

Phase Behavior of Poly(*n*-butyl acrylate) and Poly(2-ethylhexyl acrylate) in Nematic Liquid Crystal E7

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Summary: This paper reports on the phase behavior of photochemically crosslinked poly(*n*-butyl acrylate) (PABu) and poly(2-ethylhexyl acrylate) (PEHA) networks in a nematic liquid crystal (LC) solvent. The swelling properties of these networks were studied as a function of temperature using a low molecular weight LC (LMWLC), which is an eutectic mixture of cyanoparaphenylenes named E7. To obtain different polymer network densities, the ratio of the reactive monomers ABu (or EHA) to the crosslinking agent hexanedioldiacrylate (HDDA) was varied prior to polymerization/crosslinking reactions. Immersion of these networks in an excess of LC solvent allowed for the measurement of size increase by polarizing optical microscopy in terms of temperature. Diameter ratios were calculated considering swollen to dry network states of the samples. The uptake of LMWLC inside the network preferentially takes place around the nematic to isotropic transition temperature of the solvent. Phase diagrams in the concentration-temperature framework were given and discussed as a function of crosslinking degree of the polymer network and temperature and phase behavior of the solvent.

Keywords: crosslinking; density; homopolymerization; phase behavior; phase diagram; swelling

Introduction

The process of network swelling and deswelling in low molecular weight liquid crystal (LMWLC) solvents has been the subject of many intensive studies for several decades.^[1–6] More than half a century ago, Flory and Rehner^[7] 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 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.^[8–10] A large amount of data is available on these issues in the literature,^[11–16] but the problem remains a subject of debate, attesting to its complexity and richness. A fundamental theoretical work on polymer networks in anisotropic solvents was established by F. Brochard.^[17] Only a few experimental studies are focused on the swelling behavior using LC compounds.^[18–24]

The phase behavior and swelling properties of two selected well-defined polymer networks in LMWLC will be discussed in this work. The conditions of preparation, solvent quality, temperature, and crosslinking composition control, to some extent, the elasticity of the network, the presence of entanglements, and trapped

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defects.^[7,25–26] These problems are important when dealing with polymer dispersed liquid crystal (PDLC) materials.^[27–30] The preparation of well-defined polymer networks enables us to avoid difficulties related to the complex polymer network structure often obtained by the crosslinking polymerization of monomer and LC mixtures.^[31–33] Furthermore, sensitivity to parameters such as temperature and composition during crosslinking, can be enhanced.

The effect of swelling on a selected photochemically crosslinked poly(*n*-butyl acrylate/hexanedioldiacrylate) network abbreviated as poly(ABu/HDDA), was examined in detail in ref.^[34] The phase diagrams were achieved as function of temperature and composition for several isotropic solvents, such as methanol, acetone, cyclohexane, and toluene. The uptake of methanol was very low, whereas the degree of swelling for toluene reached a maximum at different temperatures. Some preliminary results obtained for a nematic LC, the eutectic mixture E7, were considered for comparison to those of isotropic solvents.

In the present work, a special emphasis was paid to the investigation of the phase behavior of polymer network/LC systems by dissolving the elaborated chemically crosslinked polymer networks in LMWLC, and following the solvent uptake as function of temperature and crosslinking degree of the network. Networks were prepared via polymerization and crosslinking of initial solutions made up of the reactive monomer butyl acrylate (ABu) (or ethylhexyl acrylate (EHA)), a crosslinker (HDDA), and a photoinitiator (Darocur 1173) by UV radiation. The concentrations of ABu (or EHA) and HDDA were varied in a wide range of composition in order to obtain different network densities, whereas the amount of the photoinitiator was not changed with respect to the monomers. A static UV lamp with a curing process under nitrogen atmosphere was used, and the UV-exposure time was fixed in order to reach complete conversion of the reactive acrylic functions.

The obtained polymer network samples were immersed in LC E7, and the swelling behavior was investigated as a function of temperature and crosslinking density. Changes in the sample sizes from dry to swollen states were measured via optical microscopy for samples in the sub-millimeter size, which is particularly suitable in the case of polymer/LC blends.

Experimental Part

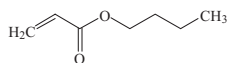
Materials

Chemical structures of the monofunctional monomers ABu and EHA, the difunctional crosslinker HDDA, and the photoinitiator Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propane-1) are given in Figure 1a. ABu and EHA were obtained from Sigma Aldrich, and Darocur 1173 from Ciba-Geigy, Rueil Malmaison (France), whereas HDDA was donated by Cray Valley (France). The eutectic LC mixture E7 was purchased from Merck KGaA, Darmstadt, Germany. E7 exhibits a single nematic-isotropic transition temperature $T_{NI} = 61^{\circ}\text{C}$ and contains 51 weight % (wt.%) of 4-cyano-4'-pentylbiphenyl (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). The chemical structures of LC components are given in Figure 1b. E7 exhibits a frozen nematic phase below -61°C , a nematic phase between -61°C and 61°C , and becomes isotropic above 61°C .

Sample Preparation

Mixtures of ABu/HDDA/Darocur 1173 and EHA/HDDA/Darocur 1173 were prepared in different weight fractions by varying the quantity of ABu (or EHA) 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 some hours before they were cast in small flat sample holders. The samples were exposed to UV radiation under nitrogen atmosphere, using

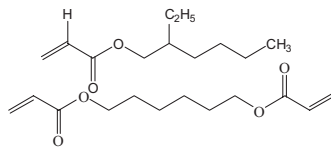
(a)

Monomer: *n*-butyl acrylate (*n*-ABu)

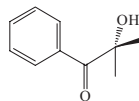
Monomer: 2-ethylhexyl acrylate (2-EHA)

Crosslinker: 1,6-hexanedioldiacrylate

(HDDA)



Photoinitiator: 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Darocur 1173)



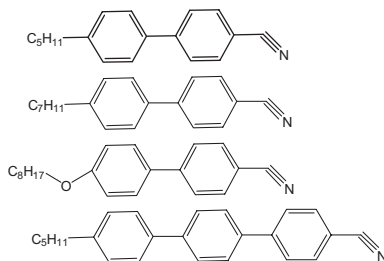
(b)

4-cyano-4'-pentylbiphenyl (5CB): 51 wt. %

4-cyano-4'-heptylbiphenyl (7CB): 25 wt. %

4-cyano-4'-oxyoctylbiphenyl (8OCB): 16 wt. %

4-cyano-4'-pentyl-p-terphenyl (5CT): 8 wt. %

**Figure 1.**

Chemical structures of the initial components of the mixtures (prior to UV curing): (a) 1-ABu, 2-EHA, HDDA, Darocur 1173; and (b) the liquid crystal mixture E7.

Philips TL08 UV lamps with a wavelength $\lambda = 365$ nm and an intensity $I_0 = 1.5$ mW/cm². The exposure time was fixed to 15 min to achieve complete conversion of monomers.

Techniques and Experimental Procedures

Sub-millimeter-sized samples with circular shapes of approximately 500 μ m and thicknesses of roughly 50 μ m were prepared from crosslinked poly(ABu/HDDA) and poly(EHA/HDDA) (see Figure 2 (a) for an example). Characterization was performed by observations using a standard optical microscope 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. Four different ratios of diameters (swollen to dry states) were collected as a function of temperature.

Duplicate samples were used to check for reproducibility and averaged values of the results were used for data analysis.

Results and Discussion

Figure 2 displays micrographs obtained by optical microscopy observations showing the influence of swelling on a PaBu sample prepared with 0.5 wt. % HDDA. The initial state without solvent immersion is shown in Figure 2a. Figure 2b shows the same sample immersed in nematic E7 at room temperature ($T = 20^\circ\text{C}$). One observes a slight increase in the sample size in all directions compared to the initial state. As the ratio between diameter and thickness is rather high, the change in thickness is less important compared to the variations of the diameters.

With regards to temperature effects, a direct evaluation of the solvent uptake and network swelling at different network

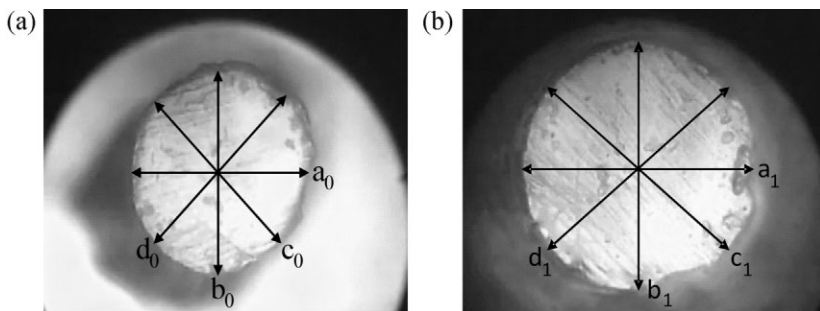


Figure 2.

Representation of different sample diameters of (a) dry and (b) swollen states. The latter shows a PaBu network with 0.5% HDDA in E7.

densities as a function of temperature is given in Figure 3 for PABu/E7 systems. Consistent results were obtained for a large number of duplicate samples prepared under the same conditions and analyzed by microscopy measurements. This graph can be divided into two different zones, following the phase behavior of E7. The first one is located between room temperature and T_{NI} , and the second one is located beyond T_{NI} . Near the room temperature, λ only slightly increases with temperature, and the swelling curves are sensitive to the amount of crosslinker HDDA. Around T_{NI} , λ increases significantly and it is now possible to clearly distinguish the loosely crosslinked networks from the highly crosslinked ones. At T_{NI} , the value of λ for poly(ABu/0.5 wt.% HDDA) is close to 1.47, whereas it is 1.35 for poly(ABu/

2.5 wt.% HDDA). Finally, above T_{NI} , only the loosely crosslinked networks continue to absorb some isotropic E7. This amount decreases if the HDDA content in the initial mixture increases. Above 100°C, all swelling curves tend to reach plateau values corresponding to saturation.

The origin of the phenomenon of important swelling of the polymer networks in the neighborhood of the nematic-isotropic transition temperature can be explained by entropic arguments: This transition from unidirectional LC ordering in the nematic phase to a disordered state in the isotropic state is accompanied by a considerable increase of the mobility of the LC molecules, making it possible to diffuse more easily in the polymeric network.

Figure 4 present the data of poly(ABu/HDDA)/E7 systems as phase diagrams, i.e.,

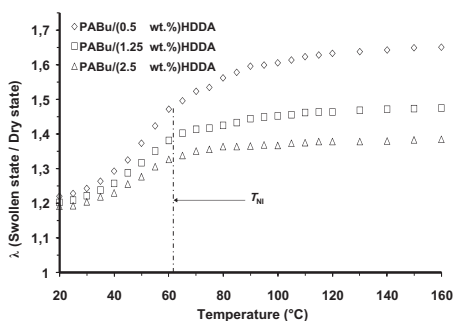


Figure 3.

Swelling behavior of crosslinked poly(ABu/HDDA) networks in the LC solvent E7 in terms of temperature and crosslinker concentration.

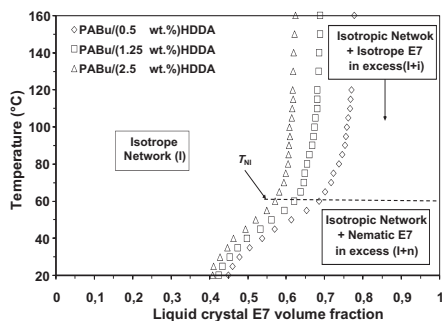


Figure 4.

Phase diagrams of poly(ABu/HDDA)/E7 systems presented in the composition/temperature frame using the same data as in Figure 3.

in a composition/temperature frame. From the optical micrographs shown on Figure 3, 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 using the formula: $\lambda^3 = (l/l_0)^3 = V/V_0$, where V represents the volume in the swollen state, and V_0 the initial volume of the dry sample. The LC volume fraction ϕ_{LC} was calculated from $\phi_{LC} = 1 - (1/\lambda^3)$, where:

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

Q represents the swelling degree in volume of the gel.

All systems show a large region on the left hand side of Figure 4, 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 4.

Under thermodynamic equilibrium conditions, an isotropic polymer network swollen in an anisotropic solvent remains always isotropic, even at temperatures lower than the isotropic-anisotropic (generally nematic) transition temperature of the LC. Detailed studies^[35] showed that quenching of a swollen polymer gel from $T > T_{NI}$ to the nematic state of the solvent leads to the formation of a segregated LC phase inside the polymer matrix. After a certain period of time at $T < T_{NI}$, which can take several weeks, the polymer/solvent system returns to the thermodynamic equilibrium conditions, and the polymer network recovers its isotropic character.

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. The effect of crosslinking density on the miscibility can be deduced from Figure 4, which shows clearly that the system containing 0.5 wt.% HDDA is miscible to a great extent with E7, whereas the 2.5% HDDA system represents a much lower compatibility with the LC. R.Vendamme et al.^[36] observed that the single LC 5CB exhibits a better compatibility with crosslinked poly(ABu/HDDA) than E7, independent of the HDDA content. These findings can be explained by the molecular nature of the components of the LC mixture, E7. Indeed, 5CB presents a higher solubility compared to the other molecular species present in E7, and can therefore diffuse more easily in the network. On the other hand, dense networks show a lower sensitivity to the difference the LC solvent due to the higher incompatibility of the LC with the network.

Figure 5 shows the swelling behavior of poly (EHA/HDDA)/E7 systems which is similar to that of the poly (ABu/HDDA)/E7 system. The variation of the volume of gel around the nematic-isotropic transition of the LC is also controlled by the crosslinking density of the network. One notes that the maximum of swelling is not reached on the given temperature scale, especially

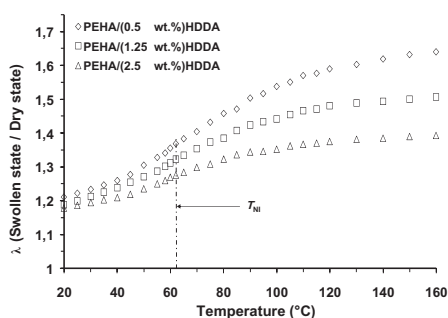


Figure 5. Swelling behavior of crosslinked poly(EHA/HDDA) networks in the LC solvent E7 in terms of temperature and concentration of HDDA.

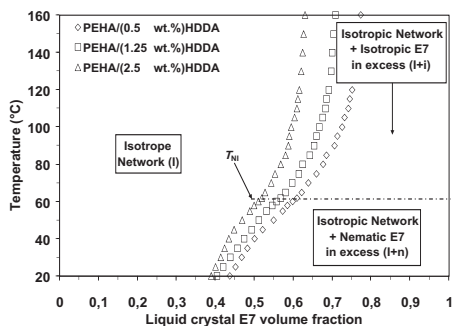


Figure 6.

Phase diagram of poly(EHA/HDDA)/E7 systems presented in the composition/temperature frame using the same data as in Figure 5.

in the case of the poly(EHA/0.5Ywt.% HDDA) system.

Comparing the phase diagrams of poly(ABu/HDDA) (Figure 4) and poly(EHA/HDDA) (Figure 6) networks, one notes that around the LC transition temperature, the volume fractions of the first network are more significant than that of the second. One can conclude that the LC E7 is more miscible in the poly(ABU/HDDA) network.

Conclusion

The equilibrium swelling and phase behaviour of photochemically crosslinked poly(*n*-butyl acrylate) and poly(2-ethylhexyl acrylate) networks in the presence of nematic LC E7 are investigated. The phase behavior depends not only on the degree of crosslinking of the polymer and temperature but also on the nature of solvent and composition. 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, T_{NI} , of the LC. Above this temperature, the swelling ratio levels off and tends to remain constant. The quantitative studies of swelling ratios of these networks enabled us to conclude that the miscibility of poly(ABu/HDDA)/E7 systems is more

important than that of poly(EHA/HDDA)/E7.

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