Ternary mixtures of mesomorphic polymers

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The theory of ternary mixtures of mesomorphic semi-rigid polymers is reviewed. Polymer chains are modelled as elastic lines (with bend curvature) and a density functional method is used to construct a general expression for free energy of mixing which includes terms representing the entropy of mixing, the entropy of chain configuration and the mean field through pairwise interaction potentials. Expressions for the chemical potentials are derived and numerical methods used to compute phase diagrams for a specific mixture, the mesomorphic semi-rigid polymer1/solvent2/solvent3 system.

(Keywords: phase diagram; liquid crystal; semi-rigid chain; order parameter; density functional expansion)

INTRODUCTION

Over the last 20 years, many studies, both theoretical and experimental, have been made of polymers. The studies had two main interests: blends[1–3] and mesomorphic liquid crystal polymers[4–6]. One of their aims was to design polymers with specific properties for industrial applications.

Liquid crystal polymers exhibit different kinds of mesomorphic phase (nematic, cholesteric and smectic phases)[7]. We are interested here with those giving nematic phases only. To study these polymers, we need to model polymer chains. Several models have been used previously: rods to model rigid chains[8], rods connected by flexible spacers, wormlike chains[9] to model semi-rigid polymers, etc. For this study on phase diagrams of semi-rigid liquid crystal polymers, we chose the elastic line model.

Theoretical studies began as early as the 1940s on rigid rod polymers. Onsager[10] developed a virial equation explaining the occurrence of phase separation between an isotropic and an anisotropic phase in a system of rigid rods in a solvent. Flory and Huggins independently used the lattice model to study polymer chains and their studies gave rise to the well known Flory–Huggins thermodynamic equations[11,12]. Using such equations, Flory has shown that a phase transition can occur in systems consisting of rigid rods or semi-flexible chains[8] in a solvent. Flory and co-workers[13–19] applied this theory to multicomponent systems, to chains with some flexibility and to systems with a mass distribution (polydisperse). In this approach, at first only a repulsive interaction between particles was used. Attractive terms were introduced more recently.

Authors such as Khoklov, Semenov and Odijk[20,21] have used the Onsager theory to study lyotropic systems with different mechanisms of flexibility. This is related to the fact that real polymer chains are in general semi-rigid rather than rigid.

Recently, a density functional method was used to study thermodynamic properties of a space curve in which only positional degrees of freedom were taken into account[22].

In the present authors' laboratory, the functional method has been used to study the same thermodynamic properties as earlier, but orientational interactions were also taken into account. This resulted in a general expression for the free energy of mixing, which was used to study lyotropic liquid crystal polymers[23–26], mixtures of a liquid crystal polymer and a non-mesomorphic polymer and mixtures of two liquid crystal polymers[26].

In this paper, we extend these studies to ternary mixtures. The model used is summarized and the free energy of mixing is calculated for a general three-component mixture. The chemical potentials and equations which must be resolved numerically to obtain phase diagrams are derived. An example is given of a phase diagram for a specific ternary system (polymer–solvent–solvent).

CHAIN MODEL

We describe a semi-rigid polymer as an elastic curve with bend elastic constant κ and length L. We define the position and orientation at contour length 0, s and L from the origin of the chain by $(\mathbf{r}', \mathbf{w})$, $(\mathbf{r}, \mathbf{w})$ and $(\mathbf{r}'', \mathbf{w}'')$, respectively, with $\mathbf{w} = d\mathbf{r}/ds$ and $|\mathbf{w}| = 1$. The associated elastic energy of a chain is[25]

$$\frac{1}{2}\kappa \int_0^L \left(\frac{\partial \mathbf{w}}{\partial s}\right)^2 ds$$

Saito *et al.*[27] used such a model to calculate some configurational properties (such as $\langle R^2 \rangle$ and $\langle R^4 \rangle$) and obtained for the quadratic mean square end to end distance $\langle R^2 \rangle$ the expression

$$\langle R^2 \rangle = 2(\beta\kappa)L\{1 - (\beta\kappa)/L[1 - \exp(-L/\beta\kappa)]\} \quad (1)$$

which is the same as the wormlike chain expression[9] with persistence length $q = \beta\kappa$ ($\beta^{-1} = k_B T$, where k_B is the Boltzmann constant).

FREE ENERGY OF MIXING

All the developments below are a generalization to ternary mixtures of calculations given previously for binary mixtures[23–26].

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A general expression for the partition function of a ternary semi-rigid polymer mixture is

$$Z=\left[\prod_{\mathrm{K}}\frac{Z_{\mathrm{K}}^{\tilde{N}_{\mathrm{K}}}}{\tilde{N}_{\mathrm{K}}!}\right]\int\prod_{\mathrm{K}}\prod_{j=1}^{\tilde{N}_{\mathrm{K}}}\delta r_j(s)P_{\mathrm{K}}[\boldsymbol{r}_{\mathrm{K}}(s)]\exp\{-\beta V[\boldsymbol{r}_{\mathrm{K}}(s)]\}\tag{2}$$

The first term on the right-hand side gives the kinetic energy contribution to the partition function, where K denotes the polymer species. Integration is over all space curves $r_{\mathrm{K}}(s)$. The products are over all monomers (j) and polymer species (K). For a given component K,

$$P_{\mathrm{K}}[\boldsymbol{r}_{\mathrm{K}}(s)]=\exp\left[-\frac{\kappa}{2k_{\mathrm{B}}T}\int_0^{L_{\mathrm{K}}}\mathrm{d}s\left(\frac{\partial^2\boldsymbol{r}_{\mathrm{K}}(s)}{\partial s^2}\right)^2\right]$$

represents the configurational probability for an individual particle, N_{K} is the number of monomers and $\tilde{N}_{\mathrm{K}}=N_{\mathrm{K}}/L_{\mathrm{K}}$ is the number of chains, where L_{K} is the degree of polymerization (*DP*).

The interaction between different chains, $V\{\boldsymbol{r}_{\mathrm{K}}(s)\}$, is given by

$$\begin{aligned}V[\boldsymbol{r}_{\mathrm{K}}(s)]={}&\frac{1}{2}\sum_{\mathrm{a,a'}}\int_0^{L_{\mathrm{a}}}\mathrm{d}s\int_0^{L_{\mathrm{a'}}}\mathrm{d}s'V_{\mathrm{aa'}}[\boldsymbol{r}_{\mathrm{a}}(s)-\boldsymbol{r}_{\mathrm{a'}}(s')]\\&+\frac{1}{2}\sum_{\mathrm{b,b'}}\int_0^{L_{\mathrm{b}}}\mathrm{d}s\int_0^{L_{\mathrm{b'}}}\mathrm{d}s'V_{\mathrm{bb'}}[\boldsymbol{r}_{\mathrm{b}}(s)-\boldsymbol{r}_{\mathrm{b'}}(s')]\\&+\frac{1}{2}\sum_{\mathrm{c,c'}}\int_0^{L_{\mathrm{c}}}\mathrm{d}s\int_0^{L_{\mathrm{c'}}}\mathrm{d}s'V_{\mathrm{cc'}}[\boldsymbol{r}_{\mathrm{c}}(s)-\boldsymbol{r}_{\mathrm{c'}}(s')]\\&+\sum_{\mathrm{a,b}}\int_0^{L_{\mathrm{a}}}\mathrm{d}s\int_0^{L_{\mathrm{b}}}\mathrm{d}s'V_{\mathrm{ab}}[\boldsymbol{r}_{\mathrm{a}}(s)-\boldsymbol{r}_{\mathrm{b}}(s')]\\&+\sum_{\mathrm{a,c}}\int_0^{L_{\mathrm{a}}}\mathrm{d}s\int_0^{L_{\mathrm{c}}}\mathrm{d}s'V_{\mathrm{ac}}[\boldsymbol{r}_{\mathrm{a}}(s)-\boldsymbol{r}_{\mathrm{c}}(s')]\\&+\sum_{\mathrm{b,c}}\int_0^{L_{\mathrm{b}}}\mathrm{d}s\int_0^{L_{\mathrm{c}}}\mathrm{d}s'V_{\mathrm{bc}}[\boldsymbol{r}_{\mathrm{b}}(s)-\boldsymbol{r}_{\mathrm{c}}(s')]\end{aligned}\tag{3}$$

which is the sum of interactions between chains of the same nature (intrapolymer interaction) and interactions between chains of different species (interpolymer interaction). These interactions are position and orientation dependent. We consider only two-body interactions. $V_{\mathrm{KK'}}$ is the density of the interaction between K and K′.

After Hong and Noolandi[22] we introduce the microscopic density of particles at point $\boldsymbol{r}$ with orientation $\boldsymbol{w}$:

$$\hat{\rho}_K(\boldsymbol{r},\boldsymbol{w})=\sum_{K=1}^{\tilde{N}_{\mathrm{K}}}\int_0^{L_{\mathrm{K}}}\mathrm{d}s\,\delta\{\boldsymbol{r}-\boldsymbol{r}(s)\}\,\delta\{\boldsymbol{w}-\boldsymbol{w}(s)\}\tag{4}$$

with $\boldsymbol{w}(s)=\partial r(s)/\partial s$ the orientation of the space curve at point s, $|\boldsymbol{w}(s)|=1$. We rewrite the exponential in equation (2) as follows:

$$\begin{aligned}\exp\{-\beta V[\boldsymbol{r}_{\mathrm{K}}(s)]\}={}&\int\prod_{\mathrm{K}}\rho_{\mathrm{K}}\prod_{\mathrm{K}}\\&\times\delta(\rho_{\mathrm{K}}-\hat{\rho}_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w}))\exp\{-\beta W[r_{\mathrm{K}}(s)]\}\end{aligned}\tag{5}$$

$$\begin{aligned}W\{\boldsymbol{r}_{\mathrm{K}}(s)\}={}&\frac{1}{2}\sum_{\mathrm{KK'}}\int\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\,\mathrm{d}\boldsymbol{w}\,\mathrm{d}\boldsymbol{w}'\\&\times\rho_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})w_{\mathrm{KK'}}(\boldsymbol{r},\boldsymbol{w}\boldsymbol{r}',\boldsymbol{w}')\rho_{\mathrm{K}}(\boldsymbol{r}',\boldsymbol{w}')\end{aligned}\tag{6}$$

Using the integral representation of the Dirac function, we have[22]

$$\begin{aligned}\delta(\rho_{\mathrm{K}}-\hat{\rho}_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w}))={}&\alpha\int\delta u_{\mathrm{K}}\\&\times\exp\left\{\int\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{w}\,u_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})[\rho_{\mathrm{K}}-\hat{\rho}_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})]\right\}\end{aligned}\tag{7}$$

where α is the normalizing factor. Then

$$\begin{aligned}\mathrm{e}^{-\beta V}={}&\alpha\int\prod_{\mathrm{K}}\delta\rho_{\mathrm{K}}\,\delta u_{\mathrm{K}}\\&\times\exp\left\{\sum_{\mathrm{K}}\int\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{w}\,u_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})[\rho_{\mathrm{K}}-\hat{\rho}_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})]-\beta W\right\}\end{aligned}\tag{8}$$

Using these equations, we rewrite the partition function of equation (2) as

$$\begin{aligned}Z={}&\alpha\left(\prod_{\mathrm{K}}\frac{Z_{\mathrm{K}}^{\tilde{N}_{\mathrm{K}}}}{\tilde{N}_{\mathrm{K}}!}\right)\int\prod_{\mathrm{K}}\delta\rho_{\mathrm{K}}\,\delta u_{\mathrm{K}}\prod_{\mathrm{K}}Q_{\mathrm{K}}^{\tilde{N}_{\mathrm{K}}}\\&\times\exp\left[\sum_{\mathrm{K}}\int\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{w}\,u_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})\rho_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})\right]\exp(-\beta W)\end{aligned}\tag{9}$$

where

$$Q_{\mathrm{K}}=\int\delta\boldsymbol{r}\,\delta\boldsymbol{w}\,P_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})\exp\left[-\int_0^{L_{\mathrm{k}}}\mathrm{d}s\,u_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})\right]\tag{10}$$

represents the configuration of a given component, with

$$P_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})=\exp\left[-\frac{\beta\kappa}{2}\int_0^{L_{\mathrm{K}}}\mathrm{d}s\left(\frac{\partial w}{\partial s}\right)^2\right]\delta\{\boldsymbol{w}-\boldsymbol{w}(s)\}$$

for a semi-rigid polymer chain. ρ_{K} and u_{K} are here independent variables representing, respectively, the particle density and the mean field.

The partition function can then be given by the expression

$$Z=\alpha\int\prod_{\mathrm{K}}\delta\rho_{\mathrm{K}}\,\delta u_{\mathrm{K}}\exp(-\beta\mathscr{F}\{\rho_{\mathrm{K}},u_{\mathrm{K}}\})\tag{11}$$

with $\mathscr{F}\{\rho_{\mathrm{K}},u_{\mathrm{K}}\}$ representing the functional of the free energy. Using the Stirling formula and neglecting the kinetic energy contribution terms, we obtain

$$\begin{aligned}\beta\mathscr{F}\{\rho_{\mathrm{K}},u_{\mathrm{K}}\}={}&\sum_{\mathrm{K}}\frac{N_{\mathrm{K}}}{L_{\mathrm{K}}}\left(\ln\frac{N_{\mathrm{K}}}{L_{\mathrm{K}}}-1\right)-\sum_{\mathrm{K}}\frac{N_{\mathrm{K}}}{L_{\mathrm{K}}}\ln(Q_{\mathrm{K}})\\&-\sum_{\mathrm{K}}\int\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{w}\,\rho_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})u_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})+\beta W\end{aligned}\tag{12}$$

Minimizing this functional with respect to ρ_{K} and u_{K} leads to

$$\begin{aligned}u_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})&=\beta\frac{\delta W}{\delta\rho_{\mathrm{K}}}\\\rho_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})&=-\frac{N_{\mathrm{K}}}{L_{\mathrm{K}}Q_{\mathrm{K}}}\frac{\delta Q_{\mathrm{K}}}{\delta u_{\mathrm{K}}}\end{aligned}\tag{13}$$

We obtain, using equation (13), the following expression for the density and mean field at equilibrium:

$$\begin{aligned}\rho_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})={}&-\frac{N_{\mathrm{K}}}{L_{\mathrm{K}}Q_{\mathrm{K}}}\int_0^{L_{\mathrm{K}}}\mathrm{d}s\,\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{w}\,P_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})\\&\times\exp\left\{-\left[\int_0^{L_{\mathrm{K}}}\mathrm{d}s\,u_{\mathrm{K}}(\boldsymbol{r},\boldsymbol{w})\right]\right\}\end{aligned}\tag{14a}$$

$$u_{\mathrm{K}}(\boldsymbol{r}, \boldsymbol{w}) = \sum_{\mathrm{K}'} \int \mathrm{d}\boldsymbol{r}'\, \mathrm{d}\boldsymbol{w}'\, W_{\mathrm{K,K}'}(\boldsymbol{r}, \boldsymbol{r}', \boldsymbol{w}, \boldsymbol{w}')\rho_{\mathrm{K}'}(\boldsymbol{r}', \boldsymbol{w}') \quad (14\mathrm{b})$$

which are coupled equations. By inserting equation (14) into equation (13) we obtain the expression for the free energy. The free energy of mixing is given by

$$\beta\Delta\mathscr{F} = \beta\left[\mathscr{F}\{\rho_{\mathrm{K}}, u_{\mathrm{K}}\} - \sum_{\mathrm{K}} \frac{N_{\mathrm{K}}}{N_{\mathrm{K}}^0} \mathscr{F}\{\rho_{\mathrm{K}}^0, u_{\mathrm{K}}^0\}\right]$$

with $\beta\mathscr{F}\{\rho_{\mathrm{K}}^0, u_{\mathrm{K}}^0\}$ the free energy for pure materials.

From now on, we are interested only in homogeneous systems. To compute the free energy of mixing, we need to make some hypotheses:

(1) The two-particle interaction can be expanded in spherical harmonics (as was done by Nakagawa and Akahane[28]):

$$W_{\mathrm{K,K}'}(\boldsymbol{r}, \boldsymbol{r}', \boldsymbol{w}, \boldsymbol{w}') = \sum_{\substack{l,l_1,l_2\\ m,m_1,m_2}} C(ll_1l_2mm_1m_2) \times Y_l^m\left(\frac{|\boldsymbol{r}-\boldsymbol{r}'|}{\|\boldsymbol{r}-\boldsymbol{r}'\|}\right) Y_{l_1}^{m_1}(\boldsymbol{w}) Y_{l_2}^{m_2}(\boldsymbol{w}') \times W_{\mathrm{K,K}'}(|\boldsymbol{r}-\boldsymbol{r}'|, ll_1l_2) \quad (15)$$

where $Y_{l,m}(\boldsymbol{w}')$ are spherical harmonics and $C(ll_1l_2mm_1m_2)$ are Clebsh–Gordon coefficients.

(2) The density distribution depends on the orientation alone, so that $\rho_{\mathrm{K}}(\boldsymbol{r}, \boldsymbol{w}) = n_{\mathrm{K}} f_{\mathrm{K}}(\boldsymbol{w})$, where n_{K} is the number density of component K and $f_{\mathrm{K}}(\boldsymbol{w})$ is the orientational distribution function.

(3) The partial volume is the same for all species, $v_{\mathrm{K}} = v = V/N_{\mathrm{K}}$, and there is no volume change on mixing.

We introduce the volume concentration of each component as $\phi_{\mathrm{K}} = N_{\mathrm{K}}/N_{\mathrm{K}}^0$, with $\sum \phi_{\mathrm{K}} = 1$. With these assumptions, we have for the mean field potential (equation (14b)) the expression

$$u_{\mathrm{K}}(\boldsymbol{w}) = \beta \sum_{\mathrm{K}'} \{\phi'_{\mathrm{K}'}[V_{\mathrm{KK}'}(0) + V_{\mathrm{KK}'}(2)S_{\mathrm{K}'}P_2(\boldsymbol{w})]\} \quad (16)$$

We use summation over even l only (symmetry of the nematic) and choose to limit the expansion to $l = 0, 2$ to take a Maier–Saupe type potential.

The interaction parameters of each component are represented by

$$V_{\mathrm{KK}'}(l) = \frac{1}{v} \int \boldsymbol{r}^2\, \mathrm{d}\boldsymbol{r} W_{\mathrm{KK}'}(r, 0ll)\left(\frac{2l+1}{4\pi}\right)^{1/2}$$

(assuming the integrability of $W_{\mathrm{KK}'}(r, 0ll)$ and the order parameters by

$$S_{\mathrm{K}'} = \int \mathrm{d}\boldsymbol{w}' P_2(\boldsymbol{w}') f_{\mathrm{K}'}(\boldsymbol{w}')$$

The free energy of mixing per site for a ternary mixture becomes

$$\begin{aligned}\beta\Delta F = \beta \frac{\Delta\mathscr{F}}{V} v = {} & \frac{\Phi_1}{L_1} \ln \Phi_1 + \frac{\Phi_2}{L_2} \ln \Phi_2 + \frac{\Phi_3}{L_3} \ln \Phi_3 \\ & - \frac{\Phi_1}{L_1} \ln \mathscr{J}_1 - \frac{\Phi_2}{L_2} \ln \mathscr{J}_2 - \frac{\Phi_3}{L_3} \ln \mathscr{J}_3 \\ & - \frac{1}{2} \Phi_1^2 u_{11}(2)S_1^2 - \frac{1}{2} \Phi_2^2 u_{22}(2)S_2^2 - \frac{1}{2} \Phi_3^2 u_{33}(2)S_3^2 \\ & - \Phi_1\Phi_2 u_{12}(2)S_1S_2 - \Phi_1\Phi_3 u_{13}(2)S_1S_3 \\ & - \Phi_2\Phi_3 u_{23}(2)S_2S_3 + \Phi_1\Phi_2\chi_{12} \\ & + \Phi_1\Phi_3\chi_{13} + \Phi_2\Phi_3\chi_{23} \end{aligned} \quad (17)$$

where $\chi_{\mathrm{KK}'} = u_{\mathrm{KK}'}(0) - \frac{1}{2}[u_{\mathrm{KK}}(0) + u_{\mathrm{K'K'}}(0)]$ are the steric interaction parameters, as in Flory–Huggins theory, $u_{\mathrm{KK}'} = \beta V_{\mathrm{KK}'}$

$$\mathscr{J}_{\mathrm{K}} = \int \mathrm{d}\boldsymbol{w}\, \mathrm{d}\boldsymbol{w}'\, g_{\mathrm{K}}(\boldsymbol{w}, \boldsymbol{w}', L_{\mathrm{K}})$$

is the orientational partition function and

$$g_{\mathrm{K}}(\boldsymbol{w}, \boldsymbol{w}', L_{\mathrm{K}}) = \int \delta\boldsymbol{w} \exp\left\{-\beta \int_0^{L_{\mathrm{K}}} \mathrm{d}s\left[\frac{\kappa}{2}\left(\frac{\partial\boldsymbol{w}}{\partial s}\right)^2 + \sum_{\mathrm{K}'} \Phi_{\mathrm{K}'} V_{\mathrm{KK}'}(2)S_{\mathrm{K}'}P_2(\boldsymbol{w})\right]\right\} \quad (18)$$

$g_{\mathrm{K}}(\boldsymbol{w}, \boldsymbol{w}', L_{\mathrm{K}})$ represents the probability of finding a chain with orientations $\boldsymbol{w}(s=0)$ and $\boldsymbol{w}'(s = L_{\mathrm{K}})$ and solves the equations[29]

$$\left[\frac{\partial}{\partial L_{\mathrm{K}}} - \frac{1}{2\beta\kappa} \Delta_{\mathrm{w}} + u(K')P_2(\boldsymbol{w})\right] g_{\mathrm{K}}(\boldsymbol{w}, \boldsymbol{w}', L_{\mathrm{K}}) = \delta(L_{\mathrm{K}})\delta(\boldsymbol{w} - \boldsymbol{w}') \quad (19)$$

$$u(K') = \beta \sum_{\mathrm{K}} \Phi_{\mathrm{K}'} V_{\mathrm{KK}'}(2)S_{\mathrm{K}'}$$

where $K, K' = 1, 2, 3$. Note that the case $u_{\mathrm{KK}'}(2) = 0$ and $\mathscr{J}_{\mathrm{K}} = \mathrm{Cte}$ corresponds to the well known Flory–Huggins model for a ternary mixture[12].

If $\phi_3 = 0$, then

$$\begin{aligned}\beta\Delta F = {} & \frac{\Phi}{L_1} \ln \Phi + \frac{(1-\Phi)}{L_2} \ln(1-\Phi) - \frac{\Phi}{L_1} \ln \mathscr{J}_1 \\ & - \frac{(1-\Phi)}{L_2} \ln \mathscr{J}_2 - \frac{1}{2} \Phi^2 u_{11}(2)S_1^2 \\ & - \frac{1}{2} (1-\Phi)^2 u_{22}(2)S_2^2 - \Phi(1-\Phi)u_{12}(2)S_1S_2 \\ & + \Phi(1-\Phi)\chi_{12} \end{aligned} \quad (20)$$

which is the general expression for the free energy of mixing in the binary case[26] and which can be compared with that proposed by Brochard *et al.*[30].

PHASE DIAGRAMS

The phase diagrams are obtained through the calculation of the chemical potentials of the different polymers in the different phases. Instead of the chemical potentials, we will use the following quantities:

$$\mu_1^0 = \beta \frac{\partial\Delta F}{\partial\phi_1} \qquad \mu_2^0 = \beta \frac{\partial\Delta F}{\partial\phi_2} \qquad \Pi = \beta\Delta F - \phi_1\mu_1^0 - \phi_2\mu_2^0$$

which are related to the chemical potential by

$$\mu_1^{\mathrm{ch}} = L_1(\Pi + \mu_1^0) \qquad \mu_2^{\mathrm{ch}} = L_2(\Pi + \mu_2^0) \qquad \mu_3^{\mathrm{ch}} = L_3(\Pi)$$

We take as independent variables ϕ_1 and ϕ_2 ($\phi_3 = 1 - \phi_1 - \phi_2$) and obtain

$$\mu_1^0 = \frac{\ln \phi_1}{L_1} + \left(\frac{1}{L_1} - \frac{1}{L_3}\right) - \frac{\ln \phi_3}{L_3} - \frac{\ln \mathscr{J}_1}{L_1} + \frac{\ln \mathscr{J}_3}{L_3} + \phi_2(\chi_{12} - \chi_{23}) + (\phi_3 - \phi_1)\chi_{13} \quad (21)$$

$$\mu_2^0 = \frac{\ln \phi_2}{L_2} + \left(\frac{1}{L_2} - \frac{1}{L_3}\right) - \frac{\ln \phi_3}{L_3} - \frac{\ln \mathcal{J}_2}{L_2} + \frac{\ln \mathcal{J}_3}{L_3} + \phi_1(\chi_{12} - \chi_{13}) + (\phi_3 - \phi_2)\chi_{23} \tag{22}$$

$$\Pi = \frac{\ln \phi_3}{L_3} - \frac{\ln \mathcal{J}_3}{L_3} - \frac{\phi_1}{L_1} - \frac{\phi_2}{L_2} + \frac{1 - \phi_3}{L_3} - \frac{1}{2} u_{11}(2) S_1^2 \phi_1^2 - \frac{1}{2} u_{22}(2) S_2^2 \phi_2^2 - \frac{1}{2} u_{33}(2) S_3^2 \phi_3^2 - \phi_1 \phi_2 u_{12}(2) S_1 S_2 - \phi_1 \phi_3 u_{13}(2) S_1 S_3 - \phi_2 \phi_3 u_{23}(2) S_2 S_3 + (\phi_1 + \phi_2)(\phi_1 \chi_{13} + \phi_2 \chi_{23}) - \phi_1 \phi_2 \chi_{12} \tag{23}$$

The equalities of these quantities in the different phases in equilibrium, together with the equilibrium value of the order parameter ($\partial \Delta F / \partial S_K = 0$), solve the problem and require numerical calculation. Thus we can obtain equations for the various types of biphasic equilibrium: isotropic–isotropic biphase

$$\mu_K^0(\mathrm{I}) = \mu_K'^0(\mathrm{I}) \qquad \Pi(\mathrm{I}) = \Pi'(\mathrm{I})$$

where I = isotrope, K = 1, 2; isotropic–nematic biphase

$$\mu_K^0(\mathrm{I}) = \mu_K^0(\mathrm{N}) \qquad \Pi(\mathrm{I}) = \Pi(\mathrm{N})$$

where N = nematic; nematic–nematic biphase

$$\mu_K^0(\mathrm{N}) = \mu_K'^0(\mathrm{N}) \qquad \Pi(\mathrm{N}) = \Pi'(\mathrm{N})$$

Similarly, we can look for the possible existence of triphasic zones.

ILLUSTRATION OF THE THEORY

We focus our attention on a semi-rigid mesomorphic polymer (length L_1, persistence length q_1) in a mixture of two solvents. Orientational correlation between the polymer and the solvents is not considered (1 = polymer; 2, 3 = solvents).

The expression for the free energy of mixing per site becomes

$$\beta \Delta F = \frac{\phi_1}{L_1} \ln \phi_1 + \frac{\phi_2}{L_2} \ln \phi_2 + \frac{\phi_3}{L_3} \ln \phi_3 - \frac{\phi_1}{L_1} \ln \mathcal{J}_1 - \frac{1}{2} \phi_1^2 u_{11}(2) S_1^2 + \phi_1 \phi_2 \chi_{12} + \phi_1 \phi_3 \chi_{13} + \phi_2 \phi_3 \chi_{23} \tag{24}$$

To illustrate the phase diagrams, we start first with the simplest case where the two solvents have the same geometrical dimensions ($L_2 = L_3 = 1$). We take $L_1 = 2.5$, so the critical values of the isotropic interactions are $\chi_{12c} = \chi_{13c} = 1.3$ and $\chi_{23c} = 2$. We use, as usual[26]

$$\chi_{ijc} = \frac{1}{2}[L_i^{-1/2} + L_j^{-1/2}]^2$$

The expressions for the μ_K^0 and Π become in this case

$$\mu_1^0 = \frac{\ln \phi_1}{L_1} - \frac{\ln \mathcal{J}_1}{L_1} + \phi_2(\chi_{12} - \chi_{23}) - \ln \phi_3 + (\phi_3 - \phi_1)\chi_{13} - \left(1 - \frac{1}{L_1}\right) \tag{25}$$

$$\mu_2^0 = \ln \phi_2 - \ln \phi_3 + \phi_1(\chi_{12} - \chi_{13}) + (\phi_3 - \phi_2)\chi_{23} \tag{26}$$

$$\Pi = \ln \phi_3 + \phi_1\left(1 - \frac{1}{L_1}\right) - \frac{1}{2} \phi_1^2 u_{11}(2) S_1^2 + (\phi_1 + \phi_2)(\phi_1 \chi_{13} + \phi_2 \chi_{23}) - \phi_1 \phi_2 \chi_{12} \tag{27}$$

In the following, we are interested only in the calculation of biphasic areas. The equations for phase equilibrium are (indicating one phase by a prime, ′)

$$0 = \frac{1}{L_1} \ln \frac{\phi_1'}{\phi_1} - \ln \frac{\phi_3'}{\phi_3} - \frac{1}{L_1} \ln \frac{\mathcal{J}_1'}{\mathcal{J}_1} + (\phi_2' - \phi_2)(\chi_{12} - \chi_{23}) + [(\phi_3' - \phi_3) - (\phi_1' - \phi_1)]\chi_{13} \tag{28}$$

$$0 = \ln \frac{\phi_2'}{\phi_2} - \ln \frac{\phi_3'}{\phi_3} + (\phi_1' - \phi_1)(\chi_{12} - \chi_{13}) + [(\phi_3' - \phi_3) - (\phi_2' - \phi_2)]\chi_{23} \tag{29}$$

$$0 = \ln \frac{\phi_3'}{\phi_3} + (\phi_1' - \phi_1)\left(1 - \frac{1}{L_1}\right) - \frac{1}{2} u_{11}(2)[(S_1'^2 \phi_1'^2) - (S_1^2 \phi_1^2)] - \phi_1' \phi_2' \chi_{12} + \phi_1 \phi_2 \chi_{12} + (\phi_1' + \phi_2')(\phi_1' \chi_{13} + \phi_2' \chi_{23}) - (\phi_1 + \phi_2)(\phi_1 \chi_{13} + \phi_2 \chi_{23}) \tag{30}$$

These are three coupled equations which must be calculated numerically to obtain phase diagrams. Another equation giving the order parameter ($\partial \Delta F / \partial S = 0$) is required to achieve the resolution of the problem.

Consider a trivial case where the two solvents are taken to have the same characteristics, so that $\chi_{23} = 0$, and to have the same affinity with the polymer, so that $\chi_{12} = \chi_{13}$. We will call it the symmetrical case. The equations of equilibrium become

$$0 = \frac{1}{L_1} \ln \frac{\phi_1'}{\phi_1} - \ln \frac{\phi_3'}{\phi_3} - \frac{1}{L_1} \ln \frac{\mathcal{J}_1'}{\mathcal{J}_1} - 2(\phi_1' - \phi_1)\chi_{13} \tag{31}$$

$$0 = \ln \frac{\phi_2'}{\phi_2} - \ln \frac{\phi_3'}{\phi_3} \tag{32}$$

$$0 = \ln \frac{\phi_3'}{\phi_3} + (\phi_1' - \phi_1)\left(1 - \frac{1}{L_1}\right) - \frac{1}{2} u_{11}(2)[(\phi_1'^2 S_1'^2) - (\phi_1^2 S_1^2)] + (\phi_1'^2 - \phi_1^2)\chi_{13} \tag{33}$$

As equation (32) implies that

$$(\phi_2' + \phi_3')/(\phi_2 + \phi_3) = \phi_S'/\phi_S = (1 - \phi_1')/(1 - \phi_1) \tag{34}$$

we obtain two coupled equations which are the same as those corresponding to a binary mixture of a polymer (ϕ_1) in a solvent ($\phi_S = 1 - \phi_1$); here the solvent is a mixture of two solvents[26].

This leads to the ternary phase diagrams shown in *Figure 1*. Three slices are shown at reduced temperatures $T/T_t = 0.95$, 0.85 and 0.80 (T_t being the transition temperature of the pure polymer, which is assumed to be thermotropic). Monophasic areas (anisotropic (A) or isotropic (I)) and biphasic areas (anisotropic–isotropic: A/I, isotropic–isotropic: I/I) can be seen.

A cut of these ternary phase diagrams at a given

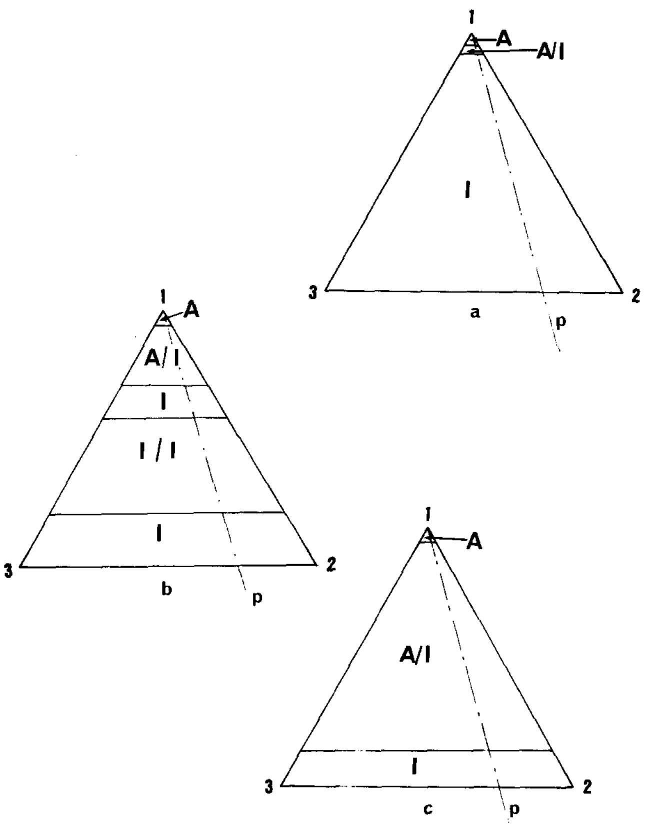

Figure 1 Phase diagrams for a ternary mixture: mesomorphic polymer1/solvent2/solvent3 (symmetrical case); $L_1/L_2 = L_1/L_3 = 2.5$, $\chi_{12} = \chi_{13}$, $\chi_{23} = 0$. The diagrams are given at three reduced temperatures (a) $T/T_t = 0.95$; (b) 0.85; (c) 0.80. A, anisotropic phase; I, isotropic phase; A/I, anisotropic–isotropic biphase; I/I, isotropic–isotropic biphase

proportion of the two solvents leads to the binary-like phase diagram given in *Figure 2b* (reduced temperature as a function of polymer concentration). Every plane p (see *Figure 1*) will lead to the same phase diagram, which does not depend on the relative proportion of the two solvents.

All these results are obvious. But now, consider what happens if the situation is dissymmetrized a little by taking solvent 3 to be a 'good' solvent for the polymer (we choose $\chi_{13} = 0$) and keeping all other conditions the same as above. The results are given in *Figure 3*. The ternary phase diagrams are not symmetrical, and the various biphasic areas have decreased on the part of the diagram where the proportion of solvent 3 is important (compare *Figure 1b* and *Figure 3b*). This is what we may have expected from physical considerations.

The order parameter S of the polymer in the anisotropic phases (monophasic or biphasic) is given in *Figure 4*, where S is plotted against $T/\phi T_t$. This graph is the same as that calculated for a thermotropic polymer with $L/q = 2.5$. This is due to the fact that we have not considered any orientational correlation between the polymer and the solvent, so that the effect of the solvent is only to dilute the orientational interactions between the monomers. For a given T/T_t and a concentration ϕ in the polymer of the anisotropic phase under consideration, *Figure 4* gives the associated order parameter S. We can see that, for $\phi = 1$ and $T = T_t$, $S = 0.3430$, the predicted order parameter at the transition for a monodisperse thermotropic polymer with $L/q = 2.5$ (References 25 and 26).

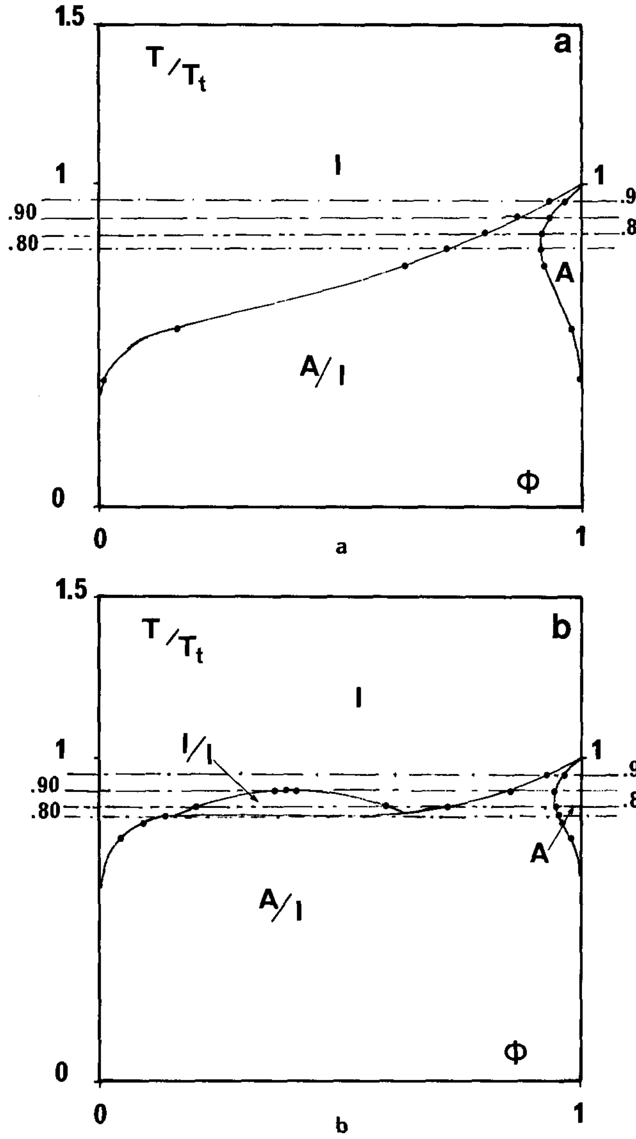

Figure 2 Phase diagrams for two binary mixtures: mesomorphic polymer 1–solvent 2 or 3. Reduced temperature T/T_t is shown as a function of polymer concentration; $L_1/L_2 = L_1/L_3 = 2.5$. (a) Solvent 3, $\chi_{13} = 0$; (b) solvent 2, $\chi_{12} = 1.2T_t/T$

CONCLUSIONS

We have presented a new theory for ternary mesomorphic polymer mixtures. Complete treatment of the problem is long and difficult and depends on many parameters (length, interaction, rigidity, etc.) and variables (concentration, temperature, etc.). An exhaustive study was beyond the scope of this paper so our work was limited to:

(1) an extension to the ternary mixture of the available theories on thermotropic and binary mixture developed previously in the present authors' laboratory[25,26];
(2) the derivation of the equations of phase equilibria for a ternary mesomorphic polymer mixture;
(3) the beginning of a numerical resolution of a particular case (semi-rigid polymer in mixed solvents).

Starting from the 'symmetrical' case (a didactic one), we have shown that the introduction of preferential affinity of the polymer with one of the solvents dissymmetrizes the ternary phase diagram and reduces the various biphasic areas.

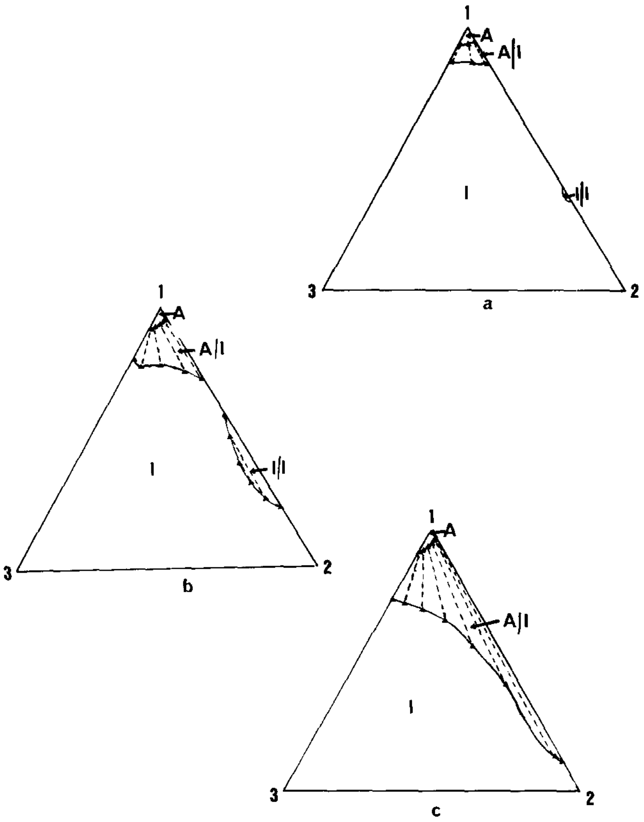

Figure 3 Phase diagram for ternary mixture: mesomorphic polymer1/solvent2/solvent3; $L_1/L_2=L_1/L_3=2.5$ $L_1/q_1=2.5$, $\chi_{13}=\chi_{23}=0$. (a) $T/T_t=0.90$, $\chi_{12}=1.33$; (b) $T/T_t=0.85$, $\chi_{12}=1.41$; (c) $T/T_t=0.80$. ▲, Calculated binodal points. ---, Lines joining points which give concentrations of the phases at equilibrium

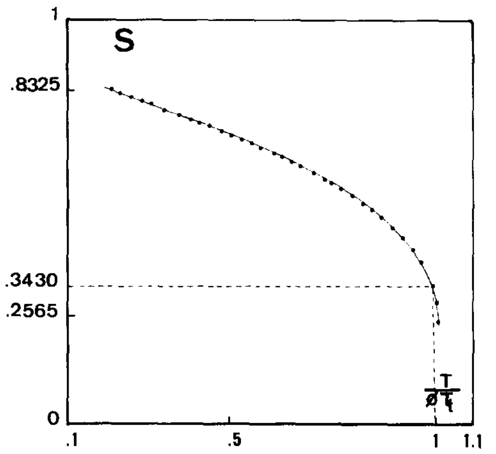

Figure 4 Order parameter for a polymer with $L_1/q_1=2.5$ as a function of $T/T_t\phi$

Note that throughout the present study we have not been interested in problems of stability of the free energy or demixing, which together with the influence of the various parameters and polydispersity, will be studied later. In future studies, we will pay particular attention to the possible existence of triphasic zones. We will also consider some typical examples of particular interest for comparison with experimental results.

The present theory deals with nematic mesomorphic polymers, while experimental results[31-35] are often concerned with cholesteric mesomorphic polymers (cellulose derivatives for example). It will be necessary to solve the cholesteric problem to achieve a complete treatment for this kind of interesting and widespread mesophase.

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