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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Kajiyama, Tisato , Yonekura, Osamu , Nishiwaki, Jun-Ichiro and Kikuchi, Hirotsugu(1994) 'Interfacial Interaction of Polymer/Liquid Crystal Molecules and Electrooptical Properties of their Composite Systems', Journal of Macromolecular Science, Part A, 31: 11, 1847 – 1865

To link to this Article: DOI: 10.1080/10601329408545886

URL: <http://dx.doi.org/10.1080/10601329408545886>

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INTERFACIAL INTERACTION OF POLYMER/LIQUID CRYSTAL MOLECULES AND ELECTROOPTICAL PROPERTIES OF THEIR COMPOSITE SYSTEMS

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Key Words: Polymer/liquid crystal composite film; Bicontinuous phase separation; Anchoring effect; Dipole polarization; Nonlinear dielectric property

ABSTRACT

Polymer/liquid crystal composite films were prepared from a solution of polymer and nematic liquid crystal (LC) by a solvent casting method. The phase-separated structure of the composite film was controlled by the solvent evaporation rate. The light-scattering profile of a poly(diisopropyl fumarate)/LC: 40/60 w/w solution during solvent evaporation exhibited a periodic structure, indicating that the phase-separated structure was formed by spinodal decomposition. The aggregation structure of the composite film was investigated with a scanning electron microscope (SEM). SEM observation of the composite film suggested the presence of periodicity and dual connectivity of polymer and LC phases. The faster the solvent was evaporated, the smaller the LC channel (domain) size in the composite film. The composite film, composed of poly(methyl methacrylate) (PMMA) and a nematic LC (E44) with a positive dielectric anisotropy, exhibited remarkable and reversible light-scattering-light-transmission switching, under the modulation of

an ac electric field. The light-scattering state was dependent on such optical heterogeneities as spatial distribution of the nematic directors and/or mismatching in the refractive indices of the components. The electrooptical behavior of the composite film was strongly dependent on the LC channel (domain) size in the composite film. The transmittance increased and the rise and decay response times (τ_R and τ_D), decreased and increased, respectively, with an increase in the size of the LC channel (domain).

The electrooptical switching properties for the polymer/LC composite film should be influenced by miscibility between the polymer and the LC phases. The miscibility between both phases was evaluated from a distribution of relaxation time for interfacial polarization. The anchoring effect was also investigated by measuring the nonlinearity of the dielectric constant for the composite system.

INTRODUCTION

Recently, new types of LC display devices in which contrast is obtained on the basis of the light-scattering–light-transmittance change have been proposed [1–3]. Two typical aggregation structures of polymer/LC composite systems have been reported: polymer-dispersed LC (PDLC) [2, 3] and bicontinuous LC (BCLC) or self-supported LC (SSLC) [1, 4, 5]. The BCLC or SSLC films, in which continuous LC domains were formed in a three-dimensional network of the matrix polymer, have been paid much attention since they show excellent mechanical properties, ease of fabrication, effective permselectivity toward gases and ions [6, 7], and excellent electrooptical response [1, 4, 5, 8, 9]. The polymer/LC composite film exhibits reversible light-scattering–light-transmission switching under an off-and-on ac electric field. The composite film is useful for large-area and flexible displays or as a light control valve.

The light-scattering state in an ac electric field is dependent on such optical heterogeneities as spatial distortion of the nematic directors and/or mismatching in the refractive indices of the components. Therefore, the light-scattering and light-switching properties of the composite film are decisively influenced by the phase-separated structure of the composite films. The sizes of an LC channel (domain) can be controlled through the solvent evaporation rate during the preparation of the composite film.

The decay response time of a polymer/LC composite system increases abnormally in the glass-transition temperature range of the matrix polymer [10]. Also, the polymer/LC composite system has an apparent hysteresis behavior on the light transmittance–imposed voltage relationship [11]. The electrooptical responses of LC molecules are strongly influenced by the anchoring strength of LC molecules on the polymeric wall.

In this study, the electrooptical effects of large-area and flexible self-supported polymer/LC composite films and the possible mechanism of light-scattering–light-transmission switching are discussed. Also, the phase-separated structure–electrooptical property relationships of the composite films are discussed. Furthermore, the

interfacial interaction between the polymer matrix and the LC molecules is discussed on the basis of the distribution of relaxation time for an interfacial polarization process and for the nonlinear dielectric characteristics.

EXPERIMENTAL

The chemical structure of polymers and LCs are given in Fig. 1. Poly(methyl methacrylate) (PMMA), polystyrene (PSt), and poly(diisopropyl fumarate) (Pdi-iPF) were used as the matrices for the polymer/LC composite system. The nematic LCs used were 4-pentyl-4'-cyanobiphenyl (5CB) and commercially available E8 and GR-63, which exhibited a positive dielectric anisotropy. The composite films were cast from a chloroform solution of a mixture of polymer and LC materials. Figure 2 shows the measuring system of the light-scattering intensity and the weight change of a solution during the film formation process. The weight change was monitored by using a strain gauge. Light-scattering and light-transmittance behaviors were studied by using a He-Ne gas laser ($\lambda = 632.8 \text{ nm}$) as an incident light beam. The transmitted light intensity was measured by a photodiode which was positioned at the direction of the incident beam. The scattered intensity profile from the cast solution was detected by a photodiode array. The photodiode array can record the light-scattering profile in a $0\text{--}10^\circ$ range of the scattering angle. The solvent evaporation rate was controlled by regulating the pressure in the solvent evaporation chamber. This was done by using the needle valve and vacuum pump as shown in Fig. 2. The weight ratio of Pdi-iPF/E8 was 40/60 (w/w%), and the initial concentration of the solute was 3–8 wt%. The thickness of the composite films finally obtained ranged from 8 to 15 μm .

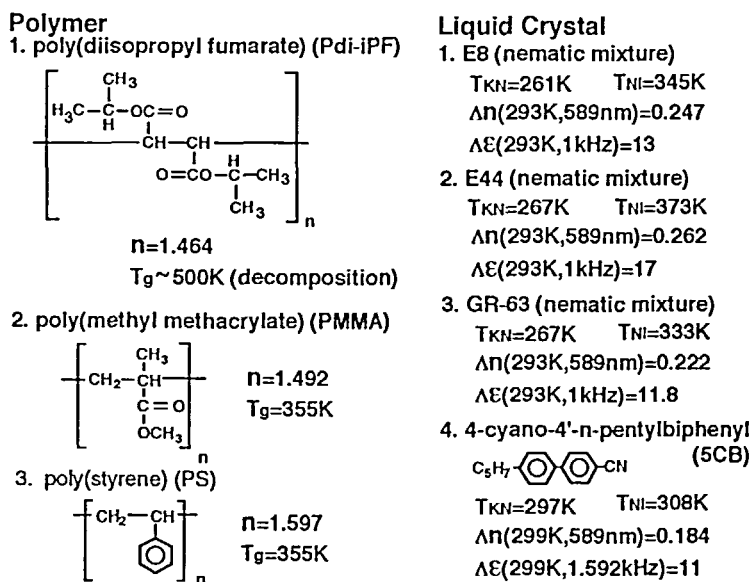


FIG. 1. Chemical structure of polymer and liquid crystal.

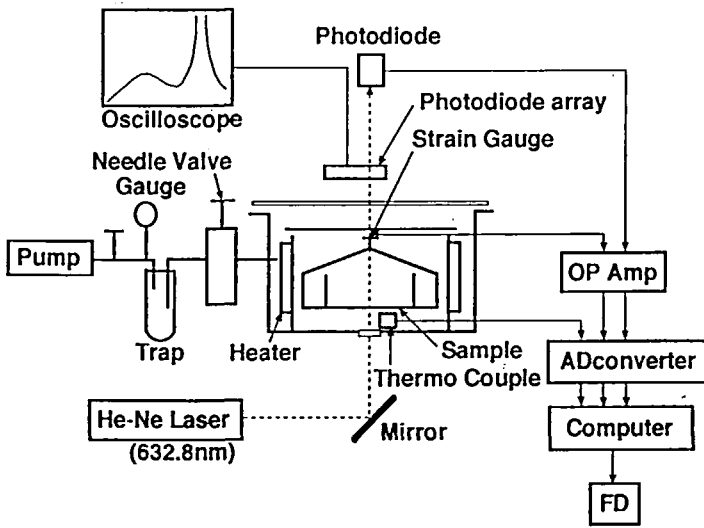


FIG. 2. Measuring system of light scattering intensity profile and weight change of the (polymer/LC) solution during the film formation process.

In order to evaluate the electrooptical properties of the composite film, the light-scattering and light-transmittance changes upon application of an ac electric field were studied by the experimental setup shown in Fig. 3. The composite films were sandwiched between two ITO coated glasses. He-Ne laser was used as the incident light source. Measurement of the transmitted light intensity through the composite films without any polarizers was carried out with a photodiode under modulation of an ac electric field. The output of the photodiode was normalized by the intensity of incident light through the differential amplifier.

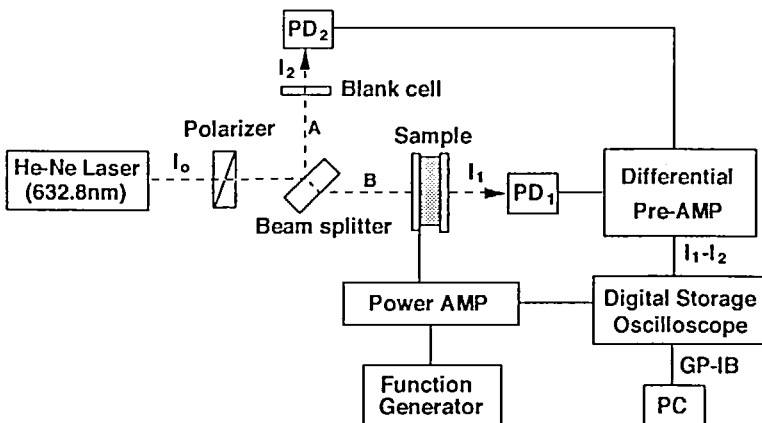


FIG. 3. Schematic diagram of the measuring system of electrooptical properties of the composite film.

The aggregation state of the composite film was investigated with a scanning electron microscope (SEM, Hitachi S-430). The composite film was fractured in liquid nitrogen, and then the LC phase of the composite film was extracted with *n*-hexane at room temperature for SEM observation.

The compatibility of a polymer-LC interface was evaluated on the basis of the distribution of relaxation time for an interfacial polarization process. Also, the anchoring strength of LC molecules on the polymeric surface was studied on the basis of a nonlinear dielectric response.

RESULTS AND DISCUSSION

Phase Separation Behavior of the Composite Film during Solvent Evaporation Process

The light-scattering state and the electrooptical response of the composite film depend strongly on the phase separated structure in the composite film. The phase separated structure can be controlled by preparation conditions, such as the temperature or solvent evaporation rate during the composite film formation process. Also, the initial concentration and the kind of solvent determine the state of phase separation.

Figure 4 shows the transmitted light intensity and the weight change of the solution during the film formation process of the Pdi-PF/E8:40/60 composite film at 308 K. The solvent evaporation rate was $3.2 \text{ g} \cdot \text{h}^{-1}$. Based on the transmittance state, the film formation process can be divided into Stages A, B, and C. No change of the transmittance was observed in Stage A. The transmittance decreased abruptly

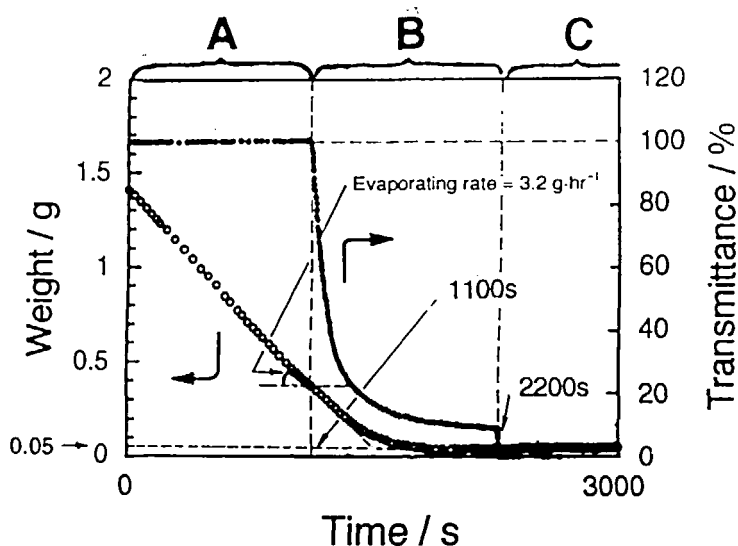


FIG. 4. Transmitted light intensity and weight changes of the Pdi-iPF/E8:40/60 chloroform solution during the solvent evaporation process at 308 K.

at the beginning of Stage B, and strong light scattering was observed in Stage C. In Stage A, the solution was optically uniform and did not have any light-scattering factor. The solution separated into polymer-rich and polymer-poor phases at the beginning of Stage B. Then, polymer and isotropic LC phases were separately formed at the end of Stage B as the solvent evaporated. Almost all of the solvent was evaporated at the end of Stage B. It was confirmed that the anisotropic LC phase appeared in Stage C, based on the light transmittance observation under crossed nicols.

The time evolution of light scattering was monitored with a charge coupled device (CCD) camera as a two-dimensional detector. A light-scattering maximum was observed at constant scattering angle in Stage B. Strong light scattering due to multiple scattering of the anisotropic LC phase was observed at Stage C. In order to carry out a more quantitative analysis of the light-scattering behavior during the solvent evaporation process, a photodiode array was used as a one-dimensional detector. There was no remarkable change of the light-scattering profile until 1060 seconds after solvent evaporation started. This corresponds to the end of Stage A in Fig. 4. The maximum peak of the light-scattering profile appeared after 1060 seconds. Also, the maximum peak of the light-scattering profile disappeared after 2280 seconds of solvent evaporation. The light-scattering maximum indicates the existence of periodicity in the solution. The sharpest maximum of the light-scattering profile was observed at 1230 seconds, and then the peak became broader. This means that the periodicity of the phase separated structure in the solution increased and then decreased with the solvent evaporation time in Stage B. However, the maximum peak angle of light-scattering profile did not change strikingly with time in Stage B.

Figure 5 shows the time dependence of the magnitudes of the structural periodicity as calculated from the light-scattering maximum. In Stage B, the magnitude

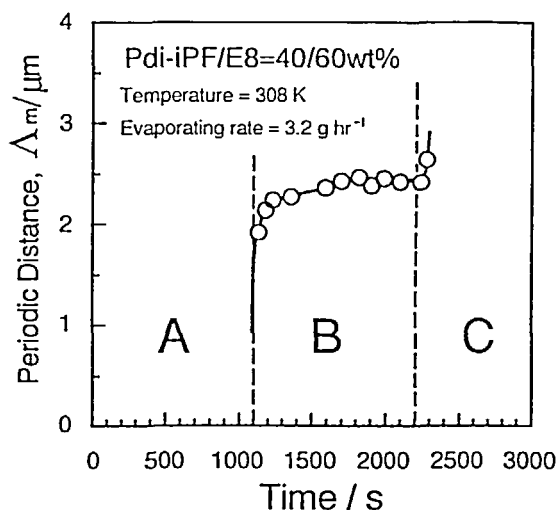
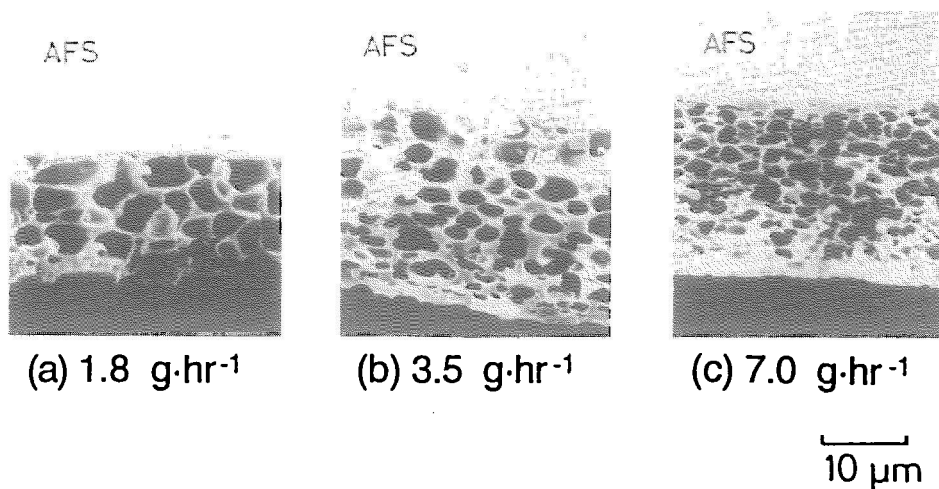


FIG. 5. Variation of structural periodic distance with solvent evaporation time for the Pdi-iPF/E8:40/60 solution at 308 K.



Pdi-iPF / E8 = 40 / 60

Evaporating Temp.: 293 K

Solvent : Chloroform

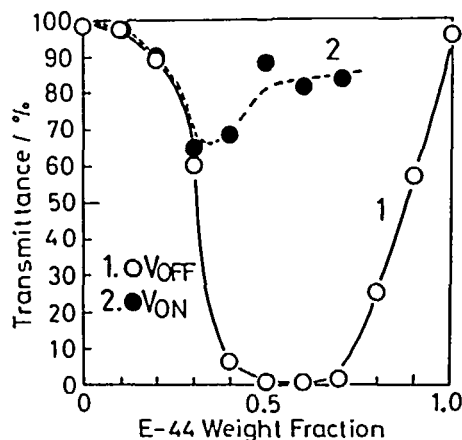
FIG. 6. Scanning electron micrographs of the Pdi-iPF/E8:40/60 composite films prepared under various solvent evaporation rates.

periodicity was almost constant, which corresponds to the typical behavior of the initial stage of spinodal decomposition [12–14]. Finally, a composite film with a bicontinuous phase of matrix polymer and LC, that is, a “modulated structure,” was obtained. It can be reasonably concluded from the SEM photographs and the light-scattering study that the morphology of the composite film is frozen in Stage B. Figure 6 shows SEM micrographs of the Pdi-iPF/E8:40/60 composite films prepared at solvent evaporation rates of 1.8, 3.5, and 7.0 $\text{g} \cdot \text{h}^{-1}$. The solvent evaporation rate was determined by the slope of the weight change of solvent with time, as shown in Fig. 4. A smaller LC channel size was formed at a faster solvent evaporation rate. When the composite film is case under unequilibrium state conditions at a fast solvent evaporation rate, the polymer and LC may be frozen in an infiltrated state. Therefore, in the process of spinodal decomposition, the faster the solvent evaporation rate is, the smaller the periodicity of solute fluctuation is.

Origins of Light Scattering in the Polymer/LC Composite System

The electrooptical effect of the composite film based on light scattering was investigated by modulating the magnitude and the frequency of an ac electric field. Reversible turbid and transparent changes was observed for the PMMA/E44:40/60 composite film in an off-and-on 60 Hz ac electric fields with $130V_{\text{rms}}$, respectively. The important factors for the good performance of a polymer/LC composite thin film is the contrast and the response speed.

Figure 7 shows the variation of transmittance through PMMA/E44 composite film with a weight fraction of E44 under the application and the absence of an ac electric field. In the absence of an ac electric field, the transmittance of the composite film showed a minimum value of 3% transmittance over an LC weight fraction range of 0.5 to 0.6. The optical heterogeneity must be optimum in this LC weight fraction region in order to scatter the visible light. In the presence of the ac electric field, the transmittance exhibited a minimum at an LC weight fraction range of 0.3 to 0.4 but the highly transparent state was observed above an LC weight fraction of 0.5. Therefore, the strong light intensity contrast (the maximum difference between the magnitudes of transmittance upon on- and non-ac electric fields) appears in an LC weight fraction range of 0.5 to 0.7. Therefore, it is concluded that a polymer/LC weight ratio of 40/60 (w/w) is satisfactorily from the point of view of both light intensity contrast and mechanical durability. Variation of the aggregation state with LC fraction was studied by SEM after extraction of E44. In the case of an LC weight fraction below 0.3–0.4, the spherical isolated LC droplets were randomly dispersed in the polymer matrix but they were hardly connected to each other. The size of the spherical LC droplets became larger with an increase in the LC weight fraction. In an LC weight fraction range above 0.4–0.5, curved LC domains or channels were formed as a continuous phase within the spongy polymer matrix. The degree of He-Ne laser light scattering in the absence of an ac electric field was abruptly enhanced at a LC weight fraction of 0.4–0.5, where continuous LC channels with various curvatures were formed. Therefore, the abrupt decrease of trans-



Temp. 300K
 Thickness 45 μm
 Frequency 1 kHz
 a.c. Voltage 250V_{p-p}

FIG. 7. Variation of light transmittance through PMMA/E44 composite thin film with weight % of E44 without an applied field and under the conditions of a 1 kHz ac field of 90V_{rms} at 300 K.

mittance at this LC fraction may indicate that the formation of curved, continuous LC channels is important to obtain strong light scattering. Since the dimension of the LC domains in the strong light-scattering composite films are larger ($10\text{--}20\ \mu\text{m}$) than the wavelength of visible light, the results may indicate that there is a strong optical heterogeneity in the curved, continuous LC channel. Also, a highly transparent state was achieved by the application of an ac electric field when the LC domain size or channel dimension was relatively large ($10\text{--}20\ \mu\text{m}$) as realized over an LC weight fraction range of 0.5 to 0.7. On the other hand, in the case where the size of the spherical LC droplets (an LC weight fraction of 0.2–0.3) was a few microns or less, the light-intensity contrast upon off-and-on ac electric fields was hardly observed. The optical heterogeneity for light scattering decreased in this LC fraction range, although the LC domain size was comparable to the wavelength. The light-intensity contrast upon off-and-on ac electric fields is strongly dependent on the shape, size, and quantity of the LC domains, and the light-scattering characteristic is dependent on not only the optical heterogeneity between the components but also in the LC domains. Since the orientation of LC molecules or nematic directors must be strongly restricted by the surface interaction between the polymeric wall and LC molecules, optical heterogeneity in the PMMA/E44 composite film is mainly induced by a compulsory distortion of nematic directors.

Figure 8 shows a schematic representation of the turbid and transparent states for the composite film. The composite film in an LC state is remarkably turbid due to its strong light scattering in the case of an off ac electric field (Fig. 8a). On the other hand, the composite film in an isotropic state becomes highly transparent in spite of an off ac electric field (Fig. 8c). These results indicate that an anisotropic

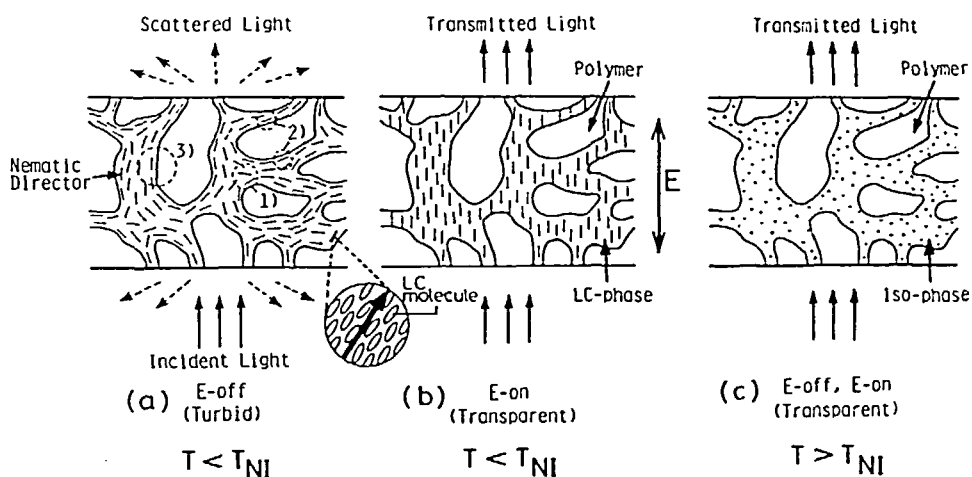


FIG. 8. Schematic representation of the turbid and transparent states for the composite film: (a) in the absence of an electric field (turbid, nematic state), (b) in the presence of an electric field (transparent, nematic state), (c) nonresponse against an electric field (transparent, isotropic state). T_{NI} is the nematic-isotropic phase transition temperature of LC materials. Possible origins of light scattering are shown by 1–3 in Fig. 8(a).

nature for LC molecules is indispensable to exhibit strong light scattering. That is, a nematic director plays an important role on the light scattering of the composite system. The turbid state of the composite film (Fig. 8a) becomes a transparent one (Fig. 8b) with a response time of milliseconds upon the application of an ac electric field. Nematic directors will orient along the direction of an applied electric field due to the positive dielectric anisotropy of LC molecules. Therefore, in the case of an off ac electric field, it is reasonable to consider that polymer-LC interfacial interaction may induce a random orientation or vigorous spatial distortion of nematic directors with various curvatures. The dimensions of the spatial fluctuation of nematic directors must be comparable or larger than the wavelength of visible light because of its strong light scattering.

In addition, a mismatch in refractive indices between the polymer matrix and the LC domain relates to the light scattering of the composite film because it causes optical heterogeneity. In the absence of an ac electric field, the difference between the refractive index of the polymer (n_p) and the spatial average refractive index (n_{ave}) in the LC domain is important for determining the light-scattering intensity. However, in the presence of an ac electric field, the difference between n_p and the ordinary refractive index (n_0) of LC molecules contributes to a degree of transparency. Since the calculated results of the mismatch in refractive indices are consistent with the experimental results of transmittance, the mismatch in refractive indices between the components plays an important role as the origin of optical heterogeneity as well as the spatial distortion of nematic directors. Based on the light-scattering phenomena of the polymer/LC composite film mentioned above, three origins may be proposed in the absence of an ac electric field: (i) a spatial distortion of nematic directors compulsorily induced by nonparallel or curved matrix walls, (ii) a discontinuous change of nematic directors among neighboring LC domains separated by thin polymeric walls, and (iii) an optical boundary owing to a difference between refractive indices in the LC phase and the polymer matrix. These possible origins are schematically shown by the (1)–(3) circles of broken lines in Fig. 8(a), respectively. The term “dynamic scattering” was introduced to describe the phenomenon of light-scattering state which is generated by hydrodynamic shear forces leading to turbulent flow induced upon the application of an ac electric field to nematic LC molecules with negative dielectric anisotropy. A strong interfacial interaction between the polymeric walls and the LC molecules also generates the light-scattering state without any application of an ac electric field, as shown in Fig. 8(a). Therefore, the light-scattering state of our polymer/LC composite system under an off ac electric field can be termed “static scattering state” [4, 8, 9, 15].

The magnitude of contribution to the total light scattering from the spatial distortion of a nematic director and the mismatch in refractive indices can be roughly separated on the basis of the temperature dependence of the transmittance of the polymer/LC composite films in the case of an off ac electric field state. This is schematically shown in Fig. 9. Since the contribution due to the existence of nematic directors to total light scattering disappears above T_{NI} , light scattering above T_{NI} may arise mainly from the mismatch in refractive indices. This fact corresponds to an increase in transmittance from room temperature to a temperature above T_{NI} . The contribution from the mismatch in refractive indices to total light scattering is around 30–50%.

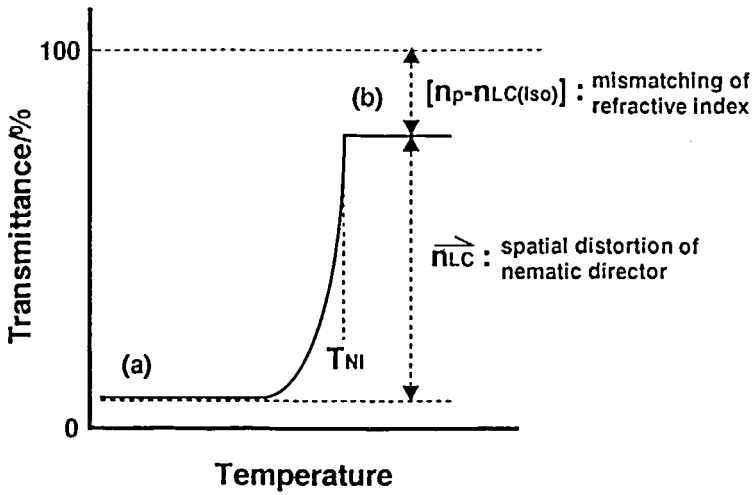


FIG. 9. Contributions of refractive index mismatching, $n_p - n_{LC(iso)}$, and spatial distortion of nematic director, n_{LC} , to the magnitude of light scattering for polymer/LC composite film.

LC Channel Size Dependence of Electrooptical Property of the Composite Films

Figure 10 shows the domain size dependence of the rise time, τ_R , the decay time, τ_D , the degree of transmittance, and the threshold voltage for the phase-separated composite films with various LC channel sizes under the conditions of ac electric field off-and-on states. The magnitudes of τ_R and τ_D were defined as the time periods to change from 10 to 90% transmittance after the application of an ac electric field and that for the reverse transmittance phenomena after turning off an ac electric field state, respectively. The magnitude of τ_R decreased with an increase in domain size due to a decrease of interfacial interaction between the matrix polymer and LC phases. This is ascribed to the anchoring effect being induced by both interfaces. On the other hand, since the interfacial interaction between the matrix polymer and LC phases acts to restore the force for random orientation of LC molecules when an ac electric field is removed, the magnitude of τ_D increased with LC channel size. Also, the transmittance for ac electric field on-and-off states increased with LC channel size. In the absence of an ac electric field, the difference between the refractive index of polymer, n_p , and the spatial average refractive index in the LC domain is important to decide the light-scattering intensity. Also, a spatial distortion of nematic directors is compulsorily induced by nonparallel or curved matrix polymer walls, and a discontinuous change of nematic directors among neighboring LC channels separated by thin polymeric walls contributes to the origin of light scattering. The slight increase in transmittance with an increase of LC channel size may arise from a decrease in interfacial interaction between the matrix polymer and LC phase. In the presence of an ac electric field, the difference between n_p and the ordinary refractive index, n_0 , of LC is important for the degree of

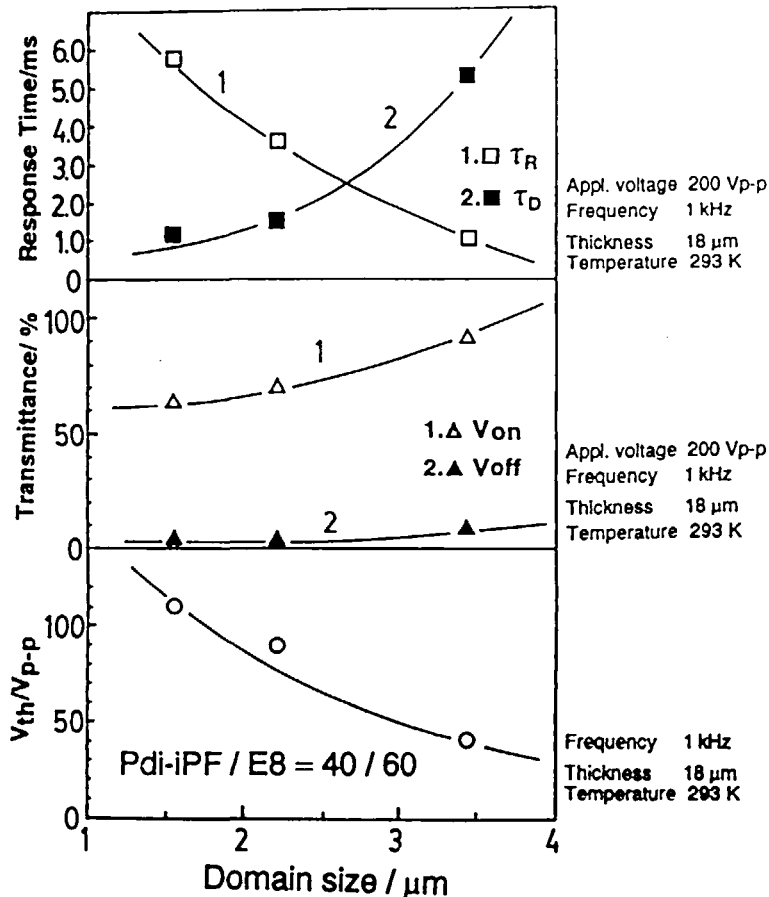


FIG. 10. Variation of response time, transmittance, and threshold voltage for the Pdi-iPF/E8 composite films. A, B, and C correspond to the composite films shown in Fig. 6.

transparency. A decrease in transmittance with a decrease in LC channel size may be attributed to an increase in the number of LC molecules for which a larger anchoring force is exerted from the polymeric walls. The threshold voltage of the composite film decreases as the LC channel sizes increase. This can also be explained on the basis of the magnitude of the anchoring force induced by the polymeric walls. The electrooptical characteristics mentioned above can be explained because the number of light-scattering points, in other words, the polymer-LC interfacial region, increases with decreasing LC channel size.

Electrooptical Hysteresis of the Polymer/LC Composite Films

The interface between the liquid crystal phase and the polymer matrix also plays an important role in electrooptical response behavior. Figure 11 shows the temperature dependence of the rise response time, τ_R , and the decay response time, τ_D , for the PMMA/E44:40/60, polystyrene(PS)/E44:40/60, and Pdi-iPF/E44:40/

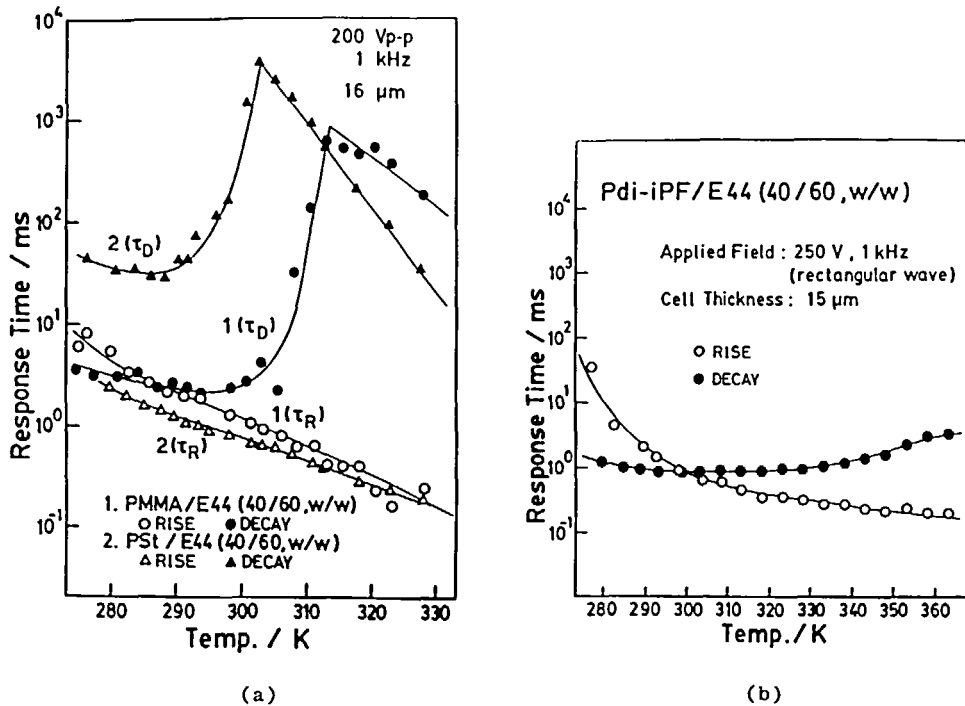


FIG. 11. Temperature dependence of rise time, τ_R , and the decay time, τ_D , for (a) PMMA/E44:40/60 and Pst/E44:40/60 composite films, and (b) Pdi-iPF/E44 composite film.

60 composite systems. τ_R of the PS/E44 composite film was shorter than that for the PMMA/E44 composite, though the polymer/LC interface area for the PS/E44 composite system was larger than that of the PMMA/E44 composite system [4]. Therefore, it may be concluded that τ_R is affected by the anchoring strength of LC molecules to the polymeric wall. τ_D of the PMMA/E44 and PS/E44 composite films increased drastically in the glass-transition temperature range of the polymer matrices. On the other hand, such a discontinuous increase of τ_D was not observed for the Pdi-iPF/E44 composite film which did not exhibit any micro-Brownian motion in a LC temperature range. These results indicate that the remarkable increase of τ_D for the PMMA/E44 and PS/E44 composite films might be involved with the thermal molecular motion of the matrix polymer. Also, in reciprocating processes of increasing and decreasing an electric voltage, an electrooptical hysteresis was observed for the polymer/LC composite film. A remarkable increase of τ_D in the glass transition temperature range and the electrooptical hysteresis mentioned above may be strongly related to an molecular aggregation structure at the polymer-LC interface.

Figure 12 shows the frequency dependence of the dielectric loss energy, P_{loss} , for the composite systems. P_{loss} was evaluated from the magnitude of a response electric current upon an imposed electric field. In the case of an adiabatic state, it was estimated from the magnitudes of P_{loss} and the specific heat of the composite

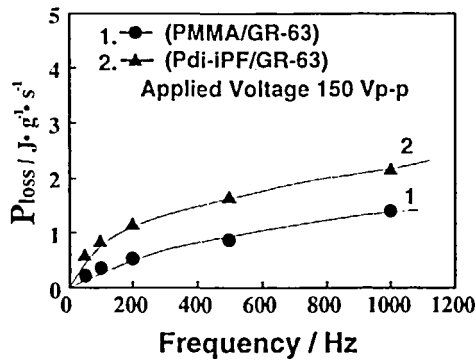


FIG. 12. Frequency dependence of dielectric loss energy for the composite film.

that the temperature rises of the PMMA/GR-63:40/60 and Pdi-iPF/GR-63:40/60 composites were 0.6 and 1.0 K/s, respectively. The magnitude of heat generated in the application of an electric field might be large enough to change the interfacial aggregation structure of the two components. Figure 13 shows the compatibility model between polymer and LC based on a dielectric composite model. The degree of compatibility might be evaluated from the distribution of relaxation time for an interfacial polarization process. Therefore, the magnitude of interfacial mixing between a polymer matrix and LC molecules can be evaluated on the basis of a Cole-Cole plot in which the imaginary components of the complex dielectric constant (ϵ'') are plotted against the real component (ϵ') corresponding to one frequency. The magnitude of deviation from a semicircular arc on the Cole-Cole plot (β) for composite systems corresponds to that of relaxation time distribution. Figure

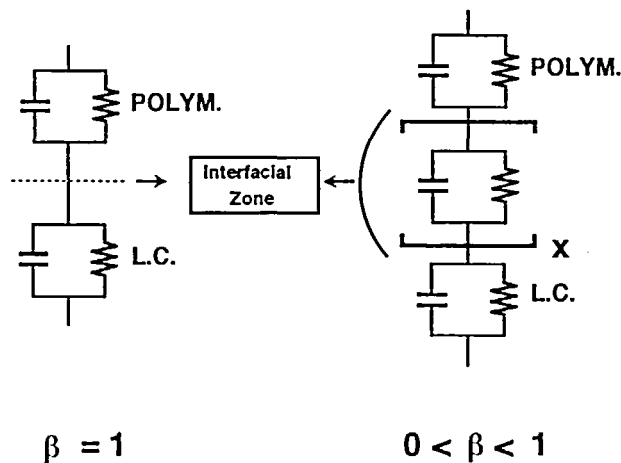


FIG. 13. Compatibility model between polymer and LC based on a dielectric composite model.

14 shows the temperature dependence of a compatibility parameter, β , for the PMMA/GR-63:40/60 and Pdi-iPF/GR-63:40/60 composite systems. The interfacial mixing induced by dielectric heating increased with an increase in temperature, more remarkably in the case of PMMA with a flexible main chain than in the case of Pdi-iPF with rigid chain characteristics [16]. When an interfacial aggregation structure is changed by a dielectric loss energy, mismatching of the refractive indices between polymer and LC decreases, resulting in an increase of light transmission for an ac electric field on state. It is concluded that an interfacial structural change induced by a dielectric loss energy is one important origin for hysteresis in an electrooptical switching.

Anchoring Effect on Polymeric Wall of Liquid Crystal Composite Film

The electrooptical response of LC molecules is strongly influenced by the anchoring strength of LC molecules on the substrate wall. In order to evaluate the anchoring strength, the dielectric response method was applied. A glass-sandwiched cell of polymer-LC-polymer parallel layers was used as a model of the composite film, and the anchoring effects of LC molecules on the polymeric walls with different surface characteristics were investigated. A rubbed polyvinyl alcohol (PVA) film and an untreated PVA film were used as the polymer substrates. The nematic LC molecules were a cyanobiphenyl-type nematic mixture which exhibited a positive dielectric anisotropy.

Figure 15 shows a schematic representation of the nonlinear dielectric characteristic of LC molecules. When an electric field above the threshold value was applied to LC molecules with homogeneous orientation, the LC molecules oriented along the imposed direction of an electric field, resulting in an induced nonlinear dipole polarization as shown in Fig. 15. Molecular orientating behaviors of LC molecules are schematically shown in Fig. 16 for the cases of strong and weak anchoring states. In the case of a weak anchoring state, an apparent extrapolation length should be considered in which LC molecules do not change their molecular orientation.

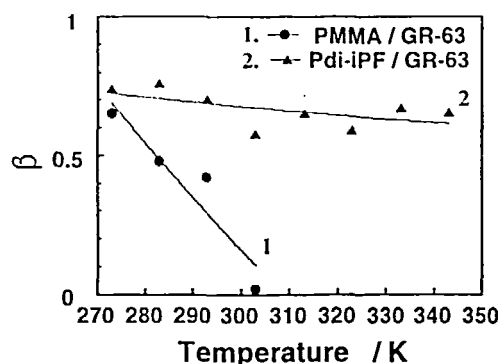


FIG. 14. Temperature dependence of a compatibility parameter β for the composite film.

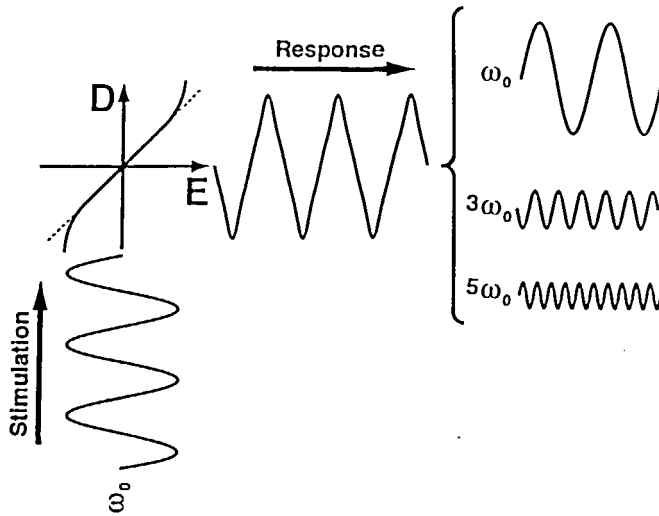


FIG. 15. Schematic representation of nonlinear dielectric characteristic of LC molecules.

In order to investigate the relationship between nonlinear dielectric characteristics and an anchoring strength of LC molecules to the polymer surface, the magnitude of nonlinear dielectric characteristics has been evaluated on the basis of the following assumption.

$$Q = C_0 V \quad (V < V_{th})$$

$$Q = CV = C_0(1 + \alpha V' + \beta V'^2)V \quad (V \geq V_{th}) \quad (1)$$

$$V = V_0 \sin \omega t, \quad V' = (V - V_{th})/V_{th}, \quad V_{th} = V_{th0}/(1 + 2d_e/d) \quad (2)$$

where Q , C_0 , V_{th} , V_{th0} , d , and d_e are the magnitude of the electric charge, capacitance, threshold voltage, threshold voltage for $d_e = 0$, specimen thickness, and extrapolation length, respectively. Also, α and β are the constants which are related

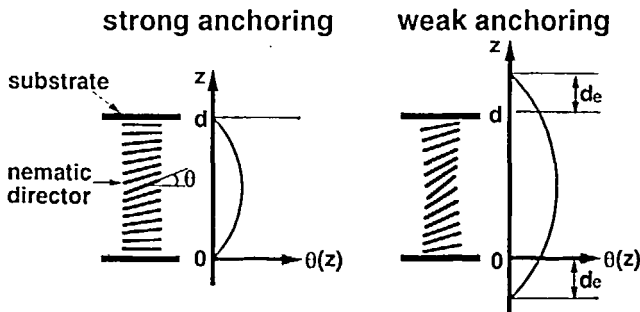


FIG. 16. Schematic representation of molecular orientating behaviors of LC molecules.

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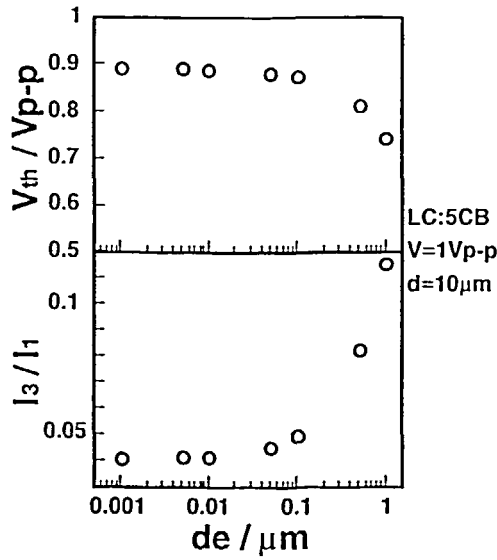


FIG. 17. Extrapolation dependence of calculated V_{th} and the dielectric nonlinearity, I_3/I_1 .

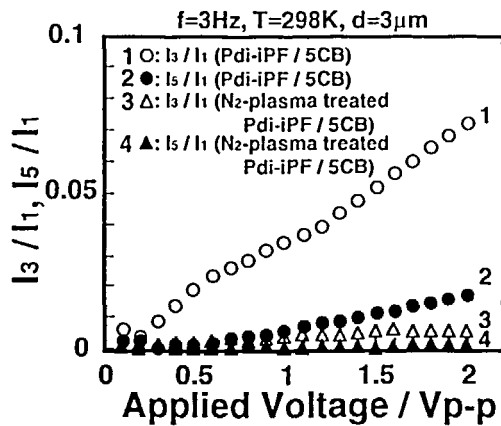


FIG. 18. Applied voltage dependence of I_3/I_1 and I_5/I_1 for the Pdi-iPF/5CB and the N_2 -plasma-treated Pdi-iPF/5CB composite systems.

to the dielectric constant and the elastic constant of LC molecules. The anchoring strength can be evaluated from the extrapolation length, d_e .

When an electric field above the threshold value is applied to the glass-sandwiched LC cell in which LC molecules align homogeneously, the dipole polarization of LC molecules increases nonlinearly by the orientation of LC molecules along the direction of an applied electric field. Then the response wave of charge to an applied fundamental wave is deformed due to nonlinearity of the dipole polarization of LC molecules. The anchoring effect of LC molecules on the polymeric wall is strongly related with the degree of realignment of LC molecules. Therefore, when a low-frequency sinusoidal electric field is applied to LC molecules, the anchoring strength on the polymeric wall may be evaluated by the magnitude of distortion of the high-order response wave (odd-order nonlinear dielectric property). Figure 17 shows the extrapolation dependence of V_{th} and the dielectric nonlinearity, I_3/I_1 . Since the magnitude of dielectric nonlinearity, I_3/I_1 , increases and V_{th} decreases with an increase of d_e as shown in Fig. 17, it is reasonable to conclude that the magnitude of I_3/I_1 can be used as a criterion for the anchoring strength of LC molecules to the polymer matrix surface.

Figure 18 shows the applied voltage dependence of I_3/I_1 and I_5/I_1 for the Pdi-iPF/5CB and the N_2 -plasma-treated Pdi-iPF/5CB composite systems. In the lower electric field region, nonlinearity of the Pdi-iPF/5CB cell remarkably increased in comparison with that of the N_2 -plasma-treated Pdi-iPF/5CB cell. This result indicates that the anchoring strength of the LC molecules on the N_2 -plasma-treated Pdi-iPF wall is stronger than that on the untreated Pdi-iPF cell.

CONCLUSIONS

SEM observation of a composite film after extraction of the LC phase indicated the periodicity and dual connectivity of the polymer and LC phases. The variation in the light-scattering profile of the solution with evaporation time can be divided into three stages: initial, intermediate, and final. In the intermediate stage, the light-scattering profile exhibited a spinodal ring which showed a constant magnitude of periodicity. The faster the solvent was evaporated, the smaller the LC channel (domain) size in the composite film was.

Based on the light-scattering phenomena of the polymer/LC composite film, three origins have been proposed in the absence of an ac electric field: (i) a spatial distortion of nematic directors compulsorily induced by the nonparallel or curved matrix walls, (ii) a discontinuous change of nematic directors among neighboring LC domains separated by thin polymeric walls, and (iii) an optical boundary owing to the difference between refractive indices in the LC phase and the polymer matrix.

The electrooptical switching properties for a polymer/LC composite film should be influenced by miscibility between the polymer and LC phases and also by an anchoring effect of liquid crystal molecules on the polymeric wall. The anchoring effect of LC molecules on the polymeric wall was strongly related with the degree of realignment of LC molecules. When a low-frequency sinusoidal electric field was applied to LC molecules, the anchoring strength on the polymeric wall might be evaluated by the distortion of a high-order response wave (odd-order nonlinear dielectric property, I_3/I_1 and I_5/I_1). In the lower electric field region, nonlinearity

of the Pdi-iPF/5CB cell increased remarkably in comparison with that of the N₂-plasma treated Pdi-iPF/5CB cell. This result indicates that the anchoring strength of the LC molecules on the N₂-plasma treated Pdi-iPF wall is stronger than that on the untreated Pdi-iPF cell.

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