Macromol. Symp. 2014, 336, 61–67 DOI: 10.1002/masy.201300016

Phase Diagrams of PolyAcrylic Networks and Liquid Crystal E7

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Summary: Equilibrium phase diagrams of polymer networks and a nematic liquid crystal blend were investigated. The polymer network used was PolyABu (poly(*n*-butyl-acrylate)), obtained by exposure to UV radiation of initial solutions composed of a reactive monomer, a small amount of a crosslinking agent, and a photoinitiator. Experimental phase diagrams were established using polarizing optical microscopy, and the results were analyzed within the predictions of the combined Flory-Rehner theory of rubber elasticity and the Maier-Saupe theory of nematic ordering.

Keywords: Flory-Rehner; liquid crystal; Maier-Saupe; phase diagrams; polymer networks

Introduction

A phase diagram provides valuable information about the thermodynamic stability of the coexisting phases as function of temperature and composition. Establishment of phase diagrams is thus the beginning point in any research on blends of Liquid Crystals (LCs) and polymers (linear or crosslinked). More than half a century ago, Flory and Rehner[1] developed a theory of rubber elasticity for the latter case, suggesting that the swelling equilibrium is reached when the osmotic pressure of small solvent molecules that promote swelling is balanced by the elastic forces at the crosslinks opposing network strand extension. Many other theories were developed on the basis of a variety of arguments. For example, the concepts of scaling and the blob hypothesis suggested by de Gennes for polymers in strong solutions or in melts were extended to networks.[2–4] A large amount of data is available on these issues in the literature,[5–10] but the problem remains a subject of debate, attesting to its complexity and richness.

This work can be viewed as part of the systematic studies undertaken in our laboratories to explore the physical properties of composite materials made of polymers and Low Molecular Weight Liquid Crystals (LMWLCs), such as polymer-dispersed liquid crystals (PDLCs).[11–15] Two main problems emerge when one deals with these materials with regards to their performances in terms of aging, thermal stability, mechanical strength, electro-optical responses, and relaxation processes. The miscibility of molecular constituents in the precursor mixture is the first problem. To characterize the specific features of the swelling behavior when small molecules are anisotropic, it is useful to undertake a comparative study with a model network in the presence of LCs. Systems made of ultraviolet (UV)-cured poly(n –butyl acrylate) network [poly(ABu)] and the known nematic LC E7 blend were considered. A low concentration of crosslinker, the difunctional monomer hexane diol-di-acrylate (HDDA), was added because (ABu) is a mono

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functional monomer, that alone would lead to linear polymer chains. Three different quantities of HDDA, i.e., 0.5, 1.25, and 2.5 wt-%, allow to obtain either a loosely crosslinked network with more efficient swelling in good solvents (0.5 wt-% HDDA) or more dense networks with limited swelling properties (1.25 and 2.5 wt-% HDDA). The amount of the photoinitiator was not changed with respect to the monomers (ABu and HDDA). It is clear that the conditions of preparation, the solvent quality, temperature and composition at crosslinking, control to some extent the elasticity of the polymer network sample. A comparative study of theoretical phase diagrams on selected networks and LC E7, using the combined Flory-Rehner theory of rubber elasticity and Maier-Saupe theory of nematic ordering, is also presented. The analysis of the results makes it possible to obtain useful information for the comprehension of the polymer/solvent interactions.

Experimental Part

Materials

The chosen monomer for this study, n-butyl-acrylate (99%) designated (ABu), was obtained from Sigma-Aldrich. The crosslinking agent is 1.6- Hexanedioldiacrylate (HDDA), supplied by Cray Valley (France). 2-hydroxy- 2-methyl- 1-phenyl-propane-1 (Darocur 1173) from Ciba-Geigy is used as a photoinitiator. The LC (anisotropic solvent) selected for this study is E7, an eutectic LC mixture, obtained from Merck KgaA, Darmstadt, Germany. E7 contains 51 wt.% of 4-cyano-4'-pentyl-biphenyl (5CB), 25 wt.% of 4-cyano-4'-heptylbiphenyl (7CB), 16 wt.% of 4-cyano-4'-oxyoctylbiphenyl (8OCB), and 8 wt.% of 4-cyano-4'-pentyl-p-terphenyl (5CT). E7 exhibits a glassy phase below – 61 °C, a nematic phase between –61 °C and 61 °C, and becomes isotropic above 61 °C.

The purity of the different products used in the study was checked by means of the NMR analysis method.

Sample Preparation

Mixtures of ABu/HDDA/Darocur 1173 were prepared in different weight fractions by varying the quantity of ABu and HDDA and keeping the amount of Darocur 1173 constant (ABu/HDDA/Darocur 1173 = 99/0.5/0.5, 98.25/1.25/0.5, and 97/2.5/0.5 wt %). The initial mixtures were stirred mechanically for 24 hours before they were cast in small flat sample holders. The samples were exposed to UV radiation under nitrogen atmosphere, using two Philips TL08 UV lamps with a wavelength $\lambda = 365$ nm and an intensity $I_0 = 1.5$ mW/cm^2. The exposure time was fixed to 15min to achieve a complete conversion of monomers.

Techniques and Experimental Procedures

Sub-millimeter-sized samples with circular shapes of approximately 500μm and thicknesses of roughly50 μm were prepared from the above mentioned crosslinked poly(ABu/HDDA) (see Figure 1a for an example). These samples were immersed in the LC solvent at room temperature for two days to allow thermodynamic equilibrium state to be reached.

Characterization of the swelling of the immersed polymer networks in the LC solvent was performed by observations via optical microscopy, by increasing the temperature from 20°C to 160°C. Micrographs were taken in intervals of 2°C until the swollen polymer samples reached thermodynamic equilibrium at each given temperature. Smaller temperature intervals were chosen in the vicinity of the nematic-isotropic phase transition temperature of the LC. A Linkham heating stage (THMS 600) and a temperature controlling unit (TMS 92) were used together with a Leitz polarizing optical microscope. Duplicate samples were used to check for reproducibility and averaged values of the results were employed for data analysis.

From the optical micrographs presented on Figure 1, the unidirectional swelling degree (l), in the thermodynamic equilibrium, can be obtained from average diameters in the dry (l_0) and the swollen (l) state

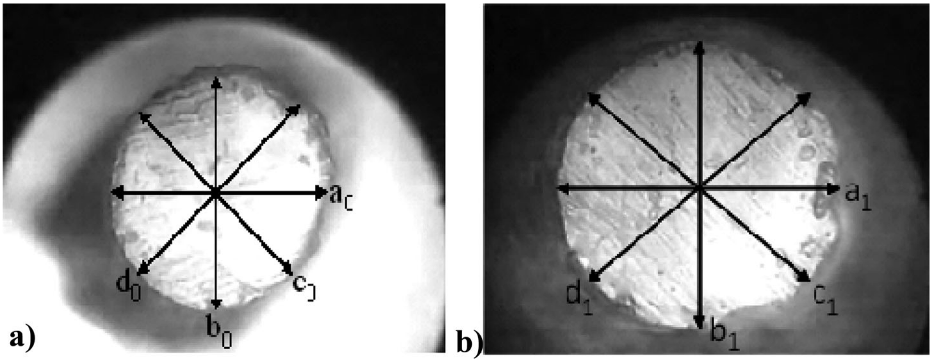

Figure 1.
Schematic representation of different diameters of a submillimeter-sized chemically crosslinked polymer network a) in the dry state and b) swollen in LC.

using the formula: $\lambda^3 = (l/l_0)^3 = V/V_0$, where V represents the volume in the swollen state, and V_0 is the initial volume of the dry sample. The LC volume fraction φ_{LC} was calculated from $\varphi_{LC} = 1-(1/\lambda^3)$, yielding

$$\lambda = Q^{\frac{1}{3}} = \frac{1}{4} \times \left(\frac{a_1}{a_0} + \frac{b_1}{b_0} + \frac{c_1}{c_0} + \frac{d_1}{d_0}\right) \qquad (1)$$

where Q stands for the swelling degree in volume of the gel.

Theoretical Phase Diagrams for Polymer Network/LC Systems

Usually, one assumes that the total free energy, describing the phase diagram of chemically crosslinked polymer network/LC blends, can be expressed by a simple summation of the free energy density of isotropic mixing, the free energy density due to network elasticity and the free energy density of nematic ordering. The phase properties can be then be deduced using standard thermodynamic methods. This combination of mean field models was already found to describe quite well the phase properties of polymer/LC mixtures.[12]

$$g = g^{iso} + g^{n} \qquad (2)$$

where g is the total free energy density of the binary system, g^{iso} represents the isotropic free energy density, and g^{n} stands for the free energy density of nematic ordering. More generally, the superscripts *iso* and *n* will be related to the isotropic and nematic parts, respectively.

The Isotropic Binodal

The phase diagram in the isotropic state can be described within the Flory-Rehner model.[1] The swelling of the crosslinked polymer in the low molecular weight solvent depends on the elasticity of the network. The isotropic free energy density is a sum of two contributions

$$g^{iso} = g^{e} + g^{m} \qquad (3)$$

where g^{e} is the free energy density due to the network elasticity given by

$$\frac{g^{e}}{k_B T} = \frac{3\alpha}{2N_c}\varphi_0^{\frac{2}{3}}\left[\varphi_2^{\frac{1}{3}} - \varphi_2\right] + \frac{\beta\varphi_2}{N_c}\ln\varphi_2 \qquad (4)$$

The second contribution to the isotropic free energy of eq. (3) is given by the free energy of isotropic mixing

$$g^{m} = \frac{\varphi_1 \ln\varphi_1}{N_1} + \chi\varphi_1\varphi_2 \qquad (5)$$

k_B is the Boltzmann constant and T represents the absolute temperature. The subscripts 1 and 2 refer to the LC and the polymer network, respectively. φ_1 and φ_2 are their respective volume fractions, satisfying the incompressibility condition $\varphi_1 = 1 - \varphi_2$.

N_1 stands for the volume ratio of solvent molecules to monomeric units of the polymer such that the total volume can be expressed as a number of repeat units $n_t = n_1 N_1 + n_2$. Here, n_1 is the number of solvent molecules and n_2 represents the number of monomeric repeat units in the network.

α and β are the rubber elasticity parameters and there values are model dependent. In the Flory affine network model,[16] one has $\alpha = 1$ and $\beta = 2/f$, f being the functionality of the monomers. The phantom network model proposed by James and Guth[17] suggest other values of these parameters. Indeed, they suggests to let $\alpha = 1$ and $\beta = 0$. Recently, Petrovic et al.[18] proposed a linear dependence of α and β on volume fraction of the polymer network of the form $\alpha = \frac{f-2+\varphi_2}{f}$ and $\beta = \frac{2\varphi_2}{f}$. It should be noted in the latter model that the limit $\varphi_2 \rightarrow 1$ corresponds to the Flory affine network model, whereas the limit $\varphi_2 \rightarrow 0$ corresponds to the James and Guth phantom model. N_c represents the number of segments between adjacent crosslinks (or adjacent chemical junctions points), and φ_0 is the volume fraction of the polymer network in the reference (unswollen) state.

χ, the Flory-Huggins isotropic mixing interaction parameter, is taken to be an inverse function of temperature of the form

$$\chi = A + \frac{B}{T} \tag{6}$$

where A and B are constants independent of T. They are chosen to obtain the best fit with the experimental data in the part of the diagram where the isotropic interaction is most significant.

The Maier Saupe Model

Nematic LCs are aligned along a reference axis in the z direction with an angular distribution. In addition to the isotropic free energy discussed earlier, one has a contribution due to the nematic interaction which can be described by the Maier-Saupe theory.[19,20] The nematic free energy is given by

$$\frac{g^n}{k_B T} = \frac{G^n}{N_T k_B T} = \varphi_1 \left[-\ln Z + \frac{1}{2} \nu \varphi_1 s^2 \right] \tag{7}$$

where G^n represents the nematic free energy for the whole lattice and g^n its value for a single lattice site (i. e., the free energy density). Z is the nematic partition function

$$Z = \int e^{-U(\theta)/(k_B T)} d(\cos\theta) \tag{8}$$

where the orientational potential $U(\theta)$ is given by

$$U(\theta) = -\frac{m}{2} \left[3\cos^2\theta - 1 \right] \tag{9}$$

m is a mean field parameter representing the potential strength. Minimization of the nematic free energy with respect to s yields

$$m = \varphi_1 \nu s \tag{10}$$

where ν is the Maier-Saupe quadrupole interaction parameter

$$\nu = 4.54 \frac{T_{NI}}{T} \tag{11}$$

T_{NI} is the nematic-isotropic transition temperature of the LC. The nematic order parameter s is given by

$$s = \frac{1}{2} \left[3 < \cos^2\theta > -1 \right] \tag{12}$$

θ is the angle between a reference axis and the director of the LC; the symbol <…> represents the average with respect to the orientational distribution function.

Results and Discussion: Phase Diagrams

Figure 2 show both experimental and theoretical binodals of poly (ABu/HDDA)/E7. The symbols are experimental Polarizing

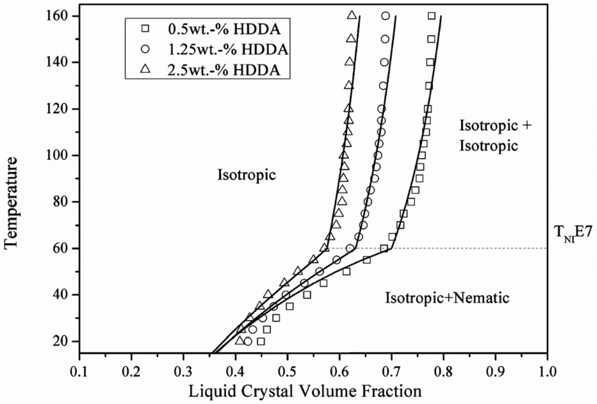

Figure 2.
Theoretical phase diagrams for the PolyABu/E7 system.

Optical Microscopy data and the LC volume fraction was calculated from eq. 1.

All systems show a large region on the left hand side of Figure 2, where a single isotropic phase appears at low LC volume fractions. A biphasic region of isotropic polymer network and isotropic LC can be found in the upper right hand side of the diagrams, above the nematic-isotropic transition temperature of E7. Below this temperature, the LC presents a nematic phase. Consequently, the phase diagrams exhibit a biphasic region of isotropic polymer network and nematic E7 in the lower right hand side of Figure 2.

One observes that in the zone (I + N), the volume fraction of LC increases quickly as function of temperature, whereas in the zone (I + I), the volume fraction tends towards a plateau and the difference between the curves becomes more significant. The miscibility of the crosslinked polymer network with LC decreases with increasing HDDA content in the initial mixture. A maximum amount of LC can be admitted within the network, above which the network reaches saturation. This amount decreases if the crosslinking density increases. The effect of crosslinking density on the miscibility can be deduced from Figure 2, which shows clearly that the system containing 0.5 wt.% HDDA is miscible to a great extent with E7, whereas the 2.5 wt.% HDDA system represents a much lower compatibility with the LC. Therefore, E7 is a good solvent in its isotropic phase compared to its nematic phase, however, toluene as isotropic solvent presents still better swelling characteristics.[21]

The solid lines represent the theoretical binodals from theoretical fitting obtained starting from the combination of the theories of Flory-Rehner (isotropic mixing) and Maier-Saupe (nematic contribution). They are obtained by solving the whole set of equations expressing the chemical potentials equality between the coexistence phases, which are given in the next section.

Chemical Potentials and Fitting Procedures

Two methods are currently available to construct the phase diagrams (binodal curves): either graphically using the double tangent method, or analytically by equating the chemical potentials of constituents 1 and 2 in the coexisting phases. Here, the latter method will be adopted by solving numerically the set of equations

$$\begin{cases} \mu_1^i = \mu_1^{ii} \\ \mu_2^i = \mu_2^{ii} \end{cases} \tag{13}$$

The chemical potentials are given by differentiating the free energy compared to the number of molecules n_1 and n_2. One has:

$$\begin{cases} \mu_1 = \left(\dfrac{\partial G}{\partial n_1}\right)_{n_2} \\ \mu_2 = \left(\dfrac{\partial G}{\partial n_2}\right)_{n_1} \end{cases} \tag{14}$$

It is sometimes convenient to express the chemical potentials in terms of the derivative of the free energy density $\frac{dg}{d\varphi_2}$

$$\begin{cases} \mu_1 = N_1\left(g - \varphi_2 \dfrac{dg}{d\varphi_2}\right) \\ \mu_2 = N_2\left(g - \varphi_1 \dfrac{dg}{d\varphi_1}\right) \end{cases} \tag{15}$$

For a crosslinked polymer, μ_1 is given by the first term in Eq. (15), but μ_2 has to be adapted to the network, which can be viewed as a single molecule $(N_2 = 1)$.[22] Then one can write:

$$\mu_2 = g - \varphi_1 \frac{dg}{d\varphi_1} \tag{16}$$

The calculation of binodals is somewhat different in the case of a crosslinked polymer than in the case of linear polymer/LC blends.[23] Since no free chains are present in the mixture, the biphasic region consists of a phase made of a network swollen by isotropically dispersed LC molecules coexisting with a pure LC phase (i. e., its polymer volume fraction $\varphi_2^{(\mathrm{ii})}$ is zero). i. e:

$$\frac{\mu_1}{k_B T} = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} = 0 \tag{17}$$

Above the transition temperature T_{NI} of the LC, a swollen isotropic network coexists with a pure LC in its isotropic state. The polymer volume fraction of the swollen network is obtained by solving the equation $\mu_1^i = \mu_1^{ii} = 0$. Below T_{NI}, where the anisotropic ordering forces must be taken into account, one needs to write the equality of chemical potentials of LC within the network (isotropic phase) and within the pure nematic LC phase. However, since the volume fraction in the pure nematic phase is $\varphi_1^{(ii)} = 1$, one still has a substantial simplification since one recovers one equation with a single variable

$$\mu_1^i = \mu_1^{ii} \tag{18}$$

with $\varphi_1^{(ii)} = 1$.

This equality of chemical potentials yields the LC composition $\varphi_1^{(i)}$ of the isotropic phase. The result of this calculation leads to the binodals of Figure 2.

On the basis of these considerations, the phase diagrams were calculated by taking into account the number of monomer units between two consecutive crosslinks, N_c, and the interaction parameter χ (given in eq. 6), for various network densities and LC E7. Theoretical fits gave us the χ parameter as a function of temperature for each system studied. In all cases α and β were kept constant, according to the Petrovic et al.[18] model; $f = 3$, $N_1 = 1$ and $\varphi_0 = 1$.

Table 1 gathers the different parameters used to calculate the theoretical phase diagrams. A good agreement was observed between the experimental data and the theoretical curves. Below 60°C, a slight shift of the theoretical curves is found for the loosely crosslinked poly (n-ABu/HDDA) system. This can be attributed to the multicomponent nature of E7. Indeed, the solvent E7 is a mixture of four different LCs (5CB, 7CB, 8OCB and 5CT), which might possess each one a different miscibility with the polymer network. Thus, the composition of LC will not be exactly the same in the three zones of the phase diagrams. Such an effect can be related to the preferential solubility[24] of one or more of the LCs towards the polymer network. For example, one can imagine that 5CB has a higher miscibility with

Table 1.
Different parameters used for the theoretical calculations for the different systems.

System		PolyABu	
HDDA (%)	0.5	1.25	2.5
N_c	21	9	6
A	−0.18	−0.19	−0.1
B	224	209	175

the polymer network than 5CT, and consequently the exact composition of E7, which swell the network, will be different from the initial composition.

Conclusion

All phase diagrams present three phases in coexistence: isotropic phase (I), isotropic network + isotropic solvent (I + I), and isotropic network + nematic solvent (I + N). These three phases are delimited with a coexistence curve called binodal. The experimental results show that the phase behavior depends on the degree of crosslinking of the polymer network and temperature. For a loosely crosslinked network, swelling enhances with temperature, but at high crosslinking density, the swelling behavior is not very sensitive to temperature. However, this increase seems to be significant only around the nematic to isotropic transition temperature. Above this temperature, the swelling ratio levels off and tends to remain constant. These results were discussed with a network model according to the Flory–Rehner theory of rubber elasticity, and the Maier–Saupe theory for nematic ordering. A good agreement between theoretical and experimental phase diagrams was observed above T_{NI}. Below this temperature, some discrepancies were observed between theory and experimental findings.

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