

Microphase Separation and Rheological Properties of Polyurethane Melts. 3. Effect of Block Incompatibility on the Viscoelastic Properties

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Received May 25, 1999; Revised Manuscript Received October 29, 1999

ABSTRACT: The accompanying paper described the structural characterization of polyurethane multi-block copolymers that varied block incompatibility at fixed block length and composition. Their linear viscoelastic properties are presented in this paper. Dynamic mechanical experiments in temperature sweep mode confirmed that the materials ranged from almost homogeneous to highly microphase-separated. Dynamic mechanical frequency sweep experiments showed a Rouse-like frequency response in all materials at high temperatures, including those polyurethanes that were highly microphase-separated. This is in stark contrast to the numerous reports on microphase-separated block copolymers that show nonliquidlike terminal behavior at low frequencies. We attribute this homopolymer-like response of microphase-separated polyurethanes to a lack of long-range order in their microphase-separated structure and regard it to be a crucial feature of most commercial multiblock copolymers. The apparent activation energy for terminal flow was found to be insensitive to the extent of microphase separation, indicating that the thermodynamic penalty χN expected for chain motion in block copolymers plays an insignificant role in the dynamics of the present materials. We demonstrate that bare effects (primarily proximity to the T_g) and dynamic asymmetry (friction in one block much larger than in the other) play a major role in the dynamics of polyurethanes. The latter is expected to be especially important in the dynamics of elastomeric block copolymers whose blocks usually have widely separated T_g 's.

1. Introduction

Polyurethanes are $(AB)_n$ type multiblock copolymers composed of "hard" and "soft" segments that microphase-separate due to thermodynamic incompatibility. The resulting microstructure of low- T_g soft-segment-rich domains reinforced by rigid hard-segment-rich domains has excellent elastomeric properties, making polyurethanes useful as thermoplastic elastomers, coatings, textiles, etc.¹ The most important parameters that influence the properties of multiblock copolymers are block length N , block incompatibility χ , and composition. The first paper in this series investigated the effect of block length on the structure and the viscoelastic properties at constant incompatibility and composition.² In that work, we studied the "E-series" of materials with polycaprolactone soft segments and isophorone diisocyanate/1,4-butanediol hard segments as a function of block length. There were three primary conclusions regarding the viscoelastic properties of polyurethanes in that paper. First, block length had a very large effect on the terminal properties of polyurethane melts with terminal viscosity varying as approximately (block length)^{4.5}. Second, at sufficiently high temperature the polyurethanes had a relaxation spectrum similar to that of a homopolymer of low molecular weight, indicating that either the polyurethanes were homogeneous at high temperatures or microphase separation did not affect the relaxation spectrum. Finally, the shift factors at sufficiently high temperatures could be adequately represented by the WLF equation with "universal" values of the constants C_{1g} and C_{2g} , provided the reference temperature was taken to be the thermal T_g that the polyurethane would have if it were single phase.

In this second part of the study of viscoelastic properties of polyurethanes, the effects of block incompatibility on the structure and viscoelastic properties of polyure-

thane elastomers are investigated. The accompanying paper³ describes the synthesis and structural characterization of polyurethanes with varying block incompatibility; this paper describes their viscoelastic properties. An unusual feature of these materials is that the segmental incompatibility was changed after synthesis of the polyurethanes, and hence, the effects of incompatibility are measured at constant molecular weight. It is demonstrated that bare effects (i.e., those present even in homogeneous samples) and the effects of dynamic asymmetry (i.e., a large difference in the friction coefficients of the blocks) are extremely important in determining the terminal relaxation properties. In addition, it is shown that even highly microphase-separated samples show relaxation spectra similar to those of homopolymer melts. This observation is directly related to the lack of long-range order in the microphase-separated state of polyurethanes.

2. Experimental Section

The materials used in this work were polyurethane cationomers with poly(propylene oxide) (PPO) soft segments and hard segments based on isophorone diisocyanate and *N,N*-dimethylamino-1,2-propanediol (DMP). They have been described in detail in the accompanying paper.³ Briefly, the DMP chain extender can be quaternized with iodomethane, thereby varying the incompatibility of the two blocks in a controlled fashion without changing the overall molecular weight of the polyurethane. The materials are designated as I x - y where x refers to the molecular weight of the soft segment and y refers to the percentage of DMP groups that have been quaternized. Three polyurethanes were synthesized by using three different PPO molecular weights, 725, 1000, and 2000. These polyurethanes were quaternized to various extents to yield three series of materials with varying block incompatibility which increases with quaternization. All these polyurethanes were amorphous and had about 50 wt % of soft segment. They are almost certainly unentangled due to their low molecular weights (Table 1 in the accompanying paper³).

Samples for rheometric experiments were cut from films prepared by casting from solution and drying in a vacuum.

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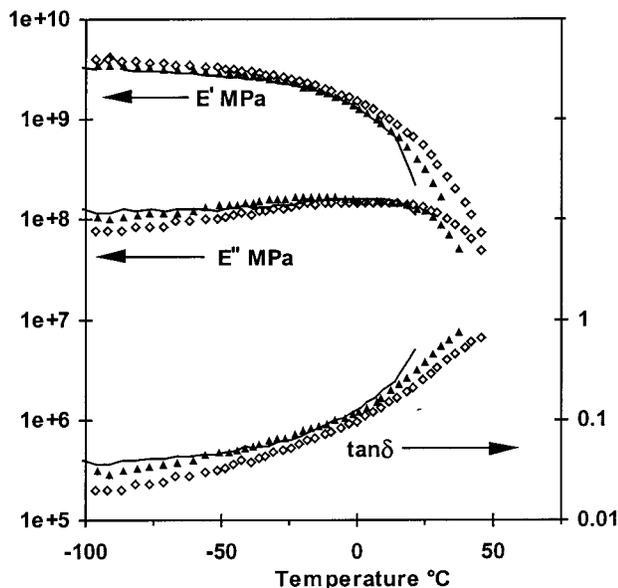


Figure 1. Dynamic mechanical temperature sweep data for the I725 series: solid line, I725-0; filled triangles, I725-25; open diamonds, I725-40. I725-12 has been omitted for clarity.

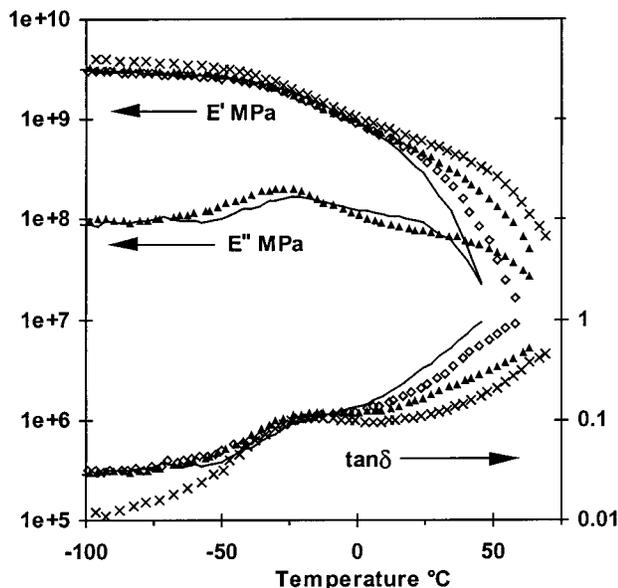


Figure 2. Dynamic mechanical temperature sweep data for the I1000 series: solid line, I1000-0; open diamonds, I1000-13; filled triangles, I1000-32; + symbols, I725-40. E' data for I1000-13 and I1000-40 have been omitted for clarity.

All samples were subjected to annealing at 55 °C for 12–14 h immediately prior to experiment in order to obtain reproducible data. High-frequency dynamic mechanical temperature sweep experiments were conducted in tensile mode as previously described.² Dynamic mechanical frequency sweep experiments in the linear viscoelastic region were conducted in parallel plate geometry between 0.01 and 100 rad/s in the temperature range 30–140 °C. At high temperatures, frequency sweeps were restricted to high frequencies, making the experimental times short enough to ignore dequaternization. Other details of sample preparation and experimental procedure have been presented elsewhere.^{2,4}

3. Results

3.1. Temperature Sweep Experiments. Figures 1–3 show the results of dynamic mechanical temperature sweep experiments at a high test frequency (80 rad/s) for the polyurethane cationomers. Figure 1 shows no

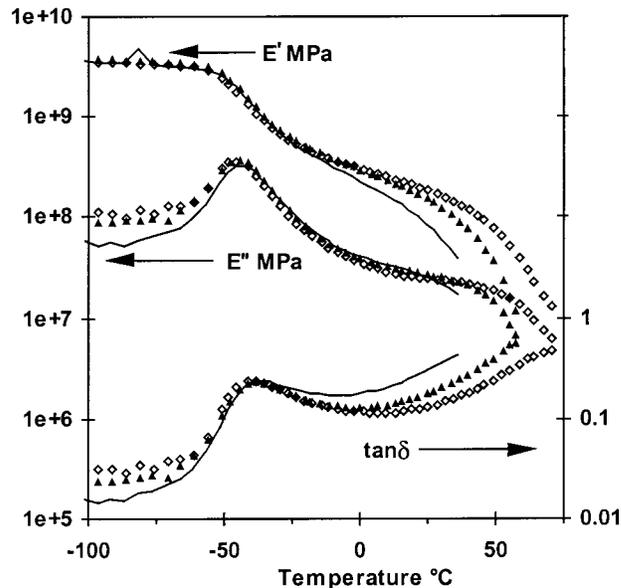


Figure 3. Dynamic mechanical temperature sweep data for the I2000 series: solid line, I2000-0; filled triangles, I2000-14; open diamonds, I2000-40.

peaks in E' or $\tan \delta$ at low temperatures, indicating that all the I725 materials are almost completely homogeneous. In the accompanying paper it was pointed out that this is not strictly true and that these materials have at least a small amount of microphase separation. Evidently, microphase separation is too weak to be observed in high-frequency dynamic mechanical experiments.

Figure 2 shows that I1000-0 has a broad peak in E' at about -20 °C, which corresponds to the glass transition temperature of the soft-segment-rich microphase. E' shows a broad decrease around this temperature, followed by a slight plateau indicative of some microphase-separated hard-segment domains. Increasing quaternization causes a decrease in the T_g and a broadening of the E' plateau, both indicative of better microphase separation.

Finally, Figure 3 shows that all I2000 materials have sharp, well-defined peaks in E' at about -45 °C and well-defined plateaus in E' above the soft-segment glass transition, indicating that all I2000 polyurethanes are highly microphase-separated. There is no shift in the E' peak (i.e., T_g of soft-segment-rich microphase) with quaternization in accordance with DSC data.⁴

In all cases, increasing quaternization causes an increase in storage modulus at high temperatures and a correspondingly higher temperature for flow. This increasingly solidlike behavior with quaternization, which will be demonstrated more clearly in the next section, has three distinct causes that have been described briefly by Hamersky et al.⁵ To have a physical picture in mind while examining further experimental data, they are explained here for the specific case of a block copolymer comprised of blocks A and B with ϕ being the volume fraction of block A.

The first cause for the increasingly solidlike behavior is "bare" effects, i.e., those effects that are unrelated to microphase separation. These would be present even if the χ parameter were to be zero (athermal blocks), making the copolymers completely homogeneous. In that case, one may define a monomeric friction coefficient ζ^{sp} for this single-phase copolymer

$$\zeta^{\text{sp}} = \mathbf{F}(\zeta_{\text{A}}^0, \zeta_{\text{B}}^0, \phi, T, \chi=0) \quad (1)$$

where ζ_{A}^0 and ζ_{B}^0 are the monomeric friction coefficients of the pure homopolymers with the same molecular weights as the blocks, at the same temperature. ζ^{sp} may be related to experimentally measurable dynamic properties such as viscosity or diffusivity by some appropriate molecular model such as Rouse theory. By definition, differences in the ζ^{sp} of different copolymers constitute the above-mentioned "bare" effects, i.e., effects unrelated to microphase separation.

Such a single-phase copolymer would have only one glass transition, henceforth referred to as the "single-phase glass transition", at a temperature denoted by T_{g}^{sp} . This is generally a function of the T_{g} 's of the blocks and their volume fractions:

$$T_{\text{g}}^{\text{sp}} = \mathbf{G}(\phi, T_{\text{gA}}, T_{\text{gB}}, \chi=0) \quad (2)$$

with equations such as the Fox equation being commonly applicable forms for \mathbf{G} .

Chapman et al.⁶ have demonstrated that in such a single-phase system the T_{g}^{sp} is the primary determinant of ζ^{sp} . Accordingly, the ζ^{sp} 's of the various polyurethanes studied here are expected to depend primarily on their T_{g}^{sp} 's since there are no significant differences between their chemical structures. How does T_{g}^{sp} vary with quaternization? It has been shown that the T_{g} of the pure hard segment increases with quaternization (Figure 1 in the companion paper³). Accordingly, the T_{g}^{sp} (and therefore ζ^{sp}) is also expected to increase with quaternization. Therefore, at least some of the increase in storage modulus and flow temperature with quaternization may be attributed to the bare effects of increasing the single-phase T_{g} .

In addition to these bare effects, the viscoelastic properties of the present materials are influenced by microphase separation in two qualitatively distinct ways. The first of these is important when one of the components has a much higher monomeric friction coefficient ζ than the other. This situation is very common in block copolymer elastomers; e.g., in SIS, SBS, or polyurethane elastomers, $\zeta_{\text{hard}} \gg \zeta_{\text{soft}}$ mainly because $T_{\text{g,hard}} \gg T_{\text{g,soft}}$. In such a case, microphase separation causes the local composition to deviate from the average composition ϕ , and hence the local monomeric friction coefficient ζ also varies throughout the sample. Thus, in the case of SIS triblock elastomers, styrene-rich regions have much lower mobility (much higher ζ) than the isoprene-rich regions, thereby increasing the viscosity of the microphase-separated sample. This will be referred to as the "dynamic asymmetry" effect of microphase separation; i.e., it depends on the difference in friction coefficients of the components. It does *not* depend on the χ parameter, except through the effect of χ on the extent of microphase separation. The second effect of microphase separation is the "thermodynamic" aspect which is the energy penalty ($\propto \chi$) of dragging a hard segment through the soft-segment-rich microphase, and vice versa. This energy penalty, which also impedes chain motion and thereby increases the viscosity, is independent of the relative friction coefficients of the two blocks.

Thus, if we consider the I2000 series of materials as a concrete example, the viscosity at a given temperature would increase with quaternization even if these ma-

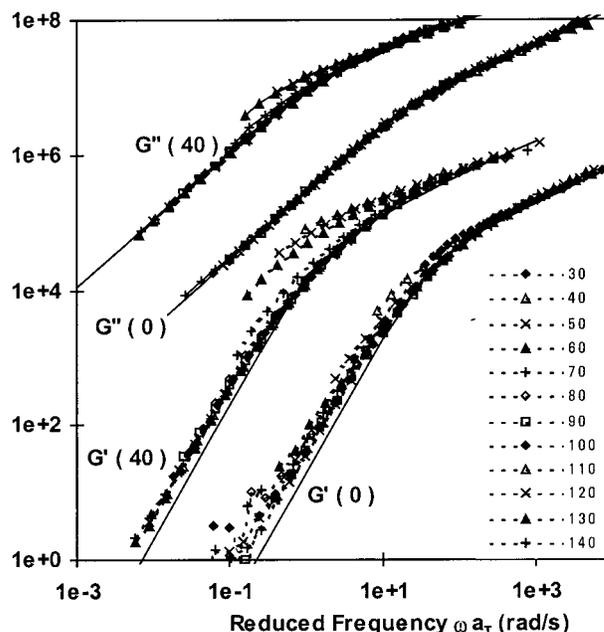


Figure 4. Dynamic mechanical frequency sweep data for I725 series. Quantities in parentheses refer to the extent of quaternization. The y-scale is in units of Pa and refers to the two G' curves. The G'' curves have been moved up by a factor of 200 for clarity. The solid lines are fit to Rouse theory.

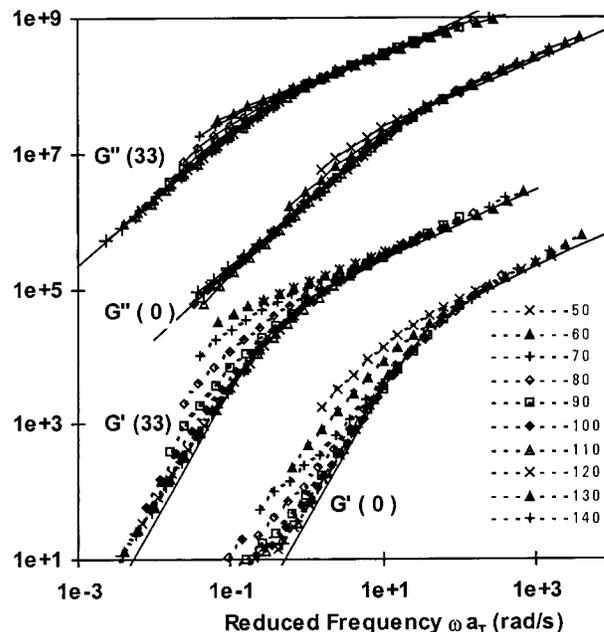


Figure 5. Dynamic mechanical frequency sweep data for I1000 series. Quantities in parentheses refer to the extent of quaternization. The y-scale is in units of Pa and refers to the two G' curves. The G'' curves have been moved up by a factor of 1000 for clarity. The solid lines are fit to Rouse theory.

terials were homogeneous because T_{g}^{sp} increases with quaternization. In addition, since quaternization increases microphase separation, it further increases the viscosity for the reasons cited in the previous paragraph. Can the effects of microphase separation be separated from the bare effects? This question will be dealt with in section 4.2.

3.2. Frequency Sweep Experiments: Qualitative Analysis of Master Curves. Figures 4–6 show the modulus vs reduced frequency master curves using a reference temperature of 90 °C for some of the polyure-

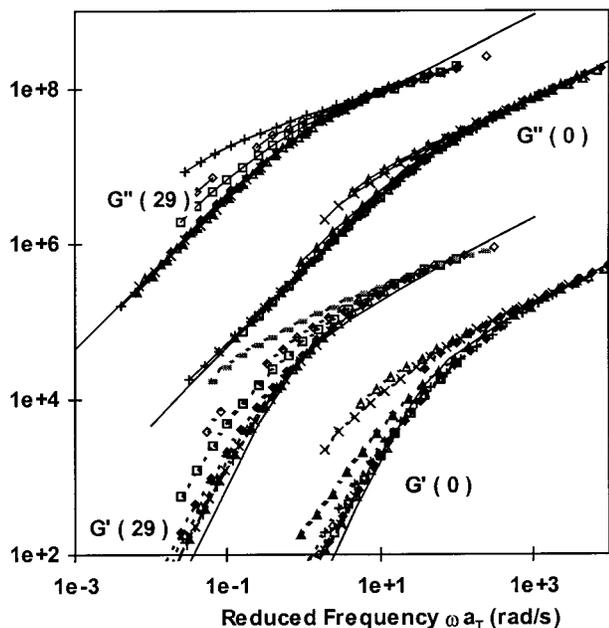


Figure 6. Dynamic mechanical frequency sweep data for I2000 series. Quantities in parentheses refer to the extent of quaternization. Symbols have the same meaning as in Figure 4. The y -scale is in units of Pa and refers to the two G' curves. The G'' curves have been moved up by a factor of 400 for clarity. The solid lines are fit to Rouse theory.

thane cationomers studied. Data on other materials have been omitted here since their master curves are qualitatively similar to those shown in Figures 4–6. Some qualitative conclusions may be drawn from these data. At sufficiently high temperatures, time–temperature superposition is seen to work for all materials in the experimental frequency range. These master curves may be described almost quantitatively using the results of Rouse theory⁷

$$G' = \frac{6\eta_0\tau_R}{\pi^2} \sum_{p=1}^{\infty} \frac{\omega^2 p^4}{1 + \tau_R^2 \omega^2 p^4}; \quad G'' = \frac{6\eta_0}{\pi^2} \sum_{p=1}^{\infty} \frac{\omega p^2}{1 + \tau_R^2 \omega^2 p^4} \quad (3)$$

where η_0 and τ_R are the terminal viscosity and relaxation times, respectively, used as fitting parameters. These fits to eq 3 are shown as solid lines in Figures 4–6, and the corresponding terminal viscosities and relaxation times listed in Table 1. In general, increasing quaternization is seen to increase both the terminal viscosity and the terminal relaxation time of the polyurethanes. It must be reemphasized that not all the increase in moduli, viscosity, and relaxation times can be attributed to microphase separation. At least some of it is due to bare effects; i.e., at the reference temperature of 90 °C, polyurethanes with higher levels of quaternization are expected to be both more microphase-separated and closer to their single-phase T_g as discussed in section 3.1.

At lower temperatures, a failure of superposition is seen for materials with large block length or large block incompatibility. Specifically, since high-frequency data were used for superposition, the failure is seen at low frequencies in the form of a smaller terminal slope at low temperatures. It is apparent from Figures 4–6 that as quaternization increases, superposition fails at successively higher temperatures. Such failure of super-

Table 1. Dynamic Characteristics of Polyurethane Cationomers

sample	Rouse parameters ^a		E_{act} for η_0 , kcal/(mol K) ^b	glass transitions, °C	
	η_0 , Pa·s	t_R , s		exptl ^c	WLF ^d
I725-0	850	0.021	33.2	3.6	−3.4
I725-12	1640	0.05	31.3	3.2	−1.4
I725-25	7100	0.225	29.1	6.1	4.6
I725-40	33500	0.55	32.0	3.9	9.6
I1000-0	1100	0.03	34.3	<i>e</i>	6.6
I1000-13	8300	0.18	34.2	<i>e</i>	<i>f</i>
I1000-32	130000	2.5	33.0	−33.1	<i>f</i>
I1000-40	280000	5.5	30.6	−34.5	<i>f</i>
I2000-0	700	0.02	35.8	−52.1	6.6
I2000-14	10500	0.2	36.8	−55	24.6
I2000-29	64000	1.1	34.8	−55	21.6

^a Apply to mastercurves at $T_{ref} = 90$ °C. ^b Slopes of broken lines in Figure 9. ^c See Velankar and Cooper.³ ^d T_g required to fit eq 4 to data in Figure 7; solid lines are the fit. ^e Too indistinct to be reliably measured. ^f WLF fits not possible.

position has often been demonstrated to be due to an order–disorder transition (ODT) or due to composition fluctuations.⁸ However, small-angle X-ray scattering experiments have shown that the scattering curves of all the polyurethane cationomers except I2000-0 show almost no change with temperature.³ Clearly, the failure of superposition of the cationomers cannot be attributed to microphase mixing. In fact, failure of superposition is seen for both almost-homogeneous materials such as I725-40 (Figure 4) and highly microphase-separated materials such as I1000-32 (Figure 5). The most likely explanation for this thermorheological complexity is the relatively high hard-segment T_g of these materials; time–temperature superposition is not expected to apply so close to the T_g . From the results of the temperature sweep data of Figures 1–3, it is evident that failure of superposition is roughly coincident with sample flow, which in turn depends on the T_g of the hard-segment-rich microphase. This lends support to the hypothesis that failure of superposition occurs due to the proximity to the glass transition of the hard-segment-rich microphase. It is interesting to note that the rheological “signature” of approaching the glass transition is very similar to that of increasing microphase separation.² Clearly, it is not generally advisable to deduce changes in microphase behavior from rheological data alone in the absence of independent confirmation by other means.

3.3. Shift Factors. The shift factors used for constructing modulus-reduced frequency master curves are plotted as a function of temperature in Figure 7. The data have been fit by two methods. Data that were approximately linear have been fit by straight lines (i.e., Arrhenius equation). Data that showed curvature have been fitted by the Williams–Landel–Ferry (WLF) equation⁷

$$\log(a_T^g) = \frac{-C_{1g}(T - T_g)}{C_{2g} + T - T_g} \quad (4)$$

where a_T^g is the shift factor with respect to the reference temperature chosen to be equal to the glass transition temperature, and C_{1g} and C_{2g} are empirical fitting parameters that are often found to be close to 17.66 and 51.6 K for many homopolymers. While the WLF equation is not expected to be generally applicable to block copolymers, the “concave up” shape of the a_T

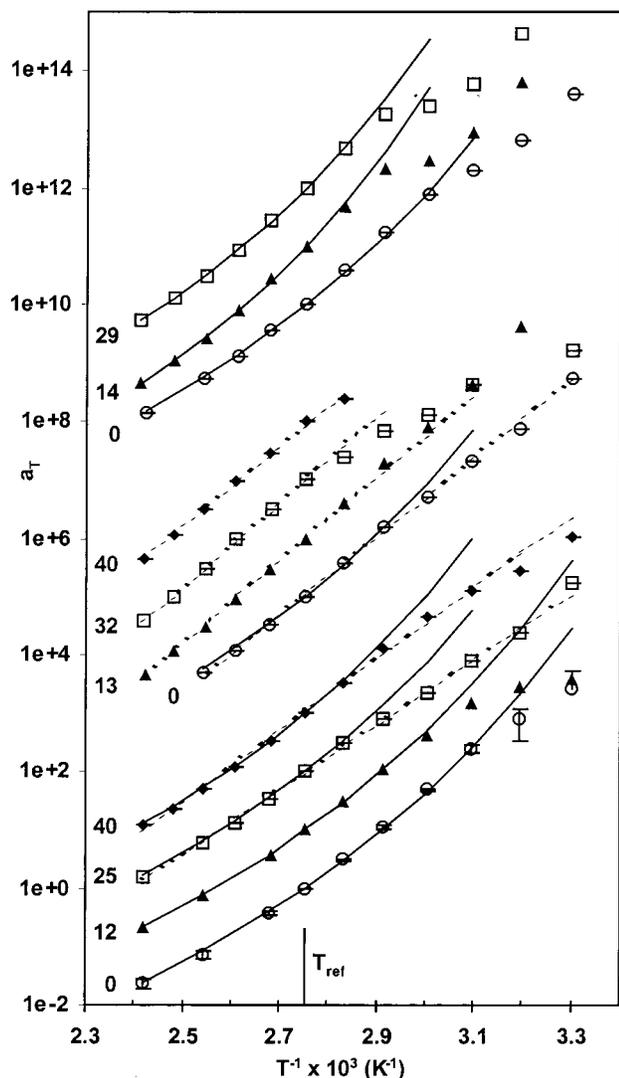


Figure 7. Shift factors used in drawing the master curves in Figures 4–6. Solid lines are fits to WLF eq 4, and dashed lines are Arrhenius fits. The lowest four refer to the I725 series, the middle four to the I1000 series, and the top three to the I2000 series. The data have been moved vertically relative to each other, and the y -axis refers to the I725-0 data only.

vs T^{-1} data of Figure 7 suggests its use. As has been discussed before,² a polyurethane often has two T_g 's, and it is not clear which one or what combination of the two be used in eq 4. Hence, as described previously,² we use $C_{1g} = 17.66$ and $C_{2g} = 51.6$ K and T_g as the only fitting parameter; the values of T_g that best fit the a_T are denoted $T_{g,WLF}$. Note that the reference temperature used for generating the master curves in Figures 4–6 was 90 °C, and the results of eq 4 must be translated to this temperature. For this,

$$\log(a_T) = \log(a_T^g) - \log(a_{T_{ref}}^g) \quad (5)$$

where a_T are the experimental shift factors (i.e., with respect to $T_{ref} = 90$ °C) and $a_{T_{ref}}^g$ are the shift factors of T_{ref} with respect to T_g .

At low levels of quaternization, the shift factors of the I725 series can be fitted well with the WLF equation (4). Upon increasing quaternization, the Arrhenius equation seems to fit the data better, although the high-temperature data may still be fit with the WLF equation within experimental error. The data for all the I1000

materials except I1000-0 have almost no curvature, making WLF fits impossible. Finally, shift factors for the I2000 series also show pronounced curvature and may be fitted well with the WLF equation. Although I725 and I2000 materials may both be fitted with the WLF equation; there is nevertheless a significant difference in their behavior. Specifically, values of $T_{g,WLF}$ for the I725 materials are roughly comparable to the measured thermal T_g 's (Table 1). Since the I725 series is almost homogeneous ($T_g^{sp} \approx$ measured T_g), we may conclude that for the I725 series $T_{g,WLF} \approx$ measured $T_g \approx T_g^{sp}$; this is in accordance with the results for the E-series² mentioned in the Introduction. To what extent is this true for the I2000 series? All I2000 materials are strongly microphase-separated (measured $T_g \ll T_g^{sp}$), and their homogeneous state could not be quenched from high temperatures; hence, their T_g^{sp} 's are not experimentally available. Unfortunately, nor can their T_g^{sp} 's be reliably estimated³ from common schemes such as the Fox equation⁹ or the Couchman equation.¹⁰ Nevertheless, from the calculations using Couchman's equation,³ it is reasonable to expect that the T_g^{sp} 's for the I2000 series are *lower* than those for the I725 series. On the other hand, the $T_{g,WLF}$ values for the I2000 series are considerably *higher* than those for the I725 series. This indicates that the T_g^{sp} 's of the I2000 materials are far lower than their $T_{g,WLF}$, in contradiction to the observation for the E-series.² We speculate that in I2000 series $T_{g,WLF}$'s may be comparable to the T_g 's of their hard-segment-rich microphases. If true, this implies that the relatively small separation between the experimental temperatures and the T_g of the hard-segment microphase causes the temperature dependence of a_T to be dominated by that of the dynamics of the hard-segment-rich microphase.

3.4. Viscosities and Relaxation Times. Figure 8 shows that terminal viscosity varies roughly exponentially with the extent of quaternization. By fitting the "raw" moduli vs frequency data (i.e., data prior to time-temperature superposition) to the Rouse equations (3), it is possible to obtain a terminal relaxation time for each material at each temperature. This terminal relaxation time t_R has an almost identical dependence on the extent of quaternization; i.e., t_R and η_0 are affected to the same extent by segmental incompatibility. Graphs of t_R vs quaternization have not been shown because there is some arbitrariness in obtaining t_R and because of their strong similarity to Figure 8.⁴ It is not possible to extract quantitative thermodynamic information from Figure 8 since the relationship between χ and the extent of quaternization is not known. Yet, the situation is somewhat better than the traditional means of varying the segmental incompatibility in polyurethanes by changing the soft segment (e.g., PCL, PEO, PPO, PTMO). In that case, even the relative incompatibilities of the different soft segments with the hard segment may not be known, and quantification would not be possible at all.

The data of Figure 8 are plotted as a function of temperature in Figure 9. Because time-temperature superposition is not strictly valid at all frequencies, η_0 has a somewhat different temperature dependence than a_T . The data seem to be adequately represented by the Arrhenius equation, and the apparent activation energies have been tabulated in Table 1. Data at low

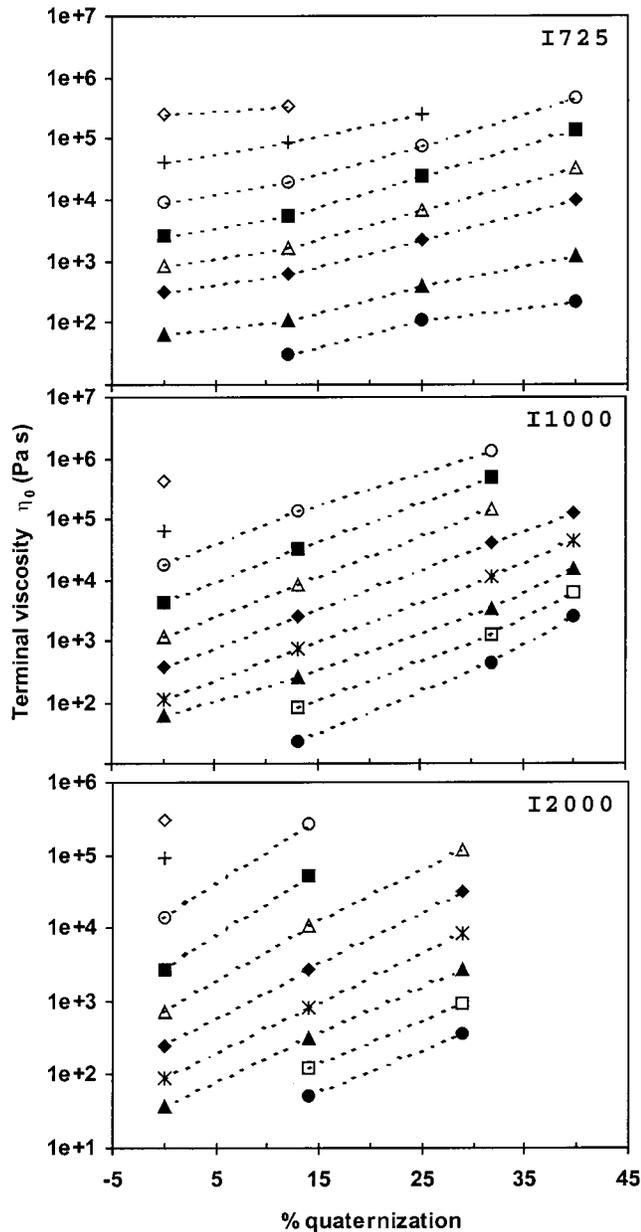


Figure 8. Dependence of terminal viscosity on the extent of quaternization: \diamond , 50 °C; +, 60 °C; \circ , 70 °C; \blacksquare , 80 °C; \triangle , 90 °C; \blacklozenge , 100 °C; *, 110 °C; \blacktriangle , 120 °C; \square , 130 °C; \bullet , 140 °C.

temperatures have been preferentially used in calculating these activation energies since the strong signal minimizes the error in measuring the moduli. There is a slight increase in activation energy upon increasing the segment length; however, considering the arbitrariness in drawing straight-line fits in Figure 9, these activation energies may be considered to be almost equal for all 11 polyurethanes. More importantly, the apparent activation energies within each series show almost no dependence on the extent of quaternization, i.e., on the extent of microphase separation. It is quite remarkable that an almost homogeneous material like I725-0 has roughly the same activation energy as I2000-29, which is highly microphase-separated. A similar insensitivity to the extent of microphase separation was found for the viscosity and relaxation times in the E-series poly(ester urethane)s.² The implications of this will be considered in the following section.

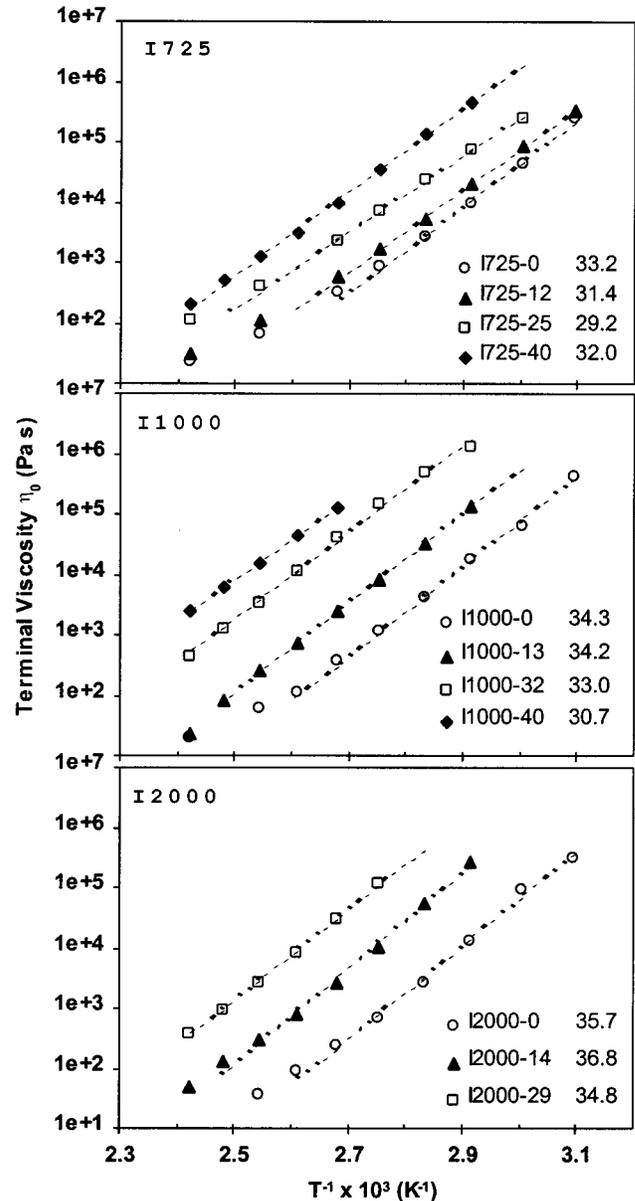


Figure 9. Dependence of terminal viscosity on temperature. Broken lines are Arrhenius fits, and the numbers adjacent to the legend are the corresponding activation energies in kcal/(mol K).

4. Discussion

4.1. Dynamics of Disordered Microphase-Separated Block Copolymers. This section attempts to draw conclusions about the dynamics of polyurethane melts using the combined results of this and the previous two papers.^{2,3} Specifically, two unexpected results are addressed here. First, the apparent activation energies for terminal viscosity and terminal relaxation time are almost insensitive to the block length or to the block incompatibility, i.e., to the extent of microphase separation. This temperature dependence of the terminal rheological properties includes the temperature dependence of each of the three factors (bare effects, dynamic asymmetry, and energy penalty χN) mentioned in section 3.1. The first two will be considered later; suffice to say that increasing quaternization is certainly not expected to decrease their temperature dependence. The last factor, related to the energy penalty, may be expected to scale as $\exp(-\chi N)$ where

χN is the thermodynamic penalty of dragging a soft segment block through the hard-segment-rich phase, and vice versa. This may be expected to increase the apparent activation energy for terminal dynamics by χN . No such systematic dependence of activation energy on incompatibility is seen in the present work, and none on block length was seen previously.² Thus, inasmuch as the measured terminal dynamic viscosity is related to chain diffusivity (or to the monomeric friction ζ), we conclude that microphase separation does not impose large energy barriers to chain motion. Similar results have been seen by Dalvi et al.¹¹ for symmetric diblocks and Yokoyama et al.¹² for asymmetric diblocks. Both Dalvi and Yokoyama found that the diffusivity of low-molecular-weight polystyrene/poly(vinylpyridine) diblock copolymers was comparable to that of polystyrene of equal molecular weight, even if the diblocks were below their ODT temperatures. A thermodynamic penalty that scaled as χN was observed only if the diblock copolymer was entangled.^{12,13} Such behavior has been predicted by theories of the dynamics of block copolymers,^{14–17} and in general one may conclude that in *unentangled* block copolymers microphase separation hinders chain motion the least. This is especially true for *lamellar* microstructures in which chain motion parallel to lamellae has no thermodynamic penalty.^{8,11} Dalvi et al.'s conclusions are more rigorous than the present ones since they are based on measuring chain diffusivity that is directly related to chain motion, rather than the terminal dynamic viscosity measured here. Moreover, due to the easy accessibility of the homogeneous state, Dalvi et al. were able to normalize the diffusivities of the diblock copolymers to their bare diffusivities and thus find the precise dependence of the thermodynamic penalty on χN .¹³ The homogeneous state is not available for all the polyurethanes studied here; more comment will be made on this issue below.

The second unexpected observation is that not only the terminal viscosity but also the entire frequency response is insensitive to the extent of microphase separation. That is, regardless of microphase separation, the high-temperature master curves for the I-series as well as the E-series² are qualitatively similar to rheological master curves of low-molecular-weight homopolymer melts. In fact, all modulus–frequency data except at the lowest temperatures may be described by Rouse theory reasonably well, even for materials such as I1000-40 and I2000-29 that are highly microphase-separated. At first sight, this merely seems to be a stronger validation of the theoretical expectation that chain motion in unentangled block copolymers is insensitive to microphase separation. However, Figures 4–6 are not the frequency response of a single chain; they refer to the frequency response of the entire microstructure. In microphase-separated block copolymers, such linear viscoelastic response in the terminal region is not controlled by single-chain diffusivity, it is controlled by the large correlation length (grain size) of the ordered microphase.^{8,18} This presence of long-range order in block copolymers with monodisperse blocks leads to nonliquidlike terminal behavior⁸ (often $G' \sim \omega^{0.5}$, $G'' \sim \omega^{0.5}$) below the ODT, though of course, this cannot be the true terminal behavior.¹⁸ The fact that even highly microphase-separated polyurethanes such as I2000-29 show homopolymer-like relaxation and not the commonly observed nonliquidlike terminal response is a direct consequence of the fact that these, and most other

polyurethanes,^{2,19} have a microphase-separated state without long-range order. This effect of a small correlation length (grain size) in polyurethanes on the terminal rheological properties has been mentioned before.² What are the reasons for this lack of long-range order? In polyurethanes, this lack of long-range order may be attributed to the high polydispersity in block length. The effect of a lack of long-range order may also be seen at the early stages of the ordering process when the block copolymer is microphase-separated but not ordered and therefore shows a liquidlike terminal response.^{20,21} It may also be seen in block copolymers with highly asymmetric block lengths which creates microphase-separated morphology without long-range order.^{21,22} Presumably, other factors such as chain branching with branch size comparable to the block length, strong specific interactions that prevent reordering of a disordered structure, etc., may also hinder long-range order. Thus, we further qualify the statement in the last paragraph by saying that the effects of microphase separation on linear viscoelastic relaxation are least evident when the block copolymers are *unentangled* and *lamellar* and have *no long-range order*. This must be borne in mind when interpreting viscoelastic data of block copolymers that are unlikely to have long-range order. For example, from the liquidlike terminal behavior of polyetherester multiblock copolymer melts, Veenstra et al.²³ concluded that these melts were single-phase; this cannot be regarded as conclusive in the absence of scattering data.

It is worthwhile speculating that this lack of long-range order may be useful from an experimental viewpoint. For instance, Dalvi et al.¹¹ studied the effects of microphase separation on chain dynamics in diblock copolymers as mentioned above. These materials had monodisperse blocks, and their corresponding microphase-separated states had long-range order; thus, information about chain dynamics (i.e., the friction coefficient ζ) was obtained by diffusivity measurements. It is possible that if these samples had no long-range order, the same results may have been obtained by mechanical rheometry, which is far more convenient from an experimental viewpoint. Of course, to be rigorous, the equivalence between the friction coefficients obtained from viscosity and diffusivity would first have to be demonstrated in microphase-separated samples without long-range order.

The above discussion does not however imply that polyurethane viscoelasticity is altogether insensitive to microphase separation; in fact, the increase in terminal viscosities and relaxation times with microphase separation have already been demonstrated (Figure 8 of this paper and Figure 18 in Velankar and Cooper²). If this cannot be interpreted in terms of activation barriers to chain motion, what mechanism is responsible for this increase in viscosity and relaxation time? The explanation must lie in bare effects and in the dynamic asymmetry aspects of microphase separation as discussed in section 3.1. While a great deal of theoretical effort^{8,15,17,24} has been expended in understanding the “thermodynamic” aspects of chain motion (i.e., the energy penalty χN), bare effects and dynamic asymmetry have been addressed only to a limited extent.^{5,17,25} The latter are expected to be especially important in the dynamics of elastomeric block copolymers in which one component usually has a much lower mobility than the other.

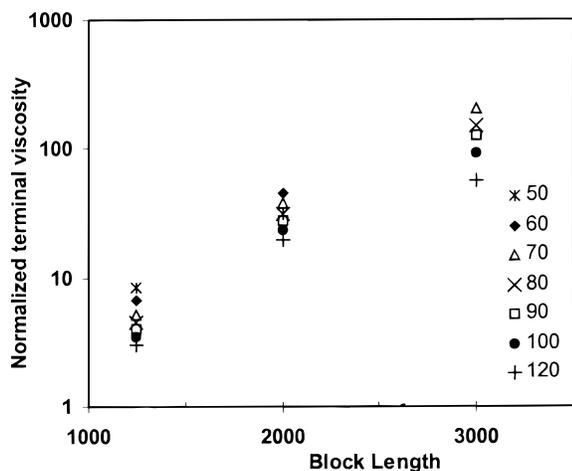


Figure 10. Effect of microphase separation on the E-series assuming that E830 is truly homogeneous (see text). Data have been corrected for differences in overall molecular weight assuming Rouse dynamics (viscosity \propto molecular weight) using the molecular weights cited previously.²

4.2. Microphase Separation vs Bare Effects in Polyurethanes: Importance of the Homogeneous State. Finally, we deal with the question raised at the end of section 3.1: is it possible to separate the effects of microphase separation from those of bare effects? To do this quantitatively would involve comparing experimentally measured dynamic properties (in this case viscosity η_0) with the value for the same property (η^{sp}) if the material were single-phase. Clearly, some means of measuring or estimating the single-phase viscosity must be available. In this respect, a serious limitation of polyurethanes is that polyurethane hard segments are capable of hydrogen bonding and hence associate very strongly. This is expected to make it much more difficult to achieve a truly homogeneous state in polyurethanes than in copolymers whose blocks are incompatible due to nonspecific repulsions. Thus, while η_0 is required to evaluate the effects of microphase separation quantitatively, it is not clear how it may be estimated for the polyurethanes studied here. For the present purposes, it would be most convenient if one of the polyurethanes in a series were demonstrably homogeneous. Of all the polyurethanes studied in this series of papers,^{2,3} the truly homogeneous state without significant composition fluctuations is most likely to be obtained in the E-series studied previously.² This is because the polyester soft segment, which is also capable of hydrogen bonding, minimizes the preferential association of the hard segments by hydrogen bonding. Since the E-series involves varying the block length, the sample with the lowest block length, E830, is the most homogeneous in that series. Assuming homogeneity of E830 for the moment, the viscosities of the E-series, normalized by the viscosity of E830, are plotted as a function of N in Figure 10. These data have been corrected for differences in overall molecular weight (Table 1 in Velankar and Cooper²) assuming Rouse dynamics (viscosity $\propto MW^{-1}$). These corrections are at most a factor of about 2. If χ were known, it would be possible to combine data at different temperatures and plot them against χN . If E830 were homogeneous, this graph would represent the effect of microphase separation after "subtracting out" any bare effects. Clearly, the net effect of microphase separation on the terminal viscosity is quite considerable; moreover, this effect is

believed to be entirely due to dynamic asymmetry as per the discussion of section 4.1.

To what extent can E830 be regarded as homogeneous? As far as the DSC data are concerned, E830 is almost completely homogeneous. Yet, that does not rule out composition fluctuations that affect the dynamics but are too weak (or decay too fast) to affect the DSC trace. E830 also showed very weak SAXS patterns, thereby indicating homogeneity; however, the electron density contrast between the segments was calculated to be very poor, which would cause weak scattering even if there were a small amount of microphase separation. Thus, how may homogeneity be conclusively demonstrated? One possibility is to verify that the dynamics of the block copolymer are dependent on chain length alone. For example, Dalvi et al. found that diffusivity of a homogeneous diblock copolymer could be well-represented by (overall length)⁻¹ at low molecular weight as per Rouse theory¹¹ or (overall length)⁻² at high molecular weight as per reptation scaling;²⁶ i.e., there was no dependence on block length per se. This suggests one possible criterion to test whether E830 is homogeneous: compare its viscosity with that of a similar polymer with even lower block length. If E830 is homogeneous, all differences in viscosity should demonstrably be due to different overall molecular weight. Note that before correlating η_0 to molecular weight, it may have to be corrected to account for the increase in T_g with block length. This verification of homogeneity of E830 has not been done due to the difficulty of obtaining polycaprolactone of lower molecular weight and good functionality.

A graph similar to Figure 10 could be drawn for the I725 series by assuming that I725-0 is homogeneous; however, the fact that the soft-segment PPO cannot undergo hydrogen bonding makes association between hard segments much more likely, and hence, homogeneity of I725-0 is a more questionable assumption. The I1000 and I2000 series are, of course, known to be microphase-separated, and no plausible candidate for their homogeneous states is available at all.

Thus, we hope to have demonstrated that information about the dynamics of the homogeneous state is absolutely essential in order to separate the effects of microphase separation from any bare effects. This is especially important when testing theories of dynamics of block copolymers that usually predict the effects of microphase separation over and above any bare effects.

5. Summary

This paper describes the effect of varying the segmental incompatibility on the linear viscoelastic properties of a series of polyurethane elastomers. We first briefly summarize the experimental results. It was found that the moduli and the relaxation times of the polyurethanes increased with block incompatibility. Increasing block length or incompatibility caused a failure of time-temperature superposition due to proximity to the T_g of the hard-segment-rich microphase. This failure was very similar to that observed with increasing microphase separation, viz. failure due to a lower terminal slope at low temperatures.

This work made two unusual observations: that the apparent activation energy of terminal relaxation was independent of microphase separation and that the terminal frequency response was liquidlike ($G' \sim \omega^2$; $G'' \sim \omega$) even for highly microphase-separated polyure-

thanes. The first observation indicates that microphase separation in unentangled systems does not greatly hinder chain motion, in accordance with previous experimental results^{12,13} and theoretical expectations.^{14–17} The second observation that strongly contrasts the nonliquidlike terminal behavior of block copolymers with monodisperse blocks⁸ reiterates the role of the disordered nature of the microphase-separated state in polyurethanes. Both these observations indicate that the effects of microphase separation in polyurethanes are felt due to the large dynamic asymmetry (difference in friction coefficients of the blocks), rather than an inability of the blocks to move through thermodynamically unfavorable regions.

It is important to note that the increase in terminal viscosity and relaxation times with microphase separation can be explained, at least qualitatively, on the basis of dynamic asymmetry alone. An energy penalty ($\propto \chi N$) for dragging a block through an inhospitable region is not consistent with the experimental data. We speculate that the effects of dynamic asymmetry are likely to dominate over those of the thermodynamic penalty^{5,25} in the dynamics of block copolymers that are designed to be elastomers. This is because the blocks of block copolymer elastomers often have a very large difference (at least 100 °C) in their T_g 's, leading to friction coefficients that can differ by several orders of magnitude. This is in contrast to the commonly studied PEP/PEE block copolymers,^{13,27} as well as other block copolymers such as PS/PVP^{11,12} or various pairs of PDMS, PI, PEO, PPO, PEP, and PEE blocks where the difference in T_g 's of the blocks (and hence the dynamic asymmetry) is relatively modest.

Polyurethanes are not suitable candidates for detailed studies of dynamic asymmetry effects or for testing theories that attempt to predict the dynamics of microphase-separated block copolymers. They have the desirable property of not possessing long-range order upon microphase separation, which may allow terminal rheological behavior to be accessed by mechanical rheometry rather than diffusion measurements. However, they have the serious disadvantage of not having an easily accessible homogeneous state, which is crucial to for any quantitative evaluation of any theory. In addition, the glass transition of the hard-segment-rich microphase is very rarely discernible in DSC traces of polyurethanes; thus, obtaining the microphase compositions accurately is relatively difficult. Finally, synthesis of hard-segment blocks of desired molecular weight to obtain the dependence of the T_g on block molecular weight is also difficult. Other materials such as polyetheresters may be more suitable for experimentation on multiblock copolymer since their homogeneous state is much more likely to be attainable.

Finally, one caveat must be borne in mind. All the experiments performed here were dynamic mechanical

experiments in the linear viscoelastic region, i.e., small-deformation experiments. The discussion above has implicitly assumed the Cox–Mertz rule that the terminal viscosity measured in dynamic experiments is equal to the Newtonian viscosity measured in the limit of low shear. Limited experiments have demonstrated that this is a good assumption, at least at the relatively high temperatures (i.e., low viscosities) at which steady shear experiments are possible. However, a more rigorous test of the insensitivity of the activation energy of terminal dynamics to microphase separation would involve more detailed steady shear experiments at low shear rates.

Acknowledgment. We are grateful to Dr. Roger Phillips, Montell Inc., USA, for valuable comments on this manuscript and to the Army Research Office for funding.

References and Notes

- (1) Hepburn, C. *Polyurethane Elastomers*, 2nd ed.; Elsevier Applied Science Publ.: London, 1991.
- (2) Velankar, S.; Cooper, S. L. *Macromolecules* **1998**, *31*, 9181.
- (3) Velankar, S.; Cooper, S. L. *Macromolecules* **2000**, *33*, 382.
- (4) Velankar, S. Ph.D., University of Delaware, 1999.
- (5) Hamersky, M. W.; Tirrell, M.; Lodge, T. P. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 2899.
- (6) Chapman, B. R.; Hamersky, M. W.; Milhaupt, J. M.; Kostecky, C.; Lodge, T. P.; von Meerwall, E. D.; Smith, S. D. *Macromolecules* **1998**, *31*, 4562.
- (7) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley and Sons: New York, 1980.
- (8) Fredrickson, G. H.; Bates, F. S. *Annual Review of Materials Science*; Annual Reviews Inc.: Palo Alto, CA, 1996; Vol. 26.
- (9) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
- (10) Couchman, P. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 117.
- (11) Dalvi, M. C.; Eastman, C. E.; Lodge, T. P. *Phys. Rev. Lett.* **1993**, *71*, 2591.
- (12) Yokoyama, H.; Kramer, E. J. *Macromolecules* **1998**, *31*, 7871.
- (13) Lodge, T. P.; Dalvi, M. C. *Phys. Rev. Lett.* **1995**, *75*, 657.
- (14) Barrat, J. L.; Fredrickson, G. H. *Macromolecules* **1991**, *24*, 6378.
- (15) Genz, U.; Vilgis, T. A. *J. Chem. Phys.* **1994**, *101*, 7111.
- (16) Tang, H.; Schweizer, K. S. *J. Chem. Phys.* **1995**, *103*, 6296.
- (17) Guenza, M.; Tang, H.; Schweizer, K. S. *J. Chem. Phys.* **1998**, *108*, 1257.
- (18) Colby, R. H. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 454.
- (19) Ryan, A. J.; Macosko, C. W.; Bras, W. *Macromolecules* **1992**, *25*, 6277.
- (20) Winter, H. H.; Scott, D. B.; Gronski, W.; Okamoto, S.; Hashimoto, T. *Macromolecules* **1993**, *26*, 7236.
- (21) Adams, J. L.; Quiram, D. J.; Graessley, W. W.; Register, R. A.; Marchand, G. R. *Macromolecules* **1996**, *29*, 2929.
- (22) Sakamoto, N.; Hashimoto, T.; Han, C. D.; Kim, D.; Vaidya, N. Y. *Macromolecules* **1997**, *30*, 1621.
- (23) Veenstra, H.; Hoogvliet, R. M.; Norder, B.; Boer, A. d. *J. Polym. Sci., Polym. Phys. Ed.* **1998**, *36*.
- (24) Leibig, C. M.; Fredrickson, G. H. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 163.
- (25) Lodge, T. P.; Blazey, M. A.; Liu, Z. *Macromol. Chem. Phys.* **1997**, *198*, 983.
- (26) Dalvi, M. C.; Lodge, T. P. *Macromolecules* **1994**, *27*, 3487.
- (27) Bates, F. S.; Rosedale, J. H.; Bair, H. E.; Russell, T. P. *Macromolecules* **1989**, *22*, 2557.

MA9908189