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Phase Behavior of Mixtures of Low Molecular Weight Nematic Liquid Crystals and Photochemically Crosslinked Polyacrylates

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Phase Behavior of Mixtures of Low Molecular Weight Nematic Liquid Crystals and Photochemically Crosslinked Polyacrylates

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*The present work deals with theoretical and experimental studies to explore some physical properties of composite materials made of crosslinked poly(*n*-butylacrylate) networks and low molecular weight nematic liquid crystals (LCs). The chemically crosslinked polymers were obtained by exposure to UV radiation of initial solutions composed of a reactive monomer, *n*-butylacrylate, a small amount of a crosslinking agent, hexanedioldiacrylate, and a photoinitiator. To obtain different polymer network densities, the ratio of *n*-butylacrylate to hexanedioldiacrylate was varied prior to exposure to UV irradiation. Immersion in excess LC solvent of the obtained polymer networks allowed for the measurement of the solvent uptake by determining the size increase as function of temperature by polarized optical microscopy. A strong change of the swelling ratio was found around the nematic-isotropic transition temperatures of the two LCs involved, i.e., 4-cyano-4'-*n*-pentylbiphenyl known as 5CB, and the eutectic commercial mixture of cyanoparaphenylene derivatives (E7).*

The obtained swelling data were used to establish phase diagrams in terms of composition and temperature for three different network densities and two LCs. The phase diagrams exhibit upper critical solution temperatures and isotropic network + nematic solvent (I+N), isotropic network + isotropic solvent (I+I), and isotropic swollen network (I) coexistence regions. The results were successfully analyzed within a theoretical model using a combination of the Flory-Rehner theory of isotropic mixing and the Maier-Saupe theory of nematic ordering.

Keywords Flory-Rehner theory; liquid crystals; Maier Saupe theory; phase diagrams; polybutylacrylate

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1. Introduction

The processes of network swelling (and deswelling) in low molecular weight solvents have been the subject of many intensive studies for several decades [1–5]. More than half a century ago, Flory and Rehner [6] developed a theory of rubber elasticity, 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 cross-links 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 [7–9]. A large amount of data is available on these issues in the literature [10–15], but the problem remains a subject of debate, attesting to its complexity and richness.

From a fundamental point of view, these polymer/LC systems are interesting as multi-component mixtures with widely different characteristics. From the point of view of their applications, these systems are useful in various fields such as display technology and smart windows [16–18].

In this work, we emphasize on the investigation of swelling properties of chemically crosslinked polymer networks as functions of network density and temperature. Chemically crosslinked polymer networks were elaborated providing substantial higher mechanical strength and a better thermal stability than linear polymers. Systems made of ultraviolet (UV) cured [19,20] poly(*n*-butylacrylate) and two known low molecular weight LCs, 4-cyano-4'-*n*-pentylbiphenyl (5CB), and the eutectic commercial mixture of cyanoparaphenylene derivatives (E7), were considered. Since UV exposure of *n*-butylacrylate (Abu) as monofunctional monomer leads only to linear chains, a small amount of a crosslinking agent, the difunctional monomer hexanedioldiacrylate (HDDA), was added to the initial mixture. Three different quantities of HDDA, i.e., 0.5, 2.5, and 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 (2.5 and 5 wt-% HDDA). The amount of the photoinitiator was not changed with respect to the monomers (Abu and HDDA). The preparation of well defined polymer networks enables one to avoid difficulties related to the complex polymer network structure often obtained by the crosslinking polymerisation of monomer and LC mixtures. After UV exposure of the initial solutions, the obtained polymer network samples were immersed in 5CB or E7, allowing for the measurement of the solvent uptake by determining the size increase as function of temperature by polarized optical microscopy. The obtained swelling data were used to establish phase diagrams in terms of composition and temperature for three different network densities and two LCs. The data are analyzed with a theoretical formalism based on a combination of the Flory-Rehner theory of the rubber elasticity for isotropic mixture [6] and the Maier-Saupe (MS) theory for nematic ordering [21,22].

2. Experimental

2.1. Materials

The monofunctional monomer was *n*-ABu obtained from Sigma Aldrich, the difunctional cross-linking agent was HDDA supplied by Cray Valley (France), and the

photoinitiator was 2-hydroxy-2-methyl + 1-phenylpropane-1 known as Darocur 1173 from Ciba-Geigy. The anisotropic solvents were 4-cyano-4'-*n*-pentylbiphenyl (5CB) and E7, the first one is a pure nematic LC whereas the other one is an eutectic mixture of cyanoparaphenylene derivatives. Both of them were obtained from Merck KgaA, Darmstadt (Germany). 5CB shows crystalline, nematic and isotropic phases. In the pure state, 5CB presents the following transition temperatures provided by the manufacturer [23]: crystalline-nematic transition temperature $T_{CN} = 23^\circ\text{C}$, and nematic-isotropic transition temperature $T_{NI} = 35.3^\circ\text{C}$. The nematic eutectic LC mixture E7 contains four cyanoparaphenylene derivatives, i.e., 51 weight-percent (wt.-%) 5CB, 25 wt.-% 4-cyano-4'-heptyl-biphenyl (7CB), 16 wt.-% 4-cyano-4'-octyloxybiphenyl (8OCB), and 8 wt.-% 4-cyano-4''-pentyl-p-terphenyl (5CT). This LC mixture exhibits a nematic-isotropic transition temperature at $T_{NI} = 61^\circ\text{C}$.

2.2. Sample Preparation

Mixtures of n-ABu/HDDA/Darocur 1173 were prepared in different weight fractions by varying the quantity of n-ABu and HDDA, keeping the amount of Darocur 1173 constant (n-ABu/HDDA/Darocur 1173 = 99/0.5/0.5 wt.-%, 97/2.5/0.5 wt.-%, and 94.5/5/0.5 wt.-%). The initial mixtures were stirred mechanically for several hours before they were cast in small flat sample holders made of Teflon. The samples were exposed under nitrogen atmosphere to a static UV lamp (Philips TL08) with a wavelength $\lambda = 365\text{ nm}$ and an intensity $I_0 = 1.5\text{ mW/cm}^2$. The exposure time was fixed at 15 min, although 5 min were sufficient to achieve complete conversion of the monomer.

2.3. Techniques and Experimental Procedures

Sub-millimeter-sized samples with nearly rectangular shapes of approximately $500 \times 400\ \mu\text{m}$ and thicknesses of roughly $60\ \mu\text{m}$ were prepared from crosslinked poly (n-ABu/HDDA). These samples were immersed in the LC solvents at room temperature for two days to enable thermodynamic equilibrium state to be reached. Characterization was performed by observations via a polarized optical microscope (POM) in a wide range of temperatures. Micrographs were taken in intervals of 5°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 under consideration. A Linkham heating stage (THMS 600) and temperature controlling unit (TMS 92) were used together with a Leitz polarized optical microscope. For each LC solvent, six different ratios of length (l_1, l_2), width (w_1, w_2) and diagonals (d_1, d_2) (swollen to dry states) were collected as a function of temperature. Equation (1) defines λ , the average of the six ratios of dimensions in the swollen state and the dry state. The value λ represents the cubic root of the swelling ratio Q .

$$\lambda = Q^{1/3} = \frac{1}{6} \left(\frac{\lambda_{l_{1,0}}}{\lambda_{l_1}} + \frac{\lambda_{l_{2,0}}}{\lambda_{l_2}} + \frac{\lambda_{w_{1,0}}}{\lambda_{w_1}} + \frac{\lambda_{w_{2,0}}}{\lambda_{w_2}} + \frac{\lambda_{d_{1,0}}}{\lambda_{d_1}} + \frac{\lambda_{d_{2,0}}}{\lambda_{d_2}} \right) \quad (1)$$

For each system, several samples were systematically measured and the curves in this work represent averages of results obtained from several samples prepared and analyzed under the same conditions.

3. Theoretical Part

3.1. The Isotropic Binodal

The swelling behaviour of a chemically cross-linked polymer in a low molecular weight solvent depends on the elasticity of the network. According to the Flory-Rehner theory [6], the swelling of such a crosslinked polymer network reaches equilibrium when the osmotic pressure of the low molecular weight solvent molecules promoting swelling is balanced by the elastic forces at the crosslinks. Using this theory in the isotropic state of the systems considered here, one can write the free energy density as a sum of two contributions

$$f^{(i)} = f^{(e)} + f^{(m)} \quad (2)$$

where $f^{(e)}$ is the elastic free energy density given by:

$$f^{(e)} = \frac{3\alpha}{2N_c} \varphi_0^{2/3} \left[\varphi_2^{1/3} - \varphi_2 \right] + \frac{\beta\varphi_2}{N_c} \ln \varphi_2 \quad (3)$$

and the second contribution to the isotropic free energy of equation (2) is given by the free energy density of isotropic mixing:

$$f^{(m)} = \frac{\varphi_1 \ln \varphi_1}{N_1} + \chi \varphi_1 \varphi_2 \quad (4)$$

The subscripts 1 and 2 refer to the LC and the polymer network, respectively. φ_1 and φ_2 are their respective volume fractions. N_c represents the number of segments between crosslinks (or chemical junction point), φ_2 is the volume fraction of the polymer network in the swollen state and φ_0 is the corresponding quantity before crosslinking in the reference (dry) state. α and β are the rubber elasticity parameters and their values are model dependent. Often α is equal to 1 while β is given different values. According to James and Guth [24] $\beta=0$ but Flory [25] suggested $\beta=2/f$ where the functionality of monomers at crosslinks f should not be mixed with the free energy density. This functionality could be equal to 3 or higher. In the limit where the functionality f is infinite, β vanishes and the model of James and Guth is recovered. Here we adopt the expressions suggested by Petrovic *et al.* [26] which were used before to describe the equilibrium phase behavior of crosslinked polymers and LC [27–29]. In this case, the parameters α and β depend on polymer volume fraction according to $\alpha = \frac{f-2+2\varphi_2}{f}$ and $\beta = \frac{2\varphi_2}{f}$.

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

$$\chi = A + \frac{B}{T} \quad (6)$$

where A and B are constants independent of T . They are chosen to obtain the best theoretical fit of the part of the phase diagrams where the isotropic interaction is most significant.

3.2. The Nematic Part

For nematic LC, the small molecules 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 to take into account a contribution due to the nematic interaction which can be described by the Maier-Saupe theory [21,22]. The nematic free energy density is given by

$$f^{(n)} = \varphi_1 \left[-\ln Z + \frac{1}{2} \nu \varphi_1 S^2 \right] \quad (7)$$

The normalized partition function Z is:

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

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

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

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

$$m = \varphi_1 \nu S \quad (10)$$

where ν is the Maier-Saupe quadrupole interaction parameter,

$$\nu = 4.54 \frac{T_{NI}}{T} \quad (11)$$

T_{NI} is the nematic-isotropic transition temperature of the LC.

The nematic order parameter S is

$$S = \frac{1}{2} [3 \langle \cos^2 \theta \rangle - 1] \quad (12)$$

$\langle \dots \rangle$ denotes the average with respect to the orientation distribution function; and θ is the angle between a reference axis and the director of the LC.

4. Results

4.1. Evaluation of the Solvent Uptake

Figure 1 represents the evolution of the polymer network swelling as a function of temperature for the E7 solvent at three different network densities. Consistent results were obtained for a large number of duplicate samples prepared under the same conditions and analyzed by microscopy measurements. The transition temperature T_{NI} of the E7 (60°C) is visualized on this graph by a vertical dotted line.

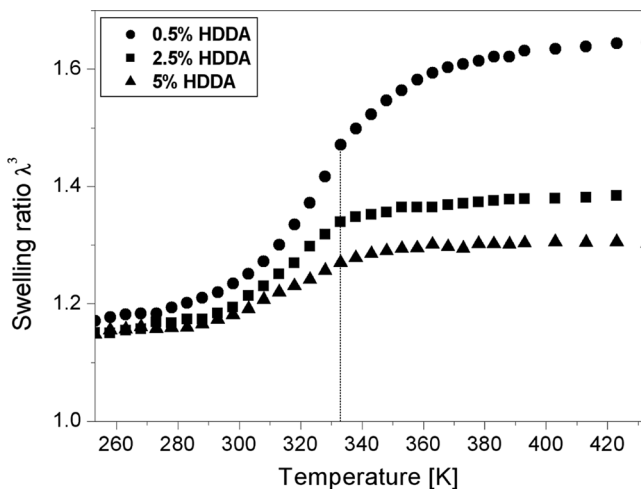


Figure 1. Swelling behavior of crosslinked poly (n-ABu/HDDA) networks in the LC solvent E7 as functions of temperature and crosslinking density of the polymer network. The dotted line corresponds to the nematic-isotropic transition temperature of E7.

Figure 1 shows two modes of quite distinct swellings. If the temperature is lower than T_{NI} where a nematic phase occurs, the effect of swelling is rather weak. On the other hand, if the temperature is higher than T_{NI} , the highly crosslinked polymer networks exhibit only slight changes whereas the effect of temperature is quite high for the loosely crosslinked network (0.5 wt.-%). A strong increase of the swelling ratio of all networks considered here was found in the vicinity of the T_{NI} of the LCs. At high temperatures, plateau-like swelling values were observed except for the 0.5 wt.-% HDDA/PABu/E7 system. This loosely crosslinked network still exhibits further solvent uptake even at higher temperatures.

The evolution of the swelling ratio of the PABu networks in pure LC 5CB as function of temperature is displayed in Figure 2, using identically prepared samples as described before with three network densities: 0.5, 2.5, et 5 wt.-% HDDA. The same general behavior was found compared to the case where the solvent is E7 (Fig. 1). Indeed, the nematic-isotropic transition temperature of 5CB (35°C) determines the beginning point of the strong increase of the swelling ratio. The loosely crosslinked network was more affected by the variation of temperature than the highly crosslinked polymers. The variation of the gel volume around T_{NI} of 5CB is also controlled by the network densities.

4.2. Phase Diagrams

Figures 3 and 4 show data of poly (ABu/HDDA)/E7 from Figure 1 and poly (ABu/HDDA)/5CB from Figure 2, presented as phase diagrams in a composition/temperature frame. The symbols are experimental POM data and the LC volume fraction φ_{LC} was calculated from $\varphi_{LC} = 1 - (1/\lambda^3)$. The phase diagrams exhibit biphasic regions of isotropic polymer network and nematic LC in the lower right hand side of Figures 3 and 4. At higher temperatures, the LCs present an isotropic phase. Consequently, a biphasic region of isotropic polymer network and isotropic

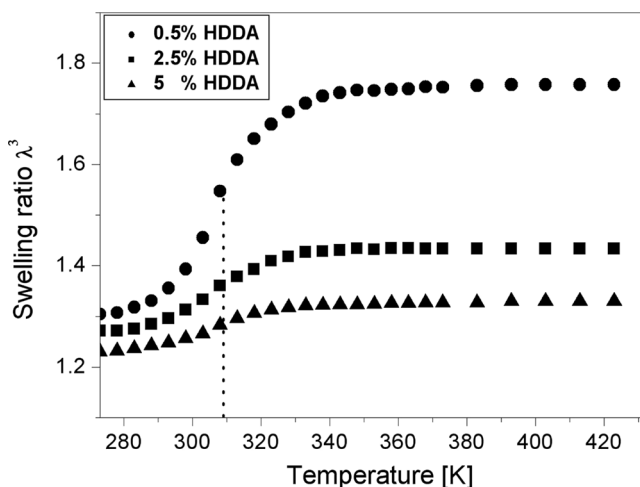


Figure 2. Swelling behavior of crosslinked poly (n-ABu/HDDA) networks in the LC solvent 5CB as functions of temperature and crosslinking density of the polymer network. The dotted line corresponds to the nematic-isotropic transition temperature of 5CB.

LC can be found in the upper right hand side of the diagrams. All systems show a large region on the left hand side, where a single isotropic phase appears at low LC volume fractions.

The solid lines in Figures 3 and 4 represent the isotropic binodals from theoretical fitting obtained starting from the combination of the theories of Flory-Rehner and Maier-Saupe. Indeed, equilibrium between two coexisting phases is generally determined by the equality of chemical potentials of each component in the two phases. For the nematic LC/crosslinked polymer system, we have a phase of swollen

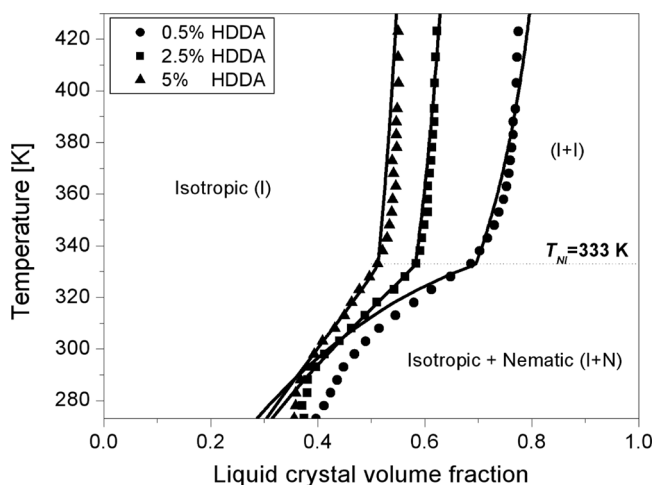


Figure 3. Equilibrium phase diagram of poly (n-ABu/HDDA)/E7 systems for different network densities. The symbols are experimental data obtained by POM using the data from Figure 1, and the solid lines represent theoretical calculations using the parameters from Table 1.

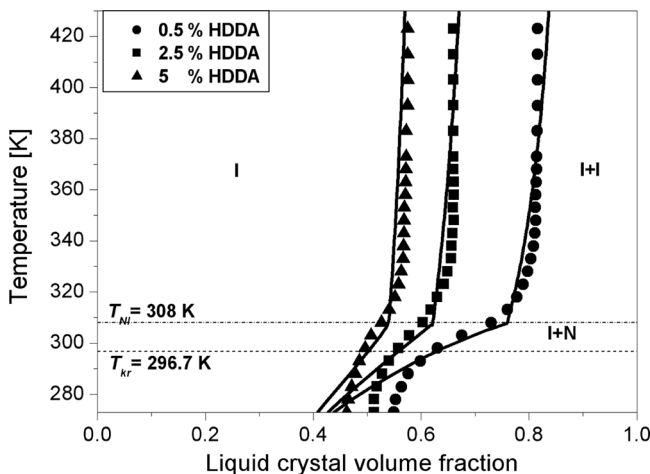


Figure 4. Equilibrium phase diagram of poly (n-ABu/HDDA)/5CB systems for different network densities. The symbols are experimental data obtained by POM using the data from Figure 2, and the solid lines represent theoretical calculations using the parameters from Table 2.

network or isotropic gel (phase α) in equilibrium with a phase of the pure solvent (Phase β). Thus the equilibrium is reached when equating the chemical potentials in the two phases (i.e. $\varphi_2^{(\beta)} = 0$ and $\mu_1^{(\alpha)} = \mu_1^{(\beta)} = 0$). The swelling of the network by the LC can occur either in the nematic phase ($T < T_{NI}$, and $\varphi_1 < \varphi_{NI}$) or in the isotropic phase ($T > T_{NI}$, and $\varphi_1 > \varphi_{NI}$). The quantity $\varphi_{NI} = T/T_{NI}$ represents the critical LC volume fraction below which nematic ordering does not exist.

The isotropic binodal calculation is thus obtained by differentiating the free energy with respect to the number of molecules which can be written in terms of f and its derivative with respect to φ_2 :

$$\mu_1^{(i)} = f^{(i)} - \varphi_2 \frac{df^{(i)}}{d\varphi_2} \quad (13)$$

$$\mu_2^{(i)} = f^{(i)} - \varphi_1 \frac{df^{(i)}}{d\varphi_1} \quad (14)$$

The chemical potentials of the constituents should be balanced in equilibrium according to the equation:

$$\begin{cases} \mu_1^{(\alpha)} = \mu_1^{(\beta)} \\ \mu_2^{(\alpha)} = \mu_2^{(\beta)} \end{cases} \quad (15)$$

In the phase α , the condition $\varphi_1^{(\alpha)} = \varphi_1^{(\beta)}$ is set. Similarly, in the phase β the condition is $\varphi_1^{(\beta)} = 1; \varphi_2^{(\beta)} = 0$. $\varphi_2^{(\beta)} = 0$ implies that the network cannot be dissolved in the LC solvent.

On the basis of these considerations, the phase diagrams were calculated taking into account the number of monomers between two consecutive crosslinks, N_c , and

Table 1. Results from theoretical calculations from Flory Rehner and Maier Saupe theories for Poly (n-ABu/HDDA)/E7 systems corresponding to different polymer network densities

HDDA (%)	0.5	2.5	5
N_c	20	5	3
A	-0.21	-0.08	-0.07
B	234	145	124

the interaction parameters χ , for various network densities and different LCs used. Theoretical fits gave us the χ parameter as a function of temperature for each system studied. In all cases α and β were kept according to $\varphi_2, f=3, N_I=1$ and $\varphi_0=1$. The results of the fitting procedures are given in Tables 1 and 2 for the both systems considering poly (n-ABu/HDDA)/E7 and poly (n-ABu/HDDA)/5CB.

Generally, a good agreement between theory and experiments was obtained in a certain range of temperature (Fig. 3 and Fig. 4). Note the emergence of the miscibility gap (I + N), whereby a swollen isotropic network coexisted with a pure nematic LC phase below T_{NI} . This transition temperature was not the same for E7 and 5CB, meaning that the region (I + N) was wider in the first case. The remarkable feature in comparison with isotropic solvents was the sudden change of the slope at T_{NI} due to the nematic term in the free energy density.

Figure 4 shows particularly for the highly crosslinked poly (n-ABu/HDDA)/5CB system, that the experimental points are likely to move away from the theoretical curves below 23°C. One should keep in mind that a pure 5CB phase can undergo crystallization processes below this temperature; which could explain this deviation. Anyway, the combination of Flory-Rehner and Maier Saupe theories allow to consider only isotropic and nematic phase transitions [21,22,30].

However in the case of E7 (Fig. 3), this shift is more pronounced for the loosely crosslinked poly (n-ABu/HDDA) system at temperatures below T_{NI} . Additional phase separation phenomena due to the four-component LC blend E7 could be a possible reason for this effect. Indeed, each of its components can present different miscibility towards the polymer networks. An attempt was made earlier by the authors to qualify and quantify these phase separation effects on linear PABu/E7 mixtures [31].

Table 2. Results from theoretical calculations from Flory Rehner and Maier Saupe theories for Poly (n-ABu/HDDA)/5CB systems corresponding to different polymer network densities

HDDA (%)	0.5	2.5	5
N_c	20	6	3
A	-0.3	-0.04	-0.04
B	215	117	85

5. Conclusions

Experimental phase diagrams were obtained from the swelling curves of chemically crosslinked PABu networks in the pure LC 5CB and in the eutectic LC mixture E7. These phase diagrams show clearly three different regions including nematic + isotropic and isotropic + isotropic biphasic regions, and a region exhibiting a single isotropic phase. A strong dependence of the phase behaviour on polymer network density was observed, particularly around the nematic-isotropic transition temperatures. The rationalization of the experimental results according to the combination of Flory-Rehner theory of rubber elasticity and Maier Saupe theory for nematic ordering led to the interaction parameter χ for all systems investigated. The theoretical analysis shows generally a good agreement with the experimental data. These results are particularly useful for the establishment of a link between the swelling behaviour of crosslinked polymer networks in LC solvents, the rubber elasticity of the networks, and the understanding of complex phase separated systems like polymer dispersed liquid crystals.

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