# 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 first 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 *exo*-OH functional groups of IS and the primary ε-NCO and 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.

KEYWORDS: *Isosorbide, Ethyl ester lysine diisocyanate, Kinetic study, Polyurethanes, Polyurethane dispersions*
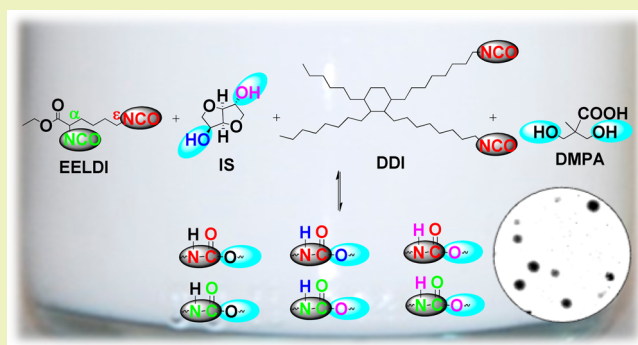
■ INTRODUCTION

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 volatility, organic compound (VOC) contents. Furthermore, they facilitate the convenient application of high molecular weight polymers due to their low viscosity. Finally, PUDs are nonflammable, show good adhesion to a variety of substrates, and have 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 nonaqueous 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, for example, diamines can be performed either in the first or in the second step.[2,9] In the first step, 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
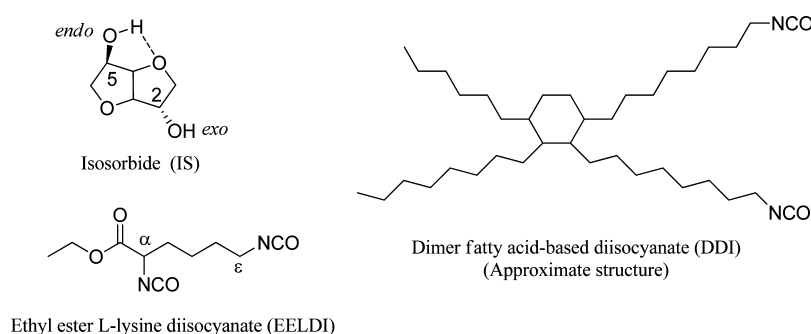
Figure 1. Structures of biomass-based isosorbide (IS),[28−30,34,35] dimer fatty acid-based diisocyanate (DDI), and ethyl ester L-lysine diisocyanate (EELDI).

through proper monomer selection and 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 affords 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 secondary isocyanate group of IPDI.[13−16] It has been reported that the reactivity of the *prim-* and *sec*-isocyanate groups of IPDI varies depending on the reaction conditions, type of counter reagent, type of catalyst, and presence and/or 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, 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), derived from from fatty acids, are interesting candidates for PU synthesis. Isosorbide is produced by the double dehydration of sorbitol, which is derived from sugar.[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 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 toward alkylation or acylation reactions. Conversely, the *endo*-oriented OH group is involved in intramolecular H-bonding with the oxygen of the neighboring tetrahydrofuran ring. In spite of the steric hindrance, this intramolecular H-bonding makes the *endo*-oriented hydroxyl group a preferred reactive center in electronically driven reactions.[32,33]

EELDI is a recently developed biomass-based bifunctional isocyanate derived from L-lysine. Its asymmetric aliphatic structure shown in Figure 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
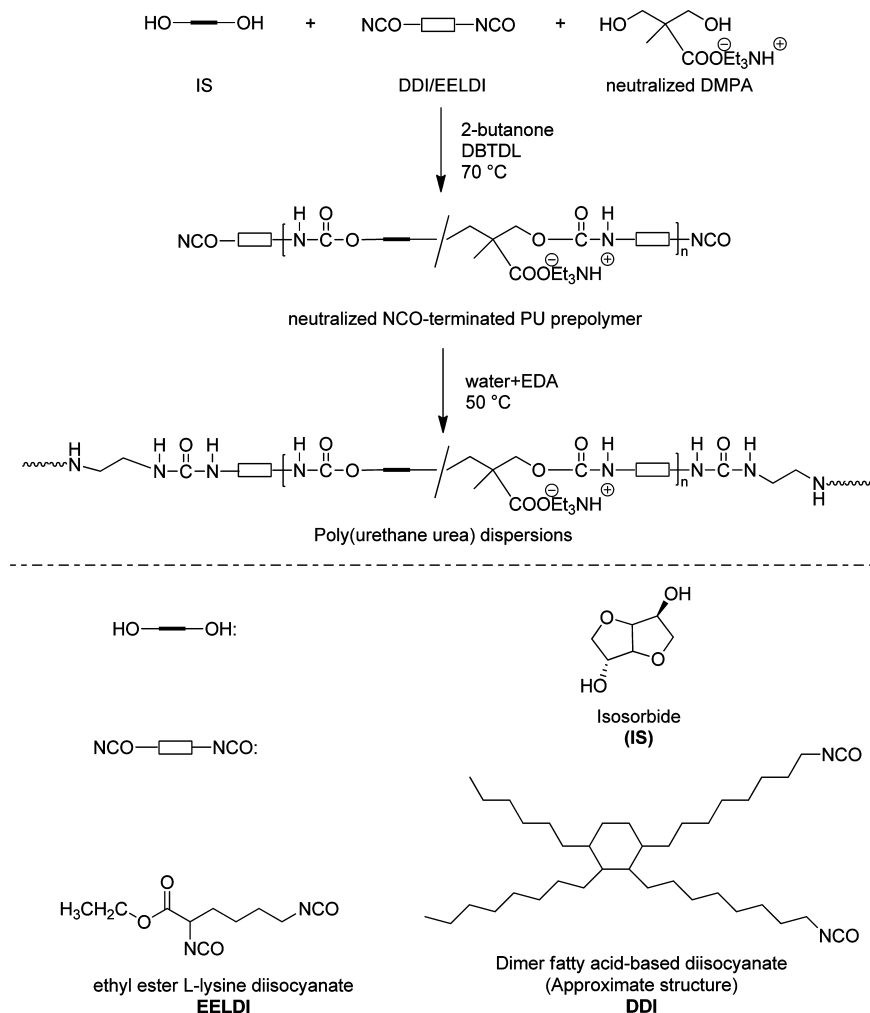
importance in replacing the conventional PU building blocks. EELDI has two isocyanate groups, an α-NCO (attached to a secondary carbon atom) and an ε-NCO (attached to a primary carbon atom) (Figure 1). As reported by Sanda et al.,[36] the α-isocyanate group may experience steric hindrance from the ethyl 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 symmetric renewable-based diisocyanate that is derived from C_{36} dimer fatty acids. Its approximate molecular structure is shown in Figure 1. Dimer fatty acid-based diols have been widely investigated as the renewable-based soft segments for PU or PUU synthesis, which exhibit good waterproof performance and mechanical properties such as hardness and tensile strength.[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 *exo*-OH groups of IS and the α- and ε-NCO groups of EELDI has never been studied in the 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 is described in their respective reactions. The monofunctional hydroxyl compound 2-butanol is used as a 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.

Scheme 1. Preparation of NCO-Terminated PU Prepolymers and Polyurethane Dispersions

neutralized NCO-terminated PU prepolymer

Poly(urethane urea) dispersions

HO━━OH:

Isosorbide
(IS)

NCO━□━NCO:

ethyl ester L-lysine diisocyanate
EELDI

Dimer fatty acid-based diisocyanate
(Approximate structure)
DDI

■ 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, ≥ 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 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-bottomed 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 2–5 h, 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 1. IS (1.023 g, 7.0 mmol) and DMPA, 0.705 g, 5.3 mmol) were weighed into a 250 mL round-bottomed 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 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) to minimize oxidation and to remove any moisture from the reactor. The reaction was carried out for 4–6 h, 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 deionized 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 1 h. Thereafter, the polymer dispersion

Scheme 2. Reaction of EELDI with 2-Butanol To Form Urethane Model Compounds
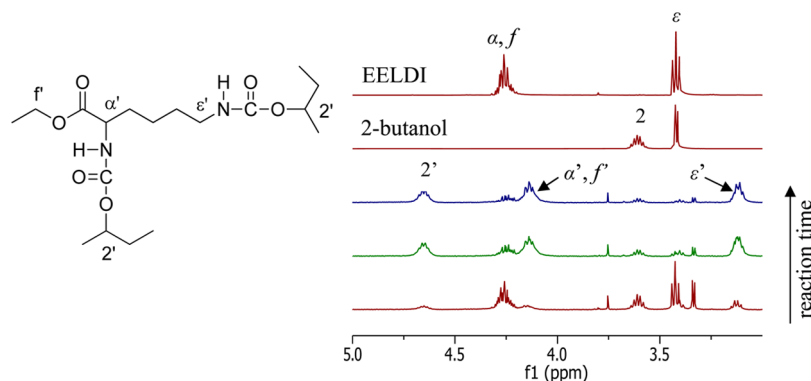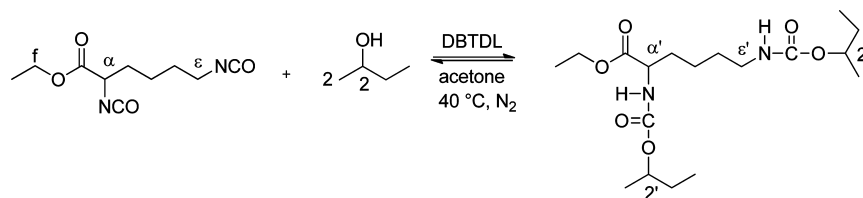
Figure 2. ^{1}H NMR spectra of the reaction EELDI:2-butanol = 1:1 (NCO:OH = 1:1) at 1, 5, and 10 min. Acetone-d_6 was used as the solvent. Signal labels refer to structures shown in this figure and Figure 3.

was discharged from the reactor. Residual 2-butanone was distilled off with a rotary evaporator at 40 °C, with pressure ranging from 100 to 200 mbar.

■ CHARACTERIZATION

^{1}H NMR. was used to follow the reaction kinetics. The conversions of both OH groups and NCO groups were followed in time. ^{1}H NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer. Acetone-d_6 was used as the solvent.

Size Exclusion Chromatography (SEC). SEC was used to determine both the molecular weight and molecular weight distribution of the prepolymers and PU dispersions. A WATERS Alliance setup equipped with a WATERS 2695 separation module, WATERS 2414 differential refractive index detector (40 °C), and 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-linear XL, 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 5000 kg/mol. Data acquisition and processing were performed using Empower software.

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy. ATR-FTIR was performed using a Bio-Rad Excalibur FTS3000MX infrared spectrometer (50 scans per spectrum, 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. 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 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} = volume of HCl solution needed for the blank (mL) and was the average of two measurements; V_{sample} = volume of HCl solution needed for sample (mL); C_{HCl} = HCl concentration in 2-propanol (mol/L); $M_{\text{prepolymer}}$ = PU prepolymer weight (g); and 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 of prepolymer solution was placed in a glass vial and dried at 60 °C for at least 24 h in vacuo until a constant weight was reached.

Dynamic Light Scattering (DLS) and ζ-Potential Measurements. 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 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 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, $\zeta = \eta\mu/\varepsilon$, 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 particle radius, respectively). Data acquisition was performed using ZetaSizer Nano software.

■ RESULTS AND DISCUSSION

Regio-Selectivity of EELDI. The regio-selectivity of EELDI was studied in reaction with 2-butanol (Scheme 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 nonpolymer generating reaction. In Scheme 1, both the α- and 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.

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

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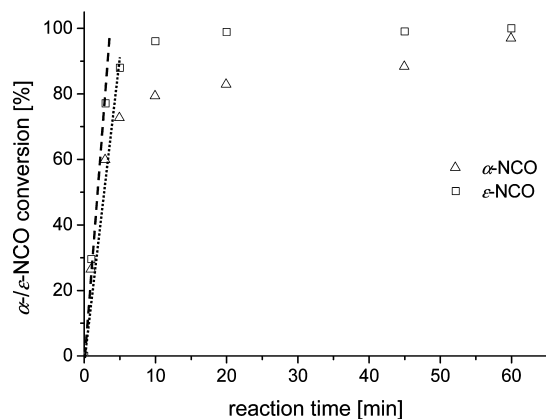
Figure 3. Conversion of α-NCO and ε-NCO in the reaction of EELDI with 2-butanol (total NCO:OH = 1:1). The results were determined by ^{1}H NMR using acetone-d_6 as the solvent.

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 secondary α-NCO of EELDI appear to be highly reactive. After about 10 min of reaction, both isocyanate groups had reached 80% conversion. Full conversion was reached within 1 h.

During the later stage of this reaction, 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.

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.

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 toward 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 a reaction temperature of 40 °C were applied using acetone as the solvent. The reaction between EELDI and isohexides is shown in Scheme 3.

On the right-hand side of the equation, an isomeric urethane mixture may form depending on the addition of the *endo*- and *exo*-oriented hydroxyl groups to the α- or 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, respectively, and α-IM-α, a-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 ^{1}H NMR analysis described previously, the formation of urethanes and the consumption of the total amount of EELDI isocyanate groups (the primary ε-NCO and 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 4. The total conversions of the EELDI isocyanate groups in the reaction with IS, II, or IM are determined from the decrease in the integrated areas under the isocyanate peaks at 2260 cm^{-1}, taking the CH$_2$ peaks at 2790–3092 cm^{-1} as a reference. The equation applied for the calculation of the isocyanate conversions is given in eq 1. Several other peaks attributed to the formation of urethane groups are observed at 3400–3210 cm^{-1} (N–H stretching), 1846–1610 cm^{-1} (amide I C=O stretching), and 1483–1608 cm^{-1} (amide II N–H deformation).

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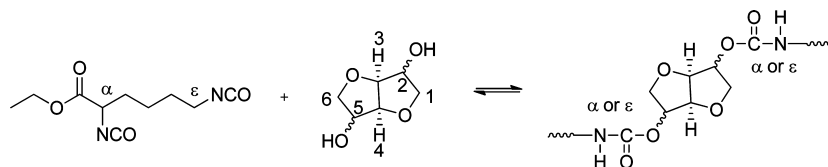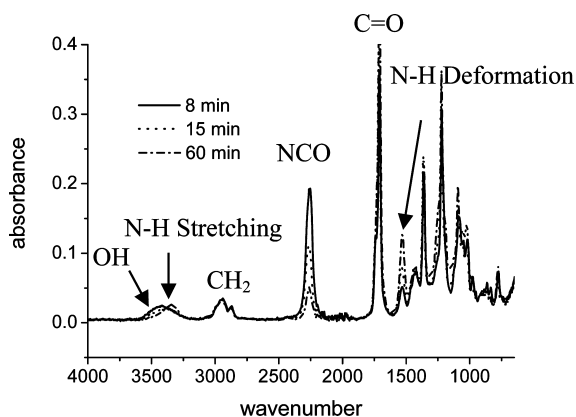
Figure 4. FT-IR spectra of the reaction at a feed ratio of EELDI:IS = 1:1. Spectra of reactions EELDI:II = 1:1 and EELDI:IM = 1:1 are very similar.

$$P_{NCOt} = \frac{[NCO]_0 - [NCO]_t}{[NCO]_0} \times 100\% \qquad (1)$$

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

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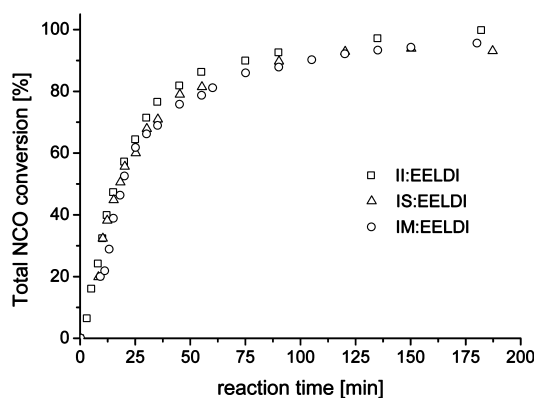
Figure 5. Total ε- and α-NCO conversion of EELDI during the course of the reaction with IM, II, and IS (NCO:OH = 1:1). The results are recorded using FT-IR and resolved using the integrated areas under the isocyanate peaks at 2260 cm^{-1}.

As becomes evident from Figure 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 equi-reactivity 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.

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. Therefore, the regio-selectivity of the α- and ε-NCO groups of EELDI was examined using an exaggerated feed ratio of IS:EELDI = 1:4 at 40 °C. Partial ^{1}H NMR spectra, focused on the relevant ppm range, are shown in Figure 6. No significant regio-selectivity has
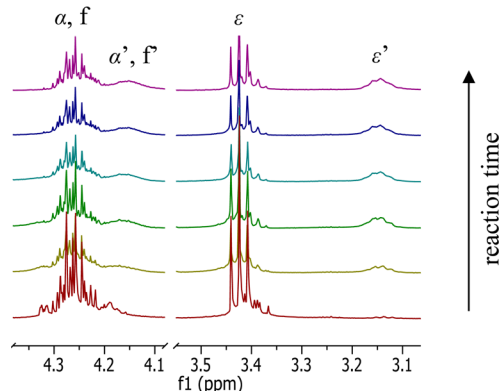
Figure 6. Partial ^{1}H NMR spectra of the reaction between IS:EELDI = 1:4 at 1, 10, 20, 30, 60, and 90 min, using acetone-d_6 as the solvent.

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.

For the same reaction, the regio-selectivity between *endo*- and *exo*-OH groups of IS has been examined as well, as shown in Figure 7. By applying a large molar excess of diisocyanates,
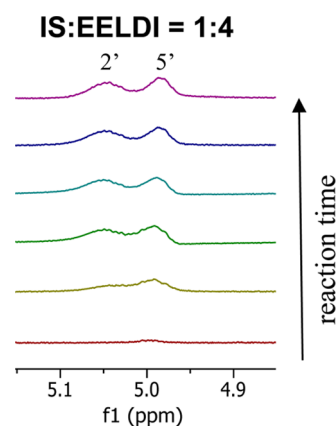
Figure 7. ^{1}H NMR signals at 4.85−5.15 ppm of reaction IS:EELDI = 1:4 at 1, 10, 20, 30, 60, and 90 min, using acetone-d_6 as the solvent. 2′ = CH adjacent to the *exo*-OH; 5′ = CH adjacent to the *endo*-OH.

both the *endo*-OH (5) and *exo*-OH (2) groups are converted (as shown for signals 2′ and 5′ in Figure 7) to a similar extent after 20 min, 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.

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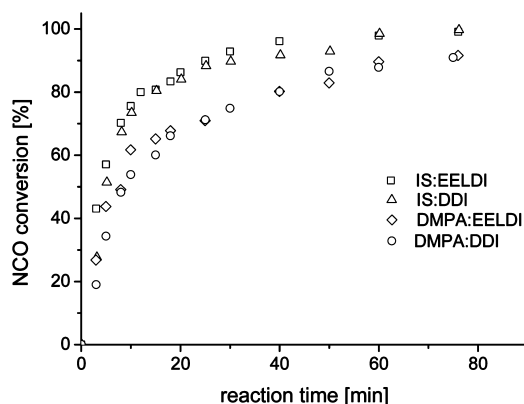
Figure 8. Total NCO conversion of DDI or EELDI (α- and ε-NCOs) during the course of the reaction with IS and DMPA (NCO:OH = 1:1), respectively. The results were recorded using FT-IR and resolved using the integrated areas under the isocyanate peaks at 2260 cm^{-1}.

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 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 min of reaction. The second-order rate constants k, determined from the first 18 min of reaction, are 3.0×10^{-1} mol^{-1} min^{-1} (IS/EELDI reaction), 2.8×10^{-1} mol^{-1} min^{-1} (IS/DDI reaction), 1.2×10^{-1} mol^{-1} min^{-1} (DMPA/EELDI reaction), and 1.1×10^{-1} mol^{-1} 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 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.

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, and 1:1 to 1:2 and by reducing the DMPA weight percentage (relative to the prepolymer weight) from 6.6 to 2.0 wt %. In this way, minimum renewable contents of 93 and 88 wt % (including triethylamine (TEA) and ethylene diamine (EDA)) are expected from such prepolymers and PUDs, respectively. 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 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 1.

As shown in Table 1, all PU prepolymers show similar M_n values around 6.0 kg/mol after the polymerization and have a
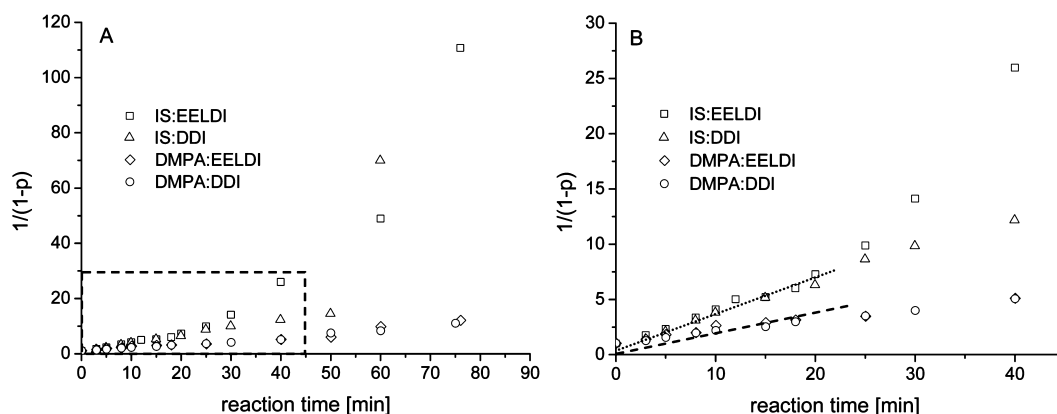
Figure 9. Second-order kinetic plot $1/(1 - p)$ versus time (A) and the enlarged area (B) of DDI or EELDI in reaction with equimolar amounts of IS and DMPA, using DBTDL as the catalyst.

**Table 1. Reaction Formulation of PU Prepolymers and Characteristics of PUDs**

PUD	DDI/EELDI/IS/DMPA (molar ratio)	DMPA (wt %)	$M_{n\,(prepol)}$ (kg/mol)	$M_{w\,(prepol)}$ (kg/mol)	$M_{n\,(PUD)}$ (kg/mol)	$M_{w\,(PUD)}$ (kg/mol)	dispersion appearance	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

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 that initially formed between the carboxylic ionic groups in the prepolymer solution[2] and to release the neutralized DMPA to migrate toward 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 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 toward 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 10 and 11.

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 approximately 90 wt %. On the basis of 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
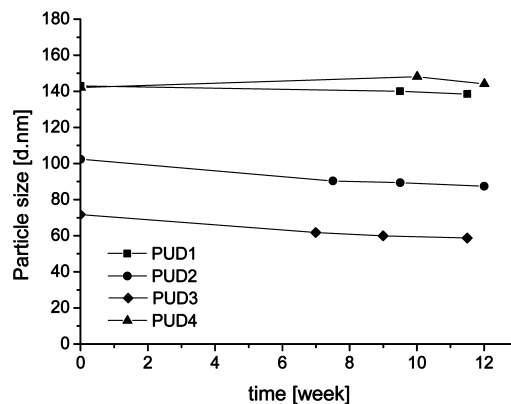
Figure 10. Particle sizes of PUDs1−4 (Table 1) measured as a function of time.
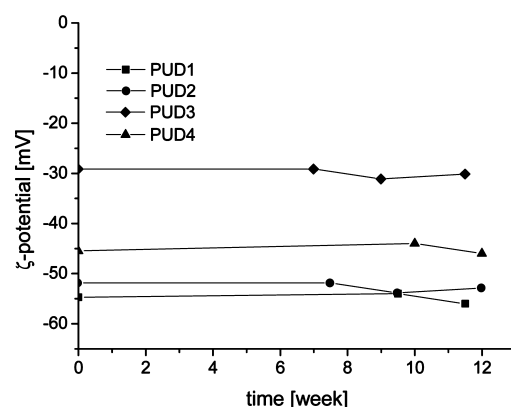
Figure 11. ζ-Potentials of PUDs1−4 (Table 1) measured as a function of time.

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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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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