

## Molecular Weight Dependence of Hysteresis in Electro-Optical Switching of (Polymer/Liquid Crystal) Composite Systems

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(Received April 9, 1999)

KEY WORDS (Polymer/Liquid Crystal) Composite System / Molecular Weight / Electro-Optical Properties / Electro-Optical Switching Hysteresis /

(Polymer/liquid crystal: LC) composite films composed of polymers and low molecular weight liquid crystals (LCs) burgeoned in the end of 1970s as a self-supported flexible film in order to develop unique characteristics of LC.<sup>1,2</sup> The composite films have been investigated as unique and novel permselective membranes for molecular filtration,<sup>1-3</sup> thermo-switching,<sup>4</sup> and optical resolution of amino acid salts.<sup>5</sup>

Recently, the composite films have become a subject of high interest because of their potential applications as optical devices such as a large-area flexible displays without polarizers, bright projections, light shutters, switchable windows and so on.<sup>6-8</sup> The composite films exhibit novel electro-optical properties based on light scattering. The light scattering state in the field-off state can be switched into a transparent state by application of an a.c. electric field.<sup>6-8</sup> It has been reported that the electro-optical properties depend on various factors such as the size of LC domains in the polymer matrix,<sup>9,10</sup> the electric properties of polymer and LC,<sup>11,12</sup> and also, the interfacial interaction between polymer and LC.<sup>13,14</sup>

The hysteresis in the electro-optical switching has been generally observed upon an increase process and a decrease one of applied voltage for the (polymer/LC) composite system. This problem must be solved for practical applications as display materials. There have been a few papers reported on the electro-optical switching hysteresis for the (polymer/LC) composite systems, but its mechanism has not been sufficiently clear yet. Vaz *et al.* concluded that it might arise from charging effects.<sup>15</sup> Drzaic proposed the mechanism that some differences of the configuration in LC particles induced the hysteresis.<sup>16</sup> Also, Li *et al.* concluded that the existence of slow components in a relaxation process after removing voltage and also, an inherent bistability of the director configuration in the droplets were responsible for the switching hysteresis, because the switching hysteresis responding to a magnetic field was similar to that of an a.c. electric field.<sup>17</sup> The author concluded that the compatibility between matrix polymer and LC is one of the origins for the switching hysteresis and furthermore, the phase-mixing at the polymer-LC interface being induced upon the application of an a.c.

electric field is a main cause of hysteresis in electro-optical switching.<sup>14</sup>

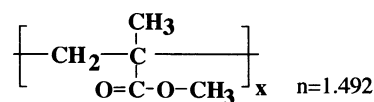
In this paper, the polymer molecular weight dependence of the hysteresis in electro-optical switching has been investigated by using two types of poly(methyl methacrylate)s (PMMA) with significantly different molecular weights. The relationship between phase-mixing at the polymer-LC interface and switching hysteresis has been discussed.

### EXPERIMENTAL

#### Materials and Preparation of the Composite System

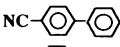
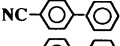
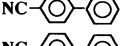
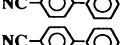
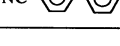
The chemical structures and the physico-chemical properties of polymers and LC are given in Figure 1. PMMA was purchased from Aldrich Co. and used as the matrix for the (polymer/LC) composite system. The

#### Polymer Poly(methylmethacrylate) (PMMA)



Code	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
low Mw PMMA	15k	1.68
high Mw PMMA	996k	2.94

#### Liquid crystal E8(Nematic mixture)

Code	Chemical structure	Wt %
K-15	NC-  -C <sub>5</sub> H <sub>11</sub>	45%
M-9	NC-  -O C <sub>3</sub> H <sub>7</sub>	16%
M-15	NC-  -O C <sub>5</sub> H <sub>11</sub>	12%
M-24	NC-  -O C <sub>8</sub> H <sub>17</sub>	16%
T-15	NC-  -C <sub>5</sub> H <sub>11</sub>	11%

$T_{KN}=261\text{K}$ ,  $T_{NI}=345\text{K}$ ,  $n_{\parallel}=1.774$ ,  $n_{\perp}=1.527$ ,  
 $\Delta n=0.247$ ,  $n_{AVE}=1.609$ ,  $\epsilon_{\parallel}=21.3$ ,  $\epsilon_{\perp}=5.7$ ,  
 $\Delta \epsilon=15.6$

Figure 1. Chemical structures and physico-chemical properties of the matrix polymer and LC for the composite systems.

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weight-average molecular weight,  $M_w$ , and the molecular weight distribution,  $M_w/M_n$  were determined *via* gel permeation chromatography (GPC) with polystyrene standards. The LC employed in this study was E8 (BDH), which is a nematic mixture consisting of several cyanophenyl type LCs with a positive dielectric anisotropy.

In order to prepare the composite systems, PMMA and E8 were mixed above the nematic-isotropic transition temperature ( $T_{NI}$ ) of E8 and sandwiched between indium tin oxide (ITO)-coated glass substrates by a capillary action at 358 K in a vacuum chamber. The cell gap between ITO electrodes was maintained with a PET spacer to be about 12  $\mu\text{m}$  thick. After a period of about an hour, the (PMMA/E8) phase separated composite was prepared by a thermally induced phase separation method and the rate of temperature drops from 358 K to room temperature was controlled about 11 K  $\text{min}^{-1}$ . The (low  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) and the (high  $M_w$ -PMMA/E8 = 3/97 wt%) composites were employed to investigate the electro-optical switching hysteresis under the same amplitude of the applied voltage as mentioned later.

#### Phase Transition Behavior and Aggregation States of the Composite System

The phase transition behavior and aggregation states of the composite system annealed at 358 K for 3 h were investigated by means of differential scanning calorimetry (DSC) and polarizing optical microscope (POM). The DSC thermograms were recorded at the cooling rate of 1 K  $\text{min}^{-1}$  and the heating rate of 5 K  $\text{min}^{-1}$  using Mac Science DSC 3200 under a dry nitrogen purge. Polarizing optical micrographs were taken under crossed Nicols using the Nikon POM.

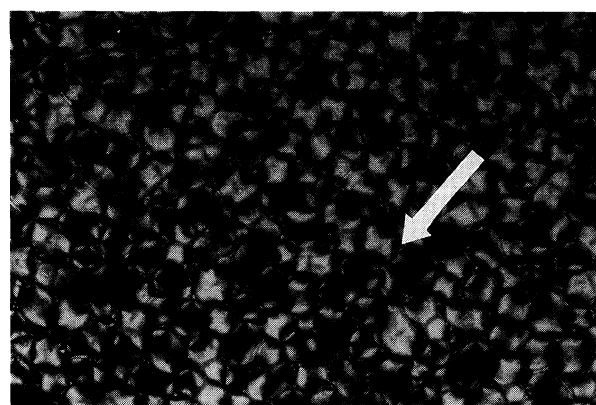
#### Electro-Optical Measurement of the Composite System

In order to evaluate the electro-optical properties of the composite films, light scattering and light transmittance changes upon a.c. electric field-off and -on states were measured by an experimental setup as mentioned in previous paper.<sup>14</sup> A He-Ne gas laser (wavelength: 632.8 nm) was used as an incident light source. A rectangular-wave with the frequency of 1 kHz was modulated by a triangular-wave and was used to drive the sample cell. The modulation of an a.c. electric field was carried out with the two function generators and the reciprocating period corresponding to the switching rate was controlled by a frequency of triangular-wave. The transmitted light intensity through the sample cell was normalized by the intensity of the incident light through a blank cell. The distance between sample cell and photodiode was 305 mm and the sensing area of the photodiode was 6.6  $\text{mm}^2$ .

## RESULTS AND DISCUSSION

#### Phase Transition Behavior and Aggregation States of the Composite System

Figures 2(a) and 2(b) show the POM micrographs of the (PMMA/E8) composite systems with  $M_w = 15$  k (low  $M_w$ ) and  $M_w = 996$  k (high  $M_w$ ), respectively. The micrographs apparently exhibited that both composite systems formed the phase-separated structure. In the case



(a) (low  $M_w$ -PMMA/E8)

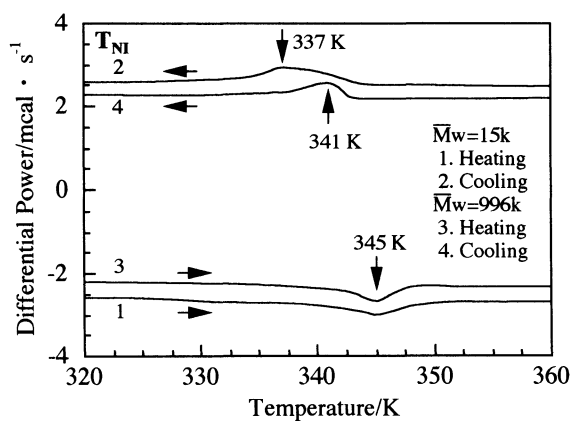
100  $\mu\text{m}$



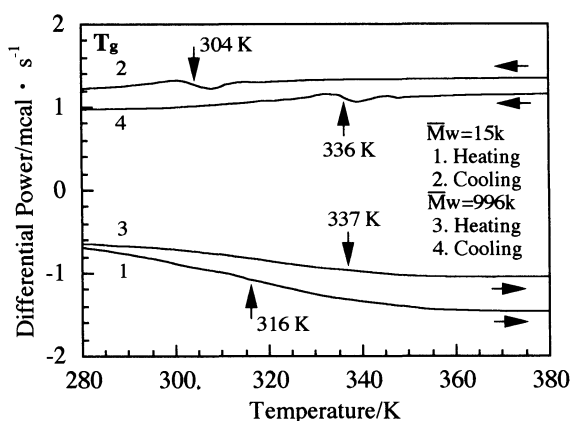
(b) (high  $M_w$ -PMMA/E8)

**Figure 2.** Polarizing microscopy textures of the (low  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) (a) and the (high  $M_w$ -PMMA/E8 = 3/97 wt%) (b) composite systems.

of the (low  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) composite system, the fibrillar PMMA network was observed as shown by the arrows in Figure 2(a). On the other hand, the apparent PMMA network was not observed (Figure 2(b)) for the (high  $M_w$ -PMMA/E8 = 3/97 wt%) composite system. Figures 2(a) and 2(b) indicate that the size of the E8 domains in the composite system was larger for the case of low  $M_w$  PMMA than that of high  $M_w$  PMMA. The same trend was observed for the (PMMA/E8 = 20/ 80 wt%) composite films with different  $M_w$  of PMMA prepared by a solvent cast method.<sup>18</sup> The phase separation behavior in the (polymer/LC) composite system could be explained on the basis of the spinodal decomposition mechanism.<sup>10,19</sup> The formation process for the (polymer/LC) composite system could be roughly divided into the stages I, II, and III based on the magnitude of light transmittance.<sup>20,21</sup> It has been reported that the optically isotropic phases were separated in the solution during the stage II. Also, an optical anisotropy was recognized in the stage III based on the polarized optical analysis under crossed Nicols and this result clearly indicates that an optical anisotropy of the LC-rich phase appeared in the stage III.<sup>20</sup> At the temperature above  $T_{NI}$  of E8, the (PMMA/E8) composite system is optically isotropic solution as the stage I. The PMMA-rich phase and the optically isotropic E8-rich



(a) (low  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) and (high  $M_w$ -PMMA/E8 = 3/97 wt%)



(b) (low  $M_w$ -PMMA/E8 = 10/90 wt%) and (high  $M_w$ -PMMA/E8 = 10/90 wt%)

Figure 3. DSC thermograms of the (PMMA/E8) composite systems.

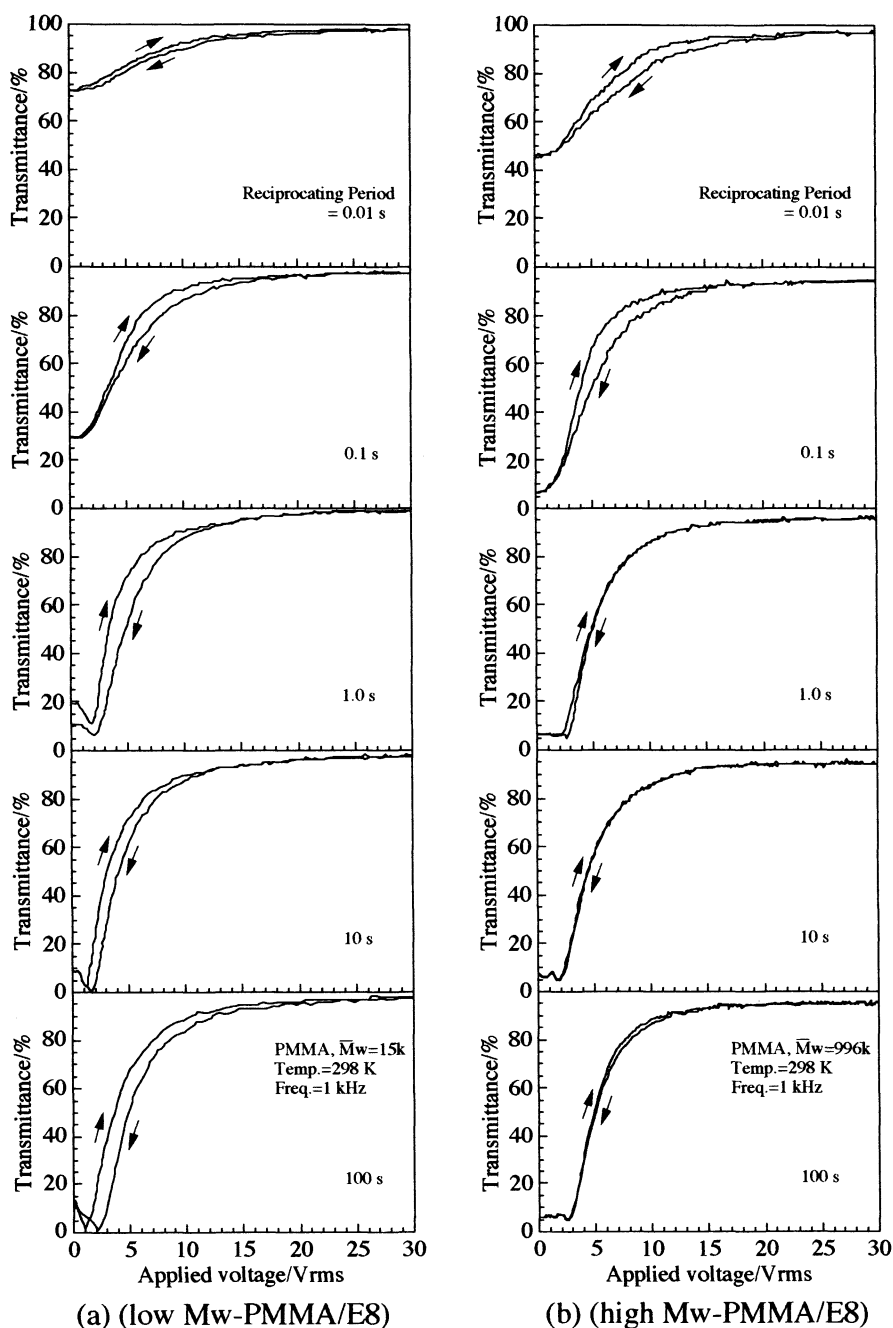
phase are separated in the isotropic (PMMA/E8) solution during the stage II by decreasing of the cell temperature. Finally, an optical anisotropy of the E8-rich phase appeared in the stage III. Here, the size of the E8 domains in the composite system was determined during the process from the stage II to the stage III and strongly depended on the diffusion velocity of PMMA chains. Therefore, it is reasonable to consider from the spinodal decomposition mechanism that the size of the E8 domains was increased in the case of a higher diffusion velocity of the polymer chains. Generally, the diffusion velocity of PMMA chains is higher for the case of low  $M_w$  PMMA chains than the case of high  $M_w$  one. Therefore, in the case of (low  $M_w$ -PMMA/E8) composite system, it seems reasonable to consider that the larger size of the E8 domains was formed due to a higher diffusion velocity of low  $M_w$  PMMA chains.

Glass transition temperatures ( $T_g$ 's) and  $T_{NI}$ 's of the (PMMA/E8) composite systems were decided as the middle of the transition range of the thermogram as shown in Figure 3, respectively. When the DSC thermograms were recorded at the cooling rate of  $1 \text{ K min}^{-1}$ ,  $T_{NI}$ 's of E8 in the (low  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) and the (high  $M_w$ -PMMA/E8 = 3/97 wt%) composite systems were observed at about 337 and 341 K, respectively, while  $T_g$ 's of PMMA were not clearly ob-

served. These results indicate that the E8-rich domains might contain molecularly dispersed PMMA chains. In other words, the long-range order of E8 was little perturbed by molecularly dispersed PMMA chains in the E8-rich phases. Figure 3(a) shows a remarkable reduction of  $T_{NI}$  of E8 in the (low  $M_w$ -PMMA/E8) composite system in comparison with the (high  $M_w$ -PMMA/E8) one. This result may be attributed an increase in the compatibility between PMMA and E8 with a decrease in the  $M_w$  of PMMA. This prediction could be confirmed by the degree of  $T_g$  reduction due to a plasticizer effect of E8 to PMMA in the (PMMA/E8 = 90/10 wt%) composite system in comparison with  $T_g$  (low  $M_w$ -PMMA = 360 K, high  $M_w$ -PMMA = 391 K) of PMMA alone, as shown in Figure 3(b). Therefore, it seems reasonable to conclude that the compatibility between PMMA and E8 in the (PMMA/E8) composite system increased with a decrease in the  $M_w$  of PMMA.

#### Electro-Optical Switching of the (Polymer/LC) Composite System

The (low  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) and the (high  $M_w$ -PMMA/E8 = 3/97 wt%) composites were employed to investigate the electro-optical switching hysteresis under the same amplitude of the applied voltage since the (high  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) composite system showed the higher applied voltage ( $> 30 \text{ Vrms}$ ) than that of the (low  $M_w$ -PMMA/E8 = 3.9/96.1 wt%) composite system. Figures 4(a) and 4(b) show the applied voltage dependence of the light transmittance for the (PMMA/E8) composite systems at 298 K. The transmittance-voltage curves for an increasing and a decreasing process of an applied voltage are shown as a function of reciprocating period. When the reciprocal period was longer than 1.0 s, the electro-optical switching hysteresis of the (high  $M_w$ -PMMA/E8) composite system was hardly observed in the reciprocating process as shown in Figure 4(b). However, the degree of the hysteresis became more apparent with reducing the reciprocating period. These results were similar to these of (poly(diisopropylfumarate)/E8) composite films for which the electro-optical hysteresis was not observed due to an incompatible characteristic between poly(diisopropylfumarate) and E8.<sup>14</sup> The same trend was also observed for the (PMMA/E8 = 20/80 wt%) composite films with different  $M_w$  of PMMA prepared by a solvent cast method.<sup>18</sup> The hysteresis in the shorter range of reciprocating period shown in Figure 4(b) seems to be responsible for the retardation of the LC molecular reorientation upon the amplitude modulation of an applied electric field. Since the decay time of the electro-optical switching for the composite system is in the order of ms, the time lag of the electro-optical response cannot be negligible in the range of the reciprocating period shorter than 0.1 s. As shown in Figure 4(a), more apparent hystereses were observed in all cases of reciprocating period from 0.01 to 100 s in comparison with the results shown in Figure 4(b). It has been reported that the compatibility between matrix polymer and LC was one of the origins on the switching hysteresis.<sup>14</sup> In other words, the phase-mixing at the polymer-LC interface being induced upon the application of an a.c. electric field was a main cause of the switching



**Figure 4.** Applied voltage dependence of the light transmittance for the (low  $M_w$ -PMMA/E8=3.9/96.1 wt%) (a) and the (high  $M_w$ -PMMA/E8=3/97 wt%) (b) composite systems.

hysteresis observed in all cases of reciprocating period. As mentioned in Figure 3, the compatibility between PMMA and E8 was dependent on the  $M_w$  of PMMA and decreased with an increase in the  $M_w$  of PMMA. Therefore, it seems reasonable to conclude that the remarkably reduction of the switching hysteresis in the case of the (high  $M_w$ -PMMA/E8) composite system was due to a decrease in phase-mixing at the PMMA-E8 interface with an increase in the  $M_w$  of PMMA.

## CONCLUSIONS

The relationship between molecular weight of matrix polymer and hysteresis in electro-optical switching was investigated for the (PMMA/E8) composite systems. The size of the E8 domains in the (PMMA/E8) composite

system was larger for the case of low  $M_w$  PMMA than the case of high  $M_w$  PMMA. This result can be explained by the magnitude of diffusion velocity depending on the  $M_w$  of PMMA. It was revealed that the electro-optical switching hysteresis of the (high  $M_w$ -PMMA/E8) composite system decreased remarkably compared with the (low  $M_w$ -PMMA/E8) composite system. This phenomenon might be explained on the basis of the different compatibility between PMMA and E8, which was directly dependent on the  $M_w$  of PMMA.

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