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Quantitative Study of Chain Connectivity Inducing Effective Glass Transition Temperatures in Miscible Polymer Blends

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ABSTRACT: To explore the ability of the “effective concentration” model to quantitatively predict the individual local dynamics of each component in miscible polymer blends, three model systems [polystyrene/poly(vinyl methyl ether), polystyrene/poly(*o*-chlorostyrene), and poly(vinyl methyl ether)/poly(*o*-chlorostyrene)] are studied using differential scanning calorimetry and thermally stimulated depolarization current, this second technique allowing to measure the effective T_g of the dielectrically active component in the blend. Final results show a very good agreement between measured effective glass transition temperatures and those predicted by the model.

Introduction

The understanding of the complex segmental dynamics taking place in miscible polymer blends has been a controversial subject during the past 10 years. While some authors have considered a single mobility for both blend components and emphasized the role of local concentration fluctuations in broadening the relaxation time distribution of each component, some others have pointed out the presence of intrinsic mobility differences of the components. This second idea seems to be confirmed by the direct observation of different component dynamics in various miscible blends, using a wide range of experimental techniques (NMR,[1,2] dielectric spectroscopy,[3] dynamic stress−optical measurements,[4] fluorescence anisotropy decay measurements,[5] quasi-elastic neutron scattering,[6] and dynamic mechanical measurements[7]).

Part of these experimental results can actually be rationalized by the concentration fluctuation based model of Kumar et al.,[8] which predicts bimodal distribution functions of local environments. Nevertheless, this model seems to fail in explaining the different segmental mobilities observed for the two blend components well above the glass transition temperature, where the concentration fluctuations do not play a significant role in the segmental dynamics.[2,6] Such limitation of the concentration fluctuation model therefore calls for the introduction of new concepts such as that of “effective concentration”, which was proposed by Chung et al.:[1] 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. The effective local concentration sensed by a polymer segment is thus given by

$$\phi_{\mathrm{eff}} = \phi_{\mathrm{s}} + (1 - \phi_{\mathrm{s}})\phi \tag{1}$$

where ϕ_s is the “self-concentration” of the considered polymer segment. A possible way of calculating ϕ_s was recently proposed by Lodge and McLeish.[9] It is based on the idea that the length scale relevant to the monomeric friction factor should be of the same order as the Kuhn length (l_K).[10] This assumption seems to be supported by recent neutron scattering results corresponding to a polyisoprene/polyvinylethylene (50/50) miscible blend.[6] In such a work, the characteristic time for chain dynamics of each component in the blend is investigated as a function of the momentum transfer Q and at high temperatures where the effect of concentration fluctuations should not be relevant. The main result reported is that distinctly different chain motions are only observed at Q values higher than those corresponding to the crossover from Rouse behavior to local segmental motions. This crossover in Q roughly corresponds to the Kuhn length scale.

Lodge and McLeish assume that the relaxation of the Kuhn segment is influenced by the concentration of monomers within a volume $V = gl_K^3$ (g being a geometric factor) and calculate ϕ_s as the volume fraction occupied by a Kuhn length’s worth of monomers inside V:

$$\phi_{\mathrm{s}} = \frac{C_\infty M_0}{k\rho N_{\mathrm{av}} V} \tag{2}$$

where M_0 is the molar mass of repeat unit, N_{av} is the Avogadro number, k is the number of backbone bonds per repeat unit, ρ is the density, and C_∞ is the characteristic ratio.[10]

To test their model, Lodge and McLeish[9] propose to calculate the effective glass transition temperature $T_{g_{\mathrm{eff}}}(\phi)$ of each blend component as a function of concentration ϕ from the calorimetric glass transition temperature $T_g(\phi)$ using the following equation:

$$T_{g_{\mathrm{eff}}}(\phi) = T_{g}(\phi_{\mathrm{eff}}) \tag{3}$$

Comparison of calculated effective glass transition temperatures with literature data thus shows relatively good qualitative agreement for a variety of miscible blends.[9] Nevertheless, even for the more significative systems,[1,3] experimental effective T_g used are obtained from isothermal measurements (NMR[1] or ac dielectric spectroscopy[3]) by selecting a particular value of the

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relaxation time. Apart from requiring some extrapolations of raw data (NMR), this procedure suppose a known relation between calorimetric T_g and the isothermal relaxation time, which is not clear when the relaxation becomes highly nonexponential.

The aim of the present communication is to test in a more quantitative way the accuracy of the "effective concentration" model as defined by Lodge and McLeish.[9] Three model miscible blends have thus been studied by differential scanning calorimetry (DSC) and thermally stimulated depolarization current (TSDC). The interest of this second technique[11] is that it can be considered as a dielectric sensitive equivalent of DSC (see Experimental Section) which allows to measure the glass transition temperature sensed by the dielectrically active segments present in the blend.

The three systems studied take profit of this selectivity. In the first one, PVME/PS[3] (poly(vinyl methyl ether)/polystyrene), only the lower T_g component (PVME) is dielectrically active. Consequently, TSDC will allow us to directly measure the effective glass transition temperature of this component. Moreover, this effective T_g being obtained for the same time−temperature stimulation as in DSC (see Experimental Section), it should be much more reliable than the effective T_g previously used by Lodge and McLeish for their qualitative tests.[9] The second blend studied, PS/PoClS[12] (polystyrene/poly(*o*-chlorostyrene)), illustrates a different situation, as this time the poly(*o*-chlorostyrene) is the dielectrically active and higher T_g component. Finally, in the last blend, PVME/PoClS,[13] both components are dielectrically active but with a very high T_g difference, which should allow to separate both dielectric contributions.[14]

Experimental Section

Poly(*o*-chlorostyrene) ($\bar{M}_w = 225\,000$ 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 ($\bar{M}_w = 740$ g/mol; $\bar{M}_w/\bar{M}_n = 1.06$) purchased Polymer Source was used for PS/PoClS blends in order to increase the difference between the T_g of the components. All binary blends were prepared by solution casting using toluene as the solvent. 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.

DSC experiments were performed at 10 K/min with samples of about 10−15 mg that were previously cooled at −40 K/min from the melt to about 40 K below the glass transition temperature of the lowest T_g component of the blend. The calorimetric glass transition temperatures T_g were subsequently determined using the midpoint of heat capacity change as a criterion. DSC temperature calibration was done by using indium (T_m = 429.75 K) and dodecane (T_m = 263.5 K) standards.

In the TSDC technique,[11] a given polymer sample is placed between electrodes maintained at a fixed distance (with Teflon spacers of 0.063 mm in our case) and polarized by applying an electric field (we used a polarization voltage of 200 V) at a temperature above its glass transition (typically 30 K above the calorimetric T_g). After that, the sample is cooled, with the electric field on, down to a temperature well below its T_g (T_g − 100 K typically) in order to freeze in the sample's polarization. The polarization voltage is then switched off, and the sample is heated at constant rate. By recording as a function of time the electric current produced by the depolarization process during this temperature ramp, a peak is obtained when the dipoles present in the polymer chains become mobile enough to randomize, that is to say, at the glass transition temperature sensed by the dielectrically active segments in the chains. Consequently, by making our TSDC measurements at the same heating rate as for DSC experiments (10 K/min), we obtain an effective T_g of the dielectrically active segments that can be directly compared with the bulk T_g obtained in DSC.

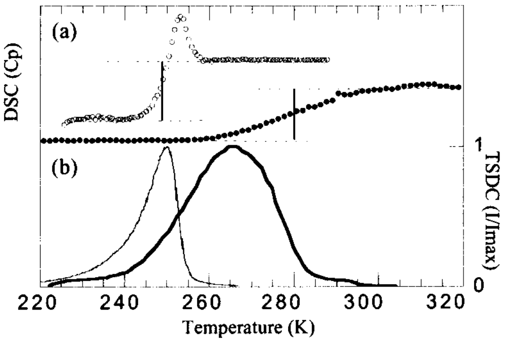

Figure 1. Comparison of DSC (a) and TSDC curves (b) for a pure PVME (empty circles and thin line) and a 50/50 PVME/PS blend (filled circles and thick line). Vertical lines show the midpoint glass transition temperatures obtained on the DSC curves.

Results

DSC measurements showed single heat capacity step (see Figure 1) for all blends, confirming their miscibility. Midpoint T_g values found for the PVME/PoClS and PVME/PS blends were in agreement with literature results.[13,15]

Some typical TSDC measurements are illustrated by Figure 1, taking the case of pure PVME and 50/50 PVME/PS blend: For the pure polymer, the midpoint T_g (249.5 K) of the DSC curve is almost equal to the temperature at which the depolarization current reaches its maximum (T_{max} = 250.4 K). However, in the blend, the TSDC maximum peak occurs at a significantly lower temperature (T_{max} = 263 K) than the calorimetric T_g (278 K), showing that the effective local T_g sensed by the dipoles present in the PVME chain is lower than the macroscopic T_g of the blend. A similar situation is observed for the PS/PoClS blends where the TSDC peaks maxima always occur at higher temperatures than the calorimetric T_g found in DSC. An intermediate situation is found for PVME/PoClS blends where two overlapped but clearly defined peaks are observed on the TSDC curves, their maxima being respectively lower and higher than the calorimetric T_g.

All DSC and TSDC results obtained for the three blends (PVME/PS, PS/PoClS, and PVME/PoClS) are plotted in Figures 2 and 3. This makes clear the difference between calorimetric T_g and individual component's T_{max} ($=T_{g_{eff}}$) obtained by TSDC as well as its evolution with blends' composition.

Discussion

For each blend, we first fitted the evolution of bulk glass transition temperature measured by DSC, using the Brekner equation (dashed lines in Figures 2 and 3):

$$T_g(\phi_B) = T_{gA} + (T_{gB} - T_{gA})[(1 + K_1)\phi_B - (K_1 + K_2)\phi_B^{\ 2} + K_2\phi_B^{\ 3}] \quad (4)$$

where ϕ_B is the bulk concentration in higher T_g component B, T_{gA} and T_{gB} are the respective glass transition temperatures of pure polymers A and B, and K_1 and K_2

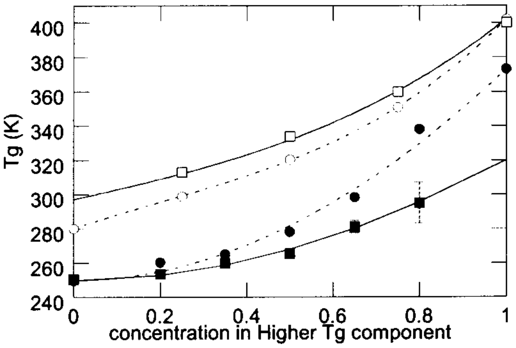

Figure 2. Glass transition temperatures in PVME/PS and $PS_{oligomer}$/PoClS blends: experimental DSC results (filled circles, PVME/PS; empty circles, $PS_{oligomer}$/PoClS), TSDC results (filled squares, PVME/PS; empty squares, $PS_{oligomer}$/PoClS), fits of calorimetric T_g by Brekner's equation (dashed lines), and predictions of the effective concentration model (solid lines).

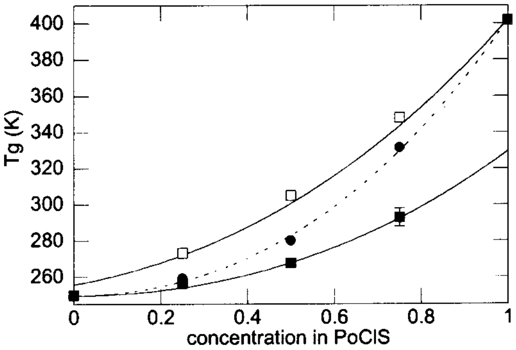

Figure 3. PVME/PoClS blend: evolution of blend's calorimetric $T_g(\phi)$ (circles, DSC experiments; dashed line, Brekner equation) and effective glass transition temperatures of PVME ($T_g(\phi)_{PVME}$: filled squares, TSDC experiments; solid line, effective concentration model) and PoClS ($T_g(\phi)_{PoClS}$: empty squares, TSDC experiments; solid line, effective concentration model).

Table 1. Parameters of Brekner's Equation (Eq 4) for the Different Blends Studied

blend A/B	T_{gA} (K)	T_{gB} (K)	K_1	K_2
PVME/PS	249.5	373.0	−0.707	0.462
$PS_{oligomer}$/PoClS	280.0	402.0	−0.296	0.792
PVME/PoClS	249.5	402.0	−0.99	0.277

are fitting parameters. All these parameters are listed in Table 1 for each blend.

In a second step, we calculated the evolution of the effective glass transition temperature $T_{g_{eff}}$ of each dielectrically active component following the same procedure as Lodge and McLeish,[9] i.e., by combining eqs 1, 3, and 4. If we take component B, for example, that gives

$$T_{gB_{eff}}(\phi_B) = T_{gA} + (T_{gB} - T_{gA})[(1 + K_1)\phi_{B_{eff}} - (K_1 + K_2)\phi_{B_{eff}}^{\ 2} + K_2\phi_{B_{eff}}^{\ 3}] \quad (5)$$

where T_{gA}, T_{gB}, K_1, and K_2 are given by the calorimetric results and $\phi_{B_{eff}}$ is calculated from the bulk concentration ϕ_B, using eq 1. The "self-concentrations" used for calculations were ($\phi_{sPVME} = 0.25$)[9] and ($\phi_{sPoClS} = 0.22$).[16] They both assume that as a first approximation the geometric factor g used to calculate the volume V is equal to unity ($V = l_K^3$).

A remarkably good quantitative agreement between TSDC results and calculated $T_{g_{eff}}$ curves can be observed for all measured blends (see Figures 2 and 3). This result, which tends to demonstrate the quantitative efficiency of the "effective concentration" model, is however quite surprising. Actually, as Lodge and McLeish[9] insist, their model should describe the effective glass transition temperatures sensed on the length scale relevant to the monomeric friction factor, that is to say, for probably longer length scales than that of the dipolar relaxation we sense in the TSDC experiments. Another interesting point is that the assumption made on the geometric factor g seems reasonable. In fact, if we now use the TSDC measurements to evaluate experimentally that factor, taking into account the experimental error bars on effective glass transition temperatures, we obtain $g_{PVME} = 1.00 \pm 0.16$ and $g_{PoClS} = 1.10 \pm 0.16$.

Conclusions

Thanks to the use of the TSDC technique, we have been able to investigate the individual effective glass transition temperatures in three model blends. On the basis of the results obtained, we can conclude that the "effective concentration" model proposed by Lodge and McLeish[9] allows not only to rationalize but also to quantitatively predict these effective glass transition temperatures, which are linked to the average segmental mobility of each polymer in the blend. This leads us to think that local concentration variations at length scales of the same order as the Kuhn length, induced by chain connectivity, are probably the predominant factor leading to the apparent distinct component mobilities experimentally observed in miscible blends. Consequently, the "effective concentration" concept should be taken into account as a fundamental ingredient when trying to develop a model able to describe all the issues of miscible polymer blends' dynamics. Work in this direction is now in progress.

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(16) The self-concentration of PoClS, ϕ_{sPoClS}, was estimated from eq 2, using $M_0 = 138.5$ g/mol and $\rho = 1.14$ g/cm^3 (Zacharius, S. L.; Brinke, G. T.; MacKnight, W. J.; Karasz, F. E. *Macromolecules* **1983**, *16*, 381−387) and $k = 2$. C_∞ was calculated from measurements of K_θ in toluene solution (Matsumura, K. *Polym. J.* **1970**, *1*, 322−326), using the following equation: $C_\infty = (K_\theta/\Phi)^{2/3}(M_0/2l^2)$, where l is the average backbone length ($l = 1.53$ Å), ϕ is Flory's universal constant ($\Phi = 2.6 \times 10^{21}$), and $K_\theta = 6.14 \times 10^{-4}$.

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