SYNTHESIS AND STRUCTURE PROPERTIES RELATIONSHIP (SPR) POLYIMIDE CONTAINING SILICONE SEGMENT FOR OPTOELECTRONIC APPLICATION

by

MUHAMMAD BISYRUL HAFI BIN OTHMAN

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DECLARATION

I declare that this thesis is the result of my own research that it does not incorporate without acknowledgment any material submitted for a degree or diploma in any university that it does not contain any materials previously published, written or produced by another person except where due the references made in the text.

Signed:
Candidate’s name: Muhammad Bisyrul Hafi Bin Othman
Dated:

Signed:
Supervisor’s name: Prof Madya Zulkifli Bin Ahmad
Dated:

Signed:
Co-Supervisor’s name: Prof Madya Hazizan Bin Md Akil
Dated:

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"Who is trying to, he will succeed"

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LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
BAPP	4-(4-1-(4-(4-aminophenoxy) phenyl)-1-methylethyl) phenoxy) aniline
BPDA	3, 3’, 4, 4’-Biphenyltetracarboxylic dianhydride
C	Carbon
COOH	Carboxylic acid group
CO_2	Carbon dioxide
DC	Dielectric constant
DL	Dielectric loss
DMA	Dynamic mechanical analysis
DMAc	Dimethyl acetemide
DMF	Dimethyl formamide
DMS	Bis-(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane
DMSO	Dimethyl sulfoxide
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric
EA	Elemental Analysis
FTIR	Fourier Transform Infra Red
GPC	Gel Permeation Chromatography
H	Hydrogen
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HNMR	Proton Nuclear Magnetic Resonance

H_2O	Water
H_2SO_4	Sulphuric acid
IV	Inherent Viscosity
MSDS	Material Safety Data Sheets
MWD	Molecular weight distribution
N	Nitrogen
NH	Amide group
NH_2	Amine group
NMP	N-methyl pyrolidone
N_2	Nitrogen gas
OH	Hydroxyl group
PAA	Polyamic acid
PDI	Polydispersity Index
PDMS	Poly dimethylsiloxane
PI	Polyimide
PIs	Polyimides
PIS	Polyimidesiloxane
PS-1	Parent polyamic acid/ polyimide precursor
PS-2	Polyamic acid containing DMS
PS-3	Polyamic acid containing PDMS
PS-4	Polyamic acid containing TEOS
S-1	Parent polyimide
S-2	Polyimide containing DMS
S-3	Polyimide containing PDMS
S-4	Polyimide containing TEOS

SEM	Scanning electron Microscope
TGA	Thermogravimetric Analysis
TEOS	Tetra-ethylorthosilicate
THF	Tetrahydrofuran
UV	Ultra Violet
UV-Vis	Ultra Violet Visible

LIST OF MAIN SYMBOL(s)

%	Percentage
<	Less than
>	More than
^{o}	Degree
^oC	Degree Celsius
$^oCmin^{-1}$	Degree Celsius per minute
Δ	Heating
ΔH	Delta H/ Enthalpy
[ ]	Concentration
cm	Centimetre
h	Hour
Hz	Hertz
gcm^{-1}	Gram per centimetre
gdL^{-1}	Gram per decilitre
gL^{-1}	Gram per litter
$gmol^{-1}$	Gram per mole
GPa	Giga Pascal
J	Joule
JK^{-1}	Joule per Kelvin
K	Kelvin
KHz	Kilo Hertz
L	Litre
m	Metre

min	Minute
mL	Millilitre
mm	Millimetre
MPa	Mega Pascal
n	Repeated unit n
nm	Nanometre
Pa	Pascal
ppm	Part per million
rpm	Rotation per minute
s	Second
Tb	Boiling temperature
Tg	Glass transition temperature
Tm	Crystalline melting temperature
wt %	Weight percent
w/w %	Weight per weight Percentage
w/V %	Weight per volume Percentage
x	Repeated unit, x
y	Repeated unit, y
z	Repeated unit, z

SINTESIS DAN STRUKTUR SIFAT-SIFAT HUBUNGAN (SPR) POLIMIDA YANG MENGANDUNGI SEGMEN SILICONE UNTUK APLIKASI OPTOELEKTRONIK

ABSTRAK

Suatu sistem polimida (PI), yang berasaskan monomer BAPP dan BPDA telah disintesis dengan jayanya dan struktur-sifat-sifat-perhubungan (SPR), silikon tersegmentasi yang berperanan terhadap sistem PI telah diselidiki. Dua kaedah berbeza telah digunakan, bagi memperkenalkan segmen Si-O-Si kedalam rantai tulang belakang dan matrik PI, melalui kaedah kopolimerisasi konvensional dan kaedah sol gel, masing-masingnya untuk menyediakan kopolimer poliimidasiloxane (PIS) dan komposit polyimide silika hibrid (PSH). PI yang telah disintesis berperatusan > 80%, mempunyai kelikatan inheren dan berat molekul sederhana dengan taburan berat molekul sempit. Adanya segmen silikon pada rantai tulang belakang PI telah berjaya disahkan oleh FT-IR, HNMR dan EA, dengan filem-filem PI telah sepenuhnya imidisasikan. Biasanya PI yang matang menunjukkan kestabilan didalam medium berasid dan beralkali serta penggabungan Si-O-Si kedalam tulang belakang atau partikel-partikel kedalam matrik meningkatkan keterlarutannya didalam pelarut aprotik berkutub. SEM menunjukkan fasa yang hampir sekata antara PI dan segmen silikon untuk sistem PI S-2 dan S-3, sedangkan sistem PI S-4 mendedahkan partikel-partikel tak organik ditebarkan kedalam PI matrik secara sekata. Pengenalan segmen Si-O-Si kedalam tulang belakang PI, secara konsistennya mengurangkan suhu peralihan kaca, kekerasan, indeks biasan, pemalar dielektrik dan kehilangan dielektrik jika dibandingkan dengan induknya (S-1). Sedangkan pengenalan partikel-partikel Si-O-Si kedalam matrik meningkatkan suhu peralihan kaca, kekerasan, indeks biasan, pemalar dielektrik dan kehilangan dielektrik sistem PI jika dibandingkan dengan induknya. Kajian TGA menunjukkan suhu degradasi akhir (Char residu 55 - 60% pada 800 ^{o}C) telah dipertingkatkan disebabkan kehadiran segmen Si-O-Si, baik pada tulang belakang mahupun matrik-matrik PI. Sistem PI memaparkan warna kekuningan dengan konsistennya, sesuai dengan peralihan π - π^* sebagai akibat peralihan muatan kompleks (CTC) aromatik pada panjang gelombang 450 nm. Data optik dan elektrik menunjukkan keputusan ujikaji berada dalam julat yang diterima untuk aplikasi peranti optoelektronik.

SYNTHESIS AND STRUCTURE PROPERTIES RELATIONSHIP (SPR) POLYIMIDE CONTAINING SILICONE SEGMENT FOR OPTOELECTRONIC APPLICATION

ABSTRACT

Polyimide (PI) system which derived from monomer BAPP/BPDA were successfully synthesized and structure-properties-relationship (SPR), silicon segment whose role on PI system has been investigated. Two different methods were used to introduce segments of Si-O-Si which are into the backbone chain through conventional copolymerization and the matrix of PI via sol-gel methods, respectively to prepare the copolymer polydimethylsiloxane (PIS) and the composite polyimide silica hybrid (PSH). The synthesized PIs yield > 80%, with moderate inherent viscosity and molecular weight is with a narrow molecular weight distribution. The presence of silicone segments in the PI backbone has been successfully verified by FT-IR, HNMR and EA, the PI films were completely imidized. Typically the cured PI showed stability in acidic and alkaline medium and the combination Si-O-Si into chain backbone or particles into the matrix increases its solubility in common polar aprotic solvents. SEM showed an almost homogenous phase between PI and silicon segment for the PI system S-2 and S-3, while the PI system S-4 revealed the inorganic particles are distributed uniformly in the PI matrix. Introduction Si-O-Si segment into the PI backbone, consistently reducing the glass transition temperature, hardness, refractive index, dielectric constant and dielectric loss compared to the parent (S-1). While the introduction Si-O-Si particles into the PI matrix increased glass transition temperature, hardness, refractive index, dielectric constant and dielectric loss of PI system in comparison with its parent PI. TGA studies showed that the final degradation temperature (char residues 55 to 60% at 800 ° C) segment has been enhanced due to the presence of Si-O-Si, both in the backbone or matrix-matrix PI. PI System yellowish color display with a consistently, suitable to the transition π - π * transition due to the complex charge (CTC) aromatic wavelength 450 nm. Optical and electrical data shows the experimental results within the range accepted for optoelectronic device applications.

CHAPTER 1

1 Introduction

1.1 Overview

The research presented in this dissertation is focused on the preparation of polyimide (PI), poly (imide siloxane) (PIS) copolymer, and polyimide silicone blend (PSH), especially for optoelectronic applications. As shown in **Figure 1.1**, the incorporated silicone unit (silicon segment) on polyimide, requires a fundamental understanding of the structure-properties relationship. Therefore chemical properties, morphology properties, thermal properties, mechanical properties, interfacial properties (although not discussed herein), optical properties, and electrical properties, depend as well on the activities manipulated by the silicone segment. Therefore, PIS and PSH are high performance polymers, derived from PI that are manipulated using silicone segments. These areas are addressed in terms of the PI structure, derived from monomer4-(4-(1-(4-(4-aminophenoxy) phenyl)-1-methylethyl) phenoxy) aniline BAPP/3, 3’, 4, 4’-Biphenyltetracarboxylic dianhydride BPDA employed.

Chapter 1 presents the scope of the research, divided into four parts, which are an overview of the study, a statement of the problem, the objective of the study, and initial hypotheses. Chapter 2 discusses the idea of polyimide synthesis and characterisation; however, only the important fundamentals regarding the PI, PIS and PSH synthesis based on 'aromatic' polyimides as they constitute the major category of such materials, are covered.

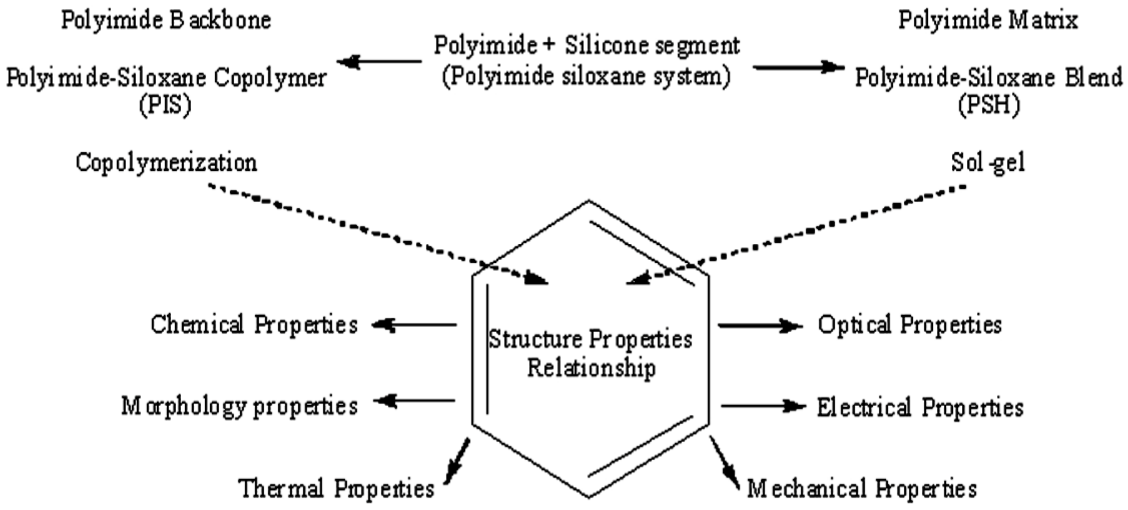


Figure 1.1: Structure-properties relationship of Polyimide-Siloxane system

The properties of polyimides can be rapidly altered by minor variations in their structure. The subtle variations of silicone placement, either in the PI backbone or the PI matrix, have a tremendous effect on the properties of the final polyimide. Accordingly, Chapter 2 reviews several such features that are important towards understanding these structure-property relationships. Chapter 3 presents the method of the experiment. The four series of polyimides, synthesized and prepared for characterisation respectively, are standard series, series of silicone segment, in PI backbone, and a series of silicone segment in PI matrix. Chapter 4 presents the synthesis consideration of PI, structure conformation of PI, and analysis of the polyimide series. Finally, Chapter 5 formulates the overall findings obtained from this study.

1.2 Problems Statement

1.2.1 Properties of PI films

Polyimide (PI) based on an aromatic backbone, is known as a high performance polymer, due to many desirable characteristics, such as excellent mechanical properties, superior chemical resistance, excellent electrical properties (low dielectric constant and high voltage breakdown), good thermal and optical properties, resistance to climate change, and formability, as reported by Cha *et al* (1996), Feger *et al* (1988), Ghosh and Mittal (1996a), and Sillion *et al* (2003). Although many applications of PI have been developed recently, such as adhesive applications (Dueber *et al,* 2004; Ellison and Taylor, 1997; Progar and Clair, 1990), encapsulation and packaging applications (Li *et al,* 2005; Razeghi, 2008; Sekitani *et al,* 2002; Tiwari *et al,* 2004), solar cell applications (Landis and Naselow, 1987; Romeo *et al,*2006; Wang *et al,*2010), fuels cell and membrane applications (Higuchi *et al,* 2006; Woo *et al,* 2003; Zou and Anthamatten, 2007), insulation applications (David 1992; Hostler 1990), optical applications (Ando *et al,* 1995; Kim *et al,* 2001), coating applications (Angelo *et al,*1980; Sidorov *et al,* 1999), and others, through those, PI characteristics have showed their ability to be used as materials for high performance application.

In the last half century, hundreds of polyimides of different structures have been studied, but there are still problems to be solved, such as the balance between higher service temperature and processability, due to its extreme glass transition temperature, the poor solubility in most organic solvents, in fully imidized form and cost, etc. (Ding 2007; Ghosh and Mittal 1996a; Kricheldorf and Burger 1996; Mittal 1984a). Therefore, much effort has been concentrated on synthesizing tractable PIs, which maintain reasonable characteristics, such as high mechanical strength and high thermal stability, without sacrificing their excellent properties. Various techniques have been attempted and extensively studied to overcome serious processing difficulties and to utilise the PI, including incorporating flexible segmented or manipulate bulky side group into a rigid PI backbone (Brum *et al,* 2008; Kricheldorf and Burger,1996; Yi *et al,* 1997) and introduce an inorganic segment network into the PI matrix, to enhance processing (Kricheldorf and Burger, 1996; Mittal, 1984a;c). Therefore, the polyimide can be synthesized at low temperature and is soluble in most organic solvents, as reported by Wu *et al,* (2004) and Wu *et al,* (2008).

1.2.2 Incorporation of silicone into the PI backbone and the PI matrix

The incorporation of silicone segment was identified as able to solve the difficulties in processing and at a same time improve the qualities of the existing PI properties. These silicone units have been manipulated, either into the PI backbone or the PI matrix, resulting in a modified PI, with properties that have been enhanced for use in extreme conditions. For incorporation of silicone segment into the PI backbone, various methods have been studied. Amongst others, are the effect of silicone unit length (Nagase *et al,* 2007), the effect of arrangement of silicone segment in PI repeated unit, the effect of type silicone segment, the effect of the mol ratio of silicone segment, and others, which will not be discussed in this paper. While, the introduction of silicone segments into the PI matrix has focused only on the effect of the silicone segment used. However, both of these methods were discussed in a separate paper and no collaboration has been done to reflect the relationship between these two, as well as an increased understanding in the knowledge base.

Silicone polymers, such as polydimethylsiloxane (PDMS) amine terminated, have $Si(CH_3)_2$-O bond, which exhibited high chain flexibility, low temperature flexibility, good hydrophobicity behaviour, high oxidative stability, and excellent thermal stability (Furukawa *et al,*1999; Liu *et al,*2008; Nakata *et al,*1993; Stern *et* *al,*1990). The copolymerization method of silicone segment into the polyimide backbone produced excellent mechanical properties, heat resistance, and electrical properties, with an excellent film forming ability, and has an excellent solvent resistance, elasticity, and adhesive properties (Chang and Wu 1998; Furukawa *et al,*1999; Stern *et al,*1990). However PDMS has poor compatibility between soft segments of PDMS and hard segments in polyimide, which usually exhibits microphase separation and separate glass transition temperature (T_g) values, due to thermodynamic incompatibilities, which were either macroscopically immiscible or exuded from the cross linked matrix during the curing procedure Liu *et al,* (2008). As reported by Ghosh and Mittal (1996b) and Kricheldorf and Burger (1996) these phase separations could be prevented by introducing less 20%wt PDMS into the PI.

On the other hand, incorporating silicone segment into the PI matrix (blending system) using the sol-gel process (Sanchez and Ribot 1994; Sanchez *et al,*1999) had shown a significant increase of mechanical properties, such as elongation and tensile strength, impact strength, toughness/hardness, and thermal properties (Furukawa *et al,*1999; Morikawa *et al,*1992; Wen and Wilkes(1996a; Zhu *et al,*1999a). These is because, the polyimide silicone hybrid can provide chemical bonding between the organics phase of PI and the inorganics phase of silicone segment (Smaihi *et al,* 1999; Wang *et al,* 1994). The sol gel process is very popular in the preparation of polyimide hybrids, where silica particles are dispersed in a PI matrix; the resultant PI will have similar properties, almost to composite properties (Liu *et al,* 2008; Wang *et al,* 1994). Furthermore, this makes the properties of the modified PI better than the parent PI. Therefore, the copolymerization silicone segment method and the sol gel method appeared compromising as a function for manipulating the desirable properties of PI.

1.2.3 Characterisation of PI silicone system

Polyimide incorporated with silicone segment and parent polyimide can be characterised in terms of their purities, intrinsic properties, such as molecular weight distribution (MWD), inherent viscosity (IV), degree of cyclization and the presence of an introducing unit, and physical form, such as colour of PI precursor and PI film, the ability of precipitation, and uniformity. Furthermore, the quality and properties of Polyimide incorporated with silicone segment and parent polyimide may vary, as many factors can influence the characteristics of a final product, such as the purity of monomer/solvent and the processing parameter. Numerous methods could be applied to determine the purity of the final synthetic product, in terms of molecular weight, such as FT-IR, H-NMR, GPC, Viscosity, and GCMS. But except for the viscosity method, all others are costly and require difficult sample preparation. Therefore in this study, the most suitable method needs to be the simplest, quickest, and most effective in determining/estimating the molecular weight of PI incorporated with silicone segment and parent PI in the synthesis.

To investigate the change in molecular weight, degree imidization, morphology, chemical structure, and bonding of the PI incorporated silicone segment and parent PI film, required the correct method. Therefore, the tool selected for the characterising of PI incorporated with silicone segment and parent PI needed to be identified. The chemical structure analysis, such as FT-IR and H-NMR, is prior to thermal, mechanical, etc. testing, since the properties of final product are influenced by a structural relationship. Therefore, the structural properties relationship of PI incorporated silicone segment and parent PI, were studied and determined.

1.3 Objective of the study

Recognising the importance of understanding the diversity of the nature of PI derived from the same monomer, it should be very interesting to systematically study two different methods, for obtaining an optimal performance of PI. The introduction of silicone segment into the backbone and the matrix of the PI, would result in a PI with different characteristics, even though the monomer used does not change. For this research, the aims are listed below:

1- To investigate the role of silicone segment on properties of the PI and study the morphological, thermal, mechanical, optical and electrical of PI system
2- To synthesis a series of PI, derived from the monomer 4-(4-1-(4-(4-aminophenoxy) phenyl)-1-methylethyl) phenoxy) aniline (BAPP) and 3, 3', 4, 4'-Biphenyltetracarboxylic dianhydride (BPDA).
3- To incorporate two types of silicone segment into the PI backbone through copolymerization, which are Bis-(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (DMS) as a short silicone segment and Poly (dimethylsiloxane), bis (3-aminopropyl) terminated (PDMS) as long silicone segment, respectively.
4- To introduce tetra ethyl orthosilicate (TEOS) as silicone segment into the matrix of the PI, derived from the monomer BAPP/BPDA, through the sol gel process.
5- To ensure the completion of the PI precursor synthesis, the perfection of imidization, and the successful incorporation of silicone segment into the PI backbone and the PI matrix, by characteristics, using Elemental Analysis

(EA), Fourier Transform Infra-Red (FT-IR), and proton Nuclear Magnetic Resonance (H NMR).

1.3 Statement of hypothesis

The primary hypothesis was that the PI synthesised, containing a high molecular and high purity would produce PI film with good properties and the PI would be imidized completely. High molecular weight was attributed to the polymerization of the monomer dianiline / dianhydride, derived from BAPP/BPDA and would be driven without interference from the impurities that can also cause reactions. While fully imidized PI would improve chemical stability, thermal properties, and mechanical properties of PI, due to the stability of the imide linkage. As an approach, the purification of PI is still considered as a means to remove the unreacted monomer, while PI precursor would cure step-wisely. To test this hypothesis, PI precursor were analysed by an Ubbelohde viscometer to determine the molecular weight and the PI was analysed using FT-IR, H-NMR, and solubility testing, to determine the chemical stability of the PI.

The secondary hypothesis, was that the incorporation of silicone segment into the PI backbone would be successful without showing a microphase separation; meaning that between the silicone segments and the PI, should be a homogenous system. Microphase separation in the PI will be the critical point that will result in a point defect. While, introducing silicone segmented into the PI matrix should be homogenously dispersed without agglomeration. Besides that, the silicone segment particle sizes are in the nano-range. This agglomeration would cause the silicone segment to be outside of the PI matrix and create phases that could be observed. To test this hypothesis, both modified PI were analysed using FT-IR and FESEM.

The tertiary hypothesis, was that by introducing silicone segment, either into the PI backbone or the PI matrix, respectively, roles of the morphological, thermal, mechanical, and electrical of the PI, which have modified. The polymer, derived from the monomer BAPP/BPDA, would enhance the chain flexibility, while incorporating silicone segmented into the PI backbone. This was attributed to the contribution of the flexibility group of Si-O-Si from silicone segment, which extends the capability of the PI backbone chain to be mobile. In addition, the introduction of silicone segment into the matrix of the PI, would limit the chain mobility of the PI, derived from the monomer BAPP/BPDA. This silicone segment would occupy empty spaces in the PI matrix, and subsequently reduce the free volume. Therefore, the capability of the PI backbone movement would be limited. To test this hypothesis, modified PI were analysed by TGA, DSC, DMA, CTE, Durometer, and tensile testing. Optical properties and electrical properties of the modified PI were also determined.

CHAPTER 2

2 LITERATURE REVIEW

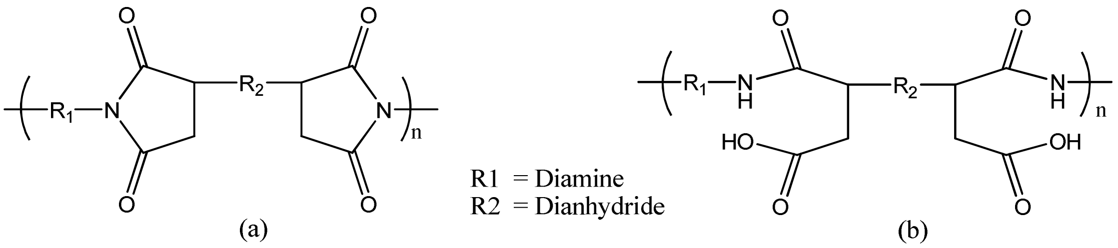
2.1 Introduction

The growth of modern technology has caused a continually increasing need for materials that perform well under harsh conditions, such as elevated temperatures. The initial excitement when DuPont introduced Polyimides (PIs) in the 1960s was over the outstanding thermo-oxidative stability of the materials (Critchley *et al,* 1983). Both academic and industrial research aims to discover the optimum method for producing polyimide (PI) materials tailored to growing manufacturing interest. Early investigations revealed aromatic PIs possess a desirable array of other important characteristics as well. These include radiation/chemical resistance, a low dielectric constant, a selective permeability to gases, film toughness under rigorous conditions of air aging, and a retention of high mechanical strength over a wide temperature range (Sroog *et al,* 1965). These versatile properties have stimulated interest in expanding the applications for PIs for the manufacturing of modern aerospace/automotive transportation vehicles and microelectronics devices.

This dissertation is a contributing research segment with regard to synthesis and characterization of thermosetting PI targeted for use as dielectric thin films in electronics applications. This chapter is divided into five sections which will review developments in PI synthesis and structure/property modifications as revealed in the published literature. The first two sections focus on a common synthetic method for the preparation of PI synthesis. The third sections describe the introduction of silicone to the PI system. The fourth section in this chapter summarizes the latest theories of characterizing PI. The final was summarized the fundamental aspects in optoelectronic application.

2.2 Polyimide (PI) synthesis

PIs are characterized by a backbone structure consisting of cyclic imide (tertiary amine) groups interconnected to two group of C=O from dianhydride and diamines (Feger *et al,* 1988; Mittal 2003, 2009; Sroog (1976). PIs are synthesized from dianhydride and diamine monomers through a two-step polymerization method. **Figure 2.1** shows the general PI structure and its precursor. Aromatic PIs are comprised of five-membered heterocyclic imide units and aromatic rings. Compared to aliphatic PIs, aromatic PI material is more suitable as a high performance polymer for high performance applications. The interconnection of an aromatic group in cyclic imide (tertiary amine) groups is a major factor that strengthens the PIs.



(a) (b)

Figure 2.1 General structures of PI (a) and its precursor (b).

The structure of these “cyclic chain” systems makes PIs insoluble/intractable and, thus, not recommended for traditional solution/melt polycondensation reactions. These characteristics contribute to chemical stability, thermal stability, mechanical strength, and electrical properties as an insulator (Feger *et al,*1988; Ghosh and Mittal, 1996b; Mittal, 2009). Despite the good characteristics contributed by the backbone, manipulations of its monomers can improve the optical and physical properties. Many researchers conclude that PIs have desirable characteristics, such as excellent thermal and mechanical properties, superior chemical and weather resistance, low thermal expansion coefficients, and their suitability for a variety of advanced technologies. For these reasons, PIs are widely utilised as high temperature insulators and dielectrics, coating and adhesive, and matrices for high performance composites (Abadie and Sillion, 2009; Feger *et al,* 1988; Ghosh and Mittal, 1996b).

In 1908, Bogert and Renshaw (1908) discovered a PI based on 4-amino-o-phthalic acid and some of its derivatives. The authors reported that 4-aminophthalic anhydride made it possible to form a "polymolecular imide" in water at elevated temperatures. Almost 50 years later, Edwards et al synthesized PIs via a more practical approach using dianhydrides, or derivatives thereof, and diamines. Using these in the melt or in solution resulted in precipitation of intractable low molecular weight PIs (Edwards 1955; Mecham 2001; Wang 2005). This led to the commercialization of the first aromatic PI called Poly(4,4'-oxydiphenylene- pyromellitimide) or PMDA-ODA PI or Kapton® by DuPont scientist, Dr. A. Endrey in 1965 (Kute and Banerjee,2007; Laszlo, 1965). He invented a method of obtaining PIs through a reaction of soluble/processable intermediates known as poly(amic acid)s (PAAs). This type of reaction consisted of two steps: the solution polycondensation of an aromatic diamine and a dianhydride to form poly(amic acid) (PAA), which then could be processed into a useful shape, followed by cyclodehydration of the amide-acid to form PI (Edwards, 1955; Sroog *et al,* 1965).

2.2.1 Two-Step Method

The two-step method was the first introduced by DuPont scientists to synthesize high molecular weight aromatic PIs (Laszlo, 1965). The first step consists of preparing a solution of the aromatic diamine monomer in a polar aprotic solvent. Next, an equimolar amount of a tetracarboxylic dianhydride monomer is added. The formation of PAA or PI precursors occur at an ambient temperature depending on monomer reactivity, solvent purity, side reactions and other possible side effects which will be discussed later. The high molecular weight PAA produces is fully soluble in the reaction solvent and, thus, may be cast into a film on a suitable substrate. The good solubility of the PAA allows the polymer to be processed in the form of the poly(amic acid)s. The second step includes the cyclodehydration of the PAA solution. This is accomplished by heating it at elevated temperatures or by incorporating a chemical dehydrating agent. The final product is usually insoluble and infusible. The overall reaction scheme for the two-step method is depicted in **Figure 2.2**.

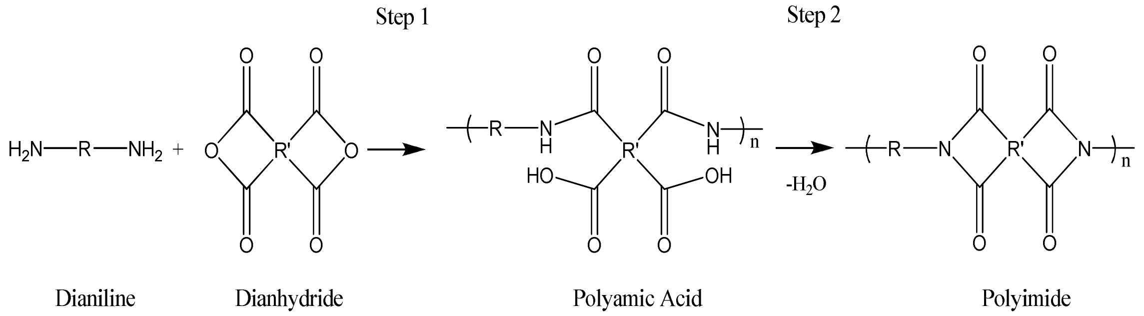


Figure 2.2 The overall reaction scheme for the two-step method

2.2.1.1 Formation of polyamic acid

The reaction mechanism of PAA formation instituted when nucleophilic acyl substitution occurs at one of the carbonyl carbons of a phthalic anhydride unit comprising the tetracarboxylic acid anhydride and shown **Figure 2.3**.

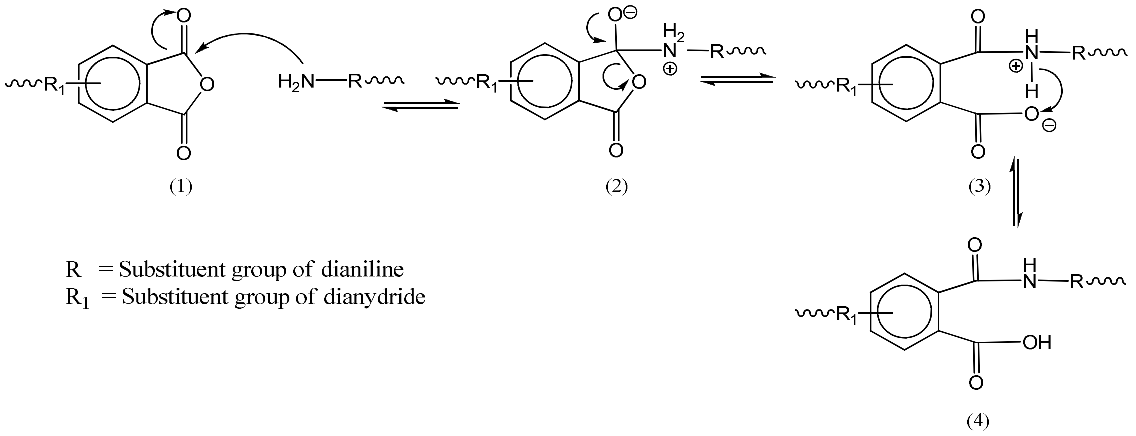


Figure 2.3 Mechanism for forming poly(amic acid)

The reactivity of carbonyl compounds is due to the polarity of carbonyl groups, resulting because oxygen is more electronegative than carbon. Therefore, carbonyl carbon is an electrophile and will predictably be attacked by nucleophiles consisting of nitrogen from the aromatic diamine with its unshared pair of electrons, (1). This causes carbon-oxygen π bond breaks, resulting in bonding of carbonyl carbon and nitrogen, producing a cyclic intermediate to be formed when the pi electrons shift into oxygen, (2). The intermediate is called a *tetrahedral intermediate* because the trigonal sp2 carbon has become tetrahedral sp3, (2). Generally, sp3 carbon bonded to an oxygen atom will be unstable if it bonded to another electronegative atom, because the lone pair electron from the oxygen reform the π bond and simultaneously cause the bond between the carbon and a “leaving group” to break. The bond that must break in this step yields linear amide-acid, which releases the central oxygen of the cyclic intermediate, thereby resulting in a carboxylate leaving group,(3).

If the bond breaks between the nitrogen and the developing sp2 carbon instead, the reaction is reversed, yielding a starting species free from amine and anhydride groups. The rate of the forward reaction must occur more rapidly than the reverse to achieve a high molecular weight polyamic acid. Since the carboxylate group is chemically bonded, it cannot be systematically removed to drive equilibrium in the forward direction. It can however be “deactivated” through hydrogen bonding with a basic solvent, further discussed in section 2.2.1.1.2 (the effect of solvent). Whether aromatic diamines or carboxylate anhydride groups are expelled depends on their relative basicities.

The weaker base is preferentially expelled because the weak base does not share its electron as well as the strong base does. A weaker base forms a weaker bond, one that is easy to break. In addition, the expelled compound is related with the acidities and the conjugate acid of some leaving groups. **Table 2.1** shows the acidities of the conjugate acid of some leaving groups. A high molecular weight PAA can be obtained by meeting the following requirements: Monomers must be highly pure (>99.9%), one-to-one stoichiometric of monomers must be employed, monomers must be difunctional and reacting groups must be mutually accessible, length of reaction time must be sufficient for high conversion and side reactions must be minimal or absent.

Table 2.1 The acidities of the conjugate acid of some leaving group

Conjugate base (leaving group)	*pKa*	Acid	Basicity	Nucleophilicity
H_2O	-1.7	H_3O^+		
CH_3COO^-	4.8	CH_3COOH	Increase ↓	Increase in aprotic solvent ↓ Increase in a gas phase ↓ Increase in a protic solvent ↑
CN^-	9.1	HCN		
NH_3	9.4	NH_4^+		
$N(CH_3)_3$	10.8	$NH(CH_3)_3+$		
CH_3O^-	15.5	CH3OH		
HO^-	15.7	H_2O		
NH_2^-	36	NH_3		

As shown in the **Table 2.1**, carboxylate anhydride groups have less basicity and are expelled more readily than other amine groups. However, equilibrium in PAA formation reactions must satisfy the additional requirement of providing a high molecular weight polymer; the forward reaction must be significantly faster than the reverse. Many researchers agree on the major cause concerning reaction rates and how they are affected by various factors, including monomer-structure, temperature, solvent composition and side reactions (Ghosh and Mittal, 1996b; Mittal, 1984a).

•Effect of monomer reactivity

The formation of PAA involves a nucleophilic substitution reaction of the carbonyl carbon atom of the dianhydride monomer with a diamine monomer. The reaction is expected to depend upon the electrophilicity of the carbonyl groups of the dianhydride monomer and the nucleophilicity of the amino nitrogen atom of the diamine monomer. As reported by Carey and Sundberg (2007), the aromatic acid anhydrides monomer, are highly electrophilic acylation agents toward amines monomer. The enhanced electrophilicity results from strong electron-withdrawing effects exerted by the ortho-placement of the carbonyl groups. However, nearly all tetracarboxylic acid anhydrides contain bridging groups or atoms between the two phthalic anhydride units which affect the electron-accepting ability, or electrophilicity, of the carbonyl carbons. The ability to accept an incoming electron pair from nucleophiles is contingent on the electron affinity (Ea) of the dianhydride monomer. Common isomeric aromatic dianhydrides can be referred in ***Appendix A-1***.

The electrophilicity is strongly influenced by the bridging group, ordered: PMDA >DSDA >BTDA >BPDA >ODPA for bridged dianhydride, and DSDPA >BTDA >BzDPA >DPEDPA >HQDPA for bridged bis-ether dianhydrides. However, the reaction rates of the diamines with a given dianhydride usually increase with rising ionization potential. Common isomeric dianiline may be referred in ***Appendix A-2***.As reported by Harris (1990), the structure of the diamines affects the reaction rate significantly more than changes in the dianhydride structure. More basic diamines, such as PPD and ODA, showed relatively higher reaction rates. The electron withdrawing nature of the bridge group also affected the acylation rate of diamines. Both the pKa and acylation rate of DABP were relatively low due to the electron withdrawing Carbonyl Bridge. Monomer reactivity is important in controlling equilibrium to favour the formation of PAAs. High molecular weight PAA is obtained when the electron affinity of the dianhydride and the basicity of the diamine are both high.

•Effect of solvent and temperature

Dine Hart and Wright (1967), Bower and Frost (1963) and Kaas (1981) report that high molecular weight PAA could be produced by using a higher concentration of monomer, and would perform at lower reaction temperatures. They also found that the viscosity of PAA rapidly decreased when stored in a solution after preparation, due to the sensitivity of amic acid toward hydrolysis. However, later work showed this phenomenon is actually associated with the reversibility of the propagation reaction (Tao *et al,* 2009). Although the rate constant is very small, a few reactions can have a dramatic effect on the molecular weight. This is because the solvent plays an important role in polyamic synthesis.

Common solvents utilized are dimethylformamide (DMF), dimethylacetamide (DMAc), N-methylpyrolidone (NMP), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), tetramethylurea (TMU), and dimethylpropaleneurea (DMPU). All of these solvents are polar aprotic solvents which have a lone pair of electrons and act as Lewis bases. The aprotic solvents do not solvate (stabilize) anions well, resulting in highly reactive anions attacking electrophiles. This is general reason to utilize a dipolar aprotic solvent, such as NMP and DMAc to increase the forward reaction of hydrogen bonding (Koton *et al,* 1974; Pravednikov *et al,* 1973). Otherwise, a less polar solvent such as

THF, having an ether linkage with the ability to form complex hydrogen bonding with the carboxyl groups is used. In these types of reactions, a substitution product is formed more slowly. However, it has been suggested that the free carboxyl proton also participates in catalyzing the forward reaction by causing protonation of the carbonyl group of the dianhydride (Kaas, 1981). It was found that the reaction rates of different solvents increased in as the following order: NMP> TMU>DMAc>DMSO>DMF>THF (Mittal, 2009).

Harris (1990) also reported that the monomer concentration affected the reaction equilibrium as well. Very dilute solutions have been found to decrease molecular weight. This is because the forward reaction is bimolecular and the reverse reaction unimolecular, increasing the concentration of monomers and favoring high molecular weights. It also important to note that the formation of PAA is exothermic and equilibrium is favored at lower temperatures (Harris, 1990). However, lowering the temperature further usually does not show any detectable effect on the reaction. Kaas (1981) has systematically tested the effect of equilibration temperatures on molecular weight. The author found Mw with increasing equilibration temperature. Since Mw was used as the basis for comparison, another factor must be taken into consideration: the dissolution of solid dianhydride in the reaction solution is slower at lower temperatures. This means that polymerization can occur at the solid-liquid interface more extensively at lower temperatures.

•Effect of side reaction and others

Several side reactions could occur in PAA synthesis, accompanying a main chain reaction, resulting in an undesired yield product and also will affect both the MWD and polydispersity index (PDI). To achieve high enough molecular weights, the side reactions need to be minimized. Harris (1990) reported that the propagation of the reverse reaction of PAA to yield the dianhydride and dianiline monomer cannot be completely eliminated due to the intermolecular acidolysis, which yields dianhydride as a result of the pendant carboxylic group at the ortho-position. In contrast, the acylation reaction of amine with benzoic dianhydride is irreversible. This does not prevent the formation of high molecular weight products, as the magnitude of the equilibrium constant is still high (Ghosh and Mittal, 1996b; Mittal, 1984b).

The competition between dianhydride and water during the propagation reaction often takes place, and results in dianhydride being removed from the equilibrium and upsetting the monomer stoichiometric (Harris, 1990). Water always represents an impurity in a monomer or solvent. Therefore, enhances its nucleophilicity, causing proton transfers and further reducing the hydrolytic stability of PAA. **Figure 2.4** represents the explanation for the hydrolytic stability of the PAA system.

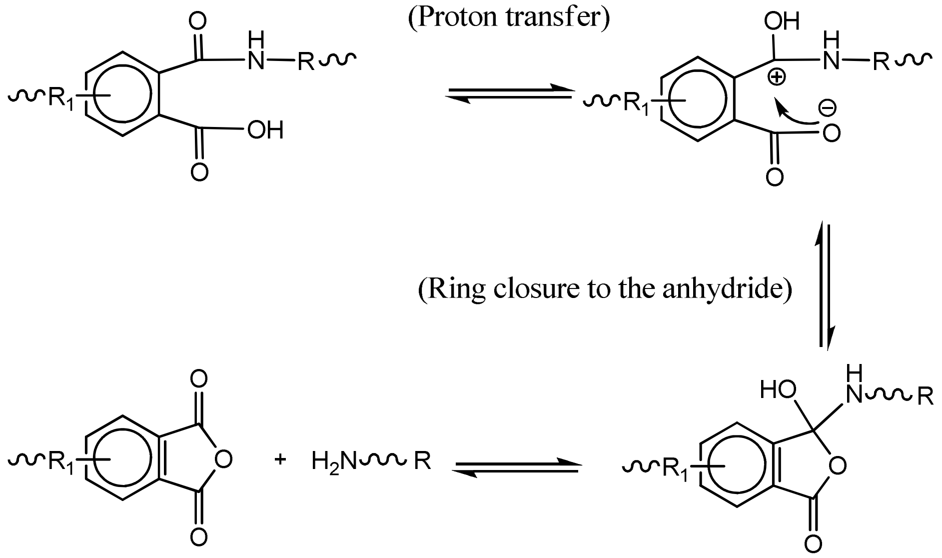


Figure 2.4 The formation of dianhydride and diamine results in backbone cleavage.

Other impurities, like mono-functional amines, possibly present in the amide solvent, can have a devastating effect on the main chain synthesis reaction (Harris, 1990). The competition between monomeric diamine and these mono-functional impurities can upset the monomer stoichiometry and lead to formation of unreactive chain ends during propagation reactions (**Figure 2.5**). Further propagation reactions will be terminated, resulting low molecular weight.

Propagation Reaction;

R = Substituent group of dianiline
R_1 = Substituent group of dianydride
R_3 = Substituent group of mono-funtional dianiline

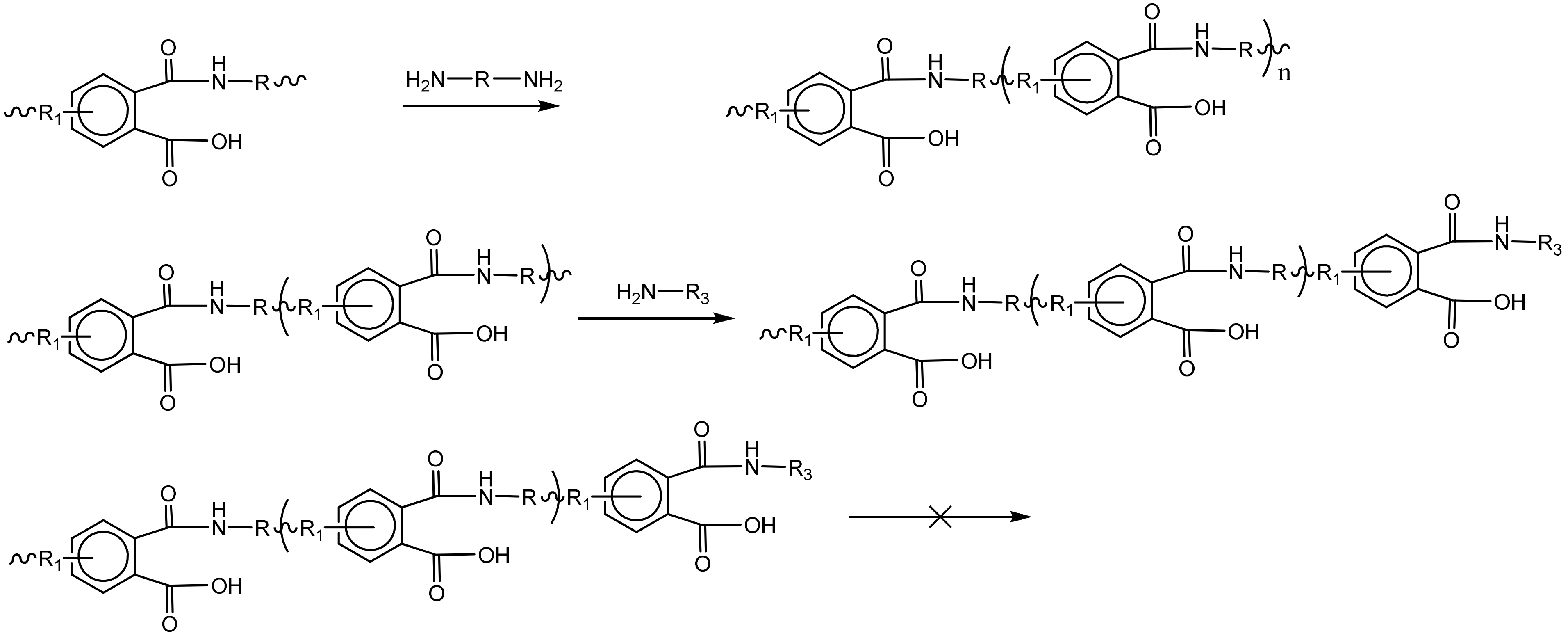


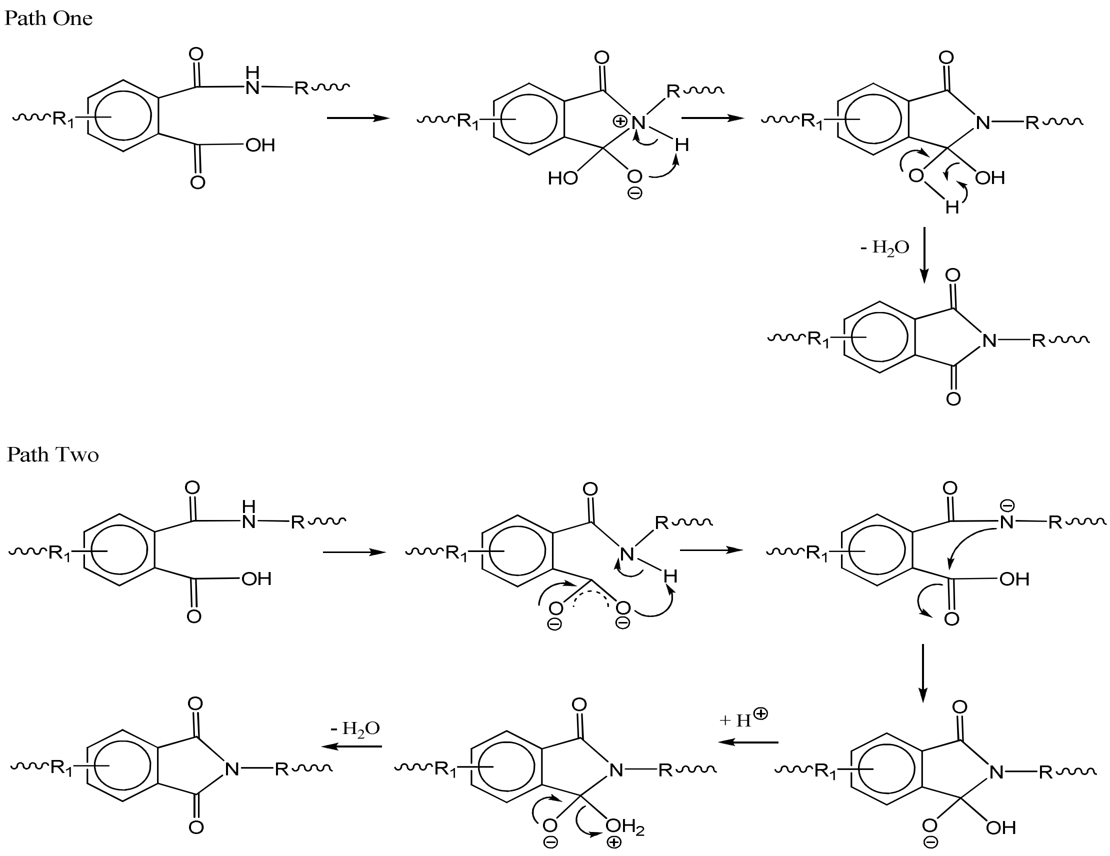
Figure 2.5 The formation of uncreative chain end

2.2.1.2 Cyclodehydration of PAA /Imidization

Cyclodehydration of PAA is the last stage of two-step method to form an imide ring by removing solvents and water by-products. The final product is usually insoluble and infusible depending on the processing type and method used. This step was accomplished by heating at elevated temperature through thermal imidization or by incorporating a chemical dehydrating agent through solution and chemical imidization.

Thermal imidization, also known as the bulk imidization method, is widely used in industry by heating PAA at elevated temperatures for a certain amount of time. The PAA solutions are cast onto a suitable substrate, followed by gradual heating to remove and the cyclodehydration reaction to form PI. The thermal imidization leads to a ring-closed structure with water as by-product. As suggested by Kreuz *et al* (1966), there are two possible pathways for thermal imidization as shown in **Figure 2.6**.

Regarding Johnston *et al* (1987), at the initial stage, a small amount of the PAA undergoes the reverse reaction to anhydride and amine instead of forming the imide ring, which contributes to a decrease in molecular weight. The irreversible cyclodehydration reaction at high temperature leads to a higher molecular weight. Baise (1986) has studied the effect of film thickness during curing and found a thin film (5 micron) is the easiest way to achieve a high degree of imidization (>99%, 230~250°C in 10 min). The solvent retained in the thin film facilitates imidization.


Path One

Path Two

Figure 2.6 Two possible pathways of thermal imidization

There are some disadvantages to implementing thermal imidization. It should be considered to maintain a high degree imidization. During the cyclodehydration, a rigid cyclic imide structure is formed and the Tg dramatically increases, rising above the reaction temperature (Ghosh and Mittal 1996b; Volksen and Cotts, 1984). This could result in the decrease of chain mobility, which could hinder the intra-molecular conformation from favouring the cyclodehydration reaction. Since entropy is decreased, conformation that is unfavourable to imide formation remains rigidly fixed and the rate of cyclization will decrease (Sroog, 1991). Also, residual solvent molecules, such as NMP, can hinder attainment of imidization-favouring conformations (in the glassy state), by forming intermolecular hydrogen bonds with the reactive groups. Hence, the final PI film contains residual uncyclized amic-acid structures, which are hydrolytically