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Doctoral Dissertation

**Syntheses and chromism of bio-based
polymers with metal binding groups from
4-amino cinnamic acid**

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Abstract

The research in this thesis focused on the synthesis of high performance polyamides derivatives from bio-based 4-aminocinnamic acid. The development of these high performance bio-based polymers was crucial to establish sustainable low-carbon society. The important and interesting results throughout this study are summarized in the following parts.

In Chapter 2, bio-based aromatic diamine 4, 4'-diamino- α -truxillic acid was successfully prepared as a photodimer of 4-aminocinnamic acid, bio-available from genetically-manipulated *Escherichia coli*, even though the direct biosynthesis of aromatic diamines had never been reported. Photo-irradiation was a good synthesis method because it can be accurately targeted and highly selective. The single crystal of 4, 4'-diamino- α -truxillic acid dihydrochloride was used to confirm the *trans*- stereoisomer product after UV irradiation. It also indicated that 4, 4'-diamino- α -truxillic acid dihydrochloride and 4,4'-diamino- α -truxillic acid methyl ester had high purity because small needles of crystal were able to be prepared. The polyamides were prepared from 4, 4'-diamino- α -truxillic acid methyl ester and phthalate acids, both bio-available compounds. The relationship of its molecular structure and properties was clarified. The polyamide showed high thermal stability and high T_g . Nevertheless, their hydrolyzability was the crucial problems when used as high performance polymer in manufacturing process. Also in Chapter 2 described the synthesis of high performance bio-based PU which were used in place of the polyamide. The synthesis of PUs was classify and quick. The reaction time only needed 2 hours at 100 °C. The PUs showed high molecular weight and good thermal properties. In case of PUs, they showed ultra high thermal resistance of T_g over 300 °C and the solubility of PUs showed improvement because polyureas can dissolve in DMF/water mixed solvent.

In Chapter 3, based on the carboxylic acid I have successfully modified polymer under the film formed by the metal cation. I confirmed the mechanism of the modified film by FT-IR and research the modified film from thermal, mechanical and optical properties. The films modified by metal cations increased the mechanical property to 43.00 MPa (tensile strength) and 1.81 GPa (tensile modulus) by controlling different metal salt. At the same time the optical property was controlled.

Not only thermal and mechanical properties, but also degradations of PUs were studied in Chapter 4. Because there are functional group, cyclobutane, existed, it became possible that the degradation products completely broke into small molecules. For the degradation, the photolysis speed was fast, only 28-32 hs and hydrolysis speed was slow, 7 days, and the products include the diamino which could be the renewable compound for methyl diphenyl isocyanate and from the photolysis the products also had the cinnamon compound.

In summary (Chapter 5), the development of aromatic polyureas not only showed good performance on the thermal and mechanical properties but also showed excellent degradation process by UV and hydrolysis. On one hand the polyureas' thermal property just was a little

weaker than polyamides; on the other hand the mechanical property was stronger than the polyamides. The degradation products of the polyureas could be the renewable sources for the polymers, which was useful to establish sustainable green society. They could be used to reduce the serious problems of plastic waste and petroleum source.

Keyword: bio-based monomer, polyamide, polyurea, modification films, bio-degradation.

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CHAPTER 1

General Introduction

Chapter 1

1-1 Background of plastic and environment problem

Human activities are responsible for a major decline of the world's biological diversity could have environmental problem that combined critical human impacts [1]. Overconsumption of nonrenewable resources as well as concomitant wasted production has brought the world to a crossroads. Sustainability is rapidly moving from the wings to centre stage. To reach the ultimate goals of cleaner production and sustainable development, new improved syntheses of chemicals have to meet economics, ecological and social criteria [2, 3]. Green chemistry (environmentally benign chemistry) is a fast emerging discipline aiming at understanding the fate of pollutants in ecosystems and at designing novel chemical products and/or processes that reduce or eliminate the use and generation of hazardous substances that are safe for ecosystems [4, 5, 6]. In addition to using and producing better chemicals with less waste, green chemistry also involves reducing other associated processes [7]. The design of environmentally benign products and processes may be guided by the 12 Principles of Green Chemistry (Figure 1-1) [8]. These principles are a categorization of the fundamental approaches taken to achieve the green chemistry goals of benign products and processes, and have been used as guidelines and design criteria by molecular scientists. Such as in green chemistry and green engineering, the researches

should bring about changes in the hazard of a product at the most fundamental level, that is, the molecular level and have the power to impact on the entire life cycle of a product or process and make it more environmentally safe and sustainable [9,10,11].

The 12 Principles of Green chemistry

- It is better to prevent waste than to treat or clean up waste after it has been created.
- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- Chemical products should be designed to affect their desired function while minimizing their toxicity.
- The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Figure 1-1 The 12 Principles of Green chemistry.

In the recent years, the plastic problems become a new challenge for the world researches, such as carbon dioxide effected the global warming, the petrol source came from energy consume, and wasted plastic polluted the environment of the sea and forest. The main parts of waste plastics stream came from petroleum based

polyolefin's such as polyethylene, polypropylene, polyvinylchloride, polystyrene, etc. contributing greatly environmental and social problems due to the loss natural resources and the limited amount of petroleum. Therefore, the use of environmentally friendly polymers originating renewable starting materials and/or which degrade in the environment is significant materials with respect to the reduction of waste. Bio-based polyesters play a predominant role as degradable plastics owing to their potentially hydrolysable ester [12]. However some aliphatic bio-based polyesters, such as poly(hydroxyalkoate)s, poly(butylenes succinate), and so on, show low performance and less functions which are not enough to use as super-engineering plastics [13, 14, 15]. Moreover, these polyesters have become substitutes for only a small amount percentage of the currently used plastic materials. A number of polymers such as EcoflexTM and BiomaxTM are used to improve durability and performance [16, 17]. However, they still have problem due to their degradation. Polymers that are able to cleavage and change to oligomer or monomer, and have a performance closer to that of engineering plastics would be highly desirable for easily degradation, not hazard for environment.

1-2 Bio-based polymers

In an age of increasing petroleum consumption, global warming, and other environmental problems (such as, pollution), the field of polymers derived from non-petrochemical feedstock has recently got many attentions [18]. The design of thermo-sustainable plastics should consider all the stages involved in their life cycle,

including extraction of the raw materials, synthetic and modification processes, processing and manufacture into final products, service life, and subsequent waste management of the residues [19-21] (Fig. 1-2). Considering the definition of sustainable thermoplastics, a wide range of raw materials can be used for their design with taking into account the restriction of energy consumption and the chemical processes. The environmental impact on the waste management processes the effective return of the material and energetic value of the product [22-23].

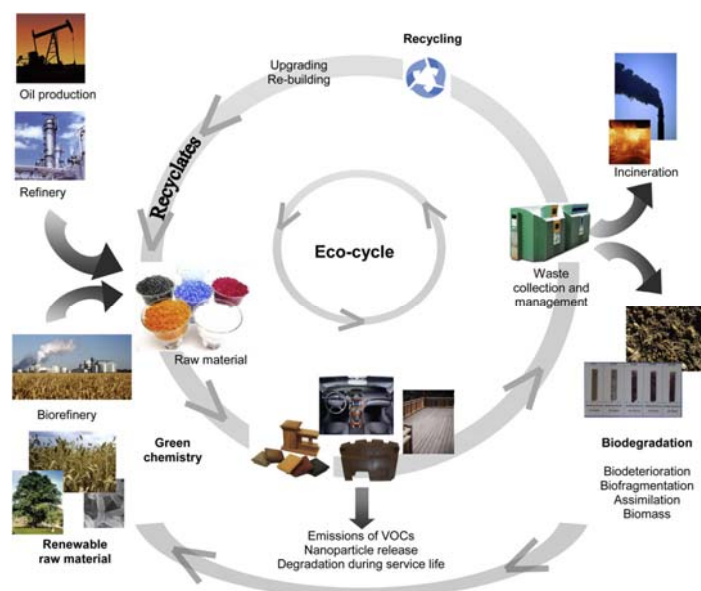


Figure 1-2 Life cycles of sustainable plastics Based on the environmental consideration, various bio-based polymer families could be utilized as follows:

- (i) Natural polymers extracted from renewable resources, such as starch, cellulose, proteins, and chitin.
- (ii) Polymers produced by microbes, such as poly (hydroxyalkanoates).
- (iii) Polymers synthesized via chemical or enzymatic processes, whose monomers are obtained from renewable resources, such as poly(lactides) or renewable epoxy resins synthesized from vegetal oils.
- (iv) Recyclable synthetic polymers that can be upgraded for new applications by the addition of natural reinforcements.

An inclination request for the decision of unique crude materials ought to be characterized regarding supportability to outline new items. Preferably, the assembling of green bio-based polymers ought to infer that both the framework and the repairman property emerge from renewable assets; the utilization of common polymers as networks and technician property ought to be particularly empowered when conceivable [24-27]. The utilization of microbial polymers, e.g. the group of poly(hydroxyalkanoates) (PHAs) and the union of new biopolymers utilizing monomers from renewable assets seems, by all accounts, to be an exceptionally encouraging course for outlining polymeric frameworks with custom-made properties; the eco-productivity of their combination and assembling courses ought to likewise be evaluated as far as manageability. The usage of reused engineered thermoplastic ought to be considered as a good stride in the manageability of material innovation [28]. The gainful impact is twofold; on one hand the waste stream volumes of disposed of engineered non-degradable polymers are minimized and the fiery and material estimation of once blended and handled polymers are kept up by their new use in second-life applications.

Maintainability in material science and particularly in polymers and composites is characterized not just by the decision of renewable or naturally inviting assets for their production, additionally by the advancement of mellow synthetic procedures that keep away from the use and generation of risky substances and along these lines minimize their natural effect. This methodology ought to be hence executed in every

progression of the assembling procedure for biopolymer and bio-composite materials, including their union and change. Green science rationality includes the usage of benevolent solvents (watery and ionic media or supercritical liquids) in synthetic responses, the minimization and/or utilization of option vitality sources in compound changes, and the utilization of non-risky synergist frameworks [29]. In polymer science, these ideas have been presented and connected in the late years to the amalgamation of customized biopolymers, by utilizing renewable materials, by utilizing catalysts and microorganisms for polymer combination, by reusing and/or evacuation of metal impetuses, and by performing manufactured responses in watery or ionic media [30-32]. The coordination of green science hones into the future bio-refineries is crucial for the manageability of such operations and procedures [33]. This advantageous interaction will promise not just that renewable assets are utilized in the assembling of new chemicals and materials, additionally that the concoction procedures are naturally inviting and won't influence future eras. The outline of materials for the 21st century ought not just consider the decision of renewable assets as crude materials for their planning, additionally ought to be totally practical, including amalgamation, use, and waste administration [34]. On account of practical perspective, the primary test lies in the outline of items that are basically and practically stable amid their application, utilizing kind blend and adjustment forms [35-42], together with fitting waste administration methods (reusing) that finish the arrival of the material and/or vigorous worth to the earth. Recyclability of maintainable bio-based polymers can be troublesome however very phenomenal.

Bio-based polymers displaying smooth debasement have been generally contemplated as ecologically neighborly polymeric materials [42]. In any case, aliphatic bio-based polymers, for example, poly(hydroxyalkanoate)s, poly(ethylene succinate), thus on debase too quickly to really be utilized [43-45]. EcoflexTM and BiomaxTM are more tough and show more noteworthy execution levels than do the aliphatic bio-based polymers however the issues of ecological lethality and accessibility of terephthalic corrosive are not kidding [46-47]. Poly(lactic acid)s (PLA) has been surprisingly all around created as a result of their high mechanical quality [48]. On the other hand, it was assessed that these polyesters will get to be substitutes for just a little rate of non-degradable plastics presently being used since use of the aliphatic polyesters is constrained because of their poor level of thermoresistance in applications as a designing plastic. At that point, superior exhibitions, bio-based polymers that debase into normal atoms are genuinely sought for enhancing human life. Non-degradable building plastics have an inflexible part of a benzene ring and super designing plastics have a consistent structure of benzene and hetero rings, for example, benzimide, benzoxazole, benzimidazole, or benzthiazole [49]. Albeit no consistent unbending structure in the polymer spine exist in nature, the polysaccharides have numerous hetero rings. Despite the fact that the polysaccharides at times show too low a level of processability to be made into a valuable material, they do have an enormous measure of potential for utilization as elite bio-based polymers since cellulose demonstrates a high Young's modulus (more than 10 GPa). In spite of the fact that the utilization of

high quality filler, for example, bacterial cellulose or altered lignin drastically expands the plastic properties, the grid polymers focus the natural composite execution [50-51]. The presentation of a sweet-smelling segment into a thermoplastic polymer spine is a proficient system for inherently enhancing material execution [52]. Moreover, the consistent arrangement of sweet-smelling rings can be a mesogenic gathering. Embellishment in the thermotropic fluid crystalline (LC) state can prompt sub-atomic introduction giving anisotropic properties to the mechanical execution, which some of the time significantly increments mechanical quality and Young's modulus. Then again, there has been no endeavor to utilize a fragrant bio-based monomer as a constituent of a bio-based polymer.

1-3 Introduction of bio-based monomer

Bio-based monomers play an important role in the syntheses of bio-based polymers and were the main focus in this research. The bio-based monomers which were used in the research are as follows.

1-3-1 Cinnamic acid and Cinnamate derivatives

It is known that many bio-monomers exist in plants such as tyrosine, vanillic acid, coumaric acid derivatives, and cinnamic acid derivatives and so on. Cinnamic acid is a white crystalline compound with a formula $C_6H_5CHCHCO_2H$ and slightly soluble in water but freely soluble in many organic solvents. It exists as both a *cis* and a *trans* isomer, although the latter is more common.

There are a number of cinnamate derivatives representing aromatic biomolecular in living organisms from photosynthetic bacteria [53] to higher plants [54] such as *p*-coumaric acid (4HCA), *m*-coumaric acid (3HCA), caffeic acid (DHCA), ferulic acid (MHCA) and 4-aminocinnamic acid (4ACA; Figure 1-3). Cinnamates have been

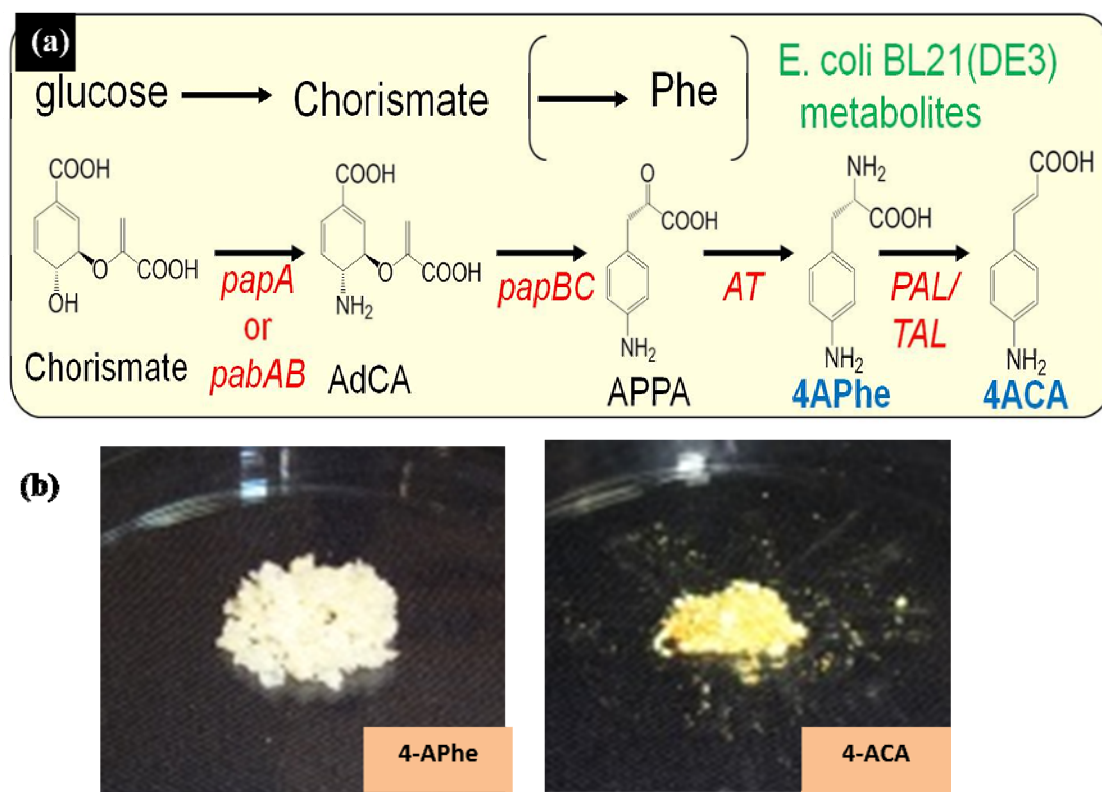


Figure 1-3 (a) 4ACA biosynthesis pathways from 4APhe and (b) physical appearances of 4APhe and 4ACA obtained from biosynthesis.

used in a photoreactions to produce various chemical materials [55]. Therefore, 4-aminocinnamic acid is an attractive option because the [2+2] photocycloaddition of the cinnamates is one of the most efficient chemical reactions if the reaction condition is well arranged.

A report has shown that some bacteria produced 4-aminophenylalanine (4-APhe) as an intermediate of antibiotics [56]. There are established systems for fermenting glucose

or biomass to produce 4-APhe [57-58]. 4ACA can be obtained from 4APhe under a kind of phenylalanine ammonia lyases, which delaminate α -amino residue of phenylalanine (or its derivatives) to generate cinnamic acid (or its derivatives) (Figure 1-4). However, the bioavailability of 4-ACA is unclear. I accordingly investigated the deamination of 4APhe to synthesize biomass-derived

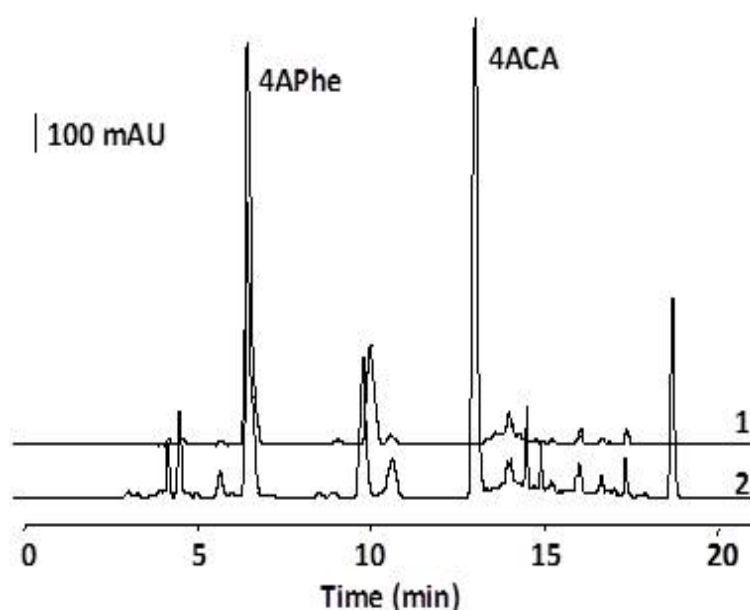


Figure 1-4 High-performance liquid chromatography (HPLC) separation of 4ACA bio-converted from 4APhe. The AtPal4 producing recombinant *E. coli* was incubated with 10 mM 4APhe at 37 °C for 0 hour (line 1) and 12 h (line 2).

4-ACA by using recombinant phenylalanine ammonia lyases. One isozyme, phenylalanine ammonia lyase 4 (AtPal4) of *Arabidopsis thaliana*, was functionally produced in recombinant *Escherichia coli*. The strain produced 1.4×10^{-2} and 3.8×10^{-4} $\mu\text{mol min}^{-1} \text{mg}^{-1}$ of phenylalanine- and 4-APhe- ammonia lyase activity, respectively, indicating that AtPal4 used 4-APhe as a substrate. Incubating the bacterial cells with 4APhe decreased the amount of 4-APhe produced and generated 0.13 g/L of 4-ACA

(Figure 1-4). This indicated that combination of this process and the 4-APhe fermenting system produced 4-ACA from the biomass.

1-3-2 Phthalic acid

Phthalic acid (Benzenedicarboxylic acid), both isophthalate acid and terephthalate acid was bio-derived production of forest microorganisms after decomposed dimethyl phthalate from wasted water of PET production process (Figure 1-5) [59-60]. It is implicated as responsible for the heat resistance of the endospore. However, the amount of products are only limited in the laboratory.

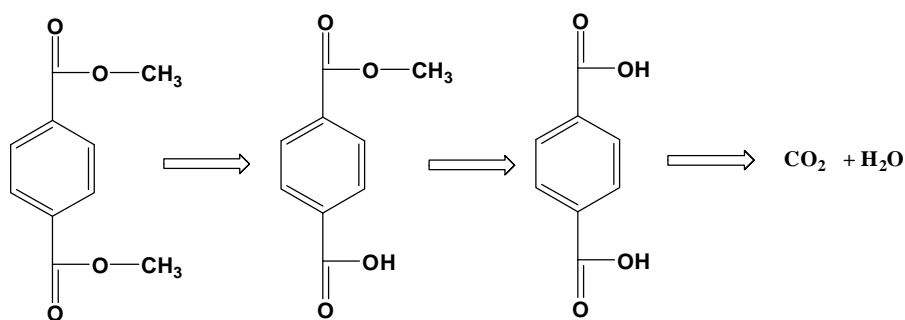
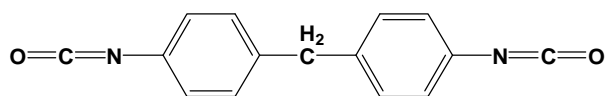


Figure 1-5 Proposed biochemical degradation pathway for dimethyl terephthalate by bacteria from mangrove sediment.

1-3-3 Methylene diphenyl isocyanate

Methylene diphenyl isocyanate (MDI) (Figure1-6) is prepared from renewable phenyl aniline which is produced by the renewable benzene of the invention as feedstock in two steps [61]. First, benzene is nitrated using a concentrated mixture of nitric acid and sulfuric acid at 50 °C. to 60 °C. The nitrobenzene product is hydrogenated in presence of various metal catalysts. The reaction can be at 200 °C to 300 °C. Alternatively, renewable benzene can be used as feedstock to produce phenol, which

can be converted to aniline by reaction with ammonia. Methods for producing aniline from benzene are known to those of skill in the art [62-63]. Since the renewable carbon content of aniline is determined by that of the renewable benzene feedstock, renewable aniline can have renewable carbon content anywhere from about 1 % to about 100%. Thus, aniline having 100 % renewable carbon content can be produced using a benzene feedstock having 100% renewable carbon. Renewable aniline can be distinguished from non-renewable aniline in that the proportion of radiocarbon to total carbon in the renewable aniline is greater than that of the non-renewable aniline.



Methylene diphenyl isocyanate

Figure 1-6 The chemical structure of MDI

1-4 High performance polymers

High performance polymers exhibit exceptional stability upon exposure to some harsh environmental conditions and have properties that surpass those of traditional polymers. These materials are defined in many ways depending on the application and, to some extent, the organized systems used for developing or employing the materials. They have properties that include outstanding thermal resistance and/or mechanical strength, low specific density, high conductivity, high thermal, electrical, or sound insulation properties or superior flame resistance [64]. The factors that contribute to the high performance and heat resistance properties of these polymers are: resonance

stabilization, primary bond strength, molecular symmetry, secondary bonding forces, molecular weight and distribution, rigid interchain structure, cross-linking, mechanism of bond cleavage and additives or reinforcements (fillers, clays, miscellaneous nanoparticles) [65]. They have been used in many industries ranging from communication to medicine and to transportation [66]. Because of the superior performance characteristics of high performance polymers, the demand for this type of polymeric materials is growing steadily. Although several applications do not require usage at high temperature, the fabrication process leading to the parts or components requires the polymer to be thermally stable. Here, I focused on two kinds of high performance polymers: polyamide and polyimide.

1-4-1 Polyamide

Polyamides are high molecular weight materials containing intermittent amide units and the hydrocarbon segments that can be aliphatic, partially aromatic, or wholly aromatic. The type of hydrocarbon segment employed has effects on the chain flexibility and structural regularity, with the latter important in the formation of crystalline phase. Polyamides are often called nylons, the trade name given to them by DuPont. Partially aromatic and wholly aromatic polyamides have been successfully developed [67]. They have good mechanical properties due to formation of hydrogen bonds. The hydrogen bond increases the chain interaction resulting in higher yield stress, fracture stress, impact strength, tear strength, and abrasion resistance [64]. Polyamides have been used essentially as fibers, films, and filler-containing

engineering plastics for special applications [68]. Most of the reinforced polyamides are filled with glass fibers and to a lesser extent with particles, e.g., talc, kaolin, and mica. For engineering plastics applications, dimensional stability at high temperatures is often sought. Wholly aromatic polyamides can be processed from solution either into films or into fibers. These polymers have very good dimensional stability [64] and excellent heat resistance [69-70]. Partially aromatic polyamides have higher glass transition and melting temperatures compared to their aliphatic counterparts. They can be prepared by various methods, e.g., mono-add systems which both acid and amine functionalities are on the same molecule and di-add systems such as diacids, diacid chlorides or diesters in combination with either aromatic or aliphatic diamines, as well as, the reactions between diisocyanates and diacids which are commonly used for this purpose. Wholly aromatic polyamides have high glass transition temperature ($>200\text{ }^{\circ}\text{C}$) and, when in the form of crystalline, show very high melting temperature ($>500\text{ }^{\circ}\text{C}$). High-molecular-weight polymers cannot be prepared by melting or melt processing, because many aromatic diacids are decarboxylates and aromatic diamines are readily oxidized and have a tendency to sublime at elevated temperature. Their synthesis is usually carried out in solution and due to the very low solubility, special solvents are required to obtain high-molecular-weight polymers.

1-4-2 Polyureas

Microcapsulation in several fields, including agriculture, food, pharmaceuticals, cosmetics, printing, textiles, and protective/smart coatings, has been used to encapsulate many active materials like pesticides, flavors, drugs, enzymes, inks, dyes,

and healing agents [71-73]. Microcapsules have been prepared from a variety of material such as PU, polyurea, ureaformaldehyde (UF), phenol formaldehyde (PF), melamine formaldehyde (MF), etc [74].

Thermoplastic segmented polyurea elastomers are block copolymers of the $(AB)_n$ type, consisting of alternating soft and hard segments. Generally, the bulk synthesis of segmented polyureas is carried out by reacting a mixture of aromatic diamines with aromatic isocyanates by reaction injection molding (RIM), because the rates of reaction are such that RIM is the only suitable process to form these engineering polymers [75-81].

1-5 Aim and scope of this study

The main motivation for this work is the scientific curiosity to synthesize and characterize new polymers and expect to apply these materials in technically relevant polymeric systems. One aim is to design new monomers from renewable photo-monomers to prepare high performance or functional polymers. The most important objective of the investigations described in this thesis, is to study properties and analyze their structures. To achieve these goals, a detailed understanding of the chemistry and functionality of the different monomers and the resulting polymers was required. Crucial polymer characteristics, such as functionality, glass transition temperature, and molecular weight were investigated to be able to design polymeric architectures. Hence, in my research I try to synthesize the polymer with sufficiently high thermal performances (especially process temperature and glass transition

temperature) during use on one hand and on the other hand the polymer can keep the mechanical property and also the degradability under specific condition (photodegradation, hydrolysis) almost similar with PLA.

CHAPTER 2

Syntheses and characterization of aromatic polyamides and polyureas

Chapter 2

2-1 Introduction

Plastic fields are not only familiar products such as clothes, packing, but also advanced ones such as electronics and automobile [82]. Most of plastic is produced from petrochemistry. However there are series problems associated with the limit amount of fossil resources and the long term resistance of plastic to the degrading action of living system affected on the pollutant environment [83]. Development of environmentally-friendly polymer and bio-based plastic that are derived from renewable biomass resources are extensively interesting. To synthesize these polymers, there are three major ways: one is directly from naturally-occurring polymer, another is derived from biologically-controlled method such as bacterial fermentation, and the last one is chemical polymerization from bio-based monomer such as DNA, amino acid. The chemical polymerization usually focuses on bio-derived plastics which can be decomposed through microbial activity or plant function [84]. Due to mechanical performance, flame retardance and chemical resistance, polymers have wide application as plastic materials in a variety of industrial fields. However the development of the polymer degradation is limited by its strong resistance. To solve the problem, bio-based/derived environment- friendly polymer was interesting because it was able to reduce plastic wasted and the amounts petroleum consumption by environment functions

such as sun, light, rain and biological activity such as microorganism. Bio-based/derived polymer was synthesized from biological resources, such as DNA, proteins, and other metabolites including cinnamic acid derivative and phthalate which was used in this research. .

Cinnamic acid, a kind of bio-derived material and easily obtained from benzoin and cinnamon, could be converted to starting materials to synthesize bio-based monomers and was widely known as photo-reactivity chemical compounds [85]. These bio-based monomers could be polymerized to create a number of bio-based polymers: polyethylene, poly (propylene carbonate), aliphatic polyester, such as poly (hydroxyl alkanate)s, poly (butyl succinate)s and poly (lactic acid)s [86-87]; semi-aromatic polyester, like poly (ethylene terephthalate)s and poly (trimethylene terephthalate)s; and some polyamides. Nevertheless, the applications of bio-based polyethylene, polycarbonate and polyester are limited due to their low thermal stability which was unsuitable for high temperature processing. I focused on polyamides with aromatic ring which have high thermal, mechanical and chemical resistant properties.

I try to describe the synthesis of the aromatic diamino monomers, polyamides and polyureas from bio-derived compound 4-amino cinnamic acid (4-ACA), even aromatic diannilines are difficult to directly derive from microorganisms due to their toxicity. Photo cyclo-[2+2] addition reaction is selected to synthesize photodimer, 4, 4'-diamino- α -truxillic acid (4-ATA). There are reasons. Light, as a remote stimulus, is an attractive nano-object disassembling driving force, which have been intensively investigated for two advantages: 1) light can be accurately targeted and highly selective;

2) light is pure, in contrast to chemical stimuli, no acid, no bases, or other reagents have to be brought into the reaction system, which in many cases could be technically challenging. Moreover, the two kinds of dichloride, isophthalic chloride and terephthalic chloride, can be derived from bio-based isophthalic acid and terephthalic acid [59-60]. Finally, bio-available 4-ATA and dichloride acid are used as monomer to polymerize polyamide in next step to reduce the problem of plastic.

The aromatic polyamides can be widely used in many fields instead of low performance plastic [85-87]. But the polyamides modification to improve the weakness property is difficult. The urea function group with similar structure as amide is more easily to control the modification. It serves an important role in the metabolism of nitrogen-containing compounds by animals and is the main nitrogen-containing substance in the urine of mammals. Urea degradation is easy and common in the environment [93]. The process will follow the formation like Figure [94]. The aromatic polyurea' structure is similar like aromatic polyamide: polyurea has two hydrogen bonds and polyamide one. Polyurea performances are a little weaker than aromatic polyamide and polyimide in thermal stability and mechanical [95] but the degradability of polyureas is quite fast than polyamide and polyimide [96]. More than this, the productions of the polyurea degradation can be resource of the polymers.

Because of the polyureas thermal property and toxicless, the material is the first choice for coating steel or water containment's surface and lining also the material can be used for the coating of the clothes by the abrasion resistance, water repellency, leather appearance. Not only kinds of coating, the polyureas also could be the materials of

spray molding. Polyurea can be spray, open pour or reaction injected into molds. Many automotive fascia parts have been molded from polyurea RIM systems. Now many sprays in mold uses are becoming popular in replacing parts commonly made from fiberglass.

Comparing the polyureas which are wide used, our new polyureas have some differences from them: firstly, our polyureas are aromatic and others usually are alkyl, second is that our polyureas are synthesized from bio-based monomers and others' resource is petroleum. According to these differences, our polyureas' properties may be distinguished with others.

2-2 Experiment

2-2-1 Chemicals

4-amino cinnamic acid (4-ACA: from TCI), trimethylsilyl chloride (TMSCl: from Sigma-Aldrich Co. LLC.) Dimethyl acetamide [anhydrous from Kanto Chemical Co. Ltd.(Kanto)] and N-methyl-2-pyridine (NMP: 99.8% anhydrous from Kanto) were used as received. The acetone and methanol (Wako Pure Chemical Industries Co. Ltd.) used as a wash solvent were used as received. Terephthalate chloride and isophthalate chloride were used after recrystallization by hexane. 4,4'-diphenylmethane diisocyanate (MDI, TCI) was purified by distillation at 160°C under vacuum before use. Sodium hydroxide (NaOH, Kanto), Hydrochloride acid (HCl, Kanto) were used as received.

2-2-2 Characterizations

The molecular weights of the polyureas were determined by gel permeation chromatography (GPC; Shodex GPC-101 with a connection column system of 803 and 807) that was calibrated with polystyrene standards at 40 °C (eluent: Dimethylformamide). FT-IR spectra were recorded with Perkin Elmer, Spectrum One. The NMR spectra were obtained on a Bruker DRX 500 spectrometer operating at 400.13 MHz for ^1H NMR. A deuterated solvent of dimethylsulfoxide- d_6 (DMSO- d_6) was used. The thermal properties were analyzed by differential scanning calorimetry (DSC; EXSTAR 6100, Seiko Instruments Inc.) and thermogravimetric analysis (TGA; SSC/5520 SII Seiko Instruments Inc.) Samples were scanned from 50 °C to 250 °C at scanning rate of 10 °C/min under a nitrogen atmosphere with a flow rate about 80mL/min. Glass transition temperature (T_g) were measured using data generated during second heating cycle. The thermal degradation behavior of the samples was observed from TGA curves by heating from 50 °C to 800 °C at a rate of 10°C/min under a nitrogen atmosphere with a flow rate about 200ml/min.

2-2-3 Monomer Synthesis

Synthesis of photo-dimer with different side chains from 4-amino cinnamic acid

To produce 4-aminocinnamic acid hydrochloride (4-ACA hydrochloride) 12 N Hydrochloric acid was dropwise added into a solution of 4-ACA (1.63 g, 100.00 mmol) in Acetone (60 ml) till the pH<1, then filtered the solid and washed three times by acetone to obtain the white power. Mixture solution of 4-ACA hydrochloride (1.5 g) and hexane anhydrous (50 mL) were placed in 100 mL round bottom flask and

irradiated (250-450 nm Mercury lamp; 2.4 uW/cm², 10-12 h) by [2+2] photocycloaddition. Subsequently, 4, 4'-diaminotruaxillate dihydrochloride (4-ATA hydrochloride) was synthesized in two necked round-bottomed flask by methylation of [2+2] photocyclo- addition product using trimethylsilyl chloride [(CH₃)₃SiCl] and methanol (1:2:40 molar ratio) under a nitrogen atmosphere at room temperature. After filtering the mixture, dissolved the solid into water and neutralized by 3M NaOH. Filtered the precipitate and dried the white powder to get the production.

2-2-4 Polyamides syntheses

Syntheses of Polyamides with methyl group as the side chain

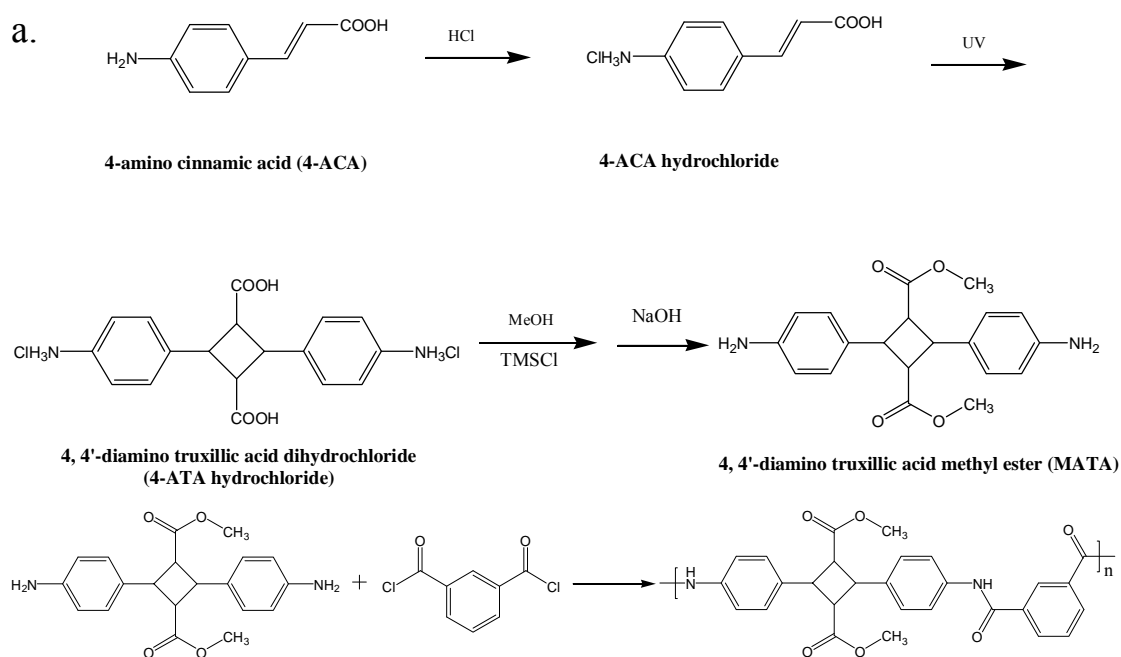
A typical polymerization procedure for the synthesis of polyamide acid (PAA) was synthesized by addition polymerization of equimolar amounts of dianhydride and diamino (Scheme 2-1.b) in NMP such as: 4,4'-diamino-dimethyltruxillate (177.1 mg, 0.5 mmol) and terephthaloyl chloride (105.9 mg, 0.5 mmol) were placed in a 10ml tube under a nitrogen balloon and added NMP (1 ml) in the tube. Then stirred the mixture at room temperature for 1 h and raised the temperature to 100 °C to react over night. Drop wise added the solution into Methanol to precipitate white powder which was collected by filtration after the reaction, washed thoroughly with MeOH. Then the solid was dried in a vacuum drying oven.

Syntheses of the polyamide with different side chain group based on the hydrolysis reaction

The method of synthesize the polyamide with different side chain group is followed as

Scheme 2-2. First, get the basis side chain group –COOH from the deprotection of methyl group by 3M NaOH. Then, mix the production, the side chain group and the catalyst in the solvent to synthesize the aimed polymer.

Dissolved 150 mg PMATA/IPA in 1ml DMSO and put the solution in 10ml tube. Added 3ml 3M NaOH into the tube then stirred 24 hs. After the reaction finished, dropped the solution to 100ml Ethanol to get the precipitate and dried at 60 °C in the dry oven. Mixed the production and the different side chain groups (Table 1) in the 3ml sample bottles and stirred 2 hs. Then raised the temperature and synthesized the polymer with different side chain groups.

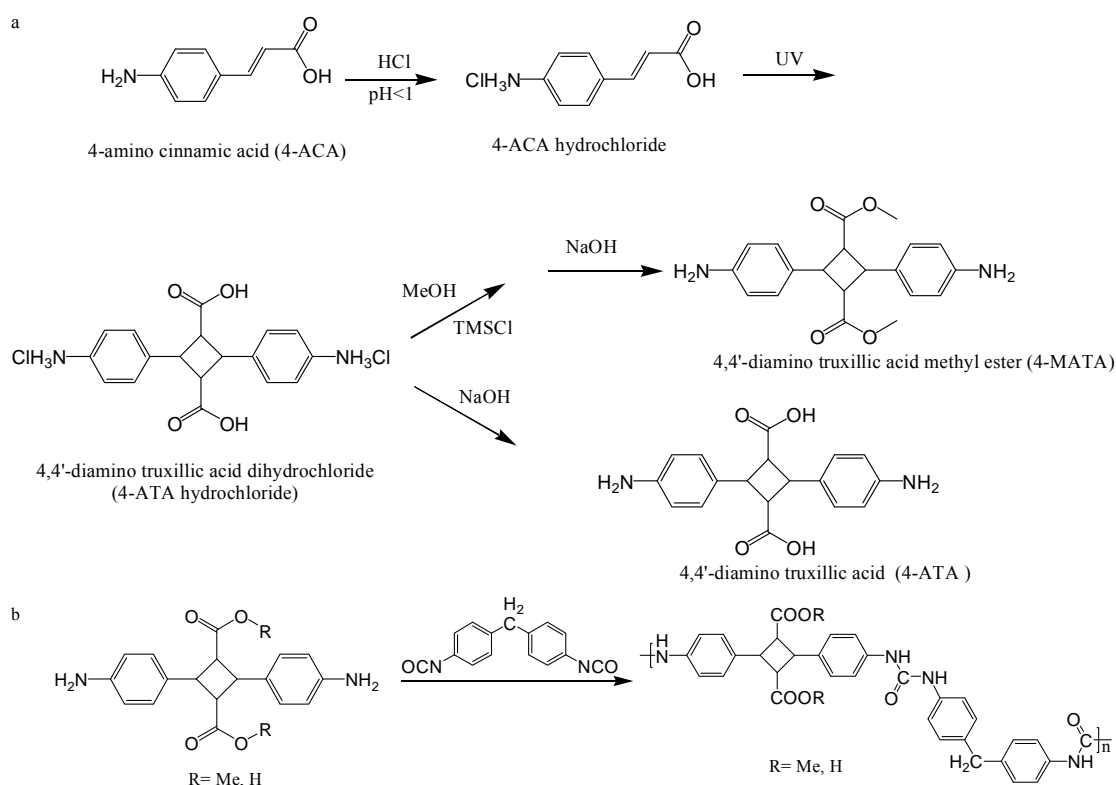


Scheme 2-1 Syntheses of the monomers and polyamide from photodimer : a) syntheses of the monomer with methyl ester as side chain, b) syntheses of the polyamide with isophthalic chloride

2-2-5 Polyureas syntheses

The representative polymerization procedure of 4ATA is shown as follows. 4ATA

(326 mg, 1 mmol) was mixed with MDI (250 mg, 1 mol) in DMAc (5 ml) at the molar rate 1:1 and heated to make a homogeneous solution at 50 °C in a 100 ml nitrogen-purged round-bottom flask. After the polymerization proceeded by agitation for 1 hour, the reaction solution became viscous. After polymerization, the reaction solution was cooled to room temperature and was poured into ethanol to precipitate the fibrous polymers. The polymers were collected by filtration and dried *in vacuo* (yield; 90 wt%). The aimed structures were confirmed by ¹H NMR and molecular weights were determined by GPC. The polymerization of 4ATA dimethyl ester with DMI was made by the analogous procedure with 4ATA polymerization (yield; 94 wt%).



Scheme 2-2 Syntheses of the monomers and polyureas from photodimer with different side chains: a) syntheses of the monomers with different side chain, b) syntheses of the polyureas from comonomers and MDI

2-3 Results and Discussion

2-3-1 Syntheses and characterization of monomer

4,4'-diamino- α -truxillic acid dihydrochloride was synthesized by a perfect [2+2] photocycloaddition of 4ACA hydrochloride salt (scheme 2.1). The cyclobutane ring of α -truxillic acid, a dimer, was occurred with ultraviolet light source above 260 nm which was stable at elevated temperature [36]. However, photolabile under deep ultraviolet light, below 260 nm, cyclobutane was cleaved to the initial of 4-ACA. The crude of 4, 4'-diamino- α -truxillic acid dihydrochloride (4-ATA hydrochloride) was recrystallized by treating with conc. HCl at refluxed temperature to receive the small needles with white color (Figure 2-1 b). And after neutralized product reacted MeOH with TMSCl, 4, 4'-diamino- α -truxillic acid dimethyl ester (MATA) was recrystallized by treating with MeOH and distilled water at 0°C to receive the needles with yellow color (Figure 2-1 c).

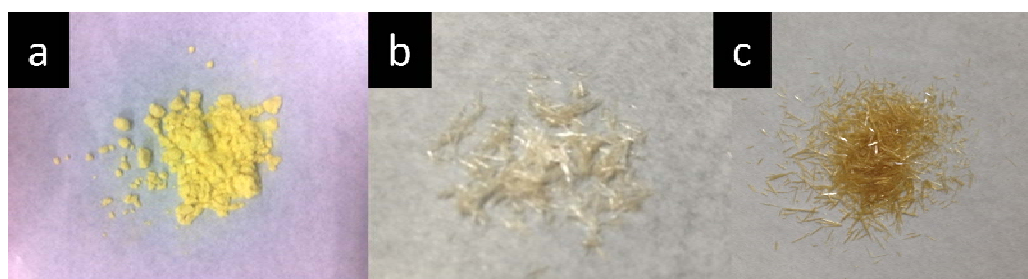


Figure 2-1 The physical appearance of (a) 4-ACA (b) the crystal of 4, 4'-diamino- α -truxillic acid dihydrochloride and (c) the crystal of 4, 4'-diamino- α -truxillic acid dimethyl ester (MATA)

4-ACA showed dark yellow powder while the crystal of 4-ATA dihydrochloride

showed white color and MATA showed yellow color (Figure 2-1). The photodimer's structure was confirmed by ^1H NMR, ^{13}C NMR and X-ray crystallography.

^1H NMR spectra of 4-ACA and 4-ATA hydrochloride produced by [2+2] photocycloaddition were shown on Figure 2-3. Compared the spectra before and after photo irradiation, it resulted in disappearance of vinylene proton signals of 7.40-7.44 and 6.12-6.15 ppm and instead of them appearance of cyclobutane proton signals at 3.81-4.33, at the same time proton signals assigned to carboxylic acids, aminos and phenyl group shifted slightly. When 4-ACA in a non-salt state was photo-irradiated, double bond transferred instead of [2+2] cycloaddition [11]. The salt state of 4-ACA was easiest former for the photocycloaddition [12]. 4-ATA has two amino groups and two carboxylic acids and then was difficult to directly use as a monomer for polyamides. Then 4-ATA hydrochloride was subsequently esterified in the dispersion state of reactant alcohol solvents such as methanol in presence of $(\text{CH}_3)_3\text{SiCl}$ (TMSCl). After 4-ATA was esterified, the product was dissolved in the solvent to react smoothly. As a result, ^1H NMR signals of methyl ester was confirmed as shown in Figure 2-2 [4, 4'-diamino - α -truxillic acid methyl ester (MATA)].

As to the ^{13}C NMR, the resonance signals of 4,4'-diamino- α -truxillic acid dihydrochloride showed seven main signals (Figure 2-3a), while those of 4,4'-diamino- α -truxillic acid methylester dihydrochloride (Figure 2-3b) showed one more signals that belonged to methyl group at 46.6 ppm.

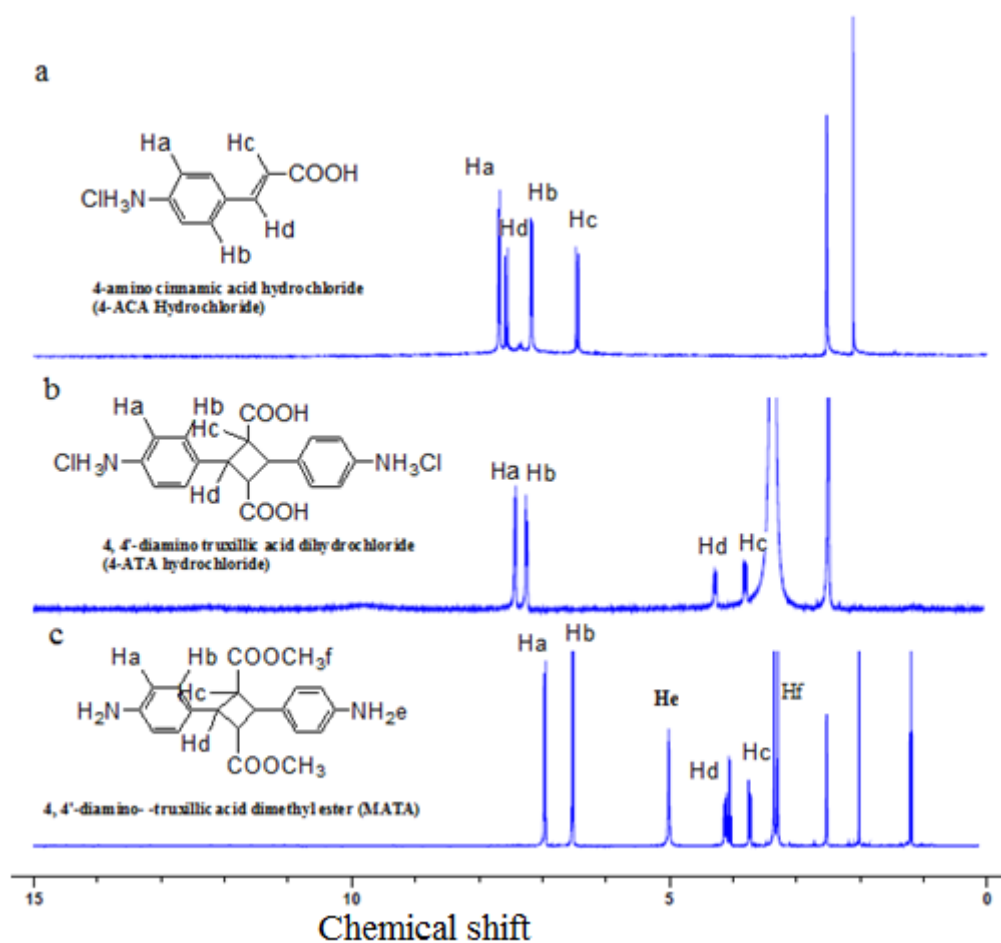


Figure 2-2 ^1H NMR spectra of: a) 4-ACA hydrochloride, b) 4,4'-diamino- α -truxillic acid dihydrochloride and c) 4,4'-diamino- α -truxillic acid methylester

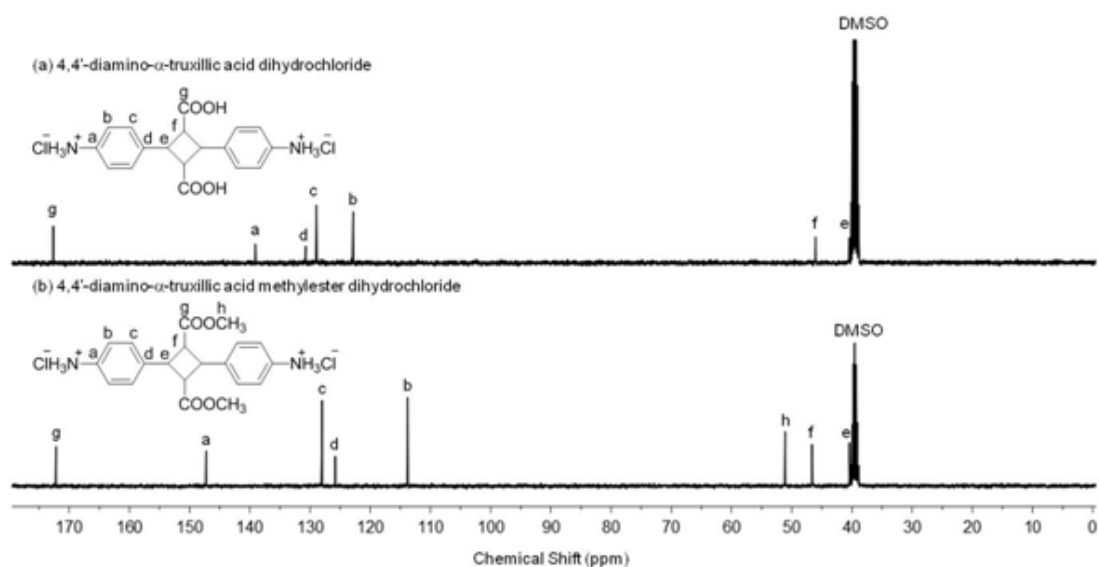


Figure 2-3 ^{13}C NMR spectra of: a) 4,4'-diamino- α -truxillic acid dihydrochloride and b) 4,4'-diamino- α -truxillic acid methylester dihydrochloride

FT-IR spectra of 4-ATA hydrochloride and MATA were shown in Figure 2-5. A broad hydroxyl peak at 2865 cm^{-1} was disappeared and carbonyls at 1700 cm^{-1} shifted toward the higher wavelength at 1713 cm^{-1} as a result of carboxylic acid reacted to be esters.

2-3-2 Syntheses and characterization of polyamides

Because the monomer with the carboxylic acid side chain cannot directly synthesize the aimed polyamides, all polyamides with different side chain groups were based on polyamides with methyl ester as side chain. The synthesis routes of aromatic polyamides with methyl ester as side chain (Scheme 2-1b) were prepared based on the polymerization of MATA and isophthalate chloride (IPC) / terephthalate chloride (TPC) in NMP solvent at $120\text{ }^{\circ}\text{C}$ under nitrogen atmosphere for 12h. The result products showed yellow solutions which were shown a little changed in viscosity.

Polyamides fibers were prepared by precipitation of polyamide solution in methanol and dried under vacuum overnight. They appeared white fibrils Figure 2.7 and then dissolved polymer fibrils with concentration of 0.2 g/mL in DMAc. Polymer solution was casted on glass plate and heating at $60\text{ }^{\circ}\text{C}$. The obtained polyamides showed light yellow color transparency and flexible film.

^1H NMR and FT-IR were used to characterize polyamide structures. The ^1H NMR signals (Figure 2-4.b and c) showed the presence of amino proton at 10.3 ppm , the aromatic dicarboxylic protons and the aromatic diamino protons of benzene ring were observed in the range of $8.3\text{-}8.4\text{ ppm}$ and $7.4\text{-}7.9\text{ ppm}$, respectively. Cyclobutane protons were assigned at $4.0\text{-}4.5\text{ ppm}$ and methyl proton was slightly overlapped with water at 3.3 ppm .

The FT-IR spectra of polyamides (Figure 2-5, c and d) showed the amide region at 3322 cm^{-1} (N-H stretching of amide), the alkyl absorption peak of diamines at 2949 cm^{-1} (C-H stretching of methylester), the phenyl ring peaks of diamines at 1435 cm^{-1} (C-H overtone aromatic ring), 1515 cm^{-1} (C=C stretching of aromatic ring). Moreover the differences of polyamides, PMATA/IPA and PMATA/TPA, were shown on the dichloride acid phenyl ring absorption and C=O stretching absorption. In PMATA/IPA, the phenyl ring absorption peaks appeared at 1597 cm^{-1} and 1651 cm^{-1} , and C=O absorption peak at 1724 cm^{-1} . At the same time in PMATATPC the peaks shifted into 1599 cm^{-1} , 1652 cm^{-1} and 1722 cm^{-1} . These results indicated the expected polyamides.

2-3-3 Molecular weight of Polyamides

The results of GPC to determine the weight-average molecular weight of (M_w), the number-average molecular weight (M_n) and the distribution of polymer molecular weight (PDI) showed on Table 2-1. The obtained polyamides showed low molecular weight.

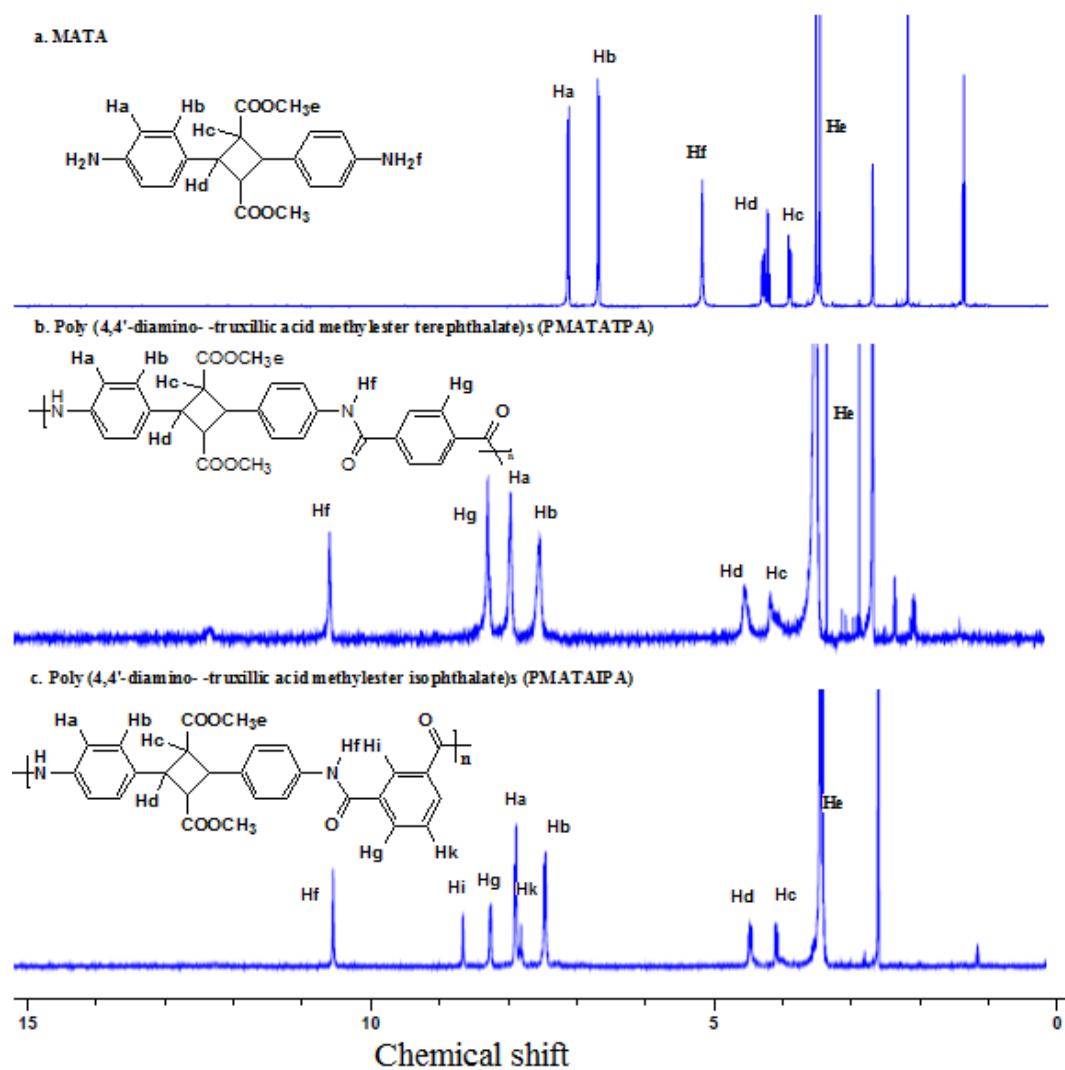


Figure 2-4 ^1H NMR spectra of; a) MATA, b) poly (4,4'-diamino- α -truxillic acid methylester terephthalate)s (PMATATPC) and c) poly (4,4'-diamino- α -truxillic acid methylester isophthalate)s (PMATAIPC)

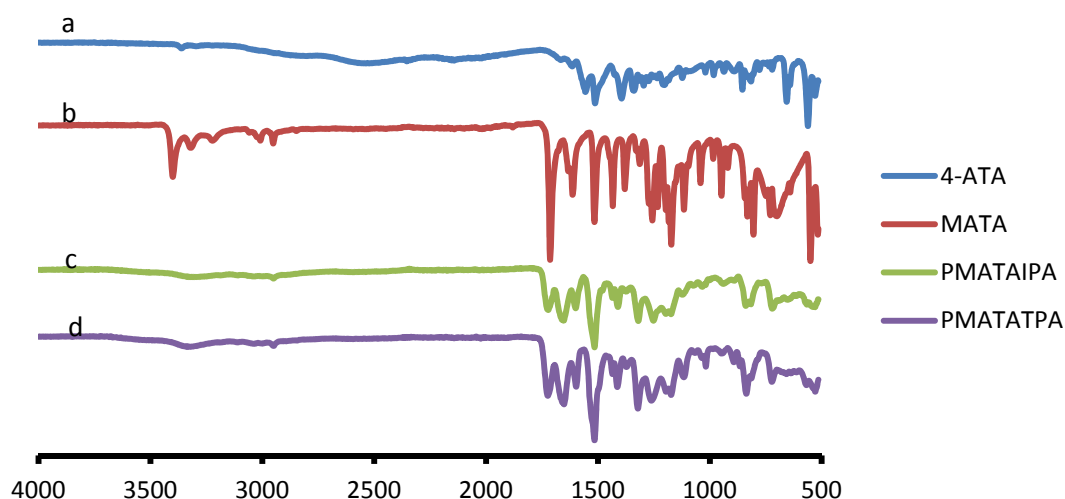


Figure 2-5 FT-IR spectra of: a) 4-ATA, b) MATA, c) PMATA/IPA d) PMATA/TPA

2-3-4 Thermal properties of Polyamides

The thermal properties of polyamides were analyzed by TGA and DSC (Figure 2-6,7). For industrial applications, the thermal properties of polyamides were important. Thermogravimetric curves (Figure 2-6) showed the TGA thermograms of PMATA/IPA and PMATA/TPA, which indicated single step thermal degradation. PMATA/IPA and PMATA/TPA showed 5% weight loss (T_5) at 340 °C and 342 °C, respectively, and 10 % weight loss (T_{10}) at 350 °C and 355 °C, respectively. The weight residue at 600 °C for PMATA/IPA and PMATA/TPA were 40 % and 50 %, respectively. The TGA measurement of the polymers revealed that these new polymers exhibited good thermal stability and these polymers are stable up to 350 °C. More than this, from DSC analysis, the glass transition temperature (T_g) of polyamides also were shown on Table 2-1. And T_g are from the results, all of T_{10} were more than 300 °C and T_g more than 130 °C, but PMACATPC's thermostabilities are higher than PMACAIPC because

the dichloride functional groups were different position on the benzene ring. These thermostability values are very high for the industrial application.

Table 2-1 The results of M_n , M_w and PDI of Polyamides

	$M_n(\times 10^3)^a$	$M_w(\times 10^3)^a$	PDI^a	$T_{10}/^\circ C^b$	$T_g/^\circ C^c$
PMATA/TPA	7	14.4	2.06	355	145
PMATA/IPA	7.4	8.4	1.13	350	130

^a Number-average molecular weights, M_n , weight-average molecular weights, M_w , and polydispersity index(M_w/M_n). ^b The 10% weight-loss temperature, T_{10} . ^c Glass transition temperature, T_g .

2-3-5 Solubility test of Polyamides

The solubility of polyamides was tested (Table 2-2) by dissolving them in three groups of solvents: (1) non-polar solvent such as toluene, hexane, chloroform, diethyl ether and dichloromethane, (2) polar protic solvent such as distilled water, methanol and ethanol and (3) polar aprotic solvent such as acetone, acetonitrile, DMF, NMP, DMAc, DMSO, THF and ethyl acetate. The polyamides were soluble in polar aprotic solvent such as DMF, NMP, DMAc and DMSO at room temperature. These results could be confirmed that polyamides have high chemical resistance.

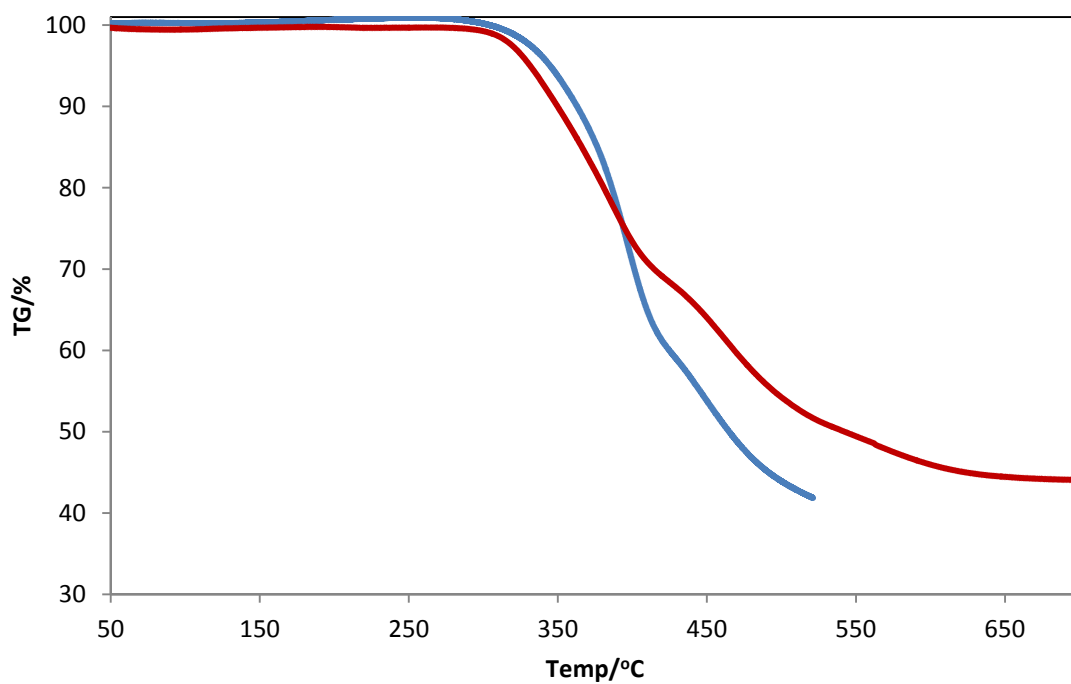


Figure 2-6 TGA curves of polyamides: red line is PMATA/IPA, blue line is PMATA/TPA

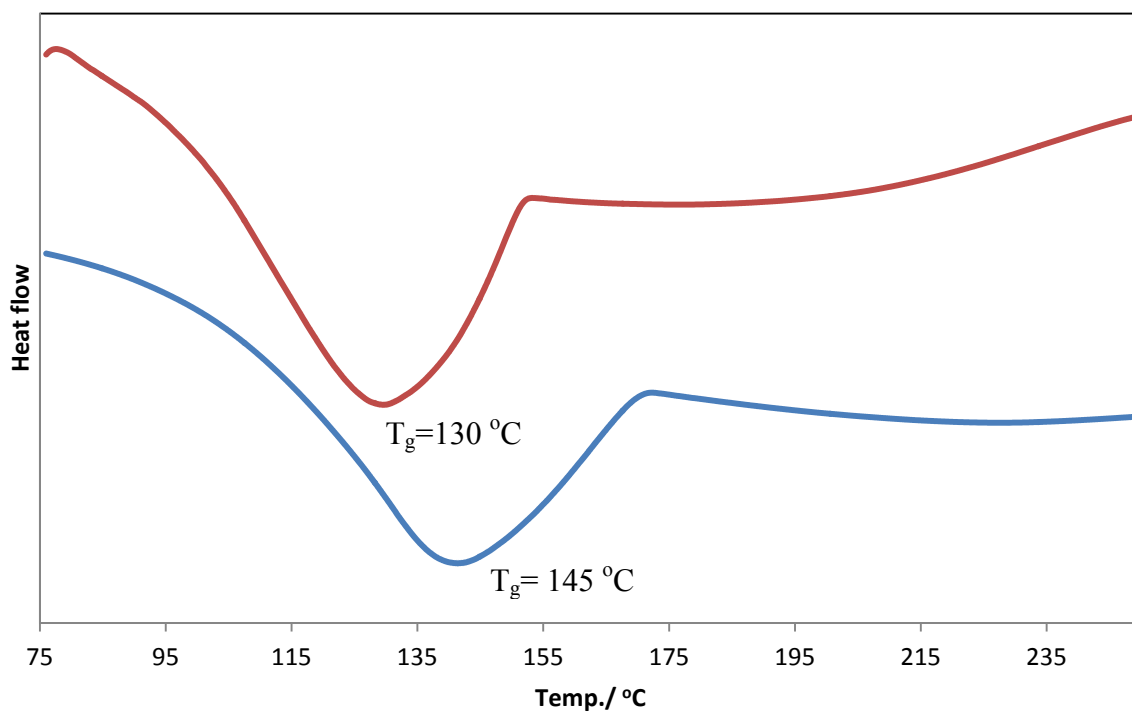


Figure 2-7 DSC curves of polyamides: red line is PMATA/IPA, blue line is PMATA/TPA

Table 2-2 The solubility of aromatic polyamides

	H ₂ O	MeOH	EtOH	Acetone	Hexane	DMF	NMP	EtOAc	DMSO
PMACATPC	-	-	-	-	-	+	+	-	+
PMACAIPC	-	-	-	-	-	+	+	-	+

2-3-6 synthesis and characterization of polyureas

I have already tried to study the possibility of isocyanate reaction with carboxylate by ¹H NMR, IR and ¹³C NMR spectra which were shown in Figure 2-8, 9, 10. If the carboxylic acid group reacted with isocyanate in the polymerization, the final polymer is the polyamide, not the polyurea. In this case ¹³C NMR spectra and ¹H NMR will be quite different. In ¹³C NMR the numbers of carbon peaks will be lost one because of carbon dioxide in production part, and in ¹H NMR spectra, the amide group peaks will be one single peak but not like present, double peak. From these spectra, we confirmed the carboxylic acid group reacted negligibly with isocyanate in this condition, presumably due to the high reactivity with amine groups.

Polyureas (PUs) with different side chain groups were prepared by the polycondensation of the diaminos of 4-ATA esters with stoichiometric amounts of MDI. The ¹H NMR spectra of all polyureas are shown in Figure 2-8. In the spectra for PUs, the main chain proton signals for aromatics, ureas methyl and cyclobutyl groups appears around 7.0-7.5, 8.5-8.6, 3.5 and 3.3-4.3 ppm. The various side chain groups show the different proton signals at different places: methyl ester appears 3.2ppm, carboxylic acid 12.2ppm and carboxyl ester both 1.1ppm and 3.2ppm. Similarly, NMR studies confirmed the formation of Pus derived from the aromatic diamino of 4-ATA

ethyl ester with MDI.

The FT-IR spectra of polyureas (Figure 3-2c, d) showed the urea region at 3340 cm^{-1} (N-H stretching of urea), the phenyl ring peaks of diamines at 1434 cm^{-1} (C-H overtone aromatic ring), 1538 cm^{-1} (C=C stretching of aromatic ring for diamine) and 1508 cm^{-1} (C=C stretching of aromatic ring for diisocyanate). Moreover the differences of polyureas, PATA/MDU and PMATA/MDU, were shown on the side chain group, methyl ester and carboxylic acid. In PMATA/MDU, the absorption methyl ester show at 2948 cm^{-1} . At the same time in PATA/MDU the absorption peak of carboxylic acid appeared at 2359 cm^{-1} . These results indicated the expected polyureas.

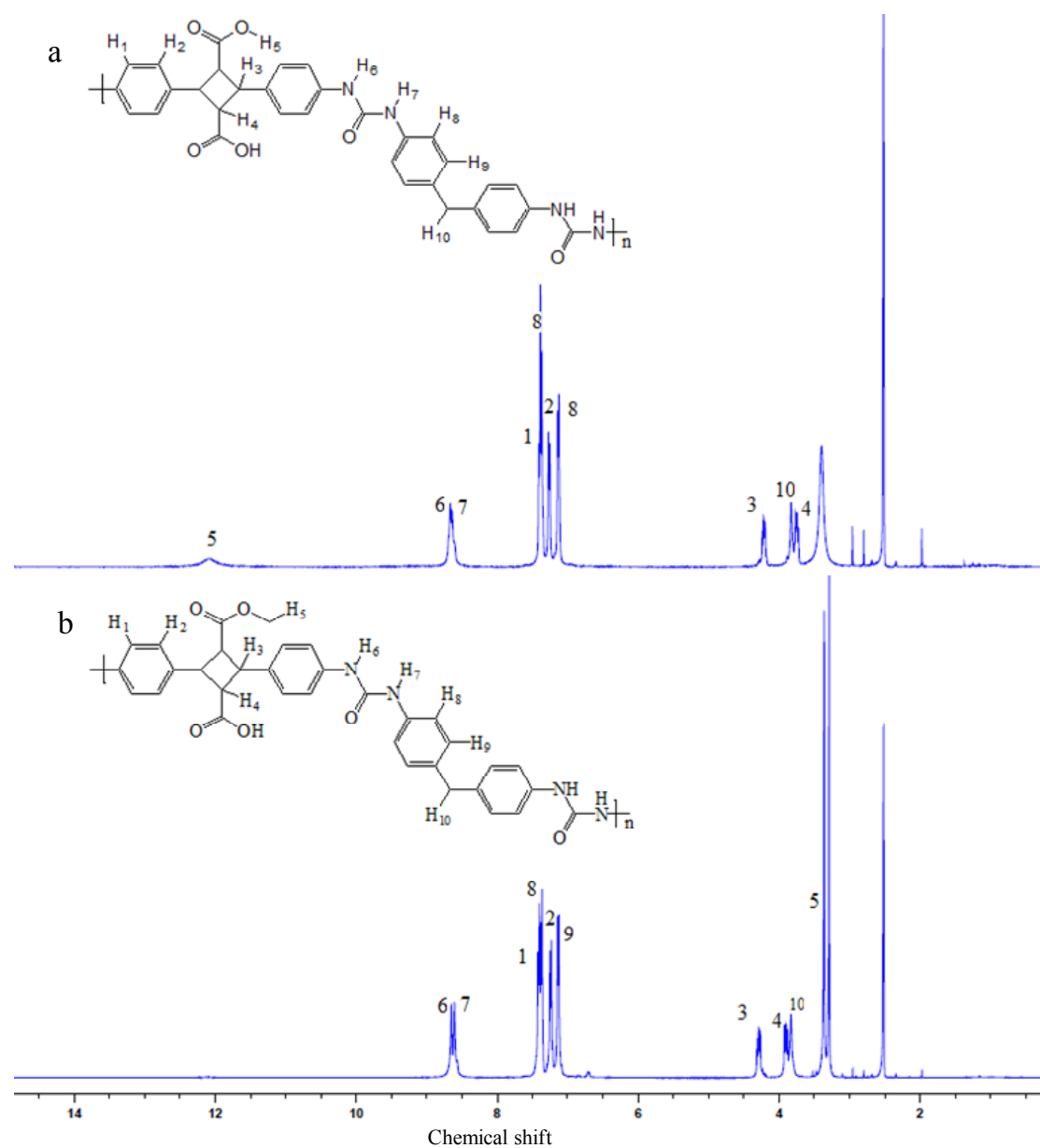


Figure 2-8 ^1H NMR spectra and the structure of polyureas: a) polyurea with carboxylic acid (PATA/MDU), b) polyurea with methyl ester side chain (PMATA/MDU),

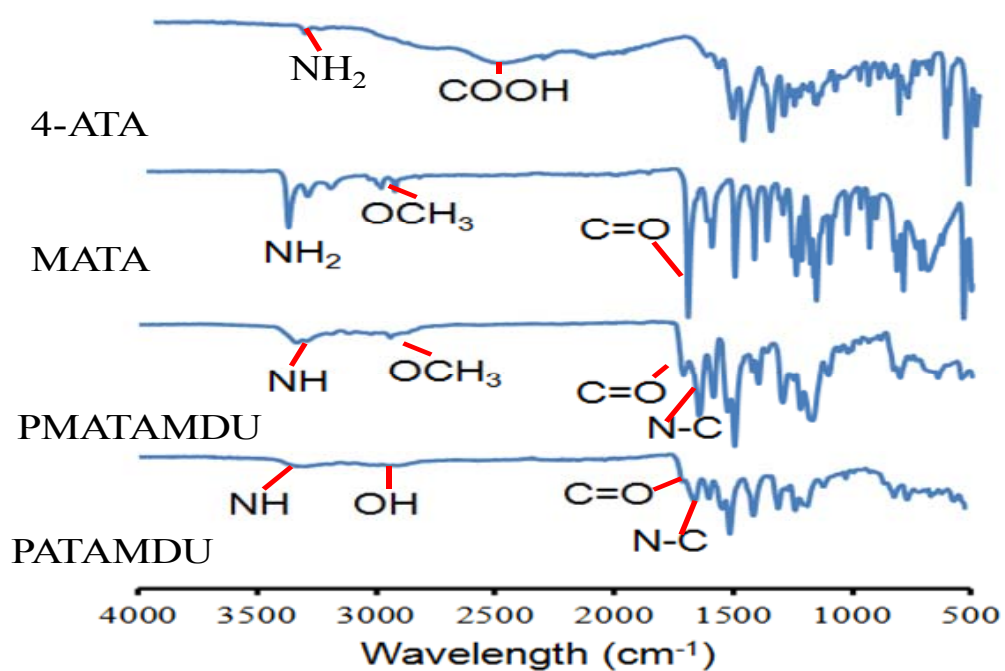


Figure 2-9 FT-IR spectra of : a) 4-ATA b) MATA c) PMATA/MDU d)

PATA/MDU

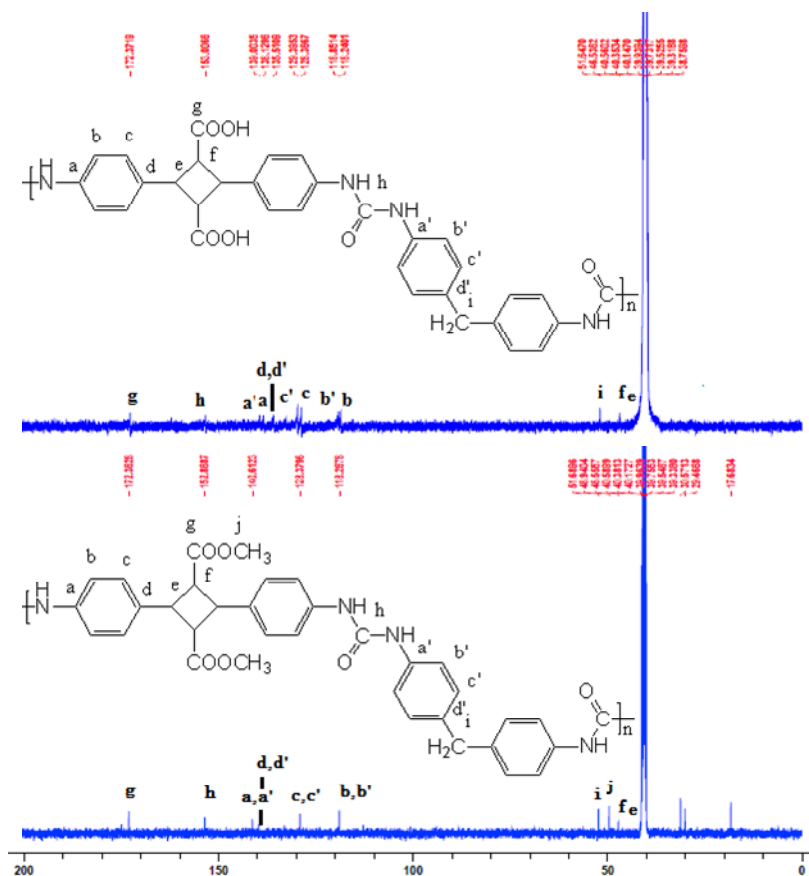


Figure 2-10. ¹³C spectra of polyureas : a) PATA/MDU b) PMATA/MDU

2-3-6 Molecular weights of Polyureas

The weight average molecular weight (M_w), the number average molecular weight (M_n) and the molecular weight distribution (PDI) were determined using PUs and are summarized in Table 1. PUs had high M_w and M_n value in range of $2.41-4.93 \times 10^5$ and $1.89-2.43 \times 10^5$, and the PDI ranged 1.28, 1.39 and 2.03. The obtained polyureas showed high molecular weight.

Table 2-3 Molecular weight and thermogravimetric of polyureas

Polymer	$M_n^a (\times 10^5)$	$M_w^a (\times 10^5)$	PDI ^a	$T_{10}^b / ^\circ\text{C}$	$T_g^c / ^\circ\text{C}$	FP ^e
PATA/MDU	1.89	2.41	1.28	270	180	Flexible
PMATA/MDU	1.81	2.51	1.39	280	210	Flexible

^a Number-average molecular weights, M_n , weight-average molecular weights, M_w , and polydispersity index (M_w/M_n). ^b The 10% weight-loss temperature, T_{10} . ^c Glass transition temperature, T_g .

2-3-7 Thermo-Mechanical Properties

The thermal degradation of PUs which were synthesized under 60°C was investigated by thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ and the 10% weight loss temperatures (T_{10}) was determined in Figure 2-11.a. After drying at 160°C the TGA curve of PMATA/MDU shown on the Figure 2-11.b and the mechanical curves of PMATA/MDU and PATA/MDU films were shown on Figure 2-12.a, d. The films thermal properties are almost the same as the powders thermal properties before drying. After drying under heat, T_{10} increased to 290°C which was a little lower than the same structure polymer synthesized from high temperature.

The glass transition temperature (T_g) values of the PUs were determined by thermo-mechanical analysis (TMA) under a nitrogen atmosphere and summarized in Table 2-4. PATA/MDU and PMATA/MDU showed T_g values of 180°C and 210°C. The T_g values of both of PUs depended on the backbone structure of the aromatic component.

The mechanical properties of the PU films were measured by a tensile test. The films of PMATA/MDU and PATA/MDU had tensile strength values of 21.23 and 16.73 MPa, tensile moduli of 1.23 and 1.13 GPa and gross mechanical failure at strains of 2.72% and 2.09%.

In the thermal property and mechanical property the values of PMATA/MDU are higher than PATA/MDU because of side chain group, methyl ester stronger than carboxylic acid.

Table 2-4 Tensile strength, Modulus, Elongation of Polyureas

Polymer	σ^a(MPa)	ε^a (%)	E^a(MPa)	RI^b	Density
PMATA/MDU	21.23 ±11.22	2.72 ±1.04	$1.2 \times 10^3 \pm 235.8$	1.61	1.26
PATA/MDU	16.73 ±1.56	2.09 ±0.43	$1.1 \times 10^3 \pm 27.17$	1.63	1.18

^a Mark σ , ε and E refer to the mechanical strength, Young's modulus and strain at break, respectively. ^b Refractive index was measured by Abbe refractometer.

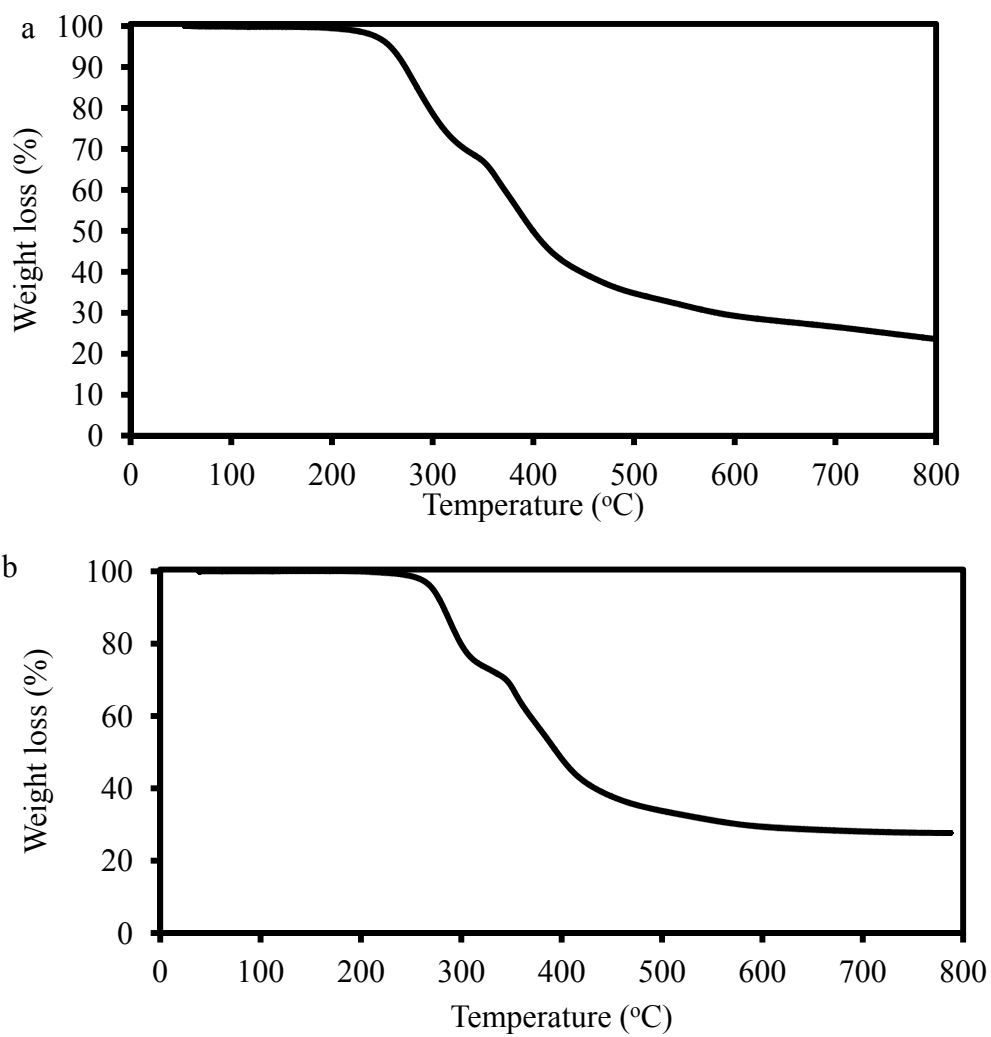


Figure 2-11 TGA curves of Polyureas' films: a) PATA/MDU b) PMATA/MDU

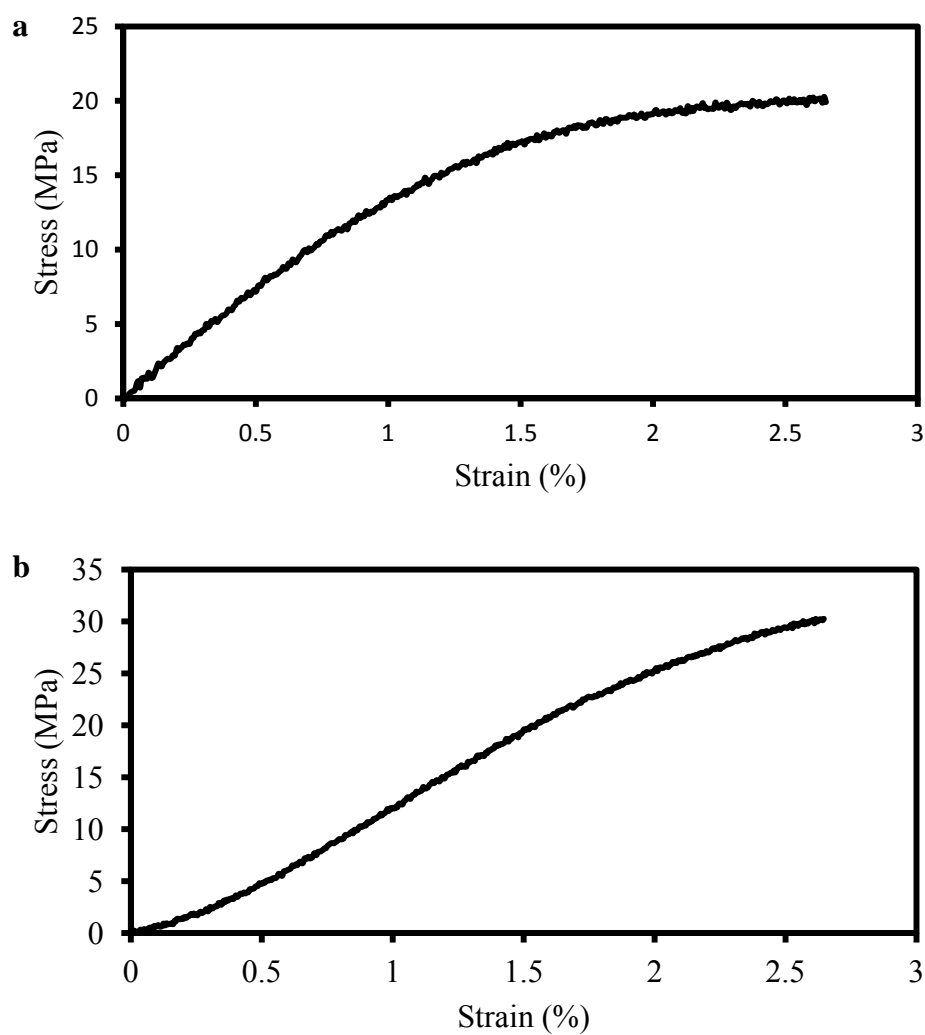


Figure 2-12 Stress-strain curves for a) PMATA/MDU and b) PATA/MDU

2-3-8 Optical Properties

Figure 2-13 showed the UV-Vis transmission spectra of PATA/MDU film and PMATA/MDU film. The absorbed spectra were normalized at a thickness $5\mu\text{m}$, optical transparency at 450 nm (λ_{450}) and the cutoff wavelengths (λ_0) of UV-Vis spectra were 91% , 310nm and 85%, 310nm.

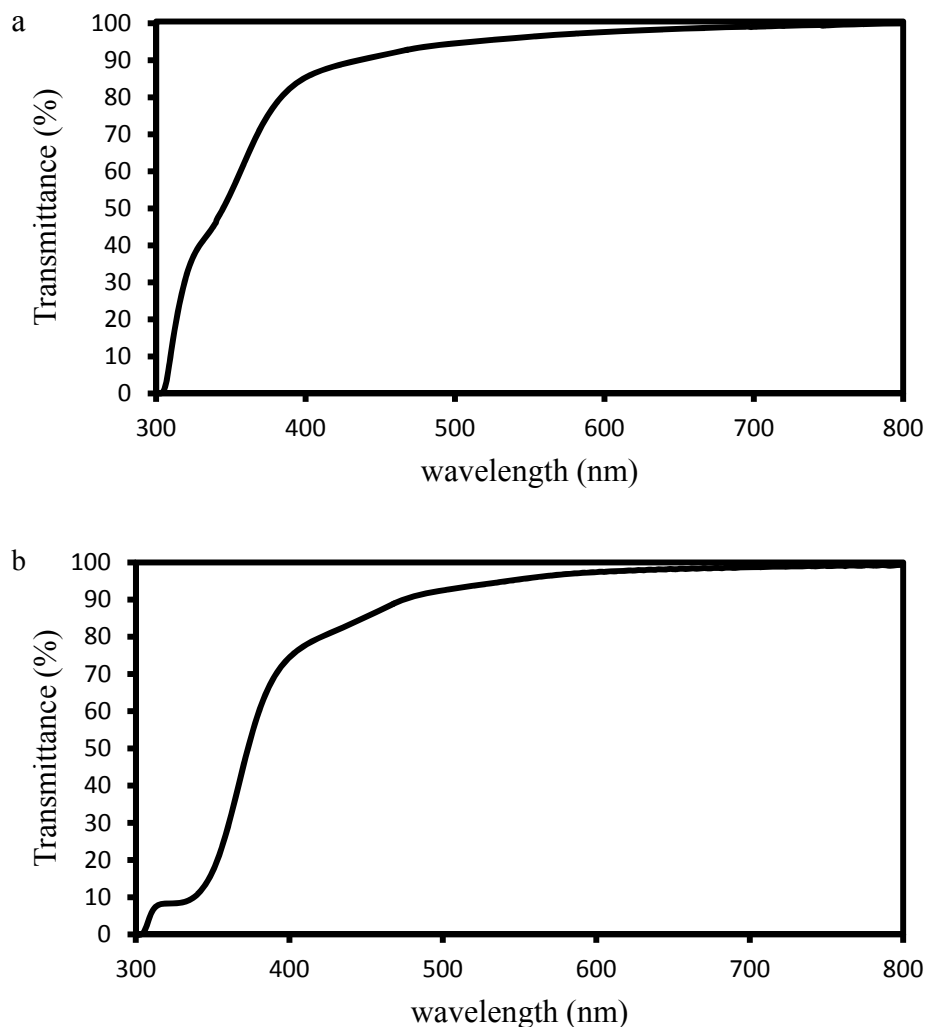


Figure 2-13 UV-Vis spectra of a) PMATA/MDU film and b) PATA/MDU film

2-3-9 Solubility of Polyureas

The solubility of polyureas was tested by dissolving them in three groups of solvents: (1) non-polar solvent such as toluene, hexane, chloroform, diethyl ether and dichloromethane, (2) polar protic solvent such as distilled water, methanol and ethanol and (3) polar aprotic solvent such as acetone, acetonitrile, DMF, NMP, DMAc, DMSO, THF and ethyl acetate. The polyureas were soluble in polar aprotic solvent such as DMF, NMP, DMAc and DMSO at room temperature and PCATAMDU was partial soluble in DMF/water mixture. These results could be confirmed that modified the side

chain group can improve the solubility of polyureas.

Table 2-5 Solubility for polyureas with different side chains

	PU-COOH	PU-COOMe
H ₂ O	-	-
MeOH	-	-
EtOH	-	-
Acetone	-	-
Hexane	-	-
THF	-	-
DMF	+	+
DMSO	+	+
NMP	+	+
H₂O:DMF(1:4)	+	+

2-4 Conclusions

New kinds of aromatic polyamides and polyureas based on new aromatic diamino derived from bio-based 4-ACA were successfully prepared. The aromatic polyureas such as PMATA/MDU and PATA/MDU had weak thermal property, T_{10} 275°C and T_g 180°C, compared with the aromatic polyamides such as PMATA/IPA's thermal property, T_{10} 325°C and T_g 210°C. However, the mechanical property of the polyureas was better than the polyamide because the polyamides films were too brittle and the polyureas films were flexible.

CHAPTER 3

Modified films of aromatic polyurea by the metal cation salts

Chapter 3

3-1 Introduction

Modified polymers can be gotten by copolymerization of monomers with distinctive practical gatherings or by post-adjustment of polymerized items. There is one example for polyacrylamide (PAA) with amide bunches which are stable in the intermediate (or neutral) pH range that can be changed over to -COOH by hydrolysis, to -OH by formaldehyde, to -NH_2 by the Hofmann reaction [106, 107]. By modified the hydrogen gel from heavy metal, the polymers' main chain were crosslinked by the hydrogen bond [108]. Crosslink made the polymer structure network and following the crosslinking degree changed, the polymer's properties were improved.

In the example, the ability of PAA to swell the heavy metal is facilitated by the carboxylic acid groups on the polymer chain, which strongly associate with water molecules [108]. These groups are readily ionizable and sensitive to the effects of pH and ionic strength.

In Chapter 2, I synthesized the aromatic polyamides and polyureas from bio-based 4-ACA, and made films from the polymers. The films of the aromatic polyamides were brittle and the ones of the aromatic polyureas were better than the polyamides. The mechanical property of the films from polyureas was nearly like Polystyrene (PS). For improved the properties, not only mechanical property but also

others, I needed modify the materials of the polyureas based on the urea group and side chain, carboxylic acid.

Here, I attempt to describe the modified films of PATA/MDU by some metal cation salts from the mechanical and thermal properties. The side chain group, carboxylic acid, of PATA/MDU can easily form the hydrogen bond between the cations. This hydrogen bond may be attributed to the aromatic donor-acceptor interaction between phenyl rings connecting with electron-donating nitrogen and electron-withdrawing carbonyl which can bring the properties change for the films.

3-2 Characterizations

The number average molecular weight (M_n), weight average molecular weight (M_w) and molecular weight distribution (PDI) of the polymers (conc. 5mg/L, filtrated after stirring over night) were determined by gel permeation chromatography [GPC, Shodex GPC-101 with a connection column system of KD-803 and KD-807(Shodex)] that was calibrated with pollulan standards at 40°C in DMF (eluent: Dimethylformamide) at the flow rate 0.5ml/min using the RI signal detector (Shodex). NMR measurements were performed by Bruker Biospin AG 400MHz, 54 mm spectrometer using DMSO- d_6 as a solvent. FT-IR spectra were recorded with a Perkin-Elmer Spectrum One spectrometer between 4000 and 600 cm^{-1} using a diamond-attenuated total reflection (ATR) accessory. The ultraviolet-visible (UV-vis) absorption spectra were recorded by Perkin Elmer, Lambda 25 UV/Vis spectrophotometer at room temperature over the range of 200-800

nm in the quartz cell under Na light source. The refractive indices of thin films were evaluated by an Abbe refractometer (Atago, NRA,1T) employing 1-bromonaphthalene as a contact liquid at room temperature. Measurements of thermogravimetry (TGA) and thermo-mechanical analysis (TMA) were performed on HITACHI, STA 7200 and HITACHI, TMA 7100, respectively, under nitrogen atmosphere at a heating rate of 10 °C/min. The polymer specimens were dried at 160 °C for 1 hour to remove any absorbed moisture before TGA and TMA. The inherent viscosities were measured using an Ubbelohde viscometer at 30 °C in DMAc at a polymer concentration of 0.5 g/dL. The tensile measurements were carried out at an elongation speed of 0.5 mm/min on a densitometer (Instron 3365) at room temperature with the polymer rectangle film.

3-3 Films modified by the metal cation

3-3-1 Films modified by the metal cation solution

Dissolved 100mg polymers in DMAc to formed 5-10wt% solution, then dropwise added on the glass which was heat at 60°C. Kept the glass at 40-50°C for 4 hs or longer to make sure the solvent dry then got the original films. Swollen the films in the different metal cation for two days and dried in the room temperature for one day to get the modified films (Figure 3-1).



Figure 3-1 Films of PATA/MDU after swollen the metal cautions

3-3-2 Absorption and Optical effect from the metal cation for the polymer

Causing the side chain group of PATA/MDU, carboxylic acid, the polymers was modified by the nitrate salts with heavy metal cations. In Figure 3-2. b, λ_{550} showed the concentration dependence on the cations. With the increase of cations concentration, λ_{550} shifted to the low transparency. Also the mechanical property (Figure 3-3) such as tensile strength and tensile modulus of the films (Table 3-1) showed the similar dependence on the concentration of the metal cations. First, when the metal cations reinforced on the films, the mechanical increased quickly. After the cations absorption amount on the films increased following the concentration increased, the mechanical property also increased but the amplification was slower than beginning. I added transmittance spectra of a model compound of the polyurea, diphenyl urea, in different concentrations, which was shown in Figure 3-5. We found both peaks around 440 and

610 nm are found in high concentration sample of diphenyl urea. Then we can guess that these peaks can be attributed to the pi-pi* transition of benzene rings of diphenyl urea moiety of the polyurea.

Table 3-1. Effects of Eu concentration on adsorption to PATA/MDU films

Eu concentration (mol/L)	Adsorption degree (mol/mol)	Abs at λ_{550}	Strength at break (MPa)	Elongation at break (%)	Young's moduli (GPa)
0	0	91	17	2.1	1.1
0.1	0.011	79	20	3.0	1.1
0.2	0.031	76	21	2.8	1.2
0.5	0.10	65	25	2.1	1.2
1	0.19	63	33	2.7	1.3

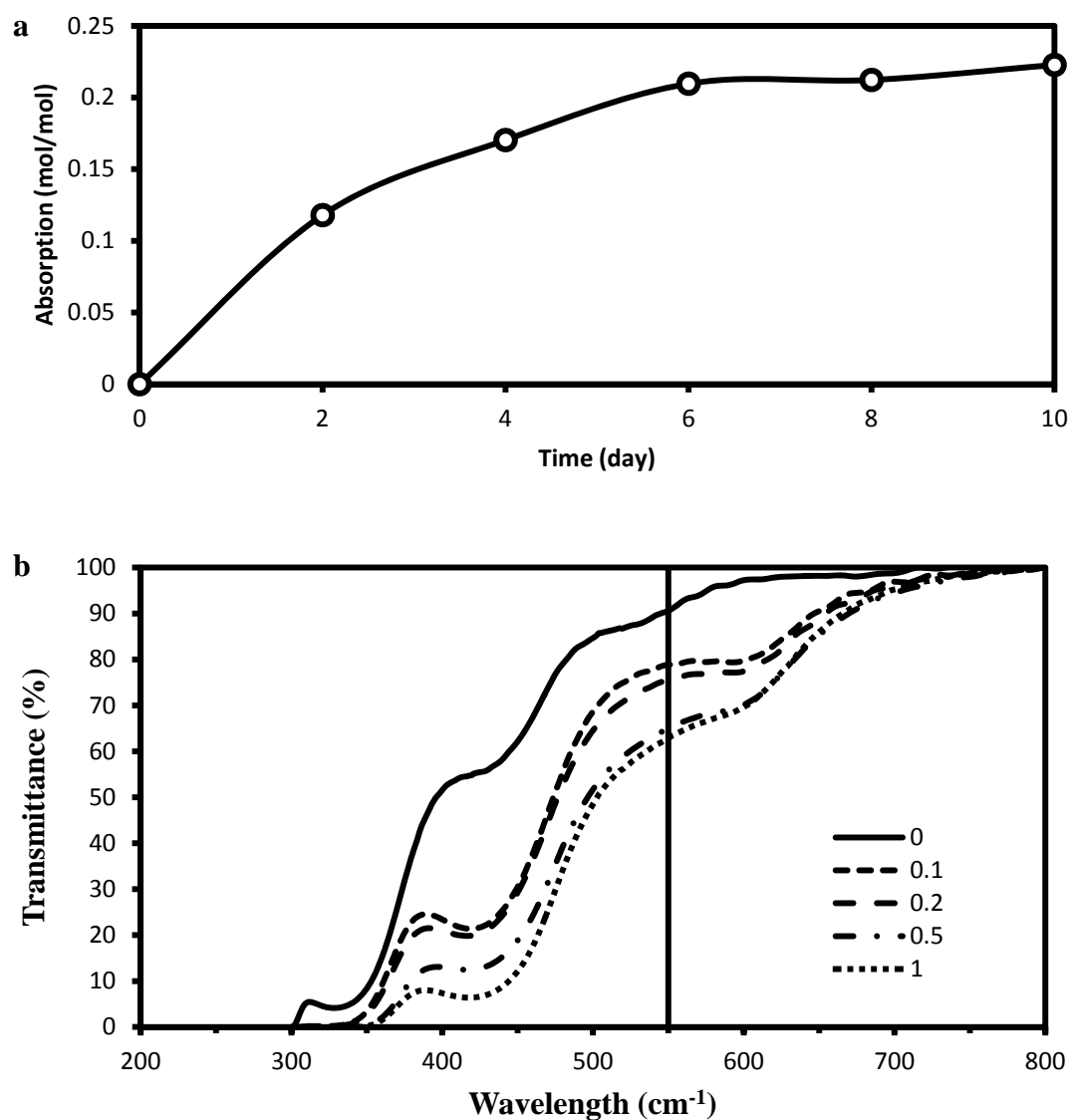


Figure 3-2 a) Concentration dependence of molar ratio of absorbed metal ions to polymer repeating units. b) UV-vis spectra of films Eu³⁺-adsorbed in different concentrations

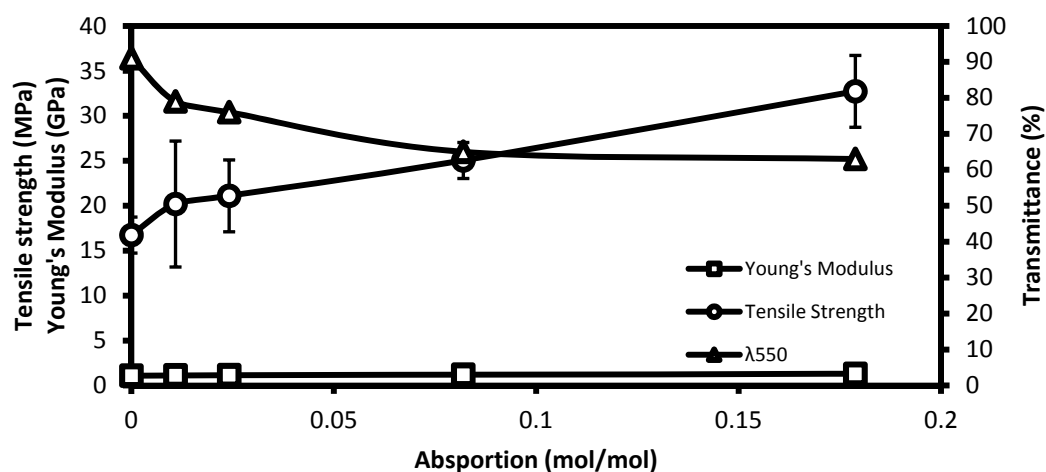


Figure 3-3. Tensile strengths at break and Young's moduli of $\text{Eu}(\text{NO}_3)_3$ -adsorbed films at various salt concentrations.

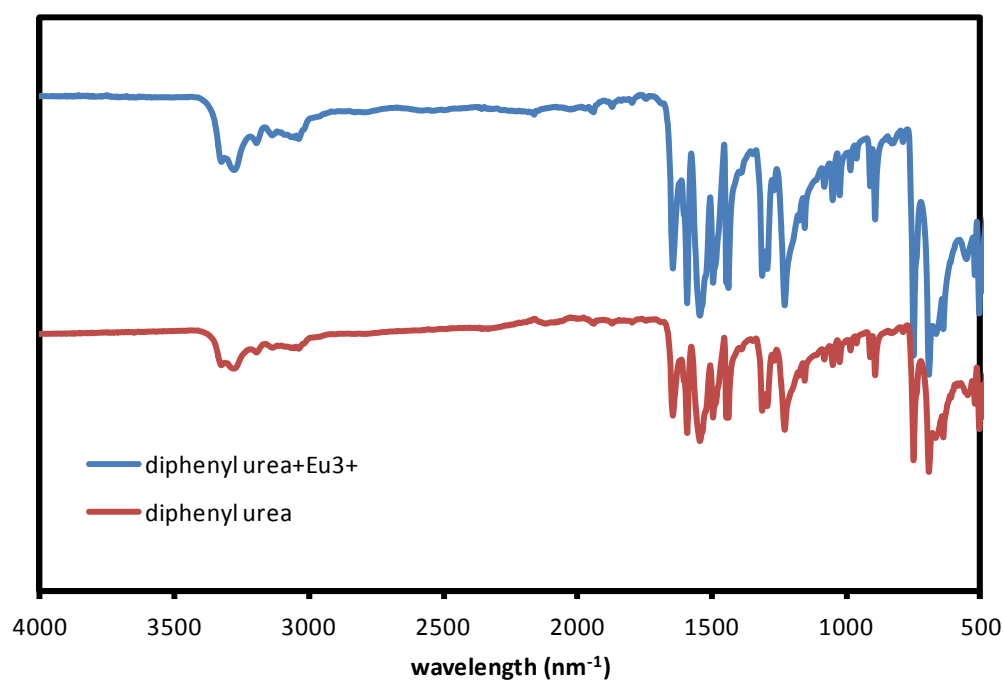


Figure 3-4. IR spectra of the model and the mixture with the salt $\text{Eu}(\text{NO}_3)_3$ which is the same compound to modify the polyureas film

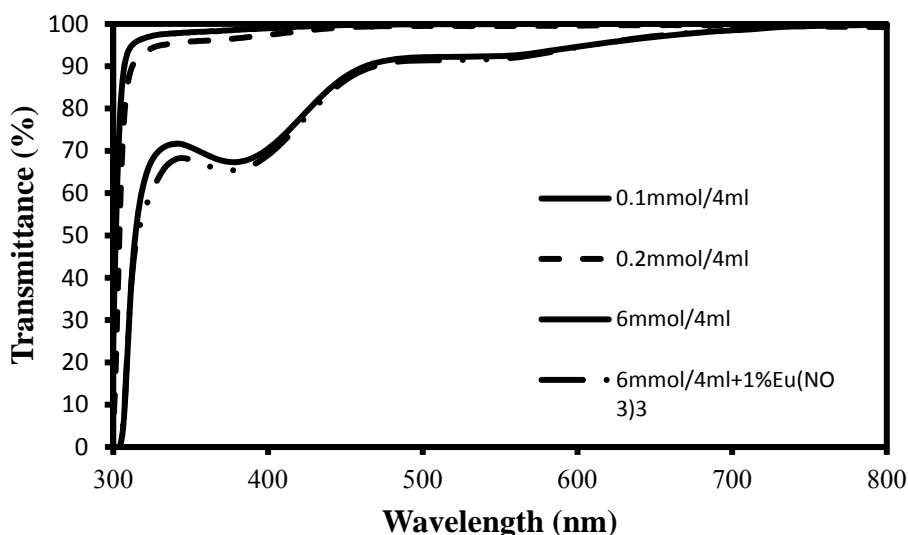


Figure 3-5. Transmittance spectra of 1, 3-diphenyl urea in the different concentrations and $\text{Eu}(\text{NO}_3)_3$ solution

3-3-3 molecular mechanism of ionic effect on the urea group

Before confirmed the mechanism of the ionic effect on the polymers, I used the low-molecular weight compound 1, 3-diphenyl urea as the model by IR spectra and UV transmittance to compare with the polymers (Figure 3-4, 5). In the IR spectra of polyureas before and after modification, I compared the change of the phenyl peaks. There is no obvious shift in the phenyl part. I also used the diphenyl urea as the model of polyurea mixed the salt $\text{Eu}(\text{NO}_3)_3$ to confirm chelation effects and charge-transfer interactions in Figure 3-4.

Confirm the structure of the metal cation how to contact with the polymer by infrared spectrum of three kinds of samples: one is without metal salt, second is that mixed the metal standard solution into the polymer solution and the third is put the polymer film in the metal standard solution to swollen. The results show on Figure 3-4. The pure

PATA/MDU film and the mixture with salt showed a sharp urea IR peak at 1678 cm^{-1} and 1605 cm^{-1} which belong to C=O of carboxylic acid and urea group. However the salt-hybridized film showed different spectra; for the part of urea group which formed the hydrogen bond with nitrate anion, a new peak appeared at 1613 cm^{-1} from the old peak shifted, and for the carboxylic acid group absorbed the metal cation, there was a big shoulder shifted from the C=O of carboxylic acid. This reveals nitrate anion adsorption by the urea group (Figure 3-7) [103-105]. Nitrate absorbing to urea cross-linked the PU chains and reinforced the films under the support of metal adsorption to carboxylic acid, and the increased interchain interaction caused the increase in mechanical properties.

The optical property (λ_{550}) and mechanical properties such as tensile strength and tensile modulus of the films depended on the concentration of the Eu^{3+} salt (Figure 3-8). Following the Eu^{3+} cation absorbed on the films the amount of hydrogen bond also increased, which made the interactions between the backbones more closely. First, this made the backbones distance changed, also meant π -electron interactions from the aromatic group between the backbones changed, caused the transparent of the films worse, and on the other hand this effects also showed on the mechanical property was that the mechanical strength and Young's moduli increased with an increase in the amount of Eu^{3+} cation absorption on the films. This suggesting that metal cation adsorption had a reinforcing effect on the films.

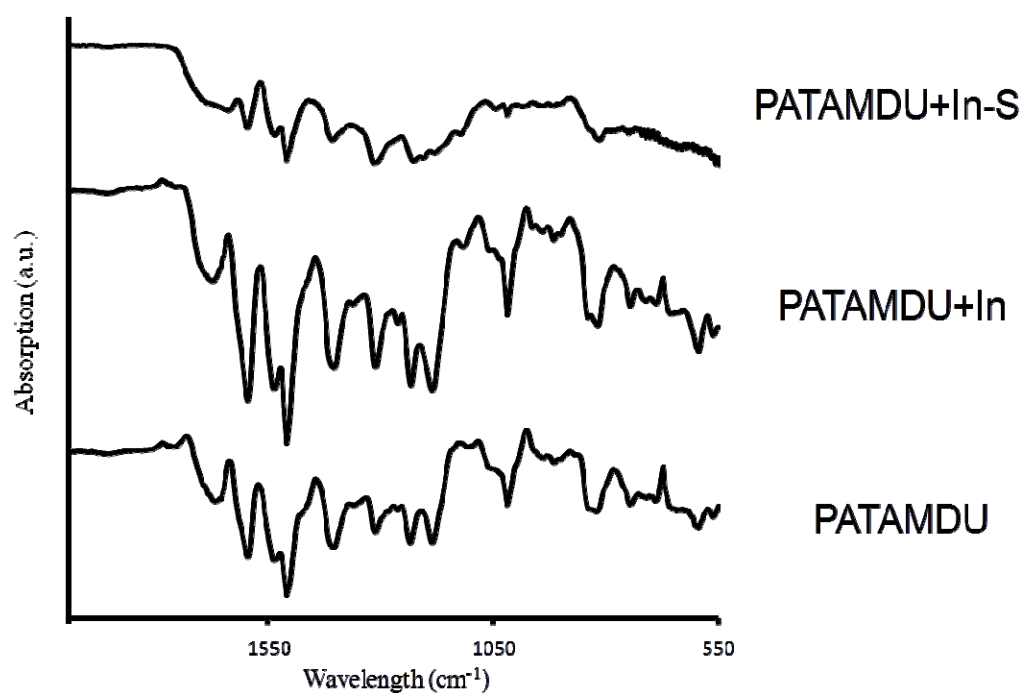


Figure 3-6 FT-IR spectra of PATA/MDU films modified by different methods

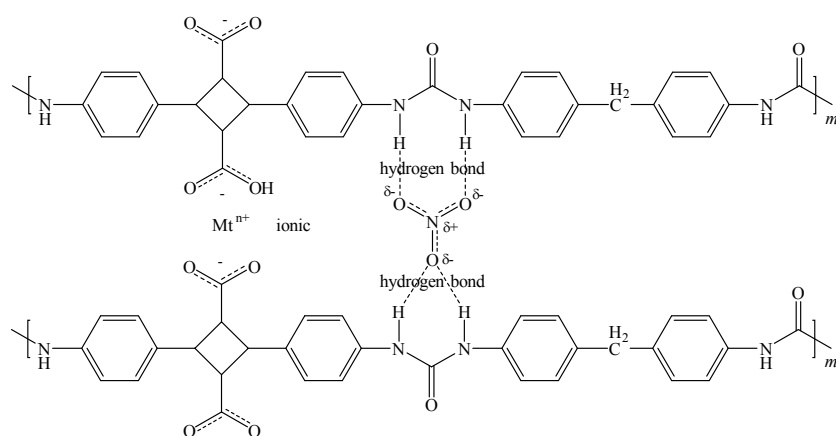


Figure 3-7 Molecular mechanism of ion forming the hydrogen bond with urea group

3-3-4 Effect on thermal and mechanical property

Compare to T_{10} of PATA/MDU, the degradation temperature of the modified films are weaker, especially the film swollen in the NaNO_3 solution ($T_{10}=256^\circ\text{C}$). This pointed out the hydrogen bond make the film's thermal property decrease.

Table 3-2. Thermal and mechanical properties of films with different metal nitrate salts

Polymers	Ionic radii ^a (Å)	Absorption (mol/mol)	σ (MPa)	ε (%)	E (GPa)	T_{d10} (°C)	λ_{550} (%)
PATA/MDU	-	-	21±2.0	2.1±0.40	1.2 ± 0.03	275	95
PATA/MDU-Na ⁺	102	0.26	41 ± 4.0	3.6±0.34	1.7 ± 0.03	260	90
PATA/MDU-Mg ²⁺	72	0.17	41 ± 0.6	2.7±0.26	1.3 ± 0.09	260	90
PATA/MDU-Fe ²⁺	64	0.14	37 ±2.1	2.7±0.47	1.6 ± 0.07	255	85
PATA/MDU-Nd ³⁺	98	0.25	43 ± 1.3	2.6±0.38	1.8 ± 0.01	265	75
PATA/MDU-Eu ³⁺	94	0.19	33 ± 0.9	2.7±0.29	1.3 ± 0.05	260	65
PATA/MDU-In ³⁺	80	0.14	29 ± 4.8	2.6±0.42	1.5 ± 0.02	255	89

^a Data of ionic radii are shown based on the *Elsevier's* periodic table of the elements.

The mechanical properties of the films were measured by a tensile test (Table 3-2). The films had tensile strength values from 29.29 to 43.00 MPa, tensile modules from 1.3 to 1.8 GPa and gross mechanical failure at strains of 2.56 to 3.58%. The increase of the mechanical property was due to the hydrogen bond forming between the urea group and the ionic which was not only the metal cation but also the nitrate group [110-112]. Although all the metal nitrate salt help improve the mechanical property of the films sodium nitrate and Neodymium nitrate had the best effect which made the tensile strength to 41.39 and 43.00 MPa and tensile modulus to 1.73 and 1.81 GPa.

3-3-5 Effect on optical property

After swollen the metal salts the films of the polymer had changes on the transmittance because of the hydrogen bond forming. The effect results showed on Figure 3-6. There showed the optical property had big change on optical transparency at 550 nm (λ_{550})

and the cutoff wavelengths (λ_0), especially, λ_0 of the sample with Neodymium nitrate at 425nm.

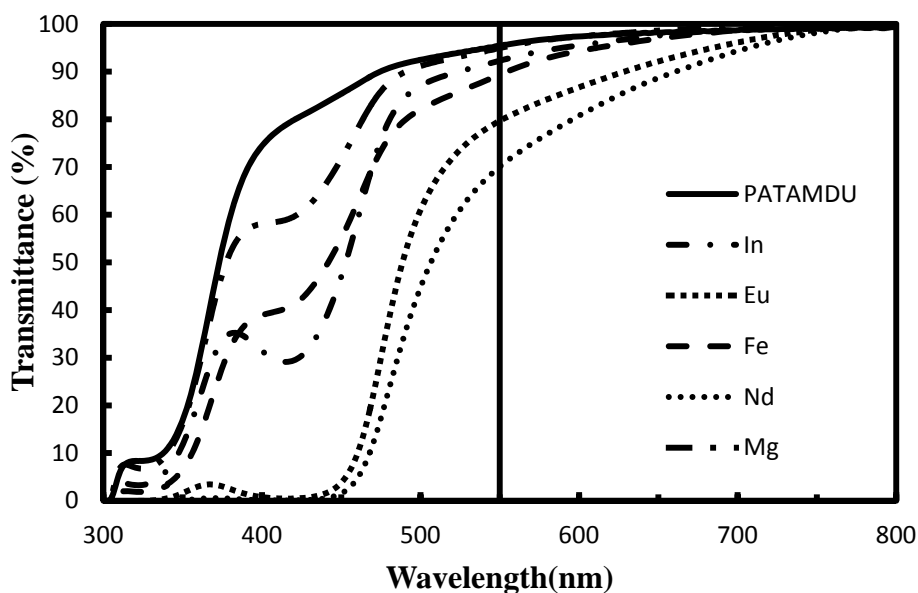


Figure 3-6 UV-vis spectrums of films mixed with metal cautions

3-4 Conclusions

I successfully modify PATA/MDU under the film form by the metal cation. I confirm the mechanism of the modified film by FT-IR that is hydrogen bond between carboxylic acid and metal cations, and research the modified film from thermal, mechanical and optical properties. The films modified by metal cations increased the mechanical property to 43.00 MPa (tensile strength) and 1.81 GPa (tensile modulus) by controlling different metal salt. At the same time the optical property was controlled, film's color turns to green from yellow which meant by different metal cation, λ_{550} can be controlled.

CHAPTER 4

Degradation of aromatic polyureas with different side chains

Chapter 4

4-1 Introduction

Synthetic polymers are important in many branches of industry, for example in the packaging industry. However, wasted plastic pollution is a serious global problem for environment. How to degrade the plastic cheap and easily becomes a hot interesting research for all scientists. Methylene diphenyl diisocyanate (MDI) is manufactured and used on a large scale, greater than one billion (1×10^9) kg/year worldwide [97]. . MDI is most often used as an oligomeric mixture, commonly known as “polymeric” MDI (PMDI), containing about 50% of the monomer, 4,4' -MDI. Most of the hydrolysis studies reported in the literature were carried out on smaller molecules (mono- and bis-ureas) in solution utilizing a mixture of water with organic solvents. The reported hydrolysis rate for the diphenyl urea made from 4,4' -methylenediphenyl diisocyanate (4,4' -MDI) at 70°C in DMSO/water is $6.43 \times 10^{-4} \text{ h}^{-1}$, a half-life of about 45 days [98]. Hydrolysis of a series of substituted ureas over a range of temperatures was studied by Audu and Heyn [99].

The effect of ultraviolet (UV) light irradiation on the color and chemical structure of water-cured polymeric diphenylmethane diisocyanate (PMDI) was investigated using a UV long-life fade meter. Control treatment was performed without UV light irradiation using a thermohygrostat for comparison. Many studies regarding the photo-

degradation of polyurethanes consisting of PMDI have been reported [100-102].

However, there is no reported of biodegradation of polyurea yet.

Here, I try to describe all of three degradation methods for the polyureas with different side chains, and try to characterize the process and product of the degradation by ^1H NMR and molecular weight. The monomer 4-ATA should be easier to degrade than other parts because cyclobutane stability is weakness. The cyclobutane can be hydrolysis by base or photolysis by UV ($<254\text{nm}$). For the biodegradation, usually the aromatic polymers were hardness for the microorganism. But in our case the urea part will be the key to break the polymer by microorganism.

4-2 Experiments

4-2-1 Chemicals

All polyureas were synthesized from Chapter 3. Dimethyl sulfoxide- d_6 (DMSO, from Kanto), methanol [MeOH(Plus), special for LC/MS, from Kanto] were used as received. The Hunter trace elements solution were prepared as below:

$\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$	5 g
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	2.2 g
H_3BO_3	1.14 g
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	506 mg
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	499 mg
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	161 mg

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	157 mg
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	110 mg
Distilled water	100 mL

Adjust the pH to 6.5-6.8 with KOH (~1.6 g). Store the solution in a refrigerator (5°C). The solution should have turned to violet color before use. This process takes a few days and was necessary.

4-2-2 Characterizations

The molecular weights of the polyureas were determined by gel permeation chromatography (GPC; Shodex GPC-101 with a connection column system of 803 and 807) that was calibrated with polystyrene standards at 40°C (eluent: Dimethylformamide). The NMR spectra were obtained on a Bruker DRX 500 spectrometer operating at 400.13 MHz for ^1H NMR. A deuterated solvent of dimethylsulfoxide- d_6 ($\text{DMSO-}d_6$) was used. The degradation products were not only confirmed by high performance liquid chromatography (HPLC, GL-7400 system from GL Sciences Ltd.) that ran at 40°C and the eluents were distilled water, MeOH (Plus) and TFA but also by liquid chromatography-mass spectrometry (LC-MS) that the solution was MeOH(Plus) and ultraviolet-visible (UV-vis) optical absorption spectra were recorded Perkin Elmer, Lambda 25 UV/Vis spectrophotometer at room temperature over the range of 200-800nm..

4-2-3 Photolysis reaction for the polyureas

For the photolysis reaction, I selected the light of 250nm-385nm wavelength from the Xenon lamp as the light source. First, dissolved 50mg polymer in 0.5 ml DMSO- d_6 to put into the quartz NMR tube or the sample bottle then shot the sample from the bottom of the tube. I checked NMR and GPC per four hours.

4-2-4 Hydrolysis reaction for the polyureas

For the hydrolysis of the polyureas 5wt% solutions which was 50mg polymer dissolved in 1ml solvent were put into a 3ml sample bottles to mixed with NaOH (10 wt%) and stirred. These two tests' processes were checked by NMR and GPC.

4-2-5 Biodegradation test for polyureas

The biodegradation test was like following: Microorganisms were collected in environment in forest soil around Tsukuba university campus. Every soil sample took one gram from nature and mixed with 3ml sterile water. 30 μ l water solvent with soil sample was inoculated on agar plate contented different polyureas. Sample plates were incubated under 30°C for growth of microorganism colonies. When microorganism colonies attained suitable size sample of every single microorganism colony was taken separately and swept onto other agar plates with the same polyurea samples as the carbon source to grow. At this stage new colonies of microorganism were recognized to isolate, when colony size was developed. The microorganisms were isolated by their sizes, shapes, and colors and again were separated to grow in several steps to complete the isolation. After isolated the single microorganisms on

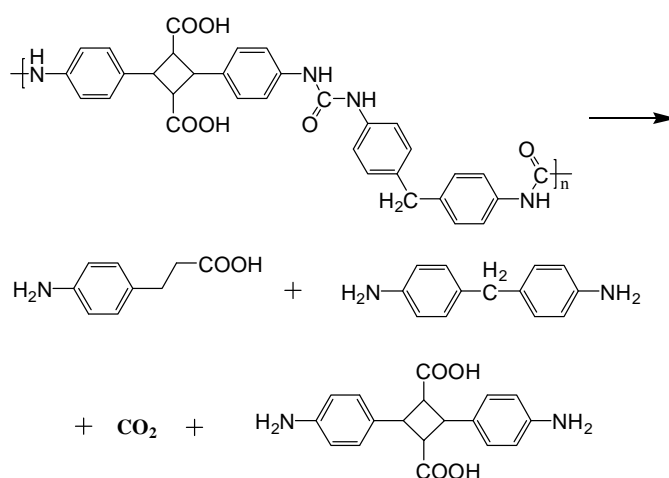
the plates, the microorganisms were transplanted into the tubes with liquid medium including the same polyurea as the single carbon source. After grown for a few days, the liquid media was separated the liquid part and insoluble part to test. The liquid parts were checked by HPLC and the insoluble parts were confirmed by GPC after dissolved into DMF.

4-3 Results and Discussion

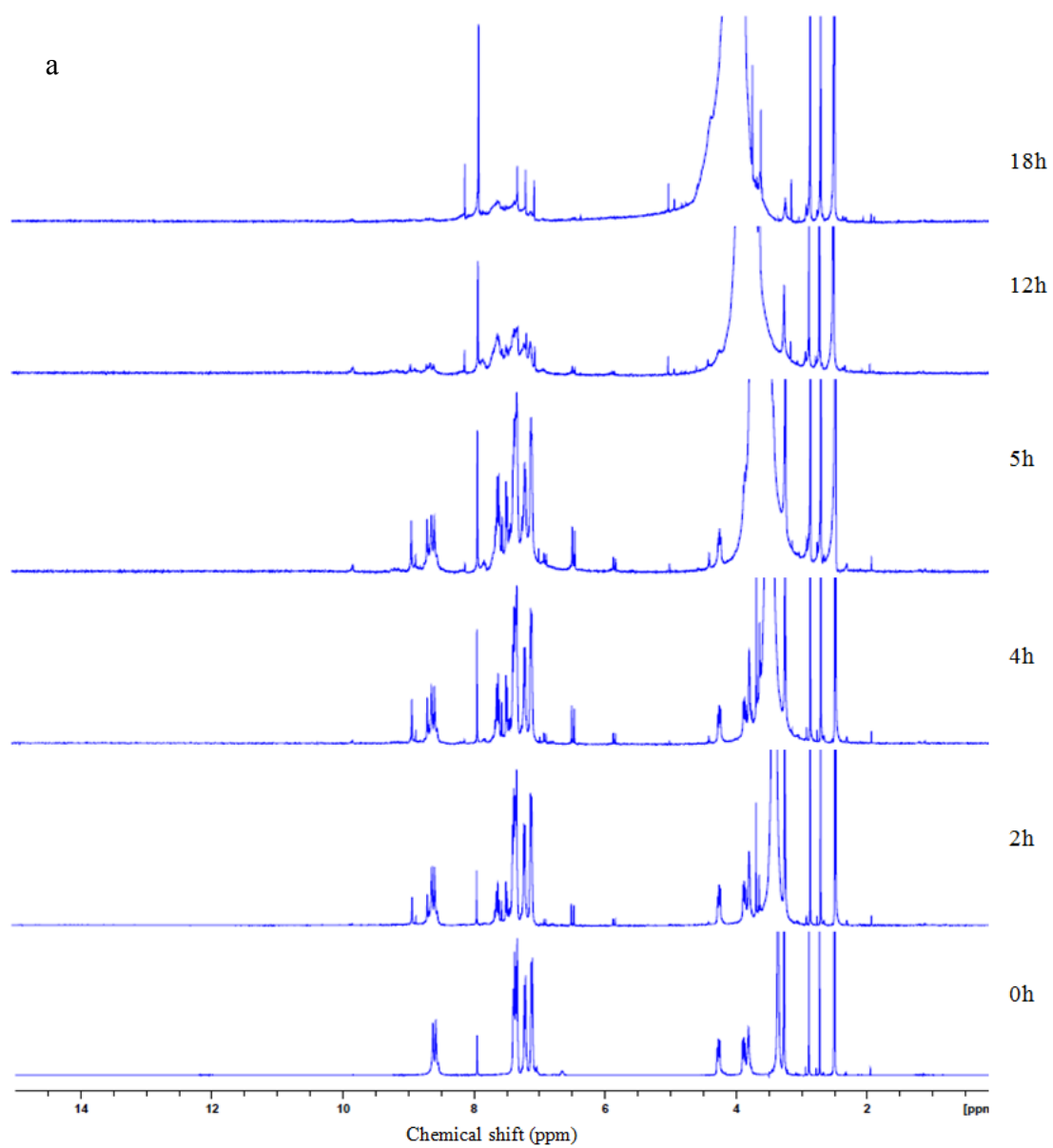
4-3-1 Characterizations of Photolysis reaction

The photolysis reaction was test on PATA/MDU and PMATA/MDU, and the processes were following by ^1H NMR and GPC (Figure 4, 5). From ^1H NMR spectra of both PATA/MDU and PMATA/MDU, the signal proton peak was changed and on PMATA/MDU result, the benzene ring peaks became sharp after degradation and also the cyclobutyl ring's peaks were changed. Also from NMR results, I can calculate the degradation speed of cyclobutane and urea group. For PATA/MDU degradation percent of cyclobutane was 40% in 24hs and after 16hs there was no change, which meant that the cyclobutane only can be degraded 40% in 16h for the whole degradation, and for the urea group, there was 60% degraded in 24h and showed a half life time was 14 hours. Not only PATA/MDU but also for PMATA/MDU degradation, the degraded percent of cyclobutane was more than 60% and after 24h there have an interesting phenomenon, the degradation and the photoaddition running at the same time, which meant that the cyclobutane can be degraded 60% in 24h but after a certain concentration, the photoaddition speeds will be higher than degradation, and for the urea group, there was

also 60% degraded in 24h and showed a half life time was 14 hours. Compared PATA/MDU and PMATA/MDU, all urea groups can be degraded 60% in 24hs, but the cyclobutane groups were quite different, one is 40% and one is 60%. At the same time on GPC results the peaks belonged to polymers decreased by time and oligmer peaks increased instead. These determined that the PUs has been degraded by UV irradiation. For the speed the degradation under UV irradiation was quite fast, only 28h for PATA/MDU and 32h for PMATA/MDU. The solution's color turned light and there is no precipitate after dropped the solution into water finally. The final solution was analyzed by LC-MS to confirm the structures of products and the photolysis reaction ran like Scheme 2 according the mass result.



Scheme 4-1 The scheme of the polyureas degradation by UV irradiation



b

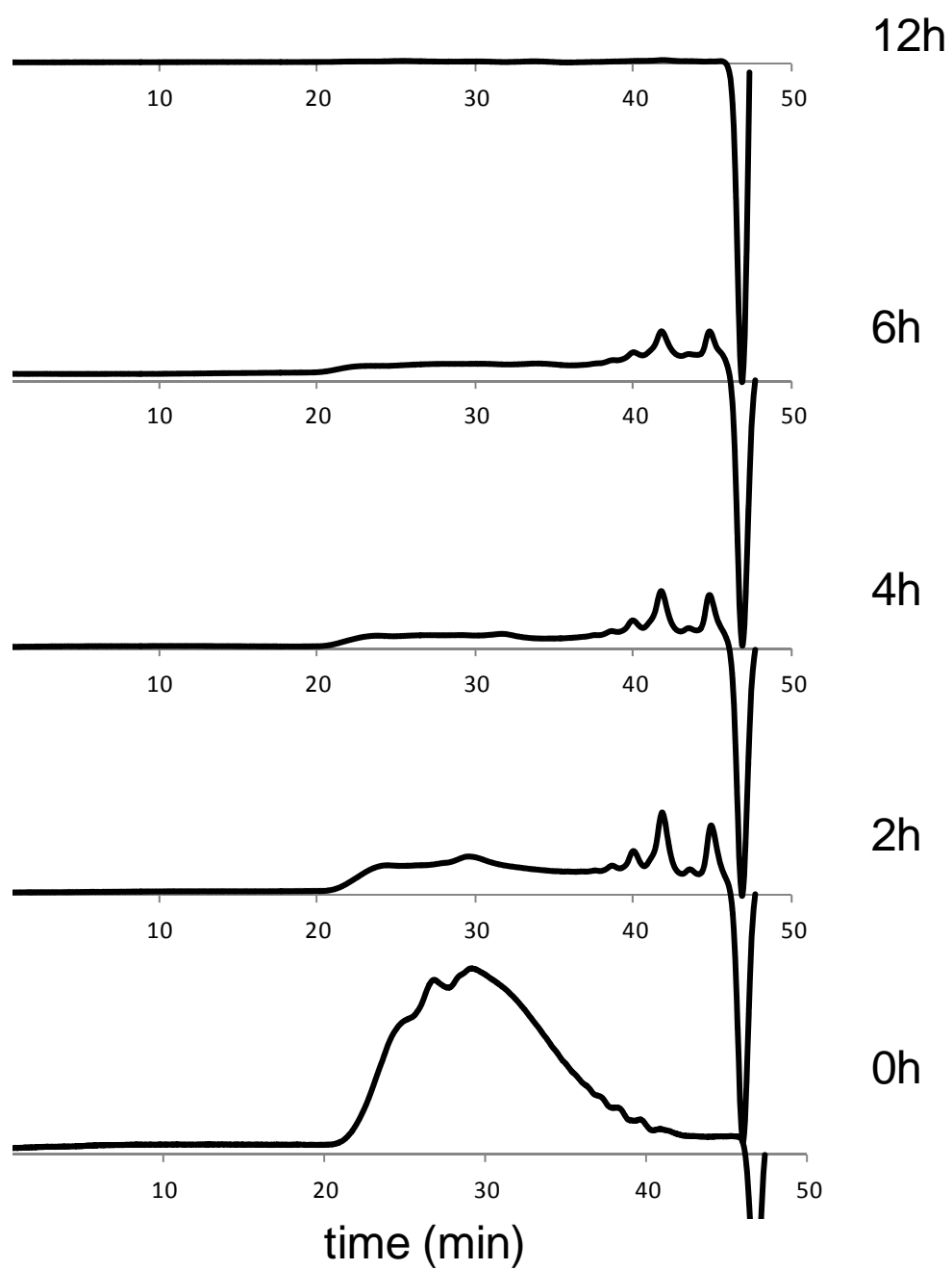


Figure 4-1 Photolysis of PMATA/MDU in low molecular weight: a) H NMR b) RI of GPC

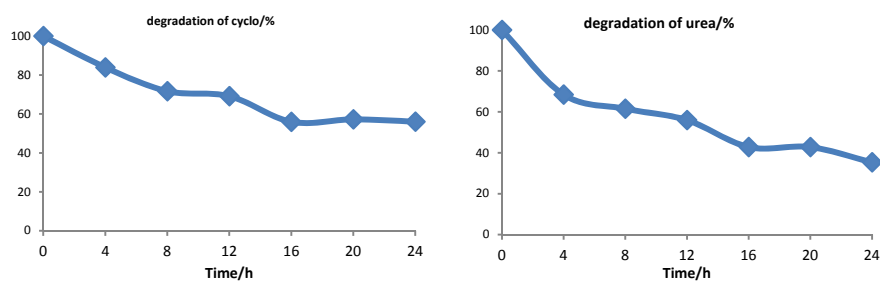


Figure 4-2 Degradation speed of photolysis on PATA/MDU for different functional group: a) cyclobutane b) urea

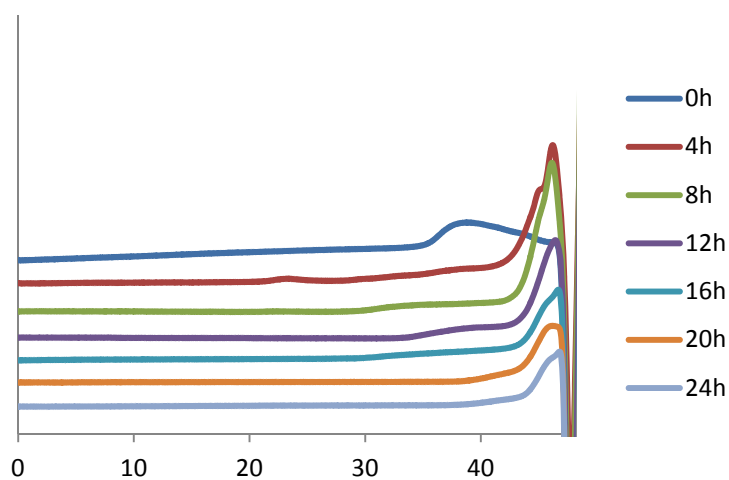


Figure 4-3 ^1H NMR spectra and GPC curves of PATA/MDU degrading by UV irradiation

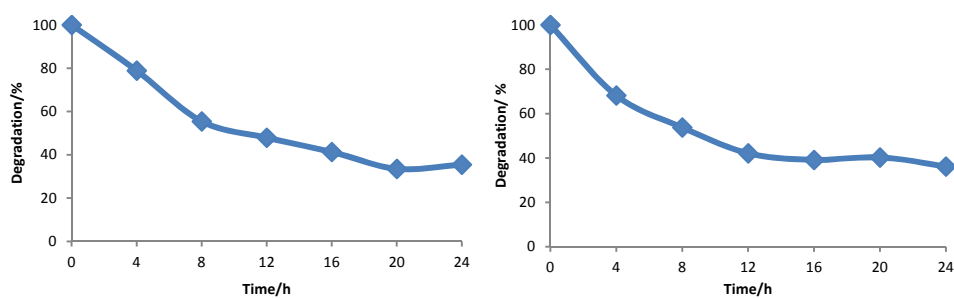
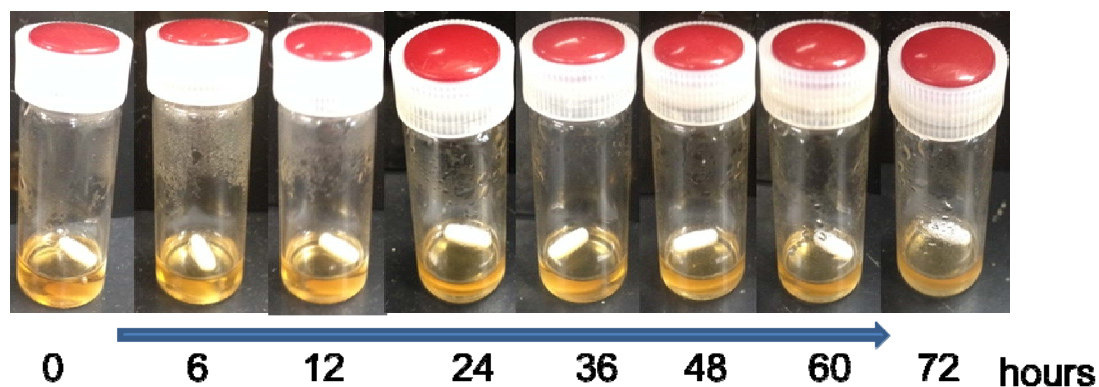


Figure 4-4 Degradation speed of photolysis on PMATA/MDU for different functional group: a) cyclobutane b) urea

4-3-2 Characterizations of hydrolysis reaction

The PATA/MDU was hydrolyzed by NaOH in DMSO solution and the degradation process was checked by ^1H NMR and recorded in photos following the time which showed on Figure 3 and Picture 1. In the NMR spectra it shows in the first 24 hours the polymer quickly broke into the oligomer and in following the oligomer degradation is very slow until 72h the hydrolysis reaction finished. For PATA/MDU the degradation percent of urea was 40% in 24hs and other functional groups like phenyl group and cyclobutane group were not change which meant there was only urea group broken in the hydrolysis. Also for PMATA/MDU in 24hs there was only 20% of urea group degraded. Compared with PATA/MDU degradation, this speed is much slower. From Picture 1 Following the process going, the solution become mucky and for a long time, the precipitate appeared in the sample bottle, meaning the oligomer solubility is a little different from polymer.



Picture 4-1 Hydrolysis process of PATA/MDU

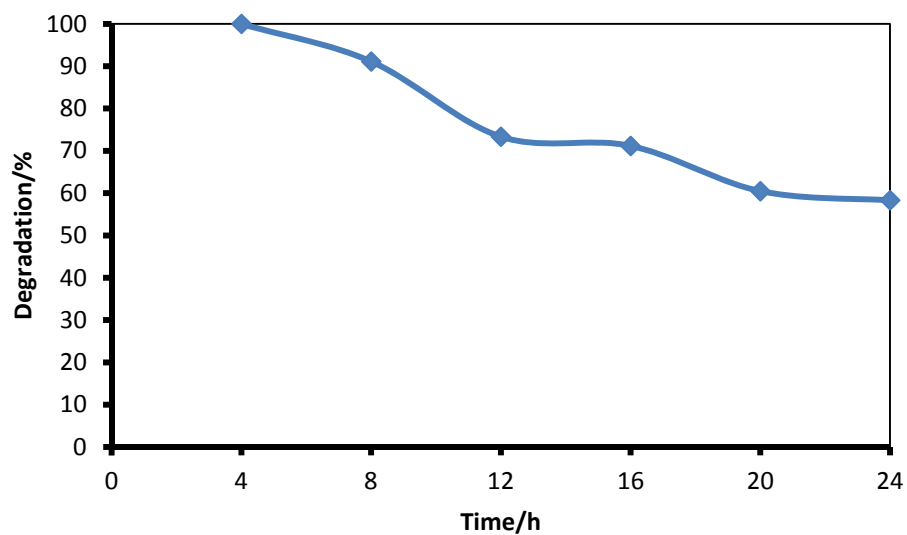


Figure 4-5 Degradation Speed of hydrolysis on PATA/MDU for urea group

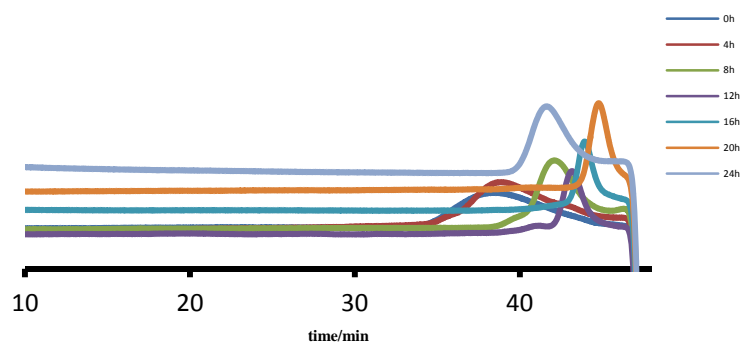


Figure 4-6 GPC curves of PATA/MDU hydrolysis procession

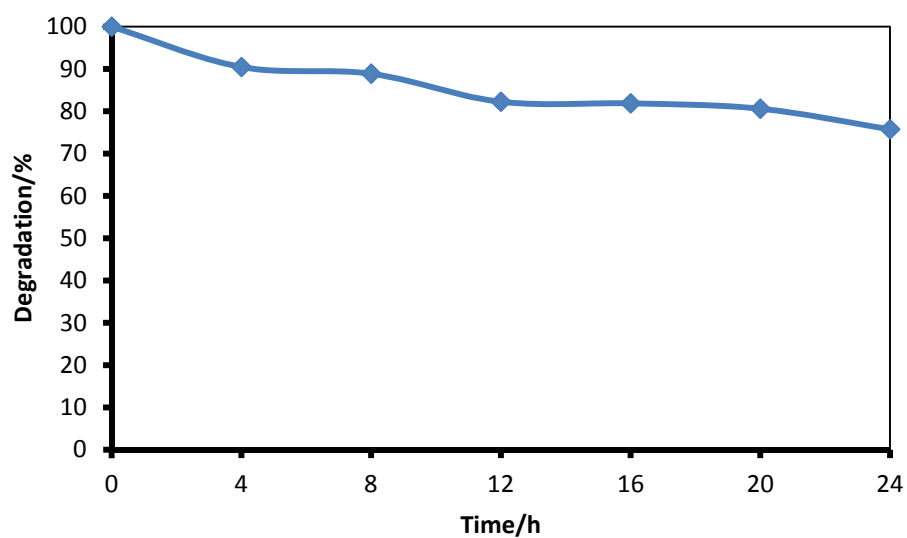


Figure 4-7 Degradation Speed of hydrolysis on PMATA/MDU for urea group

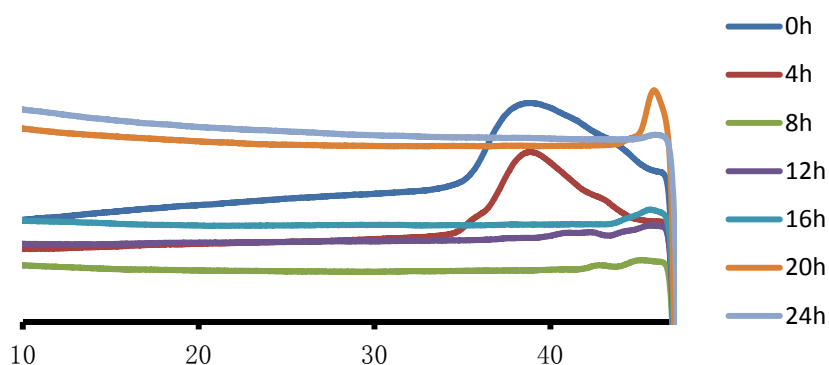


Figure 4-8 ^1H NMR spectra and GPC curves of PMATA/MDU hydrolysis procession

4-3-3 Analyze the biodegradation

For the biodegradation, the microorganism selection was first step and after obtain the single microorganisms colonies, transplanted the microorganisms into the liquid medium tubes with polyureas (Figure 4-8). After 5 days, the bacteria spots can be observed by sight which indicated that the there was no toxicity for the polyureas at least and I evaluated the results by GPC for the insoluble parts and HPLC for the liquid parts (Figure 4-9, 10, 11). On GPC results of both Methyl ester side chain and Carbitol ester side chain, compared with sample 0 which is without the microorganism the peak of polyureas decreased, even disappeared and at the same time the oligomer or dimer's peaks almost kept in all samples. This indicated that the microorganisms can degrade the polyureas with different side chain and the low-molecular polymers are hardly degradable with the same microorganism. Compared the peaks from 23min to 26 min in HPLC results from all samples, it clearly shown that there is no peak on the samples without the microorganisms but on

the other samples with microorganisms there are two peaks appeared. In this case the results meant that there are some water-soluble compounds produced after degradation. In summary of GPC and HPLC results, I confirmed that microorganisms have degraded the polyureas with different side chain and the productions can be water-soluble.

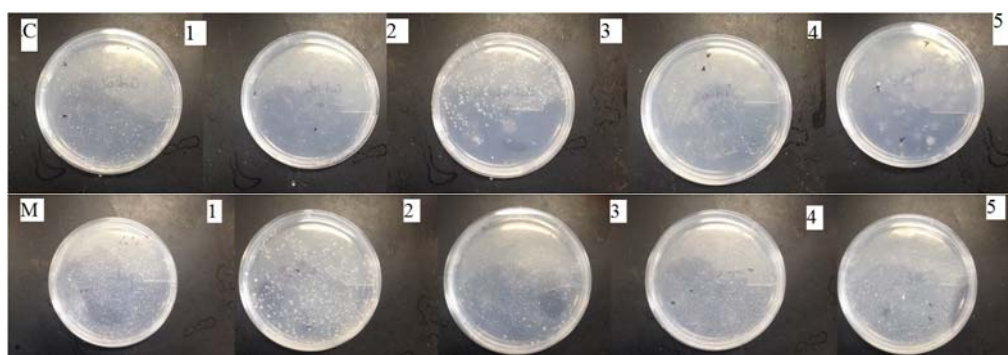


Figure 4-9 The microorganism growth on the polymer surface: C) PCATAMDU, M)

PMATA/MDU

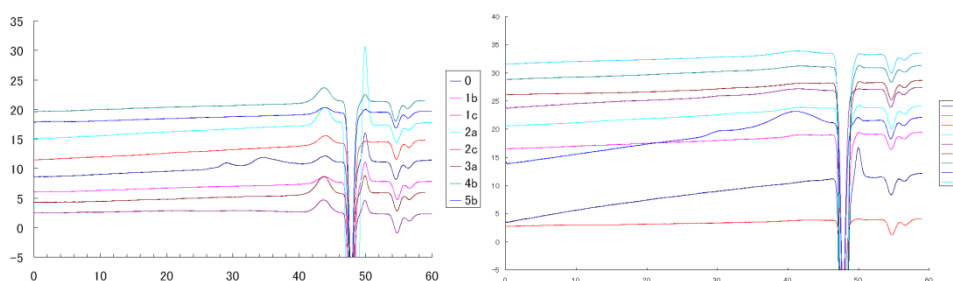
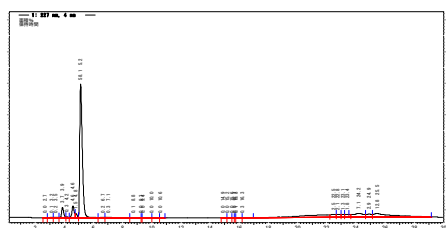
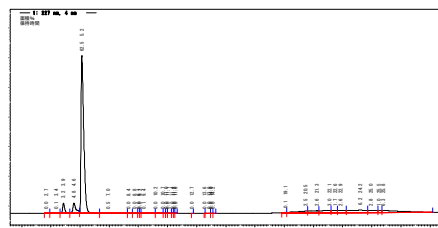


Figure 4-10 The GPC results for the insoluble parts from the degraded production.

a) GPC curves of polyurea with Methyl ester side chain after 5 days under microorganisms. b) GPC curves of polyurea with Carbitol ester side chain after 5 days under microorganisms

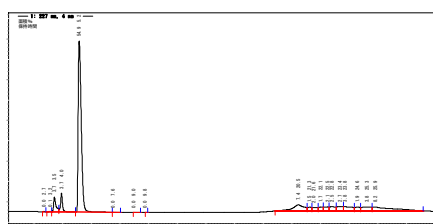


a) PU-COOCarbitol-0: None bacteria

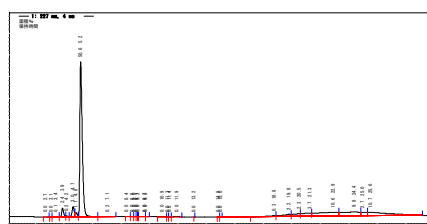


d) PU-COOCarbitol-3a: Bacteria 3-a

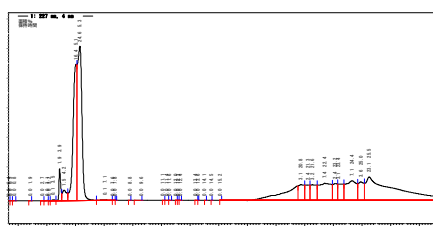
and only include the polymer.



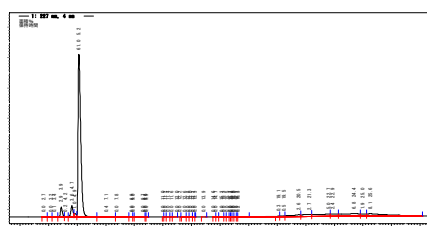
b) PU-COOCarbitol-1a: Bacteria 1-a



e) PU-COOCarbitol-4b: Bacteria 4-b

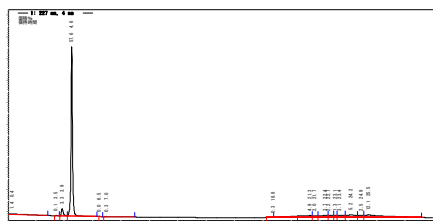


c) PU-COOCarbitol-2b: Bacteria 2-b



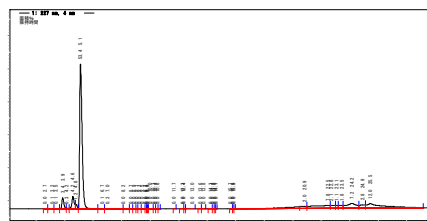
f) PU-COOCarbitol-5a: Bacteria 5-a

Figure 4-11 HPLC results for the polyurea with carbitol ester side chain under different microorganism conditions

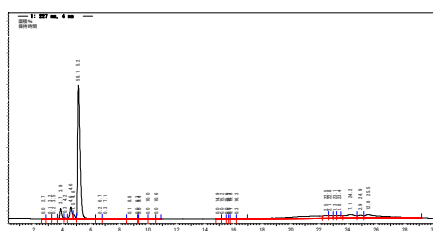


a) PU-COOMe-0: None bacteria and only

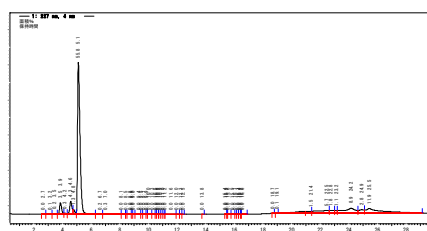
include the polymer.



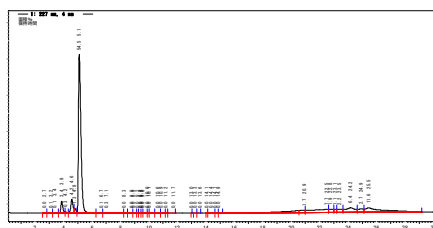
d) PU-COOMe-3a: Bacteria 3-a



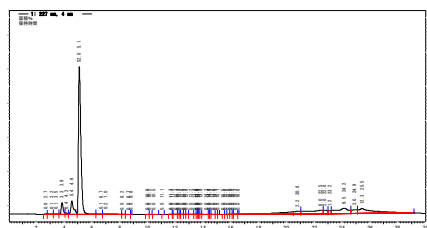
b) PU-COOMe-1b: Bacteria 1b



e) PU-COOMe-4b: Bacteria 4-b



c) PU-COOMe-2a: Bacteria 2-a



f) PU-COOMe-5b: Bacteria 5-b

Figure 4-12 HPLC results for the polyurea with methyl ester side chain under different microorganism conditions

4-4 Conclusion

I tested the photolysis and hydrolysis for the two kinds of polyureas with carboxylic acid and methyl ester as the side chain and characterized the process by ^1H NMR and GPC. For NMR spectra, I calculated the degradation speed of different polyureas under different conditions. Compared all situations by NMR, the degradation of PMATA/MDU under UV is fastest. And from GPC curves, I confirmed that all of the

polyureas can be degraded from polymer to oligomer and after oligomer the degradations became slow.

CHAPTER 5

CONCLUSION REMARKS

Chapter 5

The research in this thesis focused on the syntheses of high performance bio-based polymers including polyamides (PAs) and polyureas (PUs) derived from bio-compound 4-aminocinnamate. The development of these high performance bio-based polymers was crucial to establish sustainable low-carbon society. The important and interesting results throughout this study are summarized as follows.

In **Chapter 2**, bio-based aromatic diamine 4,4'-diamino- α -truxillic acid was successfully prepared as a photodimer of 4-aminocinnamic acid, bioavailable from genetically-manipulated *Escherichia coli*, even though the direct biosynthesis of aromatic diamines has never been reported[109]. Photo-irradiation was a good synthesis method because it can be accurately targeted and highly selective. The single crystal of 4,4'-diamino- α -truxillic acid dihydrochloride was used to confirm the *trans*-stereoisomer product after UV irradiation. It also indicated that 4, 4'-diamino- α -truxillic acid dihydrochloride and 4,4'-diamino- α -truxillic acid methyl ester had high purity because small needles of crystal were able to be prepared. The polyamides was prepared from 4, 4'-diamino- α -truxillic acid methylester and phthalate acids, both bioavailable compounds. The relationship of its molecular structure and properties was clarified. The polyamide showed high thermal stability T_{10} at about 350°C and T_g at about 140°C. Nevertheless, their hydrolyzability were the crucial problems when used as high performance polymer in manufacturing process and the mechanical property

was also a little weak. So I also synthesized high performance bio-based PU which were used in place of the polyamide. The synthesis of PUs was classify and quick. The reaction time only needs 12 hours at 80°C. The PUs showed high molecular weight and good thermal properties. In case fo PUs, they showed ultra high thermal resistance of T_g around 300°C and the solubility of PUs showed improvement because polyureas can dissolve in DMF/water mixed solvent. The molecular weights were high, up to 2.5×10^5 g/mol and T_{d10} and T_s were 270 °C and 180 °C, respectively. The polymer films had strong mechanical properties with a tensile strength 20 MPa and tensile modulus around 1.2 GPa.

In **Chapter 3** based on the carboxylic acid I have successfully modified polymer under the film form by the metal cation. I confirmed the mechanism of the modified film by FT-IR. At the same time I researched the modified film from thermal, mechanical and optical properties. The film adsorbed metal nitrate salts to strengthen the mechanical properties to 43 MPa for tensile strength and 1.8 GPa for tensile modulus. The addition of salt caused a color change to green or yellow, presumably due to nitrate hydrogen bonding with the urea linkage connecting with the benzene ring. Thus, the polyureas prepared here were reinforced by the combined effects of the metal cations and nitrate anions of added salts.

Not only thermal and mechanical properties, but also degradations of PUs were studied in **Chapter 4**. Because there are functional group, cyclobutane, existed, it become possible that the degradation products completely broke into small molecular. For the degradation, the photolysis speed was fast, only 28-32hs and hydrolysis speed

was slow, 7 days, and the products include the diamino which could be the renewable compound for methyl diphenyl isocyanate and from the photolysis the products also had the cinnamon compound.

The development of high-performance PUs generally showed excellent degradation process by UV and hydrolysis. The products could be the renewable sources for the polymers, which was useful to establish sustainable green society. They could be reduced the serious problems of plastic waste and petroleum source.

Achievement

Conferences

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