Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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P. Maïssa[a]; P. Sixou[a]

[a] U. A. 190, Physique de la Matière Condensée, Nice Cedex, France

To cite this Article Maïssa, P. and Sixou, P.(1989) 'Mixtures of liquid-crystalline polymers', Liquid Crystals, 5: 6, 1861 — 1873

To link to this Article: DOI: 10.1080/02678298908045694

URL: http://dx.doi.org/10.1080/02678298908045694

Liquid Crystals, 1989, Vol. 5, No. 6, 1861–1873

Mixtures of liquid-crystalline polymers

by P. MAÏSSA and P. SIXOU

U.A. 190, Physique de la Matière Condensée, Parc Valrose, 06034 Nice Cedex, France

A density-functional expansion method is used to derive the free energy of a polymer mixture. The expression obtained includes the entropy of mixing, the entropy of configuration of the chains and the interactions (both isotropic and anisotropic ones). The chains are modelled as interacting elastic lines (bend curvature). The method is very general, and we only focus our attention on binary mixtures. The phase diagram and the order parameters are calculated. We show some results for two types of mixtures: a nematic polymer in a non-mesomorphic particle (polymer or solvent) and in another nematic liquid crystal (small-molecule or polymer). We discuss the influence of the molecular weights, the persistence length and the interactions on the phase separation.

1. Introduction

A considerable amount of experimental and theoretical work has been done on liquid-crystalline polymers (LCP) in recent years [1–3]. These substances are of interest from both fundamental and practical points of view. They constitute a new family of materials, which have a number of industrial applications (fibres, sensors, electro-optic components etc.) [4, 5]. They are characterized by the existence of a phase transition from an isotropic to an orientationally ordered state through variation of temperature (thermotropic polymers) or concentration (lyotropic polymers).

As in the case of a small-molecule liquid crystal (SMLC), the anisotropic phases may be of different types—nematic, cholesteric and smectic. A variety of experimental methods have been used to observe and characterize these mesomorphic phases, which are optically birefringent: optical microscopy, viscosity measurements and differential scanning calorimetry have been employed in determining the transition temperature, the critical concentrations and the biphasic ranges [6–10] and also in the study of the textures [6, 11]; nuclear magnetic resonance has been used [12–14] for the determination of the order; while the cholesteric pitch has been determined by light scattering and spectrophotometry [15, 16].

Main-chain LCPs can be modelled in various ways: as rigid chains (rod-like or helical rod-like, as for polypeptides); rod-like mesogens alternating with flexible spacers (as for polyesters); semi-rigid chains (bend elastic lines or worm-like chains for cellulose derivatives, for example) [17, 18].

The chain rigidity of the polymer structure, the chain length and the interactions between monomers—both isotropic (which are of great importance in flexible polymers) and anisotropic (which also exist in SMLC)—are the main parameters that can be adjusted to modify the properties (viscosity, biphasic areas, cholesteric pitch) of LCPs both in the melt and in mixtures). Moreover, from a theoretical point of view, simple variation of the degree of polymerization, from one monomer to hundred of units, allows study of the properties of a wide range of particles, from SMLCs to ‘near-infinite’ long-chain polymers. We do not take into account here of the detailed chemical structure of real polymer chains, which is of great importance [19] but is not necessary in determining qualitative general trends and some quantitative predictions.

LCPs exhibit biphasic areas that are generally much wider than those observed in SMLCs, although some LCP mixtures seem to be miscible [20].

Prediction of the occurrence of these biphasic areas is one of the main aims of theoretical work on LCPs. Previous studies have been based mainly on two approaches: the Onsager approach [21–24] and the lattice model of Flory [25, 26]. They have been concerned primarily with rod-like polymers in the athermic case [27–34] and include work on multicomponent systems [28–32] and polydispersity [27]. They have also been used in the study of SMLC/flexible-polymer mixtures [35–37]. Some studies have also taken account of the influence of the semiflexibility of the polymer through a model of rod-like particles connected by flexible joints [32, 38] or the influence of anisotropic interactions [34, 39]. Different flexibility mechanisms have also been investigated for nematic polymer melts [22–24]. A wide range of shapes of phase diagrams were investigated in a model [40] combining the Flory–Huggins approach (for the free energy of mixing and the isotropic interactions) and the Maier–Saupe mean-field theory for SMLCs (for the anisotropic interactions); however, this approach ignores the semirigidity of the polymer, and is better adapted for side chain polymers [40].

In another approach an elastic-line-type model for the semirigidity of the chain [18] has been used for the study of the lyotropic [41] and thermotropic behaviour [42, 43] of an LCP and for the prediction of the so-called pseudo-transition in binary mixtures of an LCP and a SMLC [44]. It has also been used in the case of side-chain polymers [45].

More recently, a density-functional expansion has been used for the determination of the free energy of LCP mixtures [46], and an LCP in solution in a simple molecular solvent has been investigated [46, 47]. This density-functional approach had been used previously for SMLC nematics [48] and for flexible isotropic polymers [49].

In this paper we shall be concerned with binary nematic polymer mixtures. In the first part we recall the general procedure for obtaining the free energy of mixing. We then develop the calculation of the phase diagram, the order parameters and the equation of stability (spinodal). We then give two examples: a nematic-polymer/non-mesomorphic-polymer mixture and a two-nematic-polymer mixture. We show the phase diagrams, the evolution of the order parameters, the influence of some parameters, and finally give some concluding remarks.

2. Free energy of mixing

2.1. *General procedure* [46, 49]

The partition function of a binary mixture of particles A and B, which can be simple molecules, SMLCs, flexible polymers or PLCs, is given by (K represents either the A or the B component)

$$Z = \prod_K \frac{Z_K^{\tilde{N}_K}}{\tilde{N}_K!} \int \prod_K \prod_{\tilde{N}_K} \delta\left(\{\mathbf{r}_K(s)\}\right) P_K\left(\{\mathbf{r}_K(s)\}\right) \exp(-\beta V), \qquad (1)$$

in which we have separated the kinetic contributions Z_K.

$\tilde{N}_K = N_K/L_K$ is the number of particles of the K component, N_K being the number of monomers and L_K the degree of polymerization (in the case of a small molecule

$L_K = 1$). $P_K(\{\mathbf{r}_K(s)\})$ is the configurational probability of an individual particle of the K species described by a curve $\mathbf{r}(s)$; it depends of the molecular model chosen and describes intramolecular interactions. V represents the intermolecular interactions; it will be expressed in a general form by (we only consider two-body interactions and assume additivity of the various contributions)

$$\beta V = \frac{1}{2}\sum_{K,K'} W^{KK'}, \tag{2}$$

where

$$W^{KK'} = \begin{cases} \sum_{i,i'} W^{\mathrm{SS}'}(\mathbf{r}_i - \mathbf{r}_{i'}) & \text{(2 small molecules)},\\ \sum_{i,j}\int ds\, W^{\mathrm{SP}}[\mathbf{r}_i - \mathbf{r}_j(s)] & \text{(polymer/small molecule)},\\ \sum_{j,j'}\int ds\, ds'\, W^{\mathrm{PP}'}[\mathbf{r}_j(s) - \mathbf{r}_{j'}(s')] & \text{(2 polymers)}. \end{cases}$$

By introducing the microscopic particle density $\hat{\varrho}_K(\mathbf{r}, \mathbf{w})$ at position $\mathbf{r}$ with orientation $\mathbf{w}$, with $\mathbf{w}(s) = \partial\mathbf{r}(s)/\partial s$, so that for a polymer

$$\hat{\varrho}_{\mathrm{P}}(\mathbf{r}, \mathbf{w}) = \sum_{j=1}^{\tilde{N}_{\mathrm{P}}}\int_0^{L_{\mathrm{P}}} ds\, \delta[\mathbf{r} - \mathbf{r}_j(s)]\delta[\mathbf{w} - \mathbf{w}_j(s)], \tag{3a}$$

and for a small molecule

$$\hat{\varrho}_{\mathrm{S}}(\mathbf{r}, \mathbf{w}) = \sum_{i=1}^{N_{\mathrm{S}}} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{w} - \mathbf{w}_i), \tag{3b}$$

we get

$$\exp(-\beta V) = \int \prod_K \delta\varrho_K \prod_K \delta[\varrho_K - \hat{\varrho}_K(\mathbf{r}, \mathbf{w})]\exp(-W), \tag{4}$$

with

$$W = \frac{1}{2}\sum_{K,K'}\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{w}\, d\mathbf{w}'\, \varrho_K(\mathbf{r}, \mathbf{w})\, W^{KK'}(\mathbf{r}, \mathbf{r}', \mathbf{w}, \mathbf{w}')\varrho_{K'}(\mathbf{r}'\mathbf{w}'). \tag{5}$$

Using the integral representation of the δ function, (1) becomes

$$Z = \prod_K \frac{Z_K^{\tilde{N}_K}}{\tilde{N}_K!}\eta \int \prod_K \delta\varrho_K\, \delta u_K \times \prod_K Q_K^{\tilde{N}_K} \exp\left[\sum_K \int d\mathbf{r}\, d\mathbf{w}\, u_K(\mathbf{r}, \mathbf{w})\varrho_K(\mathbf{r}, \mathbf{w}) - W\right], \tag{6}$$

where

$$Q_K = \begin{cases} \int \delta\mathbf{r}\, \delta\mathbf{w}\, P_K(\{\mathbf{r}(s)\})\exp\left[-\int_0^{L_K} ds\, u_K(\mathbf{r}, \mathbf{w})\right] & \text{for a polymer},\\ \int d\mathbf{r}\, d\mathbf{w} \exp[-u_K(\mathbf{r}, \mathbf{w})] & \text{for a small molecule}. \end{cases} \tag{7}$$

The quantity Q_K represents the molecular model for component K in the mean-field u_k with configurational probability $P_K\{\mathbf{r}(s)\}$. η is a normalization constant.

We can write the partition function in terms of a free-energy functional:

$$Z = \eta \int \prod_K \delta\varrho_K \, \delta u_K \exp[-\beta\mathscr{F}(\varrho_K, u_K)], \tag{8}$$

so that, using Stirling's formula, we obtain an expression for the free energy (neglecting kinetic contributions)

$$\begin{aligned} \beta\mathscr{F}(\varrho_K, u_K) = {} & \sum_K \frac{N_K}{L_K}\left(\ln \frac{N_K}{L_K} - 1\right) - \sum_K \frac{N_K}{L_K} \ln Q_K \\ & - \sum_K \int d\mathbf{r}\, d\mathbf{w} \varrho_K(\mathbf{r}, \mathbf{w}) u_K(\mathbf{r}, \mathbf{w}) + W. \end{aligned} \tag{9}$$

We use the saddle-function method to minimize the functional $(\mathscr{F}(\varrho_K, u_K)$ with respect to ϱ_K and u_K. We obtain coupled equations for the equilibrium densities and mean fields:

$$\left.\begin{aligned} \varrho_K(\mathbf{r}, \mathbf{w}) &= -\frac{N_K}{L_K Q_K}\frac{\delta Q_K}{\delta u_K}, \quad \text{with} \int d\mathbf{r}\, d\mathbf{w} \varrho(\mathbf{r}, \mathbf{w}) = N_K, \\ u_K(\mathbf{r}, \mathbf{w}) &= \frac{\delta W}{\delta \varrho_K}. \end{aligned}\right\} \tag{10}$$

In pure component K the free energy is (we use label 0 for the pure components)

$$\begin{aligned} \beta\mathscr{F}_K(\varrho_K^0, u_K^0) = {} & \frac{N_K^0}{L_K}\left(\ln \frac{N_K^0}{L_K} - 1\right) - \frac{N_K^0}{L_K} \ln Q_K^0 - \int d\mathbf{r}\, d\mathbf{w}\, \varrho_K^0(\mathbf{r}, \mathbf{w}) u_K^0(\mathbf{r}, \mathbf{w}) \\ & + \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{w}\, d\mathbf{w}'\, \varrho_K^0(\mathbf{r}, \mathbf{w}) W^{KK'}(\mathbf{r}, \mathbf{r}', \mathbf{w}, \mathbf{w}')\, \varrho_{K'}^0(\mathbf{r}', \mathbf{w}'), \end{aligned}$$

So that the free energy of mixing is

$$\Delta\mathscr{F} = \mathscr{F} - \sum_K \frac{N_K}{N_K^0} \mathscr{F}_K(\varrho_K^0, u_K^0). \tag{11}$$

2.2. *Uniform-density case*

First we separate position and orientation dependence, with $\varrho_K(\mathbf{r}, \mathbf{w}) = \varrho_K(\mathbf{r}) f_K(\mathbf{w})$, $f_K(\mathbf{w})$ being the orientational distribution function for K. The two-body interaction $W^{KK'}$ is expanded in spherical harmonics [50], so that

$$\begin{aligned} W^{KK'}(\mathbf{r}, \mathbf{r}', \mathbf{w}, \mathbf{w}') &= W^{KK'}(\mathbf{r}, \mathbf{w}, \mathbf{w}') \\ &= \sum_{\substack{l, l_1, l_2 \\ m, m_1, m_2}} W^{KK'}(r, l, l_1, l_2) C(l l_1 l_2 m m_1 m_2) \\ &\quad \times Y_{lm}(\mathbf{r}/|\mathbf{r}|) Y_{l_1 m_1}(\mathbf{w}) Y_{l_2 m_2}^*(\mathbf{w}'), \end{aligned} \tag{12}$$

where $C(l l_1 l_2 m m_1 m_2)$ are the Clebsch–Gordan coefficients and $\mathbf{r} = \mathbf{r} - \mathbf{r}'$.

We shall proceed with systems of uniform density, so that the density distribution will depend on orientation alone. We introduce the number densities $n_K = N_K/V$ (V is the total sample volume) and the volume fraction $X_K = n_K v_K$, v_K the unit volume of K, so that $\varrho_K(\mathbf{r}, \mathbf{w}) = n_K f_K(\mathbf{w})$ and, with the use of (7) and (12), the expression (10) become

$$f_K(\mathbf{w}) = \frac{1}{L_K Q_K} \int \delta\mathbf{r}\, \delta\mathbf{w}\, P_K(\{\mathbf{r}\}) \exp\left\{- \int_0^{L_K} ds\, u_K[\mathbf{r}(s)]\right\} \int_0^{L_K} \delta[\mathbf{w} - \mathbf{w}(s)]\, ds,$$

$$u_K(\mathbf{w}) = \sum_{K'} X_{K'} \sum_{l,m} (-1)^l W^{KK'}(0, l, l) Y_{lm}(\mathbf{w}) \bar{Y}_{K'lm}, \tag{14}$$

where

$$W^{KK'}(0, l, l) = \int dr\, r^2 W^{KK'}(r, 0, l, l) \Big/ v_{K'} \left(\frac{2l+1}{4\pi}\right)^{1/2}$$

$$\bar{Y}_{K'lm} = \int f_{K'}(\mathbf{w}) Y_{lm}(\mathbf{w}')\, d\mathbf{w}'$$

2.3. *Polymer-chain model*

We choose the model of a semirigid polymer [18] with bend elastic constant x_K, which is represented by an elastic line $\mathbf{r}_K(s)$; $\mathbf{w}_K(s) = \partial\mathbf{r}_K(s)/\partial s$ is the tangent to the curve at the point s from the origin of the chain, $\mathbf{w}_{K'}$ and $\mathbf{w}_{K''}$ being respectively the initial ($s = 0$) and final ($s = L_K$) orientations of the chain. The persistence length of the isolated chain is [18] $q_K = \beta x_K$ and the configurational probability is ($|\mathbf{w}_K(s)| = 1$)

$$P_K(\{\mathbf{r}(s)\}) = \exp\left\{- \tfrac{1}{2}\beta x_K \int_0^{L_K} ds \left[\frac{\partial^2 \mathbf{r}_K(s)}{\partial s^2}\right]^2\right\}. \tag{15}$$

The mean-field potential that corresponds to the intermolecular interactions will be taken to be of Maier–Saupe type (we limit the expansion in (14) to $l = 0, 2$ with $m = 0$ (symmetry of the nematic):

$$u_K(\mathbf{w}) = \beta \sum_{K'} X_{K'} [u_0^{KK'} - u_2^{KK'} P_2(\mathbf{w}) S_{K'}]. \tag{16}$$

$\beta u_l^{KK'} = [(2l + 1)/(4\pi)] |W^{KK'}(0, l, l)|$ represent the strength of the effective interactions, both isotropic repulsive ($l = 0$) and anisotropic attractive ($l = 2$). From (13), (16) and the use of the Green function, the order parameter and orientational distribution function are given by [47]

$$S_K = \int f_K(\mathbf{w}') P_2(\mathbf{w}')\, d\mathbf{w}' \tag{17}$$

$$f_K(\mathbf{w}) = \frac{1}{L_K Q_K} \int_0^{L_K} ds \int d\mathbf{w}'\, d\mathbf{w}''\, G_K(\mathbf{w}', \mathbf{w}; 0, s) G(\mathbf{w}, \mathbf{w}''; s, L_K), \tag{18}$$

$$Q_K = \int d\mathbf{w}'\, d\mathbf{w}''\, G_K(\mathbf{w}', \mathbf{w}''; 0, L_K),$$

$$G_K(\mathbf{w}', \mathbf{w}''; 0, L_K) = \int_{\mathbf{w}(0)=\mathbf{w}'}^{\mathbf{w}(L_K)=\mathbf{w}''} \delta(\mathbf{w}) \exp\left\{- \int_0^{L_K} ds \left[\tfrac{1}{2}\beta x_K \left(\frac{\partial \mathbf{w}}{\partial s}\right)^2 + u_K(\mathbf{w})\right]\right\}.$$

$G_K(\mathbf{w}', \mathbf{w}''; 0, L_K)$ is a solution of the Schrödinger-type equation [47, 51]

$$\left[\frac{\partial}{\partial s} - \frac{1}{2\beta x_K}\Delta_{\mathrm{w}} + u_K(\mathbf{w})\right] G_K(\mathbf{w}, \mathbf{w}'; 0, s) = \delta(s)\delta(\mathbf{w} - \mathbf{w}'). \tag{19}$$

Finally the free energy of mixing per site for a binary PLC mixture is given by (with $v_K = v$)

$$\begin{aligned} f_{\mathrm{M}} &= \frac{v\,\Delta\mathcal{F}}{VkT} \\ &= \frac{X}{L_{\mathrm{A}}}\ln X + \frac{1-X}{L_{\mathrm{B}}}\ln(1-X) - \frac{X}{L_{\mathrm{A}}}\ln z_{\mathrm{A}} - \frac{1-X}{L_{\mathrm{B}}}\ln z_{\mathrm{B}} + X(1-X)\chi_0 \\ &\quad + \tfrac{1}{2}X^2 u^{\mathrm{AA}} S_{\mathrm{A}}^2 + \tfrac{1}{2}(1-X)^2 u^{\mathrm{BB}} S_{\mathrm{B}}^2 + X(1-X)u^{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}} \\ &\quad + \text{terms linear in } X, \end{aligned} \tag{20}$$

where $\chi_0 = \beta(u_0^{\mathrm{AB}} - \frac{1}{2}u_0^{\mathrm{AA}} - \frac{1}{2}u_0^{\mathrm{BB}}) = \beta u_0$ is the isotropic interaction parameter (Flory), $u^{ij} = \beta u_2^{ij}$ are the anisotropic interaction parameters, X is the volume fraction of polymer $A(X = X_{\mathrm{A}}, 1 - X = X_{\mathrm{B}})$ and

$$Z_K = Q_K \exp\left(\beta L_K \sum_{K'} x_{K'} u_0^{KK'}\right).$$

Four types of terms are present: the entropy of mixing, the polymer configuration, the isotropic interaction and the anisotropic interactions.

A and B can be polymers or small molecules ($L_K = 1$), leading to mesomorphic phases or not ($u^{ii} = 0$). A polymer can be flexible ($q_K \ll 1$), semirigid or rod-like ($q_K \to \infty$) [52].

If we neglect isotropic interaction in the case $q_K \to \infty$, we can recover the case of an SMLC mixture [53]; while if the anisotropic interactions are neglected, we recover the Flory–Huggins model of polymer solutions [54].

3. Phase diagrams

To calculate the phase diagrams, we need expressions for the chemical potential $\mu = \partial f_M/\partial X$ and the pressure $\Pi = f_M - X\mu$ [40]. The respective equalities of the chemical potentials and the pressures in the phases in equilibrium, together with the equations giving the equilibrium order parameter, $\partial f_M/\partial S_K = 0$, in these phases solves the problem [40]; this requires numerical calculation (the derivation of the order parameter has been described in detail elsewhere [44, 47]). We can have three types of biphase isotropic/isotropic (I/I), isotropic/nematic (I/N) and nematic/nematic (N/N). The equations are

$$\mathrm{I/I}\ \begin{cases} \mu_{\mathrm{I}_1}(X_{\mathrm{I}_1}, T) = \mu_{\mathrm{I}_2}(X_{\mathrm{I}_2}, T), \\ \Pi_{\mathrm{I}_1}(X_{\mathrm{I}_1}, T) = \Pi_{\mathrm{I}_2}(X_{\mathrm{I}_2}, T), \\ S_K = 0; \end{cases} \tag{21a}$$

$$\mathrm{I/N}\ \begin{cases} \mu_{\mathrm{I}}(X_{\mathrm{I}}, T, 0, 0) = \mu_{\mathrm{N}}(X_{\mathrm{N}}, T, S_{\mathrm{A}}, S_{\mathrm{B}}), \\ \Pi_{\mathrm{I}}(X_{\mathrm{I}}, T, 0, 0) = \Pi_{\mathrm{N}}(X_{\mathrm{N}}, T, S_{\mathrm{A}}, S_{\mathrm{B}}), \\ \partial f_M/\partial S_K = 0; \end{cases} \tag{21b}$$

$$\text{N/N}\quad \left\{\begin{aligned} \mu_{\mathrm{N}_1}(X_{\mathrm{N}_1}, T, S^1_{\mathrm{A}}, S^1_{\mathrm{B}}) &= \mu_{\mathrm{N}_2}(X_{\mathrm{N}_2}, T, S^2_{\mathrm{A}}, S^2_{\mathrm{B}}),\\ \Pi_{\mathrm{N}_1}(X_{\mathrm{N}_1}, T, S^1_{\mathrm{A}}, S^1_{\mathrm{B}}) &= \Pi_{\mathrm{N}_2}(X_{\mathrm{N}_2}, T, S^2_{\mathrm{A}}, S^2_{\mathrm{B}}),\\ \partial f_M/\partial S^i_K &= 0,\ i = 1, 2. \end{aligned}\right. \tag{21c}$$

4. Spinodal curves

These are obtained by equating to zero the second derivative of the free energy with respect to the polymer volume fraction X, and give the region of instability of the phases. This leads to a fourth-order equation:

$$\begin{aligned} \frac{\partial^2 f_M}{\partial X^2} &= \frac{\partial \mu}{\partial X}\\ &= \frac{1}{X(1-X)\Delta}(aX^4 + bX^3 + cX^2 + dX + e)\\ &= 0, \end{aligned} \tag{22}$$

with a, b, c, d, e and Δ functions of all the molecular parameters, the order parameter and the temperature.

For the I/I biphase ($S_{\mathrm{A}} = S_{\mathrm{B}} = 0$) we recover the usual equation

$$2\chi_0 L_{\mathrm{A}} X^2 + \left(\frac{L_{\mathrm{A}}}{L_{\mathrm{B}}} - 1 - 2\chi_0 L_{\mathrm{A}}\right) X + 1 = 0,$$

and the critical point is given by [55]

$$\left.\begin{aligned} \chi_0 L_{\mathrm{Ac}} &= \frac{1}{2}\left[\left(\frac{L_{\mathrm{A}}}{L_{\mathrm{B}}}\right)^{1/2} + 1\right]^2,\\ X_{\mathrm{c}} &= \left[1 + \left(\frac{L_{\mathrm{A}}}{L_{\mathrm{B}}}\right)^{1/2}\right]^{-1}. \end{aligned}\right\} \tag{23}$$

For the I/N and N/N biphases we have the equation given above (22). If we ignore the isotropic interaction then $\chi_0 L_{\mathrm{A}} = 0$, and we have an equation of only third order ($a = 0$ in (22)).

5. Typical phase diagrams

In order to illustrate the above discussion, we shall consider two examples: two types of mixtures.

5.1. *A mesomorphic-polymer/non-mesomorphic-polymer mixture*

This includes solutions of an LCP in a solvent, which were the main subjects of previous work [46, 47]. We have $u^{BB} = 0$, and we choose a special case with $u^{AB} = 0$, i.e. no orientationally induced order in the non-mesomorphic component (no orientational correlation between A and B). The parameters are the ratio $L_{\mathrm{A}}/L_{\mathrm{B}}$ of the lengths of the two components, $\chi_0 L_{\mathrm{A}}$ (or $\chi_0 L_{\mathrm{B}}$) the isotropic interaction at a given temperature (here we choose the transition temperature T_{t} of the pure LCP A) and the ratio $L_{\mathrm{A}}/q_{\mathrm{A}}$ of the length to the persistence length of the LCP, which characterizes the relative rigidity of the polymer.

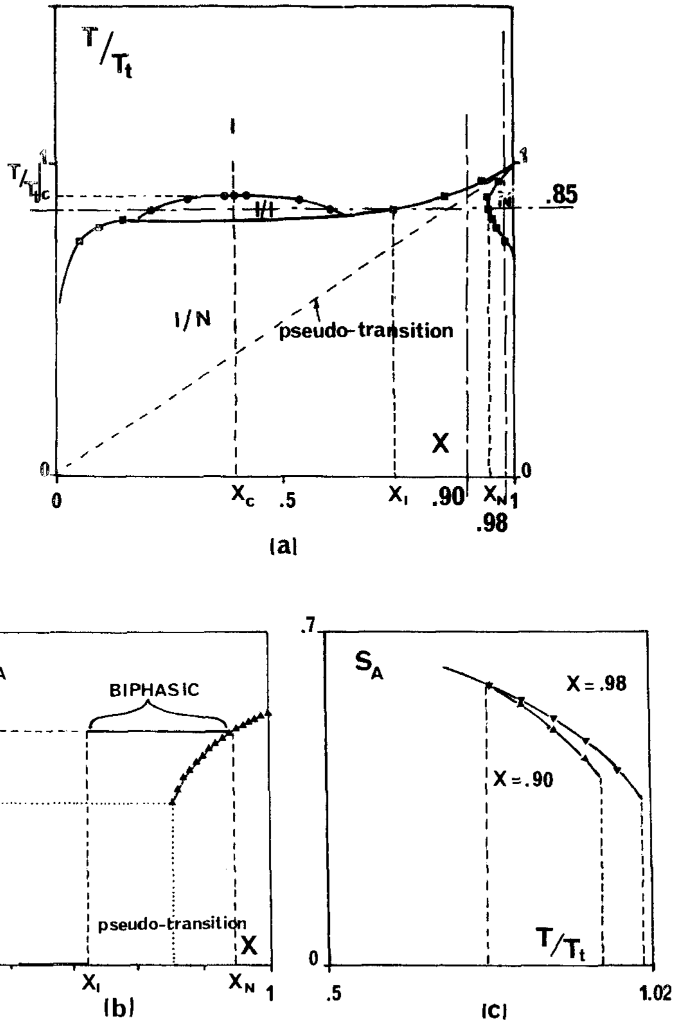

Figure 1. Mesomorphic-A/non-mesomorphic-B mixture; $L_A/q_A = 2\cdot5$, $L_A/L_B = 2\cdot5$, $\chi_0 \cdot L_A = 3$. (*a*) Phase diagram. (*b*) Order parameter at $T/T_t = 0\cdot85$ as a function of volume fraction X. (*c*) Order parameter at $X = 0\cdot98$ and $0\cdot90$ as a function of reduced temperature T/T_t.

Figure 1 (*a*) shows the phase diagram, as a plot of the reduced temperature T/T_t versus the volume fraction X of the LCP A for $L_A/q_A = 2\cdot5$, $L_A/L_B = 2\cdot5$ and $\chi_0 L_A(T_t) = 3$. We do not need the value of the anisotropic interaction because the L_A/q_A value fixes its value at the transition temperature T_t in the melt [47] and we use the reduced temperature. In this example the critical point obtained from (23), $\chi_0 L_{Ac} = 3\cdot3311$ and $X_c = 0\cdot3874$, corresponds to a reduced temperature $T/T_{tc} \approx 0\cdot90$. We can see an I/I biphasic area together with a large I/A biphasic region. The pseudo-transition [56] is also shown. We can see the evolution of the order parameter of the polymer A at a fixed reduced temperature ($T/T_t = 0\cdot85$) as a function of volume fraction X (figure 1 (*b*)) and at fixed volume fractions ($X = 0\cdot98$ and $0\cdot95$) as a function of reduced temperature (figure 1 (*c*)). The order parameter is nearly one and a half times greater in the biphase as at the pseudo-transition. This may explain

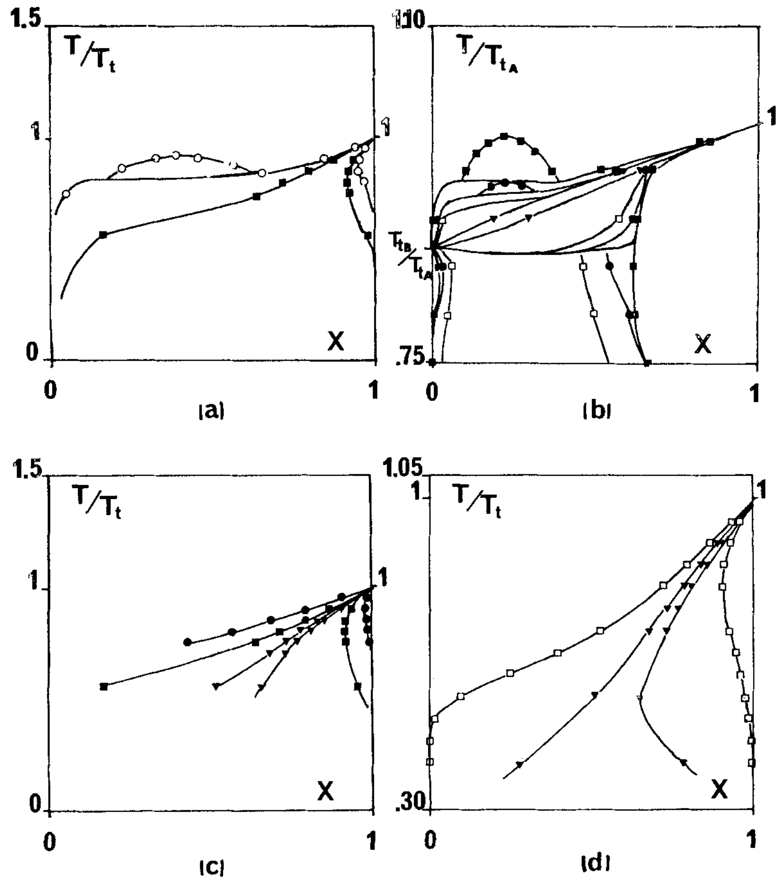

Figure 2. Influence of the molecular parameters on the phase diagram of a mesomorphic-A/non-mesomorphic-B mixture: (*a*) fixed $L_A/q_A = 2{\cdot}5$, $L_A/L_B = 2{\cdot}5$ and $\chi_0 L_A = 3$ (○), 0 (■); (*c*) fixed $L_A/q_A = 2{\cdot}5$, $\chi_0 L_A = 0$ and $L_A/L_B = 1$ (●), 2·5 (■), 10 (▼); (*d*) fixed $L_A/L_B = 10$, $\chi_0 L_A = 0$ and $L_A/q_A = 10$ (□), 2·5 (▼). (*b*) Phase diagram of a mesomorphic-A/mesomorphic-B mixture; fixed $L_A/q_A = 32{\cdot}7$, $L_B/q_B = 2{\cdot}5$, $L_A/L_B = 13{\cdot}08$, $u_2^{AA} = u_2^{BB} = u_2^{AB}$ and $\chi_0 L_A = 10{\cdot}5$ (■), 10 (●), 9 (□), 0, (▼).

certain discrepancies that have been found between experiment and theory. Figure 2 shows the influence of the various parameters, $\chi_0 L_A$ (figure 2(*a*)), L_A/L_B (figure 2(*c*)) and L_A/q_A (figure 2(*d*)). The biphasic area increases with increasing isotropic interaction, decreasing ratio of the length of the mesomorphic component to that of the flexible one, and decreasing of rigidity (increasing L_A/q_A). This is in agreement with experiment and our knowledge of polymers where large steric repulsions give rise to a wide region of phase separation, and a mixture of two polymers give rise to a larger biphasic area than a polymer/solvent one. Figure 3 shows the spinodal curves related to the phase diagram of figure 1(*a*). We can see an unusual branch, which is related to the anisotropic part of the free energy (the 'limit' line corresponds to the limit of existence of this anisotropic part of the free energy).

5.2. *A two LCP mixture*

The number of parameters is now increased; we need the same parameters as above together with L_B/q_B, u_2^{BB}/u_2^{AA} and u_2^{AB}. We only consider the case where

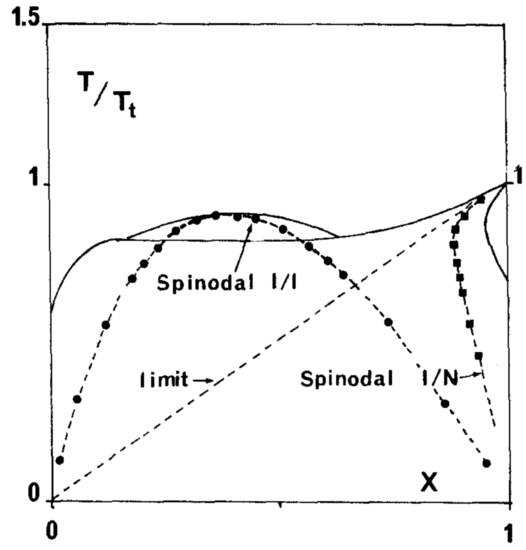

Figure 3. Spinodal curves for the mixture of figure 1.

$(u_2^{AB})^2 = u_2^{AA} u_2^{BB}$ (the orientational interaction between the two species is the geometric mean of the interaction of each component).

Figure 4 shows the phase diagram (*a*) in reduced units (T/T_{tA} as a function of the volume fraction X of A, T_{tA} being the transition temperature of the pure LCP A), and the variations of the order parameters of the two components A and B as functions of volume fraction X at two values of the reduced temperature: 0·90 (*b*) (in the I/N biphasic) and 0·85 (*c*) (in the N/N biphasic). The parameters are $L_A/q_A = 32{\cdot}7$, $L_B/q_B = 2{\cdot}5$, $L_A/L_B = 13{\cdot}08$, $\chi_0 L_A(T_{tA}) = 10{\cdot}5$ and $u^{BB}/u^{AA} = 1$. Then $\chi_0 L_{Ac} = 10{\cdot}6566$ and $X_c = 0{\cdot}2166$, which corresponds to $T/T_{tAc} = 0{\cdot}985$. We see the existence of I/I, I/N and N/N biphases. In the N/N area we see coexistence of two nematic phases, with two different order parameters for each component. Figure 2(*b*) shows the influence of the isotropic interaction parameter, which causes all the biphasic areas to grow as it increases—which is to be expected.

6. Conclusions

The theory presented here takes into account the influence of semirigidity of polymer chains and interactions (isotropic and anisotropic). The persistence length, and so the semirigidity of the polymers, are parameters that can be estimated quite easily, for example through intrinsic viscosity measurements [57, 58] and the use of Yamakawa's theory for worm-like chains [59]. For a thermotropic particle the anisotropic interaction parameter can be obtained from the experimental transition temperature of the pure melt [47]. We have shown examples of phase diagrams and order parameters associated with I/I, I/N and N/N biphasic regions. The present theory includes theories of flexible polymers and SMLC mixtures as limiting cases.

Further publications will include systematic studies of mesomorphic/non-mesomorphic mixtures and mesomorphic/mesomorphic ones. Special attention will be given to the influence of the parameters on the shape of the phase diagram. The spinodal curves will also be refined. Applications to real polymer mixtures, including

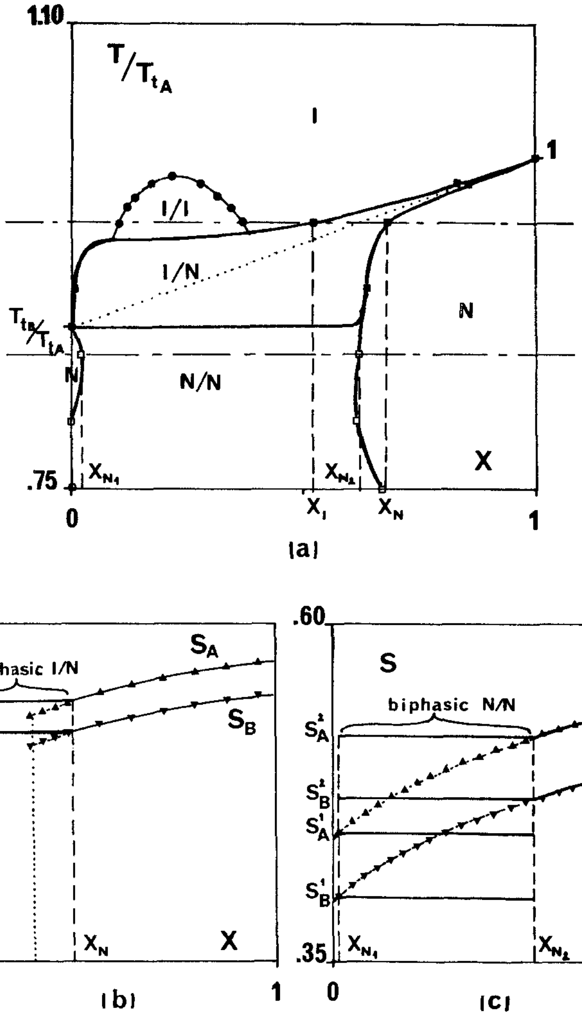

Figure 4. Mesomorphic-A/mesomorphic-B mixture; $L_A/q_A = 32{\cdot}7$, $L_B/q_B = 2{\cdot}5$, $L_A/L_B = 13{\cdot}08$, χ_0. $L_A = 10{\cdot}5$, $u_2^{AA} = u_2^{BB} = u_2^{AB}$: phase diagram (*a*); and order parameters at fixed reduced temperature $T/T_{tA} = 0{\cdot}95$ (*b*) and $0{\cdot}85$ (*c*) versus volume fraction X of polymer A.

comparisons with experimental data, will also be investigated. Multicomponent systems (e.g. ternary systems [60–63], which constitute a wide class of practical interest, since mixture of only two polymers is often impossible and needs the use of a third component, a solvent) will also be treated using this model.

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