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Synthesis and Properties
of
Novel Polyimides Utilizing Hydrazine

by

Hossein Ghassemi

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

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IN THE NAME OF GOD
THE BENEFICIENT
THE MERCIFUL

Acknowledgments

I would like to express my sincere debt of gratitude to my research advisor, professor Allan S. Hay for giving me encouragement and support throughout the formative stages of this project and preparation of this thesis.

I am indebted to Dr. Martino Paventi for his valuable comments and providing the French translation of the abstract.

My thanks are conveyed to Edmund Elce and Gennaro Barbiero for suggesting changes which I believe have improved this presentation.

I wish to express my appreciation of the scientific discussions and increasingly friendly environment given me by all my colleagues.

The assistance and the advice of Dr. Jean Zhu during the photoluminescence study and preparation of chapter 6 are highly appreciated. Thanks also to Dr. Nadim Saade for mass spectrum analyses.

Generous financial assistance from NSERC (Natural Sciences and Engineering Research Council of Canada) and MCHE (Ministry of Culture and Higher Education) of Iran is gratefully acknowledged.

Finally, I must thank my family for their patience and understanding in allowing me to spend precious time staying in Montreal.

Abstract

Hydrazine reacts with phthalic anhydride to give a mixture of cyclic hydrazide and N-aminophthalimide. However, the N-aminoimide is exclusively formed in high yield by the reaction of 1,8-naphthalic anhydride with hydrazine. N-aminoimides act as amines and react further with cyclic anhydrides to yield stable bisimides containing an N-N linkage. The syntheses of several bis(N-aminoimide)s from the corresponding bisanhydrides which contain the naphthalic anhydride moiety have been described. Novel high molecular weight polyimides have been synthesized by the reaction of these bis(N-aminoimide)s with cyclic dianhydrides. Most of the polymers are amorphous and are soluble in solvents such as chloroform, *o*-dichlorobenzene, N-methylpyrrolidinone and *m*-cresol. Only those polyimides having less flexible groups in their structure or containing a significant amount of perylene units show some degree of crystallinity.

All of the polymers show remarkably high glass transition temperatures, as high as 455 °C. Their 5% weight loss by thermogravimetric analysis in an atmosphere of air or nitrogen are all above 440 °C. Most of these polymers are highly fluorescent. Their emission spectra are in the visible region and show some evidence for an excited energy transfer and molecular aggregation.

Sommaire

La réaction de l'hydrazine avec l'anhydride phthalique produit un mélange de 1,2,3,4-tetrahydro-1,4-dioxophthalazine et de N-aminophthalimide. Toutefois, le N-aminoimide se forme exclusivement, avec un grand rendement, par la réaction de l'anhydride 1,8-naphthalique et l'hydrazine. Les N-aminoimides agissent comme des amines et réagissent, en consequence, avec les anhydrides cycliques produisant des bisimides stables contenant la liaison N-N. On décrit ici les synthèses de plusieurs bis(N-aminoimide)s à partir des bisanhydrides qui contiennent le grouppement anhydride naphthalique. Ainsi on synthétise des nouveaux polyimides de grand poids par la réaction de ces bis(N-aminoimide)s avec les bisanhydrides cycliques. La plus part des polymères sont amorphes et solubles dans les solvants comme le chloroforme, le o-dichlorobenzene, le N-methylpyrrolidinone et le m-crésol. Seulement les polyimides qui contiennent des grouppements moins flexibles dans leur structures ou qui contiennent un montant élevé d'unités de pérylène, démontrent un certain degré de crystallinité.

Tous les polymères démontrent des hautes températures de transition de verre, aussi haute que 455°C. Une réduction de poids de 5 %, déterminée par l'analyse thermogravimetrique sous une atmosphère d'air ou d'azote, survienne en dépassant 400°C. Plusieurs des polymères sont tres fluorescents. Leur spectres d'émission parviennent dans la region visible et démontrent quelque évidence de transferte d'énergie du stade excité et une aggregation moleculaire.

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GLOSSARY OF ABBREVIATIONS AND SYMBOLS

CT	charge transfer
CT^*	excited charge transfer
d	chemical shift
DMAc	N,N'-dimethylacetamide
DMF	N,N'-dimethylformamide
DSC	differential scanning calorimeter
ε	extinction coefficient
E'	Young's modulus
em	emission
exc	excitation
GPa	giga (10^9) Pascal
GPC	gel permeation chromatography
HPLC	high pressure liquid chromatography
IC	internal conversion
IR	infrared
ISC	intersystem crossing
J	coupling constant
l	wavelength
Mn	number average molecular weight
mp	melting point
MS	mass spectrum
Mw	weight average molecular weight
Mw/Mn	polydispersity
NMP	N-methylpyrolidinone
NMR	nuclear magnetic resonance
S	singlet excited state
S_o	ground state
T	triplet state
tan δ	ratio of loss moduli to storage moduli (E'/E")
Tg	glass transition temperature
TGA	thermogravimetric analysis
Tm	crystalline melting temperature

TMA	thermomechanical analysis
TMS	tetramethylsilane
Ultem®	poly(phenyl-2,2-bis(phthalimide-3-oxy-phenyl) propane)
UV	ultraviolet

CHAPTER 1

THE SCOPE OF POLYMER CHEMISTRY

1.1. Introduction

Polymers are macromolecules composed of many (tens to tens of thousands) simple repeat units, which are usually nearly equivalent to the starting monomers, chemically linked together. Some polymers are found naturally, such as wood, leather and cotton, and have been used since prehistoric times. With the discovery of synthetic polymers new classes of artificial polymers became available for the manufacture of the articles needed for a modern life. Synthetic polymers have been known since 1846 when cellulose nitrate was described as the first synthetic plastic by Schobien,[1] however it was not until after World War II that a rapid increase in the development of a broad range of new fibers, plastics, elastomers, adhesives and resins took place.[2-4] Now the number and variety of synthetic polymers is incredible and their impact on our daily life is very hard to calculate.

Polymeric materials are one of the fastest growing segments of the chemical industry. It has been estimated that more than 25% of the chemical research funds are spent on polymers.[5] In the United State alone synthetic polymers are produced at an annual rate of 35 million tons which means over 150 lb annually for every person. Table 1.1 shows the annual sales of plastics in the US for the year 1993.[6,7] On the manufacturing level, the number of persons employed in the synthetic polymer industry alone is on par with those employed in all the metal-based industries combined. More than 60% of all chemical industrial employment in the US involves synthetic polymers (Table 1.2).[6]

Table 1.1. U.S. plastics sales in 1993 (millions of pounds)

Thermosetting resins	
Epoxy	543
Polyester, unsaturated	1252
Urea and melamine	1997
Phenolic	3070
Thermoplastics	
Polyethylene, low density	13299
Polyethylene, high density	10527
Polyesters, thermoplastic	2966
Polypropylene and copolymers	8961
Styrene-acrylonitrile	112
Polystyrene	5479
Acrylonitrile-butadiene-styrene	1362
Nylon	726
Polyvinyl chloride and copolymers	10409

Table 1.2. U.S. Chemical industrial employment (in thousands)

	1975	1985
Industrial inorganic	149	143
Drugs	167	203
Soaps, cleaners, etc.	142	148
Industrial organics	150	164
Agriculture	65	60
Synthetic polymers	888	1026

1.2. Classification of synthetic polymers

Polymers can be classified in different ways. The earliest distinction between types of polymers was made long before any concrete knowledge of their molecular structure existed. It was purely based on their reaction to heating and cooling. It was noted that certain polymers would reversibly soften upon heating and solidify when cooled again. These polymers are known as *thermoplastics*. Other polymers are called *thermosets* which although they might have softening points, heating causes them to undergo a curing reaction and after curing they form a crosslinked network. Further heating of these crosslinked polymers ultimately leads only to degradation and not to softening.

Polymers can also be divided into three groups from the standpoint of their marketplace and applications. The first group called *commodity* polymers, are produced in very large quantities and have very low prices, for example, polyethylene and most vinylic polymers such as polyvinylchloride and polystyrene. The second and third groups of polymers (*engineering* and *specialty* polymers) have use temperatures higher than commodity polymers and offer much better physical and mechanical properties and therefore they are only used in special areas such as aerospace, automobile and electronic industries. Polycarbonate and polyimides are examples of these two groups, respectively.

1.3. Synthesis of polymers

Synthetic polymers may be prepared from simple monomers through two general methods. These methods are *chain (addition)* polymerization and *step (condensation)* polymerization. The first method involves the action of a free radical, a strong Lewis acid or a Lewis base which initiates the polymerization reaction. Polymerization through multiple bonds (e.g. polyethylene from ethylene) or ring opening polymerizations (e.g. nylon 6 from caprolactam) are in this category.

The second method, step polymerization, covers all procedures in which polymers are synthesized from monomers containing reactive functional groups which react with exclusion of a small molecule. Nucleophilic aromatic substitution polymerization (e.g. synthesis of poly(aryl ethers)) and condensation of diamines and dianhydrides (e.g. synthesis of polyimides) are two examples of this type which will be discussed in more detail in chapters 3 and 4, respectively.

Theoretically, polymerization reactions can proceed to an infinite degree of polymerization with formation of one single polymeric chain, but practically this never happens. In practice a number of chains having a limited degree of polymerization are formed. There are many different reasons why polymerization reactions reach a limit in their chain growth. The most important ones are the presence of impurities in the starting materials and stoichiometric imbalance (in cases where two or more monomers are involved). There are other factors, such as reaction temperature, solvent, catalysts, etc., which affect the molecular weight and the structure of the resulting polymers. These structural variations in turn influence the properties of the polymers.

1.4. Polymer structure

Generally speaking, two morphologies are characteristic of polymers, *amorphous* and *crystalline*. The former is a physical state characterized by almost complete lack of order among the polymer chains. The latter refers to a situation where polymer chains are oriented or aligned in a regular array. Depending on the structure of the monomer, and the amount of regularity, polymers may show partial crystallinity within their amorphous regions. Crystalline polymers which have a high level of regularity in their structure are generally stiffer, more opaque, more resistant to solvents, and of higher density than their amorphous counterparts. They melt over a relatively narrow range which may be observed most conveniently by thermal analysis. This value is called the *crystalline melting point*, T_m.

The amorphous state is characteristic of those polymers in the solid state that exhibit no tendency toward crystallinity. These polymers retain their amorphous nature when cooling from melt to solid and resemble a glass in the solid state. One of the most important characteristics of the amorphous state is the behavior of a polymer during its transition from solid to liquid. If an amorphous polymer is heated at a certain temperature the polymer loses its glasslike properties and goes into the rubbery state. The temperature at which this change takes place is called the *glass transition temperature*, T_g. It is one of the fundamental polymer properties which determines the temperature of processing.

1.5. Polymer characterization

There are several methods used for the characterization of polymers. Some of these methods are also used for organic compounds and some of them are used specifically for macromolecules. Here we will briefly mention the most important ones.

(a) *Chromatographic methods*: Synthetic polymers vary widely in molecular weight distribution from monodisperse to very wide polydispersities and unimodal to multimodal. One of the accurate and routine methods for the determination of molecular weight distribution is gel permeation chromatography (GPC).[8] Using this technique polymers can be separated by the size dependence of the degree of solute penetration into a porous packing (e.g. rigid crosslinked polystyrene gels). GPC has been widely used for polymer characterization and quality control, in particular in determination of molecular weight distribution and for characterizing low molecular weight polymers and small molecules.

(b) *Spectroscopic methods*: Nuclear magnetic resonance (NMR) spectroscopy is a most effective and significant method for observing the structure and dynamics of polymer chains both in solution and in the solid state.[9] Vibrational spectroscopy is another technique to determine the molecular composition.[10] The IR spectra of polymers can be readily obtained on polymer solutions or polymer films prepared from the melt or cast from solution. Emission spectroscopy can be used in a number of different ways in polymer chemistry including identifying different polymer samples and their impurities. It is also used in the study of inter- and intramolecular dynamics of polymer chains.

(c) *Diffraction and scattering methods*: The inherent nature of long chain molecules like the synthetic polymers where the basic chemical repeat is connected in a linear array creates a matrix. As it was mentioned earlier, polymers can contain local crystalline domains with amorphous regions in between. The presence of crystalline domains in polymers strongly influences their properties. This influence is most profound on the mechanical properties. X-ray diffraction patterns of polymers provides useful information on any types of orientation or disordering within the polymeric sample as well as dimensions and geometry of the chain conformation.[11]

(d) *Thermal methods*: These methods are based on techniques in which physical properties of polymers, such as glass transition temperature, crystalline melting point, thermal degradation and tensile strength, are measured as a function of temperature. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are static analytical techniques and thermal mechanical analysis (TMA) is a dynamic one. All these techniques are currently widely used methods of thermal analysis in polymer science.[12]

1.6. Applications of polymers

The demand for plastics is still growing rapidly in all different industrial areas. One important reason for the increasing demand is the need to replace traditional materials with plastics. Commodity plastics in our daily lives are used in the form of fiber (carpeting), film (packaging), blow- and injection-molded articles (squeeze bottles). Additionally, high performance polymers (engineering and specialty plastics) are increasingly going beyond these classical applications and have found use in automobile, aerospace and electronic industries. The wide range of applications for plastics is due to their highly adaptability to new market requirements. The substitution of plastics for metal, glass, and ceramics is strongly driven by technological and economical considerations. For example, a modern automobile engine and body contains over 200 lbs of plastics.[5] Similarly, the applications of polymers in the building construction industry are already impressive and will become even more so in the future.

Microelectronics is one of the fastest growing industries which demands specialty polymers. For example, photoresists and polyimides are used in fabrication of integrated circuits (ICs). Polyesters and polyimides are employed in flexible circuit board manufacture. IC encapsulating materials and die attach adhesives are also primarily polymers.[13]

In the aerospace industry, resinous polymers find use in a wide variety of hardware applications for aircraft, missiles, and space structures. In aircraft, resins are used as matrix materials for fiber-reinforced composite structures, adhesives for bonding of metals and composite hardware components, sealants, etc.[14]

1.7. High temperature polymers

During the early effort on thermally stable polymers in the late 1950s and early 1960s, attention focused primarily on polymers with high thermo-oxidative stability. The driving force for the development of high temperature polymers has come from the demand of the aerospace industry for new materials. Investigations in this field have resulted in the development of numerous classes of thermally and oxidatively stable polymers. Most of this effort has been expended on the synthesis and evaluation of the thermal stability of new organic, organometallic, and inorganic polymers.[15]

Thermally stable polymers constitute those groups of polymers which maintain their desirable properties in continuous use temperatures above 150°C. They are expected to be chemically inert, especially to oxygen and water, show low weight loss at elevated temperatures (e.g. 370 °C or higher) for short period of time combined with low flammability as well as good electrical properties (e.g. as insulators).

Basic chemical structures of these polymers are composed of a highly resonance-stabilized aromatic or other thermally unreactive ring systems such as heteroaromatic rings containing oxygen, nitrogen, or sulfur atoms with high bond and cohesive energy density. Resonance stabilization of aromatic and heterocyclic structures, such as benzene or quinoxaline, contribute substantially to bond strength. The resonance energies of these structures range from 40 to 70 KCal/mole.[16] Due to the attractive combination of properties conferred by the presence of the heteroaromatic units in the polymeric structure, thermally stable polymers are becoming increasingly important industrially.

One synthetic approach to high temperature polymers involves the use of aromatic and heteroaromatic rings with only a few isolated single bonds in the backbone which give intrinsically rigid structures. There are other approaches to enhance thermal stability which are generally based on increasing softening temperatures of polymers, for example by introducing interchain cohesive forces. Hydrogen bonding and dipole-dipole interaction between the chains are the most important of these type. The hydrogen bonding in polyamides and polyurethanes, for instance, plays an effective role to increase softening temperature of these polymers which produces additional thermal stability. The ultimate degree of interchain cohesive forces can be achieved by crosslinking of polymer chains with chemical bonds. This approach produces three-dimensional networks which are thermosetting and can withstand high temperatures without softening.

The most promising thermally stable polymers which are attracting commercial attention include polyimides, polyphenylquinoxalines, polybenzimidazoles and polybenzothiazoles.

1.7.1. Improvements in high temperature polymers

The very structural principles that provide the outstanding combinations of properties such as high thermal and chemical stability in high temperature polymers also cause many problems with respect to processability. The high symmetry inherent in aromatic and heteroaromatic rings and their high softening or melting temperatures causing insolubility and intractability of most high temperature polymers which make their fabrication into useful forms difficuit, if not impossible. The most important representative examples are polyimides which have softening temperatures above 200°C and in many cases show no melt temperature up to 400°C.[17]

It was realized that some new methods would have to be developed in order to improve the process characteristics of the high temperature polymers. These methods, in general, are (a) structural modification of polymers or (b) making low molecular weight oligomers with low melt viscosities and then polymerize them into high molecular weight polymers during the fabrication steps. In the first method the main idea is to lower the melt and softening temperature of the final materials and increase their solubility. This means partly sacrificing thermal stability and solvent resistance of the polymers for facile processing by melt extrusion or solution fabrication techniques. There are several approaches for the chemical modification of polymers which will be discussed in more detail in the following chapters.

The method which uses oligomers as precursors for high molecular weight polymers consists of preparing linear oligomers with reactive functional end-groups or making cyclic oligomers. These oligomers join together at the processing temperature to form high molecular weight linear polymers or networks. We will give only a few examples of this method in chapter 4.

1.8. Goals of this thesis

In general, there are two options which a polymer chemist can chose in order to prepare materials with new properties suitable for a demanding market. Either modifying the existing polymers or designing new monomers which form polymers with desired properties. This thesis deals with the second option and demonstrates the synthesis of new monomers and polymers. The main goal is to prepare new polyimides utilizing hydrazine. The general idea is to use hydrazine-aromatic anhydride chemistry to synthesis new monomers with hydrazine's amine functional groups in order to replace classical aromatic diamines. The advantages of these new monomers are their higher reactivity versus classical diamines and they are prepared more easily.

The chemistry of hydrazine and its reactions, especially with aromatic anhydrides, will be discussed in chapter 2. Chapters 3 to 5 are concerned with the synthesis and characterization of a series of novel monomers and polymers. A photophysical study of some of these polymers will be presented in chapter 6.

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CHAPTER 2

HYDRAZINE - AROMATIC ANHYDRIDES CHEMISTRY

2.1. Introduction

The chemistry of hydrazine has been studied extensively for more than a century since it was isolated for the first time as hydrazine monohydrate, and several of its salts, by Curtius and his co-workers in 1887.[1] It was then developed and expanded to such an extent that it was believed that all combinations of hydrazine with the various types of organic compounds, similar to those prepared from ammonia and amines, could be prepared from this very reactive material. In fact hydrazine is the second hydronitrogen (after ammonia) to have been isolated in the free state. Having two amino functional groups hydrazine can also be considered as the simplest diamino compound. The combination of high reactivity, availability and versatility to form various types of organic nitrogen compounds makes it an interesting subject for study.

2.1.1. Preparation, properties and reactions of hydrazine

Hydrazine is commercially prepared by the partial oxidation of ammonia with alkaline hypochlorite via the intermediate formation of chloramine.[15] Pure hydrazine is a colorless fuming liquid with an ammoniacal odor. It is soluble in polar solvents such as water, alcohol and amines. Hydrazine is a slightly weaker base than ammonia. Its salts from organic and inorganic acids are generally white, crystalline solids stable at room temperature.

Hydrazine and its salts are good reducing agents. They reduces many metal ions to lower valence states or to the metals themselves. In organic chemistry, hydrazide and hydrazone derivatives of many carboxylic acids, aldehydes and ketones have been synthesized and used for identification of these compounds. Reactions of hydrazine with cyclic anhydrides have been studied extensively by several chemists. In these reactions hydrazine can form cyclic products which are very interesting from different points of view. We will discuss in this chapter some of these cyclic products in detail.

Some of the most important reactions of hydrazine with organic compounds are listed in Table 2.1.[16-18]

2.2. Background

The condensation of hydrazine with phthalic anhydride **2.1a** to form 2,3-dihydrophthalazine-1,4-dione (cyclophthalhydrazide) **2.3a** was reported for the first time by Curtius and Fosterling.[2] Further studies on the series of cyclophthalhydrazides have been carried out to understand the chemistry of the reaction as well for the study of the chemiluminescent properties of these heterocyclic compounds. Discovery of their luminescence behavior generated a great deal of excitement which focused a large effort on their applications to the luminescent problem.[3-6] 5-Amino-2,3-dihydrophthalazine-1,4-dione **2.3g** (Table 2.2), commonly known as luminol, is made by reduction of the nitro derivative of 2,3-dihydrophthalazine-1,4-dione **2.3b** formed by thermal dehydration of the salt of 3-nitrophthalic acid formed with hydrazine. Luminol shows a powerful yellow chemiluminescence with alkaline oxidizing agents.[7]

Table 2.1. Some of the reactions of hydrazine

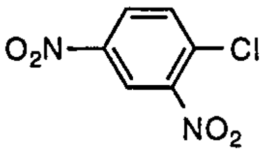
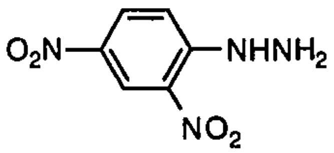
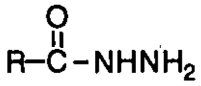
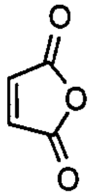
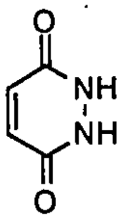
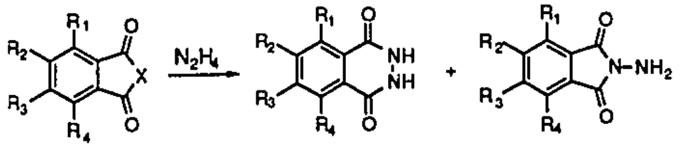
Reactants		Products
O_2		$N_2 + 2H_2O$
$Fe + H_2O$		$Fe_3O_4 + NH_3$
RX		$RNHNH_2 + HX$
		$H_2NNHCH_2CH_2OH$
		$H_2NNHCH_2CH_2NH_2$
$H_2C=CHCN$		$H_2NNHCH_2CH_2CN$
	$\xrightarrow{N_2H_4}$	
$R-COOR$		 $R-\overset{\overset{O}{\|}}{C}-NHNH_2$
		
R_2CO		$R_2C=N-N=CR_2$

Table 2.2. Results of the reaction of hydrazine with phthalic anhydrides and phthalimides



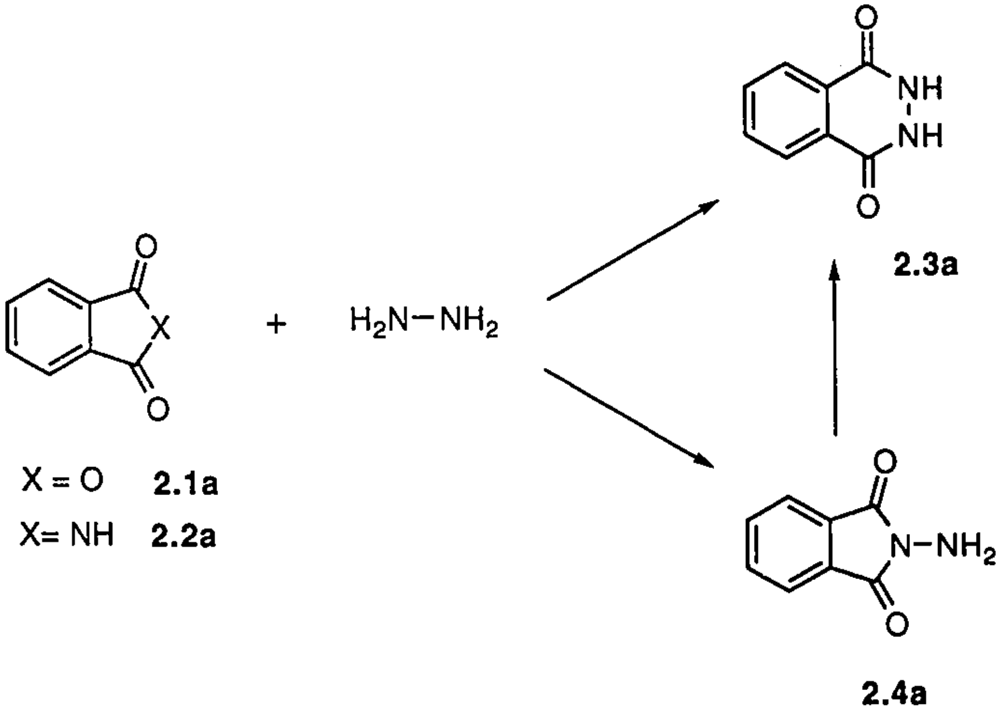
X=O **2.1**
X=NH **2.2**
2.3
2.4

2.1 or **2.2**	R_1	R_2	R_3	R_4	Product
a	H	H	H	H	**2.3a, 2.4a**
b	NO_2	H	H	H	**2.3b**
c	H	NO_2	H	H	**2.3c**
d	Cl	H	H	H	**2.3d, 2.4d***
e	Cl	H	H	Cl	**2.4e***
f	Cl	Cl	Cl	Cl	**2.4f***
g	NH_2	H	H	H	**2.3g, 2.4g***
h	OH	H	H	H	**2.3h**
i	H	NH_2	H	H	**2.3i***
j	H	Cl	Cl	H	**2.3j***
k	H	Cl	H	H	**2.3k, 2.4k**
m	H	ArO	H	H	**2.3m**
n	ph	H	H	ph	**2.4n**

* Data taken from reference 3

In spite of intensive studies on the chemistry of hydrazine, there are only a few examples in the literature of the hydrazine-aromatic anhydride chemistry. Drew and his co-workers performed the first and only systematic study in the 1930's on the chemistry of hydrazine and phthalic anhydrides and suggested correct structures for their products. They showed that the reaction of hydrazine with phthalic anhydride **2.1a** or phthalimide **2.2a** takes place via two pathways and gives two products.[2] These two products, which are considered as kinetic and thermodynamic products, are the result of two possible pathways with ring closure reaction. One way gives the five-membered ring N-aminoimide **2.4a** as the kinetic product and the other gives the six-membered ring cyclohydrazide **2.3a** as the thermodynamic product (Scheme 2.1).

Scheme 2.1



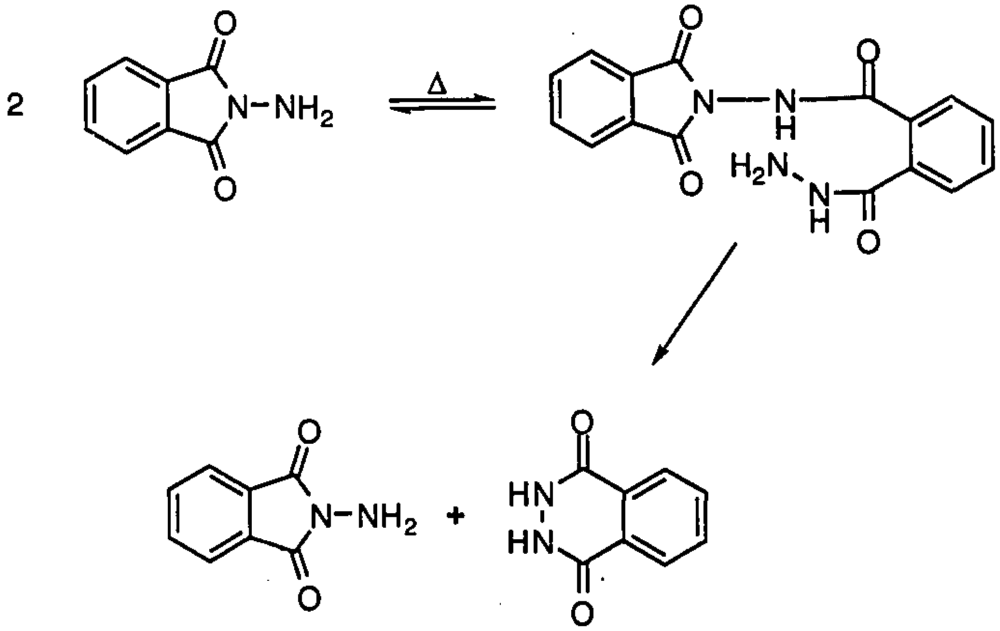
X = O **2.1a**
X= NH **2.2a**

2.3a

2.4a

The ratio of two products strongly depends on different factors, such as the mole ratio of starting materials, solvent, reaction time and temperature. When **2.1a** or **2.2a** reacts with hydrazine in boiling glacial acetic acid cyclohydrazide **2.3a** is the only product. If this reaction is run for only a few minutes, a mixture of **2.3a** and **2.4a** are isolated in various proportions, although cyclohydrazide **2.3a** is always the major product. When ethanol is used as a solvent and the reaction is quenched after two minutes the yield of **2.4a** increases to almost 50%. Employing **2.2a** instead of **2.1a** increases the isolated yield of **2.4a**, since **2.3a** stays in solution as an ammonium salt and **2.4a** precipitates from the reaction mixture in the form of light yellow crystals. N-amino-phthalimide **2.4a** is a stable compound, however, it readily rearranges to the six-membered ring phthalhydrazide **2.3a** at its melt temperature (203-205°C; lit. 200-205[2]). This rearrangement occurs at much lower temperatures in solution. The mechanism of this rearrangement is probably through reaction of two molecules of **2.4a** and subsequent ring closure as shown in Scheme 2.2.

Scheme 2.2

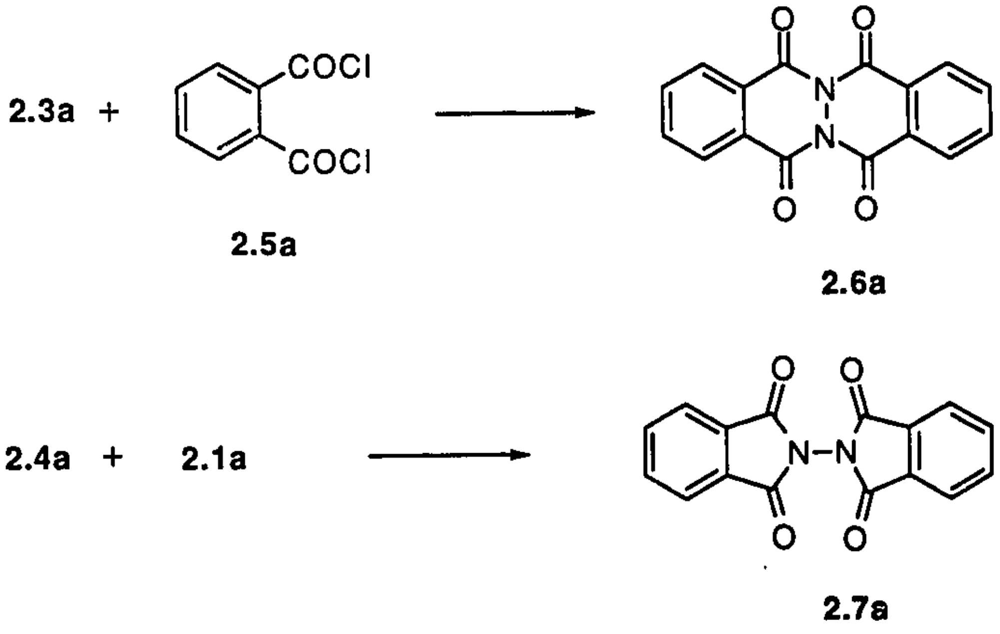


The spontaneous displacement of the diamine component of polyimides from the 5-membered ring, with the simultaneous formation of the 6-membered ring cyclohydrazide, is further evidence which illustrates the stability gained by loss of ring strain in the imide and the gain in resonance energy in the cyclohydrazide.[8]

N-aminoimides have characteristics of both aliphatic and aromatic amines. Some reactions of N-aminoimides have been reported,[2] such as condensation with aldehydes, ketones, carboxylic acids and anhydrides. Reaction of N-aminoimide **2.4a** with phthalic anhydride **2.1a** in glacial acetic acid leads to the formation of N-phthalimidophthalimide **2.7a** in quantitative yield (Scheme 2.3). This reaction seems to be faster and takes place at lower temperatures compared with reaction of aniline and phthalic anhydride.[10] Bisimide **2.7a** unlike N-aminoimide **2.4a** is stable at elevated temperatures. Compound **2.4a** also reacts with aldehydes and ketones in a manner similar to other amines.

Reactions of 2,3-dihydrophthalazine-1,4-diones **2.3a** seem to be more complicated because of the different resonance structure of this compound which adds more reactive sites to the molecule. Acetylation of **2.3a**, for instance, gives a mixture of products containing N-acetylated, O-acetylated and diacetylated compounds.[2] Condensation of **2.3a** with phthaloyl dichloride **2.5a** in nitrobenzene, interestingly, favors formation of the 2,3-phthalophthalazine-1,4-dione **2.6a** in quantitative yield (Scheme 2.3).

Scheme 2.3



2.3. Goals

The chemistry of hydrazine is very versatile and because of its ready availability it is still able to excite academic interest in the synthesis of new materials.

We wanted to better understand the chemistry of the condensation of hydrazine with anhydrides and imides. We were quite confident that this study would help us to develop new derivatives of hydrazine which could be used in the synthesis of new polymers. Specifically, we were interested in N-aminoimides which are the kinetic product of the reaction of hydrazine with anhydrides. As mentioned before, N-aminoimide acts as an amine and undergoes a condensation reaction with carboxylic acids and their derivatives.

This chapter aims to summarize the scope of the work done previously and present some new results from our study on the effect of substituents on the pathway of the reaction of phthalic anhydrides or phthalimides with hydrazine.

2.4. Results and discussion

2.4.1. Reaction of hydrazine with nitrophthalic anhydrides

The effect of substituents on the ring closure of phthalhydrazides has been studied.[3] It has been shown that ring closure of an open-ring hydrazide intermediate is mainly controlled by the nature of the substituents. Reactions of nitrophthalic anhydrides **2.1b** and **2.1c** with hydrazine was shown to give only cyclohydrazides **2.3b** and **2.3c**, respectively (Table 2.2). Our efforts to synthesize nitro-N-aminophthalimides **2.4b, 2.4c** using different solvents and reaction conditions failed and phthalhydrazides **2.3b, 2.3c** were obtained as the only products. When the reaction was conducted under controlled conditions, a mixture of hydrazides were detected by ^{1}H NMR which showed broad signals corresponding to the NH groups.

2.4.2. Reaction of hydrazine with chlorinated phthalic anhydrides

While 3-nitrophthalic anhydride **2.1b** forms a 6-membered ring product, 3-chlorophthalic anhydride **2.1d** prefers to give the 5-membered ring **2.4d** under the same reaction conditions. When we used 4-chlorophthalic anhydride **2.1k** in a similar way to prepare 4-chloro-N-aminophthalimide **2.4k**, the maximum yield of the N-amino compound was 35% while in the case of **2.1d**, according to Drew's work[3] the yield is very high. Moreover in the case of **2.1d** by changing the reaction condition either product **2.3d** or **2.4d** can be exclusively obtained. It has also been reported that when 3,6-dichlorophthalic anhydride **2.1e** or tetrachlorophthalic anhydride **2.1f** was used the formation of the 6-membered ring hydrazide was not favored and N-aminoimides **2.4e** and **2.4f** were obtained, respectively (Table 2.2).[3]

The different results from 3-nitro **2.1b** and 3-chloro **2.1d** can be attributed to the strong electron withdrawing effect of the nitro group. The positive charge on the nitrogen of the nitro group probably interacts with the lone pair electrons of the carbonyl oxygen and makes the 6-membered ring closure more favored (Figure 2.1).

From the data presented in Table 2.1, One can also conclude that some stereoelectronic effects are important in the ring closure of the substituted hydrazides.

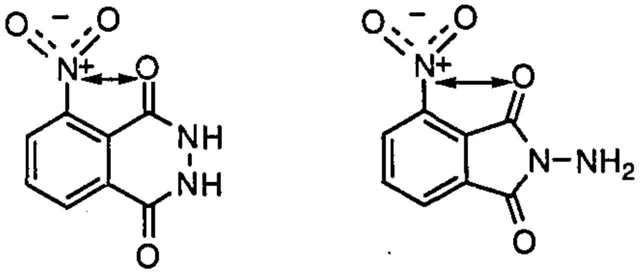
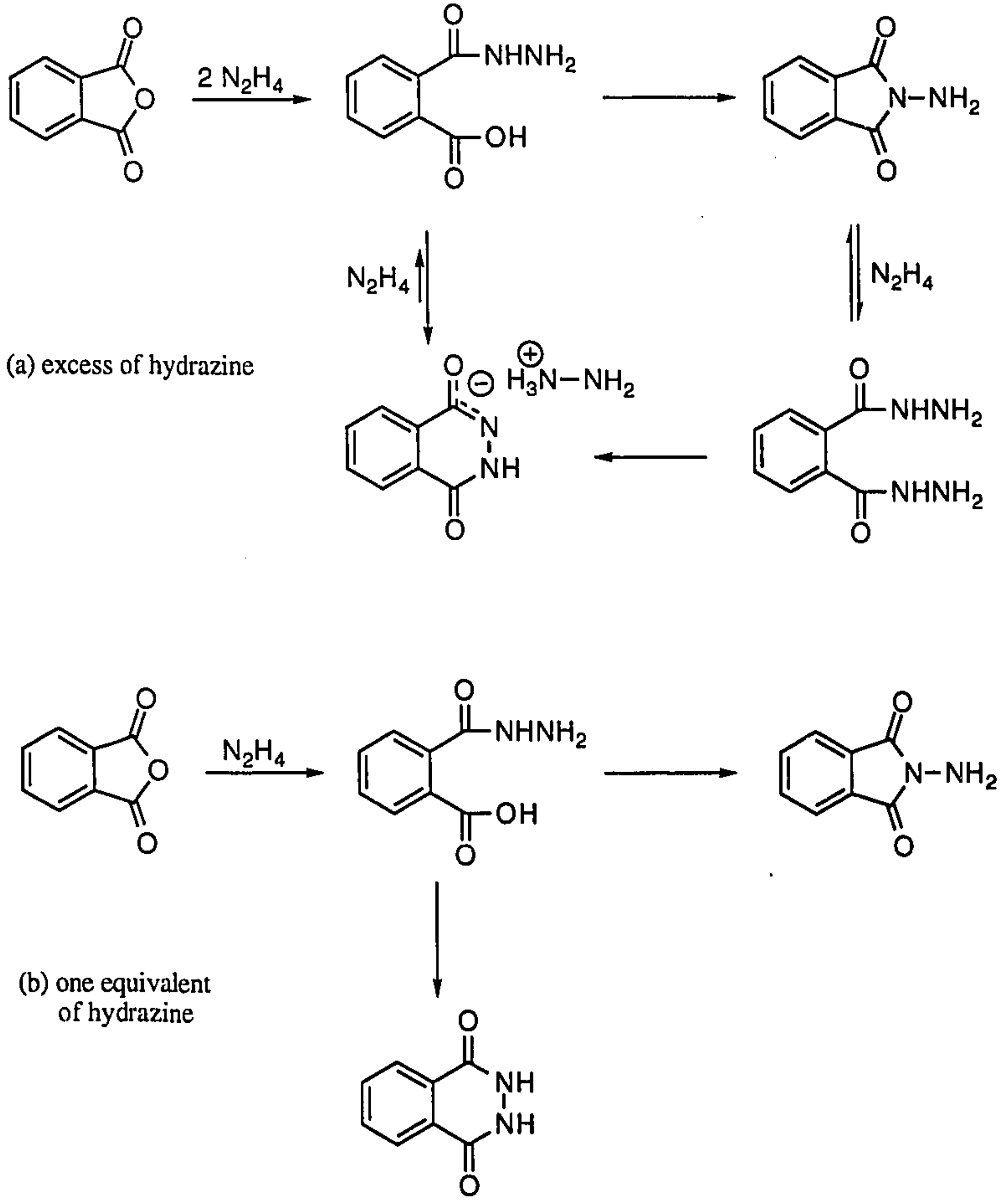


Figure 2.1. Electrostatic interaction in 3-nitrophthalimide

Experimental results show that the amount of hydrazine added to the reaction has a significant influence on the composition of the final products. For example, the ratio of 6- and 5-membered ring products in the reaction of phthalic anhydride with hydrazine strongly depends on the amount of hydrazine. 2,3-Dihydro phthalazine-1,4-dione is the only product when hydrazine is used in excess and a mixture of two products forms when one equivalent of hydrazine is used. This may be explained by the relative stability of the cyclohydrazides and the corresponding N-aminoimides in solution. In the presence of an excess amount of hydrazine, the N-aminoimides will be in equilibrium with their open ring intermediate while the cyclohydrazides will probably form stable hydrazinium salts (Scheme 2.4).

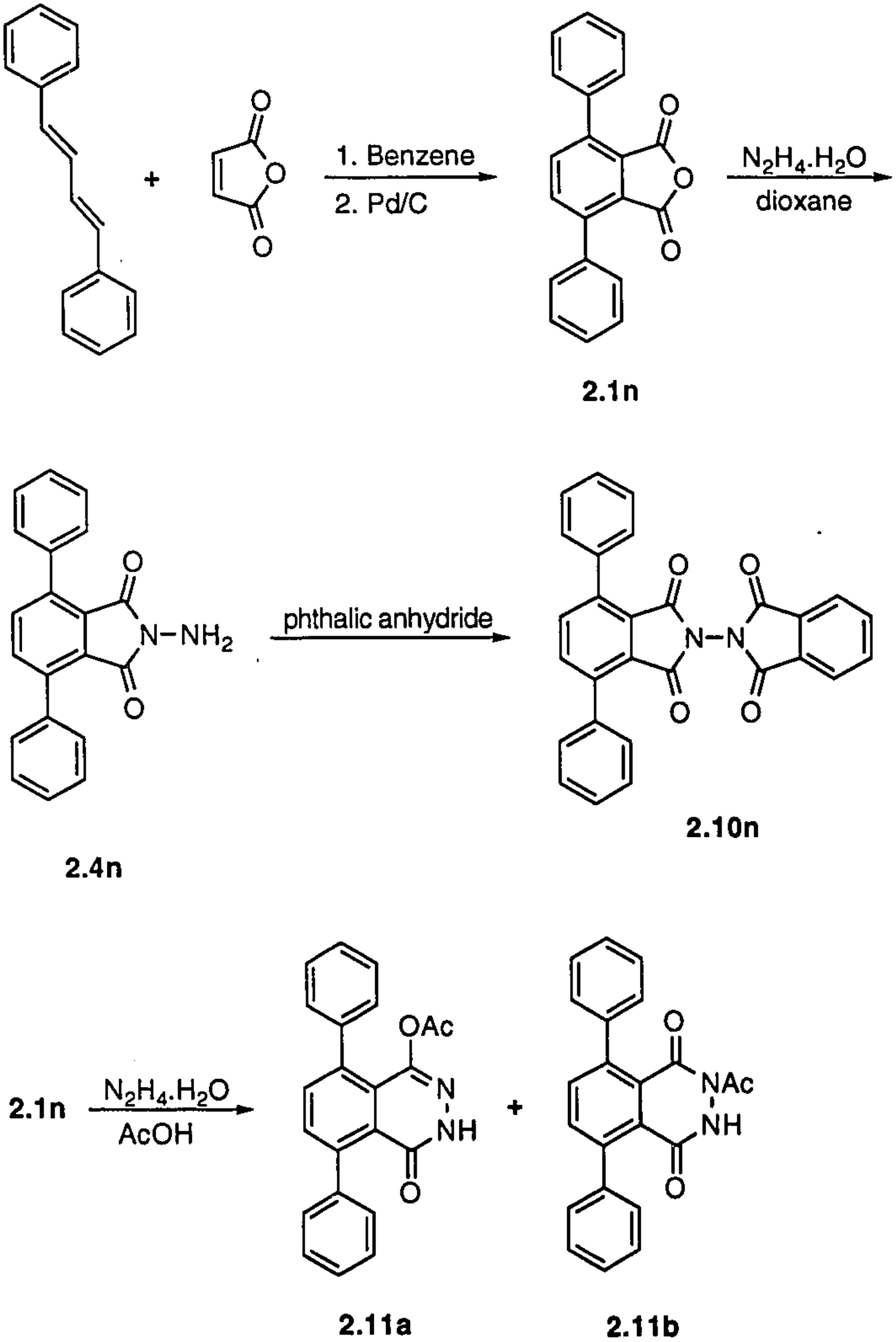
Scheme 2.4


2 N_2H_4
$NHNH_2$
OH
N–NH_2
N_2H_4
N_2H_4
(a) excess of hydrazine
H_3N^+–NH_2
N
NH
NHNH$_2$
NHNH$_2$
N_2H_4
NHNH$_2$
OH
N–NH_2
(b) one equivalent of hydrazine
NH
NH

2.4.3. Effect of bulky groups on the ring closure of phthalhydrazide

We further studied the effect of bulky substituents on the ring closure step by synthesizing 3,6-diphenylphthalic anhydride **2.1n** (Scheme 2.5). The hindered anhydride **2.1n** readily reacts with hydrazine but the ring closure step requires reaction in boiling ethanol for several hours. Using higher boiling point solvents such as dioxane facilitates the ring closure step and N-aminoimide **2.4n** was obtained as the only product in quantitative yield. Hindered anhydrides, such as **2.1n**, are generally more sensitive to moisture than the unsubstituted ones and undergo dehydration with more difficulty due to the steric effect of the substituents. When **2.1n** was reacted with hydrazine in glacial acetic acid a mixture of the acetylated cyclohydrazide **2.11a** and **2.11b** was isolated as yellow crystals (Scheme 2.5). Although formation of the 6-membered ring cyclohydrazides is usually favored, due to a thermodynamic effect, the presence of the bulky phenyl groups in anhydride **2.1n** forces the equilibrium between the two different ring closure pathways toward the N-aminoimide **2.4n** which is less sterically hindered than its 6-membered ring isomer **2.3n**. Further evidence for the stability of **2.4n** is that, in contrast to N-aminoimide **2.4a**, **2.4n** is quite stable above its melting temperature up to 300°C and does not rearrange to the corresponding 2,3-dihydrophthalazine-1,4-dione. Using acetic acid as a solvent apparently had a dramatic effect on the resulting product. The isolated product was a mixture of acetylated phthalazine-1,4-dione **2.11a,b** instead of imide **2.4n**. One possible explanation for this unexpected result is that the acetylated phthalazine-1,4-dione is less reactive in reaction with hydrazine than unacetylated hydrazide, such as **2.3a**, therefore it can not be easily in equilibrium with the open-ring hydrazide and hence rearrange to its imide form. Under these conditions all the anhydrides were gradually converted to acetylated hydrazide, as shown by monitoring ^{1}H NMR.

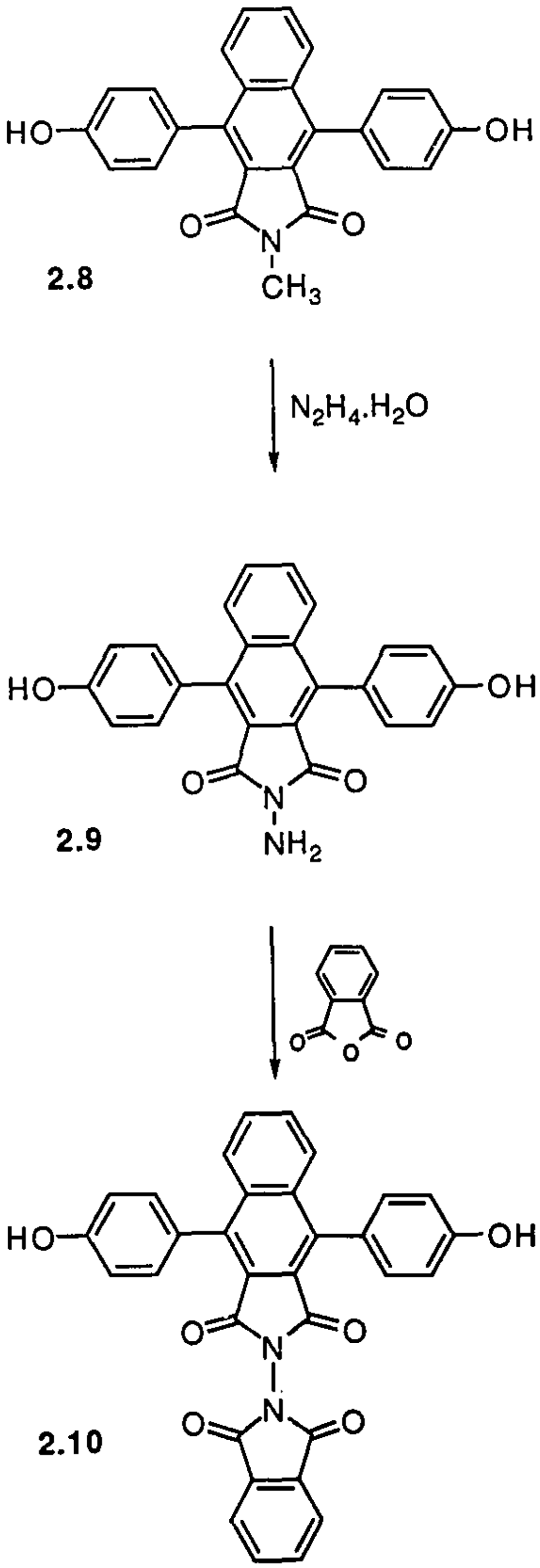
Scheme 2.5


+
1. Benzene
2. Pd/C
$N_2H_4.H_2O$
dioxane
2.1n
$N-NH_2$
phthalic anhydride
N−N
2.4n
2.10n
2.1n
$N_2H_4.H_2O$
AcOH
OAc
N
NH
+
NAc
NH
2.11a
2.11b

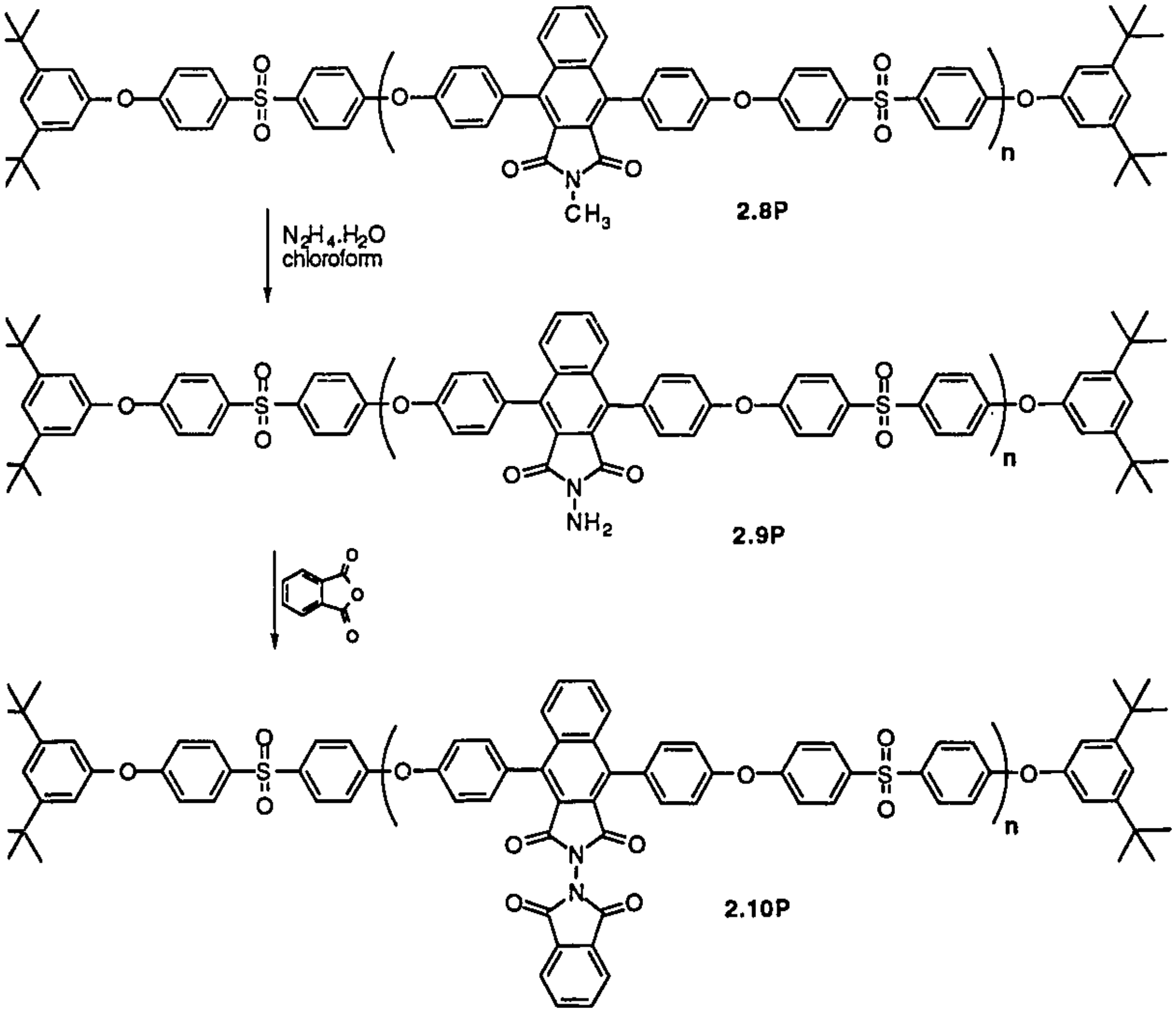
The reaction of 4,4'-imidoaryl biphenol **2.8**, as a hindered imide, with hydrazine was also examined. This imide reacts with an excess of hydrazine, in the absence of any other solvent, and gives N-aminoimide **2.9** as the only product in quantitative yield. N-aminioimide **2.9** easily condenses with phthalic anhydride to give bisimide **2.10** in high yield (Scheme 2.6). The same reaction was carried out on poly(aryl ether sulfone) **2.8P** containing 4,4'-imidoaryl biphenyl moieties as part of the structure of the repeat units. A solution of the polymer **2.8P** in chloroform was reacted with hydrazine and after removing the solvent and excess hydrazine, poly(aryl ether sulfone) **2.9P** with N-aminoimide side groups was obtained (Scheme 2.7). ^{1}H NMR showed complete conversion of the imide rings and no 6-membered ring structure was detected. Polymer **2.9P** readily undergoes a crosslinking reaction by curing above its glass transition temperature (313°C). Condensation of two N-aminoimide groups is the most likely explanation for the crosslinking reaction which could result in bisimide linkages similar to **2.10** (Scheme 2.8). The glass transition temperature (Tg) of the polymer was increased from 313 to 345°C after curing for 5 min. at 320°C and it became insoluble in chloroform. Polymer **2.10P** was also made by capping amino groups in polymer **2.9P** using phthalic anhydride. Polymer **2.10P** showed a Tg around 327°C which did not change after heating the polymer above its Tg.

All of the polymers were end-capped with 3,5-di-*tert*-butylphenyl groups. Integration of the protons of *tert*-butyl end groups and the other aromatic protons by ^{1}H NMR showed no change in the molecular weight of the polymers after each reaction step.

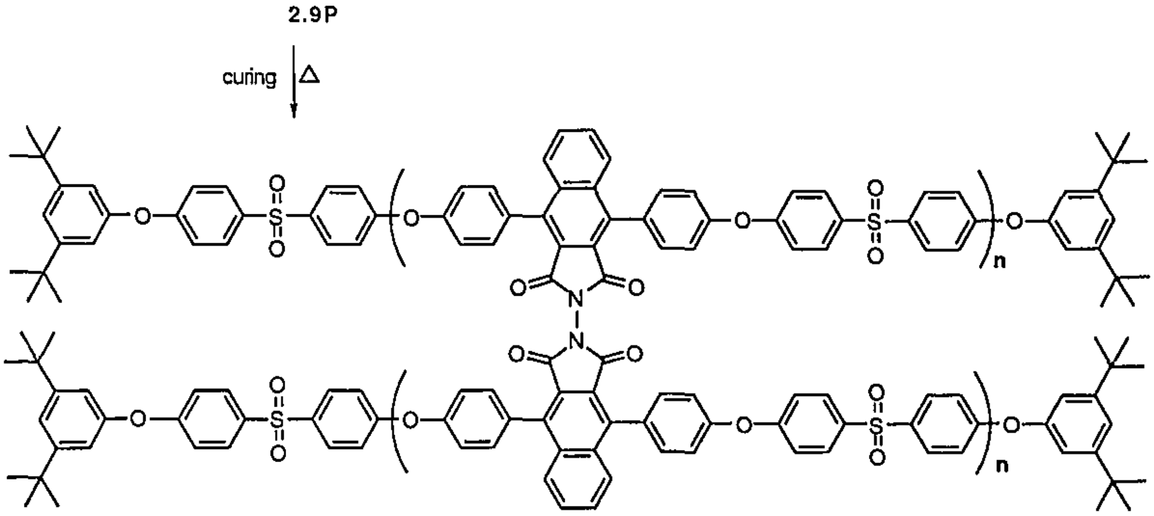
Scheme 2.6



Scheme 2.7



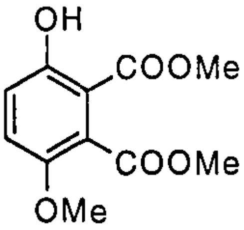
Scheme 2.8



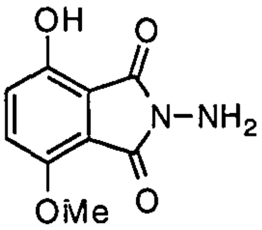
2.4.4. Effect of electron donating groups on the ring closure of phthalhydrazide

Phthalic anhydrides and phthalimides containing electron donating groups were also used to study the ring closure of hydrazides. It has been reported that 3-hydroxyphthalic anhydride **2.1h** and 3-aminophthalic anhydride **2.1g** or their phthalimides **2.2h** and **2.2g**, react with an excess of hydrazine giving the 6-membered ring cyclohydrazide exclusively (Table 2.2).[3] Another group of investigators has shown that dimethyl 3,6-dimethoxyphthalate **2.12** and dimethyl 3-hydroxy-6-methoxyphthalate **2.13** also follow the same ring closure pathway under similar conditions to give 6-membered ring product.[11] There is only one example in Drew's report which shows that the reaction of 3-aminophthalimide **2.2g** with one equivalent of hydrazine in water gives the 5-membered ring compound **2.4g** as the sole product and in all other cases hydrazine was reported to be used in excess. When we reacted 3-hydroxyphthalimide **2.2h** with one equivalent of hydrazine only hydrazide **2.3h** was obtained. ^{1}H NMR of the product showed two peaks at δ 12.82 ppm for OH and a relatively broad peak centered at 12 ppm corresponding to the NH group. Our NMR data for **2.3h** did not agree with the results published by Parrick.[11] He reported that when hydroxyphthalate **2.13** was reacted with hydrazine the product, after oxidation with ceric ammunium nitrate (CAN), was N-aminoimide **2.14**. However, the ^{1}H NMR data given for **2.14** (in which the peaks at δ 12.84 and 12.12 ppm were assigned as the protons of OH and NH_2 groups, respectively) was very similar to those of hydrazide **2.3h**. The results are questionable because the chemical shifts for NH_2 groups in N-aminoimides in DMSO-d_6 usually appear around 4-6 ppm and the acidic protons of the NH in cyclohydrazides appear around 11-12 ppm. Moreover, when compound **2.3h** and phthalic anhydride were reacted, there was no evidence of formation of bisimide which is characteristic of N-aminoimides. This experiment and the NMR study proved that compound **2.3h** was a hydrazide.

The effect of relatively weak electron donating groups, such as aryloxy, on the final product of the ring closure of hydrazide seemed worthwhile to study. For this reason 4-aryloxyphthalic anhydride **2.1m**, was prepared from 4-nitro-N-methylphthalimide in 3 steps (Scheme 2.9). Reaction of **2.1m** with hydrazine at room temperature was slower than phthalic anhydride **2.1a** as expected from the electron donating effect of aryloxy group. This reaction was run under different conditions and in all cases the 2,3-dihydrophthalazine-1,4-dione **2.3m** and **2.3l** were isolated as the major products.

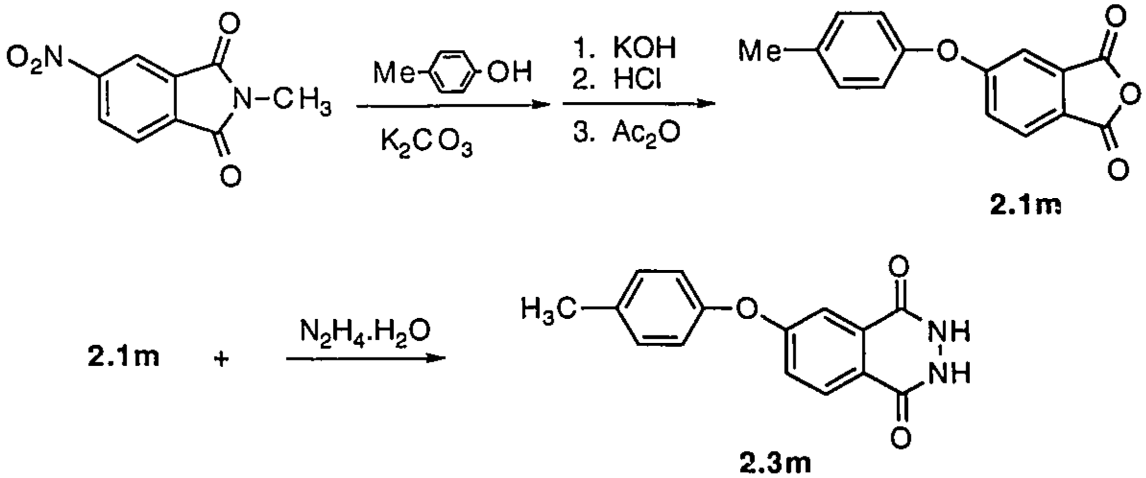


2.13



2.14

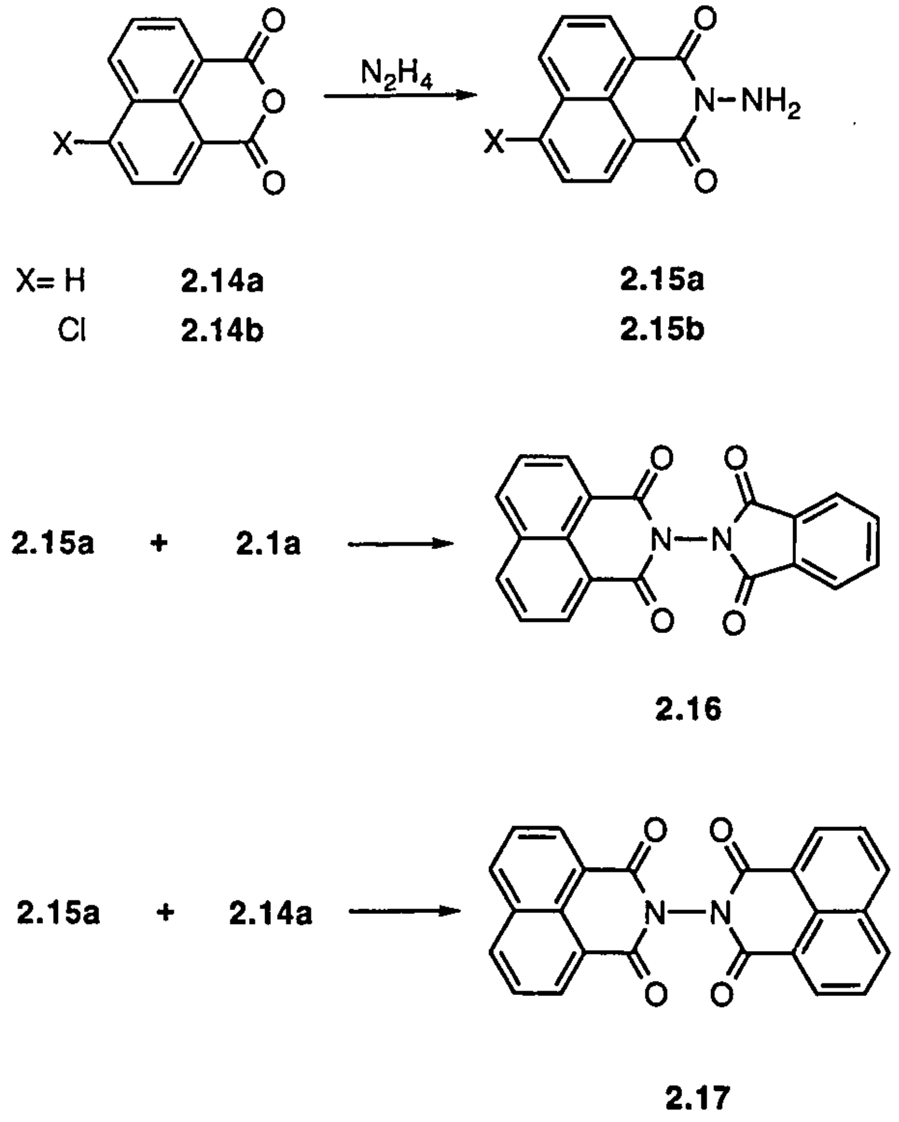
Scheme 2.9



2.4.5. Reactions of naphthalic anhydride with hydrazine

The reaction of the 6-membered ring naphthalic anhydride **2.14a** with hydrazine, interestingly, gives N-aminoimide **2.15a** as the sole product in quantitative yield. N-aminoimides **2.15a,b** condense with anhydrides, aldehydes and ketones similarly to N-aminophthalimide **2.4a**. Several derivatives of **2.15a** have been known since 1911. Reactions of **2.15a** with phthalic anhydride **2.1a** and naphthalic anhydride **2.14a**, reported by Bistrzycki [9], give bisimides **2.16** and **2.17**, respectively in quantitative yield. The condensation takes place either in high temperature solvents, such as 1,2-dichlorobenzene or in the melt. Condensation of **2.15a** with phthalic anhydride in melt under atmospheric pressure requires an excess amount of anhydride in order to form a homogeneous mixture (Scheme 2.10).

Scheme 2.10


N$_2$H$_4$
X
O
N-NH$_2$
X= H
Cl
2.14a
2.14b
2.15a
2.15b
2.15a + 2.1a
N—N
2.16
2.15a + 2.14a
2.17

2.4.6. Oxidation of N-aminoimide 2.15a

The oxidation of aromatic amines in the presence of copper (I) chloride and pyridine with oxygen gives diazo compounds.[19] There is no information about the oxidation of N-aminoimides in the literature. We attempted to oxidize N-aminoimide **2.15a** with oxygen in a Cu/pyridine system in order to see if similar N-N coupling product forms. The result showed cleavage of the N-N bond and formation of naphthalimide instead and no coupling product was detected. However, this experiment does not eliminate the possibility of formation of the dimer with a tetraazo structure which might be formed as a short-lived intermediate during the course of the reaction.

2.5. Conclusions

Studies of the reaction of hydrazine with aromatic anhydrides have demonstrated that the 6-membered ring 2,3-dihydrophthalazine-1,4-diones are thermodynamically more stable than the 5-membered ring imides and in most cases form as the major product. However, substitutions on the phthalic ring have a considerable stereoelectronic effect on the ring closure pathway. Substitutions on the 4-position of phthalic anhydride or phthalimide have almost no steric effect on the ring closure. On the other hand 3-substituted anhydrides may give either the 5- or 6-membered ring products. The ratio of these two products depends on different factors, such as the nature of the substituent, the amount of hydrazine used, solvent, temperature and reaction time. When strong electron withdrawing or donating substituents are present in either the 3- or 4-position the electronic effect becomes dominant and the 6-membered ring forms as the major product. The only exception was **2.1g** which was reported to give the 5-membered ring product. The steric effect becomes very significant when 3,6-disubstituted anhydrides or imides are used and the 5-membered ring products form exclusively.

2.6. Experimental

General Methods

The ^1H NMR spectra were measured with a Varian XL200 or Varian Unity-500 instrument, using deuterochloroform ($CDCl_3$) or dimethyl-d_6 sulfoxide (DMSO-d_6) as a solvent. The chemical shifts were calibrated using tetramethylsilane (TMS). The chemical shift (δ) and coupling constant (J) data are quoted in ppm and hertz, respectively. Mass spectra were obtained on a Du Pont 21-492B instrument. Melting points were measured on a Mettler-FP-85 DSC apparatus. 1,8-Naphthalic anhydride **2.14** was obtained from Aldrich Chemical Co., and was purified by recrystallization first from toluene and then acetic anhydride prior to use. 1,4-Diphenylbutadiene **2.5**, bisphenol **2.8** and polymer **2.8P** were synthesized previously in our organic lab.[20] 4-Nitro-N-methylphthalimide and 4-Chlorophthalic anhydride **2.1k** were kindly supplied by General Electric Company and were used without further purification. 3-Hydroxyphthalic anhydride **2.1h** (Aldrich) was converted to 3-hydroxyphthalimide **2.2h** by treating with ammonium hydroxide and then recrystallized from water before use.

N-amino-phthalimide 2.4a.

To a mixture of 7.3 g (50 mmol) of phthalimide in 100 mL of ethanol (96%) was added 2.5 mL (50 mmol) hydrazine monohydrate. The reaction mixture was stirred for 5 min. at room temperature and then transfered to a preheated hot plate and refluxed for 2 min. By adding 100 mL of cold water pale yellow crystals formed after a few hours. The resulting crystals were filtered and recrystallized from ethanol to give N-amino-phthalimide in 40% yield : mp 203-205°C (lit. 200-205°C)[2] it solidifies around 250 and melts at 352-355°C; ^1H NMR (200 MHz, DMSO-d_6) δ 7.83 (m, 4 H, C_6H_4). 4.94 (s, 2 H, exchanged with D_2O, NH_2).

N-phthalimidophthalimide 2.7a.

To a mixture of 1.48 g (10 mmol) of phthalic anhydride in glacial acetic acid (30 mL) was added 1.62 g (10 mmol) of N-aminophthalimide. The reaction mixture was refluxed for 30 min. and then it was allowed to cool for several hours. The white solid was filtered and washed with 50 mL ammonium hydroxide solution (5%). The yield was 99% : mp 311-313°C (lit. 311-313°C)[2]; ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.02-8.15 (m, 8 H, 2 C_6H_4)

Phthalophthalhydrazide 2.6a.

In a round bottom flask equipped with a condenser and a nitrogen inlet was added 1.62 g (10 mmol) of phthalhydrazide, 2.03 g (10 mmol) of phthaloyl dichloride and 20 mL nitro benzene. The reaction mixture was heated at 160°C for 1h and then at 200°C for 15 min. When the evolution of HCl had ceased the mixture was allowed to cool for several hours . The white solid was filtered and washed many times with ammonium hydroxide solution (5%). The yield of phthalophthalhydrazide was 98% : mp > 400°C (lit. 350-360°C)[2]; ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.88-8.08 (m, 2 C_6H_4).

3,6-diphenylcyclohexene anhydride 2.7.

To a solution of 2.06 g (10 mmol) of 1,4-diphenyl butadiene in 10 mL of benzene was added 1.96 g (20 mmol) of maleic anhydride. The reaction mixture was refluxed for 16 h. Upon cooling to room temperature white crystals formed which recrystallized from *o*-xylene giving the desired product in 90% yield: mp 209-211°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 3.69-3.84 (m, 4 H, PhCH-CH-CO), 6.53 (s, 2 H, CH=CH), 7.32-7.42 (m, 10 H, 2 C_6H_5).

3,6-diphenyl phthalic anhydride 2.1n.

The procedure reported by Weizmann [12] was used with some modification. To 9.12 g (30 mmol) of 3,6-diphenylcyclohexene anhydride was added 0.5 g of Pd/C (5%) under nitrogen. The reaction mixture was heated at 240°C for 10h. After cooling to room temperature it was washed with 50 mL chloroform and filtered to give a yellow solution. The solvent was removed under reduced pressure and the resulting solid was recrystallized from chloroform giving 3.15 g pale yellow crystals in 35% yield : mp 234-236°C (lit. 224°C); ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.47-7.61 (m, 10H, $2C_6H_5$), 7.83 (s, 2H, C_6H_2).

N-amino-3,6-diphenyl phthalimide 2.4n.

To a mixture of 3 g (10 mmol) of 3,6-diphenylphthalic anhydride in 20 mL of 1,4-dioxane was added 1 mL (20 mmol) of hydrazine monohydrate. The reaction mixture was refluxed for 12h then cooled to room temperature to furnish product in the form of white crystals (2.8 g, 90%) : mp 215-217°C (Found: C, 76.67; H, 4.65; N, 9.16. $C_{20}H_{14}N_2O_2$ calcd. C, 76.42; H, 4.49; N, 8.91%) ^{1}H NMR (200 MHz, DMSO-d_6) δ 4.83 (s, 2H, exchanged with D_2O, NH_2),7.45-7.59 (m, 10H, $2C_6H_5$), 7.72 (s, 2H, C_6H_2). HRMS (CI with NH_3) m/e (calcd for $C_{20}H_{14}N_2O_2$+H^+, 315.1133; found, 315.1133) 315 (100), 289 (8), 226 (12).

Acetylated 3,6-diphenyl phthalhydrazides 2.11a or 2.11b.

The reaction conditions and the amount of reactants were similar to the synthesis of compound **2.4n** except that 20 mL of glacial acetic acid was used instead of 1,4-dioxane and the reaction run for 2 h. The isolated product was 3.1 g (86% yield) : mp 265-268°C HRMS (EI with DI) m/e (calcd for $C_{22}H_{16}N_2O_3$ 356.1161 found, 356.1169); ^{1}H NMR (200 MHz, DMSO-d_6) δ 2.01 (s, 3H, CH_3), 7.45-7.61 (m, 10H, $2C_6H_5$), 7.84 (s, 2H, C_6H_2), 10.61 (s, 1H, exchanged with D_2O, NH).

When the reaction was run for longer time the peak at 10.61 ppm disappeared and a new peak at 2.11 ppm corresponding to the protons of a new acetyl CH_3 group appeared.

N-phthalimido-3,6-diphenyl phthalimide 2.10.

To a mixture of 3.14 g (10 mmol) of N-amino-3,6-diphenyl phthalimide in 20 mL of glacial acetic acid was added 1.48 g (10 mmol) of phthalic anhydride. The reaction mixture was heated to reflux for 4h. After cooling the product was formed as white crystals in 95% yield: mp 223-226°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.47-7.66 (m, 10H, $2C_6H_5$), 7.96 (s, 2H, C_6H_2), 7.99-8.12(m, 4H, C_6H_4).

4-Chloro phthalimide 2.2k.

A mixture of 9.1 g (50 mmol) of 4-chlorophthalic anhydride and 10 mL of ammonium hydroxide (27%) was heated for 2 h until evolution of water had ceased and a clear liquid formed . After cooling the product solidifed. It was ground up to form a powder (8.3 g, 91% yield) : mp 214-217°C (lit. 210°C).[13]

4-Chloro-N-aminophthalimide 2.4k.

To a cooled mixture of 1.81 g (10 mmol) of 4-chlorophthalic anhydride in 20 mL of ethanol (96%) was added 0.5 mL (10 mmol) of hydrazine monohydrate. The reaction mixture was stirred for 2 min. at room temperature and 2 min. at reflux. After adding 50 mL of cold water pale yellow crystals formed. The resulting crystals were filtered and recrystallized from ethanol to give 4-chloro-N-aminophthalimide in 20% yield: mp 172-175°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 4.90 (s, 2H, exchanged with D_2O, NH_2), 7.82-7.92 (m, 3H, C_6H_3); it solidifies after melting and melts again around 345°C. HRMS (CI with NH_3) m/e (calcd for $C_8H_5N_2O_2Cl$ 196.0039 found, 196.0034)

6-Chloro 2,3-dihydrophthalazine-1,4-dione 2.3k.

The filtrate of the reaction mixture of 4-chloro-N-amino phthalimide was acidified with dilute HCl (2%). The white precipitate was filtered and washed several times with water and dried to give 1.2 g (61%) of product.: mp 351-355°C (lit. 348-350°C)[14]; ^{1}H NMR

(200 MHz, DMSO-d_6) δ 11.73 (s, 2H, exchanged with D_2O, NH), 7.88-8.09 (m, 3H, C_6H_3).

3-Hydroxyphthalimide 2.2h.

It was prepared in a manner similar to imide **2.2k** and was isolated as white needles in 70% yield after recrystallization from water, mp 266-267°C (lit. 255-256°C).[3]

4-(4-Methylphenoxy) phthalimide 2.2m.

To a round bottom flask equipped with Dean-Stark trap and nitrogen inlet was added 4.12 g (20 mmol) of N-methyl-4-nitrophthalimide, 2.16 g (20 mmol) of *p*-cresol, 2.07 g (15 mmol) of potassium carbonate, 30 mL of DMF and 10 mL of benzene. The reaction mixture was refluxed for 6 hours during which water and most of the benzene was removed by azeotropic distillation. Then it was allowed to cool for several hours and poured into water. The crude product was extracted with methylene chloride and the organic layer was washed with an aqueous solution of potassium bicarbonate and dilute HCl and finally dried over anhydrous magnesium sulfate. The solvent was removed and after treating with ether white crystals formed. It gave 3.5 g (70%) 4-aryloxy-N-methylphthalimide after drying. mp 97-100°C. The product was hydrolyzed with 10 mL of 50% aqueous KOH for 24 h and after acidifying with dilute HCl 4-(4-methylphenoxy) phthalic acid was obtained. This was dried for the next step. A 2 g portion of this acid was dissolved in 20 mL of 30% ammonium hydroxide. The mixture was heated until all the hydroxide solution evaporated and then the temperature was increased to melt the imide product. The melt was kept at 200°C until the evolution of ammonia had ceased then the melt was allowed to cool to room temperature. The solid was crushed and recrystallized from ethanol to give 1.5 g (89%) product **2.2m** (overall yield was 60%). mp 171-173°C.

6-(4-Methylphenoxy) phthalhydrazide 2.3m.

To a cooled mixture of 1.28 g (5 mmol) **2.2m** in 25 mL of ethanol (96%) was added 0.25 mL (5 mmol) of hydrazine monohydrate. The reaction mixture was stirred for 2 min. at room temperature and 20 min. at reflux. Upon cooling to room temperature product was precipitat which was filtered and dried to give 1.15 g (87%) **2.3m** : mp 271-274°C, (Found: C, 66.90; H, 4.49; N, 10.43. $C_{15}H_{12}N_2O_3$ calcd. C, 67.16; H, 4.51; N, 10.44 %), ^{1}H NMR (200 MHz, DMSO-d_6) δ 2.34 (s, 3H, CH_3), 7.05-7.29 (d, J_{HH}=8.5, 4H, C_6H_4), 7.22-8.07 (m, 3H, C_6H_3), 11.49 (s, 2H, exchanged with D_2O, NH).

N-aminoarylimide 2.9.

A solution of 0.395 g (1 mmol) of **2.8** in 10 mL of hydrazine monohydrate was stirred at room temperature for 2 h. Hydrazine was removed completely under reduced pressure and the resulting solid was dried under vacuum at 80°C for 24 h to give 0.39 g (100%) of the pale yellow solid **2.9**. mp > 400°C, HRMS (CI with NH_3) m/e (calcd for $C_{24}H_{16}N_2O_4$ 396.1110; found, 396.1113) ^{1}H NMR (200 MHz, DMSO-d_6) δ 4.88 (s, 2H, exchanged with D_2O, NH_2), 6.93 (d, J_{HH} = 10.5,4H), 7.23 (d, J_{HH} = 10.5,4H), 7.61-7.81 (m, 4H), 9.70 (s, 2H, exchanged with D_2O, OH).

Bisimide 2.10.

A mixture of 0.39 g (1 mmol) of **2.9** and 0.20 g (1.3 mmol) of phthalic anhydride in 50 mL of acetic acid was refluxed for 2h. The solvent was distilled off under atmospheric pressure and the resulting yellow solid was recrystallized from ethanol/H_2O (50:50) to give 0.46 g (90%) bisimide **2.10** as fine needles : mp 330-335°C, HRMS (CI with NH_3) m/e (calcd for $C_{32}H_{18}N_2O_6$ 526.1165 found, 526.1149); ^{1}H NMR (200 MHz, DMSO-d_6) δ 6.94 (d, J_{HH}=10.4,4H), 7.32 (d, J_{HH}=10.5,4H), 7.76-7.91 (m, 4H), 7.90-8.12 (m, 4H) 9.78 (s, 2H, exchanged with D_2O, OH).

Poly(aryl ether sulfone) 2.9P.

To a solution of 1 g polymer **2.8P** in 10 mL of chloroform was added 1 mL of hydrazine monohydrate and the mixture was refluxed for 1 h. The polymer which precipitated during the reaction was isolated and redissolved in hot *sym*-tetrachloroethane (TCE) and reprecipitated into methanol to give pale yellow fibers. The resulting polymer was dried under vacuum at 180-200°C for 2 h to give polymer **2.9P** in quantitative yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30 (s, 36H, $C(CH_3)_3$), 4.18 (s, 2H, exchanged with D_2O, NH_2), 7.14-7.98 (m, 20H, all aromatics).

Poly(aryl ether sulfone) 2.10P.

To a solution of 0.5 g of polymer **2.9P** in 10 mL of TCE was added 1 g of phthalic anhydride and the mixture was heated at 120°C for 1 h. The resulting solution precipitated into methanol to give pale yellow fibers which were dried under vacuum at 180-200°C for 2 h to give polymer **2.10P** in quantitative yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (s, 36H, $C(CH_3)_3$), 7.12-7.82 (m, 20H, aromatics), 7.84-7.96 (m, 4H, phthalimide).

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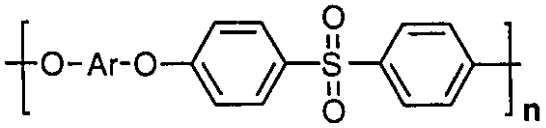
CHAPTER 3

SYNTHESIS OF NEW DIFUNCTIONAL MOLECULES AND THEIR POLYMERIZATION WITH BISPHENOLS THROUGH AN AROMATIC NUCLEOPHILIC DISPLACEMENT REACTION

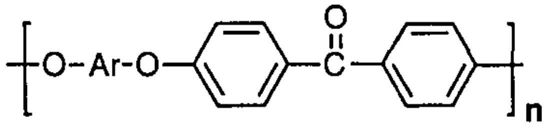
3.1. Introduction

Displacement of halogens from activated arylhalides by nucleophiles in dipolar aprotic solvents is a well known reaction. This method has been found a useful and versatile synthetic tool and many aromatic polymers have been prepared by reaction of bisphenates with activated aromatic dihalides.[1-4] Poly(ether sulfone)s (PES) **3.1**, poly(ether ether ketone)s (PEEK) **3.2** and poly(ether ketone)s (PEK) **3.3** are among the most important commercial polymers of this type (Figure 3.1).

The nucleophilic displacement of aromatic nitro groups has been known for many years. The important keys to the success of this reaction are: presence of strong electron-withdrawing groups to activate nitro displacement and use of dipolar aprotic solvents. Among the activating groups cyano group is the most effective followed by N-substituted imide, keto and ester groups.[5-6]



3.1



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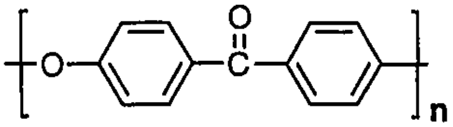

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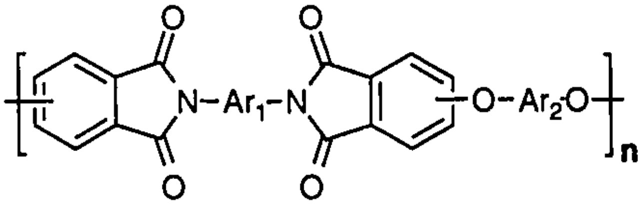
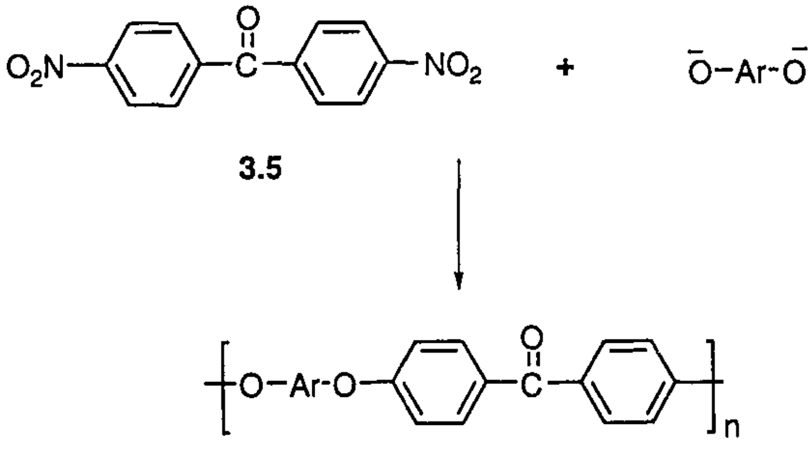


3.4

Figure 3.1. General structure of four commercial polymers

Scheme 3.1



3.5

3.2

Radlmann was the first to report the synthesis of the high molecular weight aromatic polyethers by taking the advantage of the quantitative yield obtained in nitro displacement reactions.[7] These reactions were carried out in dimethyl sulfoxide (DMSO) as solvent using 4,4'-dinitrobenzophenone **3.5** and bisphenols (Scheme 3.1). Displacement of the nitro group by phenoxides in nitrophthalic esters proceeded in reasonably high yield.[5] A number of high molecular weight aromatic poly(ether nitrile)s, poly(ether ketone)s and poly(ether imide)s have been prepared by this method.

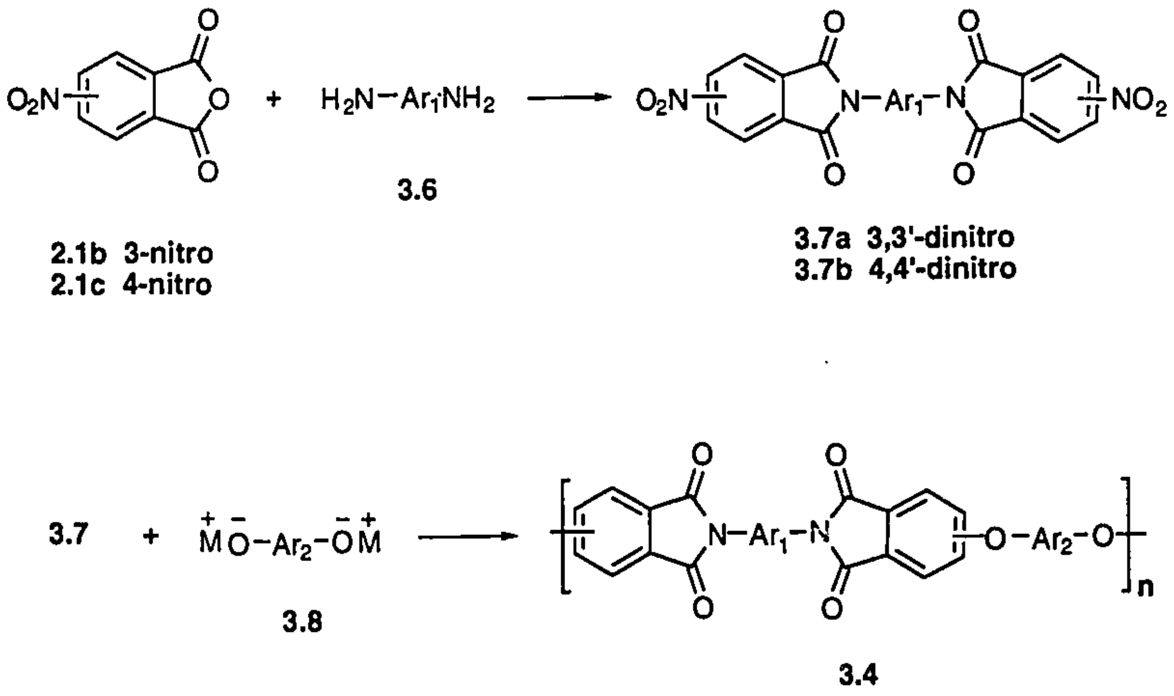
3.1.1. Poly(ether imide)s by nucleophilic displacement polymerization

Poly(ether imide)s of the general structure **3.4** (Figure 3.1) can be prepared in two steps including *cyclization* and *displacement*. In the cyclization step, which is also called the imidization step, the imide ring is formed and in the displacement step the ether linkage is formed. The order of these two steps in polymerization leads to two general methods of synthesis of poly(ether imide)s. When cyclization is followed by displacement the method is called displacement polymerization.

Studies on the model reaction of aniline with 3 or 4-nitrophthalic anhydride **2.1b,c** show that N-phenylphthalimides can be readily obtained as crystalline products in high yield.[6] The high yield of these model reactions was the basis for making different bisnitroimides **3.7a,b** from aromatic diamines and anhydrides **2.1b,c**. Among the various aromatic diamines **3.6** (Scheme 3.2) which have been used, phenylene diamines and 4,4'-diaminobiphenyl give the highest melting bisimides. Diamines such as oxydianiline and methylenedianiline produce relatively lower melting bisimides.[6]

Bisnitroimides **3.7a,b** are subsequently subjected to nitro displacement polymerization with various bisphenol salts **3.8** in dipolar aprotic solvents (Scheme 3.2). Nitro groups activated by two carbonyls are very labile to nucleophilic displacement. The high reactivity of N-substituted nitrophthalimides is attributed to the strong electron-withdrawing effect of two carbonyl groups as well as their coplanarity in relation to the plane of the benzene ring. Similarly, bishaloimides were reported to undergo displacement polymerization [8-9], but the reaction requires higher temperatures as compared to nitro displacement which occurs at room temperature. The relative reactivity of different leaving groups toward nucleophilic displacement is: $NO_2 > F > Cl$.[10]

Scheme 3.2



2.1b 3-nitro
2.1c 4-nitro

3.6

3.7a 3,3'-dinitro
3.7b 4,4'-dinitro

3.7

3.8

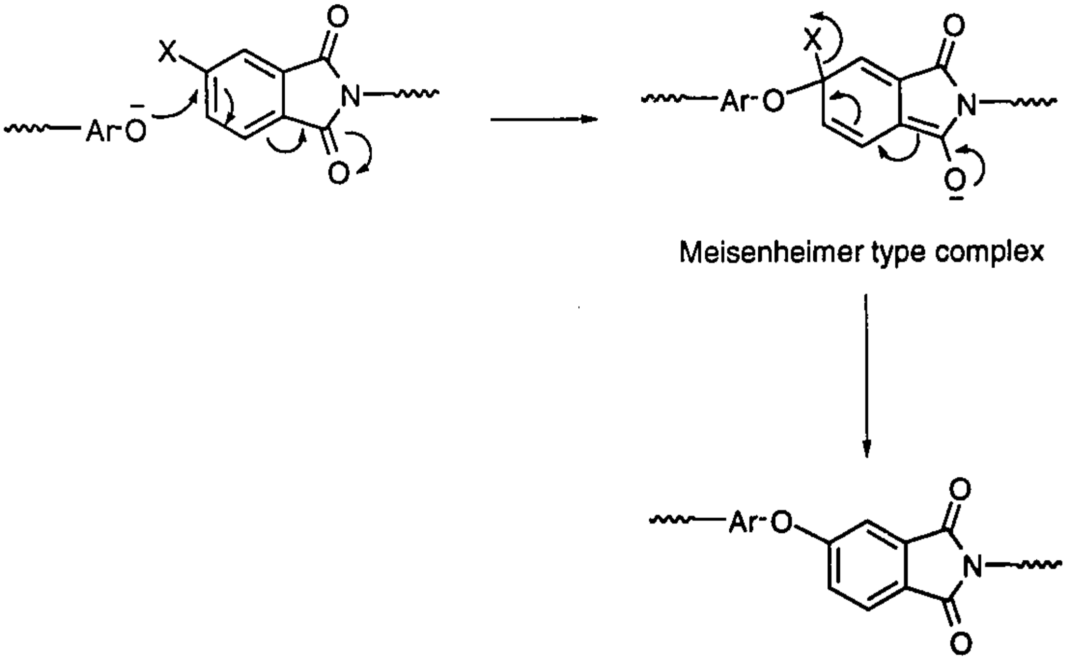
3.4

The major requirement in the displacement step is the formation of anhydrous bisphenol salt before the polymerization can take place. Different procedures have been used to dehydrate bisphenols to form anhydrous salts.[6,17] These procedures basically consist of using a base in a mixture of an aprotic solvent such as DMSO and a cosolvent, usually toluene, for azeotropic distilation of water. Potassium or sodium hydroxide and potassium carbonate are the most comonly used bases.[6,11] It is important when using hydroxides that the exact amount of base be used or a stoichiometric imbalance could lead to side reactions and termination of polymerization. However, in the case of carbonates an excess amount of base can frequently be used without causing any problem.[11]

3.1.2. Mechanism of nucleophilic displacement reaction

Displacement of the activated nitro or halo groups is believed to occur in two steps. The first step is attack of the nucleophile, phenolate, and formation of a Meisenheimer type complex. The negative charge in this intermediate is delocalized by the contribution of the electron-withdrawing groups, carbonyls of the imide ring in the case of phthalimides (Scheme 3.3). The next step is the elimination of the leaving group and formation of the ether linkage. The rate determining step can be either of these two steps depending on the nature of the leaving group and the stability of the intermediate. For better leaving groups on unactivated rings the addition of a nucleophile would be the rate limiting step and in the case of poor leaving groups on activated rings the elimination step is usually the rate limiting step. The position of the leaving groups has a significant effect on the overall rate of the reaction, for example, 3-nitrophthalimide undergoes displacement reaction much faster than 4-nitrophthalimide.[12] This is probably because of the steric hinderance between the nitro and the carbonyl groups in 3-nitrophthalimide which favours formation of the less hindered intermediate.

Scheme 3.3

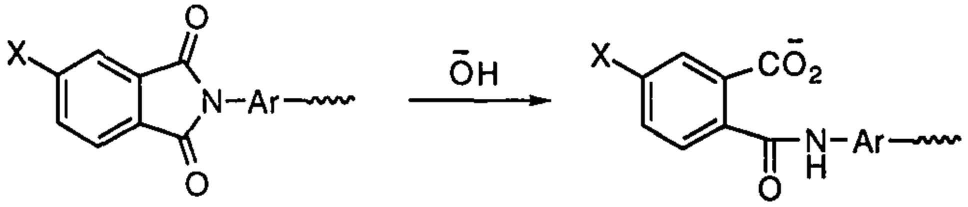


3.1.3. The most critical factor in nucleophilic displacement polymerization

The most critical factor in nucleophilic displacement polymerization is the control of stoichiometry of monomers. Therefore, the formation of the bisphenol salts and complete removal of water is a critical step in the polymerization. This step becomes even more important in the case of polyimides since the imide groups can be ring-opened under basic conditions. Dehydration of bisphenols in the presence of a base by azeotropic distillation is not usually an efficient way to ensure complete dehydration and sometimes, especially in case of polyimides, it is necessary to use other means, such as molecular sieves or calcium hydride, to remove trace amounts of water from the reaction. Inefficient removal of water will cause formation of hydroxide ion from an equilibrium reaction between bisphenolate and water. Hydroxide ions readily attack imides and produce amic acid salts (Scheme 3.4). These side reactions cause two major problems in the course of polymerization. One is that some of the bisphenolates are converted back to bisphenols, which are not active nucleophiles, and the second is the hydrolysis of imides to amide acids which terminate the polymerization since the amic acid is no longer reactive toward the nucleophilic displacement reaction.

Scheme 3.4

$$2\bar{O}H \quad + \quad HO{-}Ar{-}OH \quad \rightleftharpoons \quad \bar{O}{-}Ar{-}\bar{O} \quad + \quad 2H_2O$$



3.2. Goals

It is known that polyimides containing ether linkages, so called poly(ether imide)s, have excellent physical and thermal properties as well as good processability by conventional processing techniques. Poly(ether imide)s can be made by nucleophilic displacement polymerization from a difunctional bisimide and a bisphenol.

We have already discussed the synthesis and properties of bisphthalimides and bisphthalhydrazides from hydrazine in chapter 2. They are thermally stable materials. We set out to synthesize polyimides from hydrazine-derived compounds by preparing some new difunctional bisphthalimides and bisphthalhydrazides followed by polymerization of these monomers with different bisphenols via the aromatic nucleophilic displacement reaction.

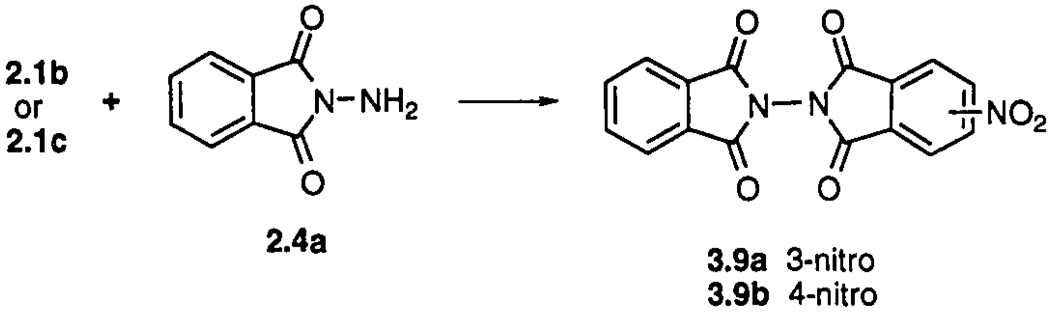
Since the synthesis of dinitro compounds from hydrazine and phthalic anhydride has some limitations as discussed in chapter 2, we decided to concentrate our attempt on the preparation of some dichloro and chloro-nitro compounds and study their polymerization with bisphenols under different reaction conditions.

3.3. Monomer synthesis

3.3.1. Synthesis of nitro-N-phthalimidophthalimide 3.9a,b as a model compound

As mentioned in section 3.1.1, displacement of the nitro group in N-substituted nitrophthalimides is a low temperature, quantitative reaction. We found no examples of similar reactions on substituted N-phthalimidophthalimide in the literature. The major question to be answered was whether the N-N linked bisimide structures would survive under the displacement reaction conditions. In order to answer this question, two isomers of 3 and 4-nitro-N-phthalimidophthalimide **3.9a,b** were synthesised by the reaction of N-aminophthalimide **2.4a** with 3 and 4-nitrophthalic anhydride **2.1b,c** according to the procedure described in chapter 2 (Scheme 3.5). The reactions took place like the classical type of anhydride-amine reaction in acetic acid and the products formed within a few minutes in boiling solvent and were isolated as pale yellow crystals in high yields (95-96%).

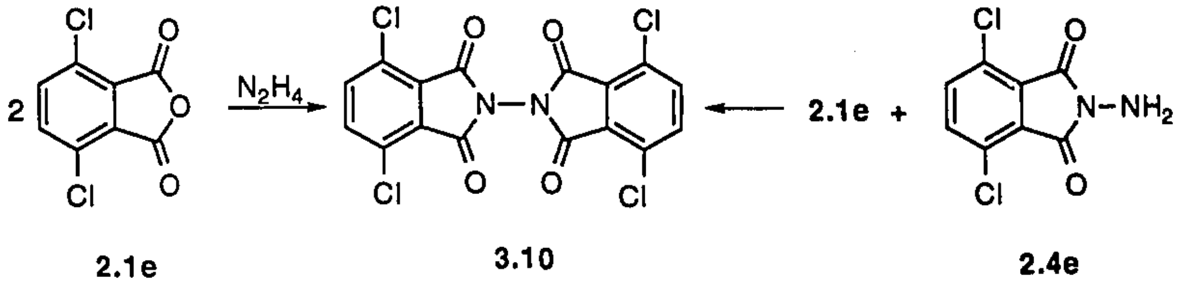
Scheme 3.5



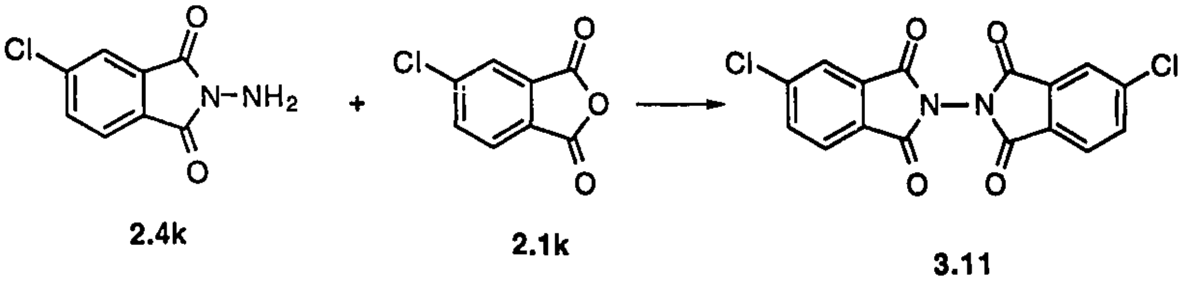
3.3.2. Synthesis of 4,4'-dichloro-N-phthalimidophthalimide 3.11

Drew and Pearman showed that the 3,3',6,6'-tetrachloro-N-phthalimidophthalimide **3.10** can be prepared from the condensation of 3,6-dichloro-N-aminophthalimide **2.4e** with 3,6-dichlorophthalic anhydride **2.1e** in acetic acid. It was also shown that this reaction takes place in one pot simply be mixing 2M of anhydride **2.1e** with 1M of hydrazine in boiling acetic acid (Scheme 3.6). This is a high yield reaction due to the effect of bulky chlorines which favors the 5-membered imide ring formation (refer to section 2.4.2 in chapter 2). Since the reaction of 4-chlorophthalic anhydride with hydrazine must be done under controlled conditions to obtain 5-membered ring product in its highest possible yield, it was decided to prepare 4,4'-dichloro-N-phthalimidophthalimide **3.11** by condensation of 4-chloro-N-aminophthalimide **2.4k** with 4-chlorophthalic anhydride **3.15** instead of using the one-pot method. Thus we prepared dichloro compound **3.11** from **2.4k** and **2.1k** in acetic acid as solvent (Scheme 3.7). The reaction is very fast and the product forms in a few minutes.

Scheme 3.6



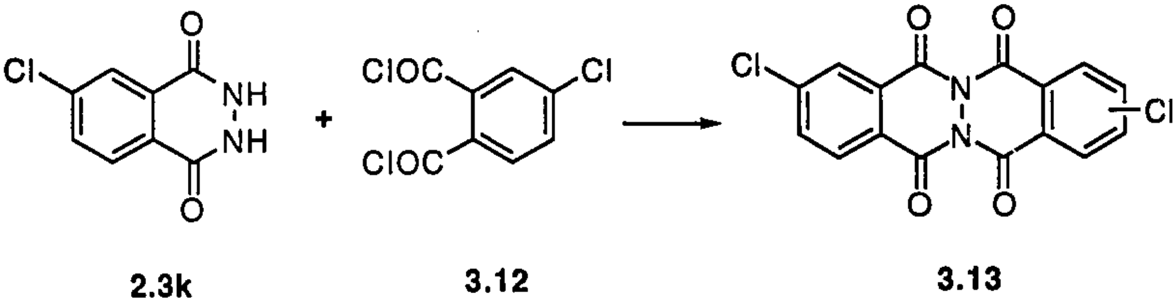
Scheme 3.7



3.3.3. Synthesis of 6,6'-dichloro-N-phthalophthalhydrazide 3.13

Synthesis of both isomers of nitrophthalophthalhydrazide from the reaction of nitrophthalhydrazides with phthaloyl dichloride or nitrophthaloyl dichlorides with phthalhydrazide has been reported to be low yield reaction giving a mixture of products compared with the same reaction using unsubstituted starting materials which is almost quantitative.[16] This is probably because of the strong electronic effect of the nitro group which promotes side reactions. It seems reasonable to expect that the condensation of nitrophthalhydrazides with nitrophthaloyl dichlorides for preparation of dinitrophthalophthalhydrazides should be a low yield reaction. When we tried reaction of 6-chlorophthalhydrazide **2.3k** with 4-chlorophthaloyl dichloride **3.12** the desired product, dichlorophthalophthalhydrazide **3.13**, was isolated in 58% yield after 2h reaction in hot nitrobenzene (Scheme 3.8). The melting point of compound **3.13** (300-307°C) is considerably lower than the unsubstituted one and has a broad range which is probably because of the presence of two isomers.

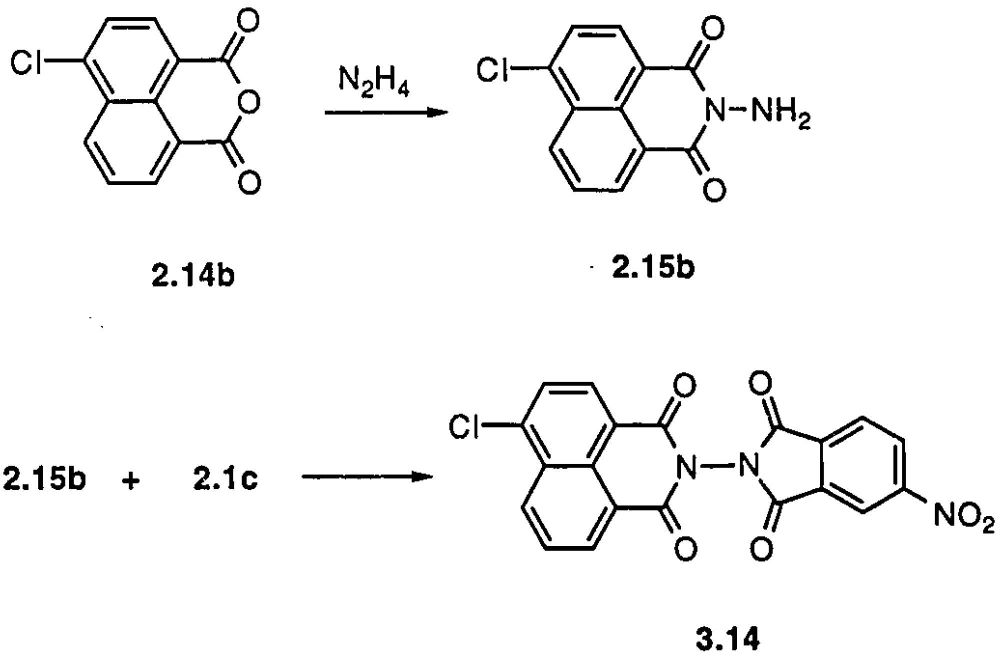
Scheme 3.8



3.3.4. Synthesis of unsymmetric bisimide 3.14

Since the unsymmetric bisimides can be obtained in quantitative yield from the condensation of N-amino-1,8-naphthalimide with phthalic anhydride, it seemed possible to obtain difunctional bisimides for use as monomers in displacement polymerization by using substituted starting materials. Therefore, N-amino-4-chloro-1,8-naphthalimide **2.15b**, which was prepared by the reaction of 4-chloro-1,8-naphthalenedicarboxylic anhydride **2.14b** with hydrazine, was condensed with anhydride **2.1c** and the unsymmetric chloronitrobisimide **3.14** obtained in high yield (95%). The reaction was very fast and the product precipitated from the reaction mixture within a few seconds (Scheme 3.9).

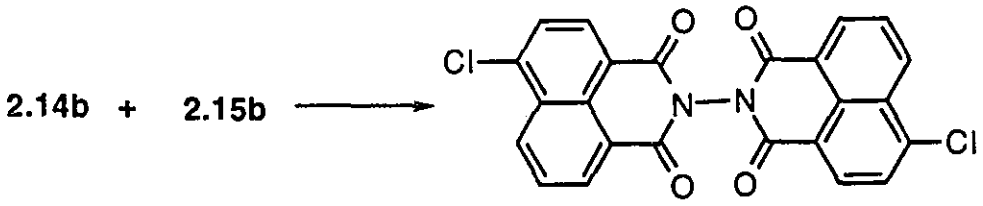
Scheme 3.9



3.3.5. Synthesis of dichloro bisnaphthalimides 3.17a,b from dianhydrides

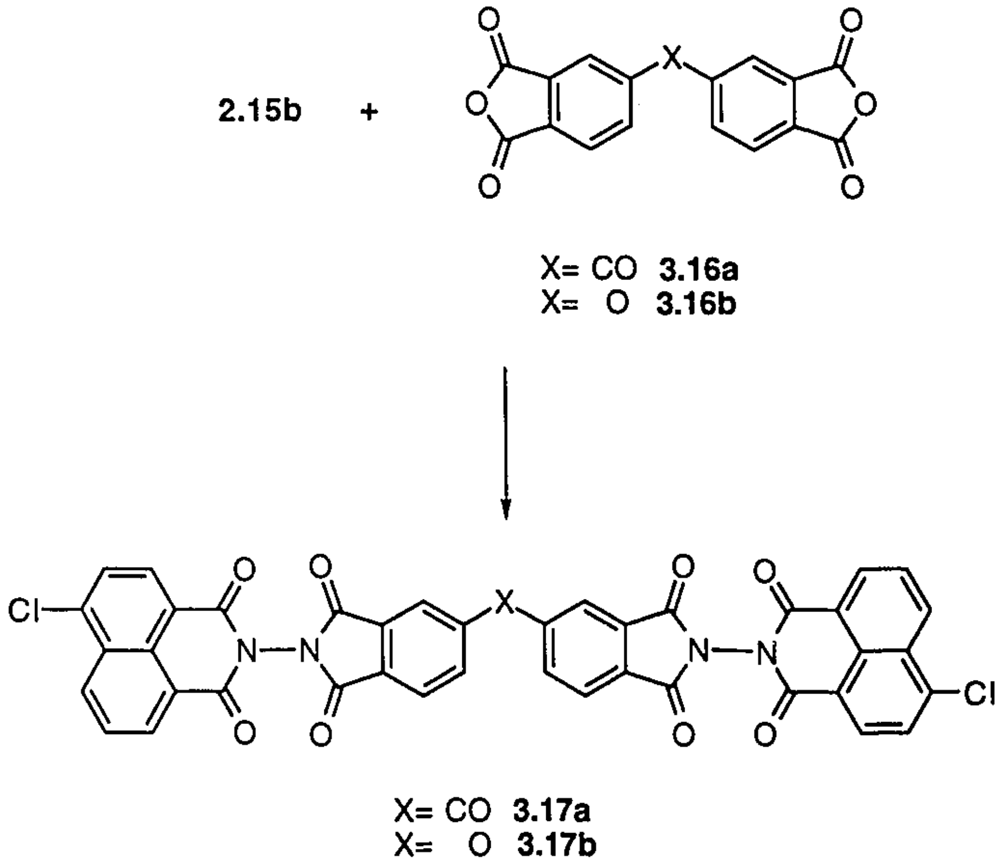
Even though bisimide **3.14** can be used as a polymerizable monomer, its unsymmetric structure and different functional groups may cause some problems in the polymerization stage owing to the difference in the reactivity of chloro and nitro groups. An alternative option involved the preparation of a bischloronaphthalimide. This was done by reaction of N-aminoimide **2.15b** with anhydride **2.14b** resulting in bischloronaphthalimide **3.15** (Scheme 3.10). But this compound was very insoluble in most solvents and therefore not very suitable for polymerization. In order to enhance the solubility of this monomer, the same reaction was conducted between **2.15b** and a dianhydride. Benzophenone tetracarboxylic dianhydride (BTDA) **3.16a** and oxydiphthalic anhydride (ODPA) **3.16b** were selected because they contain solubilizing flexible linkages. Dianhydrides **3.16a** and **3.16b** reacted with **2.15b** to give dichloro compounds **3.17a** and **3.17b**, respectively (Scheme 3.11). Both compounds were slightly soluble in NMP and DMSO at room temperature.

Scheme 3.10



3.15

Scheme 3.11



3.4. Polymer synthesis

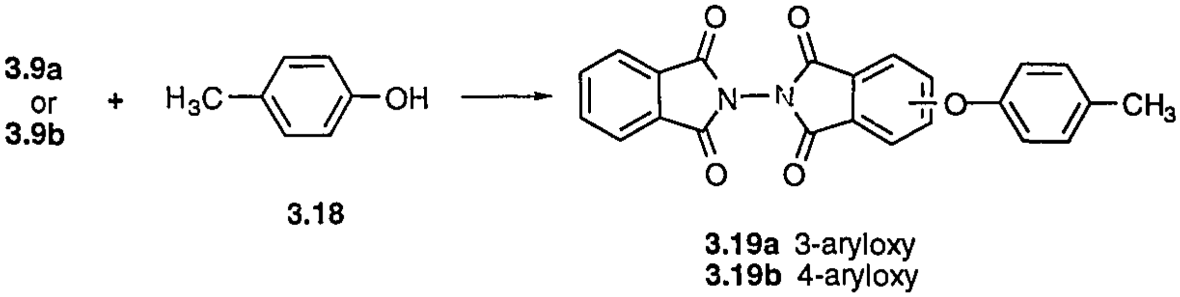
3.4.1. Displacement reaction on model compounds 3.9a,b

The reactivity of the nitro group toward the displacement reaction and the stability of the bisimide structure containing an N-N linkage under conditions similar to those used in the polymerization reaction was investigated in a model reaction with nitro compounds **3.9a** and **3.9b**. It was very important to know the yield of this reaction, which is a key factor in any condensation polymerization, in order to determine the possibility of using this type of bisimide as polymerizable monomers. Since the nitro group in phthalimide is known to be very labile and can be easily displaced, we expected to obtain similar results in the hydrazine-derived bisimide and bishydrazide systems. However, since these bisimides and bishydrazides with a direct N-N linkage show considerably lower stability in a basic environment, one may expect to see some hydrolysis side reactions during the displacement polymerization reaction. Although dichloro compounds **3.11** and **3.13** have been used for the polymerization step, we decided to conduct our model reaction on the nitro compounds which are the most frequently used materials of this type. This allowed us to compare our results with others and also optimize our reaction conditions.

Two methods of preparation of bisphenolate salts were examined to determine the most efficient manner for displacement of the nitro group. The first procedure involved using NaOH in DMSO and the second is based on K_2CO_3 in DMAc or NMP. In both methods the phenolate salt of p-cresol **3.18** was prepared in a dehydration step before addition of the nitro compound.

Both bisimides **3.9a** and **3.9b** react with the phenolate salt very rapidly at temperatures around 60-80°C. The yield of the reaction for both isomers in the NaOH method was higher (80-90%) than the K_2CO_3 method (70-80%). In the K_2CO_3 method an excess amount of carbonate was used which might have caused side reactions to occur with the imide ring or nitro group. The presence of some colored materials, especially in the K_2CO_3 method, which were very soluble in methanol indicated the existence of these side reactions.

Scheme 3.12

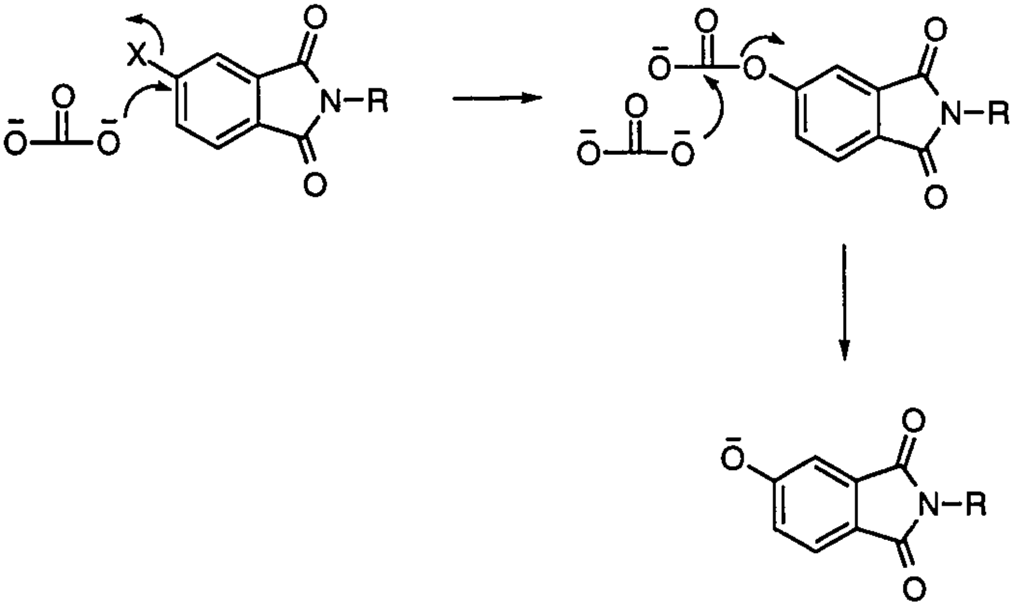


Phenolate salt formation in the NaOH system is faster and more efficient than the K_2CO_3 method. In the K_2CO_3 method stoichiometric control of the base is not necessary and it can be used in excess, therefore the K_2CO_3 method is preferred in many condensation reactions. However, since it is known that in the case of displacement reaction on imides complete formation of anhydrous phenolate salt before addition of imide is essential (see section 3.1.3) then it is likely that the presence of K_2CO_3 in excess may cause some undesirable side reactions such as attack on the imide ring or displacement of nitro or halo groups (Scheme 3.13). Although the results of the model reactions showed that the NaOH method gives higher yield and less side reactions, we decided to examine both methods as well as some other new methods in our polymerization attempts.

3.4.2. Attempt to polymerise bisimide 3.11 and bishydrazide 3.13

Since the nitro displacement reaction on model compounds **3.10a,b** showed some promising results, it was then decided to conduct polymerization reactions using the dichloro monomers **3.11** and **3.13** prepared previously. Unfortunatly, when these monomers were reacted with bisphenol-A (BPA) **3.22** in DMAc or NMP/toluene using potassium carbonate as a base only low molecular weight polymers were obtained in low yield (yield < 60%).

Scheme 3.13

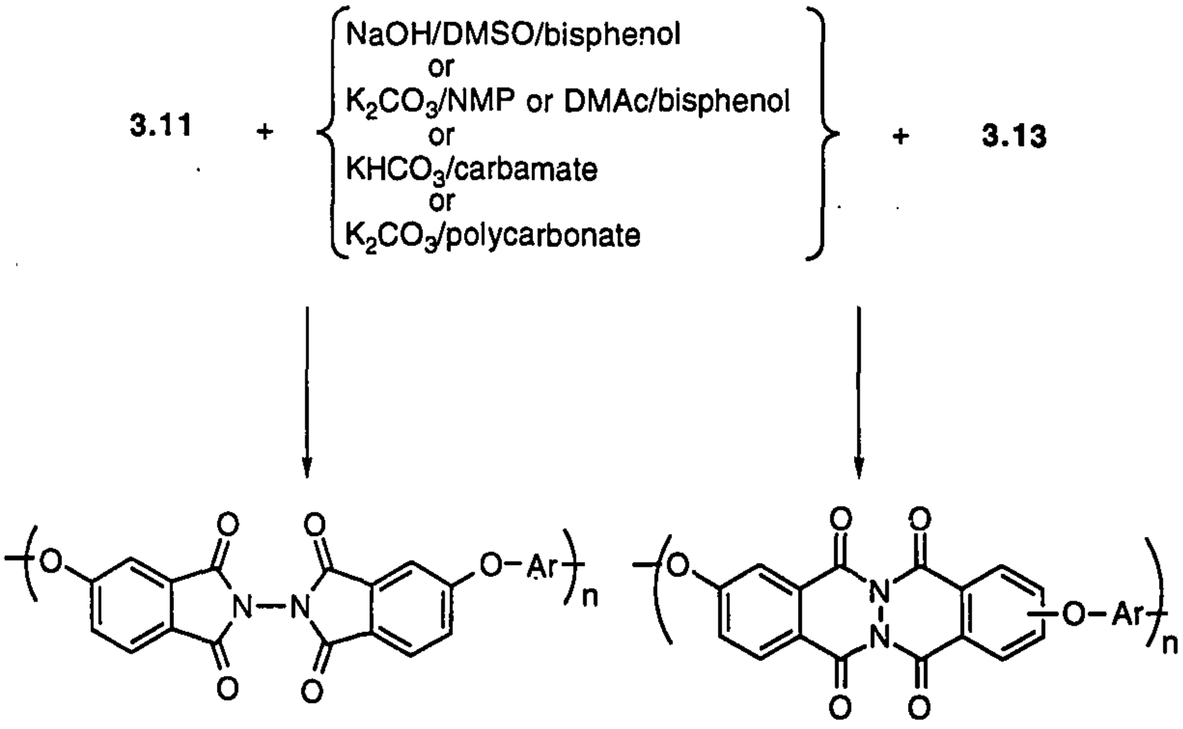


The yield of the reaction was not improved by employing a calcium hydride drying tube for further removal of trace amounts of water, assuming that the azeotropic distillation was not efficient enough in the water removing step. The same result was obtained when BPA **3.22** was replaced with bisphenol fluorenone (BPF) **3.23** (Figure 3.2). As we learned from the model reactions, we expected to obtain better results by using the NaOH system, therefore similar experiments were carried out using sodium hydroxide as base. First, the bisphenolate salt was prepared in the presence of a stoichiometric amount of NaOH and after complete dehydration, the dichloro compound was added to the mixture. This technique improved the yield in the polymerization in some cases up to 80%. Inherent viscosities of the resulting materials also showed some increase in molecular weight, but it was still below the minimum amount (≈ 0.3 dL/g) required for a polymer to be considered high enough in molecular weight. The results of different experiments using the NaOH procedure showed that the polymers **3.20** made from bisimide **3.11** had higher viscosities than the polymers **3.21** formed from bishydrazide **3.13**. This was surprising because the bishydrazide with a fused six-membered ring structure was expected to be hydrolytically more stable than the corresponding bisimide. Although the NaOH route produced higher molecular weight polymers, some difficulties in controlling the stoichiometry of the reagents in the dehydration step and bisphenolate insolubility pose a problem in the polymerization reaction. It was of interest therefore to examine other methods for our purposes.

The use of masked bisphenols was recently found to be a convenient method for the synthesis of some polymers.[14] In this method carbamate or carbonate derivatives of bisphenols are first prepared from the reaction of an alkyl isocyanate or dialkyl carbonate with a bisphenol, respectively. Both carbamates and carbonates of bisphenols are rapidly cleaved in the polymerization reaction mixture by potassium hydrogen carbonate to generate potassium bisphenolate *in situ*. The volatile by-products, carbon dioxide or alkylamine, are easily removed from the reaction system. Lexan **3.25**, which is a commercial polycarbonate, is another form of masked bisphenol and has been successfully used in the synthesis of poly(arylene ether)s.[14] The major advantage of using masked bisphenols is that no water is formed during the polymerization and therefore it should be a good choice for water sensitive polymerization reactions.

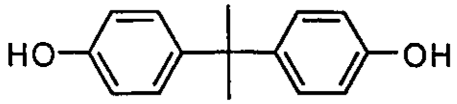
Since we believe that the main reason for obtaining low viscosity products in low yield was the hydrolysis of the imide ring, it was decided to take the advantage of the masked bisphenol method in our polymerization systems to investigate how water-free conditions would affect the results of polymerization. Therefore, bisphenol-A dicarbamate **3.24** (Figure 3.2) was prepared from n-propyl isocyanate and bisphenol-A and then introduced to the bisimide **3.11** in NMP in the presence of potassium hydrogen carbonate. Formation of a gray suspension in the early stage of polymerization indicated that some ring opening took place during the reaction. A small aliquot removed from the reaction mixture was completely soluble in methanol which was further evidence of the ring opening side-reaction. Moreover, there was no evolution of n-propylamine, as monitored by pH paper. This observation was initially surprising, but then it was realized that n-propylamine could be consumed by a reaction with the bisimide ring and interfere with the polymerization reaction. We then moved our attention to the polycarbonate system. Polycarbonate **3.25** (Figure 3.2) in the presence of potassium carbonate decomposes to potassium bisphenolate and carbon dioxide. Unfortunatly, the results of using this system showed not much improvement and a similar gray suspension appeared during the polymerisation.

Scheme 3.14

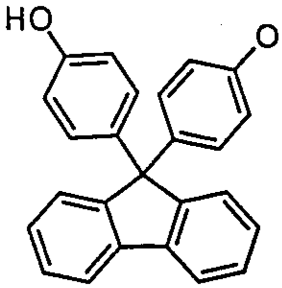


3.20

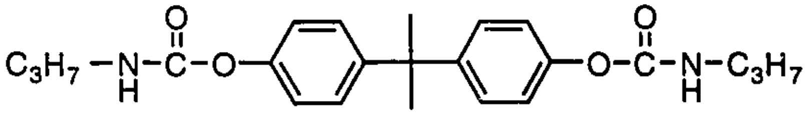
3.21



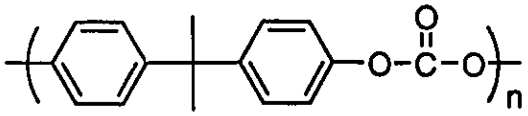
3.22



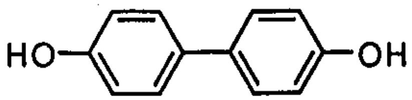
3.23



3.24



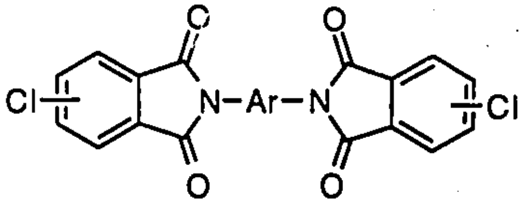
3.25



3.26

Figure 3.2. Bisphenols and masked bisphenols

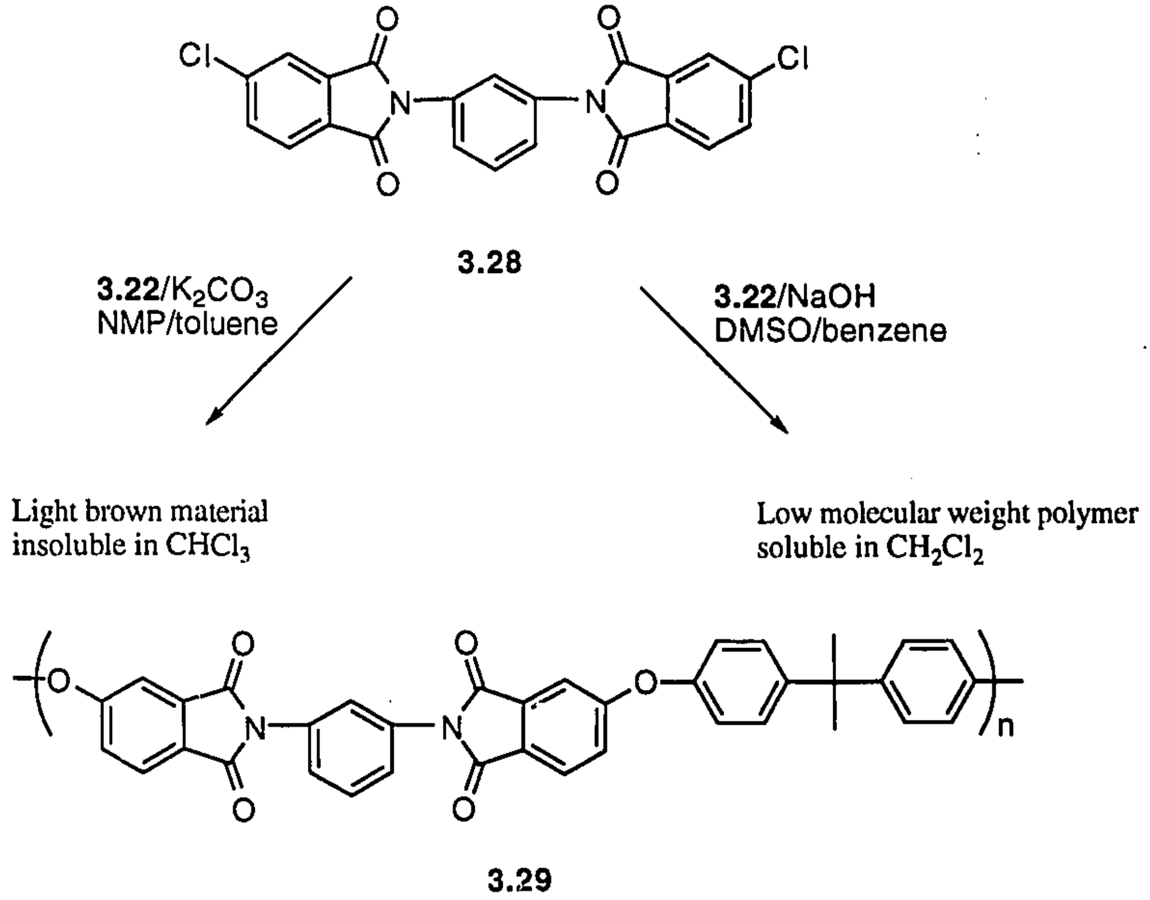
Considering all these observations, the most likely explanation for the unsuccessful polymerization of bisimide **3.11** and bishydrazide **3.13** is that these monomers are not stable under the reaction conditions and undergo ring-opening by the attack of nucleophiles such as phenolates or carbonate. These side reactions become more significant in the case of the chloro displacement reaction which is relatively slow. There is some supporting evidence in the literature which indicates that the chloro displacement polymerization of different bischlorophthalimides of the type **3.27** (Figure 3.3) generally forms low molecular weight polymers with intrinsic viscosities around 0.1-0.2 dL/g. This was further confirmed by polymerization of dichloro bisimide **3.28** with BPA **3.22** under two different reaction conditions. Both conditions would produce a poly(ether imide) commercially known as ULTEM **3.29** (Scheme 3.15). When potassium carbonate was used the reaction mixture was not homogeneous and showed a light brown color and the resulting material was insoluble in chloroform. The same reaction in DMSO/NaOH gave low molecular weight polymer as a white powder which was readily soluble in methylene chloride as would be expected for ULTEM. This experiment added more evidence to the possibility of side reactions involving opening of the imide ring in the presense of K_2CO_3.



3.27

Figure 3.3. Bischlorophthalimide

Scheme 3.15

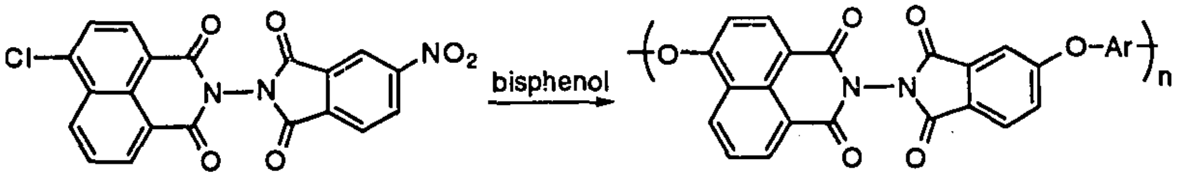


3.4.3. Polymerization of unsymmetric bisimide 3.14

While chloro displacement in phthalimides is a relatively slow reaction and needs longer reaction times and higher temperatures, it has been shown that chloronaphthalimides undergo the same reaction under milder conditions.[15] Therefore, we were interested to find out how bisimide **3.14**, with different functional groups, would react with bisphenolates. It was expected that by increasing the reactivity of the monomer toward the displacement, the relative amount of the side reactions involving cleavage of the imide ring would decrease.

Several experiments were carried out using polycarbonate or bisphenol/potassium carbonate systems at lower temperatures. In all cases the appearance of a gray suspension similar to that obtained in previous experiments was noticed, indicating the occurrence of ring opening side reactions. However, the results looked promising and indicated that more reactive monomers improve the yield of the reaction and hence the molecular weight of the resulting polymers. The same reaction using the NaOH procedure gave better results, as was expected, and low molecular weight polymer **3.30** was obtained with inherent viscosity of 0.13 dL/g. Table 3.1 shows the results of these reactions.

Table 3.1. Reaction conditions and results of polymerization of 3.14



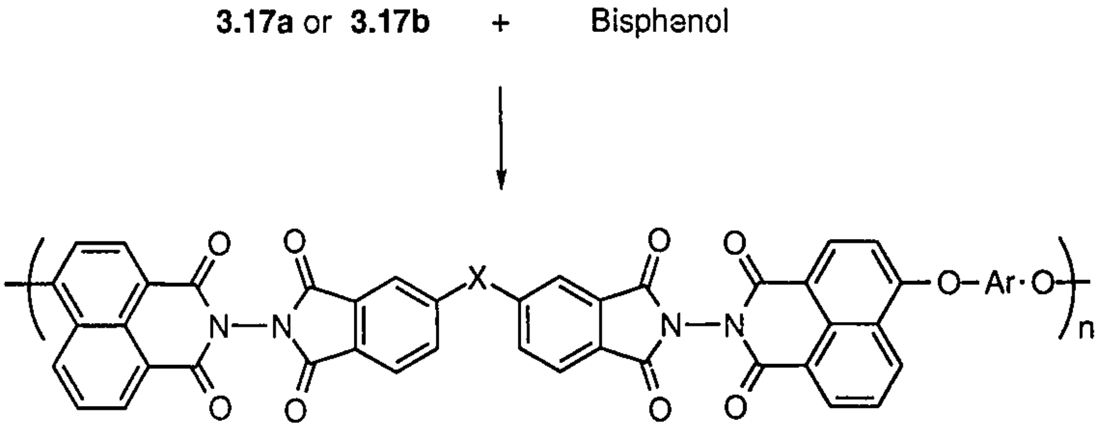
3.14 **3.30**

Reagents	Solvents	Time (h)	T (°C)	Yield (%)	η_{inh}(dL/g) ($CHCl_3$)	Solubility in $CHCl_3$
3.22/K_2CO_3	DMAc/toluene	48	30-120	67	-	partially soluble
3.26/K_2CO_3	NMP/toluene	24	70-90	54	-	partially soluble
3.22/NaOH	NMP/toluene	6	80-100	60	0.13	soluble
3.24/K_2CO_3	NMP/benzene	12	50-100	58	-	partially soluble

3.4.4. Poly(ether imide)s from dichloro compounds **3.17a** and **3.17b**

Having determined that the chloronaphthalimide system showed some improvement over the phthalimide system, we examined this system further to see if the scope of this reaction could be extended to symmetric bischloronaphthalimide compounds. This was done by reacting dichloro compounds **3.17a** and **3.17b** with bisphenols under different reaction conditions (Scheme 3.16). The results, which are summarized in table 3.2, showed that polymers **3.31a,b** with inherent viscosities up to 0.24 dL/g were obtainable. Lack of solubility of these monomers in most common solvents below 60°C was a major problem and required higher reaction temperatures which increased the possibility of ring opening side reactions. Again, the presence of a brown color during the polymerization and the color of the resulting polymers was good evidence for the presence of some side reactions.

Scheme 3.16



X= CO **3.31a**
X= O **3.31b**

Table 3.2. Reaction conditions and results of polymerization of 3.17a,b

Reagents	Solvents	Time (h)	T (°C)	Yield (%)	η_{inh}(dL/g) (NMP)	Solubility
3.17a/3.22/K_2CO_3	NMP/toluene	4	100-120	87	0.19	NMP
3.17a/3.22/K_2CO_3	sulfolane/toluene	12	150-180	86	0.24	NMP
3.17a/3.23/K_2CO_3	sulfolane/phCl	6	120-150	-	0.17	NMP
3.17b/3.22/K_2CO_3	NMP/toluene	20	140-160	93	0.11	NMP
3.17b/3.22/K_2CO_3	DMSO/toluene	20	100	89	0.14	NMP

3.5. Conclusion

A number of bisimide and bishydrazide monomers were prepared from hydrazine and different aromatic anhydrides. The overall yields for the synthesis of these monomers are good to excellent. They were subjected to the nucleophilic displacement polymerization reaction in order to synthesize new types of poly(ether imide)s and poly(ether hydrazide)s. In all of the cases formation of some insoluble materials during the polymerization reaction was observed. The products were partially soluble in a mixture of methanol and water, indicating the existence of side reactions on the imide and hydrazide rings. Generally, the sodium hydroxide system gave better results in polymerization reactions compared to the potassium carbonate method. It was found that the imide ring in **3.11** and hydrazide ring in **3.13** are not hydrolytically stable in the presence of potassium carbonate. The chloro group in phthalimide and phthalhydrazide systems is not reactive enough for displacement and the polymerization reaction was acompanied by hydrolysis of the imide and hydrazide rings. With the more reactive naphthalimide system, as in the case of dichloro monomers **3.17a** and **3.17b**, the amount of side reactions was significantly reduced. By using the potassium carbonate method and dichloro monomers **3.17a,b** low molecular weight polymers were obtained in relatively high yield.

3.6. Experimental

General methods

N-methylpyrrolidinone (NMP; Aldrich), dimethylsulfoxide (DMSO, BDH) and dimethylacetamide (DMAc; Aldrich) were dried by distilling over calcium hydride and stored over 4Å molecular sieves. 4,4'-(Isopropylidine) bisphenol (BPA) **3.22**, 4,4'-biphenol, 9,9'-bis(4-hydroxyphenyl)fluorene (BPF) **3.23**, polycarbonate **3.25** (Mw=69000, D=2.88), 4-chlorophthalic anhydride **2.1k** and 4-nitro-N-methylphthalimide were kindly supplied in high purity from the General Electric Company and were used as recieved. 3,3',4,4'-Benzophenone tetracarboxylic dianhydride **3.16a** (BTDA; Aldrich) was first recrystallized from acetic anhydride and then sublimed under reduced pressure. 4,4'-Oxydiphthalic anhydride **3.16b** (ODPA; Chriskev) was sublimed under reduced pressure before use. 4-chloro-1,8-naphthalic anhydride **2.14b** was recrystallized once from toluene and then from acetic anhydride. Tetramethylene sulfone (sulfolane; Aldrich), toluene (A&C), p-cresol (Aldrich), chlorobenzene (Aldrich), anhydrous potassium carbonate (Baker), anhydrous potassium bicarbonate (Aldrich), phosphorous pentachloride (Aldrich), 18N aq sodium hydroxide (BDH), n-propyl isocyanate and hydrazine monohydrate (Aldrich) were used as obtained.

3-nitro-N-phthalimido phthalimide 3.9a

This compound was prepared from the reaction of **2.1b** and **2.4a** according to the procedure described in the literature.[16] The product was isolated as pale yellow crystals (95% yield), mp 249-252°C (lit. 249-250°C).

4-nitro-N-phthalimidophthalimide 3.9b

This compound was prepared from reaction of **2.1c** and **2.4a** similar to the procedure used for **3.9a**. The product was isolated as pale yellow crystals (96% yield), mp 254-256°C (lit. 250°C).[16]

Model reactions to make 3.19a using potassium carbonate

To a 50 mL 3-neck flask equipped with a Dean-Stark trap, water condenser, nitrogen gas inlet and thermometer was added 0.35 g (3 mmol) **3.18**, 0.3 g (2.1 mmol) potassium carbonate, 5 mL DMAc and 3 mL toluene. The mixture was heated to reflux for 4h and then toluene was slowly removed from the Dean-Stark trap and the mixture was allowed to cool down. When the temperature of the mixture reached 50°C, **3.9a** was added and the mixture was stirred at this temperature for 6h and then at 80°C for 2h. The reaction mixture was cooled to room temperature and poured into water. The crude solid was filtered and recrystallized from methanol to give the product **3.19a** (0.83 g, 72%), mp 232-235°C, 1H NMR (200 MHz, DMSO-d6) δ 2.32 (s, 3H,PhCH_3), 7.14-7.33 (m, 4H, $C_6H_4CH_3$), 7.76-4.95 (m, 3H, C_6H_3), 8.03-8.15 (m, 4H, C_6H_4).

Model reactions to make 3.19b using potassium carbonate

Compound **3.19b** was prepared similar to **3.19a** in 80% yield. mp 236-238°C, 1H NMR (200 MHz, DMSO-d6) δ 2.33 (s, 3H,phCH3), 7.12-7.31 (m, 4H, $C_6H_4CH_3$), 7.74-4.96 (m, 3H, C_6H_3), 8.04-8.17 (m, 4H, C_6H_4).

Model reactions to make 3.19a and 3.19b using sodium hydroxide

These two compounds were also synthesized using this method with the following changes. Potassium carbonate was replaced by aqueous sodium hydroxide, DMSO was used as solvent instead of DMAc. The yields of the reactions for **3.19a** and **3.19b** were 86% and 90%, respectively.

4,4'-Dichloro-N-phthalimidophthalimide 3.11.

To a mixture of 0.44 g (2.4 mmol) 4-chlorophthalic anhydride in glacial acetic acid (10 ml) was added 0.47 g (2.4 mmol) 4-chloro-N-amino-phthalimide **2.4k**. The reaction mixture was refluxed for 30 min. and then it was allowed to cool for several hours. The white solid was filtered and washed with 50 mL of ammonium hydroxide solution (5%) to give 4,4'-dichloro-N-phthalimido phthalimide **3.11** (0.74 g, 85%). mp 303-305°C (Found: C, 53.07; H, 1.91; N, 7.85. $C_{16}H_6N_2O_4Cl_2$ calcd. C, 53.21; H, 1.67; N, 7.76%) ^1H NMR (200 MHz, DMSO-d6) δ 8.10-8.25 (m, C_6H_3).

4-Chlorophthaloyl dichloride 3.12

It was prepared from reaction of phosphorous pentachloride with **2.1k** as described in the literature.[13]

6,6'-Dichloro-2,3-dihydrophthalazine-1,4-dione 3.13.

In a 100 mL round bottom flask equipped with condenser and nitrogen inlet was added 1.96 g (10 mmol) 6-chloro 2,3-dihydrophthalazine-1,4-dione **2.3k**, 2.37 g (10 mmol) 4-chloro phthaloyl dichloride **3.12** and 20 mL of nitrobenzene. The reaction mixture was heated at 160°C for 1h and then at 200°C for 15 min. and then it was allowed to cool for several hours. The white precipitate was filtered and washed several times with ammonium hydroxide solution (5%) to give a mixture of isomers of 6,6'-dichloro 2,3-dihydrophthalazine-1,4-dione (2.1 g, 58%). mp 300-307°C (Found: C, 53.11; H, 1.63; N, 7.58. $C_{16}H_6N_2O_4Cl_2$ calcd. C, 53.21; H, 1.67; N, 7.76%); 1H NMR (200 MHz, DMSO-d6) δ 8.05-8.26 (m, C_6H_3).

Unsymetric bisimide 3.14

To a 100 mL flask equipped with a condenser was added 2.46 g (10 mmol) **2.15b** (preparation described in chapter 2), 1.93 g (10 mmol) **2.1c** and 20 mL acetic acid. The mixture was refluxed for 15 min and then cooled down to 50°C. The pale yellow precipitate was filtered and dried to give product **3.14** (3.98 g, 95%). mp > 400°C (Found: C, 56.42; H, 1.99; N, 9.74. $C_{20}H_8N_3O_6Cl$ calcd. C, 56.96; H, 1.91; N, 9.96%)

Dichlorobisnaphthalimide 3.17a

To a 50 mL flask equipped with Dean-Stark trap and nitrogen inlet was added 0.49 g (2 mmol) **2.15b**, 0.32 g (1 mmol) **3.16a** and 10 mL chlorobenzene. The mixture was distilled for 30 min. and after cooling to 50°C the white precipitate was filtered and washed with acetone and extracted with hot ethanol. After drying 0.75 g (96%) of the dichlorobisimide **3.17a** was recovered. mp >400°C, MS (CI) m/e (calcd for $C_{41}H_{16}N_4O_9Cl_2$+H+, 779.0372; found, 779.0371) 779 (MH+, 17) 613 (31) 460 (100).

Dichlorobisnaphthalimide 3.17b

Compound **3.17b** was prepared similar to **3.17a**. The yield of the reaction was 92%. mp >400°C.

Polymer synthesis

Typical method: to a 50 mL 3-neck flask equipped with a Dean-Stark trap, water condenser, nitrogen inlet and thermometer was added 0.456 g (2 mmol) **3.22**, 0.332 g (2.4 mmol) potassium carbonate, 5.5 g sulfolane and 3 mL toluene. The mixture was heated to reflux for 4h and then the Dean-Stark trap was replaced with a calcium hydride tube and the mixture was refluxed for another 1h. The Dean-Stark trap was used again to remove the toluene slowly. The mixture was allowed to cool down until the temperature of the mixture reached 50°C. Then 1.556 g (2 mmol) **3.17a** was added and the mixture was stirred at this temperature for 1 h and slowly raised to 180°C during a period of 16 h. The reaction mixture became viscous so it was diluted with 5 mL chlorobenzene. After cooling to room temperature it was poured into mixture of 300 mL methanol and 100 mL water. The pale yellow material was filtered and extracted with acetone and dried to give 1.6 g (86%) of product. In some polymerization reactions aqueous NaOH was used instead of potassium carbonate.

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(16) Reference 2 in chapter 2

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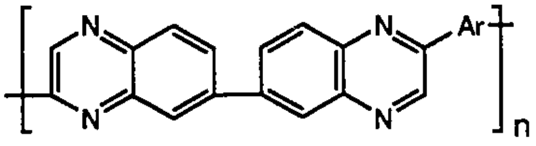
CHAPTER 4

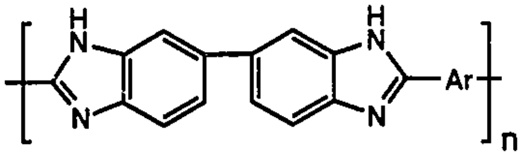
NOVEL POLY(ETHER IMIDE)S WITH REMARKABLY HIGH GLASS TRANSITION TEMPERATURES

4.1. Introduction

Polyimides are a class of high temperature stable polymers which have gained considerable importance in many engineering applications due to their excellent electrical, thermal and mechanical properties at elevated temperatures.[1-3] Among the different types of high temperature polyheterocycles attracting commercial attention such as polyquinoxalines[4] **4.1**, polybenzimidazoles[5] **4.2**, polybenzothiazoles[6] **4.3**, only aromatic polyimides **4.4** are important in a commercial context (Figure 4.1). Approximately 22% of the 1988 market of $ 2.3 billion for high temperature polymers was accounted for by polyimides which was exceeded only by those of fluoropolymers (e.g. PTFE) and aramides (e.g. Kevlar).[33] The main reason for the reputation of polyimides, beside their outstanding properties, is that they can be prepared from a variety of starting materials via different synthetic routes. This versatility allows the synthesis of polymers with a large range of properties and has led to the use of polyimides in a wide range of applications.



4.1



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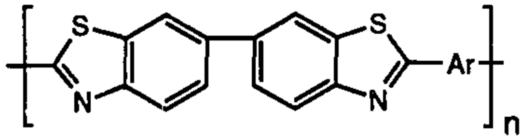

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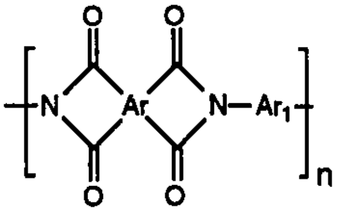


4.4

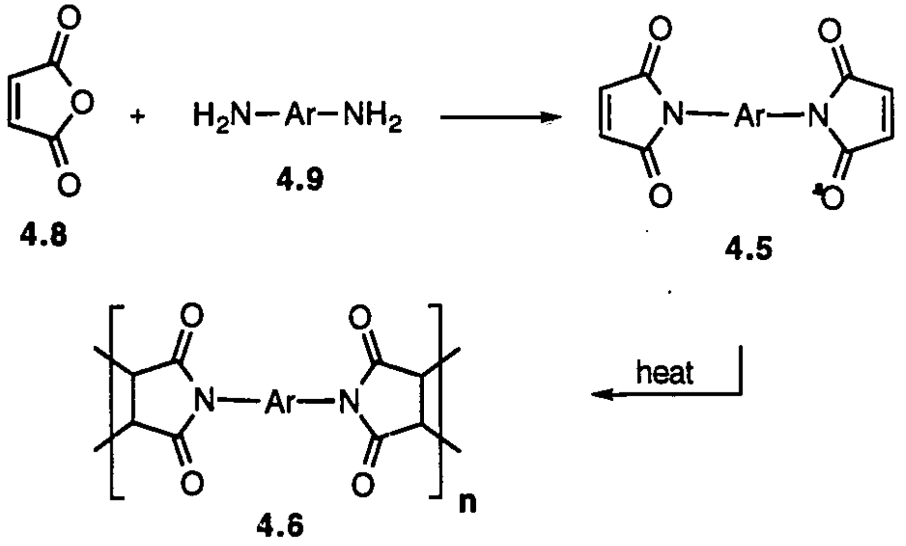
Figure 4.1. High temperature polyheterocycles

The major areas of application for polyimides include aerospace, automotive, general engineering and microelectronics.[1,2,7] In the aerospace industry, polyimides are used in structural composites and as high temperature adhesives. They also find use in load bearing structures in the automotive industry. General engineering application include high temperature bearings and seals. Polyimides have also found widespread use in microelectronics and electrical applications, as a dielectric for integrated circuits (ICs) and in electrical insulation.[51]

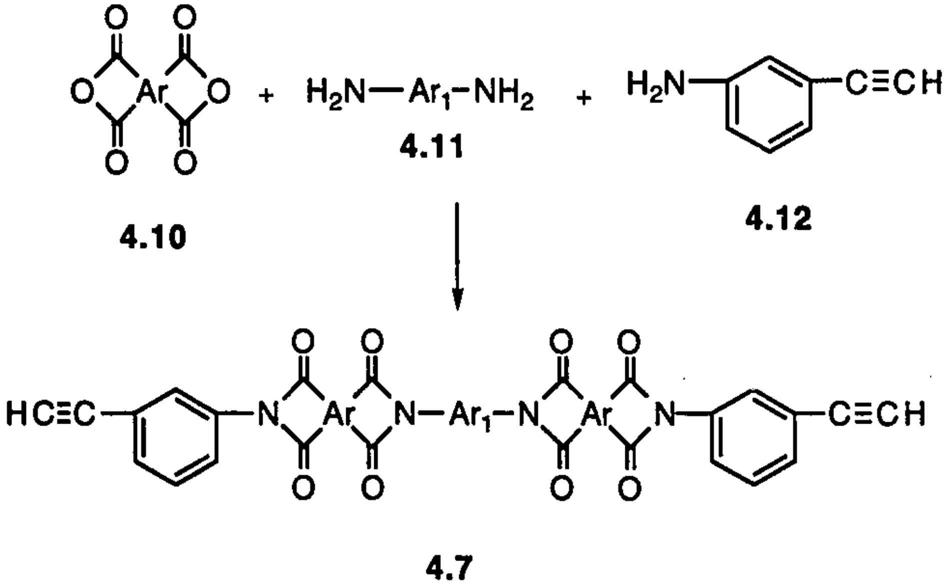
4.1.1. Preparation of polyimides

Different methods reported in the literature for the preparation of polyimides can be classified into two main routes: (i) *polyaddition.* (ii) *polycondensation.* Polyaddition is mainly carried out by addition of difunctional monomers or prepolymers which carry imide moieties in their backbone structure and are terminated by reactive groups such as maleimide **4.5** (Scheme 4.1) or acetylene **4.7** (Scheme 4.2). Since they give cross-linked networks after the curing process they are called thermosetting polyimides. Bismaleimides (BMI) **4.5** are used mainly in advanced composites. Kerimid 601® is a commercial BMI used in the manufacture of various aircraft engine parts.[1]

Scheme 4.1



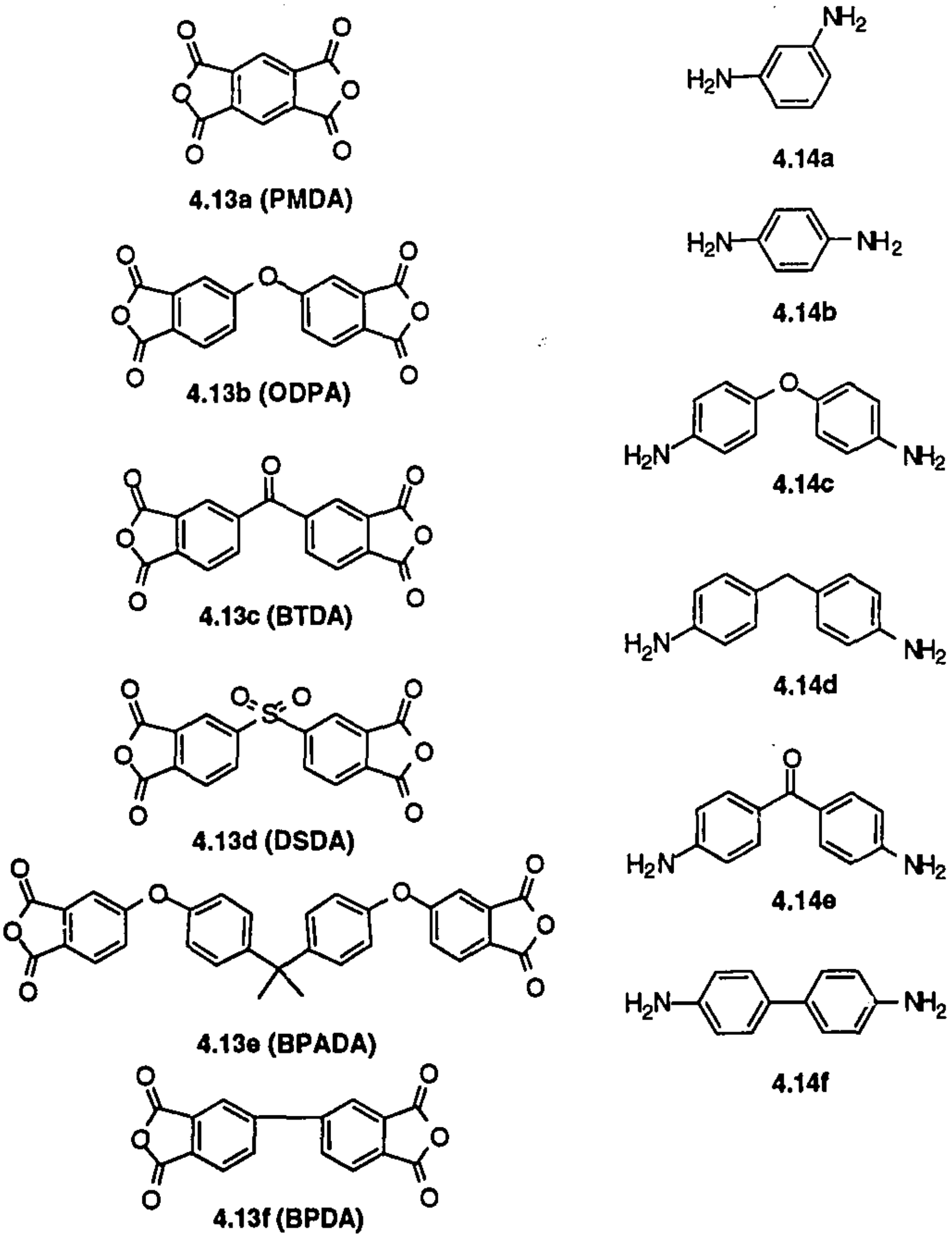
Scheme 4.2



The second route, polycondensation, is the most commonly used method in polyimide preparation. As for any classical condensation polymerization reaction it is characterized by the elimination of a small molecule which is evolved as a volatile by-product. Many different methods of synthesis have been used depending on the starting materials and condition of the reaction. Some of these methods are:

(i) Condensation of dianhydrides and diamines.
(ii) Displacement polymerization using bisphenols and dinitro bisimides.
(iii) Displacement polymerization using bisphenols and dihalo bisimides.
(iv) Condensation of dianhydrides and diisocyanates.
(v) Imide-amine exchange reaction.
(vi) Condensation of bisimides and aliphatic dichlorides.
(vii) Interchange reaction of aryloxy-substituted bisimides and bisphenols.

The first route which involves the condensation of aromatic tetracarboxylic acid dianhydrides **4.10** with primary aromatic diamines **4.11** is the oldest and most general method for preparing polyimides **4.4**. Many commercially available dianhydrides and diamines have been used (Figure 4.2). The reaction is carried out by both one and two-step methods.



4.13a (PMDA)

4.13b (ODPA)

4.13c (BTDA)

4.13d (DSDA)

4.13e (BPADA)

4.13f (BPDA)

4.14a

4.14b

4.14c

4.14d

4.14e

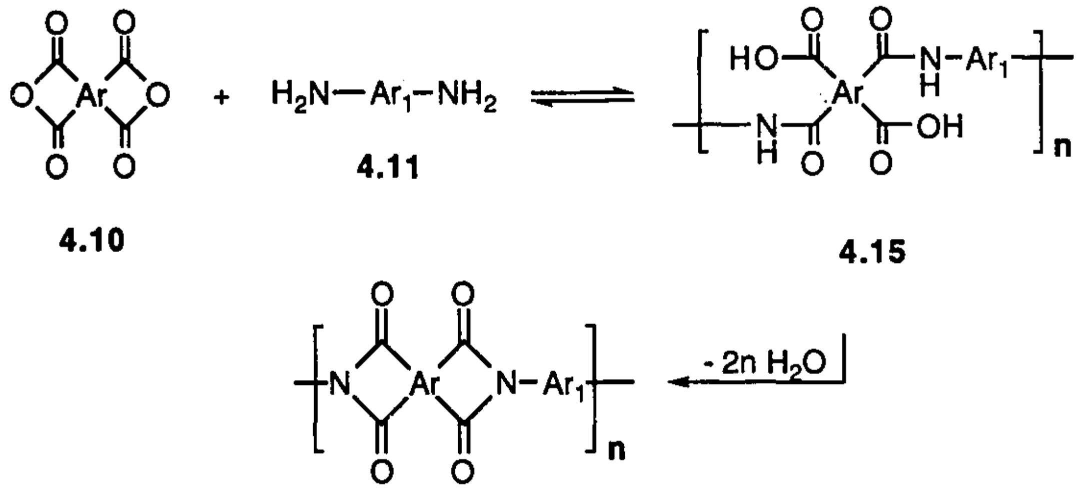
4.14f

Figure 4.2. The most commonly used dianhydrides and diamines

In the *two-step method* a tetracarboxylic acid dianhydride **4.10** reacts with an aromatic diamine **4.11** in a polar aprotic solvent (e.g. NMP, DMAc, DMSO), usually at ambient temperature, to produce a soluble polyamic acid **4.15** solution. This step is reversible, but in polar aprotic solvents the reverse reaction is not favored, therefore the reaction proceeds to high molecular weight polymer. Polyamic acid formation step is exothermic and decreasing the reaction temperature should therefore shift the equilibrium to the right and increase the polyamic acid molecular weight. The obtained polyamic acid is then converted to the corresponding polyimide **4.4** by either thermal or chemical imidization (cyclodehydration) (Scheme 4.3). Thermal imidization is induced by heating the polyamic acid **4.15** to 250-400°C in the solid state. Cyclisation can lead to either imide **4.23** or isoimide **4.24** structures, but if the latter is formed, it probably thermally rearranges to the imide. Scheme 4.4 shows one of the proposed mechanisms for thermal imidization. Chemical imidization of the polyamic acid is normally carried out by treatment with an aliphatic anhydride and a tertiary amine. The first step involves acylation of the acid to the corresponding anhydride **4.20**, followed by ring closure to either isoimide **4.24** or imide **4.23**. Rearrangement of the isoimide to the imide is catalyzed by the acetate ion (Scheme 4.5).

The most effective way to prepare polyimides that are soluble in organic solvents is via the *one-step method.* In this method dianhydride condenses with diamine in a high-boiling organic solvent such as *m*-cresol. The water generated is removed by using an azeotroping cosolvent such as toluene or chlorobenzene. Since most aromatic polyimides in imidized form are not soluble in their polymerization solvent (because of that they are made via the two-step method) relatively less studies have been done on the mechanism and kinetics of the one-step procedure. This method is sometimes useful for polymerization of unreactive monomers.

Scheme 4.3

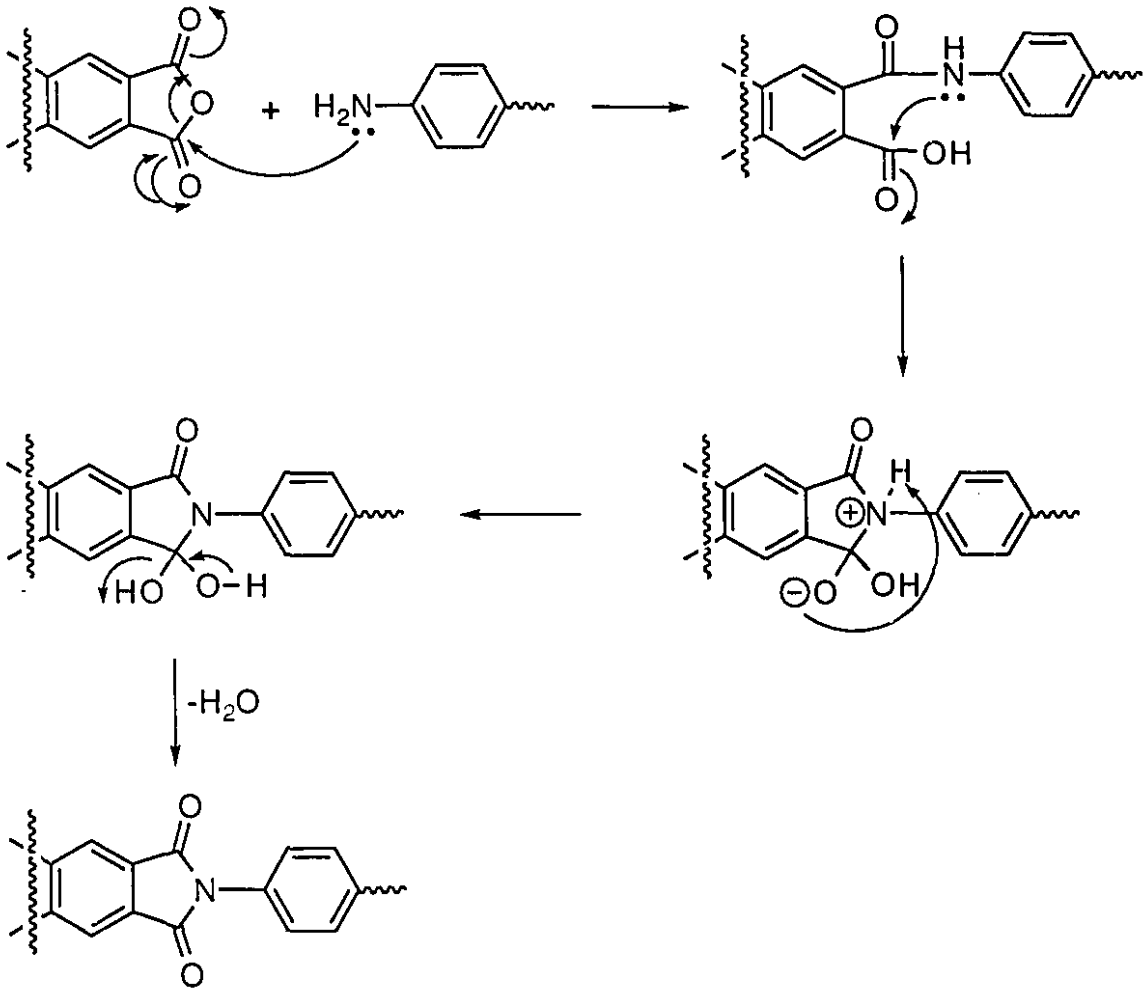


4.10

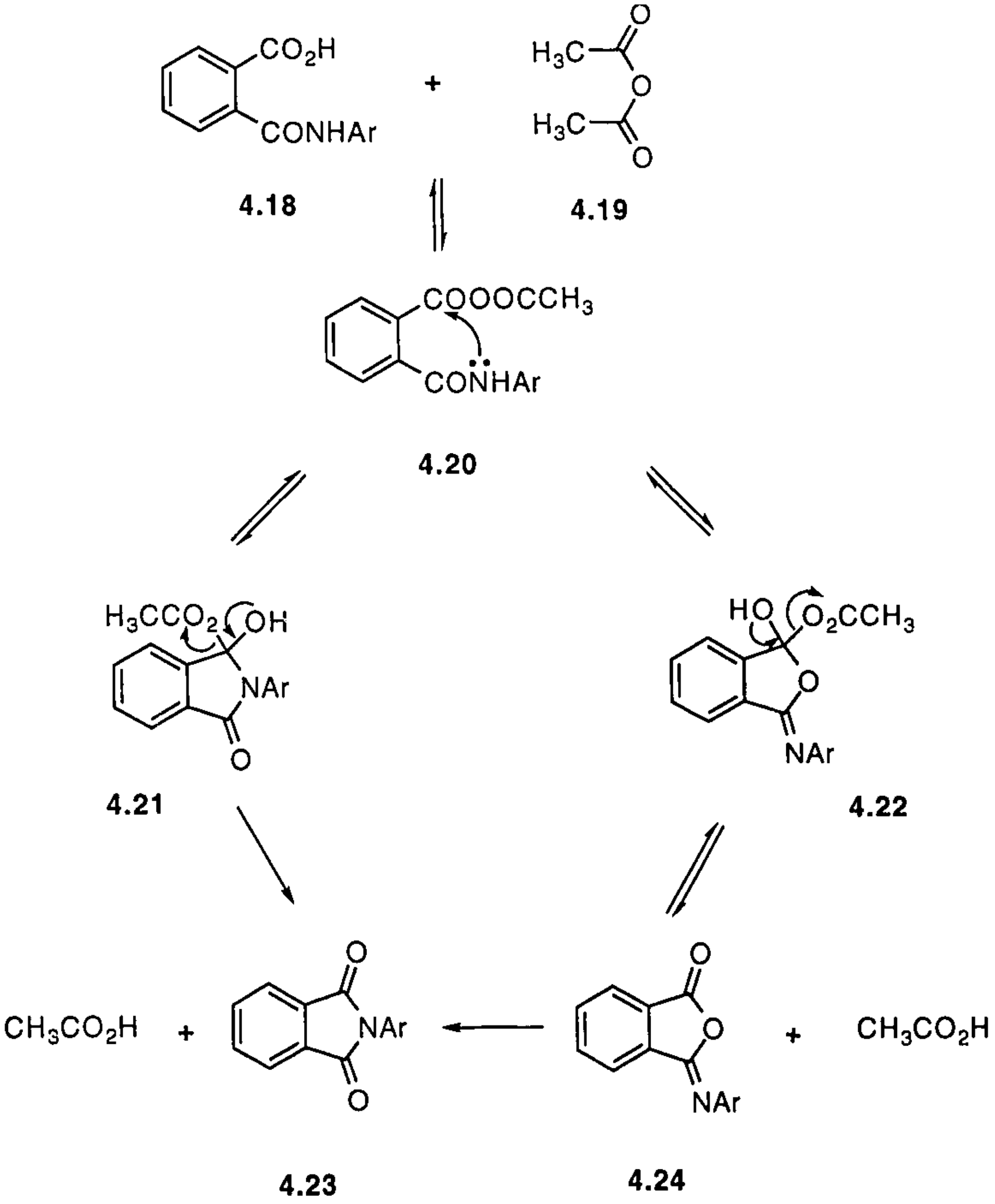
4.15

4.4

Scheme 4.4



Scheme 4.5

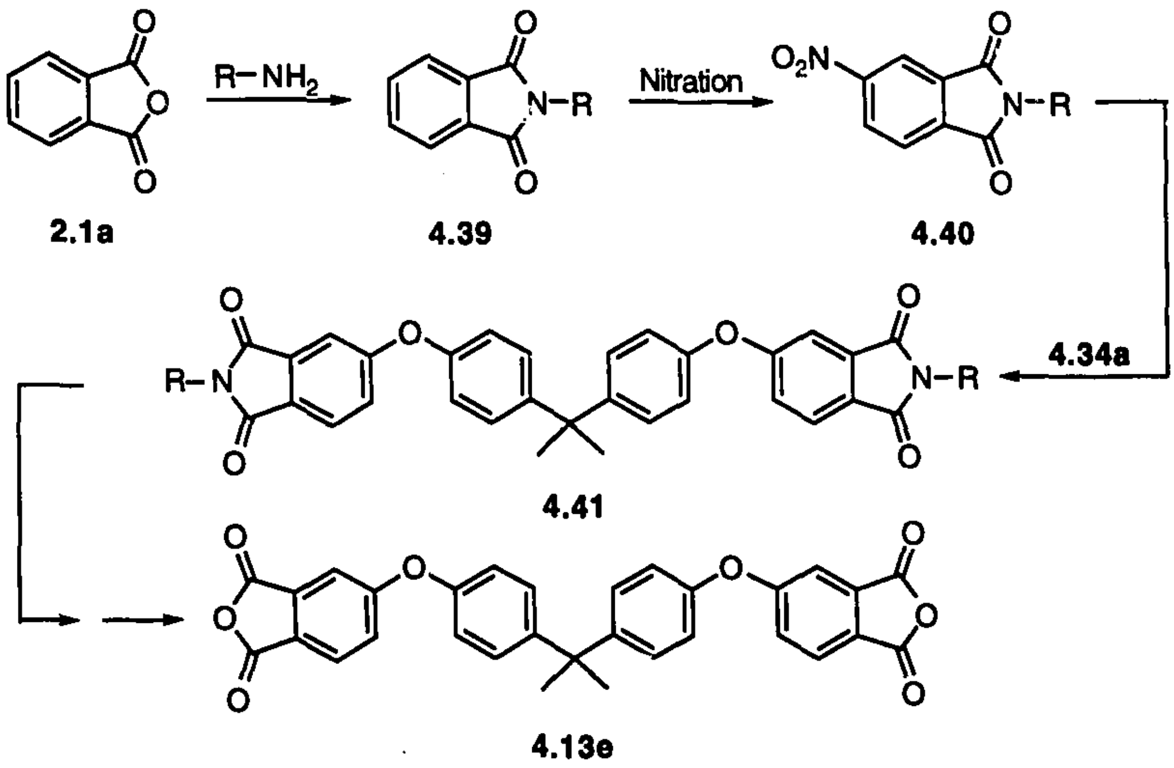

CO2H
CONHAr
+
H3C
O
H3C
O
O
4.18
4.19
COOOCCH3
CONHAr
4.20
H3CCO2
OH
NAr
O
4.21
HO
O2CCH3
O
NAr
4.22
CH3CO2H
+
O
NAr
O
4.23
O
O
NAr
4.24
+
CH3CO2H

4.1.2. Bis(ether anhydride)s by nucleophilic displacement reaction

The nucleophilic displacement polymerization has been found to be a relatively less practical approach in making polyimides. However, ether-containing dianhydrides are readily synthesized via a nucleophilic-displacement reaction. These dianhydrides have been used to make polyimides by the conventional diamine-dianhydride reaction. N-substituted-3-or 4-nitrophthalimides and various bisphenol salts were used in a displacement reaction under conditions similar to those previously mentioned (chapter 3). The resulting bis(ether imide)s were conveniently hydrolyzed to the corresponding tetracarboxylic acids in an aqueous sodium hydroxide solution. Dehydration of the tetracarboxylic acids can be accomplished either by reacting with acetic anhydride in boiling acetic acid or by simply heating at ca. 200°C. A more practical procedure to convert bis(ether imide)s to bis(ether anhydride)s in one step, consists of a reaction of bis(ether imide)s with phthalic anhydride at high temperature which gives the dianhydrides and the N-substituted phthalimides.[54]

Dianhydride **4.13e** is a commercial compound which is made from phthalic anhydride **2.1a** and BPA **4.34a** in a multi step synthesis. The first step is the preparation of N-substituted phthalimide **4.39** (usually N-methyl) by condensation of methyl amine with **2.1a** which is then followed by nitration using fuming sulfuric acid and concentrated nitric acid. The nitration step is a critical step and special care must be taken to avoid hydrolysis of the imide ring. Other methods such as chlorination of phthalic anhydride **2.1a** or phthalimide **4.39** give a mixture of the 3- and 4-isomers which is hard to separate. Chlorine, on the other hand, is a poor leaving group compared to nitro and gives a low yield in the displacement reaction. The next step in the preparation of **4.13e** is displacement of the nitro group with the disodium or dipotassium salt of **4.34a** to form diimide **4.41**. Hydrolysis of this diimide followed by cyclodehydration of the resultant tetracarboxylic acid affords **4.13e** (Scheme 4.6).

Scheme 4.6

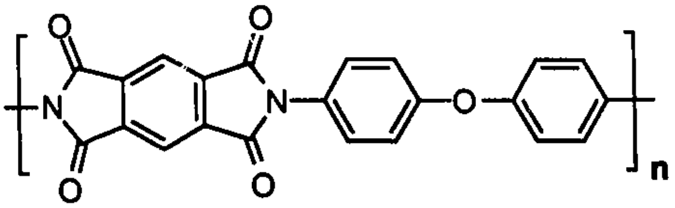


In general, reactions between phenoxides and substituted phthalimides proceed quantitatively in polar aprotic solvents at 25-60 °C. Rates of the reaction depend on the nature of the leaving group and its position (refer to chapter 3 for detail). When nitro phthalic anhydride is used instead of **4.40**, the yield of the displacement reaction decreases. This happens because anhydrides are hydrolytically less stable than their corresponding imides and ring opening intermediates and by-products form during the reaction.

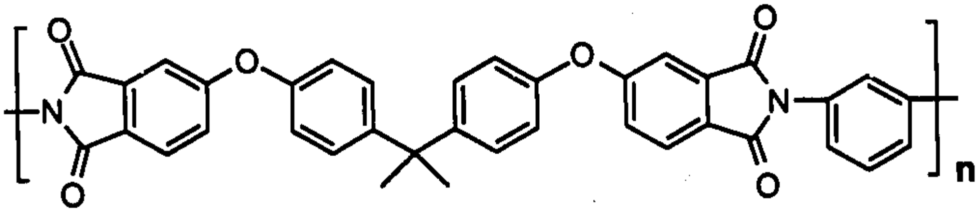
4.1.3. Development of polyimides

Although polyimides are well accepted as highly thermally stable engineering plastics and have been widely used as high performance materials, the technological application of many polyimides are often limited. One of the most important limitation for their application is insolubility and lack of processability.[8] Most commercial polyimides in their fully imidized form are not soluble in organic solvents, so they can not be processed in solution form. Their high melting points also makes it impossible to use melt processing techniques.

The initial method of overcoming the intractability of the polyimides utilized the polyamic acid **4.15** stage (precursor of polyimide) which could be fabricated into certain end-use forms by virtue of its good solubility in aprotic solvents (e.g. NMP, DMAc). Subsequent cyclodehydration of the polyamic acid resulted in the polyimide form of the end-use article. This process has been employed successfully only for thin films (Kapton® **4.16** (Figure 4.3) is a commercial polyimide available in the form of film). Problems associated with the necessary removal of volatiles (usually water) in the cyclodehydration step makes this technique unsatisfactory for other fabrication methods such as thick laminated composites, compression molded materials and fibers. In addition, the polyamic acid solution is thermally and hydrolytically unstable and depolymerizes to constituent anhydride and amine. Therefore care must be taken when handling and storing the solution.[9] The mechanism of depolymerization is shown in scheme 4.7.



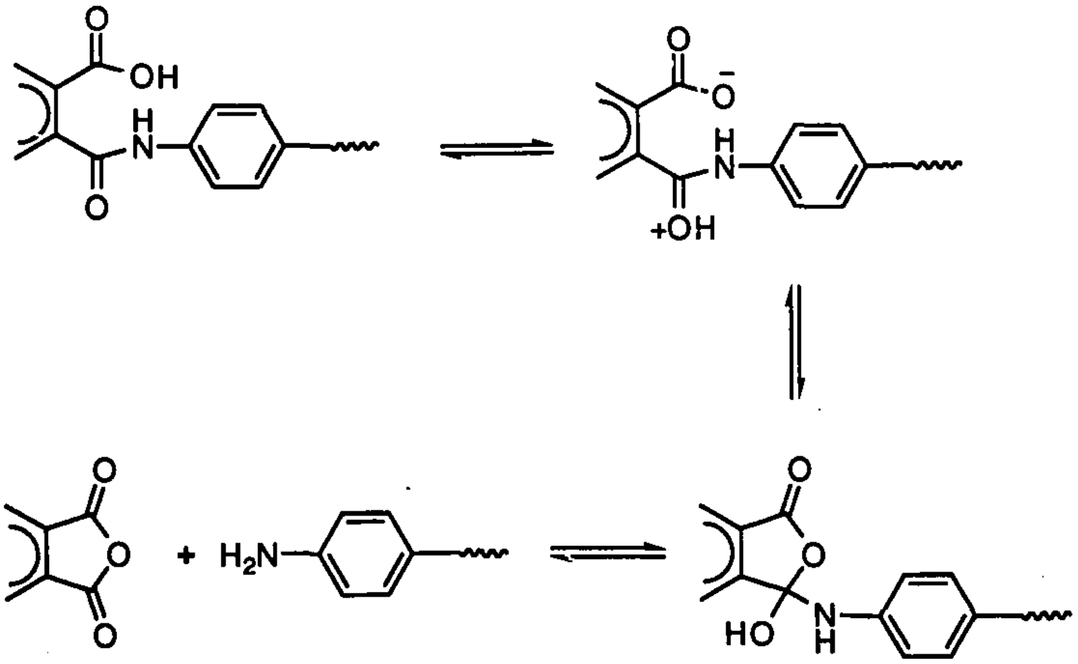
4.16



4.17

Figure 4.3. Two commercial polyimides

Scheme 4.7



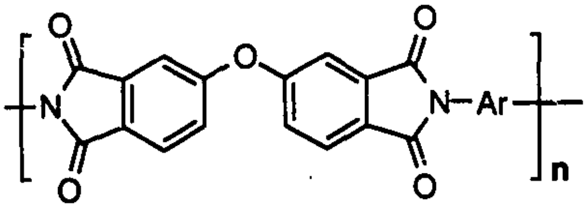
Considerable effort has been devoted to find other ways for improving the solubility and processability of polyimides without lowering the Tg and sacrificing thermal stability.[13-14] Most of these efforts have been focused on developing new structurally modified polyimides. In this way, two important factors have been considered by chemists to meet the industrial demands : (a) new monomers should be synthesized from relatively cheap and readily available starting materials. (b) polyimides derived from those new monomers should exhibit high Tg and be thermo-oxidatively stable as well as having good solubility in organic solvents. Three different strategies have been employed by chemists to overcome this problem in recent years: (i) introducing flexible linkages in the polymer backbone; (ii) incorporating kinked comonomer or noncoplanarity in the structure of polymer; (iii) incorporating bulky units along the polymer chain.

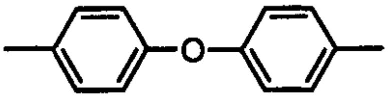
(i) It has been generally recognized that polar and rigid planar structures of high symmetry associated with aromatic imide systems are responsible for the lack of processability of these polymers. Inserting flexible linkages in the aromatic main chains has been proven to provide the polymer with a significantly lower energy of internal rotation.[10-11] However, such a structural modification leads to lower glass transition temperatures (Tg) and crystalline melting temperatures (Tm), as well as significant improvement in solubility and other process characteristics of the polymers (table 4.1). ULTEM® resin **4.17** manufactured by General Electric Company is a commercial poly(ether imide) based on bisphenol A and m-phenylenediamine.[12] The aromatic imide units provide stiffness, while ether linkages allow for good melt-flow characteristics, solubility and, therefore, processability.

(ii) Polyimides with rod-like structure are basically intractable, due to chain-chain crystalline interaction via a charge-transfer or electronic polarization mechanism. Some of the possible structural modifications to obtain processible polyimides are the incorporation of meta linkages, noncoplanar aromatic rings or certain amounts of comonomers which introduce a kink in the polymer backbone. Tables 4.1 to 4.3 provide some examples of different modified monomers and their effect on the Tg and solubility of polyimides.

(iii) One of the successful approaches to increase solubility and processability of polyimides without sacrificing their high thermal stability is the introduction of pendant bulky groups or fluorinated moieties into the polymer backbone (table 4.4).[13,14,28,43] Aryl substituents and fluorinated groups were selected in order to maintain good thermal properties. A few examples of these new monomers recently reported in the literature are shown in Fig 4.4.

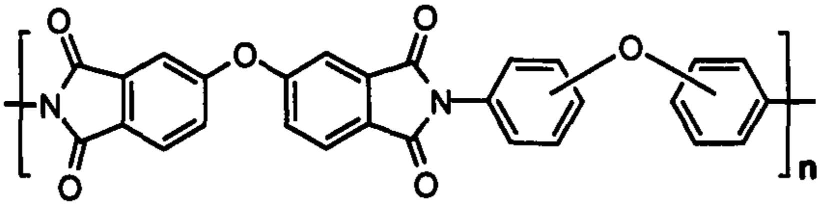
Table 4.1. Effect of flexible ether linkage on the Tg and solubility of polyimides



Ar	Tg(°C)	Solubility*	Ref.
	> 300	i	[25]
	270	s	[25]

* in *m*-cresol

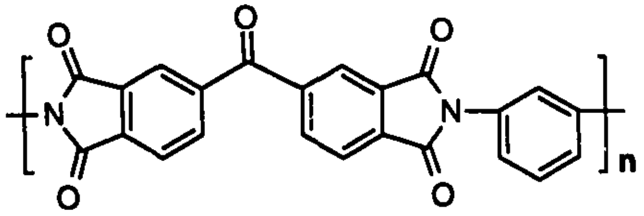
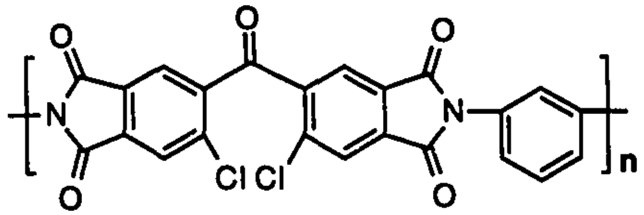
Table 4.2. Effect of isomeric attachment on the Tg and solubility of polyimides



Isomeric effect	Tg(°C)	Solubility*	Ref.
4,4'	273	i	[26]
3,3'	186	s	[26]

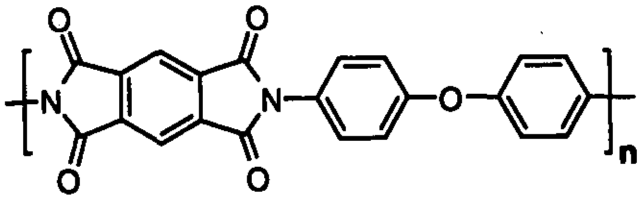
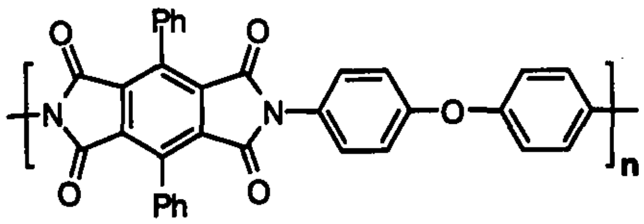
* in chloroform

Table 4.3. Effect of noncoplanar conformation on the Tg and solubility of polyimides

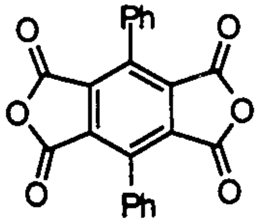
Polymer	Tg/°C	Solubility*	Ref.
	300	i	[19]
	313	s	[27]

* in NMP

Table 4.4. Effect of bulky substituents on the Tg and solubility of polyimides

Polymer	Tg/°C	Solubility*	Ref.
	377	i	[25]
	310	s	[28]

* in *m*-cresol



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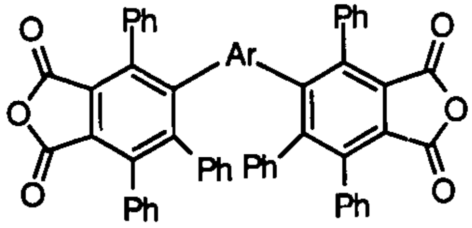

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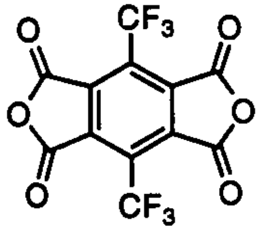
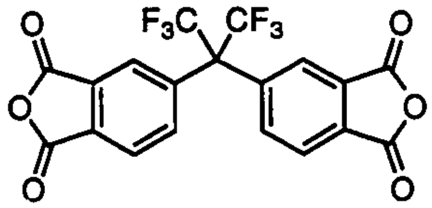


4.27



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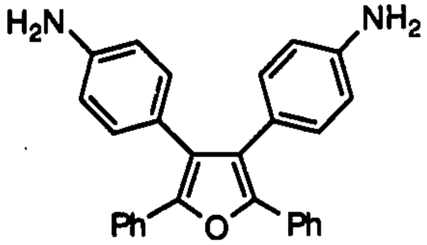

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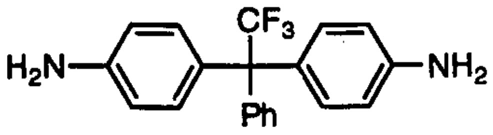
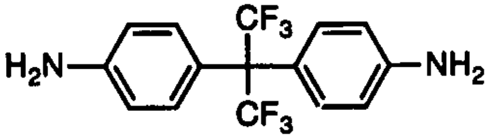
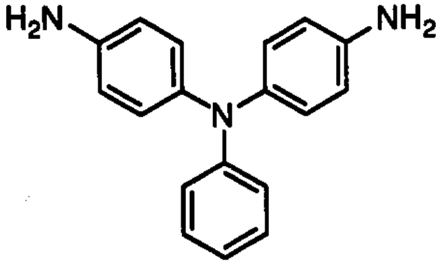


4.30



4.31



4.32

Figure 4.4. Some examples of the new dianhydrides and diamines

Most of these approaches still suffer from either having a multi step and low yielding monomer synthesis or they need relatively expensive starting materials and reagents. This means that they can not be readily commercialized. There is a continuing search in this field to make new polyimides which meet industrial demands.

4.1.4 . Problems associated with aromatic amines

Aromatic diamines such as *m*- and *p*-phenylene diamine (**4.14a** and **4.14b**) are usually made in two steps starting with a nitration reaction followed by reduction of the dinitro compound to diamine. In case of the other commercial diamines such as oxydianiline, methylene dianiline and diaminobenzophenone (**4.14c-e**) further steps are required to obtain the final products. Preparation of these diamines usually suffer from problems associated with separation of isomers and purification of the products. Aromatic amines are known as light and air-sensitive materials.[52, 53] Unless carefully purified, they soon darken on standing in air. Even the simplest aromatic amine, aniline, can give rise to numerous and frequently complex oxidation products. In addition to the amino group oxidative coupling reactions which result in the formation of C-C or C-N linkage and hydroxylation reaction of ring can occur. Several aromatic diamines used in polyimide synthesis are suspected carcinogens and should be handled with caution.[49]

4.2. Goals

The goals of our work was first to utilize interesting aromatic anhydride-hydrazine chemistry in preparation of novel diamines, and second to employ these diamines in polymerization reactions with dianhydrides to form new types of aromatic polyimides. Thus novel aromatic polyimides could be prepared without using any aromatic diamines, by using hydrazine to form N-aminoimides in order to make new diamines. These proposed diamines would be good candidates to replace existing aromatic diamines (Figure 4.2). This would eliminate many problems associated with commonly used aromatic diamines which are not easy to prepare and handle especially in large scale.

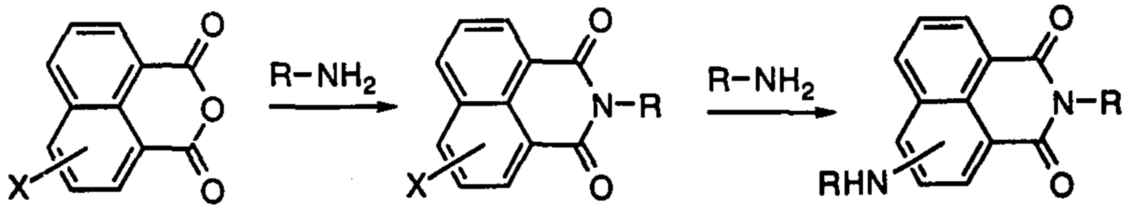
In particular, we decided to make bis(N-aminoimide) aryl ethers **4.35a-c** using hydrazine and a substituted naphthalic anhydride which are relatively inexpensive and readily available compounds. Hydrazine is able to form an N-aminoimide in reaction with one molecule of naphthalic anhydride. The N-aminoimide can be condensed with any aromatic anhydride to form bisimide in quantitative yield. The bisimides moiety with direct nitrogen-nitrogen linkage shows good thermal stability (refer to chapter 2). Different bis(N-aminoimide)aryl ethers **4.35a-c** have been proposed from 4-chloro-1,8-naphthalic tetracarboxylic dianhydride **4.32**, hydrazine and bisphenols **4.34a-c**. Schemes 4.9 and 4.10 illustrate the proposed synthetic route to **4.35a-c** and polyimides **4.36a-f** and **4.37a-d,f** which can be obtained by one-step condensation polymerization reaction with different dianhydrides.

4.3. Synthesis of Monomers

Six-membered ring aromatic anhydrides, unlike five-membered ring analogs, in reaction with hydrazine give N-aminonaphthalimide as the only product in quantitative yield (refer to section 2.4.5). This important advantage, besides the readily availability of some of the naphthalic anhydrides, were part of the driving force to make **4.35a-c**. In order to do that, we used the method developed by the General Electric Co. for making BPADA **4.13e** which is based on an aromatic nucleophilic substitution reaction (refer to section 4.1.2).

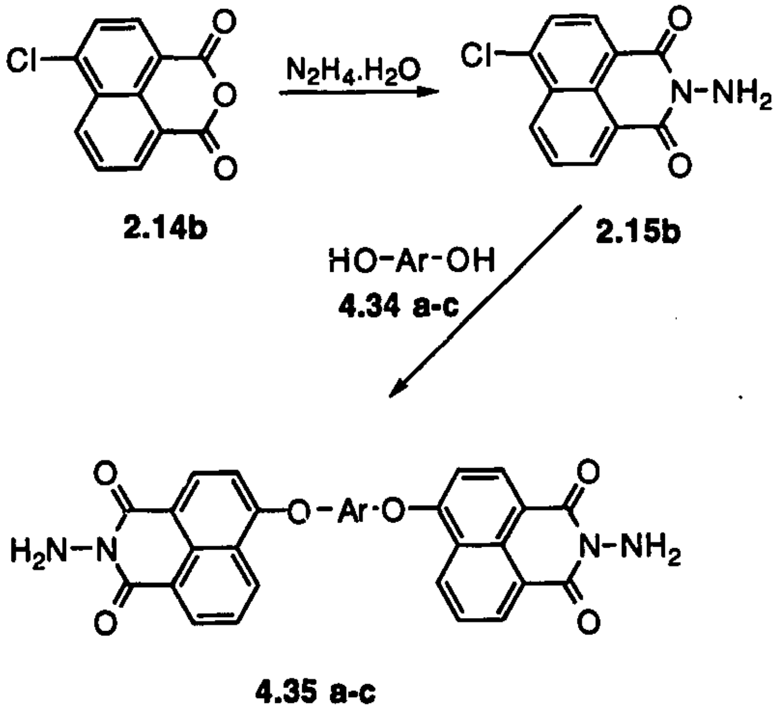
Nucleophilic displacement reactions on nitro and halonaphthalic-1,8-anhydrides **4.42** have been previously studied. Most of these efforts were aimed as finding a method to introduce an alkylamino substituent in the naphthalene ring and studying the fluorescent behavior of the products formed. Tyman and coworkers have reported the synthesis of a series of alkylamino substituted naphthalimides **4.44** using **4.42** and different amines (Scheme 4.8).[15] They showed that **4.42**, when X is halogen or nitro in the 2-, or 4-position, reacts with different nucleophiles such as alkylamines and hydrazine in warm ethanol to give the corresponding naphthalimide **4.43** without displacement of nitro or halo group. They also reported that **4.43**, when X is chloro or bromo in the 2- and 4-positions, undergoes very smooth reaction in polar aprotic solvents with a variety of amines to give the corresponding 2- and 4-substituted product **4.44**. When X is a nitro group a displacement reaction readily occurred leading to by-product formation which presents purification problems. Naphthalimide **4.43** with substitutions at the 3-position are unreactive to nucleophilic displacement reaction under similar condition. These findings demonstrates that nucleophilic displacement reaction on substituted naphthalimides is much easier than phthalimides under similar conditions.

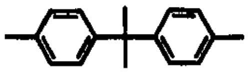
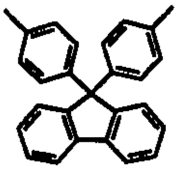
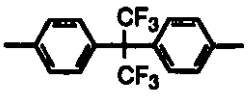
Scheme 4.8



4.42 **4.43** **4.44**

Scheme 4.9



Ar	**4.34 , 4.35**
	**a**
	**b**
	**c**

4.3.1. Synthesis of N-amino-4-chloronaphthalimide 2.15b

Chloronaphthalic anhydride **2.14b** reacts with hydrazine in ethanol to give N-amino-4-chloronaphthalimide **2.15b**, which crystallized out of the reaction mixture in the form of yellow needles pure enough to be used in the next step. Dissolution of **2.14b** in hot ethanol is very slow. Ethanol eventually reacts with **2.14b** to form the monoethyl ester which is more soluble in ethanol. Addition of hydrazine to this solution gives a yellow color in a few seconds which indicates formation of **2.15b**. There was no indication of a chlorine displacement reaction even though a slight excess of hydrazine was used.

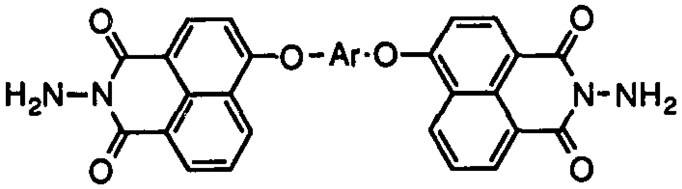
4.3.2. Nucleophilic displacement and formation of bis (N-aminonaphthalimide) aryl ethers 4.35a-c

Chloro displacement reactions were achieved using bisphenols **4.34a-c** and potassium carbonate to prepare bis(N-aminonaphthalimide)s **4.35a-c** (Scheme 4.9). Several procedures for generating the bisphenolate salt were discussed in chapter 3.

Dipotassium salts of **4.34a-c** were prepared in potassium carbonate / N,N'-dimethylacetamide (DMAc) system and the water of reaction was removed as an azeotrope using toluene as a cosolvent. 4-Chloronaphthalimide **4.32** was added later to the bisphenolate and reaction continued for few more hours at 80°C. Displacement of the chloro group takes place under mild conditions almost quantitatively to form bis-N-aminonaphthalimide **4.35a-c**. It was clear from the HPLC results that the bisphenols were used up almost completely after 3 h. The purity of the resulting diamines **4.35a-c** after recrystallyzation from 1,2-dichlorobenzene (DCB) or chlorobenzene was high according to TLC and ^{1}H NMR.

All the diamino compounds **4.35a-c** are yellow powders and are slightly soluble in chloroform. They are quite stable at their melting point (280-300 °C) and, unlike aromatic amines **4.14a-f**, are very stable when exposed to light and air, therefore they are easy to handle and to store. Table 4.5 summarizes some of the properties of the bis(N-aminoimide)s **4.35a-c**. This method provides a variety of bis (N-aminonaphthalimide) aryl ethers which can be prepared from different bisphenols.

Table 4.5. Properties of Bis(N-aminoimide)s



4.35a-c

Diamine	**Yield (%)**	**m.p. (°C)**	**appearance**	**chemical shift (δ) of NH_2 in ^1H NMR**
4.35a	75	285-290	yellow powder	5.52
4.35b	84	302-308	yellow powder	4.14
4.35c	67	297-302	yellow powder	5.65

4.4. Polymer synthesis

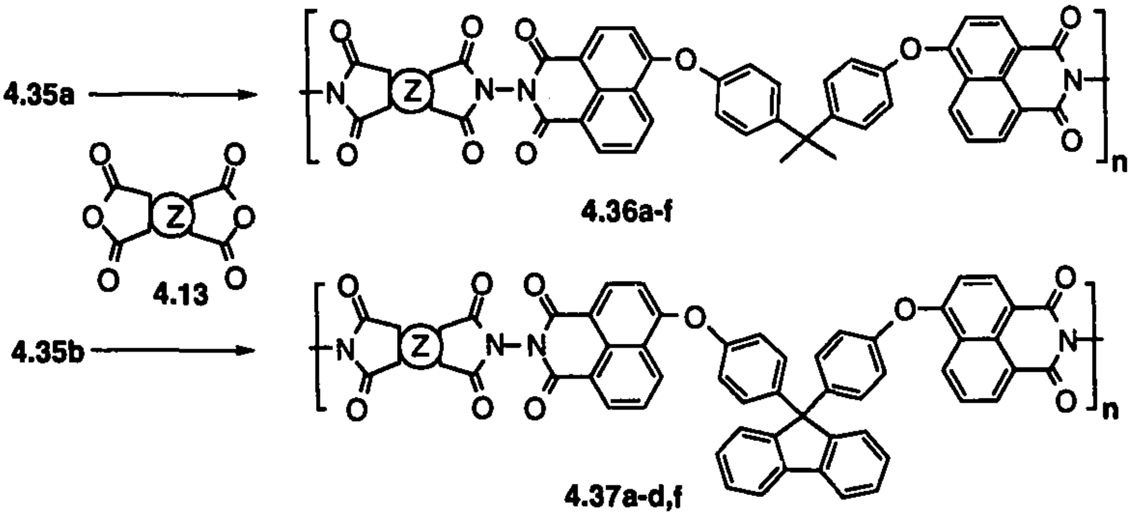
4.4.1. Polymerization reaction of bis(N-aminonaphthalimide) aryl ethers 4.35a-b with dianhydrides 4.13a-f

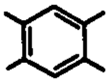
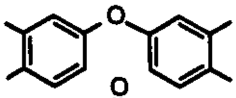
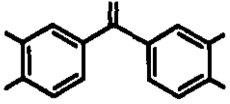
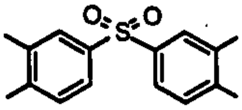
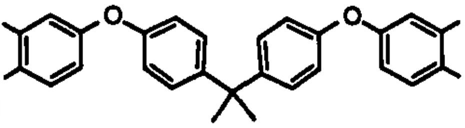
Soluble aromatic polyimides containing flexible linkages are generally prepared via a one step process.[19] In the one step synthesis, the polymerization and imidization are carried out in high boiling solvents around 200 °C. Different reaction systems have been described in the literature, but phenolic solvents (phenol, m-cresol, or p-chlorophenol) are commonly used in combination with a catalyst or accelerator, such as isoquinoline, tertiary amines or p-hydroxybenzoic acid.[19,23] In the case of the two-step process imidization of the polyamic acid **4.15** is the most difficult step and needs high temperatures under vacuum for long periods of time or requires the use of dehydrating agents such as acetic anhydride at ambient temperature (Scheme 4.4). In the one step process, the rate determining step is the reaction between the anhydride and the amine and subsequent imidization is very fast.[20] The reaction likely proceeds via formation of polyamic acid, but it appears that the amic acid is an extremely short-lived intermediate. In fact, under these reaction conditions chain growth and imidization occur essentially spontaneously.[24] From the structure of the bis-N-aminoimides **4.35a,b** having aryl ether units it was expected that they would form soluble polyimides. This was confirmed later by reacting **4.35a,b** with dianhydrides **4.13a-f** in a mixture of *m*-cresol and 1,2-dichlorobenzene (DCB) to form high molecular weight polyimides **4.36a-f** and **4.37a-d,f** (Scheme 4.10). The polymerization results were carried out in 20% (w/v) solids concentration at reflux temperature. The reaction mixture remained homogeneous, but it became very viscous at the end of the reaction and the solids concentrations were reduced to 10% by adding DCB. Water from the imidization reaction was allowed to distill from the reaction mixture so that the polyimides were generated in one step. The reaction is usually over within less than 3 to 4 h. Running the reaction for a longer time has little effect on the molecular weight of the polymer and only improves the molecular weight distribution of the resulting polymer. This was determined by Gel Permeation Chromatography (GPC) and by measuring their inherent viscosities. All the polyimides **4.36a-f** and **4.37a-d,f** were soluble in their imidization mixtures and were isolated by precipitation in methanol. Inherent viscosities of the polyimides **4.36a-f** were in the range of 0.36-0.58 dL/g at a concentration of 0.5 g/dL in NMP at 60°C (Table 4.9). Similar results were obtained for polyimides **4.37a-d,f** which showed inherent viscosities of 0.34-0.46 dL/g (Table 4.10). These results indicate that all the polymers were high molecular weight and this was also shown by solution casting to form clear tough creasable films. Films were made from a solution of 150 mg of polymer in 2 mL of DCB. Only in the case of **4.36a,f** and **4.37a,f** was the addition of a few drops of *m*-cresol to DCB necessary in order to make a clear solution.

Infrared spectroscopy which is a common way to indicate formation of polyimides is not very helpful in this case. Imide rings in **4.35a-c** made it difficult to use IR in order to prove formation of the imide ring during the polymerization reaction. However, ^{1}H NMR of the polymer **4.36e** in chloroform, as an alternative way of characterization, did not show any signal that could be attributed to the unreacted NH group or free carboxylic acid.

The IR spectrum of the polymer **4.36e** is shown in Figure 4.7. It shows imide absorption at 1795, 1714, 1691, 1076 and 738 cm^{-1} and N-N absorption at 1107 cm^{-1} which is similar to bisimide **2.16**.

Scheme 4.10



4.36	4.37	4.13	Z
a	a	a	
b	b	b	
c	c	c	
d	d	d	
e	-	e	
f	f	f	

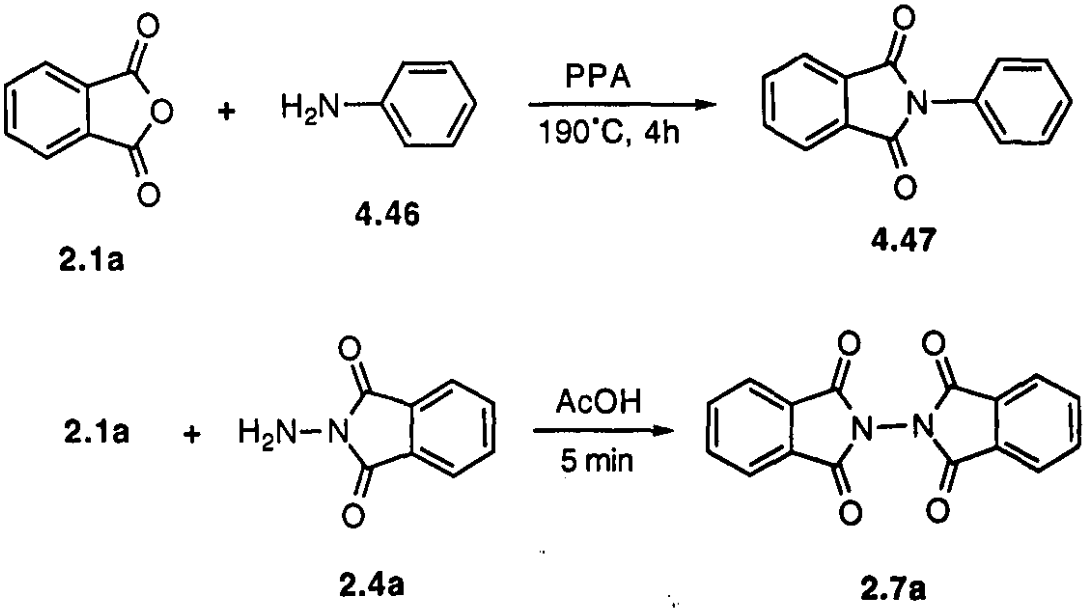
4.5. Result and Discussion

4.5.1. Reactivity of diamines 4.35a-c compared to aromatic amines

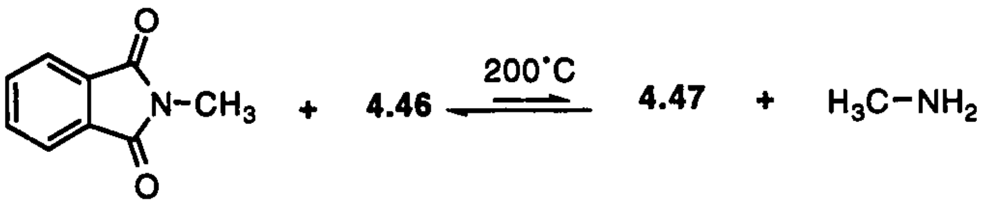
Studies show that there is a correlation between the basicity of the starting diamines and the rate of their reaction with anhydrides. The higher the pK_a of the diamine, the higher the rate constant of the reaction.[20] The effect of the monomer structure on acylation rate constants has been extensively investigated by some researchers.[37] It was reported that there is a relationship between the rate constant (log k) and ionization potential (IP) for diamines. The greater the IP, the lower the acylation rate. Similar studies showed that the acylation rate for dianhydrides increases with increasing electron affinity (EA) of dianhydrides. The reactivity of the diamine is more critical in the case of the two-step polymerization method. Different studies show that 100% degrees of imidization have never been achieved and a small percent of unimidized rings, which has unfavorable effects on the properties of the polymer, always remains. This problem is worse in the case of less reactive diamines such as 4,4'-carbonylbisbenzeneamine **4.14e**, because competition between cyclization and depolymerization is observed (Scheme 4.7). Although the one-step method has been suggested for less reactive diamines, its application is somewhat limited due to the solubility problem associated with most polyimides.

To the best of our knowledge until now there is no information in the literature about the basicity or nucleophilicity and therefore reactivity of any N-aminoimides (e.g. **2.4a** or **2.15b**). From what we know about hydrazine, substituted hydrazines and other aromatic and aliphatic amines, hydrazine and its derivatives are among the most reactive amines. Since N-aminoimides (e.g. **2.4a**) are considered as hydrazine derivatives it would be reasonable to compare their reactivity with aromatic amines. The first comparison is in imide-ring formation reaction. Reaction of aniline **4.46** and phthalic anhydride **2.1a** in polyphosphoric acid (PPA) was investigated as a model reaction to study the kinetics of polyimide formation.[41] The reaction was carried out at 190 °C for 4 hours to obtain fully ring-closed N-phenylphthalimide **4.47**. Reactions using N-aminophthalimide **2.4a** instead of **4.46** in acetic acid at reflux temperature take place in less than 5 min (Scheme 4.11) (refer to chapter 2). The basicity and nucleophilicity of an amino group attached to an aromatic ring is relatively low because of delocalization of the lone pair electrons of nitrogen through Π orbitals of the aromatic ring. This is known to contribute to the low pKa values of aromatic amines compared to aliphatic amines (e.g. 4.6 and 10.6 for aniline and methylamine, respectively). In the case of **2.4a** which has an isolated amino group, there is no resonance effect between the NH_2 and the phenyl ring and the only possible effect on the basicity of amino group is the electron withdrawing effect of the imide ring through inductive effects. Scheme 4.12 shows the equilibrium reaction of aliphatic and aromatic amines in a transimidization reaction. The higher reactivity and nucleophilicity of methylamine shifts the equilibrium toward the formation of N-methylimide **4.45**.[45]

Scheme 4.11



Scheme 4.12



4.45 (99.2%) (0.8%)

4.5.2. Color of the polyimides

Polyimides are known as colored polymers.[46] One of the theories to explain the source of the color of polyimides deals with the probability of the formation of charge transfer complex between the electron donating (usually amine) and the electron accepting (usually imide) parts of the polymer chain. This theory has been applied to some of the polyimides made from aromatic diamines. They usually are yellow or pale yellow in color. Another explanation suggests that the color in polyimides may have originated from chromophoric units in the polymers. These chromophoric units can be either part of the repeating units of the polymer or as impurities from starting materials.[15] Most of the commercial available dianhydrides, diamines and the imides made from their reaction are colorless in their pure form. Isoimide structure **4.24** (Scheme 4.5) which is believed to form during the imidization step, is also reported to be a possible origin of the color.[15] Isoimides convert to more stable imide structure during the process of thermal or chemical imidization (scheme 4.5). Chromophoric units in polyimides can be formed from impurities either present in starting materials or they may form during the polymerization reaction. These effects can be significantly reduced by using highly purified materials and running the reaction under an inert atmosphere.

In diamines **4.35a-c** the naphthalimide moiety with an arylether group attached to the naphthalene ring is the origin of the yellow color. This chromophoric structure remains almost unchanged after polymerization, and therefore the resulting polymers **4.36a-f, 4.37a-d,f** are also yellow. Naphthalimides with electron donating substituents are colored compounds and have many applications as fluorescent dyes.[47]

4.5.3. Solubility of polymers

All the polymers **4.36a-f, 4.37a-d,f** are soluble in *m*-cresol and N-methyl pyrrolidinone (NMP) at room temperature (Table 4.6). Polyimides **4.36b,c,d** which have more flexible groups in their anhydride unit show better solubility and are soluble in DCB at room temperature. However, polyimides **4.36a, f** are also soluble in DCB by adding a few drops of *m*-cresol. Polyimide **4.36e** which has two flexible BPA groups in every repeating units is readily soluble in chloroform at room temperature. Polyimides **4.37a-d,f** show almost the same solubility behavior as **4.36a-d,f** in DCB and *m*-cresol.

4.5.4. Glass transition temperatures (Tg) of the polyimides

There are numerous factors contributing to the glass transition temperature of polymers. Those which are believed to increase the Tg are : (a) presence of bulky pendant groups such as phenyl; (b) stiffening groups such as 1,4-phenylene; (c) chain symmetry as in the para-isomers; (d) polar groups such as carbonyl and sulfonyl. Glass transition temperature decreases with the introduction of: (a) flexible linkages such as ether linkage between rings which increase opportunities for bond rotation; (b) non polar groups such as methylene bridges and (c) dissymetry and structural disorder of chains (as meta-para isomers). All of these factors are "internal" which means they refer to either intra or intermolecular interaction of the polymer chains. "External" factors such as additives and plasticizers also lower the Tg. Those flexibilizing groups which lower Tg also cause a lessening of thermal stability almost without exception.

The polar rigid structure of imide groups in the backbone of polyimides is the major reason for their high Tgs. Depending on the type of monomer, Tg values of the polyimides range from less than 200°C to more than 400°C. Pyromellitic dianhydride **4.13a** (PMDA), biphenyl dianhydride **4.13f** (BPDA), *p*-phenylene diamine **4.14b** and 4,4'-diamino biphenyl **4.14f**, which have more symmetry in their structure, give the most rigid polyimides. This is shown by their very high Tg values. Intermolecular forces also strongly influence the Tg of polyimides. Interaction of polar carbonyl groups through Van der Waal forces tends to increase chain packing and therefore raise the Tg. Charge transfer complex formation between polymer chains is another inter-chain force which leads to higher glass transition temperature. This interaction is between aromatic rings of two adjacent polymer chains.[25]

Glass transition temperatures were measured by means of differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA). All the polyimides **4.36a-f** and **4.37a-d,f** show remarkably high Tgs (307-436 °C) (Table 4.7 and 4.8). Polyimides **4.37a-d,f** have higher (50-60 °C) Tgs compared to their analogs **4.36a-d,f**. This is presumably because of the effect of the more bulky fluorene group which gives higher restriction in free movement of polymer chains compared to the isopropyllidene group in BPA. The lowest Tg value (307°C, measured by DSC) belongs to **4.36e** which has two flexible BPA groups in every repeating unit. The highest Tg values are obtained for polyimides **4.36a,f** and **4.37a,f** which have more rigid BPDA and PMDA units. The Tg of polyimide **4.36a** was not detectable by DSC. Figures 4.8 and 4.9 show DSC traces of some of these polyimides. The rigid structure of the bisimide moiety along with the noncoplanarity of the two aromatic rings and the lack of free rotation along the nitrogen nitrogen bond are probably responsible for the high Tg values of these polyimides. Figure 4.5 shows a 3D structure of the unsymmetric bisimide **2.16**. Restricted rotation about the N-N bond is believed to be a result of repulsion between the lone electron pair on the two nitrogens[22] and steric hindrance caused by four imide carbonyls.

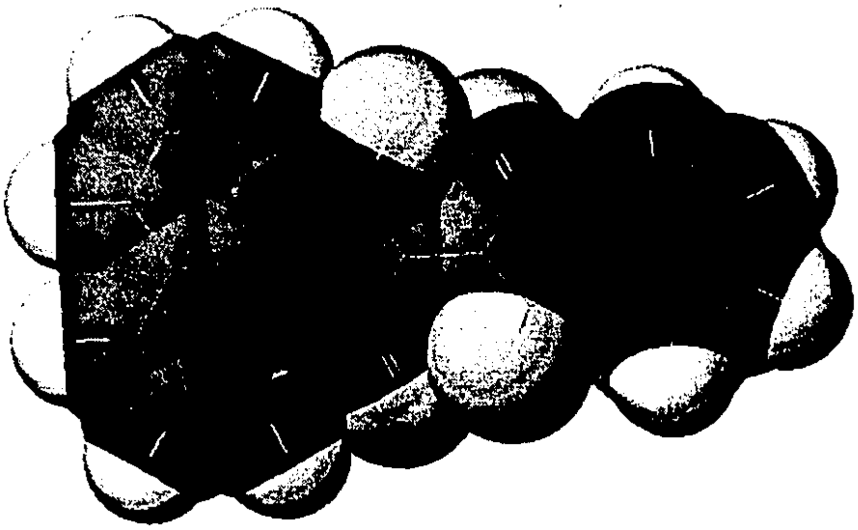


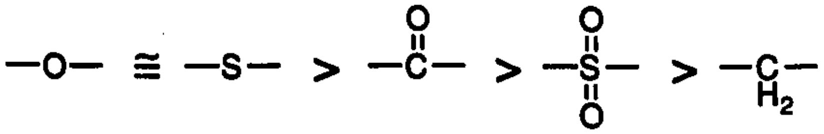
Figure 4.5. 3D structure of an unsymmetric bisimide

Glass transition temperatures of polyimides **4.36a-f** obtained from DSC are 8-17°C higher than the numbers obtained from TMA/SS measurements. Polyimides **4.37a-d,f**, in contrast, showed higher Tg values in TMA/SS compared to the DSC scans. In the case of polyimides **4.37a** and **4.37f** the difference is as much as 10 and 12 °C, respectively. These contradictory observations can be explained in terms of the difference in thermo-oxidative stability of the two series of polyimides **4.36a-f** and **4.37a-d,f** under different experimental conditions of the measurements in DSC and TMA instruments. Polymers with aliphatic hydrogens are generally less thermo-oxidatively stable than polymers with similar structure without aliphatic hydrogens.[21] The isopropylidene hydrogens of BPA unit, for instance, are believed to be responsible for thermo-oxidative degradation of the polymers, such as ULTEM and poly(ether sulfone)s, at elevated temperatures. BPA-containing poly(ether imide)s **4.36a-f**, similarly, decompose faster than poly(ether imide)s **4.37a-d,f** near their Tgs under the experimental condition of the TMA measurement, i.e., longer time (2-3 h) under an atmosphere of static air, compared with experimental condition in DSC (20 min under a nitrogen atmosphere) and therefore Tg values of polymers **4.36a-f** in TMA are lower than those obtained from DSC.

4.5.5. Thermal stability of the polyimides

Thermal stabilities of the poly(ether imide)s were determined by thermogravimetric analysis (TGA) which provides information about the threshold temperature at which major fragmentation occurs and is therefore an indication of the inherent stability of the polymer structure. Since the temperature rise rates employed in this analysis are relatively rapid (5-30 °C/min), TGA curves are generally regarded as an index of short-term stability.

As one would expect, polyimides of **4.37a-d,f** possess higher thermal stability in air and nitrogen compared to polyimides of **4.36a-f** (Table 4.7 and 4.8). This result is in agreement with the results found by several investigators. The findings show that in a series of polymers with similar structure those with biphenyl groups are usually the most stable and those with aliphatic hydrogens are the least stable one. The order of stability for interconnecting groups is reported [48] to be :



$$-O- \cong -S- > -\overset{\overset{O}{\|}}{C}- > -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}- > -\underset{H_2}{C}-$$

The values for bond dissociation energies in organic compounds also suggest that the benzylic bonds are relatively weak (84±2 Kcal mol^{-1}).[55]

The TGA results also indicated that the nitrogen-nitrogen linkage between the two imides is quite stable at elevated temperatures. This was shown for polyimides **4.37a-d,f** with 5% weight losses at 507-521 °C in air. Figures 4.10 and 4.11 show the TGA traces of some of these polyimides.

4.5.6. Isothermal studies of the polyimides

The weight loss as a function of time at a specific temperature which is done by isothermal thermogravimetric analysis (ITGA) in flowing air or nitrogen gives supplemental information on long-term stability of the polymers. The results of isothermal experiments on poly(ether imide)s **4.37a-d,f** shows that all of them had less than 3% total weight loss at 400 °C after 8 h in nitrogen (Table 4.11). When the atmosphere was air under similar condition the weight loss was between 5-8%, except for PMDA which was 10.8%.

As expected for poly(ether imide)s of series **4.36** rapid degradation occurred (4% weight loss / h in 8 h experiment) due to the instability of the isopropylidene group which is relatively less stable in long-term exposure at elevated temperatures.

4.5.7. Mechanical properties of the polyimides

Thermomechanical analysis/stress-strain (TMA/SS) measurements were carried out on thin films that were cast from chloroform (**4.36e**), DCB (**4.36b-d** and **4.37b-d**) or a mixture of DCB and a small amount of m-cresol (**4.36a,f** and **4.37a,f**) solutions. All the samples were dried at 300°C under vacuum for 2-3 hours before use. This process removes most of the DCB and m-cresol, however later experiments confirmed that a brief drying period near the glass transition temperature was necessary to almost quantitatively remove the latter solvent. The tensile moduli of all the samples were in the range of 1.3-3 GPa at 25°C (Table 4.12 and 4.13). These properties are nearly identical to commercially available polyimides and poly(ether imide)s which have tensile moduli in the range of 2-3 GPa. The films of polyimides **4.36a-f** maintained their mechanical properties at 200 °C as indicated by tensile moduli of 1.0-2.0 GPa. They start to loss their mechanical properties rapidly around 220°C for **4.36e,** which has the lowest Tg, and 340°C for **4.36a,** which has the highest Tg. Polyimides **4.37a-d,f** show similar values of tensile moduli (2.3-3 GPa) at 25 °C. When they were heated to 200 °C only small changes were observed in their tensile moduli due to their high glass transition temperatures and they maintained their mechanical properties even at temperatures around 300°C. Figure 4.12 shows the TMA thermogram of polyimide **4.37b.**

4.5.8. Comparison with other polyimides

Table 4.14 compares some of the properties of known poly(ether imide)s and polyimides with polymers **4.36a-f** and **4.37a-d,f.**

Polyimides are known as high performance and thermooxidatively stable polymers. However, all of them suffer from processing problems due to insolubility in organic solvents. Poly(ether imide)s with aromatic ether linkages in the main chain were to satisfy the need for polyimides which could be readily processed by conventional methods. In general, such a structural modification leads to the reduction of energy of the internal rotation of the chain, resulting in lowering Tgs which means sacrificing their use temperature. On the other hand, the demand for polymers capable of withstanding elevated temperatures of above 200°C is increasingly growing. This means that new materials with Tgs above 350 °C that are still soluble in organic solvents are required.

As summarized in table 4.14, polyimides **4.36a-f** and **4.37a-d,f** have both good solubility in organic solvents such as NMP, DCB and m-cresol and remarkably high Tgs. Compared with ULTEM® resin **4.17** which is the only commercially available poly(ether imide) based on BPADA **4.13e** and *m*-phenylenediamine **4.14a** with a Tg of 217°C the series of polyimides **4.36a-f** exhibit glass transition temperatures in the range of 307 to 380°C which is 90 to 160°C higher than ULTEM® **4.17** and even higher than any other known poly(ether imide)s. Some organic-soluble aromatic polyimides have been recently demonstrated using phenylated or fluorinated tetracarboxylic dianhydrides and aromatic diamines. Tgs of these polyimides was reported to be as high as 430°C.[14] Most of these diamines are synthesized from relatively expensive fluorinated starting materials such as hexafluoroacetone and trifluoroacetophenone. One of the important advantages of polyimides **4.36a-f** and **4.37a-d,f** is that they can be made from readily available starting materials. The other important point is that they can be modified by simply changing the bisphenol group to meet the desired Tg for specific purposes. As demonstrated in table 4.14, changing the bisphenol group from BPA to BPF increased the Tg of the poly(ether imide)s significantly (40-50°C).

The thermal stability of polyimides **4.36a-f** are similar, while polyimides **4.37a-d,f** are higher than those of known poly(ether imide)s made from bisphenol dianhydrides. Some polyimides with naphthalene units which have been recently synthesized also show similar thermal stability. TGA curves for polyimide made from diaminophenylether **4.14c** and PMDA **4.13a**, known as Kapton® **4.16** in commercial form, begins to lose weight in both air and nitrogen at about 510°C.[50]

4.6. Conclusion

A new class of diamines has been prepared in two steps and in high yields from hydrazine, chloronaphthalic anhydride **2.14b** and bisphenols **4.34a-c** which are readily available. They are, unlike aromatic amines, stable under exposure to air and light. Compared to aromatic diamines where amino groups are attached directly to an aromatic ring bis(N-aminoimide)s are, in fact, substituted hydrazines and hence their amino group are more reactive than an amino group in aromatic amines. Bis(N-aminoimide)s were polymerized to a series of high molecular weight novel poly(ether imide)s in the one step method using different aromatic dianhydrides. This work opens up a new class of high temperature aromatic poly(ether imide)s with extremely high glass transition temperatures (as high as 436°C) and exceptional thermal stability using hydrazine as the diamine. The presence of naphthalene groups and the rigidity of the bisimide moiety in the back bone of the polymer chains are presumably responsible for the high Tg values while the ether linkages introduce flexibility and make the resulting polymers soluble in organic solvents such as NMP, m-cresol, DCB and in one case even chloroform. The thermomechanical studies showed that all the polyimides maintain their properties at elevated temperatures (200-300°C).

4.7. Experimental

General methods

The ^{1}H NMR and ^{13}C NMR spectra were measured with a Varian XL200 or Varian Unity-500 instrument, using deuterochloroform ($CDCl_3$) or dimethyl-d_6 sulfoxide (DMSO-d_6) as a solvent. The chemical shifts were calibrated using tetramethylsilane (TMS). The chemical shift (δ) and coupling constant (J) data are quoted in ppm and hertz respectively. Inherent viscosity was determined at 0.5 g/dL concentration in NMP at 60° C using a Ubbelohde dilution viscometer. Apparent molecular weights were determined by gel permeation chromatography using polystyrene standards with NMP as the solvent on a Waters 150 CV HPLC with a UV detector and one Water's μStyragel HT linear column.

The polymer decomposition temperatures and isothermal aging were measured by thermogravimetric analysis (TGA) with a Seiko TG/DTA 220. TGA's were run at a heating rate of 10°C/min in nitrogen or air with flow rate of 200 mL/min. The differential scanning calorimeter (DSC) was run under a nitrogen stream at a flow rate of 50 cm^3/min and at a heating rate of 20°C/min using a Seiko DSC. The Tgs were taken from the midpoint of the change in slope of the baseline. Melting points were measured on a Mettler FP80 at a heating rate of 5°C/min and values were taken from the onset of the change in slope to the maximum of the endothermic peak. Thermomechanical study was performed on a Seiko 120 thermomechanical analyzer thermal stress-strain analyzer (TMA/SS) with a heating rate of 3°C/min. Films for the thermomechanical analyzer were cast from mixture of 1,2-dichlorobenzene and m-cresol (10:1) at 145°C and dried under vacuum at 100°C for 4h, 200°C for 2h and 300°C for 1h.

4-Chloro-1,8-naphthalic anhydride **2.14b** was obtained from Aldrich Chemical Co., and was purified by recrystallization first from toluene and then acetic anhydride. N-Methyl-2-pyrrolidinone (NMP) obtained from J.T.Baker and N,N'-dimethylacetamide (DMAc) obtained from Aldrich Chemical Co. were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. 1,2-Dichlorobenzene (DCB) , m-cresol , toluene , hydrazine monohydrate were purchased from Aldrich Chemical Co and used without further purification. Bisphenols 4,4'-(1-methylethylidene)bisphenol (BPA) **4.34a** and bisphenol fluorenone (BPF) **4.34b** were supplied by General Electric Co and 4,4'-(hexafluoroisopropylidine)diphenol (BPA-F6) **4.34c** was purchased from Aldrich and all were used as received. 3,3',4,4'-benzophenetetracarboxylic dianhydride (BTDA) **4.13c** and 3,3',4,4'-biphenyltetracarbaxylic dianhydride (BPDA) **4.13f** were obtained from Aldrich and recrystallized from acetic anhydride and sublimed before use. 4,4'-oxydiphthalic anhydride (ODPA) **4.13b** and 4,4'-sulfonyldiphthalic anhydride (DSDA) **4.13d** were purchased from Chriskev Company, INC. and purified by sublimation under reduced pressure. Bisphenol-A-dianhydride (BPA-DA) **4.13e** was supplied by General Electric Co. and recrystallized from acetic anhydride.

4-Chloro-N-amino-1,8-naphthalimide 2.15b.

4-Chloro-N-amino-1,8-naphthalimide **2.15b** was prepared by the reaction of hydrazine monohydrate with 4-chloro-1,8-naphthalic anhydride **2.14b**. First 2.32 g (10 mmole) **2.14b** was dissolved in 1300 mL of 96% ethanol. To this solution was added 0.5 mL (10 mmol) of hydrazine monohydrate at room temperature . This solution was boiled to remove 400 mL of solvent. Upon cooling to room temperature 1.8 g of 4-chloro-N-amino-1,8-naphthalimide **2.15b** precipitated out in the form of yellow crystals (74% yield): mp 225-228°C; ^{1}H NMR (200 MHz, DMSO-d6) δ 6.3 (s, 2H, NH2), 8.5-8.9 (m, 5H, aromatic); MS (EI) m/e calcd for $C_{12}H_7N_2O_2Cl$: 246.02, found 245.87; 246 (100, M+), 219 (29.8), 217 (92.1), 188 (11.7), 160 (20.7), 126 (16.8). IR (mineral oil) : 3204 (1.02), 3247 (1.31), 1700 (2.05), 1666 (2.11), 1643 (2.26), 1611 (1.07), 1567 (1.59), 1557 (1.50), 1239 (2.41), 976 (2.57).

2,2-Bis[4-(N-amino, 4,5-dicarboximidonaphthoxy) phenyl] propane 4.35a .

In a 100 mL , three necked flask equipped with a Dean-Stark trap, magnetic stirrer and nitrogen inlet were placed 2.28 g (10 mmol) of bisphenol A (BPA) **4.34a** , 3.31 g (24 mmol) of anhydrous potassium carbonate , 20 mL of dimethyl acetamide (DMAc) and 10 mL of toluene. The mixture was heated on an oil bath at 145°C for 12h. During this time 12 mL of an azeotropic mixture were removed. After cooling to room temperature , 5.42 g (22 mmol) of 4-chloro-N-aminonaphthalimide **2.15b** and 20 mL of DMAc were added and the resulting mixture was heated at 80°C for 24h during which time all the BPA was used up. The reaction mixture was cooled and extracted with 3x200 mL of chloroform . It was washed twice with sodium bicarbonate solution (5%) and once with aqueous HCl (5%) then with sodium bicarbonate solution (5%). The organic layer was dried using anhydrous magnesium sulfate, filtered and the filtrate was evaporated to dryness. The yellow solid was ground up and washed several times with boiling ethanol (96%) and recrystallized from 1,2-dichlorobenzene to give **4.35a** in 75% yield: mp 285-290°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (s, 6H, $C(CH_3)_2$), 5.52 (s, 4H, NH_2), other aromatic hydrogens are consistent with the structure (Figure 4.6). HRMS (CI with NH_3) m/e calcd for $C_{39}H_{28}N_4O_6$+H: 649.2090, found 649.2087; 649 (24.1, MH+), 307 (48.8), 289 (38.9), 279 (19.3), 273 (14.9), 219 (14.4), 178 (15.0), 167 (15.3), 165 (23.1), 154 (100), 152 (34.7), 149 (41.7), 138 (82.5), 136 (100), 107 (80.9). IR (mineral oil) : 3344 (0.03), 3260 (0.03), 1774 (0.02), 1734 (0.02), 1695 (0.03), 1211 (0.04), 1176 (0.04), 1115 (0.04), 1096 (0.04).

9,9-Bis[4-(N-amino,4,5-dicarboximidonaphthoxy) phenyl] fluorene 4.35b.
Bis(N-aminoimide) **4.35b** was prepared similar to **4.35a** and it was isolated as a yellow solid, 6.5 g (84% yield): mp 302-308 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (s, 4H, NH_2), other aromatic hydrogens are consistent with the structure (Figure 4.6). HRMS (CI with NH_3) m/e (calcd for $C_{49}H_{30}N_4O_6$+H, 771.2241; found, 771.2243) 771 (41, MH+), 467 (17.3), 307 (13.5), 289 (13.3), 239 (14.9), 154 (100), 137 (52.7), 120 (12.8). IR (mineral oil) : 3229 (1.56), 3156 (1.25), 1699 (1.71), 1651 (2.03), 1574 (1.78), 1541 (1.16), 1237 (2.40), 1212 (1.78), 1173 (1.35), 1109 (1.17).

2,2-Bis[4-(N-amino-4,5-dicarboximidonaphthoxy)phenyl]hexafluoropropane 4.35c.
Bis(N-aminoimide) **4.35c** was prepared similar to **4.35a** to give 5.1 g (67% yield) as a yellow powder: mp 297-302°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.65 (s, 4H, NH_2), other aromatic hydrogens are consistent with the structure. HRMS (CI with NH_3) m/e (calcd. for $C_{39}H_{22}N_4O_6F_6$+H : 757.1521; found, 757.1521) 757 (31.2, MH+), 307 (17.6), 289 (10.7), 279 (15.3), 154 (100), 136 (73.4). IR (mineral oil) : 3347 (0.34), 1701 (0.52), 1658 (0.91), 1580 (0.55), 1241 (1.58), 1199 (0.59), 1170 (0.74).

Polymer synthesis

A typical example of a polymerization reaction is as follows: To a three-neck flask equipped with a nitrogen inlet, reverse Dean-Stark and condenser was added 1.0089 g (1.55 mmol) of **4.35a** , 0.4962 g (1.54 mmol) of BTDA **4.13c**, 8 mL of 1,2-dichlorobenzene and 2 mL of m-cresol under a nitrogen atmosphere. The reaction mixture was heated with vigorous stirring at 190-200°C for 20 h in a dry nitrogen atmosphere during which time water was removed by azeotropic distillation. The solution became viscous so it was diluted with 10 mL of 1,2-dichlorobenzene and the polymer solution was trickled into 400 mL methanol giving rise to a fibrous yellow precipitate which was washed thoroughly with methanol, collected by filtration, and dried. The yield was 1.4 g (95%). The inherent viscosity of the polymer in NMP at 60°C was 0.54 dL/g.

4.8. References

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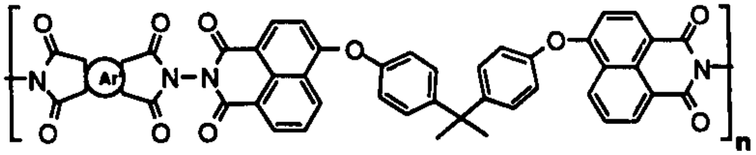
Table 4.6. Solubility of poly(ether imide)s

Polymer	Solvent				
	sulfuric acid	*m*-cresol	1,2-dichlorobenzene	chloroform	NMP
4.36a	++	++	+	-	++
4.36b	++	++	++	-	++
4.36c	++	++	++	-	++
4.36d	++	++	++	-	++
4.36e	++	++	++	++	++
4.36f	++	++	+	-	++
4.37a	++	++	+	-	++
4.37b	++	++	++	-	++
4.37c	++	++	++	-	++
4.37d	++	++	++	-	++
4.37f	++	++	+	-	++

(++) Soluble at room temperature: (+) Partially soluble on heating; (-) Insoluble.

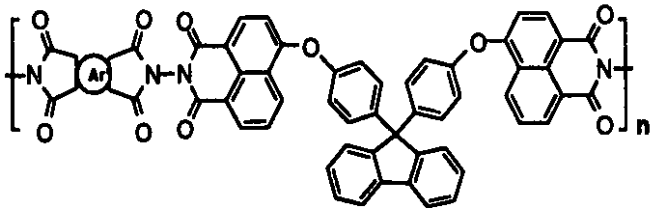
Table 4.7. Physical and thermal properties of poly(ether imide)s 4.36a-f



Polymer[a]	Reaction time (h)	Yield (%)	Tg (°C)	TGA (°C)[b] N_2	TGA (°C)[b] air	Solubility
4.36a	20	93	-	455	457	NMP, DCB[c]
4.36b	20	97	357	470	477	NMP, phCl
4.36c	18	96	360	454	475	NMP, DCB
4.36d	20	93	362	452	466	NMP, DCB
4.36e	28	92	307	474	467	$CHCl_3$
4.36f	20	93	375	468	478	NMP, DCB

(a) Polymerization solvent is a mixture of *m*-cresol and 1,2-dichlorobenzene (DCB)
(b) 5% wt loss. (c) 1,2-dichlorobenzene

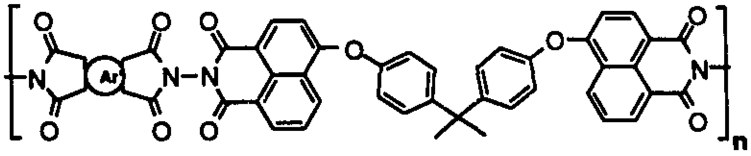
Table 4.8. Physical and thermal properties of poly(ether imide)s 4.37a-d,f



Polymer[a]	Reaction time (h)	Yield (%)	Tg (°C)	TGA (°C)[b] N_2	air	Solubility
4.37a	18	96	436	506	507	NMP, DCB[c]
4.37b	24	91	398	510	520	NMP, phCl
4.37c	20	96	404	509	521	NMP, DCB
4.37d	20	95	400	500	510	NMP, DCB
4.37f	22	94	429	515	515	NMP, DCB

(a) Polymerization solvent is a mixture of *m*-cresol and 1,2-dichlorobenzene (DCB)
(b) 5% wt loss. (c) 1,2-dichlorobenzene

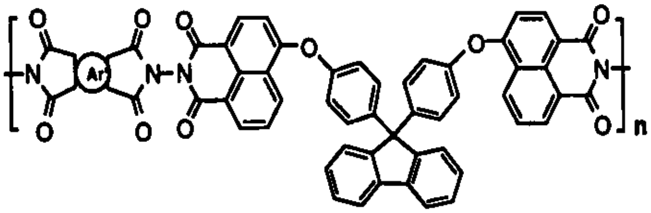
Table 4.9. Solution properties of poly(ether imide)s 4.36a-f



Polymer	η_{inh} (dL/g)	Solvent for solution casting	GPC[a] Mwx10^{-4}	Mnx10^{-4}	Mw/Mn
4.36a	0.47	DCB[b]/*m*-cresol	-	-	-
4.36b	0.58	DCB	154.3	33.6	4.57
4.36c	0.54	DCB	156.0	25.5	6.10
4.36d	0.37	DCB	123.1	26.1	4.70
4.36e	0.36	chloroform	171.0	47.7	3.58
4.36f	0.47	DCB/*m*-cresol	199.3	64.5	3.08

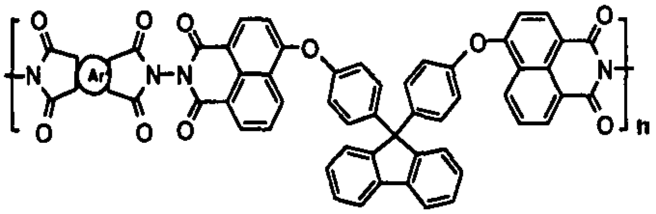
(a) Gel permeation chromatography, in NMP using polystyrene standards.
(b) 1,2-dichlorobenzene.

Table 4.10. Solution properties of poly(ether imide)s 4.37a-d,f



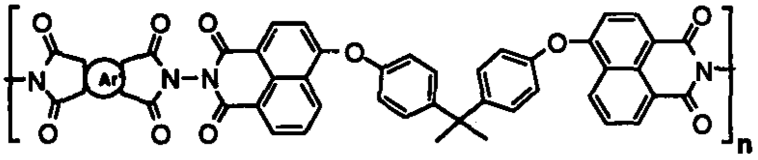
Polymer	η_{inh} (dL/g)	Solvent for solution casting
4.37a	0.46	DCB/*m*-cresol
4.37b	0.44	DCB
4.37c	0.45	DCB
4.37d	0.34	DCB
4.37f	0.42	DCB/*m*-cresol

Table 4.11. Isothermal aging of poly(ether imide)s 4.37a-d,f at 400°C



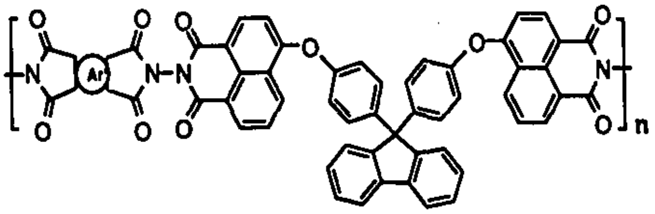
Polymer	weight loss(%) N_2	weight loss(%) air	weight loss(%)/h N_2	weight loss(%)/h air
4.37a	2.6	10.8	0.32	1.35
4.37b	2.3	5.0	0.29	0.62
4.37c	2.2	5.5	0.27	0.68
4.37d	3.0	7.8	0.37	0.97
4.37f	1.6	7.9	0.20	0.99

Table 4.12. Thermomechanical properties of poly(ether imide)s 4.36a-f



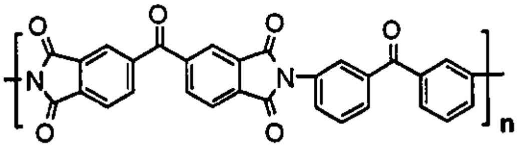
Polymer	tanδ (max) (°C)	Young's modulus (GPa) at 25°C	Young's modulus (GPa) at 200°C
4.36a	380	2.22	1.92
4.36b	340	1.81	1.48
4.36c	345	2.06	1.67
4.36d	352	2.52	2.03
4.36e	291	1.27	1.01
4.36f	366	2.08	1.81

Table 4.13. Thermomechanical properties of poly(ether imide)s 4.37a-d,f



Polymer	tanδ (max) (°C)	Young's modulus (GPa) at 25°C	200°C	370°C
4.37a	448	2.39	2.01	1.31
4.37b	401	2.31	1.92	0.54
4.37c	401	2.46	2.13	0.17
4.37d	406	2.96	2.46	0.47
4.37f	439	2.45	2.01	1.05

Table 4.14. Comparison of poly(ether imide)s 4.36a-f and 4.37a-d,f with commercial polyimides



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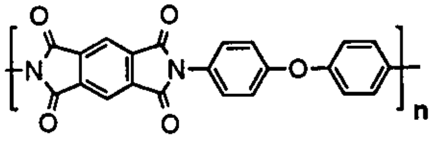

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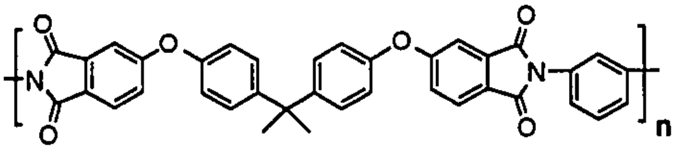

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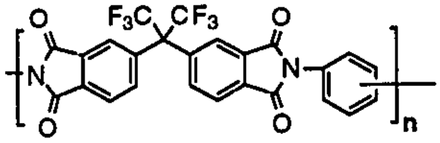

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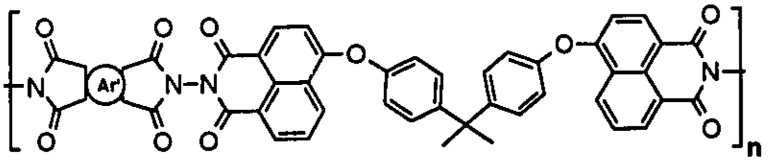
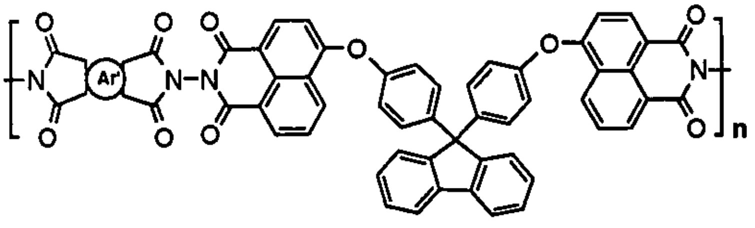


4.36a-f



4.37a-d,f

Polymer	Tg (°C)	Solubility	Reference
Kapton (**4.16**)	385	fuming HNO_3	[32]
LaRC-TPI (**4.50**)	250	sparingly in *m*-cresol	[30][31]
Avimid N (**4.51**)	352	*m*-cresol, NMP	[30][31]
ULTEM (**4.17**)	217	$CHCl_3$	[11]
4.36a-f	307-380	DCB, NMP	
4.37a-d,f	398-436	DCB, NMP	

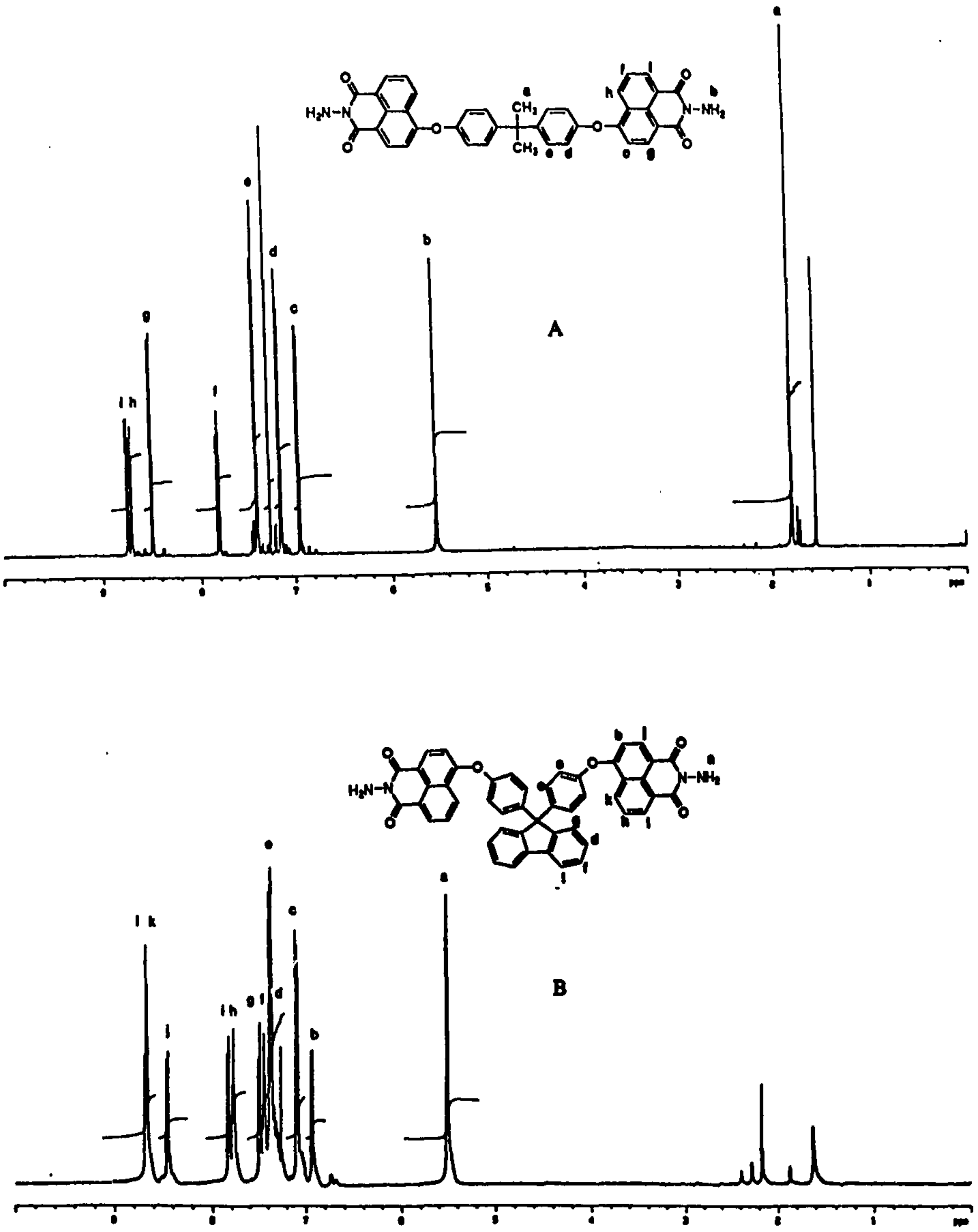


Figure 4.6. ^1H NMR (500 MHz, $CDCl_3$) of bis(N-aminoimide) 4.35a (A) and 4.35b (B).

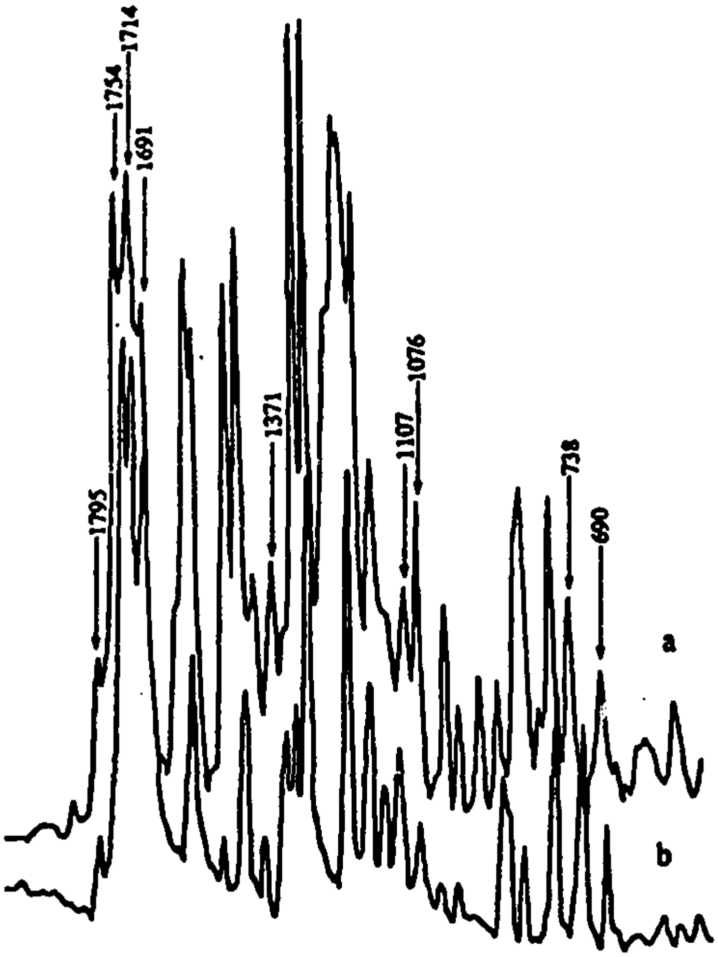


Figure 4.7. IR spectrum of (a) poly(ether imide) 4.36e and (b) unsymmetric bisimide 2.16.

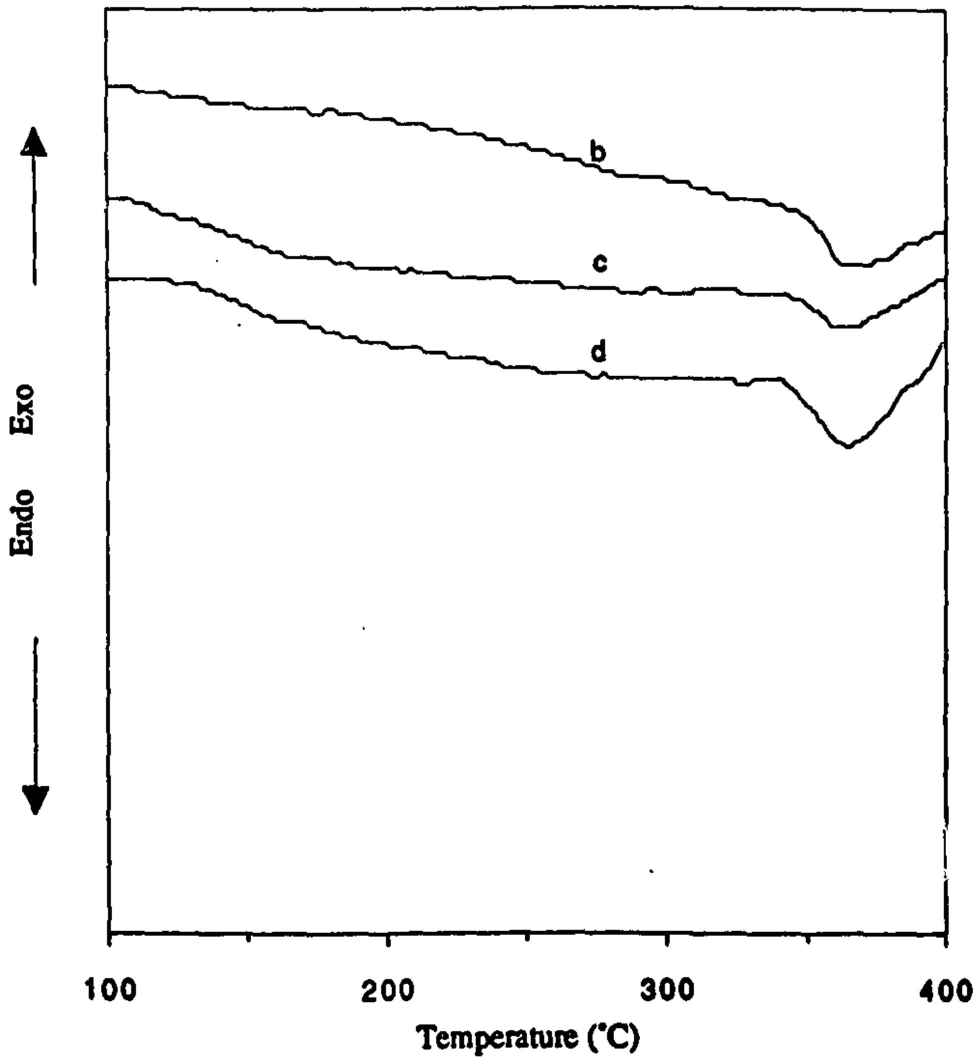


Figure 4.8. DSC analysis of poly(ether imide)s **4.36b-d** under an atmosphere of nitrogen.

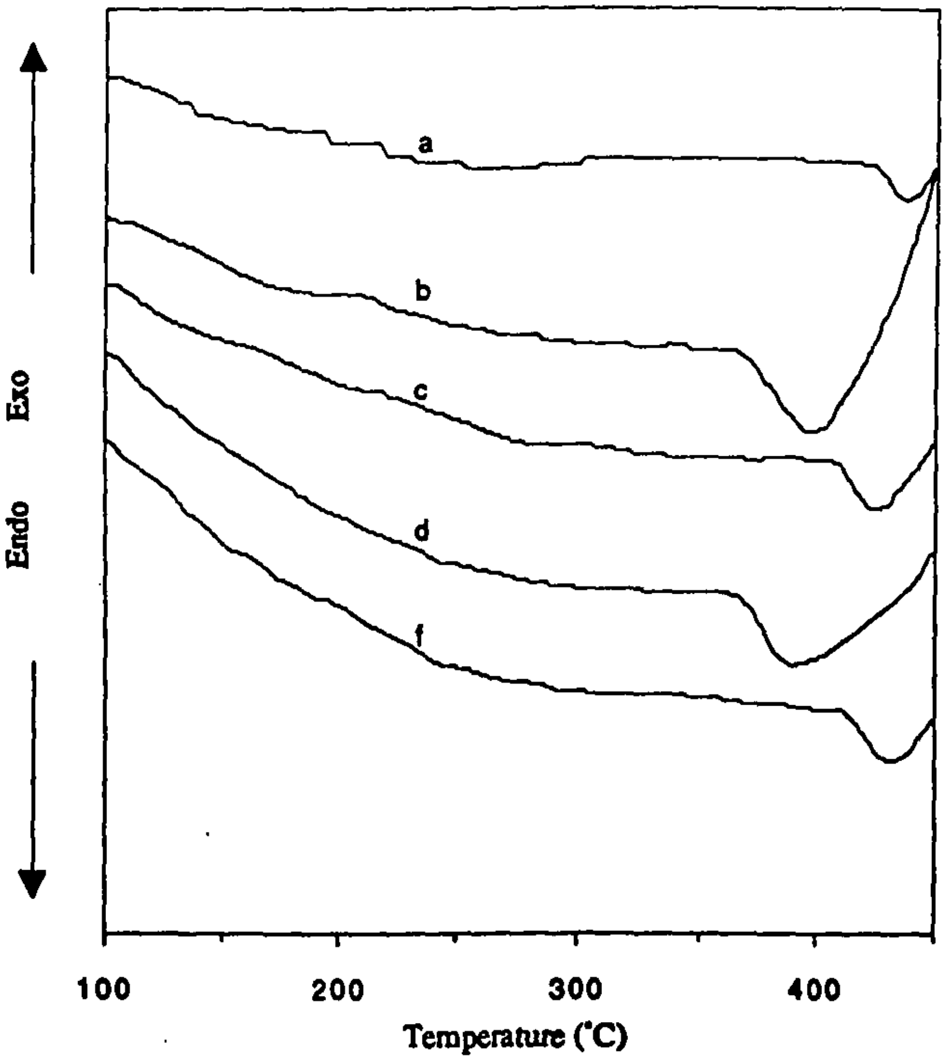


Figure 4.9. DSC analysis of poly(ether imide)s **4.37a-d,f** under an atmosphere of nitrogen.

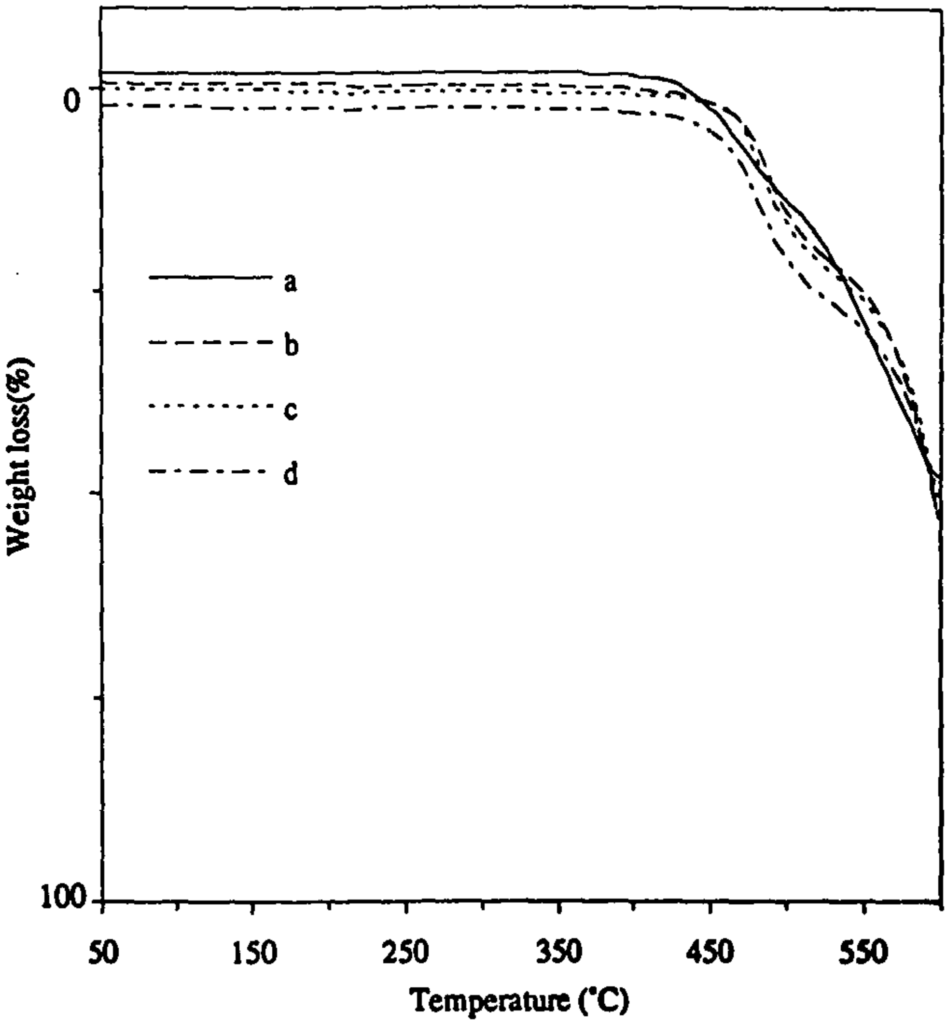


Figure 4.10. TGA thermograms for poly(ether imide)s 4.36a-d under an atmosphere of air. Offset for clarity.

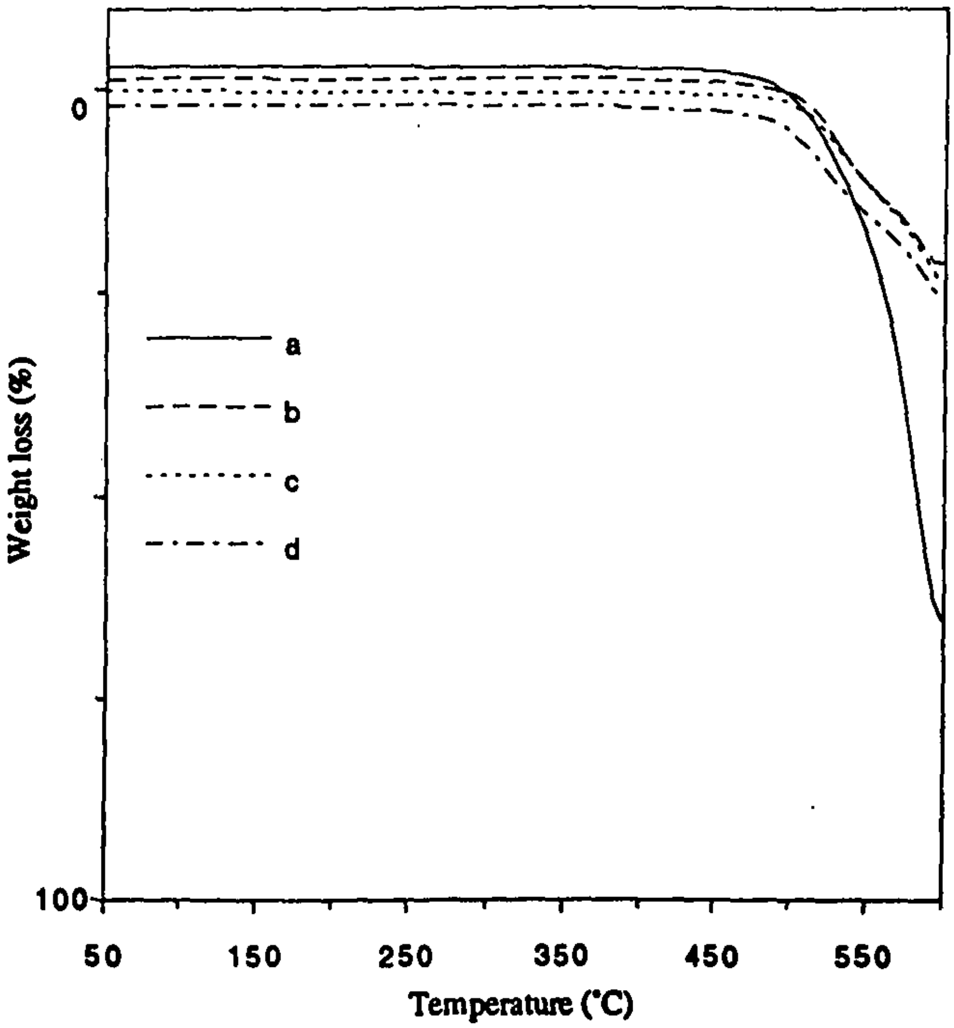


Figure 4.11. TGA thermograms for poly(ether imide)s 4.37a-d under an atmosphere of air. Offset for clarity.

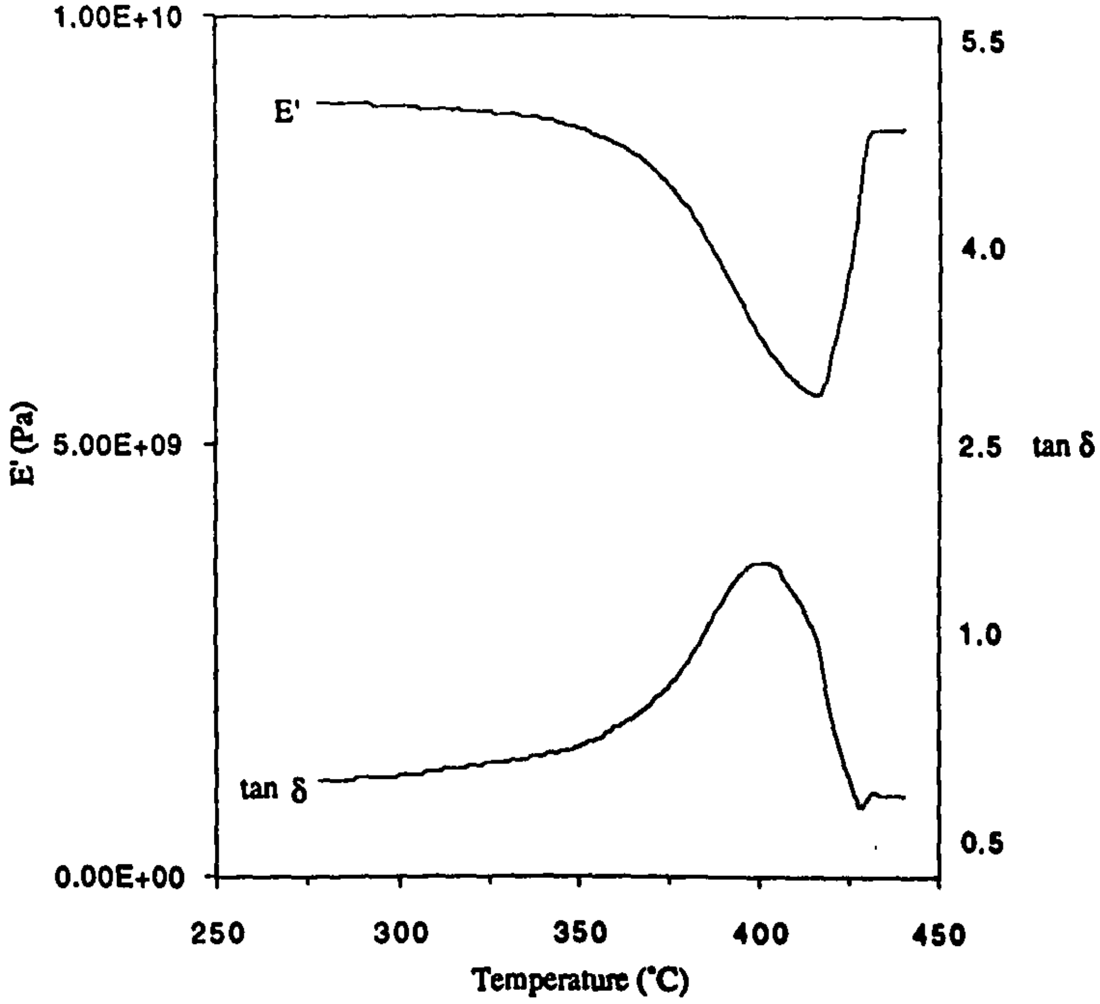


Figure 4.12. Young's modulus (E') and tan δ versus temperature for poly(ether imide) **4.37b.**

CHAPTER 5

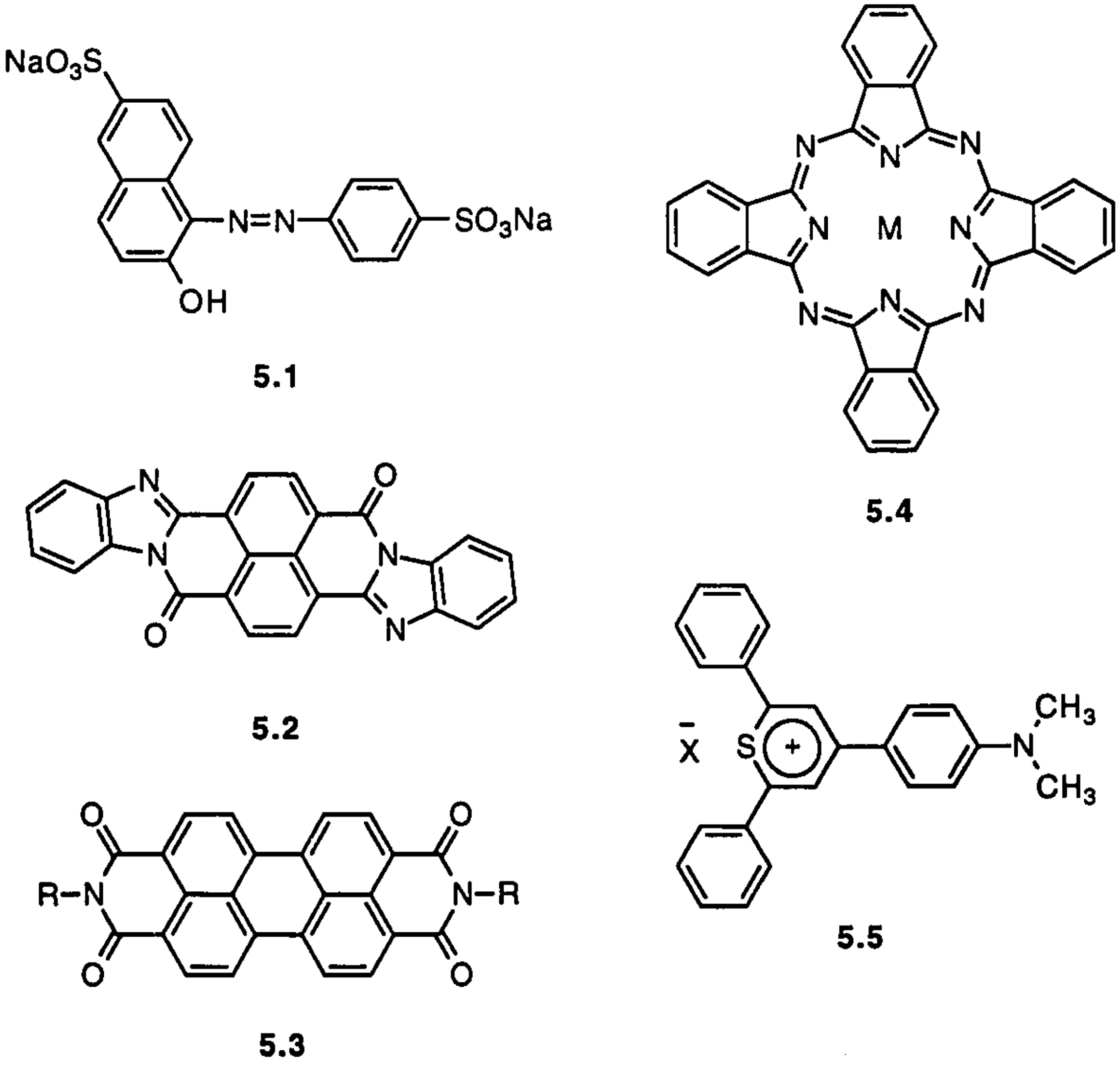
COLORED POLYMERS CONTAINING NAPHTHALENE AND PERYLENE UNITS; SYNTHESIS AND PROPERTIES

5.1. Introduction to dye molecules

Dye molecules, such as diazo compounds and derivatives of naphthalene and perylene, which are intrinsically or structurally colored materials, have been studied for many years. They have received increasing attention because of the expectation that these materials would be photoactive and some of them are photoconductive and can be used in optical devices.[1-2] Use in photovoltaic and photoelectrochemical instruments for solar energy conversion is one of the applications of these materials. Although most of the attention was paid to inorganic photoactive materials, such as silicon, zinc oxide, cadmium sulfide, etc., it was realized that using organic photoactive materials in solar cells has many potential advantages, such as low cost and ease of fabrication.[1] Another fast-growing application for the photoactive materials which are photoconductive is as xerographic photoreceptors in copiers and laser printers.[2,21] An explosive research activity in this area of science and technology has fostered this growth. The first copy machine was introduced by Xerox in 1949 and today copiers are present everywhere and have revolutionized the office. Today color copiers are used not only to duplicate the document, but also to create the document as laser printers. Organic photocoductive materials have played a key role in the process of xerography which consists of generation of electrostatic images and then development of these images into hard copy.

5.1.1. Photoconductive materials and their application in xerography

Photoconductive compounds are a group of photosensitive materials which are good insulators in the dark and become conductive upon exposure to light. A combination of a charge generation material and a charge-transporting material on a conductive substrate forms a photoreceptor layer (Figure 5.2). Many different classes of organic photoconductive compounds have been synthesized and used in commercial photoreceptors (Figure 5.1). These include diazo pigments **5.1**, naphthimidazoles **5.2**, N,N'-disubstituted-perylene-3,4,9,10-tetracarboxylic acid diimide **5.3**, phthalocyanines **5.4** and thiopyrylium salt **5.5**. There are many ways to utilize these pigments in photoreceptors. A common way is to disperse the pigment particles into a solution of polymer binder which is then coated onto a conductive substrate, by either dip coating or solution casting, to form a thin charge-generation layer.[3] While the method of using a binder has the advantages such as mechanical flexibility and low production cost, it has been found that low environmental stability in organic photoreceptors can often be traced back to the binder material itself.[4] In addition, issues related to particle size and morphology of pigments, dispersion quality of pigment, variability of material properties, uniformity of the thin generator layer, etc., generally require tremendous research effort to maximize photoreceptor yield, lifetime and copy quality in the xerographic process. Alternatively, vacuum evaporation techniques have been used to overcome the difficulties associated with applying the pigment particles as dispersions in a binder. Organic pigments with good thermal stability, like perylenes and phthalocyanines, can be deposited as uniform, thin films.[4]



5.1

5.2

5.3

5.4

5.5

Figure 5.1. Organic compounds used as photoconductors

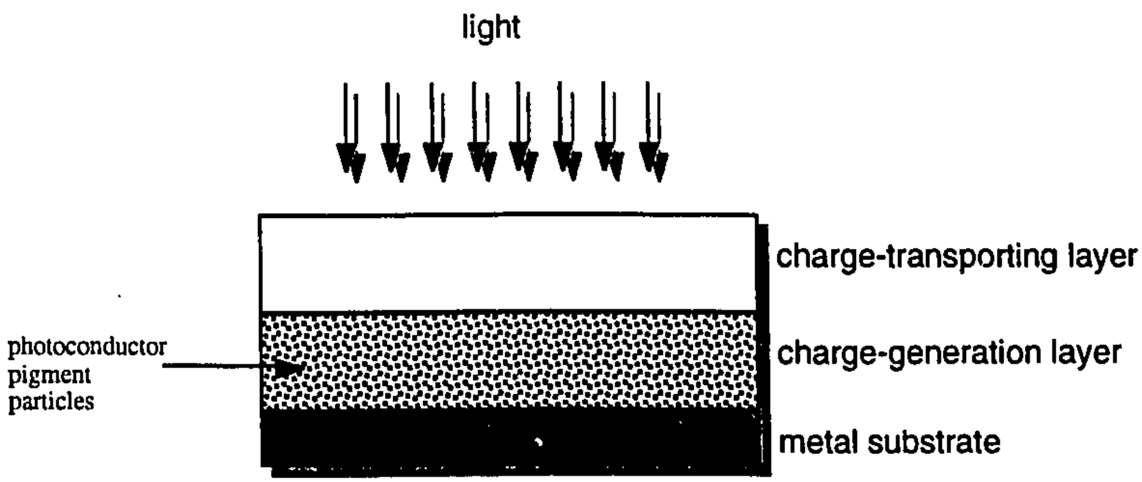


Figure 5.2. Photoreceptor

5.1.2. Dye-containing polymers

Incorporation of dye molecules into polymers is a potentially useful approach to alleviate some of the problems already mentioned with the dispersion technique.[5] Using this approach eliminates the need for a binder because the pigment moieties are molecularly dispersed in the polymer. In order to achieve this goal in a polymer system, the monomers should be selected and designed so that the resulting materials have good reliability and long-term performance as well as easy processability by conventional methods, such as solution casting. In order to make polymeric dyes one can use various synthetic approaches.[22] A common way is to attach dye molecules as pendent groups to the polymer backbone (Figure 5.3a). This approach is especially important when the direct routes (Figure 5.3b) starting from dye-containing monomers have low chemical and thermal stability characteristic of many dyes, such as azo pigments, and/or the low reactivity of the monomers themselves. Poly(1-vinylpyrene)s **5.6** is an example of the side-group approach in which pyrene rings are attached to the polyethylene backbone as pendants (Figure 5.4).[24] For dyes containing fused aromatic rings such as naphthalenes and perylenes one can imagine that any polymers containing these units directly into the backbone would be intractable and therefore not easy to prepare. This is due to the rigid planar structure of these macroaromatic structures and their propensity to uniformly pack and crystallize. The low solubility and high melting point of these aromatic pigments are their outstanding characteristics. Polybenzimidazo-benzophenanthrolines ladder polymers, such as **5.7** and **5.8** (Figure 5.4), have been reported by Xerox researchers to be useful polymeric photoconductors.[5] These ladder polymers are made by a polycondensation reaction in polyphosphoric acid (PPA) as solvent. Preparation of thin films from these polymers needs powerful solvents such as aluminum chloride/nitromethane and special equipment.

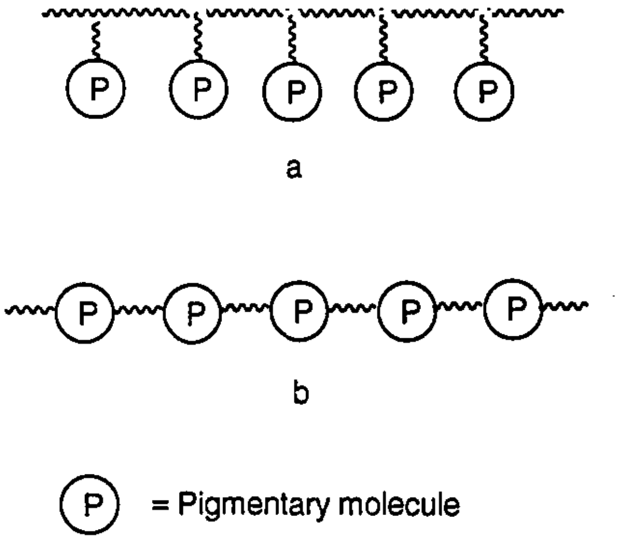
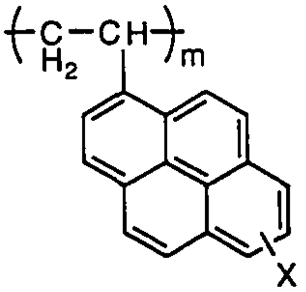
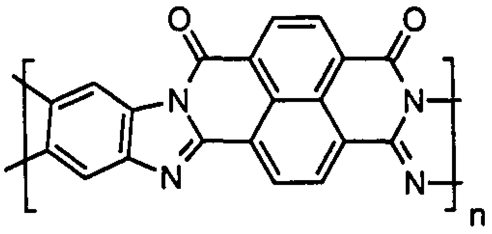


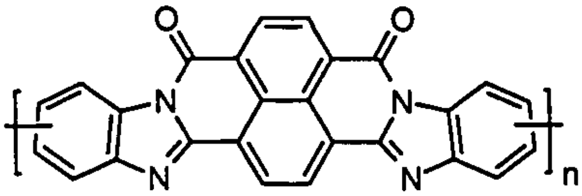
Figure 5.3. Two ways of incorporating dye molecules into a polymer backbone



5.6



5.7



5.8

Figure 5.4. Dye-containing polymers

5.1.3. Dye-containing polyimide

Polyimides are known as one of the most important high temperature commercial polymers.[6] However, the rigid and polar structure of the imide group imparts a high melting point and low solubility to the polyimides and creates some serious problems in the processing steps. It has been shown that aromatic diamines and dianhydrides with flexible linkages or solublizing pendent groups can significantly increase the processability of polyimides (refer to chapter 4 for more detail).[7] For example, Rehahn recently reported the synthesis of rigid-rod polyimides with dye-containing side groups using solubilizing alkyl side chains and a polymeric precursor route.[14] But the commercialization of these monomers have limitations due to the complexity of their synthesis and high cost of starting materials and reagents. Furthermore, aromatic amines are known as air and light-sensitive materials and they are carcinogens requiring special handling and apparatus for their bulk manufacturing which ultimately increases costs. The only commercialized monomer of this type with flexible linkages is bisphenol-A dianhydride (BPADA) **4.13e** which is made from bisphenol-A **4.34a** and nitrophthalimide **4.40** in a multi-step synthesis (refer to Scheme 4.6).[8] Dianhydride **4.13e** and m-phenylene diamine **4.14a** are used to prepare the only melt and solution processable commercial polyimide (ULTEM) **4.17** (see Figure 4.3).[9] In order to incorporate simple rigid dianhydrides such as pyromellitic dianhydride (PMDA) **4.13a** into the organic-soluble polyimides, diamines with solubilizing groups and linkages have to be used. This criterion is even more difficult in the case of aromatic dianhydrides with poly-fused aromatic ring-systems such as 1,4,5,8-naphthalenetetracarboxylic dianhydride **5.9a** and 3,4,9,10-perylenetetracarboxylic dianhydride **5.10a**. For example, it has been shown that the reaction of **5.9a** with oxydianiline (ODA) **4.14c** gives a polyimide which is only soluble in concentrated sulfuric or nitric acid.[10] A Russian group was able to react **5.10a** with a modified caprolactam in several stages in order to make colored polyimides. However, the presence of polyamic acid byproduct and formation of amine salts caused formation of an undesired gel during the reaction.[11] These examples demonstrate that the classical approach to polyimides utilizing a dianhydride and an aromatic diamine is not a practical way to incorporate poly-fused aromatic rings into the polymeric backbone.

Reaction of **5.9a** with hydrazine to form N,N'-diamino-1,4,5,8-naphthalenetetracarboxy bisimide **5.9b** was reported by Dine-Hart.[15] He attempted to make polymers by reacting this diamino compound with pyromellitic dianhydride and dianhydride **5.9a**. These attempts failed and only low molecular weight materials were obtained due to the intractability of the resulting products which were only slightly soluble in concentrated sulfuric acid.[16] They were not completely characterized, but the early studies on these low molecular weight materials and some model compounds indicated that they should have high thermal stability at elevated temperatures.[17]

5.2 Goals

We were interested in extending the hydrazine-aromatic anhydride approach to the synthesis of polyimides containing the more rigid naphthalene and perylene molecules using aromatic dianhydrides containing flexible linkages. In chapter 4, we described the synthesis of several novel bis(N-aminoimide)s **4.35a-c** from hydrazine, chloronaphthalic anhydride **2.14b** and different bisphenols **4.34a-c**. These bis(N-aminoimide)s act as diamines and upon reaction with aromatic dianhydrides containing flexible moieties gave high molecular weight poly(ether imide)s **4.36a-f** and **4.37a-d,f**.[12]

We decided to reinvestigate the polymerization of N,N'-diamino-1,4,5,8-naphthalenetetracarboxy bisimide **5.9b** with different dianhydrides in order to make soluble polyimides and further study their thermal, mechanical and physical properties.

We were also interested in exploring the potential application of the N-aminoimide chemistry for the introduction of larger aromatic dye molecules into the polyimide chain. We therefor synthesized bis(N-aminoimide) **5.10b** from perylene 3,4,9,10-tetracarboxylic dianhydride **5.10a** and investigated its polymerization with dianhydrides.

5.3. Monomer synthesis

5.3.1. Synthesis of N,N'-diamino-1,4,5,8-naphthalenetetracarboxy bisimide 5.9b

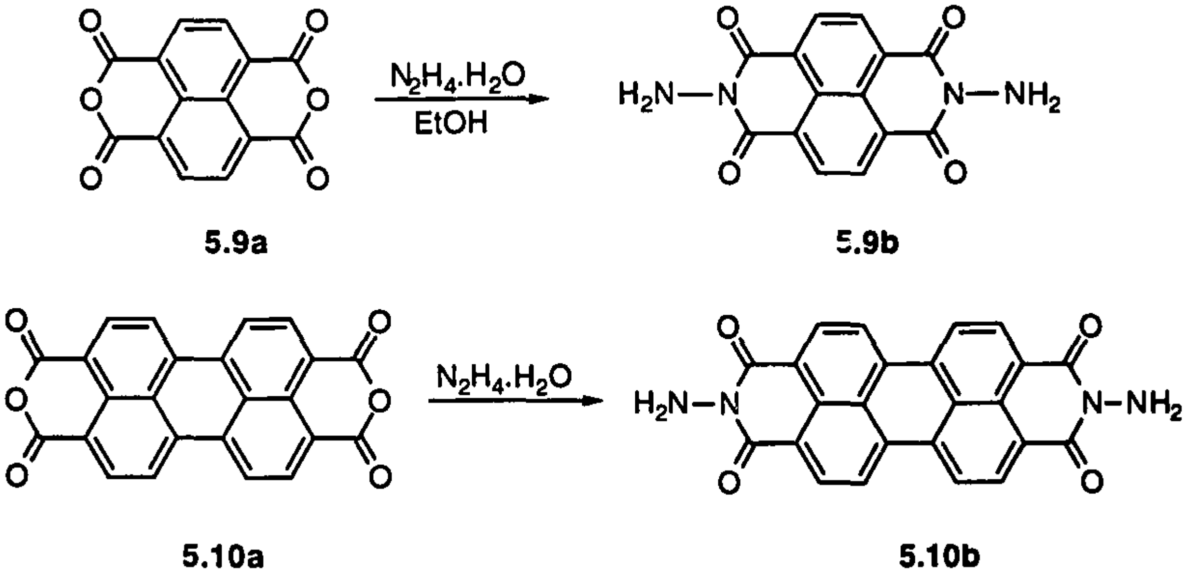
The monomer N,N'-diamino-1,4,5,8-naphthalenetetracarboxy bisimide **5.9b** was synthesized from the reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride **5.9a** with hydrazine according to the method described in chapter 4 for the synthesis of 4-chloro-N-aminonaphthalimide. Dissolution of dianhydride **5.9a** in hot ethanol takes place slowly and by addition of a slight excess of hydrazine monohydrate yellow material forms in a few seconds which is not soluble in the boiling solvent. Hot filtration of the mixture gives crude product which contains bis(N-aminoimide) **5.9b** and probably some open ring hydrazides intermediates which are converted to imide **5.9b** upon drying under vacuum. The yield of the reaction is almost quantitative (Scheme 5.1).

5.3.2. Synthesis of N,N'-diamino-3,4,9,10-perylenetetracarboxy bisimide 5.10b

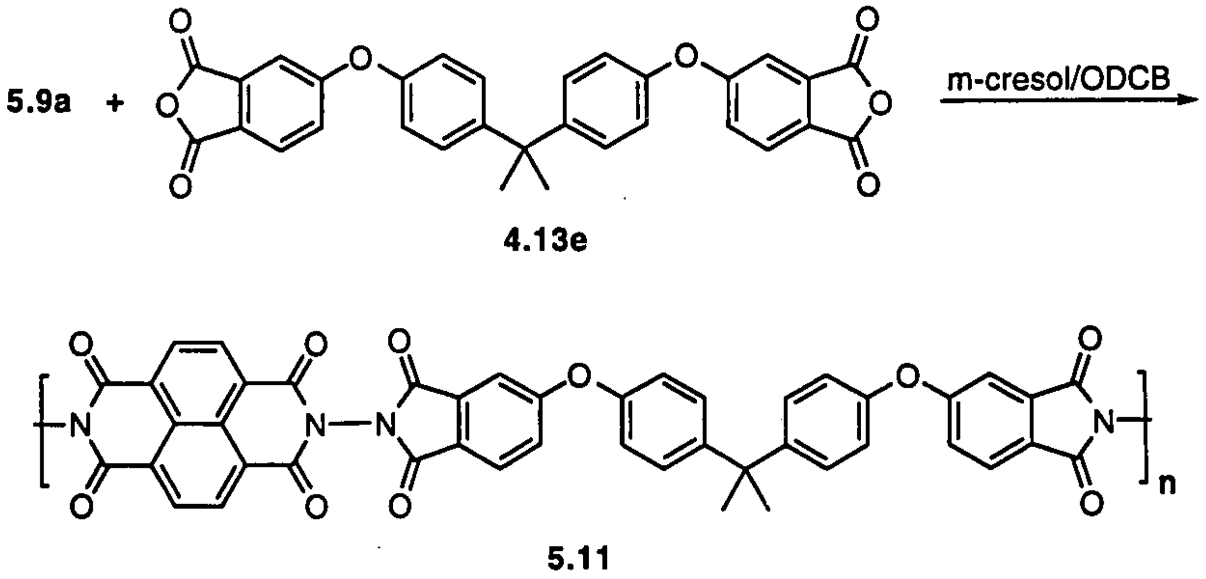
The perylene monomer **5.10b** was synthesized from 3,4,9,10-perylenetetracarboxylic dianhydride **5.10a** and hydrazine monohydrate. Perylene **5.10a** readily reacts with excess hydrazine monhydrate, which also acts as a reaction solvent, forming a dark purple slurry. The excess of hydrazine was removed under high vacuum at 150°C to give **5.10b** as a dark purple powder in quantitative yield (Scheme 5.1). Both monomers **5.9b** and **5.10b** were used in subsequent steps without further purification.

Monomer **5.9b** is soluble in hot *m*-cresol and slightly soluble in hot NMP while monomer **5.10b** is practically insoluble in organic solvents. It readily dissolves in concentrated sulfuric acid at room temperature and slightly in hot *m*-cresol and p-chlorophenol (PCP). Generally, the solubility of these monomers increases by increasing the acidity of the solvents.

Scheme 5.1



Scheme 5.2



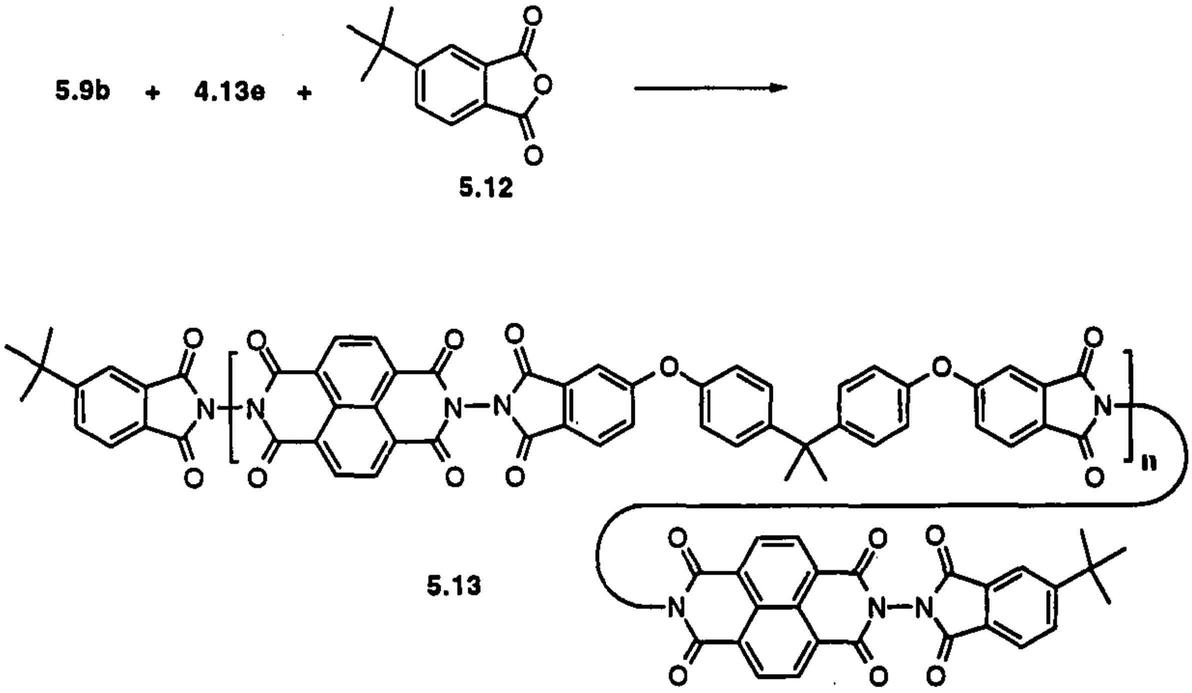
5.4. Polymer synthesis

5.4.1. Homopolymerization of 5.9b with bisphenol-A dianhydride (BPADA) 4.13e.

Monomer **5.9b** was polymerized with dianhydride **4.13e** in a one-step solution polymerization reaction using *m*-cresol and 1,2-dichlorobenzene (DCB) to form high molecular weight homopolymer **5.11** (Scheme 5.2).

To determine the absolute number-average molecular weight of poly(ether imide) **5.11**, an end-capped polymer was prepared with a calculated degree of polymerization of 50 . The reaction was run using monomers **5.9b** and **4.13e** in the presence of 4-*tert*-butyl phthalic anhydride **5.12** as an end-capping agent to give poly(ether imide) **5.13** with 4-*tert*-butyl phthalimide terminal groups (Scheme 5.3). The exact number-average molecular weight was determined for these capped materials by ^{1}H NMR studies which showed the degree of polymerization n ≈ 51. The protons of the *tert*-butyl groups show resonances at δ 1.41 and those of the isopropylidene moiety at δ 1.78 and from the ratio of the integrated peaks we can determine the degree of polymerization. The assigned ^{1}H NMR spectrum for polymer **5.13** is given in Figure 5.5.

Scheme 5.3



5.9b + **4.13e** + **5.12**

5.13

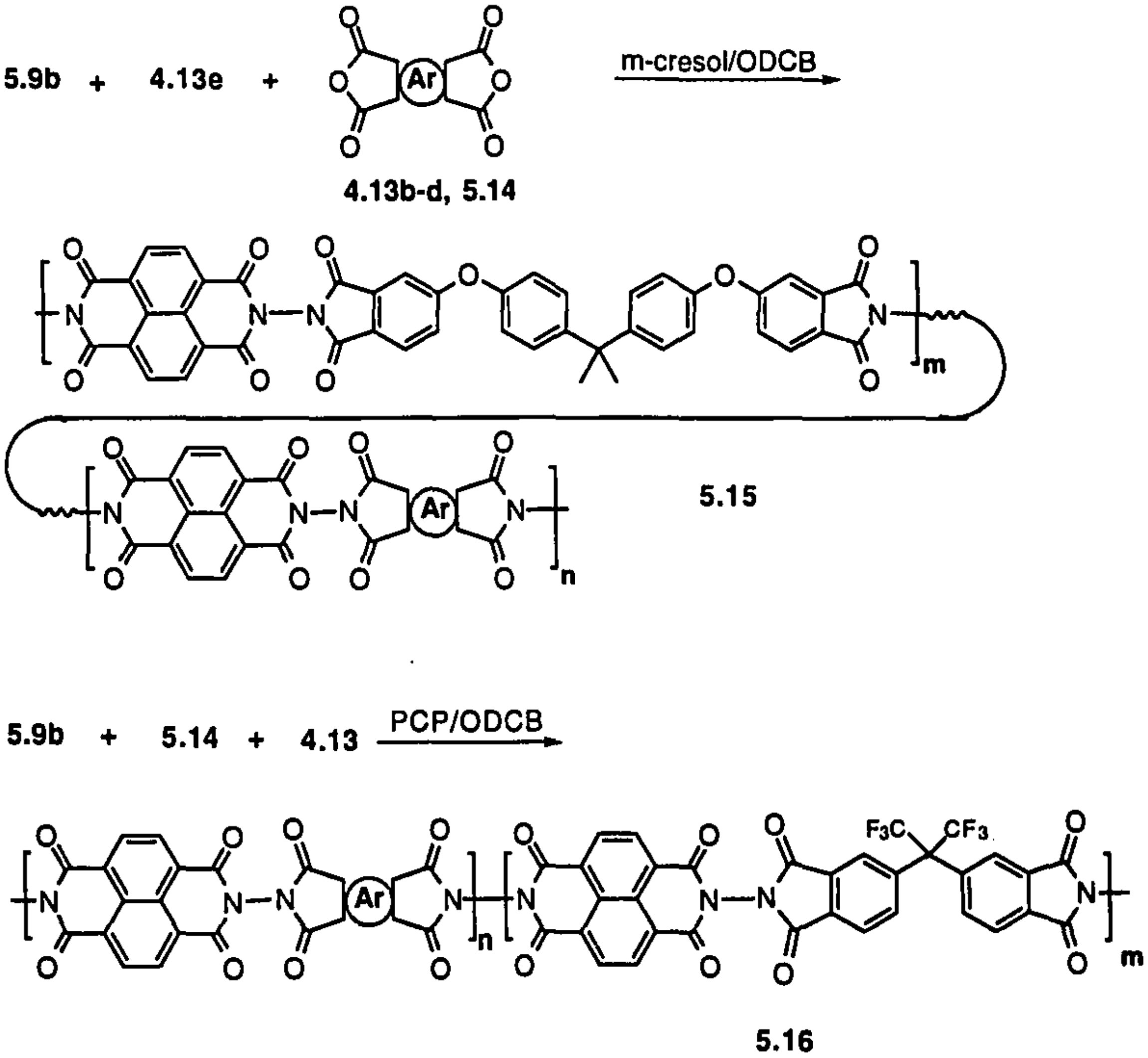
5.4.2. Oligomers from 5.9b and other dianhydrides

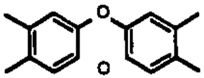
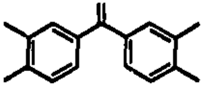
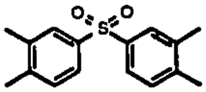
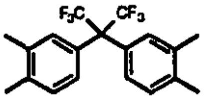
Attempt to make homopolymers from naphthalene **5.9b** and other dianhydrides via the one-step method failed due to insolubility of the oligomers which formed in the early stage of polymerization. Employing the two-step polymerization method which gives poly amic acid at the first step using NMP as solvent showed no improvement, presumably because of insolubility of compound **5.9b** in NMP at ambient temperature.

5.4.3. Copolymers 5.15a-d and 5.16a-c from 5.9b and dianhydrides 4.13b-e and 5.14

High molecular weight copolyetherimides **5.15a-d** were successfully prepared from **5.9b**, **4.13e** and different dianhydrides (**4.13b-d**, **5.14**) in a one-step solution polymerization reaction using *m*-cresol as solvent with a solids concentration of 18% (Scheme 5.4). The mole ratio of dianhydride **4.13e** to other dianhydrides was 2:1. Decreasing the relative amount of **4.13e** dramatically affected the solubility of the resulting copolymers in all cases and low molecular weight materials precipitated out of the reaction mixture during the polymerization. Lowering the monomer concentration has little effect on the resulting products. Since copolymers generally show significant improvement in solubility, copolymers were synthesized using a mixture of two dianhydrides. High molecular weight copoly(ether imide)s **5.16a-c** were prepared (Scheme 5.4) from **5.9b**, 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) **5.14** and another dianhydride (**4.13b-d**) as a comonomer using the one-step method in PCP/DCB solvent system. The solids concentration in this case was reduced to 8% to lower the viscosity of the solution. All the copolymers of series **5.15** and **5.16** remained totally soluble during the course of reaction and only in case of copolymers **5.16a-c** did some cloudiness appeared when the molecular weight increased. The solution became viscous during the reactions indicating that substantial polymerization had occurred. In all of these polymerization reactions, 2 mol% phthalic anhydride was used as end-capping agent in order to control the molecular weight of the resulting materials.

Scheme 5.4



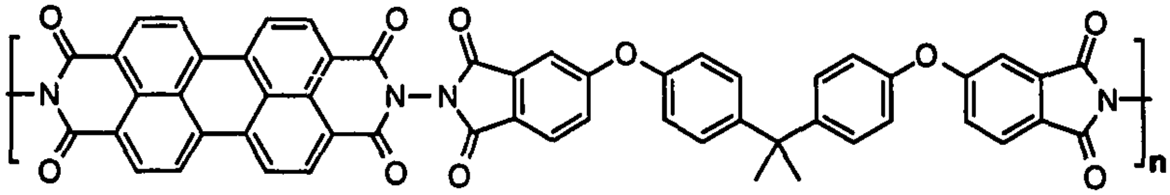
dianhydride	5.15	5.16	Ar
4.13b	a	a	
4.13c	b	b	
4.13d	c	c	
5.14	d		

5.4.4. Homopolymers from 5.10b and BPADA 4.13e

Polymerization of N,N'-diamino-3,4,9,10-perylenetetracarboxy bisimide **5.10b** with BPADA **4.13e** was conducted in a mixture of PCP and DCB as solvents. The reaction required 4 days at 200°C in order to form high molecular weight poly(ether imide) **5.17** (Scheme 5.5). When *m*-cresol was used instead of PCP as a solvent high molecular weight homopolymer was obtained after 8 days. The reason for such long reaction times is related to the lack of solubility of perylene **5.10b** in *m*-cresol which is less acidic than PCP. We postulate that the rate of the polymerization reaction is controlled by the dissolution of perylene **5.10b**.

Scheme 5.5

$$\mathbf{5.10b} + \mathbf{4.13e} \xrightarrow[\text{ODCB}]{p\text{-chlorophenol}}$$



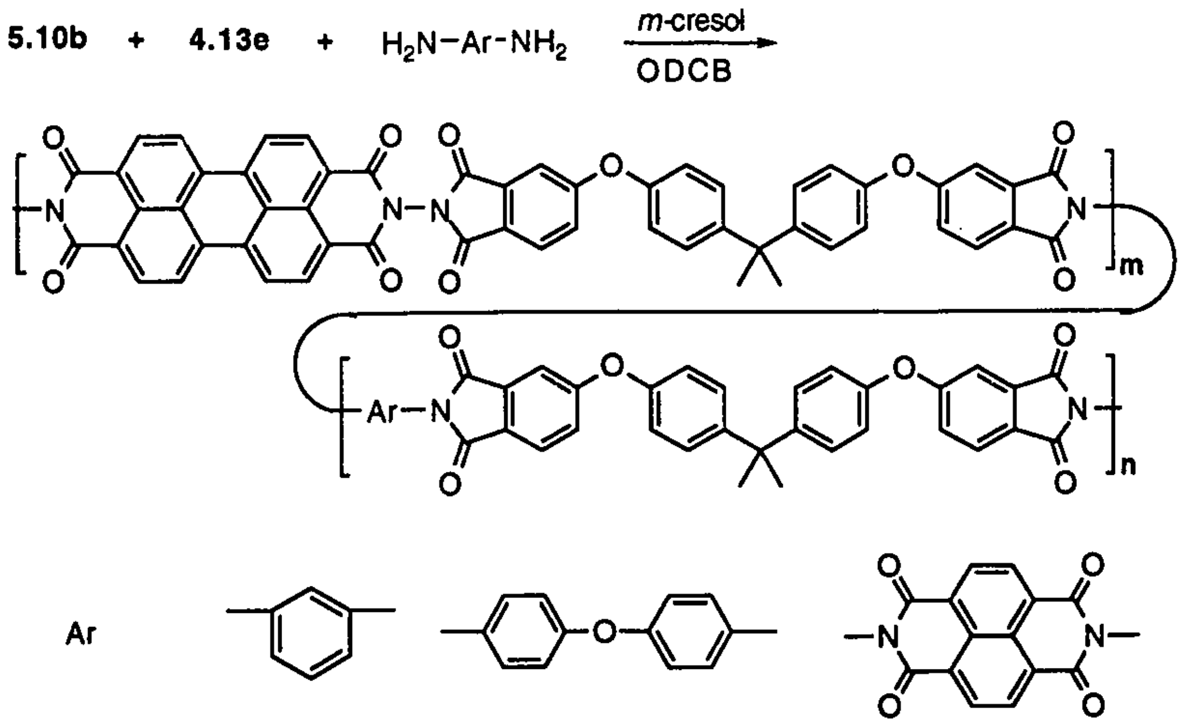
5.17

5.4.5. Copolymers 5.18a-c, 5.19a-c and 5.20 from 5.10b, BPADA 4.13e and a diamine as a comonomer

In order to investigate the effect of concentration of perylene units on the properties of the resulting polymers, copoly(ether imide)s **5.18a-c** and **5.19a-c** were prepared from monomers **5.10b** and **4.13e** using *m*-phenylene diamine (MPD) **4.14a** and ODA **4.14c** as comonomers respectively (Scheme 5.6). The polymerization reactions were carried out in *m*-cresol/DCB. Reaction times became significantly shorter when a lower concentration of perylene monomer was used. High molecular weight copolymers **5.18c** and **5.19c** containing 20 mol% perylene monomer and 80 mol% of other diamines were isolated after 4 days. These copolymers are readily soluble in chloroform at room temperature. Copolymers **5.18b** and **5.19b** which contain 50 mol% perylene **5.10b** are readily soluble in *sym*-tetrachloroethane (TCE) and *m*-cresol at room temperature. However, when the amount of monomer **5.10b** was raised to 80 mol% as in copolymers **5.18a** and **5.19a** or for homopolymer **5.17**, the resulting materials only swell in TCE but are very soluble in *m*-cresol at room temperature. Solution viscosities of the polymers in the appropriate solvent (Table 5.3) are between 0.34-0.53 dL/g.

Copolymer **5.20** was also prepared by reacting monomers **5.10b** and **5.9b** in 1:1 mol ratio with dianhydride **4.13e** in a similar way using *m*-cresol/DCB as a solvent system. It forms a red colored transparent film by casting from solution of *m*-cresol. All of the above materials were used for a further investigation of their photophysical properties (Chapter 6).

Scheme 5.6



diamine	**4.14a** (MPD)	**4.14c** (ODA)	**5.9b**
copolymer	**5.18**	**5.19**	**5.20**

copolymer, **5.18** or **5.19**	a	b	c
mol% of **5.10b**	80	50	20
mol% of **4.14a** or **4.14c**	20	50	80

5.5. Results and discussions

5.5.1. NMR and IR study of polymers

The ^1H NMR spectra of copolymers **5.18b,c** and **5.19c** in chloroform or TCE exhibit a broad peak around δ 8.1-8.7 which corresponds to all the protons of the perylene ring. Integration of this peak and comparison with the peak for the isopropylidene group shows good agreement with the calculated amount of perylene monomer **5.10b** used in the polycondensation. Characteristically, the signals of the protons in the bay-region of a perylene appear as a broad peak at lower field.[25] This broadness does not seem to be due to slow motion of the perylene ring in the backbone of the polymer which may stack together in the solution. This was demonstrated by studying the effect of temperature on the shape of this broad peak which remained unchanged up to 100°C. The isopropylidene moiety shows a resonance at δ 1.75 and other aromatic protons from BPADA appear around δ 7.0-8.0. Figure 5.9 shows a ^1H NMR spectrum of the aromatic region of copolymer **5.18c** in which the mole ratio of perylene monomer to *m*-phenylene diamine is 20:80. The assignments given in this figure were made by comparison with the spectra of known polymers, e.g. ULTEM **4.17**. This spectrum shows two new peaks in addition to the broad peak of the perylene group which were assigned as proton b and j in the BPADA **4.13e** unit attached to the perylene group (see Figure 5.9 at the end of this chapter). The change in the environment of the protons in **4.13e** is due to the attachment of the electron withdrawing perylene diimide. This effect on proton j of the phthalimide moiety is more than 50 Hz and in case of proton b is smaller (around 30 Hz) due to a longer range effect. There are probably similar changes on the chemical shift of the other protons of BPADA which overlap and therefore are not easily resolved. The ^1H NMR spectra of homopolymer **5.11** or **5.13** shows a similar down field shift of the BPADA protons as compared to ULTEM which is additional evidence to support our hypothesis.

The I.R. spectra of the polymers **5.11** and **5.15a-d** and **5.16a-c**, show absorption bands characteristic of aromatic polyimides i.e. in the range of 1606-1618, 1710-1719, 1739-1753 cm^{-1}. The absorption bands for polymers **5.17**, **5.18a-c** and **5.19a-c** are in the range 1693-1701, 1712-1726 and 1740-1750 cm^{-1}. A weak absorption band is observed in all cases around 1101-1112 cm^{-1} which is characteristic of the N-N bond of hydrazines.[27]

5.5.2. T_g of polymers

Glass transition temperatures of the polymers made from monomer **5.9b** are listed in Table 5.1. All the T_g values are above 340°C. Poly(ether imide)s **5.15c** and **5.15d** do not show a detectable T_g signal in a differential scanning calorimetry measurement and their T_g's were determined from tanδ (max) measured by thermo-mechanical analysis (Table 5.2). From the copolymers of series **5.16** only copolymer **5.16a** shows a very weak T_g at 438°C in DSC and the other copolymers of this series have no clear transition. Attempts to detect their T_g's in TMA failed owing to brittleness of their films cast from PCP/DCB and only the film of copolymer **5.16c** clearly showed a T_g at 456°C according to its tanδ (max) (Table 5.2). The rigid structure of the naphthalene bisimide moiety in the backbone of the polymer and restriction in rotation along the N-N bond are presumably responsible for the high T_g values of the polymers, while BPA groups and ether linkages introduce flexibility and hence impart solubility to the polymer. In order to demonstrate the effect of using bis(N-aminoimide) **5.9b** as a diamine on the T_g of other known poly(ether imide)s the copolymer **5.21** was prepared by replacing 50% of m-phenylenediamine **4.14a** in ULTEM **4.17** with monomer **5.9b**. The resulting copolymer is soluble in chloroform at room temperature while the T_g increases to 288°C which is 73°C higher than the cognate ULTEM.

Tables 5.3 and 5.4 show the glass transition temperatures and the temperature of maximum tanδ for poly(ether imide) **5.17** and other copoly(ether imide)s **5.18a-c**,

5.19a-c and **5.20** from DSC and TMA measurements, respectively. The T_g of the highly crystalline homopolymer **5.17** was only detected in the TMA at 405°C. Its theoretical Tg calculated from the Fox equation is 427°C.[26]

By incorporating *m*-phenylenediamine **4.14a** or ODA **4.14c** as comonomers in **5.18a-c** and **5.19a-c** the T_g's were clearly detectable in DSC and their values drop rapidly as a result of the lowering of the amount of perylene used in the copolymers. The lowest T_g's are 250 and 247°C for **5.18c** and **5.19c** respectively. The T_g values of copolymers of series **5.19** are slightly lower than those of series **5.18** owing to the less restricted rotation present in the flexible ether linkage of the ODA moiety in copolymers **5.19a-c**. The T_g values obtained from TMA are a few degrees higher than the corresponding values from DSC. Figure 5.12 shows DSC thermograms of copolymers **5.18a** and **5.18b**.

5.5.3. Solution properties of polymers

Homopolymer **5.11** is readily soluble in chloroform at room temperature while copolymers **5.15a-d** and **5.16a-c** are soluble in a mixture of *m*-cresol/DCB or PCP/DCB at room temperature, respectively. All the polymers made from monomer **5.9b** are readily processed from solution to give flexible, yellow transparent films. Films of the copolymers of series **5.16** are less flexible and have darker color than the others and appear brownish yellow. Inherent viscosities of polymer **5.11** and other copolymers are in the range of 0.41-1.51 dL/g (Table 5.1).

All of the polymers from perylene **5.10b** can be readily cast into flexible transparent red films. The quality of the films depends on the concentration of perylene groups in the polymer, thickness of the films and the mode of preparation. Homopolymer **5.17** and copolymers **5.18a** and **5.19a** which contained higher amounts of perylene units give less flexible dark red films. Slow evaporation of solvent during the casting of these materials results in more brittle opaque films due to crystallization of the polymers. Only when a low solution concentration of these polymers is employed along with a rapid evaporation of solvent are relatively flexible thin films obtained from these materials. The other copolymers form tough flexible red films from chloroform or TCE.

5.5.4. TGA study of polymers

The thermooxidative stability of polymer **5.11** and copolymers **5.15a-d** are lower than copolymers **5.16a-c**. Their TGA thermograms show 5% weight loss in air around 456-465°C (Figure 5.6). The poorer stabilities can be attributed to the susceptibility of isopropylidene groups to oxidation. The 5% weight losses of all the samples in air under the experimental condition are higher than in nitrogen (Table 5.2). The thermooxidative and thermal stabilities of copolymers **5.16a-c**, which contain no aliphatic hydrogens, are considerably higher. Their TGA thermograms show 5% weight losses around 497-500°C in nitrogen and 506-526°C in air (Figure 5.7).

All polymers from monomer **5.10b** demonstrate excellent thermal stability by thermogravimetric analysis (TGA), with a 5% weight loss under an atmosphere of air and nitrogen in the temperature range 453-507°C (Table 5.2).

5.5.5. Mechanical properties of polymers

Table 5.2 summarizes tensile properties of the films of the polyimides. The films had tensile moduli of 1.5-2.7 GPa at 25°C. They maintain most of their mechanical properties up to 200°C and a major change appears around 300°C. The low modulus value (1.1 GPa) for copolymer **5.16c** is probably due to the presence of the solvent remaines in the film. The high T_g values make drying of these materials very difficult. Figure 5.8 shows the TMA trace of homopolymer **5.11**.

The films of polymers and copolymers from perylene showed tensile moduli of between 0.6-2.4 GPa at 25°C. Their moduli remained almost unchanged and in some cases showed some increase when the temperature was raised to 200°C (Table 5.4). The increase of tensile moduli is quite significant in copolymers with lower amounts of perylene, especially in copolymers containing ODA moiety. This unexpected behavior presumably relates to the tendency of perylene-containing polymers to crystallize. Copolymers with 50 or 20 mol% of perylene monomers which have relatively lower Tg values probably form some crystalline domains at elevated temperatures. Crystallinity would be enhanced at high temperatures while a stress/strain condition is applied to the polymer film.

5.5.6. X-ray study of polymers

X-ray diffraction experiments on solution-cast film of homopolymer **5.17** shows a high degree of crystallinity. Copolymers **5.18a** and **5.19a** where 20% of perylene monomer was replaced by another diamine show only a relatively low degree of crystallinity. X-ray diffraction patterns of **5.17** and **5.18a** are shown in Figure 5.10. The high degree of crystallinity in homopolymer **5.17** is due to the regularity of the macromolecular chains and the packing of perylene macrocyclic rings together (Figure 5.11). In copolymers this regularity is disrupted because of random distribution of repeating units in the backbone. Copolymers **5.18c** and **5.19c** are amorphous whereas the copolymers **5.18b** and **5.19b** show a small amount of crystallinity only when they are stretched at temperatures close to their T_g's.

5.6. Conclusions

Bis(N-amino imide)s have been prepared from hydrazine and two polycyclic aromatic dianhydrides. These bis(N-amino imide)s act as diamines and undergo condensation polymerization with dianhydrides to give polyimides and copolyimides in excellent yield. The polymerization reaction are conducted in *m*-cresol or *p*-chlorophenol using 1,2-dichlorobenzene as azeotropic agent at temperatures between 190-220°C to give high molecular weight polymers. Glass transition temperatures of these materials in most cases are above 300°C. They show 5% weight losses above 450°C in air, indicative of their high thermal stability. All of the polymers and copolymers can be readily processed from solution to give flexible yellow or red films. Their photophysical properties make them an excellent material for further investigation into their potential, for application in related areas.

5.7. Experimental

General Methods.

The ^{1}H NMR spectra (500 MHz) were measured with a Varian Unity-500 instrument, using deuteriochloroform, DMSO-d6 or TCE as a solvent. The chemical shifts were calibrated using tetramethylsilane (TMS). The chemical shift (δ) and coupling constant (J) data are quoted in ppm and hertz respectively. UV spectra were performed on a SP-800 Unicam ultraviolet spectrophotometer. Inherent viscosities were determined at 0.5 g/dL concentration in chloroform at 25° C, m-cresol at 50° C or in PCP at 50° C using a Ubbelohde dilution viscometer.

p-Chlorophenol (PCP) was purchased from Aldrich and used without purification.

The 1,4,5,8-naphthalenetetracarboxylic dianhydride **5.9a** (from Aldrich Chemical Co.) was purified according to the procedure described in the literature with some modifications.[13] Thus, 50 g of the dianhydride **5.9a** was dissolved in 200 mL of aqueous 21% KOH solution. The dark brown solution was heated at 70°C with charcoal for 20 min, then filtered and heated again with charcoal for 10 min. After filtration, the yellow filtrate was cooled to room temperature and dilute HCl added until acidic to pH paper (pH 1-12). The white precipitate of tetraacid was filtered, washed with water and acetone and dried in vacuum at 60°C overnight. This powder was boiled with a mixture of 600 mL glacial acetic acid and 150 mL acetic anhydride for 2 h.The cream-colored product was filtered washed with methanol and ethyl ether and dried under vacuum at 80°C.

The 3,4,9,10-perylenetetracarboxylic dianhydride **5.10a** was purified in a same way except that 20 g of dianhydride was dissolved in 200 mL of KOH solution. The color of tetrapotassium salt in aqueous solution is dark green. The red color of the dianhydride **5.10a** after boiling with a mixture of glacial acetic acid and acetic anhydride was brighter than before purification.

Other characterization methods and chemicals used in this chapter were described in the experimental section of chapter 4.

Monomer synthesis

Naphthalene-N,N'-bisaminoimide 5.9b.

The procedure reported by Dine-Hart[16] was used with some modification. To a solution of 5 g (18.6 mmol) of 1,4,5,8-naphthalene tetracarboxylic dianhydride **5.9a** in 1 L of hot ethanol (96%) was added 2 mL (40 mmol) of hydrazine monohydrate. A yellow solid formed which was stirred in boiling ethanol for 4 h to give light brown colored material. This was filtered and dried under vacuum at 100°C for 24 h: yield 90%; mp > 400°C (lit. 440-450°C)[16]; MS (FAB, using nitrobenyl alcohol-NBA as a matrix) 297 (65.3, MH+); Anal. Calcd for $C_{12}H_8N_4O_4$: C, 56.76; H, 2.72; N, 18.91. Found: C, 56.65; H, 2.73; N, 18.76; ^1H NMR (500 MHz, DMSO-d6) δ 5.88 (s, 4H, $2NH_2$), 8.71 (s, 4H, naphthalene).

Perylene-N,N'-bisaminoimide 5.10b.

Hydrazine monohydrate (20 mL) and 8 g of 3,4,9,10-perylenetetracarboxylic dianhydride **5.10a** were stirred for 1 h at 50 °C. Excess of hydrazine was removed slowly by a constant stream of nitrogen while the temperature was maintained around 50 °C. The resulting solid was dried in vacuum oven at 80 °C for 48 h to give 7.9 g product as a dark purple powder in quantitative yield; mp > 400°C; MS (FAB, using NBA as a matrix) 421 (7.9, MH+); Anal. Calcd for $C_{24}H_{12}N_4O_4$: C, 68.57; H, 2.88; N, 13.33. Found: C, 68.13; H, 3.07; N, 13.31.

Polymer synthesis

Poly(ether imide) 5.11 from bis(N-aminoimide) 5.9b and dianhydride 4.13e.

To a stirred solution of 2.6024 g (5.00 mmol) **4.13e** in a mixture of 6 mL of *m*-cresol and 6 mL of 1,2-dichlorobenzene (DCB) under nitrogen was added 1.5108 g (5.1 mmol) of **5.9b** and 0.0296 g (0.2 mmol) of phthalic anhydride. After the reaction mixture was stirred for 1 h, it was heated to reflux (ca. 190-200°C) and maintained at that temperature for 6 h. During this time, the water of imidization was removed azeotropically from the reaction mixture. The solution was allowed to cool to ambient temperature, diluted with 20 mL DCB, and then slowly added into 800 mL of methanol while stirring. The precipitated polymer was collected by filtration washed with acetone and dried under reduced pressure at 80°C for 24 h. The polymer was reprecipitated from chloroform with methanol. The yield was 91%. The inherent viscosity of a 0.5 g/dL polymer solution in chloroform was 0.41 dL/g at 25°C.

Copoly(ether imide) 5.15b from 5.9b, 4.13e and 4.13c.

To a stirred solution of 1.0410 g (2.00 mmol) **4.13e** in a mixture of 5 mL *m*-cresol and 5 mL DCB under nitrogen was added 0.9065 g (3.06 mmol) **5.9b**, 0.3222 g (1.00 mmol) **4.13c** and 0.0178 g (0.12 mmol) phthalic anhydride. The reaction mixture was heated and worked up as for the preparation of **5.11**. The precipitated polymer was collected by filtration washed with acetone and dried under reduced pressure at 300 °C for 3 h to yield

96% yellow fibers. The inherent viscosity of a 0.5 g/dL polymer solution in *m*-cresol was 0.52 dL/g at 50 °C. Using the above reaction conditions, copolymers **5.15a,c,d** and **5.21** were isolated in a period of 6-8 h.

The copoly(ether imide)s **5.16a-c** were prepared in a similar fashion as **5.15b** with 2.04 mmol of **5.9b**, 1 mmol of **5.14**, 1 mmol of one of the comonomers **4.13b-c** and 0.08 mmol of phthalic anhydride except that PCP was used instead of *m*-cresol, and the reaction was run at 210-220°C.

Poly(ether imide) 5.17 from 5.10b, and 4.13e.

To a stirred solution of 2.0819 g (4.00 mmol) **4.13e** in a mixture of 12 g *p*-chlorophenol (PCP) and 4 mL DCB under nitrogen was added 0.1681 g (0.4 mmol) **5.10b**. After the reaction mixture was stirred for 1 h, it was heated to reflux (ca. 200-210°C) and maintained at that temperature for 4 days. During this time, the water of imidization was removed azeotropically from the reaction mixture. The dark red colored solution was allowed to cool to ambient temperature, it was diluted with 10 mL *m*-cresol and then slowly added to 800 mL acetone. The precipitated polymer was collected by filtration and washed with acetone. The red fibrous material was dried under reduced pressure at 200 °C for 3 h and 300°C for 1h to yield 94% light purple polymer. The inherent viscosity of a 0.5 g/dL polymer solution in *m*-cresol was 0.48 dL/g at 50 °C.

Copoly(ether imide) 5.18b from 5.10b, 4.13e and m-phenylene diamine 4.14a.

To a stirred solution of 2.0819 g (4.00 mmol) **4.13e** in a mixture of 10 mL *m*-cresol and 5 mL DCB under nitrogen was added 0.8576 g (2.04 mmol) **5.10b** and 0.2163 g (2.00 mmol) m-phenylene diamine. After the reaction mixture was stirred for 1 h, it was heated to reflux (ca. 200-210°C) and maintained at that temperature for 4 days. During this time, the water of imidization was removed azeotropically from the reaction mixture. The solution was allowed to cool to ambient temperature, it was diluted with 20 mL DCB and then slowly added into 800 mL of methanol while stirring . The precipitated polymer was collected by filtration washed with acetone and dried under reduced pressure at 200 °C for 3 h to yield 93% of red polymer. The inherent viscosity of a 0.5 g/dL polymer solution in chloroform was 0.53 dL/g at 25 °C.

The copoly(ether imide)s of series **5.18** and **5.19** were prepared in a similar fashion as **5.18b** (the mole ratio of starting monomers are given in Scheme 5.6).

Copoly(ether imide) 5.18c

^{1}H NMR (500 MHz, $CDCl_3$) (refer to Figure 5.9) δ 1.75 (s, 6H, $2CH_3$), 7.03 and 7.09(2d, J=8.4 Hz, 4H, a,b),7.33 (d, J=8.6 Hz, 6H, c,d), 7.41 (s, 2H, e), 7.48 (d, J=1.6, 1H, f), 7.59 (d, J=8.2 Hz, 1H, g), 7.62 (s, 1H, h), 7.87 and 7.98 (2d, J=8.3 Hz, 2H, i,j); UV ($CDCl_3$) λ_{max} 542 nm (ε= 47600), 505 nm (ε= 34000).

Poly(ether imide) 5.13

It was prepared in a similar way as poly(ether imide) **5.11** except that 4-*tert*-butyl phthalic anhydride was used as end-capping agent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (s, 18H, $2C(CH_3)_3$), 1.78 (s, 6H, $2CH_3$), 7.06 (d, J=8.7 Hz, 4H, 2*ortho*-C_6H_4O-), 7.34 (d, J=8.7 Hz, 4H, 2*meta*-C_6H_4O-), 7.42 (d, J=8.8 Hz, 2H, 5-C_6H_3O-), 7.48 (s, 2H, 3-C_6H_3O-), 7.95 (d, J=8.2 Hz, 2H, 6-C_6H_3O-); UV ($CHCl_3$) λ_{max} 378 nm (ε= 39000), 358 nm (ε= 35000).

5.8. References

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Table 5.1
Physical Properties of Poly(ether imide)s

Polymer	η_{inh} (dL/g)[a]	Tg (°C)
5.11	0.41	340
5.15a	0.66	360
5.15b	0.52	367
5.15c	0.70	ND
5.15d	1.51	ND
5.16a	0.65	438
5.16b	0.56	ND
5.16c	0.41	ND
5.21	0.44	288

a. Inherent viscosities were measured at a concentration of 0.5 g/dL in *m*-cresol at 50°C except for **5.11** and **5.21** which was measured in chloroform at 25°C, and **5.16a-c** in PCP at 50°C.

Table 5.2
Thermal and Mechanical Properties of Poly(ether imide)s

Polymer	TGA (°C)[a]		modulus (GPa) at		tanδ (max)
	N_2	air	(25°C)	(200°C)	(°C)
5.11	450	456	2.3	2.0	347
5.15a	444	462	2.4	1.4	365
5.15b	446	456	1.9	1.2	371
5.15c	446	459	2.7	1.9	380
5.15d	451	465	1.5	1.4	390
5.16a	500	506	-	-	-
5.16b	495	526	-	-	-
5.16c	497	515	1.1	1.1	456
5.21	435	453	2.0	1.7	283

a. Reported for 5% weight loss.

Table 5.3. Physical Properties of Poly(ether imide)s

Polymer	Perylene **5.10b** (mol %)[a]	η_{inh}(dL/g)[b]	Tg(°C)	Solubility[c]	film
5.17	100	0.48	ND	*m*-cresol	dark red, brittle
5.18a	80	0.43	359	*m*-cresol, TCE	dark red, flexible
5.18b	50	0.53	317	TCE	red, creasable
5.18c	20	0.34	250	chloroform	red, creasable
5.19a	80	0.47	353	*m*-cresol,TCE	dark red, flexible
5.19b	50	0.36	304	TCE	dark red, creasable
5.19c	20	0.50	247	chloroform	red, creasable
5.20	50	0.35	348	*m*-cresol	red, flexible

a. Based on total amount of diamino compound. b. Inherent viscosities were measured at a concentration of 0.5 g/dL in *m*-cresol at 50°C except for **5.18c** and **5.19c** which was measured in chloroform at 25°C. c. at room temperature.

Table 5.4. Thermal and Mechanical Properties of Poly(ether imide)s

Polymer	TGA (°C)[a]		modulus (GPa)		tanδ (max)
	N_2	air	(25°C)	(200°C)	(°C)
5.17	459	470	1.1	0.5	405
5.18a	453	468	1.5	1.1	366
5.18b	464	475	1.9	1.4	328
5.18c	496	505	0.9	1.4	245
5.19a	466	474	2.5	1.9	358
5.19b	470	489	2.1	2.4	315
5.19c	503	507	0.6	0.7	247
5.20	442	451			

a. Reported for 5% weight loss.

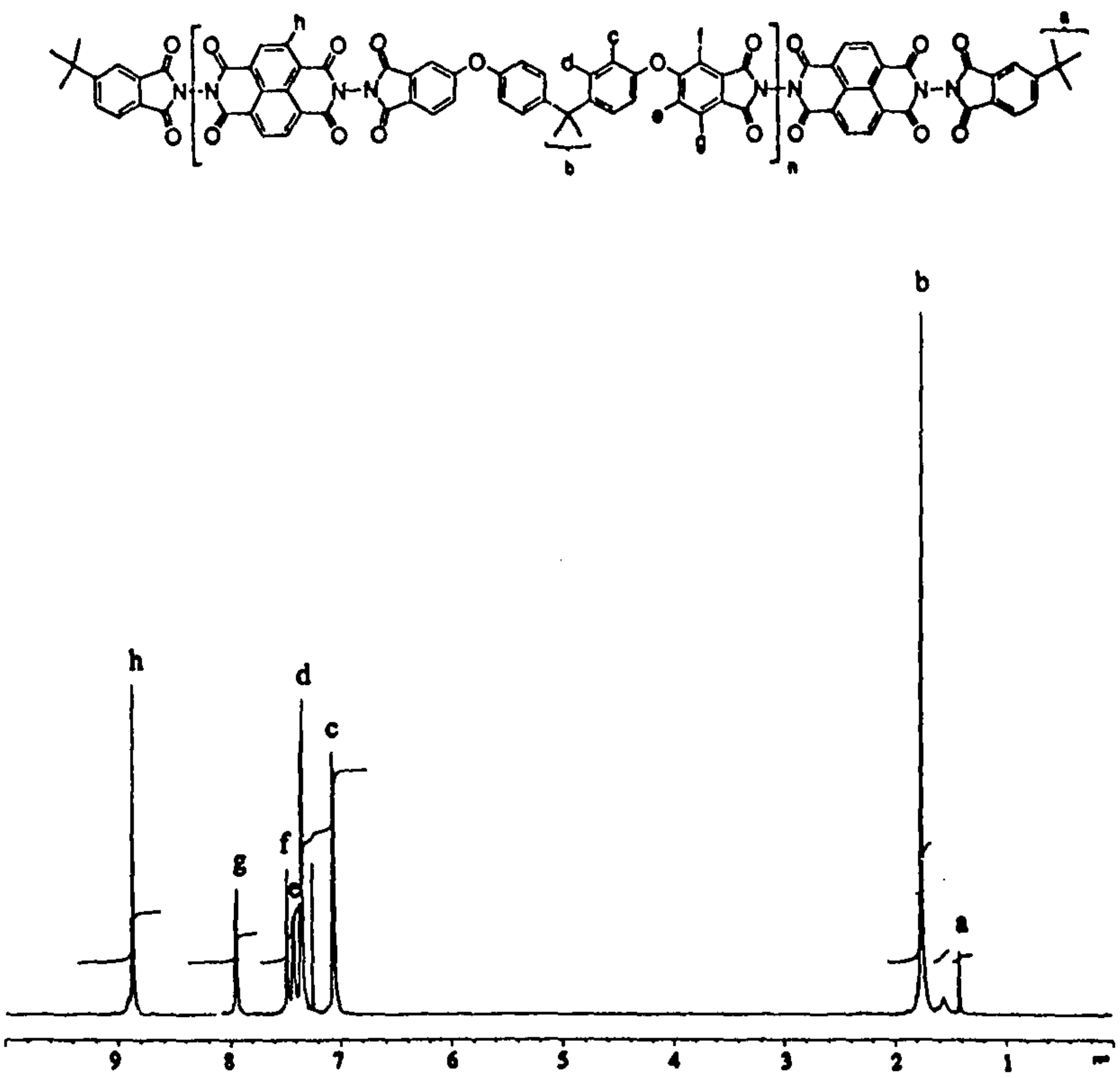


Figure 5.5 ${}^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of end-capped poly(ether imide) **5.13**.

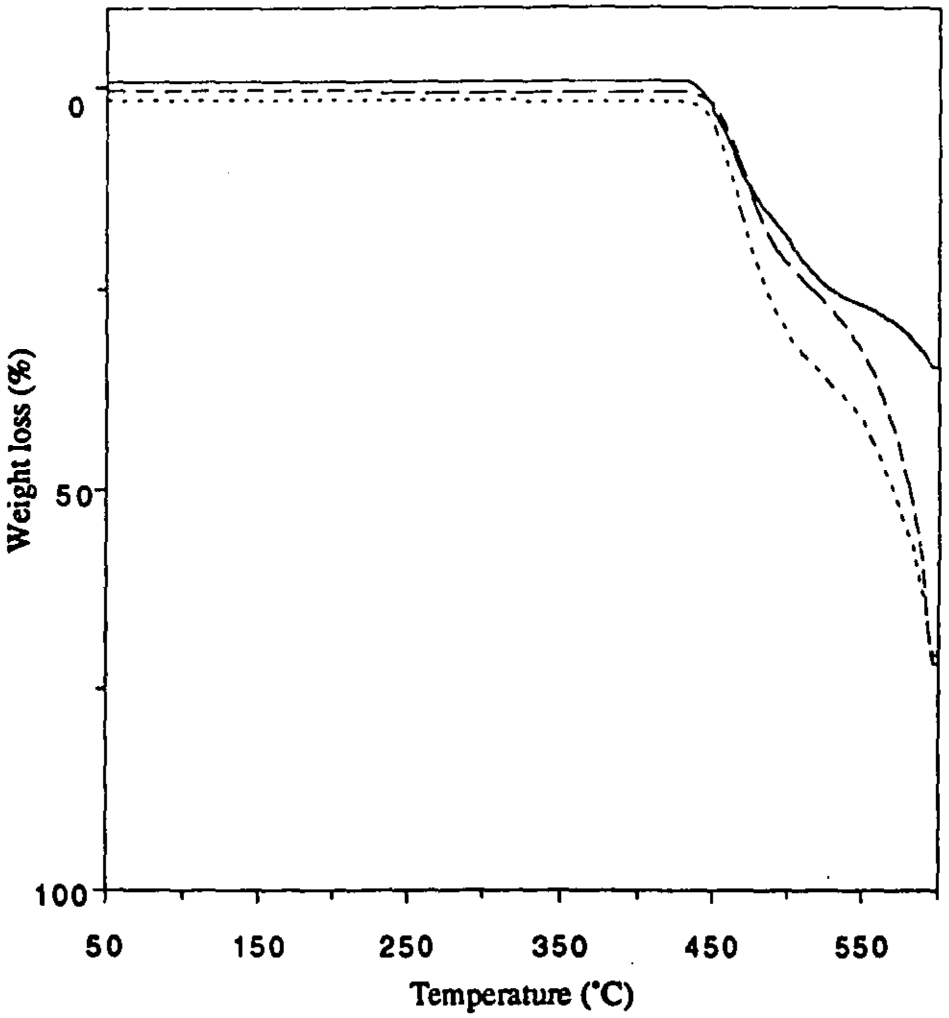


Figure 5.6. TGA thermograms for poly(ether imide) **5.11** (—)and copoly(ether imide)s **5.15a** (– –) and **5.15b** (---)under an atmosphere of air. Offset for clarity.

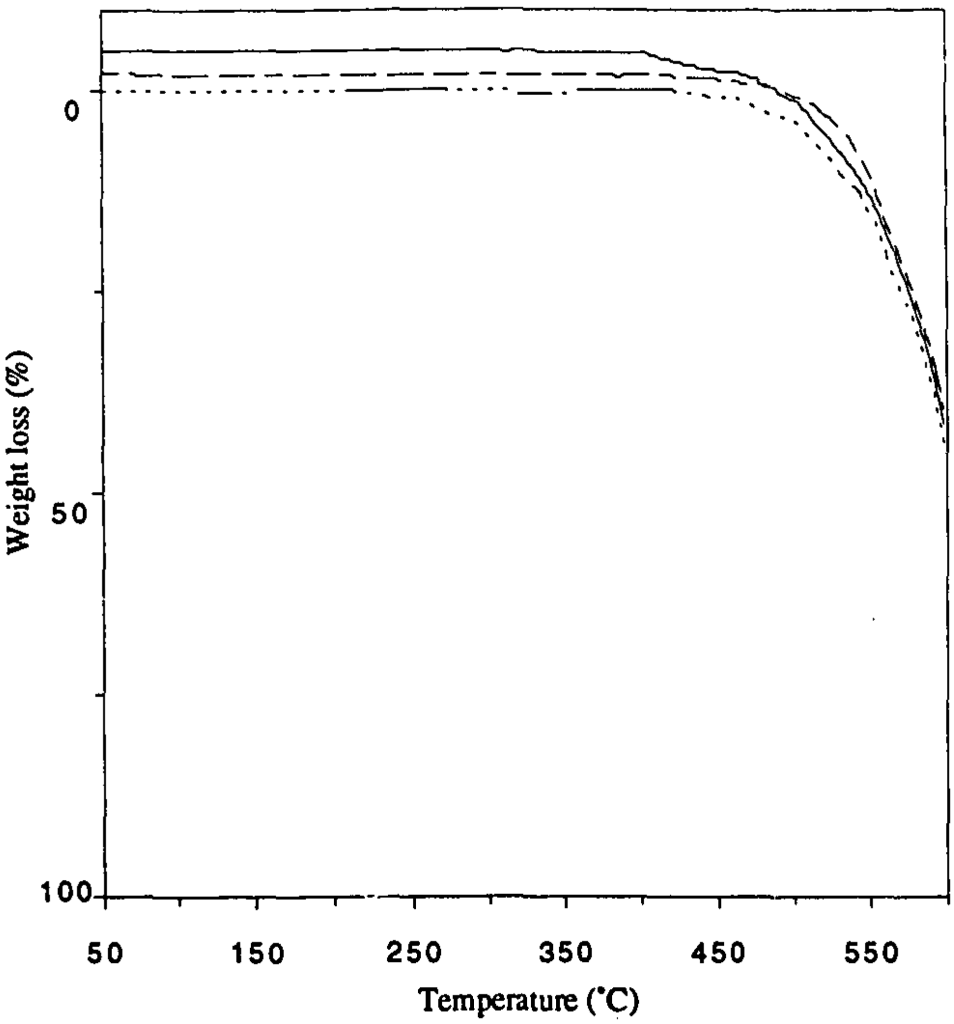


Figure 5.7. TGA thermograms for copoly(ether imide)s **5.16a** (—), **5.16b** (– –) and **5.16c** (---) under an atmosphere of air. Offset for clarity.

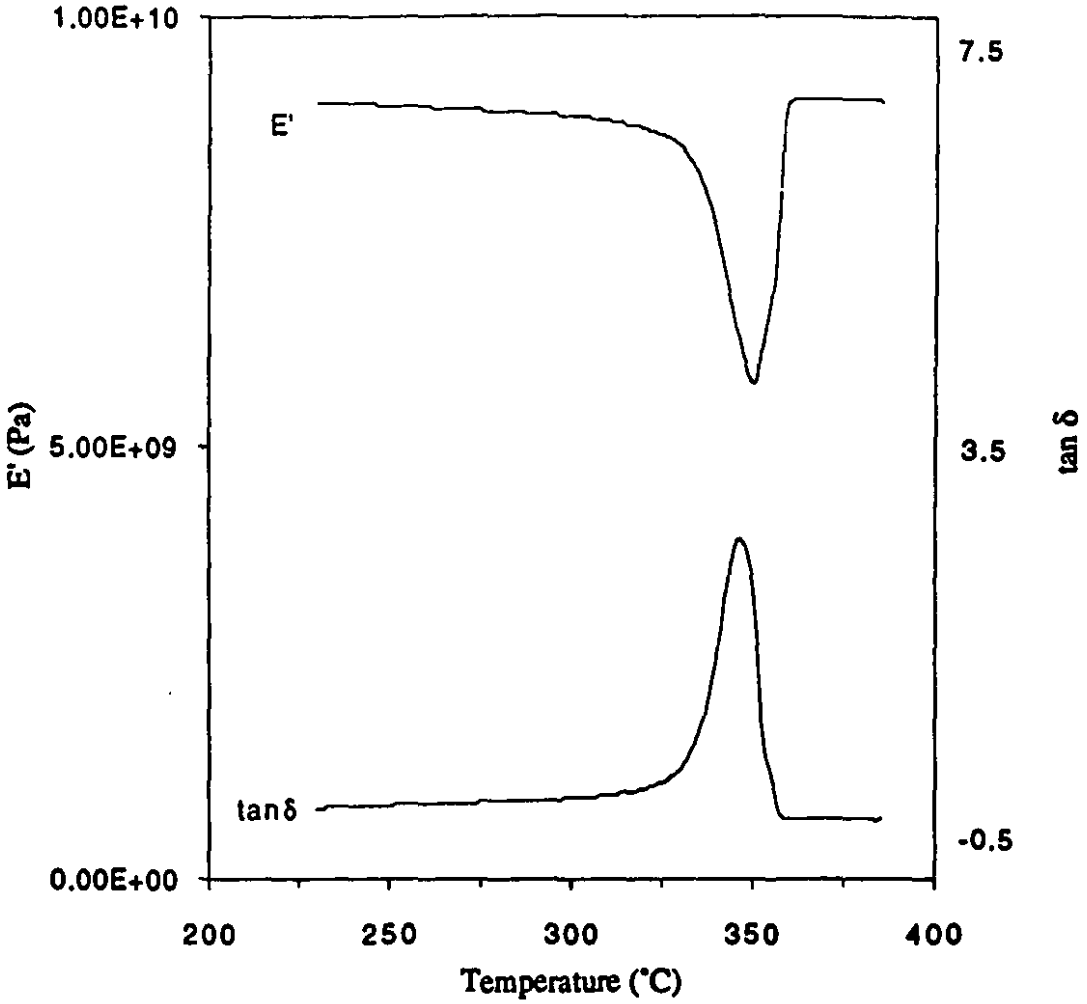


Figure 5.8. Young's modulus (E') and tanδ versus temperature for poly(ether imide) **5.11.**

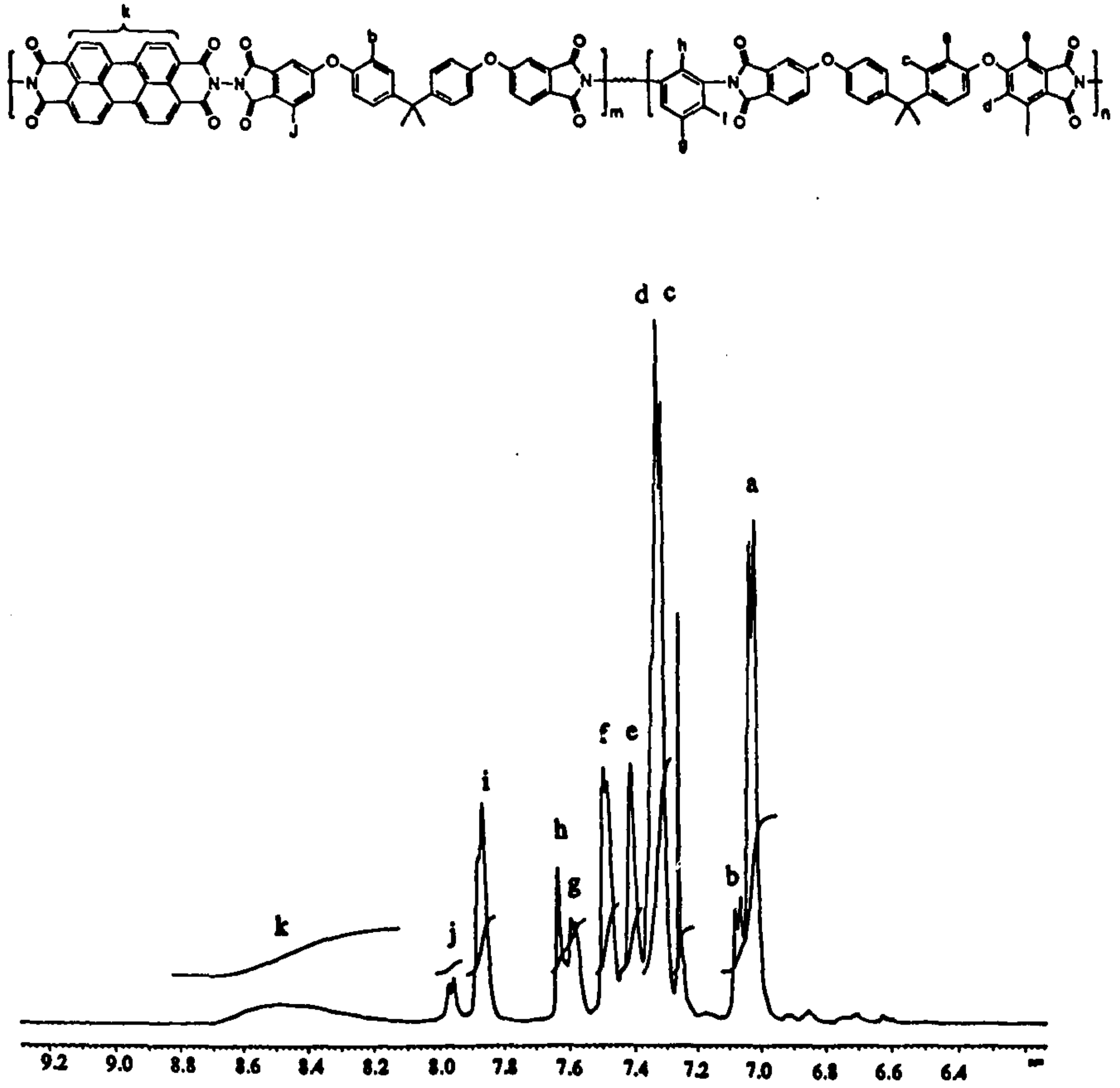


Figure 5.9 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of aromatic region for copoly(ether imide) **5.18c**.

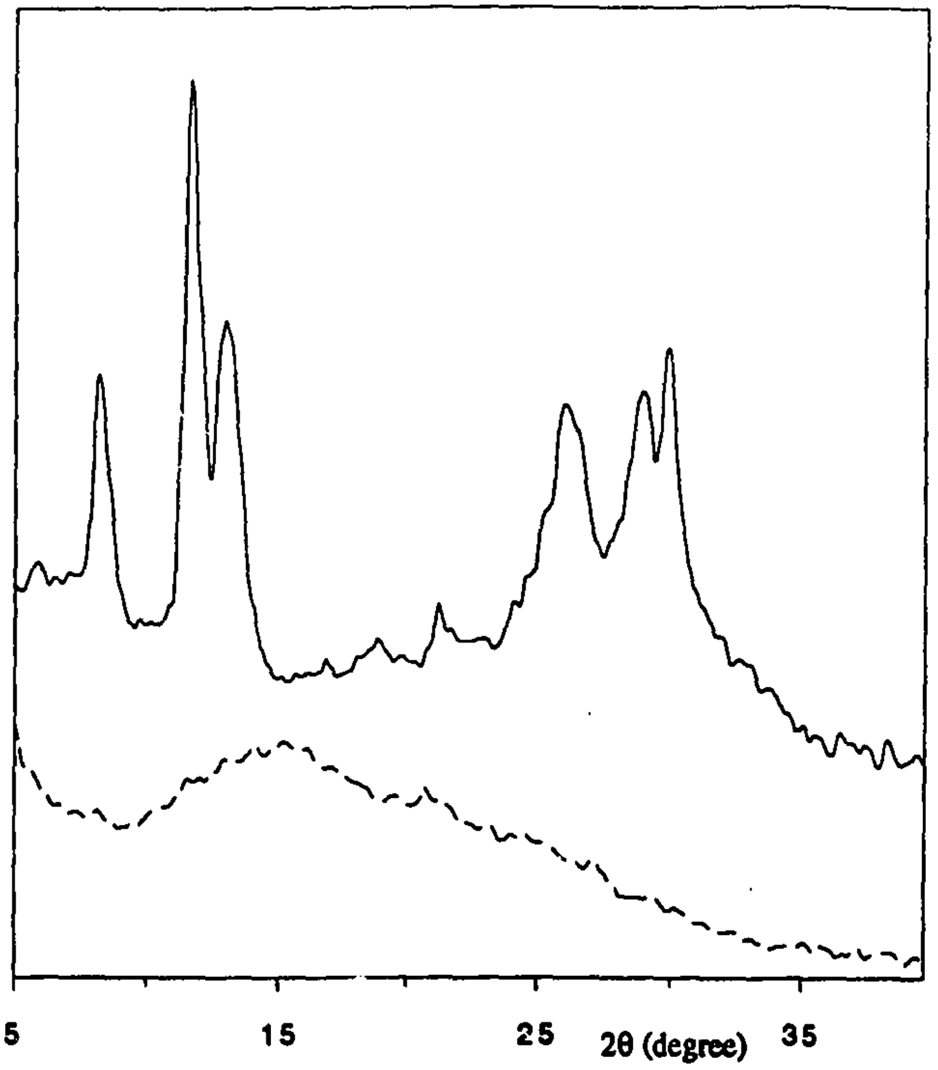


Figure 5.10. X-ray diffraction diagrams of poly(ether imide) **5.17** (—) and copoly(ether imide) **5.18a** (--).

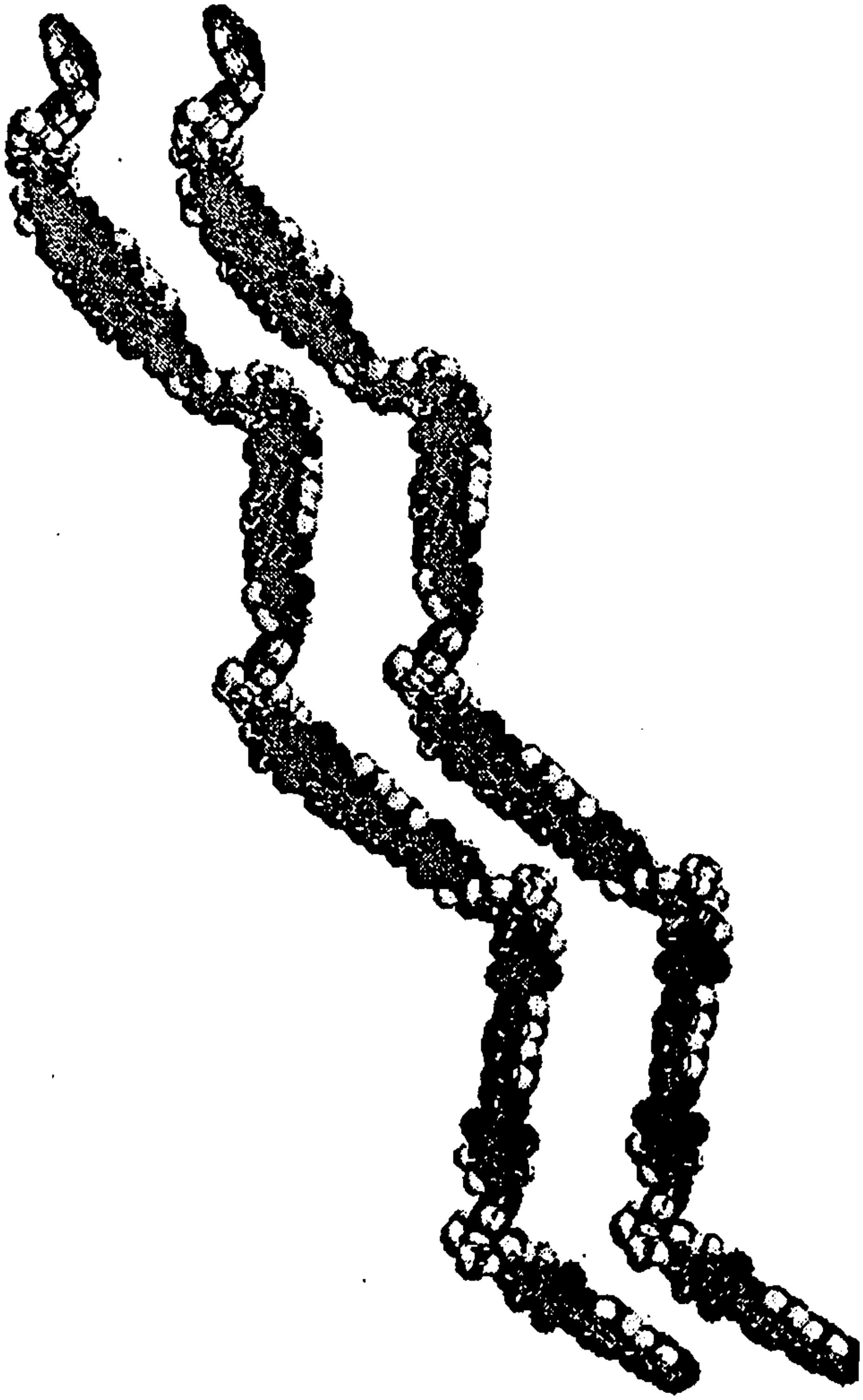


Figure 5.11 3D view of two chains of poly(ether imide) **5.17**.

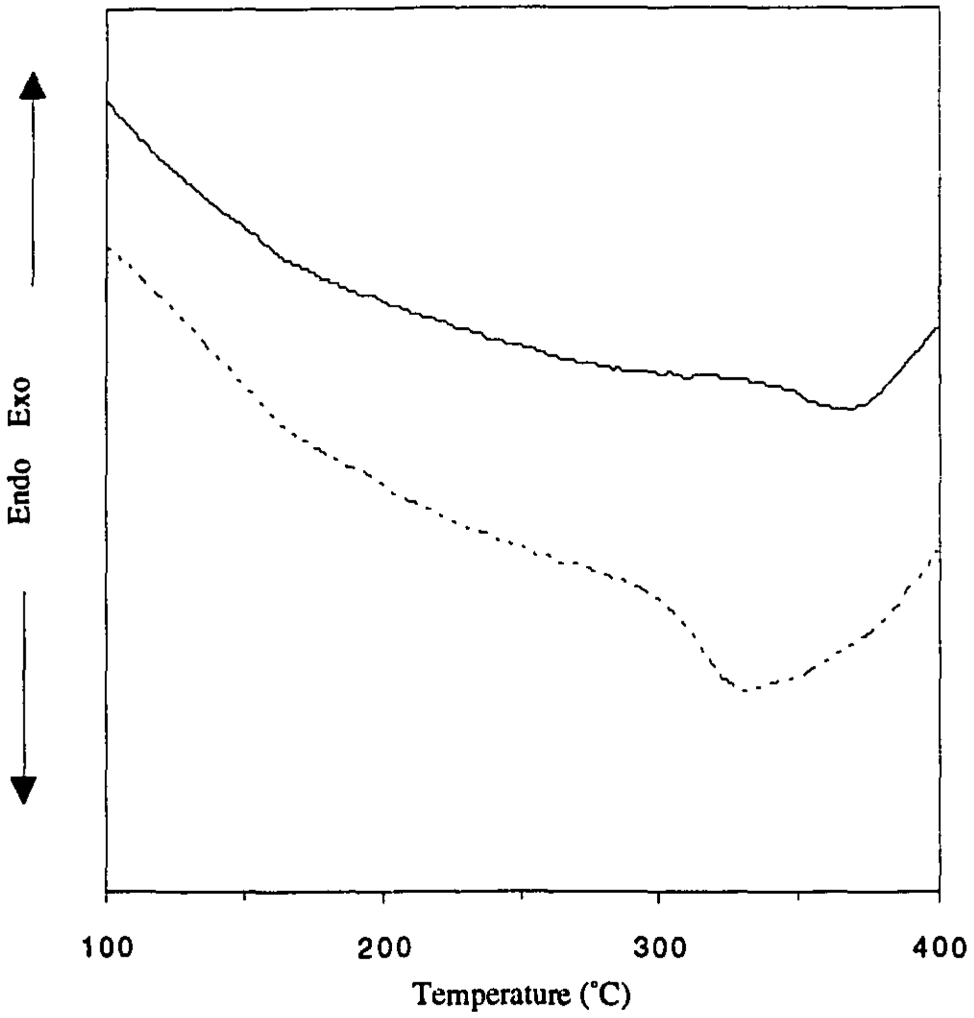


Figure 5.12. DSC analysis of copoly(ether imide)s **5.18a** (—) and **5.18b** (---) under an atmosphere of nitrogen.

CHAPTER 6

FLUORESCENCE PROPERTIES OF NAPHTHALENE AND PERYLENE-CONTAINING POLYIMIDES

6.1. Introduction

The term luminescence indicates an emission of light which represents the energy emitted when a substance returns from an excited or higher energy states to its normal or lower energy state. Luminescence phenomenona may fall into different classifications. The most common cases are fluorescence and phosphorescence. The techniques of luminescence as an experimental tool, in different fields of science, have been established over the past 50 years. During this period luminescence analysis has become a sophisticated and popular technique in the hands of analytical chemists, biochemists, physical chemists and physicists.[1-3]

Photoluminescence is a term applied to a fluorescence or phosphorescence produced by the direct application of light as a source of excitation to a substance. Fluorescence is distinguished from phosphorescence by the fact that the lifetime of an excited molecule in the singlet excited state in the case of fluorescence is very short (10^{-7}-10^{-10} s).[4] The fluorescence spectra are of two types: (a) *fluorescence emission spectra*, obtained by scanning for fluorescence emission with a fixed excitation wavelength (λ_{exc}), and (b) *fluorescence excitation spectra*, obtained by scanning for fluorescence excitation with a fixed emission wavelength (λ_{em}). There are processes other than fluorescence in which a singlet excited state (S_1) may dissipale energy in returning to the ground state (S_o), such as photochemical reactions, intersystem crossing (ISC) to the triplet state (T_1) and non-radiative decay.[1-3] The energy diagram in Figure 6.1 shows the process of absorption of light and different ways of losing energy on the molecular scale.

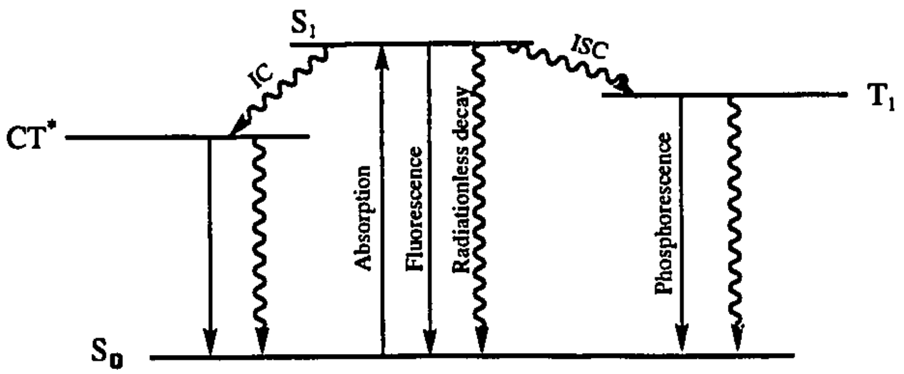


Figure 6.1. Schematic diagram and energy levels showing photophysical processes in a hypothetical material

A typical energy relationship between absorption, fluorescence and phosphorescence spectra is shown in Figure 6.2. On an energy scale, fluorescence always appears at lower-energy (red-shift or longer wavelength) with respect to the absorption and phosphorescence has a red-shift relative to fluorescence reflecting the lower electronic energy level of the triplet state.

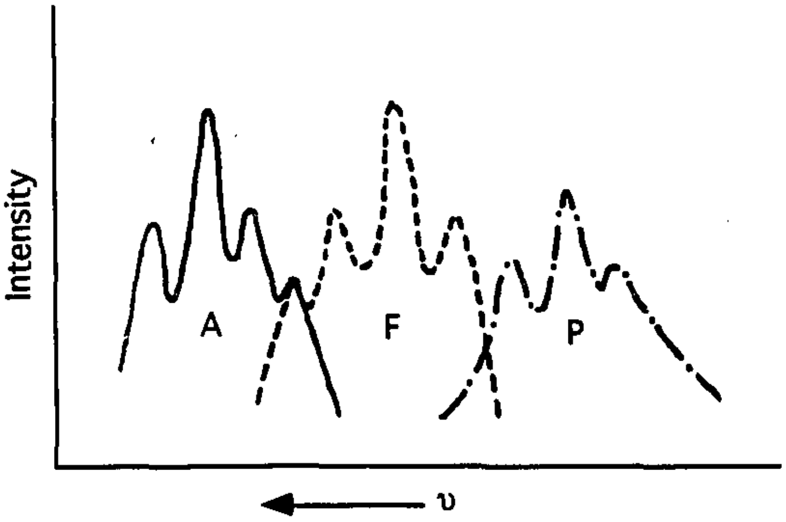


Figure 6.2. Energy relationship between absorption, A, fluorescence, F, and phosphorescence, P.

6.1.1. Photoluminescence spectroscopy of polymers

Polymer photophysics and photochemistry have evolved over the past two decades, providing the polymer scientific area with a viable tool for probing polymer structure on a molecular scale. By investigating photophysical phenomena of polymer systems, one can develop an accurate picture of how polymers exist in solution and solid phases. The interaction of light with monomer, polymer and their additives also serves useful purposes in the understanding of polymer structure and its behavior in an environment and is utilized in industry. These applications, such as photopolymerisation, photocrosslinking, photostabilisation, microelectronics and optical devices have evolved from basic research into industrial products.[7,9]

Studies involving luminescence characterization of polymers in solution and solid phase have included energy transfer and excimer formation and dissociation.[4-11] Energy transfer and migration in polymers seems to be a function of the nature of the chromophores involved and the distance between them. This phenomenon has been under intense investigation for many years. It is generally admitted that these phenomena certainly occur in polymers such as polystyrene, poly(vinyltoluene), poly(vinylnaphthalene), poly(vinylcarbazole) and poly(vinylpyrene).[10,12,13]

Luminescence techniques provide valuable information in several areas of science and technology where polymers have found applications. For example, fluorescence spectroscopy is used to study the photochemical and photophysical properties of photoresist polymers. These polymers are selected among the thermally stable photopolymers and used for pattern-generation by phototechniques.[14] The photodegradation of polymers, such as polyimides used for high temperature adhesives, coatings or photodegradable polymers, is another area in which luminescence spectroscopy is used to study the different aspects of degradation.[15a-f] Some of the polymers used as coatings may be subjected to corrosive environments including prolonged exposure to ultraviolet radiation.

Charge transfer (CT) fluorescence spectroscopy has been applied in monitoring the thermal imidization of polyimides and as a useful method for evaluating the miscibility of polyimide blends.[16d] Studies by different investigators show that both the intra- and intermolecular charge transfer processes exist in polyimides and are sensitive to the aggregation of polymer chains.[16a-d] A CT complex is formed between two molecules, or two different sites of a molecule, one of which behaves as an electron donor, D, and another as the acceptor, A. This complex can form in polymers when both the electron donor and the acceptor sites in the polymer chain interact with each other. Much of this research is based on the spectral absorption which shows new bands at higher wavelength of the UV-visible region and emission which is red-shifted.

6.2. Goals

We have outlined (in chapters 4 and 5) the syntheses of different series of polyimides and poly(ether imide)s containing naphthalene and perylene rings. These polymers all exhibit extremely high glass transition temperatures and excellent thermal stability. They form yellow to red transparent films from solution casting.

A prerequisite for the potential applications of the polyimides especially **5.17-5.20** which contain perylene groups, in optical devices is the study of their photophysical properties.

In cases where coatings and adhesives with good physical and mechanical properties are needed, polyimides are an excellent choice. In some of these applications a prolonged exposure to ultra-violet and visible radiation might be expected. Since the polyimides introduced in this thesis can be used as high temperature coating and adhesives, we found it worthwhile to use absorption and fluorescence spectroscopy to probe their optical properties including those of the starting monomers.

It has been observed that the fluorescence spectra of polyimides are partially due to CT interaction between imide and amine moieties.[16a-c] Polyimides usually show different fluorescence spectra in solution and film because of the effect of the molecular aggregation in the solid phase which makes the formation of interchain CT likely. In order to investigate this effect on the hydrazine-derived polyimides it was decided to study fluorescence emission of the polymers in solution using different solvents and compare the results with their spectra in solid form.

The goal of this chapter is to present and discuss some preliminary photophysical measurements made on several materials discussed in this thesis. A more detailed investigation is beyond the scope of our research group and needs a collaboration with scientists with more expertise in this field.

6.3. Results and discussions

6.3.1. Absorption and emission study of the copolymers containing perylene units

The absorption spectra of the copoly(ether imide)s **5.18b** and **5.19c** containing perylene diimide units and the perylene monomer **5.10b** are shown in Figures 6.4 and 6.5. The spectra clearly demostrate the identical absorption bands in the 400-600 nm region for the perylene monomer before and after polymerization. It also shows that using *m*-cresol or concentrated sulfuric acid has no effect on the absorption bands. This indicates that the absorption bands for the copolymer **5.18b** and its monomer peaking at λ 544 (ε=48000 M^{-1} cm^{-1}), 505 (ε=35000 M^{-1} cm^{-1}) and 475 (ε=18000 M^{-1} cm^{-1}) nm can be assigned as the π-π^* transition of perylene. The reason for this assignment comes from the evidence which shows that the polarity of the solvents (concentrated sulfuric acid versus *m*-cresol) affect the position of the n-π^* state more significantly than the π-π^* state.[2]

The n-π^* transition occurs in molecules which contain non-bonding electrons (n-electrons or lone pairs) associated with heteroatoms such as oxygen or nitrogen. The n-π^* states also differ quite markedly from the π-π^* states in that they have a much lower extinction coefficients (< 10^3).

The amine groups of N-aminoimides in monomer **5.10b** are strongly basic and are readily protonated by acids, therefore the perylene **5.10b** in acid solution is most likely present in the form of the diammonium salt whereas in *m*-cresol it exists mostly in its neutral form. If n-electrons of the amino nitrogen and the carbonyl oxygen in monomer **5.10b** or copolymer **5.18b** were directly involved in the absorption process then a significant shift in their respective absorption maxima ought to be expected.

Moreover, the absorption spectra of the copoly(ether imide) **5.18b** (Figure 6.4) and the absorption spectra of perylene and polyarylenes oligomers containing perylene and naphthalene rings show no difference in their pattern.[17,18] The absorption spectra of monomer **5.10b** and copoly(ether imide) **5.18b** show a red shift of about 80 nm compared with the perylene unit itself which is due to the presence of imide rings causing more conjugation in the system. It is known that the energy of S (π, π^*) falls rapidly with increasing conjugation.[16c]

The excitation and emission spectra of copolyimides **5.18c** and **5.19c** are shown in Figures 6.7 to 6.10. The fluorescence emission spectra of chloroform solutions of these copolymers are identical and show a peak around 630 nm (excited around 550 nm). New emission bands around 580 and 540 nm appear as the energy of the excitation is increased to 430 and 365 nm. However, the emission band at 630 nm in both cases remains as the lowest band (Figures 6.7 and 6.8). The emission bands at 630 and 580 nm are assigned to be from perylene units which are similar to the emission bands observed from monomer **5.10b** (Figure 6.6). The shape and the band positions in excitation and absorption spectra of these copolymers and the perylene monomer are very similar. The excitation of the other chromophores in the polymer structure does not affect the emission spectra due to the presence of an efficient intramolecular energy transfer within the polymer chains.

Using *m*-cresol instead of chloroform sharply decreases the emission intensity of these copolymers to an undetectable level. Solution fluorescence of the perylene monomer **5.10b** is also strongly solvent dependent. The *m*-cresol solution of this monomer is non-fluorescent while it shows a strong fluorescence emission in concentrated sulfuric acid solution peaking at 575, 623 and 670 nm (Figure 6.6).

Solvent effects, commonly observed in fluorescence measurements, are manifested by wavelength shifts and/or quenching of fluorescence. These changes are in some instances accompanied by comparable changes in the fluorescence excitation spectra. Displacements of the maxima in the absorption and fluorescence emission spectra imply interaction with solvent in both the ground state and the excited state of the molecule. When the fluorescence excitation and emission spectra are affected by change of solvent (as in the case of perylene monomer **5.10b**), interaction between solvent and both the ground state and the excited state is indicated. The excitation spectra of monomer **5.10b** in sulfuric acid and the copolymers **5.18c** and **5.19c** in chloroform show a shift of about 30 nm.

The excitation and emission spectra of the films prepared from copolymers **5.18c** and **5.19c** are broad and structureless (Figures 6.9 and 6.10). A red shift of about 30 to 45 nm is observed in the emission spectra of **5.18c** (λ_{exc}=500. λ_{em}=675) and **5.19c** (λ_{exc}=580, λ_{em}=660) compared with the lowest energy band in their solution emission spectra. The red shift observed in the fluorescence emission and the broad excitation spectra of the polymer films can be accounted for by the different conformation of the polymer chains in solution and solid phase and the effect of environment in these two phases. Obviously, the electronic structure of the chromophoric units in the polymer chains in solution will be quite different from that in a glassy phase where the repeat units have frozen orientation.

The broad structureless excitation spectra of these films reveals that an energy transfer takes place. In contrast to the solution spectra of these copolymers the spectra of film samples are not identical and show a red shift of about 15-20 nm for copolymer **5.18c** compared to **5.19c**. This band shift is caused by the structural difference in these copolymers (*m*-phenylene diamine group in **5.18c** versus oxydianiline in **5.19c**) and the effect of aggregation of polymer chains in the solid phase. The aggregation of chains enhances interchain energy transfer and CT formation. The CT complexes form between perylene rings and *m*-phenylene diamine and oxydianilin moieties in copolymers **5.18c** and **5.19c**, respectively.

Generally, emission and excitation spectra of polyimides are sensitive to any change in molecular orientation and aggregation, e.g. caused by annealing. Therefore one can obtain information from the change of the emission spectra induced by change of molecular aggregation without introduction of any emission probe into the system.

We have already observed the fluorescence spectra of two perylene-containing copolyimides **5.18c** and **5.19c**. In order to examine the relationship between the molecular aggregation and the fluorescence spectra of these copolyimides, the effects of annealing on the emission and excitation spectra of these copolymers were studied. Experiments showed that the emission and excitation spectra of both copolymers after annealing at 280°C for 2 h decreased sharply. The copolymers **5.18c** and **5.19c** were chemically stable during the process of annealing. This was examined by redissolving of the annealed polymers in chloroform and measuring their fluorescence which showed exactly the same excitation and emission spectra as the unannealed copolymers.

It has been shown that the fluorescence spectra of classical polyimides, which are commonly derived from condensation of aromatic diamines and dianhydrides, are due to CT interaction between imide and amine moieties.[16a-c] It is also believed that the sharp increase of the fluorescence intensity after annealing for most classical polyimides is attributed to the intermolecular CT formation. However, in the case of polyimides derived from hydrazine, which contain no direct linkage between aromatic amines and perylene rings only formation of the intermolecular CT is possible. The amount of intermolecular CT in the polymers strongly depends on the degree of molecular aggregation. The molecular aggregation in turn is sensitive to the repeat unit structure and the thermal history of polymers. Therefore, the decrease in the emission intensities of copolymers **5.18c** and **5.19c** after annealing above their Tg's can be due to the stacking of perylene rings together or with other chromophores. These interactions enhance formation of excimers and exciplexes.

Excimer formation has been observed in many organic molecules (such as pyrene, naphthalene, etc.) and polymers bearing aromatic side groups (such as, polystyrene, poly(vinylnaphthalene), etc.).[2,11] Formation of excimers in most cases are accompanied by appearance of new emission bands at higher wavelengths compared to the normal emission. Unfortunately, we were unable to scan the spectra to the infra red region in order to investigate formation of excimer or exciplex bands owing to instrumental limitations.

6.3.2. Absorption and emission study of the polymer 5.11 containing naphthalenedimide units.

The absorption spectra of the polymer **5.11** (Figure 6.11), synthesized by condensation of naphthalene diimide **5.9b** with BPADA **4.13e** (see chapter 5), and its starting monomer **5.9b** (Figure 6.12) appears to be different from the perylene-containing polymers. The absorption band for **5.9b** in *m*-cresol has a broad gaussian shape with a maximum around 360 nm which tails up to 450 nm while in concentrated sulfuric acid it shows three maxima at 378, 358 and 335 nm with no absorption above 400 nm. The tailing into the visible region of **5.9b** in *m*-cresol explains why the solution is yellow while in concentrated sulfuric acid it is colorless. The solution of polymer **5.11** in *m*-cresol and chloroform shows two different features of absorption bands similar to the monomer **5.9b** (Figure 6.11). The absorption spectrum of the monomer **5.9b** in *m*-cresol is slightly red-shifted compared with that of polymer **5.11** (Figure 6.13). The absorption bands for the naphthalene monomer **5.9b** and the polymer **5.11** can be assigned to be the π, π^* transition using the same argument mention previously for the perylene compound. However, these results reveal that there is a ground state interaction between *m*-cresol molecules and the naphthalene bisimide moiety of monomer **5.9b** and polymer **5.11**.

The studies of the effects of proton-donating solvents on the absorption and fluorescence of many organic compounds show that using a strong proton-donating solvent usually enhances the molar absorptivity (ε) values and fluorescence intensities.[19] The influence of solvent molecules on different types of electronic transition is a known phenomena. Molecular energies may be reduced by solvation, and the extent of this reduction depends on the nature of solvent. Absorption intensities may also be affected by perturbations brought about by the proximity of solvent molecules. Formation of CT complexes between solute and solvent molecules is also believed to be responsible for the red shift in the absorption spectra and the changes in the ε values. These effects in the case of polymer **5.11** and monomer **5.9b** in *m*-cresol are manifested by a broadening of the absorption band and tailing into the visible part of spectrum and also by a decrease of the extinction coefficient.

The solution fluorescence of polymer **5.11** is shown in Figure 6.14. The dilute chloroform solution of this polymer shows fluorescence emission bands around 400 nm and a broad band around 550 nm. The intensity of the band at 550 nm (λ_{exc}=355 nm) increases dramatically as the solution concentration is increased and a new excitation peak appears around 440 nm. The excitation and emission bands from dilute polymer **5.11** solution are mirror images and very similar to the absorption spectra of this polymer and the monomer **5.9b**. The excitation and emission spectra of monomer **5.9b** in sulfuric acid (Figure 6.15) are also very similar to **5.11** in dilute solution. This indicates that the origin of the bands in dilute polymer solution are from the naphthalene group. As the concentration of the polymer solution increases the aggregation of polymer chains becomes more important causing formation of an intermolecular CT complex which emits at longer wavelength.

Similar to perylene monomer **5.10b**, naphthalene bisimide monomer **5.9b** shows a weak fluorescence in *m*-cresol but strongly emits in concentrated sulfuric acid solution.

A film of polymer **5.11** has an emission band around 580-600 nm (Figure 6.16) which is similar to the long wavelength emission of this polymer in concentrated solution. The intermolecular CT complex and excimer formation are accounted for by this emission band.

6.3.3. Absorption and emission study of the copolymer 5.20 containing both naphthalene and perylene units and a blend of copolymers 5.18c and polymer 5.11

Copolymer **5.20** having both perylene and naphthalene rings in the backbone shows fluorescence emission and excitation spectra (Figure 6.18) very similar to copolymer **5.18c** (Figure 6.9) and no emission around 550-600 nm corresponding to naphthalene-containing segments was obseved. This indicates that energy transfer efficiently takes place. Unfortunately, it was not possible to have the spectrum of the copolymer **5.20** in chloroform for comparison with the solution spectra of polymers **5.18c** and **5.11** due to the lack of solubility of the copolymer **5.20** in common solvents. The absorption spectrum of **5.20** in *m*-cresol shows bands from both perylene and naphthalene moieties (Figure 6.17).

Fluorescence spectroscopy is known to be a useful tool in the investigation of the molecular aggregation in polyimides. It has been shown that fluorescence spectroscopy is a very sensitive method for monitoring and evaluating the miscibility of polymer blends.[16d] In order to study the fluorescence behavior of the polyimide alloy containing naphthalene and perylene rings, a blend of polymers **5.11** and **5.18c** was prepared by solution casting of a mixture of these polymers in chloroform.

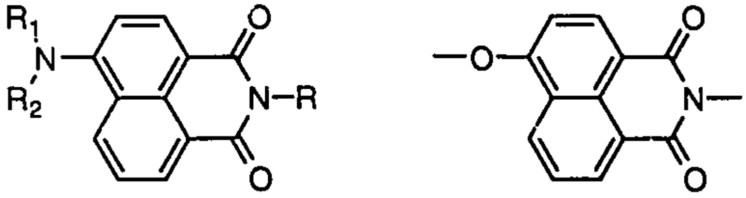
Figure 6.19 shows the excitation and emission spectra of the blend (**5.11/5.18c**). Fluorescence emission maximum of the blend appears at 665 nm (excited at 500 nm). We did not observe any emission from naphthalimide moieties of the polymer **5.11**. This indicates a high degree of miscibility between these two polyimides which cause efficient energy transfer among the chromophores. The relatively weak fluorescence behavior of the polymer blend (**5.11/5.18c**) may be due to the partial stacking of perylene and naphthalene rings and excimer and/or exciplex formation, similar to polymers **5.18c** and **5.19c**.

Similar to what was observed in the case of polyimides **5.18c** and **5.19c**, the annealing of the blend (**5.11/5.18c**) at 280°C (above the Tg of copolymer **5.18c**) for 2 h showed a sharp decrease of the emission intensity. The annealing process enhances the stacking of chromophores and hence formation of excimers and exciplexs which always appear at longer wavelength (in this case in the infra red region).

6.3.4. Absorption and emission study of the polymers containing arylether bisnaphthalimide units

The absorption spectra of the monomers **4.35a** and **4.35b** and the polymers **4.36b** and **4.37b** derived from these monomers in chloroform demonstrate broad absorption bands which extend well into the visible region (Figure 6.20 and 6.21). Both the monomers and their polymers absorb light at a maximum of 380 nm. This indicates that the chromophoric naphthalimide moiety **6.2** (Figure 6.3) is the major participant in the absorption band and its electronic structure remains unchanged after polymerization. The electron donating effect of the oxygen of the ether linkage attached to the naphthalene ring and the electron deficiency of imide moiety in **6.2** presumably causes the formation of a ground state donor-acceptor CT. Transformation of charge through the naphthalene conjugated π system which affects the energy of π, π^* transition and the formation of CT can be implied from the broad absorption band of these naphthalene monomers and their polymers which tail into the visible region. A slight red shift in the absorption spectra of the monomers **4.35a** and **4.35b** compared to their corresponding polymers shows that another CT may exist between amine groups and imide ring. This CT vanishes after polymerization when the amino groups form new imide rings.

Amine-substituted naphthalimides **6.1** (Figure 6.3), which have similar chromophoric structure as monomers **4.35a** and **4.35b**, are yellow compounds and are known fluorescent dyes with several applications such as fluorescent probes in the field of non-destructive testing.[20]



6.1 **6.2**

Figure 6.3. Substituted naphthalimides

Figures 6.22 and 6.23 demonstrate the fluorescence emission and excitation spectra of polymers **4.36b** and **4.37b** in chloroform solution. Both polymers demonstrate strong emission compared to their monomers **4.35a,b**. The chloroform solutions of both monomers **4.35a,b** show relatively weak fluorescence emissions at 500 nm (exciting at 435 nm) which is almost a 60 nm red shift relative to their polymer emission bands (Figures 6.26 and 6.27). The excitation spectra of these monomers peak around 435 nm whereas their absorption spectra have maxima around 375 nm (Figures 6.20 and 6.21). The comparison of the excitation and absorption spectra of the monomers show that a ground state CT exist. This CT has very low concentration but emits efficiently once excited.

The excitation and emission spectra of polymers do not show CT emission similar to the monomers. However, their excitation spectra show two distinct bands around 400 and 300 nm indicating energy transfer along the polymer chains.

Figures 6.24 and 6.25 show fluorescence spectra of polymer films of **4.36b** and **4.37b**. Emission spectra of polymer **4.36b** shows intense fluorescence at 490 nm and two others at 510 and 550 nm (excited at 420 or 435 nm) which is evidence of formation of excimers and exciplexes. In spectra of polymer **4.37b** excimer and exciplex peaks are not as clear as polymer **4.36b** and appear as weak shoulders.

6.4. Conclusions

In this chapter, the results for UV and fluorescence analysis of several polymers containing naphthalene and perylene rings and their monomers have been presented. We have discussed the effect of chemical structure, solvent and annealing on the absorption and emission spectra of these materials. It is found that the perylene ring among the various structural units of polymers **5.18b,c** contributes mainly to the longest wavelength bands. The bands were assigned as π, π^* transition. It is shown that the absorption spectrum of naphthalene-containing polymer **5.11** changes with solvents indicating the presence of solvent solute interaction. The emission spectra of the perylene-containing polymers and monomer were measured under several conditions. We assigned the strong emission spectra to normal fluorescence and a sharp decrease of emission intensity in the case of monomer **5.10b** in *m*-cresol as a solvent effect. It is evident from the results that the energy transfer from the phthalimide chromophores to the naphthalene or perylene ring is quite efficient. Remarkable decrease of intensities in the emission and excitation spectra of polyimide **5.18c** and blend (**5.18c/5.11**) are caused by annealing and are attributed to change in the degree of molecular aggregation and possible formation of excimers and exciplexes. Excimer bands were also observed from emission spectra of polymers **4.36b** and **4.37b**.

This chapter only presents a preliminary study on the dye-containing polymers introduced in this thesis and there are many questions about the photophysical properties of these materials which are still unanswered. The potential applications of these pigmentary materials, as e.g. photoconductive materials, would require more detailed investigation on their luminescence behavior.

6.5. Experimental

All the monomers and the polymers were synthesized according to the procedures described in the previous chapters. Spectro-grade chloroform (BDH) and reagent grade sulfuric acid (A&C) were used. *m*-Cresol (Aldrich) was distilled before use. Films of polymers were cast onto a glass plate from chloroform solution followed by drying at 200°C for 4h.

The fluorescence and UV-visible absorption spectra were measured at room temperature in air using a fluorometer (Spex model-F112) and spectrophotometer (Unicam SP.800), respectively. The solution samples were excited at various wavelengths in a side-face arrangement in standard quartz cell and front-face arrangement was used for film samples to minimize self-absorption. The band passes are 0.3 and 2.0 mm for the excitation and emission monochromators, respectively. The excitation and emission spectra were corrected for wavelength-dependent lamp intensity and detector sensitivity in the range of 200-700 nm by rhodamine B solution.

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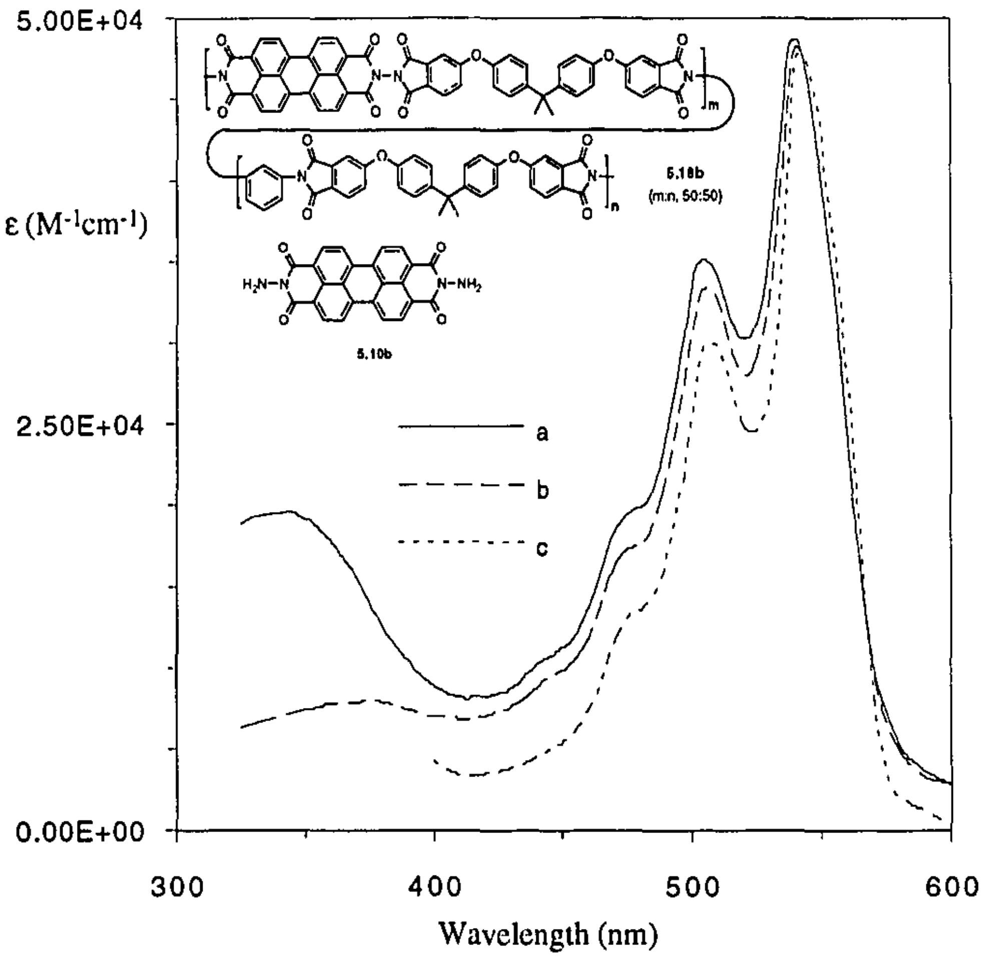

Figure 6.4. Absorption spectra of (a) polyimide **5.18b**, (b) monomer **5.10b** in *m*-cresol and (c) monomer **5.10b** in concentrated sulfuric acid

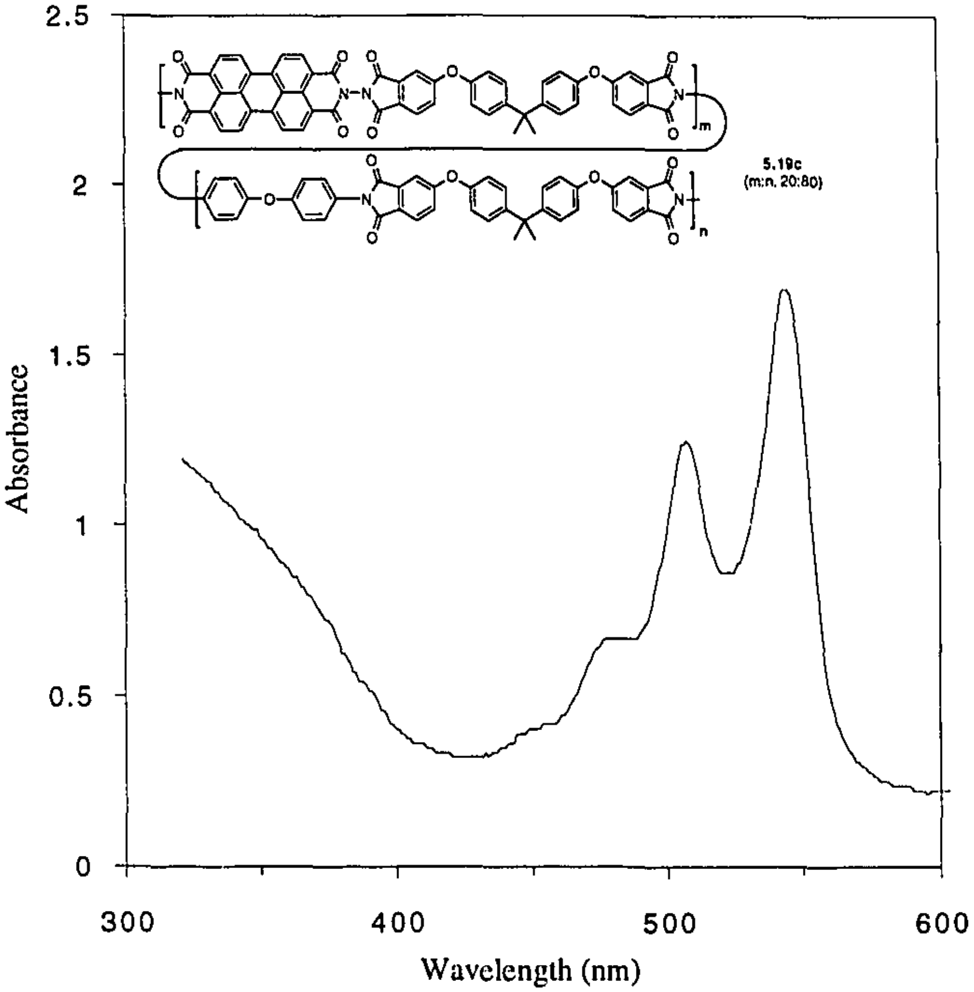

Figure 6.5. Absorption spectrum of copoly(ether imide) **5.19c** in chloroform

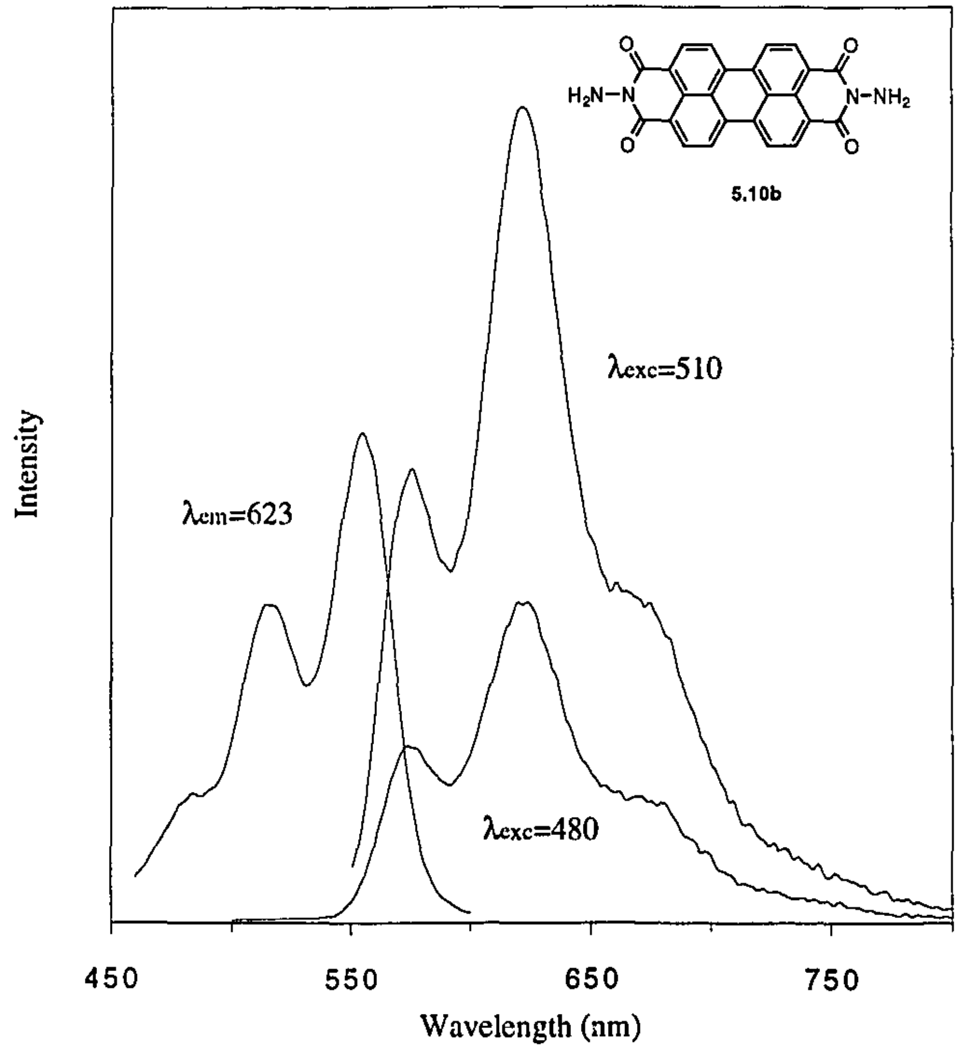

Figure 6.6. Fluorescence excitation and emission spectra of concentrated sulfuric acid solution of perylene **5.10b**
(excitation spectra always appear on the left side of the emission spectra)

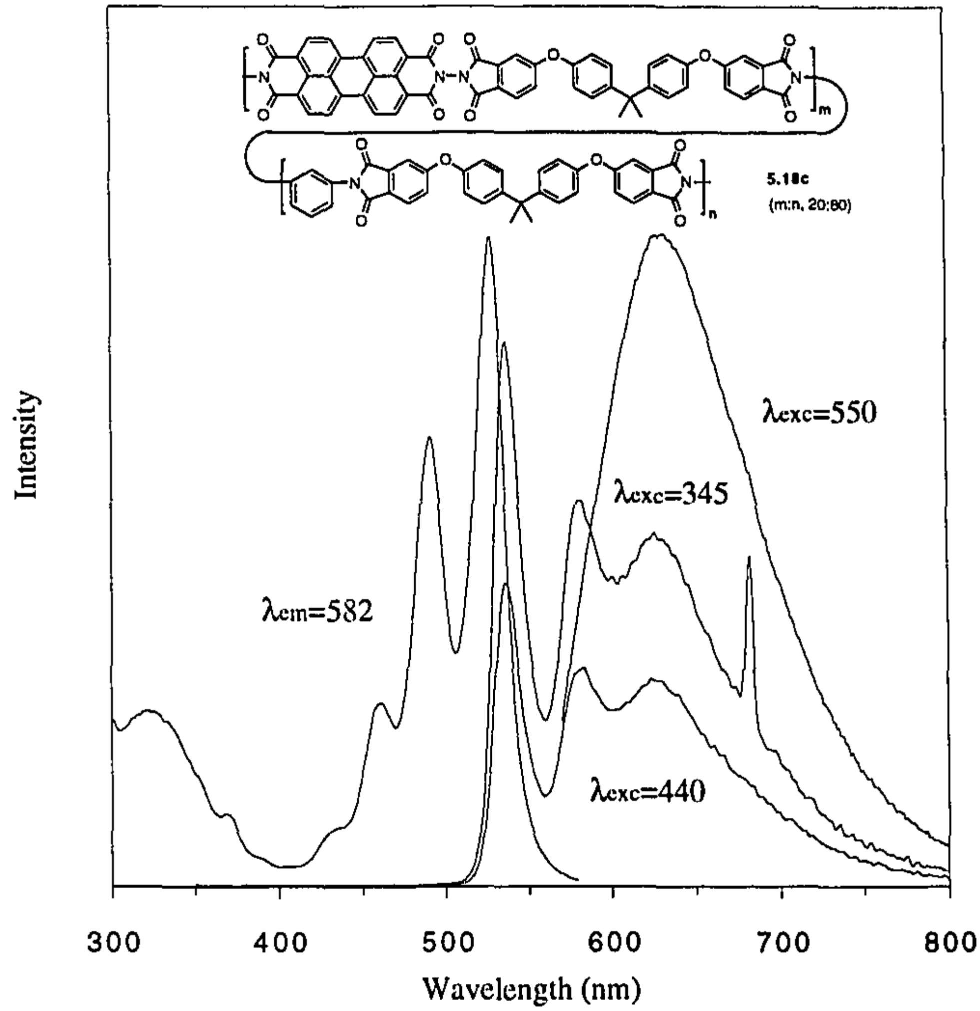

Figure 6.7. Fluorescence excitation and emission spectra of chloroform solution of copoly(ether imide) **5.18c**

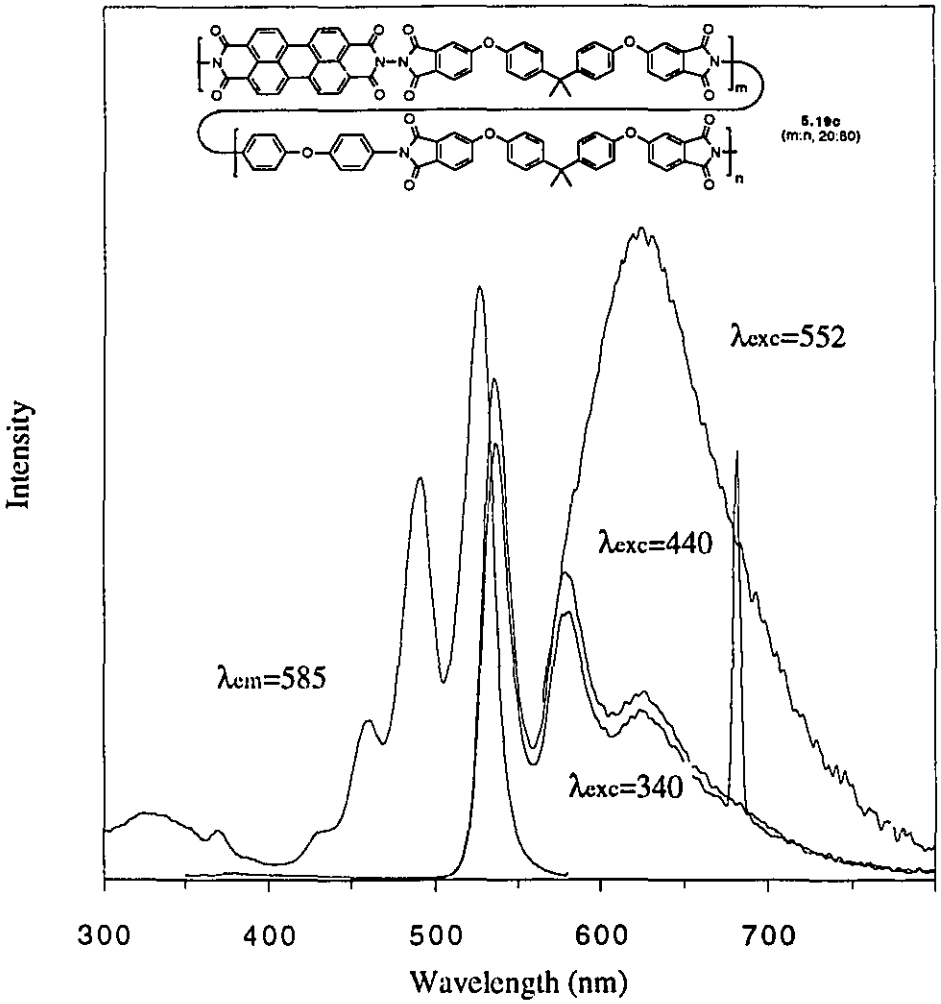

Figure 6.8. Fluorescence excitation and emission spectra of chloroform solution of copoly(ether imide) **5.19c**

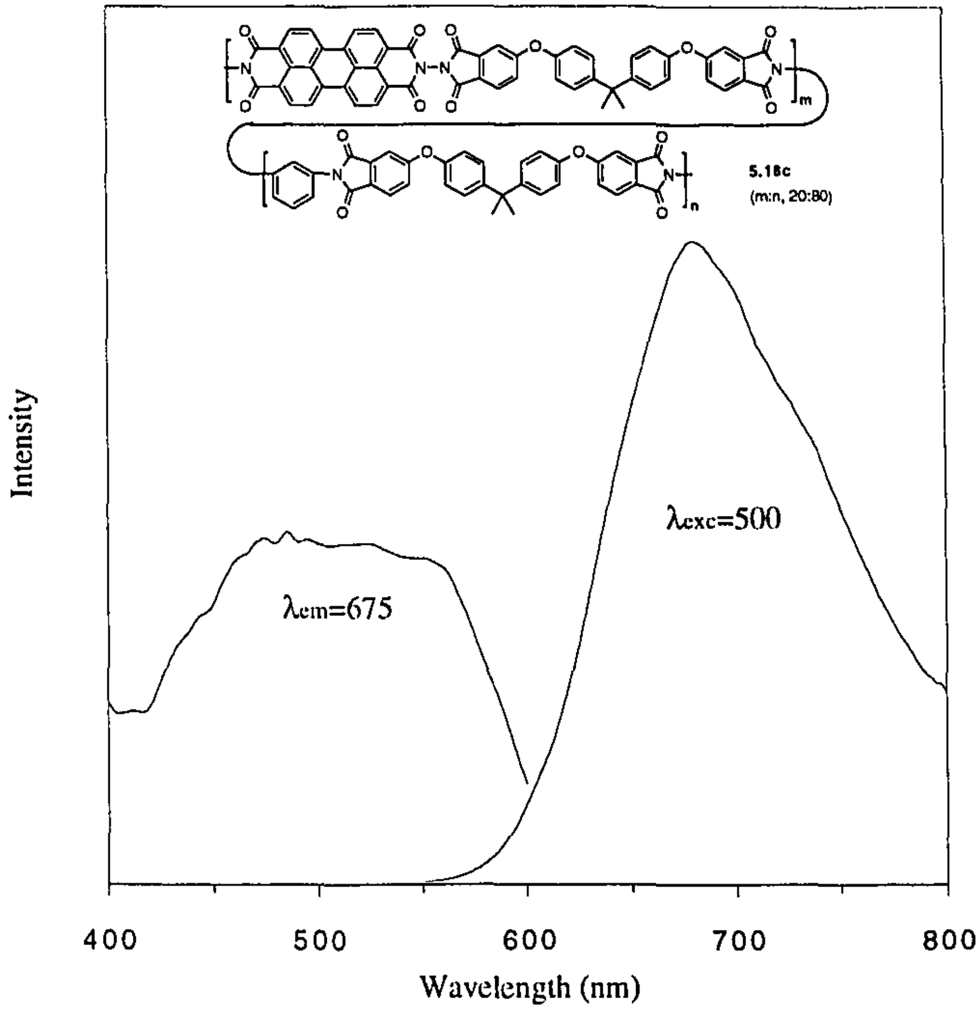

Figure 6.9. Fluorescence excitation and emission spectra of copoly(ether imide) **5.18c** film

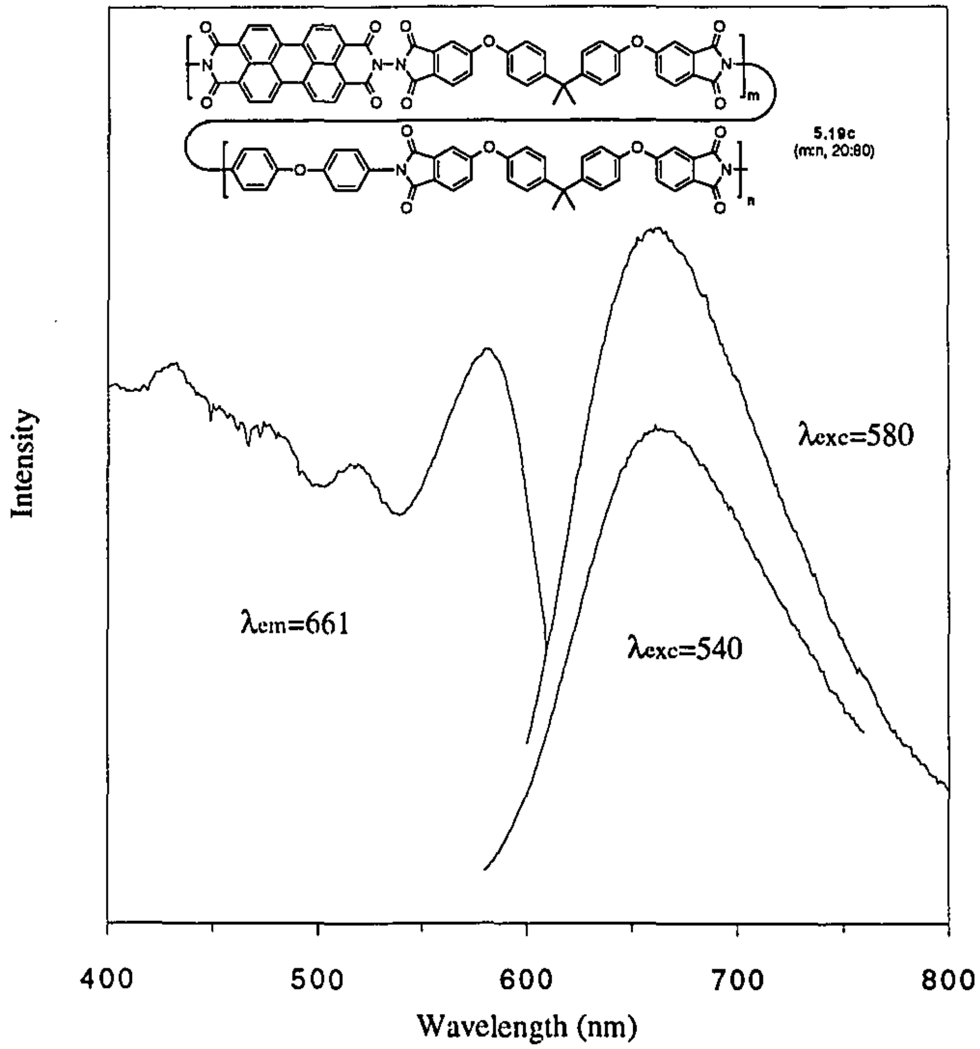

Figure 6.10. Fluorescence excitation and emission spectra of copoly(ether imide) **5.19c** film

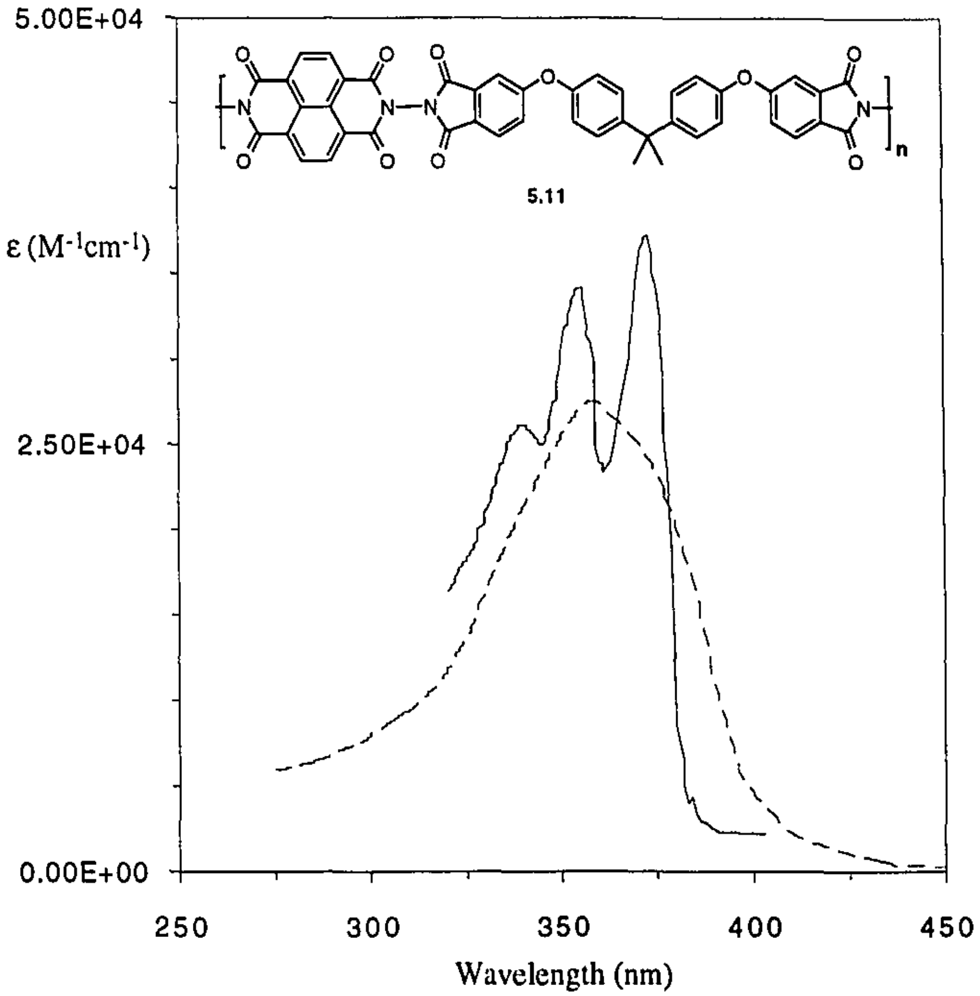

Figure 6.11. Absorption spectra of poly(ether imide) **5.11** in (—) chloroform and (---) *m*-cresol

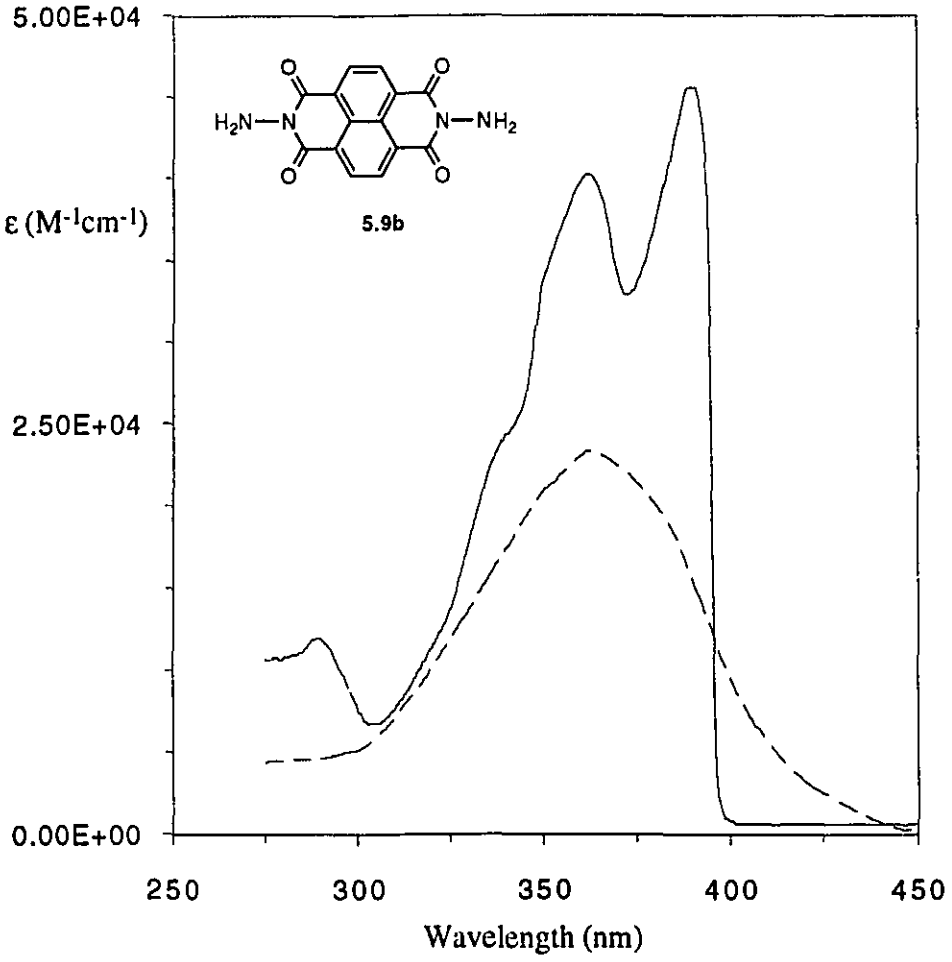

Figure 6.12. Absorption spectra of monomer **5.9b** in (—) concentrated sulfuric acid and (---) in *m*-cresol

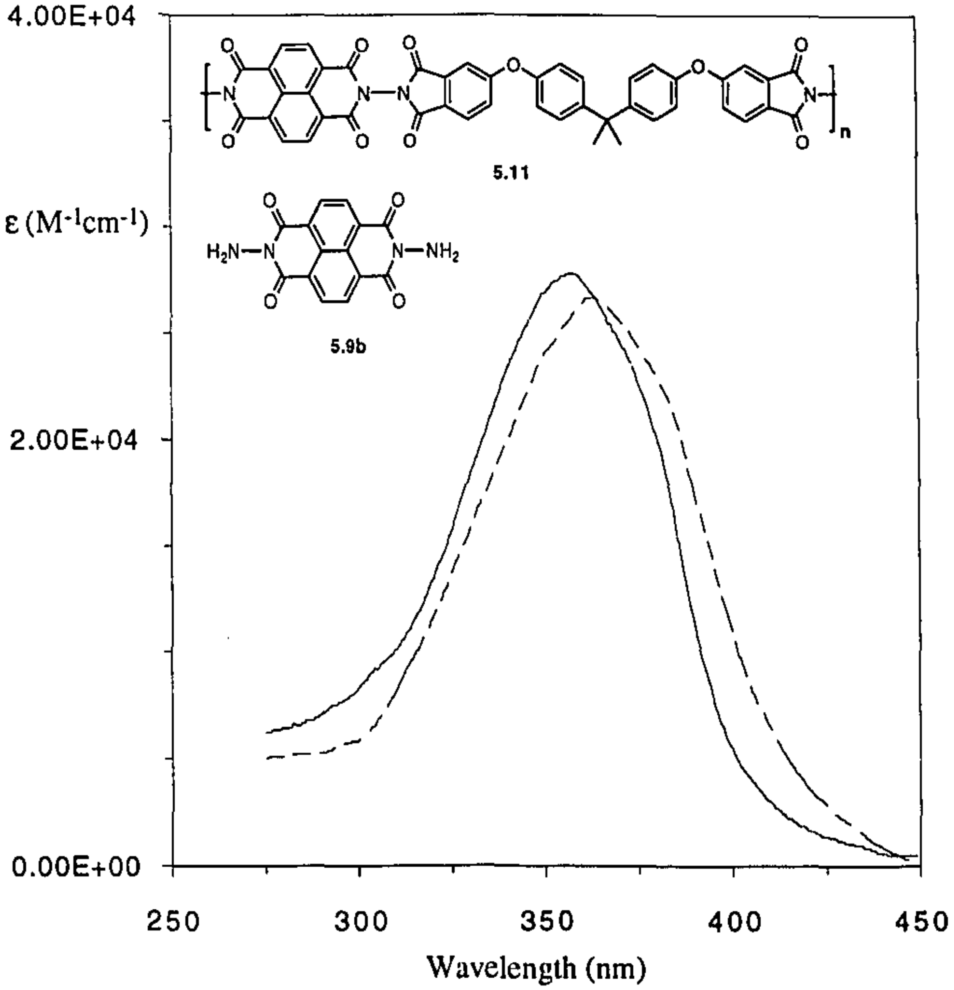

Figure 6.13. Absorption spectra of poly(ether imide) **5.11** (—) and monomer **5.9b** (---) in *m*-cresol

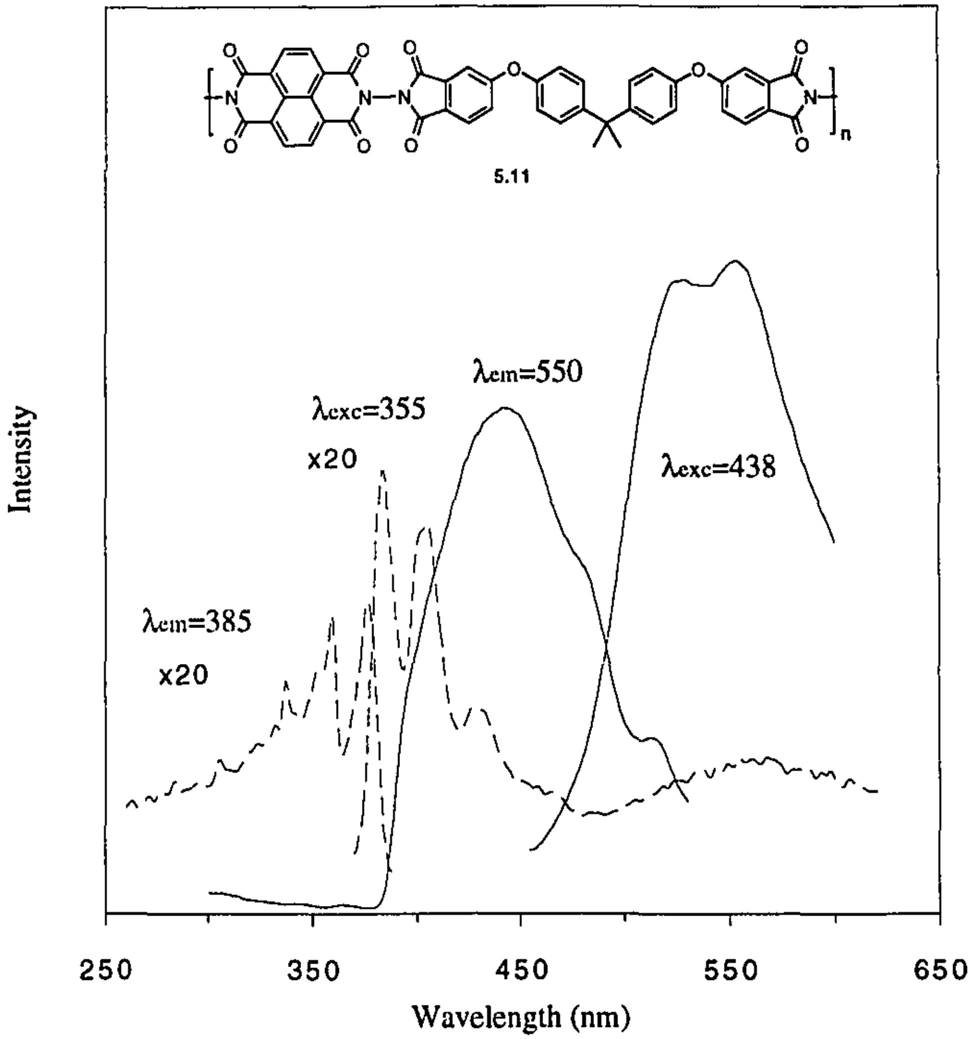

Figure 6.14. Fluorescence excitation and emission spectra of dilute (----) and concentrated (—) chloroform solution of polyimide **5.11**

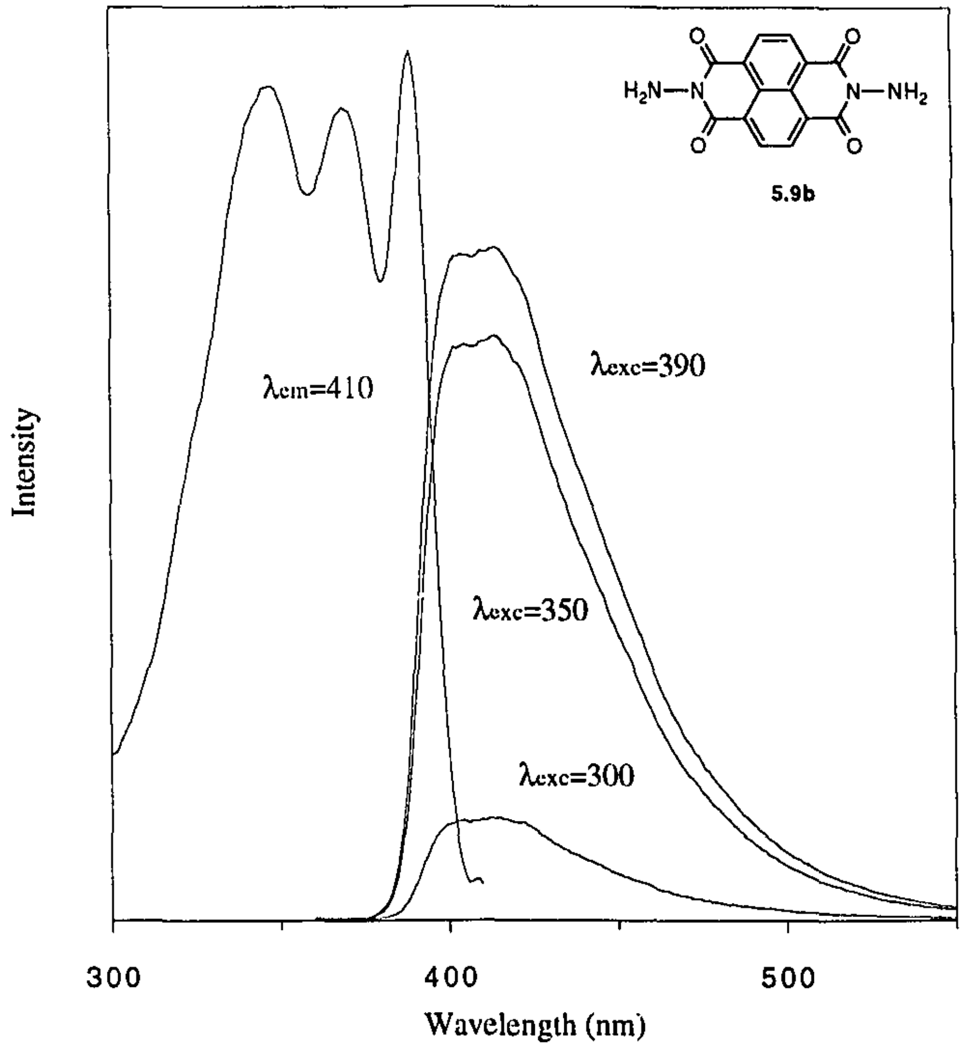

Figure 6.15. Fluorescence excitation and emission spectra of concentrated sulfuric acid solution of monomer **5.9b**

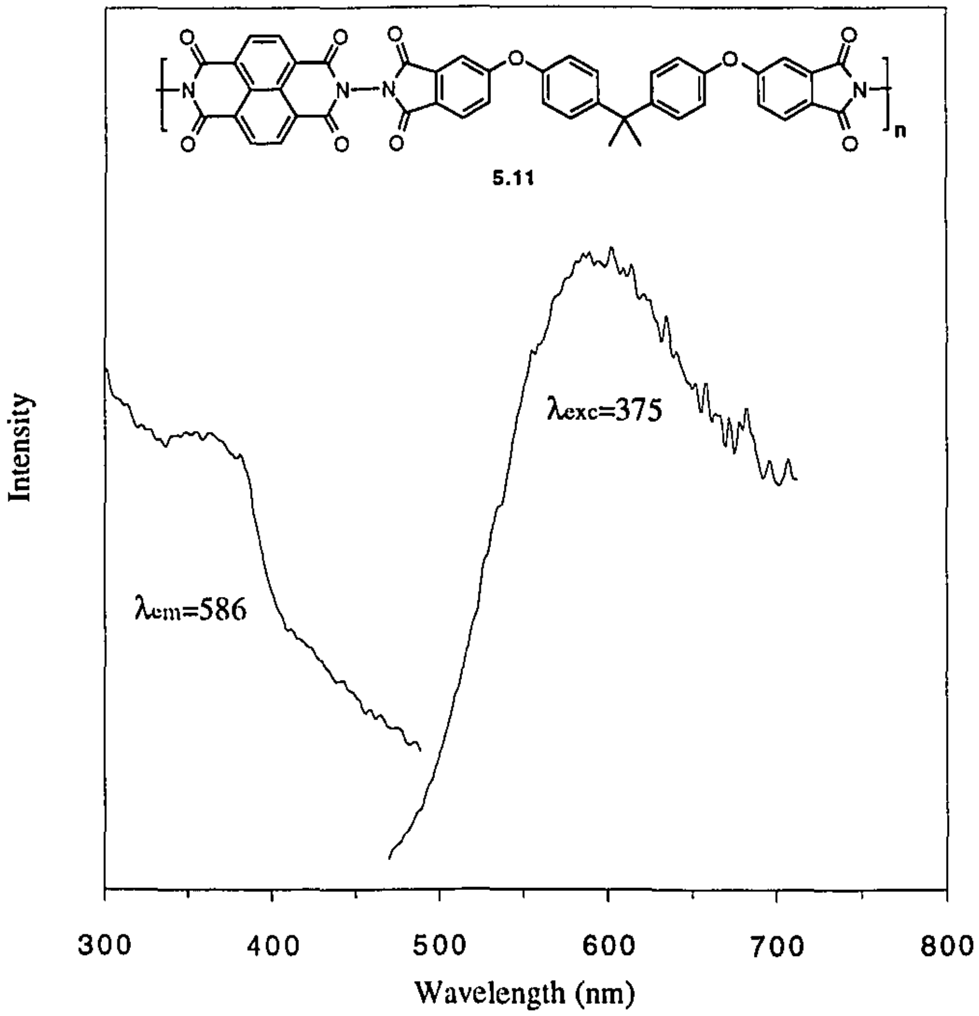

Figure 6.16. Fluorescence excitation and emission spectra of polyimide **5.11** film

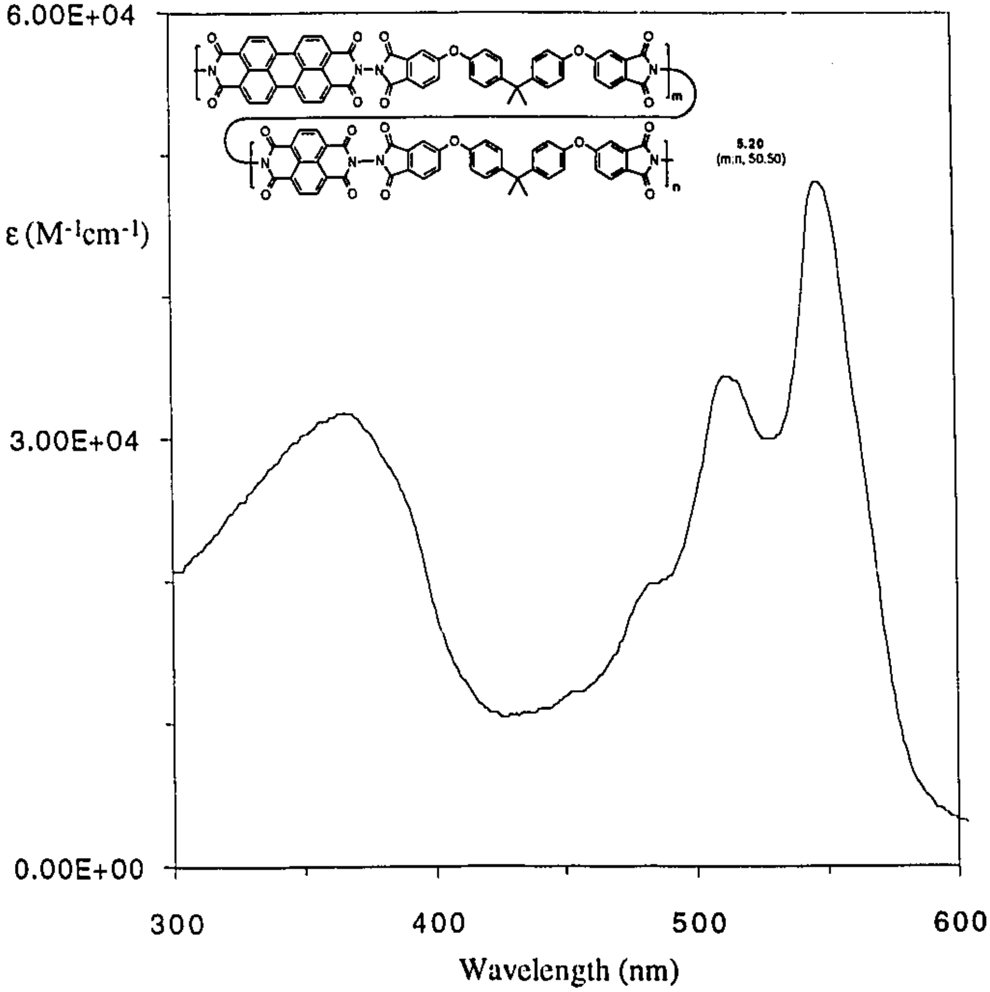

Figure 6.17. Absorption spectrum of copolyimide **5.20** in *m*-cresol

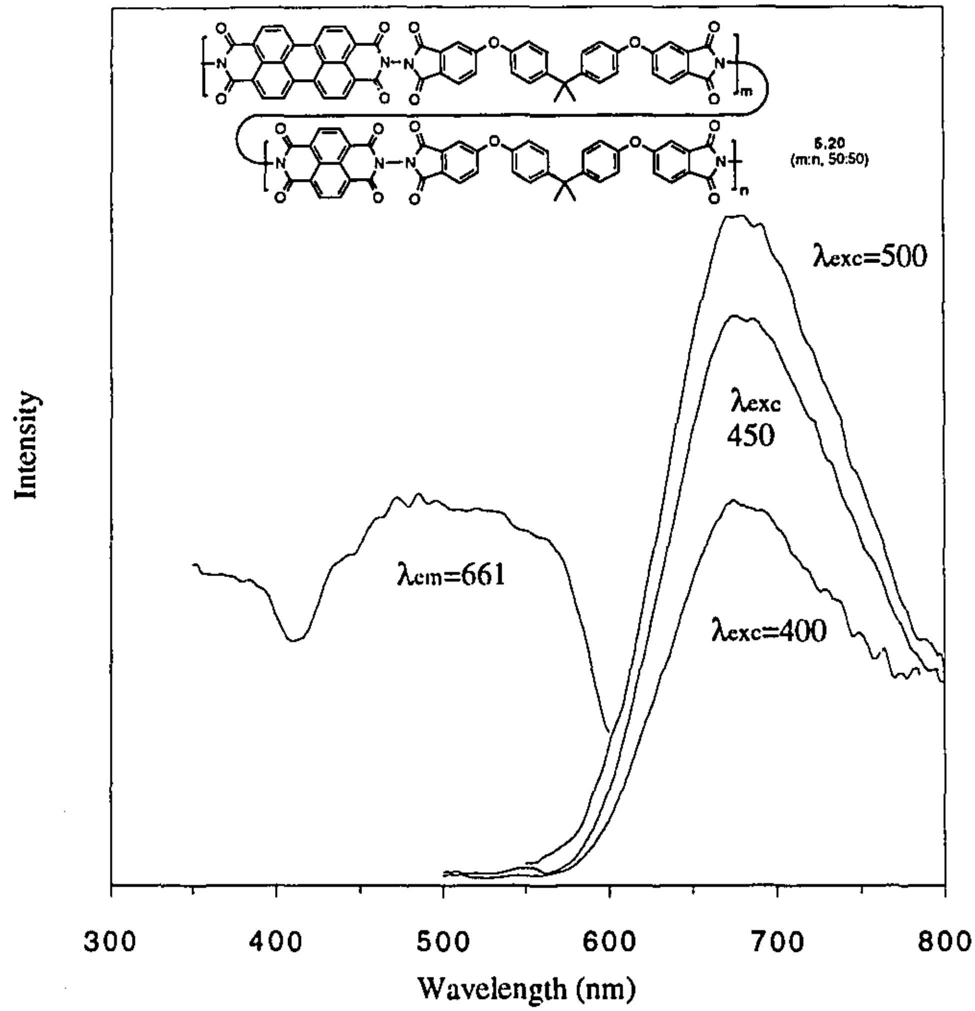

Figure 6.18. Fluorescence excitation and emission spectra of copoly(ether imide) **5.20** film

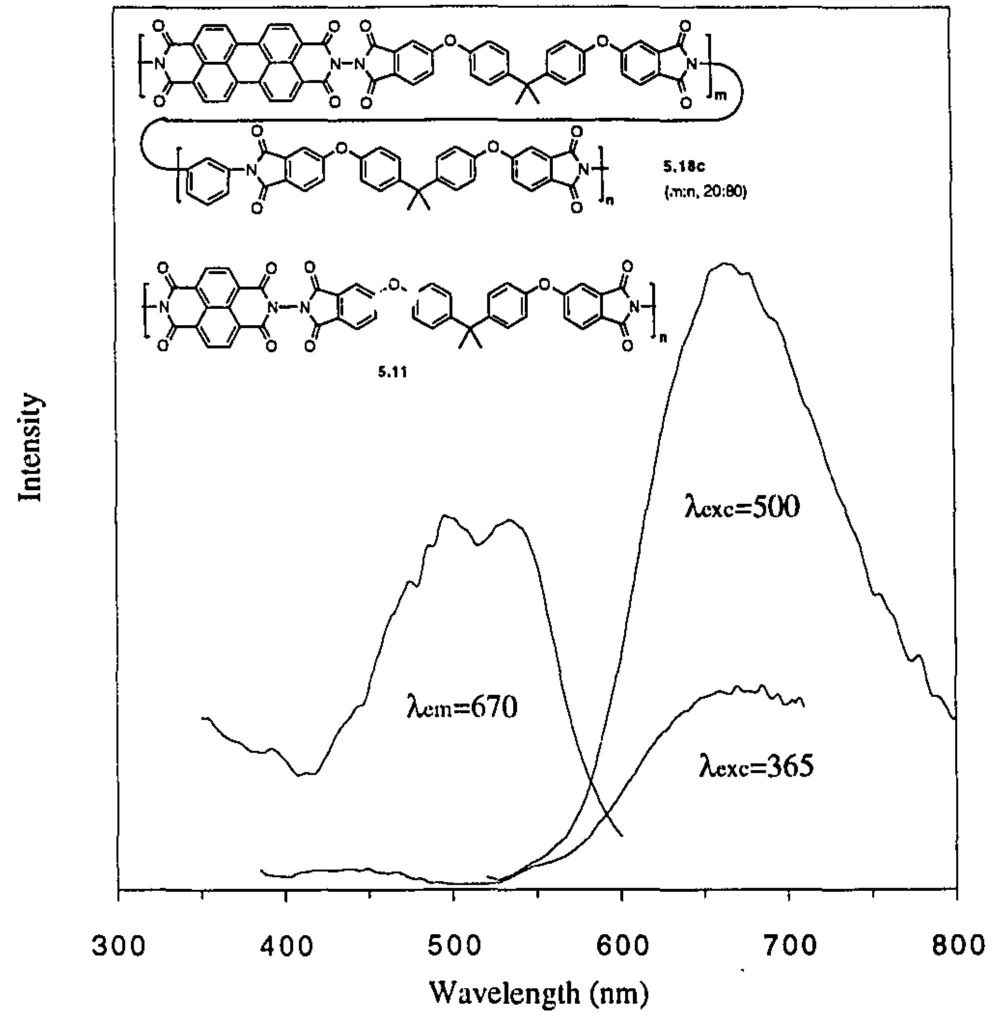

Figure 6.19. Fluorescence excitation and emission spectra of polymer blend **(5.18c / 5.11)**

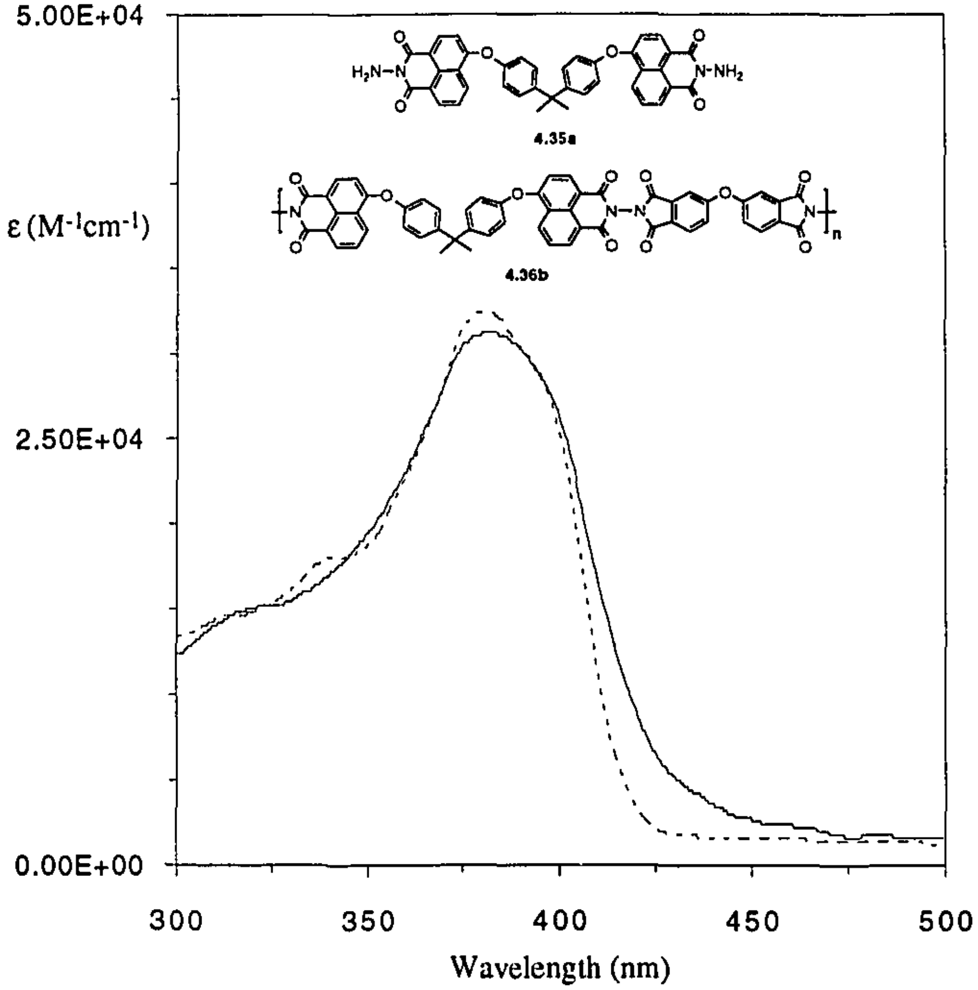

Figure 6.20. Absorption spectra of monomer **4.35a** (—) and poly(ether imide) **4.36b** (---) in chloroform

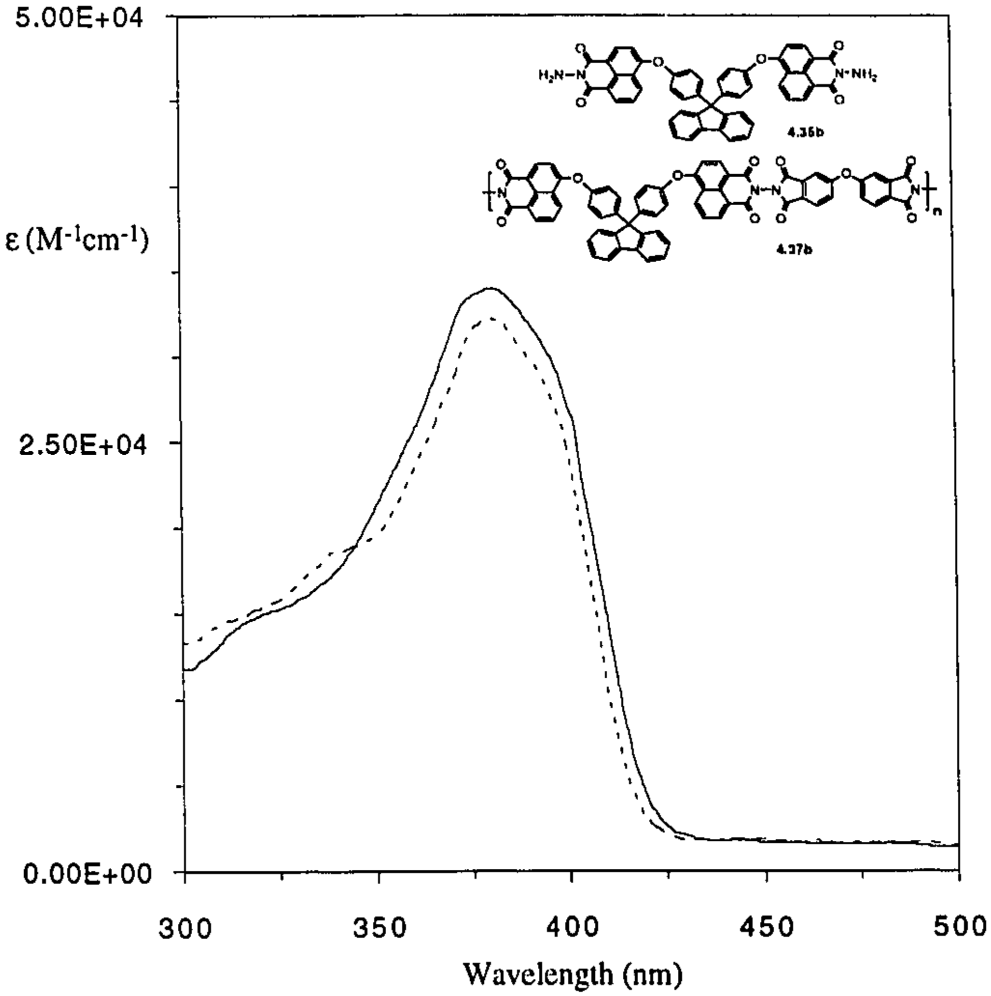

Figure 6.21. Absorption spectra of monomer **4.35b** (—) and poly(ether imide) **4.37b** (---) in chloroform

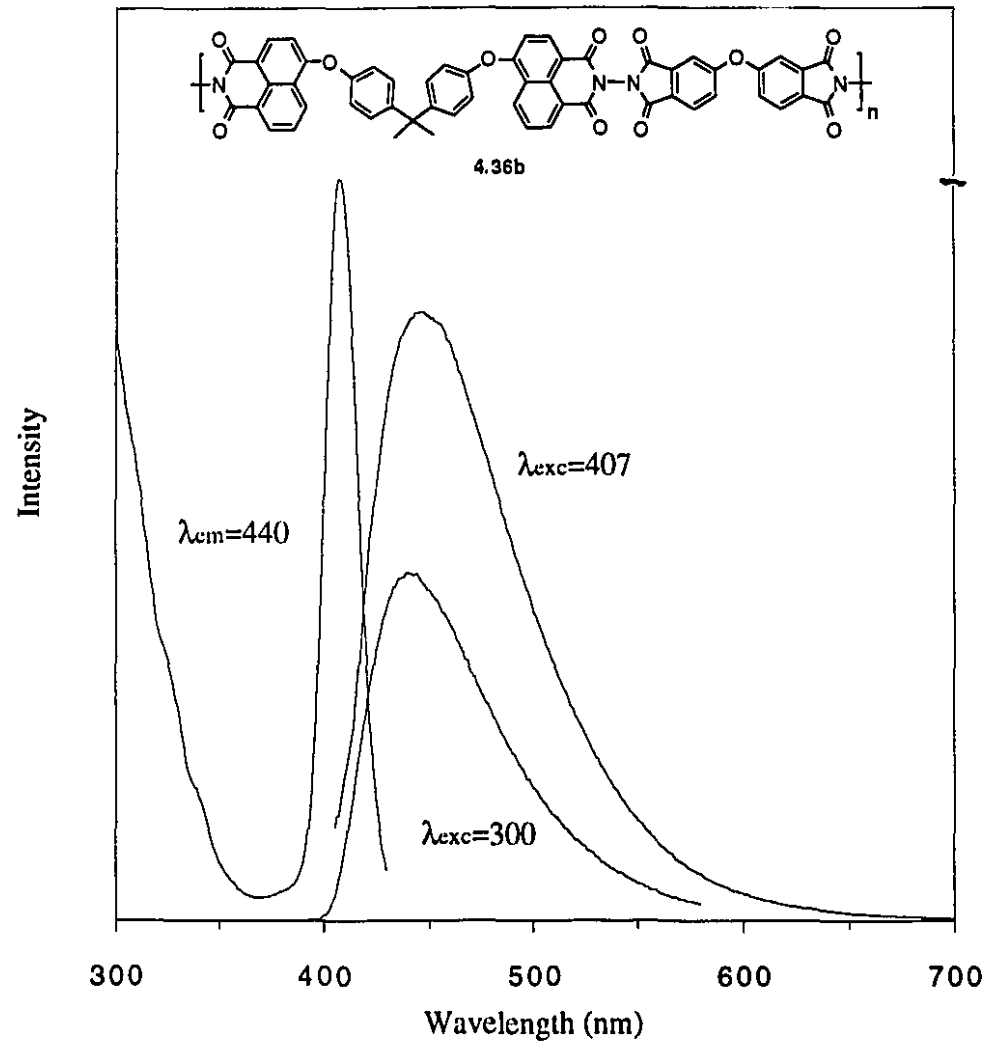

Figure 6.22. Fluorescence excitation and emission spectra of chloroform solution of poly(ether imide) **4.36b**

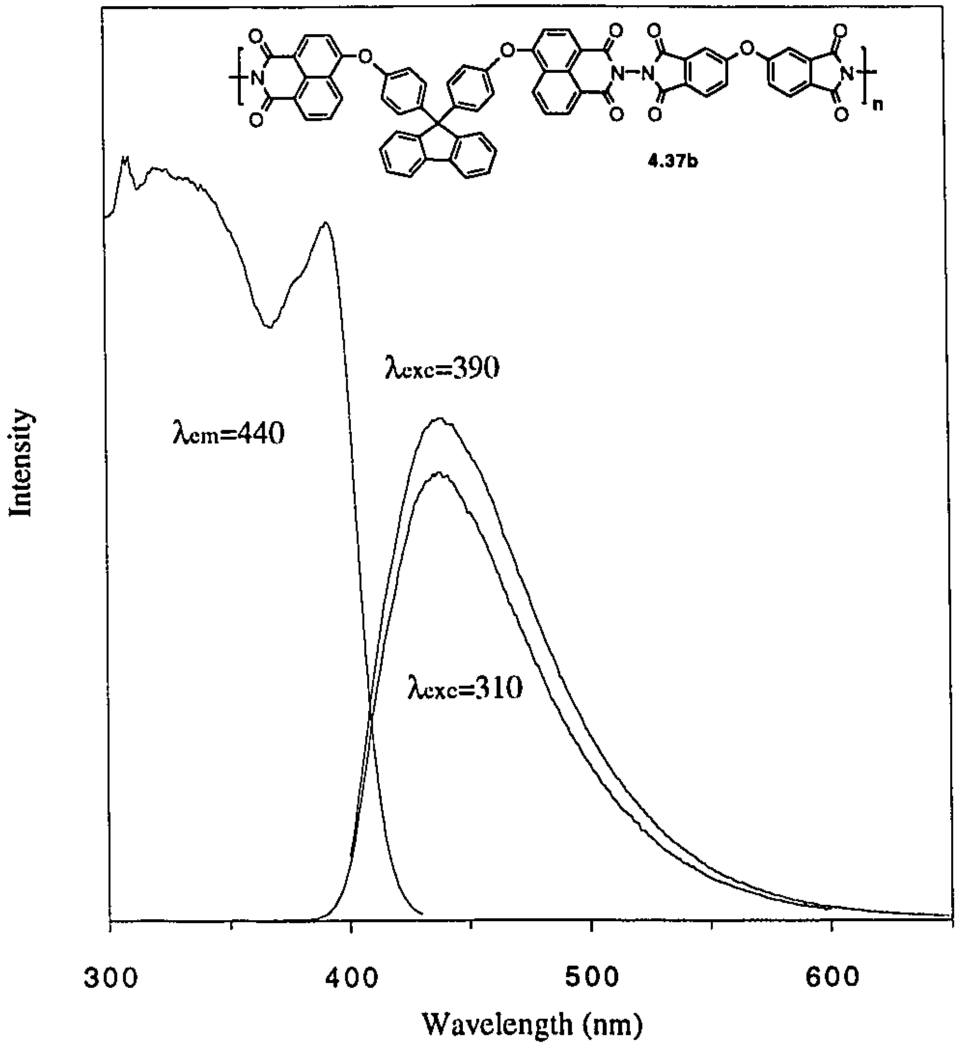

Figure 6.23. Fluorescence excitation and emission spectra of chloroform solution of poly(ether imide) **4.37b**

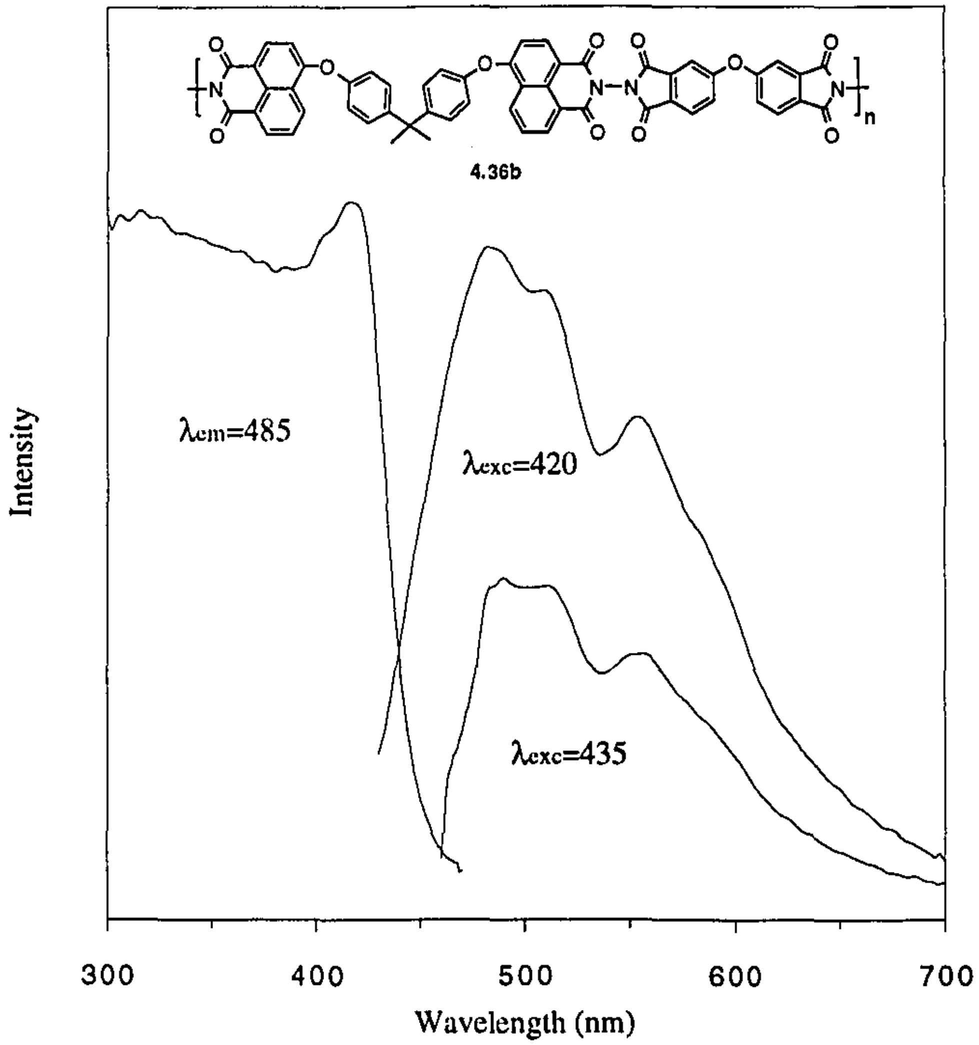

Figure 6.24. Fluorescence excitation and emission spectra of poly(ether imide) **4.36b** film

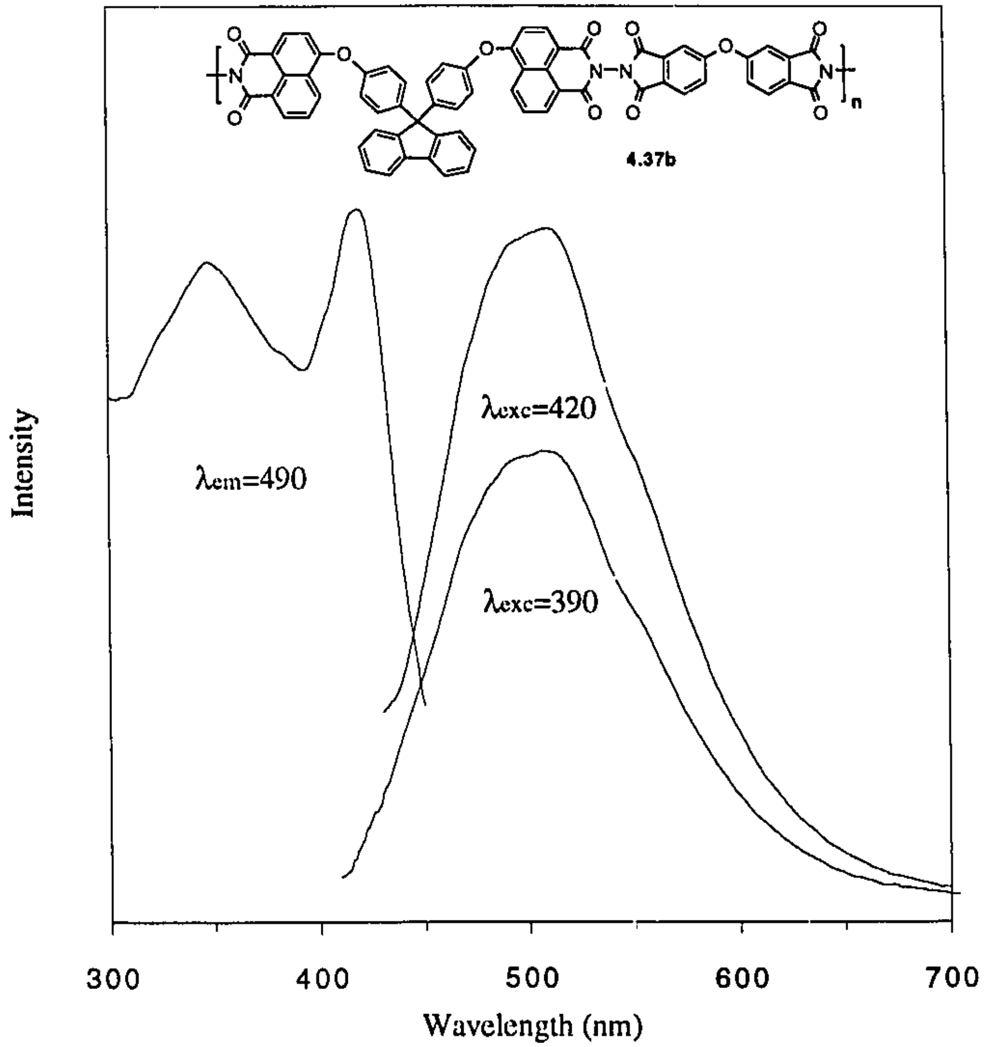

Figure 6.25. Fluorescence excitation and emission spectra of poly(ether imide) **4.37b** film

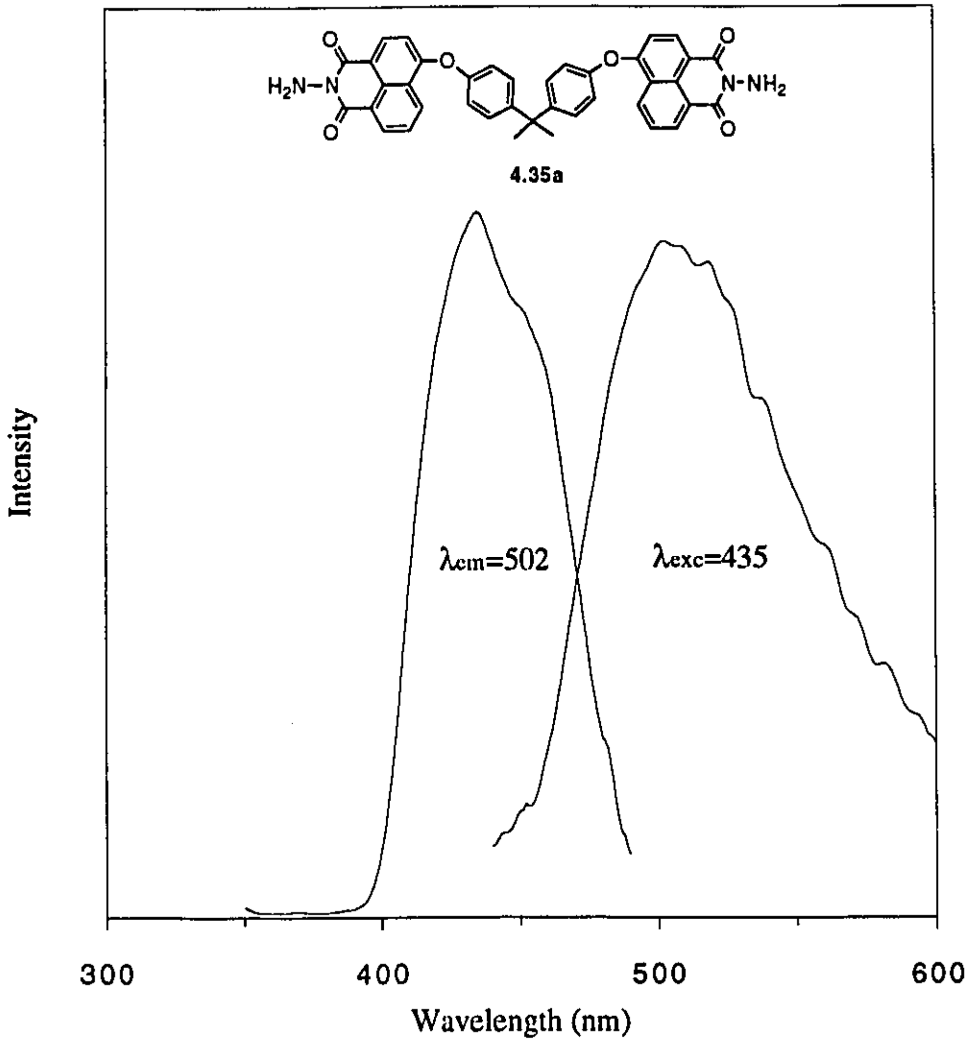

Figure 6.26. Fluorescence excitation and emission spectra of chloroform solution of monomer **4.35a**

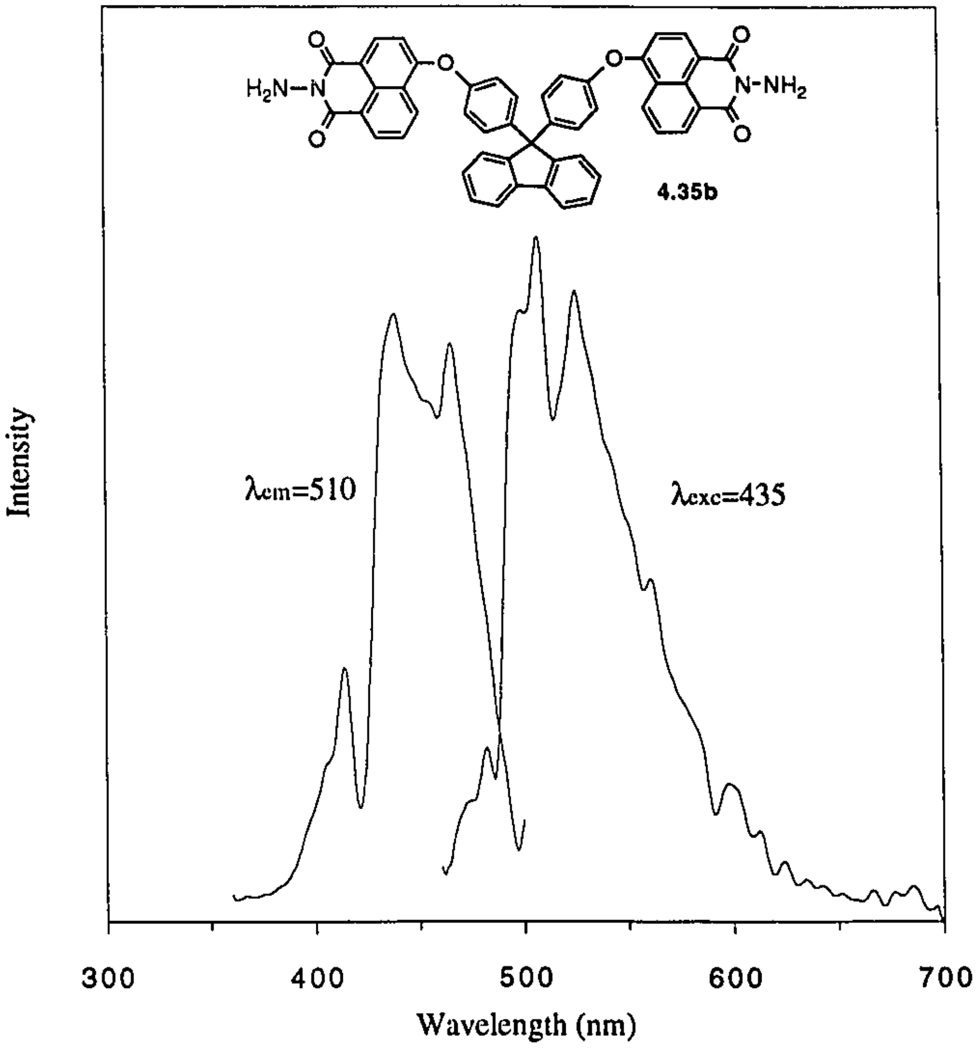

Figure 6.27. Fluorescence excitation and emission spectra of chloroform solution of monomer **4.35b**

Contributions to Knowledge

The contributions to knowledge resulting from this study are:

1) The reactions of hydrazine monohydrate with aromatic anhydrides were investigated. Phthalic anhydride with two phenyl groups adjacent to the anhydride ring on reaction with hydrazine gives only five membered-ring N-aminoimide in quantitative yield. The hindered N-aminoimide is thermally stable and unlike the unsubstitued N-aminoimide does not rearrange to the six-membered ring hydrazide. Using the same chemistry an N-aminoimidoaryl bisphenol was prepared which can be polymerized through its phenolic hydroxyl groups with an aromatic dihalide monomer to form a poly(imido aryl ether) having amino pendent groups along the chain. The amino groups in the poly(imido aryl ether) are very reactive and can potentially be used to make graft copolymers. As a model reaction, the amine-containing poly(imido aryl ether) was reacted with an anhydride, e.g. phthalic anhydride, to form a polymer with bisimide side groups, quantitatively. The amine-containing polymer can potentially be grafted to several type of commercial polymers such as polycarbonates and nylons. These graft copolymers may act as compatibilizing agents for immiscible polymer pairs, e.g. polysulfones and polyamides.

2) New difunctional bisimides and bishydrazide monomers were synthesized starting from hydrazine and chloro or nitrophthalic anhydride. Most of the monomers suffer from lack of solubility in organic solvents and therefore are hard to purify. Additionally, they are not hydrolytically stable and in the presence of a base and a bisphenol under the nucleophilic displacement polymerization reaction conditions are partially hydrolyzed. Hydrolysis of the bisimides and bishydrazide prevents the polymerization from proceeding and only low molecular weight oligomers form.

3) New monomers, bis(N-aminoimide)s, were synthesized from hydrazine, 4-chloronaphthalic anhydride and several bisphenols. Bis(N-aminoimide)s are, unlike aromatic amines, stable under exposure to air and light and therefore easy to purify and store. They behave as amines and react with aromatic dianhydrides to form high molecular weight poly(ether imide)s. The polymers show excellent thermooxidative stability as indicated by thermogravimetric analysis, have extremely high glass transition temperatures and are still soluble in organic solvents. This work opens up a new class of high temperature aromatic polyimides which can be prepared from readily available materials. The polymers are potentially suitable candidates for replacing existing polyimides which suffer from lack of processability due to their low solubility in most organic solvents. They can be readily cast from solution to give tough, flexible films which may be useful as high temperature coatings.

4) New high molecular weight poly(ether imide)s and copoly(ether imide)s were also synthesized from N,N'-diamino-1,4,5,8-naphthalenetetracarboxy bisimide, N,N'-diamino-3,4,9,10-perylenetetracarboxy bisimide (both derived from hydrazine) and several aromatic dianhydrides. One-step solution polymerization of the perylene diimide monomer, which is an extremely insoluble compound in most organic solvents, to form a high molecular weight polyimide has been demonstrated. Several derivatives of naphthalene and perylene dianhydrides have been used as dyes. Due to the photoconductive properties of the perylene diimides they have also found use in xerography as charge generation materials where the photoconductive compound has to be carefully dispersed into a binder polymer. Perylene based polyimides, which readily form red flexible fluorescent films by casting from solution, provide a new approach to facilitate the preparation of charge generation layers.