

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 (~ 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 transitions² 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) model⁴ 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_g s in two additional miscible blend systems [poly(*o*-chlorostyrene)/poly(vinyl methyl ether) (PoCIS/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_g s 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 PoCIS/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.^{11,12,21,27} 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 stated⁹ 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 ~ 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

84 Unlike PEO blends, the low T_g component in this system (PI) has
85 been well studied in other blends with various methods⁵ and shows
86 typical behavior. In addition, since this is the only system studied
87 to date that has a ΔT_g comparable with the PEO/PMMA system,
88 the comparison of these two systems is of interest.

89 For miscible PI/P4tBS blends, we resolve two distinct calorimetric
90 glass transitions by both conventional and temperature-modulated
91 DSC for blends of intermediate composition (25%–
92 50% PI). Good agreement was found between the component T_g
93 values measured by the two methods. Fitting of the measured T_g
94 values to the Lodge–McLeish model gives a ϕ_{self} of around 0.63
95 for the PI component in this blend and 0.03 for the P4tBS
96 component. Similar to the PEO/PMMA system, our results imply
97 enhanced dynamics of the fast component in a miscible polymer
98 blend at temperatures below the glass transition of the slow
99 component. This observation is consistent with the presence of a
100 nonequilibrium or confinement effect,^{17,25,28} which results in
101 enhanced dynamics of the fast component below the T_g of the
102 slow component.

103 Experimental Section

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

108 **Miscibility.** Small-angle neutron scattering (SANS) measure-
109 ments were previously used by Yurekli et al. to study the
110 miscibility of PI/P4tBS blends.¹⁴ Measurements were done on
111 blends of deuterated polybutadiene with PI, P4tBS, and PI/
112 P4tBS blends. From these scattering experiments, negative χ
113 values were extracted for PI/P4tBS (molecular weight 40 and
114 33 kDa, respectively) blends with various compositions up to
115 443 K. The increase of χ with increased temperature indicates
116 LCST behavior for this system. Small-angle X-ray scattering
117 (SAXS) experiments were done on a 8/2 PI/P4tBS (molecular
118 weight 20 and 70 kDa, respectively) blend between 298 and
119 343 K in a study by Watanabe et al. A homogeneous state was
120 indicated from the data for this blend in the temperature range
121 studied.¹⁵ Miscibility of blends containing lower molecular
122 weight PIs is further supported by our DSC data, which will
123 be discussed in detail below.

124 **Blend Preparation.** A total of about 20 mg of PI/P4tBS with
125 the desired composition was dissolved in tetrahydrofuran to
126 form a 1% solution. The solution was stirred for at least 10 h,
127 after which solvent was evaporated in an N_2 environment
128 until the polymer concentration was around 50%. This concen-
129 trated solution was transferred into a DSC pan and further
130 evaporated in a vacuum oven at room temperature for at least
131 10 h. The oven temperature was then raised by 30 K and held for
132 3 h before the weight of the sample was determined. This
133 procedure was repeated until oven temperature was 383 K
134 (~50 K above the average T_g of a 25% PI/P4tBS blend). The
135 sample was then held in the vacuum oven at 383 K and weighed
136 every hour until the weight was constant to ensure complete
137 evaporation of solvent. To confirm evaporation of the solvent
138 by this procedure, we took one 25% PI/P4tBS sample (the blend
139 with the highest average T_g) after the DSC measurement and set
140 it in the vacuum oven at 433 K (13 K above the T_g of pure P4t-
141 BS) for 5 h. DSC measurements were then repeated on this
142 sample, with the results in excellent agreement with the previous
143 measurement.

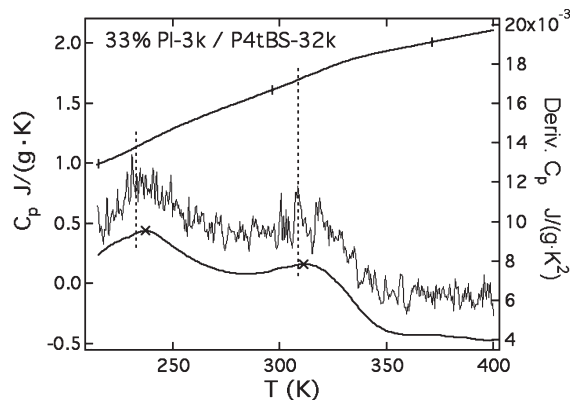


Figure 1. From top to bottom, the heat capacity C_p , the temperature
derivative of C_p , and the temperature derivative of C_p smoothed over
30 K, for a representative blend showing two DSC glass transitions.
Vertical shifts were applied. Vertical bars on the C_p curve indicate
the visually selected 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.

144 **DSC Measurements.** For each blend sample, both conven-
145 tional DSC and temperature-modulated DSC (TMDSC) were
146 performed. The conventional DSC has a higher scanning rate,
147 which offers a higher sensitivity and shorter acquisition time.
148 TMDSC offers the advantage of selectively observing the rever-
149 sible glass transition signals; in addition, its lower scanning rate
150 results in better temperature resolution.

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

172 Results

173 Figure 1 shows representative conventional DSC traces for a
174 33% PI-3k/P4tBS-32k blend. The top curve is the total heat
175 capacity C_p . The middle curve is the temperature derivative of C_p .
176 We investigated multiple methods for determining the two
177 component T_g values. As one method, we visually picked the
178 two transition ranges as indicated by the vertical bars on the C_p
179 curve. Given these transition ranges, the glass transition tem-
180 peratures indicated by the dotted vertical lines were determined
181 by the TA Universal Analysis program as the inflection points of
182 the C_p curve. Although this is a standard method to determine the
183 glass transition temperature, the procedure involves an arbitrary
184 selection of the transition ranges for each DSC trace. To simplify
185 the procedure as well as eliminate human bias, a more objective
186 procedure of defining the glass transitions is proposed here.

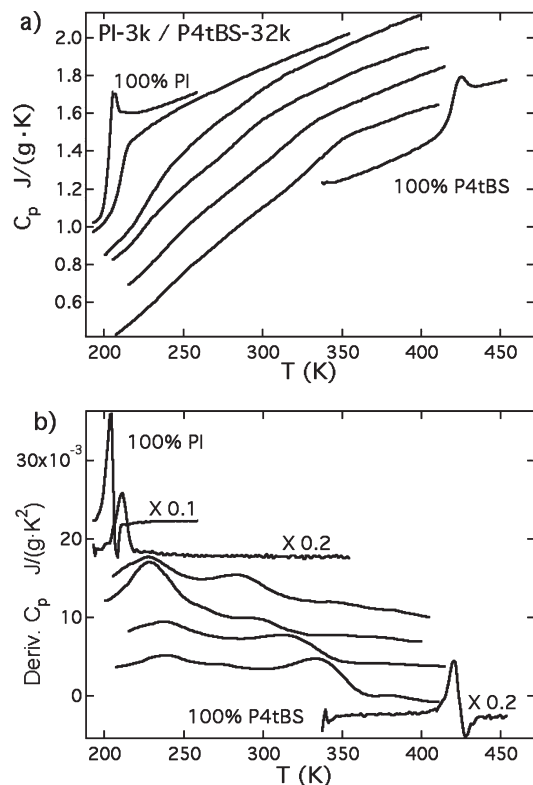


Figure 2. Conventional DSC thermograms of PI-3k/P4tBS-32k blends. From pure PI to pure P4tBS, curves represent blends with PI compositions of 75%, 50%, 40%, 33%, and 25%, respectively. (a) C_p curves. (b) Temperature derivative of C_p curves. For three curves, the data have been scaled by the factors indicated. In all other cases, the data have been smoothed over 30 K. Vertical shifts have been used for clarity.

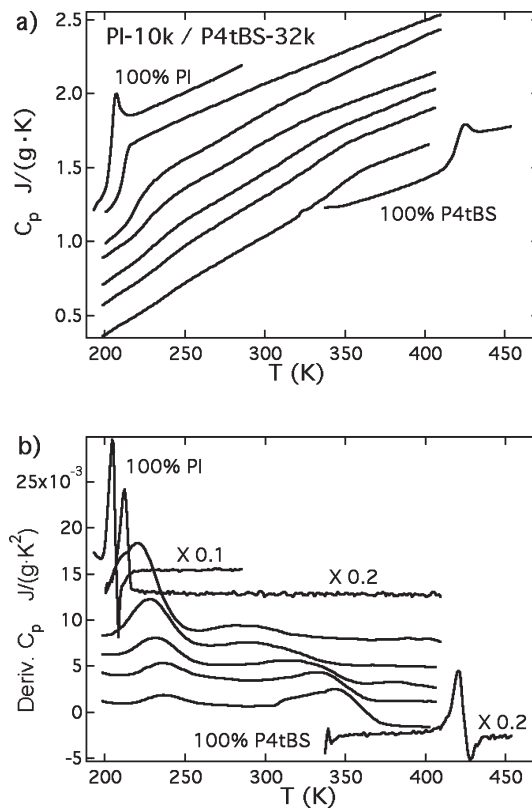


Figure 3. Conventional DSC thermograms of PI-10k/P4tBS-32k blends. From pure PI to pure P4tBS, curves represent blends with PI compositions of 75%, 50%, 40%, 33%, 29%, and 25%, respectively. (a) C_p curves. (b) Temperature derivative of C_p curves. For three curves, the data have been scaled by the factors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

187 The bottom curve in Figure 1 is the temperature derivative of
 188 C_p smoothed over 30 K. The glass transition temperatures for this
 189 blend were determined as the temperatures corresponding to the
 190 peaks of the smoothed curve (indicated by the crosses). The
 191 T_g values determined by this procedure were reasonably consistent
 192 with those determined by the previous method (differing by
 193 less than 5 K). Thus, this smoothing procedure was adopted to
 194 determine the component T_g values for the rest of the study.
 195

196 Figure 2 shows the conventional DSC thermograms of PI-3k,
 197 P4tBS-32k, and their blends with compositions ranging from 25%
 198 to 75% PI. For blends with PI compositions between 25% and
 199 50%, two glass transitions are clearly observed both in the original
 200 C_p curves and the smoothed derivative C_p curves. For pure PI,
 201 pure P4tBS, and 75% PI/P4tBS blends, the transitions were sharp
 202 and well-defined; thus, no smoothing was performed. In order for
 203 the data for these three compositions to be plotted with the others,
 204 their derivative C_p curves were scaled by the amount indicated in
 205 the figure. From many previous studies on segmental dynamics in
 206 miscible polymer blends, it is known that the components in these
 207 systems have distinct segmental dynamics, each biased toward the
 208 dynamics of their pure homopolymers. Thus, it is reasonable to
 209 assume that the high-temperature transition is the glass transition
 210 of the slower P4tBS component in this blend while the low-
 211 temperature transition belongs to the faster PI component. In
 212 addition, as the composition of PI increases, the glass transition
 213 of both components shift to lower temperatures, which is also consistent
 214 with the shifting trend of component segmental dynamics. We
 215 will discuss the interpretation of the two glass transitions below.
 216 Parallel experiments were carried out on PI-10K and its blends
 217 with P4tBS-32k to study the effect of molecular weight on the
 218 glass transition behavior of this blend. The corresponding data

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

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

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

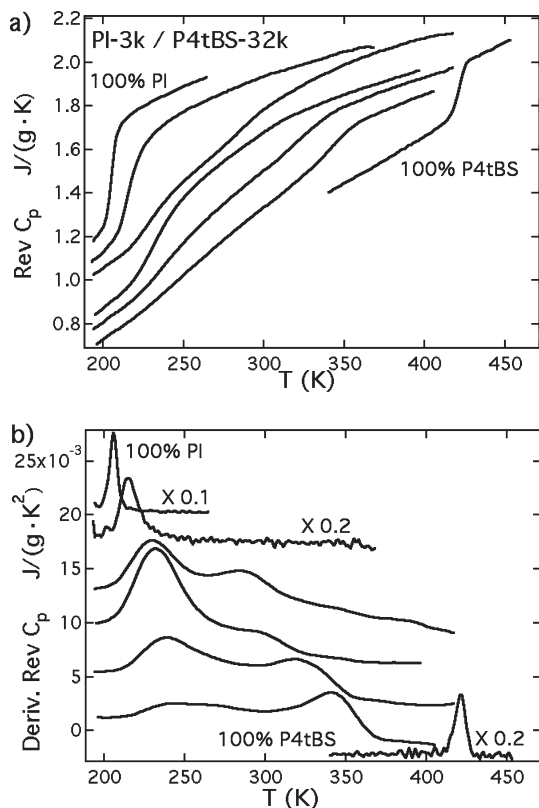


Figure 4. Temperature-modulated DSC thermograms of PI-3k/P4tBS-32k blends. From pure PI to pure P4tBS, curves represent blends with PI compositions of 75%, 50%, 40%, 33%, and 25%, respectively. (a) Reversible C_p curves. (b) Temperature derivative of reversible C_p curves. For three curves, the data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

250 25% and 50% PI-3k/P4tBS-32k blends to test the reproducibility
 251 of both the conventional DSC and TMDSC measurement. Error
 252 bars indicating the range of these values are shown in Figure 5.
 253 Except for T_g (P4tBS) in 50% PI-3k/P4tBS-32k blend measured
 254 by conventional DSC, the deviations between other replicate
 255 experiments are smaller than the size of the symbols and thus
 256 are not visible.

257 Discussion

258 **Lodge–McLeish Model.** The LM model⁴ assumes that the
 259 chemical composition of the region within one cubic Kuhn
 260 length (l_K) of a given polymer segment determines the
 261 mobility of that segment. This local concentration (ϕ_{eff}) is
 262 calculated by considering the bulk concentration (ϕ) and the
 263 self-concentration (ϕ_{self}):

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

264 LM estimate the self-concentration ϕ_{self} as

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

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

268 In this model, polymer segments of a given type (e.g., A)
 269 have an effective glass transition temperature that is different
 270 from the macroscopic blend T_g because $\phi_{\text{eff},A}$ differs from
 271 ϕ_A . In our implementation of the LM model, we have used

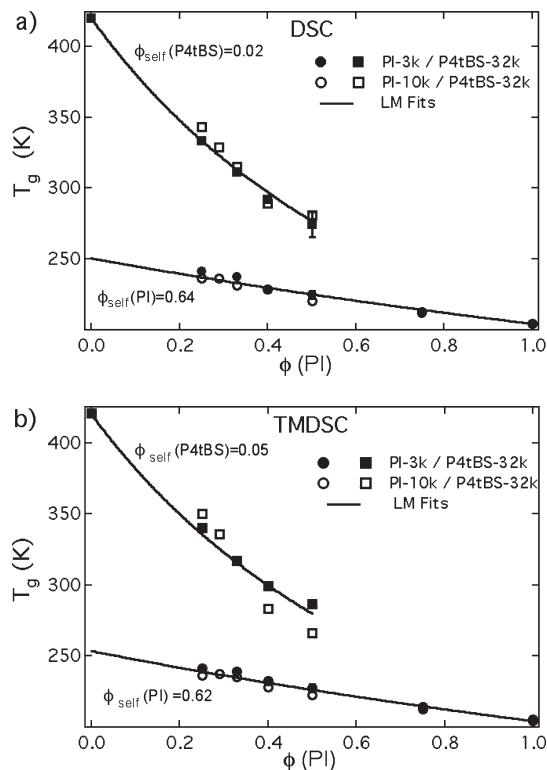


Figure 5. Component T_g values obtained from (a) conventional DSC and (b) TMDSC for PI-3k/P4tBS-32k blends and PI-10k/P4tBS-32k blends. The lines are fits of the data to the Lodge–McLeish model with the self-concentration values indicated.

the Fox equation to calculate this effective T_g :

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

We assume that $T_{g,\text{eff}}$ 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 $T_{g,\text{eff}}$ 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 determina-
 tions 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 exten-
 sively studied by NMR, dielectric relaxation, and rheology

302 measurements over a broad time, temperature, and composi-
 303 tion range.^{5,21–24} The ϕ_{self} value of 0.45 predicted⁴ by the LM
 304 model was found to give an excellent description of the
 305 dynamics of PI in this system. As another example, for low
 306 molecular weight blends of PI and polystyrene, a ϕ_{self} of 0.33
 307 was obtained for the PI component.³²

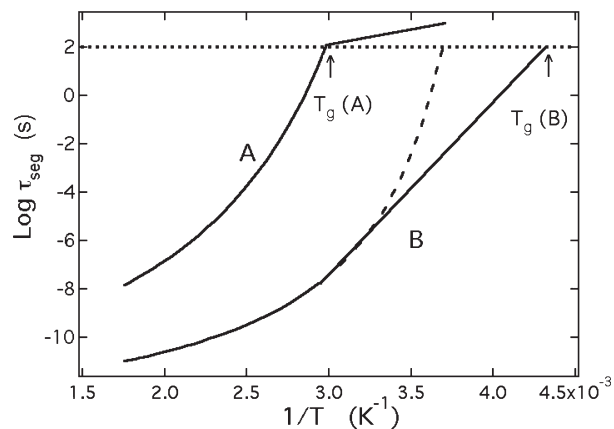
308 Only one other miscible blend component has been re-
 309 ported to have a ϕ_{self} value as large as that determined here
 310 for PI in P4tBS. Large ϕ_{self} values were determined for PEO
 311 in blends with PMMA as studied with various methods^{9,11,12}
 312 and PEO in blends with poly(vinyl acetate) (PVAc) as
 313 studied with DSC.¹⁰ This insensitivity of the dynamics of
 314 PEO upon blending indicates that the motions of PEO chains
 315 are less dependent on the cooperative motion of the blending
 316 partner and was previously attributed to the lack of side
 317 groups for PEO.¹¹ As PI contains a side group, this explana-
 318 tion cannot be used to explain the data presented here.

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

329 In 2006, Lipson and Milner modified the LM model by
 330 taking into account of a self-consistency requirement³⁴
 331 between the self-concentration values for the two compo-
 332 nents; i.e., the calculated volume fraction of the blend should
 333 be the same whether the calculation is based upon the
 334 environment of A segments or the environment of B seg-
 335 ments. Unlike the original LM model in which the effective
 336 T_g s of each component can be independently fitted by a
 337 single ϕ_{self} value, the self-consistent LM model allows only
 338 certain pairs of ϕ_{self} values. The self-consistent model³⁴ could
 339 not yield good fits to the DSC data reported (see Supporting
 340 Information for details). Thus, while recognizing the limita-
 341 tions of the original LM model, we utilize it in this work for
 342 lack of a suitable alternative. At a minimum, the original LM
 343 in conjunction with the Fox equation provides a basis for the
 344 intercomparison of results on different blend systems, as all
 345 of these results have been fitted in an equivalent manner.

346 **Nonequilibrium and Confinement.** Recent quasi-elastic neu-
 347 tron scattering measurements on PEO in a blend with PMMA
 348 provide a useful context for the experiments reported here.
 349 Genix et al.²⁵ reported that as the temperature is lowered
 350 below the T_g of PMMA, the dynamics of PEO are signifi-
 351 cantly faster (and more broadly distributed) than would be
 352 expected based upon extrapolation from high temperatures.
 353 The authors argue that the vitrified PMMA chains “confine”
 354 the mobile PEO chains and caused a qualitative change in the
 355 dynamics of PEO at low temperatures. One could pose the
 356 issue in somewhat more general terms:^{17,25,28} Why should the
 357 dynamics of the fast component continue to follow the trend
 358 established in thermodynamic equilibrium if the system has
 359 left equilibrium (and thus does not have the extrapolated
 360 volume or structure)?

361 We imagine that these ideas^{17,25,28} are applicable to all
 362 miscible blends where the interactions between segments
 363 on different chains are not too strong. Here we apply these
 364 ideas to PI in P4tBS. Figure 6 schematically illustrates the
 365 idea. At temperatures above the effective T_g of the slow
 366 component, the system is in equilibrium. In this temperature
 367 range, the component dynamics exhibit a VTF tempera-
 368 ture dependence, which can be at least qualitatively



369 **Figure 6.** Sketch of the segmental dynamics of the slow (A) and fast
 370 (B) components in a miscible A/B polymer blend. The dotted line
 371 represents a segmental relaxation time of 100 s, and effective glass
 372 transition temperatures of the components are indicated. For compo-
 373 nent B, below the effective T_g of A, the dashed curve represents the VTF
 374 extension of its high-temperature dynamics, while the thick solid line
 375 represents the enhanced dynamics that result from the vitrification of
 376 the blend.

377 predicted from their pure homopolymer dynamics and the
 378 LM model.^{5,6,29–33} At temperatures below the effective T_g
 379 of the slow component, the dynamics of the slow component
 380 exhibit a roughly Arrhenius temperature dependence. The
 381 vitrification of the slow component in the blend causes the
 382 entire system to fall out of equilibrium, and thus the dynam-
 383 ics of the fast component deviate from the LM prediction
 384 even though the temperature is above its effective T_g .

385 In Figure 6, the dynamics of the fast component are
 386 illustrated as enhanced and nearly Arrhenius below the effec-
 387 tive T_g of the slow component. As the components are in
 388 intimate contact with each other, the dynamics of the fast
 389 component are expected to change in the same direction as
 390 the dynamics of the slow component. Experimental support
 391 for the view that the fast component switches to Arrhenius
 392 behavior below the slow component T_g can be found in work
 393 on other systems in addition to the PEO/PMMA work^{17,25}
 394 mentioned above. For poly(vinylidene fluoride) (PVF) in
 395 blends with poly(methyl methacrylate), dielectric α relaxa-
 396 tion times of 10^{-9} – 10^{-1} s were measured by Sy et al.¹⁸ As the
 397 temperature is lowered, the VTF temperature dependence of
 398 τ_α transforms into a weaker Arrhenius temperature depen-
 399 dence. In Figure 6, we extend this behavior to even lower
 400 temperatures where the effective T_g of the fast component is
 401 reached.

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

411 Recently Chen et al. reported dynamic mechanical and
412 DSC measurements on PI/P4tBS blends containing 50% and
413 70% PI.¹⁹ These authors extracted effective T_g values from a
414 VTF analysis of dielectric and viscoelastic measurements at
415 high temperatures where the blend is in the equilibrium state.
416 We took the reported effective T_g values and fit them to the
417 LM model. The ϕ_{self} extracted for the P4tBS component in
418 this blend is 0.0, qualitatively consistent with the value that
419 we extracted from the DSC measurements. The ϕ_{self} value
420 extracted for the PI component in the 50% PI blend is 0.4.
421 This value is similar to that reported for the PI component in
422 blends with PVE and smaller than that extracted from our
423 DSC measurements. Since the viscoelastic and dielectric
424 measurements were carried out in the equilibrium state, this
425 difference is consistent with Figure 6. Although two glass
426 transitions were not clearly resolved in DSC, Chen et al.
427 comment that “the blends exhibit broad, almost two step
428 glass transition”. (For the blend containing 70% PI, we
429 determined a larger ϕ_{self} value from the dielectric and viscoelastic
430 measurements.¹⁹ Since the dynamics of the PI component
431 change little in the concentrated region, this extracted
432 ϕ_{self} value is associated with a relatively large error bar and
433 was thus not used in the comparison.)

434 Further evidence for the effect shown in Figure 6 can be
435 found in DSC measurements on polymer–solvent mixtures.
436 According to the LM model, self-concentration is a result of
437 enhanced local concentration due to chain connectivity.
438 Hence, for a homogeneous small molecule/polymer mixture,
439 a ϕ_{self} of 0 is expected for the small molecule. In a paper
440 published in 2003,²⁰ Savin et al. reported two-step glass
441 transitions in PS solutions with bis(2-ethylhexyl) phthalate
442 (DOP), di-*n*-butyl phthalate (DBP), and dimethyl phthalate
443 (DMP). For all three solvents, an apparent self-concentration
444 effect was indicated from the data. For DMP in PS, a
445 ϕ_{self} value as large as 0.6 can be calculated from the reported
446 DMP glass transition temperatures. This result is consistent
447 with Figure 6 and the idea that a ϕ_{self} value for a small
448 molecule determined from only equilibrium data would be
449 much closer to 0. Indeed, Ediger et al. have reported exactly
450 this result, albeit for somewhat larger “solvent” molecules.²⁶

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

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

466 The DSC traces show no dependence on molecular weight
467 as the molecular weight of the PI component increases from 3
468 to 10 kg/mol. Higher molecular weight blends always have a
469 higher tendency toward phase separation. If the higher
470 molecular weight blend or both blends were phase separated,
471 it would be completely unexpected for these two blends to
472 show similar DSC traces and the same component T_g values.
473 To further check this point, we carried out additional DSC
474 measurements on blends with an even higher molecular
475 weight PI (PI-17k). For PI-17k/P4tBS-32k blends containing
476 25% and 75% PI, the observed component glass transitions
477 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_g s shift systematically
with blend composition. As described above, neutron scattering
measurements¹⁴ 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_g s 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 tempera-
ture 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 inter-
mediate 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 tem-
peratures 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 independ-
ent 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

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543 these PI/P4tBS blends. Similarly large ϕ_{self} values were deduced
 544 for PEO in its blends by Gaikwad et al.¹⁰ The large ϕ_{self} value for
 545 PI is consistent with the existence of a confinement or vitrification
 546 effect in blends with large dynamic asymmetry, as previously
 547 reported for PEO/PMMA²⁵ and PVME/PS²⁸ blends. At temper-
 548 atures below the effective T_g of the slow component, the blend is
 549 not in equilibrium, and this has a strong influence on the
 550 dynamics of the fast component. For DSC and TMDSC mea-
 551 surements, this rationalizes the unexpectedly large ϕ_{self} value
 552 determined for PI in P4tBS blends. A general picture of compo-
 553 nent dynamics in miscible polymer blends across a wide temper-
 554 ature range is summarized in Figure 6.

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 556 the National Science Foundation (DMR-0355470).

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

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