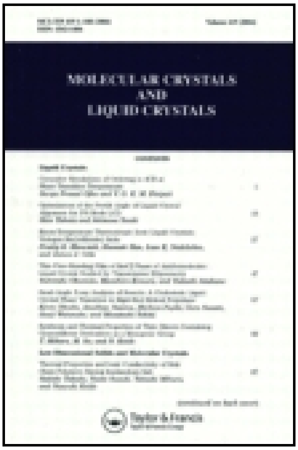

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On the Miscibility of Crosslinked Networks and Solvents with and without Nematic Order

Farida Benmouna [a] [b] , Ulrich Maschke [c] , Laurent Leclercq [b] , Bernd Ewen [b] , Xavier Coqueret [c] & Mustapha Benmouna [a] [b]

[a] Université Aboubakr Belkaïd, Institut de Physique et Chimie, Bel Horizon, BP119, 13000, Tlemcen, Algeria

[b] Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, Germany

[c] Université des Sciences et Technologies de Lille, Laboratoire de Chimie Macromoléculaire, CNRS URA N[ddot] 351, 59655, Villeneuve d'Ascq, Cedex, France

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On the Miscibility of Crosslinked Networks and Solvents with and without Nematic Order

FARIDA BENMOUNA[ab], ULRICH MASCHKE[c],
LAURENT LECLERCQ[b], BERND EWEN[b], XAVIER COQUERET[c]
and MUSTAPHA BENMOUNA[ab]

[a]*Université Aboubakr Belkaïd, Institut de Physique et Chimie, Bel Horizon, BP119, 13000 Tlemcen, Algeria,* [b]*Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany and* [c]*Université des Sciences et Technologies de Lille, Laboratoire de Chimie Macromoléculaire, CNRS URA N° 351, 59655 Villeneuve d'Ascq Cedex, France*

The phase behavior of crosslinked polymer networks and solvents with and without nematic order is investigated. The Flory-Huggins interaction parameter χ is assumed to be function of temperature and polymer volume fraction. Effects of these variations on the miscibility of networks and low molecular weight solvents are discussed. Under certain conditions, equilibrium between collapsed and swollen networks is observed. This behavior was not observed in previous studies where χ was assumed independent of polymer volume fraction. If the low molecular weight component is a liquid crystal (LC), below the nematic-isotropic transition temperature nematic order induces a drastic loss of miscibility in the dilute polymer range. If the nematogens are attached to the polymer network as side chain LC groups, the loss of miscibility is even larger but localized in the dense polymer region. The phase diagram in the whole range of composition is discussed.

Keywords: Phase behavior; miscibility; Flory-Huggins interaction parameter; crosslinked polymer network; nematic liquid crystals

INTRODUCTION

Phase mixing of crosslinked polymers and low molecular weight solvents driven by isotropic interaction has been the subject of intensive studies for a long time[1-5]. However, more efforts are needed to understand the combined effects of crosslinks and anisotropic forces on the phase behavior and clearly identify discrepancies with linear polymer systems[6-11]. These efforts are useful to improve the quality of these materials in practical applications which are numerous and diversified. These applications may be based upon electro-optical response properties, sensitivity of the system subject to external fields, texture of phases under various conditions of temperature, composition and pressure, etc.[12-14]. In view of the variety of fundamental and practical problems encountered in these systems, it would be useful to understand the effects of architecture of the polymer and its interactions with the solvent or LC on the phase properties of the mixture. The excess elasticity of the polymer network due to crosslinks, the model characterizing the constants of elasticity and the density of crosslinks have a particular influence on the phase behavior of these systems. Variations of the Flory-Huggins interaction parameter with temperature and polymer composition induces new features in the phase diagram[15] which are interesting to investigate with or without nematic order. In isotropic mixing conditions, when the χ-parameter depends on the polymer volume fraction, equilibrium of collapsed and swollen networks is observed. Recent studies of phase properties of mixtures of linear polymers and nematic LCs were reported[7,8]. Little attention has been given to crosslinked polymer networks and LC. In this paper, we discuss the phase behavior of mixtures of polymer networks with side chain LC groups and low molecular weight isotropic molecules which are referred to as solvent molecules. Both the Flory-Huggins[16] interaction parameter χ and the parameters of rubber elasticity of the network α and β are assumed to be functions of composition. We will examine how nematic interactions below the nematic-isotropic transition temperature reduce the miscibility of the mixture.

GENERAL THERMODYNAMIC PROPERTIES

For the mixtures under consideration, the free energy is a sum of two terms

$$F = N_T f = [n_1 N_1 + n_2][f^i + f^n] \tag{1}$$

Capital F represents the free energy for the whole lattice with N_T sites; lower case f represents the free energy per site, f^i and f^n are the isotropic and nematic contributions. n_1 is the total number of LC or solvent molecules, each molecule having N_1 repeat units and n_2 is the total number of repeat units in the network. The volume fractions of solvent and polymer are denoted φ_1 and φ_2

$$\varphi_1 = \frac{n_1 N_1 v_1}{V_0}; \varphi_2 = \frac{N_2 v_2}{V_0}; V_0 = N_2 v_2 + n_1 N_1 v_1 \tag{2}$$

v_1, v_2 and V_0 are the molar volumes of molecules 1 and 2 and the total volume of the system, respectively. We will let $v_1=v_2$ which means that volume fractions coincide with number fractions. The phase diagram contains biphasic regions of coexisting phases a and b. Their compositions are obtained by solving the set of equations

$$\mu_1^a = \mu_1^b \tag{3}$$

$$\mu_2^a = \mu_2^b \tag{4}$$

Where the chemical potentials μ_i are calculated using

$$\mu_1 = \frac{1}{k_B T}(\frac{\partial F}{\partial n_1})_{n_2} = N_1\left[f - \varphi_2 \frac{df}{d\varphi_2}\right] \tag{5}$$

$$\mu_2 = \frac{1}{k_B T}(\frac{\partial F}{\partial n_2})_{n_1} = \left[f + \varphi_1 \frac{df}{d\varphi_2}\right] \tag{6}$$

Eqs.(3) to (6) yield

$$f-\varphi_2\frac{df}{d\varphi_2}\bigg|^{a}=f-\varphi_2\frac{df}{d\varphi_2}\bigg|^{b} \qquad (7)$$

$$\frac{df}{d\varphi_2}\bigg|^{a}=\frac{df}{d\varphi_2}\bigg|^{b} \qquad (8)$$

The isotropic free energy

From the classical rubber elasticity theories, one obtains the isotropic free energy of crosslinked polymers and solvents as

$$\frac{f^{i}}{k_B T}=\frac{F^{i}}{N_T k_B T}=\frac{3\alpha}{2N_C}(\varphi_0^{2/3}\varphi_2^{1/3}-\varphi_2)+\frac{\beta\varphi_2}{N_C}\ln\frac{\varphi_2}{\varphi_0}+\frac{\varphi_1\ln\varphi_1}{N_1}+\chi\varphi_1\varphi_2 \qquad (9)$$

φ_0 is the volume fraction of polymer at crosslinking. We shall give the value 1 to this quantity implying that crosslinking takes place in the bulk. N_C represents the number of units between two consecutive crosslinks; for numerical applications we use $N_C=10^3$ and $N_1=1$. The constants of the network α and β depend on the model of rubber elasticity; α often takes the value 1 while β is either 0, 1 or 2/functionality of monomers at crosslinks. Here, we choose yet another model in which α and β are allowed to be functions of polymer volume fraction φ_2,

$$\alpha=\frac{1}{f}(f-2+2\varphi_2) \qquad \beta=\frac{2\varphi_2}{f} \qquad (10)$$

where the functionality of the crosslinks is $f=3$. The Flory-Huggins interaction parameter χ varies with φ_2 according to

$$\chi=\chi_0+\chi_1\varphi_2+\chi_2\varphi_2^2 \qquad (11)$$

For the sake of illustration, the parameters χ_1 and χ_2 are chosen arbitrarily as χ_1=0.3 and χ_2=0.04 while χ_0 varies with temperature following

$$\chi_0 = -0.35 + 342/T \tag{12}$$

This form leads to an upper critical solution temperature (UCST) diagram. This diagram requires the resolution of Eqs.(7) and (8) for which one needs the derivative of the free energy. Considering the isotropic part, a straightforward calculation gives

$$\begin{aligned}\frac{df^i}{d\varphi_2} = &\frac{\alpha}{2N_C}(\varphi_2^{-2/3} - 3) + (\frac{3(\varphi_2^{1/3} - \varphi_2)}{fN_C}) + \frac{\beta}{N_C}(\ln\varphi_2 + 1) + \frac{2\varphi_2 \ln\varphi_2}{fN_C} \\ &- \frac{\ln\varphi_1 + 1}{N_C} + \chi_0(1 - 2\varphi_2) + \chi_1\varphi_2(2 - 3\varphi_2) + \chi_2\varphi_2^2(3 - 4\varphi_2)\end{aligned} \tag{13}$$

The nematic free energy

The nematic free energy is modelled using the Maier-Saupe[17-19] mean field theory. In recent years, this model has been used quite extensively to mixtures of polymers and nematic LC. Here, we consider the case of a polymer network with side chain mesogen groups and isotropic solvent molecules. In order to characterize the phase behavior of these mixtures, one needs the nematic part of the free energy

$$\frac{f^n}{k_BT} = \frac{F^n}{N_Tk_BT} = \varphi_2(-\ln Z_2 + \frac{v_2\varphi_2^2 s_2^2}{2}) \tag{14}$$

The subscript 2 is deliberately used in all the quantities involved in this equation to stress the fact that nematic groups are hooked to the polymer. Z_2 is the nematic partition function

$$Z_2 = \int e^{\frac{m_2[3\cos^2\theta - 1]}{2}} d(\cos\theta) \tag{15}$$

θ is the angle between a reference axis and the LC molecules and m_2 is the strength of nematic interaction; s_2 is the orientational order parameter

$$s_2 = \frac{1}{2}[3 < \cos^2\theta > -1] \tag{16}$$

In Eq.(14), v_2 represents the nematic interaction parameter and is inversely proportional to the temperature according to

$$v_2 = 4.54\frac{T_{NI2}}{T} \tag{17}$$

T_{NI2} is the nematic-isotropic transition temperature of the side chain LC polymer network. As it was pointed out earlier, one needs the derivative of the free energy in order to determine the composition of coexisting phases. The nematic part is

$$\frac{df^n}{d\varphi_2} = \ln Z_2 \tag{18}$$

RESULTS AND DISCUSSIONS

Combining Eqs.(7) - (9), (13), (14), and (18) yields the phase diagram of Figure 1 for T_{NI2}=80°C. Several regions are visualized in this diagram. Above the binodal curve, a single isotropic phase where the network is homogeneously dissolved in the low molecular weight solvent is observed. The corresponding region in isotropic mixtures is much larger indicating that the nematic interaction reduces significantly the miscibility. Note that above point A, the network is uniform and isotropic although the system is 60°C below the isotropic-nematic transition temperature. On the left hand side of the diagram, a single nematic dense polymer phase is observed. This nematic phase is quite different from the one observed in mixtures involving low molecular weight

LC molecules and linear polymers in the vicinity of $\varphi_1=1$. In this case, the single nematic phase region is much more extended and covers a large domain of temperatures and polymer volume fractions. This diagram shows several biphasic regions. The first one is delimited on the left hand side by the single nematic phase, upward by the isotropic phase and from below by the dashed line passing through point A. The two coexisting phases here are both highly dense networks with a small amount of solvent but one of them is a nematic phase and the other is an isotropic phase. As T approaches T_{NI2}, polymer contents of the two phases approach each other. When the transition temperature is reached, a single isotropic phase merges with a different degree of swelling depending on solvent volume fraction. Another biphasic region is surrounded on the left by the single nematic phase, above by the dashed line passing through point A and on the right by the vertical axis at $\varphi_1=1$. Here, a

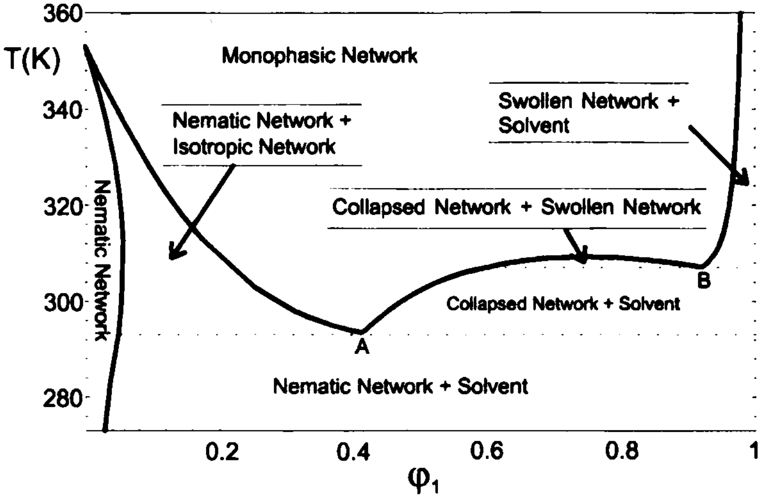

FIGURE 1 Phase diagram of a side chain liquid crystal network and an isotropic solvent with $\chi=\chi_0+\chi_1\varphi_2+\chi_2\varphi_2^2$; $\chi_0=-0.35+342/T$; $\chi_1=0.3$; $\chi_2=0.04$; $\alpha=[f-2+2\varphi_2]/f$; $\beta=2\varphi_2/f$; $T_{NI2}=80°C$; $N_1=1$; $N_C=10^3$; and $f=3$. The nature of phases in each region is clearly identified on the figure.

dense collapsed nematic network is in equilibrium with a pure solvent phase. This region is limited to temperatures below 20°C but covers a large domain of composition varying practically from the bulk polymer to the pure solvent. The region between the two dashed lines passing through points A and B contains an isotropic collapsed network coexisting with a pure solvent phase. Here, the network admits more solvent as the temperature increases until the upper dashed line is reached at approximately 35°C. This is a tricritical temperature where a third phase made of a swollen network is in equilibrium with a collapsed network and a pure solvent. Above 35°C, for compositions less than 86% all the solvent available in the solution is absorbed by the swollen network and the system reaches an equilibrium between collapsed and swollen isotropic networks. On the right hand side of the diagram, one finds a region of equilibrium between a swollen isotropic network and a pure solvent phase.

CONCLUSION

The phase properties of side chain LC network polymers presents striking differences with the case of linear polymers and low molecular weight LC. Dense polymer nematic phases are found in contrast with the tiny region of a single nematic phase observed in linear polymer-LC mixtures. Allowing the Flory-Huggins parameter for isotropic mixing to depend on polymer volume fraction, leads to a rich diagram with various regions of coexisting phases. In particular, collapsed and swollen networks reach equilibrium under certain conditions of temperature and composition. In general, nematic interactions favor unmixing and lead to completely different phase diagram whether one has a low molecular weight LC or a polymer network with side chain LC groups.

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References

[1] K. Dusek, and W. Prins, *Adv. Polymer Sci.*, **6,** 1 (1969).

[2] P.J. Flory, and B. Herman, *Macromolecules,* **15,** 800, (1982).

[3] Z.S. Petrovic, W.J. Macknight, R. Koningsveld and K. Dusek, *Macromolecules* **20,** 1088 (1987).

[4] R. Briber, and B.J. Bauer, *Macromolecules* **24,** 1899 (1991).

[5] B.J. Bauer, R. Briber and C.C. Han, *Macromolecules* **22,** 940 (1989).

[6] C. Shen and T. Kyu, *J. Chem. Phys.*, **102,** 556 (1995).

[7] H.W. Chiu and T Kyu, *J. Chem. Phys.*, **103,** 7471 (1995).

[8] C.Shen, Phase Equilibrium and Phase Separation Dynamics in Polymer Dispersed Liquid Crystals, PhD dissertation (University of Akron, 1995).

[9] U. Maschke, X. Coqueret, M. Benmouna, *Polym. Networks Blends* **7,** 23 (1997).

[10] F. Benmouna, L. Bedjaoui, U. Maschke, X.. Coqueret and M. Benmouna, *Macromolecular Theory and Simulations,* In Press.

[11] F. Benmouna, U. Maschke, X. Coqueret and M. Benmouna, *Macromolecules,* In Press.

[12] J.W. Doane, Polymer Dispersed Liquid Crystal Displays, in: *Liquid Crystals: Applications and Uses,* edited by B. Bahadur (World Scientific, Singapore, 1990).

[13] P.S. Drzaic, *Liquid Crystal Dispersions,* (World Scientific, Singapore, 1995).

[14] a) U. Maschke, X. Coqueret and C. Loucheux, *J. Appl. Polym. Sci.,* **56,** 1547 (1995); b) U. Maschke, A Traisnel, J.-D. Turgis, and X. Coqueret, *Mol. Cryst. Liq Cryst.,* **299,** 371 (1997); c) U. Maschke, N. Gogibus, A. Traisnel, and X. Coqueret, *Liq. Cryst.* **23,** 457 (1997).

[15] R. Moerkerke, R. Koningsveld, H. Berghmans, K. Dusek, and K. Solc, *Macromolecules* **28,** 1103 (1995).

[16] H.M.J. Boots, J.G. Kloosterboer, C. Serbutoviez, and F.J. Touwslager, *Macromolecules* **29,** 7683 (1996).

[17] W. Maier and A. Saupe, *Z. Naturforschung,* **14a,** 882 (1959).

[18] W. Maier and A. Saupe, *Z. Naturforschung,* **15a,** 287 (1960).

[19] P.G. de Gennes, *The Physics of Liquid Crystals,* (Oxford University Press, Ely House, London, 1974).