

Bio-based poly(urethane urea) dispersions : chemistry, colloidal stabilization and properties

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Bio-based Poly(urethane urea) Dispersions

chemistry, colloidal stabilization and properties

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op
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voor een commissie aangewezen door het College voor Promoties, in het openbaar te
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door

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To my dearest parents, husband and son

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Glossary

^1H NMR	proton Nuclear Magnetic Resonance spectroscopy
α	Debye-Hückel parameter
ADH	adipic dihydrazide
ADMET	acyclic diene methathesis polymerization
AFM	Atomic Force Microscopy
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared spectroscopy
BD	1,4-butanediol
BDA	1,4-butane diamine
BuRicin	butanol ricinoleate
CLSO	carbonated linseed oil
CSBO	carbonated soybean oil
DAH	1,4:3,6-dianhydrohexitol (isohexitol)
DBA	dibutylamine
DBTDL	dibutyltin dilaurate
DDI®1410 or DDI	dimer fatty acid-based diisocyanate
DIO	1,8-diisocyanatooctane
DITO	1-isocyanato-10-[(isocyanatomethyl)thio]decane
DLS	Dynamic Light Scattering
DMA	Dynamic Mechanical Analysis
DMA _d	dimethyl adipate
DMPA	dimethylolpropionic acid
DMS	dimethyl succinate
DSC	Differential Scanning Calorimetry
ϵ	dielectric constant
η	viscosity
E'	storage modulus
E''	loss modulus
EDA	ethylene diamine
EELDI	ethyl ester L-lysine diisocyanate (ethyl-2,6-diisocyanatohexanoate)
EMO	epoxidized methyl oleate
f_{noH}	number-average hydroxyl functionality
HCl	hydrogen chloride
HDI	hexamethylene diisocyanate
HETU	11-[(2-hydroxyethyl)thio]undecan-1-ol
HFIP	hexafluoroisopropanol

HMDI	hydrogenated 4,4'-diphenylmethane diisocyanate
HPMDI	1,7-heptamethylene diisocyanate
ICFAD	internal-carbonated fatty acid diester
II	isoidide (1,4:3,6-dianhydro-L-iditol)
IM	isomannide (1,4:3,6-dianhydro-D-mannitol)
IPDI	isophorone diisocyanate
IS	isosorbide (1,4:3,6-dianhydro-D-glucitol)
κ	Debye-Hückel parameter
KOH	potassium hydroxide
LDI	L-lysine diisocyanate
μ	electrophoretic mobility
MDI	4,4'-diphenylmethane diisocyanate
MEDA	N-methyl diethanol amine
MHHDC	methyl-N-11-hydroxy-9- <i>cis</i> -heptadecene carbamate
M_n	number-average molecular weight (g/mol)
M_w	weight-average molecular weight (g/mol)
NaOH	sodium hydroxide
NDO	1,9-nonanediol
NIPU	non-isocyanate polyurethane
ODEDO	1,18-octadec-9-enediol
OLT	1,3,5-(8-hydroxyoctyl)-2,4,6-octylbenzene
PDI	polydispersity index
PDMEA	poly(1,2-dimethylethylene adipate)
PDMES	poly(1,2-dimethylethylene succinate)
PMMA	poly(methyl methacrylate)
PPG	poly(propylene glycol)
PPGda	diamine-terminated poly(propylene glycol)
PS	polystyrene
PSD	particle size distribution
PU	polyurethane
PUD	polyurethane dispersion
PUU	poly(urethane urea)
SEC	Size Exclusion Chromatography
SPUU	segmented poly(urethane urea)
SSC	soft segment content
T	temperature [°C]
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene

T_{CE}	chain extension temperature [°C]
TCFAD	terminal-carbonated fatty acid diester
$T_{d, 5\%}$	temperature of 5% mass loss [°C]
$T_{d, 50\%}$	temperature of 50% mass loss [°C]
TDI	toluene diisocyanate
TEA	triethylamine
T_{fl}	flow temperature [°C]
T_{g}	glass transition temperature [°C]
$T_{\text{g}1}$	the 1 st glass transition temperature [°C]
$T_{\text{g}2}$	the 2 nd glass transition temperature [°C]
TGA	Thermogravimetric Analysis
T_{m}	melting temperature [°C]
TPU	thermoplastic polyurethanes
UDT	1,3,5-(9-hydroxynonyl)benzene
VOC	volatile organic compounds
V_{OH}	hydroxyl number (KOH/g)

Summary

Major concerns over fossil oil reserves and the environment have inspired people to explore renewable alternatives to reduce the dependence of the polymer industry on the exhaustible fossil feedstock. Intensive efforts are being invested in deriving useful starting chemicals from renewable resources. These new chemicals can further be used to synthesize novel polymers. Biomass-derived polyurethane (PU) building blocks or PU-related products have become an important field of research. However, limited by the current availability of bio-based diisocyanates and internal stabilizing agents for making aqueous PU dispersions, the preparation of fully renewable-based PUs or PU dispersions, commonly applied in various coating and adhesive applications, remains an important challenge. Purity issues and the less well-defined functionality and reactivity of these new chemicals, as well as the inherently flexible nature of plant oil-derived building blocks have restricted the control over the molecular weight of the derived polyurethanes, the polymer composition and the polymer performance. This work aimed to develop fully biomass-based aqueous poly(urethane urea) (PUU) dispersions. Application of these dispersions should result in sustainable coating materials with satisfactory properties. An in-depth study was performed concerning the PU chemistry, the colloidal stability and the chemical composition-properties correlations of such poly(urethane urea) polymers.

The first target was the development of well-controlled isocyanate end-capped PU prepolymers from renewable building blocks, including a dimer fatty acid-based diisocyanate (DDI), the sugar-based 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) and lysine-derived ethyl ester L-lysine diisocyanate (EELDI), combined with the petro-based dimethylolpropionic acid (DMPA), which was chosen as the internal stabilizing agent. The combination of the relatively hydrophobic DDI with the hydrophilic DMPA, as well as the incorporation of the asymmetric monomers IS and EELDI, could have restricted the control over the polymer composition and the chain end-groups. Fundamental kinetics studies have been carried out to probe the regio-selectivity of IS and EELDI and the reactivity of these four compounds in their respective reactions. The results have shown that slight differences in reactivity exist between the *endo*- and the *exo*-hydroxyl groups of isosorbide, as well as between the ε - and α -isocyanate groups of EELDI. Because of the high reaction rate of EELDI, combined with the fact that EELDI was typically present in excess, the less reactive *endo*-OH and the α -NCO groups did not significantly hinder the polymerization reactions. Moreover, compared to hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), EELDI proved to be suitable for the preparation of PU dispersions, mainly due to its fast reaction rate and the asymmetric structure. To our

surprise, DMPA exhibited a relatively low reactivity compared to that of isosorbide. This was thought to be the result of the steric hindrance of the CH₃ and COOH groups, as well as the electron-withdrawing effect of the carboxylic acid groups (COOH) of DMPA. Through this study, PU prepolymers with well-defined isocyanate chain end-groups could be prepared at appropriate reaction conditions and at the desired monomer feeds.

In prepolymer dispersions, the isocyanate-water side-reaction is the major obstacle for diamine or diol chain extension reactions, as it influences the reaction stoichiometry. To achieve high molecular weight, chain-extended poly(urethane urea)s (PUUs), the influence of the reaction temperature, the moment of diamine (ethylene diamine (EDA) and adipic dihydrazide (ADH)) addition, or only water, as well as the use of a catalyst (triethylamine) were investigated. As a result, a significant increase of the final PUU molecular weight was achieved by using only water as the chain extender at 50 °C and using triethylamine as the catalyst. EDA could extend NCO-end capped prepolymer chains at both 30 and 50 °C in the presence of water, due to the fast reaction of its primary amines with isocyanate groups. ADH chain extension seemed to be limited by its low solubility in 2-butanone, which was used as a solvent in which the prepolymers were prepared. Upon addition of water, the initially formed polymer particles were swollen with 2-butanone, the solvent used to prepare the PU prepolymers, which severely hampers ADH to react with the isocyanate end-groups. In addition, the reaction temperature, the moment of diamine addition and the use of triethylamine have shown to have an influence on the particle diameter of the dispersions and on their colloidal stability.

The internal stabilizing agent DMPA is a petrochemical-based component. To minimize the content of DMPA in the polymer composition, while maintaining a good colloidal stability of the dispersions, was another target of this research. The incorporation of EELDI into the PU backbone, as a rigid replacement of DDI, appeared to facilitate the stabilization of the formed dispersions. The corresponding hypothesis was that the hydrolysis of the ester groups present in EELDI results in carboxylic acid groups, which stabilize dispersions after being neutralized with TEA. Therefore, with the increase of the EELDI content, the amount of DMPA could be significantly reduced (to the lowest content reported). Accordingly, nearly fully renewable PU dispersions were obtained, containing up to 97 wt% bio-based monomers.

In the final section, the investigation has focused on the thermal and mechanical properties of the poly(urethane urea) dispersion-cast films as well as on the polymer phase morphology in correlation with the polymer composition. Significant dependencies of these properties and the morphology on the polymer composition were observed. The

flexible nature of fatty acid-derived PU building blocks typically resulted in polymers with low glass transition temperatures (T_g) and low tensile stress values. By means of partially replacing the flexible DDI by the rigid EELDI in the monomer feed, the T_g values of dispersion-cast films were significantly enhanced from approximately 20 to 58 °C (1st T_g) and to above 70 °C (2nd T_g). An enhanced thermal stability is observed for films containing a relatively high DDI content, which is attributed to the reduced content of thermally labile urethane and urea groups. In addition, H-bonds-induced micro-phase separation was evidenced from the combination of DSC, AFM and FT-IR measurements and was correlated with the polymer composition. The properties of these dispersion-cast films met the requirements of conventional coating materials with respect to their good acetone resistance and moderate impact resistance (at high IS and EELDI contents), as well as their excellent adhesion to aluminum.

This work is expected to contribute to the development of sustainable industrial PU coatings from renewable resources.

Samenvatting

Serieuze bezorgdheid over fossiele olievoorraden en het milieu hebben mensen geïnspireerd om duurzame alternatieven te onderzoeken. Dit onderzoek heeft als doel om de afhankelijkheid van de polymeerindustrie van niet onuitputtelijk voorradige fossiele grondstoffen te verminderen. Veel moeite wordt gestoken in het maken van basis chemicaliën uit hernieuwbare bronnen. Deze kunnen dan worden gebruikt als grondstof om nieuwe polymeren te synthetiseren. Uit biomassa voortkomende polyurethaan (PU) bouwstenen of PU-gerelateerde producten zijn een belangrijk gebied van onderzoek.

Echter, wegens de huidige beperkte beschikbaarheid van bio-gebaseerde diisocyanaten en interne stabilisatoren voor het maken van waterige PU dispersies, blijft de bereiding van volledig hernieuwbare PU of PU dispersies, zoals algemeen toegepast in diverse coating en lijm toepassingen, een serieuze uitdaging. Onzuiverheden en de beperkte functionaliteit en reactiviteit van deze nieuwe stoffen, alsook de inherente flexibiliteit van plantaardige olie afgeleide bouwstenen maken het moeilijk het molecuulgewicht van de vervaardigde polyurethanen te controleren. Hierdoor variëren de polymeersamenstelling en dus ook de kwaliteit en eigenschappen van de polymeren.

Dit werk is gericht op de ontwikkeling van volledig biomassa-gebaseerde, waterige poly(urethaan urea) (PUU) dispersies. Toepassing van deze dispersies moet leiden tot duurzame materialen met bevredigende materiaaleigenschappen. Een diepgaande studie werd uitgevoerd met betrekking tot de PU chemie, de colloïdale stabiliteit en de chemische samenstelling - eigenschappen correlaties van deze poly(urethaan urea)s.

Het eerste doel was de ontwikkeling van PU prepolymeren met isocyanaat-eindgroepen uit hernieuwbare bouwstenen. Hiertoe werden een dimeer vetzuur-gebaseerde diisocyanaat (DDI), suiker-gebaseerd 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) en lysine-afgeleide ethylester L-lysine diisocyanaat (EELDI) gecombineerd met het petrochemie-gebaseerde dimethylolpropionzuur (DMPA). DMPA werd gekozen als interne stabilisator van de uiteindelijke PU dispersies.

De combinatie van het relatief hydrofobe DDI en het hydrofiele DMPA, evenals de integratie van de asymmetrische monomeren IS en EELDI, zou de controle over de polymeersamenstelling en de keten eindgroepen kunnen beperken. Fundamentele kinetiek studies zijn uitgevoerd om de regio- selectiviteit van IS en EELDI en de reactiviteit van deze vier verbindingen in hun respectievelijke reacties te bepalen.

De resultaten hebben aangetoond dat kleine verschillen in reactiviteit bestaan tussen de *endo*- en *exo*-hydroxylgroepen van isosorbide alsmede tussen de ε - en α -isocyanaat

groepen van EELDI. De hoge reactiesnelheid van EELDI, gecombineerd met het feit dat EELDI typisch in overmaat aanwezig was, betekent dat de minder reactieve *endo*-OH en α -NCO groepen de polymerisatiereacties niet significant belemmeren. Bovendien bleek dat, in vergelijking met hexamethyleendiisocynaat (HDI) en isoforondiisocynaat (IPDI), EELDI geschikt is voor de bereiding van PU dispersies. Dit is voornamelijk te danken aan de snelle reactiesnelheid en de asymmetrische structuur van EELDI. Tot onze verrassing vertoonde DMPA een relatief lage reactiviteit vergeleken met die van isosorbide. Sterische hindering van de CH₃ en COOH-groepen, en het elektron-zuigend effect van de carbonzorgroepen (COOH) van DMPA zijn hier waarschijnlijk de oorzaak van. Hierdoor konden PU prepolymeren met goed gedefinieerde isocynaat keindgroepen worden bereid onder gepaste reactie omstandigheden en met gewenste monomeervoedingen.

Omdat het de reactiostoichiometrie beïnvloedt, is de isocynaat-water reactie het belangrijkste obstakel voor diamine of diol ketenverlengingsreacties in de bereiding van polyurethaan dispersies.

Het doel is om hoog molgewicht, ketenverlengde poly(urethaan urea)s (PUUs) te maken. Daarom is de invloed van de reactietemperatuur, het moment van diamine (ethyleendiamine (EDA) en adipinezuurdihydrazide (ADH)) toevoeging, toevoeging van water evenals het gebruik van een katalysator (triethylamine, TEA) op het molecuulgewicht onderzocht. Dit resulteerde erin dat een significante toename van het uiteindelijke PUU molecuulgewicht werd bereikt met gebruik van alleen water als ketenverlenger bij 50 °C en met triethylamine als katalysator. EDA bleek de NCO-getermineerde prepolymerketens te kunnen verlengen bij zowel 30 en 50 °C in aanwezigheid van water. Dit is het gevolg van de snelle reactie van de primaire aminegroepen met de isocynaatgroepen.

ADH ketenverlenging bleek te worden beperkt door de lage oplosbaarheid van ADH in 2-butanon, dat werd gebruikt als een oplosmiddel voor de bereiding van de prepolymeren. Na toevoeging van water zwollen de aanvankelijk gevormde polymeerdeeltjes op met 2-butanon, wat de ADH reactie met de isocynaat eindgroepen ernstig belemmerde. De reactietemperatuur, het moment van diamine toevoeging en het gebruik van triethylamine blijken invloed te hebben op de deeltjesdiameter en op de colloïdale stabiliteit van de dispersies.

De interne stabilisator DMPA is een petrochemisch gemaakte component. Een volgend doel van dit onderzoek was om het DMPA gehalte in de polymeersamenstelling te minimaliseren, met behoud van een goede colloïdale stabiliteit van de dispersies. De incorporatie van EELDI in de PU hoofdketen, als een starre vervanging van DDI, bleek de stabilisatie van de gevormde dispersies te vergemakkelijken. De bijbehorende hypothese

was dat de hydrolyse van de ester groepen in EELDI leidt tot carbonzuurgroepen, die dispersies stabiliseren nadat ze geneutraliseerd zijn met TEA. Daarom, onder invloed van een toenemend EELDI gehalte, kon de hoeveelheid DMPA aanzienlijk worden verminderd tot de laagste in literatuur gerapporteerde waarde. Dienovereenkomstig werden bijna volledig hernieuwbare PU dispersies verkregen, met een gehalte tot aan 97 gew% bio-gebaseerde monomeren.

In het laatste gedeelte van het proefschrift is het onderzoek omschreven dat was gericht op de thermische en mechanische eigenschappen van dispersie-gegoten poly(urethaan urea) films in relatie tot de polymeersamenstelling. Daarnaast is gekeken naar de relatie tussen de polymormorfologie en de polymeersamenstelling. Zowel de eigenschappen als de morfologie bleek sterk afhankelijk van de polymeersamenstelling. Het flexibele karakter van vetzuren-gebaseerde PU bouwstenen resulteerde meestal in polymeren met een lage glasovergangstemperatuur (T_g) en lage trekspanningswaarden. Door gedeeltelijke vervanging van het flexibele DDI door het stijve EELDI in de monomeervoeding, werden de T_g waarden van dispersie-gegoten PUU films aanzienlijk verbeterd van 20 naar 58 °C (eerste T_g) en boven 70 °C (tweede T_g). Een verbeterde thermische stabiliteit wordt waargenomen voor films met een relatief hoog DDI gehalte. Dit wordt toegeschreven aan de verminderde hoeveelheid thermisch instabiele urethaan- en ureagroepen. Daarnaast werd waterstofbrug-geïnduceerde micro-fasescheiding waargenomen met een combinatie van DSC, AFM en FT-IR metingen. Deze fasescheiding is gecorreleerd met de polymeersamenstelling. Deze dispersie-gegoten PUU films voldoen aan de vereiste eigenschappen van coatingmaterialen wat betreft de goede acetonresistentie, de gematigde slagvastheid (bij hoge IS en EELDI gehalten) en de uitstekende hechting aan aluminium.

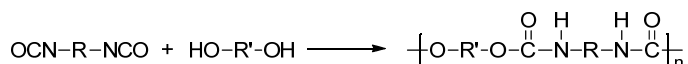
Dit werk zal naar verwachting bijdragen aan de ontwikkeling van duurzame, industriële PU coatings uit hernieuwbare bronnen.

1

Introduction

1.1 Polyurethanes

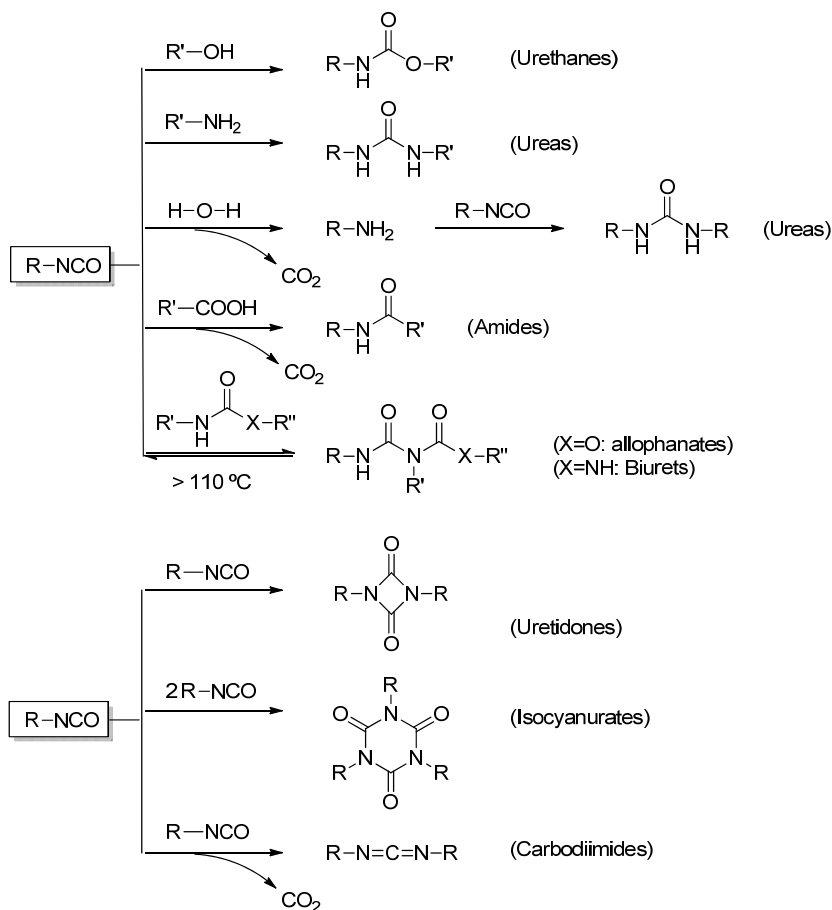
Polyurethanes (PU) are an important class of polymers, characterized by urethane (carbamate) linkages between the monomer residues. PUs are typically built up starting from polyols (polyether or polyester type) and diisocyanates (**Scheme 1-1**). The first polyurethanes were synthesized from octamethylene diisocyanate and 1,4-butanediol by Otto Bayer et al. ^[1] in 1937 in Germany. Since then, the polyurethane industry has shown a fast development in the 1950s, stimulated by the appearance of various diisocyanates (4,4'-diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI), hydrogenated MDI (HMDI)) and oligomeric polyols (polyesters, polyethers and polycarbonates). These polymers often integrate flexibility and rigidity in one material, affording great versatility in terms of their material properties. ^[2] Due to their excellent adhesion to many substrates and their good chemical resistance, polyurethane products have been applied in a broad spectrum of applications, ranging from fibers to foams, adhesives, coatings, sealants and elastomers.



Scheme 1-1. Synthesis of polyurethanes.

1.1.1 Isocyanate chemistry

Diisocyanates, one of the major classes of chemicals used for PU synthesis, are highly reactive toward nucleophilic reagents, affording the opportunity to synthesize different sorts of polymers. The pronounced positive charge of the carbon atom in the isocyanate group is a result of the electronegativity of the adjacent oxygen and nitrogen atoms, favorable for nucleophilic attack. Isocyanate reactions can be divided into addition reactions with nucleophiles containing reactive hydrogen atoms and self-addition reactions. Examples of these two types of isocyanate reactions are summarized in **Scheme 1-2**.



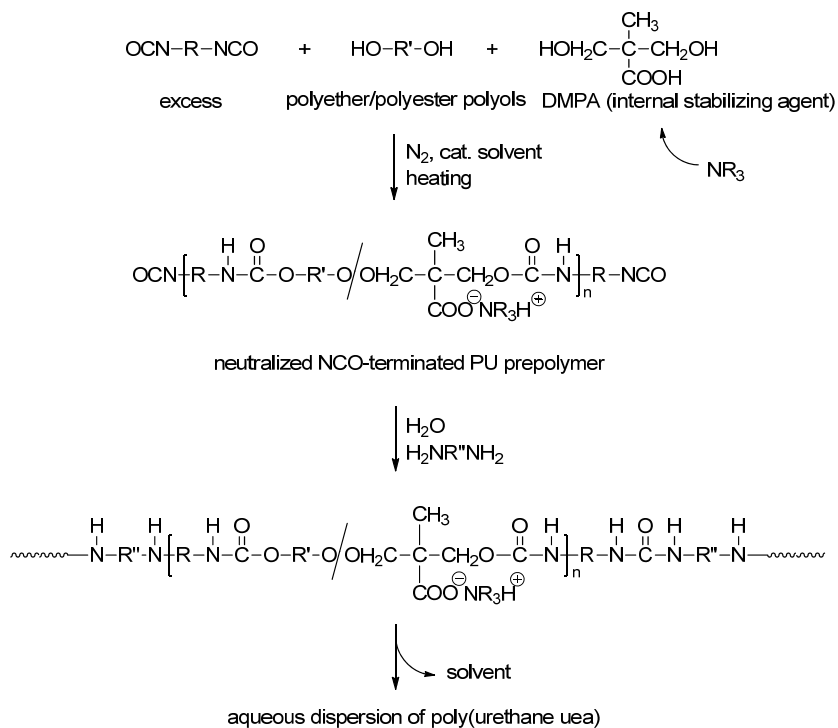
Scheme 1-2. Overview of isocyanate reactions, addition reactions with nucleophiles containing reactive hydrogen atoms (top) and self-additions (bottom).^[3-5]

1.2 Aqueous polyurethane dispersions

In coating applications, water-borne PU dispersions, together with high solids and powder coatings, form one of the most rapidly developing branches of PU chemistry, a.o. due to their low volatile organic compounds (VOC) contents.^[6-7] Water-borne PU coatings exhibit advantageously low viscosities even at high molecular weights, low-flammability, good adhesion and resistance to solvents, and have therefore gained extensive industrial importance.^[4, 8-11]

A water-borne polyurethane dispersion (PUD) is a binary colloid system in which polyurethane particles, containing internal stabilizing groups, are dispersed in the continuous aqueous medium.^[3, 8-9] The internal stabilizing agents are either of the non-ionic (e.g. poly(ethylene oxide)), cationic (e.g. quaternary ammonium salts) or anionic (e.g. carboxylate and sulfonate) type.^[4, 9] Also combinations of non-ionic and ionic types are possible. Although non-ionic dispersions, compared to their ionic counterparts, exhibit better stability in electrolytes and at relatively high temperatures, ionic stabilization is commonly applied due to its high efficacy in obtaining stable dispersions with relatively small average particle sizes.^[12-13] In this thesis, anionic polyurethane dispersions based on renewable resources are described (Chapters 3 to 6).

A conventional, two-step procedure to prepare PU dispersions consists of the synthesis of NCO-terminated prepolymers in bulk or in a low boiling solvent, followed by their dispersion in water and chain-extension, typically using diamines. Subsequently the low boiling solvent is removed by evaporation. In both steps, moderate reaction temperatures and atmosphere pressure are sufficient. The transition from the single-phase prepolymers to the two-phase dispersions is facilitated by the incorporation of hydrophilic or amphiphilic internal stabilizing agents into the hydrophobic prepolymer backbone, and assisted by mechanical stirring. A schematic representation of the so-called solvent-assisted process is depicted in **Scheme 1-3**. In this process, NCO-end capped PU prepolymers are synthesized in a low boiling point solvent by reacting an excess of diisocyanates with polyols, in the presence of the (neutralized) anionic stabilizing agent dimethylolpropionic acid (DMPA). The neutralization of the DMPA COOH groups with e.g. tertiary amines can also be performed after the prepolymer formation. High molecular weight, aqueous poly(urethane urea) dispersions are obtained by adding water and diamine chain extenders to the as-prepared, NCO-terminated prepolymers. After that, the used low boiling point solvent is removed by evaporation.



Scheme 1-3. Schematic approach to prepare anionic aqueous poly(urethane urea) dispersions, using DMPA as the internal stabilizing agent and diamine as the chain extender. ^[9, 14]

In ionic aqueous dispersions, the colloidal stability and average particle size are influenced by parameters such as the ionic content, the degree of neutralization, the structure and molecular weight of the prepolymers, as well as the polarity of the prepolymer backbone. ^[15-18] Even though the average particle size of such dispersions does not directly influence the final properties of the dispersion-cast coatings, it does influence the drying process during application, which may in turn have an effect on the final coating properties. ^[19]

1.3 Biomass and renewable PU building blocks

The concerns over dwindling fossil-fuel supplies and the environment in relation to global warming have inspired intensive research exploring renewable alternatives for petrochemicals, aiming to reduce the dependence of the polymer industry on fossil

feedstock. Inspired by the abundant availability of many varieties of biomass, their low toxicity and the relatively low cost, extensive effort has been spent to explore biomass-based chemicals or polymer precursors for the synthesis of the corresponding polymer materials.^[20-37] The most frequently applied classes of biomass in non-fuel applications include lipids (fats, glycerides and phospholipids), polysaccharides (cellulose, chitin and starch), proteins (amino acids, polypeptides) and lignin (**Figure 1-1**).^[28] This feedstock and its derivatives facilitate the synthesis of renewable polyesters,^[38-41] polyamides^[42-43], epoxy resins^[44] and polyurethane materials,^[21, 45-50] among others.

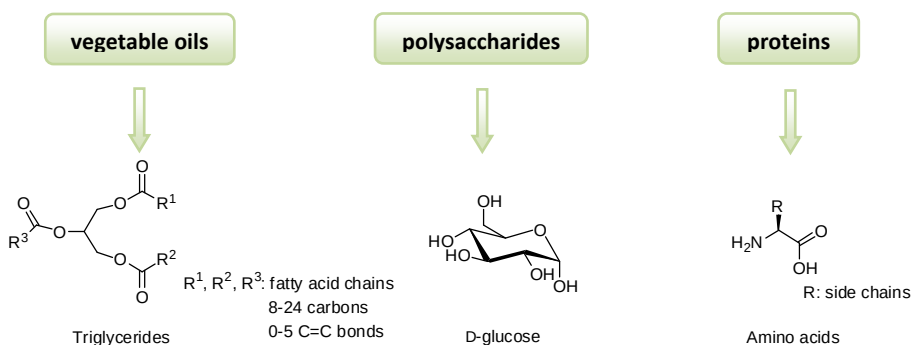


Figure 1-1. Examples of chemicals derived from vegetable oils, polysaccharides and proteins.

1.3.1 Renewable PU building blocks

The importance of polyurethanes and aqueous PU dispersions in industrial applications, together with the drive towards more sustainable polymeric materials, has sparked the research interest in developing high-performance PU products from renewable resources. Research has been ongoing to derive renewable PU building blocks and to prepare the corresponding PU products. Early investigations of polyurethanes containing castor oil (derivatives) date back to the 1960s.^[51] Since then, a wide range of plant oils such as castor, soybean and sunflower oils have been considered for the synthesis of polyurethanes. Numerous publications and patents have become available, covering renewable polyurethanes synthesized from vegetable oil-based polyols^[52-54] and diisocyanates,^[53, 55-56] sugar-based polyols^[7, 57-59] as well as amino acid-based diisocyanates.^[60-62] Along with academia, nowadays, several chemical companies, active in producing PU building blocks or the final PU products, are developing various

renewable-based products. Examples of commercialized renewable PU building blocks and their applications are listed in **Table 1-1**. However, to the best of our knowledge, fully renewable PU dispersions have not been achieved, due to the limited availability of bio-based diisocyanates and internal stabilizing agents.

Table 1-1. Examples of commercialized renewable PU building blocks and applications. ^[2]

Companies	PU building blocks	Renewable resources	Applications
DuPont	Cerenol TM	saccharides	fibers, elastomers ^[63-64]
Roquette	Neosorb®, Polysorb®	saccharides	Polyurethanes, polyesters
Huntsman	Jeffadd TM B650	soybean oil	foams, coatings, adhesives
Bayer	BAYDUR®PUL2500	soybean oil	flexible and rigid foams ^[65]
DOW CHEMICAL	Renuva TM	soybean oil	flexible foams coatings, and elastomers
CRODA	PRIPOL TM , PRIPLAST TM	vegetable oil	Polyurethanes, polyesters
Biobased Technologies	Agrol®	soybean oil	polyurethanes
BASF (Cognis)	Sovermol®, DDI®1410	vegetable oil	Coatings, adhesive, sealant
BASF	LUPRANOL®BALANCE50	castor oil	flexible and rigid foams ^[66]
HOBUM OLEOCHEMICALS	MERGINOL	castor oil, linseed oil and soybean oil	foams, dispersions, and coatings

1.3.2 Renewable PU building blocks used in this research

A dimer fatty acid-based diisocyanate (DDI®1410 or DDI), sugar-based diol 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) and amino acid-derived ethyl-2,6-diisocyanatohexanoate or ethyl ester L-lysine diisocyanate (EELDI) have been selected as the renewable PU building blocks in the work described in this thesis. The structures of these three renewable monomers are depicted in **Figure 1-2**.

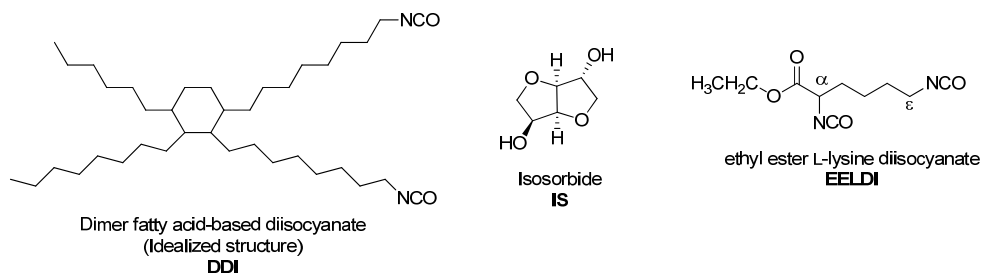


Figure 1-2. Chemical structures of DDI (idealized), IS and EELDI.

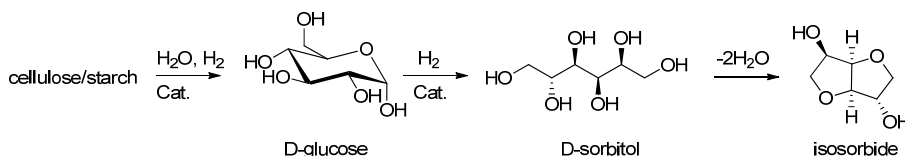
Dimer fatty acid-based diisocyanate (DDI)

DDI is a vegetable oil-based commercial product from Cognis (now part of BASF). According to the manufacturer it contains 36 carbon atoms and two terminal isocyanate functionalities. The cyclohexene structure present in this molecule is the result of the dimerization of fatty acids. Although the preparation method of this diisocyanate is not disclosed by the producer, the dimerization reaction is probably similar to that of dimerized fatty acid diols. In this process, taking linoleic acid as an example, the isomerization of linoleic acids yields conjugated molecules, which consist of positional and geometrical isomers.^[67-68] One conjugated molecule undergoes a Diels-Alder reaction with a second linoleic acid, resulting in an aliphatic, branched cyclohexene moiety as the main product, with a small fraction of (unreacted) mono and tri-functional compounds.^[2, 69] A hydrogenation step of the cyclohexene moiety is usually performed afterwards to prevent the yellowing of the products. Subsequently, these ester groups are reduced to produce dimer fatty diols.^[70] Further modification of these hydroxyl groups yields diamines, which can then be converted into diisocyanates through the phosgenation route.

DDI is a bulky, aliphatic fatty acid moiety. Similarly to the other vegetable oil-based polyols, it exhibits outstanding flexibility and hydrophobicity, potentially affording good impact resistance and water resistance to the resulting polymer materials.^[21, 71-74] In addition, its unreactive side chains would function as plasticizers for the resulting PU polymers.^[75-76] On the other hand, this substantial flexibility may significantly reduce the T_g values and the thermo-mechanical properties of the corresponding polymers, precluding its application when high rigidity and high modulus are required.^[75, 77]

Isosorbide

1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) is one of the most important, commercialized renewable diol building blocks for polymer synthesis.^[34] Together with isoidide (1,4:3,6-dianhydro-L-iditol, II) and isomannide (1,4:3,6-dianhydro-D-mannitol), they form the three 1,4:3-6-dianhydrohexitol (DAH) isomers. These DAH isomers or so-called isohexitols can be derived from polysaccharides through a three-step (bio)organic transformation, including 1) depolymerization of polysaccharides into monosaccharides (D-fructose, D-glucose), 2) hydrogenation of these monosaccharides into hexitols (D-glucitol, D-mannitol) and 3) dehydration of hexitols into DAH isomers (**Scheme 1-4**).^[78-80]



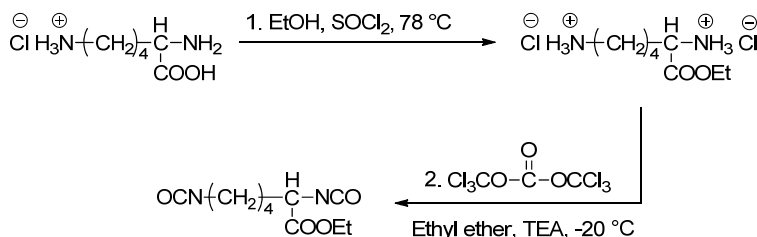
Scheme 1-4. The synthetic approach for the production of isosorbide from sugar.^[81]

Even though isosorbide contains two secondary hydroxyl group of moderate reactivity, it is exceptionally suitable for use as a polyurethane building block for several reasons. The molecular structure of isosorbide contains two fused ether rings, providing rigidity to the polymeric molecules.^[57, 82] Isosorbide is thermally stable up to 280 °C and hence, can withstand rather high reaction temperatures if required. Furthermore, the relatively low reactivity of the secondary hydroxyl groups (*endo* and *exo*) is not necessarily an issue in PU reactions, due to the highly reactive isocyanate moieties of the comonomers. In addition, the *endo*-oriented OH group is involved in intra-molecular H-bonding with the oxygen of the neighboring tetrahydrofuran ring. In spite of the steric hindrance, this intra-molecular H-bonding makes the *endo*-oriented hydroxyl group a preferred reactive center in electronically driven reactions.^[83-84] As a result, moderate reaction temperatures are sufficient to achieve high molecular weight polymers.^[85] The yellowing of isohexitols caused by the thermal oxidation at high reaction temperature can therefore be avoided. Moreover, the asymmetric and cyclic ring structure of IS is favorable for producing soluble PU prepolymers by the enlarged free volume between the polymer chains, which is an

advantage when making aqueous PU dispersions. In addition, amorphous poly(urethane urea)s are expected to be produced, which are preferably used in coating applications.

Ethyl ester L-lysine diisocyanate

Ethyl ester L-lysine diisocyanate (EELDI) is a recently commercialized diisocyanate derived from the amino acid lysine. This renewable diisocyanate is not commonly used to produce industrial PU products due to the limited number of producers, the relatively low production volume and the related high cost. The synthetic procedure of EELDI from L-lysine monohydrochloride generally includes the preparation of L-lysine ethyl ester dihydrochloride and the generation of L-lysine ethyl ester diisocyanate using a phosgenation method (**Scheme 1-5**).^[60-61] To reduce the hazardous risk of using gaseous phosgene, triphosgene and an organic solution of phosgene both have been used as alternatives in the second step, with relatively high yields between 72-95%.^[60]



Scheme 1-5. The synthesis of ethyl ester L-lysine diisocyanate from L-lysine monohydrochloride.^[61]

EELDI contains asymmetric terminal isocyanate groups, viz. the α -NCO (*secondary*-NCO) and the ϵ -NCO (*primary*-NCO) (see **Figure 1-2**). It contains five carbons between the two isocyanate groups. The overall isocyanate reactivity of EELDI and the urethane-bond density are expected to be nearly comparable to those of hexamethylene diisocyanate (HDI), though the secondary NCO group of EELDI may exhibit a somewhat reduced reactivity, restricted by the steric hindrance caused by the pendant ester group.^[86] Compared to the long chain vegetable oil-based PUs, EELDI-based polyurethanes contain a higher urethane-bond density at the same molecular weight. It potentially increases the rigidity of the resulting polymers, hence, increasing thermo-mechanical properties of

materials. Similarly to the asymmetry of IS and the petrochemical isophorone diisocyanate (IPDI), EELDI affords the possibility to obtain soluble PU prepolymers and amorphous polymeric structures, suitable for coating applications.

1.4 Property requirements

To replace petrochemistry-based PU products, renewable polyurethanes should have properties competing with or even exceeding those of their conventional counterparts. Compared to conventional PU building blocks, biomass-based PU reagents exhibit very distinctive chemical structures and physical properties, depending on their molecular structure, molecular weight, number and position of functional groups, monomer purity and polarity. Because of these differences, they may behave differently in typical PU reactions and provide different properties to the resulting polymers. Concerning PU dispersions, these new building blocks can also influence the formation of PU dispersions and their colloidal stability. Therefore, monomers from renewable resources should in most cases be considered as new and unique building blocks, rather than as drop-in replacements for petroleum-based polymers. Their chemical behavior in PU reactions and their influence on preparing PU dispersions, as well as their chemical structure-determined material properties, must therefore be investigated in detail.

1.5 Research aim and scope

The objective of this work was to develop fully biomass-based aqueous polyurethane dispersions, containing dimer fatty acid-based diisocyanates (DDI®1410 or DDI), sugar-based 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) and lysine-derived ethyl ester L-lysine diisocyanate (EELDI). The petro-based DMPA was used as the internal stabilizing agent, as no proven alternative was available. The ideal outcome of the dispersion-cast films and coatings should meet the quality requirements of conventional coating materials, with respect to thermal stability, polymer rigidity and modulus, impact resistance and chemical resistance, as well as adhesive properties.

To reach this main goal, a stepwise investigation needed to be carried out. The first target was to investigate the chemical behavior of these four chemicals in PU reactions, especially in the synthesis of isocyanate-terminated prepolymers. The potentially low compatibility between the relatively hydrophobic DDI and the hydrophilic DMPA, as well as the regio-selectivity of the asymmetric difunctional groups present in IS and EELDI,

might influence the control over the polymer composition and chain-end groups. Based on these results, the aim in the second step was to prepare anionically stabilized dispersions of (high molecular weight) chain-extended poly(urethane urea)s, containing DDI, IS and DMPA residues. To reach this objective, the dispersion process and the chain extension reactions, varying the type of chain extenders, the moment of chain extender addition and the reaction temperature, etc., needed to be investigated and optimized. The third step was an investigation on how to achieve stable, nearly fully renewable PU dispersions from DDI, IS and EELDI, by means of reducing the DMPA content. Correspondingly, the influence of the changes in polymer composition on the dispersion formation and colloidal stability had to be addressed as well. The last sub-objective was to achieve aqueous poly(urethane urea) dispersions, which after film casting resulted in satisfactory and well-controlled coating properties. To reach this goal, the properties of dispersion-cast films and coatings in terms of the T_g , thermal stability, hardness, modulus, solvent resistance and adhesion properties must be investigated.

This PhD project was sponsored by the Dutch Polymer Institute (DPI) and is entitled “PUDDING”, which stands for “PolyUrethane Dispersion Development: It’s New and Green”. In the first two and a half years of this project, a collaboration existed between Food & Biobased Research in Wageningen (FBR, part of the Wageningen University and Research Centre, WUR) and the Laboratory of Polymer Chemistry (SPC) of the Eindhoven University of Technology (TU/e).

1.6 Outline of the thesis

This study, of which the results are presented in this thesis, comprises a broad array of disciplines, ranging from kinetics studies of PU synthesis to the optimization of chain extension in aqueous dispersions, the colloidal stabilization of these PU dispersions and the properties investigation of PUU coating materials, as well as the employment of various analytical and characterization techniques. This thesis consists of seven chapters, describing the development of novel biomass-based aqueous poly(urethane urea) dispersions and the corresponding coating materials.

To obtain an overview concerning the state of the art of renewable PUs and aqueous PU dispersions, **Chapter 2** describes the recent advances in the development of bio-based PU building blocks and the corresponding PU products. It focuses on the influence of chemical structure and physical properties of renewable PU building blocks on the properties of the final polyurethane materials and the colloidal stability of aqueous PU dispersions.

Chapter 3 deals with the reactivity and regio-selectivity of DDI, EELDI, IS and DMPA in their respective PU reactions and especially in isocyanate-terminated PU prepolymer synthesis. These results are highly useful to obtain PU prepolymers with well-controlled polymer compositions and reactive end-groups.

Based on the outcome of Chapter 3, i.e. PU prepolymers with well-controlled end-groups, **Chapter 4** describes the dispersion in water and the chain extension of these PU prepolymer dispersions (PUDs), containing DDI, IS and DMPA residues in the main chain. By varying the reaction temperatures, the type of chain extender, the moment of chain extender addition and the use of catalysts, poly(urethane urea) dispersions with enhanced molecular weight were targeted.

To reduce the non-renewable DMPA content, **Chapter 5** focuses on the preparation of PU dispersions containing DDI, IS, EELDI and DMPA with a reduced DMPA content. The influence of the changes of the polymer composition on the colloidal stability and the thermal and thermo-mechanical properties of dispersion-cast films was described.

Aiming to achieve applicable PUU coatings with satisfactory and well-controlled properties, **Chapter 6** deals with the property investigation of dispersion-cast films and coatings. The thermal and mechanical properties of the dispersion-cast films, as well as the polymer phase morphology were described in correlation with the monomer properties and the polymer composition.

The final section of this thesis, **Chapter 7**, highlights the major achievements of the work presented in Chapters 3 to 6. The potential industrial applications of these PU dispersions and a few expectations regarding their further development are described in the “technology assessment” and the “outlook” section, respectively.

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2

Recent Advances in Bio-based Polyurethanes and Aqueous Polyurethane Dispersions

Abstract

Already for a few decades, biomass has been increasingly used as a feasible, renewable feedstock to reduce the dependence of polymer chemistry on fossil-fuel supplies. Both in the past and nowadays, polyurethanes (PU) and aqueous PU dispersions have shown significant importance in various industrial applications. Due to the world-wide availability, the low toxicity and the relatively low price, vegetable oil is one of the most promising biomass resources for the development of renewable PU chemistry. Partially or fully bio-based polyurethane building blocks have been developed in recent years. Challenged by the heterogeneity and the less well-defined functionality of these bio-based PU monomers, as well as their different chemical nature compared to the petroleum-based ones, a direct drop-in replacement of petroleum-based PU building blocks by these renewable-based counterparts appears to be restricted. This chapter addresses the recent developments in the area of renewable PU building blocks and their application in the synthesis of renewable polyurethanes. Particularly, it highlights the influence of the chemical nature of vegetable oil-based PU building blocks on the final properties of the resulting PU materials, as well as on the colloidal stability of aqueous PU dispersions. Moreover, the recent developments of renewable polyurethanes obtained via isocyanate-free routes are also briefly discussed.

2.1 Introduction

2.1.1 Background

Recently, taking into account the dwindling petroleum supplies and the concerns over environment in relation to global warming, as well as the abundant availability of biomass, extensive efforts have been spent to explore biomass-based chemicals or polymer precursors for the synthesis of renewable polymer materials.^[1-21] In non-fuel applications, the most frequently applied classes of biomass include lipids (fats, glycerides and phospholipids), polysaccharides (cellulose, chitin and starch), proteins (amino acids, polypeptides) and lignin.^[9, 11, 14-15, 19, 22-24] Their derivatives often contain hydroxyl, amine and carboxylic acid functional groups, and hence are potentially suitable for the synthesis of renewable polyesters,^[25-27] polyamides,^[28] and polyurethane materials,^[2, 29] etc., through step-growth polymerization. Examples of vegetable oil-, starch- and polypeptide-derived chemicals, such as triglycerides, D-glucose and amino acids, respectively, are depicted in **Figure 2-1**.

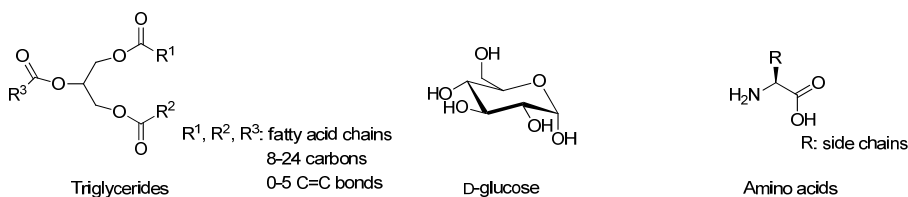
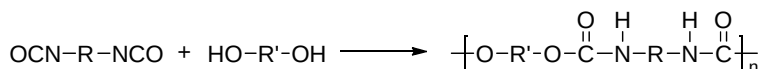


Figure 2-1. Molecular structures of triglyceride,^[30] D-glucose and amino acids as examples of biomass-based chemicals.

2.1.2 Polyurethanes

Polyurethanes (PU) are an important class of polymers exhibiting versatile polymer properties.^[31] These polymers contain urethane (carbamate) linkages formed between the monomer units, typically synthesized from diisocyanates and (polyether, polyester or polycarbonate) polyols (**Scheme 2-1**). Depending on the monomer functionality, thermosetting (chemically cross-linked) and thermoplastic (linear segmented) PUs can both be synthesized. Because of often exhibiting combined flexibility and rigidity, provided by the corresponding segments present in one and the same material, good chemical resistance and excellent adhesion to many substrates, PU materials have been applied in a

broad spectrum of industrial applications, ranging from fibers, foams, adhesives, coatings, to elastomers and sealants. In coating applications, water-borne PU dispersions form one of the most rapidly developing branches of PU chemistry, a.o. due to their low volatile organic compounds (VOC) contents.^[32] In addition, water-borne PU coatings also exhibit advantageous low viscosities even at high molecular weights, low-flammability, good adhesion and resistance to solvents^[33-36] and therefore have gained extensive industrial importance.



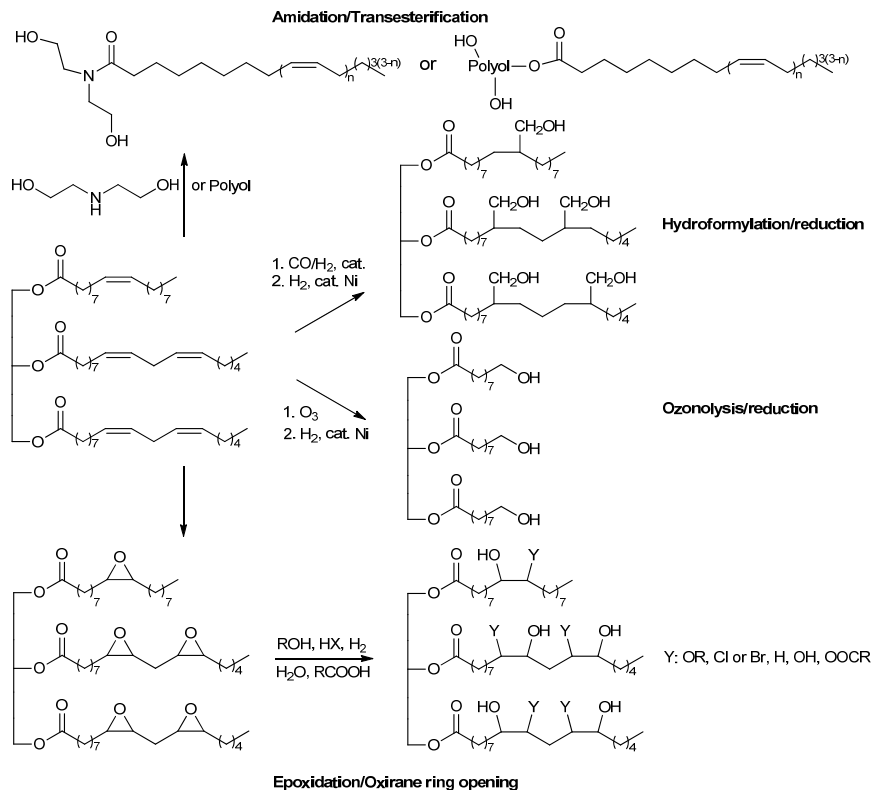
Scheme 2-1. Synthesis of a polyurethane from a diisocyanate and a diol.

2.1.3 Renewable PU building blocks

In recent years, a considerable number of PU building blocks, including polyols, diamines and diisocyanates, have been synthesized from renewable resources. Of these new building blocks, vegetable oil polyols form the most abundant fraction, owing to their availability, low toxicity and relatively low cost.^[30, 36-41] In addition to oil-derived polyols, vegetable oil-based diisocyanates,^[37, 40] sugar-based polyols^[14, 19, 42-53] and diisocyanates,^[54-58] as well as amino acid-derived diisocyanates,^[59-61] etc., are also currently available, constituting an important contribution to the library of renewable PU building blocks.

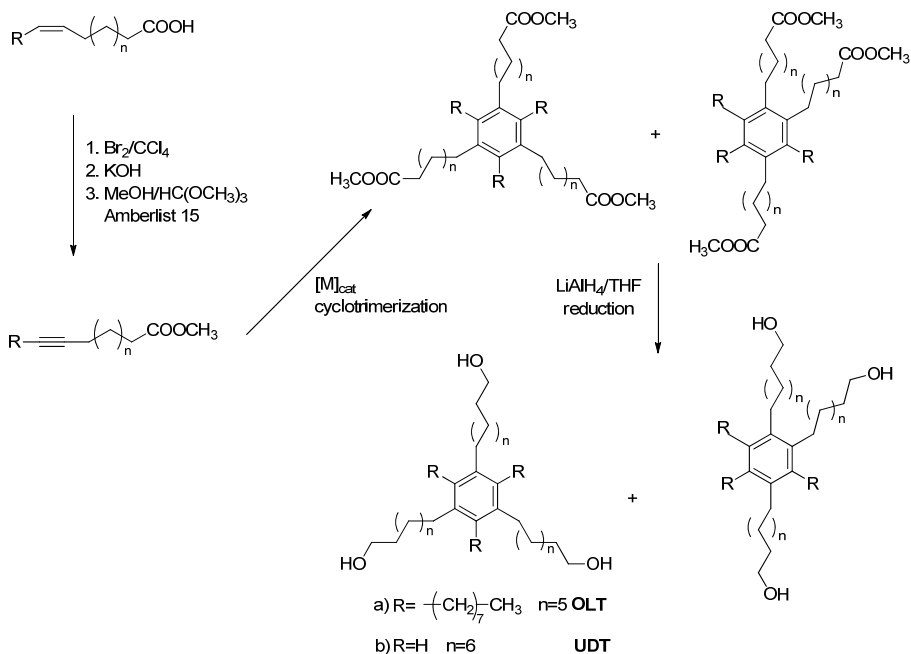
From vegetable oils

In the category of vegetable oil-based polyols, castor oil is the only commercially available, naturally hydroxylated triglyceride, and it can be directly used for PU synthesis.^[22, 62] Other vegetable oils, such as soybean oil and sunflower oil, can be converted to the corresponding polyols through one of the following methods: 1) the direct oxidation of oils by epoxidation of the olefin functional groups, followed by ring opening substitution,^[31, 63] 2) the hydroformylation/reduction of carbon-carbon double bonds present in the fatty acid backbone,^[31, 64] 3) ozonolysis/reduction of the carbon-carbon double bonds, resulting in primary and short alcohols,^[31, 65] and 4) transesterification/amidation of triglycerides with glycols or diethanolamine^[66] (**Scheme 2-2**)^[1, 31] Depending on the synthetic approaches and the triglyceride structure, the resulting polyols may vary in their molecular structures and the position and number of hydroxyl functionalities.



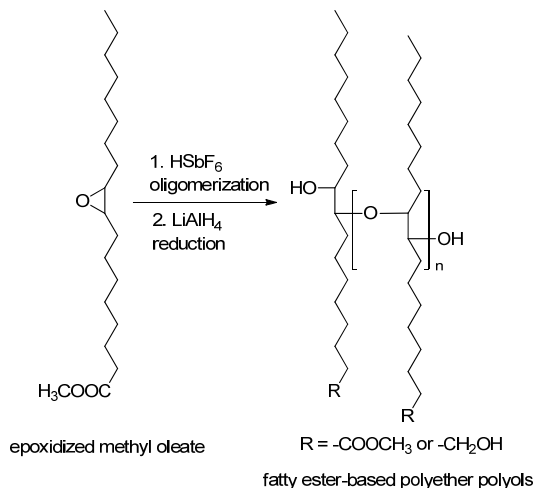
Scheme 2-2. Schematic presentation of the synthetic methods to obtain vegetable oil-based polyols.^[30] (©2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

In addition to these most common approaches, other methods such as cyclotrimerization of alkyne fatty esters^[67] and oligomerization of epoxidized methyl oleate^[68-69] have also been used to derive vegetable oil-based polyols of different molecular structures. For instance, castor oil and sunflower oil-based terminal aromatic triols, 1,3,5-(9-hydroxynonyl)benzene (UDT) and 1,3,5-(8-hydroxyoctyl)-2,4,6-octylbenzene (OLT), have been synthesized through two major steps: the cyclotrimerization of alkyne fatty esters and the subsequent reduction of the carboxylate groups to yield primary hydroxyl groups (Scheme 2-3).^[67]



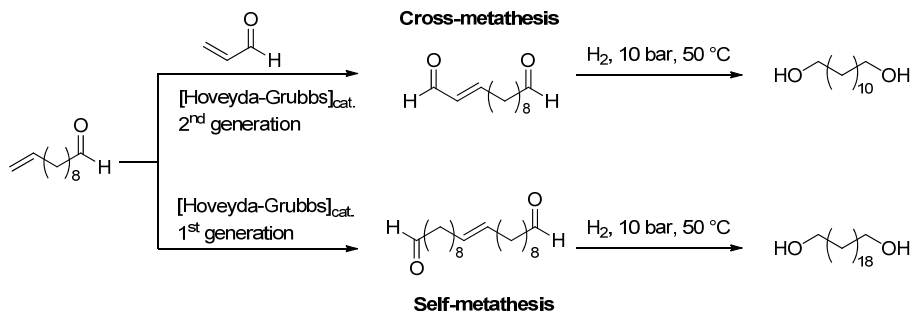
Scheme 2-3. Synthesis of castor oil and sunflower oil-based OLT and UDT, as well as the asymmetric triol products. ^[67]

Lligadas et al. have synthesized fatty ester-based polyether polyols from the oligomerization of epoxidized methyl oleate (EMO), followed by the controlled reduction of the ester groups to hydroxyl groups (**Scheme 2-4**). ^[68-69] The degree of ester reduction can be varied to obtain polyols with a wide range of hydroxyl contents. By reacting these polyols of different hydroxyl contents with diisocyanates (MDI or L-lysine diisocyanate), with or without the presence of chain extenders, a variety of thermosetting PUs were synthesized. ^[68-71]



Scheme 2-4. Synthesis of fatty ester-based polyether polyols from epoxidized methyl oleate. ^[30, 68-69]

Another very interesting approach to produce vegetable oil polyols is *via* olefin metathesis. The olefin metathesis of vegetable oils has shown to be an efficient, straightforward method to synthesize vegetable oil-based polyols with linear or branched molecular structures. ^[26, 72-75] The carbon-carbon double bonds present in the fatty acid chains can be modified through self- or cross-metathesis. A few examples of olefin metathesis of vegetable oils are depicted in **Scheme 2-5**. In addition to a number of publications, a review describing the recent progress in this field of research has been published by de Espinosa et al. ^[72]



Scheme 2-5. Synthesis of α,ω -diols from castor oil-based 10-undecenal. ^[72]

Compared to vegetable oil-based polyols, renewable diisocyanates are much less developed. ^[37, 40] Their preparation is hampered by the challenges involved when introducing primary amines onto a vegetable oil backbone. Hence, the common phosgenation route to convert primary amines into isocyanates is typically not applicable. Furthermore, this route is not considered as eco-friendly and sustainable as it involves the extremely toxic compound phosgene and the resulting toxic isocyanates. The successful introduction of terminal diisocyanates on linear saturated fatty acid chains was achieved by Narine and coworkers. ^[40] Those diisocyanates were synthesized from oleic acid *via* the Curtius rearrangement. One commercialized vegetable oil-derived aliphatic diisocyanate (Cognis, now BASF, product DDI®1410) is prepared from dimerized fatty acids. ^[2] More et al. have also successfully derived two linear aliphatic diisocyanates, 1-isocyanato-10-[(isocyanatomethyl)thio]decane (DITO) and 1,8-diisocyanatooctane (DIO) (**Figure 2-2**), from fatty acid moieties through a non-phosgene method. ^[37]

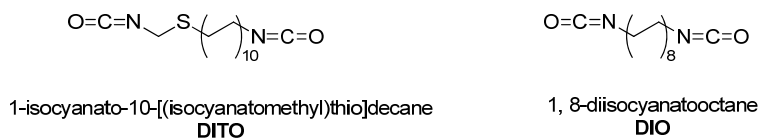


Figure 2-2. The molecular structures of DITO and DIO.

From sugar (polysaccharides)

Sugar-derived polyols form another important category of renewable PU building blocks. Early studies of sugar-derived 1,4:3,6-dianhydrohexitols date back to 1940s. ^[76-77] In recent years, various polysaccharides-based polyols have been developed, ranging from 1,3-propanediol (from glucose fermentation), polytrimethylene ether glycol (polymerized 1,3-propanediol), ^[78] to various sugar alcohols (sorbitol, mannitol and L-iditol) and their further derivatives (isosorbide, isomannide and isoidide). Isosorbide is the only sugar diol technically produced in relatively large quantities (multi-ton scale), and it is currently an increasingly important, commercialized building block for polymer synthesis. ^[15] Further modification of sugar diols to produce diisocyanate monomers has been achieved through a cold and hot two-step phosgenation procedure. ^[54-55] A few patents describing the derivation of sugar-based isocyanates phosgene-free approaches have been filed. ^[56-58]

To explore the use of sugar derivatives to a large extent, Muñoz-Guerra and Galbis et al. have developed a variety of carbohydrate-based chemicals, containing hydroxyl, amine and carboxylic acid functionalities. A few examples of these sugar derivatives are depicted in **Figure 2-3**. These building blocks are mainly applied as monomers for the synthesis of degradable polyesters, polycarbonate, polyamines and polyurethanes. ^[19, 48-53, 79-81]

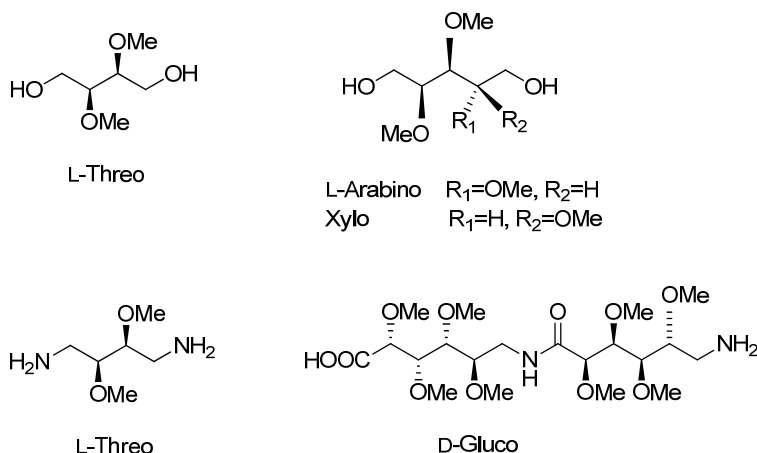
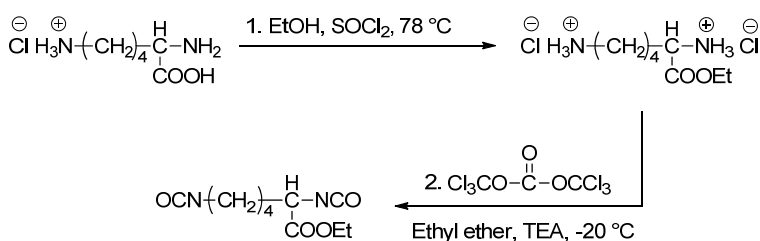


Figure 2-3. Sugar derivatives containing hydroxyl, amine and carboxylic acid groups. ^[19]

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From amino acids

Though sparsely available, ethyl-2,6-diisocyanatohexanoate (ethyl ester L-lysine diisocyanate) and lysine triisocyanates represent two recently developed isocyanate-functional compounds from amino acids. The L-lysine diisocyanate (LDI) can be obtained through a two-step reaction (**Scheme 2-6**): the preparation of the amino acid ester dihydrochloride from L-lysine monohydrochloride and the subsequent generation of the L-lysine ethyl ester diisocyanate using a phosgenation method. ^[59-60] This type of diisocyanate has been mainly used to prepare non-toxic, degradable PU materials for tissue engineering and biomedical materials. ^[60-61, 82-84]



Scheme 2-6. The synthesis of ethyl-2,6-diisocyanatohexanoate. ^[60]

A few excellent reviews, describing the more detailed derivation of renewable PU building blocks, vegetable oil-based polyols in particular, are available for interested readers. ^[2, 15, 30-31, 85]

2.1.4 A brief history of renewable PUs

Early applications of vegetable oil-based PUs building blocks date back to the 1960s, when castor oil was applied to prepare PU foams. ^[86-87] In the 1980s-90s, sugar-based isohexitols, such as isosorbide and 2,5-diamino-1,4:3,6-dianhydro-2,5-dideoxyalditols (with D-gluco-, D-manno-, and L-ido-configuration), were also used as PU monomers for the synthesis of polyurethane-based plastics or elastomers. ^[88-91] Recently, partially or fully bio-based polyurethane products have been developed at an increasing pace. Numerous publications and patents have become available, covering renewable polyurethanes synthesized from vegetable oil-based polyols ^[30, 38-39] and diisocyanates, ^[30, 40-41] , sugar-

based polyols^[48-53, 92-95] as well as amino acid-based diisocyanates.^[59-60, 69, 71, 82-84, 96-99] Concurrently, a large number of chemical companies also increasingly spend efforts on developing various renewable-based PU products.^[31, 78, 100-101] Of these companies, CRODA has commercialized several vegetable-derived polyols such as PRIPOLTM (fatty acid-based dimers) and PRIPLASTTM (polyether polyols), with a renewable content ranging from 36% to 100%. Cognis, nowadays part of BASF, developed a large range of polyols (Sovermol[®]) from vegetable oils. Cargill has commercialized soybean oil-based polyol BIOH[®] for flexible foam applications. This bio-based polyol has a renewable carbon content of higher than 95% and has won the Presidential Green Chemistry Award in 2007.^[31] The polyurethanes based on such newly developed PU building blocks cover a broad range of applications from foams, thermoplastic and thermoset elastomers, to coatings and adhesives.^[22]

2.1.5 Property requirements

To replace petrochemical-based PU products, renewable polyurethanes should have properties competing with or even exceeding those of their conventional counterparts. Compared to conventional PU building blocks, biomass-based PU reagents are different in terms of their molecular structure, molecular weight, number and position of functional groups, monomer purity and polarity. Hence, the polymer properties of renewable-based polyurethanes are expected to be rather different as well from those of conventional petro-based polyurethanes.

Concerning vegetable oil-based polyols, one should bear in mind that these polyols are a mixture of various triglycerides of different molecular structures.^[9, 11, 30, 39, 72] Depending on the derivation methods, their hydroxyl functionality can vary from primary to secondary, from pendant to terminal and from di- to multi-functional. These variations may lead to complications when striving to obtain a well-defined polymer composition and to achieve the desired polymer properties. Moreover, the bulky, aliphatic fatty acid moieties present in vegetable oil-based polyols exhibit outstanding flexibility and hydrophobicity, improving the material's impact resistance and water resistance.^[102-103] On the other hand, this kind of monomer structure may significantly reduce the T_g values and the thermo-mechanical properties of the corresponding polymers, significantly limiting the scope of their applications where high temperature shape stability and material rigidity are required.^[104-105] Therefore, tremendous efforts have been spent to improve the properties of vegetable oil-based PUs.

2.1.6 Scope of this review

Regarding the development of vegetable oil-based polyurethanes, (sugar-based PUs have been reviewed in previous publications ^[15, 19, 89, 106]) a number of reviews are available. ^[2, 9, 18, 30-31, 39] These reviews comprehensively cover the synthetic methods to prepare vegetable oil-derived polyols and their incorporation into renewable thermosetting and thermoplastic PU products, as well as into water-borne polyurethane dispersions. None of the existing reviews, except for the one published by Petrović, ^[2] did extensively address the polymer properties in correlation with the chemical structure and physical properties of these new biobased raw materials. This current review intends to provide an overview of the recent developments in the field of renewable polyurethanes, including thermosetting and thermoplastic PUs as well as aqueous PU dispersions. In addition, it highlights the importance of the chemical structure and physical properties of the renewable PU building blocks, vegetable oil-based ones in particular, in correlation with the polymer properties. Furthermore, some recent advances in the development of vegetable oil-containing polyurethanes synthesized through isocyanate-free routes are also addressed.

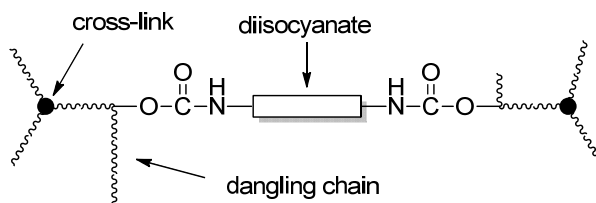
2.2 Chemical structure - property correlation of oil-containing polyurethanes

2.2.1 Thermosetting polyurethanes

Thermosetting (thermoset) polyurethanes are chemically cross-linked polymers, obtained by reacting multi-functional polyols with polyisocyanates. Because of their chemically cross-linked network topology, PU thermosets are characterized by high moduli, strength, durability, chemical resistance and excellent thermo-mechanical properties. The applications of PU thermosets range from flexible or rigid foams to elastomers and coatings. ^[29]

To prepare thermosetting polyurethanes, tri- or multi-functional hydroxyl or isocyanate compounds are required. Vegetable oil-based and sugar-based polyols are the most promising candidates because of their multi-functionality. However, conventional polyols have terminal primary or secondary hydroxyl groups. Their molecular weights are in the range of 400-6000 g/mol. Differently, vegetable oil polyols, such as castor oil and polyols obtained from epoxidation/ring opening of vegetable oils, have pendant hydroxyl groups, located along the polyol structure (**Scheme 2-2**). ^[30-31] Their molecular weights are commonly below 1000 g/mol, lower than that of most conventional polyols. ^[2] By reacting

these polyols (containing pendant hydroxyl groups and relatively low molecular weights) with isocyanates, a significantly shorter average chain length between cross-links is expected. In addition, the short pendant side chains, also called dangling chains (as shown in **Scheme 2-7**), would function as a plasticizer. They provide additional viscoelasticity to the materials, but also reduce their rigidity. Due to the steric hindrance of dangling chains, further cross-linking is hampered.^[105, 107]



Scheme 2-7. Schematic PU network chain structure containing dangling chains and cross-links.^[2]

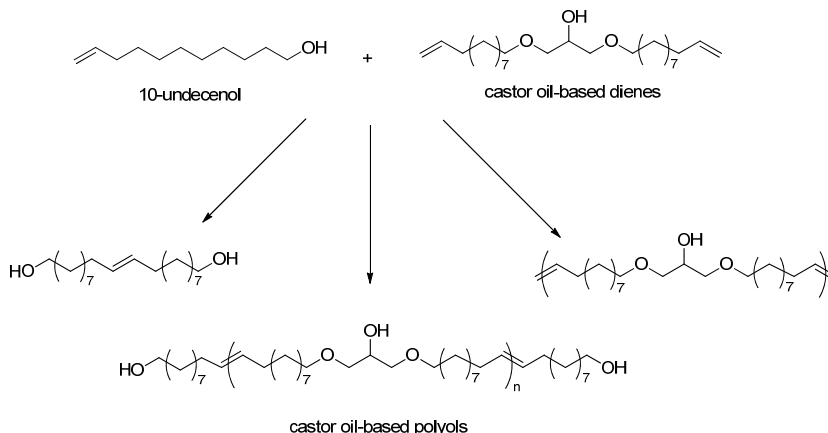
Various methods have been investigated to prepare polyurethane thermosets with satisfactory rigidity and thermo-mechanical properties. These methods include: 1) using alternative methods to derive polyols having reduced pendant hydroxyl groups but increased terminal OH groups, 2) increasing cross-linking density, 3) incorporating rigid comonomers and 4) applying a segmented polymer structure. Due to the limited availability of renewable diisocyanates, the currently prepared renewable PU thermosets mainly contain conventional diisocyanates, such as 2,4-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI) and isophorone diisocyanate (IPDI).

Vegetable oil polyols derivatization methods

As mentioned previously, vegetable oil-based polyols can be synthesized through four main types of reactions (**Scheme 2-2**). Castor oil and the polyols obtained from the epoxidation of unsaturations along the fatty acid structure and the subsequent ring opening contain pendant, secondary hydroxyl functionalities. These secondary hydroxyl groups usually exhibit limited reactivity in PU synthesis and thus limit the cross-linking density. A relatively high amount of catalyst or high reaction temperatures are normally

required to achieve high conversions.^[108] Using hydroformylation/reduction,^[64] ozonolysis^[109-110] and transesterification reactions, primary hydroxyl groups can be obtained. However, the pendant, primary hydroxyl groups obtained through hydroformylation may still result in significant amounts of dangling chains, plasticizing the resulting PU materials, in just the same way as the earlier mentioned secondary alcohol containing vegetable oil polyols.^[111] On the contrary, both ozonolysis and transesterification reactions introduce terminal, primary OH groups to polyols. Still, the polyols prepared through transesterification contain the fatty acid backbone as a side chain, again reducing the rigidity of the derived polyurethanes. Only polyols prepared through ozonolysis lack such dangling chains. In spite of their relatively low hydroxyl functionality (typically tri-functional), compared to the products obtained from epoxidation and hydroformylation, the corresponding polyurethanes exhibit much improved mechanical properties.^[2, 107, 112]

Moreover, the olefin metathesis of vegetable oils provides a broad range of opportunities to obtain polyols with desired linear molecular structures and terminal hydroxyl functionalities. In addition, the chain length of the polyols can be controlled by cross-metathesis. Del Río et al. have prepared castor oil-based polyols of different molecular weights by the acyclic diene metathesis polymerization (ADMET) of castor oil-based dienes (1,3-di-10-undecenoxy-2-propanol) with 10-undecenol (**Scheme 2-8**). The addition of a varying amount of 10-undecenol was used to end-cap the diene groups and control the chain length of the polyols. The as-prepared castor oil-based polyols were reacted with MDI to produce cross-linked polyurethanes. The T_g values increased from 8 °C to 28 °C with increasing 10-undecenol content.



Scheme 2-8. The ADMET polymerization of castor oil-based dienes and 10-undecenol. ^[74]

Increasing the cross-link density

The increase of the cross-link density in vegetable oil-based PUs can be achieved either by changing the monomer ratio or by increasing the functionality of the comonomers. For instance, a soy-based polyol (number average functionality, $f_{\text{noH}} = 3.6$) was reacted with MDI at different NCO/OH ratios, ranging from 0.4 to 1.05. ^[104] Polyurethanes with various cross-link densities were obtained. With increasing NCO/OH ratio, the T_g values of the resulting polymers increased from below 0 °C to 64 °C. The corresponding tensile strength increased and the elongation at break decreased.

Petrović and coworkers have synthesized polyols through the partial hydrogenation of epoxidized soybean oil. ^[113] These polyols have hydroxyl numbers ranging from 82 to 225 mg KOH/g and number-average functionalities (f_{noH}) ranging from 1.4 to 3.8. The influence of their structural heterogeneity on network formation and properties were investigated. Polyurethanes containing polyols with high hydroxyl numbers (> 200 mg KOH/g) are glassy polymers, while polyols having relatively low hydroxyl values yield rubbery materials. Because of the low (average) hydroxyl numbers, imperfect and heterogeneous networks were formed, resulting in relatively low elongation at break and low tensile strengths.

Incorporation of rigid, short comonomers

To improve the thermal and mechanical properties of vegetable oil-based polyurethanes, conventional rigid diisocyanate comonomers such as TDI^[114], IPDI^[115] and MDI^[116] have been used. The research group of Petrović has evaluated the effect of nine different isocyanates (**Figure 2-4**) on the properties of polyurethanes, using soy polyol ($V_{OH} = 206$ mg KOH/g) as the counter reagent.^[114] The resulting PU showed glass transitions decreasing from using aromatic triisocyanates ($T_g = 93$ °C and higher) to aromatic and cycloaliphatic diisocyanates ($T_g = 47$ -59 °C) to aliphatic triisocyanates ($T_g \sim 25$ °C) and finally using aliphatic diisocyanates ($T_g = 10$ °C). The tensile strength of these polymers decreased in the same order.

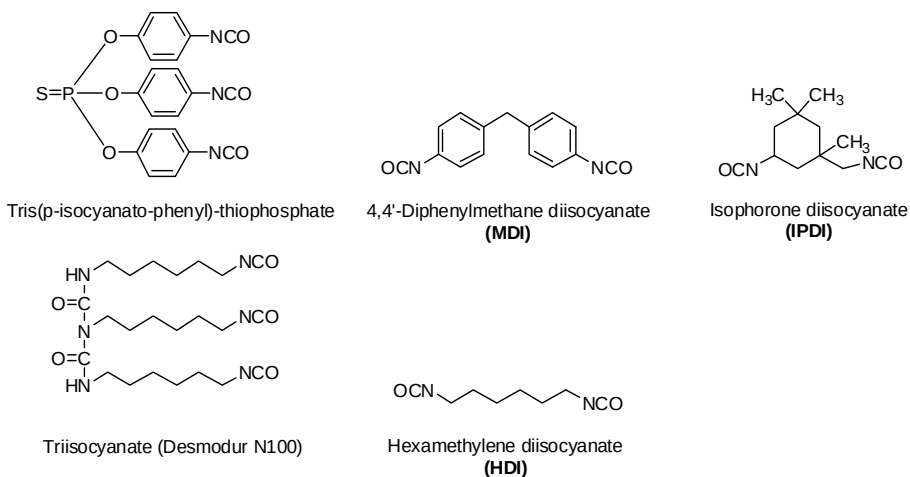


Figure 2-4. Examples of isocyanates ranging from aromatic trifunctional to aromatic and cycloaliphatic difunctional, and to aliphatic trifunctional and difunctional.

The same research group also observed that by cross-linking castor oil with distilled MDI instead of crude MDI, the T_g values increased from -40 to -5 °C.^[116] Obviously, a much improved MDI purity and consequently higher cross-linking density was obtained by using distilled MDI.

Segmented polymer structures

Preparing thermosets with segmented structures is another commonly applied method to improve the T_g values and the mechanical performance of these materials. Corcuera et al. have prepared segmented PU elastomers from castor oil polyols ($f_{\text{OH}} = 3$) as the soft segment. The hard segment consists of 1,4-butanediol (BD) after reaction with hexamethylene diisocyanate (HDI) or MDI.^[117] By changing the polyol : diisocyanate : BD ratio from 1 : 3 : 2 to 1 : 11 : 10, the T_g values of the hard segments increased up to 50 and 62 °C for HDI- and MDI-based polyurethanes, respectively. These T_g values are much higher than those of the solely soft segments-based PUs, -51 and -42 °C, respectively. In addition, HDI-based PUs presented a relatively high degree of phase separation and high hard segment crystallinity, as well as a superior thermal stability compared to the MDI-based PUs.

A series of poly(ether urethane) networks were synthesized by reacting polyether polyols (epoxidized methyl oleate, structure depicted in **Scheme 2-4**) with MDI or L-lysine diisocyanate (2,6-diisocyanato methyl caproate, LDI) (**Figure 2-5**).^[71] By increasing the hydroxyl content of the polyols, the DSC-derived T_g values increased from -29 °C to 49 °C and from -25 °C to 23 °C for MDI- and LDI-based PUs, respectively. The Young's modulus and tensile strength at break of these PUs also increased accordingly. In the same work, 1,3-propanediol was added as a chain extender to obtain segmented poly(ether urethane) networks. By varying the amount of 1,3-propanediol and keeping the hydroxyl content of polyols constant, segmented PU networks with calculated hard segment contents ranging from 15% to 47% were obtained. Micro-phase separation was observed in both MDI- and LDI-based PUs. The hard segment T_g values were about 53–56 °C and 40–50 °C for MDI- and LDI-based PUs, respectively. The relatively low hard segment T_g of LDI-based PUs was assigned to the irregular aliphatic structure of LDI. For the same reason, LDI-based PUs exhibited a relatively low Young's modulus and tensile strength.^[69, 71]

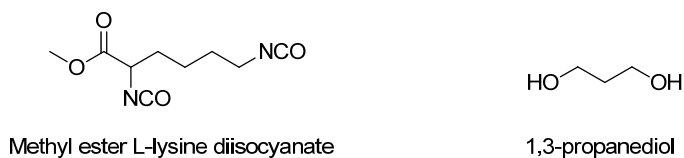


Figure 2-5. The molecular structure of L-lysine diisocyanate and 1,3-propanediol.^[71]

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Yeganeh et al. ^[118] used modified castor oil polyol ($f_{\text{noH}} = 2$), combined with the relatively short 1,4-butanediol, to react with TDI and then cured the products with toluene diisocyanate dimer (uretdione). By increasing the amount of short diol (1,4-butanediol) and TDI in the monomer feed, the T_g values reached 52 °C. Other properties, such as the tensile strength, modulus and tear strength of the produced elastomers, also increased accordingly. These increases were assigned to the increased hard segment content and the intermolecular interactions.

To extend the scope of applications of renewable polyurethanes, efforts have been made to incorporate aromatic compounds into vegetable oil-based polyurethanes, affording additional rigid properties. ^[67] Segmented PUs were synthesized from castor oil- and sunflower oil-based terminal aromatic triols (**Figure 2-6**), 1,4-butanediol and MDI. The synthesis of these aromatic triols (OLT and UDT) refers to **Scheme 2-3**. The hard segment content was varied from 44% to 52%. Higher T_g values were observed in polyurethanes with higher amounts of hard segments, where semi-crystallinity and phase separation were observed. Materials with lower hard-segment contents exhibited better phase mixing.

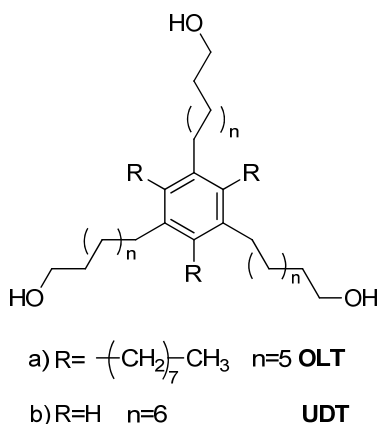


Figure 2-6. Castor oil- and sunflower oil-based triols. ^[67]

2.2.2. Thermoplastic polyurethanes

Thermoplastic polyurethanes (TPU) are block copolymers containing alternating rigid and flexible blocks, mainly used to prepare thermoplastic elastomers, adhesives and coatings.

[2, 119-120] The soft segment usually contains polyether or polyester oligomeric diols, having molecular weights between 400 and 2000 g/mol. The hard domains typically consist of the diisocyanate residue in combination with a short chain diol or diamine chain extender. As a result, the hard segments contain the urethane and/or urea moieties, providing chain rigidity and physical cross-linking through hydrogen-bonding. Because of the immiscibility between the short, rigid domains and the flexible long chain matrix, as well as the self-organization of the hard segments through H-bonding, phase-separated polymer morphologies are often present. Various studies have shown that the phase morphology of segmented PUs can be influenced by the structure of the soft/hard segments, as well as their chain length and the soft/hard content in the polymer composition. [2, 120] The obtained polymer phase morphology directly influences the physical properties of the materials.

Thermoplastic polyurethanes can only be obtained when using linear, difunctional and preferably symmetrical diisocyanate, diol and/or diamine monomers, affording the desired segmented polymer structure. Vegetable oil-based polyols in general contain multiple hydroxyl groups and hence have not been commonly applied to prepare TPUs. However, a few di-functional polyols and isocyanates, newly derived from vegetable oil, have shown potential in the preparation of vegetable oil-based TPUs. [121-123] Since these diols and diisocyanates do not always contain pendant functional groups, the effect of the dangling chains is less pronounced in these TPU materials.

TPUs containing vegetable oil-based diols

Petrović et al. have synthesized the polyricinoleate diol (**Figure 2-7**) from castor oil, having an M_n of 2580 g/mol. Segmented polyurethanes were prepared using this polyricinoleate diol as the soft segment and MDI/BD as the hard segment. The soft segment contents (SSC) are varied from 40 to 70%. The effect of the SSC on the phase morphology of the resulting polyurethanes and the related material properties were investigated. Their results showed that phase separation was observed in all polymers. A reduced modulus from more stiff to elastic was observed with increasing soft segment content. Surprisingly, the presence of the six-carbon dangling chains in the soft segments did not seriously limit the material properties. [122]

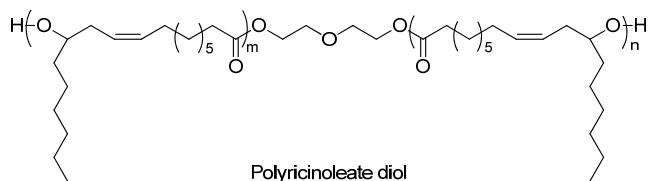


Figure 2-7. The structure of polyricinoleate diol. ^[122]

TPUs containing vegetable oil-based diisocyanates

The production of 1,7-heptamethylene diisocyanate (HPMDI) (**Figure 2-8**) from fatty acids, consisting of linear saturated chains with terminal isocyanate groups, was established by Narine and coworkers.^[40] This diisocyanate was then copolymerized with 1,18-octadec-9-enediol (ODEDO) and chain extended with 1,9-nonanediol (NDO). Both diols were derived from oleic acid. HDI was used as a reference to compare with HPMDI. As a result, entirely renewable linear segmented polyurethanes were prepared.^[123] These fully renewable PUs have shown a similar phase morphology as their HDI-based counterparts. Compared to the corresponding HDI-based TPUs, HPMDI-containing TPUs exhibit a weak H-bonding strength and a reduced ordered crystal structure, leading to a reduced tensile strength and elongation at break. This was assigned to the effect of the odd number of methylene groups present in HPMDI. The hydrogen-bonding profile of the TPUs containing HDI and HPMDI is depicted in **Figure 2-9**.

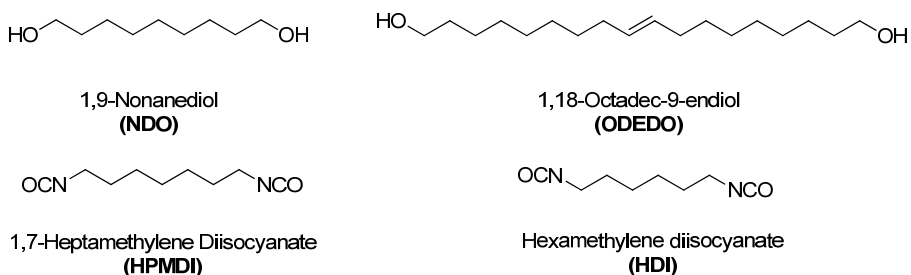


Figure 2-8. The chemical structures of NDO, OEEDO, HPMDI and HDI.

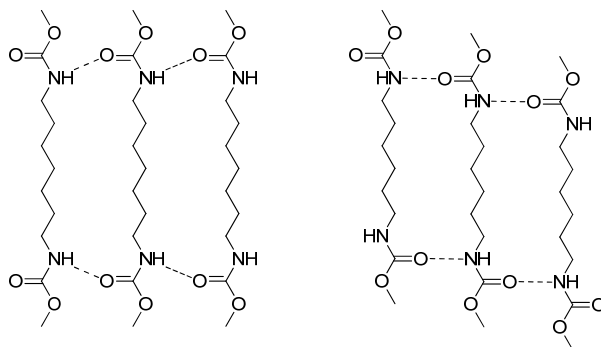


Figure 2-9. Hydrogen-bonding profile of TPUs containing HPMDI (left, odd number) and HDI (right, even number of methylene groups) as the diisocyanates. ^[123]

Two diisocyanates synthesized through a non-phosgene method, mentioned previously (**Figure 2-2**), were reacted with various diols to obtain partially and fully bio-based thermoplastic polyurethanes. The used diols range from 1,3-propanediol, 1,12-dodecanediol, butanol ricinoleate (BuRicin), 11-[(2-hydroxyethyl)thio]undecan-1-ol (HETU), isosorbide to pripol 2033 (**Figure 2-10**). The influence of the diol structures on the polymer properties was investigated. As a result, the diols with methylene dangling chains (Pripol 2033) or cyclic structure (IS and Pripol 2033) showed to enhance the amorphous feature of the polyurethanes, due to the disruption to the close packed polymer chains and the increased free volume, respectively. ^[37]

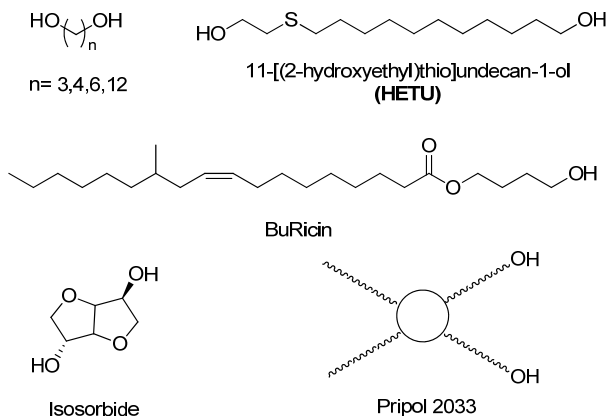


Figure 2-10. Structures of the used polyol precursors.

TPUs containing other renewable polyols

In addition to fatty acid derivatives, other renewable polyols, such as poly(1,2-dimethylethylene adipate) (PDMEA) and poly(1,2-dimethylethylene succinate) (PDMES) (**Figure 2-11**), having M_n values between 700-800 g/mol, have been developed to synthesize thermoplastic PUs. ^[124] These novel renewable polyols were synthesized from 2,3-butanediol and dimethyl adipate (DMAd) or dimethyl succinate (DMS) through transesterification. ^[125] The number of repeating units in these polyols is tunable by changing the monomer feed ratio or the reaction time. PDMEA- and PDMES-based amorphous PUs exhibit approximately 20 and 40 °C higher T_g values (determined using DSC) than those based on poly(propylene glycol)s (PPGs) of comparable M_n , respectively. The tunable chain length of this type of polyols makes them interesting for a broad variety of applications.

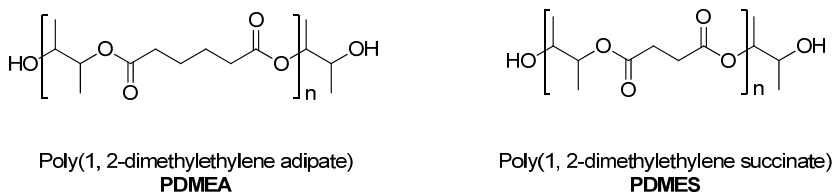


Figure 2-11. Structures of PDMEA and PDMES. ^[124-125]

2.2.3. Aqueous polyurethane dispersions

A water-borne polyurethane dispersion (PUD) is a binary colloid system in which polyurethane particles, containing colloiddally stabilizing groups (ionic or non-ionic), are dispersed in the continuous aqueous medium.^[33-34, 126] The commonly applied two-step procedure to prepare PU dispersions consists of the synthesis of NCO-terminated prepolymers in a low boiling point solvent or in bulk, followed by their dispersion in water and chain-extension, typically using diamines. Subsequently, the low boiling point solvent, having assisted the dispersion process, is removed by evaporation. Ionic stabilization is commonly applied due to its high efficiency for obtaining stable dispersions with relatively small average particle sizes. In ionic aqueous dispersions, the colloidal stability and average particle size are usually influenced by parameters such as the ionic content, the degree of neutralization, the structure and molecular weight of the prepolymers, as well as the polarity of the prepolymer backbone.^[127-130] Even though the average particle size of such dispersions does not necessarily directly influence the final properties of the dispersion-cast coatings, it does influence the drying process during application, which may in turn have an effect on the final coating properties.^[131] Therefore, it is of great importance to study the average particle size and the colloidal stability of the dispersions in correlation with the aforementioned parameters. In addition, the influence of the used monomer structures and the polymer composition on the product properties must also be assessed.

Athawale^[132] and Pfister^[30] have summarized the studies of PUDs containing renewable vegetable oil resources. These studies include anionic and cationic PU dispersions containing polyols derived from castor oil,^[133-134] rapeseed oil^[135-136] and soybean oil^[133, 137-139]. The influence of these new polyols, including their hydroxyl functionality and structure, and the degree of neutralization on the average particle size of the dispersions were investigated. The properties of dispersion-cast films were also discussed correspondingly. The main findings of these studies are summarized hereafter.

Influence of hydroxyl functionality on average particle size

Series of anionic PU dispersions containing methoxylated soybean oil polyols^[139], IPDI and dimethylolpropionic acid (DMPA) were prepared by varying the hydroxyl functionality from 2.4 to 4.0. The average particle size of these dispersions increased from about 12 to 130 nm in diameter with increasing OH functionality from 2.4 to 4.0. An increased weight percentage of DMPA was used to keep a constant molar ratio between the functional

groups of DMPA, polyol and IPDI. When increasing the hydroxyl functionality of the polyol, the increased average particle size was mainly due to the increase of the polymer cross-linking, which was proven by the soluble fraction measurements of dry films. The dispersion-cast films exhibited DSC-determined T_g values ranging from 8.9 to 33 °C, increasing with increasing hydroxyl functionality. The degree of intermolecular hydrogen bonding can be effectively controlled by the hard segment content, yielding PU materials ranging from elastomeric polymers to ductile plastics and rigid plastics.

Influence of DMPA neutralization on average particle size

Rapeseed oil-derived polyol ($f_{\text{noH}} \sim 2.75$) was reacted with IPDI to prepare anionic polyurethane dispersions. These dispersions were stabilized with triethylamine (TEA)-neutralized DMPA and chain extended with ethylene diamine (EDA).^[135] The effect of the hydrophobicity of the triglyceride backbone on the dispersion-cast films and the influence of the degree of DMPA neutralization on the dispersion stabilization were investigated. DMPA neutralization degrees lower than 70% were found to be insufficient to stabilize the dispersions. Interestingly, a small average particle size was found at 90% of neutralization instead of 100%. One proposed explanation was that the neutralization of DMPA occurred in two stages: the neutralization in the prepolymer organic phase and the post-neutralization in the two-phase dispersions. The post-neutralization refers to a small fraction of DMPA that was “trapped” inside the particles during the dispersion process, which was only neutralized after the dispersion formation. The increased hydrophilicity by the newly formed ion pairs inside the particles attracted water to swell the particles. Due to the hydrophobic polyol backbone, the resulting films show good water and ethanol resistance. An impact resistance comparable to petroleum-based polyurethane films was claimed.

Influence of polyol structure on average particle size

An investigation of cationic water-borne PUDs prepared from vegetable oil polyols (castor oil with $f_{\text{noH}} = 2.7$, methoxylated soybean oil with $f_{\text{noH}} = 2.8$ or 4.0 and acrylated epoxidized soybean oil with $f_{\text{noH}} = 3.4$) has been carried out by Lu et al.^[133] MDI was used as the diisocyanate comonomer and N-methyl diethanol amine (MDEA) was used as the internal cationic stabilizing agent, neutralized with acetic acid. In addition to the previously mentioned influence of hydroxyl functionality on the average particle size, the authors have also noticed minor structure-induced differences in the average particle size, even though the reason was unclear. The T_g values determined by Dynamic Mechanical Analysis (DMA) of the dispersion-cast films increased from 46 to 79 °C with the increase of the OH functionality, as a result of the increased cross-link density. In contrast to the anionic

PUDs, these cationic dispersions exhibited high adhesion onto anionic substrates, such as leather and glass.

Influence of L-lysine diisocyanate on the average particle size and film properties

Several recent studies were carried out concerning the utilization of a dimer fatty acid-based diisocyanate (DDI®1410 or DDI), isosorbide (IS) and ethyl ester L-lysine diisocyanate (EELDI) in PUD preparation and have shown promising results. ^[140-144] EELDI is an asymmetric aliphatic diisocyanate, derived from lysine. Compared to DDI, EELDI is a relatively short and rigid diisocyanate. By partially replacing DDI with EELDI, an increased polymer rigidity and hydrophilicity are expected due to the increase of the amount of urethane/urea bonds per unit of chain length. In these studies, the ratio of DDI : EELDI was varied from 1 : 0.5 to 1 : 1 and 1 : 2. Concurrently, the DMPA content was reduced from 6% to 2.5% and the IS content was increased to keep a constant overall NCO : OH ratio. The influence of EELDI and the increased IS content on the average particle size and the film properties were investigated. With increasing EELDI and isosorbide contents in the polymer composition, the DSC-derived T_g values increased from approximately 20 °C to 60 °C. ^[142-143] The thermal stability of dispersion-cast films decreased due to the increased content of thermally labile urethane/urea bonds. Interestingly, at low DMPA contents, the average particle diameter remained below 200 nm and the dispersions were colloidally stable. Since similar results were not observed for dispersions based solely on DDI (i.e. without EELDI), it appears that the incorporation of EELDI facilitates the formation of colloidally stable dispersions. The reduction of the content of the petrochemistry-based DMPA led to dispersions having a renewable content of at least 92 wt% and even up to 97 wt%.

Influence of diol structure on film properties

The combination of vegetable oil- and sugar-based PU dispersions has been investigated by the research group of Larock. ^[92] A series of anionic water-borne poly(urethane urea) (PUU) dispersions has been successfully prepared from the combination of soybean oil-based amide diol (*N,N*-bis(2-hydroxyethyl)soybean amide) and isosorbide (IS), using HDI as the diisocyanate comonomer. DMPA was used as the internal stabilizing agent and EDA was used as the chain extender. With the increase of the isosorbide content, ranging from 0 to 20 wt% of the total diol content, the DSC-derived T_g values of dispersion-cast films increased from 45 to 65 °C. Concurrently, the Young's modulus increased from 2.3 to 63 MPa and the ultimate tensile strength increased from 0.7 to 8.2 MPa. However, the thermal stability decreased slightly with the incorporation of isosorbide, due to the increase of the thermally labile urethane/urea contents in the poly(urethane urea)s. In this

work, a detailed description concerning the influence of the reactants on the colloidal stability was not addressed.

Dispersion modifications

Castor oil polyol- or rapeseed oil polyol-based anionic water-borne PUDs have also been blended with thermoplastic starch to modify the properties of starch films.^[134, 136] The blends exhibit higher miscibility at PU contents lower than 15 wt%, due to the hydrogen-bonding interaction between urethanes (C=O) and starch (OH groups). Furthermore, significantly improved mechanical properties and reduced water sensitivity were observed, compared to the original starch films. The incorporation of 4-20 wt% PUs enhanced the Young's modulus from 40 to 75 MPa, the tensile strength from 3.4 to 5.1 MPa and the elongation at break from 116 to 176%. Moreover, these hydrophobic PUs improved the overall hydrophobicity and water resistance of the blends.

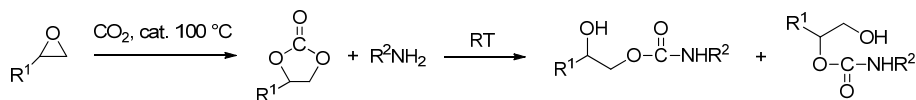
2.3. Isocyanate-free routes to bio-based polyurethanes

Even though numerous papers and patents describing PUs and PUDs prepared from renewable resources are available, still many research activities are ongoing to seek for an even more environmentally benign approach. A number of publications^[145-153] and a review^[154] describing the synthesis of renewable PUs through non-isocyanate routes are available. In these works, three major approaches have been discussed, including curing of carbonated fatty acid moieties with diamines,^[145-147, 150-151, 155] self-polycondensation of hydroxyl-containing acyl azide^[149] and transurethanization of urethanes by amines or hydroxyl compounds.^[148, 152-153]

2.3.1 Through carbonate-amine reactions

Non-isocyanate polyurethanes (NIPU) were prepared by curing carbonated soybean oil (CSBO) and linseed oil (CLSO) with different diamines (EDA, 1,4-butane diamine (BDA) and IPDA).^[145-146] These carbonated vegetable oils were obtained by reacting epoxidized vegetable oil with carbon dioxide, catalyzed by tetrabutylammonium bromide (**Scheme 2-9**). The PUs cured with isophorone diamine have relatively high T_g values ranging from 20 to 60 °C, which are higher than the glass transition temperatures obtained when using other diamines. An increase in the Young's modulus was observed in the same PUs when IPDA was used instead of the linear aliphatic diamines, while the elongation at break was

reduced. These developed NIPUs showed the potential to meet the demands of engineering applications.



Scheme 2-9. Schematic representation of the reaction of an oxirane with CO₂ ^[146, 156] and of the resulting cyclic carbonate with a primary amine. ^[146, 157]

Using a similar approach, Boyer et al. ^[150] has synthesized linear PUs from diamines (EDA and IPDA) and oleic acid methyl ester-based dicarbonates. These dicarbonates are internal- and terminal-carbonated fatty acid diesters, ICFAD and TCFAD, respectively (**Figure 2-12**). As observed, the terminal carbonated fatty acid diester was relatively more reactive than the internal counterparts. The *T_g* values of the resulting PU films were relatively low, ranging from -25 °C to -13 °C. Interestingly, the amine-ester side reactions were not observed from the polyurethanes containing secondary amines. These, however, usually occur in the PUs containing primary amines.

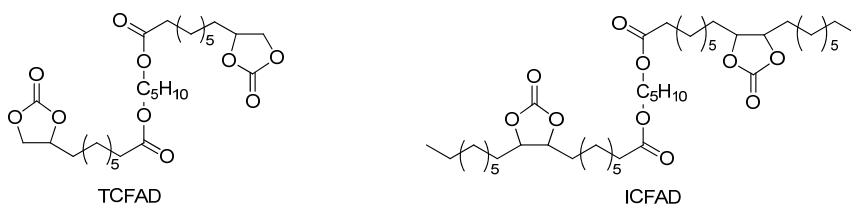
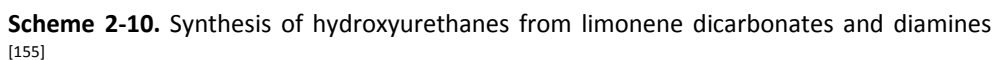


Figure 2-12. Structures of terminal- and internal-carbonated fatty acid diesters. ^[150]

In another study, linear and cross-linked polyurethanes were synthesized from cyclic limonene dicarbonate (terpene-based) and di- or polyfunctional amines (**Scheme 2-10**). ^[155] Compared to the typical vegetable oil-derived cyclic carbonates, these terpene-based cyclic carbonates contain no ester groups. The amine-ester side reactions can be therefore avoided during curing. Despite the fact that the resulting linear polyurethanes have *M_n*

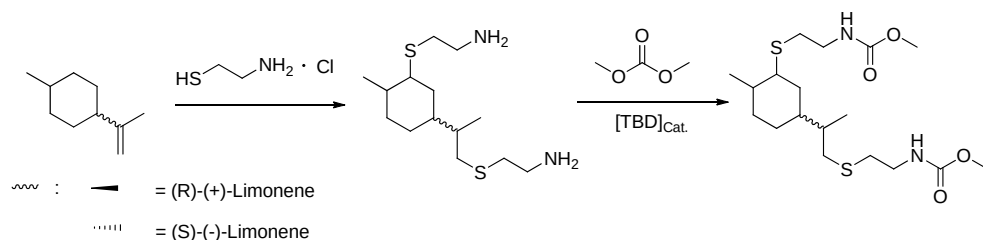


Unverferth et al. have prepared fully renewable PUs through transurethanization of castor oil-derived dimethyl dicarbamates and diols. This reaction was catalyzed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (**Scheme 2-11**).^[153] Because of the high linearity of both comonomers, the resulting linear polyurethanes exhibited T_m values above 120 °C.



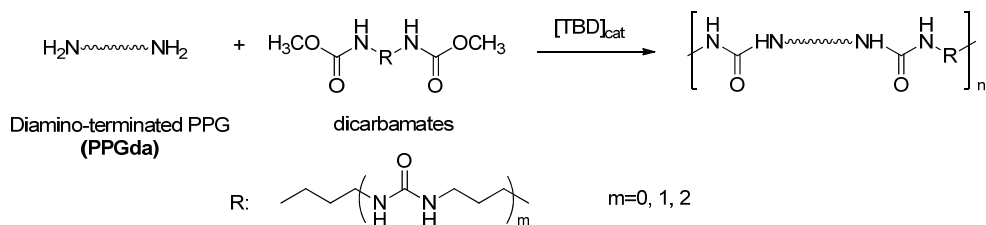
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reactions between the resulting diamines and dimethyl carbonate.^[152] By reacting these dicarbamates with 1,6-hexanediol, limonene- or linear fatty acid-based diols, amorphous or semi-crystalline polyurethanes were obtained. Their DSC-derived T_g values were all around room temperature.



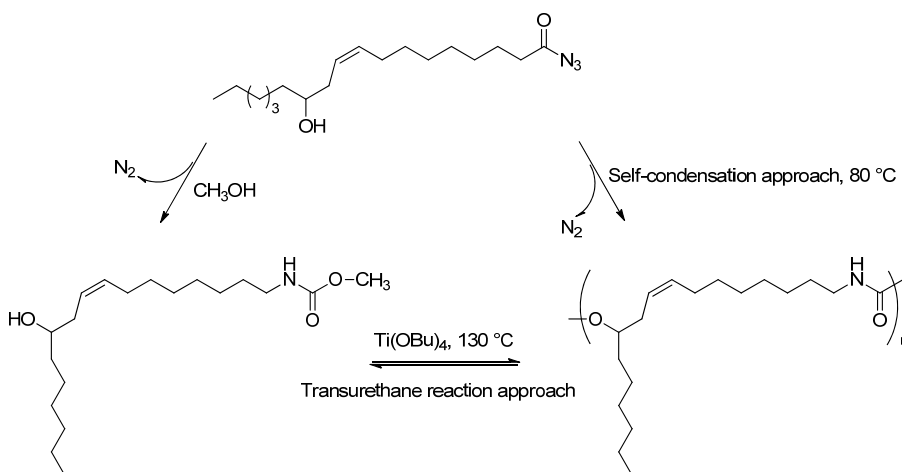
Scheme 2-12. Synthesis of limonene-based dicarbonates from (R)-(+) and (S)-(-)-limonene.^[152]

In another example, isocyanate-free thermoplastic PUs were synthesized from diamine-terminated poly(propylene glycol) (PPGda) and dicarbamates (obtained from 1,4-diaminobutane and dimethyl carbonate) *via* a transurethanization process, catalyzed by the organic catalyst TBD (**Scheme 2-13**).^[148] These potentially renewable segmented PUs contain mono-disperse hard segments and a well-defined structure. Variation in the soft (PPGda) and hard (dicarbonate) segment length was used to tailor the properties of the PU materials, making them promising for applications such as adhesives, soft elastomers, or rigid plastics.



Scheme 2-13. Synthesis of PUs through transurethanization of PPGda and dicarbonates.^[148]

In addition to transurethanization, self-polycondensation was also applied to prepare AB-type PUs from methyl oleate (derived from sunflower oil) and ricinoleic acid (derived from castor oil) (**Scheme 2-14**).^[149] By refluxing an excess of methanol with the ricinoleic acid-derived acyl azide (12-hydroxy-9-cis-octadecenoyl azide), methyl-N-11-hydroxy-9-cis-heptadecene carbamate (MHHDC) was synthesized. Either by self-condensation of the acyl azide or by transurethanization polycondensation of MHHDC at 130 °C, catalyzed by titanium tetrabutoxide, AB-type polyurethanes were obtained. These polyurethanes exhibit two different T_g values, representing the soft and hard segments, thus demonstrating a phase-separated morphology, although the authors did not clearly define the content of the soft and hard segments.



Scheme 2-14. Self-condensation of hydroxyl-containing acyl azide and transurethanization of urethanes by hydroxyl compounds.^[149]

2.4 Conclusions

Renewable resources have proved to be a useful feedstock for the derivation of numerous polyurethane building blocks. A variety of renewable thermosetting and thermoplastic polyurethanes as well as water-borne polyurethane dispersions have been successfully prepared. Compared to the petrochemical-based counterparts, monomers from renewable resources should in most cases be considered as new types of building blocks, providing different polymer properties when incorporated into the corresponding PUs,

rather than as a drop-in replacement for petroleum-based polymers. Within this contribution, we discussed the influence of the chemical nature of vegetable oil-based PU monomers on the final properties of the PU materials, as well as on the colloidal stability of aqueous PU dispersions. Concerning the limitations of these vegetable oil-based monomers, a number of modification possibilities has been identified. Furthermore, a few recent developments of vegetable oil-based polyurethanes prepared through non-isocyanate routes are discussed. These new approaches represent a very interesting field of research and may open a large potential for the further developments of renewable polyurethanes.

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3

Reactivity and Regio-selectivity of Renewable Building Blocks for the Synthesis of Water-Dispersible Polyurethane Prepolymers

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Abstract

To prepare water-borne polyurethane dispersions (PUD) from novel renewable-based, asymmetric bifunctional building blocks it is important to understand the reactivity and regio-selectivity differences between the various functional groups and reagents, respectively. This paper firstly describes the mutual reactivity and regio-selectivity of biomass-derived, asymmetric 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) and ethyl ester L-lysine diisocyanate (EELDI) in polyurethane (PU) syntheses. The regio-selectivities of the endo- and the exo-OH functional groups of IS and the primary ϵ -NCO and the secondary α -NCO of EELDI were found to have only minor consequences for the formation of NCO-terminated PU prepolymers. In addition, a model study of IS, dimethylolpropionic acid (DMPA), EELDI and a dimer fatty acid-based diisocyanate (DDI) in their respective PU reactions revealed the reaction rate differences between these four compounds. Surprisingly, a comparatively low reaction rate of DMPA was observed. For the PU prepolymers synthesized from the four mentioned components, an enrichment in DMPA near the polymer chain ends may thus be expected. Finally, PU dispersions prepared from these four-component prepolymers showed a good storage stability. The relatively small particle size at a low DMPA content and a high EELDI and IS content is predominantly regarded as the result of the hydrophilicity of EELDI, IS and possibly the enhanced DMPA concentration near the chain ends of the PU prepolymer.

3.1 Introduction

Water-borne polyurethane dispersions (PUD) are binary colloid systems in which polyurethane particles containing stabilizing groups are dispersed in the continuous aqueous medium.^[1-2] Polyurethanes are an important class of materials due to their versatile properties, which make them useful in applications such as foams, elastomers, sealants, adhesives and coatings.^[3-7] Compared to solvent-borne coating systems, aqueous polyurethane dispersions have advantageous low volatile organic compound (VOC) contents. Furthermore, they facilitate the convenient application of high molecular weight polymers due to their low viscosity. Finally, PUDs are non-flammable, show good adhesion to a variety of substrates and excellent resistance to chemicals and solvents.^[1-2, 8]

The industrially applied synthetic approach to prepare polyurethane dispersions consists of two stages. The first stage is the synthesis of low molecular weight polyurethane (PU) prepolymers containing isocyanate (NCO) end groups and an internal dispersing agent, e.g. dimethylolpropionic acid (DMPA), in a non-aqueous medium exhibiting a lower boiling point than water. The internal dispersing agent can be neutralized with for instance a tertiary amine either before or after the prepolymer synthesis. In the second stage, the aqueous PU dispersions are prepared by adding water to the prepolymer solution or vice versa, after which the (water soluble) low boiling organic solvent is removed. Chain extension with e.g. diamines can be performed either in the first or in the second step.^[2, 9] In the first step, the control of the DMPA distribution along the polymer chain and the end-group character is crucial, as it ultimately determines whether or not stable dispersions of high molecular weight poly(urethane urea)s (PUUs) are obtained. This control can be realized through proper monomer selection, reaction stoichiometry and by taking potential differences in reactivity of the used components into account.

Isophorone diisocyanate (IPDI) is often used in conventional PU and PUD systems, its aliphatic ring structure affording PU polymers with high rigidity and good UV stability, while aromatic polymers are less suitable due to yellowing when used outdoors.^[10-12] Many studies have been carried out to investigate the reactivity difference between the primary and the secondary isocyanate group of IPDI.^[13-16] It has been reported that the reactivity of the *prim*- and the *sec*-isocyanate groups of IPDI varies depending on the reaction conditions, the type of counter reagent, the type of catalyst, and the presence and/or the type of solvent.^[16-17] As a result, the reaction rate of IPDI-based PU syntheses is mainly limited by its less reactive isocyanate group.

Recently, renewable-based polyurethane building blocks have been developed from starch, fatty acids and amino acids, etc., as more sustainable alternatives for fossil fuel-based raw materials.^[18-20] Isosorbide (IS), derived from starch, ethyl ester L-lysine diisocyanate (EELDI), derived from L-lysine, and dimer fatty acid-based diisocyanate (DDI) obtained from fatty acids are interesting candidates for PU synthesis. Isosorbide is produced by the double dehydration of sorbitol, which is derived from glucose.^[21-25] Because of its intrinsically high thermal stability (up to 280 °C) and its relatively low price compared to other biomass-based feed stock, isosorbide is an important candidate monomer to produce renewable step-growth polymers such as polyesters and polycarbonates.^[26-28] In polyurethane coating applications, isosorbide is also preferably used thanks to its rigid and asymmetric structure, as shown in **Figure 3-1**, which is known to result in amorphous polymers with good thermal and mechanical properties.^{[27], [29]} In isosorbide, two hydroxyl groups having either an *endo* or an *exo* orientation are attached to the two fused ether rings.^[28, 30-31] The *exo*-oriented hydroxyl group is more accessible towards alkylation or acylation reactions. Conversely, the *endo*-oriented OH group is involved in intra-molecular H-bonding with the oxygen of the neighboring tetrahydrofuran ring. In spite of the steric hindrance, this intra-molecular H-bonding makes the *endo*-oriented hydroxyl group a preferred reactive center in electronically driven reactions.^[32-33]

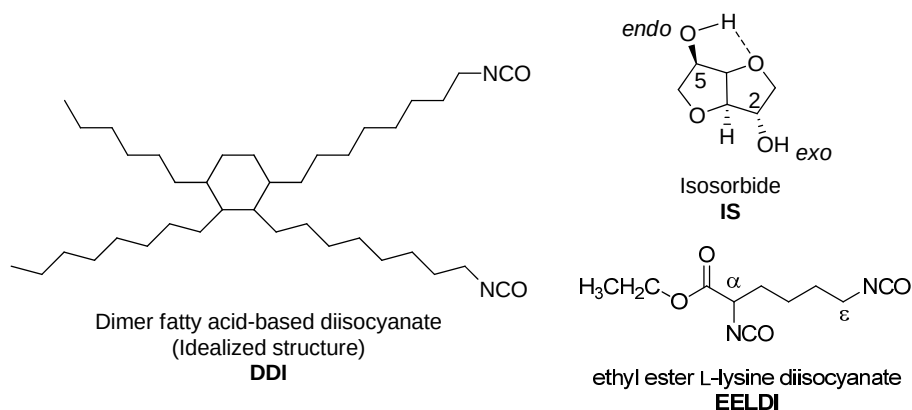


Figure 3-1. The structures of biomass-based isosorbide (IS),^[28-30, 34-35] dimer fatty acid-based diisocyanate (DDI, idealized structure) and ethyl ester L-lysine diisocyanate (EELDI).

EELDI is a recently developed biomass-based bifunctional isocyanate derived from L-lysine. Its asymmetric aliphatic structure shown in **Figure 3-1** may facilitate the formation of PUs

with an amorphous structure. Therefore, the combination of IS and EELDI may result in amorphous and rigid PU polymers with good UV stability. Besides these advantages, the reactivity of IS and EELDI and their regio-selectivity are of importance in replacing the conventional PU building blocks. EELDI has two isocyanate groups, an α -NCO (attached to a secondary carbon atom) and an ϵ -NCO (attached to a primary carbon atom) (see **Figure 3-1**). As reported by Sanda et al.^[36] the α -isocyanate group may experience steric hindrance from the ethyl ester substitute attached to the secondary carbon. On the other hand, this adjacent ethoxycarbonyl group has an electron-withdrawing character that induces an enhanced positive charge on the isocyanate carbon atom, increasing its reactivity. The combined effect of these two factors determines its overall reactivity. In addition, EELDI is expected to be more reactive than IPDI because of its structural similarity to the highly reactive hexamethylene diisocyanate (HDI).

DDI is a renewable-based diisocyanate that is derived from C₃₆ dimer fatty acids. Its idealized molecular structure is shown in **Figure 3-1**. Dimer fatty acid-based diols have been widely investigated as the renewable-based soft segments for PU or PUU synthesis, which exhibited good waterproof performance and mechanical properties such as impact resistance.^[34-35] Dimer fatty acid-based diisocyanate is expected to provide similar properties.

The reactivity of isosorbide in reactions to prepare polyesters, polycarbonates and polyurethanes has been described previously.^[29, 37-40] In these studies, only symmetric components were mentioned as the counter-reagents of isosorbide. To the best of our knowledge, in polyurethane syntheses the regio-selectivity of the *endo*- and the *exo*-OH groups of IS and the α - and ϵ -NCO groups of EELDI has never been studied in their respective reactions. In addition, dimer fatty acid-based diisocyanates have never been reported for PU synthesis and PU dispersions preparation. In order to develop new, biobased PUDs suitable for production through industrially relevant processes, knowledge of the monomer reactivities and dispersion stability is crucial.

In this study, the regio-selectivity of EELDI and IS are described in their respective reactions. The mono-functional hydroxyl compound 2-butanol is used as model alcohol to identify the regio-selectivity of EELDI. Isoidide (II) and isomannide (IM), being the two isomeric compounds of IS, are used to confirm the observations. In addition, the reaction rates of IS, DMPA, DDI and EELDI in their respective reactions are compared in a model study as well. The results yield information concerning the DMPA distribution over the prepolymer chains. Finally, the influence of DMPA distribution and the EELDI and IS content on the dispersion stability and the particle size are discussed.

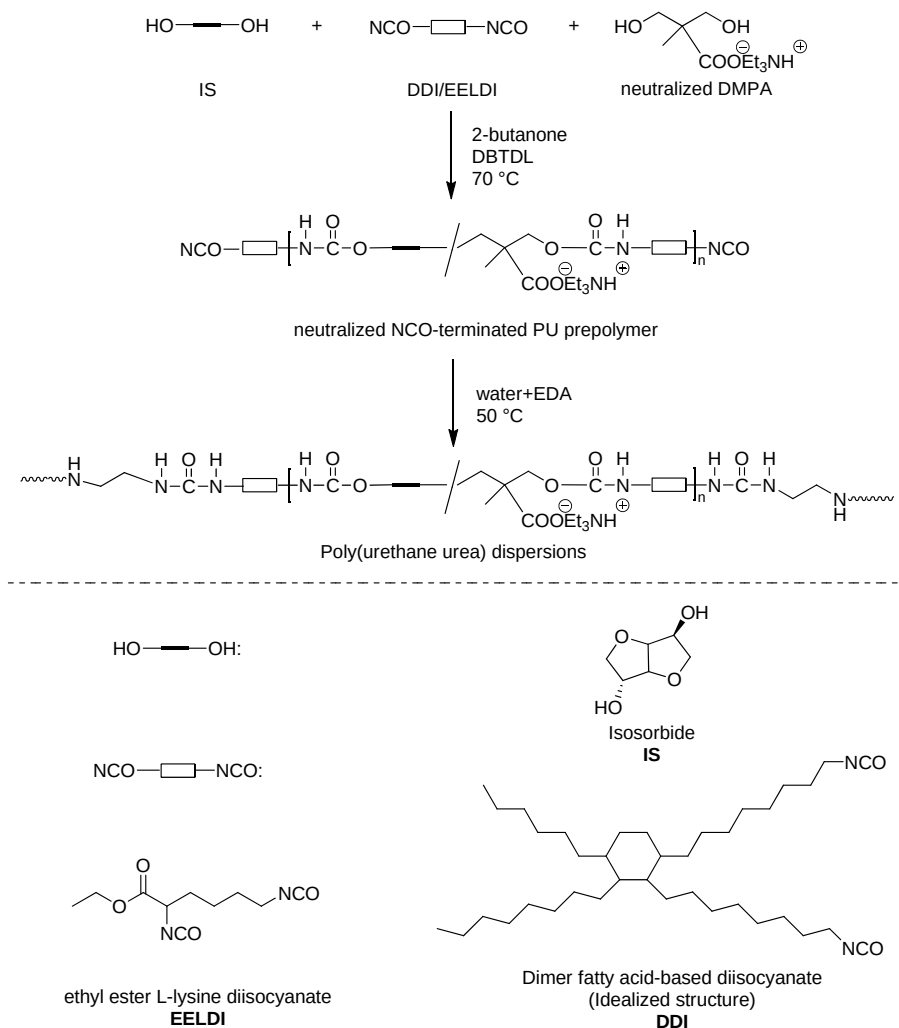
3.2 Experimental section

Materials. Isosorbide (IS, polymer grade, trade name Polysorb® P, 98.5%) and isoidide (II, 99.8%) were received as gifts from Roquette Frères. Isomannide (IM, 95%) was purchased from Sigma. Dimer fatty acid-based diisocyanate (DDI, 92%, titration value) was kindly provided as a free sample by Cognis. Dibutyltin dilaurate (DBTDL, 95%), triethylamine (TEA, $\geq 99.5\%$) and dimethylolpropionic acid (DMPA, 98%) were purchased from Aldrich. Ethyl ester L-lysine diisocyanate (EELDI, 95%) was ordered from Infine Chemicals Co., Limited, China. Dry acetone ($> 99.0\%$) and dry 2-butanone ($> 99.5\%$, AcroSeal®) were bought from MERCK and Acros respectively, and were kept under inert gas (N_2) together with 4 Å molsieves. Isosorbide, isomannide and isoidide were recrystallized from dry ethyl acetate and vacuum dried before use. All diisocyanates, IS, IM and II were kept under inert gas and in the fridge at 4 °C. Before use, DMPA was dried at 60 °C for 48 hours in a vacuum oven. Other chemicals were used as received.

Procedure of model reactions. Model reactions were carried out according to the following typical procedure. Before and during the reaction, the setup was continuously flushed with inert gas (N_2) to prevent oxidation and to keep the reaction devoid of moisture. II (0.49 g, 7 mmol) was weighed into a 5 mL round bottom flask. Acetone (1.6 mL) was added to dissolve II. Once a clear solution was obtained, EELDI (0.76 g, 7 mmol) was injected. While stirring, the mixture was heated to 40 °C using an oil bath. DBTDL (~ 0.56 wt%) was added to the mixture. The reaction was continued for two to five hours, and samples were taken at regular time intervals for ^1H NMR and FT-IR analysis. Several reactions were randomly selected and repeated to check repeatability. In some instances, 2-butanone was used instead of acetone, and the reaction temperature was controlled at 70 °C as indicated in the Results and Discussion section.

NCO-end capped PU prepolymer synthesis and dispersion preparation. A typical procedure to prepare PU dispersions includes the NCO-end capped prepolymer synthesis and the water dispersions process, as shown in **Scheme 3-1**. IS (1.023 g, 7.0 mmol) and DMPA, 0.705 g, 5.3 mmol) were weighed into a 250 mL round bottom glass flange reactor. Approximately half of the total solvent 2-butanone (5-6 mL) was used to dissolve the diols mixture. TEA (0.54 g, for 100% neutralization of DMPA) was injected into the diol mixture to help obtain a clear diol solution. Subsequently, DBTDL (0.56 wt% relative to the total solids content) was injected into the diol mixture. While being stirred mechanically, the mixture was heated up to 70 °C using a heating mantle. DDI (8.991 g, 14.1 mmol) was then added to this diols solution at 70 °C. The rest of the 2-butanone was then instantly added to dilute the total reaction mixture to a 50 wt% solids content. Before the reaction started as well as during the reaction, the reaction setup was continuously flushed with inert gas (N_2). The reaction was carried out for 4-6 hours, counted from the moment that all the DDI had been added. Subsequently, the NCO content of the resulting PU prepolymer was determined by titration.

After the PU prepolymer synthesis, the reaction temperature was decreased to 50 °C and additional solvent (4 mL) was used to adjust the solids content of the prepolymer mixture to 50 wt%. A solution of approximately 70 mL of de-ionized water and ethylene diamine (EDA) was injected continually into the prepolymer mixture and dispersing was assisted by vigorous stirring. Subsequently, the chain extension reaction was allowed to run for one hour. Thereafter, the polymer dispersion was discharged from the reactor. Residual 2-butanone was distilled off with a rotary evaporator at 40 °C, the pressure ranging from 100 to 200 mbar.



Scheme 3-1. Preparation of NCO-terminated PU prepolymers and polyurethane dispersions.

Chapter 3

Characterization

¹H NMR was used to follow the reaction kinetics. The conversions of both OH- and NCO-groups were followed in time. ¹H NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer. Acetone-*d*₆ was used as the solvent.

Size exclusion chromatography (SEC) was used to determine both the molecular weight and molecular weight distribution of the prepolymers and PU dispersions. A Waters Alliance set-up equipped with a Waters 2695 separation module, a Waters 2414 differential refractive index detector (40 °C) and a Waters 2487 dual absorbance detector were used with THF, containing 1 vol.% acetic acid, as eluent. The injection volume was 50 µL. PSS (2× SDV and guard-linearXL, 5 m, 8×300 mm, 40 °C) columns were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using poly(styrene) (PS) standards with molecular weights ranging from 500 g/mol to 5,000 kg/mol. Data acquisition and processing were performed using Empower software.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Bio-Rad Excalibur FTS3000MX infrared spectrometer (fifty scans per spectrum, spectral resolution of 4 cm⁻¹) with an ATR diamond unit (Golden Gate). The measurement was performed by applying the polyurethane or the dispersion-cast poly(urethane urea) films onto the ATR diamond. The spectrum was taken between 4000 and 650 cm⁻¹.

Potentiometric titrations of isocyanate groups were performed using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The isocyanate functional groups were converted through the reaction with a molar excess of dibutylamine (DBA). The DBA residue was titrated with a normalized 1 N HCl isopropanol solution. Blank measurements were carried out using the same amount of dibutylamine. The NCO content was defined according to the following equation:

$$NCO\% = \frac{(V_{blank} - V_{sample}) \times C_{HCl} \times 4.2}{M_{prepolymer}} \%$$

where V_{blank} is the volume of HCl solution needed for the blank [mL] (average of two measurements), V_{sample} the volume of HCl solution needed for sample [mL], C_{HCl} the HCl concentration in 2-propanol [mol/L] and $M_{prepolymer}$ is the PU prepolymer weight [g]. Titration measurements were performed in duplo.

The PU prepolymer weight was obtained by the difference in weight before and after solvent evaporation. About 0.5 g prepolymer solution was placed in a glass vial and dried at 60 °C for at least 24 hours *in vacuo*, until a constant weight was reached.

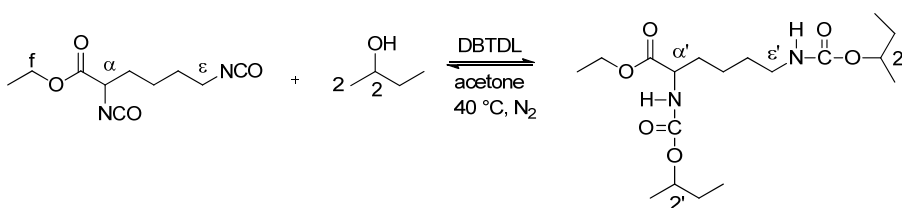
Dynamic Light Scattering (DLS) and **ζ-potential measurements** were used to determine the dispersion characteristics on a Malvern ZetaSizer Nano ZS at 20 °C, (polyurethane refractive index: 1.59). The average particle size and the particle size distribution of dispersions containing ~ 0.1 wt%

solids were determined according to ISO 13321 (1996). The pH dependence measurements of particle size and dispersion stability (ζ -potential) were performed by adding a 5×10^{-3} M aqueous HCl solution to the dispersion using a Malvern ZetaSizer MPT-2 Autotitrator, starting at the pH of the as prepared dispersion. The pH value was reduced in steps of ~ 1 and the resulting mixture was left for 1 min at this pH prior to the next ζ -potential and particle size determination, until a pH value of 3 was reached. The base titration was performed by adding 5×10^{-3} M NaOH aqueous solution to the dispersion, increasing the pH in steps of ~ 1 , until a pH of 12 was reached. The ζ -potential was calculated from the electrophoretic mobility (μ) using the Smoluchowski relationship, $\zeta = \eta\mu/\epsilon$ where $\kappa\alpha \gg 1$ (where η is the solution viscosity, ϵ is the dielectric constant of the medium, and κ and α are the Debye-Hückel parameter and the particle radius, respectively). Data acquisition was performed using the ZetaSizer Nano software.

3.3 Results and discussion

3.3.1 Regio-selectivity of EELDI

The regio-selectivity of EELDI was studied in reaction with 2-butanol (**Scheme 3-2**). This monofunctional, secondary alcohol was selected as a model compound to study the regio-selectivity between the α - and ϵ -NCO groups of EELDI in a non-polymer generating reaction. In **Scheme 3-2**, both the α - and the ϵ -isocyanate groups are shown to have reacted with the OH-group of 2-butanol to form a urethane group. In reality, either one of the two or both may react.



Scheme 3-2. The reaction of EELDI with 2-butanol to form urethane model compounds.

^1H NMR measurements were used to follow the conversion of the functional groups, as shown in **Figure 3-2**.

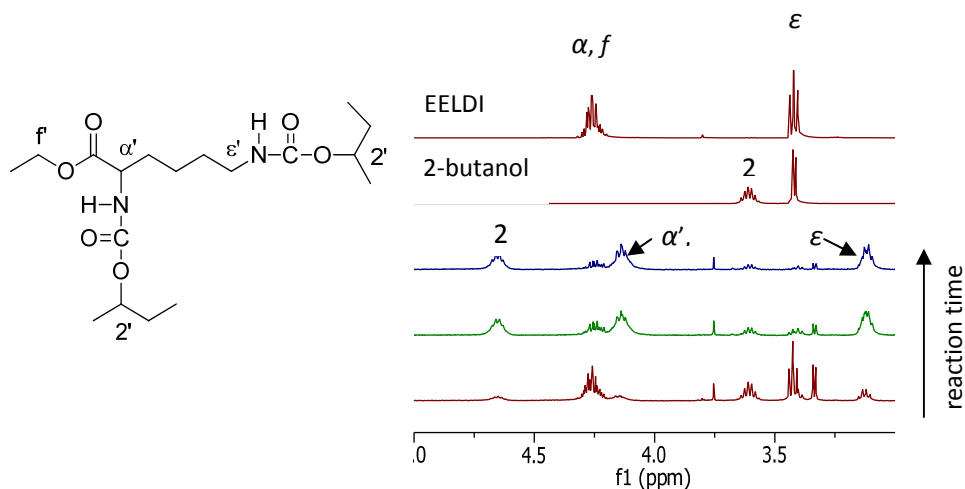


Figure 3-2. The ^1H NMR spectra of the reaction EELDI : 2-butanol = 1 : 1 (NCO : OH = 1 : 1) at 1, 5 and 10 minutes. Acetone- d_6 was used as the solvent. Signal labels refer to structures shown in **Scheme 3-2** and **Figure 3-2**.

Using this figure, from the disappearance of peak ϵ and the appearance of ϵ' , the conversion of the CH_2 group adjacent to the ϵ -NCO groups upon reaction with the OH group of 2-butanol was evaluated by integrating peak ϵ' and the sum of peaks ϵ and ϵ' . Applying the same method, the conversion of 2-butanol was derived by integrating peak 2' and the sum of peaks 2 and 2'. In addition, the change in the shift of peak α to α' indicated that the α -NCO group had been converted. Because of overlapping signals, *viz.* α and f as well as α' and f' , the α -NCO conversion was indirectly quantified by deducting the ϵ -NCO conversion from the total 2-butanol conversion. **Figure 3-3** shows the conversion curves of the two isocyanate groups as a function of reaction time with 2-butanol at a feed ratio of NCO : OH = 1 : 1. Two tangents are drawn to guide the eye to notice the subtle difference in initial reaction speed. Both the primary ϵ -NCO and the secondary α -NCO of EELDI appear to be highly reactive. After about 10 minutes of reaction, both isocyanate groups had reached 80% conversion. Full conversion was reached within one hour. During the later stage of this reaction, the α -NCO appeared to be slightly less reactive than the primary ϵ -NCO, by a factor of about 0.8. This reduced reactivity of the α -NCO indicates that the retarding steric hindrance is more effective than the enhancing electron-withdrawing effect of the adjacent ester group.

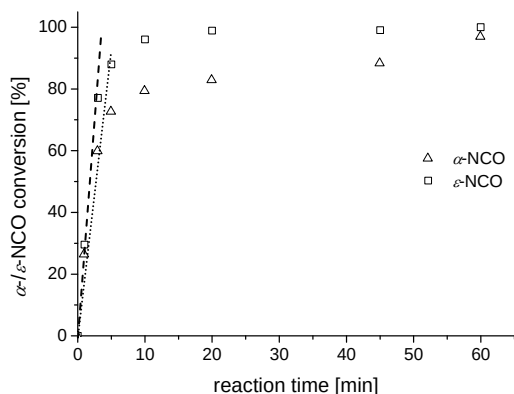
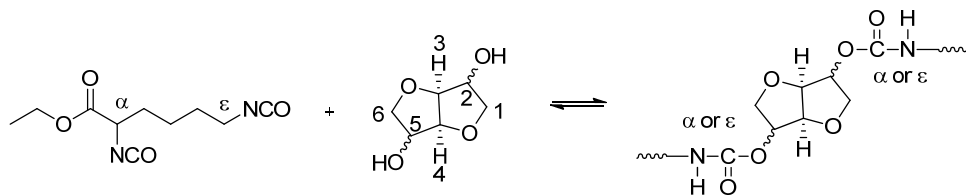


Figure 3-3. The conversion of α -NCO and ϵ -NCO in the reaction of EELDI with 2-butanol (total NCO : OH = 1 : 1). The results were determined by ^1H NMR, using acetone- d_6 as the solvent.

Having examined the relative reactivities of the two EELDI isocyanate groups, it appears that both isocyanate groups are sufficiently reactive and will react to 100% conversion. This means that PU prepolymers having reactive isocyanate end-groups can be prepared using EELDI, regardless of which isocyanate group (α or ϵ) resides at the chain end.

3.3.2 Regio-selectivity of IS

After the reactivity of the L-lysine-based diisocyanate (EELDI) was elucidated, the relative reactivity of the *endo*- and *exo*-OH of isosorbide towards the NCO groups of EELDI could be investigated, even though this reaction leads to oligomer formation already. Its two isomers, isoidide (II, *exo*, *exo*) and isomannide (IM, *endo*, *endo*), carrying two similar secondary OH groups in each molecule, were used to facilitate the comparison. A molar ratio of NCO : OH = 1 : 1 and the reaction temperature at 40 °C were applied, using acetone as the solvent. The reaction between EELDI and isohexides is shown in **Scheme 3-3**.



Scheme 3-3. The reaction of EELDI with isohexides to form polyurethanes, including IM containing two *endo*-oriented OH-groups, II containing two *exo*-oriented OH-groups and IS containing one *endo*-oriented OH and the other *exo*-oriented OH-group.

On the right-hand side of the equation, an isomeric urethane mixture may form depending on the addition of the *endo*-/ *exo*-oriented hydroxyl groups to the α - or the ϵ -NCO groups of EELDI. Therefore, upon full conversion, three different urethane isomers can be formed when using II and IM as the hydroxyl reagents (α -II- α , α -II- ϵ , ϵ -II- ϵ resp. α -IM- α , α -IM- ϵ , ϵ -IM- ϵ), and four urethane isomers can be expected for IS (α -IS- α , α -*endo*IS-*exo*IS- ϵ , α -*exo*IS-*endo*IS- ϵ , ϵ -IS- ϵ).

In addition to the ^1H NMR analysis described previously, the formation of urethanes and the consumption of the total amount of EELDI isocyanate groups (the primary ϵ -NCO and the secondary α -NCO cannot be distinguished in FT-IR measurements) have also been monitored by FT-IR measurements. FT-IR spectra recorded during the reaction EELDI : IS = 1 : 1 are shown as an example in **Figure 3-4**. The total conversions of the EELDI isocyanate groups in the reaction with IS, II or IM are determined from the decrease of the integrated areas under the isocyanate peaks at 2260 cm^{-1} , taking the CH_2 peaks at $3092\text{--}2790\text{ cm}^{-1}$ as a reference. The equation applied for the calculation of the isocyanate conversions is given in **eq. 3-1**. Several other peaks, attributed to the formation of urethane groups, are observed at $3400\text{--}3210\text{ cm}^{-1}$ (N-H stretching), $1846\text{--}1610\text{ cm}^{-1}$ (amide I C=O stretching) and $1483\text{--}1608\text{ cm}^{-1}$ (amide II N-H deformation).

$$\text{Equation 3-1. } P_{NCOt} = \frac{[NCO]_0 - [NCO]_t}{[NCO]_0} \times 100\%$$

P_{NCOt} is the total EELDI NCO conversion at time t , $[NCO]_0$ the integrated intensity of the NCO stretch at 2260 cm^{-1} at $t = 0$ and $[NCO]_t$ is the integrated intensity of the NCO stretch at 2260 cm^{-1} at time t .

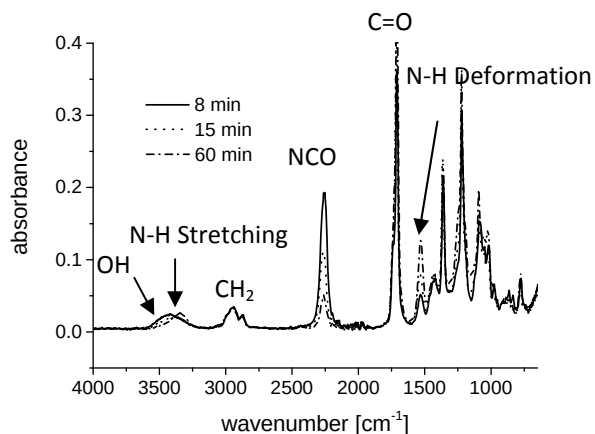


Figure 3-4. FT-IR spectra of the reaction at a feed ratio of EELDI : IS = 1 : 1. Spectra of reactions EELDI : II = 1 : 1 and EELDI : IM = 1 : 1 are very similar.

The total isocyanate conversion of EELDI derived from the FT-IR measurements are plotted in **Figure 3-5**.

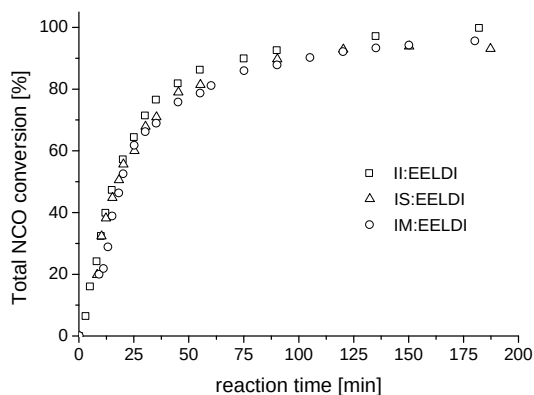


Figure 3-5. The total ϵ - and α -NCO conversion of EELDI during the course of the reaction with IM, II and IS (NCO : OH = 1 : 1). The results are recorded using FT-IR, and resolved using the integrated areas under the isocyanate peaks at 2260 cm^{-1} .

As becomes evident from **Figure 3-5**, the three dianhydrohexitols in general show similar reactivities with the two NCO-groups of EELDI. Their similarity in conversion is probably

the result of the equal 1 : 1 stoichiometry of reactive groups and the high reactivity of the isocyanates. An equireactivity between the *endo*- and *exo*-hydroxyl groups of isosorbide toward aromatic isocyanates was previously observed by Cognet-Georjon et al. ^[29] under the used experimental conditions (in THF, at 50 °C, using dibutyltin dilaurate as the catalyst). In isocyanate-terminated prepolymer synthesis, the full conversion of isosorbide and a similar regio-selectivity of the *endo*- and the *exo*-hydroxyl groups are expected.

3.3.3 NCO-terminated PU prepolymers containing EELDI and IS

As previously introduced, the first step in preparing a polyurethane dispersion is to synthesize isocyanate-terminated PU prepolymers by using an excess of diisocyanates in the reaction with (mixtures of) diols. The regio-selectivity of the α - and the ϵ -NCO groups of EELDI therefore was examined using an exaggerated feed ratio of IS : EELDI=1 : 4 at 40 °C. Partial ^1H NMR spectra, focused on the relevant ppm range, are shown in **Figure 3-6**. No significant regio-selectivity has been observed between the α - and the ϵ -NCO groups. The peak area of the converted ϵ -NCO group (ϵ') seems to be slightly larger than that of the converted α -NCO group (α'). However, because of the overlapping α and f peaks as well as overlapping α' and f' peaks, a quantitative comparison could not be derived. It is clear, however, that both NCO groups of EELDI are reacted, confirming their similar reactivities.

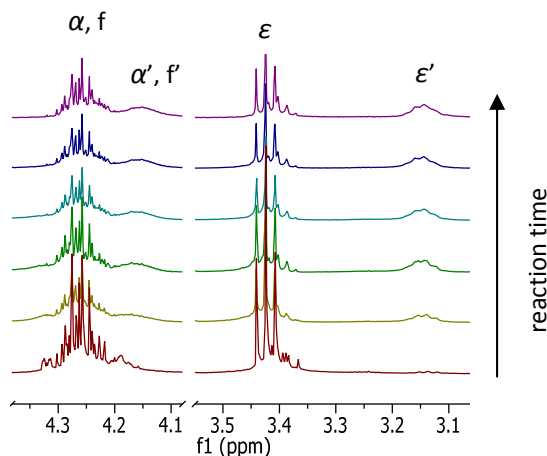


Figure 3-6. The partial ^1H NMR spectra of the reaction between IS : EELDI = 1 : 4 at 1, 10, 20, 30, 60 and 90 minutes, using acetone- d_6 as the solvent.

For the same reaction, the regio-selectivity between *endo*- and *exo*-OH groups of IS has been examined as well, as shown in **Figure 3-7**. By applying a large molar excess of diisocyanates, both the *endo*- (5) and the *exo*-OH (2) groups are converted (as shown for signals 2' and 5' in **Figure 3-7**) to a similar extent after 20 minutes, indicating that only a minor difference exists in their reactivities. This result indicates that the regio-selectivity of the *endo*- and *exo*-OH groups of IS is negligible during the synthesis of NCO-terminated prepolymer. Both hydroxyl groups can be fully converted during a similar reaction time.

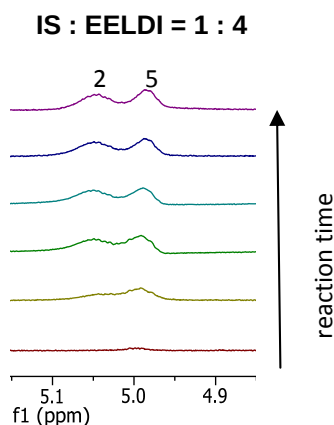


Figure 3-7. The ^1H NMR signals at 4.85-5.15 ppm of reaction IS : EELDI = 1 : 4 at 1, 10, 20, 30, 60 and 90 minutes, using acetone- d_6 as the solvent. 2' = CH adjacent to the *exo*-OH, 5' = CH adjacent to the *endo*-OH.

3.3.4 DDI and EELDI in reaction with IS and DMPA

The relative reactivities of the symmetric difunctional monomers (namely dimer fatty acid-based diisocyanate (DDI) and dimethylolpropionic acid (DMPA), being the hydrophobic segment and the internal stabilizing agent, respectively) were investigated as well. Similarly to the previously described asymmetric, biobased building blocks, these model reactions have been carried out at 70 °C in 2-butanone solution. Stoichiometric ratios for DDI/EELDI and IS/DMPA, respectively, were applied. The corresponding total NCO conversions, derived from FT-IR measurements, are plotted in **Figure 3-8**.

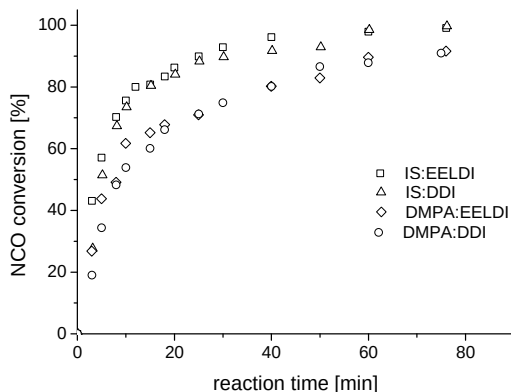


Figure 3-8. The total NCO conversion of DDI or EELDI (α - and ϵ -NCOs) during the course of the reaction with IS and DMPA (NCO : OH = 1 : 1), respectively. The results were recorded using FT-IR, and resolved using the integrated areas under the isocyanate peaks at 2260 cm^{-1} .

For reactions of mono- and diisocyanates furnishing (poly)urethanes, second order kinetic equations are known to provide the most adequate way of describing the kinetics.^[13, 41-45]

A positive deviation at high conversions is generally observed as a result of the autocatalytic effect induced by urethanes or by side reactions of isocyanates. The second order kinetic plot of DDI or EELDI in reaction with IS and DMPA is depicted in **Figure 3-9**, using $1/(1 - p)$ as a function of reaction time, where p is the conversion of the functional groups, NCO or OH.

The linearity of the plots is obvious for all four reactions until 80% (IS containing reaction) and 66% (DMPA containing reaction) conversion was reached after 18 minutes of reaction. The second order rate constants k , determined from the first 18 minutes of reaction, are $3.0 \times 10^{-1}\text{ mol}^{-1} \cdot \text{min}^{-1}$ (IS/EELDI reaction), $2.8 \times 10^{-1}\text{ mol}^{-1} \cdot \text{min}^{-1}$ (IS/DDI reaction), $1.2 \times 10^{-1}\text{ mol}^{-1} \cdot \text{min}^{-1}$ (DMPA/EELDI reaction) and $1.1 \times 10^{-1}\text{ mol}^{-1} \cdot \text{min}^{-1}$ (DMPA/DDI reaction). There is no significant difference observed for the reaction rate of DDI and EELDI in reaction with the two diols. This result confirms that only a slight effect of regio-selectivity exists of the α - and ϵ -NCO groups of EELDI. NCO-terminated prepolymers containing both EELDI and DDI at the chain ends are expected. Surprisingly DMPA, having two primary hydroxyl groups, shows a relatively low reactivity compared to IS, which contains two secondary OH groups. The relatively low reactivity of DMPA is determined by its molecular structure.^[46]

On the one hand, the steric effects of the CH_3 group and the carboxylic acid group hinder the hydroxyl groups in reaction with isocyanates. On the other hand, the electron-withdrawing effect of the COOH group reduces the nucleophilicity of the OH groups. In addition, compared to pure DMPA, the neutralized DMPA has an increased hydrophilicity, which may reduce the phase mixing with the relatively more hydrophobic diisocyanates. As a result of the low reaction rate of DMPA compared to that of isosorbide, a relatively high DMPA concentration near the polymer chain ends is expected, as isosorbide is probably incorporated faster than DMPA.

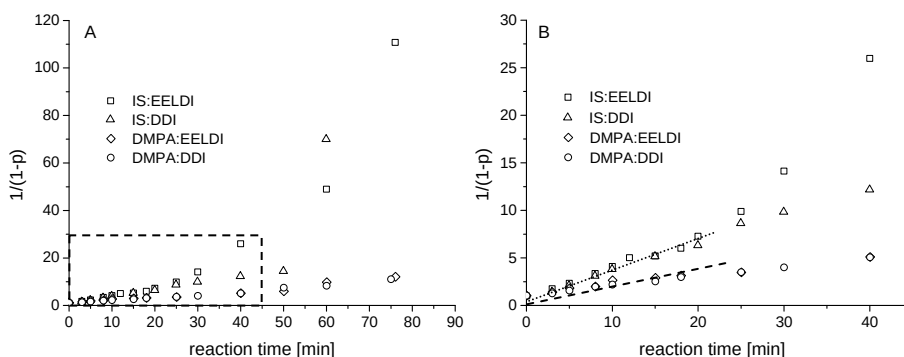


Figure 3-9. The second order kinetic plot $1/(1-p)$ versus time (A) and the enlarged area (B) of DDI or EELDI in reaction with equimolar amounts of IS and DMPA, using DBTDL as the catalyst.

3.3.5 Preparation of polyurethane dispersions

The preparation of waterborne PU dispersions by a solvent assisted route was conducted according to a two-step process: 1) the synthesis of isocyanate-terminated PU prepolymers in solution and 2) water dispersion. The prepolymer formulation was varied by decreasing the molar ratio of DDI/EELDI from 1 : 0, 1 : 0.5, 1 : 1 to 1 : 2 and by reducing the DMPA weight percentage (relative to the prepolymer weight) from 6.6 to 2.0 wt% respectively. In this way, a minimum renewable content of 93 wt% and 88 wt% are expected from such prepolymers and PUDs, respectively, by taking the petrochemical-based triethylamine (TEA) and ethylene diamine (EDA) into account as well. The overall NCO/OH molar ratio in all reaction formulations was kept constant at 1.1 : 1. The chain extender ethylenediamine (EDA) was added together with water into the prepolymer

Chapter 3

solution to prepare dispersions and to effectuate chain extension. The reaction formulation and the results of prepolymer synthesis and PUD preparation are summarized in Table 3-1.

Table 3-1. The reaction formulation of PU prepolymers and the characteristics of PUDs.

Entry	DDI:EELDI:IS:DMPA [molar ratio]	DMPA [wt%]	M_n (prepol) ^a [kg/mol]	M_w (prepol) ^a [kg/mol]	M_n (PUD) ^b [kg/mol]	M_w (PUD) ^b [kg/mol]	dispersion appearance	Av. particle diameter [nm]
1	53.5 : 0 : 26.6 : 19.9	6.6	6.4	13.5	11.2	28.2	White	143
2	35.3 : 17.6 : 35.9 : 11.2	4.5	5.9	10.7	10.7	28.3	Bluish white	102
3	26.3 : 26.3 : 37.3 : 10	4.5	5.6	11.2	11.4	29.8	Yellowish	72
4	17.4 : 34.9 : 42.8 : 4.9	2.5	6.2	13.2	15.6	51.1	White	142

^{a)} The molecular weight of PU prepolymers after the prepolymer synthesis; ^{b)} The molecular weight of PUDs after one hour of chain extension with EDA.

As can be seen from **Table 3-1**, all PU prepolymers show similar M_n values around 6.0 kg/mol after the polymerization and have a PDI around 2. The EDA chain-extended PU dispersions have M_n values between 10.7 and 15.6 kg/mol, which are lower than expected. Further research on optimizing the chain extension process is currently carried out in a separate study. It is noticed that PUD1, formulated with the highest DMPA (6.6 wt%) and DDI content, shows a relatively large average particle size compared to PUD2 and PUD3, and similar to that of PUD4. This result does not reflect the statement mentioned by Nanda et al.^[47-49] and Kwak et al.^[50] that the particle size decreases with increasing ionic content. It reveals that DDI is likely unfavorable for the formation of small particles. Its relatively high hydrophobicity is thought to limit the migration of water into the prepolymer chains. The function of water is to dissociate the ionic interactions which initially formed between the carboxylic ionic groups in the prepolymer solution^[2] and to release the neutralized DMPA to migrate towards the water interface to form particles. Contrary to DDI, EELDI and IS seem to facilitate the formation of smaller particles. The occurrence of this phenomenon is supported by the particle size differences between the dispersions using the same DMPA percentage and different EELDI and IS content, as shown in **Table 3-1** for PUD2 and PUD3. In addition, 2.5 wt% of DMPA used in PUD4 is already sufficient to stabilize the formed dispersions at a high EELDI and IS content. These

results can be understood when considering two aspects. On the one hand, the potential DMPA enrichment near the flexible chain ends may assist the polar DMPA to migrate to the particle surface to a certain extent, thereby forming more stable dispersions.^[51] On the other hand, the increased hydrophilicity of the PU polymers containing more EELDI and IS leads to increased water attraction, supporting the dissociation of the ionic pairs. As a result, more free ionic groups are able to migrate towards the water phase and to form smaller stable particles. The relatively large particle size of PUD4 is probably a result of the low DMPA content.

All dispersions show good storage and electrostatic stability. The particle size and the ζ -potential are nearly constant for at least three months. The results obtained from DLS and ζ -potential measurements are shown in **Figures 3-10** and **3-11**.

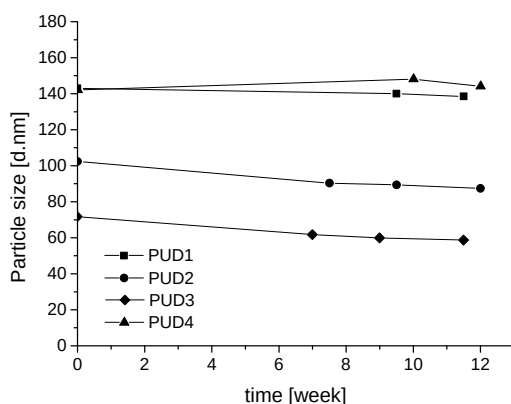


Figure 3-10. The particle sizes of PUDs1-4 (see **Table 3-1**) measured as a function of time.

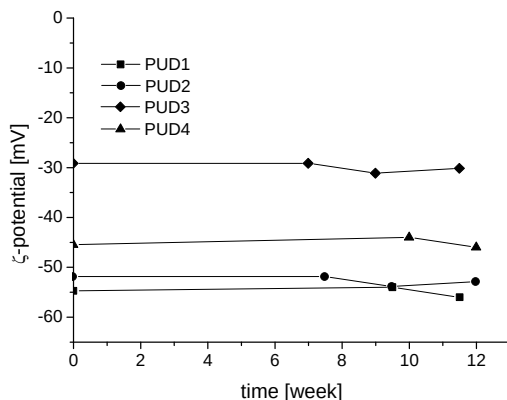


Figure 3-11. The ζ -potentials of PUDs1-4 (see **Table 3-1**) measured as a function of time.

3.4 Conclusions

In this paper, symmetric and asymmetric PU building blocks were considered for the synthesis of NCO-terminated PU prepolymers and subsequent PUD preparation with an overall renewable content of approx. 90 wt%. Based on the results obtained by performing model reactions it was concluded that, although slight reactivity differences do exist between the α - and ϵ -NCO groups of EELDI and the *endo*- and *exo*-oriented OH-groups of isosorbide, respectively, this is not expected to significantly hamper the formation of NCO-terminated PU prepolymers. In addition, the reaction rate comparisons between IS, DMPA, DDI and EELDI in their respective PU reactions reveal a rather low reactivity of DMPA compared to isosorbide. Therefore, the PU prepolymers synthesized based on these four components may contain a relatively high content of DMPA near the prepolymer chain ends, which most probably facilitates their dispersion in water. Finally, the waterborne PU dispersions prepared from these four-component prepolymers show a good storage stability and a small particle size at low DMPA contents, especially at high EELDI and IS contents. With this study, we have obtained the chemical tools to construct renewable-based polyurethanes and PU dispersions from DDI, EELDI, IS and DMPA in a more controlled way.

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4

Chain Extension of Dimer Fatty Acid- and Sugar-based Polyurethanes in Aqueous Dispersions

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Abstract:

The chain extension process of renewable water-borne polyurethane dispersions (PUDs) prepared from a dimer fatty acid-based diisocyanate (DDI) and isosorbide (IS), using dimethylolpropionic acid (DMPA) as the internal dispersing agent, was investigated. Ethylene diamine (EDA), adipic dihydrazide (ADH) and water were evaluated as chain extenders. Other variables such as the chain extension temperature, the sequence of addition of the chain extender with respect to the dispersion step and the utilization of a catalyst (triethylamine, TEA) were investigated as well. It was found that EDA extended the NCO-functional prepolymer chains at both 30 and 50 °C, independent of the moment of its addition. A limited extent of chain extension by ADH was observed, which was thought to be caused by the low solubility of ADH in the solvent 2-butanone, used for the prepolymer synthesis. ADH chain extension only took place after removal of the 2-butanone. Water chain extension was observed at temperatures ranging from 50 °C to 70 °C. A good balance was found at 50 °C, where a stable dispersion with a relatively high molecular weight, a small average particle size and a narrow particle size distribution were obtained. The usage of TEA during the dispersion process promoted the water chain extension reaction, however, at the cost of dispersion stability. An increased DMPA level has shown to improve the dispersion stability. Dispersion-cast poly(urethane urea) films were found to be thermally stable up to 249 °C (5 wt% mass loss) and had T_g values around room temperature.

4.1 Introduction

Polyurethanes offer excellent versatility in terms of their mechanical properties and are widely applied as protective coatings for automotive applications, packaging, textiles and furniture.^[1-4] Waterborne polyurethane dispersions (PUDs) have been widely used in the coating industry since the 1960s.^[5-7] They form a class of latex systems in which organic poly(urethane urea) (PUU) particles are dispersed in an aqueous medium aided by internal, polymer-bound dispersing agents. Since water is used as the continuous phase instead of organic solvents, WBPUDs have a low VOC (volatile organic compound) content and are environmentally benign. Apart from this, WBPUDs offer high molecular weight poly(urethane urea) polymer particles with low dispersion viscosity, allowing convenient film formation.^[8-10]

Among alternative dispersion processes such as the prepolymer mixing process,^{[5], [8, 10]} the melt dispersion process^[5, 8, 10] and the ketimine-ketazine process,^[5, 8, 10] the ketone-assisted dispersion process^[5, 8, 10] is industrially the most widely used process to prepare WBPUDs. Initially, NCO-end capped hydrophobic PU prepolymers are synthesized in the ketone solvent, using a slight excess of diisocyanates in reaction with polyether or polyester polyols and an internal stabilizing agent precursor, mostly dimethylolpropionic acid (DMPA). The neutralization of DMPA is carried out either before (used in this study) or after the prepolymer synthesis by for example a volatile tertiary amine or by an alkali metal hydroxide. In the second step, water is used to disperse the prepolymers solution under vigorous stirring. The resulting prepolymer dispersion is chain extended with diamines, diols or water to obtain high molecular weight PUU products. Finally, the ketone is removed from the dispersions, resulting in a solvent-free PUD system. The urea linkage introduced through the diamine-based chain extension reaction is known to improve the final mechanical properties of the films, such as its modulus and tear strength, by hydrogen-bonding.

In recent years, triggered by the increased oil price and environmental concerns, many biomass-based PUU building blocks, such as lysine-based diisocyanate (LDI), a dimer fatty acid-based diisocyanate (DDI), plant oil-based polyols, sugar-based dianhydrohexitol (DAH) isomers and their corresponding diamines, have become available for the preparation of predominantly renewable-based waterborne PUU coating systems.^[11-19] Many studies have been published concerning plant oil-based PUs and PUDs, primarily starting from soybean oil-, linseed oil- and castor oil-derived polyols^[20-27] in reaction with conventional, petrochemical-based diisocyanates. Due to their soft and hydrophobic character, the

resulting PU products show great potential in applications such as thermoplastic PU elastomers, foams and coatings, with promising impact resistance and water resistance properties.^[21, 27] However, PU systems from plant oil-based diisocyanates have rarely been reported,^[24, 28] while similar physical properties can be expected, such as chain flexibility and hydrophobicity. Furthermore, the chain extension process of renewable-based PUDs has not yet been given much attention, while some chain extension studies are available related to the petrochemical-based PU dispersions.^[29-32]

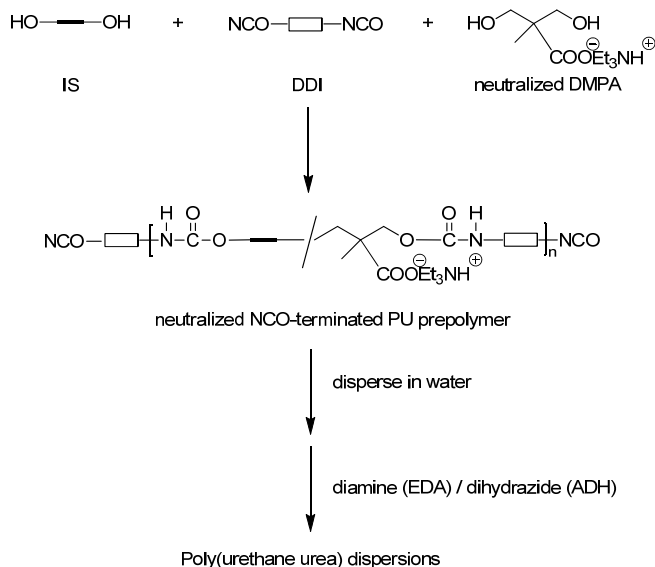
In this work, the preparation and the chain extension of renewable-based polyurethane dispersions has been described. These dispersions contain a fatty acid-based diisocyanate (DDI) and 1,4:3,6-dianhydro-D-sorbitol (isosorbide, IS) as the renewable building blocks, neutralized DMPA (non-renewable) as the internal dispersing agent, and EDA, ADH and/or water as the chain extenders. To optimize the degree of chain extension, several parameters such as the temperature applied during chain extension, the dosing moment of the chain extender with respect to the dispersion step, and the presence or absence of a catalyst (triethylamine (TEA)) were varied. The resulting dispersions were examined with respect to their molecular weight, the particle size and the colloidal stabilization. The thermal stability and the thermal transition temperatures of the dispersion-cast films were studied using TGA and DSC measurements, respectively.

4.2 Experimental section

Materials. Fatty acid-based diisocyanate (DDI®1410, 92%, titration value) was kindly supplied by Cognis. Isosorbide (IS, polymer grade, trade name Polysorb® P, 98.5%) was received as a gift from Roquette Frères. Dimethylolpropionic acid (DMPA, 98%), dibutyltin dilaurate (DBTDL, 95%), triethylamine (TEA, ≥ 99.5%) and ethylene diamine (EDA, 99.0%) were purchased from Aldrich. Adipic dihydrazide (ADH) was kindly supplied by DSM Coating Resins and used without purification. Dry 2-butanone was bought from Acros (> 99.5 %, AcroSeal®). DDI and IS were kept under inert gas and in the fridge at 4 °C. Before use, DMPA was dried at 60 °C for 48 hours in a vacuum oven. All other chemicals were used as received.

Preparation of polyurethane dispersions. A typical procedure to prepare PU dispersions includes the NCO-end capped prepolymer synthesis and the subsequent water dispersion process, as shown in **Scheme 4-1**. The PU prepolymer synthesis was performed as follows: Isosorbide (IS, 1.02 g, 7.0 mmol) and dimethylolpropionic acid (DMPA, 0.71 g, 5.3 mmol) were weighed into a 250 mL round bottom glass flange reactor. Triethylamine (TEA, 0.54 g, for 100% neutralization of DMPA) was injected into the diol mixture to obtain a clear diol solution. Subsequently, dibutyltin dilaurate (DBTDL, 0.56 wt% relative to the total solution) was injected into the diol mixture. While being

stirred mechanically, the mixture was heated up to 70 °C using a heating mantle. About 7 mL of 2-butanone was used to dilute the diol mixture. DDI (8.991 g, 14.1 mmol) was then added to this diol solution at 70 °C. Immediately, an additional amount (~6 mL) of 2-butanone was added to dilute the total reaction mixture to a solids content of 50 wt%. Before as well as during the reaction, the reaction setup was continuously flushed with inert gas (N₂). The reaction was allowed to proceed for 4-6 hours, counted from the moment that all the DDI had been added. Subsequently, the NCO content of the resulting PU prepolymer was determined by titration. After the PU prepolymer synthesis, the reaction temperature was decreased to 50 °C and additional solvent was added to correct for solvent loss and to keep the prepolymer concentration around 50 wt%. Approximately 70 mL of de-ionized water was injected in a controlled, continuous way into the prepolymer mixture and the dispersing process was effectuated by vigorous stirring. Subsequently, the chain extender (CE) EDA was added dropwise during a few minutes to the initially formed dispersion and the chain extension reaction was allowed to run for one hour. Thereafter, the polymer dispersion was discharged from the reactor. Residual 2-butanone was distilled off at 40 °C under reduced pressure.



Scheme 4-1. Preparation of polyurethane dispersions through an anionic, ketone-assisted process.

Characterization

Size exclusion chromatography (SEC) was used to determine both the molecular weights and molecular weight distributions of the prepolymers and PU dispersions. A Waters Alliance set-up equipped with a Waters 2695 separation module, a Waters 2414 differential refractive index detector (40 °C) and a Waters 2487 dual absorbance detector were used with THF, containing 1 vol.% acetic acid, as eluent. The injection volume was 50 µL. PSS (2× SDV, guard-linearXL, 5 m, 8×300 mm, 40 °C) columns were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using polystyrene (PS) standards with molecular weights ranging from 500 g/mol to 5,000 kg/mol. Data acquisition and processing were performed using Empower software.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Bio-Rad Excalibur FTS3000MX infrared spectrometer (fifty scans per spectrum, spectral resolution of 4 cm⁻¹) with an ATR diamond unit (Golden Gate). The measurement was performed by applying the polyurethane or the dispersion-cast poly(urethane urea) films onto the ATR diamond. The spectrum was recorded between 4000 and 650 cm⁻¹.

Potentiometric titrations were performed using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The isocyanate-functional groups were converted through the reaction with a molar excess of dibutylamine (DBA). The DBA residue was titrated with a normalized 1 N HCl isopropanol solution. Blank measurements were carried out using the same amount of dibutylamine. The NCO content was defined according to the following equation:

$$NCO\% = \frac{(V_{blank} - V_{sample}) \times C_{HCl} \times 4.2}{M_{prepolymer}} \%$$

where V_{blank} is the volume of HCl solution needed for the blank [mL] (average of two measurements), V_{sample} the volume of HCl solution needed for the sample [mL], C_{HCl} the HCl concentration in 2-propanol [mol/L] and $M_{prepolymer}$ is the PU prepolymer weight [g]. Titration measurements were performed in duplo.

The PU prepolymer weight was obtained by the difference in weight before and after solvent evaporation. About 0.5 g prepolymer solution was placed in a glass vial and dried at 60 °C for at least 24 hours *in vacuo*, until a constant weight was reached.

Dynamic Light Scattering (DLS) and ζ -potential measurements were used to determine the dispersion characteristics on a Malvern ZetaSizer Nano ZS at 20 °C, (polyurethane refractive index: 1.59). The average particle size and the particle size distribution (PSD) of dispersions containing ~0.1 wt% solids were determined according to ISO 13321 (1996). The pH dependence measurements of particle size and dispersion stability (ζ -potential) were performed by adding a 5×10⁻³ M aqueous HCl solution to the dispersion using a Malvern ZetaSizer MPT-2 Autotitrator, starting at the pH of the as prepared dispersion. The pH value was reduced in steps of ~ 1 and the resulting mixture was left for

1 min at this pH prior to the next ζ -potential and particle size determination, until a pH value of 3 was reached. The base titration was performed by adding 5×10^{-3} M aqueous NaOH solution to the dispersion, increasing the pH in steps of ~ 1 , until a pH of 12 was reached. The ζ -potential was calculated from the electrophoretic mobility (μ) using the Smoluchowski relationship, $\zeta = \eta\mu/\epsilon$ where $\kappa\alpha \gg 1$ (where η is the solution viscosity, ϵ is the dielectric constant of the medium, and κ and α are the Debye-Hückel parameter and the particle radius, respectively). Data acquisitions were performed using the ZetaSizer Nano software.

Thermogravimetric analyses (TGA) were performed on a TGA Q500 apparatus from TA instruments under a N_2 flow of 60 mL/min. Samples were heated from 30 to 600 °C at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC Q100 calorimeter. Samples were heated from -80 to 150 °C at a heating rate of 20 °C/min followed by an isothermal step for 5 min. A cooling cycle to -80 °C at a rate of 20 °C/min was performed prior to a second heating run to 150 °C at the aforementioned heating rate. The T_g was determined from the second heating run. The Universal Analysis 2000 software was used for data acquisition.

4.3 Results and discussion

4.3.1 PU prepolymer synthesis

The solution polymerization of PU prepolymers was carried out in 2-butanone at 70 °C, using an overall NCO/OH ratio of 1.15, aiming for a 1.54 wt% residual NCO content with a targeted molecular weight of 5.4 kg/mol. The measured molecular weights of the resulting prepolymers are shown in **Table 4-1**.

It was observed that after four hours of reaction in all cases the resulting prepolymer mixture was a clear yellowish solution with an increased viscosity compared to the starting mixture. This is a result of the increased molecular weight, ionic association and hydrogen-bond formation between the polymer chains.^[10, 33-34] As shown in **Table 4-1**, the M_n of all PU prepolymers is close to the targeted molecular weight of 5.4 kg/mol, with a polydispersity index (PDI) of around 2. The NCO content monitored by NCO back-titration reached the theoretical value and was used to calculate the amount of chain extender needed for the next step.

Table 4-1. Reaction formulations and results of PU prepolymers and PU dispersions obtained using different chain extension methods.

Entry	DMPA [wt%]	$M_{n(\text{prepol})}$ [kg/mol]	$\text{PDI}_{(\text{prepol})}$ ^a	$M_{w(\text{disp:repol})}$ ^a [kg/mol]	C.E. EDA/ADH/H ₂ O/TEA+H ₂ O	T _{CE} [°C]	$M_n(\text{PU})$ ^b [kg/mol]	$\text{PDI}_{(\text{PU})}$ ^b	$M_w(\text{PU})$ ^b [kg/mol]	Dispersion	Av. particle diameter [nm]	PSD ^e
1	6.6	5.1	1.9	9.5	EDA after dispersing	30	8.3	2.4	19.7	Stable	145	0.27
2	6.6	6.5	2.2	14.0	EDA after dispersing	50	10.1	2.5	25.0	Stable	101	0.17
3	6.6	6.4	2.1	13.5	EDA during dispersing	50	11.2	2.5	28.2	Stable	143	0.25
4	7.3	6.0	2.2	13.1	ADH after dispersing	30	7.4	2.2	16.1	Stable	121	0.19
5	7.3	6.6	1.9	12.8	ADH during dispersing	30	7.7	2.2	16.9	Stable	135	0.18
6	7.3	5.9	2.2	13.2	ADH during dispersing	50	11.4	3.1	35.1	Stable	136	0.27
7	6.3	7.3	2.2	16.3	H ₂ O during dispersing	50	12.0	2.9	34.7	Stable	68	0.25
8	6.3	5.8	2.1	12.2	H ₂ O during dispersing	60	13.4	2.9	39.6	Stable	124	0.29
9	6.3	6.6	2.2	14.2	H ₂ O during dispersing	70	13.3	2.5	33.7	Stable	195	0.35
10	6.3	5.4	2.1	11.2	TEA+H ₂ O during dispersing	50	27.3 ^c	6.1	167.5 ^c	Partially stable ^d	288	0.53
11	7.5	6.1	2.2	13.7	TEA+H ₂ O	50	18.5	2.5	46.4	Stable	189	0.20

^{a)} The molecular weight and PDI of PU prepolymers after the prepolymer synthesis; ^{b)} The molecular weight and PDI of PUDs after one hour of chain extension;

^{c)} These values might not be completely representative due to the inhomogeneity of this particular sample; ^{d)} A small fraction of this dispersion precipitated and formed aggregates; ^{e)} Particle size distribution.

4.3.2 EDA chain-extended PU dispersions

PU dispersions were prepared by adding water under vigorous stirring to the prepolymer mixture at moderate temperatures. Based on a few initial chain extension experiments, it was found that using a NH_2/NCO ratio from 0.75 to 1.0 did not result in significant differences in the molecular weight of the chain-extended PUDs, probably as a result of the partial hydrolysis of isocyanate groups. Therefore in this current study a NH_2 (from EDA) /NCO ratio of approximately 0.75 was applied. Three dispersions were prepared and chain-extended with EDA. The first two dispersions (PUD1 and PUD2) were chain-extended with EDA after the formation of the initial aqueous dispersion while the reaction temperature was controlled at $T_{\text{CE}} = 30^\circ\text{C}$ and 50°C , respectively. In the third case (PUD3), EDA was added together with the water to prepare the dispersion at $T_{\text{CE}} = 50^\circ\text{C}$.

FT-IR spectra

To demonstrate the urea formation and the occurrence of the chain extension reaction, FT-IR measurements were performed. Taking PUD3 as an example, **Figure 4-1A** shows the FT-IR spectra after the PU prepolymer synthesis and after EDA chain extension reaction, respectively. The enlarged carbonyl region of these two spectra is shown in **Figure 4-1B**.

In **Figure 4-1A**, in the spectrum recorded after the prepolymer synthesis (PU), the broad peak at 3355 cm^{-1} is attributed to the stretching vibration of urethane N-H moieties. A single peak at 2274 cm^{-1} corresponds to the remaining isocyanate groups. The absorption band at 1714 cm^{-1} is attributed to the urethane C=O groups. After EDA chain extension, the N-H stretching vibration at 3355 cm^{-1} becomes narrow and is centered around 3327 cm^{-1} due to the urea formation. The isocyanate peak at 2274 cm^{-1} has completely disappeared, mainly due to the isocyanate-amine chain extension reactions. The absorption band at 1697 cm^{-1} is attributed to the H-bonded urethane C=O. Three small shoulders at $1676\text{--}1610\text{ cm}^{-1}$ belong to the urea C=O stretching. The increased peak areas at 1530 and 1240 cm^{-1} are attributed to the amine II (C-N stretching and N-H bending) and amide III (C-N stretching and N-H deformation) regions, respectively.^[35-36] Band assignments of the enlarged carbonyl area in PU prepolymers and in PUU films are listed in **Table 4-2**. Similar characteristic peaks have been reported by Lou et al. and Hu et al.^[9, 36-38]

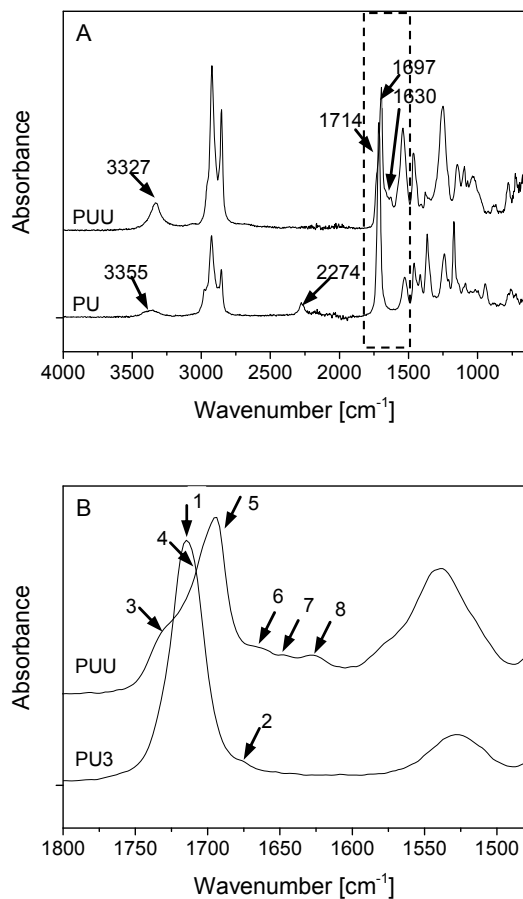


Figure 4-1. FT-IR spectra of PUD3 A) PU prepolymers and dispersion-cast PUU films obtained from EDA chain-extended dispersions; B) The enlarged carbonyl region of A.

Table 4-2. Assignment of absorption bands in the carbonyl region in **Figure 4-1B**.

No.	Wavenumber[cm^{-1}]	Assignment
1	1760-1680	free carbonyl stretching of urethane linkage (PU)
2	1680-1670	H-bonded urethane carbonyl (PU)
3	1760-1720	free carbonyl stretching of urethane (PUU)
4	1720-1696	disordered H-bonded urethane carbonyl (PUU)
5	1696-1676	ordered H-bonded urethane carbonyl (PUU)
6	1676-1672	free carbonyl stretching of urea (PUU)
7	1652-1638	disordered H-bonded urea carbonyl (PUU)
8	1638-1610	ordered H-bonded urea carbonyl (PUU)

Molecular weight

It is noticed that the M_n values of all three EDA chain-extended dispersions are approximately doubled with respect to the M_n values of the corresponding prepolymers (**Table 4-1**). No significant differences in M_n values have been observed between these three dispersions. After one hour of chain extension no further increase of the molecular weights has been observed. These results indicate that ethylene diamine is able to extend the prepolymer chains at both 30 and 50 °C, independent of the moment of EDA addition (moment of CE addition is indicated in **Table 4-1**). Nonetheless, the molecular weight of these dispersions in general is lower than expected. This might primarily be due to the relatively low purity (92%, titration value) and functionality of the dimer fatty acid-based diisocyanate. Prepolymers with single isocyanate end-groups may exist, which act as chain stoppers.

Average particle size

DLS was used to determine the average particle size and the particle size distribution of the resulting dispersions. The average particle sizes of all three dispersions PUD1-PUD3 vary between 101 and 145 nm, whereas the particle size distributions range from 0.17 to 0.27. The slight differences in particle size are most probably caused by the differences in

the dispersion and chain extension processes. For instance, PUD2 prepared at 50 °C has a smaller average particle size than PUD1 dispersed at 30 °C. PUD3 shows an increased particle size compared to PUD2 by adding EDA together with water to prepare dispersions. To understand these influences on particle size, the polymeric interactions need to be considered. Two types of interactions (i.e. ionic and H-bonding interactions) between the polymer chains exist. As can be expected, these interactions increase with increasing the polymer chain length, resulting in an increased polymer viscosity and a reduced chain mobility. The as-prepared PU prepolymers have a similar molecular weight and a comparable polymeric structure. Upon increasing the temperature to 50 °C (i.e. when preparing PUD2), these weak polymeric interactions (ionic and H-bonding) will be reduced and the chains will become more dissociated, which improves the chain mobility.^[36-37, 39] As a result, the migration of DMPA to the particle's surface is facilitated, forming smaller particles than in the case of PUD1. However, PUD3 obtained at 50 °C exhibits a relatively large particle size compared to PUD2. This might be a result of EDA chain extension happening at the moment of dispersion formation by adding EDA together with water. Consequently, the polymer chain length increases and the chain mobility is reduced. Less DMPA moieties are able to migrate to the particle's surface. Important to mention is that all resulting dispersions show good storage stability for at least several months.

4.3.3 Adipic dihydrazide (ADH) chain-extended PU dispersions

ADH was selected as a chain extender as it contains primary amine groups and has a different molecular structure than EDA. Its chain extension behavior may differ from EDA by the slightly changed molecular hydrophobicity of ADH. In addition, ADH is not soluble in 2-butanone even at 50 °C, which may influence the chain extension process. Similarly to EDA chain extension, the influence of the chain extension temperature and the sequence of ADH addition relative to the dispersion process were investigated. In the first reaction, ADH was added after the formation of the dispersion at 30 °C. In the second system, ADH was added together with water to prepare dispersions at the same temperature. In the final dispersion, ADH was again added together with water to the prepolymer mixture at 50 °C. The resulting PU prepolymers and PUDs show similar FT-IR spectra as those of the EDA chain-extended PUDs.

Molecular weight

After one hour of chain extension, the M_n values of PUD4 and PUD5 are very similar to those of their corresponding prepolymers. An increase of the M_n to about the double of the prepolymer molecular weight has only been observed in both dispersions after removing 2-butanone at 40 °C, as shown in **Figure 4-2**. To make sure that the potential side-reaction between ADH and the ketone ^[40-41] solvent does not hamper the molecular weight build-up, FT-IR measurements were performed. No significant occurrence of the side-reaction was observed. Therefore, this result may indicate that the ketone solvent, which swells the dispersed particles, limits the access of ADH to the particles. Taking into account our preliminary results, showing that water hardly extends prepolymer chains at 40 °C within one hour, the increase of M_n values to 11.3 (PUD4) and 11.0 kg/mol (PUD5) after removing the solvent indicates the occurrence of ADH chain extension. These M_n values show strong similarity to those of EDA chain-extended PUDs, implying a comparable chain extension effect of ADH to EDA. Based on these observations, a controlled ADH chain extension by either the presence or the absence of the ketone solvent can be realized. The third ADH chain-extended dispersion (PUD6) exhibits an increased molecular weight at 50 °C without removing the solvent, which is regarded as a result of the occurrence of water chain extension (*vide infra*).

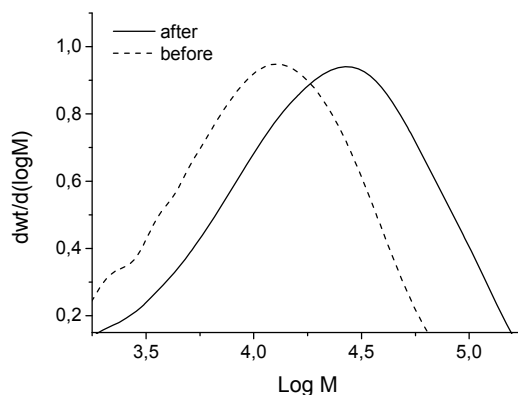


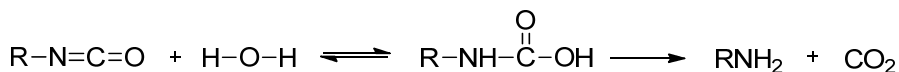
Figure 4-2. The molecular weight plots of PUD4 before and after removing 2-butanone. Chain extension reaction took place at 30 °C.

Particle size

The average particle sizes of these three ADH chain-extended dispersions are similar, ranging from 121 nm to 136 nm. The particle size distribution varies from 0.17 to 0.27 (**Table 4-1**). The chain extension temperature and the moment of ADH addition show limited influences on the particle size. These dispersions are stable for at least a few months.

4.3.4 H₂O chain-extended PU dispersions

When using water as the chain extender, the first reaction step consists of the formation of an instable carbamic acid, which subsequently decarboxylates to form an amine functionality, as shown in **Scheme 4-2**. This amine group can subsequently react with another isocyanate group to effectuate chain extension by urea formation.



Scheme 4-2. The amine formation of the chain extension reaction with water. ^[30-31]

The amount of water used to make dispersions was the same as in the previous cases. Three reactions were carried out to assess the effect of the chain extension temperature, ranging from 50, 60 to 70 °C, on the degree of chain extension. Chain extension temperatures lower or higher than this range were found to result in either slow chain extension or instable dispersions, respectively.

Molecular weight

After one hour of chain extension, the M_n values of the three dispersions show similar values around 13 kg/mol. These results indicate that instantaneous (i.e. within one hour) water chain extension took place at 50, 60 and 70 °C. In spite of the complete disappearance of the isocyanate groups observed from FT-IR measurements (meaning that the NCO concentration was below the detection limit of FT-IR), further slight increases in molecular weight up to 15.8 kg/mol have been observed for these three dispersions after one day. Slight differences in chain extension temperature from 50 up to

70 °C do not show further enhancement of the molecular weight, indicating that after reaching an M_n value of 15.8 kg/mol no NCO groups are available anymore for the chain extension process.

Average particle size and ζ -potential

As shown in **Table 4-1**, the average particle size and the particle size distribution were significantly affected by the reaction temperatures. At 70 °C, the largest average particle size around 195 nm and a bi-modal distribution are observed, while the average particle size of the dispersions obtained at 50 °C is approximately 68 nm and the system shows a mono-modal distribution. Both particle size curves are depicted in **Figure 4-3**. G. Morral-Ruiz et al. and H. Sardon et al. have reported similar results, i.e. particle size increasing with increasing temperature.^[42-43]

The electrostatic stabilization of the obtained dispersions was demonstrated using ζ -potential measurements. Typically, ζ -potential values either above 30mV or below -30mV indicate a stable system. The negative ζ -potential values of these three dispersions increased slightly with increasing T_{CE} , as shown in **Figure 4-4**, indicating a slightly reduced electrostatic repulsion between the particles. This reduction of the absolute ζ -potential is in agreement with the increase of the particle size.

To summarize the influence of the chain extension temperature on the molecular weight and particle size of the dispersions obtained, T_{CE} at 50 °C provides a better balance between the degree of chain extension and the stability of the dispersions.

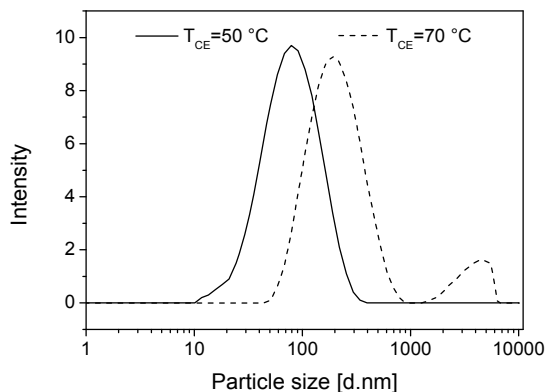


Figure 4-3. The average particle size and particle size distribution of dispersions chain-extended with water at 50 °C (PUD7) and at 70 °C (PUD9).

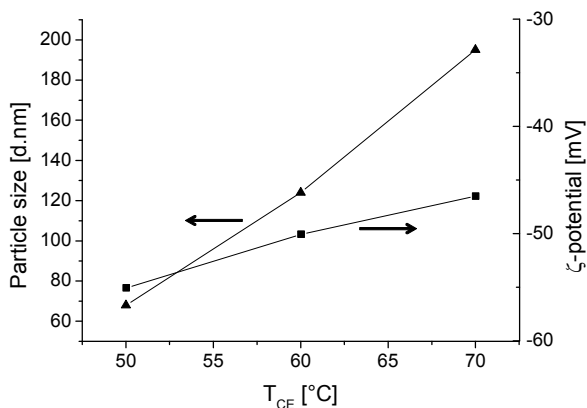


Figure 4-4. The average particle size (▲) and ζ -potential (■) measurements of dispersions prepared at 50 °C, 60 °C and 70 °C.

4.3.5 TEA-catalyzed water chain extension

Compared to primary amines, water has a much lower reactivity in reaction with isocyanates at moderate temperatures. Direct evidence can be found in PUD7-PUD9. Their M_n values kept increasing after one hour of chain extension at 50 °C. These water-

isocyanate reactions are usually facilitated by using a catalyst such as tertiary amines and organotin compounds. In spite of the high catalytic activity of organotin compounds, in this study triethylamine (TEA) was selected as a tertiary amine catalyst for its high solubility in water as well as in 2-butanone. The influences of TEA on water chain extension and the dispersion stability were investigated. The proposed mechanism of tertiary amine catalyzing the isocyanate-water reaction has been published by Ni et al.,^[44] as shown in **Scheme 4-3**. A reduced activation energy was achieved by the formation of the negatively charged isocyanate intermediate.

Average particle size and ζ -potential

The dispersion PUD10 is partially stable, showing a small fraction of precipitated aggregates after being prepared. It has an average particle size of around 288 nm, much larger than the previous dispersions using a similar amount of DMPA. PUD11, prepared using 7.5 wt% of DMPA, also showed a relatively large average particle size compared to PUD7, prepared using 6.3 wt% of DMPA and without adding extra TEA. The reduced dispersion stability introduced by the additional amount of TEA could not be related to swelling of the particle by TEA and might instead be a result of the increased concentration of TEA, which disturbs the electrical bilayer to some extent. As a result of more delocalized positive charges (protonated TEA) below or in the *Stern layer*, the absolute amount of negatively charged DMPA residues at the particle surface might be reduced. Subsequently, large particles were formed. Similar results have been observed by other researchers, in which the particle size of PU dispersions containing rapeseed oil, IPDI and DMPA proved to increase with increasing TEA content when above 100% of DMPA neutralization.^[45]

The ζ -potential of PUD11 is -61 mV, which is almost the same as that of PUD8 although more DMPA is used in PUD11. This result confirms the negative influence of TEA on the ζ -potential. In addition, the ζ -potential and the particle size of PUD11 were investigated as a function of pH and results are plotted in **Figure 4-5**.

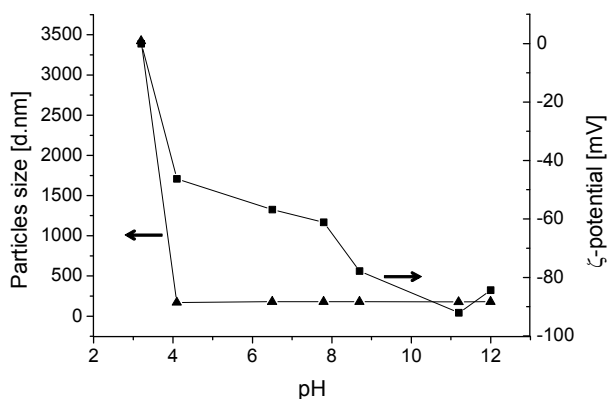


Figure 4-5. The plot of ζ -potential and average particle size measurements of PUD11 as a function of pH.

As shown in **Figure 4-5**, the particle size was nearly constant at pH values ranging from 4.1 to 12. At pH 3.2, the particle size increased significantly up to 3420 nm. Concurrently, the ζ -potential increases sharply to around 0 mV. This was due to the partial deactivation of DMPA upon the addition of acid. Large aggregates precipitated out from the dispersion. The electrostatic stability of this dispersion is presented in the same figure. From pH 4.1 to 12, the ζ -potential decreased from -46 mV to -84 mV, confirming the stability of the dispersions in a basic environment.

4.3.6 TGA and DSC measurements

The thermal stability and the thermal transitions of the dry films have been investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The TGA traces of several dry films indicated as F7, F8, F9 and F11, corresponding to the dispersions PUD7, 8, 9 and 11 in **Table 4-1**, are depicted in **Figure 4-6**.

Figure 4-6 shows that these dry films, prepared from the indicated dispersions and chain-extended with water, undergo more than one thermal degradation step. The urethane and urea decomposition step is observed in the range of 240-350 °C. Depending on the type of decomposition mechanism, the resulting degradation products may include isocyanates, alcohols, amines, olefins and carbon dioxide.^[21, 46-48] The degradation process in the temperature range of 330-405 °C corresponds to the fatty acid chain scission.^[46] The last stage of the degradation process centered around a temperature of 450-460 °C is attributed to the gasification of any remaining organic components.^[49] The amount of solid residues above 500 °C is in the range of 1.8-3.5% of the initial weight, most likely constituting the degradation products of isohexide moieties.^[50] Upon 5 wt% mass loss, the temperatures (ranging from 249 to 272 °C) fall into the range of urethane and urea decomposition (**Table 4-3**). It is also noticed that at 5 wt% mass loss, these decomposition temperatures decrease with increasing T_{CE} from 50 – 70 °C. From these results, slight differences in urethane and urea contents are expected between these films.

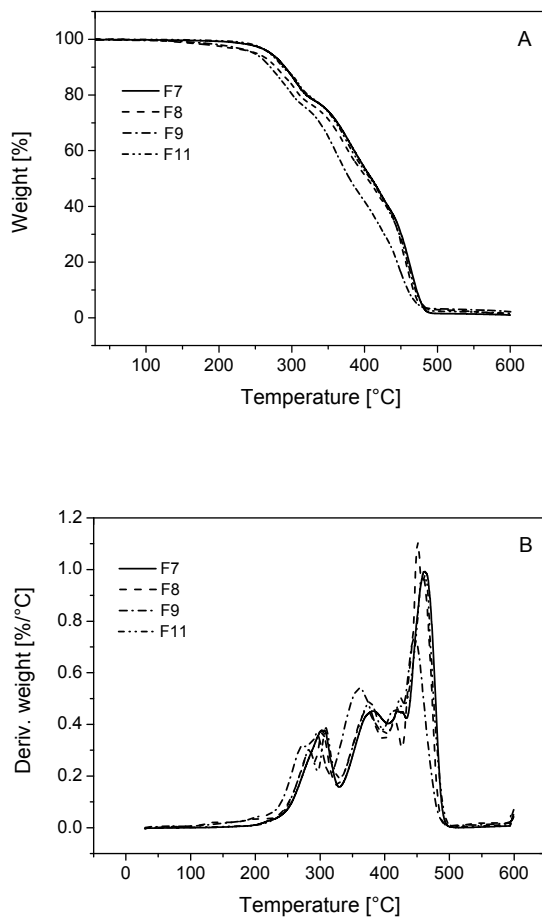


Figure 4-6. TGA curves (A) and the corresponding derivative plots (B) of dry films prepared from water chain-extended dispersions recorded from 30-600 °C at 10 °C/min under N₂ atmosphere.

Table 4-3. Thermal properties and transition temperatures derived from TGA and DSC curves.

Film*	TGA		DSC	
	$T_{d, 5\%}^a$	$T_{d, 50\%}^b$	T_{g1}^c	T_{g2}^c
	[°C]	[°C]	[°C]	[°C]
F7	272	410	19	76
F8	250	403	18	73
F9	249	379	15	73
F11	270	408	18	-

* The film numbers refer to the dispersions in **Table 4-1**. a) $T_{d, 5\%}$ is the 5% weight loss temperature measured by TGA (10 °C min⁻¹); $T_{d, 50\%}$ is the 50% weight loss temperature measured by TGA; c) The 1st and the 2nd heating T_g determined from the second DSC heating run (20 °C min⁻¹).

To seek for the evidence illustrating the differences in urethane and urea contents between these films, FT-IR measurements were performed for films F7, F8 and F9. These three films have an increased T_{CE} temperature ranging from 50, 60 to 70 °C, respectively. **Figure 4-7** shows the normalized FT-IR spectra of these three films, focusing on the N-H region and the carbonyl region of urethanes and ureas.

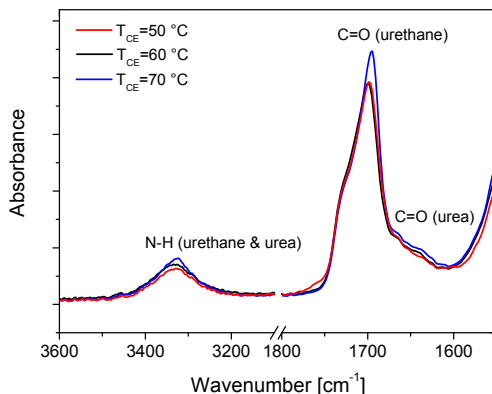


Figure 4-7. FT-IR spectra of dispersion-cast PUU films (F7, F8 and F9) corresponding to dispersions PUD7, PUD8 and PUD9 chain-extended at 50, 60 and 70 °C.

As shown in **Figure 4-7**, by increasing T_{CE} from 50 to 70 °C a slight increase in peak height was observed at 3320 cm^{-1} and at 1672-1620 cm^{-1} , attributed to the urethane and urea N-H stretching and urea C=O groups, respectively. These results indicate that the urea formation is slightly promoted by increasing chain extension temperature, even though clear evidence was not obtained from the molecular weight measurements. The relatively high temperature might have provided more activation energy for water-isocyanate reaction. The relatively large peak at 1700 cm^{-1} , attributed to the H-bonded urethane carbonyl of F9 ($T_{CE} = 70$ °C), possibly is a result of the improved chain mobility that enhances the formation of H-bonds.

The DSC curves of the dispersion-cast films prepared from the same dispersions are depicted in **Figure 4-8**. The T_g values of these dry films prepared from different dispersions are rather similar and relatively low, viz. in the range of 15-19 °C (**Table 4-3**), which is a result of using a large weight ratio of DDI in the prepolymer content. A second T_g around 75 °C is observed in samples F7, F8 and F9, implying the existence of a slight phase separation, which is possibly a result of the H-bonded urethanes and ureas. No melting temperature peak has been observed for any of the films, indicating an amorphous structure. The T_g values below 20 °C imply that one can expect film formation to readily occur at room temperature.

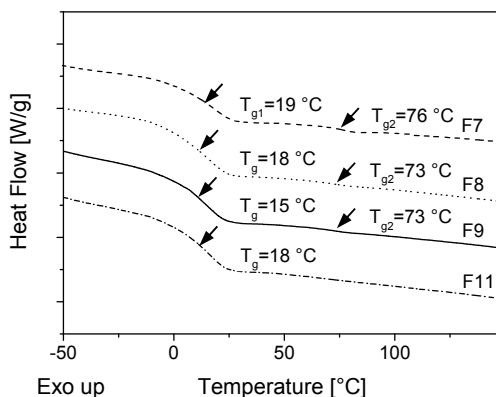


Figure 4-8. The second heating DSC curves of dry PUU films recorded from -80 to 150 °C at a heating rate of 20 °C/min.

4.4 Conclusions

Aqueous polyurethane prepolymer dispersions have been successfully prepared from a dimer fatty acid-based diisocyanate (DDI), DMPA and isosorbide, containing at least 92 wt% of renewable compounds. EDA, ADH and water have shown different chain extension behavior. EDA extended the prepolymer chains at 30 and 50 °C, independent of the moment of their addition to the prepolymer dispersions. A limited extent of ADH chain extension was observed and that was related to the low solubility of ADH in the solvent 2-butanone. The ADH chain extension took place only after removal of the 2-butanone. Hence, a controlled chain extension by either the presence or absence of 2-butanone can be realized. Water chain extension took place at temperatures ranging from 50 °C to 70 °C. A good balance was found at 50 °C, where a stable dispersion with a relatively high molecular weight, a small particle size and a narrow particle size distribution were obtained. The usage of TEA (above 100% DMPA neutralization) during the dispersion process promoted the water chain extension reaction, however, at the cost of dispersion stability. An increased DMPA level (from 6.3% to 7.5%) has shown to provide the dispersions with sufficient storage and electrostatic stability. The dispersion-cast poly(urethane urea) films showed a three-stage thermal degradation process and were thermally stable up to 249 °C (5 wt% mass loss). The T_g values determined by DSC measurements were all around room temperature, which facilitates film formation at

ambient temperature. A small second T_g transition around 75 °C exist in some of the films, indicating a H-bonding induced micro-phase separation. Still, the PUU coatings prepared in this study were too soft for many industrial applications. However, there is ample potential to increase the T_g values by for instance cross-linking or the incorporation of rigid comonomers, which would allow for more demanding coating applications.

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5

Bio-based Poly(urethane urea) Dispersions with a Low Internal Stabilizing Agent Content and Tunable Thermal Properties

Abstract

The natural flexibility of vegetable oil-derived polyols and diisocyanates hampers the development of polymer materials based thereon with T_g above room temperature. Combined with the limited availability of renewable diisocyanates and internal stabilizing agents, used to colloidally stabilize water-borne polyurethane dispersions (PUD), this explains why fully renewable-based aqueous PU dispersions with satisfactory film T_g values ($T_g > 30\text{ }^\circ\text{C}$) have not yet been developed. The aim of this work is to prepare fully bio-based linear poly(urethane urea) dispersions with a sufficiently high T_g . Dimer fatty acid-based diisocyanate (DDI), lysine-derived ethyl ester L-lysine diisocyanate (EELDI) and 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) were selected as the main PU building blocks. The petrochemical-based dimethylolpropionic acid (DMPA) was used as the internal stabilizing agent. The selection of EELDI was based on its similarity to hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) with respect to urethane-bond density and asymmetric functionality, respectively. The replacement of DDI by EELDI and the incorporation of IS into the polymer composition effectively reduced the required amount of DMPA from 6.0 to 2.0 wt% to render stable dispersions and significantly enhanced the T_g of dispersion-cast films to $60\text{ }^\circ\text{C}$ ($1^{\text{st}} T_g$) and to above $70\text{ }^\circ\text{C}$ ($2^{\text{nd}} T_g$), however, at the expense of slightly reduced thermal stability. The asymmetric structure of EELDI and its pendant ester group potentially facilitated the dispersion stability, the latter through possible (partial) hydrolysis. Accordingly, aqueous PU dispersions with a renewable content up to 97 wt% and sufficiently high, tunable film T_g values have been obtained.

5.1 Introduction

Water-borne polyurethane dispersions (PUD) represent one of the most rapidly developing branches of polyurethane (PU) chemistry for coating applications. Compared to solvent-borne systems, water-borne PU dispersions have advantageous properties, including low volatile organic compounds (VOC) contents, enhanced ease of application because of their low viscosities, non-flammable nature and good adhesion.^[1-7] Inspired by the availability of biomass and the environmental concerns about exhaustible fossil feed stocks, the preparation of aqueous PU dispersions from biomass-derived polyols and isocyanates has become an active field of research.^[8-16] However, the limited availability of bio-based diisocyanates and internal stabilizing agents, as monomers to prepare aqueous PU dispersions, have hampered the development of fully bio-based PUs or PU dispersions. Furthermore, although the flexible and hydrophobic nature of fatty acid-derived PU building blocks affords excellent impact resistance and water resistance, the relatively low glass transition temperature ($T_g < 40\text{ }^\circ\text{C}$) of these PU materials restricts their applications where high T_g and high rigidity are required.^[17-18]

Cross-linking^[19-23] of polyurethane prepolymers and the design of segmented polyurethane structures^[24-28] are the most common approaches towards improving the thermal and mechanical properties of fatty acid-containing polyurethanes. Miao et al.^[23] successfully improved T_g values up to $96\text{ }^\circ\text{C}$ by using the petrochemical-based 4,4'-diphenylmethane diisocyanate (MDI) to cross-link hydroxyl-functionalized soybean oil. Aromatic, rigid aliphatic diisocyanates^[24] and rosin acid^[25] have effectively improved the mechanical properties of fatty acid-containing segmented polyurethanes. A relatively new approach developed by More et al.^[26] involves the use of short fatty acid-based building blocks. These fatty acid-derived diisocyanates, containing 8 or 10 carbons in the monomer backbone, were polymerized with isosorbide, reaching T_g values of up to $56\text{ }^\circ\text{C}$.

Previously, we successfully prepared polyurethane dispersions from dimer fatty acid-based diisocyanate (DDI) (**Figure 5-1**) and glucose-derived isosorbide (1,4:3,6-dianhydro-D-glucitol, IS), using dimethylolpropionic acid (DMPA) as the internal stabilizing agent.^[29] Since a large amount of the hydrophobic, flexible DDI^[30] is present in the final polymers, a relatively high amount of petrochemical-based DMPA was required to stabilize the dispersions and the use of the more rigid isosorbide alone was not sufficient to bring the T_g to above $20\text{ }^\circ\text{C}$. Therefore, additional renewable rigid and relatively more hydrophilic PU building blocks are necessary to reduce the required DMPA content and improve the T_g .

The L-lysine-derivative ethyl ester L-lysine diisocyanate (EELDI) seems to be a suitable candidate. It has five carbons between the two isocyanate groups, providing a urethane

bond density similar to hexamethylene diisocyanate (HDI) as well as a relatively rigid and hydrophilic molecular structure compared to DDI. A similar reactivity of EELDI to that of HDI is expected. By partially replacing DDI with EELDI, enhanced T_g values and a higher polymer hydrophilicity, caused by the increased urethane-bond density, can be expected. Moreover, similarly to isophorone diisocyanate (IPDI), EELDI has asymmetric functionalities.^[31] It is known that the asymmetric and cyclic molecular structure of IPDI enhances the solubility of the resulting polyurethanes by generating more free volume between the polymer chains, which is favorable for making dispersions.^[32] In this respect, EELDI-based polyurethanes are thought to have similar advantages as well, attributed to its asymmetric functionality.

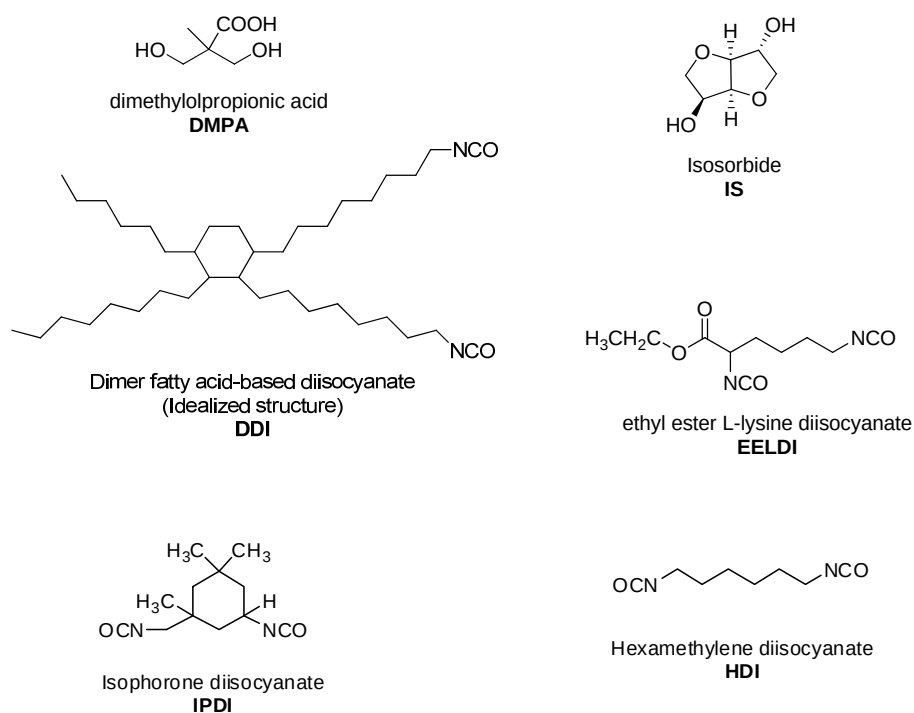


Figure 5-1. The molecular structures of DMPA, IS, DDI, EELDI, IPDI and HDI.

The aim of this work is to 1) investigate if EELDI is suited to prepare PU dispersions by considering its reactivity and molecular structure; 2) prepare water-borne polyurethane dispersions from DDI, IS, EELDI and DMPA, maximizing the content of renewable monomers by means of reducing the DMPA content as much as possible; 3) to improve the thermo-mechanical properties and thermal transition temperatures of dispersion-cast films by incorporating the rigid diol IS and the diisocyanate EELDI into the polymer backbone. Series of poly(urethane urea) dispersions were prepared with a reduced amount of DMPA and an increased EELDI-to-DDI ratio. A model study concerning the potential hydrolysis of the EELDI ester groups in correlation with the stabilizing power of EELDI in PUDs was carried out. The influence of the changes in the polymer composition on the average particle diameter of the dispersions, on the dispersion stability, on the thermal transitions and on the thermo-mechanical properties of the dispersion-cast films was investigated. Concurrently, the asymmetric molecular structure of EELDI was evaluated in the perspective of preparing dispersions, using HDI as a reference.

5.2 Experimental section

Materials. Fatty acid-based diisocyanate (DDI®1410, 92%, titration value) was kindly supplied by Cognis. Isosorbide (IS, polymer grade, trade name Polysorb® P, 98.5%) was received as a gift from Roquette Frères. Ethyl ester lysine diisocyanate (EELDI, 95%) was purchased from Infine Chemicals Co., Limited, China. Dry acetone (> 99.0%) and dry 2-butanone (> 99.5 %, AcroSeal®) were bought from MERCK and Acros respectively, and were kept under inert gas (N_2) together with 4 Å molsieves. Dimethylolpropionic acid (DMPA, 98%), isophorone diisocyanate (IPDI, 98%, Z-/E-stereoisomers = 3:1), hexamethylene diisocyanate (HDI, 99.0%), dibutyltin dilaurate (DBTDL, 95%), triethylamine (TEA, ≥99.5%) and ethylene diamine (EDA) were purchased from Aldrich. All diisocyanates and isosorbide were kept under inert gas and in the fridge at 4 °C. Before use, DMPA was dried at 60 °C for 48 hours in a vacuum oven. Other chemicals were used as received.

Model reaction procedure to elucidate diisocyanates reactivity. Model reactions were carried out according to the following typical procedure, as described in Chapter 3. Before and during the reaction, the setup was continuously flushed with inert gas (N_2) to prevent oxidation of the reactants and to keep the reaction devoid of moisture. IS (0.49 g, 7 mmol) was weighed into a 5 mL round bottom flask. Acetone (1.6 mL) was added to dissolve IS. Once a clear solution was obtained, EELDI (0.76 g, 7 mmol) was injected. While stirring, the mixture was heated to 40 °C using an oil bath. DBTDL (~0.56 wt%) was added to the mixture. The reaction was continued for two to five hours and samples were taken at regular time intervals for FT-IR analysis. The same procedure was applied for HDI- and IPDI-based model reactions. Several reactions were randomly selected and repeated to check repeatability.

NCO-end capped PU prepolymer synthesis and dispersion preparation. A typical procedure to prepare PU dispersions includes the synthesis of an NCO-end capped prepolymer and its dispersion in water, as described in Chapters 3 and 4. The PU prepolymer synthesis was performed as follows. IS (1.50 g, 10.3 mmol) and DMPA (0.64 g, 4.8 mmol) were weighed into a 250 mL round bottom glass flange reactor. TEA (0.48 g, 4.8 mmol, for 100% neutralization of DMPA) was injected into the diol mixture to obtain a clear diol solution. Subsequently, DBTDL (concentration: 0.56 wt% relative to the total solids content) was injected into the diol mixture. While being stirred mechanically, the mixture was heated up to 70 °C using a heating mantle. Approximately half of the totally added amount of solvent 2-butanone (7 mL) was used to dissolve the diols mixture. EELDI (1.34 g, 5.6 mmol) and DDI (7.17 g, 11.3 mmol) were then added to this diol solution at 70 °C. The rest of the 2-butanone was then instantly added to dilute the total reaction mixture to 50 wt%. Before as well as during the reaction, the reaction setup was continuously flushed with inert gas (N₂). The reaction was carried out for 4-6 hours, counted from the moment that all the DDI and EELDI was added. Subsequently, the NCO content of the resulting PU prepolymer was determined by titration. After the PU prepolymer synthesis, the reaction temperature was decreased to 50 °C and additional solvent was added to correct for solvent losses and to readjust the prepolymer concentration to around 50 wt%. A mixture of EDA (0.13 g) and de-ionized water (~40 mL) was injected in a controlled way into the prepolymer mixture and the dispersing process was facilitated by vigorous stirring. Subsequently, the chain extension reaction was allowed to proceed for one hour at 50 °C. Thereafter, the polymer dispersion was discharged from the reactor. Residual 2-butanone was distilled off at 40 °C at reduced pressure.

Model reaction procedure of EELDI hydrolysis. The model reaction of EELDI hydrolysis was carried out in two steps: the preparation of the EELDI model compound and the EELDI model hydrolysis. These two steps were carried out according to the following procedure: 1-butanol (0.99 g, 13.4 mmol) was weighed into a 5 mL round bottom flask. 2-butanone (2.5 g, 3.1 mL) was added to dilute the 1-butanol. While stirring, the solution was heated to 50 °C using an oil bath. DBTDL (~0.56 wt% relative to the amount of 1-butanol) was added to the solution. EELDI (1.51 g, 6.7 mmol) was then injected. Before and during the reaction, the setup was continuously flushed with inert gas (N₂) to prevent oxidation and to keep the reaction devoid of moisture. The reaction was continued for three hours, and samples were taken at regular time intervals for ¹H NMR analysis. Upon the completion of this reaction, as confirmed by ¹H NMR, a solution of EDA in water having a pH of 12 (the same as used to make dispersions) was added to the reactor by using a molar ratio of H₂O : EELDI = 3.5 : 1). Samples were taken after one hour of reaction for FT-IR measurements.

Characterization

Size exclusion chromatography (SEC) was used to determine both the molecular weight and the molecular weight distributions of the prepolymers and the PU dispersions. A Waters Alliance set-up equipped with a Waters 2695 separation module, a Waters 2414 differential refractive index detector (40 °C) and a Waters 2487 dual absorbance detector were used with tetrahydrofuran (THF), containing 1 vol.% acetic acid, as eluent (unless indicated otherwise). The injection volume was 50

μL . PSS (2 $\times$ SDV guard-linearXL, 5 m, 8 $\times$ 300 mm, 40 °C) columns were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using polystyrene (PS) standards (unless indicated otherwise) with molecular weights ranging from 500 g/mol to 5,000 kg/mol. Data acquisition and processing were performed using the Empower software.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Bio-Rad Excalibur FTS3000MX infrared spectrometer (fifty scans per spectrum, spectral resolution of 4 cm^{-1}) with an ATR diamond unit (Golden Gate). The measurement was performed by applying the PU prepolymer mixture or the PU dispersion onto the ATR diamond. The spectra were taken between 4000 and 650 cm^{-1} .

Proton Nuclear Magnetic Resonance Spectroscopy (^1H NMR) was used to follow the formation of the EELDI model compound. The conversions of both OH- and NCO-groups were followed in time. ^1H NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer. Acetone- d_6 was used as the solvent.

Potentiometric titrations were performed using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The isocyanate functional groups were converted through the reaction with a molar excess of dibutylamine (DBA). The DBA residue was titrated with a normalized 1 N HCl isopropanol solution. Blank measurements were carried out using the same amount of dibutylamine. The NCO content was defined according to the following equation:

$$\text{NCO}\% = \frac{(V_{\text{blank}} - V_{\text{sample}}) \times C_{\text{HCl}} \times 4.2}{M_{\text{prepolymer}}} \%$$

where V_{blank} is the volume of HCl solution needed for the blank [mL] (average of two measurements), V_{sample} the volume of HCl solution needed for sample [mL], C_{HCl} the HCl concentration in 2-propanol [mol/L] and $M_{\text{prepolymer}}$ is the PU prepolymer weight [g]. Titration measurements were performed in duplo.

A vacuum drying method was applied to obtain the polymer solid content by heating the dispersions at 60 °C for 24 hours *in vacuo*, until a constant weight was reached.

Dynamic Light Scattering (DLS) and ζ -potential measurements were performed to determine the dispersion characteristics on a Malvern ZetaSizer Nano ZS at 20 °C, (polyurethane refractive index: 1.59). The average particle size and the particle size distribution of dispersions containing ~0.1 wt% solids were determined according to ISO 13321 (1996). The pH dependence measurements of average particle size and dispersion stability (ζ -potential) were performed by adding a 5.0×10^{-3} M aqueous HCl solution to the dispersion using a Malvern ZetaSizer MPT-2 Autotitrator, starting at the pH of the as-prepared dispersion. The pH value was reduced in steps of ~ 1 and the resulting mixture was left for 1 min at this pH prior to the next ζ -potential and particle size determination, until a pH value of 3 was reached. The base titration was performed by adding a 5.0×10^{-3} M NaOH aqueous solution to the dispersion, increasing the pH in steps of ~ 1, until a pH of 12 was reached. The ζ -

potential was calculated from the electrophoretic mobility (μ) using the Smoluchowski relationship, $\zeta = \eta\mu/\epsilon$ where $\kappa\alpha \gg 1$ (where η is the solution viscosity, ϵ is the dielectric constant of the medium, and κ and α are the Debye-Hückel parameter and the particle radius, respectively). Data acquisitions were performed using the ZetaSizer Nano software.

Thermogravimetric analyses (TGA) were performed on a TGA Q500 apparatus from TA Instruments under a N_2 flow of 60 mL/min. Samples were heated from 30 to 600 °C at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC Q100 calorimeter. Samples were heated from -80 to 150 °C at a heating rate of 20 °C/min followed by an isothermal step for 5 min. A cooling cycle to -80 °C at a rate of 20 °C/min was performed prior to a second heating run to 150 °C at the aforementioned heating rate. The T_g was determined from the second heating run. The Universal Analysis 2000 software was used for data acquisition.

5.3 Results and discussion

Our previous work ^[29] showed that relatively non-polar PU dispersions containing DDI as the only diisocyanate had low T_g values (< 20 °C) and required high DMPA contents (> 6.3 wt%) for colloidal stabilization. By replacing DDI with a shorter, more rigid diisocyanate, an increased polymer hydrophilicity and rigidity are expected, because of the increased urethane-bond density. EELDI is a potential candidate to replace DDI and has a molecular structure similar to HDI (5 vs. 6 carbons between urethane links). A comparable reactivity between EELDI and HDI is expected. In addition, similar to isophorone diisocyanate (IPDI), EELDI has an asymmetric molecular structure, which can favor dispersion preparation with the required prepolymer solubility and lack of crystallinity.

5.3.1 Reactivity comparison between EELDI and HDI/IPDI

As the starting point, the relative reactivity of EELDI compared to that of HDI and IPDI was assessed. Model reactions between these three diisocyanates and isosorbide comonomer were performed, respectively. Because of the fast reaction of HDI at NCO : OH = 1 : 1, limiting the possibility of sampling to the initial stages of the reaction only, a molar ratio of OH : NCO = 1 : 0.6 was applied. The FT-IR derived total isocyanate conversions are plotted in **Figures 5-2** and **5-3**, by using the peaks of the unreactive CH_2 groups ($3092\text{-}2790\text{cm}^{-1}$) as the internal standard. **Figure 5-2** shows that HDI is slightly more reactive (about a factor of 1.4) than EELDI. This relatively low reactivity of EELDI was due to the steric hindrance on

the α -NCO group.^[31] In **Figure 5-3**, a higher initial reaction rate of EELDI (an approximate factor of 2.9, calculated from the second order kinetic equations) compared to that of IPDI was observed. The relatively low reaction rate of IPDI is due to its bulky molecular structure. Hence, compared to IPDI, a significantly reduced reaction time is expected when using bio-based EELDI to synthesize PU prepolymers. Moving to the second step, the influence of the asymmetric molecular structure of EELDI on the prepolymer synthesis and dispersion stabilization was analyzed.

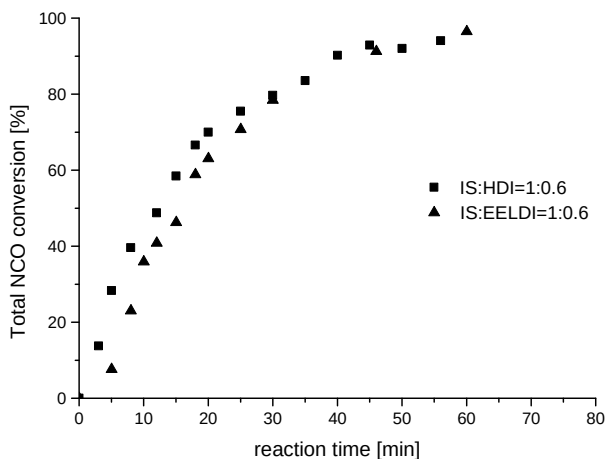


Figure 5-2. The isocyanate conversions of HDI and EELDI during the course of the reactions with IS (OH : NCO = 1 : 0.6). The results were recorded by FT-IR measurements, using the area integration of the isocyanate peak around 2260 cm^{-1} .

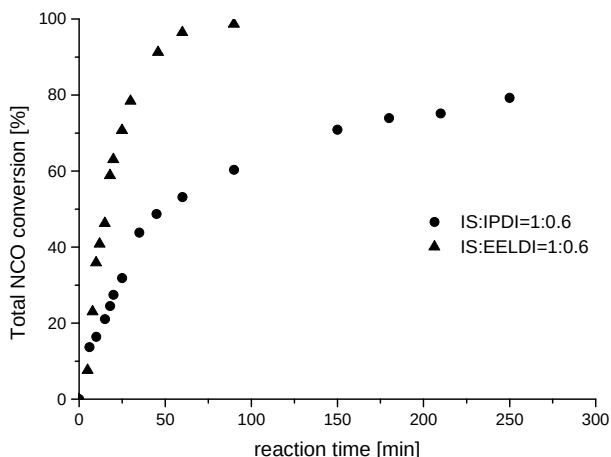


Figure 5-3. The total isocyanate conversions of IPDI and EELDI during the course of their reactions with IS (OH : NCO = 1 : 0.6). The results were recorded by FT-IR, using the area integration of the isocyanate peak around 2260 cm^{-1} .

5.3.2 PUDs prepared from DDI, EELDI, IS and DMPA

The preparation of water-borne PU dispersions by a ketone-assisted route was conducted according to a two-step process. The first step was the synthesis of NCO-terminated PU prepolymers by reacting a slight molar excess of the diisocyanates, DDI and EELDI, with IS and the neutralized DMPA in 2-butanone. In the second step, an aqueous solution of ethylene diamine (EDA) was added to the prepolymer solution for dispersion formation and chain extension. The different prepolymer compositions were prepared by varying the molar ratio of DDI-to-EELDI from 2 : 1, 1 : 1 to 1 : 2 on the one hand. On the other hand, the DMPA weight percentage was decreased at each constant DDI-to-EELDI ratio. In all formulations, the overall isocyanate-to-hydroxyl molar ratio was maintained at NCO : OH = 1.1 : 1. The reaction formulation and the results of the prepolymer synthesis and the subsequent PUD preparation are summarized in **Table 5-1**. All prepolymers were yellowish clear solutions and the experimental results were repeatable. As expected, these prepolymers were well soluble in the solvent 2-butanone without crystallization. The M_n values of the prepolymers are approximately 6.0 kg/mol and the PDI is around 2, a typical value for step-growth polymerization.^[33-34] The relatively low $M_n(\text{prepol})$ value of polymer 1 was probably a result of the less reactive DMPA compared to IS and the possible micro-

phase separation between the DMPA ionic groups and the non-polar polymers. The relatively low reactivity of DMPA is determined by its molecular structure.^[31, 35] On the one hand, the steric effects of the CH_3 group and the carboxylic acid group hinder the hydroxyl groups in their reaction with isocyanates. On the other hand, the electron-withdrawing effect of the COOH group reduces the nucleophilicity of the OH groups. Compared to the prepolymers, the molecular weights of the chain-extended poly(urethane urea)s (PUUs) were approximately twice as high. Compared to the conventional chain-extended PUU dispersions,^[36-38] these M_n values are still rather low. The M_n (PUD) values seem to increase with decreasing DDI-to-EELDI molar ratio. This is attributed to the higher purity of EELDI (95%) compared to that of DDI (92%), facilitating a slightly more effective chain extension.

Table 5-1. Reaction formulation and polymeric characteristics of PU prepolymers and EDA chain-extended poly(urethane urea) dispersions.

Entry	DDI:EELDI:IS:DMPA [molar ratio]	DMPA [wt%]	M_n (prepol) ^a [kg/mol]	M_w (prepol) ^a [kg/mol]	M_n (PUD) ^b [kg/mol]	M_w (PUD) ^b [kg/mol]	Av. particle diameter [nm]	PSD ^c	ζ -Potential [mV]
1	35.3 : 17.6 : 32.2 : 14.9	6.0	4.3	7.4	8.5	20.4	160	0.12	-50
2	35.3 : 17.6 : 35.9 : 11.2	4.5	5.9	10.7	10.7	28.3	102	0.09	-47
3	26.3 : 26.3 : 37.3 : 10.0	4.5	5.6	11.2	11.4	29.8	72	0.17	-47
4	26.3 : 26.3 : 39.7 : 7.8	3.5	6.8	14.2	12.5	36.3	64	0.19	-45
5	26.3 : 26.3 : 41.8 : 5.6	2.5	6.2	13.5	13.1	37.0	79	0.12	-49
6	17.4 : 34.9 : 42.8 : 4.9	2.5	6.2	13.2	15.6	51.1	142	0.11	-48
7	17.4 : 34.9 : 43.8 : 3.9	2.0	6.1	14.1	16.8	45.0	190	0.16	-46

^{a)} The molecular weight of PU prepolymers after the prepolymer synthesis; ^{b)} The molecular weight of PUDs after one hour of chain extension with EDA; ^{c)} PSD: particle size distribution.

5.3.3 PU prepolymers and dispersions characterized by FT-IR spectroscopy

The PU prepolymers and the dispersion-cast PUU films were characterized by using FT-IR spectroscopy. Examples of FT-IR spectra recorded for the PU prepolymer and dry film of polymer 3 are depicted in **Figure 5-4**. The carbonyl region of these two spectra is enlarged in **Figure 5-4B**. These FT-IR spectra are very similar to our previously published results.^[29]

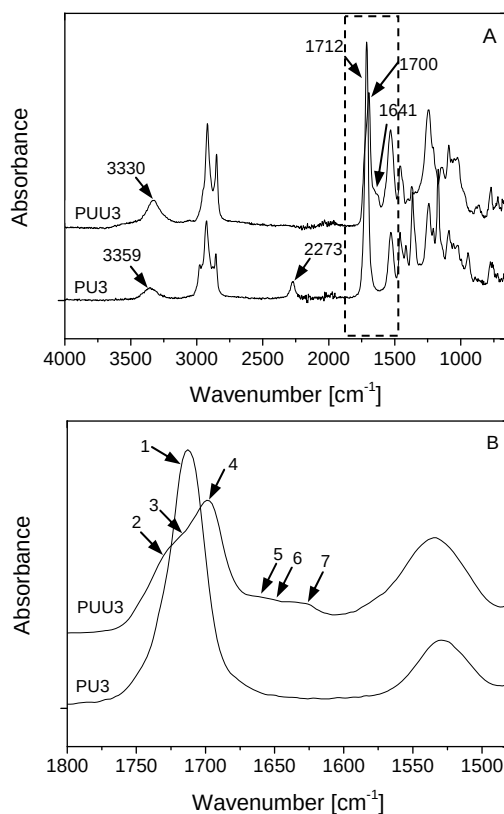


Figure 5-4. FT-IR spectra of polymer 3, A) after prepolymer synthesis (PU3) and EDA chain extension (PUU3); B) the enlarged carbonyl region of A.

In **Figure 5-4A**, after the prepolymer synthesis but before chain extension, the broad peak at 3359 cm^{-1} is attributed to the stretching vibration of urethane N-H (adjacent to amide I). A single peak at 2273 cm^{-1} is attributed to the asymmetrical stretching of the remaining isocyanate groups. The absorption band at 1712 cm^{-1} is attributed to the urethane C=O groups. After EDA chain extension, the N-H stretching vibration at 3355 cm^{-1} becomes narrow and is centered around 3300 cm^{-1} due to the urea formation. The isocyanate peak at 2273 cm^{-1} is now completely absent as a result of NCO-amine or NCO-water reactions. The absorption band at 1700 cm^{-1} is attributed to the H-bonded urethane C=O. Three small shoulders at $1666\text{-}1610\text{ cm}^{-1}$ correspond to the urea C=O stretching. Band assignments of the enlarged carbonyl area in the PU prepolymer and in the PUU are listed in **Table 5-2**. Similar characteristic peaks were reported by Hu et al. and Lou et al. ^[39-43]

Table 5-2. Assignment of FT-IR absorption bands in the carbonyl region (**Figure 5-4B**).

No.	Wavenumber [cm^{-1}]	Assignment
1	1797-1627	Free carbonyl stretching of urethane linkage (PU)
2	1780-1718	Free carbonyl stretching of urethane (PUU)
3	1718-1710	Disordered H-bonded urethane carbonyl (PUU)
4	1710-1674	Ordered H-bonded urethane carbonyl (PUU)
5	1666-1654	Free carbonyl stretching of urea (PUU)
6	1654-1644	Disordered H-bonded urea carbonyl (PUU)
7	1644-1610	Ordered H-bonded urea carbonyl (PUU)

5.3.4 Influence of polymer composition on the particle size of PUU dispersions

The average particle size of the dispersions was evaluated using Zeta-DLS measurements. The average particle diameter of these dispersions ranges from 64 to 190 nm, depending on the monomer feed ratio, the DMPA content and the amount of the hydrophilic IS and EELDI present in the PU backbone. Firstly, the amount of DMPA required to obtain stable dispersions strongly depends on the DDI-to-EELDI ratio. For each constant DDI-to-EELDI ratio, the incorporated amount of DMPA required to achieve stable dispersions was

optimized to a minimum value. Secondly, the average particle size is clearly influenced by the DDI-to-EELDI feed ratio. Larger particles were obtained at both high and low DDI-to-EELDI ratio (DDI : EELDI = 2 : 1 and 1 : 2), at DMPA contents of 4.5-6.0 wt% and 2.0-2.5 wt%, respectively. The smallest average particle size was found at DDI : EELDI = 1 : 1 and a moderate DMPA content (2.5-4.5 wt%). At high DDI-to-EELDI ratios, the larger particles probably result from the large weight percentage of DDI present in the PU. Its high hydrophobicity tends to restrict the interactions between the hydrophobic polymers and water, leading to a reduced extent of ion migration to the particle surface. At reduced DDI contents (dispersions 3-7), this hydrophobic effect might be reduced, indicating a more noticeable influence of the DMPA content on the particle diameter. Thirdly, it is also noticed that at the same DDI-to-EELDI ratio, the average particle size does not always increase with reducing the DMPA content, which is different from the studies carried out by other investigators.^[38, 44-47] For instance, compared to dispersion 1 containing 6.0 wt% of DMPA, the average particle size of dispersion 2 (4.5 wt% of DMPA) is smaller. The reduced particle size of dispersion 2 seems to be influenced by the increased amount of IS in the monomer feed, which potentially introduces additional hydrophilicity into the prepolymer chains and eases the migration of ionic groups to the particle surface.^[7] On the other hand, dispersion 5, containing more IS, has a larger particle diameter than dispersion 4. This is probably caused by a pronounced influence of DMPA at a very low content. Moreover, the average particle size of dispersion 6 is much larger compared to that of dispersion 5, despite the fact that the same amount of DMPA and a significantly reduced amount of DDI were used. Other parameters limiting the effectiveness of the stabilizing agents seem to be involved as well. For instance, the hydrogen bonds formed between the carbonyl (C=O) and the amine (N-H) groups of urethanes and ureas at high EELDI contents (*vide infra*) could significantly reduce the chain mobility, limiting the migration of the ionic DMPA groups to the outer side of the particles to stabilize the dispersions.

5.3.5 Influence of asymmetric functionality of EELDI on dispersions

To evaluate the influence of the asymmetric molecular structure of EELDI on the dispersion process, hexamethylene diisocyanate (HDI) was selected as a reference for comparison. It has six carbon atoms between the isocyanate groups (**Figure 5-1**). The distance between the urethane linkages of HDI is almost similar to that of EELDI, having five carbon atoms between the isocyanate groups (**Figure 5-1**), and hence a more or less comparable urethane-bond density per unit of chain length is expected, certainly with

respect to DDI-based residues. Nevertheless, the ester group of EELDI may induce a somewhat higher polarity as well as more steric hindrance in H-bond formation, due to the presence of the bulky ester group directly next to the urethane linkage. The preparation of HDI-based PU dispersions was performed following the same procedure as for their EELDI-based counterparts. Their reaction formulations and the characteristics of the prepolymers and EDA chain-extended dispersions are summarized in **Table 5-3**.

Table 5-3. Reaction formulation and the polymeric properties of PU prepolymers and EDA chain-extended poly(urethane urea) dispersions.

Entry	DDI:HDI /EELDI	DMPA [wt%]	M_n (prepol) ^a [kg/mol]	M_w (prepol) ^a [kg/mol]	M_n (PUD) ^b [kg/mol]	M_w (PUD) ^b [kg/mol]	Av. particle diameter [nm]	PSD ^c
8	2:1 (HDI)	6.0	5.2 (2.2 ^d)	10.0 (3.5 ^d)	9.5	23.9	105	0.11
1	2:1 (EELDI)	6.0	4.3	7.4	8.5	20.4	160	0.12
9	1:1 (HDI)	4.5	3.3 ^d	8.3 ^d	10.8	35.3	-	-
3	1:1 (EELDI)	4.5	5.6	11.2	11.4	29.8	72	0.17
10	1:2 (HDI)	2.5	2.1 ^d	5.6 ^d	6.7 ^d	12.4 ^d	-	-
6	1:2 (EELDI)	2.5	6.2	13.2	15.6	51.1	142	0.11

^a) The molecular weight of PU prepolymers; ^b) The molecular weight of PU dispersions after one hour of EDA chain extension; ^c) PSD: particle size distribution; ^d) SEC measurements in hexafluoroisopropanol (HFIP) relative to poly(methyl methacrylate) (PMMA) standards (due to limited solubility of semi-crystalline HDI-based PU samples).

The M_n values of the prepolymers containing a DDI-to-HDI molar ratio of 2 : 1 are similar to those of the corresponding EELDI-based PUs. At higher HDI contents, semi-crystalline prepolymers were formed which were insoluble in 2-butanone and THF (for SEC measurements). The occurrence of prepolymer precipitation may result in polyurethanes with a relatively low molecular weight, as observed for dispersion 10. Also, the repeatability of the HDI-based prepolymer synthesis is obviously troublesome due to the observed precipitation. Accordingly, the molecular weight characterization of the HDI-

based materials at lower DDI-to-HDI ratios could only be performed using hexafluoroisopropanol (HFIP) as the solvent and PMMA as the calibration standard. The correlation between these two SEC methods was investigated using polymer 8, which was soluble in both solvents. For polymer 8, SEC in THF indicated an M_n of 5.2 kg/mol, whereas SEC in HFIP yielded a value of 2.2 kg/mol (**Table 5-3**). It is therefore considered that polymers 9 and 10, which both show M_n values similar to that of polymer 8 in HFIP-SEC, have molar masses in the same order of magnitude as polymers 3 and 6, respectively.

The dispersion 8, prepared using DDI : HDI = 2 : 1, was stable. Its particle diameter was around 105 nm, close to that of the corresponding EELDI-based dispersion (160 nm). However, the dispersion prepared using DDI : HDI = 1 : 1 was only stable for one day. No dispersion was formed in the case of DDI : HDI = 1 : 2, contrary to the observations done for EELDI-based dispersions. HDI-based dispersions potentially contain a high fraction of semi-crystalline prepolymer material as a result of the linear structure of HDI. The significant amount of HDI used in polymers 9 and 10 is obviously unfavorable for the solubility of prepolymers and the preparation of stable dispersions, especially for relatively low DMPA contents of the PUDs. Therefore, the asymmetric structure of EELDI compares favorably to HDI in terms of preparing soluble PU prepolymers and stable dispersions. In the following section, the potential hydrolysis of the pendant ester group of EELDI, which might play a role in stabilizing the dispersions, is investigated.

5.3.6 Hydrolysis investigation of pendant ester groups in EELDI

When decreasing the DDI content in the prepolymer composition, the EELDI content is automatically increased to maintain the correct stoichiometry between hydroxyl and isocyanate functional groups. In addition to its asymmetric functionality, other potential influences of EELDI on the average particle size and the colloidal stability must be assessed. It is known that ester groups can be hydrolyzed in a basic environment. ^[48-50] These as-prepared EDA chain-extended dispersions typically have a pH between 9 and 10. Hydrolysis of pendant EELDI ester groups may thus occur upon the addition of water and EDA, resulting in free carboxylic acid groups (mostly carboxylate anions in solution, at this pH) along the PU main chain, which might enhance the stability of the PUDs. Consequently, the direct detection of the potentially formed carboxylic acid groups is less feasible. Therefore, a two-step model reaction was carried out and monitored with ^1H NMR and FT-IR spectroscopy. In the first step, a model compound was prepared by reacting EELDI with 1-butanol in 2-butanone at 40 °C until all isocyanate groups were converted. The completion of this reaction was confirmed by ^1H NMR measurements. The

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^1H NMR spectra of EELDI, 1-butanol and the resulting model compound after 160 minutes of reaction are depicted in **Figure 5-5**. In the second step, a solution of EDA in water (the same weight ratio as used for making dispersions) was added to this model compound at 50 °C and the hydrolysis (**Scheme 5-1**) was allowed to proceed for one hour (the same duration as the chain extension process). Samples were taken for FT-IR measurements after 60 minutes of reaction.

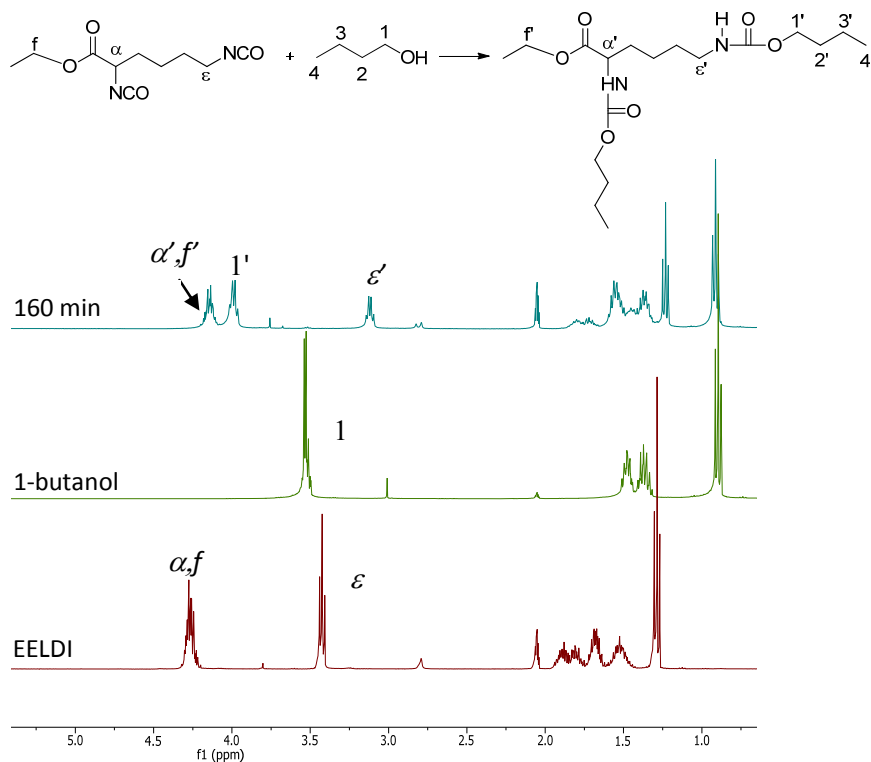
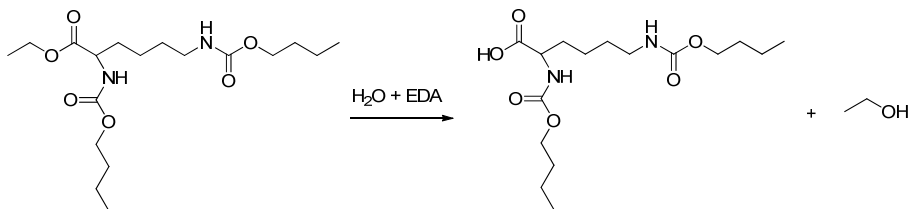


Figure 5-5. The ^1H NMR spectra of EELDI, 1-butanol and EELDI in the model reaction with 1-butanol at 160 minutes of reaction. Acetone- d_6 is used as the solvent.



Scheme 5-1. The possible hydrolysis of EELDI ester groups of the model compound, potentially catalyzed by EDA.

The FT-IR spectra of the model compound before and after the hydrolysis (acidic work-up) are shown in **Figure 5-6**. In the carbonyl region, taking the sample at 60 minutes of reaction as an example, a new peak appearing at 1665 cm^{-1} is attributed to the formation of the carboxylic acid groups.^[51] A broad peak appearing at 3353 cm^{-1} , belonging to the un-hydrolyzed model compound, is attributed to the stretching vibration of urethane N-H. After one hour of reaction, the appearance of the broader peak around $3700\text{--}3100\text{ cm}^{-1}$ area is thought to be the mixture of the formed ethanol and the generated carboxylic acid groups, as well as residual water present in the sample. Hence, the model reaction clearly demonstrates that the EELDI ester groups can be (partially) hydrolyzed under the conditions applied to make the PUDs.

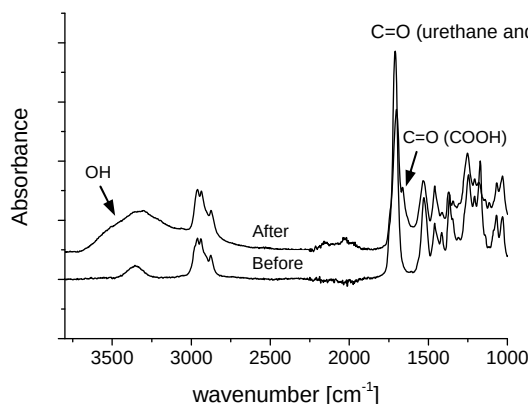


Figure 5-6. The FT-IR spectra before and after one hour of hydrolysis of the 1-butanol end-capped EELDI-based model compound.

In spite of the indirect evidence obtained for the EELDI ester hydrolysis, at DMPA contents lower than 2.0 wt% it proved impossible to prepare stable dispersions. This is probably due to the fact that a minimum amount of neutralized DMPA is necessary to initially assist the dispersion formation. The hydrolysis of EELDI ester groups and the neutralization of the newly formed carboxylic acid groups require time. To the best of our knowledge, DMPA weight percentages of 2.0-2.5 wt% (see **Table 5-1**) are the lowest DMPA concentrations ever used to obtain stable PUDs with average particle diameters lower than 200 nm. ^[38, 52-53]

5.3.7 The electrostatic stability of PU dispersions

ζ -potential measurements were performed to investigate the electrostatic stability of the as-prepared dispersions (1-7). The ζ -potential values of all dispersions are in the range of -45 to -50 mV, as shown in **Table 5-1**. These values indicate a strong electrostatic stabilization of dispersions at their initial pH values (between 9 and 10). The applied DMPA contents, ranging from 2.0 wt% to 6.0 wt% depending on the DDI-to-EELDI ratio, were sufficient to stabilize the particles by electrostatic interactions. Moreover, to investigate the electrostatic stability of ionic dispersions exposed to acidic and basic environments, the pH values of the dispersions were varied from about 4 to 12 by adding 5.0×10^{-3} M HCl solution and 5.0×10^{-3} M NaOH solution, separately. Taking dispersions 3, 5 and 6 as examples, the results obtained for average particle size and ζ -potential measurements are depicted in **Figure 5-7**. In general, these three dispersions exhibit a similar behavior. Their average particle size increased with decreasing pH values from 12 to nearly 4. This is due to the disturbed electrical bilayer by the addition of an acid. Concurrently, the absolute value of ζ -potential decreased step-wise. At pH values lower than 5, these absolute ζ -potential values of all dispersions are around or lower than 30 mV, where dispersions start to coagulate. At pH values higher than the initial pH of the dispersions, the electrostatic stabilization is strengthened, indicated as the slightly increased absolute ζ -potential values and the nearly constant average particle size.

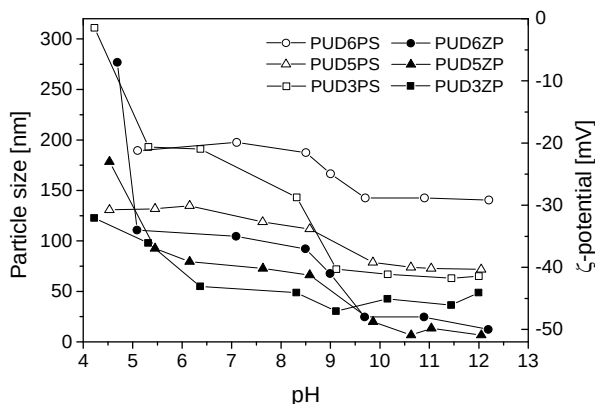


Figure 5-7. The ζ -potential (solid symbols) and average particle size (hollow symbols) curves of dispersions 3, 5 and 6 as a function of pH.

5.3.8 Thermal properties determined by DSC and TGA measurements

Thermal transitions and thermal stability of dispersion-cast PUU films were investigated using differential scanning calorimetry (DSC) measurements and thermogravimetric analysis (TGA), respectively. **Figure 5-8** depicts the DSC traces of these dispersion-cast films. The corresponding transition temperatures are listed in **Table 5-4**. Several thermal transitions comprising a 1st and a 2nd glass transition (T_{g1} and T_{g2}) can be observed in **Figure 5-8**. Corresponding to the films F1- F7, the first T_g values increased from 28 to 60 °C. This is a result of the increased incorporation of the relatively rigid EELDI (compared to DDI) and IS in the polymer composition. As shown in the derivative DSC curve (**Figure 5-8B**), the additional glass transitions were only clearly observed in a few DSC curves above 70 °C, for films F1 and F2. After that, these glass transitions merged into an endothermic peak (also shown in F6), where the disruption of some ordered domains took place upon heating. These ordered domains were possibly formed between the H-bonds as a result of aging. The appearance of the additional glass transitions implies a micro-phase separated morphology. In addition, the mentioned endothermic region falls into the temperature range of urethane and urea H-bonding dissociation.^[39-43, 54-57] Hence, H-bonding may be responsible for this kind of phase morphology. Contrary to films F1 and F2, no or less obvious second T_g was observed in films F3-F5 and F6-F7. The existence of one T_g indicates an improved phase mixing behavior. Earlier studies^[13, 24, 42, 54, 58-59] also described that the phase morphology of segmented poly(urethane urea)s (SPUUs) was influenced by the H-

bonding behavior, which was closely correlated to the polymer composition.^[13, 58] Therefore, the morphology differences between these films were considered to result from the differences in polymer composition. Provided that films F1 and F2 contain a large molar ratio of the large, non-polar DDI unit and a small fraction of EELDI, the number of the formed urethane and urea linkages is limited. Therefore, a sparse distribution of the polar rigid domains, resulting from H-bonding, over the soft matrix induces phase separation. With the increase of the EELDI content, subsequently, the amount of urethane and urea linkages increases. This potentially leads to an overall increase in H-bonded rigid segments. Phase mixing is hence promoted.

Table 5-4. Thermal properties and transition temperatures derived from TGA and DSC curves.

Film*	TGA		DSC	
	$T_{d, 5\%}^a$	$T_{d, 50\%}^b$	T_{g1}^c	T_{g2}^c
	[°C]	[°C]	[°C]	[°C]
F1	257	381	28	72
F2	262	385	35	83
F3	247	362	40	81
F4	262	378	47	-
F5	276	375	47	100
F6	246	326	56	-
F7	259	365	60	-

* The film numbers refer to the PUDs in **Table 5-1**. ^{a)} $T_{d, 5\%}$ is the 5% weight loss temperature measured by TGA (10 °C min⁻¹); ^{b)} $T_{d, 50\%}$ is the 50% weight loss temperature measured by TGA; ^{c)} The 1st and the 2nd T_g determined from the second DSC heating run (20 °C min⁻¹).

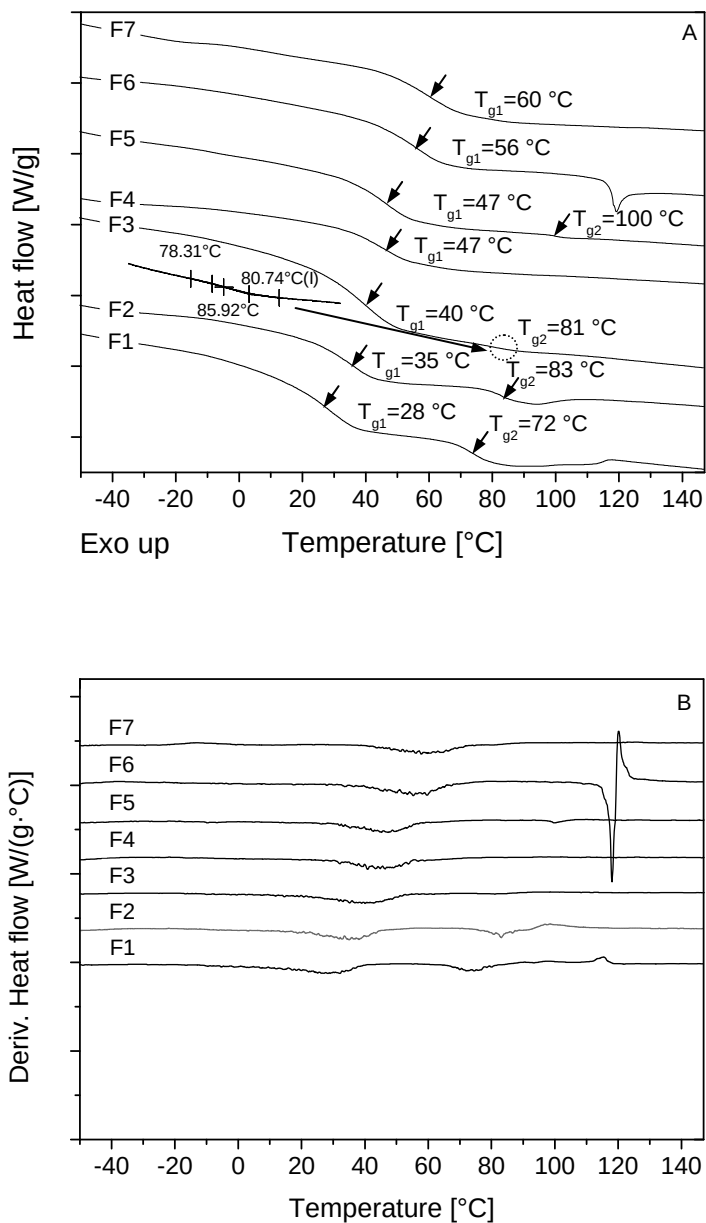


Figure 5-8. The second heating (A) DSC curves and (B) temperature-derivative DSC curves of dry PUU films, recorded from -80 - 150 °C at a heating rate of 20 °C/min.

The TGA traces of these films are depicted in **Figure 5-9**. Similarly to the PUU films containing DDI, IS and DMPA, ^[29] these four-component films usually undergo a three-stage thermal degradation, although films F6 and F7 exhibited a less obvious degradation in the second stage. The first stage is interpreted to be the urethane decomposition step in the temperature range of 250-360 °C, while the fatty acid chain scission takes place in the second stage between 340-445 °C. ^[60] In this temperature range, the decomposition peaks of films F1-F7 appear to be less intense. This is a result of the decreased DDI content in the prepolymer formulation. The last stage of the degradation process occurs around a temperature of 450-480 °C and is attributed to the gasification of any other components. ^[23] Moreover, upon 5 wt% and 50 wt% mass loss (**Table 5-4**), films with a relatively high IS content but the same DDI-to-EELDI ratio tend to be more thermally stable. This can possibly be attributed to the increased weight percentage of diol in the polymer composition by replacing DMPA with IS. ^[61] The amount of thermally labile urethanes is reduced. At the same DMPA content (F2 and F3 or F5 and F6), the thermal stability increases with increasing DDI content. This is also due to the reduced urethane content ^[22, 62] by incorporating more of the large DDI residues.

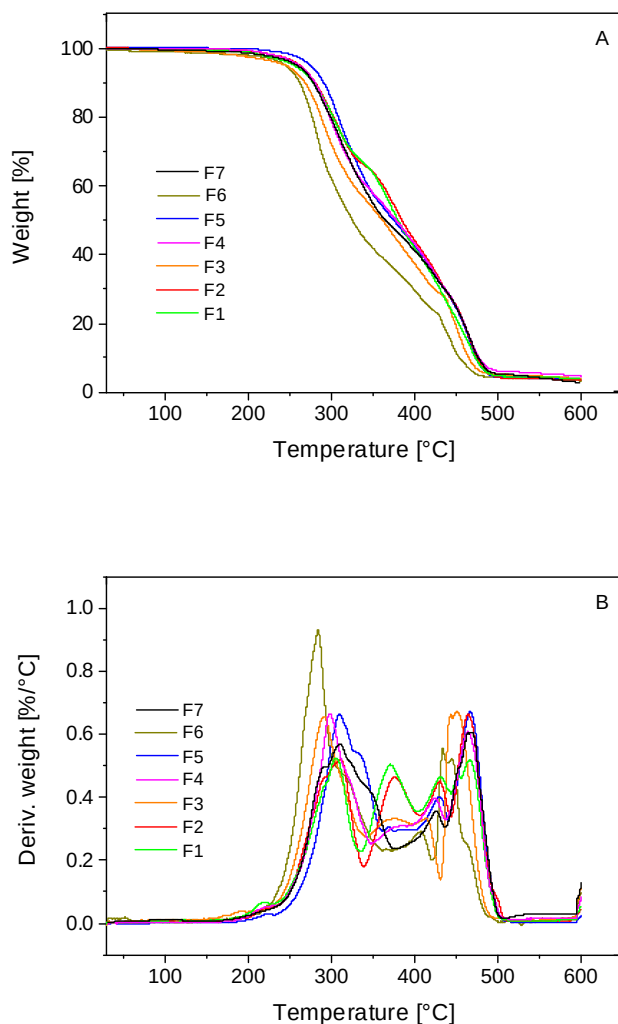


Figure 5-9. The TGA curves (A) and the derivative plots (B) of dry PUU films prepared from EDA chain-extended dispersions containing different DDI/EELDI ratio and IS contents, recorded from 30-600 °C at 10 °C/min under N₂ atmosphere.

5.4 Conclusions

This work describes the preparation of nearly fully (97 wt%) renewable aqueous poly(urethane urea) dispersions from DDI, IS, DMPA and EELDI. EELDI exhibited a similar

reactivity as HDI and a significantly higher reactivity than IPDI. Its asymmetric structure was shown to contribute to its suitability for the preparation of PU dispersions. The replacement of DDI by EELDI and the incorporation of IS into the prepolymer composition have reduced the requirement for the DMPA (petrochemical-based) content from 6.0 to 2.0 wt% to render stable PUDs. DDI and IS have shown a stronger impact on the average particle diameter than EELDI. In addition, the hydrolysis of the EELDI ester groups seemed to facilitate the dispersion stabilization. By increasingly replacing the flexible (DDI) with the rigid (EELDI), as well as by increasing the IS contents, the T_g values of these dispersion-cast films were significantly enhanced from 28 to 60 °C (1st T_g) and to above 70 °C (2nd T_g). The thermal stability of these films increased with increasing DDI and IS contents, as a result of the reduced amount of thermally labile urethanes and ureas. The significantly enhanced T_g certainly widens the potential scope of these renewable PUU polymers in coating applications.

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6

Property Profile of Poly(urethane urea) Dispersions Containing Dimer fatty acid-, Sugar- and Amino acid-based Building Blocks

Abstract

The inherently flexible nature of fatty acids has shown to restrict the rigidity and thermo-mechanical properties of the corresponding polymers based thereon. Extensive effort is being invested in improving the mechanical properties of fatty acid-derived polyurethane (PU) materials. To achieve this, the understanding of the polymer composition - properties relationship is of great importance. In this work, an in-depth study concerning the properties of waterborne poly(urethane urea) coatings and free-standing films containing dimer fatty acid-based diisocyanate (DDI), ethyl ester L-lysine diisocyanate (EELDI), 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) and dimethylolpropionic acid (DMPA) residues has been carried out. The investigation focuses on the thermal and mechanical properties of the polyurethane dispersion-cast films as well as on the morphology in correlation with the polymer composition. Significant dependencies of these properties and morphology on the polymer composition are observed. These dispersion-cast films were thermally stable up to 245 °C (5% weight loss). An enhanced thermal stability was observed for films containing a relatively high DDI content, which results in reduced urethane and urea contents. By partially replacing the flexible DDI with the rigid EELDI as well as by increasing the isosorbide contents in the monomer feed, the T_g as measured by DSC was significantly enhanced from 18 to 58 °C (1st T_g) and to above 70 °C (2nd T_g). As evidenced from the DSC, AFM and FT-IR measurements, the H-bonding-induced micro-phase separation was influenced by the polymer composition. The observed improved phase mixing at relatively high EELDI-to-DDI ratio was related to the increased EELDI content and the corresponding urethane/urea bonds. The viscoelastic behavior of these dispersion-cast films showed a strong dependence on the ratio of the flexible DDI to the rigid EELDI and were less dependent on the IS and DMPA contents. The coatings applied onto aluminum panels exhibited good acetone resistance and good adhesion to aluminum, but moderate impact resistance at high IS and EELDI contents.

6.1 Introduction

Water-borne polyurethane dispersions (PUD) have emerged as important alternatives to their solvent-based counterparts for coating applications due to their reduced volatile organic compound (VOC) contents and the related environmental benefits.^[1-7] Their excellent properties such as solvent resistance, impact resistance, film-forming ability at room temperature and adhesion to many substrates such as wood, textile and metal make them suitable for applications such as foams, coatings and adhesives.^[4, 8-11]

Recently, stimulated by the high, unstable crude oil price and the awareness of the importance of the sustainable development of polymer materials, research in the field of biomass-based polyurethanes (PU) and aqueous PU dispersions has flourished.^[12-16] However, restricted by the inherently flexible nature of fatty acid-derived PU building blocks, the corresponding PU materials often exhibit low T_g , low strength and low modulus. By means of cross-linking^[17] and designing segmented polymer structures^[18-21], the rigidity of the PU materials containing fatty acid derivatives has been significantly improved.

Compared to the chemically cross-linked polymer structure, segmented poly(urethane urea)s (SPUU) have advantageous flexibility to tailor the PU polymers for specific applications.^[22-27] The combination of the flexible and rigid chain segments, the type and structure of the building blocks and the presence or absence of physical cross-links (i.e. H-bonds) have shown to influence the polymer properties.^[23-29] In aqueous PU dispersions, in addition to the amount of internal stabilizing agent, the segmented polymeric structure has also shown to influence the average particle size and the dispersion stability of the PU dispersions.^[26-28] Lee et al.^[27] and coworkers observed a reduction of the average particle size of dispersions by increasing the molecular weight of the soft polyol segments, due to the increased chain flexibility (see Chapter 4). Therefore, to understand the correlation between the polymer composition, the structure and type of PU building blocks on the one hand and the thermal and mechanical properties of SPUUs on the other, is of great importance.

In our previous study,^[30] the combination of the flexible dimer fatty acid-based diisocyanate (DDI) with the rigid isosorbide (1,4:3,6-dianhydro-D-glucitol, IS) and ethyl ester L-lysine diisocyanate (EELDI), using the non-renewable dimethylolpropionic acid (DMPA) as the internal stabilizing agent and ethylene diamine (EDA) as the chain extender, has generated dispersion-cast films with tunable glass transition temperatures (T_g) ranging from 28-60 °C. In addition, both IS and EELDI seem to facilitate the dispersion formation due to their relatively high hydrophilicity and the possible hydrolysis of the pendant ester

group of EELDI. So far, however, the mechanical properties of dispersion-cast films and their correlation with the polymer composition and the polymer morphology have not been investigated.

This study is aimed at preparing polyurethane dispersions using DDI, DMPA, IS and EELDI as the main PU building blocks, using water (instead of EDA) as the chain extender and TEA as the neutralization agent for DMPA and as the catalyst for water chain extension. The investigation focused on evaluation of the thermal and mechanical properties of dispersion-cast films as well as the polymer architecture in correlation with the polymer composition. Other coating properties such as the acetone resistance, impact resistance and the adhesion to aluminum were investigated as well.

6.2 Experimental Section

Materials. Fatty acid-based diisocyanate (DDI®1410, 92% pure based on the NCO titration value) was kindly supplied by Cognis. Isosorbide (IS, polymer grade, trade name Polysorb® P, 98.5%) was received as a gift from Roquette Frères. Ethyl ester lysine diisocyanate (EELDI, 95%) was purchased from Infine Chemicals Co., Limited, China. Dry 2-butanone was bought from Acros (> 99.5%, AcroSeal®). Dimethylolpropionic acid (DMPA, 98%), dibutyltin dilaurate (DBTDL, 95%) and triethylamine (TEA, ≥ 99.5%) were purchased from Aldrich. Both diisocyanates and isosorbide were kept under inert gas and in a refrigerator at 4 °C. Before use, DMPA was dried at 60 °C for 48 hours in a vacuum oven. Other chemicals were used as received.

NCO-end capped PU prepolymer synthesis and dispersion preparation. A typical procedure to prepare PU dispersions includes the NCO-terminated prepolymer synthesis in a ketone solvent and the subsequent water dispersion process, as described in our previous work (Chapters 2 and 3). The PU prepolymer synthesis was executed as follows: isosorbide (IS, 1.50 g, 10.3 mmol) and dimethylolpropionic acid (DMPA, 0.64 g, 4.8 mmol) were weighed into a 250 mL round bottom glass flange reactor. Triethylamine (TEA, 0.48 g, 4.8 mmol, for 100% neutralization of DMPA) was injected into the diol mixture to obtain a clear diol solution. Subsequently, dibutyltin dilaurate (DBTDL, concentration: 0.56 wt% relative to the total solution) was injected into the diol mixture. While being stirred mechanically, the mixture was heated to 70 °C using a heating mantle. Approximately half of the total solvent 2-butanone (7 mL) was used to dilute the diol mixture. EELDI (1.34 g, 5.6 mmol) and DDI (7.17 g, 11.3 mmol) were then added to this diol solution at 70 °C. The remaining 2-butanone was then instantly added to dilute the total reaction mixture to reach a solids content of 50 wt%. Before as well as during the reaction, the reaction setup was continuously flushed with inert gas (N₂). The reaction was carried out for 4-6 hours, counted from the moment that all the DDI and EELDI had been added. Subsequently, the NCO content of the resulting PU prepolymer was determined by titration. After the PU prepolymer synthesis, the reaction temperature was

decreased to 50 °C and additional solvent was added to compensate for losses and to adjust the prepolymer concentration to around 50 wt%. A mixture of TEA (0.22 g) and de-ionized water (~ 40 mL) was injected in a controlled way into the prepolymer mixture and the dispersing process was effectuated by vigorous stirring. Subsequently, the water chain extension reaction was allowed to proceed for one hour. Thereafter, the aqueous polymer dispersion was discharged from the reactor. Residual 2-butanone was distilled off at 40 °C at a reduced pressure, reaching the theoretical solids content of 20 wt%.

Preparation of coatings and free-standing films. Aqueous PU dispersions were applied onto aluminum panels using a doctor blade, which allows a wet film thickness up to 250 µm. The films were left to dry at room temperature until a constant weight was reached. The resulting poly(urethane urea) (PUU) films had thicknesses between 30 and 40 µm and were used for an acetone resistance test, an adhesion test and an impact resistance test. Free-standing films were prepared by casting the dispersions into aluminum pans and subsequent drying in an oven at 60 °C for at least 48 hours, until a constant weight was reached. After drying, the films were peeled off from the aluminum pans for thermal (TGA and DSC) and mechanical (DMA) measurements.

Characterization of PU prepolymers and PU dispersions

Size exclusion chromatography (SEC) was used to determine the molecular weight distributions of the prepolymers and the PU dispersions. A Waters Alliance set-up equipped with a Waters 2695 separation module, a Waters 2414 differential refractive index detector (operating at 40 °C) and a Waters 2487 dual absorbance detector were used with tetrahydrofuran (THF), containing 1 vol.% acetic acid, as eluent. The injection volume was 50 µL. PSS (2× SDV, guard-linearXL, 5 m, 8×300 mm, 40 °C) columns were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using poly(styrene) (PS) standards with molecular weights ranging from 500 g/mol to 5,000 kg/mol. Data acquisition and processing were performed using Empower software.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Bio-Rad Excalibur FTS3000MX infrared spectrometer (fifty scans per spectrum, spectral resolution of 4 cm⁻¹) with an ATR diamond unit (Golden Gate). The measurement was performed by applying the polyurethane or the poly(urethane urea) onto the ATR diamond. The spectra were recorded between 4000 and 650 cm⁻¹. The Varian Resolution Pro software was used for the analysis of all spectra.

Potentiometric titrations were performed using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The isocyanate functional groups were converted into urea groups through the reaction with a known molar excess of dibutylamine (DBA). The unreacted DBA residue was titrated with a normalized 1 N HCl isopropanol solution. Blank measurements were carried out using the same amount of dibutylamine. The NCO content was defined according to the following equation:

$$NCO\% = \frac{(V_{blank} - V_{sample}) \times C_{HCl} \times 4.2}{M_{prepolymer}} \%$$

where V_{blank} is the volume of HCl solution needed for the blank [mL] (average of two measurements), V_{sample} the volume of HCl solution needed for sample [mL], C_{HCl} the HCl concentration in 2-propanol [mol/L] and $M_{prepolymer}$ is the PU prepolymer weight [g]. Titration measurements were performed in duplo.

The PU prepolymer weight was obtained by the difference in weight before and after solvent evaporation. About 0.5 g prepolymer solution was placed in a glass vial and dried at 60 °C for at least 24 hours *in vacuo*, until a constant weight was reached.

Dynamic Light Scattering (DLS) and ζ -potential measurements were performed to determine the characteristics of the aqueous dispersions on a Malvern ZetaSizer Nano ZS at 20 °C, (polyurethane refractive index: 1.59). The average particle size and the particle size distribution of dispersions containing ~0.1 wt% solids were determined according to ISO 13321 (1996). The pH dependence measurements of the average particle size and dispersion stability (ζ -potential) were performed by adding a 5.0×10^{-3} M aqueous HCl solution to the dispersion using a Malvern ZetaSizer MPT-2 Autotitrator, starting at the pH of the as prepared dispersion. The pH value was reduced in steps of ~ 1 and the resulting mixture was left for 1 min at this pH prior to the next ζ -potential and particle size determination, until a pH value of 3 was reached. The base titration was performed by adding a 5.0×10^{-3} M aqueous NaOH solution to the dispersion, increasing the pH in steps of ~ 1, until a pH of 12 was reached. The ζ -potential was calculated from the electrophoretic mobility (μ) using the Smoluchowski relationship, $\zeta = \eta\mu/\epsilon$ where " $\kappa a \gg 1$ " (where η is the solution viscosity, ϵ is the dielectric constant of the medium, and κ and a are the Debye-Hückel parameter and the particle radius, respectively). Data acquisitions were performed using the ZetaSizer Nano software.

Characterization of free-standing films

Thermogravimetric analyses (TGA) were performed on a TGA Q500 apparatus from TA Instruments under a N_2 flow of 60 mL/min. Samples were heated from 30 to 600 °C with a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC Q100 calorimeter. Samples were heated from -80 to 150 °C at a heating rate of 20 °C/min followed by an isothermal step for 5 min. A cooling cycle to -80 °C at a rate of 20 °C/min was performed prior to a second heating run to 150 °C at the aforementioned heating rate. The T_g was determined from the second heating run. The TA Universal Analysis 2000 software was used for data acquisition.

Transmission FT-IR spectroscopy applied for the H-bonding detection (**Figures 6-5 and 6-6**) of PUU films was performed with a Varian 670-IR spectrometer equipped with a FT-IR 610 microscope. The spectra were recorded in transmission mode with a zinc selenide (ZnSe) disk and heated from 30 to 160 °C. A Linkam THMS600 hotstage with the controller was used to set temperatures at 10 °C

increments per heating step. The Varian Resolutions Pro software was used for the analysis of all spectra.

Dynamic Mechanical Analysis (DMA) was carried out using a TA Instruments Q800 Dynamic Analyzer in film tension mode to determine the storage modulus (E') and the loss modulus (E''). Free-standing films were cut into a rectangular shape (approximately 13 x 5.3 x 0.2 mm) for DMA measurements. The measurements were performed at a preload of 0.01 N and at a frequency of 1 Hz, with a temperature ramp of 2 °C/min, starting from zero degree Celsius (to determine the dynamic T_g) and up to 120 °C. Data analysis was done with TA Universal Analysis 2000 software.

Atomic Force Microscopy (AFM) was used to investigate the surface structure of the films, focusing on topography as well as on phase. The measurements were performed at room temperature (~20 °C) and at elevated temperature (65±3 °C) on an NT-MDT NTegra Aura, in semi-contact mode, using NSG11 cantilevers (NT-MDT) with a typical spring constant of 5.5 N/m and a typical resonance frequency of 150 KHz. The sample scan size is 2 × 2 μm.

Characterization of coatings

The thicknesses of the obtained coatings were measured using an electronic thickness gauge (TQC LD0400 by Thermimport Quality Control). The performance of coatings formulated on aluminum panels at 20 °C was evaluated using the acetone resistance test, a rapid deformation test and an adhesion test. In the acetone resistance test, the samples were rubbed with a cloth drenched in acetone. If no damage was visible after more than 150 double rubs, the coating was qualified as having good acetone resistance. The rapid deformation test was evaluated according to the ASTM D 2794 method. The adhesive property of coatings was evaluated according to the ISO 2409:2007 standard (cross-hatch adhesion test). A 6-blade cutting device K1542 with 1 mm spacing (Elecometer SA, Belgium) and an adhesive tape (Scotch, 3M) were used. Coatings formulated on aluminum substrates were examined at 20 °C. The detachment of the coating was analyzed according to a classification from 0 (intact coating) to 5 (> 65% damage of coating). The values obtained were the average of three replicates.

6.3 Results and Discussion

6.3.1 PUDs prepared from DDI, EELDI, IS and DMPA

The preparation of waterborne PU dispersions by a ketone-assisted route was conducted according to a two-step process, i.e. the synthesis of NCO-terminated PU prepolymers in solution, followed by their dispersion and chain extension in and with water, after which the ketone solvent was removed *in vacuo*. The prepolymer composition was varied by separately decreasing the molar ratio of DDI-to-EELDI from 2 : 1, via 1 : 1 to 1 : 2 and the

DMPA weight percentage (relative to the prepolymer weight) from 6.0 to 2.5 wt%. DMPA was 100% neutralized with TEA prior to the reaction. The overall NCO : OH molar ratio in all reaction formulations was kept constant at 1.1 : 1. Additional TEA was used in the dispersion step to catalyze the water chain extension process. The reaction formulations and the results of the prepolymer syntheses and PUD preparation are summarized in **Table 6-1**.

6.3.2 Molecular weight characterization

The M_n values of the prepolymers were approximately 5.0 kg/mol and the PDI values were around 2, a typical value for step-growth polymerizations.^[31-32] After one hour of chain extension with water, the molecular weights of the chain-extended PUUs ($M_{n(PUD)}$, see **Table 6-1**) in the dispersions had increased. Similarly to our previous observations,^[30] the average $M_{n(PUD)}$ seemed to increase with decreasing DDI-to-LDI molar ratio. This was probably caused by the higher purity of EELDI (95%) compared to that of DDI (92%), which most probably contains a non-negligible amount of mono-functional isocyanate resulting in unreactive chain ends. More free isocyanate end-groups were therefore present in the EELDI-rich prepolymers, allowing for an improved chain extension reaction. Compared to the results obtained in our previous work,^[33] where the molecular weight of chain-extended PUD polymers, containing only DDI, IS and DMPA as the urethane backbone, showed a remarkable improvement by the addition of extra TEA, this current study did not show the same trend. This can be understood from the potential hydrolysis of the ester groups present in EELDI upon the addition of TEA and water.^[34-36] The newly created carboxylic acid groups from EELDI ester groups would partially consume the additional TEA (molar ratio EELDI(ester) : TEA(additional) = 2.56) by neutralization and therefore limit its overall catalytic effect on the isocyanate-hydroxyl reaction.

Table 6-1. Reaction formulations and characteristics of PU prepolymers and water chain-extended poly(urethane urea) dispersions.

Entry	DDI:EELDI:IS:DMPA	DMPA [wt%]	M_n (prepol) ^a [kg/mol]	M_w (prepol) ^a [kg/mol]	M_n (PUD) ^b [kg/mol]	M_w (PUD) ^b [kg/mol]	Av. particle diameter [nm]	PSD ^d	ζ -Potential [mV]
1	35.3 : 17.6 : 32.2 : 14.9	6.0	4.6	8.3	11.0	32.0	164	0.18	-54
2	35.3 : 17.6 : 35.9 : 11.2	4.5	5.0	9.2	9.1	26.3	87	0.10	-53
3	26.3 : 26.3 : 37.3 : 10	4.5	4.4	7.8	10.4	27.3	95	0.12	-50
4	26.3 : 26.3 : 39.7 : 7.8	3.5	6.1	13.6	11.4	39.7	79	0.20	-47
5	17.3 : 34.7 : 40.7 : 7.3	3.5	5.7	12.5	17.3	50.9	63	0.21	-42
6	17.4 : 34.9 : 41.6 : 6.1	3.0	5.6	12.8	18.3	54.9	85	0.12	-44
7	17.4 : 34.9 : 42.8 : 4.9	2.5	6.3	16.0	28.9 ^c	94.7 ^c	288	0.32	-

^{a)} The molecular weight of PU prepolymers after the prepolymer synthesis; ^{b)} The molecular weight of PUDs after one hour of chain extension with water; ^{c)} These values might not be fully representative results, due to the inhomogeneity of this particular sample; ^{d)} PSD: particle size distribution.

6.3.3 PU prepolymers and dispersions characterized by FT-IR spectroscopy

The PU prepolymers and the dry poly(urethane urea) (PUU) films of chain-extended PUDs were characterized using FT-IR spectroscopy. Examples of FT-IR spectra of the synthesized PU prepolymers and PUU dry films corresponding to PUD3 (**Table 6-1**) are depicted in **Figure 6-1**.

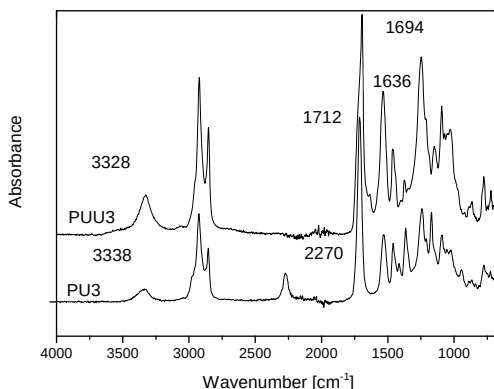


Figure 6-1. FT-IR spectra of polymer 3 after prepolymer synthesis (PU3) and subsequent water chain extension (PUU3).

After the prepolymer synthesis (PU3), the broad signal at 3338 cm⁻¹ is attributed to the stretching vibration of the urethane N-H moiety. The peak at 2270 cm⁻¹ is attributed to the remaining isocyanate end-groups. The absorption band at 1712 cm⁻¹ corresponds to the urethane C=O (amide I) groups. Upon chain extension with water (PUU3), the N-H stretching vibration at 3338 cm⁻¹ becomes more narrow and is centered around 3328 cm⁻¹ as a result of the formation of urea groups. The isocyanate groups have reacted with the amine groups being formed by the reaction of water with NCO (followed by the elimination of CO₂), leading to the disappearance of the signal at 2270 cm⁻¹. The band at 1694 cm⁻¹ is attributed to the H-bonded urethane C=O and a small shoulder at 1636 cm⁻¹ corresponds to the urea C=O stretching.

6.3.4 Influence of the polymer composition on the particle size of PUU dispersions

As listed in **Table 6-1**, the average particle diameters of the obtained dispersions range from 63 to 288 nm. A reduction of the DMPA content would typically result in larger particles.^[37-41] However, the variation in the average particle size is not directly correlated to the DMPA content alone. As explained in our previous study,^[42] the average particle size is determined by the combined effects of DMPA, IS and EELDI contents. Both the hydrophilicity of EELDI and IS as well as the potential hydrolysis of the pendant ester groups present in EELDI may lead to a reduction of the average particle size. The influence of EELDI on the particle size can be noticed when comparing dispersions 4 and 5. At DMPA contents lower than 3.5 wt%, the dispersion stability and the particle size seem to be rather sensitive to the DMPA content, as the average particle size increases from 63 (dispersion 5) to 288 (dispersion 7) nm when the DMPA content is reduced from 3.5 to 2.5 wt%. Additional TEA has no apparent influence on the particle size. As mentioned previously, the potential hydrolysis of the ester groups of EELDI would reduce the concentration of TEA, as the base would be partially consumed by neutralization of the formed carboxylic acid groups along the PU chain. Except for dispersion 7, all these dispersions have a storage stability of at least three months.

6.3.5 The electrostatic stability of PU dispersions

ζ -potential measurements were performed to determine the electrostatic stability of the PU dispersions. The as-prepared dispersions have initial pH values between 9 and 10. Except for dispersion 7, all dispersions have ζ -potential values ranging from -42 to -54 mV, as shown in **Table 6-1**. These results indicate that 3.0-6.0 wt% of DMPA is sufficient to stabilize the particles by electrostatic interactions. Dispersion 7, however, was not stable due to its low DMPA content (2.5 wt%) and rapidly sedimented after being prepared. Typically, the ζ -potential of ionic dispersions is influenced by the surrounding acid and base environment. To investigate the electrostatic stability of dispersions in this chemical environment, the pH values of dispersions were varied from approximately 4 to 12 by adding a 5.0×10^{-3} M HCl solution or a 5.0×10^{-3} M NaOH solution, respectively. The dependencies of average particle size and ζ -potential on different pH values were studied and the results of a few examples are depicted in **Figure 6-2**. In this figure, the average particle diameter of dispersions 2, 3 and 4 increased up to 180 nm with decreasing pH values from 12 to nearly 4. At the same pH range, the absolute value of the ζ -potentials steadily decreased towards 30 mV, demonstrating a gradually reduced electrostatic

stability. This reduced stability is a result of the disturbed electrical bilayer by the addition of the acid. Subsequently, large coagulates were observed in all dispersions when pH values were slightly lower than 4 (not indicated in **Figure 6-2**). Different from the dispersions chain-extended with ethylene diamine (EDA) (Chapter 5), these dispersions appeared to be more stable at low pH values. This is possibly correlated to the TEA added during the dispersion process, which weakens the total effect of the acid on the electrical bilayer.

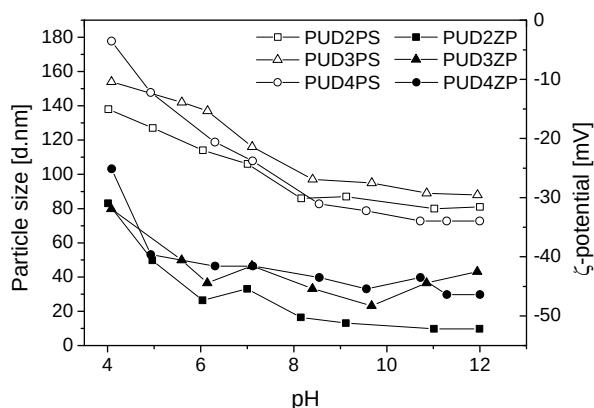


Figure 6-2. Plots of average particle size (open symbol) and ζ -potential (solid symbol) of dispersions 2-4 as a function of pH.

6.3.6 Properties of coatings and free-standing films

DSC and TGA measurements

The thermal properties of dispersion-cast films were examined by performing TGA and DSC measurements. A PUU film containing DDI alone (i.e. no EELDI, entry F0 in **Tables 6-2** and **6-3**) was used for comparison. The other films ranging from F1 to F6, as shown in **Tables 6-2** and **6-3**, correspond to the chain-extended dispersions from entries 1 to 6, respectively. The DSC traces of all PUU films are depicted in **Figure 6-3** and the corresponding transition temperatures are listed in **Table 6-2**. Similar to EDA chain-extended dispersions (Chapter 5), the low T_g values of these dispersion-cast films (indicated as T_{g1} in **Figure 6-3** and in **Table 6-2**) range from 18 to 58 °C, increasing with the increasing rigid EELDI and IS contents. A second T_g (indicated as T_{g2} in **Figure 6-3A** and in

Table 6-2) present in films F1 and F2 merges into the curvature of an endothermic peak. This endothermic peak indicates the disruption of some ordered domains upon heating, which were possibly formed between the H-bonds as a result of aging. Together with the T_{g2} of F3, these additional glass transitions point to the presence of a more rigid segment structure, which is apparently micro-phase separated from the soft segment-rich phase. Different from what was observed in the films F1 - F3, no clear indication of a second T_g was observed in F4, F5 and F6. This indicates an enhanced phase mixing behavior of the polymer composition. Another indication of this enhanced phase mixing was found in the derivative DSC curve of F3, where a broad T_{g1} curve was observed, in comparison to that of F1 and F2.

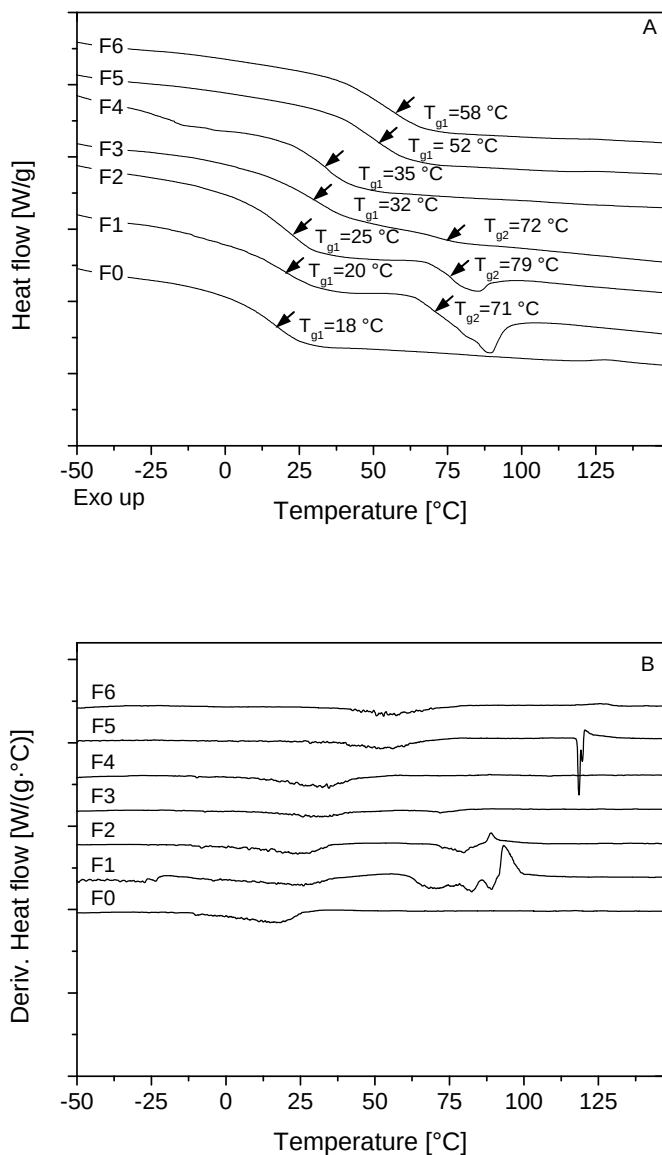


Figure 6-3. The second heating (A) DSC curves and (B) temperature-derivative DSC curves of dry free- standing PUU films containing different DDI-to-EELDI ratios and IS contents, recorded from -80-150 °C at a heating rate of 20 °C/min.

Table 6-2. Thermal properties and transition temperatures of free-standing films derived from TGA and DSC/DMA ($\tan \delta$) curves.

Film*	TGA		DSC		DMA
	$T_{d, 5\%}^a$	$T_{d, 50\%}^b$	T_{g1}^c	T_{g2}^c	T_g
	[°C]	[°C]	[°C]	[°C]	[°C]
F0	270	408	18	-	24
F1	258	380	20	71	36
F2	250	390	25	79	33
F3	258	382	32	72	52
F4	245	352	35	-	51
F5	256	354	52	-	67
F6	253	349	58	-	68

* The film numbers refer to the PUDs in **Table 6-1**. ^{a)} $T_{d, 5\%}$ is the 5% weight loss temperature measured by TGA (10 °C min⁻¹); ^{b)} $T_{d, 50\%}$ is the 50% weight loss temperature measured by TGA; ^{c)} The 1st and the 2nd T_g determined from the second DSC heating run (20 °C min⁻¹).

The TGA traces of these seven films are depicted in **Figure 6-4**. Similarly to the PUU films described in our previous work ^[33] and in Chapter 5, these dry films usually undergo a three-stage thermal degradation, although films F5 and F6 exhibited a less obvious degradation in the second stage. The first stage comprises urethane/urea decomposition in the temperature range of 220-360 °C. The degradation of fatty acid chains corresponds to the second stage, ^[43] in the temperature range of 330-400 °C. The last stage of thermal degradation takes place at 440-460 °C, correlated to the gasification of any remaining components. ^[17, 44] The incorporation of DDI shows an improved decomposition temperature upon 5 wt% and 50 wt% mass loss (**Table 6-2**), as a result of the reduced thermal labile urethane and urea contents. ^[45-46]

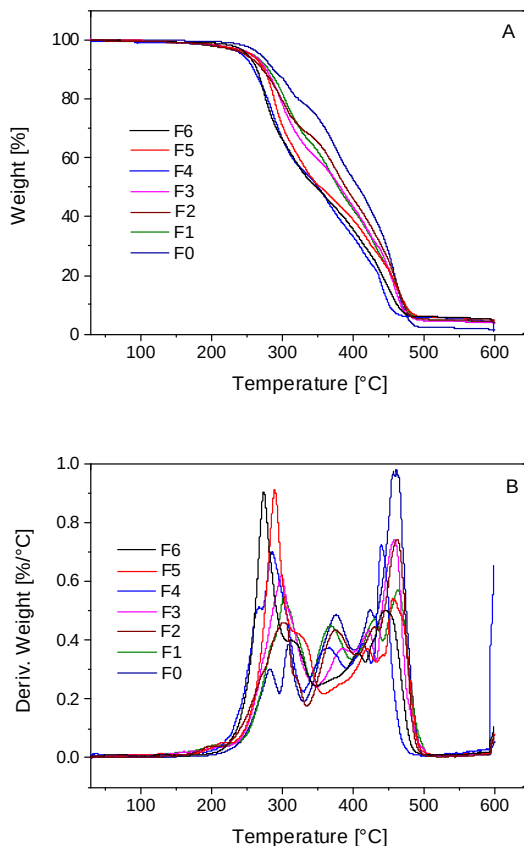


Figure 6-4. TGA curves (A) and the corresponding derivative plots (B) of dry free-standing films prepared from H₂O chain-extended dispersions containing different DDI-to-EELDI ratios and IS contents, recorded from 30-600 °C at 10 °C/min under N₂ atmosphere.

H-bonded urea carbonyl groups in free-standing PUU films monitored by FT-IR

FT-IR measurements are commonly used to investigate the H-bonded urethane and urea carbonyl groups of PUU films,^[47-51] where the H-bonded carbonyl groups are generally separated from the free carbonyl groups in the FT-IR spectrum. The peak attributed to H-bonded urea carbonyl groups of film F1 was studied as a function of temperature, ranging from 30 to 160 °C. **Figure 6-5** shows the relevant part of the FT-IR spectra of this film recorded at 30, 50, 70 and 90 °C. The absorption band at 1650-1610 cm⁻¹, attributed to the

ordered H-bonded urea carbonyls (H-bonds formed in the ordered region),^[47-51] completely disappears between 70 and 90 °C. This result confirms that the endothermic transitions at 70-80 °C, observed in the DSC curves, are most likely attributed to the H-bond dissociation. The formation of the free urea carbonyl groups was not detected because of the low peak intensity and the overlap between urethane and urea carbonyl peaks. At temperatures between 90-160 °C, the FT-IR spectra remain the same.

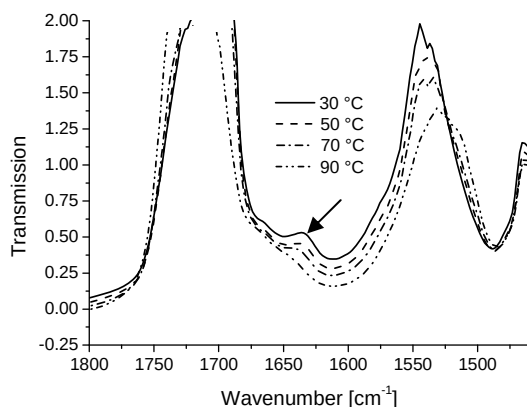


Figure 6-5. The FT-IR spectra of the ordered H-bonded urea carbonyl of free-standing film F1 as a function of temperature.

To demonstrate the correlation between the H-bonding induced differences in phase morphology and the polymer composition, FT-IR measurements of free-standing PUU films F1- F6 were performed, focusing on the ordered H-bonded urea carbonyl groups at 1643-1620 cm^{-1} . The resulting FT-IR spectra are depicted in **Figure 6-6**. It is noticed that with increasing EELDI and IS contents, a reduced peak intensity in the ordered H-bonded urea carbonyl region is observed, in the order of F1 – F6. This reduced ordered H-bonded area, induced by increasing the overall compatibility of polymers towards a rigid and soft co-continuous phase morphology^[52-53] between the flexible and rigid units, seems to confirm the enhanced phase mixing, as observed in the DSC curves.

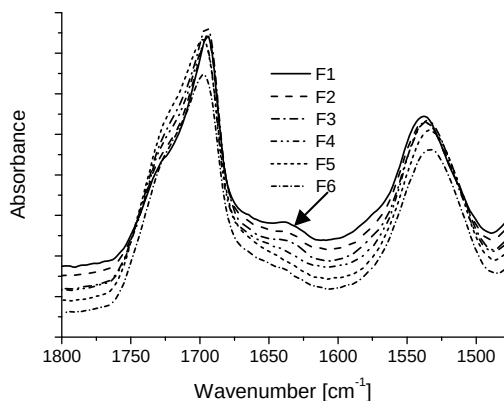


Figure 6-6. The FT-IR spectra of free-standing PUU films F1-6 at 30 °C, focusing on the urea carbonyl area.

Surface characterization by AFM

Atomic Force Microscopy (AFM) in tapping mode is often used to detect the surface topography and to perform compositional surface mapping of heterogeneous samples by providing phase and height contrast.^[54-56] The AFM 3D height and phase images of coatings F0, F1, F3 and F6 prepared at 60 °C on a glass substrate are shown in **Figures 6-7** and **6-8**, respectively. The topographical features of these 3D height images are in the order of 20-80 nm in the Z-direction and an X-Y scale of 2.0 μm is used. The detected surfaces of the films in general were rather uniform and exhibited an undulating surface structure. The average roughness (R_a , arithmetical mean deviation) of the films, calculated by the Nova software according to ISO4287, was 9.5, 6.5, 2.5 and 2.1 nm for F1, F0, F3 and F6, respectively. In the phase images (**Figure 6-8**), no clear phase contrast was observed in F0 (A). F3 (C) and F6 (D) showed similar phase profiles, exhibiting an alternate distribution between the small dark areas (soft character) and the small light areas (hard character), indicating a rigid and soft co-continuous phase morphology. In the phase image of F1(B), the size of the dark and light areas was clearly larger than that in F3 and F6, analogous to rigid domains dispersed in the soft matrix.^[52]

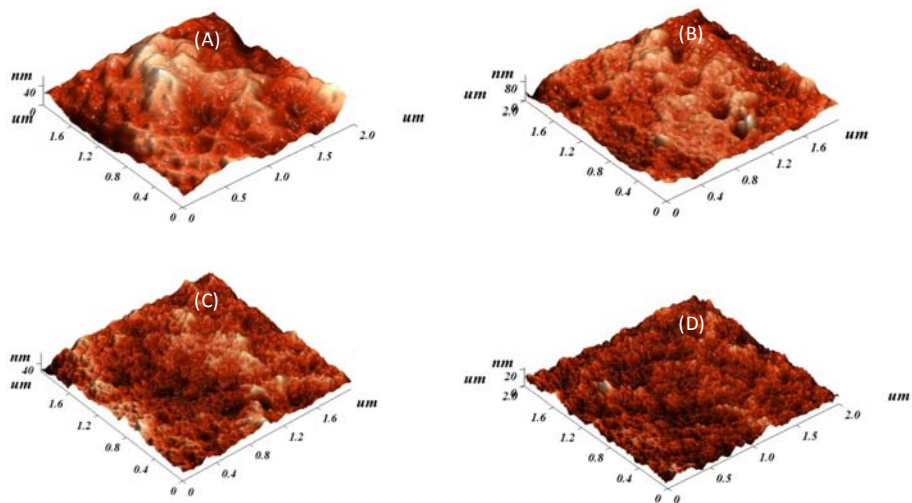


Figure 6-7. AFM 3D height images at 20 °C of films A) F0 (DDI : EELDI = 1 : 0), B) F1 (DDI : EELDI = 1 : 0.5), C) F3 (DDI : EELDI = 1 : 1) and D) F6 (DDI : EELDI = 1 : 2).

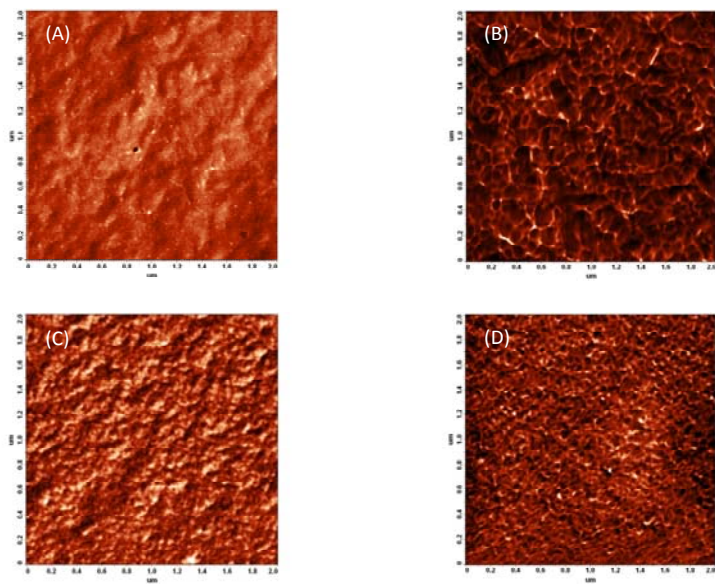


Figure 6-8. AFM phase images of coating films A) F0 (DDI : EELDI = 1 : 0), B) F1 (DDI : EELDI = 1 : 0.5), C) F3 (DDI : EELDI = 1 : 1) and D) F6 (DDI : EELDI = 1 : 2) at 20 °C.

To demonstrate the influence of H-bonding on the phase morphology of the examined films, AFM was carried out at 65 ± 3 °C (around the H-bonding dissociation temperature), focusing on the phase behavior of the films and using the semi-contact mode. Taking F1 and F6 as examples, their phase images at approx. 65 °C are depicted in **Figure 6-9**. It is clearly observed that the phase image of F1 exhibits a heterogeneous phase morphology with the large dark area of irregular shape randomly dispersed in the continuous light area, indicating micro-phase separation.^[52] Compared to F1, F6 exhibits a very low dark-light phase contrast at approximately 65 °C, demonstrating a virtually homogeneous phase morphology. Compared to F1, F6 exhibits an enhanced phase mixing.

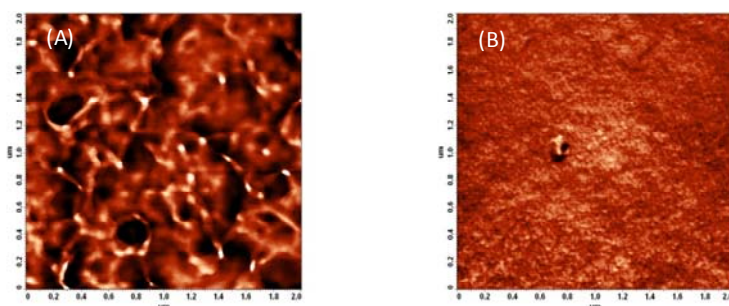


Figure 6-9. AFM phase images of coating films F1 (left) and F6 (right) prepared at 60 °C and measured at 65 ± 3 °C.

Viscoelastic properties of free-standing films

Dynamic mechanical analysis (DMA) was performed to investigate the thermo-mechanical behavior of dispersion-cast, free-standing films as a function of temperature. The storage modulus (E' , measuring the elastic behavior of the material), the loss modulus (E'' , measuring the viscous response of the material) and the $\tan \delta$ values are depicted in **Figures 6-10A**, **6-10B** and **6-10C**, respectively. In general, E' and E'' decrease with increasing temperature. The sharp decrease of the E' curves with increasing temperature indicates the transition from the glassy state to the rubbery state. A strong dependence of the shape of the E' , E'' and $\tan \delta$ curves on the ratio between the flexible DDI and the rigid EELDI residues is observed in **Figure 6-10**, in which the films containing the same DDI-to-EELDI ratio show close similarity. The maximum $\tan \delta$ values with respect to temperature transitions were found lowest for F0, where DDI is exclusively present. The dependence of

both moduli on the DMPA and IS contents, however, is limited. The maximum values derived from the $\tan \delta$ curves were used to indicate the dynamic glass transition temperature (listed in **Table 6-2**). These $\tan \delta$ -derived glass transition temperatures show strong similarity for the films containing the same DDI-to-EELDI ratio. Additional transitions were observed around 90-110 °C in films F4-F6. These transitions could be the second T_g of these films, although the DSC curves did not show the same transition. These relatively rigid amorphous domains might be too small to be accurately detected by DSC measurements. The other films (F1-F3) started to flow around 80 °C. Therefore, no second glass transitions were observed.

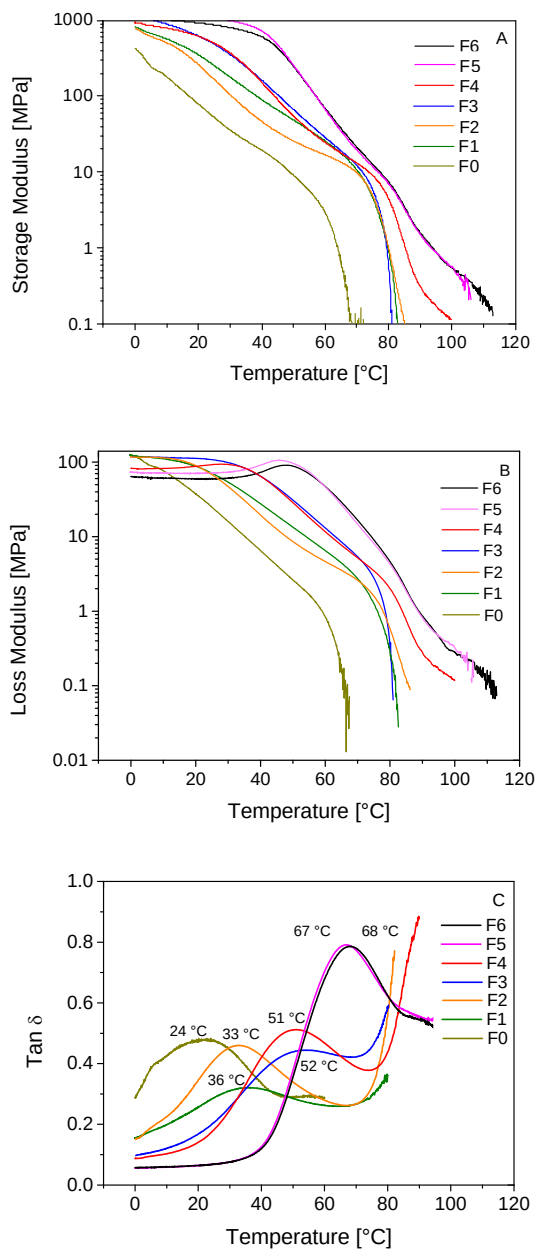


Figure 6-10. Dynamic mechanical properties of the dispersion-cast, free-standing films: A) storage modulus; B) loss modulus; C) $\tan \delta$.

Coating properties

Typical coating properties such as the acetone resistance as well as the falling dart reverse-impact resistance of coatings formulated on aluminum panels, and the adhesion to aluminum were evaluated. The reaction formulation and results are summarized in **Table 6-3**.

Table 6-3. Reaction formulation and results obtained from coating property tests.

Film*	DDI:EELDI:IS:DMPA [molar ratio]	DMPA [wt%]	$M_{n(PUD)}^a$ [kg/mol]	Av. film thickness [μm]	Acetone resistance ^b	Impact test ^b [1kg, 100cm]	Adhesion test ^c [class]
F0	53.5 : 0 : 23.7 : 22.8	7.5	18.5	25	-	+	1
F1	35.3 : 17.6 : 32.2 : 14.9	6.0	11.0	33	-	+	1
F2	35.3 : 17.6 : 35.9 : 11.2	4.5	9.1	36	-	+	1
F3	26.3 : 26.3 : 37.3 : 10	4.5	10.4	36	-/+	-/+	1
F4	26.3 : 26.3 : 39.7 : 7.8	3.5	11.4	33	-/+	+	0
F5	17.3 : 34.7 : 40.7 : 7.3	3.5	17.3	41	+	-/+	0
F6	17.4 : 34.9 : 41.6 : 6.1	3.0	18.3	40	+	-/+	0

* The film numbers refer to the PUDs in **Table 6-1.a**) The molecular weight of PUDs after one hour of chain extension with water; b) -: Poor, -/+: Moderate, +: Good; c) The adhesion is classified on a scale from 0 to 5: 0) coating intact; 1) detached area < 5%; 2) 5% < detached area < 15%; 3) 15% < detached area < 35%; 4) 35% < detached area < 65%; 5) > 65%.

In general, the coatings on aluminum panels have a thickness between 25 – 41 μm. F0 - F4, having high DDI contents, showed poor or moderate acetone resistance. This is regarded to be caused by the relatively low molecular weight of the linear PUU polymers and the limited H-bond formation in the formulation dominated by DDI. By partially replacing DDI with the relatively short EELDI in F5 and F6, the increased molecular weight and the potentially enhanced physical network (increased concentration of H-bonds) improved the acetone resistance. On the other hand, the flexibility of the DDI residues together with the relatively low T_g (18-35 °C in F0-F4) of the PUU polymers containing a high DDI content is obviously favorable for the impact resistance. By the incorporation of the more rigid IS into the polymer backbone in the PUUs of F5 and F6, the impact resistance was slightly reduced. The 'cross-hatch' adhesion test results, giving the

assessment of the damaged coating surface after removal the adhesive tape, are summarized in **Table 6-3**. The values illustrate that the degree of damage varies between 0 and 1, indicating excellent adhesion of all the poly(urethane urea) coatings to aluminum substrates.^[57]

6.4 Conclusions

In this work, the thermal and mechanical properties of the poly(urethane urea) dispersion-cast films, as well as the morphology were investigated in correlation to the polymer composition. These aqueous PUU dispersions contain DDI, EELDI, IS and DMPA as the main PU building blocks and water as the chain extender. The as-prepared dispersions showed a good electrostatic stability at pH values ranging from approximately 4-12. Significant dependencies of these properties and the phase morphology on the polymer composition were observed. These dispersion-cast films were thermally stable up to 245 °C (5% weight loss). An enhanced thermal stability was observed for films containing a relatively high DDI content, which was related to the reduced concentration of urethane and urea contents. By means of partially replacing the flexible DDI with the rigid EELDI as well as increasing the isosorbide contents in the monomer feed, the DSC-derived T_g was significantly increased from 18 to 58 °C (1st T_g) and to above 70 °C (2nd T_g). As evidenced from the DSC, AFM and FT-IR measurements, the H-bond-induced micro-phase separation depends on the polymer composition. An improved phase mixing was related to the overall increased concentration of urethane/urea bonds, as a result of increasing EELDI contents. The storage modulus, loss modulus and $\tan \delta$ data showed a strong dependence on the ratio of the flexible DDI to the rigid EELDI but are less dependent on the IS and DMPA contents. The coatings applied on aluminum panels have good acetone resistance and moderate impact resistance at high EELDI and IS contents, and excellent adhesion to aluminum.

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7

Epilogue

7.1 Highlights

The work described in this thesis concerning biomass-based aqueous polyurethane dispersions (PUD) and the investigation of the properties of the corresponding dispersion-cast coatings and free-standing films has provided a broad range of insights into the chemistry and reactivity of several polyurethane (PU) building blocks, the colloidal stability of polyurethane dispersions and the application properties of dispersion-cast films and coating materials derived from renewable resources.

An important highlight is the development of well-defined isocyanate-end capped PU prepolymers from renewable-based PU building blocks, including a dimer fatty acid-based diisocyanate (DDI), the glucose-based 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) and the lysine-derived ethyl ester L-lysine diisocyanate (EELDI), combined with the petro-based dimethylolpropionic acid (DMPA), which functions as the internal stabilizing agent of the PU dispersions. The combination of the relatively hydrophobic DDI with the hydrophilic DMPA, as well as the incorporation of the asymmetric molecules IS and EELDI, could have restricted the control over the polymer composition and the polyurethane end-groups. Fundamental kinetics studies have been carried out to probe the regio-selectivity of IS and EELDI and the reactivity of the mentioned four compounds in their respective reactions. The results have shown that at the appropriate reaction conditions and at the right monomer feed ratios, the desired PU prepolymers with well-defined end-groups can be prepared.

When dispersing isocyanate-terminated PU prepolymers in water, the isocyanate-water side-reaction is the major obstacle for the diamine or diol chain extension reaction, as this side-reaction influences the reaction stoichiometry. To achieve high molecular weight, chain-extended polyurethanes, the influence of the reaction temperature, of the sequence of diamine or water addition as well as of the use of additional catalysts were investigated. Through these studies, we were able to significantly enhance the degree of chain extension and thus increase the final PUD molecular weight. This was done by using only water as the chain extender at optimized reaction conditions and using triethylamine (TEA) as the catalyst.

Due to the limited availability of renewable-based internal stabilizing agents, the petrochemical-based DMPA is still often used when preparing anionic PU dispersions. To minimize the content of the DMPA in the polymer composition while maintaining a good colloidal stability of the polyurethane dispersions is another challenge. The amino acid-based EELDI which was incorporated into the PU backbone as a rigid diisocyanate to replace the fatty acid-based, apolar DDI appears to facilitate the stabilization of the

formed dispersions. The corresponding hypothesis is that the (partial) hydrolysis of the pendant ester groups present in the EELDI residues results in carboxylic acid groups, which help to stabilize the dispersions upon neutralization with TEA. Therefore, with increasing EELDI content in the polymer composition, the amount of DMPA could be significantly reduced (to approximately 2.5 wt%, the lowest content reported to our knowledge). Consequently, almost fully (approximately 97 wt%) renewable-based PU dispersions were obtained.

Finally, the high segment mobility of the fatty acid-derived PU building blocks typically results in polymers with low glass transition temperatures (T_g) and low tensile stress. By means of partially replacing the flexible DDI with the rigid EELDI in the monomer feed, it proved possible to significantly improve the T_g values of dispersion-cast films from approximately 20 to 58 °C (1st T_g) and to above 70 °C (2nd T_g). Moreover, an understanding of the thermal and mechanical properties and the morphology in correlation with the polymer composition was achieved.

7.2 Technology assessment

This research deals with the development of renewable aqueous PU dispersions, dedicated for sustainable coating applications. Several renewable building blocks investigated in this work show great suitability to prepare PU dispersions. Their combinations also result in films and coatings with satisfactory thermal and mechanical properties, suitable for real life applications. Therefore, this work is of interest to paint-producing companies and their raw material suppliers, some of which were actively involved in the project within the Dutch Polymer Institute (DPI) framework. In addition, the major approach used in this work to prepare aqueous polyurethane dispersions is the conventional, industrially applied acetone or 2-butanone (ketone) process. This process involves prepolymerization reactions carried out at moderate reaction temperature, under an inert reaction environment and atmosphere pressure. Therefore, the translation of the laboratory experiments described in this thesis to an industrial production process will not require major adaptations to currently available hardware. The subsequent process to remove the volatile solvent, used to prepare the initial prepolymer in solution, proceeds along the same lines as methods already applied in industry. Furthermore, the application of these dispersions to produce coating materials can be easily carried out at ambient temperature and under atmospheric conditions. One of the most promising aspects of this work is the preparation of dispersion-cast films with a tunable T_g by replacing the flexible DDI with the rigid EELDI in the monomer feed. The importance of this finding was

recognized by the industrial partners (participating within the framework of DPI) involved in this project. A patent application regarding this flexible coating system has been filed.

The limited availability and the relatively high price of DDI, EELDI and IS form the major drawbacks of these biomass-derived chemicals toward industrial implementation. Though isosorbide is currently produced with high purity and on a multi-ton scale, EELDI is much more expensive and only available at limited scale from a small number of producers in Asia, as a result of the complex and costly preparation. The availability of DDI is even more limited, as during the course of this PhD investigation it was only produced by Cognis (now BASF).

7.3 Outlook

Based on the results obtained for the linear poly(urethane urea) products prepared in this work, curing with multi-functional isocyanate cross-linkers (for amine chain end groups) is regarded as a good option to further enhance T_g , leading to a broader variety of corresponding possible applications. Concurrently, improved mechanical performance and solvent resistance can also be expected from these cross-linked materials. However, one should bear in mind that this curing process would be an additional process step, increasing the production cost. One of the major achievements described in this thesis is the preparation of nearly fully renewable, relatively high molecular weight PU dispersions through conventional diisocyanate-polyol reactions, not requiring curing after film formation. With the development of diamines and (cyclic) carbonates based on renewable resources, fully renewable PU dispersions may be developed through less toxic non-isocyanate approaches. Moreover, even though only ~ 0.56 wt% (relative to the amount of prepolymer) of the tin-based catalyst dibutyltin dilaurate (DBTDL) is used in this work, its high toxicity triggers researchers to seek for other types of catalysts, where a reduced toxicity should be combined with satisfactory catalytic activity. Furthermore, water-borne polyurethane dispersions in general have solids contents up to 50 wt%. To increase the polymer concentration by for example mixing dispersions of different particle size is another very interesting topic for future research. It is also worth mentioning that polyurethanes with moderate molar masses and low T_g values, due to the fact that they mainly contain DDI, which provides excellent adhesion to non-polar surfaces, are interesting for adhesive applications.

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After moving from Beijing to Maastricht in Jan 2007, I followed the Master's program at the Eindhoven University of Technology. In this period, when doing two research projects at the group of the Laboratory of Polymer Chemistry (SPC), I got to know many nice SPCers and some interesting research projects. Hence, directly after the Master's program, I started the PhD research in this group in Sept 2008. To recall these years at SPC (later became SPM), it has been intensive and stressful, but also pleasant and unforgettable. While now approaching the end of the PhD, I would like to especially thank many people, for their great help and support in these years. Without them, the completion of this thesis could have not been achieved.

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Curriculum Vitae

Yingyuan Li was born on 15 April 1977 in Beijing, China. After finishing her high school in 1996, she started the bachelor studies on Polymer Materials Science and Engineering at Sichuan University in China. In 2000, she graduated within the group of Prof. Gu Yi on the research topic “A Primary Research On Benzoxazine (BEN) As Electronic Packaging Material For Microelectronic Devices”. From 2001 to 2006, she successively worked at Charna, DSM and Hofung Technology within the function of commercial assistant and sales, dealing with commercializing chemical products and process technology in China. In 2007, she started Master’s study on Polymer and Composite at the faculty of Chemical Engineering of Eindhoven University of Technology. One and a half years later, she graduated on the Master’s dissertation entitled “Enzymatic ring-opening polymerization of polyesters for bio-applications (nerve guide tubes)” at the Laboratory of Polymer Chemistry (SPC). Immediately after graduation, in 2008 Sept, she started her PhD research under the supervision of Prof.dr. Cor Koning at SPC (later renamed as Laboratory of Polymer Materials, SPM) and Prof.dr. Rolf A.T.M. van Benthem from the Laboratory of Materials and Interface Chemistry (SMG). Dr. Bart A.J. Noordermeer became her coach later. Her PhD research topic focused on the development of bio-based poly(urethane urea) dispersions for coating applications. The most important results obtained in this research are described in this dissertation.

List of publications

Scientific papers:

1. Y. Li; B.A.J. Noordover; R.A.T.M. van Benthem; C.E. Koning, "Property Profile of Poly(urethane urea) Dispersions Containing Dimer fatty acid-, Sugar- and Amino acid-based Building Blocks" *Eur. Polym. J.* submitted.
2. Y. Li; B.A.J. Noordover; R.A.T.M. van Benthem; C.E. Koning "Bio-based Poly(urethane urea) Dispersions with a Low Internal Stabilizing Agent Content and Tunable Thermal Properties" *Prog. Org. Coat.* to be submitted.
3. Y. Li; B.A.J. Noordover; R.A.T.M. van Benthem; C.E. Koning "Recent Advances in Bio-based Polyurethanes and Aqueous Polyurethane Dispersions" to be submitted.
4. Y. Li; B.A.J. Noordover; R.A.T.M. van Benthem; C.E. Koning "Reactivity and Regio-Selectivity of Renewable Building Blocks for the Synthesis of Water-Dispersible Polyurethane Prepolymers" *ACS Sust. Chem. Eng.* **2014**, 2, 788-797.
5. Y. Li; B.A.J. Noordover; R.A.T.M. van Benthem; C.E. Koning "Chain Extension of Dimer Fatty Acid- and Sugar-based Polyurethanes in Aqueous Dispersions" *Eur. Polym. J.* **2014**, 52, 12-22.
6. I. van der Meulen; Y. Li; R. Deumens; E.A.J. Joosten; C.E. Koning; A. Heise "Copolymers from Unsaturated Macrolactones: Toward the Design of Cross-Linked Biodegradable Polyesters" *Biomacromolecules* **2011**, 12, 837-843.*

* The publication does not belong to the work described in this thesis.

Patent:

1. Y. Li; R.A.T.M. Van Benthem; C.E. Koning; J. Van Haveren EU/WO2011098272(A2) to the Stichting Dutch Polymer Institute, **2011**.

