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นายเทอดไท เทอดจิตธรรม

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IMPROVEMENT OF MECHANICAL PROPERTIES OF NANOPOROUS
POLYIMIDE FILM

Mr. Therdthai Therdjittoam

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

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Thesis Title IMPROVEMENT OF MECHANICAL PROPERTIES OF
 NANOPOROUS POLYIMIDE FILM

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(IMPROVEMENT OF MECHANICAL PROPERTIES OF NANOPOROUS POLYIMIDE FILM)

อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. มล. ศุภกนก ทองใหญ่ 48 หน้า.

พอลิอิมิด์ฟิล์มที่มีรูพรุนขนาดนาโนให้ค่าคงที่ไดอิเล็กทริกที่ต่ำลงเมื่อเทียบกับพอลิอิมิด์ฟิล์มปกติ แต่ยังคงรักษาสมบัติเชิงกลที่ดี พอลิอิมิด์ฟิล์มที่มีรูพรุนขนาดนาโนสามารถเตรียมได้โดยการสลายตัวทางความร้อนของโคพอลิเมอร์แบบกึ่งระหว่างพอลิอิมิด์และพอลิเอทิลีนไกลคอลที่สังเคราะห์มาจากปฏิกิริยาสังเคราะห์หมู่อีเทอร์ของวิลเลียมสัน (Williamson ether synthesis) ระหว่างพอลิอิมิด์ที่มีหมู่ไฮดรอกซิลในโครงสร้างและพอลิเอทิลีนไกลคอลที่ผ่านการเติมโบรมีนที่ปลายโครงสร้าง พอลิอิมิด์สังเคราะห์ด้วยวิธีที่การันตีที่มี FDA ODA และ DHBP เป็นโมโนเมอร์ทั้งนี้การยืนยันผลการเตรียมโคพอลิเมอร์แบบกึ่งระหว่างพอลิอิมิด์และพอลิเอทิลีนไกลคอลทำได้โดยการวิเคราะห์จาก เครื่องวิเคราะห์เอ็นเอ็มอาร์ (NMR spectroscopy) เครื่องวิเคราะห์การเปลี่ยนแปลงน้ำหนักของสารโดยอาศัยคุณสมบัติทางความร้อน (TGA analysis) และเครื่องวิเคราะห์น้ำหนักโมเลกุลด้วยการสกัดหยาบ (GPC) ซึ่งให้ผลที่สอดคล้องกัน เนื่องจากความสามารถในการทนความร้อนที่ต่างกัน จึงสามารถสร้างรูพรุนให้เกิดขึ้นบนฟิล์มพอลิอิมิด์ จากการสลายตัวทางความร้อนของวัฏภาคของพอลิเอทิลีนไกลคอลด้วยการอบที่อุณหภูมิที่เหมาะสม นอกจากนี้ยังมีการศึกษาผลที่เกิดจากการเปลี่ยนแปลงสองประการคือ เพลอร์เซนต์โมล DHBP ที่มีผลโดยตรงกับการเข้าประกอบของพอลิเอทิลีนไกลคอลในโครงสร้างพอลิอิมิด์ และการเปลี่ยนแปลงขนาดโมเลกุลของพอลิเอทิลีนไกลคอล ขนาดของรูพรุนและการกระจายตัวของรูพรุนที่เกิดขึ้นสามารถตรวจสอบโดยกล้องจุลทรรศน์อิเล็กตรอนแบบสแกน (SEM) และวัดสมบัติเชิงกลและค่าคงที่ไดอิเล็กทริกด้วยเครื่องวัดยูนิเวอรัลแมชชีน (Universal testing machine) และเครื่องวัดความต้านทานแอลซีอาร์ (LCR meter) ตามลำดับ ค่าแทนไซส์ต่ำสุดอยู่ที่ประมาณ ๘๐ เมกะปาสคัล และค่าคงที่ไดอิเล็กทริกต่ำสุดอยู่ที่ ๓.๘

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THERDTHAI THERDJITTOAM: IMPROVEMENT OF MECHANICAL PROPERTIES OF NANOPOROUS POLYIMIDE FILM. ADVISOR: ASSOC. PROF. ML. SUPAKANOK THONGYAI, Ph.D., 48 pp.

Nanoporous Polyimide has a lower dielectric constant than pristine polyimide but remained good physical properties. Nanoporous polyimide was prepared from thermal decomposition of polyimide-g-poly(ethylene glycol) copolymer, synthesized via Williamson ether synthesis reaction from OH-contained polyimide and Br-terminated poly(ethylene glycol). The incorporated poly(ethylene glycol) in polyimide was investigated by Nuclear Magnetic Resonance (NMR), Thermogravimetric Analysis (TGA) and Gel Permeation Chromatography (GPC). Because of the differences in thermal stability between polyimide and poly(ethylene glycol), Pores can be generated while polymer film was being cured at 250 °C. Moreover, the effects of two variations were investigated. One was the effect of changing ratio DHBP:6FDA which directly influenced on the incorporated poly(ethylene glycol) content in polyimide structure. Another was the effect from changing molecular weight of poly(ethylene glycol). Pore size and pore distribution was investigated by Scanning Electron Microscope (SEM). Mechanical properties were measured by Universal Testing Machine. Dielectric constant was measured by LCR Meter. The lowest tensile strength is 70 MPa and the lowest dielectric constant is 3.8.

Department : ...Chemical Engineering... Student's Signature

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

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CHAPTER I

Introduction

Nowadays, microelectronics are substantially important, because they have not only decreasing size of the devices but also increasing efficiency and capability of the device accordingly. When devices are more substantially small, as a consequence, interconnecting delay, cross talk noise and power dissipation are higher.[1] The low dielectric materials have been developed in order to replace silicon dioxide as an interlayer insulator (dielectric constant < 3.5). At initial, insulator film could have dielectric constant approximately 3.0, which polyimide has possessed this property and widely used for this specification so it has been produced in commercial scale. After the further decrease of device size, the dielectric constant of insulation must be close to 2.0 or below. Recently fluorinated polyimide has become important as a film insulator with dielectric constant approximately 2.5.

Mesoporous and Nanoporous material are interesting when applied in modern electronic device. [2-9] Main idea of using air in voids of material to reduce dielectric constant because dielectric constant of air is 1.0, is well known. Although there are many types of porous material, few of porous polymer materials are met the requirements such as good thermal stability, low water uptake and high mechanical properties. Because common properties of polyimide are met this requirements, we emphasize the study and improvement of polyimide by this method.

In current studies, there are two main routes for preparation; one is thermal decomposition of blends of copolymer [3, 4], another is through blend between stable polymer and labile polymer that can be removed with thermal decomposition or solvent extraction[5, 8]. For this study, porous polyimide will be prepared by grafted polyimide with polyethylene glycol as copolymer and use thermal decomposition to remove polyethylene glycol out form backbone of polyimide. PEG will be grafted by Williamson ether synthesis reaction between hydroxyl groups, contained in structure of polyimide, and bromine from bromination of PEG structure.

Beside the preparation of porous polyimide, we test the lamination of polyimide in order to improve mechanical properties of porous polyimide, prepared by previous research. Because of low mechanical properties of porous polyimides, the lamination of them on pure polyimide might improve mechanical properties of the total sheet. Interaction between layers will improve the strength but not decrease the insulator capability, because the upper layer still was porous polyimide and the lower layer was polyimide, which held structure of one another. Moreover, the polymer sheet can be utilized as porous substrate for printed electronics.

The Objective of This Thesis

1. To study the possibility of the method to improve mechanical properties of nanoporous polyimide via lamination on polyimide film.
2. To investigate the new easier method to prepare nanoporous polyimide via thermal decomposition of polyimide-g-poly(ethylene glycol).

The Scope of This Thesis

1. Preparation OH-contained polyimide from 4,4'-oxydianiline (ODA), - 4, 4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 4,4'-diamino-3,3'-biphenyldiol (DHBP)
2. Vary percent mol of DHBP at 1.000%, 0.500%, 0.250% and 0.125%
3. Preparation polyimide-g-poly(ethylene glycol) via Williamson ether synthesis from polyimide and poly(ethylene glycol) $M_n = 750$
4. Preparation polyimide-g-poly(ethylene glycol) via Williamson ether synthesis from polyimide and poly(ethylene glycol) $M_n = 200$
5. Demonstrate incorporation of poly(ethylene glycol) in polyimide
6. Characterize properties of nanoporous polyimide

The Benefit of This Thesis

1. Developing the novel method to prepare porous polyimide.
2. Investigation Williamson ether synthesis in polyimide structure
3. This knowledge can be applied to the new other interested research

CHAPTER II

Theories

Polyimide is a group of high performance organic polymer with imide functional group along each monomer joint. It is the very important material in both scientific and commercial because of its various superior performances such as exceptionally thermo-oxidative stability, high mechanical properties, high modulus, excellent electrical properties and good chemical resistant. Polyimide has been used in many applications nowadays, with major application as dielectric layer of electronic device and aircraft material.

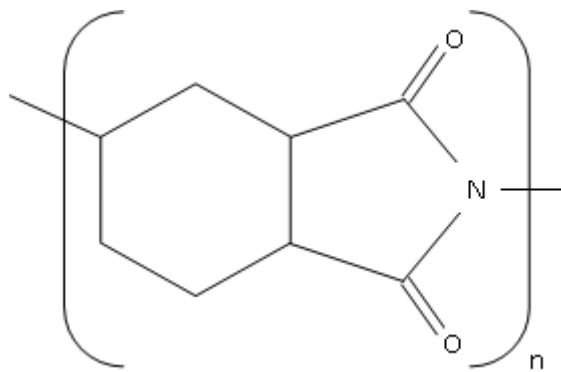


Figure 2-1 Aromatic polyimide

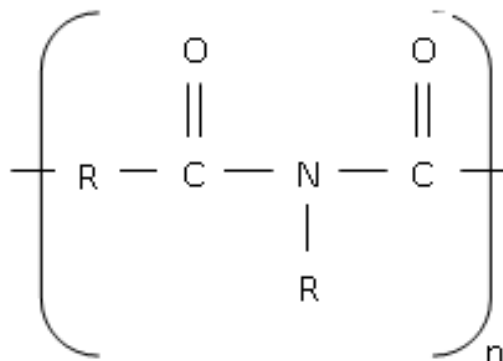


Figure 2-2 Linear polyimide

Polyimide is classified by considering the atom arrangement of imide group as two forms. The first one is linear polyimide (Fig2-2) which atom in imide structure arrange in linear form. Another is aromatic heterocyclic (Fig 2-1) polyimide which atom in imide structure arrange in heterocyclic form; linkage of C=O between aromatic ring and nitrogen atom. Therefore linear polyimide has inferior properties, in both mechanical and thermal properties, and almost all industrial usage polyimide is heterocyclic aromatic polyimide. Rigid structure of aromatic polyimide provides high glass transition temperature ($>300\text{ }^{\circ}\text{C}$), good mechanical strength and high modulus.

2.1 Synthesis of Polyimide

Normally polyimide is insoluble/intractable polymer so casting is nearly impossible after polymerization. In the early attempt, to synthesize aromatic polyimide film was failed because product was intractable by direct synthesis method from diamine salt.[10, 11] The first successful attempt to synthesize high molecular weight aromatic polyimide film was achieved in 1960s by DuPont Researcher. They reported that there were two steps for polyimide synthesis. Initial step was the preparation of poly(amic acid) precursor by reaction between dianhydride and diamine monomer in polar aprotic solvent. Final step was the conversion of polyamic acid into polyimide. This invention utilized soluble and processable intermediate, poly(amic acid).

After the first success, aromatic polyimide became interesting and initiated more research and activated industrial activity. The additional monomers were investigated more. To reduce the complication for the preparation via two steps method, then one-step method was developed. Moreover, there were many more methods to prepare polyimide as can be explained as follows.

2.1.1 Classical Two-step Method

The method that could achieve high molecular weight polyimide was firstly reported in DuPont patent by Endrey in 1962.[12] The main idea of two-step method is the conversion of polyamic acid to polyimide after the polyamic acid was casting as

a thin film on flat substrate such a glass or metal or was spinning into fiber form before conversion.

The initial step is the formation of poly(amic acid) which is conducted by reaction of diamine and dianhydride at ambient temperature in polar aprotic solvent such a NMP, DMAc or DMF. This step may be called “Polycondensation” and the requirements should be obtained for high molecular weight polyimide; that is high purity monomer, one to one stoichiometry of dianhydride and diamine and sufficient reaction time. The final step is the cyclodehydration of poly(amic acid), imidization, which can be proceeded by both thermal and chemical treatment.

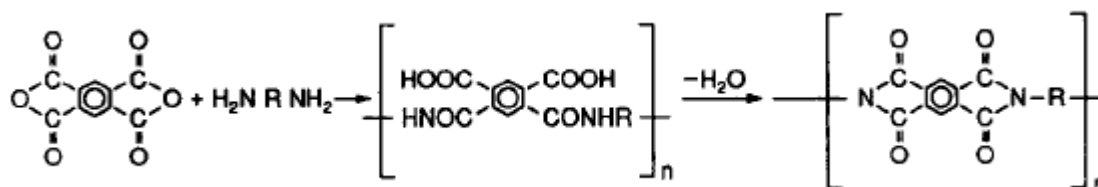


Figure 2-3 Two step method of polyimide synthesis[13]

Poly(amic acid) films can be prepared by casting of polymerized mixture on suitable substrate with an drying in vacuum oven at 80 °C for a hour. Poly(amic acid) fiber can be spun from solution and solid of poly(amic acid) can be precipitated in ethanol or xylene. All forms can be converted to polyimides, which can be tractable and useful.

There are some reports, mention that higher molecular weight polyamic acid can be prepared at lower temperature because it is the nature of exothermic reaction. Nevertheless, the typical requirements of high molecular weight formation should be met.

1. High purity monomer
2. 1:1 stoichiometry between dianhydride and diamine monomer
3. Long time reaction for high conversion
4. Side reaction be minimal

Table 2-1 Electron affinities of dianhydride[13-15]

Dianhydride	Electron affinity, Attojoules
PMDA	0.304
BTDA	0.263
DSO2DA	0.260
BPDA	0.221
ODPA	0.205

Moreover, monomer structure has affected on reaction as well as monomer type and reaction condition. Differences in amine basicity and anhydride acidity have significant effects on the success of poly(amic acid) synthesis. C. E. Sroog mentioned in his review that Soviet researchers have studied acid/basic relationship of diamine and dianhydride in polyimide synthesis and indicated that polycondensation in aprotic solvent is favorable by increased monomer basicity and acidity.[13-15]

Table 2-2 Ionization potentials of diamines[13-15]

Diamine	Ionization potential, Attojoules
PPD	1.10
BZ	1.13
ODA	1.16
MPD	1.19
4,4'-DABP	1.23

Conversion of poly(amic acid)

There are two main methods to convert poly(amic acid) to polyimide. The first method is thermal conversion; the film is heated up to 300 °C and keeps at this temperature for several hours. The second method is the chemical conversion by using dehydrate agent with basic solution. Thermal conversion is demonstrated by disappeared signal in FT-IR followed table 2-3.

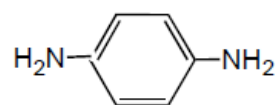
Thermal conversion consists of two rate reactions; initial fast reaction and followed by slow reaction. It is suggested that decreasing of the reaction rate could be related to polymer drying with the possibility that solvent assists in ring closure and that its loss retards imidization.[16] Similarly, Harris suggest that residual solvent act as electron donor/acceptor and thereby facilitates using ring closure.[17]

Typically, chemical conversion procedure is immersion of poly(amic acid) film at room temperature in a bath containing a benzene solution of acetic anhydride and pyridine and follow by drying and removal of solvent after several hours immersion.

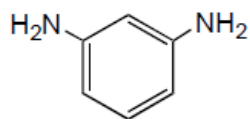
A variation of the chemical conversion methodology permits direct addition of ingredients for chemical conversion to the cold poly(amicacid), such system can be cast into film, or fiber, and heated, thereby avoiding tedious and potentially hazardous handling of large baths of corrosive, flammable toxic substances. In all conversion methods, final heating at temperatures in excess of 300°C is essential to ensuring complete conversion to polyimide.

Table 2-3 Infrared Absorption Bands of Imides and Related Compounds.

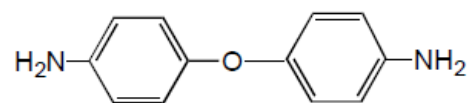
	Absorption Band (cm ⁻¹)	Intensity	Origin
Aromatic Imides	1780	s	C=O asymmetrical stretch
	1720	vs	C=O symmetrical stretch
	1380	s	C-N stretch
	725		C=O bending
Amic Acids	2900-3200	m	COOH and NH ₂
	1710	s	C=O (COOH)
	1660 amide I	s	C=O (CONH)
	1550 amide II	m	C-NH
Anhydrides	1820	m	C=O
	1780	s	C=O
	720	s	C=O
Amines	~3200 two bands	w	NH ₂ symmetrical structure NH ₂ asymmetrical structure



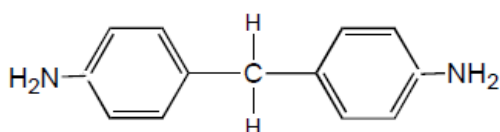
p-phenylene diamine
p-PDA



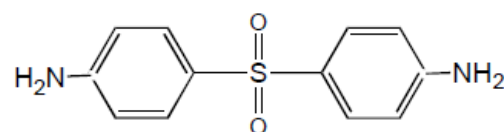
m-phenylene diamine
m-PDA



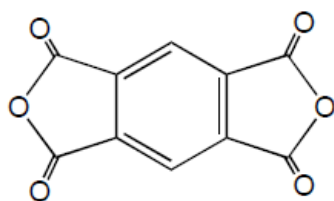
4,4'-diaminodiphenyl ether ODA



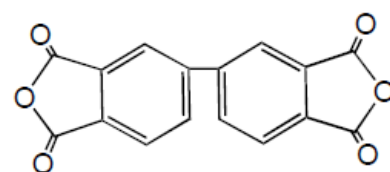
4,4'-methylene dianiline MDA



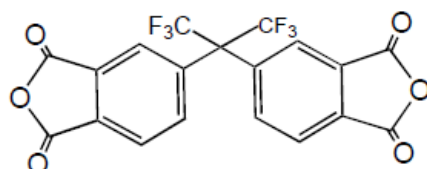
4,4'-diaminodiphenyl sulfone DDS



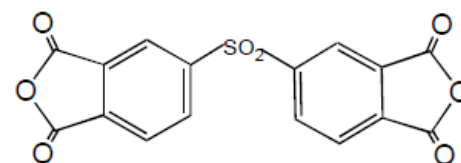
pyromellitic dianhydride PMDA



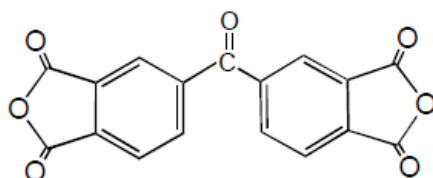
3,3',4,4'-biphenyltetracarboxylic
dianhydride BPDA



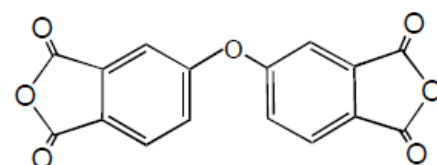
4,4'-hexafluoroisopropylidenebis(phthalic anhydride)
6FDA



4,4',5,5'-sulfonyldiphthalic anhydride DSDA



3,3',4,4'-benzophenonetetracarboxylic dianhydride
BTDA



3,3',4,4'-oxydiphthalic anhydride ODPA

Figure 2-4 Useful monomer

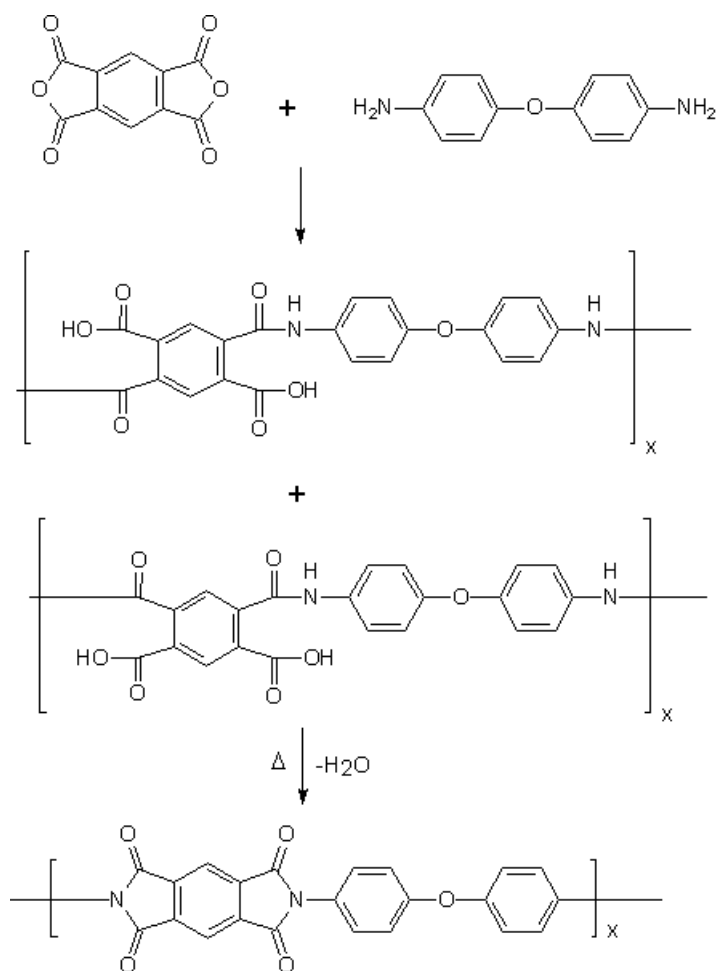


Figure 2-5 Kapton (DupontTM) preparation via two-step method¹

2.1.2 One-step Method

From previous substances, monomer structure affects reactivity in polycondensation step in two-step polymerization method. Thus, it is difficult to polymerize additional monomer, which is inappropriate acidity and basicity via Two-step method. This motion leads to the investigation of novel method of polymerization. In 1970 S.V. Vinogradova et al. reported that polymerization of

¹<http://chem.chem.rochester.edu/~chem424/pimid1.htm>

aromatic polyimide in one stage occur in phenol with presence tertiary amine and polyphosphoric acid at 180 °C[18] afterward there were some research to explore and investigate the method and found that monomers which hinder sterically and inappropriate acid/base relationship or lower-active monomer in two-step method can be successfully synthesized by One-step method.[19-23]

Table 2-4 Phenolic solvents used for polyimide synthesis

Phenolic solvent
phenol
p-chlorophenol
m-cresol
p-cresol
2,4-dichlorophenol
o-chlorophenol
p-methoxyphenol

Various phenolic solvents have been utilized follow Table 2-4. However, One-step method may use other high temperature solvent such a NMP and DMAc as solvent with presence of azeotropic solvent such a toluene. Water, which generated by imidization during reaction, was removed via azeotropic distillation.

Typically, one-step method of polyimide polymerization is carried out by heating diamine and dianhydride in the solvent and then casting polyimide solution in phenolic solvent. Several commercially important polyimides have been prepared by this route. These include ODA-BPDA, 3-3'dimethylbenzidine-PMDA and a variety of PMDA/BPDA copolymers. However, the polyimide PPD/BPDA, the polymer used for Upilex S film, has not been reported as soluble in phenolic solvents. In addition to casting films, these phenolic systems have been used for insulation lacquers and for the spinning of polyimide fibers.

2.1.3 Others Method

Polyimide synthesis by vapor deposition

Polyimide coatings have been prepared by directly printing mixed vapor stream of diamine and dianhydride in 200 °C mixing chamber onto target film. Polyimide

formation was successfully demonstrated for ODA-PMDA, PPD-PMDA, and PPD with trimellitic anhydride acid chloride, onto substrates of Kapton ® or PET film. On this method, polyimide coatings have significant lower oxygen permeability than coating applied conventionally and have good adhesive strength.[24-26]

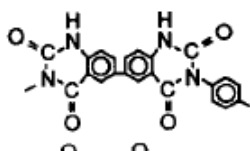
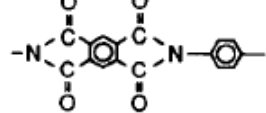

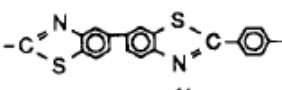
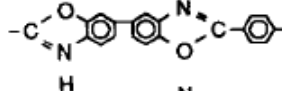
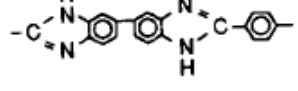
2.2 Properties of Polyimide for dielectric interlayer

2.2.1 Thermal Properties

Thermal stability

This subject has been reviewed by St Clair and Bessonovin terms of temperature for 5% weight loss in air.[27, 28] (Summarized in Table 15) It is evident that for all-aromatic systems, polyimides have outstanding thermal durability versus other heterocyclic systems.

Table 2-5 Thermal stability of aromatic polymer[28]

Structure	Name	Nominal temperature for 5% weight loss in air °C
	Quinazolidinedione	575
	Pyromellitimide	575
	Phenylquinoxaline	575
	Benzothiazole	550
	Benzoxazole	540
	Benzimidazole	520

Moreover, Thermal stability has been observed in other conditions such as air environment for thermo-oxidative degradation and inert environment for thermal

degradation. In Sroog's review, he has noted about investigation of thermal stability that structure of monomer in both air and inert condition affects thermal stability of polyimide. For polyimides derived from ODA, the order of decreasing stability was found to be PMDA > ODPA > BTDA > DSDA.[13]

2.2.2 Electrical Properties

Dielectric Constant

A dielectric material is an electronic material that can be polarized by applied electric field. Electric charges do not flow through material like a conductor but they only shift from their position through the alignment of induction and permanent type causing dielectric polarization. The insulating ability of a dielectric is described by its dielectric constant, ϵ_r . The ϵ_r is defined as the ratio of the measured capacitance of a capacitor filled with the dielectric material to the capacitance of an identical capacitor measured using a vacuum as the dielectric medium. The ϵ_r values for polyimides vary according to structure, but typically range lines between 3.0 and 3.8. The manifestation of a low ϵ_r value is of primary importance in using polyimides for dielectric film.

Dissipation Factor

During application of an alternating current electrical field (AC), the dielectric material absorbs some of the electrical energy as it becomes polarized [117]. Some of this energy can be lost by conversion to heat in the material and, thus, the dielectric constant (or "permittivity") is comprised of a complex value consisting of two components: the real component, ϵ' (the dielectric constant), and the imaginary component, ϵ'' , the dielectric loss component (or dissipation factor). The ratio of these values is designated as the dielectric loss tangent or dissipation factor:

$$\tan \delta = \epsilon'' / \epsilon'$$

The typical value for the dissipation factor of polyimides is 0.002. Low values of $\tan \delta$ indicated the minimal conversion of electrical energy to heat and, thus, signified minimal of overall power loss in the dielectric. It is advantageous to have

low values for both the dissipation factor and the dielectric constant because electrical signals will lose smaller intensity in the dielectric medium.

CHAPTER III

Literatures Review

Nanofoam or Nanoporous polymeric material have two main preparation routes. These included the degradation of block or graft copolymer and the removal of labile phase in stable phase matrix by solvent dissolution. Recently, there are varieties of investigation in order to prepare porous polymeric material by novel method such as blending porous material directly through polymer matrix.

For example, a group of study about degradation of copolymer, in 1997, Kenneth R. Carter and coworker[3] investigated the preparation of nanofoam polyimides form thermal degradation of polyimide/poly(propylene oxide) copolymer. They utilized phase separation of poly(propylene oxide) in polyimide matrix to generate pore via thermal degradation at 250 °C. Polyimide copolymer was synthesized by pyromellitic dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (PMDA/4-BDAF) monomer with addition of poly(propylene oxide) terminated amine and diamine for block-copolymer and graft-copolymer respectively (Fig 3-1). Nanoporous polyimides were achieved and demonstrated by SEM and SXAS. Moreover, nanofoam thin film had good mechanical properties and dielectric constant approximately 2.4 which improved from previous report, pure PMDA/4-BDAF had dielectric constant of 2.8.

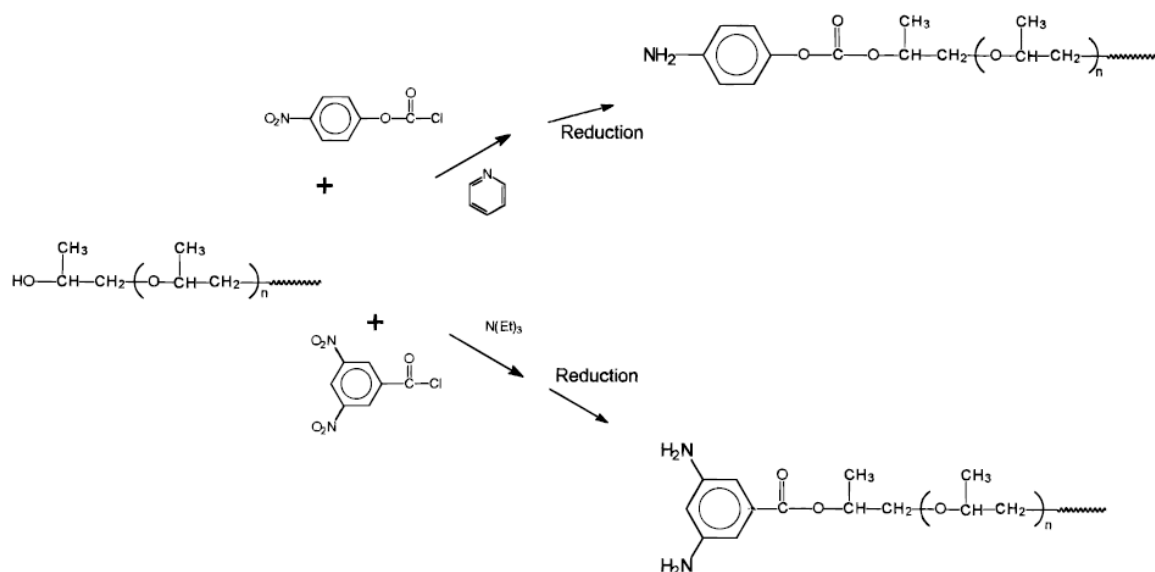


Figure 3-1 Show preparation of terminated amine and diamine PPO [3]

Afterward, in 2001, Kenneth R. Carter and coworker reported a novel nanofoam polyimide synthesis from highly fluorinate polyimide.[4] In this research, they utilized poly(propylene oxide) as a labile phase, follow fig 3-2, while a separated phase of polyimide acted as stable phase. The polyimide was synthesized form 2,2-bis(4-aminophenyl) hexafluoropropane (6FDA) or 9,9-bis(trifluoromethyl) xanthenetetra carboxylic dianhydride (6FXDA). The dielectric constant of nanofoam polyimide obtained was approximately 2.3 and the films had good mechanical properties. Nanopore was achieved and demonstrated by TEM and XSAX.

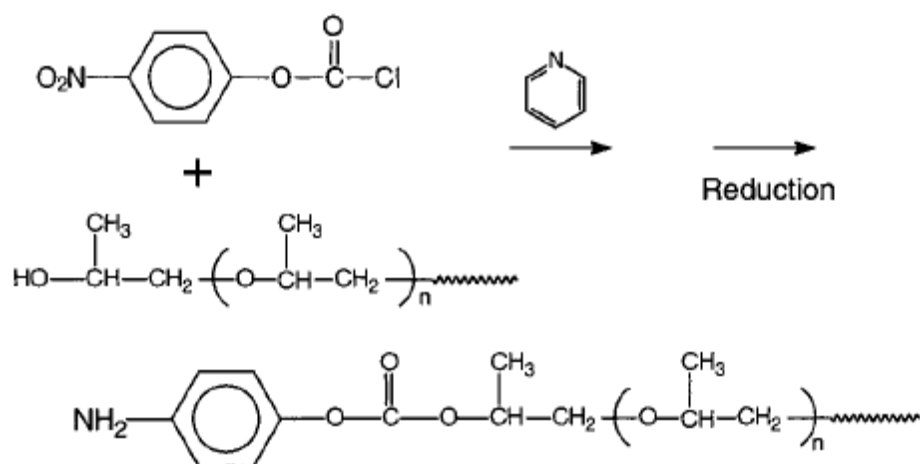


Figure 3-2 Show preparation of terminated amine PPO [4]

In 2004, Changwoon Nah and coworker reported the preparation of nanofoam polyimide from the thermal treatment of poly(amic acid) grafted poly(propylene glycol).[29] Poly(propylene glycol) acted as labile phase and was removed by thermal degradation while poly(amic acid) was cured to produce polyimide. When sufficient thermal treatment time was attained, poly(amic acid) was converted to polyimide completely and poly(propylene glycol) leaved pores in polyimide matrix. Copolymer was prepared by esterification of Br-terminated poly(propylene glycol) and carboxylic group of poly(amic acid). Poly(propylene glycol) content was determined by FT-NMR and pore size was demonstrated by SAXS, TEM and FE-SEM. (Fig 3-3 and 3-4)

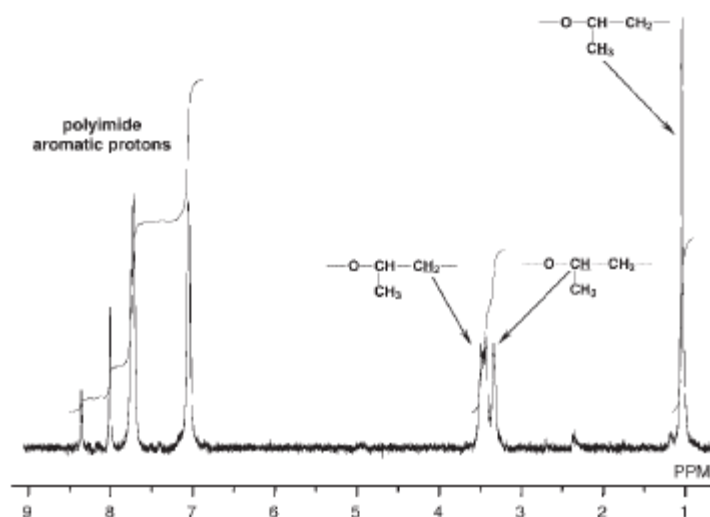


Figure 3-3 FT-NMR to confirm PPO incorporation [29]

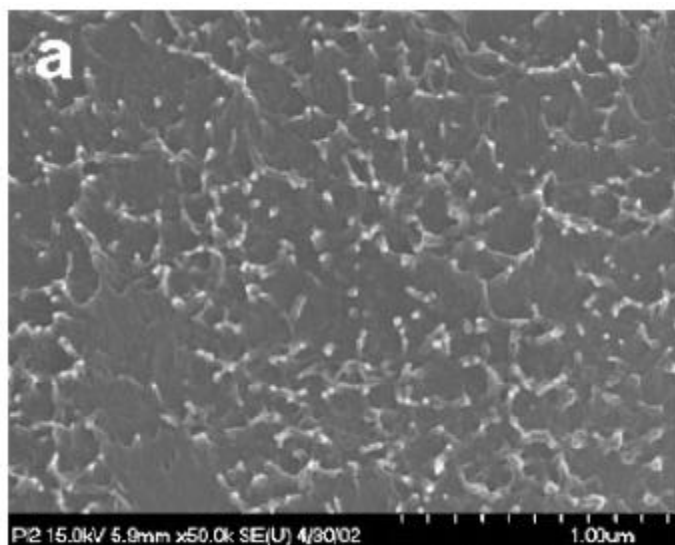


Figure 3-4 SEM nanofoam polyimide film [29]

In 2008, Chan Moon Chung and coworker, have investigated the preparation and characterization of nanoporous polyimide form triblock copolymer.[30] Triblock copolymer was prepared from Amine terminated poly(propylene glycol), 2,2-bis(4-aminophenyl) hexafluoropropane (6FDA), p-phenylenediamine (PDA) and 4,4'-oxydianiline (ODA). The poly(propylene glycol) content was varied by adjusting diamine and dianhydride ratio and was confirmed by FT-NMR. In order to avoid the decomposition of poly(propylene glycol) in thermal imidization step, instead, chemical imidization was performed by using Acetic anhydride and pyridine. Then triblock copolymer was casted on glass and heated to 250 °C to remove poly(propylene). Macro phase separation of poly(propylene glycol) in thin film was removed and leave pore in polyimide matrix. Pore size was larger than 100 nm and was confirmed by SEM. (Fig 3-5) Moreover, this research clearly indicated the significant disadvantage of preparation of porous polyimide form thermal decomposition of block copolymer, that was it made both macro phase and macro pore in matrix film.

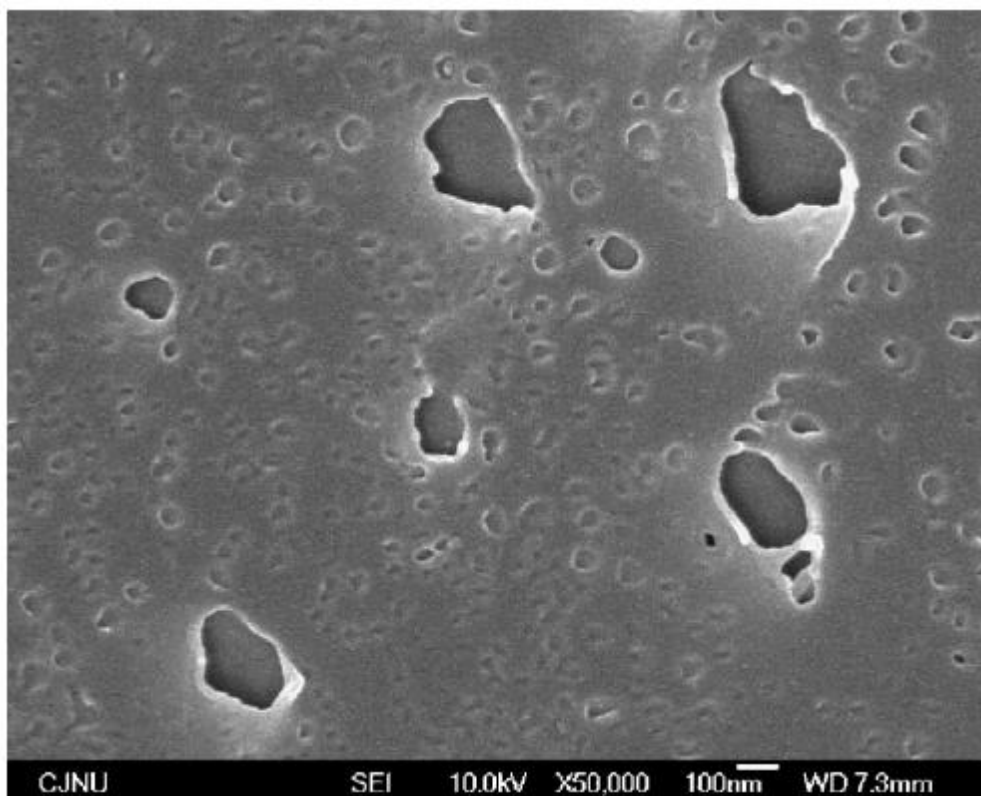


Figure 3-5 SEM porous polyimide film [30]

In the other hand, another route of preparation nanoporous polyimide has been investigated and reported continuously, B. Krause and coworker was studied and reported the preparation of nanoporous polyimide via introduce saturated CO_2 into many types of polymeric films. In 2001 - 2002, [6-9, 31] they reported about the morphology of nanoporous film of polysulfone, polyethersulfone, polyetherimide, polyimide and cyclic olefin copolymer. They introduce CO_2 into polymer film directly by CO_2 treatment in high-pressure chamber. CO_2 in the chamber was in the state of supercritical fluid at high pressure and could permeate into polymer matrix. Then the saturated thin film was taken to heat bath over T_g of polymer rapidly, while CO_2 expanded itself inside the film and generated the pores. Pore sizes depended on type of polymer film, temperature of heat bath and time for CO_2 treatment. Different polymers have different mechanical strength and higher the strength, harder the generation of the pores. In the same amount of CO_2 in film, it gave different pore size

and pore distribution. So in these researches, successfully introduction of the new method to preparation nanoporous thin film could establish.

Initially, B. Krause and coworker had investigated the preparation of foaming polymer from permeability of supercritical fluid CO₂ in polymer medium. Early polymers utilized were polysulfone, polyethersulfone and polycyclic hydrocarbon. (Fig 3-6) These results indicated that any polymeric system has different permeability of CO₂ and it determines with pore size, pore distribution and pore structure in polymer. Moreover, treatment condition has influence with quantity of CO₂ in polymer.

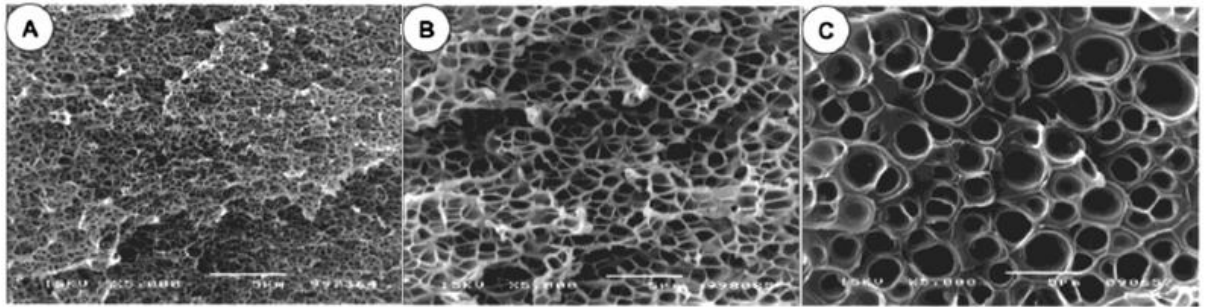
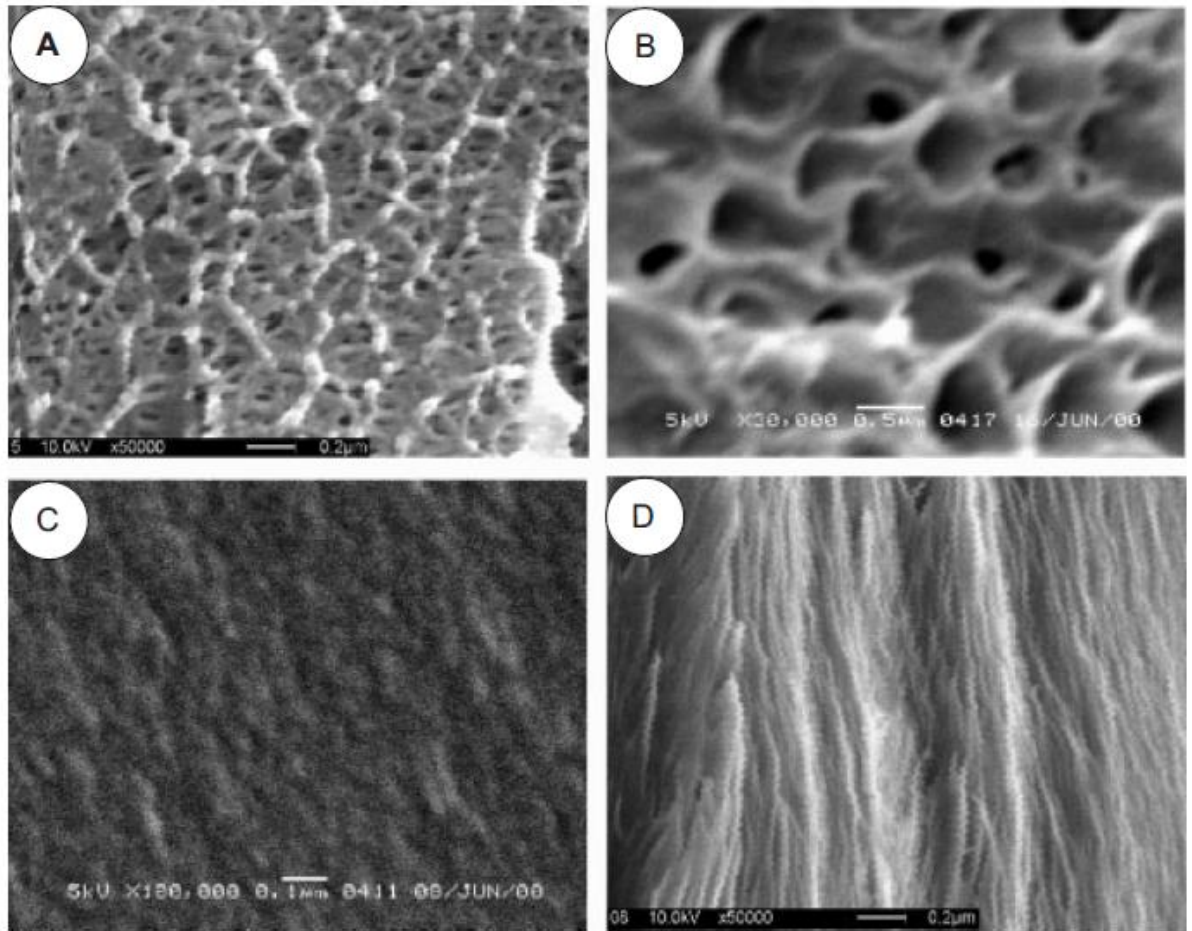


Figure 3-6 Pore structure in A) polysulfone B) polyethersulfone C) polycyclic hydrocarbon [6]

Later, B. Krause and coworker investigated the possibility of using foaming method as same as previous research to polyimide. It was shown that supercritical CO₂ foaming method could be used in polyimide film and succeeded for the preparation of nanofoam from polyimide film. In 2002, they investigated nanofoaming in varieties of polyimide. The results indicated that supercritical CO₂ foaming method could be applied to almost all polyimide but the structures in polymer films were different causing different strength of polyimide film; For example, layer structure in Kapton and porous structure in 6-FDAhydride/6FDAmine.



**Figure 3-7 Structure in film A) Matrimid B) and C) 6FDAhydride/6FDAmine
D) Kapton [8]**

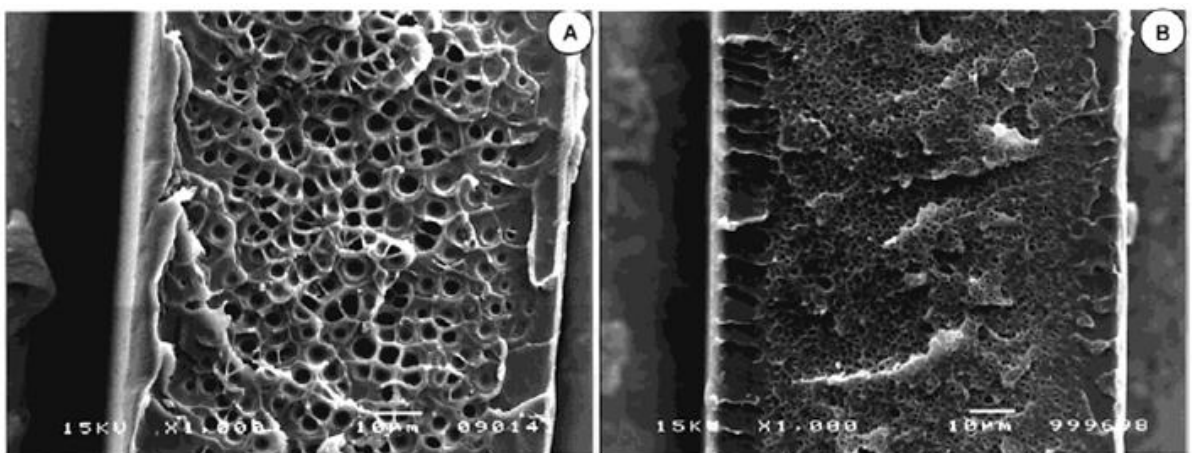


Figure 3-8 SEM of polyetherimide treated saturated CO₂ at A) 5 bar and B) 30 bar [9]

In 2011, Zhaohui Su had reported the preparation of nanoporous polyimide via layer-by-layer self-assembly of cowpea mosaic virus (CPMV) and poly(amic acid).[32] CPMV acted as labile phase in polyimide matrix. They were introduced in poly(amic acid) and were assemble in polymer at nitrogen atom, in order to be compatible with protein surface of CPMV. Then upon thermal treatment, the CPMV particles were removed and the PAA was converted into polyimide in one step, resulted in porous low- κ polyimide thin films. The dielectric constant of the nanoporous polyimide film prepared was 2.32 compared to 3.40 of the corresponding neat polyimide.

CHPATER IV

Experiment

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) dipthalicanhydride (6FDA) from Aldrich Inc.
2. 4,4'-oxydianiline (ODA) from Aldrich Inc.
3. 4,4'-diamino-3,3'-biphenyldiol (DHBP) from Chriskev Company Inc.
4. Monomethoxypoly(ethylene glycol) Mn = 750 form Aldrich Inc.
5. Tetraethylene glycol from Aldrich Inc.
6. Sodium hydride from Aldrich Inc.

4.2 Preparation OH-contained polyimide

Copolymerization was synthesized by dissolve equimolar diamine and dianhydride monomer in NMP at 0.15 g/ml that diamine monomer ratio was DHBP:6FDA by mol equals 1:50. After adding toluene into solution, reactor was stirred and heated to 180 °C for 4 hours in Argon atmosphere with Dean stark trap and reflux condenser. Product solution was precipitated and filtered in 1:1 methanol water before dry in vacuum oven at 90 °C. Repeated in same procedures at each ratio of diamine monomer; 1:100, 1:200 and 1:400 respectively.

4.3 Bromination of polyethylene glycol

Bromination was occurred by the procedure of Buckmann et al.[8] Dissolved PEG in 30 ml of toluene at 0.1 g/ml before added 3 ml thionyl bromide into solution rapidly and stirred solution at 130 °C for 12 hours with reflux condenser. After that, toluene was removed by rotary evaporator. ¹³C-NMR, CDCl₃ (δ, ppm): 30.4 (-CH₂Br), 71.2 (-O-CH₂-CH₂Br), 70.5 (Carbon main chain).

4.4 Preparation polyimide-g-polyethylene glycol

Resolved polyimide in 20 ml of NMP at 0.05 g/ml and add 0.05 g NaH and stir at room temperature for 30 minute. After that, add Br-PEG crude and heat to 90 °C

long enough. Product was precipitated in water/methanol and filtrated. Filtrated powder was dried in vacuum oven.

4.5 Preparation of porous polyimide

Polyimide-g-polyethylene glycol (PI-g-PEG) powder was resolved in NMP at 0.15 g/ml and casted on glass substrate. After dried in vacuum oven at 90 °C for 2 hour, PI-g-PEG on substrate was cured at certain temperature and long enough to generate pore.

4.6 Characterization Instrument

4.6.1 Nuclear Magnetic Resonance

Chemical structure was characterized by Bruker 400 Hz Spectrometer. Polyimide and polyethylene glycol can be dissolved in DMSO-d₆ so they can be interpreted by Nuclear Magnetic Resonance (NMR) technique. Atoms in polymer structure can absorbed magnetic wave which is radiated by NMR and different kind of atoms absord different wave frequency. Then, we can record these frequency to analyse structure of polymer. In this study, NMR was utilized to confirm the incorporation of polyethylene glycol in polyimide structure. Moreover, it could calculate polyethylene glycol content in polyimide by integration of ¹H-NMR.

4.6.2 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) is the measurement of weight loss from sample while temperature in chamber is increasing. Because of thermal degradation, weight of sample when heated was decreased and we could calculate thermal stability of sample and content of copolymer. In this study, PEG content in polyimide structure and decomposed temperature of PEG were characterized by Diamond TG/DTA of Perkin Elmer Ltd.

4.6.3 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a type of size exclusion chromatography (SEC) that separates sample on the basis of size. The technique is often used for the molecular analysis of polymers. In this study, GPC, Shimadzu LC-10A dvp, was used as an instrument to measure molecular weight of polymer. We

could observe the increasing of molecular weight of polyimide after grafting reaction and could calculate PEG content to compare with other measurements. Sample was prepared by dissolution in THF at 0.1 g/ml.

4.6.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a type of electron microscope that images sample by electron beam. Electrons interact with atom of sample and reflection to detector. Electron exchange energy with sample so detector can detect current from electron reflected to image sample. In this sample, pore size and pore distribution could be imaged by SEM, while polymer film has been coated by Platinum after it was cut to be small part.

4.6.5 Universal testing Machine

Tensile properties were characterized by using an Instron universal testing machine with a test speed of 5 mm/min and sample size of 2 x 5 cm². The tensile testing machine of a constant-rate-of-crosshead movement was used. It has a fixed or essentially stationary member carried one grip, and another moveable member carried a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and movable member to prevent the alignment problem. An extension indicator was used for determination of the distance between two designated points located within the length of the test specimen as the specimen is stretched.

4.6.6 LCR Meter

LCR meter is instrument to measure inductance, capacitance and resistance in same sample piece. In this study, LCR meter was characterized the capacitance of polymer film, was cut to be suitable piece, by parallel plate method. The results can be used for calculation of dielectric constant by the followed equation,

$$C_P = \epsilon_0 \epsilon_r \frac{d}{A}$$

When C_P is Capacitance

ϵ_0 is electric constant equal to $8.854 \times 10^{-12} \text{ F m}^{-1}$

ϵ_r is relative permittivity or dielectric constant

d is distance between two plate in this case is thickness of sample

A is area of sample

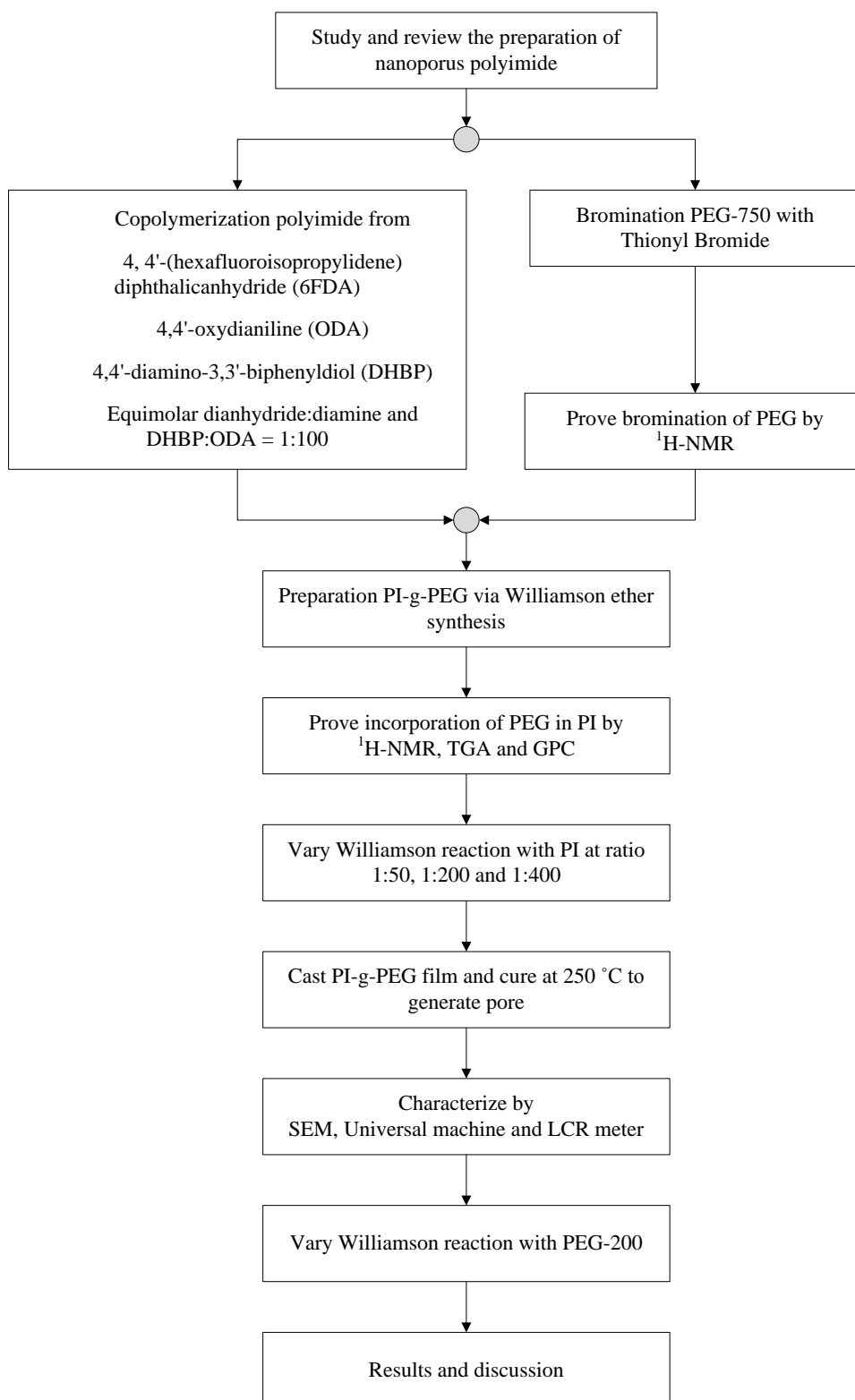


Figure 4-1 Research methodology diagram

CHAPTER V

Results and discussion

The all of polyimides in this study were synthesized via One-step method. Three kinds of monomers were used for polyimide synthesis, as shown in table 5-1 Solvent for these syntheses is N-Methyl-2-pyrrolidone (NMP) with a few amount of toluene for removal water, generated from reaction, via azeotropic distillation in Dean-Strak trap. Monomers reacted in three-neck round bottom flask, heated to certain temperature by heater with silicone oil as heat carrier. Argon was fed into flask continuously while reaction is proceeding.

Table 5-1 List of monomer used in this thesis

Monomer	Abbreviation
4,4' (hexafluoroisopropylidene) diphthalicanhydride	6FDA
4,4'-diamino-3,3'-biphenyldiol	DHBP
4,4'-oxydianiline	ODA

After the reaction completed, product solution was cooled down and was slowly dropped into water/methanol mixture by droplet. The color of droplet polymer was yellow. There were four variations of mol ratio DHBP:6FDA as shown in table 5-2

Table 5-2 Variation of mol ratio DHBP:6FDA

Mol ratio DHBP:6FDA	Percentage mol DHBP
1:50	1.000 %
1:100	0.500 %
1:200	0.250 %
1:400	0.125 %

Intrinsic viscosities of any ratio polyimide were not significant difference from each other's but the amount of hydroxyl groups in polyimide were the direct variation by adjusting the mol percent DHBP. Hydroxyl groups were the reaction took place

when reacted them with brominated poly(ethylene glycol) via Williamson ether synthesis therefore the amount of hydroxyl group has mainly affected to the amount of graft-poly(ethylene glycol), incorporated into polyimide.

Bromination of poly(ethylene glycol) was reacted from thionyl bromide and poly(ethylene glycol). Poly(ethylene glycol) not only can be dissolved in polar solvent both polar aprotic and polar protic solvent but also can be dissolved in aromatic solvent as well as. The clear solution obtained when poly(ethylene glycol) was dissolved in toluene. The first heating was the moisture removal. Water in poly(ethylene glycol), should be removed much as possible, was distilled to Dean-Stark trap via azeotropic distillation because thionyl bromide was highly active with water. After added thionyl bromide, the solution changed color to be clear orange solution. Toluene was evaporated much as possible by rotary evaporation. It is too difficult to separate Br-PEG from PEG so we use crude product in the next step.

Polyimide was redissolved in NMP at low concentration to obtain clear yellow solution before beginning of Williamson ether synthesis. Viscosity of polyimide solution at low concentration was adjusted to be suitable for Williamson reaction, because approachability was crucial for the incorporation of poly(ethylene glycol) into polyimide backbone. When Sodium Hydride (NaH) was added into solution, bubbles had appeared rapidly in solution. These bubbles occurred from gas hydrogen, generated from reaction between hydroxyl group and sodium hydride. They were the evidences for the formation of sodium alkoxide, that were the exited sites of polyimide ready for the reaction with brominated poly(ethylene glycol). After the slowly addition of brominated poly(ethylene glycol), the color of polyimide solution changed from clear yellow to clear orange-red. Product was purified by precipitation into water/methanol solution and appeared as yellow powder. Polymer powder was investigated by $^1\text{H-NMR}$, TGA and GPC during this step.

Polyimide-g-poly(ethylene glycol) was redissolved and cast on a glass substrate to make thin film. Clear yellow-orange thin films, obtained after drying in vacuum oven, have changed into dark-orange film after cured at certain temperature. Thin film could be peeled off the glass substrate when cooled down to room temperature. A part

of thin film was cut into small pieces and was investigated the surface by SEM. The other parts were cut into $2 \times 5 \text{ cm}^2$ and $1.5 \times 1.5 \text{ cm}^2$ for tensile testing and dielectric constant measurement respectively.

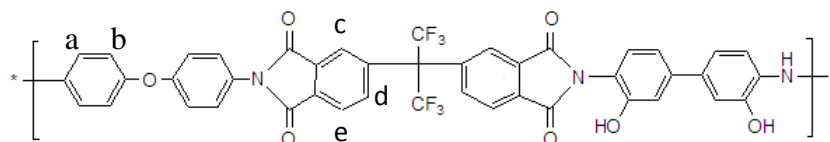


Figure 5-1 Structure of A) 4,4' ODA and B) 6FDA in polyimide structure

5.1 Nuclear Magnetic Resonance study

Polyimide and Polyimide-g-PEG was soluble in DMSO- d_6 so NMR detail and structures elucidated by NMR was possibly interpreted by 400 Hz Bruker. $^1\text{H-NMR}$ of Polyimide-g-PEG in fig. 5-2 showed that the attached proton on aromatic ring showed in chemical peaks shift 7.0-8.5 ppm.[33] Protons of ODA were in chemical peak shift 7.0-7.5 ppm, consisted of doublet at 7.235 and 7.256 ppm (H_a , 4H) and doublet at 7.492 and 7.513 ppm (H_b , 4H). Protons of 6FDA were in chemical peak shift 7.5-8.5 ppm, consist of singlet at 7.766 ppm (H_c , 2H), doublet at 7.958 and 7.577 pm (H_d , 2H) and doublet at 8.179 and 8.199 ppm (H_e , 2H).

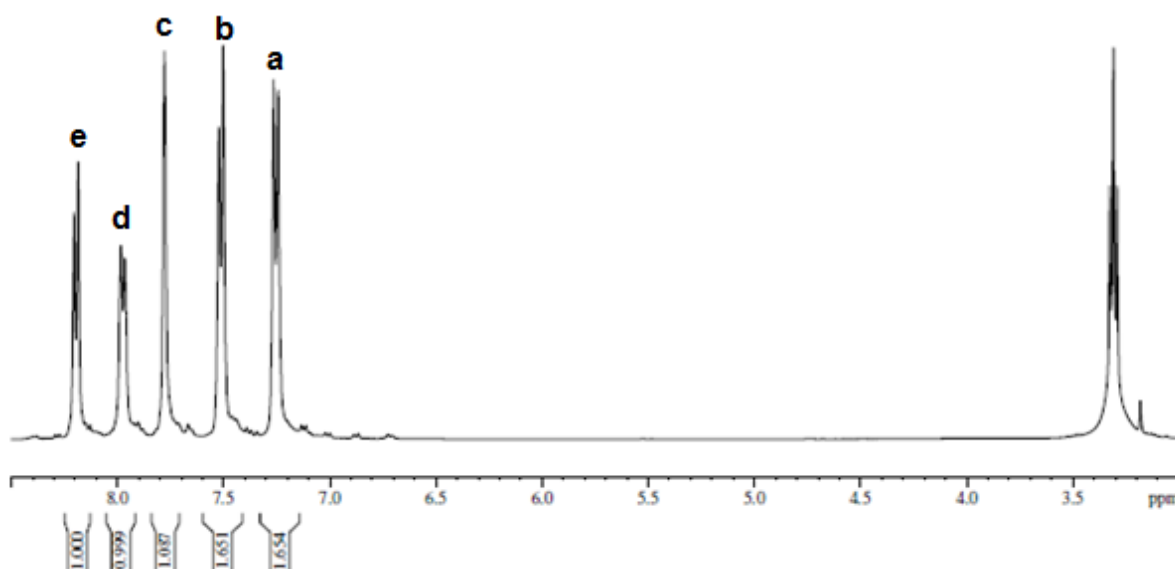
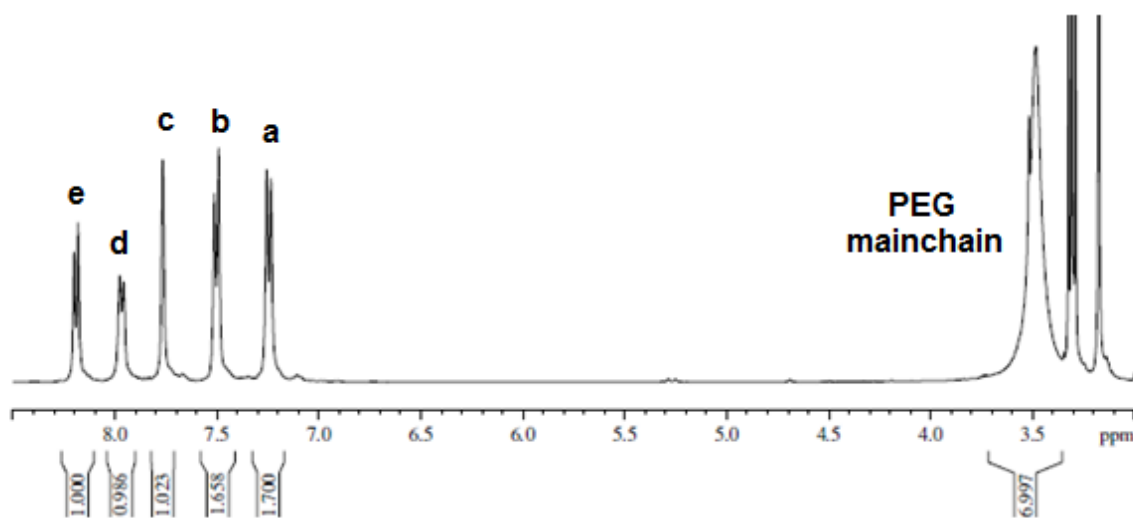


Figure 5-2 $^1\text{H-NMR}$ of Polyimide at percent mol DBHP = 0.5%

After polyimide reacted with brominated poly(ethylene glycol) via Williamson ether synthesis, the significant different was found that chemical peak shift of poly(ethylene glycol) main chain at 3.5 ppm is existed.(Fig 5-3) The intergration of aromatic in polyimide structure was a constant. It confirmed that no degradation of polyimide during Williamson ether synthesis. The calculation of poly(ethylene glycol) content could be possible by intregation of $^1\text{H-NMR}$ (Fig 5-2). Poly(ethylene glycol) content was calculated from NMR, compared with results from GPC and TGA as can be seen in table 5-1. The integration of poly(ethylene glycol) in fig 5-3 was the atom ratio of proton in mainchain of poly(etyhlene glycol) per proton in 6FDA and dividedeach component by total proton to obtain mol ratio of PEG:6FDA. Then, we could calculate the percent weight of poly(ethylene glycol)in polyimide by convert the mol ratio into weight ratio based on 100 repeating unit of polyimide (100 units of 6FDA), that was the approximate molecular weight of polyimide.



**Figure 5-3 $^1\text{H-NMR}$ of Polyimide-g-poly(ethylene glycol) at percent mol
DBHP = 0.5%**

5.2 Thermal Gravimetric Analysis study

Thermo-oxidative degradation of poly(ethylene glycol) was observed by Diamond TG/DTA. The thermal decomposition of nascent poly(ethylene glycol) in atmosphere was confirmed the initial decomposition at low temp ($\approx 100\text{ }^\circ\text{C}$) but in nitrogen atmosphere it start decomposition at around $250\text{ }^\circ\text{C}$. [34] We could calculate percent weight of poly(ethylene glycol) in polyimide-g-PEG by TGA by observe

percent weight loss in range 200 to 500 °C. There is different derivative weight loss at 200 °C, that is changing from solvent evaporation to decomposition of poly(ethylene glycol). Thermal decomposition of PEG is around 230-450 °C and thermal decomposition of polyimide is around 450 °C. The first step of weight loss around 150°-200°C might be the evaporation of solvent in matrix film. Next step weight loss around 230°C was contributed from the decomposition of poly(ethylene glycol). The last step weight loss at 450°C was contributed from polyimide degradation. (Fig 5-4)

The point of percent weight loss (POINT A) was behind the first slope, represented the percent weight of copolymer without solvent (PI+PEG). This point could be identified by the zero value of derivative weight loss and was found to be around 92.2% wt. When polymer temperature was around 250 °C, poly(ethylene glycol) was beginning to decompose. The slope of PEG decomposition range was not smooth because of the differences in decomposition rate of arbitrary phase size (Micro and Macro phase) in polyimide. The end point with significant changing of derivative weight loss (POINT B), indicated the beginning region of decomposition of polyimide. Then, the percent weight at this point, assumed as the percent weight of polyimide with completion of poly(ethylene glycol) removal (PI only), was found to be around 84.2%. The difference of percent weight loss between two points (A and B), represented the percent weight of PEG in polyimide, was found to be around 8.0%.

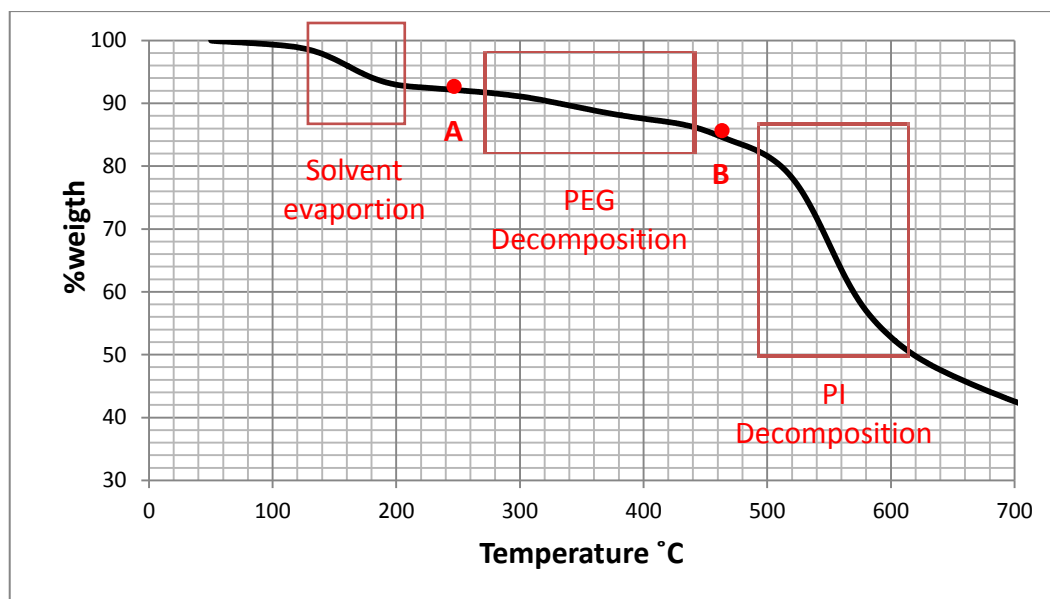


Figure 5-4 TGA of Polyimide-g-PEG

5.3 Gel permeation chromatography

Polyimide and polyimide-g-PEG resolved in THF at 1 mg/ml and was injected into Shimadzu LC-10A dvp. The average molecular weight of polyimide and polyimide-g-PEG is 85,000 and 92,000 respectively. (Table 1) From GPC results, the increase in molecular weight of polyimide-g-poly(ethylene glycol) is 8.23% when compare with nascent polyimide. $(\%wt\ PEG = \frac{\Delta M_w}{M_{w0}} \times 100\%)$

Table 5-3 Summarize results of poly(ethylene glycol) calculation

Sample	%PEG NMR	%PEG TGA	Mw
Polyimide	-	-	85,00
Polyimide-g-PEG	11.7	8.0	92,00

There were the similar results obtained from different instruments. The similar results confirmed the equal amount of PEG incorporated in polyimide of the same sample and assured that the incorporation of poly(ethylene glycol) in polyimide structure was possible. $^1\text{H-NMR}$ results show the incorporation value was 11.7% from ration of proton main chain of PEG and proton monomer of polyimide confirmed that grafted PEG were in polyimide structure via Williamson ether synthesis reaction.

TGA results showed the incorporation value of 8.0% by the thermal decomposition of PEG in range of 250-450 °C and were able to calculate in %wt by different weight loss per total weight. GPC results showed the incorporation value of 8.23% by calculated the increasing of molecular weight of polyimide after grafted with PEG. Then, polyimide-g-PEG could confirm to be prepared by our method with similar results from different equipment.

5.4 Scanning Electron Spectroscopy

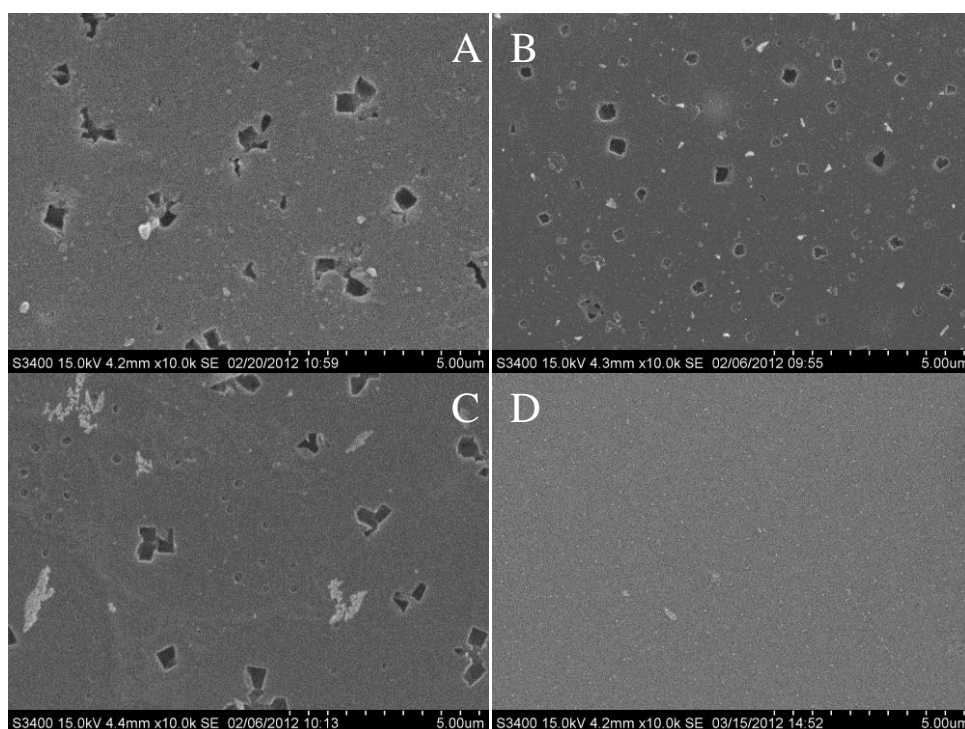


Figure 5-5 SEM of Polyimide-g-poly(ethylene glycol) – Mn = 750 after cured at 250 °C percent mol DHBP at A) 1% B) 0.5% C) 0.25% D) 0.125%

After polyimide-g-poly(ethylene glycol) was cast on glass substrate, and cured long enough in oven at certain temperature. A part of film was investigated by SEM. Fig 5-5 show surface of porous polyimide film. Fig 5-5A is porous polyimide picture, prepared from polyimide at percent mol DHBP = 1% with PEG molecular weight 750. Majority of pores are in the range of 0.5-1.0 μm because of high poly(ethylene glycol) content in polyimide structure. Poly(ethylene glycol) phase accumulate each

others to form macro phase, so that large size pores were obtained. Moreover, high poly(ethylene glycol) content affected the pore distribution. If the distribution of the pores was low, the wall of macro pore might be collapsed into each other and enhance size of macro pore.

We could reduce distribution of poly(ethylene glycol) content by vary ratio of DHBP:6FDA. Good pore distribution was found in percent mol DHBP at 0.5%. Almost of all pore are smaller than $< 0.1\mu\text{m}$ and have good distribution. In other hand, percent mol DHBP = 0.25% gave a porous film which contained both macro pore as same as micro pore. Polyimide with percent mol DHBP = 0.125% has no pore observed because poly(ethylene glycol) content is too low to generate pore or poly(ethylene glycol) phase is underneath polyimide surface because the oxygen cannot attack PEG easily.

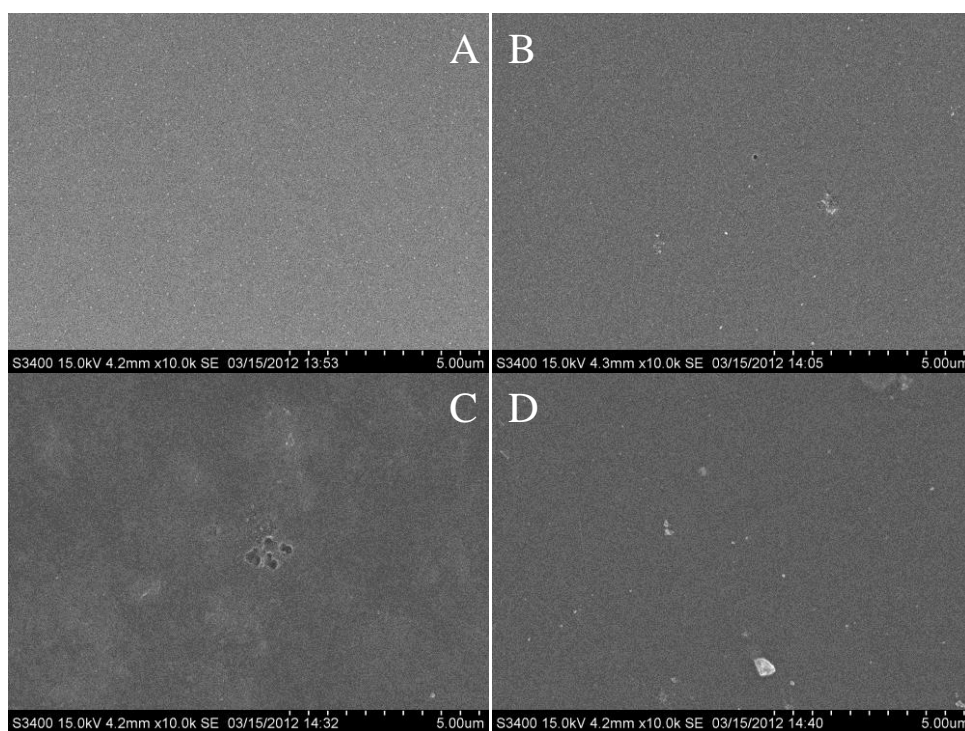


Figure 5-6 SEM of Polyimide-g-poly(ethylene glycol) – Mn = 200 after cured at 250 °C percent mol DHBP at A) 1% B) 0.5% C) 0.25% D) 0.125%

There are no pores observed in polyimide-g-poly(ethylene glycol)(Mn=200). Because poly(ethylene glycol) content is too low or the pore is too small to observe. It is too hard to found pore on surface film with SEM. Molecular weight of

poly(ethylene glycol) has affected to each phase size and phase distribution regardless of agglomeration of PEG Phase. When separated phase size is too small and well distribute, separated phases are warped underneath by polyimide surface and make the PEG domain to be in close system. Temperature in close separated phase might lower than environment, as oven chamber, because polyimide acted as heat insulator and permeability of oxygen is too low in polyimide matrix, so the under-heated PEG did not attach to Oxygen. Thermo-oxidative decomposition of poly(ethylene glycol) was almost impossible at short time but slowly thermal decompose process might be possible if the time in oven is long enough.

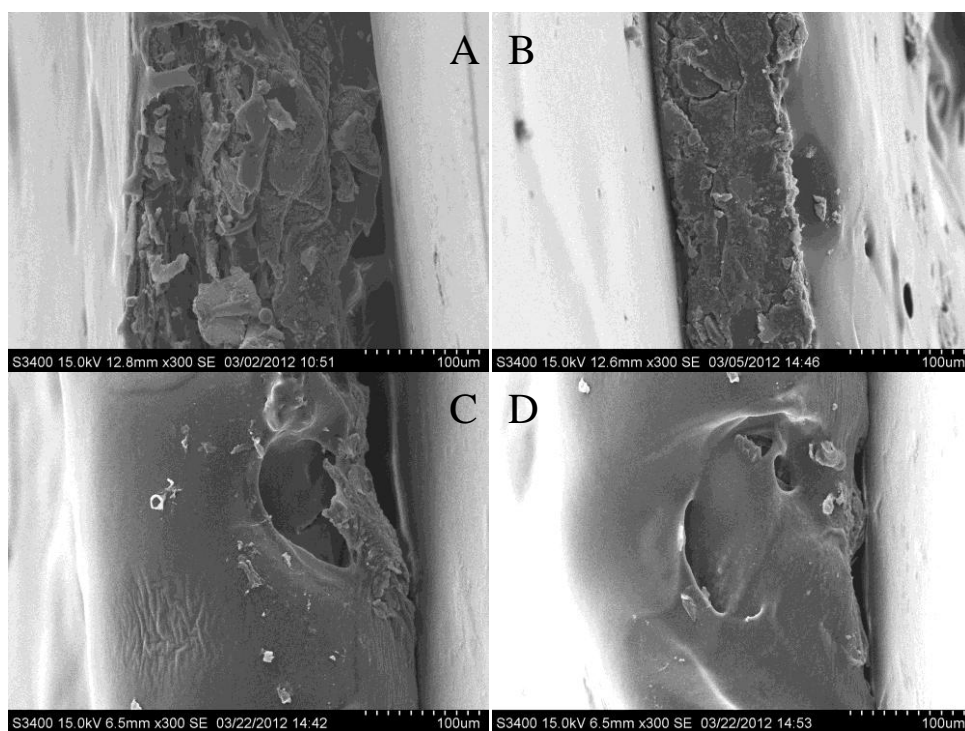


Figure 5-7 SEM of cross-section polyimide-g-poly(ethylene glycol) after cured at 250 °C percent mol DHBP = 0.25% A) fracturing in liquid nitrogen B) cross-section come from cutter C) and D) cross-section come from scissors

For investigation pores of porous polyimide underneath the surface of polyimide, cross section is needed. In this study, varieties of methods to cross section film were investigated and compared. Fracturing in liquid nitrogen is one of the three investigated methods. Even through fracturing in cryogenic condition is useful for many polymeric materials, for polyimide, this method cannot be used because of the

high toughness of polyimide even at cryogenic temperature. Cross section surface by this method caused rough fracturing and further spread into flakes. (Fig 5-7 A)

Section by cutter gave the smoother surface than fracturing in liquid nitrogen. However, the smoothest surface was received from cross-section from scissors. (Fig 5-7C and D) Majority of cross-section surface was dense even so few macro pores were found. Macro pores were around 50 μm that possibly generated from bubbling in casting or accumulation of gas during thermal decomposition of PEG.

It was possible that pores were located underneath polyimide surface, if the pores were macro pore. Although we cannot observe the smaller underneath pore by cross-section SEM, the others properties of polyimide might indicate the existence of micro pore in polyimide films.

5.5 Physical properties

Strengths of porous films were inversely proportional to poly(ethylene glycol) content in polyimide as same as percent mol DHBP. Mechanical properties consist of tensile strength, % elongation and modulus, were characterized by Universal testing machine.

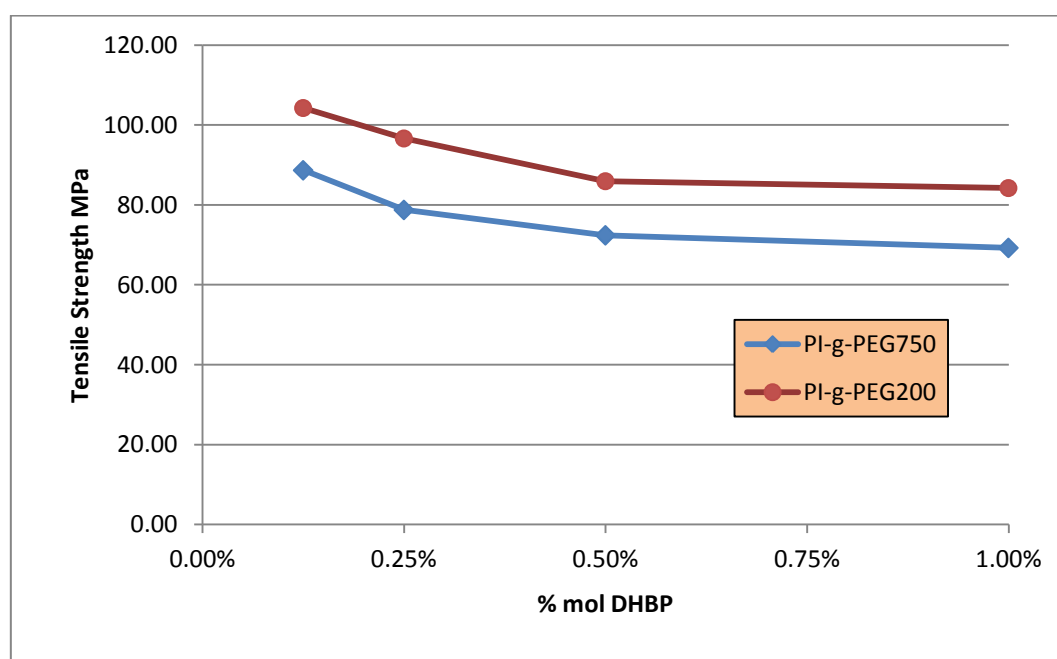


Figure 5-8 Show Tensile strength of porous polyimide film

The comparison of tensile strength of porous polyimide with the same size of poly(ethylene glycol), indicated that tensile strength is decreased by increasing percent mol DHBP as increase amount of poly(ethylene glycol) content per unit of polyimide, typical behavior of copolymer. At low poly(ethylene glycol) content or low percent mol DHBP, tensile strength got close to value of pristine polyimide (113 MPa). The weakest porous polyimide film gave tensile strength at 70 MPa which still could be prepared as standing free film.

In other direction, the comparison of porous polyimide from different size poly(ethylene glycol) while keeping the constant percent mol DHBP. Lower molecular weight PEG incorporated in Polyimide gave higher tensile strength content. In other words, porous polyimide, came from poly(ethylene glycol) – Mn 200, were stronger than porous polyimide, came from poly(ethylene glycol) – Mn 750.

Table 5-4 Summarized of thickness, Modulus and Elongation

Percent mol DHBP	PI-g-PEG-750			PI-g-PEG-200		
	Thickness μm	Modulus GPa	Elongation %	Thickness μm	Modulus GPa	Elongation %
1.000	42	1.95	4.30	49	2.35	4.38
0.500	50	2.24	3.40	46	2.50	3.12
0.250	41	2.07	4.24	63	2.10	6.18
0.125	54	2.16	3.26	66	2.10	5.07
Kapton	25	3.00	70	-	-	-

From table 5-2, Modulus of porous polyimide film is between 2.0 to 2.5 GPa regardless of molecular weight of incorporated PEG. However, there was a tendency that the modulus will slightly increase when decreasing the molecular weight of PEG which is coinciding with tensile properties. Moreover, it seemed that at % mol DHBP equal 0.25 %, the modulus was highest and decrease down as the increase percent DHBP because the second phase in the copolymer made the copolymer harder to stretch, so the modulus is temporarily increase. However, when percent mol DHBP lower toward 1% mol DHBP, the modulus is decrease down because the void in the copolymer did not contribute to the mechanical properties, so the modulus drop.

Elongation showed the flexibility of material, so the thickest sample, contain most PEG that did not decomposed, show the highest elongation and reduced down to thinner sample. The most porous film show the more elongation because of the void enhanced the stretch to flexible before break more than un-porous samples. It indicated that porosity is not significant factor to be effect to flexibility of film because some PEG is remained underneath polyimide and contribute to mechanical properties. At low % mol of DHBP, porous films give similar modulus because of closing pristine polyimide film behavior.

5.6 Dielectric constant

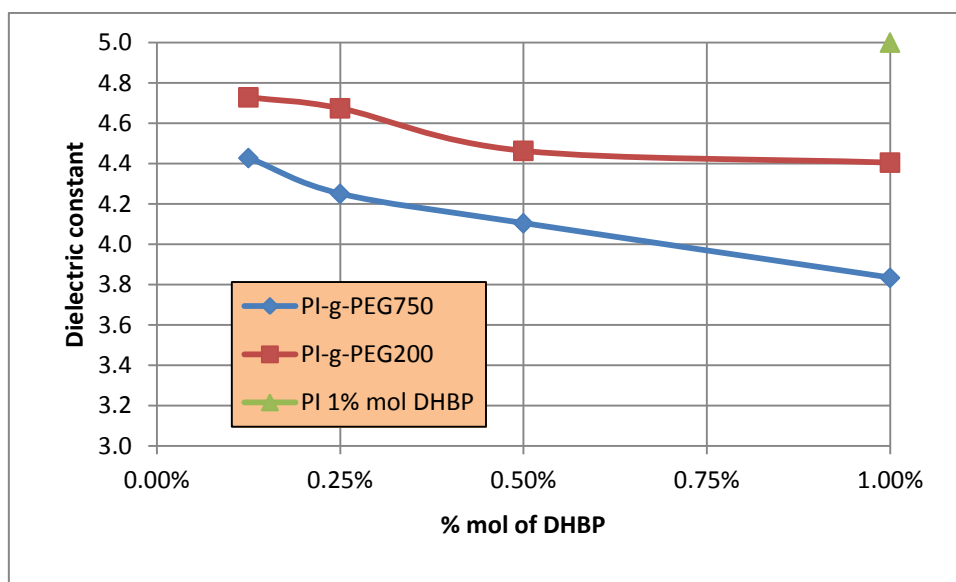


Figure 5-9 Dielectric constant of porous polyimide film

Dielectric constants of porous films were measured by LCR meter with parallel plating. Dielectric constant of porous film decreased from nascent polyimide film at 5.1 to 3.8 for percent mol of DHBP equal 1 % with poly(ethylene glycol) $M_n = 750$. Follow discussion in 5.4 that thermo-oxidative decompose is almost impossible at low poly(ethylene glycol) content and slowly thermal decompose might be possible. Then, higher dielectric constant was obtained at lower poly(ethylene glycol) content which has less void. Char residue came from thermal decomposition of PEG, that made dielectric constant increased. Moreover, poly(ethylene glycol) that still remained in matrix film possibly affected the dielectric constant as well as (higher).

The different slopes of the two curves can be seen in fig 5-9. The different molecular weight poly(ethylene glycol) gave different poly(ethylene glycol) content in polyimide, that affected to dielectric constant directly. The decrease in pore size and the decrease of oxygen accessibility were obtained when copolymer was synthesized from lower molecular weight poly(ethylene glycol). So, it made more difficult to decompose poly(ethylene glycol)-Mn 200 in polyimide film. The lowest dielectric constant obtained by poly(ethylene glycol) Mn=200 approximate 4.4 which showed porous characteristic.

CHAPTER VI

Conclusion

In this study, preparation of polyimide-g-poly(ethylene glycol) was possible by Williamson ether synthesis method and could be demonstrated the similar incorporation of PEG by $^1\text{H-NMR}$, TGA and GPC. $^1\text{H-NMR}$ results showed that grafted poly(ethylene glycol) were attached to polyimide structure via Williamson ether synthesis reaction and able to calculate in %wt by ration of proton main chain of PEG and proton monomer of polyimide. TGA results showed thermal decomposition of poly(ethylene glycol) in range 250-450 °C and able to calculate in %wt by monitoring %wt change according to PEG. GPC results showed the increasing of molecular weight of polyimide after grafted with poly(ethylene glycol). Then, polyimide-g-poly(ethylene glycol) can be prepared and further used for nanoporous polyimide film preparation.

Nanoporous polyimide film was prepared from thermal decomposition of polyimide-g-poly(ethylene glycol) via thermal curing at certain temperature and time, because the thermal decomposition temperature should be lower than T_g of polymer film, otherwise collapse of pore would attain. There were two series of polyimide-g-poly(ethylene glycol). One was polyimide-g-poly(ethylene glycol) with poly(ethylene glycol) molecular weight 750. Another one was poly(ethylene glycol) molecular weight 200. SEM results found that there were pores on surface of polyimide film and pore size and pore distribution varied with effects from poly(ethylene glycol) content in polyimide film for higher molecular weight poly(ethylene glycol). For lower molecular weight poly(ethylene glycol), no pores were found by SEM. Cross-section SEM shown that there are few pores underneath polyimide surface with both two poly(ethylene glycol)s series and suitable cross-section surface was obtained from scissor cutting. All of SEM results indicated that porous polyimide film, prepared from this method, need to be thin film ($< 20 \mu\text{m}$) in order to improve oxygen attack easier for thermal-oxidative decomposition.

The physical properties and electrical properties were inversely varied with poly(ethylene glycol) content. Higher poly(ethylene glycol) content given lower dielectric constant and lower tensile strength. The lowest tensile strength was approximate 70 MPa and the lowest dielectric constant was 3.8. From these, this method was not recommended for producing insulation polyimide because high dielectric constant film would attained even through their strength were acceptable but this method is a novel method which is easier to prepare porous polyimide than previous method.

Knowledge from this thesis

1. Graft copolymer of polyimide can be synthesized via Williamson ether synthesis.
2. For thermal-oxidative decomposition of polymer film, thin film should be prepared. It is the most important factor to prepare porous polyimide film via this method.
3. The low molecular weight poly(ethylene glycol) not only make smaller size pore but also make lower accessibility of oxygen using in decomposition.
4. Cross-section of polyimide film should be cut by scissors
5. The thermal decomposition temperature should be lower than the glass transition temperature of the matrix polyimide in order not to obtain collapse pore (no pore attained at all).

Recommendations

1. Vary ratio DHBP:6FDA more than 1:50 which was used preparation of polyimide-g-poly(ethylene glycol)
2. Apply spin coat method to preparation polyimide-g-poly(ethylene glycol) thin film
3. The preparation of polyimide-g-poly(ethylene glycol) should be modified by react between Chloride-attached Polyimide, replace the OH-attached polyimide, and OH in poly(ethylene glycol) because the dielectric constant of porous polyimide film can be reduced.

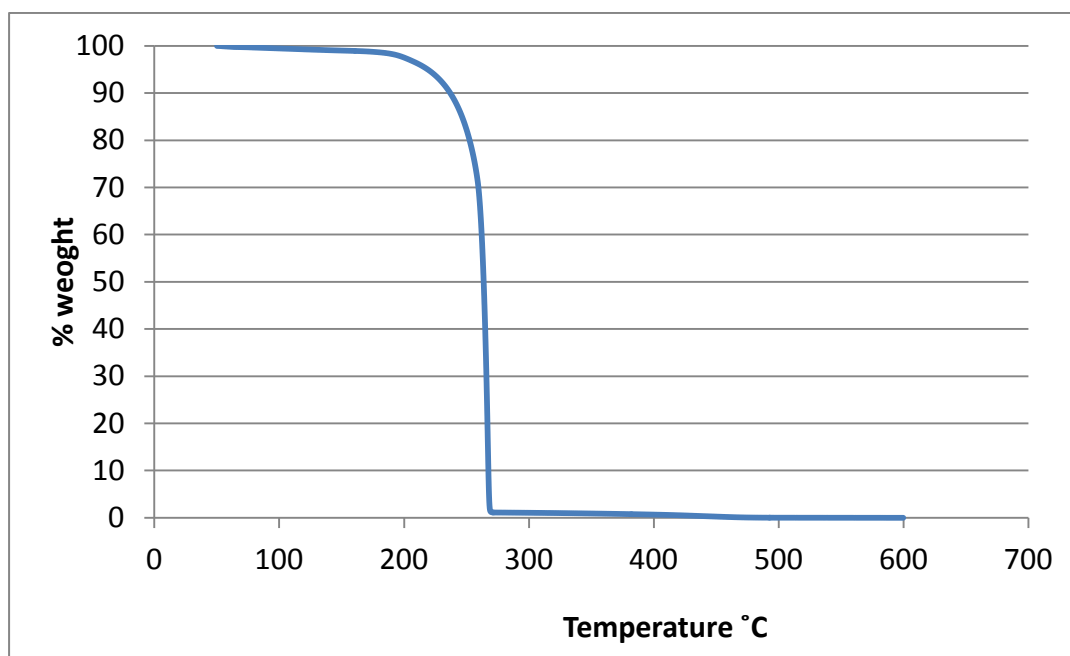
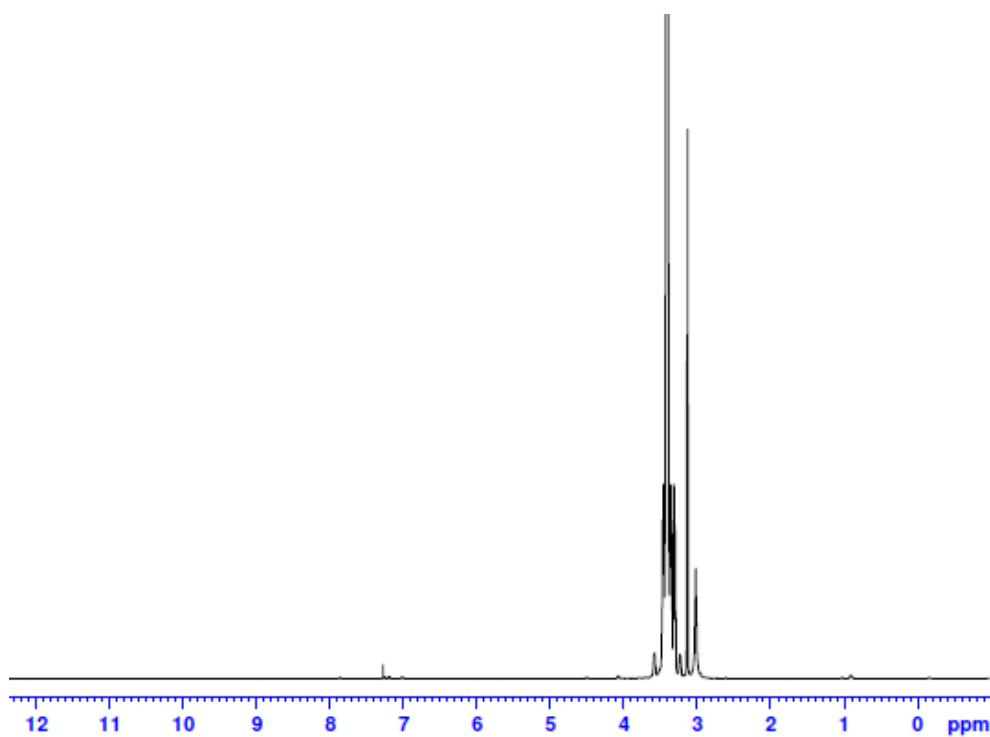
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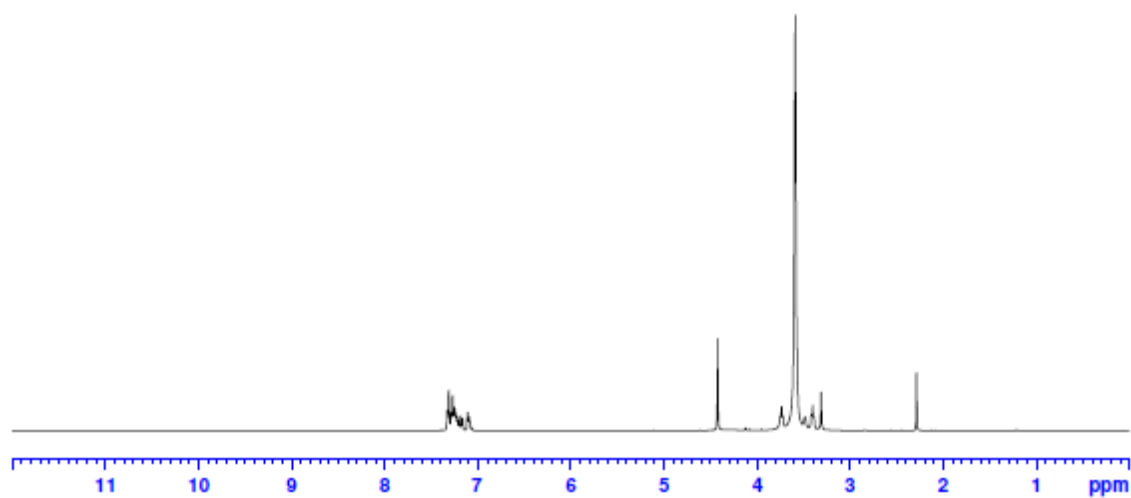
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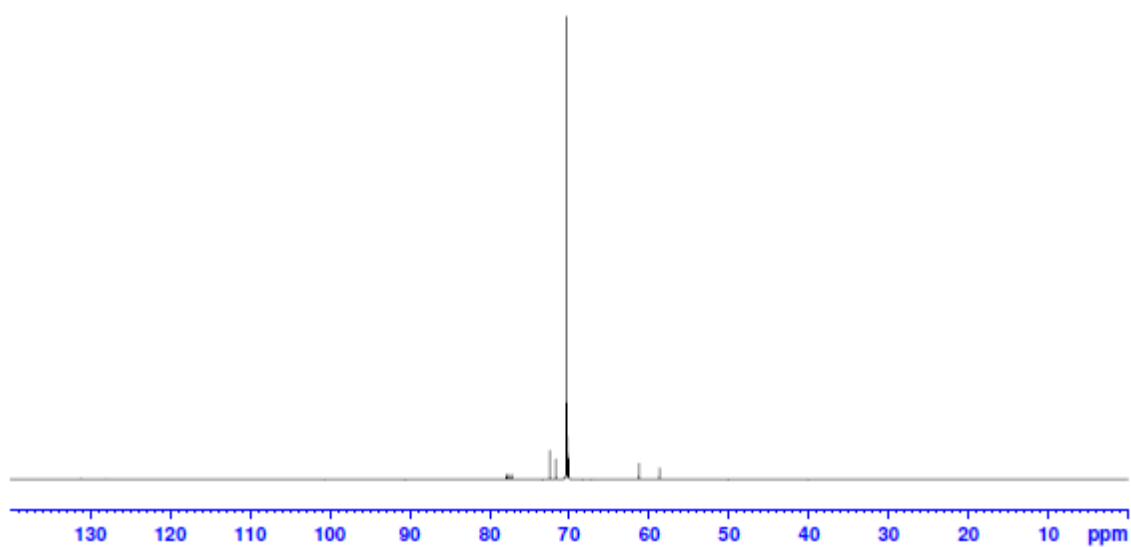
APPENDIX

Appendix

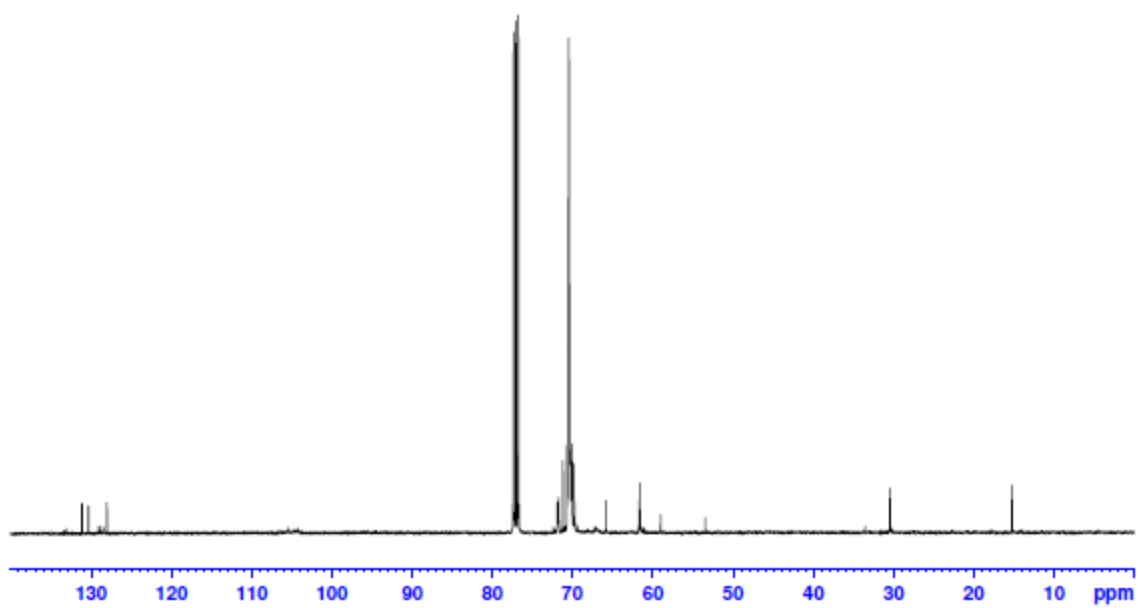
TG curve of PEG in O₂ rate 10°C/min¹H-NMR of poly(ethylene glycol)



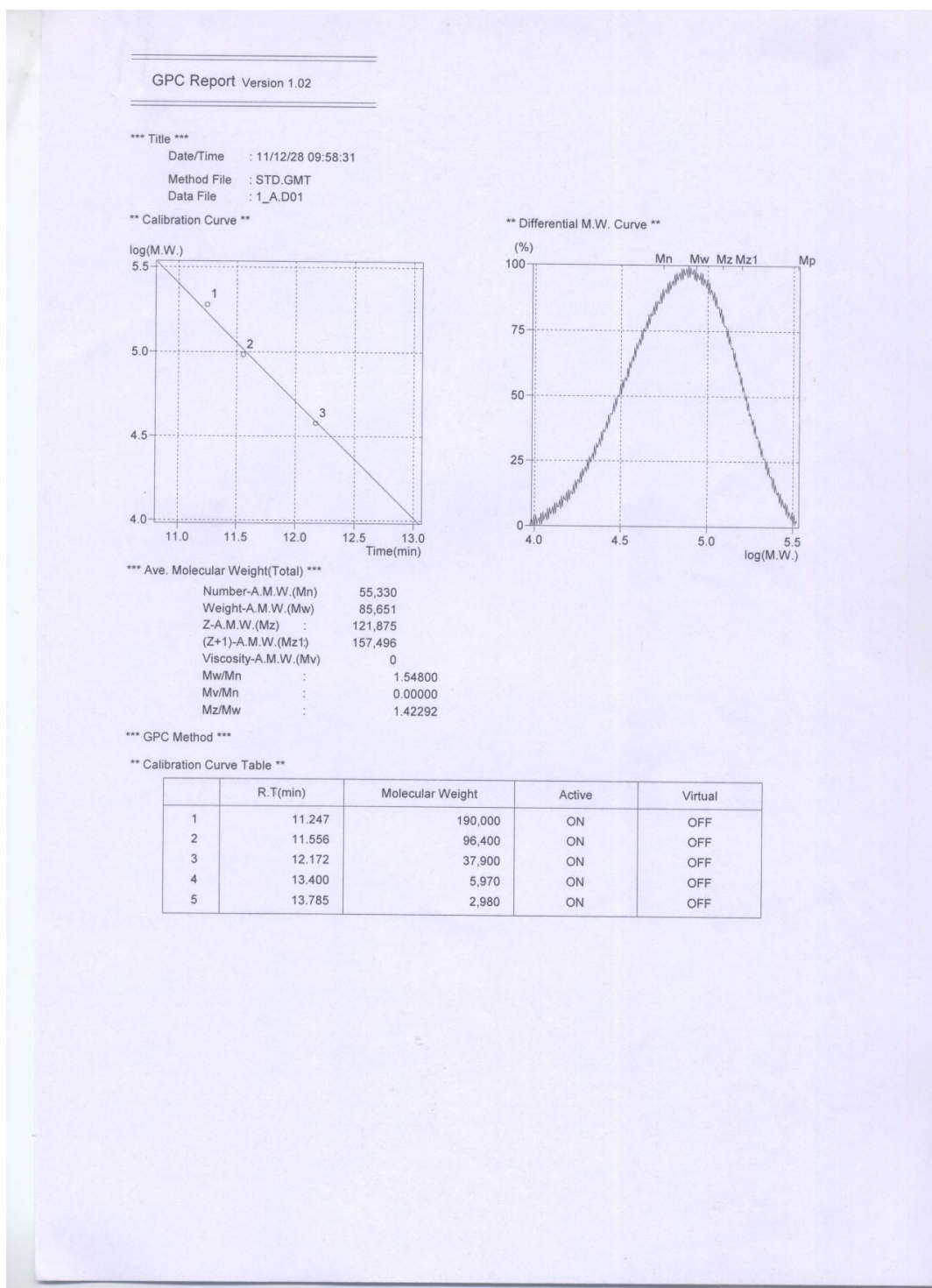
$^1\text{H-NMR}$ of Brominated poly(ethylene glycol)



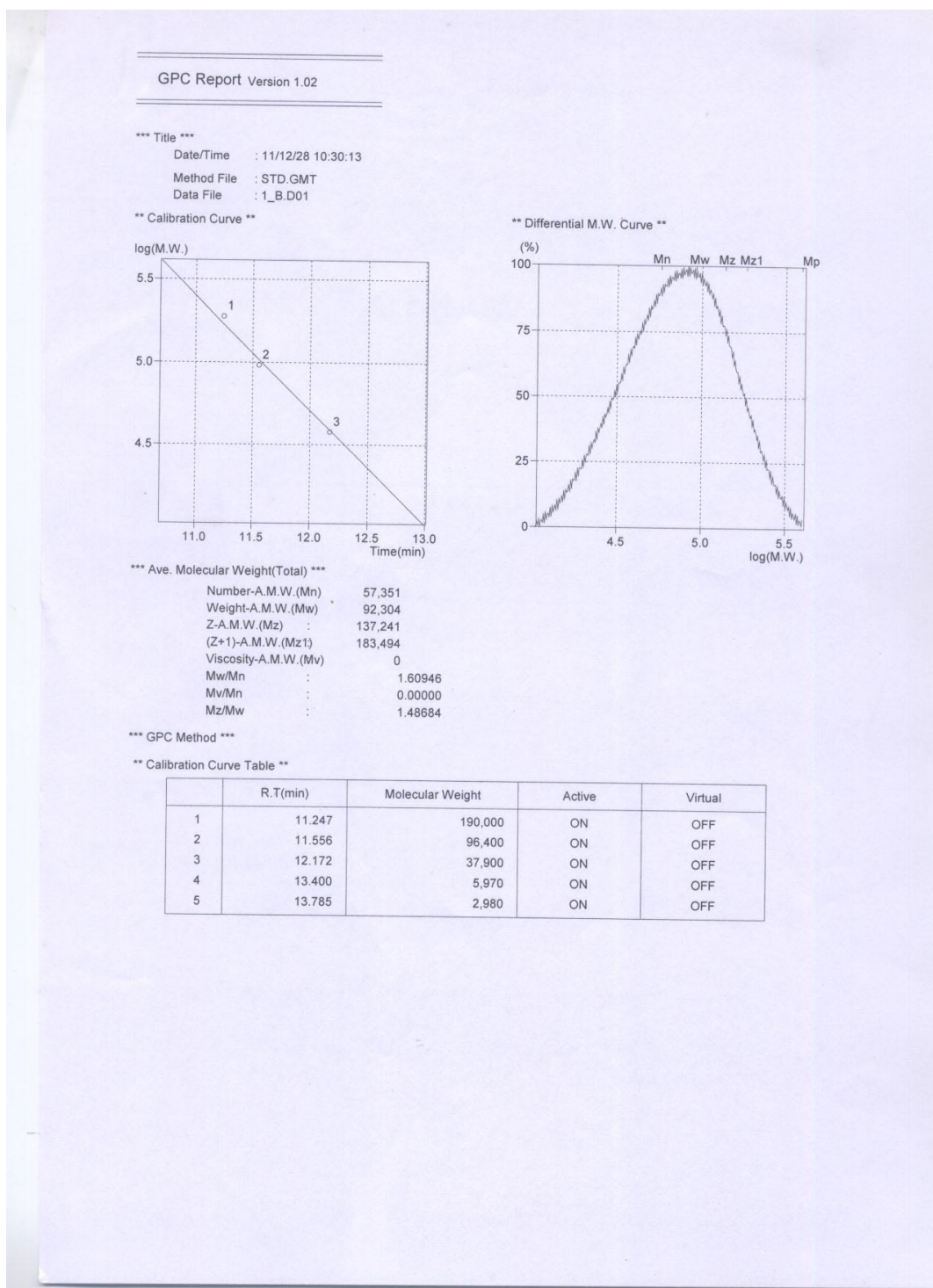
$^{13}\text{C-NMR}$ of Poly(ethylene glycol)



^{13}C -NMR of Brominated poly(ethylene glycol)



GPC result of OH-contained polyimide



GPC result of polyimide-g-poly(ethylene glycol)

VITAE

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List of publication :

Therthai Therdjittoam, Supakanok Thongyai and Piyasan Prasertthdam, "Preparation Of Polyimide Copolymer Based For Nanoporous Polyimide Film" Pure and Applied Chemistry International Conference 2012, Changmai, Thailand, January, 2012.