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Glass Transition Temperature of a Component near Infinite Dilution in Binary Polymer Blends: Determination via Fluorescence Spectroscopy

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Supporting Information

INTRODUCTION

In 1982, Lau et al.[1] reported the first "double glass transitions" in miscible blends by differential scanning calorimetry (DSC). Using ^{2}H NMR, in 1994 Chung et al.[2,3] reported two segmental relaxations in a miscible blend. They proposed a picture based on self-concentration (SC), where chain connectivity results in a component experiencing a local environment richer in its repeat units than the overall blend. Thus, the component glass transition temperature (T_g) is expected to be intermediate to the blend T_g (reported as a single value) and pure component T_g. In 2000, Lodge and McLeish[4] further developed the SC concept, indicating that the effective T_g ($T_{g,eff}$) of component i is equivalent to the blend T_g at a different effective concentration (ϕ^i_{eff}), which in turn is related to the component SC (ϕ^i_{self}):

$$\phi^i_{eff} = \phi^i_{self} + (1 - \phi^i_{self})\phi^i_{bulk} \tag{1}$$

$$T_{g,\,eff}(\phi^i_{bulk}) = T_g(\phi^i_{eff}) \tag{2}$$

Concentration fluctuations (CF) within a local distribution of volumes have also been proposed as the cause of distinct segmental relaxations.[5,6] Related miscible blend dynamics studies are reviewed in ref 7.

Many studies have reported component segmental mobilities in miscible blends and rationalized their findings in terms of SC,[8−25] CF,[26,27] or a combination.[28−32] Such studies typically cannot probe component dynamics or T_g with precision when the component is present at less than ~10−15%. This is important given that in the Lodge−McLeish (LM) model[4] $\phi^i_{eff} = \phi^i_{self}$ in the limit of infinitely dilute blends.[33] In this limit, concentration fluctuations go to zero,[33] and the SC of a single chain surrounded by a second component can be determined. Lutz et al.[13,34] used ^{2}H NMR to study components as dilute as 0.5 wt %; their approach requires measuring dynamics far above T_g (> T_g + 50 K) and extrapolating the Vogel−Fulcher−Tamman equation to estimate T_g. No direct measurement of a near-infinite-dilution component T_g has been reported.

Here, we employ fluorescence to yield the first direct probe of T_g of a component near infinite dilution in a polymer blend. (By direct we mean monitored in the temperature range where the component changes from rubbery to glassy.) Intrinsic polystyrene (PS) fluorescence has long been used to study chain conformations in dilute solution[35−37] and the kinetics of phase separation in blends[38,39] via an excimer to monomer intensity ratio. We have shown[40,41] that intrinsic fluorescence of styrene−X block copolymer present near infinite dilution in polyX can be used to determine critical micelle concentrations, below which copolymers exist as unimers in polyX. With block copolymers as unimers, the styrene block fluorescence is essentially all monomer, with excimer fluorescence appearing at concentrations where micelles are present. Here we use the temperature (T) dependence of fluorescence to measure T_g in various blends. This includes near-infinite-dilution blends where PS is dissolved in the matrix regardless of whether the blend is miscible or immiscible when both components are nondilute. We show that ϕ_{self} for PS near infinite dilution is matrix dependent, in disagreement with a tenet of the LM model.[4]

EXPERIMENTAL SECTION

Binary blends of PS with poly(*tert*-butyl acrylate) (PtBA), poly(methyl methacrylate) (PMMA), and poly(*n*-butyl methacrylate) (PnBMA) and blends of PMMA with poly(ethylene oxide) and styrene/acrylonitrile copolymer (SAN) with poly(ethyl methacrylate) PEMA were prepared by codissolution in toluene or chloroform and solvent casting onto quartz slides. Blends were near infinite dilution (≤ 0.1 wt % PS or 1.0 wt % SAN) and nondilute (≥ 7.0 wt % PS, SAN, or PMMA). 1-Pyrenylmethyl methacrylate (MPy) was copolymerized with styrene or methyl methacrylate to yield MPy-labeled PS or PMMA with trace (< 0.7 mol %) label. Separate blends were made using labeled and unlabled PS to compare methods for determining T_g. To obtain T_g in unlabeled blends, the T dependence of PS or SAN integrated fluorescence intensity was monitored. For MPy-labeled PS or PMMA blends, T_g was determined via the T dependence of the intensity ratio of the third to first vibronic band peaks of the pyrene label.[42,43] Details are given in the Supporting Information.

RESULTS AND DISCUSSION

Figure 1a compares intrinsic PS fluorescence from 0.1 and 7.0 wt % PS in PtBA blends. In the 7.0 wt % blend, both monomer fluorescence (intensity peak at ~285 nm)[44] and excimer fluorescence (intensity peak at ~328 nm)[44] are evident, with excimer

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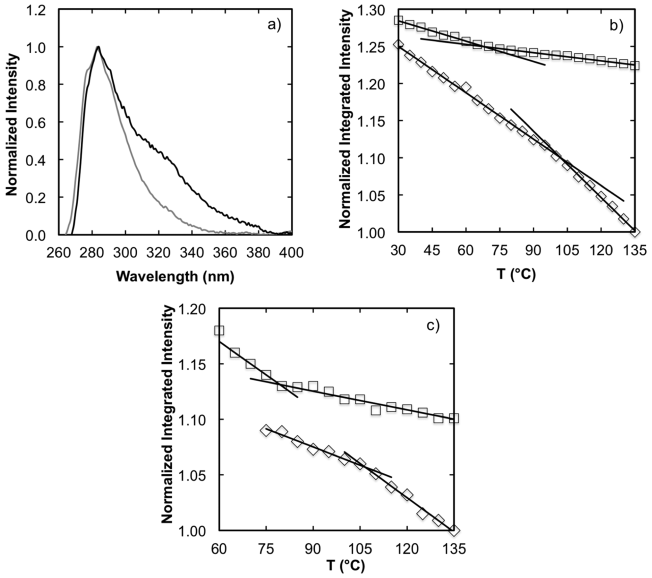

Figure 1. (a) Intrinsic PS fluorescence for a 0.1 wt % (gray curve) and 7.0 wt % (black curve) PS in PtBA-37 blend (see Table 1 for description of PtBA-37). Spectra were measured at 60 °C and normalized to 1.0 at the monomer fluorescence peak. (b) Normalized, integrated intrinsic PS fluorescence for a 0.1 wt % (squares) and 7.0 wt % (diamonds) PS in PtBA-37 blends. (c) Normalized, integrated PS fluorescence for 1.0 wt % SAN/PEMA blend (squares) and 100 wt % SAN (diamonds). All sample data in (b) and (c) have been normalized to 1.00 at 135 °C. The 0.1 and 1.0 wt % samples have been shifted vertically for clarity. [In the dilute cases of (b) and (c), the slope becomes steeper below T_g, a result in agreement with ref 44 and anticipated for spectra with essentially pure monomer fluorescence rather than a combination of monomer and excimer fluorescence.[47]]

Table 1. Polymer T_g Values and Molecular Weights

polymers	T_g (°C)	M_n (kg/mol)
PS	101^a	50^b
MPy-labeled PS	103^a	800^c
PMMA	125^a	56^b
MPy-labeled PMMA	123^a	276^c
PtBA-75	42^a	75^c
PtBA-37	45^a	37^c
PnBMA	27^a	55^c
SAN^d	108^a	81^c
PEMA	75^a	390^c
PEO	-78^e	0.3^b

[a] Determined from DSC T_g onset values. [b] Reported by supplier. [c] Determined by GPC using PS standards and appropriate Mark–Houwink parameters in THF. [d] 75% styrene, 25% acrylonitrile. [e] Reported in ref 16.

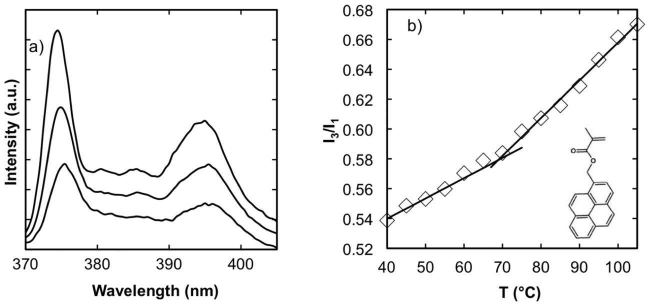

Figure 2. (a) Extrinsic fluorescence of MPy-labeled PS at 105 °C (lowest curve), 75 °C (middle curve), and 45 °C (highest curve). The first and third vibronic band peaks appear at ∼377 and ∼387 nm, respectively.[42] (b) Intensity ratio I_3/I_1 as a function of temperature for a 0.1 wt % MPy-labeled PS in PtBA-75 blend (see Table 2 for description of PtBA-75) along with the MPy monomer structure.

fluorescence appearing as a shoulder. (Monomer fluorescence is emission from a single excited-state phenyl ring; excimer fluorescence is emission from an excited-state dimer of two phenyl rings arranged in a parallel, overlapping configuration with a ∼0.3 nm separation.[45]) In the 0.1 wt % blend, fluorescence is monomer, with no evident excimer fluorescence. Previous studies employing intrinsic fluorescence to monitor micelle concentrations in styrene/X block copolymer blends with polyX homopolymer[40,41] showed that the absence of excimer fluorescence is a signature of block copolymer dissolved as unimers in homopolymer. Thus, the 0.1 wt % blend fluorescence is characteristic of individual PS chains dissolved in PtBA. In contrast, the combined monomer and excimer fluorescence in the nondilute blend is characteristic of a system in which PS is phase separated,[38,39] in agreement with the immiscibility of this blend outside the near-infinite-dilution limit.

Figure 1b shows the T dependence of the normalized integrated fluorescence intensities of 0.1 and 7.0 wt % PS-in-PtBA blends, with different T dependences in the rubbery and glassy states and intersections yielding T_g.[44,46] The stronger (weaker) T dependence in the rubbery state for the nondilute (near-infinite-dilution) blend agrees with studies of styrene-containing random copolymers showing that this behavior is observed in systems exhibiting both excimer and monomer fluorescence (only or nearly only monomer fluorescence).[44,47] The PS T_gs are 102 and 67 °C in the nondilute and near-infinite-dilution blends, respectively. The nondilute PS T_g agrees with the neat PS T_g (101 °C, see Table 1), indicating that PS phase separates into (nearly) pure domains in that blend. The near-infinite-dilution blend PS T_g is closer to the T_g of neat PtBA (45 °C; see Table 1) than of neat PS.

Figure 1c shows related data for the miscible SAN/PEMA blend, with intrinsic fluorescence from the SAN styrene units. Neat SAN exhibits T_g = 108 °C while 1.0 wt % SAN in PEMA exhibits T_g = 80 °C, close to neat PEMA T_g (75 °C; see Table 1). A 20 wt % SAN in PEMA blend yields a SAN T_g of 86 °C, which is closer to that of neat PEMA than that of neat SAN[48] and is consistent with the miscibility of this blend at all compositions.[49]

Figure 2a shows the T dependence of extrinsic fluorescence for MPy-labeled PS in PtBA. We recently showed that MPy-labeled PS yields T_g via the T dependence of the third vibronic band to the first vibronic band intensity ratio, I_3/I_1.[42,43] (For some pyrene-type dyes, I_3/I_1 also exhibits sensitivity to local polarity.[50,51]) Figure 2b shows the T dependence of I_3/I_1 for 0.1 wt % MPy-labeled PS in PtBA, yielding a PS T_g via the intersection of the rubbery- and glassy-state T dependences. The 68 °C T_g is within error identical to that obtained via intrinsic fluorescence.

Similar characterization has been done for PS/PMMA and PS/PnBMA blends, with T_gs for all blends summarized in Table 2. For 0.01 wt % PS (0.1 wt % PS) blends with PMMA (PnBMA), fluorescence is monomer, and the PS T_g is much closer to that of the matrix than of neat PS. At 7.0 and 20 wt % PS, the PS T_gs are

Table 2. PS, SAN, and PMMA T_g Values in Various Blends and Self-Concentrations Determined from Fitting eqs 1 and 2 from the Lodge−McLeish Model[4] with eq 3 to Experimental Data

blends	wt % PS, SAN, PMMA	T_g (°C) ± 1	ϕ_{self}^{PS}, ϕ_{self}^{SAN}
PS/PtBA-37	0.1	67	0.43 ± 0.02
	7.0	102	
MPy-labeled PS/PtBA-75	0.1	68	0.47 ± 0.02
PS/PMMA	0.01	119	0.23 ± 0.05
	7.0	99	
MPy-labeled PS/PMMA	0.1	118	0.29 ± 0.06
PS/PnBMA	0.1	38	0.18 ± 0.02
	20	98	
SAN/PEMA	1.0	80	0.16 ± 0.03
	20	86	0.20 ± 0.03
	100	108	
MPy-labeled PMMA/PEO	75	87	
	90	100	

very close to that of neat PS, characteristic of well-phase-separated PS, which is expected based on the immiscibility of these blends away from the near-infinite-dilution limit. The T_g determined from a dilute MPy-labeled PS blend in PMMA agrees within error with the T_g from intrinsic fluorescence.

We have also done T_g measurements with extrinsic pyrene-labeled PMMA. Blends of MPy-labeled PMMA at 10 and 25 wt % in 300 g/mol PEO were made to study component T_gs in fully miscible blends. The T_g values determined via extrinsic fluorescence, 100 and 87 °C in a 90 and 75 wt % PMMA blends with PEO, respectively, agree with T_g values from DSC in studies by Lodge et al.[16] for the same blend system.

Along with component T_gs obtained via fluorescence, Table 2 lists ϕ_{self} values obtained using eqs 1 and 2 along with the Fox−Flory equation to determine the overall blend T_g:

$$T_g = (\phi_A/T_{g,A} + \phi_B/T_{g,B})^{-1} \quad (3)$$

In PnBMA blends containing 0.1 wt % PS, a ϕ_{self} of 0.18 is determined, which is close to the SAN ϕ_{self} values of 0.16 and 0.20 for 1.0 and 20 wt % blends in PEMA. The ϕ_{self} for PS calculated using the LM model[4] is 0.27 based on the PS Kuhn length, and our results indicate that the PS in PnBMA blend experiences dynamics more influenced by the matrix than anticipated. In contrast, with 0.1 wt % PS in PtBA, $\phi_{self} = 0.45 \pm 0.04$ independent of whether T_g is determined by intrinsic or extrinsic fluorescence. (A dependence of ϕ_{self} on blend partner for a given component has been previously reported and discussed.[9,13]) The ϕ_{self} value for PS in PtBA is more than twice that in the PnBMA dilute blend and may possibly be related to the higher Flory−Huggins interaction parameter in PS/PtBA blends.[52] This would result in a greater self-concentration of styrene repeat units when single PS chains are dissolved in PtBA (in contrast to the theta-condition experienced by PS in the neat melt state.[53]) Further study is warranted.

The intrinsic fluorescence method may be extended to a styrene/X block copolymer dissolved as unimer in polyX, yielding examination of how covalent bonding of an X block affects the T_g and ϕ_{self} of the styrene block in a miscible blend. The extrinsic fluorescence method may be extended in multiple ways, from using MPy-label to examine ϕ_{self} of repeat units in polymers lacking intrinsically fluorescent moieties in blends with other polymer (e.g., our PMMA/PEO blends), to using label types placing the pyrenyl dye farther away from the chain backbone (by copolymerization with 1-pyrenylbutyl methacrylate[54]) to probe local concentrations of apparent ϕ_{self} as a function of distance from the backbone. Fluorescence methods are exquisitely designed for such investigations in the limit of infinite dilution. Studies are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional experimental information on polymer synthesis, sample preparation, and fluorescence measurement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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(47) As noted in ref 44, the normalized integrated intensity of PS fluorescence has a steeper temperature dependence below T_g when the spectrum is essentially pure monomer fluorescence. This behavior was observed in a styrene/methyl methacrylate random copolymer with 22 mol % styrene content and is in contrast to systems exhibiting a combination of monomer and excimer fluorescence where a less steep temperature dependence is observed below T_g (styrene/methyl methacrylate random copolymers with 39 and 58 mol % styrene content). The T_g determined by fluorescence for bulk random copolymer films agreed with DSC T_g determinations over the entire range of styrene contents. The difference in the steepness of the slopes is related to the manner in which excimer fluorescence quenches monomer fluorescence and its temperature dependences in glassy and rubbery states. The cause of the stronger T dependence in the glassy state for monomer-only fluorescence spectra is yet to be determined.

(48) In the case of SAN/PEMA blends, an attempt was made to compare SAN T_g values measured by fluorescence with T_g measured by DSC. For a 20 wt % SAN in PEMA blend, DSC measurements revealed a broad transition between the component T_gs, and determination of a SAN effective T_g was not possible.

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