Component Relaxation Dynamics in a Miscible Polymer Blend: Poly(ethylene oxide)/Poly(methyl methacrylate)

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ABSTRACT: Relaxation dynamics in the miscible blend of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) are studied subsequent to a linear step strain using the simultaneous measurement of infrared dichroism and birefringence. Blends ranging in composition from 20 to 60% by weight PMMA are prepared from nearly monodisperse PMMA (M_w = 337 000), PEO (M_w = 112 000), and deuterated PEO (M_w = 122 000). IR dichroism in these blends is governed solely by the segmental orientation of the deuterium-labeled PEO and therefore may be used to recover the characteristic PEO relaxation time. Birefringence, on the other hand, is a measure of both PEO and PMMA orientation, and it is shown that from the long-time behavior of this observable the characteristic relaxation time of PMMA may be recovered. Component relaxation times computed in this fashion are monitored as functions of blend composition and $T - T_g$. To extend the range of compositions and provide a basis for comparison to the pure state, results from dynamic mechanical experiments on the pure components and 70 and 80% PMMA blends are included in the analysis. It is observed that in the blend components maintain distinct relaxation times but that the presence of dissimilar chains certainly affects component relaxation behavior. PEO relaxation times are found to be more strongly composition dependent and pass through a maximum near 40–50% PMMA. Several mechanisms possibly responsible for this behavior are discussed. In addition, it was observed that for PMMA-rich blends each component manifests a separate temperature dependence, while for PEO-rich systems the blends appear to be thermorheologically simple.

1. Introduction

Significant attention has been devoted in recent years to the development and characterization of miscible polymer blends due to the unique combination of properties that blends offer. Numerous rheological studies on a variety of blends have been performed,[1-13] yet much experimenting remains to be conducted in order to establish a firm basis for the development of molecular-based blend rheology theories. In an attempt to expand the knowledge of component contributions to blend rheology, this paper investigates component relaxation dynamics in the miscible blend of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) via the simultaneous measurement of infrared dichroism and birefringence. This blend has been chosen since it does not exhibit strong enthalpic interactions, which might complicate the rheology. In addition, the components possess widely separated glass transition temperatures, entanglement molecular weights, and WLF coefficients, facilitating the identification of each component's influence. This work is distinguished from previous rheological studies on this and other miscible blends by several advantages: (1) the technique used is capable of simultaneously monitoring in situ the microstructural orientation of both the bulk and a selectively labeled component (in contrast to mechanical rheometry, which cannot isolate a single component); (2) the apparatus has sufficient sensitivity to be used in the limit of linear viscoelasticity (in contrast to other IR polarimetry studies);[11,13] (3) both blend components exhibit a narrow molecular weight distribution, making it possible to clearly identify component contributions to blend rheology and accurately determine their temperature dependences.

The discussion of current results will include comparisons to three previous rheological studies on PEO/PMMA blends. The first of these was conducted by Wu,[6] who examined the full range of blend compositions using mechanical rheometry. In that study the familiar time–temperature superposition principle was found to hold, suggesting that the blends manifest a single segmental friction factor. Blend friction factors were computed from shear creep measurements and were found to exhibit positive deviations from linear composition dependence, implying that in the blend friction is enhanced by attractive interactions between the dissimilar components.

Colby employed oscillatory shear rheometry to investigate the full range of compositions at a constant temperature above the glass transition[7] and to examine the temperature dependence of an 80% by weight PMMA blend.[10] All blends were prepared from components with narrow molecular weight distributions (M_w/M_n < 1.3 for all samples). The most significant finding of this work is that the time–temperature superposition principle failed. From the dynamic loss modulus relaxation times for both components in an 80% PMMA blend were determined and found to have distinct temperature dependences, resulting in the failure of time–temperature superposition. From this it was argued that separate friction factors are required to characterize each component, contradicting the results of Wu. It was suggested that the apparent validity of time–temperature superposition reported by Wu may have been due to polydispersity of the pure components used (M_w/M_n = 2.46 for PMMA; M_w/M_n was not reported for PEO)[6] since polydispersity tends to smear out details in the loss modulus. In addition, it was found that at constant $T - T_g$ PMMA relaxation is hindered in the blend (consistent with Wu) but PEO relaxation is accelerated (in contrast to Wu).

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Table I
Molecular Weight Characteristics of Blend Components

polymer	M_w	M_w/M_n	degree of polymerization
PEO	112 000	<1.26	2550
d-PEO	122 000	<1.36	2540
PMMA	337 000	<1.3	3370

A third study was reported by Zhao, Jasse, and Mon-nerie,[11] who used infrared dichroism, birefringence (in the visible regime), and mechanical rheometry to study blends ranging from 80 to 100% PMMA subjected to nonlinear, uniaxial stretching. From infrared dichroism measurements at 749 cm^{-1} PMMA orientation was measured as a function of draw ratio 21 °C above the glass transition in an experiment at constant elongation rate. PMMA orientation was enhanced in the blends, indicating that PMMA relaxation is slowed by the presence of PEO (as found by Wu and Colby). Also, PMMA orientation was found to increase with increasing PEO molecular weight, implying a cooperative effect of interchain interactions. Birefringence was unable to detect any PEO orientation in the blends at the uniaxial draw ratios studied due to the very fast relaxation of this component. From mechanical rheometry hindered relaxation of PMMA was observed in the blends, consistent with the dichroism measurements. The validity of time–temperature superposition could not be rigorously tested due to the low PEO molecular weights ($M_{w,PEO}$ = 4000 and 20 000) used in the blends studied by mechanical rheometry. For such low molecular weights the longest relaxation time of PEO is too small to measure in both mechanical and optical experiments.

2. Experimental Section

2.1. Materials. Blend components were prepared by anionic polymerization to yield a narrow distribution of molecular weights. The PMMA was synthesized at Eastman Kodak Company, while PEO and perdeuterated PEO samples having the same degree of polymerization were obtained from Polymer Laboratories. Component molecular weights and distributions are given in Table I. Highly isotactic PMMA is known to be immiscible with PEO[14,15] and is therefore undesirable. Triad analysis of ^{1}H NMR revealed the PMMA used here is 78% syndiotactic, 21% heterotactic, and only 1% isotactic.

Blends containing 20, 30, 40, 50, and 60% by weight PMMA are studied here, all of which contain 8% by weight deuterated PEO. This choice of deuterated PEO composition reflects a balance between the transmitted light intensity and the strength of the sample's dichroism (higher deuterated PEO content yields stronger dichroism but poorer light transmittance since the C–D bonds of deuterated PEO absorb at the IR wavelength used here). High glass transition temperatures exhibited by blends containing more than 60% PMMA set an upper limit on the composition range that may be studied with the current technique. Samples were prepared by dissolving the three components in 40 °C acetone and film casting the solutions at room temperature. To further reduce solvent content, films were placed in a room-temperature vacuum for 12 h followed by a heated (80–100 °C) vacuum for 24–48 h.

2.2. Thermal Analysis and Miscibility. Glass transition behavior for the pure components and blends was measured using a Du Pont 910 differential scanning calorimeter. The glass transition temperature, T_g, was taken to be the midpoint of the transition observed in an upward scan at 20 °C/min. To suppress PEO crystallization, samples (except pure PMMA and blends with $T_g > T_{m,PEO}$) were quenched from +80 °C (above the PEO melting point, 65 °C) to –100 °C just prior to analysis. In general, this quenching scheme was successful and resulted in reproducible DSC scans having virtually no melting peak and a single glass transition with T_g's following Fox equation behavior. These results are plotted in Figure 1. In the range of 40–60% PMMA,
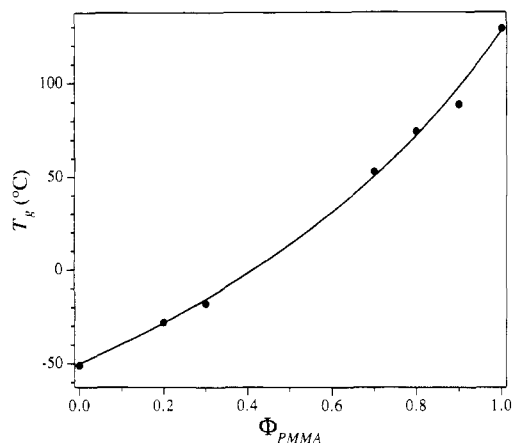

Figure 1. Glass transition temperatures found by DSC. The solid curve corresponds to the Fox equation using the pure-component T_g's.

for unknown reasons, adequate suppression of PEO crystallization could not be achieved and consequently reliable measurements of T_g could not be made. Apparent T_g's in this composition range were not reproducible and were not always observable. Unusual glass transition behavior over this composition range has been previously reported by Martuscelli[16] and Assman and Schneider.[17] The rheological results presented here are not subject to complications introduced by the degree of PEO crystallinity since the experiments are conducted in the melt regime above the PEO melting point. For analysis Fox equation predictions are used over the full composition range, based on the pure-component T_g's ($T_{g,PEO}$ = –50 °C and $T_{g,PMMA}$ = 128 °C).

Due to extremely weak enthalpic interaction in PEO/PMMA blends, miscibility in this system is marginal. The general consensus of numerous studies on the system's phase behavior (see ref 10 and references therein) is that PEO and PMMA do form a miscible blend. However, the reported values for the Flory–Huggins interaction parameter χ are not strongly negative, indicating that miscibility has not been absolutely proven, and the system is marginally miscible at best. To verify that the components used here form a single-phase blend over the ranges of composition and temperature studied, the thermal behavior and optical properties were closely analyzed. Noting that the pure components have T_g's that differ by roughly 180 °C, the presence of a single blend glass transition observed using DSC at a temperature intermediate to the two pure-component T_g's strongly suggests miscibility.[18] DSC was also used to monitor the PEO melting point, $T_{m,PEO}$, on unquenched samples, taking the extrapolated onset temperature of the endothermic melting peak to be $T_{m,PEO}$. Samples were allowed to crystallize at T_c = 40 °C prior to the DSC run. The composition dependence of the PEO melting point was found to be nearly linear, varying from $T_{m,PEO}$ = 65 °C for pure PEO to $T_{m,PEO}$ = 57.5 °C for the 50% PMMA blend. Similar melting point behavior was observed by Martuscelli[16] on samples crystallized at room temperature. Since the observed melting points are not equilibrium values (i.e., the observed melting points were not extrapolated to $T_m = T_c$), the composition dependence of the observed T_m may be taken as an indication of thermodynamic melting point depression (indicative of mixing on a molecular level) *only* if T_m varies linearly with T_c and the constant of proportionality varies only slightly with composition. Martuscelli[19] and Assman and Schneider[17] demonstrated that the above assumptions hold over wide ranges of composition.

Optical microscopy of a 0.015 in. (0.38 mm) thick sample between a crossed polarizer and analyzer confirmed the melting point depression behavior observed by DSC and demonstrated the absence of any large-scale inhomogeneity in the blends. At temperatures below the PEO melting point Maltese crosses arising from PEO spherulites were observed at all blend compositions studied here. Near the expected melting region, temperature was increased in increments of 0.5 °C, after which the system was allowed to equilibrate for 2 min. The temperature at which the Maltese crosses vanished was taken as the melting point of PEO. Above this temperature (up to 120 °C) no light was
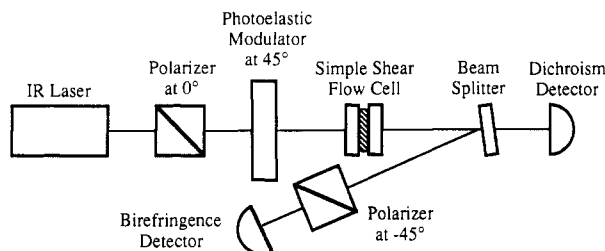
Figure 2. Schematic of the optical train.

Figure 3. Typical normalized birefringence and dichroism profiles obtained from a 40% PMMA blend at $T - T_g = 82$ °C. The solid curves show the double-exponential fit for birefringence (time constants = 5.3 and 84 s) and the single-exponential fit for dichroism (time constant = 5.6 s).

transmitted, indicating that no large-scale concentration fluctuations occur in these blends above $T_{m,PEO}$. The melting points obtained by this method were consistent with the DSC results.

Perhaps the most convincing evidence of miscibility is the measurement of PEO orientation following a step strain using IR dichroism (discussed below) at times orders of magnitude larger than the pure PEO relaxation time. If the system were not homogeneous, PEO would be expected to relax on roughly the same time scale as in the pure state (on the order of 0.01 s for the temperatures studied here). The fact that dichroism persists for seconds in the blends suggests that there is intimate contact between the component chains.

2.3. Method. The dynamic response of blends of various compositions was monitored subsequent to a simple shear step strain using the simultaneous measurement of infrared dichroism and birefringence. For the study of blend rheology, this optical technique has an advantage over more conventional mechanical methods in that it can monitor the behavior of a selectively labeled component as well as that of bulk, whereas mechanical rheometry can only probe the overall, bulk behavior. Since details regarding the theory of these optical measurements and the construction of the optical train used in this study may be found elsewhere,[20] only a brief overview is given here. Subsequent to mechanical deformation, polymeric materials typically exhibit anisotropic optical properties due to microstructural orientation. In this study the two optical anisotropies measured are birefringence, the anisotropic retardation of light, and dichroism, the anisotropic attenuation of light. These optical properties are proportional to the degree of orientation of the chain segments responsible for the material's so-called optical anisotropy, where the degree of orientation is characterized by the second moment of the distribution of chain segment orientations. Since both PEO and PMMA chain segments retard light of the wavelength used in this study (4.6 μm), both components contribute to the birefringence, making birefringence a measure of bulk orientation. That each component possesses a separate intrinsic birefringence is inconsequential since it is the time dependence of the blend birefringence that is of primary interest here and not the magnitude. In contrast, neither component absorbs light of the wavelength used here, and as a result the blends are not naturally dichroic at 4.6 μm. However, replacing certain hydrogens with deuterium in one component's repeat unit introduces carbon–deuterium bonds, which strongly absorb at 4.6 μm. Thus, it is possible to selectively label one component by deuteration and monitor that component's orientation via dichroism. In the present work only blends with deuterated PEO are studied, and it is assumed that the deuterium substitution does not alter the rheology of the blend.

A schematic of the optical train is shown in Figure 2. The light source used here is a diode laser (2190 cm^{-1}). The collimated beam passes through a polarizer oriented at 0° followed by a photoelastic modulator with a frequency of 42 kHz oriented at 45°. The polarization-modulated beam then passes through a temperature-controlled parallel-plate flow cell containing the sample. The surfaces of the transparent parallel plates are normal to the optical axis, and shearing is applied in the 0° direction. Sample thicknesses ranging from 0.015 to 0.020 in. (from 0.38 to 0.51 mm) are used, and strains of 50–65% are applied. The response time of the flow cell to complete such step strains is 25 ms. To ensure that the applied strains lie within the linear viscoelastic regime, results from 40–70% strain experiments were compared and found to be consistent. After leaving the flow cell, the beam is divided by a beam splitter oriented at less than 5° with respect to the optical axis. The transmitted beam is
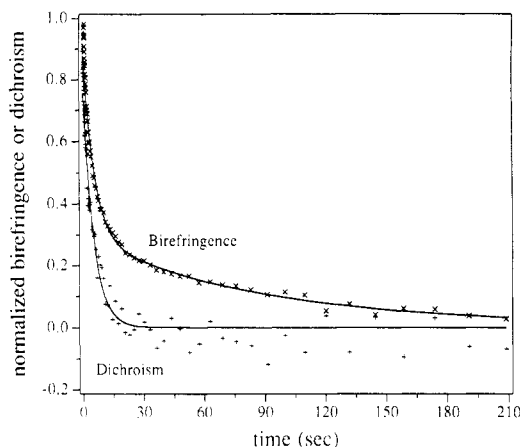
directly observed by photodetector 1, while the reflected beam passes through an analyzer oriented at –45° before being received by detector 2. The intensity from detector 1 is used to recover dichroism, and the signal from detector 2 yields birefringence. With the choice of flow cell orientation used here it is possible to observe microstructural anisotropy in the plane defined by the shearing and vorticity directions.

To recover pure-component relaxation times, mechanical oscillatory shear rheometry using a Rheometrics System Four rheometer was employed. Parallel-plate geometry with 25-mm-diameter plates and a 1–2-mm gap height was studied over the frequency range of 2.5 × 10^{-4}–100 rad/s. Further details on the method used may be found in ref 10.

3. Results

Birefringence and dichroism were measured as functions of time for blends containing 20, 30, 40, 50, and 60% by weight PMMA at temperatures ranging from 65 to 120 °C above the blend T_g. Typical normalized birefringence and dichroism profiles are presented in Figure 3. The raw data were rescaled with respect to the signal at 10 ms (the initial data point), yielding normalized profiles that decay from unity at $t = 10$ ms to zero as $t \rightarrow \infty$. All profiles manifest exponential decays, a characteristic of stress relaxation in polymer melts.[21] Since dichroism is a measure of PEO orientation in the blends, a single-exponential fit of this signal yields the PEO component relaxation time. However, a single-exponential fit was found to be inadequate for the birefringence profiles. This is as expected since both PEO and PMMA orientation contribute to birefringence, and in general each component is expected to relax on a separate time scale. Using a double-exponential fit, two relaxation times were recovered for each birefringence profile. In all cases the two time scales differed by at least an order of magnitude and the two preexponential factors were of the same order, making accurate recovery of both relaxation times possible. The longer time constant is attributed to PMMA relaxation and the shorter to PEO relaxation since in the pure state at the same $T - T_g$ PMMA exhibits a much larger relaxation time for the molecular weights studied here. This assumption is supported by excellent agreement between the shorter birefringence time scale and the single dichroism time scale (i.e., both agree within the margin of uncertainty).

Due to the modest signal-to-noise ratio of dichroism (typically about 10:1), the possible presence of a second, slower relaxing contribution of much lower amplitude than that characterized by the exponential fit cannot be ruled
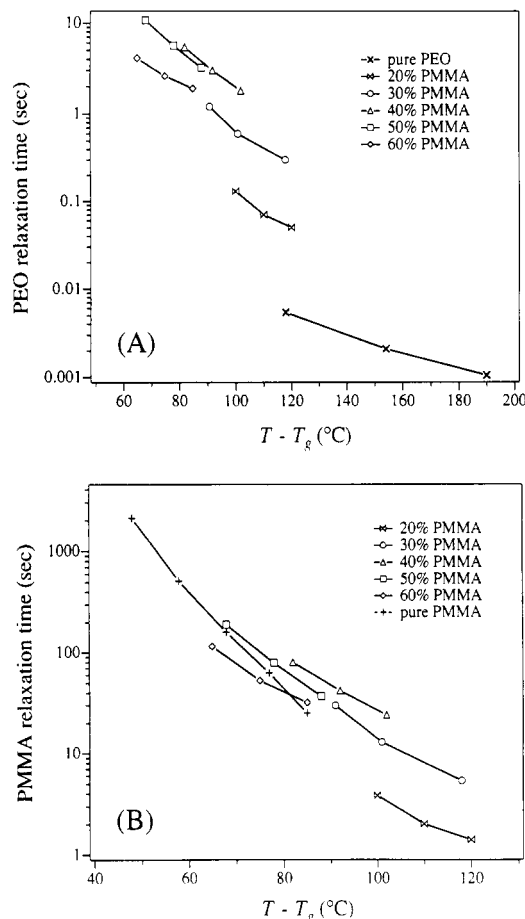
Figure 4. Temperature dependence of relaxation times for PEO (A) and PMMA (B) at various compositions. Pure-component relaxation times were found by mechanical oscillatory shear rheometry.

Figure 5. Composition dependence of component relaxation times at $T - T_g = 100$ °C. Solid data points were computed from optical experiments, while hollow data points were estimated from mechanical experiments.

out. Orientational coupling interactions[22,23] as well as mild specific interactions between the two components might be expected to produce such a contribution. The fact that no long time scale comparable to that of PMMA in the blend is evident in the dichroism signal suggests that orientational coupling interactions and specific interactions between PEO and PMMA are relatively weak. Due to the noise level in the dichroism signal, though, a more quantitative assessment is not possible.

It is worth noting that for all experiments the birefringence signal remains positive, even long after the PEO orientation has vanished (as can be seen by comparing the birefringence and dichroism profiles in Figure 3). This implies that PMMA has a positive stress-optical coefficient at the IR wavelength of 4.6 μm. In contrast, it has been reported[8,24] that in the visible range PMMA has a negative stress-optical coefficient (although a change of sign has been observed at high temperatures).[25] Since PMMA exhibits only a small birefringence effect in both wavelength regimes, it may be argued that differences in the wavelength dependences of backbone bond polarizabilities and side-group bond polarizabilities may account for this difference in the stress-optical coefficient.

Component relaxation times over the range of blend compositions and temperatures studied are plotted in Figure 4. PEO relaxation times were taken to be the dichroism exponential time constant, while PMMA relaxation times were acquired from the longer birefringence time constant. A total of 50–180 step strain profiles were averaged for each temperature and composition studied (more signal averaging was required at higher tempera-
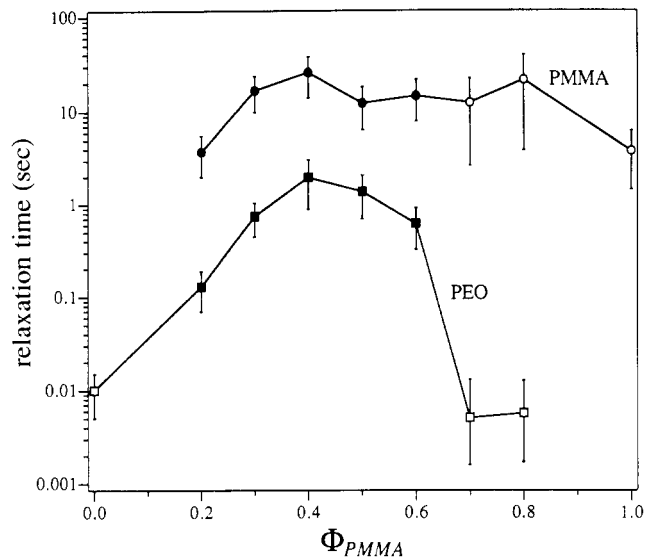
tures where a poorer signal-to-noise ratio was observed). Also plotted are the pure PEO and pure PMMA relaxation times obtained from dynamic mechanical experiments. Mechanical oscillatory shear rheometry was used to recover the pure-component relaxation times since pure PEO relaxes too quickly to monitor using step strains in the temperature range of interest and pure PMMA requires temperatures exceeding those accessible with the present apparatus due to its high T_g. A higher molecular weight PEO ($M_w = 235\ 000$) was used in the mechanical experiments, and the resulting relaxation time was rescaled assuming a 3.4 power law dependence on molecular weight.

From Figure 4 it can be seen that over the composition range of 20–60% PMMA, PEO exhibits much slower relaxation in the blend than in the pure state at a given $T - T_g$, while PMMA relaxation times are on the same order as in the pure state. The fact that one component is hindered and the other remains more or less unaffected seems consistent with Wu's observation[6] of positive deviations from linearity for overall blend friction. Although PMMA relaxation times in the blend are on the same order as in the pure state, in general there is a mild hindrance of relaxation, which is consistent with the findings of Colby[10] and Zhao et al.[11] The dramatic retardation in PEO relaxation, however, is in contrast with these studies. Colby found a slight reduction of PEO relaxation times in the blend, while Zhao et al. were unable to capture any PEO orientation within the time scale of their experiment (0.01 s), indicating that PEO is not hindered (at least not to the extent observed here). Noting that the present study focuses on a different composition range than these two previous studies, this contrast in results implies a complicated composition dependence of component relaxation times. This complex dependence is demonstrated in Figure 5, where relaxation times are plotted as a function of composition for a fixed $T - T_g$ of 100 °C. In addition to the relaxation times recovered optically on 20–60% PMMA blends, relaxation times at 70 and 80% PMMA estimated from mechanical experiments are plotted. Although stress rather than optical anisotropy is measured in mechanical experiments, the observables of the two techniques are related through the stress-optical law, meaning that both experiments monitor the same physical phenomenon (i.e., the relaxation of segmental orientation). Mechanical results for the 80%
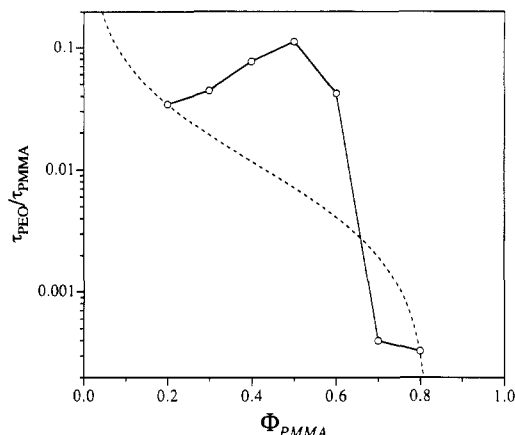
Figure 6. Ratio of component relaxation times at $T - T_g = 100$ °C. Similar behavior was reported for PS/PXE blends.[26] The dashed line corresponds to predictions of the Brochard-Wyart model based on a fit at $\Phi_{PMMA} = 0.2$ and 0.8.

PMMA blend were previously reported.[10] To account for differences in the molecular weights of the components used in that study, the data at 70 and 80% PMMA were rescaled using a 3.4 power law. This shifting is likely to introduce some error to the data but not enough to significantly distort the dramatic behavior illustrated in Figure 5. Over the temperature range investigated, the qualitative trends illustrated in Figure 5 do not vary.

The credibility of this remarkable trend is reinforced by a similar observation for a blend of polystyrene (PS) and poly(xylenyl ether) (PXE) by Composto, Kramer, and White.[26] Forward recoil spectrometry was used to measure tracer diffusion coefficients in that blend, which in turn were used to compute monomeric friction factors for each component ($\zeta_{o,PS}$ and $\zeta_{o,PXE}$) as a function of composition. According to reptation theory, the monomeric friction coefficient is proportional to the relaxation time,[21] and it was verified that for the PS/PXE blends reptation is the dominant mode of diffusion.[26] Thus, trends in the friction factor data of that study may be directly compared to trends in relaxation times of the present work. In the PS/PXE blends the faster relaxing component, PS, exhibits the more dramatic behavior, with $\zeta_{o,PS}$ spanning 2 orders of magnitude and passing through a maximum near the weight fraction $\Phi_{PXE} = 0.25$ (see Figure 4b of ref 26). Such behavior is analogous to that of the faster relaxing component in the present study, PEO, only the height and peak composition vary slightly. The diffusion/relaxation behavior of the slower relaxing component in both blends is less sensitive to composition, varying by less than an order of magnitude over the full range of composition.

Further comparison to the PS/PXE blend may be found by examining the ratio of the two component relaxation times as a function of composition. Figure 6 illustrates this behavior at $T - T_g = 100$ °C. As with the PS/PXE blend there is a maximum in this ratio at an intermediate composition (near $\Phi_{PMMA} = 0.6$ for the present system and near $\Phi_{PXE} = 0.15$ for the PS/PXE system). As shown by Composto et al., with the data plotted in this fashion it is possible to check whether the system follows the Brochard-Wyart theory for chain friction in blends.[27] According to that model, three friction coefficients ($\zeta_{PEO,PEO}$, $\zeta_{PEO,PMMA}$, $\zeta_{PMMA,PMMA}$) give rise to the two observed monomeric friction factors

$$\zeta_{o,PEO} = \Phi_{PEO}\zeta_{PEO,PEO} + \Phi_{PMMA}\zeta_{PEO,PMMA} \quad (1)$$

$$\zeta_{o,PMMA} = \Phi_{PEO}\zeta_{PEO,PMMA} + \Phi_{PMMA}\zeta_{PMMA,PMMA} \quad (2)$$

which can be rewritten as

$$\frac{\zeta_{o,PEO}}{\zeta_{o,PMMA}} = \frac{\Phi_{PEO}(\zeta_{PEO,PEO}/\zeta_{PEO,PMMA}) + \Phi_{PMMA}}{\Phi_{PEO} + \Phi_{PMMA}(\zeta_{PMMA,PMMA}/\zeta_{PEO,PMMA})} \quad (3)$$

With knowledge of the degree of polymerization and chain segment length, the observed ratios of relaxation times may be converted to ratios of monomeric friction factors using reptation theory[21] and then fit to eq 3 using any two points on Figure 6. The dashed line on Figure 6 represents the Brochard-Wyart prediction for τ ratios based on a fit at $\Phi_{PMMA} = 0.2$ and 0.8. As found with the PS/PXE blend, the model yields a poor fit for the current system, indicating that the Brochard-Wyart approach does not accurately capture the composition dependence of component chain friction in the blend.

In addition to dramatic composition dependence, component relaxation dynamics in the current system exhibit remarkable temperature behavior. Since the range of temperatures studied was limited, accurate recovery of WLF coefficients was not possible. However, since the data extend beyond 100 °C and into the range where WLF behavior typically gives way to Arrhenius type behavior, the data are fit to the Arrhenius model and it is assumed that the apparent Arrhenius activation energies serve as adequate measures of the relaxation temperature dependences for the current discussion. It was found that relaxation times in the blends studied here follow Arrhenius behavior over the limited temperature ranges investigated:

$$\frac{\tau(T)}{\tau(T_0)} = \exp\left[\frac{\Delta H_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (4)$$

where T_0 is a reference temperature and ΔH_a is interpreted as an activation energy for an elementary flow process.[28] Linearity was observed in plots of $\ln \tau$ vs $1/T$, the slopes of which were used to calculate ΔH_a values, presented as a function of composition in Figure 7. $\Delta H_{a,PEO}$ is nearly composition independent, while $\Delta H_{a,PMMA}$ is strongly influenced by the presence of PEO, falling monotonically to roughly 25% of its pure-component value at 20% PMMA.

4. Discussion

In analyzing the composition dependence of the component relaxation times, the first point to consider is whether a constant $T - T_g$ really corresponds to a constant free volume state. This approximation assumes that the free volume at T_g and the thermal expansion of free volume are composition-independent parameters. More sophisticated estimates could be made[28] if relaxation times spanning wider ranges of temperatures could have been measured. Composto et al.[26] applied two strategies to estimate temperatures of constant free volume, which resulted in slightly different results. In each of these approaches, however, the friction factor of the faster relaxing species, PS, still showed a clear maximum. Furthermore, any changes in the temperatures used in the analysis will alter the relaxation times of *both* components, so no reasonable calculation of iso-free-volume temperatures will permit monotonic concentration dependences for both relaxation times. Thus, we believe the maximum in PEO relaxation time shown in Figure 5 to be real, irrespective of the choice of $T - T_g$ as the free
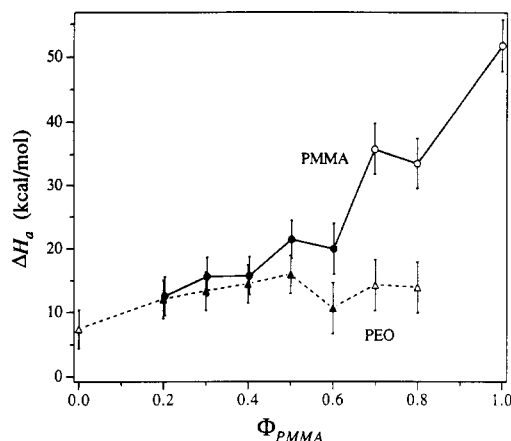
Figure 7. Composition dependence of Arrhenius activation energies for each component. Solid data points were computed from optical experiments, while hollow data points were estimated from mechanical experiments.

volume state. We offer below a tentative explanation for this maximum in terms of a trade-off between specific interactions slowing the relaxation of PEO and the tube diameter widening as PMMA is added to the blend, speeding the relaxation of PEO.

Although specific interactions between PEO and PMMA are small, from FTIR experiments they are known to cause PEO to preferentially adopt trans conformations in the blend, as opposed to the primarily helical structure PEO takes on in the pure state.[29,30] The effect of this conformational change on dynamics is not clear, but it is conceivable that it could cause a reduction in mobility and hindered relaxation for PEO as PMMA is introduced (as observed in Figure 5). A possible competing effect involves chain entanglements. From the results of Wu,[6] the tube diameter of the blend is expected to increase with PMMA concentration since PMMA experiences fewer entanglements than PEO ($M_{e,PEO}$ = 2200 and $M_{e,PMMA}$ = 9100, corresponding to tube diameters[21] of 39 and 61 Å for PEO and PMMA, respectively). This tube widening could account for the observed behaviors of both PEO and PMMA relaxation times in PMMA-rich blends (Φ_{PMMA} > 0.4), as both component relaxation times decrease with increasing PMMA concentration in this range (see Figure 5).

The drop in PMMA relaxation time observed at low PMMA concentrations (see Figure 5) is presumably due to constraint release becoming important.[31] A crude estimation based on ref 31 with the experimentally observed prefactor for constraint release[32] leads to the expectation that tube reptation should be the dominant mode of relaxation for Φ_{PMMA} < 0.5 (ordinary chain reptation is anticipated for Φ_{PMMA} > 0.5). Consequently, τ_{PMMA} is expected to monotonically decrease with decreasing Φ_{PMMA} for Φ_{PMMA} < 0.5.

The temperature dependence of component relaxation times contains information concerning monomeric friction factors in the blends and the validity of time–temperature superposition. As mentioned in the introduction, there is conflicting evidence in the literature regarding whether the components of this miscible blend should exhibit a single friction factor or separate ones. The temperature dependence of relaxation times is given by the ratio of the friction factor and absolute temperature ($\tau \sim \zeta_0/T$). Consequently, if both components in a blend have identical friction factors, the relaxation times of both components must exhibit the same temperature dependence. From Figure 7 it can be seen that for PMMA-rich

blends this is not the case. Each component clearly exhibits a separate temperature dependence (evidenced by separate activation energies), and therefore each must have a separate ζ_0. This uniqueness of component friction factors underlies the failure of the time–temperature superposition observed for the 80% PMMA blend.[10] Such thermorheological complexity has also been observed in miscible blends of polybutadienes with different microstructures.[33] As PMMA concentration is decreased, however, PEO and PMMA adopt nearly identical temperature dependences (demonstrated by similar activation energies in the 20–40% PMMA blends), suggesting the existence of a single blend friction factor and thermorheologically simple behavior at low PMMA concentrations.

The composition dependence of the apparent activation energies observed in Figure 7 is nontrivial, and similar behavior has not been reported in other blends. A possibly related peculiarity regarding PEO/PMMA blends is the reported composition dependence of the Flory–Huggins interaction parameter χ obtained from neutron scattering by Ito et al.[34] They found that χ increases monotonically from -5×10^{-3} at Φ_{PMMA} = 0.3 to 1×10^{-3} at Φ_{PMMA} = 0.9. Using the random-phase approximation,[35] this leads to a correlation length for concentration fluctuations which increases from roughly 20 to 60 Å as the PMMA concentration increases from 0.3 to 0.9. Since we are dealing with the single-phase region of the phase diagram, the magnitude of these concentration fluctuations is expected to be small. Nonetheless, it may not be coincidental that the temperature dependences of both species merge at low PMMA concentrations when this correlation length becomes small and χ becomes most strongly negative (i.e., attractive interactions are strongest). However, a full understanding of the validity/breakdown of the time–temperature superposition principle in miscible blends will have to await studies on dynamics of other miscible blend systems.

5. Conclusions

From the composition and temperature dependences of component relaxation times it is clear that each component in the PEO/PMMA blend retains a separate rheological identity, although the presence of dissimilar chains certainly influences component relaxation behavior. This is evidence that both intra- and intermolecular forces play crucial roles in the relaxation dynamics of the blend. Two observations significant to the development of blend rheology models were made. First, component relaxation dynamics manifest a dramatic and complex sensitivity to blend composition. The maximum in the composition dependence of the PEO relaxation time suggests that there is not a single mechanism responsible for this sensitivity to composition but rather multiple mechanisms, each dominating relaxation dynamics in a separate concentration regime. Such behavior has been observed in at least one other blend, PS/PXE.[26] Furthermore, from the temperature dependence of the component relaxation times it is apparent that in PMMA-rich blends each component adopts a separate friction factor with a unique temperature dependence, while in PEO-rich blends thermorheologically simple behavior arises.

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