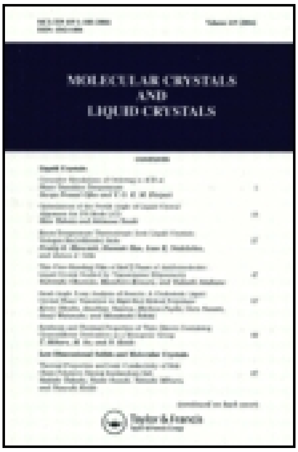

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A Thermodynamic Model for Solubilities in Phase-Separated Systems: Polymer-Dispersed Liquid Crystals

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A Thermodynamic Model for Solubilities in Phase-Separated Systems: Polymer-Dispersed Liquid Crystals

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A thermodynamically based model for phase separation in polymer-dispersed liquid crystals (PDLCs) is developed. Using Flory-Huggins theory and the lever rule, it quantitatively describes liquid crystal (LC) solubility in a polymer matrix as a function of temperature. From the spinodal compositions, the model yields upper bounds for the solubility limits of LC in polymer and of polymer in LC. The solubility limits are related to the Flory-Huggins interaction parameter, χ, and hence to solubility parameters, δ. This model may prove useful in selecting materials for which maximum segregation of liquid crystal into microdroplets is desired.

Keywords: polymer-dispersed liquid crystals, phase separation, liquid crystals, solubility, Flory-Huggins theory

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films,[1,2] dispersions of micron-sized droplets of liquid crystal (LC) in a polymer matrix, have considerable potential for a variety of applications, including displays and variable transmittance windows. One of the goals of recent research is the maximization of the amount of liquid crystal entrapped in the microdroplets (rather than dissolved in the polymer matrix). To accomplish this goal it is important to use a LC/polymer matrix combination for which A, the liquid crystal solubility limit in the matrix, is low. A low value of A results in an enhanced degree of phase separation of LC from the cured matrix, thus helping to maximize α, the fraction of liquid crystal in the droplets.

An ad hoc mathematical model for α in terms of A and the liquid crystal concentration has been previously developed.[3–5] Although calorimetric evidence[4–6] has agreed with the model rather well, a thermodynamic basis would provide additional support and could enable us to relate α to solubility parameters of the LC and the polymer matrix. Perhaps we might then be able to predict the best combinations of components (in terms of efficient use of liquid crystal).

The purpose of the present paper is to develop such a thermodynamic basis. The calculations will be based on the Flory-Huggins theory[7,8] of phase behavior of binary polymer mixtures, as expanded upon by Nishi,[9-11] Sanchez,[12] and others. In particular, we shall compute the spinodal temperature-concentration curve and then apply the lever rule[13] to determine either the fraction of polymer-rich phase or the fraction of liquid-crystal phase as a function of temperature. [As we shall see, the use of the spinodal for this purpose is not strictly legitimate. However, we shall argue that it is a physically meaningful approach which allows us to calculate upper bounds for solubility limits and to introduce the temperature dependences of A and α in closed form.]

In the next two sections we shall review our previous model for A and α in PDLC systems and briefly discuss the Flory-Huggins model.

BACKGROUND: CALORIMETRIC MODEL

Smith and Vaz[3] pointed out that α, the fractional amount of liquid crystal contained in PDLC microdroplets, can be determined from calorimetric determinations of ΔH_{NI}, the PDLC nematic-isotropic transition enthalpy per unit mass. They provided a simple equation for α:

$$\alpha \equiv m_{\mathrm{LC}}^{D}/m_{\mathrm{LC}} = (1 + m_p/m_{\mathrm{LC}})P(x) \tag{1}$$

where m_{LC}^{D} is the mass of LC in the droplets, m_{LC} and m_p are the masses of liquid crystal and polymer in the PDLC, x is the LC concentration, and

$$P(x) = \Delta H_{\mathrm{NI}}(x)/\Delta H_{\mathrm{NI}}(LC), \tag{2}$$

the ratio of the nematic-isotropic transition enthalpy for the PDLC to that for the pure LC. The value of $\Delta H_{\mathrm{NI}}(x)$ can be determined by integration of the nematic-isotropic transition peak from differential scanning calorimetry (DSC) spectra like that shown in Figure 1. [Basically $P(x)$ is equal to $m_{\mathrm{LC}}^{D}/m_{\mathrm{tot}}$, where m_{tot} is the total PDLC mass. Strictly speaking, m_{LC}^{D} is the mass of the liquid crystal which has phase-

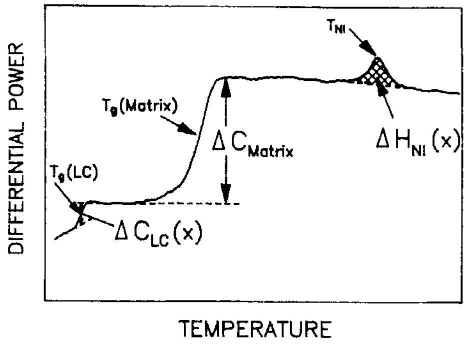

FIGURE 1 A typical DSC thermal spectrum for a PDLC. The three transitions shown are (from low to high temperature): the LC glass transition; the polymer matrix glass transition; and the nematic-isotropic transition. Only the first and third transitions are discussed in this paper. (Endothermic transitions are taken to be upward going.)

separated from the polymer and which would contain a small amount of polymer-precursor material in solution. For low enough values of x all such "free" LC is contained in the droplets; for large values of x, some, or all, of the free LC may be present as a continuous phase. The remainder of the LC is dissolved in the polymer matrix.]

Subsequently, Smith[4,5] showed that a linear relationship exists between $P(x)$ and x:

$$\begin{aligned} P(x) &= 0 && (x < A), \\ P(x) &= (x - A)/(1 - A) && (x \geqslant A), \end{aligned} \tag{3}$$

where $P(x)$ is either the enthalpy ratio of Equation 2 or the ratio of specific heat increments defined in Equation 4:

$$P(x) = \Delta C_{\mathrm{LC}}(x) \Delta C_{\mathrm{LC}}(\mathrm{LC}), \tag{4}$$

where $\Delta C_{\mathrm{LC}}(x)$ is the incremental increase in specific heat (per unit mass) at $T_g(\mathrm{LC})$, the liquid crystal glass transition temperature for the PDLC (Figure 1). $\Delta C_{\mathrm{LC}}(\mathrm{LC})$ is the increment for the pure liquid crystal.

Two basic assumptions are required for the derivation of Equation 3: 1) only liquid crystal not dissolved in the polymer matrix (i.e., free LC) contributes to either $\Delta C_{\mathrm{LC}}(x)$ or $\Delta H_{\mathrm{NI}}(x)$; 2) the amount of liquid crystal which a given mass of polymer matrix can dissolve is the same for all LC concentrations greater than A. Since $P(x)$ is a mass (or weight) ratio, Equation 3 is exact only for x expressed as a weight fraction. [If $P(x)$ were a volumetric ratio, Equation 3 would be exact only for x expressed as a volume fraction.] However, if the densities of the polymer and LC in the PDLC are almost equal, Equation 3 is a good approximation for x expressed as a volume fraction.[4,5] Generally these densities are, indeed, comparable, so that volume and weight fractions are nearly equal, and Equation 3 is valid for either.

The dependence of the enthalpy and specific heat increment ratios on liquid crystal concentration for two PDLCs are plotted in Figure 2. As has been previously shown,[4,5] the data satisfy the linear dependence of Equation 3 fairly well. However, the value of the solubility limit, A, derived from ΔC_{LC} is generally somewhat smaller than that from ΔH_{NI}. It has been pointed out[5,14] that, since $\Delta C_{\mathrm{LC}}(x)$ was measured at a temperature more than 100°C lower than ΔH_{NI} (for the 7CB/epoxy PDLC, ~ -68°C versus ~ 44°C) a lower solubility limit, A, from ΔC_{LC} might be expected.

Given Equation 3, it is easy to derive an expression for α, the fraction of liquid crystal contained in the microdroplets. Like $P(x)$, α depends only upon A and x[4,5]

$$\begin{aligned} \alpha &= 0 && (x < A) \\ \alpha &= (1/x)(x - A)/(1 - A) && (x \geqslant A) \end{aligned} \tag{5}$$

Equation 5 is equally valid for x expressed either as a weight or a volume fraction (provided A is similarly expressed). The most efficient usage of liquid crystal will occur if $\alpha \rightarrow 1$; for this to occur, A should be as close to 0 as possible.

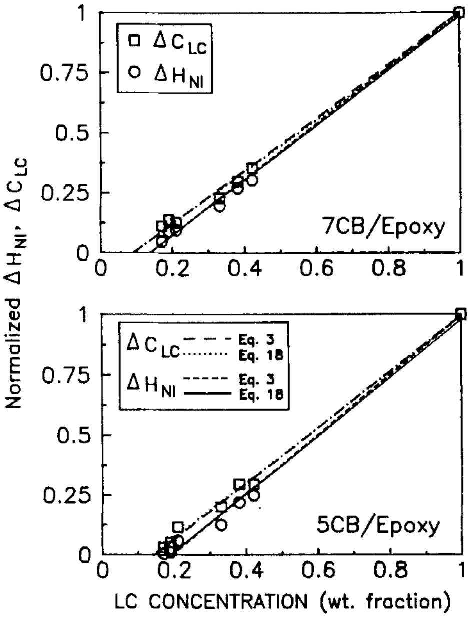

FIGURE 2 $\Delta H_{NI}(x)/\Delta H_{NI}(LC)$ and $\Delta C_{LC}(x)/\Delta C_{LC}(LC)$ versus liquid crystal concentration for two epoxy-based PDLCs.[5] Points are results of calorimetric experiments. Lines are best fits of Equations 3 $[P(x)]$ and 18 $[\Pi_{LC}(x)]$ which appear to be essentially equivalent. Values of the solubility limit derived from Equation 3: for the 7CB/epoxy system $A(\Delta C_{LC}) = 0.0925$, $A(\Delta H_{NI}) = 0.138$; for the 5CB/epoxy system $A(\Delta C_{LC}) = 0.140$, $A(\Delta H_{NI}) = 0.191$.

BACKGROUND: FLORY-HUGGINS MODEL

The phase stability of a binary mixture of two components (at least one of which is a polymer) can be well understood in terms of the lattice theory of Flory[7] and Huggins.[8] The starting point of the model is the Gibbs free energy of mixing, ΔG_{mix}, given by

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}, \tag{6}$$

where ΔH_{mix} is the enthalpy of mixing, ΔS_{mix} the entropy of mixing, and T the absolute temperature. For mixing of the two components to occur, ΔG_{mix} should be less than 0. According to the F-H theory, ΔS_{mix} is

$$\Delta S_{mix} = -NR[(1 - \phi)\ln(1 - \phi)/m_1 + \phi \ln \phi/m_2]. \tag{7}$$

Here m_1 and m_2 are the degree of polymerization of components 1 and 2, ϕ is the volume fraction of component 2, R is the gas constant, and N is the number of polymer segments in the system. It is apparent from Equation 7 that as m_1 and m_2 increase, ΔS_{mix} will approach 0, making it difficult for high polymers to mix unless ΔH_{mix} becomes small or negative. Indeed, 95% of all binary polymer blends are incompatible.[12]

The F-H enthalpy of mixing can be expressed as

$$\Delta H_{\text{mix}} = NRT\chi\phi(1 - \phi) \tag{8}$$

where χ is the well-known Flory-Huggins interaction parameter. The temperature dependence of χ is often given by[9–11,15]

$$\chi(T) = C + D/T, \tag{9}$$

where C and D are frequently taken to be constants. Equation 9 introduces the temperature into phase diagrams derived from the F-H theory. For some systems χ may be a function of ϕ as well[15]; however, we shall not consider a ϕ-dependence in the present discussion. Polydispersity of m_2 is also neglected.

Nishi[9,10] has pointed out that two different types of binary phase diagrams can be obtained from the F-H model by the appropriate choice of the signs of C and D: i) For $C > 0$ and $D < 0$, the polymers separate into two phases upon heating; the temperature-concentration ($T - \phi$) diagram of such systems has a minimum temperature, the lower critical solution temperature (LCST), below which the system forms a single phase. ii) For $C < 0$ and $D > 0$, phase separation occurs upon cooling; in this case the $T - \phi$ diagram has a maximum temperature, the upper critical solution temperature (UCST) above which a single phase forms. Type i) behavior is much more common than type ii) among binary polymer systems; in fact, there are no known examples of high molecular weight binary blends which exhibit UCST behavior.[12] However, systems in which at least one component (say #1) has a low molecular weight can exhibit type ii) behavior. As we shall see, PDLCs all seem to have UCST phase diagrams.[16–18]

Given Equations 6–9, one can construct phase diagrams for various values of m_1, m_2, C, and D. Figure 3 shows curves of ΔG_{mix} versus ϕ for a type ii) system at three different temperatures. At the lowest temperature (T_1) ΔG_{mix} is positive for all values of ϕ except those near 0 and 1. Thus, the equilibrium state at this temperature is one of almost complete phase separation. At high temperature (T_3) ΔG_{mix} is everywhere negative; in this case the two components are completely mixed. The curve for intermediate temperature (T_2), which shows two local minima, is plotted on an expanded scale in Figure 4.

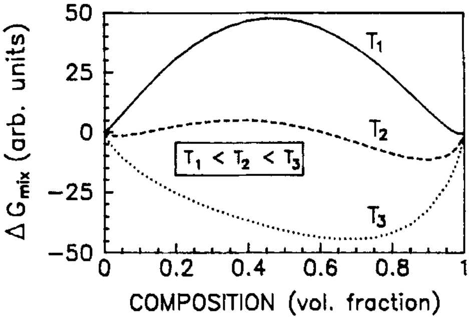

FIGURE 3 Curves of ΔG_{mix} versus ϕ at three different temperatures for a binary system with $m_1 = 4$ and $m_2 = 10$, $C = -0.4$, and $D = 500$ K, as computed from the F-H model.

Figure 4 is helpful in defining two basic concepts important to our description of phase separation in PDLCs: the binodal and spinodal curves. (Useful discussions of these curves are given in References 12, 19, and 20). In the figure the binodal concentrations, ϕ_b' and ϕ_b'', are the equilibrium compositions of the system. Thus, ΔG_{mix} for the mixture is a minimum when the system consists of two phases having concentrations ϕ_b' and ϕ_b''. A line drawn through ϕ_b' and ϕ_b'' is tangent to the ΔG_{mix} curve at both points.[12] [It is important to note that the binodal concentrations usually do not coincide with the local minima of the free energy curve. Such coincidence occurs only when $\Delta G_{\text{mix}}(\phi)$ is symmetrical (i.e., $m_1 = m_2$).] The amounts of the two phases can be calculated from the binodal compositions using the lever rule.[13] The binodal temperature-concentration curve can be constructed by determining ϕ_b' and ϕ_b'' for a number of temperatures and then plotting $T - \phi$ diagrams.

The spinodal compositions in Figure 4 are indicated by ϕ_s' and ϕ_s''. At these points $\delta^2(\Delta G_{\text{mix}})/\delta\phi^2 = 0$. The significance of the spinodal compositions can be visualized as follows: Consider a sample of composition $\phi(\phi_s' < \phi < \phi_s'')$ held initially at a

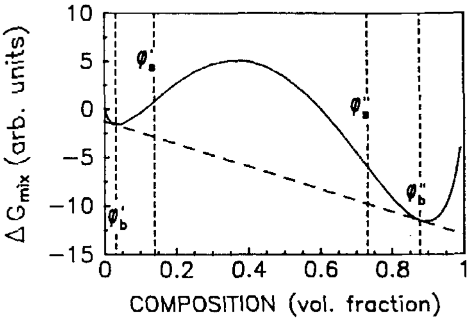

FIGURE 4 Expanded plot of ΔG_{mix} of Figure 3 for intermediate temperature T_2. The binodal compositions are indicated by ϕ_b' and ϕ_b''; spinodal compositions by ϕ_s' and ϕ_s''.

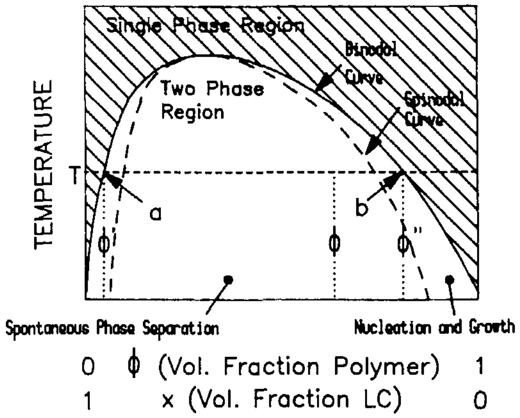

FIGURE 5 Schematic binary UCST phase diagram for a LC/polymer system. In the two phase region, phase separation occurs either spontaneously (inside the spinodal curve) or by nucleation and growth (between the spinodal and binodal). The tie-line between points *a* and *b* is used to illustrate the application of the lever rule to determine the fraction of LC-rich phase, *a*, or polymer-rich phase, *b*.

TABLE I

Differences between SD and NG

Spinodal Decomposition	Nucleation and Growth	Reference
SD requires viscous mixture. Two-phase structure is uniform and highly interconnected.	NG can intervene for low viscosity. Two-phase structure is not uniform and not highly interconnected.	12
Morphology is initially interconnected. It can then coarsen to form droplets.	Morphology is initially dispersed. Droplet sizes then increase by growth and coalescence.	19
Minor phase composition changes continuously with time. Interface between phases is diffuse. Separated phases are generally non-spherical and interconnected. Complex regularity in size and distribution of phases.	Minor phase composition constant. Interface between phases is sharp. Minor phase tends to be spherical droplets and not interconnected. Tendency for random distribution of sizes and positions of phases.	20
Modulated structure initially.	Droplet-like structure initially.	21
SD not defined thermodynamically. SD occurs near center of miscibility gap.	Binodal is an equilibrium line. NG occurs just inside binodal curve.	22
If 2 phases are commensurate, neither is minor or major phase; both are continuous and interpenetrating.	At low and high concentrations the minor phase is dispersed as droplets in the major one.	23
Not all interconnected systems are due to SD. NG plus coalescence can lead to similar structures.	Morphology of NG has sharp boundary between phases. In initial stages minor phase shows droplet structure.	24

Note: Doremus[25] has pointed out that phase-separating isotropic systems (e.g., liquids or glasses) can have interconnected structures. Morphology is not a sure method for identifying SD. If the phases have comparable volumes, they can initially exhibit individual particles.

high temperature T_3, where it is a single phase system. If the sample is subsequently cooled to T_2, it will spontaneously separate into two phases[20]; the equilibrium composition of the two phases will, of course, be ϕ_b' and ϕ_b''. This process is called spinodal decomposition (SD). On the other hand, if a sample with $\phi_b' < \phi < \phi_s'$ or $\phi_s'' < \phi < \phi_b''$ is cooled to T_2, phase separation will not be spontaneous. Rather, an energy barrier will have to be overcome, and phase separation will occur by a nucleation and growth (NG) mechanism.[20,21] A schematic phase diagram, illustrating both the binodal and spinodal curves, is given in Figure 5. Attributes of systems undergoing spinodal decomposition and nucleation and growth have been extensively discussed in the literature (Table I). As can be seen from the table, there is some confusion concerning the morphology exhibited during the two phase separation processes. However, generally speaking, during the early stages of phase separation, SD is characterized by a bi-continuous, interconnected structure, whereas NG shows a texture in which the minor phase is dispersed as droplets in the major phase.

Ideally, in order to construct an equilibrium T-ϕ phase diagram for our binary system, we wish to calculate the binodal curves. Unfortunately, this cannot be done in closed form using the F-H theory; iterative methods are required.[9,10] On the other hand, spinodal curves can be computed in closed form, making it much more convenient to use them in an initial approach to modelling phase separation in PDLCs. We shall calculate spinodal curves and use them to determine the amounts of the two phases (polymer-rich and liquid-crystal-rich). Strictly speaking, this is not legitimate because the binodal, not the spinodal curve determines the equilibrium concentrations of the binary system. However, there are reasons why our approach is physically meaningful: 1) As we shall see, for our two-phase system the dependence of Π_p, the fraction of polymer-rich phase (or Π_{LC}, the fraction of liquid-crystal-rich phase), upon ϕ is determined by the lever rule, not by the details of the T-ϕ plot. Only when we calculate the temperature dependence of Π_p and Π_{LC} does the nature of the phase diagram enter the picture. 2) Since the shape of the spinodal curve can mimic that of the binodal, its use provides a convenient way in which to introduce a temperature dependence into calculations of Π_p and Π_{LC}. The parametric temperature dependence (Equation 9) is the same for both the binodal and spinodal curves. From Π_{LC} we can then compute $P(x)$, α, and A. 3) As discussed by Nishi[10], the gap between the binodal and spinodal curves may sometimes be narrow enough that phase separation is dominated by spinodal decomposition. 4) If spinodal decomposition governs the phase separation process by which a PDLC is formed and if the polymer matrix hardens rapidly during formation, the "frozen in" concentration may be a non-equilibrium value given by the spinodal curve. Kim and Palffy-Muhoray[26] have studied phase separation kinetics of PDLC formation and interpreted their results in terms of a spinodal decomposition model. On the other hand, Tanaka and Nishi[21] have suggested that a droplet structure is consistent with the nucleation and growth mechanism and a periodically modulated structure with spinodal decomposition. 5) It has been pointed out that the usefulness of the F-H theory is restricted by limitations[15] which include the ϕ-dependence of χ. Thus, basing our arguments on a spinodal curve derived from F-H, although thermodynamically problematical, may still be almost as helpful as the use of the binodal. 6) Perhaps the most significant argument in favor of the use of the spinodal is the fact that it is legitimate to use spinodal compositions as upper ($0 < \phi_b' < \phi_s'$) or lower ($\phi_s'' < \phi_b'' < 1$) bounds for the binodal compositions.

We shall model the PDLC as a liquid-crystal/polymer system. We shall first compute spinodal curves for such a system. Then we shall show how the lever rule can give an expression (analogous to Equation 3) for Π_{LC}, the fraction of LC phase. This will enable us to calculate α, the fraction of LC in the droplets (rather than dissolved in the matrix). Finally, by using the spinodal compositions together with the lever rule we can incorporate the temperature into our calculations. In the next section we describe the calculation of spinodal curves.

CALCULATION OF SPINODAL CURVES

The equation for the spinodal T-ϕ curve is obtained by setting the second derivative of equation 6 equal to zero to yield

$$T = [-C/D + (1/2D)\{1/(m_1(1 - \phi)) + 1/(m_2\phi)\}]^{-1}. \qquad (10)$$

We require the spinodal compositions in order to calculate the temperature dependence of phase fractions using the lever rule. Therefore, we invert Equation 10 to obtain

$$\phi = [-Q(T) \pm \{Q(T)^2 - 8\chi(T)m_1^2 m_2\}^{1/2}]/(4\chi(T)m_1 m_2), \tag{11}$$

where

$$Q(T) = m_2 - m_1 - 2\chi(T)m_1 m_2, \tag{12}$$

and $\chi(T)$ is given by Equation 9. The spinodal compositions, ϕ_s' and ϕ_s'', are given respectively by ϕ_- and ϕ_+, the two roots of Equation 11.

The critical concentration, ϕ_c, and temperature, T_c, (i.e., the coordinates of the maxima of the UCST curve) are given by

$$\phi_c = [1 + (m_2/m_1)^{1/2}]^{-1} \tag{13}$$

and

$$T_c = (-D/C)\{1 - (1/(2C))[m_1^{-1/2} + m_2^{-1/2}]^2\}^{-1}. \tag{14}$$

The choice of the parameters m_1, m_2, C, and D can appreciably shift the T-ϕ spinodal curves, but it is possible to make judicious selections with which we can obtain reasonable results. A family of spinodal curves calculated from the F-H model is given in Figure 6. For this system we take component 1 to be the liquid crystal and let $m_1 = 2$ (in accord with its low molecular weight). We allow m_2, the degree of polymerization of the polymer component, to increase from 1 to 160. Choosing $C < 0$ and $D > 0$ automatically leads to UCST behavior.[9,10] There is evidence that polymer-dispersed liquid crystals all have UCST phase diagrams, no matter how they are formed. We shall examine that evidence briefly in the next paragraph.

The Kent State group[16,17] have reviewed the three PDLC formation processes: PIPS (polymerization-induced phase separation), TIPS (thermally-induced phase

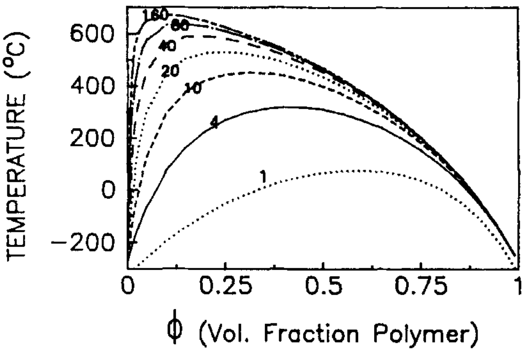

FIGURE 6 Family of UCST spinodal curves derived from the F-H model for $C = -0.4$, $D = 670$ K, $m_1 = 2$, and $m_2 = 1, 4, 10, 20, 40, 80$, and 160.

separation), and SIPS (solvent-induced phase separation). The latter two cases involve the use of thermoplastic polymer matrices in which the liquid crystal is initially dissolved; phase separation is produced either by cooling or solvent extraction, and in both cases a system with a UCST phase diagram is produced[16,17] In the PIPS process the LC is initially dissolved in a low molecular weight polymer precursor. Polymerization of the precursor leads to an increase in molecular weight of the matrix, with concomitant reduction in the mutual solubility of the components which, in turn, leads to phase separation. If a polymer precursor with a low functionality is used, the PIPS process (like TIPS and SIPS) yields a thermoplasic system (which, as already discussed, has a UCST diagram). On the other hand, use of a high functionality polymer precursor produces a highly cross-linked matrix (i.e., a thermoset). Evidence for UCST behavior of a thermoset PDLC is indirect, since formation of a single phase by heating such a system cannot be achieved without decomposition. However, Hirai, *et al.*[18] have computationally simulated phase separation for a thermoset PIPS system with different degrees of cure, obtaining UCST diagrams. Furthermore, the temperature dependence of the solubility limits of thermoset PDLCs measured by Smith, *et al.*[5] is consistent with UCST behavior.

Having reviewed the method for calculating spinodal curves for mixed high and low molecular weight systems, we shall, in the next section, turn our attention to the use of the lever rule to calculate Π_{LC} ($=P$), A, and α.

APPLICATION OF THE LEVER RULE

As we have already mentioned, the temperatures and shapes of the spinodal curves are sensitive to the choices of m_1, m_2, C, and D. We shall let $m_1 = 2$, but shall adjust m_2, C, and D to yield the best agreement with calorimetric results (subject to the restriction that $C < 0$ and $D > 0$). But first, we need to examine the lever rule which will allow us to calculate the amount of polymer-rich or liquid-crystal-rich phase. As we shall see, without even resorting to F-H, application of the lever rule yields an expression analogous to that for $P(x)$ (Equation 3).

We illustrate the use of the lever rule by the schematic UCST temperature-concentration diagram of Figure 5. A mixture with polymer concentration ϕ at temperature T will separate into two phases: a) a liquid-crystal-rich phase with polymer concentration ϕ', and b) a polymer-rich phase with concentration ϕ''. The fractions of phases a) and b) are given by the lever rule[13]:

$$\Pi_{LC}(\phi) \equiv V_a/V_{tot} = (\phi'' - \phi)/(\phi'' - \phi') \quad \text{(LC-rich phase)} \tag{15}$$

$$\Pi_p(\phi) \equiv V_b/V_{tot} = 1 - \Pi_{LC} = (\phi - \phi')/(\phi'' - \phi') \quad \text{(polymer-rich phase),} \tag{16}$$

where V_a, V_b, and V_{tot} are the volumes of the a- and b-phases and the PDLC. (Since LC and polymer densities are comparable, either masses or volumes can be used.)

We are primarily interested in the fraction of liquid-crystal rich phase in terms of the LC concentrations, x, where

$$x \equiv 1 - \phi. \tag{17}$$

Therefore we substitute $(1 - x)$ for ϕ in Equation 15 to obtain

$$\Pi_{LC}(x) = (x - x'')/(x' - x''). \tag{18}$$

It is apparent that Equation 18 is similar to Equation 3. For a high degree of polymerization ($m_2 \rightarrow \infty$), Equation 11 shows that $x' \rightarrow 1$; if we then let $x'' = A$, Equations 3 and 18 become identical so that:

$$\Pi_{LC}(x) = P(x) \qquad (\text{for } m_2 \rightarrow \infty). \tag{19}$$

This use of the lever rule to derive an expression equivalent to Equation 3 is more fundamental than the original calorimetric argument. Equation 18 is more general than Equation 3 since it allows a non-zero solubility of the polymer in the liquid crystal. Nevertheless, as will be seen in the next paragraph, Equation 3 is still an excellent representation of PDLC solubility behavior.

Smith, *et al.*[5] have measured $P(x)$ for two epoxy-based PDLC systems, each employing a single component liquid crystal, 7CB and 5CB. Their data are plotted in Figure 2 along with best fits of Equations 3 and 18. Derived values of x', x'', and A are given in Table II. Since $x'' \simeq A$ and $x' \simeq 1$, it appears that Equation 18 reduces to Equation 3 as far as PDLC solubility behavior is concerned. (The fact that the x'-values exceed unity is physically unrealistic; however, the excess is <0.02, smaller than the experimental uncertainty).

The fraction of liquid crystal which is "free" (i.e., not dissolved in the matrix) is then given by the analogue of Equation 5:

$$\alpha = (1/x)(x - x'')/(x' - x''). \tag{20}$$

In the next section we shall use equations 15 and 20 together with the spinodal compositions to compute the temperature dependences of Π_{LC} and of a.

TABLE II

Parameters for Equations 18 and 3

System & DSC Quantity	x' (Equation 18)	x'' (Equation 18)	A (Equation 3)
7CB/Epoxy PDLC			
$\Delta C_{LC}(x)/\Delta C_{LC}$ (−68°C)	1.012	0.0896	0.0925
$\Delta H_{NI}(x)/\Delta H_{NI}$(LC) (44°C)	1.012	0.136	0.138
5CB/Epoxy PDLC			
$\Delta C_{LC}(x)/\Delta C_{LC}$ (−68°C)	1.006	0.139	0.140
$\Delta H_{NI}(x)/\Delta H_{NI}$(LC) (41°C)	1.017	0.189	0.191

JOINT USE OF LEVER RULE AND SPINODAL TO CALCULATE TEMPERATURE DEPENDENCE OF Π_{LC} AND α

In order to calculate the temperature dependence of Π_{LC}, the amount of the liquid-crystal-rich phase (expressed as a volume fraction of the total PDLC), we use the lever rule together with Equation 11. However, it is important to keep in mind the caveats regarding the use of the spinodal rather than the binodal composition (see above). The calculation is straightforward: for a specific temperature, the two roots of Equation 11 give ϕ_s' and ϕ_s''. For each selected value of ϕ, the polymer volume fraction, Equations 17 and 18 give Π_{LC}, the fraction of liquid-crystal-rich phase, as a function x, the liquid crystal concentration. Similarly, α, the fraction of LC which is "free" (and, for sufficiently low x, contained in the microdroplets), can be computed from Equation 20.

Determining the values of F-H parameters. In order to perform the calculations, we needed to select appropriate values for the four parameters in the Flory-Huggins model: m_1, m_2, C, and D. The steps in the selection process involved trial and error to some extent: 1) We set $m_1 = 2$ since component 1 is a low molecular weight LC. 2) We then let $m_2 = 40$, since, as will be seen, spinodal compositions are fairly insensitive to the variations in m_2 for $m_2 \geqslant 40$. 3) The best values of the two χ-parameters for the PDLCs of Table II were selected by comparing theoretical and experimental plots of α vs. x for two temperatures: with $m_1 = 2$ and $m_2 = 40$, C and D were each varied to obtain simultaneously the best agreement between the calculated x-dependences of α and those determined calorimetrically [from ΔC_{LC} (at T_g(LC) ~ -70°C) and from ΔH_{NI} (at $T_{NI} \sim 40$°C)]. The selections were constrained by the requirements that $C < 0$ and $D > 0$. For the 7CB/epoxy system we obtained $C = -0.4$ and $D = 670$ K; for 5CB/epoxy, $C = -0.05$, $D = 410$ K.

Having determined best values for the F-H parameters, we were then able to calculate spinodal T-ϕ curves (from Equation 10) for the two PDLC systems (Figure 7). Justification for selecting $m_2 = 40$ is seen in Figure 6: it is clear that, for temperatures well below T_c ($=592.3$°C), ϕ_s' and ϕ_s'' do not change much with m_2 for $m_2 > 40$. (The sensitivity of ϕ_b' and ϕ_b'', the binodal concentrations, to m_2 should

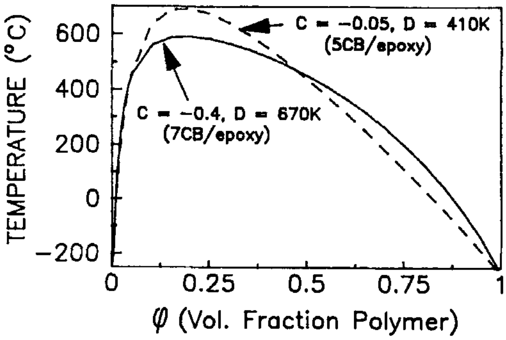

FIGURE 7 Spinodal curves calculated for the two systems of Figure 2, assuming $m_1 = 2$, $m_2 = 40$, and the indicated C- and D-values.

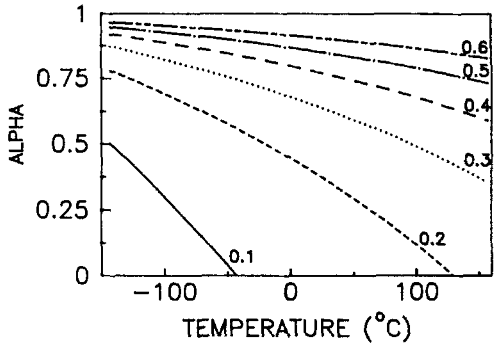

FIGURE 8 Temperature dependence of α, the fraction of LC which is phase-separated, calculated from Equation 20 for LC volume fractions ranging from 0.1 to 0.6. Values of the F-H parameters: $m_1 = 2$, $m_2 = 40$, $C = -0.4$, and $D = 670$ K.

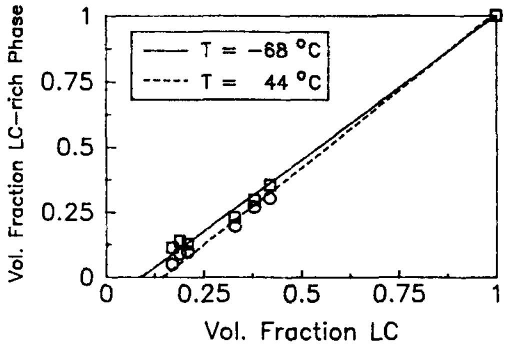

FIGURE 9 Dependence of volume fraction of LC-rich phase on LC concentration, x, for the 7CB/epoxy PDLC. Squares are data for ΔC_{LC}, circles for ΔH_{NI} (from Equations 4 and 2 respectively). Lines are $\Pi_{LC}(x)$ values calculated from Equation 18 for the temperatures at which ΔC_{LC} and ΔH_{NI} were measured (−68°C and 44°C respectively), using values of the F-H parameters: $m_1 = 2$, $m_2 = 40$, $C = -0.4$, and $D = 670$ K.

be greater, especially for low m_2). Since, for low m_2, the liquid phase consists of both LC and low molecular weight polymer, we cannot use the model to study the phase separation of LC from polymer as a function of degree of polymerization. Nevertheless, as discussed above, we do feel confident in the temperature dependences of $\Pi_{LC}(x)$ $[=P(x)]$ and α calculated for high degrees of matrix polymerization ($m_2 \geq 40$).

Calculated plots of α vs. temperature are given in Figure 8 for $m_1 = 2$, $m_2 = 40$, $C = -0.4$, $D = 670$ K, and x-values ranging from 0.1 to 0.6. It is clear that the fraction of free LC decreases with increasing temperature, as expected for a UCST system. For low values of the LC concentration and sufficiently high temperatures, all the liquid crystal is dissolved in the polymer matrix. Figure 8 also shows that, for this system at ambient temperatures (0 to 100°C), large values of α (>0.8) are attained only with LC concentrations near or above $x = 0.4$. For lower values of x, α can be considerably smaller (~0.6 or less), resulting in much less efficient use of liquid crystal.

Let us now turn our attention to the implications of the model for the calorimetric

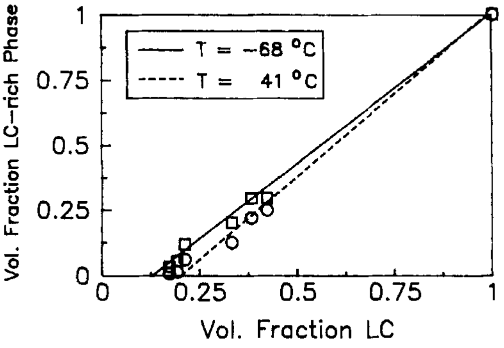

FIGURE 10 Dependence of volume fraction of LC-rich phase on x for the 5CB/epoxy PDLC. Lines are $\Pi_{LC}(x)$ values calculated from Equation 18 for the temperatures at which ΔC_{LC} and ΔH_{NI} were measured (−68°C and 41°C). Values of the F-H parameters: $m_1 = 2$, $m_2 = 40$, $C = -0.05$, and $D = 410$ K. Data points as in Figure 9.

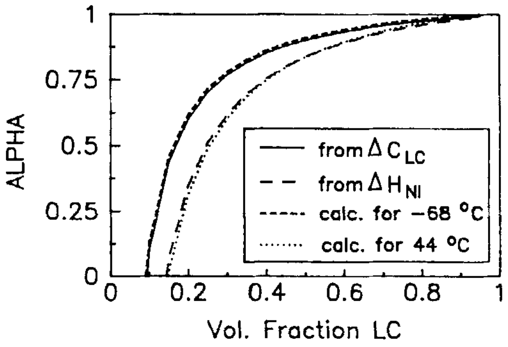

FIGURE 11 Calorimetrically determined dependence of fraction of phase-separated LC, α, on x, for the 7CB/epoxy PDLC, compared to the dependence calculated from Equation 20 for F-H parameters of Figure 9.

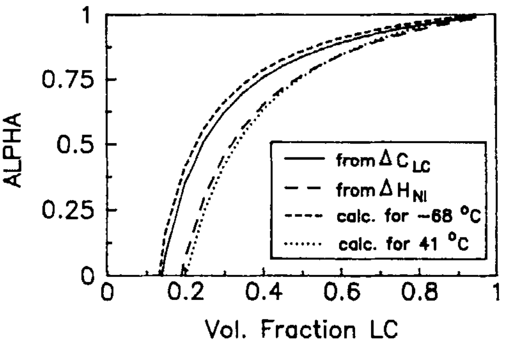

FIGURE 12 Calorimetrically determined dependence of fraction of phase-separated LC, α, on x, for the 5CB/epoxy PDLC, compared to the dependence calculated from Equation 20 for F-H parameters of Figure 10.

results. Experimental P-values are plotted in Figures 9 and 10 together with curves of Π_{LC} calculated from equation 18 for the temperatures at which ΔC_{LC} and ΔH_{NI} were determined. In each figure the pairs of lines are similar to the best fits shown in Figure 2, with one difference: the use of F-H has now built the temperature dependence into the calculation. Agreement of experiment and theory is good. (In the figures the LC concentrations for the data are weight fractions, whereas the calculations use volumetric fractions. However, since LC and matrix densities are comparable, weight and volume fractions are almost identical.) In Figures 11 and 12 are the calculated and experimental curves of α, comparison of which allowed us to select C and D in the first place. It can be seen that the curve optimization process succeeded fairly well, in spite of the constraints involved in selecting the parameters.

The potential usefulness of the model for assessing solubility parameter effects and implications for selection of liquid crystal/polymer combinations will be discussed in the next section.

DISCUSSION

It appears that the present model, based on Flory-Huggins theory and the lever rule, is of some value in interpreting phase separation behavior in polymer-dispersed liquid crystal systems. The use of spinodal curves, rather than binodal, is certainly problematical, but we feel that the convenience of operating with closed form expressions outweighs the thermodynamic consideration, especially when one considers the limitations inherent in F-H itself. As we have stated above and shall demonstrate below, the model is a legitimate way to estimate an upper bound for the solubility limit, A.

Relation of χ to Solubility Parameters

The fact that the Flory-Huggins interaction parameter is related to solubility parameters has been extensively discussed.[11,15,27–30] It has been pointed out[15,27,29,30] that χ for a two-component mixture can be taken to be the sum of an entropic and an enthalpic term:

$$\chi = \chi_S + \chi_H, \tag{21}$$

where the enthalpic term is given by[29]:

$$\chi_H = V_1(\delta_1 - \delta_2)^2/RT. \tag{22}$$

Here V_1 is the molar volume of component 1 (the low molecular weight component), δ_1 and δ_2 are the solubility parameters of components 1 and 2, and R is the gas constant. It is evident that Equations 21 and 22 provide a justification for the form of Equation 9. Equating the temperature-dependent term of Equation 9 to Equation 22 gives:

$$D = V_1(\delta_1 - \delta_2)^2/R, \tag{23}$$

which would allow us to calculate D if we knew the molar volume of component 1 and the solubility parameters. Roginskaya *et al.*[29] have calculated solubility parameters for epoxy/rubber mixtures using the theory of group contributions,[15] obtaining reasonable agreement with experiment. They also found χ_S ($\equiv C$) values ranging from -0.1 to -2.35, comparable to the results obtained from our best fits to α ($C = -0.4$ and -0.05). Their determinations of χ_H ($\equiv D/T$) give D values ranging from 275 K to 1350 K, bracketing out determinations (670 K and 410 K). Such agreement may not be significant for two such different types of systems, but the fact that the results are not wildly different is satisfying, given the limitations of the present work.

It would seem that careful determination of the F-H interaction parameters for PDLCs should provide information about the solubility parameters of the components. Conversely, it should be possible to maximize the degree of phase separation of a PDLC by choosing components according to their solubility parameters. A complication is the need to take account of solubilities before and after formation of PDLCs by PIPS. What is needed are solubilities which are high prior to polymerization but low afterwards, perhaps with the decrease assisted by a change in temperature during cure. Further discussion of this point is beyond the scope of the present work.

Upper Bounds for Solubility Limits

Although the use of spinodal curves in the present model imposes limitations on certain aspects of its validity, at the very worst the spinodal compositions allow us to compute upper bounds for the solubilities of LC in the matrix and of the polymer in the liquid crystal. Assuming a large degree of polymerization for the matrix ($m_2 \to \infty$) we can use the two roots of Equation 11 (ϕ_- and ϕ_+), to write approximate expressions for the solubility limits of polymer in LC and LC in polymer. The upper bound for the solubility limit of polymer in LC, is:

$$\phi_s' \equiv \phi_- \simeq 1/(1 + 2\chi m_2 - m_2/m_1). \tag{24}$$

The expression for x_s'', the upper bound for A, the solubility limit of LC in the polymer matrix, is:

$$A \leq x_s'' \equiv 1 - \phi_+ \simeq 1/(2\chi m_1) - 1/(2\chi m_2) + 1/(1 + 2\chi m_2 - m_2/m_1). \tag{25}$$

If $m_2 \to \infty$ and $T << \text{UCST}$, Equations 24 and 25 reduce to:

$$\phi_s' \simeq 0, \tag{26}$$

and

$$A \leq x_s'' \simeq 1/(2\chi m_1). \tag{27}$$

As always, χ is given by Equation 9. For low temperatures ($T << T_c$), Equation 27 is a very good approximation to the exact expression.

Equation 27 is useful in that it relates the solubility limit of the LC in the polymer to the degree of polymerization of the liquid crystal molecule (i.e., to its size) as well as to the F-H interaction parameter. The equation indicates that large molecules should be less likely to dissolve in the matrix than small molecules, in agreement with recent experiments[31] and with Table II in which it is seen that the smaller molecule, 5CB, has higher A-values than 7CB.

It is instructive to calculate solubility limits for a model PDLC using Equations 24 and 25. If we assume $m_1 = 2$, $m_2 = 40$, $C = -0.4$, $D = 670$ K, and $T = 300$ K (23°C), we obtain $\phi_s' \simeq 0.008$ and $A \simeq 0.136$; thus, the solubility of the LC in the polymer is more than an order of magnitude greater than that of the polymer in the LC. The result for A is consistent with calorimetric measurements[2–6] which indicate that some 15 to 20% of the LC is dissolved in the polymer matrix.

Equation 27 could, in principle, be used to evaluate the two constants in Equation 9 from measurements of A at two temperatures. Unfortunately, such measurements are not presently precise enough to provide accurate values of C and D. As an example, consider the case of the 7CB-based PDLC. Taking $A\ (-68°\mathrm{C}) = 0.093$ and $A\ (44°\mathrm{C}) = 0.14$, we find $C = 0.1$ and $D = 528$ K; if instead we let $A\ (-68°\mathrm{C}) = 0.085$, we obtain $C = -0.3$ and $D = 661$ K. Because of the constraints on the F-H constants ($C < 0$, $D > 0$), it appears that it is more fruitful to determine C and D by comparison of theoretical and experimental α-curves (subject to the constraints) than by solving Equation 27. However, knowledge of δ-values may in the future allow us to predict A-values from Equations 21–23 and 27. If this becomes possible, we may then be able to computationally optimize compositions of PDLCs prior to their fabrication.

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References

1. J. W. Doane, N. A. Vaz, B.-G. Wu and S. Zumer, *Appl. Phys. Lett.*, **48**, 269 (1986).
2. N. A. Vaz, G. W. Smith and G. P. Montgomery, Jr., *Mol. Cryst. Liq. Cryst.*, **146**, 1 (1987); N. A. Vaz, G. W. Smith and G. P. Montgomery, Jr., *Mol. Cryst. Liq. Cryst.*, **146**, 17 (1987).
3. G. W. Smith and N. A. Vaz, *Liq. Cryst.*, **3**, 543 (1988).
4. G. W. Smith, *Mol. Cryst. Liq. Cryst.*, **180B**, 201 (1990). Note that in the present paper we express liquid crystal concentration as a fractional quantity, x, rather than as a percentage, X ($= 100x$).
5. G. W. Smith, G. M. Ventouris and J. L. West, *Mol. Cryst. Liq. Cryst.*, **213**, 11 (1992).
6. G. W. Smith and N. A. Vaz (in preparation).
7. P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
8. M. L. Huggins, *Ann. NY Acad. Sci.*, **43**, 1 (1942).
9. T. Nishi, *Rep. Prog. Polymer Phys.*, Japan **20**, 225 (1977). Unfortunately, the UCST region in Figure 1 of this paper is incorrect. It should lie in the fourth quadrant between the x-axis and the line $C = -D/T$ (in Nishi's notation: the line $A = -B/RT$).
10. T. Nishi, *J. Macromol. Sci.-Phys.*, **B17**, 517 (1980). The error of reference 9 is repeated in Figure 3 of this paper.
11. T. Nishi, *CRC Critical Revs. in Sol. State and Mater. Sci.*, **12**, 329 (1985).
12. I. C. Sanchez, *Ann. Rev. Mater. Sci.*, **13**, 387 (1983).

13. L. H. Van Vlack, *Elements of Materials Science and Engineering*, 3rd Ed., Addison-Wesley Pub. Co., Reading, MA (1975), pp. 310–312.
14. First ALCOM Symposium on Dispersions of Liquid Crystals and Polymers, Cuyahoga Falls, OH, June 12–13, 1991.
15. A. F. M. Barton, *Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL (1983), p. 263ff; A. F. M. Barton, *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press, Boca Raton, FL (1990), p. 3ff.
16. J. W. Doane, A. Golemme, J. L. West, J. B. Whitehead, Jr. and B. G. Wu, *Mol. Cryst. Liq. Cryst.*, **165**, 511 (1988).
17. J. L. West, *Mol. Cryst. Liq. Cryst.*, **157**, 427 (1988); J. L. West, *ACS Symp. Ser.*, **435**, 475 (1990).
18. Y. Hirai, S. Niiyama, H. Kubai and T. Gunjima, SPIE **1257**, 2 (1990). See also Reports Res. Lab. Asahi Glass Co., *Ltd.*, **40**(2), 285 (1990).
19. O. Olabisi, L. M. Robeson and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, NY (1979), pp. 31–35.
20. C. N. R. Rao and K. J. Rao, *Phase Transitions in Solids*, McGraw-Hill, NY (1978), pp. 133–136.
21. H. Tanaka and T. Nishi, *Phys. Rev. Letters*, **55**, 1102 (1985).
22. D. de Fontaine, in *Treatise on Solid State Chemistry, Vol. 5, Changes of State*, N. B. Hannay, ed., Plenum Press, NY, 1975, pp. 153–154.
23. R. M. Hikmet, S. Callister and A. Keller, *Polymer* **29**, 1378 (1988).
24. H. S.-Y. Hsich, *Polymer Eng. & Sci.*, **30**, 493 (1990).
25. R. H. Doremus, *Rates of Phase Transformations*, Academic Press, Orlando, FL, 1985, pp. 78–83.
26. J. Y. Kim and P. Palffy-Muhoray, *Mol. Cryst. Liq. Cryst.*, **203**, 93 (1991).
27. S. Chen, *J. Appl. Polymer Sci.*, **15**, 1247 (1971).
28. D. M. Koenhen and C. A. Smolders, *J. Appl. Polymer Sci.*, ***19***, 1163 (1975).
29. G. F. Roginskaya, V. P. Volkov, A. Ye. Chalykh, N. N. Avdeyev and B. A. Rozenberg, *Polymer Sci. U.S.S.R.*, **21**, 2331 (1980); G. F. Roginskaya, V. P. Volkov, A. I. Kuzayev, A. Ye. Chalykh and B. A. Rozenberg, *Polymer Sci. U.S.S.R.*, **26**, 1139 (1984).
30. G. A. Lipson, A. Ye. Chalykh, N. N. Avdeyev, V. V. Matveyev, V. V. Arslanov and V. A. Ogarev, *Polymer Sci. U.S.S.R.*, **26**, 2081 (1984).
31. P. Nolan, Merck Ltd, Poole, England (private communication).