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SYNTHESIS AND CHARACTERIZATION OF CHIRAL AMIDE POSS AND POLYIMIDE

Miss Kulthida Sukchol

A Thesis Submitted in Partial Fulfillment of the Requirements
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Field of study	Chemical Engineering
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กุลธิดา สุขชล: การสังเคราะห์และวิเคราะห์คุณลักษณะของไครอลเอไมด์พอสและพอลิอิไมด์ (SYNTHESIS AND CHARACTERIZATION OF CHIRAL AMIDE POSS AND POLYIMIDE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. มล. ศุภกนก ทองใหญ่, 71หน้า

วัตถุประสงค์ของงานวิจัยนี้มุ่งเน้นที่จะศึกษาถึงการสังเคราะห์และวิเคราะห์คุณลักษณะของไครอลเอไมด์ในพอสและพอลิอิไมด์ ซึ่งเป็นการศึกษาปฏิกิริยาระหว่างหมู่เอมีนและสารไครอลทำปฏิกิริยากันเกิดเป็นหมู่เอไมด์ ดังนั้นในงานวิจัยนี้จึงเลือกใช้พอสชนิด OAPS ที่เตรียมขึ้นโดยมีหมู่เอมีนเป็นหมู่ฟังก์ชันเป็นตัวแทนในการศึกษาปฏิกิริยาระหว่างหมู่เอมีนและสารไครอลได้แก่ menthyl chloroformate และ mandelic acid จากนั้นอาศัยปฏิกิริยาที่ศึกษาได้ข้างต้นเพื่อทำการเตรียมพอลิอิไมด์ที่มีสารไครอลเป็นโซ่ข้าง พอลิอิไมด์ถูกเตรียมขึ้นได้โดยวิธี 2-steps polymerization จาก 4, 4'-6FDA, 3, 4'-ODA และ 3, 3'-4AM เป็นสารตั้งต้นในตัวทำละลาย NMP จากการทดลองนี้เราสามารถตรวจสอบโครงสร้างของ OAPS/mandelic acid amide, OAPS/menthyl chloroformate, PI4AM/mandelic acid amide และ PI4AM/menthyl chloroformate ได้จาก FTIR และ ^{1}H NMR ตรวจสอบคุณสมบัติทางความร้อนและลักษณะพื้นผิวด้วยเครื่อง TGA และ optical microscope ตามลำดับ จากผลการทดลองจะเห็นได้ว่าไครอลเอไมด์สามารถเตรียมได้โดยอาศัยปฏิกิริยาการควบแน่นของ OAPS และ polyimide กับสารไครอลทั้งสองชนิด และจากผลของ FT-IR และ NMR เป็นการยืนยันได้ว่ามีการเกิดปฏิกิริยาและมีการเชื่อมต่อกันเกิดเป็นพันธะเอไมด์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
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KULTHIDA SUKCHOL: SYNTHESIS AND CHACTERIZATION OF CHIRAL AMIDE POSS AND POLYIMIDE.
THESIS ADVISOR: ASSOC.PROF.ML.SUPAKANOK THONGYAI, Ph.D., 71pp.

The objectives of this work are to demonstrate facile routes to synthesize novel chiral molecular derivatives by reacting chiral compounds; menthyl chloroformate or mandelic acid; with octaaminophenyl silsesquioxane (OAPS) to be basic information for studying the reaction of amine functional groups and chiral compounds. Their chemical structures were confirmed by Fourrier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance spectroscopy (^{1}H NMR). A further objective is to synthesize polyimide (PI) films containing chirals in side chain. The polyimide was prepared by two steps copolymerization of 4,4´-hexafluoroisopropylidene diphthalic anhydride (6FDA), 4,4´-oxydianiline (ODA) and 3,3'-diaminobezidine (4AM) in N-methyl-2-pyrrolodone (NMP), and chemical structure of PI was confirmed by FT-IR and the texture of PI film was shown by optical microscope. Then PI containing side-chains was prepared and its chemical structure was confirmed by FT-IR and ^{1}H NMR and the texture of PI film was shown by optical microscope. It can be see that the chiral amide was prepared by condensation reaction of OAPS and polyimide with chiral compounds; mandelic acid and menthyl chloroformate. From FT-IR and ^{1}H NMR spectrum, they confirmed the functional group of amide which indicated the incorporation of OAPS and polyimide with mandelic acid or menthyl chloroformate.

Department: Chemical Engineering Student’s Signature:
Field of Study: Chemical Engineering Advisor’s Signature:
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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 a very interesting group of incredibly strong and astoundingly heat and chemical resistant polymers. Their strength and chemical resistance are so great that these materials often replace glass and metals, such as steel, in many demanding industrial applications. Polyimides are even used in many everyday applications [1]. During the past three decades since the commercialization of Kapton polyimide, many impressive varieties of polyimides have been synthesized because of both scientific and commercial interests [2]. Besides, due to excellent mechanical performance, high temperature durability, low moisture absorption, good radiation and chemical corrosion resistance as well as good adhesion to inorganic materials, polyimides (PIs) are currently used at any stage of the chain in fabrication of integrated circuits, inkjet printer heads and flexible circuitry. Alignment layers for liquid crystal display devices (LCDs) constitute now an extremely active area of research, development and production of new polyimides. [3-4].

Traditional LCDs, which adopt the rubbed parallel alignment layer to achieve uniform alignment of liquid crystals (LCs), have shown some defects, such as narrow viewing angle, low contrast ratio and slow response time [5-7]. In conventional LCDs for notebook computers and desktop monitors, twisted nematic (TN) LCDs are widely used [8]. Defect free alignment of LC molecules is a key issue in manufacturing LCDs. To realize defect free LCD, the introduction of chiral dopant is required [9].

In this study, the reaction of amine functional groups and chiral compounds were studied as basic information at the beginning. Firstly, the octa(aminophenyl) silsesquioxane (OAPS), that can be easily synthesized with amine functional groups according to procedures by Laine’s group [10], was reacted with chiral compounds in order to create chairal recognition compound. Secondly, polyimide films, that have excess amine in the main chain, were prepared by two steps polymerization. Finally, a polyimide containing chiral in side chains was prepared by the same reaction as OAPS and chiral compounds in order to fabricate twisted nematic LCDs. Lifting the degeneracy of reversely twisted nematic domain is resulted from chirality of PI surfaces that can be used instead of rubbing polyimide for twisted nematic LCDs display.

1.1 The Objectives of This Thesis

1.1.1 To study on the synthesis of OAPS.

1.1.2 To study on the reaction of amine functional groups and chiral compounds by reacting chiral compounds with OAPS**.**

1.1.3 To synthesize chiral polyimide for twisted nematic liquid crystal display.

1.2 The Scope of This Thesis

1.2.1 Synthesized octa(aminophenyl)silsesquioxane (OAPS) in two steps by nitration of octaphenyl silsesquioxane (OPS) in fuming nitric acid to form octa(nitrophenyl)silsesquioxane (ONPS). ONPS is transformed to OAPS by hydrogenation reaction.

1.2.2 Synthesized chiral molecular derivatives by reacting OAPS and menthyl chloroformate or mandelic acid.

1.2.3 Synthesized polyimide from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride(6FDA), 4,4′-oxidianiline(4,4′-ODA) and 3,3'-diaminobezidine (4AM) in N-methyl-2-pyrrolodone (NMP) by two-steps polymerization method.

1.2.4 Synthesize polyimide containing chirals in the side chains based on menthyl chloroformate or mandelic acid as chiral molecules.

1.2.5 Characterize the chiral polyimide properties by conventional techniques: FTIR, NMR TGA and optical microscope.

This thesis is divided into six chapters as follows:

Chapter I provides an overview of the chiral polyimide films and objective and scope of this thesis.

Chapter II explains the basic theory about this work such as introduction of cubic silsesquioxane, polyimide definition, type of polyimide polymerization, liquid crystal definition, liquid crystal display technique.

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

Chapter IV shows the experimental equipments and experimental procedures to synthesis octa(aminophenyl) silsesquioxane (OAPS), the reaction of OAPS and chiral compounds and polyimide films with chiral in the side chains. Including, instruments and techniques used for characterizing the resulting polymers.

Chapter V exhibits the experimental results on the synthesis of OAPS, the reaction of OAPS and chiral compounds and the preparation of chiral polyimide films.

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

CHAPTER II

THEORIES

2.1 Polyimides

Polyimides are a very strong and astoundingly heat and chemical resistant polymers. Because of their strength and heat and chemical resistance, these materials often replace glass and metals in many demanding industrial applications. Polyimides are even used in many everyday applications. They are also used in the construction of many appliances as well as microwave cookware and food packaging because of their thermal stability, resistance to oils, greases, and fats, and their transparency to microwave radiation. They can also be used in circuit boards, insulation, fibers for protective clothing, composites, and adhesives.

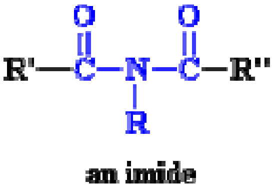
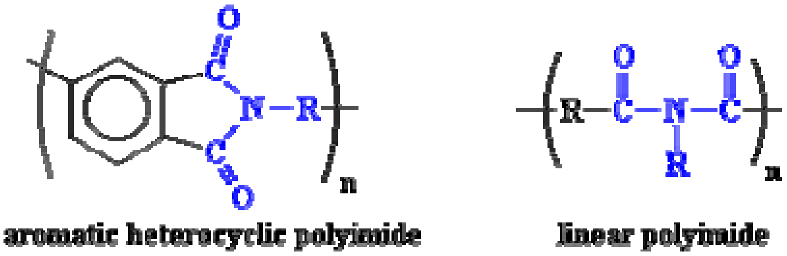


Figure 2.1 Structure of an imide group


aromatic heterocyclic polyimide

linear polyimide

Figure 2.2 Structure of types of polymide

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.

Analytical methods useful to determine the degree of chemical transformations in the solid state are limited. The most commonly used method is infrared spectroscopy. Some of the absorption bands useful for the quantitative or qualitative analysis of imidization are listed in Table 1.

Table 2.1 Infrared Absorption Bands of Imides and Related Compound

	Absorption band (cm^{-1})	Intensity	Origin
Aromatic imides	1780	S	C=0 asym. Stretch
	1720	Vs	C=O svm. Stretch
	1380	S	C-N stretch
	725		C=0 bending
Isoimides	1795-1820	S	Iminolactone
	1700	M	Iminolactone
	921-934	Vs	Iminolactone
Amic acids	2900-3200	M	COOH and NH,
	1710	S	C=O (COOH)
	1660 amide I	S	C=O (CONH)
	1550 amide II	m	C-NH
Anhydrides	1820	m	C=O
	1780	S	C=O
	720	S	C=O
Amines	~3200 two bands	W	NH, symmetrical structure (v_s) NH, asymmetrical structure (v_{as}) $v_s = 345.53 + 0.876v_{as}$

vs, very strong; s, strong; m, medium; w, weak

Several characteristic absorption bands are used for the quantification of five-membered aromatic imides. The strongest absorption occurs at 1720 cm^{-1} (C=O symmetrical stretching). However, the band partially overlaps with strong carboxylic acid band (1700 cm^{-1}, C=O) of poly(amic acid). The more useful bands of imide groups are 1780 cm^{-1} (C=O asymmetrical stretching), 1380 cm^{-1} (C-N stretching), and 725 cm^{-1} (C=O bending). The absorption of anhydrides also occurs at 1780 and around 720 cm^{-1}. When a mixture of imide and anhydride groups is analyzed, these bands may partially overlap together, requiring proper correction. The carboxylic acid bands, 1700 cm^{-1} (C=O) and 2800-3200 cm^{-1}, (OH), and amide bands, 1660 cm^{-1} (C=O, amideI), 1550 cm^{-1} (C-NH, amideII) and bands at 3200-3300 cm^{-1} (NH) often appear as broad peaks, particularly when they are strongly associated with hydrogen bonds. Nevertheless, they are useful for the qualitative assessment during imidization process.

2.2 Synthesis Method

2.2.1 One-step method

1. High-Temperature Solution 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 solvent or a mixture of solvents in a temperature range of 140-250°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 condensation water. During polymerization, water is distilled off continually as an azeotrope along with the cosolvent. 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°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°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. Gerashchenko et al. studied one-step solution polycondensation in nitrobenzene employing soluble polyimide system based on 9,9-bis(4-aminophenyl)fluorene with PMDA or 4,4'oxydiphthalic anhydride.

The kinetic profile was composed of a fast second-order reaction at initial stage and the following slow first-order reaction. The high-temperature solution imidization in nitrobenzene showed that it was a second-order reaction. Similar results were also reported by Vinogradova et al. Lavrov et al. studied imidization of a model compound N-phenylphthalamic acid to N-phenylphthalimide in various solvents. The rate profile showed an initial fast second-order kinetic and much slower second-order reaction after 40-60% conversion. The rate was slower in basic aprotic amide solvents and faster in acidic solvent, m-cresol. In general, imidization reaction has been shown to be catalyzed by acid. Kreuz et al. observed that thermal imidization of poly(amic acid)s was catalyzed by tertiary amines. High-temperature solution polymerization in m-cresol is often performed in the presence of high boiling tertiary amines such as quinoline as catalyst. Dialkylaminopyridines and other tertiary amines were effective catalysts in neutral solvents such as dichlorobenzene. Alkali metal and zinc salts of carboxylic acids and salts of certain organophosphorus compounds were also very efficient catalysts in one-step polycondensation of polyimides.

2. Low-Temperature Solution Polymerization

Kim and Moore synthesized a dicyanomethylidene derivative of phthalic anhydride, as shown in Figure 2.3. The compound reacted with aniline in NMP to produce an intermediate of amic acid analog that gradually transformed during 24 h at room temperature to N-phenylphthalimide, co producing malonitrile as condensation byproduct. Subsequently, bis(dicyanomethylidene) derivative of PMDA and ODA were reacted in NMP to afford poly(amic acid) analog intermediate, which underwent partial imidization at room temperature in the homogeneous solution, as illustrated in Figure 2.4.

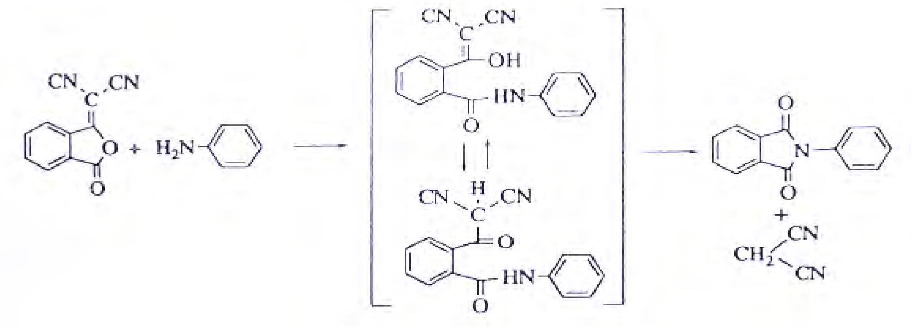


Figure 2.3: Reaction of dicyanomethylidenephthalide with aniline

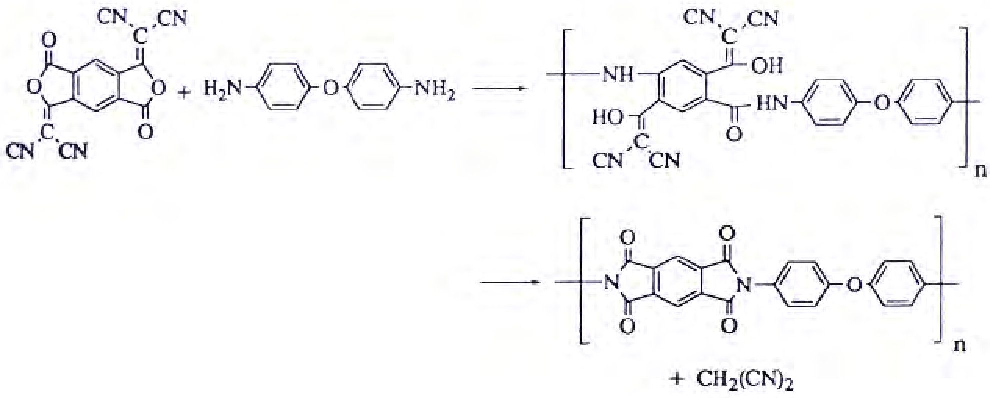


Figure 2.4: Polymerization of bisdicyanomethylidene derivative of PMDA with ODA

The extent of imidization reached approximately 75% over 24 h, after which time the polymer began to precipitate. The solid-state imidization of films prepared from the poly(amic acid) analog intermediate behaved similarly to that of poly(amic acid). However, the imidization could be achieved at lower temperature; it was nearly complete at 120°C in 20 h.

2.2.2 Two-step method via poly(amic acids)

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. Figure 2.5 presents 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 namely Du Pont’s Kapton^{TM} and it is still the method of choice in majority of applications.

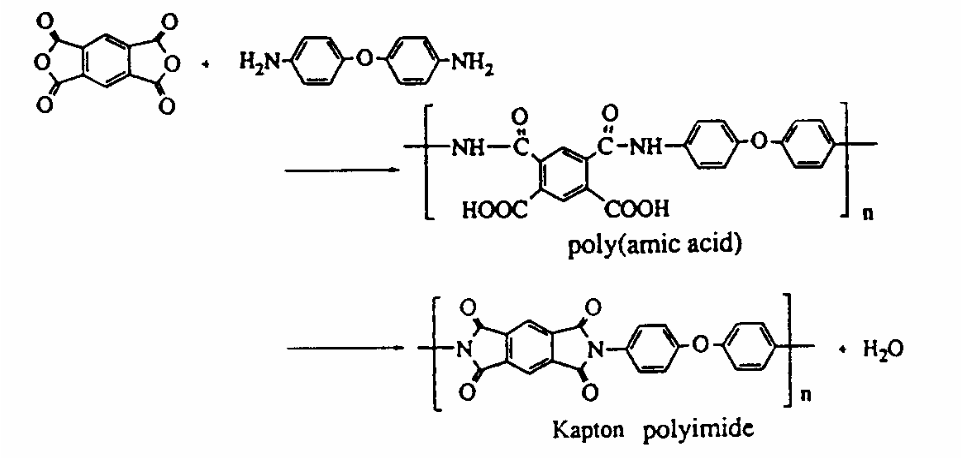


Figure 2.5: Preparation of Kapton polyimide

The two-step poly(amic acid) process is the most commonly practiced procedure of making polyimides. In this process ,a dianhydride and a diamine react at ambient temperature in a dipolar aprotic solvent such as N-methyl-2-pyrrolidinone (NMP) or N,N dimethylacetamide (DMAc) to form a poly(amic acid) ,which is then cyclized into the polyimide product. The reaction of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) and 4,4′-diaminodiphdiphenylether (ODA) proceed rapidly at room temperature to form a viscous solution of poly(amic acid), which is an ortho-carboxylated aromatic polyamide.

Poly(amic acid)s are shaped into articles such as films and fibers by removal of solvent. The shaped poly(amic acid) films, for example, are thermally or chemically converted to the final polyimide products. The conversion produces water as a by-product. Because water must be removed during this in-situ imidization, the process is generally suitable only for the preparation of thin object such as films. The arrows in poly(amic acid) structure denote isomerism (Figure 2.6), indicating that the main chain is composed of mixture of 1,3 and 1,4-phenylenebisamide linkages.

1. Formation of Poly(amic acid)

When a diamine and a dianhydride are added into a dipolar aprotic solvent such as N,N-dimethylacetamide, poly(amic acid) is rapidly formed at ambient temperatures. The reaction mechanism involves the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group, followed by the opening of the anhydride ring to form amic acid group as illustrated in Figure 2.5.

The most important aspect of this process is that it is an equilibrium reaction [28-29]. 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 acids).

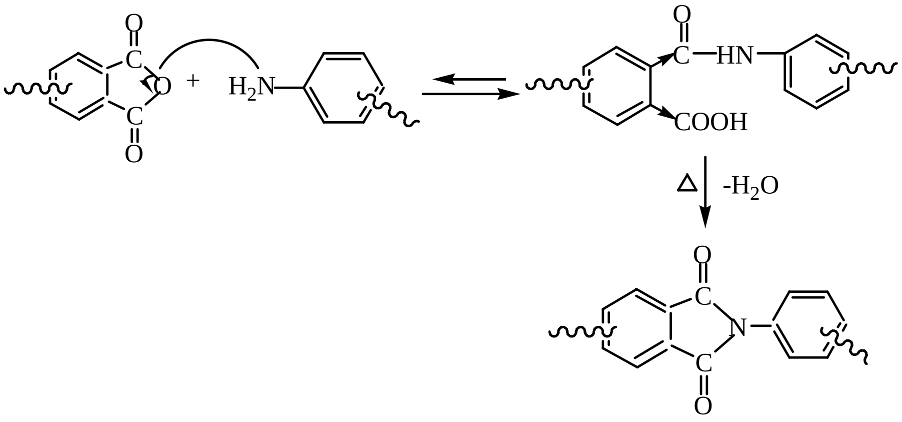


Figure 2.6:Reaction mechanism of imide formation

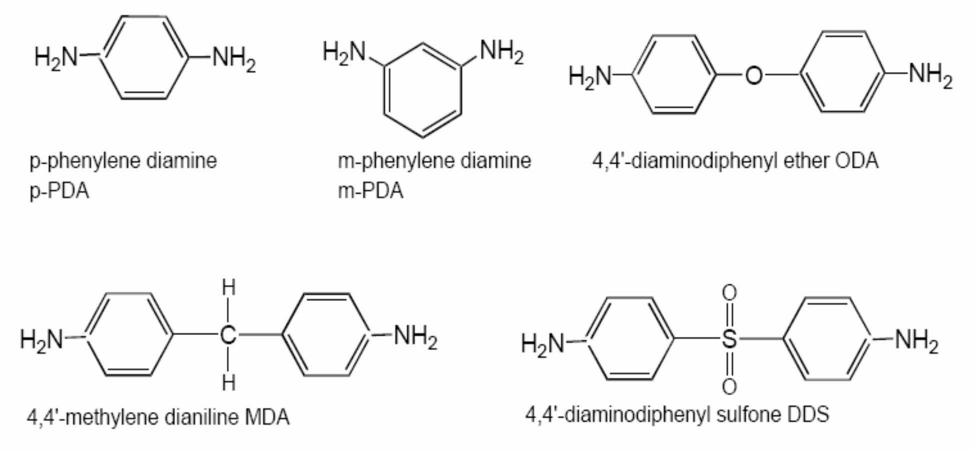


Figure 2.7: Commonly used diamine monomers

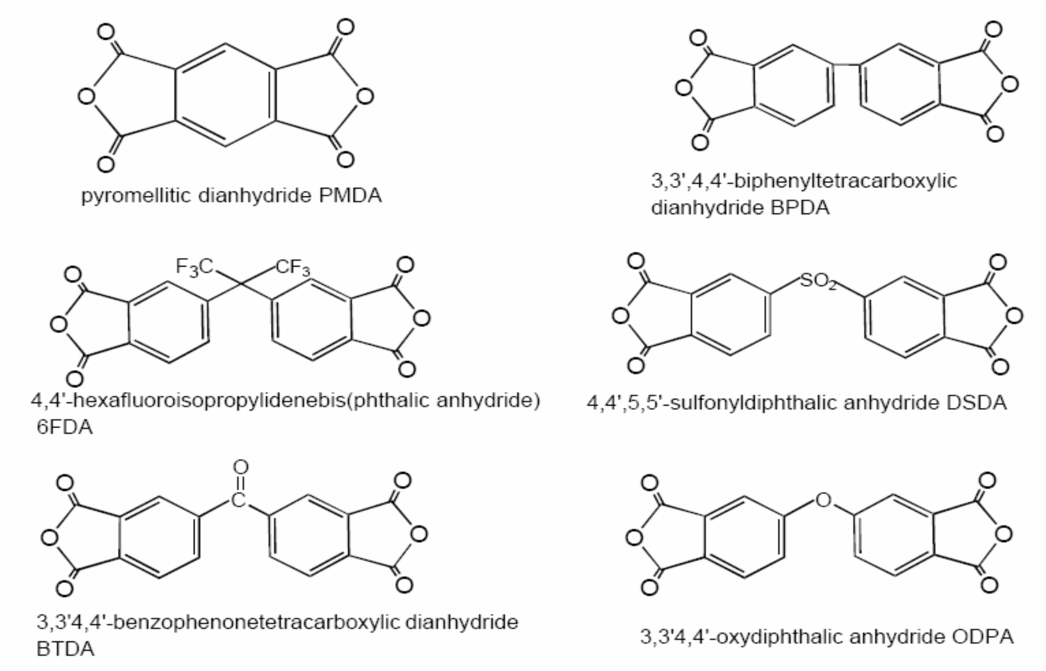


Figure 2.8: Commonly used dianhydride monomers

2. Thermal Imidization of Poly(amic acid)

Conversion of poly(amic acid)s to the corresponding polyimides is most commonly performed thermally in “solid state”. This method is suitable for preparation of thin objects such as films, coatings, fibers, and powders in order to allow the diffusion of by-product and solvent without forming brittles and voids in the final polyimide products. The cast films are dried and heated gradually up to 250-350^{o}C, depending upon the stability and glass transition temperature (T_g) of the polymer. Too rapid a heating may cause the formation of bubbles in the sample. When a DMAc solution of poly(amic acid) is cast and “dried” at ambient temperature to a nontacky state, the resulting film still contains a substantial amount of the solvent (typically up to 25% by weight, depending on the drying conditions). In the subsequent heating, imidization reaction takes place not in a true solid state but rather in a very concentrated viscous solution, at least during the initial and the intermediate stages of thermal imidization. The presence of residual solvent plays an important role in the film forming behaviors. The imidization proceeds with faster rate in the presence of dipolar amide solvents. The observation is attributed to the specific solvation to allow the favorable conformation of amic acid group to cyclize. It may also be explained by the plasticizing effect of the solvent to increase the mobility of the reacting functional groups. The favorable property of amide solvent also suggests that its basicity to accept protons may be responsible for the specific effect. The proton of the carboxylic group is strongly hydrogen-bonded to the carbonyl group of the amide solvent. The cyclization of o-carboxyaminde group results in dehydrogen bonding and release of the solvent molecule along with water of condensation. The thermal imidization process of poly(amic acid)s is complex. It is normally unlikely to describe the thermal imidization reaction by simple kinetic expression as the process typically involves several interrelated elementary reactions.

3. Mechanism of Chemical Imidization

The kinetic study of model compounds revealed that isoimides and imides are formed via a mixed-anhydride intermediate (7), which is formed by acylation of the carboxylic group of amic acid (6), as illustrated in Figure 2.9.

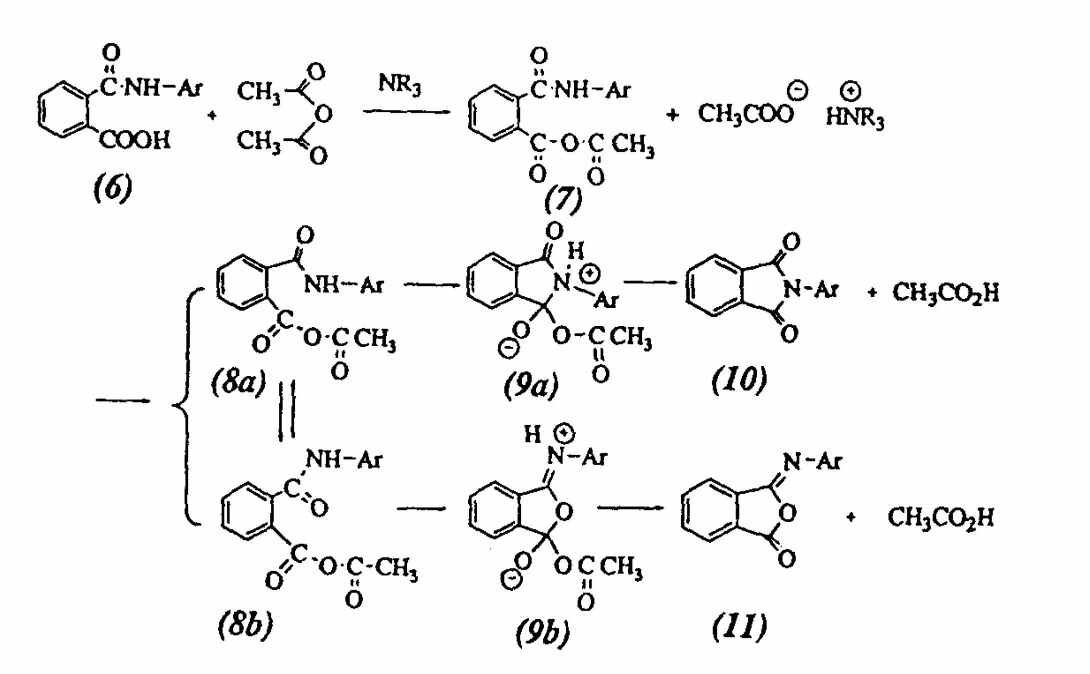


Figure 2.9: Mechanism involved in chemical dehydration of amic acid. R, ethyl;Ar;phenyl

The presence of the intermediate mixed-anhydride was detected by IR as well as proton nuclear magnetic resonance (NMR). Convincing evidence was also presented when di- functional acid chloride such as sebacoyl chloride was used instead of acetyl chloride for cyclization of poly(amic acid). The solution viscosity temporarily increased during the reaction because of the interchain mixed-anhydnide formation. The viscosity gradually decreased back to the normal level as the cyclization proceeded. Imides are formed by intramolecular nucleophilic substitution at the anhydride carbonyl by the amide nitrogen atom *(8a-9a)*, while isoimides are formed as a result of substitution by the amide oxygen *(8b-9b)*. The cyclization of N-phenylphthalamic acids with acetic anhydride proceeds smoothly at room temperature in DMAc in the presence of a tertiary amine. The amine acts as a catalyst as well as an acid acceptor. Use of a less than stoichiometric amount of amine still leads to completion of the reaction, only at a slower rate. Use of triethylamine (pk_a 10.6) as a catalyst produced exclusively normal imides. However, a mixture of imide and isoimide was formed when less basic pyridine (pk_a 5.2) was used as a catalyst.

2.3 Polyhedral oligomeric silsesquioxanes (POSS)

Polyhedral oligomeric silsesquioxanes (sometimes abbreviated POSS) is a hybrid organic/inorganic nano-material that comprise Silica cage linked with carbon molecules and usually made with 8 Silica atoms at the cubic corners that also linked with benzene as the corner ligands as shown below figure.

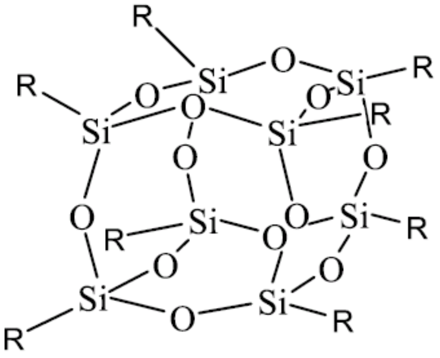


Figure 2.10: Diagram showing the chemistry of POSS

POSS frameworks have been reported with synthetically useful functional groups. They are most often prepared via hydrolytic condensation reactions of trifunctional organosilicon monomers, e.g., $RSiCl_3$ or $RSi(OMe)_3$.

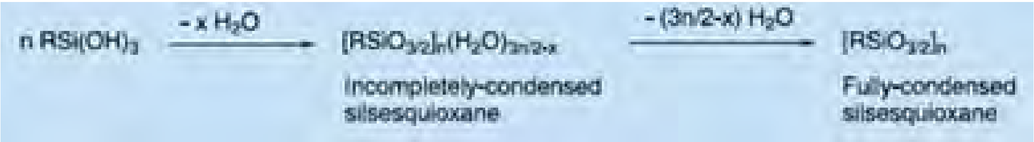


Figure 2.11: Diagram showing the process for preparing POSS frameworks using the hydrolytic condensation reactions of trifunctional organosilicon monomers**.**

The structures of the POSS frameworks depend a great deal on the method of their preparation. They are uniquely sensitive to a highly interdependent combination of experimental factors, including product solubilities, initial monomer concentration, nature and stability of the solvent, temperature, pH, the amount of free water available, and the type of catalyst (acid or base) used to facilitate condensation. Careful hydrolysis leads to well-defined, fully condensed, prismatic, POSS structures T_8^R, T_{10}^R, T_{12}^R (Figure 2.12)

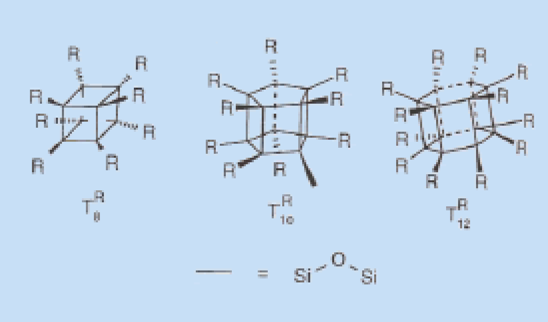
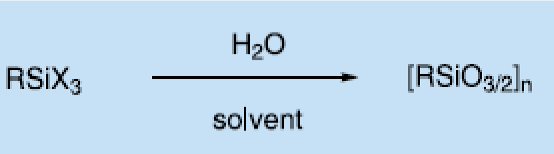


Figure 2.12: Diagram showing the fully condensed and prismatic POSS structures, T_8^R, T_{10}^R, T_{12}^R

POSS Precursors ($RsiX_3$) and Intermediates

POSS frameworks may be prepared using trifunctional organosilicon monomers or POSS silanols.



$$RSiX_3 \xrightarrow[\text{solvent}]{H_2O} [RSiO_{3/2}]_n$$

Figure 2.13: Diagram showing how POSS frameworks may be prepared using trifunctional organosilicon monomers or POSS silanols.

POSS Polymers - Polymerization/Grafting Methods, Physical Properties and Processing Techniques

POSS monomers can be polymerized or grafted using standard techniques to yield inorganic-organic hybrid homopolymers and copolymers. As illustrated below in Figure 2.14, the size of the pendant POSS cage is comparable to the dimensions of the linear polymer, enabling POSS to control the motions of the chains at the molecular level. Thus, an enhancement in the physical properties is observed, while the processability and mechanical properties of the base resin are retained. POSS copolymers are typically soluble in THF and toluene. Using both solution and melt techniques, they can be processed into fibers, foams, films, and monolithic pieces.

Figure 2.14: Diagram showing the size of the pendant POSS cage

Octa(aminophenyl) silsesquioxane (OAPS)

Octahedral or cubic silsesquioxanes (cubes) and the related polyhedral oligomeric silsesquioxanes (POSS) offer one solution to the need in that the providing the opportunity to design and construct materials with extremely well-defined dimensions and behavior. There are many variety of octafunction cubes with polymerizable moieties. The synthesis of octa(aminophenyl) silsesquioxane, an aromatic amine-functionalized silsesquioxane free from aliphatic components.

2.4 Liquid Crystals

Liquid crystals are materials in an intermediate state of aggregation between the solid state and the conventional isotropic liquid phase. Unlike normal solids, mesogenic materials melt to form highly anisotropy fluids in which a significant part of the molecular order is retained. Upon heating, these solids melt and form viscous fluids exhibiting birefringence and anisotropic physical properties.

2.4.1 Liquid crystal phases

Liquid crystals are divided into two major categories: thermotropic liquid crystals whose properties change with temperature and lyotropic liquid crystals that are multicomponent mixtures in solution. Thermo rod-shaped organics compounds are subdivided into three distinctive structural categories: the smectic, nematic and cholesteric edifices. However, cholesteric substances are sometimes presented as a subclass of nematic liquid crystals. The simplified design of Fig.2.15 shows that these structures differ by the nature of the residual molecular order achieved in the temperature range of liquid crystallinity.

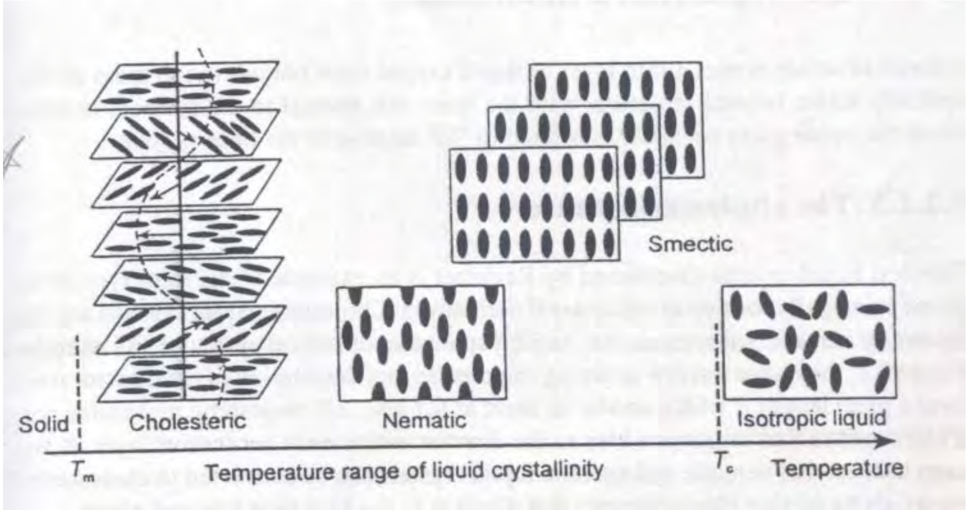


Figure 2.15: Phase structures of thermotropic liquid crystals between first melting temperature and clearing temperature

Thermotropic liquid crystals

1. The smectic phase

The smectic phases, which are found at lower temperatures than the nematic, form well-defined layers that can slide over one another like soap. The smectics are thus positionally ordered along one direction. In the Smectic A phase, the molecules are oriented along the layer normal, while in the Smectic C phase they are tilted away from the layer normal. These phases are liquid-like within the layers. There is a very large number of different smectic phases, all characterized by different types and degrees of positional and orientational order.

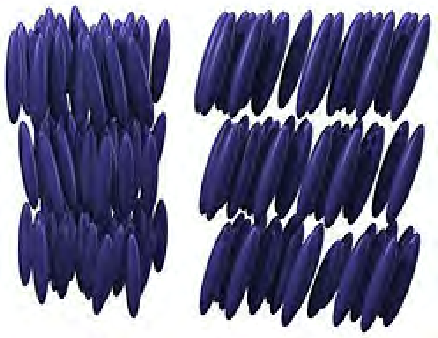


Figure 2.16: Schematic of mesogen alignment in the smectic phases.

2. The nematic phase

One of the most common LC phases is the nematic, where the molecules have no positional order, but they have long-range orientational order. Thus, the molecules flow and their center of mass positions are randomly distributed as in a liquid, but they all point in the same direction (within each domain). Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent (can be approximated as cylinders). Some liquid crystals are biaxial nematics, meaning that in addition to orienting their long axis, they also orient along a secondary axis. The word *nematic* comes from the Greek, which means 'thread.' This term originates from the thread-like topological defects observed in nematics, which are formally called 'disclinations'. Nematics also exhibit so-called hedgehog topological defects. Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can be easily aligned by an external magnetic or electric field. An aligned nematic has the optical properties of a uniaxial crystal and this makes them extremely useful in liquid crystal displays (LCD).

Figure 2.17: Schematic of mesogen ordering in a nematic phase.

3. The cholesteric phase

The chiral nematic phase exhibits chirality (handedness). This phase is often called the *cholesteric* phase because it was first observed for cholesterol derivatives. Only chiral molecules (i.e., those that lack inversion symmetry) can give rise to such a phase. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director. The finite twist angle between adjacent molecules is due to their asymmetric packing, which results in longer-range chiral order. In the smectic C* phase (an asterisk denotes a chiral phase), the molecules have positional ordering in a layered structure (as in the other smectic phases), with the molecules tilted by a finite angle with respect to the layer normal. The chirality induces a finite azimuthal twist from one layer to the next, producing a spiral twisting of the molecular axis along the layer normal.

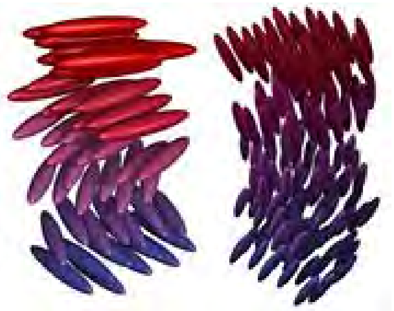


Figure 2.18: Schematic of mesogen ordering in chiral liquid crystal phases.

Lyotropic liquid crystals

A lyotropic liquid crystal consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic liquid crystals, these lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases. A compound which has two immiscible hydrophilic and hydrophobic parts within the same molecule is called an amphiphilic molecule. Many amphiphilic molecules show lyotropic liquid-crystalline phase sequences depending on the volume balances between the hydrophilic part and hydrophobic part. These structures are formed through the micro-phase segregation of two incompatible components on a nanometer scale. Soap is an everyday example of a lyotropic liquid crystal. The content of water or other solvent molecules changes the self-assembled structures. At very low amphiphile concentration, the molecules will be dispersed randomly without any ordering. At slightly higher (but still low) concentration, amphiphilic molecules will spontaneously assemble into micelles or vesicles. This is done so as to 'hide' the hydrophobic tail of the amphiphile inside the micelle core, exposing a hydrophilic (water-soluble) surface to aqueous solution. These spherical objects do not order themselves in solution, however. At higher concentration, the assemblies will become ordered. A typical phase is a hexagonal columnar phase, where the amphiphiles form long cylinders (again with a hydrophilic surface) that arrange themselves into a roughly hexagonal lattice. This is called the middle soap phase. At still higher concentration, a lamellar phase (neat soap phase) may form, wherein extended sheets of amphiphiles are separated by thin layers of water. For some systems, a cubic (also called viscous isotropic) phase may exist between the hexagonal and lamellar phases, wherein spheres are formed that create a dense cubic lattice. These spheres may also be connected to one another, forming a bicontinuous cubic phase.

2.4.2 Twisted nematics

The twisted nematic device is formed of a liquid crystal layer homogeneously aligned on two glass substrates that are twisted by 90°. As shown in Figure 2.19, this structure rotates the nematic director and, accordingly the plane of polarization of light from one boundary surface to the other.

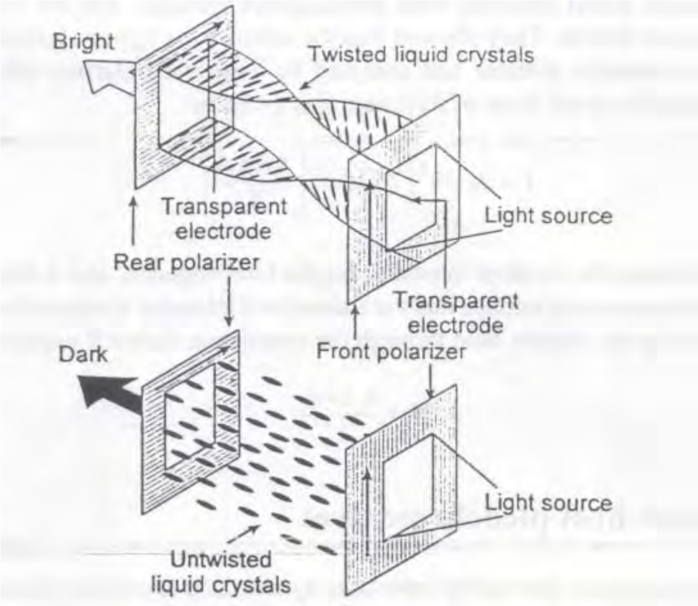


Figure 2.19: Operation of a conventional 90° twisted nematic cell with polarized light transmitted through the nematic helix

CHAPTER III

LITERATURE REVIEWS

3.1 Octa(aminophenyl)silsesquioxanes (OAPS) synthesis.

Richard M. Laine et al. [11] synthesized OAPS in two steps by nitration of octaphenylsilsesquioxane (OPS) in fuming nitric acid to form octa(nitrophenyl)silsesquioxane (ONPS), followed by mild reduction. OPS nitration was described briefly 40 years ago, but the resulting product was poorly characterized, and the material was reported to be unreactive. They slightly modified the previous procedure. ONPS is easily transformed to OAPS by hydrogenation reaction using Pd/C catalyst at 60°C for 24 h. Besides, they have prepared a wide variety of octafunctional cubes with polymerizable moieties that offer access to highly cross-linked (thermoset) nanocomposites having: (1) controlled porosities with high surface areas, (2) novel mechanical properties, and (3) high thermal stabilities. Their approach to generating functionalized cubic silsesquioxane macromonomers that offer access to nanocomposites has relied primarily on introducing functionality by hydrosilylation using $(HSiO_{1.5})_8$ or $(HMe_2SiOSiO_{1.5})_8$ nanoplatforms. They have successfully introduced functional groups including methacrylates, mesogenic groups, epoxies and alcohols.

3.2 The reaction of amine functional groups and chiral compounds.

Koichi Tanaka et al. [12] previously have designed chiral alcohol host compounds derived from tartaric acid, and found them to be very useful hosts for the optical resolution of racemic guests and for the enantioselective reaction of prochiral guests. They have now designed and synthesized novel chiral amide host compounds derived from mandelic acid, which have a rigid amide group connected to the benzene or cyclohexane framework, bulky phenyl substituents, and an OH group for possible hydrogen bonding to guest molecules.. The amide host compounds were synthesized by the condensation reaction of (R)-(-)-mandelic acid and (R,R)-(-)-trans-1,2-

cyclohexanediamine, respectively, in the presence of N-hydroxysuccinic anhydride and dicyclohexylcarbodiimide (DCC) as a condensing agent.

3.3 Chiral/polyimide liquid crystal displays

Hideo Takezoe et al. [13] demonstrated a method for LC alignment using chiral PI films. They succeeded in lifting the degeneracy of the two twisted domains in 90° TN cells, even though the pretilt angle at the rubbed PI is low ($\Theta \leq 1°$). They noted that this technique merits applying LCD manufacturing to provide defect-free and reproducible alignment of LCs in flat panel displays. They fabricated 90° TN cells from fused-quartz slides with two different surfaces: (1) slides coated with racemic achiral PI with equal ratio of *S*- and *R conformers* and (2) slides coated with chiral PI with 100% *enantiomer*. The PI films were spin cast on the slides and cured at 180 °C for 1 h. Rubbing was carried out by using a commercial rubbing machine using velvet under a moderate rubbing strength. The nominal 90° TN cell thickness was maintained by bead spacers with 5 m. in diameter. The LCs were inserted at room temperature (RT) and the cells were aged thermally below the isotropic-nematic *(T*NI) transition temperature for 30 min to obtain a good twisted alignment of the director. They confirmed that defect free uniform TN alignment with pretilt angles below 1° cannot be realized. On the other hand, the textures of TN cells coated with chiral PI films under cross polarizers at RT show perfectly defect-free TN alignment without marble defect lines compare with. Figure.3.1 showing the texture of two twisted domains with reverse twisting. The cell fabricated was coated with commercialized PI (AL 1524, JSR) possessing low pretilt angle ($\Theta \leq 1°$) and commercially available nematic material (MLC-6650, Merck) was introduced. Figure. 3.2 showing the cells consisting of chiral PI films under cross polarizers at RT. Both TN cells filled with (a) 5CB and (b) MLC 6650 show defect-free TN alignment without marble defect lines.

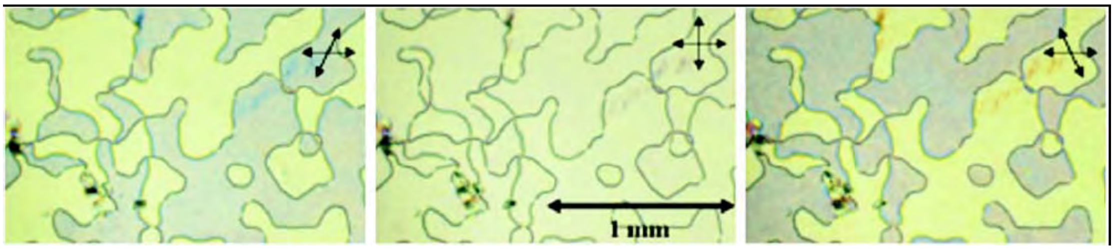


Figure. 3.1: (Color online) Polarizing optical microphotographs of two twisted domains with reverse twisting. The cell fabricated was coated with commercialized PI (AL 1524, JSR) possessing low pretilt angle (Θ≤1°) and commercially available nematic material (MLC-6650, Merck) was introduced.

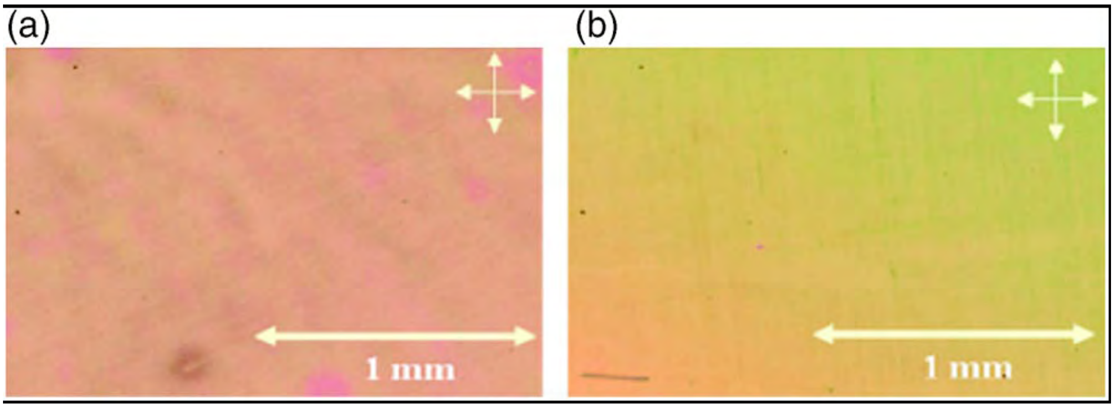


Figure. 3.2: (Color online) Polarizing optical microphotographs of the cells consisting of chiral PI films under cross polarizers at RT. Both TN cells filled with (a) 5CB and (b) MLC-6650 show defect-free TN alignment without marble defect lines.

Zhijie Liu et al. [14] synthesized a series of diamines with a side chain containing rigid biphenyl unit and nonpolar alkoxy side end group for preparing side-chain-type PI films. Besides, an aromatic PI without a side chain was also prepared as a reference. The effect of the length of alkoxy side end group on alignment behavior of LC. Then three polyimides (PIs) were prepared by copolymerization of pyromellitic dianhydride (PMDA), 4,4’-methylenedianiline (MDA) and BBDA in N-methyl-2-pyrrolodone (NMP). Liquid crystal (LC) cells were fabricated using these PIs as the alignment layer for characterization of the alignment properties of LCs.

CHAPTER IV

EXPERIMENT

In this research, the experimental procedures divided into seven parts as below,

i. Chemicals and Equipments.
ii. Preparation of octa(nitrophenyl)silsesquioxane (ONPS).
iii. Preparation of octa(aminophenyl)silsesquioxane (OAPS).
iv. The reaction of OAPS and chiral compounds.
v. Preparation of polyimide films.
vi. Preparation of polyimide/chiral films.
vii. Characterization of polyimide/chiral films.

4.1 Chemicals and Equipments

4.1.1 Chemicals

1. Octaphenylsilsesquioxane (OPS) was prepared by Laine’s group.
2. Fumimg nitric acid (HNO_3) was purchased from Merck KGa Germany.
3. Palladium 5% on activated carbon catalyst was purchased from Aldrich chemical Company, Inc.
4. (s)-(+)-Mandelic acid (99+%) was purchased from Alfar Aser.
5. (1R)-(-)-Menthyl chloroformate (95%) was purchased from Alfar Aser.
6. N-Hydroxy Succinimide (98%) was purchased from Aldrich chemical Company, Inc.
7. Dicyclohexylcarbodiimide (99%) was purchased from Aldrich chemical Company, Inc.
8. Triethylamine ($C_6H_{15}N$; 99.5%) was purchased from Aldrich chemical Company, Inc.
9. 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) was purchased from Aldrich chemical Company, Inc.
10. 3,4′-Oxydianiline (ODA) was purchased from Aldrich chemical Company, Inc.

11. 3,3'-Diaminobenzidine (4AM) was purchased from Aldrich chemical Company, Inc.
12. N-Methyl-2-pyrrolidinone (NMP) purchased from Merck KGaA Germany
13. Dimethyl sulfoxide (DMSO) purchased from Aldrich chemical Company ,Inc .
14. 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.
15. Acetone (Analytical grade) was purchased from SR lab.

4.1.2 Equipments

All equipments used in the OAPS preparation and polyimide film preparation are listed as below:

4.1.2.1 OAPS synthesis part

(a) Reactor

The synthesis reactor was a large Parr bomb reactor. The reactor was assembled with the top and bottom parts and tightening with hex screws, equipped with a thermometer, a magnetic stir bar and placed in the silicone oil bath as shown in Figure 4.1.

Figure 4.1: Parr bomb reactor

(b) Magnetic Stirrer and Hot Plate

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

(c) Hydrogen gas tank

4.1.2.2 Chiral polyimide synthesis 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) 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 0.1 ppm. The glove box is shown in Figure 4.2.

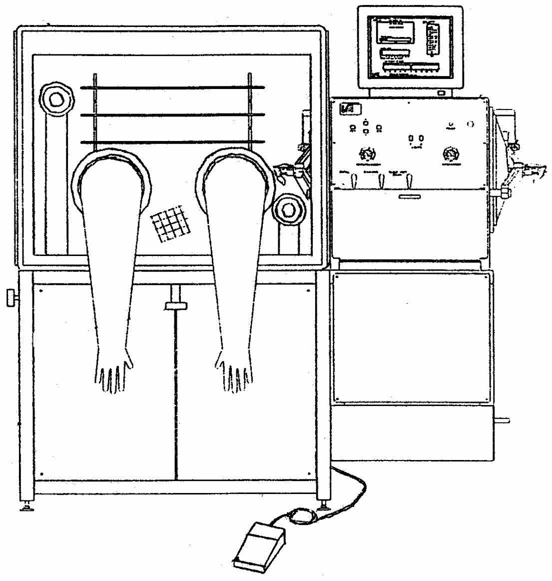


Figure 4.2: Glove box

(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 4.3.

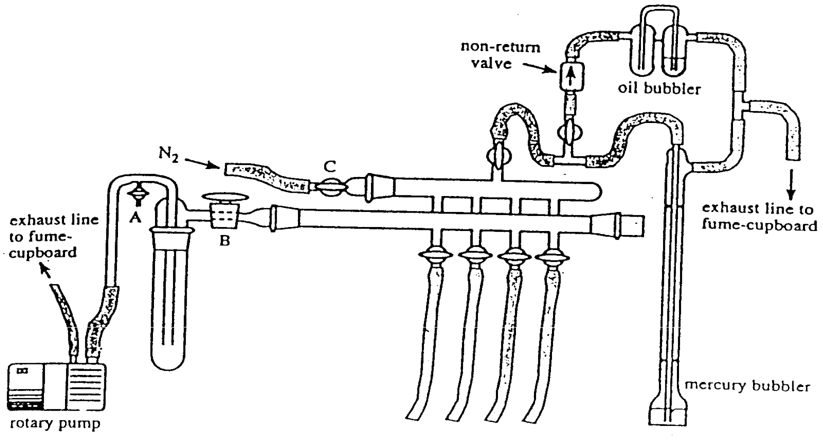


Figure 4.3: Schlenk line

(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 4.4.

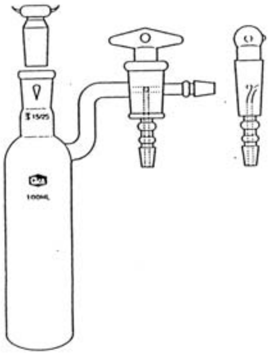


Figure 4.4: Schlenk tube

(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 4.5.

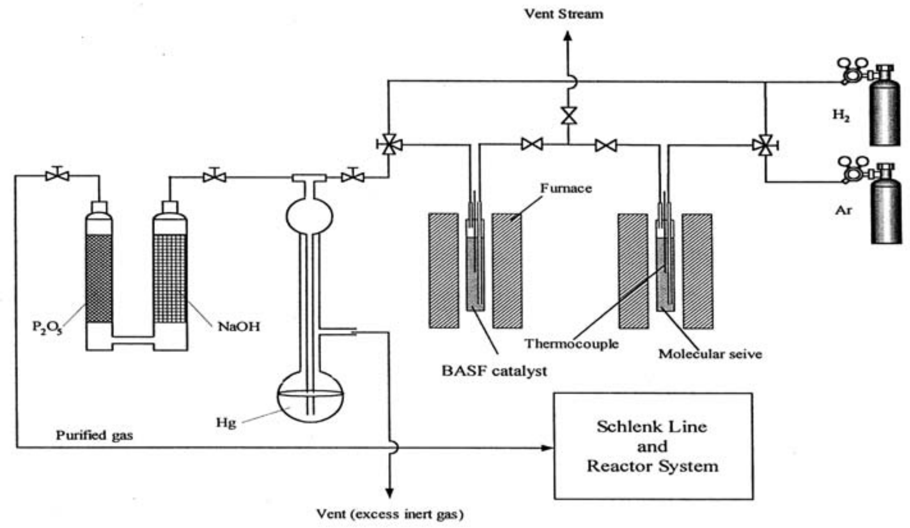


Figure 4.5: Inert gas supply system

(e) Magnetic Stirrer and Hot Plate

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

(f) Syringe, Needle

The syringe used in these experiments had a volume of 10 ,5 ,1 ml and 100 μl, respectively.

(g) 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 4.6.

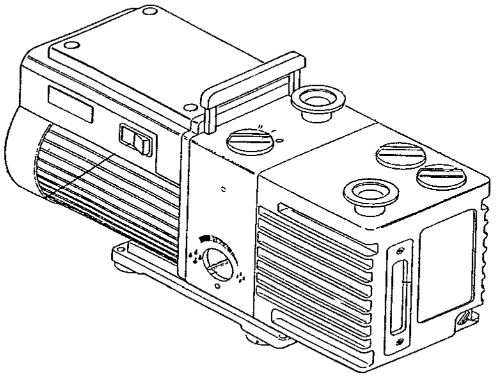


Figure 4.6: Vacuum pump

4.1.2.3 Film preparation Part

(a) High temperature oven

A Cole-Parmer high temperature ovens model 282A was used for removing solvent from freshly cast films. This high temperature oven can be programmed. All functions can be set from digital panel and display their status on LCD. The temperature, pressure and time are controllable variables. The maximum working temperature of this machine is 400°C.

4.2 Preparation of octa(nitrophenyl)silsesquioxane (ONPS)

To a 1-L Erlenmeyer flask was added 600 ml. of HNO_3 and was the placed in an ice bath. After 15 min, OPS was slowly added (5 g. every 5 min, total = 100 g., 96.8 mmol). The solution was stirred in the ice bath for 2 h and then stirred at room temperature overnight. The solution was filtered using glass wool and celite and then precipitated into 500 g. of the ice. Once the ice melts, the solution was filtered through a filter paper and washed the powder with deionized water until the pH of the filtrate is neutral.

4.3 Preparation of octa(aminophenyl)silsesquioxane (OAPS)

To the Parr bomb reactor was added (30 g., 21.52 mmol) of ONPS and 0.3 g. of Pd/C. Distilled THF was added as solvent. Hydrogen gas (400-500 psi) was filled to the reactor. The solution was stirred at 60 °C for 2 days. The solution was filtered through glass wool and celite and then precipitated in hexane.

4.4 The reaction of OAPS and chiral compounds

4.4.1 Reaction of Octa(aminophenyl)silsesquioxanes (OAPS) with mandelic acid.

Mandelic acid (1.2 g, 6.94 mmol), OAPS (0.5 g, 3.47 mmol), N-hydroxysuccinic anhydride (1.02 g, 8.68 mmol) and dicyclohexylcarbodiimide (1.8 g, 8.68 mmol) were added to a 50 ml. one-neck flask with stirrer bar. Anhydrous THF (30 ml.) was then added by syringe. The mixture was stirred at room temperature for 24 h The solvent was removed under reduced pressure by rotary evaporation. The residue was dissolved in ethyl acetate and washed successively with 5% sodium carbonate, water, 1N HCL, water and brine and dried over $MgSO_4$. The product was further purified by recrystallization.

4.4.2 Reaction of Octa(aminophenyl)silsesquioxanes (OAPS) with menthyl chloroformate.

OAPS (0.5 g, 3.47 mmol) was added to a 25 ml. one-neck flask with stirrer bar. Distilled THF (10 ml.) was then added as solvent by a syringe. The mixture was stirred under N_2 at room temperature until the OAPS dissolved completely ~5-10 mins, followed by the menthyl chloroformate (1.5 ml) and triethylamine (0.75 ml) by a syringe. The mixture was stirred under N_2 at room temperature for 24 h The solution was then filtered using glass wool and celite to remove unreacted products and the remains were precipitated in hexane (100 ml). The solution was then filtered, and the product was further purified by recrystallization.

4.5 Preparation of polyimide film

Polyimides were synthesized by two steps polymerization of 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6 FDA), 3,4′-Oxydianiline (ODA) in NMP. Then the polyimide film was re-dissolved in NMP and dropped into the solution of 3,3'-Diaminobenzidine (4AM) to obtain polyimide containing amine functional groups.

The polyimide was prepared in glove box from polymerization of 3 equiv. diamine and 4 equiv. dianhydride by mol at 15% solid content in NMP as follow:
The diamine (ODA; 0.676 g, 0.00337 mol) was completely dissolved in NMP (17.84 ml.) with stirring to obtain the ODA solution(15% by wt/v). After stirring, the dianhydride (6FDA; 2 g, 0.0045 mol) was added into ODA solution. The mixture was stirred continuously for 1 h to form the poly(amic acid) (PAA) solution. The PAA solution was then cast onto clean, dry plate glass and subjected to thermal imidization for 1 h each at 100^o C, 150^o C and 250^o C to produce PI films.

The PI4AM film was prepared in glove box from grafting of 3 equiv. dianhydride and 4 equiv. amine. by mol at 15% solid content in NMP as follow:
The core (polyimide film; 1 g, 0.000444 mol) was dissolved in NMP (7.459 ml.) with stirring. The core solution was added by drop wise into the 4AM (0.119 g, 0.000555 mol) solution. The mixture was stirred continuously for 1 h to form the poly(amic acid) (PAA) solution. The PAA solution was then cast onto clean, dry plate glass and subjected to thermal imidization for 1 h each at 100^o C, 150^o C and 250^o C to produce PI4AM films containing amine functional groups.

4.6 Preparation of polyimide/chiral.

4.6.1 Reaction of amine group in polyimide with menthyl chloroformate.

PI4AM film (1 g, -NH_2 0.267 mmol) was dissolved in NMP (30 ml) at 150^o C for 24 h The PI4AM solution was added to a 100 ml. three-neck flask with stirrer bar. Menthyl chloroformate (0.534 mmol, 0.24 ml.) was then added to the flask, followed by thriethylamine (0.267 mmol, 0.08 ml.) The mixture was stirred under Ar at room temperature for 24 h The solution was then filtered using glass wool and celite to remove unreacted products and the remains were then cast onto clean, dry plate glass and subjected to thermal imidization for 1 h each at 100^o C, 150^o C and 250^o C.

4.6.2 Reaction of amine group in polyimide with mandelic acid.

PI4AM film (1 g, -NH_2 0.267 mmol) was dissolved in NMP (30 ml) at 150^o C for 24 h Mandelic acid (0.184 g, 0.534 mmol), N-hydroxysuccinic anhydride (0.319 g, 1.36 mmol) and dicyclohexylcarbodiimide (0.566 g, 1.36 mmol) were added to a 100 ml. three-neck flask with stirrer bar. The mixture was stirred at room temperature for 24 h The solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate and washed successively with 5% sodium carbonate, water, 1N HCL, water and brine and dried over $MgSO_4$. The solution was then filtered using glass wool and celite to remove unreacted products and the remained solvent was evaporated under vacuum at 60 °C for overnight. The cast films were thermally treated at 5 °C/min heated rate and the holding time was 0.5 h for 200 °C and 300 °C each to remove reaction water in a temperature controlled oven. After the thermal treatment, the films were removed from the glass substrate by immersing into water and dried at 100 °C for 24°C. PI4AM films containing amine functional groups were obtained as transparent, flexible, dark brown to yellow colored.

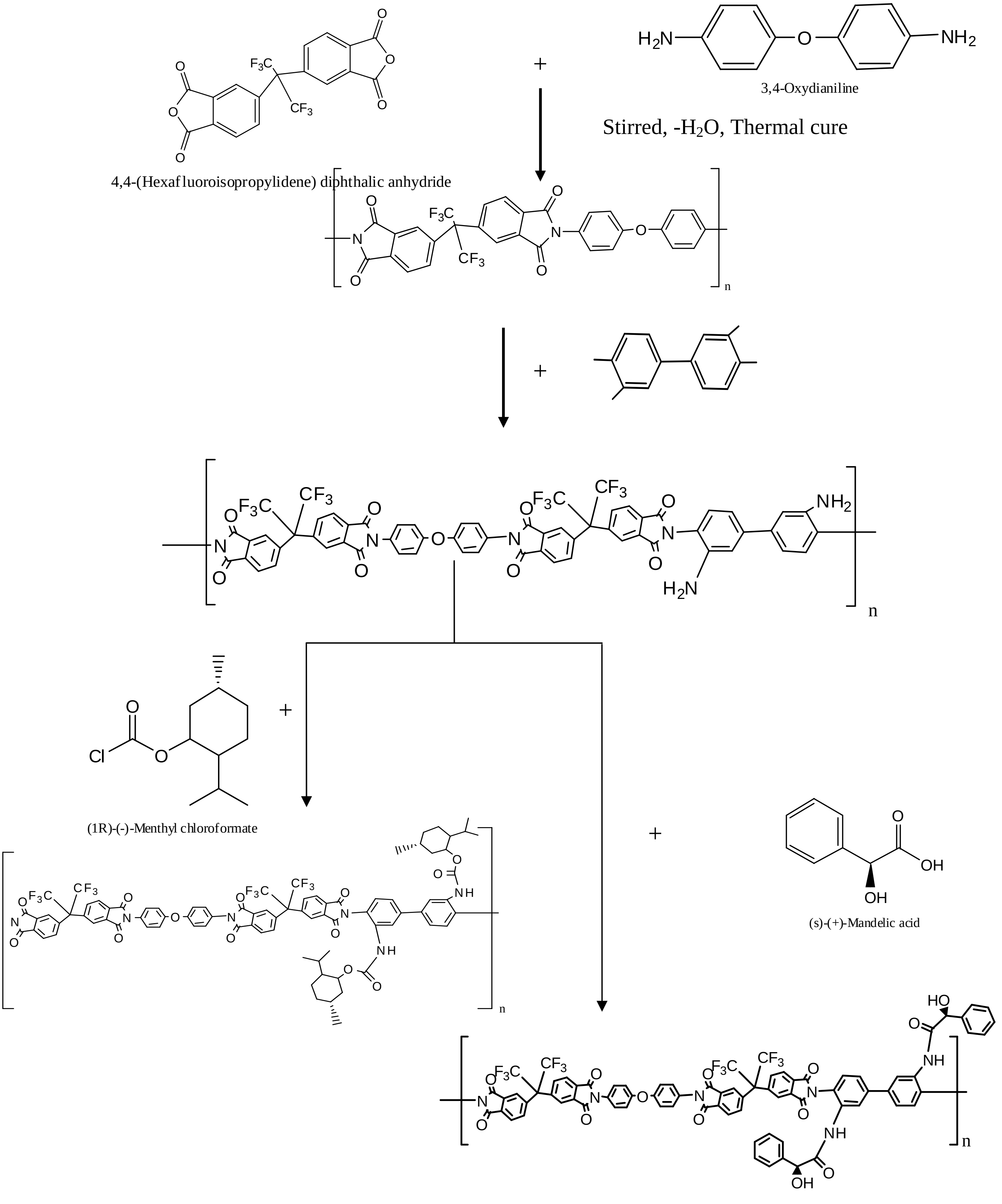


Figure 4.7: The synthesis procedure of chiral polyimides.

4.7 Characterization Instruments

4.7.1 Infrared Spectroscopy (FTIR)

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

Figure 4.8: Fourier Transform Infrared Spectroscopy (FTIR) Equipment

4.7.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^{1}H-NMR spectra were recorded with Bruker 400 UltraShield ^{1}H NMR spectrometer. The scanning numbers are 128 times. The samples were dissolved in DMSO deuterates and ran under high temperature at 120 °C.

Figure 4.9: Nuclear Magnetic Resonance (NMR) Equipment

4.7.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) thermograms were performed using a Diamond TG/DTA Thermogravimetric/Differrential Thermal Analyzer. The sample weights were 3-10 mg. The temperature is range of 50-900°C at a heating rate of 10°C/min with nitrogen purge flow rate 100 ml/min.

Figure 4.10: Thermogravimetric analysis (TGA) Equipment

4.7.4 Optical Microscope

The textures of polyimide and polyimide/chiral films were characterized using optical microscope. The sample films were investigated range from 0.67X-4.5X and zoom ratio at 6,7:1.

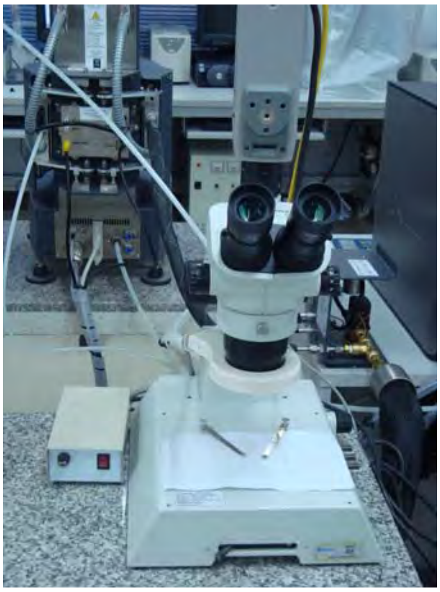


Figure 4.11: Optical Microscope Equipment

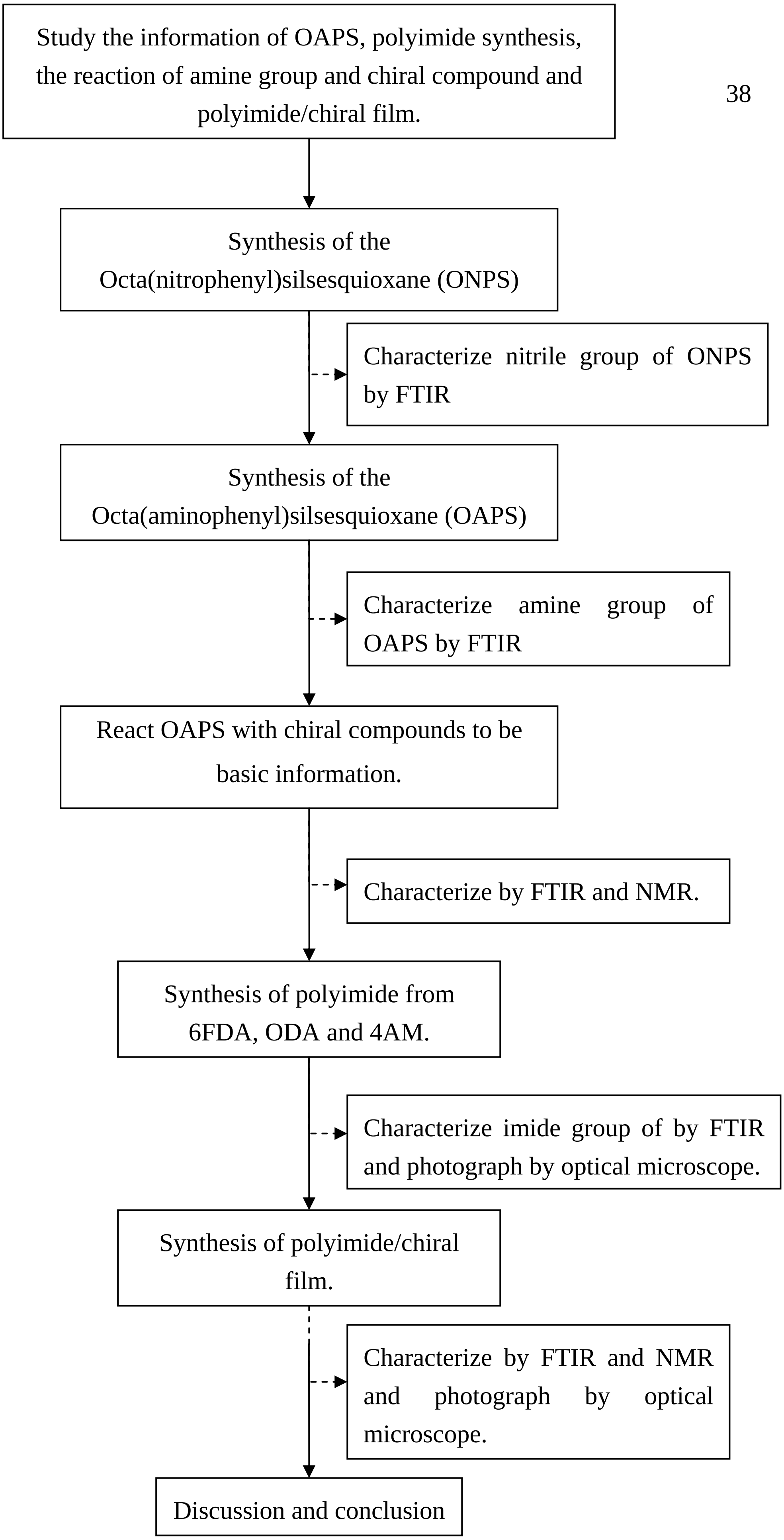


Figure 4.12: Flow diagram of research methodology

CHAPTER V

RESULTS AND DISCUSSION

This chapter provides the identification information of the properties of the OAPS synthesis, the reaction of OAPS and chiral compound, the polyimide/chiral film synthesis and the characterization information of polyimide/chiral film.

5.1 The Preparation of octa(aminophenyl)silsesquioxane (OAPS)

OAPS was prepared by two-steps reaction.

i) Nitration reaction of OPS to form ONPS

ii) Hydrogenation reaction of ONPS to form OAPS.

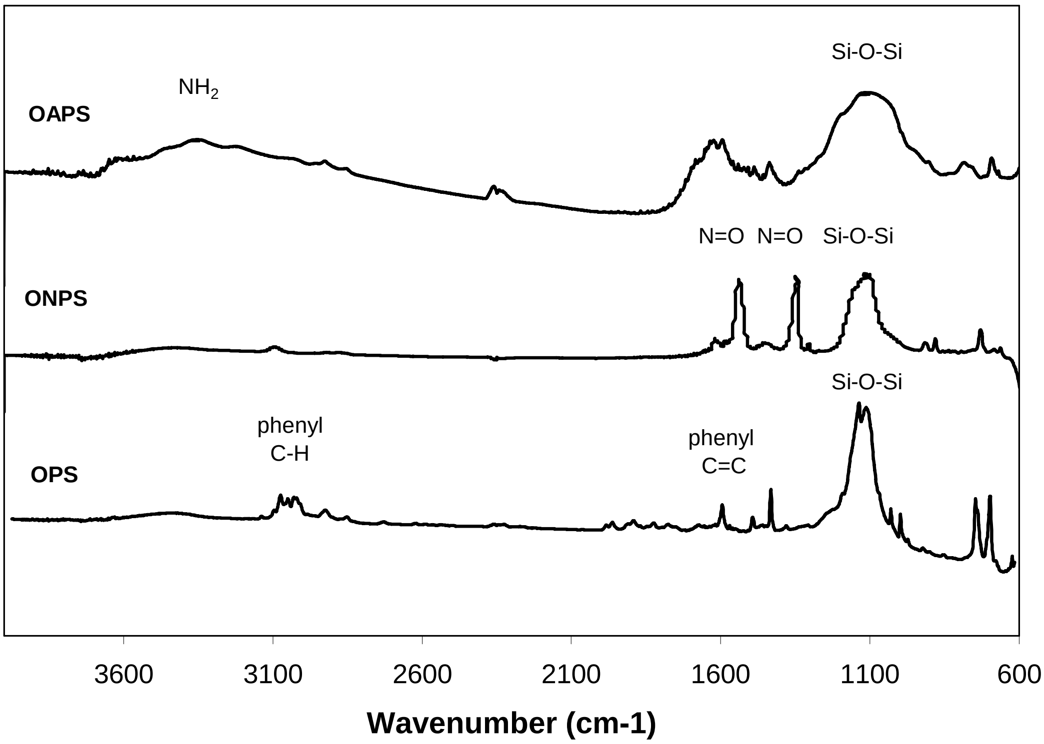


Figure 5.1: FT-IR spectra of OPS, ONPS and OAPS.

In Figure 5.1, FT-IR of the products from those reactions can be shown and can confirm the functional groups of the ONPS and OAPS. Functional groups after nitration of OPS to form ONPS were confirmed at the peak of 1347 and 1540 cm^{-1}

resulting from asymmetric and symmetric stretching vibration of $-NO_2$ groups. These peaks were disappeared after ONPS was reduced by hydrogenation to form OAPS. The FTIR spectra of OAPS indicated a complete hydrogenation of nitro-compound into amine functional because the peaks of $-NO_2$ groups were disappeared while band of $-NH_2$ groups were instate presented at 3376 cm^{-1} and 1620 cm^{-1}.

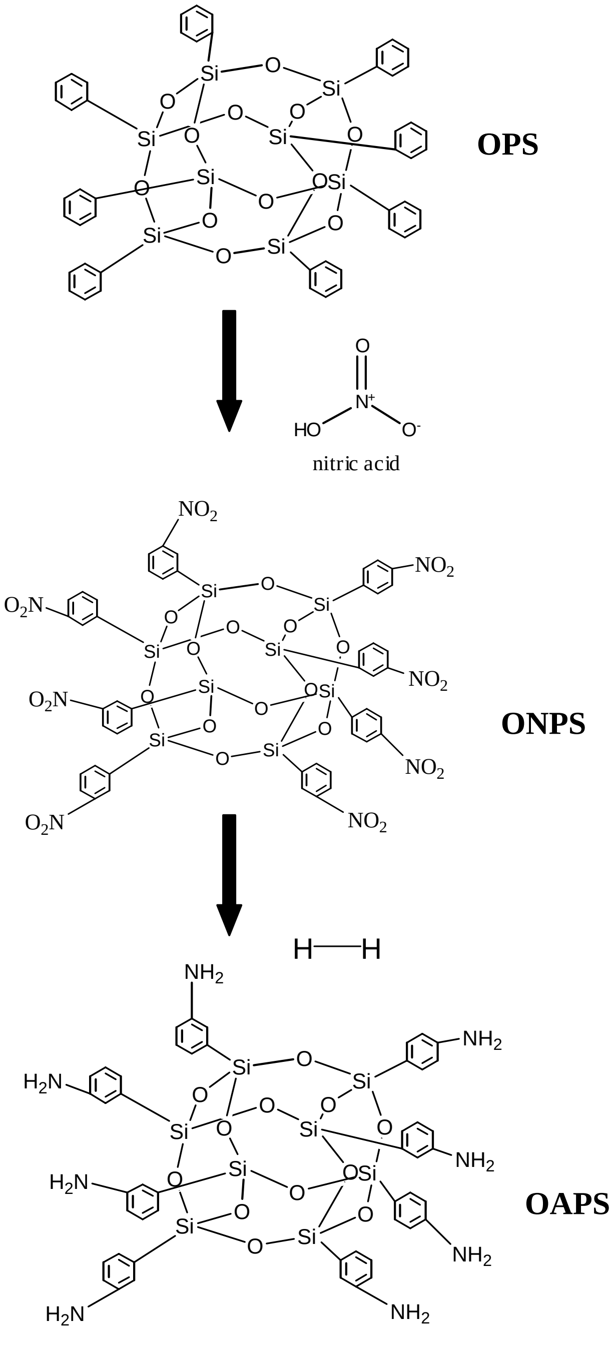


Figure 5.2: The chemical structures of OPS, ONPS and OAPS

5.2 The reaction of OAPS and chiral compounds

Since OAPS offers 3-dimension symmetry with eight aminophenyl functional groups and combining unique inorganic-organic chemical compositions with nano-sized cage structures have long been important and interesting class of materials. Therefore, in this section we studied the reaction of OAPS and chiral compounds to provide new method for the reaction of amine groups and chiral compound to be basic information. However, octaaminophenyl silsesquioxanes (OAPS) is absence of chiral-centers in their molecule that are needed to perform symmetric molecules. The OAPS/mandelic acid amine and OAPS/menthyl chloroformate were successfully synthesized.

5.2.1 Reaction of Octa(aminophenyl)silsesquioxanes (OAPS) with mandelic acid.

The OAPS/mandelic acid amides were successfully synthesized by condensation reaction or dehydration reaction of OAPS and mandelic acid using N-hydroxysuccinic anhydride and dicyclohexylcarbodiimide as condensing agents. The chemical structures were confirmed by FTIR and ^{1}H-NMR. The thermal properties were characterized by TGA and their textures were characterized by optical microscope.

5.2.1.1 FTIR spectrum

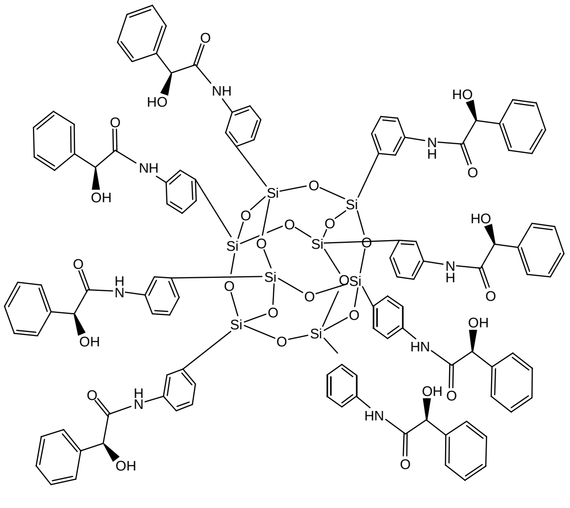


Figure 5.3: Chemical structure of OAPS/mandelic acid amide

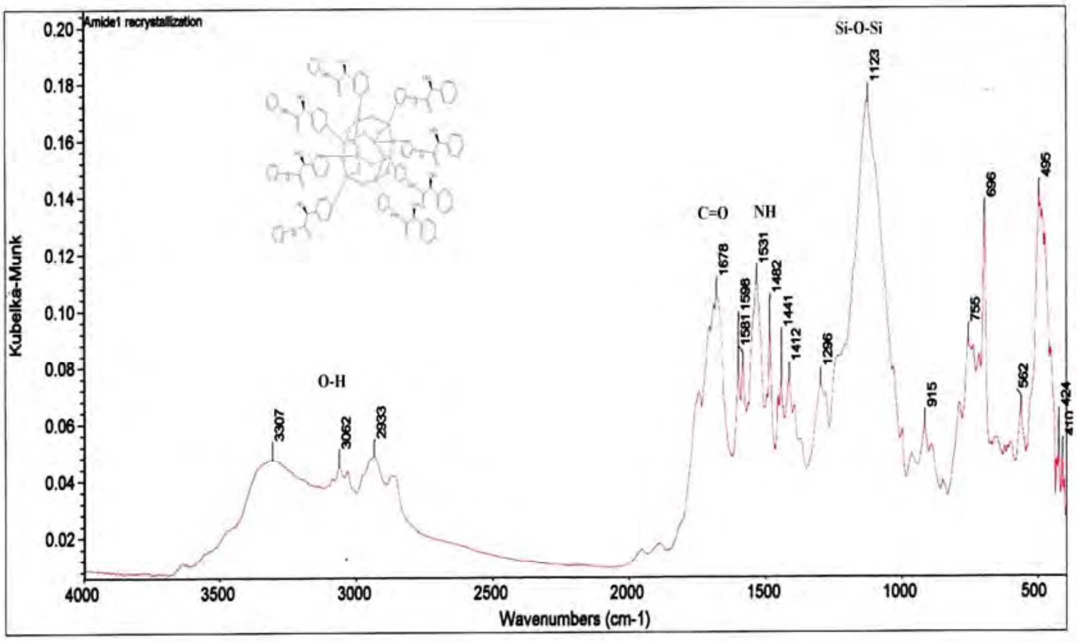


Figure 5.4: FTIR spectrum of OAPS/mandelic acid amide

Figure 5.4 shows the FTIR spectra of OAPS/madelic acid amide. The OAPS/madelic acid amide exhibits the characteristic absorption band at 1123 cm^{-1} resulting from Siloxane (Si-O-Si) groups, which confirmed that the product still contained the POSS cage. The characteristic absorption band of amide groups, which confirmed the incorporation of OAPS and mandelic acid to form amide, can be observed at 1531 cm^{-1} and 1678 cm^{-1} resulting from bending vibration of amide band (N-H) and stretching vibration band of amide (C=O) respectively. The broad band of stretching O-H at 2933-3307 cm^{-1} corresponded to the characteristic of mandelic acid.

Figure 5.5 shows ^{1}H NMR (DMSO-d4, 400 MHz) spectrum of OAPS/mandelic acid amide.The chemical structures were confirmed by ^{1}H NMR analysis. The peaks appearing at 7.24 ppm confirmed the presence of NH proton resulting from attachment directly of proton to nitrogen to form amide. This amide confirmed the incorporation of OAPS and mandelic acid. The sharp peak at 3.59 ppm resulted from OH proton and the peak appearing at 7.34-7.49 ppm resulted from phenyl protons.

5.2.1.2 ^{1}H NMR spectrum

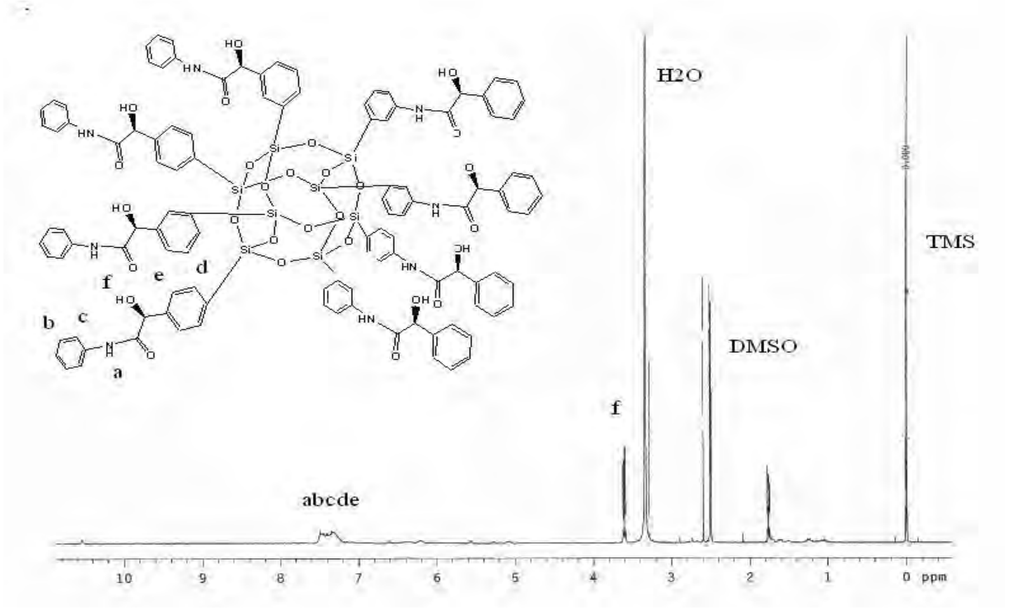


Figure 5.5: ^{1}H NMR spectrum of OAPS/mandelic acid amide.

5.2.1.3 Thermal properties

The thermal properties of OAPS/mandelic acid amide were investigated by TGA under nitrogen atmosphere at 10 °C/min heating rate. In Figure 5.6, the initial decomposition temperature (Td5%) of OAPS/mandelic acid amide is 220 °C. The initial decomposition temperature (Td10%) at 250°C and char yield is 14.93%. Thermal properties were summarized in table 5.1.

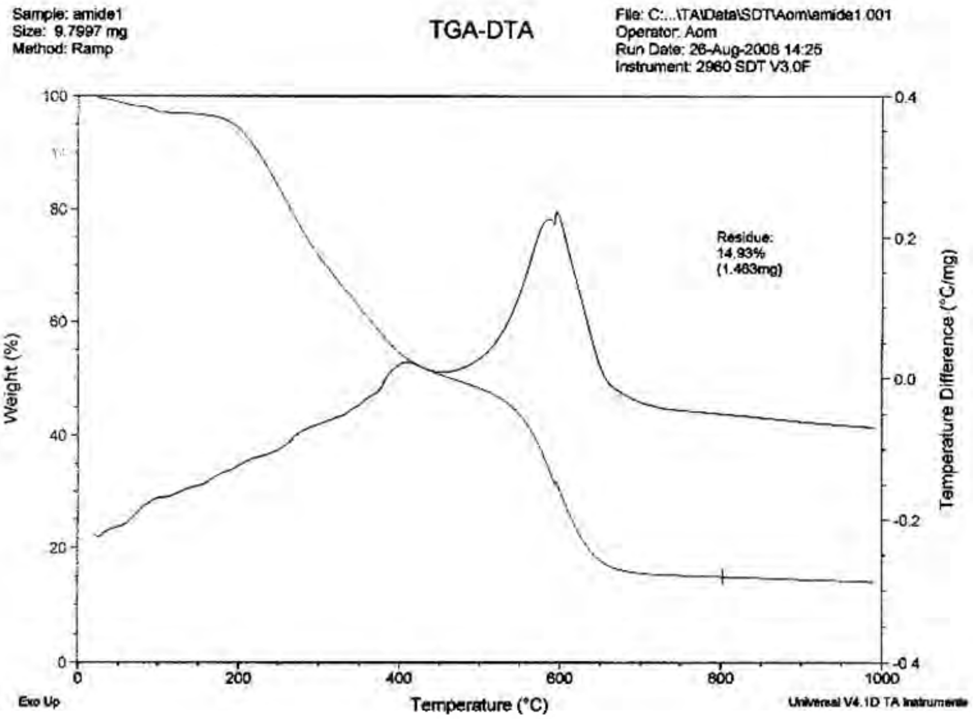


Figure 5.6: TGA curve of OAPS/mandelic acid amide.

Table 5.1 Thermal properties of OAPS/mandelic acid amide.

% CharYield	14.93 wt %
5% Weight loss	220°C
10% Weight loss	250°C

5.2.2 Reaction of Octa(aminophenyl)silsesquioxanes (OAPS) with menthyl chloroformate.

The OAPS/menthyl chloroformate were successfully synthesized by condensation reaction of OAPS and menthyl chloroformate to form amide and also form HCl molecule. Triethylamine was used for catching the by product, HCl, from this reaction. The chemical structures were confirmed by FTIR and ^{1}H-NMR. The thermal properties were characterized by TGA.

5.2.2.1 FTIR spectrum

Figure 5.8 shows the FTIR spectra of OAPS/menthyl chloroformate. The OAPS/menthyl chloroformate exhibited characteristic absorption band at 1134cm^{-1} resulting from Siloxane (Si-O-Si) groups, which confirmed that the product still contained the POSS cage. The characteristic absorption band of amide groups, which confirmed the incorporation of OAPS and menthyl chloroformate to form amide, can be observed at 1525cm^{-1} and 1717 cm^{-1} resulting from bending vibration of amide band (N-H) and stretching vibration band of amide (C=O) respectively. The broad band of stretching O-H can be seen at 2500-3500 cm^{-1}.

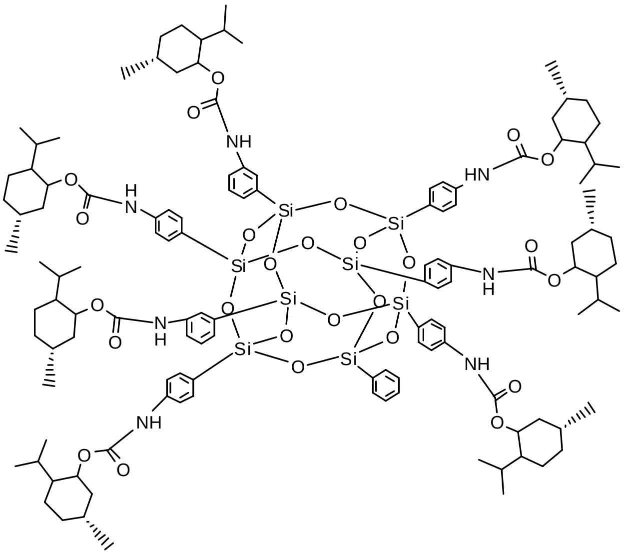


Figure 5.7: The chemical structure of OAPS/menthyl chloroformate

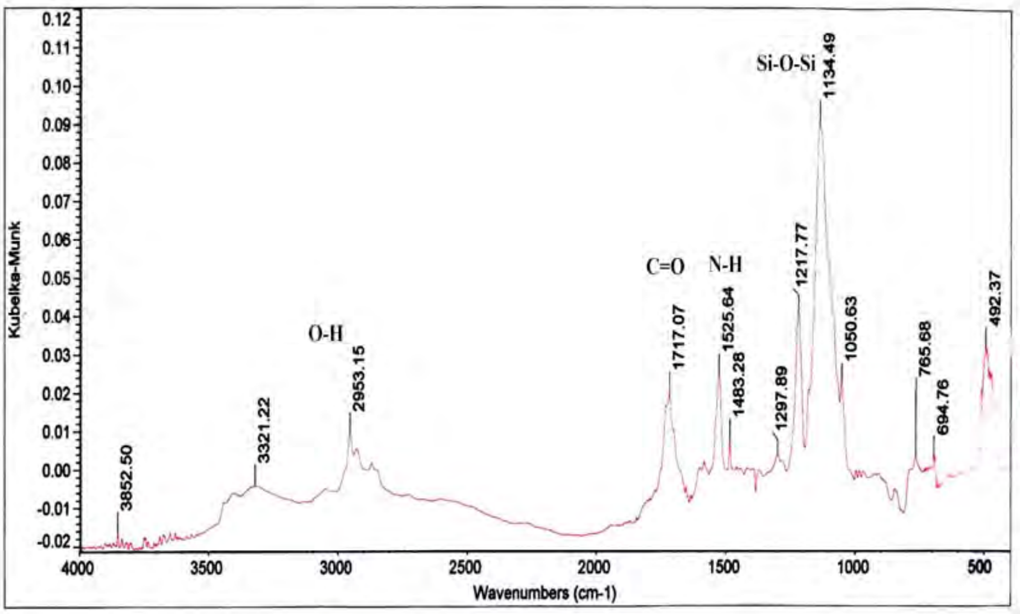


Figure 5.8: FTIR spectrum of OAPS/menthyl chloroformate.

5.2.2.2 ^{1}H NMR spectrum

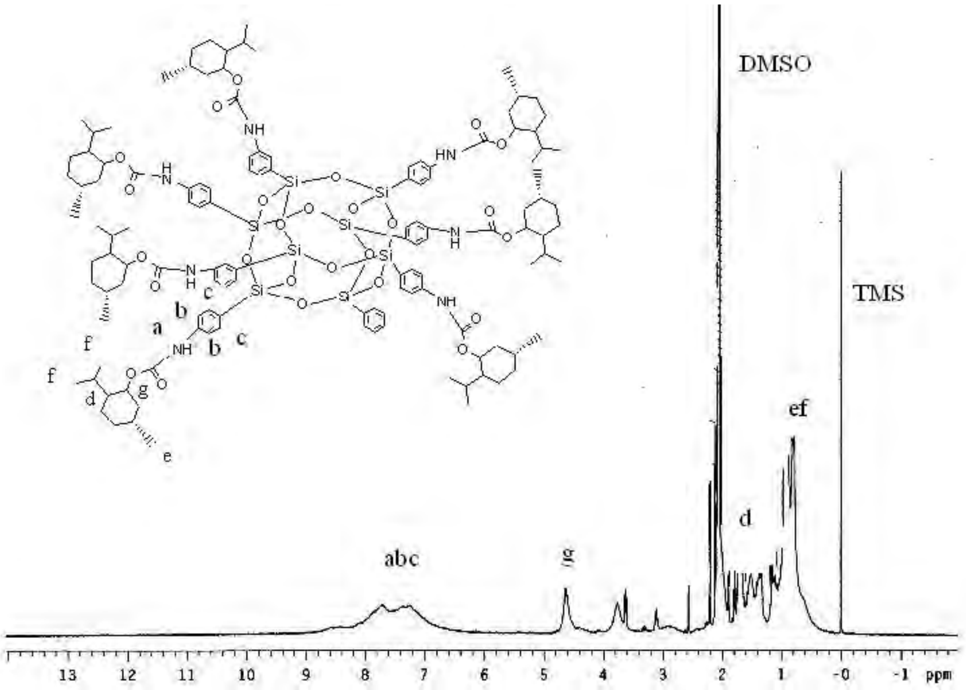


Figure 5.9: ^{1}H NMR spectrum of OAPS/menthyl chloroformate.

Figure 5.9 shows ^{1}H NMR (DMSO-d4, 400 MHz) spectrum of OAPS/menthyl chloroformate. The chemical structures were confirmed by ^{1}H NMR analysis. The peaks appearing at 8.59 ppm confirmed the presence of NH proton resulting from attachment directly of proton to nitrogen to form amide. This amide confirmed the incorporation of OAPS and menthyl chloroformate. The sharp peak shows at 4.65 ppm resulting from phenyl-OH proton and the peak appearing at 7.81and 7.83 ppm resulted from phenyl protons.

5.2.2.3 Thermal properties

The thermal properties of OAPS/menthyl chloroformate were investigated by TGA under nitrogen atmosphere at 10 °C/min heating rate. In Figure 5.10, the initial decomposition temperature (Td5%) of OAPS/ menthyl chloroformate is 180 °C. The initial decomposition temperature (Td10%) at 250°C and char yield is 20.25%. Thermal properties were summarized in table 5.2.

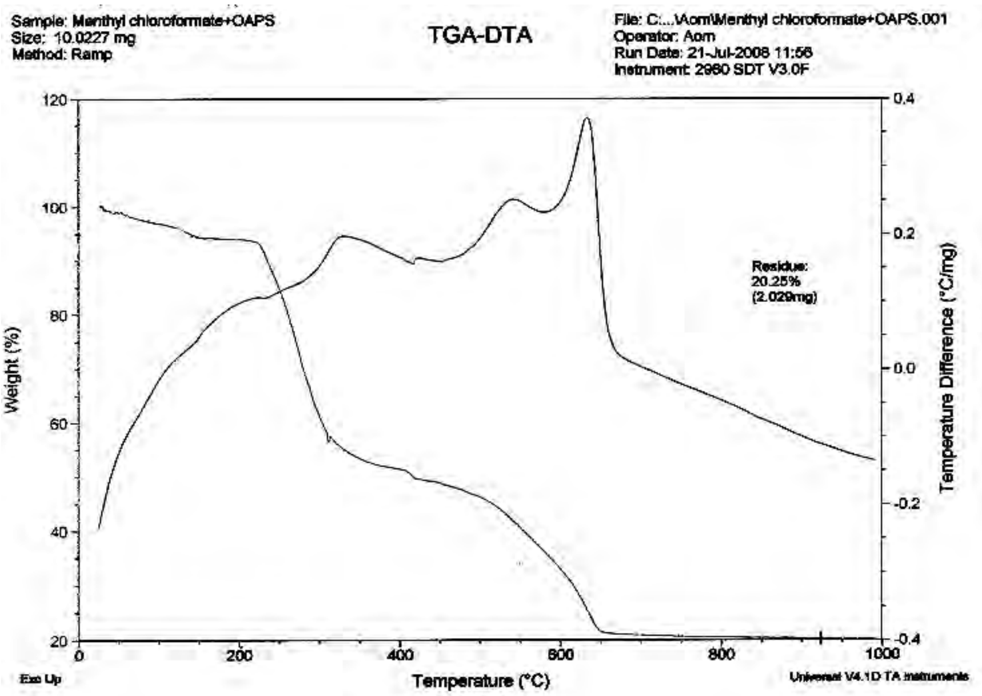


Figure 5.10: TGA curve of OAPS/menthyl chloroformate.

Table 5.2 Thermal properties of OAPS/menthyl chloroformate

% CharYield	20.25 wt %
5% Weight loss	180°C
10% Weight loss	250°C

5.3 Preparation of polyimide/chiral

Polyimides were synthesized by two steps polymerization of 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6 FDA), 3,4′-Oxydianiline (ODA) Then the polyimide film was re-dissolved in NMP and dropped into the solution of 3,3'-Diaminobenzidine (4AM) to obtain polyimide containing amine functional groups.

The polyimide was prepared from polymerization of 3 equiv. diamine and 4 equiv. dianhydride. The unbalance of molar ratio was used to obtain low molecular weight polyimide for easier dissolution than high molecular weight polyimide. The calculation is shown in Appendices A.

The PI4AM film was prepared from grafting of 3 equiv. dianhydride and 4 equiv. amine by slowly added PI solution into 4AM solution to obtain PI containing amine functional groups in the main chain. The chiral compounds, mandelic acid and menthyl chloroformate, are connected to the main chain as side-chains by condensation reaction of amine groups in the main chain and chiral compounds. The chemical structures were confirmed by FTIR. Structural identification was performed by ^{1}H NMR. The thermal properties and the texture were shown by TGA and optical microscope respectively.

5.3.1 Reaction of amine group in polyimide with menthyl chloroformate.

Polyimides were synthesized by two steps polymerization of 6 FDA and ODA. Then the polyimide film was reacted with 3,3'-Diaminobenzidine (4AM) to obtain polyimide containing amine functional groups known as PI4AM. Afterwards, PI4AM/methyl chloroformate was successfully synthesized by the same method as the reaction of OAPS/menthyl chloroformate.

5.3.1.1 FTIR spectrum

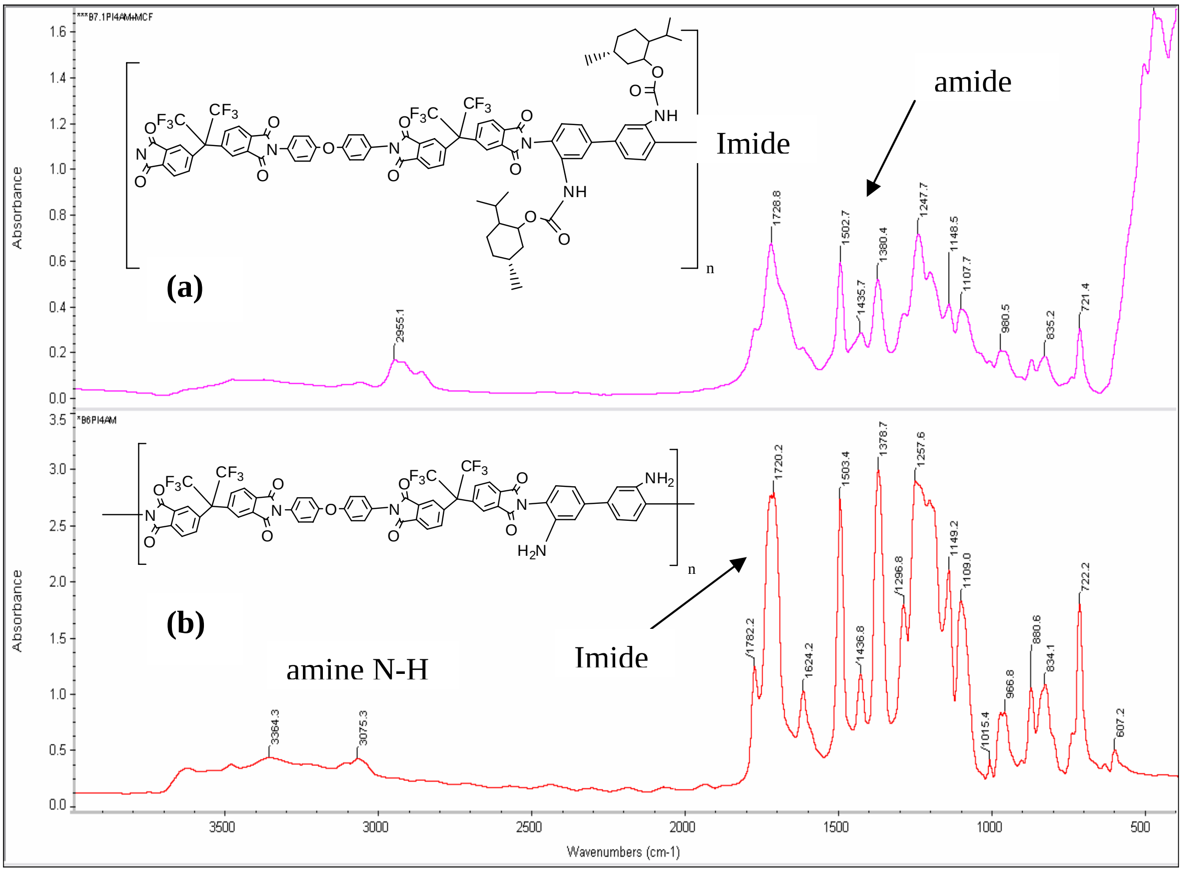


Figure 5.11: FTIR spectrum of (a) PI4AM/menthyl chloroformate (b) PI4AM

Figure 5.11 shows the FTIR spectra of PI4AM/menthyl chloroformate and PI4AM. Functional groups after condensation of PI4AM to form PI4AM/menthyl chloroformate were confirmed at the peaks of 1502 cm^{-1}, 1720 and 1782 cm^{-1} resulting from bending vibration of amide –NH groups, asymmetric and symmetric of imide ring C=O respectively. The imide bond confirmed the complete imidization. The amine –NH$_2$ broad peaks at 2500-3500 cm^{-1}are disappeared after condensation of PI4AM to form amide with menthyl chloroformate. This disappearance confirmed the condensation reaction.

5.3.1.2 1H NMR spectrum

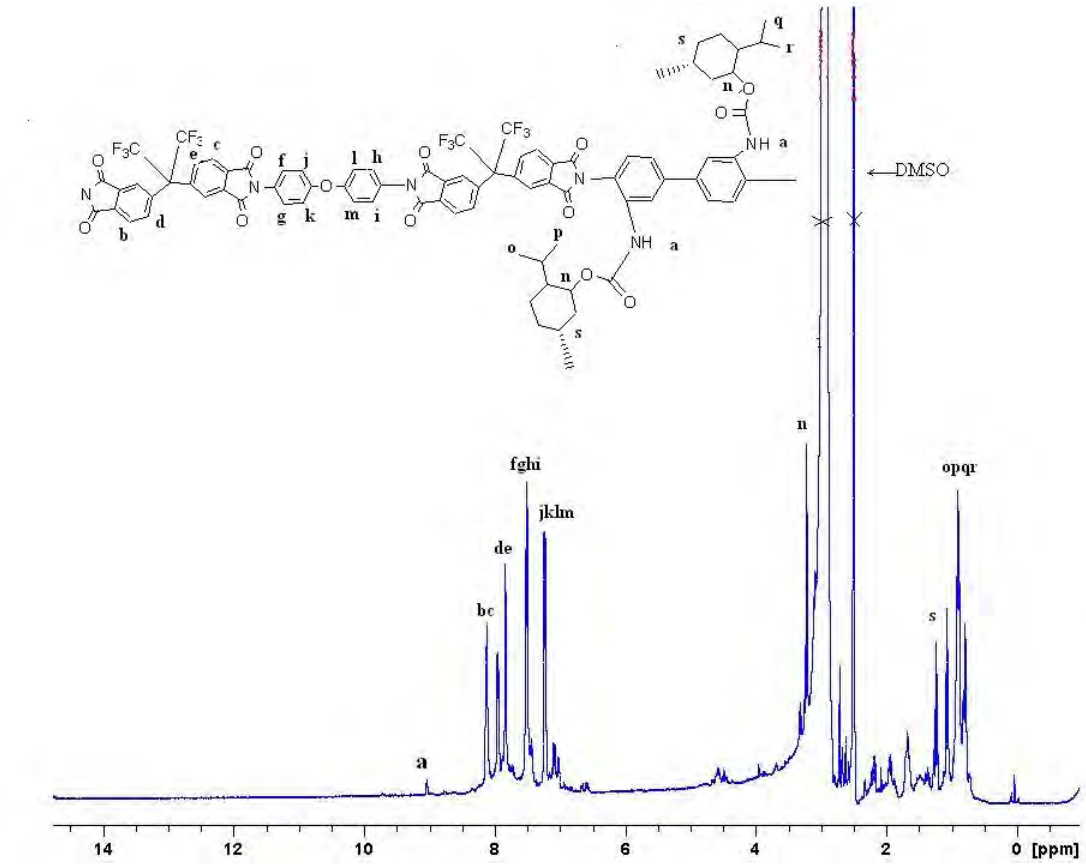


Figure 5.12: NMR spectrum of PI4AM/menthyl chloroformate**.**

Figure 5.12 shows ^{1}H NMR spectrum of OAPS/menthyl chloroformate. The chemical structures were confirmed by ^{1}H NMR analysis. The peaks appearing at 9.15 ppm confirmed the presence of NH proton resulting from attachment directly of proton to nitrogen to form amide. This amide confirmed the incorporation of OAPS and menthyl chloroformate. The sharp peaks presented at 6.99, 7.25, 7.83 and 8.02 ppm resulting from phenyl rings-H proton and the peak appearing at 0.91 and 0.96 ppm resulted from C-H proton.

5.3.1.3 Thermal properties

The thermal properties of PI4AM/menthyl chloroformate were investigated by TGA under nitrogen atmosphere at 10 °C/min heating rate. In Figure 5.13, the initial decomposition temperature (Td5%) of OAPS/ menthyl chloroformate is 209 °C. The initial decomposition temperature (Td10%) at 242°C and char yield is 36.27%. Thermal properties were summarized in table 5.3.

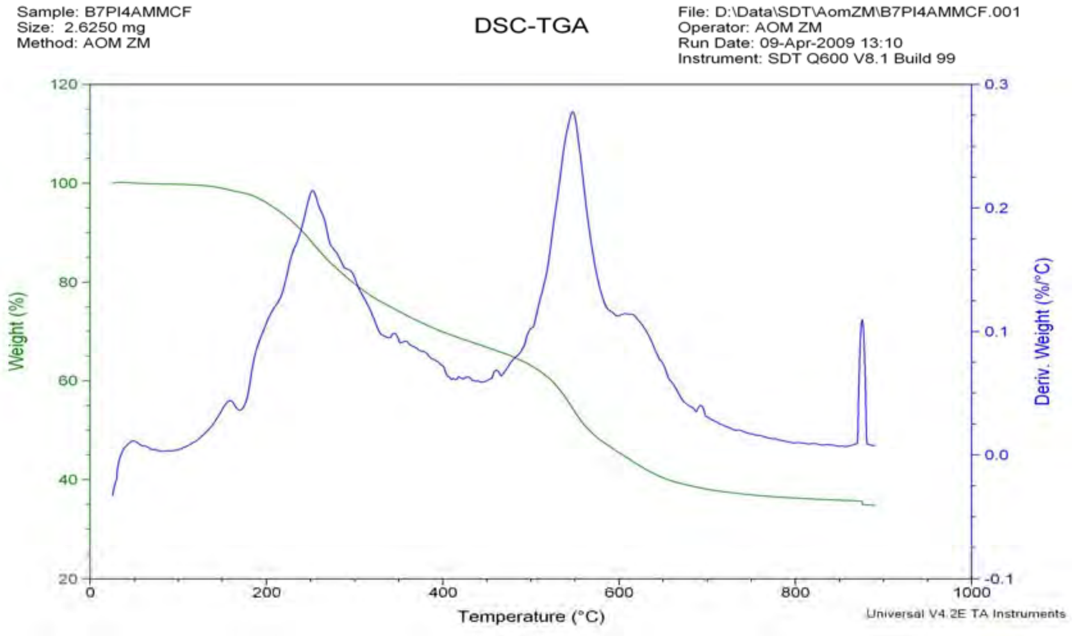


Figure 5.13: TGA curve of PI4AM/menthyl chloroformate**.**

Table 5.3 Thermal properties of PI4AM/menthyl chloroformate

% CharYield	36.27wt %
5% Weight loss	209°C
10% Weight loss	242°C

5.3.1.4 Optical microphotographs

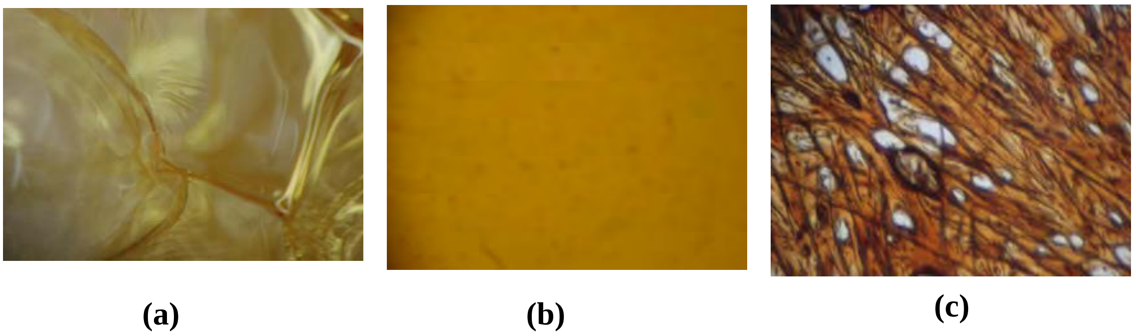


Figure 5.14: Optical microphotographs show the texture of (a) PI (b) PI4AM and (c) PI4AM/menthyl chloroformate

Figure 5.14 an example showing the texture of (a) PI (b) PI4AM and (c) PI4AM/menthyl chloroformate to confirm the complete reacted in each steps. The effect of containing the chiral compounds as side-chains in polyimide shows the texture of PI4AM/menthyl chloroformate (c) which has symmetric configuration.

5.3.2. Reaction of amine group in polyimide with mandelic acid.

Polyimides were synthesized by two steps polymerization of 6FDA and ODA. Then the polyimide film was reacted with 3,3'-Diaminobenzidine (4AM) to obtain polyimide containing amine functional groups known as PI4AM. Afterwards, PI4AM/mandelic acid amide was successfully synthesized by the same method as the reaction of OAPS/mandelic acid amide.

5.3.2.1 FTIR spectrum

Figure 5.15 shows the FTIR spectra of PI4AM/ mandelic acid amide and PI4AM. Functional groups after condensation of PI4AM to form PI4AM/ mandelic acid amide were confirmed at the peak of 1501 cm^{-1} and 1726 cm^{-1} resulting from bending vibration of amide –NH groups and symmetric of imide ring C=O respectively. The imide and amide bond confirmed the complete imidization and condensation. The amine $–NH_2$ broad peaks at 2500-3500 cm^{-1} were disappeared after condensation of PI4AM to form amide with mandelic acid, while the bands of –OH group were instate presented.

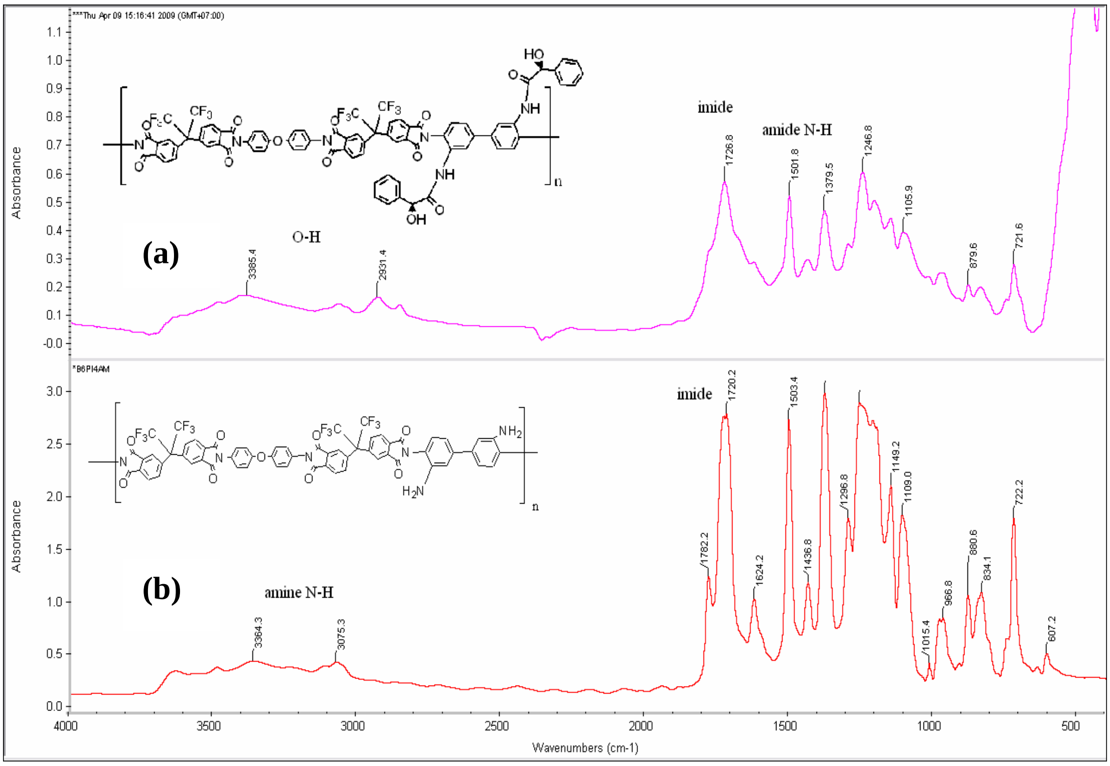


Figure 5.15: FTIR spectrum of (a) PI4AM/mandelic acid amide (b) PI4AM

5.3.2.2 ^{1}H NMR spectrum

Figure 5.16 shows ^{1}H NMR spectrum of PI4AM/mandelic acid amide. The chemical structures were confirmed by ^{1}H NMR analysis. The peak appearing at 7.24 ppm confirmed the presence of NH proton resulting from attachment directly of proton to nitrogen to form amide. This amide confirmed the incorporation of PI4AM and menthyl chloroformate. The peaks presented at 6.99, 7.25, 7.83 and 8.02 ppm resulting from phenyl rings-H proton and the peak appearing at 3.65 ppm resulted from O-H proton.

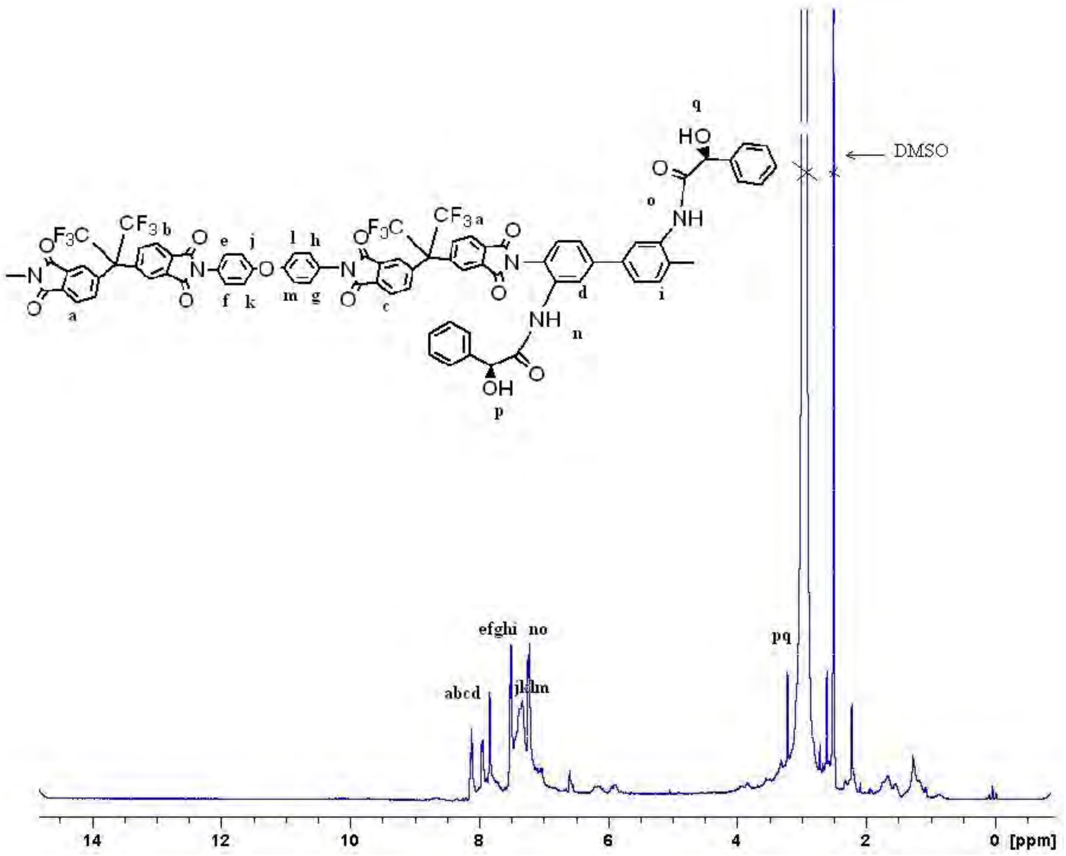


Figure 5.16: ^{1}H NMR spectrum of PI4AM/mandelic acid amide

5.3.2.3 Thermal properties

The thermal properties of PI4AM/mandelic acid amide were investigated by TGA under nitrogen atmosphere at 10 °C/min heating rate. In Figure 5.17, the initial decomposition temperature (Td5%) of OAPS/ menthyl chloroformate is 254 °C. The initial decomposition temperature (Td10%) at 280 °C and char yield is 40.90%. Thermal properties were summarized in table 5.4.

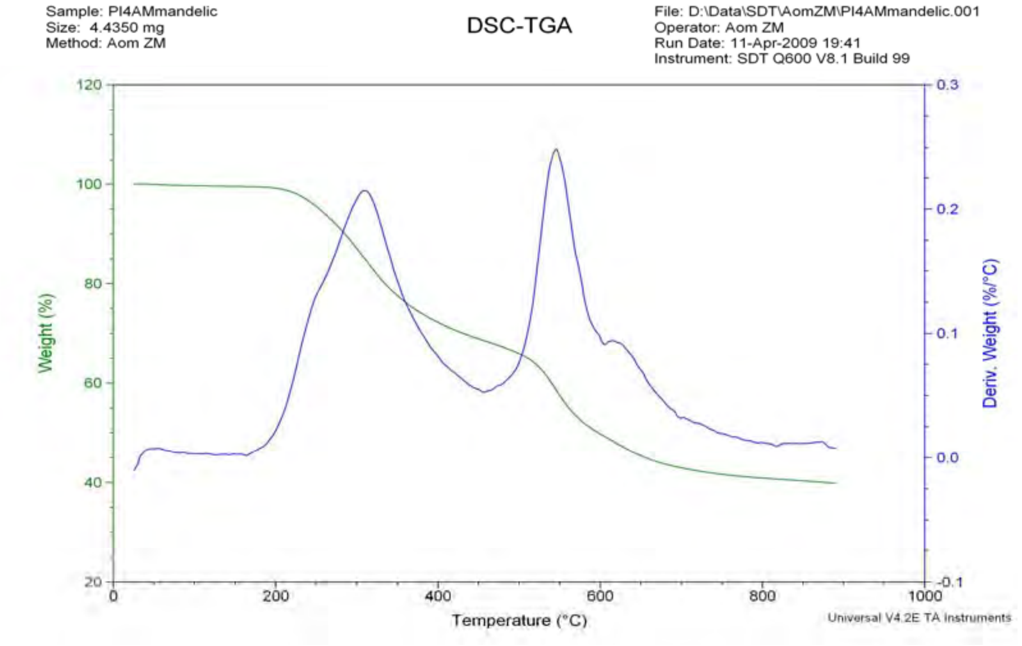


Figure 5.17: TGA curve of PI4AM/mandelic acid amide

Table 5.4 Thermal properties of PI4AM/menthyl chloroformate

% CharYield	40.90wt %
5% Weight loss	254°C
10% Weight loss	280°C

5.3.2.4 Optical microphotographs

(a) (b) (c)

Figure 5.18: Optical microphotographs show the texture of (a) PI (b) PI4AM and (c) PI4AM/mandelic acid amide

Figure 5.18 an example showing the texture of (a) PI (b) PI4AM and (c) PI4AM/mandelic acid amide to confirm the complete reacted in each steps. The effect of containing the chiral compounds as side-chains in polyimide shows the texture of PI4AM/mandelic acid amine (c) which has symmetric configuration.

5.4 Summary thermal properties

Table 5.5 Summary the degradation temperature of chiral amide POSS and polyimide

Chemicals	Td 5% (^{o}c)	Td 10% (^{o}c)	Char yield (%)
OAPS/mandelic acid amide	220	250	14.93
OAPS/menthylchloroformate	180	250	20.25
PI4AM/mandelic acid	254	280	40.90
PI4AM/menthyl chloroformate	209	242	36.27

From table 5.5, it showed the thermal decomposition temperature of 5% mass loss, thermal decomposition temperature of 10% mass loss and char yield of chiral amide of POSS and polyimide. The increasing thermal stability of PI4AM/mandelic acid and PI4AM/menthyl chloroformate as the containing of polyimide chains.

CHAPTER VI

CONCLUSIONS & RECOMMENDATIONS

6.1 Conclusions

In this research, the synthesis of OAPS and the reaction of OAPS and chiral compounds were firstly investigated. From the reactions of chiral, the basic information for studying the reaction of amine functional groups and chiral compounds was established. Moreover, the synthesis of polyimide and the reaction of PI4AM and chiral compounds were investigated. The conclusion of this research can be summarized as follows;

6.1.1 The synthesis of OAPS

OAPS was prepared by two-steps reaction of nitration reaction of OPS to form ONPS and hydrogenation reaction of ONPS to form OAPS. FT-IR spectrum confirmed the existing of functional group of POSS in OAPS.

6.1.2 The reaction of OAPS with mandelic acid or menthyl chloroformate.

The OAPS/mandelic acid amides or OAPS/menthyl chloroformate were synthesized by condensation reaction of OAPS with mandelic acid or menthyl chloroformate. From FT-IR and H^1NMR spectrum, they confirmed the functional group of amide which indicated the incorporation of OAPS with mandelic acid or menthyl chloroformate.

6.1.3 The reaction of PI4AM with mandelic acid or menthyl chloroformate

The PI and PI4AM were prepared by two-steps polymerization of dianhydride and diamine. The PI4AM/mandelic acid and PI4AM/menthyl chloroformate were synthesized by condensation reaction following the reaction of OAPS with mandelic acid or menthyl chloroformate in previous study. The chemical structures of PI, PI4AM, PI4AM/mandelic acid and PI4AM/menthyl chloroformate were confirmed by FTIR and H^1NMR, which affirmed the amide functional group of amide.

6.2 Recommendations

6.2.1 There should be more investigation in the inserting of Liquid Crystals (LCs) cell and the alignment of LCs according to the chiral PI films.

6.2.2 The method of developing the separation column should be continuously examined and verified.

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APPENDICES

APPENDIX A

THE CALCULATION OF POLYIMIDE SYNTHESIS

Calculation of quantitative of 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 3,4′-Oxydianiline (ODA) to synthesized PI.

6FDA+ODA

6FDA: Acid, ODA: Amine

Define

Mole 6FDA: Mole ODA= 4:3 Concentration =15% wt by vol

From

$$r = \frac{\text{Short}}{\text{Long}} = \frac{\text{Amine}}{\text{Acid}} = \frac{\text{ODA}}{\text{6FDA}} = 0.75$$

DP = (1+r)/(1-r) = 7

Let 6FDA (Mw = 444.25 g/mol) = 2 g.
= 0.0045 mol
ODA (Mw = 200.23 g/mol) = 0.00337 mol
= 0.676 g.
Total weight = 2.676 g.
NMP = 17.84 ml.

$$\text{Mw}_{\text{PI}} = \frac{[(\text{Mw of 6FDA}) \times (\text{mol of 6FDA})]+[(\text{Mw of ODA}) \times (\text{mol of ODA})]-[(\text{DP})(\text{Mw of water})]}{\text{Total mol/DP}}$$

= 2251.69 g/mol

PI(6FDA+ODA) + 4AM

PI: Acid, 4AM: Amine

Define

Mole PI: Mole 4AM = 3:4 Concentration =15% wt by vol

From

$$r = \frac{\text{Short}}{\text{Long}} = \frac{\text{PI}}{\text{Amine}} = 0.75$$

DP = (1+r)/(1-r) = 7

Let PI (Mw = 2251.69g/mol) = 1 g.

= 0.000444 mol

4AM (Mw = 214 g/mol) = 0.000592 mol

= 0.1267 g.

Total weight = 1.1267 g.

NMP = 7.5 ml.

$$\text{Mw}_{\text{PI}} = \frac{[(\text{Mw of PI}) \times (\text{mol of PI})]+[(\text{Mw of 4AM}) \times (\text{mol of 4AM})]-[(\text{DP})(\text{Mw of water})]}{\text{Total mol/DP}}$$

= 7,485.07 g/mol

APPENDIX B

Determination of Materials Loading

Material loading that was added into the reaction of OAPS/mandelic acid amide, OAPS/menthyl chloroformate, PI4AM/mandelic acid and PI4AM/menthyl chloroformate were calculated as shown below.

OAPS/mandelic acid amide

$$C_{48}H_{32}Si_8O_{12}NH_8 + 8C_8H_8O_3 \longrightarrow C_{112}H_{104}Si_8O_{12} + 8H_2O$$

Molecular weight of OAPS ($C_{48}H_{32}Si_8O_{12}NH_8$) = 1,154 g/mol

Molecular weight of mandelic acid ($C_8H_8O_3$) = 152.14 g/mol

For example, preparation of material by using 0.5 g of OAPS

$$n = M / Mw$$

where n = mole molecule (mol)

M = mass (g)

Mw = molecular weight (g/mol)

$$\text{Mole of OAPS} = 0.5\ (g) / 1,154\ (g/mol)$$
$$= 0.43\ mmol$$

From mechanism we used 1 mol of OAPS react with 8 mol of mandelic acid, thus loading of mandelic acid was calculated as shown below.

$$\text{Mole of mandelic acid} = \frac{0.43\ (\text{mmol}) \times 8\ (\text{mol})}{1\ (\text{mol})}$$

= 3.47 mmol

When we used 2 excess of mandelic acid = 6.94 mmol

$M = n \times Mw$

Mass of mandelic acid = 6.94 (mmol) x 152.14 (g/mol)

= 1.06 g

When purity of mandelic acid is 99%

Mass of mandelic acid = 1.06 g /0.99%

= 1.07 g

OAPS/menthyl chloroformate

$$C_{48}H_{32}Si_8O_{12}NH_8 + 8C_{11}H_{19}ClO_2 \longrightarrow C_{136}H_{184}Si_8O_{12} + 8HCl$$

Molecular weight of OAPS ($C_{48}H_{32}Si_8O_{12}Br_8$) = 1,154 g/mol

Molecular weight of menthyl chloroformate ($C_{10}H_{12}$) = 218.72 g/mol

For example, preparation of material by using 0.5 g of OAPS

$$n = M / Mw$$

where n = mole molecule (mol)

M = mass (g)

Mw = molecular weight (g/mol)

$$\text{Mole of OAPS} = 0.5\ (g) / 1{,}154\ (g/mol)$$

$$= 0.43\ mmol$$

From mechanism we used 1 mol of OAPS react with 8 mol of menthyl chloroformate, thus loading of menthyl chloroformate was calculated as shown below.

$$\text{Mole of menthyl chloroformate} = \frac{0.43\ (mmol) \times 8\ (mol)}{1\ (mol)}$$

$$= 3.47\ mmol$$

When we used 2 excess of mandelic acid = 6.94 mmol

$$M = n \times Mw$$

Mass of menthyl chloroformate = 6.94 (mmol) x 218.72 (g/mol)

= 1.52 g

$$D = M / V$$

Where D = density (g/cm^3)

M = mass (g)

V = volume (cm^3)

Volume of menthyl chloroformate = 1.52 (g) / 1.02 (g/cm^3)

= 1.5 cm^3

PI4AM/mandelic acid amide

Molecular weight of PI4AM = 7485.07 g/mol

Molecular weight of mandelic acid ($C_8H_8O_3$) = 152.14 g/mol

For example, preparation of material by using 1 g of PI4AM

$$n = M / Mw$$

where n = mole molecule (mol)

M = mass (g)

Mw = molecular weight (g/mol)

$$\text{Mole of PI4AM} = 1\ (\text{g}) / 7485.07\ (\text{g/mol})$$

$$= 0.13\ \text{mmol}$$

We used 1 mol of PI4AM react with 4 mol of mandelic acid, thus loading of mandelic acid was calculated as shown below.

$$\text{Mole of mandelic acid} = \frac{0.13\ (\text{mmol}) \times 4\ (\text{mol})}{1\ (\text{mol})}$$

$$= 0.534\ \text{mmol}$$

When we used 2 excess of mandelic acid = 1.068 mmol

$$M = n \times Mw$$

$$\text{Mass of mandelic acid} = 1.068\ (\text{mmol}) \times 152.14\ (\text{g/mol})$$

$$= 0.162\ \text{g}$$

When purity of mandelic acid is 99%

$$\text{Mass of mandelic acid} = 0.162\ \text{g} / 0.99\%$$

$$= 0.164\ \text{g}$$

PI4AM/menthyl chloroformate

Molecular weight of PI4AM = 7485.07 g/mol

Molecular weight of menthyl chloroformate ($C_{10}H_{12}$) = 218.72 g/mol

For example, preparation of material by using 1 g of PI4AM

$$n = M / Mw$$

where n = mole molecule (mol)

M = mass (g)

Mw = molecular weight (g/mol)

$$\text{Mole of PI4AM} = 1 \text{ (g)} / 7485.07 \text{ (g/mol)}$$

$$= 0.13 \text{ mmol}$$

We used 1 mol of PI4AM react with 4 mol of menthyl chloroformate, thus loading of menthyl chloroformate was calculated as shown below.

$$\text{Mole of menthyl chloroformate} = \frac{0.13 \text{ (mmol)} \times 4 \text{ (mol)}}{1 \text{ (mol)}}$$

$$= 0.534 \text{ mmol}$$

When we used 2 excess of menthyl chloroformate = 1.068 mmol

$$M = n \times Mw$$

$$\text{Mass of menthyl chloroformate} = 1.068 \text{ (mmol)} \times 218.72 \text{ (g/mol)}$$

$$= 0.23 \text{ g}$$

When purity of menthyl chloroformate is 95%

$$\text{Mass of menthyl chloroformate} = 0.23 \text{ g} / 0.99\%$$

$$= 0.24 \text{ g}$$

$$D = M / V$$

Where D = density (g/cm^3)

M = mass (g)

V = volume (cm^3)

Volume of menthyl chloroformate = 0.24 (g) / 1.02 (g/cm^3)

= 0.24 cm^3

VITA

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