7. COMPARING THE SOLID STATE STRUCTURE-PROPERTY BEHAVIOR OF HIGHLY BRANCHED SEGMENTED POLYURETHANEUREA COPOLYMERS WITH THEIR LINEAR ANALOGS

7.1 CHAPTER SUMMARY
The solid state structure-property and solution rheological behavior of highly branched segmented polyurethaneurea (PUU) copolymers and their linear analogs was investigated. The linear PUUs were synthesized by the two-step prepolymer method whereas the oligomeric $A_2+B_3$ methodology was utilized to synthesize the highly branched materials. Hydroxyl terminated poly(tetramethylene oxide) (PTMO) of $MW \ 2000 \ g/mol$ and MWD 1.87 or poly(propylene oxide) (PPO) of MW ranging from 2200 to 12200 $g/mol$ and MWD less than 1.1 were utilized as the soft segments. The hard segments (HS) of the linear PUUs were based on hydrogenated diphenylmethane diisocyanate (HMDI) and 2-methyl-1,5-diaminopentane (Dytek) whereas HMDI, tris(2-aminoethyl)amine (TRIS), and cyclohexyl isocyanate (CHI) were utilized as the HS moieties for the highly branched PUUs; CHI was utilized to end-cap the terminal amine functional groups of the highly branched PUUs and therefore promote potential intermolecular hydrogen bonding. All copolymers utilized in this study contained 28 wt % HS. DMA and SAXS indicated that the linear as well as the highly branched PUUs were able to develop a microphase morphology. DMA also demonstrated that the SS $T_g$ of the highly branched PUUs was similar to their linear analogs. However, the latter copolymers exhibited broader and more temperature insensitive rubbery plateaus primarily due to their higher entanglement density and the longer HS as compared to those of the highly branched materials. Particularly noteworthy, and surprising, was the observation of weak second order interference shoulders in the SAXS profiles of the highly branched samples based on PPO of MW 8200 and 12200, indicating the presence of at least some level of long-range order of the hard domains in these samples. Tapping-mode AFM phase images of these two samples, which clearly confirmed the SAXS results, indicated the presence of particulate hard domains with an average inter-domain spacing of ca. 200 Å. In addition to the strain induced crystallization of the PTMO MW 2000 $g/mol$ based linear PUU, the highly
branched analog of this sample also exhibited similar behavior at ambient temperature and uniaxial deformation of \( \text{ca.} \ 400\% \) strain. WAXS was utilized to confirm the above observation. The stress-strain, stress-relaxation and mechanical hysteresis of the highly branched PUUs were also compared with their linear analogs. In general, the mechanical response of the highly branched analogs was slightly poorer than their linear analogs. However, the ambient temperature solution viscosity of the former samples was substantially lower than that of the linear samples, which is distinctly advantageous with regard to solution or melt processing of these highly branched copolymers.

7.2 INTRODUCTION

Since their initial discovery, the synthesis of hyperbranched counterparts of almost all common linear polymers has been reported [1-4]. Researchers have targeted hyperbranched polymers for applications in drug delivery systems, coating and sealant materials, non-linear optics, modification of the properties of linear polymers, \textit{etc.} [4]. The DSM corporation in the Netherlands recently reported [5] perhaps the first commercialization of hyperbranched polymers, namely polyesteramides which are targeted for applications such as improving the dyeability of polypropylene fibers, and improving the control of the rheological behavior of paper coating dispersions. Hyperbranched polymers, unlike dendrimers, are generally prepared by a one-step condensation synthesis. Thus, the cumbersome and expensive multi-step synthesis required for synthesizing and purifying dendrimers is avoided. Consequently, hyperbranched polymers have ‘defects’ and usually a large number of ‘geometrical isomers’ are produced due to the random placement of each monomer on the branched structure. Hyperbranched polymers also have an associated polydispersity, which is larger than that of conventional linear polymers of MW for an equal extent of conversion [6].

Hyperbranched polymers are typically synthesized by the polymerization of \( \text{AB}_x \) monomers, where \( x \) is 2 or higher. Another approach is the copolymerization of \( \text{A}_2 \) and \( \text{B}_3 \) monomers. Limiting the conversion or manipulating the multifunctional monomer stoichiometry is typically used in such a reaction scheme to prevent gelation. In both synthetic strategies, as expected, the reaction between A and B functional groups of the same molecule will terminate growth of that ‘arm’ due to cyclization. The \( \text{A}_2+\text{B}_3 \) approach is often
a more attractive alternative due to a ready commercial availability of many A$_2$ and B$_3$
monomers. As noted above, a wide range of hyperbranched polymers have been produced
that include polyesters, polyethers, poly(ether ketone)s, poly(ether sulfone)s, poly(ether
imide)s, polyamides, poly(siloxysilane)s, polystyrenes, poly(acrylates), polyurethanes,
polyureas, etc. [1-4]. However, there are very few reports on the synthesis of hyperbranched
systems utilizing the latter two chemistries [7-11]. Spindler and Frétchet [7] were the first;
they utilized protected or blocked isocyanates to synthesize hyperbranched polyurethanes.
Later, Kumar and Ramakrishnan [8,9] produced wholly aromatic hyperbranched polymers
with urethane linkages by the polymerization of 3,5-dihydroxy benzozyl azide. An important
observation made by these authors was that the $T_g$ (measured by DSC) of the hyperbranched
polymer without the oxyethylene spacer ($x = 0$) was 106°C and it decreased to 13°C when
the length of the spacer was increased to $x = 2$. The degradation temperature on the other
hand increased from 240°C ($x = 0$) to 310°C ($x = 2$). The same research group also
synthesized hyperbranched polymers with urea linkages [10] by using the polycondensation
commercially available A$_2$ and CB$_n$ ($n = 2$ or higher) monomers to produce hyperbranched
polymers with urethane and urea linkages.

Clearly, the polyurethanes, polyureas, or polyurethaneureas discussed above are not
segmented because unlike the presence of alternating hard and soft segments along the chain
backbone of conventional linear segmented copolymers, the hyperbranched systems consist
of only the ‘hard segment’ moieties. The oxyethylene spacers incorporated by Kumar and
Ramakrishnan in their hyperbranched polyurethanes cannot be considered as soft segments
since they are very short in length and as expected, no $T_g$ due to these segments was reported
to be observed. However, an important step in the direction towards the synthesis of ‘truly’
segmented polyurethanes or polyureas that could display useful structural properties is
provided when the observation of the decrease in $T_g$ with increase in the length of the
oxyethylene spacer is combined with the A$_2$+B$_3$ synthesis approach.

Recently, Prof. Timothy E. Long’s group and Dr. Iskender Yilgor in conjunction with
the author and Prof. Garth L. Wilkes reported the synthesis of segmented, highly branched
polyurethaneureas (PUUs) based on the oligomeric A$_2$+B$_3$ approach [12]. Isocyanate end-
capped poly(tetramethylene oxide) (PTMO) or polypropylene oxide (PPO) was utilized as
the oligomeric $A_2$ while tris(2-aminoethyl)amine was used as the $B_3$ monomer. The solid state structure-property and solution rheological behavior of these PUUs is presented in this chapter. Specifically, (1) the highly branched copolymers are compared with equivalent linear, segmented PUUs, (2) in light of the ability of PTMO and the inability of PPO to strain induce crystallize, linear and highly branched PUUs based on PTMO (MW 2000 g/mol, MWD 1.87) are also compared with those based on PPO (MW 2200 g/mol, MWD 1.03), and (3) PPO (MWD < 1.1) of MW below and above its critical MW between entanglements, $M_c$ (7700 g/mol [13]) is utilized to study the effect of SS entanglements on the structure-property behavior of the highly branched PUUs. The $M_c$ values of PTMO and PPO that are quoted above are for homopolymers and it is realized that copolymerization and chain architecture may influence the MW at which the onset of SS entanglement is noted. The samples utilized in this study, with one exception, contain 28 wt % HS. The usage of the term ‘highly branched’ instead of the more common ‘hyperbranched’ to describe the branched copolymers utilized in this study is justified on the basis that for a given overall MW, the use of oligomeric $A_2$ precursors inevitably produces copolymers with a lower degree of branching than those that would result from monomeric $A_2$ precursors. The reader is referred to Chapter 2 for a detailed discussion on the morphological aspects of linear segmented polyurethaneurea copolymers.

7.3 EXPERIMENTAL

7.3.1 Materials

The linear and highly branched segmented PUU copolymers were synthesized according to the scheme similar to the reaction procedure described in detail in a joint publication with Prof. Timothy E. Long’s group at Virginia Tech [12]. In brief, the prepolymer method was utilized to synthesize the linear PUUs based on hydroxyl terminated poly(tetramethylene oxide) (PTMO) or poly(propylene oxide) (PPO) as the SS, bis(4-isocyanatocyclohexyl)methane (HMDI) as the diisocyanate, and 2-methyl-1,5-diamnopentane (Dytek) as the chain extender. The $A_2+B_3$ synthesis strategy was adopted to synthesize the highly branched analogs. Hydroxyl terminated PTMO or PPO were end-capped with HMDI in bulk or in isopropyl alcohol respectively. A calculated excess amount of HMDI and TRIS
were utilized in order to achieve 28 wt % HS content in the final copolymer. The end-capped polyether \( (A_2) \) was introduced drop-wise into a solution of \( B_3 \). The chemical, tris(2-aminoethyl)amine (TRIS) was utilized as \( B_3 \). It was dissolved in a mixture of tetrahydrofuran/isopropyl alcohol (25/75 vol/vol) or in isopropyl alcohol to synthesize PTMO based and PPO based highly branched PUUs, respectively. While equal molar amounts of \( A_2 \) (mixture HMDI plus PTMO-NCO or HMDI plus PPO-NCO) and \( B_3 \) (TRIS) were utilized during the synthesis of PUUs based on PTMO of MW 2000 g/mol and PPO of MW 2200 g/mol, 10 % excess \( B_3 \) was utilized to synthesize PUUs based on PPO of MW 4200, 8200, or 12200 g/mol. During the reaction no gelation was observed, which indicates the absence of a cross-linked network. However, this observation also suggests internal cyclization in the highly branched PUUs. After polymerization, the excess -NH\(_2\) groups in the all the highly branched PUUs except one were end-capped with cyclohexyl isocyanate (CHI) to form terminal urea linkages, which would facilitate terminal bidentate hydrogen bonding with the other highly branched PUU molecules in a sample. The copolymers utilized in this chapter are based on a constant HS content of 28 wt %; HMDI+Dytek constitute the HS in linear PUUs and HMDI+TRIS+CHI as that in the highly branched analogs. The samples are listed in Table 7.1 and identified by the nomenclature:

**SS type and MW- Chain architecture**

For example, a linear sample based on PTMO of MW 2000 g/mol is identified as ‘T2-L’ whereas a highly branched sample based on PPO of MW 8200 g/mol is identified as ‘P8-H’. The molar ratios of precursors, the absolute \( <\text{M}_w> \) and MWD of these copolymers are also listed in Table 7.1. The reader’s attention is drawn to the fact that equimolar amounts of HMDI terminated PPO (or PTMO) and TRIS were utilized to synthesize P-2H (or T-2H). However, in order to maintain a constant HS content in the highly branched copolymers, excess HMDI and TRIS had to be utilized as the SS (PPO) MW was raised above 2200 g/mol. As can be readily imagined, the required excess (see Table 7.1) increased with increasing PPO MW. Due to this fact, the extent of HS branching level in a given HS will also increase with PPO MW in the highly branched PUUs.
7.3.2 Methods

A Seiko Instruments model DMS210 was used for dynamic mechanical analysis (DMA). Under a dry nitrogen atmosphere, thoroughly dried solution cast films were quenched from room temperature to -150°C using liquid nitrogen and immediately thereafter subjected to a 2°C/min heating scan; $\tan \delta$ and storage modulus, $E'$, data were obtained at a frequency of 1 Hz.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar Composition</th>
<th>$&lt;M_w&gt;$</th>
<th>$M_w/M_n$</th>
<th>Young’s Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS/HMDI/Amine CHI</td>
<td>(g/mol)</td>
<td>(g/mol)</td>
<td>(MPa)</td>
</tr>
<tr>
<td>T2-L</td>
<td>1.0/2.0/2.0/-</td>
<td>220000</td>
<td>4.41</td>
<td>7.5</td>
</tr>
<tr>
<td>T2-H</td>
<td>1.0/2.0/1.0/1.0</td>
<td>92000</td>
<td>5.78</td>
<td>10.3</td>
</tr>
<tr>
<td>T2-H-noCHI</td>
<td>1.0/2.0/1.0/-</td>
<td></td>
<td></td>
<td>6.4</td>
</tr>
<tr>
<td>P2-L</td>
<td>1.0/2.0/2.0/-</td>
<td>45000</td>
<td>2.59</td>
<td>2.8</td>
</tr>
<tr>
<td>P2-H</td>
<td>1.0/2.0/1.0/1.0</td>
<td>110000</td>
<td>7.14</td>
<td>1.3</td>
</tr>
<tr>
<td>P4-L</td>
<td>1.0/4.1/4.1/-</td>
<td>94000</td>
<td>2.30</td>
<td>4.3</td>
</tr>
<tr>
<td>P4-H</td>
<td>1.0/3.7/2.4/2.0</td>
<td>150000</td>
<td>7.72</td>
<td>3.2</td>
</tr>
<tr>
<td>P8-L</td>
<td>1.0/8.2/8.2/-</td>
<td>120000</td>
<td>2.10</td>
<td>3.5</td>
</tr>
<tr>
<td>P8-H</td>
<td>1.0/6.8/5.3/4.2</td>
<td>76000</td>
<td>4.11</td>
<td>1.0</td>
</tr>
<tr>
<td>P12-L</td>
<td>1.0/12.4/12.4/1</td>
<td>77000</td>
<td>2.18</td>
<td>1.5</td>
</tr>
<tr>
<td>P12-H</td>
<td>1.0/9.9/8.1/6.5</td>
<td>53000</td>
<td>4.06</td>
<td>1.1</td>
</tr>
</tbody>
</table>

$^a$ Linear (L) PUU copolymers utilize Dytek as the amine and the highly branched analogs utilize TRI as the amine.

$^b$ $<M_w>$ values are absolute MWs determined by triple angle laser light scattering and for measurements the samples were dissolved in HFIP [14].

$^c$ $<M_n>$ values are absolute and were measured by differential viscometry [14].

Ambient temperature tensile testing was conducted by utilizing an Instron model 4400R equipped with a 1-kN tension load cell and calibrated with a 2 kg standard (19.61 N). “Dog-bone” shaped film specimens, 2.9 mm wide and having a grip separation distance of 10 mm were used to generate the stress-strain curves at a crosshead speed of 25 mm/min. Three samples were tested for each copolymer and the average Young’s modulus of these three runs is reported. Only representative stress-strain responses are presented in the appropriate
figure. Stress relaxation studies were also performed on similar dog-bone shaped specimens where the strain levels of 25 % or 500 % were utilized. Mechanical hysteresis experiments were conducted by also utilizing strain levels of 25 % or 500% for two uniaxial deformation cycles each and at a crosshead speed of 25 mm/min. A given deformation cycle was started immediately after the completion of the previous one.

Pin-hole collimated small angle x-ray scattering (SAXS) profiles were collected at ambient temperature using a Rigaku Ultrax18 rotating anode X-ray generator operated at 40 kV and 60 mA. Further instrumentation details can be found in Section 4.3.2.

A Digital Instruments (now Veeco) Dimension 3000 scanning probe microscope, which was controlled by a Nanoscope IIIa controller, was utilized for tapping-mode atomic force microscopy (AFM). Images of the free surface of thoroughly dried solution cast films were captured at a magnification of 2 µm x 2 µm and a set-point ratio of ca. 0.6. Nanosensors’ TESP 7 or Veeco’s TAP 300 tips having a spring constant of 35-40 N/m were utilized for imaging.

TA Instruments’ AR1000 rheometer with 2°, 40 mm diameter cone-and-plate attachment was utilized to measure the viscosity of 15 wt % copolymer solutions of the respective materials in dimethyl formamide (DMF) at room temperature [15]. The solution viscosity of a sample was determined from the slope of shear stress versus shear rate within the Newtonian or linear region of this plot. The reported viscosity numbers are averages of 3-4 samples.

7.4 RESULTS AND DISCUSSION

7.4.1 Dynamic Mechanical Analysis

The storage modulus, \( E' \) and \( \tan \delta \) responses as a function of temperature of linear and highly branched PUUs based on PTMO and PPO are presented in Fig. 7.1. The DMA behavior of PTMO-2000 based copolymers presented in Fig. 7.1(a) is addressed first. Focusing on \( E' \) of the linear sample, T-2L as expected, behaves as a rigid solid up to ca. -100°C. Thereafter, \( E' \) begins to decrease due to the glass transition of the PTMO SS (\( T_g \))
-78°C, $\tan \delta$ peak value). Not surprisingly, the SS $T_g$ is slightly higher than that of the pure PTMO oligomer (-85°C [16]) due to restrictions experienced by the SS from the covalently linked urea HS. After the SS glass transition induced drop in $E'$, a relatively temperature insensitive rubbery plateau can be observed that extends up to 200°C. As is well known, in structural applications, this plateau is also referred to as the ‘service window’ of the copolymer. Finally, another drop in $E'$ occurs due to the softening of the hard phase. The low $T_g$ of the SS coupled with the broad and nearly temperature insensitive rubbery plateau indicate that the sample possesses a microphase morphology. From this sample’s $\tan \delta$ behavior, two distinct transitions can be noted that correspond to the respective transitions in $E'$. A damping peak centered at -78°C occurs due to the SS glass transition and an increase in $\tan \delta$ values above 200°C is noted due to the softening of the hard phase and possible onset of degradation of the material.

*Figure 7.1* DMA response of linear and highly branched PUUs (a) T2-L and T2-H; (b) P2-L and P2-H; (c) P4-L and P4-H; (d) P8-L and P8-H; (e) P12-L and P12-H.
The DMA behavior of the PTMO based highly branched analog, T-2H is also presented in Fig.7.1a. Interestingly, below 50°C the $E'$ and $\tan \delta$ responses of T-2H are very similar to T-2L. The former sample also displays a drop in $E'$ from ca. -100 to -50°C due to the SS glass transition and a rubbery plateau extends thereafter. The average plateau moduli of both samples are also quite comparable up to 50°C. However, the rubbery plateau is significantly narrower in T-2H than it is in T-2L. The narrower rubbery plateau of T-2H is expected to arise due to (1) its lower $M_w$ as compared to T-2L (recall Table 7.1), (2) fewer chain entanglements in its highly branched architecture as compared to T-2L, and (3) the slightly shorter average length of the HS in its branched architecture, which is expected to promote increased inter-segmental mixing and therefore also result in a narrower rubbery plateau. Furthermore, it is noted that while calculating the HS content of the highly branched samples, the terminal end-capping moieties, namely CHI, are considered to be part of the HS. From the $\tan \delta$ response of T-2H, it can be again noted that the breadth of the SS glass transition and the peak transition temperature, $T_g$ (-78°C) are very similar to T-2L. However, due to reasons noted above, the rise in $\tan \delta$, which corresponds to the decrease in $E'$ occurs at a lower temperature (ca. 50°C) than in T-2L (200°C).

In Fig. 7.1a the DMA response of the CHI end-capped T-2H (28 wt % HS content) is compared with its counterpart that is without the end-cap moiety (T-2H no CHI, 25 wt % HS content). Note that despite the slightly lower HS content and the likely reduced, if any, inter-molecular bidentate hydrogen bonding of the latter, no significant differences are noticeable between the two highly branched PTMO 2000 g/mol based highly branched samples.

Turning attention to Fig. 7.1b, it can be observed that the DMA behavior of PPO 2200 g/mol based linear and highly branched samples is very similar to that of the corresponding PTMO 2000 based samples presented in Fig. 7.1a. However, noteworthy differences can be observed. Firstly, the PPO SS $T_g$ occurs at -57°C as compared to the PTMO SS $T_g$ at -78°C, that is principally due to the differences in the chemical structures of the two types of SS and also due to potential differences in the extent of the copolymers’ microphase separation (see below). Note that the $T_g$ of the pure PPO oligomers is reported to be ca. -73°C [17] whereas that of the PTMO oligomers is -85°C [16]. Secondly, the average rubbery plateau modulus of the PTMO based copolymers is ca. 3 times higher than the PPO
based materials. Such a difference arises primarily due to the higher entanglement density in the PTMO-2000 segments as compared to the PPO-2200 segments. It may be noted that $M_c$ of PTMO is 2500 g/mol whereas for PPO it is significantly higher at 7700 g/mol [13]. The above results underscore the importance of the SS MW in relation to $M_c$ as a means of controlling the stiffness of the copolymer within its rubbery plateau region. Tong and Jerome [18] also note that in triblock copolymers, such as poly(methyl methacrylate)-b-poly(alkyl acrylate)-b-poly(methyl methacrylate) and polystyrene-b-polyisoprene-b-polystyrene of comparable hard block content (ca. 30 wt%), the entanglements of the central soft block play a critical role in governing the tensile strength of the material. Lastly, the rubbery plateau of the PTMO-2000 based samples is significantly broader than that of the PPO-2200 based counterparts because unlike in the latter, which are based on PPO of narrow MWD (1.03), the PTMO MWD of 1.87 means that there is a significant fraction of the SS in PTMO based PUUs that are of higher molar mass (and therefore, longer in length) than the average. These longer SS are expected to play an important role in broadening the rubbery plateau of PTMO based PUUs. In addition, the overall $<M_w>$ of P-2L and P-2H is substantially lower than that of T-2L (recall Table 7.1), which also results in a narrower rubbery plateau for the PPO-2200 based samples.

Considering the series of copolymers based on PPO, note that the overall $<M_w>$ of these copolymers, with the exception of P-2L and P-12H, is comparable and in the range of 100,000 g/mol. Schollenberger and Dinbergs [19] note that the mechanical properties of linear segmented polyurethanes reaches a plateau value around $<M_w>$ between 100,000 and 200,000 g/mol. The reasons for such behavior are discussed in greater detail in Chapter 2 where their results were cited. The differences in $E'$ and $Tan \delta$ responses between the PPO based linear PUU and its highly branched analog also arise due to similar reasons as discussed above. When the MW of the PPO SS is increased from 2200 to 4200, 8200 and finally to 12200 g/mol (Figs. 7.1c-e), a systematic decrease in the SS $T_g$ and also the breadth of the SS glass transition can be observed (from both the $E'$ and $Tan \delta$ responses) with increasing PPO MW. Such a trend is observed because of the fewer restrictions experienced by the longer SS, which therefore form fewer junctions with the HS. In the linear PUUs shown in Figs. 7.1c-e, as the PPO SS MW in increased, the rubbery plateaus become more temperature insensitive and extend up to higher temperature (ca. 200°C) primarily due to an
improved extent of microphase separation in these samples. In comparison to the linear PUUs, the rubbery plateau of each of the highly branched analogs based on PPO-4200 and PPO-8200 begin to decay earlier due to reasons similar to those noted in the above discussion, which are (1) their branched architecture, (2) shorter HS length as compared to their linear analogs, and (3) relatively lower extent of microphase separation as compared to their linear analogs. Of particular interest is the observation that the breadth of the rubbery plateau of P-12H is nearly comparable to its linear analog, P-12L. The fact that the SS MW in these two copolymers is well above the $M_c$ of PPO may be responsible for such behavior. Another reason why the rubbery plateau of P-12H is comparable to P-12L is the low $<M_w>$ of the former sample (53,200 g/mol), which means that the degree of branching in this sample is only modest.

In general, from the DMA data it can be noted that despite the incorporation of branching, that is HS branching, the SS $T_g$ (and therefore, the extent of microphase separation) of the highly branched PUUs is very similar to their particular linear analogs. Such behavior is consistent with the results presented in Chapter 6, wherein increasing extent of HS branching was introduced in model PUUs having a constant 22 wt % HS content. During synthesis as many as 25 % of the -NCO groups contributed by a diisocyanate were replaced with those contributed by a triisocyanate. Despite this fact, the SS $T_g$ of the copolymers (determined by DSC) was similar to that of its linear counterpart. The reader may recall that SAXS profiles of those model PUUs also confirmed the DSC results.

7.4.2 Small Angle X-Ray Scattering

The pin-hole collimated ambient temperature SAXS profiles of PPO and PTMO based linear and highly branched PUU copolymers are presented in Fig. 7.2. The absolute intensities are plotted as a function of the scattering vector, $s (= 2\sin(\theta/2)/\lambda$, where $\theta$ is the radial scattering angle and $\lambda$ (= 1.542 Å) the wavelength of incident radiation). The absolute intensities have been translated vertically for clarity. The scattering profiles of all eleven samples exhibit a distinct first order interference peak in their respective scattering profiles. The SAXS data clearly suggests that the samples posses a microphase separated morphology and therefore it is consistent with the respective ambient temperature DMA responses. The inter-domain
spacing of a given sample, which is approximated by $1/s_{\text{max}}$, according to Bragg’s law, is noted next to the respective legend in Fig. 7.2.

The linear PUUs based on PPO as the SS component are presented in Fig. 7.2a. From this figure it can be observed that with increasing SS MW, the inter-domain spacing, as expected, increases from ca. 80 Å in the PPO-2200 based PUU to 145 Å in the PPO-12200 based PUU. The absolute intensity of the first order interference peak also increases with SS MW. On the other hand, the breadth of the first order interference peak decreases systematically. Although not directly quantified, the latter two observations together indicate that the relative extent of microphase separation is increasing with increasing SS MW. The samples P-8L and P-12L also show a very weak interference shoulder in their respective scattering profiles at larger
scattering vectors suggesting that these two samples may possess at least some level of long-range order of the hard domains.

Focusing on the highly branched PUUs based on PPO, which are presented in Fig. 7.2b, a systematic narrowing of the breadth of the first order interference peak can be also observed as was noted in the linear samples. Interestingly, a distinct weak higher order interference shoulder can be observed in the scattering profiles of P-8H as well as P-12H. In both the samples, its position corresponds to a ‘d’ spacing that is half of the respective spacing of the first order interference peak. It must also be noted that unlike in the PPO based linear samples, the inter-domain spacing of the first order interference peak of the PPO-12200 sample at ca. 180 Å is smaller than that of PPO-8200 based copolymer (ca. 200 Å). The underlying reasons for such behavior are not fully understood at this point.

In light of the SAXS results presented in this section the reader’s attention is directed to the report by Ryan et al. [20]. They noted that their extensive search of the literature did not yield any instance of a linear segmented polyurethane’s SAXS profile exhibiting higher order reflections in addition to the primary (or first order) reflection. In that publication, the authors also referred to the theoretical work of Fredrickson et al. [21,22], which predicts that random block copolymer melts will lack long-range order due to a broader distribution of the segment lengths. Thus, the higher order interference shoulder(s) in the PPO-8200 and 12200 based linear and highly branched PUUs are perhaps the first such observation in a segmented PUU. The very narrow MWD of the PPO soft segments (<1.1) in conjunctions with the relatively short HS in these two copolymers is conjectured to be the primary reason for such behavior. Note that the block copolymers, such as diblocks or triblocks based on polystyrene and polyisoprene, which are synthesized anionically, and thus have a very narrow MWD of both of the constituent blocks, routinely exhibit several distinct higher order interference peaks in their SAXS profiles. In the present study, what is also interesting is the fact that the highly branched samples display more prominent higher order interference shoulders. Considering the relatively high extent of HS branching in P-8H and P-12H the higher order interference shoulders in these branched copolymers is particularly surprising. Nonetheless, AFM provides further direct confirmation of the SAXS interpretation as will be discussed later.
The SAXS profiles of the PTMO based linear and highly branched PUUs are presented in Fig. 7.2c. These three samples also exhibit first order interference peaks, which indicate the presence of a microphase morphology. The inter-domain spacing of these PTMO-2000 based samples is higher than that of the PPO-2200 counterparts. This difference in the inter-domain spacing arises due to (1) difference in the average number of backbone bonds along the backbone of PTMO-2000 (ca. 140) and PPO-2200 (ca. 114) and also the chain dimensions between PTMO and PPO of comparable average MW, and (2) the broader MWD of the PTMO segments (1.87) as compared to the PPO segments (<1.03). O’Sickey et al. [23] have also observed similar differences in the inter-domain spacing in polyurethaneureas based on PPO of narrow MWD (< 1.03) and PTMO with a broader MWD (ca. 2).

7.4.3 Atomic Force Microscopy

Both DMA and SAXS results discussed above indicate that the segmented PUUs addressed in this study possess a microphase morphology at ambient temperature. In addition, at this temperature, the soft phase is well above its $T_g$ while that of the hard domains is below. Thus, due to the ability of tapping-mode AFM phase imaging to generate a visual map of the free surface based on the relative hardness of the scanned regions, the ambient temperature morphology of these copolymers is especially amenable to investigation by AFM. The tapping-mode AFM phase images of the free surface of solution cast PPO based PUUs captured at ambient temperature are presented in Fig. 7.3. The dark and the light regions correspond to soft and hard domains, respectively. From the phase images of PPO-2200 based linear (Fig. 7.3a) and highly branched (Fig. 7.3b) PUU we observe the presence of light and dark regions, indicative of a microphase separated morphology. The hard (or bright) regions in these two images are not very distinct or well separated because the average inter-domain spacing in these samples as indicated by SAXS (Fig. 7.2) is only ca. 80 Å. This suggests that the average hard domains size is expected to be 40-50 Å and the particular AFM tips utilized to capture the images in Fig. 7.3 are unable to clearly resolve morphological features of this size. The phase image of the P-4L (Fig. 7.3c) is very similar to the PPO-4200 based counterpart.
Figure 7.3 AFM phase images of the free surface of linear and highly branched PUUs (a) P2-L; (b) P2-H; (c) P4-L; (d) P4-H; (e) P8-L; (f) P8-H; (g) P12-L; and (h) P12-H. Note: The length of the magnification bar corresponds to 200 nm.
As compared to P-2H (Fig. 7.3b), the long-range connectivity of the HS is distinctly more improved in sample P-4H (Fig. 7.3d) and its hard domains chiefly appear to adopt a more short rod-like shape. While the hard phase in this sample may at first appear to possess considerable degree of hard phase percolation, as will be shown later, its corresponding stress-strain curve does not exhibit any yielding behavior, strongly indicating that the hard phase in P-4H is not percolated.
Focusing on the phase image of P-8L (Fig. 7.3e), one can readily observe more spherical hard domains that are dispersed in the soft matrix. The phase image of its highly branched analog, P-8H (Fig. 7.3f) is even more striking. For the sake of clarity the same phase image as can be seen in Fig. 7.3f is reproduced at a higher magnification in Fig. 7.4 along with the SAXS profile of P-8H as an inset. The hard domains in this sample clearly are either spherical or particulate-like and the average spacing between the domains is ca. 200 Å, which corresponds with this sample’s first order SAXS interference peak (196 Å). Moreover, from this phase image the presence of at least some long-range order of the hard domains can be readily observed. Thus, the AFM results clearly support the second order interference shoulders that were observed in this sample’s SAXS profile. However, the type of hard domain packing (e.g. simple cubic or face centered cubic) cannot be confidently ascertained from this phase image. Turning attention to the final set of images, the morphology of the P-12L (Fig. 7.3g) appears to be very similar to that of P-8L (Fig. 7.3e). The phase image of the highly branched material, P-12H (Fig. 7.3h) also exhibits some signs of a long-range order of predominantly particulate-like hard domains; again, the HS constitute 28 wt % of the copolymer.

### 7.4.4 Mechanical Properties

In this section the stress-strain response, the extent of stress relaxation, and the mechanical hysteresis behavior of the linear and highly branched PUU copolymers are presented and compared. The stress-strain results of the PTMO and PPO based samples are presented in Fig. 7.5. The Young’s moduli of these samples are listed in Table 7.2. Focusing on Fig. 7.5a, the PTMO-2000 based samples, no distinct yield point can be observed, which indicates that in these particular systems, 28 wt % HS is not sufficient to enable extensive percolation of the hard phase. In fact, the AFM images of the PPO-2200 based samples also indicated insufficient percolation of the hard phase. The Young’s modulus of T-2L (listed in Table 7.2) is, surprisingly, lower than T-2H. However, the highly branched copolymer without end-capping, T-2H-no CHI, displays the lowest Young’s modulus amongst the three PTMO based copolymers due to (1) the potentially lower extent of terminal bidentate hydrogen bonding between various molecules in the sample, and (2) the slightly lower HS content in this sample (25 wt %) as compared to T-2L and T-2H (28 wt %). The strain hardening at
higher extensions that is noted in the linear sample, T-2L, undoubtedly occurs due to the well
know ability of PTMO (MW > ca. 1500 g/mol) to strain induced crystallize at greater than
csa. 400 % strain.

Figure 7.5 Stress-strain behavior of linear and highly branched PUUs based on PPO-2200
and PTMO-2000 (a), and PPO of MW 4200, 8200 and 12200 g/mol (b).

Wide-angle X-ray scattering was utilized to investigate the similar strain hardening behavior
of the highly branched sample T-2H. The 2D ambient temperature WAXS pattern (Fig. 7.6)
of T-2H uniaxially deformed to ca. 400 % strain demonstrates two distinct equatorial
reflections at ‘d’ spacings of ca. 4.5 and 3.3 Å due to the crystalline PTMO phase [24]. In
view of the above results, the strain hardening behavior of the sample, T-2H-no CHI, is also
expected to arise due to the strain induced crystallization of the PTMO phase, as was also
noted in T-2H. Such behavior in a copolymer with a highly branched architecture is indeed
surprising and to the author’s knowledge, it is perhaps the first such observation.
Table 7.2 Young’s moduli of linear and highly branched PUUs determined at ambient temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus$^a$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2-L</td>
<td>7.5</td>
</tr>
<tr>
<td>T2-H</td>
<td>10.3</td>
</tr>
<tr>
<td>T2-H-no CHI</td>
<td>6.4</td>
</tr>
<tr>
<td>P2-L</td>
<td>2.8</td>
</tr>
<tr>
<td>P2-H</td>
<td>1.3</td>
</tr>
<tr>
<td>P4-L</td>
<td>4.3</td>
</tr>
<tr>
<td>P4-H</td>
<td>3.2</td>
</tr>
<tr>
<td>P8-L</td>
<td>3.5</td>
</tr>
<tr>
<td>P8-H</td>
<td>1.0</td>
</tr>
<tr>
<td>P12-L</td>
<td>1.5</td>
</tr>
<tr>
<td>P12-H</td>
<td>1.1</td>
</tr>
</tbody>
</table>

$^a$The Young’s modulus values are averages of three repeat runs. The standard deviation in Young’s modulus is less than ± 10%.

Figure 7.6 Wide angle X-ray scattering pattern of the sample, T-2H deformed uniaxially at ambient temperature to ca. 400 % strain. The deformation direction is vertical.

In addition, while the tensile strength of T-2L is higher than that of T-2H and T-2H-no CHI (possibly due to its substantially higher overall $<M_w>$), the latter two samples display a slightly higher elongation at break. It is also noted that while the DMA and SAXS behavior
of the latter two samples are very similar, the benefit of end-capping the chain ends of the highly branched copolymer with a moiety that can form bidentate hydrogen bonds is clearly supported by the former material’s higher Young’s modulus and tensile strength. It must also be noted that both the ambient temperature \( E' \) (DMA, Fig. 7.1a) as well as Young’s modulus exhibit similar dependence on structural features of the three PTMO based copolymers thus demonstrating the consistency between these two methods.

The stress-strain behavior of the linear and highly branched PPO-2200 based samples are also presented in Fig. 7.5a. As expected, these two samples, like their PTMO counterparts, do not display a distinct yield point. In addition, the inability of the atactic PPO SS to strain induce crystallize and also their comparatively lower overall \( <M_w> \) (Table 7.1) clearly results in copolymers with lower tensile strength as compared to the PTMO based copolymers. However, the PPO-2200 based samples display a remarkably high strain at break of \( ca. \) 1200 %. Upon comparison of the effect of PPO SS MW on the stress-strain response of the linear and highly branched PUUs (Fig. 7.5a and b), it can be noted that the PPO-4200 and 8200 based materials display the highest Young’s modulus (values listed in Table 7.2), tensile strength, and elongation at break amongst the series. While the overall \( <M_w> \) of the linear copolymers influences the ultimate properties of the samples, the generally superior stress-strain behavior exhibited by the PPO-4200 and 8200 based samples in comparison to the PPO-2200 and 12200 based counterparts is not fully understood at this point. However, as expected, the tensile performance of the linear copolymers is distinctly superior to that of the highly branched analogs.

Stress relaxation of the copolymers is another mechanical property of practical interest for systems intended for structural applications. In light of the highly branched copolymer’s greater difficulty to entangle, the extent of stress relaxation in these materials is expected to be higher than in their linear analogs. The extent of stress relaxation of the copolymers addressed here is presented in Fig. 7.7 and it is quantified as the ratio of the absolute decrease in the stress at \( t = 10,000 \) seconds (\( ca. \) 3 hours) to the stress recorded immediately after the sample was first stretched. The samples were stretched to the two different strain levels, 25 % or 500 % and different samples were utilized for each test. A crosshead speed of 150 mm/min was utilized to reach the required strain. At both strain levels, as expected, the extent of stress relaxation in the highly branched PTMO based
copolymers is higher than in the linear analog. In addition, due to the absence of the end
capping moieties (CHI), which results in a reduced level of inter-molecular hydrogen
bonding in T-2H-no CHI, it displays higher stress relaxation than the CHI end-capped T-2H.
When we compare the T-2L and T-2H with P-2L and P-2H, we note that due to the ability of
PTMO to strain induce crystallize, the former two samples relax a smaller extent of their
initial stress as compared to the respective PPO-2200 based samples. Amongst the PPO
based samples, in general, at 25 % strain the extent of stress relaxation exhibited by the
highly branched PUUs is higher than the linear analogs. At 500 % strain, a similar trend can
be observed in the PPO-2200 and 4200 based copolymers. The sample, P-8H failed ca. 1000
seconds after it was stretched to 500 % strain, and the stress relaxation of P-12H could not be
measured because its extension at break of P-12H is only ca. 400 % (recall Fig. 7.5).

![Figure 7.7](image)

**Figure 7.7** Extent of ambient temperature stress relaxation in linear and highly branched
PUUs uniaxially elongated to 25 % and 500 % strain.

The mechanical hysteresis behavior of materials is also of practical importance and it
was utilized to further compare the linear segmented PUUs with their highly branched
analogs. The mechanical hysteresis of the PTMO and PPO based copolymers during two
consecutive cycles to 25 % and 500 % strain is presented in Figs. 7.7a and b respectively. In
general, at both strain levels the mechanical hysteresis during cycle 1 is greater than during
cycle 2. Such behavior is not surprising due to the fact that once the original microstructure becomes disrupted during the first cycle it does not have enough time to completely ‘heal’ before the next cycle is initiated. At 25 % strain, as expected, the mechanical hysteresis of linear PTMO-2000 and PPO-2200 based PUUs is distinctly lower than their highly branched analogs. However, for the other PPO based materials the difference in the mechanical hysteresis between the linear and highly branched samples is not significant. Surprisingly, at 500 % (Fig. 7.8b) strain the percent mechanical hysteresis of the linear materials and their highly branched analogs are quite comparable. Such behavior indicates that the substantial disruption of the microstructure upon deforming the copolymers to 500 % strain apparently overrides differences in the entanglement density between the linear and highly branched materials. Interestingly, at 500 %, despite the strain induced crystallization of the PTMO-2000 SS in T-2L and T-2H, they display comparable mechanical hysteresis as their PPO-2200 based counterparts.

Figure 7.8 Ambient temperature mechanical hysteresis of linear and highly branched PUUs during cyclic deformation to 25 % and 500 % strain. Note: Cycle 2 was initiated immediately after the completion of Cycle 1.
7.4.5 Solution Viscosity And Implications For Processability

The above discussion on the comparison of the mechanical properties of the copolymers addressed in this chapter indicate that the tensile performance of the highly branched PUUs is, in general, lower than analogous linear PUUs with identical SS MW and overall HS content. The difficulty of the highly branched architecture to entangle is undoubtedly a major reason for such a difference in tensile properties. However, it is well known that in dilute solutions, the hydrodynamic volume of a branched polymer is lower than that of linear polymer of comparable MW. In addition, when the concentration of the polymer solution is increased such that it is in the concentrated regime, the lower entanglement density of branched polymers also lowers the viscosity of the polymer. Since a material of lower viscosity can be more easily processed, controlled incorporation of branching can be utilized to improve the processability of polymers. In order to investigate the effect of architecture on viscosity a cone-and-plate rheometer was utilized to measure the ambient temperature solution viscosity of selected PUUs addressed in this chapter. The results are presented in Table 7.3.

Table 7.3 Ambient temperature solution viscosity (15 wt % in DMF) of selected linear and highly branched PUUs. The sample’s \(<M_w>\) values are also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(&lt;M_w&gt;) (g/mol)</th>
<th>Solution Viscosity (mPa.s)</th>
<th>Shear stress (mPa) linear up to shear rate (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2-L</td>
<td>222500</td>
<td>very viscous</td>
<td>-</td>
</tr>
<tr>
<td>T2-H</td>
<td>91900</td>
<td>410</td>
<td>500</td>
</tr>
<tr>
<td>P2-L</td>
<td>44900</td>
<td>79</td>
<td>3000</td>
</tr>
<tr>
<td>P2-H</td>
<td>111000</td>
<td>30</td>
<td>3000</td>
</tr>
<tr>
<td>P4-L</td>
<td>93450</td>
<td>1840</td>
<td>40</td>
</tr>
<tr>
<td>P4-H</td>
<td>147500</td>
<td>51</td>
<td>3000</td>
</tr>
<tr>
<td>P12-L</td>
<td>77300</td>
<td>550</td>
<td>80</td>
</tr>
<tr>
<td>P12-H</td>
<td>53200</td>
<td>27</td>
<td>3000</td>
</tr>
</tbody>
</table>

Note: The solution viscosity values are averages of three to four repeat runs. The standard deviation is less than ± 7 %.

The Newtonian (zero shear) solution viscosity of a given sample was determined from the slope of the linear region of the shear stress versus shear rate plot; the upper shear rate limit
of this linear region (before the onset of shear thinning) is also listed in Table 7.3. The PTMO based linear sample was too viscous for the instrument to measure. In light of its substantially high overall $<M_w>$ such behavior is not surprising. However, the solution viscosity of T-2H was measured to be 410 mPa.s. The lower solution viscosity of T-2H is believed to be primarily due to the reduced entanglements of its highly branched molecules. The lower overall $<M_w>$ of T-2H is also expected to be a contributing factor. On the other hand, the solution viscosity of the linear samples based on PPO-2200 as well as PPO-4200 is higher than its highly branched analogs despite the significantly higher $<M_w>$ of P-2H. Such behavior provides further support to the argument that polymer chains with a highly branched architecture encounter considerable difficulty to entangle in the semi-dilute regime and consequently the reduced entanglement density of the highly branched polymers lowers their solution viscosity.

7.5 CONCLUSIONS

In conclusion, the solid state structure-property behavior of truly highly branched segmented PUUs, synthesized by the oligomeric $A_2+B_3$ methodology, was compared with their linear analogs. The two-step prepolymer route was utilized to synthesize the latter materials. While the HS content of the copolymers was maintained constant at 28 wt %, the SS type (PPO or PTMO), its MW, and MWD were changed in order to investigate the effect of the SS structure on the behavior of the linear and highly branched PUUs. The effect of intermolecular hydrogen bonding in the highly branched PUUs was also investigated.

DMA indicated that all the copolymers addressed in this chapter possessed a microphase morphology. The breadth of the SS glass transition and the SS $T_g$, as determined from the peak position of the samples’ $\tan\delta$ response, was nearly identical for a given set of linear PUUs and its highly branched analog. However, the SS $T_g$ systematically moved to lower temperatures as the SS (PPO) MW increase due to the comparatively fewer restrictions imposed on the longer PPO SS. The systematic decrease in SS $T_g$ with increasing SS MW may also indicate a potential improvement in the extent of microphase separation. In addition, the upper temperature limit of the rubbery plateau also increased with increasing PPO SS MW. In the linear PPO based samples such behavior arises due to the increasing
length of the HS and the ability of the SS to more effectively entangle in samples based on PPO ($M_c$ 7700 g/mol) of MW 8200 and 12200 g/mol. While the latter point is also expected to be applicable for the highly branched samples, the improved upper temperature limit stability of the rubbery plateau in the highly branched PUUs is not fully understood at present.

SAXS confirmed the presence of a microphase separated morphology in these copolymers. In addition, a distinct weak second order interference shoulder in the SAXS profiles of the highly branched samples based on PPO of MW 8200 and 12200 were noted, indicating the presence of at least some long-range order of the hard domains in both these samples. Tapping-mode AFM phase images of the free surface of these two samples clearly confirmed the SAXS results. However, the type of packing of the hard domains in these samples could not be absolutely ascertained by SAXS due to the absence of further higher order interference peaks.

Another noteworthy result of this study was the observation of the strain induced crystallization of the SS phase in the PTMO (MW 2000 g/mol) based highly branched PUU at ambient temperature. A distinct strain hardening of this sample occurred above ca. 400% strain. The WAXS pattern of the sample, also deformed to ca. 400% strain at ambient temperature, clearly exhibited equatorial reflects due to the PTMO crystalline phase. Due to such behavior, the stress-strain response of the highly branched PUU was similar to its PTMO based linear analog. However, when the terminal functional groups of the former sample were not end-capped with a moiety that could establish intermolecular bidentate hydrogen bonding, the stress-strain response was markedly poorer as compared to its linear analog, although strain hardening could still be observed in the sample.

The stress-strain response of the PTMO or PPO based copolymers did not exhibit any yield point, thereby suggesting that at 28 wt % there was not sufficient percolation of the hard phase through the soft matrix. Tapping-mode AFM phase images of these samples further confirmed the lack of the hard phase percolation. In general, the stress-strain response, the extent of stress relaxation, and the mechanical hysteresis of the highly branched PUUs were poorer in comparison to their linear analogs, there being one exception. Surprisingly, the mechanical hysteresis of the highly branched PUUs at high deformation (500% strain) was comparable to the linear samples.
Ambient temperature solution rheological experiments indicated that the highly branched PUUs had significantly lower viscosity than their linear analogs. Thus, despite slightly poorer mechanical properties of the highly branched segmented PUUs as compared to linear analogs, the branched architecture are expected to be distinctly easier and more economical to process.