Chapter 4: Influence of Soft Segment Molecular Weight and Hard Segment Content on Structure-Property Relationships of Poly(urethane-urea)s

This first results chapter details the influence of varying soft segment molecular weight and hard segment content over a limited range on PUU elastomer morphology and properties. It reflects studies by other researchers conducted on PU and PUU elastomers with non-ultralow monol content PPG soft segments, principally PTMEG and conventional base catalyzed PPG. In addition to assessing the influence of soft segment length and hard segment content, this study provided insight with respect to morphological, mechanical, and thermal property trends in PUUs. This insight is essential to understanding the work presented in subsequent chapters. As stated previously, much of work presented in this chapter is drawn from a manuscript submitted to and accepted by the Journal of Applied Polymer Science. Dr. Bruce Lawrey, who provided materials and synthesis information, and Professor Garth Wilkes were co-authors of that manuscript. Redundant elements relating to experimental procedure and nomenclature, previously described in Chapter 3, have been omitted for brevity.

Section 4-1: Overview

Structure-property relationships in poly(urethane-urea)s synthesized with ultra-low monol content poly(propylene glycol) soft segments were investigated as soft segment molecular weight (2000, 4000, and 8000 g/mol) and hard segment content (6.3 and 9.0 wt%) were varied. Morphological features such as interdomain spacing and interphase thickness were quantified and revealed with SAXS and AFM. The thermal and mechanical behavior was assessed through application of DMA, DSC, and stress-strain tests. Hard segment content, over the limited range studied, had little effect on the morphology and soft segment thermal and mechanical properties. The molecular weight of the soft segments had considerably more influence on the morphology and mechanical properties. Increasing soft segment molecular weight resulted in greater interdomain spacings as seen by SAXS and a noticeable change in the structure shown by atomic force microscopy. Additionally, as soft segment molecular weight decreased, it was seen that the soft segment glass transition broadened and rose to higher temperatures.

Section 4-2: Introduction & Literature Review

The role of elastomers within the field of polymer science has been and is one of key importance. Elastomeric materials, and particularly synthetic elastomers, are virtually indispensable with regard to their myriad industrial, medical and consumer applications. They continue to make up a considerable portion of annual polymer production and sales.[1-4] Those elastomeric materials based upon poly(urethane) and/or poly(urethane-urea) chemistry have a rich history, both in terms of practical application and research.[1-19] Much of the insight gained through the study of poly(urethane) elastomers applies readily to poly(urethane-urea) elastomers as well.[9-10, 20]

To act as an elastomer, linear segmented poly(urethane-urea) copolymers must consist of a sequence of alternating blocks. One of these blocks must possess a glass transition temperature below the use temperature. This first type of block is designated the soft block or segment and is commonly a polyether or polyester. The second variety of block is required to have a glass transition above the use temperature and therefore acts as a hard glassy material and is known as the hard block or segment. It is also possible to affect elastomer behavior by being below the melting temperature of the hard segments in those instances when the hard segments are crystallizable. However, within this study, it was observed with wide angle x-ray scattering (WAXS) and differential scanning calorimetry (DSC) that the hard segments, and in fact the elastomer on the whole, did not appear to possess crystallizability. In most cases, the soft and hard segments are chemically incompatible and would phase separate were they not covalently linked to one another.[5,20] However, hard and soft segments will aggregate with their own kind, forming phases rich in hard and soft segments respectively.[20] Phase separation behavior is chiefly dependent upon temperature, composition, and segmental molecular weight. The physical network resulting from this morphology possesses many attributes of conventional covalently crosslinked rubber.

Many variables govern the behavior of physically crosslinked networks including, though not exclusively, the volume fractions of each segment, the chemical composition of each segment, the molecular weight and molecular weight distribution of each segment, and many processing variables. These variables affect the morphology of the elastomer, which in turn influences mechanical properties. In terms of materials using polyethers for the soft segments, there exists a formidable volume of literature on the use of poly(tetramethylene oxide) and to a lesser extent poly(ethylene oxide) and poly(propylene oxide) polyols. However, the majority of previous studies into the structure-property behavior of elastomers using the propylene oxide based polyether polyols (PPG) for soft segment material employed PPG synthesized through a base catalyzed reaction scheme for which it was found that quality elastomers were difficult to obtain.[1,3-4,13-14,21-23] This difficulty arose largely from the high monol content within the polypropylene glycol. It is well known that not only does the base catalyze the addition of propylene oxide to the growing polyol molecule, but it also catalyzes a side reaction involving the isomerization of propylene oxide to allyl alcohol. Since allyl alcohol acts as a new monofunctional starter, its hydroxyl group is propoxylated along with the growing polyol chain. The relatively low molecular weight propoxylated allyl alcohol is monofunctional and known as "monol".[3-4] Monol acts as a chain terminator, disrupting the chain reaction required to build a high molecular weight polymer. Thus as the monol content increases, the functionality of the polyol decreases. The effect of reducing polyol functionality on limiting an elastomer's theoretical molecular weight can be estimated from the Carothers equation.[24] As monol content rises, the ultimate molecular weight of any segmented elastomer formed from the macroglycol is diminished, as seen in Figure 2-5 for a 2000 g/mol PPG based elastomer. Hence the ultimate mechanical properties suffer dramatically.[3-4] Considerable improvement in lowering the monol content (Table 4-1), narrowing of the molecular weight distribution, and increasing the molecular weight of the polyol was achieved with the development and use of double metal cyanide (DMC) catalysts.[25-27] However, economically useful high performance elastomers were still difficult to obtain. In the early 1990s , ARCO Chemical developed a catalyst system allowing for the efficient production of atactic

Table 4-1. Monol Content of Conventional and Ultra-low Monol PPG.[33]

Polyol	Unsaturation or Monol (meq/g)	Functionality	Mole % Monol
1000 MW Diols			
• Conventional (KOH)	0.011	1.989	1.1%
• Ultra-low Monol	0.004	1.996	0.4%
2000 MW Diols			
• Conventional (KOH)	0.03	1.94	6%
• Ultra-low Monol	0.005	1.99	1%
4000 MW Diols			
• Conventional (KOH)	0.10	1.67	33%
• Ultra-low Monol	0.005	1.98	2%
8000 MW Diols			
• Conventional (KOH)	NA	NA	NA
• Ultra-low Monol	0.005	1.96	4%
12000 MW Diols			
• Conventional (KOH)	NA	NA	NA
• Ultra-low Monol	0.005	1.92	8%

propylene oxide based polyols (marketed as Acclaim® polyols), with monol contents significantly lower than those produced with conventional DMC catalysts. These polyols have proven to be of greater utility in the development of polyurethane and poly(urethane-urea) elastomers. A comparison of the molecular weight distributions of conventional and ultra-low monol 4000 g/mol diols is shown in Figure 2-7.[3-4] The GPC trace of the conventional base catalyzed PPG polyol exhibits a second lower molecular peak due to monol. The rate of monol formation increases as the concentration of hydroxyl species in the reactor decreases.

It was the purpose of this specific report to investigate the structure-property relationships of a systematic series of poly(urethane-urea) elastomers based upon this new generation of low monol PPG polyether polyols. As alluded to earlier, most previous investigations involving PPG, and a number of other polyether polyols as well, have been limited to relatively low polyol molecular weight (e.g. $\leq$ 2000 g/mol), broad molecular weight distribution polyols, and elastomers suffering from the effects of higher monol contents. The present study stands apart from much of the previous work in this well studied area in that it examines higher quality elastomers based upon PPG polyols which contain little monol, have narrower molecular weight distributions (1.02-1.15), and may be of higher average molecular weight than previously investigated. The PPG based poly(urethane)s and poly(urethane-urea)s previously investigated were often either foams or low-end elastomers.[11-12,21-22] The elastomers produced with ultra-low monol PPGs have significantly enhanced properties in contrast to those based upon conventional base catalyzed PPG. This allows for the fabrication and use of PPG based poly(urethane-urea)s in areas previously thought unfeasible, such as higher performance elastomers and fibers.

Particular emphasis within this study will be devoted to the microphase separation characteristics, morphology, mechanical and thermal properties as a function of soft segment molecular weight and content. Subsequent publications will investigate the effect of polyol molecular weight distribution, variation of the type of polyol, as well as blends of polyols for use as soft segments.

In the present study, the molecular weight of the PPG soft segment was varied systematically for two different levels of hard segment content. Several experimental techniques were used to characterize these materials including small x-ray scattering (SAXS), atomic force microscopy (AFM), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and a variety of bulk mechanical tests. As noted earlier, it is feasible that these poly(urethane-urea)s may prove useful in fiber applications, such as spandex. Therefore, although the present work was done exclusively on film samples, much of the mechanical property evaluation was conducted using fiber testing protocols.

Section 4-3: Experimental-Materials

In this study, six different model poly(urethane-urea) elastomers were examined, three for each of two different levels of hard segment content. The hard segment contents were calculated on the basis of urea content, as described by Flory (Eqn 3-1). It was felt that this method best represents the material residing in the hard phases.[17] As can be seen, *Eqn 3-1. considers only the portion of isocyanate, which reacts with amine* , whereas hard segment contents are often calculated to include the urethane linkages connecting the soft and hard segments (Eqn. 3-2.). Eqn. 3-2 leads to higher values of hard segment content. The calculated hard segment contents obtained using both of the methods are shown in Table 4-2. The two hard segment levels, as calculated by Eqn 3-1., chosen for this study were 6.3 wt% and 9.0 wt%. At each of these levels, three poly(urethane-urea)s based upon 2000 g/mol, 4000 g/mol, and 8000 g/mol PPG polyols were synthesized. The hard segments are comprised of MDI and a blend of 80 wt% ethylene diamine (EDA) and 20 wt% propylene diamine (PDA). The synthesis of the materials and sample nomenclature used in this study was previously described in Section 3-1. The compositions of the materials used within this study, as well as the sample nomenclature, are

Table 4-2. Sample Nomenclature and Hard Segment Contents

PPG Soft Segment MW	NCO/OH ratio	Wt% Hard Segment Content (urea)[a]	Wt% Hard Segment Content (urea and urethane)[b]	Sample Nomenclature
2000	1.48	6.25	16.67	{(P2K)}-2K-6.3
2000	1.71	8.98	19.09	{(P2K)}-2K-9.0
4000	1.907	6.25	11.77	{(P4K)}-4K-6.3
4000	2.342	8.98	14.34	{(P4K)}-4K-9.0
8000	2.856	6.25	9.04	{(P8K)}-8K-6.3
8000	3.713	8.98	11.62	{(P8K)}-8K-9.0

a) Calculated using Equation 1.
b) Calculated using Equation 2.

tabulated in Table 4-2. The polyols used in this study had monol contents as shown in Table 4-1 and the prepolymers formed from them had rheological properties similar to those shown in Table 4-3, which summarizes the effects of stoichiometry and polyol molecular weight on prepolymer viscosity as determined with a concentric cylinder DV III Brookfield viscometer, using either a 25 or 34 spindle. The trends are similar to those observed in previous MDI elastomer work, however the NCO contents are lower than those typically used in making cast elastomers.[3-4] As expected, for a given polyol molecular weight, prepolymer viscosity decreased as the NCO/OH ratio increased (% free NCO increased). As is well known, many higher performance poly(urethane-urea) elastomers and spandex fibers have PTMEG soft segments, so it is instructive to contrast the properties of such systems to those currently being studied. It was seen that, for comparable number average molecular weight polyols and NCO/OH ratios, PPG-based prepolymers generally have lower solution viscosities than PTMEG-based

Table 4-3. Viscosities of Prepolymers Used in Poly(urethane-urea) Synthesis.

Polyol	$\frac{NCO}{OH}$	% NCO	Viscosity @ 40°C	Viscosity @ 60°C
2000 g/mol PPG[#]	1.7	2.24	20,100	5,290
2000 g/mol PPG[#]	1.85	2.73	12,580	3,430
4000 g/mol PPG[%]	1.7	1.22	29,540	9,698
4000 g/mol PPG[%]	2.35	2.28	8,140	2,780
4000 g/mol PPG[%]	2.6	2.79	5,740	1,960
4000 g/mol PPG[%]	2.85	3.15	4,400	1,520
2000 g/mol PTMEG *	1.7	2.30	194,360	54,290
2000 g/mo PTMEG w/ 10 wt.% 4000 g/mol PPG	1.7	2.07	127,570	41,120
2000 g/mo PTMEG w/ 40 wt.% 4000 g/mol PPG	1.7	1.80	85,540	27,470

ACCLAIM 2200 (Bayer's ultra-low monol PPG-2000)
% ACCLAIM 4200 (Bayer's ultra-low monol PPG-4000)
*T-2000 = Terathane®-2000 (DuPont's PTMEG-2000)

prepolymers (Table 4-3). The advantages of lower prepolymer viscosity include easier handling, processing, and higher solids content for comparable viscosities.

Solutions of 22 wt% solids in DMAc were prepared for polymers formulated from 2000 and 4000 g/mol PPG polyols. At this concentration, it was found that polymers formulated from 8000 g/mol PPG polyols could undergo an association process in which a gel-like material was formed which was not conducive to film preparation. For this reason, the formulations based on 8000 g/mol PPG polyols were provided at lower (18% and 15%) weight percent solids for hard segment content levels of 6.3% and 9.0% respectively. Films were cast from the polymer-DMAc solutions upon glass plates using a doctor blade to achieve final (post-drying) film thickness ranging from 0.1 to 0.30 mm. Immediately upon casting, the coated glass plates were placed within a circulating hot air oven heated to 80°C for a period no less than 2 hours. A similar procedure was used to coat thin films upon glass Fisherbrand® microscope slides for purposes of AFM analysis. Experimental procedure has been previously presented in Section 3-3.

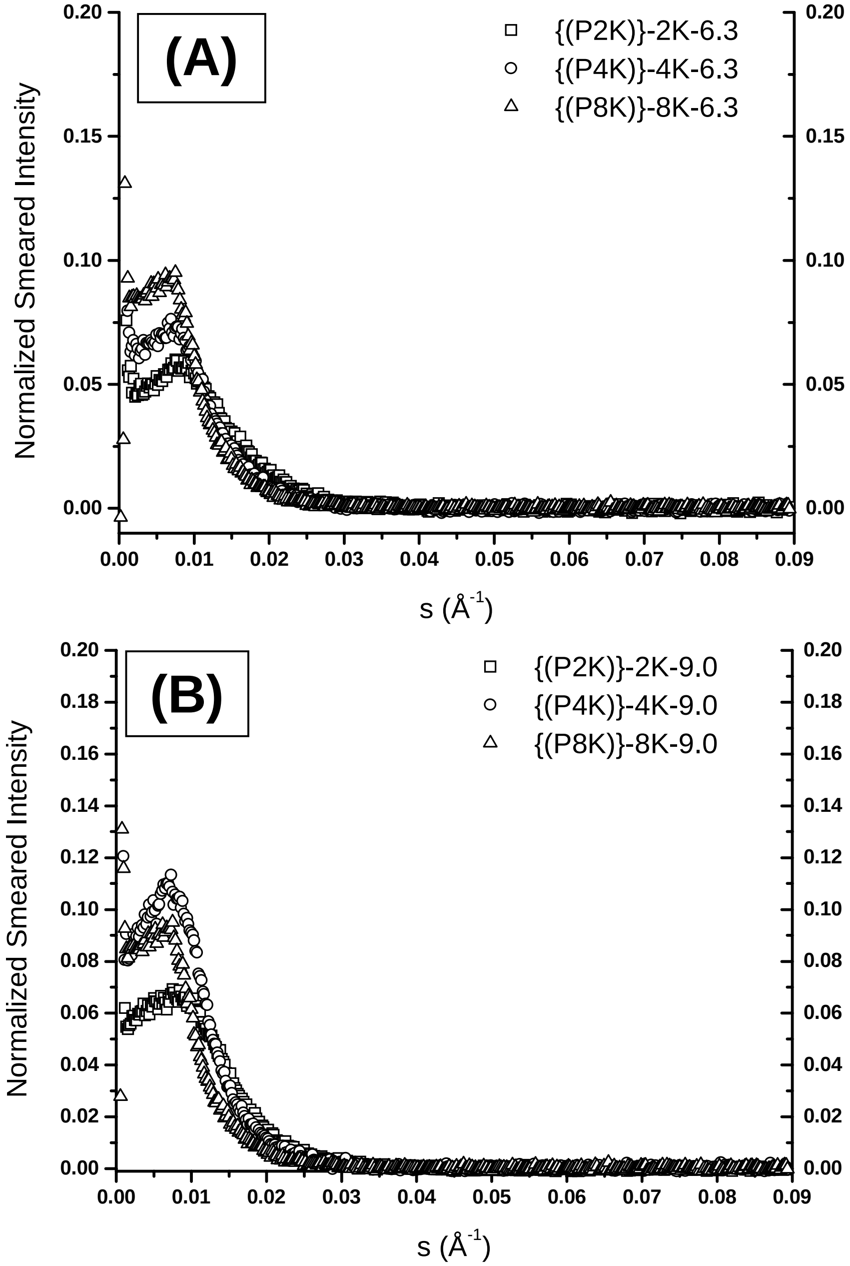


Figure 4-1. SAXS Curves for A) 6.3% and B) 9.0% Hard Segment Content Poly(urethane- urea)s

Section 4-4: Experimental Results

The interdomain spacings and interphase thickness parameters, obtained by SAXS are tabulated in Table 4-4 and the scattering curves are shown in Figs. 4-1a and 4-1b. Recall again, that the intensity data presented is slit-smeared. It is clearly seen from the two sets of scattering curves in Figs. 4-1a and 4-1b that the *estimated* spacing between hard domains increases with increasing soft segment length as expected, though there is little change (ca. 10 Å) in the spacing when comparing materials with differing amounts of hard segment content. It is intuitive that, as the length of the soft segment increases, the distance between the hard domains should also increase and these results reflect those obtained for other segmented poly(urethane-urea)s.[12,28-29] What is less intuitive is how hard segment content affects the interdomain spacing, for in only one case, that of the 8000 g/mol polyols, does the interdomain spacing significantly change as hard segment content is increased. The relatively minor increase in interdomain spacing seen for this case of hard segment content variation was from 160Å (6.3% HS) to ~175Å (9.0% HS). Further investigation is

Table 4-4. Interdomain Spacings and Interphase Thicknesses of PPG-based Poly(urethane-urea)s

Sample Designation	Inter-domain spacing, d (Å)	Interphase thickness, σ Koberstein (Å)	Interphase thickness, σ Bonart (Å)
{(P2K)}-2K-6.3	120	4.3	6.0
{(P2K)}-2K-9.0	120	3.7	5.0
{(P4K)}-4K-6.3	140	5.5	5.5
{(P4K)}-4K-9.0	145	3.9	5.6
{(P8K)}-8K-6.3	160	4.3	6.1
{(P8K)}-8K-9.0	175-180	4.2	4.8

required in order to ascertain the source of this change, though it may reflect the onset of significant change in morphology, such as formation of more cylindrical hard domains instead of a more spherical shape. In brief, for the range of hard segment contents in this study, when the hard segment content was increased there was generally no appreciable change in the interdomain spacing. Another feature of the scattering results is that there is an increase in the intensity of the scattering curves, as the molecular weight of the soft segment increases, which implies better phase separation between hard and soft phases. The intensity also rises as the hard segment content increases as expected in the range studied. However, due to changes in the electron density character of the elastomer, the interpretation is not as straight forward as when soft segment length increases for fixed hard segment content. The one exception to this observed trend, is the case of the material based upon the 8000 g/mol polyol and 9.0% hard segment content, which will be discussed in more detail shortly. It should be noted, that the increases in the intensity of the peaks in the scattering curves are not dramatic.

Estimation of the interfacial thickness parameter, σ, shown in Figures 4-2a and 4-2b, which provides a relative measure of the thickness of the interphase region between hard and soft domains, shows little statistically appreciable change in the interfacial thickness *as soft segment length is varied or as the hard segment content is varied*. This implies that for the ranges of these two variables studied, regardless of hard segment content or soft segment length, the interphase is essentially of constant thickness and it may be further hypothesized

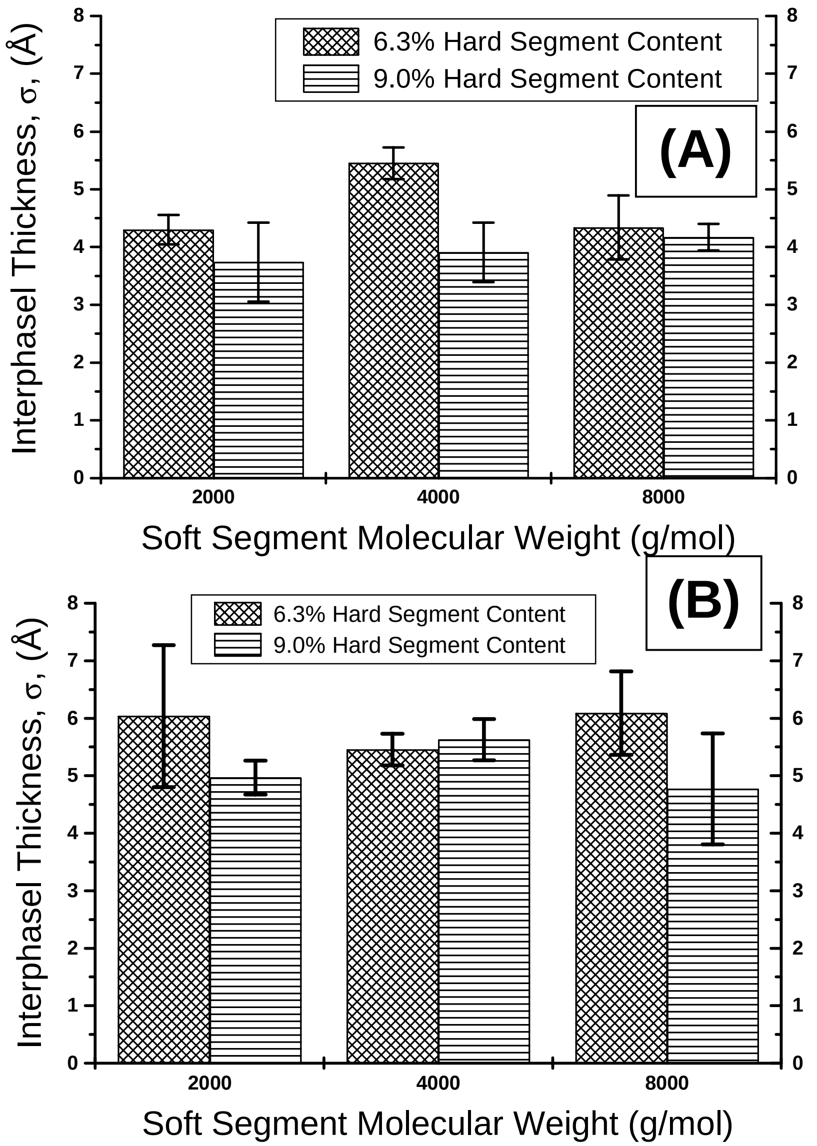


Figure 4-2. A) Interphase Thicknesses Using Koberstein's Method of Analysis and, B) Using Bonart's Method of Analysis

that for any given PPG polyol, a nearly constant portion of its length will be incorporated in the interphase. It should be noted, that the interfacial area is not directly measurable, and that due to this consideration, the amount of interfacial material could indeed be changing as soft segment length is varied. Certainly as the polyol molecular weight is increased, one would expect that there is a decreasing percentage of this segment to be mixed with hard segments in the interphase between hard and soft domains. Thus, it *would appear* that there would be better phase separation as polyol molecular weight increased and indeed that is suggested by Figures 4-2a and 4-2b.

It was noted during film sample preparation, that sample {(P8K)}-8K-9.0 was somewhat turbid suggesting that there may be some "gelled" material in this specific formulation of higher soft segment molecular weight. This phenomenon has been observed in other poly(urethane-urea) materials investigated outside of this study and has been attributed to association of longer hard segments in solution.[31] More will be discussed with regards to this subject when the atomic force microscopy results are presented below.

Tapping mode AFM was used to further verify the results obtained from SAXS and appropriate tapping strengths were determined by varying the ratio of set point to free air amplitude, r_{sp} (Figure 4-3). It was found that r_{sp} of 0.5-0.6 resulted in consistent, quality images. AFM phase images of the surfaces of the six formulations are shown in Figure 4-4, where the *darker areas are indicative of softer material and the lighter areas are indicative of harder material*.[30,32-33] The images support the trends observed and commented upon during the SAXS analysis. Specifically, as the hard segment content increases, there is a discernible, albeit not dramatic, increase in the amount of light colored region seen in the images, bearing in mind that the increase in the hard segment content was only 3wt%. Also, as the hard segment content increases, the distinction between light and dark regions appears more clear which may support findings of both the interfacial thickness analysis and peak intensity increases

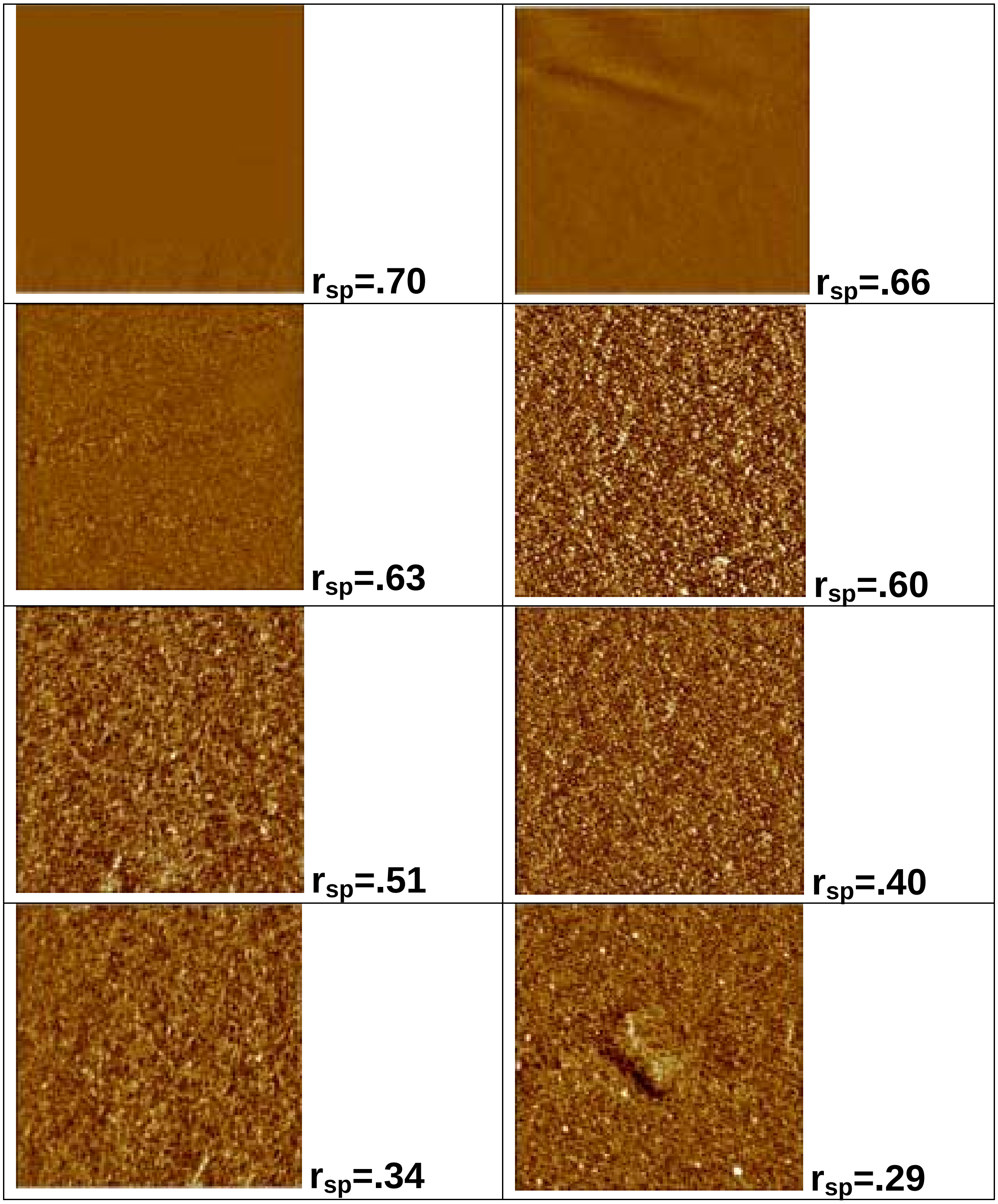


Figure 4-3. AFM phase images of {(P2K)}-2K-9.0, illustrating the influence of tapping strength. Ratio of set point to free air amplitude, r_{sp}, is shown for each.

seen in the SAXS experiments. Furthermore, as molecular weight of the polyol increases there distinctly exists a larger spacing between the light colored or

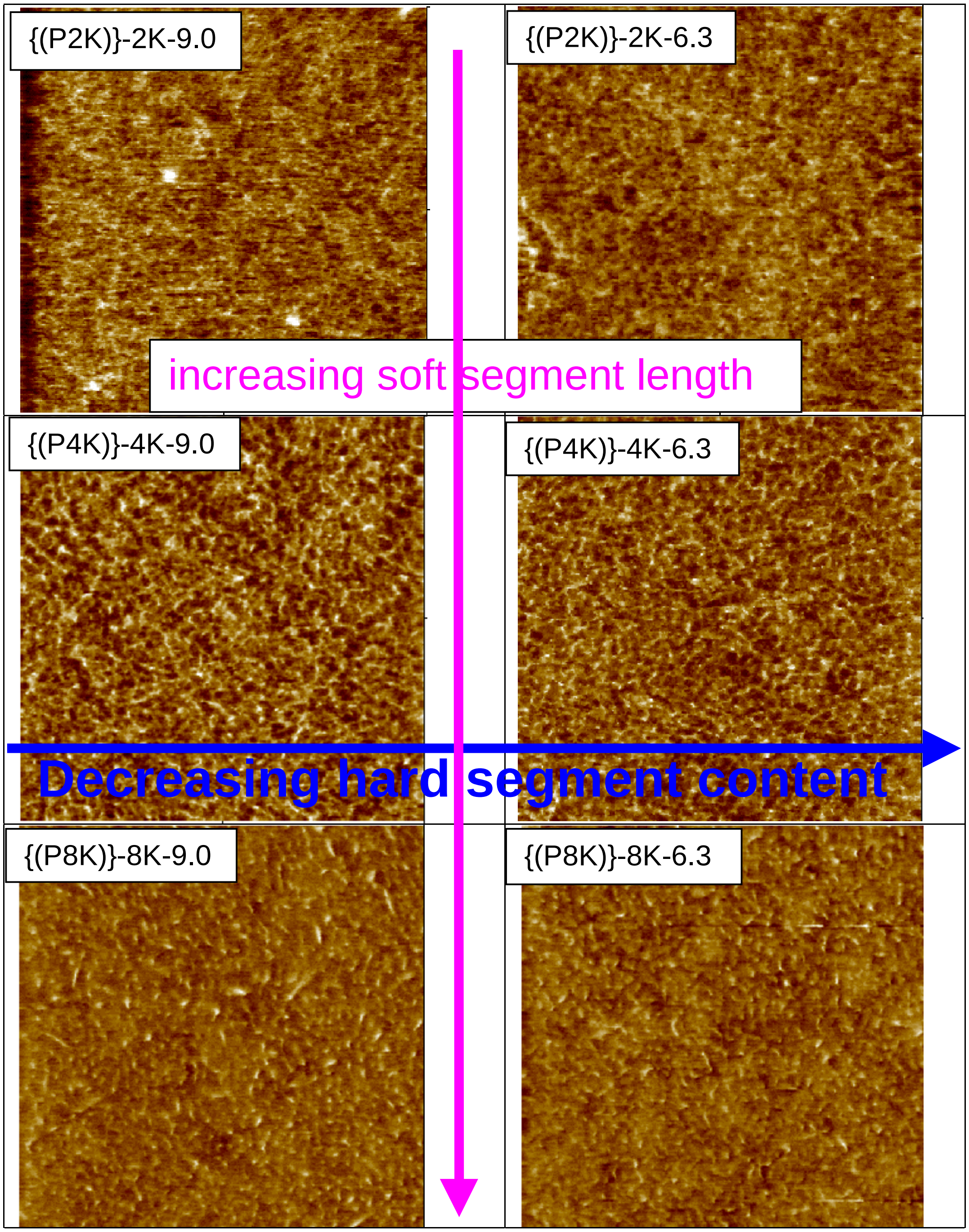
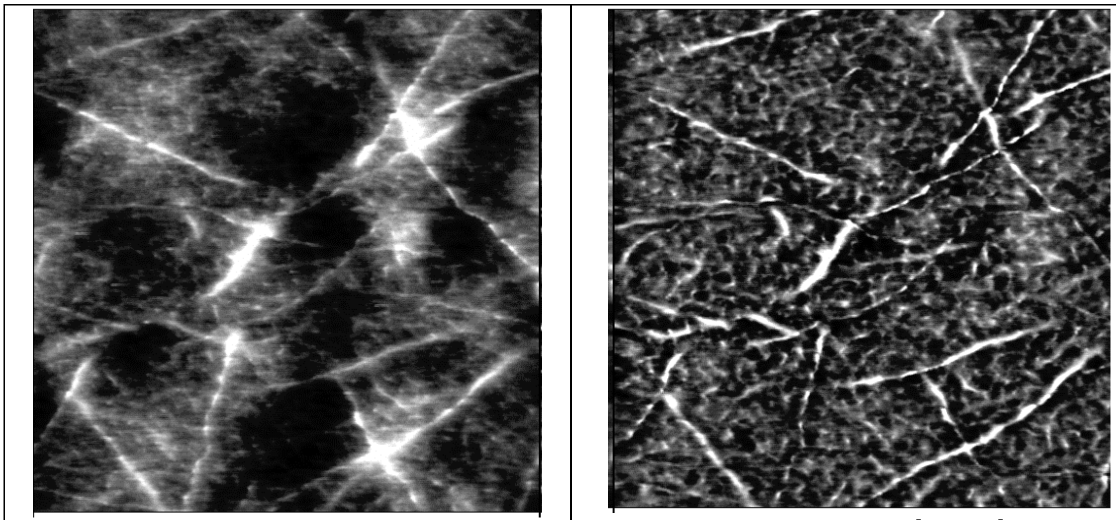


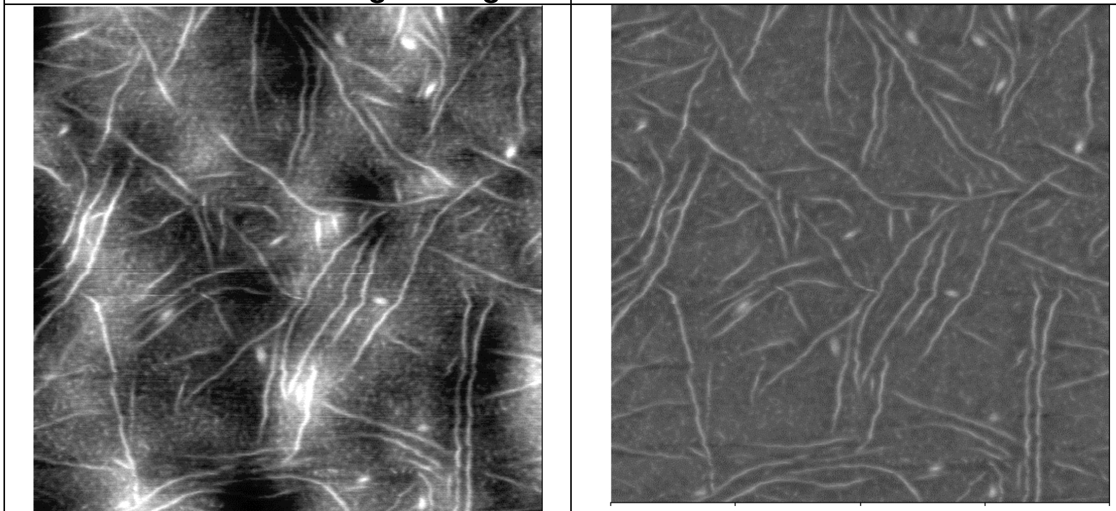
Figure 4-4. AFM tapping mode phase images (500 nm x 500 nm) of PUUs as function of HS content and SS length.

hard regions, confirming the trend seen with SAXS with regard to interdomain spacing. An interesting feature is again found in the image of the {(P8K)}-8K-9.0 material. In that image, there appear to be oblong regions of hard material that are not observed to any great extent in the other images. This is reminiscent of AFM images, shown in Figure 4-5, taken of a material of comparable composition, which was strongly suspected of having formed a hard segment based gel phase within solution. In this image, there exist “string-like” hard regions, which are believed to be the hard segment based "gelled" material, as



500 nm x 500 nm height image

500 nm x 500 nm phase image



1μm x 1μm height image

1μm x 1μm phase image

Figure 4-5. AFM of Hard Segment Gelled Material {(P8K)}-8K-9.0. Top set of images taken using relatively hard tapping (r_{sp} = ~0.55), bottom set of images taken using relatively soft tapping (r_{sp} = ~0.70)

well as the grain-like pattern present in AFM images of films cast from solution not suspected of having any "gelled" material. It is a reasonable supposition that , when reflecting upon thermodynamic and solubility considerations and the effects of increasing molecular weight with that of the length distribution of hard segments, it will be those of longer length that will be more apt to form into the string-like superstructures. If large amounts of longer hard segment material are isolated in these string-like superstructures, there will be by necessity shorter hard segments for the remaining nonstring-like or "typical" hard domains, which are more commonly encountered in this study. With a lower hard segment concentration and shorter hard segments to draw from, the circular appearing hard domains may be fewer and/or somewhat smaller. If there are fewer circular appearing hard domains, and if they are of the size seen when there are no string-like hard segment superstructures present, they would by necessity be further apart, which is in agreement with the slightly increased spacings observed with SAXS for the gel containing materials. It was also observed that these domains, when compared to AFM results where there are few or no string-like hard domains, show less tendency to be linked to one another with hard segment material. The results and conclusions regarding these string-like hard segment super-structures were further verified by examining a set of materials fabricated in a manner to intentionally include "gelled" material. These materials, shown in the lower set of images in Figure 4-5, were designed to facilitate hard segment association and strikingly exhibited string-like super-structures when examined with AFM.

The two methods, SAXS and AFM, lead to mutually supportive conclusions regarding the microphase separation characteristics. It should again be recalled that the SAXS results presented here are slit-smeared data. Hence the interdomain spacings obtained from SAXS are therefore, slightly larger than in reality and will not correlate directly to visual inspection of the corresponding AFM images.

Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were both used to follow the behavior of the soft segment glass transition as the soft segment length and hard segment content were varied. The breadth of the glass transition can provide insight into the phase separation behavior of segmented poly(urethane-urea)s, while the location of the glass transition may indicate how the hard domains restrict soft segment mobility. It is seen from the dynamic mechanical analysis shown in Figs. 4-6a and 4-6b, that a decrease in the molecular weight of the soft segment leads to both increases in and broadening of the soft segment glass transition temperature. The broadening of the glass transition implies greater restriction of the soft segments by the hard phase as soft segment molecular weight decreases and supports the conclusions already put forth in the discussion of the SAXS and AFM results. As soft segment molecular decreases, the percentage of the soft segment being restricted by the hard domain will increase, even though the actual length of that restricted portion of the chains will be essentially unchanged. To reiterate, as soft segment molecular weight was lowered, the intensity of the scattering peaks decreased, which is an indication of less complete phase separation. It was

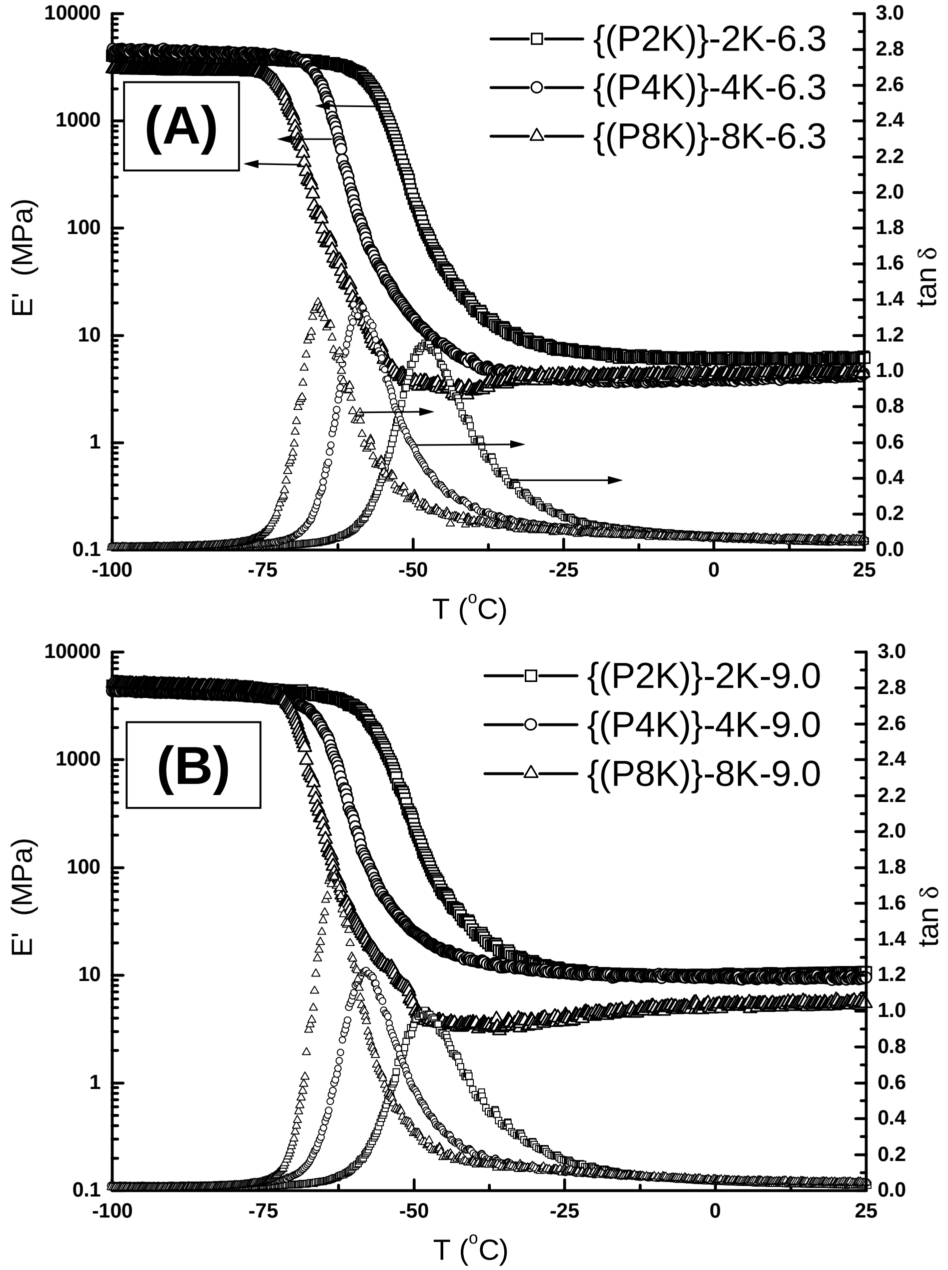


Figure 4-6. DMA of A) 6.3% and B) 9.0% HS Poly(urethane-urea) Elastomers

seen that the interfacial thickness parameter did not vary significantly as a function of soft segment molecular weight, implying that, regardless of soft segment length, there is a relatively constant interface in terms of thickness, with

Table 4-5. Soft Segment Glass Transition Temperatures of PPG-based Poly(urethane-urea)s

Soft segment MW (g/mol)	DMA #		DSC *	
	6.3% HS	9.0% HS	6.3% HS	9.0% HS
2000	-47.9 ºC	-48.1 ºC	-48.9 ºC	-49.7ºC
4000	-59.2 ºC	-58.0 ºC	-58.4ºC	-59.1ºC
8000	-65.9 ºC	-63.4 ºC	-62.3ºC	-62.3ºC

\# Determined from the peaks of the DMA tan delta curves
* Determined from inflection points of the T_g region of the DSC curves

again the possibility of more interfacial area or volume. Within this interfacial region, the soft segments will be more restricted in their ability to move due to a tethering action of the hard domains. For smaller segments (e.g. 2000 g/mol), a greater percentage of their overall length will be thus influenced or tethered, leading to the observed rise in the soft segment glass transition temperature as soft segment molecular weight decreases. Similarly, as a greater percentage of a given soft segment experiences restricted mobility, that soft segment will promote less damping, as shown by the peak height of the tan delta curves. It is readily seen that, as soft segment molecular weight is decreased, there is a corresponding broadening of and decrease of height in the tan delta curves which reflects upon the soft segment damping characteristics. There were only minor increases in the glass transition temperature as hard segment content was increased and increases in modulus were observed, as typically expected for materials of this nature. It has been seen that over the range of hard segment content studied, changes in microphase separation characteristics are relatively minor though observable. DMA tests appeared insensitive to anomalies associated with those formulations that potentially contained gelled material.

DSC, like DMA, is a useful tool for investigating the influence of soft segment length and hard segment content on the soft segment glass transition and its breadth, and as such was used to confirm the trends observed in the dynamic mechanical analysis. Figure 4-7 clearly shows that, as the soft segment molecular decreases, there is broadening of the glass transition, as well as a shift to higher temperatures, in accordance with the arguments put forth in the DMA discussion. Again, the broadening of the glass transition may suggest increased phase mixing or an increase in the amount of interphase material, which supports

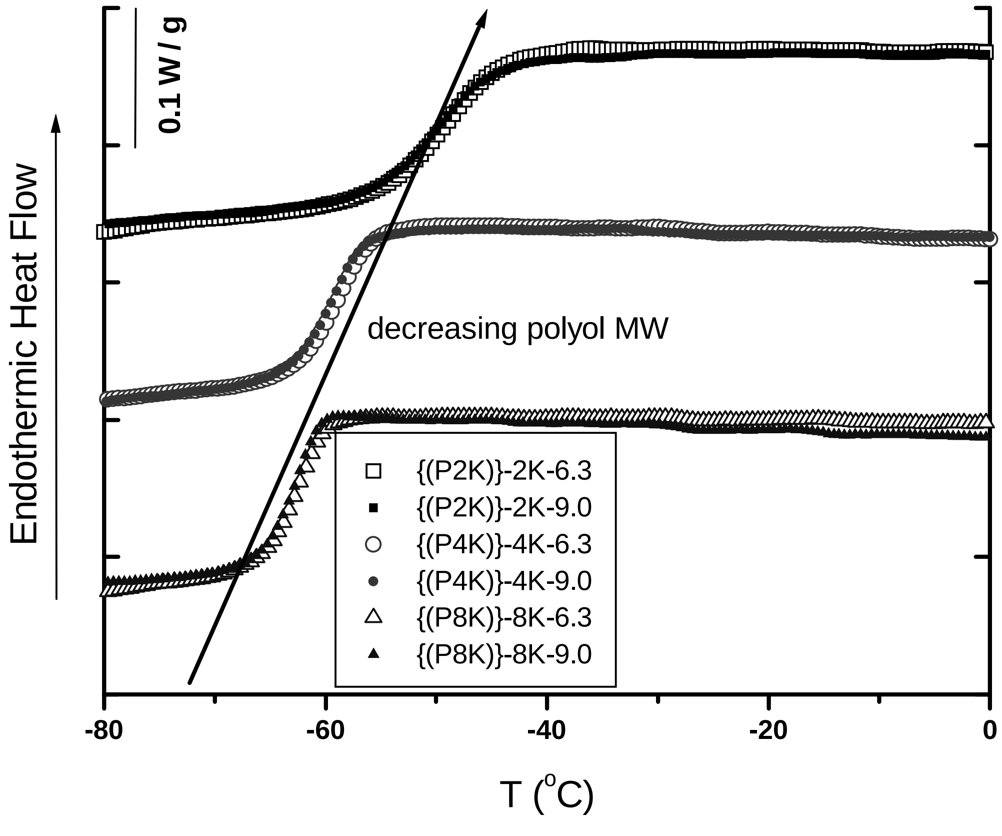


Figure 4-7. DSC of 6.3% & 9.0% HS Poly(urethane-urea) Elastomers

those results put forth in the SAXS, AFM, and DMA discussions. Increasing hard segment content from 6.3 wt% to 9.0 wt% does not appear to have a significant effect upon the breadth of the glass transition or its location, but again, it should be noted that the range of hard segment contents was in itself rather small. Studies by Petrovic on PPG based polyurethanes and PTMEG based polyurethanes have shown over a much greater range of hard segment content, 30 wt%-70 wt%, that the soft segment glass transition is only nominally affected by changes in hard segment content. [1-2] Sung and coworkers similarly found that, through a hard segment content range of ca. 25-55%, the soft segment glass transition in poly(urethane-urea)s based upon PTMEG soft segments was independent of hard segment content.[15-17]

Addressing the mechanical behavior, we observed for materials with less hard segment content that the percent elongation was greater and tenacity was lower. It was also seen that for most cases the percent elongation tended to increase as the soft segment molecular weight increased. These results, shown in Table 4-5., are in agreement with a number of the arguments already put forth, particularly that as soft segment molecular weight increased the hard domains influence a lower percent of the soft segment material (e.g. less interphase area or volume). Therefore, longer soft segments will be better able to respond to deformations and will lead to higher elongations. Similar arguments may be made for the decrease in percent elongation observed as hard segment content increased.

Table 4-6. Mechanical Properties of PPG-based Poly(urethane-urea)s

Sample	ULP @ 100% (MPa)	ULP @ 300% (MPa)	Tenacity (MPa)	% Elongation	30 Sec. Set (%)
{(P2K)}-2K-6.3	0.553	2.71	14.0	1686	33.3
{(P2K)}-2K-9.0	0.815	4.69	45.1	1115	33.8
{(P4K)}-4K-6.3	0.529	2.52	6.8+	1301+	26.4
{(P4K)}-4K-9.0	0.655	3.38	20.4	1816	28.1
{(P8K)}-8K-6.3	0.666	2.48	15.6+	1869+	13.9
{(P8K)}-8K-9.0	0.798	3.34	23.7	1602	13.6

+ Sample did not break at limit of crosshead travel

Two conclusions may be readily drawn from the 30s set experiments (Table 17). First, over the range studied, hard segment content had very little effect upon the 30s set . Second, set decreased as a function of increasing soft segment molecular weight, which is in accordance with the conclusions drawn from the structural, thermal, and mechanical characterization. Simply put, longer soft segments are less influenced by the restricting behavior of the hard domains and will be accordingly more capable of accommodating deformation without breaking and will retract more readily resisting set.

In all cases, the unload power (Table 17.) was seen to increase as the hard segment content was increased, though no clear trend due to variation in soft segment molecular weight was seen. Increasing hard segment contents over the range studied can be considered to be increasing the number and/or size of the physical crosslinks. Hence, the network nature of the poly(urethane-urea) would be enhanced, leading to the observed increased retractive power.

The stress-strain behavior of poly(urethane) elastomers fabricated with 4000 g/mol conventional base catalyzed, DMC catalyzed, and Acclaim PPG is shown in Figure 51 where it is seen that the ultimate tensile properties of the

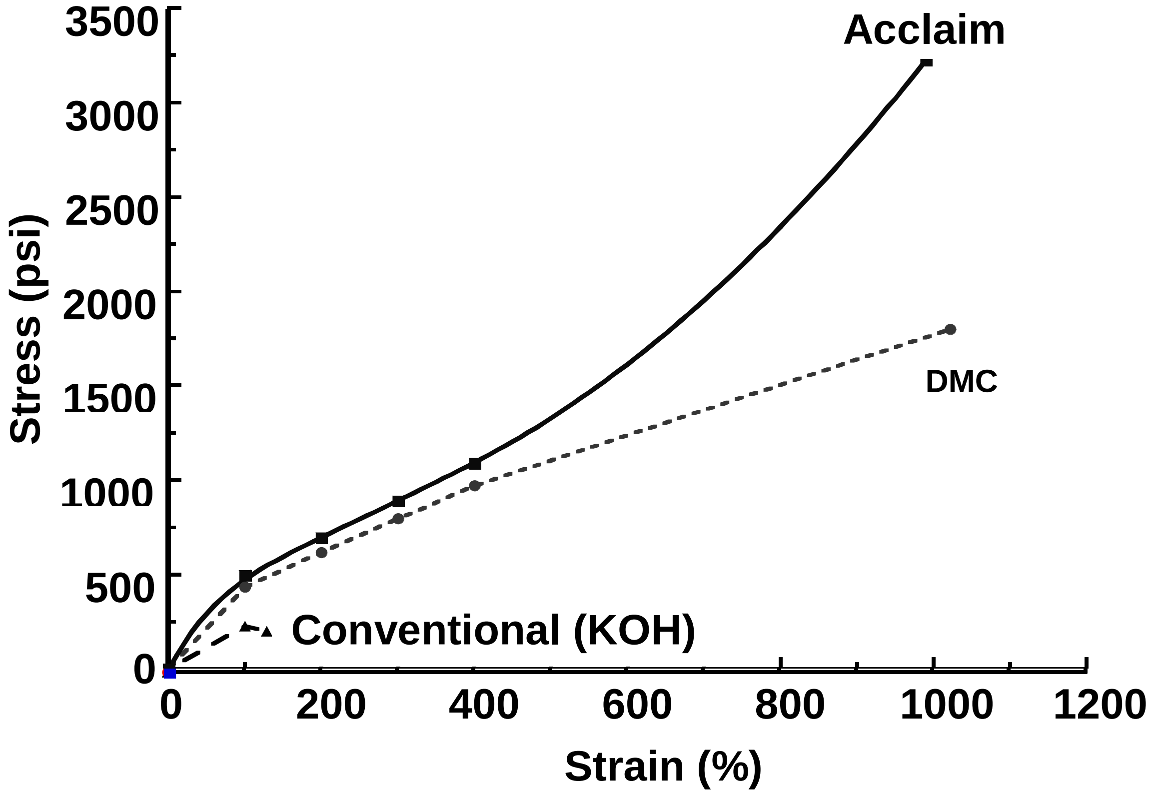


Figure 4-8. Stress-strain Curves of Different Poly(urethane) Elastomers With 4000 g/mol PPG-based MDI-endcapped Prepolymers, Cured With BDO.

Acclaim based elastomer are superior. In each case the poly(urethane)s are made with PPG-MDI prepolymers and extended with butane diol. The improvement over formulations using the base catalyzed PPG is dramatic.

Section 4-5: Conclusions

A series of model poly(urethane-urea) compounds based upon a narrow molecular weight distribution PPG polyol were developed and investigated with regards to their microphase separation, morphological, and mechanical characteristics. It was seen that increases in the molecular weight of the PPG soft segment led to increased phase separation which, in part, resulted in greater soft segment mobility and lower glass transition temperature of the soft segments. Furthermore, the presence of gelled hard segments was implied by an unexpected increase of the interdomain spacing as determined by SAXS and was clearly seen with AFM. The effect of varying the hard segment content was seen to be minor in much of the structural analysis, yet discernible, in comparison to the effect of varying the soft segment molecular weight. However, the mechanical properties, particularly the unload power, were seen to be dependent upon the hard segment content. It is apparent, from the discussion above, that developing useful elastomers from the ultra-low monol poly(propylene glycol)s will require careful consideration of the influence of chemical variables upon the morphology of the materials.

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