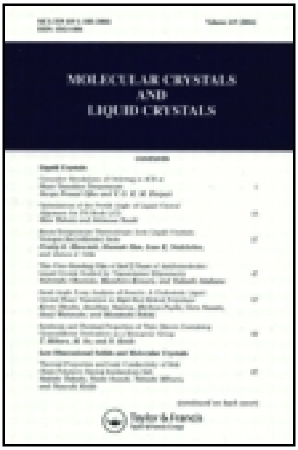

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Mixtures of Polymer Networks and Nematic Liquid Crystals

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To cite this article: Farida Benmouna, Ulrich Maschke, Xavier Coqueret & Mustapha Benmouna (1999): Mixtures of Polymer Networks and Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 475-482

To link to this article: http://dx.doi.org/10.1080/10587259908025624

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 475-482
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Printed in Malaysia

Mixtures of Polymer Networks and Nematic Liquid Crystals

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A theoretical investigation of the miscibility of polymer networks and nematic liquid crystals is presented. The results are compared with the case of mixtures involving linear polymers. Phase diagrams are extremely distorted in the presence of a crosslinked polymer. Hypothetical mixtures characterized by parameter values comparable with literature data are used to illustrate some examples of these distortions.

Keywords: Phase diagram; Flory-Huggins interaction parameter; linear polymers; crosslinked polymer networks; nematic liquid crystals

INTRODUCTION

The need for studying miscibility of mixtures made of polymers and nematic liquid crystals (LCs) is motivated by the large number of practical applications and the fundamental interest these materials present as multicomponent systems[1]. In this paper, a theoretical study of the phase properties of hypothetical polymer/LC mixtures is performed. This could be useful in the identification of trends to improve the performance in the application of polymer-LC based materials and eventually in the design of new materials.

Understanding the phase properties of these mixtures combines the thermodynamic models developed separately for polymers and LC. In the case of blends of linear flexible polymers, the free energy of mixing is described by the Flory-Huggins model[2]. If a mesogen is present in the system, then another contribution to the free energy should be included to take into account the effect of anisotropic ordering forces. There exists a transition temperature T_{NI} below which a nematic phase appears and an appropriate thermodynamic description requires the introduction of a nematic contribution to the free energy.

The phase properties are quite sensitive to the nature and architecture of both polymer and LC in the mixture. Large differences are found by changing the nature, architecture and size of polymer and/or LC. This information is included in the free energy

$$F/N_T = f^{(i)} + f^{(n)} \tag{1}$$

Where the superscripts i and n refer to isotropic and nematic, respectively; F is the total free energy for the whole lattice and N_T the number of sites in the system.

ISOTROPIC FREE ENERGY

In the present paper, we consider mixtures of crosslinked networks and low molecular weight LC. The crosslinking density is defined by the number of monomers between two consecutive crosslinks N_C which has some control on the phase behavior since the miscibility increases with N_C.

The network can be visualized as a single molecule occupying n_2 sites and the total number of sites is $N_T=n_2+n_1N_1$. The network is mixed with n_1 LC molecules each of them having N_1 repeat units. The isotropic free energy of this mixture is a sum of an elastic and an entropic parts in addition to the isotropic interaction term[3-5]

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

The constants α and β are model dependent; here α is given the commonly used value 1 while β is equal to ½ which, according to Flory would correspond to crosslinks with a fonctionality 4.[5]

For a network with isotropic swelling, expansion is defined by the ratio $(\varphi_0/\varphi_2)^{1/3}$ where φ_0 is the volume fraction of polymer at crosslinking and is given the value 1/2. Assuming that all sites occupy the same volume and that the mixture is incompressible, the volume fractions φ_1 and φ_2 satisfy the condition

$$\varphi_1 = \frac{n_1 N_1}{N_T} = 1 - \varphi_2 \quad (3)$$

Here the Flory-Huggins parameter χ varies with temperature according to

$$\chi = A + \frac{B}{T} \quad (4)$$

where A and B are constants characteristic of the mixture.

Nematic free energy

In this work, we are interested on flexible polymers and nematic LC. Within the framework of the Maier-Saupe[6,7] theory, one has

$$\frac{f^{(n)}}{k_B T} = \frac{F^{(n)}}{N_T k_B T} = \frac{\varphi_1}{N_1}\left[-\ln Z + \frac{1}{2}\nu\varphi_1 S^2\right] \quad (5)$$

where S is the orientational order parameter expressed in terms of the average $<\cos^2\theta>$, θ being the angle between a reference axis and the LC molecules

$$S = \frac{1}{2}\left[3\langle\cos^2\theta\rangle - 1\right] \tag{6}$$

v is the Maier-Saupe interaction parameter which is inversely proportional to the temperature T

$$\nu = 4.54\frac{T_{NI}}{T} \tag{7}$$

and Z represents the anisotropic partition function

$$Z = \int e^{\frac{m(3\cos^2\theta-1)}{2}} d(\cos\theta) \tag{8}$$

The parameter m is directly proportional to S, φ_1 and ν

$$m = \varphi_1 \nu S \tag{9}$$

The anisotropic driving forces for nematic ordering are non zero only if the order parameter S is non zero which is the case below the characteristic temperature T_{NI} and the characteristic composition φ_{NI}.

RESULTS AND DISCUSSIONS

The figure below represents the phase diagram for a crosslinked network/LC mixture. It shows striking differences with the case of a mixture involving a linear polymer. There are regions where two phases (α) and (β) are in equilibrium. Compositions of these phases are usually determined using equality of chemical potentials

$$\mu_1^{(\alpha)} = \mu_1^{(\beta)} \quad ; \quad \mu_2^{(\alpha)} = \mu_2^{(\beta)} \tag{10}$$

where the chemical potentials are given by

$$\mu_1^{(\alpha)} = \left(\frac{\partial F}{\partial n_1}\right)_{n_2}^{(\alpha)} \tag{11}$$

$$\mu_2^{(\alpha)} = \left(\frac{\partial F}{\partial n_2}\right)_{n_1}^{(\alpha)} \tag{12}$$

For a crosslinked network, the calculation of the binodal presents some simplification as compared to a linear polymer[8-12]. Assuming that no free chains are present in the mixture, any biphasic region in this diagram consists of a network phase α swollen by isotropically dispersed LC molecules in equilibrium with a pure LC phase β. In the latter phase, the equilibrium is reached by equating the chemical potential of liquid crystal to zero

$$\mu_1 = \frac{1}{k_B T}\left(\frac{\partial F}{\partial n_1}\right)_{n_2} = 0 \tag{13}$$

In the conditions where the mixture is driven by isotropic mixing, the binodal equation is obtained by combining Eqs.(4) and (13). The result is

$$T^{-1} = -\frac{A}{B} - \frac{1}{B\varphi_2}\left|\frac{\alpha(\varphi_0\varphi_2)^{2/3} - \beta}{N_C} + \frac{\varphi_2 + \ln\varphi_1}{N_1\varphi_2}\right| \tag{14}$$

This equation is valid above T_{NI}. It is clear that the binodal in this system is much simpler than in the case of a linear polymer where one has to solve numerically a set of coupled equations. Below T_{NI}, anisotropic ordering forces must be taken into account and one needs to return to the standard procedure based on Eq.(10). The chemical potentials of LC within the network (isotropic phase) and within the pure LC nematic phase should be equated. Since the volume fraction in the pure nematic phase is $\varphi_1^{(\beta)} = 1$, one still has a simple problem of solving a single equation with one variable

$$\mu_1^{(\alpha)} = \mu_1^{(\beta)} \quad \text{with} \quad \varphi_1^{(\beta)} = 1 \tag{15}$$

This equation yields the LC composition $\varphi_1^{(\alpha)}$ inside the network.

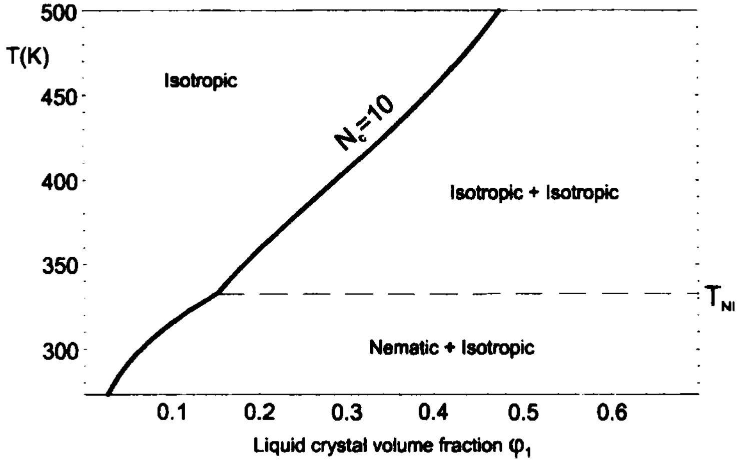

FIGURE 1 Phase diagram for a polymer network/LC mixture using N_l=4, N_C=10, T_{NI}=60°C and χ=-0.34+225/T. The nature of phases in each region is clearly indicated. Note the presence of a pure nematic region on the bottom right hand side of the diagram.

The phase diagram shown in Figure 1 distinguishes three parts. The first part covers the area on the left hand side and corresponds to an isotropic single phase. This region becomes wider as N_C increases implying a lower density of crosslinking points. In this case, the network offers more volume to the LC molecules enhancing miscibility of the mixture. The region limited on the left hand side by the binodal, on the right hand side by the axis φ_1=1 and downward by the line T=T_{NI} is characterized by two isotropic coexisting phases, one of them is a pure LC whose molecules are randomly oriented. The area of this region decreases with increasing N_C because of enhanced compatibility of the mixture. The third region is immediately below and contains a swollen isotropic network in equilibrium with a pure nematic LC phase. This region is weakly sensitive to the value of N_C. These results show that the phase diagram is substantially distorted in the presence of crosslinks. Discrepancies exist with linear polymers at any degree of crosslinking although they tend to be reduced when N_C increases and miscibility of the mixture is enhanced. Comparison of phase diagrams of blends involving crosslinked and linear polymers in similar conditions leads to the following remarks. 1. In both cases, an isotropic region emerges in the upper part of the diagram above the binodal curve. 2. For crosslinked polymer systems, at any temperature a biphasic region exists when the axis $\varphi_1=1$ is approached. This region becomes wider for a lower value of N_C. 3. The single nematic phase emerging in the vicinity of $\varphi_1=1$ for linear polymers cannot be found in the case of a crosslinked network. 4. These observations should be reconsidered if the mixture contains a certain fraction of linear chains no matter how small it is.

CONCLUSIONS

The phase behavior of a crosslinked network and a nematic LC mixture is investigated. This behavior is quite different in the presence of crosslinks. Since the network can be viewed as a single large molecule, one has only an equilibrium between a swollen network and a nematic phase of pure LC below T_{NI}. The binodal is obtained by solving much simpler equations than in the case of linear polymers since polymer is absent from the single LC phase. The rubber elasticity parameters of the crosslinked network α and β are model dependent and bear slight influence on the phase properties. The density of crosslinks represented by N_r and the volume fraction of the network in the relaxed reference state φ_0 affect more the phase behavior. Decreasing N_C widens the miscibility gap but only the case $\varphi_0=½$ was considered here.

Neither the effects of the glass transition temperature nor the presence of free monomers or oligomers in the mixture were included in these discussions.

Acknowledgement

M. Benmouna acknowledges support received from the Organizing Committee of the 16th ILCC, Kent, USA.

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