

Phase Separation of Polymer/Liquid Crystal Composites

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Introduction

Polymer-dispersed liquid crystals (PDLCs) are of technological importance in the development of switchable windows, electro-optic shutters, displays, and, most recently, switchable gratings. The most versatile method for forming PDLC structures is photoinitiated polymerization of an initially homogenous mixture containing reactive monomers and liquid crystal (LC) molecules. These prepolymer syrups are typically solvent-free and have low viscosity. Large variations in the final two-phase structure can be obtained by varying either the LC composition, the intensity of the curing radiation, or the photo-polymerization chemistry (free-radical or step-growth). The breadth of the accessible two-phase structure results in a broad range of electro-optical properties [1].

The optical characteristics of the PDLC film depend on the nature and rate of polymerization of the matrix polymer, the presence of small molecule additives, and the polymerization protocol. Understanding and controlling the polymerization mechanism are especially important for holographic curing of PDLC films, in which a spatial variation of light intensity results in a patterned LC droplet distribution.

This work examines the resultant morphology of photoinitiated phase separation of a penta-acrylate/LC system. The structural heterogeneity observed with increasing LC concentration underscores the importance of the polymerization mechanism in controlling the two-phase morphology in PDLCs.

We used x-ray scattering to observe the changes that occur in a system when variations are made to the prepolymer syrup recipe and when different curing conditions are utilized. The small q region required for evaluation of the data is not accessible with conventional small-angle x-ray scattering, so we used ultrasmall-angle x-ray scattering (USAXS). The region of interest lies within $0.00001 \leq q (\text{\AA}^{-1}) \leq 0.1$, the range covered by the UNI-CAT USAXS instrument at the APS.

Methods and Materials

The prepolymer syrups consisted of a penta-acrylate monomer (82.9%), photoinitiator (0.6%), coinitiator (1.5%), homogenizer (10%), and acid (5%). This isotropic syrup was thoroughly mixed with the LC E7 (EM

Industries), leading to systems containing 0-50% E7. (All percentages refer to the weight percent.) Films 1-mm thick were exposed to two 20-W halogen lamps (one on each side) for approximately 20 minutes. The incident power on the samples was approximately 120 mW/cm^2 . Four different LC concentrations were prepared: 0, 10, 35, and 50%.

Results

Figure 1 compares the USAXS profiles for the four LC concentrations. From these data, we learn to what extent changing the LC concentration affects the degree of phase separation. As the matrix polymer polymerizes, the system progresses from a continuous polymer matrix with dissolved LC to a discontinuous system with distinct LC domains.

To evaluate the degree of phase separation, we calculated the Porod invariant Q_P :

$$Q_P = \int_0^{\infty} I(q) \cdot q^2 dq. \quad (1)$$

To calculate Q_P , we divided the $I(q)$ versus q plot (Fig. 2) into two regions: the main region (Region 1) where the fit tracks the data, and the Porod tail region (Region 2) where we must make an analytical extrapolation. The diverging data at low q are not due to the LC domains and are therefore ignored.

To determine the invariant for Region 2, we assume the intensity decays as a pure power law with exponent $-P$. Then the analytical extrapolation is simply

$$Q_{tail} = \frac{B}{P-2} (q_{max})^{3-P}. \quad (2)$$

We used the unified fit to the $I(q)$ versus q data to create a new plot, $I(q)q^2$ versus q (Fig. 3). This plot shows that the data are adequate in the sense that there is very little area under the missing beginning and tail portions of the curve. This plot was used to determine the invariant for Region 1 by following Eq. (1) and integrating from zero to some q_{max} , beyond which the data follow a power law. The invariant, therefore, is the sum of the area under the appropriate region of the curve in Fig. 2 and Eq. (2).

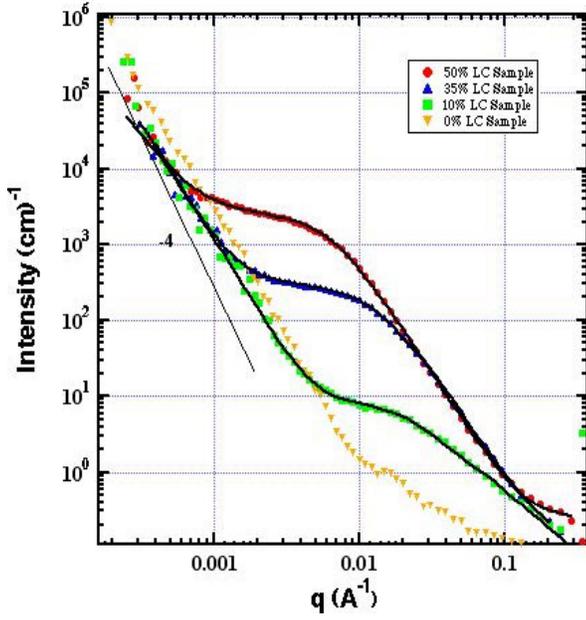


FIG. 1. USAXS profiles of samples with four different LC concentrations: 0, 10, 35, and 50%. The lines are unified fits to the data.

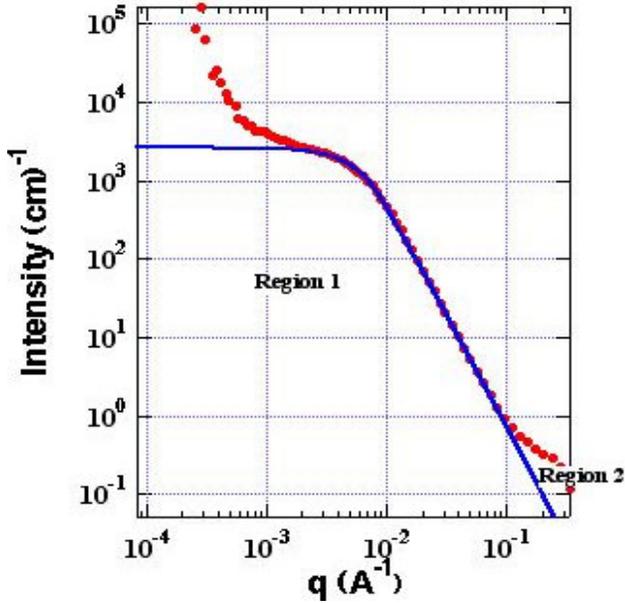


FIG. 2. Plot of $I(q)$ versus q for an LC composition of 50%. Region 1 and Region 2 are defined. The blue line was used for evaluation of Q_p .

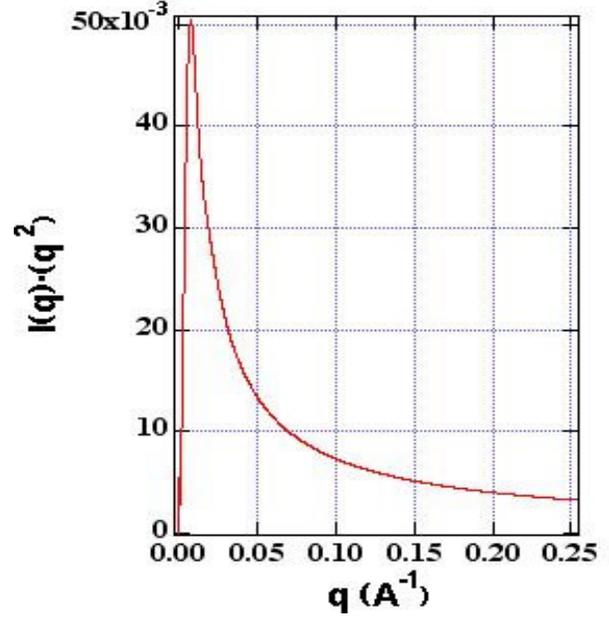


FIG. 3. Plot of $I(q)q^2$ versus q . The area under this curve is the invariant for Region 1 and is calculated by using Eq. (1).

Discussion

The invariant quantifies the extent of separation. For simple two-phase systems,

$$Q_p = (\Delta\rho)^2 \varphi (1 - \varphi), \quad (3)$$

where $\Delta\rho$ is the x-ray contrast and φ is the volume fraction of the minority phase. Thus, an increase in Q_p signals either more contrast due to purer or denser phases or a greater volume fraction of the minority LC phase. In either case, increased Q_p means less compatibility.

At 0% LC, no phase separation could be seen because no LC was present. At 35% LC, we calculated that $Q = 0.0040096$. At 50% LC, we calculated that $Q = 0.0049243$.

At 10% LC, it is impossible to calculate Q_p since the integral in Eq. (1) diverges. This situation arises because, in spite of considerable scattering, there is no phase separation. Strong correlations are observed, but there are no interfaces in the system. The correlations observed in Fig. 1 in this case are probably the result of disorderly dendritic growth. As a result of the curing of the polymer, the disordered structure is frozen before it can evolve into distinct domains.

Acknowledgments

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Reference

[1] T.J. Bunning and D.W. Tomlin et al., "Two-phase nanoscale morphology of polymer/LC composites," *Polymer* **42**, 1055-1065 (2001).