Equilibrium Phase Diagrams of Interpenetrating Polymer Networks and Liquid Crystals

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Summary: Swelling and deswelling of photochemically crosslinked interpenetrating polymer networks in anisotropic solvents were examined. Phase diagrams were established in terms of composition and temperature using two low-molecular-weight nematic liquid crystals, 4-cyano-4-*n*'-pentylbiphenyl and an eutectic mixture of cyanoparaphenylenes. Networks were formed by ultraviolet curing in the presence of a difunctional monomer and a photoinitiator. Immersion in excess of solvent allowed us to measure the solvent uptake by weight and to determine the size increase by optical microscopy in terms of temperature. We calculated weight and diameter ratios considering the swollen-to-dry network states of the samples.

Keywords: crosslinking; interpenetrating networks (IPN); phase diagrams; photochemistry; swelling

Introduction

Polymer gels have attracted considerable attention from the point of view of various physical and chemical properties.[1–5] For example, hydroelectrolyte gels show a dramatic change in volume in response to change in solvent composition, pH, ionic strength, and temperature. They contract upon application of an electric field. The properties of polymer gels are closely related to their structures and dynamics. Thus, establishment of methods determining structures and dynamics is very important for making reliable polymer gel design and developing new advanced polymer gels.

The combination of two polymer networks of different chemical nature and different physical properties makes it possible to obtain new materials (Interpenetrating Polymer Networks) with interesting performances compared to the homopolymers.[6]

Blends of polymers and low molecular weight liquid crystals (LCs) are the subject of fundamental and technological interest.[7] Polymer Dispersed Liquid Crystals (PDLCs) consisting of micron-sized LC domains droplets dispersed in a polymer matrix have a considerable potential for a variety of opto-electronic applications.[8] From the fundamental point of view, these systems are interesting as multi-component mixtures where the individual species may have quite different thermodynamic properties. Mixing LC molecules with various ordered structures and a polymer matrix gives rise to a variety of phase diagrams from which we can learn a lot on the state of matter and interaction between different species.[9] In recent years, several studies have been reported along these lines, focussing generally on the determination of the clearing temperature versus composition by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and light scattering (LS) techniques.[10–13]

In the present work, an investigation of the phase behavior of interpenetrating polymer network/LC systems as a function

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of temperature is presented. Experimental phase diagrams are established using optical microscopy observations.

Experimental Part

Materials

The chosen monomers for this study, n-butyl-acrylate (99 wt.%) and 2-ethyl-hexylacrylate (98 wt.%) designated (ABu) and (EHA) respectively, were obtained from Aldrich. The crosslinking agent was 1,6-Hexanedioldiacrylate (HDDA), supplied by Cray Valley (France). 2-hydroxy-2-methyl-1-phenyl-propane-1 (Darocur 1173) from Ciba-Geigy was used as a photoinitiator. The anisotropic solvents selected for this study are 4-Cyano-4'-n-pentylbiphenyl (5CB) and E7, an eutectic mixture of LCs, both obtained from Merck KgaA, Darmstadt, Germany.

Sample Preparations

Two sequential IPNs were synthesized. The first one consists of a PABu polymer network (made up from a UV-cured blend of 99 wt.% ABu, 0.5 wt.% HDDA and 0.5 wt.% photoinitiator, swollen up to saturation level in a solution containing 99 wt.% EHA, 0.5 wt.% HDDA, and 0.5 wt.% photoinitiator. The swollen sample was then exposed to a UV lamp (Philips TL08, $\lambda = 350\,\text{nm}$) with intensity $I_0 = 1.5\,\text{mW/cm}^2$, under nitrogen atmosphere. The exposure time was fixed to 15 min although 5 min is sufficient to achieve complete conversion of all monomers in the precursor system. The resulting network will be called IPN1. The second IPN is obtained using the same method as described above, except that at first a PEHA network was formed, which was swollen in a second step by a solution containing ABu, as mentioned before. The resulting network will be called IPN2.

Swelling Behavior

Initially, sub-millimeter-sized samples with nearly rectangular shapes of approximately 50 μm thickness were prepared. We cut out of this film a rectangle of 100 μm × 100 μm approximately. The sample obtained was placed in the measuring cell (Linkham heating stage (THMS 600) and temperature controlling unit (TMS 92)). Characterization was performed by observations via a standard optical microscope in a wide range of temperatures. Micrographs were taken in intervals of 1 to 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. Six different ratios of length, width, and diagonals (swollen to dry states) were collected as a function of temperature (for illustration, see Figure 1a - dry state and Figure 1b - swollen state). Duplicate samples were used to check reproducibility, and averaged values of the results were used in data analysis. Further details for the sample preparation technique are given in references 14-15.

Results and Discussion

Investigations on swelling kinetics were carried out on IPN1, IPN2, PolyEHA, and PolyABu networks. The influence of the crosslinking density and the chemical nature of the solvent on the swelling behavior of the networks was also examined.

Figure 2 represents the evolution of swelling ratio of the interpenetrating polymer networks and their precursory networks according to the temperature in LC 5CB. Thus, these curves constitute a measure of the quantity of 5CB absorbed by the different networks. The nematic-isotropic phase transition temperature of the 5CB solvent ($T_{NI}^{5CB} = 35.3\,^\circ\text{C}$) is visualized on this figure by a vertical dotted line.

Below T_{NI}, the swelling ratio of the polymeric networks is weak, which means that the anisotropic solvent 5CB is a bad solvent in its nematic phase. When the temperature was increased, we note a significant growth of the swelling ratio in

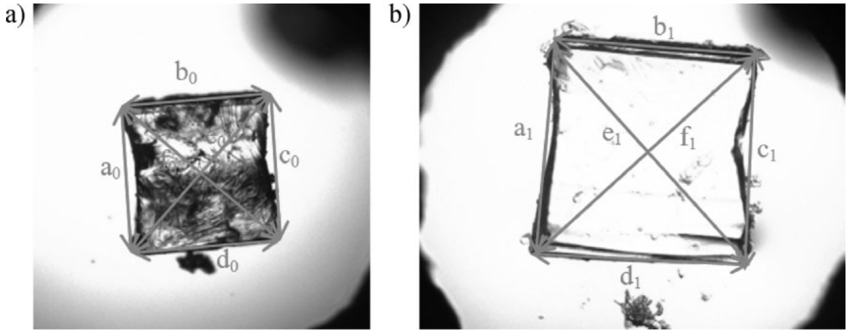

Figure 1.
Typical example of different length ratios of a IPN1 network sample with 0.5% HDDA; a) dry state and b) swollen state in E7.

the vicinity of the nematic-isotropic phase transition temperature, in particular that of IPN2, which increases from 1.21 (34 °C) to 1.31 (36 °C) and that of IPN1, 1.24 (34 °C) to 1.29 (36 °C). After this abrupt increase swelling starts to reach a plateau value at approximately 100 °C. The remarkable swelling enhancement of the IPNs with temperature, in the vicinity of the nematic-isotropic transition temperature of the LC, can be explained as a consequence of polymer-solvent interactions. The miscibility of the LC is strongly reduced below T_{NI} due to entropic reasons, inducing phase separation effects. As a consequence, at $T < T_{\text{NI}}$, the LC molecules are expelled outside the IPNs and the polymer gels shrink considerably.

It should be noted that the gel volume can be controlled by the crosslinking density which varies from the IPN to the simple network. The swelling ratios of the two simple networks (PolyABu and Poly-EHA) are higher by comparing them with those of the IPNs (IPN1 and IPN2). Figure 3 represents the evolution of the swelling ratio of the IPN_S and their precursory networks according to the temperature in the eutectic mixture E7. Analysis of the various curves of this figure allows us to conclude that below the nematic-isotropic phase transition temperature of E7 ($T_{\text{NI}}^{\text{E7}} = 60\,^{\circ}\text{C}$) the swelling ratios of the different systems remain low. As the temperature increases and approaches T_{NI}, a rather strong increase

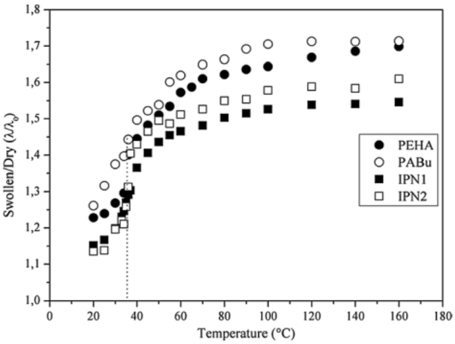

Figure 2.
Swelling properties of crosslinked polymer networks in the LC solvent 5CB as function of temperature. The dotted line represents the nematic-isotropic transition temperature of 5CB.

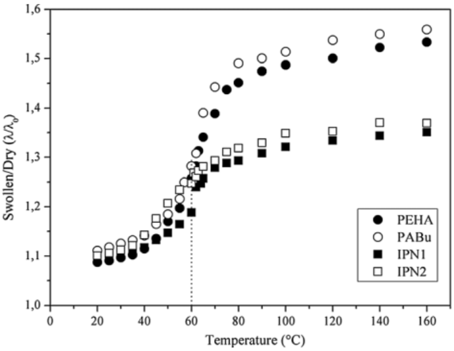

Figure 3.
Swelling properties of crosslinked polymer networks in the LC solvent E7 in terms of temperature. The dotted line represents the nematic-isotropic transition temperature of E7.

is noticed but the absolute values do not exceed 1.4. Above T_{NI}, swelling of the IPN networks is remarkable but does not undergo great modifications compared to that of the precursory networks.

Figure 4 shows the data of polymer network/5CB systems from Figure 2 as phase diagrams, i.e., in a composition/ temperature frame. The volume fractions of the components in thermodynamic equilibrium were obtained from the averaged length, width, and diagonals in the dry (l_0) and the swollen (l) state under the assumptions of isotropic swelling and additivity of volumes following $\lambda^3 = (l/l_0\ )^3 = V/V_0$, where l represents the swelling ratio, V 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 $\varphi_{LC} = 1\text{-}(1/\lambda^3)$. This diagram comprises three characteristic regions; the first one corresponds to the isotropic phase (Phase I), occupying the left part of the diagram.

The region (I + I) which is in the top right of the diagram appears for higher temperatures than T_{NI} and corresponds to an isotropic polymer network swollen in excess of isotropic LC. In the region (I + N), at the right part on the bottom of the diagram, the volume fraction increases quickly according to the temperature. The excess solvent is in the nematic phase because the temperature is now lower than T_{NI}. However the gel remains always isotropic because the isotropic polymer chains prevent the formation of a stable LC phase inside the network. Figure 5 represents the experimental phase diagrams of the IPN/E7 systems and their precursory networks. Three different regions were found where by the isotropic region (Phase I) extends to the left part of the phase diagrams. One finds also the I + N phase which occupies the lower part on the right-hand side of the diagram, which is limited by T_{NI}^{E7}. And finally the region I + I located on the upper right hand side of the phase diagrams which represents an isotropic gel in excess solvent in the isotropic state.

One observes an increase of the LC volume fraction when the crosslinking density decreases i.e PEHA and PaBu polymer networks compared to the IPNs. In region (I + N), the LC volume fraction increases quickly according to the temperature. In region (I + I), the LC volume fraction tends towards a constant value and the difference between the curves representing IPNs and the curves representing the pure polymer networks Poly-EHA and PolyABu becomes more important.

By observing these figures, one notices that the increase in the swelling ratio becomes significant in the vicinity of the nematic-isotropic transition temperature of the LC solvent. Below this temperature where the solvent is in its nematic phase,

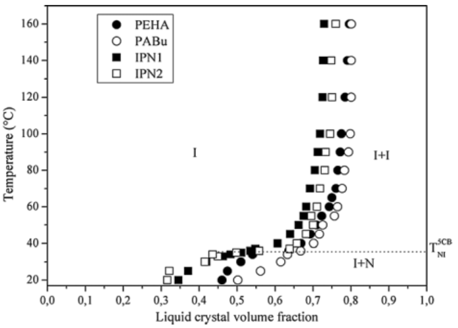

Figure 4.
Phase diagram of polymer network/5CB systems presented in the composition/temperature frame using the data from Figure 2.

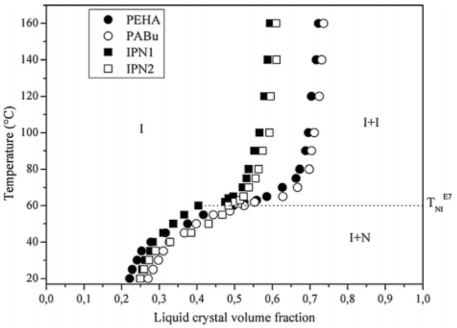

Figure 5.
Phase diagram of polymer network/E7 systems presented in the composition/temperature frame using the same data as in Figure 3.

swelling is rather weak. This can be explained by the impossibility of forming a stable LC phase inside the polymer network. On the other hand, above the T_{NI} of the LC solvent, the two systems are in the isotropic state and miscibility between LC and polymer network becomes more important.

Conclusion

The swelling ratio of various isotropic networks (PolyABu, PolyEHA, IPN1 and IPN2) was determined in two different LC-solvents. The quantitative study of the swelling ratio of these networks enable us to conclude that the miscibility between the polymer networks and solvent was enhanced with decreasing crosslinking density. It also appeared that swelling was more important in the isotropic phase of solvent than in its nematic phase. The change between these two modes results in a clear inflection of the swelling curves in the vicinity of the nematic-isotropic transition temperature of the LC solvent.

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