

MODELS FOR THE COMPONENT DYNAMICS IN BLENDS AND MIXTURES

K. L. NGAI, C. M. ROLAND*

NAVAL RESEARCH LABORATORY, WASHINGTON DC 20375-5342

ABSTRACT

Four models for the component dynamics in polymer blends are briefly reviewed, with an emphasis on their ability to describe anomalous segmental relaxation behavior, secondary relaxations in blends, mixtures which include small molecules, and properties in the concentration limits of probe molecules and neat polymers. While general features of the segmental dynamics of polymer blends can be accounted for by all of these models, only that of the authors addresses all these particular aspects of blend dynamics. Our conclusion is that assessment of blend dynamics models should extend beyond intuitive appeal or general properties, with due attention given to the more subtle and exceptional behaviors.

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I. INTRODUCTION

There is longstanding interest in the segmental relaxation behavior of polymer blends. Various phenomena have been observed, such as thermorheological complexity, unusual concentration dependences, asymmetric broadening of the relaxation function, the emergence of secondary peaks, and component dynamics differing qualitatively from that of the pure components. The initial obstacle for analyzing blends is the resolution of the component dynamics. The first direct evidence that the segmental dynamics for the respective components of a miscible polymer blend are different came from solid state ^{13}C MAS NMR measurements on 1,4-polyisoprene (PIP) / polyvinylethylene (PVE) blends.¹ The solid state ^{13}C MAS NMR technique allows the components of a blend to be differentiated by their isotropic chemical shifts. Combined mechanical and dielectric spectroscopies were also used to probe the component dynamics in this same blend,² yielding results in quantitative agreement³ with subsequent deuterium NMR measurements.⁴ NMR experiments have also been used to demonstrate dynamic heterogeneity in blends of polyvinylmethylether (PVME) and polystyrene (PS).⁵⁻⁷

Perhaps the first published model addressing the component dynamics of binary polymer blends was by Roland and Ngai (RN).^{2,3,8-11} This approach was based on the coupling model, that has general applicability to the dynamics of polymeric and non-polymeric materials.^{12,13} The coupling model's description of homopolymer dynamics¹⁴⁻²⁰ was extended to blends by incorporating dynamic heterogeneity, due both to the intrinsic mobility differences of the components

* Corresponding author. Ph: 202-762-1719; Fax: 202-769-0594; email: roland@nrl.navy.mil

and to the local compositional heterogeneity from concentration fluctuations. The dynamics of a relaxing species in a blend is determined by its chemical structure, as well as by the local environment, since the latter governs the intermolecular cooperativity associated with the relaxation. Thus, the relaxation of a given species reflects its intrinsic mobility and the degree of intermolecular coupling, or constraints, imposed by neighboring segments, the latter obviously being composition dependent.

In the intervening years, other models of component dynamics in polymer blends have been proposed. Fischer and Zetsche (FZ)²¹⁻²³ developed a model that specifically addressed the effect of local composition on the glass transition temperature, and hence on the dynamics of segments comprising that local environment. Kumar and coworkers²⁴⁻²⁷ extended the FZ concentration fluctuation model. While concentration fluctuations still give rise to subvolumes, each governed by a local glass temperature, Kumar *et al.* invoke the idea that experimental probes of the dynamics only sense compositions fluctuations which occur over a certain cooperative volume. Rather than a constant length scale, the cooperative volume is governed by the local composition. Lodge and McLeish (LM)²⁸⁻³⁰ observed that, when making comparisons to experimental results, the cooperative length scale required to fit the data is too large, on the order of 10 nm or more in both the FZ and the Kumar *et al.* models. LM proposed an alternative model based on the Kuhn length, l_K , of the polymer chain. The segmental relaxation rate of a segment of component A, in a binary blend of polymers A and B, is determined by the composition of its local volume with a length scale of l_K of A. Because of chain connectivity, this local volume is on average richer in A units than the average bulk concentration ϕ_A ("self-concentration" effect). This enhanced local concentration of A is given by $\phi_{\text{eff}} = \phi_A + \phi_{sA}(1 - \phi_A)$, where ϕ_{sA} is the "self-concentration" of A, determined by the volume fraction occupied by A repeat units in a volume of size $(l_K)^3$. Concentration fluctuations have not been taken into consideration. They are unnecessary for the prediction of component relaxation times in the LM model; however, without taking concentration fluctuation into account, the LM model cannot address either the spectral dispersions of the components or their change with composition.

The purpose of the present paper is to reexamine these models. First, we assess their consistency with the available experimental facts, including secondary relaxation phenomena. Secondly, we describe similarities of the component dynamics among polymer blends, mixtures of polymers with small-molecule liquids, and binary mixtures of molecular glass-formers. In some of these systems, anomalous component dynamics were found. The relevant question is whether the polymer blend models can be extended to mixtures containing small molecules or to the anomalous cases. Finally, we examine the predictions of the various models for the dynamics of component A in two limits, $\phi_A \rightarrow 0$ (it becomes a probe molecule), and $\phi_A \rightarrow 1$ (the blend becomes a neat polymer).

II. COMPARISON WITH COMPONENT DYNAMICS DATA FOR POLYMER BLENDS

The above-noted models for component dynamics in polymer blends can all explain some aspects of experimental data. However, at least some of them cannot be right, since they have an entirely different physical basis (excepting the FZ and the Kumar *et al.* models). Of course, conceivably, none of these models are correct. Notwithstanding any intuitive appeal or pervasiveness of a model, the objective criterion must be consistency *in toto* between predictions and experimental results. For the purpose of testing a model, more falsifiable predictions are better, if it withstands the tests. While a model might be credited for one or another explanation, if even one of its predictions is falsified by experiment, then the obvious alternative is to reject the model, at least in its present form. We view this approach to judging models as the best way for progress to be made in scientific research.

There is a recent experiment on component dynamics of polymer blends that can be used to

critically test all four models. This is the NMR study of miscible blends of deuterated poly(ethylene oxide) (d_4 PEO) and poly(methyl methacrylate) (PMMA) by Lutz *et al.*³¹ The authors found that the segmental dynamics of d_4 PEO is nearly independent of composition for blends with 0.5, 3, 6, 10, and 30% d_4 PEO, over a wide temperature range covering both $T < T_g(\phi)$ and $T > T_g(\phi)$, or $T < T_g(\phi_{\text{eff}})$ and $T > T_g(\phi_{\text{eff}})$. As pointed out by Lutz *et al.*,³¹ such behavior is quite different from that of other miscible blends, and is immediately at odds with the predictions of the FZ and Kumar *et al.* models. Moreover, the fits to the data at 10, 20 and 30% d_4 PEO by the LM model requires a value of ϕ_{sA} equal to 0.57, whereas the predicted value of ϕ_{sA} is 0.15.³¹ It is not clear whether the LM model will fit the data at lower concentrations. In any case, these discrepancies led Lutz *et al.*³¹ to conclude that the d_4 PEO segmental dynamics for blends from 0.5% to 30% d_4 PEO cannot be described by these three models. On the other hand, we have tested the RN model against the NMR data of Lutz *et al.*³¹ for the d_4 PEO/PMMA blends, and found that the predictions of the RN model are consistent with the d_4 PEO segmental dynamics over the entire composition range.³² The noteworthy feature of the d_4 PEO/PMMA blends, the insensitivity to composition of the d_4 PEO dynamics, as probed at high frequencies by NMR, is a natural consequence in the RN model of the high frequency and temperature of the NMR experiments. The d_4 PEO independent relaxation time in the NMR experiments approaches the cross-over time for intermolecular coupling (~ 2 ps) of the coupling model.¹³ The RN model predicts accordingly that the effect of local environment on the d_4 PEO component dynamics becomes negligible.

Despite the problems in applying the FZ, Kumar *et al.* and LM models to these experimental data, some constructs of the models - concentration fluctuation in the FZ and Kumar *et al.* models and self-concentration in the LM model - are correct and necessary aspects of a rigorous treatment. However, these inputs are not sufficient, and some additional physics is required to explain more generally the component dynamics in blends. Concentration fluctuations are an essential feature of the RN model, and self-concentration effects, though not explicitly accounted for, make a well-known contribution to the thermodynamics of polymer blends.^{33,34} The additional physics in the RN model is the intermolecular coupling and its dependence on local composition. Since the RN model stems from the coupling model, there is a primitive relaxation time, τ_{0A} , along with a crossover time, $t_c \approx 2$ ps, both of which exert a crucial effect on the d_4 PEO dynamics in d_4 PEO/PMMA blends.³² There are other aspects of the relaxation behavior of glass-forming systems, beyond segmental dynamics in binary polymer blends, for which intermolecular coupling is needed to explain the observed effects. These examples are introduced in the sections to follow.

III. EFFECT OF COMPONENT DYNAMICS ON SECONDARY RELAXATIONS IN POLYMER BLENDS

A more ambitious model of polymer blends addresses dynamics beyond the segmental relaxation. The change of segmental dynamics of component A with concentration may also be accompanied by a change of the secondary, Johari-Goldstein (JG) relaxation.^{35,36} The nomenclature JG implies that the motion involves the polymer backbone, to distinguish it from secondary relaxations of only a side group. The secondary relaxations in poly(*n*-methyl methacrylate) and poly(*n*-ethyl methacrylate) involve not only an 180° flip of the $-\text{O}-(\text{C}=\text{O})-$ plane of the pendant moiety, but also the rocking motion of part of the repeat unit on the main chain.^{37,38} This means that this process is a JG relaxation, as is, by inference, the secondary relaxation of poly(*n*-butyl methacrylate) (PBMA), the next higher member of the poly(*n*-alkyl methacrylate) series. The JG secondary relaxation is the precursor to the primary structural relaxation,^{17,39,40} and thus of some import in studies of blend segmental dynamics.

On increasing the styrene content from 0 to 66 mol% in a series of PBMA copolymers, a monotonic increase in the separation of the JG relaxation from the segmental relaxation was

measured.⁴¹ This separation can be quantified as the difference between the logarithm of the respective relaxation times, τ_{α} and τ_{β} , for segmental and JG motions

$$\Delta_A \equiv \{\log[\tau_{\alpha A}(T_{gA})] - \log[\tau_{\beta A}(T_{gA})]\}, \quad (1)$$

at the dielectric glass temperature T_{gA} of the PnBMA component. The usual changes in the segmental dynamics of the PBMA component were also observed. In the context of the RN model, the intermolecular coupling parameters of PBMA, n_{Ai} , in its various local environments $\{i\}$ are enhanced by the presence of the less mobile styrene repeat units; thus, as the styrene content of the blend increases, the intermolecular coupling of the PBMA units increases. This increase is then explained by the coupling model⁴²: [i] $\tau_{\beta A}(T_{gA})$ is approximately the same as the primitive relaxation time $\tau_{0A}(T_{gA})$ because they are of the same character^{17,39,40} and [ii]

$$\Delta_A \approx \{\log[\tau_{\alpha A}(T_{gA})] - \log[\tau_{0A}(T_{gA})]\} = 11.7n_A + n\log[\tau_{\alpha A}(T_{gA})], \quad (2)$$

where n_A is the most probable n_{Ai} among the distribution of environments. The large increase of Δ_A with styrene content implies a correspondingly large increase of n_A . The latter is supported by the large increase of the steepness (fragility) index m with styrene content.⁴² There is a well-established empirical correlation between n_A and m ,^{20,43,44} which hold especially well for glass-formers of the same chemical same family.

On the other hand, miscible blends of poly(4-vinylphenol) and poly(ethyl methacrylate) (PVPh/PEMA)⁴⁵ exhibit slight broadening of the segmental relaxation dispersion, consistent with suppressed concentration fluctuations due to hydrogen bonding between the PVPh and PEMA. Also, there is little change in m with composition. These observations indicate a small change in the intermolecular coupling parameter n_A of either PEMA or PVPh in their blends. Thus, the observed small change in the separation $\{\log[\tau_{\alpha A}(T_{gA})] - \tau_{\beta A}(T_{gA})\}$ for either component PEMA or PVPh is a result expected from Equation (2) and our blend model.

Neat PVME has two distinct secondary peaks, located at high frequencies. At T_g , one loss peak is (already) above 10^8 Hz, and the other is at even higher frequency.⁴⁶ Such short relaxation times cannot be reconciled with $\tau_{\alpha A}(T_{gA})$ for any reasonable value of n_A , especially given the low steepness index and T_g of neat PVME. Thus, it is likely these peaks reflect local motion of the O-CH₃ side group, rather than a JG relaxation involving all atoms of the repeat unit. Indeed, simulations have shown free and restricted rotational motion of the methyl ether group about the O-C bond.⁴⁶ When the dielectric loss ϵ'' of neat PVME is displayed in a double logarithmic plot versus frequency, the high frequency flank of the α -peak exhibits an unusually slow decrease with increasing frequency, after which ϵ'' rises again to form a secondary peak above 10^8 Hz. We expect that the (universal) JG relaxation is hidden under this high frequency flank of the α -process, because the separation, Δ_A , estimated as $\{\log[\tau_{\alpha A}(T_{gA})] - \log[\tau_{0A}(T_{gA})]\}$, is not large given the small magnitude of n_A . Dielectric data presented in terms of $\tan\delta \equiv \epsilon''/\epsilon'$ apparently have higher sensitivity for detection of the JG relaxation. In fact Pathmanathan and Johari⁴⁷ found the resolved Johari-Goldstein relaxation from their $\tan\delta$ data at frequencies not much higher than the α -loss peak frequency. A straight-forward prediction of the RN model applied to PVME/PS blends¹⁰ is the increase of n_A for the PVME component with increasing content of the less mobile PS. Therefore, from Equation (2), an ancillary prediction of the RN model is an increase of the separation Δ_A with increasing PS concentration. For blends with large enough PS concentrations, Δ_A will be sufficient for the JG relaxation of PVME to be resolved as a distinct peak. This prediction is borne out by dielectric relaxation data for blends with 70% or higher PS concentrations.⁴⁸ For these compositions, a new relaxation loss peak appears, at a frequency intermediate between that of the α -peak and the high frequency secondary relaxation peak. The

new peak has an Arrhenius temperature dependence at temperatures below T_{gA} of the PVME component, and its dielectric strength increases with temperature [see Figure 5 of Reference 48]. These characteristics indicate that the relaxation is indeed a JG process. This JG process of the PVME component in such compositions is resolved as a separate peak in blends with high PS content because of the large n_A , and its relaxation time τ_β is further separated from τ_α , as follows from Equation (2) The isochronal dielectric data at 1 kHz for 70% PVME mixed with 30% poly(2-chlorostyrene)⁴⁶ also show a resolved JG secondary relaxation, and a similar explanation from the RN model applies. Essentially, these same effects are seen in mixtures of small molecule liquids, as discussed in the next section. The generality of this behavior of JG relaxations is anticipated by the RN model.

IV. ANOMALOUS DYNAMICS IN BLENDS AND MIXTURES

From the experimental viewpoint, the component segmental dynamics of polymer blends should be no different from the local dynamics of the components in polymer solutions or mixtures of two small molecules (SM mixtures). Similar to polymer blends, in these other systems (i) concentration fluctuations exist, (ii) each component has its own local dynamics, which differ from that in the pure state, (iii) there is asymmetric broadening of the local relaxation function, and (iv) there is a breakdown of time-temperature superpositioning. For polymer solutions, as far as we are aware, the first experimental evidence of component dynamics was presented by Plazek *et al.*⁴⁹ for polystyrene/tricresylphosphate mixtures, in which each component exhibits its own glass transition temperature. The phenomena of modification of solvent dynamics by the presence of polymer^{50,51} is analogous to the component dynamics in polymer blends. One expects models for polymer blends (*e.g.*, RN, FZ, Kumar *et al.*, and LM) to be applicable to the segmental dynamics in polymer solutions. In fact, some of the common features of the component dynamics observed in some polymer solutions are consistent with predictions from all models.

However, anomalous component dynamics are found in some polymer solutions, and these need to be addressed by a viable model of blend dynamics. Anomalous dynamics were found in polymer solutions having components of nearly equal T_g 's. The glass transition temperature of the blend and the segmental relaxation times of the components can be less than those of either neat component, as seen in mixtures of PVE with polychlorinated biphenyl⁵²⁻⁵⁴ and poly(methylphenylsiloxane) with 1,1-bis-(p-methoxyphenyl) cyclohexane.^{55,56} This same anomaly was also seen in a polymer blend, epoxidized natural rubber with polychloroprene.⁵⁷ The opposite anomaly, in which T_g 's and relaxation times in the blend are greater than those of either neat component, has been observed as well, in blends of PVME with polyepichlorohydrin.^{58,59} Models based on a distribution of local T_g 's due to concentration fluctuations, like those of FZ and Kumar *et al.*, as well as the LM model based on self concentration, all use the Fox-Flory equation, $1/T_g(\phi) = \phi/T_{gA} + (1-\phi)/T_{gB}$, to generate the component relaxation times in one fashion or another. The glass transition temperature of the mixture and the relaxation times of the components predicted by these models, therefore, cannot lie outside the bounds determined by the neat components. Hence, the models of FZ, Kumar *et al.* and LM do not explain the aforementioned anomalies. Of course, when an anomaly is caused by some factor external to a model's purview, such as a large excess volume or strong interaction between the components which changes their chemical nature, failure to account for such an anomaly cannot be used to indict the model. Rather, the model needs to be extended to incorporate the additional effects. Notwithstanding, the RN model has been shown to account for at least some of the aforementioned anomalies.^{53,55,56}

A recent work on creep compliance of mixtures of polystyrene with tri-cresyl-phosphate (TCP)¹⁵ has shown that the glass-rubber softening dispersion of the PS component as well as the

T_g -scaled temperature dependence of its segmental relaxation time can be made to resemble neat polyisobutylene at some concentration. These properties of the PS/TCP mixtures were explained by the reduction of intermolecular coupling of the polystyrene component in the presence of the solvent, which is conceptually the basis of the RN model for blends.

The explanation from the RN model also applies to results for tris(2-ethyl-hexyl) phosphate (TOP), which has an opposite effect on the γ -relaxation times in bis-phenol-A-polycarbonate (BPA-PC), as does tetramethyl-bis-phenol-A-polycarbonate (TMBPA-PC). Dynamic mechanical⁶⁰ and dielectric relaxation⁶¹ measurements showed that addition of TOP to TMBPA-PC increases the relaxation rate of the γ -process; however, the opposite effect was found when TOP was added to BPA-PC – the γ -process became slower. NMR experimental data on the same mixtures confirmed these findings.⁶²

In the preceding section, we discussed the effect on the JG relaxation of polymer A, when it is blended with another polymer B, the latter having a much higher T_g . The interesting case is when the JG relaxation cannot be easily resolved in neat polymer A, having a small coupling parameter n_A , whereby the separation, $\Delta_A \equiv \{\log[\tau_{\alpha A}(T_{gA})] - \log[\tau_{\beta A}(T_{gA})]\}$ of the JG relaxation from the α -relaxation is small. In the RN model for component segmental dynamics, adding a sufficient amount of polymer B, having a much higher T_g , increases n_A , and hence it follows from Equation (2) that the separation Δ_A is increased, whereby the JG relaxation is further separated and hence resolved. This scenario pertains whether or not either A or B is polymeric. In fact, the effect was found in mixtures of picoline with ortho-terphenyl⁶³ and with tri-styrene,^{64,65} in which picoline corresponds to component A. Neat picoline has a small n_A , equal to *ca.* 0.30 near $T_g = 133$ K. Consequently, from Equation (2), the JG relaxation is not well separated from the α -relaxation, and indeed, the JG relaxation of neat picoline has never been resolved experimentally. On mixing with ortho-terphenyl ($T_g = 247$ K) or tri-styrene ($T_g = 233$ K), n_A is enhanced and the separation Δ_A becomes larger. As expected, a distinct JG relaxation for picoline is seen in these blends and Δ_A increases monotonically with the concentration of the higher T_g component B. Using the combination of Equations (1) and (2), one can deduce n_A from the experimentally determined Δ_A .⁶⁶ Thus, taking advantage of the extra prediction of the coupling model for the JG relaxation of component A, the important parameter n_A of the dynamics of the α -relaxation of component A in mixtures is determined. Another example is sorbitol, which has a larger n_A than picoline, and a well resolved JG relaxation.^{67,68} When mixed with the more mobile glycerol, n_A of sorbitol should decrease, which makes the separation Δ_A smaller, as has been observed.⁶⁹

V. PROBE DYNAMICS ($\phi_A \rightarrow 0$)

At very low concentrations, ϕ_A , the component A is reduced to the role of a probe. Each probe molecule experiences the same environment, which eliminates complications from concentration fluctuations. Although not necessary, it is certainly desirable for a model of component dynamics of mixtures to have valid predictions for this limiting case. Since the crux of the FZ and the Kumar *et al.* models is concentration fluctuations, they cannot address probe molecule dynamics. If the probe is not a polymer, the LM model is no longer applicable. In the RN model, which is applicable to the dynamics of small molecules as well as polymers, the essential physics is intermolecular coupling, which remains active at all concentrations. For a probe molecule A dispersed in host B, the degree of intermolecular coupling, measured by the coupling parameter n_A , depends on the respective chemical structures, as well as on the mobility difference between A and B. The latter can be measured by the ratio, τ_c/τ_α , where τ_c is the rotation correlation time of probe A and τ_α is the α -relaxation time of the bulk sample (which is just $\tau_{\alpha B}$). According to the RN model, the larger the ratio of τ_α to τ_c , the larger n_A will be for the probe molecule. In the absence of concentration fluctuations, the predicted correlation function of the probe rotation is just the Kohlrausch function. Indeed, this correlation function is found in probe

rotation experiments.⁷⁰⁻⁷³ Thus, in the absence of concentration fluctuations, there is no distribution of any kind. The coupling parameter n_A can be determined directly from the measured probe rotational correlation function, and the prediction of its increase with the ratio, τ_c/τ_c , can be falsified or verified. The data (see, for example Figure 2 in Reference 73) show that n_A increases in the predicted way with increasing τ_c/τ_c . These results from probe dynamics experiments corroborate a principal aspect of the RN blend model, concerning the role of local environment on the relaxation function of a constituent.

VI. HOMOPOLYMER SEGMENTAL DYNAMICS ($\phi_A \rightarrow 1$)

When $\phi_A \rightarrow 1$, the study of the component dynamics in a blend becomes the study of the segmental dynamics of a neat polymer. The FZ, Kumar *et al.* and LM models all reduce to the empirical Vogel-Fulcher-Tammann equation (or equivalent WLF equation) in this case. These models add no new physics to familiar phenomenology, nor do they attempt to further describe segmental relaxation. However, it can be argued that if model does not (or cannot) address neat materials (a limiting case), there are limited prospects for successfully addressing the diverse segmental relaxation behavior, encompassing many anomalies and even new physics, seen in polymer blends.

A large body of work^{16,18,20,74-79} has shown that intermolecular coupling is an essential aspect of the segmental dynamics. The size of the coupling parameter n_A appearing in the correlation function depends on the chemical structure of the repeat unit through its capacity for intermolecular coupling. This explains the differences in n_A from one polymer to another, as well as trends in the change of n_A with changing local environment.^{16,18,20,74-79} There are other predictions concerning the segmental dynamics which stem from n_A .⁸⁰ One example is the anomalous dependence on the scattering vector (Q) of segmental relaxation times. Instead of the normal Q^2 -dependence, it is observed⁸¹ that this dependence can be easily derived from the coupling model.⁸⁰

VII. MOLECULAR DYNAMICS SIMULATIONS

The important ansatz of the RN blend model is that each environment i of polymer A is associated with a coupling parameter, n_{Ai} , the magnitude of which depends on the intermolecular constraints imposed on the segmental motion of A. The correlation function is given by the Kohlrausch function

$$\Phi_{Ai}(t) = \exp[-(t/\tau_{Ai})^{1-n_{Ai}}] \quad (3)$$

with the relaxation time τ_{Ai} given by

$$\tau_{Ai} = [t_c^{-n_{Ai}} \tau_0]^{1/(1-n_{Ai})} \quad (4)$$

This ansatz can be obtained via some formal mathematical procedures;^{82,83} however, here we support the idea with results from molecular dynamics simulations of an analog system.

Scheidler *et al.*⁸⁴ carried out molecular dynamics simulations of a binary LJ liquid thin film confined by frozen configurations of the same system. The film thickness was 15.0 in units of the length parameter, z , of the Lennard-Jones potential, with the film center at a distance $z = 7.5$ from the confining walls. An important feature of the simulation⁸⁴ is the interaction of the mobile particles in the film with the immobile particles comprising the confining walls. Interaction between the mobile and the immobile particles occurs via the Lennard-Jones potential, the same

as between mobile particles. The particles in the immediate vicinity of the wall are highly constrained (*i.e.* strongly coupled) because of the neighboring immobile particles of the wall (the analogue of the component *B* that has much higher T_g in mixture with *A*). Thus, the ansatz of the RN model leads to the expectation that the first layer of particles will have a large n . The advantage of simulation is that the self part of the intermediate scattering function, $F_s(q, z, t)$, can be calculated for layers at any chosen distance z from the wall. All particles at the same distance from the wall are equivalent, including those in the first layer. In fact, for z_1 corresponding to the first layer, $F_s(q, z_1, t)$ obtained by simulation has the Kohlrausch form,

$$F_s(q, z_1, t) = A(z_1) \exp[-(t/\tau(z_1))^{1-n(z_1)}] \quad (5)$$

with $n(z_1)$ much larger and the relaxation time $\tau(z_1)$ much longer than the corresponding quantities for particles in the bulk. Thus, the dynamics of the first layer are consistent with the RN ansatz of larger $n(z_1)$ because of proximity to the wall, and the RN result of large $\tau(z_1)$. The particles in the second layer at z_2 are constrained by the partially immobilized particles (*i.e.*, having longer $\tau(z_1)$) of the first layer. According to RN, they will have their own $n(z_2)$ and $F_s(q, z_1, t)$. The constraints on the particles in the second layer are weaker than on the first layer, because unlike the wall, the first layer is not totally immobilized. Hence, we expect that $n(z_2)$ is less than $n(z_1)$, and that $\tau(z_2)$ is shorter than $\tau(z_1)$. Continuing application of our ansatz to the j^{th} layer, we have $n(z_1) > n(z_2) > \dots > n(z_j) > n(z_{j+1})$, and $\tau(z_1) > \tau(z_2) > \dots > \tau(z_j) > \tau(z_{j+1})$. Eventually at a sufficiently large distance from the wall, the enhancement of constraints vanishes, and the coupling parameter and relaxation time assume their bulk values. The data from the simulations are in complete accord with this description.

Furthermore, the relaxation time $\tau(z_j)$ and the coupling parameter $n(z_j)$ obtained from the simulation were shown⁸⁵ to follow Equation 4 approximately for all j , with the same primitive relaxation time τ_0 . This was the same assumption (*i.e.*, τ_0 is independent of local environment) employed in the application of our RN model to data on conventional polymer blends.

When all particles in the confined thin film are included in the calculation, the intermediate scattering function, $F_s(q, t)$, does not have the Kohlrausch stretched exponential time dependence. Instead, it exhibits a long-time tail, which when Fourier transformed causes asymmetric broadening towards low frequencies. This effect is similar to the dielectric frequency dispersion of a polymer blended with a less mobile component, such as PVME mixed with polystyrene,⁸⁶ as described by the RN model.¹⁰

VIII. DISCUSSION AND CONCLUSION

The physical chemistry of polymers is an interdisciplinary field, involving researchers whose technical backgrounds span chemistry, materials science and physics. The criteria for what constitutes an acceptable explanation of component dynamics can be quite different, depending on the individual's background. We highlight two views.

(i) One viewpoint is that if a model can explain the best-known features of the component dynamics, it is considered to be acceptable, although it might not explain, or is even at odds with, anomalous or obscure aspects of blend behavior. Anomalies are thus categorized as special cases, having some attribute that makes them exceptional. Possibilities for such attributes include strong specific interactions (*e.g.*, hydrogen bonding) between the components, which effectively give rise to new chemical species, or large changes in volume due to mixing, which introduces an additional mechanism not usually addressed by models for blend dynamics.

An example of an anomaly is the dynamics of d_4 PEO found in d_4 PEO/PMMA blends.^{31,32} As discussed above, this situation cannot be explained by the models of FZ, Kumar *et al.*, or LM,

and has been rationalized as an exceptional case, due to the absence of any side-groups in PEO.³¹ However, essentially the same anomaly was found in the PVME component of PVME/PS blends, and PVME has a pendant group. Of course, since chemical structure does not enter into the FZ, Kumar *et al.*, or LM models, it is not clear why their applicability should be restricted with regard to details of the chemical structure. Evidently, the anomalous d₄PEO dynamics in d₄PEO/PMMA blends violates the predictions of these three models.

Another anomaly described above concerns polymer solutions, and this anomaly has been observed in several systems. From the constructs of the FZ, Kumar *et al.* and LM models, these should be applicable to polymer solutions. Thus, various solutions also represent violations of the three models. However, if the success of a model is determined by its viability for the general cases and best-known properties, the anomalies found in a handful of systems may be viewed as unimportant exceptions, a consequence of special attributes of particular systems.

(ii) The alternative view emphasizes the anomalies, since they can offer critical tests of competing ideas. A model is considered deficient if it cannot address the special cases. Moreover, if a model makes predictions that are contradicted by experiments, then the model has to be rejected, notwithstanding how intuitively appealing or generally useful a model may seem to be. Failure to describe some specific aspect of behavior reveals a critical defect in the model's underlying basis. From this viewpoint, the anomalies in the dynamics of either d₄PEO or PVME in blends, as well as the anomalous polymer solution dynamics, are a sufficient basis to reject the FZ, Kumar *et al.*, and LM models, at least as presently constructed.

Of course, there are other aspects of a model, which bear on its utility and acceptability. One aspect is the rigor underlying its derivation. Although the dynamics in condensed matter, certainly including polymers, is too complex for any first-principles calculations at the present time, the use of general physical principles at the model-building stage is certainly reassuring. Another desirable aspect of a model is a lack, or minimum number, of adjustable parameters. Moreover, the values of any parameters should be independently verifiable, and not only available from data fitting. A case in point is the LM model, whose only parameter is the self-concentration ϕ_{sA} of component A. ϕ_{sA} can be calculated from known characteristics of the neat polymer A. Of course, some assumptions have to be made in order to minimize the number of parameters; nevertheless, it is quite impressive when predictions of the relaxation time of component A for various concentrations are found to be in agreement with experiment (although some disagreements with experiment have been reported.⁸⁷ The neglect of concentration fluctuation does not allow the LM model to address the shape of the dispersion, nor can this model describe non-polymeric component dynamics.

Finally, we note that the RN model does not give a prescription for calculating either the coupling parameter n_A nor its distribution. In this regard it is less ambitious than the LM model, which has effectively no unknown parameters. However, the LM model makes no attempt to address the spectral dispersion of the component dynamics, which in the RN model is described by the distribution of n_{Ai} . The spectral dispersion and the characteristic relaxation time of a component are two distinct pieces of information. Hence, extension of the LM model to address the shape of the relaxation spectra would necessarily require additional parameters to be introduced. In a similar fashion, the FZ and the Kumar *et al.* models have distribution parameters, which are used to fit the dispersion. However, unlike the RN model, these distribution parameters are not related to the relaxation time. The RN model, and the coupling model on which it is based, is the only approach in which the dispersion has a direct bearing on the magnitude of the relaxation time.

From n_A of the neat component, the RN model predicts the qualitative changes in n_A with composition, accounting for the asymmetric broadening of the dispersion for the more mobile component. From the changes in n_A , the RN model describes the variation in the difference

between the α -relaxation time and the Johari-Goldstein secondary relaxation time for the component. And of most general utility, this model addresses the dynamics of component A in the two limits: $\phi_A \rightarrow 0$ (it becomes a probe molecule) and $\phi_A \rightarrow 1$ (a neat polymer).

IX. ACKNOWLEDGEMENTS

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