2. LITERATURE REVIEW

Thermoplastic polyurethanes (TPU) are a subcategory of copolymers called *thermoplastic* elastomers (TPE). They were one of the first segmented copolymers to be made commercially available. In the United States, TPUs were marketed for the first time in the 1960s by Goodrich, Mobay and Upjohn under the trade names Estane®, Texin®, and Pellethane® respectively. Other widely used TPEs include tri-block copolymers based on polystyrene and polyisoprene (or polybutadiene) blocks, and segmented copolymers such as poly(etherester)s, poly(ether-block-amide)s, etc. As noted earlier, their ability to develop a microphase separated morphology and the consequent association of the hard blocks or segments into hard domains is one of the most characteristic features of this category of copolymers.

The remarkable physical behavior of TPUs immediately attracted academic and industrial interest after their commercialization in the 1960s. While investigating the morphology of a linear segmented ester-based TPU, Schollenberger *et al.* [1,2] demonstrated that it exhibited high extensibility and elasticity in an unvulcanized form. Such a behavior they noted was due to the presence of virtual (physical) cross-links that were made-up of hard segments (HS). These physical cross-links allowed TPUs to behave as TPEs, as opposed to covalently cross-linked elastomers, such as from vulcanized natural rubber, which cannot be thermally reprocessed. It is generally accepted that Schollenberger *et al.* were the first to introduce the concept of virtual cross-links. In a later study, from the laboratory of A. Tobolsky [3], it was shown that the enhanced width of the relatively temperature insensitive storage modulus of a polyester-based TPU possessed similarities to that displayed by styrene-butadiene-styrene (S-B-S) tri-block copolymers. The segregation of the constituent HS from the soft segments (SS) and the consequent formation of physical cross-link sites made-up of the HS were offered as an explanation for the observed behavior in both the systems. They further pointed out that since the polystyrene blocks are unable to form hydrogen bonds like their polyurethane counterparts, hydrogen bonding was not essential to achieve an improved rubbery plateau behavior when compared with respect to the width of the service window. Thus, Tobolsky *et al.* [3] were one of the first to explicitly recognize the importance of
As stated earlier, one of the central objectives of this dissertation is to investigate the role played by hydrogen bonding, over and above microphase separation, in influencing the structure/property-processing of segmented copolymers. In the following discussion, some general but important aspects of block copolymers are briefly addressed first. A more focused review of the chemistry and structure-property behavior of segmented polyurethane copolymers follows thereafter.

2.1 BLOCK COPOLYMERS

Helfand and Wasserman [4] state that, “Like a child contemplating the results of tying the cat’s tail to that of the dog, scientists perhaps find a certain mischievous delight in considering the effect of joining two immiscible polymer blocks into one macromolecule.” Thanks to such curiosity, scientists have been able to push the ‘applications envelope’ of block polymers. Thus, besides their current widespread use as thermoplastic elastomers, based on today’s research it would be safe to say that in the near future block copolymers will strongly contribute to the next generation of devices having applications in electronics (e.g. for data storage) to those in biotechnology (e.g. controlled drug delivery) [5]. Examples of common AB block copolymer architectures are illustrated in Fig. 2.1.

![Block Copolymer Architectures](image)

**Figure 2.1** Various diblock copolymer architectures [adapted from Ref. 6].
Living anionic polymerization, step-growth polymerization, *etc.* have been used to produce block copolymers and the former has been successfully utilized commercially to produce well-defined (MWD < 1.1) block copolymer architectures. Moreover, theoretical development has been mostly restricted to amorphous monodisperse diblock copolymers [4,7,8] although limited development of the theoretical aspects of multi-block copolymers and also theories that take into account the polydispersity of the blocks can be found in the literature [9-13]. Meier [7] was perhaps the first to have identified the important elements of a statistical thermodynamic theory of linear block copolymers. More recently, a theory for the prediction of the phase diagrams of non-linear block copolymers (having a star architecture) has been also developed [14].

For high MW polymers, the entropy of mixing per unit volume is low. In fact, in the limit of infinite MW, the entropy of mixing is zero. Thus, in the case of a symmetric diblock copolymer (volume fraction of a block, \( f = 0.5 \)) in the disordered or mixed state, when \( N \), the overall degree of polymerization is sufficiently large, a reduction in temperature (equivalent to increasing \( \chi \); see eqn. 1 and wherein \( A \) and \( B > 0 \) are constants) gives rise to excess free energy, which is minimized by the local compositional ordering or segregation of the constituent blocks.

\[
\chi = A + \frac{B}{T} \tag{1}
\]

Such *microphase separation* is also commonly referred to as the *order disorder transition* (ODT). As noted earlier, the ODT in the case of diblock copolymers without any specific interactions is governed by the parameter \( \chi N \). Thus, the ODT in such systems can be crossed, to achieve microphase separation, either by decreasing the temperature (and therefore increasing \( \chi \)) at a constant \( N \) or by increasing \( N \) with \( \chi \) being held constant. It may be noted that \( \chi \) is also dependent on thermodynamic changes, such as crystallization, in addition to temperature. As expected, microphase separation is achieved at the expense of some loss in translational and configurational entropy of the chains [15]. The ordered and disordered states of a diblock copolymer are schematically illustrated in Fig. 2.2.

The early theories established \( f \) and the product \( \chi N \) as important parameters in describing the ODT for diblock copolymers having no specific interactions. It may be noted that in these theories the temperature dependence of \( \chi \) was defined by eq. (1). The narrow
interphase approximation based self-consistent theory by Helfand et al. [4,16] and the random phase approximation based theory by Leibler [8] are two of the most important theoretical treatments of block copolymers. The former theory, as the name suggests, is based on the assumption that the interface between domains is narrow compared to the domain size. The highlights of this theory are (1) the desire to reduce the domain surface-to-volume ratio results in reducing the interfacial free energy thereby promoting domain growth, (2) the localization of the joint between blocks at the domain matrix boundary opposes domain growth, thus preventing significant excursions of one block into a region occupied by the other, and (3) there is a loss of conformational entropy near the phase boundary due to the overwhelming drive to maintain a constant density throughout the condensed system. This prevents further domain growth. Leibler’s random phase approximation based theory describes the behavior of amorphous diblock copolymers near the ODT, where the blocks are weakly segregated \( \chi N < 10 \). The free energy of the copolymer near the ODT is modeled on the basis of the Landau-Ginzburg theory and the monomer density functions in a disordered phase are based on the generalization of the ‘random phase approximation’ method developed by de Gennes. Leibler’s theory is able to predict the domain symmetry, the range of density fluctuations of maximum growth, the phase diagram at the ODT and the transitions between the mesophases.

![Schematic representation of order and disorder in a symmetric monodisperse diblock copolymer. Lamellar morphology is shown in the ordered state [15].](image)

However, the above two theories cannot explain the entire structure and dynamics of a diblock copolymer system. Thus, researchers have attempted to explain their experimental results in different regimes (strong versus weak segregation limit) by utilizing the appropriate
one of the above noted two theories. Transmission electron microscopy, small angle x-ray, and neutron scattering have been widely utilized by investigators to verify various aspects of these theories [6,17-21]. Currently atomic force microscopy, a surface technique, is also being increasing utilized [22].

The experimentally determined phase diagram for a polystyrene (PS)-polyisoprene (PI) diblock copolymer in the parameter space of $\chi N$ and $f$ is presented in Fig. 2.3.

![Phase diagram for polystyrene-polyisoprene diblock copolymer.](image)

Figure 2.3 Phase diagram for polystyrene-polyisoprene diblock copolymer. The mean-field theory prediction of the ODT is represented by the dash-dot curve [23].

Identified in this figure are five experimentally observed microphase structures of a PS-PI diblock copolymer, which occur above the ODT and at different values of the PI volume fraction, $f_{PI}$. When $f_{PI}$ is ca. 0.2, it packs into spherical microdomains in a matrix of PS. At higher PI contents cylindrical morphology of the PI microdomains is observed. Also shown in Fig. 2.3 are narrow regions above the ODT where the bicontinuous (or gyroid) and perforated layer morphologies are noted. For nearly symmetric diblocks ($f = 0.5$), the
lamellar morphology is the stable structure. For a diblock copolymer with \( f = 0.5 \), the mean field theory [8] predicts the ODT at a critical \( \chi_N = 10.5 \). Lodge and Muthukumar [24] note that under equivalent conditions, if the two blocks were simply blended together instead of being covalently linked to form a diblock copolymer, the critical \( \chi_N \) would be ca. 2, as was first shown by Flory [25]. It may be noted that the self-consistent field theory, developed by Matsen and coworkers [12, Refs. in 6], unifies the separate theories developed for the strong and weak segregation limits. It can be used to predict chain conformation, composition profiles, and equilibrium phase behavior. This theory is also based on mean-field assumptions.

While \( \chi_N \) is also an important parameter governing the ODT in segmented copolymers, rigorous application of the theories noted above is difficult in copolymers, such as polyurethanes and poly(ether-block-amide)s, due to the presence of strong secondary interactions (e.g. hydrogen bonding) [26,27]. Furthermore, possible crystallizability of the hard and/or the soft segments, which also affects the extent of microphase separation, also prevents direct application of theories developed for amorphous A-B diblock copolymers. The inherent polydispersity of these segmented copolymers (ca. 2) produced via step-growth polymerization, the greatly increased number of junction points (or covalent links) between the soft and the hard segments in segmented copolymer as compared to those in block copolymers of comparable overall MW, and the considerable variation of \( \chi \) along the segmented copolymer chain are some of the other factors that make the development of a rigorous theoretical treatment difficult. The research presented in the subsequent chapters clearly demonstrates that microphase separation in segmented copolymers is also influenced by backbone symmetry and chain architecture. The issue of microphase separation in polyurethanes (PU) and some common factors that influence such behavior are discussed in Section 2.2.1, after a brief review of PU chemistry.

2.2 POLYURETHANES

2.2.1 Chemistry
Otto Bayer and his coworkers at I. G. Farbenindustrie (now Bayer AG) developed PU chemistry in the late 1930s as a competitive response to the synthetic polyamide fibers
developed by DuPont [28]. While the initial commercial product had poor properties, it was soon realized that PUs with good elastomeric characteristics could be synthesized simply by reacting a linear diol terminated polyester with α,ω-diisocyanate and water. End-capping of the polyester with isocyanate in the first step and chain extension with water to generate urea linkages between the hard and soft segments was offered as a possible reaction scheme. It was later recognized that a diol-terminated polyether could be used instead of a polyester and water could be replaced by a low molecular weight diol or diamine as a CE. In the late 1950s DuPont introduced spandex fibers (PUs with greater than 80 % elastomer component) under the trade name Fiber K (now Lycra®). This material was based on diphenylmethane-4,4’-diisocyanate, a macrodiol as the soft segment (SS) component, and a diamine as the chain extender (CE). Urethane linkages connected the hard to the soft segments and urea linkages existed within the hard segments (HS). It may be noted that due to the strong hydrogen bonding within the urea HS of spandex materials, they are not thermoplastic in the true sense of the word since the degradation temperature of the urea linkages is lower than the HS’s softening point. Later research demonstrated that TPUs resulted when the urea linkages were eliminated, by replacing the diamine CE with a diol; 1,4-butane diol is commonly utilized. As noted earlier, TPUs were commercially introduced in the early 1960s [28-30].

In general, any group containing active hydrogens can react with an isocyanate [30-32]. Three of the most commonly utilized isocyanate reactions in PU chemistry are presented in Scheme 2.1 (a & b). Reactions (a) and (b) result in urethane and urea linkages respectively between the soft and the hard segments. On the other hand, the evolution of CO₂ upon the decomposition of the unstable carbamic acid in reaction (c) is advantageously utilized to generate flexible polyurethaneurea foams with urethane and urea linkages based HS. The flexible polyurethaneurea foams are also commonly referred to as ‘polyurethane’ foams. Reaction of the isocyanate with active hydrogens on the urethane or urea groups is also possible and it gives rise to branching or cross-linking, as presented below in Scheme 2.2 (a & b). During the synthesis of linear PUs, these side reactions are minimized by controlling the order of addition of precursors and proper choice of temperature and catalyst [31]. A variety of diisocyanates, oligomeric diols or diamines as the soft component, and diols or diamines as CE can be used to make segmented copolymers based on the isocyanate
chemistry described above. The chemical structures of some of these precursors are presented in Table 2.1 (on page 15).

\[
\begin{align*}
R-N=C=O + R'-OH & \rightarrow R-N-C-O-R' \quad (a) \\
& \text{Urethane linkage} \\
R-N=C=O + R''-NH_2 & \rightarrow R-N-C-N-R'' \quad (b) \\
& \text{Urea linkage} \\
R-N=C=O + H_2O & \rightarrow R-N-C-OH \quad (c) \\
& \text{Carbamic Acid} \\
\end{align*}
\]

Scheme 2.1

\[
\begin{align*}
R-N=C=O + R-N-C-O-R' & \rightarrow R-N-C-O-R' \quad (a) \\
& \text{alophanate linkage} \\
R-N=C=O + R-N-C-N-R'' & \rightarrow R-N-C-N-R'' \quad (b) \\
& \text{biuret linkage} \\
\end{align*}
\]

Scheme 2.2
Table 2.1 Chemical structure of various precursors utilized in PU chemistry [30-32].

<table>
<thead>
<tr>
<th>Soft Segments</th>
<th>Polyethers</th>
<th>Polyesters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PTMO</td>
<td>PCL</td>
</tr>
<tr>
<td></td>
<td>PEO</td>
<td>Polysiloxane</td>
</tr>
<tr>
<td></td>
<td>PPO</td>
<td>PDMS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diisocyanates</th>
<th>Aliphatic</th>
<th>Aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HMDI</td>
<td>MDI</td>
</tr>
<tr>
<td></td>
<td>HDI</td>
<td>TDI</td>
</tr>
<tr>
<td></td>
<td>CHDI</td>
<td>pPDI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mPDI</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chain Extenders</th>
<th>Diol</th>
<th>Diamine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BD or BDO</td>
<td>EDA</td>
</tr>
</tbody>
</table>

Note: Soft segments and chain extenders presented above could also be diamine terminated. In such case, polyurethaneureas or polyureas (see below) are produced.

The most commonly utilized SS components are either diol or diamine terminated polyesters and polyethers. Other compounds, such as polydimethylsiloxane (PDMS) are also
utilized. Polyester s generally exhibit better oil resistance and strength but possess inferior hydrolytic stability than polyethers. Polyethylene oxide (PEO), polypropylene oxide (PPO), polytetramethylene oxide (PTMO), and random copolymers of ethylene oxide and propylene oxide, are some of the most commonly used polyethers. PEO has two primary hydroxyl groups and it is hygroscopic in nature. PPO on the other hand has one primary and one secondary hydroxyl group. Thus the reactivities of PEO and PPO are different. Moreover, the hygroscopic nature of the former limits its use in many applications. PPO is hydrophobic and the atacticity of commercially available PPO prevents it from packing into a crystalline lattice. Such a feature can be advantageously utilized in applications requiring elastomeric response at lower temperatures than possible with many other polyether or polyester diols. PTMO of MW > ca. 1500 g/mol, can also strain induce crystallize at ambient temperature. PDMS has some very unique characteristics because of the nature of the Si-O bond in its repeat unit. The discussion in Chapter 4 on PDMS based segmented polyurethanes and polyureas addresses the advantages and disadvantages of PDMS in greater detail. As noted earlier, the $T_g$ or $T_m$ of the SS governs the lower temperature limit of the service window of a segmented thermoplastic elastomer.

The diisocyanates utilized in PU chemistry can be either aliphatic or aromatic. Linear aliphatic diisocyanates, such as hexamethylene diisocyanate (HDI), hydrogenated diphenylmethane diisocyanate (HMDI), etc. or cycloaliphatic diisocyanates, such as cyclohexyl diisocyanate (CHDI) are more UV stable than their aromatic counterparts, such as diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), para-phenylene diisocyanate (pPDI), meta-phenylene diisocyanate (mPDI), etc. Those diisocyanates that have a symmetric structure, such as HDI, HMDI, CHDI, pPDI, MDI, etc. can, under appropriate conditions, crystallize and this generally results in more cohesive hard domains. The aromatic diisocyanates are generally more reactive (due to the resonance stabilization of the phenyl ring) than aliphatic diisocyanates. Thus in some cases a catalyst, whose use may give rise to undesired side reactions, can be completely avoided. The diisocyanate and the CE govern the nature of the HS. Ethylenediamine (EDA) and 1,4-butanediol (BD) are two of the most commonly used CE. They generate urea and urethane linkages respectively between the isocyanate end-capped SS (prepolymer) and the HS [30-32].
Segmented PUs can be polymerized via a one-step reaction or a two-step ‘prepolymer’ method. A schematic representation of the latter is presented in Scheme 2.3. When the diol CE is replaced by a diamine, the resulting linear segmented copolymers are called polyurethaneureas (eg. spandex). Polyureas are synthesized when both the diol terminated oligomer and the chain extender are replaced by diamine-terminated species.

\[
\text{HO-} - \text{OCN-R-NCO} + \text{OCN-R'-NCO} \rightarrow \text{OCN-R'}-\text{OCN-R-NCO}
\]

\[
\text{OCN-R'}-\text{OCN-R-NCO} + \text{OCN-R-NCO} + \text{HO-R'-OH} \rightarrow \text{linear segmented polyurethane}
\]

**Scheme 2.3**

A theoretical treatment on the effect of one- versus two-stage polymerization on the HS length distribution in multi-block copolymers was developed by Peebles [33,34] he showed that a narrower distribution of the HS lengths resulted when a two-stage polymerization was utilized instead of the one-stage procedure. Later, the effect of one- versus two-stage polymerization on the morphology and properties of polyether (PTMO) or polyester (polytetramethylene adipate) based segmented polyurethanes with MDI-BD HS was investigated by Abouzahr and Wilkes [35]. They found that the polyester based PU polymerized by the one-stage process exhibited slightly poorer physical properties (eg. lower extension at break, enhanced stress relaxation, mechanical hysteresis, etc.) than their two-stage counterparts. A greater hard-soft segmental mixing in the former, owing to their greater HS length distribution, was proposed as the reason for such behavior. The aforementioned mechanical properties of polyether based PU were not as sensitive to the type of polymerization process due to the lower inherent interaction between the polyether SS and the urethane HS as compared to that between polyester SS and the urethane HS (see below).
2.2.2 Microphase Separation in Polyurethanes

Due to reasons noted previously, the development of a theory that describes the microphase separation behavior in segmented PUs is extremely limited and is mostly semi-empirical in nature; the studies by Camberlin and Pascault [26,27] being the most noteworthy. The authors utilized four PUs with the same HS (BD extended MDI; HS content ca. 30 wt %) but different SS. They estimated the solubility parameter, $\delta$, of the pure HS from group contributions [36] and thereby calculated the Flory-Huggins interaction parameter, $\chi$, of the four PUs; the values of the SS $\delta$ were taken from literature. The values of $\chi$ were then related to the percent segregation of the soft phase from the hard phase. The ratio $\Delta C_{P2}/\Delta C_{P1}$, where $\Delta C_{P1}$ is the heat capacity change per gram of the pure SS oligomer and $\Delta C_{P2}$ the heat capacity change per gram of the SS in the PU, was utilized as a measure of the degree of microphase separation of the soft from the hard phase. Note that both $\Delta C_{P2}$ and $\Delta C_{P1}$ are determined via differential scanning calorimetry. In the case of no microphase segregation, $\Delta C_{P2}$ equals $\Delta C_{P1}$ and the ratio $\Delta C_{P2}/\Delta C_{P1}$ becomes unity. When the percent microphase separation was plotted against $\chi$ of a given PU, a straight line resulted. A linear extrapolation to 50 % microphase separation gave a critical interaction parameter $\chi_c$ value of 2.7. For comparison, it may be recalled that the mean field theory of Leibler [8] predicts the value of $\chi_c$ to be 10.5 in the case of an amorphous, monodisperse diblock copolymer having no strong secondary interactions. No correlation between $\chi_c$ and the equilibrium degree of microphase separation was noted by the authors. The utilization of $\Delta C_{P2}/\Delta C_{P1}$ as a measure of the degree of microphase separation is open to discussion. However, to this author’s knowledge, the above study was the first attempt to relate the phenomenon of microphase separation in segmented PU to the thermodynamic quantity, $\chi$ of these copolymers.

Over the years various investigators have reported the effect of chemical or process variables on the level of microphase separation in PUs. Many of these studies are summarized in excellent review chapters in various handbooks [28-32,37,38]. In the following discussion only a few representative studies of the effect of chemical variables on the level of microphase separation in polyether or polyester based PUs are brought to the reader’s attention. For example, polyether or polyester based PU with semicrystalline HS (based on the symmetric 2,6 TDI) were reported by Schneider and Sung [39] to exhibit a
higher degree of microphase separation than the corresponding PU with amorphous HS (based on the asymmetric 2,4 TDI). The microphase separation in a series of commercially available polyether or polyester based PU (Estane® from B. F. Goodrich, Vibrathane® from Uniroyal Chemical, and Rucothane® from Hooker Chemical) was investigated by Lilaonitkul and Cooper [40]. Using various characterization tools they were able to determine that increasing the HS content (equivalent to increasing the HS length; if the SS MW is held constant) or SS MW (equivalent to decreasing the HS content) led to an increase in the extent of microphase separation. In another study on polyether or polyester based polyurethaneureas, Takahara et al. [41] also observed an improvement in the extent of microphase separation with increasing the SS MW. Such behavior was further assisted if the constituent SS could crystallize, just as crystallizable HS promoted greater microphase separation.

While many studies have addressed the influence of SS MW on the extent of microphase separation, Schollenberger and Dinbergs [42] studied the effect of increasing the overall MW of the segmented copolymer on the mechanical properties of BD extended MDI HS and polyester SS based PUs. In this study, the overall HS content was maintained constant at 20 wt %. They found that the tensile strength and elongation at break increased with increasing MW. Other properties such hysteresis, stress relaxation, and permanent set decreased with increasing overall copolymer MW. However, the increase (or decrease) in these properties reached a plateau value in the range of $<M_w>$ 100,000 to 200,000. Such behavior, the investigators suggested, was primarily due to the unresponsiveness of the physical cross-linked network and no further reduction in the free volume (by the decrease in the concentration of free chain ends) with an increase in chain MW beyond a certain point, which they called the ‘inflection’ MW. It is noted that an increase in the number of chain entanglements and the relaxation times with increasing overall MW of the copolymer also lead to improvement in ultimate tensile properties. Hydrogen bonding, which also affects the extent of microphase separation in segmented PUs, is discussed in the next section.

The influence of temperature on the microphase separation behavior of a commercial PU (Rucothane® – a polyester based PU with MDI-BD HS) was first investigated by Wilkes et al. [43]. They demonstrated that a breakdown in the microphase separated morphology could be achieved by raising the temperature above the ODT temperature. An unstable
morphology consisting of segregated HS associated into domains resulted when the temperature was lowered below the ODT temperature. Such an unstable morphology matured with time as indicated by the increase in the Young’s modulus ($E$) of the copolymer or decrease in the SS $T_g$. For the particular segmented PU investigated, at ambient temperature, both $E$ and SS $T_g$ began to reach a plateau after ca. 3-5 hours. Thereafter, $E$ and SS $T_g$ increased slightly for a period of ca. 2 weeks, beyond which time no further changes were noted. The reversibility of the microphase separated morphology was illustrated by the authors via a simplified schematic which is reproduced in Fig. 2.4. In this figure the labels A, B, C, D, and E indicate partially extended SS, HS microdomain, coiled or ‘relaxed’ SS, and HS microdomain with lower order (as compared to B) respectively.

![Simplified schematic model depicting the morphology of a segmented PU (a) long time; (b) following heat treatment above ODT](image)

**Figure 2.4** Simplified schematic model depicting the morphology of a segmented PU (a) long time; (b) following heat treatment above ODT [43].

Subsequent to the above study, the same research group [44,45] also demonstrated the time-dependent behavior in other PU (e.g. based on polyester or polyether SS). In these studies, the development of microphase separation with time was followed by small angle x-ray scattering (SAXS), which confirmed the earlier observations made dynamic mechanical analysis (DMA). Other research groups [46,47] have also confirmed the above noted behavior in segmented PUs.

### 2.2.3 Hydrogen Bonding in Polyurethanes

Fourier transform infrared spectroscopy (FT-IR) is perhaps the most important tool utilized by various research groups [48-55] to investigate hydrogen bonding in PUs. The C=O stretching absorption region ($ca.1600-1800 \text{ cm}^{-1}$) and the N-H stretching absorption region
(ca. 3200-3400 cm$^{-1}$) are generally monitored. Hydrogen bonding has been utilized to quantify the extent of microphase separation [49,50] in PUs as a function of backbone chemistry/composition. Thermal transitions (e.g. SS $T_g$) of PUs have been related to hydrogen bonding by following the latter as a function of temperature [52,53]. Various aspects of hydrogen bonding that are pertinent to the present discussion are now addressed.

Based on the ‘three dimensional’ solubility parameter theory proposed of Hansen [56], hydrogen bonding ($\delta_h$) is one of three forces that may contribute to the solubility parameter, $\delta$ of a chemical group. The other two forces are permanent dipole interactions ($\delta_d$) and van der Waals or London dispersive forces ($\delta_p$). Thus according to Hansen,

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

(2)

The Flory-Huggins interaction parameter $\chi$ and the solubility parameter are related by,

$$\chi = \frac{\bar{v}(\delta_1 - \delta_2)^2}{RT}$$

(3)

where $\delta_1$ and $\delta_2$ are the solubility parameters of species 1 and 2, $\bar{v}$ is the molar segmental volume of species 1 and 2 (assumed to be the same), R is the universal gas constant, and T is the temperature in degrees K. The units of $\delta$ are (J/cm$^3$)$^{1/2}$ or (cal/cm$^3$)$^{1/2}$ and $\chi$ is dimensionless [56]. Thus, from the above discussion, it is evident that hydrogen bonding influences $\chi$, which in turn will have important implications on the microphase separation behavior of block/segmented copolymers.

Some relevant moieties’ $\delta$ and the contribution of hydrogen bonding to the respective $\delta$ are presented in Table 2.2. From this table it is noted that the values of $\delta$ and $\delta_h$ of the urea moiety are the highest. Furthermore, it is interesting to note that for the urethane moiety, the contribution of $\delta_h$ to $\delta$ is 68%. The contribution increases to 70% in the case of n-methylurea and is the highest for the urea moiety at 75%. These values thus indicate that the hydrogen bonding in urea is stronger than the hydrogen bonding in urethane (see below). As a reference, it may be noted from this same table that for water the contribution of $\delta_h$ to $\delta$ is as high as 88.5%. 

21
Table 2.2 Solubility parameter values of some relevant moieties [57-59].

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\delta$ (J/cm$^3$)$^{1/2}$</th>
<th>$\delta_{h}$ (J/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>urethane</td>
<td>37.2</td>
<td>25.4</td>
</tr>
<tr>
<td>n-methylurea</td>
<td>39.7</td>
<td>27.8</td>
</tr>
<tr>
<td>urea</td>
<td>45.6</td>
<td>34.2</td>
</tr>
<tr>
<td>Polycaprolactone</td>
<td>18.4</td>
<td>—</td>
</tr>
<tr>
<td>PPO</td>
<td>17.6, 18.6</td>
<td>—</td>
</tr>
<tr>
<td>PDMS</td>
<td>15.6</td>
<td>—</td>
</tr>
<tr>
<td>Water</td>
<td>47.9</td>
<td>42.4</td>
</tr>
</tbody>
</table>

The nature of hydrogen bonding in segmented polyurethane and polyurea copolymers is illustrated in Scheme 2.4. The hydrogen bonding between two urethane moieties is known as *monodentate* and that between two urea moieties is known as *bidentate*. As noted above, bidentate hydrogen bonding is stronger than monodentate hydrogen bonding. Urethane-ether or urea-ether (or the respective ester counterparts) hydrogen bonding interactions are also possible. Semi-empirical quantum mechanical calculations [60] based on the density functional theory have indicated that the urea-ether hydrogen bonding interaction energy is 19.2 kJ/mol, which is comparable to the urethane-urethane 18.4 kJ/mol interaction energy. These inter-segmental hydrogen bond interactions have been shown by Sung and Schneider...
[61] to promote greater microphase mixing and also reduce the ability of the SS to crystallize. In fact, they also demonstrated that the polyester SS contribute to greater phase mixing than polyethers. On the other hand, the possibility of urea-siloxane hydrogen bonds at 7.5 kJ/mol is very small. Yilgor et al. [60] point out that 7.5 kJ/mol is substantially lower than typical hydrogen bond energies and thus they suggest that the urea-siloxane interaction may be a dipole-dipole type interaction. In fact, it was further noted by the same authors that the extremely non-polar nature of PDMS promotes a very high degree of microphase separation in PU as compared to those based on polyether SS.

![Scheme 2.4](image)

No discussion on the role of hydrogen bonding in PUs can be complete without a reference to the unique model PUs prepared by Harrell et al. [62]. These materials were synthesized in a controlled manner to produce PU samples with monodisperse HS containing one, two, three, or four repeat units. Moreover, these HS had no –NH groups since the nitrogen atoms were in a piperazine ring. Thus, no hydrogen bonding within these model segmented PUs was possible. A detailed structure-property behavior study of these materials by Samuels and Wilkes [63] revealed that despite the lack of hydrogen bonding within the hard domains, these copolymers were microphase separated and exhibited storage modulus, tensile strength and elongation at break values that were similar to commercial ester based PUs (with hydrogen bonding). The ambient temperature storage modulus decreased when the distribution of the HS lengths was increased by blending two samples with monodisperse HS lengths. As an aside, small angle light scattering and scanning electron microscopy experiments by the same research group revealed the presence of a spherulitic superstructure in these model segmented PUs [64]. Thirty years later, Aneja and Wilkes [65] used atomic force microscopy to reexamine the morphology of these same copolymers. Remarkably, this
technique not only provided additional direct visual confirmation of the presence of a spherulitic superstructure but also further aided in resolving the preferential orientation of the crystalline HS; which is along the tangential direction of the spherulites.

From the preceding discussion it is seen that microphase separation is the essential morphological characteristic that is responsible for the remarkable elastomeric properties of these materials. However, unlike the monodisperse HS of the model PUs noted above, the HS in commercial PUs are polydisperse. In such materials, due to viscous restrictions, some shorter HS may be more prone to become trapped or dissolved in the soft matrix [43,66]. Without the ability of the HS to form hydrogen bonds, the fraction of such dissolved HS would be undoubtedly greater, thereby further reducing the extent of microphase separation in the copolymer. Thus, in most segmented PUs of commercial importance, the issues of microphase separation and hydrogen bonding are not easily separable. As noted earlier, Chapter 5 of this document, amongst other focus areas, pertains to the utilization of lithium chloride as a molecular probe to address the importance of hydrogen bonding in oligomeric model trisegment polyurethaneureas. The objective of that study was to investigate the influence of hydrogen bonding, over and above microphase separation, in mediating the long-range connectivity of the HS in polyurethaneureas.

2.3 FLEXIBLE POLYURETHANE FOAMS AND THEIR PLAQUES

One of the largest commercial uses of PU chemistry is in the manufacture of flexible slabstock or molded PU foams. Slabstock or molded foams differ mainly in the type of catalyst package and the polyol (polyfunctional oligomeric alcohol) utilized during production. The molded PU foams, as the name suggests, are produced within a mold. The process economics for molded PU foams manufacture require short mold times. Thus, higher MW and more reactive polyol (than for slabstock foams) are used to produce them. Additional cross-linking agents, such as diethanolamine (DEOA), are also often used to further reduce cycle time. On the other hand, slabstock foams are manufactured as rectangular blocks or slabs, which are then allowed to cure over a period of several days. Since the first demonstration of PU foam formation in 1941, the technology has matured enough to cater to a wide variety of applications in various fields, such as in the automotive
sector, home furnishings, etc. The development of the one-shot technology was primarily responsible for this commercial success [67,68]. While the foam manufacture technology merits detailed discussion by itself, in light of the research goals stated earlier and the material covered in Chapter 5, the limited discussion in this chapter briefly considers only the chemistry and morphology of flexible slabstock PU foams.

2.3.1 Polyurethane Foam Chemistry

Flexible PU foams consist of an open-cell structure, which is a result of two simultaneous exothermic reactions shown in Scheme 2.5.

**Blow reaction:**
\[ R-N=C=O + H_2O \xrightarrow{-\Delta} R-N=C-OH \]

\[ \text{Carbamic Acid} \]

\[ \text{Carbamic Acid} \xrightarrow{-\Delta} -CO_2 \uparrow \]

**Gelation reaction:**
\[ R-N=C=O + R'-OH \xrightarrow{-\Delta} R-N=C-O-R' \]

Scheme 2.5

An isocyanate group of a difunctional isocyanate can either react with a water molecule or an alcohol group of a polyol. Often, the polyol is a glycerin extended polyfunctional alcohol of MW 1000-3000 g/mol. The reaction of an isocyanate with water results in an unstable carbamic acid, which decomposes to an amine with the release of CO₂ and heat. Urea HS result when the amine-terminated moiety is chain extended by its reaction with an isocyanate. This reaction is called the **blow reaction**. The reaction of the isocyanate with a polyol results in chemical cross-linking and the build-up of the MW, which ultimately results in the formation of a gel. Thus this reaction is called the **gelation reaction**. The reaction of an isocyanate with water is the rate-limiting step [67]. It may be noted that the blow reaction is identical to reaction (c) of Scheme 2.1 discussed in Section 2.2.1. A catalyst package
consisting of amine (NR₃) and tin (L₄Sn; L represents a ligand) catalysts is usually used in the commercial manufacture of PU foams. The cross-linked network generated by the above reactions is ‘blown’ into a cellular structure by the heat expanded CO₂ and entrapped air. At some point during these reactions the thermodynamic boundary for microphase separation, governed by the product χN, is crossed and a microphase separated morphology results. In practice, on the industrial scale, the precursors are mixed in a ‘mixing head’, which results in a heterogeneous (but stoichiometrically accurate) mixture of reactants. Thus, microphase separation in such a system does not occur at the same time throughout the reaction mass, as may be implied from the above discussion. Aggregation of the HS, assisted by hydrogen bonding, leads to the formation of hard domains that are dispersed in the soft polyol matrix. The HS content of the foam is governed by the level of water and diisocyanate in the formulation. A sufficient HS content leads to the development of an interconnected hard domain morphology, which coexists with the covalent cross-linked network. In most commercial flexible PU foams, an 80:20 2,4:2,6 isomeric mixture of toluene diisocyanate (TDI) is usually used as the diisocyanate. A low boiling solvent, which serves as a physical blowing agent, is also sometimes used to assist the blowing process. The choice of such solvents is restricted to a very few due to the ozone-depleting nature of some of these solvents. Surfactants are another important ingredient in foam formulations. These are usually silicone based and serve, amongst other purposes, to lower the bulk surface tension, promote nucleation of bubbles during mixing, and stabilize the foam cell [67,68]. The general morphology of water-blown flexible PU foams that results during the above reactions is presented in the following section.

2.3.2 Development of Flexible Polyurethane Foam Morphology

Several length scales characterize the PU foam morphology and underscore its complexity. Indeed, to the author’s knowledge aside from cross-linked polyethylene, very few other commercial polymer based products possess a morphology that consists of coexisting covalent and physical cross-linked networks. The evidence of the presence of a microphase separated morphology in slabstock PU foams was first presented by Wilkes et al. [69] in a brief study. A more in-depth morphological investigation of TDI and PPO based water blown flexible PU foams from the same research group [70] followed thereafter. These studies
confirmed the fact that conventional flexible PU foams possessed a microphase separated morphology. Moreover, based on the results of techniques such as DSC, DMA, SAXS, etc. the degree of microphase separation in conventional slabstock foams was found to be independent of the water content. At low water content, small hard domains were randomly distributed in the soft matrix. At higher water content, the development of an interconnected hard domain morphology was suggested. The formation of larger hard urea ‘aggregates’ or urea ‘balls’ (ca. 300 nm in size) were also seen. These were a result of the precipitation of the urea HS during the foaming reactions. Their formation was noted when the growing urea carbonyl IR absorbance peak shifted from 1715 cm\(^{-1}\) to 1640 cm\(^{-1}\) due to the formation of bidentate hydrogen bonding with the urea HS [71-73]. Model studies on diphenyl urea conducted earlier [Refs. in 70] had demonstrated that in good solvents, the urea carbonyl IR absorbance occurred at 1715 cm\(^{-1}\) whereas in poor solvents, the absorbance was noted at 1640 cm\(^{-1}\).

Depicted in Fig. 2.5 is a simplified model of the various morphological features in typical flexible PU foams. Illustrated in this figure are hard domains formed by the aggregation of 30-50 Å long HS with an average inter-domain spacing of ca. 100 Å. Aggregation of the urea hard domains results in the formation of HS rich ‘urea balls’ which are ca. 3000 Å in diameter. A copolymer particle, 2000-5000 Å in diameter, is a polymeric filler particle (added to PU foams to produce open-cell foams with higher hardness) whose surface is usually grafted with the polyol in order to avoid flocculation. Copolymer particles are more commonly employed in molded foams. It is also noted from Fig. 2.5 that the dimensions of a typical single foam cell in slabstock or molded PU foams are at least three orders of magnitude larger than the size of a urea ball.

Recently, Elwell et al. [74,75] conducted an in-situ investigation by FT-IR spectroscopy, synchrotron SAXS, and dynamic rheology of the structure development during the reactive processing of model PU foams. Foams based on MDI and either a polyether polyl (f’>2) or a mono-functional ether (referred to as monol) were used. A catalyst and a silicone surfactant were also utilized. For the polyl based system they noted that the SAXS invariant, Q (see eq. 4) started to increase (indicating progress towards microphase separation) prior to the growth in the concentration of urea hydrogen bonded carbonyl species.
The SAXS invariant is a measure of the degree of microphase separation and can be calculated from the following equation:

$$Q = \int_0^\infty I(q)q^2 dq$$  \hspace{1cm} (4)$$

where

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$  \hspace{1cm} (5)$$

In the above equation, $\lambda$ is the wavelength of incident radiation and $\theta$ is the scattering angle.

The increase in viscosity (indicated by the reaction mixture’s elastic shear modulus, $G'$) lagged the growth in both the SAXS invariant and urea hydrogen bonded carbonyl species. Thus these results, the investigators noted, indicated that after the onset of microphase separation, the hydrogen bonds anchored the structure in place. Later,
vitrification of the copolymer further locked in the structure. The monol based PU foams also demonstrated a similar behavior. However, some important differences were also observed, the most significant being the much higher rate of association of the urea HS in the monol based system as compared to that in the polyol based system. Such rapid aggregation in the former resulted in the macrophase separation (precipitation) of the urea aggregates due to insufficient linkages (urethane) between the urea HS and the polyether SS. By comparing the overall behavior of the polyol based PU foam to its monol based counterpart, Elwell et al. concluded that the covalent cross-links in the polyol based system delayed the onset of microphase separation of the urea HS. However, they also noted that the molecular connectivity between the microphases (via urethane linkages) were essential in achieving useful mechanical/physical properties.

A more in-depth review of the literature pertaining to each of the research topics addressed in this dissertation is presented at the beginning of each of the following chapters.