

Viscoelastic Effects on the Early Stages of Phase Separation in Polymer Blends

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ABSTRACT: We modify the Cahn–Hilliard theory of concentration fluctuation dynamics to account for the short-time networklike nature of high molecular weight polymers. We propose an additional term in the free energy, due to elastic energy arising from the finite lifetime of entanglements. If we assume a single-exponential decay time for the entanglements, the equation of motion is governed by two exponential modes. For quenches into the two-phase region, the faster mode always decays with time, and the slower mode grows. The theory successfully accounts for data from spinodal decomposition of polymer blends containing at least one component of very high molecular weight.

Introduction

When a polymer blend is quenched from the miscible region of the phase diagram into the immiscible two-phase region, phase separation occurs via the mechanism of spinodal decomposition. A description of the early-stage dynamics is provided by the Cahn–Hilliard model,¹ which considers the dynamic behavior of concentration fluctuations near equilibrium. It is predicted that concentration fluctuations with wavevectors below some critical value, q_c , will grow exponentially with time, with a particular wavevector, q_m , having the maximum growth rate.

Recent experiments² have shown that anomalous phenomena are associated with the early-stage dynamics of phase separation in certain polymer blends. Typical plots of the growth with time of the light scattering intensity at a fixed wavevector are shown in Figure 1 for two blends of polystyrene, molecular weight 1.61×10^6 (PS1610) or 2.75×10^5 (PS275), with poly(vinyl methyl ether) of molecular weight 9.5×10^4 (PVME), after a temperature jump of 3 K into the spinodal. These experiments indicate that there is a delay in the onset of phase separation, of up to 200 s after the jump into the two-phase region for the PVME/PS1610 blend, whereas there is no significant delay for the PVME/PS275 blend. The relative composition for the PS1610/PVME blend is 10/90, which is very close to the critical composition of the blend; hence, we would not expect there to be nucleation phenomena in passing a metastable gap. Rheological measurements, at the relevant temperatures, indicate that the relaxation time of the PS1610 component is on the order of 50 s.

Since the only difference between the two blends is the very highly entangled nature of the PS1610 component when compared with the PS275 component, we are led to address the question of the effect of entanglements on the dynamics of concentration fluctuations in polymer blends. We believe that the driving force for the dynamics must be modified to account for the transient elastic energy of the network. Previously, the

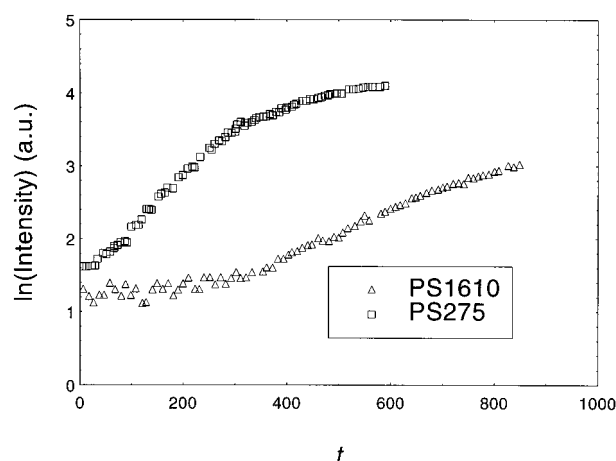


Figure 1. Growth of light scattering intensity in the equal time structure factor at a value of $q = 6.6 \times 10^6 \text{ m}^{-1}$, for two blends of PS/PVME after a temperature jump of 3 K inside the spinodal. The PVME molecular weight for both blends is 9.5×10^4 .

effects of entanglements on the mobility,^{3,4} late stage growth,⁵ and the dynamics of concentration fluctuations in the presence of either a macroscopic flow field⁶ or a hypothetical microscopic flow field,⁷ referred to as the “tube velocity”, have been considered. This work has been explored further by Onuki;⁸ it was proposed that coupling between stress and the dynamics of concentration fluctuations occurred in asymmetric blends (i.e., those in which the molecular weights of the two components are different). Binder *et al.*,⁹ in a formal treatment, developed a general theory for the dynamics of concentration fluctuations in the presence of slowly relaxing structural variables. Although primarily concerned with effects close to the glass transition, it was also indicated that entanglement effects may lead to similar physical behavior. Due to a recent increase in the interest in viscoelastic effects on phase separation of polymer blends, and in light of recent experiments (the results of some of which are presented here), it is timely to further explore these ideas.

Cahn–Hilliard Theory

Within this model the equation of motion for concentration fluctuations is written as

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$$\frac{\partial \rho_q(t)}{\partial t} = -q^2 M(q) \frac{\partial F[\rho_q(t)]}{\partial \rho_q(t)} \quad (1)$$

where $F[\rho_q(t)]$ is the free energy functional for the system, $\rho_q(t)$ is the Fourier transform of the difference of the local concentration from the average, and $M(q)$ is the q -dependent mobility. The free energy for a polymer blend is often written in the modified Flory–Huggins^{10,11} form as

$$F_{\text{FH}}[\rho_q] = \sum_q [\chi_c - \chi + \kappa q^2] \rho_q^2 \quad (2)$$

where χ is the Flory–Huggins interaction parameter, χ_c is its value on the spinodal curve, and κ is the interfacial free energy cost due to gradients in the concentration. Equations 1 and 2 lead to the following relaxation equation:

$$\rho_q(t) = \rho_q(0) \exp\{-q^2 M(q) [\chi_c - \chi + \kappa q^2] t\} \quad (3)$$

When a temperature jump into the two-phase region is performed, so that $\chi_c < \chi$, the thermodynamic term becomes negative for wavevectors $q < q_c$; such concentration fluctuations grow rather than decay. The critical and fastest-growing wavevectors are

$$q_c = \sqrt{(\chi - \chi_c)/\kappa}; \quad q_m = \sqrt{(\chi - \chi_c)2/\kappa} \quad (4)$$

respectively.

Polymer Entanglements

The effect of entanglements on the driving force of concentration fluctuation dynamics may be addressed by first considering the free energy of a polymer blend in which one or both components are permanently cross-linked. The stretching of chains, between fixed cross-links, which must occur to accommodate concentration fluctuations, gives rise to an elastic term in the free energy. There are two cases of interest; either both components are mutually entangled, forming an A–B network, or only one component is effectively entangled, forming an A–A network. The former models at short times blends in which both components have similar molecular weights. The latter models blends in which the A component has a much larger molecular weight than the B component, because at times intermediate between the reptation of short and long polymers the only topological constraints affecting the long chains are entanglements with each other. This is the case in the experiments referred to in the Introduction. In both cases the elastic energy, to a good approximation, may be written as¹²

$$\begin{aligned} F[\rho_q] &= F_{\text{FH}}[\rho_q] + F_{\text{el}}[\rho_q] \\ &= \sum_q [\chi_c - \chi + \kappa q^2] \rho_q^2 + c_0(q) |\rho_q - \rho_{0q}|^2 \end{aligned} \quad (5)$$

Hence, the elastic energy is dependent not on the magnitude of the fluctuation but on the difference between the magnitude of the fluctuation and the “frozen-in” initial fluctuation, ρ_{0q} .

The difference between the two cases arises in the coefficient c_0 , which represents the magnitude of the elastic energy. For A–B entanglements, it was shown by de Gennes using an analogy between local cross-link

density and charge polarization in dielectric media that¹³

$$c_0(q) = 36/N_e^2 b^2 q^2 \quad (6)$$

where N_e is the distance between cross-links in a network, which corresponds to the entanglement distance in homopolymer blends, and b is the statistical segment length. For A–A entanglements the elastic energy arises due to swelling of the entanglement network, with an elastic energy¹⁴

$$c_0(q) = 3\phi_A/N_e \quad (7)$$

where ϕ_A is the volume fraction of polymer A. Note that in both eqs 6 and 7 the numerical prefactors are not exact and are treated as phenomenological. A natural consequence of eqs 6 and 7 is that our discussion is valid only for length scales greater than the distance between entanglements, i.e., $1/q > N_e b^2$.

From the preceding discussion we see how to account for the transient elastic energy arising from the existence of entanglements. The total elastic energy at any time t is the sum of all contributions arising from the difference between the concentration fluctuation at time t and the frozen-in and unrelaxed concentration fluctuations from all previous times. This arises from direct analogy with the network case, but in an entangled blend the frozen-in fluctuations are not permanent.

First, we consider the contribution to the elastic energy arising from fluctuations at some previous time, t' . The fraction of entanglements which existed at this time, and are unrelaxed at time t , is denoted by $g(t-t')$; it is these entanglements which represent the frozen-in fluctuation. Hence, the contribution to the elastic energy is the product of F_{el} and the fraction of entanglements unrelaxed, i.e.

$$E_q(t, t') = \{c_0(q) [\rho_q(t) - \rho_q(t')]^2\} g(t-t') \quad (8)$$

It is possible⁴ to imagine other effects giving rise to elastic energy contributions similar in form to eq 8; however, in this paper we restrict our attention to polymer entanglements.

We now sum contributions from all previous times. Since a new set of entanglements is only born after a characteristic lifetime, τ_v , the total elastic energy may be written as

$$E_q(t) = c_0(q) \sum_{j=0}^{\infty} [\rho_q(t) - \rho_q(t-j\tau_v)]^2 g(j\tau_v) \quad (9)$$

Substituting $t' = j\tau_v$ and taking the continuous limit, we have

$$E_q(t) = c_0(q) \int_{-\infty}^t [\rho_q(t) - \rho_q(t')]^2 g(t-t') \frac{dt'}{\tau_v} \quad (10)$$

By including this elastic contribution in the driving force for small concentration fluctuations away from equilibrium, we arrive at the following equation of motion for $\rho_q(t)$:

$$\begin{aligned} \frac{\partial \rho_q(t)}{\partial t} &= -q^2 M(q) \frac{\partial}{\partial \rho_q(t)} \left\{ [\chi_c - \chi + \kappa q^2] \rho_q^2(t) + \right. \\ &\quad \left. c_0(q) \int_{-\infty}^t dt' \frac{g(t-t')}{\tau_v} |\rho_q(t) - \rho_q(t')|^2 \right\} \end{aligned} \quad (11)$$

This is the first principal result of this paper. A similar equation of motion was derived in ref 7; however, only the decay dynamics of concentration fluctuations were explored in full. In ref 8 Binder *et al.* investigated the resultant dynamics governed by a general form of eq 11, but without a molecular interpretation.

Equation 11 may be solved if we make two reasonable approximations. First, the decay of entanglements by reptation is approximated by a simple single-exponential decay

$$g(t-t') = \exp\{-(t-t')/\tau_v\} \quad (12)$$

Clearly, the form of eq 12 is such that the physical effect of eq 8 is most significant when the viscoelastic relaxation time is long.

Second, taking the time of the temperature jump (or quench) to be $t = 0$, we neglect any contributions to the elastic energy from fluctuations for which $t < 0$; i.e., we take the fluctuations in ρ_q at $t = 0$ as a boundary condition and assume that no elastic energy is associated with them in the first instance. The time-dependent scattering function is found from

$$S_q(t) \equiv \langle \rho_q(t) \rho_q(0) \rangle$$

Equation 11 may then be solved, using the Laplace transform technique, to give

$$S_q(t) = S_q(0) [A_1 \exp\{-R_1 t\} + (1 - A_1) \exp\{-R_2 t\}] \quad (13)$$

where

$$A_1 = \frac{1}{2} \left[1 - \frac{2a - b}{\sqrt{b^2 - 4c}} \right]$$

$$R_1 = \frac{1}{2} [b + \sqrt{b^2 - 4c}]$$

$$R_2 = \frac{1}{2} [b - \sqrt{b^2 - 4c}]$$

with $a = R_v$, $b = R_T + R_v + R_{c0}$, and $c = R_T R_v$. The following definitions have been used for the three effective dynamic rates:

$$\begin{aligned} R_T &= 2q^2 M [\chi_c - \chi + \kappa q^2] \\ R_{c0} &= 2c_0(q) M q^2 \\ R_v &= 1/\tau_v \end{aligned} \quad (14)$$

The first of which, R_T , can be recognized as the Cahn–Hilliard relaxation, or growth, rate. For simplicity we assume that the mobility, M , is independent of q .

Discussion

Despite the complicated dependence on the various thermodynamic and viscoelastic variables of the relaxation amplitudes and rates, some general comments can be made based on the observation that of the three rates in eq 14 only R_T can be negative.

The most significant property is that R_1 is always positive, even if R_T is negative. It can also be seen that $R_1 > R_2$; i.e., R_1 represents the fast decay mode and R_2

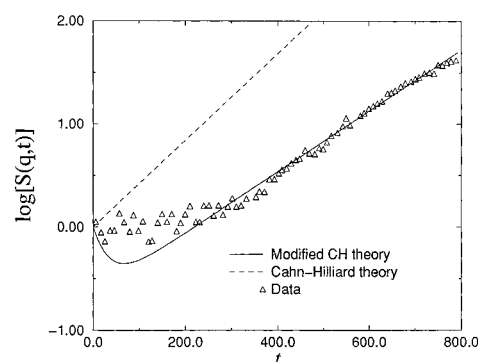


Figure 2. Time dependence of the theoretical scattering curve (eq 13) for an A–A entangled blend. The values used are (i) $\chi - \chi_c = 0.0005$, for a temperature jump of 3 K with experimentally determined χ parameters;¹⁹ (ii) $q = 6.6 \times 10^6 \text{ m}^{-1}$ corresponding to the data in Figure 1; (iii) $q_m = 14.4 \times 10^6 \text{ m}^{-1}$ (see ref 2), (iv) $R_v = 1/50$, taken from rheological measurements; (v) $c_0 = 3.8 \times 10^{-3}$, which although chosen to give a good fit to the experimental data, is very close to the theoretical value predicted by eq 7 with²⁰ $N_e = 145$ for PS1610; and (vi) $M = 2 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, which gives approximately the correct slope for the growth rate. The experimental data are for the PS1610/PVME95 blend. For comparison the prediction of Cahn–Hilliard theory for the same parameters is also included.

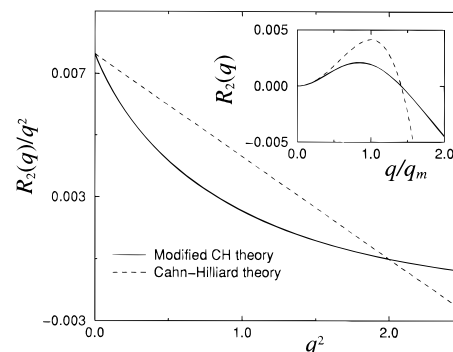


Figure 3. A plot of $R_2(q)/q^2$ against q^2 for the same parameters used in Figure 2. Cahn–Hilliard theory predicts a linear relation. Inset: the q dependence of the growth rate, $R_2(q)$.

represents the slow mode. In Figure 2 the time dependence of the scattering curve, based on eq 13 with the use of eq 7, is shown and compared to the scattering data presented in Figure 1. For A–B entangled blends, the q dependence of the growth rate is identical to that established for Cahn–Hilliard theory (see eq 4), the only difference being that the growth rate is slowed. However, for A–A entangled blends the q dependence of the growth rate is altered noticeably, as illustrated in Figure 3, from which it can be seen that, although q_c is unchanged from Cahn–Hilliard theory, q_m is shifted to smaller q values. In Figure 4 we compare the theoretical prediction with experimental data taken from the PS1610/PVME95 blend; the fitting parameters are identical to those used in fitting the time-dependent curve. Further details of the experimental method will be published in the near future.¹⁵

We briefly mention the phenomenon of thermal noise which could be the explanation for the experimental scattering function being constant during the delay time. The method developed by Cook¹⁶ to include thermal noise in the Cahn–Hilliard theory cannot be applied to the above development; the white noise approximation which is valid for correlation functions with a single-exponential decay mode is not valid for more complex decay modes. In principle, it is possible

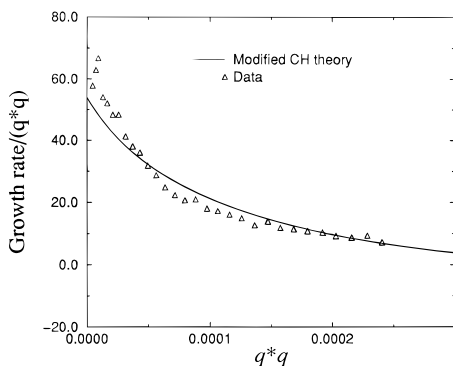


Figure 4. Comparison of $R_2(q)/q^2$ against q^2 , using the same parameters used in Figure 2, with experimental data² for the PS1610/PVME95 blend.

to calculate the frequency-dependent noise spectrum, based on the method of Lifshitz and Pitaevskii,¹⁷ but in practice this leads to an intractable equation of motion.

In the limit of $R_T \ll R_{c0}$, R_v , i.e., if modes arising from the viscoelastic nature of entangled polymers are much faster than the thermodynamic mode, the solution may be decoupled into a purely viscoelastic mode, and a modified thermodynamic (or Cahn–Hilliard) mode

$$S_q(t)/S_q(0) \approx A_1 \exp\{-(R_v + R_{c0})t\} + (1 - A_1) \exp\{-R_T(1 + R_{c0}/R_v)^{-1}t\} \quad (15)$$

The validity of the various comments made in the preceding paragraph, regarding the dynamic behavior of concentration fluctuations, is clear when examining this form of the equation of motion. An initial negative slope in the time-dependent structure factor after a quench in the two-phase region arises because the initial fluctuation has elastic energy associated with it. This begins to relax by quenching the fluctuations before phase separation has time to occur. At longer time scales the remaining concentration fluctuation is free to grow, albeit more slowly, as entanglements disappear.

With reference to eqs 6 and 7 we can see that for a blend dominated by A–B entanglements the decay mode is q independent, whereas for a blend dominated by A–A entanglements the decay rate will be quadratic in q . It is also worth noting that in our theoretical development we have not modified the equilibrium free energy nor have we simply modified the kinetic coefficient.

The modified Cahn–Hilliard mode of eq 15 is similar to the results of ref 8, in which a “retarded” growth rate is also predicted; however, the present theory shows that a slowed growth rate occurs regardless of whether the two components are asymmetric. The assumption that the phase separation time scale is much greater than the viscoelastic time scale is also made in ref 8; our results strongly suggest that the most interesting features, which arise from the coupling of viscoelasticity and concentration fluctuation dynamics, occur when the time scales are not widely separated. Furthermore, it is not apparent that, for asymmetric blends, a model which only includes one viscoelastic time scale is appropriate, unless one component has a much greater relaxation time than the other. The latter scenario corresponds to our A–A network. Below we discuss a model for asymmetric blends which incorporates two time scales.

It is possible to go beyond the single-exponential rheological relaxation function given by eq 12 and use the full reptation spectrum given by¹⁸

$$g(t) = \frac{8}{\pi^2} \sum_{p, \text{odd}} \frac{1}{p^2} \exp\{-p^2 t / \tau_v\} \quad (16)$$

The solution to eq 11 is then a sum of exponentials; initial numerical analysis which includes only the first correction to eq 12 shows that the behavior as illustrated in Figures 2 and 3 is not noticeably changed. In a future paper we hope to investigate the behavior due to more complex relaxation spectra, such as that associated with entangled star polymers.

Another interesting extension of the theory is to consider blends which are not dominated by either pure A–A or pure A–B networks. This will arise when the two components are well entangled but still have different rheological relaxation times. In this case we can imagine the system to contain three types of temporary networks, each with its own relaxation time and contribution to the free energy. A simple extension of eq 11 which describes this behavior is

$$\begin{aligned} \frac{\partial \rho_q(t)}{\partial t} = & -q^2 M(q) \frac{\partial}{\partial \rho_q(t)} \left\{ [\chi_c - \chi + \kappa q^2] \rho_q^2(t) + \right. \\ & \phi_A^2 c_{AA}(q) \int_{-\infty}^t dt' \frac{g_A(t-t')}{\tau_{vA}} \left| \rho_q(t) - \rho_q(t') \right|^2 + \\ & 2\phi_A \phi_B c_{AB}(q) \int_{-\infty}^t dt' \frac{g_{A,B}(t-t')}{\tau_{vA,B}} \left| \rho_q(t) - \rho_q(t') \right|^2 + \\ & \left. \phi_B^2 c_{BB}(q) \int_{-\infty}^t dt' \frac{g_B(t-t')}{\tau_{vB}} \left| \rho_q(t) - \rho_q(t') \right|^2 \right\} \quad (17) \end{aligned}$$

where g_A and g_B are the relaxation functions for the A and B components with relaxation times τ_{vA} and τ_{vB} , respectively; $g_{A,B}$ is the relaxation function of the faster component, with $\tau_{vA,B}$ being the corresponding relaxation time, i.e.

$$\tau_{vA,B} = \min[\tau_{vA}, \tau_{vB}]$$

The elastic energy magnitudes, c_{AA} and c_{BB} , are given by eq 7; c_{AB} is given by eq 6. Such a complete analysis is only readily applicable to blends in which both components have the same entanglement molecular weight; no expression for N_e to use in the calculation of c_{AB} exists when the two components have different entanglement molecular weights.

A complete solution of eq 17 is possible if we again use the same assumptions that facilitated solution of eq 11, and we define B to be the slower component; its general form is

$$S_q(t) = S_q(0) [A_\alpha \exp\{-R_\alpha t\} + A_\beta \exp\{-R_\beta t\} + A_\gamma \exp\{-R_\gamma t\}] \quad (18)$$

The dependence of the three rates and amplitudes on the various thermodynamic and elastic parameters is now very complex; the rates are the three solutions of the cubic equation

$$s^3 + (R_\sigma + R_{vA} + R_{vB})s^2 + (R_\sigma R_{vA} + R_\sigma R_{vB} + R_{vA} R_{vB})s + R_\sigma R_{vA} R_{vB} - R_\mu - R_\pi = 0 \quad (19)$$

and the corresponding amplitudes, which satisfy the

condition $A_\alpha + A_\beta + A_\gamma = 1$, are given by

$$\begin{aligned} A_\alpha &= \frac{(R_\alpha + R_{vA})(R_\alpha + R_{vB})}{(R_\alpha - R_\beta)(R_\alpha - R_\gamma)} \\ A_\beta &= \frac{(R_\beta + R_{vA})(R_\beta + R_{vB})}{(R_\beta - R_\alpha)(R_\beta - R_\gamma)} \\ A_\gamma &= \frac{(R_\gamma + R_{vA})(R_\gamma + R_{vB})}{(R_\gamma - R_\alpha)(R_\gamma - R_\beta)} \end{aligned} \quad (20)$$

where

$$R_\sigma = 2q^2 M \{ [\chi_c - \chi + \kappa q^2] + \phi_A^2 c_{AA}(q) + \phi_A \phi_B c_{AB}(q) + \phi_B^2 c_{BB}(q) \}$$

$$R_\mu = \frac{\phi_A^2 c_{AA}(q)}{\tau_{vA}}; \quad R_\pi = \frac{1}{\tau_{vB}} [\phi_A \phi_B c_{AB}(q) + \phi_B^2 c_{BB}(q)]$$

$$R_{vA} = 1/\tau_{vA}; \quad R_{vB} = 1/\tau_{vB} \quad (21)$$

We would expect that the roots of eq 19 are real and that for a quench into the two-phase region only one rate would become negative; numerical solutions with various trial parameters suggest that this is the case. Despite the apparent complexity of eq 18, the results are still amenable to comparison with experiment.

Conclusions

In summary, we predict that the effect of viscoelasticity due to entanglements is to delay the onset of phase separation. This is, to some degree, in accord with the experimental evidence illustrated in Figure 1. The delay time is dependent on both the magnitude of the elastic energy and the entanglement lifetime. Clearly, a delay is only likely to be observable, on the time scales usually associated with phase separation, if the entanglement lifetime or the reptation time is significant compared with the growth rate. The reptation of

PS1610 in a PVME95 matrix satisfies this condition. Physically the delay corresponds to the need for the blend to relax any excess elastic energy before a (slowed) growth process may proceed; in other words, the A component initially reacts as if it were a cross-linked network and the blend is consequently still within the one-phase region of the phase diagram until the entanglements have relaxed. Another method of achieving viscoelastic relaxation times comparable to phase separation time scales is if the temperature is such that one component is close to its glass transition temperature.

Finally we note that the ideas presented also provide a candidate explanation for the unusual q dependency of the growth rate, at least for blends with high molecular weights.

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