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Phase-separated composite films: Experiment and theory

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A different phase-separation process is capable of producing a composite system consisting of a very thin layer of liquid crystal in contact with a similarly thin layer of polymer. The morphology of the polymer depends on the composition of the prepolymer-liquid crystal mixture and the rate of polymerization. A simple one-dimensional theory is able to describe the essential features of this process.

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I. INTRODUCTION

It has recently been shown to be possible to prepare cells containing very thin layers of liquid crystal (LC) by means of a phase-separation process [1]. The technique used to produce these systems, which are referred to as phase-separated composite films (PSCOF's), involved shining ultraviolet (UV) light onto one side of a cell containing a mixture of LC and prepolymer. At low levels of illumination a sufficient amount of diffusion can occur to allow the complete separation of LC and polymer.

In this paper we briefly report some experimental observations of the effect of changing the intensity of the illumination. We then present a simplified theoretical analysis of the phase-separation process, and draw some conclusions as to the effect of changing various parameters in the model.

II. EXPERIMENT

The technique used to construct the PSCOF structure (Fig. 1) is essentially the same as that used for making polymer-dispersed liquid crystal (PDLC) devices [2]. One starts with a pair of substrates coated with transparent electrodes of indium-tin-oxide. One of the substrates was spin-coated with a layer of a commonly used polymer, such as polyvinyl alcohol, and then rubbed to enforce LC alignment. The other substrate was left untreated. They were separated by the glass-bead spacers commonly used in the LC display industry. The PSCOF structure has been designed to form between these two substrates such that the LC and the polymer layers are in contact with the rubbed and the untreated substrates, respectively. As a result, the LC layer is aligned by the rubbed substrate, while the polymer layer, which does not need to be aligned, is formed next to the untreated substrate. Commercially available photocurable prepolymer NOA-65 (Norland) and various liquid crystals were used. The prepolymer and the LC were mixed at some ratio, typically 60:40, and then introduced into the cell by capillary action at a temperature well above the clearing point of the LC. Phase separation was carried out at a temperature of around 100 °C by exposing the cell to UV light incident normally on the untreated substrate. The source of UV light was a xenon lamp operated at 200 W of electrical power, and exposure times around 5 min were used. The prepolymer-LC mixture is in the isotropic phase at the temperature and the mixture ratio listed above. The relatively high temperature is above the nematic-isotropic transition point of the LC. This makes the system less viscous, which hastens the phase-separation process. The ratio close to 50:50 was chosen because it leads to better separation of the LC and the polymer, as will be shown in Sec. III. After the completion of the phase separation, the sample was cooled to room temperature.

To determine the internal structure of the devices obtained in this manner, their optical texture was examined under a polarizing microscope. It was found that the LC acquires a homogeneous alignment due to the effect of the rubbed polymer-coated substrate. Several cells were opened and washed with a solvent to remove the LC, and then observed under a scanning electron microscope.

The mechanism responsible for the formation of PSCOF is nonuniform polymerization [3]. The LC molecules absorb UV light more strongly than anything else in the mixture at wavelengths near 350 nm. As a result, an intensity gradient is produced in the sample. Consequently, NOA-65 molecules first undergo polymerization near the substrate closest to the UV source and the LC molecules are expelled from the polymerized volume. The rate of phase separation, which can be controlled by varying the intensity and the exposure time, is the most important factor in determining the resultant structure. Four samples, with 40 wt% of the LC Felix-15-100 (commercial mixture from Hoechst) and 60% prepolymer NOA-65, were prepared using 5 μm spacers to observe the effect of UV exposure on the final structure. All components of the LC mixtures we used are miscible with the prepolymer and immiscible with the polymer. Microscopic textures shown in Figs. 2(a)–2(d) illustrate how the resultant structure changes from PSCOF to PDLC as the total UV dosage applied in a given time varies over the range

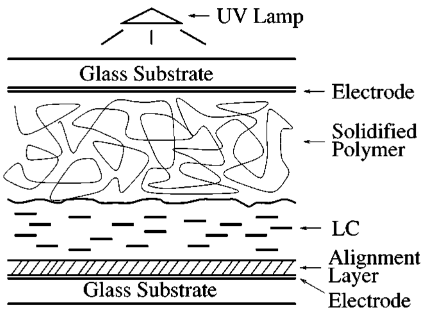

FIG. 1. Schemtic of the PSCOF structure.

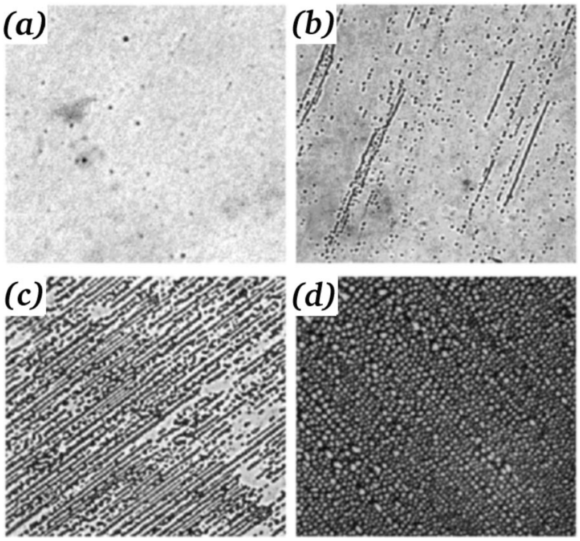

FIG. 2. Photographs taken through a microscope with samples between crossed polarizers. From (a) to (d), the UV dosage applied varied from 0.75 to 20 mJ/cm^2.

0.75,7.5,15, and 20 mJ/cm^2, respectively. These photographs were taken with the sample between crossed polarizers. It is seen that high irradiance leads to the formation of heterogeneous structures characteristic of a PDLC. The diameters of the droplets visible in Fig. 2(d) are of the order of $2-4$ μm. The PSCOF structure formed at low irradiance gives a nearly uniform optical texture [Fig. 2(a)]. Figures 2(b) and 2(c) show the formation of droplets elongated along the substrate rubbing direction at intermediate irradiance. Because the LC is in its isotropic phase at the temperatures used for polymerization, it must be assumed that the anisotropic morphology seen in Figs. 2(b) and 2(c) is a consequence of the effects of the rubbed substrate surface on the flow of LC during phase separation [1]. Measurements on PSCOF cells prepared with different concentrations of the nematic LC E7 (commercial mixture from Merck) show that the thickness of the LC layer depends directly on the amount of LC in the LC-prepolymer mixture and that only a small amount $(2-5\%)$ of the LC is trapped in the polymer film. The transition temperature of the LC obtained after complete phase separation deviates from that of the original LC sample by less than 1 °C. This small change is most likely the consequence of an increase in impurity concentration resulting from the expulsion into the LC of impurities originally contained in the prepolymer.

III. THEORY

A complete theory of the formation of PSCOF's would describe the evolution of the phase-separated system in terms of spatial and temporal distribution of LC, prepolymer, polymer, and all the intermediate oligomers. It would also include the effect of a rubbed substrate surface on the inducement of nematic ordering in the otherwise isotropic LC mixture, and its consequence for the polymer morphology.

In this treatment we adopt a much simpler model. We assume that the essence of the phase-separation process can be expressed in terms of the concentrations of just three constituents of the system. These are the volume fractions ψ of LC, ϕ of prepolymer, and η of immobile polymer, and are assumed to be functions only of time, t, and distance, z, from the substrate on the side of the cell that is illuminated. In reducing the description to concentrations, we note that all the components involved in the phase separation are hydrocarbon compounds with comparable densities. Because the total volume is assumed constant, $\psi+\phi+\eta=1$, and there are only two independent variables describing the local composition. A third variable, however, does enter the model, as it is necessary to specify the irradiance I of the UV light.

In the absence of absorption of the UV light by the system, the radiant incidence would be uniform, and the photopolymerization rate would not vary with distance from the illuminated surface. The random nature of the polymerization process would then lead to a time-varying distribution of degree of polymerization, but such a distribution would be the same in different regions of the cell. The volume fraction of polymer molecules would increase with accumulated irradiation, and phase separation would occur, but there would always be a macroscopically uniform volume fraction of polymer throughout the cell.

The real situation, however, is that UV light is predominantly absorbed by the LC molecules, and so an intensity gradient is present in the solution from the beginning of the irradiation process [1]. As a consequence, the polymerization rate is higher close to the illuminated surface and thus more prepolymer molecules are consumed there. A gradient of the prepolymer concentration is therefore produced, and this leads to a migration of the prepolymer molecules from the bulk to the illuminated surface and also a migration of the LC molecules from the illuminated surface to the bulk. Meanwhile, the migration of small molecules (prepolymer and LC) is much faster than that of the large polymer molecules, which eventually form the immobile polymer gel.

We consider both the migration of small molecules and the formation of the immobile polymer network. For this purpose, we treat the distribution of polymerization degree or molecular weight in a simplified way. Of the three species present—LC, prepolymer, and polymer—the LC molecules undergo diffusion only. The prepolymer molecules undergo diffusion, and are also consumed as the polymerization proceeds. The polymer is treated as immobile, and hence does not diffuse, but has a local volume fraction that keeps growing as long as there are still prepolymer molecules at that location.

Our model is one-dimensional, along the substrate normal, here defined as the z direction in which the intensity gradient is produced. The basic equations are as follows. First, the concentration ψ of the LC molecules changes through a diffusion current J_{ψ}, defined as the volume of LC passing through unit area per unit time, so that

$$\frac{\partial\psi}{\partial t}=-\nabla\cdot J_{\psi}. \tag{1}$$

Second, the concentration ϕ of the prepolymer molecules changes both through a diffusion current J_{ϕ} and through polymerization, which increases the concentration η of the immobile polymer network. We thus have

$$\frac{\partial\phi}{\partial t}=-\nabla\cdot J_{\phi}-\frac{\partial\eta}{\partial t}. \tag{2}$$

Third, the volume fraction η of the polymer network changes in proportion to irradiance I, and the product of the concentrations of the reactants, which are assumed to be that of the prepolymer, ϕ, and that of the sum, $\phi+\eta$, of the prepolymer and polymer. We are thus assuming a model of polyfunctional polymerization in which a reacting monomer can combine with another monomer or attach at any point on an existing polymer molecule. This gives us

$$\frac{\partial\eta}{\partial t}=kI\phi(\phi+\eta). \tag{3}$$

The real dependence of $\partial\eta/\partial t$ on the concentrations of the reactants is actually very complicated and usually determined empirically. But this complexity should not affect the qualitative agreement between our theory and the experimental observations, which we will show below. Finally, the irradiance I decays with distance z from the illuminated substrate at a rate assumed to be linear in the concentration of the constituents, giving the equation

$$\frac{\partial I}{\partial z}=-I(a\phi+b\psi+c). \tag{4}$$

Here k is a constant reflecting the rate of photopolymerization, and a,b,c are constants related to the absorption of light by the different species. Since the absorption is predominantly by the LC molecules, here we simply neglect a and c.

According to the mean-field kinetic theory of phase separation, the current J_ϕ of prepolymer molecules, which is related to the LC current J_ψ by $J_\phi=-J_\psi$, is given by [4]

$$J_\phi=D\left(-\psi\frac{\partial\phi}{\partial z}+\phi\frac{\partial\psi}{\partial z}-\chi_1\phi\psi\frac{\partial\psi}{\partial z}\right), \tag{5}$$

where χ_1 is the interaction parameter in the Flory-Huggins (FH) theory [5]. The first two terms on the right-hand-side of Eq. (5) are due to entropy-driven diffusion, while the third term is due to molecule-molecule interactions. Starting from a system with a given ratio of prepolymer to LC, i.e., $\phi:\psi$, in a LC cell of thickness d, the final volume-fraction profile of polymer network and LC are established when the supply of prepolymer molecules is exhausted. It is easy to put Eqs. (1)–(4) into dimensionless form by using d as the unit of length and d^2/D as the unit of time. It is then readily seen that the final profiles of polymer network and LC are completely determined by four dimensionless numbers. They are (1) the initial ratio of $\phi(z,t=0)=\phi_0$ to $\psi(z,t=0)=\psi_0$; (2) the relative polymerization rate, defined as $R\equiv kI(z=0)d^2/D$ (illuminated surface defined at $z=0$); (3) the relative absorption length of light, defined as $L\equiv 1/bd$; and (4) the FH interaction parameter χ_1.

A finite difference scheme has been used to solve simultaneously the differential equations (1)–(4). The numerical results show that, depending on the values of ϕ_0/ψ_0, R, L, and χ_1, both PSCOF and PDLC structures can be formed. In particular, to form PSCOF's with clear boundaries between polymer and LC requires the following: (1) A large gradient of irradiance must exist in the LC cell, i.e., the absorption length must be much shorter than the cell thickness, so that $L\ll 1$. (2) Photopolymerization must be slow compared with the diffusion of the small molecules, so that $R\ll 1$. (3) The volume fractions of prepolymer and LC should not be too different from each other, and hence ϕ_0/ψ_0 should be of order unity. (4) The FH parameter χ_1 should be reasonably large, but not so great as to cause the instability that leads to the formation of PDLC's.

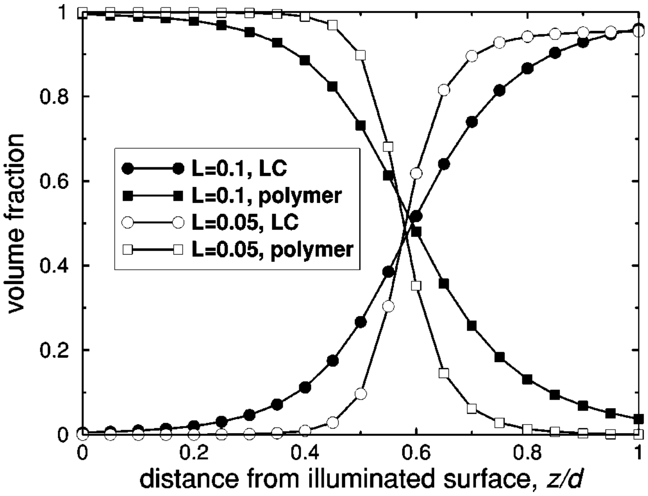

FIG. 3. Final volume fractions of LC and polymer, which show better separation for shorter absorption length of light. The parameters used for calculation are $\phi_0/\psi_0=60/40$, $L=0.10$ and 0.05, $R=0.05$, and $\chi_1=0$.

The numerical results that support these conclusions are illustrated in Figs. 3, 4, 5, and 6. Figure 3 shows that a sharper boundary occurs when L is reduced from 0.10 to 0.05. Here $\phi_0/\psi_0=60/40$, $R=0.05$, and $\chi_1=0$. In Fig. 4 we see that slow polymerization, represented by small values of R, leads to a more sharply defined boundary. Here $L=0.10$, $\phi_0/\psi_0=60/40$, and $\chi_1=2$. Figure 5 shows that more equal initial volume fractions of LC and prepolymer produce a crisper boundary when $L=0.05$, $R=0.05$, and $\chi_1=2$. Finally, Fig. 6 illustrates the sharper separation found for larger values of χ_1 when $L=0.05$, $\phi_0/\psi_0=60/40$, and $R=0.05$.

These conclusions are in qualitative agreement with the experimental observations, which showed the importance of slow photopolymerization and roughly equal proportions of

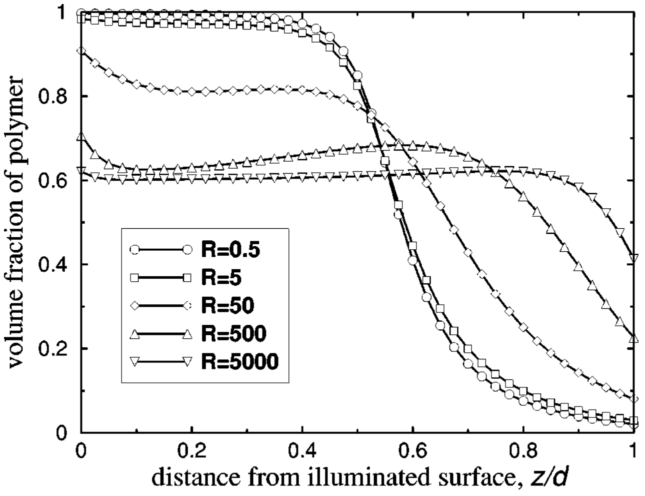

FIG. 4. Final volume fraction of polymer, which shows better separation for slower polymerization. The parameters used for calculation are $\phi_0/\psi_0=60/40$, $L=0.10$, $R=0.5,5,50,500$, and 5000, and $\chi_1=2.0$.

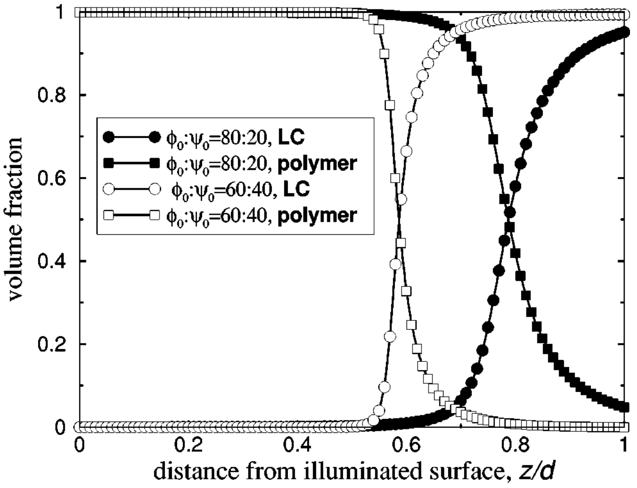

FIG. 5. Final volume fractions of LC and polymer, which show better separation for more equal initial volume fractions of prepolymer and LC. The parameters used for calculation are $\phi_0/\psi_0 = 80/20$ and 60/40, $L = 0.05$, $R = 0.05$, and $\chi_1 = 2.0$.

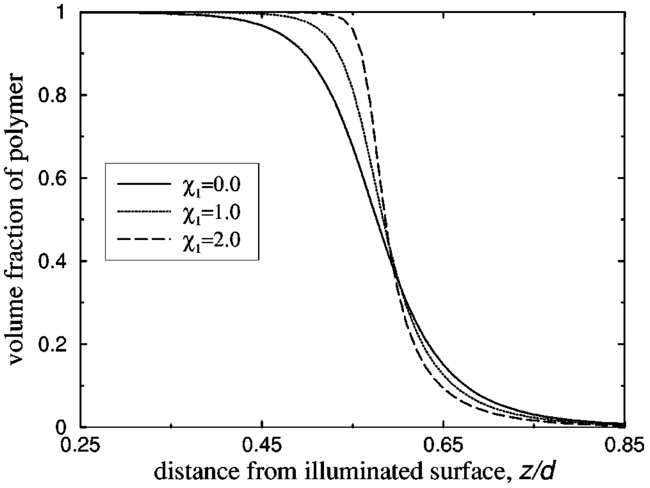

FIG. 6. Final volume fractions of polymer, which show better separation for larger χ_1. The parameters used for calculation are $\phi_0/\psi_0 = 60/40$, $L = 0.05$, $R = 0.05$, and $\chi_1 = 0$, 1.0, and 2.0.

prepolymer and LC. In our numerical results, the degree of the separation is measured by the thickness of a transition layer formed between the regions of $\eta \simeq 1$ (polymer layer) and $\psi \simeq 1$ (LC layer). This transition layer, distributed around the position z_t defined by $\eta(z_t) = \psi(z_t) = 0.5$, is composed of a mixture of polymer and LC, i.e., PDLC. Since we have reduced the theoretical description to various concentrations in a one-dimensional space, the simplified nature of the theory did not permit any prediction of the detailed morphology of the polymer network. Experimentally, we can estimate the completeness of the phase separation by examining the optical texture of the sample between crossed polarizers (see Fig. 2). The PSCOF structure, with a negligibly thin transition layer, leads to a nearly uniform optical texture with a LC layer aligned by the rubbed substrate [Fig. 2(a)]. The PDLC structure, if present in a layer that is thick enough to be observable optically, leads to a heterogeneous texture [the amount of PDLC-structured mixture increases from Fig. 2(b) to Fig. 2(d)]. The importance of slow polymerization to phase separation is thus clearly illustrated in Figs. 2(a)–2(d) and these experimental observations are at least in qualitative agreement with the numerical results shown in Fig. 4. We can also obtain scanning-electron-microscope micrographs by removing the rubbed substrate and washing away the LC. It is possible the polymer network may become compacted when the LC is extracted, but regardless of this possibility, whether the polymer surface so observed is smooth or grooved still provides some qualitative measure of the degree of separation. Micrographs show that the polymer film formed at $\phi_0/\psi_0 = 60/40$ has a much smoother surface than that formed at $\phi_0/\psi_0 = 80/20$ (see Fig. 2 in Ref. [1]). This observation is also in qualitative agreement with the numerical results shown in Fig. 5. Finally, we point out that the effective Flory-Huggins parameter χ_1 is not known for this system, and so the fourth theoretical prediction could not be verified.

IV. CONCLUSION

In summary, the formation of PSCOF is a joint effect of strong light absorption, slow polymerization, phase separation, and fast diffusion of small molecules. A theoretical study of this phenomenon has been carried out in a model that takes into account the absorption of light, the diffusion of prepolymer and LC molecules, the formation of an immobile polymer network via polymerization and phase separation, and the polymer-LC interaction. The effects of varying composition and irradiance have been obtained within this model, and are in qualitative agreement with experimental observations. Finally, we point out that our macroscopic model could be improved by incorporating the existence of polymer molecules of different weight and different mobility and by considering the phase separation kinetics that determine the microscopic structure of the polymer network. Work in this direction is currently proceeding.

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