SYNTHESIS OF WATERBORNE, BRANCHED, FUNCTIONAL POLY(URETHANE)s and THEIR APPLICATIONS

by

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SYNTHESIS OF WATERBORNE, BRANCHED, FUNCTIONAL
POLY(URETHANE)s and THEIR APPLICATIONS

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To my beloved family…

SYNTHESIS OF WATERBORNE, BRANCHED, FUNCTIONAL POLY(URETHANE)s and THEIR APPLICATIONS

Nihan Ongun

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Abstract

Polyurethanes are an important class of polymers that have wide application in a number of different industrial sectors. Their versatile chemistry enables researchers to design novel materials ranging from liquid, soft and rubbery solids to rigid thermoplastic and thermoset polymer for elastomeric materials, coating and adhesive. The present study focuses on synthesizing waterborne, branched and chemically functional polyurethanes with unique architectures via novel methodologies for coating and adhesive applications using the oligomeric $A_2 + B_n$ strategy where a multifunctional isocyanate B_n (n>2) was polymerized with an A_2 oligomer or an A_2 monomer. In order to prepare these novel polyurethanes in the form of waterborne dispersions, novel polyurethane ionomer architectures were designed with ionic groups either pendant along the polymer chain or placed at the chain end-groups. The effect of functionality, type and content of soft segment and type and location of emulsifying agent were critical parameters that were investigated in this study. The $A_2 + B_n$ strategy used in this study also permitted the control of the molar mass between branch points which led to interesting macromolecular properties, such as tunable mechanical properties, improved processibility, and a multitude of functional blocked isocyanate end-groups. Highly functional polyurethanes were formulated with hydroxyl functional components and model self-standing thermoset films were obtained, which showed interesting thermo-mechanical properties. Dynamic mechanical analyses demostrated that higher functionality increased the storage modulus by increasing crosslink density at equivalent soft segment molar mass whereas higher soft segment content decreased the

storage modulus yet increased the elastic nature ofthese films. These characterizations results clearly revealed that novel synthethic approaches developed in this study were useful to prepare highly functional waterborne polyurethanes that could be used as a new component to prepare one component formulations with shelf-life stability to obtain thermoset films and coatings with tunable mechanical properties.

SU BAZLI, DALLANMIŞ, FONKSİYONEL POLİÜRETANLARIN SENTEZLENMESİ ve UYGULAMALARI

Nihan Ongun

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Anahtar kelimeler: Poliüretanlar, su bazlı, dallanmış, fonksiyonel poliüretanlar, A_2 + B_n sentez stratejisi, poliüretan filmler

Özet

Poliüretanlar, çok sayıdaki farklı sanayi sektöründeki uygulamalarda yer alan polimerlerin önemli bir sınıfıdır. Onların çok yönlü kimyaları, araştırmacılara sıvı, yumuşak ve lastik katıdan, elastomerik, kaplama ve yapıştırıcı için gerekli sert termoplastik ve termoset polimer arasında değişen yeni malzeme tasarımı için olanak sağlarlar. Bu çalışma, çok fonksiyonlu izosiyanat B_n grubunun, oligomer veya monomer A_2 yumuşak segment ile polimerize edildiği oligomerik A_2 + B_n stratejisini kullanarak kaplama ve yapıştırıcı uygulamaları için yeni metodolojiler aracılığıyla gelen eşsiz mimarileri sayesinde su bazlı, dallı ve kimyasal fonksiyonel poliüretan sentezlemek üzerinde durmaktadır. Bu yeni poliüretanların su bazlı dispersiyonlar şeklinde hazırlanması için, iyonik grupların polimer zinciri boyunca sallandığı veya zincirin sonuna yerleştirildiği yeni poliüretan iyonomerleri tasarlanmıştır. Fonksiyonalite, yumuşak segmenti oluşturan malzemenin yapısını ve çeşidi ve emülsiyon yapıcı malzeme zincir üzerindeki lokasyonunun nihai ürün üzerinde etkisi sırasıyla incelenmiştir. Bu çalışma aynı zamanda üstün mekanik performans, daha yüksek kristallik, daha iyi işlenebilirlik ve kalabalık fonksiyonel blok izosiyanat uç grupları gibi ilginç makromoleküler özelliklere yol açan dallı noktalar arasındaki molar kütle kontrolüne izin vermiştir. Hidroksil fonksiyonel bileşenleri ile formüle edilen çok fonksiyonel poliüretanlardan ilginç termo-mekanik özellikler gösteren termoset filmler elde edildi. Ayrıca çalışmalar bu işlevsel poliüretanların serbestçe duran filmlerini hazırlamak üzerinde durmuştur. DMA analiz sonuçlarına göre, aynı miktarda yumuşak segment içeren poliüretan filmler kıyaslandığında artan fonksiyonalite ile birlikte çağraz bağlanma ve kristallenme olasılığı da artmış ve böylelikle $E^{'}$ için de bir artış

gözlenmiştir. Bununla birlikte aynı fonksiyonaliteye sahip poliüretanlar kıyaslandığında, yumuşak segmentin artışı ile birlikte $E^{'}$ azalmıştır. Bu karakterizasyonların sonucu açıkça göstermektedir ki, bu çalışmada geliştirilen yeni sentetik yaklaşımlar ayarlanabilir mekanik özelliklere sahip termoset filmler ve kaplamalar elde etmek için raf ömrü sabit olan bir bileşen formülasyonlarının hazırlanmasını sağlayan çok fonksiyonel su bazlı poliüretanların sentezi için uygundur.

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CHAPTER 1

1.   Introduction

The increasing need to reduce volatile organic compounds and hazardous air pollutants' emissions has forced many polyurethane manufacturing industries to formulate environment friendly waterborne systems for use as coatings, adhesives and related end uses. As a green technology, waterborne polyurethanes are versatile eco-friendly materials used increasingly in adhesives, coatings and sealants due to a variety of advantages [2]. Because of environmental restrictions on solventborne resins, waterborne polyurethane dispersions have received much attention in recent years and are expected to replace the solvent-based coatings. The release of volatile organic components to the atmosphere in these systems is considerably reduced compared to conventionally employed solvent-based systems. Waterborne polyurethane dispersions can offer the many advantages such as viscosity and flow properties independent of molecular weight, the absence of external emulsifiers, flexibility, good behaviour at low temperature and high strength, nontoxicity, nonflammablity, environmental safety, good adhesion and rheological characteristics that allow them to be used in wide range of application areas. Waterborne polyurethane dispersions present also drawbacks such as poor surface properties, deficiency in chemical resistance and limited thermal, mechanical and electrolytic stability caused principally by low crosslinking density. The high reactivity of isocyanate groups toward water is the main problem for synthesizing waterborne polyurethane dispersions. Therefore, waterborne polyurethanes are not able to be obtained by conventional water synthesis methods such as emulsion or suspension polymerization and alternative synthesis have to be employed. Several processes have been developed for the synthesis of polyurethane water dispersions [3]. However, there are still limited number of successful studies on the development of waterborne polyurethanes based on aromatic isocyanates.

$A_2 + B_n$ polymerization has received significant attention in the last decade to synthesize highly branched polymers with a multitude of functional end-groups. Several types of difunctional (A_2) and trifunctional monomers or oligomers (B_3) are commercially available. The wide range commercially available A_2 and B_n reagents also allow tailoring the polymer structure due to various choices of monomer pairs and provide more facile routes to many families of highly branched polymers. Therefore, a fundamental understanding of branching and how it influences polymer properties is essential for tailoring the structure of a polymeric material for desired high performance applications [4].

In this thesis, novel synthethic approaches were developed to prepare a series of highly branched, chemically functional polyurethanes in the form of waterborne dispersions by modifying the "oligomeric $A_2 + B_3$" approach. This study explores new possibilities for tailoring the functionality of waterborne polyurethanes by controlled branching and discusses the structure-property relations based on novel molecular architectures. In order to establish these structure-property relations and to demonstrate the usefulness of these novel waterborne functional branched polyurethanes for future applications, thermally cured thermoset films with a tunable thermo-mechanical properties were prepared as revealed by the dynamic mechanical analyses.

CHAPTER 2

2.   Literature Review

2.1.   Polyurethanes

2.1.1.   Introduction to Polyurethanes

Although polyurethanes can be formed by different methods, the most widely used production method is an exothermic polyaddition reaction between a multifunctional isocyanate containing two or more isocyanate groups per molecule with a polyol containing two or more reactive hydroxyl groups per molecule in the presence of a suitable catalyst and additives. Polyurethanes are organic polymers that consist of urethane group in the main chain. Aside from the urethane linkage, these materials may also contain several other types of linkages such as aromatic an aliphatic hydrocarbons, oxazolidone groups, allophanate groups, amides, urea groups, biuret groups, isocyanure groups, carbodiimide groups, ethers, and esters. The general reaction of an isocyanate with an alcohol to form urethane linkages can be shown as:

$$R-N=C=O \; + \; OH-R' \; \longrightarrow \; R-\overset{H}{\underset{|}{N}}-\overset{O}{\overset{||}{C}}-O-R'$$
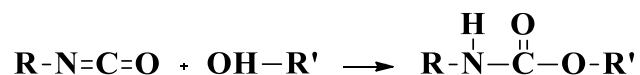
Figure 2.1 Reaction of isocyanate with alcohol to form urethane

R makes an aliphatic, aromatic or alicyclic radical acquired from the isocyanate monomer and R` is acquired from polyester or polyether. The type of isocyanates and polyols in the polymerization reaction determines final properties of the polyurethanes.. Increasing the functionality of isocyanate or hydroxyl-containing components results in

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the formation of branched or cross-linked polymers. Other structural changes can be made as well. For instance, the nature of R` may be altered severely by changing molecular weight and type of the polyol component. Mixtures of polyol compounds can also be preferred. Similarly, the nature of R can be altered depending on the structure of diisocyanate [5].

Characteristic properties of polyurethanes can be influenced by the chemical structure of each component and microphase-separated morphology. Polyurethanes are blocked copolymers that comprise of hard and soft segments linked together by covalent bonds [6]. Hard segments of a polyurethane are produced by the reaction of short-chain diol and diisocyanate. Hard segments consist of glassy or semicystalline domains and give important properties to the chain. They are basically low molecular weight polyurethanes or polyurethane-ureas that can easily cross-link through the formation of non-covalent hydrogen bonds with a leaning to form hard segment domains in the morphology. They can implement unique and elastomeric properties, increase the mechanical strength of the chain, control the hardness and tear strength. On the other hand, soft segments of polyurethanes are incorporate into the chain by the reaction of diisocyanate and long-chain polyols such as polyester or polyether diols. Soft segment chains form an amorphous latex in which the hard segments are dispersed and give flexibility and absorb external stress by extending and unfolding. They also impart some chemical behaviours to polymer chains such as resistance to solvents [7].
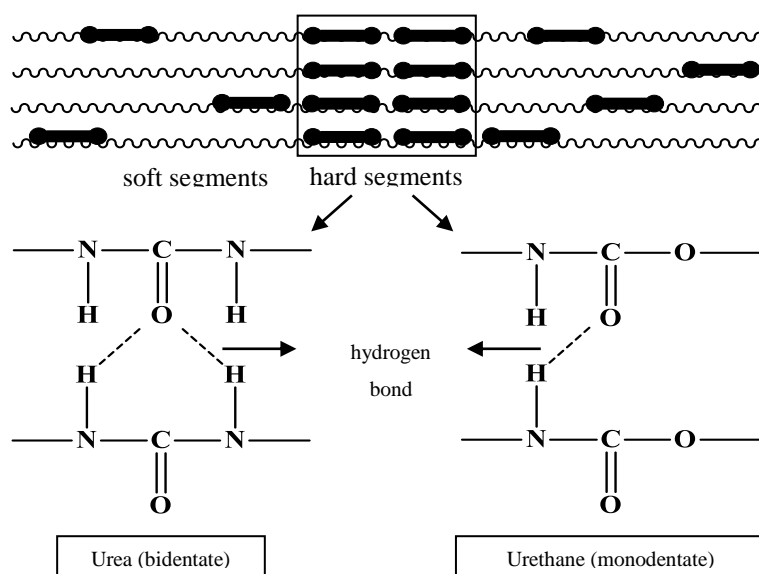
Figure 2.2 Illustration of the hard and soft segments of a blocked polyurethane

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As shown in Figure 2.2 oxygen and nitrogen atoms with available unshared pairs of valence electrons provide these valence electrons to the hydrogen atom of neighboring molecule to form hydrogen bonding between the two molecules in polyurethane chain. These bonds improve physical properties of polyurethanes significantly [8].

A wide range of application areas for polyurethanes arise from their unique and versatile performance properties, which can be modified by choosing appropriate starting monomers and components. Polyurethane's versatile chemistry enables researchers to design novel materials ranging from liquid, soft and rubbery solids to rigid thermoplastic and thermoset polymers for coating, adhesive, and elastomeric materials. All these factors make polyurethanes unique and suitable for such applications [5, 9].
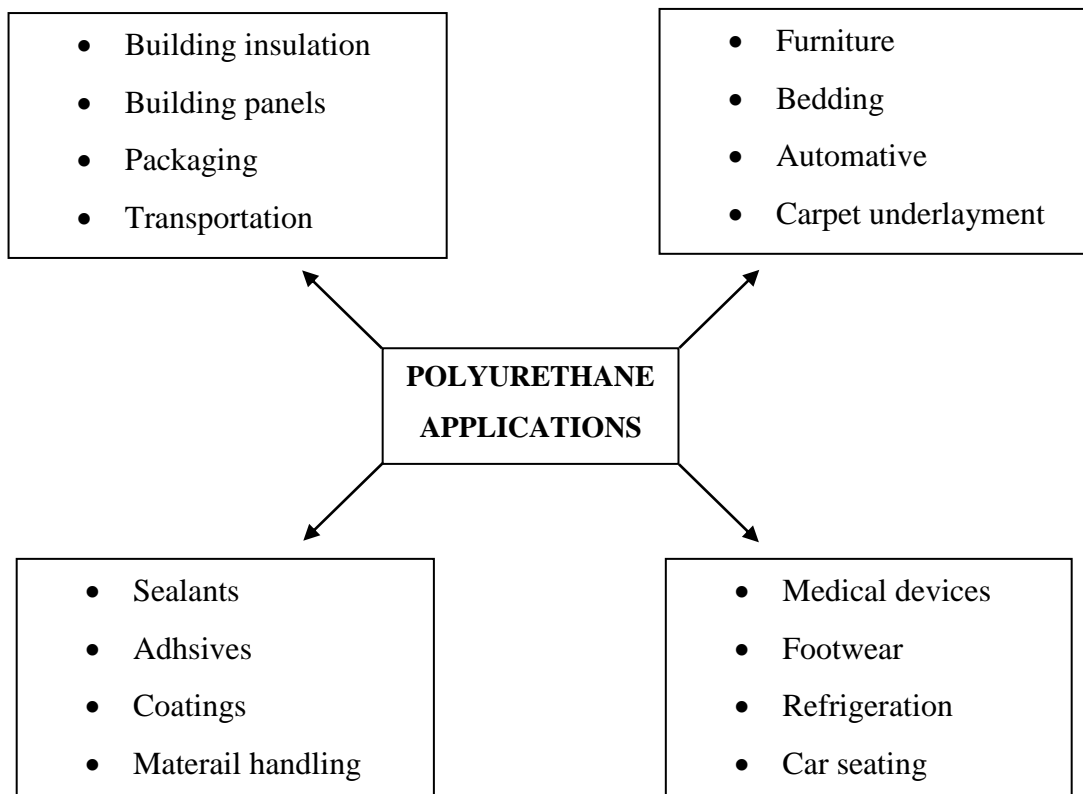
Figure 2.3 Application of polyurethanes

2.1.2. Reactions of Isocyanates

Isocyanates are key monomers for polyurethane synthesis. Multiple reactions of isocyanates are possible due to their high energy content and polarizability of the double bonds. Monoisocyanates are used as intermediate products due to their less significance. Diisocyanates consist of two isocyanate groups in the molecule, whereas polyisocyanates are formed with two or more isocyanate functionalities in the molecule [10]. The isocyanate functionality is highly reactive toward proton carrying nucleophiles. The lack of electrons on the carbon explains the susceptibility of isocyanates towards nucleophilic attack, for that reason most reaction take place across the C=N bond. Aliphatic isocyanates are less reactive then aromatic isocyanates due to the existence of electron withdrawing substituents linked with R to increase the positive charge on carbon in aromatic isocyanates, thereby increasing reactivity of the isocyanate group towards nucleophilic attack. On the other hand, the reactivity of isocyanate groups are easily decreased by electron donating groups [8].

Isocyanates are highly reactive towards all compounds that contain "active" hydrogen atoms under suitable conditions. These are compounds that consist of –OH and –NH groups such as alcohols, amines and water. Production of polyurethanes can be done by the polyaddition reaction of a polyisocyanate with polyol in the presence of a catalyst. Urethane, urea and amide linkages are produced when the isocyanate group reacts with alcohols, amines, carboxylic acids and water, respectively [11]. The resonance structure of an isocyanate group is shown in Figure 2.4, in which the electron density is the highest in oxygen atom, lower in nitrogen atom and lowest in carbon atom.

$$\left[R-\overset{\ominus}{N}-\overset{\oplus}{C}=O \quad\longleftrightarrow\quad R-N=C=O \quad\longleftrightarrow\quad R-N=\overset{\oplus}{C}-\overset{\ominus}{O} \right]$$
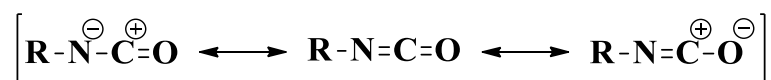
Figure 2.4 Typical ressonance structures of the isocyanate group [5]

The most important reaction of isocyanates is the production of carbamic acid derivatives by the addition of components with active H-atom across the C-N double bond.

$$R\text{-}N=C=O + HX \longrightarrow R\text{-}NH\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}X$$
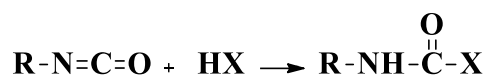
Figure 2.5 Addition of reductants to the carbon-nitrogen double bond [12]

This reaction in Figure 2.5 proceeds easily at lower temperatures by increasing nucleophilic character of HX. The regeneration of isocyanates and reactants can bedone at higher temperatures. This is approach enables one to temporarily block the isocyanate with nucheophiles which can be unblocked readily at elevated temperatures.

- **With alcohol to urethane**

The reaction mechanism of urethane bond formation was discovered by Wurtz in 1848 whereas the polymerization method which is called ''polyaddition reaction'' forming polyurethanes was first defined in detail by Otto Bayer in 1937 [13]. The reaction of isocyanate with hydroxyl groups is an exothermic reaction. The structure of isocyanate or the alcohol affects the reaction rate. Aliphatic primary alcohols react faster than secondary and tertiary alcohols because of the steric hindrance of neighboring methyl group. Phenols also react with isocyanates but much more slower than aliphatic alcohols and the product is urethane group [1]. The reaction rate of isocyanate with different types of alcohols is as follows [14].

primary OH > water> Secondary OH > Tertiary OH > Phenolic OH

The hydrogen at the end of the diol includes a partial positive charge which attacks the nucleophile and the more negative oxygen atom reacts with a carbon located in an isocyanate group. Moreover, the nitrogen on the isocyanate group is left to be negative. This negative charge of the nitrogen is given out to the hydrogen atom on the alcohol group, eventually by forming a urethane bond. This is a polyaddition reaction because no small compounds are formed during the reaction.

$$R\text{-}N=C=O + R'\text{-}OH \longrightarrow R\text{-}NH\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OR'$$

- **With amine to urea**

Another important reaction in polyurethane chemistry is the reaction of isocyanates with amines. Isocyanates react with primary and secondary amines to produce urea linkages.

Tertiary amines do not react with isocyanates due to the absence of an active hydrogen. The reactivity of the amines is mainly dependent on their basicity. The reaction is much faster than the reaction of isocyanate with alcohol [10, 15].

$$R-N{=}C{=}O \; + \; H_2NR' \; \longrightarrow \; R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NHR'$$
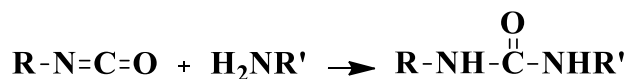
- **With water to urea**

The next fundamental reaction of isocyanate is with water. Carbondioxide is produced as a blowing agent which is useful in urethane foam industry. In this case, the primary addition product is an unstable intermediate which is called carbamic acid. Then, it decomposes to form corresponding amine, which immediately reacts with isocyanate that is still present in the reaction mixture to produce urea[8, 15].

$$R-N{=}C{=}O \; + \; H_2O \; \longrightarrow \; \left[R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-OH \right] \; \longrightarrow \; R-NH_2 \; + \; CO_2$$
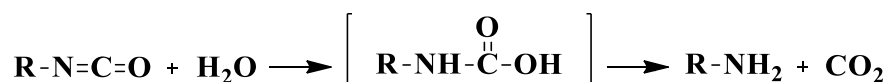
2.1.3. Waterborne Polyurethane Dispersions

The increasing requirements to protect the environment and people's health has led to development of new waterborne formulations to be used as adhesives, coatings and sealants for automotive, construction and footwear industries [2]. In addition to fundamental chemical components of polyurethanes such as diisocyanates, polyols, amines, catalysts and additives, waterborne polyurethanes comprise of anionic, non-ionic or cationic components as external or internal emulsifiers for the stabilization of the dispersion in water [16]. Waterborne polyurethanes are environmentally friendly materials that contain and release water during their drying stage which makes them free of volatile organic compounds and pollutants. In addition, waterborne polyurethanes offer advantages such as low viscosity at high molecular weight, flexibility and high strength even at low temperature, nontoxicity, nonflammability and good adhesion that allows them to be used in high-performance application areas. On the other hand, waterborne polyurethanes have some drawbacks due to their poor surface properties, deficiency in chemical resistance and limited mechanical strength

induced mainly by hydrophilic nature. In fact, production of highly crosslinked waterborne polyurethanes is a challange due to high viscosity problem of prepolymers or possible poor combination of the formulated dispersion [16, 17]. Many studies have been reported in the literature to synthesis polymers containing urethane and urea groups in the form of two-phase waterborne systems. The main principle consists of two steps. The first step is to prepare a medium molecular weight isocyanate prepolymer from diols and multifunctional isocyanates. The second step is to chain extend the prepolymer and disperse in water by presenting hydrophilic solubilizing groups [16, 18].

There are several methods to synthesize polyurethane dispersions. The most common methods are listed as; acetone process, prepolymer mixing process, melt dispersion process and ketamine-ketazine process [16].

The prepolymer mixing process is the most common method to form polyurethane dispersions. Water is mixed with a hydrophilic prepolymer which contains free isocyanate groups. Then, chain extension of the isocyanate terminated prepolymer with amines in the aqueous phase is achieved [3]. In the literature, various early studies on the synthesis and characterization of waterborne polyurethane dispersions and their applications have been reported [16]. The first efforts were directed towards producing polymers with a high number of hydrophilic groups to obtain solubility in water. However, the high reactivity of isocyanate groups towards water created a problem to form waterborne polyurethanes. Dietheric and his coworker studied firstly on aqueous emulsion and dispersion of polyurethane for one package systems [19, 20]. Barni et al., Wicks et al. and Wei et al. studied polyurethane aqueous dispersions in two-step procedure [21-23]. Recently, Contraires et al. [24] claimed that it is possible to form hydrophobic polyurethane dispersions in water in one step procedure using the miniemulsion process.

On the other hand, waterborne urethanes are linear thermoplastic polymers which are easily resoluable in solvents. Important efforts have been made in recent work to bring about a new classes of thermosetting polymers that are chemically crosslinked. Coogan and Boghossian showed that waterborne urethanes with a limited number of crosslink sites show significant improvements [24, 25]. After that, Wicks et al. studied on two

package waterborne urethane systems and reported the use of polyisocyanates to cross-link a variety of waterborne coreactants [18]. Later, low molecular isocyanate-containing prepolymers were emulsified and chain-extended. John et al. showed the influences of the chain extension on the waterborne polyurethanes' particle size [26].

2.1.4. Blocked Isocyanates

2.1.4.1. Chemistry

The history of blocked isocyanates goes back to World War II and since then numerous papers and patents emphasizing advantages and applications of blocked isocyanates have been reported in the literature [27]. As mentioned before, isocyanates are highly reactive and they are sensitive to water or even moisture either from solvents or high humidity. In order to control the reaction of isocyanates, they can be temporarily blocked. A blocked-isocyanate structure can be explained as an isocyanate reaction product which is stable at room temperature consisting a relatively weak bond formed by the reaction of an isocyanate and a compound containing an active hydrogen atom. At higher temperatures, the weak urethane or urea bond dissociates to regenerate the isocyanate and blocking agent. This regenerated isocyanate can immediately react with a compound containing the hydroxyl functional group to produce desired, thermally more stable urea or urethane linkages [28, 29].

➢ Blocked isocyanate reaction:

$$R-N=C=O \ + \ BL-H \ \longrightarrow \ R-N-\overset{\overset{\displaystyle O}{\|}}{C}-BL$$
$$\underset{H}{|}$$

➢ Deblocking reaction:

$$R-\underset{\underset{H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-BL \ + \ HO\sim \ \rightleftharpoons \ R-\underset{\underset{H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O \ + \ HBL$$
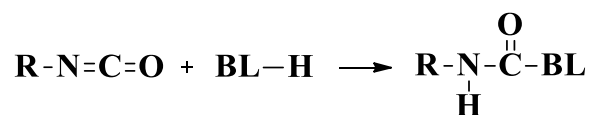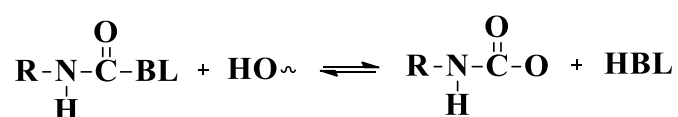
BL represents the blocking agent in the reactions above. There are several different blocking agents that contain active hydrogens. By the help of this active hydrogen,

blocking agent can be attached to the isocyanate group and form weak urethane or urea linkages. Then blocked isocyanates can be deblocked in the presence of heat and an isocyanate reactive reagent. Interestingly, different blocking agents also unblock at different tempretures as shown in Table 2.1 [30]. A blocked isocyanate can react with a nucleophile in two different ways to form urethane as shown below. In the elimination-addition reaction, the blocked isocyanate breaks up to the free isocyanate and the blocking group. Thereafter, the isocyanate reacts with a nucleophile to produce final product. In the addition-elimination reaction, the nucleophile reacts directly with the blocked isocyanate to yield an intermediate. After that, the blocking agent is eliminated [29].

A. Elimination-Addition Reaction

$$\underset{\underset{H}{|}}{R-N-\overset{\overset{O}{\|}}{C}-BL} \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad R-N{=}C{=}O \;+\; BL{-}H \tag{1}$$

$$R-N{=}C{=}O \;+\; Nu{-}H \quad \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad \underset{\underset{H}{|}}{R-N-\overset{\overset{O}{\|}}{C}-Nu} \tag{2}$$

B. Addition-Elimination Reaction

$$\underset{\underset{H}{|}}{R-N-\overset{\overset{O}{\|}}{C}-BL} \;+\; NuH \quad \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \quad \underset{\underset{H}{|}\;\underset{Nu}{|}}{R-N-\overset{\overset{OH}{|}}{C}-BL} \tag{3}$$

$$\underset{\underset{H}{|}\;\underset{Nu}{|}}{R-N-\overset{\overset{OH}{|}}{C}-BL} \quad \overset{k_4}{\longrightarrow} \quad \underset{\underset{H}{|}\;\underset{Nu}{|}}{R-N-\overset{\overset{OH}{|}}{C}-BL} \;+\; BH \tag{4}$$
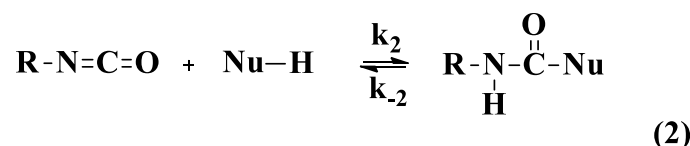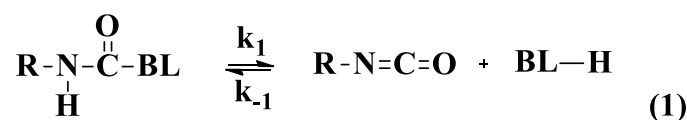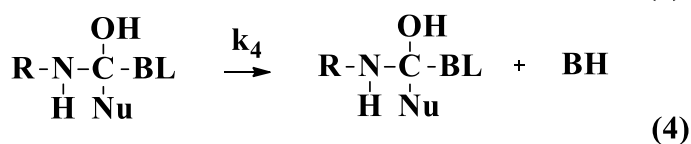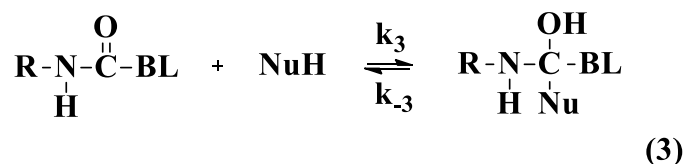
The deblocking reaction rely upon the structure of the isocyanate and blocking agent including substituents, solvents, temperature and the thermal stability of the isocyanate-blocking agent bond [27, 28, 31]. Urethane linkages formed from the aromatic reactants are unstable at higher temperatures. Because of that reason, aromatic isocyanates or phenol are commonly prefered in blocking reactions [32]. Among these blocking agents, phenols are mostly studied blocking agents in the literature because it is easy to introduce number of substituents on the benzene ring [33]. The most extensively used blocking agents are phenols, alcohols, oximes, ε-caprolactam and amines such as

diethylamine with their chemical structures shown below. Additionally, a number of reports showed that imidazoles, triazoles and imidazolines and have been choosed as blocking agents for isocyanates. It is important to note that, the dissociation temperatures of blocked polyisocyanates with various blocking agent increase in following order: methyl ethyl ketoxime > phenols > ε-caprolactam > alcohols [34].
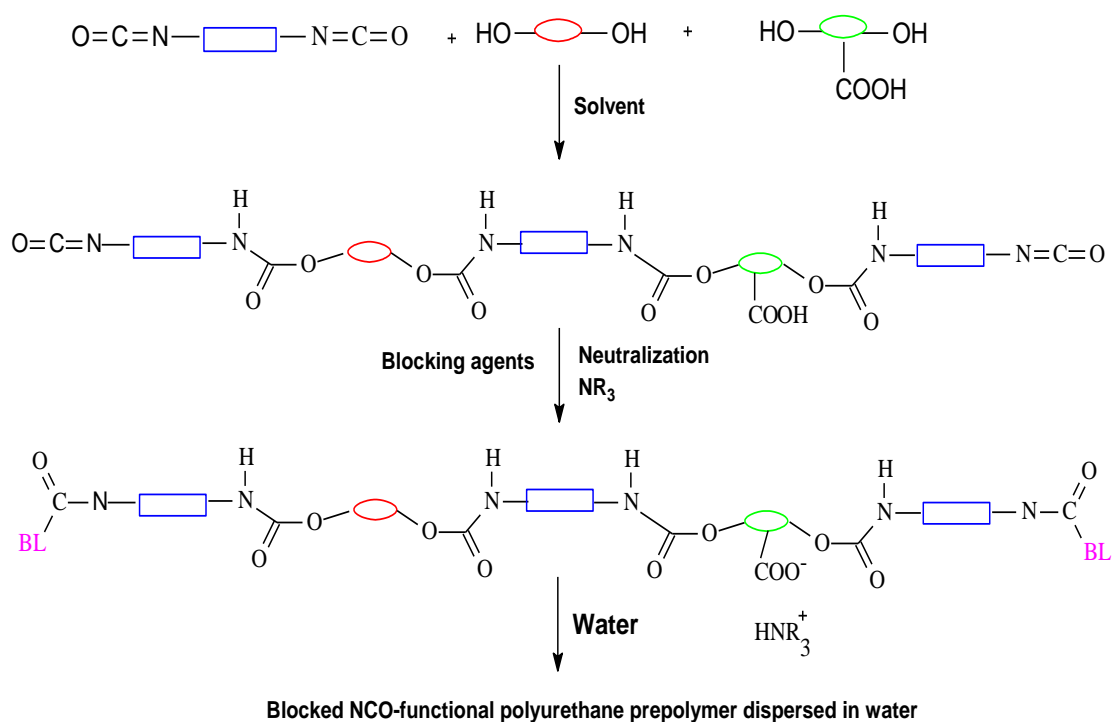
Figure 2.6 Synthetic Strategy for Waterborne Blocked Polyurethane
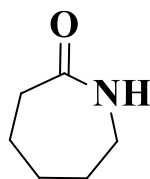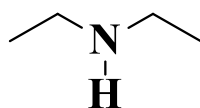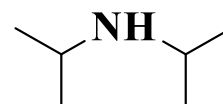
ε-   Diethylamine   Diisopropylamine
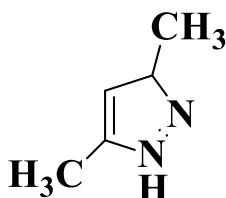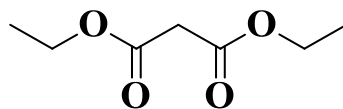
3,5-Dimethylpyrazole   Diethyl malonate   2-Butanone oxime
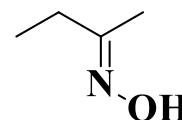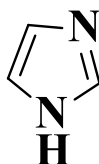
2-imidazoline   Imidazole   1,2,3-Triazole
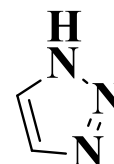
Table 2.1 Initial Crosslinking Temperatures of Different Blocking Agents [27]

Blocking Agent	Initial Crosslinking Temperature (ºC)
ε-caprolactam	160-180
Diethylamine	170-180
Diisopropylamine	130-140
3,5-Dimethylpyrazole	150-160
Diethyl malonate	100-120
2-Butanone oxime	140-150
2-Imidazoline	120-130
Imidazole	110-130
1,2,3-Triazole	120-130

Normally, blocked aromatic isocyanates have lower deblocking temperatures than blocked aliphatic isocyanates due to the larger electron withdrawing potential of an aromatic ring. Electron donor groups reduce deblocking reaction rates though electron-withdrawing groups raise deblocking reaction rates [29]. Kothandaraman et al. reported the thermal dissociation temperature and the kinetic parameters for phenolic reactions of a group of blocked toluene diisocyanates [35-37]. In another work, Müblebach showed that deblocking rates of p-substituted phenols increase in the presence of electron acceptor substituents the rate of p-NO2>p-Br>p-Cl>p-F> H>p-Me [38].

As shown in the literature, a wide varity of alcohols have been also preferred to block isocyanates which were reported in thousand patents and papers. Mostly, deblocking temperatures of alcohols are highest. Isopropanol, 2-ethyl hexanol, n-butanol and cyclohexanol are reported as blocking agents by Subramani [28]. Isocyanates that are blocked by alcohols have magnificent stability in waterborne coatings because of their very low reactivity [29]. Also, Moriarity et al. [39] and Gimpel et al. [40] reported their studies in which furfuryl alcohol and cyclohexyl alcohol were used as blocking agents, respectively.

Besides all these, ε-caprolactam is an essential and broadly used blocking agent for isocyanates. It has higher deblocking temperature than oxime. The high deblocking temperature provides benefits in some applications as reported by Wicks et al. [29]. Further, a great variety of other blocking agents such as aryl mercaptans, aliphatic mercaptans, aromatic amines, ethyl carbamate, amides and acetic acid have been reported [27].

Waterborne dispersions of polyurethanes with blocked isocyanate functionalities can be synthesized as shown in Figure 2.6. These products have a great potential in formulating one-component waterborne formulations that give a thermoset product upon drying and curing by deblocking reactions at elevated temperatures. It is therefore essential to develop novel waterborne polyurethane dispersions with increased blocked isocyanate functionalities.

2.1.4.2. Applications of Blocked Isocyanates

Blocked isocyanates are preferred for a wide variety of applications. There are many patents and papers mentioning the applications of blocked polyurethanes in various areas such as powder coatings, coil coatings, automotive coatings, paper coatings, wire coatings and tire cord adhesives in the literature. Blocked isocyanates have feasible advantages for packaging area. It is easy to formulate one package coatings with blocked isocyanates. Moreover, the usage of blocked isocyanates in powder coatings applications are mentioned in very large number of papers and patents. The curing of thermoset polyester and urethane powder coatings can be achieved by ε-caprolactam blocked isocyanates. In addition to that, various blocked isocyanates are preferred to achieve wet strength of crosslinked paper. Moreover, cotton fabric has been treated with blocked isocyanates for stable press properties. Also, the improvement in elongation at break for Nylon-6 fiber was provided by phenol-blocked TDI and MDI. Heat-sensitive, hot-melt adhesives containing phenol-blocked prepolymers are demanded as fabric laminating adhesives. Furthermore, various patents explain the usage of blocked isocyanates in fabric coatings, especially for adhesion to nylon fabrics [27].

2.2. Branching in Step-Growth Polymerization

2.2.1. A_2+B_3 Polymerization

AB_n type monomers that include one "A" functional group and n "B" functional groups undergo self-polycondensation or copolymerize with AB type monomers to create highly branched polymers [41]. One of the alternative method to synthesize highly branched polymers has been A_2 and B_n where n≥3. In this recent method, A_2 refers difunctional monomers whereas B_3 refers trifunctional monomers. As mentioned in the literature, eventhough AB_n type monomers have several drawbacks during polymerization such as the risk of premature polymerization, they are effective methods to synthesize highly branched polymers [4].
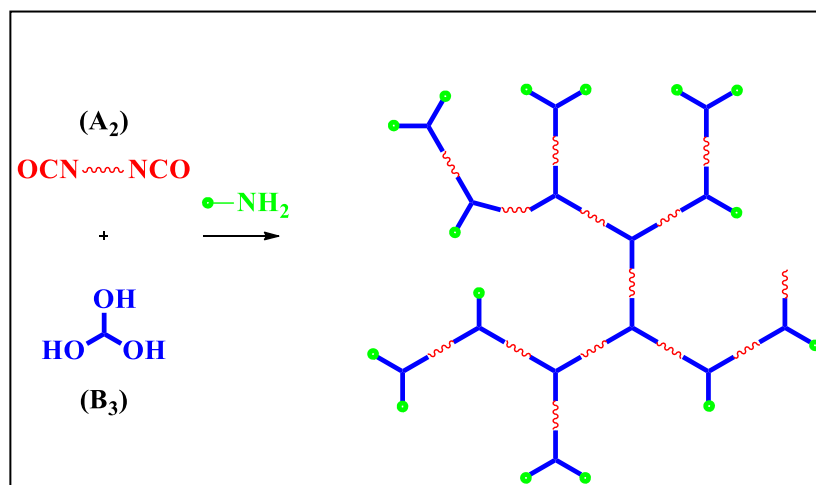
Figure 2.7 Oligomeric $A_2 + B_3$ approach to hyperbranched, segmented polymers [1]

Flory has statistically analyzed the network formation in a copolymerization of two-functional (A_2) and three-functional (B_3) monomers over half a century ago [41]. According to Flory`s theory, A_2:B_3 molar ratio and functional group conversion directly can be controlled to avoid gelation upon the polymerization of A_2 and B_3 monomers and result in high molecular weight, highly branched polymers as shown in Figure 2.7. In spite of the risk of gelation, feasibility of the $A_2 + B_3$ polymerization has huge application potential for many industries. Because of that reason, understanding of key reaction parameters to eliminate the gelation problem becomes prominent. The first two reports that describe the synthesis of highly branched polymerization by using the $A_2 +$ B_3 method appeared in 1999. After that, Kakimoto et al. claimed synthesis of hyperbranched aromatic polyamides from aromatic diamines (A_2) and trimesic acid (B_3) [42]. Then, Fréchet et al. demonstrated the synthesis of hyperbranched polyether epoxies via proton-transfer polymerization from 1,2,7,8-diepoxyoctane (A_2) and 1,1,1-tris(hydroxymethyl)ethane (B_3) [43]. Moreover, several types of highly branched polymers, such as aromatic polyamides, polyimides, and polyesters were synthesized successfully via the $A_2 + B_3$ polymerization.

Flory has shown that depending on the stoichiometry of the monomers and extent of the reaction, step-growth polymerization reactions involving a mixture of difunctional (A_2) and multifunctional (B_n) monomers lead to the formation of hyperbranched or crosslinked polymers [1, 4]. According to Flory, for an A_2+B_n system with all

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monomers initially present in the reaction mixture, assuming no side reactions, the critical monomer conversions at gel point can be calculated by using Eq. (2. 1):

$$\alpha = r \times P_A^2 = P_B^2 / r \tag{2. 1}$$

where (α) is the probability of branching which means the probability that a given functional group of a branch unit (B_n) is linked to another branch unit, (α_c) is the probability of branching for gelation, (pA and pB) are the extent of reaction for A and B type monomers and (r) is the ratio of the A groups to that of B groups [1, 4]. The critical branching coefficient (α_c) is calculated by using Eq. (2. 2):

$$\alpha_c = \frac{1}{(f - 1)} \tag{2. 2}$$

in which f indicates the average functionality of multifunctional monomers in the system. Consequently, α_c turns into 0.5 for an A_2 + B_3 polymerization if only trifunctional monomer is used as a multifunctional monomer [1]. In Flory's theory, when $\alpha < \alpha_c$,a fully soluble product are present and a sol-gel mixture begins to appear when α becomes greater than α_c with increasing monomer conversion [1, 4]. As can be calculated from Equation (2. 1), maximum α value can be equal to one, which corresponds to a fully crosslinked system. The value of α can also be associated to the degree of branching of a product, which clearly increases as a function of monomer conversion [1]. Furthermore, it is essential to determine the P_{Ac} and P_{Bc} values at the gel point for different r values, based on Equation (2. 1) and Equation (2. 2) in an A_2 + B_3 polymerization to avoid gelation.

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Table 2.2 Calculation of gel point in $A_2 + B_3$ polymerization (α_c=0.5) for various monomer ratios using Equation (2.1) and Equation (2.2) [1]

A_2:B_3	r = A:B	P_{Ac}	P_{Bc}
0.75:1.00	0.50	1.000	0.500
0.90:1.00	0.60	0.913	0.548
1.00:1.00	0.67	0.866	0.577
1.25:1.00	0.83	0.775	0.645
1.50:1.00	1.00	0.707	0.707
2.00:1.00	1.33	0.612	0.816
3.00:1.00	2.00	0.500	1.000

Table 2.2 summarizes the critical conversion of A and B groups for various A to B ratios. As the molar ratio of A to B functional groups is increased, the gel point is reached sooner, at a lower monomer conversion, and gelation becomes more difficult to prevent.

The functionality of a compound is directly related to the number of reactive sites it possesses. The functionality of a monomer is mentioned as the number of bonds which each monomer molecule can make. In step-growth polymerization, bi-functional monomers are able to produce linear chain polymers whereas tri- or higher-functional monomers form a cross linked polymer. Topology of a polymer is the principal tool for setting the physical properties and functionality of polymers. Branching on polymers affect the processability and physical properties, thus applications of the produced polymer [44, 45]. On the other hand, branched and functional polymer or oligomers can be used for further reactions to form thermosetting polymer systems as commonly used in composite structures.

The crosslinking that is formed by using multifunctional polyols (having a functionality greater than 2) locates in the soft segments and creates urethane bonds in the main polymer chain. Properties and structure of resulting polyurethanes are firmly dependent on the functionality (number of hydroxyl groups in the molecule) and the molecular

weight of the polyol used. For the formation of crosslinked polyurethanes, polyols are those having functionality in the range $2<f<8$ (where f refers to polyol functionality meaning as the number of OH groups per 1 mole of compound) are commonly preffered. Moreover, low functional polyols ($2<f<3$ OH/mol) form weakly crosslinked elastic polyurethanes by reacting with diisocyanates. Highyl crosslinked and rigid polyurethanes are typically produced by using high functional polyols (3-8 groups OH/mol) [46].
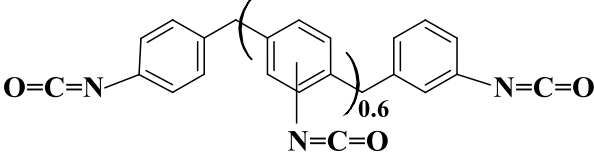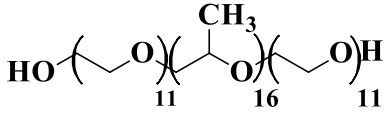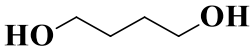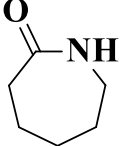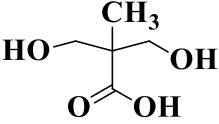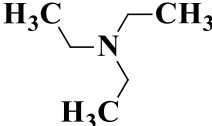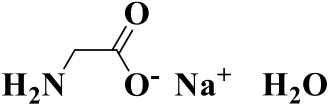
CHAPTER 3

3. Experimental

3.1. Materials

Polyisocyanates, polyester polyols, Bayhydrol UH XP 2658 and PEG 600 were kindly supplied by Bayer MaterialScience AG. Pluronic PE 3500 was provided by BASF Turkey. ε-caprolactam was purchased from Merck. Anhydrous triethylamine (TEA) (99%), Glycine sodium salt hydrate (GSS) (98%) were purchased from Sigma Aldrich. Acetone and methyl ethyl ketone (MEK) were also purchased from Sigma-Aldrich Chemical Company, USA and dried over 3 Å molecular sieves for 7 days prior to use. Ethyl acetate was obtained form Riedel-de Haën AG, USA. 1,4-Butanediol (99+%) was purchased from Acros Organics, USA. Dimethylolpropionic acid (DMPA) was donated by Geo Chemicals, USA and dried at 100ºC for 1 hour in an oven prior to use. All other reagents were used as received unless otherwise stated. The structures of key reagents were shown in the Table 3.1.

Table 3.1 The structure of the reagents for the synthesis of the waterborne polyurethane

Structure	Name
$O=C=N$ — (aromatic) — $N=C=O$, $N=C=O$, subscript 0.6	Polyisocyanate
HO—(—O—)$_{11}$(—CH_3,O—)$_{16}$(—O—)$_{11}$H	Pluronic PE 3500
HO ~~~~ OH	1,4-Butanediol
O=, —NH (ring)	Ɛ-caprolactam
HO—, CH_3, OH, $O=$, OH	Dimethylolpropionic acid (DMPA)
H_3C, CH_3, N, H_3C	Triethylamine (TEA)
H_2N, O, O^- Na^+, H_2O	Glycine sodium salt hydrate (GSS)

3.2. Synthesis

In our approach, each of the synthesized polymer is labeled as ''NO-1-x'', in which x denotes the order of synthesis.
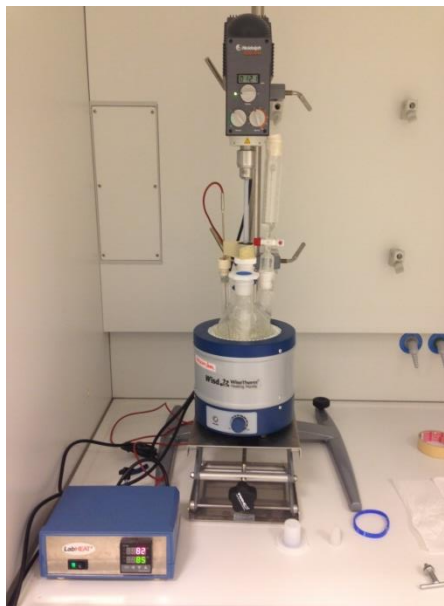
Figure 3.1 Prepolymer synthesis set up
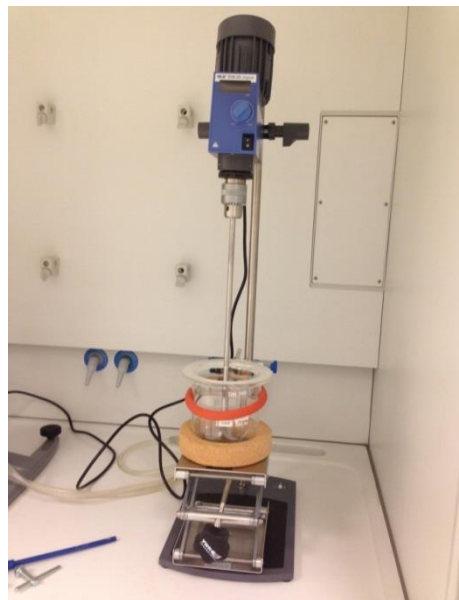
Figure 3.2 Dispersion set up
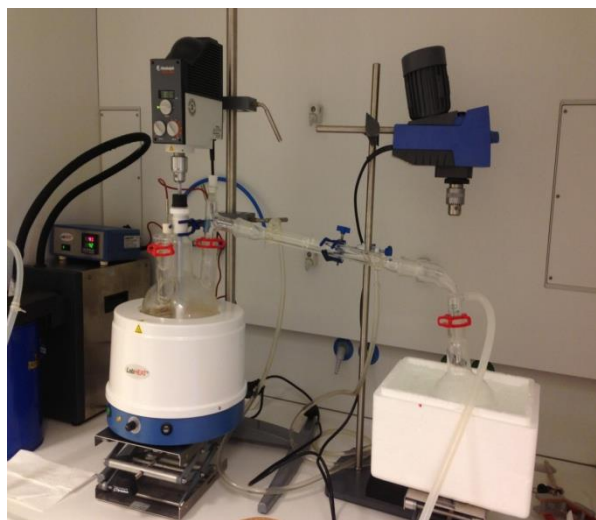
Figure 3.3 Distillation set up

Synthesis Branched PUDs Possessing Internal Ionic Groups on the Polymer Chain (Route I)

Prepolymer Synthesis Pluronic PE 3500 and DMPA were charged into the dried 500 ml, four necked, round-bottomed flask that was equipped with an overhead mechanical stirrer, condenser, addition funnel, and thermocouple that was connected to a a heating mantle to control the reaction temperature. Temperature was set to 75 °C and contents were dewatered by applying vacuum (~2 mbar) was for 15 min. Vacuum was released and multifunctional isocyanate was added dropwise over 25 min into the reaction mixture at 75 °C and the mixture was stirred for another 5 h at 75°C. The synthesis of NCO-terminated prepolymer was followed by FT-IR spectroscopy based on a decrease in the NCO signal at 2260 cm^{-1}, and appearence of urethane carbonyl peaks at 1711 cm^{-1}.

Blocking Reaction Upon the completion of the prepolymer reaction, ε-caprolactam was slowly added over 2 h at 80°C. The completion of the blocking reaction was confirmed using FT-IR spectroscopy based on the disappearence of the NCO peak and appeareance of the urea carbonyl at 1655 cm^{-1}. Upon the completion of the blocking reaction, the reaction mixture was dissolved in acetone while cooling to 50°C. As neutralization agent, TEA was added into the reaction mixture to react with carboxylic group in the DMPA and stirred 30 min at 50°C.

Dispersion Step Dispersion of the polyurethane product was accomplished by slowly adding the polyurethane/acetone solution into distilled water at room temperature while agitating at >500 rpm. Addition of all polyurethane solution was done in a 10 min period to obtain the polyurethane dispersion in water with acetone.

Distillation Step The polyurethane dispersion and acetone mixture was then heated to 42°C and acetone removal by a slow distillation process began. For the complete removal of acetone, 50 mbar vacuum and 42°C was achieved. The resulting product, a stable waterborne polyurethane dispersion with a solids content of about 30%, was collected by filtering through a ~50 micron filtration media.

Notebook number starting from NO-1-013 to NO-1-035 were synthesized according to the procedure above with varying chemical compositions and parameters as summarized in Table 3.2.

Table 3.2 Chemical compositions of functional, branched and waterborne polyurethanes in Route I

PU	NO-1-013	NO-1-018	NO-1-021	NO-1-022	NO-1-023	NO-1-024	NO-1-026	NO-1-029	NO-1-031	NO-1-032	NO-1-033
Isocyanate (B_n)	2.1	2.6	2.9	2.9	2.6	2.9	2.9	2.9	2.9	2.6	2.6
Polyol (A_2)	Pluronic PE 3500	Pluronic PE 3500	Pluronic PE 3500	Pluronic PE 3500	Pluronic PE 3500	Pluronic PE 3500	Polyester polyol	Polyester polyol	Polyester polyol	Polyester polyol	Polyester polyol
Ionic center (A_2)	DMPA	DMPA	DMPA	DMPA	DMPA	DMPA	DMPA	DMPA	DMPA	DMPA	DMPA
Chain extender	-	-	-	1,4-Butanediol	-	-	-	-	-	-	-
Blocking agent	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam
Neutralizing agent	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA
Solvent	Acetone	Acetone	Acetone	Acetone	Acetone	Acetone	Acetone	Ethylacetate	E.acetate and acetone mix	E.acetate and acetone mix	Acetone
Final functionality	2.2	gel	4.6	gel	3.5	4.8	gel	gel	gel	gel	gel
Soft segment % in TRS	19.56	gel	21.15	gel	18.96	18.63	gel	gel	gel	gel	gel
COOH % by weight	2.00	gel	2.8	gel	2.93	2.44	gel	gel	gel	gel	gel
A_2:B_3 ratio	0.57	0.74	0.68	0.82	0.70	0.70	0.78	0.78	0.78	0.68	0.65
Particle size (nm)	22*	gel	11*	gel	59*	30*	gel	gel	gel	gel	gel

*: Bi-modal

Synthesis of Polyurethane Dispersions Possessing Ionic End-Groups
(Route II)

Prepolymer Synthesis The same prepolymer process mentioned in Route I above was followed using a polyester polyol in place of Pluronic PE 3500.

Blocking Reaction Upon the completion of the prepolymer reaction, ε-caprolactam was slowly added over 40 min at 80°C. Upon the completion of the blocking reaction, GSS and distilled water mixture was added at 45°C.

Dispersion Step Dispersion of the polyurethane product was accomplished by slowly adding distilled water into the polyurethane/methyl ethyl ketone (MEK) solution at room temperature while agitating at >500 rpm. Addition of all dispersing water was done in a 10 min period to obtain the polyurethane dispersion in water with MEK.

Distillation Step The polyurethane dispersion and MEK mixture was then heated to 42°C and MEK removal by a slow distillation process began. For the complete removal of MEK, 50 mbar vacuum and 42°C was achieved. The resulting product, a stable waterborne polyurethane dispersion with a solids content of about 30%, was collected by filtering through a ~50 micron filtration media.

Notebook number starting from NO-1-035 to NO-1-063 were synthesized according to the procedure above with varying chemical compositions and parameters as summarized in Table 3.3.

Table 3.3 Chemical compositions of functional, branched and waterborne polyurethanes in Route II

PU	NO-1-035	NO-1-036	NO-1-037	NO-1-038	NO-1-039	NO-1-040	NO-1-041	NO-1-042	NO-1-043
Isocyanate (B_n)	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Polyol (A_2)	Polyester polyol	Polyester polyol	Polyester polyol	-	Polyester polyol	Polyester polyol	Polyester polyol	-	-
Chain extender	-	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol
Blocking agent	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam
Emulsifying agent	GSS	GSS	GSS	GSS	GSS	GSS	GSS	GSS	GSS
Solvent	MEK	MEK	MEK	MEK	MEK	MEK	MEK	MEK	MEK
Final functionality	3.08	3.08	3.09	3.23	gel	3.19	3.20	3.22	3.23
Soft segment % in TRS	17.06	21.84	3.52	-	gel	14,67	14.20	-	-
COOH % by weight	2.23	2.50	3.50	3.50	gel	2.50	2.75	3.25	3.50
Particle size (nm)	108	72	49	23	gel	19*	64*	314*	41*
A_2:B_3 ratio	0.54	0.56	0.63	0.66	0.63	0.61	0.61	0.63	0.66
Note	Emuls. at 45ºC	Emuls. at 45ºC	Emulsification at 45ºC	Emuls. at 45ºC	gel	Emuls. at 45ºC	Emuls. at 45ºC	Emuls. at 45ºC	Emuls. at 45ºC

*: Bi-modal

Table 3.4 Chemical compositions of functional, branched and waterborne polyurethanes in Route II

PU	NO-1-056A	NO-1-057	NO-1-058	NO-1-059	NO-1-060	NO-1-061	NO-1-063
Isocyanate (B_n)	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Polyol (A_2)	Polyester polyol	Polyester polyol	Polyester polyol	Polyester polyol	Polyester polyol	Polyester polyol	Polyester polyol
Chain extender	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol	1,4-Butanediol
Blocking agent	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam	ε-caprolactam
Emulsifying agent	GSS	GSS	GSS	GSS	GSS	GSS	GSS
Solvent	MEK	MEK	MEK	MEK	MEK	MEK	MEK
Final functionality	4.20	gel	3.82	gel	gel	4.20	4.20
Soft segment % in TRS	3.50	gel	3.47	gel	gel	1.00	3.50
COOH % by weight	2.25	gel	2.93	gel	gel	2.44	2.30
Particle size (nm)	30*	gel	73	gel	gel	87	334
A_2:B_3 ratio	0.73	0.73	0.72	0.75	0.69	0.74	0.74
Note	Emulsif. at 7ºC	gel	Emulsif. at 7ºC	gel	gel	Emulsif. at 7ºC	Emulsif. at 7ºC

*: Bi-modal

Preparation of Waterborne Polyurethane Dispersion Films

For coating applications, calculated amounts of synthesized polyurethane dispersions and PEG 600 or Bayhydrol UH XP 268 were mixed to obtain 1:1 NCO:OH ratio and cast onto a 20x30 glass plate at room temperature. Cast films were dried in an oven at 90 °C for 30 min to ensure the complete removal of water. Then, films were cured at 120 °C and 180 °C for 30 min and solid polyurethane films were obtained.

3.3. Characterization

The mean particle size and the average particle size distribution of PUDs were measured using Nanoseries Zetasizer provided with laser diffraction and polarised light of three wavelengths (P.I.D.S.) detectors. The samples were diluted with deionized water to adjust solid content and a small amount of aqueous dispersion was directly placed in the cell. The statistical model used to obtain the particle size distributions assumes that the particles are polyurethane and taking into account the refraction index of the polyurethane (1.5) and the water (1.333). The measurements were carried out at room temperature. Polymerization reactions were followed using a Nicolet IS10 Fourier Transform Infrared Spectrometer equipped with an ATR system. Dynamic mechanical analysis (DMA) was performed on Netzsch DMA. The experiments were carried out in tension mode by heating the sample from 24 to 200 ºC, using a heating rate of 10ºC /min, a frequency of 1Hz, maximum amplitude of 10 μm peak to peak and maximum dynamic force of 3N. Zwick-Roell Z100 Universal Testing Machine (UTM) was used for tensile stress tests. The stress–strain behavior of the films was determined using micro-tensile dog-bone test speciments films with 2.9 mm width, 10 mm grip separation distance, and 25 mm/min cross-head speed according to ASTM D1708 test method. Three to five samples were measured and their results were averaged.

CHAPTER 4

4.   Results and Discussion

4.1.   Synthesis of Functional, Branched Waterborne Polyurethane Dispersions

This study has focused on the development of novel synthethic approaches for the development of chemically functional, branched polyurethanes in the form of waterborne dispersions. For this purpose, synthetic approaches to obtain waterborne polyurethane dispersions were combined with the branching methodology in step-growth polymerization, so called A_2+B_n (n>2) approach. The $A_2 + B_n$ approach allowed us to design and obtain highly branched polyurethanes with a multitude of blocked isocyanate functionality. In order to synthesize such functional, branched polyurethanes in the form of waterborne dispersions, ionic groups that acted as emulsifying agents were deliberately incorporated either along polymer chains as pendant groups, or at polymer chain-ends as telechelic groups as shown in Scheme 4.1 and Scheme 4.2 using synthetic Routes I and II, respectively as discussed in detail below. Branched polyurethane dispersions in this thesis were synthesized by a modified acetone process.
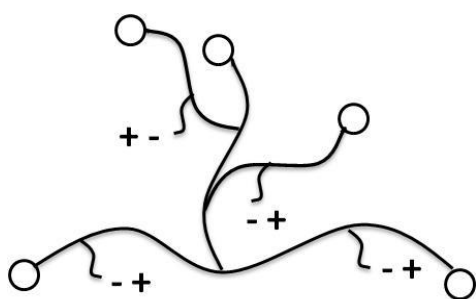
Scheme 4.1 Pendant ionic groups placed along the polymer backbone
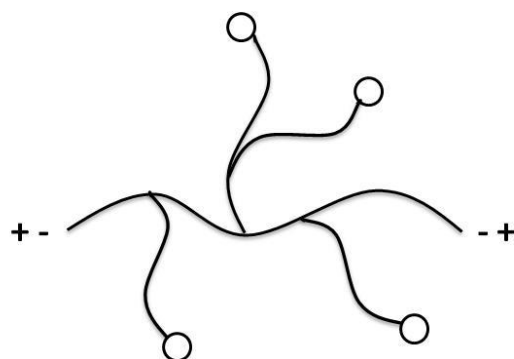
Scheme 4.2 Ionic groups placed on the polymer chain ends
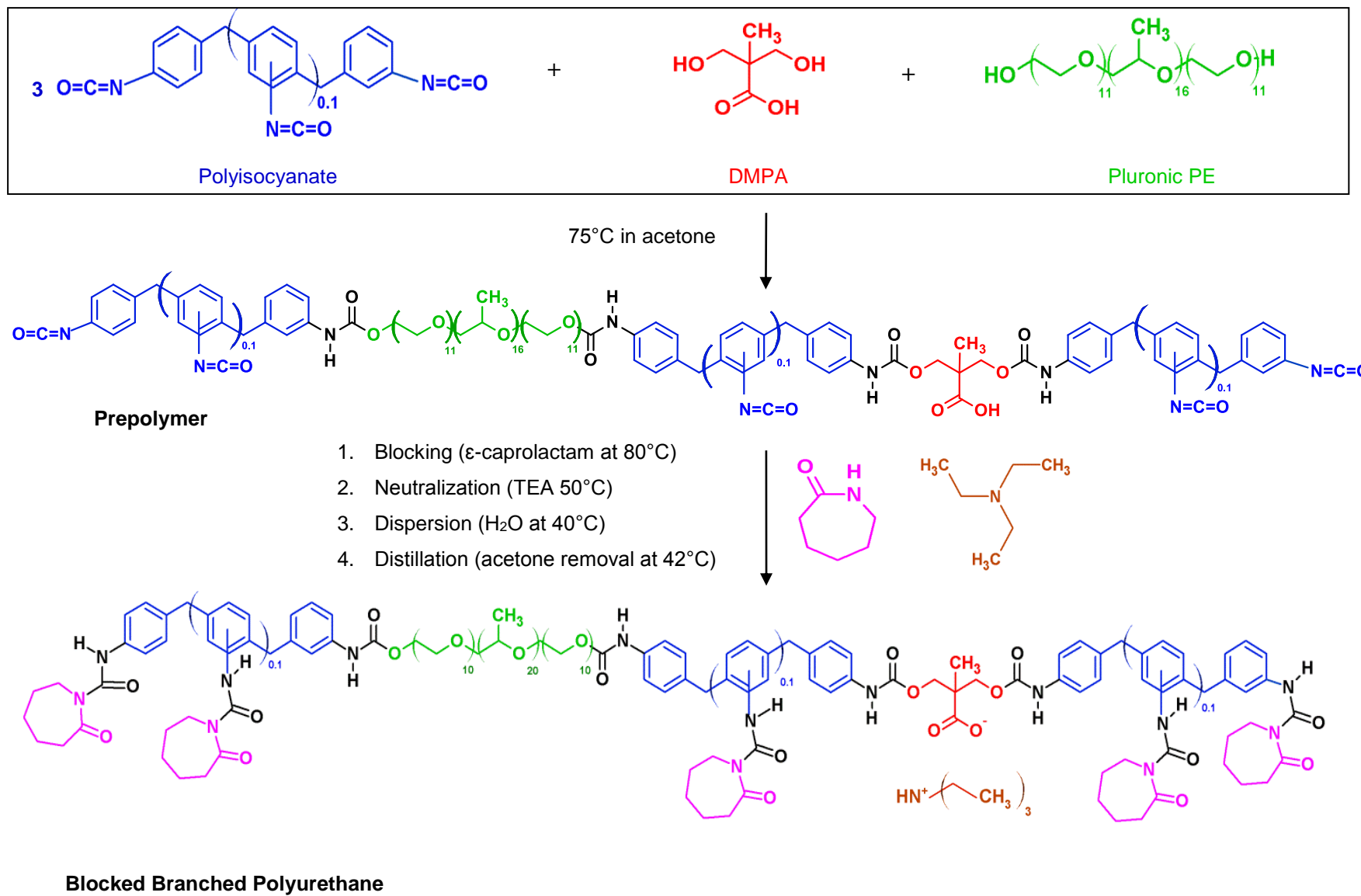
Scheme 4.3 The preparation process of the branched, waterborne polyurethaneL dispersion
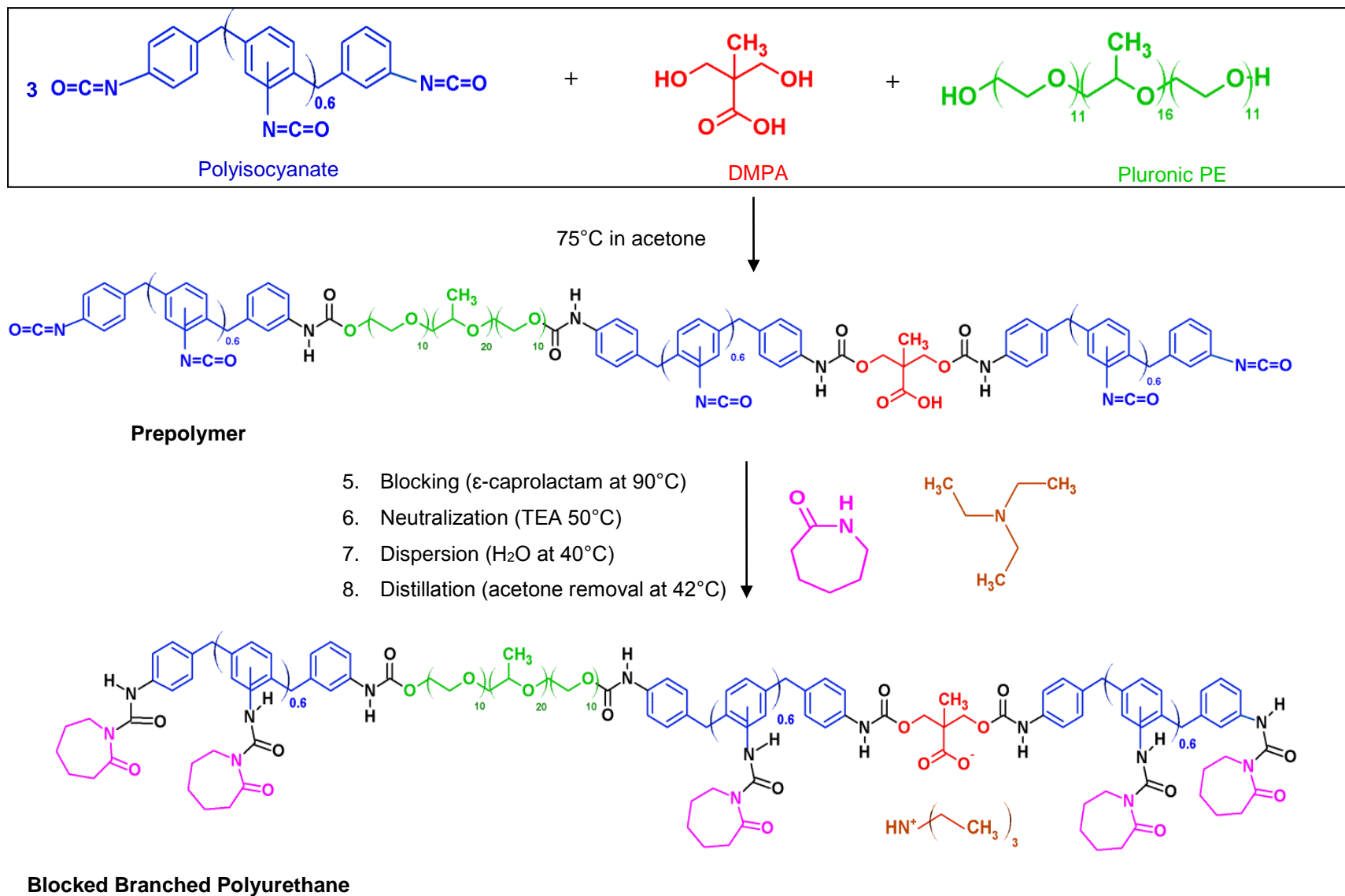
Scheme 4.4 The preparation process of the branched, waterborne polyurethane dispersion
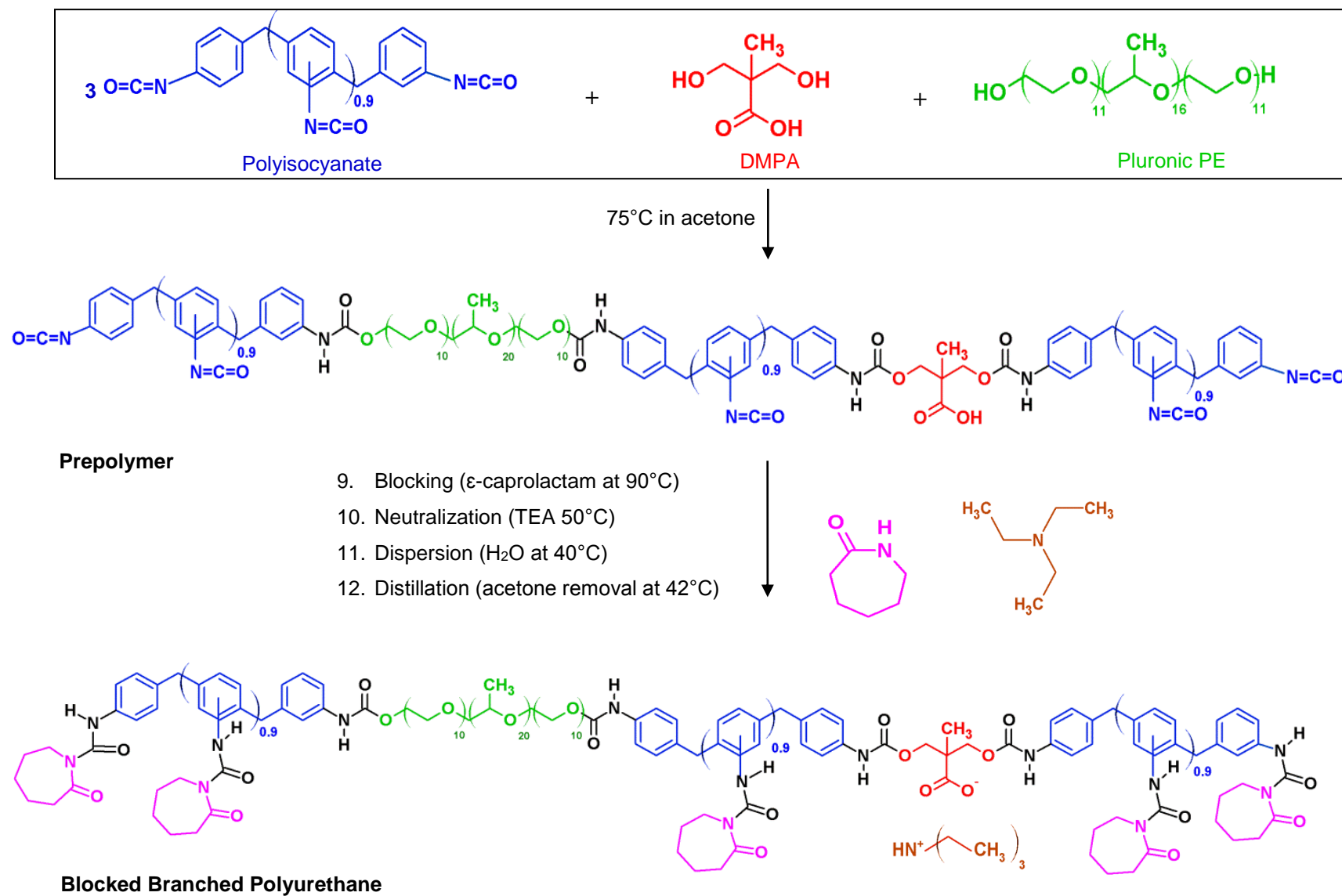
Scheme 4.5 The preparation process of the branched, waterborne polyurethane dispersion

4.1.1. Route I: Branched PU Possessing Internal Ionic Groups on the Backbone

Highyl branched, functional and waterborne polyurethane dispersions were synthesized via the oligomeric $A_2 + B_n$ approach where a multifunctional isocyanate (B_n, n>2) was reacted with A_2 type oligomers or monomers such as polyether polyol and short diols in such ratios that NCO-terminated branched polyurethane prepolymers were obtained without any gelation. For this purpose, the ratio of the $A_2 : B_n$ molecules (thus A:B groups) was critical, as emphasized in Table 2.2. It is important to note that, in addition to the branched topology that was achieved by the $A_2 + B_n$ approach, in order to obtain a polymer in the form of waterborne dispersion, ionic groups were incorporated into the polyurethane backbone using DMPA as one of the A_2 monomers as depicted in Scheme 4.1. As shown in Scheme 4.3, Scheme 4.4 and Scheme 4.5, DMPA molecule is a short-diol with a pendant carboxylic acid group, which can be neutralized with tertiary amines such as TEA to obtain a hydrophilic triethylammonium carboxylate salt group.

In waterborne polymer dispersions, the size and distribution of polymer latex particles play a critical role in the colloidal stability of these dispersions to avoid undesirable precipitation or phase separation of the polymer during storage. The optimum amount of COOH was determined as 2-3% with the aid of non-ionic Pluronic PE 3500 at 18-22% content in this study when an aromatic MDI-based polyisocyanate was used as shown in Scheme 4.5. This has enabled us to achieve stable dispersions having uniform particle size distributions with average particle size below 300 nm. The prepolymer synthesis step in Scheme 4.3 was monitored by FT-IR spectroscopy, in which the NCO peak at 2260 cm^{-1} was reduced as the reaction proceeded and remained constant upon the consumption of all hydroxyl groups of A_2 components. In addition, urethane carbonyls began to form as shown in Figure 4.2 at 1711 cm^{-1}. Pluronic PE 3500, which is a diol of a PPG-PEG copolymer (50:50 ratio, M_n: 1900 g/mol) that was used as the soft segment also has a hydrophilic nature and therefore acts as a non-ionic emulsifying agent in the polyurethane chain while imparting a flexible nature to the polyurethane product.

The order and rate of monomer addition were critical factors to obtain a homogeneous, gel-free reaction mixture. In general, a slow addition of A_2 into B_n monomer in dilute

solution avoids premature gelation. Thus, functional waterborne polyurethanes were synthesized in this study based on the slow addition of A_2 into B_n approach. The polymerization procedure, where A_2 was added slowly onto B_n, is quite different than the conventional procedures employed for the preparation of step-growth polymers, which usually involves the addition of all reactants into the reactor at the beginning of the reaction. Isocyanates are highly reactive and they are sensitive to moisture either from solvents or high humidity. Slow addition of A_2 onto a large excess of B_n is expected to provide a more controlled topology during the polymer formation. It will also reduce the formation of side reactions and more importantly the risk of gel formation during reactions, since the stoichiometric balance of the reactants will be controlled throughout the reaction. A_2 and B_n can also be mixed directly at the beginning of the reaction. In order to have a gel-free polymer, A:B ratio should be much more lower than the critical rate shown in Table 2.2. When A:B ratio close to that of the critical ratio, slow addition of A_2 into B_n even in dilute solution might be necessary to control topology and to avoid undesired gelation.

In the synthethic approach Route I utilized in this study, the prepolymer and blocking reactions were carried out in bulk without any solvent following the prepolymer synthesis at 80°C. At the end of the blocking reaction of isocyanate end groups with ε-caprolactam, the reaction mixture was usually highly viscous. This reaction was also followed and confirmed by FT-IR spectroscopy due to complete disapparence of isocyanate peaks at 2260 cm^{-1} and appearance of urea peaks at 1655 cm^{-1}. Acetone is commonly employed in waterborne polyurethane synthesis as a temporary solvent to dissolve polyurethane chains and to transfer and emulsify them in water. Another advantage acetone offers is the ability to easily remove it from the polymer/water mixture by vacuum distillation upon the completion of the reaction. In our Route I synthethic approach, acetone was determined to be a suitable solvent for the prepolymer and ε-caprolactam blocked polyurethane since it easily dissolved the viscous product obtained after the blocking reaction. In this way, the viscosity and temperature of the reaction mixture was reduced, therefore neutralization of carboxylic acid pendant groups on the polymer chains with TEA were achieved at 50 – 55 °C, at a temperature below TEA's boiling point. More importantly, the reduced viscosity of the final product enabled us to disperse and emulsify it in water easily by adding the polymer/acetone

solution into water under high agitation rates (>400 rpm). The emulsification step would not be possible in the absence of acetone or a similar solvent.

Commercially available MDI-based polyisocyanates with average functionalities of 2.1, 2.6 and 2.9, respectively, (Table 3.1) were used as B_n multifunctional monomers. These monomers also formed the hard segment of polyurethanes synthesized in this study. As shown in Scheme 4.3, an isocyanate end-capped prepolymer was synthesized through the reaction of polyisocyanates with Pluronic PE 3500 and DMPA, in which excess equivalents of NCO groups with respect to hydroxyl groups was present. After obtaining NCO-terminated prepolymer, these NCO end-groups were blocked with ε-caprolactam at 80°C and the reaction was confirmed by FT-IR spectroscopy by the disappearance of NCO peak at 2260 cm^{-1}. After the blocking reaction, the product was dissolved in acetone and cooled to 42°C. Then triethylamine (TEA) was added to neutralize the carboxylic acid in the DMPA to form pendant ionic groups on the polymer chains. In FTIR spectra of prepolymer and polyurethane dispersion in Figure 4.1 and Figure 4.2, the gradual disappearance of isocyanate groups after 50%, 75% and 100% ε-caprolactam addition (in weight percent) can be observed. The NCO group has characteristic absorption peak at around 2260 cm^{-1} which is due to the antisymmetric stretching. The absence of characteristic NCO absorption around 2260 cm^{-1} indicated the absence of free NCO groups. This indicated that the NCO groups of the isocyanate molecule were almost completely blocked with the blocking agents in Figure 4.2. Strong absorptions at 1700 cm^{-1} (C=O stretching), 3250–3300 cm^{-1} (N–H stretching), 1530–1560 cm^{-1} (N–H bending) and 1210–1240 cm^{-1} (the stretching vibration of the C=O group of urea combined with the N–H group) and the stretching band of C-O appears in 1000-1150 cm^{-1} confirmed the formation of blocked polyisocyanate containing polyurethane product.

In our synthesis, isocyanate end-groups were blocked with stoichiometric equivalent of blocking agent, ε-caprolactam, to obtain NCO-blocked end-groups. It is important to note that for successful syntheses, one should ensure complete blocking of isocyanate end-groups with ε-caprolactam before neutralization and dispersion steps. If these isocyanate end-groups are not completely blocked, when the neutralizing agent TEA is added into the reaction, a rapid gelation may occur primarily due to the catalytic effect of TEA towards aromatic isocyanate reactions. In fact it is well-known that TEA and

similar tertiary amines are commonly employed as catalysts during polyurethane synthesis. Thus, one should ensure that all aromatic isocyanate groups are blocked or reacted prior to the neutralization step by TEA addition. In addition, if an MDI-based PU prepolymer without blocking was dispersed in water, the NCO groups would rapidly react with water, which would cause uncontrolled chain extension of this multitude of end-groups with water to result in a highly cross-linked product, therefore undesired gelation. In our studies, successful synthesis resulted in a clear, low viscosity polymer solution in acetone after neutralization before dispersion steps as shown as in Figure 4.3. In fact FT-IR spectroscopy was used as a powerful tool to follow the reaction step by step as shown in Figure 4.2. In addition, the absence of any undesired gel products during the neutralization or dispersion step also confirms complete blocking of isocyanate groups, which otherwise would go under side reactions upon TEA addition or react with excess water present in the dispersion step and form gel particles. Therefore, blocking of isocyanate end-groups with ε-caprolactam enabled us to not only obtain thermally reactive end-groups but also protect these end-groups before the dispersion step to prevent the reaction of isocyanate groups with water. The advantages of blocked isocyanates include their ease of handling, non-reactivity and lack of sensitivity to atmospheric humidity at room temperature or temperatures up to 80°C.

As summarized in Table 3.2, among several reactions from NO-1-013 to NO-1-035, some attempts such as NO-1-018, NO-1-022, NO-1-026, NO-1-029, NO-1-031, NO-1-032 and NO-1-033 were unsuccessful to synthesize waterborne, functional polyurethanes. Hence, it was very critical in this study to understand and figure out reasons behind premature gelations that occurred during these syntheses. As discussed in the previous paragraph, it was very critical to ensure the absence of any isocyanate groups prior to the TEA addition for neutralization purposes. For example, in NO-1-018 and NO-1-022 gelation occured immediately after the addition of triethylamine shown as in Figure 4.4. In these cases, TEA catalyzed the excess isocyanate to react with potentially "active" hydrogen atom in urethane and urea groups in the reaction mixture to form allophanate and biuret groups, which resulted in an insoluble crosslinked network in acetone. Pluronic PE 3500, which is a diol of a PPG-PEG copolymer (50:50 ratio, M_n: 1900 g/mol), was used as an A_2 oligomer in an attempt to control the distance between branch points in this study. It was a long polyether polyol which created long distances between crosslink points. In an attempt to shorten the distance between branch

points, a shorter diol of a polyester oligomer was used as the A_2 oligomer. Reactions prematurely resulted in gelation due to limited solubility of the new product in acetone (NO-1-026 and NO-1-033, Table 3.2). Acetone has a low boiling point (56°C) and this temperature was not sufficient enough to complete the reaction at the beginning to obtain NCO-terminated prepolymer and blocking reactions and thus acetone was always utilized prior to the neturalization step. As summarized in Table 3.2 in NO-1-029, NO-1-031 and NO-1-033, a higher boiling point solvent, ethyl acetate was used as a co-solvent to assist acetone; however, these reactions also resulted in gelation. In fact, when ethyl acetate utilized as the only solvent, gelation occurred during blocking reactions, showing poor solubility of the new product. It was presumed that when shorter diol of a polyester oligomer was used in place of Pluronic PE 3500 the polymerization reaction resulted in a more compact product with a higher average degree of branching and a more aromatic nature, which, therefore was insoluble in common solvents that could be used waterborne polyurethane synthesis.
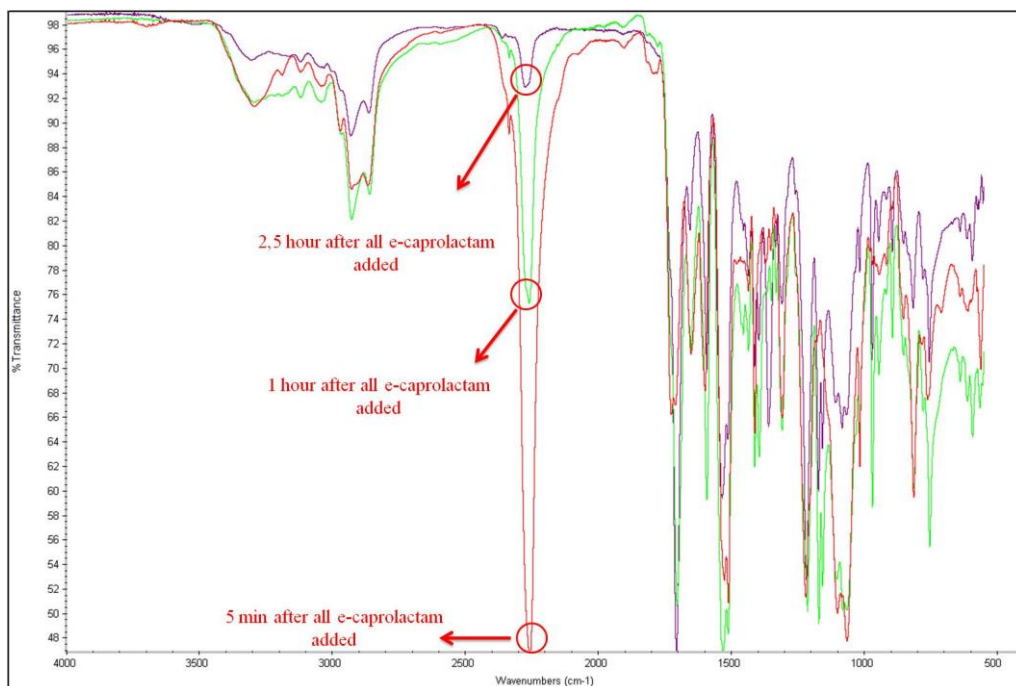
Figure 4.1 FTIR spectrum of polyurethane dispersion after the completed reaction
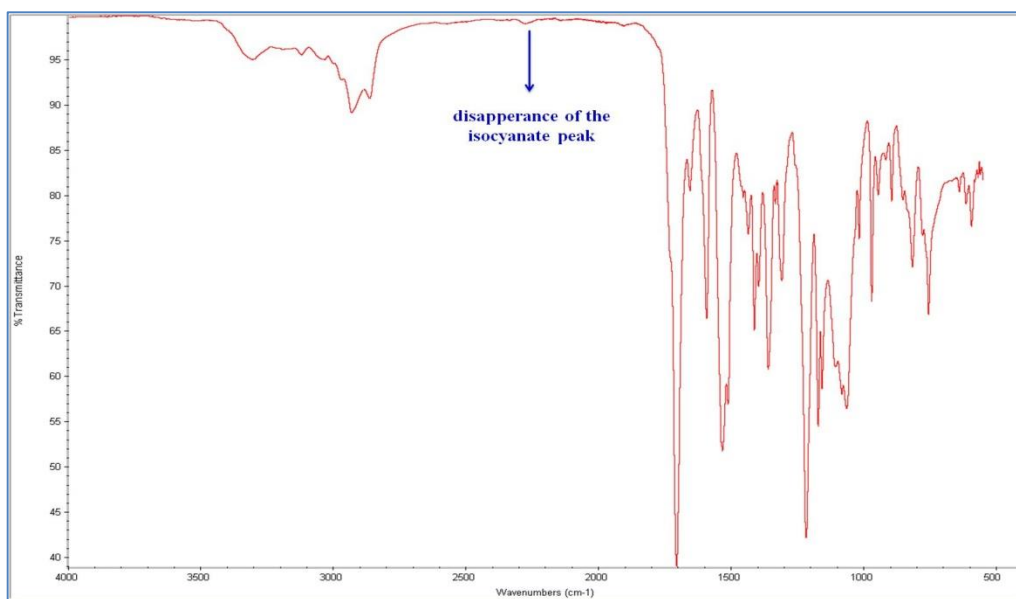
Figure 4.2 FTIR spectrum of ε-caprolactam endcapped prepolymer

Figure 4.3 Blocked polyurethane/acetone solution before dispersion

Figure 4.4 Gelation after triethylamine addition

To sum up, a new synthethic approach, Route I, was developed successfully based on an A_2+B_n polymerization strategy to prepare branched, chemically functional polyurethanes possessing pendant ionic groups along the chain, which allowed us to emulsify these products in water to obtain waterborne dispersions. Two critical reasons were discovered for possible premature gelation of the product during the syntheses. By controlling key reaction conditions and parameters, such as the solution concentration, molar ratio and addition order of monomers, relative reactivity of the functional groups, and preferred partial monomer conversion gelation was effectively avoided. It was very critical to ensure complete reaction of isocyanate groups prior to the introduction of TEA for neutralization purposes, since TEA could catalyze residual isocyanate groups in the reaction mixture to form branched allaphonate and biuret structures resulting in premature gelation during syntheses. In addition, the choice of solvent, acetone was found to offer limited solvating power when the distance between branch points was shortened with from ~1800 to 200 daltons.

4.1.1.1. Principles of Branching by A_2 + B_n (n>2)

Although Route I was successfully developed to synthesize waterborne, branched polyurethanes with pendant ionic groups, premature gelation issues encountered during the polymerization reaction limited the applicability of this synthethic route to a wide range of chemical components. In addition, it was critical to pre-calculate the average functionality of the final branched polymer based on the ratio of the A_2 : B_n molecules or A:B groups. For this purpose, one needs to re-visit the principles of A_2 + Bn polymerization process, which is known to be a feasible method to obtain highly branched products with a multitude of functional end-groups and controlled distance between branch points. Flory has demonstrated that depending on the stoichiometry of the monomers and extent of reaction, step-growth polymerization reactions involving a mixture of difunctional (A_2) and multifunctional (B_n) monomers lead to the formation of hyperbranched or crosslinked polymers. According to Flory, for an A_2+B_n system with all monomers initially present in the reaction mixture, assuming no side reactions, the critical monomer conversions at gel point can be calculated by using the following equations;

$$\alpha = r \times P_A^2 = P_B^2/r \qquad (4.\ 1)$$

$$\alpha_c = \frac{1}{(f-1)} \qquad (4.\ 2)$$

where (α) is the probability of branching which means the probability that a given functional group of a branch unit (B_n) is linked to another branch unit, (α_c) is the probability of branching for gelation, (f) average functionality of multifunctional monomers in the system, (pA and pB) are the extent of reaction for A and B type monomers and (r) is the ratio of the A groups to that of B groups. Therefore, α_c becomes 0.53 for an A_2 + B_n polymerization if only trifunctional monomer is present as a multifunctional monomer. As calculated from Equation (4. 1), the maximum α value is equal to one, which resembles a fully crosslinked system. In an A_2 + B_n polymerization, it is important to calculate the critical conversion of A and B groups (P_{Ac} and P_{Bc}) at the

gel point for various r values, based on equations. Flory showed that when $\alpha < \alpha_c$, gel formation is impossible, but may be possible when $\alpha > \alpha_c$. Therefore, in our synthesis it was critical take α and α_c values into account to ensure gel-free, highly branched products. Another critical parameter in our synthesis was the average final functionality of branched polyurethanes that were synthesized via the A_2+B_n polymerization. For this purpose, in order to statistically calculate the final average functionality of a polymer which is synthesized by $A_2 + B_n$ (where n>2) polymerization method, Equation (4. 3) was proposed;

$$f_{final} = \frac{NB - NA}{nB_x - nA_2} \tag{4. 3}$$

where NB is the number of B equivalent groups, NA is the number of A equivalent groups, nB_n is the number of moles of B_n and nA_2 is the number of moles of A_2. For example, if 3 moles of B_3 monomer (possessing 9B equivalent groups) and 2 moles of an A_2 monomer (possesing 4A equivalents) are mixed to react with each other, final average functionality can be calculated as five using the Equation (4. 3) as also simply shown in Figure 4.5. Since it is well-known that step-growth polymers always have a polydispersity, thus composed of different size of molecules, this equation will always give an average functionality value, although this functionality will have a polydispersity based on the molecular weight distribution of the final product.

$$f_{final} = ((3*3B) - (2*2A))/(3 - 2) = 5$$
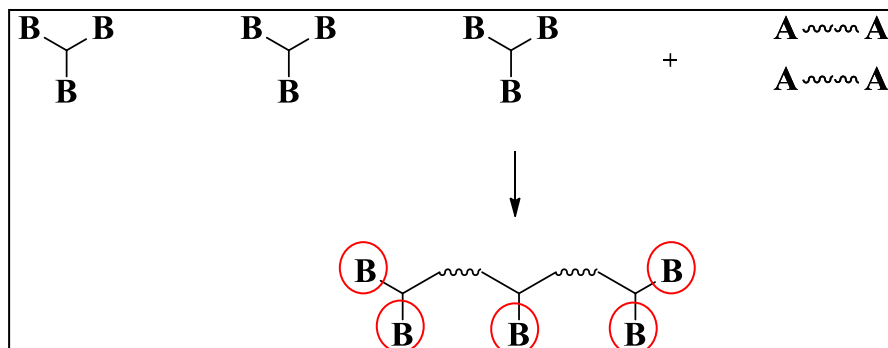
Figure 4.5 Final average functionality calculation of the synthesized polymer from $3B_3$ and $2A_2$ molecules

The ability to pre-calculate the average functionality of final products in this study enabled us to precisely control this paremeter. As summarized in Table 3.2, when Equation (4. 3) was applied to polyurethanes synthesized by Route I, it was demonstrated that branched polyurethanes with final average functionalities ranging from 2.2 to 4.8 were obtained simply by controlling the degree of branching simply with two paremeters in our syntheses: (i) $A_2 : B_n$ or A:B ratio and (ii) functionality of the starting B_n reagent.

4.1.2. Route II : Branched PU Possessing Internal Ionic Groups on Chain Ends

In addition to premature gelation issues, limited solubility of reaction products in acetone was a critical limitation in increasing the average functionality of final products in Route I. For this reason, a new strategy, Route II, was developed to obtain gel-free branched polyurethane dispersions with higher average functionalities in our studies. In Route II, a new solvent, methyl ethyl ketone was used in place of acetone, and ionic groups were deliberately at polymer chain-ends as shown in Scheme 4.2. Highyl branched, functional and waterborne polyurethane dispersions were synthesized via the oligomeric $A_2 + B_n$ approach where a multifunctional isocyanate (B_n) was reacted with a a diol of a polyester oligomer in such ratios that NCO-terminated branched polyurethane prepolymers were obtained without any gelation. It is important to note that, in addition to the branched topology that was achieved by the $A_2 + B_n$ approach, in order to obtain a waterborne polymer, ionic groups were incorporated into the polyurethane chain ends using GSS as the emulsifying agent monomer as depicted in Scheme 4.2. GSS molecule is a mono-amino compound possessing a sodium carboxylate group. It was again essential to optimize the reaction conditions to obtain gel-free, fully soluble products in our studies in Route II. In this case, using a new ionic monomer incorporated at polymer chain ends allowed us to study the influence of it on the properties of the final product. Also, poor acetone solubility problem in Route I syntheses was overcome by using MEK as the solvent. MEK was a suitable solvent since both the starting materials and the final product were completely soluble. In fact, MEK.has similar solvent properties to acetone but boils at a higher temperature (79.64 °C), still lower than water, which enables us to remove it from the polyurethane/water/MEK mixture at the end of the reaction by vacuum distillation to obtain co-solvent free, completely waterborne products. In waterborne polymer dispersions, the size and distribution of polymer latex particles play a critical role in the stability of these dispersions to avoid undesirable precipitation of the polymer during storage as mentioned before. The PUD's with larger particle size generally undergoes agglomeration, thus possesses shorter shelf life compared to dispersions containing smaller particle size. The higher surface energy of smaller size dispersions facilitates the better film formation. The concentration of hydrophilic group, stirring speed, prepolymer viscosity and the rate of water addition can certainly influence the particle

size of the PUD. Among the various influencing factors, the particle size is greatly influenced by the concentration of carboxylic acid (hydrophilic group). To have a stable dipsersion, the optimum amount of COOH was determined as 2.2-3.5% with the emulsifying agent, glycine sodium salt in our studies. These have enabled us to achieve stable dispersions below 350 nm. The particle sizes of the synthesised PUD's were presented in Table 3.3 and Table 3.4.

For syntheses in Route II, α and α_c were calculated from the Equations (4. 1) and (4. 2), which enabled us to do final functionality calculations using Equation (4. 3). As expected, in our experimental studies no gelation was observed during the prepolymer step (reaction of A_2 and B_n) as long as α value was not greater than α_c.

Key reaction parameters of the polyurethane dispersions for Route II were listed in Table 3.3 and Table 3.4. In Route II syntheses, Pluronic PE 3500 was replaced with short a diol of a polyester oligomer in an attempt to shorten the distance between branch points. A shorter polyester polyol provided shorter distance between branch points to achieve polyurethanes with a more branched topology functionality. Limited solubility of the product in acetone and ethylacetate in Route I was due to high degree of branching, urea contents and aromatic structure of monomers. Shorter polyester polyol increased the aromaticity in polymer chain and lowered the solubility of the product in solvent by forming gelation. Another problem encountered in Route II was gelation before the addition of triethylamine. In cases where ε-caprolactam was not allowed to completely react, even the presence of residual isocyanate groups remained in the reaction mixture would immediately result in side reactions. To eliminate these gelation issues, ionic emulsifying agent DMPA was replaced with GSS, which allowed us to introduce sodium carboxylate ionic groups at polyurethanes' chain ends. The quantitative disappearance of isocyanate groups was confirmed by using FTIR and standard back titration method (ASTM D841). After completion of the blocking reaction, temperature was set to 45°C for the emulsification step. Aqueous GSS (50%) was added dropwise at 45°C to obtain a polyurethane solution in MEK with a small amount of water. It is important to note that GSS was only miscible and reactive with the reaction product when added in an aqueous solution.

Incorporating chain extenders, such as diols of low molecular weight enhances the elastomeric properties of the resulting polyurethanes, because the small diols react with diisocyanates and form hard domains to serve as the physical crosslink for the polyurethane systems. In combination with hard segments, using long polyols that form the soft segment in polyurethanes results in thermoplastic polyurethanes with elastomeric nature. This versatility in polyurethanes enables one to synthesize polyurethanes with any desired properties based on the ratio and chemical nature of hard and soft segments. In our syntheses, 1,4-Butanediol was used as the chain extender, which formed the hard segment with MDI-based isocyanate, was used with a short diol of a polyester oligomer with Mn = 400 g/mol that formed the soft segment. As summarized in Table 3.3, while maintaining an A:B ratio (OH:NCO) to ensure α value remains below the $α_c$ value, a variety of products were successfully synthesized with soft segment contents from 0 to 14 wt%. Similarly, by varying the A:B ratio (OH:NCO) and maintaining the α value below the $α_c$ value, branched polyurethanes with final average functionalities ranging from 3.08 to 5.27 was synthesized successfully. However, since NCO end-groups were endcapped with both ε-caprolactam and GSS as shown in Scheme 4.3, ε-caprolactam end-capped functionality of each product was also calculated from the molar ratio of ε–caprolactam and GSS in each reaction and shown in Table 3.3 and Table 3.4.

Particle size of the polyurethane dispersion depends on many factors, such as type of isocyanates, polyols, emulsifying agent (hydrophilicity), blocking agents used, and viscosity of the prepolymer and varies with their content and neutralization degree. The neutralization degree is the percentage of the carboxylic groups that are neutralized to become carboxylic ions and in our studies due to the structure of the GSS all carboxylic acid groups were in sodium carboxylate form. As stated in the literature, the typical mean particle size below 300 - 400 nm, preferably below 200 nm is acceptable to have stable latex dispersions of most polymers. The stability of polyurethane dispersion is affected by a large number of factors, both internal and external. The attracting Van der Waals forces between particles in the dispersion are counteracted by various repelling interactions. One of these is the electrostatic repulsion of the charged particles which is the dominant effect in ionically stabilized polyurethane dispersions. In addition to that, with increasing hydrophilicity, the particle size decreases, the viscosity increases and the dispersion becomes more stable. Table 3.3 and Table 3.4 shows the compositions of

the synthesize polyurethane in route II. Even though bimodal distributions were observed, stable polyurethane dispersions with mean particle sizes below 350 nm were obtained. In Route II syntheses, a rapid increase was observed in the viscosity of the reaction mixture during the isocyanate terminated polymer formation by the reaction of polyol and chain extending diol with multi-functional isocyanate. MEK was an effective solvent in reducing this viscosity and allowing the blocking reaction with e-caprolactam. Using MEK reduced the viscosity of the polyurethane and maintained effective agitation in the following emulsification and dispersion steps. The amount of solvent was calculated based on the desired final concentration of the polyurethane solution, typically a 30 wt% polyurethane/MEK solution was used, which was then dispersed in water to obtain a 30 wt% dispersion upon the removal of MEK by vacuum distillation.

While some syntheses in Route II have resulted in gelation, optimization of key reaction conditions discussed above has resulted in a novel synthethic process to obtain branched and functional polyurethanes with mainly aromatic nature in the dispersion form. As a result, this study is one of the first examples in the literature both for the synthesis of aromatic polyurethane dispersions and synthesis of highly branched, functional polyurethane dispersions.

4.1.3. Preparation and Characterization of Thermoset Polyurethane Films

In order to demonstrate the usefulness of these novel functional polyurethane dispersions synthesized in this study, they were formulated with hydroxyl bearing components such as poly(ethylene glycol) (PEG 600) or waterborne dispersion of a hydroxyl terminated poly(ester urethane) (Bahydrol UH XP 2698) at equimolar NCO:OH ratios similar to two-component formulations used in the coatings industry as shown in Scheme 4.6. In this part of the study, the effect of the presence of a soft segment in the branched polyurethane and the effect of the average final functionality on the thermo-mechanical properties of final thermoset films were investigated. These formulations were stable at room temperature due to lack of a reaction between blocked isocyanate and hydroxyl groups.

PEG 600
Bayhydrol UH XP 2698

Blocked Branched Polyurethane   Poly(ester urethane) network
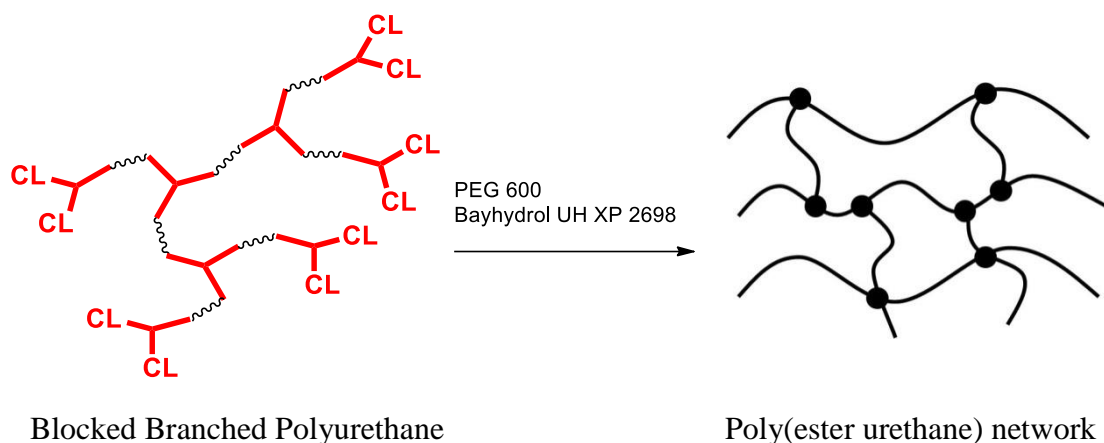
Scheme 4.6 Preparation of a poly(ester urethane) network

However, once dried and heated to up to 180ºC shortly in order to initiate de-blocking of functional end-groups, continuous, self-standing films were formed upon the reaction "de-blocked" isocyanate end-groups with hydroxyl groups present in the formulation as depicted in Figure 4.6.
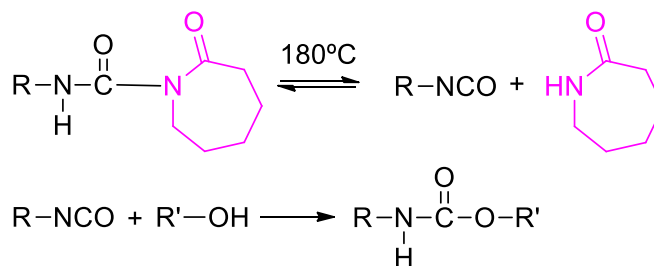

Figure 4.6 Blocking, deblocking and cross-linking reaction of isocyanate group

Figure 4. 7 NO-1-041 based self-standing thermoset polyurethane film

As a result, these novel, functional, waterborne polyurethane formulations gave self-standing thermoset films as shown in Figure 4. 7 and their thermo-mechanical and tensile properties were investigated as a function of key structural parameters such as soft segment content, average. Dynamic mechanical analysis (DMA) was used to probe the dependence of storage modulus (E') and tan delta on temperature for resulting polyurethane thermoset films. Figure 4.8 and Figure 4.9 depict the comparative DMA behavior of polyurethane films obtained from the reaction of PEG-600 with NO-1-041 and N0-1-043. As summarized in Table 3.3, both NO-1-041 and NO-1-043 had an average functionality of 3.20. However, NO-1-041 contains 14.20 wt% polyester soft segment (short diol of a polyester oligomer), whereas NO-1-043 contains 0 wt% soft segment.The storage modulus and tan delta versus temperature plots show a significant difference in both storage modulus and glass transitions values observed. The influence of soft segment structure on the storage modulus is related to the intermolecular association and crystallization during streching. Huh and Cooper (1971) have reported that polyurethane may exhibit two separate glass transition in the hard and soft segment domains, respectively. However, depending on the chemical composition, length, ratio of the components, method of preparation, and subsequent processing steps, there may be considerable interphase mixing between the molecules of the two segments. In our syntheses, the presence of an aromatic polyester soft segment was found to have a pronounced effect on the glass transition. A glass transition primarily due to aromatic hard segments was observed at 99.27°C for NO-1-043, and this glass transition value decreased to 35.79°C in the case of NO-1-041 than contained 14 wt% aromatic polyester soft segment. In addition, such a difference in glass transition values could also be explained by the degree of crosslinking difference between the two films since the degree of crosslinking is dictated by the distance between branch points in the precursor polymers we synthesized in this study. In NO-1-043-based films, the degree of crosslinking is expected be higher since the distance between branch points in NO-1-043 only arises from the length of 1,4-butanediol, whereas this distance increases with the polyester polyol in NO-1-041. As a result, the presence, length and and type of a soft segment in the branched polyurethane was found to be critical in determining elastomeric nature of corresponding thermoset films prepared from them.
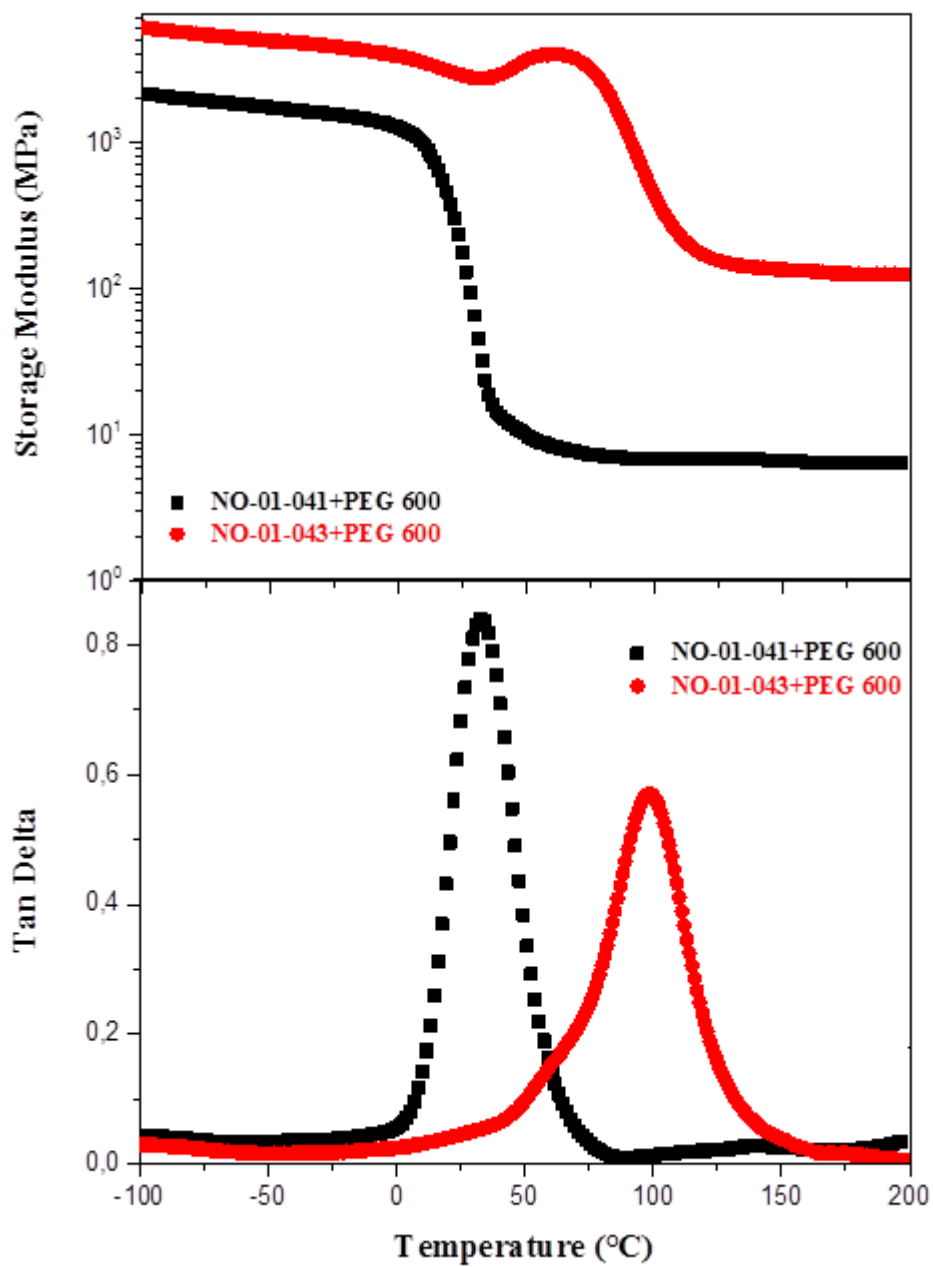
Figure 4.8 Investigation of the effect of soft segment on the thermoset polyurethane films

Figure 4.9 depicts the comparative DMA behavior of polyurethane films of NO-1-058 and N0-1-063 obtained from the reaction of PEG-600. As summarized in Table 3.4, both NO-1-058 and NO-1-063 contain 3.50 wt% short diol of a polyester oligomer. However, NO-1-058 had an average functionality of 3.8 whereas NO-1-063 had an average functionality of 4.2. The influence of the functionality on the storage modulus is related to the degree of branching on the pre-synthesized polymer. When the functionality of the branched polyurethane increased, degree of crosslinking in the corresponding thermoset film increased. This resulted in increased storage modulus and the film became more rigid. As a result, NO-1-063 resulted in thermoset films with higher storage modulus due to its higher functionality.

The rigidity of the polyurethane backbone increased with the increased number of urethane linkages in NO-1-043. However, in this case, NO-1-058 and NO-1-063 thermoset polyurethane films had the same hard segment content. The interactions between the urethane groups were the same. Therefore their T_g's are nearly the same as 103.05ºC for NO-1-058-based thermoset polyurethane film and 103.11ºC for NO-1-063-based thermoset polyurethane film.
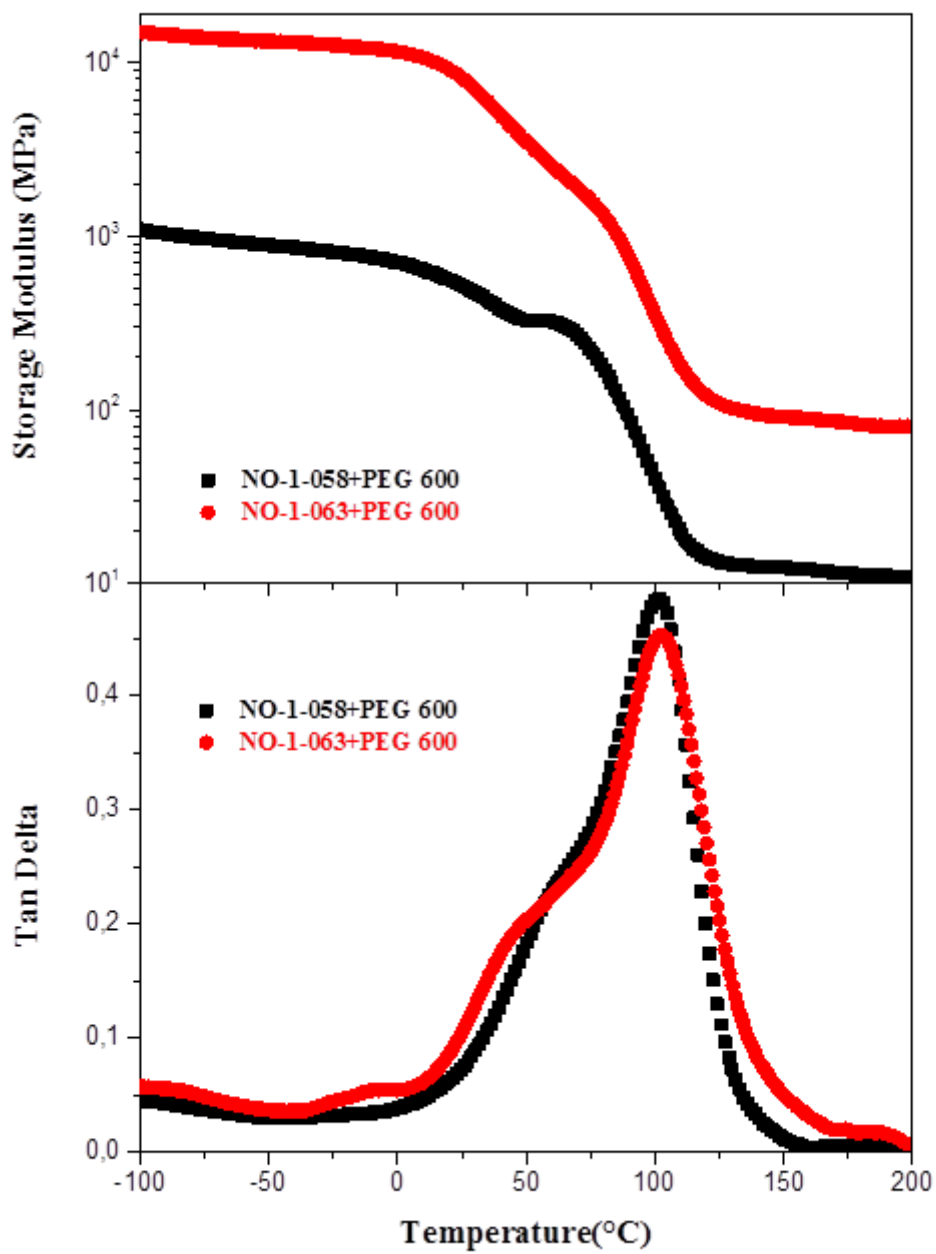
Figure 4.9 Investigation of the effect of final functionality on the thermoset polyurethane films

Figure 4.10 depicts the comparative stress-strain behaviour of polyurethane films obtained from the reaction of Bayhydrol UH XP 2698 with NO-1-041 and N0-1-043. As summarized in Table 3.3, both NO-1-041 and NO-1-043 had an average functionalities of 3.20. However, NO-1-041 contains 14.20 wt%, whereas NO-1-043 contains 0 wt% soft segment.

The chemical structure of the whole polymer has an effect on the mechanical properties. The soft polyol segment was responsible for the elastic behavior of the polymer film. Polyester soft segment increased the chain mobility by increasing the elasticity. On the other hand the presence of more urethane carbonyls available for hydrogen bonding with lead to the formation of more rigid polyurethane film in NO-1-043 due to the absence of soft segment, which resulted in films with poor elastic properties. Hence, the cured film of NO-1-043 showed lower value of elongation at break than the cured film of NO-1-041 due to its highly crosslinked structure and higher hard segment content. These results demonstrate that mechanical and elastic properties of final cured polyurethane films are highly dependent on the soft segment content.
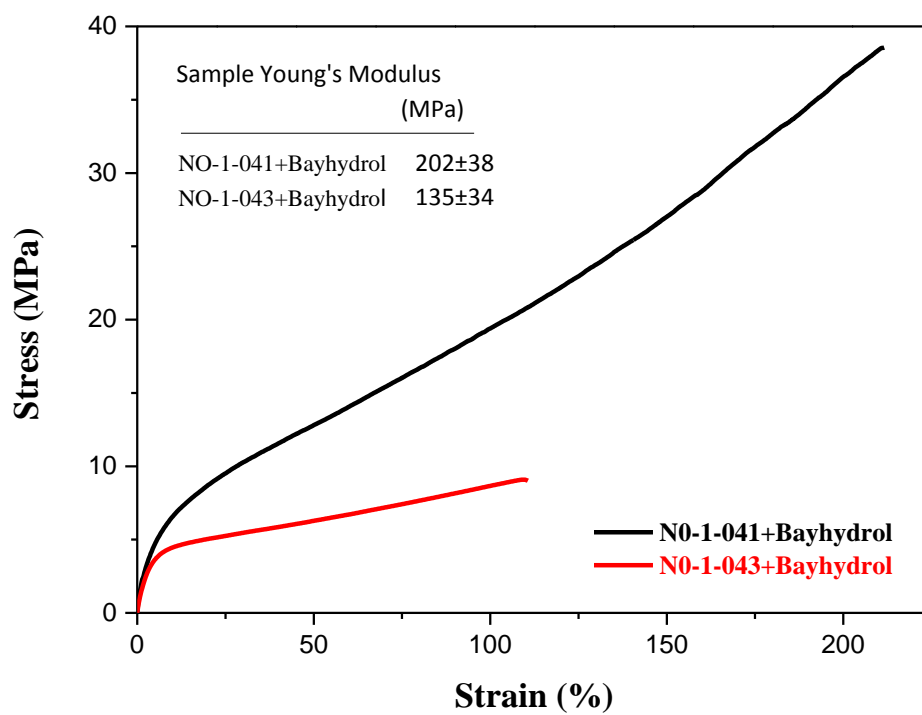
Figure 4.10 Investigation of the effect of soft segment on the the stress-strain

behavior of thermoset polyurethane films

CHAPTER 5

5.   Conclusion

Novel segmented chemically functional, branched and waterborne polyurethanes were developed via the $A_2 + B_n$ polymerization approach. The $A_2 + B_n$ polymerization approach allowed us to control the degree of branching to design and obtain highly branched polyurethanes with a multitude of chemically functional end-groups. In addition to the branched topology that was achieved by the $A_2 + B_n$ approach, in order to synthesize such functional, branched polyurethanes in the form of waterborne dispersions, ionic groups that acted as emulsifying agents were deliberately incorporated into the polyurethane backbone. For this purpose, two different synthethic processes were developed. In the first approach, ionic groups were incorporated along polymer chains as pendant groups, whereas in the second approach, ionic groups were placedat polymer chain-ends as telechelic groups. These branched polyurethanes synthesized in this study were designed to possess thermally reactive e-caprolactam blocked-isocyanate functional end-groups. DSC analysis of these functional polyurethanes demonstrated that de-blocking reactions of the blocked-isocyanate groups start occurring >130ºC, optimally at 160 – 180ºC. In order to demonstrate their usefulness, these branched polyurethanes possessing blocked-isocyanate functionalities were formulated with hydroxyl-functional oligomers to obtain cross-linked thermoset films or coatings. DMA and tensile-test results of these films clearly demonstrated that thermoset films can be obtained with desirable thermo-mechanical properties depending on the chemical composition and average functionality of the branched polyurethane in the formulation. For example, by increasing average final functionality, the degree of crosslinking in the polymer increased. As a result, the modulus of films increased as well. On the other hand, the presence and type of a soft segment in the branched polyurethane was found to be critical in determining elastomeric nature of these films.

In conclusion, this thesis provides novel synthethic methodologies that successfully resulted in chemically functional polyurethanes with ionic emulsifying groups located either along polymer chains as pendant groups, or at polymer chain-ends as telechelic groups. Hence, these novel syntheses illustrate clearly that it is possible to synthesize polyurethane dispersions with different compositions including aromatic components such as aromatic isocyanates or aromatic polyols and a variety of chemicaly functional end-groups such as thermally reactive blocked-isocyanate groups, post-reactive hydroxyl, amine or thiol groups, radiation curable acrylates, hydrophilic or hydrophobic groups, ionic groups, non-covalently interacting groups. Such chemically functional, branched and waterborne polymers have a huge potential to be used in a variety of applications in the the field of coating and adhesives due to their versatile chemistry and tunable reactivities to obtain films and coatings with desirable properties.

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