Title	バイオベースポリウレアの合成とその実現
Author(s)	熊倉，拓哉
Citation	
Issue Date	2023-03
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/18433
Rights	
Description	Supervisor: 金子 達雄，先端科学技術研究科，博士

Doctoral Dissertation

Syntheses and Materialization of Bio-based Polyureas

Takuya KUMAKURA

Supervisor: Tatsuo Kaneko
Graduate School of Advanced Science and Technology
Japan Advanced Institute of Science and Technology
Materials Science

March 2023

Abstract

Due to the limited availability of products derived from oil fields and petroleum, biobased materials are essential for building a low-carbon society. Researchers are trying to reduce the consumption of non-renewable resources produced by synthetics by utilizing alternative materials such as natural biopolymers. The relationship between polymer structure and physical properties is critical in materials design. Engineering plastics from biomolecules are well suited for such materials in terms of available volume and cost. Development of such high-performance and high-performance biobased polymers is very important for building a sustainable low-carbon society.

In this paper, we focus our research on the synthesis of high-performance polyureas from bio-based furan, aromatic, and heterocyclic compounds. The development of such high-performance biobased polymers is essential for the realization of a sustainable low-carbon society. Important and interesting results obtained through this research are summarized in the following parts.

In Chapter 2, syntheses of polyureas with furan as the main chain using AMF and the addition of sol-gel transition, self-healing, and cross-healing functionalities via the Diels-Alder (DA) reaction. Bio-based polyureas with furan rings in the main chain were synthesized from 2,5-bis(aminomethyl)furan in DMAc and various diisocyanate compounds via a one-step solution polymerization route. The physical properties of the polyurea samples were determined by H-nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy. Thermophysical properties of polyurea samples have been investigated by differential scanning calorimetry and thermogravimetric analysis. A reversible DA reaction between furan and maleimide was used to successfully crosslink furan polyurea and bismaleimide. The polyurea gel exhibited repair properties based on dynamic bond recovery and was found to adhere to the fracture site at 60°C. Reversible sol-gel transition based on DA reaction provided temperature-responsive gels.

In Chapter 3, aromatic diamine 2-(4-aminophenyl) ethylamine (4APEA) was produced by fermentation using genetically engineered Escherichia coli and its condition optimization was evaluated. The fermented 4APEA was purified from the medium and polymerized with methylene diphenyl diisocyanate and hexamethylene diisocyanate to produce polyureas. 10% weight loss temperature (T_{d10}) results were above 276°C, respectively, which is comparable to other heat-resistant aromatic temperatures of other thermostable aromatic polyureas. This study is the first to synthesize polyureas from microbial aromatic diamines. Their excellent thermal stability will be useful in the industrial production of heat-resistant polymeric materials.

Chapter 4 presents the synthesis of functional polymers that promote degradability by imparting photo-induced hydrophilicity to biobased polyureas. Itaconic acid, which can be produced from biological sources, is used to synthesize diamine oligomers. We will then synthesize various polyureas by reacting them with typical diisocyanates and compare them with biogenic polyureas we have prepared so far and evaluate the structure-property relationship. The preliminary review will introduce the synthesis of new itaconic acid-derived polyurea and the evaluation of its thermosphysical and photo responsiveness properties.

As conclusions, the development of biologically derived polyureas showed good thermal and mechanical performance. The introduction of a furan ring into the main chain was accompanied by thermo-reversible reactions, enabling self-healing properties and controlled sol-gel transition. These polyurea materials are not only expected to be applied to temperature-responsive actuators, self-healing agents, and heat-resistant coatings, but also to help build a sustainable green society.

Keywords：bio-based monomer, polyurea, aromatics, self-healing, stimulus responsiveness

Acknowledgements

I, the author of this dissertation, would like to express my deepest gratitude to my respected supervisor Professor Tatsuo Kaneko for his valuable guidance, supervision, encouragement, and support during my study in Japan Advanced Institute of Science and Technology (JAIST).

I would like to extend my appreciation to my thesis committee: my second supervisor *Professor Toshiaki Taniike, Professor Kazuaki Matsumura, Professor Masayuki Yamaguchi* at JAIST, *Associate Professor Ryohei Ishige* from Tokyo Institute of Technology, and I would like to thank Professor Naoki Takaya from Tsukuba University for allowing me to cite his paper.

I am very grateful to my advisor for minor research *Visiting Professor Yoshitake Iyoku* and *Visiting Professor Hiroyuki Shinbo.*

Assistant Professor Kenji Takada, and *Dr. Maiko Okajima* for their excellent guidance and kind encouragement at professional and personal level. This work would never have performed without their great supporting.

Finally, I would like to give his sincere thanks to my family and members of Kaneko laboratory for their supporting.

March 2023

Takuya KUMAKURA

Contents

Chapter 1

General Introduction

1-1 Background of plastic and environment problem

In the modern era, plastics and other polymeric materials are found in a wide variety of consumer goods, including money, instant adhesives, furniture, transportation materials, aircraft, and spacecraft. Among them, the factors that contribute to the popularity of plastics are their processability, relative low cost, availability of raw materials, heat and chemical resistance. Thus, they are widely used in society in various forms and have become an essential part of people's lives. Depending on their composition and application, petroleum-based plastics can be either disposable or highly durable materials. The first man-made plastic material was celluloid, invented by Thomas Hancock in 1851 [1]. Also, in the mid-1800, the development of synthetic polymers gained momentum after American scientist Charles Goodyear accidentally discovered vulcanized rubber [2]–[7] Bakelite [8]–[10](discovered by Leo Bakeland in 1907), neoprene [11] (discovered by A. Nieuwland and Arnold Collins in the early 1900), nylon [12]–[14] (discovered by Wallace Carothers and his chemistry team in the early 1930), polyvinyl chloride[15]–[18] (discovered by Eugen Baum), and polystyrene [19], [20] (discovered by Eduard Simon), among others, were to open up the future of polymers. At the end of 1945, petrochemical-based polymers replaced metal materials, ceramic materials, wood, and mankind entered the era of plastics[21]; since 1989, the production of plastics has overtaken that of steel, with about 322 million tons of plastic produced in 2015[22]. Furthermore, as technology advances, applications of polymeric materials are moving beyond the realm of glass and metals, and into new fields with new functions that have never been seen before, and it is expected that demand will continue to grow and functionality will continue to improve. However, most of them are made from fossil fuel resources such as petroleum, which accounts for more than 99% [23]. However, the petroleum-based plastics manufacturing process has been criticized for causing serious environmental problems globally, such as waste problems, air pollution, and resource problems. [24], [25]

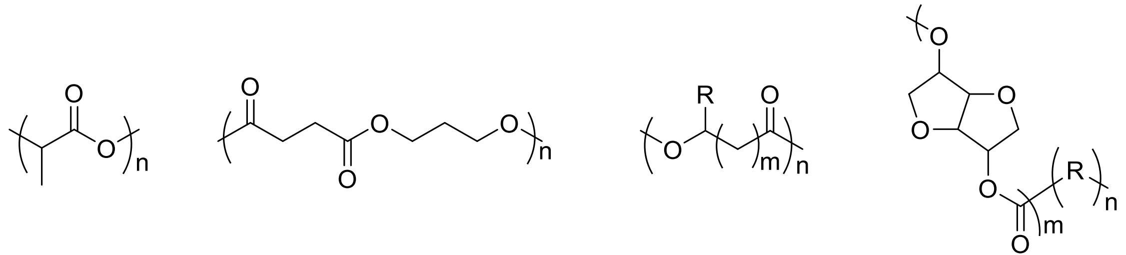
Various initiatives are underway to address these problems. Recycling of plastic products and energy recovery are among the preferred options to achieve a sustainable society[26][27][28]. In view of global environmental problems, resource depletion, and consequent price increases, there is a need for biobased polymers that do not depend on fossil fuel resources, whose reserves are finite, but are made from renewable resources such as plants and bacteria [29][30].

1-2 Bio-based polymer

Biobased polymers make an important contribution to the natural environment by providing a renewable manufactured alternative to the use of fossil fuel-based chemicals[31]. One of the key elements to be achieved by biobased polymers is the concept of carbon neutrality. This advocates the use of materials derived from plants and microorganisms as raw materials for plastics to reduce carbon dioxide in the atmosphere, since carbon dioxide-derived carbon can be immobilized in the materials. Furthermore, the extended durability of biobased plastics is expected to play a role in carbon storage in the form of plastics. Therefore, the development and commercial[32]ization of biobased polymers and the expansion of their applications are very important issues for the realization of a low-carbon and sustainable society. Furthermore, the Sustainable Development Goals (SDGs) were adopted by all member states of the United Nations in 2015 for a sustainable society in the future. One effective approach to achieve these goals is the production of biobased polymers, produced from biomass resources such as plants, animals, and microbial metabolic materials [33], [34]. Bio-based polymers include polymers produced by microbial fermentation and polymers synthetically produced from bio-based monomers. Numerous studies have been conducted on these polymers [35]–[40], and in recent years, the development of biobased polymeric materials has attracted interest from researchers in the field of polymer chemistry and industry.

In particular, infrastructure materials such as heat-resistant materials and insulating materials for electrical appliances, automotive parts, and power cables are promising applications for carbon neutrality. Currently, commercially available biobased polymers include polylactic acid[7][41], poly(butylene succinate) [42], poly(hydroxyalkanoate) [43], and polycarbonate (DURABIO™ [44]) (Figure 1). In order to further expand the practical use and applications of biobased polymers, the development of biobased polymers with superior material properties and functionality is desired.

The control of physicochemical properties and molecular design are required to expand the application of biobased polymers in various fields. In the case of naturally occurring biobased polymers and their derivatives, the fundamental chemical structure of these materials cannot be significantly modified. Therefore, they have limitations in controlling their properties. Synthetic biobased polymers, on the other hand, have the advantage of being able to design their molecular structure on a monomer-by-monomer basis, indicating the ability to tailor polymer materials with desired properties.



Poly(lactic acid) Poly(butylene succinate) Poly(hydroxyalkanoates) Polycarbonate

Figure 1-1. Structures of commercialized bio-based polymers.

With the growing interest in biobased polymers, researchers are focusing not only on polymer synthesis but also on the synthesis of monomers derived from biomass resources to develop novel biobased polymers. In the last years, biobased aromatic monomers such as polybenzimidazole and polyimides have been developed [45] [46]. These polymers exhibit superior properties compared with common high-performance polymers derived from petroleum resources, of which the diversity of structural variations is a member. Therefore, the development of novel and useful biobased polymers and their derivatives/precursors are an important issue for decarbonized and carbon neutral society in the future.

1-3 Introduction of biomass monomer

Biobased monomers are a vital molecule in the synthesis of biobased polymers. In this study, we focused on these biobased monomers. The biobased monomers used in this study are as follows.

1-3-1 Furan

Various natural and biogenic monomers such as vegetable oils, sugars, and woody biomass have been investigated to construct biorefineries. Among them, 5-hydroxymethylfurfural (HMF) has been reported to be a valuable biomass resource because it can be produced from woody biomass and other plant sources such as cellulose, glucose, and inulin [47]–[49], HMF is said to be a potentially valuable monomer because it can be converted into various products such as biofuels, pharmaceutical intermediates, and functional chemicals [50]–[53]. It is said to be a potentially valuable monomer because it can be converted into various manufactured products such as biofuels, pharmaceutical intermediates, and functional chemicals.

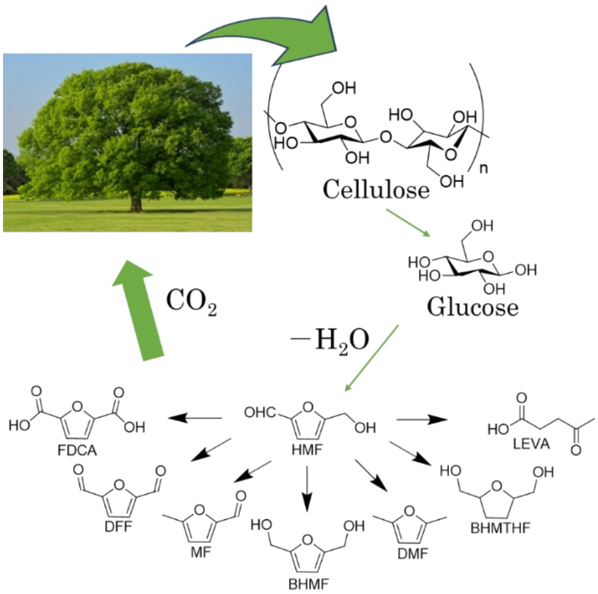


Figure 1-2. Furan monomer structures from biomass.

Another advantage is that it can be introduced into the polymer chain, which is reported to provide performance and functionality derived from the furan structure. As an example, furandicarboxylic acid, an oxidation product of HMF, can be polycondensed with diol as an alternative to terephthalic acid to obtain polyethylene furanoate (PEF) [53]. PEF has properties comparable to polyethylene terephthalate (PET) and thermomechanical properties such as glass transition temperature (T_g) and yield stress superior to those of PET[54]. In addition, gas barrier properties have been added, and it has been confirmed that it exhibits superior physical properties and new properties to petroleum-derived plastics[55]. For this reason, it is being considered as an alternative biomass plastic to PET bottles.

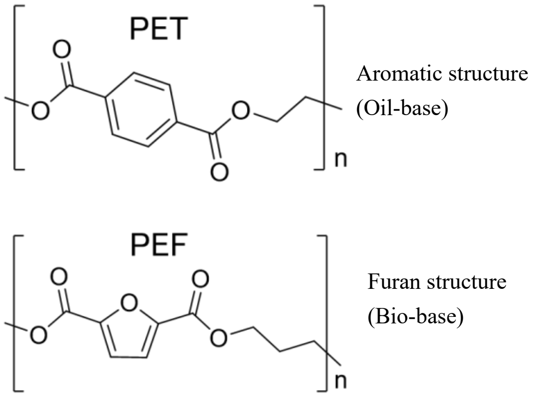


Figure 1-3. Molecular structures and mechanical properties of structure differences of PET and PEF [53]

Table 1-1. Thermal and mechanical properties of PET and PEF [54]

	Thermal properties (°C)		Mechanical properties
	T_m	T_g	σ_ε (Gpa)
PET	250-270	76	50-60
PEF	210-230	88	90-100

T_m refers to melting temperature. T_g refers to glass transition temperature. σ_ε refers toYield stress.

Among diamines, monomers with aromatic group are used as raw materials for engineering plastics with excellent physical properties such as polyamide and polyimide. However, it is difficult to obtain aromatic diamines directly from plants and microorganisms because of their high toxicity to living organisms [56]. Therefore, efforts have been made to develop a method to obtain biogenic aromatic diamines by chemically modifying biogenic substances.

In addition, most of the furan-containing polymers mentioned above are derived from dicarboxylic acids or diols, which tend to reduce the heat resistance of the produced polymers. In order to expand the application of furan-containing polymers, there is a need for furan diamine monomers that can be polymerized into a variety of high-performance polymers, and studies and research are currently underway to develop such monomers. In the past, there have been few examples of synthesis of nitrogen-containing furan polymers due to the difficulty of derivation from HMF to diamine, and there have been few studies on the reactivity of the nitrogen-containing furan polymers. However, with the development of catalytic chemistry, it has become possible to produce furans with diamines.

2,5-bis(aminomethyl)furan (AMF) [49], [57], [58] is a diamine monomer that can be synthesized by oxidative and reductive amination using microbial HMF as a catalyst. It is thought that the polymers polymerized from AMF can be given thermoresponsive properties and consequent reparability while retaining the excellent physical properties of furan-derived polymers. In addition, since there are few examples of synthesis of polymers based on sequential polymerization using furan diamine as a raw material and chemical modification of the furan ring in the main chain, we believe that this approach is feasible. Figure 1-4 shows that, unlike furan dicarboxylic acid, AMF has a methylene next to the furan ring, which is expected to give flexibility to the resulting polymers.

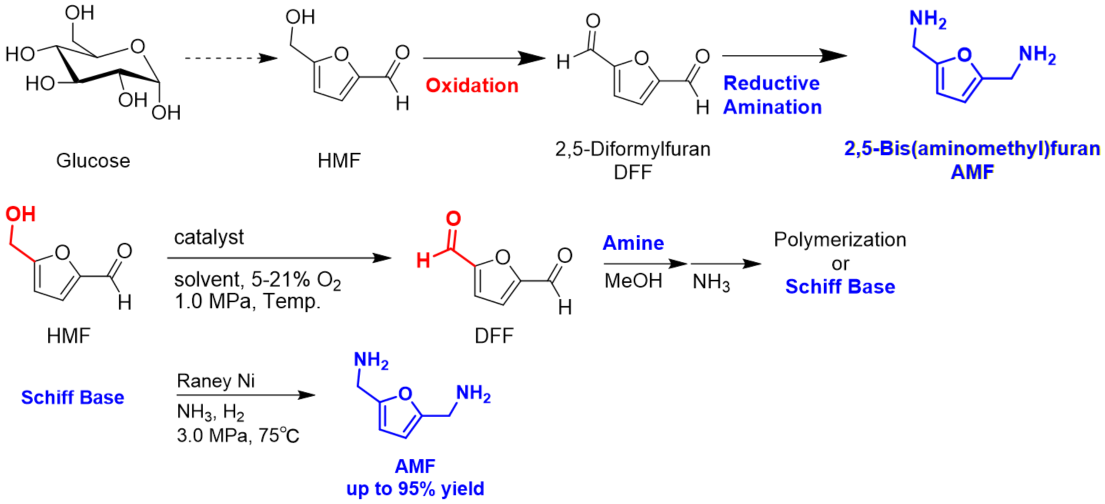


Figure 1-4. Synthesis of AMF from HMF: Oxidation and Reductive Amination.

1-3-2 Aminophenylaranine

4-Amino-L-phenylalanine (4APhe) is an amino derivative of the amino acid phenylalanine. It is produced by bacteria as an intermediate for antibiotics [59] or by fermentation of glucose or biomass [60]. Recently, a method has been established to produce it more efficiently from sugar metabolism in genetically engineered *Escherichia coli* [61][62]. L-phenylalanine (Phe) is biologically converted to L-tyrosine, which is further converted to L-DOPA, which in turn is converted to dopamine, norepinephrine (noradrenaline) and epinephrine (adrenaline). The latter three are called catecholamines; Phe is a natural substance found in mammalian breast milk, used in the manufacture of foods and beverages and in dietary supplements, and has other analgesic and antidepressant properties. It is also a direct precursor to the neuromodulator phenylethylamine. 4APhe can also be produced chemically by nitrating phenylalanine and reducing it to introduce an amine group. It can be produced chemically from phenylalanine by first nitration with nitric/sulfuric acid followed by reduction with Pd/C. Thus, the production of 4APhe is a well-established method [63] (Figure 1-5).

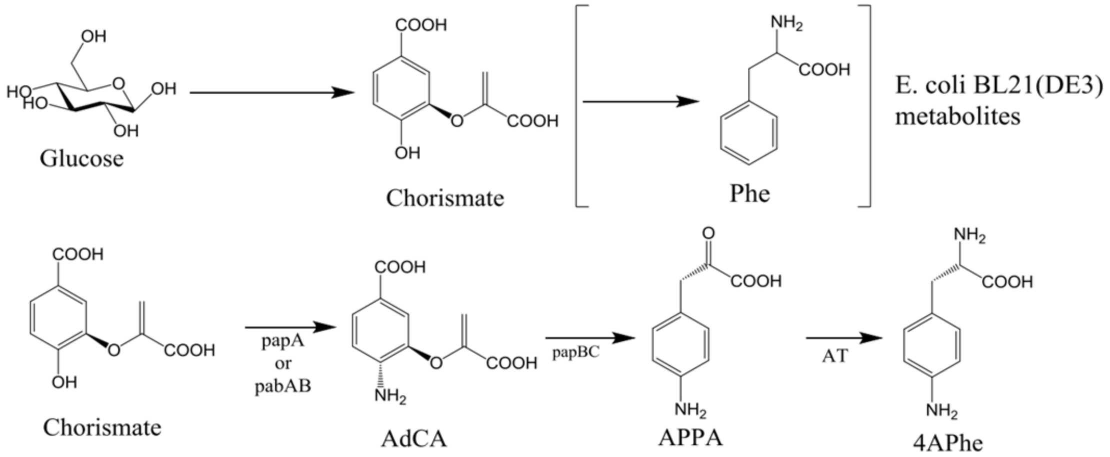


Figure 1-5 Biosynthetic pathway to produce 4-APhe using *E. coli.*

4APhe is an attractive starting material for realizing new biobased monomers because of its three modification points: carboxylic acid, aromatic amine, and alpha-carbon amine. It is also possible to synthesize diamine monomers from it, which can be derived to 2-(4-aminophenyl) ethylamine (4APEA) with one aliphatic and one aromatic amine residue (Figure 1-6). This diamine can be used to obtain high-performance polymer materials [61].

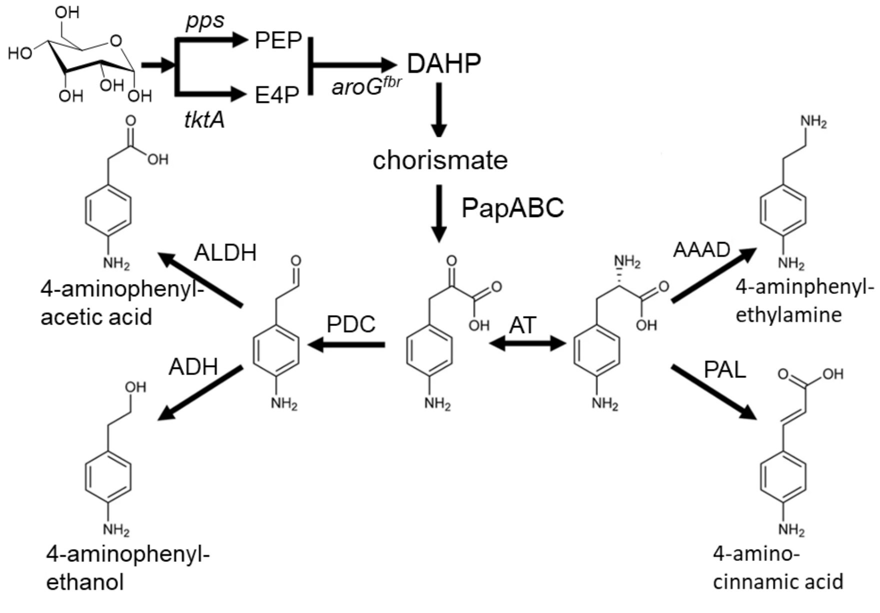


Figure 1-6 Artificial pathway to produce aromatic amines [61]. (AAAD, aromatic amino acid

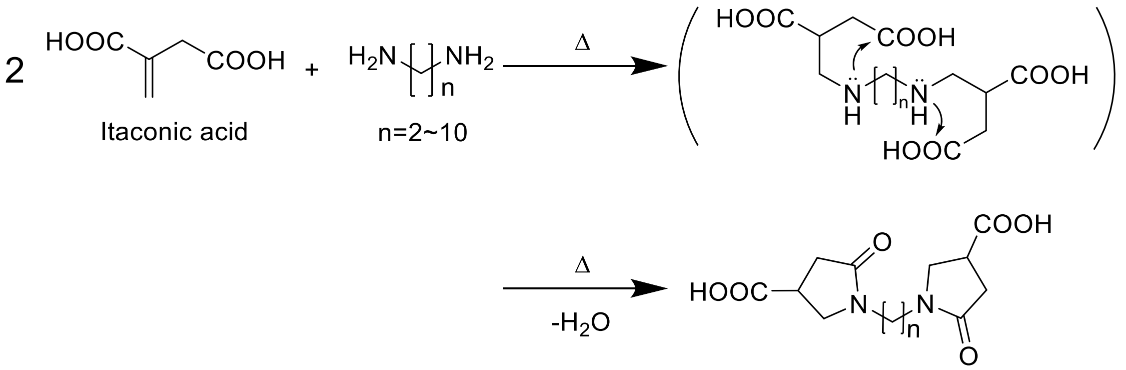
decarboxylase; ADH, aldehyde dehydrogenase; ALDH, alcohol dehydrogenase; AT, aminotransferase; PAL, phenylalanine ammonia lyase; PapA, 4-amino-4-deoxychorismate synthase; PapB, 4-amino-4-deoxychorismate mutase; PapC, 4-amino-4-deoxyprephenate dehydrogenase; PDC, phenylpyruvate decarboxylase. Host cell genes encoded aroG4fbr, feedback resistant isozyme of DAHP synthase; pps, PEP synthase; tktA, transketolase.)

1-3-3 Itaconic acid

Itaconic acid (IA) is a diacid bio-monomer derived from hexose [64]–[68]. Not only can it be used as a dicarboxylic acid monomer, but it also contains a highly reactive vinylidene group [69]. Therefore, itaconic acid can be used as an interesting renewable building block for a variety of applications. Thus, it can be easily incorporated into polymers and could replace the petrochemicals acrylic acid and methacrylic acid. It is also used in the manufacture of synthetic fibers, as a coating, adhesive, and thickener. The production process preferentially employs fermentation of carbohydrates by fungi, and the current market size is about 30,000 tons per year. New biotechnological approaches such as immobilization techniques, screening programs, and genetic engineering may lead to higher productivity [70] IA is also recognized as one of the highest value-added chemicals, derived from carbohydrate biomass [71].

Originally, itaconic acid is a compound obtained by the thermal decomposition of citric acid, but now a method has been established to produce it by fermentation of Aspergillus terreus, and it is already produced in large quantities in Japan and abroad. The substance is produced at a lower cost by fermentation than by petrochemical production methods. This molecule is one of the compounds that have attracted attention in the field of biorefineries, and recently, the U.S. Department of Energy (DOE) proposed 19 key substances for biorefineries (sorbitol, 2,5-furan dicarboxylic acid, glycerol, levulinic acid etc.). Vinyl polymers with itaconic acid as part of the raw material have been known for a long time, and its usefulness as a polymer raw material is widely recognized [72].

Previous studies have reported that in IA, primary amines react with vinyl groups in an azamichael addition-condensation sequence to form imines, which then dehydration-condense with carboxylic acids far from the double bond to form pyrrolidone rings (five-membered rings). It is also possible that the imine reacts with the carboxylic acid located nearby, but the probability of this reaction is extremely low because of the instability of the four-membered ring that is formed. If diamines are used in this reaction, N-substituted nylons can be obtained and heterocycles can be introduced into the main frame (Scheme 1-1) [73]–[75]. Polycondensation of these dicarboxylic acids with various diamines yields polyamides with controlled size alkylidene spacers. The resulting amphiphilic polycondensates are suggested to exhibit a tunable hydrophilic-hydrophobic balance.



Scheme 1-1 Cyclization reaction of pyrrolidone ring formed by heating the itaconic acid and diamine.

1-3-4 Hexamethylenediamine

Hexamethylenediamine (HMDA) is one of the key intermediates in the preparation of nylon 66 by polycondensation with adipic acid. Currently, the well-known commercial production of HMDA is through hydrocyanation of butadiene and adiponitrile from adipic acid. However, they are derived from petroleum and have toxicity risks. Therefore, it is highly desirable to consider greener alternatives that achieve HMDA in fewer steps. Two examples are the production of HMDA from starch derived from corn and potatoes or 5-hydroxymethylamine. Major methods include synthesis of sugar-derived

HMF as derivatives or microbial fermentation [76] Since HMF is readily available from carbohydrates by catalytic dehydration reactions, we will explore its potential as a building block for the production of bio-HMDA. For this purpose, comparative studies on economics and LCA have been reported for three biobased routes starting from fructose (high fructose syrup, HFS) [77]. starting from fructose (HFS) for HMF production, intermediates produced directly from HMF (There are three potential biobased routes, including DFF, THFDM, and AM-THF [78]–[81].

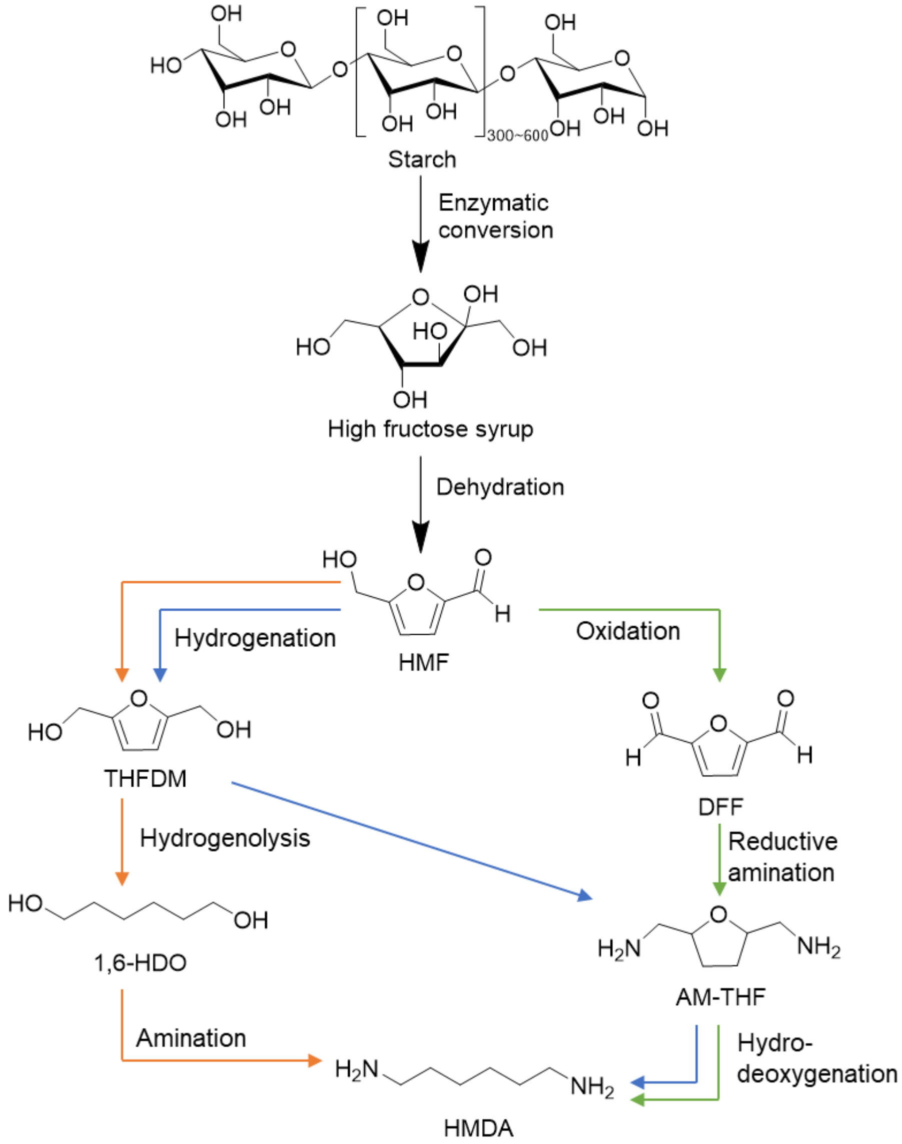


Figure 1-7 Potential routes towards bio-HMDA using platform molecules issued from biomass[77].

1-3-5 Diisocyanates

Diisocyanate compounds have also been developed from biomass sources. Representative biobased diisocyanates include lysine diisocyanate (LDI) and lysine triisocyanate (LTI) [82][83], dimer diisocyanate (DDI), 1,5-pentamethylene diisocyanate (PDI) [84][85]and other long chain aliphatic diisocyanates [86]–[88]. All are produced from vegetable oils and amino acids. Methylenediphenyldiisocyanate (MDI) is also prepared from renewable aniline [89]. A genetically engineered strain of *Corynebacterium Glutamicum* fermentation produces sugar and ammonia to aminobenzoic acid The ammonia is then heated and decarboxylated. Biobased aniline is then obtained by heating and decarboxylation. Alternatively, phenol can be produced from renewable benzene, which can be converted to aniline by reaction with ammonia. Benzene feedstock with 100% renewable carbon can be used to produce aniline with 100% renewable carbon content. Therefore, it is considered effective against carbon neutrality.

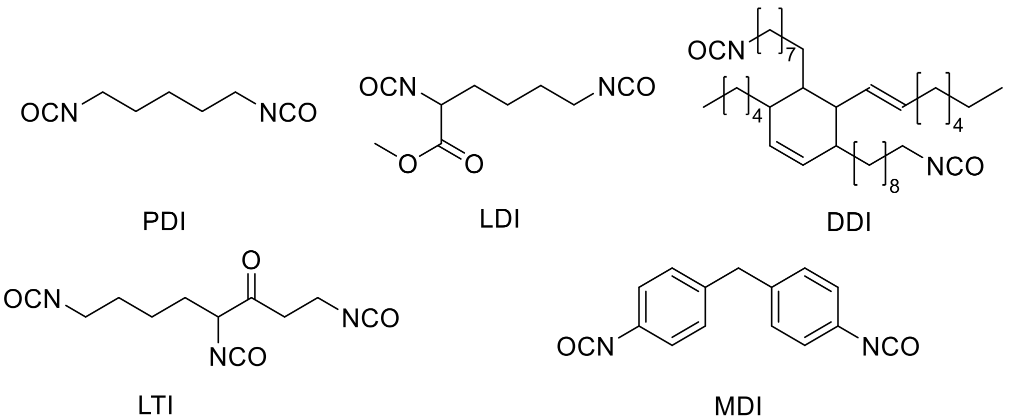


Figure 1-8 The chemical structure of Di/Triisocyanates

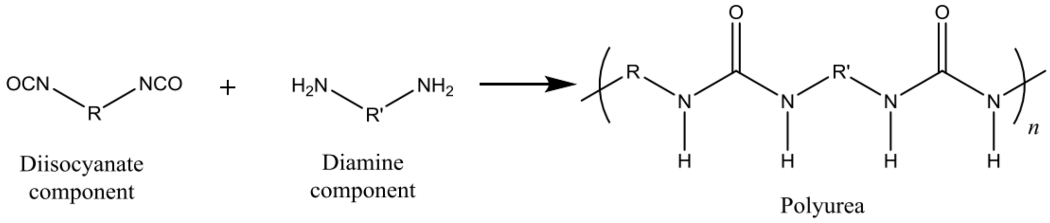
1-4 High performance polymers

High-performance polymers are a group of polymer materials known for their ability to maintain their mechanical, thermal, and chemical properties under extreme conditions such as high temperatures, high pressures, and corrosive chemicals. For example, they have excellent mechanical strength, heat resistance, high electrical conductivity, low specific gravity, high electrical, flame resistance, and acoustic insulation[90] [91]. The important factors contributing to the high performance of these polymers include resonance stabilization, primary bond strength, molecular symmetry, secondary bond strength, molecular weight/molecular weight distribution, rigid inter-chain structure, and cross-linking. In addition, additives or reinforcing agents (fillers, clays, nanoparticles) can impart high-performance properties beyond those of commodity plastics [92][93]. Such materials are variously defined by their applications and have been applied in fields ranging from telecommunications to medical, aerospace, transportation, energy electronics, automotive, and other areas that are more challenging than those of conventional polymers [94].

The demand for these high-performance polymers is steadily increasing in industrial society, as they are used as metal substitutes due to their excellent performance characteristics. Although some applications do not require high temperatures, the manufacturing process leading to parts and components requires that polymeric materials be thermally stable. Various categories of high-performance polymers include poly(phenylene ether), polysulfone, poly(aryl ether ketone), polyoxadiazole, and polyimide. Here we focus on one type of high-performance polymer, polyurea.

1-5 Polyurea

Polyurea (PU) is a thermosetting resin with a urea bond (-NH-CO-NH-) and is synthesized by a polyaddition reaction with diisocyanate and diamine. PU has high transparency due to the absence of charge bias. It is also known to have strength and flexibility derived from bidentate hydrogen bonding interactions and C-N bonds [95] (Scheme 2). PU is a very useful material, and its physical and chemical properties allow it to be used in a wide range of applications. Advantages of PUs include weather resistance (resistance to temperature and water), excellent tensile strength, tear strength, elongation at break, high heat resistance, pigment compatibility, formulation stability, ease of compositing, fast curing, chemical resistance, hydrolytic stability, and low flammability. In addition, they have multiple applications in many fields due to their excellent adhesion to all types of surfaces, especially metals [96]–[101]. It also shows sufficient reactivity without catalysts and produces no by-products, making it very clean as a green chemistry. It is mainly used in industrial coatings such as linings and is one of the most successful materials in the coatings industry [102][103]. Many methods are used to prepare PUs, but as indicated above, the rapid polyaddition reaction of two diamines and diisocyanates is the most common method. Polyurea with urea bonds can be rapidly prepared by simply mixing these two commercial components. In addition, the reaction of isocyanate with water can also form polyurea via a carbamic acid intermediate. This acid decomposes to amine and carbon dioxide. The amine further reacts with another isocyanate group to form urea bonds.



Scheme 1-2 Synthesize of polyurea using two main components.

Some PUs have been reported to be very tough coating materials, with tensile strengths reaching 40 MPa and elongations exceeding 500 % [104]. PU coatings have been a boon to the shipping industry because they last 25 to 30 years, unlike asphalt coatings, which last 3 to 4 years. In addition to its use as a coating material, the copolymer of PU and polyurethane has been used in the development of Spandex™. Initially used as a slim suit and body shaper, a fiber material has been used in a variety of products known for its excellent elasticity and durability equivalent to natural rubber [105]. Other applications include microencapsulation of PU. Microencapsulation has been used in a variety of fields, including agriculture, cosmetics, pharmaceuticals, food, textiles, printing, and protective and smart coatings [106][107]. In addition, thermoplastic segmented PU elastomers are

(AB)n block copolymers with alternating soft and hard segments. Generally, segmented PUs are obtained by reacting a mixture of diamines and isocyanates in reaction injection molding. This allows for rapid reactions and can also be applied to develop copolymers such as polyurethane-urea and polyamide-urea [108]–[112].

However, conventional PU can withstand temperatures up to about 150 ℃, but thermally degrades at temperatures above 200 ℃ [113][114]. This limits its use as an engineering material. Numerous studies have been conducted to improve the thermal stability of PU by introducing rigid structures, blending or copolymerization with polymers with higher thermal stability, and so on [114][115]. In addition, these PUs are prepared from petroleum-derived chemicals, and there is a need to substitute biologically derived raw materials. With growing environmental awareness, PUs are an effective and economical choice for businesses and industrial society in need of coating, elastomers, films and structural materials. For example, material improvements and condition studies on hardness, curing time, durability, aging resistance, etc. are conducted daily. Furthermore, dispensing equipment and spray tip technology are progressing more rapidly than ever to meet the demand for more efficient means of spraying PU in place. The number of papers published on the subject of bio-based PUs is small, and the number of pure PUs, excluding copolymers with polyurethanes, is negligible (718 results from Google Scholar). Therefore, there is room for scientific research on the subject of bio-based PUs.

1-6 Aim and scope of this study

This thesis aims to develop high-performance functional materials from renewable resources for the realization of a sustainable society. The main objective is to synthesize and characterize new high-performance and high-performance PUs from biogenic monomers. To achieve these goals, a detailed understanding of the chemistry and functionality of various monomers is necessary. Important polymer properties such as functionality, thermophysical properties, and structure can now be investigated and polymer structures can be designed. Therefore, my research attempts to synthesize polymers with sufficiently high thermal performance.

I hope to apply the developed materials to technically relevant polymer systems and extend the use of biobased polymers. The main motivation for this research is scientific curiosity in the synthesis and characterization of new polymers. The purpose of this paper is as follows.

・ To develop high-strength and thermostable polyurea from a new monomer, 2,5-bis(aminomethyl)furan(AMF) (Chapter 2).

・We will develop thermoresponsive and self-healing gels using furan polyurea (Chapter 2).

・Synthesis of high performance PU from diamine 2-(4-aminophenyl)ethylamine (4APEA) derived from microorganisms (Chapter 3).

・ Synthesis of new diamine oligomers from itaconic acid and development of photoinduced hydrolysable PU (Chapter 4).

・We will test the effectiveness of these materials in various applications and compare their physical parameters with those of previous studies (Chapter 5).

1-7 References and notes

[1] M. E. Springate, “Cellulose Nitrate Plastic (Celluloid) in Archaeological Assemblages: Identification and Care,” *Northeast Hist. Archaeology*, **1997**, *26*, 1, 63–72, doi: 10.22191/neha/vol26/iss1/5.

[2] D. Hosler, S. L. Burkett, and M. J. Tarkanian, “Prehistoric polymers: Rubber processing in ancient Mesoamerica,” *Science (80-.).*, **1999**, *284*, 5422, 1988–1991, doi: 10.1126/science.284.5422.1988.

[3] A. Gursel, E. Akca, and N. Sen, “A review on devulcanization of waste tire rubber,” *Period. Eng. Nat. Sci.*, **2018**, *6*, 1, 154–160, doi: 10.21533/pen.v6i1.167.

[4] C. M. Roland, *Structure Characterization in the Science and Technology of Elastomers*, Fourth Edi. Elsevier Inc., **2013.**

[5] W. B. Jensen, “Ask the Historian The Origin of the Term ‘ Base’”, *J. Chem. Educ.*, **2006**, *83*, 12, 45221

[6] M. E. SantosMiranda *et al.*, “Automatic continuous online monitoring of polymerization reactions (ACOMP),” *Polym Int*, **2008,** *57*, 3, 390–396, doi: 10.1002/pi.

[7] M. Karamanlioglu, R. Preziosi, and G. D. Robson, “Abiotic and biotic environmental degradation of the bioplastic polymer poly(lactic acid): A review,” *Polym. Degrad. Stab.*, **2017**, *137*, 122–130, doi: 10.1016/j.polymdegradstab.2017.01.009.

[8] L. H. Baekeland, “Method of making insoluble products of phenol and formaldehyde,” *United States Pat. Off.*, **1909**, 3.

[9] M. Nečemer, P. Kump, P. Šket, J. Plavec, J. Grdadolnik, and M. Žvaunt, “A novel analytical technique suitable for the identification of plastics,” *Acta Chim. Slov.*, **2013**, *60*, 3, 701–705

[10] K. Hirano and M. Asami, “Phenolic resins-100 years of progress and their future,” *React. Funct. Polym.*,**2014**, *73*, 2, 256–269, doi: 10.1016/j.reactfunctpolym.2012.07.003.

[11] M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, and R. L. Clough, “Correlation of chemical and mechanical property changes during oxidative degradation of neoprene,” *Polym. Degrad. Stab.*, **2000,** *68*, 2, 171–184, doi: 10.1016/S0141-3910(99)00183-4.

[12] T. A. Schools and N. E. Archaeology, “The history of nylon,” *Dip. di Chim. IFM dell’Università di Torino, Via P. Giuria 7 Torino, Italy*, **2012**, *61*, 4, 238–252

[13] K. Hosino, “Studies on Synthetic Fibers (I). Decomposition and Synthesis of ‘Nylon,’” *Bull. Chem. Soc. Jpn.*, **1943**, *18*, 3, 97–104, doi: 10.1246/bcsj.18.97.

[14] M. M. Lakouraj and M. Mokhtary, “Synthesis of polyamides from p-Xylylene glycol and dinitriles,” *J. Polym. Res.*, **2009**, *16*, 6, 681–686, doi: 10.1007/s10965-009-9273-z.

[15] Z. Zhang, H. Peng, D. Yang, G. Zhang, J. Zhang, and F. Ju, “Polyvinyl chloride degradation by a bacterium isolated from the gut of insect larvae,” *Nat. Commun.*, **2022**, *13*, 1, doi: 10.1038/s41467-022-32903-y.

[16] B. Y. Peng *et al.*, “Biodegradation of Polyvinyl Chloride (PVC) in Tenebrio molitor (Coleoptera: Tenebrionidae) larvae,” *Environ. Int.*, **2020**, *145*, 106106, doi: 10.1016/j.envint.2020.106106.

[17] R. Mohammed, G. A. El-Hiti, A. Ahmed, and E. Yousif, “Poly(Vinyl Chloride) Doped by 2-(4-Isobutylphenyl)Propanoate Metal Complexes: Enhanced Resistance to UV Irradiation,” *Arab. J. Sci. Eng.*, **2017**, *42*, 10, 4307–4315, doi: 10.1007/s13369-016-2323-z.

[18] W. H. Starnes, *Structural and mechanistic aspects of the thermal degradation of poly(vinyl chloride)*, **2022**, *27*, 10

[19] E. M. K. and N. H. A. H. S.T. Rabie, A.M. Mahran, “Photodegradation of Polystyrene Stabilized with Uracil Derivatives,” *J. Appl. Sci. Res.*, **2008**, *4*, 12, 2018–2026

[20] W. D. Watson and T. C. Wallace, “Polystyrene and Styrene Copolymers.,” *ACS Symp. Ser.*, **1985**, 363–382, doi: 10.1016/b0-08-043152-6/01389-9.

[21] J. Hammer, M. H. S. Kraak, and J. R. Parsons, *Plastics in the Marine Environment: The Dark Side*

of a Modern Gift, **2012**, *220*

[22] R. Geyer, J. R. Jambeck, and K. L. Law, “Production, use, and fate of all plastics ever made,” *Sci. Adv.*, **2017**, *3*, 7, 25–29, doi: 10.1126/sciadv.1700782.

[23] BP, “Statistical Review of World Energy globally consistent data on world energy markets and authoritative publications in the field of energy,” *BP Energy Outlook*, **2021**, *70*, 8–20

[24] D. V. Quayle, “Plastics in the Marine Environment: Problems and Solutions,” *Chem. Ecol.*, **1992**, *6*, 1–4, 69–78, doi: 10.1080/02757549208035263.

[25] R. C. P. Monteiro, J. A. Ivar do Sul, and M. F. Costa, “Plastic pollution in islands of the Atlantic Ocean,” *Environ. Pollut.*, **2018**, *238*, 103–110, doi: 10.1016/j.envpol.2018.01.096.

[26] K. Pivnenko, M. K. Eriksen, J. A. Martín-Fernández, E. Eriksson, and T. F. Astrup, “Recycling of plastic waste: Presence of phthalates in plastics from households and industry,” *Waste Manag.*, **2016**, *54*, 44–52, doi: 10.1016/j.wasman.2016.05.014.

[27] C. Aciu, D. A. Ilutiu-Varvara, D. L. Manea, Y. A. Orban, and F. Babota, “Recycling of plastic waste materials in the composition of ecological mortars,” *Procedia Manuf.*, **2018**, *22*, 274–279, doi: 10.1016/j.promfg.2018.03.042.

[28] C. Doyle, E. T. Tanner, and W. Bonfield, “In vitro and in vivo evaluation of polyhydroxybutyrate and of polyhydroxybutyrate reinforced with hydroxyapatite,” *Biomaterials*, **1991**, *12*, 9, 841–847, doi: 10.1016/0142-9612(91)90072-I.

[29] B. Saharan and D. Sharma, “Bioplastics-For Sustainable Development : A Review Bioplastics-For Sustainable Development : A Review,” *Int. J. Microb. Resour. Technol.*, **2015**, 1, 10–23.

[30] N. Jabeen, I. Majid, and G. A. Nayik, “Bioplastics and food packaging: A review,” *Cogent Food Agric.*,**2015**, *1*, 1, 1–6, doi: 10.1080/23311932.2015.1117749.

[31] R. P. Babu, K. O’Connor, and R. Seeram, “Current progress on bio-based polymers and their future trends,” *Prog. Biomater.*, **2013**, *2*, 1, 8 doi: 10.1186/2194-0517-2-8.

[32] D. Garlotta, “A Literature Review of Poly (Lactic Acid),” *J. Polym. Environ.*, **2019**, *9*, 2, 63–84.

[33] W. D. Jang, J. H. Hwang, H. U. Kim, J. Y. Ryu, and S. Y. Lee, “Bacterial cellulose as an example product for sustainable production and consumption,” *Microb. Biotechnol.*,**2017**, *10*, 5, 1181–1185, doi: 10.1111/1751-7915.12744.

[34] S. RameshKumar, P. Shaiju, K. E. O’Connor, and R. B. P, “Bio-based and biodegradable polymers - State-of-the-art, challenges and emerging trends,” *Curr. Opin. Green Sustain. Chem.*, **2020**, *21*, 75–81, doi: 10.1016/j.cogsc.2019.12.005.

[35] Daniel Elieh-Ali-Komi and M. R. Hamblin, “Chitin and Chitosan: Production and Application of Versatile Biomedical Nanomaterials Daniel,” *Int. J. Adv. Res.*, **2016**, *4*, 3, 411–427, doi: 10.2307/4145104.

[36] K. Azuma, S. Ifuku, T. Osaki, Y. Okamoto, and S. Minami, “Preparation and biomedical applications of chitin and chitosan nanofibers,” *J. Biomed. Nanotechnol.*, **2014**, *10*, 10, 2891–2920, doi: 10.1166/jbn.2014.1882.

[37] L. A. Petrasovits, M. P. Purnell, L. K. Nielsen, and S. M. Brumbley, “Production of polyhydroxybutyrate in sugarcane,” *Plant Biotechnol. J.*, **2007**, *5*, 1, 162–172, doi: 10.1111/j.1467-7652.2006.00229.x.

[38] O. Nechyporchuk, M. N. Belgacem, and J. Bras, “Production of cellulose nanofibrils: A review of recent advances,” *Ind. Crops Prod.*, **2016,** *93*, 2–25, doi: 10.1016/j.indcrop.2016.02.016.

[39] R. E. Burgeson and N. P. Morris, “The Collagen Family of Proteins,” *Connect. Tissue Dis.*, **2021**, *60*, 3–28, doi: 10.1201/9781003210016-2.

[40] Erich Adler, “Lignin Chemistry-Past, Present, and Future,” *Wood Sci. anci Technol.*, **1977**, *11*, 169–218, doi: 10.1021/ba-1976-0157.ch001.

[41] D. E. Henton, P. Gruber, J. Lunt, and J. Randall, “Polylactic acid technology,” *Nat. Fibers, Biopolym. Biocomposites*, **2005**, *48674*, 23, 527–577, doi: 10.1002/1521-

4095(200012)12:23<1841::aid-adma1841>3.3.co;2-5.

[42] M. Gigli, M. Fabbri, N. Lotti, R. Gamberini, B. Rimini, and A. Munari, “Poly(butylene succinate)-based polyesters for biomedical applications: A review in memory of our beloved colleague and friend Dr. Lara Finelli.,” *Eur. Polym. J.*, **2016**, *75*, 431–460, doi: 10.1016/j.eurpolymj.2016.01.016.

[43] C. Phithakrotchanakoon, V. Champreda, S. I. Aiba, K. Pootanakit, and S. Tanapongpipat, “Engineered Escherichia coli for short-chain-length medium-chain-length polyhydroxyalkanoate copolymer biosynthesis from glycerol and dodecanoate,” *Biosci. Biotechnol. Biochem.*, **2013**, *77*, 6, 1262–1268, doi: 10.1271/bbb.130073.

[44] T. Rokkonen, E. Luoma, A. Tribot, and H. Peltola, “Sustainable material options for polymer films,” **2021**, 1–57.

[45] A. Nag *et al.*, “Ultrahigh Thermoresistant Lightweight Bioplastics Developed from Fermentation Products of Cellulosic Feedstock,” *Adv. Sustain. Syst.*, **2021**, *5*, 1, doi: 10.1002/adsu.202000193.

[46] P. Suvannasara *et al.*, “Biobased polyimides from 4-aminocinnamic acid photodimer,” *Macromolecules*, **2014**, *47*, 5, 1586–1593, doi: 10.1021/ma402499m.

[47] A. Mukherjee, M. J. Dumont, and V. Raghavan, “Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities,” *Biomass and Bioenergy*, vol. 72, 143–183, 2015, doi: 10.1016/j.biombioe.2014.11.007.

[48] A. Gandini, T. M. Lacerda, A. J. F. Carvalho, and E. Trovatti, “Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides,” *Chem. Rev.*, **2016**, *116*, 3, 1637–1669, doi: 10.1021/acs.chemrev.5b00264.

[49] I. Delidovich, P. J. C. Hausoul, L. Deng, R. Pfützenreuter, M. Rose, and R. Palkovits, “Alternative Monomers Based on Lignocellulose and Their Use for Polymer Production,” *Chem. Rev.*, **2016**, *116*, 3, 1540–1599, doi: 10.1021/acs.chemrev.5b00354.

[50] A. Gandini, “Furans as offspring of sugars and polysaccharides and progenitors of a family of

remarkable polymers: A review of recent progress," *Polym. Chem.*, **2010**, *1*, 3, 245–251, doi: 10.1039/b9py00233b.

[51] T. Thananatthanachon and T. B. Rauchfuss, "Efficient route to hydroxymethylfurans from sugars via transfer hydrogenation," *ChemSusChem*, **2010**, *3*, 10, 1139–1141, doi: 10.1002/cssc.201000209.

[52] P. A. Russo *et al.*, "Mesoporous carbon-silica solid acid catalysts for producing useful bio-products within the sugar-platform of biorefineries," *Green Chem.*, **2014**, *16*, 9, 4292–4305, doi: 10.1039/c4gc01037j.

[53] R. J. I. Knoop, W. Vogelzang, J. Van Haveren, and D. S. Van Es, "High molecular weight poly(ethylene-2,5-furanoate); Critical aspects in synthesis and mechanical property determination," *J. Polym. Sci. Part A Polym. Chem.*, **2013**, *51*, 19, 4191–4199, doi: 10.1002/pola.26833.

[54] S. K. Burgess, J. E. Leisen, B. E. Kraftschik, C. R. Mubarak, R. M. Kriegel, and W. J. Koros, "Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate)," *Macromolecules*, **2014**, *47*, 1383–1391.

[55] S. K. Burgess, O. Karvan, J. R. Johnson, R. M. Kriegel, and W. J. Koros, "Oxygen sorption and transport in amorphous poly(ethylene furanoate)," *Polymer (Guildf).*, **2014**, *55*, 18, 4748–4756, doi: 10.1016/j.polymer.2014.07.041.

[56] R. Benigni and L. Passerini, "Carcinogenicity of the aromatic amines: From structure-activity relationships to mechanisms of action and risk assessment," *Mutat. Res. - Rev. Mutat. Res.*, **2002**, *511*, 3, 191–206, doi: 10.1016/S1383-5742(02)00008-X.

[57] O. R. Schade, P. K. Dannecker, K. F. Kalz, D. Steinbach, M. A. R. Meier, and J. D. Grunwaldt, "Direct Catalytic Route to Biomass-Derived 2,5-Furandicarboxylic Acid and Its Use as Monomer in a Multicomponent Polymerization," *ACS Omega*, **2019**, *4*, 16, 16972–16979, doi: 10.1021/acsomega.9b02373.

[58] H. Yuan, B. T. Kusema, Z. Yan, S. Streiff, and F. Shi, "Highly selective synthesis of 2,5-

bis(aminomethyl)furan: Via catalytic amination of 5-(hydroxymethyl)furfural with NH3 over a bifunctional catalyst," *RSC Adv.*, **2019**, *9*, 66, 38877–38881, doi: 10.1039/c9ra08560b.

[59] R. A. Mehl *et al.*, "Generation of a bacterium with a 21 amino acid genetic code," *J. Am. Chem. Soc.*, **2003**, *125*, 4, 935–939, doi: 10.1021/ja0284153.

[60] K. Yanai, N. Sumida, K. Okakura, T. Moriya, M. Watanabe, and T. Murakami, "Para-position derivatives of fungal anthelmintic cyclodepsipeptides engineered with Streptomyces venezuelae antibiotic biosynthetic genes," *Nat. Biotechnol.*, **2004**, *22*, 7, 848–855, doi: 10.1038/nbt978.

[61] S. Masuo, S. Zhou, T. Kaneko, and N. Takaya, "Bacterial fermentation platform for producing artificial aromatic amines," *Sci. Rep.*, **2016**, *6*, 1–9, doi: 10.1038/srep25764.

[62] M. J. Bibb *et al.*, "New insights into chloramphenicol biosynthesis in Streptomyces venezuelae ATCC 10712," *Antimicrob. Agents Chemother.*, **2014**, *58*, 12, 7441–7450, doi: 10.1128/AAC.04272-14.

[63] J. He, N. Magarvey, M. Piraee, and L. C. Vining, "The gene cluster for chloramphenicol biosynthesis in Streptomyces venezuelae ISP5230 includes novel shikimate pathway homologues and a monomodular non-ribosomal peptide synthetase gene," *Microbiology*, **2001**, *147*, 10, 2817–2829, doi: 10.1099/00221287-147-10-2817.

[64] V. F. Pfeifer, C. Vojnovich, and E. N. Heger, "Itaconic Acid by Fermentation with Aspergillus terreus," *Ind. Eng. Chem.*, **1952**, *44*, 12, 2975–2980

[65] H. Horitsu, Y. Takahashi, J. Tsuda, K. Kawai, and Y. Kawano, "Production of itaconic acid by Aspergillus terreus immobilized in polyacrylamide gels," *Eur. J. Appl. Microbiol. Biotechnol.*, **1983**, *18*, 6, 358–360, doi: 10.1007/BF00504745.

[66] T. Boruta and M. Bizukojc, "Production of lovastatin and itaconic acid by Aspergillus terreus: a comparative perspective," *World J. Microbiol. Biotechnol.*, **2017**, *33*, 2, 1–12, doi: 10.1007/s11274-017-2206-9.

[67] M. Okabe, D. Lies, S. Kanamasa, and E. Y. Park, “Biotechnological production of itaconic acid and its biosynthesis in Aspergillus terreus,” *Appl. Microbiol. Biotechnol.*, **2009**, *84*, 4, 597–606, doi: 10.1007/s00253-009-2132-3.

[68] P. Bonnarme, B. Gillet, A. M. Sepulchre, C. Role, J. C. Beloeil, and C. Ducrocq, “Itaconate biosynthesis in Aspergillus terreus,” *J. Bacteriol.*, **1995**, *177*, 12, 3573–3578, doi: 10.1128/jb.177.12.3573-3578.1995.

[69] P. L. Paytash, E. Sparrow, and J. C. Gathe, “The Reaction of Itaconic Acid with Primary Amines,” *J. Am. Chem. Soc.*, **1950**, *1415*, 3, 1415–1416.

[70] T. Willke and K. D. Vorlop, “Biotechnological production of itaconic acid,” *Appl. Microbiol. Biotechnol.*, **2001**, *56*, 3–4, 289–295, doi: 10.1007/s002530100685.

[71] T. Werpy and G. Petersen, “Results of Screening for Potential Candidates from Sugars and Synthesis Gas,” *Top Value Added Chem. from Biomass*, **2004**, 76 , doi: 10.2172/15008859.

[72] E. De Jong, H. Stichnothe, G. Bell, and H. Jorgensen, *Bio-Based Chemicals: A 2020 Update*., IEA *Bioenergy Task 42 Biorefinery*, **2020**, 1-79.

[73] P. L. Paytash, M. J. Thompson, and M. E. Fykes, “Itaconic Acid Derivatives of Sulfanilamide,” *J. Am. Chem. Soc.*, **1952**, *74*, 18, 4549–4552, doi: 10.1021/ja01138a027.

[74] M. A. Ali, S. Tateyama, Y. Oka, D. Kaneko, M. K. Okajima, and T. Kaneko, “Syntheses of high-performance biopolyamides derived from itaconic acid and their environmental corrosion,” *Macromolecules*, **2013**, *46*, 10, 3719–3725, doi: 10.1021/ma400395b.

[75] F. Ayadi, S. Mamzed, C. Portella, and P. Dole, “Synthesis of bis(pyrrolidone-4-carboxylic acid)-based polyamides derived from renewable itaconic acid - Application as a compatibilizer in biopolymer blends,” *Polym. J.*, **2013**, *45*, 7, 766–774, doi: 10.1038/pj.2012.206.

[76] X. Wang *et al.*, “The production of biobased diamines from renewable carbon sources: Current advances and perspectives,” *Chinese J. Chem. Eng.*, **2021**, *30*, 4–13, doi:

10.1016/j.cjche.2020.12.009.

[77] F. D. C. and M. P.-T. A. B. Dros, O. Larue, A. Reimond, “Hexamethylenediamine (HMDA) from Fossil vs. Bio-based Routes: an Economic and Life Cycle Assessment Comparative Study,” *Green Chem.*, **2015**, *17*, 4760–4772, doi: 10.1039/b000000x.

[78] D. Pham Minh, M. Besson, C. Pinel, P. Fuertes, and C. Petitjean, “Aqueous-phase hydrogenation of biomass-based succinic acid to 1,4-butanediol over supported bimetallic catalysts,” *Top. Catal.*, **2010**, *53*, 15–18, 1270–1273, doi: 10.1007/s11244-010-9580-y.

[79] G. W. Huber, R. D. Cortright, and J. A. Dumesic, “Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates,” *Angew. Chemie - Int. Ed.*, **2004**, *43*, 12, 1549–1551, doi: 10.1002/anie.200353050.

[80] B. M. Stadler, C. Wulf, T. Werner, S. Tin, and J. G. De Vries, “Catalytic Approaches to Monomers for Polymers Based on Renewables,” *ACS Catal.*,**2019**, *9*, 9, 8012–8067, doi: 10.1021/acscatal.9b01665.

[81] R. Datta, S. Tsai, P. Bonsignore, S. Moon, and J. R. Frank, “Technological and economic potential of poly(lactic acid) and lactic acid derivatives,” *FEMS Microbiol. Rev.*, **1995**, *16*, 221–231.

[82] J. H. De Groot, R. De Vrijer, B. S. Wildeboer, C. S. Spaans, and A. J. Pennings, “New biomedical polyurethane ureas with high tear strengths,” *Polym. Bull.*, **1997**, *38*, 2, 211–218, doi: 10.1007/s002890050040.

[83] M. K. Hassan, K. A. Mauritz, R. F. Storey, and J. S. Wiggins, “Biodegradable Aliphatic Thermoplastic Polyurethane Based on Poly(e-caprolactone) and L-Lysine Diisocyanate,” *J. Polym. Sci. Part A Polym. Chem.*, **2006**, *44*, 9, 2990–3000, doi: 10.1002/pola.

[84] W. Li, H. Li, C. Wu, B. Han, P. Ouyang, and K. Chen, “An effective synthesis of bio-based pentamethylene diisocyanate in a jet loop reactor,” *Chem. Eng. J.*, **2021**, *425*, 131527, doi: 10.1016/j.cej.2021.131527.

[85] M. Charlon, B. Heinrich, Y. Matter, E. Couzigné, B. Donnio, and L. Avérous, "Synthesis, structure and properties of fully biobased thermoplastic polyurethanes, obtained from a diisocyanate based on modified dimer fatty acids, and different renewable diols," *Eur. Polym. J.*, **2014**, *61*, 197–205, doi: 10.1016/j.eurpolymj.2014.10.012.

[86] L. Hojabri, X. Kong, and S. S. Narine, "Fatty Acid-Derived diisocyanate and biobased polyurethane produced from vegetable oil: Synthesis, polymerization, and characterization," *Biomacromolecules*, **2009**, *10*, 4, 884–891, doi: 10.1021/bm801411w.

[87] L. Hojabri, X. Kong, and S. S. Narine, "Functional thermoplastics from linear diols and diisocyanates produced entirely from renewable lipid sources," *Biomacromolecules*, **2010**, *11*, 4, 911–918, doi: 10.1021/bm901308c.

[88] L. Hojabri, X. Kong, and S. S. Narine, "Novel long chain unsaturated diisocyanate from fatty acid: Synthesis, characterization, and application in bio-based polyurethane," *J. Polym. Sci. Part A Polym. Chem.*, **2010**, *48*, 15, 3302–3310, doi: 10.1002/pola.24114.

[89] B. Winter, R. Meys, and A. Bardow, "Towards aromatics from biomass: Prospective Life Cycle Assessment of bio-based aniline," *J. Clean. Prod.*, **2021**, *290*, 11, 125818, doi: 10.1016/j.jclepro.2021.125818.

[90] Vikas Mittal, *High Performance Polymers and Engineering Plastics*. **2011**, 1-454

[91] K. Cao *et al.*, "Reactive aramid nanostructures as high-performance polymeric building blocks for advanced composites," *Adv. Funct. Mater.*, **2013**, *23*, 16, 2072–2080, doi: 10.1002/adfm.201202466.

[92] S. Mallakpour and M. Dinari, "High Performance Polymers in Ionic Liquids: A Review on Prospects for Green Polymer Chemistry. Part I: Polyamides," *Iran. Polym. J.*, **2010**, *19*, 12, 983–1004.

[93] H. M. Ng *et al.*, "Extraction of cellulose nanocrystals from plant sources for application as

reinforcing agent in polymers," *Compos. Part B Eng.*, **2015**, *75*, 176–200, doi: 10.1016/j.compositesb.2015.01.008.

[94] J. M. García, F. C. García, F. Serna, and J. L. de la Peña, "High-performance aromatic polyamides," *Prog. Polym. Sci.*, **2010**, *35*, 5, 623–686, doi: 10.1016/j.progpolymsci.2009.09.002.

[95] P. Wang, X. Ma, Q. Li, B. Yang, J. Shang, and Y. Deng, "Green synthesis of polyureas from CO2 and diamines with a functional ionic liquid as the catalyst," *RSC Adv.*, **2016**, *6*, 59, 54013–54019, doi: 10.1039/c6ra07452a.

[96] V. Sendijarevic, A. Sendijarevic, I. Sendijarevic, R. E. Bailey, D. Pemberton, and K. A. Reimann, "Hydrolytic Stability of Toluene Diisocyanate and Polymeric Methylenediphenyl Diisocyanate Based Polyureas under Environmental Conditions," *Environ. Sci. Technol.*, **2004**, *38*, 4, 1066–1072, doi: 10.1021/es035072f.

[97] J. L. Stanford, "Effects of soft-segment prepolymer functionality on the thermal and mechanical properties of RIM copolymers," *Polym. Int.*, **1996**, *41*, 3, 283–292, doi: 10.1002/(sici)1097-0126(199611)41:3<283::aid-pi594>3.3.co;2-p.

[98] A.Mahammad Ibrahim, V.Mahadevan, and M.Srinivasan, "Synthetic studies on aliphatic-aromatic co-polyureas," *Eur. Polym. J.*, **1989**, *25*, 4, 427–429.

[99] W. Sakai, K. Chiga, and N. Tsutsumi, "Nonlinear optical (NLO) polymers. IV. Second-order optical nonlinearity of NLO polyurea and copolyurea with NLO dipole moments aligned transverse to the main backbone," *J. Polym. Sci. Part B Polym. Phys.*, **2001**, *39*, 2, 247–255, doi: 10.1002/1099-0488(20010115)39:2<247::AID-POLB70>3.0.CO;2-Y.

[100] J. R. Hwu and K. Y. King, "Design, synthesis, and photodegradation of silicon-containing polyureas," *Chem. - A Eur. J.*, **2005**, *11*, 13, 3805–3815, doi: 10.1002/chem.200401321.

[101] B. Shojaei, M. Najafi, A. Yazdanbakhsh, M. Abtahi, and C. Zhang, "A review on the applications of polyurea in the construction industry," *Polym. Adv. Technol.*, **2021**, *32*, 8, pp. 2797–2812, doi:

10.1002/pat.5277.

[102] G. Toader *et al.*, "A facile synthesis route of hybrid polyurea-polyurethane- mwcnts nanocomposite coatings for ballistic protection and experimental testing in dynamic regime," *Polymers (Basel).*, **2021**, *13*, 10, 1618, doi: 10.3390/polym13101618.

[103] N. Iqbal, M. Tripathi, S. Parthasarathy, D. Kumar, and P. K. Roy, "Tuning the properties of segmented polyurea by regulating soft-segment length," *J. Appl. Polym. Sci.*, **2018**, *135*, 21, 1–8, doi: 10.1002/app.46284.

[104] R. Zhang, W. Huang, P. Lyu, S. Yan, X. Wang, and J. Ju, "Polyurea for Blast and Impact Protection: A Review," *Polymers (Basel).*, **2022**, *14*, 13, 2670, doi: 10.3390/polym14132670.

[105] K. Won-In and P. Dararutana, "Morphology, Thermal Degradation and Dynamic Mechanical Properties of Polyurea used as Explosive-Proof Elastomer," *IOP Conf. Ser. Mater. Sci. Eng.*, **2020**, *894*, 1, doi: 10.1088/1757-899X/894/1/012010.

[106] V. V. Tyagi, S. C. Kaushik, S. K. Tyagi, and T. Akiyama, "Development of phase change materials based microencapsulated technology for buildings: A review," *Renew. Sustain. Energy Rev.*, **2011**, *15*, 2, 1373–1391, doi: 10.1016/j.rser.2010.10.006.

[107] S. N. Rodrigues, I. Fernandes, I. M. Martins, V. G. Mata, F. Barreiro, and A. E. Rodrigues, "Microencapsulation of limonene for textile application," *Ind. Eng. Chem. Res.*, **2008**, *47*, 12, 4142–4147, doi: 10.1021/ie800090c.

[108] N. Samson, F. Mechin, and J. P. Pascault, "Relationships between synthesis and mechanical properties of new polyurea materials," *J. Appl. Polym. Sci.*, **1997**, *65*, 12, 2265–2280, doi: 10.1002/(sici)1097-4628(19970919)65:12<2265::aid-app2>3.3.co;2-s.

[109] J. Nam, E. Jeon, S. Y. Moon, and J. W. Park, "Rearranged copolyurea networks for selective carbon dioxide adsorption at room temperature," *Polymers (Basel).*, **2021**, *13*, 22, 1–9, doi: 10.3390/polym13224004.

[110] J. Yi, M. C. Boyce, G. F. Lee, and E. Balizer, “Large deformation rate-dependent stress-strain behavior of polyurea and polyurethanes,” *Polymer (Guildf).*, **2006**, *47*, 1, 319–329, doi: 10.1016/j.polymer.2005.10.107.

[111] A. Pangon, G. P. Dillon, and J. Runt, “Influence of mixed soft segments on microphase separation of polyurea elastomers,” *Polymer (Guildf).*, **2014**, *55*, 7, 1837–1844, doi: 10.1016/j.polymer.2014.02.009.

[112] Q. Liu *et al.*, “Mechanical behavior and failure mechanism of polyurea nanocomposites under quasi-static and dynamic compressive loading,” *Def. Technol.*, **2021**, *17*, 2, 495–504, doi: 10.1016/j.dt.2020.02.006.

[113] K. Hong and S. Park, “Preparation of polyurea microcapsules with different composition ratios: Structures and thermal properties,” *Mater. Sci. Eng. A*, **1999**, *272*, 2, 418–421, doi: 10.1016/S0921-5093(99)00509-2.

[114] S. Hasnain, M. Zulfequar, and N. Nishat, “Adsorption properties of thermally stable and biologically active polyurea: Its synthesis and spectral aspects,” *Polym. Adv. Technol.*, **2012**, *23*, 6, 1002–1010, doi: 10.1002/pat.2004.

[115] Q. Zhu, S. Feng, and C. Zhang, “Synthesis and thermal properties of polyurethane-polysiloxane crosslinked polymer networks,” *J. Appl. Polym. Sci.*, **2003**, *90*, 1, 310–315, doi: 10.1002/app.12790.

Chapter 2

Self- and Cross-fusing of Furan-based Polyurea Gels Dynamically Cross-linked with Maleimides

2-1 Introduction

A polymer will dissolve if it has an affinity for a solvent. However, chemical or physical cross-linking of polymer chains results in gels that are insoluble in good solvents. It is believed that gels first came to widespread industrial attention about 180 years ago, after Goodyear's development of cross-linking by vulcanization of rubber. Goodyear's discovery led to the development of cross-linked rubber, a highly functional gel with shape memory properties. This cross-linked rubber is still an important material used today as the basis for technologies that support the manufacture of industrial goods such as tires, for example. The development of gels, which began with Goodyear's discovery of cross-linking polymer chains, has since been used in a wide range of fields, including food, medicine, and cosmetics. In particular, products utilizing the high retention and sustained-release properties of gels, which utilize the three-dimensional network structure characteristic of gels, continue to be developed, and products based on hydrogel materials are becoming increasingly sophisticated. Although hydrogels are now indispensable materials in our daily lives, from an academic viewpoint, until about half a century ago, no evaluation system had been established for the physicochemical properties of gels, and the gelation phenomenon that occurs during polymer synthesis was more often reported as a negative result. However, starting with the detailed theoretical proof and evaluation of physical properties by Flory, Stockmayer, and Toyokazu Tanaka, gel research quickly became one of the major disciplines in polymer research. Hydrogel research is characterized by the fact that it has been conducted by numerous scientists across a very wide range of fields in polymer science, including synthesis, structural analysis, characterization, and application. Therefore, gels have provided new research subjects for a wide range of research fields, such as polymer synthesis, biology, medicine, and pharmacology, and have enabled cutting-edge research. As described above, with the focus on both academic and applied aspects, new hydrogel cross-linking points and cross-linking modes have been discovered, and highly functional hydrogels that were previously considered difficult to develop have been developed in collaboration with smart polymers developed through advanced polymer research. For example, stimulus-responsive gels that show phase transitions in response to the external environment such as temperature and pH, ultra-high-strength gels with rubber-like strength and flexibility, and self-healing gels that repair wounds and breaks on their own, have been developed that overturn conventional concepts of gel properties and characteristics. These gels are called "smart gels" and have become the flower of hydrogel development. In addition, since hydrogels have many similarities with soft tissues of the human body, they are being actively applied to the biomedical field.

Polymer gels have a three-dimensional (3D) network structure that contains a solvent. Owing to their excellent solvent absorption properties, polymer gels have ap-plications in a variety of fields, including biomedical engineering and electronics [1]–[8]. Conventional polymer gels composed of covalent 3D networks exhibit thermo-mechanical stability superior to physical gels. However, because the 3D network structure of covalently cross-linked polymers (CLP) is permanent, they lack the ability to undergo reprocessing. One promising approach to overcome this problem is to use dynamic covalent bonds (DCBs) in CLPs [9]–[11]. The introduction of DCBs regenerates covalent bonds inside and at the interface of polymeric materials via transesterification [12], olefin metathesis [13][14], reversible boronate ester formation [15][16], and dichalcogenide bond exchange [17][18]. Furthermore, studies on CLPs containing DCBs have revealed that they exhibit properties such as self-healing [19][20], shape memory [21], and the ability to undergo reversible sol- 0 gel reactions [22]. Self-healing based on bond exchange reactions prevents catastrophic structural collapse and ex-tends the lifetime of materials. Therefore, self-healing polymers have been extensively studied, from their microscopic repair mechanisms to their macroscopic properties [23]–[27]. Recently, direct adhesion between hydrogels using the inclusion function of cyclodextrins [28] and by covalent bond formation via the Suzuki/Miyaura cross-coupling reaction have been reported [29][30]. Both are based on reactions between functional groups of the side chains. Depending on their composition, CLPs exhibit a range of properties, from soft gels to hard thermoset materials, and are utilized in diverse applications in our daily lives. However, crosslinked polymers cannot dis-solve or melt, making it difficult to mix and integrate different crosslinked polymers. To overcome these challenges it is necessary to employ heterojunction technology for CLP, where molecular chains are connected in a 3D mesh-like pattern. In this context, we focused on 2,5-bis(aminomethyl)furan (AMF), a diamine monomer synthesized via catalytic processes from microorganism-derived 5-(hydroxymethyl)furfural (HMF) [31]. Polymers based on AMF introduce a furan in the main chain that provides a site for further functionalization. The furan-maleimide Diels-Alder (DA) reaction allows for reversible dynamic covalent cross-linking to be introduced, which imparts abilities to heal, recycle, and repair the polymeric materials [32]–[36]. We believe this approach is worthy of investigation, as there are few examples of polymer synthesis focused on chemical modifications of furandiamines and their main-chain furan rings. Unlike furan dicarboxylic acids, we expect AMFs to lend flexibility to the resulting polymers owing to the presence of methylenes adjacent to the furan rings. This may allow for the synthesis of polymers with excellent thermal and mechanical properties. Herein, we focus on a polyurea (PU) formed by the reaction of a diisocyanate and diamine [37][38]. Molecularly, it is similar to polyamide, but has a structure where significant hydrogen bonding occurs between the polymer chains, enhancing the mechanical properties [39][40]. Recently, the use of PUs in films, foams, and composites such as vertical body panels, spray foams, and microcellular foam liquid plastics, has attracted attention in industrial applications [41]–[43]. A further advantage of PUs is that they do not require catalysts or rapid heating to undergo molding [44].

Here, we describe the synthesis and characterization of a bio-based PU from a microorganism-derived AMF via polyaddition reaction with various diisocyanate compounds. Some PUs showed thermally reversible sol-gel transitions, achieved by adding cross-linking agents. In particular, heterojunctions between different PU gels are formed by the dynamic covalent bonding of CLPs while maintaining the gel state by heating. This design includes furan group in the main chain and cross-linking reaction of different polymer chains by the DA reaction, which expected to exhibit the high performance and self-healing properties.

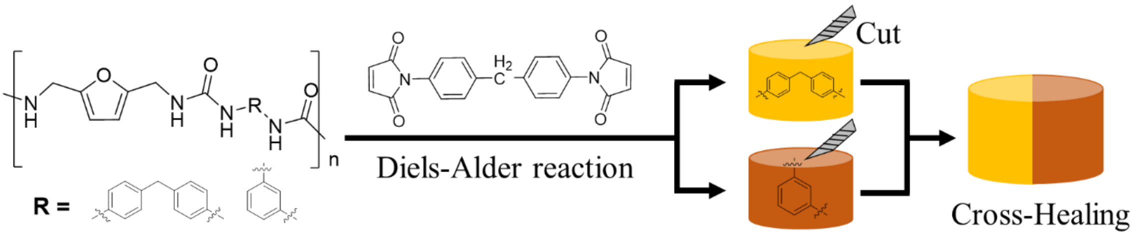


Figure 2-1 Process of polymer synthesis using AMF and cross-linked and cross-healing polymer synthesis by Diels-Alder reaction

2-2 Materials and Methods

2-2-1 Materials

2,5-Bis(aminomethyl)furan (99% purity) was provided from Nippon Shokubai Co., Ltd(Tokyo, Japan), Methylene diphenyl diisocyanate (MDI), 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,3-phenylenediisocyanate (m-PDI), 1,4-phenylenediisocyanate (p-PDI), m-Xylylene Diisocyanate (XDI), 1,5-Diisocyanatonaphthalene (NDI), Dicyclohexylmethane 4,4'-Diisocyanate (CDI), Isophorone diisocyanate (IDI), Hexamethylene diisocyanate (HDI), 4,4'-Diphenylmethane bismaleimide (BMI) were purchased from Tokyo Chemical Industry Co., LTD. 4,4'-Diisocyanato-3,3'-dimethylbiphenyl (DMMDI), N,N-Dimethylacetamide (DMAc) were purchased from Kanto Chemical Co., Inc. 1,4-Butane diisocyanate (BDI), 1,8-Octane Diisocyanate (ODI) were purchased from Sigma-Aldrich Co., Inc. All reagents were used without further purification.

2-2-2 Instruments

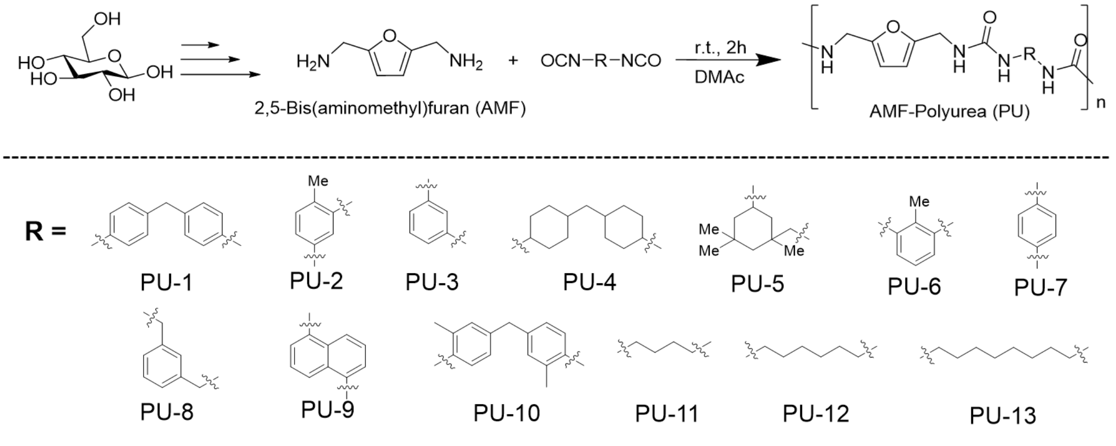
^{1}H NMR measurements were performed using a Bruker Bio-spin AG 400 MHz spectrometer. FT-IR spectra were used with a Perkin–Elmer Spectrum One spectrometer, between 4000 and 600 cm^{-1}, using a diamond-attenuated total reflection accessory. The gel permeation chromatography (GPC) were performed on a Shodex column (SB 806M × 2), column oven (GL Science, CO 631A, set at 40 °C), degassing unit (GL Science, DG 660 B), pump (JASCO, PU-2080 Plus), refractive index detector (JASCO, 830-RI), and ultraviolet detector (JASCO, UV-2075 plus) using a 0.01 mol L^{-1} LiBr solution in DMF as an eluent (flow rate, 1 mL min^{-1}). Thermal gravimetric analysis (TGA) was carried out using a HITACHI STA 7200 under nitrogen flow (flow rate, 200 mL min^{-1}) from 25 °C to 800 °C (heating rate, 5 °C min^{-1}) to determine the 5 % and 10 % decom-position temperatures (T_{d5} and T_{d10}). Differential scanning calorimetry (DSC) were performed with a SEIKO X-DSC7000T to measure the glass transition temperature (T_g), from 25 to 300 °C at a heating rate of 10 °C min^{-1} with ca. 5 mg of sample. The ultraviolet-visible (UV-Vis) absorption spectroscopy were performed with a V-670

(JASCO) instrument in the 200–800 nm range. Finally, a tensile testing machine (INSTRON 3365-L5) were performed with a 1 mm s^{-1} movement at room temperature. The rectangular polymer film dimensions were 2 × 0.5 cm with a thickness of 2.5 μm.

2-2-3 Syntheses of bio-base polyurea using AMF

For synthesis of PUs, 2,5-bis(aminomethyl)furan (AMF) (126.2 mL, 1.0 mmol) was dissolved in dimethylacetamide (DMAc, 2.0 mL) and dropped it, very slowly, into an MDI (250.3 mg, 1.0 mmol) solution in DMAc (2.0 mL) with stirring (Scheme 1). An ice–water bath cooled the mixture. The obtained solution with sufficient viscosity ap-proximately 2 h after the drop, which indicated formation of the PUs. The solution was diluted the reaction mixture with a DMAc solution before reprecipitation by dropping into methanol. The precipitate was collected by suction filtration and dried under reduced pressure for 12 h. Powdery or fibrous white polyurea resulted (365.1 mg, yield 97.0 %, Scheme 1). We synthesized PUs from AMF and other diisocyanate monomers using an analogous procedure (Scheme 1).

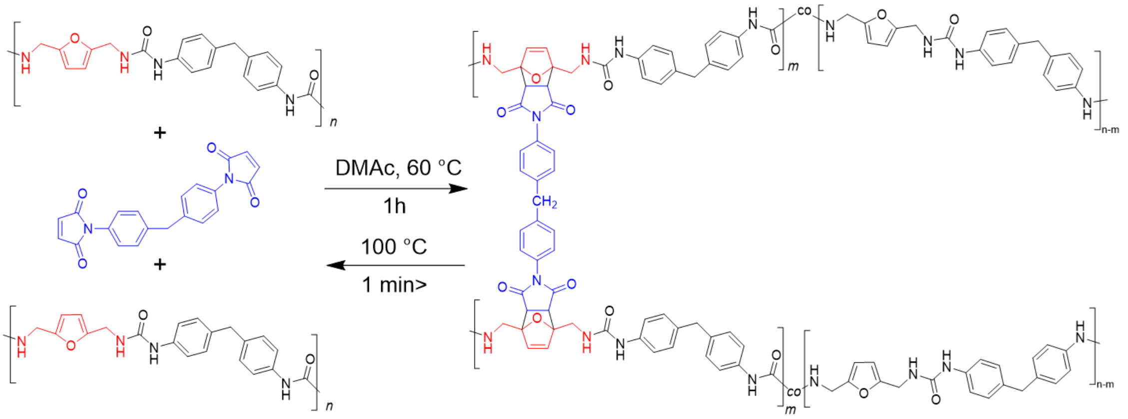
Scheme 2-1 Syntheses of PUs from 2,5-bis(aminomethyl)furane and various diisocyanates



2-2-4 Syntheses of bio-base polyurea gel using PU and BMI

PU-1 (100.0 mg, 264.9 mmol) was dissolved into DMAc (1.5 mL), to which was added into a solution of 4,4'-bismaleimidodiphenylmethane (BMI) (9.5 mg, 26.5 mmol) in DMAc (0.5 mL). The reaction was carried out the addition at room temperature before heating to 50 °C with stirring for 1 h. Yellow gels formed as the reaction progressed. When the gel was heated to 100 °C, it disappeared (Scheme 2).

Scheme 2-2 Cross-linking reaction of PUs by Diels-Alder reaction.

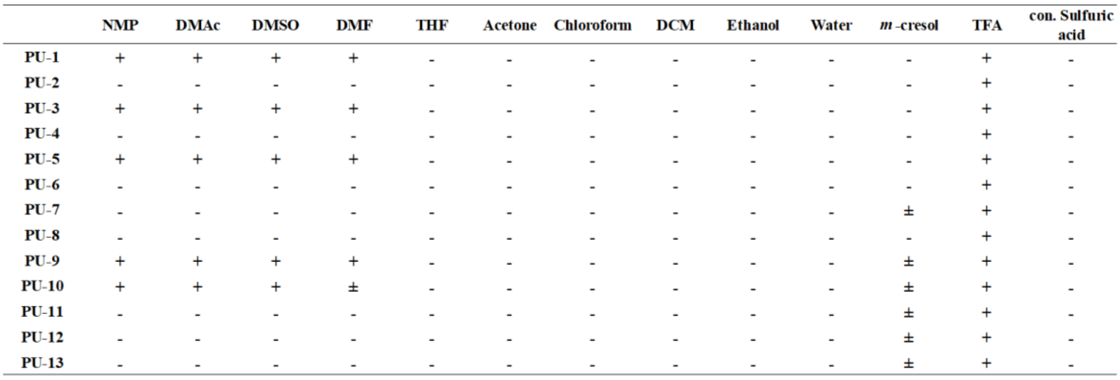


2-3 Results and discussion

2-3-1 Synthesis and characterization of bio-based polyurea (PU-1~PU-5)

PU with furan rings in the main chain was prepared by the polyaddition of 2,5-bis(aminomethyl)furan with a stoichiometric amount of a diisocyanate compound. The solubility of PUs were tested using non-polar solvents such as hexane, chloroform, and dichloromethane; polar protic solvents such as distilled water, methanol, and ethanol; and polar non-protic solvents such as acetone, THF, DMF, DMAc, DMSO, NMP. PU-1 to PU-5 were soluble at room temperature in some polar nonprotic solvents of DMF, NMP, DMAc, and DMSO (Table 2-1). The reason why solubility was not observed for the aliphatic PUs is suggested by their high aggregation potential.

Table 2-1 Solubility of the synthesized PUs from various diisocyanates (a



	NMP	DMAc	DMSO	DMF	THF	Acetone	Chloroform	DCM	Ethanol	Water	*m*-cresol	TFA	con. Sulfuric acid
PU-1	+	+	+	+	-	-	-	-	-	-	-	+	-
PU-2	-	-	-	-	-	-	-	-	-	-	-	+	-
PU-3	+	+	+	+	-	-	-	-	-	-	-	+	-
PU-4	-	-	-	-	-	-	-	-	-	-	-	+	-
PU-5	+	+	+	+	-	-	-	-	-	-	-	+	-
PU-6	-	-	-	-	-	-	-	-	-	-	-	+	-
PU-7	-	-	-	-	-	-	-	-	-	-	±	+	-
PU-8	-	-	-	-	-	-	-	-	-	-	-	+	-
PU-9	+	+	+	+	-	-	-	-	-	-	±	+	-
PU-10	+	+	+	±	-	-	-	-	-	-	±	+	-
PU-11	-	-	-	-	-	-	-	-	-	-	±	+	-
PU-12	-	-	-	-	-	-	-	-	-	-	±	+	-
PU-13	-	-	-	-	-	-	-	-	-	-	±	+	-

a) sample 5 mg / solvent 1 mL + :easily soluble, - : insoluble. ± : dissolved by heating

Based on the solubility data, NMR measurement of the resulting polyurea was performed, and the proton derived from the furan ring around 6.2 ppm and the proton of the amide group contained in the urea bond around 8.5 ppm was confirmed, suggesting that the target product was obtained (Figure 2-2).

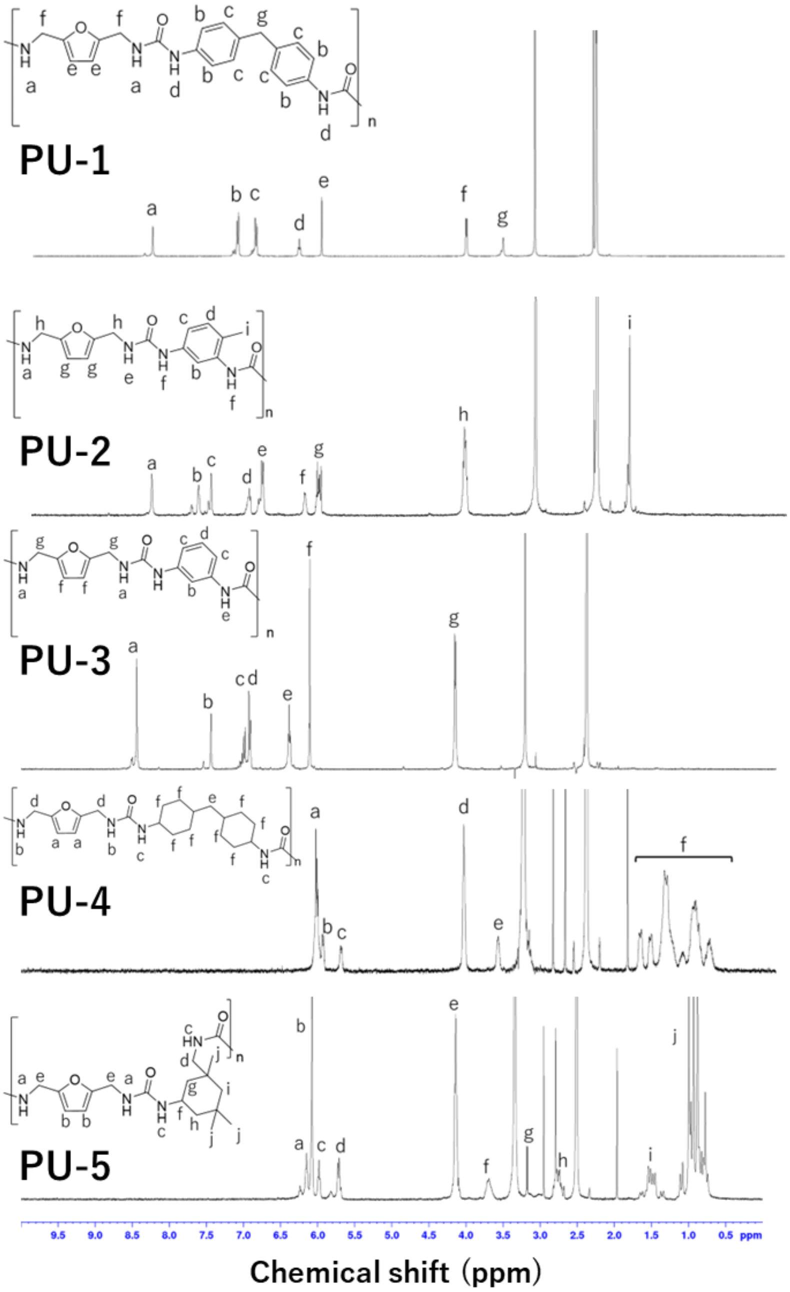


Figure 2-2 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of PU-1 to PU-5.

Among the obtained PUs, the results of IR structural analysis of PU-1 to PU-5 are shown (Figure 2-3). Absorption originating from the N-H stretching vibration was confirmed near 1620 cm^{-1} and 3450 cm^{-1}, indicating that urea bonds were formed and the desired polyurea was obtained.

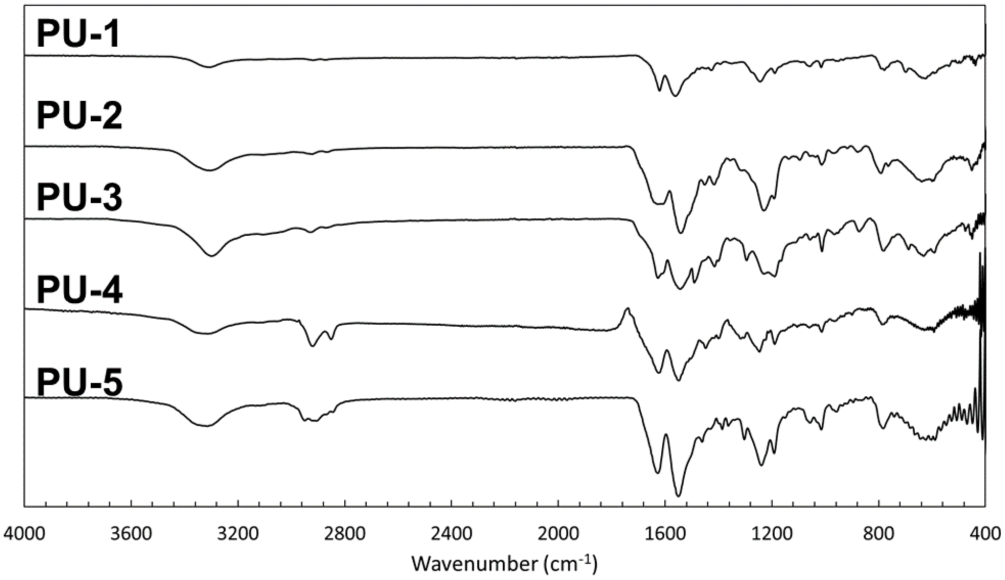


Figure2-3 IR spectrum of PU-1 to PU-5 using AMF and various diisocyanates.

The film was cast from a 50 M concentration of DMAc solution by dropping the solution onto glass and allowing it to dry at 100°C for at least 1 hour. The films were tough and flexible and exhibited relatively high transparency of 61.3~66.1% at 450 nm.

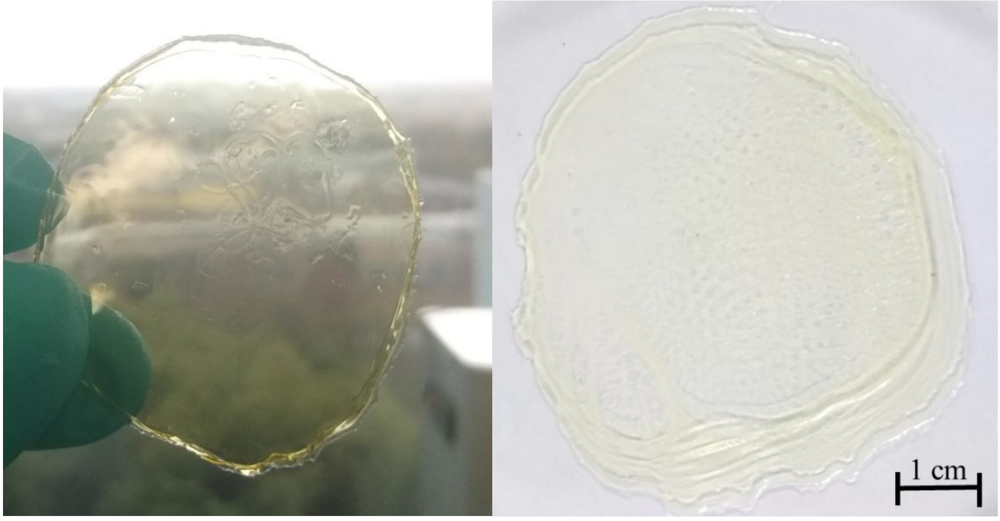
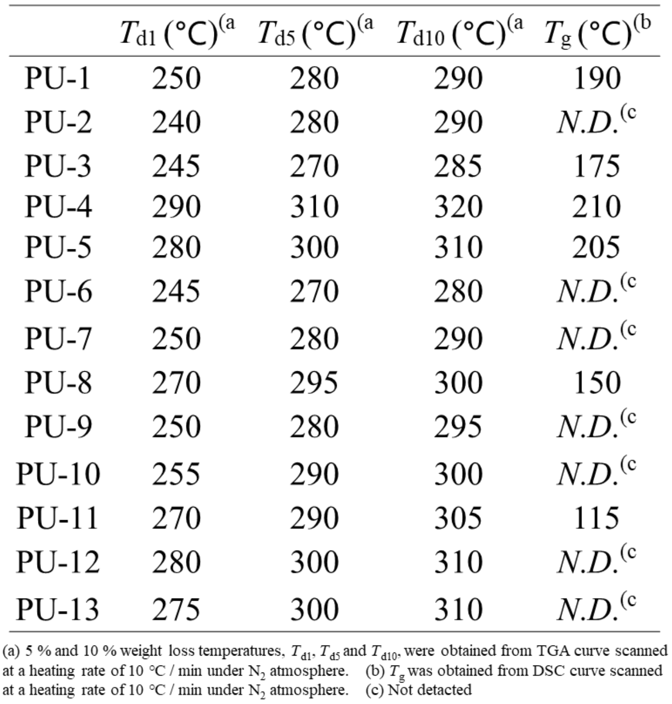


Figure 2-4 Films of synthesized PU-1 using AMF.

Pyrolysis of PU was investigated by thermogravimetric analysis in a nitrogen atmosphere at a heating rate of 10 °C min-1 to determine a 10% weight loss temperature (T_{d10}). Samples were dried at 100 °C prior to measurement. The T_{d1} of the various PUs were all above 240 °C, and the confirmed T_g was also above 110 °C (Table 2-2).

Table 2-2 Weight loss temperature and glass-transition temperature of the synthesized PUs using AMF and various diisocyanates



	T_{d1} (°C)$^{(a}$	T_{d5} (°C)$^{(a}$	T_{d10} (°C)$^{(a}$	T_g (°C)$^{(b}$
PU-1	250	280	290	190
PU-2	240	280	290	*N.D.*$^{(c}$
PU-3	245	270	285	175
PU-4	290	310	320	210
PU-5	280	300	310	205
PU-6	245	270	280	*N.D.*$^{(c}$
PU-7	250	280	290	*N.D.*$^{(c}$
PU-8	270	295	300	150
PU-9	250	280	295	*N.D.*$^{(c}$
PU-10	255	290	300	*N.D.*$^{(c}$
PU-11	270	290	305	115
PU-12	280	300	310	*N.D.*$^{(c}$
PU-13	275	300	310	*N.D.*$^{(c}$

(a) 5 % and 10 % weight loss temperatures, T_{d1}, T_{d5} and T_{d10}, were obtained from TGA curve scanned at a heating rate of 10 °C / min under N_2 atmosphere. (b) T_g was obtained from DSC curve scanned at a heating rate of 10 °C / min under N_2 atmosphere. (c) Not detected

Among them, PU-4 showed the best heat resistance with a T_{d1} value of 291 ºC. Similarly, PU-4 showed the highest T_g value of 212 °C. The large difference between T_{d1} and T_g of PU-11 (151 °C) and the melting point of PU-1 (195 °C) indicate that these two PU have excellent moldability. Among the synthesized AMF PUs, no T_g was detected in the range of room temperature to 250 °C for the PUs. This suggests that the PUs synthesized in this study have T_g above 250 °C. Comparing the diisocyanate monomer structure and weight loss temperature, there was no difference in PUs with an aromatic main chain, while PUs with aliphatic and alicyclic structures in the main chain showed higher heat resistance. One of the reasons for this is thought to be the intermolecular interaction due to packing properties [46]. Polymers with highly rigid structures or alkyl chains in the main chain formed crystallinity due to packing, which may have affected the thermophysical properties. In addition, thermal decomposition tends to start from thermally unstable portions in the polymer chain. Therefore, if the number of unstable structural sites in the main chain structure is small, the pyrolysis initiation temperature will be higher [47]. We speculate that aliphatic PUs have high thermostability because they have fewer unstable structures that induce thermal decomposition.

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution (M_w/M_n) were determined and summarized in Table 2-3. The synthesized PU yielded high molecular weights. Among them, PU-2 had the highest molecular weight with M_n 16,000 and M_w 94,000. On the other hand, PU-1 and PU-4 had relatively low M_w values of about 20,000. The reason for this is expected to be the time required for polymerization due to the bulky structure of the diisocyanate. Therefore, we believe that this problem can be solved by lengthening the reaction time.

Tensile testing of PU films was performed to understand their mechanical properties; PU-1 to 5 films exhibited tensile strengths of 21 and 17 MPa, tensile moduli of 1.2 and 1.1 GPa, and elongations at break of respectively 2.7% and 2.1% elongation at break. PU-1 exhibited the highest mechanical strength, with a tensile strength of 65 MPa and a Young's modulus of 820 MPa. The reason for this is thought to be that the methylenediphenyl groups in the main chain contributed to the strength and flexibility. The main chain of the PU was aromatic because of the methylenediphenyl group, and the methylene group between the aromatic and methylene groups provided flexibility in the structure. The maximum elongation of all PUs was 8.9 %, and although they showed flexibility, they did not exhibit the high elongation seen in conventional PUs. The reason for this is thought to be the introduction of the furan structure. In general PU, two amino groups and one carbonyl group form a bidentate hydrogen bond, which gives flexibility. On the other hand, when furan is introduced, hydrogen bonds are formed between the oxygen atom in the furan and the urea bonding site, and this interaction is stronger than that of general PUs (Figure 2-5). The T_d, T_g, and mechanical properties of the synthesized resins in the dry state were measured and are summarized. (Table 2-3).

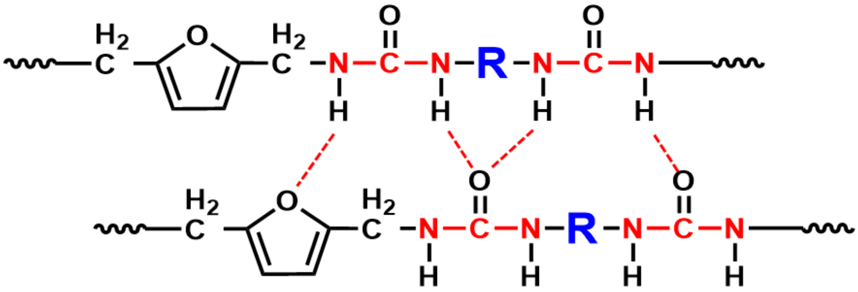


Figure 2-5 Hydrogen bond interaction between urea bond and furan structure.

Table 2-3 Molecular weight, thermal, mechanical, and optical properties of the obtained PU-1 to 5

Polymer	M_n [a]	M_w [a]	M_w/M_n [a]	T_{d5} / °C [b]	T_{d10} / °C [b]	T_g / °C [c]	Strength, σ / MPa	Young's modulus, E / GPa	Elongation at break, ε / %	Transparency (400 nm) / %	Transparency (450 nm) / %
PU-1	7.4×10^3	2.1×10^4	2.84	277	288	193	65	0.8	8.6	31.7	63.9
PU-2	16×10^3	94×10^4	6.01	277	287	*N.D.* [f]	25	0.5	6.8	53.3	64.9
PU-3	8.8×10^3	2.0×10^4	2.32	273	284	175	38	0.7	8.4	56.2	66.1
PU-4	8.0×10^3	2.0×10^4	2.65	307	318	212	16	0.3	8.9	44.7	61.3
PU-5	3.0×10^3	1.0×10^4	3.46	301	308	205	5	0.2	2.7	3.6	20.9

a) Determined by SEC measurement using DMF LiBr solution b) 5 % and 10 % weight loss temperatures, T_{d5} and T_{d10}, were obtained from TGA curve scanned at a heating rate of 10 °C / min under N_2 atmosphere. c) T_g was obtained from DSC curve scanned at a heating rate of 10 °C / min under N_2 atmosphere. d) Not detected

2-3-2 Crosslinked structure characterization

BMI was added into PU-1 dissolved in DMAc and allowed them to cross-link via the DA reaction. When BMI was mixed with PU-1 and stirred at room temperature, no cross-linking was observed even after several days. The mixture became a gel upon heating to 50 °C, and its apparent elasticity increased with time. The gelation was observed at 50, 60, 70, and 80 °C, and the gelation time decreased at higher temperatures. However, when heated between 85 and 95 °C, a small amount of solution began to elute from the gel, and above 95 °C, the gel returned to solution in approximately 10 min (Figure 2-6). This may be due to the decomposition of the cross-linked structure via retro-Diels-Alder (retro-DA) reaction. Subsequently, the solution gelled again by cooling to 80-60 °C over approximately 1 h, indicating a reversible process.

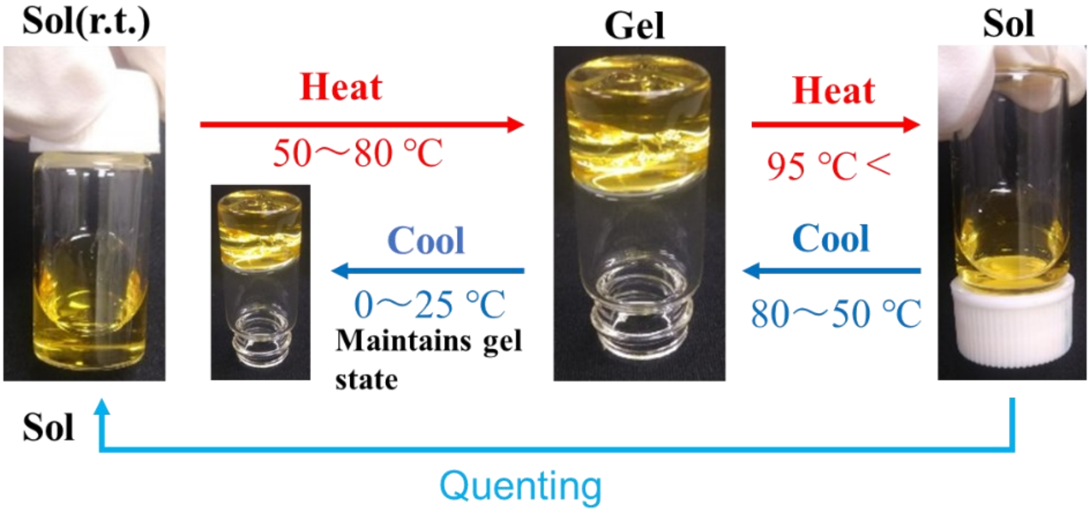


Figure 2-6 Thermal behavior of polyurea.

The DA reaction was observed by ^{1}H NMR measurements of PU-1 (Figure 2-7a) and a mixture of PU-1 with BMI at various temperatures (Figure 2-7b-d), showing the reaction of PU with the crosslinkers. In Figure 2a and b, all signals in the spectra obtained at 25 °C to the protons of PU and BMI were assigned. At 60 °C, proton signals were broadened, except for unreacted free BMI, indicating gelation. Additionally, proton signals from cross-linking points were barely detected at 3.6 ppm (m) and 6.4 ppm (l) (Figure 2-7c). Upon heating to 100 °C, these same signals reappeared clearly, and there was no detection of cross-linking points (Figure 2-7d), confirming both the retro-Diels-Alder reaction and gel-sol transition.

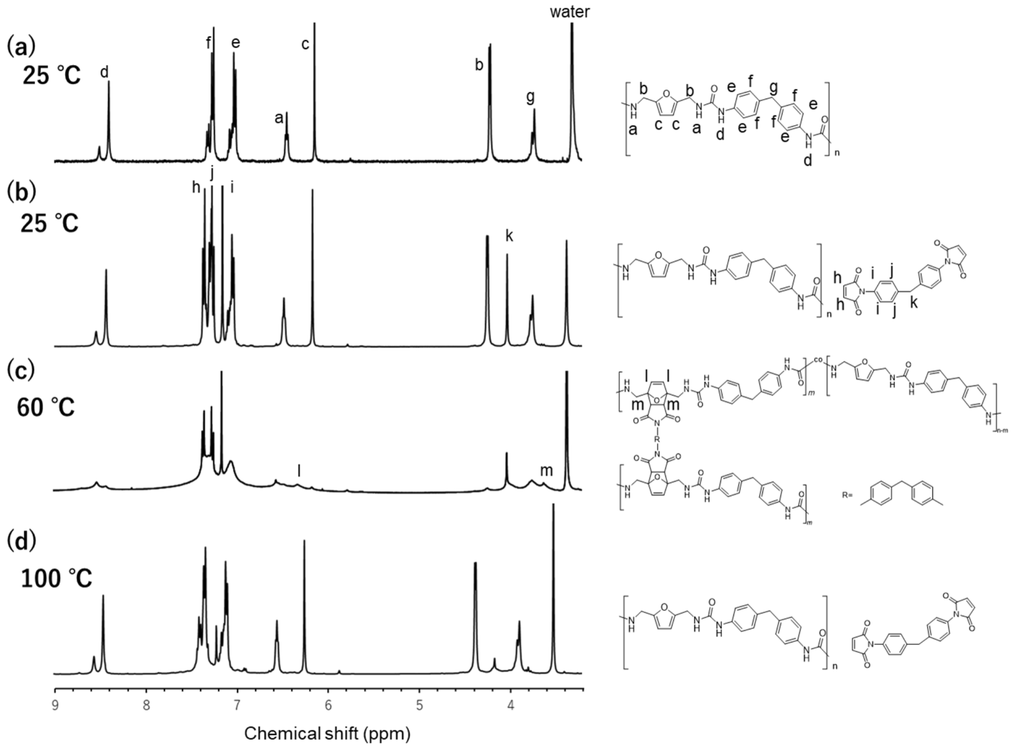


Figure 2-8 1H NMR (400 MHz, DMSO-d6) spectra of (a) PU-1 taken at 25 °C, (b) PU-1 mixed with BMI at 25 °C, (c) PU-1 mixed with BMI at 60 °C, (d) PU-1 mixed with BMI at 100 °C.

The compressive strength of the PU gels depended on the amount of BMI added, and we obtained gels with high elasticity when adding more than 10 mol % BMI (Figure 2-9). Among the gels, those containing 80 mol % BMI showed an initial modulus of elasticity of 0.8 kPa. In contrast, the modulus of elasticity tended to decrease from 0.2 to 0.5 kPa when the amount of BMI exceeded 100 mol % (Table S3). This attribution was an undesired reaction between excess BMI and the furan structure in the main chain, which makes it difficult to form a cross-linked structure.

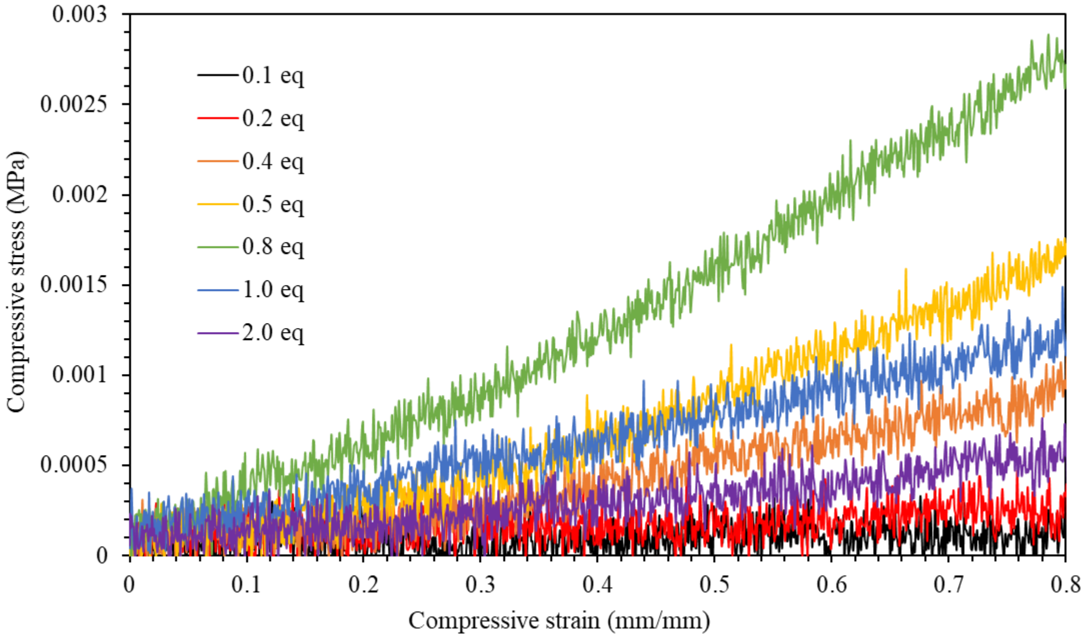


Figure 2-9 Stress-strain curves of PU-1 gels with different of amount of BMI addition.

Table 2-4 Mechanical properties of obtained PU-1 gels

Amount of BMI(mol%)	Elastic moduli E_0(kPa)
0.1	0.12 ± 0.01
0.2	0.18 ± 0.05
0.4	0.73 ± 0.04
0.5	0.72 ± 0.07
0.8	0.78 ± 0.2
1.0	0.51 ± 0.03
2.0	0.18 ± 0.04

Additionally, the solution did not gel upon quenching from 80 °C to about 15 °C in a water bath, even after 24 h of incubation. One reason for the hysteretic behavior of gelation is the slow recovery of the gel state, and the molecular mobility is too low to allow for a DA reaction to occur at room temperature. When a substituent is attached to either the 2- or 5-position of the furan ring, its reactivity is very high, whereas when substituents are attached to both positions, the reactivity is reported to be lower than monosubstituted examples [48]. In addition, the furan structure in the main chain has a lower molecular mobility than the substituted furan ring in the side chain. The low reactivity of 2,5-disubstituted furan may be related to the retro-DA reaction under conditions present at 80 °C. A thermoreversible sol-gel transition was also observed in DMAc, DMSO, and NMP. Soluble PUs other than PU-1 (PU-2 to PU-5) showed similar gelation behavior toward DMAc (Figure 2-10).

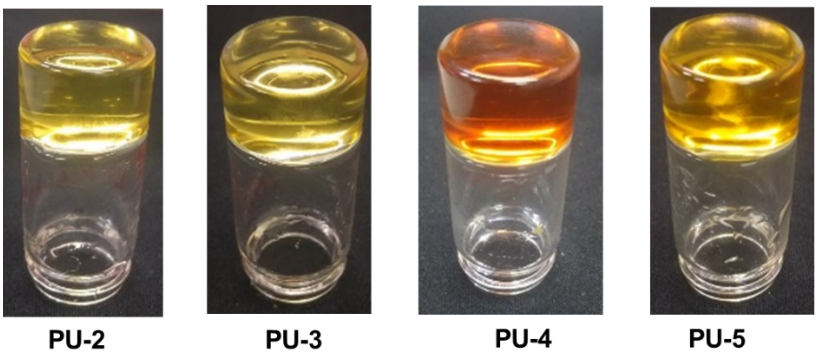


Figure 2-10 Photographs of gelation of various PUs

2.3. Thermal reversibility and reprocessing performance

A knife heated to approximately 100 °C was used to scar the PU-1 gel. The gel then stood at room temperature, and over a period of 1 to 2 min, the surface scar gradually disappeared (Figure 2-11). Spontaneous healing occurred during cooling, as seen in the photograph at the right side of Figure 3. From this result, it was conclude that the heated knife turned the surface into a solution via retro-DA reaction, which flowed and filled the incision. Healing then occurred due to the dynamic DA reaction.

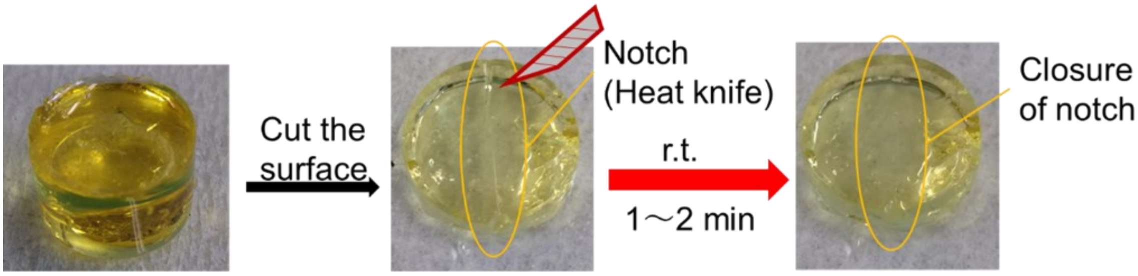


Figure 2-11 Rapid self-healing process of PU-1 gel surface cut by a heated knife.

Next, the formed gels were cut with an unheated knife at approximately 20 °C and placed the cut surfaces in contact with one other at room temperature. Healing did not occur. When the cut surfaces were placed in contact with each other for 1 h at 60 °C, it was confirmed adhesion of the cut surfaces. The adhesive was pulled using a spatula; however, the adhesive did not detach from the cut surfaces, and the gel was not torn at the bonded area (Figure 2-12). This phenomenon is different from healing based on the gelation of the solution, as the sample is already a gel at room temperature. In other words, self-healing occurred entirely within the gel state, where the DA reaction of the network occurred at the gel surface (Figure 2-12a). The gels PU-1 and PU-3, having dif-ferent types of network main chains, were cut using a knife at room temperature and placed in contact with each other at 60 °C. Healing was observed, forming a hetero-junction between PU-1 and PU-3. The pigments in each gel diffused throughout (Figure 2-12b). Usually, different polymers are not miscible with each other, as both networks are unable to intercalate at the molecular level. Such cross-healing behavior can only be based on the DA reaction on the outer surface of each gel.

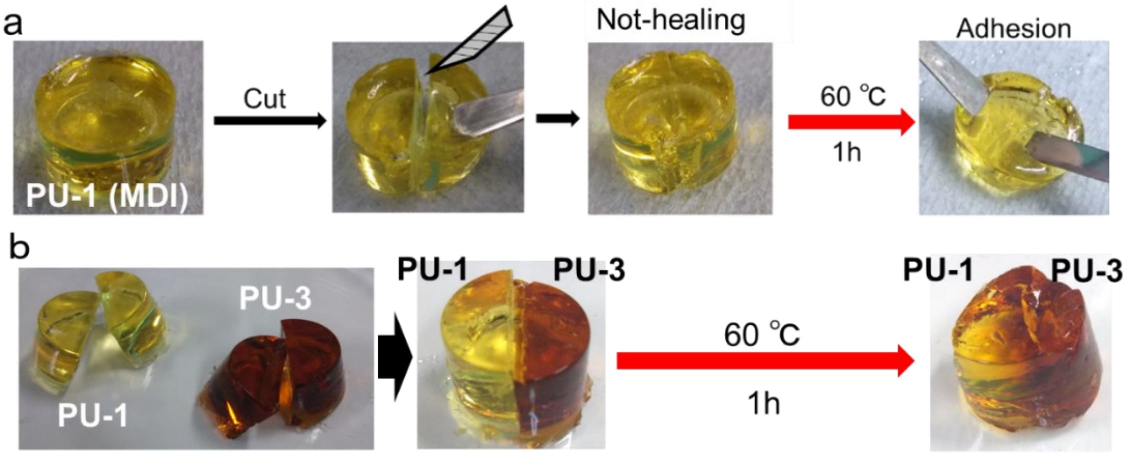


Figure 2-12 Self-healing of cross-linking PU gels by Diels-Alder reaction. (a) Self-healing of notch on PU-1 gel surface by heat, (b) Self-healing and adhesion between cross-linking PU-1 and PU-3 gels.

The results of compressive stress and fracture strain before and after self-repair for each cross-linker amount are shown below (Table 2-5). In addition, gels fractured by the compression tests were occurred by the Diels-alder reaction, processed again into gels, and then subjected to the same tests. The gel with 50 mol% had the highest strength, and the strength decreased with higher additions. the strength of the gels after repair by DA reaction increased for all but the 80 mol% sample from that before repair. The fracture strain was slightly lower than before repair. As in Figure 2-9, it is suggested that the physical properties decrease when the amount of BMI added exceeds a certain level because the furan structure in the main chain is excessively modified by BMI, making it difficult to form cross-links (Figure 2-13).

Table 2-5 Mechanical properties of obtained PUs gels and recovery of mechanical properties by DA reaction.

Amount of BMI(mol%)	Compressive strength, σ(kPa)	Compressive strength after self-healing, σ (kPa)	Compression strain, ε (mm/mm)	Compression strain after self-healing, ε (mm/mm)
10	17.2	23.2	0.9	0.8
50	39.4	60.5	0.6	0.6
80	23.9	15.5	0.5	0.4
100	33.6	38.4	0.6	0.6

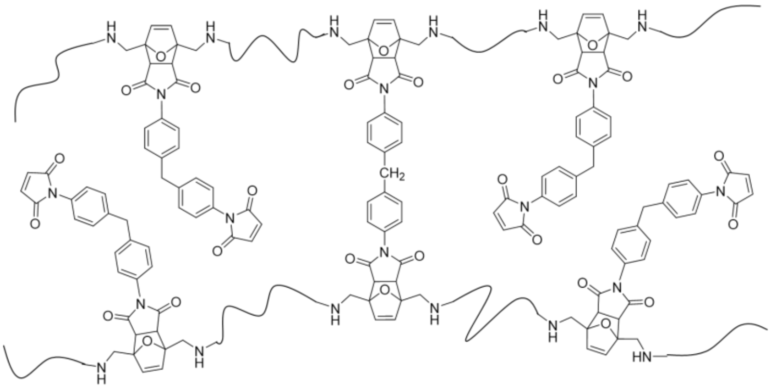


Figure 2-13 Decrease in crosslink density due to excessive addition of BMI.

2-4 Conclusions

The synthesis of furan-containing PUs by a polyaddition reaction of AMF with thirteen different diisocyanate compounds were reported. In the dry state, the PUs exhibited greater thermoresistance and hardness than conventional ones. Five PUs were soluble in polar solvents such as DMSO, DMAc, DMF, and NMP. The existence of a reversible DA reaction between the main chain furan ring and maleimide of the crosslinkers to generate a network structure was confirmed by NMR. The PUs were not gelated in the presence of bismaleimide at room temperature, but rather by heating to 50-80 °C. At temperatures higher than 80 °C, the gel transforms into a solution state as a result of retro-DA reactions. The solution showed gelation behavior with slow cooling but maintained the solution state upon rapid quenching to room temperature. Dy-namic covalent bonding extended to the healing behavior of the gels. While the cut surfaces did not adhere to each other at room temperature, we observed self-healing behavior at 60 °C. We also confirmed this healing phenomenon when we placed the cut surfaces of different PU gels in contact at 60 °C. This suggests that the outer surface of the cross-linked networks underwent a chemical reaction to form a heterojunction. The application of this phenomenon can be extended to the fabrication of self-healing films, gels, and elastomers.

2-5 References

[1] A. S. Hoffman, “Hydrogels for biomedical applications,” *Adv. Drug Deliv. Rev.*, **2012,** *64*, 18–23, doi: 10.1016/j.addr.2012.09.010.

[2] N. A. Peppas, P. Bures, W. Leobandung, and H. Ichikawa, “Hydrogels in pharmaceutical formulations,” *Eur. J. Pharm. Biopharm.*, **2000**, *50*, 1, 27–46, doi: 10.1016/S0939-6411(00)00090-4.

[3] D. Seliktar, “Designing Cell-Compatible Hydrogels,” *Science*, **2012**, *336*, 6085, 1124–112.

[4] C. Yang and Z. Suo, “Hydrogel ionotronics,” *Nat. Rev. Mater.*, **2018**, *3*, 6, 125–142, doi: 10.1038/s41578-018-0018-7.

[5] T. Jing, B. Xu, Y. Yang, M. Li, and Y. Gao, “Organogel electrode enables highly transparent and stretchable triboelectric nanogenerators of high power density for robust and reliable energy harvesting,” *Nano Energy*, **2020**,. *78*, 105373, doi: 10.1016/j.nanoen.2020.105373.

[6] J. Y. Song, Y. Y. Wang, and C. C. Wan, “Review of gel-type polymer electrolytes for lithium-ion batteries,” *J. Power Sources*, **1999**, *77*, 183–197.

[7] C. Keplinger, J. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, and Z. Suo, “Stretchable, Transparent, Ionic Conductors,” *Am. Assoc. Adv. Sci.*, **2013**, *341*, 984–98.

[8] Y. Kitazawa, K. Ueno, and M. Watanabe, “Advanced Materials Based on Polymers and Ionic Liquids,” *Chem. Rec.*, **2018**, *18*, 4, 391–409, **2018**, doi: 10.1002/tcr.201700041.

[9] N. Roy, B. Bruchmann, and J. M. Lehn, “DYNAMERS: Dynamic polymers as self-healing materials,” *Chem. Soc. Rev.*, **2015**, *44*, 11, 3786–3807, doi: 10.1039/c5cs00194c.

[10] T. Maeda, H. Otsuka, and A. Takahara, “Dynamic covalent polymers: Reorganizable polymers with dynamic covalent bonds,” *Prog. Polym. Sci.*, **2009**, *34*, 7, 581–604, doi: 10.1016/j.progpolymsci.2009.03.001.

[11] F. García and M. M. J. Smulders, “Dynamic covalent polymers,” *J. Polym. Sci. Part A Polym.*

Chem., **2016**, *54*, 22, 3551–3577, doi: 10.1002/pola.28260.

[12] L. L. D. Montarnal, M. Capelot, F. Tournilhac, "Silica-Like Malleable Materials from Permanent Organic Networks," *Am. Assoc. Adv. Sci.*, **2011**, *334*, 965–969.

[13] T. Maeda, S. Kamimura, T. Ohishi, A. Takahara, and H. Otsuka, "Synthesis of polyethylene/polyester copolymers through main chain exchange reactions via olefin metathesis," *Polymer*, **2014**, *55*, 24, 6245–6251, doi: 10.1016/j.polymer.2014.10.001.

[14] Y. Lu and Z. Guan, "Olefin Metathesis for Effective Polymer Healing via Dynamic Exchange of Strong Carbon − Carbon Double Bonds," *J. Am. Chem. Soc.*, **2012**,. *134*, 34, 14226–14231.

[15] J. J. Cash, T. Kubo, A. P. Bapat, and B. S. Sumerlin, "Room-temperature self-healing polymers based on dynamic-covalent boronic esters," *Macromolecules*, **2015**, *48*, 7, 2098–2106, doi: 10.1021/acs.macromol.5b00210.

[16] Y. Chen, D. D. Dussan, D. Wu, W. Wang, Y. Y. Peng, A. B. Asha, D. G. Hall, K. Ishihara, R. Narain, "Bioinspired Self-Healing Hydrogel Based on Benzoxaborole-Catechol Dynamic Covalent Chemistry for 3D Cell Encapsulation," *ACS Macro Lett.*, **2018**, *7*, 8, 904–908, doi: 10.1021/acsmacrolett.8b00434.

[17] S. Ji, W. Cao, Y. Yu, and H. Xu, "Dynamic diselenide bonds: Exchange reaction induced by visible light without catalysis," *Angew. Chemie - Int. Ed.*, **2014**,. *53*, 26, 6781–6785, doi: 10.1002/anie.201403442.

[18] H. Otsuka, S. Nagano, Y. Kobashi, T. Maeda, and A. Takahara, "A dynamic covalent polymer driven by disulfide metathesis under photoirradiation," *Chem. Commun.*, **2010**, *46*, 7, 1150–1152, doi: 10.1039/b916128g.

[19] F. W. Xiangxu Chen, Matheus A Dam, Kanji Ono, Ajit Mal, Hongbin Shen, Steven R Nutt, Kevin Sheran, K. Sheran, and F. Wudl, "A thermally re-mendable cross-linked polymeric material," *Science*, **2002**, *295*, 5560, 1698–1702, doi: 10.1126/science.1065879.

[20] K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara, and H. Otsuka, "Self-healing of chemical gels cross-linked by diarylbibenzofuranone-based trigger-free dynamic covalent bonds at room temperature," *Angew. Chemie - Int. Ed.*, **2012**, *51*, 5, 1138–1142, doi: 10.1002/anie.201104069.

[21] B. T. Michal, C. A. Jaye, E. J. Spencer, and S. J. Rowan, "Inherently photohealable and thermal shape-memory polydisulfide networks," *ACS Macro Lett.*, **2013**, *2*, 8, 694–699, doi: 10.1021/mz400318m.

[22] J. Shen, L. Chang, D. Chen, Y. Wang, W. Li, Y. He, J. Qin, "Cross-linking induced thermo-responsive self-healing hydrogel with gel-sol–gel transition constructed on dynamic covalent bond," *J. Polym. Res.*, **2021**, *28*, 132, doi: 10.1007/s10965-021-02492-3.

[23] Y. Higaki, H. Otsuka, and A. Takahara, "A thermodynamic polymer cross-linking system based on radically exchangeable covalent bonds," *Macromolecules*, **2006**, *39*, 6, 2121–2125, doi: 10.1021/ma052093g.

[24] K. Yu, A. Xin, and Q. Wang, "Mechanics of self-healing polymer networks crosslinked by dynamic bonds," *J. Mech. Phys. Solids*, **2018**, *121*, 409–431, doi: 10.1016/j.jmps.2018.08.007.

[25] X. He, D. W. Hanzon, and K. Yu, "Cyclic welding behavior of covalent adaptable network polymers," *J. Polym. Sci. Part B Polym. Phys.*, **2018**,. *56*, 5, 402–413, doi: 10.1002/polb.24553.

[26] A. Susa, R. K. Bose, A. M. Grande, S. Van Der Zwaag, and S. J. Garcia, "Effect of the Dianhydride/Branched Diamine Ratio on the Architecture and Room Temperature Healing Behavior of Polyetherimides," *ACS Appl. Mater. Interfaces*, **2016**, *8*, 49, 34068–34079, doi: 10.1021/acsami.6b10433.

[27] E. B. Stukalin, L. H. Cai, N. A. Kumar, L. Leibler, and M. Rubinstein, "Self-healing of unentangled polymer networks with reversible bonds," *Macromolecules*, **2013**, *46*, 18, 7525–7541, doi: 10.1021/ma401111n.

[28] M. Nakahata, Y. Takashima, and A. Harada, “Cutting-Edge Science of Cyclodextrin Supramolecular Polymeric Materials Containing Cyclodextrins,” *Chem. Pharm. Bull.*, **2017**, *65*, 4, 330–335.

[29] T. Sekine, T. Kakuta, T. Nakamura, Y. Kobayashi, Y. Takashima, and A. Harada, “A macroscopic reaction: Direct covalent bond formation between materials using a Suzuki-Miyaura cross-coupling reaction,” *Sci. Rep.*, **2014**,. *4*, 1–6, doi: 10.1038/srep06348.

[30] N. Miyaura and A. Suzuki, “Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds,” *Chem. Rev.*, **1995**, *95*, 7, 2457–2483, doi: 10.1021/cr00039a007.

[31] O. R. Schade, P. K. Dannecker, K. F. Kalz, D. Steinbach, M. A. R. Meier, and J. D. Grunwaldt, “Direct Catalytic Route to Biomass-Derived 2,5-Furandicarboxylic Acid and Its Use as Monomer in a Multicomponent Polymerization,” *ACS Omega*, **2019**, *4*, 16, 16972–16979, doi: 10.1021/acsomega.9b02373.

[32] X. Chen, F. Wudl, A. K. Mal, H. Shen, and S. R. Nutt, “New thermally remendable highly cross-linked polymeric materials,” *Macromolecules*, **2003**, *36*, 6, 1802–1807, doi: 10.1021/ma0210675.

[33] R. Gheneim, C. Perez-Berumen, and A. Gandini, “Diels-Alder reactions with novel polymeric dienes and dienophiles: Synthesis of reversibly cross-linked elastomers,” *Macromolecules*, **2002**, *35*, 19, 7246–7253, doi: 10.1021/ma020343c.

[34] A. M. Peterson, R. E. Jensen, and G. R. Palmese, “Room-temperature healing of a thermosetting polymer using the diels-alder reaction,” *ACS Appl. Mater. Interfaces*, **2010**, *2*, 4, 1141–1149, doi: 10.1021/am9009378.

[35] P. A. Pratama, M. Sharifi, A. M. Peterson, and G. R. Palmese, “Room temperature self-healing thermoset based on the diels-alder reaction,” *ACS Appl. Mater. Interfaces*, **2013**, *5*, 23, 12425–12431, doi: 10.1021/am403459e.

[36] Y. S. Patel and H. S. Patel, “Thermoplastic-thermosetting merged polyimides via furan-maleimide Diels–Alder polymerization,” *Arab. J. Chem.*, **2017**, *10*, 1373–1380, doi: 10.1016/j.arabjc.2013.04.010.

[37] B. Shojaei, M. Najafi, A. Yazdanbakhsh, M. Abtahi, and C. Zhang, “A review on the applications of polyurea in the construction industry,” *Polym. Adv. Technol.*, **2021**, *32*, 8, 2797–2812, doi: 10.1002/pat.5277.

[38] J. A. Pathak, J. N. Twigg, K. E. Nugent, D. L. Ho, E. K. Lin, P. H. Mott, C. G. Robertson, M. K. Vukmir, T. H. Epps, C. M. Roland, “Structure evolution in a polyurea segmented block copolymer because of mechanical deformation,” *Macromolecules*, **2008**, *41*, 20, 7543–7548, doi: 10.1021/ma8011009.

[39] G. Toader, A. Diacon, E. Rusen,F. Rizea, M. Teodorescu, P. O. Stanescu, C. Damian, A. Rotariu, E. Trana, F. Bucur, R. Ginghina, “A facile synthesis route of hybrid polyurea-polyurethane-mwcnts nanocomposite coatings for ballistic protection and experimental testing in dynamic regime,” *Polymers (Basel).*, **2021**, *13*, 10, 1618, doi: 10.3390/polym13101618.

[40] F. J. De Zwart, P. C. M. Laan, N. S. V. Leeuwen, E. O. Bobylev, E. R. A. V. Hove, S. Mathew, N. Yan, J. Flapper, K. J. V. D. Berg, J. N. H. Reek, B. D. Bruin., “Isocyanate-Free Polyurea Synthesis via Ru-Catalyzed Carbene Insertion into the N-H Bonds of Urea,” *Macromolecules*, **2022**, *55*, 9690–9696, doi: 10.1021/acs.macromol.2c01457.

[41] A. Sánchez-Ferrer, D. Rogez, and P. Martinoty, “Synthesis and characterization of new polyurea elastomers by Sol/Gel chemistry,” *Macromol. Chem. Phys.*, **2010**, *211*, 15, 1712–1721, doi: 10.1002/macp.201000117.

[42] E. Gauch, J. LeBlanc, and A. Shukla, “Near field underwater explosion response of polyurea coated composite cylinders,” *Compos. Struct.*, **2018**, *202*, 836–852, doi: 10.1016/j.compstruct.2018.04.048.

[43] M. Broekaert, “Polyurea spray coatings: The technology and latest developments,” *Paint Coatings Ind.*, **2022**, *18*, 10, 80–93.

[44] H. Chen, Z. Sun, H. Lin, C. He, and D. Mao, “Neuron Inspired All-Around Universal Telechelic Polyurea with High Stiffness, Excellent Crack Tolerance, Record-High Adhesion, Outstanding Triboelectricity, and AIE Fluorescence,” *Adv. Funct. Mater.*, **2022**, *32*, 36, 1–12, doi: 10.1002/adfm.202204263.

[45] M. Manivannan and S. Rajendran, “Investigation of Inhibitive Action of Urea- Zn 2 + System in the Corrosion Control of,” *Int. J. Eng. Sci. Technol.*, **2011**, *3*, 11, 8048–8060.

[46] S. K. Burgess, J. E. Leisen, B. E. Kraftschik, C. R. Mubarak, R. M. Kriegel, and W. J. Koros, “Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate),” *Macromolecules*, **2014**, *47*, 1383–1391.

[47] D. C. Xue-lian Li and State, “Synthesis and Characterization of Aromatic/Aliphatic Co-polyureas,” *J. Appl. Polym. Sci.*, **2010**, *116*, 5, 2658–2667, doi: 10.1002/a

[48] A. Gandini, “The furan/maleimide Diels-Alder reaction: A versatile click-unclick tool in macromolecular synthesis,” *Prog. Polym. Sci.*, **2013**, *38*, 1, 1–29, doi: 10.1016/j.progpolymsci.2012.04.002.

Chapter 3

Fermentative production of 2-(4-aminophenyl) ethylamine to synthesize a novel heat-resistant biopolyurea

3-1 Introduction

Aromatic diamines are monomers that can be polymerized to create thermoresistant aramids, polyimides, polybenzimidazoles, and polybenzoxazoles with broad industrial applications [1–5]. Examples include p-phenylenediamine, 4,4'-diaminodiphenyl oxide, 3,3',4,4'-tetraaminodiphenyl, and 4,6-diaminoresorcinol, from which the popular super engineering plastics, Kevlar®, Kapton®, Celazole®, and Zylon®, are respectively generated. These monomers harbor two amino residues directly bound to benzene rings. Aliphatic diamines are monomers of popular nylons, as well as of potential raw materials for synthesizing high-performance materials including liquid crystals [6-8]. Polyureas (PUs) are produced using monomeric aromatic and aliphatic diamines [9, 10]. Such PUs with excellent tensile strength and thermochemical resistance are condensation products of diamine and diisocyanate monomers, and they are applied as commodity plastics, foams, and coating agents, and biomedical materials [11, 12]. Most diamine monomers are products of petroleum chemistry, but they could be replaced with those derived from biomass, which would support a sustainable society. Synthetic biology using microbial fermentation is under development to enable the production of biomaterials including biomonomers for bioplastic synthesis [13–15]. Fermented putrescine and cadaverine are counter diamines that generate the aliphatic polyamide nylons 4, 6, and 5, 6 when condensed with dicarboxylic acids [16, 17]. Genetically manipulated bacteria are being developed for fermenting aromatic diamines. We constructed a microbial fermentation platform that converts biomass-derived glucose to 4-aminophenylalanine, 4-aminocinnamic acid, and other aromatic amines [13, 14]. The 4-Aminophenylalanine is a natural diamine, and the 4-aminocinnamic acid is photodimerized to generate artificial diamine 4,4'-diaminotruxillic acid. These compounds are polycondensed into aromatic polyamides [18] and polyimides [19] with extremely high heat resistance, compared with biomass-derived plastics, as their decomposition temperatures (T_{d10}) are 367 °C and 374 °C at 10% weight loss, respectively. Thermostable bio-based PUs can also be developed from diamine monomer 4-aminophenylalanine and 4,4'-diaminotruxillic acid [20, 21]. Microbial diamines are thus novel monomers for producing aromatic biopolymers.

High-performance polymer materials are synthesized from diamine 2-(4-aminophenyl)ethylamine (4APEA) that has one aliphatic and one aromatic amine residue (Fig. 1a). For example, when condensed with isophthalic acid, 4APEA produces a highly thermoresistant aramid [22]. Our fermentation platform produces 4APEA using glucose as the raw material [13]. A recombinant Escherichia coli strain expresses the Pseudomonas fluorescens papABC genes, which convert cellular chorismate to 4-aminophenylpyruvate, and endogenous aminotransferases aminate 4-aminophenylpyruvate to 4-aminophenylalanine (4APhe). Introducing the exogenous L-amino acid decarboxylase (AADC) gene of Solanum lycopersicum (tomato) to the E. coli strain converted 4-aminophenlyalanine to 4APEA (Fig.1a). This study optimized the fermentation conditions of 4APEA. Controlling the dissolved oxygen (DO) concentration during fermentation is critical for the maximal production (3.5 g/L) of 4APEA and to prevent oxidative 4APEA degradation. We purified 4APEA from fermentation medium, then condensed it with hexamethylene diisocyanate or methylenediphenyl 4,4'-diisocyanate to produce novel semi-bio-based aromatic PUs with high thermoresistance.

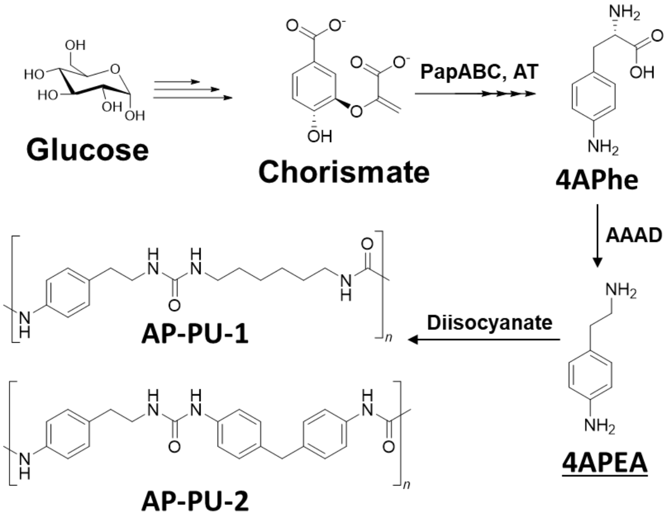


Figure 3-1 Effect of glucose and media on 4APEA production by *E. coli* NDPGADa

3-2 Materials and Methods

3-2-1 Synthesis of AP-PU-1 and AP-PU-2

Purified 4APEA (0.10 g, 0.76 mmol) and methylenediphenyl 4,4'-diisocyanate (0.19 g, 0.76 mmol) were dissolved in 1 mL of dimethyl sulfoxide (DMSO) and incubated at room temperature under nitrogen for 48 h. Reaction products were precipitated with pure methanol to obtain PU-1 as a pale brown powder with quantitative yield. Under the same reaction conditions, 4APEA was polymerized with hexamethylene diisocyanate (0.13 g, 0.76 mmol) to obtain a quantitative yield of PU-2.

3-2-2 Analytical methods

The proton nuclear magnetic resonance (^{1}H-NMR) of 0.5-mM specimens in DMSO-d6 was measured in borosilicate glass NMR test tubes (ϕ 4.932–4.970 × 7 in; Fujifilm Wako Pure Chemical Co., Osaka, Japan) using an AG 400 MHz, 54-mm spectrometer (Bruker Biospin Corp., Billerica, MA, USA). Thermal stability and the decomposition temperatures required for 10% weight loss (T_{d10}) were assessed by increasing temperatures at a rate of 5°C/min using an STA7000 thermogravimetric analyzer (Hitachi High-Technologies Co., Tokyo, Japan).

3-3 Results and discussion

3-3-4 Synthesis of AP-PU-1 and AP-PU-2 derived from biomass.

The fermented 4APEA was polymerized with diisocyanates by a polyaddition reaction to yield PUs. The red liquid preparation of fermented 4APEA was polymerized with diphenyl diisocyanate and hexamethylene diisocyanate because 4APEA·HCl could not be polymerized. The resulting pale brown and grayish-white powders were respectively designated AP-PU-1 and AP-PU-2 (Figure 3-4b, c)

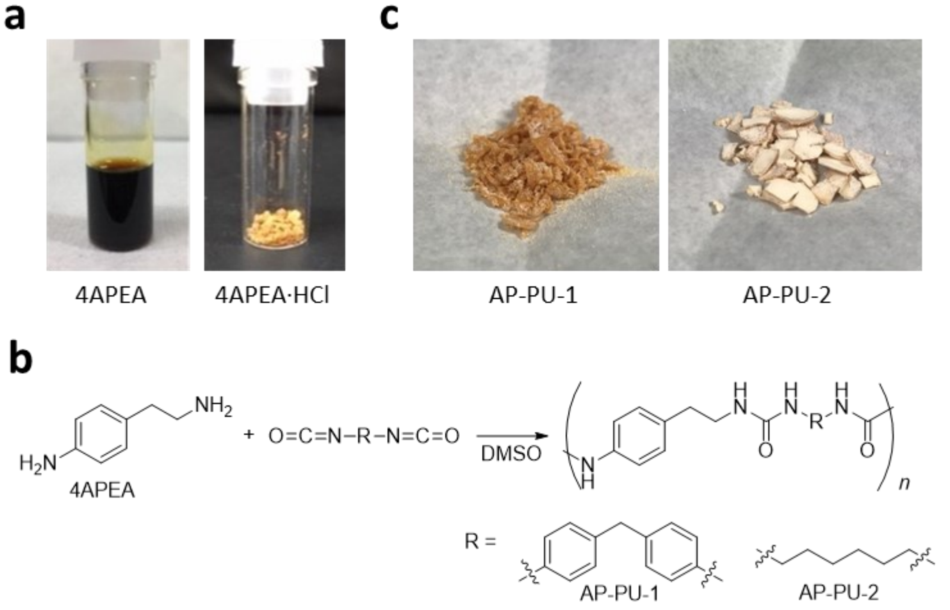


Figure 3-4 Polyurea synthesis from purified fermented 4APEA. (a) Purified 4APEA (*left*) and 4APEA· HCl (*right*). (b) AP-PU-1 and AP-PU-2 were synthesized by polymerizing purified 4APEA with methylene diisocyanate and hexamethylene diisocyanate, respectively. (c) Corresponding PUs.

Structure characterization

The ^{1}H-NMR spectra of PUs revealed peaks of aromatic protons at 6.7–7.5 and 6.5–7.3 ppm, respectively, and urea protons at 8.3–8.6, and 5.7–5.9, and 8.3 ppm, respectively (Figure 3-5). Integration ratio of aromatic protons to NH proton of urea bonds was in agreement with the predicted structure. These results confirmed the targeted structure of the PUs.

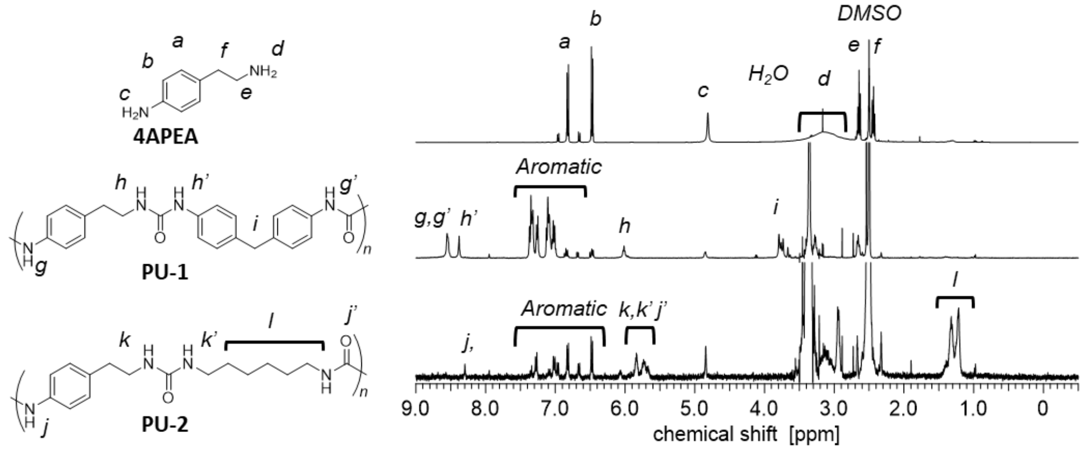


Figure 3-5 ^{1}H NMR spectra at 400 MHz measured in DMSO-d_6.

Infrared spectra also indicated that the obtained PUs. In AP-PU-1, an N-H stretch was identified around 3300 cm^{-1}, and in AP-PU-2, an N-H stretch around 3300 cm^{-1} and a C-H stretch at 2600-2900 cm^{-1} were identified. This is suggested to be due to the amine origin of the urea bond and the saturated aliphatic chain (Figure 3-6).

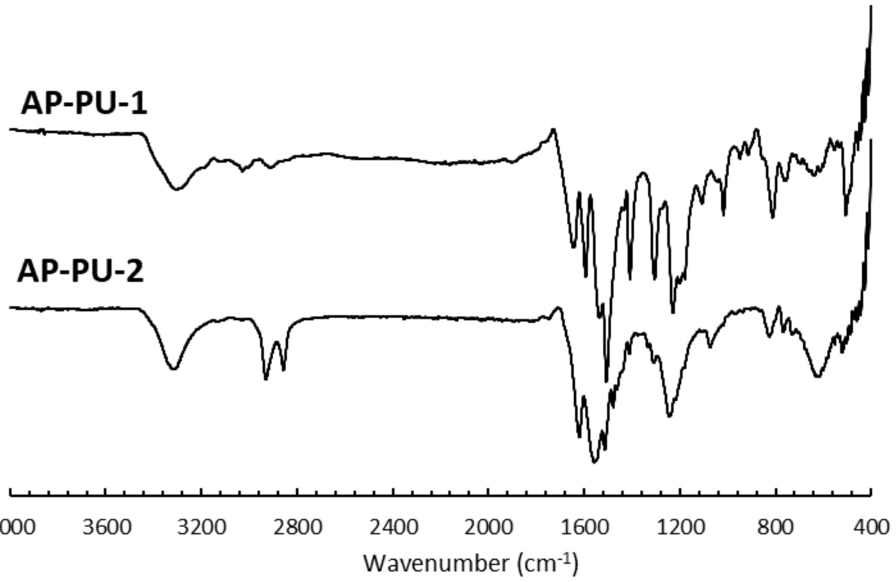


Figure 3-6 FT-IR spectra of the PUs using bio-based 4APEA.

The molecular weights of PUs were not measured since they were not solubilized in common organic solvents (*N, N'*-dimethylformamide, chloroform, tetrahydrofuran, and dimethylacetamide) for GPC. Number-average molecular weights of the soluble PUs were estimated from integration ratios of the monomer unit (peaks *i* and *j* for AP-PU-1, and peaks *r, q* and *q'* for AP-PU-2) and predicted protons at the chain ends of the polymers(δ = 4.8 ppm for PUs), and found to be 6,800 and 1,000, respectively. This suggests that the soluble PUs comprise oligomeric PUs (Figure 3-5). This study could not assign the structure of insoluble PUs using NMR. They are predicted to consist of highly condensed PUs while it is possible that they may also include diisocyanate polymers and other polymers.

Thermal properties

The thermal degradation properties of PUs were analyzed by thermogravimetric analysis (TGA) under nitrogen (Figure 3-7). T_{d10} for PUs were 276 °C and 302 °C, respectively. These temperatures were similar to those of another thermotolerant bio-based PUs prepared from the biobased diamine 4,4'-diaminotruxillic acid and diisocyanate (T_{d10} = 275°C) [20], and other biomass-derived PUs. Residual char remaining after heating PUs at 800 °C was ≤ 5%, indicating that considerable amounts of PUs were pyrolytically degraded.

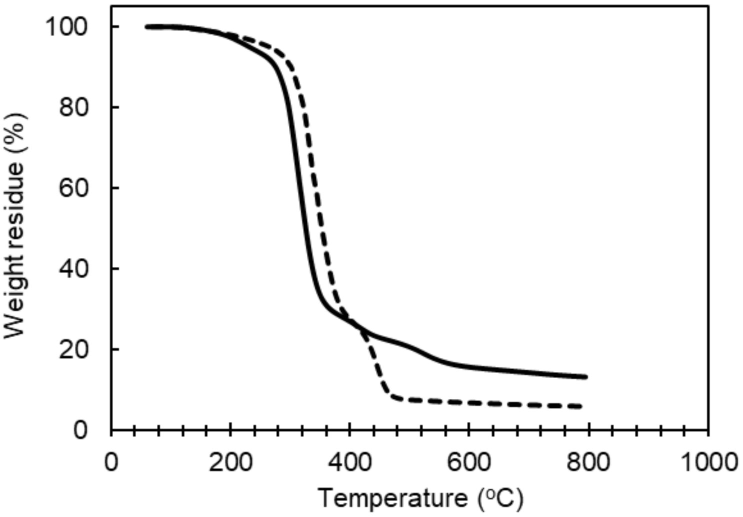


Figure 3-7 Thermogravimetric analysis of PUs under nitrogen.

Differential scanning calorimetry (DSC) of PUs showed no obvious glass transition temperature (T_g) and melting points (T_m) in the analytical range from 25 °C-50 °C (Figure 3-8)

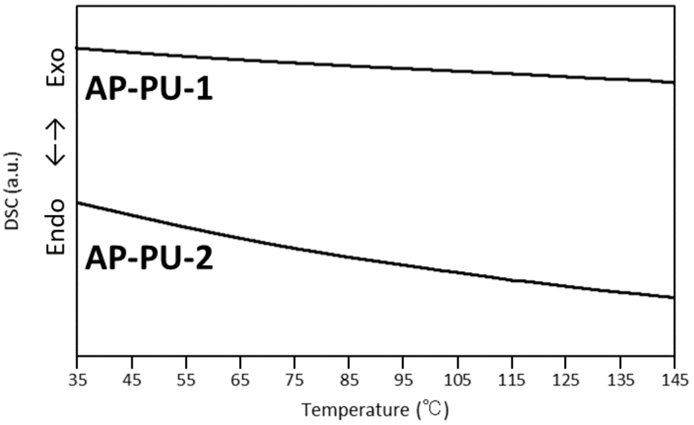


Figure 3-8 Differential scanning calorimetry thermograms of AP-PU-1 (*upper*) and AP-PU-2 (*lower*) upon heating. Arrow indicates directions of endothermic (endo) and exothermic (exo) heat flows.

3-4 Conclusions

In this study, we produced diamines derived from microorganisms and optimized the conditions for their production. The resulting diamine monomers were reacted with diisocyanate compounds to obtain aliphatic and aromatic PUs.

The development of bio-based polymers requires the production of the purest monomers in sufficient quantities to optimize the conditions for chemical polymerization. Here, fermentation conditions were optimized to produce 4APEA at the gram order level in a bench-top jar fermenter. This allowed for repeated purification of immediately polymerizable compounds of subgram order. It optimizes polymerization and contributes to obtaining highly polymerized biopolymers. In addition, fine-tuning of fermentation conditions, genetic modification, and process engineering will improve the production efficiency of 4APEA and contribute to the development of new polyamides and polyimides from microbially derived 4APEA. One of the key factors to improve fermentation productivity is to control and inhibit oxidative degradation of 4APEA. Oxidation by the host E. coli degrades some of the 4APEA accumulated during fermentation [21]. However, aromatic amines and diamines, which are easily oxidized under physiological conditions, are susceptible to biological oxidation via oxygen supplied to the culture vessel [22, 23]. In any case, since both biotic and abiotic reactions require molecular oxygen, the control of oxygen supply as shown in this study should be important.

In this study, biomass-derived 4APEA was polymerized with petroleum-derived diisocyanate to produce partially biomass-derived AP-PU-1 and AP-PU-2. Both showed excellent thermophysical properties, with T_{d10} values of 270-300 °C or higher. This is more than 100 °C higher than that of conventional petroleum-derived polyureas. Although petroleum-derived diisocyanate was used in this study, it can be replaced with a biomass-derived diisocyanate to produce a completely biomass-derived PU. In recent years, there has also been great interest in the production of the monomer hexamethylenediamine from renewable resources [24, 25]. Since the chemical industry currently produces hexamethylene diisocyanate, the counter-diamine of AP-PU-2, from hexamethylene diamine, the combination of this technology and our results should constitute a sustainable technology. In summary, this study is the first example of synthesis of aromatic PU from diamines derived from microorganisms. This is expected to open new possibilities for the application of biomass-derived polymers, which is necessary for the development of a sustainable society.

3-5 References

[1] Trigo-López M, Sanjuán AM, Mendía A, et al. Heteroaromatic polyamides with improved thermal and mechanical properties. *Polymers (Basel),* **2020**, *12,* 1793.

[2] Kubota Y, Nakada S, Sugi Y. New heat-resistant and soluble aramids synthesized by palladium-catalyzed carbonylation-polycondensation. *Mater Trans* **2002**, *43,* 326–331.

[3] Reglero Ruiz JA, Trigo-López M, García FC, García JM. Functional aromatic polyamides. *Polymers (Basel),* **2017,** *9*, 414.

[4] Yang CP, Lin JH. Syntheses and properties of aromatic polyamides and polyimides based on 3,3-bis[4-(4-aminophenoxy)phenyl]- phthalimidine. *Polymer (Guildf),* **1995,** *36*, 2607–2614.

[5] Park ES, Sieber J, Guttman C, et al. Methodology for detecting residual phosphoric acid in polybenzoxazole fibers. *Anal Chem,* **2009**; *81*, 9607–9617.

[6] Inoue T, Kakimoto MA, Imai Y, Watanabe J. First observation of a thermotropic liquid crystal in a simple polyimide derived from 1, 11-diaminoundecane and 4, 4''-terphenyltetracarboxylic acid. *Macromolecules*, **1995**, *28*, 6368-6370.

[7] Zhuang Y, Seong JG, Lee YM. Polyimides containing aliphatic/alicyclic segments in the main chains. *Prog Polym Sci,* **2019,** *92*, 35-88.

[8] Zou W, Lin X, Terentjev EM. Amine-acrylate liquid single crystal elastomers reinforced by hydrogen bonding. *Adv Mater,* **2021**, *33*, 2101955.

[9] Santana JS, Cardoso ES, Triboni ER, Politi MJ. Polyureas Versatile Polymers for New Academic and Technological Applications. *Polymers,* **2021**, *13,* 4393.

[10] Toader G, Rusen E, Teodorescu M, et al. Novel polyurea polymers with enhanced mechanical properties. *J Appl Polym Sci,* **2016,** *133*, 1–7.

[11] Mohotti D, Ngo T, Raman SN, et al. Plastic deformation of polyurea coated composite aluminium plates subjected to low velocity impact. *Mater Des*, **2014,** *56*, 696–713.

[12] Restani RB, Morgado PI, Ribeiro MP, et al. Biocompatible Polyurea Dendrimers with pH-Dependent Fluorescence. *Angew Chem Int Ed.*, **2012,** *51*, 5162-5165.

[13] Masuo S, Zhou S, Kaneko T, Takaya N. Bacterial fermentation platform for producing artificial aromatic amines. *Sci Rep,* **2016,** *6,* 25764.

[14] Kawasaki Y, Aniruddha N, Minakawa H, et al. Novel polycondensed biopolyamide generated from biomass-derived 4-aminohydrocinnamic acid. *Appl Microbiol Biotechnol,* **2018,** *102,* 631–639.

[15] Zahoor A, Lindner SN, Wendisch VF. Metabolic engineering of Corynebacterium glutamicum aimed at alternative carbon sources and new products. *Comput Struct Biotechnol J*, **2012,** *3,* e201210004.

[16] Schneider J, Wendisch VF. Putrescine production by engineered *Corynebacterium glutamicum*. *Appl Microbiol Biotechnol,* **2010**, *88*, 859–868.

[17] Xue C, Hsu KM, Chiu CY, et al. Fabrication of bio-based polyamide 56 and antibacterial nanofiber membrane from cadaverine. *Chemosphere,* **2021,** *266,* 128967.

[18] Tateyama S, Masuo S, Suvannasara P, et al. Ultrastrong, transparent polytruxillamides derived from microbial photodimers. *Macromolecules,* **2016,** *49*, 3336–3342.

[19] Minakawa H, Masuo S, Kaneko T, Takaya N. Fermentation and purification of microbial monomer 4-amminocinnamic acid to produce ultra-high performance bioplastics. *Process Biochem,* **2019,** *77*, 100–105.

[20] Jin X, Tateyama S, Kaneko T. Salt-induced reinforcement of anionic bio-polyureas with high transparency. *Polym J,* **2015,** *47*, 727–732.

[21] Díaz E, Ferrández A, Prieto MA, García JL. Biodegradation of aromatic compounds by *Escherichia coli*. *Microbiol Mol Biol Rev,* **2001**, *65*, 523-569.

[22] Kovtun GA, Aleksandrov AL. Amine oxidation by molecular oxygen. *Russ Chem Bull,* **1977**, *26*, 29–35.

[23] Murahashi S, Imada Y. Amine oxidation. *Transition Metals for Organic Synthesis, Vol.2, 2^{nd} ed. (Eds.), Wiley-VCH, Weinheim*, **2004**, 497-507

[24] Wang HH, Wu SP. Synthesis of aromatic poly(urea-imide) with heterocyclic side-chain structure. *J Appl Polym Sci,* **1999,** *74,* 1719-1730.

[25] Dros AB, Larue O, Reimond A, et al. Hexamethylenediamine (HMDA) from fossil- vs. bio-based routes: an economic and life cycle assessment comparative study. *Green Chem,* **2015,** *17,* 4760-4772.

Chapter 4

Syntheses of photo-induced hydrolysis polyurea using itaconic acid

4-1 Introduction

The depletion of fossil raw materials and the use of conventional plastics have proven to contribute to major environmental problems such as water and air pollution [1]. To this end, the production of materials with low environmental impact is essential for the realization of a sustainable, low-carbon society. For example, through the development of degradable materials and the reuse and recycling of existing materials, we are looking for ways to make polymers suitable for the circular economy [2, 3], and as a step toward sustainable chemistry [4, 5], bio-based molecules synthesized from renewable raw materials can provide an alternative monomer source for polymers can be used. As a result, bio-based polymers such as biopolyesters [6] and biopolyamides [7] are being actively developed. However, their thermodynamic performance is not very high, and they face stiff competition from commodity plastics [8, 9], making their widespread use difficult. In addition, the variety of biobased polymers is not comparable to that of petroleum-derived polymers, and many of them have limited applications. Rigid polyamides containing aromatic and heterocyclic rings have high strength, high fatigue resistance, and high wear resistance due to the presence of strong intermolecular hydrogen bonds. The presence of ring-based intermolecular hydrogen bonding and π-electron stacking results in high strength, high fatigue resistance, and high wear resistance [10, 11].

One biomass monomer is itaconic acid (IA); IA is obtained by thermal conversion of citric acid [12] and is used in a variety of polymers. It was also used as a fermentation product of Aspergillus terreus in the presence of carbohydrate-containing substances such as cornstarch [13]. It is thus readily available at low cost; due to the presence of one unsaturated group and two carboxylic acid moieties, IA reacts readily with diamines, and heterocyclic 3-carboxy-2-pyrrolidines are readily formed by azamichael addition and amidation [14]. In addition, for polymers with pyrrolidone rings, photoirradiation causes ring-opening reaction of the pyrrolidone ring, giving carboxylic acids on the side chains; photoinduced solubilization of polyamides in water was reportedly observed after UV irradiation using high-pressure mercury vapor lamps in the 250-450 nm wavelength range [15]. In addition, corrosion behavior in soil and solubilization behavior in water by UV irradiation are also shown. The water solubilizing functionality is expected to prevent accidental ingestion by marine organisms, promote biodegradation by microorganisms, and solve disposal problems in landfills [15]. Besides, it has also been reported to be affected by enzymatic actions, such as shape collapse by pepsin, suggesting the possibility of biodegradation [16, 17]. Thus, molecular designs containing pyrrolidone rings in the main chain can expand the field of green and sustainable polymers.

To apply these in prior fields, it is necessary to elucidate the structure-property relationships of IA-type polymers with pyrrolidone rings. Prior studies have developed a variety of IA-derived polyamides with higher thermodynamic performance than previous aliphatic polyamides. However, no examples of such materials have been reported other than polyamides and inorganic/metal oxide composites, which limits their use to polyamides only at this time. Therefore, we focused on the synthesis of diamine monomers containing pyrrolidone rings from IA, which would enable the synthesis of polyimides and PUs in addition to polyamides. In this chapter, we aimed to synthesize photoinduced hydrophilic PUs incorporating pyrrolidone rings in the main chain and to evaluate their physical properties and functionality. The physical properties of the obtained PUs will be compared with those of the PUs in the chapters to clarify the structure-property correlations.

4-2 Materials and methods

4-2-1 Materials

2,5-Bis(aminomethyl)furan (99% purity) was provided from Nippon Shokubai Co., Ltd (Tokyo, Japan), Itaconic acid (IA) was dedicated as a bio-derived diacid from Iwata chemical co. ltd. Dimethyl Itaconate(TCI), hexamethylenediamine (TCI) and Boc-hexamethyleneamine (TCI) as diamine monomers were used as received without purification. (4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride : DMT-MM) (TCI) as condensation agent were used as received without purification. Solvents such as dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), ethyl acetate (EtOAc), acetone, hexane, *N, N*-dimethylformamide (DMF), *N, N'*-dimethylacetamide (DMAc), trifluoroacetic acid (TFA), dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP) were purchased from Wako Pure Chemical Industries Ltd. (Osaka Japan) used as received.

4-2-2 Characterizations

^{1}H NMR spectra were performed by a Bruker Biospin AG 400 MHz, 54 mm spectrometer using DMSO-d_6 as the solvent. The FT-IR spectra were recorded with a Perkin-Elmer Spectrum One spectrometer between 4000 and 400 cm^{-1} using a diamond-attenuated total reflection (ATR) accessory.

The mass spectra were measured using a FT-ICR MS (Solarix) equipped with a Nanospray source operating in the nebulizer-assisted ESI mode used in the negative ion mode and scanned from m/z 50 to m/z 1000.

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC, concentration 1 g/L, 10 mM LiBr/DMF eluent) after calibration with polystyrene standards using two of OHpack SB-806M HQ column (Shodex). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out by Seiko Instruments SII, SSC/5200 and Seiko Instruments SII, X-DSC7000T, respectively, at a heating rate of 5 °C/min under a nitrogen atmosphere.

Remaining solvent and absorbed moisture in polymer samples were removed at 200 °C for 1 hour before TGA and DSC measurement.

4-2-3 Monomer syntheses

4-2-3-1 Synthesis of bis-pyrrolidone ring 6i diamine monomer.

Synthesis of bis-pyrrolidone ring 6i-1.5 mer dicarboxylic acid (BP6iDC)

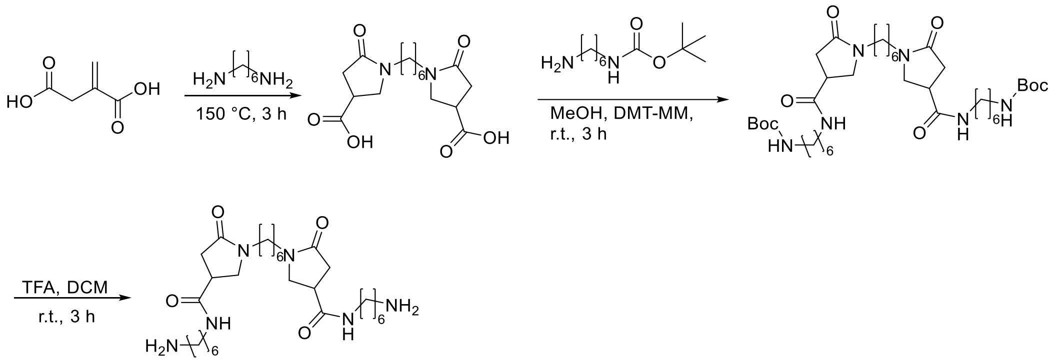
Hexamethylenediamine (15.5 g, 129.51 mmol) and itaconic acid (2.5 equivalents) at 160 °C for 3 hours. It was heated and stirred without solvent for a time, then dissolved with methanol and added dropwise to ethyl acetate to precipitate a light-yellow powder. This was suction-filtered and vacuum-dried to prepare a 1.5 mer bis-pyrrolidone ring 6i dicarboxylic acid (BP6iDC). In addition, when a small amount of hexane is added, precipitation of the product may be promoted. The product was confirmed by ^{1}H NMR (yield: 26.88 g, 61.0%.) ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm):

Synthesis of Boc-Bis-pyrrolidone ring 6i-2.5 mer (Boc-BP6i)

Boc-bis(pyrrolidone) 6i-2.5 mer (Boc-BP6i) is a bis-pyrrolidone ring dicarboxylic acid (BP6iDC) (6.79 g 19.95 mmol) and Boc-Hexamethyleneamine (2.3 equivalents), condensation agent (DMT-MM) (2.3 equivalents) It was prepared by stirring at room temperature for 3 hours. The solvent was removed from the sample with an evaporator, RO water was added therein and stirred for 1 hour. Thereafter, the grayish-white powder was recovered by suction filtration and vacuum-dried to obtain Boc-BP6i (yield: 8.75 g, 59.51 %). Identification of the product was confirmed by ^{1}H NMR. (400 MHz, DMSO-d6, δ, ppm):

Synthesis of bis-pyrrolidone ring 6i-2.5 mer diamine monomer (BP6iDA)

Boc-BP6i (4.00 g, 5.43 mmol) was dissolved with dichloromethane (DCM) and 3.0 mL of trifluoroacetic acid (TFA) was added dropwise at 0 °C～room temperature. After stirring for 3 hours, the solvent was removed with an evaporator, a saturated sodium bicarbonate aqueous solution was added, and EtOAc was used to separate the solution. The obtained aqueous phase was distilled away with an evaporator to obtain a yellow viscosity powder (Scheme 4-1) (yield: 888.7 mg, 30.49%). ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm):



Scheme 4-1 Synthesis of bio-based bis-pyrrolidone diamines from itaconic acid.

4-2-3-2 Synthesis of bis-pyrrolidone ring Fi diamine monomer.

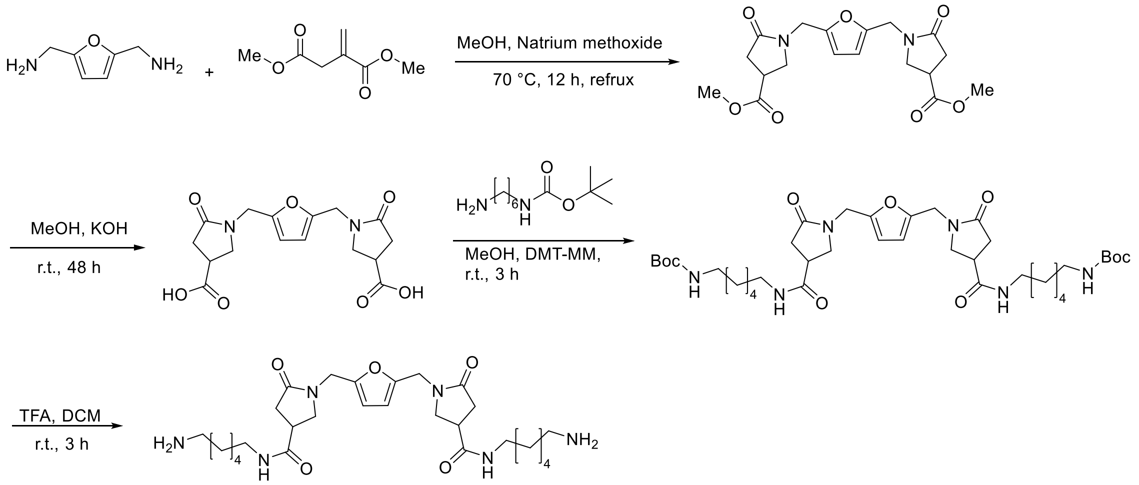
Synthesis of bis-pyrrolidone ring Fi-1.5 mer dicarboxylic acid dimethyl (BPFiMe)

AMF (6.0 g, 47.6 mmol), dimethyl Itaconate (2.5 equivalents), and sodium methylate adding 3 wt% at 70 °C for 12 hours. The mixture was then heated to pH 5.0 or lower. This was heat refluxed in MeOH for 24 h. The solvent was removed by evaporator and hydrochloric acid was added until pH 5.0 or less. Water was added and stirred, and the mixture was divided using ethyl acetate. The organic layer was collected and concentrated using an evaporator to prepare 1.5 mel bis-pyrrolidone ring Fi dicarboxylic acid dimethyl (BPFiMe). The product was confirmed by ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm)

Synthesis of bis-pyrrolidone ring Fi-1.5 mer dicarboxylic acid (BPFiDA)

BPFiMe 16.0 g (42.3 mmol) was dissolved in 48 mL of MeOH and 32.0 g potassium hydride was added. After stirring at room temperature for 72 h, the disappearance of the methyl ester group was confirmed by NMR. The solvent was removed with an evaporator and hydrochloric acid was added to bring the pH below 5.0. Water was added, and ethyl acetate was used for the preparative operation. The organic layer was allowed to concentrate and the oil-like BPFiDA was collected

(Scheme4-2).



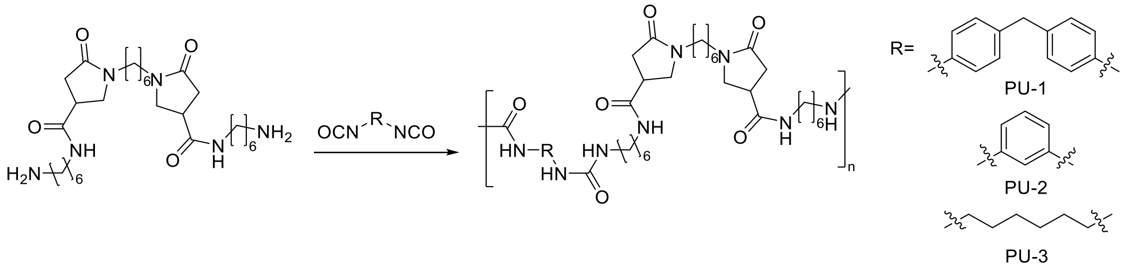
Scheme 4-2 Synthesis of bio-based bis-pyrrolidone diamines from AMF and itaconic acid.

However, because of the difficulty of purification, it was not possible to obtain diamine monomers with furan. Therefore, we proceeded with our research, focusing mainly on 2.5 dimer diamines with an easy structure to synthesize.

4-2-4 Polymer syntheses

4-2-4-1 Synthesis of 6i-PU-1

BP6iDA (1.0 g, 536.8 mmol) and diisocyanates (1.0 equivalent) were mixed at 70 ℃ in DMAc solvent. After 4 hours, a highly viscous solution was obtained. The reaction solution was added dropwise to methanol, and white powder precipitated. After suction filtration and vacuum drying (Scheme 4-3).



Scheme 4-3 Synthesis of bio-based polyurea from BP6iDA monomer.

4-3 Results and discussion

4-3-1 Monomer syntheses

Bulk mixture of itaconic acid and hexamethylenediamine in a 3:1 ratio, followed by azamichael addition and condensation reactions, and purification with methanol and ethyl acetate afforded BP6iDC. The product was easily synthesized and purified. (a) to (c) peaks indicate protons of the pyrrolidone ring, suggesting cyclization (Figure 4-1). Mass spectrometry showed that the molecular weight was the same as the theoretical molecular weight, confirming that itaconic acid and diamine form 1.5 dimer (Figure 4-2).

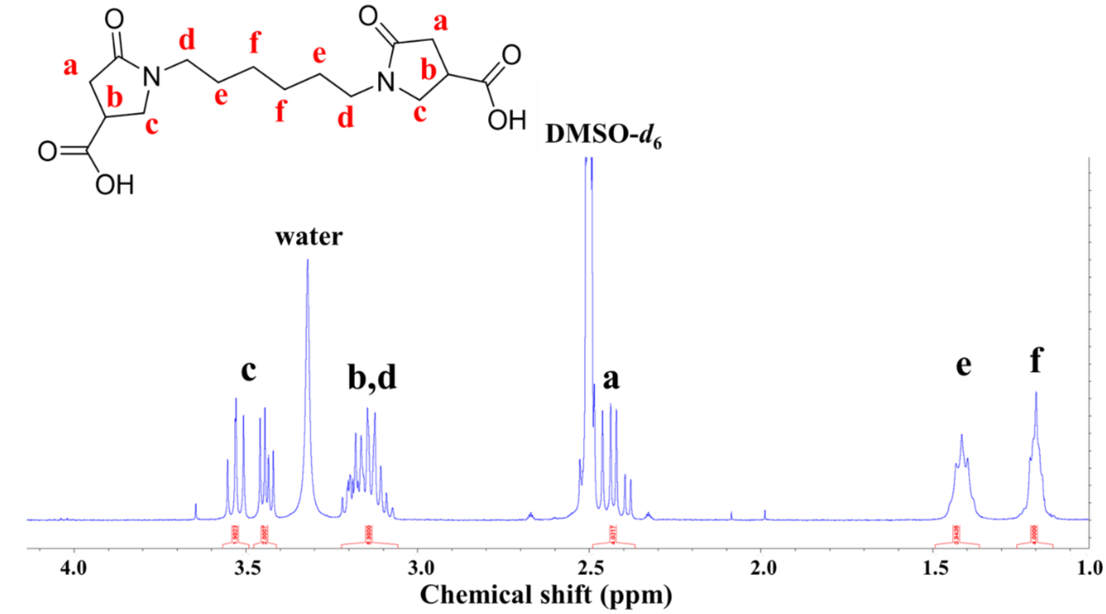
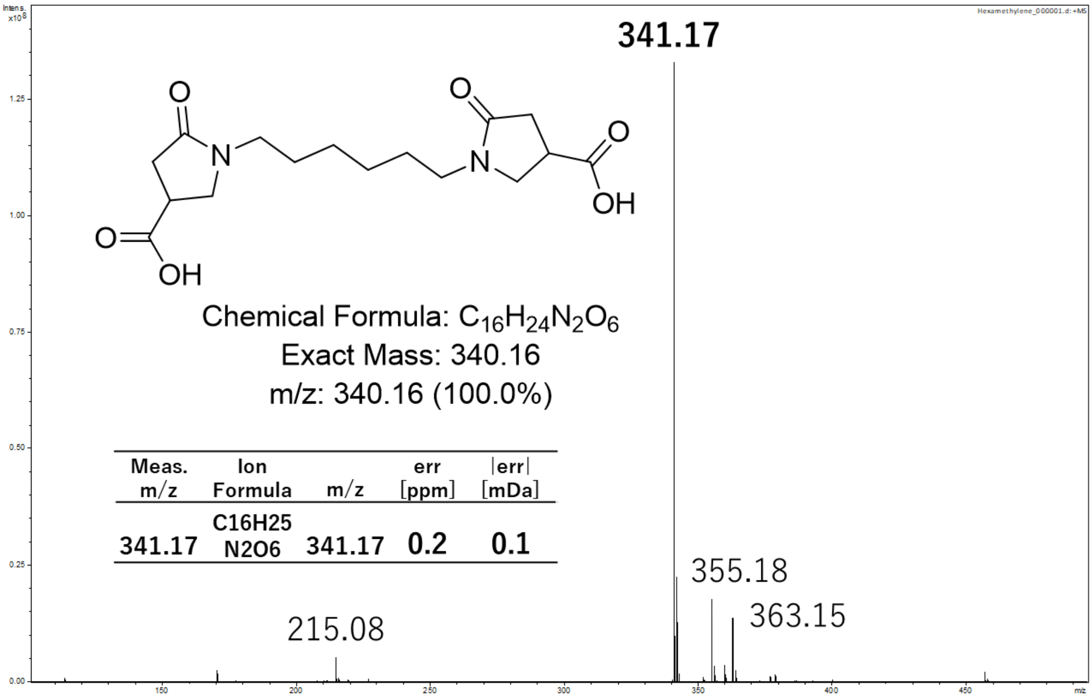


Figure 4-1 1H-NMR spectrum (400 MHz, DMSO-d_6) of the product using itaconic acid and hexamethylenediamine (Enlarged view 1.0~4.0 ppm)



Meas. m/z	Ion Formula	m/z	err [ppm]	|err| [mDa]
341.17	C16H25 N2O6	341.17	**0.2**	**0.1**

Figure 4-2 MS spectrum of Hexamethylene-bis (pyrrolidone dicarboxylic acid) (ESI-FT-ICR MS Positive mode)

Condensation with BP6i and hexamethylenediamine modified with Boc groups was followed by purification and deprotection. After neutralization and aliquoting, the resulting solid viscous product was evaluated by ^{1}H NMR (Figures 4-3, 4). The peak around 8.00 ppm was attributed to the amide bond, and the integrated value was consistent with the number of protons, suggesting that the BP6iDC was modified at both ends with hexamethylenediamine.

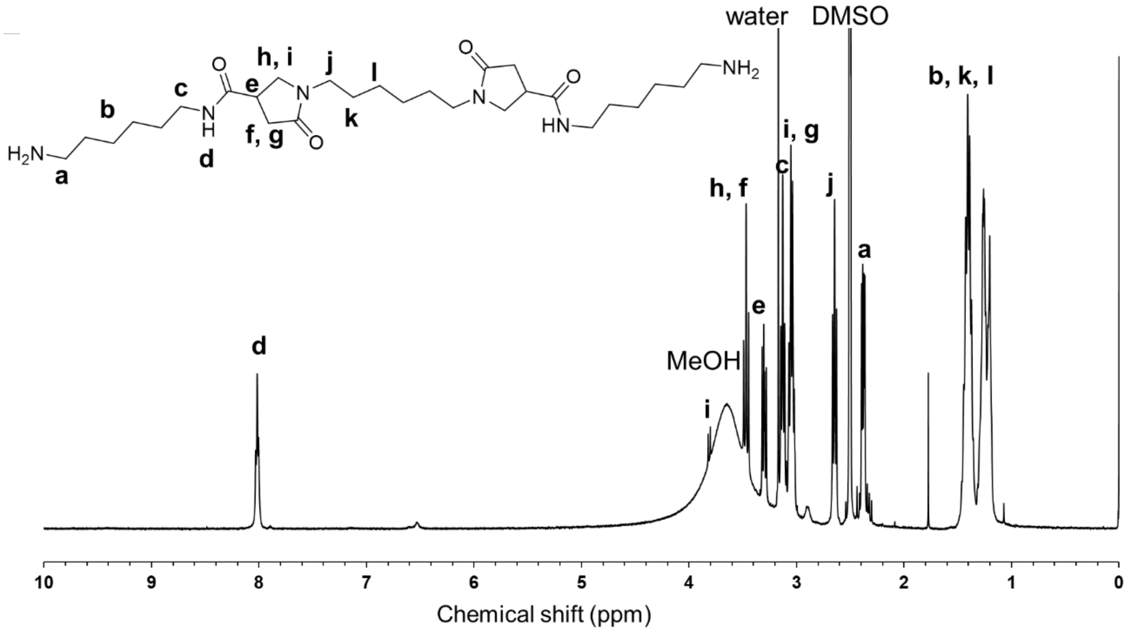


Figure 4-3 ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of the bis(pyrrolidone) 6i diamine monomer using itaconic acid and hexamethylenediamine.

Figure 4-4 The physical appearance of BP6iDA

4-3-2 Polymer syntheses

BP6iPU-1 to 3 with furan rings and bis(pyrrolidone) rings in the main chain was prepared by the polyaddition of BP6iDA with a stoichiometric amount of a diisocyanate compound. The solubility of PUs were tested using non-polar solvents such as hexane, chloroform, and dichloromethane; polar protic solvents such as distilled water and methanol, and polar non-protic solvents such as acetone, THF, DMF, DMAc, DMSO, NMP. PU-1 and 2 were soluble at room temperature in some polar nonprotic solvents of DMF, NMP, DMAc, and DMSO (Table 4-1). The reason why solubility was not observed for the aliphatic BP6iPU-3 is suggested by their high aggregation potential. This suggests that urea bonds and fatty chains contribute to improved cohesion.

Table 4-1 Solubility of the synthesized PUs from various diisocyanates. (a

	NMP	DMAc	DMSO	DMF	THF	Acetone	$CHCl_3$	DCM	MeOH	Water
BP6iPU-1	+	+	+	+	-	-	-	-	-	-
BP6iPU-2	+	+	+	+	-	-	-	-	-	-
BP6iPU-3	-	-	-	-	-	-	-	-	-	-

a) Sample 1 mg / solvent 1 mL + : easily soluble, - : insoluble

Based on the solubility data, NMR measurement of the resulting PU was performed, and the proton derived from the furan ring around 6.0 ppm and the proton of the amide group contained in the urea bond around 8.0, 8.5 ppm was confirmed, suggesting that the target product was obtained (Figure 4-5).

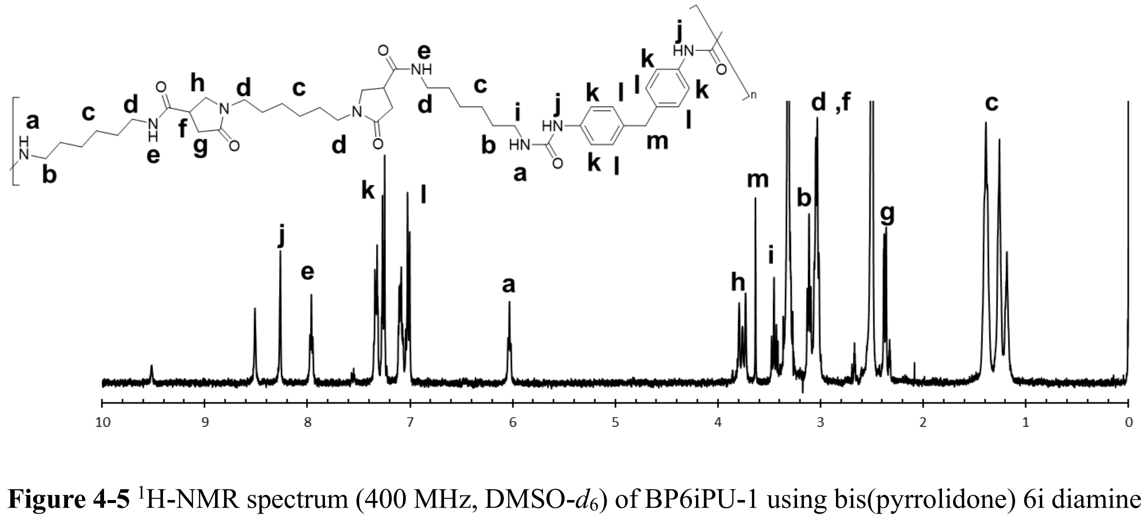


Figure 4-5 ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of BP6iPU-1 using bis(pyrrolidone) 6i diamine monomer and methylenediphenyldiisocyanate.

4-3-3 Properties.

Among the obtained PUs, the results of IR structural analysis of BP6iPU-1 to 3 are shown (Figure 4-6). Absorption originating from the N-H stretching vibration was confirmed near 1620 cm^{-1} and 3450 cm^{-1}, indicating that urea bonds were formed and the desired PUs were obtained.

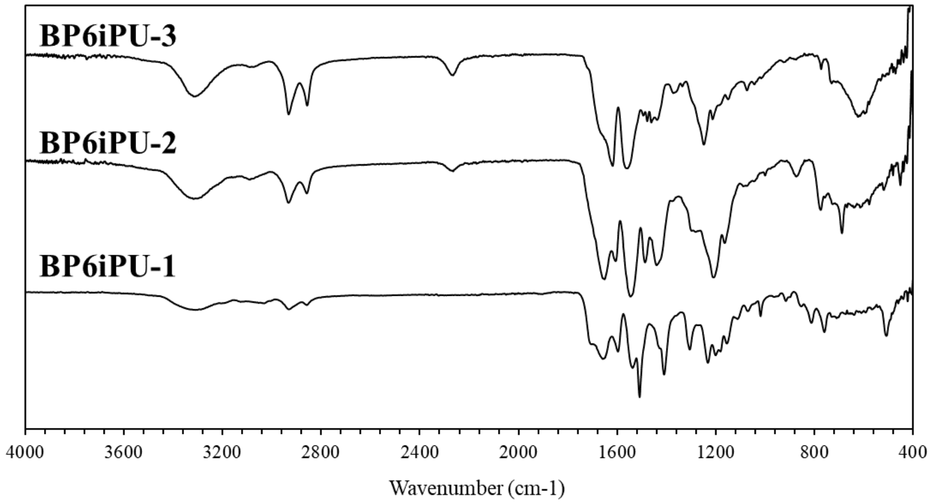


Figure 4-6 IR spectrum of BP6iPU-1 to 3 using itaconic acid and various diisocyanates.

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution (M_w/M_n) were determined and summarized (Table 4-2). The synthesized PU yielded high molecular weights about 10,000. The data for BP6iPU-3 could not be obtained because of its low solubility in DMF. The reason for the low molecular weight of both BP6iPU-1 and 2 is the bulky structure of the monomer. Therefore, we believe that this problem can be solved by increasing the reaction time.

Table 4-2 Molecular weight of the synthesized PUs using AMF and various diisocyanates[a)]

	$M_n \times 10^3$	$M_w \times 10^4$	M_w/M_n
BP6iPU-1	8.2	1.2	1.49
BP6iPU-2	7.0	1.0	1.41
BP6iPU-3	*N.D.*[b)]	*N.D.*[b)]	*N.D.*[b)]

(a) Determined by SEC measurement using DMF/LiBr. Polystyrene as standards. (b) not data.

Thermogravimetric analysis (TGA) was conducted of PU under a nitrogen atmosphere with a heating rate of 10 °C min^{-1} to determine the 5% weight loss temperature (T_{d5}) and 10% weight loss temperature (T_{d10}) (Figure 4-7). Additionally, differential scanning calorimetry (DSC) was performed under identical conditions to determine the glass transition temperature (T_g) and melting point (T_m) within the temperature range of -20 to 230 °C (Figure 4-8). T_g was observed in the range of 170 to 180 °C for both PUs.

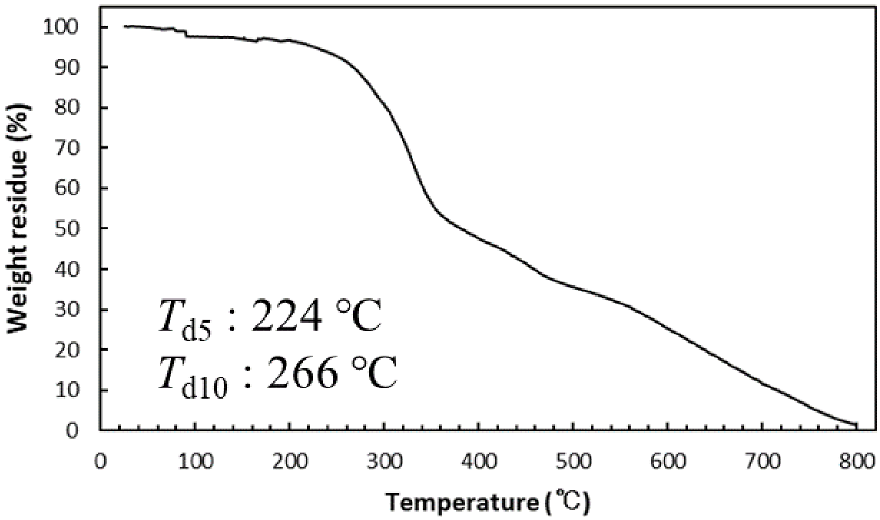


Figure 4-7 TGA curves of BP6i-PU1.

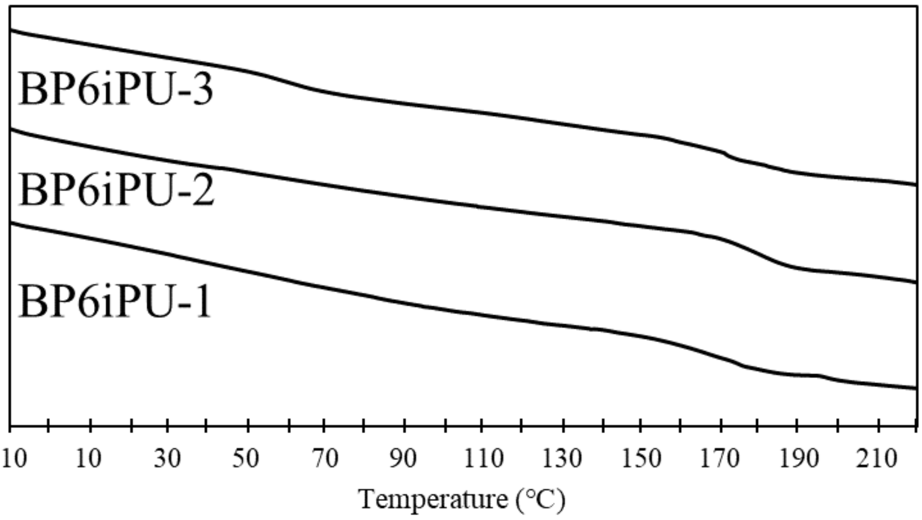


Figure 4-8 Differential scanning calorimetry thermograms of BP6iPU-1 to 3 upon heating.

Among the synthesized PUs, T_g values of 165, 172, and 171 °C were observed for BP6iPU-1, BP6iPU-2, and BP6iPU-3, respectively, in the range of -20 to 230 °C. BP6iPU-1 also exhibited a pyrolysis temperature of 266 °C. Thus, the PU synthesized in this chapter is also considered to be a polymer with excellent heat resistance, and the calculated values are comparable to those of a typical polycarbonate. The reason for this is suggested to be the introduction of two pyrrolidone rings per unit. However, the reason for the relatively lower values than the aromatic PU synthesized in Chapters 2 and 3 is thought to be the incorporation of more fatty chains. The reason why there is no significant difference between the aliphatic and aromatic units in the diisocyanate is thought to be intermolecular interaction due to the packing nature of the aliphatic chains.

4-3-4 Photo-responsive of BP6i-PU1

The photo-induced hydrophilicity of BP6i-PU1 upon light irradiation was confirmed. UV irradiation using a high-pressure mercury lamp in the wavelength range of 250-450 nm caused the PU to become discolored, brittle, and dispersed after 6 hours. Upon filtration, a solution was obtained, and photo-induced solubility of PU in water was observed (Figure 4-9). Heating and stirring at 80 °C did not result in dissolution without UV irradiation. This suggests that photo-induced solubility was enhanced by light irradiation.

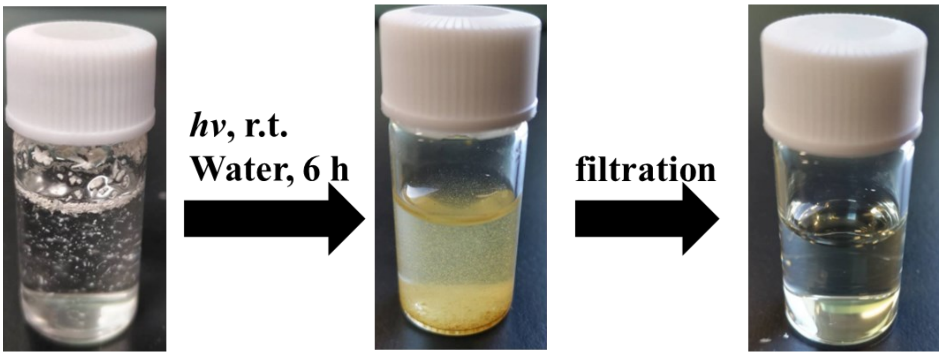


Figure 4-9 Water-solubilization behavior of BP6i-PU1 derived from itaconic acid by high-pressure mercury lamp irradiation with a wavelength range 250–450 nm.

4-4 Conclusion

As described above, we have succeeded in synthesizing a new diamine compound from itaconic acid that is close to an oligomer. The synthesized oligomers can be used as new monomers and are expected to be applied to polyamide and polyimide, which are high performance polymers, in addition to polyurea handled in this study. Synthesis of new PUs were achieved using the obtained monomers. The obtained PUs having Bis(pyrrolidone) as the main chain had high thermophysical properties, and T_g around 170 °C was confirmed for all of them. This suggests that the introduction of the pyrrolidone ring improves the physical properties. The PUs with a hetero ring without aromaticity have higher thermophysical properties than conventional PUs, although they do not have the same heat resistance as the biobased furan PUs and aromatic PUs that have been synthesized so far. Applications of this polymer are expected to include microcapsules, fibers, and films. Furthermore, the synthesized PU has been demonstrated to confer hydrophilicity under UV irradiation. This is believed to be due to the formation of carboxylic acid side chains by the ring-opening reaction of the pyrrolidone ring. This phenomenon is important in overcoming the issues of plastic waste, particularly the danger of synthetic fibers used in fishing lines and nets to marine life and ocean pollution. As these UV wavelengths are present in sunlight, it is expected that irradiating these plastics will induce hydrophilicity in seawater.

4-5 References

[1] Marsh K, Bugusu B. Food packaging - Roles, materials, and environmental issues: Scientific status summary. *J Food Sci.*, **2007**, *72*(3). doi:10.1111/j.1750-3841.2007.00301.x

[2] Gross RA, Kalra B. Biodegradable polymers for the environment. *Science (80-)*. **2002**, *297*, 5582, 803-807. doi:10.1126/science.297.5582.803

[3] Swift G. Directions for Environmentally Biodegradable Polymer Research. *Acc Chem Res*. **1993**, *26*(3), 105-110. doi:10.1021/ar00027a005

[4] Winkler M, Lacerda TM, Mack F, Meier MAR. Renewable polymers from itaconic acid by polycondensation and ring-opening-metathesis polymerization. *Macromolecules*. **2015**, *48*(5), 1398-1403. doi:10.1021/acs.macromol.5b00052

[5] Ranucci E, Liu Y, Lindblad MS, Albertsson AC. New biodegradable polymers from renewable sources. High molecular weight poly(ester carbonate)s from succinic acid and 1,3-propanediol. *Macromol Rapid Commun.*, **2000**, *21*(10), 680-684. doi:10.1002/1521-3927(20000601)21:10<680::AID-MARC680>3.0.CO;2-Y

[6] Sousa AF, Gandini A, Silvestre AJD, Net, CP. Synthesis and characterization of novel biopolyesters from suberin and model comonomers. *Chem Sus Chem*, **2008,** *1,* 1020-1025,

[7] Asif Ali M, Tateyama S, Oka Y, Kaneko D , Okajima MK, Kaneko T. Syntheses of highperformance biopolyamides derived from itaconic acid and their environmental corrosion. *Macromolecules*, **2013**; *46,* 3719-3725.

[8] Kaneko T, Tran HT, Shi DJ, Akashi M. Environmentally degradable, high-performance thermoplastics from phenolic phytomonomers. *Nat Mater,* **2006,** *5,* 966-970.

[9] Shere AJ, Sethumadhavan M, Stein RS. Kerr. Effect and wide angle light-scattering studies of a para-aromatic polyamide in dilute solution. *Macromolecules*, **1996**; *29*, 2088-94.

[10] Garcia J M, Garcia FC, Serna F, De la pena JL. High-performance aromatic polyamides., *Prog*

Polm Sci, **2010,** *35,* 623-686,

[11] Hao Y, Chen M, Zhao J, Zhang Z, Yang W. Synthesis and Properties of Polyesteramides Having Short Nylon-61 Segments in the main chains through polycondensation and chain extension. *Ind Eng Chem Res*, **2013,** *52,* 6410-6421,

[12] Willke T, Vorlop KD. Biotechnological production of itaconic acid. *Appl Microbiol Biotechnol.* 2001;56(3-4):289-295. doi:10.1007/s002530100685

[13] Mralidharao D, Jaheer Hussain SMD, Rangadu VP, Subramanyam K, Krishna GS, Swamy AVN. Fermentatative production of itaconic acid by aspergillus terreus using Jatropha seed cake. *Afr J Biotechnol,* **2007**, *18,* 2140-2142.

[14] Gallagher T, Derrick I, Durkin MP, Haseler CA, Hirschhauser C, Magrone P. Intramolecular 1,6-addition to 2-pyridones mechanism and synthetic scope. *J Org Chem,* **2010,** *75,* 3766-3774.

[15] Pengxu Qi, Hsiao-Li Chen, Ha Thi Hoang Nguyen. Chu-Chieh Linb and Stephen A. Miller, *Green Chem.*, **2016**, *18*, 4170-4175

[16] Roy M, Noordzij GJ, Van Den Boomen Y, Rastogi S, Wilsens CHRM. Renewable (Bis)pyrrolidone Based Monomers as Components for Thermally Curable and Enzymatically Depolymerizable 2-Oxazoline Thermoset Resins. *ACS Sustain Chem Eng*. **2018**, *6*(4), 5053-5066. doi:10.1021/acssuschemeng.7b04716

[17] Ali MA, Kaneko T. High-Performance BioNylons from Itaconic and Amino Acids with Pepsin Degradability. *Adv Sustain Syst.* **2022**, *6*(2). doi:10.1002/adsu.202100052

Chapter 5

General Conclusions

Conclusion

The research in this thesis focused on the syntheses of high performance bio-based polyureas (PUs) derived from various bio-compounsd. The development of these high-performance biobased polymers is essential to the realization of a sustainable low-carbon society. The following is a summary of the important and interesting results obtained throughout this research through this study.

In Chapter 2, polyurea was successfully synthesized using AMF. The thermophysical properties of the 13 furan PUs obtained were evaluated and showed higher T_g than those of previously reported PUs and main-chain furan polymers. This is due to the aromaticity of the furan structure and the interaction between the oxygen atom in the 1-position and the amino group of the urea bond, resulting in higher crystallinity. Furthermore, the heat resistance of all the PUs was high, with 5 % T_d ranging from 273 to 307 °C. Furthermore, the reversible DA reaction of furan and maleimide successfully cross-linked furan polyurea with maleimide and bismaleimide. The polyurea gel showed reparability based on dynamic bond recovery and was found to adhere to the fracture site at 60°C heat. This suggests that polyurea gels can be repaired even at lower temperatures than the dissociation temperature of the dynamic bond because of the recombination of the free furan and maleimide groups around the fracture site. a reversible sol-gel transition based on the DA reaction was observed, indicating that a thermo-responsive gel was obtained. The reaction was also used to achieve interfacial adhesion of polyurea gels with different main chains, which is expected to lead to further functional developments in adhesion chemistry and network polymers.

In Chapter 3, we produced diamines derived from microorganisms and optimized the conditions for their production. The resulting diamine monomers were reacted with diisocyanate compounds to obtain aliphatic and aromatic polyureas. The development of biopolymers requires the production of the purest monomers in sufficient quantities to optimize the conditions for chemical polymerization. Here, fermentation conditions were optimized to produce 4APEA at the gram order level in a bench-top jar fermenter. This allowed for repeated purification of immediately polymerizable compounds of subgram order. It optimizes polymerization and contributes to obtaining highly polymerized biopolymers. In addition, fine-tuning of fermentation conditions, genetic modification, and process engineering will improve the production efficiency of 4APEA and contribute to the development of new polyamides and polyimides from microbially derived 4APEA. One of the key factors to improve fermentation productivity is to control and inhibit oxidative degradation of 4APEA. Oxidation by the host E. coli degrades some of the 4APEA accumulated during fermentation. However, aromatic amines and diamines, which are easily oxidized under physiological conditions, are susceptible to biological oxidation via oxygen supplied to the culture vessel. In any case, since both biotic and abiotic reactions require molecular oxygen, the control of oxygen supply as shown in this study should be important. In this study, biomass-derived 4APEA was polymerized with petroleum-derived diisocyanate to produce partially biomass-derived AP-PU-1 and AP-PU-2. Both showed excellent thermophysical properties, with T_{d10} values of 270-300 °C or higher. This is more than 100 °C higher than that of conventional petroleum-derived polyureas. Although petroleum-derived diisocyanate was used in this study, it can be replaced with a biomass-derived diisocyanate to produce a completely biomass-derived PU. In recent years, there has also been great interest in the production of the monomer hexamethylenediamine from renewable resources. Since the chemical industry currently produces hexamethylene diisocyanate, the counter-diamine of AP-PU-2, from hexamethylene diamine, the combination of this technology and our results should constitute a sustainable technology. In summary, this study is the first example of synthesis of aromatic PU from diamines derived from microorganisms. This is expected to open up new possibilities for the application of biomass-derived polymers, which is necessary for the development of a sustainable society.

In Chapter 4, we synthesized high-performance and photoinduced hydrolyzable polyureas by introducing itaconic acid-derived bis(pyrrolidone) into the main chain. Diamine oligomers were successfully synthesized using itaconic acid. The high thermal properties were maintained equivalent to conventional heat-resistant PU, while achieving hydrophilic properties through light irradiation. This suggests that contribution to the imparting of hydrolytic degradability is possible and further expansion of applications for bio-based PU is expected. This is expected to have applications in engineering plastics/super engineering plastics such as polyamide, polyimide, and polyazomethine in addition to polyurea.

As a result, this product can alleviate the serious problem of plastic waste and petroleum resources. Not only that, it suggests that biobased polymers can enter new areas and expand their applications.

Academic achievements

Publications:

[1] Takuya Kumakura, Kenji Takada, Tatsuo Kaneko, Self- and Cross-fusing of Furan-based Polyurea Gels Dynamically Cross-linked with. *Polymers*, **2023,** *15*(2), 341 https://doi.org/10.3390/polym15020341

[2] Hajime Minakawa, Shunsuke Masuo, Kenji Takada, Takuya Kumakura, Nozomi Katsuki, Tatsuo Kaneko, Naoki Takaya, Fermentative production of 2-(4-aminophenyl)ethylamine to synthesize a novel heat-resistant biopolyurea. *Bioscience, Biotechnology, and Biochemistry*, **2022**, *86* (8), 1114–1121. https://doi.org/10.1093/bbb/zbac077

Proceedings

[1] 熊倉拓哉, 高田健司, 金子達雄.「2,5-ビス(アミノメチル)フランを用いた刺激応答性バイオポリウレア架橋体の合成とその物性評価」、第 28 回日本ポリイミド・芳香族系高分子会議, 2021 年 3 月

Patent:

[1] 金子達雄, 高田健司, 熊倉拓哉, 赤松善弘(代理人),「ウレアポリマー」, 特願 2019-164777, 出願日：2019 年 9 月

Conferences:

[1] Takuya Kumakura, Kenji Takada, Tatsuo Kaneko, “Synthes of Bio-based polyurea using 2,5-Bis(aminomethyl)furan”, The 48th World Polymer Congress IUPAC-MACRO 2020+, Korea(Online), May. 2021 (Short presentation video)

[2] Takuya Kumakura, Kenji Takada, Tatsuo Kaneko, “Thermo-responsive organogels of 2,5-bis(aminomethyl)furan-based polyureas and bismaleimides”, Pacifichem 2020(Online), December. 2021 (Poster)

[3] 熊倉拓哉, 野田拓海, 高田健司, 金子達雄,「キラルな桂皮酸二量体を用いた芳香族バイオベースポリマーの合成と熱力学的物性の評価」, 第 1 回 COI 学会, 大阪府, 2018 年 10 月, (Poster)

[4] 熊倉拓哉, 野田拓海, 高田健司, 金子達雄,「キラルトルキシン酸誘導体を用いた芳香族ポリウレアの合成とその熱力学的特性」、高分子若手会, 富山県, 2018.11 月, (Poster)

[5] 熊倉拓哉, 野田拓海, 川下友輝, 高田健司, 金子達雄.「立体配置の異なる桂皮酸二量体をベースとしたバイオポリウレアの構造物性相関」,第 68 回高分子学会年次大会, 大阪府, 2019.5 月, (Poster)

[6] 熊倉拓哉, Kumar Amit, 高田健司, 金子達雄.「バイオマス由来 2,5-ビス(アミノメチル)フランをベースとしたポリウレアの合成」,第 68 回高分子討論会, 福井県, 2019 年 9 月, (Poster)

[7] 熊倉拓哉, 高田健司, 金子達雄.「2,5-ビス(アミノメチル)フランを用いたバイオベースポリウレアの合成と熱応答性の評価」, 第 68 回高分子学会北陸支部研究発表会, 石川県, 2019 年 11 月, (Oral)

[8] 熊倉拓哉, 高田健司, 金子達雄,「グルコース由来アミノ化フランを用いた熱応答性ポリウレアゲルの合成」, 第 31 回高分子ゲル研究討論会, 東京都, 2020 年 1 月 (Poster)

[9] 熊倉拓哉, Kumar Amit, 高田健司, 金子達雄.「バイオ由来ジアミノフランを用いたポリウレア架橋体の刺激応答性」, 第 69 回高分子学会年次大会, 2020 年 5 月, (Oral), 中止

[10] 熊倉拓哉, Kumar Amit, 高田健司, 金子達雄.「主鎖にフラン骨格を有したバイオベースポリウレアゲルの合成とその熱応答性評価」, 第 69 回高分子討論会, オンライン開催, 2020 年 9 月(Oral・依頼講演)

[11] 熊倉拓哉, 高田健司, 金子達雄, 「2,5-ビス(アミノメチル)フランを用いた刺激応答性バイオポリウレア架橋体の合成とその物性評価」, 第 28 回日本ポリイミド・芳香族系高分子会議, 群馬県, 2020.12 月, (Poster)

[12] 熊倉拓哉, 高田健司, 金子達雄. 「バイオ由来フランジアミンを用いたポリウレアゲルの合成とその熱的性質の評価」,第 70 回高分子学会年次大会, オンライン開催, 2021 年 5 月, (Poster)

[13] 熊倉拓哉, Wang Huaiyu, Maninder Singh, Mohammad Asif Ali, 高田健司, 金子達雄, 「イタコン酸由来バイオベースポリアミドの合成と環境分解性の評価」, 第 70 回高分子討論会, オンライン開催, 2021 年 9 月(Oral・依頼講演)

[14] 熊倉拓哉, Mohammad Asif Ali, 立山誠治, 高田健司, 金子達雄, 「水と光で生分解するバイオナイロンプラスチック」, 第 12 回スイゼンジノリ・サクラン研究会年次大会エクセレントコア「サスティナブルマテリアル」国際シンポジウム, オンライン開催, 2021 年 11 月, (Oral)

[15] 熊倉拓哉, 高田健司, 金子達雄, 「バイオマス由来ポリフラン-ウレアゲルの合成とその熱応答性の評価」, 第 71 回高分子討論会, オンライン開催, 2022 年 9 月, (Oral)

Awards:

[1] 熊倉拓哉, 2019 年度第 68 回高分子討論会優秀ポスター賞 受賞, 2019 年 10 月

[2] 熊倉拓哉, 2019 年度高分子学会北陸支部優秀研究賞 受賞, 2019 年 11 月

[3] Takuya Kumakura, Kenji Takada, Tatsuo Kaneko, The 48th World Polymer Congress IUPAC-MACRO 2020+ Online Short Talk Student Award, May. 2021