Swelling of Acrylic Interpenetrating Polymer Networks in Liquid Crystals

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Summary: The swelling properties of acrylate based polymer networks in anisotropic solvents (LCs) are examined. Two Interpenetrating Polymer Networks (IPNs) consisting of crosslinked poly(ethyl hexyl-acrylate) (PolyEHA) and poly(n butyl-acrylate) (PolyABu) are investigated. The samples are prepared by sequential UV-curing of the monomers in the presence of a cross-linking agent and a photo-initiator. Microscopy observations are used to measure the diameter of the samples in the dry and swollen states and to deduce the kinetics of polymer-solvent swelling for different systems. The theoretical calculations based on the Fick model are presented.

Keywords: anisotropic solvents; fick model; interpenetrating polymer networks (IPN); refractive index; swelling kinetics

Introduction

Mixtures of polymers and liquid crystals constitute an important field in the polymer- material-science, in particular for Polymer Dispersed Liquid Crystals systems (PDLC). These systems are in general thin films which consist of micron-sized droplets of ordered LC molecules dispersed in a polymer matrix. Recently, great importance is given to these systems from a fundamental point of view[1–2] and because of their applications.[3–4]

Interpenetrating Polymer Networks (IPNS) represent an important class of materials: they are combinations of two or more polymer networks.[5–7] This type of polymeric materials makes it possible to obtain new performances, better as those of the starting components. IPNs were employed during the last decades to improve physical properties of homopolymers like impact resistance, flexibility and thermal stability.[8–15] IPNs can be divided in two major categories, depending on their preparation method: sequential and simultaneous IPNs. In the first case, a solution containing the monomers, crosslinking agents and photoinitiators of the second network are swollen into the first polymer network, followed by chemical crosslinking reactions. Simutaneous IPNs called SINs are prepared by mixing different monomers, crosslinking agent and photoinitiator together, which will be simultaneously polymerized.[16–17]

The kinetics of swelling of the interpenetrating polymer networks determines also their potential applications. Bouchaour et al.[18–20] reports on swelling and deswelling of PolyABu networks in different isotropic solvents, allowing to extract the polymer-solvent interaction parameter according to the temperature. Bedjaoui et al.[21] performed a study on the phase diagrams of the mixtures of linear polyABu and the commercial LC mixture E7. Kara Slimane et al.[22] worked on theoretical phase diagrams of systems made up of binary mixtures of linear PEHA and the LCs 5CB and E7. In a previous paper,[23] a fundamental study was presented on the swelling properties of the interpenetrating

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polymer networks in isotropic solvents (methanol, toluene and cyclohexane). It was found that the swelling of the polymer networks depends on the concentration of the cross-linking agent in the network. In this work, the kinetics of swelling of interpenetrating polymer networks in anisotropic solvents (5CB and E7) was examined. The analysis of the results of swelling makes it possible to obtain useful information on polymer/solvent interactions.

Experimental Part

Materials

The chosen monomers for this study, *n-butyl-acrylate* (99%) and *2-ethyl-hexyl-acrylate* (98%) designated (Abu) and (EHA) respectively, were obtained from Aldrich. The crosslinking agent is *1.6-Hexanediol diacrylate* (HDDA), supplied by Cray Valley (France). *2-hydroxy-2-methyl-1-phenyl-propane-1* (DAROCUR 1173) from Ciba-Geigy is used as a photo-initiator. The anisotropic solvents selected for this study are *4-Cyano-4′-n-pentyl-biphenyl* (5CB) and E7, an eutectic mixture of LCs, both obtained from Merck KgaA, Darmstadt, Germany.

Sample Preparations

Two sequential IPNs are 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.% Darocur), swollen in a solution containing 99 wt.% EHA, 0.5 wt.% HDDA, and 0.5 wt.% Darocur. The swollen sample is then exposed to a UV lamp (Philips TL08, $\lambda = 350$ nm) with intensity $I_0 = 1.5$ 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 with the same method 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.

Study of Swelling

After polymerization and unmoulding of samples, they are cut in nearly disk shaped pieces of some millimeters in diameter and a thickness of about 100 μm. The observation of the swelling of IPN network samples in anisotropic solvents was carried out at room temperature using optical microscopy, by recording the evolution of the diameters of the samples as a function of time.

The swelling ratio can be estimated using the following equation:

$$\textit{Swelling ratio} = \left(\frac{D_g - D_i}{D_i}\right) \times 100 \qquad (1)$$

where D_g and D_i are the diameters of the sample in swollen and dry states, respectively.

Results and Discussion

The swelling kinetics were carried out on IPN1, IPN2, PolyEHA, and PolyABu networks. For this purpose, two anisotropic solvents were used, 5CB and E7. The influence of the crosslinking density and the chemical nature of the solvent on the swelling behavior of the networks was also examined.

Figure 1 and 2 represent the swelling kinetics of IPN1 and IPN2 in 5CB and E7 during 24 hours, respectively. In each case, plateau values were obtained after 9 hours of immersion of the sample in the solvent. Figure 1 shows a more important swelling effect in 5CB compared to that in E7. Indeed, a swelling ratio of about 22% was reached after 24 hours of immersion in E7, whereas a plateau value of approximately 35% was found for 5CB. In the case of IPN2 shown in Figure 2, this difference between the swelling behaviour in E7 and 5CB is even much greater. Surprisingly, the plateau value for E7 in Figure 2 was found close to that of Figure 1, but 5CB shows

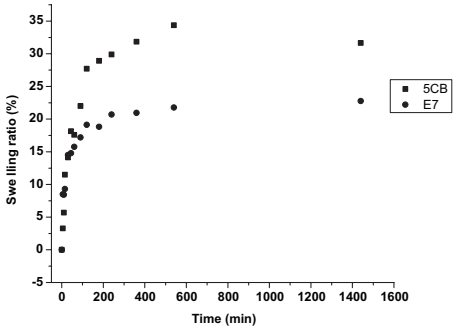

Figure 1.
Kinetics of swelling of IPN1 in anisotropic solvents at $T = 24\ ^{\circ}C$.

nearly a two-fold value by comparing the results from Figure 2 with Figure 1.

Solubility Parameter

One of the most convenient methods to predict the miscibility of polymers with low molecular weight molecules is the determination of the Hildebrand solubility parameter (δ) for the components of the mixture. The solubility parameters were given by the method of Fedors[24] and the results are gathered in Table 1.

The solubility of a polymer P in a solvent S is proportional to $(\delta_P - \delta_s)^2$, where δ_P and δ_s are the solubility parameters of polymer and solvent, respectively. The interest of this method consist to predict the behavior of each network in the chosen anisotropic solvent, as described in Table 2.

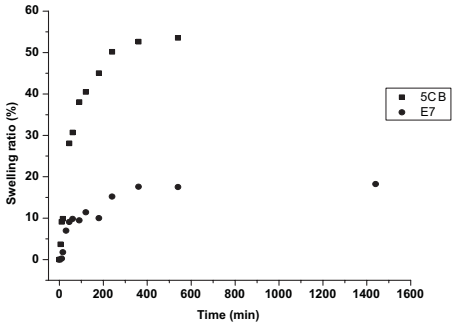

Figure 2.
Kinetics of swelling of IPN2 in anisotropic solvents with $T = 24\ ^{\circ}C$.

Table 1.
Solubility parameters of the components calculated from the method of Fedors. The values marked by (*) were taken from[21] and those of (**) are from.[25]

Component	δ (j$^{1/2}$.cm$^{-3/2}$)
PEHA(0.5 wt.%HDDA)*	17.198
PABu(0.5 wt.%HDDA)*	18.957
IPN1	17.435
IPN2	18.535
5CB**	22.4
E7**	22.2

Qualitative Analysis

The analysis of the swelling data of the networks (IPN1, IPN2, PEHA and PABu) in the LCs 5CB and E7 allows to make the following remarks: In general, networks immersed in 5CB show a larger swelling ratio compared to E7. The variation of the swelling ratio of the two networks IPN1 and IPN2 in 5CB and E7 can be explained by the calculated solubility of the networks in these LCs. Indeed, if the classification given in Table 2 is taken into account, one notices that the PABu network represents the most soluble network in 5CB and E7, followed by IPN2, where the PABu network is dominating, since the initially synthesized PEHA network is swollen in an excess of a mixture containing Abu. Network IPN1 (where the network PEHA is dominating) is less soluble in the LCs compared to IPN2. The pure PEHA network represents the lowest solubility of all networks considered here.

Theoretical Exploitation of the Experimental Results

The swelling kinetics can be rationalized by using the Fick model:

$$\frac{D_t}{D_\infty} = 1 - A\exp(-k_2 t) \qquad (2)$$

Table 2.
The solubility classification of the polymer networks.

	The solubility increases from the left to the right						
5CB:	PEHA	–	IPN1	–	IPN2	–	PABu
E7:	PEHA	–	IPN1	–	IPN2	–	PABu

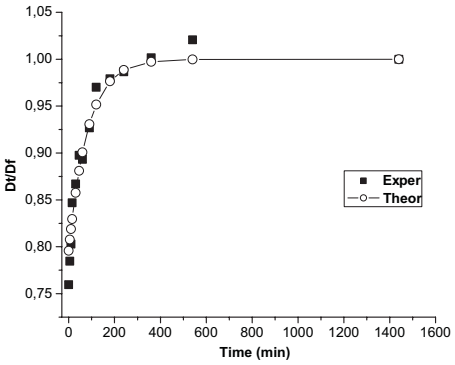

Figure 3.
Experimental and theoretical swelling curves for IPN1 in 5CB.

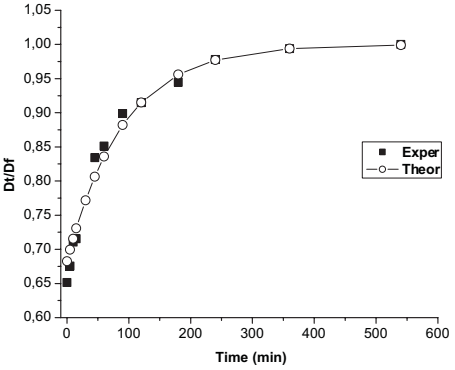

Figure 5.
Experimental and theoretical swelling curves for IPN2 in 5CB.

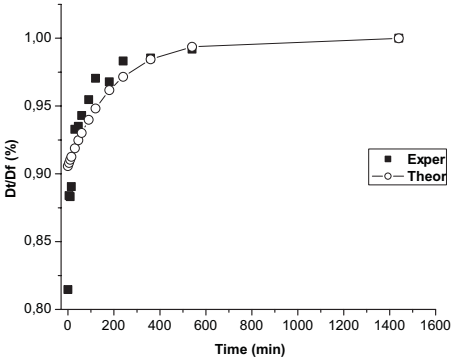

Figure 4.
Experimental and theoretical swelling curves for IPN1 in E7.

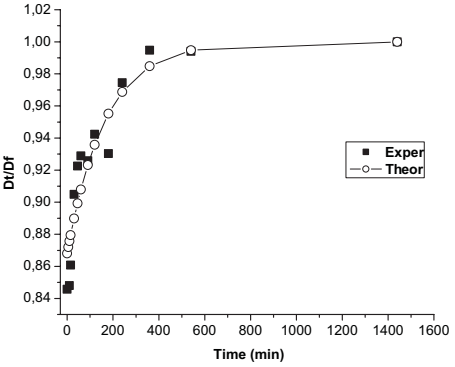

Figure 6.
Experimental and theoretical swelling curves for IPN2 in E7.

where A and k_2 are constants, which can be calculated from the slopes and intercepts of the plots of $\ln(\frac{1-D_t}{D_f})$ versus time t at times greater than those corresponding to $(\frac{D_t}{D_f}) = 0.60$. The values obtained are summarized in Table 3. In general, a good agreement is obtained between theory and experimental data as shown in Figure 3–6.

Table 3.
Parameters k_2 and A for IPN1 and IPN2 in different solvents.

	IPN1		IPN2	
	$k_2(min^{-1})$	A	$k_2(min^{-1})$	A
5CB	0.012	0.2041	0.006	0.1319
E7	0.009	0.1177	0.011	0.3175

Conclusion

In this study, sequential IPNs were prepared from Abu and EHA as starting materials. It was shown that the swelling of these networks did not depend only on the network architecture but also on the nature of solvent. 5CB shows an important rate of swelling compared to E7. The kinetics of swelling allows to deduce solubility parameters and to establish the theoretical curves based on the Fick model.

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