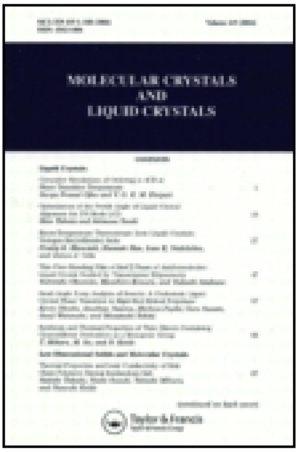

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Polymerization-induced Phase Separation of a Liquid Crystal-Polymer Mixture

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We study the phase separation, induced by polymerization, of a liquid crystal-polymer mixture by using the Flory-Huggins mean-field free energy and a simple kinetic model of polymerization. Equilibrium phase behavior and the kinetic processes are analyzed separately. These results are then combined under the assumption that the polymerization rate is sufficiently slow, or the diffusive processes sufficiently rapid, that phase separation occurs at a well defined degree of polymerization. This allows the calculation of the critical time at which phase separation begins.

Keywords: phase separation, polymerization kinetics

I. INTRODUCTION

The phase separation of a binary mixture following a thermal quench is a process that has been studied for many years, and is now comparatively well understood in the cases of polymers[1] and low-molecular-weight systems.[2–3] Phase separation, however, can also be driven by other means, and in particular by the polymerization of one of the components of a mixture. This is the method that is often utilized to form the dispersion of liquid crystal droplets in a polymer matrix necessary for the operation of some optical devices.[4] This process is less well understood, and forms the subject of the theoretical study to be presented below.

An interesting aspect of the process of phase separation under polymerization lies in the fact that two competing processes occur, each of which has its own distinctive time scale. The phase separation process is driven by the dependence of the free energy on composition, and acts on a time scale governed by diffusion. The polymerization process, on the other hand, proceeds at a rate governed by the kinetics of chemical reactions. If this rate is much slower than that for diffusive processes, then the phase separation process can be considered as determined by the local free energy.

The simplest treatment of phase separation in a polymeric system is that of Flory[5] and Huggins,[6] who proposed a mean-field expression for the free energy. This was combined with the theory of spinodal decomposition of Cahn[7] and Hilliard[8] by Kim and Palffy-Muhoray[9] in a discussion of their experiments on polymer-dispersed liquid crystal samples.

In the present work we calculate the characteristic time t_s that will elapse before phase separation occurs in a polymerizing mixture. We assume that the polymerization process is sufficiently slow that the spinodal curve of the mixture at any time determines whether phase separation will occur. The characteristic time for phase separation is then the time that it takes for the spinodal curve to cross the point on the composition-temperature phase diagram representing the sample.

The calculation thus proceeds in two stages. We first make use of the Flory-Huggins approximation to note the variation of the phase diagram with degree of polymerization. We then use a simple kinetic theory to estimate the variation of the degree of polymerization with time. These results are then combined to determine the dependence on composition of the characteristic time for phase separation.

II. PHASE DIAGRAM IN EQUILIBRIUM

The model we consider is a system that is initially composed of two components, which we will refer to as monomer and liquid crystal, in molecular proportions p and $1-p$ respectively. As time proceeds, molecules of monomer combine chemically with each other to form oligomers and then polymers. The general composition is thus a mixture of liquid crystal and a polydisperse polymer.

In the Flory-Huggins mean-field model of a solution of monodisperse polymer of degree of polymerization N, the free energy f per molecule initially present is given by the expression

$$\frac{f(\varphi)}{k_B T} = \frac{\varphi}{N}\ln(\varphi) + (1 - \varphi)\ln(1 - \varphi) + \chi\varphi(1 - \varphi), \tag{1}$$

where φ (≥ 0, and ≤ 1) is the local molecular concentration of monomeric units forming the polymer. The energies of intermolecular interaction ε_{pl}, ε_{pp}, and ε_{ll} between polymer and liquid crystal components enter this expression through the term

$$\chi = \frac{1}{k_B T}\left[\varepsilon_{pl} - \frac{1}{2}(\varepsilon_{pp} + \varepsilon_{ll})\right], \tag{2}$$

where T is the temperature and k_B is Boltzmann's constant.

This expression for $f(\varphi)$ allows the usual derivation to be made of the phase diagram and spinodal lines. Phase separation is favored when $f(\varphi)$ has the form shown in Figure 1(b), but not when it is as in Figure 1(a). The tangent-line construction to find the phase boundaries in equilibrium is indicated in Figure 1(b), but for spontaneous phase separation in a homogeneous mixture to occur the

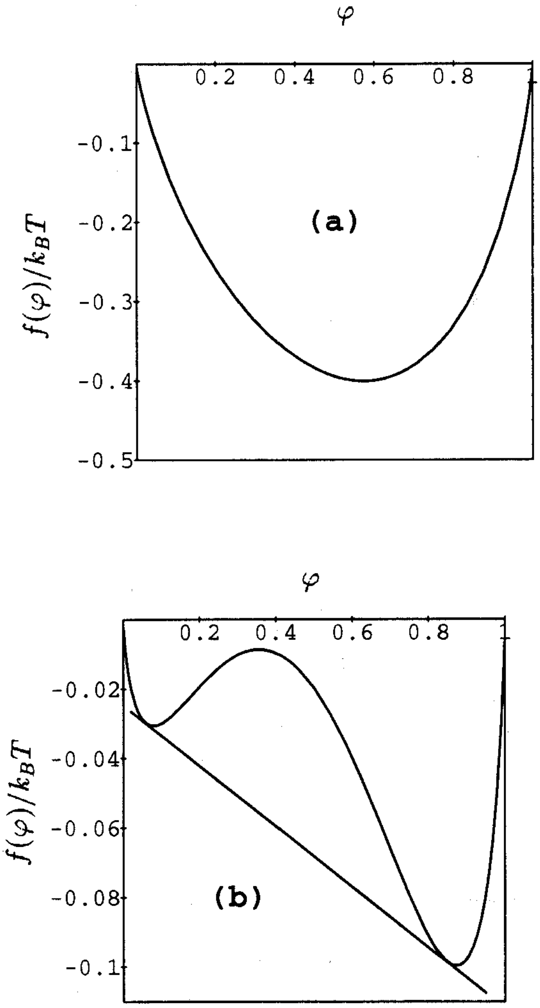

FIGURE 1 This shows two possible forms of the free energy as a function of composition φ. While in case (a) $f''(\varphi) > 0$ for all φ, in case (b) there is region a where $f''(\varphi) < 0$. The straight line is tangent to the curve.

composition must lie within the spinodal lines given by the condition $f''(\varphi) = 0$. In the Flory-Huggins model these occur at a given temperature at compositions

$$\varphi_{\pm} = \frac{1}{4\chi}\left[\left(2\chi - 1 + \frac{1}{N}\right) \pm \sqrt{\left(2\chi - 1 + \frac{1}{N}\right)^2 - 8\chi\frac{1}{N}}\right]. \qquad (3)$$

In Figure 2 we show the form of the spinodal lines (solid lines) at various values of degree of polymerization N. Before polymerization occurs, when $N = 1$, the spinodal is a simple parabola. As polymerization proceeds, the curve rises asym-

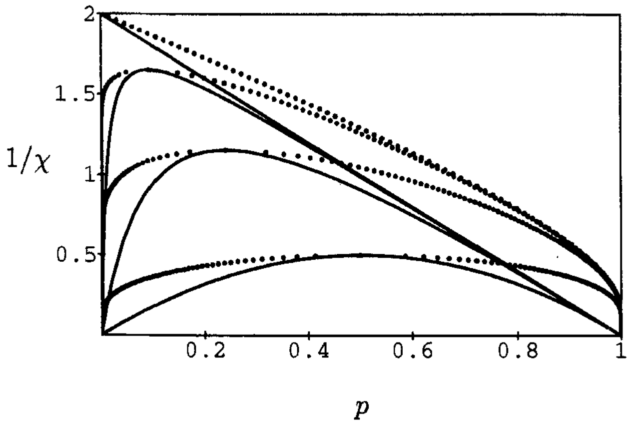

FIGURE 2 Spinodal lines (solid lines) and phase boundaries (dotted lines) in the temperature ($1/\chi$) and composition (p) parameter-space at various degrees of polymerization. From top to bottom, $1/N$ = 0, 0.01, 0.1 and 1 respectively.

metrically, until at large times, when $N \to \infty$, the spinodal has become a triangle whose left-hand side has vertical slope. The actual phase boundaries are shown by the dotted curves in Figure 2.

In contrast to the process of phase separation by thermal quench, in which the operating point on the phase diagram descends vertically until the two-phase region is entered, phase separation due to polymerization is represented as a stationary point on the phase diagram which then becomes engulfed by the moving spinodal curve.

III. KINETIC PROCESS OF POLYMERIZATION

Although the Flory-Huggins theory is formulated in terms of a monodisperse polymer, the actual process of polymerization proceeds through a series of polydisperse states in which various values of N will be present. In the spirit of the mean-field approach we make the assumption that the appropriate value of N to use will be the inverse of the average reciprocal degree of polymerization. That is we make use of Equation (3) with $1/N$ replaced by its average $\langle 1/N \rangle$ over the distribution of values of N present at any given time. We thus require an expression for $P(N, t)$, the probability that any site is occupied by a monomer forming part of a polymer of degree of polymerization N. We use a simple mean-field model for polymerization, similar to that of Stockmayer,[10] and assume that the rate of change of $P(N, t)$ can be written as

$$\frac{d}{dt} P(N, t) = \frac{\kappa N}{2} \sum_{m+n=N} A(m)P(m, t)A(n)P(n, t)\Delta_{\bar{N}}(m, n)$$
$$- \kappa N A(N) P(N, t) \sum_{m=1}^{\infty} P(m, t)\Delta_{\bar{N}}(m, N). \quad (4)$$

Here the first term on the right-hand side represents the rate at which a polymer of size N is formed by the reaction of one of size m with one of size $n = N - m$, while the second represents the rate of removal of polymer of size N by reaction with others of all sizes. The function $A(N)$ describes the type of polymerization process. For a multifunctional reaction in which each site on a polymer chain is equally likely to react we have $A(N) = 1$, while for linear polymerization we might have $A(N) = 2/N$. The cut-off function $\Delta_{\bar{N}}(m, n)$ is introduced in order to avoid a difficulty arising from the possible divergence of the infinite sums when the percolation limit is reached, and is defined as

$$\Delta_{\bar{N}}(m, n) = \begin{cases} 1 & \text{for } \min(m, n) \leq \bar{N}, \\ 0 & \text{otherwise.} \end{cases} \tag{5}$$

This function eliminates reactions between polymers with degree of polymerization larger than the cut-off value $\bar{N}$. Its effect is purely formal, as $\bar{N}$ will be allowed to become infinite at a later stage in the calculation. The temperature-dependent reaction rate constant κ determines the time scale of the process, and the factor of $\frac{1}{2}$ avoids double counting. The factor of N takes into account the fact that each reaction either removes or adds N monomer units.

We now specialize to the multifunctional process for which $A(N) = 1$. The initial conditions are

$$P(1, 0) = p; \qquad P(N, 0) = 0, \quad \text{for } N > 1, \tag{6}$$

where p is the initial molecular proportion of monomer in the mixture. The kinetic equation for $P(1, t)$ can be obtained from Equation (4) by imposing the boundary condition

$$P(0, t) = 0. \tag{7}$$

By combining Equations (4)–(7), the average value of $1/N$ can be determined. The result[11] is

$$\left\langle \frac{1}{N} \right\rangle = \frac{\sum_{N=1}^{\infty} \frac{1}{N} P(N, t)}{\sum_{N=1}^{\infty} P(N, t)}$$

$$= \begin{cases} 1 - \dfrac{1}{2}\tau, & \text{for } \tau \leq 1; \\[2ex] \dfrac{1}{\tau}\left(\bar{\tau} - \dfrac{1}{2}\bar{\tau}^2\right), & \text{for } \tau > 1; \end{cases} \tag{8}$$

where $\tau \equiv \kappa p t$ is the reduced time and $\bar{\tau}$ is a function of τ defined by the relation

$\tau e^{-\tau} = \bar{\tau} e^{-\bar{\tau}}$ with $\bar{\tau} < \tau$. The discontinuity in the second derivative of $\langle 1/N \rangle$ at $\tau = 1$ marks the formation of material for which the degree of polymerization is infinite. When τ is large, we find

$$\left\langle \frac{1}{N} \right\rangle \simeq e^{-\tau}, \tag{9}$$

and so the average of the reciprocal of the degree of polymerization is seen to decay exponentially with time in this model.

IV. CRITICAL TIME FOR PHASE SEPARATION

We have now formed expressions for the location of the spinodal in terms of $1/N$ and T, and for the time dependence of $\langle 1/N \rangle$. By replacing the term in $1/N$ in Equation (3) by its average $\langle 1/N \rangle$ we are now in a position to evaluate the critical time t_s at which the phase separation process begins.

For separation to occur at all, the starting point must lie between the spinodal lines for $N = 1$ and $N = \infty$ on Figure 2, i.e. inside the triangle but outside the parabola. For points initially close to either side of the triangle, separation only occurs at very large times. A plot of t_s as a function of initial monomer concentration p for fixed temperature thus has the form shown in Figure 3. For the majority of the range of initial concentrations the time to separation decreases with increasing p, but then rises sharply as p approaches the infinite-time spinodal line.

This form of variation of separation time with concentration is seen qualitatively

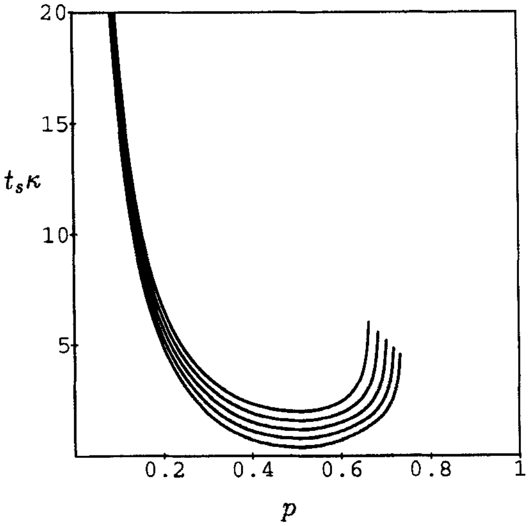

FIGURE 3 The critical time as a function of composition of polymer at various coupling parameters. From top to bottom, $\chi = 1.5, 1.6, 1.7, 1.8$, and 1.9 respectively.

in the experimental work of Kim and Palffy-Muhoray,[9] who observed the time evolution of the structure factor when the liquid crystal *E7* was mixed with the expoxy *Epon28* and curing agent Capcure 3–800. The rapid drop in t_s with increasing p is seen, but not the subsequent rise, as the experiments were not performed for large p.

V. CONCLUSIONS

We have seen that the separation process that can occur during polymerization may be modeled by using the simple framework of Flory-Huggins theory and a kinetic model of polymerization of a branched polymer. This model allows a prediction to be made of the qualitative form of the phase-separation time t_s as a function of the monomer concentration and other relevant parameters, but does not suffice to make realistic estimates for the properties of actual materials. In particular, the spatial dependence of the concentration has not been treated, and so no prediction of the form of the structure factor can be made using the methods described here.

The next step in understanding the phenomenon of phase separation under polymerization will require a more careful approach to the problem of phase behavior away from equilibrium, i.e. when the time scales for diffusion and polymerization are comparable. It will also be desirable to perform numerical simulations for realistic models in three dimensions, since at present it appears that only some preliminary two-dimensional studies have been made.[12–13]

Acknowledgment

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