Segmental Dynamics in Miscible Polymer Blends: Modeling the Combined Effects of Chain Connectivity and Concentration Fluctuations

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ABSTRACT: The dynamic heterogeneity of the segmental dynamics in miscible polymer blends has been alternatively interpreted in terms of either chain connectivity effects or thermal concentration fluctuations. Taking into account that both phenomena seem to be relevant, in this work we propose a minimal model which combines these two effects. This model basically assumes the self-concentration approach recently proposed by Lodge and McLeish [*Macromolecules* **2000**, *33*, 5278] and introduces a distribution of the effective concentration around a given segment mainly due to the effect of thermal concentration fluctuations. The proposed model has been checked in two blend systems, PVME/PS and PoCLS/PS700. Each of these systems allows to selectively observe by dielectric spectroscopy either the low- or high-glass transition temperature component of the blend, respectively. The model provides a good quantitative description of the dielectric segmental relaxation in both cases with only one free parameter: the variance of the distribution of the effective concentration. This parameter results to be hardly dependent on temperature, at least in the two blends investigated.

I. Introduction

The study of polymer blends has been a very active field in polymer physics during the past 20 years (see refs 1−15 and references therein). From the point of view of the polymer blend dynamics, the so-called “dynamic miscibility”, i.e., the question concerning how the dynamics of each component is modified in the blend, has been deeply investigated. In an ideal two-component miscible polymer blend one could, in principle, expect a completely homogeneous dynamic behavior, in the meaning that the time scale as well as the relaxation function of each component becomes similar in the blend. Although this has been observed in some particular cases,[8] weakly interacting athermal miscible polymer blends are in general dynamically heterogeneous. This heterogeneity, which yields a failure of the time−temperature superposition principle,[10] has two manifestations.[1−7] On one hand, when the dynamics of a single component of a blend is selectively investigated, it is found that the response extends over a very broad time/frequency range, mainly in the vicinity of the glass transition temperature T_g. On the other hand, distinctly different segmental mobility for the two blend components have been observed in many blends, mainly at temperatures well above T_g. Thus, each of these two manifestations seems to dominate the blend dynamics, depending on the temperature range considered. Namely, at high temperature the response of each component has the shape corresponding to the pure polymer, and therefore the distinct segmental mobility of the components is apparent. However, at low temperature the response of each component extends over a very broad time range, and the distinct segmental mobility of the two components is not so evident. Whether these two manifestations have the same microscopic origin or they put in evidence two different aspects of the polymer blend dynamics is still controversial.

The models or theoretical approaches for polymer blend dynamics proposed up to date can be classified in two separate groups, depending on which of these sources of dynamical heterogeneity is considered to be the most relevant. The so-called thermal concentration fluctuation models[11,12] are based on the idea that the local concentration fluctuations, inherent to any miscible blend, are quasi-stationary near the glass transition (typically for $T_g < T < T_g + 60$ K) because their average relaxation time is much longer than that of segmental dynamics in that temperature range. This leads to a distribution of local concentration throughout the blend and thereby to a distribution of characteristic relaxation times for the segmental dynamics of each component. This explains qualitatively the dramatic relaxation broadening observed experimentally when a single component of a blend is selectively investigated. The first formal development of this idea was proposed by Fischer and co-workers.[11] The resulting model allowed to give a quantitative description of the α-relaxation broadening in various miscible blends. Later on, Kumar et al. proposed a more refined model[12] willing to describe also the different time scales of the two components in terms of thermal concentration fluctuations. Their model indeed can predict bimodal distribution functions of local environments of each blend component under some conditions. Nevertheless, the thermal concentration fluctuations approach fails in explaining the persistence of different segmental mobility for the two blend components well above the glass transition temperature (typically $T_g + 100$ K). As aforementioned, in this temperature range the shape of the component response is indistinguishable from that observed in the pure polymer,[2,3,6] providing evi-

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dence that the concentration fluctuations do not play a significant role in determining the shape of the segmental dynamics relaxation. Nevertheless, the difference between the characteristic times of the two components remains.

On the other hand, there are other models that consider that the chain connectivity[1,13] is the main factor responsible for the dynamic heterogeneity of polymer blends. This approach, first proposed by Chung et al.,[1] gives a comprehensive understanding of the dynamic heterogeneity without any particular temperature range restriction. The basic idea is that in a miscible blend of polymers A and B chain connectivity imposes that the local environment of a segment of polymer A is (on average) necessarily richer in polymer A compared to the bulk composition. This source of local concentration variation, which is, in principle, independent from thermal concentration fluctuations, implies that the average relaxation time of the lowest T_g component segments in the blend will always be significantly smaller than that of the highest T_g component segments. In a recent publication,[14] we showed that the formulation of this approach proposed by Lodge and McLeish[13] can be used to quantify this difference in mobility through the quantitative prediction of two distinct effective glass transition temperatures corresponding to each blend component. However, this formalism does not account for the strong broadening of the component response observed in the vicinity of T_g.

Only recently, a computer simulation study on the local concentration of miscible polymer blends has discussed the combined effect of thermal concentration fluctuations and chain connectivity.[16] In that investigation, it is found that both the thermal concentration fluctuations and the chain connectivity can be responsible for the local concentration variations.

An important question to be commented at this point is that the length scale relevant for the blend segmental dynamics derived when the thermal concentration fluctuations or the chain connectivity effects are considered as the main factor controlling the component dynamics seem to be different. The approach proposed by Lodge and McLeish[13] for calculating the effects of chain connectivity considers the Kuhn length l_K, as the characteristic spatial scale of the segmental dynamics. Accordingly, the self-concentration of each component is calculated as the volume fraction occupied by a Kuhn length's worth of monomers inside a cube of size l_K.[13] As aforementioned, this approach is able to account quantitatively for the different time scales of the components, even in the neighborhood of the glass transition range. On the basis of these results, one can consider that the chain connectivity effects are relevant for spatial scales of the order of, or shorter than, 1 nm. The neutron scattering results available point out on characteristic length scales for dynamic heterogeneity of polymer blends at high temperatures of this order of magnitude.[17] It is noteworthy that the effects of chain connectivity would vanish rapidly if the relevant spatial scale is significantly bigger. As an example, by following the procedure used by Lodge and McLeish to evaluate the chain connectivity effects, it is found that these effects are already negligible for characteristic lengths 3 times larger. On the other hand, the thermal concentration fluctuations are also very sensitive to the volume size explored; the thermal concentration fluctuation increases as the volume size decreases. When this approach has been applied to account for the relaxation broadening of a single component of miscible polymer blends, length scales of the order of 10 nm have been derived near the glass transition range.[11,12,15] As has been commented on above, for these length scales the chain connectivity effects nearly vanish.

Thereby, despite the rather different length scales derived when each of those effects are considered separately for describing the polymer blend dynamics, the two mechanims chain connectivity and thermal concentration fluctuations seem to be highly complementary. The chain connectivity would control the average mobility of each component reflecting, in some way, the intrinsic differences in mobility. Additionaly, the thermal concentration fluctuations would induce a spatial heterogeneity (in the time scale of the segmental dynamics) which would be responsible for a distribution of each component's mobility.

On the basis of these ideas, in this work we propose to combine both mechanisms in order to define a minimal model which allows to describe quantitatively the main features of the complex segmental dynamics taking place in miscible polymer blends. As a test, such a model will be then used to describe the segmental dynamics of two canonical miscible blends. The two systems studied take profit of the selectivity of dielectric spectroscopy. In the first one, PVME/PS (poly(vinyl methyl ether)/polystyrene), only PVME is dielectrically active.[14] Consequently, this blend will allow us to illustrate the effect of blending on the dynamics of the lower T_g component of the blend (PVME here). The second blend studied, PS/PoClS (polystyrene/poly(*o*-chlorostyrene)), in which only PoClS is dielectrically active,[14] illustrates the complementary case, as PoClS is also the higher T_g component of the blend.

II. Modeling

The proposed model is based on the following qualitative picture. The dynamics of a given polymer segment in a miscible blend is controlled by the local composition in some small region around the segment. The distribution of local compositions is mainly driven by two effects: statistical thermal concentration fluctuations and chain connectivity. These two effects are assumed to be independent in a simple first approach. With these ideas in mind, the main goal of the model is to calculate the distribution of the local concentration around segments of the two polymer components A and B. This is done by means of the following assumptions:

(i) In a polymer blend of concentration Φ on the component A the segments of the two polymer components A and B are chemically bounded to two segments of the same type. Therefore, they will experience effective local concentrations Φ_{effA} and Φ_{effB} given by

$$\Phi_{effA} = \Phi_{sA} + (1 - \Phi_{sA})\Phi \tag{1}$$

$$\Phi_{effB} = \Phi_{sB} + (1 - \Phi_{sB})(1 - \Phi) \tag{2}$$

where Φ_{sA} and Φ_{sB} are the respective "self-concentrations" of the components. If the size of the relevant volume for the segmental dynamics is large, Φ_s is nearly zero, and therefore, $\Phi_{eff} = \Phi$; i.e., one could expect a homogeneous dynamical behavior of the two blend components. On the contrary, if the size of the relevant volume is very small, Φ_s is close to one and therefore

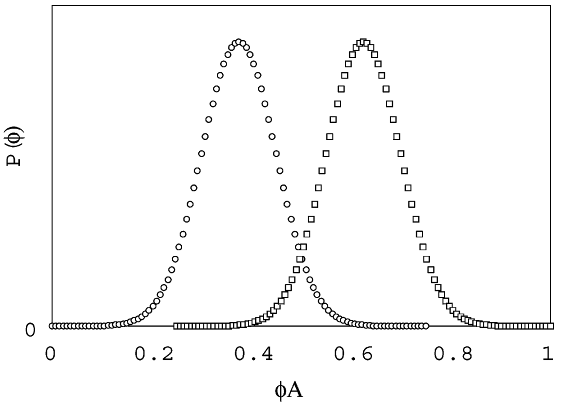

Figure 1. Example of local concentration distributions due to the combined effect of chain connectivity and thermal fluctuations of concentration: distribution of local environments of polymer A segments (squares) and polymer B segments (circles).

$\Phi_{\text{eff}} \approx 1$; i.e., one should expect a dynamical behavior of the component in the blend similar to that of the pure component. This latter situation is what is found, for instance, when studying the local secondary relaxations in polymer blends.[3] Following Lodge and McLeish, we calculate Φ_s for each component as the volume fraction occupied by a Kuhn length's worth of monomers inside a cube of size l_K (the Kuhn length).[13] This implies that the relevant volume for the segmental dynamics is assumed to be of the order of l_K^3.

Note that we are considering the self-concentration value of each component to be a perfectly defined quantity. However, in general one could consider a distribution of self-concentration values as well. Such a distribution has been suggested from computer simulation investigations.[16] Nevertheless, for the sake of simplicity, in the present work we have preferred to use the simplest approach of a unique value of self-concentration for each component.

(ii) The presence of statistical thermal concentration fluctuations would produce distributions of the effective concentration around the average value corresponding to each component. We assume these distributions to be Gaussian-like, i.e.

$$P(\Phi_{\text{eff}}) \propto \exp\left[-\frac{(\Phi_{\text{eff}} - \langle\Phi_{\text{eff}}\rangle)^2}{2\langle(\delta\Phi_{\text{eff}})^2\rangle}\right] \qquad (3)$$

with $\langle\Phi_{\text{eff}}\rangle$ being the average effective concentration calculated for a particular component from the average blend concentration Φ and $\langle(\delta\Phi_{\text{eff}})^2\rangle$ the corresponding variance which, in general, depends on the temperature and on the size of the relevant volume for the dynamics of the component considered. Note that there are two distinct distributions characterizing the environments experienced by the two polymer components in the blend, and each is, therefore, the relevant one for determining the segmental dynamics of the corresponding component. In Figure 1, we show an illustration of the two distinct distributions sensed by the two components. For constructing this plot we have considered a polymer blend in which the average concentration would be equal to 0.5, the self-concentrations Φ_{sA} and Φ_{sB} would be both equal to 0.25, and the variance of the distribution produced by the thermal concentration fluctuations would be characterized by $\langle(\delta\Phi_{\text{eff}})^2\rangle = 0.075$ in both cases.

A. Component Dynamics. In the following, we will show how this model can be used to calculate the contribution of a single component of a miscible blend to the dielectric relaxation response. Because of the different local compositions, the blend is considered as divided in different regions, and the dielectric relaxation of a given component of the blend is calculated assuming that in each region the shape of the dielectric relaxation function $\epsilon^*(\omega)$ is the same as that of the pure polymer. Thus, the blend response (the dielectric losses $\epsilon''(\omega)$ in our case) can be calculated as

$$\epsilon''(\omega) = \int_{-\infty}^{\infty} H(\log\tau)\,\text{Im}[\epsilon^*(\log\omega + \log\tau)]\,\text{d}\log\tau \qquad (4)$$

where the contribution of each region to the blend relaxation is given by the dielectric permittivity function of the pure polymer shifted in the frequency axis in accordance with the influence of the environment on the characteristic relaxation time. Note that this assumption implies that the dynamic properties inside each region can be modeled on the basis of the dynamic properties of the pure polymer.

The distribution of dielectric relaxation times $H(\log\tau)$ in eq 4 reflects the fact that the time scale of the dynamics of a given component changes from region to region because the different local concentrations. Thus, $H(\log\tau)$ must be obtained from the distribution of effective concentration as

$$H(\log\tau) = \frac{\Phi_{\text{eff}} - \Phi_s}{\langle\Phi_{\text{eff}}\rangle - \Phi_s} P(\Phi_{\text{eff}}) \left(\frac{\text{d}\Phi_{\text{eff}}}{\text{d}\log\tau}\right) \qquad (5)$$

where now Φ_{eff} corresponds to the local effective concentration of the polymer considered (A or B) and the factor $(\Phi_{\text{eff}} - \Phi_s)/(\langle\Phi_{\text{eff}}\rangle - \Phi_s)$ accounts for the fact that the dielectric contribution of this polymer in each region is proportional to the polymer content on it. This transformation calls for a formal relationship between the effective concentration of a given region and the characteristic relaxation time of the component in this region. This can be obtained by means of the Williams–Landel–Ferry (WLF) equation in the following way. For pure polymers, the WLF equation gives a direct relationship between the glass transition temperature and the relaxation time, which reads as

$$\log\tau(T) = \log\tau_g - \frac{C_1(T - T_g)}{C_2 + T - T_g} \qquad (6)$$

$\log\tau_g$, C_1, and C_2 being polymer dependent. When applying this equation to the different regions of a polymer blend, Fischer and co-workers used the concentration dependence of the macroscopic glass transition temperature (i.e., that determined by DSC experiments). However, by using such an approach the influence of the chain connectivity on the time scale of the component dynamics is missed. In our approach, we take into account the chain connectivity effects by relating the characteristic time of the component in each region of the blend with the effective glass transition temperature T_{geff} of the component considered (the lower the value of T_{geff}, the higher the mobility of the corresponding component). Lodge and McLeish proposed to calculate T_{geff} from the effective concentration as

$$T_{\text{gef}} = T_g(\Phi)|_{\Phi=\Phi_{\text{eff}}} \qquad (7)$$

where $T_g(\Phi)$ corresponds to the macroscopic glass transition temperature of the blend of average concentration Φ. Here we will use the same way to calculate the effective glass transition temperature of a given component in each region. To carry out the calculation, we will use as $T_g(\Phi)$ the one determined by fitting the macroscopic T_g values obtained by means of standard DSC experiments using the Brekner equation:

$$T_g(\bar{\Phi}_A) = T_{g_A} + (T_{g_B} - T_{g_A})[(1 + K_1)(1 - \bar{\Phi}_A) - (K_1 + K_2)(1 - \bar{\Phi}_A)^2 + K_2(1 - \bar{\Phi}_A)^3] \quad (8)$$

Here, $\bar{\Phi}_A$ is the average blend concentration in polymer A, T_{g_A} and T_{g_B} are respectively the glass transition temperatures of pure polymers A and B, and K_1 and K_2 are fitting parameters. Thus, the characteristic relaxation time of the component in each region is calculated as

$$\log \tau(T) = \log \tau_g - \frac{C_1(T - T_{\text{geff}})}{C_2 + T - T_{\text{geff}}} \quad (9)$$

Moreover, for using eq 9, we need the input of the three parameters C_1, C_2, and $\log \tau_g$, which might depend on the component concentration. As in the case of ref 11, we will assume a linear interpolation of the parameters C_1 and C_2 with the component average concentration. However, a similar choice of $\log \tau_g$ is not consistent with our approach, due to the intrinsically distinct time scales of the components. Our method to determine $\log \tau_g(\Phi)$ is based on the measurement of the dynamics of the different blends at any temperature well above the corresponding glass transition range. In the following we will refer to this high temperature as T^*. Note that at this high temperatures the effect of the thermal concentration fluctuations on the blend response is weak. With the experimental value of $\tau(T^*)$ from the blend with average concentration Φ on the component considered and rewriting eq 9, the value of $\log \tau_g$ is determined as

$$\log \tau_g = \log \tau(T^*) + \frac{C_1(T^* - T_{\text{geff}})}{C_2 + T^* - T_{\text{geff}}} \quad (10)$$

where we use the previously determined Φ dependences of C_1, C_2, and T_{geff}. This method introduces the contribution of self-concentration to the dynamical heterogeneity of the blend, which will persist at high temperatures where the possible effects of the thermal concentration fluctuations should be weak.

In this framework, the variance of $P(\Phi_{\text{eff}})$, $\langle(\delta\Phi_{\text{eff}})^2\rangle$, is the single free parameter to be adjusted in order to properly describe the experimental curves of the blends at each temperature.

III. Experimental Section

Poly(*o*-chlorostyrene) ($\bar{M}_w$ = 22 5000 g/mol, $\bar{M}_w/\bar{M}_n = 1.7$) and poly(vinyl methyl ether) ($\bar{M}_w$ = 21 900 g/mol, $\bar{M}_w/\bar{M}_n = 3$) were obtained from Lark Enterprises and Aldrich Chemical, respectively. For PVME/PS blend, a polystyrene ($\bar{M}_w$ = 66 000 g/mol, $\bar{M}_w/\bar{M}_n = 1.03$) obtained from Polymer Laboratories was used. In contrast, a polystyrene oligomer, PS_{700} ($\bar{M}_w$ = 740 g/mol, $\bar{M}_w/\bar{M}_n = 1.06$), purchased Polymer Source was used for PS_{700}/PoClS blends in order to increase the difference between the T_g values of the components.

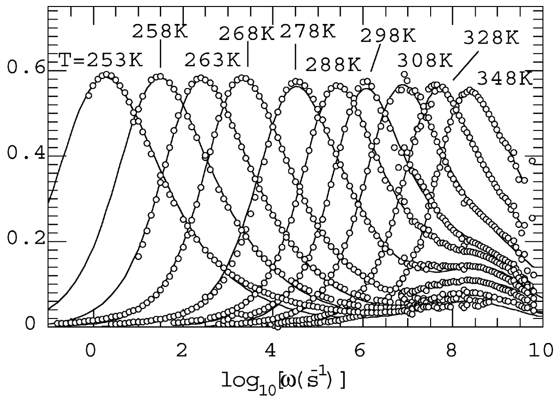

Figure 2. Dielectric relaxation curves of pure PVME: experimental results (symbols) and fitting curves (solid lines). The β-relaxation contribution was also included in the fitting.

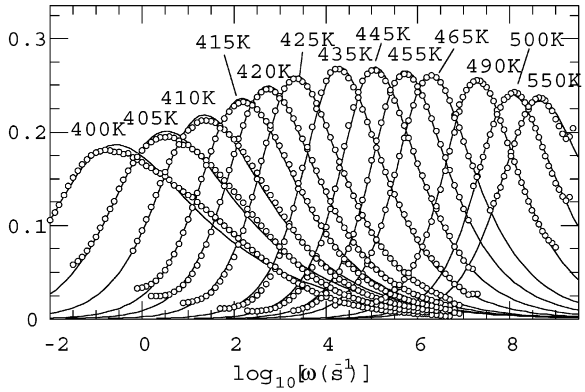

Figure 3. Dielectric relaxation curves of pure PoClS: experimental results (symbols) and fitting curves (solid lines).

Blends were prepared by solution casting using toluene as the solvent. The obtained films were carefully dried under vacuum, above their glass transition temperatures for 72 h, to remove the solvent completely. Reference samples of PVME, PoClS, and PS were prepared in a similar way. Dielectric relaxation measurements were performed on two different setups supplied by Novocontrol GmbH. For the frequency range from 10^{-3} to 10^7 Hz the setup consisted of a Solartron-Schlumberger frequency response analyzer SI 1260 supplemented by a high-impedance preamplifier of variable gain. For the frequency range from 10^6 to 10^9 Hz a Hewlett-Packard impedance analyzer HP4191A was used. For both ranges the sample was kept between two condenser plates (gold-plated electrodes, 20 and 5 mm diameter) that were maintained at a fixed distance. Frequency sweeps were performed at constant temperature with a temperature stability better than 0.05 K.

IV. Results

A. Dielectric Relaxation of Pure Polymers. Figures 2 and 3 show dielectric relaxation curves obtained for pure PVME and pure PoClS, respectively. In the case of PVME, we observe two relaxation processes: the secondary β-process and the segmental α-relaxation. As shown in a previous paper by our team,[3] the β-process can be described as the superposition of Debye-like thermally activated processes, and it is unaffected by blending with PS. These results are particularly important as they will allow us to calculate the β-process contribution to the PS/PVME blends dielectric relaxation curves and to remove it, so that we can focus only on the effect of blending on the α-relaxation.

For both polymers (pure PVME and pure PoClS), the α-relaxation was described using the Alvarez−Alegría−

Table 1. Estimated Parameters of WLF Equation Obtained for the Different Pure Polymers

polymer	C_1	C_2 (K)	$\log \tau_g$
PVME	13.2	49.5	0.158
PS	11.7	47.0	−0.801
PoClS	11.3	53.1	−0.129
PS_{700}	12.3	53.7	0.511

Colmenero function,[18,19] which is a particular case of the Havriliak−Negami function[3]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau_{HN})^{\alpha})^{\gamma}} \tag{11}$$

where $\Delta\epsilon$ is the relaxation strength and exponents α and γ are related by

$$\gamma(\alpha) = 1 - 0.812(1 - \alpha)^{0.387} \tag{12}$$

This constraint allows to reduce the number of free parameters and also to deduce from this frequency domain fit the parameters of the corresponding time domain Kohlrausch−Williams−Watts (KWW) function:[3]

$$\beta = (\alpha\gamma(\alpha))^{1/1.23} \tag{13}$$

$$\log \tau_{KWW} = \log \tau_{HN} - 2.6(1 - \beta)^{0.5} \exp[-3\beta] \tag{14}$$

Therefore, the dielectric relaxation corresponding to the polymer segmental dynamics is described at each temperature by only three parameters: β, $\log \tau_{KWW}$ (or α and $\log \tau_{HN}$), and the relaxation strength $\Delta\epsilon$.

For both pure polymers, the parameter β was found to increase with temperature above T_g, reaching a constant value at higher temperatures, $\beta = 0.50$ for PVME and $\beta = 0.45$ for PoClS. This temperature dependence, more pronounced in the case of PoClS, is in agreement with literature results[20] and has been also observed for different polymers.[21]

The KWW relaxation time of the two pure polymers followed the WLF equation with the parameters listed in Table 1. The corresponding values determined in a similar way for PS and PS_{700} are also included in the table.

B. Dielectric Relaxation of Polymer Blends. Figures 4a and 5a show the dielectric relaxation curves obtained for PS/PVME blends of compositions 50/50 and 35/65, respectively.[3] The observed relaxation processes have essentially the same characteristics than the relaxation curves reported in the literature for this system,[13] although both the frequency and the temperature ranges explored are wider in the present case. In both cases, the contribution of β-process has been calculated[3] and subtracted, so that the peak observed corresponds only to the α-relaxation of PVME in the blend. In comparison with pure PVME (Figure 2), we observe a huge broadening of the relaxation at temperatures close to the calorimetric glass transition temperatures of the blends ($T_g = 265$ K for 35/65 blend and $T_g = 282$ K for 50/50 blend). The effect is stronger in the case of the 50/50 blend.

The dielectric relaxation curves obtained for PoClS/PS blends of compositions 50/50 ($T_g = 320$ K) and 25/75 ($T_g = 300$ K) are shown in Figures 6a and 7a, respectively. Again, the relaxation broadening is stronger in the second blend which contains the lowest dielectrically active component fraction. Nevertheless, in both PoClS/PS blends, the broadening effect seems less pronounced than for the PS/PVME system.

Table 2. Parameters Used for Effective T_g Calculations Different Blends Studied[14]

blend A/B	Φ_{sB}	T_{gA} (K)	T_{gB} (K)	K_1	K_2
PS/PVME	0.25	373	249.5	−0.707	0.462
PS_{700}/PoClS	0.22	280	402	−0.296	0.792

V. Test of the Model

As commented above, for the application of the model to the blends investigated we need the input of a series of parameters that should be calculated starting from the data of the pure polymers. One of these parameters is that describing the relaxation shape. For the pure polymers investigated here, the shape of the relaxation has been found to be slightly temperature dependent. Nevertheless, this temperature dependence tends to disappear at high temperatures (typically $T > T_g + 30$ K). For our calculations, we will assume the shape parameters to be temperature independent and equal to those obtained experimentally from the fitting at high temperatures ($\beta = 0.5$ for PVME and $\beta = 0.45$ for PoClS). This choice is the simplest approximation and will likely produce a small, but systematic, overestimation of $\langle(\delta\Phi_{eff})^2\rangle$ at low temperatures. Nevertheless, there is not a clear alternative to this procedure since, when considering a variation of β with temperature, rather different approximations are possible. For example, one can use the value of β of the corresponding component at the measuring temperature or, alternatively, at the same temperature distance from the corresponding T_g. Another possibility is to associate the value of β to the characteristic time of the component, and in that case, because of the relaxation time distribution, a distribution of β values would be needed at each temperature. We will also take a temperature-independent $\Delta\epsilon$ value in the calculations equal to the average of the experimental values determined from the high-temperature measurements in the corresponding blends.

Concerning the evaluation of $\log \tau(T)$, we have used the WLF parameters $C_1 = C_{1A}\bar{\Phi}_A + C_{1B}(1 - \bar{\Phi}_A)$ and $C_2 = C_{2A}\bar{\Phi}_A + C_{2B}(1 - \bar{\Phi}_A)$ with the values for the homopolymers listed in Table 1. The corresponding values of T_{geff} have been calculated by means of the Breknel equation (8) with the parameters[14] listed in Table 2. Finally, we have calculated the values of $\log \tau_g$ for the dielectrically active component of the blends using eq 10, following the procedure described above. Note that the values of $\log \tau_g$ so obtained depend on the mixing rule used for calculating C_1 and C_2. The calculations yield for the PVME/PS blends $\log \tau_{gpvme}$ values compatible with that corresponding to pure PVME (0.14). This result is consistent with the results of a previous phenomenological analysis of the PVME/PS dielectric response[3] where it was found that the WLF parameters for the average relaxation time of the PVME segments in PS/PVME blends can be maintained to be the same that those of pure PVME. On the contrary, for PoCls/PS blends the values obtained for $\log \tau_{gpocls}$ are systematically higher than that in pure PoClS (−0.13); $\log \tau_{gpocls} = 0.54$ in the 50/50 PS/PoClS blend and $\log \tau_{gpocls} = 0.84$ in the 75/25 PS/PoClS blend. To answer whether these results correspond to general features of respectively the low-T_g and high-T_g compo-

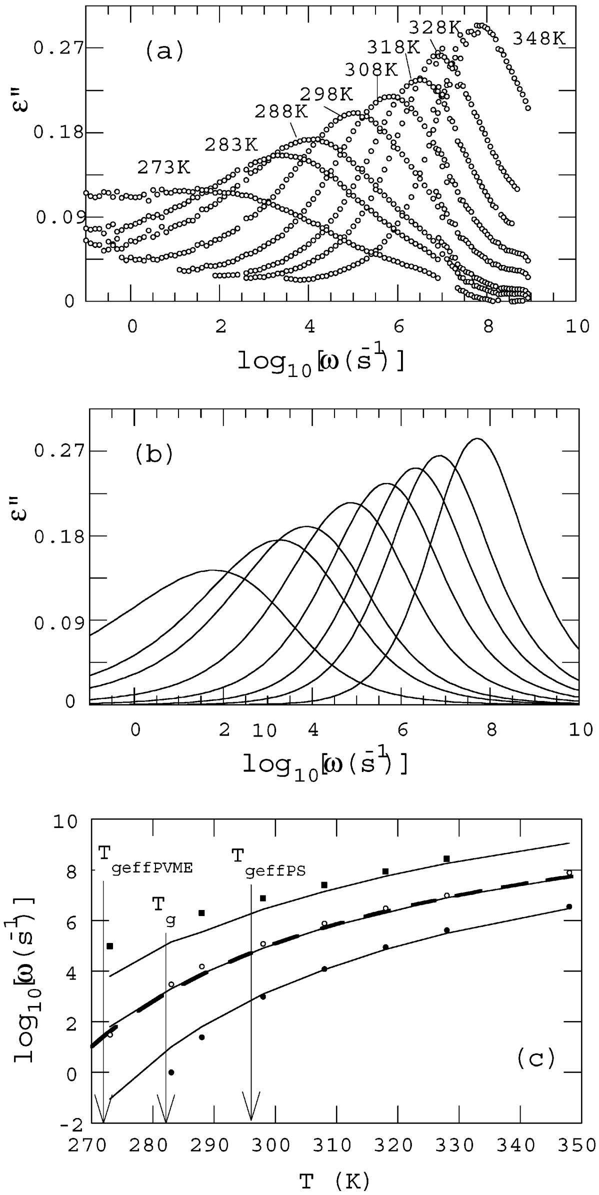

Figure 4. PS/PVME blend of composition 50/50: (a) experimental dielectric relaxation curves, once removed the β-relaxation contribution; (b) calculated curves with the model proposed; and (c) comparison of the experimental positions of peak maxima (empty circles) and half-height on both the low-frequency side (filled circles) and the high-frequency side (filled squares), with model predictions (solid lines). The three vertical arrows indicate the calorimetric T_g of the blend (282 K) and the two corresponding effective T_g of PS (296 K) and PVME (272 K). The dashed line has been calculated directly using the WLF equation with $T_{\mathrm{geff,\ PVME}}$.

nents of miscible polymer blends would need the application of this approach to other blend systems.

A. PS/PVME Blends. First we will comment on the comparison between model and experimental results on the 50/50 PS/PVME blend (Figure 4). Figure 4b show the calculated curves for the 50/50 PS/PVME, using the parameters given above and allowing the distribution variance $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$ as the single fitting parameter at each temperature. The agreement with the experimental curves is illustrated by Figure 4c where we have plotted the frequencies at the peak maximum and at half-height (both on low- and high-frequency sides) for both the experimental curves (symbols) and the model predictions (solid line). In this plot, we have also included three vertical arrows marking the calorimetric T_g (282 K) of the blend as well as the corresponding effective T_g values of both PS (296 K) and PVME (272 K) resulting from the effective concentration approach.[13,14]

It can be seen that the temperature evolution of peak frequency is remarkably well described for all temperatures above the effective T_g of PVME. The description of the half-height position on the lowest frequency side is also well described except for temperatures below the effective T_g of PS, where the model begins to underestimate the broadening. According to the SANS measurements of Takeno et al.,[22] the thermal concentration fluctuations start to freeze around 295 K and are completely frozen for temperatures below the calorimetric T_g of the blend. Consequently, it is not surprising that our approach fails in this temperature range. A similar behavior is observed for the half-height position on the highest frequency side. Nevertheless, in this case, the small but systematic disagreement occurs even at temperatures slightly higher than T_{geffPS}, i.e., when the thermal concentration fluctuations are in equilibrium. Thus, the difference between experiment and model predictions in these high frequencies should have other origin. From a previous phenomenological analysis of relaxation of PS/PVME blends,[3] it was observed that, close to T_g, the dynamics of some PVME segments seems to be faster in the blend than in pure polymer. This phenomenon was attributed to the result of the lack of packing in the blend leading to regions with greater "free volume" than that in pure PVME. Moreover, it has been recently suggested that this phenomenon could also be related to the nonequilibrium effects which would result in the motion of PVME segments in an environment rich on frozen PS chains.[23] A similar interpretation has been suggested in a very recently published work[24] for explaining that, in blends of poly(ethylene oxide) and poly(methyl methacrylate) with low concentration on the former, the motion of this component in the T_g range of the blend occurs with a time scale about 12 orders of magnitude faster than that observed for the other component. Again, this kind of phenomenology cannot be taken into account by the model we are considering here.

These intrinsic limitations of the model justifies the choice of testing it for blend compositions with a PS content not exceeding the 50%. Effectively, for higher compositions the two effects described above (thermal concentration fluctuations freezing and lack of packing) would be necessarily more important, so that the model would fail in describing accurately the experimental relaxation curves in the range of interest, i.e., for temperatures near the calorimetric T_g of the blend.

We now turn to the 35/65 PS/PVME blend for which calculated curves are showed in Figure 5b and compared in the same way to experiments in Figure 5c. As for the previous case, we observe a very good agreement between the model predictions and experimental values of peak maximum and half-height positions except when the temperature comes very close or below the calorimetric T_g of the blend (265 K). Note that the agreement between the calculated and the experimental values is for this composition even better than for the 50/50 PS/PVME blend. The reason is that for this composition the temperature range below the effective glass transition of PS where experimental data exist is narrower.

The values of $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$ obtained for the two PS/PVME blends are plotted as a function of temperature in Figure

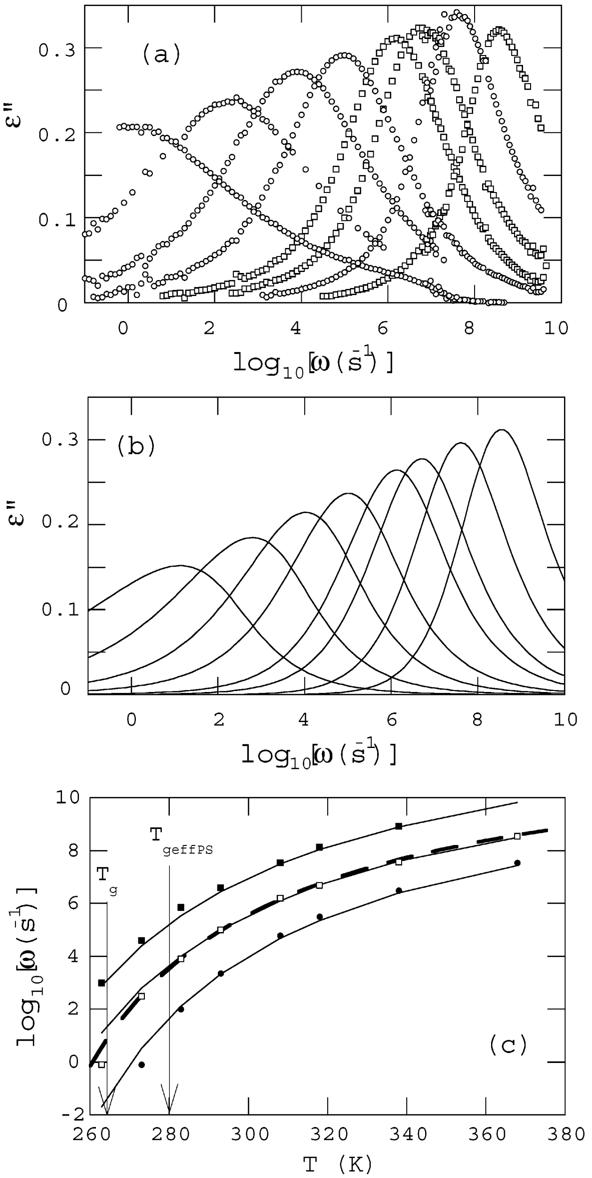

Figure 5. PS/PVME blend of composition 35/65: (a) experimental dielectric relaxation curves, once removed the β-relaxation contribution; (b) calculated curves with the model proposed; and (c) comparison of the experimental positions of peak maxima (empty circles) and half-height on both the low-frequency side (filled circles) and the high-frequency side (filled squares), with model predictions (solid lines). The two vertical arrows indicate the calorimetric T_g of the blend (263 K) and the corresponding effective T_g of PS (280 K). The dashed line has been calculated directly using the WLF equation with $T_{\mathrm{geff,PVME}}$.

8. In both cases we found a weak, but systematic, increasing of $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$ with temperature.

B. PoClS/PS$_{700}$ Blends. In contrast with the previous system, the application of the model in this system is expected to work over the whole experimental temperature and composition ranges, since the dielectrically active component (PoClS) is that showing the highest T_g. Therefore, no freezing of the thermal concentration fluctuations is expected in the temperature range of interest. Note that the dielectric response in these cases can be observed only for temperatures above $T_{\mathrm{geffPoClS}}$, which is higher than the calorimetric T_g of the blend.

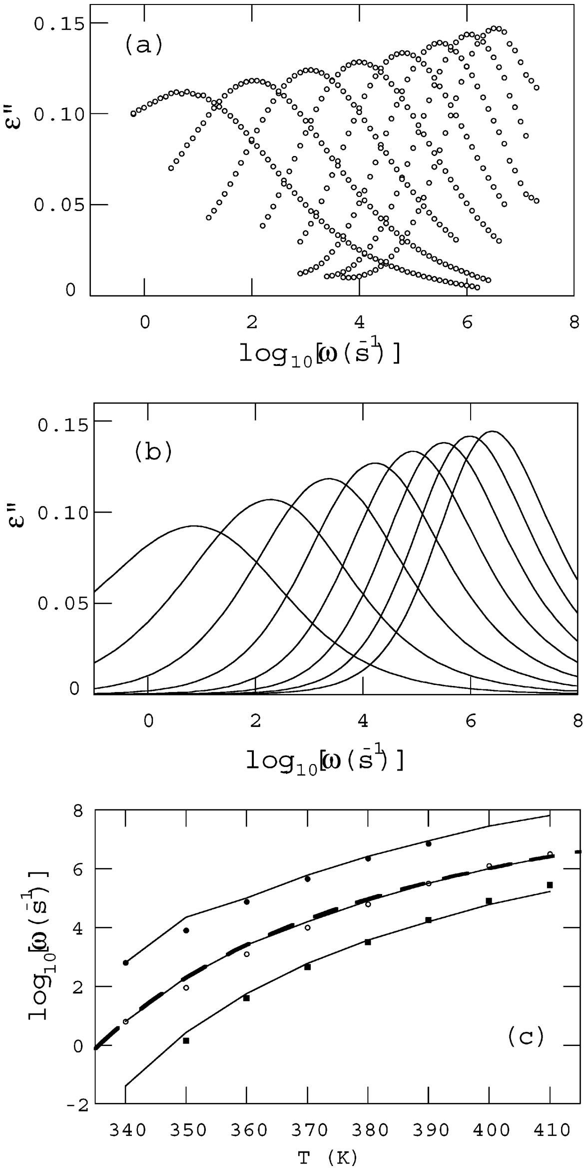

Figure 6. PoClS/PS$_{700}$ blend of composition 50/50: (a) experimental dielectric relaxation curves; (b) calculated curves with the model proposed; and (c) comparison of the experimental positions of peak maxima (empty circles) and half-height on both the low-frequency side (filled circles) and the high-frequency side (filled squares), with model predictions (solid lines). The dashed line has been calculated directly using the WLF equation with $T_{\mathrm{geff,PoClS}}$.

Figures 6b,c and 7b,c show the results obtained when applying the model for the 50PoClS/50PS$_{700}$ and the 25PoClS/75PS$_{700}$ blends, respectively. For both compositions, the lower temperatures measured are above the average glass transition of the corresponding blend (320 and 300 K, respectively) and also above the effective T_g of PoClS ($T_{\mathrm{geffPoClS}}$: 335 and 315 K, respectively), and therefore the corresponding arrows are not included in the figures. As for PS/PVME, the model allows a remarkably good description of relaxation process for both compositions. The values of the variance $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$ were found to be much lower than for PS/PVME blends and nearly temperature independent for the two compositions: $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle = 0.0050$ for the 50/50 blend and $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle = 0.0095$ for the 25/75 blend. These smaller values can be attributed to the fact that we have used a PS oligomer. Effectively, a previous study on the same system[25] showed that the broadening effect of blending highly depends on PS molar mass, the broadening being smaller for lower PS molar masses. Note that any possible weak temperature dependence of $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$

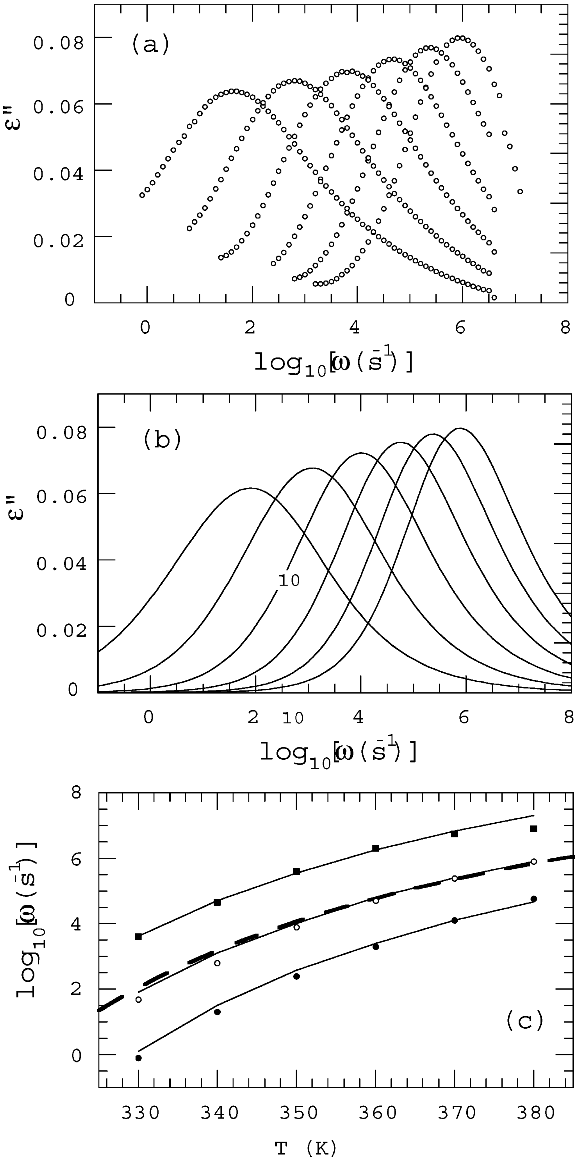

Figure 7. PoClS/PS$_{700}$ blend of composition 25/75: (a) experimental dielectric relaxation curves; (b) calculated curves with the model proposed; and (c) comparison of the experimental positions of peak maxima (empty circles) and half-height on both the low-frequency side (filled circles) and the high-frequency side (filled squares), with model predictions (solid lines). The dashed line has been calculated directly using the WLF equation with $T_{\mathrm{geff,PoClS}}$.

cannot be resolved for these blends because the resulting differences in the model curves would be within the experimental uncertainties.

VI. Discussion

In the previous section we have shown that the simple model proposed here is able to describe quantitatively the dynamics of the components of miscible polymer blends using a single free parameter: the variance of the effective concentration fluctuations $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$. This parameter contains information about two independent effects, namely self-concentration and thermal concentration fluctuations. Moreover, our results indicate that $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$ is hardly dependent on temperature, at least in the systems investigated.

On the other hand, it is notewordly that in this simple model a characteristic length scale for the segmental dynamics is implicitly involved: the Kuhn length of each component, which is used to estimate the self-concentration values. It is also important to point out that the temperature dependence of the relaxation peak frequency of a given component is perfectly described by taking into account only the self-concentration effects at that length scale, independent of the thermal concentration fluctuations effects. This fact is illustrated in Figures 4c, 5c, 6c, and 7c where a dashed line calculated by using the WLF formula directly with the parameters used in the model is included. Thereby, that relevant length scale seems to be nearly temperature independent over the whole temperature range investigated ($T_g \leftrightarrow T_g + 100$ K).

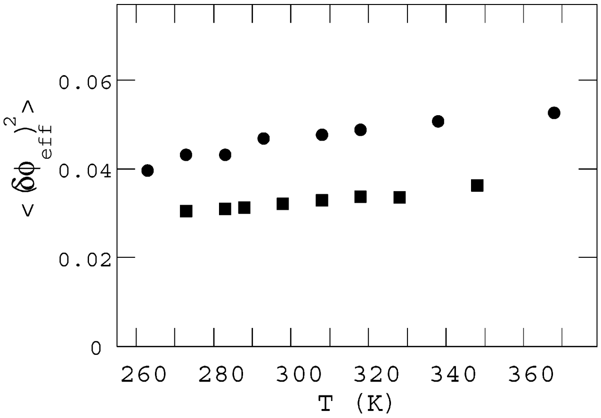

Figure 8. Values of the distribution variance for the PVME component in PS/PVME blends, composition 50/50 (squares) and 35/65 (circles), obtained at each temperature to fit the experimental data.

When comparing these results with previous estimations[11,12] of the relevant length scale for the segmental dynamics in polymer blends, a disagreement becomes apparent. The values of the relevant length scales so derived strongly depend on temperature and are markedly larger than the typical Kuhn length.[11,12] However, it is worthy of remark that the approaches abovementioned only consider the thermal concentration fluctuations effects. In that framework, the relevant length scale is evaluated from the concentration distribution variance[11,12] on the basis of the modification of the formalism of Ruland[26] for density fluctuations. This formalism gives the variance of the number of particles inside a reference volume as a function of both the volume size and the static structure factor. To apply this formalism to polymer blends, it is habitually assumed that the concentration fluctuations in this case are equivalent to what is obtained in a mixture of particles and holes. The particles are replaced by segments of polymer A, and the holes are replaced by segments of polymer B.[11] It is obvious that such a procedure does not take the chain connectivity into account, and thereby, its validity would be restricted to sufficient large volumes where the chain connectivity effects would be negligible. On the contrary, in the model proposed here, the dynamics of a segment are affected significantly by two effects, chain connectivity and thermal concentration fluctuations. Unfortunately, to our knowledge, there is not a theory for concentration fluctuations taking the chain connectivity effect into account able to establish a formal relationship between the distribution variance $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$ and the relevant length scale for the component dynamics. Nevertheless, the fact that the model proposed here—which directly involves the Kuhn length—describes quantitatively the component segmental dynamics, for both the low- and the high-T_g component, suggests that this relevant length scale should not be very different from that Kuhn length. A similar conclusion has been obtained from different arguments in a recent publication.[27]

VII. Conclusion

The combination of two existing approaches (the self-concentration concept and the thermal concentration fluctuations approach) leads to a simple model for describing the main features of the segmental dynamics in miscible polymer blends. This model basically takes the idea of an effective concentration for a given polymer segment in the blend and, in addition, assumes a distribution of effective concentrations mainly due to the effect of thermal concentration fluctuations. The model also assumes that the relevant length scale for the segmental dynamics of a given component is the corresponding Khun length.

The model has been used to calculate the dielectric relaxation curves of two model polymer blend systems (PVME/PS and PoClS/PS) where only one component (either the low-T_g ore the high-T_g) dominates the dielectric response in each case. A very good quantitative description is obtained in both cases with only one free parameter, $\langle(\delta\Phi_{\mathrm{eff}})^2\rangle$. At least for the two systems investigated this parameter hardly depends on temperature.

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