

Control of Polymer Structures in Phase-Separated Liquid Crystal-Polymer Composite Systems

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(Received October 20, 2004; accepted January 17, 2005; published May 10, 2005)

The formation of different structures in phase-separated composite films (PSCOFs) from formulations of liquid crystals and photocurable monomers has been investigated using polarizing optical and scanning electron microscopies. Two processes, spatially nonuniform polymerization and diffusion of small molecules, play important roles in determining a specific PSCOF polymer structure. The variations in UV irradiation intensity and temperature, at which phase separation is carried out, strongly influence these two processes and can change the resultant structure from a homogeneous PSCOF bilayer structure to a heterogeneous polymer dispersed liquid crystal (PDLC) structure. A variation in cell thickness changes the distance through which small molecules have to diffuse during phase separation and, thus, affects the structure obtained in thick and thin cells. [DOI: 10.1143/JJAP.44.3115]

KEYWORDS: liquid crystal, polymerization, phase separation, polymer morphology, polymer dispersed liquid crystal

1. Introduction

The phase-separated composite film¹⁾ (PSCOF) method has attracted considerable attention because of its applications in many novel liquid crystal display (LCD)^{2–5)} and photonics devices^{5,6)} with unique internal polymer/liquid crystal (LC) bilayer structures. Typically, a PSCOF device is fabricated by initiating the polymerization reaction by irradiating UV light onto one side of a cell containing a solution of LC and a photocurable monomer. The spatially nonuniform rate of polymerization⁷⁾ is affected by the gradient of UV intensity along the substrate normal. The intensity gradient is produced by strong absorption of UV mostly by LC. The final result is complete separation of LC and the resulting polymer into different volumes within the cell. A bilayer structure is obtained with the polymer layer in contact with the substrate closer to the UV source, and the LC layer is formed between the polymer layer and the second substrate. The optic axis of the LC layer is controlled with the help of a unidirectionally rubbed alignment layer on the second substrate that is in contact with the LC layer, as shown in Fig. 1. This unique internal structure provides PSCOF devices with a strong resistance to mechanical deformations. With this technology, flexible plastic LCDs, microlens arrays, and single-substrate devices have been fabricated.^{2–6)}

The electro-optical performance and mechanical robustness of PSCOF devices depend on their internal polymer structure and morphology. It is important to understand the underlying process to design and optimize the fabrication process. Qian *et al.* calculated the essential features of this process using a simple one-dimensional model⁸⁾ and predicted that the formation of PSCOF is a result of nonuniform UV illumination caused by the strong UV absorption, slow polymerization and phase separation of the LC and prepolymer mixture. Here, we report the results of our experimental investigations of internal polymer structures of nematic PSCOF devices. Our investigations focus on how curing temperature, UV intensity, and cell thickness influence the formation of PSCOF architectures.

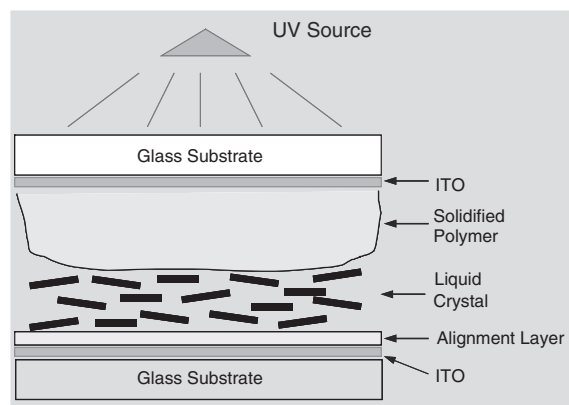


Fig. 1. Scheme of PSCOF structure.

2. Experimental Details

We used scanning electron microscopy and polarized optical microscopy, to determine the shape and morphology of the polymer and LC/polymer structures, as described below.

2.1 Materials

The materials and procedures used to construct the PSCOF devices and their structures are similar to those previously used in preparing polymer-dispersed liquid crystal (PDLC)^{9,10)} devices. We used the nematic LC E7 obtained from E. Merck, Inc. The UV curable monomer NOA65 (Norland Product, Inc.) was added to E7 in the ratio of 1 : 1 by weight. The mixture was stirred well for 15 min at a temperature above the clearing point of the LC for uniform mixing. After stirring, the whole mixture remained stable in a homogeneously isotropic phase at room temperature (25°C).

2.2 PSCOF sample preparation

Cells were constructed with a pair of glass substrates coated with transparent electrodes of indium tin oxide (ITO). A thin layer of a commonly used polymer, polyvinyl alcohol (PVA), was spin-coated on one of the substrates and then

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uniaxially rubbed to induce LC alignment. The other substrate was left untreated. Glass fiber spacers were used to maintain cell gap. Several spacer sizes of 1.5 μm , 3 μm , 5 μm , and 10 μm were used to fabricate cells with different cell gaps. Empty cells were filled with the LC/monomer mixture by capillary action. Phase separation was carried out by exposing the cell to a collimated UV beam, incident normally to the untreated substrate of the cell. This exposure was carried out at UV intensities of: 0.05 mW/cm^2 , 0.1 mW/cm^2 , 0.5 mW/cm^2 and 5 mW/cm^2 . Sample temperature was controlled with a Mettler FP-82HT hot stage. We investigated the phase separation at different temperatures: 30°C, 50°C, 70°C and 90°C.

2.3 Optical and scanning electron microscopy

The internal architecture and electrooptical properties of the resulting samples were characterized using polarizing optical microscopy and scanning electron microscopy (SEM). To determine the polymer morphology and structures by SEM, the PSCOF devices were opened and soaked in hexane for one day to dissolve and remove the liquid crystals. The substrate closer to the UV source during photopolymerization was rinsed with fresh hexane to ensure that the liquid crystal material was fully removed, dried, and then placed in a sputtering system to coat it with a thin layer of gold. Portions of polymer deposits on the substrate were removed with a sharp blade to expose the bare glass substrate on one side and permit an edge-on view of the film. The substrate was then placed in the SEM chamber and its structure examined.

2.4 Viscosity measurement

The zero-shear bulk viscosity of the E7+NOA65 mixture was measured using an ARES Rheometer (Rheometric Scientific Inc.). A cone-and-plate geometry ($d = 5.0$ cm, angle = 0.02 rad) was used and the gap zero was set at 55°C. The sample was loaded and the gap was fixed according to the cone truncation. Steady state viscosities were recorded at 25°C, 40°C, 50°C, 60°C, 70°C, 80°C and 85°C.

3. Results and Analysis

The mechanism responsible for the formation of PSCOF is the spatially nonuniform rate of polymerization caused by an intensity gradient inside the cell due to a strong absorption of UV by the LC+monomer mixture. Monomers first undergo polymerization near the substrate close to the UV source and LC molecules are expelled from the polymerized volume. The LC molecules diffuse into the unpolymerized volume away from the UV source. Figure 2 shows the UV-vis transmission spectra of a bare ITO-coated glass substrate (curve 1), a cell with pure NOA65 (curve 2), and a cell with the mixture of E7+NOA65 in a ratio of 50 : 50 (curve 3), respectively. The cell thickness is 10 μm . As evident from curve 3, E7+NOA65 strongly absorbs UV light for wavelengths in the range of 300–350 nm. The absorption is mostly contributed by E7 molecules because the NOA65 monomer's spectrum does not show significant absorption in this range. Continued UV irradiation eventually consumes more and more monomers and causes LC molecules to move out of the polymerized volume. The final outcome is a complete separation of the polymer and LC.

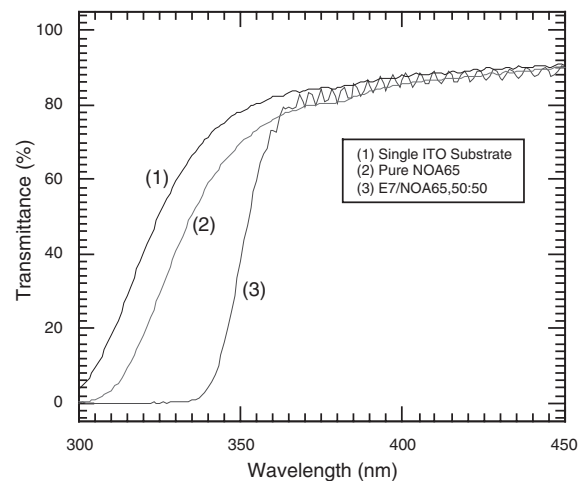


Fig. 2. UV-vis transmission spectra of (1) bare ITO glass substrate, (2) cell with pure NOA65 monomer and (3) cell with mixture of E7/NOA65 (50 : 50). The cell thickness for (2) and (3) is 10 μm .

The intensity gradient is the crucial factor in the formation of PSCOF.

3.1 Effect of UV intensity on PSCOF

UV intensity has a strong impact on polymerization and the rate of phase separation, which are the most important factors in determining the resultant structure of PSCOF. The samples prepared at 50°C with UV irradiations at 0.05, 0.1, 0.5 and 5 mW/cm^2 (measured for $\lambda = 350$ nm) were observed under a polarized light microscope (Nikon Labophot-Pol). As can be easily seen from the microscopic images shown in Fig. 3(a), at a low intensity, the rate of phase separation is slow and results in a complete phase separation of LC and the polymer, i.e., a PSCOF cell with uniform optical texture and alignment. On the other hand, nonuniform PDLC-like textures, Fig. 3(d), are observed for the samples irradiated at higher UV intensities at high polymerization rates. At intermediate UV intensities, elongated LC droplets along the rubbing direction are obtained as a consequence of the anisotropic wetting by LCs of the rubbed PVA surface during the phase separation [Figs. 3(b) and 3(c)]. LC molecules aligned along the rubbing direction of PVA, as confirmed by rotating the samples between crossed polarizers [Figs. 3(a) to 3(c)].

The SEM results provide clear evidence of how the resultant polymer structures change gradually from a smooth PSCOF structure to a heterogeneous PDLC structure as UV intensity varies from 0.05 mW/cm^2 to 5 mW/cm^2 . Figure 4(a) shows a solid polymer layer with a uniform and smooth surface, which indicates a complete separation of LC and the polymer under a low UV intensity of 0.05 mW/cm^2 . The surface reveals a weak remanence in the LC alignment along the rubbing direction. It seems that the alignment pattern is imprinted on the LC-polymer interface. Increasing the UV intensity to 0.1 mW/cm^2 leads to a stronger remanence in the LC alignment on the polymers surface and induces an elongated groove structure along the rubbing direction [Fig. 4(b)]. This reveals a consequence of the effect of an anisotropic flow of E7 LC molecules on the uniaxially rubbed alignment layer surface during phase separation.¹⁾ The surfaces of the groove bottom are still

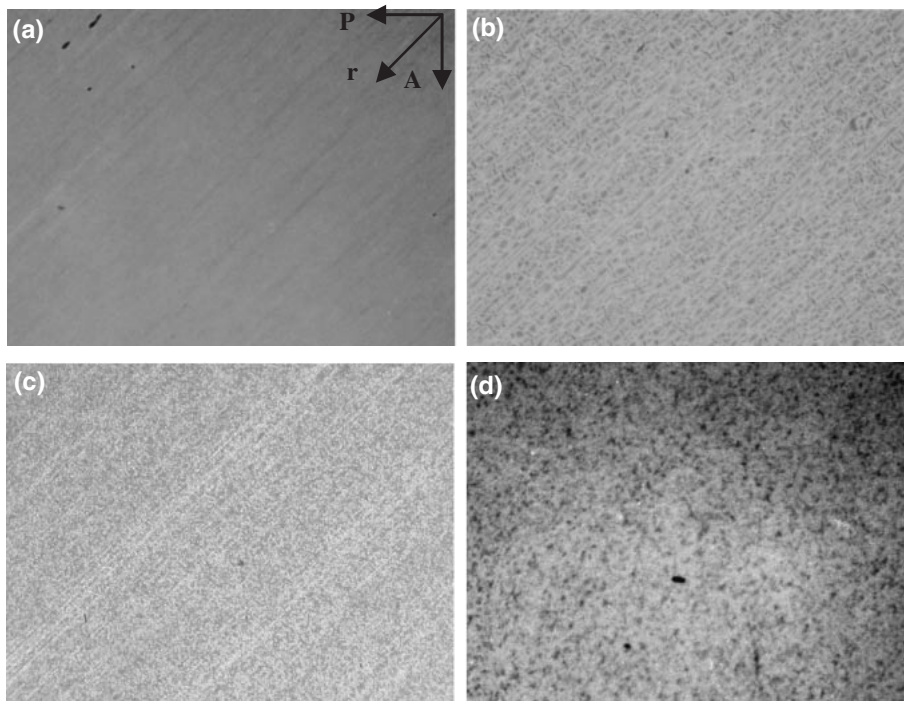


Fig. 3. Microscopic texture (200 \times) of cells prepared with UV irradiation at (a) 0.05 mW/cm², (b) 0.1 mW/cm², (c) 0.5 mW/cm² and (d) 5 mW/cm². All the samples have the same cell thickness of 3 μ m and have been cured at 50°C. P, A, and r mark the directions of the polarizer, analyzer and rubbing of the alignment layer, respectively.

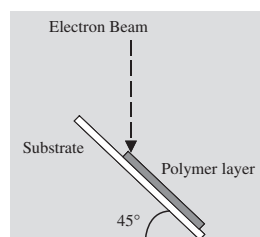
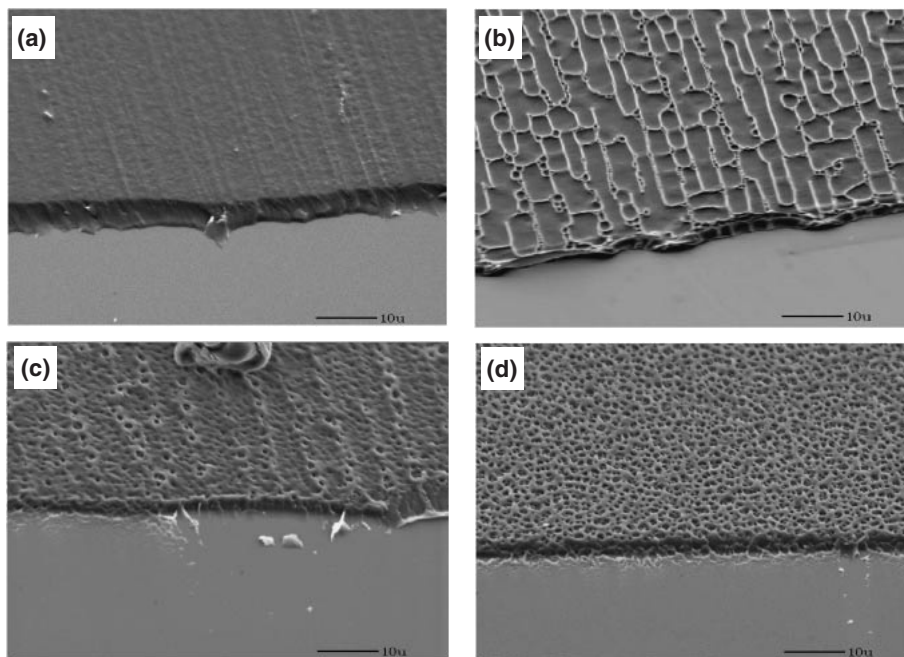


Fig. 4. SEM images of polymer morphology. The UV intensities used were (a) 0.05 mW/cm², (b) 0.1 mW/cm², (c) 0.5 mW/cm² and (d) 5 mW/cm². All the samples were tilted 45°. The scaled bars represent 10 μ m.

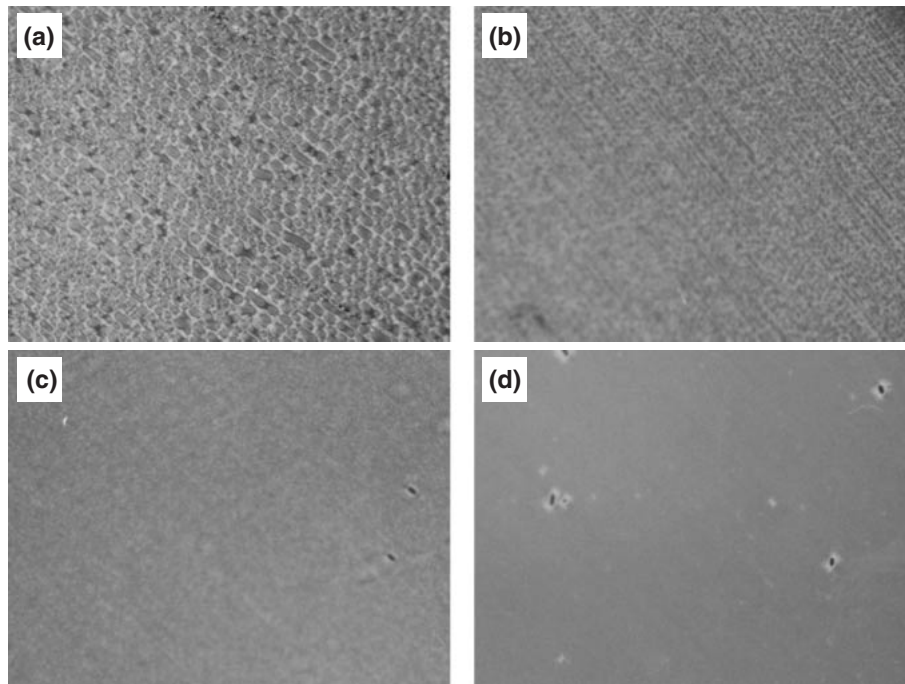


Fig. 5. Microscopic textures of cells prepared at curing temperatures of (a) 30°C, (b) 50°C, (c) 70°C and (d) 90°C, at a magnification of 200.

fairly smooth, which indicates that most LC is phase-separated out from the polymer. When the UV irradiation intensity is increased to 0.5 mW/cm^2 , the groove structure on the polymer surface almost fades away. The resulting polymer surface is very rough and its structure closely resembles that of PDLC. The surface had many small cavities occupied by LC droplets, which were later washed away with hexane during the sample preparation for SEM [Fig. 4(c)]. These small cavities on the rough polymer surface indicate that some LC failed to separate out from the polymerized volume because of the fast polymerization under strong UV irradiation. When the UV intensity approaches 5 mW/cm^2 , the resultant polymer structure becomes a regular PDLC structure [Fig. 4(d)]. The groove structure completely fades away and many micron-size cavities ($1\text{--}3 \mu\text{m}$) formed inside the polymer volume indicate that the LC molecules failed to completely separate from the polymerized volume under strong UV irradiation. The SEM results are in very good agreement with our optical microscopy observations.

We believe that the gradual structural changes from smooth PSCOF to heterogeneous PDLC are a consequence of the competition between two processes: the nonuniform polymerization of prepolymer molecules and the diffusion of LC and prepolymer molecules. These processes show different dependences on UV intensity. At low UV intensities, the polymerization rate is slow; and this produces a gradient in monomer concentration, leading to a net migration of monomers from the un-polymerized bulk towards the irradiated surface, where they participate in polymerization and are consumed. Also, the concentration of LC molecules increases near the polymerized volume as LC molecules are expelled from the polymer. LC molecules undergo a net migration, due to diffusion away from the UV source and towards the un-polymerized bulk. Continued

irradiation eventually results in a complete separation of LC and polymer forming a PSCOF structure with uniform bilayer structure. At high UV intensities, the polymerization rate is higher, while the diffusion rate of small molecules remains the same. LC molecules tend to get trapped in small pockets in the polymer volume. This results in the formation of PDLC-like structures.

3.2 Effect of curing temperature on PSCOF

The temperature at which the phase separation takes place also plays an important role in determining polymer structure and morphology. This is highly noticeable from the results of optical microscopy (Fig. 5) and SEM (Fig. 6). Samples were prepared using $5 \mu\text{m}$ -thick cells and cured at four different temperatures and a fixed UV intensity of

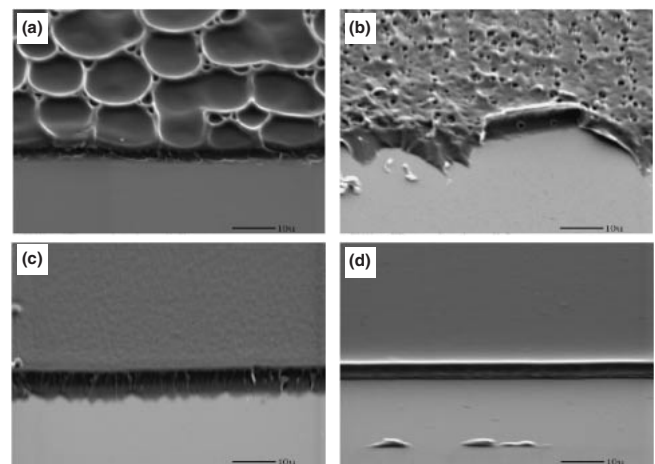


Fig. 6. SEM images of polymer structures with curing temperatures of (a) 30°C, (b) 50°C, (c) 70°C and (d) 90°C. All the samples were tilted 45° for the sectional view. The scaled bars represent $10 \mu\text{m}$.

0.5 mW/cm². The optical microscopy images of the samples [Figs. 5(a)–5(d)] show how the resultant texture gradually changes from a PDLC-like texture with elongated LC droplets to a uniform PSCOF texture as the curing temperature is raised from 30°C, 50°C and 70°C to 90°C, respectively.

The SEM images in Fig. 6 further reveal how the changes in phase separation temperature affect the PSCOF structures. At a low temperature of 30°C, PDLC-like structures with many spheroidal cavities on the polymer films' surface are formed. The average diameter of the oblate cavities is approximately 10 μm. At an intermediate temperature of 50°C, the average diameter of the cavities becomes smaller in the range of approximately 1–2 μm. This indicates that a smaller amount of LC is trapped in the polymer. At high temperatures of 70°C and 90°C, uniform polymer films with a very smooth surface are formed. Their corresponding sectional SEM images [Figs. 6(c) and 6(d)] show a complete absence of cavities inside the polymer or at its surface. This indicates that a complete separation of LC and the polymer occurs at high temperatures.

The effect of temperature on the polymer films' morphology is profound and can be understood with the help of the simple mechanism discussed above. Generally, the polymerization rate of NOA65 mostly depends on the intensity of UV irradiation and does not change much with temperature. The rates of diffusion of LC and monomer molecules strongly depend on the mixture's bulk viscosity, which shows a strong temperature dependence (Fig. 7). At low temperatures, the diffusion rates of LC and monomer molecules are low because the bulk viscosity of the E7/NOA65 mixture is high. Thus, the polymerization dominates among the two processes, and PDLC-like structures are formed because LC molecules cannot efficiently separate from the polymer. At high temperatures, small LC and

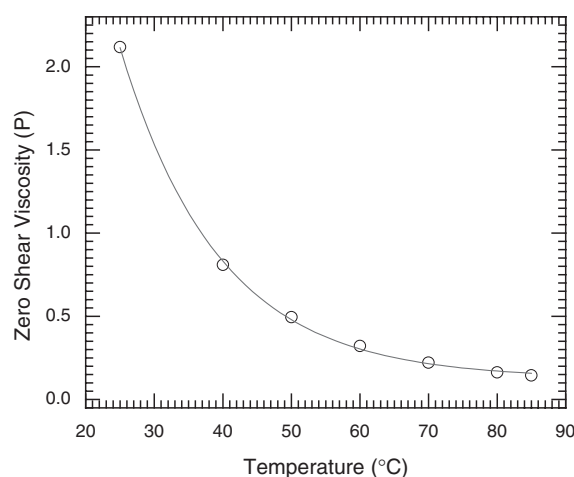


Fig. 7. Temperature dependence of bulk viscosity of E7/NOA65 mixture (50 : 50 by weight).

prepolymer molecules migrate much faster due to lower bulk viscosity. Evidently, one should obtain uniform bilayer PSCOF structures with a smooth LC-polymer interface.

3.3 Cell thickness dependence of PSCOF formation

The effect of cell thickness on PSCOF formation was also investigated. By preparing cells with thicknesses of 1.5 μm, 5 μm and 10 μm and cured under UV at 0.5 mW/cm² at 50°C. The optical microscopy images reveal a change from a well-aligned and uniform PSCOF texture to a PDLC texture [Figs. 8(a) to 8(c)] as cell thickness is increased from 1.5 μm to 10 μm. The results of SEM (Fig. 9) also show a change from a uniform PSCOF layer structure to PDLC-type structures. In thick cells, monomers (LC molecules) have to travel a longer distance to reach the area close to (farther from) the UV source than that in thin cells. Since the

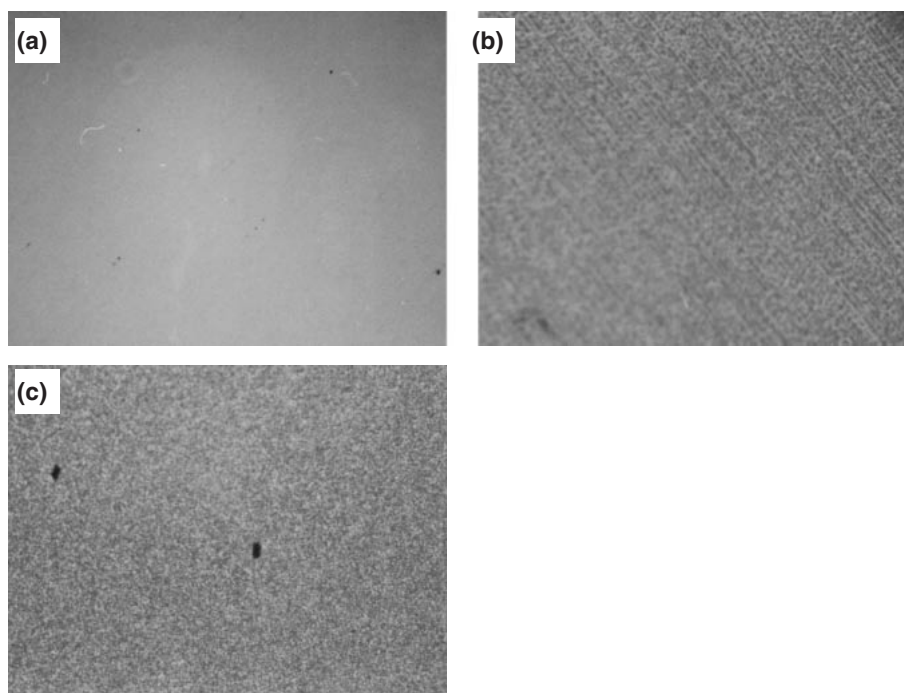


Fig. 8. Microscopic textures with crossed polarizers, magnification = 200. The samples' cell gaps are (a) 1.5 μm, (b) 5 μm and (c) 10 μm respectively.

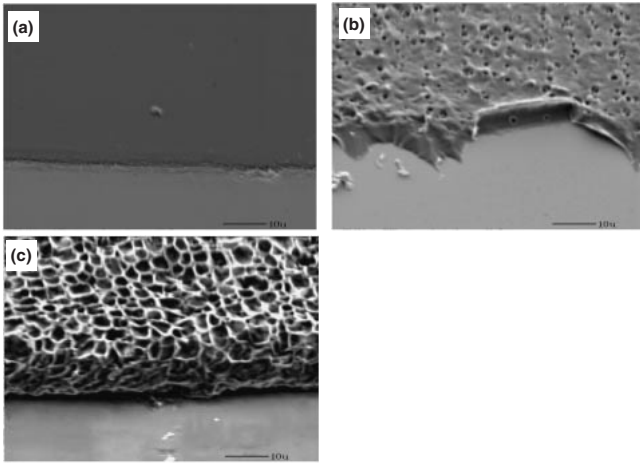


Fig. 9. SEM images of polymer structure formed in samples with cell gaps of (a) 1.5 μm , (b) 5 μm and (c) 10 μm , respectively. All the samples were tilted 45° for the section view. The scaled bars denote 10 μm .

polymerization reaction proceeds faster than monomer diffusion, most monomers are polymerized before they migrate to the other side, which is close to the UV source. Consequently, PDLC-like structures with LC microdroplets are formed in samples with a cell gap larger than 5 μm [Figs. 9(b) and 9(c)]. This result suggests that thin cells should be used to obtain good PSCOF structures.

4. Conclusions

The results of our investigation into the effects of variations in UV intensity, curing temperature, and cell thickness on the formation of PSCOF have been reported. An interaction between two competing processes involved spatially nonuniform polymerization and the diffusion of LC and monomer molecules plays the decisive role in determining the morphology of the resulting polymer structures.

A fast diffusion of molecules in a solution with a low bulk viscosity at high curing temperatures or slow polymerization

under a relatively low UV intensity leads to the formation of homogenous and uniform polymer layer structure with little LC trapped in it. On the other hand, a fast polymerization or a slow LC and monomer diffusion at low curing temperatures leads to the formation of heterogeneous PDLC structures. Short diffusion distances in thin cells result in homogeneous PSCOF structures. The one-dimensional model proposed by Qian *et al.*⁸⁾ predicates that a slow polymerization at low-intensity-UV irradiation allows a complete separation of LC and the resulting polymer and leads to a uniform PSCOF structure, while high-intensity-UV irradiation results in the formation of heterogeneous structures characteristic of PDLC. Our experimental observations on the structure changes of PSCOF with UV intensity are in good agreement with the prediction of the model.

Acknowledgment

The authors would like to thank Dr. Oleg D. Lavrentovich for providing access to the SEM facility. This work was supported, in part, by the National Science Foundation under the grant DMR-0312792 and by a Research Challenge award from the Ohio Board of Regents.

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