Dielectric Property–Electrooptical Effect Relationships of Polymer/Liquid-Crystal Composite Films

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Received October 3, 1990; Revised Manuscript Received February 7, 1991

ABSTRACT: The dielectric properties of a polymer/liquid-crystal (LC) composite film and their influence on the electrooptical response have been investigated. The composite film in which an LC material is embedded as a continuous phase in a three-dimensional spongy polymer matrix shows an electrooptical effect based on a novel concept of light scattering. The electrooptical response speed for the composite film is proportional to $\sim\Delta\epsilon E^2$, where $\Delta\epsilon$ is the dielectric anisotropy of the LC, and E is the electric field. The dielectric properties of the composite film are approximately explained by the series-connected dielectric composite model consisting of the polymer matrix and the LC phases. Since the magnitude of the ratio of the dielectric constants of both polymer and LC phases, $\epsilon'_P/\epsilon'_{LC}$, is not always the same as that of the electric conductivities, σ_P/σ_{LC}, the magnitude of an ac electric field in the LC phase is modulated and depends on the frequency of the externally applied ac electric field. Further, the frequency dependence of the magnitude of an ac electric field in the LC domain is calculated on the basis of the series-connected dielectric composite model. The calculated result explains qualitatively the frequency dependence of the electrooptical response rise time for the composite film. Also, it is concluded, from the dielectric model calculation, that the electrooptical response rise speed in a wide frequency range of electric field could be improved by using a polymer matrix with greater magnitudes of both electric conductivity and dielectric constant.

1. Introduction

A novel electrooptical effect based on the light scattering–light transmission switching of a polymer/liquid-crystal (LC) composite system has been investigated for possible application to a large-area, flexible display device.[1-6] The composite film is interesting for this application because it has a sufficient viewability and a high light transmittance compared with a twisted nematic mode and, in addition, has good moldability and processability. A prototype of the polymer/LC composite film was first developed by us.[7,8] The first application for the electrooptical device of the polymer/LC composite system was attempted by Craighead and co-workers.[1] We have reported the electrooptical properties of the polymer/LC composite film in which an LC is embedded as a continuous phase, i.e., the self-supported LC film.[5,6,9-11] The reversible light scattering–light transmission switching may be caused by the optical heterogeneity–homogeneity change, which is dependent on the magnitude and the frequency of an ac electric field. These optical heterogeneity–homogeneity states correspond to the random–unidirectional orientation of LC directors, being induced by the modulation of the external electric field, respectively.[10,11] Fergason proposed that the opaque "electric field-off state" was caused by the mismatch of the refractive indexes between the polymer matrix and a nematic curvilinear aligned phase (NCAP).[2] We have suggested that the spatial distortion of nematic directors in the curved or distorted LC continuous channel is also an important cause for the optical heterogeneity in addition to the mismatch of refractive indexes.[10,11] Therefore, the degree of light scattering is greatly dependent on various factors such as the shape or size of the LC domains, the birefringence of the LC material used, the refractive indexes of both phases, and the compatibility between the matrix polymer and LC.[12]

The polymer/LC composite film can be treated as a binary dielectric composite because of its phase-separated nature. In such a heterogeneous dielectric composite, the magnitude of an ac electric field in an LC domain is not generally equal to that of the externally applied one, where the externally applied field means simply the voltage divided by the sample thickness. Since the electrical response speed of LC molecules in the LC domain is proportional to the square of the magnitude of the ac electric field in the LC phase, it is important to understand the factors that affect the effective electric field in the LC phase. This knowledge is necessary to achieve rapid response speed in an electrooptical device using the polymer/LC composite system.

In this paper, we investigated (1) the dielectric properties of the composite film, (2) the relationship between the dielectric properties and the light switching characteristics of the composite film, and (3) the way to improve the response characteristics on the basis of the modulation of electric properties of the matrix polymer.

2. Experimental Section

2.1. Materials. The chemical structures of the constituent polymers and LC materials for the composite films are given in Figure 1. Poly(methyl methacrylate) (PMMA) [$\bar{M}_w$ = (9.8–11) × 10^4, $\bar{M}_w/\bar{M}_n$ = 1.8–2.0] and acrylonitrile–butadiene–rubber (NBR) (48% of acrylonitrile monomer unit) were used as matrix polymers. E44 (a nematic mixture with positive dielectric anisotropy, purchased from BDH Chemical Co. Ltd.) and 4-(heptyloxy)-4′-cyanobiphenyl (7OCB) were used as LC materials.

2.2. Preparation of the Composite Film. Polymer/LC composite films were prepared by casting 5–10 wt % chloroform solutions on a glass plate. A fraction of LC of 60 wt % was chosen to produce a composite film combining sufficiently large electrooptical contrast with satisfactory mechanical durability.[11] The thickness of the composite film was ~50 μm.

2.3. Investigation of Dielectric Properties. In order to investigate the dielectric properties, the composite films were sandwiched between two indium/tin oxide (ITO) coated glass plates. The area and the surface resistance of the ITO electrode were 1 cm² and 10 Ω·cm⁻², respectively. The dielectric properties

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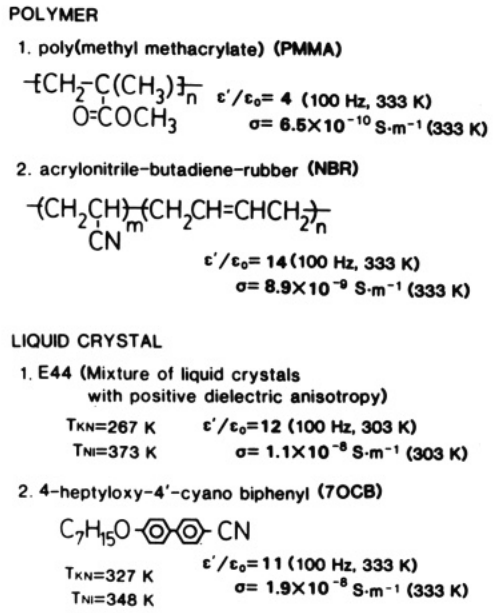

Figure 1. Chemical structures of the constituents for the polymer/liquid-crystal composite films.

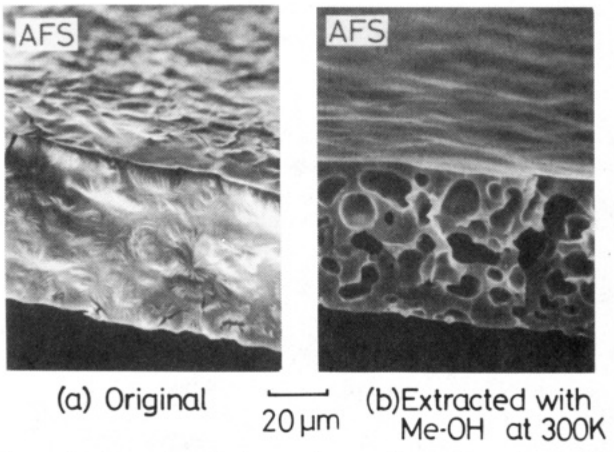

Figure 2. Scanning electron microscopic photographs for the PMMA/E44 (40/60, w/w) composite film (a) as-cast from a chloroform solution and (b) after extraction of E44 with methanol at 303 K. The upper part and the lower part are an air facing surface (AFS) and a fractured surface, respectively.

were evaluated from the measurement of both capacitance and conductance for the composite film by using an impedance analyzer (Model 4192A, Yokogawa-Hewlett-Packard Ltd.).

2.4. Electrooptical Measurements. The electrooptical measurements were carried out by using the same cell used for the dielectric study. A He/Ne laser (wavelength of 632.8 nm) was used as an incident light, being irradiated normal to the film surface. An external ac electric field was applied across the composite film. The transmitted light intensity through the cell without any polarizers was measured with a photodiode under the modulation of an applied ac electric field. The intensity of transmitted light was recorded with a digital storage oscilloscope (Kawasaki KDS-102). The distance between the cell and the photodiode was 305 nm.

3. Results and Discussion

3.1. Dielectric Analysis of the Polymer/LC Composite Film. Figure 2 shows scanning electron microscopic (SEM) photographs of the PMMA/E44 (40/60, w/w) composite film, (a) as-cast from a chloroform solution and (b) after extracting an LC (E44) with methanol at 303 K. It is apparent that the LC material forms a phase-separated continuous phase in a three-dimensional polymer network.[13] It seems reasonable from the phase-separated structure as shown in Figure 2 that the polymer/LC composite film can be treated as a binary dielectric composite composed of the two different dielectrics (polymer matrix and LC). In the case of a mutual interpenetrating dielectric composite composed of the polymer matrix and the LC phases, the same strength as an externally applied ac electric field across the composite film cannot be imposed on the LC phase, since the magnitude of an ac electric field in the LC phase is strongly dependent on the dielectric heterogeneous structure in the composite film.

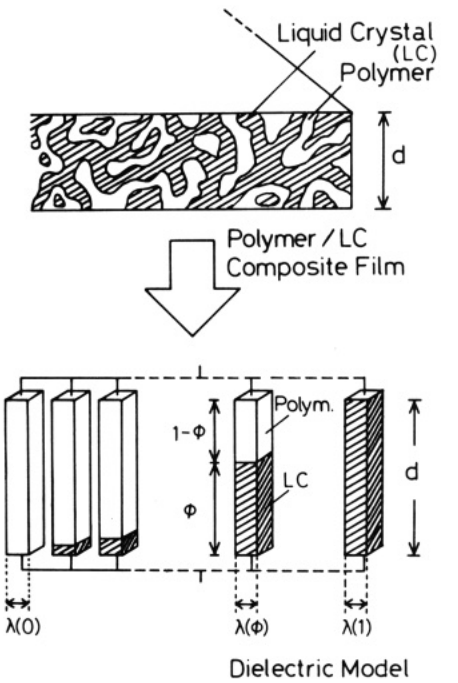

Figure 3. Schematic representation of the cross-sectional area of the composite film and the corresponding dielectric composite model. The $\lambda(\phi)$ is the distribution function of the dielectric microunit in which the LC volume fraction is ϕ.

We tried to describe the dielectrically heterogeneous structure of the composite film by using a dielectric composite model composed of an assembly of microunits connected in series by the polymer and LC phases, as shown in Figure 3. Actually, each microunit has a multilayer structure composed of the matrix polymer and the LC phases. However, from the point of view of a dielectric composite model, such a multilayer structure can be simplified by a two-layer one under the assumption that the structural boundary between the matrix polymer and the LC phases is parallel to the film surface. With this assumption, the polymer/LC composite system is replaced by the dielectric composite model shown in the lower part of Figure 3. In this model, several factors that affect the dielectric properties are neglected, that is, (1) the shape of the LC domains, (2) the LC molecular orientation on the polymeric wall, which is restricted by the anchoring effect of the LC molecules, (3) the dipole–dipole interaction between domains, (4) the migration of conductive ions in a direction that is not parallel to the direction of the applied ac electric field, (5) the refraction of the lines of electric force and of electric displacement, and so on. Therefore, it is assumed that the complex dielectric constant of the polymeric phase, ϵ^*_{P}, or that of the LC phase, ϵ^*_{LC}, in the composite film is independent of position within each phase. In Figure 3, the $\lambda(\phi)$ means the distribution function of the microunit in which the LC volume fraction

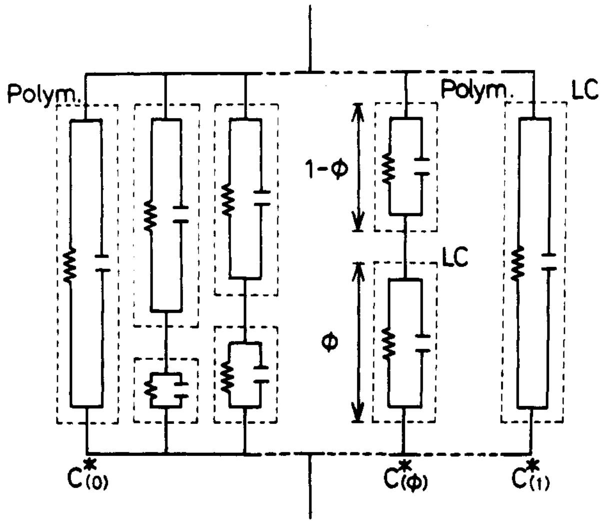

Figure 4. Electrically equivalent circuit of the dielectric composite model. $C^*(\phi)$ is the complex capacitance of the microunit with the LC volume fraction ϕ.

is ϕ, and this function is normalized by

$$\int_0^1 \lambda(\phi)\, d\phi = 1 \tag{1}$$

Further, the entire volume fraction of the LC domain, Φ_{LC}, is described as follows.

$$\Phi_{LC} = \int_0^1 \phi\lambda(\phi)\, d\phi \tag{2}$$

When an external electric field, e_{EXT}, is imposed to the microunit, eq 3 is satisfied since the normal component

$$\epsilon^*(\phi)e_{EXT} = \epsilon^*_P e_P(\phi) = \epsilon^*_{LC} e_{LC}(\phi) \tag{3}$$

of the electric displacement is continuous across a dielectric boundary. $\epsilon^*(\phi)$ and $e(\phi)$ are a complex dielectric constant and an electric field in the microunit in which an LC volume fraction is ϕ, and the subscripts P and LC represent the polymeric and the LC phases, respectively. Also, the following boundary condition concerning the electric field is satisfied in the microunit.

$$e_{EXT} = \phi e_{LC}(\phi) + (1-\phi)e_P(\phi) \tag{4}$$

Then, eq 5 is derived from eqs 3 and 4. Further, the

$$\epsilon^*(\phi) = (\epsilon^*_P \epsilon^*_{LC})/\{(1-\phi)\epsilon^*_{LC} + \phi\epsilon^*_P\} \tag{5}$$

complex dielectric constant, ϵ^*_{COMP}, of the entire composite model is expressed by eq 6. When eq 5 is substituted in

$$\epsilon^*_{COMP} = \int_0^1 \epsilon^*(\phi)\lambda(\phi)\, d\phi \tag{6}$$

eq 6, we obtain eq 7.

$$\epsilon^*_{COMP} = \int_0^1 [(\epsilon^*_P \epsilon^*_{LC})/\{(1-\phi)\epsilon^*_{LC} + \phi\epsilon^*_P\}]\lambda(\phi)\, d\phi \tag{7}$$

Figure 4 illustrates the electrically equivalent circuit that corresponds to the dielectric composite model shown in Figure 3. Each polymeric or LC domain is expressed by a parallel connection of both a capacitance and a resistance. Further, the complex capacitance of each microunit with the LC volume fraction ϕ is described as $C^*(\phi)$. Therefore, the entire complex capacitance of this equivalent circuit, C^*_{COMP}, is expressed by eq 8. The relationship between the complex dielectric constant and the complex capacitance is written as eqs 9a and 9b, where C_0

$$C^*_{COMP} = \int_0^1 C^*(\phi)\lambda(\phi)\, d\phi \tag{8}$$

$$C^*(\phi) = C_0(\phi)(\epsilon^*(\phi)/\epsilon_0) \tag{9a}$$

$$C^*_{COMP} = C_{0\,COMP}(\epsilon^*_{COMP}/\epsilon_0) \tag{9b}$$

and ϵ_0 are the vacuum capacitance and the vacuum dielectric constant, respectively.

Actually, the value of ϵ^*_{COMP} for the composite film was experimentally obtained by means of an impedance analyzer measurement. Also, ϵ^*_{COMP} can be calculated from eq 7 for the dielectric composite model with the parameters ϕ and $\lambda(\phi)$. Further, the relative dielectric constant, $\epsilon'_{COMP}/\epsilon_0$, and the relative dielectric loss factor, $\epsilon''_{COMP}/\epsilon_0$, for the dielectric composite model are expressed as the real and the imaginary parts of eq 7, respectively. The appropriate dielectric model was determined by comparing the experimental frequency dependence of the relative dielectric constant, ϵ'/ϵ_0, of the composite film with that of the dielectric composite model corresponding to eq 7.

In order to calculate ϵ^*_{COMP} for the dielectric composite model based on eq 7, it is necessary to measure both the ϵ^*_{LC} and ϵ^*_P independently. We used the spatially averaged complex dielectric constant of the LC phase described by eq 10 as the magnitude of ϵ^*_{LC}, because the

$$\epsilon^*_{LC} = (^1/_3)(\epsilon^*_{LC(\parallel)} + 2\epsilon^*_{LC(\perp)}) \tag{10}$$

nematic directors in the LC domain were randomly oriented due to strong polymeric surface/LC molecule interaction on the curved or nonparallel polymer walls in the case of the absence of an ac electric field.[11] In eq 10, $\epsilon^*_{LC(\parallel)}$ and $\epsilon^*_{LC(\perp)}$ are the complex dielectric constants of the LC phase, which are parallel and perpendicular to the long axis of the LC molecule, respectively. The $\epsilon^*_{LC(\parallel)}$ and $\epsilon^*_{LC(\perp)}$ were measured by using the surface-modified cells in which LC molecules were oriented in homeotropic or homogeneous states. Also, as the magnitude of ϵ^*_P, the complex dielectric constant of PMMA dissolving E44 of 10 wt % was used instead of the pure PMMA value, because it was confirmed, from the results of both differential scanning calorimetric (DSC) study and SEM observation, that LC molecules were molecularly dispersed up to ~10 wt % in the PMMA matrix at 303 K.[11,13]

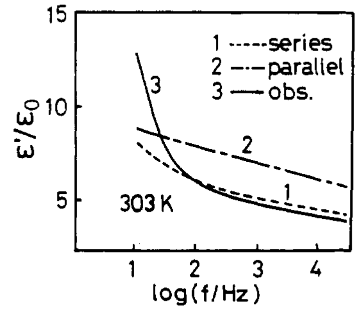

Figure 5. Frequency dependence of the relative dielectric constants, ϵ'/ϵ_0, for the series dielectric composite model (curve 1) and for the parallel dielectric composite model (curve 2) and the experimental results for the PMMA/E44 (40/60, w/w) composite film (curve 3). The measuring temperature was 303 K.

Figure 5 shows the frequency dependence of the relative dielectric constants, ϵ'/ϵ_0, for the dielectric composite models (curves 1 and 2) in which the polymer and the LC phases are connected in series or in parallel, respectively and, also, the PMMA/E44 (40/60, w/w) composite film (curve 3). Under the assumption that the matrix PMMA involved E44 of 10 wt %, the entire volume fraction, Φ_{LC}, of the phase-separated LC domain in the PMMA/E44 (40/60, w/w) composite film was estimated to be 58 vol % at 303 K on the basis of the density measurement for the E44 and the PMMA/E44 (90/10, w/w) composite film. Therefore, curves 1 and 2 correspond to the calculated results for the case of $\lambda(0.58) = 1$ (a series connection) and $\lambda(1) = 0.58$ (a parallel connection), respectively. The experimental result (curve 3) was in close agreement with the calculated curve (curve 1) based on the series-connected dielectric composite model [λ (0.58) = 1] in a frequency range above ~100 Hz. The considerable increase of the observed magnitude of ϵ'/ϵ_0 in the frequency range below 100 Hz might be due to an increase of ionic conduction in the LC phase. Figure 5 indicates that the dielectrically heterogeneous structure of the polymer/LC composite film may be qualitatively described as the series-connected dielectric composite model (i.e. a two-layer dielectric model).

3.2. Relationship between Dielectric Properties and Light Switching Behavior of the Composite Film. We now consider the relationship between an externally applied ac electric field and the resulting electric field in an LC domain. Since each microunit in the dielectric composite model is parallel to the direction of the applied ac electric field, as shown in Figure 3, the magnitude of the ac electric field in each microunit is equal to that of the externally applied ac electric field, $e_{EXT}(t)$. The $e_{EXT}(t)$ is given by eq 11, where e^0_{EXT} is the amplitude of the external ac electric field.

$$e_{EXT}(t) = e^0_{EXT} \exp(j\omega t) \tag{11}$$

The electric fields in the polymeric phase, $e_P(\phi,t)$, and in the LC phase, $e_{LC}(\phi,t)$, for the case of the microunit with the LC volume fraction of ϕ are given by eqs 12a and 12b, where $e^0_i(\phi)$ means the amplitude of the ac electric field in the polymeric or the LC phase (i = P or LC) in the microunit, respectively.

$$e_P(\phi,t) = e^0_P(\phi) \exp(j\omega t) \tag{12a}$$

$$e_{LC}(\phi,t) = e^0_{LC}(\phi) \exp(j\omega t) \tag{12b}$$

The ratio of the amplitudes of the ac electric field in the LC phase to the field in the polymeric phase, $e^0_{LC}(\phi)/e^0_P(\phi)$ in the microunit, is expressed by eq 13. The complex dielectric constant is

$$e^0_{LC}(\phi)/e^0_P(\phi) = |\epsilon^*_P|/|\epsilon^*_{LC}| \tag{13}$$

$$\epsilon^* = \epsilon' - j\epsilon'' \tag{14}$$

where ϵ' and ϵ'' are the dielectric constant and the dielectric loss factor, respectively. Therefore, eq 13 can be replaced by eq 15. In a frequency range where relaxation phenomena due to molecular motions are not observed, the relationship between the dielectric loss factor, ϵ'', and the electric conductivity, σ, is expressed by eq 16, where ω is an angular frequency and subscript i means either the P (polymeric) or LC phase. Therefore, eq 15 is rewritten as eq 17.

$$e^0_{LC}(\phi)/e^0_P(\phi) = \sqrt{(\epsilon'^2_P + \epsilon''^2_P)/(\epsilon'^2_{LC} + \epsilon''^2_{LC})} \tag{15}$$

$$\epsilon''_i = \sigma_i/\omega \tag{16}$$

$$e^0_{LC}(\phi)/e^0_P(\phi) = \sqrt{(\omega^2\epsilon'^2_P + \sigma_P^2)/(\omega^2\epsilon'^2_{LC} + \sigma_{LC}^2)} \tag{17}$$

When the frequency of the applied ac electric field is modulated, the extreme cases of eq 17, for $\omega \to 0$ and $\omega \to \infty$ respectively, are expressed by eqs 18a and 18b. The ratio of LC field to external field, $e^0_{LC}(\phi)/e^0_{EXT}$, is written as eq 19. In the limits of low and high frequencies, eq 19 takes the forms given by eqs 20a and 20b.

$$\lim_{\omega\to 0}\{e^0_{LC}(\phi)/e^0_P(\phi)\} = \sigma_P/\sigma_{LC} \tag{18a}$$

$$\lim_{\omega\to\infty}\{e^0_{LC}(\phi)/e^0_P(\phi)\} = \epsilon'_P/\epsilon'_{LC} \tag{18b}$$

$$e^0_{LC}(\phi)/e^0_{EXT} = |\epsilon^*(\phi)|/|\epsilon^*_{LC}| \tag{19}$$

$$\lim_{\omega\to 0}\{e^0_{LC}(\phi)/e^0_{EXT}\} = \sigma_P/\{\phi\sigma_P + (1-\phi)\sigma_{LC}\} \tag{20a}$$

$$\lim_{\omega\to\infty}\{e^0_{LC}(\phi)/e^0_{EXT}\} = \epsilon'_P/\{\phi\epsilon'_P + (1-\phi)\epsilon'_{LC}\} \tag{20b}$$

Actually, it is reasonable to consider that the magnitude of an electric field in each polymer and LC phase has a distribution according to the distribution function, $\lambda(\phi)$, for the dielectric composite model. However, in order to compare the ac electric fields in each phase, the average amplitudes, E^0_P and E^0_{LC} of the ac electric field for each phase, which are described by eqs 21a and 21b, can be used to explain qualitatively the experimental results. As mentioned in section 3.1, it is apparent that the dielectric heterogeneous structure of the composite film may be adequately characterized by the series-connected dielectric model composed of the polymer and the LC phases. In this case, the ϕ and $\lambda(\phi)$ in eqs 21a and 21b can be replaced by the volume fraction of the pure LC domain Φ_{LC}, and 1.0, respectively. Then, the boundary condition of eq 4 is replaced by eq 22. Therefore, eq 13 and eq 19 are rewritten as eq 23 and eq 24, respectively. Also, eqs 18a,b and eqs 20a,b are rewritten as eqs 25a,b and eqs 26a,b, respectively. Equations 25a,b or eqs 26a,b indicate that

$$E^0_P = \int_0^1 e^0_P(\phi)\lambda(\phi)\,d\phi \tag{21a}$$

$$E^0_{LC} = \int_0^1 e^0_{LC}(\phi)\lambda(\phi)\,d\phi \tag{21b}$$

$$E^0_{EXT} = \Phi_{LC}E^0_{LC} + (1-\Phi_{LC})E^0_P \tag{22}$$

$$E^0_{LC}/E^0_P = |\epsilon^*_P|/|\epsilon^*_{LC}| \tag{23}$$

$$E^0_{LC}/E^0_{EXT} = |\epsilon^*_{COMP}|/|\epsilon^*_{LC}| \tag{24}$$

$$\lim_{\omega\to 0}\{E^0_{LC}/E^0_P\} = \sigma_P/\sigma_{LC} \tag{25a}$$

$$\lim_{\omega\to\infty}\{E^0_{LC}/E^0_P\} = \epsilon'_P/\epsilon'_{LC} \tag{25b}$$

$$\lim_{\omega\to 0}\{E^0_{LC}/E^0_{EXT}\} = \sigma_P/\{\Phi_{LC}\sigma_P + (1-\Phi_{LC})\sigma_{LC}\} \tag{26a}$$

$$\lim_{\omega\to\infty}\{E^0_{LC}/E^0_{EXT}\} = \epsilon'_P/\{\Phi_{LC}\epsilon'_P + (1-\Phi_{LC})\epsilon'_{LC}\} \tag{26b}$$

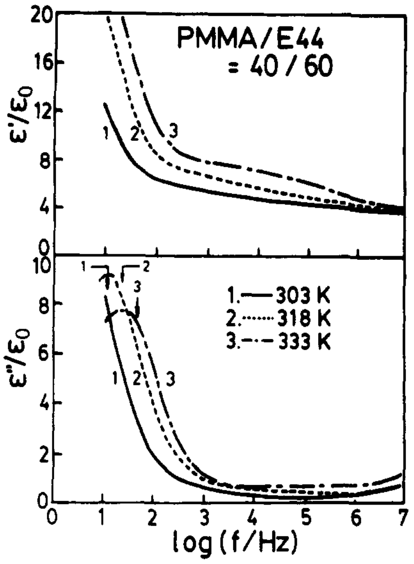

Figure 6. Frequency dependence of the relative dielectric constant, ϵ'/ϵ_0, and the relative dielectric loss factor, ϵ''/ϵ_0, for the PMMA/E44 (40/60, w/w) composite film as a function of temperature. The arrows show the relaxation frequencies of the interfacial polarization for the series-connected dielectric composite model.

the ac electric field in the LC phase is governed mainly by electric conductivities of both polymer and LC phases when the frequency of an applied ac field is low, and mainly by dielectric constants when the frequency is high.

Moreover, since eq 27 below holds in most cases of a series-connected dielectric composite, the magnitude of E^0_{LC}/E^0_P or E^0_{LC}/E^0_{EXT} is modulated by the frequency of

$$\sigma_P/\sigma_{LC} \neq \epsilon'_P/\epsilon'_{LC} \quad (27)$$

the applied ac electric field. When eq 27 is satisfied, an *interfacial polarization* is necessarily induced in such a binary dielectric composite with the series-connected component, even though nondielectric relaxation phenomena due to molecular motions are observed. Figure 6 shows the frequency dependence of the relative dielectric constant, ϵ'/ϵ_0, and the relative dielectric loss factor, ϵ''/ϵ_0, for the PMMA/E44 (40/60, w/w) composite film at 303, 318, and 333 K. The maxima of ϵ''/ϵ_0 were observed at around 10–100 Hz and shifted to a higher frequency region with an increase in temperature. The relaxation frequency for the interfacial polarization, f_0, for the simple series-connected dielectric composite is given by eq 28,

$$f_0 = (^1/_{2\pi})[\{\Phi_{LC}\sigma_P + (1 - \Phi_{LC})\sigma_{LC}\}/\{\Phi_{LC}\epsilon'_P + (1 - \Phi_{LC})\epsilon'_P\}] \quad (28)$$

which is derived from the condition of $\partial\epsilon''_{COMP}(\omega)/\partial\omega = 0$. The arrows in Figure 6 correspond to the relaxation frequencies at different temperatures for the series-connected dielectric composite model, which are calculated by using eq 28. Since the calculated relaxation frequencies fall near the measured maxima of ϵ''/ϵ_0, the maxima of ϵ''/ϵ_0 are attributed to the interfacial polarization.

Figure 7 shows the frequency dependence of E^0_{LC}/E^0_{EXT}, which is calculated by using eq 24 for the series-connected dielectric composite model as a function of temperature. The arrows in Figure 7 show the calculated relaxation frequencies for the interfacial polarization as shown in Figure 6. It is apparent from Figure 7 that the magnitude of E^0_{LC}/E^0_{EXT} drastically decreases below around the relaxation frequency of the interfacial polarization. This result can be attributed to the fact that the magnitude of σ_P/σ_{LC} is generally smaller than that of $\epsilon'_P/\epsilon'_{LC}$ since the ionic conductivity in the LC domain is greater than that in the polymeric phase. Further, since the ionic conductivities of both polymeric and LC phases increase with an increase in temperature, the value of f_0 is shifted to a higher frequency region, much in the same manner as the calculated results based on eq 28. Moreover, the increase of E^0_{LC}/E^0_{EXT} with an increase in temperature in the frequency region above ~300 Hz may be attributed to the increase of the value of ϵ'_P. Therefore, it is expected that the electrooptical response for the composite film is dependent on the modulation of the frequency of an applied ac electric field, as explained next.

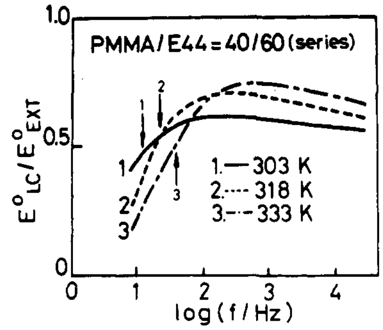

Figure 7. Frequency dependence of the E^0_{LC}/E^0_{EXT}, calculated for the series-connected dielectric composite model composed of polymer and liquid-crystalline phases. The arrows show the relaxation frequencies of the interfacial polarization.

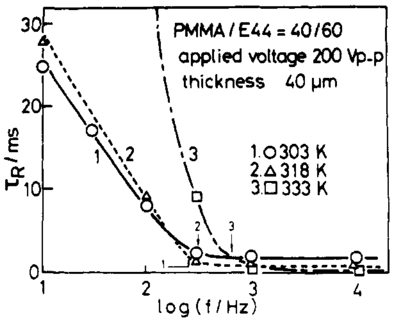

Figure 8. Frequency dependence of electrooptical rise time, τ_R, for the PMMA/E44 (40/60, w/w) composite film under the application of 200 V_{p-p} ac voltage at different temperatures. The thickness of the composite film was 40 μm.

Figure 8 shows the frequency dependence of the response rise time, τ_R, for the PMMA/E44 (40/60, w/w) composite film under the condition of an applied ac voltage of 200 V_{p-p}, at several temperatures. As usual, τ_R is defined as the time period required for a change of transmission intensity between 10% and 90%. Since the driving force to make homeotoropic orientation of LC molecules under the ac electric field is proportion to $\sim\Delta\epsilon E^2$($\Delta\epsilon$ is the dielectric anisotropy of the LC), the magnitude of τ_R is proportional to the reciprocal of the square of the magnitude of the ac electric field in the LC phase.[11] In the high-frequency region above ~1 kHz, the magnitude of τ_R decreases slightly with an increase in temperature. This result could be explained mainly by two factors: (1) the decrease of the viscosity of the LC phase and/or the decrease of the binding strength of the LC molecules to the polymeric walls (the degree of polymer/LC interaction) with an increase in temperature, and (2) the increase of the magnitude of E^0_{LC}/E^0_{EXT} due to the increase of the magnitude of ϵ'_P with an increase in temperature, as shown in Figure 7. In contrast, in the frequency region between ~300 Hz, the magnitude of τ_R increases with a decrease in frequency of the ac applied field and also increases with

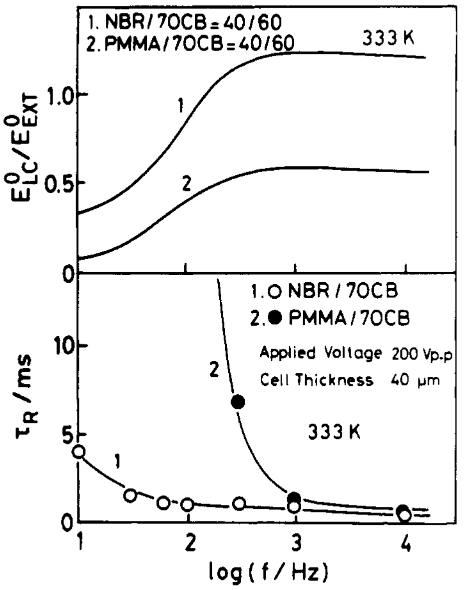

Figure 9. Frequency dependence of calculated E^0_{LC}/E^0_{EXT} based on the series-connected dielectric composite model and measured electrooptical rise time, τ_R, under the application of 200 V_{p-p} ac voltage for (1) the NBR/7OCB (40/60, w/w) and (2) the PMMA/7OCB (40/60, w/w) composite films. The measuring temperature was 333 K.

an increase in temperature, although it is expected that the viscosity in the LC phase and/or the binding strength of the LC molecules to the polymer walls decreases. The frequency at which the magnitude of τ_R starts to increase is shifted to a higher frequency region with an increase in temperature, as shown by the arrows. The frequency dependence of τ_R is similar to that shown by E^0_{LC}/E^0_{EXT} in Figure 7. Therefore, it appears that the frequency dependence of τ_R as shown in Figure 8 could be attributed to that of E^0_{LC}/E^0_{EXT} described by eqs 26a,b.

3.3. How To Improve the Electric Response Speed Based on Modulation of the Dielectric Heterogeneous Structure of the Composite Film. As section 3.2 shows, the strength of an ac electric field in both phases of the composite film is modulated by the frequency of the applied ac electric field. Since the magnitude of σ_P/σ_{LC} is generally smaller than that of $\epsilon'_P/\epsilon'_{LC}$, the magnitude of the effective ac electric field in the LC phase drastically decreases with a decrease in the frequency of the applied ac electric field, as expected from eqs 25a,b. Therefore, the electrooptical response speed, τ_R^{-1}, decreases when the frequency of an imposed ac electric field is lower than the relaxation frequency of the interfacial polarization. There are two approaches to improve the slow response in the low-frequency region. As expected from eq 28, one of the methods is to reduce the ionic conductivities of both matrix polymer and LC materials in order to make the relaxation frequency of the interfacial polarization as low as possible. Another technique is to use a matrix polymer with greater magnitudes of both electric conductivity, σ, and dielectric constant, ϵ', as suggested by eqs 25 and 26.[14]

Figure 9 shows the frequency dependence calculated for E^0_{LC}/E^0_{EXT} and the measured electrooptical rise time, τ_R, for the NBR/7OCB (40/60, w/w) and PMMA/7OCB (40/60, w/w) composite films at 333 K. The relative dielectric constants (ϵ'/ϵ_0) of PMMA and NBR are 4 and 14, respectively, under the conditions of 100 Hz and 333 K. Also, the electrical conductivities of PMMA and NBR are respectively 6.5×10^{-10} and 8.9×10^{-9} S·m^{-1}, at 333 K. As shown in the upper part of Figure 9, E^0_{LC}/E^0_{EXT} for the NBR/7OCB composite film is larger than that for the PMMA/7OCB composite film for all frequencies. The τ_R for the PMMA/7OCB composite film drastically increases with a decrease in frequency below 1 kHz. However, in the case of the NBR/7OCB composite film, τ_R shows only a small increase from 1 to 4 ms in the same frequency region. Therefore, the frequency dependence of τ_R is consistent with expectations based on the calculated E^0_{LC}/E^0_{EXT}, as shown in the upper part of Figure 9. Thus, Figure 9 tells us that the electrooptical response speed can be remarkably improved in a wide range of frequencies by using a matrix polymer with the greater magnitude of dielectric constant and electrical conductivity as suggested by the eqs 25 and 26.

4. Conclusion

The dielectric heterogeneous structure of the composite film was approximated as the binary series-connected dielectric composite model composed of polymer matrix and LC phases. Since an interfacial polarization is generally induced in the composite film, under an externally applied ac electric field, the effective strength of the ac electric field in the LC phase is modulated by the frequency of the applied field. From the dielectric model calculations, it is suggested that the ratio of the effective field in the LC phase to the externally applied field is relatively larger when the matrix polymer has both a large dielectric constant and a large electrical conductivity. Further, it is experimentally demonstrated that the electrooptical response speed can be remarkably improved in a wide frequency range by using a matrix polymer with both a large dielectric constant and a large electrical conductivity.

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Registry No. PMMA, 9011-14-7; E44, 81209-18-9; 7OCB, 52364-72-4.