Available online at www.sciencedirect.com
ScienceDirect
Colloids and Surfaces A: Physicochem. Eng. Aspects 295 (2007) 113–122
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Swelling equilibria in mixtures of isotropic gels and low molar weight smectic-A liquid crystals

Richard Vendamme [a,1], Tewfik Bouchaour [b], Tadeusz Pakula [a], Ulrich Maschke [c,*]

[a] *Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany*
[b] *Laboratoire de Recherche sur les Macromolécules, Faculté des Sciences, Université Aboubakr Belkaïd, BP119, 13000 Tlemcen, Algeria*
[c] *Laboratoire de Chimie Macromoléculaire—CNRS (UMR 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq, France*

Received 22 December 2005; received in revised form 13 August 2006; accepted 16 August 2006
Available online 22 August 2006

Abstract

The phase behaviour of poly(*n*-butyl acrylate) gels swollen in smectic-A low molar weight liquid crystals (LMWLC) was investigated, in view of the increasing importance of such systems in advanced optical devices. Polyacrylate networks were prepared by ultraviolet (UV) irradiation of reactive formulations including a monomer (*n*-butyl acrylate), a crosslinker (hexane diol diacrylate, HDDA) and a photoinitiator (2-hydroxy-2-methyl-1-phenyl-propane-1-one). The obtained dry polymer networks were characterized by a combination of physical techniques, and immersed in an excess of smectic-A LMWLC (4-*n*-octyl-4′-cyanobiphenyl (8CB) and 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB)), forming polymer gels. A detailed study by polarized optical microscopy (POM) allowed us to determine the swelling degree of the gels and the phase behaviour of the solvent inside the polymer matrix in a wide range of temperature. It was found that the LC inside the swollen poly(*n*-butyl acrylate) networks remains isotropic, even if the surrounding solvent is liquid crystalline. The uptake of LMWLC inside the network preferentially takes place between the smectic to nematic and the nematic to isotropic transition temperatures of the solvent. Phase diagrams in the concentration–temperature framework were given and discussed as a function of crosslinking degree of the polymer network and temperature, and phase behaviour of the solvent. Finally, results were critically examined and compared to the few studies found in the literature.

Keywords: Polymer networks; Liquid crystals; Swelling; Phase behaviour; Photo-polymerization

1. Introduction

In recent years, material scientists have devoted substantial effort to the development of new materials for advanced optical device applications. The reasons for continued interest in this area are manifold, encompassing both economic and technological realms. Although conventional liquid crystal (LC) systems like twisted nematics currently remain the material of choice for many display applications, these materials are still relatively expensive and moderately difficult to fabricate. As a result, new applications requiring alternative materials are presently under development [1]. In this context, mixtures of LCs and polymers have received considerable attention in many laboratories around the world. This interest is motivated by their potential use in many fields of high technology involving electronic equipments, display systems, commutable windows, etc.

In particular, polymer dispersed liquid crystals (PDLCs) represent an important class of materials for advanced devices because they can be switched electrically from a light scattering off-state to a transparent on-state [2,3]. They consist commonly of micron-sized droplets of low molecular weight LC (LMWLC) dispersed in a solid polymer matrix. The sample morphology including the size, shape, and number density of LC domains embedded in the polymer matrix particularly influences the electro-optical properties of these films [4]. In these heterogenous systems, segregated LC molecules are present in domains, and it has to be noted that a certain amount of LC remains dissolved in the polymer matrix [5–7].

---

[*] Corresponding author. Tel.: +33 3 20 33 63 81; fax: +33 3 20 43 43 45.
E-mail address: maschke@univ-lille1.fr (U. Maschke).

[1] Present address: Frontier Research System (FRS), The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako-shi, Saitama 351-0198, Japan.

0927-7757/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2006.08.039

In order to avoid these difficulties and others related to the complex polymer network structure often obtained by crosslinking polymerization of mixtures of monomers and LC, the polymer networks discussed in this work were prepared independently, i.e. in the absence of LC, characterized, and than submitted to the LC solvent. To the best of our knowledge, only two groups except us [8–10] have previously studied the swelling properties of isotropic polymer in anisotropic solvents. First, Ballauf and Orendi studied the swelling behaviour of poly(butadiene) (PB) networks in the nematic LCs *p*-azoxyanisole (PAA) and *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) [11,12]. They emphasized on the swelling behaviour of the gel around the nematic to isotropic transition and did not discuss the phase behaviour of EBBA inside the PB matrix. Recently, Urayama et al. also investigated the swelling properties of cylindrical shaped poly(butadiene) [13,14] and poly(styrene) (PS) [15] networks in few nematic LCs including EBBA and studied the phase behaviour of a nematic LC inside an isotropic network.

These authors showed that the phase behaviour of poly(butadiene) network in EBBA strongly depends on whether there is surrounding EBBA or not [13,14]. Without the surrounding solvent, EBBA in PB networks fails to form the nematic phase but in the presence of the surrounding EBBA, the nematic phase is formed inside the gels. These results suggest that a high order of molecular alignment in the surrounding EBBA induces the formation of a nematic phase inside the gels and that these effects overcome the high dilution of the impurity (PB) on the anisotropic interactions between EBBA molecules. In the case of a gel surrounded by an excess of EBBA, Urayama notes that the nematic to isotropic transition temperature of the gel is slightly lower than T_{NI} of the pure solvent (approximately 2 °C).

More recently, these authors studied the swelling of poly(styrene) network in a nematic LC solvent [15]. In this article, they found a LC phase inside the polymer network and show some polarized optical microscopy (POM) pictures of the nematic gel. To explain this result, Urayama et al. assumed that the solvent molecules may be allowed to localise in the network meshes so they can form the nearly pure nematic domains. They also observed that the non-mesomorphic network does not markedly influence the nematicity of the solvent, even if its volume fraction was around 0.5.

The phase behaviour of polymer/LC solvents systems with crosslinked polymer architecture has received far less experimental interest in the past than the case of polymers made of linear chains. In the present work, a special emphasis was paid to the investigation of the phase behaviour of polymer network/LC systems by dissolving the elaborated chemically crosslinked polymer networks in LMWLCs, and following the solvent uptake as a function of temperature and crosslinking degree of the network. In particular, analysis of the swollen polymer network was carried out to make evidence of the presence of a segregated LC phase inside the isotropic polymer.

In the first step of this study, the preparation of ultraviolet (UV)-cured poly(*n*-butyl acrylate) networks will be considered. Then, immersion of these networks in two smectic-A LMWLCs with chemical formula 4-*n*-octyl-4′-cyanobiphenyl (8CB) and 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) allowed to investigate miscibility and phase diagrams of these new polymer/LC systems.

2. Experimental

2.1. Materials

The monomer *n*-butyl acrylate (Abu) was obtained from Aldrich and the photoinitiator 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) from Ciba, Rueil Malmaison (France), whereas hexane diol diacrylate (HDDA) was donated by Cray Valley (France). The smectic LMWLC 8CB and 8OCB were purchased from Merck KgaA (Darmstadt, Germany). All chemicals were used as received. 8CB is characterized by a crystalline to smectic-A transition temperature $T_{CrS} = 22.8$ °C, a smectic-A to nematic transition temperature $T_{SN} = 33.6$ °C, and a nematic to isotropic transition temperature $T_{NI} = 40.9$ °C. For 8OCB, these characteristics temperatures are, respectively, $T_{CrS} = 55.4$ °C, $T_{SN} = 68.4$ °C, and $T_{NI} = 80.6$ °C. Chemical structures of the molecules employed in this study are given in Fig. 1.

2.2. Sample preparation

Mixtures of Abu/HDDA/Darocur 1173 were prepared in different weight fractions by varying the quantity of Abu and HDDA and keeping the amount of the photoinitiator constant (Abu/HDDA/Darocur 1173 = 99.4/0.1/0.5 wt.%, 99.0/0.5/0.5 wt.%, 97.0/2.5/0.5 wt.%, 94.5/5/0.5 wt.%, 92.0/7.5/0.5 wt.%). The initial mixtures were stirred mechanically for several hours before they were transferred into teflon holders. These holders were placed inside a reaction chamber filled with nitrogen and exposed to a UV lamp (Philips TL08) with a wavelength of 365 nm and an intensity of 1.5 mW/cm^2. The

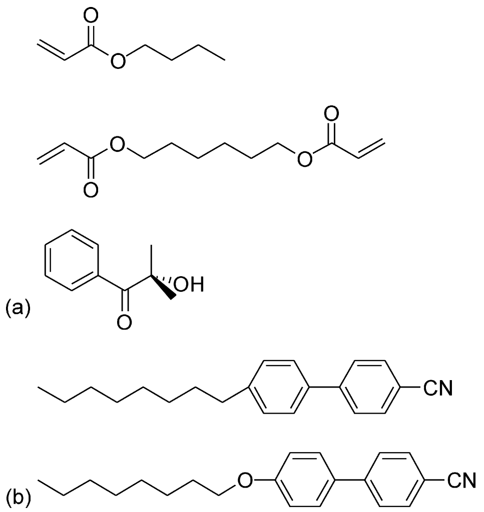

Fig. 1. Molecular structures of the employed molecules. (a) Polymer network precursors: *n*-butyl acrylate (n-ABU); 1,6-hexane-diol-di-acrylate (HDDA); 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Darocur 1173); (b) LMWLCs: 4-*n*-octyl-4′-cyanobiphenyl (8CB) and 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB).