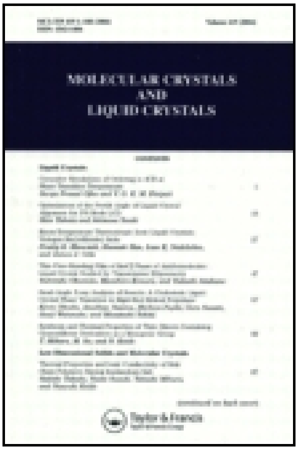

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SWELLING AND DESWELLING OF POLY (n-BUTYLACRYLATE) NETWORKS IN ISOTROPIC AND NEMATIC SOLVENTS

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We report swelling/deswelling data of Poly(n-butyl acrylate) networks in isotropic and anisotropic solvents. The investigated systems are prepared via polymerization induced phase separation processes of initial mixtures composed of a reactive polymer precursor, a cross-linker, a photoinitiator and a low molecular weight solvent by ultraviolet (UV) radiation. A comparison of data obtained from isotropic organic solvents and a low molecular weight nematic liquid crystal is made in terms of temperature and cross-linking density of the network. Hexanediol-diacrylate (HDDA), a di-functional monomer is used as a cross-linker and the conditions of preparation are set in order to obtain well defined model networks. Effects of temperature and composition

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are evaluated by measuring the size via microscopy and the mass of dry and swollen networks. Simple modelling is used to rationalize the data.

Keywords: isotropic and nematic solvents; liquid crystal; networks; optical microscopy; photopolymerization; swelling

INTRODUCTION

Swelling and deswelling properties of networks in isotropic solvents is the subject of a particular attention for decades [1–7]. Long time ago, Flory and Rehner [4,5] suggested a theory of rubber elasticity based on the idea of a swelling equilibrium between the osmotic pressure of solvent favoring swelling and the elastic forces at cross-links opposing network strands extension. Besides Flory-Rehner theory, a variety of other concepts were developed and in particular those based on scaling arguments and blob hypothesis [6]. From the experimental point of view, a significant effort was made [8–9] but the problem still remains a subject of debate in the literature. Novel and interesting applications emerged, some of them are related with the concepts of artificial muscles and responsive gels undergoing changes under external stimuli such as stretching, compression or shear stress [10,11].

Cooling a system that originally is in a stable homogeneous state generates a phase separation phenomenon whereby an equilibrium sets in between a dense network and a pure solvent phase. Swelling experiments and measurement of solvent uptake are still the subject of high interest in the literature in view of the fact that many fundamental questions remain to be answered.

This paper reports data describing swelling and deswelling properties of UV-cured poly(n-butylacrylate) and several low molecular weight solvents including liquid crystal 4-cyano-4′-n-pentyl-biphenyl (5CB). A small amount of hexanedioldiacrylate (HDDA, a di-functional monomer) is added to the initial mixture prior to UV exposure as a cross-linking agent.

It is clear that the conditions of preparation, the solvent quality, temperature and composition at cross-linking control to some extent the elasticity of the network, the presence of entanglements and trapped defects. Therefore, a precise knowledge of these conditions is crucial in any investigation of swelling/deswelling processes. These problems are also important when dealing with polymer dispersed liquid crystals (PDLCs). The question of miscibility arises in the same way whether one deals with a low molecular weight liquid crystal or an isotropic solvent. This is the reason why both cases are considered here to collect information on the swelling and deswelling of network in different solvents. Swelling is analyzed by measuring the mass of the system in dry and swollen states.

This yields the amount of solvent uptake that is quite sensitive to the polymer/solvent interaction. Changes in the sample sizes are also measured via optical microscopy for samples in the sub-millimeter size which is particularly suitable in the case of PDLCs [12–15]. For a lack of space, we focus on the results of 5CB and give a brief comparison with those obtained with standard solvents.

Model networks are prepared according to well established methods using UV-curing technique. This enables us to circumvent difficulties related with the complex network structure and sensitivity to parameters such as temperature and composition at cross-linking.

EXPERIMENTAL PART

Materials

The monomers n-butyl-acrylate (Abu) and 1,6 Hexane-diol-di-acrylate (HDDA) were donated by Cray Valley (France). The photoinitiator used is Darocur 1173 (2-hydroxy-2-methyl + 1-phenyl-propane-1) and the liquid crystal is 4-cyano-4′-n-pentyl-biphenyl (5CB). The results are compared with those of methanol, acetone, THF, toluene and cyclohexane.

Sample Preparation

Mixtures of Abu/HDDA/Darocur 1173 are prepared in the weight fractions 99/0.5/0.5 wt% and exposed to a UV lamp (Philips TL08) having a wavelength $\lambda = 350\,\text{nm}$ and an intensity $I_0 = 1.5\,\text{mW/cm}^2$ under nitrogen atmosphere. The exposure time was fixed at 15 min although 5 min were sufficient to achieve complete conversion of all the monomers in the precursor system. Initially, these systems exhibit a single homogeneous phase. The obtained cross-linked polymer networks were immersed in the liquid crystal or solvent for a period of 12 hours until the swollen gel reached the final equilibrium state at saturation.

Techniques and Experimental Procedures

For isotropic solvents, small (sub-mm sized) and large (cm sized) samples were prepared. In the case of the liquid crystal 5CB only sub-millimeter sized samples were prepared to reduce cost. All samples were nearly disk shaped. The small ones were characterized by microscopy revealing diameters in the range of few mm and thicknesses over 100 μm. Ratios of swollen to dry diameters of those samples were recorded. Large samples of few cm diameter and few mm thickness were characterized both by measuring the mass (nearly 1 g) and microscopy. Ratios of diameters and masses (swollen/dry) were obtained as a function of temperature for all the systems investigated. In each case, duplicate samples were used to check the reproducibility of the results.

RESULTS AND DISCUSSION

Typical results of microscopy showing the extent of swelling of PolyAbu/5CB are given in Figure 1a and b where two temperatures and two concentrations of the cross-linker HDDA are used. The former figure corresponds to the lower concentration of HDDA meaning that the network is loosely cross-linked. If the network is highly cross-linked as in the case of 5 wt.-% HDDA, the effect of temperature is weak even in the presence of the low molar weight LC molecules. Results of the loosely cross-linked network obtained with 0.5 wt.-% HDDA are illustrated in Figure 1b where the effect of temperature is quite high. For example at 25°C one observes nematic droplets dispersed in the polymer matrix whereas at 40°C, few large isotropic droplets are dispersed in the network. This is consistent with the phase diagram of this system established before, showing a miscibility gap at 40°C where two coexisting isotropic phases are found. For a highly cross-linked network (5 wt.-% HDDA), the swelling behavior is similar to that of cyclohexane but if the network is loosely cross-linked (0.5 wt.-% HDDA), the swollen polymer in 5CB is remarkably sensitive

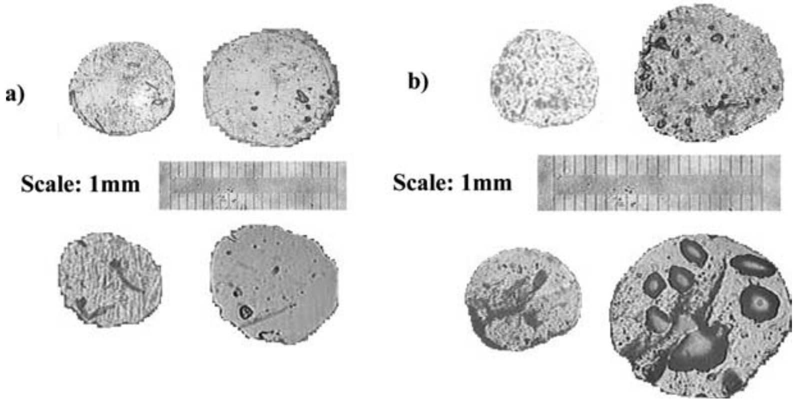

FIGURE 1 Camera pictures made during microscopy observations of poly(n-butylacrylate)/HDDA networks a) Network prepared with 5 wt% HDDA. Dry (top, left) and swollen (top right) networks at 25°C. Dry (bottom, left) and swollen (bottom right) networks at 40°C. b) The same as panel a) for samples prepared with 0.5 wt% HDDA.

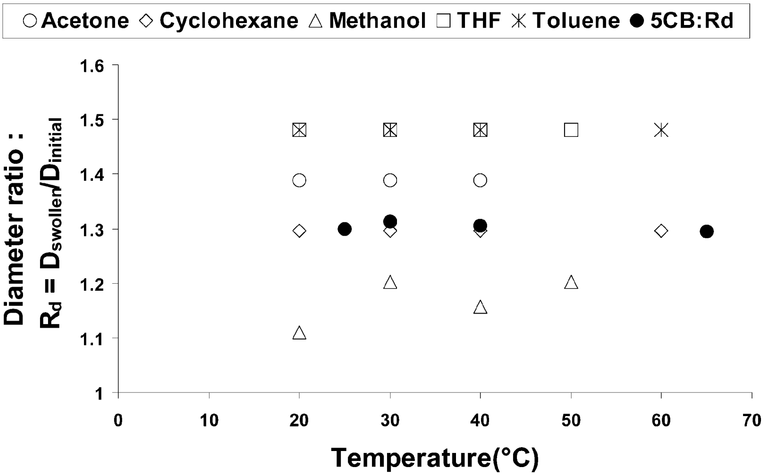

FIGURE 2 Swelling ratios (swollen/dry) of diameters R_D for poly(n-butylacrylate)/5 wt% HDDA/solvent versus temperature. Different symbols are used to distinguish the results for each of the 5 solvents in addition to 5CB as indicated on the figure.

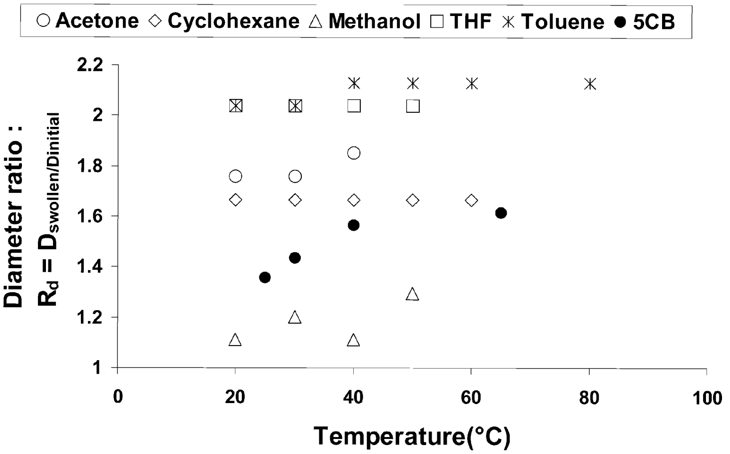

FIGURE 3 Swelling ratios (swollen/dry) of diameters R_D for poly(n-butylacrylate)/0.5 wt% HDDA/solvent versus temperature. Different symbols are used to distinguish the results for each of the 5 solvents in addition to 5CB as indicated on the figure.

to temperature variations. This sensitivity of swelling to the temperature is found in the non solvent methanol whereas other solvents investigated here showed practically no temperature dependence. In order to illustrate these features, we plot in Figures 2 and 3 diameter ratios of swollen to dry networks versus temperature for 0.5 and 5 wt.-% HDDA, respectively. We have collected in these figures the results for the five isotropic solvents cited above together with those of 5CB. This allows us to estimate the extent of miscibility of 5CB and PolyAbu in comparison with the isotropic solvents. Interestingly, Figure 3 reveals a qualitative change at the nematic – isotropic transition temperature T_{NI} (i.e., 35.3°C) of the polymer network swelling in the presence of 5CB. Below this temperature, the diameter ratio increases and tends to level off if the T_{NI} of the liquid crystal is exceeded.

It is known that the ratio of swollen to dry network masses can be several times higher than the ratio of diameters [5,8,16]. It means that large quantities of solvent are admitted inside the network eventhough strand swelling remains moderate. These features are confirmed in the present work for both isotropic and anisotropic solvents such as 5CB.

CONCLUSIONS

The swelling of cross-linked PolyAbu/5CB networks depends not only on the degree of cross-linking and temperature but also on the nature of solvent. By analyzing the ratio of diameters for the dry and swollen samples at two concentrations of the cross-linker, an attempt is made to confirm these dependencies. Several isotropic organic solvents are considered for the sake of comparison with 5CB. At high cross-linking density, 5CB exhibits a similar swelling behavior to cyclohexane and is not very sensitive to temperature. For a loosely cross-linked network, the swelling enhances with temperature. However, this increase seems to be significant only below the nematic to isotropic transition temperature T_{NI} of the liquid crystal. Above this temperature, the swelling ratio levels off and tends to remain constant.

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