# Self-Concentrations and Effective Glass Transition Temperatures in Polymer Blends

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ABSTRACT: In a miscible polymer blend the local environment of a monomer of type A will, on average, be rich in A compared to the bulk composition, $\phi$, and similarly for B; this is a direct consequence of chain connectivity. As a result, the local dynamics of the two chains may exhibit different dependences on temperature and overall composition. By assigning a length scale (or volume) to particular dynamic mode, the relevant "self-concentration" $\phi_s$ can be estimated. For example, we associate the Kuhn length of the chain, $l_K$, with the monomeric friction factor, $\zeta$, and thus the composition and temperature dependences of $\zeta$ should be influenced by $\phi_s$ calculated for a volume $V \sim l_K^3$. An effective local composition, $\phi_{eff}$, can then be calculated from $\phi_s$ and $\phi$. As lower $T_g$ polymers are generally more flexible, the associated $\phi_s$ is larger, and the local dynamics in the mixture may be quite similar to the pure material. The higher $T_g$ component, on the other hand, may have a smaller $\phi_s$, and thus its dynamics in the mixture would be more representative of the average blend composition. An effective glass transition temperature for each component, $T_g^{eff}$, can be estimated from the composition-dependent bulk average $T_g$ as $T_g(\phi_{eff})$. This analysis provides a direct estimate of the difference in the apparent $T_g$'s for the two components in miscible blends, in reasonable agreement with those reported in the literature for four different systems. Furthermore, this approach can reconcile other features of miscible blend dynamics, including the asymmetric broadening of the calorimetric $T_g$, the differing effects of blending on the segmental relaxation times of the two components, and the failure of time−temperature superposition.

## Introduction

The dynamic properties of polymer mixtures are a topic of great current interest. One overall goal is to be able to predict the viscoelastic response of a given blend solely on the basis of knowledge of the composition and the component molecular weights and architectures. This problem may be conveniently divided into two parts. The first involves adapting mechanisms of molecular motion that describe single-component systems to mixtures. For example, in the framework of reptation this may be accomplished through the concept of "double reptation"; the main issues are the mixing rule for the entanglement spacing or tube diameter and the treatment of constraint release effects for components with greatly differing longest relaxation times. The second part of the problem is the temperature ($T$) and composition (volume fraction, $\phi$) dependence of the time scale for relaxation of the fastest "Rouse" mode, i.e., the behavior of the monomeric friction factor, $\zeta_i(\phi,T)$, for each component $i$. This paper is directed at the latter topic.

Experimental information about $\zeta_i(\phi,T)$ has been obtained for a variety of miscible blends, including polystyrene (PS)/poly(phenylene oxide) (PPO),[1−6] PS/poly(tetramethyl carbonate) (PTMC),[7,8] PS/poly(vinyl methyl ether) (PVME),[9−11] polyisoprene (PI)/poly(vinyl ethylene) (PVE),[12−19] and poly(methyl methacrylate) (PMMA)/poly(styrene-*s*-acrylonitrile) (PSAN).[20,21] Immiscible systems such as PS/PI[22,23] and PS/PMMA[24] have also begun to receive attention. The data as a whole indicate a great deal of complexity, as exemplified by the following three observations: (i) it is not yet possible to predict the "tracer" friction factors $\zeta_A(\phi=0,T)$ and $\zeta_B(\phi=1,T)$ in a binary system based on knowledge of the "self" friction factors $\zeta_A(\phi=1,T)$ and $\zeta_B(\phi=0,T)$; (ii) knowledge of the two tracer and two self-friction factors is not sufficient to enable prediction of the mixing rules for arbitrary $\phi$; (iii) direct measurements of segmental dynamics are not easily related to $\zeta$ as determined from chain dynamics.

The behavior of $\zeta(\phi,T)$ is most directly extracted from chain diffusivities. In this case the measurement averages extensively in both time and space, which makes the persistent complexity of the results even more remarkable. Other techniques, such as NMR, dielectric relaxation, or optical probe dynamics, which can gain insight on shorter time and length scales, have also been directed at polymer mixtures. Of particular interest are indications of local heterogeneity, such as different temperature dependences for the dynamics of different components, differential degrees of broadening of the two component relaxation time distributions upon cooling, suggestions of one component exhibiting two (or more) distinct relaxation time distributions in one blend, and inference that the two components experience different glass transition temperatures ($T_g$) within a miscible blend.

Recent discussions of local heterogeneity have been couched in terms of "concentration fluctuations", i.e., local regions spontaneously rich in either A or B segments. To apply this concept, it is necessary to

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consider the length scale or volume of the relevant local region, as the probability of a fluctuation of a given amplitude should decrease as the associated volume increases. At least four different approaches have been described. Chin et al. applied 2D solid-state NMR to local motions in PS/PPO and found that the data for each component could be interpreted in terms of two or even three relaxation modes.[5,6] These were considered to arise from monomers of one type having differing numbers of nearest neighbors of the other. Thus, the relevant length scale is taken to be the monomer size ($\leq$1 nm). Fischer and co-workers[25,26] took the length scale from the Donth model of the glass transition,[27,28] in which the volume of a cooperatively rearranging region (as originally proposed by Adam and Gibbs[29]) is predicted to diverge with $(T - T_0)^{-2}$, where $T_0$ is the Vogel temperature.[30] The probability of a given concentration fluctuation within that volume is related to the static structure factor (in the appropriate $q$ range), and then that volume is assigned a $T_g$ given by the macroscopic $T_g(\phi)$. This approach is apparently very successful in capturing the broadening of dielectric relaxation with both $\phi$ and $T$.[26] However, the fitting parameters indicate cooperative length scales in excess of 10 nm near $T_g$, whereas the original Donth model values (and other measures of cooperative length scales near $T_g$[31−33]) are clustered around 2 nm. Chung et al. used 2D deuteron exchange NMR to examine PI/PVE blends near $T_g$.[13,14] They found not only broadening of each component's dynamics but also a different effective $T_g$ for each component ($T_g$ being defined by a fixed value of a given relaxation time). They incorporated the cooperative volume concept following Fischer but also considered the self-concentration, i.e., the idea that a local region around an A segment is always somewhat enriched in A segments due to chain connectivity. They concluded, however, that this approach could not describe both the broadening and the separation of the component dynamics concurrently. They therefore proposed that some accounting for inherent dynamic differences between the components must also be incorporated in a successful model. More recently, Kumar et al.[34] extended the cooperative volume concept by requiring that each volume correspond to the $T-T_0$ that applies to that local concentration; a region rich in the lower $T_g$ component will have a larger $T-T_0$ and therefore a smaller volume. This approach can, under some circumstances, predict that one component can exist in two distinctly different environments. However, as with the Fischer approach, cooperative length scales on the order of 10 nm or more are apparently necessary to fit the data.

In this paper we propose an alternative way to consider part of this problem. First, we suggest that for the monomeric friction factor, or any local probe that senses similar dynamics, the relevant length scale is the Kuhn length of the chain. We therefore consider the possibility that the existence of dynamic heterogeneity might be understood without recourse to a diverging length scale or cooperative volume. Second, we emphasize the self-concentration as providing a significant and inevitable bias to the mean concentration experienced by each component. These two concepts combine to provide simple explanations for several experimental phenomena, including the broadening of the calorimetric (dsc) $T_g$ in polymer blends relative to the pure components; the fact that a 75:25 blend will generally have a broader (narrower) dsc transition when the majority component has the higher (lower) $T_g$; the fact that the local dynamics of the lower $T_g$ component in the blend will be closer to those in its pure melt, whereas those of the higher $T_g$ component will be closer to a blend average; the relative magnitudes of the self- and tracer monomeric friction factors in some blends; the possibility that the lower $T_g$ component in the blend can exhibit two distinct relaxation times; the failure of time−temperature superposition in some blends with a large difference in component $T_g$'s. We next describe the model itself and then provide some comparisons with experiment. The paper concludes with a discussion of the strengths and weaknesses of this approach.

## Model

The model is based on two postulates. The first concerns the length scale relevant to the monomeric friction factor. Specifically, we suggest that this length scale is determined primarily by the Kuhn length, $l_K$, which is a well-defined property of any polymer chain:

$$l_K = C_\infty l \tag{1}$$

where $C_\infty$ is the characteristic ratio and $l$ is the length of the average backbone bond. Thus, the conformational relaxation of a Kuhn length is taken to correspond to the fastest Rouse mode of the chain, and this relaxation is influenced by the concentration of monomers within a volume $V \sim l_K^3$. This volume will presumably be only weakly dependent on temperature, in contrast to the cooperative volume or cooperatively rearranging region invoked in various other treatments, which is assumed to diverge at the Vogel temperature. Inoue, Osaki, and co-workers have shown via a combination of rheological and rheo-optical measurements that the "rubbery" relaxation spectrum terminates with a fastest Rouse mode that, for many polymers, corresponds well to $l_K$.[35] This intuitively reasonable result is thus consistent with our first postulate.

The second postulate is that within the volume $V$ centered on a monomer of type A there will be, on average, an excess of A monomers, relative to the bulk average concentration. This is nothing more than a local manifestation of the well-known correlation hole effect and is simply due to chain connectivity; the appearance of an A monomer of a long chain at a particular site guarantees a certain number of other A monomers in the vicinity. Consequently, we assume that in a binary blend a typical A monomer (i.e., not near a chain end) experiences *on average* an effective local concentration $\phi_{\text{eff}}$ given by

$$\phi_{\text{eff}} = \phi_s + (1 - \phi_s)\phi \tag{2}$$

where $\phi_s$ is termed the "self-concentration". We determine $\phi_s$ from the volume actually occupied by a Kuhn length's worth of monomers, divided by $V$:

$$\phi_s = \frac{C_\infty M_0}{k \rho N_{\text{av}} V} \tag{3}$$

where $M_0$ is the repeat unit molar mass, $k$ is the number of backbone bonds per repeat unit, and $\rho$ is the density. This definition could easily be modified by a multiplicative constant of order unity. For example, a spherical or cylindrical volume could be chosen instead of a cube. However, this would only effect the numerical results

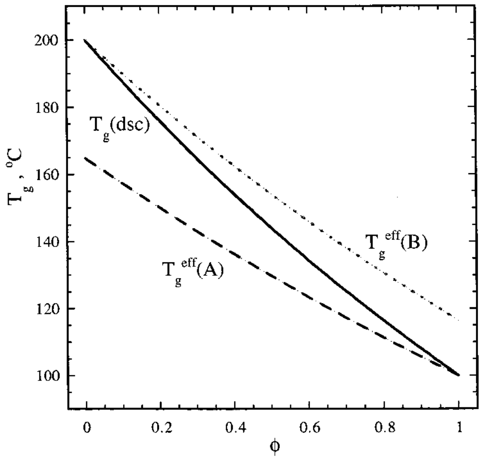

**Figure 1.** Calculated effective component glass transition temperatures as a function of composition, for a model blend in which component A has a $T_g$ of 100 °C and component B a $T_g$ of 200 °C, and the calorimetric $T_g$ follows the Fox equation.

and not the more important qualitative effects; we therefore retain the definition in eq 3 because of its simplicity. The main consequence is that, in any binary polymer blend, A monomers experience local environments that tend to be rich in A and B monomers local environments rich in B. This calculation of $\phi_{\mathrm{eff}}$ assumes an athermal mixture, in other words that there is no energetic preference for A segments to be next to A segments rather than B segments. Therefore, the local variations in concentration are due entirely to the statistics of random packing of connected objects. It is conceivable that near a phase boundary large-amplitude concentration fluctuations will come into play, but we set that possibility aside for now. The interesting dynamic effects that have been reported in most miscible blends apparently bear no obvious correlation with the sign or magnitude of the interaction parameter $\chi$, so this is a reasonable simplification. Furthermore, based on Boltzmann weights, the small $\chi$ typically found in miscible blends (e.g., $|\chi| < 0.01$) should not bias the local packing significantly. This calculation of $\phi_s$ is similar in spirit to that of Chung et al.[13] but differs in the important selection of the relevant length scale. We now consider the implications for the glass transition temperatures.

Suppose that for a binary blend the calorimetric $T_g(\phi)$ has been determined, say as the inflection point in the dsc trace. We propose that the monomeric friction factor of component A actually senses a different *effective* $T_g$, determined by

$$T_g^{\mathrm{eff}}(\phi) = T_g(\phi)|_{\phi=\phi_{\mathrm{eff}}} \tag{4}$$

and the corresponding expression for B. In other words, the effective $T_g$ for A is determined from the macroscopic $T_g(\phi)$ but evaluated at $\phi_{\mathrm{eff}}$ rather than $\phi$. Taking A as the lower $T_g$ ("faster") component, the chain dynamics of A will sense a lower $T_g$ and the dynamics of B a higher $T_g$, than the bulk average. (Note that we use the term $T_g$ rather loosely here; we take the effective $T_g$ as a *reference temperature* for dynamics, not necessarily as the temperature of a macroscopic departure from equilibrium. Furthermore, we are not equating the Kuhn length with the fundamental length scale for the glass transition.) The effect of eq 4 is plotted in Figure 1 for a hypothetical blend in which $T_{g,A} = 100$ °C, $T_{g,B} = 200$ °C, and $T_g(\phi)$ follows the Fox equation

$$\frac{1}{T_g(\phi)} = \frac{\phi}{T_{g,A}} + \frac{1-\phi}{T_{g,B}} \tag{5}$$

The self-concentrations of components A and B are taken as 0.3 and 0.2, respectively. These are plausible values and within the range for real systems (vide infra). Component A is assigned a larger value because lower $T_g$ materials tend to be more flexible, and the smaller the Kuhn length, the larger $\phi_s$ will be. The results are quite striking; for example, in the 50:50 mixture the effective $T_g$'s differ by 25 °C.

Estimates of $\phi_s$ based on eq 3 are listed in Table 1 for eight polymer structures that have been featured in studies of miscible blends, along with estimates for the necessary input data. As noted above, the prefactor in eq 3 is open to discussion, and thus one should emphasize the relative values of $\phi_s$. Overall, the correlation between high $T_g$ and low $\phi_s$ is maintained; poly(1,4-isoprene) has the lowest $T_g$ (−60 °C) and the largest $\phi_s$ (0.45), and PPO and TMPC have the highest $T_g$'s (220 and 200 °C) and the lowest $\phi_s$ (0.13 and 0.08). However, PS, PMMA, PVE, and PVME have $T_g$'s varying over 150 °C but apparently have little variation in $\phi_s$, so this correlation does not hold in detail. (It is perhaps worth noting that it may be important to use the Kuhn length or characteristic ratio, and not the statistical segment length, $b$, in estimating the relevant length scale; for example, PS and PI differ by a factor of 2 in $l_K$ but by only 15% or so in $b$.)

The simple arguments presented above have a series of interesting consequences. For example, assuming that the calorimetric $T_g$ reflects the differing local environments in some kind of volume-fraction-weighted way, this analysis implies that (i) dsc traces in blends should be broader than in the pure components and that (ii) a 25:75 blend should have a broader transition than a 75:25 blend of the same components (the lower $T_g$ component listed first). This asymmetry arises primarily from the fact that $|\partial T_g/\partial\phi|$ is greater for B-rich blends. Both of these predictions are qualitatively consistent with experiments on PS/TMPC, PMMA/PSAN, PI/PVE, and PS/PVME (vide infra). This broadening is simulated in Figure 2, for the same hypothetical blend as in Figure 1. The dsc traces were approximated by hyperbolic tangent functions, with 10 °C half-widths for the pure components. The mixture traces were volume-fraction-weighted sums of the component traces centered on their respective effective $T_g$'s, with half-widths taken as one-half of the difference between the two effective $T_g$'s. Furthermore, (iii) the difference between the effective and calorimetric $T_g$'s should be greatest for a tracer polymer in another melt, an effect that can only be explored when the experimental technique has sufficient sensitivity to monitor the dynamics of a tracer. Then, (iv) the larger the self-concentration, the more the average dynamics of that component in the mixture will resemble the dynamics in the pure component. Because of the approximate correlation between $T_g$ and flexibility, it will often be the case that the faster component should show dynamics more reminiscent of its melt, whereas the slower component will be closer to the average dynamics of the blend. The dielectric relaxation in PI/PVE clearly exhibits this phenomenon.[18,19] This observation has been emphasized as evidence for the cooperative volume approach,[18] but here it is a natural

**Table 1. Estimates of Relevant Parameters for Various Polymers**[a]

| | $\langle R^2\rangle/M$ (Å$^2$ mol/g) | $T$ (°C) | $\rho$ (g/mL) | $M_0$ (g/mol) | $l_K$ (Å) | $C_\infty$ | $\phi_s$ | $T_g$ (°C) |
|---|---|---|---|---|---|---|---|---|
| PI | 0.596 | 25 | 0.913 | 68 | 6.8 | 4.5 | 0.45 | −60 |
| PVME | 0.58 | 30 | 1.05 | 58 | 10.9 | 7.1 | 0.25 | −25 |
| PVE | 0.664 | 25 | 0.889 | 54 | 11.6 | 7.6 | 0.25 | 0 |
| PS | 0.434 | 140 | 0.969 | 104 | 14.7 | 9.5 | 0.27 | 105 |
| PSAN[b] | | 140 | 1.01 | 92 | 15 | 9.6 | 0.22 | 110 |
| PMMA | 0.425 | 140 | 1.13 | 100 | 13.8 | 9.0 | 0.25 | 125 |
| PTMC | 1[c] | 200 | 1.14 | 127 | 18.1 | 7.0 | 0.08 | 200 |
| PPO | 0.741 | 220 | 1.00 | 120 | 16.5 | 3.0 | 0.13 | 220 |

[a] Values obtained from Fetters et al.[38,39] unless otherwise indicated. [b] Data estimated for a statistical copolymer containing 23% acrylonitrile.[40] [c] Approximate coil dimensions assumed to be comparable to bisphenol A polycarbonate.

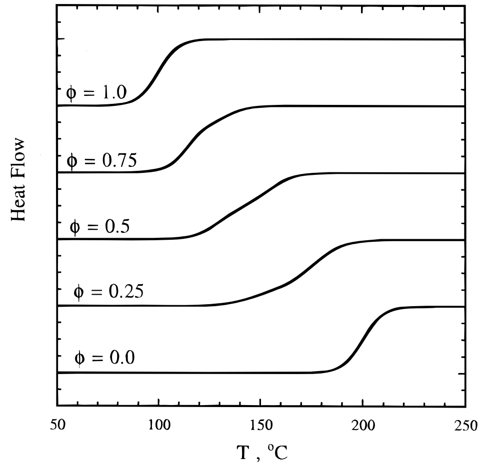

**Figure 2.** Simulation of dsc curves for the blends of Figure 1, calculated as described in the text.

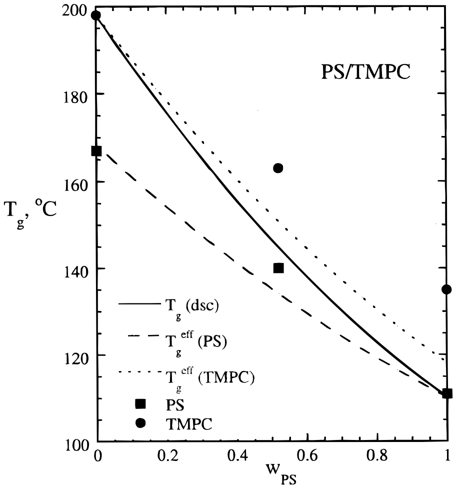

**Figure 3.** Effective glass transition temperatures for PS/TMPC blends; data from Kim et al.[8]

consequence of the arguments presented above. Finally, (v) the failure of time−temperature superposition in some blends may be easily understood, if the effective component $T_g$'s are sufficiently far apart; this, in turn, requires that the pure component $T_g$'s be well separated.

## Comparison with Experiments

We consider first the PS/TMPC system examined by Kim et al.[8] They measured tracer diffusivities via forward recoil spectrometry and extracted $\zeta$ for each component over the full range of concentration and as a function of $T$ for some compositions. Using this $T$ dependence, they were able to extrapolate the self-friction factors $\zeta_{PS}(\phi=1)$ and $\zeta_{TMPC}(\phi=0)$ to their respective dsc $T_g$'s. The two values were virtually identical (ca. 22.5 dyn s/cm). This suggested defining a component $T_g$ in the mixture as that $T$ for which $\zeta = 22.5$. The results are shown in Figure 3, for the two tracer values ($\zeta_{PS}(\phi=0)$ and $\zeta_{TMPC}(\phi=1)$) and for both components in a 50:50 blend. A smooth trace representing the calorimetric $T_g$ is also shown. The main experimental observation is that $T_g^{eff}$ for PS in TMPC-containing blends lies consistently below $T_g$(dsc), whereas that for TMPC is consistently above. The corresponding predictions of our model are also included in the figure. The qualitative features are captured very well, and in particular, we predict that a tracer PS chain in TMPC should experience a $T_g^{eff}$ of 166 °C, in quantitative agreement with the experimentally inferred value. The calculation apparently underestimates the effect of self-concentration for TMPC, which may be related to the approximate parameter values in Table 1. However, it is the qualitative features of the results that we seek to capture with this simple model, and so we do not pursue the comparison in more detail. Kim et al. also noted that the $T$ dependences of $\zeta$ for the two components and for different $\phi$ became essentially the same, once referenced to the component $T_g^{eff}$.[8] Thus, in this system it is possible to construct a simple reference state such that, at a constant temperature increment above the reference temperature, the friction factors of both components are identical and essentially independent of $\phi$. This is a remarkably simple result, which raises the possibility that much of the unusual phenomenology of $\zeta(\phi,T)$ can be rationalized when appropriate reference temperatures are found. However, it is not presently possible to pursue this issue with systems such as PS/PVME[9] and PS/PPO,[4] because the temperature dependence of $\zeta(\phi)$ is apparently not yet available.

Kim et al. also examined PMMA/SAN blends by similar techniques.[20] The results are shown in Figure 4a, where in this case $T_g^{eff}$ was defined by $\zeta_{SAN} = 1000$ and $\zeta_{PMMA} = 83$ dyn s/cm; thus, the two components have differing self-friction factors at their respective $T_g$'s. (However, a change in the value of $T_g$ by less than 5 °C would be more than sufficient to make these values equal.) The data do not extend to the tracer friction factors, but nevertheless the trends are similar to the PS/TMPC system and in qualitative agreement with our predictions shown in Figure 4a. Once again the calculation underestimates the effect for the higher $T_g$ material. However, it should be noted that the $T$ axis is greatly expanded; the experimental points only lie a few degrees off the corresponding curves. The dsc traces for the same blends reported by Kim et al. are reproduced in Figure 4b.[20] They reveal clearly the larger broadening in the transition for the blend with weight fraction $w = 0.2$ than for $w = 0.8$, as anticipated in Figure 4a and in good qualitative agreement with Figure 2.

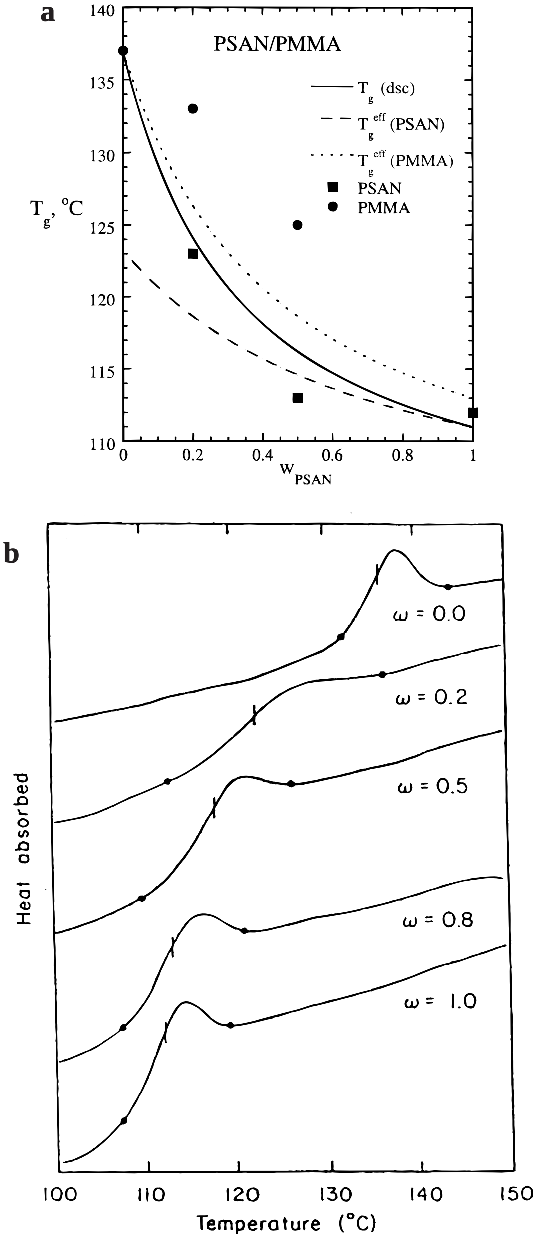

**Figure 4.** (a) Effective glass transition temperatures and (b) dsc traces for PSAN/PMMA blends; data from Kim et al.[20]

Chung et al. examined PI/PVE blends by NMR relaxation and inferred component effective $T_g$'s by selecting a particular value of the segmental relaxation time.[14] Their results and our predictions are shown in Figure 5a. In this case the agreement is excellent for the higher $T_g$ component, PVE, but the effect is overestimated for PI. This is a direct result of the large self-concentration value for PI (Table 1). The dsc traces are also reproduced in Figure 5b and are again in good qualitative agreement with Figure 2. Finally, Cendoya et al. examined the dielectric relaxation of PVME/PS blends, and by equating $T_g$ with the temperature at which the PVME dielectric relaxation time was 1 s, they extracted a $T_g^{\text{eff}}$ for PVME as a function of composition.[10] The results are shown in Figure 6, along with the corresponding predictions. In this instance the agreement is nearly quantitative. It should be noted that for this system the dsc $T_g$ is based on the earlier work of Yang et al.,[36] which leads to the slight mismatch in $T_g$ for 100% PVME in the figure. Thus, in summary, for four different systems this simple model anticipates the relative broadening of the dsc transitions and provides a semiquantitative rationale for the existence and values of the effective component $T_g$'s.

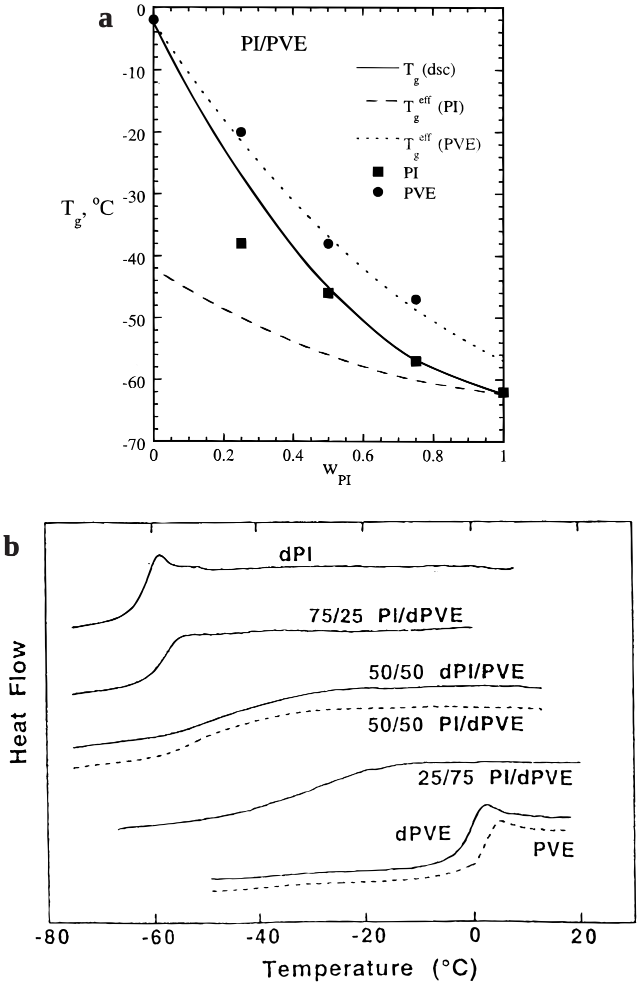

**Figure 5.** (a) Effective glass transition temperatures and (b) dsc traces for PI/PVME blends; data from Chung et al.[13]

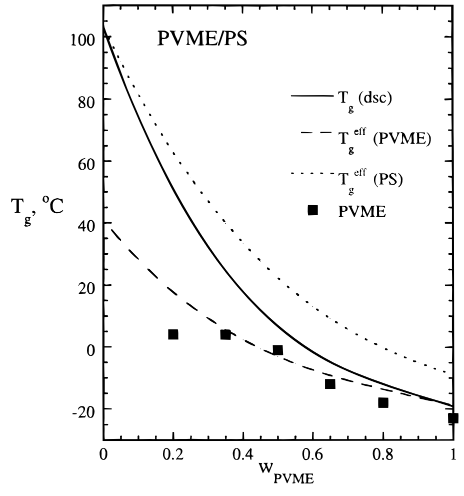

**Figure 6.** Effective glass transition temperatures for PVME/PS blends; data from Cendoya et al.[10]

## Discussion

The model we have proposed rests on two concepts: the self-concentration and the Kuhn length as the relevant length scale for the monomeric friction factor.

The comparison with experiment shows that these two concepts may be sufficient to explain various features of dynamics in miscible blends and particularly the observation of distinct component effective $T_g$'s, or reference temperatures, in a mixture. The apparent success of this approach is largely attributable to the incorporation of the self-concentration; the appropriateness of the Kuhn length as the associated length scale has not really been tested critically. Still, it is apparent that a diverging length scale is not required to reconcile those features of the data that have been emphasized here; by the same token, a diverging length scale is not precluded. It should be noted that Ediger, for example, has discussed how density/entropy fluctuations could account for increasingly heterogeneous dynamics near $T_g$, with a temperature-independent length scale.[37]

The basic model could certainly be refined. For example, the prefactor relating the self-concentration to a volume proportional to the Kuhn length cubed could be polymer-specific; one might employ experimentally determined component effective $T_g$'s to fit this parameter. One might also employ a decaying function of distance, rather than abrupt cutoff at the Kuhn length, to estimate the self-concentration. On a more fundamental level, the relevant quantity is more likely the *dynamic* Kuhn length, which is conceptually distinct from the equilibrium Kuhn length employed here. As temperature is lowered toward $T_g$, the barriers to local rearrangements will exert a stronger influence and imbue the associated self-concentration with an additional temperature dependence which could become very strong as $T_g$ is approached. It is also important to recognize that different experimental probes for dynamics in a given system will be influenced by the concentrations over differing length scales. For example, in some systems dielectric relaxation apparently senses relaxation on a significantly shorter length scale than does the monomeric friction factor extracted from rheology or diffusion.[11] It will therefore tend to reflect larger effects of local concentration differences than the chain dynamics. The approach introduced here should be directly extendable to other experimentally accessible quantities, providing that the relevant length scale can be estimated.

The analysis emphasizes the *average* composition experienced by a segment and not the distribution of compositions or the distribution of relaxation times. Nevertheless, some important qualitative conclusions may be drawn about these distributions. The more flexible component will have the larger self-concentration because the associated volume is smaller. The concentration fluctuations within this volume will be relatively large, implying a broader distribution of relaxation times. However, the less flexible component will likely be the higher $T_g$ component, and therefore $|\partial T_g/\partial\phi|$ will be larger in regions rich in that component; this will also play an important role in the breadth of the relaxation time distribution. The observation of two relaxation time distributions for the faster component in some systems has been advanced as evidence for the concentration fluctuation/diverging length scale model.[34] The model presented here does not exclude this phenomenon, however. For a flexible polymer such that $\phi_s$ approaches 50%, or for a segmental mode that is operative on a shorter length scale than the Kuhn length, it is easy to see that the remaining volume may frequently be taken up by only one other chain. Thus, there would be two typical environments, one almost pure A and the other almost 50:50 A and B. For systems where A and B have vastly different $T_g$'s, this could lead directly to a bimodal distribution of relaxation times for A.

Our approach assigns an average concentration within a volume centered on a given segment. Thus, within any volume segments on different chains may be relaxing at different rates, and any segment is contributing simultaneously to the properties of many different volumes. In this sense, these volumes do not "tile" space. This should be contrasted with treatments in which space is divided into volume elements, each with a particular concentration and $T_g$. In such cases the segments within a volume are assumed to relax cooperatively, for example as in the model of Adam and Gibbs,[29] although in subsequent treatments the degree of cooperation is often not clearly defined. For example, it is not immediately clear in some cooperative volume treatments how the two components can relax at markedly different rates within a given cooperative volume.

## Summary

We emphasize the importance of the self-concentration in understanding the dynamics of polymer blends. The self-concentration accounts approximately for the fact that a monomer of type A will always experience a local average concentration that is rich in A, relative to the macroscopic composition; this is a direct consequence of chain connectivity. The self-concentration, and therefore the effective average local composition, may be estimated once the relevant volume is selected. For the particular case of the monomeric friction factor, i.e., the associated fastest bead−spring "Rouse" mode, we propose that this volume is proportional to the cube of the Kuhn length. This model is used to estimate the "effective glass transition temperature" experienced by each component in the blend. These quantities are compared with published experimental results for four miscible blends, and the agreement is generally encouraging. Furthermore, this approach (i) anticipates the asymmetric broadening of dsc traces in miscible blends, (ii) accounts for the observation that the lower $T_g$ component tends to have segmental dynamics in the blend closer to its own bulk, whereas the higher $T_g$ component senses a blend average, (iii) can rationalize the possibility of the higher $T_g$ component exhibiting two distinct segmental relaxation times, and (iv) anticipates the failure of time−temperature superposition in miscible blends with large differences in the component $T_g$'s. Consequently, this model suggests that it may be possible to understand many features of the dynamics of miscible blends without invoking a cooperative length scale that diverges at or below $T_g$.

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