

Structure–Property Relationships of Poly(urethane-urea)s with Ultralow Monol Content Poly(propylene glycol) Soft Segments. III. Influence of Mixed Soft Segments of Ultralow Monol Poly(propylene glycol), Poly(tetramethylene ether glycol), and Tri(propylene glycol)

Matthew J. O'Sickey,¹ Bruce D. Lawrey,² Garth L. Wilkes^{1,2}

¹Department of Chemical Engineering, Virginia Polytechnic Institute & State University, Blacksburg, Virginia 24061
²Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Received 17 July 2002; accepted 15 December 2002

ABSTRACT: Recent advances in the catalyst technology associated with the production of poly(propylene glycol) (PPG) have allowed for the fabrication of ultralow monol content PPG macrodiols (Acclaim™ polyols), which are highly bifunctional and can be produced in substantially higher molecular weights and with narrower molecular weight distributions than previously possible. These factors have enabled the preparation of higher value elastomers and may allow for the first manufacture of economically attractive PPG-based poly(urethane-urea) (PUU) fibers. In the past, many performance polyurethane and PUU elastomers used poly(tetramethylene ether glycol) (PTMEG) for the soft segments either alone or in combination with other macrodiols. The work presented here details the investigation of the morphological features of PUU systems with mixed soft segments of PPG, PTMEG, and a low molecular analog of PPG, tri(propylene glycol) (TPG) in an effort to ascertain the influence of structural features on the mechanical and thermal properties of the elastomers. Also of interest was

whether the incorporation of PPG and TPG would either prohibit or greatly hinder the formation of strain-induced PTMEG crystallites. It was found that, even when only 60 wt % of the soft segments consisted of PTMEG, those soft segments were still able to undergo recognizable strain-induced crystallization as detected by wide-angle X-ray scattering. It was also seen that, as the ratio of PPG to PTMEG was varied, there were systematic changes in the soft segment glass transition and cold crystallization characteristics. Inclusion of PPG and TPG resulted in PTMEG's diminished ability to undergo cold and strain-induced crystallization, as seen with differential scanning calorimetry and wide-angle X-ray scattering. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3520–3529, 2003

Key words: structure–property relationships; poly(urethane-urea)s; ultralow monol content; poly(propylene glycol); soft segments; poly(tetramethylene ether glycol); tri(propylene glycol)

INTRODUCTION

As a group of materials, segmented, microphase-separated poly(urethane-urea) (PUU) elastomers are important both commercially and scientifically. Numerous chemical formulations are used to fabricate materials with a range of thermal and mechanical properties, although many of the most significant industrial formulations have relied on the use of the poly(tetramethylene ether glycol) (PTMEG) as a soft segment material until recently.^{1–4} Poly(propylene glycol) (PPG) is most commonly produced through a base-catalyzed process. It has also been used as a soft segment material, which is usually in the making of foams and, less frequently and with less success, in the

production of elastomers. Because it has been conventionally produced, PPG has been limited in its applications because of an inability to maintain difunctionality while building the molecular weight of the PPG. However, advances during the 1990s in the catalysts used to produce PPG diols have led to substantial improvements in the level of difunctionality, molecular weights, and the narrowing of the molecular weight distributions of those oligomeric diols to under 1.1. These diols are referred to as ultralow monol PPG polyols, and they are marketed as Acclaim™ PPG polyols.^{5–8} In addition to the aforementioned enhancements, it was also found for two-step PUU synthesis that the melt viscosities of isocyanate end-capped prepolymers based on this latter generation of PPG diols are dramatically lower than those based on PTMEG of the same number-average molecular weight.^{5,6} For example, at 40°C, the viscosity of a 2000 g/mol PPG-based prepolymer is about 20,000 cP whereas that of a

Correspondence to: G. L. Wilkes (gwilkes@vt.edu).

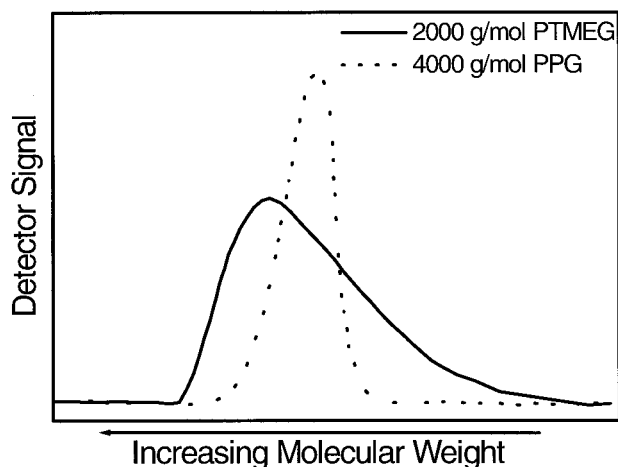


Figure 1 The molecular weight distributions of 4000 g/mol PPG and 2000 g/mol PTMEG polyols.

2000 g/mol PTMEG-based prepolymer is about 195,000 cP, which is an order of magnitude greater. This potentially accords a significant processing advantage in the fabrication of PUUs based on ultralow monol PPG, provided that the pertinent mechanical properties of such ultralow monol based elastomers were found to be suitable relative to those based on PTMEG.

Previous studies have shown the effect of varying the molecular weight of the PPG soft segment and hard segment content in elastomers cured with a combination of 4,4'-diphenyl methane diisocyanate (MDI), ethylene diamine (EDA), and propylene diamine (PDA) on the morphology, microphase separation characteristics, and thermal and mechanical properties.^{7,8} When it became clear that the mechanical properties of the PPG-based elastomers were not comparable (e.g., the permanent set was higher for PPG-based elastomers than for those based on PTMEG) to those based on PTMEG, a subsequent study was per-

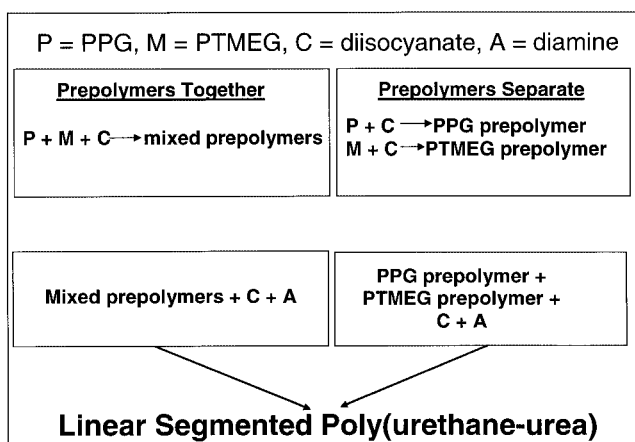


Figure 2 The synthesis methods of two-step production of mixed soft segment PUUs.

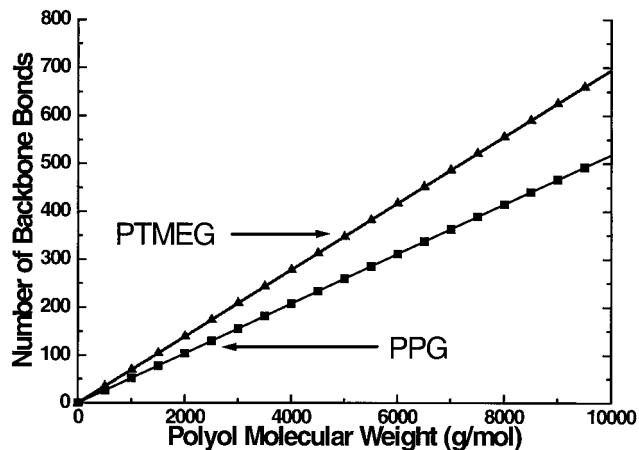


Figure 3 The difference in the number of backbone bonds associated with PPG and PTMEG as a function of the polyol molecular weight.

formed to investigate the influence of the low molecular components of the polyol molecular weight distribution. Conventional PTMEG has an appreciably broader molecular weight distribution (1.7–2.4) than Acclaim™ PPG (1.02–1.15; Fig. 1), and there are significant allotments of high and low molecular weight material in the former.⁵ The higher prepolymer solution viscosities seen in PTMEG-based systems are mainly attributed to the high molecular weight components found in the PTMEG molecular weight distribution. Additionally, it may be noted that, for the polyols, the molecular weight between entanglements for PTMEG (2500 g/mol) is less than that for PPG (7700 g/mol).⁹ Until recently, little work has been done in evaluating the role of the low molecular weight species, which is largely due to economic difficulties in obtaining PTMEG with a sufficiently narrow molecular weight distribution (i.e., polydispersity < 1.1).¹ Ultralow monol content PPG is readily produced with a narrow molecular weight distribution, and thus provided an ideal opportunity for such an investigation.^{7,8}

Previously, it was seen that use of a low molecular weight species such as tri(propylene glycol) (TPG) in PUU formulations based on PPG has a significant impact on the mechanical and morphological properties of the resulting elastomers. It was concluded that low molecular weight components of the polyol molecular weight distribution, such as TPG, principally also acted as hard segment urethane chain extenders rather than only as soft segment links and as such were incorporated in the hard domains of the microphase separated PUU.⁸

The enhancements in the mechanical properties that ultralow monol PPG-based elastomers exhibit in contrast to elastomers fabricated with conventional base catalyzed PPG have been detailed extensively.^{5–8} PPG-based systems present advantages in the pre-

TABLE I
Sample Nomenclature and Hard Segment Contents

Soft Segment MW	NCO/OH Ratio	Hard Segment Content (wt %)		Sample Nomenclature
		Urea ^a	Urea and Urethane ^b	
2000	1.723	8.954	18.98	{(M2K)}-2K-9.0
2000	1.71	8.98	19.09	{(P2K)}-2K-9.0
4000	2.342	8.98	14.34	{(P4K)}-4K-9.0
8000	3.713	8.98	11.62	{(P8K)}-8K-9.0
8000/1500	1.552	8.98	21.98	{(P8K/T1.5K)}-1.5K-9.0 R
8000/2000	1.70	8.98	19.09	{(P8K/T2.0K)}-2.0K-9.0 R
8000/2500	1.868	8.98	17.25	{(P8K/T2.5K)}-2.5K-9.0 R
	1.886	9.15	17.41	{40(P4K) + 60(M2K)}-2.50-9.0 R
	1.838	9.15	17.88	{30(P4K) + 70(M2K)}-2.35-9.0 R
	1.795	9.15	18.33	{20(P4K) + 80(M2K)}-2.22-9.0 R
	1.757	9.15	18.78	{10(P4K) + 90(M2K)}-2.11-9.0 R
	1.85	7.15	13.88	{50(P8K) + 50(M2K)}-3.2K-7.2 R
	1.85	8.23	15.98	{35(P8K) + 65(M2K)}-2.7K-8.2 R
	1.85	8.58	16.65	{30(P8K) + 70(M2K)}-2.6K-8.6 R
	1.732	9.23	19.32	{20(P4K/T2K) + 80(M2K)}-2K-9.1 R
	1.729	9.19	19.28	{30(P4K/T2K) + 70(M2K)}-2K-9.1 R
	1.726	9.16	19.25	{40(P4K/T2K) + 60(M2K)}-2K-9.1 R
	1.70			{20(P8K/T2K) + 80(M2K)}-2K-9.0 S
	1.70			{35(P8K/T2K) + 65(M2K)}-2K-9.0 S
	1.70			{50(P8K/T2K) + 50(M2K)}-2K-9.0 S

^a Calculated using Eq. (1).

^b Calculated using Eq. (2).

polymer solution viscosity and material costs in comparison to PTMEG-based systems. Having determined that inclusion of a low molecular weight component to PPG-based formulations led to enhanced mechanical properties at higher strains, it became of interest to assess what would occur when elastomers were synthesized with mixed soft segments of PPG and PTMEG. Specifically, would the low molecular weight tail of the PTMEG molecular weight distribution act similarly to TPG and would the inclusion of PPG, and in some cases TPG, prevent PTMEG from undergoing cold and strain-induced crystallization? Although the influence of using mixed hard segment chain extenders during PU and PUU synthesis has been considered by a number of researchers, there have been relatively few investigations of the effect of mixed soft segments.^{10,11}

Our previous work detailed the influence of the soft segment molecular weight, polyol molecular weight distribution, and hard segment content on the structure-property relationships of PUU elastomers based upon ultralow monol PPG.^{7,8} The materials used in those studies were synthesized via a two-step process in which PPG diols of varying molecular weight, and in some cases a mixture of PPG and TPG, were end capped with MDI to obtain a prepolymer that was later chain extended with MDI and a 80:20 mixture of EDA and PDA. The elastomers analyzed in the current study were synthesized via two different reaction schemes (Fig. 2) in order to ascertain whether the method of synthesis could appreciably influence the

elastomer morphology and properties.¹²⁻¹⁴ The first of these is essentially identical to the procedure used previously, in that all of the polyols (PPG, TPG, PTMEG) are mixed together first and then end capped with MDI. These prepolymers are then chain extended as described above. The second method differs from the first in that the PPG- and PTMEG-based prepolymers are synthesized separately. The two prepolymers are then mixed together *before* chain extending. These two different methods were used because it is understood that, during prepolymer formation, a distribution of prepolymers will be generated.¹⁵ Potential morphological differences may arise, depending on the composition of the prepolymers; and it was thought that the second method of synthesis could provide insight into this issue. When analyzing these systems, it should be kept in mind that ultralow monol PPG and PTMEG differ in one other key aspect: PTMEG has a greater number of backbone bonds than PPG for a given polyol molecular weight (Fig. 3).

EXPERIMENTAL

Materials

In this study, each of the PUU elastomers examined had about 9% hard segment content. The hard segment contents (%HS) were calculated on the basis of the urea content, as described by the Flory equation :

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

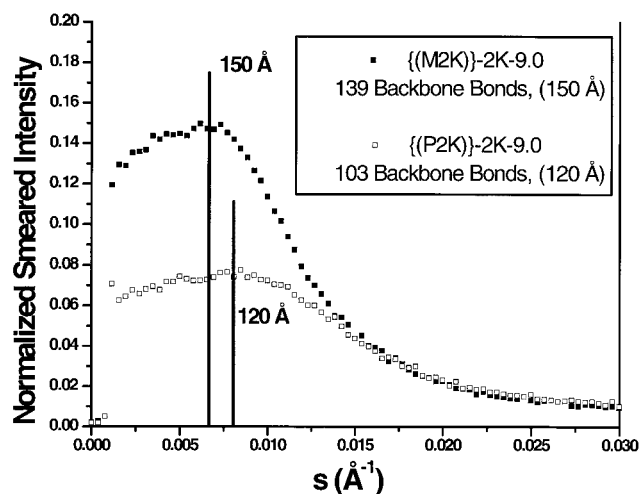


Figure 4 SAXS profiles of pure 2000 g/mol PPG and PTMEG based PUU systems.

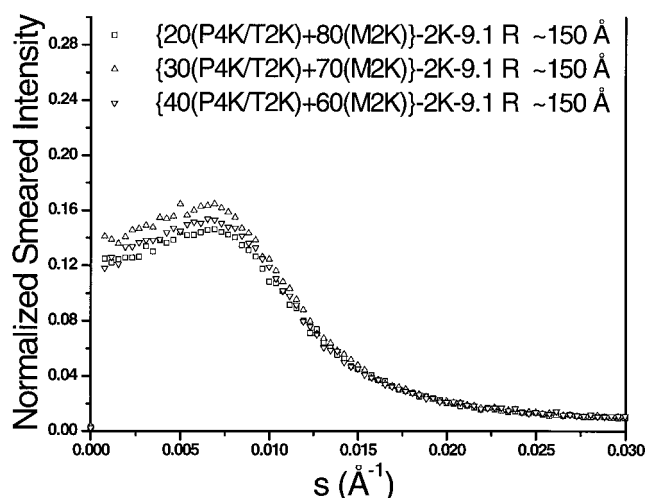


Figure 6 SAXS profiles for PUUs with randomly assembled soft segments of 4000 g/mol PPG, TPG, and 2000 g/mol PTMEG.

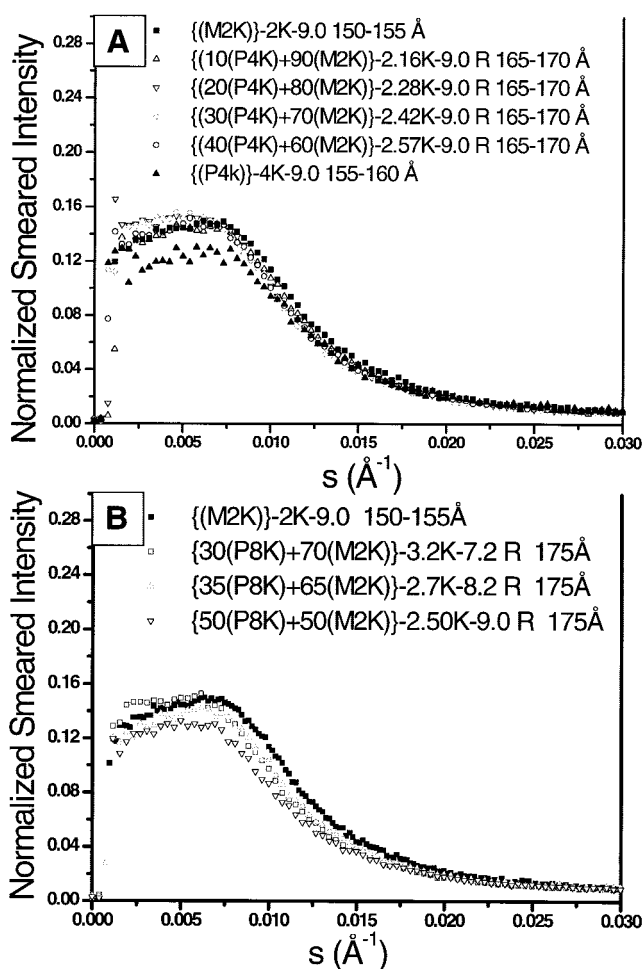


Figure 5 SAXS profiles for PUUs with mixed soft segments of (A) 4000 (B) and 8000 g/mol PPG and 2000 g/mol PTMEG.

where M is the number-average molecular weight; R is the mole ratio of isocyanate to glycol; and the subscripts g , di , and da refer to glycol, diisocyanate, and diamines (average molecular weight in moles), respectively. It was felt that this method best represents the material residing in the hard phases. As can be seen, eq. (1) considers only the portion of isocyanate that reacts with amine for the purpose of calculating the hard segment weight whereas the hard segment contents are often calculated to include the urethane linkages connecting the soft and hard segments, which leads to higher values for the hard segment content.

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

The calculated hard segment contents obtained using both of the above methods are shown in Table I. As stated earlier, the hard segments comprised MDI and a blend of 80 wt % EDA and 20 wt % PDA.

Polymer synthesis

A more detailed description of the syntheses of polymers containing only PPG soft segments and systems with PPG and TPG was previously described.^{7,8} The majority of the elastomers examined in this study were produced using these methods, where all of the various polyols are mixed together, end capped with MDI, and then chain extended with MDI and a 80:20 ratio of EDA/PDA. As noted earlier, a few of the elastomers examined in this study were synthesized via the second reaction scheme described above in which the PPG- and PTMEG-based prepolymers were made separately and then blended together before chain extending.

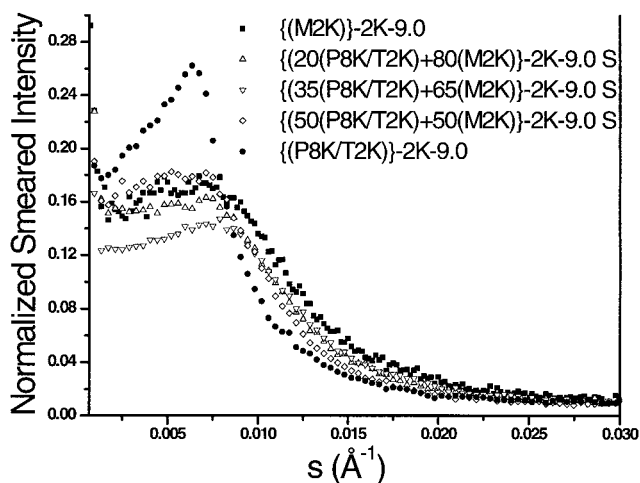


Figure 7 SAXS profiles for PUUs with mixed soft segments of 8000 g/mol PPG, TPG, and 2000 g/mol PTMEG in which the prepolymers are made separately.

Sample nomenclature

The compositions of the materials used within this study, as well as the sample nomenclature, are delineated in Table I. The nomenclature consists of two sections, information regarding the soft segments and information regarding the hard segments. The information within the parentheses indicates the type of polyol (P = PPG, M = PTMEG), the relative amount of each polyol (shown as a weight percentage preceding the type), and the molecular weight of each. The inclusion of TPG, when appropriate, is indicated immediately following the PPG polyol information (/T), which is followed by the number-average molecular weight of the PPG-TPG blend. For instance, P8K/T2K, indicates that an 8000 g/mol PPG was blended with sufficient TPG to achieve an average blend molecular weight of 2000 g/mol. Following the braces is the number-average molecular weight of all the polyols used in the fabrication of that elastomer. The final number in

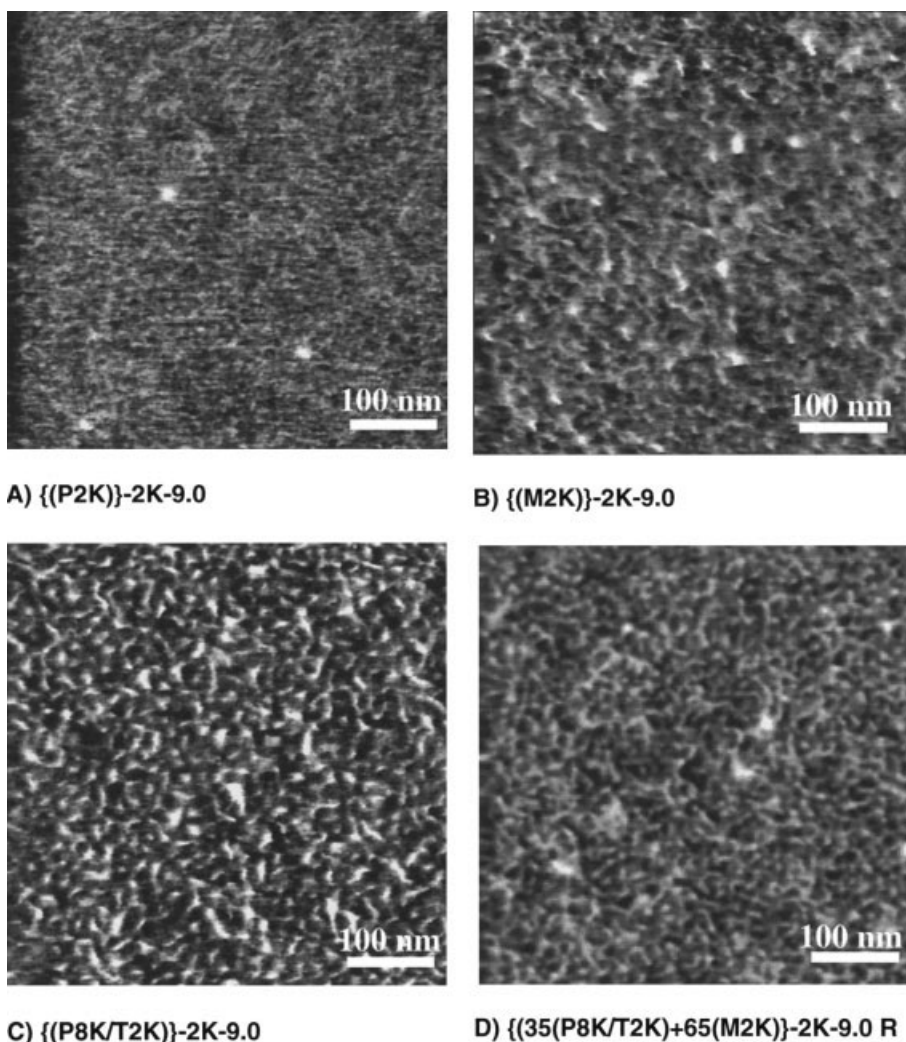


Figure 8 AFM micrographs of (A) {(P2K)}-2K-9.0, (B) {(M2K)}-2K-9.0, (C) {(P8K/T2K)}-2K-9.0, and (D) {(35(P8K/T2K)+65(M2K))}-2K-9.0.

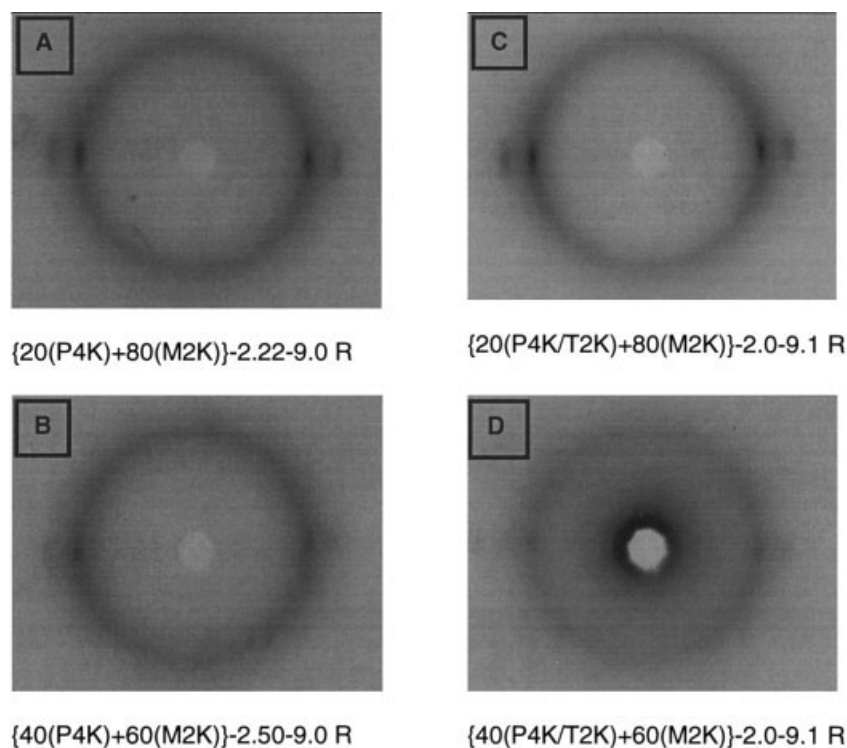


Figure 9 WAXS images of PUU films stretched to 350% elongation. (A,B) PPG-PTMEG and (C,D) PPG-TPG-PTMEG soft segment blends.

the sample nomenclature is the weight percentage of hard segment content as defined in eq. (1). In those instances when the prepolymers are produced separately before chain extension, an S is appended to the nomenclature. Similarly, when the prepolymers are produced from a blend of polyols, an R is

appended to the nomenclature. Throughout this article, when a system is referred to as being a pure or unblended PPG or PTMEG system, this simply means that this particular PUU formulation is unblended and consists of a single soft segment component, either PPG or PTMEG. Preparation of com-

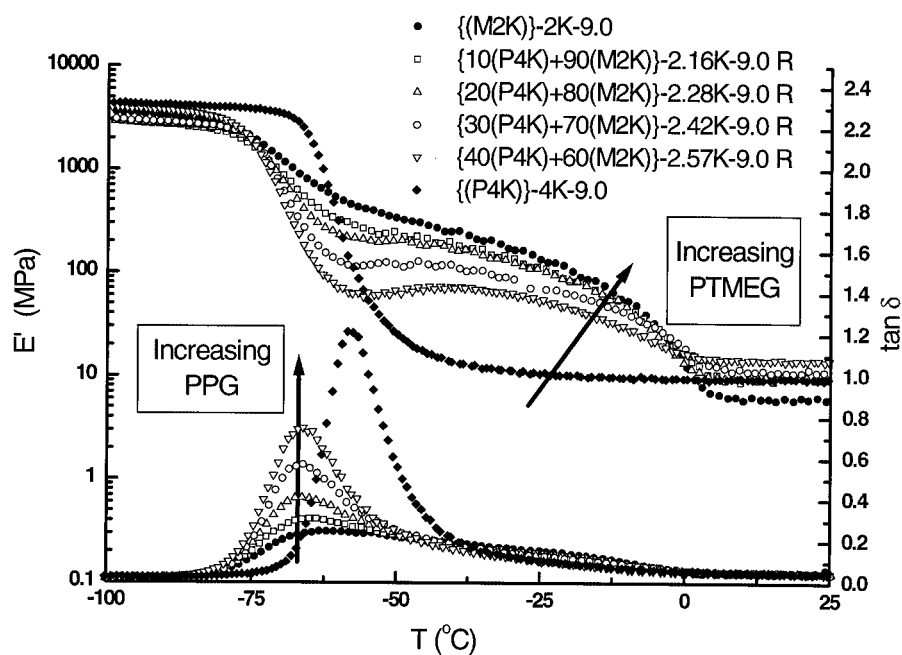


Figure 10 DMA of PUUs fabricated with mixed PPG-PTMEG soft segments that contain no TPG.

parable "unblended" or "pure" elastomer films from these materials was described previously.^{7,8}

Methods

Characterization method procedures for small-angle X-ray scattering (SAXS), atomic force microscopy (AFM), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and mechanical property characterizations were presented in earlier reports.^{7,8,16–23} Wide-angle X-ray scattering (WAXS) was performed to ascertain the strain-induced crystallization characteristics, particularly the point of onset, for those materials based upon blends of PPG and PTMEG polyols. A Phillips model PW1720 generator was operated at 40 kV and 20 mA to obtain nickel filtered $\text{CuK}\alpha$ radiation (wavelength = 1.542 Å) with 0.020 pinhole collimation. A Warhus camera with a sample to film distance of 7.3 cm was used with exposure times of 4 h for samples with a thickness of approximately 0.15 mm.

RESULTS AND DISCUSSION

In the tracking of morphological changes, one of the key experimentally determined parameters is the interdomain spacing determined from SAXS experiments. Slit smeared scattering profiles were obtained for pure 2000 g/mol PPG-based and pure PTMEG-based PUU systems, and they are shown in Figure 4. The interdomain spacing of the PTMEG-based system is greater than that of the PPG-based one, which may be attributed to two effects. First, for comparable soft segment molecular weights, there are a greater number of backbone bonds in the PTMEG-based system, allowing for greater distance between hard domains (recall Fig. 3). Second, the low molecular weight component of the PTMEG molecular weight distribution may be incorporated in the hard domains as an urethane chain extender in a fashion similar to what was seen for TPG in PPG-based PUUs. When this occurs, the hard domains increase in size while the nonmixed flexible-coil soft segments remain the same in size, thus leading to increases in the interdomain distance. In addition, the PTMEG-based system exhibits a sharpening in the scattering profile, which is also similar to results seen for systems based on a blend of PPG and TPG.

When a 4000 g/mol PPG and 2000 g/mol PTMEG were blended to generate PUUs rich in PTMEG [Fig. 5(A)], there was a broadening in the scattering profile and the interdomain spacings of the various blends were essentially the same. The spacings were slightly greater than either that of the pure PPG-based or pure PTMEG-based formulations. This may be due to extension of the soft segments during prepolymerization.¹³ The behavior seen for formulations based upon

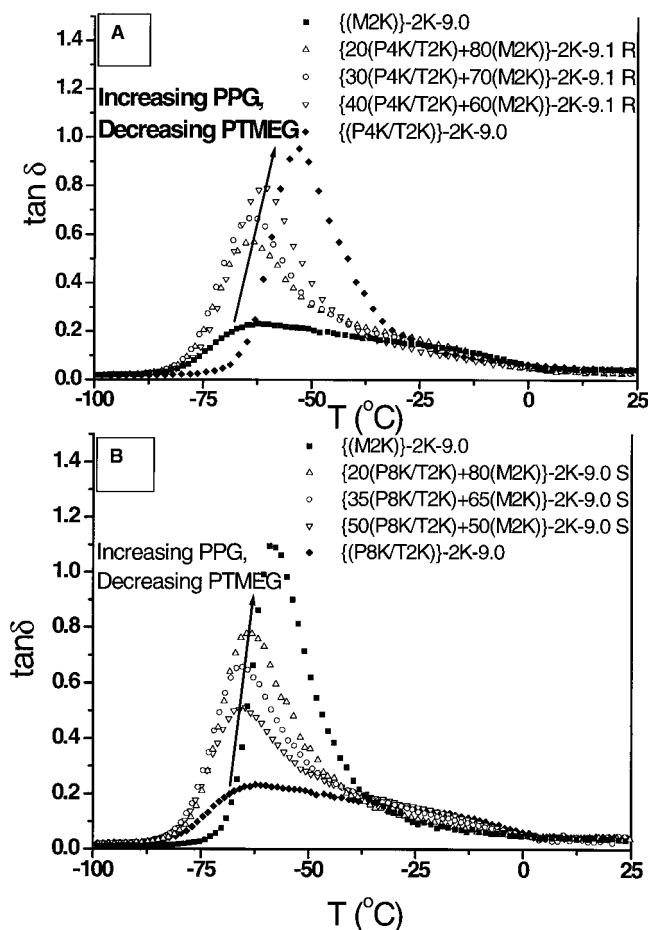


Figure 11 The $\tan \delta$ behavior from DMA for PUUs fabricated with mixed PPG-TPG-PTMEG soft segments with (A) randomly assembled prepolymers and (B) prepolymers made separately and mixed prior to chain extending.

8000 g/mol PPG and 2000 g/mol PTMEG [Fig. 5(B)] is similar in that the blend systems are all of approximately the same spacing (175 Å). The interdomain spacing for the 8000 g/mol PPG is also about 175 Å, so in this instance the interdomain spacings of the mixed soft segment systems falls within the bounds of the two pure soft segment components, albeit just barely.

If TPG is incorporated into a randomly assembled blend formulation, along with 4000 g/mol PPG and 2000 g/mol PTMEG, it is again seen that the various blends have essentially identical interdomain spacings (Fig. 6). The inclusion of TPG results in a sharpening of the scattering profiles in contrast to systems without TPG, which is consistent with what was seen for formulations based on PPG-TPG blends.⁸ Similar results are seen when the prepolymers are prepared separately (Fig. 7). In this system an 8000 g/mol PPG is blended with TPG to achieve a PPG molecular weight of 2000 g/mol before end capping with MDI. Similarly, a 2000 g/mol PTMEG is end capped with MDI. The two end-capped prepolymers are then mixed together and chain extended. Once again, the blends

TABLE II
Interdomain Spacings and Soft Segment Glass Transitions of Mixed Soft Segment Based Poly(urethane-ureas)

Sample Nomenclature	Interdomain Spacing, d (Å)	Soft Segment Glass Transition ^a (°C)	Soft Segment Glass Transition ^b (°C)
{(M2K)}-2K-9.0	150–155	–62.5	–69.8
{(P2K)}-2K-9.0	120	–48.1	–49.7
{(P4K)}-4K-9.0	145	–58.0	–59.1
{(P8K)}-8K-9.0	175–180	–63.4	–62.3
{(P8K/T1.5K)}-1.5K-9.0	160	–59.0	–61.2
{(P8K/T2.0K)}-2.0K-9.0	175	–57.6	–60.8
{(P8K/T2.5K)}-2.5K-9.0	190	–56.0	–60.6
{10(P4K) + 90(M2K)}-2.11-9.0 R	165–170	–65.0	–69.7
{20(P4K) + 80(M2K)}-2.22-9.0 R	165–170	–66.9	–69.3
{30(P4K) + 70(M2K)}-2.35-9.0 R	165–170	–66.1	–68.4
{40(P4K) + 60(M2K)}-2.50-9.0 R	165–170	–66.4	–67.0
{50(P8K) + 50(M2K)}-3.2K-7.2 R	175		
{35(P8K) + 65(M2K)}-2.7K-8.2 R	175		
{30(P8K) + 70(M2K)}-2.6K-8.6 R	175		
{20(P4K/T2K) + 80(M2K)}-2K-9.1 R	145–150	–64.5	–68.7
{30(P4K/T2K) + 70(M2K)}-2K-9.1 R	145–150	–63.1	–67.8
{40(P4K/T2K) + 60(M2K)}-2K-9.1 R	145–150	–61.2	–66.2
{20(P8K/T2K) + 80(M2K)}-2K-9.0 S	175	–68.2	
{35(P8K/T2K) + 65(M2K)}-2K-9.0 S	175	–66.6	
{50(P8K/T2K) + 50(M2K)}-2K-9.0 S	175	–66.1	

^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.

possess essentially identical interdomain spacings and there is a sharpening of the peaks in comparison with those systems without TPG.

In all cases for PUUs based on PTMEG-rich blends, the relative amount of PTMEG had virtually no major influence on the interdomain spacing as seen by SAXS. Inclusion of PTMEG and/or TPG resulted in a sharpening of the SAXS profile peak, implying a more uniform distribution of interdomain spacings, which is consistent with previous results for PPG-TPG based systems as stated above.

AFM was utilized to ascertain any changes in the near surface morphology of thin films investigated in this study [Fig. 8(A–D)]. In these AFM micrographs, the light regions correspond to hard phase material and the darker regions correspond to soft phase material. We saw that the mixed soft segment systems possessed characteristics of both the pure PPG- [Fig. 8(A)] and pure PTMEG-based systems. Formulations based upon PTMEG have a fine grain structure of hard domains within a soft matrix, and occasional larger hard domains are seen [Fig. 8(B)]. The presence of these larger hard domains is consistent with results seen for PPG-TPG based PUUs [Fig. 8(C)]. These larger hard domains also appear in the blend systems [Fig. 8(D)]. No appreciable influence of using mixed soft segments was inferred in the near surface morphology of the materials examined in this study.

In addition to determining the influence of using mixed soft segments on the morphology, it was also of interest to assess whether strain-induced crystalliza-

tion of PTMEG would be appreciably hindered by the presence of PPG and TPG. WAXS was employed to determine whether blending PTMEG with noncrystallizable PPG and TPG would hinder or prevent strain-induced crystallization of PTMEG. In all cases, film samples were stretched 350%, which is beyond the onset point of strain-induced crystallization of 2000 g/mol pure PTMEG at ambient conditions. It was seen that as the amount of PPG was increased from 20 to 40 wt % [Fig. 9(A,B)] that the amount of crystalline content as denoted by the equatorial reflections decreases, as would be expected because of decreasing the content of crystallizable material. However, even for cases where there was substantial noncrystallizable PPG material [Fig. 9(B)] present, there is still clear evidence for the occurrence of PTMEG strain-induced crystallization. However, when formulations with comparable amounts of PTMEG that contain TPG were analyzed [Fig. 9(C,D)], it appears that the strain-induced crystallization of PTMEG is hindered more than without TPG.

It is reasonable to assume that, if the presence of TPG in a PUU formulation hinders strain-induced crystallization of PTMEG, it will similarly hinder the cold crystallization of this same segment that occurs at subambient temperatures. To test this hypothesis, DMA and DSC were conducted on the samples examined in this study. The incidence of cold crystallization is readily apparent from DMA results for mixed soft segment systems both without (Fig. 10) and with TPG [Fig. 11(A,B)]. It was seen that, as the amount of crys-

tallizable soft segment material increases, the extent of cold crystallization also increases. Some crystallization occurs during the initial cooling process. As the temperature is increased above the soft segment glass transition, those formulations containing PTMEG achieve sufficient soft segment mobility to undergo crystallization. When this occurs, the moduli of PTMEG containing systems increase (Fig. 10) with respect to those without or having lower PTMEG content. When the PTMEG crystallites melt, this trend is reversed; that is, those systems with greater PPG content exhibit higher moduli than those without. Systems both with and without TPG exhibit only a single soft segment glass transition, which is very nearly that of a PUU with only PTMEG soft segments. It is interesting to see that the soft segment glass transition (Table II) of systems without TPG is nearly constant at about -66°C over the range of compositions. However, systems with TPG exhibit a shift in the soft segment glass-transition temperature to higher temperatures, as signified by the $\tan \delta$, with increasing content of TPG. This behavior occurs regardless of whether the soft segments are assembled randomly [Fig. 11(A)] or separately [Fig. 11(B)], and it is consistent with the argument put forward in previous work, asserting that TPG incorporates into the hard phase and generates additional restraints on soft segment mobility. DMA regrettably does not provide a quantitative measure of the degree of cold crystallization.

DSC was used both to verify the findings regarding the soft segment glass-transition behavior (Table II) and to attempt to quantify the influence of TPG on the cold crystallization of PTMEG soft segments. The melting temperature (T_m), as determined from the apex of the melting peak, decreases somewhat as the PPG content of the soft segment blends is increased. This may imply that PPG and PTMEG are nearly completely compatible, although interpretation is complicated by the consideration of both the crystal size and its perfection, a topic not considered in this investigation. From the DSC plots shown [Fig. 12(A,B)] it does appear, using the heat of fusion, that the inclusion of TPG in formulations does inhibit cold crystallization to some extent. However, it should be recognized that the two systems do not have completely comparable compositions. The heat of fusion for a given composition was normalized by the heat of fusion for a pure PTMEG-based PUU, $\{(\text{M2K})\}-2\text{K}-9.0$, of comparable hard segment content. These results (Fig. 13), clearly show that TPG containing formulations exhibit less cold crystallization than those of comparable composition without TPG. By inference, the presence of TPG in a formulation may also inhibit strain-induced crystallization, supporting the results seen with WAXS. These results further support the hypothesis that TPG incorporates into the hard phase, generating a greater hard phase volume and increas-

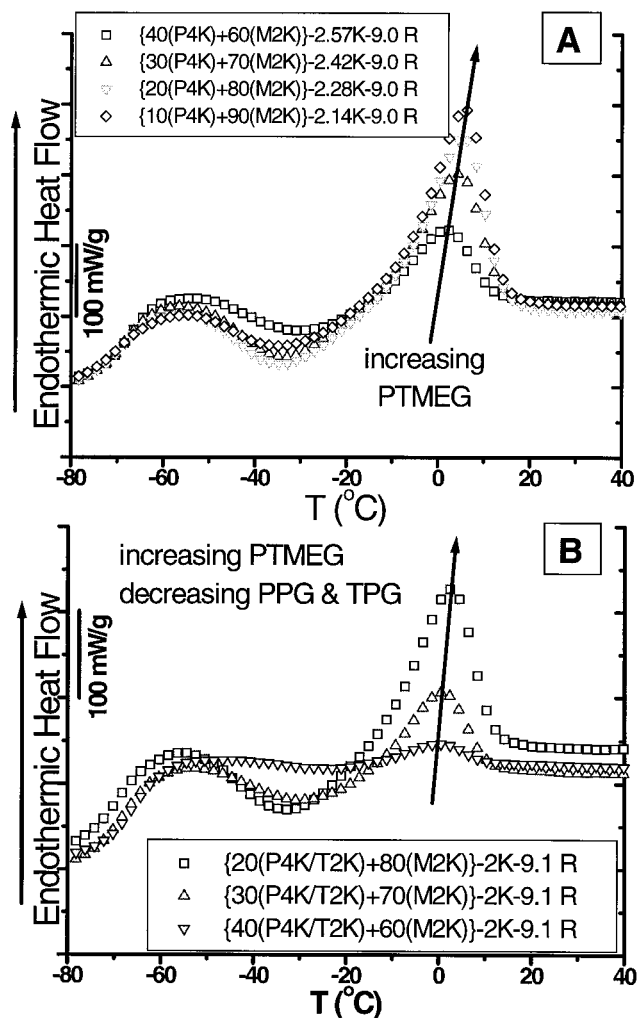


Figure 12 Second heating DSC scans of PUUs fabricated with mixed soft segments of PPG and PTMEG (A) without and (B) with TPG.

ing the phase mixing, which lead to greater restrictions on soft segment mobility and decreased crystallinity. It should also be noted that, as the PPG/TPG content increases, the PTMEG becomes less able to undergo cold crystallization.

CONCLUSIONS

We demonstrated that PUUs may be fashioned with mixed soft segments of ultralow monol content PPG and PTMEG. Such systems did not exhibit appreciable morphological differences from formulations based upon a single soft segment type. The resulting morphology of the systems examined was generally intermediate to what has been seen for pure PPG and PTMEG systems, although it should be acknowledged that the morphology of those two systems is reasonably similar. The incorporation of a noncrystallizable soft segment (PPG) in a PTMEG containing PUU did not prevent strain-induced or

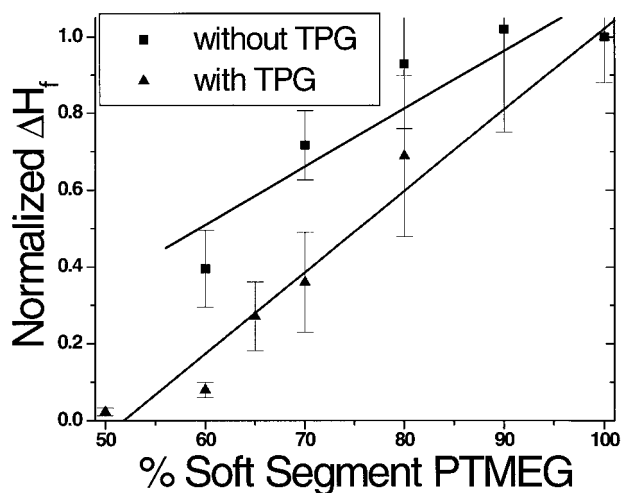


Figure 13 The normalized heat of fusion (ΔH_f) results for PUUs of mixed PTMEG and PPG soft segments with and without TPG.

cold crystallization of PTMEG from occurring, although increasing amounts of PPG increasingly inhibit the process. More dramatically, it was seen that, for equal weight percentages of PTMEG, inclusion of TPG in the formulations resulted in less crystalline material and inhibited strain-induced crystallization processes. Furthermore, TPG containing systems exhibited higher soft segment glass-transition temperatures, indicating once again that TPG should be considered more appropriately as a hard segment component. From the conclusions drawn regarding the role of TPG, the importance of the low molecular weight components of the polyol molecular weight distributions was demonstrated.

References

1. Shirasaka, H.; Inoue, S.; Asai, K.; Okamoto, H. *Macromolecules* 2000, 33, 2775.
2. Schneider, N. S.; Sung, C. S. P. *Polym Eng Sci* 1977, 17, 73.
3. Ng, H. N.; Allegranza, A. E.; Seymour, R. W.; Cooper, S. L. *Polymer* 1973, 14, 255.
4. Takahara, A.; Tashita, J.; Kajiyama, T.; Takayanagi, M.; MacKnight, W. J. *Polymer* 1985, 26, 987.
5. Seneker, S. D.; Barksby, N.; Lawrey, B. D. In *Proceedings of SPI—Polyurethanes*; Las Vegas, NV, 1996.
6. Barksby, N.; Seneker, S. D.; Allen, G. L. In *Proceedings of the PMA Conference*; Pittsburgh, PA, 1995.
7. O'Sickey, M. J.; Lawrey, B. D.; Wilkes, G. L. *J Appl Polym Sci* 2002, 84, 229.
8. O'Sickey, M. J.; Lawrey, B. D.; Wilkes, G. L. *Polymer* 2002, 43, 7399.
9. Zang, Y. H.; Carreau, P. J. *J Appl Polym Sci* 1991, 42, 1965.
10. Wen, T. C.; Tseng, H. S.; Cheng, T. T. *Ind Eng Chem Res* 2000, 39, 72.
11. Yang, C. H.; Li, Y. J.; Wen, T. C. *Ind Eng Chem Res* 1997, 36, 1614.
12. Sanchez-Adsuar, M. S.; Papon, E.; Villenave, J. J. *J Appl Polym Sci* 2000, 76, 1590.
13. Sanchez-Adsuar, M. S.; Papon, E.; Villenave, J. J. *J Appl Polym Sci* 2000, 76, 1596.
14. Sanchez-Adsuar, M. S.; Papon, E.; Villenave, J. J. *J Appl Polym Sci* 2000, 76, 1602.
15. Blomquist, R. *Urethane Sealants—Their Chemistry and Properties*. Caulks & Sealants Short Course, Dearborn, MI, 1992.
16. Bonart, R. *J Macromol Sci Phys* 1968, B2, 115.
17. Bonart, R.; Morbitzer, L.; Muller, E. H. *J Macromol Sci Phys* 1974, B9, 447.
18. Koberstein, J. T.; Stein, R. S. *J Polym Sci B Polym Phys* 1983, 21, 1439.
19. Koberstein, J. T.; Stein, R. S. *J Polym Sci B Polym Phys* 1983, 21, 2183.
20. Tyagi, D.; Yilgor, I.; McGrath, J. E.; Wilkes, G. L. *Polymer* 1984, 25, 1807.
21. Tyagi, D.; McGrath, J. E.; Wilkes, G. L. *Polym Eng Sci* 1986, 26, 1371.
22. McLean, R. S.; Sauer, B. B. *Macromolecules* 1997, 30, 8314.
23. Garrett, J. T.; Runt, J.; Lin, J. S. *Macromolecules* 2000, 33, 6353.