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Interface morphology and phase separation in polymer-dispersed liquid crystal composites

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Abstract

It is widely appreciated that electro-optic activity in polymer-dispersed liquid crystals (PDLCs) depends on separation of the polymer and liquid crystal (LC) phases. Since the phase structure develops in a non-equilibrium system, the morphology of the LC domains depends on the details of the chemical and physical processes active during domain formation. The nature of the interface between the polymer and liquid crystal phases is of particular interest. This work discusses the two-phase morphology in an acrylate-based system that develops during polymerization-induced phase separation (PIPS). Using small-angle X-ray scattering (SAXS) and ultra-small-angle X-ray scattering (USAXS), we find that interfaces in PDLCs developed from an acrylate-based recipe are more disordered than generally appreciated. Information gained from SAXS and USAXS is compared to data from scanning electron microscopy (SEM) and transmission electron microscopy (TEM). To elucidate the apparent discrepancies between imaging and scattering, we investigated the effects of SEM sample preparation. We observe significant alteration of the interface morphology due to the leaching of the LC phase.

Keywords: Small-angle X-ray scattering; Interface morphology; PIPS

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are of technological importance for electro-optic applications such as privacy windows, electro-optic shutters, and large-area flat-panel displays [1–4]. PDLCs are prepared by pre-mixing a low-molar-mass liquid crystal (LC) solvent and a monomer into a uniform syrup. These mixtures are then cured, leading to phase separation of the LC and polymer phases. Ultimately, sequestered pockets of the LC phase are embedded in a polymer matrix. These pockets may or may not be spherical, depending upon the nature of the PDLC recipe.

In most cases, the two-phase morphology that results falls into one of two categories, (1) a 'Swiss cheese' morphology where spherical LC droplets are embedded in a polymer matrix, or (2) a 'reverse morphology' where a continuous LC phase is embedded in a polymer bead-like matrix [5,6]. In the latter case, the LC phase does not have droplet character. Controlling LC domain morphology is important since it modulates the electro-optical properties of the PDLC [7,8].

In this work, we concentrate on the two-phase morphology that develops in a crosslinked acrylate polymer system by polymerization induced phase separation (PIPS). Previous work shows that the 'reverse morphology' [1,3,4,6] develops in these systems. Early in the reaction, a high-molecular-weight polymer network phase-separates as spherical beads [6] that appear aggregated into a loose network with pores varying in size and shape [4]. As polymerization continues, the polymer network becomes more rigid and traps the LC domains within the polymer matrix. These features have been attributed to liquid–gel phase separation that occurs when gelation precedes phase separation [9]. This topic and its implications for the interface morphology will be discussed in more detail later in this work. The interesting feature of these PDLCs is that, although the LC domains are not spherical droplets, the sequestered volume of LC is sufficient such that a cast film can still be electro-optically active [10,11].

Considerable research has been devoted to improving the

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optical efficiency of acrylate-based PDLCs [5]. The specific recipe discussed in this work has been investigated extensively with regard to holographically cured PDLC films (H-PDLC) [1,7,11,12]. The recipe has been optimized to sequester nanoscale LC domains (<100 nm), thereby eliminating scattering problems associated with larger two-phase structures [3]. To ensure nanoscale domains, high-functionality monomers are used as the majority constituent in the pre-polymer syrup [12]. Nanometer domains are necessary to yield PDLCs with high transmission, high diffraction efficiency, and fast poling response [1]. Bunning et al. investigated the use of highly functional monomers and solubilizers to control LC domain growth and restrict droplets to nanometer dimensions [1,7]. Using a high functionality monomer ensures fast kinetics that trap small LC droplets in the polymer matrix. Further, solubilizers are often added to increase the homogeneity of the pre-polymer syrup and reduce the viscosity generated by the highly functional monomer [12]. The use of a solubilizer reduces the crosslink density of the polymer matrix by scavenging double bonds in the penta-acrylate during the free-radical reaction [1]. Issues related to polymerization chemistry will be reported elsewhere.

Throughout the literature, most of the emphasis has concerned the relationship between inherent LC properties (elastic constants, viscosity, dielectric anisotropy, birefringence) and the electro-optical properties of the two-phase structure (contrast ratios, switching speeds). However, the optical characteristics of PDLCs are also dependent on polymer architecture and the nature and rate of polymerization, which determine the spatially varying two-phase structure [3]. Almost no research focuses on the polymer structure or the interfaces that develop between the polymer and LC phases. The bulk of the reported results rely on electron microscopy to characterize morphology [1,4,13]. For the few cases where small-angle scattering (SAS) has been used [2,3], the information available in the scattering profiles was not fully exploited.

The focus of this work is the effect of LC loading on the interface morphology and phase separation of a photo-initiated, free-radical-polymerized penta-acrylate/LC system. We used the complementary information provided by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and ultra-small angle X-ray scattering (USAXS) to characterize the nanoscale morphology on length scales from 10 Å to 1 μm. When the LC concentration is increased, we observe increased domain size by SEM and USAXS. Micrographs of the leached samples show the expected reverse morphology, with the size and smoothness of the polymer ‘beads’ increasing as LC concentration increases. The USAXS data, however, suggest that even at the highest LC loading, the polymer/LC interface is very rough, which seems inconsistent with the distinct interfacial surface observed by SEM. Transmission electron microscopy (TEM) images verify the presence of disorder observed with USAXS. We investigate the SEM sample preparation for possible explanations for the discrepancies between these two analysis techniques. Specifically, small-angle X-ray scattering (SAXS) shows sample preparation for SEM alters the interfaces between the polymer/LC phases. Through the use of USAXS and SAXS, we conclude (1) the interfaces between the polymer/LC phases are more disordered than generally acknowledged, and (2) the sample preparation for SEM compromises the interpretation of the imaging data.

2. Experimental

2.1. Materials

Pre-polymer syrups consisting of monomer dipentaerythritol penta-/hexa-acrylate (DPHPA, 38–88%), photoinitiator rose bengal (0.6%), co-initiator *n*-phenyl glycine (NPG, 1.5%), and homogenizer n-vinylpyrrolidinone (NVP, 10%) were mixed with varying concentrations of liquid crystal E7 (0, 10, 20, 30, 40, 50%). All percentages listed are weight percentages. All constituents were acquired from Aldrich except the rose bengal (Spectra Group) and the LC-E7 (EM Industries). The samples were mixed into 1 g syrups and cured as 1.5 mm thick films. It should be noted that a curing gradient could be present due to the thickness of these samples. The films were flood-cured by exposure to two 20 W halogen lamps (one on each side of the sample) for 20 min. The incident power on the samples was approximately 100 mW/cm^2. These five samples were characterized using both USAXS and SEM.

Four samples were prepared for SAXS analysis using the same constituents in the pre-polymer syrup and technique. The LC concentrations for these four samples were 0, 10, 35, and 50%. To simulate SEM preparation, the LC in these four samples was leached using methanol (MeOH) extraction. The samples were soaked in MeOH for several hours and dried under vacuum.

2.2. Characterization

X-ray scattering results from electron density contrast between constituents and provides information about geometry and three-dimensional arrangement of scattering objects. Scattering at small angles is sensitive to large-scale inhomogeneities in electron density. USAXS provides reliable information about real-space structures ranging in size from 1 nm to a few μm. Structural information is gained by measuring the scattered intensity, *I*, as a function of scattering vector, *q*, which is related to the scattering angle (θ) by

$$q = (4\pi/\lambda)\sin(\theta/2) \qquad (1)$$

where λ is the wavelength of the radiation in the medium. In our system, the intensity is measured on an absolute scale