Two DSC Glass Transitions in Miscible Blends of Polyisoprene/Poly(4-*tert*-butylstyrene)

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ABSTRACT: Conventional and temperature-modulated differential scanning calorimetry (DSC) experiments have been carried out on miscible blends of polyisoprene (PI) and poly(4-*tert*-butylstyrene) (P4tBS) over a broad composition range. This system is characterized by an extraordinarily large T_g difference ($\sim$215 K) between the two homopolymers. Two distinct calorimetric glass transitions were observed in blends of intermediate compositions (25%–50% PI) by both conventional and temperature-modulated DSC. Good agreement was found between the component T_g values measured by the two methods. Fitting of the component T_g values to the Lodge–McLeish model gives a ϕ_{self} of around 0.63 for PI in this blend and 0.03 for P4tBS. The extracted ϕ_{self} for PI is comparable to reported values for PEO in blends with PMMA and is significantly larger than values reported for PI in other blends with smaller homopolymer T_g differences. This observation is consistent with the presence of a nonequilibrium or confinement effect in PI/P4tBS blends, which results in enhanced dynamics of the fast component below the T_g of the slow component.

Introduction

Particular applications of polymeric materials often require specific properties that might include glass transition temperature (T_g), viscosity, mechanical response, and small molecule transport coefficients. The mixing of two compatible polymers is one of the most cost-effective ways to tune these properties to meet application needs.[1] However, miscible polymer blends have been known for some time to exhibit complicated dynamic phenomena including extremely broad calorimetric glass transitions[2] and the failure of time–temperature superposition.[3] Our limited understanding of these features restricts the utility of these materials.

Over the past two decades, dynamics in miscible polymer blends have been extensively studied. It is now well established that the unusual properties of these systems mainly result from the distinct segmental dynamics of the components. The Lodge–McLeish (LM) model[4] developed in 2000 is one approach that captures these features by considering the self-concentration effect (the enhanced local concentration due to chain connectivity). This model provides qualitatively correct predictions of dynamics in many miscible polymer blends in the high-temperature regime (well above the blend T_g). In some systems, quantitative agreement has been found between the model predictions and experimental results[5,6] in this regime.

However, one important phenomenon inferred by the LM model was not experimentally observed until a few years ago. The LM model predicts that, due to the enhanced self-concentration, components in a miscible blend will have distinct effective glass transitions, with the T_g values for each component biased toward its homopolymer value. On the contrary, the existence of a single broad calorimetric T_g has long been accepted as a general feature of miscible polymer blends.[1] In 2005, Sakaguchi et al. reported

that the configurational heat capacity of miscible polyisoprene/polyvinylethylene (PI/PVE) blends obtained from adiabatic calorimetry could be resolved into two sigmoidal curves.[7] By fitting an empirical equation, they were able to extract distinct T_g values for each component. Later that year, Miwa et al. reported the observation of two calorimetric T_gs in two additional miscible blend systems [poly(*o*-chlorostyrene)/poly(vinyl methyl ether) (P*o*ClS/PVME) and polystyrene (PS)/PVME blends] at selected compositions using temperature-modulated DSC.[8] In 2006 and 2008, Lodge and co-workers reported the direct observation of two DSC T_gs for three miscible blends containing poly(ethylene oxide) (PEO) across a broad composition range.[9,10]

Although the above pioneering work supports the presence of distinct effective glass transitions for components in miscible polymer blends, questions still remain about the interpretation and generality of this phenomenon. For the PI/PVE blend, the determination of two T_g values involved a complicated fitting process. For P*o*ClS/PVME and PS/PVME blends, two glass transitions were obvious only at very limited compositions. Because of the anomalous behavior of the PEO component in blends with PMMA,[11,12] PEO is considered by some researchers as an atypical blend component.[11–13,27] The crystallization of PEO in these blends is an additional complication. To suppress crystallization, very low molecular weight PEO (300–1000 g/mol) was used in the study of PEO blends, which the authors stated[9] could "place the system somewhere between 'classical' polymer solutions and polymer blends".

In this study, we perform conventional and temperature-modulated DSC (TMDSC) measurements on polyisoprene/poly(4-*tert*-butylstyrene) (PI/P4tBS) blends with several different PI molecular weights. This system features a very large pure component T_g difference of $\sim$215 K, which facilitates the calorimetric observation of two glass transitions. The molecular weights of both components used in this study are on the order of 10^3–10^4 Da.

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Table 1. Polymer Characteristics

polymer	M_n (g/mol)	M_w/M_n	T_g (K)
PI-3k	3 000	1.06	204
PI-10k	10 100	1.04	204
PI-17k	17 000	1.04	206
P4tBS-32k	32 000	1.04	420

Unlike PEO blends, the low T_g component in this system (PI) has been well studied in other blends with various methods[5] and shows typical behavior. In addition, since this is the only system studied to date that has a ΔT_g comparable with the PEO/PMMA system, the comparison of these two systems is of interest.

For miscible PI/P4tBS blends, we resolve two distinct calorimetric glass transitions by both conventional and temperature-modulated DSC for blends of intermediate composition (25%− 50% PI). Good agreement was found between the component T_g values measured by the two methods. Fitting of the measured T_g values to the Lodge−McLeish model gives a ϕ_{self} of around 0.63 for the PI component in this blend and 0.03 for the P4tBS component. Similar to the PEO/PMMA system, our results imply enhanced dynamics of the fast component in a miscible polymer blend at temperatures below the glass transition of the slow component. This observation is consistent with the presence of a nonequilibrium or confinement effect,[17,25,28] which results in enhanced dynamics of the fast component below the T_g of the slow component.

Experimental Section

Materials. All polymers were purchased from Polymer Source Inc. with molecular weights, polydispersity indices, and T_g values indicated in Table 1. All PI samples have the microstructure of 80% cis 1,4, 15% trans 1,4, and 5% 3,4.

Miscibility. Small-angle neutron scattering (SANS) measurements were previously used by Yurekli et al. to study the miscibility of PI/P4tBS blends.[14] Measurements were done on blends of dueterated polybutadiene with PI, P4tBS, and PI/P4tBS blends. From these scattering experiments, negative χ values were extracted for PI/P4tBS (molecular weight 40 and 33 kDa, respectively) blends with various compositions up to 443 K. The increase of χ with increased temperature indicates LCST behavior for this system. Small-angle X-ray scattering (SAXS) experiments were done on a 8/2 PI/P4tBS (molecular weight 20 and 70 kDa, respectively) blend between 298 and 343 K in a study by Watanabe et al.[15] A homogeneous state was indicated from the data for this blend in the temperature range studied. Miscibility of blends containing lower molecular weight PIs is further supported by our DSC data, which will be discussed in detail below.

Blend Preparation. A total of about 20 mg of PI/P4tBS with the desired composition was dissolved in tetrahydrofuran to form a 1% solution. The solution was stirred for at least 10 h, after which solvent was evaporated in an N_2 environment until the polymer concentration was around 50%. This concentrated solution was transferred into a DSC pan and further evaporated in a vacuum oven at room temperature for at least 10 h. The oven temperature was then raised by 30 K and held for 3 h before the weight of the sample was determined. This procedure was repeated until oven temperature was 383 K (∼50 K above the average T_g of a 25% PI/P4tBS blend). The sample was then held in the vacuum oven at 383 K and weighed every hour until the weight was constant to ensure complete evaporation of solvent. To confirm evaporation of the solvent by this procedure, we took one 25% PI/P4tBS sample (the blend with the highest average T_g) after the DSC measurement and set it in the vacuum oven at 433 K (13 K above the T_g of pure P4tBS) for 5 h. DSC measurements were then repeated on this sample, with the results in excellent agreement with the previous measurement.
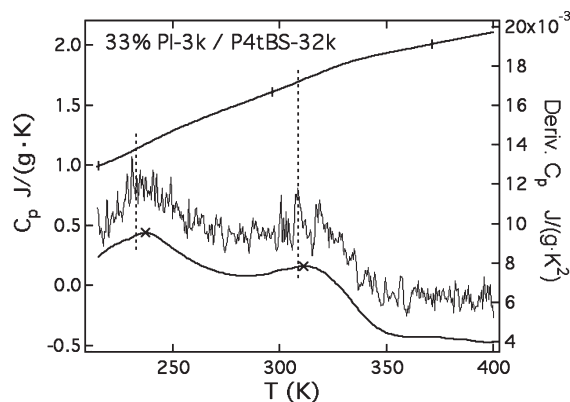

Figure 1. From top to bottom, the heat capacity C_p, the temperature derivative of C_p, and the temperature derivative of C_p smoothed over 30 K, for a representative blend showing two DSC glass transitions. Vertical shifts were applied. Vertical bars on the C_p curve indicate the visually selected range for each transition. Dotted lines indicate the T_g values determined by the TA Universal Analysis program (inflection point of C_p curve). Crosses indicate the maxima of the smoothed temperature derivative curves. These two methods of T_g determination are in good agreement.

DSC Measurements. For each blend sample, both conventional DSC and temperature-modulated DSC (TMDSC) were performed. The conventional DSC has a higher scanning rate, which offers a higher sensitivity and shorter acquisition time. TMDSC offers the advantage of selectively observing the reversible glass transition signals; in addition, its lower scanning rate results in better temperature resolution.

Blend samples of around 10 mg prepared by the above method were sealed in aluminum crimped pans provided by TA Instruments. DSC experiments were carried out with a TA Instruments Q2000 using a nitrogen purge of 50 mL/min. An empty crimped pan was used as the reference in every case. The instrument was calibrated using an indium standard (melting point 429.7 K) with a ramp rate of 10 K/min. Based on previous tests, calibrations done at different ramp rates differ by less than 0.5 K. Hence, this calibration is used for both conventional and temperature-modulated DSC measurements. To erase thermal history completely, all the samples were annealed at a temperature higher than the the T_g of either blend component in the DSC cell chamber for 3 min. This was followed by cooling at 10−40 K/min to a temperature below the T_g values of both components. (In a few cases as discussed below, a cooling rate of 1 K/min was employed.) A conventional DSC scan with a ramp rate of 10 K/min was then obtained during heating of the sample to 423 K, which was followed by a cooling cycle to 193 K. Finally, a TMDSC scan was performed during heating to 423 K at a ramp rate of 2 K/min. The modulation used in TMDSC measurement has an amplitude of 0.5 K and period of 60 s.

Results

Figure 1 shows representative conventional DSC traces for a 33% PI-3k/P4tBS-32k blend. The top curve is the total heat capacity C_p. The middle curve is the temperature derivative of C_p. We investigated multiple methods for determining the two component T_g values. As one method, we visually picked the two transition ranges as indicated by the vertical bars on the C_p curve. Given these transition ranges, the glass transition temperatures indicated by the dotted vertical lines were determined by the TA Universal Analysis program as the inflection points of the C_p curve. Although this is a standard method to determine the glass transition temperature, the procedure involves an arbitrary selection of the transition ranges for each DSC trace. To simplify the procedure as well as eliminate human bias, a more objective procedure of defining the glass transitions is proposed here.
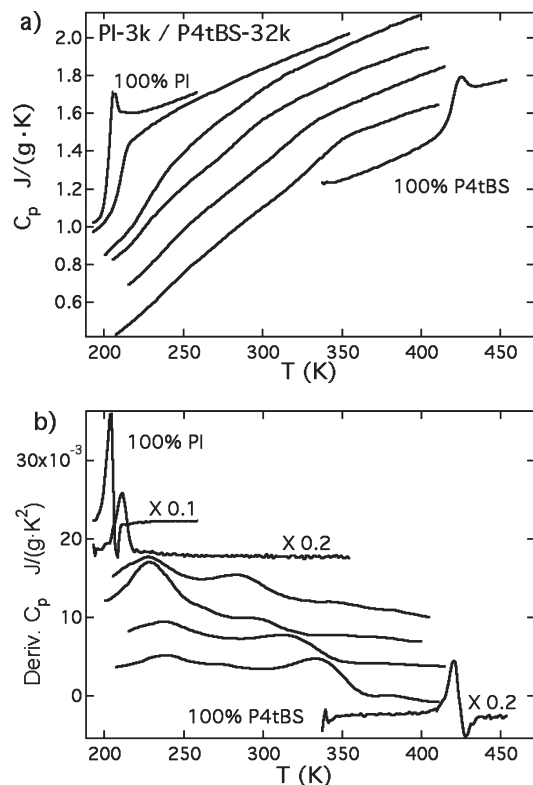
Figure 2. Conventional DSC thermograms of PI-3k/P4tBS-32k blends. From pure PI to pure P4tBS, curves represent blends with PI compositions of 75%, 50%, 40%, 33%, and 25%, respectively. (a) C_p curves. (b) Temperature derivative of C_p curves. For three curves, the data have been scaled by the factors indicated. In all other cases, the data are smoothed over 30 K. Vertical shifts have been used for clarity.

The bottom curve in Figure 1 is the temperature derivative of C_p smoothed over 30 K. The glass transition temperatures for this blend were determined as the temperatures corresponding to the peaks of the smoothed curve (indicated by the crosses). The T_g values determined by this procedure were reasonably consistent with those determined by the previous method (differing by less than 5 K). Thus, this smoothing procedure was adopted to determine the component T_g values for the rest of the study.

Figure 2 shows the conventional DSC thermograms of PI-3k, P4tBS-32k, and their blends with compositions ranging from 25% to 75% PI. For blends with PI compositions between 25% and 50%, two glass transitions are clearly observed both in the original C_p curves and the smoothed derivative C_p curves. For pure PI, pure P4tBS, and 75% PI/P4tBS blends, the transitions were sharp and well-defined; thus, no smoothing was performed. In order for the data for these three compositions to be plotted with the others, their derivative C_p curves were scaled by the amount indicated in the figure. From many previous studies on segmental dynamics in miscible polymer blends, it is known that the components in these systems have distinct segmental dynamics, each biased toward the dynamics of their pure homopolymers. Thus, it is reasonable to assume that the high-temperature transition is the glass transition of the slower P4tBS component in this blend while the low-temperature transition belongs to the faster PI component. In addition, as the composition of PI increases, the glass transition of both components shift to lower temperatures, which is also consistent with the shifting trend of component segmental dynamics. We will discuss the interpretation of the two glass transitions below. Parallel experiments were carried out on PI-10K and its blends with P4tBS-32k to study the effect of molecular weight on the glass transition behavior of this blend. The corresponding data
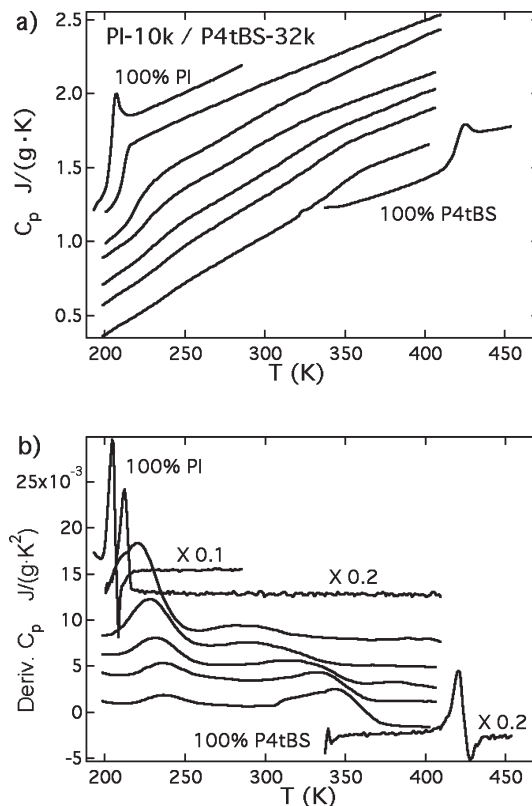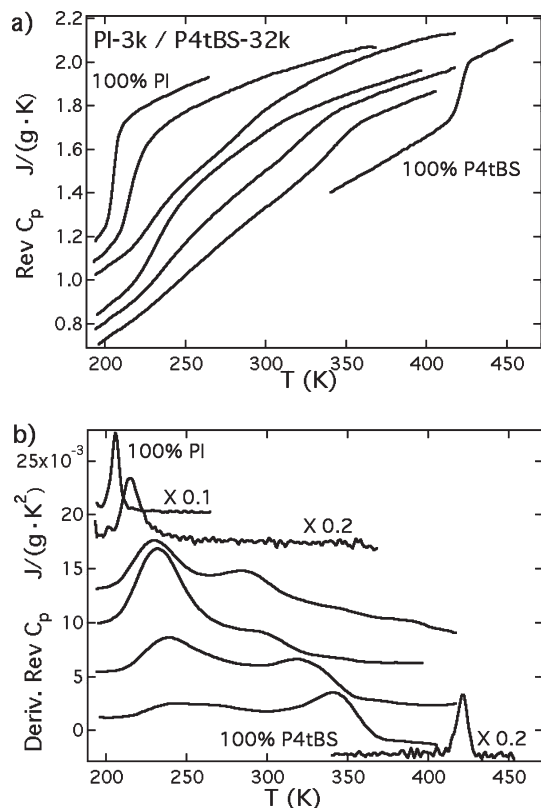

Figure 3. Conventional DSC thermograms of PI-10k/P4tBS-32k blends. From pure PI to pure P4tBS, curves represent blends with PI compositions of 75%, 50%, 40%, 33%, 29%, and 25%, respectively. (a) C_p curves. (b) Temperature derivative of C_p curves. For three curves, the data have been scaled by the factors indicated. In all other cases, the data are smoothed over 30 K.

are shown in Figure 3. Pure PI-10k has a molecular weight 3 times that of PI-3k but the same T_g (within 1 K). It is clear from Figure 3 that the glass transition behavior of PI-10k/P4tBS-32k blends is similar to that of PI-3k/P4tBS-32k blends.

Figure 4 shows the reversible TMDSC thermograms of PI-3k, P4tBS-32k, and their blends. By adding temperature modulation, this technique allows selective observation of the reversible component of the heat capacity. Figure 4 provides an alternative view of the glass transitions by eliminating the effect of irreversible heat flow (enthalpy overshoot effect). In comparison to Figure 2, the glass transition peaks are better defined in Figure 4. However, the main features of the two figures are the same. The glass transition peaks appear at similar temperatures and shift in a similar pattern with composition. The corresponding TMDSC thermograms of the PI-10k/P4tBS-32k blends are available as Supporting Information.

A quantitative comparison of the component T_g values measured for PI-3k/P4tBS-32k blends and PI-10k/P4tBS-32k blends is shown in Figure 5. Good agreement (less than 7 K deviation) between the two blend systems was found for both component T_g values at all the compositions measured by conventional DSC (Figure 5a). For the TMDSC results (Figure 5b), good agreement was found for both component T_g values at all compositions except for blends containing 40% and 50% PI, in which case deviations of up to 15 K were observed for the P4tBS component. The intensity of the glass transition for P4tBS is very weak for blends with larger PI compositions; this is reasonable given that the ΔC_p of pure P4tBS is about half that of pure PI. Hence, larger errors are associated with the determination of the T_g (P4tBS) for these blends. For this reason, we do not report P4tBS T_g values for blends with more than 50% PI. Replicate samples were made for

Figure 4. Temperature-modulated DSC thermograms of PI-3k/P4tBS-32k blends. From pure PI to pure P4tBS, curves represent blends with PI compositions of 75%, 50%, 40%, 33%, and 25%, respectively. (a) Reversible C_p curves. (b) Temperature derivative of reversible C_p curves. For three curves, the data have been scaled by the factors indicated. In all other cases, the data are smoothed over 30 K.

25% and 50% PI-3k/P4tBS-32k blends to test the reproducibility of both the conventional DSC and TMDSC measurement. Error bars indicating the range of these values are shown in Figure 5. Except for T_g (P4tBS) in 50% PI-3k/P4tBS-32k blend measured by conventional DSC, the deviations between other replicate experiments are smaller than the size of the symbols and thus are not visible.

Discussion

Lodge−McLeish Model. The LM model[4] assumes that the chemical composition of the region within one cubic Kuhn length (l_K) of a given polymer segment determines the mobility of that segment. This local concentration (ϕ_{eff}) is calculated by considering the bulk concentration (ϕ) and the self-concentration (ϕ_{self}):

$$\phi_{eff} = \phi_{self} + (1 - \phi_{self})\phi \qquad (1)$$

LM estimate the self-concentration ϕ_{self} as

$$\phi_{self} = \frac{C_\infty M_0}{\kappa \rho N_{av} V} \qquad (2)$$

Here C_∞ is the characteristic ratio, M_0 is the repeat unit molar mass, κ is the number of backbone bonds per repeat unit, ρ is the density, N_{av} is Avogadro's number, and $V = l_K^3$.

In this model, polymer segments of a given type (e.g., A) have an effective glass transition temperature that is different from the macroscopic blend T_g because $\phi_{eff,A}$ differs from ϕ_A. In our implementation of the LM model, we have used
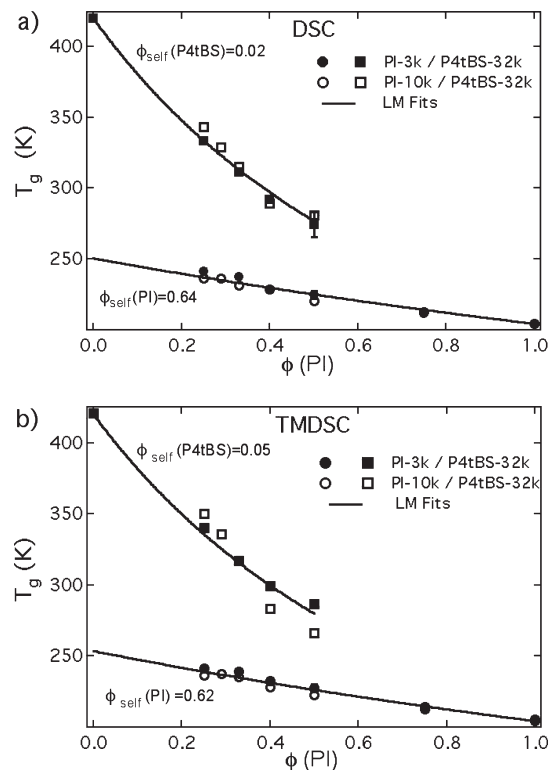
Figure 5. Component T_g values obtained from (a) conventional DSC and (b) TMDSC for PI-3k/P4tBS-32k blends and PI-10k/P4tBS-32k blends. The lines are fits of the data to the Lodge−McLeish model with the self-concentration values indicated.

the Fox equation to calculate this effective T_g:

$$\frac{1}{T_{g,eff}(A)} = \frac{\phi_{eff,A}}{T_{g,A}} + \frac{1 - \phi_{eff,A}}{T_{g,B}} \qquad (3)$$

We assume that $T_{g,eff}$ in the LM model can be identified with the component glass transition temperatures measured in our study. Thus, we make a direct comparison between our DSC measurements and the LM model in Figure 5. Here, instead of predicting the $T_{g,eff}$ values, we have used eqs 1 and 3 to fit the measured T_g values for each component and thus extracted the self-concentrations for PI and P4tBS in this blend. Since PI-3k and PI-10k pure homopolymers have the same T_g value, data on both blends were fitted with one set of parameters. Solid lines are the best fits with the extracted ϕ_{self} values for each component indicated. The self-concentration values extracted from conventional DSC and TMDSC measurements are in good agreement.

For the slow component (P4tBS), a very small ϕ_{self} value (smaller than 0.1) was extracted. This is the first experimental report on the ϕ_{self} of P4tBS. A self-concentration value of 0.2 is predicted from the LM model using eq 2 and parameters reported in the literature.[16] Although the absolute ϕ_{self} value extracted from the experiments is considerably different than that predicted from the LM model, the fitted value is qualitatively consistent with the model prediction in that the slow component usually has a stiffer backbone, larger Kuhn length, and hence a small self-concentration.[4]

For the fast component (PI), a ϕ_{self} value of 0.63 was determined by fitting the data. Given the previous determinations of ϕ_{self} for PI in various miscible blends, this value is unexpectedly large. For example, the PI/PVE blend system is often considered a model miscible blend and has been extensively studied by NMR, dielectric relaxation, and rheology

measurements over a broad time, temperature, and composition range.[5,21−24] The ϕ_{self} value of 0.45 predicted[4] by the LM model was found to give an excellent description of the dynamics of PI in this system. As another example, for low molecular weight blends of PI and polystyrene, a ϕ_{self} of 0.33 was obtained for the PI component.[32]

Only one other miscible blend component has been reported to have a ϕ_{self} value as large as that determined here for PI in P4tBS. Large ϕ_{self} values were determined for PEO in blends with PMMA as studied with various methods[9,11,12] and PEO in blends with poly(vinyl acetate) (PVAc) as studied with DSC.[10] This insensitivity of the dynamics of PEO upon blending indicates that the motions of PEO chains are less dependent on the cooperative motion of the blending partner and was previously attributed to the lack of side groups for PEO.[11] As PI contains a side group, this explanation cannot be used to explain the data presented here.

We note that the large ϕ_{self} values obtained for PEO in miscible blends have been reported for blends with large homopolymer T_g differences (e.g., 197 K for the PEO/PMMA blend). The unusually large ϕ_{self} value found here for PI in P4tBS also occurs in a system with a large homopolymer T_g difference (215 K). In contrast, the well-studied PI/PVE has a homopolymer T_g difference of only 60 K. As described below, we expect that DSC measurements will generally produce large ϕ_{self} values for the fast component when the two components have very different homopolymer T_g values.

In 2006, Lipson and Milner modified the LM model by taking into account of a self-consistency requirement[34] between the self-concentration values for the two components; i.e., the calculated volume fraction of the blend should be the same whether the calculation is based upon the environment of A segments or the environment of B segments. Unlike the original LM model in which the effective T_gs of each component can be independently fitted by a single ϕ_{self} value, the self-consistent LM model allows only certain pairs of ϕ_{self} values. The self-consistent model[34] could not yield good fits to the DSC data reported (see Supporting Information for details). Thus, while recognizing the limitations of the original LM model, we utilize it in this work for lack of a suitable alternative. At a minimum, the original LM in conjunction with the Fox equation provides a basis for the intercomparison of results on different blend systems, as all of these results have been fitted in an equivalent manner.

Nonequilibrium and Confinement. Recent quasi-elastic neutron scattering measurements on PEO in a blend with PMMA provide a useful context for the experiments reported here. Genix et al.[25] reported that as the temperature is lowered below the T_g of PMMA, the dynamics of PEO are significantly faster (and more broadly distributed) than would be expected based upon extrapolation from high temperatures. The authors argue that the vitrified PMMA chains "confine" the mobile PEO chains and caused a qualitative change in the dynamics of PEO at low temperatures. One could pose the issue in somewhat more general terms:[17,25,28] Why should the dynamics of the fast component continue to follow the trend established in thermodynamic equilibrium if the system has left equilibrium (and thus does not have the extrapolated volume or structure)?

We imagine that these ideas[17,25,28] are applicable to all miscible blends where the interactions between segments on different chains are not too strong. Here we apply these ideas to PI in P4tBS. Figure 6 schematically illustrates the concept. At temperatures above the effective T_g of the slow component, the system is in equilibrium. In this temperature range, the component dynamics exhibit a VTF temperature dependence, which can be at least qualitatively
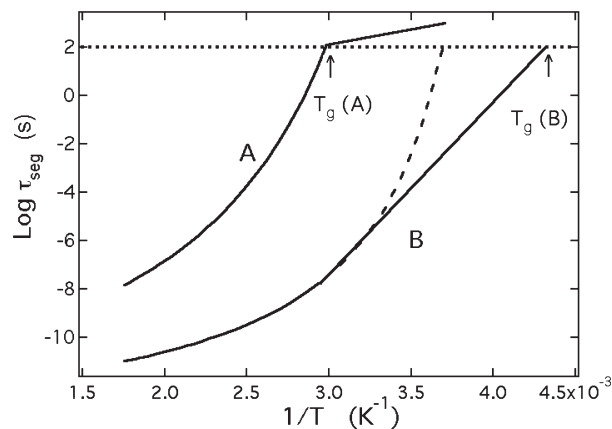
Figure 6. Sketch of the segmental dynamics of the slow (A) and fast (B) components in a miscible A/B polymer blend. The dotted line represents a segmental relaxation time of 100 s, and effective glass transition temperatures of the components are indicated. For component B, below the effective T_g of A, the dashed curve represents the VTF extension of its high-temperature dynamics, while the thick solid line represents the enhanced dynamics that result from the vitrification of the blend.

predicted from their pure homopolymer dynamics and the LM model.[5,6,29−33] At temperatures below the effective T_g of the slow component, the dynamics of the slow component exhibit a roughly Arrhenius temperature dependence. The vitrification of the slow component in the blend causes the entire system to fall out of equilibrium, and thus the dynamics of the fast component deviate from the LM prediction even though the temperature is above its effective T_g.

In Figure 6, the dynamics of the fast component are illustrated as enhanced and nearly Arrhenius below the effective T_g of the slow component. As the components are in intimate contact with each other, the dynamics of the fast component are expected to change in the same direction as the dynamics of the slow component. Experimental support for the view that the fast component switches to Arrhenius behavior below the slow component T_g can be found in work on other systems in addition to the PEO/PMMA work[17,25] mentioned above. For poly(vinylidene fluoride) (PVF) in blends with poly(methyl methacrylate), dielectric α relaxation times of $10^{-9}−10^{-1}$ s were measured by Sy et al.[18] As the temperature is lowered, the VTF temperature dependence of τ_α transforms into a weaker Arrhenius temperature dependence. In Figure 6, we extend this behavior to even lower temperatures where the effective T_g of the fast component is reached.

Figure 6 provides a qualitative explanation for the large ϕ_{self} values observed for the fast component in blends with large homopolymer T_g differences. Since the DSC T_g occurs when the segmental relaxation time of a polymer chain is roughly 100 s, the apparent T_g of the fast component is lower than would be obtained from extrapolating the high-temperature dynamics. This in turn leads to a larger ϕ_{self} value for the fast component extracted from the DSC measurement than would be expected from measurements only in the equilibrium state (or from the LM model, combined with the Fox equation). For most polymer blends like PI/PVE, the T_g difference between pure components is small enough that this effect takes place over a narrow temperature range and likely has little influence on the effective T_g of the fast component. For the case of PI/P4tBS and PEO/PMMA, however, the large T_g difference between the pure homopolymers facilitates the detection of this deviation.

Recently Chen et al. reported dynamic mechanical and DSC measurements on PI/P4tBS blends containing 50% and 70% PI.[19] These authors extracted effective T_g values from a VTF analysis of dielectric and viscoelastic measurements at high temperatures where the blend is in the equilibrium state. We took the reported effective T_g values and fit them to the LM model. The ϕ_{self} extracted for the P4tBS component in this blend is 0.0, qualitatively consistent with the value that we extracted from the DSC measurements. The ϕ_{self} value extracted for the PI component in the 50% PI blend is 0.4. This value is similar to that reported for the PI component in blends with PVE and smaller than that extracted from our DSC measurements. Since the viscoelastic and dielectric measurements were carried out in the equilibrium state, this difference is consistent with Figure 6. Although two glass transitions were not clearly resolved in DSC, Chen et al. comment that "the blends exhibit broad, almost two step glass transition". (For the blend containing 70% PI, we determined a larger ϕ_{self} value from the dielectric and viscoelastic measurements.[19] Since the dynamics of the PI component change little in the concentrated region, this extracted ϕ_{self} value is associated with a relatively large error bar and was thus not used in the comparison.)

Further evidence for the effect shown in Figure 6 can be found in DSC measurements on polymer–solvent mixtures. According to the LM model, self-concentration is a result of enhanced local concentration due to chain connectivity. Hence, for a homogeneous small molecule/polymer mixture, a ϕ_{self} of 0 is expected for the small molecule. In a paper published in 2004,[20] Savin et al. reported two-step glass transitions in PS solutions with bis(2-ethylhexyl) phthalate (DOP), di-*n*-butyl phthalate (DBP), and dimethyl phthalate (DMP). For all three solvents, an apparent self-concentration effect was indicated from the data. For DMP in PS, a ϕ_{self} value as large as 0.6 can be calculated from the reported DMP glass transition temperatures. This result is consistent with Figure 6 and the idea that a ϕ_{self} value for a small molecule determined from only equilibrium data would be much closer to 0. Indeed, Ediger et al. have reported exactly this result, albeit for somewhat larger "solvent" molecules.[26]

Finally, we note that the discussion of Figure 6 could be posed in terms of the inadequacy of the Fox equation (eq 3). An alternate method that correctly accounts for nonequilibrium effects could in principle be used to convert effective volume fractions into component T_g values. In such a scheme, self-concentration values extracted from equilibrium measurements at high temperature might agree with those extracted from DSC measurements on the low-T_g component.

Could the Two Glass Transitions Be a Result of Phase Separation? The existence of two glass transitions has long been accepted as an indication of phase separation. Thus, it is natural to ask whether the two glass transitions observed here for PI/P4tBS are a result of phase separation. Our experimental results support homogeneous mixing as described in this section.

The DSC traces show no dependence on molecular weight as the molecular weight of the PI component increases from 3 to 10 kg/mol. Higher molecular weight blends always have a higher tendency toward phase separation. If the higher molecular weight blend or both blends were phase separated, it would be completely unexpected for these two blends to show similar DSC traces and the same component T_g values. To further check this point, we carried out additional DSC measurements on blends with an even higher molecular weight PI (PI-17k). For PI-17k/P4tBS-32k blends containing 25% and 75% PI, the observed component glass transitions occurred at similar temperatures as the lower molecular

weight PI blends reported in Figures 2–4. This indicates that this higher molecular weight blend is miscible at these compositions. For PI-17k/P4tBS-32k blends with intermediate compositions, however, the observed glass transitions differed from the results in Figures 2–4 and in each case were shifted toward the T_g values of the pure homopolymers. We interpret this to indicate that the highest molecular weight blend is phase separated at these intermediate compositions.

We observe that the component T_gs shift systematically with blend composition. As described above, neutron scattering measurements[14] on PI/P4tBS blends demonstrate a LCST phase behavior. In our measurements, the highest temperature that each sample experienced was 423 K, just prior to the DSC measurements. If phase separation occurs at this temperature, the blends would likely separate into phases of the same composition regardless of their initial compositions. If this were the case, then the location of the observed glass transition temperatures would remain similar for all compositions. This is indeed what we observed for PI-17k blends with intermediate compositions. However, as it is clearly seen in Figures 2–4, the observed glass transitions shift systematically with blend composition for the lower molecular weight blends.

The DSC traces show no dependence on the thermal history of the samples. The properties of a phase-separated blend often show a dependence on their thermal history. To test this, we took the 40% PI-10k/P4tBS-32k blend (the blend with two clear DSC T_gs that is most likely to phase separate) and did a conventional DSC measurement but with a cooling rate of 1 K/min before the second heating cycle instead of the 40 K/min used in the standard measurements. Consistent with our assumption of miscibility, the DSC trace acquired after slow cooling was similar to those reported in Figure 3. In a further test, this same sample was held at the highest temperature (423 K) for 30 min as opposed to 3 min in the standard measurements, followed by rapid cooling and a heating scan. The DSC trace thus acquired was also in good agreement with those from the standard measurements.

The above observations support the full miscibility of PI-3k/P4tBS-32k and PI-10k/P4tBS-32k blends in the temperature range of interest and the partial miscibility of the PI-17k/P4tBS-32k system.

Summary

In this study, we carried out DSC and TMDSC measurements on PI/P4tBS blends with varying PI molecular weights. Self-concentration values for each component were extracted. Results were compared to other PI blends as well as the PEO/PMMA blend. There are three major findings in this work.

Two calorimetric glass transitions were clearly observed for both PI-3k/P4tBS-32k and PI-10k/P4tBS-32k blends with intermediate compositions. The results experimentally support the existence of distinct effective glass transitions for each component in miscible polymer blends as predicted by the Lodge–McLeish model. As emphasized by other recent work,[9,10] the presence of a single broad glass transition is not a universal feature of miscible polymer blends.

Both TMDSC and conventional DSC measurements yielded similar results in this study. The effective glass transition temperatures for the components in both PI-3k/P4tBS-32k and PI-10k/P4tBS-32k blends can be described by the LM model with the same self-concentration values. For these miscible blends, the dynamics responsible for the two glass transitions are independent of molecular weight.

An exceptionally large ϕ_{self} value for the low-T_g component (PI) is extracted from the DSC and TMDSC measurements on

these PI/P4tBS blends. Similarly large ϕ_{self} values were deduced for PEO in its blends by Gaikwad et al.[10] The large ϕ_{self} value for PI is consistent with the existence of a confinement or vitrification effect in blends with large dynamic asymmetry, as previously reported for PEO/PMMA[25] and PVME/PS[28] blends. At temperatures below the effective T_g of the slow component, the blend is not in equilibrium, and this has a strong influence on the dynamics of the fast component. For DSC and TMDSC measurements, this rationalizes the unexpectedly large ϕ_{self} value determined for PI in P4tBS blends. A general picture of component dynamics in miscible polymer blends across a wide temperature range is summarized in Figure 6.

Supporting Information Available: Temperature-modulated DSC thermograms of PI-10k/P4tBS-32k blends (Figure S1); detailed descriptions of our attempts to fit the DSC data to the self-consistent LM model[34] (Figure S2 and text). This material is available free of charge via the Internet at http://pubs.acs.org.

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