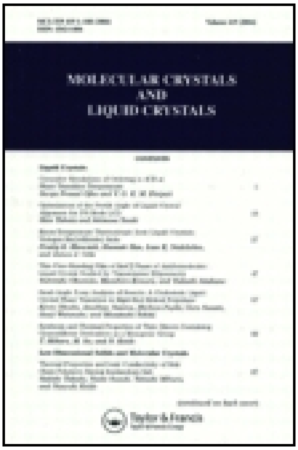

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Effect of Copolymer Composition on the Domain Morphology and Electrooptic Properties of Polymer/Lc Composite Film

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EFFECT OF COPOLYMER COMPOSITION ON THE DOMAIN MORPHOLOGY AND ELECTROOPTIC PROPERTIES OF POLYMER/LC COMPOSITE FILM

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Abstract

Morphology and electrooptic properties of poly(styrene-co-methyl methacrylate) (PSMMA)/nematic liquid crystal composite films have been studied for varying copolymer composition. Effects of copolymer composition, voltage and frequency of applied AC electric field on the optical response of the films were measured, and the results were interpreted in terms of aggregation structure of the film, the interfacial interactions between the LC and the polymer, the magnitude of external field, and refractive indices of LC and polymer.

INTRODUCTION

Polymer/liquid crystal(LC) composite films are becoming more important as an electrooptic devices because of their broad applicability ranging from light shutters to active matrix projection displays as well as easiness of fabrication of large, flexible display device.[1-5] 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.[6,7] 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.[6-8]

In this research we synthesized styrene-methyl methacrylate(MMA) copolymers(hereafter called PSMMA) with different composition, and prepared films at 40/60(by weight)(polymer/LC) composition. The effect of copolymer composition on electooptic properties were measured as a function of voltage and frequency. Attempts were made to elucidate the relationship between copolymer composition and electrooptic properties.

EXPERIMENTAL

PSMMAs of varying styrene content(0~35.7 wt%) was polymerized in benzene with azobisisobutylonitrile(AIBN) at 60℃. Average molecular weights(M_n and M_w) were determined by gel permeation chromatography(GPC), whereas the copolymer composition by refractive index(n_p) measurements(Abbe). Molecular parameters and refractive indices of PSMMAs are listed in Table I. E-44 is a mixture of nematic liquid crystal(cyanobiphenyl type, BDH Chemical) with n_o = 1.528, n_e = 1.790, T_{KN}=273K, T_{NI}=373K.

Table I . Characteristics of the Copolymers Used in the Experiment

mixture of nematic liquid crystal(cyanobiphenyl type, BDH Chemical) with n_o =
1.528, n_e = 1.790, T_{KN}=273K, T_{NI}=373K.

and cast on a ITO-coated glass plate using an applicator to control the thickness. The thickness of the dried films were ~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.

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

Figure 1 shows the SEM micrographs of the cross sections of PSMMA/LC (40/60) composite film. Morphology of composite film depends on a number of factors such as the type of polymer and LC, film composition, solvent, and film preparation conditions. As expected, PMMA or PSMMAs form three-dimensional network and LCs are imbbeded in polymer. The size of LC domains or channels are smallest with PMMA, however no significant difference is obtained with varying copolymer composition. Spatial heterogeneity is found near the air facing surface(AFS) of the film, where small drops or channels, diameter smaller than 0.5μm, are clustered. The smaller LC domains near AFS is formed by rapid solvent evapolation and solidification[12] of polymer near AFS, not allowing the LC domains to coalesce.

Figure 2 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.[13,14] Since LC used in this experiments has a positive dielectric anisotropy, LC molecules will tend to align with their nematic director along the applied field. At this time, much stronger external field should be applied when the polymer-LC interactions are stronger. It is noted that saturation transmittance for PSMMA3/LC film is the highest 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 never reaches a maximum. In the case of $n_p>n_o$ the transmittance reaches a maximum, beyond which the tranasmittance decreases silightly.[15] The refractive indices of polymer used are in the range of 1.492~1.528, therefore

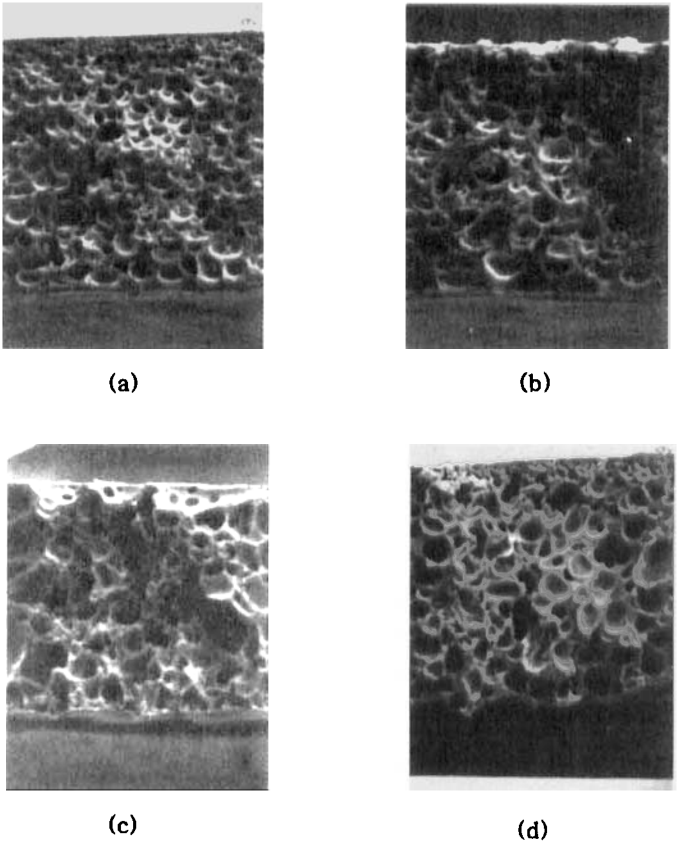


Fig. 1. SEM photographs of polymer/E44(40/60, w/w) composite films after extraction of LC with methanol : (a) PMMA/E44, (b) PSMMA1/E44, (c) PSMMA2/E44, and (d) PSMMA3/E44.

transmittance increases with increasing order of PMMA < PSMMA1 < PSMMA2 < PSMMA3 due to the decrease of $|n_p - n_o|$.

Figure 3 shows threshold voltage(V_{th}), defined as the voltage required to achieve 10% of miximum 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} is more than 250V_{p-p} for PMMA and with increasing styrene content of copolymer it decreases down to less than 150 V_{p-p}. For bipolar orientation, which occurs in most cases, the V_{th} of polymer/LC composites film is given by eq. (1),[3,16]

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

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, respectivly, and subscripts P and LC denote polymer and liquid crystal. Nematic director orientation within the LC domain is determined by correlation between eleastic force, electric force and surface interaction.[17] Equation (1) states that V_{th} depends only on ρ_P for a given LC and domain morphology. Thus PMMA is expected to show the lowest V_{th} because the ρ of PMMA is the lowest among the polymers used. However, Figure 3 shows the opposite trend. Our earlier studies[10] indicated that interfacial interaction, i. e. surface anchoring stength, is a dominant factor to control V_{th} of composite film.

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).[3,18]

Figures 4 and 5 show rise time and decay time as a function of applied voltage. With increasing applied voltage τ_R decreases rapidly in the transition

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

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

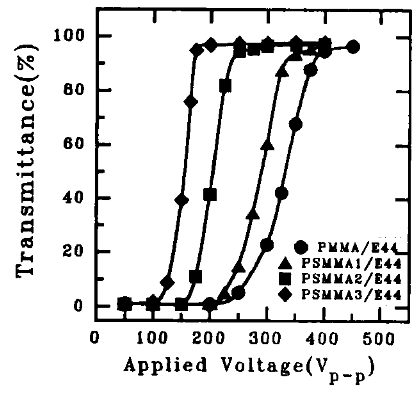


Fig. 2. Transmittance vs. applied voltage for PSMMA/LC composite film at 1kHz 25℃.

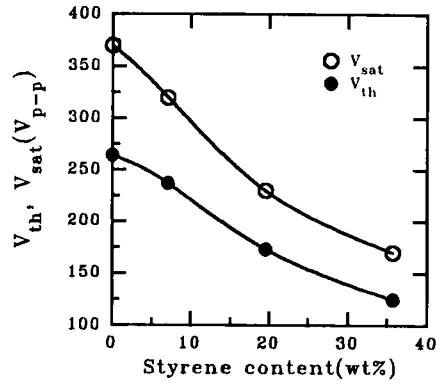


Fig. 3. Threshold voltage and saturation voltage vs. styrene content for PSMMA/LC composite film.

region and almost unchanged at > V_{sat} + $50V_{p-p}$. 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 the rise time is inversely proportional to $\sim \Delta\varepsilon E^2(E=v/d)$,[2,19] 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. Under the same voltage, τ_R decreases and τ_D increases with increasing styrene content of the copolymer. This could also be interpreted in terms of anchoring effect applied for V_{th} vs. styrene content behavior in Fig. 3. That is, as styrene content increases, anchoring strength of LC molecules toward polymer wall decreases, which leading fast rise time and slow decay time.

Figure 6 shows transmittance as a function of time at $350V_{p-p}$ for PSMMA1/LC composite film. At 30Hz, periodic flicker of transmittance is exactly twice of imposed AC electric pulse oscillating from maximum to minimum value. However, at higher external frequency, molecular motion of LC cannot follow the polarity change of external electric field,[1,20] and the amplitude of the transmitted light decreases with increasing applied frequency. Full scale oscillations, meaning the dirctor orientation between random and electric field direction, occurs only at the initial power on stage. Even at 1kHz, transmittance oscillates in full scale at the very initial power-on stage, which means there is

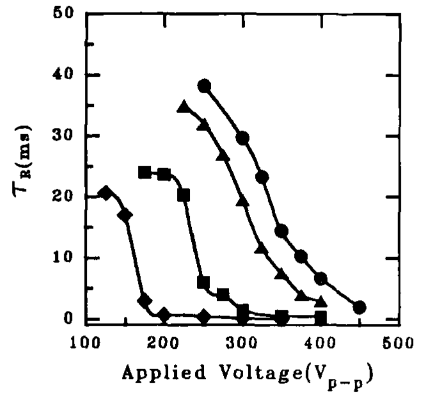


Fig. 4. Rise time vs. applied voltage for PSMMA/LC composite film(1kHz and 25℃, same caption with Fig. 2.).

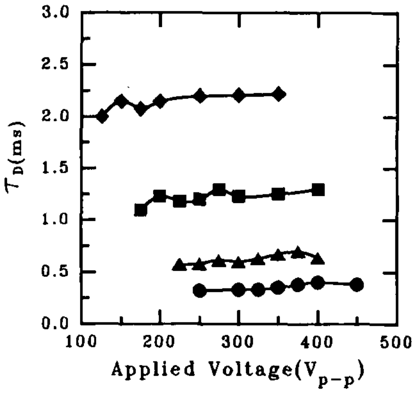


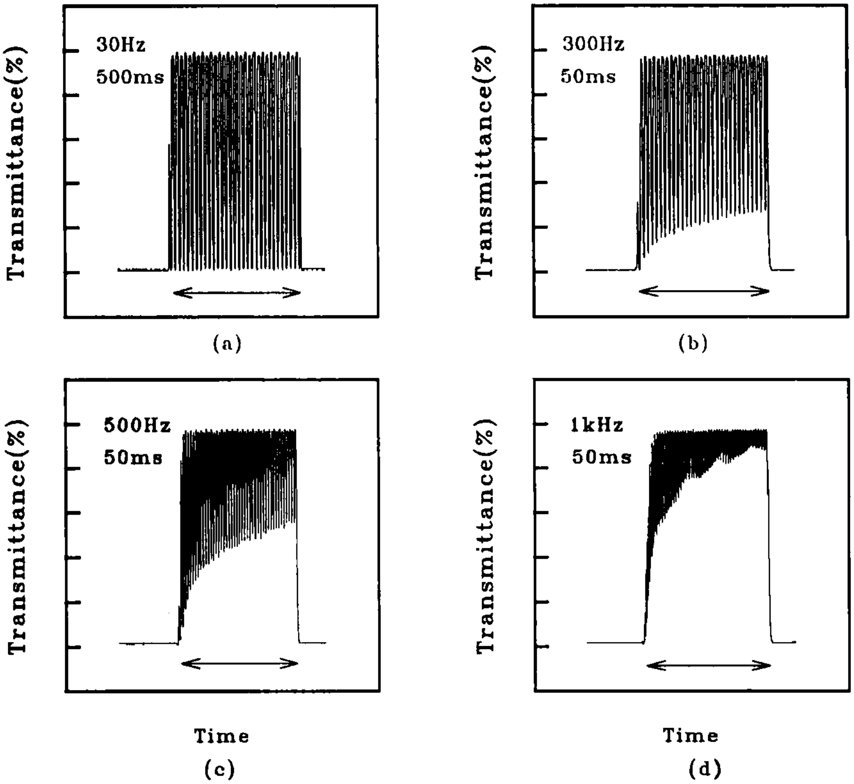
Fig. 5. Decay time vs. applied voltage for PSMMA/LC composite film(1kHz and 25℃, same caption with Fig. 2.).

nematic director reorientation. However, it disappears immediately.

Figure 7 shows transmittance as a function of electric frequency at 350 V_{p-p} for the composite film, showing on S-shaped curves, with plateaus at both frequency ends. When transmittance oscillates following external field, it is obtained by averaging maximum and minimum values. 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),[9,21]

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

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.



(a) (b) (c) (d)

Fig. 6. Transmittance as a function of time at 350V_{p-p} for PSMMA1/E44 composite film : (a) 30Hz, (b) 300Hz, (c) 500Hz, (d) 1kHz.

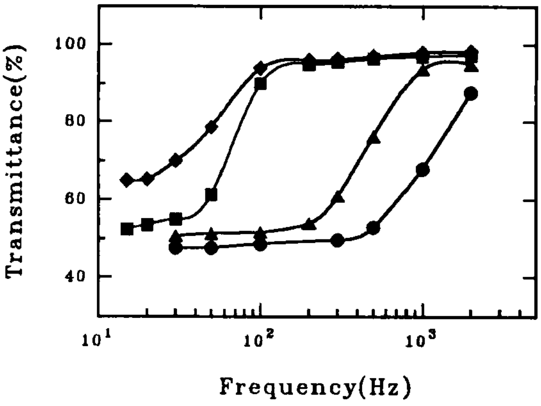
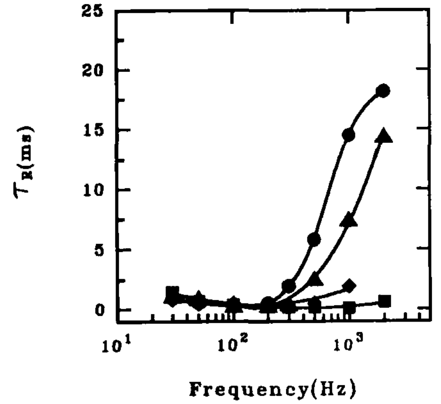


Fig. 7. Transmittance vs. frequency for PSMMA/LC composite films (350 V_{p-p}, 25℃, same caption with Fig. 2.).

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. Therefore the distribution of external electric field to polymer and LC phases strongly 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.[7,9,21] It is seen that relaxation frequency shifts to lower values with increasing styrene content, due to the decreased interfacial interaction

Figures 8 and 9 show rise time and decay time as a function of frequency. According to eq. (4), τ_R decreases with applied frequency since E_{LC} is larger at high frquency.[22] This is well agreed with PMMA/LC and PSMMA1/LC system. However, PSMMA2 and PSMMA3/LC systems show diffrent behavior. In these films, τ_R decreased with frquency below 300Hz, but increased abruptly at > 300Hz. This may result from the fact that the reorientaion of nematic director occurs before the transmittance reaches complete saturation in the initial electric field, which is often observed for liquid crystal side chain polymers.[23] τ_D also decreased with applied frquecy(Figure 9). τ_D of PSMMA3/LC system shows an obvious frequency dependence, whereas the others show marginal change. It seems that when relaxation occurs slowly(small interfacial interaction), frequency affects τ_D significantly.



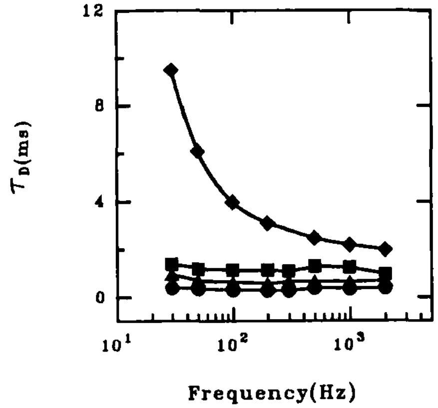


Fig. 8. Rise time vs. frequency for PSMMA/LC composite film. (350 $V_{p\text{-}p}$, 25℃, same caption with Fig. 2.)

Fig. 9. Decay time vs. frquency for PSMMA/LC composite film. (350 $V_{p\text{-}p}$, 25℃, same caption with Fig. 2.)

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