Chapter 1
INTRODUCTION

1.1. THERMOPLASTIC POLYURETHANES

The first commercial thermoplastic polyurethanes (TPUs) were established in Germany by Otto Bayer-Faben fabriken and in the U.S. by B.F. Goodrich in the 1950s. The Polyurethane Industry describes TPUs as “bridging the gap between rubber and plastics”, since TPUs offer the mechanical performance characteristics of rubber but can be processed as thermoplastics. This special type of TPUs among other polymers and elastomers imparts high elasticity combined with high abrasion resistance and results in a wide array of applications ranging from skin boots, footwear to gaskets, hoses, seals, etc.. Thermoplastic polyurethanes are randomly segmented copolymers composed of hard and soft segments forming a two-phase microstructure as shown in the Figure 1.1.

![Figure 1.1: The alternating structure of TPUs. HS: Hard segment; SS: Soft Segment.](image)

Polymers can be classified in a number of ways; one of the most basic is the division of materials into two groups, namely homopolymers and copolymers (the latter which contain a subset of materials known as block and segmented copolymers). A material is deemed a homopolymer when only one type of repeating unit (RU) is used to
form the polymer chain and as a copolymer if two or more different repeat units are used to create the chain. Employing just two repeat units, represented as A and B will form a copolymers with very different structures. If the units are chemically linked in an alternating fashion, as shown in the Scheme 1.1(1) an “alternating copolymer” is formed. If the RUs are not alternated sequentially but rather are randomly joined, then the resulting polymer is termed a “random copolymer”. An example of RUs joined randomly is shown in the Scheme 1.1(2)

If instead, RUs are grouped together into reasonably long segments or blocks of similar species, a “block copolymer” is formed as shown in the Scheme 1.1(3). In general an individual block usually contains far more repeat units than is shown below (blocks lengths in classic block copolymers are typically 10,000–100,000 g/mol). Only a few units are shown here for the sake of simplicity.

(1) A B A B A B A B A B A B
(2) A B B A A B A B B A B A B
(3) A A A A B B B B A A A A

Scheme 1.1: Alternating (1), random (2) and block (3) copolymer arrangements of repeat units ‘A’ and ‘B’.

1.2. MULTIBLOCK COPOLYMER

Block copolymers are currently produced in three main categories: diblock copolymers often referred to as AB block copolymers (here A and B indicate an entire block instead of single repeat units), triblock copolymers of the ABA type and multiblock copolymers of the (AB)n type. Other types of block copolymers do exist such
as ABC types (which are constructed from three different types of repeating units), star block copolymers, and graft copolymers (such as high-impact polystyrene)\textsuperscript{3,4}. However, these are beyond the scope of this review. Multi-block copolymer consists of alternating crystallizable rigid segments and flexible of segments\textsuperscript{5-7} are called thermoplastic elastomers (TPE’s). The flexible segments form the continuous amorphous soft phase often with a low $T_g$, which gives the material low temperature flexibility. The rigid segments can phase separate by crystallization and form continuous lamellae in the low $T_g$ phase, acting as a physical crosslink’s, gives the material dimensional stability and solvent resistivity.

The rigid segments in segmented block copolymers are normally fast crystallizing segments, such as esters or amide groups. Also, urea and urethane groups are well known for their ability to self associate via hydrogen bonding. Thermoplastic elastomers with ester, amide and urethane groups are discussed below in more detail. The morphology of segmented block copolymers is determined by the phase separation between flexible and rigid segments. Phase separation can occur by liquid-liquid demixing or crystallization. TPE’s that phase separate by crystallization have a morphology that comprises a soft phase with dispersed crystalline lamellae\textsuperscript{8-13}.

Block copolymers have attracted much scientific interest for decades owing to many fascinating microphase-separated morphologies, the associated physical properties, and for their potential applications in various fields \textsuperscript{14-22}. Yet most studies block copolymers have focused on the simplest molecular architectures: linear AB diblocks and ABA triblocks\textsuperscript{23-27}. Much less research has been directed at block copolymers characterized by sequences of four or more blocks\textsuperscript{28-37} and containing more than two types of block chemistry. Increasing the number of blocks affects the chain
configurations and overall thermodynamics of self-assembly along with the kinetically mediated paths to equilibrium and non-equilibrium morphology, hence the resulting mechanical properties. Multiblock copolymers containing 10 or more blocks are expected to have distinctive microstructures and respond mechanically than conventional diblocks and triblocks shown in the Scheme 1.2.

![Multiblock copolymer](image)

**Scheme 1.2: Schematic representation of multiblock copolymer.**

Although in past two decades we have witnessed an explosion in the number of controlled synthetic approaches to preparing block copolymers. Among these, living anionic polymerization still represents a versatile and commercially the most important, method for preparing well-defined block copolymers. This technique offers precise control over block molecular weight, dispersity and provides facile mechanisms for functionalizing one or both chain termini at various stages during the development of the molecular architecture.

### 1.3. WHY POLYURETHANES ARE DIFFERENT FROM OTHER USED POLYMERS CURRENTLY?

Most of the polymers manufactured in industry possess a fairly simple chemical structure as they are synthesized from one or two monomers therefore leading to the formation of homopolymers or copolymers. Examples of these polymers are poly(ethyleneterephthalate) (PET), poly(tetrafluoroethylene) (PTFE), poly(styrene),
poly(ethylene), poly(propylene), poly(butadiene), etc. On the other hand, polyurethanes possess more complex chemical structures that typically comprise three monomers: a diisocyanate, a macro glycol (which is an oligomeric macro monomer) and a chain extender. Because of the three “degrees of freedom” that are available when considering the synthesis of a polyurethane, one may obtain a virtually infinite number of materials with various physicochemical and mechanical characteristics. Due to this unique composition, the structure of polyurethanes is quite different from that of other polymers.

In fact, PU elastomers usually show a two-phase structure in which hard segment-enriched domains are dispersed in a matrix of soft segments. The hard segment-enriched domains are composed mainly of the diisocyanate and the chain extender, while the soft segment matrix is composed of a sequence of macroglycol moieties. For this reason, polyurethanes are often referred as segmented block copolymers. This particular molecular architecture, as well as the intrinsic properties of each ingredient used for the synthesis of polyurethanes, explained the unique characteristics of this class of materials when compared to other polymers.

1.3.1. Polyurethane Structure

Polyurethane is the general name given to a family of synthetic copolymers that contain the urethane moiety in their chemical repeat structure. Since polyurethane was first synthesized in 1937 by Otto Bayer and co-workers, it has achieved a variety of applications including elastomers, foam, paint and adhesives. Such diversity of applications originates from the tailorable chemistry of polyurethanes, i.e., the chemical composition of polyurethanes can be tailored by choosing different raw materials and processing conditions to accommodate many specific requirements. As a family of
biomaterials, polyurethanes are most frequently synthesized as segmented block copolymers. In the following sections, we are going to focus on the basic chemical reactions, raw materials, and synthesis of segmented polyurethanes.

1.3.2. Raw Materials

Segmented polyurethane is composed of three important chemical entities namely: diisocyanates, polyol, and chain extenders (diamine or diol). The final properties of the polyurethane produced are largely dependent on the chemical and physical nature of these three building blocks.

1.3.2.1. Isocyanates

Isocyanates are highly reactive compounds and readily react with groups containing active hydrogen. This reaction is the most important for the formation of polyurethane elastomers. The chemistry of polyurethanes is therefore called as chemistry of isocyanates. Several aromatic and aliphatic isocyanates are available, but most of the commercial polyurethanes are based on two of them and they are 4,4’-methylenediphenyl diisocyanate (MDI) and hexamethylene diisocyanate (HMDI).

The high reactivity of isocyanate towards nucleophilic reagents is mainly due to pronounced electropositive character of the carbon atom caused by the delocalization of electrons onto oxygen, nitrogen and aromatic group. Aromatic isocyanates are therefore more reactive than aliphatic isocyanates, due to the negative charge delocalization. Substitution on the aromatic ring can affect delocalization of negative charge as in the case of aromatic isocyanates. Electron withdrawing groups at ortho or para position can increase the reactivity of the NCO group, while an electron donating group will have the
opposite effect on the reactivity of isocyanate. The electronic structure of isocyanate group can be represented by resonance structures as shown in the Figure 1.2.

![Figure 1.2: Resonance structures of isocyanate group.](image)

Polyurethanes obtained from aromatic diisocyanates undergo slow oxidation in the presence of air and light causing discoloration, which is unacceptable in some applications. In contrast, polyurethanes obtained from aliphatic diisocyanates are colour stable, although it is necessary to add antioxidants and UV stabilizers to the formulations to maintain physical properties of the polymers with time. Because of the ring structure of the diisocyanates and the strong intermolecular interactions such as hydrogen bonding among urethane groups, the segments that contain isocyanate and chain extender are more rigid and therefore called as hard segments. Table 1.1 lists some of them commonly used as isocyanates for polyurethane synthesis.

**Table 1.1: Isocyanates used for making polyurethanes.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’-methylene diphenyl diisocyanate (MDI)</td>
<td>OCN(\text{CH}_2\text{NCO})</td>
</tr>
<tr>
<td>1,6–hexamethylene diisocyanate (HMDI)</td>
<td>OCN(\text{CH}_2\text{NCO})</td>
</tr>
</tbody>
</table>
1.3.2.2. Polyols

The addition reaction of isocyanate with a polyol is an exothermic reaction which is influenced by the structure of both reactants. Aliphatic polyols with primary hydroxyl end groups are the most reactive. They react with isocyanates about ten times faster than similar polyols with secondary hydroxyl groups. Phenols react more slowly with the isocyanates and the resulting urethane groups are easily broken on heating to yield the starting materials. The addition reaction is strongly influenced by catalysts; e.g. acid compounds (mineral acid, acid halide etc.) which slow down the reaction, whereas the basic compounds (tertiary amines) and metal compounds (Sn, Zn, Fe salts) accelerate the reaction. The reaction pathway between polyol and the diisocyanate is presented in the Scheme 1.3.

\[
\begin{align*}
R-\text{OH} & \quad + \quad \text{OCN}-R' \\
\text{Hydroxy} & \quad \text{Isocyanate} \\
\text{Ka} & \quad \text{Kb} \\
\end{align*}
\]

Scheme 1.3: Reaction of isocyanate with polyol.

Generally, polyols are hydroxyl terminated macromolecules, with molecular weights ranging from 250 to 8000. The structure of polyol is an important factor that determining the properties of polyurethane. A wide range of polyols are used for the manufacture of polyurethanes. However, most of them fall under two classes: hydroxyl terminated polyethers and hydroxyl terminated polyesters. Important characteristics of polyols are their hydroxyl group functionality, hydroxyl equivalent weight and their reactivity and compatibility with the other components used in the polyurethane formulation. Blending of polyols of different functionality, molecular weight and
reactivity can be used to tailor a polyol for a specific application. Since primary hydroxyl groups are more reactive than secondary groups, it is advantageous to produce block copolymers with terminal primary hydroxyl groups.

Unlike diisocyanate compounds and chain extenders, a polyol is oligomeric with a molecular weight normally ranging from a few hundred to a few thousand. At room temperature, polyols can be liquid or solid depending on the molecular weight. Due to their aliphatic structure and low intermolecular interaction, polyol molecules can rotate and bend easily and are therefore soft materials. Consequently, the polyol sequence in segmented polyurethane is referred to as the soft segment (SS). New polyol materials including polyalkyl\textsuperscript{41,42} polydimethylsiloxane\textsuperscript{43} and polycarbonate\textsuperscript{44} have also been developed to fulfill the critical and specific requirements intrinsic to biomedical and industrial applications. The important polyols used commercially up to now in industries are tabulated in Table 1.2.

\textit{Table 1.2: The chemical structure of the low Tg polyols.}

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td><img src="image" alt="Structure of PEO" /></td>
</tr>
<tr>
<td>Polypropylene oxide (PPO)</td>
<td><img src="image" alt="Structure of PPO" /></td>
</tr>
<tr>
<td>Polytetramethylene oxide (PTMO)</td>
<td><img src="image" alt="Structure of PTMO" /></td>
</tr>
</tbody>
</table>
Although high Tg polyols seldom used and finds applications only in high performance polymer industries, nevertheless these high Tg polyols are very important compound used in several applications like military equipments, etc., The chemical structure of the high Tg polyols are presented in the Table 1.3.

*Table 1.3: The chemical structure of the high Tg polyols.*

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulphone</td>
<td><img src="image" alt="Polysulphone Structure" /></td>
</tr>
<tr>
<td>α, ω-Dihydroxy polystyrene</td>
<td><img src="image" alt="α, ω-Dihydroxy Polystyrene Structure" /></td>
</tr>
</tbody>
</table>

1.3.2.3 Chain Extenders (Amines or alcohols)

Reaction of diisocyanates with diamines is the most important reaction in polyurethane chemistry. The reaction of isocyanates with primary amines at room temperature in the absence of catalyst is about 100 to 1000 times faster than the reaction with primary alcohols. The reactivity of amines increases with the basicity of the amine. The aliphatic amines react much faster than aromatic amines. In the case of aromatic amines, steric hindrance and electron withdrawing substituents reduces the reactivity towards isocyanate. Tertiary amines, due to the absence of active hydrogen atoms, do not react with isocyanates. The scheme of reaction between the amine and isocyanate is presented in the Scheme 1.4.
Scheme 1.4: Reaction of isocyanate with amine.

Generally, diamine terminated chain extenders are low molecular weight compounds that play an important role in polymer morphology. The choice of chain extender and diisocyanate determines the characteristics of the hard segment and to a large extent the physical properties of polyurethane. Diamines react faster than dihydroxy with isocyanates and results in the formation of the hard segment with a high density of secondary bonding which leads to high thermal stability. Table 1.4 lists commonly used diamine chain extenders for polyurethane-urea synthesis.

Table 1.4: Chain extenders used for making polyurethane-urea.

<table>
<thead>
<tr>
<th>Chain extender</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene diamine</td>
<td><img src="structure1.png" alt="Structure" /></td>
</tr>
<tr>
<td>Butane diamine</td>
<td><img src="structure2.png" alt="Structure" /></td>
</tr>
<tr>
<td>Hexamethylene diamine</td>
<td><img src="structure3.png" alt="Structure" /></td>
</tr>
<tr>
<td>6T6</td>
<td><img src="structure4.png" alt="Structure" /></td>
</tr>
<tr>
<td>6A6</td>
<td><img src="structure5.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
1.3.3. Catalyst

The catalysis of the isocyanate-hydroxyl reaction has been studied by many authors\textsuperscript{45} who found out that the reaction of aliphatic isocyanates with hydroxyl groups can be catalyzed by many metal carboxylates and organo-tin compounds. The urethane formation reaction may be greatly influenced by the use of appropriate catalysts. The catalysts most widely used commercially in polyurethane processes are tertiary amines and organo-tin compounds. In the case of the amines, promotion of urethane links related to the strength of the base and the structure are also important\textsuperscript{46}. Some of the organo-metallic compounds used in the preparation of polyurethane is ferric acetyl acetonate and cobalt naphthenate will catalyse isocyanate reactions.

The most widely used tin based catalyst is Dibutyltin dilaurate (DBTDL) which possess remarkable activity. These catalysts will promote reactions of NCO with OH groups in preference to reaction with water. For this reason, DBTDL and tin octoate are widely used. They are readily soluble in the reaction mixtures and have the advantage of low volatility and little odour. The effect of catalyst on the synthesis of polyurethane prepolymer was investigated\textsuperscript{47} and it was found that this effect extends beyond simply increasing the reaction rate. The catalysts serve to promote the slower reactions more than the faster ones. This would imply that for the preparation of polyurethane prepolymers, a catalyst might serve to equalize the reaction rates between the first and he second isocyanate groups in a diisocyanate. In general, it seem that the tertiary amines favour NCO/OH, NCO/H\textsubscript{2}O combinations while organo-tin catalysts are most effective for the NCO/NH\textsubscript{2} reaction and for influencing urea and biuret linking. In practice, a mixture of tertiary amines and tin catalyst can be used so as to achieve the appropriate balance of chain extension and cross-linking.
1.4. STRUCTURE-PROPERTY RELATIONSHIP

The physical properties of polyurethanes can vary considerably depending upon the nature and amount of the three main components namely, polyol, diisocyanate and chain extender. The mechanical properties of polyurethane are strongly dependent on the extent of microphase separation and the details of domain structure of phase separated morphology.

1.4.1. Soft Segment (SS)

The long flexible soft segment largely controls the low temperature properties, weather resistance, solvent resistance and elastic properties. The structure and the molecular weight of soft segments also influence the morphology of polyurethanes. Typically, soft segments with average molecular weights of 2000 – 2500 are used for the synthesis of thermoplastic polyurethanes.

1.4.2. Polystyrene (PS)

In a plastics family, polystyrene is a high molecular weight, linear polymer that is commercialized on a very high volume worldwide and has a wide range of applications, which is the reason why it has been classified as commodity plastic (along with polyethylene, polypropylene, polyvinyl chloride, polymethyl methyl methacrylate, etc.). The most common form of commercial PS is atactic polystyrene (aPS), which is an important thermoplastic material due to its well-balanced physical properties, easiness of moulding, good dimensional stability and its transparency\textsuperscript{48,49}.

The polymer chain stiffening effect of the pendant phenyl groups gives it a relatively high glass-transition temperature ($T_g$) of about 100 °C, which translates into a
glassy polymer under ambient conditions and a viscous liquid above the $T_g$. It should be emphasized that, from a physical properties view point, in order to have optimal strength, the PS must have a weight-average molecular weight about ten times higher than its chain entanglement molecular weight.

PS having an Mw< 150,000 is generally too brittle to be useful and therefore for general-purpose moulding and extrusion grades, the PS sold commercially has Mw> 180,000 g/mol. This result in a high melts viscosity. An extensive compilation of physical properties of PS is given elsewhere$^{50,51}$. The relationship between Tg of the polymer to that of molecular weight of PS is presented in the Table 1.5. It was concluded that the Tg values depends upon the molecular weight.

Styrenic polymers offer wide variety of benefits in many industries including:

- Light weight, water resistant and excellent thermal insulation. Rigid, with a high strength-to-weight ratio that offers energy-savings benefits in transportation and an excellent cost performance.
- Can be shatterproof and transparent if required.
- Good electrical insulation.
- Easy to process and produce in a range of attractive colours.
- Easy to recycle.

Manufacturers use styrene-based resins to produce a wide variety of everyday goods ranging from computer to yoghurt cups. Extruded polystyrene is used in insulation, kitchen appliances, toys, consumer electronics, automobile parts, and durable lightweight packaging of all kinds. Styrene polymers are present in a variety of highly demanding applications. Their unique selling point is to combine cost efficiency, high
performance and easy processing and thus, make it the material of choice for use in electronic equipment, high-end domestic appliances and state of the art packaging.

Table 1.5: The effect of molecular weight on the Tg of polystyrene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw</th>
<th>Tg(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tg(^{1})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS 1</td>
<td>1940</td>
<td>56.8</td>
</tr>
<tr>
<td>PS 2</td>
<td>4380</td>
<td>76.2</td>
</tr>
<tr>
<td>PS 3</td>
<td>5480</td>
<td>77.0</td>
</tr>
<tr>
<td>PS 4</td>
<td>12600</td>
<td>89.6</td>
</tr>
<tr>
<td>PS 5</td>
<td>35100</td>
<td>100.2</td>
</tr>
<tr>
<td>PS 6</td>
<td>65000</td>
<td>100.6</td>
</tr>
<tr>
<td>PS 7</td>
<td>275000</td>
<td>103.5</td>
</tr>
<tr>
<td>PS 8</td>
<td>950000</td>
<td>103.9</td>
</tr>
</tbody>
</table>

*1 Onset Temperature of Tg, *2 Mid-Point Temperature of Tg,*3 End Temperature of Tg.

1.4.3. Hard Segment (HS)

The elastic properties of segmented polyurethane are resulted from the microphase separation between soft and hard segment sequences. HS sequences, which are formed by the isocyanate and the chain extender molecules, can be crystalline, semi crystalline or glassy. They form a crystalline phase dispersed in the continuous phase of the soft elastomeric segments. The HS micro domains act as thermally labile physical cross-link sites as well as fillers for the rubbery SS matrix. Considerable efforts have been made to elucidate the nature of hard segments in polyurethanes\(^{52-57}\).
1.5. THE CHEMICAL NATURE OF HYDROGEN BONDING

As mentioned earlier, many polyurethanes and polyureas have the potential to form hydrogen bonds. Hydrogen bonding is an attractive force between a lone pair of electrons of an electronegative atom (N, O, or F) and a hydrogen atom that is attached directly to an N, O, or F. When electronegative oxygen is hydrogen bonded to a single electronegative atom, this is termed monodentate hydrogen bonding. When electronegative oxygen is hydrogen bonded to two electronegative atoms, this is termed bidentate hydrogen bonding. Looking at the typical polyurethane and polyurea backbone structure, one can see that the potential for H-bonding exists between the hydrogen atom or proton of a urethane group and the oxygen atom of a carbonyl group or another nearby urethane linkage (Figure 1.3). Hydrogen bonding can also arise between the urethane (or urea) group and the ether or ester group of the SS.

\[ \text{monodentate} \quad \begin{array}{c}
R' \\
N \\
\bigg\downarrow \\
R \\
O \\
\bigg\uparrow \\
H
\end{array} \quad \text{bidentate} \quad \begin{array}{c}
R' \\
N \\
\bigg\downarrow \\
R \\
O \\
\bigg\uparrow \\
H
\end{array} \]

\begin{array}{c}
\text{Urethane linkage} \\
\begin{array}{c}
R' \\
N \\
\bigg\downarrow \\
R \\
O \\
\bigg\uparrow \\
H
\end{array}
\end{array} \quad \begin{array}{c}
\text{Urea linkage} \\
\begin{array}{c}
R' \\
N \\
\bigg\downarrow \\
R \\
O \\
\bigg\uparrow \\
H
\end{array}
\end{array}

Figure 1.3: Hydrogen bonding schemes for polyurethanes and polyureas.

The strength of the hydrogen bonding in polyurethanes and polyureas has a direct effect on the final properties of these materials. Bidentate hydrogen bonding is stronger than monodentate hydrogen bonding as determined by semi-empirical quantum mechanical calculations performed by Yilgör et al.\textsuperscript{57}. His calculations based on the
density functional theory show that urea-ether hydrogen bond interaction energy is 19.2 kJ/mol (and occur in pairs), as compared to the lower urethane–urethane 18.4 kJ/mol interaction energy. Urethane–ether or urea–ether (or the respective ester counterparts) hydrogen bonding interactions are also possible. The extent of hydrogen bonding can be affected by the structure and composition of polyurethane as well as by temperature. Hydrogen bonding starts disrupting with increase in temperature above the melting point of the hard segment.

High temperature infrared studies carried on aliphatic polyurethanes by McKiernan et al.\textsuperscript{58} showed the existence and high concentration (≈75\%) of hydrogen bonding in these polyurethanes presents even in the melt. Their study also shows that hydrogen bonding controls the crystallization, packing, and morphology of polyurethanes resulting in a crystal structure analogous to that of aliphatic polyamides. Influence of the hard segment length on thermal and thermo mechanical properties by Arun et al.\textsuperscript{59} showed that the melting temperature of the MDI-endcapped PTMO\textsubscript{2000} as well as the degree of crystallinity displayed a surprising by increase with increasing HS length, which was probably due to nucleation effects of the HS crystallites. It is expected that H-bonding would be possible even in the molten state thereby providing a network structure in the melt.

The primary force for microphase separation is believed due to be the strong intermolecular interaction (hydrogen bonding) between urethane units. Thus, qualitative information of phase separation can be extracted from hydrogen bonding between the two phases. If hydrogen bonds exist only within the hard segment domains, phase separation occurs to a greater extent. On the other hand, if they can be formed between the soft and hard segments, the interphase hydrogen bonding enhances the degree of phase mixing. The strength of hydrogen bonding polyureas is higher than polyurethane\textsuperscript{60-62}.
In order to investigate hydrogen bonding in these materials, Fourier transform infrared spectroscopy (FT-IR) is a very important tool and most frequently used technique because it can often quantify the size, extent and strength of hydrogen bonding in polyurethanes and polyureas as a function of backbone chemistry\textsuperscript{63-66}. The magnitude of the frequency shifts in the peak positions of the C=O stretching absorption region (1600–1800 cm\textsuperscript{-1}) and the N–H stretching absorption region (3200–3400 cm\textsuperscript{-1}) are most often monitored. Thermal transitions of PUs such as the SS $T_g$ have been monitored via hydrogen bonding by following the N–H absorption as a function of temperature.

Wang and Cooper\textsuperscript{67} studied the effect of urea linkage, hard segment content, and block length on the extent of phase separation, domain structure and physical properties. It was observed that the presence of three dimensional hydrogen bonding between the urea groups leads to unusually strong hard domain cohesion. That is, single urea N-H group is bonded to two urea C=O in a non-planar three dimensional configuration. The FT-IR technique has been used to track the real-time development of hydrogen bonding by monitoring the shift in the urethane carbonyl group’s absorption to lower wave numbers upon hydrogen bonding\textsuperscript{68-77}. Hydrogen bonding has also been monitored during the heating and cooling of polyureas and polyurethane-urea’s.

For example, Ning and coworker\textsuperscript{74} showed that the strength and degree of monodentate hydrogen bonding in polyurethanes decreases with increasing temperature. Polyurethane-ureas do not display a large drop in storage modulus with increasing temperature as the bidentate bonding in these materials is stronger than monodentate bonding found in polyurethanes. As a result, the value of storage modulus often remains high until the material thermally degrades\textsuperscript{78}. A great deal of information is available in literature about the effect of hydrogen bonding in polyurethanes, polyureas and polyurethane -ureas\textsuperscript{79-81}. 
1.6. REVIEW OF LITERATURE

1.6.1. Based on PUU copolymer

Estes and co-workers\textsuperscript{82} were the first to propose a two phase model for polyurethane morphology with semi continuous and interpenetrating domains. Lamellar morphologies have been reported in PUs based on the TEM observations. Chi Li and co-workers\textsuperscript{83} studied the morphology of polybutadine-polyurethanes containing a wide range of hard segment content (MDI-BDO). It was observed that polyurethanes containing low hard segment content showed dispersed, short, hard segment cylinders embedded in a matrix of polybutadine soft segments.

Versteegen et al.\textsuperscript{84} have observed long stacks of hard blocks embedded in soft phase in the segmented copoly(ether urea)s having uniform hard segments. Das et al.\textsuperscript{85} studied structure-property relationship of segmented, non-chain extended polyureas. AFM imaging on these polyureas shows the presence of microphase separated structure, with thread like hard segments randomly dispersed throughout the soft segment matrix.

Revenko et al.\textsuperscript{86} studied heterophase morphology of polyurethanes containing aliphatic soft segments (HS content 30 wt \%) using tapping mode AFM. Authors have observed rod like hard domains of about 50 nm length dispersed in the soft segment matrix. Christenson et al.\textsuperscript{87} have also reported a similar morphology in polycarbonate polyurethanes. Hard segment domains were found to be cylindrical having 5-10 nm in width and 40-100 nm in length.

Hernandez et al.\textsuperscript{88} recently studied phase organization in a series of segmented polyurethanes having different soft segment. Three series of polyurethanes synthesized in this study had soft segments composed of either an aliphatic polycarbonate, polytetramethyleneoxide, or a mixed macrodiol of polyhexamethyleneoxide (PHMO)
and hydroxyl terminated PDMS. The hard segment used in this study are MDI and 1,4-butanediol. The morphological analysis demonstrates the presence of three phase core-shell morphology in PHMO/PDMS based copolymers, while in other two copolymers demonstrated two phase microstructure.

Klinedinst et al\textsuperscript{89} studied structure-property relationships of novel polyurethane and polyurea segmented copolymers and the influence of solution casting variables on the solid state structure of synthetic polypeptide films based on glutamate chemistry. The softness of the sample at the AFM imaging temperature certainly contributed to the lack of stiffness contrast for this image. AFM phase images of several polyurethane samples displaying different levels of microphase separation as shown in Figure 1.4.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{afm_images.png}
\caption{AFM phase images of several polyurethane samples displaying different levels of microphase separation: (A) pPDI–U; (B) MDI–U; (C) HDI–U; (D) CHDI–U.}
\end{figure}
Ranimol Stephen et al\textsuperscript{90} synthesized and analyzed the melt and solution polymerization of the segmented block copolymers based on polysulphone with mono dispersed amide segments. The high Tg amorphous polysulphone could be modified to a high Tg semi-crystalline PSU-T6T6T copolymer. This copolymer had a high dimensional and solvent resistance.

Vipin P.Joshi\textsuperscript{91} studied the synthesis and characterization of thermoplastic poly(urethane-urea) copolymers and consequently study the effect of controlled introduction of defects in the hard segments on the phase morphology and the ultimate properties of PUUs. The defect moieties that he has studied in this work are diarnines having long aliphatic side chains, which form short branches on the hard segments of a PU molecule.

1.6.2. PU containing amide bonds

Segmented polyurethanes based on polyamide (TPE-A) as a hard segments is the newer developments in TPE’s. A wide variety of aliphatic and aromatic amides can be used and so a wide range of property variations are available. Thermoplastic elastomers based on amides (TPE-A’s) are chemically solvent resistant than the thermoplastic elastomers based on ester linkage (TPE-E’s).

R.J.Gaymans et al\textsuperscript{92-95}, group in their paper explained the synthesis of block copolymers based on various amide segments and soft segments like poly(tetra methylene oxide) (PTMO), polyethylene oxide (PEO), etc., Niesten et al\textsuperscript{96,97} in his paper studied the synthesize, mechanical and elastic properties of the block copolymer.

Arun et al\textsuperscript{98,99} studied the synthesis, mechanical, elastic, and rheological properties of polyurethane tri-block copolymers. He also studied the influence of the
hard segment length on thermal and thermo mechanical properties. He showed that increasing the number of amide bonds in the mono-disperse hard segment increased the modulus and the hard segment melting temperature and decreased the compression set values. The low temperature properties were hardly affected by the amide length.

Edwin Biemond et al\textsuperscript{96} did similar studies on hydrogen bonding in segmented polyamides. All these studies showed that hard segments of uniform length crystallize faster and better than hard segments of non-uniform length. If the crystallized hard segments are poorly miscible i.e (phase separated in the solid) with the amorphous soft segments, hardly any hard segments will be present in the amorphous phase, resulting in a low glass transition temperature (Tg) and high melting temperature (Tm).

1.7. RESEARCH AIM

Polyurethane elastomers are industrially important polymeric materials because of their wide range of applications, and their properties, which can be controlled by changing the starting materials, preparation conditions and so on. Thermoplastic polyurethanes (PU) and their analogue polyurethane-ureas (PUU) are (AB)n type block copolymers consisting of sequences of hard and soft segments. Thermodynamic incompatibility between hard and soft segments, and/or crystallinity in the hard segment drives them to phase separate. However, phase separation is limited at the segmental level due to connectivity of the blocks. The primary driving force for domain formation is the intermolecular interactions between urethane / urea units which are capable of forming hydrogen bonds. The incorporation of urea linkages in PU hard segment has a profound effect on the phase separation and microphase morphology.
In this thesis, the synthesis and structure-property relationships of segmented block copolymers based on α,ω-dihydroxy polystyrene as amorphous segment and diisocyanate along with diamine as crystallizable segment is discussed. The main goal of this project is to synthesize dihydroxy terminated low molecular weight polystyrene and to modify the amorphous polystyrene to a semi-crystalline copolymer using crystallizable hard segments based on hexamethylene diisocyanate (HMDI) or 4-4’-methyldiphenyldiisocyanate (MDI) along with chain extenders 1,2-ethylenediamine (EDA) or 1,4-butanediamine (BDA) or 1,6-hexamethylene diamine (HMDA) or diamine-diamide (6A6 or 6T6). Polystyrene is known for its amorphous nature, but synthesized segmented block copolymer is expected to possess semi-crystallinity.

In the present work, we synthesis and characterize of poly(urethane-urea) and poly(urethane-urea-amide) by using two different diisocyanates and different chain extenders. The effect of type of hard segment and the concentration of hard segment on thermal and crystallization properties of these copolymers is studied. The crystallization properties are related to the morphology of the copolymers. Additionally, the factors that influence the crystallinity of the copolymers, such as the nature, the concentration and the length of the crystallizable segment are also investigated. Other parameters studied are the solvent resistivity and the swelling properties of the synthesized PUU and PUUA. The relationship between the solvent resistances to that of type of hard segment in the PU is investigated in detail.

1.8. OUTLINE OF THIS THESIS

Chapter 1 of this thesis describes the overall review about the polyurethane synthesis characterization and their morphologies.
Chapter 2 discusses in detail about the synthesis and characterization of functionalized polystyrene using Atom Transfer Radical Polymerization (ATRP) method with strong base techniques. This technique is used to prepare the low molecular weight polymers with desired functionality. This polymer shows poor solvent resistivity.

Chapter 3 describes the synthesis and characterization of different types of uniform amide units such as 6A6 and 6T6, which are used as crystallizable hard segments in the copolymers. The diamide-diamine units are synthesized in one step to ensure the uniformity. It act as a hard segment for improving the crystallization thereby increase the solvent resistivity.

Chapter 4 describes the synthesis and characterization of poly(urethane-urea) based on functionalized polystyrene using HMDI and various diamine EDA, BDA and HMDA. The effect of diamine extender such as EDA, BDA and HMDA on the properties of polyurethane-urea is discussed in detail. Also, the effect of HS structure and length of chain extender on the properties of the resulting polyurethanes are studied.

Chapter 5 describes the synthesis and characterization of poly (urethane-urea-amide) based on HMDI from functionalized polystyrene using different diamide-diamine segments (6T6 and 6A6). The properties of the segmented block copolymers can be improved by using uniform rigid segments.

Chapter 6 describes the synthesis and characterization of poly(urethane-urea) based on symmetrical aromatic isocyanates MDI and functionalized polystyrene. Different diamine extenders used are EDA, BDA and HMDA. The properties of the synthesized polyurethane-urea are studied in detail.
Chapter 7 describes the synthesis and characterization of poly(urethane-urea-amide) based on MDI, functionalized polystyrene and two different diamide-diamine segments (6T6 and 6A6). The properties of the synthesized segmented block copolymers are studied in detail and special attention is given to solvent resistivity.

Finally, Chapter 8 draws some important conclusions on PUU/As.
REFERENCES


