

Swelling Behaviour of Isotropic Poly(*n*-butyl acrylate) Networks in Isotropic and Anisotropic Solvents

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Summary: The swelling properties of photochemically crosslinked poly(*n*-butyl acrylate) (PABu) networks in isotropic and anisotropic solvents were investigated experimentally. The purpose of this study was to examine the swelling kinetics of PABu networks in isotropic solvents and to compare the results obtained with those observed in the case of the low molecular weight liquid crystal 4-cyano-4'-*n*-pentyl-biphenyl known as 5CB. The phase diagrams were established in terms of composition and temperature for isotropic solvents, as toluene, acetone, cyclohexane, and methanol, and 5CB, using the plateau values corresponding to equilibrium states of swelling. The polymer networks were prepared via free radical polymerization/crosslinking processes by ultraviolet (UV) radiation of initial mixtures made up from a monomer, a crosslinker, and a photoinitiator. PABu networks with several crosslinking densities were formed using different quantities of difunctional monomer hexanedioldiacrylate (HDDA). Immersion of these networks in excess solvent allows measuring the solvent uptake by determination of the weight in isotropic solvents and diameter in an anisotropic solvent (5CB). Swelling data were rationalized by calculating weight and diameter ratios considering swollen to dry network states of the samples.

Keywords: crosslinking; networks; phase behavior; photopolymerization; swelling

Introduction

The kinetics of the swelling and deswelling of an elastic body is a fundamental problem in classical physics. Gels, consisting of an elastic crosslinked polymer network and a fluid which fills the interstitial space of the network, provide an excellent system to study this fundamental problem.^[1–9] In particular, Flory and Rehner^[3] proposed 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 crosslinks opposing network strands extension. Dynamics of gel swelling and deswelling were intensively studied by Tanaka et al.^[10–12] who developed a theoretical formalism describing the gel dynamics. This approach and extensions of this theory^[13–17] were later successfully used to rationalize experimental data from swollen gels. Swelling properties of responsive gels are among the themes that retain most attention nowadays.^[7,9,18–20] The present work can be viewed as part of the systematic studies to explore the physical properties of composite materials made of polymers in presence of organic solvents and low molecular weight liquid crystals (LCs) such as Polymer Dispersed Liquid Crystals (PDLs).^[21,22] Systems made of UV-cured crosslinked poly(*n*-Butyl-Acrylate) (PABu) networks were considered. A small amount of hexanedioldiacrylate (HDDA, a difunc-

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tional monomer) was added to the initial mixture prior to UV exposure as a cross-linking agent.

The conditions of preparation, the solvent quality, temperature and composition 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 processes. The question of miscibility arises in the same way whether one deals with a low molecular weight LC or an isotropic solvent. This is the reason why both cases were considered here to collect information on the swelling of PABu networks in different solvents. To analyse the swelling behavior, samples from isotropic solvents were characterized by difference of weight from swollen to dry state, whereas optical microscopy was used to follow the evolution of sample sizes in the case of LC as solvent.

Experimental Part

Materials

The monofunctional monomer n-Butyl-Acrylate, designated ABu, was obtained from Aldrich and the difunctional cross-linking agent 1,6-hexanedioldiacrylate, designated HDDA, was supplied by Cray Valley (France). To initiate the reaction of free radical photopolymerization, we used 2-hydroxy-2-methyl-1-phenyl-propane-1 (Darocur 1173, Ciba-Geigy). Methanol, acetone, cyclohexane and toluene of high purity (>99%, Sigma Aldrich) were employed as received. The LC was

4-cyano-4'-n-pentyl-biphenyl, designated as 5CB (Merck KGaA, Darmstadt, Germany). 5CB exhibits a crystalline phase below 23 °C, a nematic phase between 23 °C and 35.3 °C, and becomes isotropic above 35.3 °C. The chemical structures of the different components are given in Figure 1.

Sample Preparation

Blends of ABu/HDDA/Darocur 1173 were prepared in different weight fractions by varying the quantity of ABu and HDDA keeping the amount of the photoinitiator constant (ABu/HDDA/Darocur 1173 = 99.4/0.1/0.5 wt.%, 99/0.5/0.5 wt.%, 98.25/1.25/0.5 wt.%, and 97/2.5/0.5 wt.%). These initial mixtures were stirred mechanically for some hours before they were cast in small flat sample holders, exhibiting a single homogeneous phase. The samples were exposed to UV radiation under nitrogen atmosphere, using Philips TL08 UV lamps exhibiting a wavelength $\lambda = 365$ nm and an intensity $I_0 = 1.5$ mW/cm². The exposure time was fixed at 15 min to achieve complete conversion of all monomers in the precursor system.^[23] The obtained optically transparent crosslinked polymer networks were immersed in an excess of organic solvent or LC at different temperatures.

Techniques and Experimental Procedures

Two series of samples with disc-like shapes were prepared. The first series exhibited rather large diameters in the order of 3 cm, which were characterized by weight measurements (initial state: 1 g). The second series corresponded to small samples destined for optical microscopy

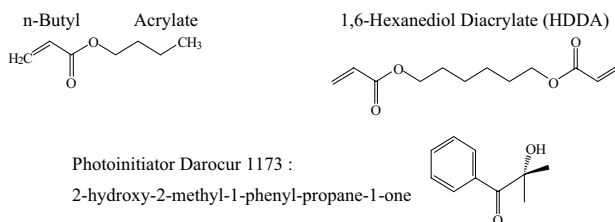


Figure 1.

Chemical structures of the components of the initial mixtures (prior to UV curing).

observations, possessing diameters in the range of 1–2 mm and thicknesses near 150 μm . For each solvent, the ratios of diameters and weights (swollen to dry states) were collected as a function of temperature. Four duplicate samples were considered systematically to check for reproducibility and averaged values of the results were used in data analysis.

Results and Discussion

Swelling studies were performed to investigate the time-dependent swelling behavior of PABu networks. Swelling behavior in terms of the swelling ratio τ in the case of an isotropic solvent is given as:

$$\tau = 100 \cdot (M_t - M_0) / M_0 \quad (1)$$

where M_t represents the swollen sample weight at time t and M_0 corresponds to the initial dry sample.

In case of optical microscopy, this ratio reads as:

$$\tau' = 100 \cdot (D_t - D_0) / D_0 \quad (2)$$

where D_t represents the swollen sample diameter at time t and D_0 corresponds to the initial dry sample.

Figure 2 shows experimental swelling curves of the PABu/0.1 wt.% HDDA networks at room temperature ($T = 18^\circ\text{C}$) in methanol, cyclohexane, acetone and toluene. A fast rise of the swelling ratio was found at the beginning of the kinetics experiments followed by a plateau characterized by constant swelling ratios. One clearly observes a strong swelling behavior from the curve corresponding to PABu network in toluene.

In the case of methanol, the plateau is reached quickly, which corresponds to a fast saturation of the network. One can notice that toluene is a good solvent for PABu networks, while methanol is a bad one. Acetone presents an intermediate swelling as compared to toluene and cyclohexane. Swelling kinetics in cyclohexane is slower than that in toluene and acetone, and its plateau value is located between those corresponding to acetone and methanol.

In order to illustrate the influence of the ratio of crosslinking on the swelling kinetics in toluene at room temperature ($T = 18^\circ\text{C}$), Figure 3 shows the corresponding experimental curves as a function of this parameter. Consistent results were obtained for a large number of duplicate samples

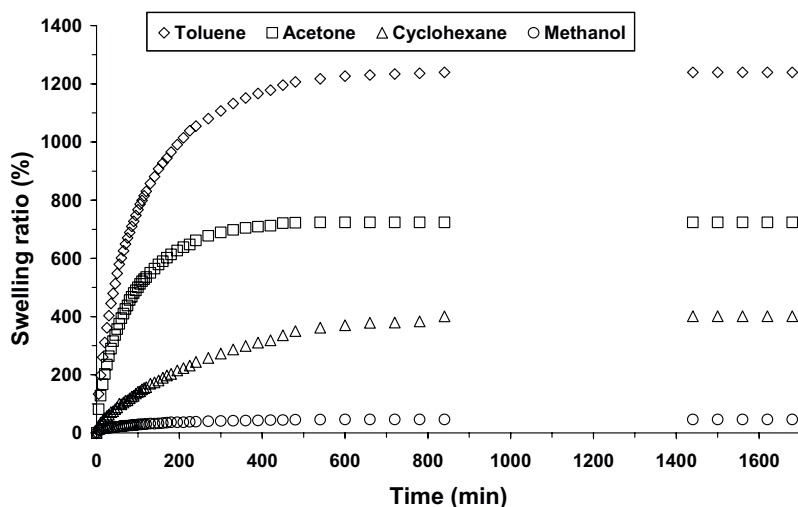


Figure 2.

Swelling behavior for PABu/0.1 wt.% HDDA networks at room temperature as a function of time for toluene, acetone, cyclohexane and methanol.

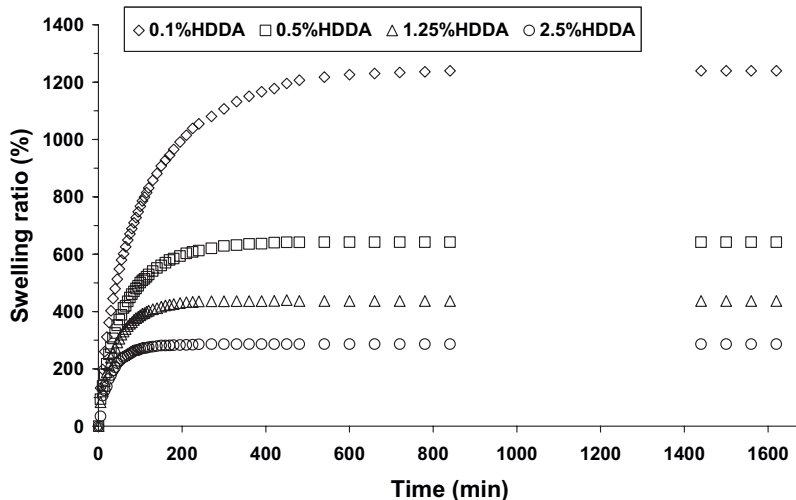


Figure 3.

Swelling behavior of PABu/HDDA networks in toluene at room temperature as a function of time for several concentrations of HDDA.

prepared under the same conditions. If the network is crosslinked by 1.25 and 2.5 wt.% HDDA, the effect of swelling is weak. Results of the loosely crosslinked networks obtained with 0.1 and 0.5 wt.% HDDA are also illustrated in Figure 3, where the effect of solvent uptake is quite high. A low concentration of the crosslinker yields a loosely crosslinked network with more efficient swelling in toluene as good solvent than for dense networks.

These results show clearly that the modification of the amount of the crosslinking agent HDDA in the initial mixtures strongly influences the swelling behavior of the PABu networks.

Figure 4 displays the dependence of the swelling ratio on the temperature for the PABu/0.1 wt.% HDDA/toluene system. In the range $0 < t < 200$ min, one notices that there is a small increase of the slope of the swelling curves with increasing tempera-

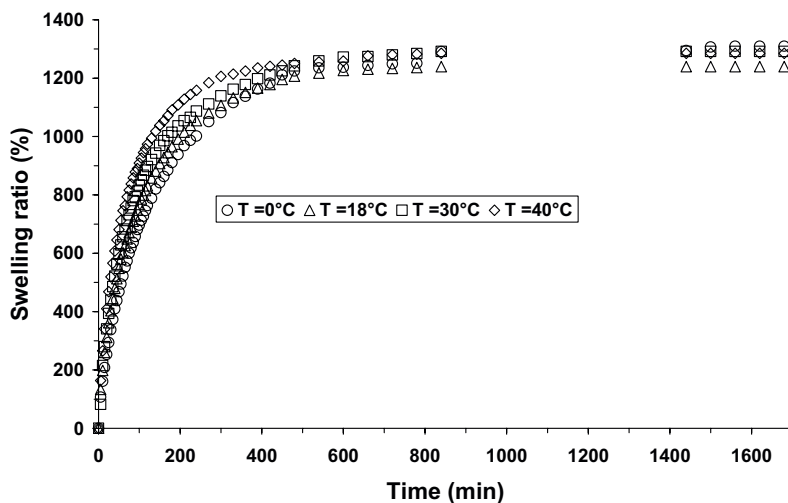


Figure 4.

Swelling behavior of PABu/0.1 wt.% HDDA networks in toluene as a function of temperature.

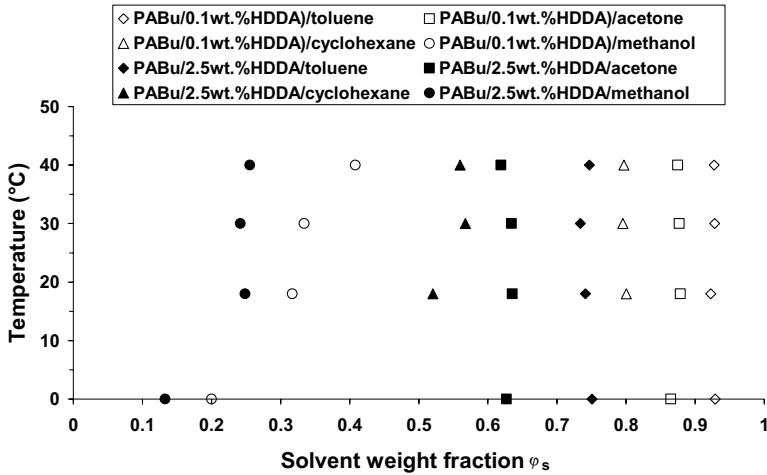


Figure 5.

Phase diagram by plotting temperature versus solvent weight fraction for the systems involving the four isotropic solvents and the two PABu-networks.

ture. This behavior is a direct consequence of the evolution of the polymer/solvent compatibility with temperature, knowing that the Flory-Huggins interaction parameter χ varies as a function of $1/T$ regardless of the isotropic or anisotropic character of the solvent molecules. Beyond $t=500$ min, swelling behavior for all temperatures is similar and the plateau values of the curves are almost identical.

One can conclude that there is no important effect of the temperature on swelling at the equilibrium state.

Figure 5 shows data of poly (Abu/HDDA)/solvent systems presented as phase diagrams, i.e. in a composition/temperature frame. The volume fractions of the components in thermodynamic equilibrium were obtained from the average measurements in the dry (D_0) and

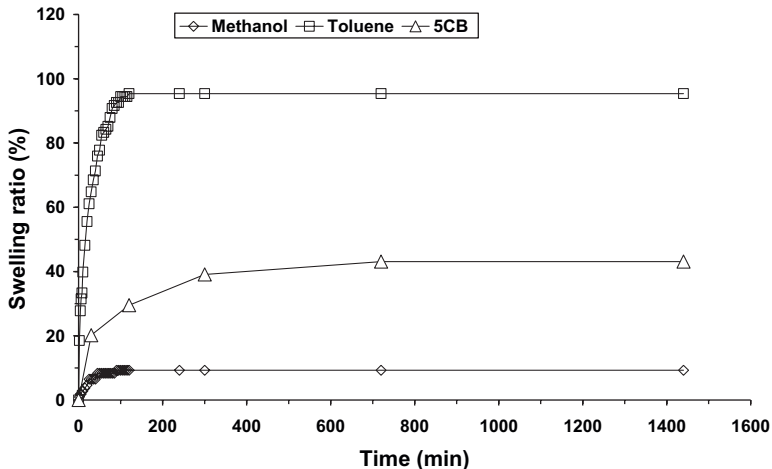


Figure 6.

Swelling ratio of PABu/0.5 wt.% HDDA networks at room temperature as a function of time for 5CB, toluene, and methanol.

swollen (D_t) state under the assumption of isotropic swelling and additivity of volumes following $\lambda^3 = (D_t/D_0)^3 = V_t/V_0$, where λ represents the swelling ratio, V_t the volume in the swollen state, and V_0 the initial volume of the dry sample. The solvent volume fraction φ_s was calculated from $\varphi_s = 1 - (1/\lambda^3)$. All systems show a large region on the left hand side of Figure 5, where a single phase appears at low solvent volume fractions. A biphasic region of polymer network and isotropic solvent can be found on the right hand of the diagram. Figure 5 shows clearly that the crosslinking density of the polymer network influences strongly the miscibility of the polymer with respect to the solvent.

Increasing the composition of HDDA in the initial mixture leads to a substantial decrease of the number of monomer units separating two consecutive crosslinks, N_c ,^[24] and to a change of the phase diagram. As a consequence, all systems with PABu/2.5 wt.% HDDA networks show reduced miscibility compared to crosslinked polymers made of PABu/0.1 wt.% HDDA.

Figure 6 shows swelling effects of PABu-networks obtained with 0.5 wt.% HDDA in the presence of an excess of 5CB and two different organic solvents. In both cases, the diameter ratio was considered. In the case of 5CB a rapid increase at early stages of swelling was observed, followed by slow solvent uptake. Plateau values were achieved at swelling times around 700 min, at a swelling ratio of 40%. The two organic solvents used for comparison were methanol as non-solvent and toluene as good solvent. For both isotropic solvents, the PABu-networks swell fast and the leveling off time was much shorter than for 5CB, i.e. at 120 min. The plateau of 5CB is located between those of methanol and toluene.

Conclusion

The swelling behavior of crosslinked PABu networks in the presence of several isotropic solvents and 5CB as anisotropic solvent was investigated. The swelling

kinetics depends not only on the degree of crosslinking and temperature but on the nature of the solvent as well. The optical technique by microscopy, which is particularly suitable for small size samples, was applied to measure the ratio of diameters for the dry and swollen polymer networks in 5CB. For a loosely crosslinked cross-linked network like PABu/0.5 wt.% HDDA, the swelling behaviour of 5CB was located between those of toluene and methanol. These aspects are modulated by polymer/solvent interactions.

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