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Predicting the Time Scale of the Component Dynamics of Miscible Polymer Blends: The Polyisoprene/Poly(vinylethylene) Case

Daniele Cangialosi,*,† Angel Alegría,‡ and Juan Colmenero†,‡

Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain, and Departamento de Física de Materiales, Facultad de Química, Universidad del País Vasco (UPV/EHU) y Unidad de Física de Materiales Centro Mixto (CSIC−UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain

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ABSTRACT: In this study, we predict the component segmental dynamics of polyisoprene/ poly(vinylethylene) (PI/PVE) blend employing a model, recently presented by Cangialosi et al. [*J. Chem. Phys.* **2005**, *123*, 144908], which combines the concept of self-concentration with the Adam−Gibbs (AG) theory of the glass transition. As the model requires the fitting of one unknown parameter connecting the characteristic length scale for segmental relaxation with the configurational entropy, PI and PVE dynamics in toluene have been investigated to extract indirectly this parameter for each of the two polymers. The employment of a mixing rule through the effective concentration to evaluate this parameter for each polymer in the blend allows the prediction of the time scale for segmental relaxation of PI and PVE in the blend. Thus, the model turns to be fully predictive. Therefore, it can be used also for those blends for which the dynamic response of the two polymers is highly overlapped as is the case of the PI/PVE blend. The characteristic length scale for segmental relaxation predicted by the model was between 1.3 and 1.8 nm for both polymers in the blend depending on the temperature.

Introduction

Mixing of polymers with different characteristics has increasingly become an attractive route to obtain materials with improved properties. For this reason, predicting the properties of polymer blends is a subject of great interest. In this framework, a wide body of studies has long been performed on the segmental dynamics of miscible polymer blends. Despite the great effort made, the underlying dynamic behavior of miscible polymer blends is still a matter of open debate. In particular, the scientific debate has been focused on the explanation of two main signatures of the segmental dynamics, namely the failure of the time−temperature superposition[1] and the presence of two distinct segmental dynamics.[2,3] The former experimental evidence can be explained advocating the role of thermodynamically driven concentration fluctuations.[4−8] These create a distribution of environments that induces a general broadening of the dynamic response. On the other hand, nowadays the scientific community has widely agreed that the presence of two distinct segmental dynamics can be mainly attributed to the effect of self-concentration,[9−11] giving rise to an effective concentration in the volume relevant for segmental relaxation different from the macroscopic one. Beyond the recognition of the crucial role of self-concentration, Lodge and McLeish[10] have formulated an additional hypothesis assuming that the characteristic length scale for segmental relaxation is temperature independent and of the order of the Kuhn segment, i.e., on the order of nanometers. More recently, Kant et al.,[12] without making any a priori hypothesis on the relevant length scale, and Cangialosi et al.,[13,14] in the framework of the Adam−Gibbs (AG) theory,[15] have suggested that an increasing length scale with decreasing temperature is compatible with the description of dynamics and, in some cases, even allows a more accurate fitting of data.[14,16]

In an attempt to apply these ideas, polyisoprene/poly(vinylethylene) (PI/PVE) system, a typical miscible polymer blend known to possess a slightly negative Flory−Huggins interaction parameter (χ), has been the subject of intense research in the past decade.[2,3,5−12,17−25] To predict the effective glass transition temperature (T_g) both PI and PVE in the blend, Lodge and co-workers[10,21] have exploited the concept of self-concentration with a temperature independent length scale of the order of the Kuhn segment, which is the base of the Lodge−McLeish model. The model turned out to be rather successful in describing the segmental dynamics of both components at temperatures well above T_g, whereas it seems to be somewhat inaccurate when attempting to predict the dynamics at temperatures closer to T_g (see, e.g., the prediction of the effective T_g(s) of the two components in Figure 5 of ref 10 and Figure 7 of ref 21). On the other hand, Kant et al.,[12] also employing the concept of self-concentration and its effect on the blend dynamics but allowing a temperature variation of the relevant length scale, successfully fitted dynamics data. However, unphysically large length scales, corresponding to self-concentration approaching zero, had to be employed to fit PVE dynamics data in the blend.

In this work, we attempt to provide a description of PI/PVE dynamics data obtained through dielectric spectroscopy by means of a model, recently presented by us.[13] The model combines the self-concentration concept with the AG theory,[15] relating the relaxation time and the characteristic length scale for structural relaxation to the configurational entropy. The model relies on the fitting of just one parameter, i.e., the proportionality constant connecting the characteristic length scale to the configurational entropy. This constant, as discussed in a very recent paper,[26] can be indirectly derived from the application of the model to concentrated solutions of the pure polymer in a solvent, making the model free of any fitting parameter, apart from those of the pure components, i.e., fully predictive. In this study, we have investigated PI and PVE solutions in toluene together with the dynamics of PI/PVE blends. Moreover,

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[†] Donostia International Physics Center.

[‡] Departamento de Física de Materiales, Facultad de Química, Universidad del País Vasco (UPV/EHU) y Unidad de Física de Materiales Centro Mixto (CSIC−UPV/EHU).

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we have refined the model assumptions compared to its original version[13] to make it more general, as will be discussed in the next section of the paper.

Model Refinement

To apply the AG theory in combination with the self-concentration concept to the dynamics of miscible blends, two main conjectures of the AG theory are exploited: (i) the relationship between structural relaxation time and configurational entropy; (ii) the growing length scale for structural relaxation with decreasing temperature as a consequence of the reduction of the configurational entropy.

The connection between the structural relaxation time and the configurational entropy for the component dynamics of polymer blends is expressed by the following relation:[15]

$$\tau = \tau_0(\phi_{\text{eff}}) \exp\left[\frac{C(\phi_{\text{eff}})}{TS_{\text{c}}(\phi_{\text{eff}})}\right] \tag{1}$$

Here T is the temperature, S_c is the configurational entropy, C is a material specific parameter, and τ_0 is the relaxation time at infinite temperature. All these parameters need to be estimated in the volume involved in the structural relaxation and, in general, will be function of the effective concentration in that volume. The effective concentration is related to the self-concentration through:[10] $\phi_{\text{eff}} = \phi + (1 - \phi_s)\phi$. The self-concentration ϕ_s is defined as the volume fraction occupied by the chain of a polymer within a sphere of radius r_c centered in a monomer of such a chain. The dependence of the configurational entropy on the effective concentration rationalizes the effect on the dynamics of one component induced by the presence of the other component and has been recently demonstrated at a molecular scale by solid-state NMR.[27,28]

The relevant volume for structural relaxation is related to the decrease of the configurational entropy of the glass-former:[15]

$$V \propto S_c^{-1} \tag{2}$$

This volume can be related to the characteristic length scale for structural relaxation, r_c through: $r_c = V^{1/n}$, where n is the fractal dimension for the growth of the relevant volume. Simulation studies well above T_g in the framework of the dynamic heterogeneity suggest that $n = 2$, with a tendency to increase with decreasing temperature.[29-31] However, the random first-order transition by Wolynes and co-workers[32] predicts an evolution to a more compact shape when the laboratory T_g is approached from above, and very recent simulation studies also suggest a three-dimensional shape of the relevant volume.[33] In this study, we have found a good agreement with experimental data for $n = 3$ (relevant volume growing in three directions). According to the previous considerations, the radius of the characteristic length scale for structural relaxation can be expressed as

$$r_c(\phi_{\text{eff}}) = \alpha\, [S_c(\phi_{\text{eff}})]^{-1/3} \tag{3}$$

where α is a material specific parameter which, as will be shown later in the paper, can be evaluated from the fitting of dynamics data or, once it is known indirectly, introduced in the model to make it fully predictive.[26] r_c can be related to the self-concentration (and therefore to the effective concentration) through simple geometric considerations involving the packing and the Kuhn length (respectively l_p and l_k).[12,13]

To apply the model, the parameters of eq 1 have to be expressed as a function of the effective concentration. In the original version of the model,[13] the preexponential factor was kept constant and equal to that of the polymer for which the segmental dynamics is examined. On the other hand, the configurational entropy S_c and the parameter C were evaluated as a linear combination of S_c and C of the pure components through the effective concentration. However, we notice that a constant preexponential factor would induce inconsistent results for those systems where the effective concentration approaches zero (infinite dilution and large characteristic volume for relaxation). In this case, the dynamics should be that of the other component of the blend, being this largely in excess in the characteristic volume for relaxation, and, therefore, according to eq 1 the preexponential factor should be that of the other component of the blend. For this reason, a mixing rule to evaluate the preexponential factor should be more appropriate and, therefore, has been employed in this work.

Moreover, in the original version of the model, the excess entropy was used instead of the configurational entropy, experimentally inaccessible, exploiting the proportionality between the two quantities.[34-37] Furthermore, it was assumed that the excess vibrational entropy, which together with the configurational entropy composes the total excess entropy, contributes in a similar way for both polymers of the blend. This means that the linear combination between the excess entropies of the pure components through the effective concentration could be employed also to calculate the configurational entropy of each component in the blend. However, it seems that the hypothesis of similar vibrational contribution to the excess entropy is not a good approximation for PI and PVE. According to the theoretical approach of DiMarzio and Dowell,[38] the configurational entropy accounts for 91% of the total excess entropy for PI, whereas it only accounts for 72% for PVE. Therefore, the configurational entropy of component A in the blend on the volume relevant for structural relaxation can be obtained starting from the excess entropies of the pure components as

$$S_c^{\text{A/Blend}} = \phi_{\text{eff}} S_c^{\text{A}} + (1 - \phi_{\text{eff}}) S_c^{\text{B}} = \phi_{\text{eff}} m S_{\text{ex}}^{\text{A}} + (1 - \phi_{\text{eff}}) n S_{\text{ex}}^{\text{B}} \tag{4}$$

where m and n are the ratio of the configurational to the excess entropy of respectively component A and B. A similar expression can be written for the configurational entropy of B in the blend. It is worth noticing that eq 4 is compatible with the Flory−Huggins approximation of polymer solutions thermodynamics. According to this theory, the entropy of mixing: $\Delta S_{\text{mix}} = S_{\text{AB}} - [\phi_A S_A + (1 - \phi_A) S_B]$, is composed by a combinatorial term ΔS_{comb} and an interaction parameter χ_S. However, the combinatorial term does not affect the dynamics and, therefore, the configurational entropy of the AG equation must be depurated of this term, and for PI/PVE blend the interaction term is negligible; namely, the blend is almost athermal.[39] Therefore, ΔS_{mix} approximately equals zero and eq 4 is obtained.

Finally, in the initial application of the model,[13,14] a single parameter α, relating the characteristic length scale for structural relaxation to the configurational entropy, was found for each polymer, independently of the other polymer in the blend and its concentration. This result suggested that α must be a material specific constant. However, it was anticipated that the model could be refined including a mixing rule also for the α parameter, which would be significant only for those binary systems with components displaying rather different intrinsic values of α. In this case, the presence of the other component in the characteristic volume for structural relaxation affects the effective value of α. As will be shown in the result section, a mixing rule for the α(s) of the pure polymers through the effective concentration is more appropriate to describe the component segmental dynamics of PI/PVE blend, since the two components of the blend display rather different values of α. In other words, each polymer contributes to the α in the blend with its own α and with a weight which depends on its effective concentration in the blend.

To summarize, the application of the model is based on the knowledge of the following parameters of the pure components: (i) dynamic parameters, i.e., C, τ_0 and T_K (the temperature where the relaxation time would diverge) of the AG equation; (ii) thermodynamic properties, i.e., the configurational entropy obtained from the excess entropy from calorimetric measurements and the knowledge of the contribution of the former quantity to the latter (*m* and *n*). In addition, the model is based on the hypothesis of ideal mixing of the two components that, in the framework of the Flory−Huggins theory of polymer solutions, implies a mixing rule of the configurational entropies of the pure components through the effective concentration to obtain the configurational entropy of each component in the blend. A similar mixing rule is also imposed for C and τ_0 of the AG equation, though in this case the assumption is empirical. This assumption is less critical the more the parameters of the pure components are similar. Finally the fractal dimension for the growth of the characteristic length scale for segmental relaxation is also assumed a priori. This means that, once all the needed parameters of the pure components of the blends are known, combining eqs 1, 3, and 4, parameter α, connecting the characteristic length scale to the configurational entropy is the only free parameter that must be fitted to experimental data.

Experimental Section

1,4-Polyisoprene (PI) and 1,2-polybutadiene (1,2PB or PVE) were purchased from Polymer Source Inc. The molecular weights were $M_n = 3 \times 10^4$ ($M_w/M_n = 1.04$) for 1,4PI and $M_n = 1.7 \times 10^4$ ($M_w/M_n = 1.04$) for PVE. It is worth noticing that PVE possesses >85% of 1,2PB dyads, the rest being 1,4 ones. The presence of 1,4PB dyads results in a slight speed-up of the segmental dynamics compared to PVE with more than 98% 1,2-dyads.[40] Toluene was purchased from Aldrich and distilled before use to reach a purity >99%.

Homogeneous blends were prepared by dissolving PI and PVE in toluene in the required proportions. The solution was then poured on the bottom electrode of the sample cell used for dielectric measurements and left at atmospheric pressure for 1 day. Then toluene was completely removed in a vacuum at 40 °C. Blends with the following PI/PVE weight proportions were prepared: 75/25, 50/50, and 25/75.

Homogeneous polymer−toluene solutions were prepared by dissolving the polymer (either PI or PVE) in excess toluene. Both PI and PVE were soluble in toluene at all concentrations. The homogeneous solution was subsequently poured on the bottom electrode of a liquid sample cell and the desired concentration obtained via toluene evaporation. The following polymer−solvent solutions were investigated: PI/toluene 80/20, 90/10, and 95/5 w/w; PVE/toluene 70/30, 80/20, 90/10, and 95/5 w/w.

Dielectric measurements were carried out on PI/PVE blends as well as on all polymer−solvent systems and on pure PI and PVE using a high precision dielectric analyzer (ALPHA, Novocontrol GmbH) and a Novocontrol Quatro cryosystem for temperature control with a precision of ±0.1 K. Measurements were performed over a wide frequency (10^{-2}−10^6 Hz) and temperature range in isothermal steps starting from the highest temperature. As a general rule, the relevant relaxation time at any temperature was obtained from dielectric relaxation spectra as the reciprocal of the angular frequency at the maximum of the permittivity loss. Structural relaxation data for toluene were taken from ref 41.

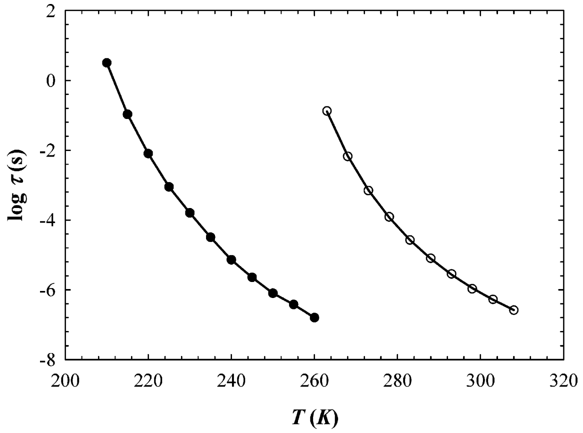

Figure 1. Logarithm of the relaxation time vs temperature for pure PI (filled circles) and pure PVE with >85% 1,2-dyads (empty circles). The solid points show the fitting through the AG equation to experimental data.

Calorimetric measurements were carried out on pure PI and PVE by means of the differential scanning calorimeter (DSC-Q1000) from TA-Instruments. Samples were annealed above T_g before measurements to remove the previous thermomechanical history. Measurements were performed in temperature modulated mode with an average heating rate of 0.1 K/min and amplitude of 0.3 K. Different oscillation frequencies were investigated and the so-obtained specific heats were extrapolated to zero frequency in order to obtain quasi-static values of the specific heat itself. The so-obtained PI specific heat is in agreement with that obtained by means of adiabatic calorimetry by Sakaguchi et al.,[23] whereas PVE specific heat is not directly comparable being in our case composed of about 85% 1,2-dyads rather than being pure PVE as in ref 23. Specific heat of toluene was taken from ref 32. The knowledge of the specific heat for PI, PVE and toluene allowed the evaluation of the excess heat capacity, well approximated by the difference between the specific heat in the liquid and the glassy state (the last one extrapolated above T_g). From the knowledge of the excess specific heat, the excess entropy was calculated as: $S_{ex}(T) = \int_{T_K}^{T} \Delta C_P(T') / T' \, dT'$. The Kauzmann temperature T_K was assumed to be equal to the temperature where the structural relaxation time tends to diverge. This implies that only the contribution to the excess entropy originating from the motion involved in the structural relaxation is calculated in such a way.[43,44] To obtain T_K relaxation time data for pure PI, PVE and toluene were fitted through the AG equation, having C, τ_0, and T_K as unknown parameters. Finally, the configurational part of the excess entropy was extracted using the approach of DiMarzio and Dowell for PI and PVE,[38] whereas a recent study on the contribution to the excess entropy of several glass forming liquids suggests that it accounts for about 65% of the excess entropy in liquid toluene.[45]

Results

1. Dynamics of Pure PI, PVE, and Toluene. Figure 1 shows the experimental dielectric relaxation times vs temperature for pure PI (filled circles) and PVE (empty circles and filled triangles). These data, together with toluene dynamics data,[41] were fitted through the AG equation: $\log \tau = \log \tau_0 + C/(TS_c)$ to obtain the preexponential factor $\log \tau_0$, the parameter C, and the Kauzmann temperature T_K. The AG equation provides a good fitting of experimental data as shown by the solid lines in Figure 1. As in refs 13 and 14, a linear expression for the excess specific heat was employed to obtain the configurational entropy. The resulting expression for the latter magnitude is: $S_c(T) = a \ln(T/T_K) + b(T - T_K)$. As from calorimetric experiments only

Table 1. Relevant Parameters for All Components of All Mixtures[a]

	T_g (K)	a (J/molK)	b (J/molK)	T_K (K)	log τ_0 (s)	C (kJ/molK)	S_c/S_{ex}	l_k (Å)	l_p (Å)
PI	213	60.2	−0.14	167 ± 2.5	−13 ± 0.8	20.4 ± 4.8	0.91	8.2	3.2
1,2PVE (>85%)	263	28.3	−0.02	228 ± 0.9	−10.6 ± 0.2	6.4 ± 1.4	0.72	14	2.8
toluene	117	105	−0.31	96 ± 0.9	−14.7 ± 0.5	37.9 ± 4.6	0.65		

[a] Data for the C parameter of the AG relation and for the parameters a and b of the specific heat are referred to a per mole of monomer basis for PI and PVE and to a per mole of toluene basis for toluene.

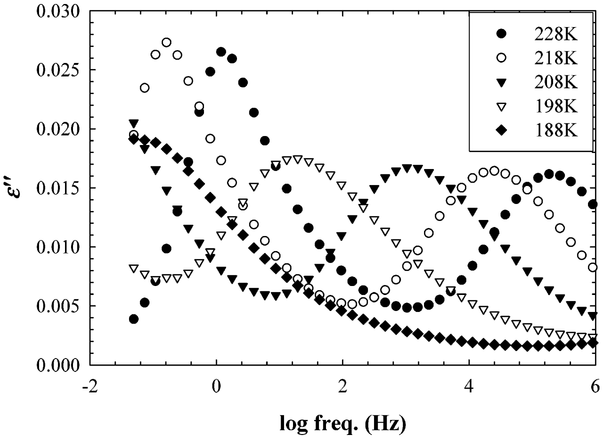

Figure 2. Permittivity loss vs logarithm of the frequency for PI/toluene system with 80 wt % PI at various temperatures.

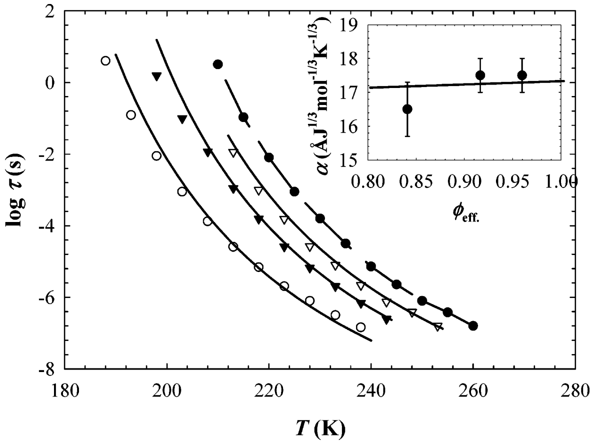

Figure 3. Logarithm of the relaxation time vs temperature for pure PI (filled circles) and for PI segmental dynamics in PI/toluene systems with the following PI weight percentages: 80% (empty circles), 90% (filled triangles), and 95% (empty triangles). The solid lines are the fitting of the model to PI segmental dynamics in toluene solutions and the dashed line is the fitting through the AG equation to pure PI dynamics data. The inset of the figure represents the variation of the α parameter with the average effective concentration (filled circles). The solid line is a linear fitting of experimental data, which, extrapolating to pure PI, allows the evaluation of the α parameter for pure PI.

the excess entropy can be calculated, the configurational entropy was determined from the knowledge of the configurational entropy portion of the excess entropy. The ratio of the configurational to the excess entropy and all the parameters from the fitting of the AG equation are summarized in Table 1. The Kauzmann temperature T_K, namely the temperature where the configurational entropy associated with the structural relaxation drops to zero, and the glass transition temperature T_g are also shown for PI, PVE, and toluene. In addition, the packing and the Kuhn lengths of PI and PVE are presented in Table 1.

When applying the AG equation to pure components, we have left free to vary the preexponential factor log τ_0, the parameter C, and the Kauzmann temperature T_K. However, it is noteworthy that if PVE preexponential factor is constrained at a more physical value such as log $\tau_0 = -13$ an acceptable fitting of data is obtained. This obviously implies a change in both C and T_K. However, this does not change the outcome of the application of the model to polymer blends in the prediction of the relevant time and length scale for segmental relaxation.

2. PI Dynamics in Toluene. PI/toluene permittivity loss vs frequency curves at several selected temperatures are displayed in Figure 2 for 80 wt % PI as an example. Similar plots were obtained for 90 and 95% PI in toluene. Two main peaks can be observed in the figure for high T_g data, which can be both attributed to PI dynamics. Toluene related dynamics is not visible in the temperature−frequency conditions for which data are shown being this much faster than PI dynamics. The low-frequency peak can be attributed to PI normal mode and will not be subject of further attention in the rest of the paper except because it is present in all systems containing PI. On the other hand, the high-frequency peak can be attributed to PI structural relaxation. A broadening of the dielectric response with decreasing temperature can be observed indicating the failure of time−temperature superposition. This feature is commonly found in polymer blends[1] as well as in binary mixtures of low molecular weight glass-formers.[46] Similar results in PI/toluene mixtures were obtained in the past by Adachi et al.[47] The relaxation times corresponding to the structural relaxation are displayed in Figure 3 for 80, 90, and 95 wt % PI in toluene and for pure PI. As expected, the presence of toluene induces a speed-up of PI segmental dynamics. The solid lines are the fitting of the model to experimental data obtained using α as the single fitting parameter. The fitting is carried out solving eq 3 as a function of the effective concentration for each value of α. The selected value of α is that providing an effective concentration that, once introduced in eq 1, is able to best reproduce the experimental relaxation times. As is possible to observe, a good agreement is found between the fitting of the model and experimental data. In the inset of Figure 3, the parameter α used to fit data is plotted as a function of the average value of the effective concentration in the volume relevant for structural relaxation.[48] The parameter α is approximately independent of the effective concentration, thus suggesting that toluene does not substantially affect the value of α of the mixtures. The weak influence, if any, of toluene on the value of α, unlike other systems like PVME/toluene recently investigated,[26] leads to a value of α essentially concentration independent and equal to: $\alpha_{PI} = 17.5 \pm 0.5$ Å $J^{1/3}$ $mol^{-1/3}$ $K^{-1/3}$. This value is referred to moles of isoprene monomer.

3. PVE Dynamics in Toluene. Figure 4 displays the permittivity loss in a wide frequency and temperature range for PVE/toluene solutions with 90% PVE. Similar plots were obtained for 70, 80, and 95% PVE in toluene. In the frequency−temperature window shown in the figure, only PVE related dynamics is visible, whereas toluene related dynamics only shows up at much lower temperatures and/or higher frequencies. Similarly to PI/toluene solutions, a clear failure of the time−temperature superposition occurs with a progressive broadening of the dielectric response with decreasing temperature. The relaxation times corresponding to the maximum of the permittivity loss-frequency curves are plotted vs temperature in Figure 5. The solid lines are the fitting of the model to the experimental

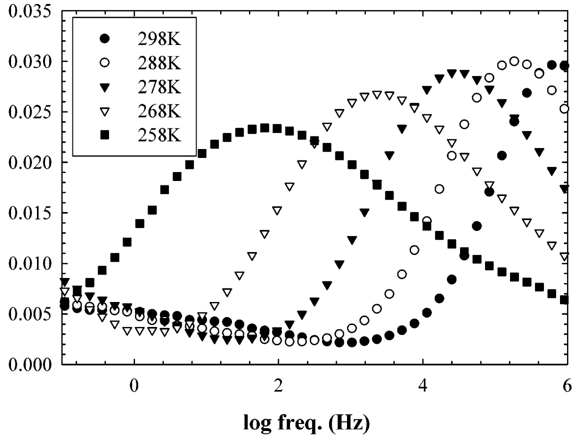

Figure 4. Permittivity loss vs logarithm of the frequency for PVE/toluene system with 90 wt % PVE at various temperatures.

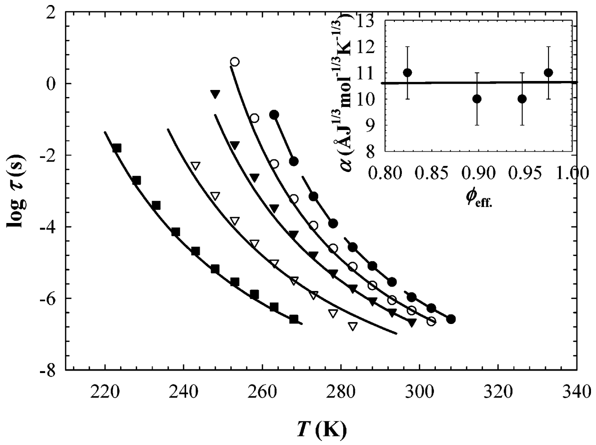

Figure 5. Logarithm of the relaxation time vs temperature for pure PVE (filled circles) and for PVE segmental dynamics in PVE/toluene systems with the following PVE weight percentages: 70% (filled squares), 80% (open triangles), 90% (filled triangles), and 95% (open squares). The solid lines are the fitting of the model to PVE segmental dynamics in toluene solutions and the dashed line is the fitting through the AG equation to pure PVE dynamics data. The inset of the figure represents the variation of the α parameter with the average effective concentration (filled circles). The solid line is a linear fitting of experimental data, which, extrapolating to pure PVE, allows the evaluation of the α parameter for pure PVE.

data. From inspection of the figure, it can be concluded that the model allows a good description of the experimental data. Similarly to PI in toluene, the α parameter needed to describe experimental data does not present any dependence with the effective concentration. Therefore, the value of α for pure PVE is: $\alpha_{PVE} = 11 \pm 0.5$ Å $J^{1/3}$ $mol^{-1/3}$ $K^{-1/3}$. In this case, the value of α is referred to moles of vinyl ethylene monomer.

4. PI/PVE Blends. Figures 6−8 show the permittivity loss vs frequency at various temperatures for PI/PVE with 75, 50, and 25 wt % PI. Apart from PI normal mode, visible at relatively low frequencies and high temperatures, two dynamics are observable, in agreement with previous observations.[2,3] The one emerging at lower frequencies can be assigned to PVE related segmental relaxation in the blend, whereas at higher frequency PI related segmental relaxation shows up. Because of the presence of some 1,4-dyads in PVE that speed up the dynamics of this polymer, the separation between PVE and PI related dynamics is weakened in comparison to previous data on the same blend.[2,3] The overlapping of the signals from the components of the blend prevents the unambiguous determination of the mean relaxation times for the two polymers in the blend from the permittivity loss−frequency curves. Nevertheless the proposed model is capable to fully predict the dynamics of both polymers in the blend, since α, the only fitting parameter required by the model, can be derived from the knowledge of the parameter α of the pure polymers, which has been determined applying the model to the dynamics of PI and PVE in toluene. Figures 9a and 10a show the model prediction of, respectively, PVE and PI related dynamics in the blend. The

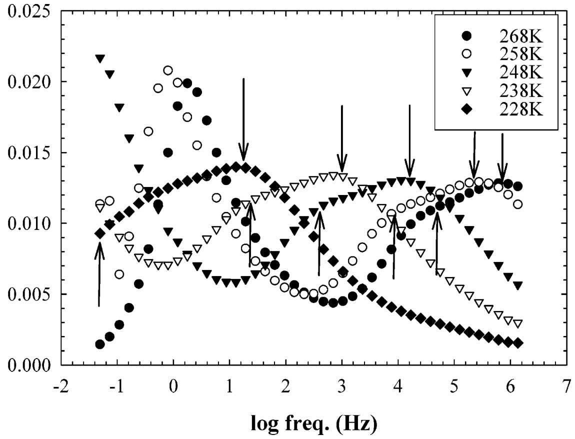

Figure 6. Permittivity loss vs logarithm of the frequency for PI/PVE system with 75 wt % PI at various temperatures. The arrows indicate the position of the average relaxation time of both PI and PVE in the blend as predicted by the model.

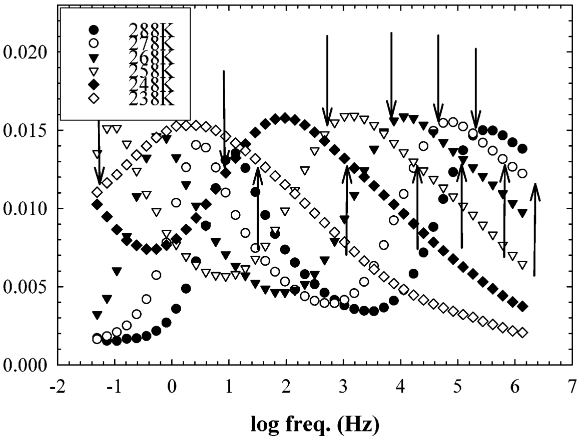

Figure 7. Permittivity loss vs logarithm of the frequency for PI/PVE system with 50 wt % PI at various temperatures. The arrows indicate the position of the average relaxation time of both PI and PVE in the blend as predicted by the model.

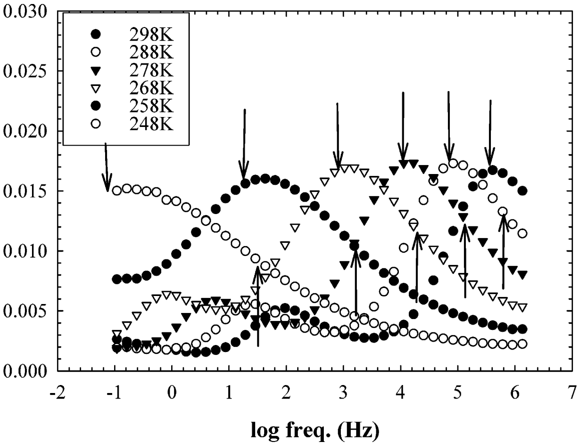

Figure 8. Permittivity loss vs logarithm of the frequency for PI/PVE system with 25 wt % PI at various temperatures. The arrows indicate the position of the average relaxation time of both PI and PVE in the blend as predicted by the model.

aforementioned mixing rule was used to obtain the α at the average effective concentration of each component in each blend.

To test whether the prediction of the model is in agreement with experimental data, in Figures 6−8 we have indicated with arrows the position of the average relaxation time as predicted by the model for PVE and PI related dynamics in all the blends studied. Two arrows are drawn for each spectrum, the one at higher frequency corresponding to PI dynamics and the other one to PVE dynamics. As can be observed, the model is able to give a reasonable prediction of the location of the average relaxation time of both PI and PVE dynamics in the blend despite the two dynamics are highly overlapped due to the broadening of the dielectric response and the similarity in the dynamics. This means that the model is also suitable to predict the component dynamics in those systems possessing T_g contrast even smaller than for PI/PVE system. In this case, due to the broadening of the response, the average relaxation time can be effectively identified through the model, once the α parameter is known indirectly from the study of other systems. It is noteworthy that the employment of a mixing rule to determine the α parameter provides a quantitatively accurate description of the dynamics of both components as evidenced by the arrows in Figures 6−8. On the other hand, the employment of the α parameter of the pure components to describe the segmental dynamics of the each of the component in the blend would result in a less accurate prediction.

Figures 9b and 10b show the diameter ($d = 2r_c$) of the relevant volume for segmental dynamics respectively for PVE and PI in the blends. In both cases the relevant diameter for segmental relaxation is in the range between 1 and 2 nm depending on the polymer, its concentration in the blend and the temperature. As a general rule, a tendency of the length scale to increase with the concentration of the rigid component (PVE) is observed, in agreement with previous observations in other miscible polymer blends.[13]

Discussion

The results presented in the previous section have highlighted three main crucial points: (i) the model based on the combination of the self-concentration concept and the AG theory in its refined version compared to that presented originally[13] successfully describes experimental data for both polymer/solvent systems and PI/PVE blends; (ii) the application of the model to polymer/toluene solutions allows determining the only unknown parameter needed by the model, apart from those of the pure components, thus making it fully predictive when describing blends dynamics data; (iii) the model provides a satisfactory prediction of PI/PVE dynamics data with a relevant length scale for structural relaxation dependent on temperature and of the order of 1−2 nm.

The first point has been already commented in the second section of the paper. The preexponential factor of the AG equation was derived more consistently through a mixing rule of the preexponential factors of the pure components of the blend, and the configurational entropy instead of the excess entropy was employed using the approach of DiMarzio and Dowell[38] to calculate the former quantity.

A crucial modification of the model consisted on the introduction of a mixing rule to determine the α parameter of the model. The employment of the mixing rule is justified by the fact that each component of the blend contributes to the α parameter with its own α in the volume relevant for segmental relaxation. This implies that once the α parameter is known, in principle it is possible to predict the structural dynamics of any polymer blend. In addition, we have shown that α can be easily obtained applying the model to concentrated solutions of the polymer under investigation with a good solvent like toluene. All these considerations suggest that α is a material specific parameter that can be empirically determined. However, it is noteworthy that in our approach we do not attempt to provide a microscopic interpretation of this magnitude. On the other hand, the AG theory[15] provides a theoretical estimation of the coefficient of proportionality between the number of particles participating to the cooperative rearrangement and the configurational entropy. According to the AG approach this proportionality constant would be equal to $N_A s_c^*$, where N_A is the Avogadro number and s_c^* is the configurational entropy associated with the rearrangement of one basic cooperative unit. However, several theoretical approaches have evidenced the inaccuracy of the AG approach to provide an estimation of the size of the relevant volume for structural relaxation.[49,50] On the other hand, several recent simulations suggest that the proportionality between the number of particles participating to the cooperative rearrangement and the inverse of the configurational entropy actually works.[31,51] Our approach offers the possibility of extracting experimentally the proportionality constant (α) through the study of the structural dynamics of bicomponent systems, exploiting the role of self-concentration.

Regarding the length scale for segmental relaxation obtained for PI and PVE, it is noteworthy that the increase of the characteristic diameter with decreasing temperature imposed by the AG theory results in an accurate description of experimental data. This result is at odds with the hypothesis of a temperature independent length scale postulated by Lodge and co-workers.[10,11] In addition, while the length scale for segmental relaxation of PVE is of the order of the Kuhn segment (between 1.3 and 1.7 nm compared to a Kuhn length = 1.4 nm), the one of PI is between 1.35 and 1.8 nm and, therefore is about twice larger than the PI Kuhn length (0.82 nm). This difference in the characteristic length scale could in principle explain the inaccuracy of the Lodge and McLeish approach to provide a precise determination of the effective T_g(s) of PI and PVE in the blend.[10,21] However, the incongruence between the length scale obtained by us and that derived from the Lodge−McLeish model may originate from the different way in which the two approaches extract relevant temperatures of the blend such as the T_g or the temperature where the relaxation time would diverge to infinite, namely the Kauzmann temperature (T_K) in the AG framework or its phenomenological equivalent, the Vogel temperature. The Lodge−McLeish model makes use of the Fox equation that for the T_g reads as follows:

$$1/T_{g(A/AB)} = \phi_{eff}/T_{g(A)} + (1 - \phi_{eff})/T_{g(B)} \qquad (5)$$

An analogous equation can be written for the other component of the blend. Despite its theoretical appeal, this equation was criticized by Leroy et al.,[52] who highlighted its inadequacy in predicting the T_g of some polymer blends. The Kauzmann (or the Vogel) temperature of component A in the blend ($T_{K(A/AB)}$) can be derived from the T_g through the following:[53]

$$T_{K(A/AB)} = T_{K(A)} + (T_{g(A/AB)} - T_{g(A)}) \qquad (6)$$

Combining eqs 5 and 6, the concentration dependence of T_K can be derived for both components of the blends. On the other hand, T_K can be obtained from our model considering that at this temperature the configurational entropy of the blend

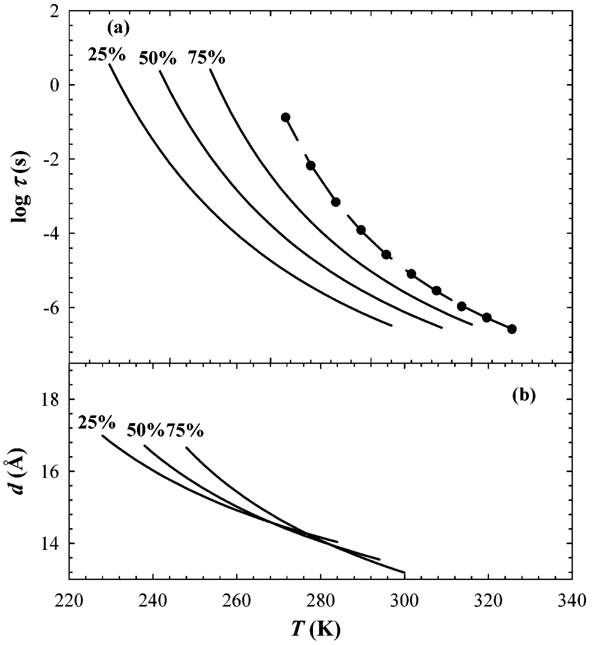

Figure 9. (a) Logarithm of the relaxation time vs temperature pure PVE (filled circles) and for PVE segmental dynamics in PI/PVE blends predicted by the model through a linear combination of the α(s) parameters of the pure polymers through the effective concentration (solid lines). The dashed line is the fitting through the AG equation to pure PVE dynamics data. (b) Diameter of the relevant volume for segmental relaxation vs temperature calculated through the model for PVE in blends with PI. Percentages refer to PVE.

vanishes to zero. Therefore, the concentration dependence of T_K can be extracted equating to zero the left-hand side of eq 4:

$$\phi S_c^A(T_{K(blend)},T_{K(A)}) + (1-\phi)S_c^B(T_{K(blend)},T_{K(B)}) = 0 \quad (7)$$

It is noteworthy that in our approach only one T_K exists, since according to the AG theory, the size of the relevant region for structural relaxation tends to diverge to infinity, thus making self-concentration effects irrelevant.

In Figure 11, we plot the concentration dependence of the Kauzmann temperature obtained from the Fox equation together with that arising from the application of our model. Clearly a notable discrepancy exists between the two approaches, overall in the dilute regime. However, the Kauzmann temperature for PI in the blend obtained through the Fox equation almost coincides with that obtained through the AG approach at concentration above 40%. This could explain the ability of the Lodge−McLeish model combined with the Fox equation to provide an accurate prediction for PI effective T_g, in contrast to the inaccuracy of the prediction for PVE one (see Figure 7 of ref 21).

A complementary check to highlight the differences between our approach and that employed by Lodge and McLeish can be performed deriving the blend T_g from the T_g(s) of the pure component. Defining the T_g as the temperature at which the relaxation time is 100s and combining the AG relation (eq 1) with eq 4, the following relation between the blend T_g and the T_g(s) of the pure component is obtained:

$$\frac{C_{blend}}{T_g^{blend}\log(100/\tau_0^{blend})} = \phi\frac{C_A}{T_g^A\log(100/\tau_0^A)} + (1-\phi)\frac{C_B}{T_g^B\log(100/\tau_0^B)} \quad (8)$$

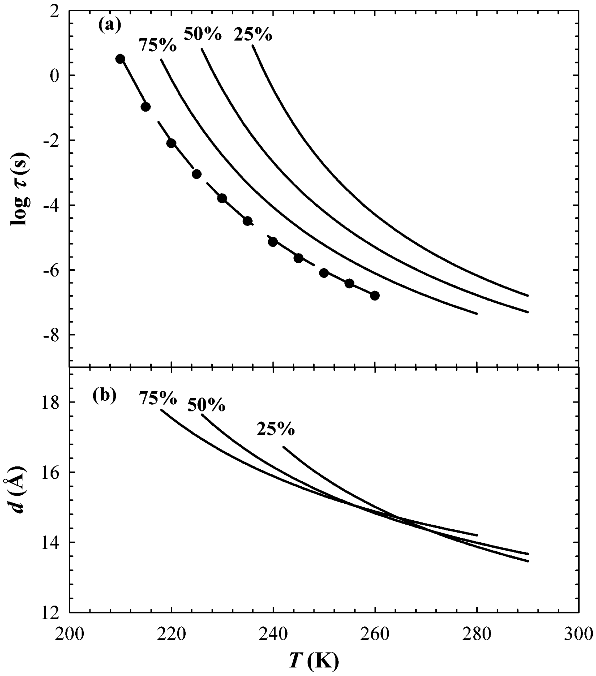

Figure 10. (a) logarithm of the relaxation time vs temperature pure PI (filled circles) and for PI segmental dynamics in PI/PVE blends predicted by the model through a linear combination of the α(s) parameters of the pure polymers through the effective concentration (solid lines). The dashed line is the fitting through the AG equation to pure PVE dynamics data. (b) Diameter of the relevant volume for segmental relaxation vs temperature calculated through the model for PI in blends with PVE. Percentages refer to PI.

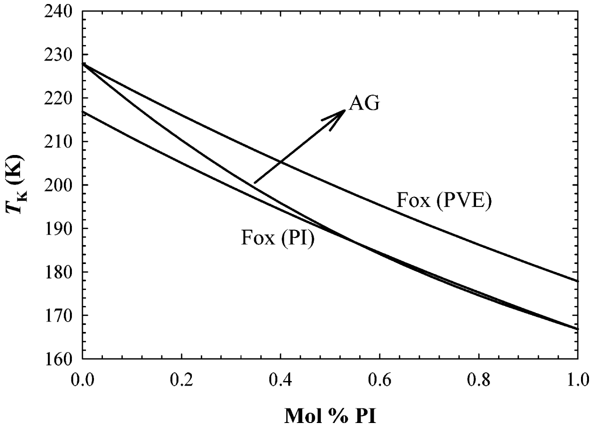

Figure 11. Concentration dependence of the Kauzmann temperature according to the Fox equation and the AG approach.

This expression is equivalent to the Fox equation only when the preexponential factor and the parameter C of the AG equation are equal for the two component of the blend. This is not the case for PI and PVE that present notable differences in both the preexponential factor and the parameter C (see Table 1). Equation 8, which is based on the AG theory, represents a more fundamental alternative route to the Fox equation to evaluate the T_g of miscible polymer blends starting from the knowledge of the dynamics and thermodynamics of the pure components of the blend. A similar approach to evaluate the T_g of polymer blends based on thermodynamic grounds has been recently proposed by Kim et al.[54]

Apart from the comparison with the length scales arising from the Lodge−McLeish model, our results can also be compared with those of Hirose et al.[22] They found that a length scale equal to the Kuhn segment was not appropriate to fit PI effective T_g and a value between 0.9 and 1.2 nm had to be employed, which is larger than the Kuhn segment but smaller than the one found by us at this concentration and temperature (about 1.5 nm). On the other hand, PVE characteristic length was found of the order of the Kuhn segment in agreement with our results.

It is interesting to note that PI, despite its rather high flexibility, displays a length scale up to 1.8 nm. In light of this relatively large length scale, the idea that the Kuhn segment controls structural dynamics in polymer blends might be questioned. On the other hand, while this concept has been proposed to relate the characteristic length scale for structural relaxation of glass-forming polymers to their flexibility, it seems too limitative as structural relaxation, giving rise to the glass transition, is a universal phenomenon involving also low molecular weight glass-formers. The results obtained in this work and in refs 13 and 14 suggest that the characteristic length scale for structural relaxation is universally found between 1 and 3 nm. Although chain flexibility seems to plays a role in affecting the value of this length scale for glass-forming polymers, a precise correlation between the characteristic length scale and the chain structure has still to be determined.

Conclusions

We have described PI/PVE segmental dynamics by means of a model based on the combination of the AG model and the self-concentration. The model was refined with respect to its original version[13] to obtain a more accurate estimation of the C parameter of the AG equation and account for the different configurational contribution to the excess entropy of PI and PVE. The so-modified model resulted in a good description of PI/PVE experimental data and, in principle, should be more suitable to be applied to a variety of multicomponent systems. In addition, the determination of the only unknown parameter of the model (α) from the application of the model itself to polymer−solvent systems provides a simple route to make the model fully predictive. This prediction has been found to work for PI/PVE blends, a system for which, to the best of our knowledge, the previously proposed approaches seem to be rather inaccurate. Furthermore, both polymers in the blends present a temperature-dependent relevant length scale for structural relaxation in the range 1.3 and 1.7 nm for PVE and between 1.35 and 1.8 nm for PI, which is of the same order of magnitude as that found for all polymer blends for which the model has been applied so far.

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