Macromolecules **2007,** *40,* 5759−5766

Dynamics of Miscible Polymer Blends: Role of Concentration Fluctuations on Characteristic Segmental Relaxation Times

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Received February 28, 2007; Revised Manuscript Received May 7, 2007

ABSTRACT: We show that the time corresponding to the peak of the segmental relaxation time distribution and the mean time of that distribution for the components of several miscible polymer blends are strongly affected by both chain connectivity and concentration fluctuations. These two measures of characteristic segmental relaxation times differ from the time corresponding to the mean composition experienced by a segment, with these differences being emphasized for blends with large glass transition contrast, lower temperatures, or increased concentration fluctuations on the nanometer scale. These findings are in contrast to self-concentration models, which generally assume that concentration fluctuations affect neither the mean nor the peak segmental relaxation times and are only relevant for determining the distribution of relaxation times. Going further, we show through the inclusion of self-concentration and concentration fluctuation effects that segmental dynamics are only affected by a local environment of size ∼1 nm surrounding a test monomer. This length scale is only weakly temperature and composition dependent, even near T_g. This estimate of a relevant dynamic length scale is in good agreement with the conjecture on which the Lodge−McLeish self-concentration model is based but is contrary to the ansatz used by many concentration fluctuation-based models which assume that this local environment size diverges in the vicinity of the glass transition.

Introduction

It is now well appreciated that the segmental dynamics of the two polymers in a miscible blend can have quite different temperature dependences,$^{1-25}$ with this effect being magnified when the component glass transition temperatures are very different. This behavior, which manifests itself as a breakdown of the empirical time−temperature superposition (tTS) principle, is rationalized as follows:[15] since the monomer of interest is bonded to other monomers on the same chain, a certain fraction of the "averaging volume" is "self-concentration". This naturally biases the mean composition experienced by this segment toward its pure constituent. In addition, the remainder of the volume is occupied by the segments of other polymers, with this concentration subject to large fluctuations.[26] The magnitudes of both the self-concentration and concentration fluctuations are controlled by the size of the averaging volume. If the two constituents have different glass transition temperatures, the system has natural dynamic contrast, which then leads to the observed breakdown of tTS. Here, we address two important unresolved questions in this field: (1) In addition to the well-accepted fact that concentration fluctuations determine the width of the relaxation time spectrum, do they play any role in determining characteristic segmental relaxation times (e.g., the mean or the peak times of the distribution)? (2) What is the size of the volume which affects the relaxation time of a segment, and how does this depend on temperature, composition, and blend partner?

The pioneering models of Kornfield[7] and Lodge and McLeish[15] have postulated that the peak or the mean segmental relaxation times of the components of miscible blends only depend on self-concentration. Concentration fluctuations are assumed to be only relevant for determining the distributions of relaxation times. While these approaches are almost quantitative in their predictive ability for segmental dynamics far above T_g, more recent work has shown that the self-concentration values necessary to describe experimental data have to be small (and sometimes even negative) in the vicinity of T_g.[7,27,28] Even more disturbingly, the value of self-concentration that fits the experimental data for a particular polymer depends on the partner with which the polymer is blended with.[29] These results suggest that some other factor needs to be considered to resolve these apparent inconsistencies. In this paper we shall show that concentration fluctuations play important roles even in determining the peak or the mean segmental relaxation times. The analysis of available experimental data for the segmental dynamics of miscible polymer blends using a model that incorporates both self-concentrations and concentration fluctuations suggests that segmental motion is controlled by a ∼1 nm sized neighborhood surrounding a test segment. This length scale is apparently independent of blend composition and blend partner and only has a weak temperature dependence. We therefore conclude that the inclusion of self-concentration and concentration fluctuation effects over this small volume should form the basis for a truly predictive model for blend dynamics.

Model Development

We base our ideas on the incompressible Flory theory of polymer blends: thus, while we shall include the effects of concentration fluctuations, we do not account for any density

10.1021/ma070502y CCC: $37.00

fluctuations (or compressibility effects) in our formalism. We introduce two distribution functions, $p(\phi_{\mathrm{eff}}^{\mathrm{A}})\, \mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}$ and $p_\tau(\ln \tau)\, \mathrm{d}\ln \tau$, the probability distributions of effective concentrations surrounding a given segment and logarithmic relaxation times experienced by that given segment, respectively. These probability distribution functions are related by the equation

$$p(\phi_{\mathrm{eff}}^{\mathrm{A}})\, \mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}} = p_\tau(\ln \tau)\, \mathrm{d} \ln \tau \qquad (1)$$

$\phi_{\mathrm{eff}}^{\mathrm{A}}$ has contributions from both self-concentration and concentration fluctuations:[15]

$$\phi_{\mathrm{eff}}^{\mathrm{A}} = \phi_{\mathrm{self}}^{\mathrm{A}} + (1 - \phi_{\mathrm{self}}^{\mathrm{A}})\phi^{\mathrm{A}} \qquad (2)$$

where ϕ^{A} represents the intermolecular concentration experienced by a test segment, while $\phi_{\mathrm{self}}^{\mathrm{A}}$ is the self-concentration. For small volumes, whose sizes are smaller than a Kuhn length, b_{A}, the self-concentration is fixed since the chain is rigid at these scales.[15,27] If we assume that the averaging volume is a sphere of radius R_{c} ($R_{\mathrm{c}} < b_{\mathrm{A}}$), we obtain

$$\phi_{\mathrm{self}}^{\mathrm{A}} = \frac{3 v_{\mathrm{A}}}{2\pi b_{\mathrm{A}} R_{\mathrm{c}}^2} \qquad (3)$$

where $v_{\mathrm{A}} = l_{\mathrm{pA}} b_{\mathrm{A}}^2$ is the volume of a single A segment, while l_{pA} and b_{A} are the packing and the Kuhn lengths of the polymer, respectively.[30] The *variation* of concentrations sampled by the test segment thus has no contributions from self-concentration effects. In this case the distribution of concentration experienced by a test segment, $p(\phi_{\mathrm{eff}}^{\mathrm{A}})$, is a Gaussian[26]

$$p(\phi_{\mathrm{eff}}^{\mathrm{A}}) = \frac{1}{\sqrt{2\pi\langle \delta\phi_{\mathrm{eff}}^{\;2}\rangle}} \exp\left\{ - \frac{(\phi_{\mathrm{eff}}^{\mathrm{A}} - \bar{\phi}_{\mathrm{eff}}^{\mathrm{A}})^2}{2\langle \delta\phi_{\mathrm{eff}}^{\;2}\rangle} \right\} \qquad (4)$$

where the mean-squared fluctuation in effective composition $\langle \delta\phi_{\mathrm{eff}}^2 \rangle$ is related to the usual mean-square concentration fluctuation $\langle \delta\phi^2 \rangle$:

$$\langle \delta\phi_{\mathrm{eff}}^{\;2}\rangle = (1 - \phi_{\mathrm{self}}^{\mathrm{A}})^2 \langle \delta\phi^2 \rangle \qquad (5)$$

$p(\phi_{\mathrm{eff}}^{\mathrm{A}})$ has a maximum at a mean effective concentration, $\bar{\phi}_{\mathrm{eff}}^{\mathrm{A}}$, which is related to the mean blend composition, Φ_{A}:

$$\bar{\phi}_{\mathrm{eff}}^{\mathrm{A}} = \phi_{\mathrm{self}}^{\mathrm{A}} + (1 - \phi_{\mathrm{self}}^{\mathrm{A}})\Phi_{\mathrm{A}} \qquad (6)$$

The companion paper[30] shows that the mean-squared concentration fluctuation for component A is given by

$$\langle \delta\phi^2 \rangle = \frac{3\sqrt{v_{\mathrm{A}} v_{\mathrm{B}}}}{2\pi R_{\mathrm{c}} \left(\dfrac{b_{\mathrm{A}}^{\;2}}{\Phi_{\mathrm{A}}} + \dfrac{b_{\mathrm{B}}^{\;2}}{\Phi_{\mathrm{B}}} \right)} \qquad (7)$$

An analogous expression can be derived for component B. Thus, both the self-concentration and the magnitude of concentration fluctuations are controlled directly by the size scale R_{c}.

Most experimental methods either measure the time corresponding to the maximum of $p_\tau(\ln \tau)$ ["most probable" time] or its mean ["mean logarithmic relaxation" time]. All self-concentration models, including the Lodge−McLeish model, convert the mean effective concentration, $\bar{\phi}_{\mathrm{eff}}^{\mathrm{A}}$, to a relaxation time, which is then compared directly to these experimental measures of mean relaxation times. The question we consider here is whether these experimental times correspond to $\bar{\phi}_{\mathrm{eff}}^{\mathrm{A}}$ as has been assumed. We first focus on the most probable time or the time corresponding to the maximum in $p_\tau(\ln \tau)$. This maximum is defined by

$$\frac{\partial p_\tau(\ln \tau)}{\partial \ln \tau} = 0$$

As discussed above, since $p_\tau(\ln \tau)$ and $p(\phi_{\mathrm{eff}}^{\mathrm{A}})$ are directly related (eq 1), this condition for the maximum transforms to

$$\frac{\partial}{\partial \ln \tau}\left[p(\phi_{\mathrm{eff}}^{\mathrm{A}}) \frac{\partial \phi_{\mathrm{eff}}^{\mathrm{A}}}{\partial \ln \tau} \right] = 0 \qquad (8)$$

We now use the Gaussian form of $p(\phi_{\mathrm{eff}}^{\mathrm{A}})$ (eq 4) to obtain

$$\phi_{\mathrm{peak}}^{\mathrm{A}} - \bar{\phi}_{\mathrm{eff}}^{\mathrm{A}} = -[1 - \phi_{\mathrm{self}}^{\mathrm{A}}]^2 \langle \delta\phi^2 \rangle \frac{\left[\dfrac{\mathrm{d}^2 \ln \tau}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}\;2}} \right]}{\left[\dfrac{\mathrm{d} \ln \tau}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}} \right]} = -\langle \delta\phi_{\mathrm{eff}}^{\;2}\rangle \frac{\mathrm{d}}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}} \ln\left[\frac{\mathrm{d} \ln \tau}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}} \right] \qquad (9)$$

Thus, the maximum of $p_\tau(\ln \tau)$ occurs at a composition that is shifted from the mean composition experienced by a segment by an amount that is directly proportional to the mean-squared concentration fluctuation. This is a central result of our paper.

We next focus on the mean of the segmental relaxation time distribution. In previous work[27] we derived an expression for the mean logarithmic relaxation time experienced by a test segment. That form is slightly incorrect, and below we show the correct Taylor series expansion for this quantity:

$$\langle \ln \tau(\phi_{\mathrm{eff}}^{\mathrm{A}}) \rangle = \ln \tau(\bar{\phi}_{\mathrm{eff}}^{\mathrm{A}}) + \frac{1}{2}\langle \delta\phi_{\mathrm{eff}}^{\;2}\rangle \frac{\mathrm{d}^2 \ln \tau}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}\;2}} + \ldots \qquad (10)$$

We can then approximately transform eq 10 as

$$\phi_{\mathrm{average}}^{\mathrm{A}} - \bar{\phi}_{\mathrm{eff}}^{\mathrm{A}} \approx \frac{\langle \ln \tau(\phi_{\mathrm{eff}}^{\mathrm{A}}) \rangle - \ln \tau(\bar{\phi}_{\mathrm{eff}}^{\mathrm{A}})}{\mathrm{d} \ln \tau / \mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}} = \frac{1}{2}\langle \delta\phi_{\mathrm{eff}}^2 \rangle \frac{\mathrm{d}}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}} \ln\left[\frac{\mathrm{d} \ln \tau}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}} \right] \qquad (11)$$

where $\phi_{\mathrm{average}}^{\mathrm{A}}$ is the effective composition corresponding to $\langle \ln \tau(\phi_{\mathrm{eff}}^{\mathrm{A}}) \rangle$. This shift relative to the mean composition, $\phi_{\mathrm{average}}^{\mathrm{A}} - \bar{\phi}_{\mathrm{eff}}^{\mathrm{A}}$, is half the magnitude and opposite in sign to the shift seen in eq 9.

The most important point that emerges from this analysis is that neither the peak relaxation time nor the mean logarithmic relaxation time rigorously equals the relaxation time that corresponds to the mean value of the effective concentration, i.e., $\bar{\phi}_{\mathrm{eff}}^{\mathrm{A}}$. While we have not discussed the numerical importance of the concentration fluctuation terms in this context,[27] we shall demonstrate below that including them in the analysis of experimental data (for either the peak time or the mean time) allows us to avoid unphysical effects such as negative values of the self-concentration.

How Important Are These Effects?

To put some numerical values into these equations, we employ the well-known Vogel−Fulcher (VF) form to describe the temperature dependence of relaxation times. [The VF functional form can be readily reduced to the Williams−

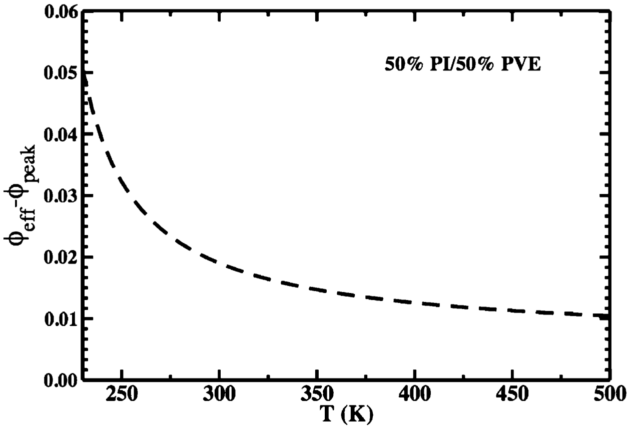

Figure 1. Difference between the mean effective composition and the composition corresponding to the peak relaxation time for PVE in a 50/50 blend of PI/PVE. We assumed an R_c value of 6 Å, a Kuhn length $b = 14$ Å, and a packing length of $l_p = 2.8$ Å. The WLF parameters used to describe this system are listed in ref 27.

Landel−Ferry form.] We assume that the blend Vogel temperature T_0 follows the Fox equation, while all other quantities are composition-independent. (It is important to note that there is no *a priori* reason to use the Fox equation, and below we shall consider the use of an alternate form, the DiMarzio expression, to describe the composition dependence of T_g. The use of this different form does not qualitatively alter the conclusions we draw.) Under these assumptions, eq 9 reduces to the form

$$\phi_{\mathrm{peak}}^{\mathrm{A}} - \bar{\phi}_{\mathrm{eff}}^{\mathrm{A}} = 2\langle\delta\phi_{\mathrm{eff}}{}^{2}\rangle T_0\left[\frac{1}{T_{0\mathrm{A}}} - \frac{1}{T_{0\mathrm{B}}}\right]\left(\frac{T}{T - T_0}\right) \qquad (12)$$

for component A, where T_{0A} and T_{0B} are the Vogel temperatures of pure components A and B, respectively. Thus, the effective concentration corresponding to the peak relaxation time is different from the mean effective composition (eq 6), with this difference becoming larger as concentration fluctuations grow, if the T_0 contrast between the two polymers is increased or as T is lowered. To get a sense of the magnitude of these numbers, we use parameters for the 50/50 PI/PVE blend system: for PVE with $R_c = 6$ Å, we obtain $\langle\delta\phi_{\mathrm{eff}}{}^2\rangle \approx 0.012$ and $\phi_{\mathrm{self}}^{\mathrm{A}} = 0.5$. As Figure 1 shows, in the high-temperature limit, this equation predicts that the difference in volume fraction between the peak and the Lodge−McLeish prediction would only be ~0.009. At T_g the difference in compositions predicted by this model is ~0.05, which would affect the relaxation times by orders of magnitude. This result reiterates our previous statement that the Lodge−McLeish approach works remarkably well when one considers blends far above their glass transition temperatures, but this model becomes less reliable at lower temperatures.[27]

We also consider the findings of Ediger and co-workers,[29] who had used NMR to obtain the *mean* relaxation times $\langle\tau(\phi_{\mathrm{eff}}^{\mathrm{A}})\rangle$ of polyisoprene, when blended with a range of different polymers. (At these high temperatures $\langle\tau(\phi_{\mathrm{eff}}^{\mathrm{A}})\rangle \approx 1 + \langle\ln \tau(\phi_{\mathrm{eff}}^{\mathrm{A}})\rangle$, and thus we simply calculate the mean logarithmic relaxation time.) These workers used the Lodge−McLeish (LM) model and treated the self-concentration as a variable. Surprisingly, they found that $\phi_{\mathrm{self}}^{\mathrm{A}}$ for PI was dependent on the blend partner. When PI was blended with higher T_g materials, the apparent $\phi_{\mathrm{self}}^{\mathrm{A}}$ was consistently smaller than the Lodge−McLeish prediction (0.45), while it showed an opposite trend when the partner had a lower T_g. To understand this result, we return to eq 11. Since the self-concentration is used as a fit parameter to describe the mean time, it follows that the resulting value of self-concentration is also affected by the presence of concentration fluctuations:

$$\phi_{\mathrm{self}}^{\mathrm{A,apparent}} - \phi_{\mathrm{self}}^{\mathrm{A}} \approx \frac{1}{2}\frac{\langle\delta\phi_{\mathrm{eff}}{}^{2}\rangle}{1 - \Phi_{\mathrm{A}}}\frac{\mathrm{d}}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}}\ln\left[\frac{\mathrm{d}\ln\tau}{\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}}\right] \qquad (13)$$

We now make the standard assumption that the relaxation time of the blend components follows the same VF form as the pure material, with T_0 given by the Fox equation. Thus, we obtain

$$\phi_{\mathrm{self}}^{\mathrm{A,apparent}} - \phi_{\mathrm{self}}^{\mathrm{A}} \approx -\frac{\langle\delta\phi_{\mathrm{eff}}{}^{2}\rangle}{1 - \Phi_{\mathrm{A}}}T_0\left[\frac{1}{T_{0\mathrm{A}}} - \frac{1}{T_{0\mathrm{B}}}\right]\frac{T}{T - T_0} \qquad (14)$$

for component A. If A is the low-T_g component, then $\phi_{\mathrm{self}}^{\mathrm{A,apparent}} < \phi_{\mathrm{self}}^{\mathrm{A}}$, and if A is the high-$T_g$ component, then $\phi_{\mathrm{self}}^{\mathrm{A,apparent}} > \phi_{\mathrm{self}}^{\mathrm{A}}$. Thus, since PI is the low-T_g component of PI/PVE blends, the apparent self-concentration extracted from the mean time should be lower than the LM prediction. Further, for a 50/50 PI/PVE blend, the magnitude of this shift in self-concentration is predicted be ~0.01 at high temperatures, while it should be ~0.06 at low temperatures. The NMR derived self-concentration[29] is $\phi_{\mathrm{self}}^{\mathrm{A,apparent}} = 0.41 \pm 0.05$ for PI in this blend, while the Lodge−McLeish prediction is $\phi_{\mathrm{self}}^{\mathrm{A}} = 0.45$. While we shall provide a more detailed analysis of this issue below, it appears that including concentration fluctuations might allow resolution of this problem.

Results and Discussion

Fits to the Peak Relaxation Times for the PI/PVE and PoCS/PVME Blends. We fit the temperature dependence of peak segmental relaxation time data from the literature to eq 9, using one temperature-independent fitting parameter, the size of the volume R_c. In all cases we minimize the “cost” function $F = \sum_i(\ln \tau[\phi_{\mathrm{eff}}^{\mathrm{A}}] - \ln \tau[\Phi_{\mathrm{A}}])_i{}^2$, where the first term on the right side is the predicted value of the logarithm of the relaxation time (corresponding to either the peak or the average value) while the second quantity is the experimental value. Knowledge of R_c immediately yields both (1) the fluctuation in effective composition $\langle\delta\phi_{\mathrm{eff}}{}^2\rangle$ (eq 7) and (2) the self-concentration $\phi_{\mathrm{self}}^{\mathrm{A}}$ (eq 3). To proceed from here to obtain the relaxation times relevant to the experiments, we need to make two assumptions: (1) the composition dependence of T_0 (using for example the Fox or DiMarzio equations) and (2) the detailed form of the temperature dependence of relaxation time.

We shall show below that the results are insensitive to both of these assumptions: we speculate that this insensitivity results because the models that work have sufficient variability resulting from adjusting the single parameter, R_c. In this sense it is powerful if the CF model presented here works better than the LM model: we argue that, in this case, the model including CF better embodies the physics. In the companion paper,[30] we fit the entire distribution of relaxation times, effectively using a single parameter, R_c, again illustrating the power of this approach.

Results. Figures 2 and 3 and Table 1 represent our best fits to the peak segmental relaxation time (or frequency) for the constituents of two different blends with a temperature-independent R_c for each blend component—poly(*o*-chlorostyrene)/poly(vinyl methyl ether)[22] and polyisoprene/poly(vinylethylene)[7,31]—following eq 9. For the PoCS/PVME blends the dependence of log τ vs composition was described by a Vogel−Fulcher form, with only T_0, the Vogel temperature, being dependent on composition. T_0 was obtained via the Fox equation.

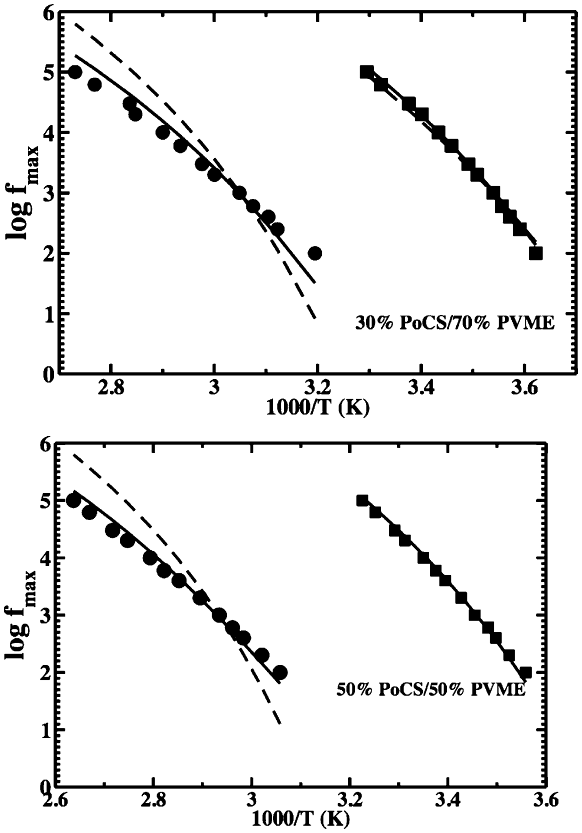

Figure 2. Frequencies (in Hz) corresponding to the peak in the dielectric relaxation spectrum for two compositions of PoCS/PVME blends.[22] The circles are PoCS, and the squares are PVME. The dashed lines are predictions of the Lodge−McLeish model with a temperature-independent self-concentration. The full lines are fits to eq 9 with R_c independent of temperature.

For the PI/PVE blends we used the WLF form with a composition-independent values of c_1 and of c_2 as we have utilized previously. (We examine the sensitivity to using a different form for the composition dependence of T_0 such as the DiMarzio equation below.) The required parameters were derived from refs 32 and 27, respectively. In both of these blends, the glass transition temperatures of the constituents are very different.

In agreement with past work on PI/PVE,[27] we find that the peak relaxation time for the faster (low-T_g) component can be well fit by using either the Lodge−McLeish mean-field approach or the model proposed here (see Figures 2 and 3 and Table 1). In all cases we use $\Delta(\log \tau)$ in Table 1 as a metric to characterize the goodness of fit. $\Delta(\log \tau)$ is the standard deviation of the fit value of log τ relative to the experimental most probable value of the relaxation time. This standard deviation is reported in decades and represents in a single number the quality of the fits over the temperature range of the available data.

We first discuss the fits obtained using only self-concentrations, i.e., the Lodge−McLeish approach. Figure 2 and Table 1 show that this approach works very well for the low-T_g component in all cases. However, in agreement with the ideas presented in previous work,[27] the Lodge−McLeish model provides a much less satisfactory fit to the relaxation time for the slower component (PoCS in the PoCS/PVME blend and PVE in the PI/PVE blend). In both blends, the experimental data for the high-T_g component show a much weaker temperature dependence than might be expected from the application of the mean-field Lodge−McLeish model. This result has been observed previously by Kornfield in the case of the PI/PVE blend.[7] Kant et al.[27] have suggested that the apparent self-concentration of PVE has to approach zero or even become negative in the vicinity of T_g to rationalize dielectric spectroscopy results for the α-relaxation time with the mean-field Lodge−McLeish model. Similarly, Roland[28] has suggested that the PoCS data from a PoCS/PVME blend has an unusually low fragility parameter. We thus conclude that the mean-field Lodge−McLeish model consistently fails for the high-T_g component near T_g. One must either use a temperature-dependent self-concentration or include some missing physics.

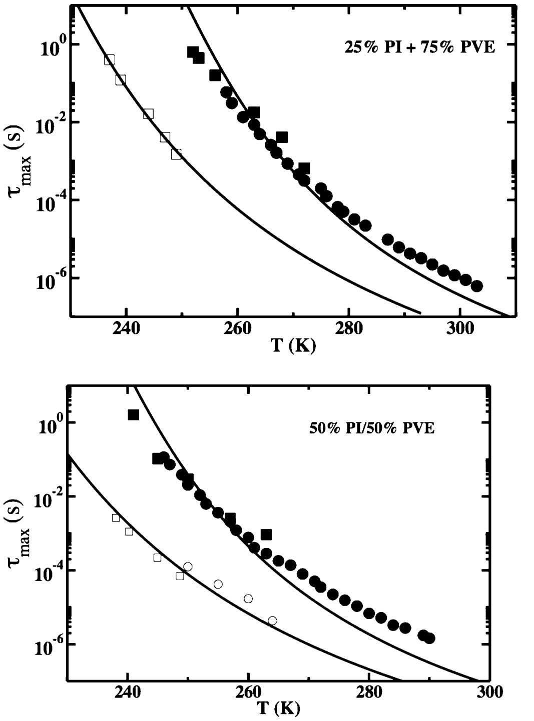

Figure 3. Temperature dependence of relaxation times corresponding to the peak in either the NMR[7] (squares) or the dielectric relaxation spectrum[31] (circles) for two compositions of the PI/PVE blend. The filled symbols are PVE while the open symbols are PI. The lines are fits to eq 9 with R_c independent of temperature. The predictions of the Lodge−McLeish model for these PI/PVE blends are reported in ref 27.

Introduction of concentration fluctuations (CF) allows us to satisfactorily resolve these problems (solid lines in Figures 2 and 3; see also Table 1). Our results show that the experimental peak relaxation times for both components in each blend can be fit by the proposed model, with smaller uncertainties than those obtained using the Lodge−McLeish model. Further, we get reasonable fits even though we have employed temperature-independent values of R_c in each case. In the worst case of PVE in the 75/25 PI/PVE blend, it is apparent that the fits to PVE are poor and even use of the CF model only allows us to fit the data to within one decade. We thus argue that R_c may need to depend weakly on temperature. We shall explore this aspect further below and in the companion paper,[30] but it is important to stress that the current results suggest that our calculations using a single temperature-independent R_c as a fit parameter offer a better description than the Lodge−McLeish model with the same number of fit parameters (a single value of ϕ_{self}^{A}). Note that while the Lodge−McLeish model without CF requires very small values of the self-concentration in some cases (e.g., the PVE in the blends with 25% or 75% PVE), the corresponding values required with the inclusion of CF (column 6 in Table 1) are always much larger, and vary less with blend composition.

Table 1. Fit Parameters for PI/PVE[2,7] and PoCS/PVME[22] Miscible Blends

system[a]	T (K)	$\phi_{\mathrm{self}}^{\mathrm{LM}\,b}$	$\Delta(\log \tau)^{\mathrm{LM}\,c}$	R_c (Å)	$\phi_{\mathrm{self}}^{\mathrm{CF}}$, $\langle \delta\phi_{\mathrm{eff}}^2 \rangle^d$	$\Delta(\log \tau)^{\mathrm{CF}\,c}$	$T_g{}^e$	$\phi_{\mathrm{self}}^{\mathrm{LM}\,f}$
30/**70** PoCS/**PVME**	276−303	0.52	0.05	7.7	0.28, 0.018	0.10	260	0.47
30/70 **PoCS**/PVME	313−366	0.32	0.60	10.1	0.33, 0.012	0.15	340	0.30
50/**50** PoCS/**PVME**	281−310	0.58	0.075	6.4	0.41, 0.020	0.04	275	0.57
50/50 **PoCS**/PVME	327−379	0.23	0.61	10.1	0.33, 0.016	0.14	353	0.16
70/**30** PoCS/**PVME**	293−322	0.54	0.14	5.9	0.48, 0.016	0.09	292	0.54
70/30 **PoCS**/PVME	368−416	0.50	0.45	7.7	0.57, 0.009	0.08	390	0.36
75/25 **PI**/PVE	214−263	0.55	0.10	6.4	0.30, 0.014	0.05	217	0.41
75/**25** PI/**PVE**	214−300	0.02	1.76	13.0	0.11, 0.011	1.62	225	0.03
50/50 **PI**/PVE	238−264	0.38	0.29	6.8	0.27, 0.024	0.26	226	0.38
50/**50** PI/**PVE**	241−290	0.25	0.67	6.85	0.40, 0.016	0.49	234	0.18
25/75 **PI**/PVE	237−249	0.40	0.14	6.4	0.31, 0.023	0.09	236.5	0.40
25/**75** PI/**PVE**	252−303	0.09	0.60	6.8	0.40, 0.016	0.38	253	0.08

[a] Each row corresponds to one component in a blend, denoted in bold. [b] Obtained by fitting the experimental data directly to the Lodge−McLeish model. [c] Standard deviations of the fits from the experimental data reported in log units. [d] The self-concentration and concentration fluctuations are calculated following eqs 3 and 7 using the R_c values reported in column 5. [e] T_g of each component for PI/PVE was obtained from Kornfield et al.,[7] while for PoCS/PVME we used data from Urakawa et al.[22] [f] These data for the self-concentration for the Lodge−McLeish model were derived following eq 17 and the data shown in column 5 (or 6).

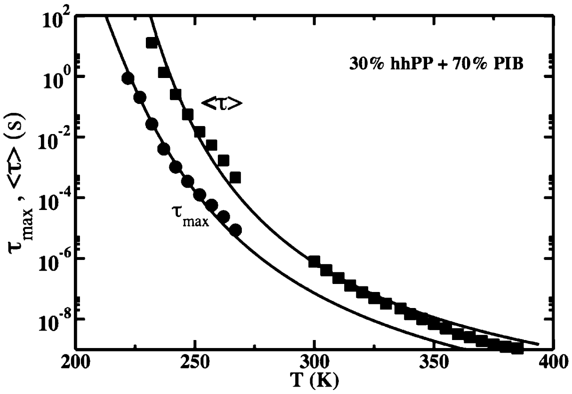

Figure 4. Temperature dependence of relaxation times corresponding to the peak in the dielectric relaxation spectrum (circles) for the hhPP component in a 30% hhPP/70% PIB blend.[33] The filled squares are the mean logarithmic relaxation times for the hhPP component: the low-temperature data are from dielectric spectroscopy, while the high-temperature data are for $\langle \tau \rangle$ from NMR (at high temperature $\exp\langle \log \tau \rangle \sim \langle \tau \rangle$, and so we consider both the NMR and dielectric data on the same footing). The lines are fits to eqs 9 and 10 with both self-concentrations and the magnitude of concentration fluctuations independent of temperature.

Fits to the Peak and Mean Relaxation Times for the hhPP/PIB Blend. Next, we proceed to the dynamics of the hhPP component in a 30% hhPP/70% PIB blend,[33] where we have data on both the peak time (from dielectric spectroscopy) and the mean logarithmic relaxation time (from NMR) as functions of temperature. Figure 4 clearly shows that these two quantities are different, with the differences becoming more pronounced as temperature is lowered. The two lines in Figure 4 correspond to the fits following eqs 9 and 10, with the same value of R_c = 6 Å. It can be seen that excellent fits are obtained, reiterating that this approach is useful for representing these different measures of segmental relaxations for the high-T_g component in miscible blends. In contrast, the LM model fails to predict either data set[33] with a single value of $\phi_{\mathrm{self}}^{\mathrm{A}}$.

Sensitivity of Results to the Fitting Procedure Employed. The data presented in Table 1 (and Figures 2 and 3) show several important trends which need to be explained. First, regardless of the model employed (LM vs CF), the data for the low-T_g component are apparently fit better than those of the high-T_g component. As a consequence, it appears that the data for the low-T_g component are less sensitive to concentration fluctuations than the high-T_g component. Is this reasonable and can we understand these trends? Second, the Lodge−McLeish model appears to provide a reasonable fit to the experimental peak relaxation time data, especially for the low-T_g component. How does this model fit data adequately, when we argue that concentration fluctuations play an important role?

First, we focus on the fact that the relaxation times for the low-T_g component always appear to be fit with lower uncertainties than the data for the high-T_g component. To understand this result, we note that both the LM model and the CF model start with expressions for the composition experienced by a test segment, which is then converted to a relaxation time. Thus, if a model predicts the relevant composition with an error of $\Delta\phi_{\mathrm{eff}}^{\mathrm{A}}$, then the error in predicted log time is $|(\mathrm{d} \log \tau)/\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}| \times |\Delta\phi_{\mathrm{eff}}^{\mathrm{A}}|$. Let us consider one representative case; the PI/PVE blend with 25% PI. We use the Fox equation, in conjunction with the WLF equation, to estimate the mean value of $|(\mathrm{d} \log \tau)/\mathrm{d}\phi_{\mathrm{eff}}^{\mathrm{A}}|$ for each component over the relevant temperature range (Table 1). This yields a value of 15 for PI and 40 for PVE (i.e., a composition error of 0.1 would change the PI relaxation time by 1.5 decades but would change the PVE relaxation time by 4 decades). These differences are not due to the temperature ranges studied, which include the apparent T_g of each component (Table 1). Since this derivative is larger for lower temperatures, we might have expected that PI would yield a larger derivative, given the narrower temperature range studied relative to PVE. Instead, the opposite trend is observed. This trend reflects the fact that, at a given distance from T_g, the derivative is larger for compositions richer in the high-T_g component. Since PVE (with its self-concentration) samples this end of the composition spectrum, it is then unsurprising that the derivatives for PVE are larger than for PI. Since the ratio of the derivatives track the relative errors of the relaxation times for the PI and PVE as predicted by our model, we conclude that the apparently lower error in the PI is not a consequence of the fact that its peak composition is predicted better than for the PVE. Rather, the magnitude of the error reflects the amplification associated with the conversion from composition to relaxation times.

Next, we focus on the apparent success of the Lodge−McLeish model in predicting the peak relaxation time of the low-T_g component over the temperature ranges considered using a constant self-concentration. To understand this result, we start with the "error" function:

$$F = \sum_i (\ln \tau[\phi_{\mathrm{LM}}^{\mathrm{A}}] - \ln \tau[\phi_{\mathrm{CF}}^{\mathrm{A}}])_i^2 \qquad (15)$$

where the first term in the brackets is the logarithm of the relaxation time predicted by the Lodge−McLeish model, while the second is the prediction of the concentration fluctuation

Table 2. Comparison of the Quality of Fits Using the Fox Equation vs the DiMarzio Equation

system	T (K)	LM−Fox	CF−Fox	LM− DiMarzio	CF− DiMarzio
75/25 **PI**/PVE	214−263	0.10	0.05	0.10	0.02
75/**25** PI/**PVE**	214−300	1.76	1.62	2.38	2.66
50/50 **PI**/PVE	238−264	0.29	0.26	0.26	0.26
50/**50** PI/**PVE**	241−290	0.67	0.49	0.54	0.46
25/75 **PI**/PVE	237−249	0.14	0.09	0.16	0.10
25/**75** PI/**PVE**	252−303	0.60	0.38	0.60	0.34
30/**70** PoCS/**PVME**	276−303	0.05	0.10	0.09	0.10
30/70 **PoCS**/PVME	313−366	0.60	0.15	0.52	0.50
50/**50** PoCS/**PVME**	281−310	0.075	0.04	0.04	0.05
50/50 **PoCS**/PVME	327−379	0.61	0.14	0.53	0.49
70/**30** PoCS/**PVME**	293−322	0.14	0.09	0.08	0.15
70/30 **PoCS**/PVME	368−416	0.45	0.08	0.37	0.35

model for the peak relaxation time (i.e., $\phi_{\mathrm{CF}}^{\mathrm{A}} = \phi_{\mathrm{peak}}^{\mathrm{A}}$ from eq 9). Thus, we treat our CF model predictions (using the concentration fluctuations and the self-concentration) as "data" which are fit to the Lodge−McLeish model. This procedure allows us to focus only on the ability of the LM model to reproduce data which are affected by concentration fluctuations. The best fit composition for the Lodge−McLeish model, $\phi_{\mathrm{LM}}^{\mathrm{A}}$, can be derived by Taylor expanding the first term about the peak concentration and truncating it at first order:

$$\frac{\partial F}{\partial \phi_{\mathrm{LM}}^{\mathrm{A}}} = 0 = \sum_i \left(\frac{\partial \ln \tau}{\partial \phi_{\mathrm{eff}}^{\mathrm{A}}}\right)_i^2 [\phi_{\mathrm{LM}}^{\mathrm{A}} - \phi_{\mathrm{peak}}^{\mathrm{A}}]_i \tag{16}$$

leading to

$$\phi_{\mathrm{LM}}^{\mathrm{A}} = \frac{\sum_i \left(\frac{\partial \ln \tau}{\partial \phi_{\mathrm{eff}}^{\mathrm{A}}}\right)_i^2 \phi_{\mathrm{peak}_i}^{\mathrm{A}}}{\sum_i \left(\frac{\partial \ln \tau}{\partial \phi_{\mathrm{eff}}^{\mathrm{A}}}\right)_i^2} \tag{17}$$

This equation can be simplified using eq 9 to relate the peak composition to the effective composition and concentration fluctuations.

$$\phi_{\mathrm{LM}}^{\mathrm{A}} = \bar{\phi}_{\mathrm{eff}}^{\mathrm{A}} - \frac{1}{2}(1 - \phi_{\mathrm{self}}^{\mathrm{A}})^2 \langle \delta\phi^2 \rangle \frac{\partial}{\partial \phi_{\mathrm{eff}}^{\mathrm{A}}}\left[\ln \sum_i \left(\frac{\partial \ln \tau}{\partial \phi_{\mathrm{eff}}^{\mathrm{A}}}\right)_i^2\right] \tag{18}$$

Further, for simplification, we replace the summation by an integral going over the temperature range of interest. On this basis, then, we can use the R_{c} (and hence the self-concentration and the concentration fluctuations as derived from our model) in conjunction with the experimental ranges of temperatures to determine the value of the self-concentration which would allow the LM model to best fit the peak relaxation time data as generated by the CF model. The last column in Table 1 shows that the proposed approach, which fits the LM model to the data generated by the CF model, nearly quantitatively reproduces the results obtained by directly fitting the LM model to experimental data. We thus conclude that the LM model can always be forced to fit experimental data which are affected by CF, but at the cost of obtaining poorer fits to the experimental data than the CF model proposed here. The differences in uncertainties, $\Delta(\log \tau)$ (i.e., compare columns 4 and 7 in Table 1), then reflect the improvement achieved in going from the Lodge−McLeish model to the concentration fluctuation based approach.

Composition Dependence of Vogel Temperature. Our fits to the peak relaxation times use the Fox equation to describe the composition dependence of the Vogel temperature T_0 (or T_{g}), while the companion paper uses the DiMarzio equation. To critically examine the consequences of this choice, we have considered data from the PI/PVE and the PoCS/PVME systems. Table 2 presents fit quality as characterized by $\Delta(\log \tau)$ in four different cases: LM−Fox, CF−Fox, LM−DiMarzio, and CF−DiMarzio. Table 2 shows that the use of the DiMarzio vs the Fox equation for describing the composition dependence of the Vogel temperature does not qualitatively alter the conclusions drawn. However, the particular choices of mixing rules for T_0 do affect the values of the fit parameters and the absolute values of the standard deviations between the fits and the experiments. For the purposes of this paper, both formalisms yield comparable quality of fits to peak relaxation time data.

Sensitivity of Results to Data Utilized. To understand the sensitivity of our results to the particular data set employed, we consider one particular representative situation: this corresponds to PI in a 75/25 PI/PVE blend. In this case we have access to relaxation time data from NMR[7] and dielectric spectroscopy.[2,31] Fits to the NMR data yield an R_{c} value of ∼6.8 Å, while corresponding fits to the two different dielectric relaxation data yielded 5.4 and 5.7 Å, respectively. It is important to note that analysis of different data sets can yield different values of R_{c}. While this is most likely due to the fact that the NMR and the dielectric data were taken over different ranges (see more on this point below), it could also be a consequence of the erroneous assumption that the WLF parameters for PI are the same for all three different data sets,. More analysis, where WLF parameters relevant to data derived from each protocol, could help to resolve this issue, but below we focus on the scenario that R_{c} must be weakly temperature dependent.

Is ϕ_{self} Independent of Temperature and Blend Partner? Finally, we consider the work of Ediger and co-workers,[10,11,29] who measured the mean segmental relaxation times of PI, when blended with a variety of other polymers. These workers found that the resulting PI self-concentrations depend on the component with which it was blended. We had argued above that, in a qualitative sense, eq 14 would allow us to rationalize these findings. Our results in Table 1 are less convincing. For the four polymers studied we find that the R_{c} values (and hence the self-concentrations) vary considerably even with changes in blend composition. In the same context, we note our discussion above which suggested that a temperature-independent value of R_{c} performed poorly in some cases, e.g., for the PVE component in a blend with 25% PI/75% PVE (Table 1). To potentially resolve these issues, we fit experimental peak relaxation time data to a separate R_{c} value at each experimental point for each component. Figure 5 shows that in all cases the resulting R_{c} are independent of composition and exhibit a modest temperature dependence. We now couple these findings to the

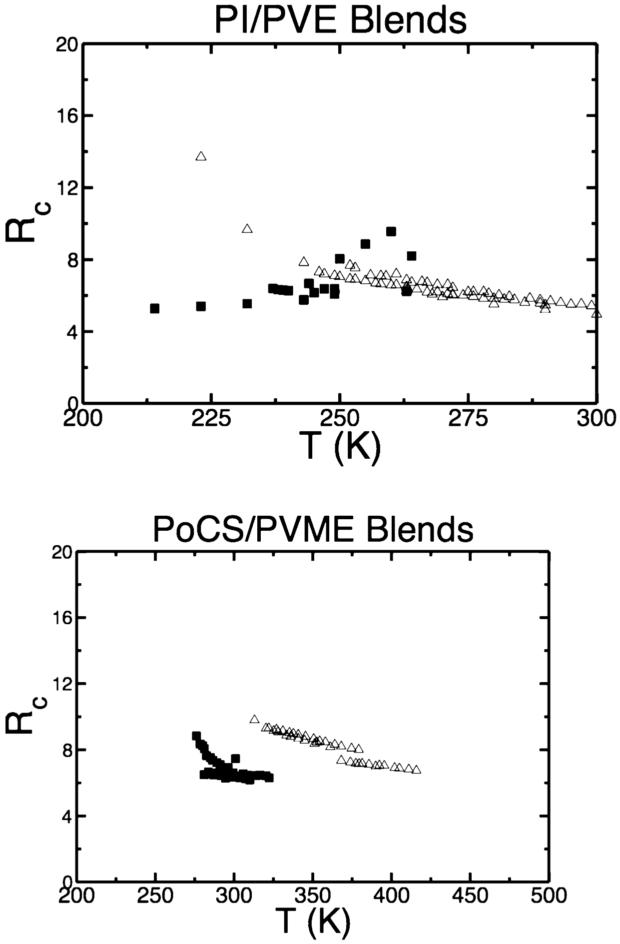

Figure 5. Temperature dependence of the radius of the spherical averaging volume (Å) for PI/PVE blends and for PVME/PoCS blends. The filled squares are the low-T_g components (PI or PVME), and the open triangles are the high-T_g components (PVE or PoCS). R_c may have a weak temperature dependence.

results presented in the companion paper, where we have applied the full concentration fluctuation model (with chain connectivity effects) to the dielectric relaxation behavior of two different blends PI/PVE and PBO/PVE.[30,34] There, we found excellent fits to the full relaxation time distribution in all cases; as will be discussed in the more detailed companion paper,[30] the resulting values of R_c are essentially independent of composition and the blend partner for PVE. However, a weak temperature dependence survives. Similarly, fits to the PS/PVME blend system yield $R_c \sim$ 5 Å for the PVME, a result which is in very good agreement with the R_c values obtained for PVME for the PoCS/PVME blend discussed in Table 1. While we thus argue for very good agreement between the results of this paper and the companion paper, differences in absolute magnitude do persist. For example, we find that R_c for PI is in the range 4.5−6.5 Å, while the companion paper finds $R_c \sim$ 4 Å. Similarly, the results in Figure 5 of the current paper for PVME in a 30/70 PVME/PoCS blend show a much stronger temperature dependence than those found in the second paper. We do not understand these differences but speculate that they might arise because we only fit to the peak time, while the companion paper fits to the overall distribution of relaxation times. With these caveats, however, in a predominant number of cases we appear to be able to fit the experimental results for blend relaxation with R_c values which are independent of the blend partner and composition. However, the resulting R_c values retain a subtle temperature dependence which appears to be a real feature of the data, possibly reflecting the weak temperature dependence of the Kuhn length or packing length. While we are not aware of data for the temperature dependence of chain dimensions for PVE, PVME, or PoCS, SANS data show that the Kuhn length of PI increases weakly with temperature,[35] consistent with R_c of PI in Figure 5.

We thus believe that we have satisfactorily resolved the question raised by Ediger: The results obtained for the dependence of self-concentration on blend partner results from ignoring concentration fluctuations, coupled to the fact that R_c has a weak temperature dependence. In this context it is important to stress that the R_c values themselves can be quite different depending on the model employed. We therefore use R_c as a fitting parameter with some relatively stringent constraints, i.e., that it be of order the Kuhn length and be independent of the blend partner and composition.

Why Are the R_c Values Here So Different in Behavior Than Those Used in Previous Versions of CF Models? Previous versions of concentration fluctuation models (e.g., by Zetsche and Fischer[26] and Kumar, Colby, and co-workers[14,31]) have found that the R_c values necessary to describe experimental relaxation time data appeared to diverge at low temperature, and values as large as 10 nm were found even 20 K above the blend glass transition temperature. In contrast, the values derived in this paper are typically ∼1 nm in size with a weak temperature dependence. It is important to ask why such a difference exists between earlier works and the current paper. The work by Zetsche and Fischer did not include the effects of self-concentration. Additionally, and probably more importantly, this work only considered blends where the dielectric relaxation was dominated by the low-T_g component, which is further from its T_g and hence less sensitive to variations in the value of R_c. The work of Kumar, Colby, and co-workers includes the effects of both self-concentration and concentration fluctuations, but the formulas used to calculate the contribution of concentration fluctuations contained uncontrolled approximations. This work overcomes these deficiencies and uses improved concentration fluctuation expressions in conjunction with a self-consistent expression for the self-concentration. In this last case, we find R_c typically in the 1 nm range, consistent with the ansatz of Lodge−McLeish. We thus assert that CF models yield dynamically relevant length scales which are consistent with the self-concentration model of Lodge−McLeish. However, we show that the inclusion of CF effects permit for an improved description of experimental blend relaxation time data.

Conclusions

Our primary conclusion is that both the mean and peak segmental relaxation times of the constituents of miscible polymer blends are affected by self-concentration and concentration fluctuations. Further, the mean and the peak times fall on different sides of the prediction by the mean-field Lodge−McLeish model, corresponding to the peak in $p(\phi_{\mathrm{eff}})$. These effects become more important as the glass transition temperature is approached, where these three predicted times differ by orders of magnitude. The inclusion of both self-concentration and concentration fluctuations allows us to rationalize experimental data on a range of blends using an averaging volume whose size is ∼1 nm, independent of blend composition and blend partner, with only a weak temperature dependence. Our results suggest that simply incorporating concentration fluctuation effects into the Lodge−McLeish model for self-concentration may thus provide a predictive model for segmental dynamics in miscible polymer blends.

Acknowledgment. We acknowledge the financial support from the National Science Foundation (DMR-0422079). Tim Lodge and Mark Ediger provided many useful comments on this paper, which truly helped us to significantly improve it. We also thank Osamu Urakawa for sending data.

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MA070502Y