

Structure–Property Relationships of Poly(urethane urea)s with Ultra-low Monol Content Poly(propylene glycol) Soft Segments. I. Influence of Soft Segment Molecular Weight and Hard Segment Content

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ABSTRACT: 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 small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM). The thermal and mechanical behavior was assessed with a dynamic mechanical analyzer (DMA) and by differential scanning calorimetry (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 shown by SAXS, and a noticeable change in the structure, as shown by AFM. Additionally, as soft segment molecular weight decreased the soft segment glass transition broadened and rose to higher temperatures. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 229–243, 2002; DOI 10.1002/app.10168

Key words: polyurethane; elastomer; AFM; SAXS; block copolymer

INTRODUCTION

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 produc-

tion and sales.^{1–4} Those elastomeric materials based on 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 (T_g) below the use temperature. This first type of block is designated the soft block or segment and is

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commonly a polyether or polyester. The second variety of block is required to have a T_g 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 promote 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 seen 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, that 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 on 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) (PTMEG) 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 poly(ether 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 poly(propylene 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. Because allyl alcohol acts as a new monofunctional starter, its hydroxyl group is propoxylated along with the growing polyol chain. The relatively low molecu-

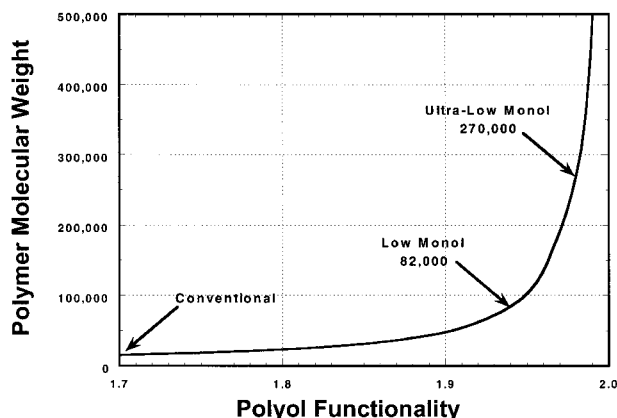


Figure 1 Effect of polyol functionality on theoretical elastomer MW as calculated from the Carother's equation. The assumed composition for this calculation was based on a MDI endcapped 4000 g/mol PPG oligomer made with a NCO/OH ratio of 4.7. Butane diol was used as a chain extender at a NCO/OH ratio of 1.03.

lar 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 the theoretical molecular weight of an elastomer 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 1. Hence the ultimate mechanical properties suffer dramatically.^{3,4} Considerable improvement in lowering the monol content (Table I), 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 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.^{3,4} The gel permeation chromatography (GPC) trace of the conventional base-catalyzed

Table I Monol Content of Conventional and Ultra-low Monol PPG^a

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%

^a Reference 42.

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 on this new generation of low monol PPG polyether polyols. As alluded to earlier, most

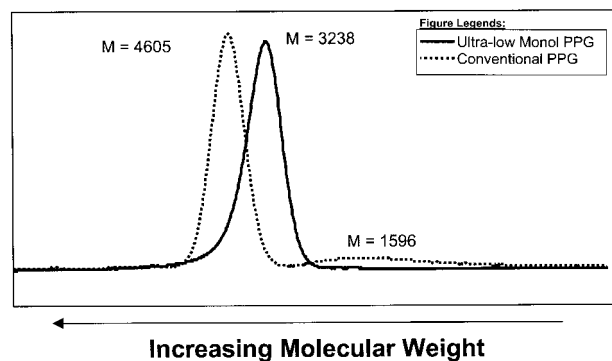


Figure 2 GPC chromatogram of a conventional, base-catalyzed 4000 MW (hydroxyl number = 28 mg KOH/g) diol compared with that of an ultra-low monol 4000 MW diol. The conventional diol exhibits a broad second peak at low molecular weight (~1596) due to its high monol (propoxylated allyl alcohol) content. The molecular weights were calculated relative to the retention times of narrow MW distribution poly(ethylene glycol) standards. Key: (—) ultra-low monol PPG; (---) conventional PPG.

previous investigations involving PPG, and a number of other polyether polyols as well, have been limited to relatively low polyol molecular weight (e.g., ≤ 2000 g/mol), broad molecular weight distribution polyols, or 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 on PPG polyols that 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 on conventional base-catalyzed PPG. This difference allows for the fabrication and use of PPG based poly(urethane urea)s in areas previously thought infeasible, 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.

Table II 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 eq. 1.^b Calculated using eq. 2.

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-angle X-ray scattering (SAXS), atomic force microscopy (AFM), dynamic mechanical analysis (DMA), 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.

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 (eq. 1):

$$\% \text{ HS} = \frac{100(R - 1)(M_{\text{di}} + M_{\text{da}})}{(M_{\text{g}} + R(M_{\text{di}}) + (R - 1)(M_{\text{da}}))} \quad (1)$$

where M is the number average molecular weight, R is the mole ratio of isocyanate to glycol, and subscripts g , di , and da refer to glycol, diisocyanate, and diamines (mole average molecular weight), respectively. It was felt that this method best represents the material residing in the hard phases.¹⁷ Equation 1 considers only the portion of isocyanate that reacts with amine, whereas hard segment contents are often calculated with eq. 2

to include the urethane linkages connecting the soft and hard segments:

$$\% \text{ HS} = \frac{100((R)(M_{\text{di}}) + (R - 1)(M_{\text{da}}))}{(M_{\text{g}} + R(M_{\text{di}}) + (R - 1)(M_{\text{da}}))} \quad (2)$$

Equation 2 leads to higher values of hard segment content. The calculated hard segment contents obtained using both of the methods just presented are shown in Table II. The two hard segment levels, as calculated by eq. 1, chosen for this study were 6.3 and 9.0 wt %. At each of these levels, three poly(urethane urea)s based on 2000, 4000, and 8000 g/mol PPG polyols were synthesized. The hard segments are comprised of MDI (Mondur M, from Bayer Corp.) and a blend of 80 wt % ethylene diamine (EDA) and 20 wt % propylene diamine (PDA). The sample nomenclature, which contains compositional information for each elastomer examined in this study, will be presented in the following section.

Prepolymer Procedure

A description of the preparation of the poly(urethane urea)s investigated in this study follows. An Acclaim™ PPG polyol of desired molecular weight was chosen and checked for water content. If necessary, the polyol was dewatered by heating at 90–100 °C under vacuum until the water level was less than ~0.01%. Excess 4,4'-MDI was added to the polyol and reacted at 80 °C (176 °F) in an inert atmosphere (i.e., nitrogen or argon) until all hydroxyl groups reacted. Typical reaction times for prepolymers made with acidified polyol were ~7–9 h.

The effects of stoichiometry and polyol molecular weight on prepolymer viscosity as deter-

Table III Viscosities of Prepolymers Used in Poly(urethane-urea) Synthesis

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

^a ACCLAIM 2200 (Bayer's ultra-low monol PPG-2000).

^b ACCLAIM 4200 (Bayer's ultra-low monol PPG-4000).

^c T-2000 = Terathane®-2000 (DuPont's PTMEG-2000).

mined with a concentric cylinder DV III Brookfield viscometer, using either a 25 or 34 spindle, are shown in Table III. The trends are similar to those observed in previous MDI elastomer work, however the isocyanate (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. For comparable number average molecular weight polyols and NCO/OH ratios, PPG-based prepolymers generally have lower solution viscosities than PTMEG-based prepolymers (Table III). The advantages of lower prepolymer viscosity include easier handling and processing.

After preparing the prepolymer, the next step was that of chain extension with an aliphatic diamine or a mixture of diamines to make the final polyurethane/urea polymer. Chain extension was carried out in a polar, aprotic solvent, typically dimethylacetamide (DMAc). The following reagents and equipment were used in the chain extension step: solvent, DMAc (Aldrich, 99.8%, anhydrous); chain extenders, EDA (Aldrich, 99.5+%); redistilled 1,2-diaminopropane (PDA, Aldrich, 99%); terminator, diethylamine (Aldrich, 99.5%, redistilled); mixer, Caframo BDC 3030 or equivalent.

The final prepolymer NCO content was measured and the prepolymer was allowed to cool to 65 °C. Having decided on the percent polymer,

desired batch size, and stoichiometry (including excess diamine level and terminator level), the required amounts of DMAc and amines were added to 8-oz. jars. Prepolymer was added to a tared plastic syringe and placed in a 65 °C oven until ready to use. A small piece of dry ice (~1 g for 50 g of polymer) was added to each jar of DMAc and amines and allowed to dissolve (solution turns milky). Then, the mixer was turned on (~1000 rpm) and the contents of the syringe containing prepolymer was injected into the DMAc solutions. The solution then built in viscosity and, after uniformly mixing for ~15 s, the mixing was stopped. Viscosity, which slowly increases with time, was typically measured after letting the solution sit at 50 °C for ~1 h (this time allows solution to warm up and for some of the entrained air to escape).

Reaction of the aliphatic diamine chain extenders with isocyanate-terminated prepolymers is extremely rapid and, unless the mixing was very rapid (on the same order as the rate of reaction), the final product was sometimes inhomogeneous, containing gels or haze, apparently due to insoluble oligo-ureas (e.g., MDI-EDA-MDI-EDA-, etc.). This inhomogeneity can have a detrimental impact on the mechanical properties of the final elastomer. The solutions for this study were produced in bench scale quantities (150 g of solution per run) in which a Caframo mixer with a Jiffy mixer blade spinning at ~1000 rpm was used for mixing purposes. In addition to mixing, the reaction itself was slowed by the addition of dry ice. Dry ice acts as a retarding agent when added to the solution of DMAc and amines, forming a turbid carbamate solution with the amines. When

complexed with the CO₂, the amine reaction with isocyanate groups is slowed down enough for the prepolymer to be added and uniformly mixed before the polymer molecular weight (and viscosity) build to unacceptable levels. A working time of 15–20 s was obtained versus <5 s without the addition of dry ice. The turbidity of the solution disappeared with evolution of CO₂, and a clear, colorless, high-viscosity polymer solution was obtained. The “CO₂ Method” has been utilized in several poly(urethane urea) synthesis patents.^{28,29}

The compositions of the materials used within this study, as well as the sample nomenclature, are tabulated in Table II. The polyols used in this study had monol contents as shown in Table I, and the prepolymers formed from them had rheological properties similar to those shown in Table III. The nomenclature consists of two sections, information regarding the soft segments and information regarding the hard segments. The information within the braces indicates the molecular weight of the PPG polyol(s) used and, if more than one polyol was used, the weight percent of each. Within this study, only a single polyol was used within a given elastomer formulation. Following the braces is the number average molecular weight of all the polyols used in the fabrication of that elastomer. Within the scope of this specific report, this aspect of the nomenclature will be redundant because, as already mentioned, only a single polyol is used within each elastomer formulation. Subsequent publications in preparation will further justify the redundant nature of this aspect of the nomenclature. The final number in the sample nomenclature is the weight percent hard segment content as defined in eq. 1.

Solutions of 22 wt % solids in DMAc were prepared for polymers formulated from 2000 and 4000 g/mol PPG polyols. At this concentration, polymers formulated from 8000 g/mol PPG polyols could undergo an association process in which a gel-like material was formed that 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 on glass plates using a doctor blade to achieve final (post-drying) film thickness ranging from 0.1 to 0.30 mm. Immediately on casting, the coated glass plates were placed within a circulating hot air oven heated to 80 °C for a period ≥2 h. A similar procedure was

used to coat thin films on glass Fischer brand microscope slides for purposes of AFM analysis.

Methods

SAXS was performed for each of the six materials to ascertain characteristics of the microphase separation; specifically, the average spacing between hard domains and a relative measure of the thickness of the interphase between the soft and hard phases. A Phillips model PW1729 generator was operated at 40 kV and 20 mA in conjunction with a slit-collimated Kratky camera (0.03 × 5 mm) with nickel filtered CuK α radiation (wavelength = 1.542 Å). A Braun OED 50-position sensitive platinum wire detector was employed with this system. Slit-smear data were obtained and were not desmeared; the interdomain spacings reported are therefore somewhat greater than in actuality. Data normalization with a Lupolen standard and correction for parasitic scattering were performed according to Kratky's procedure. Thermal fluctuations were addressed by the procedure of Vonk, and the interphase thickness parameter, σ , was obtained by a graphical approach using the methods of Bonart and Koberstein as described by Tyagi.^{30–38} Both methods evaluate negative deviations from the perfectly phase-separated state described by Porod's law and, in both cases, assume that the form of the diffuse interphase region has sigmoidal character. Graphically, a measure of the interphase thickness is obtained from the slope of the linear region (high s region) of a plot of $\ln(s^3 I_{\text{corr}})$ versus the scattering vector, s , raised to an exponent. The exponent is either 2.0 or 1.81, respectively, for Bonart's and Koberstein's methods.

Confirmation of trends seen with SAXS was obtained from AFM results. A Digital Instruments Scanning Probe Dimension 3000 Microscope with a Nanoscope IIIa controller was used for the purpose of analysis. Nanosensors, TESP (Tapping Etched Silicon Probe)-type single beam cantilevers, were used in this instrument in the tapping mode to obtain phase images of the free surfaces of the poly(urethane urea) films cast on Fischer brand glass microscope slides. The cantilevers were ~125 μm in length, with force constants of 35 ± 7 N/m, and were operated at a frequency of 290 kHz. It is recognized that the ratio of setpoint amplitude to free amplitude of oscillation (r_{sp}) may influence AFM results.³⁹ For this study, a single r_{sp} of ~0.6 was employed and other operating conditions were held constant.

Table IV 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	4.30	6.03
{(P2K)}-2K-9.0	120	3.74	4.97
{(P4K)}-4K-6.3	140	5.45	5.45
{(P4K)}-4K-9.0	145	3.91	5.63
{(P8K)}-8K-6.3	160	4.34	6.09
{(P8K)}-8K-9.0	175–180	4.17	4.77

A Seiko model 210 dynamic mechanical analyzer operated in tensile mode was used to obtain DMA data for the materials. In all cases, data were taken at a heating rate of 1 °C/min at 1 Hz. Materials of cross-sectional area between 0.7 and 2.0 mm² and with length ≥ 20 mm were mounted with a grip-to-grip distance of 10 mm and initially cooled to about -100 °C with a liquid nitrogen cooling system.

Thermal properties were assessed by DSC with a Seiko model 220 differential scanning calorimeter. Sample loading varied between ~ 7 and ~ 15 mg. In all cases, samples were cooled to about -100 °C and heated to 100 °C at a rate of 10 °C/min, cooled again to -100 °C, and heated again to 100 °C at a rate of 10 °C/min, employing a nitrogen purge gas. Results of the second heating run were normalized on a weight basis. Analysis and plotting of SAXS, DMA, and DSC results were done with Origin 4.1 from Microcal Software.

For mechanical property testing, the films were dried in air at 80°C for 2.5 h and cut with a die into 6.35-mm (0.25") wide strips. Elastic properties of films were measured in general accord with the procedures described in ASTM D 2731-72. This method was designed mainly for the testing of elastic threads and yarns rather than films. However, the parameters tested by this method are those commonly used to evaluate the elastic properties of spandex. Tests were run on a constant-rate-of-crosshead speed type tensile testing machine, with a load capacity of 50 N (11.2 lb). The samples were gripped with pneumatically operated clamps. To avoid tearing at the grips, films were sandwiched between two pieces of self-fusing Okonite No. 35 Jacketing Tape (The Okonite Company, Ramsey, NJ). Sample strips of 6.35-mm (0.25") width, ~ 0.0762 -mm (0.003") thickness, and 63.5-mm (2.5") gauge length were cycled five times at 508 mm/min (20 in./min or

800%/min) between the limits 0–300% elongation. The load curve decreases during the first few stretch and relax cycles. By the fifth cycle, the system approaches steady state equilibrium and the cycling curve is then considered to correlate with spandex behavior in fabrics. On the fifth cycle, the specimen was held in the extended state for 30 s before returning the crosshead. On this return cycle, the forces were obtained at 300, 200, and 100% elongation were recorded. By dividing the force at each of these points by the initial cross-sectional area, the unload power (i.e., return modulus or retractive power) was calculated for each of these points. To calculate percent set, after completion of the fifth cycle, we waited 30 s and then slowly lowered the crosshead until slack was just removed from the film. The extension was recorded to the nearest 0.254 mm (0.01"). Set, as calculated from the following formula, is defined as the difference between the original and final length, expressed as a percentage of the original length.

$$\text{Set (\%)} = \left[\frac{\text{Final length} - \text{Initial Length}}{\text{Initial Length}} \right] \cdot 100 \quad (3)$$

(Note: This mechanical set differs from the permanent set test in which a film or fiber is elongated at 400% for 24 h and then allowed to relax for 10 min. Set is then also calculated based on the difference between the initial and final lengths according to eq. 3.)

Tensile strength and elongation of the films were also recorded by extending the sample until a break occurred or until the crosshead reached the limit of travel.

RESULTS

The interdomain spacings and interphase thickness parameters obtained by SAXS are tabulated

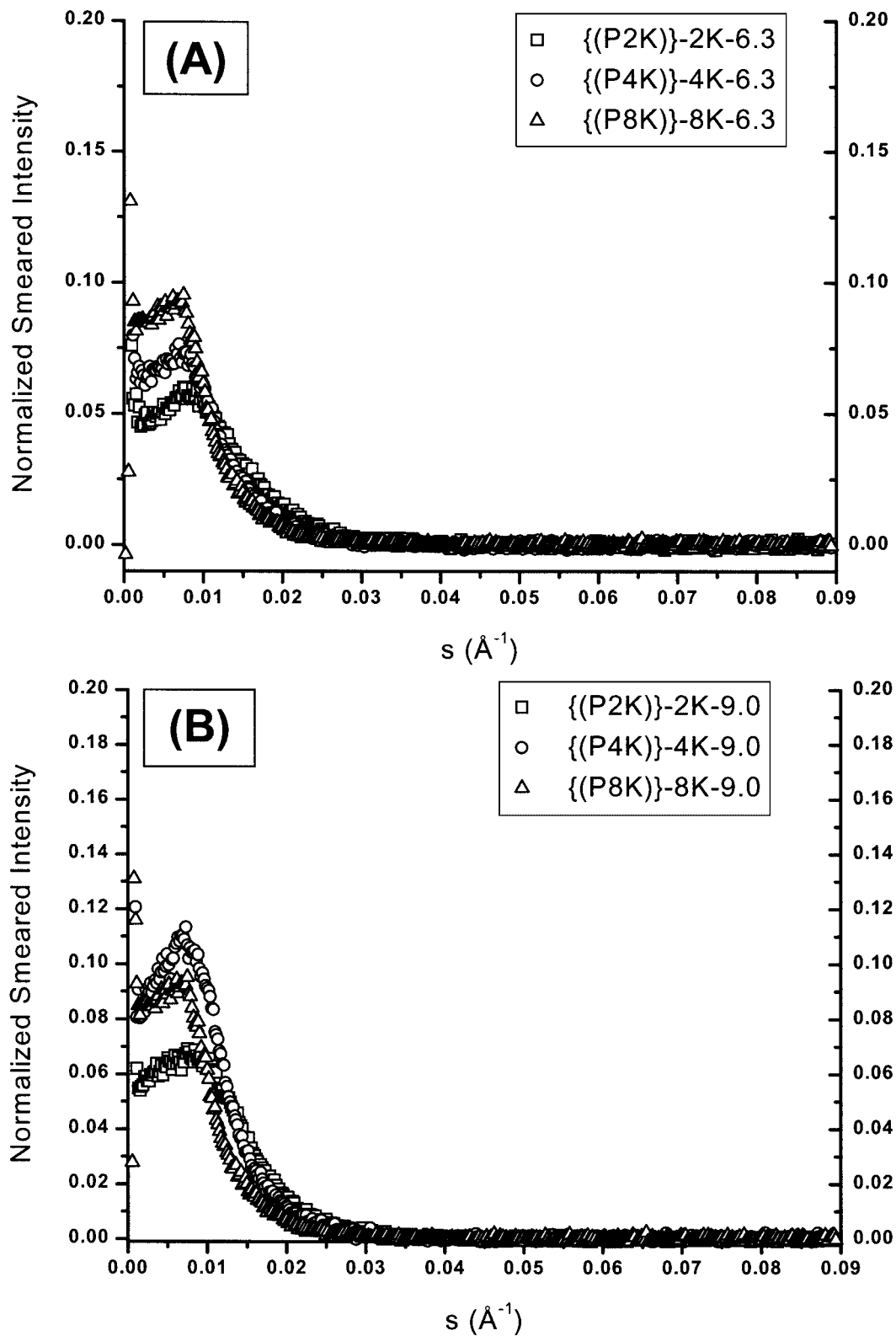


Figure 3 SAXS curves for (A) 6.3% and (B) 9.0% hard segment content poly(urethane)s.

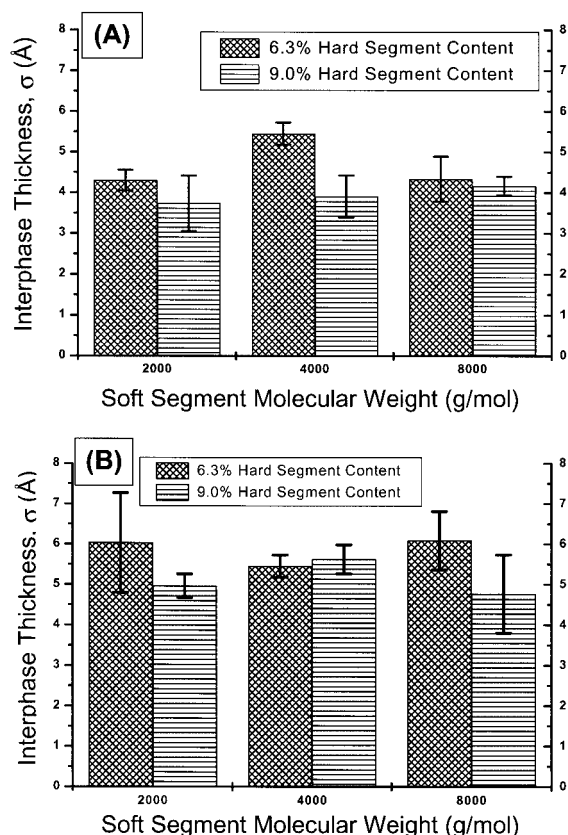


Figure 4 Interphase thicknesses using (A) Koberstein's method of analysis and (B) Bonart's method of analysis.

in Table IV, and the scattering curves are shown in Figures 3A and B. Recall again that the intensity data presented are slit-smeared. It is clearly seen from the two sets of scattering curves in Figures 3a and 3b that the estimated spacing between hard domains increases with increasing soft segment length as expected, though there is little change 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; these results reflect those obtained for other segmented poly(urethane urea)s.^{12,34,38} 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 160 Å (6.3% HS) to ~175 Å (9.0% HS). Further investigation is re-

quired to ascertain the source of this change, though it may reflect the onset of significant change in morphology, such as formation of 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 of the elastomer, the interpretation is not as straightforward 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 on 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 4a and 4b, which provides a relative measure 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 result implies that regardless of hard segment content or soft segment length, the interphase is essentially of constant thickness; it may be further hypothesized 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, therefore 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, which is indeed suggested by the results in Figures 3a and 3b.

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

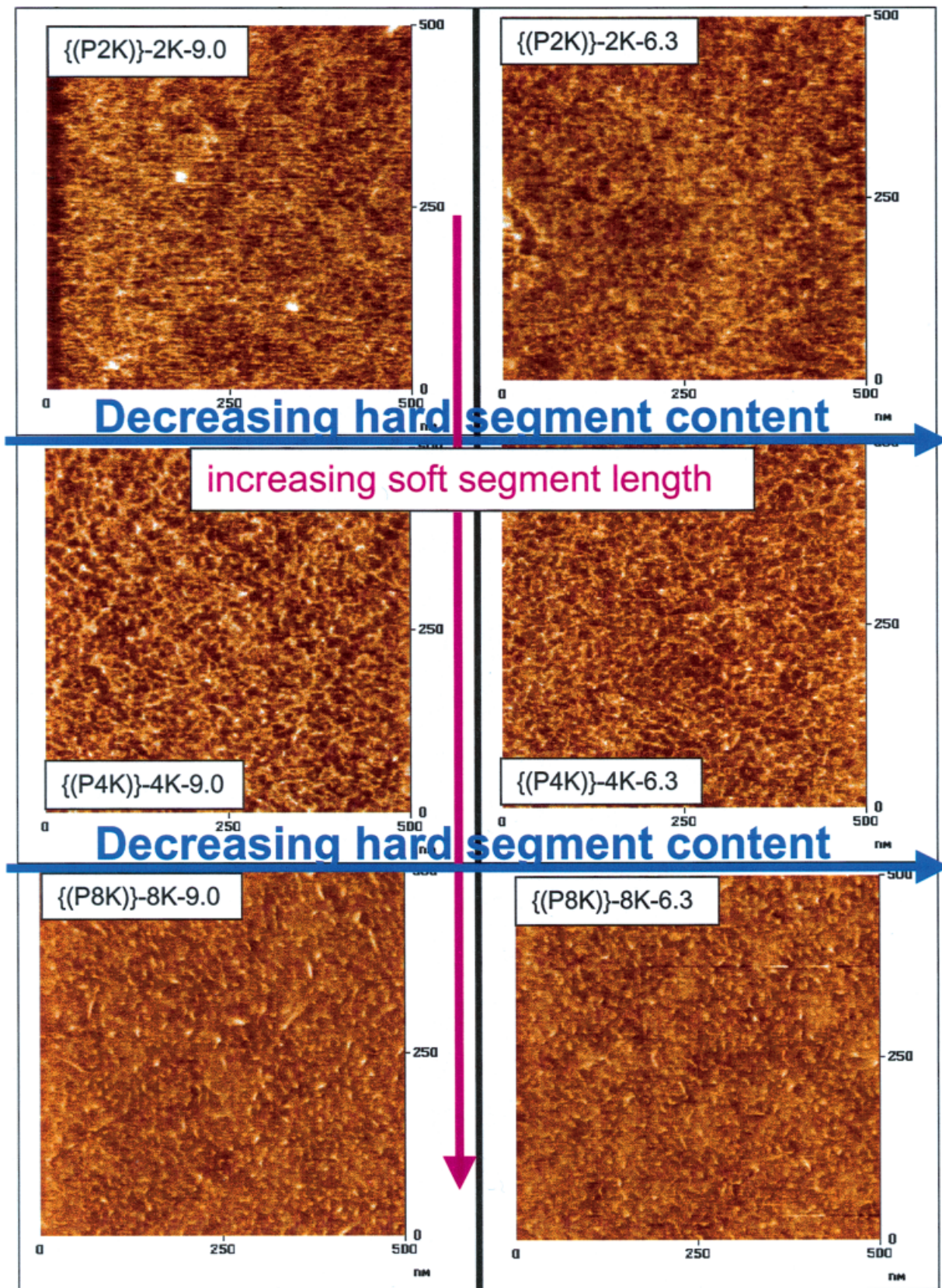


Figure 5 AFM micrographs as function of HS content and SS length.

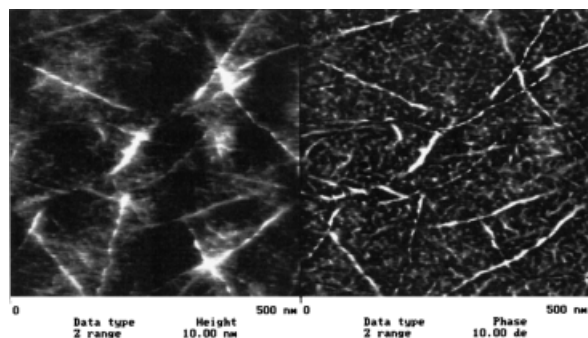


Figure 6 Height and phase AFM images of hard segment gelled material ((P8K))-8K-9.0.

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.⁴⁰ This subject will be discussed further with the AFM results.

AFM phase images of the surfaces of the six formulations are shown in Figure 5, where the darker areas are indicative of softer material and the lighter areas are indicative of harder material.^{39,41,42} The images support the trends observed and commented on during the SAXS analysis. Specifically, as the hard segment content increases, there is a discernable, 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 3 wt %. 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 seen in the SAXS experiments. Furthermore, as molecular weight of the polyol increases, there distinctly exists a larger spacing between the light-colored or 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 result is reminiscent of AFM images, shown in Figure 6, of a material of comparable composition that 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 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 on thermodynamic and solubility considerations and the effects of increasing molecular weight on 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, by necessity there will be 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 from which to draw, the circular-appearing hard domains may be fewer and/or 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 by necessity would 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 with 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 superstructures were further verified by examining a set of materials fabricated in a manner to intentionally include “gelled” material. These materials, not shown here, were designed to facilitate hard segment association and strikingly exhibited string-like superstructures when examined by 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-smear data. Hence, the interdomain spacings obtained from SAXS are slightly larger than in reality and will not correlate directly to visual inspection of the corresponding AFM images.

DMA and 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, and the location of the glass transition may indicate how the hard domains restrict soft segment mobility. The DMA results shown in Figures 7a and 7b indicate that a decrease in the molecular weight of the soft segment leads to both increases

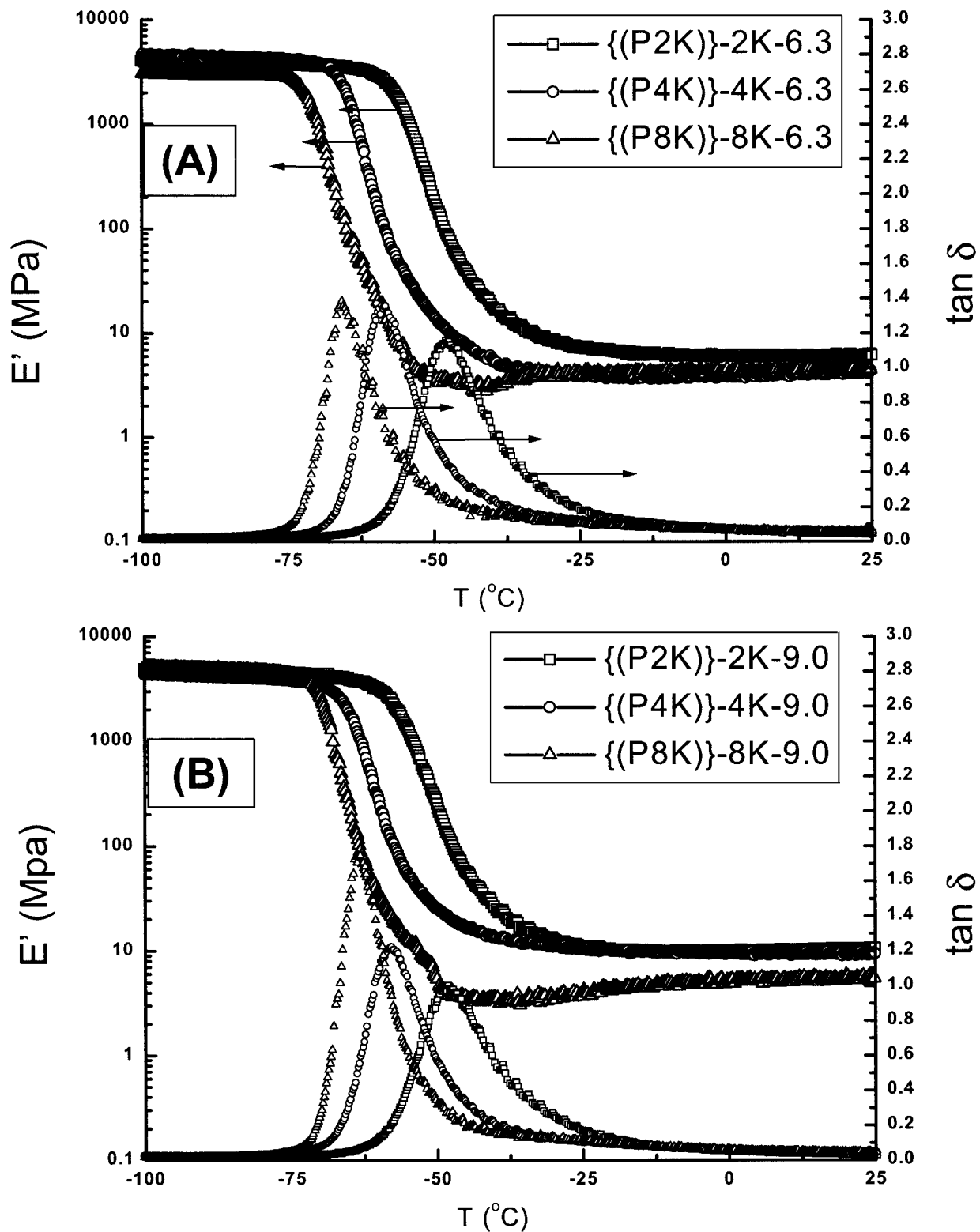


Figure 7 DMA of (A) 6.3% and (B) 9.0% HS poly(urethane urea) elastomers.

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 weight 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 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, again with 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 T_g 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 on the soft segment damping characteristics. There are only minor increases in the T_g as hard segment content increases and the expected increases in modulus are also observed. 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 DMA studies. The results in Figure 8 clearly show that as the soft segment molecular decreases, there is broadening of the glass transition as well as a shift to

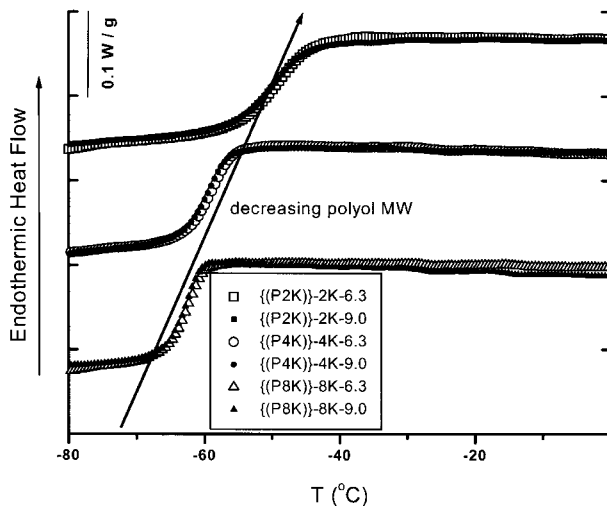


Figure 8 DSC of 6.3 and 9.0% HS poly(urethane urea) elastomers.

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 those results put forth in the SAXS, AFM, and DMA discussions. Increasing hard segment content from 6.3 to 9.0 wt % does not appear to have a significant effect on 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- and PTMEG-based polyurethanes have shown over a much greater range of hard segment content (30–70 wt %) that the soft segment glass transition is only nominally affected by changes in hard segment content.^{1,2} Sung and co-workers similarly found that through a hard segment content range of ~25–55%, the soft segment glass transition in poly(urethane urea)s based on 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 that the percent elongation tended to increase as the soft segment molecular weight increased. These results, shown in Table V, 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).

Table V Soft Segment Glass Transition Temperatures of PPG-Based Poly(urethane-urea)s

Soft Segment MW (g/mol)	DMA ^a		DSC ^b	
	6.3% HS	9.0% HS	6.3% HS	9.0% HS
2000	-47.9°C	-48.1°C	-48.9°C	-49.7°C
4000	-59.2°C	-58.0°C	-58.4°C	-59.1°C
8000	-65.9°C	-63.4°C	-62.3°C	-62.3°C

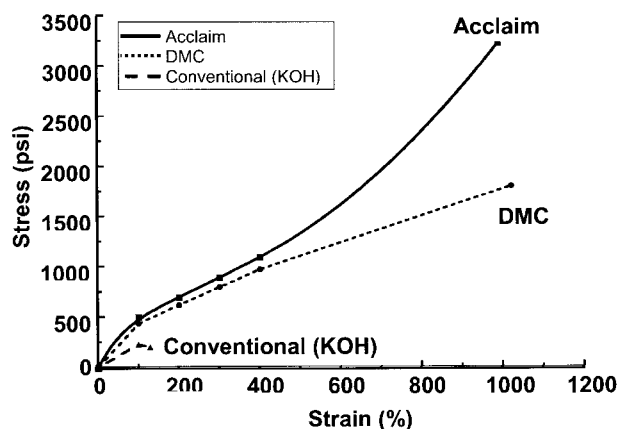
^a Determined from the peaks of the DMA tan delta curves.

^b Determined from inflection points of the T_g region of the DSC curves.

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.

Analysis of the mechanical set behavior of the materials is still ongoing, but two conclusions may be readily drawn from the 30 s set experiments (Table VI). First, over the range studied, hard segment content had very little effect on the 30 s set as defined in eq. 3. 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 VI) 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. In-

**Figure 9** Stress-strain curves of different poly(urethane) elastomers with 4000 g/mol PPG-based MDI-encapped prepolymers, cured with BDO, as stated in Figure 1.

creasing 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 9, where it is seen that the ultimate tensile properties of the 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.

CONCLUSIONS

A series of model poly(urethane urea) compounds based on a narrow molecular weight distribution

Table VI Mechanical Properties of PPG-Based Poly(urethane-urea)s

Sample	ULP @ 100% (MPa)	ULP @ 200% (MPa)	ULP @ 300% (MPa)	Tenacity (MPa)	% Elongation	30-s Set (%)
{(P2K)}-2K-6.3	0.553	1.31	2.71	14.0	1686	33.3
{(P2K)}-2K-9.0	0.815	2.03	4.69	45.1	1115	33.8
{(P4K)}-4K-6.3	0.529	1.19	2.52	6.8 ^a	1301 ^a	26.4
{(P4K)}-4K-9.0	0.655	1.51	3.38	20.4	1816	28.1
{(P8K)}-8K-6.3	0.666	1.28	2.48	15.6 ^a	1869 ^a	13.9
{(P8K)}-8K-9.0	0.798	1.56	3.34	23.7	1602	13.6

^a Sample did not break at limit of crosshead travel.

PPG polyol were developed and investigated with regards to their microphase separation, morphology, and mechanical characteristics. Increases in the molecular weight of the PPG soft segment led to increased phase separation that, in part, resulted in greater soft segment mobility and lower T_g 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 clearly seen by AFM. The effect of varying the hard segment content was seen to be minor in much of the structural analysis, yet discernable, in comparison to the effect of varying the soft segment molecular weight. However, the mechanical properties, particularly the unload power, were dependent on the hard segment content. It is apparent from the results and discussion presented that developing useful elastomers from the ultra-low monol poly(propylene glycol)s will require careful consideration of the influence of chemical variables on the morphology of the materials.

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