Chapter 7: Orientation Behavior of Ultra-low Monol Content Poly(propylene glycol) Soft Segment Poly(urethane-urea)s

The work presented in this chapter details investigations into the molecular and segmental orientation behavior of poly(urethane-urea)s with ultra-low monol content soft segments. Chapters four, five, and six were largely accounts of investigations of the morphology of the unoriented PUUs being investigated, and how the morphology influenced the mechanical and thermal properties. The studies detailed in the present chapter examine the elastomers' molecular behavior during deformation by monitoring molecular / segmental orientation.

Section 7-1: Overview

Poly(urethane-urea) elastomers with ultra-low monol content PPG soft segments were analyzed using birefringence and infrared linear dichroism to assess molecular and segmental orientation behavior during deformation as a function of soft segment molecular weight, hard segment content, hard segment type, and soft segment molecular weight distribution. The results extend from two broad groups of experiments. The first group consists of experiments in which the elastomers were deformed only a single time. The second group of experiments involve studies in which an elastomer is subjected to additional deformations beyond the first and investigates the effect of permanent set and residual orientation. The two groups of experiments were performed separately and there are appreciable differences in technique, as well as experimental complications, that are described in the section 7-3.

Section 7-2: Introduction & Literature Review

Segmented, microphase separated, poly(urethane-urea) (PUU) elastomers are, as a group of materials, important both commercially and scientifically and have been investigated extensively. The majority of this work has concerned the determination of elastomer morphology and the influence of compositional variables on thermal and mechanical properties. With respect to the copious amount of work performed in these endeavors, there has been relatively little investigation into the orientation behavior of PUUs.[1-15] Not surprisingly orientation can have a significant impact on the mechanical properties of polymeric films and fibers.[16]

As noted earlier (Section 2-13), orientational birefringence is unable to provide individual segmental orientation information and provides only the average molecular orientation for the PUU being studied. It has also been suggested that the measured birefringence of a microphase separated segmented copolymer is not explained solely by orientation effects.[3] Form birefringence may also contribute to the measured birefringence, though it is not expected to do so for the materials investigated. The isolated sphere-like hard domains in the materials of these studies are not expected to exhibit significant form birefringence. Still, the average molecular orientation as inferred from birefringence is useful in developing and supporting theories regarding PUU orientation. Infrared linear dichroism, as presented in Section 2-14, is capable of providing segmental orientation information in terms of specific segmental Hermans' orientation function, f. A number of infrared absorption bands useful for segmental orientation determination in PUUs have been tabulated in Table 6.

Absorbances are a function of the product of the extinction coefficient of a given moiety, the concentration of a given moiety, and the thickness of the specimen. It is preferred that the measured absorbances be less than 1.0 (10% transmittance) for quantitative work and less than 2.0 (1% transmittance) for qualititative comparisons. For moieties with high concentrations and high extinction coefficients (strong absorbing bands) sample thickness must be minimized to obtain good quantitative results. In contrast, weak absorbing groups in low concentrations may require thicker specimens to achieve acceptable signal to noise ratios. For soft segment orientation, bands associated with the ether linkage (ca. 1100 cm^{-1}) or methylene units (ca. 2970 cm^{-1}) are typically used.[3,5,6-8,12-14] Both absorbance bands are characterized as having strong absorption. Absorption bands associated with the carbonyls of the urea (ca. 1640 cm^{-1}) and urethane (1730 cm^{-1}) linkages are used for hard segment orientation in PUUs and PUs respectively. [3,5,6-8,12-14] These bands are not characterized as strong absorbing bands.[14]

Poly(urethane)s, poly(urethane-urea)s, and a number of other segmented block copolymers, display interesting hard segment orientation behavior when undergoing deformation that initially appears counter-intuitive. Upon initial deformation, the hard segments exhibit negative orientation with respect to the deformation direction! This phenomenon was noted by Bonart during x-ray scattering investigations of poly(urethane)s and poly(urethane-urea)s.[1-2] In addition to proposing that the hard segments form a three dimensional structure held together by bidentate hydrogen bonds (Section 2-4), he also hypothesized

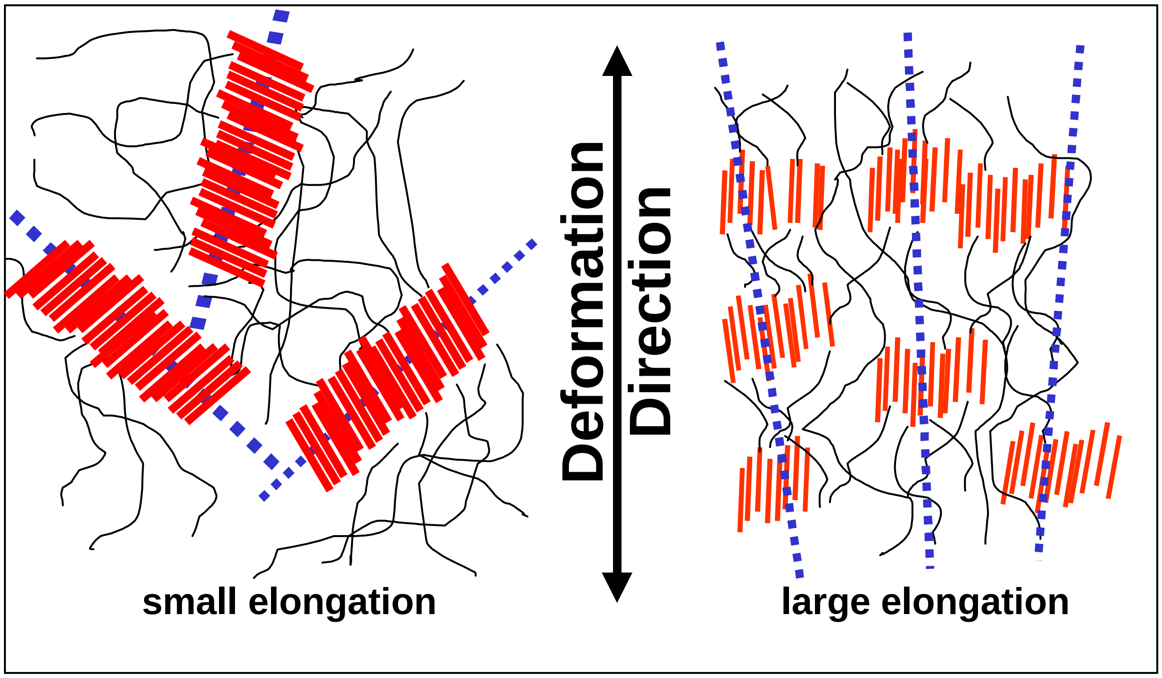

Figure 7-1. Hard segment orientation for small and large elongations.

that lath-like hard segments organize in a sheaf-like geometry which then orients as a whole in the direction of deformation (Figure 7-1).[1-2] Upon greater deformation this sheaf-like structure is ruptured and individual groups and/or single hard segments are then able to orient in the deformation direction (Figure 7-1). This hypothesis was supported and expanded upon by Cooper et al. and Ishihara et al. using infrared linear dichroism.[3-8] The initial negative orientation of hard segments has since been seen for poly(urethane)s and poly(urethane-urea)s of various and disparate composition, as well as for other segmented block copolymers, such as poly(butylene succinate)-poly(tetramethylene glycol).[3-9,12-13]

Section 7-3: Experimental

The samples for the first group of experiments were stretched using a manual stretching device which required the use of fine grain sand paper in the grips to prevent sample slippage during stretching. Films samples thinner than 1 mil in thickness had tendencies to develop tears near the grips during deformation. It was also limited to maximum elongations of 350% (DR=4.5) without remounting the samples. Remounting of sample required fixing the samples in a nested picture frame fixture (Figure 3-1), removing the fixed sample from the stretcher, remounting the sample, and finally removing the picture frame fixture. Elongations beyond 350% are therefore approximations and somewhat imprecise. It was found that thicker films survived the remounting process more reliably than thinner films. The samples were evaluated as they were stretched using infrared linear dichroism and birefringence. It was determined, using birefringence, that system average orientation did not appreciably increase with time when a sample was held fixed in a stretched state of 350% elongation (Figure 7-2).

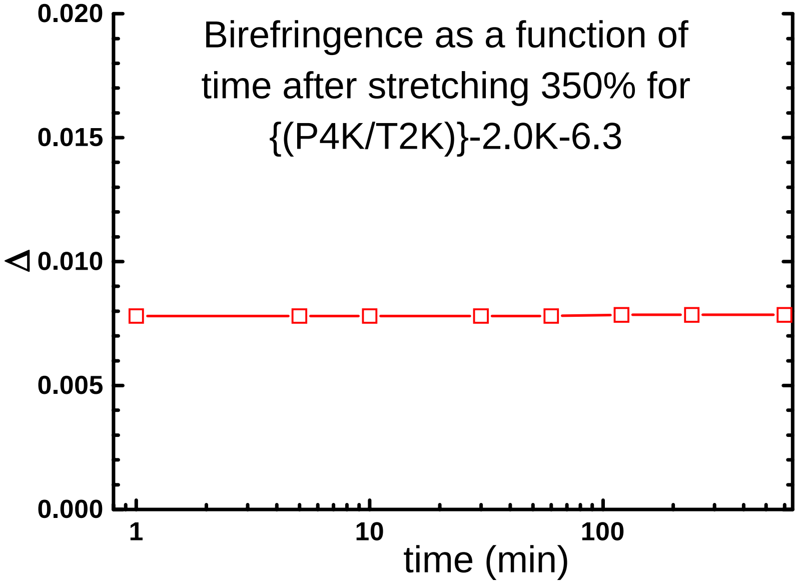

Figure 7-2. Time dependence of PUU birefringence after 350% elongation at ambient conditions.

The samples for the second group of experiments were stretched using an Instron to a desired elongation at which point they were fixed in a nested picture frame fixture and removed from the Instron. The samples were then evaluated by birefringence, infrared linear dichroism, and SAXS analysis (along the meridinal). After removing the samples from the fixture, set was measured at 30 seconds and 1 hour. Five minutes after removing from the fixture, the orientation of each sample was re-evaluated by birefringence and infrared linear dichroism. Those samples stretched to 600% elongation also had SAXS measurements performed on them in addition to birefringence and linear dichroism. An hour after removing the samples from the picture frame fixture, they are stretched a second time in the Instron and retested. A schematic of the testing procedure is

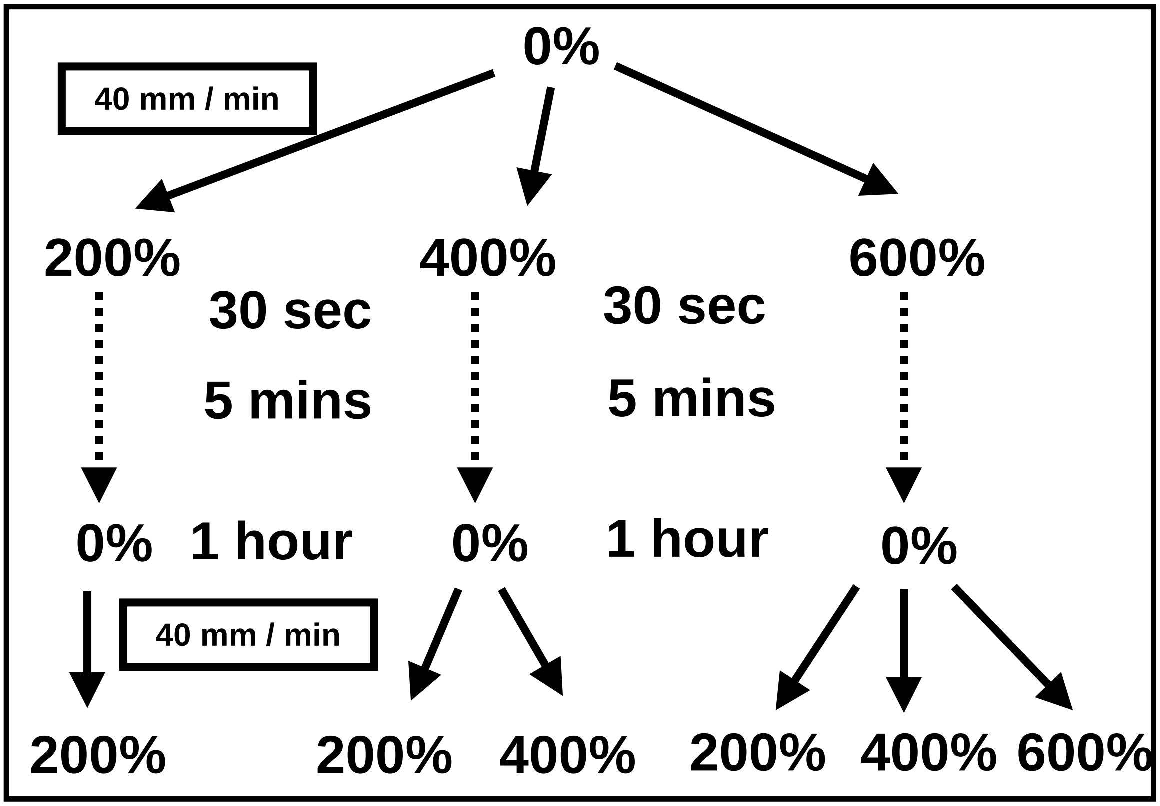

Figure 7-3: Stretching treatments for second group of orientation studies.

shown in Figure 7-3.

Evaluation of a single sample with the techniques listed above required choosing an appropriate sample thickness. It was found that sample thickness in the range of 1-2 mils were useful for birefringence, SAXS, WAXS, and hard segment orientation studies using linear dichroism. Samples of these thicknesses typically displayed absorbances well in excess of two for soft segment bands.. Depending upon initial thicknesses, at higher elongations (ca. 400+%), these samples became thin enough to conduct qualitative and in some instances quantitative linear dichroism measurements for soft segment orientation. Given that the soft segment glass transition temperature (-50C and lower) is well below room and typical use temperature, it was believed that hard segment orientation would play a significant role in development of mechanical properties. In addition, other researchers have seen that the hard segment orientation changes more appreciably than that of the soft segments for PUUs similar to ones in the present study.[12]

Section 7-4: Experimental Results

It was found using birefringence that changing the type of the hard segment by varying the ratio of ethylene diamine to propylene diamine chain extenders from 80:20 to 100:0, resulted in no significant changes in system average orientation (Figure 7-4). This was seen for formulations both with and without TPG. It is acknowledged that the range of hard segment types as defined by the chain extender ratio is somewhat limited. Additionally, it should be noted that formulations containing TPG exhibit greater birefringence, and by inference greater orientation.

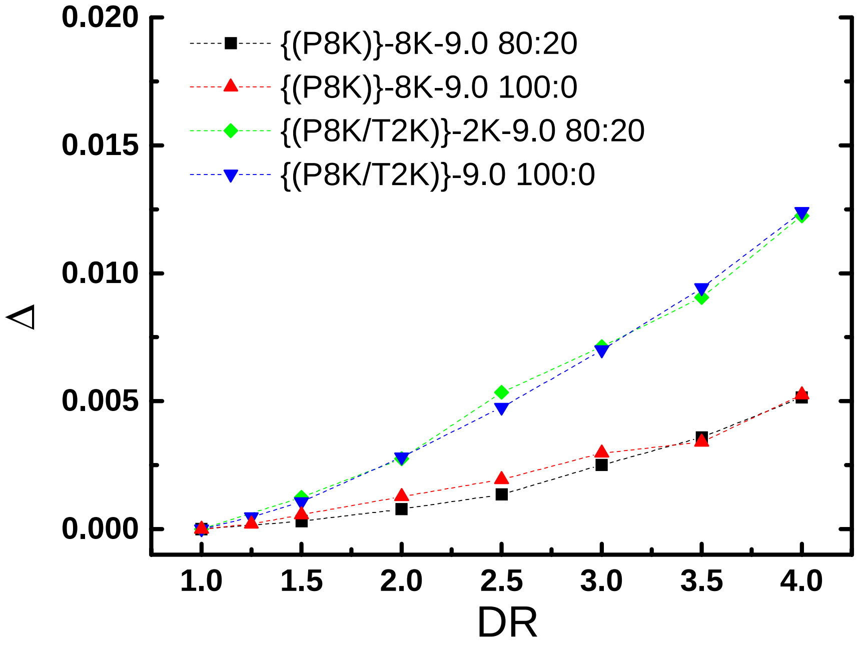

Figure 7-4: Birefringence of PUUs with hard segments of variable composition due to varying chain extender ratio of ethylene diamine to propylene diamine.

Decreasing soft segment molecular weight resulted in increased birefringence as shown in Figure 7-5. Also shown in Figure 7-5 is the influence of hard segment content on birefringence. It was seen that increased hard segment content resulted in increased birefringence and by inference higher system orientation. Recall from Chapters 4 and 5 that the molecular weight distributions of the various PPG polyols used in this study were all narrow (<1.1) and that accordingly 2000g/mol PPG polyols would have a more appreciable fraction of low molecular weight components than 4000 g/mol and 8000 g/mol PPG polyols. These low molecular weight diols can potentially act as urethane hard segment chain extenders, much as TPG was seen to do in Chapter 5. It is then consistent that the PUUs with low MW soft segments may exhibit similar orientation characteristics to PUUs with higher hard segment contents.

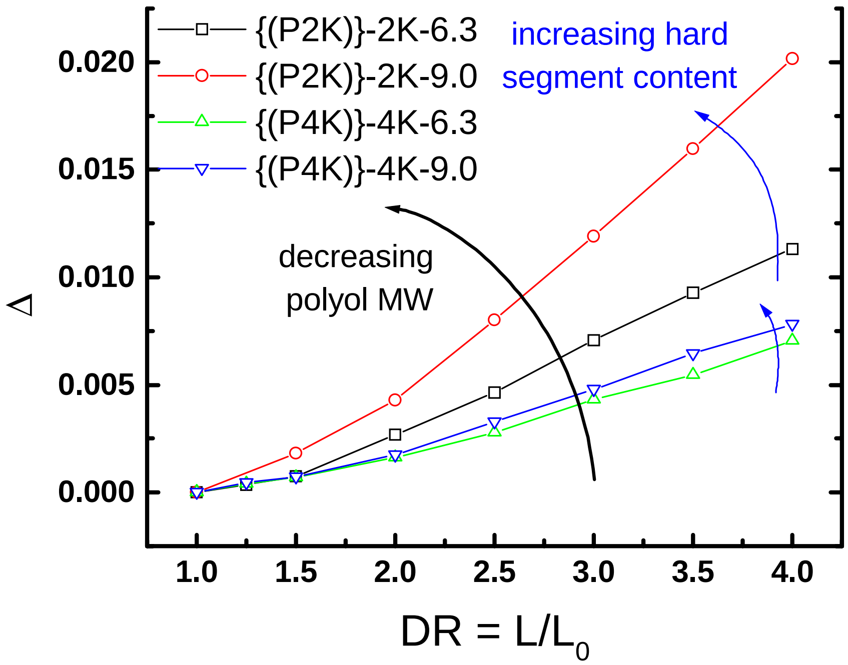

Figure 7-5: Influence of soft segment length and hard segment content on birefringence of PUUs.

Additionally, recall the argument put forth in the discussion of DMA and DSC results in Chapter 4 that as the length of a soft segment decreases, the fraction of that soft segment influenced by the hard domain will increase.. It also stands then that PUUs with shorter soft segments may show birefringence behavior similar to that seen for PUUs with greater hard segment content.

The results shown in Figures 7-4 and 7-5 support the arguments put forth in Chapter 5 regarding the role of the low molecular components of the polyol molecular weight distribution. Investigating that more explicitly (Figure 7-6), by varying the amount of TPG used in PUU formulations based upon 8000 g/mol PPG polyols, it was seen that as TPG content increases, so too does the birefringence. This is consistent with the interpretations of the data in Figures 7-4 and 7-5 as well as the work presented and discussed in Chapters 4, 5, and 6.

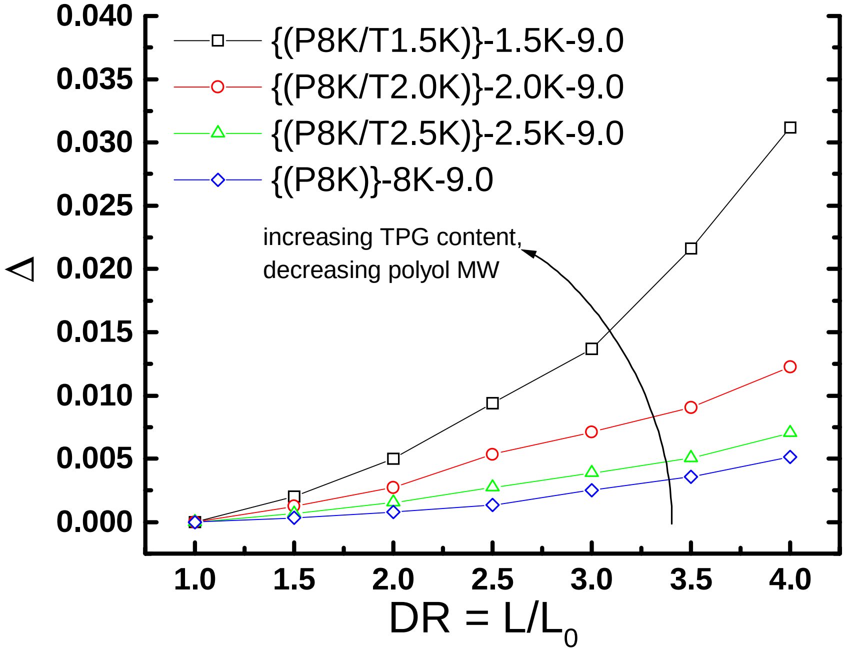

Figure 7-6: Influence of soft segment molecular weight distribution / TPG content on birefringence of PUUs.

From the birefringence results it was assessed that hard segment content was a key consideration when developing orientation in the PUUs being investigated. Accordingly, when forced to choose sample thicknesses for linear dichroism studies, thicknesses were chosen to facilitate obtaining hard segment orientation data.

Figure 7-7 demonstrates that by varying the hard segment content from 6.3 wt% to 9.0wt% there was no significant difference in hard segment orientation as denoted by the linear dichroism of the 1640 cm^{-1} urea carbonyl absorption. This is not surprising, since the hard domains are believed to be isolated as consequence of the relatively low levels of hard segment content. The initial negative orientation and subsequent upturn seen for the PUU hard segments is consistent with the conclusions of Bonart and work of Cooper et al and Ishihara et al.[1-8]

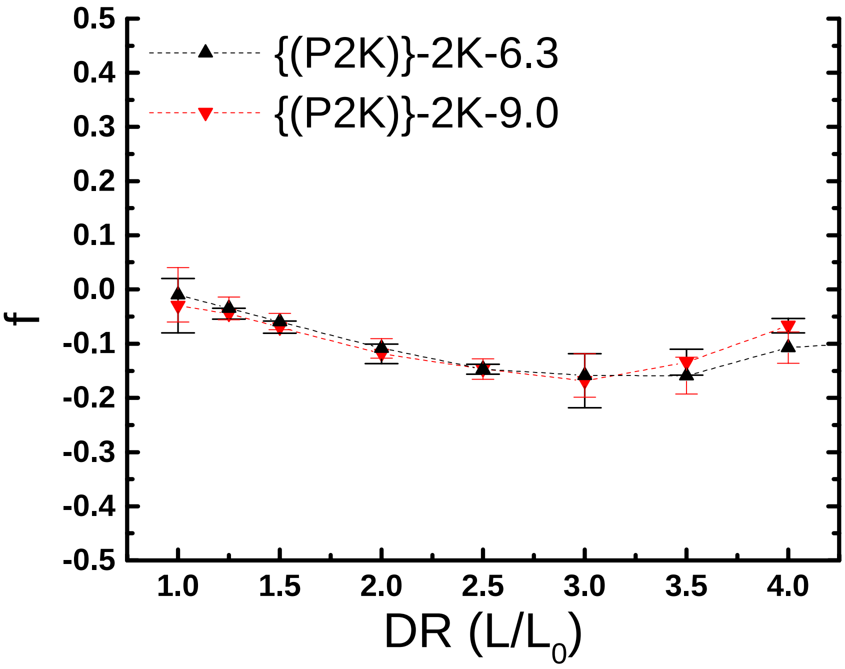

Figure 7-7: Hard segment orientation, as determined by infrared linear dichroism of 1640 cm^{-1} urea carbonyl absorption band, for PUUs with varying hard segment content.

Distinct differences in hard segment orientation behavior are noted when soft segment molecular weight is varied (Figure 7-8). To achieve the higher draw ratios shown, the samples required remounting as described in Section 7-3. Results for draw ratios above 4 are therefore less reliable for quantitative evaluation. It is seen that the hard segments of the PUU based upon a 2000 g/mol soft segment oriented less negatively than those of the 4000 g/mol and 8000 g/mol PUUs. Mechanical property results in Chapters 4 and 5 also revealed that 2000 g/mol PUUs displayed upturns in stress-strain plots at appreciably lower elongations than 4000 g/mol and 8000 g/mol based PUUs. If the hard segments are orienting in the direction of deformation more readily or quickly in lower MW soft segment systems (Figure 7-8) this may contribute to the increase in tensile strength seen in Figure 5-10. Another interesting feature of

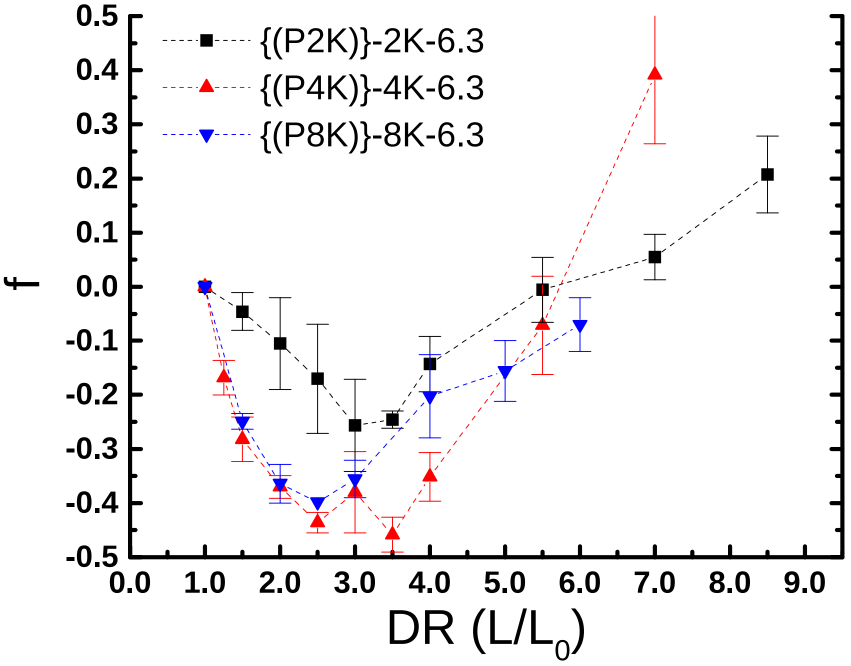

Figure 7-8: Hard segment orientation, as determined by infrared linear dichroism of 1640 cm^{-1} urea carbonyl absorption band, for PUUs with varying soft segment length.

Figure 7-8, is that it appears that the draw ratio at which the hard segment orientation becomes positive decreases for decreasing soft segment molecular weight. Longer soft segments linking the hard domains together likely allows for greater hard domain mobility during deformation. With increased ability as a domain to adjust to deformation, some hard domains may be able to resist shearing apart. However this interpretation is complicated by the magnitude of measurement error and is not particularly conclusive.

Inclusion of TPG in the formulations apparently results in a combination of the phenomena seen described above (Figure 7-9). The three formulations based upon 8000 g/mol PPG blended with TPG investigated behave similarly in terms of the magnitude of negative orientation, which is less than that seen for a

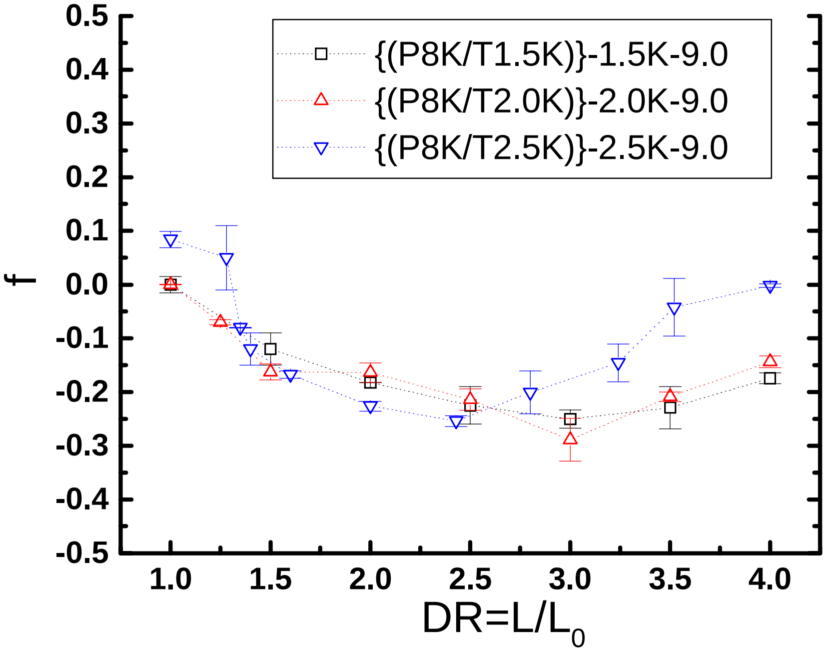

Figure 7-9: Hard segment orientation, as determined by infrared linear dichroism of 1640 cm^{-1} urea carbonyl absorption band, for PUUs with varying soft segment molecular weight distribution / TPG content.

8000 g/mol PPG-based PUUs without TPG. The TPG containing systems behave more like a 2000 g/mol PPG-based PUU with regards to the magnitude of negative orientation as well as exhibiting similar stress-strain properties (Figure 5-10). However, the TPG containing formulations behave more like an 8000 g/mol PPG-based PUU when considering the point at which they show positive orientation. This tendency reflects the soft segment glass transition behavior seen with DMA and DSC in Chapter 5, adding further credence to the argument that TPG, and other low MW components of the MWD, act as hard segment chain extenders.

It has been seen that the birefringence is seen to increase in all cases even though the hard segments exhibit negative orientation. Birefringence is a system average measure and includes contributions from both hard and soft segments. There is a modest increase in the slope of the birefringence beginning around draw ratios of 2.5-3.5 (Figures 7-4, 7-5, & 7-6). This corresponds to the range in which hard segment orientation is seen to begin increasing in linear dichroism experiments (Figures 7-7, 7-8, & 7-9).

The second group of experiments was conducted in response to the results seen in Figure 7-10. Samples were stretched to draw ratios of 5.0 and held at that extension for 3 hours before removing them from the stretcher and allowing them to relax for 15 minutes. After 15 minutes relaxing in an unstretched state, they were remounted in the stretcher and re-evaluated. It appeared that some degree of residual hard segment orientation existed in the material after the 15 minute period of relaxing in an unstretched state. The

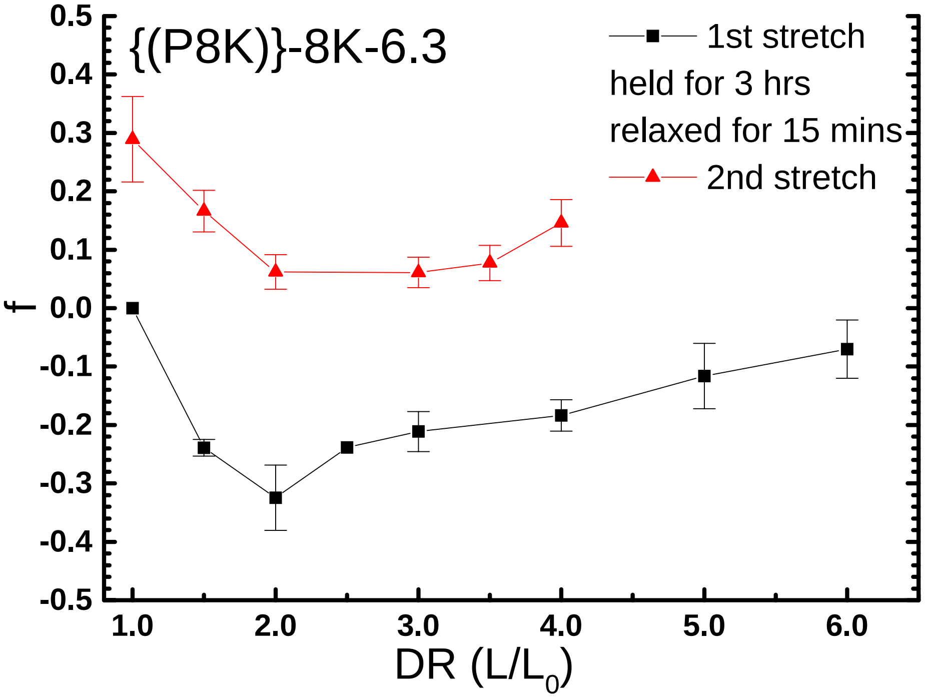

Figure 7-10: Hard segment orientation, as determined by infrared linear dichroism of 1640 cm^{-1} urea carbonyl absorption band, for a PUU that has been stretched, held for 3 hours in the stretched position, relaxed for 15 minutes and retested.

overall behavior was similar to that seen for the initial stretching that during both the first and second stretches, the hard segments exhibited orientation in the negative direction before passing through a minimum. This implies that during the relaxation process, hard domains were able to “reform” to some degree suggesting that they again be ruptured before resulting in increases in orientation. During the first stretch, the magnitude of the decrease was ca. 0.3 while it was only ca. 0.2 for the second stretch. This may indicate that it was less difficult to shear the sheaf-like hard domains apart during the second stretch. For the second group of experiments three materials were chosen for comparison: P2K-2K-9.0, P8K-8K-9.0, and P8K/T2K-2K-9.0. It has been seen that the first two of these PUUs represent two extremes of material characteristics, while the third entails aspects of each of the first two as well as being representative of the TPG containing materials.

It was seen for all three materials that samples which have been stretched and relaxed show residual birefringece (Figure 7-11). The amount of residual birefringence increased with increasing initial draw ratio. That is, samples which were stretched to draw ratios of 7 showed greater residual birefringence than samples which were only stretched to a draw ratio of 5. Additionally, the P2K-2K-9.0 materials showed the greatest residual birefringence for a given initial draw ratio, while the P8K-8K-9.0 and P8K/T2K-2K-9.0 showed residual birefringences similar to one another.

Hard segment orientation as obtained from linear dichroism for the same three samples generated supporting results (Figure 7-12). In each case, a

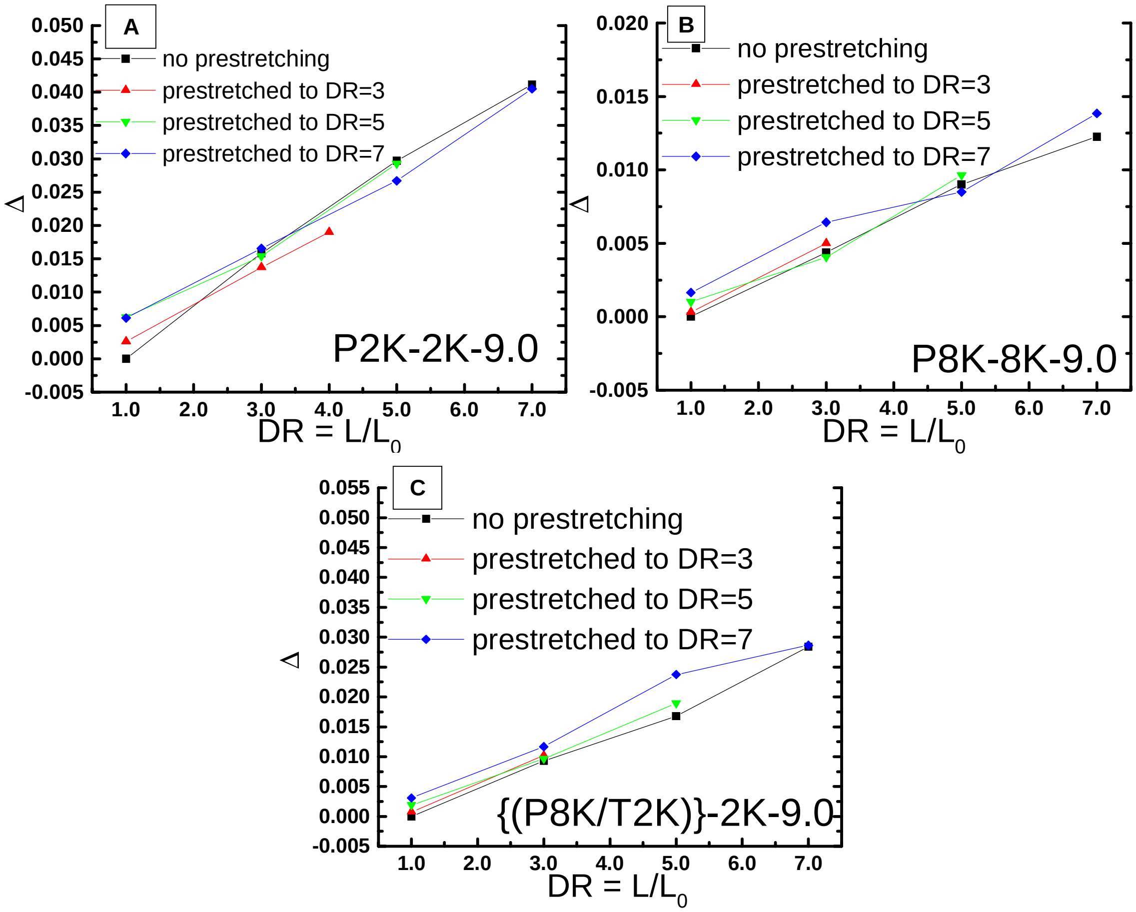

Figure 7-11. Birefringence for three PUUs (A: P2K-2K-9.0, B: P8K-8K-9.0, C: P8K/T2K-2K-9.0) that have been stretched to draw ratios of 1 (black), 3 (red), 5 (green), and 7 (blue) prior to testing.

sample that was stretched and then relaxed displayed residual orientation. Upon subsequent stretching, the samples again initially showed a decrease in hard segment orientation from an initial orientation (usually positive) to a smaller value of orientation.. The P2K-2K-9.0 system (Figure 7-12A) again showed the most dramatic evidence of residual orientation, supporting the results obtained with birefringence. Both materials based upon 8000 g/mol soft segments showed appreciably less residual hard segment orientation than the 2000 g/mol soft segment based system. The P8-8K-9.0 (Figure 7-12B) showed slightly greater

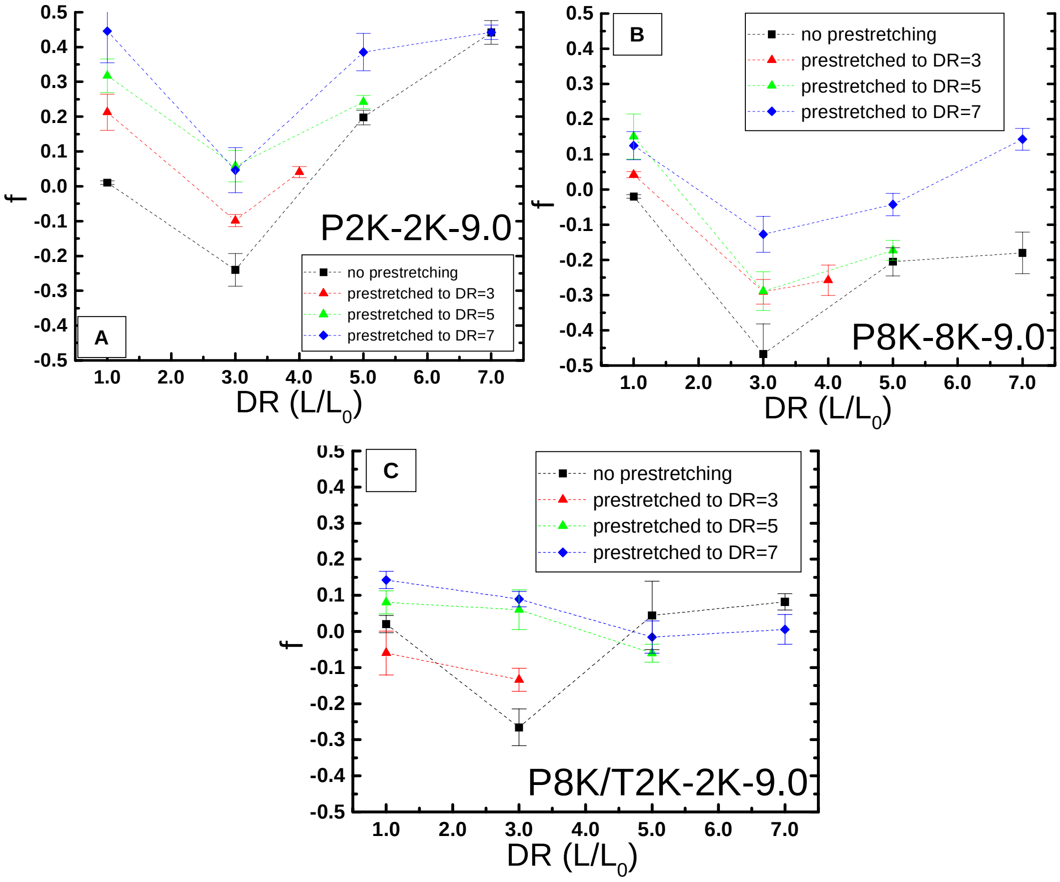

Figure 7-12. Hard segment orientation, as determined by infrared linear dichroism of 1640 cm^{-1} urea carbonyl absorption band for three PUUs (A: P2K-2K-9.0, B: P8K-8K-9.0, C: P8K/T2K-2K-9.0) that have been stretched to draw ratios of 1 (black), 3 (red), 5 (green), and 7 (blue) prior to testing.

residual hard segment orientation than the P8K/T2K-2K-9.0 (Figure 7-12C), implying that the TPG containing system was less likely to remain in an oriented state following relaxation.

These results become more interesting when coupled with the mechanical set recorded 30 seconds and one hour after releasing the samples from the nest picture frame fixture (Figure 7-13). In all cases, permanent set was seen to be greatest for the P2K-2K-9.0 material and least for the P8K/T2K-2K-9.0 material. These trends in set measurements are in agreement with those provided by Dr.

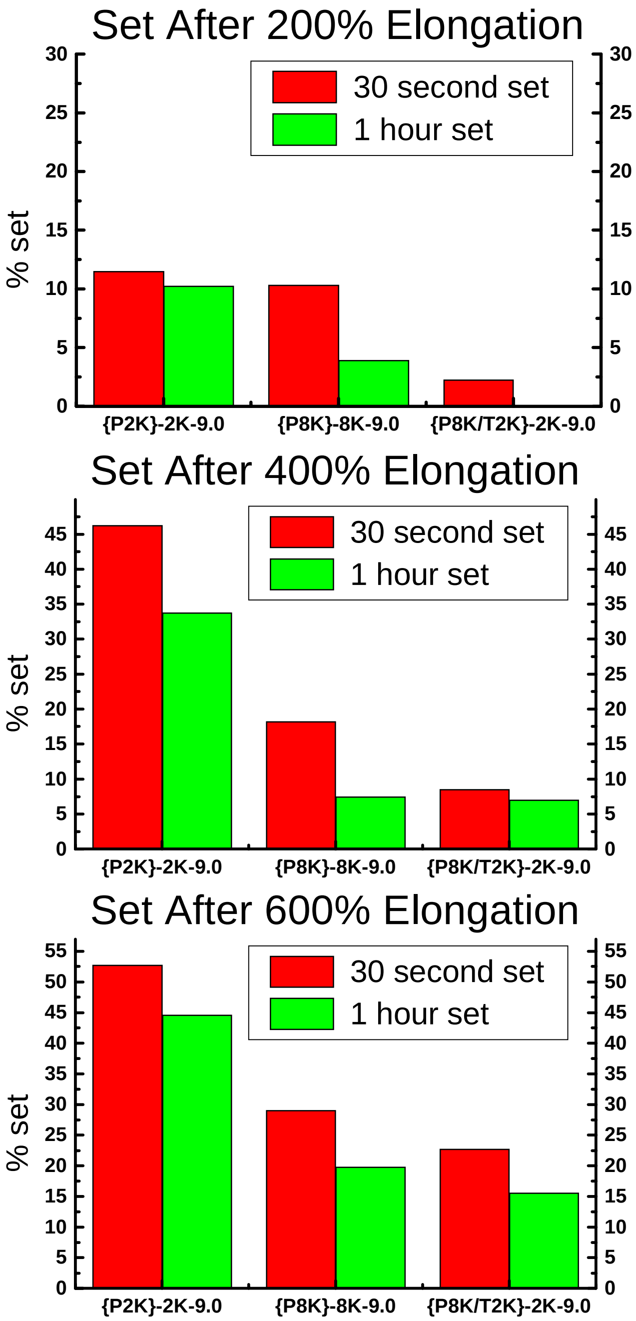

Figure 7-13. Thirty second and one hour set for three PUUs (P2K-2K-9.0, P8K-8K-9.0, P8K/T2K-2K-9.0) after elongations of 200%, 400% and 600%.

Lawrey of Bayer AG, cited in Chapters 4 and 5. Clearly, there is a correspondence between materials which exhibit higher permanent set and those which display residual birefringence and hard segment orientation.

Small angle x-ray scattering of samples before and after they have been stretched to 600% elongation are shown in Figure 7-14. It should be noted that intensities will differ due to minor changes in sample thicknesses that resulted from mechanical set induced by the deformation process. For the two non-TPG containing materials, stretching of the samples appears to have slightly enhanced the definition the shoulder or peak in the scattering pattern. This can imply a narrowing of the distribution of interdomain spacings or a greater concentration of those spacings on the meridian. It is believed by this author that the latter is more likely and that this would result in enhancement of the scattering peaks. The stretched and relaxed TPG containing material (Figure 7-14C) shows a slight increase in spacing and a minor decrease in peak sharpness. This may be a result of the greater difficulty that such materials may have in reforming their hard domains after deformation. The TPG induced hard segment urethane linkages, which are incapable of bidentate hydrogen bonding, will likely inhibit the reformation of the three dimensional hard domain network described by Bonart.[1-2] Hard domains reformed under these conditions may be less regular in size and shape, and may reform with increased phase mixing, resulting in larger and less pure hard domains.

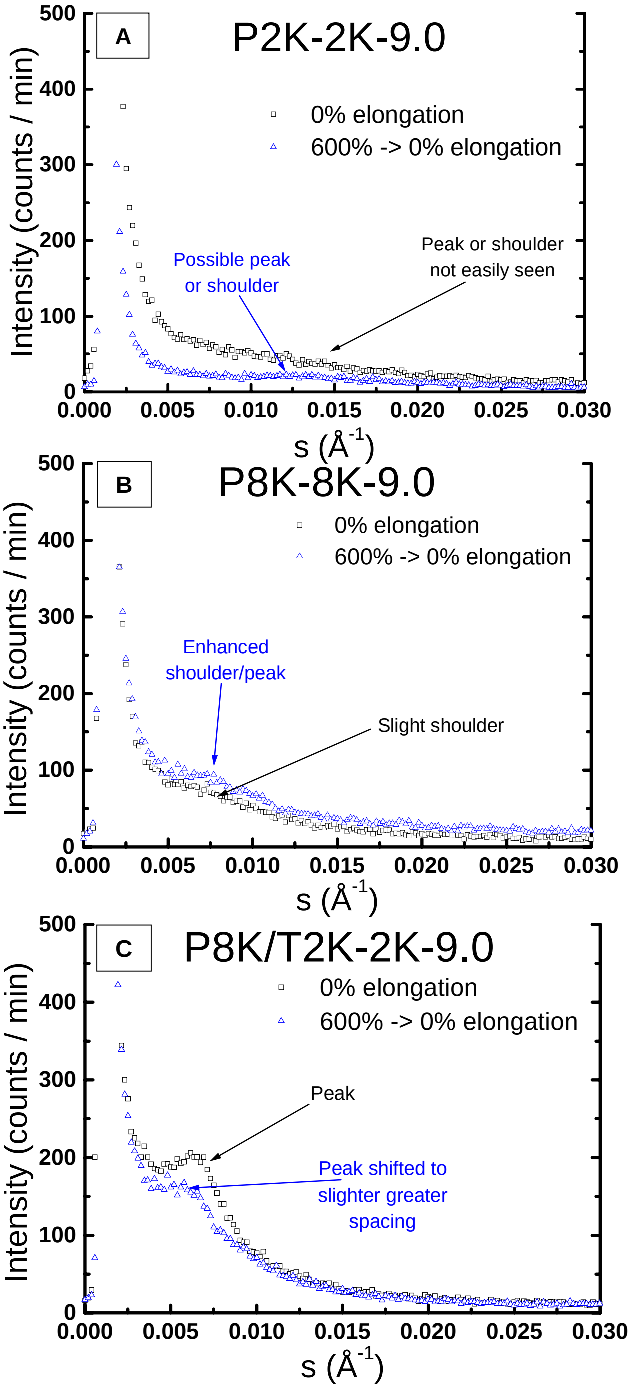

Figure 7-14. SAXS profiles for three PUUs (A: P2K-2K-9.0, B: P8K-8K-9.0, C: P8K/T2K-2K-9.0) comparing an unstretched sample (square) to a sample that has been stretched 600% and allowed to relax (triangle).

Section 7-5: Conclusions

Over the range of contents and hard segment types, it was seen that there was little difference in hard segment orientation characteristics. However, birefringence at a given set of draw conditions does show a modest increase with hard segment content. Further, decreasing average soft segment (without TPG) length also results in an increase in birefringence. TPG containing systems possess both the possibility of increased “apparent” hard segment content and decreased average soft segment length, and accordingly results in substantial increases in birefringence. For lower molecular weight soft segment, hard segments orient less negatively than those in PUUs with a soft segment of molecular weight either 4000 g/mol and 8000 g/mol. Hard domains place greater restriction on shorter soft segments and thus the domains may be less able to respond as domains to deformation, thus breaking apart more easily. From these first group of experiments, it was determined that the hard domains are the predominant factor in the orientation of the PUUs studied. Further, the second group of experiments elucidated the importance of permanent set, generally attributed as a hard domain behavior, with regards to orientation. TPG containing systems may have less cohesive hard domains due to disruption of the three-dimensional hard segment lattice. Such hard domains, having increased urethane character, may be more readily able to reorganize and reform. This tendency may be revealed by decreased set and residual orientation characteristics.

Acknowledgments

Solutions of the PUUs investigated were provided by Dr. Bruce Lawrey of Bayer Corporation.

Section 7-6: References

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