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Rheology and Dynamics near Phase Separation in a Polymer Blend: Model and Scaling Analysis

ABDELLAH AJJI* AND LIONEL CHOPLIN

Centre de recherche en sciences et ingénierie des macromolécules, Département de génie chimique, Faculté des sciences et de génie, Université Laval, Québec, PQ, Canada G1K 7P4

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The dynamics of low molecular weight polymer mixtures, in terms of concentration fluctuations near a critical point, in the homogeneous region, has shown a nonlinear behavior in a number of physical properties.[1,2] For high molecular weight mixtures, i.e., polymer blends and block copolymers, most of the studies dealt with the dynamics of phase separation and spinodal decomposition and its incidence on the scattering properties of these mixtures.[3] For the viscoelastic properties, Bates,[4,5] Gouinlock and Porter,[6] and Han[7,8] have studied block copolymers and observed important discontinuities of their dynamic properties (G' and η^*) near the microphase separation temperature (T_s) when performing temperature steps. Also, an important increase of these properties was observed at low frequencies for temperatures close to T_s.

Until recently, similar studies were missing for polymer blends exhibiting phase separation behavior.[9,10] In a recent study,[10] clear evidence of a similar behavior has been observed for blends of polystyrene with poly(vinyl methyl ether) (PS/PVME) in our laboratory. The magnitude of the changes near the phase separation temperature T_s was much smaller than those observed for block copolymers, but it was significant, i.e., an increase of G' of 100% for a frequency of 10 rad/s, in contrast to the expectation of a negligible effect if compared with that of block copolymers.[4,11]

From a theoretical point of view, Fredrickson and Larson[11] and Onuki[12] have considered the contribution of critical fluctuations to the viscoelastic properties of block copolymers near the critical point (T_s). Mean-field theory was used to predict the evolution of the viscoelastic properties (G' and G'') under oscillatory shear flow and to derive scaling laws for block copolymers. Particularly, an increase in the viscoelastic properties near T_s was predicted, in qualitative agreement with the results of Bates mentioned above.[4,5] In this paper, the treatment proposed by Fredrickson et al.[11] is extended to binary homopolymer blends, and the results of a scaling analysis are presented.

It is important to mention here that the mean-field approach can be justified by using sufficiently high molecular weights to reduce the temperature range of non-mean-field behavior.[13] These molecular weights should be also sufficiently low to allow for important concentration fluctuation effects,[14] since these effects are proportional to $1/N$ (N the number of units). Fredrickson and Larson[11] derived a mean-field expression for the critical contribution to the shear stress for near-critical polymer mixtures, the details of their development and discussion of the case of copolymers can be found in refs 11 and 14–16. For the sake of brevity, the same nomenclature as in ref 11 is used. After integration over wave-vector space, they obtained the following expressions for the dynamic storage and loss moduli G' and G'' respectively:

$$G' = \frac{k_B T\omega^2}{15\pi^2}\int_0^{k_c} \frac{k^6 S_0^{\,2}(k)}{\omega^2 + 4\bar{\omega}^2(k)}\left[\frac{\partial S_0^{-1}(k)}{\partial k^2}\right]^2 \mathrm{d}k \qquad (1)$$

$$G'' = \frac{2k_B T\omega}{15\pi^2}\int_0^{k_c} \frac{k^6 S_0^{\,2}(k)\bar{\omega}(k)}{\omega^2 + 4\bar{\omega}^2(k)}\left[\frac{\partial S_0^{-1}(k)}{\partial k^2}\right]^2 \mathrm{d}k \qquad (2)$$

$$\bar{\omega}(k) = k^2 S_0^{-1}(k)\lambda(k) \qquad (3)$$

These expressions were valid either for block copolymers or binary homopolymer blends and can be calculated by using the proper expressions for the static structure factor $S_0(k)$ and the Onsager coefficient $\lambda(k)$ for the polymeric system of interest.

Application to Homopolymer Blends. For binary homopolymer blends, we used the expression of the static structure factor (scattering function) that has already been computed by de Gennes[14] by a mean-field approach in the random phase approximation:

$$S_0^{-1}(k) = \frac{1}{\phi N_1 g_1(k)} + \frac{1}{(1-\phi)N_2 g_2(k)} - 2\chi \qquad (4)$$

where $g_i(k)$ are the Debye functions. For the Onsager coefficient, Binder[16] proposed the following expression for binary homopolymer blends near the phase separation temperature:

$$\frac{1}{\lambda(k)} = \frac{1}{\phi a_1^{\,2} W_1 g_1(k)} + \frac{1}{(1-\phi)a_2^{\,2} W_2 g_2(k)} \qquad (5)$$

where a_i is the length of a repeat unit of species i and W_i its rate of reorientation, defined by

$$W_i = 3\pi k_B T/\zeta_i \qquad (6)$$

where ζ_i is the "monomeric" friction coefficient.

The knowledge of molecular weight allows the determination of N_i and a_i and/or Rg_i can be determined experimentally (or from the literature). Only three parameters remain unknown, namely, the individual monomeric friction coefficients and the interaction parameter. We should mention also that the structure factor decreases rapidly to zero so that the integrals in eqs 1 and 2 converges easily in the terminal region, and a cutoff in the wave vector can be imposed when G' has converged.[11] Thus, values of G' and G'' for different frequencies, temperatures, and interaction parameters can be computed.

Scaling Analysis. The scaling analysis of G' and G'' in the terminal region as the critical point is approached is of particular interest. Hence, using the expansion of $g_i(k)$ to the first term, one obtains for $S_0(k)$ and $\lambda(k)$ the following expressions:

$$S_0^{-1}(k) = 2(\chi_s - \chi) + \left[\frac{1}{\phi N_1}\frac{Rg_1^{\,2}}{3} + \frac{1}{(1-\phi)N_2}\frac{Rg_2^{\,2}}{3}\right]k^2 \qquad (7)$$

$$\lambda^{-1}(k) = \frac{1}{\phi a_1^{\,2} W_1} + \frac{1}{(1-\phi)a_2^{\,2} W_2} + \left[\frac{Rg_1^{\,2}}{\phi a_1 W_1} + \frac{Rg_2^{\,2}}{(1-\phi)a_2 W_2}\right]k^2 \qquad (8)$$

where χ_s designates the interaction parameter at the spinodal ($S_0^{-1}(0) = 0$). Replacing these expressions in eqs 1 and 2 and retaining only the leading order terms as χ tends to χ_s, one obtains after integration

$$G'(w) = \frac{k_B T\omega^2}{1920\pi}\left[\frac{1}{3}\left\{\frac{Rg_1^{\,2}}{\phi N_1} + \frac{Rg_2^{\,2}}{(1-\phi)N_2}\right\}\right]^{1/2} \times \left[\frac{1}{\phi a_1^{\,2} W_1} + \frac{1}{(1-\phi)a_2^{\,2} W_2}\right]^2 [2(\chi_s - \chi)]^{-5/2} \qquad (9)$$

$$G''(w) = \frac{k_{\mathrm{B}}T\omega}{240\pi}\left[\frac{1}{3}\left\{\frac{Rg_1^{\,2}}{\phi N_1} + \frac{Rg_2^{\,2}}{(1-\phi)N_2}\right\}\right]^{-1/2} \times \left[\frac{1}{\phi a_1^{\,2}W_1} + \frac{1}{(1-\phi)a_2^{\,2}W_2}\right][2(\chi_s - \chi)]^{-1/2} \quad (10)$$

Several consequences can be drawn from these expressions: (i) G′ is proportional to $(\chi_s - \chi)^{-5/2}$, similar to the result obtained for copolymers; (ii) the dependence of G'' on $(\chi_s - \chi)^{-1/2}$ is much less pronounced than that of G' and is different from that obtained for block copolymers (an exponent of −3/2); (iii) from the expressions obtained for G' and G'', one can eliminate either the monomeric friction coefficients or the interaction parameter dependence. If the ratio $G'/G''^{\,2}$ is calculated, one obtains

$$\frac{G'}{G''^{\,2}} = \frac{30\pi}{k_{\mathrm{B}}T}[\phi(1-\phi)]^3\left[\frac{a'}{6}\{\phi(1-\phi)(\chi_s - \chi)\}^{-1/2}\right]^3 \quad (11)$$

Having in mind the expression of the correlation length of blends

$$\xi = \frac{a'}{6}\{\phi(1-\phi)(\chi_s - \chi)\}^{-1/2} \quad (12)$$

one obtains the simple relationship:

$$\frac{G'}{G''^{\,2}} = \frac{30\pi}{k_{\mathrm{B}}T}[\phi(1-\phi)]^3\xi^3 \quad (13)$$

Thus, the correlation length can be estimated near the critical region from rheological measurements:

$$\xi = \left[\frac{k_{\mathrm{B}}T}{30\pi}\frac{G''^{\,2}}{G'}\right]^{1/3}\phi(1-\phi) \quad (14)$$

It is to be noted here that the frequency dependence is eliminated. Close to the critical point (T_s), the correlation length increases drastically as a result of concentration fluctuations, giving rise to an anomalous contribution to the viscoelastic properties. Finally, lets mention that, if the ratio $G'/G''^{\,5}$ is calculated, one can eliminate the interaction parameter dependence as can be seen from eqs 9 and 10.

Discussion

Rheological measurements, in the dynamic mode, were performed on polystyrene/poly(vinyl methyl ether) (PS/PVME) blends in our laboratory. The details of the procedure and experiments were given in refs 9 and 10. The results showed an anomalous behavior below T_s in the low-frequency region for G' and much less sensitivity of G''. As shown in the preceding section, close to the phase-separation temperature, the contribution to G'' coming from concentration fluctuations is very weak compared to that of G' and copolymers, thus justifying this result. It is to be noted also that the exponent obtained for G'' is the same as the one obtained for the viscosity of low molecular weight mixtures near a critical point.[19,20]

On the other hand, representation of the ratio $G'/G''^{\,2}$ as a function of temperature was shown to be independent of temperature in the miscible region far from the phase transition temperature T_s.[10] As the temperature was increased to T_s, deviations began to be observed. This supports the theoretical predictions obtained herein. In fact, as the temperature approaches T_s, the interaction parameter χ approaches χ_s. Knowing that the ratio $G'/G''^{\,2}$ is dependent on $(\chi_s - \chi)$ only, the contribution coming from concentration fluctuations becomes significant, giving rise to the increase in the ratio $G'/G''^{\,2}$.

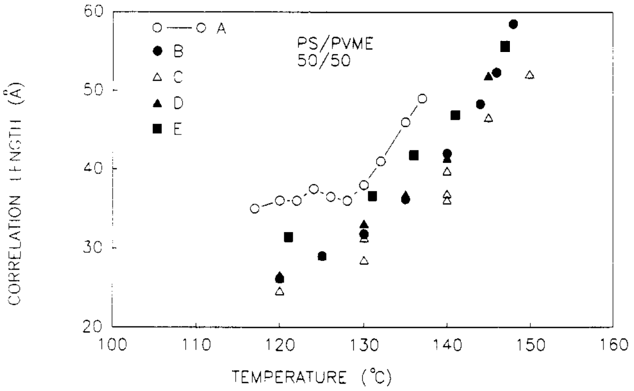

Figure 1. Temperature dependence of the correlation length for the 50/50 PS/PVME blend From rheological measurements: (A) Data of ref 10 and eq 14, M_w(PS) = 48 000 (M_w/M_n = 1.04), M_w(PVME) = 45 000 (M_w/M_n = 2.26). From SANS measurements:[21,22] (B) M_w(PS) = 593 000 (M_w/M_n = 1.48), M_w(PVME) = 1 100 000 (M_w/M_n = 1.26); (C) M_w(PS) = 230 000 (M_w/M_n = 1.14), M_w(PVME) = 389 000 (M_w/M_n = 1.25); (D) M_w(PS) = 402 000 (M_w/M_n = 1.42), M_w(PVME) = 210 000 (M_w/M_n = 1.32); (E) M_w(PS) = 255 000 (M_w/M_n = 1.11), M_w(PVME) = 99 000 (M_w/M_n = 2.13).

In Figure 1 we show the correlation length as a function of temperature as calculated from eq 14 compared to experimental data (G' and G'') obtained for the 50/50 PS/PVME blend at a frequency of 10 rad/s (results of ref 10). This representation gives us some qualitative information that one can obtain from the combination of the model proposed, in the limits of its validity, and the rheological measurements. The shape and the values obtained for ξ are well in the range of those obtained by scattering experiments. In fact, on the same figure, the experimental results obtained by small-angle neutron scattering (SANS)[21,22] for the correlation length of 50/50 PS/PVME blends of different molecular weights (M_w) are presented. It is clearly seen that the range of ξ values is comparable to that obtained by model calculations. The scattering data on ξ indicate a closer agreement as M_w decreases. It should be mentioned also that some shift in the phase separation temperature toward higher temperatures is generally obtained for blends with deuterated PS, hence the data on correlation length will be shifted in the same direction. Far from the critical point, eq 14 does not give ξ, since this equation assumes that the fluctuation contributions to G' and G'' are dominent, and this is not true except close to the critical point.

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