# Combining configurational entropy and self-concentration to describe the component dynamics in miscible polymer blends

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We provide a new approach to describe the component segmental dynamics of miscible polymer blends combining the concept of chain connectivity, expressed in terms of the self-concentration, and the Adam-Gibbs model. The results show an excellent agreement between the prediction of our approach and the experimental data. The self-concentrations obtained yield length scales between 1 and 3.2 nm depending on the temperature, the flexibility of the polymer, expressed in terms of the Kuhn segment, and its concentration in the blends, at temperatures above the glass transition range of the blend. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2052592]

## INTRODUCTION

The dynamics of miscible polymer blends displays peculiar features that make the study of these systems very attractive, from both basic and applied points of view. Among them the most striking are the failure of the time-temperature superposition,[1] approximately verified for single polymer systems, and the heterogeneous dynamics at the length scale of the segmental relaxation.[2] In the last years, a large number of studies on the dynamics of miscible blends by means of dielectric and dynamic-mechanical spectroscopies, nuclear magnetic resonance, and neutron scattering have been presented[3–17] showing the presence of two relevant time scales for the segmental dynamics (and also for the terminal dynamics) and a broadening of the dynamic response upon temperature reduction. To explain this somehow peculiar behavior, it has been considered that the dynamics of one blend component is determined by the neighbors located in a finite volume centered on it. Two main hypotheses have been formulated for the relevant feature controlling the component dynamics within this volume: (i) one based on the idea that thermally induced concentration fluctuations are mainly responsible for the dynamical features;[5,6] (ii) a second one where the effect of chain connectivity on the local effective concentration of polymer blends is highlighted.[3,4,10]

The role of concentration fluctuations was first invoked by Zetsche and Fischer[5] and later developed by Kumar and co-workers.[6,7] Despite the general agreement about the ability of concentration fluctuations to affect the distribution of relaxation times, several authors have argued about their role in determining the mean relaxation time.[10,18] In addition, when this approach is used to determine the length scale relevant for segmental dynamics, a length scale of the order of 10 nm is obtained at the glass transition temperature ($T_g$). This value is too large when compared to the size expected for the polymer segmental dynamics on the basis of the Adam and Gibbs theory,[19–21] as well as that estimated by Donth (around to 2 nm).[22]

It is now generally accepted that concentration fluctuations cannot explain the presence of two relevant time scales and the effect of chain connectivity has to be taken into account.[3,4,10] Due to chain connectivity the portion of matter relevant for segmental relaxation of one component is always richer in that component. This fact has been referred to as self-concentration effect, leading to an effective concentration higher than the blend average. As the effect of self-concentration depends on the relevant length scale for segmental relaxation, the scientific debate has now been focused on what is this length scale. Lodge and co-workers[10,11] proposed a temperature-independent length of the order of the Kuhn segment of the chain and, at least qualitatively, successfully predicted the component glass transition in several miscible blends. Leroy *et al.*[13,14] modeled the segmental dynamics data of poly(vinyl methyl ether)/polystyrene (PVME/PS) and poly(*o*-chlorostyrene)/polystyrene (PoClS/PS700) taking into account both the effect of concentration fluctuations and chain connectivity. They concluded that an essentially temperature-independent length scale could be assumed. Hirose *et al.*[15] performed dielectric spectroscopy on polyisoprene/Poyvinylethylene (PI/PVE) blends and, by

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measuring the terminal dynamics of PI and the segmental dynamics of both components, suggested that length scales of the order of the Kuhn length for PI are relevant for the segmental dynamics, whereas a larger length scale is needed for PVE. He *et al.*[16] reached similar conclusions when fitting the dynamics data for several blends with a temperature-independent self-concentration. They also found that for most of the components of the blends investigated a length scale comparable to the Kuhn length can be assumed. Finally, Kant *et al.*,[17] after demonstrating that concentration fluctuations affect the mean segmental relaxation time only close to the blend $T_g$, proposed to evaluate the relevant length scale directly from the segmental dynamics data. By this procedure, they showed that, whereas temperature variation of the relevant length scale can be neglected for the low $T_g$ component, the high $T_g$ component generally displays a rather pronounced temperature dependence.

It is worth mentioning that in all of the previously cited studies the Williams-Landel-Ferry[14,15,17] (or the Vogel-Fulcher-Tamann[11,16]) equation is employed to fit the temperature dependence of the relaxation time. This choice requires the knowledge of the $T_g$ (or the Vogel temperature) corresponding to each component to be known. The values of the component's $T_g$ can, in some cases,[13] be obtained experimentally. In order to make the models predictive, however, they should to be estimated from the pure polymer component properties. The most commonly used approach for that was proposed by Lodge and McLeish[10] and connects the effective $T_g$ of each component with a macroscopic $T_g$ value as defined using the values of the pure polymers $T_g(s)$ through the Fox equation. The implications and problems of this procedure have been highlighted by Leroy *et al.*[14]

In the present work, we propose a new model based on the combination of the effective concentration concept with the configurational entropy approach to the glass transition originally proposed by Adam and Gibbs (AG).[19] The AG theory suggests that the decrease of the available configurations upon temperature reduction is responsible for the non-Arrhenius slowing down of the segmental dynamics. On this theoretical basis, they proposed the following equation for the temperature dependence of the segmental relaxation time:

$$\tau = \tau_0 \exp\left(\frac{\Delta\mu s_c^*}{k_B T S_c}\right) = \tau_0 \exp\left(\frac{C}{T S_c}\right), \tag{1}$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $S_c$ is the configurational entropy, $\Delta\mu$ is the energy barrier per particle over which a cooperatively rearranging group must pass, $s_c^*$ is the configurational entropy associated with such a rearrangement, and $\tau_0$ is the relaxation time at infinite temperature. Both $s_c^*$ and $\Delta\mu$ are assumed to be independent of temperature. A second basic concept of the AG theory is that the decrease of the configurational entropy upon temperature reduction requires an increasing degree of cooperativity among basic relaxing units. In other words, when temperature is reduced, molecular rearrangements can occur only if an increasing number of basic relaxing units is involved in the motion. This idea gave rise to the concept of the cooperatively rearranging region (CRR), whose size is predicted

to increase upon temperature reduction. In the low-temperature limit the size of the CRR should diverge when the configurational entropy tends to zero, a condition never reached in the experimental practice. In polymer blends, the hypothesis of a temperature-dependent size of the CRR has important implications since the effect of chain connectivity will be more or less pronounced depending on the relevant volume for segmental relaxation.

With these ideas in mind, in this paper we show how the model combining the self-concentration concept and the AG approach is able to describe the component segmental dynamics of several miscible polymer blends. The model makes use of both the connection between configurational entropy and relaxation time, on the one hand, and of the concept of a temperature-dependent length scale with its implications on the local effective concentration, on the other hand. This approach allows giving an estimate of the relevant length scale for the segmental relaxation for each component in several polymer blends. Although the application of the model does not involve the predetermination of the components' effective $T_g(s)$ to account for the component dynamics, it is worth to remark that the existence of two $T_g(s)$ in the blend emerges in a natural way from the model as a consequence of the prediction of two segmental dynamics.

## MODEL

To extend the AG theory to polymer blends, thermodynamic properties of the blend need to be assessed. To do this, we make the basic assumption that the interaction between the two components in the blend is negligible (athermal mixture). This assumption means that any extensive thermodynamic property $X$ ($=H, S, V$, etc.) of a blend composed by polymers $A$ and $B$ can be expressed as

$$X^{\text{blend}} = \phi^A X^A + (1 - \phi^A) X^B, \tag{2}$$

where $X^{\text{blend}}$ and $X^{A,B}$ represent the thermodynamic property of the blend and of the pure components, respectively, and $\phi^A$ is the mole concentration of component $A$.

In polymer blends, as mentioned in the Introduction, connectivity effects have to be taken into account to evaluate the local effective concentration in the volume relevant for dynamics. Chain connectivity leads to an excess of monomers of one type, relative to the bulk concentration, when a volume $V$ centered in such a monomer is explored. For length scales of the order of several monomeric units, the effective concentration $\phi_{\text{eff}}$ can deviate significantly from the macroscopic concentration. $\phi_{\text{eff}}$ can be calculated as[10]

$$\phi_{\text{eff}} = \phi_s + (1 - \phi_s)\phi, \tag{3}$$

where $\phi$ is the macroscopic molar concentration of one of the two components and $\phi_s$ is the self-concentration of the same component, 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. Therefore, by combining Eqs. (2) and (3) we can obtain the thermodynamic property in any volume relevant for segmental dynamics in a blend as a linear combination of the thermodynamic properties of the pure components weighed by its effective concentration. On this

basis we can express $S_c$ and $C$ of the AG equation as

$$S_c^{A/\text{blend}} = \phi_{\text{eff}}^A S_c^A + (1 - \phi_{\text{eff}}^A)S_c^B, \tag{4}$$

$$C^{A/\text{blend}} = \phi_{\text{eff}}^A C^A + (1 - \phi_{\text{eff}}^A)C^B, \tag{5}$$

where $S_c^{A/\text{blend}}$ and $C^{A/\text{blend}}$ refer to regions centered around a segment of polymer $A$. Similar equations can be written for component $B$. Equations (4) and (5) allow the calculation of the parameters of the AG equation in the relevant volume for segmental relaxation in the hypothesis of negligible thermal interactions between the components of the blend.

The self-concentration in the volume considered can be estimated according to simple geometric considerations, assuming a spherical shape of the relevant volume. Depending on whether the radius of the relevant volume is smaller or larger than the Kuhn length, the self-concentration can be calculated as[17]

$$\phi_s = \frac{3l_k l_p}{2\pi r_c^2}, \quad r_c < l_k, \tag{6a}$$

$$\phi_s = \frac{3l_p}{2\pi r_c}, \quad r_c > l_k, \tag{6b}$$

where $l_k$ and $l_p$ are, respectively, the Kuhn and the packing length of the chain and $r_c$ is the radius of the relevant volume for segmental relaxation.

On the other hand, from the AG theory, we know that the number of basic structural units ($z^*$) within a CRR is inversely proportional to the configurational entropy:[19]

$$z^* \propto S_c^{-1}, \tag{7}$$

and therefore the size of such a CRR would be related to the configurational entropy by

$$r_c = \alpha S_c^{-1/3}, \tag{8}$$

where $\alpha$ is a proportionality constant that, as will be shown below, can be obtained from the fitting of the experimental data. If the volume of the CRR is identified with the relevant volume for segmental dynamics considered above, by combining Eq. (8) with Eq. (6), we can express the self-concentration as a function of the configurational entropy. Thus we obtain

$$\phi_s = \frac{3l_k l_p}{2\pi \alpha^2}S_c^{2/3} \quad \text{for } r_c < l_k \tag{9a}$$

and

$$\phi_s = \frac{3l_p}{2\pi \alpha}S_c^{1/3} \quad \text{for } r_c > l_k. \tag{9a'}$$

In order to apply the AG equation to describe the component segmental dynamics of a miscible polymer blend, we also need to make an assumption on the preexponential factor. As this parameter is representative of the high-temperature behavior of each component of the blend, namely, where the cooperative volume approaches the monomer size, we assume a temperature-independent preexponential factor and equal to that of the pure component.

Once the dynamics of the pure polymers is described according to the AG equation, under the above assumptions, the proposed model can be compared with the experimental data having just one unknown parameter for each component dynamics, namely, $\alpha$ of Eq. (8), the others being fully determined. This means that apart from the dynamics data, also the specific-heat data are required for the pure components. On the other hand, it is important to note that the estimation of the relevant length scale for segmental dynamics via Eqs. (6), (8), and (9) is performed exploiting chain connectivity effects rather than the AG theory, which is by itself unsuitable to predict relevant length scales for dynamics.[23]

Finally, it is worth remarking that in this model we are ignoring the effect of concentration fluctuations on the relaxation time. In particular, we predict the relaxation time at the average concentration of the blend, whereas relaxation times obtained from the experiments are usually more representative of the mean relaxation time. Neglecting the difference between the relaxation time at the average concentration and the experimental relaxation time can result in 10% (or more) error according to Kant et al.[17] but only at temperatures close to the blend $T_g$ (defined as the inflection point in a specific-heat-temperature trace). As will be discussed later in the paper, in this work the experimental dynamics data are fitted only at temperatures above the $T_g$ range of the blend to avoid the effect of nonequilibrium dynamics.

## IMPLEMENTATION OF THE MODEL

In order to apply our model, some additional assumptions have to be made.

(i) Since the configurational entropy $S_c$ is not experimentally accessible, we use the excess entropy, namely, the entropy of the liquid in excess of the corresponding crystal ($S_{\text{ex}} = S^{\text{melt}} - S^{\text{crystal}}$). However, due to the contribution of the excess vibrational entropy, $S_{\text{ex}}$ and $S_c$ are never the same. Therefore, here we assume a proportionality between them, i.e., $S_{\text{ex}} \propto S_c$. Although this point is still a matter of open debate, several experimental and simulation studies seem to suggest a general validity of this proportionality.[24–26]

(ii) In order to use the $S_{\text{ex}}$ in Eq. (4) it is necessary to assume that

$$\frac{S_{\text{ex}}^A}{S_c^A} \cong \frac{S_{\text{ex}}^B}{S_c^B}. \tag{10}$$

In other words, we assume that the excess vibrational entropy contributes in a similar way for both polymers of the blend. This assumption is supported by recent findings on several molecular glass formers that display similar relative vibrational contribution to the excess entropy.[25] Therefore, we can rewrite Eq. (4) as

$$S_{\text{ex}}^{A/\text{blend}} = \phi_{\text{eff}}^A S_{\text{ex}}^A + (1 - \phi_{\text{eff}}^A)S_{\text{ex}}^B \tag{11}$$

and a similar equation for the component $B$.

(iii) In order to calculate $S_{\text{ex}}$ from calorimetric measurements, we assume that the excess specific heat can be expressed as a linear function of temperature: $\Delta C_P$

TABLE I. Relevant parameters for all components of all blends. Errors are ±1 of the least significant digit unless specified.

| Polymer | $T_g$ (K) | Dynamics parameters | | | Thermodynamic parameters | | Structural parameters[a] | |
|---|---|---|---|---|---|---|---|---|
| | | $\log(\tau_0(s))$ | $C$ (kJ/mol) | $T_K$ (K) | $a$ (J/K mol) | $b$ (J/$K^2$ mol) | $l_k$ (Å) | $l_p$ (Å) |
| PoClS | 402 | −12.9 | 61.8 | 340.6 | 98.4 | −0.172 | 17.3 | 3.9[b] |
| $PS_{700}$ | 280 | −12.5 | 75.8 | 223.8 | 85.5 | −0.180 | 18 | 3.9 |
| PS | 373 | −12.4 | 60.7 | 322.2 | 99.0 | −0.171 | 18 | 3.9 |
| PVME | 249 | −13.0 | 51.6 | 203.4 | 68.3 | −0.160 | 13 | 2.7 |

[a]All parameters were taken from Ref. 17 except the Kuhn length of PoClS that was taken from Ref. 13.
[b]The packing length of PoClS has been assumed equal to that of PS due to the lack of the literature data.

$= C_P^{\text{melt}} - C_P^{\text{crystal}} = a + bT$, where $a$ and $b$ are constants. This dependence was proposed by Hodge[27] and is recognized to be the most accurate. Furthermore, as in general we cannot access the specific-heat data for fully crystalline polymers, $C_P^{\text{crystal}}$ is usually identified with $C_P^{\text{glass}}$. Therefore, the excess entropy can be calculated as

$$S_{\text{ex}}(T) = \int_{T_K}^{T} \frac{\Delta C_P(T')}{T'} dT', \tag{12}$$

where $T_K$ is the temperature where the excess entropy tends to vanish (the Kauzmann temperature). Introducing the linear dependence of $\Delta C_P$ in Eq. (12) and integrating, we obtain

$$S_{\text{ex}}(T) = a \ln(T/T_K) + b(T - T_K). \tag{13}$$

Equation (13) allows to evaluate the excess entropy of the pure components from the knowledge of the parameters $a$, $b$, and $T_K$. The former quantities can be evaluated from specific-heat-temperature traces. The latter could in principle be obtained only if the properties of crystalline polymers were known. However, in this work, we cannot obtain $T_K$ from thermodynamic properties of crystalline polymers. This brings us to the last assumption of the implementation of the model.

(iv)  We assume that $T_K$ can be identified with the temperature where the relaxation time of the $\alpha$ process tends to diverge. This has been proved to be a good approximation for a large number of fragile glass formers.[28] However, it is worth mentioning that for some glass-forming polymers secondary relaxation processes, related to some intramolecular degrees of freedom, contribute to the total excess entropy as recently demonstrated by Cangialosi *et al.*[29] Therefore, a residual excess entropy exists at the temperature where the relaxation time of the segmental dynamics diverges. In this case, the excess entropy evaluated from Eq. (13), with $T_K$ obtained from the dynamics data, will not be the total excess entropy but only the contribution related to the $\alpha$ process.

## EXPERIMENTAL DATA

In this work, we have tested the above-presented model to the dynamics of three different blends known to have neg-ligible enthalpic interactions (athermal blends). Two of these systems contain one of the components having much higher relaxation strength than the other:

(i)  polystyrene/poly(*o*-chlorostyrene)  (PS700/PoClS), where PS700 is a low molecular weight polystyrene ($M_w$=740 g/mol);
(ii)  poly(vinyl methyl ether)/polystyrene (PVME/PS). In the former case the high $T_g$ component (PoClS) is dielectrically active, whereas in the latter case it is the low $T_g$ component (PVME). In the case of the third blend considered, both components are dielectrically active:
(iii)  PVME/PoClS.

Details about the polymers used can be found in Refs. 8, 13, and 14 and in Table I of this paper. The selection of these three different polymer blends offers the possibility of exploring a wide variety of dielectrically active components in different environments. 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. Dielectric spectra for PS700/PoClS and PS/PVME blends can be found in Refs. 4, 30, and 31, whereas those for PVME/PoClS have been obtained by a broadband dielectric spectrometer based on 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 on cooling over a wide frequency ($10^{-2}$–$10^{7}$ Hz) and temperature range.

Calorimetric measurements were carried out by means of the differential scanning calorimeter (DSC-Q1000) from TA-Instruments. The samples were annealed above $T_g$ before measurements to remove the previous thermomechanical history. Measurements were performed in a 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 quasistatic values of the specific heat itself.

## RESULTS

Figure 1 shows a typical heat-capacity-temperature trace recorded for PS as an example. Specific-heat-temperature plots were obtained for all pure components as required by our model. Glass heat capacities were extrapolated above $T_g$
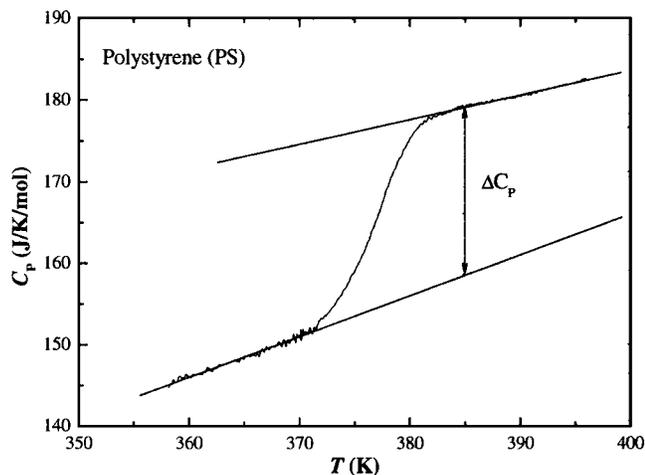
FIG. 1. Specific heat vs temperature for pure PS. The straight lines are the fittings of the specific heat of liquid and glass through a linear function of temperature.



FIG. 2. (a) Logarithm of the relaxation time vs temperature for pure PoClS (open circles), PS700 (filled circles), and PoClS in blends with PS700 with the following PoClS weight percentages: 25% (filled triangles), 50% (open triangles), and 75% (filled squares). The solid lines are the fittings of the model to the blend experimental data and the dashed lines are the fittings of pure components data through Eq. (14); (b) diameter of the relevant volume for segmental relaxation (left axis) and its ratio with the Kuhn segment (right axis) vs temperature calculated through the model for PoClS in blends with PS700. Percentages refer to PoClS.

and the excess heat capacity evaluated using the linear dependence with temperature ($\Delta C_P = a + bT$). This is shown in Fig. 1. The parameters $a$ and $b$ describing the excess heat capacity of pure polymers are summarized in Table I. Once $a$ and $b$ are known, it is possible to fit pure polymer dynamics data by means of the AG equation:

$$\tau = \tau_0 \exp\left(\frac{C}{TS_{\mathrm{ex}}}\right) = \tau_0 \exp\left[\frac{C}{T(a \ln(T/T_K) + b(T - T_K))}\right].$$
(14)

Equation (14) allows an excellent fit of the dynamics data of pure polymers as shown in Figs. 2–5, where the dynamics experimental data are shown together with the fitting of Eq. (14) (dashed lines). No appreciable difference was found with the commonly used Vogel-Fulcher-Tamann (VFT) phenomenological equation. The resulting fitting parameters ($\tau_0$, $C$, and $T_k$) for all pure polymers are listed in Table I. In this table, we also list the values of the Kuhn and packing lengths corresponding to all pure polymers. These values are used to relate the relevant volume for segmental relaxation and the self-concentration by means of Eq. (6) for all dielectrically active components in any blend.

## PS700/PoClS blends

In this blend, PoClS possesses a higher $T_g$ compared to PS700 and is the more dielectrically active component. Thus a single segmental dynamics can be detected through dielectric spectroscopy. Figure 2(a) shows the dielectric relaxation time versus temperature for blends with 25, 50, and 75 wt % of PoClS, and for pure PoClS and PS700. The continuous lines are the best fittings of the proposed model to the experimental data. The quality of the fitting is excellent. The best-fitting values of $\alpha$ for all blend compositions are summarized in Table II. It is found that the magnitude of $\alpha$ depends only slightly on composition. The knowledge of the parameter $\alpha$ allows to calculate the temperature dependence of the size of the relevant volume for segmental relaxation and of the self-concentration by means of Eqs. (8) and (9). As shown in Fig. 2(b), diameters of the relevant volume of

the order of 2.2–3 nm are obtained. The increasing length upon temperature reduction imposed by the AG theory results in a substantial temperature variation of the size of the relevant volume within the range of temperature for which the experimental data are available. Finally, it is noteworthy that an increase of the content of the rigid polymer, i.e., PoClS, results in an increase of the relevant length scale.

## PVME/PS blends

In this case the dielectrically active component of the blend is PVME, which presents a lower $T_g$ than PS. Figure 3(a) shows the dynamics experimental data for pure PVME and for blends with 50, 65, and 80 wt % of PVME. The data for PVME/PS with only these three percentages are presented, though the data at lower concentration of PVME (10%–30%) were previously obtained by some of us.[30,31] The reason is that blends with low PVME content display an Arrhenius-type behavior at relatively low temperatures. This kind of behavior was first noticed by Sy and Mijovic in poly(vinylidene fluoride)/poly(methyl methacrylate) blends,[32] and attributed to the ability of the rigid high $T_g$ polymer of the blend to confine the low $T_g$ one. Recent quasielastic neutron-scattering experiments and molecular-dynamics simulations on poly(ethylene oxide)/poly (methyl methacrylate) (PEO/PMMA) blends with a high content of the high $T_g$ component (PMMA) have shown a similar effect of confinement for the low $T_g$ component (PEO).[33] In addition, here we evidence that the effect of the high $T_g$ component on the dynamics of the low $T_g$ one should manifest even

TABLE II. Fitting parameter $\alpha$ expressed in ($\text{Å J}^{1/3} \text{ mol}^{-1/3} \text{ K}^{-1/3}$). Concentrations refer to the low $T_g$ component.

| Blend | Component | 25% | 50% | 75% | 80% |
|-------|-----------|-----|-----|-----|-----|
| PS700/PoClS | PoClS | 23.3±3 | 26.6±3 | 24.8±3 | ⋯ |
| PVME/PoClS | PoClS | ⋯ | 28.6±3 | 28.6±3 | ⋯ |
| PVME/PoClS | PVME | ⋯ | 10.7±1 | 11.2±1 | ⋯ |
| PVME/PS | PVME | ⋯ | 10.7±1 | 10.3±1[a] | 10.7±1 |

[a]This value of $\alpha$ refers to a PVME/PS with 65% of PVME.

at higher temperature where the Arrhenius behavior has not appeared yet. The high $T_g$ component falls out of equilibrium upon temperature reduction where the low $T_g$ component dynamics is still experimentally accessible. In other words, the experimental relaxation times of the low $T_g$ component below a certain temperature will be affected by the nonequilibrium dynamics imposed by the other component. In terms of the model we are proposing, below the glass transition range of the blend the high $T_g$ component would give an essentially constant contribution to the configurational entropy in the relevant volume for segmental relaxation. In PVME/PS blends the dielectric response of the PS is not detectable due to the strong contribution of PVME. However, it is possible to estimate the temperature where nonequilibrium effects should start being important from specific-heat-temperature traces presented in Ref. 30. This temperature can be identified with the point where, decreasing the temperature, the temperature derivative of the liquid heat capacity starts increasing due to the onset of the glass transition. For blends with 50, 65, and 80 wt % of PVME this temperature is, respectively, about 300, 284, and 270 K. As the model we have presented is based on equilibrium dynamics, we only determine the fitting parameter $\alpha$ form the data at temperatures where the blend is totally in equilibrium. This means that for blends with 10–30 wt % of PVME no fitting can be performed as the experimental data are only available up to 330 K. For blends with 50, 65, and 80 wt % of PVME, the lines in Fig. 3(a) are the best fitting of our model in the relevant temperature range (filled symbols). The parameters $\alpha$ for the three blend compositions are listed in Table II. As shown in the table, once again $\alpha$ is almost independent of the blend composition. Figure 3(b) shows the size of the relevant volume resulting from the model. Unlike PS700/PoClS blends, for PVME/PS blends the size of the relevant volume presents a weak temperature dependence. Sizes of the order of 1 nm are obtained. It is worth remarking that the weak temperature dependence of the relevant length scale is verified only in the range of temperature where the experimental data are available. However, within the framework of the AG theory, a diverging length scale would be obtained if the prediction of our model were extended to lower temperatures. Regarding the influence of blend concentration on the size of the relevant volume, as for PS700/PoClS blends, an increase in the concentration of the rigid component of the blend (in this case PS) results in an increase of the size of the relevant volume.
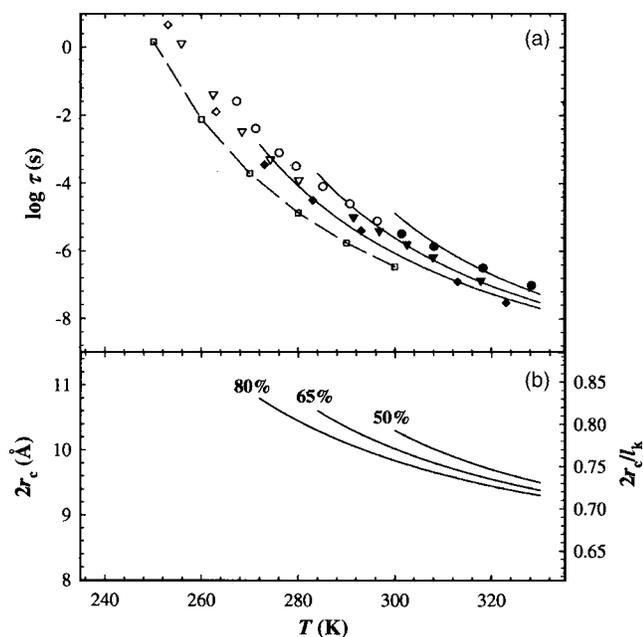


FIG. 3. (a) Logarithm of the relaxation time vs temperature for pure PVME (open square) and PVME in blends with PS with the following PVME weight percentages: 50% (filled and open circles), 65% (filled and open triangles), and 80% (filled and open diamonds). The solid symbols refer to the experimental data in the range of temperature where the model is applied. The solid lines are the fittings of the model to the blends experimental data and the dashed line is the fittings of pure PVME data through Eq. (14); (b) diameter of the relevant volume for segmental relaxation (left axis) and its ratio with the Kuhn segment (right axis) vs temperature calculated through the model for PVME in blends with PS. Percentages refer to PVME.

## PVME/PoClS blends

This blend presents both of the components dielectrically active and well separated in $T_g$. In Fig. 4(a), we plot dielectric relaxation times versus temperature for PoClS in blends with 25 and 50 wt % of PoClS and for pure PVME and PoClS. The solid lines refer to the model fitting. As in previous cases, an excellent fitting is obtained in the whole temperature range for which the experimental data are available. The fitting parameter $\alpha$ is reported in Table II. A single $\alpha$ for both compositions allows an excellent fitting of the data. The size of the relevant volume versus temperature is plotted in Fig. 4(b). As for PoClS in the blend with PS700, the relevant length scale displays significant temperature dependence and lays between of 2.4 and 3.2 nm. An increase in the size of the relevant volume is observed upon increasing the content of PoClS, in agreement with that observed for the other blends.

Figure 5(a) displays the dielectric relaxation time for PVME in blends with PoClS and for pure PVME. As for
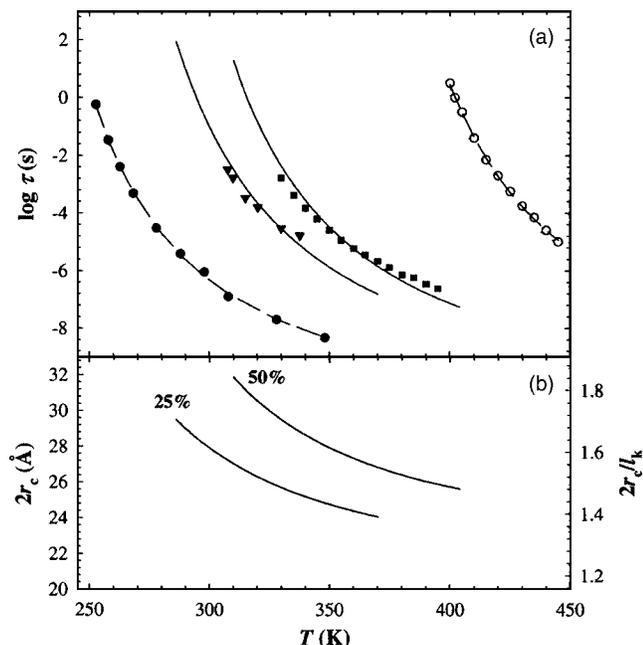
FIG. 4. (a) Logarithm of the relaxation time vs temperature for pure PoClS (open circles), pure PVME (filled circles), and PoClS in blends with PVME with the following PoClS weight percentages: 25% (filled triangles) and 50% (filled squares). The solid lines are the fittings of the model to the blend experimental data and the dashed lines are the fittings of pure components data through Eq. (14); (b) diameter of the relevant volume for segmental relaxation (left axis) and its ratio with the Kuhn segment (right axis) vs temperature calculated through the model for PoClS in blends with PVME. Percentages refer to PoClS.



FIG. 5. (a) Logarithm of the relaxation time vs temperature for pure PVME (open squares) and PVME in blends with PoClS with the following PVME weight percentages: 50% (filled and open circles) and 75% (filled and open triangles). The solid symbols refer to the experimental data in the range of temperature where the model is applied. The solid lines are the fittings of the model to the blend experimental data and the dashed line is the fitting of pure PVME data through Eq. (14); (b) diameter of the relevant volume for segmental relaxation (left axis) and its ratio with the Kuhn segment (right axis) vs temperature calculated through the model for PVME in blends with PoClS. Percentages refer to PVME.

PVME/PS blends, nonequilibrium effects due to the presence of rigid PoClS have to be taken into account when fitting the data. In this case, we can estimate the temperature where nonequilibrium effects appear from the dielectric data of PoClS in the blend. In particular, nonequilibrium will show up below the temperature where PoClS relaxation time in the blend is of the order of 100 s, namely, the time scale for a dielectric experiment. This temperature is about 290 and 310 K, respectively, for blends with 50 and 75 wt % of PVME. The solid lines in Fig. 5(a) represent the best fitting of our model to the high-temperature relaxation data. The fitting parameter $\alpha$ is reported in Table II and displays again a very weak dependence on blend concentration. In Fig. 5(b), the resulting diameter of the relevant volume versus temperature is plotted. Similar to PVME in the blend with PS, a weak temperature variation can be observed with a relevant length scale of the order of 1 nm. Again an increase of the rigid component content (PoClS) shifts upwards the diameter of the relevant volume.

## DISCUSSION

In the previous sections of the paper, we have presented a model based on the AG theory connecting dynamics and configurational entropy to predict the segmental dynamics of polymer blends starting from the knowledge of the dynamics and thermodynamics of the pure components. Apart from the parameters needed to fit dynamics and specific-heat data of pure components, the only parameter ($\alpha$) required to fit the component mean relaxation time and its temperature depen-

dence allowed an excellent fitting of the experimental data. Furthermore, under certain assumptions, the relevant length scale for segmental relaxation of that component can be obtained. As in the approach of Chung et al.,[3,4] and Lodge and Mcleish,[10] we have exploited the role of chain connectivity to describe the heterogeneous dynamics of miscible polymer blends. On the other hand, we let the relevant length scale vary with temperature according to the AG theory, predicting a growing length scale upon temperature reduction [see Eqs. (7) and (8)]. A temperature variation of the relevant length scale was also employed by Kant et al.,[17] in the framework of the Lodge-McLeish model. Unlike all previous approaches, our model does not involve any estimation of the effective $T_g$ starting from the pure components $T_g(s)$. However, since the model accounts for two distinct component dynamics, the existence of two $T_g(s)$ in a miscible polymer blend is a natural consequence of the model. Despite these differences, the size of the relevant length scale and its temperature variation obtained by us for PVME blended with PS resembles that obtained by Kant et al.[17] [see Fig. 3(b) of this work and Fig. 7(b) of Ref. 17]. In addition, the values obtained for the diameter of the relevant volume ($2r_c$) are not far from the Kuhn length in agreement with several recent findings.[10,11,14–16] A similar conclusion can be drawn for PVME blended with PoClS that presents sizes of the relevant volume close to those of PVME in PS, meaning that the relevant length scale for segmental dynamics is not very sensitive to the nature of the other component. This is true at least when PVME is blended with a polymer with higher $T_g$

and is probably due to the fact that PVME tends to maintain its identity due to the high self-concentration associated with a small relevant volume at the high temperatures, where the dynamics data are available at equilibrium.

Despite the ability of a length scale of the order of the Kuhn segment to approximately describe the segmental dynamics for PVME in PS and PoClS, it is worth noting that a weak temperature dependence of the size of the relevant volume is predicted by our model. This is in agreement with the widely accepted concept of a growing length scale upon temperature reduction in glass-forming systems. This concept becomes even more marked for the high $T_g$ components of the blends investigated in this study, namely, PoClS in blends with PS700 and PVME, where a rather pronounced temperature dependence of the relevant length scale has been obtained [see Figs. 2(b) and 4(b)]. PoClS in these blends displays a size of the relevant volume between 2.2 and 3.2 nm depending on the temperature, the other component of the blend (PVME or PS700), and its concentration, which means 1.3–1.9 larger than PoClS Kuhn length. This means that according to our treatment the Kuhn segment is accurate within a factor equal or smaller than 2. The nature of the second component of the blend does not seem to strongly affect the size of the relevant length scale, likely due to the similar mobility of PVME and PS700 that possess similar $T_g(s)$. As a general rule for all the investigated blends, a higher rigidity of the second component and/or a higher concentration of the rigid component generate larger sizes of the relevant volume for segmental dynamics. This is a plausible conclusion considering that rigid polymers generally require a larger number of basic structural units to give rise to molecular rearrangement.

It is worth remarking that, in this work, we have developed a model based on the configurational entropy only for the equilibrium relaxation data. This has limited the temperature range of application of our model to the dynamics of the low $T_g$ component of the blend. At relatively low temperatures, the dynamics of the fast component is restricted by the freezing-in of the high $T_g$ component, which eventually confines the low $T_g$ component as highlighted in several recent works.[30–33] The onset of nonequilibrium dynamics can in principle be assessed by the current model, once the dynamics of the high $T_g$ component is known. In particular, the system will fall out of equilibrium on the laboratory time scale, when the relaxation time of the high $T_g$ component is predicted to be of the order of several seconds. As a consequence of nonequilibrium, the experimental relaxation times for the low $T_g$ component obtained at temperatures where the rigid component is out of equilibrium are systematically smaller than those predicted by the model. A development of the model to out-of-equilibrium dynamics will be the subject of future work.

Finally, it is worth comparing our approach with that used by Lodge and McLeish to describe the component segmental dynamics of miscible polymer blends.[10] The latter approach attempts to provide a prediction of the segmental dynamics starting from the knowledge of the pure component dynamics alone. The Lodge and McLeish model, though successful to obtain a rough estimation of the dynamics,

yields a self-concentration value dependent on both the blend concentration and the other blend's component when a rigorous prediction of the segmental dynamics is required.[16,34,35] In our case, once pure component properties are known, the prediction of the segmental dynamics of blends requires the fitting of the parameter $\alpha$, relating the size of the relevant length scale to the configurational entropy, to the experimental data. As shown in Table II, the parameter $\alpha$ seems to be specific of the polymer independently of the other component of the blend. However, it is noteworthy that, based on very simple arguments, it is possible to refine the proposed model including a mixing rule also for the $\alpha$ parameter. Preliminary results on polymer-solvent systems seem to support this idea.[36] This would be significant only for those binary systems with components displaying rather different intrinsic values of $\alpha$. This independence would mean that, once $\alpha$ is known for one polymer, its segmental dynamics can be predicted whatever is the environment surrounding that polymer and its concentration. This makes the model potentially suitable to be also applied to predict the dynamics of multicomponents and out-of-equilibrium systems. Furthermore, the knowledge of the parameter $\alpha$ and its specificity for a given polymer can in principle be exploited to obtain information on single polymer dynamics, such as the estimation of the relevant length scale for segmental dynamics.

## CONCLUSIONS

We have proposed a model based on the AG theory of the configurational entropy and on the self-concentration to describe the component dynamics of several miscible polymer blends. In the framework of the AG theory, we have also made use of the concept of a growing length scale as temperature is reduced. Exploiting the concept of effective concentration, namely, the concentration experienced by the volume relevant for segmental dynamics, we were able to estimate the relevant length scale and its temperature variation. Apart from the fitting of dynamics and thermodynamic data for the pure components, the model requires only one fitting parameter relating the size of the relevant volume for segmental relaxation and the configurational entropy. Nevertheless, the results indicate that our model gives rise to an excellent description of the dynamics data, in the accessible temperature range. In addition, the fitting parameter does not seem to depend either on the blend concentration or the other component of the blend. This could suggest that this parameter is polymer specific and can be used to predict the segmental dynamics of other blends. The size of the relevant volume was found to lay between about 1 and 3.2 nm in agreement with any plausible expectation. In addition, the temperature variation of the relevant length scale suggests the general validity of the concept of a temperature-dependent length scale for segmental dynamics.

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