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Novel isocyanate-free Waterborne Polyurea Dispersions

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Novel Isocyanate-free Waterborne Polyurea Dispersions

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Novel Isocyanate-free Waterborne Polyurea Dispersions

ABSTRACT

The study was set out to prepare waterborne polyurea dispersions for coating application via isocyanate-free route. The dispersions are required to have good film forming ability at room temperature. The glass transition temperature (T_g) of the polyureas plays a vital role in the film formation, and the ideal T_g is considered to be in the range of 30-50 °C.

To obtain isocyanate-free polyureas, dicarbamates were employed instead of isocyanate to react with diamines. To understand the effect of the structure of the polyureas on T_g, building blocks with different structures were chosen. Apart from structure tailoring, molecular weight of polyureas, was also varied to control the T_g. The first prepolymer was prepared from dimethyl-1,4-butylenedicarbamate (BU2) and polypropylene glycol bis (2-aminopropylether) (PPGda_{400}, M_n=400), but the T_g was low(-43 °C). Therefore afterwards similar dicarbamate with different length were used. However, no evident change on T_g can be observed. After that a shorter diamine, Polypropylene glycol bis (2-aminopropylether) (PPGda_{230}, M_n=230), was employed, and the T_g of the resulting product reached to 25°C when the molecular weight was 21 kDa. Another series of prepolymeres were prepared from isophorone diamine (IPDA), BU2 and PPGda_{400}. The T_g of the resulting prepolymeres experienced a great enhancement. IPDA was utilized due to its rigid structure and the steric effect, which can enhance T_g. However, it is not guaranteed that IPDA+BU2+PPGda_{400} prepolymeres have diamine groups on both sides, which is very important in the upcoming dispersion preparation. In addition, the prepolymeres containing BU2 have solubility issues, which can hinder the formation of dispersion. This was improved when isophorone diacarbamate (IPDC) was used instead of IPDA. IPDC was used to react with 4,7,10-Trioxa-1,13-tridecanediamine (TOD), 4,9-Dioxa-1,12-dodecanediamine (DDD) to prepare prepolymeres. The obtained TOD+IPDC and DDD+IPDC prepolymeres were modified with EDTAD to prepare stable waterborne polyurea dispersions. Coatings were prepared from the dispersions under room temperature, which can pass impact tests and have reasonable solvent resistance.

The results obtained in this research include:
(1) Length of the alkyl-dicarbamate has limited effect on the $T_g$ of the alkyl-dicarbamate +BU2 prepolymer.

(2) Replacing PPGda400 with PPGda230 helps to increase the $T_g$ of the polyurea.

(3) $T_g$ of BU2+PPGda230 prepolymer can not reach 30-50°C even with high molecular weight.

(4) Increasing IPDA content can lead to polymers with higher $T_g$s.

(5) Water-borne polyurea coatings with desired Tg were prepared.
1 Introduction

Polyurethanes (PUs) are a wide variety of polymers which are characterized by their urethane linkage in the backbone. The polymers that contain urea linkage in the backbone are known as polyureas, however, they are also acknowledged as polyurethanes, for their similar physical properties and synthesis methods with polyurethanes, as well as overlapped applications. Since their invention in 1937, polyurethanes have been drawing much attention from scientists all over the world. Today, polyurethanes are still finding wide applications in car coating, flooring, furniture and foam materials, and more than 10 megatons annually are produced.

1.1 Isocyanate chemistry of polyurethanes and polyureas

In conventional polyurethane industry, PUs are synthesized from the polyaddition reaction of diols (or polyols) or diamines (or polyamines) and diisocyanates. Figure 1.1 shows the basic reactions of conventional isocyanate-based method of synthesizing linear polyurethanes and polyureas. The structure of PUs can vary from case to case because there are vast amount of starting materials can be choose from. The properties of PUs are highly dependent on the starting materials. Thus by altering the starting materials researchers can prepare PUs with desired materials properties for specific applications.

In industry, the most frequently used diisocyanates are aromatic diisocyanates, such as toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), etc., for their resulting PUs display better mechanical properties, and they can react more easily with polyols than many other diisocyanates. However, they are not appropriate for coating applications due to the poor UV resistance and weathering issues. If they are exposed to light and high temperature for long time, the color of the polymer will change with time, which is undesirable in coating applications. Therefore, PUs coatings are often prepared from aliphatic starting materials. In this work, aliphatic starting materials are utilized to prepare polyureas, because the polyureas prepared in this study are expected to be used as coatings.
1.2 Isocyanate-free chemistry of polyurethanes and polyureas

As the environmental problems accumulate in recent years, the concept of green chemistry is becoming increasingly popular in research groups and industries all over the world. It is the same in PU industry: many researchers in this area are attempting to find out an isocyanate-free method to produce PU. Since in conventional method, diisocyanates are used as starting material and they are highly toxic. In addition, the diisocyanates are usually prepared from phosgene, which is also extremely toxic.\(^4,9,10\)

There were quite many pioneering works in the isocyanate-free methods of synthesizing polyurethane/urea. For example, Ihata O. et al.,\(^11\) prepared polyurethanes using aziridines and carbon dioxide. However, aziridines are also highly toxic as phosgene and isocyanate. Palaskar et al.,\(^12\) reported a self-condensation route using A-B type monomers synthesized from plant oil to produce polyurethane. However, toxic intermediates formed during the reaction. To avoid the drawbacks of these methods, most researchers see dicarbamates and cyclic carbonates as the most favorable alternatives for diisocyanates.\(^4,13-19\) Dicarbamates can be obtained from many non-phosgene or non-diisocynate pathways, and can react with diols or diamines in bulk to form PUs via polycondensation. It means the whole process is non-toxic and free of solvent, which is environmentally friendly.\(^4\) In this thesis, dicarbamates were employed to synthesize polyureas, and the reactions related to dicarbamates and polyureas preparation will be introduced in chapter 3.
1.3 Hydrogen bonding in PUs

Hydrogen bonding exists in PUs, it is formed between urethane and/or urea linkages. Hydrogen bonding have great impact on the properties of PUs. For example, phase separation in PUs is related to hydrogen bonding, and the mechanical properties of PUs can be enhanced by hydrogen bonding. The effect of hydrogen bonding on phase separation depends on where the hydrogen bonding exists: if it exists only between hard segments, the phase separation of hard segments and soft segments will be facilitated, but if it exists between hard segments and soft segments, the hard segments and soft segments in the polyurethane tend to mix instead of separate.\textsuperscript{21} Figure 1.2 shows the hydrogen bonding of polyurethane and polyurea.

\textit{Figure 1.2 Hydrogen bonding in polyurethane and polyurea.}

As shown in the figure 1.2, in polyurethanes, the hydrogen bonding forms between one O atom and one H atom, which is also known as monodentate hydrogen bonding; In polyureas, one O atom can interact with 2 H atoms to form hydrogen bonding, also known as bidentate hydrogen bonding.\textsuperscript{22,23} It is confirmed by Yilgör, E., et al.\textsuperscript{24} that the bidentate hydrogen bonding is stronger than monodentate hydrogen bonding. Therefore, with assistance of
bidentate hydrogen bonding, the polyureas have better mechanical properties than polyurethane with similar building blocks.

1.4 Waterborne PU coatings

The properties of PUs, such as scratch resistance, excellent mechanical properties and chemical resistance etc., make PUs stand out from other polymers which also act as organic coating materials. Traditionally, PU coatings are solvent borne, however, due to the high VOC level (volatile organic compounds) of solventborne coatings, it is becoming increasingly difficult for them to meet the strict environment requirements at present. Therefore, waterborne coatings are more favored compared with solventborne coatings. Waterborne PU coatings are usually produced based on PU dispersions. In general, to disperse PU into water, the hydrophilicity of PUs should be increased via modification. The hydrophilicity of PUs is very important because it can affect the particle size distributions of PU dispersion.

The modification is carried out by introducing hydrophilic groups into the PUs backbones. The role of hydrophilic groups are internal stabilizers. According to the types of the hydrophilic groups, the PU dispersions can be classified as 3 types: cationic PU, anionic PU and non-ionic PU. For example, if carboxyl groups, tertiary amine groups and poly(ethylene oxide) groups are introduced, cationic PU, anionic PU and non-ionic PU will form, respectively. Except for the modification, adding a surfactant is another way to prepare dispersion.

When modified PUs are dispersed into water, the hydrophilic and hydrophobic parts of PUs can re-arrange, and the PUs will aggregate to form micelles. The double layers surrounding the micelles are regarded as being responsible for the stable dispersion of the PU micelles in water (see Figure 1.3). The film formation of PU waterborne coating was performed by spraying the dispersions on the substrates and evaporating the water (see Figure 1.4). With the evaporation of water, the micelles started to pack and then deformed, which was driven by the surface and capillary forces. Afterwards, the entanglement (also known as coalescence) of polymer chains from different micelles occurred, which results in the fusion of the micelles. After that, a continuous film is formed with further coalescence.
1.5 Molecular weight control

The reactions between diamines or diamines and diisocyanates or dicarbamates can be classified as step-growth polymerization. In those reactions, molecular weight control is a significant factor to consider, because their molecular weight can have significant influence on the properties of the final products. There are several molecular weight control methods available. For example, molecular weight can be controlled by stopping the reaction before 100% conversion, adding a chain stopper to introduce chain ends that can not further react with other functional end groups or altering the feed ratio between the starting materials.20 In this research, the molecular weight was controlled through altering the feed ratio of diamine to dicarbamate. To achieve this, diamine was added in excess to react with dicarbamate. The reaction stopped when the dicarbamate was consumed completely and the polymer chains produced just contain amine end functional groups. The more nonstoichiometric the two starting materials are, the smaller molecular weight can be expected. In other words, when product with a small molecular weight is needed, large feed ratio of diamine to dicarbamate is required. For PUs, apart from the molecular weight, the end functional groups of prepolymer are another essential factor to consider. Because if the end functional groups of the prepolymer can not react with a dispersing agent, carboxyl groups can not be introduced into the backbones of the polyurea in the dispersion preparation step. Thus it is very important that the prepolymer should have the same end functional groups on both sides that can react with the dispersing agent.20 In this research, prepolymer with amine end functional groups were the desired product of the prepolymer preparation step.
Figure 1.3 The cationic and anionic PU dispersions in water.

Figure 1.4 Film formation of dispersion.

Each latex particle contains several polymer chains

Water evaporation and latex particle packing

Water diffusion and particle deformation

Polymer chain interdiffusion and loss of particle boundaries

Figure 1.4 Film formation of dispersion.
1.6 Outlook

In this research, the film formation of the dispersions can proceed at room temperature, which makes the dispersion very convenient for application. In the film formation, $T_g$ is a very important factor to be considered in designing the polyureas. The range of 30-50°C is considered to be ideal in this research. Indeed, if the $T_g$ is too high, the contraction and deformation in the film formation of polyureas particles will not be achieved at room temperature, which leads to cracking of film. But if the $T_g$ is too low, the strength of the coating will not be high enough. Thus, the goal of this research is to find an isocyanate-free route to prepare the polyureas, and to design the structure of the polyureas to obtain desired $T_g$. 
2 Materials and Methods

2.1 Materials

The chemicals such as 1,2-diaminoethane (DAE), 1,3-diaminopropane (DAMPA), 1,4-diaminobutane (DAB), 1,5-diaminopentane (DAP), 1,6-diaminohexane (DAH), 1,7-diaminoheptane (DAPA), 1,8-diaminoctane (DAO), dimethylcarbonate (DMC), isophorone diamine (IPDA), 1,5,7-triazabicyclo [4,4,0]dec-5-ene (TBD), polypropylene glycol bis (2-aminopropylether) (PPGda\textsubscript{230}, M\textsubscript{n}=230 g/mol), polypropylene glycol bis (2-aminopropylether) (PPGda\textsubscript{400}, M\textsubscript{n}=400 g/mol), ethylenetetraacetic dianhydride (EDTAD), 4,7,10-trioxa-1,13-tridecanediamine (TOD), trimethylamine (TEA) and dimethylacetamide (DMAc) were purchased from Sigma-Aldrich. Priamine was purchased from Croda Europe. 4,9-dioxa-1,12-dodecanediamine (DDD) was purchased from TCI. All the other solvents were purchased from Biosolve B.V..

2.2 Method

2.2.1 Preparation of dicarbamates\textsuperscript{36}

In an typical experiment, 1.25 mol of dimethylcarbonate (DMC), 0.5 mol of 1,4-diaminobutane (DAB) and 0.01 mol of TBD were added into a 500 ml beaker. After 30 minutes reaction at room temperature, and then afterwards, 350 ml diethylether (DE) was poured into the beaker. The precipitate was filtrated and washed with DE before dissolving in chloroform for recrystallization. The crystalline solid (dicarbamate BU2) was then filtrated and dried under vacuum for 12 hours at 60 °C. The procedure of the reaction between DMC and other diamines is the same, except for IPDA.

BU2: Yield:87%; \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) δ: 4.75 ppm (d, 1H, -NHCH\textsubscript{2}), 3.61 ppm (s, 3H, -CH\textsubscript{3}), 3.2 ppm (s, 2H, -NHCH\textsubscript{2}), 1.52 ppm (d, 2H, -NHCH\textsubscript{2}CH\textsubscript{3}).\textsuperscript{36}
2.2.2 Preparation of isophorone dicarbamate

Into a 2000 mL three-neck flask equipped with a condenser, 170 g (1 mol) of IPDA and 630 g (7 mol) of DMC were added. 70 g (1 mol) of sodium methoxide was added into the mixture under a argon flow at room temperature. The mixture was heated up to 60 °C after 4 hours and continued for another 6 hours. After that, excess of chloroform was added into the mixture, and then after 1 hour the chloroform layer was separated followed by being washed with brine and dried with anhydrous sodium sulphate. In the last step, the chloroform layer was evaporated to obtain a light yellow solid (150 g, yield 52%) \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\):

- 4.75 ppm (d, 1H, -NH\(_2\)),
- 4.6 ppm (s, 1H, cy-NHCH),
- 3.8-3.6 ppm (s, 1H, cy-CH-NH + d, 6H,-OC\(_3\)H\(_3\)),
- 3.3, 2.9 ppm (d, 2H,-CH\(_2\)NH),
- 1.7-0.7 ppm (15H, cy-H). \(^{37}\)

2.2.3 Preparation of prepolymers

The prepolymers were synthesized from reaction between one dicarbamate and one or two diamines. The diamines employed were polypropylene glycol bis (2-aminopropylether) (PPGda\(_{230}\), \(M_n=230\) g/mol), polypropylene glycol bis (2-aminopropylether) (PPGda\(_{400}\), \(M_n=400\)), priamine, 4,7,10-trioxa-1,13-tridecanediamine (TOD) and 1,4-butanediol bis(3-aminopropyl) ether (DDD).

Diamines, dicarbamate and TBD were added into a flask. The reaction proceeded overnight under argon flow at 120 °C, after which, vacuum was applied for another 6 hours. The product was then washed with water and dried in vacuum oven at 80°C overnight to obtain the polyurea.

2.2.4 Preparation of poly(amic acid urea)

In a 50 mL crimp-capped vial, 4 g of prepolymer and a stoichiometric amount of EDTAD were dissolved in 12 g of DMAC, and stirred at 80 °C for 30 minutes. The solution was then quenched into toluene and washed with water before drying in oven at 80 °C for 10 h to obtain 3.94 g poly(amic acid urea) as product (yield:86%).
2.2.5 Preparation of waterborne dispersions

In a 50ml glass bottle, 0.75 g of poly(amic acid urea) was dissolved in 0.8 g of methanol(or 2-propanol). And then, the solution was neutralized with 0.01 g of TEA under stirring. After a period of about 30 minutes, the mixture was then slowly added into deionized water at 800 rpm. Eventually, a milky or transparent dispersion was formed after hours of stirring.

2.2.6 Preparation of waterborne coatings

The dispersion obtained from 2.2.5 was dropped on clean aluminium plates and spreaded with a gap applicator to form wet films. In this step, gap sizes of 120 µm and 250 µm were selected. Since the viscosity of the water dispersion is relatively low, the aluminium plates must be placed horizontally. The wet films were subsequently dried at room temperature to obtain coatings.

2.3 Characterization

2.3.1 Differential scanning calorimetry (DSC)

The glass transition temperature \( T_g \) of the prepolymer and the poly(amic acid urea)s were obtained by using TA Instruments DSC Q1000. 5-8 mg of sample were placed in an aluminium pan and equilibrated at 25°C. And the temperature stayed constant for 5 minutes, then reduced to -80°C at a rate of 10K per min, and then stayed constant for another 5 minutes. After that, the temperature increased to 150°C at a rate of 10K per min, and then return back to 25°C. The test ended after a repeating cycle.

2.3.2 Nuclear magnetic resonance spectroscopy (NMR)

H-NMR measurements were performed on a Varian Mercury Vx(400 MHz) spectrometer at room temperature, 16 scans and 2s of delay time were selected for the dicarbamates, and 32
scans and 5s were selected for the prepolymers. In addition, CDCl$_3$ or DMSO-d$_6$ were utilized as solvents to dissolve the dicarbamates or the prepolymers in sample preparation.

2.3.3 Gel Permeation Chromatography (GPC)

A gel permeation chromatography analyzer was employed to determine the molecular weight of samples, which used DMAc with Lithium chloride as eluent. The flow rate was set as 1 mL/min. The GPC analyzer is equipped with a Waters 2695 separations module and a water 2414 refractive index detector.

2.3.4 Potentiometric titration

Potentiometric titration was performed to determine the molecular weight of the prepolymers with amine end groups or the number of moles of carboxyl groups introduced into the backbones of the poly(amic acid urea)s. The sample for titration was prepared by dissolving 1 g of prepolymer or poly(amic acid urea)s into 40mL of solvent (methanol, 2-propanol, or/and HFIP). The prepolymer was titrated with 0.1 mol/L HCl solution to define the amount of amine end groups of the prepolymers. Because each prepolymer chain has 2 amine end groups, the amount of the prepolymer chains can be determined. The molecular weight can be calculate by dividing the weight of prepolymer with the amount of the prepolymer chains. The poly(amic acid urea)s was titrated with 0.1 mol/L KOH solution, and the number of the moles of carboxyl groups in the poly(amic acid urea)s was determined by the volume of KOH consumed.

2.3.5 Particle size and and ζ-potential of dispersion

The particle size and ζ-potential of the dispersions were measured with Dynamic Light Scattering and Laser doppler micro-electrophoresis techniques on a Malvern ZetaSizer Nano ZS at room temperature. Before the particle size and ζ-potential measurements, the dispersions were diluted with deionized water (1:50 by weight). The moving speed of particles related to Brownian motion was first measured through dynamic light scattering. The size and
size distribution of particles were calculated through the Stokes-Einstein equation by the computer. In the equation, the relationship between speed and size of particles is defined. Laser doppler micro-electrophoresis was used by the apparatus to measure first the velocity of the particles under an electric field. Then electrophoretic mobility was calculated according to the velocity followed by calculating the ζ-potential through the mobility.  

2.3.6 Reverse impact test and double rub test

A BYK-Gardner ISO impact tester was used to test the coating impact resistance. The coated panel was fixed on the die of the tester with the coating side facing down, and a 1kg of weight was lifted vertically up to 1.0 m from the panel and then released to hit on the panel. The solvent resistance of the coatings was determined with double rub test. The acetone, water and toluene were used as testing solvent. The coatings were double rubbed 100 times with a rag that was saturated with solvent. If the coating is not damaged after the double rub test, the coating was consider as having good solvent resistance.

2.3.7 Thickness and Hardness test

The thickness of the coatings was tested with a TQC Layer Thickness Meter. The hardness test was carried out using a scratch hardness tester. Pencils with hardness ranging from 6H to 6B were selected to scratch on the coating. The hardness of coating was determined when no sign of scratch on the coating was observed.
3 Results and discussion

3.1 Preparation of dicarbamates

In the dicarbamate synthesis, dimethylcarbonate (DMC) in excess and diamines were utilized (Figure 3.1). All the diamines and their resulting dicarbamates that used in this research were listed in Table 3.1.

![Figure 3.1 Methoxycarbonylation between diamine and dimethylcarbonate (DMC).](image)

There were 2 types of diamines were employed in this research: primary aliphatic linear diamines and primary aliphatic diamine with cyclic ring structure. Thus two different types of dicarbamates were obtained. The aliphatic linear diamines were a series of diamines with 2-8 carbons in their alkyl chains, including DAE, DAMPA, DAB, DAP, DAH, DAPA and DAO. The corresponding dicarbamate products from these diamines with linear structure were EU2, PRU2, BU2, PEU2, HU2, HEU2 and OU2, respectively. And the diamine with cyclic structure was isophorone diamine (IPDA) and the resulting dicabamate was dimethyl isophorone dicarbamate (IPDC).

![Figure 3.2 Hydrogen bonding of BU2 and PEU2](image)

This reaction between dimethylcarbonate (DMC) and diamines is exothermic, at onset of the reaction, the temperature of the mixture started to increase until high conversion of substrates was achieved. Because at the high conversion, the exothermic process became considerably slower, leading to a drop in temperature. For the reaction between the aliphatic
diamines with linear structure and DMC, when the mixture cooled down, the dicarbamates that precipitated during the reaction were washed with DE before recrystallizing in CHCl₃. The precipitation rate of the dicarbamates was closely related to their structure. The dicarbamates with odd carbon numbers generally precipitated slower than their even-numbered counterparts since the fit between the even-numbered dicarbamate is better (see Table 3.1). Such better fitting not only facilitates the formation of hydrogen bonds between the urethane moieties, but also gives better packing of aliphatic chains, leading to a faster crystallization rates.³⁹ As can be seen from Figure 3.2, as the better fit between BU2 molecules than PEU2 molecules, more hydrogen bonds can form between the BU2 molecules compared to PEU2 molecules, leading to a stronger tendency to crystallize and then precipitate. The same trend was also observed during the recrystallization of the dicarbamates. However, for the reaction between IPDA and DMC, no precipitation or recrystallization of isophorone dicarbamate (IPDC) can be observed. The incapacity of precipitation and recrystallization of IPDC is due to the high steric hindrance coming from the three pending methyl groups and cyclic rings. Such steric effect prevents the hydrogen bonds formation between the urethanes and prevents the chain packing, which will be discussed in later sections.

It is interesting to notice that in the Table 3.1, although PRU2 has the least carbon number among the dicarbamates with odd carbon number, it was the one took the longest time to precipitate and recrystallize compared to the other dicarbamates with odd carbon number. A reasonable explanation could be due to the higher concentration of the methyl end-group compare with other aliphatic dicarbamates. These methyl groups can disrupt the packing between the dicarbamates.
Table 3.1 Various diamines and related dicarbamates.

<table>
<thead>
<tr>
<th>Diamine</th>
<th>Precipitation time (hour)</th>
<th>Recrystallization time (hour)</th>
<th>Dicarbamate product</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₈N₂ (DAE)</td>
<td>0.4</td>
<td>5</td>
<td>EU2</td>
</tr>
<tr>
<td>C₃H₁₀N₂ (DAMPA)</td>
<td>12</td>
<td>160</td>
<td>PRU2</td>
</tr>
<tr>
<td>C₄H₁₂N₂ (DAB)</td>
<td>0.3</td>
<td>4</td>
<td>BU2</td>
</tr>
<tr>
<td>C₅H₁₄N₂ (DAP)</td>
<td>3</td>
<td>47</td>
<td>PEU2</td>
</tr>
<tr>
<td>C₆H₁₄N₂ (DAH)</td>
<td>0.3</td>
<td>4</td>
<td>HU2</td>
</tr>
<tr>
<td>C₇H₁₈N₂ (DAPA)</td>
<td>2</td>
<td>40</td>
<td>HEU2</td>
</tr>
<tr>
<td>C₈H₁₆N₂ (DAO)</td>
<td>0.3</td>
<td>3</td>
<td>OU2</td>
</tr>
<tr>
<td>IPDA</td>
<td>N/A*</td>
<td>N/A*</td>
<td>IPDC</td>
</tr>
</tbody>
</table>

*N/A stands for no precipitation or recrystallization can be observed.*
3.2 Preparation of prepolymer

To acquire a polyurea with better material properties, we need to introduce both soft and hard-segments in the polymer backbone. Poly(propylene glycol) diamine was chosen as the soft segment due to its flexibility and the methyl group from the propylene glycol segments can prevent the polymer from crystallization as well as improve the \( T_g \) of the material.

The first polyurea prepolymer in the project was synthesized from \( \text{PPGda}_{400} \ (M_n=400 \text{ g/mol}) \) and \( \text{BU2} \) in the presence of TBD as catalyst (see Figure 3.3).

\[
\begin{align*}
\text{PPGda}_{400} & + \text{BU2} \\
\rightarrow & - \text{CH}_3\text{OH}
\end{align*}
\]

Figure 3.3 Preparation of a diamino-terminated prepolymer and the corresponding \(^1\text{H}-\text{NMR}\) spectrum
For this reaction, the molar ratio between the two monomers determines both molecular weight of the prepolymer and what end groups the prepolymer contains. As mentioned in Chapter 1.5, larger ratio between the diamines and dicarbamates lead to lower molecular weight of the resulting prepolymers. Molecular weight is an important factor to be considered in dispersion preparation, because it has a great influence on the properties of the final coating product. If diamine is added in excess, diamino-terminated prepolymers (prepolymer that contains only amine end groups) can be produced. However, if dicarbamate is added in excess, dicarbamate-terminated prepolymer can be expected to be generated, which is unwanted in this research. Diamino-terminated prepolymer is required in the dispersion preparation because ethylenetetraacetic dianhydride (EDTAD) which acts as both the dispersing agent and chain extender can react with amine end groups instead of carbamate end groups to introduce carboxyl groups into the backbone of the polyurea. For preparing the first prepolymer, a molar ratio between diamine and dicarbamate of 1.3:1 (PPGda400 to BU2) was chosen.

According to the $^1$H-NMR spectrum of the PPGda400-BU2 prepolymer (Figure 3.4), signal a (0.8 ppm) and b (1.0 ppm) reflect the chemical shifts of protons on the two end methyl groups and those on the repeating units of PPGda400, respectively. Based on the ratio between the integration of a and b, the molecular weight of the prepolymer was calculated as follows:

$$\frac{a}{2b} = \frac{1}{(m+1) \times n}$$

where m is the number of repeating units of the prepolymer, and n is the number of repeating PPG units in PPGda400. With these repeating units, $M_n$ of prepolymer is thus determined as 3.7 kDa. However, in some cases, because of the proximity of signal a and b, overlapping of the signals a and b might be observed. If this is the case, the calculation can be performed using the ratio between signals c or d and (a+b) to determine the molecular weight.

The $T_g$ of the prepolymer was measured by DSC to be -43°C, which is too low for coating applications. To increase the $T_g$ of the prepolymer, different dicarbamates from EU2 to OU2 were chosen to polymerize with PPGda400, with a ratio of 1.3:1 (diamine: dicarbamate). This was based on the consideration that the length of the hard segments (dicarbamate) may affect the $T_g$ of the related prepolymer. Table 3.2 shows the $T_g$ and $M_n$ of these prepolymers. There is no certain trend in the $T_g$ can be observed when the length of the hard segments
(dicarbamate) change, and all of the $T_g$s are within a range of -33 °C to -44 °C. It indicates that changing the length of the hard segments might not be an effective way to enhance the $T_g$ of the prepolymers to reach the ideal $T_g$ range. This is probably due to the inability of the flexible linear aliphatic chains fail to restrict the chain motion of the polymers, which is crucial for improving the $T_g$ of the polymer. Therefore, a more effective way should be employed to enhance the $T_g$ of the prepolymer.

Table 3.2 $T_g$, $M_n$ and of molecular weight distribution dicarbamate+PPGda$_{400}$ prepolymers.

<table>
<thead>
<tr>
<th>Prepolymer (1:3:1)</th>
<th>$T_g$ (°C, DSC)</th>
<th>$M_n$ (kDa, DMAc-GPC)</th>
<th>Molecular weight distribution</th>
<th>$M_n$ (kDa, MNR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EU2+PPGda400</td>
<td>-42</td>
<td>5.2</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>PRU2+PPGda400</td>
<td>-44</td>
<td>5.9</td>
<td>1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>BU2+PPGda400</td>
<td>-36</td>
<td>8.7</td>
<td>1.7</td>
<td>3.2</td>
</tr>
<tr>
<td>PEU2+PPGda400</td>
<td>-34</td>
<td>11.2</td>
<td>1.7</td>
<td>4.8</td>
</tr>
<tr>
<td>HU2+PPGda400</td>
<td>-39</td>
<td>9.4</td>
<td>1.7</td>
<td>3.4</td>
</tr>
<tr>
<td>HEU2+PPGda400</td>
<td>-38</td>
<td>9.4</td>
<td>1.7</td>
<td>3.2</td>
</tr>
<tr>
<td>OU2+PPGda400</td>
<td>-42</td>
<td>6.9</td>
<td>1.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>

In the following polymerization experiment, a new route was chosen. In the new route, PPGda$_{400}$ was replaced by PPGda$_{230}$ to investigate if the soft segments (PPGda$_{230}$) can enhance the $T_g$ of the prepolymer. This is based on the consideration that with shorter soft segment, the concentration of the urea moieties becomes higher, the strong hydrogen bonds between which can help to restrict the chain motion of the polymer chains, thereby increasing the $T_g$. PPGda$_{400}$ and PPGda$_{230}$ are very close in structure, the only difference between these two
diamines is the number of repeat units. In the reaction, three BU2+PPGda$_{230}$ prepolymer were prepared with feed ratios (diamine to dicarbamate) of 1.3:1, 1.2:1 and 1.1:1, respectively.

The results of $M_n$ and $T_g$ of the BU2+PPGda$_{230}$ prepolymer from NMR and DSC are shown in Table 3.3. As can be seen in the Table 3.3, Compared to the overall $T_g$s of the PPGda$_{400}$ prepolymer series, the $T_g$s of the PPGda$_{230}$ series are higher and closer to the ideal range (30-50°C), it indicates that shorter soft segment can enhance the $T_g$ of the prepolymer. This is because with shorter soft segments, the density of hard segments in the BU2+PPGda$_{230}$ prepolymer is higher than that of BU2+PPGda$_{400}$ prepolymer. As a result, higher density of hydrogen bonds formed among the hard segments, and the hydrogen bonds restricted the chain motion of the BU2+PPGda$_{230}$ prepolymer chains, which results in higher $T_g$s of the prepolymer.

Apart from the soft segments, the $M_n$ of the BU2+PPGda$_{230}$ prepolymer was playing an important role in the increase of the $T_g$s as well. The $M_n$ of the BU2+PPGda$_{230}$ prepolymer was related to the feed ratio of the monomers. With increasing feed ratio (PPGda to BU2), the $M_n$ of the prepolymer from NMR rose from 2.7K to 3.5K and then 3.8K. And the corresponding $T_g$ also witnesses a rising trend from 10°C, 16°C and then 25°C. The possible reason for the rising of $T_g$ among the BU2+PPGda$_{230}$ prepolymer is that the percentage of the end chains of the prepolymer became lower when the molecular weight increased. The chain motion of end chains are considered to be greater than the internal chain, thus lower percentage of the end chains can lead to less free volume, which means higher $T_g$. It is noteworthy that there a maximum value of $T_g$ a polymer can reach, in other words, the maximum value is for the polymer with an infinite molecular weight. However, as can be seen from the Table 3.3, even with a high molecular weight of 3.8 kDa, the $T_g$ of prepolymer is still low. Thus it means even after chain extension, the $T_g$ of the polymer might still not reach the desired range of 30-50°C for the final coating application. Thus another approach should be adopted.
Table 3.3 $T_g$, $M_n$ and of molecular weight distribution of BU2+PPGda230 prepolymers.

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>$T_g$ (°C)</th>
<th>$M_n$ (kDa, DMAc-GPC)</th>
<th>Molecular weight distribution</th>
<th>$M_n$ (kDa, NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BU2+PPGda$_{230}$ (1:1:1)</td>
<td>25</td>
<td>20.7</td>
<td>2.4</td>
<td>3.8</td>
</tr>
<tr>
<td>BU2+PPGda$_{230}$ (1:2:1)</td>
<td>16</td>
<td>11.4</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>BU2+PPGda$_{230}$ (1:3:1)</td>
<td>10</td>
<td>10.0</td>
<td>1.5</td>
<td>2.7</td>
</tr>
</tbody>
</table>

As widely accepted$^{20}$, the rigidity of the backbone has a significant effect on the $T_g$ of polymer. Therefore another way we chose to increase the $T_g$ of the prepolymer was to employ IPDA (Figure 3.4) as a monomer, since IPDA has pendent methyl groups and a cyclic ring to restrict the chain motion, thereby increasing the $T_g$ of the polymer. A series of BU2+IPDA+PPGda$_{400}$ with different molar fractions of IPDA were added. Since IPDA is volatile and can escape during the reaction, the amount of IPDA incorporated in the prepolymer chains were not necessary the same as the original amount that were added at the beginning of the reaction. Thus $^1$H-NMR was used to analyze the prepolymer structure and determine the IPDA content contained in the BU2+IPDA+PPGda$_{400}$ prepolymers.

The results of a series of IPDA+PPGda$_{400}$+BU2 prepolymers obtained from DSC, NMR and GPC are summarized in Table 3.4. As shown in the table, comparing prepolymers 1 to 3, although the IPDA contents are basically the same, the prepolymers with larger $M_n$ have higher $T_g$. It indicates that the $M_n$ may be responsible for the increase of the $T_g$.

![Figure 3.4 Structure of IPDA.](image)

Apart from the $M_n$, IPDA concentration in the polymer backbone may have significant influence on the $T_g$s of the prepolymers as well. After the introduction of IPDA, the general $T_g$s of the IPDA+PPGda$_{400}$+BU2 prepolymers are much higher than those of PPGda$_{400}$+BU2
prepolymers. This is because the chain motion of polymer can be restricted by the steric effect of the cyclic structure of IPDA and the rigidity of segments that IPDA formed with BU2 (see the segment (1) in the following paragraph).

In the IPDA+PPGda$_{400}$+BU2 prepolymers, three possible types of segments could be generated instead of only one in the PPGda$_{400}$+BU2 prepolymers:

—IPDA—BU2—IPDA—BU2—IPDA—BU2—IPDA— (1)

—PPGda$_{400}$—BU2—PPGda$_{400}$—BU2—PPGda$_{400}$—BU2— (2)

—PPGda$_{400}$—BU2—IPDA—BU2—PPGda$_{400}$—BU2—PPGDA$_{400}$—BU2—IPDA— (3)

Segment (1) consists of alternative BU2 and IPDA moieties which are both hard segments. The steric effect of IPDA can make the segment chain more difficult to rotate, leading to the relatively high rigidity of the segment (1).

With the addition of IPDA, two separated $T_g$s (see Figure 3.5) can be observed in the DSC curves of some prepolymer products, especially when IPDA content is relatively low. It indicates that micro phase separation exists in the IPDA+PPGda$_{400}$+BU2 prepolymers with low IPDA content. This phenomenon was not observed in PPGda$_{230}$+BU2 and PPGda230+BU2 prepolymers. The hydrogen bonding between –NH– and –CO– groups is generally regarded as a plausible reason.

Table 3.4 $M_n$ and $T_g$ Results of IPDA+PPGda$_{400}$+BU2 prepolymers with different IPDA content.

<table>
<thead>
<tr>
<th>Polyurea Prepolymer Number</th>
<th>IPDA content (mol%)</th>
<th>$T_g$ (°C)</th>
<th>$M_n$ (kDa, GPC)</th>
<th>Molecular weight distribution</th>
<th>$M_n$ (kDa, NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34</td>
<td>87</td>
<td>8.7</td>
<td>1.6</td>
<td>4.2</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>80</td>
<td>7.5</td>
<td>1.6</td>
<td>3.2</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>39</td>
<td>4.2</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>47</td>
<td>10.0</td>
<td>1.7</td>
<td>4.4</td>
</tr>
<tr>
<td>5</td>
<td>27.5</td>
<td>19</td>
<td>7.7</td>
<td>1.6</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>-17 and 95</td>
<td>8.0</td>
<td>1.7</td>
<td>2.3</td>
</tr>
<tr>
<td>7</td>
<td>17.5</td>
<td>1 and 106</td>
<td>10.7</td>
<td>1.7</td>
<td>4.1</td>
</tr>
<tr>
<td>8</td>
<td>14.5</td>
<td>2 and 95</td>
<td>12.4</td>
<td>1.8</td>
<td>4.0</td>
</tr>
<tr>
<td>9</td>
<td>7.5</td>
<td>-27 and 71</td>
<td>8.0</td>
<td>1.5</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>-26 and 76</td>
<td>10.0</td>
<td>1.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>
for phase separation in PUs. However, this is not the case in the IPDA+PPGda400+BU2 prepolymer, because the steric effect of IPDA can hinder the formation of hydrogen bonding between the BU2 moieties. If the hydrogen bonding between the BU2 moieties was strong enough, phase separation would have been occurred in PPGda400+BU2 prepolymer already. Because without the hindrance of other moieties, hydrogen bonding can form more easily in the PPGda400+BU2 prepolymer. Given the hindrance of IPDA, it is almost impossible for hydrogen bonding to drive the phase separation in the IPDA+PPGda400+BU2 prepolymer. The micro phase separation might be explained by the LCST and UCST behavior (see Figure 3.6). The IPDA+PPGda400+BU2 prepolymer can be regarded as a mixture of those three potential segments mentioned above. The horizontal axis of Figure 3.6 is the composition of polymer mixture and the vertical axis is the temperature or the reciprocal of polymer-polymer interaction parameter $\chi^{-1}$. There is a spinodal line that separates the unstable region and the meta-stable region, and a binodal line that separates the stable region and the metastable region in the phase diagram. In the stable region, also called single phase region, different phases are miscible. The polymer mixture in the stable region can be driven by the change of composition and/or temperature to pass through the metastable region from the stable region to the unstable region, and then phase separation will occur. For the IPDA+PPGda400+BU2 prepolymer, the composition of those segments changed as the IPDA
content varied, when the IPDA content was low, the prepolymer found itself in the unstable region, leading to the phase separation.

Although the $T_g$s of IPDA+PPGda$_{400}$+BU2 prepolymers can reach the required range of 30-50 °C, there is still another challenge to be tackled. The problem is that with addition of IPDA, carbamate terminated prepolymers were also formed in some cases, which was confirmed by $^1$H-NMR (see Figure 3.7). As shown in the figure, carbamates groups related peak can be observed around 7 ppm in contrast with the spectrum of PPGda$_{400}$+BU2, where no such peak presents. It is suspected that those unreacted carbamate groups are related to hard segments domains which are mainly composed of $-$IPDA$-$BU2$-$IPDA$-$BU2$-$IPDA$-$BU2$-$IPDA$-$BU2$-$ segments. Since the segments are relatively long and rigid, their unreacted carbamate groups can easily be trapped in the domain and thus their chance of further reacting with amine groups diminished. As a result, prepolymers with unreacted carbamate groups remained, which is not desired for our further dispersion preparations.

Figure 3.6 Phase diagram of polymer mixture.

Although the $T_g$s of IPDA+PPGda$_{400}$+BU2 prepolymers can reach the required range of 30-50 °C, there is still another challenge to be tackled. The problem is that with addition of IPDA, carbamate terminated prepolymers were also formed in some cases, which was confirmed by $^1$H-NMR (see Figure 3.7). As shown in the figure, carbamates groups related peak can be observed around 7 ppm in contrast with the spectrum of PPGda$_{400}$+BU2, where no such peak presents. It is suspected that those unreacted carbamate groups are related to hard segments domains which are mainly composed of $-$IPDA$-$BU2$-$IPDA$-$BU2$-$IPDA$-$BU2$-$IPDA$-$BU2$-$ segments. Since the segments are relatively long and rigid, their unreacted carbamate groups can easily be trapped in the domain and thus their chance of further reacting with amine groups diminished. As a result, prepolymers with unreacted carbamate groups remained, which is not desired for our further dispersion preparations.
To tackle the problem, the formation of the hard segments domain mentioned above should be avoided. This can be achieved by preventing the reaction between BU2 and IPDA. To prevent the reaction, IPDA was turned to IPDA-dicarbamate (IPDC) via the following reaction displayed in Figure 3.8. IPDC can only react with diamine instead of BU2, leading to separation between IPDC and BU2 moieties within the polymer chains. Afterwards, a series of IPDC+BU2+PPGda230 prepolymers were prepared and tested. As shown in the $^1$H-NMR spectrum (see Figure 3.9), no signal around 7 ppm can be seen. It indicates that the carbamate residue in the IPDA+PPGda400+BU2 prepolymers is related to the $-\text{IPDA—BU2—IPDA—BU2—IPDA—BU2—IPDA—BU2—}$ segments.

![Figure 3.7 $^1$H-NMR spectrum of IPDA+PPGda400+BU2 prepolymers.](image)

Figure 3.7 $^1$H-NMR spectrum of IPDA+PPGda400+BU2 prepolymers.

![Figure 3.8 preparation of IPDA-dicarbamate (IPDC).](image)

Figure 3.8 preparation of IPDA-dicarbamate (IPDC).
An important phenomenon should be mentioned here is that although BU2 units have a strong tendency to pack, all the prepolymer that were prepared were amorphous polymers. It was supported by the evidence that no crystallization peak or melting peak could be found in the DSC thermograms of the prepolymer (Figure 3.10). Crystallization peak and melting peak are related to the crystallization and melting process of crystals contained in polymer, respectively. Since the existence of crystals can render coating opaque, which is unwanted in coating application.
3.3 Preparation of waterborne polyurea dispersions

The procedure for the dispersion preparation is shown in the Figure 3.11. The diamine functional polyurea prepolymer and ethylenetetraacetic dianhydride (EDTAD) were first dissolved in DMAc and stirred until the high conversion of monomers was achieved, then the mixture was poured into water to precipitate. After that, the precipitate was dried in vacuum overnight to obtain the poly(amic acid urea). Then the poly(amic acid urea) was dissolved in a polar solvent (e.g. methanol) and neutralized with NEt$_3$, afterwards the solution was slowly added into of water and stirred overnight to give the dispersion. EDTAD is chosen amongst other dianhydrides here for two reasons: first reason is that the tertiary amines in the EDTAD can neutralize the carboxyl groups to form the zwitterionic species, this can help lower the amount of neutralization agent (toxic and volatile NEt$_3$ in this case) needed for the dispersion preparation process. The second reason is that unlike most of dianhydrides, there is no aromatic ring in EDTAD. As mentioned in Chapter 1.1, aromatic structure is the culprit in color changing of coatings. The dianhydride not only serves as an internal dispersing agent, which grant the polymer backbone with carboxyl groups, but also as a chain extender that increase the molecular weight of the polymer.

Initially, several poly(amic acid urea) samples were synthesized from IPDC+BU2+PPGda$_{400}$ prepolymer and EDTAD. However, in the following steps, a problem was encountered because it was difficult to dissolve these poly(amic acid urea)s in a suitable polar solvent. This is probably associated with the packing of BU2 units. Since it is difficult to find a suitable solvent, a series of new prepolymer were prepared to replace the BU2 based ones.
The substituents for the BU2 based prepolymers were the resulting prepolymer of new diamines (see Figure 3.12) and IPDC. The diamines, TOD and DDD, are employed because of their hydrophilic characteristics. And then, by addition of EDTAD, a series of TOD + IPDC and DDD + IPDC poly(amic acid urea)s were obtained. As a consequence, carboxyl groups were introduced into the backbones of the poly(amic acid urea)s, and the resulting poly(amic acid urea)s can be easily dissolved in methanol. Just like previous preparation of the prepolymers, molar ratios (TOD/DDD:IPDC) ranging from 1.03:1 to 1.4:1 were chosen to vary the molecular weights. As can be seen from the reaction, two amine groups react with one EDTAD to form two carboxyl groups. Potentiometric titration was used to determine the total amount of amine end groups that prepolymers contains and the amount of the carboxyl groups that were introduced to the backbones of the poly(amic acid urea)s.
Theoretically, the total amount of amine end groups that prepolymers contains should be equal to that of the carboxyl groups that were introduced to the resulting poly(amic acid urea), whereas this is not the case in practice. As can be seen in Table 3.5, the titration values of amine end groups in the prepolymer is larger than that of the carboxyl groups in its resulting poly(amic acid urea). The reason is that although these amine groups were first converted to carboxyl groups, the resulting carboxyl groups further reacted with the amide groups of the poly(amic acid urea) to form an poly(imide-urea) byproduct (see Figure 3.12). Except for titration, GPC and DSC were carried out to investigate the properties of poly(amic acid urea)s. Dynamic light scattering (DLS) and ζ-potential measurements were performed to study the properties of the dispersions made from those poly(amic acid urea)s. In dispersion preparation, NEt₃ was utilized to neutralize the carboxyl groups in the poly(amic acid urea)s, and the addition amount of NEt₃ was selected from 7.5% to 100% (mole fraction) of the poly(amic acid urea)s. With more NEt₃ added, more carboxyl groups were neutralized and smaller particles of the dispersions were obtained. As shown in Figure 3.13, from the dispersion on the left side to the one on the right side, more and more NEt₃ was added, as a result the dispersions became increasingly clear due to the decrease of the particle size. In addition, it is not necessary to add 100% of NEt₃ to produce a dispersion with small particles, because when EDTAD react with the prepolymer, the tertiary amine moieties can be also introduced into the backbone of poly(amic acid urea) along with carboxyl groups. The tertiary amine moieties can also neutralize the carboxyl groups, which render the dispersion more stable. The zeta potentials of all dispersions were also obtained and listed in Table 3.5 and their values are all below -30 mv, which is an indication for the formation of stable electrical double layer around the particles of the dispersions.
Table 3.5 Results of poly(amic acid ureas) and their dispersions.

<table>
<thead>
<tr>
<th>poly(amic acid urea)</th>
<th>$M_n$ of poly(amic acid urea) (GPC) (kDa)</th>
<th>Particle size (nm)</th>
<th>NEt$_3$ (mol%)</th>
<th>Zeta potential (mv)</th>
<th>Concentration of amine end groups of prepolymer (mol/g)</th>
<th>Concentration of carboxyl groups of poly(amic acid urea) (mol/g)</th>
<th>$T_g$(°C) of poly(amic acid urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.03:1) TOD+IPDC+EDTAD</td>
<td>32</td>
<td>$22 \pm 2$</td>
<td>100%</td>
<td>-47 ± 3</td>
<td>5.62E-04</td>
<td>3.67E-04</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$24 \pm 4$</td>
<td>56%</td>
<td>-49 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$51 \pm 5$</td>
<td>30%</td>
<td>-54 ± 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$68 \pm 5$</td>
<td>18%</td>
<td>-44 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.2:1) TOD+IPDC+EDTAD</td>
<td>29</td>
<td>$5 \pm 2$</td>
<td>100%</td>
<td>-42 ± 2</td>
<td>9.76E-04</td>
<td>6.94E-04</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6 \pm 3$</td>
<td>66%</td>
<td>-44 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$8 \pm 4$</td>
<td>30%</td>
<td>-56 ± 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$64 \pm 3$</td>
<td>15%</td>
<td>-47 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.3:1) TOD+IPDC+EDTAD</td>
<td>21</td>
<td>$7 \pm 3$</td>
<td>50%</td>
<td>-52 ± 2</td>
<td>1.02E-03</td>
<td>8.04E-04</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7 \pm 2$</td>
<td>37%</td>
<td>-41 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$562 \pm 12$</td>
<td>30%</td>
<td>-46 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\infty$</td>
<td>15%</td>
<td>NA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.4:1) TOD+IPDC+EDTAD</td>
<td>28</td>
<td>$6 \pm 2$</td>
<td>45%</td>
<td>-51 ± 3</td>
<td>1.33E-03</td>
<td>1.02E-03</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$160 \pm 5$</td>
<td>22.5%</td>
<td>-41 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$115 \pm 2$</td>
<td>15%</td>
<td>-51 ± 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$298 \pm 8$</td>
<td>7.5%</td>
<td>-43 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.1:1) DDD+IPDC+EDTAD</td>
<td>21</td>
<td>$20 \pm 1$</td>
<td>80%</td>
<td>-48 ± 2</td>
<td>8.12E-04</td>
<td>3.85E-04</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$23 \pm 2$</td>
<td>56%</td>
<td>-45 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$42 \pm 2$</td>
<td>30%</td>
<td>-45 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$204 \pm 3$</td>
<td>18%</td>
<td>-47 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.2:1) DDD+IPDC+EDTAD</td>
<td>16</td>
<td>$30 \pm 2$</td>
<td>31%</td>
<td>-45 ± 2</td>
<td>1.14E-03</td>
<td>7.63E-04</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$35 \pm 1$</td>
<td>26%</td>
<td>-51 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$58 \pm 2$</td>
<td>20%</td>
<td>-43 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$110 \pm 4$</td>
<td>15%</td>
<td>-50 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.3:1) DDD+IPDC+EDTAD</td>
<td>17</td>
<td>$8 \pm 2$</td>
<td>60%</td>
<td>49 ± 1</td>
<td>1.39E-03</td>
<td>9.67E-04</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$16 \pm 1$</td>
<td>30%</td>
<td>60 ± 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$48 \pm 2$</td>
<td>15%</td>
<td>53 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$218 \pm 7$</td>
<td>7.5%</td>
<td>54 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.4:1) DDD+IPDC+EDTAD</td>
<td>17</td>
<td>$12 \pm 1$</td>
<td>30%</td>
<td>-56 ± 2</td>
<td>1.84E-03</td>
<td>1.38E-03</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$39 \pm 1$</td>
<td>16%</td>
<td>-41 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$84 \pm 3$</td>
<td>11%</td>
<td>-44 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$903 \pm 50$</td>
<td>7.5%</td>
<td>-50 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Another phenomenon should be noticed is that with higher IPDC content, the $T_g$ of poly(amic acid urea) is higher as well. The higher $T_g$ is unlikely to be related to molecular weight, because as can be seen in the case of 1.3:1 in the TOD series, although the $M_n$ is lower than that of
1.4:1, the $T_g$s of it is higher. Therefore, the most probable reason is that the rigid structure and steric effect of IPDC gave rise to the increase of $T_g$. More importantly, thanks to IPDC, some $T_g$s have already reached the ideal range of 30-50°C. This could allow us to form coating films at room temperature directly from the water dispersions.

![Figure 3.13 Dispersions of DDD+IPDC+EDTAD (1.4:1) with different particle size and amount of NEt$_3$](image)

### 3.4 Coating preparation and test

To further study the properties of the coatings, the dispersions were applied on aluminum plates with a gap applicator to form coatings at room temperature. All the dispersions can form coatings at room temperature, and Figure 3.14 shows an example of a sample before and after impact test. The results of the impact tests and solvent resistance tests are listed in Table 3.6, in which ‘+’ stands for pass and ‘-’ stands for failure. As can be seen from the table, most of the coatings passed the impact test and coatings show also good resistance to toluene and acetone, but weak resistance to water. This is quite surprising considering the dispersions, which have polymer particles well phase separated with water, are quite stable. One possible reason could be that the smaller oligomers of the polyureas are still well dissolved in the dispersion, and it is these soluble oligomers that later dissolves in the water during the coating tests, and thereby causing low water resistance. Additionally, left over of NEt$_3$ in the film could also contribute to the limited water resistance of these coatings. To balance the hydrophilic and hydrophobic properties of the coatings, priamine 1071 (see Figure 3.15), a highly hydrophobic diamine, was added in the prepolymer preparation step. However, the resulting
coatings containing priamine did not show much improvement in water and acetone resistance. Furthermore, the addition of priamine lowered the hardness of the coatings because of its flexible long chain and the long side chain that disrupts the hydrogen bonding between the urea groups.

**Figure 3.14** A coating sample before and after impact test.

**Table 3.6 Properties of coatings.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness</th>
<th>Impact test</th>
<th>Water resistance</th>
<th>Toluene resistance</th>
<th>Acetone resistance</th>
<th>Average Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.03:1) TOD+IPDC+EDTAD</td>
<td>&lt;6B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>25μm</td>
</tr>
<tr>
<td>(1.2:1) TOD+IPDC+EDTAD</td>
<td>3B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>32μm</td>
</tr>
<tr>
<td>(1.3:1) TOD+IPDC+EDTAD</td>
<td>6B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>40 μm</td>
</tr>
<tr>
<td>(1.4:1) TOD+IPDC+EDTAD</td>
<td>3B</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>35 μm</td>
</tr>
<tr>
<td>(1.1:1) DDD+IPDC+EDTAD</td>
<td>3B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>20μm</td>
</tr>
<tr>
<td>(1.2:1) DDD+IPDC+EDTAD</td>
<td>3B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>60μm</td>
</tr>
<tr>
<td>(1.3:1) DDD+IPDC+EDTAD</td>
<td>3B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>20μm</td>
</tr>
<tr>
<td>(1.4:1) DDD+IPDC+EDTAD</td>
<td>3B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>40μm</td>
</tr>
<tr>
<td>(1.4:1) TOD+20%Priamine+IPDC +EDTAD</td>
<td>5B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>32 μm</td>
</tr>
<tr>
<td>(1.4:1) DDD+20%Priamine+IPDC +EDTAD</td>
<td>4B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>50 μm</td>
</tr>
<tr>
<td>(1.4:1) DDD+40%Priamine+IPDC +EDTAD</td>
<td>6B</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>45μm</td>
</tr>
</tbody>
</table>
Figure 3.15 Structure of Priamine 1071.
4 Conclusion

In this study, a series of waterborne polyurea dispersions were prepared via isocyanate-free routes. Coatings were obtained from the dispersions at room temperature without cracking.

Higher urea moiety density leads to higher $T_g$, which can be achieved by decreasing the length of the soft segments of the polymer. In contrast, the length of the hard segments has limited effects on the $T_g$. Higher molecular weight and introduction of a rigid building block also help to increase the $T_g$ of the polymer. The hard segments domain that consists of only the hard segments with alternative IPDA and BU2 structure can trap the prepolymer chains with unreacted carbamates end groups. The unreacted carbamates end groups can cause trouble because they can not react with EDTAD (dispersion agent), which means carboxyl groups can not be introduced into the backbones of the polyurea. Without carboxyl groups, the dispersion can not be produced.

IPDC was used as the carbamate source instead of BU2 due to the solubility issue of the BU2-based polyureas. Stable dispersions were prepared with EDTAD internal dispersing agent and polyureas obtained from IPDC and TOD/DDD/priamine. The relatively low $T_g$ (between 10-40°C) of these polymers allows them to form coatings at room temperature, which can pass impact tests and have good resistance against solvents such as acetone and toluene.
5 Acknowledgement

I would like to express my sincere and deepest gratitude to the people that helped me during my research. Firstly I would like to thank my supervisor and friend S. Ma, MSc who provided considerable assistance in my research and my final report. Without his help, the research could not have been accomplished. Secondly, my gratitude goes to my graduation committee, prof. dr. R. (Remco) Tuinie, dr. A.C. (Catarina) de Carvalho Esteves, dr. R.J. (Rafaël) Sablong and dr. J.P.A. (Hans) Heuts. I would like to thank them for their assessment of my project and valuable advices on my report. Lastly, I would like to thank other colleagues of SPC group for their encouragement and support when I suffered from setbacks and frustration.
6 Reference


