

Segmental dynamics of miscible polymer blends: Comparison of the predictions of a concentration fluctuation model to experiment

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We recently proposed a concentration fluctuation model to describe the segmental dynamics of miscible polymer blends [Kumar *et al.*, J. Chem. Phys. **105**, 3777 (1996)]. This model assumes the existence of a cooperative volume, similar to that in the Adam-Gibbs picture of the glass transition, over which segments have to reorganize in a concerted fashion to facilitate stress relaxation. No molecular theory exists for the cooperative volume. Consequently, here we critically compare two alternative functional dependences for this quantity in the context of the segmental dynamics of the most extensively studied miscible polymer blend, 1,4-polyisoprene (PI) and polyvinylethylene (PVE): (a) The Donth model, which assumes the Vogel form for the temperature dependence of relaxation processes, with a relaxation time that diverges at the Vogel temperature, roughly 50 K below the glass transition, and (b) a more recent dynamic scaling model that predicts the relaxation time diverges algebraically, only about 10 K below the glass transition. We find that the dynamic scaling model provides a near-quantitative description of the segmental relaxation in PI/PVE blends. In contrast, the Donth model predicts that the relaxation time spectrum for PI, the faster relaxing component, is bimodal, in qualitative disagreement with NMR experiments and our dielectric measurements reported here. Our results therefore emphasize two findings. First, our model can describe the segmental relaxations of the components of a polymer blend in a near-quantitative manner. Second, and more fundamentally, it appears that the dynamic scaling model describes segmental dynamics of polymers near their glass transition. © 1999 American Institute of Physics. [S0021-9606(99)52137-5]

I. INTRODUCTION

The dynamics of miscible polymer blends are critical to their processing. A complication induced by the blending of polymers is that the empirical time-temperature superposition (tTS) principle,¹ which is known to be approximately valid for homopolymer systems, breaks down in some miscible polymer blends.²⁻¹⁴ This “thermorheological complexity” manifests itself in different temperature dependences of the relaxation times of each blend component.² In contrast, other miscible blends exhibit thermorheological simplicity.¹⁵⁻¹⁷ Before we can predict the viscosity and related dynamic properties it is therefore imperative to understand the rheology of model miscible blends and the critical factors controlling their thermorheological behavior.

Here we shall focus our attention on a model polymer blend which is miscible over a wide range of parameter space and whose dynamic behavior has been investigated extensively: 1,4-polyisoprene (PI) and polyvinylethylene

(PVE).⁵⁻¹⁴ Dielectric spectroscopy (DS), selectively labeled ²H-2D NMR, and linear viscoelasticity measurements corroborate the fact that this blend displays thermorheological complexity, both at the segmental level and at the chain level. In earlier work we presented a concentration fluctuation model, based on the Adam-Gibbs description of the glass transition,¹⁸ which permitted the qualitative understanding of the segmental dynamics of miscible polymer blends.^{17,19-21} Here we shall *quantitatively* compare experimental results on segmental dynamics of PI/PVE blends,^{6,7,22} disordered diblock copolymers, and blends of diblock copolymers to model predictions¹⁹ using two descriptions for dynamics near the glass transition. Thus, we shall provide a critical test of these models in the context of this well-investigated system.

We begin by examining literature DS and NMR data on the component segmental relaxations in PI/PVE blends.^{6,7,12,22,23} There are qualitative differences in the relaxation behavior as obtained from these two sources. Particularly, the NMR experiments unequivocally show that the relaxation of the PI, the faster relaxing component, is unimo-

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dal, and slowed down due to blending. In contrast, the dielectric data have been interpreted to suggest that the PI relaxation is bimodal, with one component relaxing as fast as the pure PI, while a second component relaxes with a rate that may be expected from a homogeneously mixed blend. To clarify these issues we complement these data with new DS measurements on PI/PVE blends, disordered diblock copolymers, and binary blends of diblock copolymers of several different compositions. Our DS results are consistent with the ^2H -2D NMR measurements of Kornfield and co-workers,^{6,7,12} and allow us to establish the relaxation times of the PI and PVE segments from two independent sources. We then compare these data to predictions of our concentration fluctuation model using two descriptions for the temperature and composition dependence of the cooperative volume. While Donth's model²¹ is able to qualitatively capture the experimental trends, it *cannot* give quantitative agreement. Further, it incorrectly leads to the prediction that the segmental relaxation time spectrum for the PI is bimodal. We shall then show that a dynamic scaling picture of the glass transition^{24,25} can provide an improved description of the segmental dynamics of this blend. The consequences of these results on our understanding of blend dynamics, and glass transition phenomena in general, will finally be considered.

II. EXPERIMENTAL RESULTS

A. Past work

PI and PVE have different glass transition temperatures: $T_g(\text{PI}) \approx 210$ K, $T_g(\text{PVE}) \approx 273$ K.⁶ These polymers are well known to be miscible and have a small negative Flory interaction parameter over the temperature range $200 \text{ K} < T < 280 \text{ K}$.³ The segmental dynamics of the PI/PVE blend have been studied by ^2H -2D NMR^{6,7,12} and dielectric spectroscopy^{22,23}. Kornfield and co-workers^{6,7,12} used deuterium NMR with selective deuteration to show that the two components in the blend have different segmental relaxation times than in their respective pure states. Furthermore, in each blend the relaxation times of the two polymers were different from each other. The relaxation time for the PVE was close to that expected from a homogeneous blend with averaged WLF parameters and glass transition temperatures.¹ However, the PI relaxed considerably faster. The relaxation times of both components were unimodal, and well fit by log-normal distributions.

In contrast to these NMR measurements, where the individual component dynamics can be distinguished by selective labeling, resolution of the molecular origins of observed relaxations^{22,23} in DS is difficult at best. In principle, the known dielectric strengths of the two components can be used to identify relaxations in DS, but in practice the broad overlapping spectra of the two blend components prevent clean assignments. In a typical dielectric experiment on PI/PVE blends, especially for blends rich in PI, the isothermal dielectric loss data show two distinct peaks. Colmenero and co-workers^{22,23} attributed the two relaxations to PI relaxing in a nearly pure PI environment and both PI and PVE relaxing in an environment corresponding to the mean blend com-

TABLE I. Molecular characteristics of PI/PVE diblock copolymers.^a

Composition (PI/PVE)	PI (wt%)	% Vinyl in PVE	M_w
75/25	76	94	366 000
68/32	68	97	164 000
50/50	49.5	84	316 000
25/75	25	98	242 000

^aReference 26.

position. These results, however, are in marked contrast to the NMR results of Kornfield,^{6,7,12} who shows that the relaxation of PI is *always* unimodal. It is clear that this situation has to be resolved before a more complete understanding of the segmental dynamics of these systems can be obtained. We present such results here.

B. Current work

The molecular characteristics of the diblock copolymers used in this study are discussed elsewhere²⁶ and listed in Table I. Size exclusion chromatography (SEC) shows that $M_w/M_n < 1.1$ for these anionically polymerized copolymers. Since PI and PVE homopolymers form miscible blends, the PI/PVE diblock copolymers are disordered at all temperatures studied.

Measurements of the complex dielectric function have been made with a Novocontrol BCD-S system composed of a frequency response analyzer (Solartron Schlumberger FRA 1260) and a broadband dielectric converter with an active sample cell. The latter contains six reference capacitors ranging from 25 to 1000 pF. Measurements were made in the frequency range from 10^{-2} to 10^6 Hz using a combination of three capacitors in the sample cell. The resolution in $\tan \delta$ is estimated as 2×10^{-4} between 10^{-1} and 10^5 Hz. The cell consists of two 20 mm gold-plated stainless steel plates separated by 100 μm maintained by small Teflon spacers. Care was taken to ensure that the samples uniformly filled the volume between the electrodes. Temperature was controlled between 213 and 413 K with an accuracy of ± 0.1 K.

Typical dielectric data for three diblock copolymers at comparable temperatures are shown in Fig. 1. The dielectric loss data were converted to a distribution of segmental relaxation times via Eq. (1) using a modified version of CONTIN, resulting in the inset to Fig. 1:

$$\varepsilon''(\omega) = \int_{-\infty}^{\infty} F(\ln \tau) \frac{\omega \tau}{1 + (\omega \tau)^2} d \ln \tau. \quad (1)$$

In the 75% PI and 68% PI copolymers there are clearly two relaxation processes. In the 68% PI copolymer, two local maxima in ε'' are observed, with comparable heights owing to the fact that PVE has a higher dielectric strength. The very broad DS dispersion seen for the 50% PI copolymer is also consistent with two relaxation processes. Note that, in the inset, the spectrum of relaxation times span times which are outside the frequency window probed by the dielectric spectrometer. This artifact is a consequence of using the CONTIN package, and arises since we require a continuous distribution of relaxation times. The $F(\ln \tau)$ is only meaningful in the time (frequency) ranges covered by the experiment.

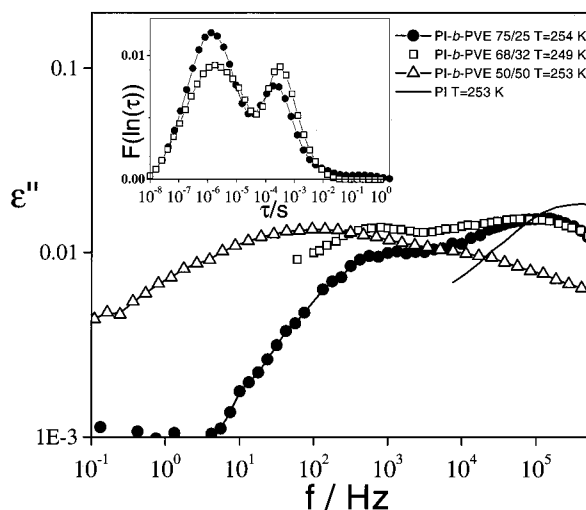


FIG. 1. Dielectric loss spectra for three PI/PVE diblock copolymers with the compositions and temperatures indicated, with the dielectric loss of pure PI shown as the solid curve. The inset shows the relaxation time distributions determined for the 75% PI and 68% PI copolymers.

In Fig. 2 we compare the dielectric spectra of a 50/50 blend of antisymmetric diblock copolymers (75% PI and 25% PI) with a 50% PI diblock copolymer (lines) at two temperatures. The two are virtually indistinguishable at high frequencies, while at low frequencies the 50% PI diblock copolymer shows a slightly broader distribution of segmental relaxations. The segmental relaxation time distributions shown in the inset to Fig. 2 indicate that two relaxation processes can be extracted from the 50% PI compositions as well. Figure 2 clearly shows that the intermolecular environment surrounding a given segment, reflected by the mean blend composition, determines the segmental relaxation time

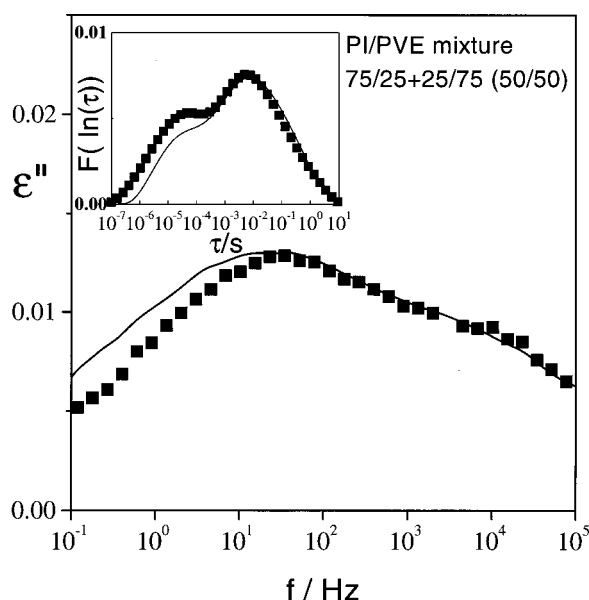


FIG. 2. Dielectric loss spectra for a 50/50 blend of two PI/PVE diblock copolymers with antisymmetric compositions (75/25 mixed with 25/75) with an overall composition of 50/50 (squares) compared to that of a single copolymer with the same overall composition (solid curve) at 248 K. The inset compares the relaxation time distributions.

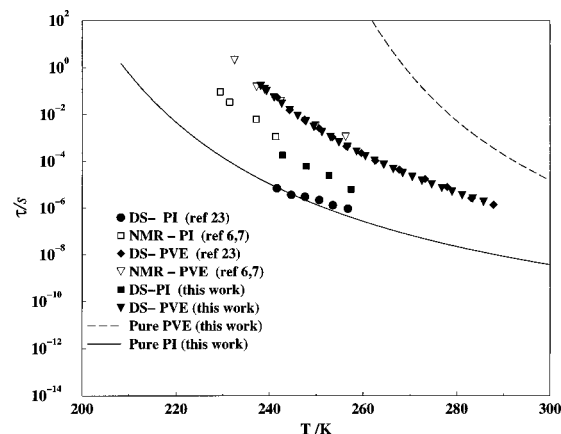


FIG. 3. Comparison of segmental relaxation times obtained from NMR and DS from various sources for 50% PI/50% PVE compositions. Also shown are segmental relaxation times for pure PI (solid curve) and pure PVE (dotted curve).

distribution. Thus, miscible blends and disordered copolymers of the same overall composition have essentially identical segmental dynamics.

The relaxation times extracted from both processes are in excellent agreement with those from NMR, as demonstrated for the 50/50 blends and diblocks in Fig. 3. Since the NMR data are unimodal for each component, this allows us to assign the fast DS relaxation to PI and the slow relaxation to PVE. Colmenero's fast relaxation does not agree with either our determination from DS nor the NMR determination for PI. This is presumably caused by the errors involved with CONTIN determination of the two relaxation processes from the single broad spectrum in ϵ'' data at 50% PI (see Fig. 1). At all temperatures, the fast process is slower than the segmental relaxation of pure PI (solid curve in Fig. 1).

III. MODEL DESCRIPTION

Here we summarize the essential features of a concentration fluctuation model that we proposed to rationalize the segmental dynamics of miscible polymer blends.¹⁹ The distribution of concentration fluctuations in an *incompressible* polymer blend is obtained from standard statistical mechanics:²⁷

$$P(\phi) \propto \exp \left[-\frac{(\phi - \bar{\phi})^2}{2\langle(\Delta\phi)^2\rangle} \right], \quad (2)$$

where $\bar{\phi}$ is the mean blend composition, and $\langle(\Delta\phi)^2\rangle$ is the mean-squared value of the concentration fluctuation,

$$\langle(\Delta\phi)^2\rangle = \frac{b^3 S(q)}{V}. \quad (3)$$

$S(q)$ is the static structure factor²⁸ corresponding to the size scale over which the fluctuation is sampled, b is the monomer size (Kuhn length), and V is the volume of the fluctuation. In the context of a dynamic experiment, we have postulated that V corresponds to the volume of a "cooperatively rearranging region" associated with each local concentration fluctuation.^{18,19} Thus, V is a function of the local composition

probed, and it would only be expected to be independent of ϕ in the special case where the two components in the blend relaxed identically.

Thus, the only important unknown in our model is the temperature and composition dependence of the “cooperative volume,” V , in Eq. (3). In the literature there are two different approaches for describing the dependence of V on system parameters. Perhaps the most commonly accepted form is the one postulated by Donth,²¹ which is based on the Adam-Gibbs formalism for the glass transition,¹⁸

$$\frac{V}{b^3} = d^3 \left(\frac{T - T_\infty}{T_\infty} \right)^{-2}, \quad (4)$$

where d is a material specific constant, and T_∞ is the Vogel temperature where the viscosity diverges. Associated with this approach is also the temperature and composition dependence of the relaxation times of each species, described through the WLF equation,¹ with the blend glass transition temperature, T_g , as the reference temperature with relaxation time τ_g ,

$$\log \frac{\tau}{\tau_g} = \frac{-c_1(T - T_g)}{T - T_g + c_2}, \quad (5)$$

where c_1 and $c_2 \equiv T_g - T_\infty$ are WLF constants. We determined c_1 and c_2 for the two pure components, and then used a *linear mixing rule* to calculate c_1 and c_2 of both components at any intermediate composition. The composition dependence of the cooperative volumes and relaxation times enter through d and T_g , with the latter simply determined by the Fox equation. In contrast, the pure component d values were used as fitting parameters, with a simple linear composition dependence of d for all blend compositions.

Dynamic scaling provides a second approach to describe relaxation in the vicinity of the glass transition.^{24,25} In this model the relaxation time scales as ξ^z , where $\xi \equiv V^{1/3}$ is the length scale of cooperative motion,

$$\frac{V}{b^3} = \left(\frac{\xi}{b} \right)^3 = B \left(\frac{T - T_c}{T_c} \right)^{-3\nu}. \quad (6)$$

Thus, the relaxation time scales as,

$$\tau = A \left(\frac{T - T_c}{T_c} \right)^{-\nu z}, \quad (7)$$

where T_c is the “critical” temperature for this dynamic transition. We will show below that the composition dependence of T_c can be described by the Fox equation, and *single, composition-independent* values of A_{PI} , A_{PVE} , and B allow description of all blend data at different compositions.

A few salient features of the model are stressed here, and the interested reader is referred to Ref. 19 for more information. These approaches yield a $P(\phi)$ as observed by a dynamic probe. For a system where V does not vary with composition, the distribution function $P(\phi)$ will be unimodal and centered at the blend composition. For blends with strong dynamic asymmetry (large disparity in component glass transitions ΔT_g) the $P(\phi)$ can be bimodal, with one peak always centered at the mean composition, and a second peak at the pure low- T_g component. The $P(\phi)$ can then be

TABLE II. Donth model parameters for PI and PVE.

Component	T_g (K)	C_1	C_2 (K)
PI	210	11.2	35
PVE	273	9.2	23

converted to a spectrum of relaxation times, i.e., $F(\ln \tau)$ by using the appropriate mapping between τ and ϕ . A final issue is the role of chain connectivity as stressed earlier by Kornfield.^{6,7} Any cooperative volume centered around a segment of type i will have a certain volume fraction of segments that are connected to the same chain to which the test segment is attached. Thus the cooperative volume centered around a PI segment will not sample compositions rich in PVE, making the only allowed compositions for PI $\phi_{PI} \geq 2b/\xi$. A similar idea also holds for the PVE segments. This intramolecular cutoff controls the compositions that can be sampled by each component, and hence is one of the primary factors in causing the two blend components to have dynamic asymmetry. We can thus obtain a spectrum of relaxation times for each component, which are then compared to experiment.

IV. COMPARISON OF THEORY AND EXPERIMENT

In this section we compare model predictions with experimental data for the segmental relaxation times and their spectra^{6,7} for blends containing 25%, 50%, and 75% PI. The model parameters used for this study are listed in Table II, taken from the literature.⁶ Following our past work, we replaced $S(q)$ by $S(0)$ in Eq. (3). The random phase approximation²⁸ leads to

$$\frac{1}{S(0)} = \frac{1}{\phi_1 N_1} + \frac{1}{\phi_2 N_2} - 2\chi, \quad (8)$$

where ϕ_1 and ϕ_2 are the volume fractions of the two components in the blend, N_1 and N_2 are the chain lengths of the two components, and $\chi = 0.0074 - 3.2/T$ is the Flory-Huggins interaction parameter.²⁹ Chain lengths were fixed at the values appropriate for Kornfield’s NMR experiments ($N_{PI} = 2650$ and $N_{PVE} = 1850$) but the results did not change significantly when the chain lengths relevant for our DS data were used ($900 < N_{PI} < 4100$, and $1000 < N_{PVE} < 3400$).

A. Donth model

We begin by utilizing Donth’s model²¹ for the temperature dependence of the cooperative volume. The WLF coefficients c_1 and c_2 for each component were calculated from WLF fits to DS data on pure PI and PVE, and a linear mixing rule was used for intermediate blend compositions. The d values for each component [Eq. (4)] are considered to be fit parameters and the model predictions were compared with experimental data for blends containing 25%, 50%, and 75% PI. Figure 4 shows comparisons of the model predictions to the experimental data for a 75% PI blend using $d_{PI} = 1.75$ and $d_{PVE} = 220$ which were the best fit values in this case. Similar results were obtained for the 50% and 25% PI blends, but it is important to note that the d_{PVE} values have to

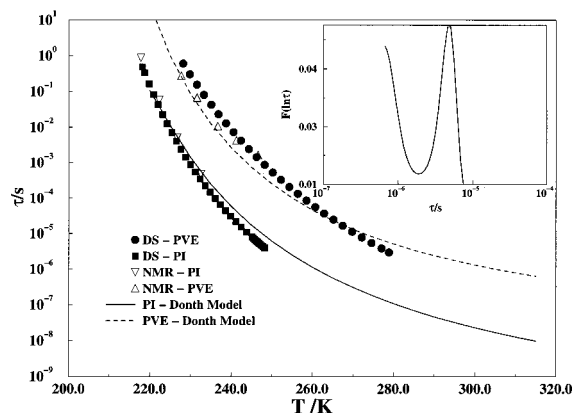


FIG. 4. Comparison of the Donth model predictions to experimental data for a 75% PI/25% PVE copolymer. The inset shows the bimodal character of the Donth model prediction for the distribution of segmental relaxations of PI in a 75% PI/25% PVE blend at 300 K.

be varied dramatically with composition: $d_{PVE}=65$ at $\phi_{PI}=0.50$ and $d_{PVE}=35$ at $\phi_{PI}=0.25$, while the d_{PI} values remain unchanged. The dependence of d_{PVE} on blend composition makes us question the utility of the Donth model. Although the model predictions seem to describe the experimental observations (see Fig. 4), these fits suffer from one major problem. We find that the relaxation time spectrum for the PI is bimodal, with one peak centered at the average blend value and another one at pure PI (see inset to Fig. 4). This result is in dramatic disagreement with experimental data, which unequivocally show that the PI relaxation time spectrum is unimodal. Of course, one can obtain a unimodal distribution of PI relaxation times by changing $d_{PVE}=7.5$, for example, but in this case the average relaxation time for the PI component becomes slower by one order-of-magnitude or more at each temperature. We have also tried several other “mixing” rules to describe the cooperative volumes at intermediate compositions, but find that these essential conclusions remain unmodified. As a consequence we are therefore forced to conclude that the Donth model in its current form cannot quantitatively capture the segmental dynamics of the two blend components.

B. Dynamic scaling model

We now consider the dynamic scaling model^{24,25} following Eqs. (6) and (7). For pure polymers, Colby²⁵ has shown that data from oscillatory shear experiments, which probe chain dynamics, and DS and NMR, which probe segmental dynamics, obey this scaling behavior with a near universal value of $\nu z=9$. Further, the T_c values obtained from all sets of data agree internally. This last result should be contrasted with fits to the WLF model where the T_∞ values derived from OS and DS can differ by as much as 40 K. Thus, there is experimental evidence that the form of the divergence of relaxation time is better described by Eq. (7) rather than Eq. (5). Further, $T_c > T_\infty$, typically $T_g - T_c \approx 10$ K and $T_g - T_\infty \approx 55$ K. This result has profound implications on segmental dynamics, since most experiments designed to measure segmental dynamics are conducted close to the glass transition temperature of the blend. The scaling approach predicts

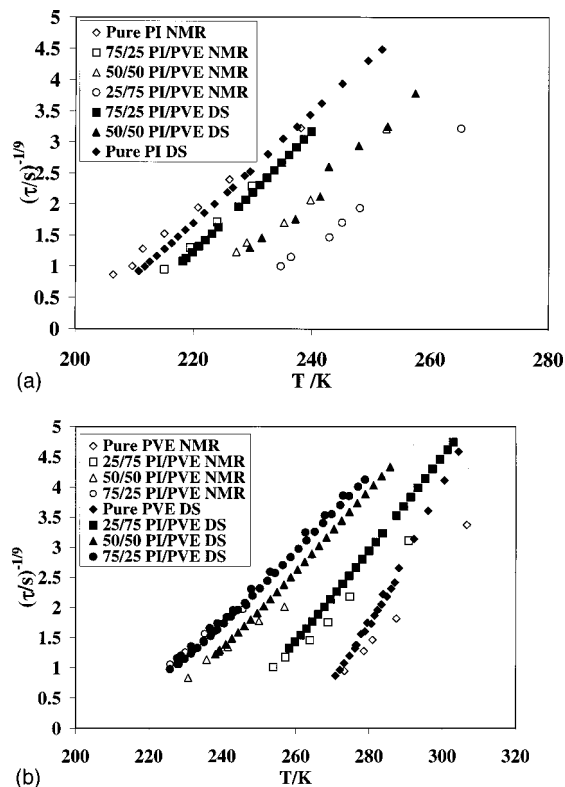


FIG. 5. Temperature dependence of segmental relaxation times from NMR on blends (Refs. 6, 7, 12) (open symbols) and DS on diblock copolymers (filled symbols) plotted in the scaling form of Eq. (7). (a) Segmental relaxation times for PI, and (b) segmental relaxation times for PVE.

stronger composition dependences of V and τ than the corresponding WLF/Donth approach. We shall show below that this significantly improves the description of the dynamics of the PI/PVE system, especially for the PI component.

As noted above, the exponent νz assumes a near “universal” value of 9 for polymeric systems.²⁵ It then follows from Eq. (6) that a plot of $\tau^{-1/9}$ vs. T should be linear, with T_c and A determined from the slope and intercept. Figure 5 shows such plots for PI and PVE relaxation times in various blends, as obtained from NMR and DS. The relaxation times of both the pure components and the blends follow this scaling, especially close to the extrapolated T_c values where the relaxation time diverges. Also, the data from dielectric as well as NMR experiments are in reasonable agreement with each other, except for PVE in blends rich in PVE (including

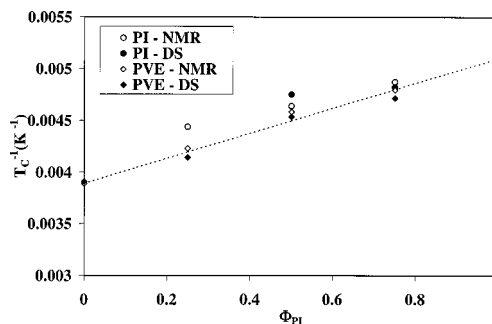


FIG. 6. Fox plot of the composition dependence of T_c . Diamonds are PVE, circles are PI, and the dotted line is the Fox equation.

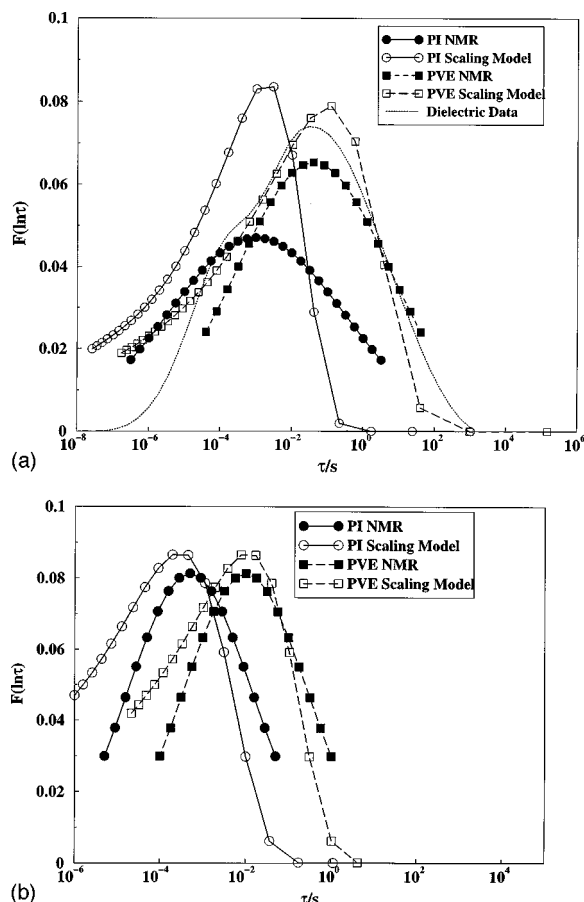


FIG. 7. Comparison of the segmental relaxation time distributions of blended PI and PVE calculated from the scaling model (open symbols) with the log Gaussian distributions from NMR (Refs. 6, 7, 12) (filled symbols) for (a) a 50% PI/50% PVE blend at 242 K, and (b) a 75% PI/25% PVE blend at 232 K. The segmental relaxation time distribution from DS (multiplied by a constant for better comparison) for a 50% PI/50% PVE diblock copolymer is also shown as the dotted curve in part (a). The solid and dashed curves are guides for the eye.

pure PVE). The relaxation of PVE at high temperatures is consistently slower in NMR than in DS, and the origin of this discrepancy is not clear. Figure 5 is used to determine T_c for each component in all blends. For all compositions, we find $T_g - T_c < 20$ K. Since we do not know how T_c varies with composition, we assume it is described by the Fox equation. Figure 6 illustrates this to be a reasonable approximation, using the pure component T_c 's. We used $\nu = 1$, and optimized A_{PI} , A_{PVE} , and B for 50% PI blends at 242 K. These values were then employed at all blend compositions to compare model predictions with data. Figure 7(a) shows a comparison of the model predictions with the log Gaussian relaxation time spectra used to analyze NMR data for PI and PVE in a 50/50 blend at 242 K.

Two points need to be emphasized about Fig. 7(a). First, our predicted distributions of relaxation times for each component are in near-quantitative agreement with experiment. The shape differences between theory and experiment are probably of little consequence, as the NMR data are shown as log Gaussian fits, but other unimodal fitting functions worked just as well.³⁰ Second, note that the PI relaxation is unimodal, again in agreement with experiment. As a further

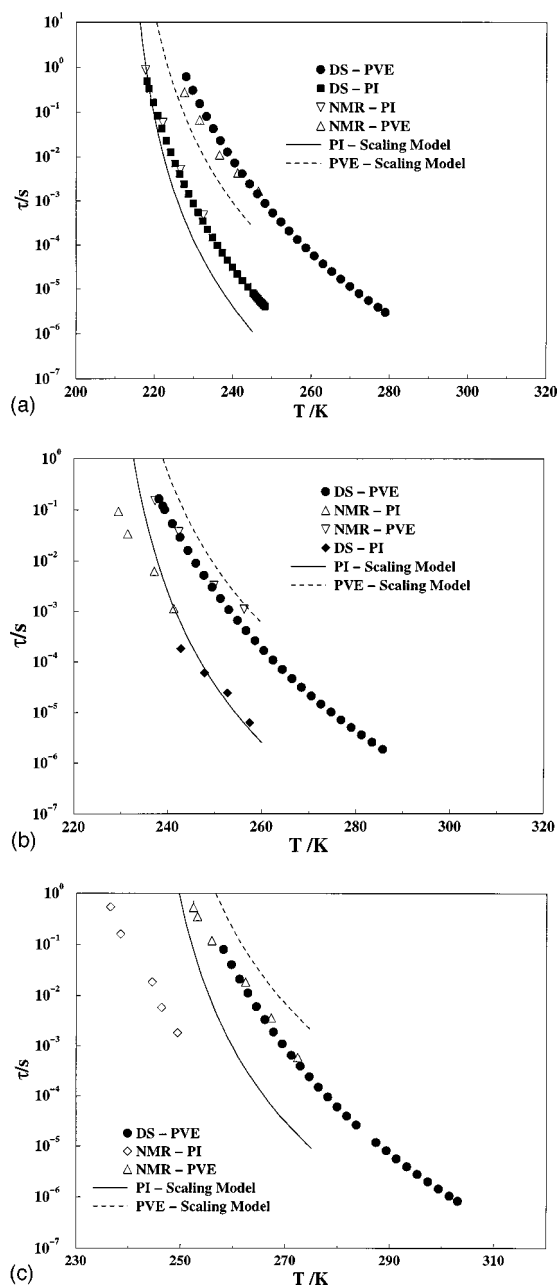


FIG. 8. Comparison of the scaling model predictions (curves) to experimental segmental relaxation times obtained from NMR on blends (Refs. 6, 7, 12) (open symbols) and DS on diblock copolymers (filled symbols) for (a) 75% PI/25% PVE, (b) 50% PI/50% PVE, and (c) 25% PI/75% PVE.

check, we predict the segmental relaxation time spectra for PI and PVE in a 75% PI blend using the same values of ν , A_{PI} , A_{PVE} , and B , in Fig. 7(b). As seen in the figure, we get good agreement for the 75% PI blend as well. Finally, we examine the predicted value of the average relaxation times for both components as a function of temperature at all three compositions in Fig. 8.

While the agreement between experimental segmental relaxation times and predictions at 50% PI and 75% PI are reasonable, the predictions at 25% PI [Fig. 8(c)] are poor, particularly for the PI segmental time. At 25% PI, the predictions would improve significantly if the T_c were lower than what is predicted by the Fox equation. Apparently, the

Fox equation does not adequately describe the composition dependence of T_c . However, the scaling model provides an adequate description of relaxation times with parameters that are independent of composition and temperature.

V. DISCUSSION

One important success of the dynamic scaling model is its prediction that the faster relaxing component (PI) has a unimodal distribution of segmental relaxation times. This result is predicted for all miscible blends with $\Delta T_g \leq 80$ K. For blends with larger dynamic asymmetry ($\Delta T_g > 80$ K) the model predicts a bimodal distribution of segmental relaxation times for the low- T_g blend component. This prediction agrees with DS results on blends with stronger dynamic asymmetry. Polystyrene/poly(methyl phenyl siloxane) with $\Delta T_g = 115$ K shows a bimodal relaxation spectrum in DS, even though the low- T_g component (PMPS) is the only component that is dielectrically active.¹⁹ A 50/50 blend of polystyrene/poly(vinyl methyl ether) with $\Delta T_g = 125$ K also shows evidence of a bimodal distribution of relaxation times, where only the low- T_g component (PVME) is dielectrically active.³¹ In both of these examples, one of the peaks appears to represent the low- T_g component relaxing in the environment of the mean blend composition, while the second (faster) relaxation corresponds to an environment that is nearly the pure low- T_g component. This finding agrees well with our model, as Eqs. (2) and (3) have two maxima in $P(\phi)$, one at $\phi = \bar{\phi}$ and the other with the smallest V , corresponding to compositions rich in the low- T_g component.

An important point that we do not fully understand yet is the fact that $\nu = 1$ provides the best description. Consideration of data on a number of glass-forming polymers²⁵ (not blends) resulted in $\nu \approx 3/2$. However, $\nu = 3/2$ is clearly incorrect for the PI/PVE blends considered here, because the peaks get much sharper with $\nu = 3/2$, and more importantly the segmental relaxation distribution for PI becomes bimodal. Since $\nu z \approx 9$ for polymers,²⁵ $\nu = 1$ suggests that $z = 9$, which seems too large. Andrade creep, universally observed for all glass-forming materials, suggests that $z = 6$.²⁵ A better understanding of these critical exponents is needed before we can claim to "understand" dynamics through dynamic scaling.

Close inspection of Figs. 7(a) and 7(b) show that, while both peaks are roughly the correct width, the predictions are cutoff sharply at the long-time end of the distribution. The origin of this cutoff lies in the calculation of the distribution of segmental relaxations $F(\ln \tau)$, from $P(\phi)$.

$$F(\ln \tau) = P(\phi) \frac{d\phi}{d \ln \tau}. \quad (9)$$

Here $P(\phi)$ goes to zero at the blend composition that has the T_c at the particular temperature [see Eqs. (2), (3), and (6)]. Similarly, the derivative $d \ln \tau / d \phi$ also diverges at the same point [Eq. (7)]. Both of these factors then directly ensure the presence of a strong cutoff in the distribution of relaxation times. For the 50% PI blend at 242 K [Fig. 7(a)] this critical composition is $\phi_{PI} = 0.25$, while the 75% PI blend at 232 K [Fig. 7(b)] has this critical composition at $\phi_{PI} = 0.4$. Thus,

for any blend where segmental relaxation is measured at a temperature below the glass transition of the high- T_g component, the long-time end of the segmental relaxation time distribution of each component will be cutoff sharply. The NMR data actually can be fit by a variety of unimodal forms as well as by the Gaussian form used in Ref. 12. Thus, the NMR experiment can neither refute nor support the predicted form of the sharp cutoff. Future experiments should be designed to look for this sharp cutoff, which is a predicted characteristic at temperatures below the T_g of the high- T_g component.

As noted above, the cutoff arises from the dependences of V and $d \ln \tau / d \phi$ on local composition. Since V enters in an exponential fashion in the calculation of $P(\phi)$, it will play a stronger role than the divergence of the quantity, $d \ln \tau / d \phi$. This point restresses the fact that the success of the scaling model in this context is based on the strong dependence of the cooperative volume on composition, especially when one operates near the glass transition of a blend with components with disparate T_g 's. This form is much stronger than Eq. (4) adopted in the Donth formalism since $T_g - T_c \ll T_g - T_\infty$. In addition to these ideas, it is also clear that the scaling approach [i.e., Eqs. (6) and (7)] is in better agreement with experimental relaxation time spectra since it predicts a unimodal distribution of relaxation times. In contrast, the Donth model predicts a bimodal distribution of relaxation times. Both approaches predict that the distributions of $P(\phi)$ are bimodal, with one peak at the mean composition and one peak at pure PI. Consequently, the scaling approach is more successful in reproducing experiment since the quantity $d \ln \tau / d \phi$ has a much stronger composition dependence than in the Donth model especially for compositions rich in PI. This fact permits for the prediction for a unimodal distribution of relaxation times. In combination, these results stress that the success of the scaling approach is attributable to the adopted functional forms for *both* V and $\ln \tau$ in Eqs. (6) and (7).

VI. CONCLUSIONS

We have used dynamic scaling in conjunction with a concentration fluctuation model to provide an improved description of segmental relaxations in miscible polymer blends. The model correctly predicts that each component in PI/PVE blends has a unimodal distribution of segmental relaxation times. Furthermore, the model provides a reasonable description of the composition and temperature dependences of the peaks of these segmental relaxation time distributions for each component. The model also predicts that blends with stronger dynamic asymmetry ($\Delta T_g > 80$ K) have bimodal segmental relaxation time distributions for the low- T_g component, consistent with available data. The success of this approach apparently arises from a better description of cooperative volume than the earlier model of Donth. However, our understanding of the cooperative volume is still rather vague, and it appears to hold the key to understanding dynamics in glass-forming liquids. Future work in our group will therefore be aimed at an improved understanding of the cooperative volume, through computer simulation.

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