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Experimental Study on the Swelling Behavior of Polymer Networks in a Nematic Solvent

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Summary: Swelling properties and phase diagrams of binary systems composed of polyacrylate networks and a low molecular mass liquid crystal (LMWLC) have been investigated. The networks were prepared by ultraviolet (UV) irradiation of reactive mixtures including a monomer, a crosslinking agent and a photo-initiator. Poly(n-butylacrylate) networks were prepared using two crosslinking agents: 1,6-hexanedioldiacrylate (HDDA) and a mesogenic acrylic acid 6-(4'-(6-acryloyloxy-hexyloxy)biphenyl-4-yl oxy) hexyl ester (AHBH). The obtained dry polyacrylates were characterized by differential scanning calorimetry, and immersed in an excess of a LMWLC solvent 4-cyano-4'-pentylbiphenyl (5CB), forming polymer gels. A detailed study by polarized optical microscopy allowed to determine the swelling degree of the gels and to follow the phase behavior of the solvent inside the polymer matrix in a wide range of temperature. Swelling data were used to establish the phase diagrams in terms of composition and temperature. It was found that the poly(n-butylacrylate) network obtained with the nematic crosslinking agent show fluctuations in the region of the nematic-isotropic transition temperature of 5CB, probably due to the presence of nematic-nematic coupling effects between the nematic solvent and the nematic moieties of AHBH.

Keywords: liquid crystals; phase diagrams; photopolymerization; polyacrylate networks; swelling

Introduction

Liquid crystals (LCs), polymers and LC polymers are soft condensed matter systems of major technological and scientific interest.[1,2] LC elastomers (LCEs) are polymeric networks containing covalent bound mesogenic groups, in a main-chain, side-chain or mixed main-chain/side-chain configuration.[3,4] Network formation can be induced chemically by copolymerization of reactive monomers with a cross-linking agent, and then the polymerization can be accomplished by adding a photoinitiator to the system and thereby exposing all under UV light.

The process of network swelling in low molecular weight solvents has been subject of intensive studies for several decades,[5,6] and particularly the phase behavior of polymer network/solvent systems possessing nematicity has attracted much attention,[7,8] because the presence of nematic interactions is expected to yield new and interesting aspects on the phase diagrams, which will extend the potential applications of polymer gels to industrial devices. One important scientific development in this field was the experimental observation of the phenomenon of a collapsing gel which consists in a sharp decrease of the gel

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volume during the swelling process, in the presence of a LC solvent.

Currently some experiments relate mainly to the case of isotropic[9–12] and mesogenic networks,[13–16] swollen in nematic solvents without applying any LC orientational effects during sample preparation, like alignment coatings or electric/magnetic fields.

In this investigation a new class of LC polymer gel systems will be considered, where the isotropic monofunctional monomer will be polymerized/crosslinked together with a small amount of a reactive difunctional mesogenic species. To the best of our knowledge, experimental studies concerning the phase behavior of such systems have not been reported before. This study deals particularly with the swelling behavior of such crosslinked systems, giving data to establish phase diagrams in terms of composition and temperature. It would be interesting to address the question of the role of the nematic interactions.

Experimental Part

Materials

The monofunctional monomer n-butyl acrylate (ABu) was obtained from Sigma-Aldrich, the difunctional isotropic crosslinking agent hexanedioldiacrylate (HDDA) was supplied by Cray Valley, the acrylic acid 6-(4'-(6-acryloyloxy-hexyloxy)biphenyl-4-yl oxy) hexyl ester (AHBH) was purchased from Synthon Chemicals; and the photo-initiator 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) was obtained from Ciba-Geigy. The LMWLC solvent (5CB), obtained from Synthon Chemicals, shows crystalline, nematic and isotropic phases. In the pure state, 5CB presents the following transition temperatures determined by POM and DSC techniques: a crystalline-nematic transition at $T_{CrN} = 23°C$, and a nematic-isotropic transition at $T_{NI} = 35.6°C$. The chemical structures of the reactive molecules and the LC are given in Figure 1.

Sample Preparation

Mixtures of ABu/HDDA/Darocur 1173 and ABu/AHBH/Darocur 1173 were prepared using the following proportions by mass 99.0/0.5/0.5%. The initial mixtures were stirred mechanically for several hours before they were put into Teflon holders. These were placed inside a reaction chamber filled with nitrogen and exposed to a UV lamp (Philips TL08) with a wavelength of 365nm and an intensity of 1.5mW/cm^2. The exposure time was fixed to 20min to achieve complete conversion of the monomers.

Thermal Analysis

Calorimetric measurements were carried out on a Perkin Elmer DSC 8000 equipped with an Intracooler system. A rate of 10°C/min during heating and cooling was used in the temperature range from -70 to +120°C. The program consists first in cooling the sample followed by three heating and cooling cycles. Data analysis was carried out on the second heating ramp.

Polarized Optical Microscopy

The thermo-microscopy studies were performed on a Olympus BX41 polarized optical microscope (POM), equipped with a Linkam heating/cooling stage LTS 350 together with a temperature-controlling unit TMS 94. For the swelling measurements, thin sheets of dry polymer networks (thickness approximately 50μm) were sliced with a scalpel, cut into approximately 500 × 500μm squares and placed on the heating/cooling stage, which allowed the thermo-microscopic observation of the samples without being sandwiched between two glass plates. The samples were placed under a nitrogen atmosphere during the experiments.

Ratios of the gel dimensions (swollen/dry states) were measured by means of micrographs taken by a camera installed on the POM, as function of time and temperature, allowing the precise determination of the swelling degree of the gel in a wide range of temperature.

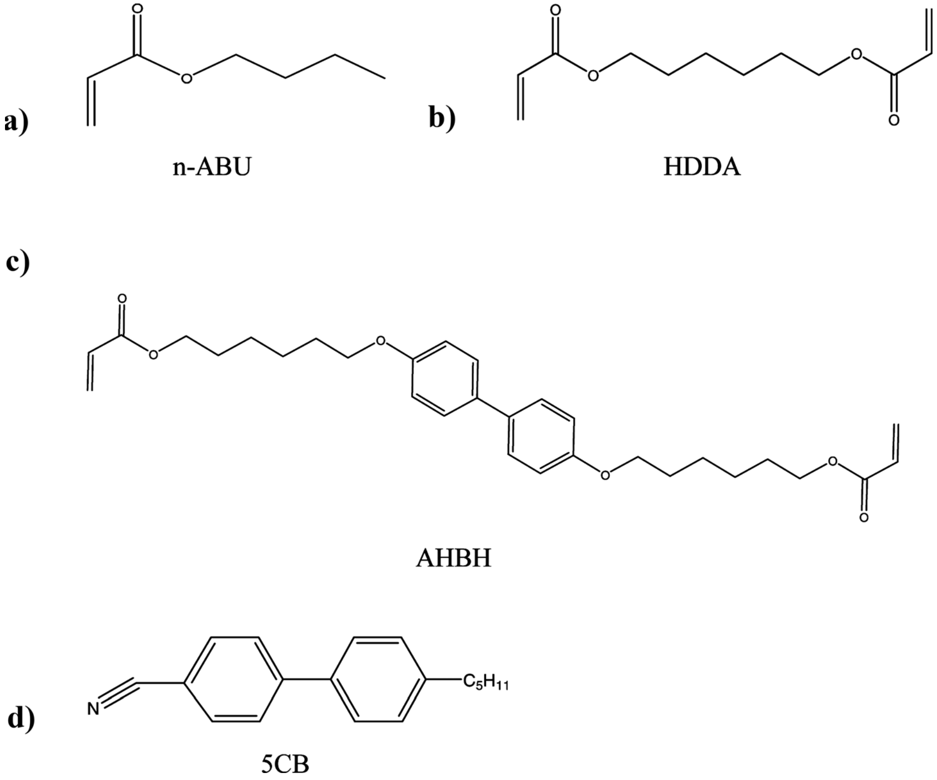

Figure 1.
Molecular structures of (a) n-butyl acrylate (n-ABU), (b) 1,6-hexanediol diacrylate (HDDA), (c) acrylic acid 6-(4'-(6-acryloyloxy-hexyloxy)biphenyl-4-yl oxy)hexyl ester (AHBH), and (d) LMWLC: 4- n-pentyl-4-cyanobiphenyl (5CB).

Swelling Investigation

Micrometer-sized samples with nearly rectangular shapes was employed to shorten the time needed for achieving the equilibrium swelling at each temperature. The swelling kinetics has been observed using different heating rates varying from 5°C/min to 0.05°C/min, in the range of temperatures from 0°C to 100°C. As a result, it was found that heating rates above 0.5°C/min do not allow to obtain reproducible results and to observe the fluctuations around the nematic-isotropic transition temperature of 5CB. Since the swelling ratios obtained by using a heating rate of 0.05°C/min were practically identical with the results obtained from 0.1°C/min, we finally decided to present the latter data. It can thus be assumed that this heating rate is sufficiently slow to achieve the condition of equilibrium swelling at each temperature. These experiments were repeated several times: At least five samples for each of the two polymer networks were evaluated and representative average values were taken into account for data analysis.

From the optical micrographs, the degree of equilibrium swelling (Q) was determined from the ratio of the diameters of the gel in the dry and swollen states. 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. Then, λ was defined as the average of these six ratios. The value λ is in fact the cubic root of the swelling ratio Q:

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

Results and Discussion

Figure 2 shows thermograms from DSC measurements of the nematic crosslinking agent (AHBH) as well as of polymer networks obtained with 0.5 weight-% (wt-%) of AHBH and 0.5 wt-% HDDA, respectively. The reactive monomer AHBH shows two specific transitions, a crystalline-nematic transition at $T = 78°C$, and a small but reproducible nematic-isotropic transition at $T = 82.7°C$. Both polymer networks exhibit a single glass transition temperature around $T = -50°C$, and no other transitions were observed in the explored range of temperatures.

The micrographs obtained by POM observations for the pure crosslinking agent (AHBH) are displayed in Figure 3, showing two phase transitions, crystalline-nematic and nematic isotropic, thus confirming the results obtained from calorimetric measurements.

The swelling behavior of the polymer networks was followed by POM, revealing that the samples always swell homogeneously in all directions, even in the liquid crystalline state. Figure 4 and 5 depict the temperature dependence of the average swelling ratio λ for the acrylate networks including HDDA and AHBH, respectively. The displayed data represent an average of

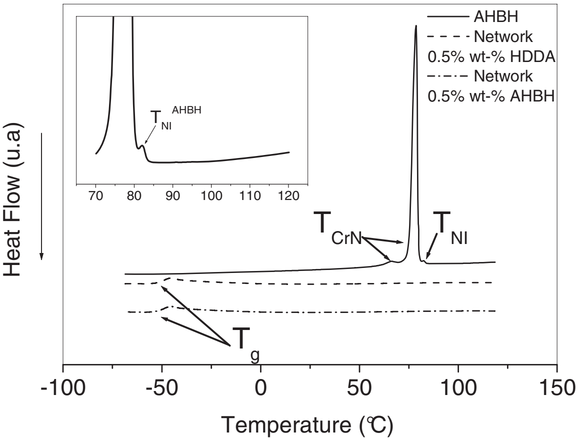

Figure 2.
Representative DSC thermograms of the crosslinking agent AHBH, and of the two polymer networks obtained with 0.5wt-% HDDA and 0.5wt-% AHBH. The inset shows an enlarged view of the AHBH thermogram to highlight the nematic to isotropic transition.

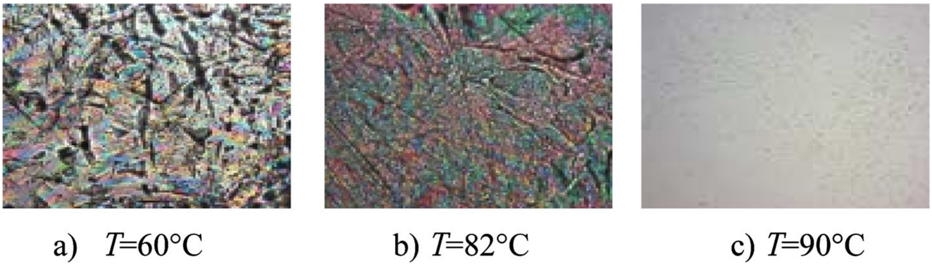
a) T=60°C b) T=82°C c) T=90°C

Figure 3.
Optical micrographs showing the phase behavior of the nematic crosslinking agent AHBH a) crystalline phase at 60°C, b) nematic phase at 82°C, c) isotropic phase at 90°C.

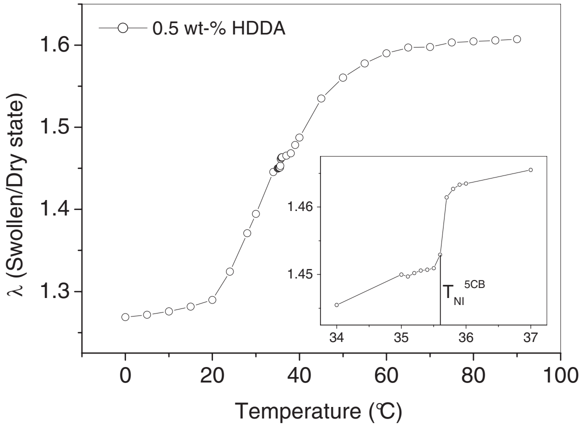

Figure 4.
Evolution of the swelling ratio of a representative sample of a crosslinked PABu network (0.5wt-% HDDA) in the nematic solvent 5CB, according to the temperature. The inset shows an enlarged view around the nematic-isotropic transition temperature of 5CB (T_{NI}).

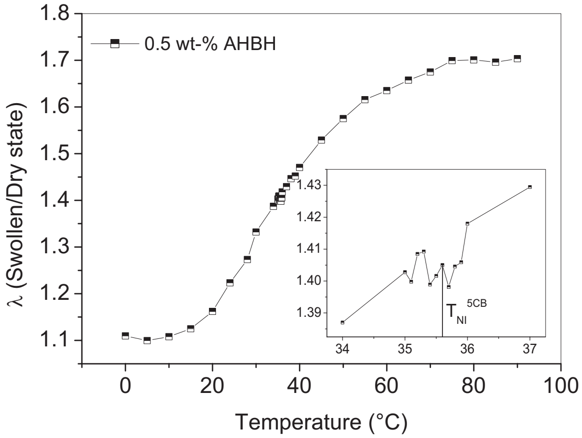

Figure 5.
Evolution of the swelling ratio of a representative sample of a crosslinked PABu network (0.5wt-% AHBH) in the nematic solvent 5CB, according to the temperature. The inset shows an enlarged view around the nematic-isotropic transition temperature of 5CB (T_{NI}).

several size measurements from five distinct samples, which have been prepared and analyzed separately, by applying the same swelling conditions.

It is interesting to note that both systems show essentially the same characteristics for the swelling behavior. For temperatures below the nematic-isotropic transition of the LC solvent, the swelling ratio of both networks is rather weak. When the temperature approaches progressively the nematic-isotropic transition temperature of the solvent, the swelling ratio starts to increase in a more pronounced way.

It should be pointed out that the high accuracy of the measurements, together with an enhanced number of samples investigated, allow to reveal that the polymer networks show a different behavior in the neighborhood of T_{NI} of the LC

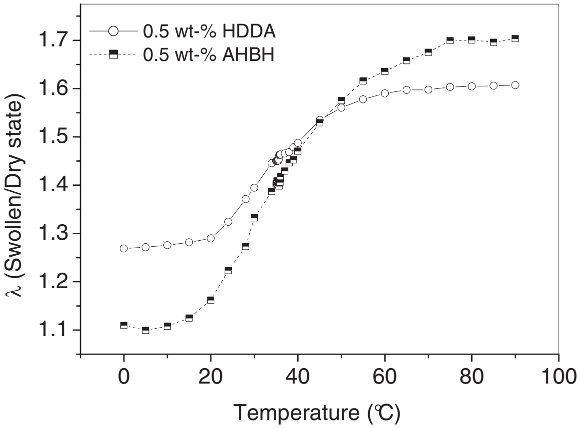

Figure 6.
Superposition of the swelling curves of PABu (0.5wt-% AHBH) and PABu (0.5wt-% HDDA) in the nematic solvent 5CB, according to the temperature.

solvent. From the insets of Figure 4 and 5 it can be deduced that both networks present first a slowing down than a relatively steep increase of the λ ratios. Only the AHBH network shows repeated fluctuations of the swelling values between 35 and 36°C, and even a small tendency for decreasing swelling ratios was noticed. Such a tendency as well as the fluctuations can be explained by a nematic coupling effect between the nematic solvent and the mesogenic parts of the AHBH network.[11–13]

Once the temperature was increased above the nematic-isotropic LC transition, the swelling ratio reaches a plateau value at around 70°C for both polymer networks.

Figure 6 represents the superposition of the swelling curves of the polymer networks containing 0.5wt-% HDDA and 0.5wt-% AHBH, respectively. Below T_{NI} of 5CB, the polymer network containing AHBH shows λ values smaller than those of the HDDA system, but above T_{NI} of 5CB, the swelling of the AHBH system becomes more important and behaves as a loosely crosslinked network reaching a plateau at $\lambda = 1.7$ while the HDDA network reached a value of $\lambda = 1.6$. It is interesting to note that the crossing temperature of these swelling curves lies in the vicinity of T_{NI} of 5CB.

In spite of the fact that identical initial concentrations of the crosslinking agent were used, the effective crosslinking density is lower in the case of the AHBH network compared to the HDDA network. It can be assumed that under the same irradiation conditions, this difference might be due to the chemical nature and the molecular weights of both crosslinking agents. The reactivity of the HDDA molecule is certainly higher than that of AHBH since HDDA contains six flexible CH_2-units between the two reactive acrylic groups, whereas the structure of the AHBH molecule includes two sterically hindered aromatic groups. The molecular weight of AHBH exceeds roughly twice that of HDDA so that the acrylic double bond density of AHBH is two times lower than that of HDDA. These explanations can help to understand that the AHBH polymer network presents a larger difference of the swelling ratios between dry and swollen state, compared to the HDDA network.

Conclusion

The elaboration of samples of photochemically crosslinked acrylate networks, swollen in a nematic LC (5CB), was considered in this work. Thin polymer films were immersed in an excess of 5CB, forming polymer gels. An extended study by POM allowed determining the size evolution of the samples, and the corresponding swelling curves could be deduced for the polymer/ LC systems. Interestingly, the swelling experiments in the nematic solvent for the polymer networks containing mesogenic moieties show fluctuations around the nematic-isotropic transition of the 5CB, probably due to the anisotropic coupling between LC solvent molecules and mesogenic parts of the polymer network. This effect is remarkable compared to the much lower intensity of the fluctuations observed within the isotropic polymer network.

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