# CORRELATING THE SYNTHESIS PROTOCOL AND PROPERTIES OF POLYIMIDE FILM FOR $CO_2$ REMOVAL

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# CORRELATING THE SYNTHESIS PROTOCOL AND PROPERTIES OF POLYIMIDE FILM FOR $CO_2$ REMOVAL

by

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Yiauw Diing Ye
June, 2018

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| Abbreviation | Description |
|---|---|
| BTDA | 3,3',4,4'-benzophenonetetracarboxylic dianhydride |
| 6FDA | 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride |
| ODPA | 4,4'-oxyphthalic dianhydride |
| DAM | 2,4,6-Trimethyl-m-phenylenediamine |
| 6FpDA | 4,4'-(Hexafluoroisopropylidene)dianiline |
| DABA | 3,5-Diaminobenzoic acid |
| ODA | 4,4 –oxydianiline |
| PAA | Poly(amic acid) |
| FFV | Free fractional volume |
| NMP | N-Methyl-2-pyrrolidone |
| $CO_2$ | Carbon dioxide |
| $H_2S$ | Hydrogen sulfide |

# MENGAITKAN PROTOKOL SINTESIS DENGAN SIFAT FILEM POLIIMIDE UNTUK PENYINGKIRAN $CO_2$

## ABSTRAK

Membran poliimide mempunyai pelbagai aplikasi, terutamanya dalam industri gas asli untuk menyingkirkan $CO_2$. Walaupun membran poliimide telah dikaji secara meluas dan digunakan dalam industri, pengaruh protokol sintesisnya terhadap sifat-sifat filem poliimide yang memihak kepada penyingkiran $CO_2$ masih lagi difahami secara mendalam. Oleh itu, poliimide-poliimide dengan kombinasi monomer yang berbeza telah disintesis melalui kedua-dua cara, iaitu imidisasi terma dan juga imidisasi kimia untuk mengetahui kesannya terhadap sifat-sifat filem poliimide yang berguna terhadap penyingkiran $CO_2$. Hasil uji kaji menunjukkan bahawa keberatan molekul poliimide yang disintesis tetap dipengaruhi oleh kaedah imidisasi, dimana keadaan sepanjang imidisasi memainkan peranan yang penting dalam pertumbuhan rantai poliimide. Kepadatan membrane turut dikawal oleh panjang rantai poliimide, selain faktor-faktor lain seperti struktur monomer dan interaksi antara molekul. Selain itu, jenis imidisasi juga mengawal susunan antara molekul yang merupakan faktor kritikal yang menentukan volum pecahan bebas membran (FFV). Ketertelapan dan juga selektiviti sangat bergantung kepada volum pecahan bebas yang membolehkan pelarasan antara selektiviti dan ketertelapan membran. Di samping itu, penghubung silang antara rantai poliimide melalui rawatan terma dalam relau bagas juga merupakan salah satu sifat dominan dalam menentukan volum pecahan bebas membran. Kesimpulannya, sifat polimide-polimide, pembentukan membran poliimide masing-masing yang menyumbang kepada prestasi pemisahan gas dapat dikawal serta ditambahbaik melalui protokol sintesis.

# CORRELATING THE SYNTHESIS PROTOCOL AND PROPERTIES OF POLYIMIDE FILM FOR $CO_2$ REMOVAL

## ABSTRACT

Polyimide membrane has a wide variety of applications, especially in natural gas industry for removing $CO_2$. Although polyimide membrane has been widely studied and used in the industry, the influence of its synthesis protocol on the properties of polyimide film that are in favor of $CO_2$ removal is still roughly understood. Hence, polyimides with different monomer combinations were synthesized via both thermal imidization and also chemical imidization in order to discover its impact on the properties of the polyimide film that were important for $CO_2$ removal. The results showed that the final polyimide molecular weight was affected by the imidization methods, which the conditions offered by each method played a major role in the growth of polyimide chain. The polyimide chain length then contributed to the membrane density, although it was also governed by other factors such as monomer structure and intermolecular interactions. Furthermore, the type of imidization also governed the intermolecular packing, which was found to be an critical factor that determined the membrane free fractional volume (FFV). The permeability and also selectivity were strongly dependent on FFV, which it served as the characteristic that allowed the tradeoff between the membrane selectivity and permeability. In addition, cross-linking the polyimide membrane via furnace treatment was also one of the dominant attributes in deciding the membrane FFV. It was concluded that properties of polyimides, their membrane formation, and hence gas separation performance were able to be controlled and improved by their synthesis protocol.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Membrane in gas separation

The discovery of the concept of membrane technology dated back as early as the eighteenth century by Abbé Jean-Antoine Nollet (Kołtuniewicz, 2006). The first synthetic membrane from nitrocellulosis was invented by Adolf Eugen Fick, a German physiologist, in 1865 (Fick, 1855). However, membrane technology is successfully applied in a wide variety of industries only in the 1960s (Prabhakar *et al.*, 2005). One of the membranes that is being developed and given tremendous focus on is polymeric membrane, which is well known for its high efficiency in gas mixtures separation. Polymeric membrane is often used in natural gas industry to remove acid gases such as $CO_2$ and $H_2S$. The amount of $CO_2$ in natural gas determines the quality of the gas, since higher $CO_2$ concentration in the gas results in a lower gas heating value. Hence, $CO_2$ content in natural gas is limited to 2-3% v/v as per suggested by the US pipeline specification (Foss and Head, 2004). Unlike conventional technologies such as cryogenic distillation that requires condensation, and amine absorption that requires solvent regeneration to constantly remove acid gases, membrane gas separation is a better alternative technology as it does not involve phase changes and consume less energy (Favvas *et al.*, 2017).

Membrane separation technology utilizes the dissimilarities of physical and chemical properties of each gas in gas mixture to achieve the targeted separation (Rufford *et al.*, 2012). For separation of gases, the membrane used is dense and non-porous, and the pore size of the membrane is at the level of gas molecular diameter, usually depicted in angstroms, Å (Wang *et al.*, 2007). The movement of gas across a membrane is facilitated by both solution and diffusion. This means that the rate of gas permeation depends on its solubility in the membrane material, as well as its diffusivity in the membrane structure (Baker, 2000). Therefore, it is suggested that the membrane structure and the type of its material strongly affects the permeability of gases, which makes these two factors as the core research considerations in membrane technology. The membrane structure is related to the synthesis method of the membrane itself, where it is determined by a few parameters that give the membrane its unique properties. Hence, depending on the synthesis method, the synthetic membrane can be applied in different fields with particular operational conditions.

## 1.2 Polyimide membrane

There are several types of polymeric membrane that are suitable for gas separation under high temperature and pressure, but polyimide membrane stands out among them due to its high mechanical strength and thermal tolerance. DuPont was the first to patent polyimide back in 1955 and commercialized its Kapton polyimide membrane around 1961, which showcased that aromatic polyimides of their great mechanical, electrical, and quite a few specific properties, besides of its good thermal stability (Yi *et al.*, 2017).

Despite its good mechanical and thermal stability, polyimide membranes struggles with the gas separation efficiency. It is simply not possible to improve gas selectivity without sacrificing membrane permeability. One of the solution is molecular design. Tong et al. (2015) reported that introducing bulky groups is able to enhance gas permeability . The membrane also exhibited fairly good $CO_2/N_2$ selectivity since the molecular cavity size is suitable for $CO_2$ separation.

The gas separation performance by polyimide membrane is closely related to its fractional free volume (FFV), other than mechanical and thermal properties. While mechanical and thermal properties may be important to characterize the aging and degradation of the polyimide membrane, thus affecting its performance, FFV is the main factor that determines the short term performance of the membrane, that is, the permeability and selectivity. The side chains, rigidity, and dipolar orientation of the monomers would have a great effect on FFV. The effect of some of the factors might not be in one way only, hence further investigation of FFV should be carried out carefully in order to design the desired, high performance polyimide membrane. Generally, monomers with bulky groups lead to a higher FFV, while straight and less-branched monomers will be more compact and have a lower FFV.

Polymeric compounds such as polyimides, can be synthesized by a two-step process. The first step is polycondensation of diamine and dianhydride to yield poly(amic acid), while it will be imidized to form polyimide in the next step. Diamine and dianhydrides are commonly used to produce poly(amic acid). With different conditions, the reaction will take place in different pathways. For example, as shown in Figure 1.1, when no catalyst is present,  reaction can be occurred via a seven-membered polycyclic intermediate, which then releases carbon dioxide to yield the final polyimide (Mehdipour-Ataei and Bahri-Laleh, 2008). However, the reaction temperature is relatively high as compared to those of  with the presence of catalyst reagent and aprotic solvents. Moreover, molecular weight of the produced polyimide were reported low, which is impractical to be used for membrane fabrication. .

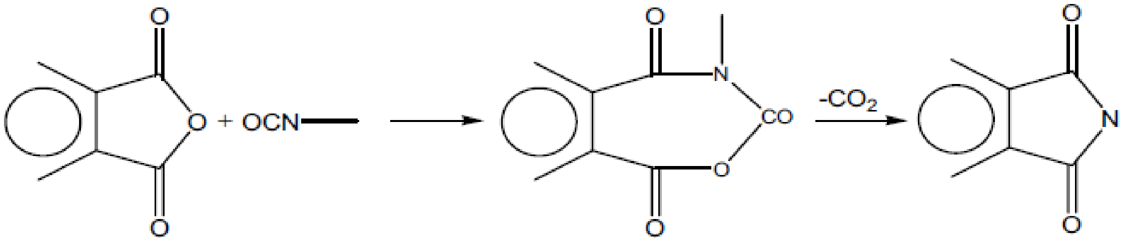


Figure 1.1: Mechanism of polyimide synthesis from dianhydrides and diisocyanates (Mehdipour-Ataei and Bahri-Laleh, 2008).

Polyimides can also be synthesized by polycondensation of diamines. For this case, diimides of tetracarboxylic acids are used and three reactions can be used to obtain the polyimide, namely: (i) Polycondensation of diimides with dihalides (Figure 1.2) (ii) Aminolysis of diimides by diamines (Figure 1.3) and (iii) Transimidization (Figure 1.4).

Polycondensation of diimides with dihalides involves the formation of polyimide by reacting an diimide with dihalide with elimination a mole of hydrogen halide. Whereas aminolysis of diimides by diamines involves a nucleophilic attack on the carbon of the imide group that opens up the diimide ring. Ammonia is then eliminated, closing the ring and forms the polyimide. Transimidation is similar to that of aminolysis, however, the reacting diimide is a tertiary diimide instead of secondary diimide, and the eliminated molecules are primary amines.

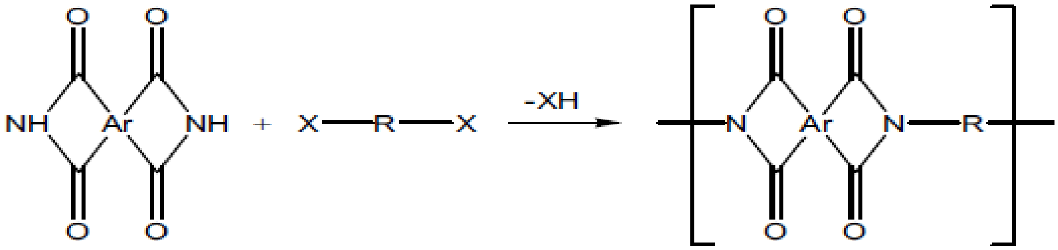


Figure 1.2: Polycondensation of diimides with halides (Mehdipour-Ataei and Bahri-Laleh, 2008).

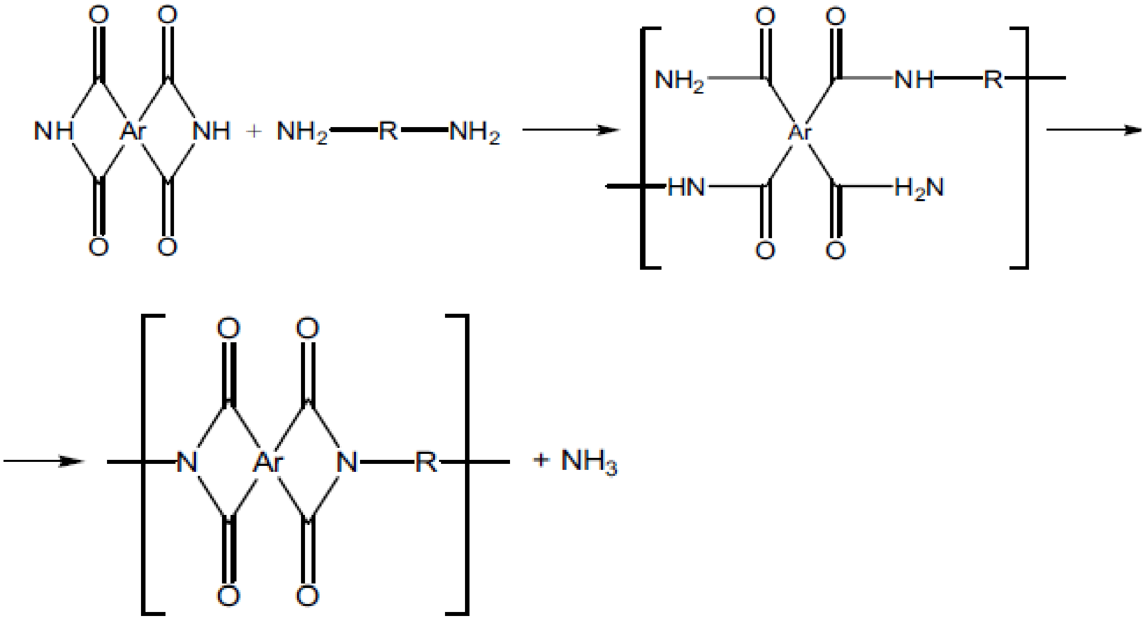


Figure 1.3: Aminolysis of diimides by diamines (Mehdipour-Ataei and Bahri-Laleh, 2008).

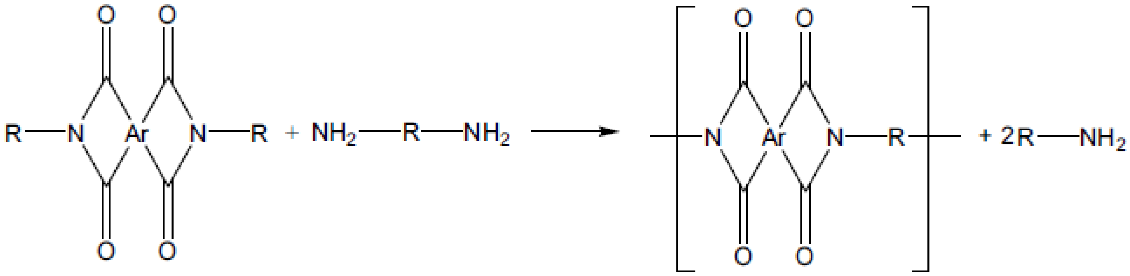


Figure 1.4: Transimidization (Mehdipour-Ataei and Bahri-Laleh, 2008).

High thermal stability of aromatic polyimide causes manufacturing issues, since it is very difficult to melt or dissolve as it has unsatisfying flow properties and insoluble in organic solvents. The unstable poly(amic acid) that would fail solution casting, water being released as by-product that causes hydrolysis, reverse reactions, and hence full imidization cannot be achieved. Numerous solutions that focused on modifying monomer structures by redesigning and creating new monomers have been proposed and applied to tackle the issues mentioned above (Vanherck *et al.*, 2013). The solutions are: (i) reducing chain stiffness by introducing aliphatic group or incorporating flexible linkages; (ii) integrating side groups that can retard crystallization and molecular arrangement. However, easing the process difficulties would require compromise from the physical and chemical properties of the polyimide itself. The easier the polyimide to be processed and modified, the more thermal stability, chemical stability, and mechanical strength would need to be sacrificed. Thus, it is important to handle the structural modifications of polyimides with proper degree in order to maintain certain properties required for particular service.

Apart from maintaining certain desired properties, there are also solutions to strengthen certain polyimide properties, in case these properties do not satisfy the service requirement. A common way to enhance thermal and mechanical properties of a polyimide membrane is by cross-linking. Polyimide membranes that have undergone cross-linking is stronger in terms of mechanical and chemical strength and have been applied in pervaporation, despite its initial development for gas separation to minimize the plasticization effect (Vanherck *et al.*, 2013). Since then, cross-linked polyimide membranes are capable to treat complete range of organic solvents in solvent resistant nanofiltration processes (Vanherck *et al.*, 2013). In fact, there are a variety of cross-linking methods, either physical or chemical, that can be used to obtain cross-linked polyimide membranes for different service requirements.

## 1.3 Problem Statement

In natural gas treatment plants and gas refineries, traces of heavy hydrocarbons in feed gas stream can cause the polymer membranes to be plasticized or become swollen, hence reducing the membrane selectivity. Thus, it is important to synthesize polyimide membranes with good thermal stability and chemical properties for commercialized use. Monomer design is an important factor to improve thermal stability of polyimide membranes. Hence, research is required to study the monomer design of polyimide by selecting dianhydride and diamine combinations with bulky group or numerous Fluoro group to improve the free fractional volume (FFV). However, polyimide membrane of some combinations might not able to form if all of them are synthesized under the same route. Thus, it is also required to study the synthesis routes, both chemical and thermal imidization, to determine the better route for polyimide membrane synthesis for each combination. Then, relate these two factors with gas separation performance such as $CO_2$ and $N_2$ removal in terms of selectivity and permeability.

## 1.4 Objectives

Polyimide polymer membranes that are tough in terms of thermal and mechanical stability, while retaining considerably good separation characteristics can be achieved by following aims such that:

1) To synthesize polyimide polymer with variety of diamine and dianhydride compounds for better polymer segmental mobility.
2) To investigate the effects of chemical and thermal imidization on physical and chemical properties of polyimide membrane.
3) To evaluate mixed gas separation properties of polyimide mixed matrix membrane in term of selectivity and permeability.

## 1.5 Scope of study

This work focused on polyimide membrane characterization by synthesizing the polyimide membrane using different combinations of dianhydride and diamine: (i) 6FDA-6FpDA:DABA The polyimide membrane preparation involved thermal and chemical imidization after obtaining poly(amic acid) by mixing dianhydride and diamine. Several physical and chemical properties of polyimide membrane were studied and investigated by utilizing a few laboratory devices; (i) Fourier transform infrared spectroscopy (FTIR) is performed on the synthesized films to evaluate the imidization degrees of the films by determining the functional groups in the polyimide films. (ii) Thermo gravimetric analysis (TGA) is performed by using the synthesized films to analyze the decomposition pattern. (iii) Differential scanning calorimetry (DSC) is utilized for thermal stability analysis. (iv)

Gel permeation chromatography (GPC) is used to measure the molecular weight distribution of the synthesized polyimide.

The polyimide membranes would ultimately be used for permeability and selectivity tests with $CO_2$ and $N_2$. The goal was to synthesize polyimide membrane successfully, then study and explain the polyimide membrane gas separation performance with the data gathered from the devices. Improvements may also be suggested based on the study and research.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Synthesis of poly(amic acid)

As mentioned in Chapter 1, polyimides can be prepared using the common synthetic pathway, which is a two-step process. The first step is the synthesis of poly(amic acid) intermediate that is soluble and able to be processed via polymerization, followed by the second step, which is the imidization of the pre-polymer to yield the final polyimide by releasing water. This approach is illustrated in Figure 2.1, which involves the reaction of a suitable diamine with a dianhydride, while using aprotic solvent. Examples of aprotic solvents are tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), or N-methylpyrrolidone (NMP). The reaction would normally occur even at ambient temperature, yielding a poly(amic acid). The poly(amic acid) then undergoes cyclisation either thermally or chemically to form the polyimide, which will be further elaborated in Section 2.2.

The formation of soluble poly(amic acid) from diamine and dianhydride is highly dependent on the symmetry of both the reacting diamine and dianhydride. The chemical nature of the dianhydride determines its ratio with the corresponding diamine (Volksen, 1994). On the other hand, the nature of the diamine determines the reaction itself. For example, aliphatic diamines that are highly basic in nature, are inappropriate for this reaction pathway since they have high tendency to form salt with the carboxyl group of the generated poly(amic acid) at initial stages of the reaction, given that diamine is in excess. Under the presence of the salt, the reaction of protonated amine groups with the anhydride is hindered, thus the stoichiometry of the initial monomer charge is altered. This leads to low molecular weight compound formation. Moreover, cross-links between the molecular chains may happen as a result of amide formation, such that the salt bond reacts to form an amide bond during the imidization of the precursor.

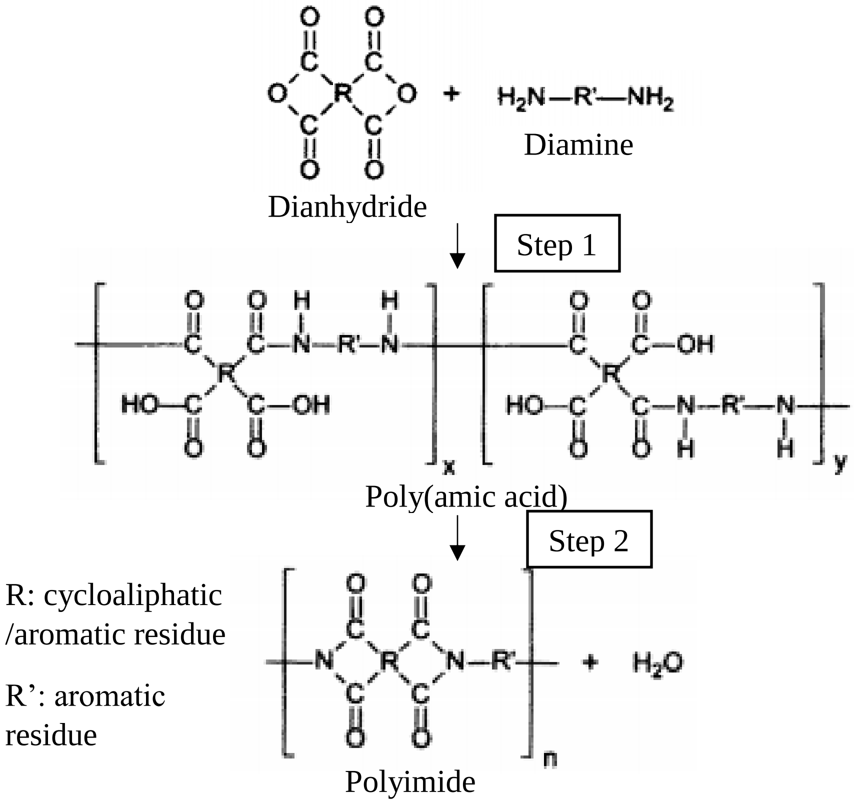


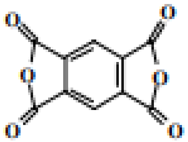
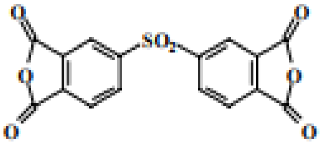
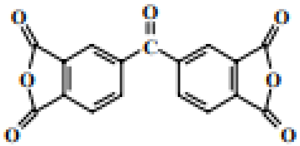
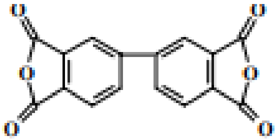
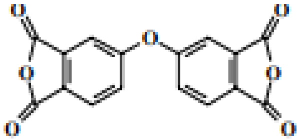
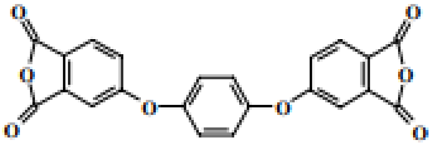
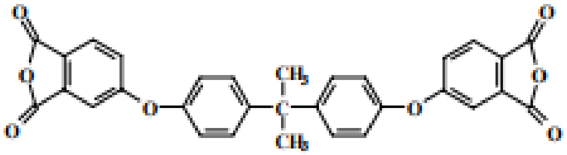
Figure 2.1 Synthesis of polyimide from poly(amic acid)

Water and moisture is a very big hindrance to poly(amic acid) formation due to hydrolysis. Therefore, the key for poly(amic acid) preparation to succeed is to utilize pure monomers and remove all the moisture. Other than that, poly(amic acid) formation is an exothermic reaction, so lower reaction temperature is preferred (Ratta, 1999). However, it was found that further lowering of the temperature below ambient temperature usually does not show any significant effect on the reaction. Besides, monomer concentration will also affect the reaction equilibrium. It was observed that the forward reaction is bimolecular, while the reverse reaction unimolecular. This indicates that high monomer concentration is favorable to form high molecular weight products (Ratta, 1999). The occurrence agrees with the study carried out by R. A. Dine-hart and W. W. Wright (1971) who suggested that low molecular weight products are formed with diluted monomer concentration due to competitive aminolysis and hydrolysis.

### 2.1.1 Monomer reactivity

As shown in Figure 2.1, it was indicated that the poly(amic acid) formation mechanism involves using a diamine for nucleophilic substitution reaction at the carbonyl carbon atom of the dianhydride. Therefore, the rate of reaction would depend on the nucleophilicity of the amino nitrogen atom of the diamine and also the electrophilicity of the carbonyl groups of the dianhydride. Electron affinity is normally used to measure the electrophilicity of the dianhydride. From Table 2.1, it was shown that PMDA that has the highest electron affinity, thus, the highest rate of reaction is anticipated when it is reacted with different diamines (Mehdipour-Ataei and Bahri-Laleh, 2008). It can also be inferred from Table 2.1 that bridging groups in dianhydrides would lower the electron affinity. Another observation is that the electron-withdrawing groups such as $SO_2$ and C=O increases the electron affinity, meanwhile electron donating groups such as ethers would result in a lower electron affinity. The difference in reactivity has several effects on the reaction equilibrium. Low electron affinity dianhydrides such as ether-containing dianhydrides are less likely to be affected by atmospheric moisture, whereas high affinity dianhydrides would require more stringent moisture control.

Table 2.1: Electron affinity of common dianhydrides (Ratta, 1999).

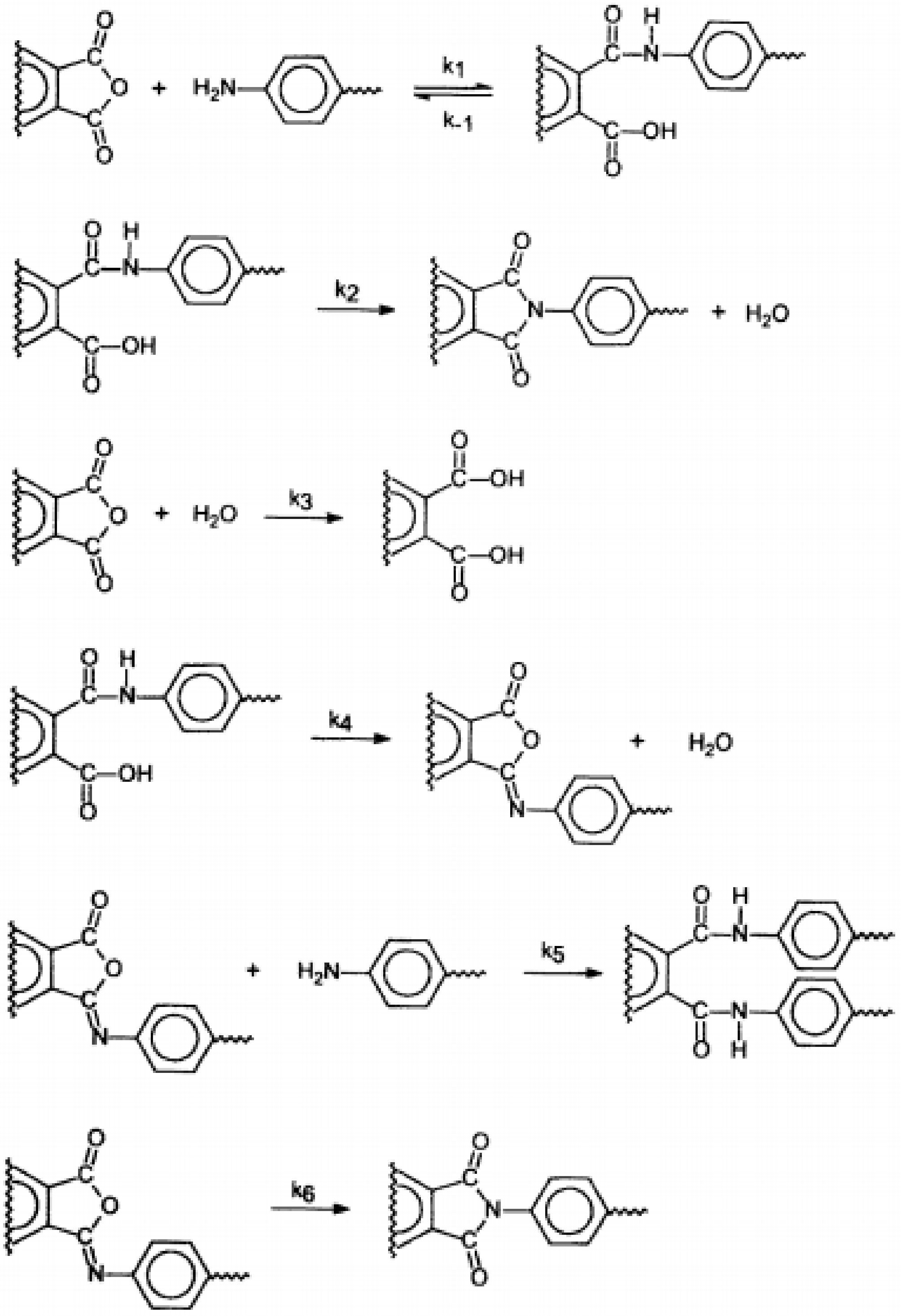
| **Dianhydride Structure** | **Name** | **Electron Affinity (eV)** |
|---|---|---|
|  | **PMDA** | **1.90** |
|  | **DSDA** | **1.57** |
|  | **BTDA** | **1.55** |
|  | **BPDA** | **1.38** |
|  | **ODPA** | **1.30** |
|  | **HQDA** | **1.19** |
|  | **BPADA** | **1.12** |

The relationship between the reactivity of the aromatic diamines with their nucleophilicity has not been reported. However, there were reports on higher reactivity achieved with increasing ionization potential of diamine (Ratta, 1999). Furthermore, reactivity also increases with diamine basicity, indicated by increasing rate constants with higher value of $pK_a$ (Wang *et al.*, 2007). Although diamine basicity promotes higher reactivity, however, it was not encouraged to use high basicity diamine due its tendency to form salt with carboxyl group of poly(amic acid). The ideal diamine basicity should be around a $pK_a$ value of 4.5-6 (Ratta, 1999).

### 2.1.2 Side reactions

Poly(amic acid) formation is actually a complex reaction that involves many side reactions, making it impossible to achieve complete conversion. As illustrated in Figure 2.2, besides the main reaction, there are five more potential reaction pathways that lead to the yield of undesired products. The situation is even more complicated when the propagation step involves an equilibrium between poly(amic acid) and starting dianhydride and diamine. Frost and Kesse (1964) were the first to discover the possibility of an equilibrium between propagation and depolymerization in 1964, which makes poly(amic acid) formation rather intricate.

In order to confirm which reaction is the main reaction pathway, rate constant data is extracted from several literature references, as shown in Table 2.2. According to Table 2.2, it was suggested that reaction (2.1) is the main reaction pathway. As shown, the hydrolysis of dianhydride by water (reaction 2.3) is five times slower than poly(amic acid) formation reaction (reaction 2.1) (Ratta, 1999). Although this rate difference may make the presence of water in the reaction seems insignificant during the initial phase of the polymerization, it should not be neglected as it might be detrimental during the later stages. Hydrolysis of dianhydride groups leads to the formation of diacid moieties that are inert and would not have any further reaction. Therefore, as the diamine concentration declines until a point where the competition with water for dianhydride becomes significant, the amount of poly(amic acid) formed will decrease significantly. In addition, it is also possible that dianhydride formed from the reverse reaction of poly(amic acid) undergoes hydrolysis and further reduces the yield of amic acid units.



(2.1)

(2.2)

(2.3)

(2.4)

(2.5)

(2.6)

Figure 2.2: Side reactions in poly(amic acid) formation (Ratta, 1999).

Table 2.2: Relative rate constants for reactions shown in Figure 2.2 (Ratta, 1999).

| **Reaction** | **Rate constant ($s^{-1}$)** |
|---|---|
| Propagation ($k_1$) | 0.1 – 0.5 |
| Depropagation ($k_{-1}$) | $10^{-5}$ – $10^{-6}$ |
| Spontaneous Imidization ($k_2$) | $10^{-8}$ – $10^{-9}$ |
| Hydrolysis ($k_3$) | $10^{-1}$ – $10^{-2}$ |
| Isoimide Formation ($k_4$) | - |
| Diamide Formation ($k_5$) | - |
| Isomerization ($k_6$) | - |

* Rate constants are estimated for a typical polymerization at ca. 10 wt% concentration, i.e. 0.5M

Concluding all the factors discussed above, measures have been taken during the poly(amic acid) synthesis to maximize the yield of poly(amic acid): (i) High concentrations of the monomers are used since it promotes the poly(amic acid) synthesis; (ii) Diamine is added first before dianhydride so that the dianhydride reacts faster with the diamine as compared with the existing moisture; (iii) Slight excess of dianhydride is applied to obtain higher molecular weights (Ratta, 1999).

## 2.2 Imidization of poly(amic acid)

Following the formation of poly(amic acid) is imidization to form polyimide. The second step is also known as the cyclodehydration of the poly(amic acid) to yield polyimide, as illustrated in Figure 2.3. Cyclodehydration reaction can be carried out via thermal or chemical imidization process (Feng and Iroh, 2013).

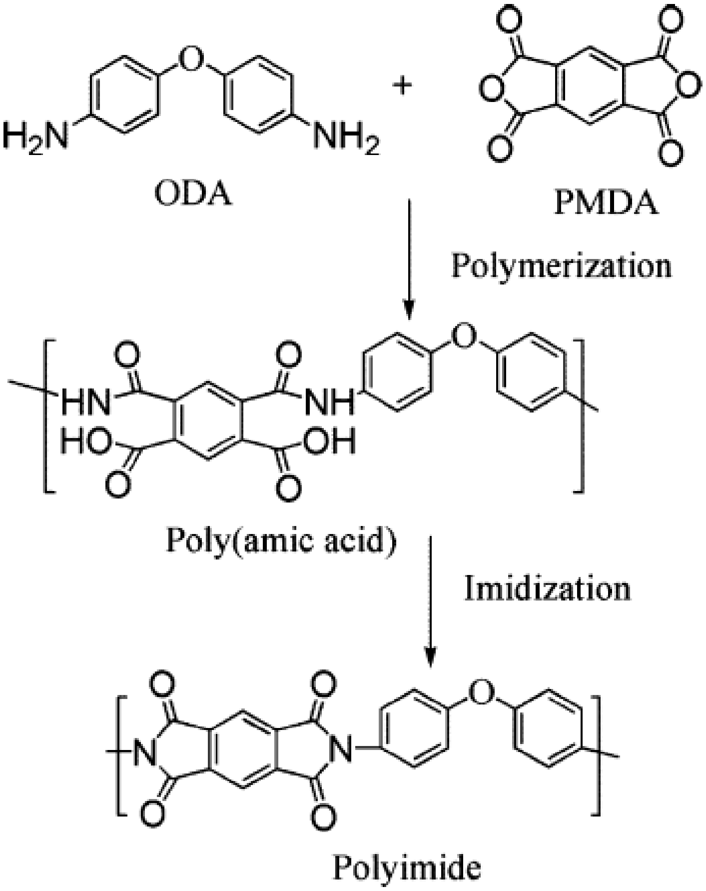


Figure 2.3: Illustration of formation of poly(amic acid) and polyimide (Kapton$^{TM}$) (Liaw *et al.*, 2012).

### 2.2.1 Thermal imidization

Commercially, straight thermal imidization of poly(amic acids) is the most practical approach for imidization, since thermal processes are most cost-effective, time saving, and allows high precision control from the perspective of industries. Thermal imidization is performed with a stepwise heating process. Imidization level of the poly(amic acid) during thermal imidization can be estimated from observing the cure profile from ambient temperature to 350°C. The volatiles evolved can be tested using mass spectrometry, as an example display in Figure 2.4. As shown, NMP solvent and water are evolved from ambient temperature to approximately 150 °C and from 150 °C to 250 °C, respectively (Ratta, 1999). The final imidization was completed when temperature approaching 250°C or above, where the solvent is completely removed.

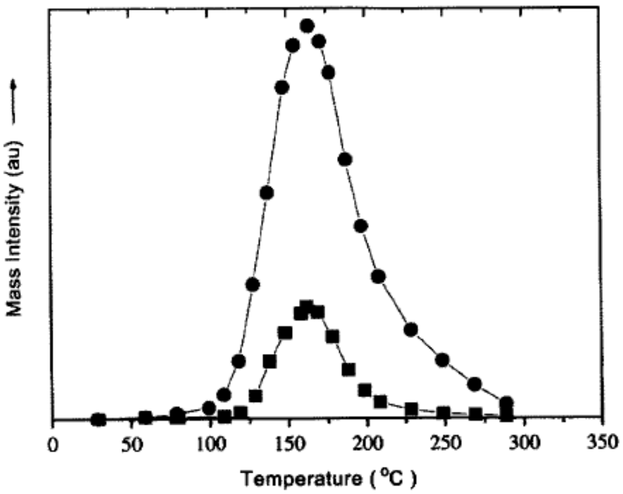


Figure 2.4: Evolution of volatiles during thermal cure of PMDA/ODA poly(amic acid). (●) Mass-18 water and (■) mass 99-NMP. Sample was pre-dried at 90°C for 1 hour (Ratta, 1999).

Temperature regime between 150 °C and 250 °C is the most crucial part in thermal imidization. In this region, remarkable shrinkage was observed and the polymer film suffers from maximum stress due to simultaneous occurrence of evolution of solvent and maximum imidization. This is the point where polymer film may have cracking problems, if the partially cured polyimide has a weak inherent mechanical strength. The apparent molecular weight of the polymer associates with the cracking problem as well (Volksen, 1994). At the end of that heating step, the mobility of the initial poly(amic acid) will be limited and the system vitrifies, since solvent is completely evaporated and imidization is mostly done. The glass transition temperature is pushed to its maximum value by further imidization. This in turn causes the final polyimide unable to regain sufficient mobility to enable recombination reactions without significant thermal degradation. Hence, it is a common practice to slowly heat the poly(amic acid) mixture to just below 150 °C to drive off the bulk solvent while preventing cracking issues. Then, rapidly ramp the temperature through the critical region to above 250°C.

Since thermal imidization evolves all the solvent and water, it is actually a very useful process for attaining a final product that is going to be used as a film or a coat on resins. Another literature suggested slightly different thermal cycle for thermal imidization. According to Takekoshi (1996), poly(amic acid) solution is cast on a support by solution casting. Next, the poly(amic acid) mixture is heated in a thermal cycle, such that heating from ambient temperature to 100°C and hold for 1 h, then raise the mixture temperature from 100°C to 200°C and hold it for another 1 h. Lastly, the mixture temperature is raised again from 200°C to 300°C and hold for further 1 h, followed by slow cooling to ambient temperature (Mehdipour-Ataei and Bahri-Laleh, 2008).

Kai Zhang et. al (2017) reported that synthesizing polyimide using different diamine ratios (ODA:DABA) through thermal imidization would lead to final polyimide membrane density changes. As the diamine ratio decreases, the density of polyimide membrane increases as DABA promotes the inter-molecular hydrogen bonding interaction . The PAA was synthesized by mechanical stirring at 25 °C, while the thermal imidization process was carried out in a vacuum oven with progressive heating of 100 °C for 1 hour, 200 °C for 1 hour, 300 °C for 1 hour, and then cooled down to room temperature. The vacuum condition is necessary to prevent oxidation during the final polyimide membrane formation. FTIR and TGA were used to study the chemical structure and thermal properties respectively.

It is worth noting that the thermal properties of polyimides synthesized from thermal imidization, such as glass transition temperature and thermal degrading temperatures, are at a higher level if they are compared with those of polyimides synthesized from chemical imidization. The dissimilarities can be explained with molecular structure orientation, for example, the molecular aggregation of the polymer chain segments that increases during thermal imidization (Ratta, 1999).

#### 2.2.1 (a) Changes in molecular weight

During thermal imidization, there is a temperature range that involves the maximum evolution of water and the solvent carrying the reacting diamine and dianhydride. In this case, the equilibrium of the polymerization reaction will be shifted in favor for hydrolysis and also depropagation. Thus, increased concomitant molecular weight breakdown is expected. This phenomenon has been observed for both soluble polyimides and for insoluble systems (Mehdipour-Ataei and Bahri-Laleh, 2008). Mass spectrometry was applied to monitor the appearance and disappearance of dianhydride groups as a function of temperature. However, when further heating is applied and water is removed, the polymer would recombine to yield the expected molecular weight. Such behavior also applies to insoluble polyimide systems, that is, a decrease in average molecular weight, followed by an increase in average molecular weight upon further imidization.

#### 2.2.1 (b) Changes in mechanical properties

As suggested by Volksen (1994), mechanical properties of a polyimide membrane is related to its average molecular weight. Based on Figure 2.5, the elongation of PMDA/ODA based polyimides increases rapidly from average molecular weights of approximately 8000 and approaches a steady value of about 12000. Do bear in mind that these molecular weight values are for the initial poly(amic acid) and they might vary to the values of the final polyimide. The higher molecular weight of initial poly(amic acids), the better their mechanical properties in terms of elongation and tensile strength. Naturally, thermal imidization of higher molecular weight poly(amic acids) would result in higher molecular weight ranges of the final polyimide. Therefore, to ensure good mechanical properties of polyimide membrane can be attained, the initial poly(amic acid) must have a molecular weight of more than 10000 (Volksen, 1994).

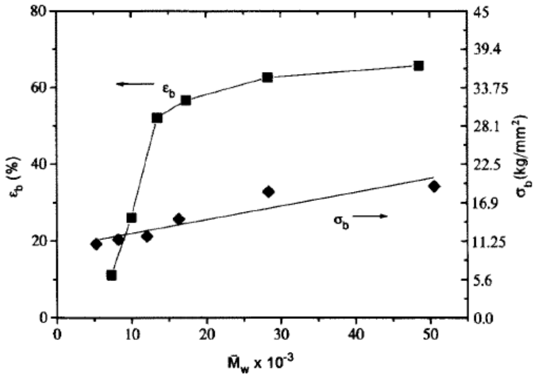


Figure 2.5: Polyimide mechanical properties as a function of the average molecular weight of initial poly(amic acid) (Volksen, 1994).

### 2.2.2 Chemical imidization

The reagent most widely used for chemical imidization of poly(amic acids) is a mixture of pyridine/acetic anhydride. The process can be carried out at ambient temperature or elevated temperatures. Increasing the temperature from 20 °C to 100°C cuts down the reaction time from 15h to 2h to achieve complete imidization (Ratta, 1999). However, Mehdipour-Ataei and Bahri-Laleh (2008) states that it might take a period of 24h to 48h for total imidization at room temperature. To distinguish with thermal imidization, chemical imidization is always performed in solution, in which the final polyimide forms a precipitate that can be collected easily. Besides, the precipitate is conveniently soluble. Unlike thermal imidization, chemical imidization results in significant amounts of isoimide linkages other than imide linkages. However, this issue can be solved if triethylamine was used instead of pyridine. Using trimethylamine also provides remarkably faster rate of reaction (Ratta, 1999). Based on Figure 2.6, it was observed that amic acid linkages will react with acetic anhydride to form a mixed anhydride. The reaction is promoted by the presence of bases, such as pyridine or triethylamine. Tautomerization of the mixed dianhydride intermediate can occur and changes from amide to iminol form. The amide tautomer cyclizes to form the imide (pathway A) as the thermodynamically favored product. Meanwhile, the iminol tautomer follows pathway B and yields the kinetically favored isoimide. Isomerization of isoimide to the more stable imide form via pathway C is also possible by introducing heat. However, isomerization occurs via the back reaction in this case. This back reaction is apparently initiated by nucleophilic attack of acetate ion on the isoimide (Vanherck *et al.,* 2013). Such behavior would be more common with stronger amines like triethylamine, since it promotes acetate formation and therefore drives the back reaction resulting in exclusive imide formation.

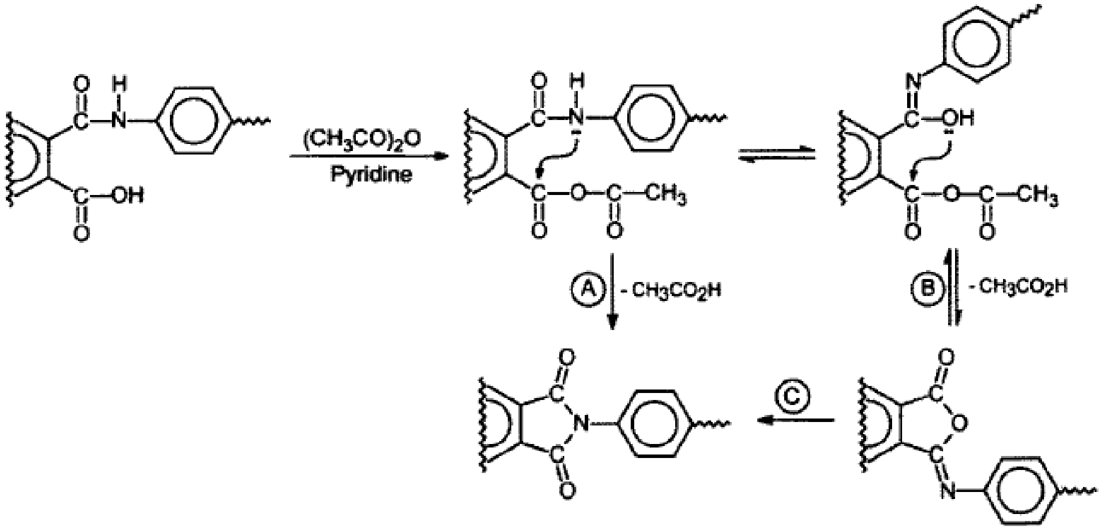


Figure 2.6: Reaction scheme of chemical imidization (Vanherck *et al.*, 2013).

A work by Mao et al. (2017) suggested that chemical imidization is a suitable polyimide synthesis route for PAA precursor comprised of ODA and PMDA. Acetic anhydride and trimethylamine with a ratio of 4:1 was used for the reaction. TGA was used