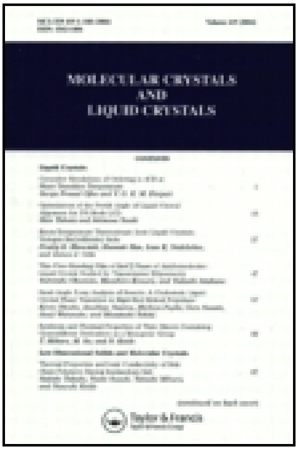

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Equilibrium Phase Properties of Polymer/Liquid Crystal Blends: Theory and Experiments

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Equilibrium Phase Properties of Polymer/Liquid Crystal Blends: Theory and Experiments

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A theoretical formalism to calculate the phase diagrams of polymer/liquid crystal mixtures is presented. Mixtures involving linear and crosslinked polymers together with low molecular weight nematic and smectic-A liquid crystals are considered. The generalization to binary mixtures of nematogens is briefly shown. The method of calculating model phase diagrams of side chain liquid crystal linear and crosslinked polymers in either isotropic or nematic solvents is presented. In nematogen mixtures, the coupling parameter induces tremendous changes in the miscibility of both linear and crosslinked polymers with low molecular weight analogous or different liquid crystals. Applications of the theoretical formalism are given.

Keywords: Polymer; liquid crystal; phase behavior; microscopy; DSC

INTRODUCTION

The phase behavior of polymers and liquid crystals (LCs) is a subject of growing interest from the fundamental and the applied points of view[1]. Mixing molecular species of different physical characteristics leads to a rich variety of phase diagrams and raises fundamental questions similar to those encountered in multi-component systems[2,3]. The knowledge of the effects of various parameters governing their phase behavior is crucial to reach a better understanding of their physical properties in general and eventually identify the ways to improve their performance in practical applications under given conditions. Most applications involve electro-optical response functions of these systems which in turn depend crucially upon their thermodynamic state[4]. For a better electro-optical response, one seeks a material with large ordered mono-domains. One possibility would be to operate the system under the conditions where it exhibits a polymer rich phase dissolving a minimum amount of LC coexisting with large nematic droplets containing pure LC. These favorable conditions are dictated not only by the nature and architecture of the molecular species present in the mixture but also on parameters that we wish to identify in the present work. In the case of linear polymers, the miscibility with LCs depends on the size of the polymer[5] and the isotropic interaction parameter. If the polymer is a crosslinked network, the phase behavior is much more complicated due to the elastic forces at the crosslinks that oppose swelling of the network. The rubber elasticity description is model dependent and remains a subject of controversial discussions in the literature[6]. Moreover, it is highly sensitive to the method of preparation of the blend such as the type of curing radiation (UV or Electron Beam) and the conditions of crosslinking for polymer networks[4]. Polymers with side chain LC groups exhibit entirely different phase properties depending on whether they are embedded in an isotropic or a nematic low molecular weight solvent. In an isotropic solvent, the fact that the LC molecules are hooked to the polymer backbone induces dramatic changes in the miscibility with the solvent[3,7]. First, the nematic-isotropic transition temperature changes by several degrees up or down when the LCs are hooked to the polymer. On the other hand, if the solvent is also nematic, the degree of coupling between nematogens leads to systems with different morphologies whether the nematic coupling is strong or weak[8]. Some of these aspects will be reviewed in this paper. Finally, an experimental example is given to illustrate the application of the theoretical formalism and show the procedure of adjusting the unknown parameters of the model to fit best the data points.

The theoretical formalism starts from a free energy model which is the sum of isotropic and anisotropic contributions. Since these free energies depend on the system under consideration, it is necessary to distinguish different cases as we shall discuss in the following section.

THEORETICAL FORMALISM

Isotropic free energy

As pointed out earlier, we consider systems with linear and crosslinked polymers. These systems correspond to different isotropic free energies that are examined separately hereafter.

The case of linear polymers

We limit ourselves to the mean field level and ignore all the complications due to strong fluctuations when approaching phase transition conditions. Within this scheme, the Flory-Huggins[9] free energy is often sufficient to describe the conditions of isotropic mixing. This part of the free energy is denoted $\Delta f^{(i)}$ and is given by

$$\frac{\Delta f^{(i)}}{k_B T} = \frac{\varphi_1}{N_1}\ln\varphi_1 + \frac{\varphi_2}{N_2}\ln\varphi_2 + \chi\varphi_1\varphi_2 \tag{1}$$

where k_B is the Boltzmann constant, T is the absolute temperature, N_1 and N_2 are the numbers of repeat units of components 1 and 2, φ_1 and φ_2 are their volume fractions.

In principle, the interaction parameter χ depends on various conditions such as temperature, composition, and the polymer molecular weight in addition to the nature and architecture of the molecules present in the mixture. To obtain the composition of the coexisting phases denoted by the symbols (') and (''), one needs to solve the set of equations

$$\begin{aligned} \Delta\mu_1^{(')} &= \Delta\mu_1^{('')} \\ \Delta\mu_2^{(')} &= \Delta\mu_2^{('')} \end{aligned} \tag{2}$$

with $\Delta\mu_1=(\partial\ \Delta F/\partial n_1)_{T,n2}$, ΔF is the total isotropic free energy of the system, $\Delta\mu_1$ is the chemical potential of component 1 and the same definition holds for $\Delta\mu_2$, n_1 and n_2 are the numbers of molecules of type 1 and 2.

The case of a crosslinked network

Here, the isotropic free energy takes into account the elastic contribution due to the crosslinks. According to the Flory-Rehner[6] theory of rubber elasticity, the isotropic free energy can be written as

$$\frac{\Delta f^{(i)}}{k_B T} = \frac{3\alpha\varphi_0^{2/3}}{2N_c}\left[\varphi_2^{1/3} - \varphi_2\right] + \frac{\beta\varphi_2}{N_c}\ln\varphi_2 + \frac{\varphi_1\ln\varphi_1}{N_1} + \chi\varphi_1\varphi_2 \tag{3}$$

where N_C is the number of repeat units between consecutive crosslinks, α and β are the rubber elasticity parameters and φ_0 is the volume fraction of polymer at crosslinking. The phase diagram of this system can be obtained by a similar procedure as linear polymer systems.

Anisotropic free energy

Low molecular weight liquid crystal with a nematic order

The nematic order is described using the Maier-Saupe[10] mean model of free energy $\Delta f^{(n)}$

$$\frac{\Delta f^{(n)}}{k_B T} = \frac{\varphi_1}{N_1}\left[-\ln Z + \frac{1}{2}\nu\varphi_1 s^2\right] \tag{4}$$

where s is the orientation order parameter, Z the nematic partition function and ν the quadrupole interaction parameter.

Low molecular weight liquid crystal with a smectic-A order

The Maier-Saupe theory of nematic order was extended by McMillan[11] to include the effect of smectic-A order. The free energy becomes function of two order parameters: the orientation order parameter and the directional order parameter along the z-axis denoted σ

$$\frac{\Delta f^{(s)}}{k_B T} = \frac{\varphi_1}{N_1}\left[-\ln Z_s + \frac{1}{2}\nu\varphi_1(s^2 + \zeta\sigma^2)\right] \tag{5}$$

where Z_s is the smectic partition function. The parameter ζ depends on the ratio of transition temperatures T_{SN}/T_{NI} and the sequence of transitions S-N-I. According to McMillan, when ζ approaches 0.981, this ratio is 1 indicating a direct transition from S to I.

Binary nematogen mixtures

Binary mixtures of side chain liquid crystal polymers (SCLCP) and LMWLCs are characterized by quite different phase properties than those of analogous systems involving single LCs. Even if the chemical structure of the LMWLC is identical to the side chain group bound to the polymer backbone, miscibility of the two components may be low. According to the rule of Arnold and Zachmann[7] one would expect similar LCs to be highly miscible but there are examples that contradict this rule[8]. Moreover, the transition temperature N-I may change up or down by several degrees or even tens of degrees when it is bound to the polymer backbone. The free energy for those mixtures was first given by Brochard et al.[2] as a generalization of the Maier-Saupe[10] theory

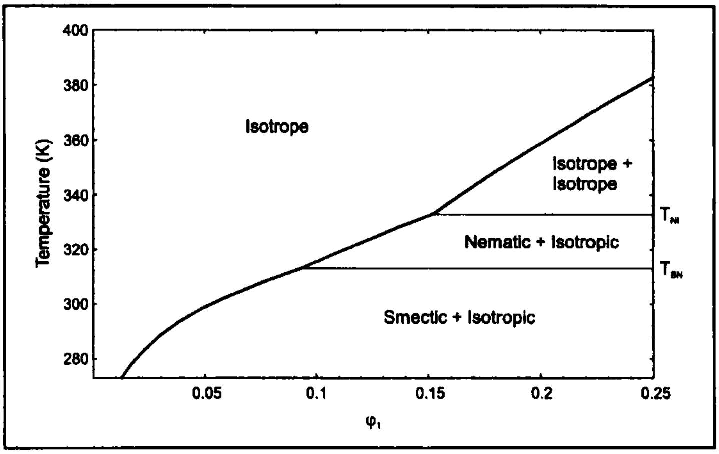

FIGURE 1 The phase diagram for a crosslinked polymer/smectic-A LMWLC mixture with N_c=10, ζ=0.851, T_{SN}=40°C, T_{NI}=60°C, N_l=4 and χ=-0.34+225/T

$$\frac{f^{(n)}}{k_B T} = -\varphi_1 \ln Z_1^{(n)} - \varphi_2 \ln Z_2^{(n)} + \frac{1}{2}\left[v_{11}\varphi_1^2 s_1^2 + v_{22}\varphi_2^2 s_2^2 + 2v_{12}\varphi_1\varphi_2 s_1 s_2\right] \quad (6)$$

where Z_1 and Z_2 are the partition functions, the quadrupole Maier-Saupe parameters v_{ij} are inversely proportional to T while the cross term $v_{12}=v_{21}$ depends on the strength of coupling between the nematogens.

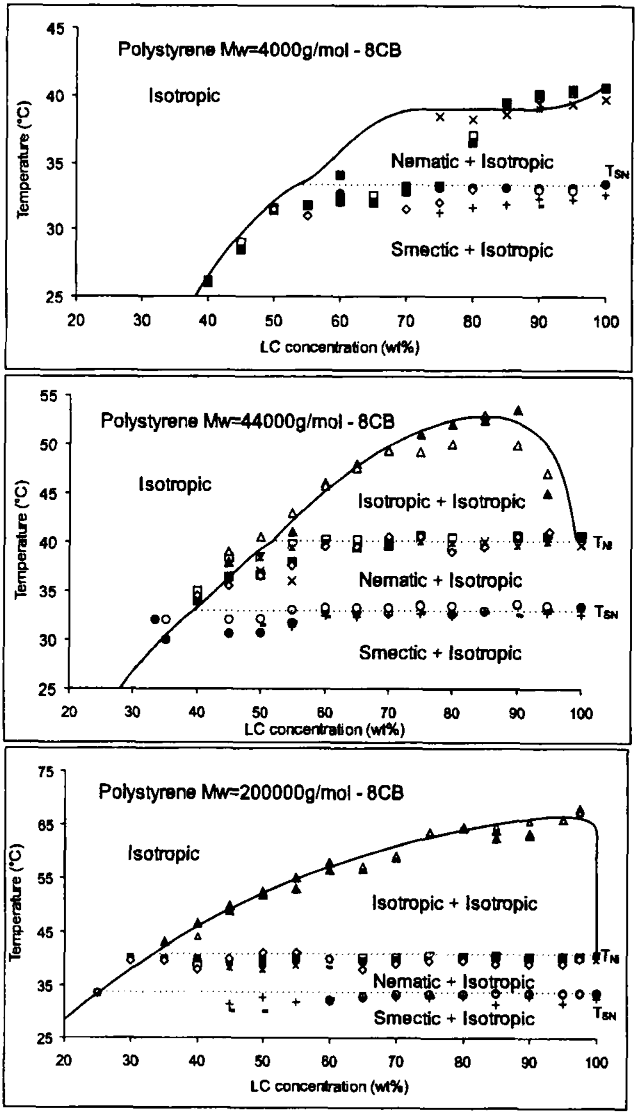

FIGURE 2 Equilibrium phase diagrams of Poly(styrene)/8CB. The symbols are data described in reference 5. The solid curves represent the calculations.

Brochard et al.[2] considered only the case where $v_{12}^2=v_{11}v_{22}$ while Chiu and Kyu[3] proposed to generalize this law assuming that v_{12} deviates from the geometric average of v_{11} and v_{22} via a constant parameter κ such that $v_{12}^2=\kappa^2 v_{11}v_{22}$. Depending on whether κ is higher, lower or equal to 1, the coupling is strong, weak or intermediate, respectively. These three limits lead to quite different phase diagrams.

APPLICATIONS

The main steps in the procedure of calculating the phase diagram is the same for different cases and are displayed elsewhere[3,5,12]. Examples are presented here to illustrate the usefulness of the formalism for hypothetical and real systems. Figure 1 shows the phase diagram of a crosslinked flexible polymer and a smectic-A LMWLC. The latter is characterized by two transition temperatures T_{SN}=40°C and T_{NI}=60°C, a smectic parameter ζ=0.851 and a sequence of transitions S-N-I. The phase diagram of several other hypothetical mixtures were reported before[12].

Figure 2a, b, and c give the experimental and theoretical phase diagrams of a polystyrene (PS)/4-cyano-4′-*n*-octyl-biphenyl (8CB) system with three different molecular weights as indicated on the figure. 8CB is a LMWLC that admits two distinct transitions. An S-N transition at 32°C and a N-I transition at 43°C. These diagrams illustrate the extent to which the miscibility of 8CB and PS decreases when the molecular weight of polymer increases.

CONCLUSIONS

This paper deals with the equilibrium phase diagrams of polymers and LCs. Formalism for calculating the phase diagram is presented with a particular emphasis on linear and crosslinked polymers, nematic and smectic-A LCs. An experimental example is presented to illustrate the miscibility reduction when the molecular weight of polymer increases. Experimental phase diagrams are successfully analyzed with a simple theoretical formalism.

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