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SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE PARTICLES

MissPhetcharat Rabingkao

A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE PARTICLES
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Field of study	Chemical Engineering
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เพชรรัตน์ ระบิงเกา : การสังเคราะห์และวิเคราะห์คุณลักษณะของอนุภาคพอลิอิไมด์
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อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. มล. ศุภกนก ทองใหญ่, 78 หน้า

การสังเคราะห์อนุภาคของพอลิอิไมด์โดยใช้วิธีคอลลอด์ยเกิดได้โดย การใช้สารละลายที่สามารถละลายสารตั้งต้นได้ดี กับสารละลายที่ไม่ทำให้เกิดการละลายตัวของสารตั้งต้น สำหรับสารตั้งต้นเป็นการทำปฏิกิริยาระหว่าง ไดแอนไฮดราย, 4,4′-(ออกซิไดแอนิลีน) และสารละลาย เอ็น-เมทิล-2-ไพโรลิโดน นำสารตั้งต้นที่ได้ทำการหยดลงในสารละลายผสมที่มีสารลดแรงตึงผิวผสมด้วยซึ่งไม่ทำให้เกิดการละลายตัวของสารตั้งต้น แล้วทำการกวนผสมและใช้เครื่องอัลตราโซนิคเพื่อทำเกิดการกระจายการแตกตัวของอนุภาคให้เล็กลง จากนั้นสารตั้งต้นพอลิเอมิคเอซิดเปลี่ยนเป็นพอลิอิไมด์โดยใช้วิธีการปิดวงของอิไมด์โดยการหยดสารเคมีลงไปในสารละลายผสม หลังจากการปิดวงอิไมด์ด้วยสารเคมีแล้ว นำอนุภาคพอลิอิไมด์ที่ได้ไปแยกส่วนออกจากสารละลายโดยการเซ็นตริฟิวค์ และนำผงของอนุภาคออกมาโดยใช้วิธีการทำให้แห้งภายใต้สุญญากาศ ทำให้ได้อนุภาคของพอลิอิไมด์ออกมา สำหรับงานวิจัยนี้ได้ทำการศึกษาชนิดของสารละลายที่ไม่ทำปฏิกิริยากับสารตั้งต้น, ชนิดของสารลดแรงตึงผิว, ชนิดของสารตั้งต้น และ เครื่องปฏิกรณ์กับใบพัดในการทำปฏิกิรยา สภาวะที่ดีที่สุดในการทำให้อนุภาคของพอลิอิไมด์มีขนาดเล็กที่สุด คือปฏิกิริยาที่ใช้เฮกเซนเป็นสารละลายที่ไม่ทำละลายสารตั้งต้น, สารลดแรงตึ้งผิวที่ใช้คือ อะคริดิกเอ-1381 และสารตั้งตั้นคือ 4,4′- (เฮกซะฟลูออโรไอโซโพรพิลิดีน)ไดฟาธาลิค แอนไฮดราย โดยการทำปฏิกิริยาที่อุณหภูมิห้องและการหยดสารเพื่อที่จะทำให้เกิดการปิดวงของอิไมด์ เครื่องปฏิกรณ์และใบพัดควรจะใช้แบบที่ทำให้เกิดแรงเฉือนมากที่สุด ทำให้ผลของขนาดอนุภาคของพอลิอิไมด์มีขนาดเล็กที่สุดประมาณ 1 ถึง 10 ไมโครเมตร สำหรับการวิเคราะห์หมู่ฟังก์ชันของพอลิอิไมด์ จะเกิดขึ้นที่ความยาวคลื่นประมาณ 1750, 1380 และ 1370 เซนติเมตร$^{-1}$ สอดคล้องกับผลของหมู่ฟังก์ชันของพอลิอิไมด์ ผลการวิเคราะห์คุณสมบัติทางความร้อนแสดงถึงค่าการเสื่อมสภาพทางความร้อนของพอลิอิไมด์ เกิดการเสื่อมสภาพที่อุณหภูมิประมาณ 450-600 องศาเซลเซียส ผลการทดลองที่ได้แสดงให้เห็นถึงความสามารถนำวัสดุอนุภาคของพอลิไมด์ที่ได้ไปประยุกต์ใช้ในอุตสาหกรรมอิเล็คโทรนิคได้อย่างมีประสิทธิภาพต่อไป

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก
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PHETCHARAT RABINGKAO: SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE PARTICLES.
ADVISOR: ASSOC. PROF. ML. SUPAKANOK THONGYAI, Ph.D., 78 pp.

The PI particles were synthesis by colloid method, which use good solvent and poor solvent. The polyimide precursor was prepared from reaction between dianhydride, 4,4΄- oxydianiline (ODA) in NMP (good solvent), which obtain Polyamic acid (PAA) precursor solution. The PAA was injected to poor solvent of hexane and suitable amount of surfactants to mix with rigorous agitation and/or sonication to break the droplet of PAA. Then, PAA colloids were obtained and the colloid was further changed to PI particle by the in-situ chemical imidization of PAA colloids in the solution. The PI particle was separated from solution by centrifuge and dried under vacuum. In this study, various types of poor solvents, various types of surfactant and reactor and propeller blade in the reaction were investigated to verify the suitable conditions for the reactions. The best condition that produced the smallest size particulate polyimide, that have the average diameters of 1 to 10 μm, are by using hexane as poor solvent and use Acrydic A-1381 as surfactant with 6-FDA as the dianhydride. The reaction can be run at room temperature, insensitive to the time delay of imidization and improve by the reactor and the propeller blade. The temperature did not change particles site and thermal propertied of PI. The synthesized functionalized PI particle features at wave number near 1750, 1380 and 1370 cm^{-1} were also observed in the FT-IR spectra correspond with imide characteristics. Their thermal properties are the degradation of polyimide particles which appeared above 450-600 ^{o}C. These results indicated the success preparation method of polyimide particle materials that have potential applications for electrical appliances.

Department : Chemical Engineering Student's Signature : ....
Field of Study : Chemical Engineering Advisor's Signature : ....

Academic Year 2009

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Finally, I would like to dedicate this thesis to my parents and my families, who generous supported and encouraged me through the year spent on this study.

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CHAPTER I

INTRODUCTION

Polyimides are prominent among the polymers employed in high-temperature applications due to their outstanding thermal and thermo-oxidative stability, excellent mechanical properties, and ease of fabrication. In view of the increasing applications for these materials, the number of commercially available polyimide precursors has grown substantially in the past. At the same time, high demands of the aerospace and aircraft industries for advance composite matrix resins for using at temperature as high as 371°C (700°F) are suitable for polyimides. These applications, which approach the limits of stability for most polymers, are intensified, addressed using polyimides[1]. In order to enhance certain mechanical and physical properties of polyimides, nanoparticles (inorganic, organically modified, carbon nanotubes) have been incorporated [2-5]. Nanocomposite films derived from 3,3’,4,4’-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4’ Oxydiamine (ODA) polyimide with organoclay (1.8% by weight) exhibited an increased in tensile modulus, similar strengths and lower elongations at break as compared to control films [2]. The coefficient of thermal expansion of various polyimide/organoclay nanocomposite films was 23% lower than that of a similar film not containing organoclay [3]. Multi-walled carbon nanotubes dispersed throughout a thermosetting asymmetric BPDA-ODA polyimide act as macroscopic crosslinks. This type of polyimide nanocomposite exhibits excellent mechanical properties and processability with a glass transition temperature above 300 °C [5].

Polyimide (PI) is one of the most promising high-performance polymeric materials possessing highly thermal stability, good mechanical properties, easy processability, and low dielectric constants (k=2.32)[6]. Therefore, PI is widely employed in the fields of microelectronics applications such as substrate of flexible printed circuitry boards, insulating layers in multilevel very-large-scale integrated (VLSI) circuits and buffer coating in electronic package. Most of the studies on PI have been focused on films, adhesive, and varnish. PI seems to exhibit good physicochemical properties in particle foams, which could be used as the coating materials of insulating parts, low dielectric filler, and spacer for liquid crystal devices. For the PI nanoparticles ranging from several tens to ca. 500 nm in size have been successfully fabricated through the “two-step imidization” i.e., chemical imidization followed by thermal imidization of poly(amic acid) (PAA) precursor nanoparticles prepared by the reprecipitation method [7]. Preparation of porous films electrophoretic-deposited by PI nanoparticles is possible. The films morphology can be controlled by changing electrical potential and dispersion concentration of PI nanoparticles. Dielectric properties films obtained are in the low reasonable ranges [6].

Employing a second polymer as the porogen to prepare porous PI nanoparticles through the reprecipitation method is applicable. Then, investigating how the porogen species and the reprecipitation conditions affected the porous structures of the resulting PI nanoparticles can be considered. The formation process of the superficial nanopores may expect to happen [8]. Fluorinated nanoparticles and nanosheets of an aromatic polyimide can be synthesized via a very simple monomer adsorption/polycondensation reaction inside the pore systems of some different mesoporous silica monoliths. The resulting nanoparticles were found as about perfect replications for both silicas under consideration. A mesoporous silica with spherical pores with a diameter of 13 nm and another with a lamellar pore morphology with an approximately 2 nm thickness can be replicated [9].

As the nanosheet structures seemed to be cohesive and quite extended, it is promising to extend the present work to the replication of three-dimensional nanostructures, e.g., membranes or separation gels by nanocoating[10], for the controlled design of high-performance membranes and filters with structural features upon the nanoscale.

In the exploration of a surfactant technology to prepare size tunable polyimide nanoparticles, there will first establish conditions ensuring the stability of polyimide nanoparticles in a nonsolvent-dominated solvent/nonsolvent mixture. A stabilization mechanism will be put forward to interpret this phenomenon. Finally, three methods (including one ultrasound integrated method) will be examined to identify their effectiveness in tuning nanoparticle sizes [11].

1.1 The Objectives of This Thesis

1.1.1 To synthesize polyimide particles using colloid method.

1.1.2 To investigate the effects of the ratio of surfactant to the amount of diamine on polyimide for improving mechanical, and thermal properties of the polyimide particles.

1.1.3 To apply polyimide particle in electronic industry.

1.2 The Scope of This Thesis

1.2.1 Formulate colloid of polyamic acid.

1.2.2 Chemical imidized colloid of polyamic acid.

1.2.3 Synthesize and characterize polyimide particle.

1.2.4 Develop and formulate the high thermal and smallest particles size of polyimide particle.

1.2.5 Apply polyimide particles in electronic field.

This thesis is divided into six chapters as follows:

Chapter I provide an overview of the polyimide and objective and scope of this thesis.

Chapter II explains the basic theory about this work such as polyimide definition, type of polyimide polymerization, colloid method and chemical imidization.

Chapter III presents literature reviews of the previous works related to this research.

Chapter IV shows the experimental equipments and experimental procedures to prepare poly(amic acid) precursor and polyimide polymerization. Including, instruments and techniques used for characterizing the resulting polymers.

Chapter V exhibits the experimental results on polyimide nanoparticle synthesized by colloid method, and effects of various surfactants, solvents, ingredients and condition of synthesis on the properties of the synthesized polyimide nanoparticles will be explained.

Chapter VI, the last chapter, shows overall conclusions of this research and recommendations for future research.

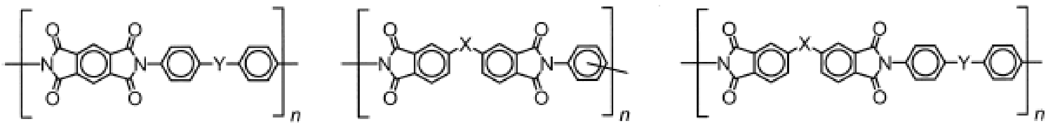
CHAPTER II

THEORIES

The basic theories about this work were mentioned here such as polyimide (PI) definition, type of fluorinated polyimide, type of method polyimide polymerization, and branched system.

2.1 Polyimide

From the early 1970s to the late 1980s, polyimides were already used as interlayer and intermetal dielectric materials (ILD/IMD) [12] .



1 2 3

Figure 2.1 General structures of aromatic polyimides

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 temperatures and processability, the poor solubility of wholly aromatic polyimides and cost, etc. Recently, polyimides based on isomeric dianhydrides or diamines have attracted increasing attention, because of characteristic properties that are of special value, both in the study of relationships between structure and properties and in applications. Their general structure is shown in Figure 2.1. Variation of the bridging groups X and Y in structures 1, 2, and 3 within the diamine and the dianhydride moieties allows the adjustment of the properties in a wide range. Many polyimides are insoluble, especially those without bulky groups X or Y. Only very few polyimides can be processed from the melt. The others must be processed via a precursor, which is the poly(amic acid) in most cases. This precursor is soluble in dipolar aprotic solvents and can be cast into films or spun into fibers.

Soluble polyimides can be prepared in the same way as insoluble ones, that is using the same approach via poly(amic acid) and thermal curing. However, they can also be imidized in solution. In this case, the poly(amic acid) is formed as usual in a dipolar aprotic solvent, and the ring closure is then achieved either thermally with or without a catalyst, or chemically. Thermal cyclization in solution usually involves the removal of the water formed by imidization as an azeotrope with an aromatic cosolvent (typically toluene or chlorobenzene). Cyclization can be accelerated by use of a base (e.g. sodium acetate or pyridine). Chemical cyclization is achieved by reaction of the poly(amic acid) with acetic anhydride to for dehydration and sodium acetate or pyridine as a catalyst. Imidization kinetics of the various procedures has been studied in details. Instead of the poly(amic acid), poly(amic esters) can be used as precursors, allowing a wider range of solvents and adjustment of the properties of the prepolymer. Chemical imidization often proceeds at least in part via the isoimide. Controlled preparation of the poly(isoimide) allows the use of this polymer class as precursor, since poly(isoimide)s even of rigid rod-like polyimides are often soluble. The isoimide linkage introduces kinks and bends into the polymer backbone. Conversion of the kinetically favored isoimide into the thermodynamically more stable imide is achieved thermally or catalytically with bases. Since it involves no water formation, this type of curing may be advantageous for polyimides, which are sensitive to moisture absorption.

An imide is a group of bonds as a molecule that has a general structure can be shown in Figure 2.2.

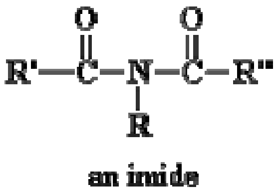


Figure 2.2 A structure of imide

So if the molecule shown above were to be polymerized, the product would be a polyimide. Polyimides usually take one of two forms. The first of these is a linear structure where the atoms of the imide group are part of a linear chain. The second of these structures is a heterocyclic structure where the imide group is part of a cyclic unit in the polymer chain has shown in Figure 2.3.

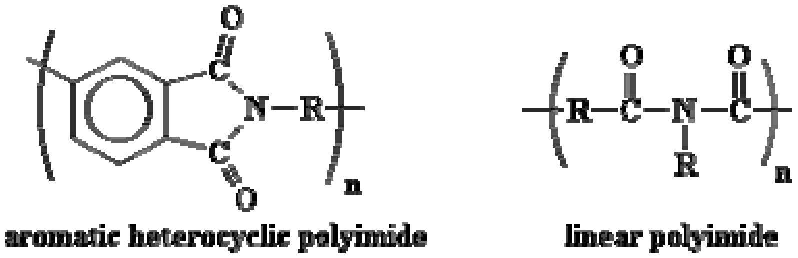


Figure 2.3 Two types of polyimides

A polymer which contains a charge transfer complex consists of two different types of monomers, a donor and an acceptor. The donor is like a rich man with more money than he knows what to do with. It has plenty of electrons to go around because of its nitrogen groups. The acceptor, then, is like a mooching houseguest. Its carbonyl groups of adjacent to imide bond will suck away its electron density. The donor doesn't mind supporting from the acceptor. In fact, with the acceptor around, the donor looks better. So the donor lends some of its electrons to the acceptor, holding them tightly together.

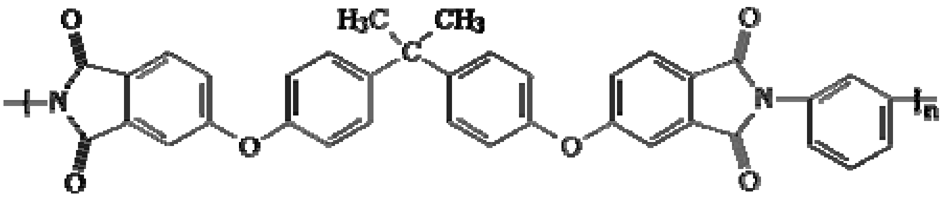


Figure 2.4 A structure of polyimides

Aromatic heterocyclic Polyimides, like the one on the left, are typical of most commercial polyimides, such as Ultem from G.E. and Dupont’s Kapton. The aromatic polyimides are therefor the polyimide that worth to spend most of our time on. At that time, the driving factor was cost rather than low dielectric constant. The structures were larger than 1 mm, and the dielectric constant of the insulating material between the metal lines was not yet an issue. However, the compatibility of polyimides with semiconductor manufacturing processes and the reliability of the resulting devices had been proven. Thus, when polymers were evaluated again for use as dielectrics, this time with the focus on low dielectric constant, polyimides seemed like the natural choice.

2.2 Structures of dianhydride

2.2.1 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA)

- Molecular Formula $C_{16}H_6O_6$
- Molecular Weight 294.22

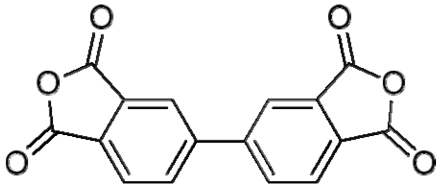


Figure 2.5 Structures of BPDA

2.2.2 Pyromellitic dianhydride (PMDA)

- Molecular Formula $C_{10}H_2O_6$
- Molecular Weight 218.12

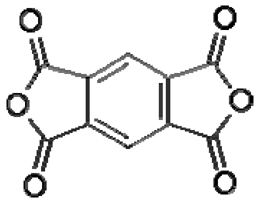


Figure 2.6 Structures of PMDA

2.2.3 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6-FDA)

- Molecular Formula $C_{19}H_6F_6O_6$
- Molecular Weight 444.24

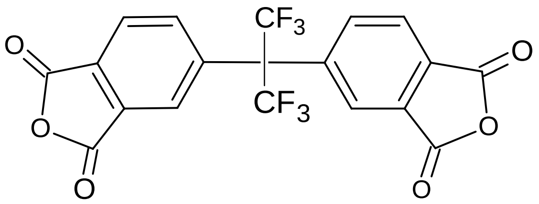


Figure 2.7 Structures of 6-FDA

2.3 Structures of diamine

2.3.1 3,4′- Oxydianiline (3,4′-ODA)

- Molecular Formula $O(C_6H_4NH_2)_2$
- Molecular Weight 200.24

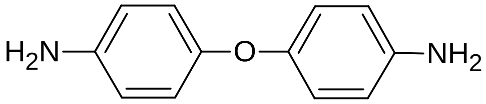


Figure 2.8 Structures of 4,4′-ODA

2.4 Structures of polyimide

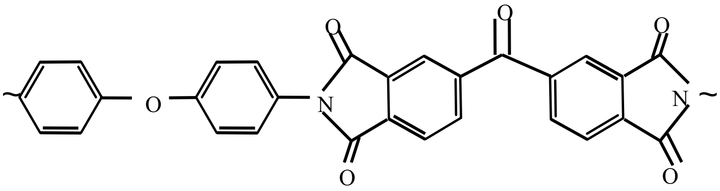


Figure 2.9 Structures of BPDA-ODA

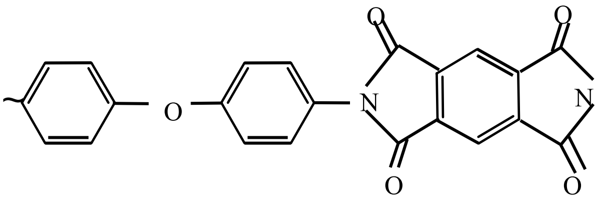


Figure 2.10 Structures of PMDA-ODA

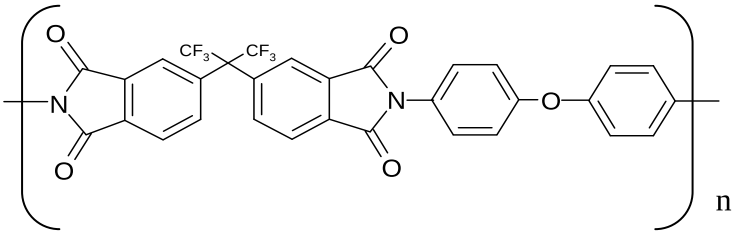


Figure 2.11 Structures of 6-FDA-ODA

2.5 Synthesis of Polyimide

Polyimide are generally prepared from precursor poly(amic acid) (PAA) solution by casting followed by thermal curing. The thermal curing process involves the simultaneous cyclicization with dehydration [16-19]. In Figure 2.12, the comparison of preparation step and the experimental procedure for the sample preparation of PMDA-ODA polyimide were illustrated. Started by the PAA solution casting on the Al plate, and followed by drying at 60°C for 24 hr under vacuum.

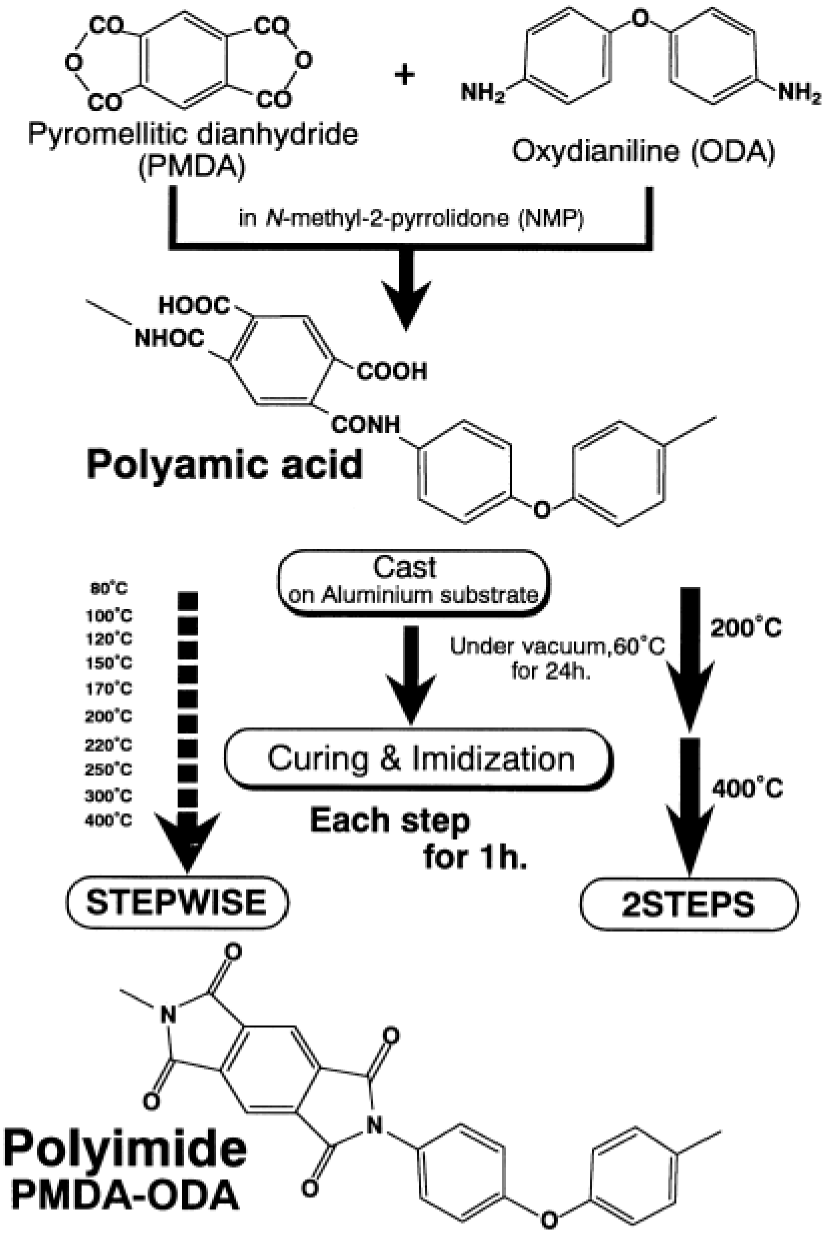


Figure 2.12 Experimental procedure for the sample preparation of PMDA–ODA polyimide [14]

2.5.1 One-step polymerization

A single-stage homogeneous solution polymerization technique can be employed for polyimides which are soluble in organic solvents at polymerization temperatures. In this process, a stoichiometric mixture of monomers is heated in a high boiling point solvent or a mixture of solvents in a temperature range of 140-250^{o}C where the imidization reaction proceeds rapidly. Commonly used solvents are nitrobenzene, benzonitrile, α-chloronaphthalene, *o*-dichlorobenzene, trichlorobenzenes and phenolic solvents such as *m*-cresol and chlorophenols in addition to dipolar aprotic amide solvents. Toluene is often used as a cosolvent to facilitate the removal of the water of condensation. During polymerization, water is distilled off continually as an azeotrope along with the solvent. Preparation of high-molecular-weight poly(amic acid) is not necessary in this procedure. Imidization still proceeds via amic acid intermediate. However, the concentration of amic acid group is very small at any time during the polymerization because it is unstable at high temperature and rapidly imidizes, or reverts to amine and anhydride. Because water is formed as the result of the imide formation, some of the anhydride groups are rapidly hydrolyzed to *o*-dicarboxylic acid. When a mixture composed of diamine, dianhydride, and a solvent is heated, a viscous solution is formed at intermediate temperature of 30-100 ^{o}C. The composition of the product is mainly poly(amic acid). At this stage, phase separation is usually observed in nonpolar solvents such as chlorinated aromatic hydrocarbons. However, on raising the temperature to 120-160 ^{o}C, a vigorous evolution of water occurs and the reaction mixture suddenly becomes homogeneous. At this stage the product is essentially a low-molecular-weight polyimide having *o*-dicarboxy and amino end groups. Thereafter, a slow stepwise polycondensation takes place according to the reaction between the end groups [8].

2.5.2 Two-step polymerization

The majorities of polyimides possess extended rigid planar aromatic and heteroaromatic structures and are infusible and insoluble. The earlier pioneers at DuPont Co. coped with this common problem of intractability generally associated with high-temperature polymers by synthesizing the soluble polymer precursor, namely "poly(amic acid)" and converting it to the final polyimide [13]. Figure 2.13 showed an example of the synthesis of Kapton polyimide. This highly elegant process made it possible to bring the first significant commercial polyimide products into the market and it has still been the method of choice in vast majorities of applications. However, the seemingly simple process involves several elementary reactions interrelated in a complex scheme. In the following sections important parameters that govern these complex interrelations will be discussed in terms of reaction mechanisms in relation to the chemical and physical natures of monomers and intermediates as well as solvents involved.

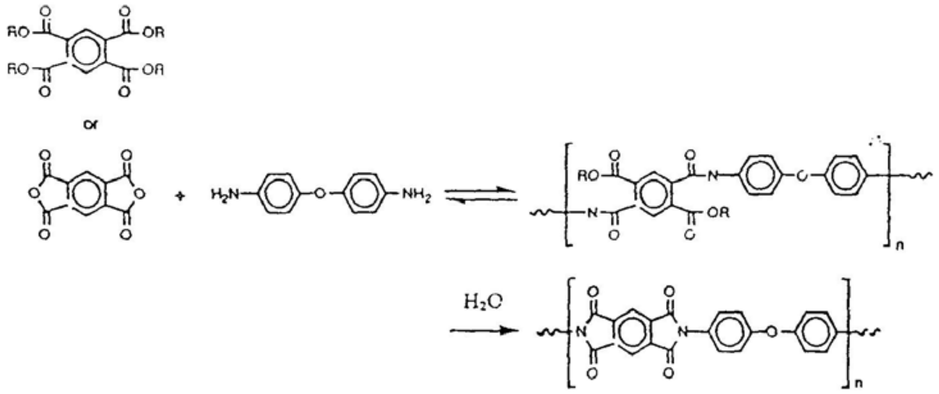


Figure 2.13 General two-step imidizatmon reaction scheme

2.5.3 Reactivity of monomers

As mentioned earlier the mechanism of poly(amic acid) formation is a nucleophilic (Figure 14) substitution reaction at one of the carbonyl carbon atoms of the dianhydride with diamine. Therefore, it is expected that the reaction rate is primarily governed by the electrophilicity of the carbomers used in the beginning. If an additional dianhydride equivalent to the unreacted amino group is added to the above solution, it reacts with the amino end groups and the molecular weight increases. Although the high molecular weight of poly(amic acid) solutions is generally preferred in terms of process requirement for applications as films and coatings, it is not necessarily good to use additional dianhydride. Although the orthodicarboxylic acid group is inactive at ambient temperature, it thermally dehydrates to the anhydride and reacts with amine at higher temperatures, thus creating an off-stoichiometric situation with the dianhydride in excess. The molecular weight of poly(amic acid) intermediate is not important for one-step homogeneous high-temperature solution polymerization and the melt polymerization of polyimides. The molecular weight of the polyimide product is primarily determined by the stoichiometric relation of the monomers.

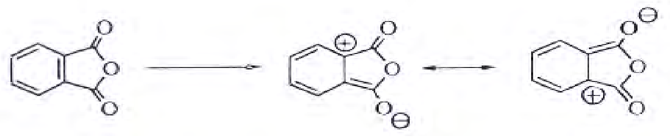


Figure 2.14 Resonance effect on phthalic anhydride group

2.5.4 Formation of polyamic acids

Addition of a dianhydride to a diamine in a dipolar aprotic solvent such as DMAc or NMP at ambient temperatures leads to the formation of the intermediate poly(amic acid) due to the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group. The scheme that is illustrated in Figure 2.15 involves a reversible reaction leading to opening of the anhydride ring to form an amic acid group. However, the forward rate constant for the reaction is several orders of magnitude larger than the reverse reaction and thus the reaction often appears irreversible if pure reagents are utilized. The formation of high molecular weight product is also dependent on this large difference in the reaction rate constants and thus it becomes important to examine the driving forces favoring the forward reaction. For the reverse reaction to take place, the carboxyl proton needs to attack the adjacent poly(amic acid) group. Thus any reagent, that hinders this reaction can decrease the rate of backward reaction and thus can shift the equilibrium to the right.

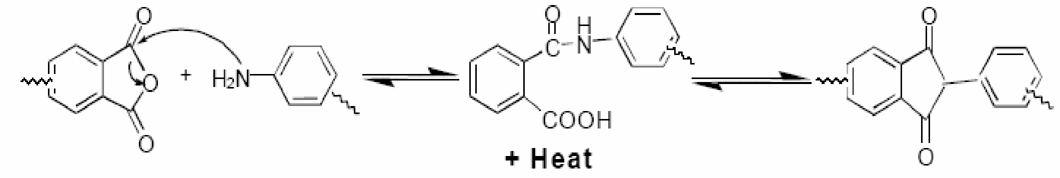


Figure 2.15 Generalized reaction mechanism of aromatic imide formation

Polar aprotic solvents form strongly hydrogen bonded complexes with the free carboxyl groups and thus lead to equilibrium constants in excess of 10^5 l/mol at ambient conditions. However, if the polymerization reaction is carried out in ether or hydrocarbon solvents, considerable differences in equilibrium constant are observed depending upon the amine’s basicity and the dianhydride’s electrophilicity. It is also important to note that the poly(amic acid) formation is exothermic and the equilibrium is favored at lower temperatures. However, the equilibrium is shifted so far to the right at ambient that further lowering of the temperature usually does not show any detectable effect on the reaction. Another important factor affecting the reaction equilibrium is the monomer concentration. As the forward reaction is bimolecular and the reverse reaction is unimolecular, increasing the monomer concentration favors high molecular weight products. For the case of very dilute solutions this feature becomes especially important and leads to decreased molecular weight of poly(amic acid).

The most important aspect of this process is that it is an equilibrium reaction. Often it appears to be an irreversible reaction because a high-molecular-weight poly(amic acid) is readily formed in most cases as long as pure reagents are used. This is because the forward reaction is much faster than the reverse reaction, often by several orders of magnitude. If the large reaction rate difference is not met, the high-molecular-weight poly(amic acid) is not formed. Therefore, it is important to examine the driving forces that favor the forward reaction over the reverse reaction. It should also be noted that the acylation reaction of amines is an exothermic reaction and that the equilibrium is favored at lower temperatures. The forward reaction in dipolar solvents is a second-order reaction and the reverse reaction is a first-order reaction. Therefore, the equilibrium is favored at high monomer concentrations to form higher -molecular-weight poly(amic acid)s.

2.5.5 Chemical imidization of poly(amic acid)

The cyclodehydration of polyamic acids to polyimides was preformed by the usage of acetic anhydride as a dehydration agent and could be readily achieved by means of chemical dehydration at ambient temperature. Commonly used reagents are acid anhydrides in dipolar aprotic solvent or in the presence of tertiary amines. Among the dehydration agent used were acetic anhydride, propionic anhydride and others. Among the amine catalysts used were pyridine, trialkylamines and others.

The imidization proceeds rapidly at the initial stage and tapers off at a plateau as same as a typical diffusion-limited kinetic process. As the degree of imidization increases, the Tg or stiffness of the polymer chain increase. When the Tg approaches the reaction temperature, the imidization rate slows down markedly. At a higher temperature, a higher degree of imidization is attained [21].

The initial rapid stage of imidization is attributed to the ring closure of amic acid in the favorable conformation. The slower rate in the later stage of imidization is attributed to the unfavorable conformation, which has to rearrange to conformation before ring closure.

Chemical imidization often proceeds at least in part via the isoimide. Controlled preparation of the poly(isoimide) allows the use of this polymer class as precursor, since poly(isoimide)s even of rigid rod-like polyimides are often soluble.

The isoimide linkage introduces kinks and bends into the polymer backbone. Conversion of the kinetically favored isoimide into the thermodynamically more stable imide is achieved thermally or catalytically with bases, which is formed by acylation of the carboxylic group of amic acid (6), as illustrated in Figure 2.16. Since it involves no water formation, this type of curing may be advantageous for polyimides, which are sensitive to moisture absorption.

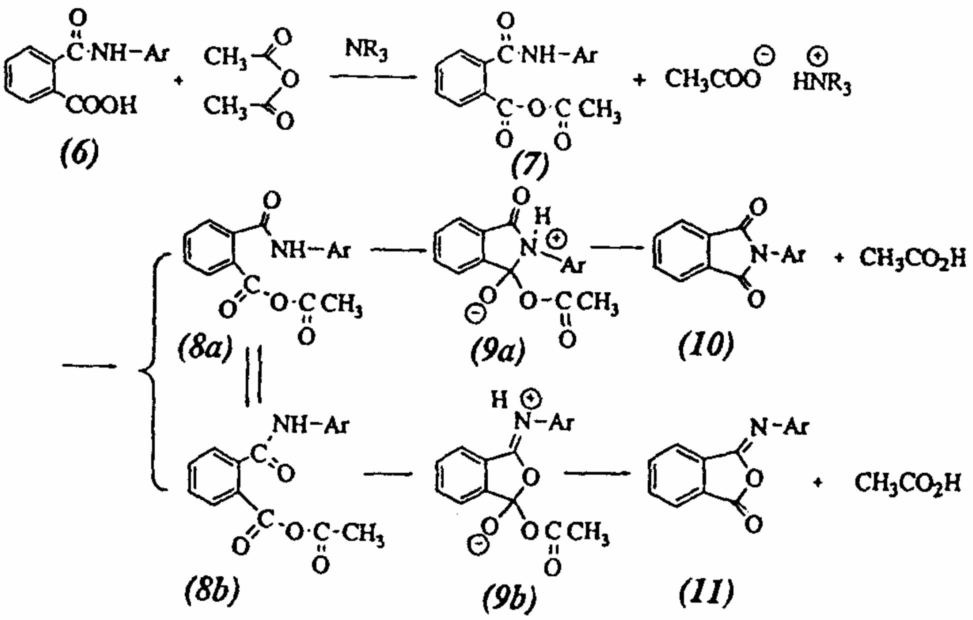


Figure 2.16 Mechanism involved in chemical dehydration of amic acid (R, Ethyl, Ar, phenyl)

2.5.6 Solution deposition

Solvents used in the formation of poly(amic acid)s play an important role. Most commonly used solvent are dipolar aprotic amide solvent such as *N*-methylpyrolidinone (NMP). However, lesser thermal stability and difficulty in removing it in the following imidization process argue against its use. One of the important properties of these solvents is the basicity (Lewis' base). It is interesting and worthy to note that the starting reagents are weakly basic aromatic amine and nonprotic anhydride, and yet the product is a strong protic acid. In other words, the starting mixture is basic and the product is an acid. The orthoamic acid is a relatively strong carboxylic acid because of the electron-withdrawing effect of the orthoamide group and the stabilization by internal hydrogen bonding of dissociated carboxylate with amide hydrogen. The strong acid-base interaction between the amic acid and the amide solvent is a major source of exothermicity of the reaction and one of the most important driving forces. Therefore, it is expected that the rate of poly(amic acid) formation is generally faster in more basic and more polar solvents.

Common source of water is in the solvents and the monomers containing water as an impurity, it should be noted that the water is also formed in situ by the imidization of amic acid groups. Although the rate of the imidization, and therefore the formation of water, is relatively slow at ambient temperatures, it is still significant enough to cause a gradual decrease in molecular weight over a long period of time.

2.6 Colliod method

A colloid is a type of chemical mixture where one substance is dispersed evenly throughout another. The particles of the dispersed substance are only suspended in the mixture, unlike a solution, where they are completely dissolved within. This occurs because the particles in a colloid are larger than in a solution - small enough to be dispersed evenly and maintain a homogenous appearance, but large enough to scatter light and not dissolve. Because of this dispersal, some colloids have the appearance of solutions. A colloidal system consists of two separate phases: a dispersed phase (or internal phase) and a continuous phase (or dispersion medium). A colloidal system may be solid, liquid, or gaseous. Many familiar substances are colloids, as shown in the chart below. The subsequent table compares particle(s) diameters of colloids, homogeneous and heterogeneous mixture [15].

2.6.1 Lyophilic and lyophobic sol (stability and instability)

Colloids are conditionally divided into two classes *lyophilic* (good solvent) and *lyophobic* (poor solvent) respectively, depending on the ease with which the system can be redispersed if once it is allowed to dry out.

Lyophilic colloid can be dispersed merely by adding a suitable solvent (that is a dispersing medium) to the dry colloid which will first swell as it takes up the liquid and well finally form a homogeneous colloidal solution.

Lyophobic colloid on the other hand can only be dispersed by vigorous mechanical agitation (or by the application of some other external source of energy).

A sol in which the particles remain separated from one another for long period of time (of the order of days at least) is said to be **stable.** For lyophilic colloids the stability result from the fact that the solution is thermodynamically stable (that is the solution has a lower Gibbs free energy than the separate component) such a sol can be stable indefinitely. For lyophobic colloid, there is always an attractive (van der Waals) force between particles.

Lyophilic colloids are not obviously affected by the salt concentration of the surrounding medium until it becomes quite high. Lyophobic colloidal sols on the other hand can be markedly affected and rendered unstable by quite low concentration of salt ($<10^{-2}$M).

2.6.2 Interaction between colloid particles

The following forces play an important role in the interaction of colloid particles:

- Excluded volume repulsion: This refers to the impossibility of any overlap between hard particles.
- Electrostatic interaction: Colloidal particles often carry an electrical charge and therefore attract or repel each other. The charges of both the continuous and the dispersed phases, as well as the mobility of the phases are factors affecting this interaction.
- van der Waals forces: This is due to interaction between two dipoles that are either permanent or induced. Even if the particles do not have a permanent dipole, fluctuations of the electron density gives rise to a temporary dipole in a particle. This temporary dipole induces a dipole in particles nearby. The temporary dipole and the induced dipoles are then attracted to each other. This is known as van der Waals force, and is always present, is short-range, and is attractive.
- Entropic forces: According to the second law of thermodynamics, a system progresses to a state in which entropy is maximized. This can result in effective forces even between hard spheres.
- Steric forces: between polymer-covered surfaces or in solutions containing non-adsorbing polymer can modulate interparticle forces, producing an additional steric repulsive force (which is predominantly entropic in origin) or an attractive depletion force between them. Such an effect is specifically searched for with tailor-made superplasticizers developed to increase the workability of concrete and to reduce its water content.

2.6.3 Steric stabilization

In effect, the surface of the lyophobic colloid was coated with a layer of lyophilic material of a polymeric (or, at any rate, of a long-chain) nature. When two of such particles approach, the interaction between the adsorbed chains causes a repulsion that can be sufficient to induce stability. Its magnitude can be calculated by estimating the effect of particle separation on the free energy of the adsorbed molecules. As they are forced together the number chain-chain contacts is increased at the expense of chain-solvent interactions and for a lyophilic (solvent-loving) polymer, which must lead to an increase in the free energy, or a repulsive force (Figure 2.17) [15].

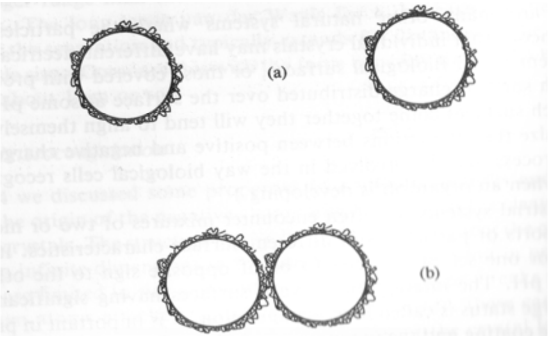


Figure 2.17 Interaction between two sterically stabilized particle

(a) Separate particle with adsorbed polymer chain interacting with the solvent

(b) Interpenetration of the polymer chain reduces the amount of polymer/solvent interaction

2.6.4 Surfactant

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

Thermodynamics of the surfactant systems are of great importance, theoretically and practically. This is because surfactant systems represent systems between ordered and disordered states of matter. Surfactant solutions may contain an ordered phase (micelles) and a disordered phase (free surfactant molecules and/or ions in the solution).

Ordinary washing up (dishwashing) detergent, for example, will promote water penetration in soil, but the effect would only last a few days (although many standard laundry detergent powders contain levels of chemicals such as sodium and boron, which can be damaging to plants, so these should not be applied to soils). Commercial soil wetting agents will continue to work for a considerable period, but they will eventually be degraded by soil micro-organisms. Some can, however, interfere with the life-cycles of some aquatic organisms, so care should be taken to prevent run-off of these products into streams, and excess product should not be washed down gutters.

A micelle (rarely micella, plural micelles) is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic tail regions in the micelle centre illumoinate in figure 2.18. This type of micelle is known as a normal phase micelle (oil-in-water micelle). Inverse micelles have the headgroups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micellae is known as micellisation and forms part of the phase behaviour of many lipids according to their polymorphism [22].

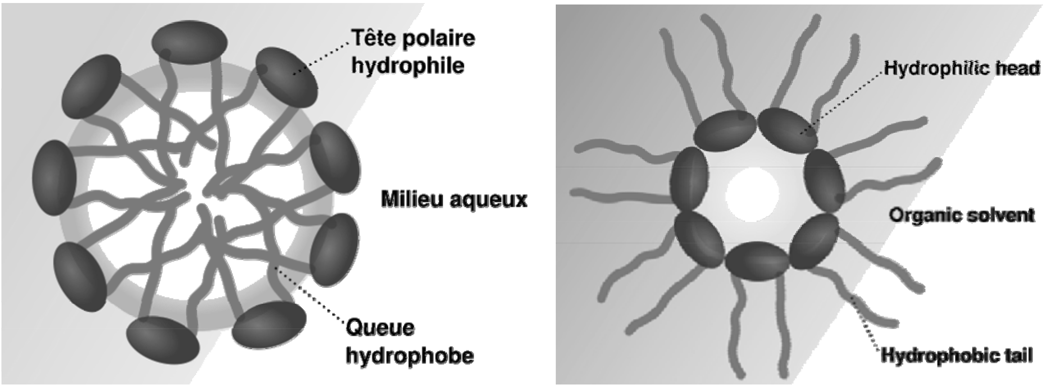


Figure 2.18 A micelle formed by phospholipids in an aqueous solution

2.7 Thermal properties

The Glass transition temperature, *T*g is the temperature at which an amorphous solid, such as glass or a polymer, becomes brittle on cooling, or soft on heating. More specifically, the glass transition is a pseudo second order phase transition in which a super cooled melt yields, on cooling, a glassy structure and properties similar to those of crystalline materials e.g. of an isotropic solid material [1]. *T*g is usually applicable to wholly or partially amorphous solids such as common glasses and plastics (organic polymers), although there is an analogous phenomenon in crystalline metals called the ductile-brittle transition temperature.

TGA can be used to examine polymer mixture by showing differences between the behaviors of the individual substance on heating. If significant temperature differences are observed, then the specific reaction of the particular components can be identified. For instance, polymer blend and polymers containing additives can all be examined in this way.

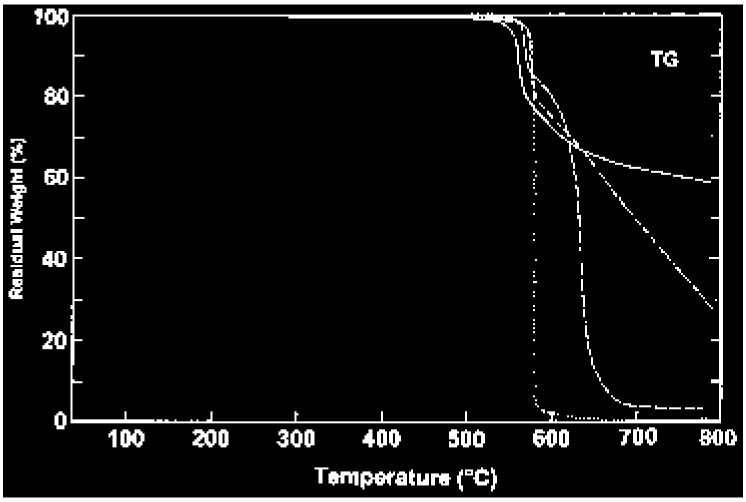


Figure 2.19 High-resolution TG curves of the thermoplastic polyimide (TPI) fine powder in at an initial heating rate of 50°C/min and resolution 4
nitrogen flow (—) helium flow (- - -)
argon flow (- · -) air flow (· · ·)

The PI belongs to a class of thermally stable polymers characterized by a higher thermostability than most of the high heat resistant polymers such as poly(phenylene ether sulfone), polysulfone, poly(p-phenylene terephthalamide) (Kevlar), poly[(poxybenzoate)-co-(p,p'-biphenylene terephthalate)] (Ekonol), poly(oxybenzoate-co-oxynaphthoate) (Vectra) and polycarbonate. The highly aromatic character and imide group of PI contribute to its excellent thermal stability. Generally, implicit in the designation "high temperature" or "thermostable" polymers are two basic criteria : 1) thermo-oxidative stability the ability to withstand performance deterioration over long periods at high temperatures in air 2) thermophysical profile specimen must retain a substantial percentage of room temperature strength and modulus at elevated use temperature and plasticity or creep should not limit the utility to temperatures below the thermo-oxidative limit. The thermal degradation of some PIs has been studied by traditional thermogravimetry (Tg) at a constant heating rate. However, there are few studies on the thermal degradation and kinetics of a new thermoplastic polyimide (TPI).

2.8 Dynamics Light Scattering Analysis

This procedure refers to the fact that when a light photon hits a moving particle, the frequency of the scattered light, as measured by a stationary observed is slightly increased or decreased depending on whether the particles is moving towards or away from the observer.

In its original form the method involved using a spectrum analyser to determine the intensity of the light scattered at a certain angle as a function of the frequency.

2.9 Properties of polyimide

- Thermosetting or Thermoplastic
- Crystalline, Semi-crystalline or Amorphorous polymer Kapton Polyimide
- Density 1.42 g/cm^3
- Glass temperature > 400 °C
- Flexural Modulus 2.48 GPa
- Tensile Strength 72 MPa
- Water absorption (ASTM D570) 0.32

ADVANTAGES/DISADVANTAGES

Classification	Advantages
Characteristic	Molecular design suitable to need
	Purification
	Heat resistance and Low smoke emission
	Chemical resistance
Technological	Elasticity
	Alpha-ray absorption and unaffected by radiation

Disadvantages
Expensive
High moisture absorption and penetration
Poor resistance to alkali and hydrolysis

CHAPTER III

LITERATURE REVIEWS

This chapter presents the literature reviews of the previous works related to this research. Polyimide synthesis part, colloid method part, polyimide particle part and variation of type surfactant part are shown as below.

3.1 Polyimide synthesis.

T. Nishino *et. al.* [14] involves simultaneous imidization of polyimide (PI) from precursor poly(amic acid) (PAA) solution processing, evaporation of solvent and crystallization, so imidization process influences the final properties of PI. The residual stress at the interface between the most popular PI (PMDA–ODA) and the aluminum substrate was measured by X-ray diffraction method and the relationship between the microstructure and the mechanical properties was investigated for PI with different imidization processes. The residual stress and the mechanical properties of PI depend on the imidization process. The skeletal structure is suggested to be changed by the amount of residual solvent during imidization process, which brings the difference in the residual stress. The selection of imidization condition (thermal treatment or evaporation speed of solvent) brought the different skeletal structure of PI (PMDA–ODA). Thus it affected the final mechanical properties of PI.

Accordingly, controlling of the imidization processes will bring high performance such as low residual stress or high elastic modulus to PI.

L. Jiang *et. al.* [23] have found a method to generate nanoporous polyimide films with low dielectric constants. The preparation consisted of two steps. Firstly, a polyimide/silica hybrid film was prepared via sol–gel process. Secondly, the hybrid film was treated with hydrofluoric acid to remove the dispersed silica particles, leaving pores with diameters between 20 and 120 nm, depending on the size of silica particles. Both hybrid and porous films were subjected to a variety of characterizations including transmission electron microscopy observation, dielectric constant measurement and tensile strength measurement.

I. Rozhanskii *et. al.* [24] examined 2,2’,3,3’-Biphenyltetracarboxylic dianhydride (i-BPDA) as a monomer for the synthesis of soluble polyimides with high thermal stability, and developed the efficient method of its preparation. Polyimides derived from i-BPDA and aromatic diamines (i.e. 4,4’-oxydianiline, 2,2’-bis(trifluoromethyl)benzidine and 9,9’-fluorenylidene-4,4’-dianiline) showed high glass transition (Tg >330 ^{o}C) and degradation (Td_5 > 550 ^{o}C), temperatures, and were soluble in organic solvents (i.e. NMP, DMF, γ-butyrolacton, $CHCl_3$), although their mechanical properties were inferior to those of polyimides composed of semirigid 3,3’,4,4’-biphenyltetracarboxylic dianhydride (s-BPDA). Random copolymers, derived from i-BPDA and s-BPDA, retained superior mechanical properties of s-BPDA-based polyimides and showed improved solubilities, depending on the i-BPDA content. A regular increase of glass transition temperatures and a decrease of inherent viscosities of copolymers with increasing content of i-BPDA were observed, whereas the dielectric constants and degradation temperatures were found to be independent of the ratios of dianhydride units.

S.-H. Xie *et. al.* [25] have prepared polyimide/aluminum nitride (AlN) composites based on pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA) by in situ polymerization. To disperse the AlN particles in the polyimide matrix homogeneously, γ-glycidoxypropyltrimethoxysilane (GPTS) was used as coupling agent for the preparation of the composites. It was found that, with the inclusion of aluminum nitride powder into the polyimide matrix, the thermal properties of the resulting polyimide–AlN composite were improved without obvious loss in the dielectric properties. The results indicated that the thermal stability and the thermal conductivity of the composite were enhanced, while the dielectric constant increased slightly and the electrical properties altered to less degree with the increase of AlN fraction. Meanwhile, the dielectric and thermally conducting properties were also influenced by the content of the coupling agent. In addition, the thermally conducting and dielectric properties of the studied composites followed the classic composite theories.

Z. Y. Ge *et. al.* [26] examined a series of novel fluorinated polyimides, which could be easily dissolve in many organic solvents to give homogeneous and stable polyimide solution with solid content as high as 35-40% wt. The polyimide films obtained by casting the polymer solution followed by thermal imidization exhibited good thermal stability with high glass transition temperature and the temperature at 5% weight loss, and have outstanding mechanical properties. In addition, the fluorinated polyimides have low dielectric constants and dissipation factor, and very low moisture absorption.

S. Carturan *et. al.* [27] fluorinated polyimide film derived from 4,4′-(hexafluoroisopropylidene) diphthalic anhydride and 2,3,5,6-tetramethyl-1,4-phenylenediamine have been obtained by spin-coating a solution of polyimide powder dissolved in chloroform. The synthesized polyimide has been characterized by Fourier transform infrared spectroscopy, optical transmission spectroscopy and fluorescence spectroscopy. Significant changes in some intrinsic fluorescence features such as the intensity, the shape and the position of the emission peaks have been observed under exposure to vapours of water, ethanol and isopropanol. These effects have been correlated to the developing of specific chemical interactions between these analytes and the macromolecules, including the formation of hydrogen bridges. In order to determine the detection capabilities and the response and recovery times towards the various analytes, single-wavelength fluorescence versus time measurements have been performed as the polyimide films were exposed to alternating pulses of pure nitrogen and different vapour concentrations. The polymer proved capable to respond to all the tested analytes, with response and recovery times in the order of the tens of seconds and detection thresholds in the 500–1000 ppm range.

3.2 Colloid Method

F. Deplace *et. al.* [22] found poor mechanical properties are usually in films cast from waterborne colloidal polymers relative to their solvent cast counterparts, these materials offer the opportunity to control structure and composition very precisely at the nanoscale. Here, we introduce a knowledge-based strategy to design what we call a "soft–soft nanocomposite" in which a percolating crosslinked phase contains a second less crosslinked dispersed phase distributed regularly throughout it. This new type of structure uses polymer colloid particles as building blocks in a bottom-up approach to obtain simultaneously very viscoelastic behaviour at small strains and an elastic behaviour at larger strains, bringing highly desirable properties for adhesives applications. For instance, the adhesion energy of the soft–soft nanocomposite on polyethylene is more than four times greater than that of a commercial material in which the particles are crosslinked and the interfaces are entangled. Our conclusions are broadly applicable to a large class of soft materials based on deformable polymeric networks, such as gels, elastomers and artificial tissues.

Y. Baimark *et. al.* [28] were prepared Nanoparticle colloids of methoxy poly(ethylene glycol)-*b*-poly(D,L-lactide) (MPEG-*b*-PDLL) diblock copolymer by a modified spontaneous emulsification solvent diffusion method using acetone/ethanol as the mixture organic solvents. The MPEG-*b*-PDLL was synthesized by ring-opening polymerization of D,L-lactide using stannous octoate and MPEG with molecular weight of 5,000 g/mol as the initiating system. The MPEG-*b*-PDLL obtained was an amorphous polymer with molecular weight of 73,600 g/mol. Influences of acetone/ethanol (v/v) ratios and Tween 80 surfactant concentrations on characteristics of the colloidal nanoparticles were investigated and discussed. Light-scattering analysis showed that average diameters of the surfactant-free colloidal nanoparticles were in the range of 86–124 nm. The nanoparticle sizes decreased as the ethanol ratio increased. The Tween 80 did not show the significant effect on the nanoparticle sizes. Scanning electron micrographs of dried nanoparticles that demonstrated the aggregation of most particles suggested they were the soft nanoparticles. However, the dried nanoparticle morphology can be observed from scanning electron microscopy as having a spherical shape and smooth surfaces.

3.3 Polyimide Particle

M. Suzuki *et. al.* [7] produced spherical polyimide nanoparticle size 20-500 nm by reprecipitation methods. The polyimide consists of 15.7% wt. concentration of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA) and 4,4'-oxydianiline

(ODA) in 1-Methyl-2-pyrrolidinone (NMP ; the good solvent). The PI have been successfully fabricated through the “two-step imidization” i.e., chemical imidization followed by thermal imidization of poly(amic acid) (PAA) precursor nanoparticles prepared by the reprecipitation method, which mixture NMP solution of PAA was first rapidly injected into a stirred cyclohexane (the poor solvent). Surfactant added in a poor solvent was Acrydic A-1381. After chemical imidization, the resulting PI nanoparticle were centrifuged at 12,000 rpm and dried in vacuo.

G. Zhao *et. al.* [8] fabricated porous polyimide (PI) nanoparticles using the reprecipitation method, with a second polymer as a porogen, and subsequent imidization. Poly(acrylic acid) (PAS) and poly(vinyl alcohol) (PVAL) were used as porogens without further purification. Chemical imidized, a mixture of pyridine and acetic anhydride was injected into dispersion phases of PAA nanoparticle. After chemical imidized PI nanoparticle were separated using a centrifuge, dried in vacuo. Then cured and thermal imidized at 270°C, result in a yellowish powder of PI nanoparticle having superficial nanopores, the sizes of which were in the range 20 - 70 nm. The sizes of the resulting PI nanoparticles were ca. 200-500 nm.

J. Y. Xiong *et. al.* [11] fabricated polyimide nanoparticles using a combined liquid–liquid phase separation and solvent/nonsolvent mixing technology. Selective solvation and electron pair donor/electron pair acceptor interaction are employed to stabilize nanoparticles. The experiments were performed in two ways, denoted as the forward titration (FT) method and backward titration (BT) method, based on the moving directions. As an extension of the BT method, the so-called ultrasound enhanced backward titration (UEBT) method, ultrasound was introduced into the nanoparticle formation system. Two polyimides, P84 and Matrimid were used as polymers. While NMP is an electron pair donor (EPD) solvent due to the presence of its lone electron pair, and ethanol is an electron pair acceptor (EPA) solvent. Experiment results, a very high level of supersaturation at a very high nucleation rate. This effect is found extremely useful in the fabrication of sub-50-nm polyimide nanoparticles. Utilizing selective solvation together with an EPD/EPA interaction, can produce sub-50-nm polyimide nanoparticles in the absence of all surfactants.

3.4 Variation of type surfactant

A. Rahimpour *et. al*. [29] study the effects of three surfactants, sodium dodecyl sulphate (SDS) as anionic surfactant, cetyle three methyl ammonium bromide (CTAB) as cationic surfactant and Triton X-100 as non-ionic surfactant on structure and performance of polyethersulfone membranes prepared from PES/PVP/DMAC system via immersion precipitation have been investigated. The mixture of water and isopropyl alcohol (IPA) (30/70% vol.) was used as gelation media. It was found that the addition of small amounts of surfactants in the casting solution increases the formation of macrovoids and finger-like pores in the sub-layer of membranes. This enhances the pure water flux and milk water permeation with slight decrease in milk protein rejection. When Triton X-100 was used as additive in the casting solution the performance of prepared membrane was higher compared to the other cases. The surface analysis of membranes showed that mean pore size, pore density and surface porosity of membranes are higher compared to the membrane prepared without surfactant.

M. Y. Khan *et. al*. [30] has been studied of Interaction between water-soluble polymers and anionic surfactants. Sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) were used as surfactant while polyacrylamide (PAA), commercial grade partially hydrolyzed polyacrylamide (PHPA), and xanthan gum were used as water-soluble polymers for the present study. The behavior of surfactant–polymer interaction was found to be dependent on both surfactant and polymer concentrations. After the critical aggregation concentration (CAC), interaction between the water soluble polymer and surfactants was started and above the polymer saturation point (PSP) polymer was saturated by surfactant with no further change of surface tension and conductivity of the solution. It has also been found that alkali (NaOH) and salts (Na_2CO_3, NaCl) have significant influence on the polymer–surfactant interaction.

R. McLemore *et. al*. [31] study to ensure a high degree of control over the gelation rate of the materials to prevent the formation of uncontrolled emboli from shear or dispersion. Through manipulation of factors affecting the kinetics of *in situ* forming polymeric systems, patients' safety can be maximized. The rate of Michael-Type Addition is known to be affected by the pH of the accompanying solution, as thiols will become nucleophilic thiolates in an aqueous environment. This work evaluates the effect of the addition of 2 and 4 % wt. of several common surfactants on the gelation rate of reverse emulsion polymeric systems as a method for augmenting control of *in vivo* Michael-type addition kinetics. This work shows that both Tween-20 (HLB 16.7) and Pluronic type surfactants (HLB ~6.7) stabilize our emulsion, with gelation rates being significantly different in the presence of Pluronic type surfactants ($p < 0.05$). This work has demonstrated the ability of surfactants to promote faster gelation at lower pH by maximizing emulsion stability and reducing cohesion of smaller bubbles, thereby maximizing surface area between the initiator and the bulk phases.

CHAPTER IV

EXPERIMENT

In the present study, the influences of various dianhydride synthesized polyimide (PI) were examined. The experiments were divided into six parts which can be explained as below,

(i) Materials and chemicals
(ii) Equipments
(iii) Preparation of poly(amic acid) (PAA) precursor
(iv) Polyimide polymerization
(v) Characterization of polyimide

The details of the experiments can be explained as followed.

4.1 Materials and chemicals

The chemicals used in these experiments were analytical grade, but only crucial materials were specified as followed:

1. 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6-FDA) 98.5%

purchased from Aldrich chemical Company, Inc .

2. Pyromellitic dianhydride (PMDA) purchased from Aldrich chemical Company, Inc.
3. 3,3’,4,4’-Biphenyl dianhydride (BPDA) purchased from Aldrich chemical Company, Inc.
4. 3,4′-Oxydianiline (ODA) purchased from Merck KGaA Germany.
5. N-Methyl-2-pyrrolidinone (NMP) purchased from Merck KGaA Germany.
6. Hexane (Commercial grade) was purchased from SR lab.
7. Cyclohexane (Commercial grade) was purchased from Chemical Express Company, Inc.
8. Carbon disulfide (CS_2) purchased from Chemical Express Company, Inc.
9. Pyridine (98.5%) purchased from Merck KGaA Germany.
10. Propionic anhydride (98%) purchased from Merck KGaA Germany.
11. Acrydic A-1381 purchased from DIC Corporation.

12. Sodium dodecyl sulfate (SDS ; 98.5%) purchased from Aldrich chemical Company, Inc.
13. Dodecyl benzene sulfonic acid sodium salt (SDBS ; 80%) purchased from Fluka-Aldrich chemical Company, Inc.
14. Methanol (Commercial grade) was purchased from SR lab.
15. Argon gas (Ultra high purity grade, 99.999 %) was purchased from Thai Industrial Gas Co.,Ltd.(TIG) and further purified by passing through columns packed with copper catalyst, NaOH, P_2O_5 and molecular sieve 4A to remove traces of oxygen and moisture.
16. Silicone Oil purchased from Merck KGaA Germany.

4.2 Equipments

The equipments, which used during the polymerization of polyimide, and the procedures to synthesize various dianhydride monomer, type of surfactant and poor solvent, are listed as below:

4.2.1 Preparation of Poly(amic acid) (PAA) precursor part

Since most of the reagents were very sensitive to the oxygen and moisture therefore the special techniques were taken during the handling of reagents and the loading of ingredient into the reactor. Such equipments utilized for this purpose are listed as follows:

(a) Glove box (Vacuum Atmospheres) is used prepare reactant, with oxygen and moisture analyzer for handling solid reagents under inert atmosphere and for storing air-sensitive reagents. Inside the glove box, oxygen and moisture levels are normally controlled to below 2 ppm. The glove box is shown in Figure 4.1.

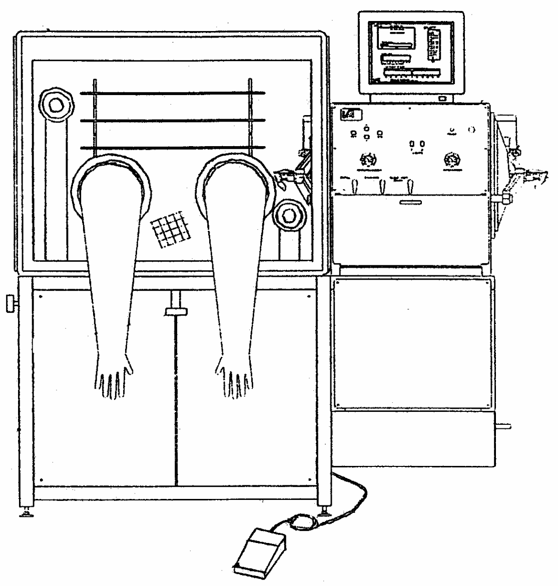


Figure 4.1 Glove box

(b) Schlenk line included of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred. The schlenk line was shown in Figure 4.2.

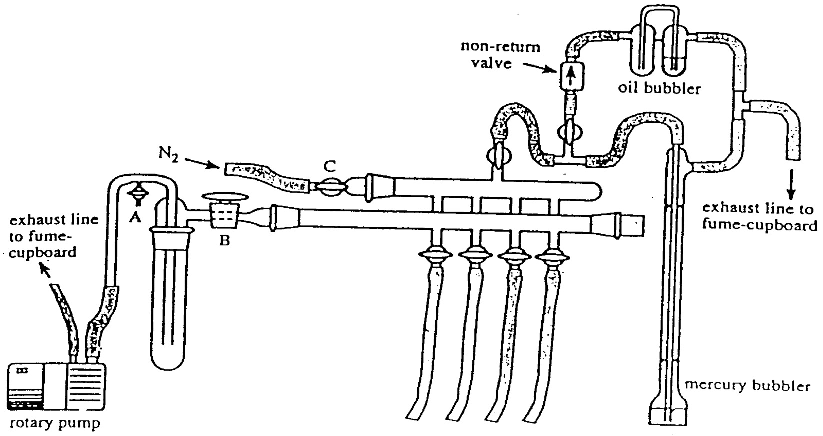


Figure 4.2 Schlenk line

(c) Schlenk tube for keeping reagents under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line. Schlenk tube is the tube with a ground joint and a side arm which connected with three ways glass valve. The Schlenk tube picture is shown in Figure 4.3.

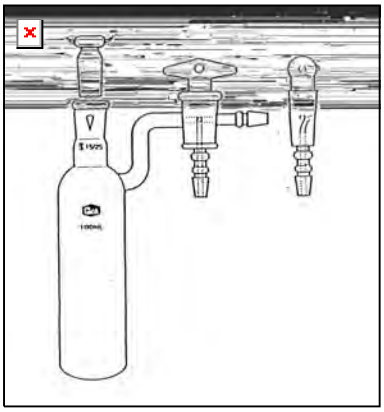


Figure 4.3 Schlenk tube

(d) The inert gas (argon) from the cylinders was passed through columns of oxygen trap (BASF catalyst, R3-11G), moisture trap (molecular sieve), sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) in order to purifying the argon gas to obtain ultra high purity argon which was used in Schlenk line and solvent distillation column. The inert gas supply system can be shown in Figure 4.4.

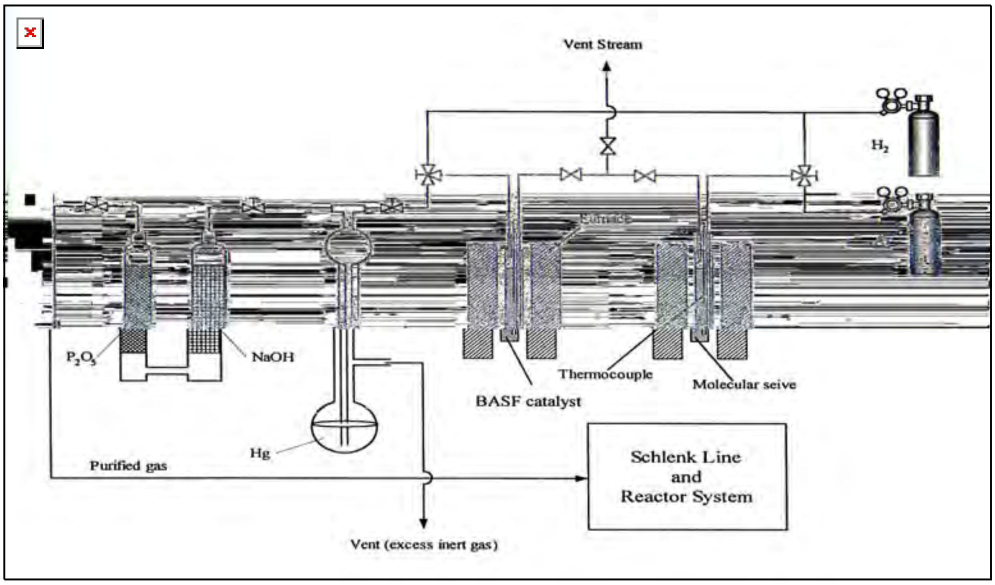


Figure 4.4 Inert gas supply system

(e) The vacuum pump model 195 from Labconco Coporation was used. The produced low pressure of 10^{-1} to 10^{-3} mmHg was adequate for utilizing as the vacuum supply to the vacuum line of the Schlenk line. The vacuum pump is shown in Figure 4.5.

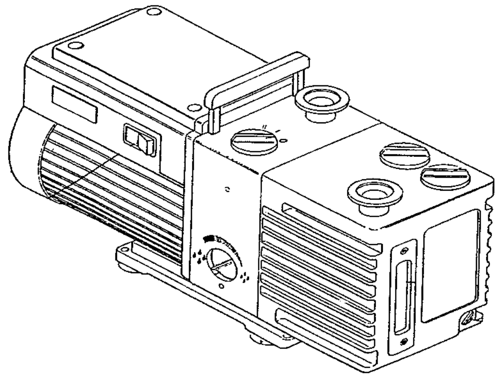


Figure 4.5 Vacuum pump

(f) Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

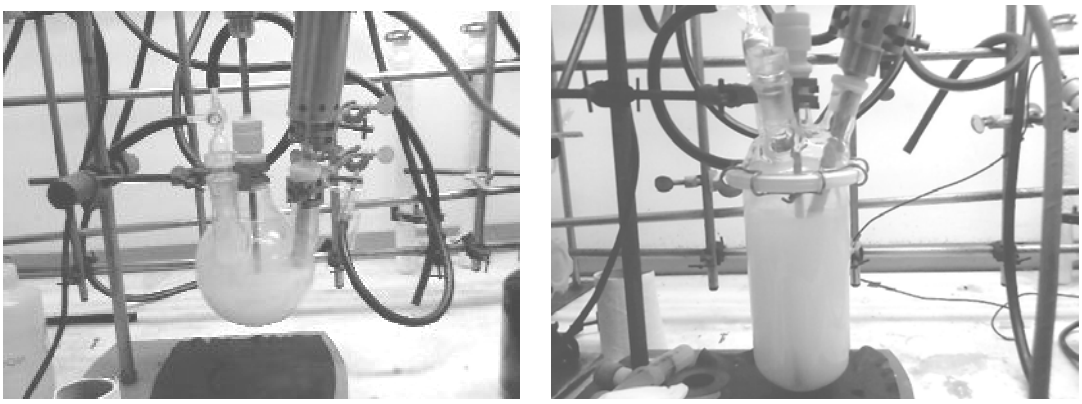
(g) Syringe and Needle

The syringe used in these experiments had a volume of 5 and 10 ml and the cooperated needles were of No. 27 and 18, respectively.

4.2.2 Polyimide Polymerization part

(a) Synthesized reactor

The polymerization reactor round bottom flask was a 1000 ml. four-neck flask. The reactor was equipped with several fittings for injecting the chemicals and purging with argon gas. A three-necked, round bottom flask equipped with an argon inlet, an ultrasonic prop, mixing impeller with mixer and a stopper valve for injection reagent. For new reactor (opening reactor flask) as same as an earliest stage reactor. The new reactor used mixing impeller for high shear, which can be shown in Figure 4.6.



Reactor for reaction earliest stage New reactor for high shear

Figure 4.6 Reactor

(b) Stirrer and propeller blade

Impellers (Figure 4.7) in agitated reactor are used to mix fluids or colloid in the reactor. This can be used to combine materials; solids, liquids, gas. Mixing the fluids in a reactor is very important if there are gradients in conditions such as temperature or concentration.

Properties

adjustable chuck size : 0.5-10 mm
feature : CE compliant, CSA approved
: Speed range I 60 - 500 rpm
: Speed range II 240 - 2000 rpm
: torque maximum 185Ncm
mfr. no. : IKA 2684601
H × W × D : 292 mm × 88 mm × 188 mm
Weight : 2.9 kg

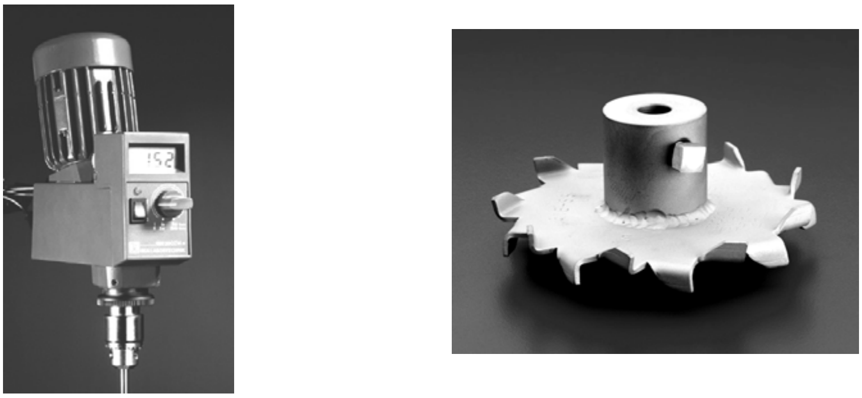


Figure 4.7 Stirrer and propeller blade

4.3 Preparation of Poly(amic acid) (PAA) precursor

The PAA precursor, which was synthesis from vary type of dianhydride and diamine in good solvent that is NMP. The solution calculate to be 5%wt. by volume (mole ratio is 1 : 1of solid). The solution stirred under argon asmosphere

4.3.1 Non-Fluorinate monomer

(a) 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA)

The stock solution of PAA precursor were prepared by addition of BPDA (0.0025mol, 0.7355g) and ODA (0.0025mol, 0.5006g) to a stirred solution with NMP (24.72ml) at ambient temperature, reaction be on schlenk tube under vacuum in the glove box.

(b) Pyromellitic dianhydride (PMDA)

The stock solution of PAA precursor consist of PMDA (0.0025mol, 0.5453g) and ODA (0.0025mol, 0.5006g) in NMP (20.9ml) at ambient temperature, reaction be on schlenk tube under vacuum in the glove box.

4.3.2 Fluorinate monomer

The PAA precursor were prepared approximate non- fluorinate monomer, that consist of 6-FDA (0.0025mol, 1.1106g) and ODA (0.0025mol, 0.5006) in NMP (42.2ml) at ambient temperature, reaction be on schlenk tube under vacuum in the glove box.

4.4 Polyimide Polymerization

In this study, various type of poor solvent and type of surfactant in the reaction.

4.4.1 Type of poor solvent

(a) Cyclohexane

The poor solvent be composed of clycloheaxane (200ml), carbon disulfide (CS_2) and surfactant. The volume fraction of CS_2 ($\square_{CS_2}$) in the mixed poor solvent 0 to 1. That was mixing cyclohexane (200ml), carbondisulfide (20ml) and suitable amount of surfactants.

(b) Haxane

Prepare of poor solvent as same as a cyclohexane too. That was mixing hexane (200ml), carbondisulfide (20ml) and suitable amount of surfactants.

4.4.2 Type of surfactant

(a) Acrydic A-1381

Description:	Mixture: consisting of the following components. Acrylic resin 50.0% Alkane, C(9~12)-iso- 50.0%

(b) Sodium Dodecylbenzenesulphonate (SDBS)

Molecular Formula	$C_{18}H_{29}NaO_3S$
Molecular Weight	348.48

(c) Sodium dodecyl sulfonate (SDS)

Molecular Formula	$C_{12}H_{25}OSO_3Na$
Molecular Weight	288.38

After prepare PAA precursor stock solution. Since PI is insoluble in a common organic solvent, the colloid method was applied to PAA (30ml) was fist rapidly inject into a vigorously stirred poor solvent (220ml) 1 hr., containing 0.1%wt of surfactant. The mixing rate of poor solvent was constant 1300 rpm and ultrasonic break (maximum frequency) of PAA particles 1 hr. Chemical imidization of PAA particles was perform by adding of propionic anhydride (for dehydration) and pyridine (for accelerated cyclization) mixture 1:1 ratio (30:30ml) into the PAA particles dispersion liquid[7] 2 hr. Finally, a yellow powder of PI particles was obtained. The fabrication procedure of PI particles is illustrated in Figure 4.8.

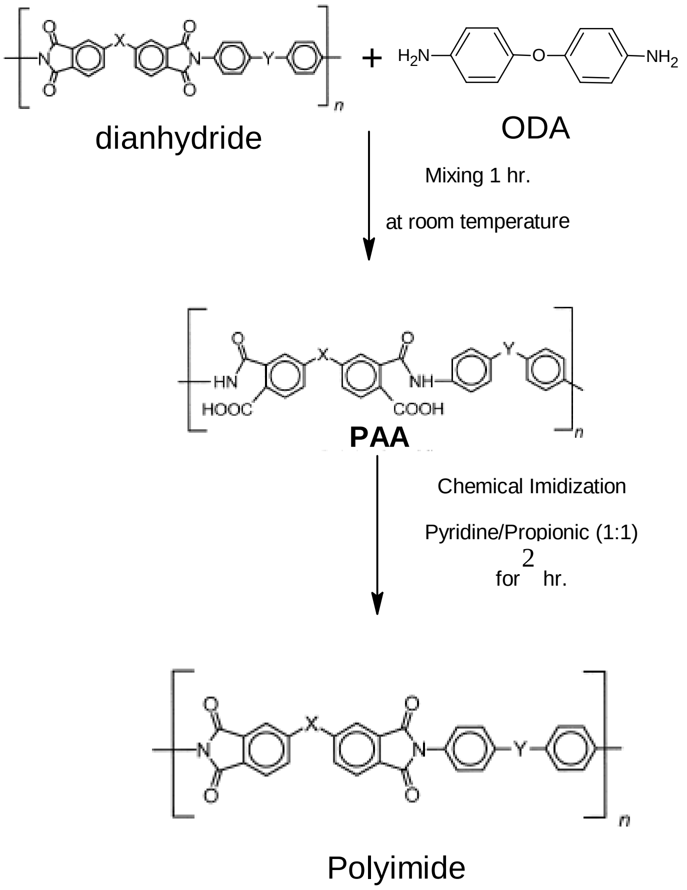


Figure 4.8 Preparation of polyimide particles

4.5 Characterization Instruments

4.5.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared survey spectra were recorded with Nicolet 6700 FT-IR spectrometer. The scanning ranged from 400 to 4000 cm^{-1} with scanning 64 times.

Figure 4.9 Fourier transform infrared spectroscopy (FT-IR) Equipment

4.5.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) thermograms were performed using a SDT Analyzer Model Q600 from TA Instruments, USA. The sample weights were 5-10 mg. The temperature range of 30-1000^{o}C at a heating rate of 10^{o}C/min with oxygen and nitrogen purge flow rate 100 ml/min.

Figure 4.10 Thermogravimetric analysis (TGA) Equipment

4.5.3 Dynamic Light Scattering (DLS)

Particles size of all polyimide products were determined by using Dynamic Light Scattering (DLS) with a Mastersizer 2000 Ver. 5.22 Serial Number MAL101847. Condition and parameters were shown in the Table below.

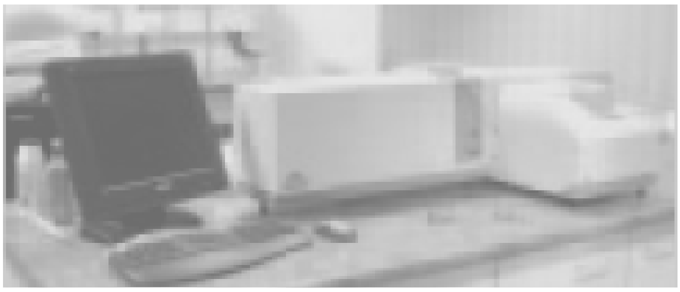


Figure 4.11 Dynamic Light Scattering (DLS) Equipment

Table 4.1 Conditions and parameter for running DLS

Conditions and parameter	**Value**
Wide dynamic range	0.01µm-2000µm
Measurement Mode	Mie scattering
Light sources	Red light : helium-neo laser Blue Light : solid-state light source

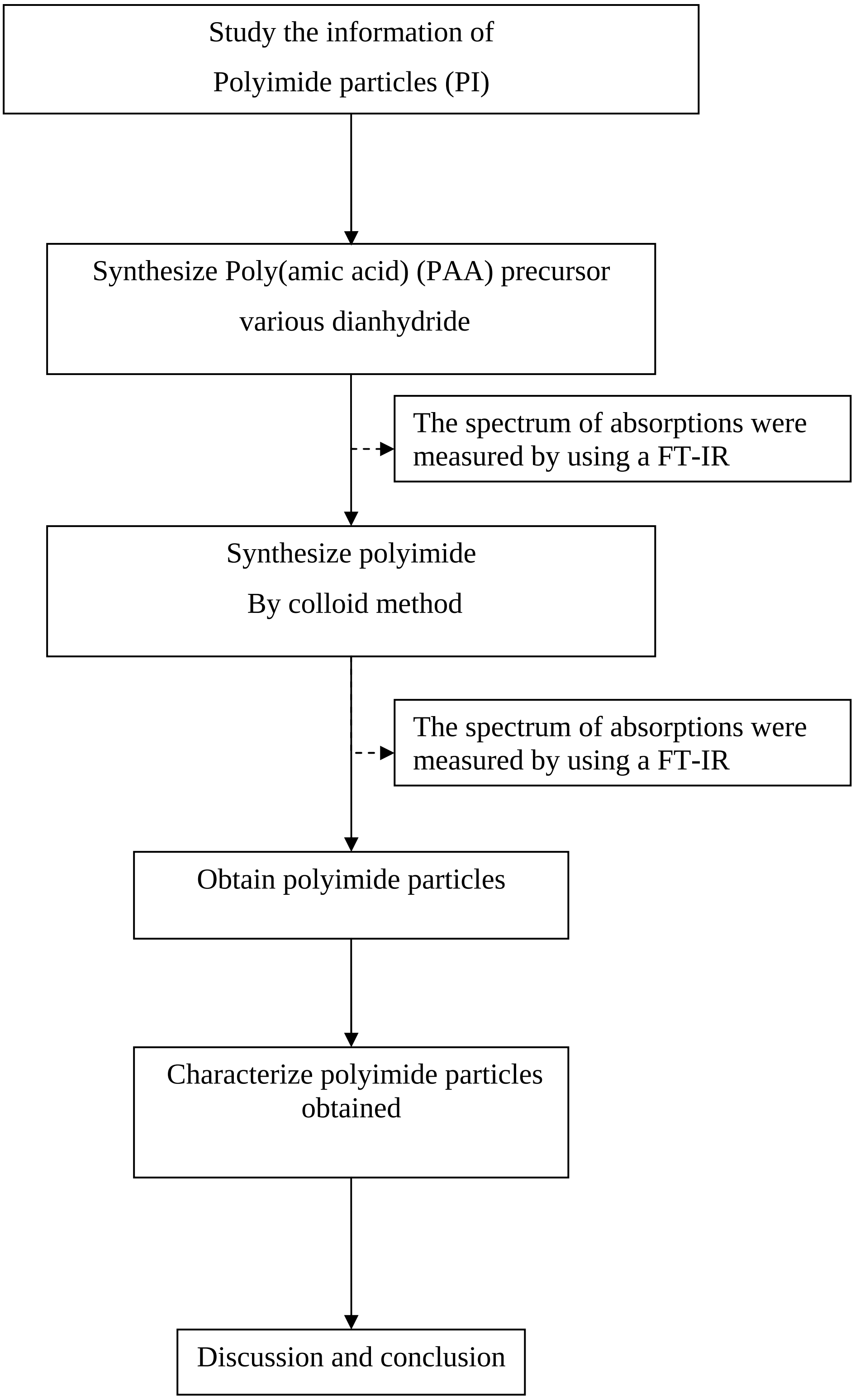


Figure 4.12 Flow diagram of research methodology

CHAPTER V

RESULTS AND DISCUSSION

This chapter provides the information about the results of polyimide (PI) particles and PI synthesis including the effects of various dianhydride monoer, surfactants and poor solvent on the properties of the synthesized PI particles, the thermal properties and particles size distribution.

5.1 Preparation of Poly(amic acid) (PAA) precursor

5.1.1 Structure of poly(amic acid) in various condition

All synthesis conditions and name definitions of synthesized polyimide are shown in B-2 (Appendix B). In this research, the polyimide are synthesized by a colloid reaction method between various dianhydride monomer with ODA (diamine monomer) which have hydroxyl functional groups in a polyimide aprotic solvents to form poly(amic acid) (PAA). The FT-IR peaks of PAA were constant regardless of the various dianhydried monomers.

PAAs 1-9 (Appendix B in Table B-2) gave the same characteristics peaks by FT-IR spectroscopy. The FT-IR spectra of Figure 5.1 showed characteristic amide around 1500 cm^{-1} (amide I: coupled vibration mode of N-H blending vibration and C-N stretching vibration in –CO-NH-amide moity) and 1543 cm^{-1} (N–H bending), 1674 (amide, C=O stretching) and carboxylic acid absorptions at 1724 (carboxylic acid, C=O stretching) common in every pair of PAA.

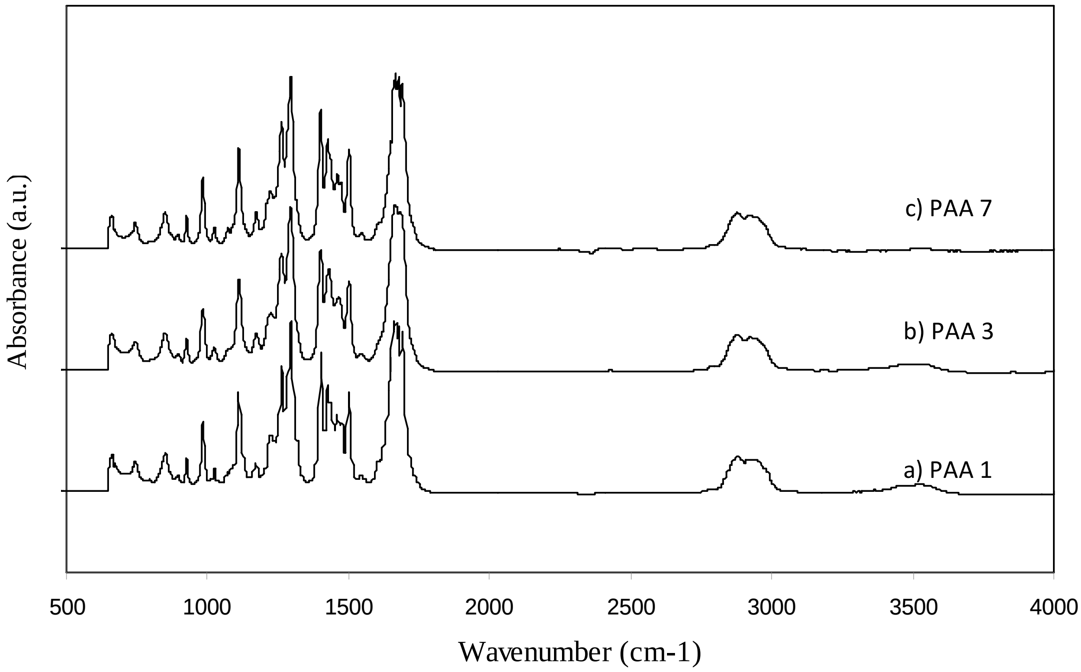


Figure 5.1 FT-IR spectra of poly(amic acid) (PAA) precursor is different dianhydride monomer

a) dianhydride is BPDA
b) dianhydride is PMDA
c) dianhydride is 6-FDA

5.1.2 Reaction scheme

Various colloid reactions were performed according to the table in the next page.

Table 5.1 The molar ratios of the compositions on the reaction mixtures

Code	Molar ratio of the composition										Note
	BPDA mol (g)	**PMDAmol (g)**	**6-FDAmol (g)**	**ODAmol (g)**	**NMP (ml)**	**PAA inject(ml)**	**Surfactant**	**poor solvent**	**pyridene (g)**	**propionic (g)**	
PI1	0.0025(0.7355)			0.0025(0.5006)	24.7	20	SDBS/0.05 (g)	cyclohexane	50	50	-
PI2		0.0025(0.545)		0.0025(0.5006)	20.9	20	SDBS/0.07 (g)	cyclohexane	50	50	-
PI3			0.0025(1.2709)	0.0025(0.568)	37	15	SDBS/0.07 (g)	cyclohexane	15	15	-
PI4			0.0025(1.2709)	0.0025(0.568)	37	15	SDBS/0.07 (g)	hexane	15	15	-
PI5			0.0025(1.2709)	0.0025(0.568)	37	30	SDS/0.318 (g)	haxane	30	30	-
PI6			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	40	40	-
PI7			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	cyclohexane	30	30	-
PI8			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	30	30	low temp.
PI9			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	40	40	fast imidized

5.2 Polyimide with various type of dianhydride monomer

In this study, various PIs were synthesized by a colloid reaction method (Figure 5.2) utilized different dianhydride such as 6-FDA, PMDA and BPDA with the same diamine ODA via poly(amic acid) (PAA). The solution of PAA was injected into poor solvent to generate colloid of PAA which would be further change into PI via the chemical imidization methods. The pyridine and proprionic anhydride were used as an chemical imidization agent by injecting into colloid solution while stirring. The PI particles were produced from the reaction and stabilized by freeze drying method.

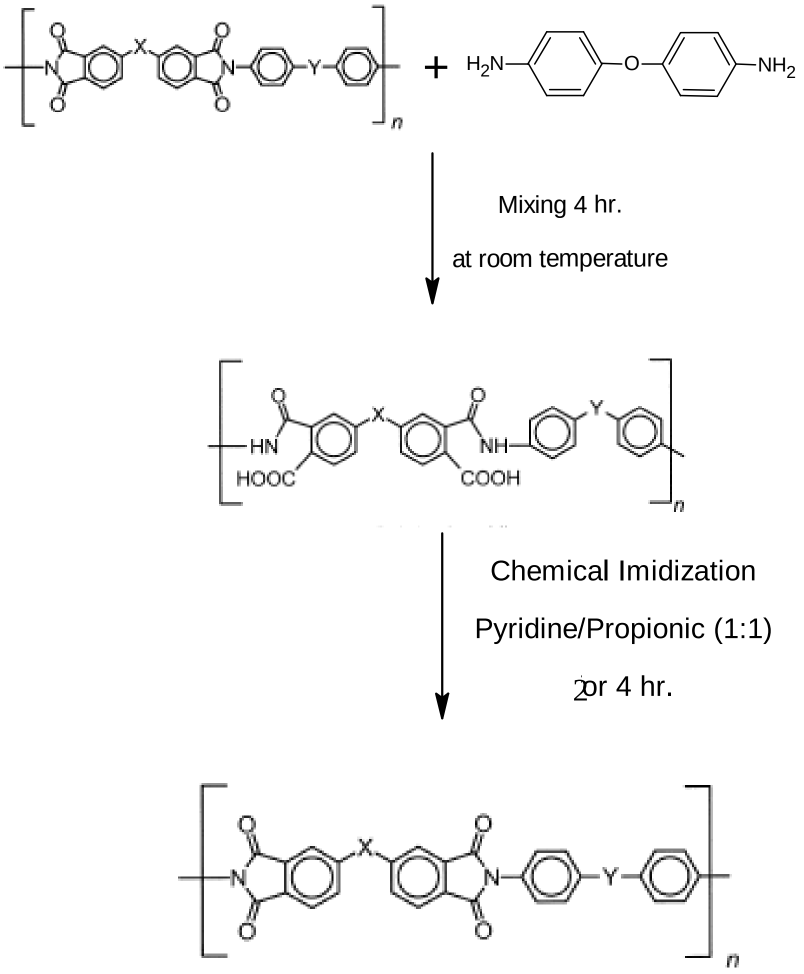


Figure 5.2 Structure of polyimide (PI)

5.2.1. Structure comparation of poly(amic acid) (PAA) precursor and Polyimide

It can be confirmed that imidization have proceeded quantitatively from IR spectra measurements. After the chemical imidization the absorption band around 1500 cm^{-1} (amide I: coupled vibration mode of N-H blending vibration and C-N stretching vibration in –CO-NH-amide moiety), while features at wave number near 1750, 1380 and 1370 cm^{-1} were observed in the FT-IR spectra correspond with imide I (stretching vibration of cyclic C=O), imide II (C-N stretching vibration) and imide IV (bending vibration of cyclic C=O) respectively, which as commonly the characteristic absorption peaks of the imide group [9]. The FT-IR spectra results indicated that the imidization reaction was completed because the totally absent of PI particles were successfully developed from PAA precursor.

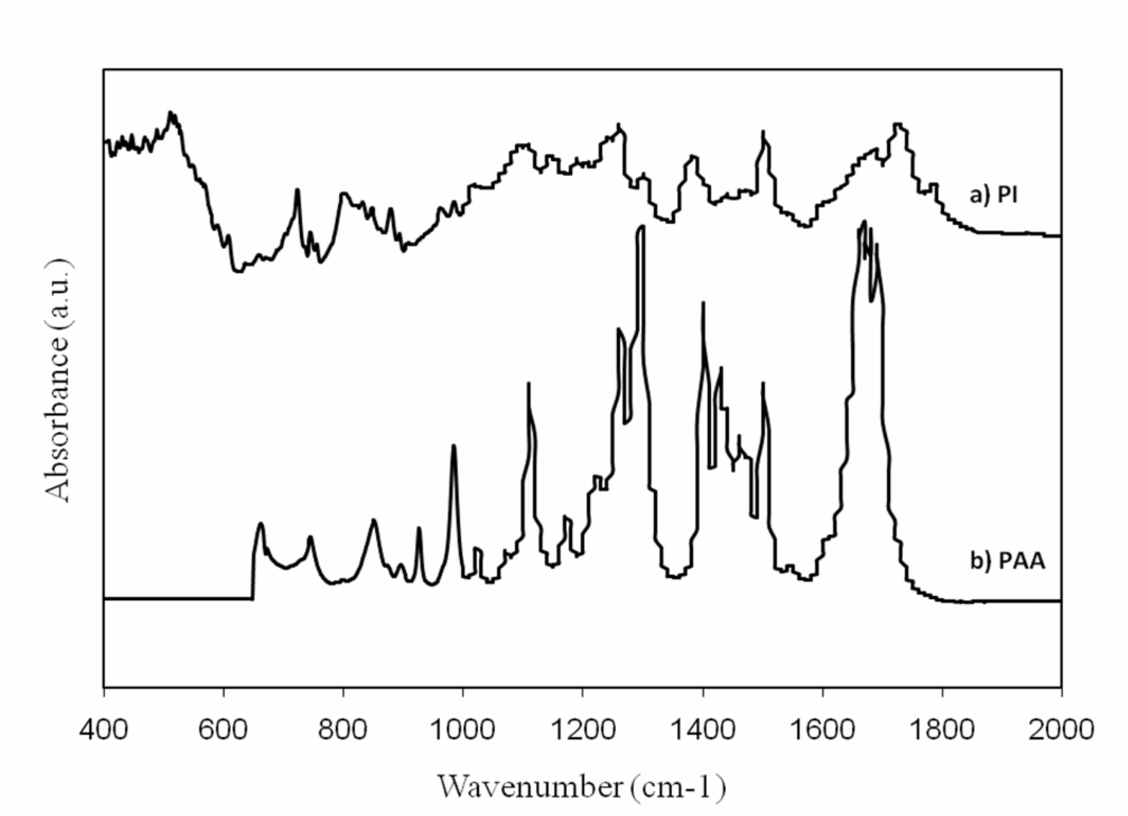


Figure 5.3 FT-IR spectra of polyimide

a) Poly(amic acid) precursor
b) Polyimide

5.2.2. Structure of polyimide in various condition

The structures of polyimides were investigated by FT-IR spectra. The solid FT-IR polyimide samples were prepared via KBr pellet. Figure 5.4 shows a typical polyimide in various condition represented by FT-IR spectrum. The FT-IR peaks of PI were similar regardless of the various types of poor solvent and surfactant. However, the peaks of some surfactant can be observed in the Figures.

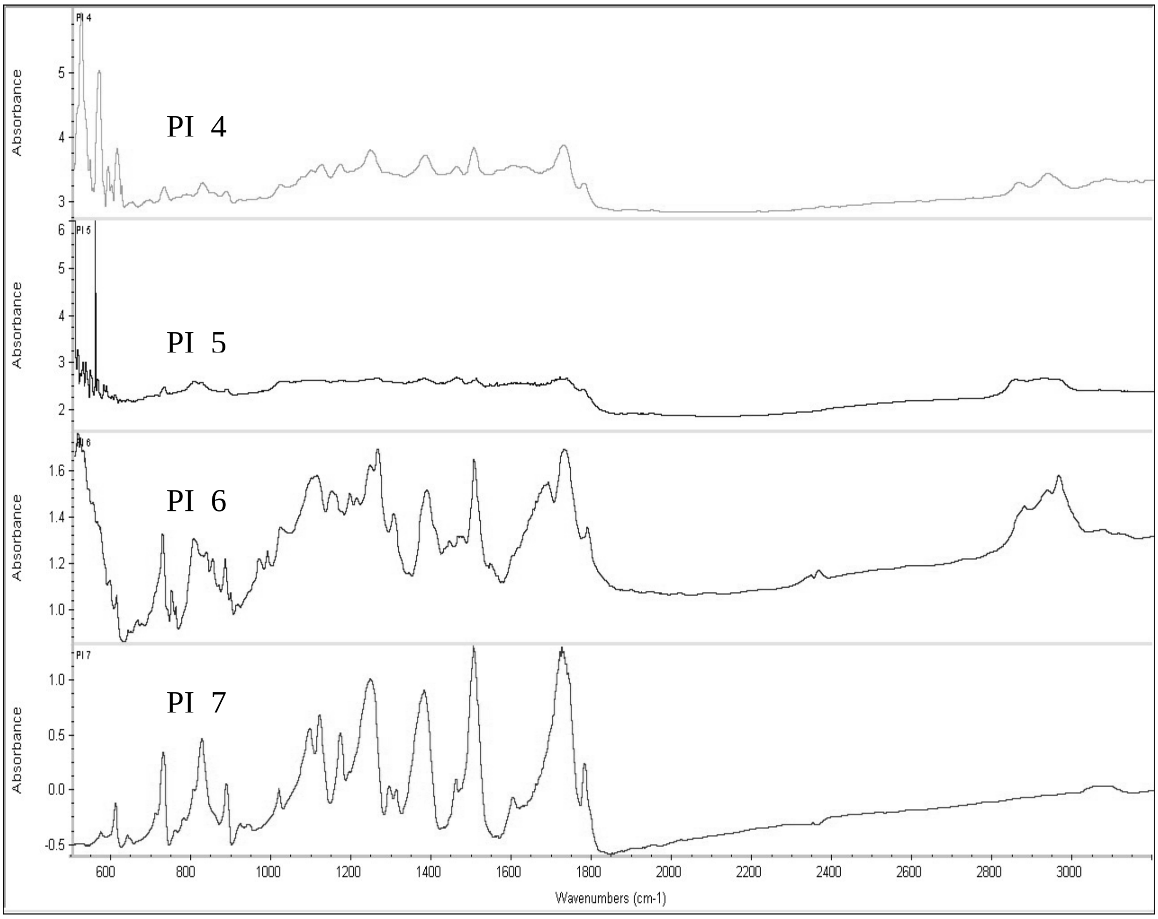


Figure 5.4 FT-IR spectra of Polyimide is different condition (follow Table. B-2)

After imidization the absorbtion band around 1750, 1380 and 1370 cm^{-1} were observed in the FT-IR spectra correspond with imide I (stretching vibration of cyclic C=O), imide II (C-N stretching vibration) and imide IV (bending vibration of cyclic C=O) respectively, which as commonly the characteristic absorption peaks of the imide group [9]. The FT-IR spectra results indicated that the imidization reaction was completed. Moreover, these results confirm that polyimide particles were successfully developed from PAA precursor.

5.2.3. Dynamic Laser Light Scattering (DLS)

The DLS measurements gave the particles size distribution of polyimide particles' samples. De-ionized water was utilized as medium for measurements and has been filtered though a 0.2 μm pore to remove any large impurity particulates beforehand. Figure 5.5 compared the particles size of the polyimide particles produced from various dianhydride. The PI particle that prepared from PMDA have average diameter of 50.8, but the PI particle prepared from 6-FDA have average diameter of 22.3 μm. The PI particles prepared from BPDA have very large diameters inadequate to be measured particles size distribution by DLS.

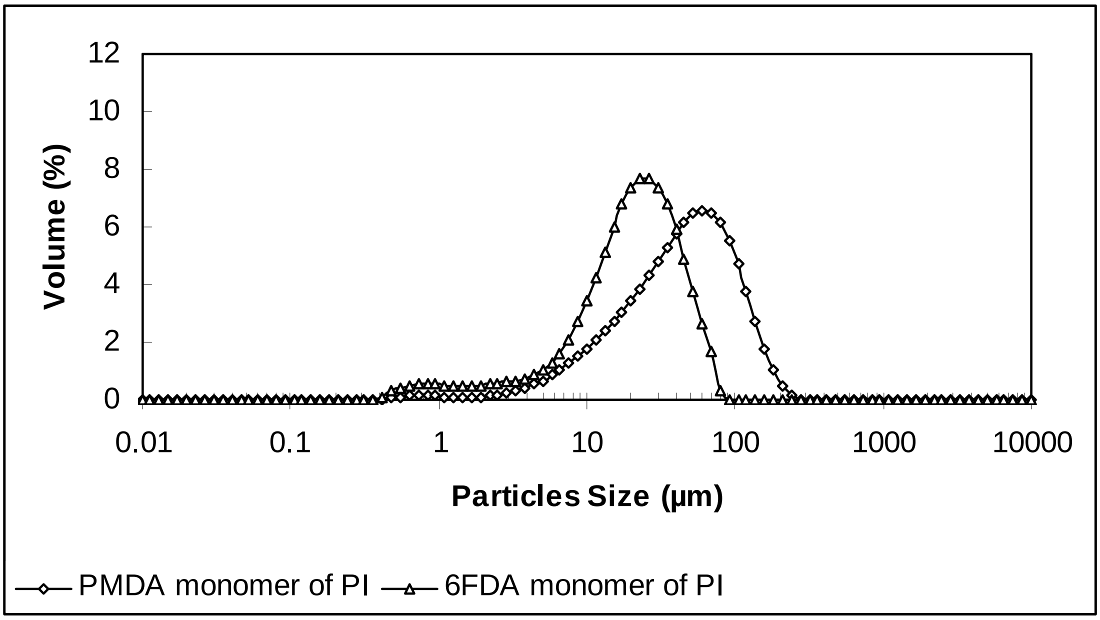


Figure 5.5 DLS measure Paticles size of Polyimde(PI) paticles in various dianhydride

5.2.4. Thermal Charaterization

The derivative weight of TGA (show data in Appendix A) showed that the degradations of polyimide particles occured in two stages. The first stage is the surfactant degradation at about 200-250 ^{o}C and the second stage is the degradation of polyimide backbone which appeared above 450-600 ^{o}C.

In Figure 5.6, the polyimide particles TGA from different polyimide composed of different dianhydride ie. PI1, PI2 and PI3 came from BPDA, PMDA and 6-FDA respectively were shown. From the figure, on the same condition of reaction (hexane as poor solvent), it was clearly seen that the series of the fastest degradation PI particles were 6-FDA, PMDA and BPDA respectively. The condition of the experiments can be found in Table B-2.

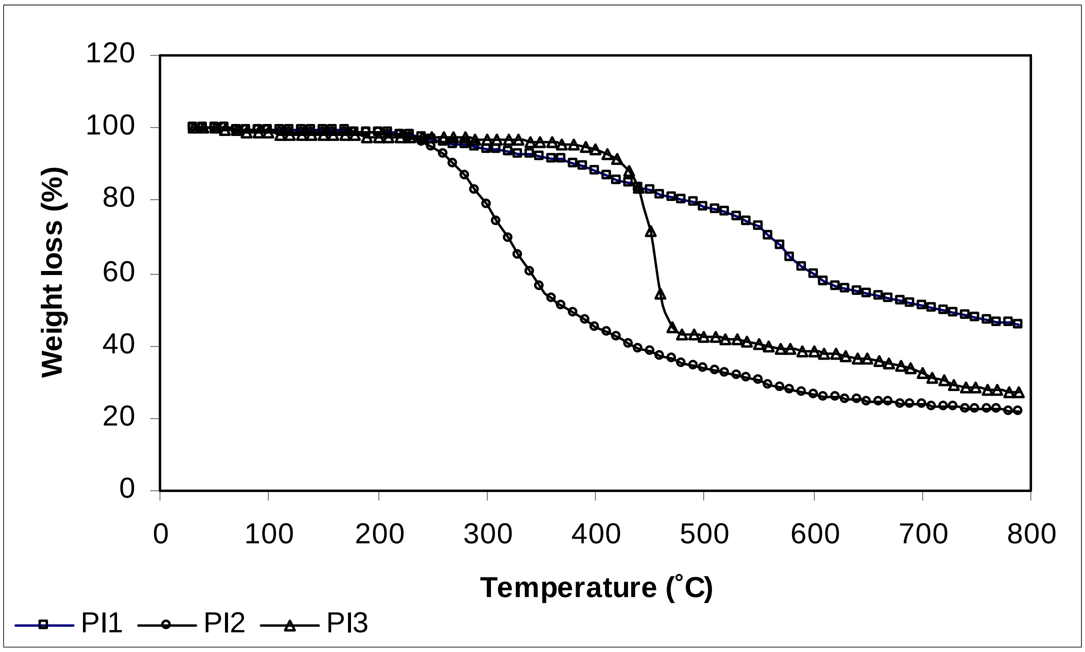


Figure 5.6 TGA curve of polyimide(PI) various dianhydride monomer in N_2

5.3 Polyimide Polymerization in various type of poor solvent

In order to compare the effect of poor solvent on the particle sizes of polyimide produced, the two reactions were performed. The details of the results can be found as follows.

5.3.1 Dynamic Laser Light Scattering (DLS)

Figure 5.7, indicated the particle size distribution of PI particle that prepared from various types of poor solvent. The particle sizes appeared to have average diameter of 741 and 427 µm correspond to cyclohexane and hexane as a poor solvent respectively. The hexane seem to have the smaller particles sizes because of the lower dielectric of the solvent (more poor solvent).

Figure 5.7 DLS measure Paticles size of Polyimde paticles in various poor solvent

5.4 Reaction of Colloid at various condition.

Figure 5.8 showed some interesting characteristic. All the three systems in the Figure were synthesis by the same material and surfactant but different condition of synthesis. The PI7 prepared by normal methods while PI8 using the fast imidization technique and PI9 performed at lower temperature than the room condition. The PI7 is the normal route of synthesis which gave the lowest degradation temperature and fastest degradation. But if the fast imidized cycle was applied in PI9, the degradation also occurred at about the same temperature but in less extent weight loss. Compare to the low temperature of synthesis as PI8, the degradation step are about the same (because they are made from the same material and surfactant) but least weight loss was observed.

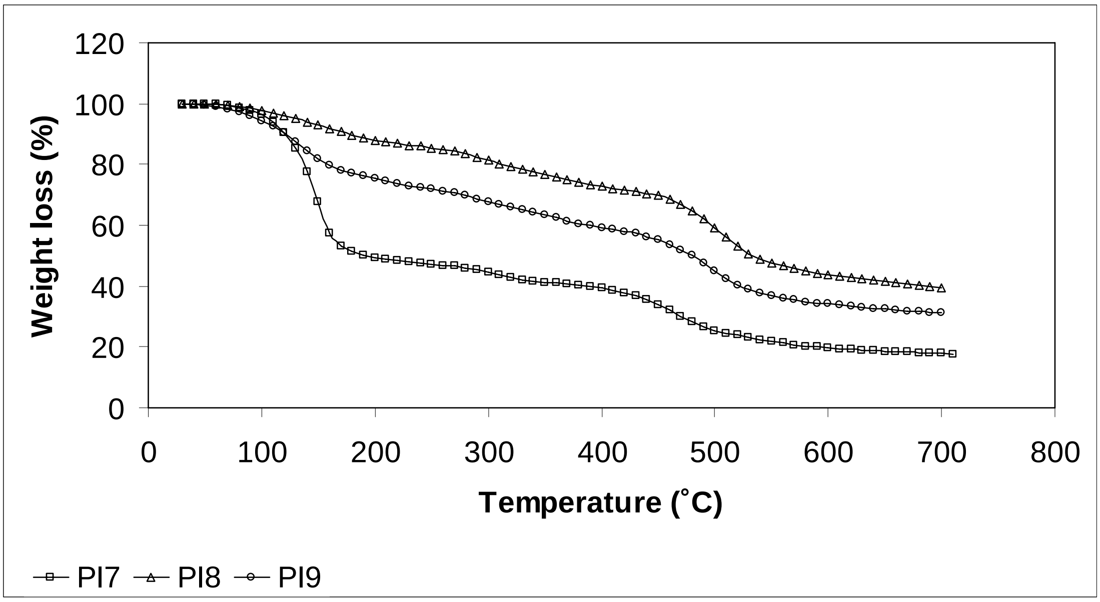


Figure 5.8 TGA curve of polyimide various Temperature and time of imidized in N_2

5.5 Polyimide Polymerization in various type of surfactant

To compare the various type of surfactant effects on particle sizes of polyimide obtained, various colloid reactions were established. The surfactant of Acrydic, SBDS, and SDS were compared.

5.5.1 Dynamic Laser Light Scattering (DLS)

The particle size distribution curve of PI particles that prepared with different surfactant can be shown in Figure 5.9. The average diameters were 22.3, 21.8 and 15.3 µm correspond to Sodium dodecyl benzene sulfonate (SBDS), Sodium dodecyl sulfate (SDS) and Acydic A-1381 respectively. The particle sizes distribution from Acrydic was the least compare with SBDS and SDS respectively.

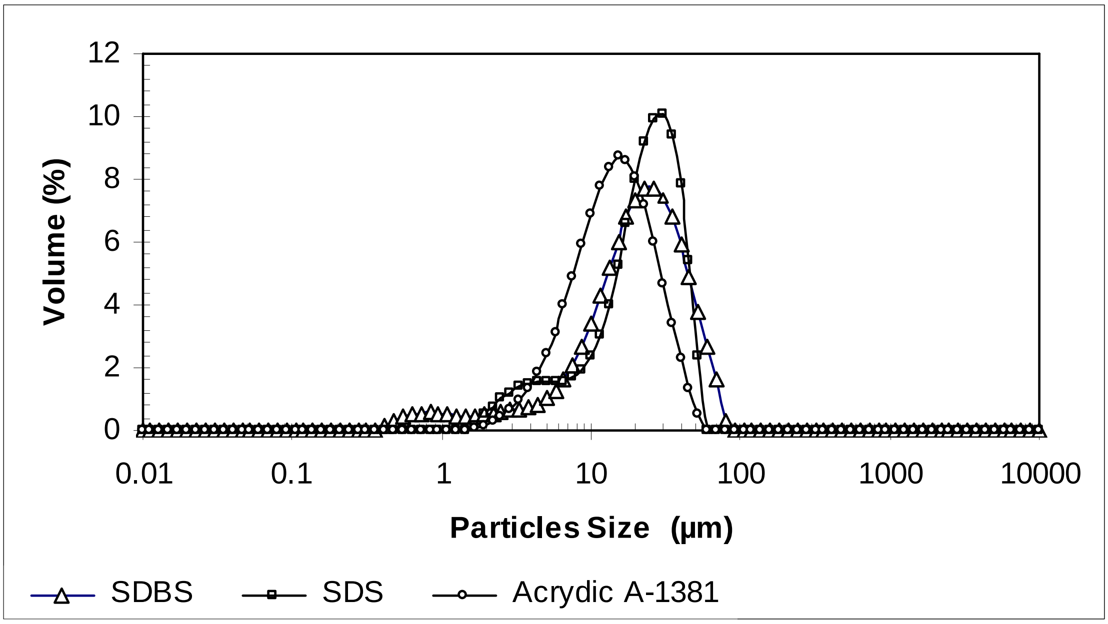


Figure 5.9 DLS measure Paticles size of Polyimde paticles in various surfactant

5.5.2 Thermal Charaterization

In Figure 5.10, the different surfactants were used according to PI4, PI5 and PI6 for SBDS, SDS and Acrydic respectively, while the other parameter was compromised. The most durable surfactant was SBDS, SDS and Acrydic respectively. The degradation temperatures of the surfactants were in the range of 200-250°C as mention before.

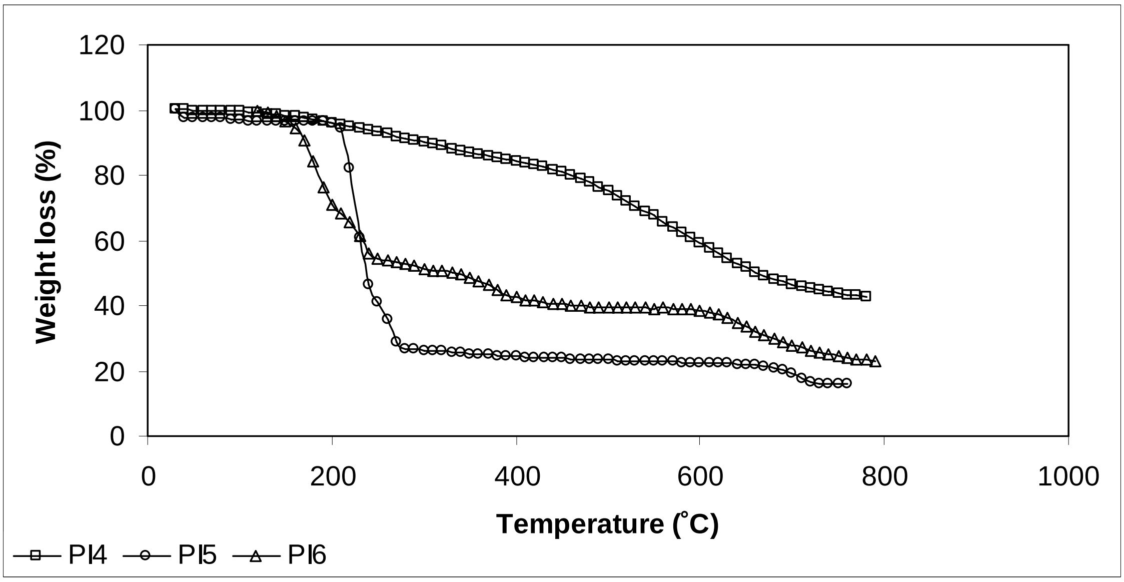


Figure 5.10 TGA curve of polyimide various surfactant in N_2

To be an example, in the sample case of PI9 in Figure 5.11, the degradations happened in two stages. The first stage is the aliphatic linkages degradation of surfactant that appeared about 200 ^{o}C and the second stage of polyimide backbone degradation appeared about 550 ^{o}C. The first layer (surfactant) degradation has lower temperature characteristic. The rest of the TGA data can be seen in appendix A.

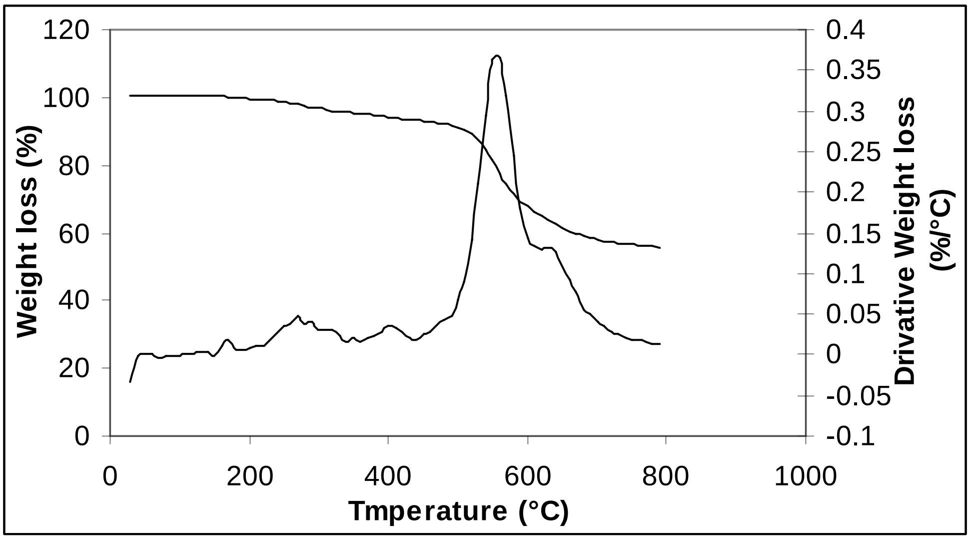


Figure 5.11 TGA curves of polyimide in N_2

5.6 Polyimide Polymerization reaction in new reactor

A result posteriori particles size of polyimide was large than expected hence the change in reactor shape and propeller blade shape were changed in order to increase the shear force exert on breaking PAA particles. The result effects on polyimide particles size were immense. The polyimide particles became smaller as can be measured with DLS.

In Figure 5.12 the average diameters of polyimide particles were 15.3, 9 and 17.5 µm correspond to hexane (old reactor with the new blade), hexane (new reactor with the new blade) and cyclohexane (new reactor with the new blade) as a poor solvent respectively.

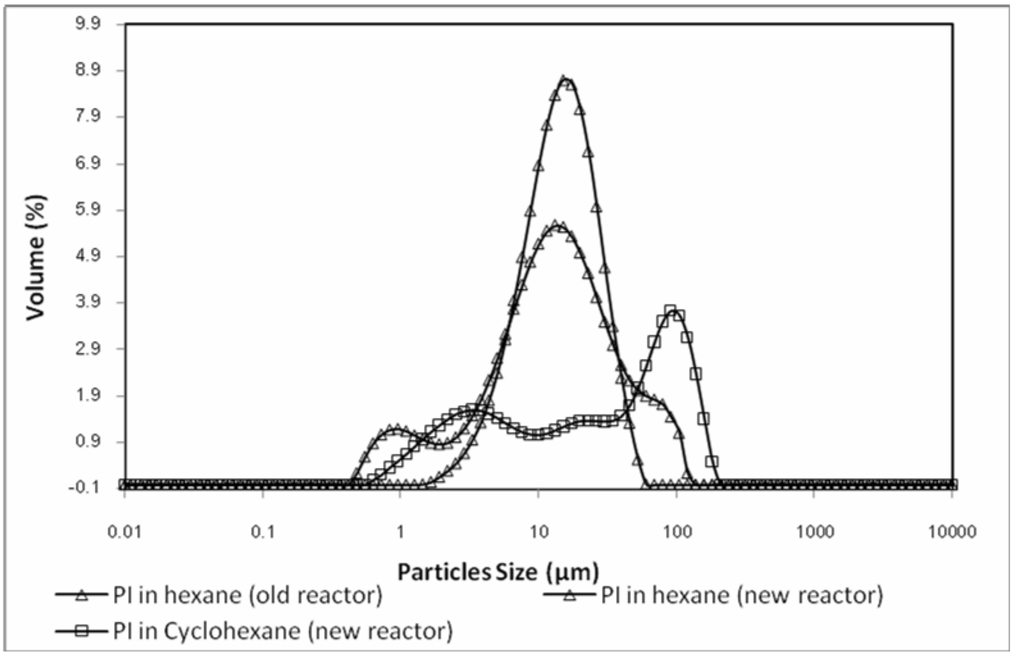


Figure 5.12 DLS measure Paticles size of Polyimde paticles in new reactor

5.7 Summary

The manufacturing of PI particles using colloid method utilizing colloid which is regarded as colloidal if the size of particles in the poor solvent falls anywhere in the range of 5-300 µm. The dianhydride of 6-FDA monomer gave the smallest particles size distribution and easiest to process compare to PMDA and BPDA respectively. In order to synthesis the polyimide paticles in the range of range 50 – 100 µm, Acrydic A-1381 gave better particles size distribution compare to sodium dodecylbenzenesulfonate. (SBDS) and sodium dodecyl sulfonate (SDS). The new reactor and the new blade resulted in smallest particles size compare with the same condition before. The temperature of the poor solvents did not affect the particles size distribution and the thermal propertied of power PI obtained. The temperature degradation of all condition can be show data in Appendix A. Time delay during the injection of chemical imidization substance for cyclodehydration of PI particles did not also affect the particles size and the thermal propertied obtained.

CHAPTER VI

CONCLUSIONS & RECOMMENDATIONS

6.1 Conclusions

In this research, the colloid synthesis polyimide properties were investigated.

6.1.1 Synthesis of polyimide of various dianhydride

The dianhydride of 6-FDA monomer gave better particles size properties and process ability compare to PMDA and BPDA respectively.

6.1.2 Synthesis of polyimide of various poor solvent

Poor solvent of hexane based polyimide paticles gave better particles size properties and process ability compare to cyclohexane.

6.1.3 Synthesis of polyimide of various type of surfactant

The choice of a good of polyimide paticles; Acrydic A-1381 gave better particles size properties compare to sodium dodecylbenzenesulfonate. (SBDS) and sodium dodecyl sulfonate (SDS).

6.1.4 Synthesis of polyimidev of time and temperature

The temperature did not change particles site and thermal propertied of PI. Time of inject chemical imidization for aliphatic linkages did not change particles size and thermal properties.

6.1.5 Polyimide polymerization reaction in new reactor

A result posteriori particles size of polyimide was larger than the produces from new reactor and the high shear blade. The extra shear forces were increased to break PAA colloid particles that affects smaller polyimide particles size as measure with DLS.

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APPENDICES

APPENDIX A

THERMOGRAVIMETRIC ANLYSIS (TGA) CHARACTERIZATION

A-1 TGA diagrams of polyimide and hyperbranch polyimide

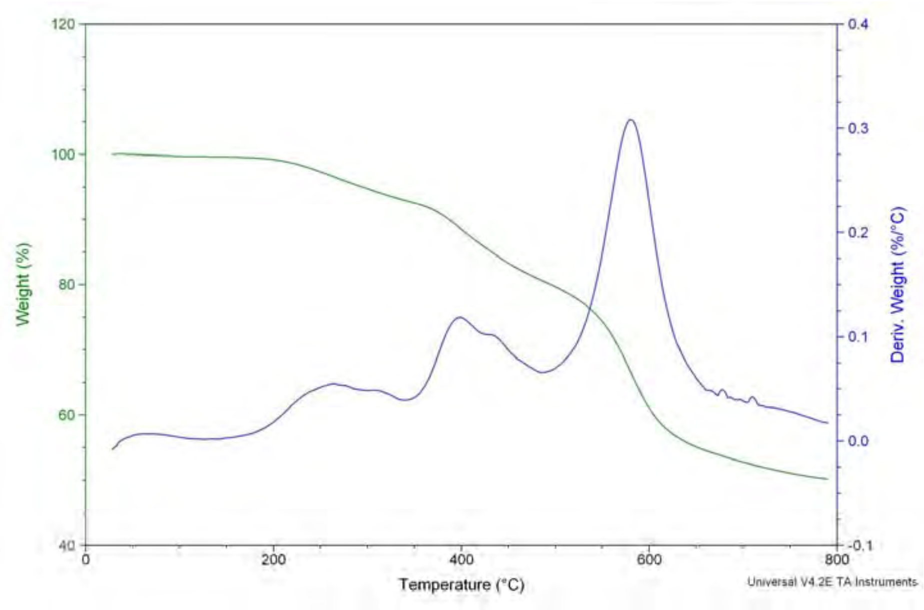

Figure A-1 Thermogravimetric analysis of polyimide 1 at rate 10°C/min, in N_2

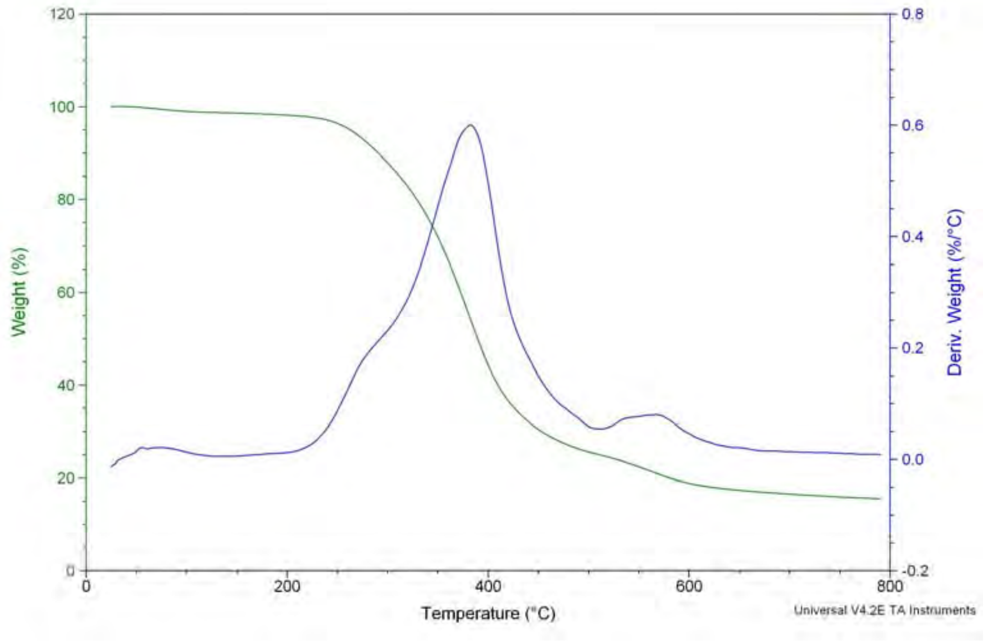

Figure A-2 Thermogravimetric analysis of polyimide 2 at rate 10°C/min, in N_2

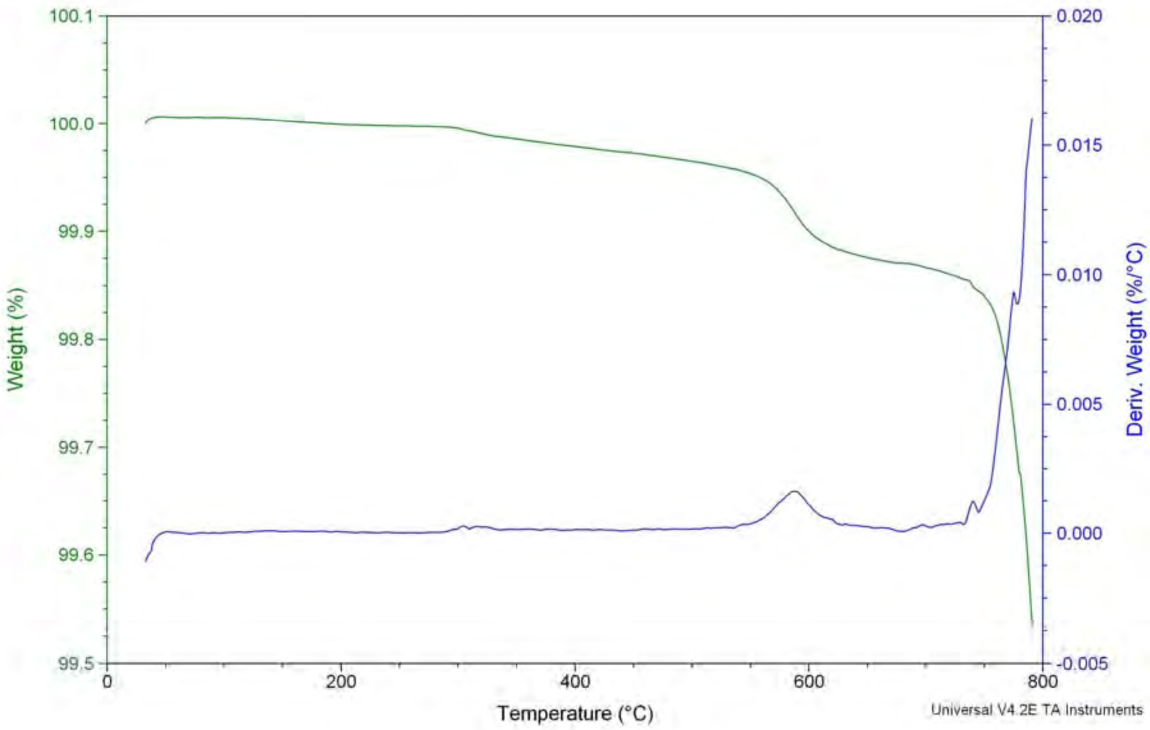

Figure A-3 Thermogravimetric analysis of polyimide 3 at rate 10^{o}C/min, in N_2

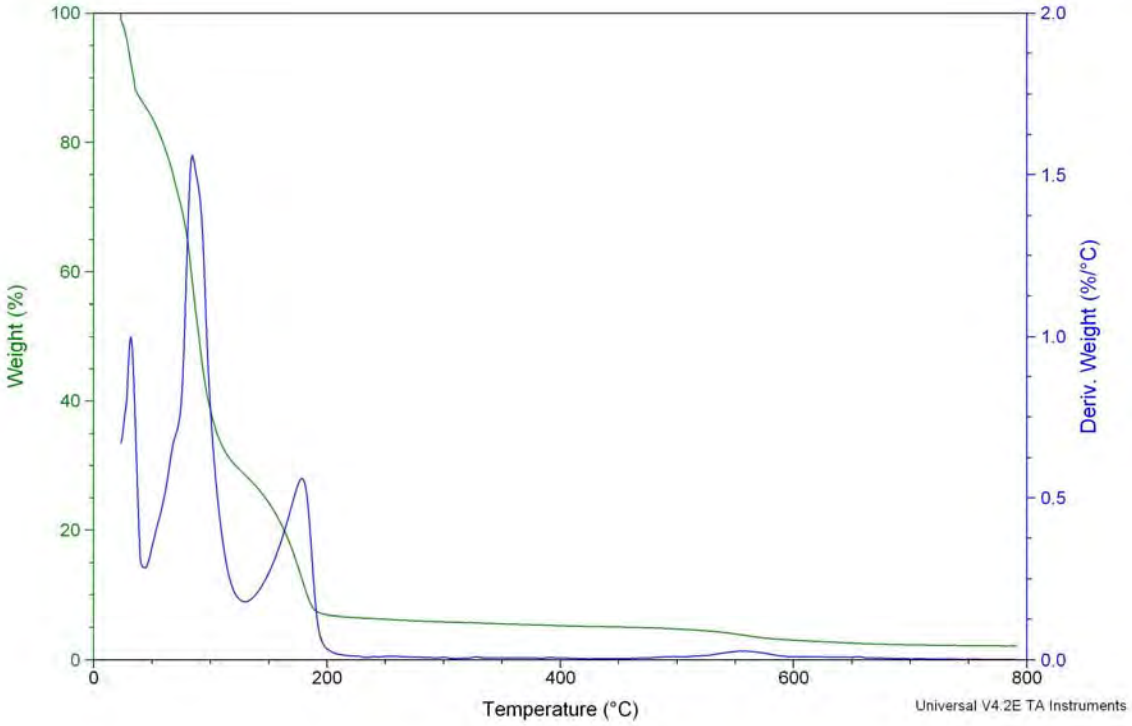

Figure A-4 Thermogravimetric analysis of polyimide 4 at rate 10^{o}C/min, in N_2

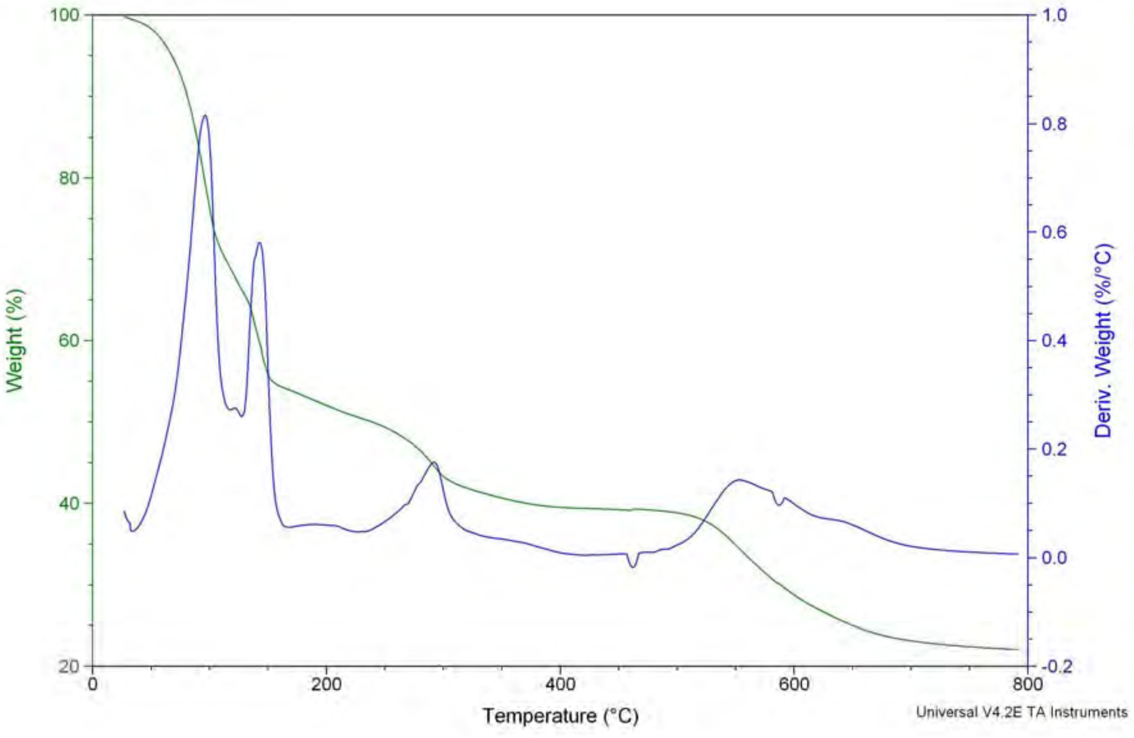

Figure A-5 Thermogravimetric analysis of polyimide 5 at rate 10^{o}C/min, in N_2

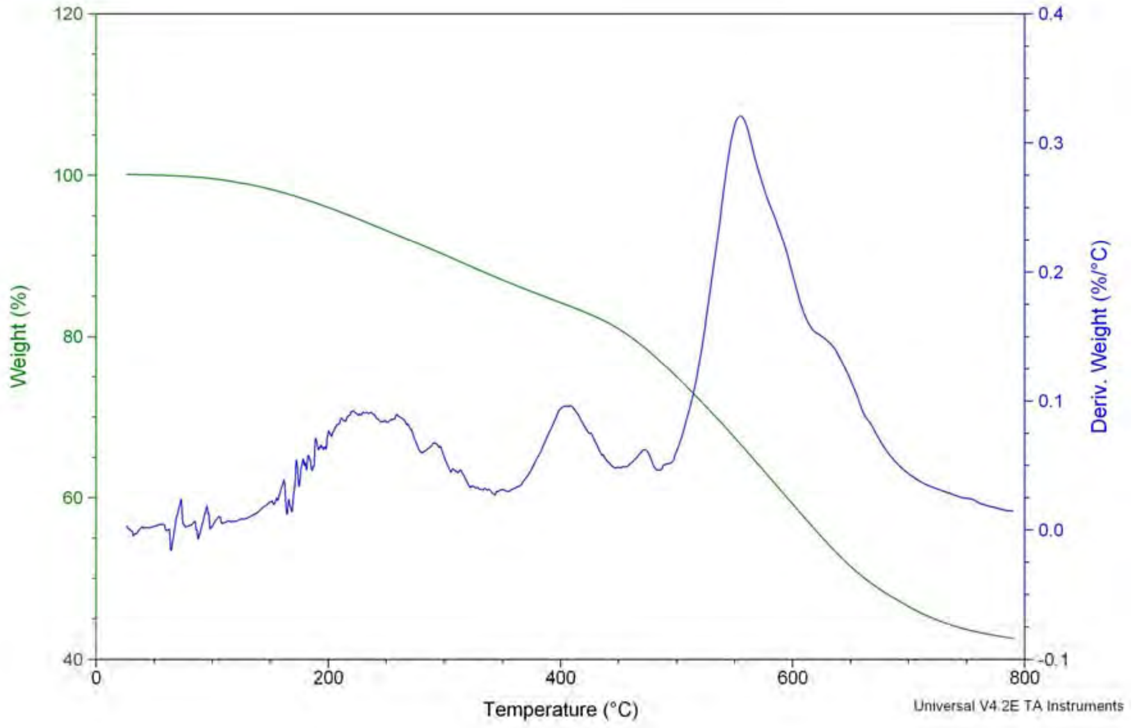

Figure A-6 Thermogravimetric analysis of polyimide 6 at rate 10^{o}C/min, in N_2

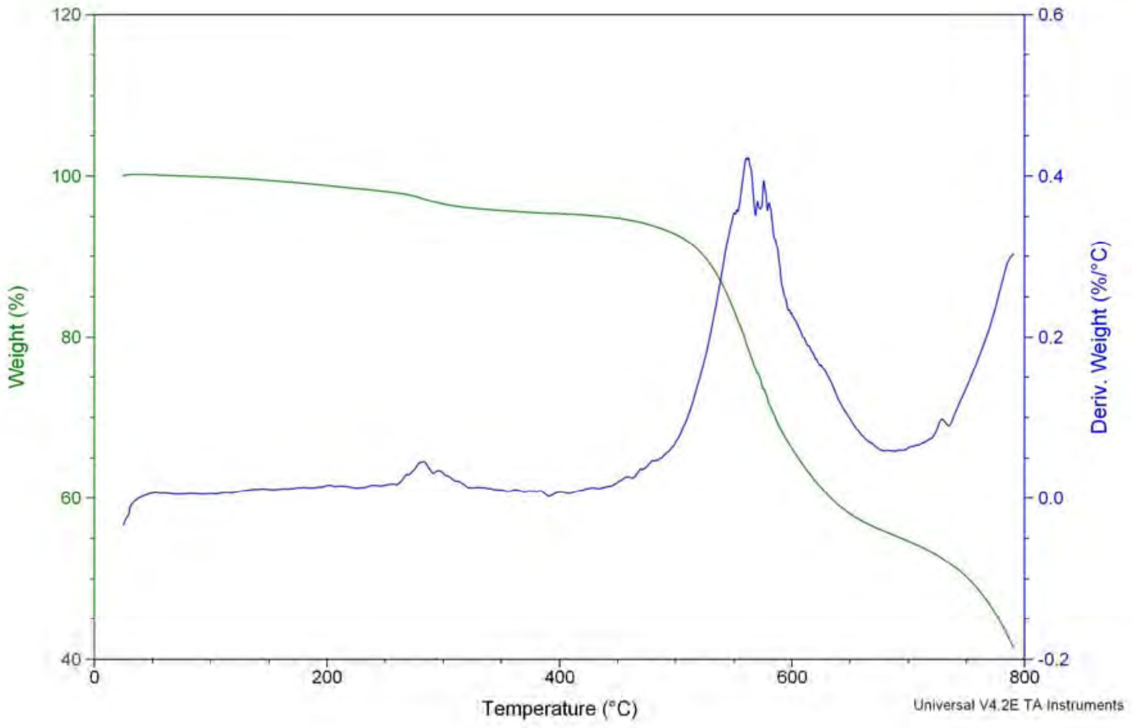

Figure A-7 Thermogravimetric analysis of polyimide 7 at rate 10^{o}C/min, in N_2

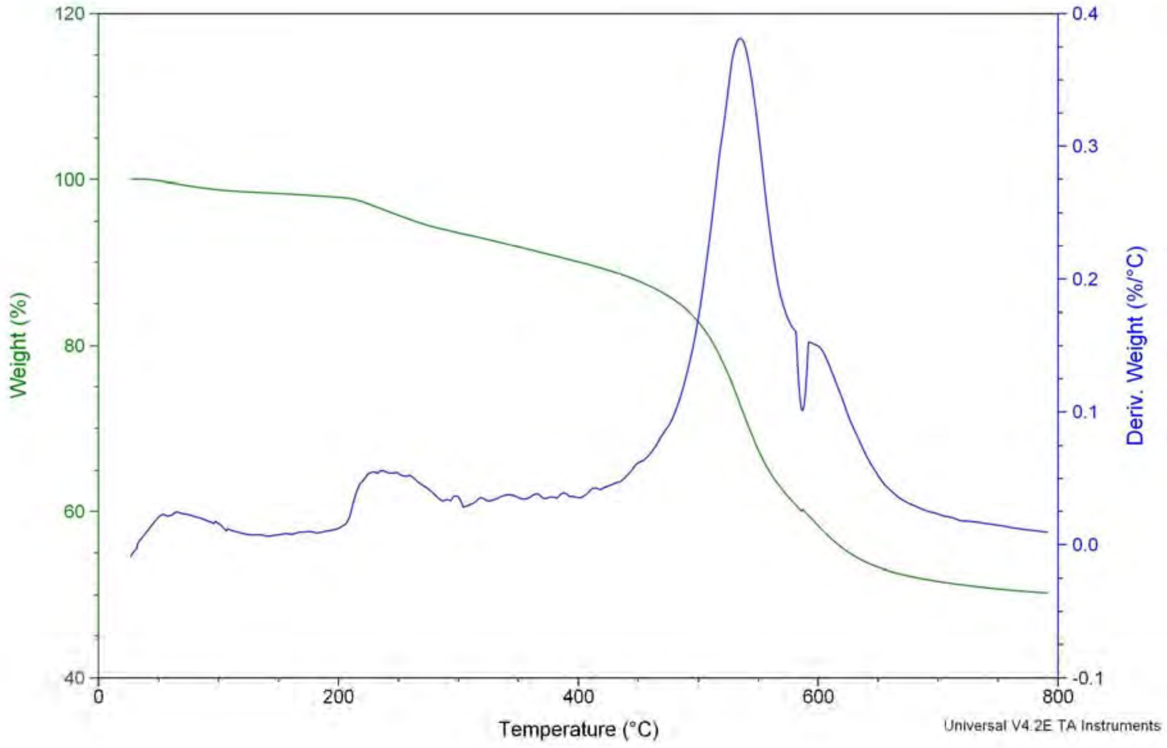

Figure A-8 Thermogravimetric analysis of polyimide 8 at rate 10^{o}C/min, in N_2

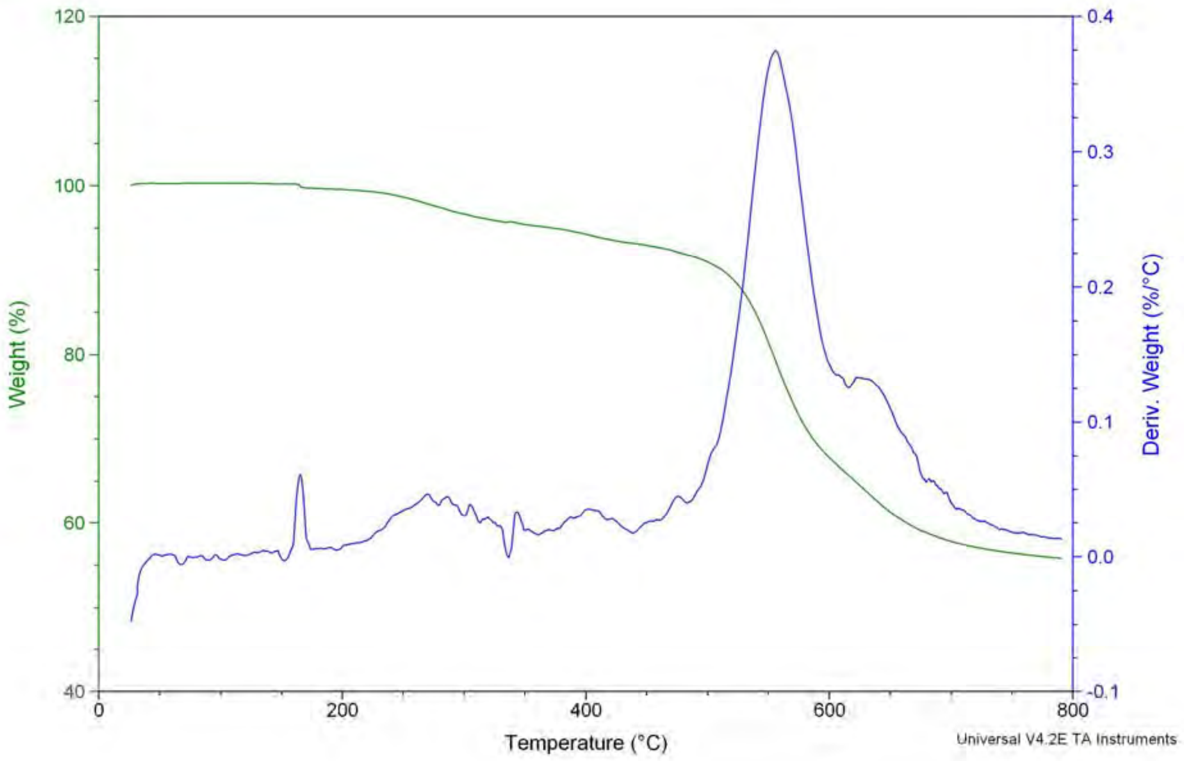

Figure A-9 Thermogravimetric analysis of polyimide 9 at rate 10^{o}C/min, in N_2

APPENDIX B

DYNAMIC LIGT SCATTERING ANLYSIS (DLS) CHARACTERIZATION

Table B-1 Data of characterized particles sized

	PI 2	**PI 4**	**PI 5**	**PI 6**	**PI 7**	**PI 9**
Size Average (µm)	127.56	17.18	16.33	367.94	96.57	16.329
Minimum Size (µm)	0.36	0.36	1.45	4.37	1.45	1.445
Maximum Size (µm)	954.99	91.20	60.26	2187.76	549.54	60.256
Average Min. Size (µm)	7.02	6.29	9.75	184.29	8.82	5.975
Average Max. Size (µm)	286.68	55.88	46.59	1592.28	184.32	34.967
Vol. Weight Meae (µm)	51.66	22.3	21.8	741.50	35.08	15.304

Figure B-1 Size distribution obtain by DLS measurement.

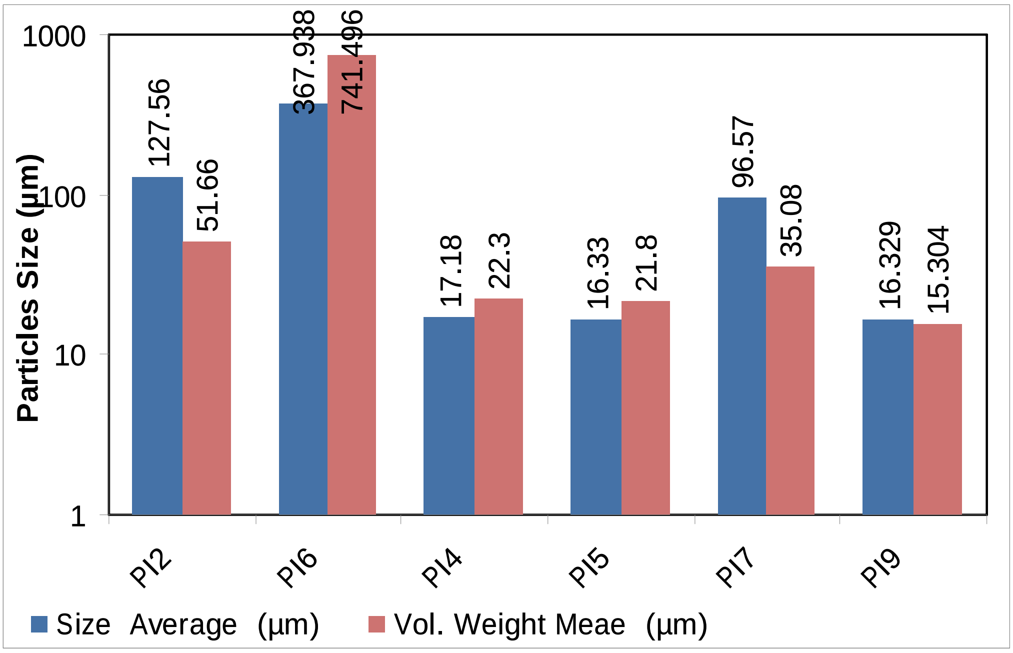

Table B-2 The molar ratios of the compositions on the reaction mixtures

Code	Molar ratio of the composition										Note
	BPDA mol (g)	**PMDAmol (g)**	**6FDAmol (g)**	**ODAmol (g)**	**NMP (ml)**	**PAA inject(ml)**	**Surfactant**	**poor solvent**	**pyridene (g)**	**propionic (g)**	
PI1	0.0025(0.7355)			0.0025(0.5006)	24.7	20	SDBS/0.05 (g)	cyclohexane	50	50	-
PI2		0.0025(0.545)		0.0025(0.5006)	20.9	20	SDBS/0.07 (g)	cyclohexane	50	50	-
PI3			0.0025(1.2709)	0.0025(0.568)	37	15	SDBS/0.07 (g)	cyclohexane	15	15	-
PI4			0.0025(1.2709)	0.0025(0.568)	37	15	SDBS/0.07 (g)	hexane	15	15	-
PI5			0.0025(1.2709)	0.0025(0.568)	37	30	SDS/0.318 (g)	haxane	30	30	-
PI6			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	40	40	-
PI7			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	cyclohexane	30	30	-
PI8			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	30	30	low temp.
PI9			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	40	40	fast imidized
PI10			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	cyclohexane	40	40	New reactor
PI11			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	40	40	New reactor

APPENDIX C

PROGRESSION REPORT “ SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE NANOPARTICLES FOR ELECTRONIC INDUCTRY”

INTRODUCTION

Polyimide (PI) particles can be used as an additive in many electrical appliance such as adhesive or insulation materials. Moreover, if the particles were coated with metal, they can be used as the conductive particles which might have many applications in electronic field. The PI particles were synthesis by colloid method, which use the good solvent such as N-methyl- 2-pyrrolidinone (NMP) to mix the polymer and the poor solvent such as carbondisulfide / hexane to disperse the colloid particles. The polyimide precursor was prepared from reaction between 4,4’-hexafluoroisopropylidenebis(phthalic anhydride) (6FDA), 4,4´- oxydianiline (ODA) and suitable amount of surfactants in NMP (good solvent), which obtain Polyamic acid (PAA) precursor solution (5 %wt in NMP). The PAA was injected to poor solvent of hexane with rigorous agitation and/or sonication to make the colloid by breaking the droplet of PAA and stabilized it in poor solvent. Then, PAA colloids were obtained and the colloid was further imidized to be PI particle by the in-situ chemical imidization of PAA colloids in the poor solution by the chemical substances. The chemical imidization substances used were the mixture of 1:1 by weight of pyridine/propionic anhydride. After the chemical imidization, the PI particles were concentrated from the solution by centrifuge. Finally, a yellow particle having average diameters of 10 to 100 μm of PI were obtained which could be confirmed by dynamic laser light scattering (DLS). The synthesized functionalized PI of the particles was confirmed by Infrared spectrum (IR). Their degradation properties were measured by Thermal Gravimetric Analysis (TGA). These results indicated the success preparation method of polyimide particle material.

THEORY

An imide is one of the chemical bond that has the general structure shown in Figure 1.

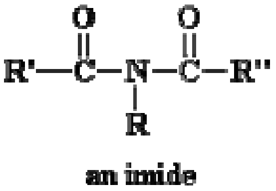

Figure 1 A structure of imide

So if the molecule shown above has polymerized, the product that contain imide repeating unit would call a polyimide. Polyimides usually take one of two forms. The first form of these is a linear structure where the atoms of the imide group are part of a linear chain. The second form of these structures is a heterocyclic structure where the imide group is part of a cyclic unit in the polymer chain has shown in Figure 2.

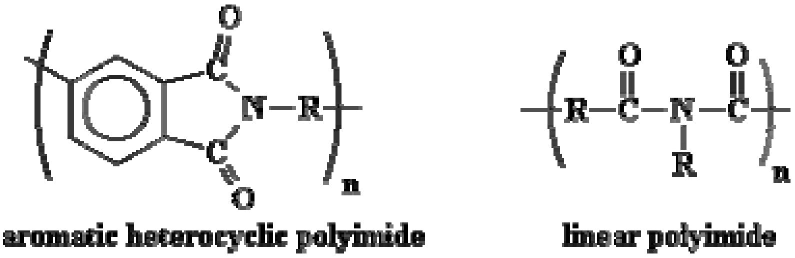

Figure 2 Two types of polyimides

Chemical imidization of polyamic acid

The cyclodehydration of polyamic acids to polyimides was preformed by the usage of propionic anhydride as a dehydration agent, that can be readily achieved by means of chemical dehydration at ambient temperature. Commonly used dehydration reagents are acid anhydrides in dipolar aprotic solvent and in the presence of tertiary amines as a catalyst. Among the dehydration agent used were acetic anhydride, propionic anhydride and others. There usually come with the amine catalyst. Among the amine catalysts used were pyridine.

Colliod method

A colloid is a type of chemical mixture where one substance is dispersed evenly throughout another. The particles of the dispersed substance are only suspended in the mixture, unlike a solution, where they are completely dissolved within. Colloids are conditionally divided into two classes *lyophilic* (good solvent) and *lyophobic* (poor solvent) respectively, depending on the ease with which the system can be redispersed if once it is allowed to dry out. The interaction between the adsorbed chains causes a repulsion that can be sufficient to induce stability. As they are forced together the number chain-chain contacts is increased at the expense of chain-solvent interactions and for a lyophilic (solvent-loving) polymer, which must lead to an increase in the free energy, or a repulsive force.

EXPERIMENT

The polymerization reactor was a 1000 ml four-neck round bottom flask. The reactor was equipped with several fittings for injecting the chemicals and purging with argon gas. A four-necked, round bottom flask equipped with an argon inlet, an ultrasonic probe, mixing impeller with mixer and a stopper valve for injection of reagent, was used as the reaction vessel which can be shown in Figure 3. The firstly, the reaction began by mixing poor solvent with surfactant under the stirrer speed of 1300 rpm for 1hr. Secondly, the polyamic aicd (PAA) precursor was injected with ultrasonic probe operated at maximum frequency while stirred for 30 min. Lastly, the chemical imidization of PAA colloids were performed by the addition of propionic anhydride (for dehydration) and pyridine (for accelerated cyclization) mixture at 1:1 ratio (30:30 ml) into the PAA dispersion colloid liquid and the reaction was proceeded for 2hr. After 2.3 hr, the ultrasonic probe was turned off while the mixture was still stirred. Finally, a yellow powder of PI particles was obtained.

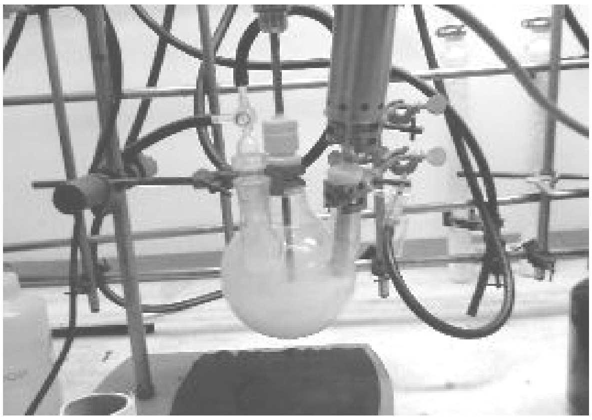

Figure 3 Reactor

Preparation of Polyamic acid (PAA) precursor

The PAA precursor, which was synthesized from various types of dianhydride and diamine (mole ratio was 1 : 1), was prepared in good solvent, NMP. The concentration of the solution was about 5%wt by volume. The solution was stirred under argon asmosphere before usage.

a) 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA)

The stock solution of PAA precursor were prepared by the addition of 1:1 mole ratio of BPDA(0.7355g) and ODA (0.5006g) into a stirring solution of NMP (24.72ml) at ambient temperature. The reaction was performed on the schlenk tube under inert atmostphere or in the glove box.

b) Pyromellitic dianhydride (PMDA)

The stock solution of PAA precursor consist of 1:1 mole ratio of PMDA (0.5453g) and ODA (0.5006g) in NMP (20.9ml) prepared at ambient temperature. The reaction was performed on the schlenk tube under inert atmostphere or in the glove box.

c) 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6-FDA)

The PAA precursor was prepared by the same way as non- fluorinate monomer. The precursor solution consist of 1:1 mole ratio of 6-FDA (1.1106g) and ODA (0.5006) in NMP (42.2ml) at ambient temperature. The reaction was performed on the schlenk tube under inert atmostphere or in the glove box.

Polyimide Polymerization

In this study, various types of poor solvents and various types of surfactant in the reaction were examined to verify the suitable substance for the reactions.

(c) Cyclohexane

The poor solvent compose of clycloheaxane (200ml), and carbon disulfide (CS_2) with the surfactant. The volume fraction of CS_2 ($\square_{CS_2}$) in the mixture of the poor solvent was 0.1 that equilibrate to mixing cyclohexane (200ml), with carbondisulfide (20ml) and suitable amount of surfactants.

(d) Hexane

The preparation of poor solvent was as same as a cyclohexane. The mixture was between hexane (200ml) and carbondisulfide (20ml) with suitable amount of surfactants.

(e) Acrydic A-1381

The amount of the donated surfactant, acrydic A-1381, was added to the poor solvent solution as above by adding acrydic A-1381 0.2 ml in CS_2 20 ml. The acrydic was donated from DIC company.

(f) Sodium Dodecylbenzenesulphonate (SDBS)

Dodecyl benzene sulfonic acid sodium salt (SDBS ; 80%) purchased from Fluka-Aldrich chemical Company, Inc. The SDBS was added at the maximum solubility of SDBS in the poor solvent that was SDBS 0.07 g in CS_2 20 ml.

(g) Sodium dodecyl sulfonate (SDS)

Sodium dodecyl sulfate (SDS ; 98.5%) purchased from Aldrich chemical Company, Inc. The SDS was added at the maximum solubility of SDS in the poor solvent, that was SDS 0.32 g in CS_2 20 ml.

RESULTS AND DISCUSSION

Study functional group of PAA and PI at different conditions

The FT-IR spectra of PAA and polyimide particles can be shown in figure 4. The FT-IR peaks of PAA were constant regardless of the various dianhydried monomers. As same as the FT-IR peaks of PI, the peaks were constant regardless of the various types of poor solvent and surfactant, but in addition, included the peaks of surfactant.

After imidization, the absorption band around 1500 cm^{-1} appeared (amide I: coupled vibration mode of N-H blending vibration and C-N stretching vibration in –CO-NH-amide moity), while features at wave number near 1750, 1380 and 1370 cm^{-1} were also observed in the FT-IR spectra correspond with imide I (stretching vibration of cyclic C=O), imide II (C-N stretching vibration) and imide IV (bending vibration of cyclic C=O) respectively, which as commonly the characteristic absorption peaks of the imide group [9]. The FT-IR spectra results indicated that the imidization reaction was completed. Moreover, these results confirmed that polyimide particles were successfully developed and could be compared with PAA precursor.

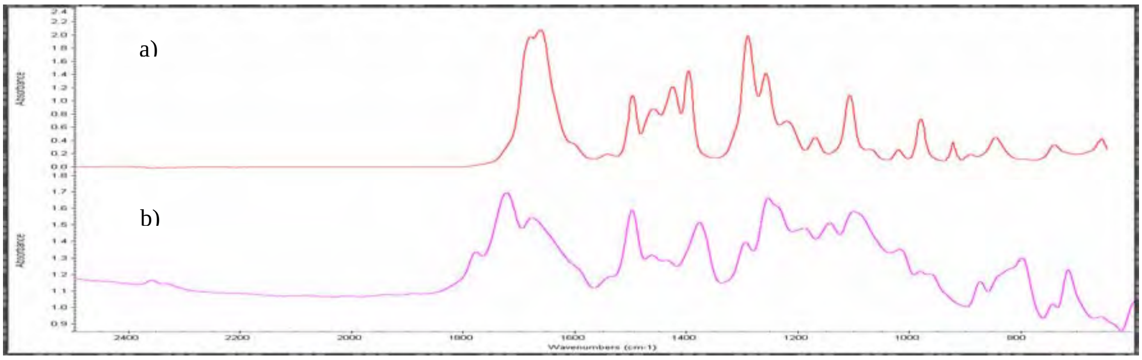

Figure 4. FTIR spectra of prepared PAA and PI particle
a) Poly (amic) acid
b) Polyimide

Dynamic Laser Light Scattering (DLS)

The DLS measurements showed the particles size distribution of samples at various type of poor solvent, surfactant and dianhydride monomer. De-ionized water used in DLS was filtered though a 0.2 μm filter to remove any large impurity particulates before the measurements. Figure 5 (a), compare the particles size of PI that prepared from various dianhydride. The PI particle that prepared from PMDA have average diameter of 50.8, but the PI particle prepared from 6-FDA have average diameter of 22.3 µm. The PI particles prepared from BPDA have very large diameters that cannot be measured particles size distribution by DLS. Figure 5 (b), indicate the particle size distribution of PI particle that prepared from various types of poor solvent. The particle sizes appeared to have average diameter of 741 and 427 µm correspond to hexane and cyclohexane as a poor solvent respectively. The particle size distribution curve of PI particles that prepared with different surfactant can be shown in Figure 5 (c). The average diameters were 22.3, 21.8 and 15.3 µm correspond to Sodium dodecyl benzene sulfonate (SBDS), Sodium dodecyl sulfate (SDS) and Acydic A-1381 respectively.

The manufacturing of PI particles using colloid method utilizing colloid which is regarded as colloidal if the size of particles in the poor solvent falls anywhere in the range of 5-300 µm. The dianhydride of 6-FDA monomer gave the smallest particles size distribution and easiest to process compare to PMDA and BPDA respectively. In order to synthesis the polyimide paticles in the range of range 50 – 100 µm, Acrydic A-1381 gave better particles size distribution compare to sodium dodecylbenzenesulfonate. (SBDS) and sodium dodecyl sulfonate (SDS). The temperature of the poor solvents did not affect the particles size distribution and the thermal propertied of power PI obtained. Time delay during the injection of chemical imidization substance for cyclodehydration of PI particles did not also affect the particles size and the thermal propertied obtained.

(a)

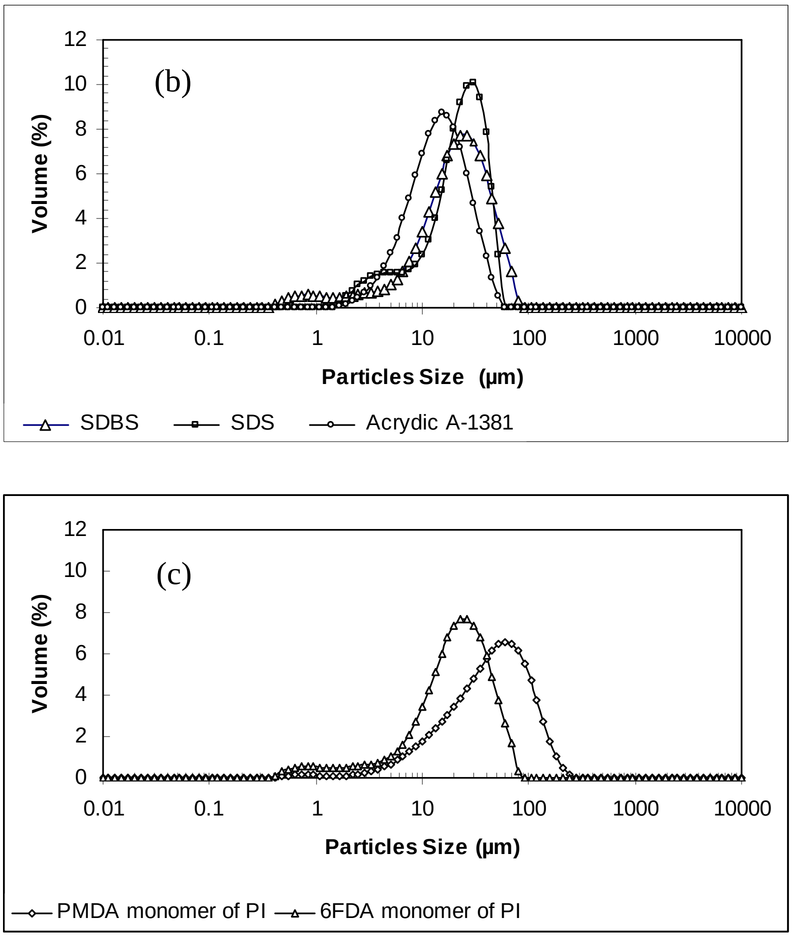

Figure 5 DLS measure Paticles size of Polyimde paticle

(a) compare type of poor solvent.(b) compare type of surfactant.(c) compare type of dianhydride.

Table 5.1 The molar ratios of the compositions on the reaction mixtures

Code	Molar ratio of the composition										Note
	BPDA mol (g)	**PMDAmol (g)**	**6FDAmol (g)**	**ODAmol (g)**	**NMP (ml)**	**PAA inject(ml)**	**Surfactant**	**poor solvent**	**pyridene (g)**	**propionic (g)**	
PI1	0.0025(0.7355)			0.0025(0.5006)	24.7	20	SDBS/0.05 (g)	cyclohexane	50	50	-
PI2		0.0025(0.545)		0.0025(0.5006)	20.9	20	SDBS/0.07 (g)	cyclohexane	50	50	-
PI3			0.0025(1.2709)	0.0025(0.568)	37	15	SDBS/0.07 (g)	cyclohexane	15	15	-
PI4			0.0025(1.2709)	0.0025(0.568)	37	15	SDBS/0.07 (g)	hexane	15	15	-
PI5			0.0025(1.2709)	0.0025(0.568)	37	30	SDS/0.318 (g)	haxane	30	30	-
PI6			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	40	40	-
PI7			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	cyclohexane	30	30	-
PI8			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	30	30	low temp.
PI9			0.0025(1.2709)	0.0025(0.568)	37	30	Acrydic A1381/0.2 (ml)	haxane	40	40	fast imidized

Thermal Charaterization

If the derivative weight of TGA were plotted (not shown here), the degradations of polyimide particles would occur in two stages. The first stage is the surfactant degradation at about 200-250 ^{o}C and the second stage is the degradation of polyimide backbone which appeared above 450-600 ^{o}C.

In Figure 6, the ingredient of the polyimide particles came from different dianhydride ie. PI1, PI2 and PI3 came from BPDA, PMDA and 6-FDA respectively. From the figrure, it clearly be seen that on the same condition of reaction (hexane as poor solvent), the fasted degradation of PI particles were 6-FDA, PMDA and BPDA respectively. The condition of the experiments can be found in Table 5.1.

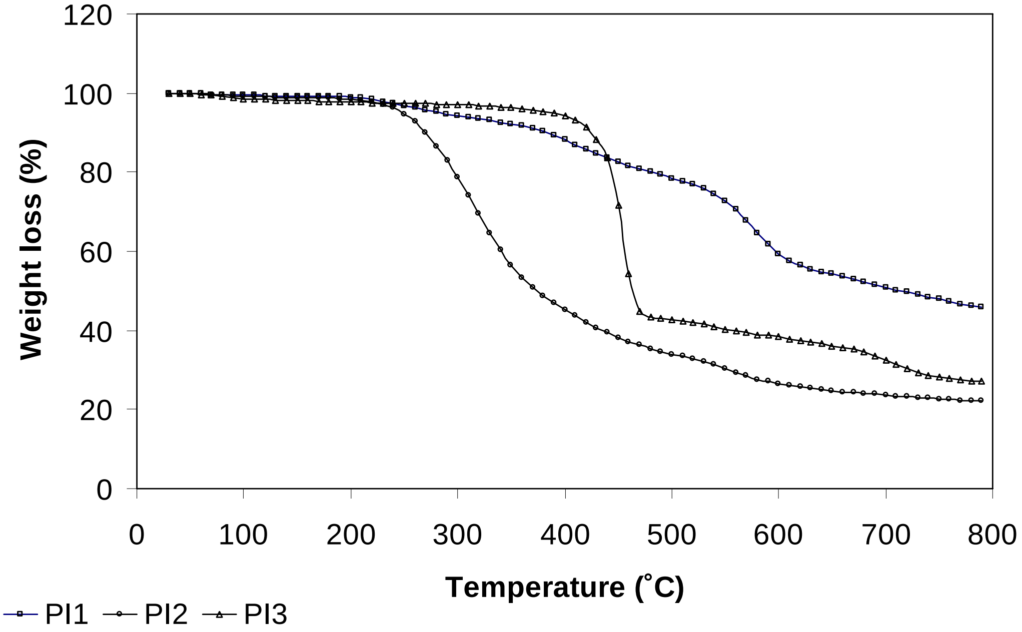

Figure 6 TGA curve of polyimide various dianhydride monomer in N_2

In Figure 7, the different surfactants were used according to PI4, PI5 and PI6 for SBDS, SDS and Acrydic respectively, while the other parameter was compromised. The most durable surfactant was SBDS, SDS and Acrydic respectively. The degradation temperature of the surfactant were in the range of 200-250°C as before.

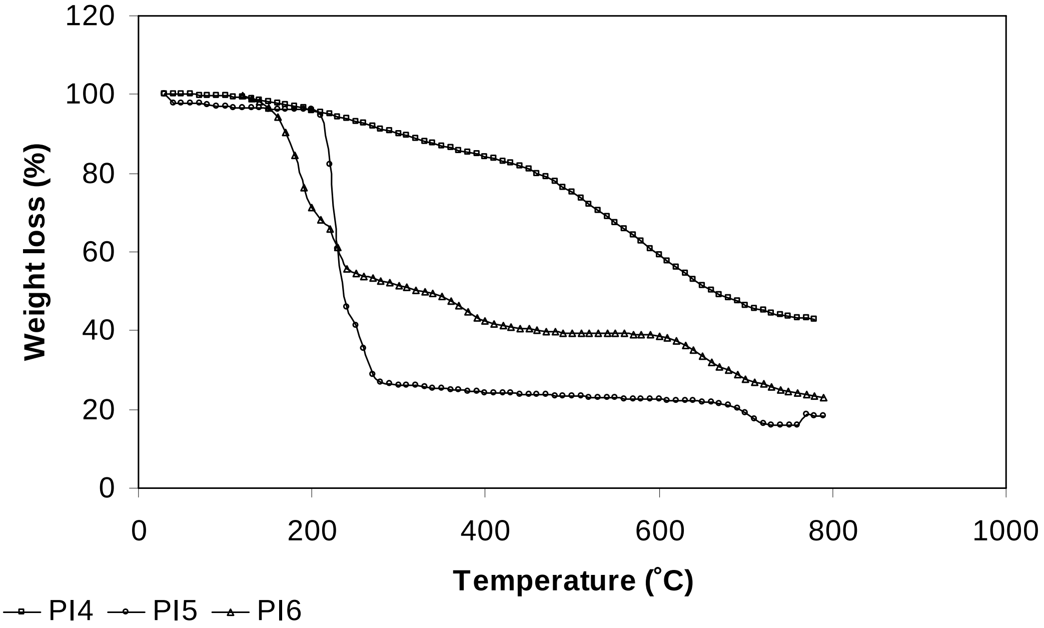

Figure 7 TGA curve of polyimide various surfactant in N_2

Figure 8 showed some interesting characteristic. All the three system were synthesis by the same material and surfactant but different condition of synthesis. The PI7 is the normal route of synthesis which gave the lowest degradation temperature and fastest degradation. But if the fast imidized cycle was applied in PI9, the degradation also occurred at about the same temperature but in less extent weight loss. Compare to the low temperature of synthesis as PI8, the degradation step are about the same (because they are made from the same material and surfactant) but least weight loss was observed.

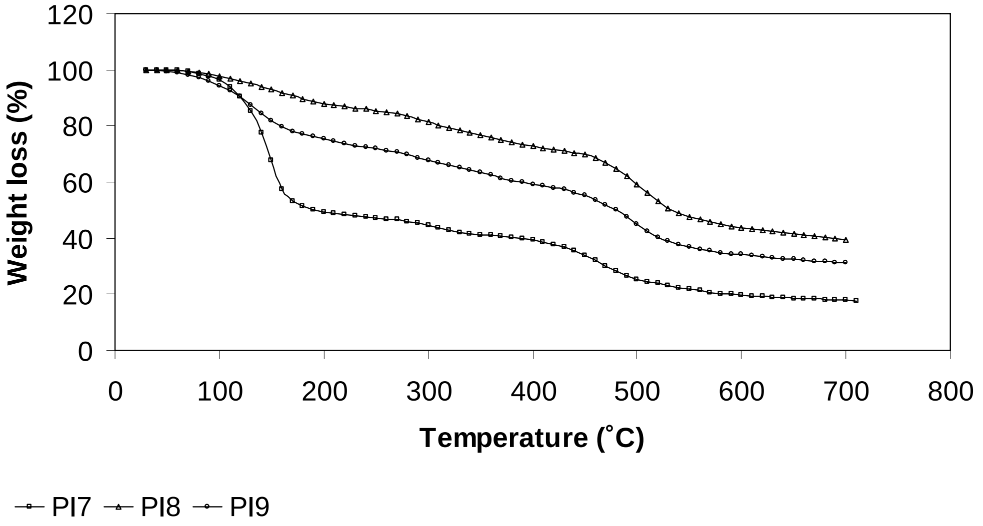

Figure 8 TGA curve of polyimide various Temperature and time of imidized in N_2

CONCLUSION

By using colloid method, the best condition that produced the smallest size particulate polyimide are by using hexane as poor solvent and use Acrydic A-1381 as surfactant with 6-FDA as the dianhydride. The reaction can be run at room temperature and insensitive to the time delay of imidization. The particle sized distribution needed to be lower by improving the reactor and the propeller blade to obtain the highest shear rate while injection of the PAA solution in the poor solvent. The temperature did not change particles site and thermal propertied of PI. Time of inject chemical imidization for aliphatic linkages did not change particles site and thermal propertied.

VITA

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