

Investigation of the effect of diisocyanate symmetry and soft segment molecular weight on the structure- property behavior of non-chain extended, segmented polyureas

by

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ABSTRACT

The effect of diisocyanate structure and soft segment molecular weight on the structure-property behavior of novel, non-chain extended, segmented polyureas were investigated. These novel polyureas were synthesized by the stoichiometric reactions of diisocyanates and amino functional oligomers. Amine terminated poly(tetramethylene oxide) (PTMO) and poly(ethylene/butylene) (PEB) oligomers were synthesized by using a two step process from commercially available hydroxyl terminated PTMO and PEB with number average molecular weights of 2000 and 3340 g/mol, respectively. In the first step, nitrile end-capped oligomers were prepared by the reaction of acrylonitrile in the presence of sodium hydride at 0 °C. Reduction of the nitrile end groups to the amine was obtained by the utilization of borane-THF complex at 0 °C. Resulting oligomers were characterized by FTIR and NMR spectroscopy. End group titration of PTMO and PEB gave number average molecular weights of 2450 and 3700 g/mol, respectively. The diisocyanates used in the preparation of polyureas were 1,6-hexamethylene diisocyanate (HDI), 1,4-phenylene diisocyanate (*p*PDI), 1,4-*trans*-cyclohexyl diisocyanate (CHDI) and 4,4'-dicyclohexylmethane diisocyanate (HMDI). All polymerization reactions were conducted at room temperature, by the dropwise addition of oligomer solution onto the diisocyanate solution under strong agitation. Hard segment contents were varied around 6.0 wt% for PTMO based polyureas and 4.5 wt% for PEB based polyureas calculated from the reaction stoichiometry. Dynamic mechanical analysis (DMA) of PTMO based polyureas showed high rubbery plateau modulus, which can be seen in conventional chain extended polyurethanes with much higher hard segment contents. It was found that the structure of the diisocyanates did not affect the stiffness of the polyurea in the rubbery plateau region. Atomic Force Microscopy (AFM) images of all PTMO based polyureas possessed microphase separated morphology with thread-like hard domains in the soft segment matrix. PTMO based polyurea films had a tensile strength of approximately 30 MPa and

elongation at break of ~1000 %, which are comparable to the commercial chain extended thermoplastic elastomers with much higher hard segment contents. DMA scans of PEB based polyurea films also indicated microphase separation, in spite of only 4.5% hard segment content. It also displayed a fairly long rubbery plateau extending between -25 °C and 150 °C.

Although the main focus of this study was the preparation of segmented polyureas through stoichiometric reactions of amine terminated oligomers and diisocyanates with very low hard segment contents, we also briefly investigated water as a chain extender to produce novel poly(urethane ureas). This brief investigation produced very interesting polymers which displayed microphase morphology and good solubility in DMF, in spite of fairly high urea contents, and very good composition dependent tensile properties.

ÖZET

Yeni bir bakış açısıyla bire bir oranda diizosiyanat ve amin sonlu oligomer kullanılarak çok kısımlı poliüre kopolimerleri sentezlendi. Diizosiyanat yapısının ve yumuşak kısmı oluşturan oligomerin zincir uzunluğunun sentezlenen poliürelerin yapısı ve fiziksel ve mekanik özelliklerine etkisi incelendi. Bu poliürelerin sentezinde kullanılan amin sonlu politetrametilen oksit (PTMO) ve polietilenbütilen (PEB) oligomerleri piyasada bulunabilen, sayı ortalama molekül ağırlıkları sırasıyla 2000 ve 3340 g/mol olan ve alkol sonlu PTMO ve PEB kullanılarak iki aşamalı bir yöntemle sentezlendi. Söz konusu dönüştürme reaksiyonlarının birinci aşamasında alkol sonlu oligomerler 0 °C'de sodyum hidrür varlığında akrilonitril ile reaksiyona sokuldular. Bu ilk aşamada elde edilen nitril sonlu oligomerler (borane-THF) kompleksi yardımıyla 0 °C'de redüklendiler ve amin sonlu oligomerler elde edildiler. Elde edilen oligomerler Fourier Transform Kızılötesi (FTIR) ve Nükleer Magnetik Rezonans (NMR) Spektroskopisi kullanılarak karakterize edildiler. Amin sonlu PTMO ve PEB oligomerlerinin titrasyonu sonucunda sayı ortalama molekül ağırlıkları sırasıyla 2450 ve 3700 g/mol olarak bulundu. Bu çalışmada, 1,6-hekzametilen diizosiyanat (HDI), 1,4-fenilen diizosiyanat (*p*PDI), 1,4-*trans*-sikloheksil diizosiyanat (CHDI) ve 4,4'-disikloheksilmetan diizosiyanat (HMDI) kullanıldı. Polimerler oligomer solüsyonunun diizosiyanat solüsyonu üzerine damla damla eklenmesi yolu ile elde edildi. Stokiyometrik hesaplamalar sonucunda PTMO ve PEB kullanılarak elde edilen poliürelerin sert kısımlarının oranı sırasıyla % 6 ve % 4.5 civarında bulundu. Dinamik Mekanik Analiz (DMA) sonuçları elde edilen polimerlerde mikrofaz ayrımı olduğunu ve bu polimerlerin yapılarında çok yüksek miktarlarda sert kısım bulunan poliüretanlarla aynı modül ve ısısal özelliklere sahip olduğunu gösterdi. Bunun yanında, kauçuksu bölgenin elastik modülüs değerinin diizosiyanat yapısı/simetrisi ile değişmediği gözlemlendi. PTMO ile hazırlanan poliürelerin Atomik Kuvvet Mikroskobu (AFM) yardımıyla yapılan analizlerinde mikro faz

ayrımli morfoloji tespit edildi. Bu morfolojik yapıda sert kısımların yumuşak matris içerisinde şeritler halinde bulunduđu gösterildi. Aynı poliürelerin çekme-kopma testleri de çok ilginç sonuçlar verdi. Kopma anındaki kuvveti ve uzaması sırasıyla 30 MPa ve % 1000 olarak bulundu. Bu değerlerin daha fazla sert kısım içeren geleneksel poliüreler ile karşılaştırılabilir büyüklükte olduđu gösterildi.

PEB oligomerleri kullanılarak elde edilen poliürelerin DMA sonuçları çok uzun bir sıcaklık aralığında (-25 °C ile 150 °C) kauçuksu plato davranışı gösterdi. Bu kadar uzun bir sıcaklık aralığını kapsayan bir kauçuksu plato davranışının görülmesi bu poliürelerin mikro faz ayrımlı bir morfolojik yapıya sahip olduğunun belirtisi olarak kabul edilebilir.

Bu çalışmanın ana konusu amin sonlu oligomerlerin ve diizosiyanatların stokiyometrik reaksiyonu sonucunda elde edilen çok kısımlı poliürelerin hazırlanması olmasına rağmen suyun zincir uzatıcı olarak kullanıldığı poliüretanüre sentezleri de sınırlı da olsa incelendi. Bu malzemeler ile yapılan araştırmada ilginç sonuçlar elde edildi. Bu polimerler oldukça yüksek sert kısım içermelerine rağmen dimetilformamit (DMF) içinde çözünme kabiliyeti ve kompozisyona bağlı çekme-kopma özellikleri gösterdiler.

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
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ABBREVIATIONS

PT2k-NH ₂	α,ω -Aminopropyl terminated PTMO
PT2k-CN	Bis(2-cyanoethyl) terminated PTMO
CHDI	<i>Trans</i> -1,4-cyclohexyl diisocyanate
DMF	Dimethylformamide
HMDI	4,4'-Dicyclohexylmethane diisocyanate
DMA	Dynamic Mechanical Analysis
FTIR	Fourier Transform Infrared Spectrometer
HDI	1,6-Hexamethylene diisocyanate
IPA	Isopropanol
MDI	4,4'-methylene bis(phenyl isocyanate)
<i>m</i> DSC	Modulated differential scanning calorimetry
<i>p</i> PDI	1,4-Phenylene diisocyanate
PEB-NH ₂	Poly(ethylene/butylene)-bis(3-oxypropylamine)
PEB-CN	Poly(ethylene/butylene)-bis(3-oxypropyl nitrile)
PEB	Poly(ethylene/butylene) glycol
PTMO	Poly(tetramethylene oxide) glycol
PUU	Polyurethaneurea
SAXS	Small-angle X-ray scattering
AFM	Atomic force microscopy
THF	Tetrahydrofuran
TDI	Toluene diisocyanate

Chapter 1

INTRODUCTION

A BRIEF SURVEY OF SEGMENTED THERMOPLASTIC ELASTOMERS

1.1 Thermoplastic Elastomers

Thermoplastic elastomers (TPEs) have been synthesized since 1940s as an alternative material to natural rubber, which has been mainly used in tire manufacturing. The most demanding property of a rubber is its ability to be stretched to moderate elongations and, on the removal of stress, to return to its original shape.[1] However, once produced, conventional rubbers cannot be reprocessed and/or reshaped for further applications due to the chemical crosslinks in its structure. These chemical bonds are irreversible in their nature that they require very high temperatures to be processed. Unfortunately, under such conditions the material will chemically decompose and lose its properties. This is one of the main problems in recycling of the car tires. However, TPEs show elastomeric properties in their service window and unlike conventional rubbers; they are melt processible because of reversible (physical) nature of their crosslinks.[2]

Depending on their chemical compositions, backbone structures and resultant microphase morphologies, TPEs can display versatile properties and find applications in many different fields. TPE market is approximately 1 % of the total polymer consumption, worldwide. World demand for thermoplastic elastomers is expected to expand 6.2 percent per year and in the year 2009, the volume of production will be approximately 3.1 million tons and it would correspond to more than US\$14 billion.[3] The demand is expected to

continue due to the replacement of natural and synthetic rubber. As shown in Figure 1.1., automotive industry is the largest market for thermoplastic elastomers with the applications in body seals, instruments and door panel skins of motor vehicles. This is followed by adhesives and sealants industry and various others.

As shown in Figure 1.2., TPEs can be divided into three main categories. The largest group is styrenic ABA type triblock copolymers, such as styrene-butadiene-styrene (SBS) copolymers. In these types of materials, polybutadiene forms the amorphous and rubbery matrix in which the glassy and rigid polystyrene segments are dispersed and act as crosslinks.

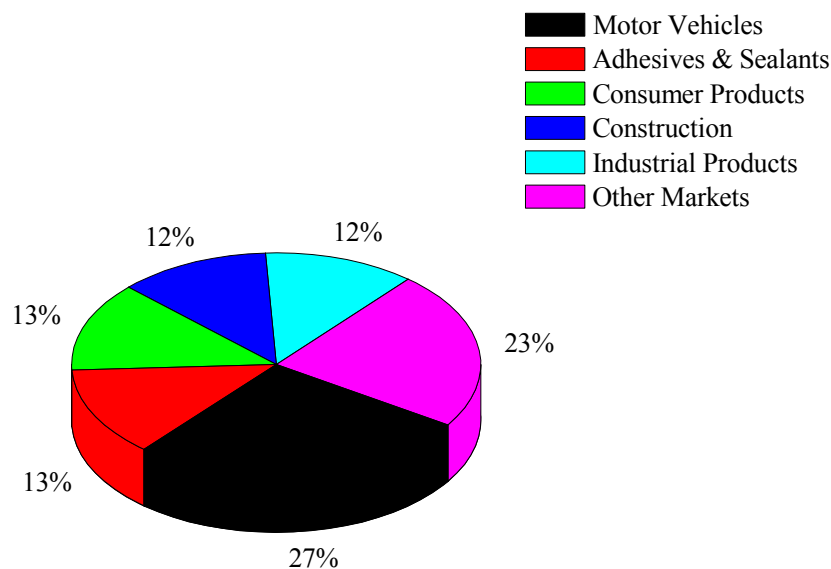


Figure 1.1: U.S. TPE demand by market, 2002[4]

Second group is the elastomeric blends, where thermoplastic polyolefins are blended with an elastomer.[5] Segmented (multi-block) copolymers form the third group. This thesis is mainly concentrated on the last group of the thermoplastic elastomers.

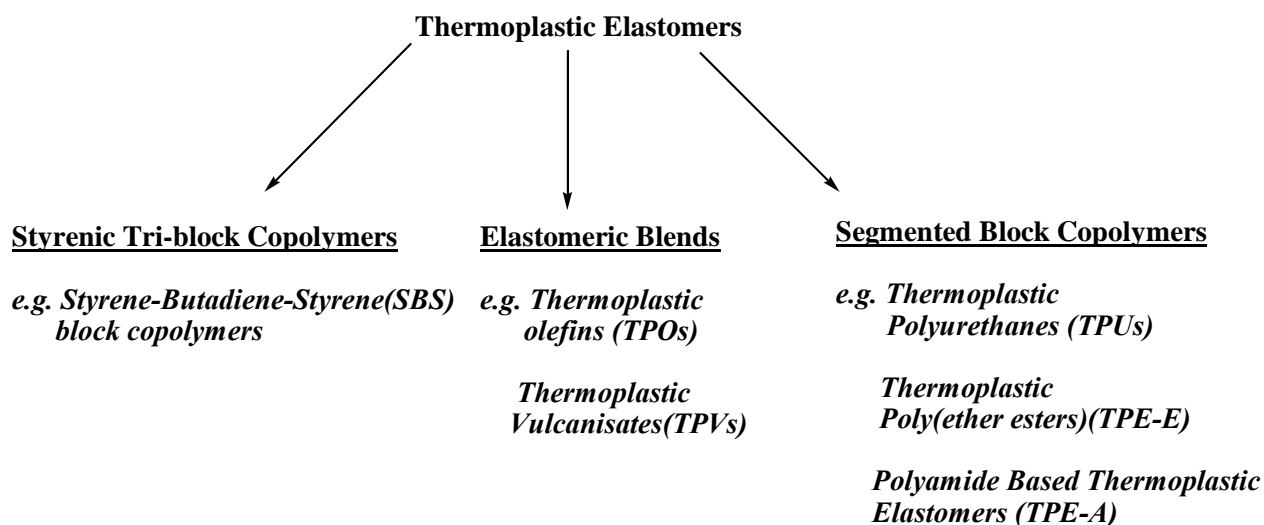


Figure 1.2: Types of thermoplastic elastomers

1.1.2 Segmented Block Copolymers

Segmented or multiblock copolymers are formed by the chemical combination of alternating rigid hard segments and flexible soft segments along a linear macromolecular backbone.[5] Schematic description of a segmented copolymer is provided in Figure 1.3. The soft segments with a low glass transition temperature (T_g) form the continuous matrix, which gives low temperature flexibility and the hard segments with high T_g or melting points (T_m) provide physical crosslinks which also behave like a reinforcing filler in the

low T_g matrix and give the material thermal and dimensional stability and solvent resistance. These physical crosslinks are reversible in nature. Upon heating, both segments soften or melt and usually form a homogeneous mixture and as a result it is possible to reprocess these materials at high temperatures. That is why they are termed as “thermoplastic” elastomers.

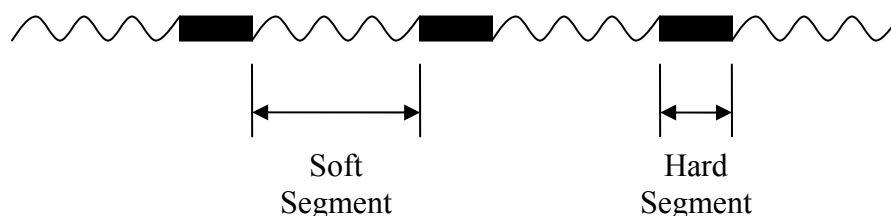


Figure 1.3: Schematic representation of a segmented block copolymer

In segmented block copolymers, hard phases usually consist of amide, ester, urea or urethane segments. Oligomeric aliphatic ethers, such as poly(ethylene oxide), poly(propylene oxide) and poly(tetramethylene oxide), aliphatic polyesters, such as poly(butylenes adipate) and polycaprolactone, oligomeric alkylenes such as poly(ethylene/butylenes) and siloxane oligomers are used as the soft segments. Covalent links between these structurally different blocks prevent macro-phase separation.[6] However, thermodynamic incompatibility of soft and hard segments causes micro-phase separation. Chemical composition and relative amounts of the hard and the soft blocks, their average molecular weights and molecular weight distributions, the method of copolymer preparation and the thermal history of the material strongly affect the degree of phase separation.[5]

A schematic representation of the micro-phase separation in segmented copolymers, which was first proposed by Cella is shown in Figure 1.4.[7]

Segmented block copolymers display elastomeric properties between the glass transition temperature of the soft segment and the glass transition or melting temperature of the hard segment. This temperature range is called the service window of a specific copolymer. In order to enhance the properties of copolymers in their service window, the parameters described in the paragraph above should be taken into consideration.

Three main types of segmented copolymers have been developed in order to fulfill the requirements of modern technology. These are; (i) poly(ether-esters), (ii) poly(ether-amides) and (iii) thermoplastic polyurethanes (TPUs), which also includes polyurethaneureas and polyureas.

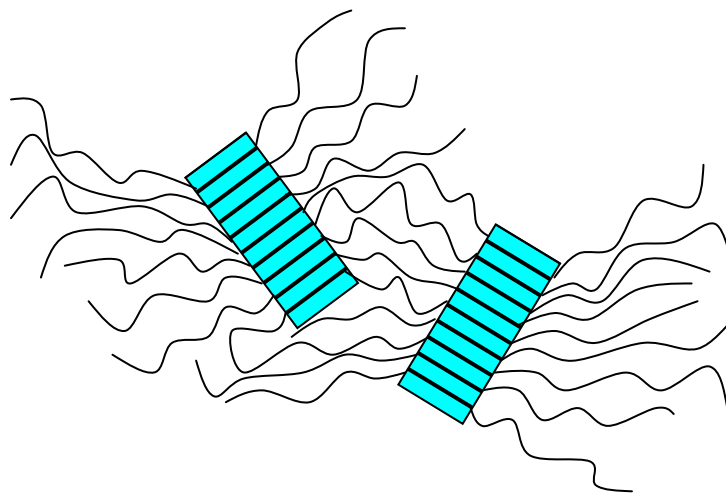




Figure 1.4: Schematic representation of the microphase separation in a segmented block copolymer. () represents hard segment and () represents the soft segment.

1.1.2.1 Thermoplastic Poly(ether esters)

Research on block copolyether-ester elastomers started in the late 1940s. D. Coleman [8] synthesized a copolyether-ester elastomer by polymerization of ethylene glycol, dimethyl terephthalate and poly(ethylene oxide) (PEO) to develop novel melt-spinnable fibers. In the late 1950s, Shivers [9] also prepared various terephthalic acid based copolyether-esters to develop melt-processable elastic fibers. Copolymers containing a PEO molecular weight of 4000 g/mol and a soft segment content of 60 wt% were reported to give the optimum elastomeric properties.

In 1972, copolyether-esters based on dimethyl terephthalate, 1,4-butanediol and poly(tetramethylene oxide)glycol (PTMO) were prepared with various compositions by Witsiepe [10]. Similar copolymers with different ester hard segments (diacids+diol), such as tetramethylene isophthalate and tetramethylene phthalate were also prepared [11-12]. All of these materials exhibited excellent thermo-mechanical properties and could be processed by conventional techniques and commercialized in 1972 as Hytrel[®] by DuPont.[10-12] A representative chemical structure for Hytrel[®] is shown in Figure 1.5. These polyester-based multi-block copolymers are mostly prepared by a two-step polycondensation reaction of a polyether glycol and a mixture of a terephthalate ester and low molecular weight diol at elevated temperatures in the presence of a catalyst.[13]

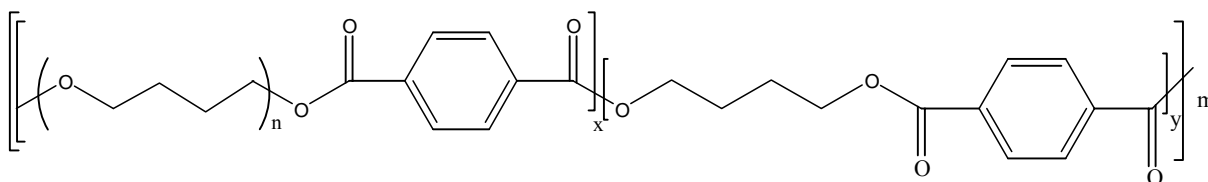


Figure 1.5: Representative chemical structure of poly(ether-ester) elastomer

The poly(ether-esters) exhibit unusual combination of strength and flexibility compared with engineering plastics. This is due to the microphase separation of crystalline ester segments from continuous polyether matrix. Their service window spans a relatively large temperature range, which depends on the structure and melting point of the ester hard segments. They also display high impact resistance at low temperatures and resistance to creep at higher temperature values.[5]

1.1.2.2 Polyamide Based TPEs

Thermoplastic polyamide elastomers consist of alternating soft segments and rigid polyamide segments. Four types of polyamide elastomers are available in the literature.[5] These are; polyesteramides (PEAs), polyetheresteramides (PEEAs), polycarbonate-esteramides (PCEAs) and polyether-*block*-amides (PE-b-As). PEA, PEEA and PCEA elastomers are prepared via the condensation of the aromatic diisocyanate, an aliphatic dicarboxylic acid and a polyester or a polyether oligomer with number average molecular weight of 500 to 5000 g/mol with aliphatic carboxylic acid end-groups. Simple synthetic schemes for the preparation of these copolymers are provided in Figure 1.6. The PE-b-A elastomers are synthesized by the melt polycondensation of the dicarboxylic acid amide block and the polyoxyalkylene glycol at elevated temperature and under high vacuum. High molecular weight segmented poly(ether-*block*-amide) could be synthesized via the development of a novel catalyst system which contains tetra alkoxide species in late 1970s by Atochem.[14] Polyamide based TPEs are more chemically resistant than their poly(ether ester) counterparts. They also possess excellent toughness, flexibility at ambient temperature and elastic recovery.

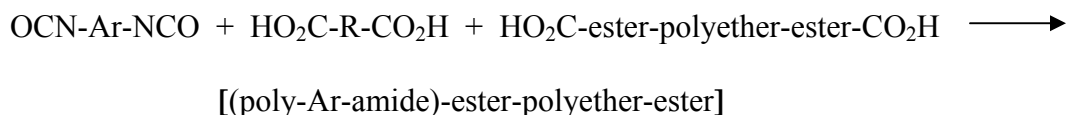
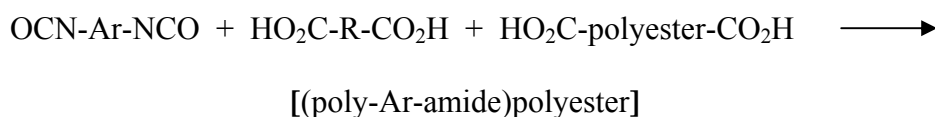
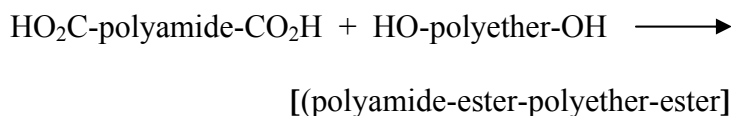
PEEA:**PEA or PCEA:****PE-b-A:**

Figure 1.6: Schematic of polyamide elastomer polymerization.[5]

1.1.2.3 Thermoplastic Polyurethanes (TPUs)

The term “polyurethanes” covers a very broad range of materials, which are used in various applications such as; coatings[15], fibers, foams, membranes, gaskets and seals, and biomaterials[16]. The class of polyurethanes covers the materials that have urethane and urea linkages in their backbone structures and other isocyanate derived groups. Urethane (carbamate) linkage is formed by the reaction of an isocyanate and a hydroxyl group whereas; urea (carbamide) is formed from the reaction of an isocyanate and an amine group, as shown in Figure 1.7.

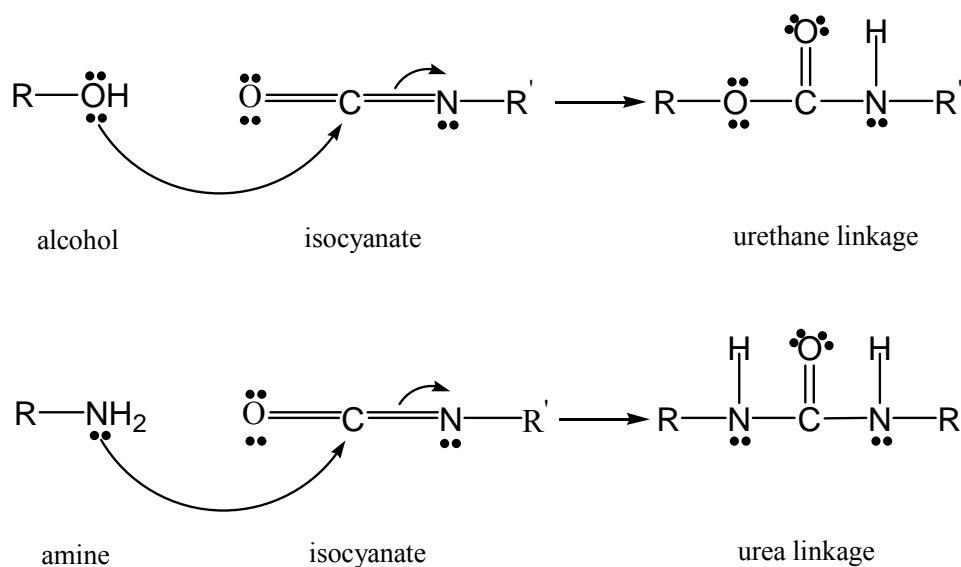


Figure 1.7: Formation reactions of the urethane and urea linkages.

These urethane and urea linkages are capable of forming monodentate and bidentate hydrogen bonding as shown in Figure 1.8. These hydrogen bonds have shown to have bond energies of 46.5 and 65.1 kJ/mol respectively, determined by quantum mechanical calculations.[17]

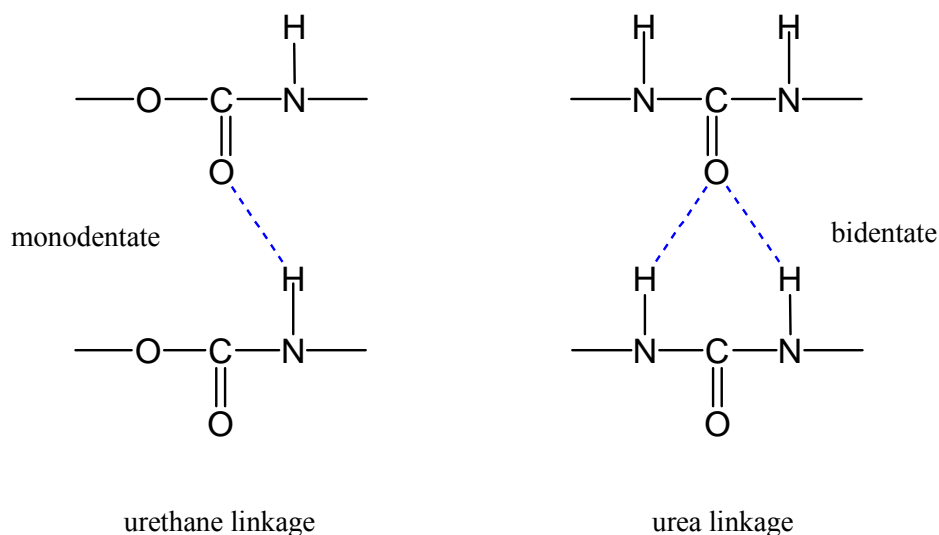


Figure 1.8: Intermolecular hydrogen bonding in urethane and urea linkages

Highly polar nature of these linkages and their ability to form hydrogen bonding can also be confirmed from the cohesive energy densities or solubility parameters of these groups. Solubility parameter (δ) can be expressed according to Equation (1.1), where E_{coh} is

$$\delta = \sqrt{E_{coh}/V} \quad (1.1)$$

the cohesive energy, V is the molar volume and δ is the solubility parameter. Solubility parameters of urethane and urea groups are 37.2 and 45.6 (J/cm³)^{0.5} respectively. This indicates that polyurethanes and polyureas are very polar materials compared with other common polymers. In addition to this, polyurethanes may also form crystalline hard segments that make these materials difficult to dissolve. Commonly, polar solvents such as;

dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide (DMAC) and the mixtures of isopropyl alcohol (IPA) and toluene in appropriate ratios is used to synthesize and dissolve these polymers.

For comparison, solubility parameter values for various polymers are provided in Table 1.1.

Table 1.1: Experimental values of solubility parameters deduced indirectly from various types of experiments. [18,19] *Calculated by using group contribution method.

Polymer	δ (j/cm ³) ^{0.5}
Polytetrafluoroethylene	12.7
Polyethylene	15.8 to 17.1
Poly(propylene oxide)	15.4 to 20.3
Polystyrene	17.4 to 19.0
Poly(vinyl chloride)	19.2 to 22.1
Polyurethane	37.2*
Polyurea	45.6*

In 1937, Otto Bayer was the first to demonstrate the synthesis of polyurethanes and fibers of this polymer, named Perlon-U. This material is considered as an alternative to polyamide, known as nylon, developed by Carothers at Du Pont. The limited thermal stability and poor mechanical properties prevented this material from commercial production and any further industrial applications.[1] However, changing short chain diol with a long chain diol improved the performance of these polyurethanes dramatically.

Preparation of segmented thermoplastic polyurethane was first reported by Schollenberger in 1955.[20-22] Later on Cooper and Tobolsky were the first to report microphase separation in segmented polyurethanes and its effect on the properties.[23-25]

Thermoplastic polyurethanes consist of three main components;

- (i) a long chain diol, mostly polyether or polyester
- (ii) a diisocyanate, usually aromatic
- (iii) a chain extender, such as water, a short chain diol or a diamine

The most commonly used polyethers glycols in the preparation of segmented polyurethanes are poly(propylene oxide) (PPO) and poly(tetramethylene oxide) (PTMO). Adipic acid based aliphatic polyester glycols, such as poly(butylene adipate), poly(neopentyl adipate) and polycaprolactone are some of the commonly used ester soft segments. Commonly used diisocyanates include 4,4'-dicyclohexylmethane diisocyanate (HMDI), 1,4-diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) and *para*-phenylene diisocyanate (*p*PDI). Most commonly used chain-extenders are ethylenediamine (EDA), hexamethylene diamine (HMDA) and hydrazine as low molecular weight diamines and ethylene glycol (EG) and 1,4-butanediol (BD) as low molecular weight diols.[5]

Segmented thermoplastic polyureas, polyurethanes or polyurethane-ureas are commonly synthesized by a two-step process, called the “prepolymer” method, where the first step consists of preparing an isocyanate terminated prepolymer through the reaction of a long chain diol with an excess of the diisocyanate. This is followed by the reaction of the prepolymer mixture with stoichiometric amounts of a difunctional chain extender to form a high molecular weight polyurethane and polyurethane-urea[2].

One of the commercially most successful TPUs is Spandex, (Lycra[®]) which was first synthesized by Joseph Shivers at Du Pont in 1959.[26] Due to its excellent stretching

and recovery properties, Spandex has been used for women undergarment and is now expanding into all types of clothing.[27] It can be stretched up to 600 % of its original length and has an ability to return to its original shape. Typical chemical structure of Spandex is represented in the Figure 1.9.

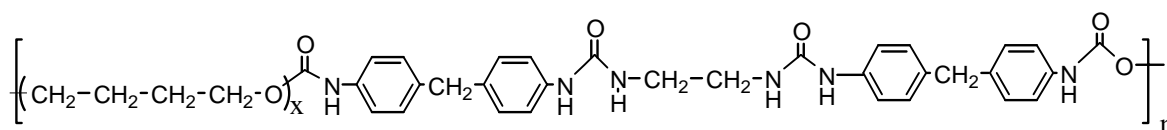


Figure 1.9: Chemical structure of LycraSpandex

LycraSpandex is also prepared by the prepolymer method. In the first step an excess of diphenylmethane diisocyanate (MDI) is reacted with PTMO-2000 to prepare the prepolymer. The prepolymer is then chain extended with stoichiometric amount of an organic diamine, such as ethylene diamine. Reactions are conducted in solution, where the solvent is usually dimethylacetamide (DMAC) or dimethylformamide (DMF). Some examples of other commercially available thermoplastic polyurethanes are Pellethane[®] by Dow and Elastollan[®] by Elastogran.

Chapter 2

STRUCTURE-PROPERTY RELATIONS IN SEGMENTED POLYURETHANES

2.1 Overview

As mentioned in the previous chapter, microphase separation plays a critical role in the performance of segmented, thermoplastic elastomers. Thermo-mechanical properties of segmented block copolymers strongly depend on the equilibrium morphology of the polymer. Important factors that influence the morphology of segmented polyurethanes can be listed as follows:

- (i) Chemical structure, number average molecular weight and molecular weight distribution of soft segments,
- (ii) Chemical structure and symmetry of diisocyanate,
- (iii) Chemical structure of the chain extender, average chain length and length distribution of hard segments,
- (iv) Relative amounts of hard and soft segments in the copolymer,
- (v) Crystallizability of hard and soft segments
- (vi) Extent of competitive hydrogen bonding between hard-hard and hard-soft segments.
- (vii) Solubility between hard and soft segments,
- (viii) Polymerization procedure used during the synthesis (one-step or two-step method),

- (ix) The nature of the interfacial region between the soft segment matrix and hard segment domains.

As schematically shown in Figure 2.1., overall properties of TPUs are strongly dependent on the polymer structure and chemical composition and resultant polymer morphology. By proper design and controlled synthesis it is possible to prepare TPUs with desired properties and performance.

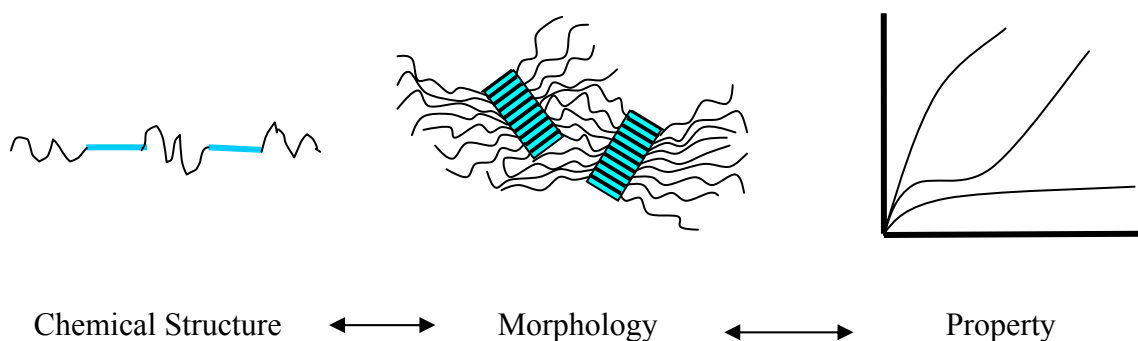


Figure 2.1: Structure-morphology-property relations in TPUs.

However, controlling chemical structure and morphology may be a very complicated issue because of a large number of parameters involved in this relationship. In order to maintain perfect control on structure and morphology of TPUs, researchers tried to understand the effect of chemical structure, average molecular weight and molecular weight distribution of both soft and hard segments on properties of segmented TPUs.[28-33] In addition to these efforts, morphological models have been developed.[34-38]

In this chapter, a brief overview of these efforts in understanding the structure-morphology-property relations will be provided. Additionally, in order to illustrate the

effect of perfect control of the structure and morphology of TPEs on performance, some studies which are related to a natural segmented TPE, spider dragline silk, will be discussed. At the end of the chapter, a comprehensive review of both non-chain extended and water chain extended segmented TPUs, which are the main foci of this study will be provided.

2.1.1 Effect of hard segment structure, molecular weight and distribution on morphology and properties of TPUs

It is known that, once an isocyanate group on a diisocyanate molecule reacts with a diol, reactivity of the other isocyanate group changes dramatically, especially in aromatic diisocyanates.[63-64] That is, the reactivity of an isocyanate unit in a growing chain and in a monomer is not similar in real reaction conditions. A statistical work was done by Peebles [28], to show the effect of nonequivalent reactivity of the two functional groups in a diisocyanate on the hard segment length distribution in chain extended, segmented block copolymers. He concluded that the number average length of the hard segment in each repeating unit at % 100 conversion is equal to C_1/C_2 when the isocyanate groups are equally reactive, where C_1 is the initial concentration of the diisocyanate and C_2 is the initial concentration of the prepolymer. In comparison, when the reactivity of the first isocyanate group is greater than that of the second isocyanate group, the number average length of the hard segment approaches $(C_1-C_2)/C_2$.

In order to understand the effect of hard and soft segment length on the thermo-mechanical properties of segmented polyurethanes, a pioneering work has been performed by Harrell [29]. He varied hard segment size and size distribution independently by special synthetic techniques. The author prepared segmented polyurethanes by the chain extension of a mixture of chloroformates with piperazine in the presence of an acid acceptor. He precisely synthesized amine terminated hard segments with various segment sizes by end-capping with phosgene to eliminate the effect of reactivity differences of end groups in a

controlled manner. Differential Scanning Calorimetry (DSC) results of this study clearly indicated sharp, endothermic peaks and segment melting point increases with the number of repeating units. Additionally, polymers which had broad hard segment distribution were prepared to compare stress-strain behavior with narrow hard segment distribution. Polymers, which had narrow distribution of hard segments produced much higher tensile strength values than that of the broad distribution.

Versteegen and co-workers have also studied the effect of uniform hard segment size for the poly(ether-urea)s based on PTMO oligomers as soft segment.[30] Applying protective group chemistry, authors managed to control the number of urea groups for each repeating unit (varying from 1 to 4). The copolymers having two urea groups in the hard block gave superior structural properties and ease of processibility. These copolymers possessed higher strain at break and toughness values than many other commercially available thermoplastic elastomers and poly(ether-urea)s based on polydisperse hard segment sizes. Authors concluded that excellent properties of these copolymers are the result of very thin, uniform hard blocks and the strong hydrogen bonding between the urea groups.[31]

2.1.2 Effect of hard segment structure on morphology and properties of TPUs

Chemical structure of the hard segment is another important parameter that strongly affects the morphology and mechanical properties of segmented copolymers. Yilgor, Wilkes and co-workers, prepared non-chain extended polyurethanes and polyureas based on *para*-phenylene diisocyanate (*p*PDI), and *meta*-phenylene diisocyanate (*m*PDI) as hard segment and PTMO as the soft segment.[33] The authors designed these copolymers due to the inspiration of outstanding properties of natural biopolymers. By controlling the level of chain symmetry and the proper choice of hydrogen bonding, they were able to obtain microphase separation in these non-chain extended, segmented copolymers. The dynamic

mechanical analysis (DMA) results exhibited higher modulus and a rubbery plateau extended to fairly high temperatures in the case of *p*PDI based polyurea which had 14 wt% hard segment. Such high modulus can be seen in conventional chain extended polyurethanes with a higher hard segment content. In comparison, *m*PDI based polyureas had much shorter rubbery plateau and weaker mechanical properties. By using similar synthetic approach, non-chain extended, segmented polyurethanes were also prepared and microphase separation and morphology development in these polyurethanes were studied by Yilgor et. al.[38] These polyurethanes were based on PTMO as the soft segment and trans-1,4-cyclohexyl diisocyanate (CHDI), 4,4'-dicyclohexylmethane diisocyanate (HMDI), MDI and *p*PDI as the hard segments. Time dependent FTIR spectra of these copolymers showed self-organization and formation of well ordered hard segments for *p*PDI and CHDI based polyurethanes. However, phase separation could not be seen in the case of unsymmetrical MDI and HMDI based polyurethanes.

2.1.3 Effect of soft segment distribution on morphology and properties of TPUs

As mentioned earlier, Harrell prepared segmented poly(ether urethane)s based on piperazine.[29] In order to investigate the effect of soft segment distribution, he used fractionated hydroxyl terminated PTMO (PD = 1.1) and a commercially available polydisperse PTMO glycol (PD = 1.7) as soft blocks in the synthesis of a series of segmented poly(ether urethane)s. He observed slightly increased strength and strain at break by lowering the polydispersity of the PTMO glycol.

Shirasaka et. al., studied block poly(ether urethane urea)s, which have fractionated PTMO glycol as soft blocks (PD = 1.1).[32] These copolymers showed a slightly lower strength and strain at break. They concluded that soft segment distribution is not very significant for these types of copolymers.

2.2 A Natural TPE: Spider Dragline Silk

Spider dragline silk is nature's high performance fiber.[39] This material exhibits a combination of high strength and high toughness comparing to other high performance synthetic fibers like, Kevlar[®] and rubber. Morphology of dragline silk is very similar to the segmented copolymers.[40] For example, *Bombyx mori* silk has β -sheet crystalline segments of (GlycineAlanineGlycineAlanineGlycineSerine)_n and *Nephila clavipes* silk has (Alanine)_n. [41,42] These crystalline β -sheet units form hard segments which are embedded into amorphous matrix composed of amino acids. Amino acid analysis has shown that dragline silk contains 42 % of glycine and 25 % of alanine and some residues with bulky side groups such as glutamine and tyrosine.[43] Repeating units of these proteins give five to seven polyalanine parts followed by glycine-rich sequences and poly(alanine) with less than 16 alanine residues tend to form crystalline β -sheet structure rather than α -helix.[44] A very well established theoretical model was provided to understand the structure of spider silk by Termonia.[45] The model has been quiet successful in indicating the experimentally found stress-strain curves for the dragline. Also his approach provided comprehensive analysis of the factors those affect the spider silk elasticity.

The outstanding properties and precise control of architecture exhibited by spider dragline silk has inspired researchers to synthesize novel materials. These materials combine elements of synthetic and natural polymers.[41,46-50] Sogah et. al., synthesized segmented copolymers in which hard blocks (for example, poly(alanine)) were derived from the crystalline regions of the silk. These hard blocks were combined with poly(ethylene glycol) (PEG) as a soft block in order to mimic amorphous, glycine-rich blocks in the spider silk. PEG is selected as the equivalence of amorphous polypeptide domain because of its availability, water solubility, biocompatibility and ease of synthesis. Shorter PEG oligomers were chosen for this application to prevent unwanted crystallization of this domain to maintain the amorphous character of the soft segment. These silk-inspired

polymers exhibited very good mechanical properties. Microphase separated morphology of these materials contained irregularly shaped 100-200 nm domains of hard segments dispersed within the PEG phase. The main drawback for the most of the synthetic silk-like copolymers is their poor solubility in conventional solvents which prevents further investigation and industrial development of these materials for commercial purposes. Shao and co-workers decided to use polyisoprene (PI) oligomer instead of PEG to replace amorphous, glycine-rich domain. X-ray analysis showed the formation of crystalline β -sheet domains which were made of 5 units of alanine blocks derived from the crystalline regions of the spider silk. Polymers based on shorter isoprene blocks, indicated micellar-like structures of hard domains.[50]

2.3 Non-chain extended TPUs

Only a few examples of non-chain extended, segmented TPEs are known in the literature.[33,51-52] Yilgör et al., [51] described polydimethylsiloxane (PDMS) based segmented, non-chain extended polyureas and studied their structure-property behavior in detail.[52] These copolymers were prepared by reacting stoichiometric amounts of amine terminated PDMS oligomers with selected diisocyanates such as, MDI, TDI and HMDI. Depending on the PDMS and diisocyanate molecular weight, they synthesized copolymers that had hard segment contents between 6 to 22 wt%. Evidence of microphase separation was obtained from the dynamic mechanical analysis (DMA) and small angle x-ray scattering (SAXS) studies. These polymers possessed relatively good elastomeric properties comparable to the crosslinked PDMS rubber, while they also were melt processible. Even the 6 wt% hard segment containing system exhibited evidence of microphase separation.[52] Recently Sheth et. al., prepared poly(tetramethylene oxide) (PTMO) based non-chain extended, segmented polyurethanes and polyureas by using *para*-phenylene diisocyanate (*p*PDI) and *meta*-phenylene diisocyanate (*m*PDI) as hard

segments.[33] In this way, authors had the opportunity to investigate the effect of the type of hydrogen bonding and diisocyanate symmetry on the morphology and properties of the resultant polymers. Atomic force microscope (AFM) images of *p*PDI based polyurethanes and polyureas showed microphase separated morphology. As for the *m*PDI based homologs, only the polyurea showed microphase morphology, whereas polyurethane was featureless, indicating no phase separation! In phase separated systems, ribbon-like hard segment phases were developed and percolated through the continuous soft segment matrix.

2.4 Water chain extended polyurethaneureas (PUUs)

Although the main focus of this study was the preparation of segmented polyureas through stoichiometric reactions of amine terminated oligomers and diisocyanates with very low hard segment contents, we also briefly investigated water as a chain extender to produce novel poly(urethane ureas). The first report on the water chain extended, segmented polyurethaneureas was recently published by Hilborn and co-workers. [61] In this synthesis route, diisocyanate end-capped prepolymers were first prepared followed by the chain extension with water vapor bubbled through the reaction mixture in solution.

In non-chain extended copolymer synthesis strategy, hard segment content can only be tailored by changing soft segment molecular weight for a specific diisocyanate. However, in the case of water chain extended polyurethaneurea synthesis strategy, hard segment content can easily be altered by changing stoichiometric ratios of diisocyanate to polyol soft segment in the reaction mixture. Water chain extended synthetic approach provides the opportunity to control the morphology and the properties of the copolymer by controlling the initial $[\text{NCO}]:[\text{OH}]$ ratio in the reaction system. This is done by using different soft segments and diisocyanates as well as easily synthesizing different lengths of hard segments.

Wilkes and co-workers [62] prepared model segmented PUU copolymers with varying amounts of hard segment to understand the hydrogen bonding capability of these building blocks. Hard segment branching were obtained by utilizing a triisocyanate along with a diisocyanate and water during the chain extension step of the synthesis. They controlled relative ratio of these two isocyanates to synthesize copolymers with varying extends of branching with a constant hard segment content. They concluded that incorporation of hard segment branching reduced the ability of the hard segment to pack and establish long-range connectivity.

Asplund et. al. [61] prepared water chain extended, segmented PUUs based on poly(caprolactone) glycol as soft segment and methyl 2,6-diisocyanatohexanoate (LDI) as the hard segment. After the pre-polymer formation, they performed the synthesis via vapor phase addition of water continuously. They concluded that as the hard segment length was increased, hydrogen bonding ability of the hard segment and elastic modulus of the copolymers were also enhanced.

2.5 Objectives of this study

The outstanding thermomechanical properties of natural polymers are directly related to their precisely defined chemical structures and resulting well-defined microphase morphologies. However, conventional synthetic techniques used for the preparation of TPUs, in general do not provide such a precise control of the chemical structure and morphology. In order to close the gap between the synthetic and natural polymers, we want to control the hard segment length distribution by designing non-chain extended, segmented TPUs with proper choice of diisocyanate and novel soft segments. To do this, we planned to study the synthesis of non-chain extended, segmented polyureas based on novel amine end-capped poly(tetramethylene oxide) (PTMO) and poly(ethylene-butylene) (PEB) soft segments and various diisocyanates as hard segments. The effect of the

molecular weight and type of the soft segment and diisocyanate structure on the mechanical, morphology and the thermal properties was investigated. In addition to non-chain extended polyureas, water chain extended PUUs based on hydroxyl terminated PTMO as a soft segment and 1,6-hexamethylene diisocyanate (HDI) and 4,4'-dicyclohexylmethane diisocyanate (HMDI) as hard segments were also synthesized. Stress-strain behaviors of these PUUs were investigated.

Chapter 3

EXPERIMENTAL

3.1 Materials and purification of reagents

1,4-Phenylene diisocyanate (*p*PDI) was purchased from Aldrich. *Trans*-1,4-cyclohexyl diisocyanate (CHDI) was purchased from Du Pont. 1,6-Hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4'-methylen bis(phenyl isocyanate) (MDI) and 4,4'-dicyclohexylmethane diisocyanate (HMDI) were kindly provided by Bayer AG. All diisocyanates, except *p*PDI were used as received. *p*PDI was sublimed at 70°C under ambient pressure before use. Purities of diisocyanates were better than 99.5 % as determined by dibutylamine back titration. Poly(tetramethylene oxide)glycol, (PT2k-OH) with $\langle M_n \rangle$ of 2050 g/mol and (PT1k-OH) 975 g/mol were kindly provided by Du Pont. Hydroxy terminated KratonTM Liquid-L-2203 (PEB-OH) was kindly supplied by Kraton Inc. The average functionality and the number average molecular weight $\langle M_n \rangle$ of KratonTM L-2203, as determined by ¹H NMR, were 1.92 and 3340 g/mol, respectively. It also had a very narrow molecular weight distribution of 1.03, as determined by SEC. Borane-tetrahydrofuran complex (1 M), 15-crown-5 (98%), NaOH pellets (purity better than 97%), reagent grade acrylonitrile, tetrahydrofuran (THF), dimethylformamide (DMF), isopropanol (IPA), methanol and toluene were purchased from Merck. Technical grade dichloromethane was purchased. THF was dried over molecular sieves and fractionally distilled. Other solvents were used as received. Sodium hydride suspension (60% in paraffin oil) was obtained from Merck.

3.2 Synthetic Procedures

3.2.1 Synthesis of bis(2-cyanoethyl) terminated PTMO, (PT2k-CN)

Poly(tetramethylene oxide) glycol, (PT2k-OH) $\langle M_n \rangle = 2050$ g/mol (20.051 g; 9.78 mmol) was dissolved in acrylonitrile (32.236 g) in a 3-neck, 250 mL Pyrex, round bottom reactor equipped with an overhead stirrer and cooled on an ice bath. NaH (8.6 mg 60 % dispersion in mineral oil) was added to this solution in the presence of a cyclic ether (15-crown-5) (2 drops) to catalyze the reaction. Reaction mixture was stirred under strong agitation for 25 min. Reaction mixture turned slightly yellow and the reaction was followed by the appearance of nitrile peak in the FTIR spectra. The reaction was terminated by the addition of one drop of concentrated HCl. 100 mL of dichloromethane was added and the yellow precipitate formed was filtered and heated to 60 °C to remove the solvents in a rotary evaporator. Resulting orange product was placed in a 60 °C vacuum oven for one day to have a completely dry product. The product was identified by FTIR and $^1\text{H-NMR}$ spectroscopy. (Yield = 89.3 %)

3.2.2 Synthesis of α,ω -aminopropyl terminated PTMO, (PT2k-NH₂)

PT2k-CN (10.091 g; 4.92 mmol) was dissolved in freshly distilled and anhydrous tetrahydrofuran (80 mL), the solution is introduced into an addition funnel and slowly added into a mixture of borane-tetrahydrofuran complex (40 mL 1M in THF, 40 mmol) in a 3-neck, 500 mL Pyrex, round bottom reactor equipped with an overhead stirrer and a nitrogen inlet. 120 mL of freshly distilled, anhydrous THF was added and the reaction was continued at 0 °C for 30 minutes under nitrogen atmosphere and strong agitation to obtain a homogeneous reaction medium. After this point, reaction mixture was stirred for additional 30 minutes at room temperature. Then the solution was refluxed for 4 hours for complete reduction of nitrile groups. In order to reduce the viscosity of the resulting mixture, 60 mL of THF was added. Methanol (40 mL) was slowly added to decompose the excess borane at

0 °C for 25 minutes (Hydrogen gas evolution). 2 mL of concentrated HCl was added and the resulting mixture was put to 70 °C in a rotary evaporator. During evaporation process 3x50 mL of methanol was added into the rotavap to remove the nitrogen containing by products. Product was then introduced into a separatory funnel and 75 mL of 1 M NaOH solution and 250 mL of dichloromethane was added to obtain phase separation. Organic phase was extracted and filtered. After evaporation of solvents, slightly orange colored PT2k-NH₂ was obtained. The product was identified by FTIR and ¹H-NMR spectroscopy. (Yield = 88.8 %).

Titration of the amine end groups with standard HCl solution gave a number average molecular weight of 2450 g/mol.

3.2.3 Synthesis of Poly(ethylene/butylene)-bis(3-oxypropyl nitrile), (PEB-CN)

Poly(ethylene/butylene) glycol (PEB-OH) $\langle M_n \rangle = 3340$ g/mol (15.96 g; 4.780 mmol) was dissolved in acrylonitrile (8.263 g) and toluene (30.96) in a 3-neck, 250 mL Pyrex, round bottom reactor, equipped with an overhead stirrer and nitrogen inlet. The homogeneous mixture was cooled on an ice bath. 15-crown-5 (4 drops) and NaH (80 mg 60 % dispersion in mineral oil) were added to this solution. Reaction mixture was stirred under strong agitation for 1 hour. The color of the reaction mixture turned slightly yellow and the reaction was followed by monitoring the disappearance of the broad hydroxyl peak centered at 3336 cm⁻¹ and formation of nitrile peak at 2253 cm⁻¹ in the FTIR spectra. The reaction was quenched by the addition of 10 drops of concentrated HCl (pH = 3). 30 mL of dichloromethane was added and the yellow precipitate formed was filtered and heated to 60 °C to remove solvents in a rotary evaporator. Resulting slightly orange product was placed in a 60 °C vacuum oven for one day to have a completely dry product. The product was identified by FTIR and ¹H-NMR spectroscopy. (Yield = 99.2 %).

3.2.4 Synthesis of Poly(ethylene/butylene)-bis(3-oxypyrrolamine), (PEB-NH₂)

PEB-CN (15.83 g; 4.74 mmol) was dissolved in freshly distilled and anhydrous THF (95 mL) in a 3-neck, 500 mL Pyrex, round bottom flask equipped with an overhead stirrer and a nitrogen inlet. A mixture of borane-tetrahydrofuran complex (50 mL of 1M in THF, 50 mmol) and freshly distilled, anhydrous THF (40 mL) was introduced into an additional funnel and slowly added onto the oligomer solution at 0 °C in about 1 hour, under strong agitation. After this point, the reaction mixture was stirred for additional 10 minutes at room temperature. Then the solution was refluxed for 7 hours for complete reduction of nitrile groups. Methanol (36 mL) was slowly added to decompose the excess borane at 0 °C for 30 minutes. 2 mL of concentrated HCl was added and the resulting mixture was transferred into a rotary evaporator at 80 °C. During the evaporation process 2×50 mL of methanol was added to remove the nitrogen containing by products. Product was then introduced into a separatory funnel and 50 mL of 1 M NaOH solution and 120 mL of dichloromethane was added to obtain phase separation. Organic phase was extracted and filtered. After evaporation of the solvents, slightly yellow colored (PEB-NH₂) was obtained. The product was identified by FTIR and ¹H-NMR spectroscopy. (Yield = 93.4 %).

Reactions of the amine end groups with stoichiometric amounts of diisocyanates gave a number average molecular weight of 3700 g/mol.

3.2.5 Preparation of PTMO based polyurea copolymers

Polymerizations were conducted in 100 mL, three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer and addition funnel. All copolymers were prepared by reacting equimolar amounts of a selected diisocyanate and PTMO oligomers. No chain extenders were utilized. Polymerization reactions were carried out at room temperature in DMF (at a concentration of about 15-20% solids) by the dropwise addition of PTMO solution onto the diisocyanate solution under strong agitation. As the molecular

weight of the polymer formed and the solution viscosity increased with conversion, the reaction mixture was diluted with adequate amounts of DMF. Completion of the reactions was determined by monitoring the disappearance of the isocyanate absorption peak around 2270 cm^{-1} with an FTIR spectrometer.

3.2.6 Preparation of PEB based polyurea copolymers

Polymerizations were conducted in a 100 mL, three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer and addition funnel. All copolymers were prepared by reacting equimolar amounts of a selected diisocyanate and PEB oligomer. No chain extenders were utilized. Polymerization reactions were carried out at room temperature in THF (at a concentration of about 10-15% solids) by the dropwise addition of PEB solution onto the diisocyanate solution under strong agitation. As the molecular weight of the polymer formed and the solution viscosity increased with conversion, the reaction mixture was diluted with adequate amount of THF. Completion of the reactions was determined by monitoring the disappearance of the isocyanate absorption peak around 2270 cm^{-1} with an FTIR spectrometer.

3.2.7 Preparation of non-chain extended polymer films for testing

Polymer films with thicknesses of 0.5 - 1 mm were obtained by pouring the solutions into Teflon molds. The molds were placed at room temperature overnight. After evaporation of the solvent, the molds were placed in a $50\text{ }^{\circ}\text{C}$ air oven for complete drying. One day later, the molds were placed at room temperature for 30 minutes. The resulting films were then removed from the Teflon molds and stored in a sealed polyethylene bag at room temperature until needed for testing.

3.2.8 Preparation of water chain extended PUUs

Polymerizations were conducted in 250 mL, three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer and addition funnel. To synthesize the

prepolymer, PT1k-OH and excess diisocyanate which was previously dissolved in DMF were introduced into the reactor and strongly agitated to obtain a homogeneous mixture. To this mixture, 1 drop of 1% T-12 was added as a catalyst and reaction was conducted at 80 °C. Completion of the prepolymer formation was determined by monitoring the disappearance of the strong and broad O-H absorption peak centered at 3470 cm^{-1} using FTIR spectroscopy. When necessary, adequate amount of DMF was added to decrease the viscosity of the prepolymer. Before water chain extension, 1 drop of 10% T-12 was added into this solution to increase the rate of diamine formation from diisocyanate. Stoichiometric amount of deionized, triple distilled water was diluted in DMF and introduced into an additional funnel. Water/DMF mixture was slowly added onto the prepolymer solution at 80 °C, under strong agitation to obtain high molecular weight chain extended polyurethaneureas. As the molecular weight of the polymer formed and the solution viscosity increased with conversion, the reaction mixture was diluted with adequate amounts of DMF. Completion of the reaction was determined by monitoring the disappearance of the isocyanate absorption peak at around 2270 cm^{-1} with an FTIR spectrometer.

3.2.9 Preparation of water chain extended polymer films for testing

Polymer films with thicknesses of 0.5 - 1 mm were obtained by pouring the solutions into Teflon molds. The molds were placed in a 50 °C air oven for drying, followed by drying in a vacuum oven at 50 °C for 24 hours. After complete removal of the solvent, the molds were kept at room temperature for 30 minutes. The resulting films were then removed from the Teflon molds and stored in a sealed polyethylene bag at room temperature until needed for testing.

3.3 Characterization Methods

3.3.1 (Nuclear Magnetic Resonance) NMR

Varian model, Unity Inova 500MHz type with a probe type of switchable ^1H - ^{19}F (^{15}N - ^{31}P) 5mm PFG was used. All samples were dissolved in CDCl_3 (purity better than 99,8% with 0.03% v/v TMS purchased from Cambridge Isotope Laboratories, Inc.) at ambient temperature. NMR spectra were collected at Sabanci University.

3.3.2 Fourier Transform Infrared Spectrometer (FTIR)

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet model Impact 400D FTIR spectrometer. FTIR scans were collected on thin films cast on KBr discs. All spectra were collected using 20 scans with a resolution of 2 cm^{-1} .

3.3.3 Tensile testing

An Instron model 4411 Universal Testing system controlled by Series IX software was used. A bench-top die (ASTM D 1708) was used to cut dog-bone-shaped samples from the solution cast films. Samples were deformed until failure at a cross-head speed of 25 mm/min, at room temperature.

3.3.4 Dynamic mechanical analysis (DMA)

A Seiko DMS 210 or a TA model Q800 instrument was used. Both instruments had an auto cooling system for precise temperature control. Rectangular samples ($16\text{ mm} \times 2\text{-}3\text{ mm}$) were cut from cast films. The dynamic mechanical spectra of samples were recorded (at a heating rate of $2^\circ\text{C}/\text{min}$), while they were deformed ($10\text{ }\mu\text{m}$ amplitude, 1 Hz frequency) in the tension mode, under a nitrogen atmosphere.

3.3.5 Tapping mode Atomic force microscopy (AFM)

Phase images of the different segmented copolymers were captured under ambient conditions using a Veeco atomic force microscope equipped with a Nanoscope IVa controller. Nanosensors™ Point Probe® plus non-contact/tapping mode, high resonance frequency with a reflective aluminum coating (PPP-NCH-50) were used for imaging. These tips had a nominal force constant of 42 N/m, resonance frequency of ~320 kHz and a radius of curvature <10 nm. Images were captured at 1Hz frequency and a set-point ratio of ~0.6 (medium to hard tapping) under ambient conditions. AFM studies were performed at Virginia Tech in the research group of Prof. Garth L. Wilkes.

3.3.6 Small-angle X-ray scattering (SAXS)

Data were collected at the Army Research Laboratory using a 3 m SAXS camera with pinhole collimation and a Molecular Metrology multi-wire area detector. Cu-K α X-rays are generated using a Rigaku Ultrax18 rotating at 40 kV and 115 mA, which was filtered with nickel foil to give a wavelength (λ) of 1.5418 Å. The sample to detector distance is approximately 1.5 m. Beam center and camera length are routinely calibrated using a silver behenate standard. The raw data are corrected for background noise and transmission prior to azimuthal averaging, and the corrected data are scaled to absolute intensity using data from a sample of type 2 glassy carbon which was previously calibrated at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. All data reduction and averaging were done using Wavemetrics' IGOR Pro v. 5.04B, and procedures written by Dr. Jan Illavsky of Argonne National Laboratory. The SAXS data are presented as intensity, I , versus scattering angle, s , where $s = \frac{2 \sin \theta}{\lambda}$, where 2θ is the radial scattering angle.

3.3.7 Modulated differential scanning calorimetry (mDSC)

A TA Instrument Q100 DSC with refrigerated cooling system was used. Samples (2-4 mg) were enclosed in aluminum hermetic pans. Samples were cooled down to -90°C , equilibrated for 15 minutes and then heated to 150°C at a heating rate of $2.5^{\circ}\text{C}/\text{min}$, with temperature modulation of 1°C at every 60 seconds.

Chapter 4

RESULTS AND DISCUSSION

4.1 Designing non-chain extended polyureas

In order to mimic the nature and prepare synthetic polymers with well defined properties and functions, similar to that of natural polymers, it is necessary to strictly control the polymerization reactions and also the chemical structure and molecular weight of the polymers formed. However, this is not a very simple task. It is especially difficult to control the step-growth polymerization reactions, which is the method of polymerization used in the preparation of segmented polyurethane and polyurea copolymers. As we have discussed previously, in addition to the chemical structure, the properties of segmented copolymers are also strongly dependent on the microphase morphology. A large number of factors affect the microphase morphology of the segmented copolymers, such as; the chemical structures of the hard and soft segments, their molecular weights and molecular weight distributions, their ratio in the copolymer, type of the chain extender, etc. In this study, we tried to minimize some of these variables by preparing non-chain extended, segmented polyurea copolymers. Since in this study all copolymers are produced by the stoichiometric reactions between diisocyanates and polymeric glycols without using any chain extenders, hard segments formed are uniform in size and chemical structure. As a result for a specific choice of the diisocyanate and the amine terminated oligomer, molecular weight distribution of the soft segment and overall molecular weight and molecular weight distribution of the copolymer become the only factors to be considered.

Previous investigations on non-chain extended, segmented polyureas based on a PTMO soft segment of molecular weight 1100 g/mol showed microphase separated

morphology.[33, 56] In order to investigate the effect of soft segment molecular weight on the morphology and properties in these systems, amine end-capped PT2k-NH₂ was prepared from hydroxyl terminated PT2k-OH.

4.1.1 Synthesis of PT2k-NH₂

To obtain primary amine end-capped PT2k-NH₂ with a number average molecular weight around 2000 g/mol, a two step process, proposed by Versteegen et. al., was used.[30] In this two-step synthetic route, cyanoethylation of PT2k-OH was followed by the reduction of the nitrile groups with borane-terahydrofuran complex. Cyanoethylation of PT2k-OH was performed via the Michael addition of acrylonitrile to the PTMO. In order to increase the nucleophilicity of the hydroxyl group, a base is used in the presence of a cyclic ether (1% amount) to catalyze the reaction. Since this reaction is exothermic and in equilibrium, the reaction was carried out at 0 °C and excess acrylonitrile (which also acts as a solvent) was used to shift the equilibrium forward. (Yield = 89.3 %) The product was characterized by both ¹H NMR and FTIR spectroscopy. 3.75 δ triplet (very weak), not identified, 3.64 δ triplet not identified, 3.51 δ triplet, 4H, -OCH₂CH₂CN, 3.41 δ multiplet (very strong) -OCH₂CH₂CH₂CH₂O-, 3.21 δ doublet (very weak) not identified, 2.65 δ triplet (very weak) not identified, 2.59 δ triplet, 4H, -OCH₂CH₂CN 1.62 δ multiplet (very strong) -OCH₂CH₂CH₂CH₂O-. ¹H NMR spectra is shown in the Figure 4.1.

Preparation of PT2k-CN was repeated for 3 times and the yield of this synthesis was enhanced from 82.0 % to 89.3 %.

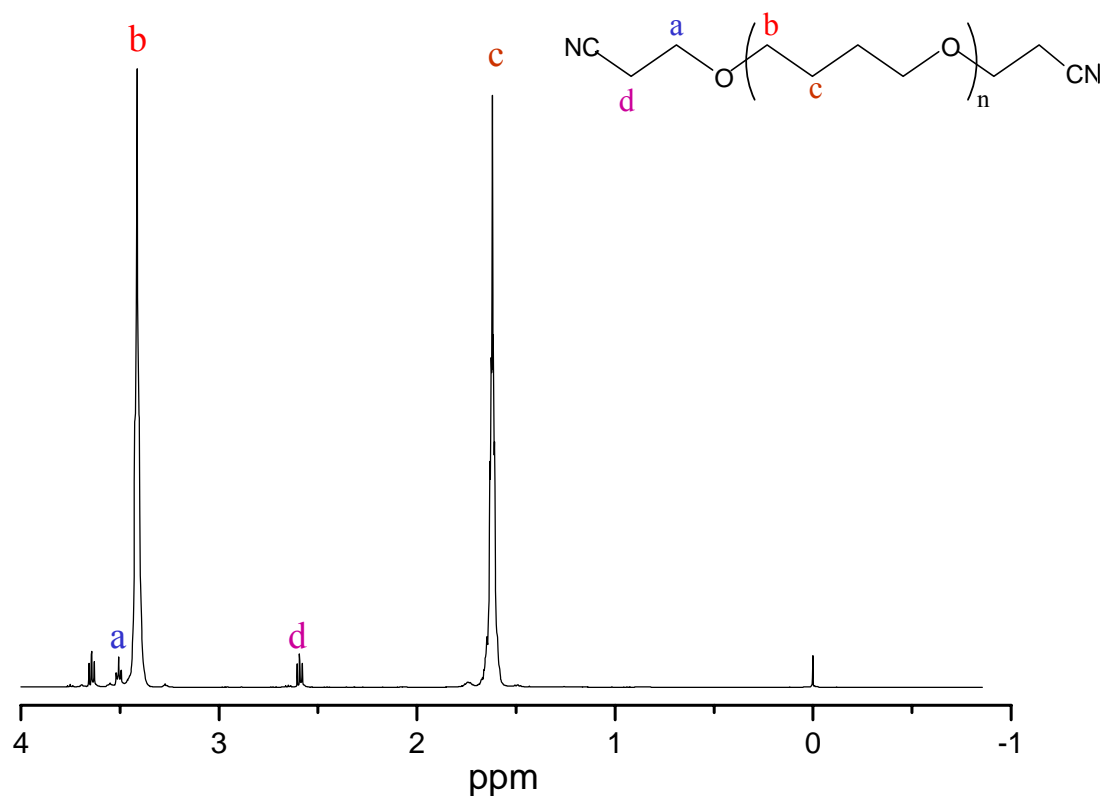


Figure 4.1: ^1H NMR spectrum of bis(2-cyanoethyl)-poly(tetrahydrofuran)

Two types of processes have been proposed to perform the homogeneous hydrogenation of nitriles to obtain amine functional species. First route is the introduction of large quantities of ammonia at high temperature and pressure. In the second route, Raney nickel is used as a catalyst at temperatures below 100 °C and at hydrogen pressures

of 50-100 atmospheres. [53] The main drawback for these two routes is the formation of oligomers with secondary and tertiary amine end-groups as by-products.

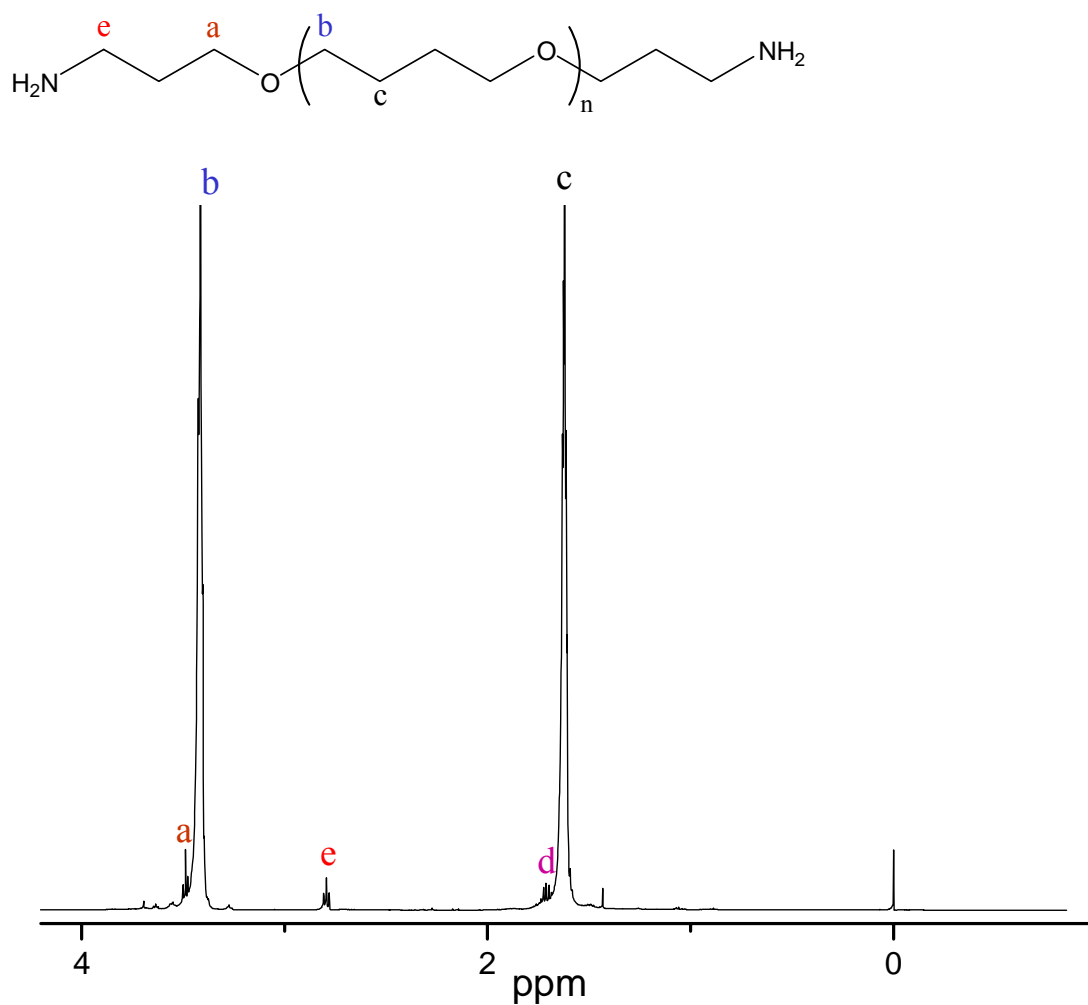


Figure 4.2: ^1H NMR spectrum of bis(3-aminopropyl)-poly(tetrahydrofuran)

Therefore none of these approaches were very attractive for our purposes. In order to obtain high molecular weight polymers with desired properties, end groups should be entirely

primary. As a result Versteegen et. al., selected to use the borane-THF complex to reduce the nitrile groups to primary amines in a controllable way. The reactions were carried under much milder conditions, at the reflux temperature of THF. Addition of concentrated acid and methanol removed the nitrogen containing by products. Extraction with basic solution and evaporation of solvents gave pure PT2k-NH₂. (Yield = 88.8 %) ¹H NMR spectra of the product is illustrated in Figure 4.2. 3.49 δ triplet, 4H, -OCH₂CH₂CH₂NH₂, 3.41 δ multiplet (very strong) -OCH₂CH₂CH₂CH₂O-, 2.79 δ triplet, 4H, -OCH₂CH₂CH₂NH₂, 2.27 δ singlet (very weak), 1.71 δ triplet -OCH₂CH₂CH₂NH₂, 1.63 δ multiplet (very strong), OCH₂CH₂CH₂CH₂O-, 1.43 δ singlet, 4H, -OCH₂CH₂CH₂NH₂, 1.26 δ singlet (very weak), not identified, 1.07 δ doublet (very weak), -OCH(CH₃)CH₂NH₂, side product.

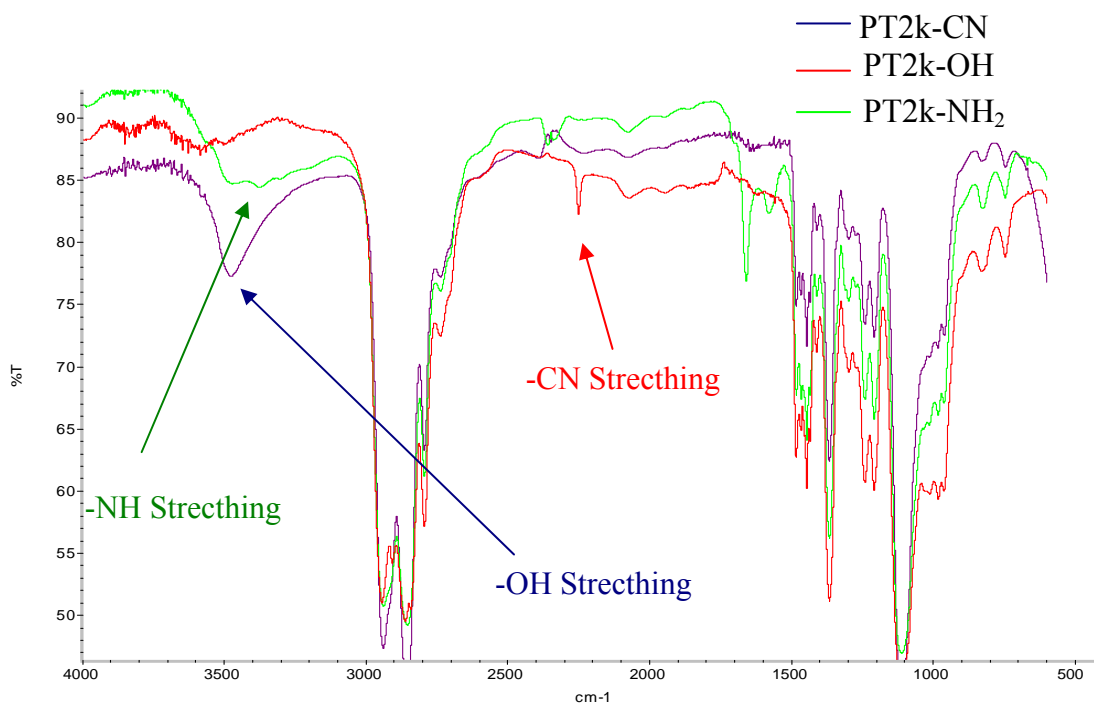


Figure 4.3: FTIR spectra of the end group functionalization reaction of PT2k-OH

Preparation of PT2k-NH₂ was repeated for 3 times and the yield of this synthesis was enhanced from 85.9 % to 88.8 %. The overall yield for the synthesis from PT2k-OH to PT2k-NH₂ was enhanced from 71.5 % to 79.3 %. Titration of the amine end groups with standard HCl solution gave a number average molecular weight of 2450 ± 7 g/mol. However, it was theoretically expected to be 2184 g/mol.

Progress and the completion of the end group conversion reaction of PTMO oligomer was monitored by FTIR spectroscopy. For comparison, IR spectra of hydroxyl, nitrile and amine end-capped PTMO oligomers are shown in Figure 4.3. Completion of the cyanoethylation reactions were confirmed by the disappearance of broad hydroxyl band centered around 3470 cm^{-1} and appearance of the nitrile stretching peak at 2290 cm^{-1} . After hydroboration, the amine terminated PTMO oligomers displayed two weak N-H stretching peaks at 3380 and 3490 cm^{-1} , typical for amines.

4.1.2 Synthesis of PEB-NH₂

In order to control the extent of phase separation in segmented copolymers, such as polyureas, one should take into account the polarity of the soft segment used during the polymer preparation. In this work, we also want to investigate the effect of soft segment polarity on the microphase separation. For this purpose, poly(ethylene butylene) (PEB) type soft segment, which has a completely nonpolar structure, was used. However, amine terminated PEB is not available commercially. Amine terminated PEB was synthesized from the commercially available hydroxyl terminated PEB in our laboratory.

Hirschberg described the two step synthesis of an amine terminated PEB by using hydroxyl end-capped PEB.[55] In this synthesis route, cyanoethylation of PEB was followed by the reduction of the nitrile groups with borane-terahydrofuran complex. In the first step of the synthesis, NaOH was used in the presence of methyltrioctylammonium chloride. Unlike the Hirschberg's route, NaH was used in this study in the presence of a crown ether to increase the nucleophilicity of the hydroxyl group. Acrylonitrile acted both

as solvent and reactant and used in excess amount to shift the equilibrium forward. The reaction was followed by FTIR by the disappearance of strong and broad O-H stretching peak centered around 3336 cm^{-1} and formation of the nitrile peak at 2253 cm^{-1} . Reaction was quenched by the addition of concentrated hydrochloric acid and the side products were removed by the filtration. (Yield = 99.2 %) The product was characterized by ^1H NMR spectroscopy, which is provided in Figure 4.4. $3.64\text{ }\delta$ triplet, 2H, PEB- CH_2O , $3.49\text{ }\delta$ multiplet, 1H, PEB- $\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}$, $2.59\text{ }\delta$ triplet, 4H, $-\text{OCH}_2\text{CH}_2\text{CN}$, $2.45\text{ }\delta$ doublet (very little) $-\text{OCH}(\text{CH}_3)\text{CN}$, $2.36\text{ }\delta$ singlet ArCH_3 impurity from toluene, $1.55\text{ }\delta$ multiplet, not identified, $1.40\text{-}0.92\text{ }\delta$ multiplet, (very strong), CH_2 backbone, $0.83\text{ }\delta$ multiplet, (strong), CH_3 backbone.

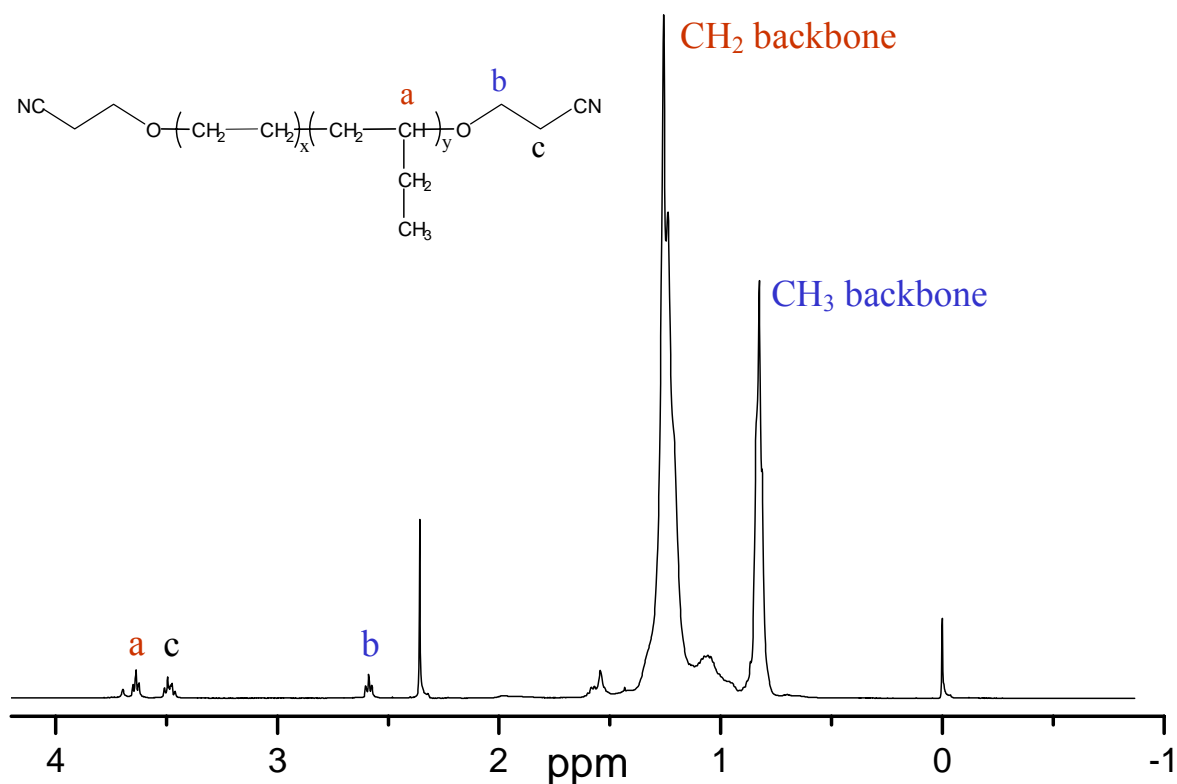


Figure 4.4: ^1H NMR α,ω -poly(ethylene/butylene)-bis(3-oxypropyl nitrile)

Preparation of PEB-CN was repeated for 2 times and the yield of this synthesis was enhanced from 84.0 % to 99.2 %. In the second step, PEB-NH₂ was synthesized by the reduction of PEB-CN with borane-THF complex at reflux temperature. The product was characterized by ¹H NMR and FTIR spectroscopy. (Yield = 93.4 %). The product was characterized by ¹H NMR, which is shown in Figure 4.5.

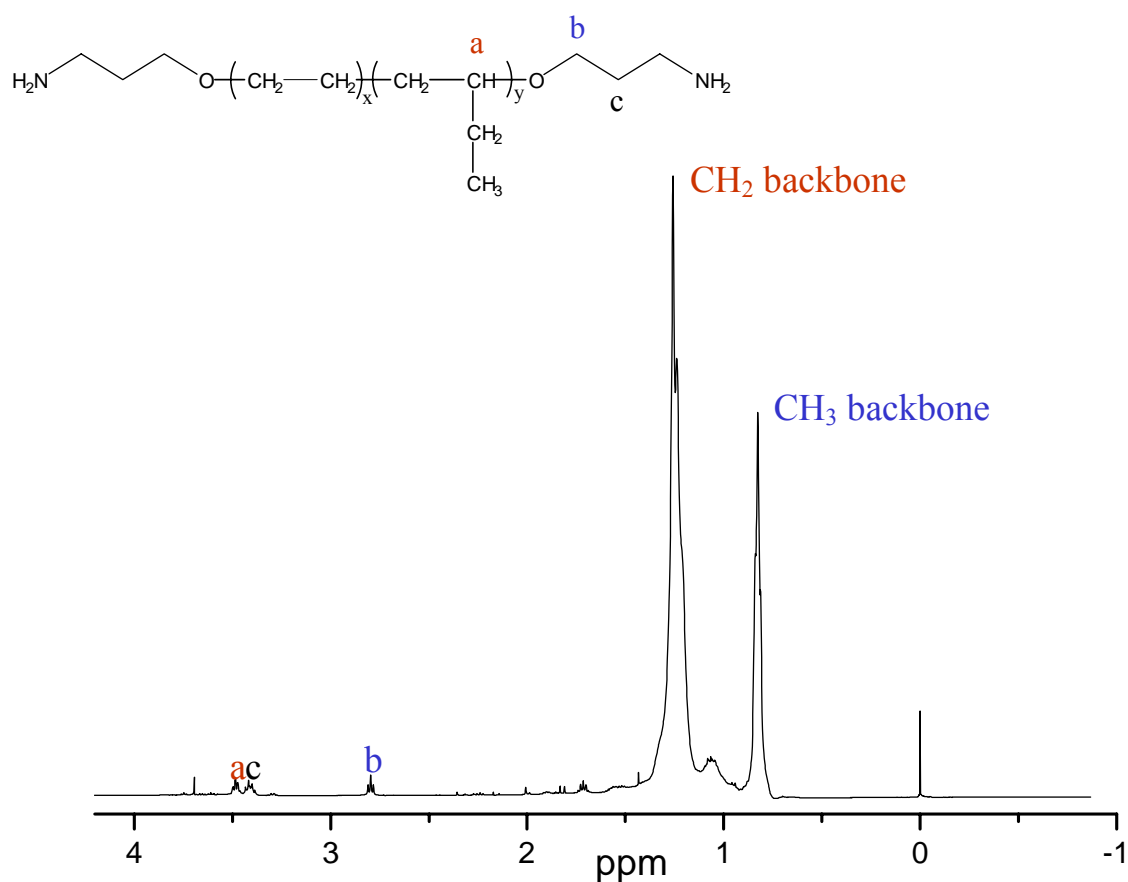


Figure 4.5: ¹H NMR α,ω -Poly(ethylene/butylene)-bis(3-oxypropylamine)

Analysis of the NMR spectrum: 3.59 δ triplet, 2H, PEB- CH_2O , 3.48 δ triplet, 4H, - $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, 3.42 δ multiplet, 1H, PEB- $\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}$, 2.80 δ triplet, 4H, - CH_2NH_2 , 2.46 δ quartet (very weak) not identified, 2.31 δ triplet (very weak) not identified, 2.16 δ doublet (very weak) not identified, 1.88 δ multiplet (very weak) not identified, 1.71 δ pentet, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, 1.54 δ multiplet (very weak) not identified, 1.44 δ singlet, not identified, 1.37-1.00 δ multiplet, (very strong), CH_2 backbone, 0.83 δ multiplet, (strong), CH_3 backbone.

Preparation of PEB- NH_2 was repeated for 2 times and the yield of this synthesis was enhanced from 72.1 % to 93.4 %. The overall yield for the synthesis of PEB- NH_2 was enhanced from 60.6 % to 92.6 %. Reactions of the amine end groups with stoichiometric amounts of diisocyanates gave a number average molecular weight of 3700 g/mol. However, it was theoretically expected to be 3474 g/mol.

4.1.3 Preparation of segmented polyureas

All copolymers were prepared by reacting equimolar amounts of a selected diisocyanate and the amine terminated PTMO or PEB oligomers. Polymerization reactions were carried out at room temperature by the dropwise addition of oligomer solution onto the diisocyanate solution under strong agitation. All non-chain extended polyureas were synthesized only once, except CHDI-PEB. Dual reactions were performed for the synthesis of this polyurea since it did not make a good film in the first trial. However, film formed after the second trial resulted in a homogenous, nice film. Polymerization reactions of non-chain extended, segmented polyureas were followed by FTIR spectroscopy. Representative IR spectra of various stages of the reaction between PT2k- NH_2 and CHDI are shown in Figure 4.6.

IR spectra of intermediate obtained after addition of 50% and 85% of PTMO onto the CHDI and that of the final polymer are provided in Figure 4.6. As can be seen from these spectra, as the reaction proceeds, the strong isocyanate absorption peak at 2270 cm^{-1}

disappears and hydrogen bonded C=O and N-H absorption peaks at in the 1508-1676 cm^{-1} range and at 3315 cm^{-1} were respectively observed.

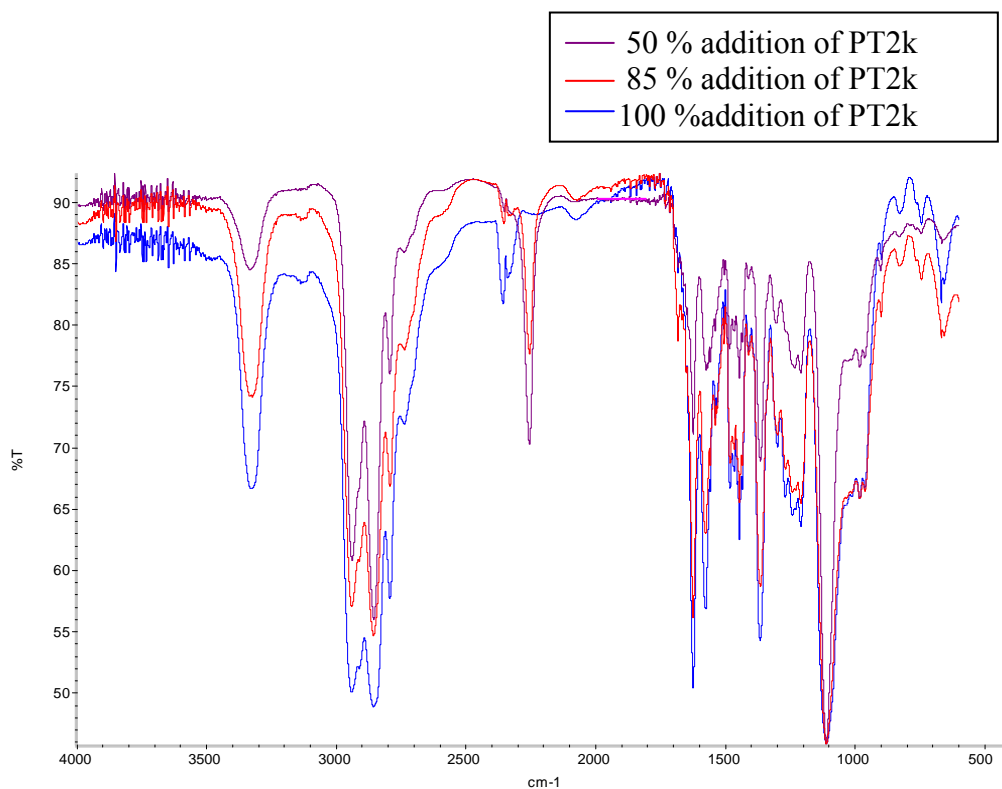
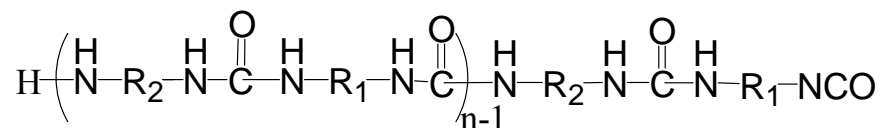


Figure 4.6: Comparative FTIR spectra of the starting materials and products in the reaction between PTMO and CHDI

Representation of the chemical structures of non-chain extended, segmented polyureas and a list of polyureas that were synthesized in this study, together with their hard segment contents are provided in the Table 4.1. Since dissolution of non-chain extended polyureas were difficult, SEC analysis could not be done in order to determine the molecular weight of the polymer.

Table 4.1: Chemical structures of segmented polyureas and list of polyureas that were synthesized in this study.



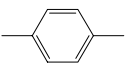
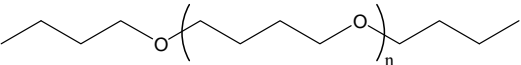
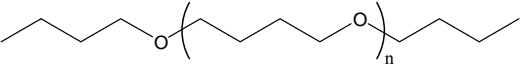
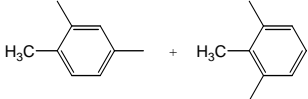
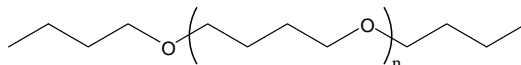
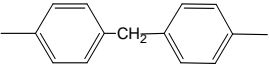
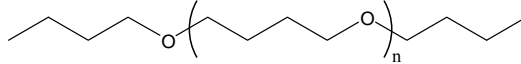

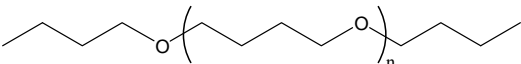

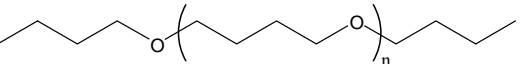
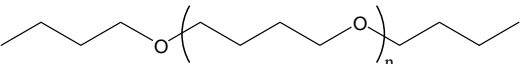

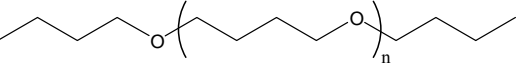
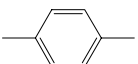
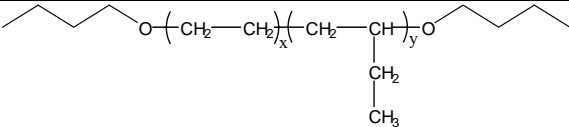
Polymer Code	R ₁	R ₂	% Hard Segment
<i>p</i> PDI-PT1k			13.8
HDI-PT1k	$-(\text{CH}_2)_6-$		13.5
TDI-PT1k			13.7
MDI-PT1k			18.5
CHDI-PT1k			13.3
<i>p</i> PDI-PT2k			6.60
HDI-PT2k	$-(\text{CH}_2)_6-$		6.40
CHDI-PT2k			6.35
<i>p</i> PDI-PEB			4.50

Table 4.1. continued

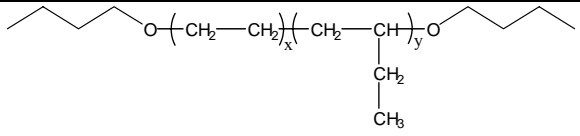
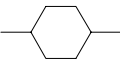
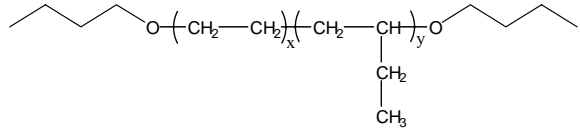
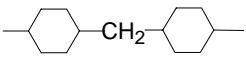
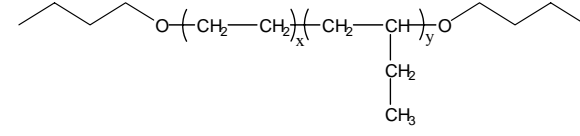
HDI-PEB	$-(\text{CH}_2)_6-$		4.30
CHDI-PEB			4.30
HMDI-PEB			6.60

Table 4.2: A detailed list and chemical compositions of water chain extended PUUs

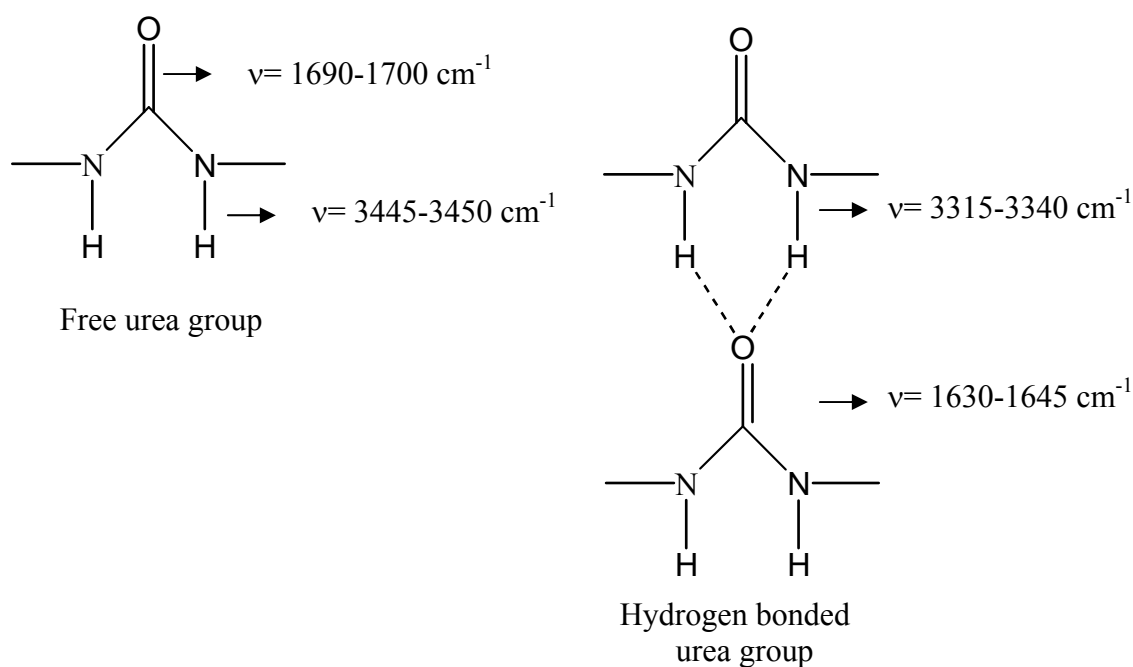
Polymer Code	Diisocyanate	Oligomer	Chain Extender	% Hard Segment
PTMO1K(1)-HMDI(2)-H ₂ O(1)	HMDI	PT1k	H ₂ O	35.7
PTMO1K(1)-HMDI(3)-H ₂ O(1)	HMDI	PT1k	H ₂ O	45.0
PTMO1K(1)-HDI(1.5)-H ₂ O(0.5)	HDI	PT1k	H ₂ O	21.7
PTMO1K(1)-HDI(2)-H ₂ O(1)	HDI	PT1k	H ₂ O	26.7

As given in Table 4.2., it is interesting to note that we were able to prepare PT1k based polyurethaneureas with extremely high urea contents of 21 to 45 % by weight, which was also soluble in DMF. On the other hand we could only prepared PEB based water chain extended polyurethaneureas with very low hard segment contents, due to solubility problems.

4.2 Studies on the determination of the extent of phase separation

FTIR spectroscopy is a very sensitive technique in determining frequency shifts in the characteristic absorption peaks which are due to the hydrogen bonding. Analysis of the

differences in the C=O and N-H regions of the FTIR spectra gives valuable information in understanding the extend of microphase separation in polyurethanes [59,60]. Characteristic IR absorption frequency ranges for free and hydrogen bonded polyureas are illustrated in Scheme 4.1.[17]



Scheme 4.1: Characteristic IR band ranges for urea groups

The frequency of a vibration can be calculated according to the Equation 4.1, where k is the force constant of a vibrating system, μ is the reduced mass and ν is the corresponding frequency.

$$\nu = 2\pi \sqrt{\frac{k}{\mu}} \quad (4.1)$$

Because of the hydrogen bonding, vibrational motion is restricted and force constant of the system is decreased. As it is seen in the scheme above, polyureas obey this trend and the frequencies of hydrogen bonded C=O and N-H were found to shift to the lower values.

Since carbonyl stretching vibration band is narrower than the N-H stretching vibration, it is more practical to analyze carbonyl region to understand the extent of phase separation. IR spectra of the carbonyl regions of *p*PDI based polyureas are provided in Figure 4.7.

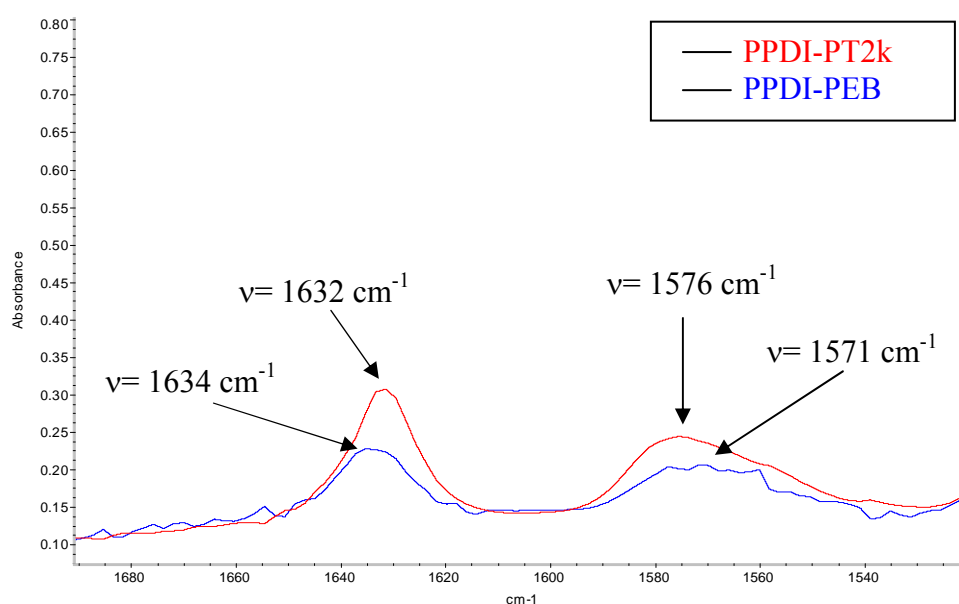


Figure 4.7: Carbonyl region of the FTIR spectra for *p*PDI based polyureas (Blue spectrum *p*PDI-PEB-urea, Red spectrum: *p*PDI-PT2k-urea)

Hydrogen bonded urea was reported to show a peak maximum at 1635 cm^{-1} [58] *p*PDI-PT2k and *p*PDI-PEB segmented polyureas displayed absorption peaks at 1632 and 1634 cm^{-1} respectively, very good agreement with the literature. Other semi-empirical evidence for hydrogen bonding is the shift in the N-H absorption peak position. N-H absorption peaks for *p*PDI-PT2k and *p*PDI-PEB were found to be centered at 3315 and

3319 cm^{-1} and these frequency values are in the range of hydrogen bonded N-H stretching in polyureas (Scheme 4.1)

Since the soft segment of PTMO based polyureas contain ether functional groups, in addition to carbonyl oxygen, ether oxygen can also interact with urea and form weak hydrogen bonding which leads to phase mixing. In order to understand the extend of phase separation in polyurethane copolymers, strong ether (C-O-C) absorption band around 1100 cm^{-1} in IR region, can be analyzed. Yilgor et. al. have reported distinct shoulder in this region for non-chain extended, PT1k based polyurethanes as an evidence for incomplete phase separation. [38] IR spectra of *p*PDI-PT2k polyurea displayed a very narrow, strong absorption peak centered at 1115 cm^{-1} with no distinct shoulder. This absorption peak is exactly the same when compared to the C-O-C peak that was found in the PT2k-NH₂ case, which can be considered as a strong evidence for complete phase separation in *p*PDI-PT2k polyurea.

4.3 Thermal properties

4.3.1 PTMO based polyureas

The dynamic mechanical analysis of non-chain extended, segmented polyureas, with the hard segments based on *p*PDI, HDI and CHDI and the soft segment based on PTMO with number average molecular weights of 1080 (PT1k) and 2450 (PT2k) are shown in Figure 4.8. In the lower temperature range between -130 °C and -100 °C, PT2k based polyureas possess higher storage moduli compared to their PT1k based analogues independent from the type of the diisocyanate. In segmented copolymers, it is known that increasing soft segment molecular weight enhances the ability to form crystalline morphology. [1] The higher moduli values in the case of 2k polyureas are most probably due to the crystalline phase of PT2k. Presence of a distinct shoulder in the $\tan \delta$ peaks between -50 °C and 0 °C also provides a strong support for this suggestion. This result is also supported by the differential scanning calorimetry responses of these polyureas, which

will be addressed later. The glass transition started at $-90\text{ }^{\circ}\text{C}$ in all the polyureas and the corresponding $\tan \delta$ exhibited a peak centered at $-60\text{ }^{\circ}\text{C}$, typical for PTMO. The moduli of the rubbery plateau region for all polyureas are lower in 2k polyureas than their 1k analogues ($\sim 1 \times 10^8$ for the 1k polyureas and $\sim 4 \times 10^7$ Pa for the corresponding 2k polyureas). The rubbery plateau modulus is lower in the case of 2k polyureas because of the higher hard segment content (approximately two times) of 1k polyureas. Such high rubbery plateau moduli are also observed in the case of chain extended polyurethanes which have much higher hard segment content than the case of our copolymers.[5] Surprisingly, diisocyanate structure or symmetry did not affect the stiffness of the polyurea in the rubbery plateau temperature range.

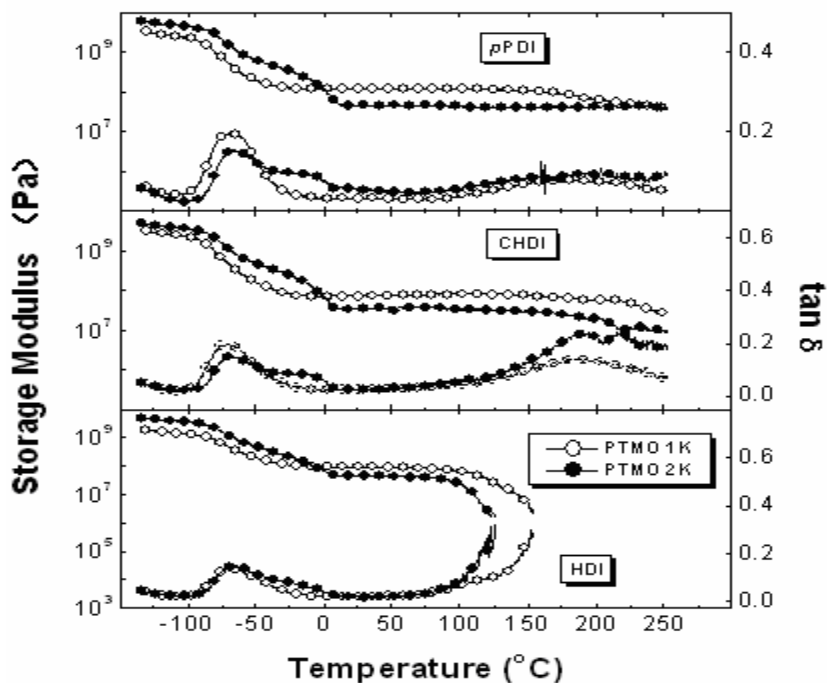


Figure 4.8: Effect of PTMO SS molecular weight and diisocyanate type on the dynamic mechanical spectra of non-chain extended, segmented polyureas.

The length of the rubbery plateau and the beginning of the softening point were found to depend on the soft segment molecular weight and the structure and symmetry of the diisocyanates. Due to the melting of PTMO crystallites in the 2k case, the starting point of the rubbery plateau shifted to a higher temperature and rubbery-viscous flow occurred at a lower temperature than their 1k analogues. HDI based 1k polyurea, which has only six methylene groups between the urea linkages, started to soften at 100 °C. Unlike the other copolyureas, the ones based on HDI were reported to be melt processible at reasonably low temperatures, because of such a low softening temperature. [57] However, the diisocyanates which contain cyclohexyl (CHDI) and phenyl rings (*p*PDI) between the urea linkages softened and flowed at significantly higher temperatures.

The effect of soft segment molecular weight is seen more obviously by differential scanning calorimetry (DSC) responses. The crystallinity of both the soft and the hard segments of HDI based polyureas were characterized by DSC and is shown in the figure below.

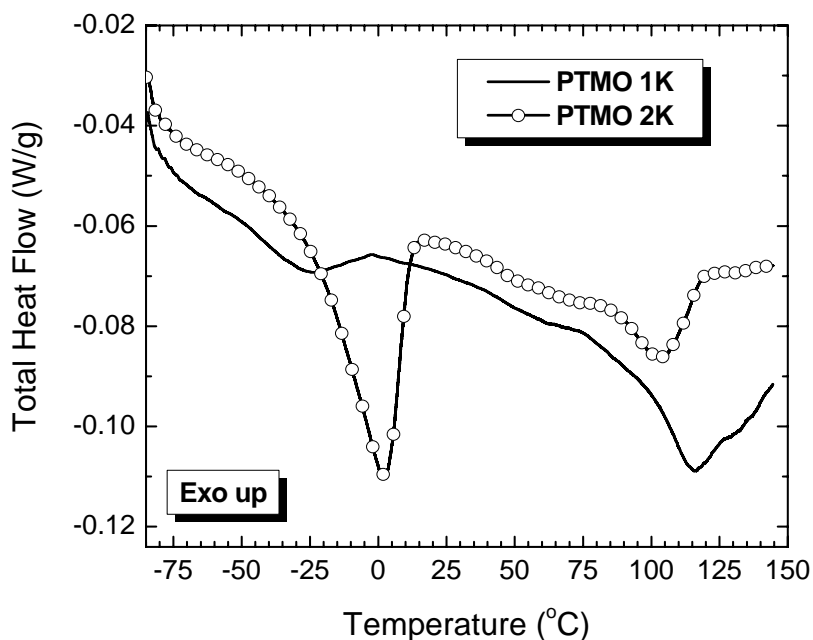


Figure 4.9: Effect of PTMO molecular weight on the DSC profiles of non-chain extended, segment polyureas based on HDI.

Both polyureas possessed an endothermic transition at about -60°C , because of the T_g of the PTMO. The 1k polyurea displayed smaller endothermic peak at about -25°C ; however, a larger endothermic melting peak was observed at about 0°C for the 2k polyurea. Hard segment melting was observed at 103°C for 2k polyurea and at 116°C for 1k polyurea. This observation also explains the difference in inception temperature of viscous flow between 1k and 2k polyureas. In addition to the effect of molecular weight, minor product from end group functionalization of PTMO may also affect the hard segment crystallinity in the 2k polyureas. Additionally, increasing soft segment molecular weight will potentially limit the chain motions of the soft segment and prevent formation of better crystallites of hard segments. The melting endotherms displayed that the heat of fusion for the hard segment melting was approximately two times greater in the case of 1k polyurea compared to their 2k analogues because of the higher hard segment content of this polyurea.

4.3.2 PEB based polyureas

The dynamic mechanical analysis of non-chain extended, segmented polyureas, with the hard segment based on HDI and HMDI and the soft segment based on PEB with number average molecular weight of ~ 3700 g/mol are shown in Figure 4.10.

In the lower temperature range between -100°C and -50°C , below T_g of PEB, interestingly both polyureas exhibited similar storage moduli ($\sim 2 \times 10^9$ Pa). The glass transition started at around -50°C in both polyureas and the corresponding $\tan \delta$ exhibited a fairly strong and symmetrical peak centered at -35°C . The moduli of the rubbery plateau were $\sim 2 \times 10^6$ Pa. Such a long rubbery plateau, extending from -50 to $+150^{\circ}\text{C}$ gave indirect evidence for the excellent phase separation, more importantly it especially indicated almost no phase mixing between hard and soft segments as observed in silicone-urea copolymers [51,52] in these copolymers also. DSC scans of these materials are required to make a conclusion about the melting point of the hard segment. Such high temperature ($\sim 180^{\circ}\text{C}$)

for the $\tan \delta$ peak that corresponds to the end point of the rubbery plateau will be due to the breakage of strong hydrogen bonding in the copolymers similar to that of silicone-urea copolymers.[52] AFM analysis of these polyureas is also required for the direct evidence of phase separation.

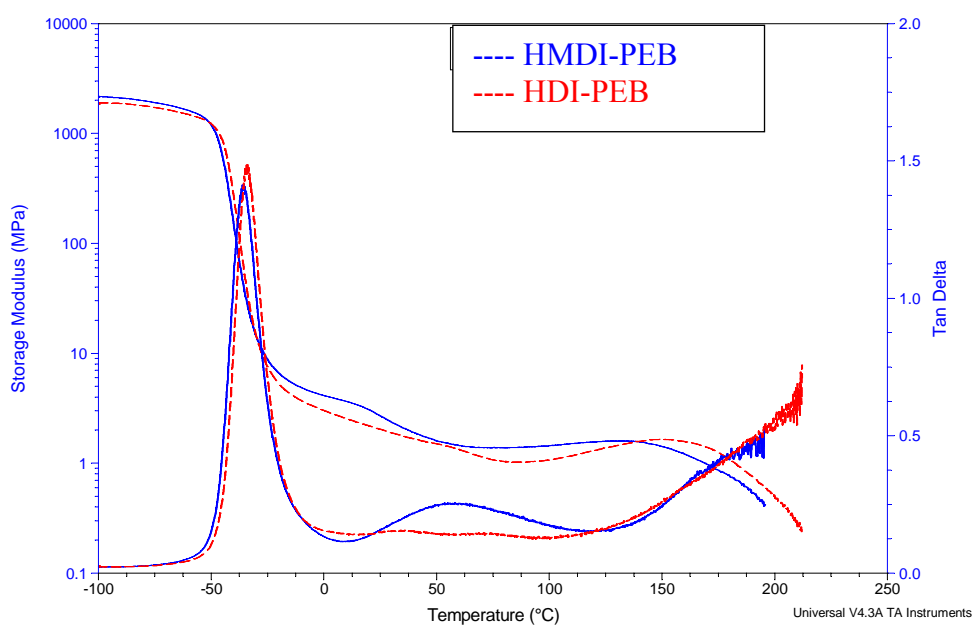


Figure 4.10: Effect of diisocyanate type on the dynamic mechanical spectra of PEB based non-chain extended, segmented polyureas.

4.4 Morphology

4.4.1 AFM studies on PTMO based polyureas

As it was verified by the DMA scans, PTMO soft segment based non-chain extended, segmented polyureas exhibited relatively high rubbery plateau modulus ($\sim 1 \times 10^8$ for the 1k polyureas and $\sim 4 \times 10^7$ Pa for the corresponding 2k polyureas). Such high storage

modulus could only be possible in these very low amounts of hard segment containing polyureas if considerable percolation of the hard segment phase exists throughout the soft segment matrix. This postulation was verified by the direct support of the tapping mode AFM, a surface characterization technique, analysis and results are shown in Figure 4.11 for polyureas based on *p*PDI and HDI hard segments.

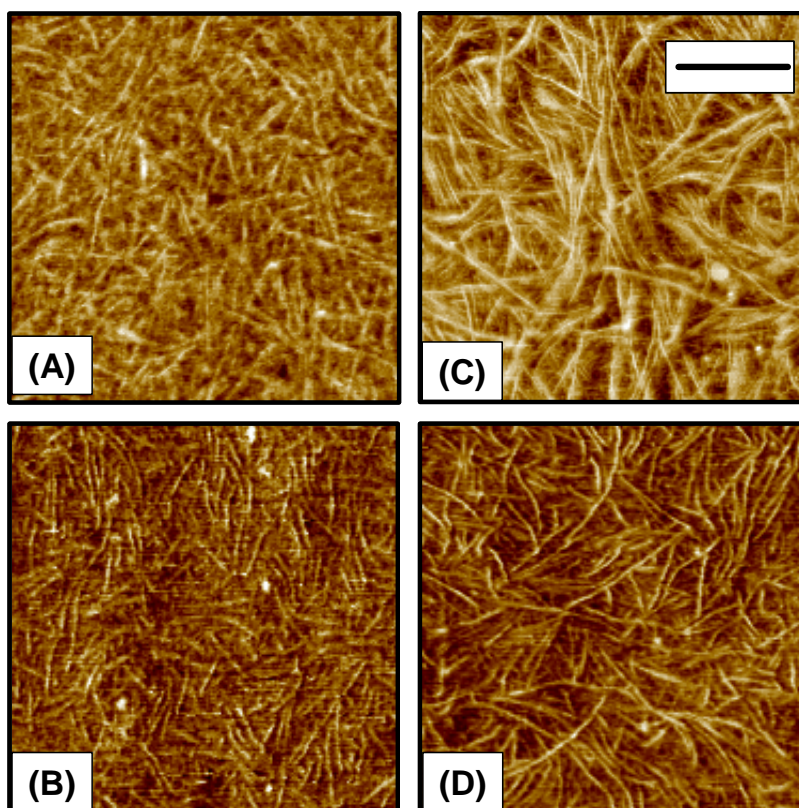


Figure 4.11: Tapping-mode AFM phase images of selected non-extended, segment polyureas: (A) PPDI-PT1k, (B) PPDI-PT2k, (C) HDI-PT1k, (D) HDI-PT2k. The bar denotes 200 nm.

Hard segments appear lighter in color than the soft segments in these images. These ordered hard domains which appeared as ribbon-like structures resulted from well ordered

packing or crystallization of *p*PDI and HDI. The lengths of these hard domains were appeared to be similar, but as expected, the density of the hard domains in 1k polyureas was higher than their 2k analogues because of almost two fold difference in the hard segment contents in these 1k and 2k polyureas. Further verification of the phase separation and the hard domain connectivity was done by SAXS measurements.

4.4.2 Small Angle X-Ray Scattering studies on PTMO based polyureas

Unlike AFM, small angle X-ray scattering (SAXS) is a bulk characterization technique. SAXS measures the scattering of the X-rays at distances very close to the primary beam. Since the scattering distance is inversely proportional to the distance in real space, SAXS therefore, is sensitive to length scales on the order of nanometers rather than angstroms. Therefore, this technique is suitable for characterization of inter-phase instead of intra-phase morphology.[1] SAXS profile of HDI based polyureas are shown in Figure 4.12. Data were represented as intensity versus scattering angle, s , and it is defined in the equation below;

$$s = \frac{2 \sin \theta}{\lambda} \quad (4.2)$$

where 2θ is the radial scattering angle and λ is the wavelength of the incoming X-ray. First order transition peak in SAXS profiles of non-chain extended, segmented HDI based polyureas is the evidence of microphase separated morphology. The position of the corresponding peak was used to calculate the average interdomain spacing. The average interdomain spacing basically gives the average length between the two repeating hard segments. As the molecular weight of the soft segment increases, the interdomain spacing should increase as an expectation. SAXS analysis of PT2k based polyurea exhibited higher interdomain spacing (103 Å) than PT1k based polyurea (79 Å). [57]

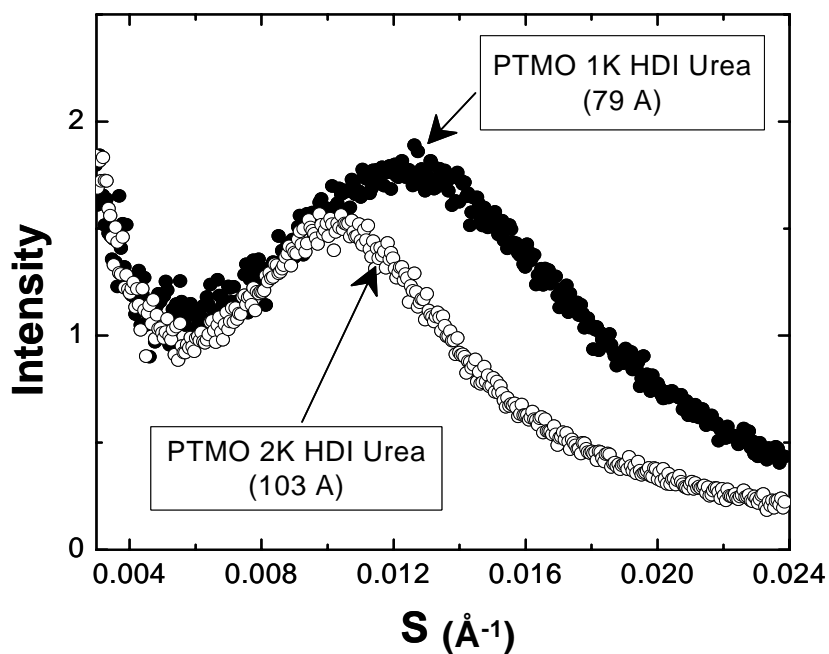


Figure 4.12: Effect of PTMO SS molecular weights on the SAXS profiles of non-chain extended, segment polyureas based on HDI hard segment.

4.5 Mechanical Properties

4.5.1 Tensile Testing

In order to examine the extent of hard phase connectivity and mechanical properties of PTMO based non-chain extended, segmented polyureas, stress-strain behavior was analyzed. Comparative stress-strain curves for PT1k and PT2k and HDI based polyureas are shown in Figure 4.13.

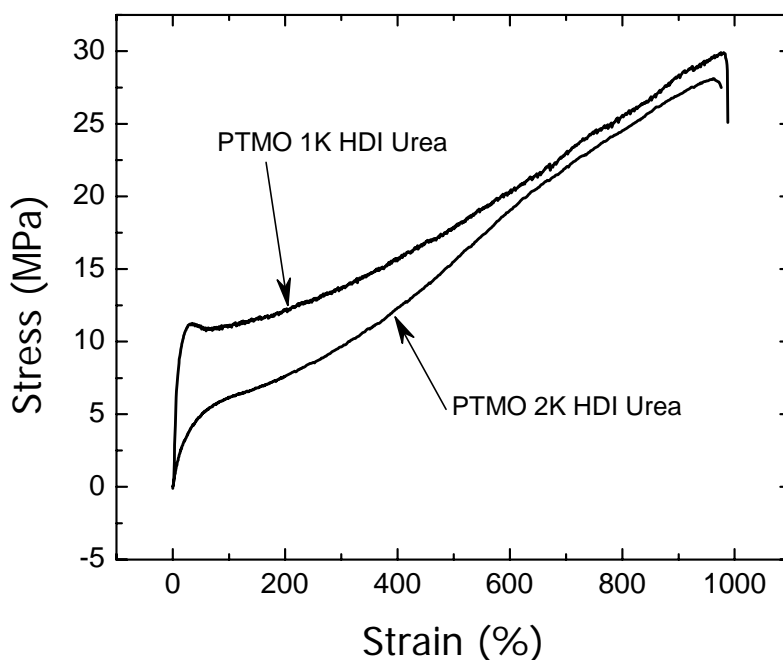


Figure 4.13: Effect of PTMO molecular weight on the tensile behavior of non-chain extended, segmented polyureas based on HDI

Unlike PT2k polyurea, PT1k polyurea exhibited a distinct yield point because of the lower interdomain spacing between repeating urea groups. Up to the yield point, energy was given to the system to break the connectivity of the hard domains. At the yield point, plastic deformation occurred and physical connectivity of hard domains was broken. Similar behavior was also reported in the PT1k soft segment containing, non-chain extended, segmented copolyureas based on other diisocyanates.[33,56] After the yield point, PT1k based polyurea behaved as a completely different material and had an ultimate tensile strength of around 30 MPa and elongation at break of about 1000 %. Very surprisingly, the PT2k based polyurea also had an approximately the same ultimate tensile strength and elongation at break. For the poly(dimethylsiloxane) based non-chain extended polyurea system, it was found that the modulus and ultimate tensile strength decreased when the molecular weight of the poly(dimethylsiloxane) was increased.[51] PTMO based

homologous copolymer systems do not seem to follow the same trend as those of the poly(dimethylsiloxane) based copolymers.

In order to investigate the effect of diisocyanate structure/symmetry on the mechanical properties, non-chain extended, segmented PT1k based polyureas were prepared. Comparative mechanical properties, which were obtained from stress-strain measurements, are shown on Table 4.3.

Table 4.3. Mechanical properties of PT1k based non-chain extended, segmented polyureas prepared by using different diisocyanates and with different hard segment contents.

Diisocyanate	Hard segment content (% weight)	Modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)
TDI	13.7	52	12.0	760
<i>p</i> PDI	12.7	76	19.5	540
MDI	18.5	80	17.0	670
CHDI	13.1	130	30.0	980
HMDI	19.3	6.6	19.6	925

As shown on Table 4.3., these polymers exhibited relatively good mechanical properties. Their moduli and ultimate tensile strengths were strongly dependent on their diisocyanate structure/symmetry. *p*PDI which is a symmetric and aromatic diisocyanate displayed higher ultimate tensile strength than other aromatic diisocyanates such as TDI and MDI. TDI is a mixture of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate and it has an unsymmetrical structure. Also, MDI has a bended structure and this type of unsymmetrical structure limits the packing ability of the hard segment. MDI based polyurea displayed lower tensile strength than symmetrical *p*PDI. Similar situation is observed in aliphatic

diisocyanate based polyureas. More symmetric CHDI based polyurea gave higher tensile strength than HMDI based polyurea.

4.6. Water chain extended PUUs

As shown on Table 4.2. it was possible to prepare water chain extended PT1k based polyurethaneureas from HMDI and HDI, with fairly high urea hard segment contents. As shown on Table 4.4., these polymers displayed very good mechanical properties. Their moduli and ultimate tensile strengths were strongly dependent on their compositions. HMDI base PUUs with fairly high urea hard segment contents showed very high ultimate tensile strength values around 40 MPa. As expected their elongation at break values were somewhat low, around 300-400%. HDI based water chain extended PUUs had lower urea hard segment contents, and as a result displayed lower moduli and tensile strength values compared to HMDI based PUUs. Elongation at break values for these materials was very high, around 700-750%, typical for elastomers.

Table 4.4. Tensile properties of PT1k based and water chain extended polyurethaneureas prepared by using different diisocyanates and with different hard segment contents.

Diisocyanate and Polymer composition	Hard segment content (wt%)	Modulus (MPa)	Ultimate Tensile strength (MPa)	Elongation at break (%)
HMDI - 1:2:1	35.7	12.5	39.0	420
HMDI - 1:3:1	45.0	110.0	44.0	290
HDI - 1:1.5:0.5	21.7	6.0	10.4	750
HDI - 1:2:1	26.7	8.0	15.6	700

Chapter 5

CONCLUSIONS

The effect of diisocyanate structure and soft segment molecular weight on the structure-property behavior of novel, non-chain extended, segmented polyureas were investigated. These polyureas displayed a microphase separated structure with randomly dispersed, crystalline hard segments in the continuous soft segment matrix. Crystalline hard segment based on a single isocyanate molecule had an aliphatic or aromatic nature, while soft segment based on a high molecular weight oligomer (PTMO or PEB) had a moderately polar or nonpolar structure.

DMA profiles of PTMO based polyureas showed somewhat higher low temperature moduli for 1k polyureas than their 2k analogues due to the higher extent of soft segment crystallinity of PT2k oligomers. However, rubbery plateau moduli of 1k polyureas were found to be higher ($\sim 1 \times 10^8$ Pa) than their 2k analogues ($\sim 4 \times 10^7$ Pa) because of the higher hard segment content and the presence of hard segment connectivity. Such high rubbery plateau moduli are typically observed in conventional chain extended polyurethanes which have much higher hard segment content than the case of our non-chain extended polyureas. Surprisingly, structure or symmetry of the diisocyanate did not affect the stiffness of the polyurea in the rubbery plateau region. AFM studies of these polyureas showed thread-like hard segment domains in the continuous soft segment matrix. Extent of the hard segment connectivity decreased as the molecular weight of the soft segment increased. The distinct yield point that was found by the stress-strain analysis showed an indirect evidence of the hard phase connectivity in 1k polyureas. The distance between the two hard domains were characterized by SAXS, which is a bulk characterization technique, and were calculated to

be 103 Å for the 2k polyurea and 79 Å for the 1k polyurea as a direct evidence for the hard segment connectivity. It was found that inception points of viscous flow of polyureas were strongly related to the melting point of hard segment. Increasing soft segment molecular weight (i.e. decrease in hard segment content) did not affect the ultimate tensile strength (~30 MPa) in a great extent, surprisingly. It may be because of the higher extent of strain induced crystallinity of PTMO soft segment by the effect of deformation. It was also found that mechanical properties of PT1k based polyureas were strongly related to structure/symmetry of the diisocyanate.

DMA profiles of PEB based non-chain extended polyureas exhibited low temperature storage moduli of $\sim 2 \times 10^9$ Pa which was very similar to PTMO based polyureas. The moduli of the rubbery plateau were $\sim 2 \times 10^6$ Pa which is lower than PTMO based polyureas due to the lower hard segment content (for HDI-PEB polyurea it is %4.30). Such a long rubbery plateau gave indirect evidence for the phase separation of these copolymers.

A brief investigation of the water as a chain extender for polyurethaneureas resulted in some very interesting polymers which displayed good solubility in DMF, in spite of fairly high urea contents, and very good composition dependent tensile properties.

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