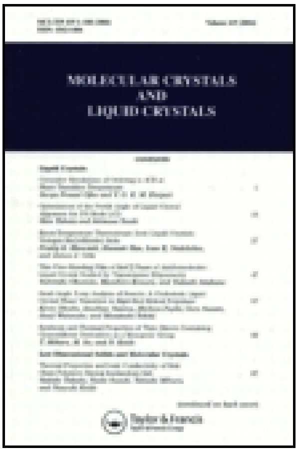

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Effect of Copolymer Composition on the Domain Morphology and Electrooptic Properties of Polymer Dispersed Liquid Crystals

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EFFECT OF COPOLYMER COMPOSITION ON THE DOMAIN MORPHOLOGY AND ELECTROOPTIC PROPERTIES OF POLYMER DISPERSED LIQUID CRYSTALS

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Abstract Film morphology and electrooptic performance of poly(styrene-co-ethylmethacrylate) (PSEMA)/E7 composite films have been studied for various copolymer compositions. The effects of copolymer composition on the optical response of the films were measured as a function of voltage and frequency of applied AC electric field. It was found that the LC domain size increased significantly with styrene content of PSEMA up to 32.5%, beyond which a decrease was noted. The electrooptic responses were mainly governed by the film morphology.

INTRODUCTION

Polymer dispersed liquid crystal(PDLC), where LC phase is imbedded in polymer matrix, gives a number of potential applications ranging from large area flexible window and signs to high resolution active matrix addressed devices, and direct view display.[1-3] These films are electrically switchable from an opaque to a transparent state. The light scattering states are essentially induced by optical heterogeneity of the film such as spatial distortion of nematic director and refractive index mismatching between polymer and LC phase.[4,5] Electrooptic properties depend on polymer/LC composition, film thickness, morphology(domain size and shape), match and mismatch of refractive indices of polymer and LC, dielectric properties of polymer and LC, and surface interaction.[4-6]

We synthesized styrene-ethylmethacrylate copolymers(hereafter called PSEMA) with different composition, and prepared films at 40/60(polymer/LC by weight) composition. The effects of copolymer composition on morphology and electooptic properties of the films were measured as a function of voltage and frequency.

EXPERIMENTAL

PSEMAs of various styrene content(0~54.6 wt%) were polymerized in benzene with azobisisobutylonitrile(AIBN) at 60℃. Number average molecular weights(M_n) and weight average molecular weight (M_w) were determined by a gel permeation chromatography(GPC), and the copolymer composition by refractive index(n_p) measurements(Abbe). Molecular parameters and refractive indices of PSEMAs are listed in Table I. E7 is a mixture of nematic liquid crystal(cyanobiphenyl type, BDH Chemical) with n_o = 1.5216, n_e = 1.7462, T_{KN}=263K, T_{NI}=341K.

Composite films were prepared by SIPS(solvent induced phase separation) technique[7-9] at room temperature. Approximately 20 wt% of PSEMA and E7 at a fixed polymer/LC composition(40/60 by weight) was dissolved in chloroform and cast on a ITO-coated glass plate using an applicator to control the thickness. The thickness of the dried film was ~25μm.

Morphologies of the composite films were studied using a scanning electron microscopy(SEM). LCs were first extracted in methanol at 25℃, and the films were dried overnight under vacuum. The dried films were cryogenically (in liquid nitrogen) fractured, and sputtered with gold before viewing under SEM.

Table I Characteristics of the copolymers synthesized.

Polymers	M_n	M_w	n_p	Styrene content(%)
PSEMA0	28467	59558	1.4845	0
PSEMA1	16033	38933	1.4951	10.3
PSEMA2	16209	38965	1.5082	22.4
PSEMA3	11600	35932	1.5191	32.5
PSEMA4	10373	31223	1.5429	54.6

For electrooptic measurements, the composite films were sandwiched between two indium/tin oxide(ITO) coated glass plates. The collimated beam of He/Ne laser(wave length of 632.8 nm) was passed normal to the film surface, and the transmitted light intensity without any polarizer was measured with a photodiode. The output from a function generator was amplified and used to drive the cell. The drive signal and the response of the photodiode were monitored on a digital storage oscilloscope(Hitachi VC-6023). The distance between the cell and photodiode was about 300mm.

RESULTS

Film morpology is a most significant factor to control the electrooptic performance of the composite film, and it depends on a number of factors such as the type of polymer and LC, film composition, type of solvent in SIPS, and film preparation details.

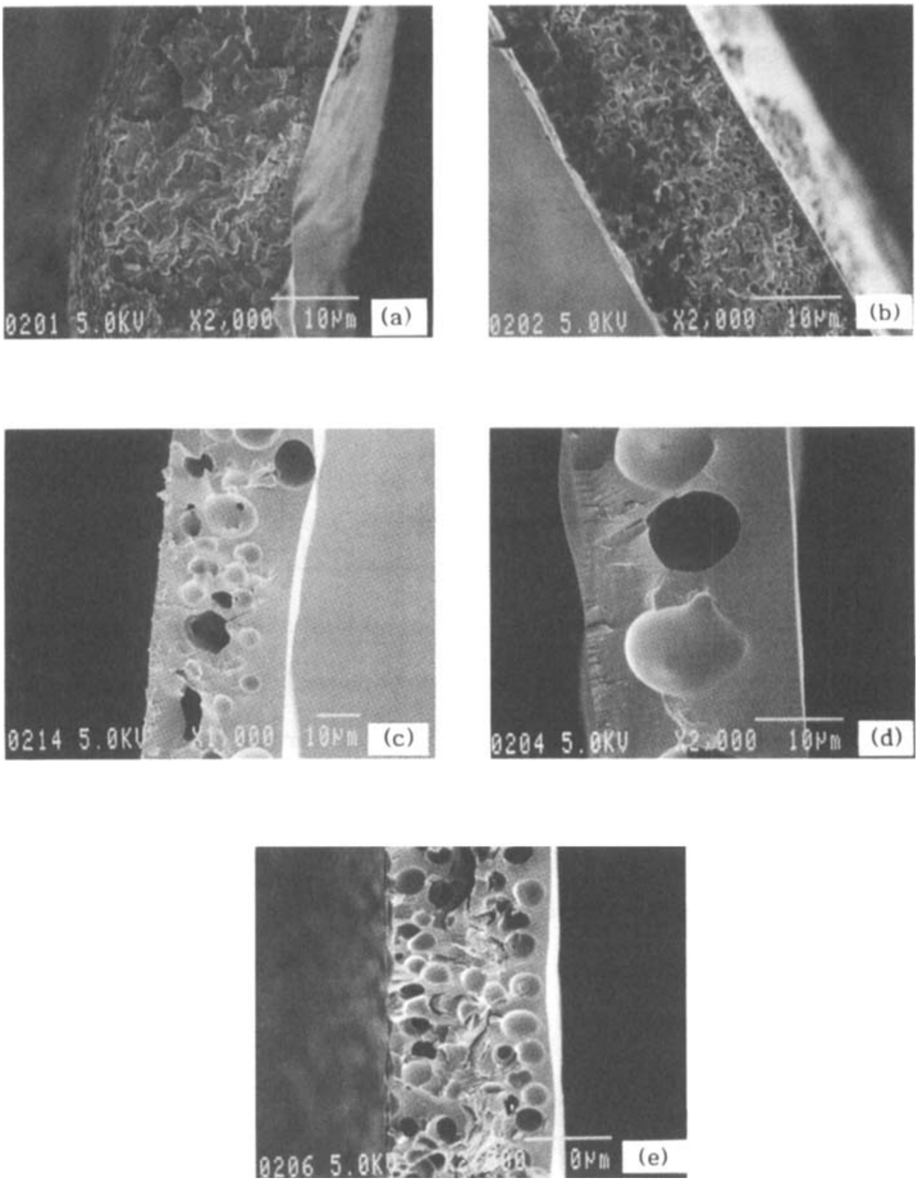

FIGURE 1. SEM photographs of polymer/E7(40/60, w/w) composite films after extraction of LC with methanol : (a) PSEMA0/E7, (b) PSEMA1/E7, (c) PSEMA2/E7, (d) PSEMA3/E7, and (e) PSEMA4/E7.

Figure 1 shows SEM morphology of the film cross sections. It is surprising that the morphology is greatly changed with only the variation of copolymer compositions. The size of LC droplet is minimum with PSEMA0 homopolymer(<0.1μm), and it increases with the styrene content of copolymer showing maximum with PSEMA3(32.5% styrene, ~10μm). The droplet size decreases with further increase of styrene content(PSEMA4, ~3μm). This dissolution of LC molecules in polymer matrix, especially in PSEMA0 and PSEMA1, is apparent from the SEM(compare the fractional area of droplet to the LC composition).

In SIPS, the LC droplet size should mainly be governed by polymer-LC interactions and the solution viscosity which, on the other hand, is determined by the molecular weight of polymer. From this point of view, the smallest droplet size with PSEMA0 is probably due to the strong PSEMA0-E7 interactions and high solution viscosity of casting. Stronger interactions with polar LC molecules are expected from the relatively high polarity of PSEMA0 as compared to the other copolymers. Polarity of the copolymers decreases with the increase of styrene content. Higher viscosity of PSEMA0 solution is simply expected from its high molecular weight(Table 1). It is noted in the Table that molecular weight of the polymer decreases with the increase of styrene content. The decrease of polarity and molecular weight of polymer with increasing styrene content should contribute to the easy coalescence of LC droplets to form larger ones, or augment polymer-LC phase separations. The reduction of LC domain size in PSEMA4, as compared to PSEMA3, is not well understood at this moment. Exact chemical formula and composition of the E7 would be necessary.

Contact angle measurements(Fig.2) gave essentially identical composition dependence with droplet size, i.e., contact angle of the film with E7 increased with styrene content of the copolymer up to 32.5% styrene, beyond which a decrease was noted.

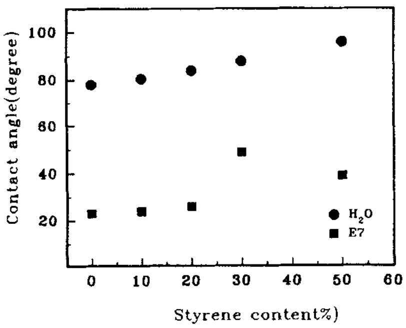

FIGURE 2. Contact angle vs. styrene content.

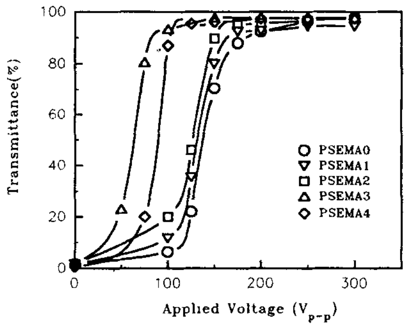

FIGURE 3. Transmittance vs. voltage for PSEMA/LC composite film at 1kHz.

Figure 3 shows transmittance as a function of applied voltage at 1kHz for the composite films. The transmittance of polymer/LC composite film is closely related to the nematic director orientation of LC molecules. In the absence of electric field, LC molecules adopt oriention of minimum free energy which is determined by interactions at polymer-LC interface.[10,11] Since LC used in this experiments has a positive dielectric anisotropy, LC molecules will tend to align with their nematic directors along the applied field. At this time, much stronger external field should be applied when the polymer-LC interactions are stronger. It may be noted that saturation transmittance of the film is the highest for PSEMA3/LC because the mismatch of refractive indices between polymer and LC is minimum for this film. For $n_p \simeq n_o$, transmittance of the film increases rapidly until a maximum value is reached, while for $n_p<n_o$ transmittance increases smoothly and never reaches a maximum. For $n_p>n_o$ the transmittance reaches a maximum, beyond which the transmittance decreases slightly.[12] This tendency is generally seen in the Figure.

Figure 4 shows threshold voltage(V_{th}), defined as the voltage required to achieve 10% of maximum transmittance, and saturation voltage(V_{sat}), required to achieve 90%, as a function of styrene content of the copolymer. It is clearly seen that V_{th}, V_{sat}, and (V_{sat}-V_{th}) strongly depend on the copolymer composition. V_{th} as well as V_{sat} decreases with increasing styrene content up to 32.5%, beyond which an increase in V_{th} and V_{sat} is obtained. The tendency is identical with morphology.

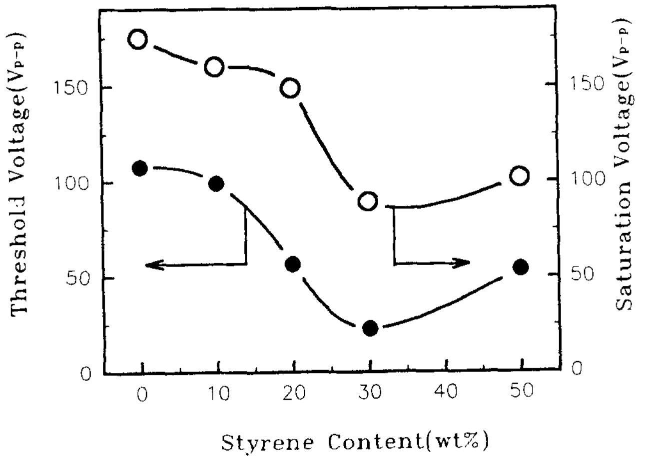

FIGURE 4. Threshold voltage and saturation voltage vs. styrene content for PSEMA/LC composite film.

For bipolar orientation, which occurs in most cases, the V_{th} of polymer/LC composites film is given by eq. (1),[3, 13]

$$V_{th} = \frac{d}{3a}\left(\frac{\rho_P}{\rho_{LC}} + 2\right)\left(\frac{K(l^2 - 1)}{\varepsilon_0 \Delta\varepsilon}\right)^{1/2} \qquad (1)$$

where d, a, ρ, K, and l represent film thickness, major dimension, resistivity, eleastic constant, and aspect ratio(major dimension/minor dimension) of LC domain, respectively, and subscripts P and LC denote polymer and liquid crystal. Nematic director orientation within the LC domain is determined by a balance between eleastic force, electric force and surface interaction.[14] Equation (1) states that V_{th} depends mainly on "a" for a given LC and domain geometry. Thus PSEMA3 is expected to show the lowest V_{th} because the its domain size is the largest. Our earlier studies[8] indicated that interfacial interaction, i. e., surface anchoring stength, is a dominant factor to control V_{th} of composite film.

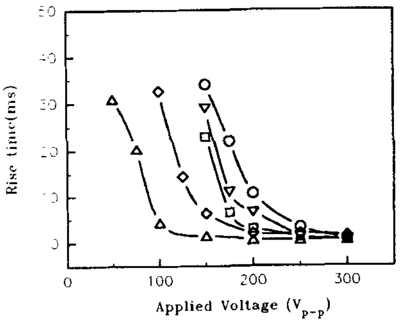

FIGURE 5. Rise time vs. voltage for PSEMA/LC composite film at 1kHz.

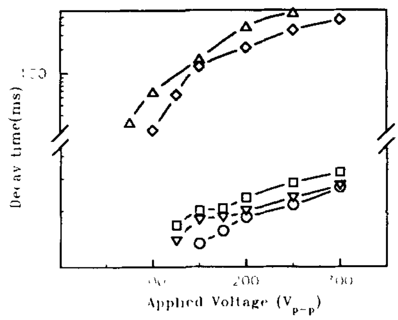

FIGURE 6. Decay time vs. voltage for PSEMA/LC composite film at 1kHz.

Rise time(τ_R) and decay time(τ_D) are defined as the time required for transmittance change from 10 to 90% upon switching the film on, and upon switching the film off, respectivly, and these are given by eq.(2) and eq.(3).[3,15] Figures 5 and 6 show rise time and decay time as a function of applied voltage. With increasing applied voltage τ_R decreases rapidly in the transition

$$\frac{1}{\tau_R} = \frac{1}{\eta}\,\frac{9\varepsilon_0 \Delta\varepsilon V^2}{d^2(\rho_P/\rho_{LC}+2)^2} + \frac{K(l^2-1)}{\eta a^2} \tag{2}$$

$$\tau_D = \frac{\eta a^2}{K(l^2-1)} \tag{3}$$

region and almost unchanged at > V_{sat} + 50$V_{p\text{-}p}$. On the other hand, τ_D does not depend on the applied voltage. In general, τ_R is dominated by the first term of eq. (2), and is inversely proportional to $\sim\Delta\varepsilon E^2(E=v/d)$,[2,16] which is qualitatively agreed with the present results. It should be noted that the τ_R is only a few ms at > V_{sat}, and this is faster than that of convensional twisted nematic type display device. With regard to the copolymer composition, τ_R decreases and τ_D increases with increasing styrene content up to 32.5%, beyond which the tendency is reversed.

Figure 7 shows transmittance as a function of electric frequency at 150 $V_{p\text{-}p}$ for the composite film. When the transmittance oscillates with external field, an average of maximum and minimum was taken. At this particular voltage, films of high styrene content are saturated(Fig. 3) and give high transmittance throughout the frequency range. Typical S-shaped curves with plateau at both frequency ends are seen for PSEMA2 and PSEMA3. In most dielectric composites composed of polymer and LC, the applied external electric field is not entirely imposed on LC phase. The distribution of external field to polymer and LC phases strongly depends on the magnitude of dielectric constants and conductivities. For a series connected dielectric composite which finds close analogy to the films of present concern, the partition of external electric field is given by eq.(3),[9]

$$\frac{E_{LC}}{E_P} = \frac{|\varepsilon^*_P|}{|\varepsilon^*_{LC}|} = \left(\frac{\omega^2\varepsilon'^2_P+\sigma^2_P}{\omega^2\varepsilon'^2_{LC}+\sigma^2_{LC}}\right)^{1/2} \tag{4}$$

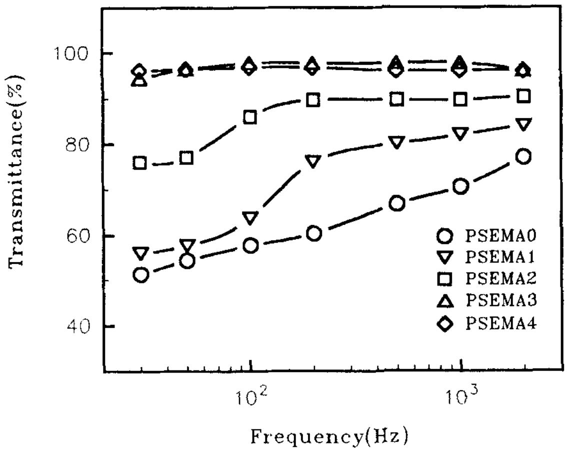

FIGURE 7. Transmittance vs. frequency for PSEMA/LC composite film at 150Vp-p.

where E, ε^*, ε', σ and ω represent electric field, complex and dielectric constants, conductivity and angular frequency, respectively. This equation states that at very low and very high enough frequencies the electric field of each phase is inversely propotional to the conductivity and dielectric constant, respectively. However, in general, the dielectric constant ratio($\varepsilon_P'/\varepsilon_{LC}'$) is not equal to the conductivity ratio(σ_P/σ_{LC}) and an interfacial polarization is induced at certain frequency range. Therefore the distribution of external electric field to LC and polymer phases generally depends on the electric frequency. Since $\varepsilon_P'/\varepsilon_{LC}'$ is generally larger than σ_P/σ_{LC}, the magnitude of E_{LC}/E_P drops dramatically in a frequency range near and below the relaxation frequency of the interfacial polarization.[5,7,9] Presently, this phenomenon is observed for PSEMA0, PSEMA1, and PSEMA2, where relaxation frequency shifts to the lower values with increasing styrene content, probably due to the decreased interfacial interaction.

The relaxation occurs in a broad range of frequency when the polymer-LC interaction is high(PSEMA0), and sharply as the interaction becomes small.

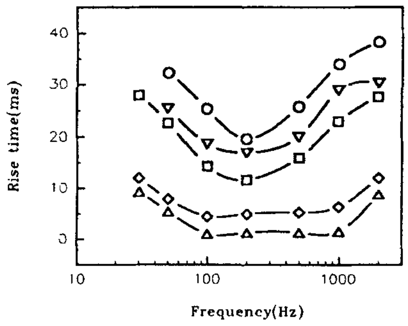

FIGURE 8. Rise time vs. frequency for PSEMA/LC composite film at 150Vp-p.

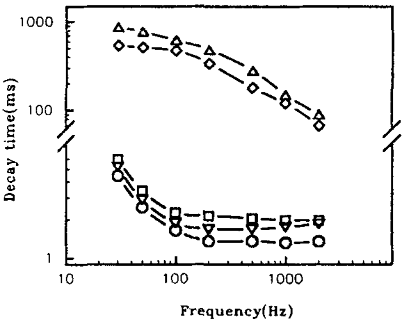

FIGURE 9. Decay time vs. frequency for PSEMA/LC composite film at 150Vp-p.

Figures 8 and 9 show rise time and decay time as a function of frequency. Rise time decreases and increases with frequency at low and high frequencies respectively, showing minimum[17,18] at 100~200 Hz for PSEMA0, PAEMA1, and PSEMA2. At low frequencies, space charge-build up occurs at polymer-LC interfaces leading to the loss of electric field.[19] The space charge-build up decreases with increasing frequency, giving minimum at 100~200 Hz. Above this frequency, dielectric dissipation becomes significant and rise time increases.

The decay response should depend on the droplet size("a" in Eq. 3), i.e., smaller droplet gives shorter decay time. With similar droplet size the decay time is governed by the polymer-LC interactions. Stronger interactions induce fast decay(compare PSEMA2 and PSEMA4).

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