

# Electrooptical Properties of Poly(diisopropyl Fumarate-co-Styrene)/Cyanobiphenyl-Type Liquid Crystal Composite Films

C. H. CHOI,<sup>1</sup> B. K. KIM,<sup>1</sup> H. KIKUCHI,<sup>2</sup> T. KAJIYAMA,<sup>2,\*</sup> N. AMAYA,<sup>3</sup> and Y. MURATA<sup>3</sup>

<sup>1</sup>Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea; <sup>2</sup>Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan;

<sup>3</sup>Tukuba Laboratory, Nippon Oil and Fats Co., Ltd., Ibaragi 30026, Japan

## SYNOPSIS

Composite films composed of poly(diisopropyl fumarate-co-styrene) (PFS) and nematic-type liquid crystal (E8) (40/60 by weight) were prepared by solvent casting in chloroform at room temperature. Scanning electron microscopy measurement showed that a liquid crystal phase is continuously embedded in a spongy-like PFS matrix. Optical responses of the composite films under the conditions of an externally imposed ac electric field (60–240 V<sub>p-p</sub>, 10–1000 Hz), temperature (290–355 K), and a film thickness (8–16 μm), were determined using a He–Ne laser (wavelength 632.8 nm). The results obtained indicated that, under the conditions imposed, the output can be continuously controlled, and the response time is only of several milliseconds or less. In addition, the response to temperature sweep, heating and cooling, was reversible with only a delay, and it was interpreted in terms of the rigidity and thermal stability of the matrix polymer. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Over the last couple of decades, liquid crystalline materials generated considerable interest with regard to use in information displays, which make use of the controllable response of liquid crystal to electrical or magnetic field.<sup>1</sup> Of these displays, the twisted nematic (TN) type has widely been employed due probably to its high visibility under ambient lightening conditions and potentials for high information content.<sup>2</sup> In such a device, however, liquid crystals are contained in a cell sandwiched between conducting glass plates, and this poses restrictions on the device geometry.

Fairly recently, composite films with liquid crystals (LC) embedded in polymeric matrix have been introduced for electrooptical applications.<sup>3–11</sup> Such polymer/LC composite film is self-supported with mechanical durability and flexibility as well, and es-

entially with no restriction on its geometry for fabrication.<sup>3,12–14</sup> Advantages of the composite film over the TN type are well documented in the literature.<sup>4</sup>

Side chain polymer liquid crystals that exhibit electrooptical effects similar to low molar mass materials, which are currently used in liquid crystal display industry, have also been discovered and tested for electrooptical applications.<sup>15,16</sup> However, polymers have a high viscosity and nematic polymers with short flexible spacer are more elastic than the chemically equivalent low molar mass nematogen. These characteristics limit their usefulness in such devices.<sup>17</sup> This paper describes the preparation of poly(diisopropyl fumarate-co-styrene) (PFS)/E8 composite films at a fixed composition of 40/60 (w/w), and their electrooptical responses as a function of film thickness, applied voltage and frequency, and temperature.

## EXPERIMENTAL

Poly(diisopropyl fumarate-co-styrene) (PFS) ( $M_w = 3 \times 10^5$ , [DPF]/[St] = 9) and a mixture of ne-

\* To whom correspondence should be addressed.

matic liquid crystal [E8, cyanobiphenyl derivatives with phase transition temperatures [ $T_{KN} = 261$  K (crystal to nematic transition temperature),  $T_{NI} = 345$  K (nematic to isotropic transition temperature)], an anisotropy of refractive indices ( $n_e = 1.774$ ,  $n_o = 1.527$ ),  $\eta$  (viscosity) = 54 cP at 293 K, and a positive dielectric anisotropy] were used to prepare the composite film. The composite film was prepared by solvent casting in chloroform at room temperature. The aggregation structure of the film was studied by a scanning electron microscopy (SEM, Hitachi S-430), from the fractured surface (in liquid nitrogen), which was sputtered with gold before viewing.

For electrooptical measurements, the composite film was first sandwiched between two indium-tin oxide (ITO)-coated glass plates. The laser (He-Ne, wavelength 632.8 nm) beam was incident, normal to the film surface, and the transmittance through the film was recorded in the digital storage oscilloscope (Kawasaki KDS-102). The distance between the cell and the photodiode was 305 mm.

## RESULTS AND DISCUSSION

### Effect of Film Thickness

The degree of light scattering in the absence of an ac electric field strongly depends on the aggregation state of the composite, which is controlled by a number of factors, namely the type of polymer, LC, or casting solvent, the composition of composite or solution, and the evaporation rate and temperature.<sup>13,18,19</sup> On the other hand, light transmittance in the presence of an ac electric field depends also on the distortion of LC directors in LC domain, in addition to the phase morphology of the composite. Following the literature, the polymer/LC composite with 40/60 (w/w) composition generally gives strong light intensity contrast and mechanical durability as well.<sup>3,13</sup>

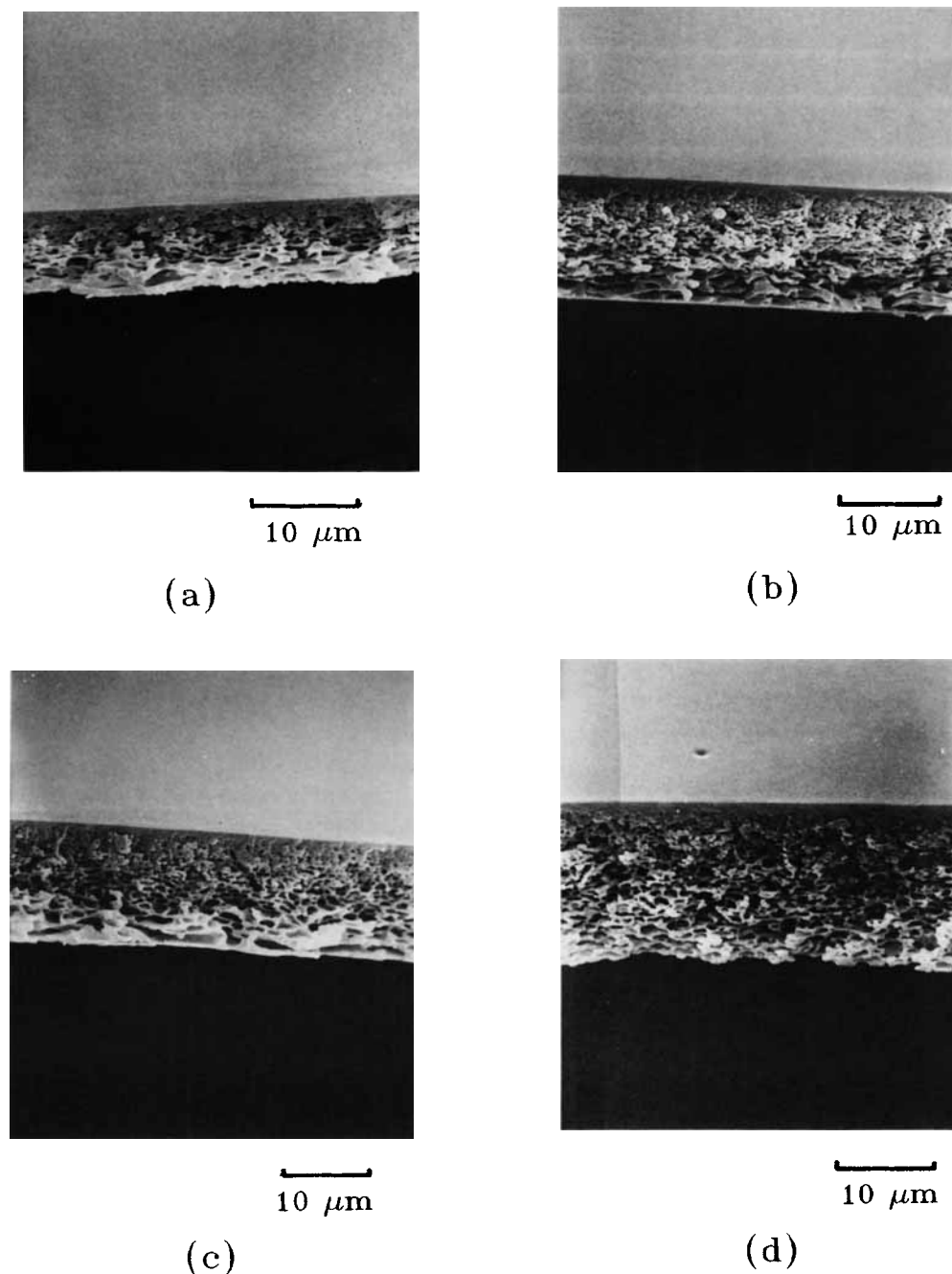
Figure 1 shows the SEM micrographs of the composite film (40/60, w/w), cast from solutions with different concentrations. The micrographs were taken after extracting LC with methanol for 10 h. The extracting condition was proved sufficient as determined from a weight change upon extraction. It is apparently observed that the polymer forms continuous phase with spongelike structure, and the LC domains, which are more or less curved and stratified, are continuously embedded in the polymer matrix. Since, in most cases of the polymer/LC composites, LC acts as lubricant or plasticizer for polymer, LC reduces viscosity and provides the

composites with flexibility.<sup>12-14</sup> The structural heterogeneity corresponds to a source of optical heterogeneity for the composite in the absence of an external field. It is apparent from Figure 1 that the film thickness increases with concentration and the dispersed domain of LC becomes smaller in size nearing the air facing surface. However, the above basic structure is almost independent of the concentration of a casting solution.

Figure 2 shows the magnitude of transmittance and the rise time as a function of film thickness in the absence and presence of an ac electric field (1 kHz, 200 V<sub>p-p</sub>) at 293 K. The purpose of this experiment is to obtain an optimum film thickness which gives maximum optical contrast. The rise time ( $\tau_R$ ) is conventionally defined as the time for transmittance change from 10 to 90% upon an electric field—on. For the composite film with thickness of 8  $\mu\text{m}$ , the transmittance in the absence and presence of an applied voltage are over 60% and about 80%, respectively, and, therefore, the contrast is insufficient for an on-off switching device due to a low light scattering intensity. On the other hand, in the case of the film thickness over 16  $\mu\text{m}$ , the contrast is again unsatisfactory due to a strong light scattering. Under conventional experimental conditions with respect to an incident light intensity or the magnitude of an applied voltage, the composite film with the thickness of 11–14  $\mu\text{m}$  gives significant optical contrast, and further experiments were proceeded with film thickness of about 12  $\mu\text{m}$ . The magnitude of rise time slightly increases with the film thickness, due probably to the decreased electric field (V<sub>p-p</sub>/film thickness).

### Voltage Dependence of Transmittance and Response Time

Transmittance as a function of voltage at 1 kHz is shown in Figure 3. Transmittance slightly increases with voltage up to approximately 100 V<sub>p-p</sub>, and increases drastically in the range 100–150 V<sub>p-p</sub>. The voltage, at which a drastic increase in transmittance sets up, is the threshold voltage ( $V_{th}$ ). It should be mentioned that the transmittance response with voltage in Figure 3 corresponds to high frequency characteristics. In a high frequency range, molecular orientation cannot follow a superposed electric polarity change, and the transmittance output varies in a fashion of simple monotonic (not periodic) asymptote.<sup>3</sup> However, in a low frequency range, a periodic flicker of transmitted light with twice of imposed frequency overlapping the asymptote was observed.<sup>4</sup>



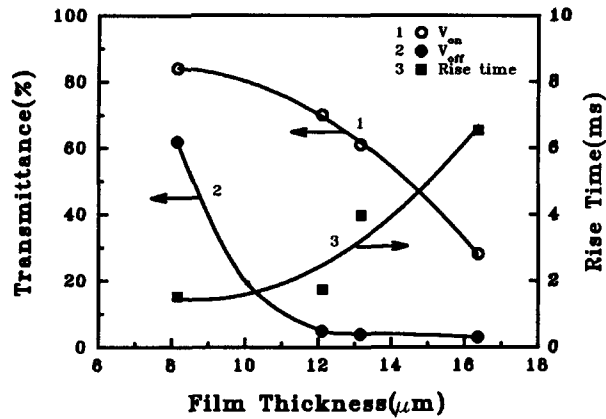
**Figure 1** SEM photographs of PFS/E8 (40/60, w/w) composite film cast at different solute concentrations (wt %): (a) 10; (b) 12; (c) 15; (d) 20.

Figure 4 shows that the voltage dependence of the magnitude of rise time ( $\tau_R$ ) and decay time ( $\tau_D$ ). The magnitude  $\tau_R$  and  $\tau_D$  are only an order of milliseconds or less, and this can be favorably compared with that of TN type.<sup>1,2</sup> It is of importance to note that  $\tau_R$  can be continuously controlled with voltage because the magnitude of  $\tau_R$  corresponds to  $V^{-2}$ . On the other hand, the magnitude of  $\tau_D$  is not closely

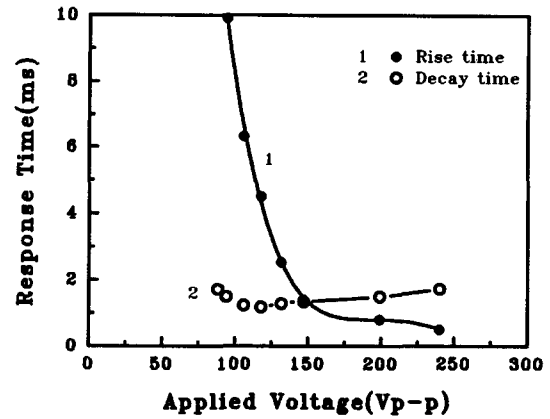
related to the magnitude of applied voltage but to the interfacial interaction between polymeric wall and LC molecules.

#### Frequency Dependence of Transmittance

Figure 5 shows the frequency dependence of transmittance for PFS/E8 (40/60) composite film.



**Figure 2** Transmittance and rise time as a function of film thickness (1 kHz, 200 V<sub>p-p</sub>, 293 K).



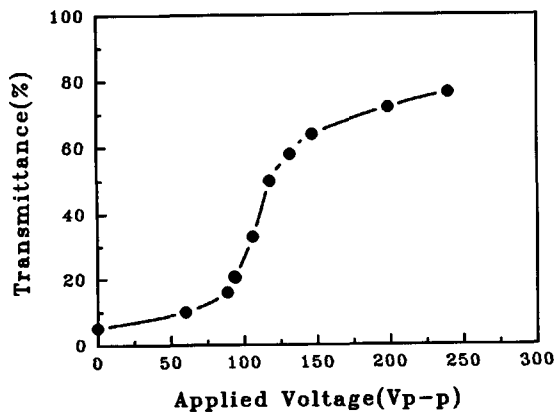
**Figure 4** Response time as a function of applied voltage (1 kHz, 298 K, 12 μm).

Transmittance increases with the increase of an external frequency, notably with a drastic increase at around 100 Hz, under the experimental conditions of 200 V<sub>p-p</sub> and 298 K. The optical response of the composite to electric frequency should be associated with the partition of external electric field ( $E_{EXT}$ ) to polymer ( $E_P$ ) and LC domains ( $E_{LC}$ ),<sup>3</sup> i.e.,  $E_P/E_{EXT}$  and  $E_{LC}/E_{EXT}$ . For example, in the composite film composed of polymer and LC in series, the ratio of  $E_{LC}$  to  $E_P$  can be written as<sup>20,21</sup>

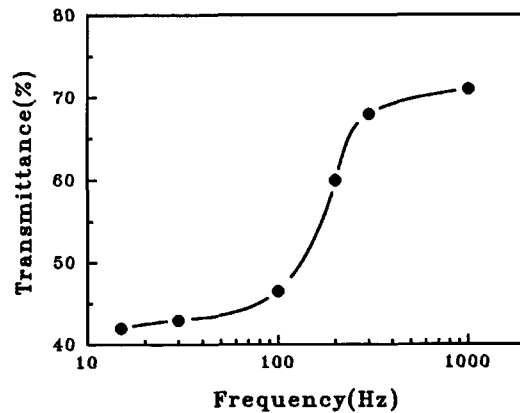
$$E_{LC}/E_P = |\epsilon_P^*|/|\epsilon_{LC}^*| = \{(\omega^2\epsilon_P'^2 + \sigma_P'^2)/(\omega^2\epsilon_{LC}'^2 + \sigma_{LC}'^2)\}^{1/2} \quad (1)$$

where  $E$ ,  $\epsilon^*$ ,  $\epsilon'$ ,  $\omega$ , and  $\sigma$  are the amplitude of external electric field, complex and in-phase component of dielectric constant, angular frequency, and conductivity, respectively. Equation (1) indicates that, at

low and high enough frequencies, the ratio respectively is inversely proportional to the conductivity and dielectric constant ratio. Since the magnitude of  $\sigma_P/\sigma_{LC}$  is generally smaller than  $\epsilon_P'/\epsilon_{LC}'$ , the magnitude of an effective ac electric field in the LC phase drastically decreases with a decrease in frequency of an ac electric field, as shown in Figure 5. Therefore, as expected from eq. (1), 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 electric conductivity. It has been experimentally demonstrated that the magnitude of transmittance and the electric response speed can be remarkably improved in a wide frequency range by using the matrix polymer with both a large dielectric constant and a large electrical conductivity.<sup>20,21</sup>



**Figure 3** Transmittance as a function of applied voltage (1 kHz, 298 K, 12 μm).

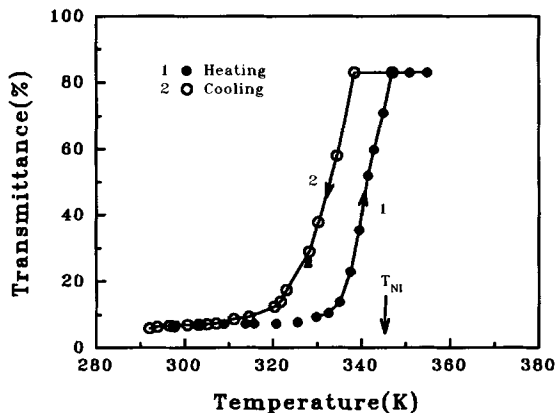


**Figure 5** Transmittance as a function of applied frequency (200 V<sub>p-p</sub>, 298 K, 12 μm).

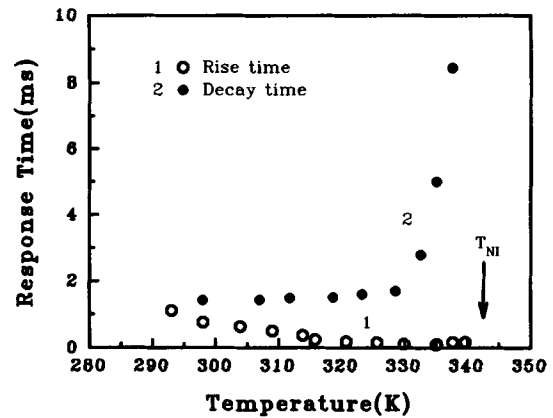
### Temperature Dependence of Transmittance and Response Time

Figure 6 shows the temperature dependence of transmittance for the PFS/E8 (40/60) composite film in the absence of electric field. The composite film was first heated, and then cooled at 10 K/min, measuring the transmittance. It is seen that the transmittance increases with temperature to a level corresponding to isotropic state. Note that the  $T_{NI}$  of the LC is 345 K. The cooling process reversibly dictates an essentially identical trend with heating, but with a delay probably due to the chain mobility of surrounding polymers. If the aggregation structure of the composite film varies with thermal treatment, the original state of scattering would not be reproduced upon cooling. The reversible nature of scattering should come from the rigidity and thermal stability of PFS.<sup>22,23</sup> Transmittance variation with temperature is mainly due to the changes of phase separated structure, mismatching in refractive indices between polymer and LC, and birefringence of LC ( $\Delta n = n_e - n_o$ ).<sup>4,8,24</sup> In this PFS/E8 system, therefore, the temperature dependence of transmittance is closely related to the birefringence of LC, which decreases with temperature.<sup>8,24</sup> Transmittance was constant above  $T_{NI}$  since refractive indices of isotropic LC and polymer are almost independent of temperature.

Figure 7 shows the response times, viz.,  $\tau_R$  and  $\tau_D$  as a function of temperature under the conditions of 200 V<sub>p-p</sub> and 1 kHz. From the figure it follows that  $\tau_R$  decreases with temperature and  $\tau_D$  is almost independent of temperature up to about 330 K, beyond which a drastic increase is shown. The rise time of pure nematics can theoretically be expressed as<sup>1</sup>



**Figure 6** Transmittance as a function of temperature in the absence of external field (12  $\mu\text{m}$ ).



**Figure 7** Response time as a function of temperature (1 kHz, 200 V<sub>p-p</sub>, 12  $\mu\text{m}$ ).

$$\tau_R = \eta L^2 / (\Delta\epsilon \cdot \epsilon_0 \cdot V^2 - K\pi^2) \quad (2)$$

where  $\eta$  is fluid viscosity,  $L$  is the cell thickness,  $\Delta\epsilon$  is the dielectric anisotropy,  $\epsilon_0$  is the absolute permittivity, and  $K$  is an elastic constant. For the composite film, the response characteristics are also affected by the dimension of LC domain, instead of  $L$ , and interfacial interaction between polymeric wall and LC molecules, i.e., the strength of anchoring.<sup>4,24</sup> From this point of view, the mild decrease of  $\tau_R$  is due to the decrease of interfacial interaction with temperature as well as the decrease of viscosity.  $\tau_D$  is obtained from eq. (2) by simply letting  $V = 0$ .<sup>1</sup> Then,  $\tau_D$  depends on a time constant, defined by  $\eta/K$ , for a film with constant domain size. However, the rapid increase of  $\tau_D$  near  $T_{NI}$  may not be properly explained by the decreased  $K$  of LC because  $\eta$  also decrease with temperature.  $\tau_D$  is therefore closely related to the thermal molecular motion on the surface of polymeric wall in addition to  $\eta/K$ . The thermal molecular motion of polymer chain may prohibit reorientation of nematic directors from homeotropic state to random orientation state.

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