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Structure–property relationships of poly(urethane–urea)s with ultra-low monol content poly(propylene glycol) soft segments. Part II. Influence of low molecular weight polyol components

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Abstract

Segmented poly(urethane–urea)s have been synthesized with mixed soft segments of ultra-low monol content poly(propylene glycol) (PPG) and tri(propylene glycol) (TPG) which allows the fabrication of quality elastomers without crosslinking. The narrow molecular weight distribution of the ultra-low monol content PPG polyols allows for the probing of the influence of the low molecular components of the molecular weight distribution through the inclusion of low molecular homologs of PPG such as TPG. Structure–property relationships for these materials were investigated as average soft segment molecular weight was varied by blending 8000 g/mol PPG with TPG to achieve molecular weights of 2500, 2000, and 1500 g/mol. Morphological features such as microphase separation, interdomain spacing and interphase thickness were quantified and revealed with SAXS. AFM was utilized to verify the microphase separation characteristics inferred by SAXS. The thermal and mechanical behavior was assessed through applications of DMA, DSC, and conventional mechanical tests. It was found that as the average soft segment molecular weight was decreased through the addition of TPG, the interdomain spacing distinctly increased contrary to the trend seen for decreasing soft segment molecular weight in PPG based systems without TPG. Additionally, the inclusion of TPG in the poly(urethane–urea) formulations resulted in the formation of larger hard domains as evidenced by AFM. These results and supporting evidence from DMA, DSC, birefringence, and mechanical testing led to the conclusion that TPG apparently acts more as a chain extender as well as, or in contrast to, a soft segment. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(urethane–urea)s; Small angle X-ray scattering; Mechanical properties

1. Introduction

Segmented, microphase separated, poly(urethane–urea) elastomers are, as a group of materials, important both commercially and scientifically. A wide range of chemical formulations are used to fabricate materials with a range of thermal and mechanical properties, though many of the most significant industrial formulations have, until recently, relied on the use of the poly(tetramethylene ether glycol) as a soft segment material. Poly(propylene glycol) (PPG), most commonly produced through a base-catalyzed process, has also been used as a soft segment material, though over a much narrower range of applications. However, due to advances during the 1990s in the catalysts used to produce PPG diols, there have been substantial improvements in the level of difunctionality, molecular weights and a narrowing of the molecular weight distributions of those polymeric diols (Fig. 1A) [1,2]. These diols are referred to as ultra-low monol PPG polyols and are marketed as ACCLAIM® (Bayer AG) PPG polyols. In addition to these enhancements, it was also found that the melt viscosities of isocyanate end-capped prepolymers based upon this latter generation of PPG diols are dramatically lower than those based upon PTMEG of the same number-average molecular weight, which accords a significant processing advantage in the fabrication of solution spun poly(urethane–urea)s based upon ultra-low monol PPG [1,2]. If the mechanical properties of such ultra-low monol based elastomers were found to be comparable to those based upon PTMEG, which, unlike PPG, can undergo strain-induced crystallization, there would be considerable incentive in terms of both material costs and processing costs to justify replacing PTMEG with ultra-low monol PPG.

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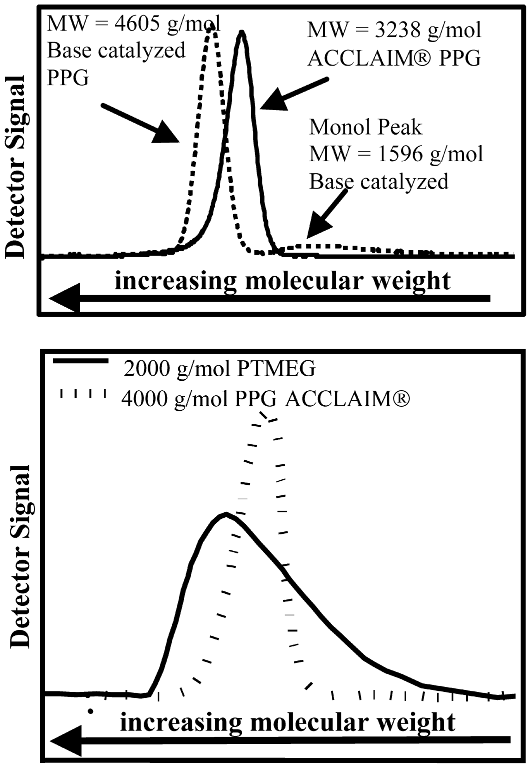

Fig. 1. Molecular weight distributions of ultra-low monol PPG and PTMEG polyols.

The use of PPGs in poly(urethane–urea) elastomers has been generally limited, in large part, to the inability to generate PPG diols with high degrees of difunctionality and appreciable molecular weight. The impact of monol on the properties of urethane elastomers has been previously documented, but in brief, monofunctional impurities present in PPG polyols act as terminators during the development of elastomer molecular weight upon chain extension with either diols (urethanes) or diamines (urethane–ureas), thus limiting the molecular weight of the final elastomer [1,2]. The elastomers thus produced generally have inadequate mechanical properties, particularly stress–strain behavior, for use in higher value elastomer applications such as spandex fibers. PTMEG in contrast, has been produced without appreciable monol content, though with broader molecular weight distribution (Fig. 1B). It has also been used with considerable success in both urethane and urethane–urea elastomer applications. Another attribute of PTMEG, which has been credited for its successful use in elastomeric applications, is its ability to undergo strain-induced crystallization at ambient temperatures. Under ambient conditions, at strains of approximately 300–400% elongation, PTMEG will exhibit the development of crystallites and a corresponding noticeable upturn in the tensile deformation curves. PPG, on the other hand, is produced in an atactic form that prevents the development of crystallinity under any conditions, and will thus not benefit from such a crystallinity dependent upturn in the stress–strain behavior.

Ultra-low monol PPG and PTMEG differ in other key aspects. For instance, PTMEG has a greater number of backbone bonds for a given polyol molecular weight. As Fig. 1A and B demonstrate, an appreciable low molecular weight component in the molecular weight distributions also exists for both the conventionally produced base-catalyzed PPG and PTMEG that is absent in the ultra-low monol content PPG. The low molecular component in the base-catalyzed PPG is due to the presence of monofunctional PPG, the implications of which were discussed above and in other works [1–3]. In contrast, the low molecular species present in the PTMEG molecular weight distribution are difunctional and do not have the deleterious impact on mechanical properties that monol does. However, there has been relatively little work to assess the impact of the low molecular diols present in the PTMEG molecular distribution due in part to difficulties in obtaining a narrow molecular distribution PTMEG for comparison purposes [4]. Use of ultra-low monol content PPG, with its narrower molecular weight distribution, presents an opportunity to make such a study on a similar poly(urethane–urea) system. Blending a low molecular weight homolog to PPG, such as tri(propylene glycol) (TPG), with the PPG diol prior to prepolymer formation provides a series of materials to contrast against those with no appreciable low molecular contribution. This paper documents the results obtained in such a study (Fig. 2).

Previous work by the authors detailed the influence of soft segment molecular weight and hard segment content on the structure–property relationships of poly(urethane–urea) elastomers based upon ultra-low monol PPG [3]. The materials used in that study were fabricated via a two-step process in which PPG diols of varying molecular weight were end-capped with 4,4′-MDI to obtain a prepolymer which was later chain extended with an 80:20 mixture of ethylene diamine and propylene diamine. Within the current work, similar elastomers were synthesized with the notable difference that TPG was first blended with the ultra-low monol PPG *before end-capping* with 4,4′-MDI. It was then

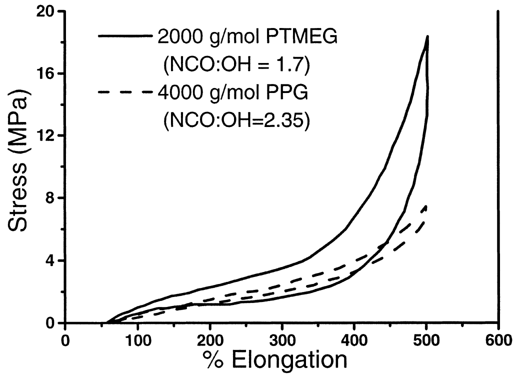

Fig. 2. Fifth cycle stress–strain curves of PUU films cycled to 500% elongation.

Table 1
Sample nomenclature and hard segment contents

PPG soft segment MW	NCO/OH ratio	wt% of hard segment content (urea)[a]	wt% of hard segment content (urea and urethane)[b]	Sample nomenclature
2000	1.5	6.3	16.7	{(P2K)}-2K-6.3
2000	1.7	9.0	19.1	{(P2K)}-2K-9.0
4000	1.9	6.3	11.8	{(P4K)}-4K-6.3
4000	2.3	9.0	14.3	{(P4K)}-4K-9.0
8000	2.9	6.3	9.0	{(P8K)}-8K-6.3
8000	3.7	9.0	11.6	{(P8K)}-8K-9.0
8000/2500	1.9	9.0	17.3	{(P8K/T2.5K)}-2.5K-9.0
8000/2000	1.7	9.0	19.1	{(P8K/T2.0K)}-2.0K-9.0
8000/1500	1.6	9.0	22.0	{(P8K/T1.5K)}-1.5K-9.0
4000/2000	1.5	6.3	16.7	{(P4K/T2K)}-2.0K-6.3
4000/2000	1.7	9.0	19.1	{(P4K/T2K)}-2.0K-9.0

[a] Calculated using Eq. (1).

[b] Calculated using Eq. (2).

possible to compare PPG-based urethane–urea elastomers with and without a low molecular weight contribution to the soft segments.

2. Experimental materials

In this study, six different model poly(urethane–urea) elastomers were examined, three for each having 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))

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

where M is number-average molecular weight, R is the mole ratio of isocyanate to glycol, subscript 'g' refers to glycol, subscript 'di' refers to diisocyanate, and subscript 'da' refers to the diamines (mole average molecular weight.)

It was felt that this method best represents the material residing in the hard phases [3]. As can be seen, Eq. (1) considers only the portion of isocyanate which reacts with amine for the purpose of calculating the hard segment weight, whereas often hard segment contents are calculated to include the urethane linkages connecting the soft and hard segments (Eq. (2)), which leads to higher

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

values of hard segment content. The calculated hard segment contents obtained using both of the above methods are shown in Table 1. The two hard segment levels, as calculated by Eq. (1), chosen for this study were 6.3 and 9.0 wt% and for each of these, three poly(urethane–urea)s based upon 2000, 4000, and 8000 g/mol PPG polyols were synthesized. As stated earlier, the hard segments are comprised of MDI and a blend of 80 wt% ethylene diamine and 20 wt% propylene diamine.

3. Polymer synthesis

A more detailed description of the synthesis of polymers containing only PPG soft segments was described previously [3]. It is useful to note that, during prepolymer formation, a distribution of prepolymer molecular weights is obtained which may be theoretically calculated [5]. The preparation of TPG-containing systems differs in that PPG and TPG are blended together to achieve the desired number-average polyol molecular weight (M_n) before end-capping with 4,4′-MDI. For sake of discussion, all hydroxyl containing species (PPG and TPG) are included in the calculation of the soft segment number-average molecular weight. TPG content for systems based upon 8000 g/mol PPG diols is shown in Fig. 3 in terms of mol% TPG and wt% TPG. The ratio of NCO to OH must be adjusted accordingly to maintain the targeted hard segment contents of 6.3 and 9.0 wt%.

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.

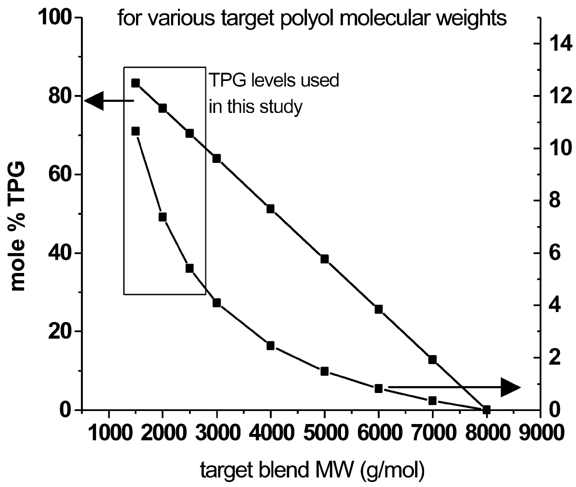

Fig. 3. TPG content in materials used in this study.

Immediately upon casting, the coated glass plates were placed within a circulating hot-air oven heated to 80 °C for a period of not less than 2 h. A similar procedure was used to coat thin films upon glass FISHERBRAND® (Fisher Scientific Company) brand microscope slides for the purposes of atomic force microscopy (AFM) analysis.

4. Sample nomenclature

The compositions of the materials used within this study, as well as the sample nomenclature, are tabulated in Table 1. The nomenclature consists of two sections, information regarding the soft segments and information regarding the hard segments. The nomenclature 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 synthesis of that elastomer. Within the scope of this specific report, this aspect of the nomenclature will be redundant since, as mentioned above, only a single polyol is used within each elastomer formulation, though subsequent publications, in which mixed soft segments are used, will justify this aspect of the nomenclature. The final number in the sample nomenclature is the weight percent hard segment content as defined in Eq. (1). Throughout this paper, when a system is referred to as being a pure PPG system this simply means that particular poly(urethane–urea) formulation is unblended and does not contain TPG. Preparation of 'unblended' elastomer films from these materials has been described previously along with their thermal, structural, and mechanical behavior [3].

5. Experimental methods

Characterization method procedures for small angle X-ray scattering (SAXS), AFM, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and stress–strain mechanical property characterization have been presented in an earlier work [3]. 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 by pneumatically operating clamps. In order 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 in.) width, approximately 0.0762 mm (0.003 in.) thickness and 63.5 mm (2.5 in.) gauge length were cycled five times at 508 mm/min (20 in./min or 800%/min) between the limits of 0 and 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 are 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 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 (a.k.a. return modulus or retractive power) was calculated for each of these points. In order to calculate %set, after completion of the fifth cycle, we waited 30 s and then slowly lowered the crosshead until slack was noted. This extension was recorded to the nearest 0.254 mm (0.01 in.). 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.

$$\text{Set }(\%) = [(\text{Final length} - \text{Initial length})/\text{Initial length}] \times 100 \tag{3}$$

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 till a break occurred or until the crosshead reached the limit of travel. Birefringence studies were conducted by manually stretching film samples to desired draw ratios and determining the birefringence using a Babinet compensator.

6. Results

It had been previously seen that as the length or molecular weight of the PPG soft segments decreased, the interdomain spacing as determined from SAXS also decreased for a given hard segment content (Fig. 4A) and that over the range of hard segment contents analyzed there was little influence of hard segment content on the interdomain spacing [3]. Also shown is a 2000 g/mol PTMEG based poly(urethane–urea) comparable to the 2000 g/mol PPG based material ({(P2K)}-2K-9.0). It is noted that the interdomain spacing of the PTMEG based poly(urethane–urea) is greater than that of the comparable 2000 g/mol PPG based formulation. This increased spacing of the PTMEG-based material could in principle be due to a larger number of backbone bonds for a given molecular weight in comparison to the PPG-based system. The principal cause of this behavior, however, is believed to be a result of the PTMEG used to formulate the poly(urethane–urea) having an appreciably broader molecular weight distribution (Fig. 1B), with low molecular weight components not present in ultra-low monol content PPG. This assertion will be developed throughout the discussion of the results. In striking contrast to the results for systems based solely upon PPG, when the

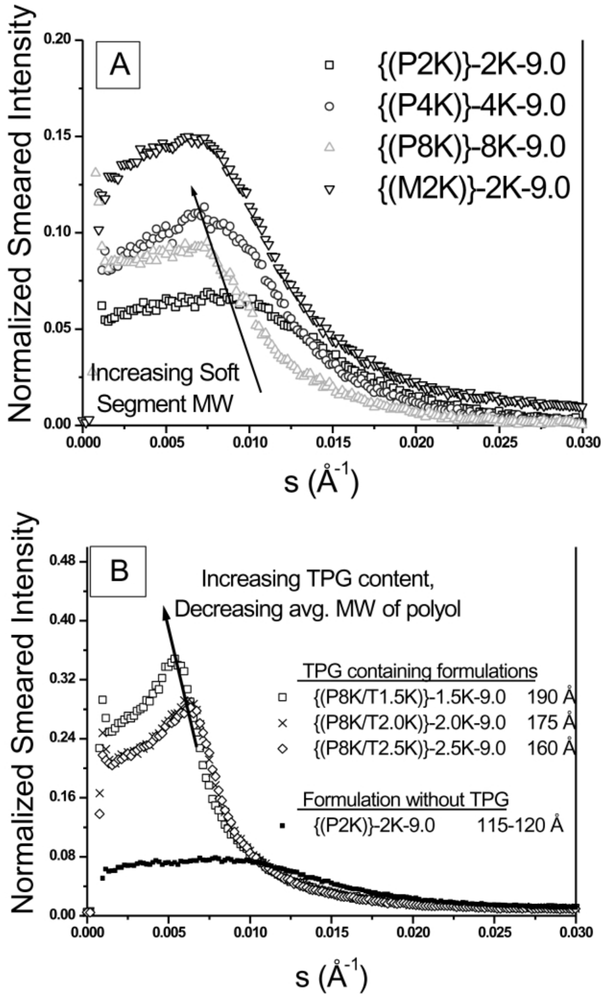

Fig. 4. SAXS results for systems (A) without, and (B) with TPG.

average soft segment molecular weight is decreased via blending with TPG, the interdomain spacing increased appreciably. For example, when a 8000 g/mol PPG is blended with TPG to give a soft segment M_n of 1500, 2000, or 2500 g/mol it is seen that the interdomain spacing varied from 190 to 160 Å (Fig. 4B; Table 2), respectively. These values of interdomain spacings are more comparable to the spacing seen for formulations based upon an 8000 g/mol PPG when no TPG was included (175–180 Å). A similar trend was seen for formulations based upon 4000 g/mol PPG diols (Table 2). It should also be noted that when TPG is included in the formulations, a very distinct sharpening of the peaks in the scattering curves and an increase in the intensity occurs. The increase in peak sharpness is an indication that a narrower distribution of interdomain spacings exists and the increase in the intensity may imply better phase separation of the hard and soft segments since the chemistry and content of each segment type was initially assumed to be constant.

Additionally, an interphase thickness analysis was performed on the smeared SAXS data using a graphical approach based upon Bonart and Koberstein's methods [6–11]. For systems based upon an 8000 g/mol PPG-containing TPG, there was a small apparent increase in the thickness of the interphase region of ~2 Å when compared to analogous systems without TPG (Fig. 5; Table 2). While the interphase thickness numbers should not be taken as absolutes, they are valuable as indicators of trends [10,11].

Fig. 6 shows the influence of varying the tapping force or ratio of setpoint amplitude to free amplitude of oscillation (r_{sp}) upon the phase images. For this study, the ratio of setpoint amplitude to free amplitude of oscillation (r_{sp}) was held at ca. 0.60. Atomic force microscopy had previously shown that as soft segment size of pure PPG-only formulations increased for the same percent HS, an increasingly larger grain structure was seen in the AFM micrographs [3]. However, when the *average* soft segment length was decreased through the addition of TPG, the results are in stark contrast to that previously observed trend (Fig. 7A–C). In the tapping mode AFM phase image micrographs shown, the brighter regions correspond to areas of the sample with higher modulus (i.e. the hard domains) [3,12–14]. It is clearly seen that as the amount of TPG within the system is increased from zero (Fig. 7A), to ~11 wt% of total polyol weight or an average soft segment molecular weight of 1500 g/mol (Fig. 7C), that the grain size dramatically increases. The increase in the amount of bright region in the micrographs is an indicator that there is a greater amount of hard domain material. However, recalling that the

Table 2
Interdomain spacings and interphase thicknesses of PPG-based poly(urethane–urea)s

Sample designation	Interdomain spacing, d (Å)	Interphase thickness, σ Koberstein (Å)	Interphase thickness, σ Bonart (Å)
{(P2K)}-2K-6.3	120	4	6
{(P2K)}-2K-9.0	120	4	5
{(P4K)}-4K-6.3	140	5	5
{(P4K)}-4K-9.0	145	4	6
{(P8K)}-8K-6.3	160	4	6
{(P8K)}-8K-9.0	175–180	4	5
{(P8K/T2.5K)}-2.5K-9.0	160	5	7
{(P8K/T2.0K)}-2.0K-9.0	175	4	5
{(P8K/T1.5K)}-1.5K-9.0	190	6	7
{(P4K/T2K)}-2.0K-6.3	150–155		
{(P4K/T2K)}-2.0K-9.0	155		

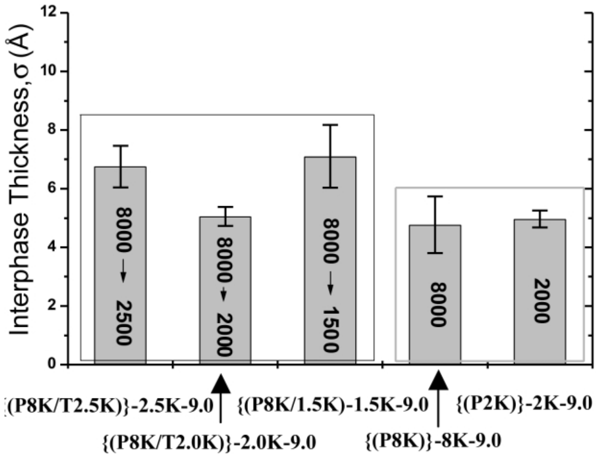

Fig. 5. Interphase thicknesses as determined via Bonart's method.

hard segment content was kept nominally fixed at 9 wt%, this is at first somewhat surprising until one considers the possibility that a significant portion of the TPG may be acting less as a soft segment and more as a chain extending diol. The validity and implications of this claim will become apparent in the following discussion of DMA and DSC results.

DMA has previously revealed that as the soft segment molecular weight decreases for pure (non-TPG-containing) systems, there is a rise and broadening of the soft segment glass transition (Fig. 8A) [3]. The curves shown are truncated at 25 °C as there is minimal change until ~170 °C at which point the sample begins undergoing thermal decomposition. There is also a slight increase in the modulus of the material above the soft segment glass transition temperature. These phenomenon were explained by recognizing that a hard domain will influence, in the interphase region, some portion of the soft segments to which it is attached. For higher molecular soft segments, the size of the restricted or influenced region will be essentially constant, though for lower molecular weights segmental solubility issues cannot be neglected. Hence, longer soft segments will possess character more similar to that of the homopolymer PPG since they experience less restriction due to the less connecting junctions hard domains [15]. When the soft segment molecular weight is decreased via blending with TPG, while there is a slight rise in the glass transition temperature, this rise is not nearly to the extent that would have been predicted from the behavior of the soft segment without TPG (Fig. 8B; Table 3). That is, if the trend in soft segment glass transition was extrapolated from that seen for PPG soft segments of 2000, 4000, and 8000 g/mol, the shift in T_g of TPG-containing systems would be expected to be more substantial. Additionally, the glass transition regions of materials containing TPG are broader than those based upon systems with the same starting PPG molecular weight, but without TPG (e.g. 4000, 8000 g/mol PPG). There is also a slight rise in the modulus above the glass transition temperature as TPG content increases (average soft segment MW decreases), which is consistent with the trends previously seen for decreasing soft segment molecular weight and for increased hard segment content (Table 3).

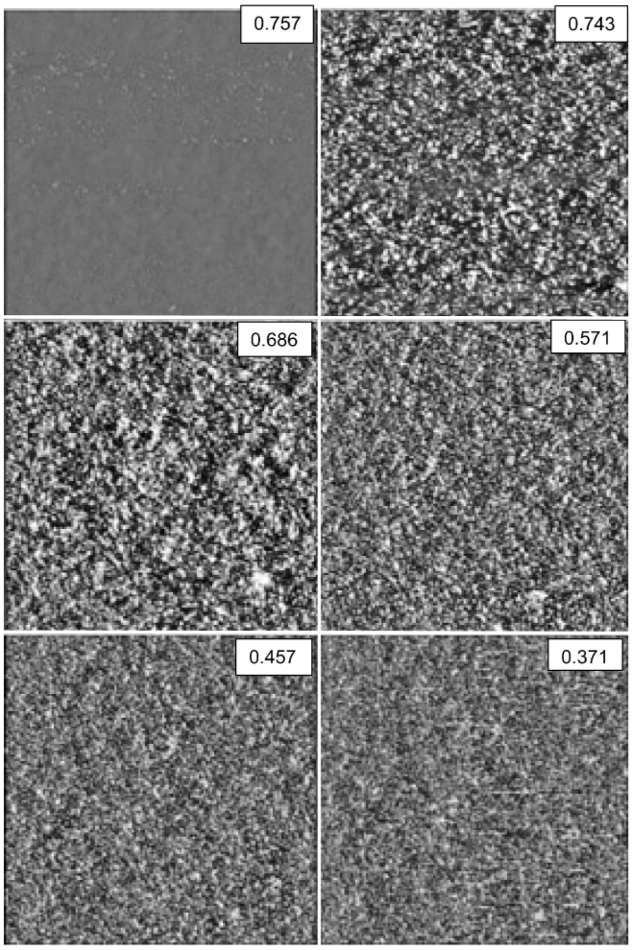

Fig. 6. Tapping mode AFM phase images for variable ratio of setpoint amplitude to free amplitude of oscillation (r_{sp}). r_{sp} is shown for each 1 μm × 1 μm image.

The trends seen in DMA were confirmed and expanded upon using DSC. For systems based upon pure 4000 and 8000 g/mol PPG, it was found that blending with TPG to achieve a final soft segment molecular weight of 2000 g/mol (Fig. 9A and B; Table 3) resulted in some broadening of the glass transition and an increase to higher temperatures. However, the shift to higher temperatures was distinctly not anywhere as great as would have been expected by the influence of pure PPG soft segment molecular weight alone (Table 3). When soft segment molecular weight was systematically decreased through the use of TPG, it was found that the soft segment glass transition shifted to slightly higher temperatures and broadened. This was in agreement with the results of DMA (Fig. 10; Table 3). The changes in structure implied from the SAXS, AFM, DMA, and DSC results as TPG is included in the formulations might well be expected to substantially impact the mechanical properties as will now be addressed.

The stress–strain curves shown in Fig. 11A and B demonstrate the significant impact that the low molecular

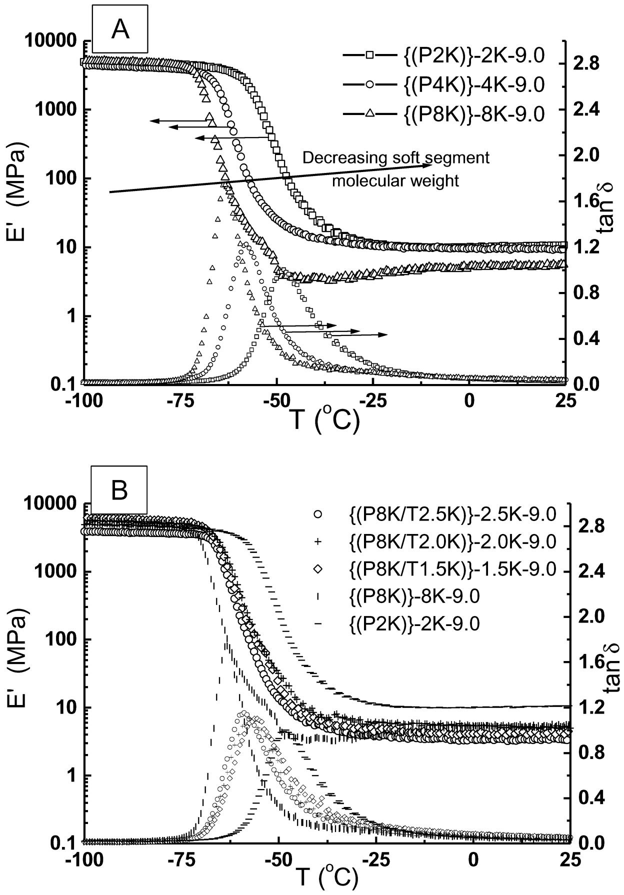

Fig. 8. DMA of poly(urethane–urea) systems (A) without TPG, and (B) with TPG.

components, such as TPG, have upon the mechanical properties of poly(urethane–urea)s. Before discussing these results, consider that the polydispersity of 2000, 4000, and 8000 g/mol PPG diols are quite similar. Thus, a pure 2000 g/mol PPG diol will have greater representation of low molecular diol species (e.g. TPG) than a pure 4000 or 8000 g/mol PPG diol. It is then not surprising that systems based upon a 4000 or 8000 g/mol PPG with TPG present will resemble more closely the 2000 g/mol based formulations. What is noticeable for the TPG-containing systems is the increase in stress for a given strain beyond low extensions, which implies that a thinner film or fiber would be required to accommodate a given force. The TPG-containing systems mimic those formulations based upon a pure 2000 g/mol PPG at higher extensions. In addition, it should be noted that inclusion of TPG results in an upturn in the stress–strain curve at lower elongations and a potentially higher ultimate tensile strength at break than the corresponding system with pure PPG of the same number-average molecular weight. This is consistent with the premise that when TPG incorporates into the hard domains, there will be

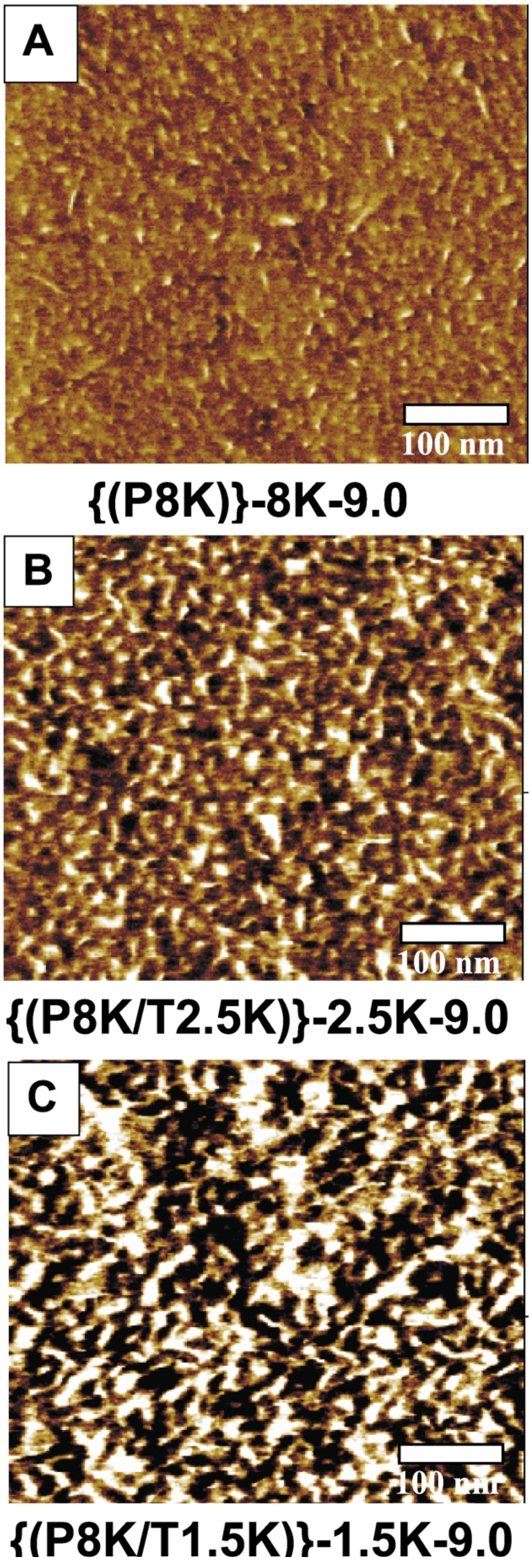

Fig. 7. Atomic force micrographs demonstrating the impact of using TPG in poly(urethane–urea) formulations. The ratio of setpoint amplitude to free amplitude of oscillation (r_{sp}) was held fixed at ca. 0.60 (A) no TPG, (B) ~5.5 wt% polyol TPG, (C) ~11 wt% polyol TPG.

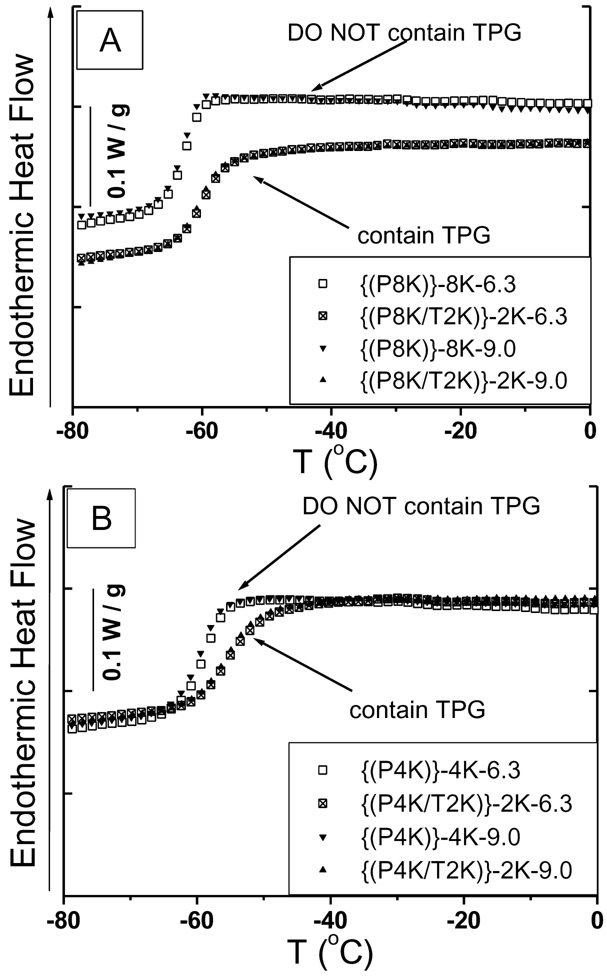

Fig. 9. DSC comparison of systems with and without TPG using base PPG polyols of (A) 8000 g/mol, and (B) 4000 g/mol.

less soft segment material, or conversely there will be a greater content of hard domain material.

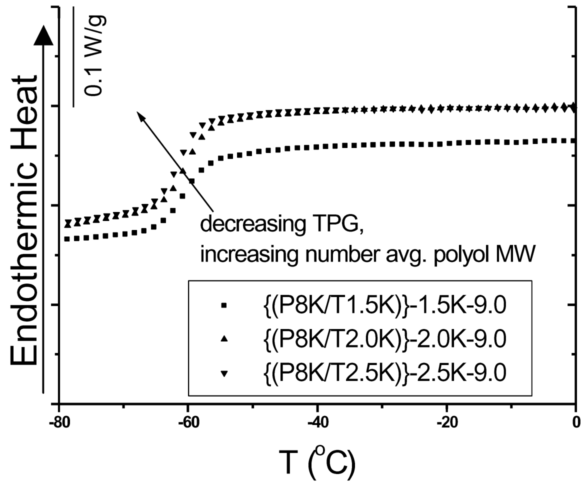

Fig. 10. Impact of varying levels of TPG on location of soft segment glass transition.

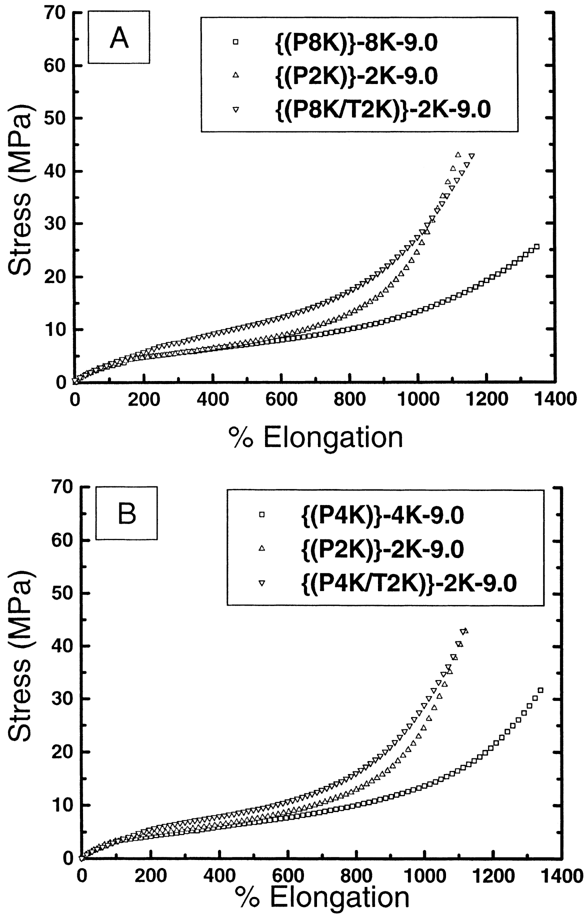

Fig. 11. Impact of TPG upon mechanical properties for systems with (A) 8000 g/mol PPG polyol, and (B) 4000 g/mol PPG polyol.

Formulations containing TPG also exhibit higher unload power and tenacity than those based solely upon pure PPG of comparable number-average molecular weight (Table 4). Similarly, for systems without TPG, it was seen that the unload power and tenacity generally increased for increasing hard segment content. Taken together, this supports the argument that the addition of TPG, and potentially other low molecular homologs of PPG and PTMEG, leads more to an increase in hard segment content than to a decrease in

Table 3
Soft segment glass transition temperatures (°C) of PPG-based poly(urethane–urea)s

Sample designation	DMA[a]	DSC[b]
{(P2K)}-2K-6.3	−48	−49
{(P2K)}-2K-9.0	−48	−50
{(P4K)}-4K-6.3	−59	−58
{(P4K)}-4K-9.0	−58	−59
{(P8K)}-8K-6.3	−66	−62
{(P8K)}-8K-9.0	−63	−62
{(P8K/T2.5K)}-2.5K-9.0	−59	−61
{(P8K/T2.0K)}-2.0K-9.0	−58	−61
{(P8K/T1.5K)}-1.5K-9.0	−56	−61
{(P4K/T2K)}-2.0K-6.3		−56
{(P4K/T2K)}-2.0K-9.0		−56

[a] Determined from the peaks of the DMA tan δ curves.
[b] Determined from inflection points of the T_g region of the DSC curves.

Table 4
Mechanical properties of PPG-based poly(urethane–urea)s

Sample	Solids (%)	ULP at 100% (MPa)	ULP at 200% (MPa)	ULP at 300% (MPa)	Tenac. (MPa)	Elong. (%)	30 s Set (%)	Prepoly. visc. at 50 °C (cP)	Solution visc. at 50 °C (cP)
{(P2K)}-2K-6.3	22	0.55	1.31	2.71	14.0	1690	33.3	11,980	1170
{(P2K)}-2K-9.0	30	0.82	2.03	4.69	45.1	1120	33.8	7010	28,190
{(P4K)}-4K-6.3	22	0.53	1.19	2.52	6.8[a]	1300[a]	26.4	5360	620
{(P4K)}-4K-9.0	22	0.66	1.51	3.38	20.4	1820	28.1	3270	740
{(P8K)}-8K-6.3	18	0.67	1.28	2.48	15.6[a]	1870[a]	13.9	5790	710
{(P8K)}-8K-9.0	15	0.80	1.56	3.34	23.7	1600	13.6	3920	280
{(P8K/T2.5K)}-2.5K-9.0	22	1.01	1.97	4.68	32.2	1290	13.3	n.a.	950
{(P8K/T2.0K)}-2.0K-9.0	22	1.15	2.15	4.96	35.2	1110	11.5	20,000	5060
{(P8K/T1.5K)}-1.5-9.0	22	0.85	1.91	4.75	35.6	1020	20.7	n.a.	6990

[a] Sample did not break at limit of crosshead travel.

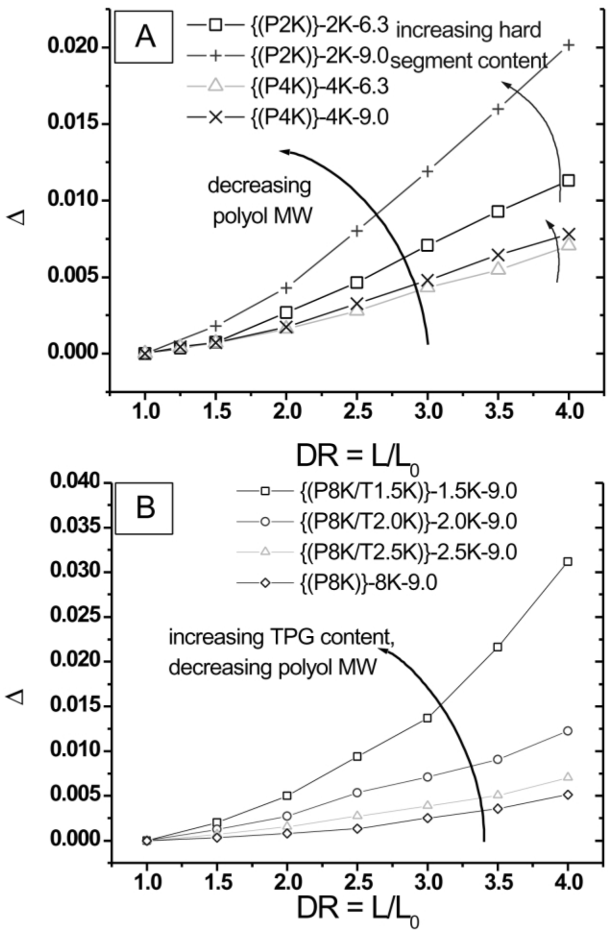

Fig. 12. Birefringence of stretched materials (A) without TPG, and (B) with TPG for various hard segment contents and soft segment lengths.

average soft segment length. The ultimate elongation of the TPG-containing materials (Table 4) was appreciably less than of those based solely upon 8000 g/mol PPG, which is again consistent with the hypothesis that TPG is acting as a hard segment chain extender.

When birefringence was investigated as a function of deformation, it was seen that as either hard segment content increased or average soft segment length decreased for pure PPG systems, there was an increase in the birefringence (Fig. 12A). Since birefringence, for a constant composition, scales with the system average orientation, it may be said that increasing the 'role' of the hard domains, either through hard segment content or restrictions upon soft segments, result in greater orientation. A necessary caveat is that while maintaining hard segment content as measured by urea linkages, there may be an increase in the amount of MDI present in the system. This is due to a varying number of urethane linkages at the interfaces of the hard and soft segments and in sequences of soft segments. Similarly, as TPG content is increased, thus decreasing the average soft segment molecular weight, there is an increase in the birefringence at a given (Fig. 12B). Complicating this interpretation is the likelihood, as seen by AFM and SAXS, that TPG will be present in both hard and soft phases. It

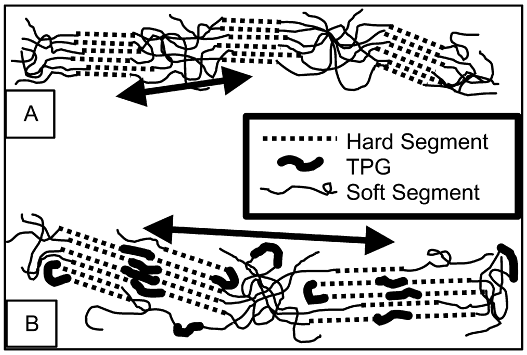

Fig. 13. Schematics of morphologies (A) without TPG, and (B) with TPG. The arrows indicate the interdomain spacings as seen by SAXS.

must also be acknowledged that the optical anisotropy of the phases will be changing as the level of TPG is increased (lower average soft segment molecular weight), due both to inclusion of TPG within the hard phase, and also the increase in urethane linkages formed from MDI and TPG.

7. Discussion

It has been suggested from the results presented that a significant portion of TPG is incorporated into the hard domains as a diol chain extender, rather than in the soft domains as a short soft segment. Atomic force microscopy clearly showed an increase in the hard domain content and size with increasing TPG content. DMA, DSC, and birefringence showed that the TPG-containing systems tended to mimic the behavior of those pure ultra-low monol PPG-based systems with shorter soft segments and/or greater hard segment content. Since TPG will be present in both hard and soft phases, it is probable that the trends seen with DMA, DSC, and birefringence are a combination of trends seen for both the variations of hard segment content and soft segment length. DMA and DSC showed that the soft segment glass transition temperature of TPG-containing systems behaved nearly like the pure unblended PPG diol, implying that the behavior of the 8000 and 4000 g/mol PPG soft segments is essentially unchanged. This suggests that though a considerable portion of the TPG acts as a chain extender in the hard domains, the long PPG soft segments still principally behave as flexible coils between the hard domains. Accepting that the hard domains are clearly larger in TPG-containing systems, if the soft segments continue to separate the hard domains by essentially the same amount as in the case of non-TPG-containing systems, then the interdomain spacing as determined by SAXS would by necessity have to be greater. Simple schematic morphological representations of formulations with and without TPG are shown in Fig. 13A and B. Assuming that the soft segments will act as flexible coils both in and out of the presence of TPG and will be essentially unchanged in length, the distance between larger domains will have to increase (Fig. 13B).

The ability to use TPG to induce strain-hardening at lower elongations in PPG-containing systems may imply that the upturn seen in the stress–strain plots for PTMEG based poly(urethane–urea)s need not solely be due to the phenomenon of strain-induced crystallization. This is, in fact, strongly supported by investigations of a variety of SBS block copolymers, which display extensive strain-hardening at high elongations yet, no segmental crystallization occurs in these well studied materials [15–18]. The low molecular components of the PTMEG molecular weight distribution may behave as diol chain extenders, much as TPG does. The difficulty in obtaining sufficiently narrow molecular weight distribution PTMEG has made this hypothesis somewhat challenging to investigate directly until recently [4].

8. Conclusions

Through the use of TPG to incorporate a low molecular weight component to the ultra-low monol PPG narrow molecular weight distribution, it was clearly seen from SAXS, AFM, thermal and mechanical analysis that the TPG moiety may contribute a significant amount of material that is incorporated into the hard domains. A reasonable assumption would be that other low molecular diols found in the tail of the PPG and PTMEG molecular weight distributions would similarly influence the elastomer morphology. This supposition greatly highlights the need to understand the nature of the molecular weight distribution of the reagents used in the fabrication of poly(urethane–urea)s.

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