

(Polymer/Liquid Crystal) Composite Systems with Steep Electro-optical Response and Elucidation of its Mechanism based on Light Scattering and Dielectric Property

Ken-ichi IZUMI, Quin NIU, Hirotsugu KIKUCHI*, Yasuhiro IMAMURA¹,
Norihiro KAIYA¹, Naoyuki AMAYA¹, Huai YANG², K. RAJESH², Reiko KIMURA², Tomoki
GUNJIMA², Haruumi HASUO³, Tisato KAJIYAMA⁴

Department Applied chemistry, Faculty of Engineering, Kyushu University
6-10-1 Hakozaki, Higashi-ku Fukuoka 812-8581, Japan

¹NOF Corporation

Yebis Garden Place Tower, 20-3 Ebisu 4-chome, Shibuya-ku, Tokyo 150-6019, Japan

²FUKUOKA IST

Acros Fukuoka Nishi Office 9F, 1-1-1 Tenjin, Chuo-ku, Fukuoka 810-0000, Japan

³Fukuoka Industry Technology Center

332-1 Kamikoga, Chikushino, Fukuoka 818-8540

⁴Kyushu University

6-10-1 Hakozaki, Higashi-ku Fukuoka 812-8581, Japan

Fax: 81-092-651-5606 e-mail: hkikutcf@cstf.kyushu-u.ac.jp

(Polymer/liquid crystal: LC) composite films consisting of a continuous LC phase embedded in a three-dimensional network of a polymer matrix were prepared by a photo-polymerization-induced phase separation method. The steepness of the electro-optical switching depends on the morphology and the orientation of the LC directors. In this study, the (polymer/LC) composite systems with the steep electro-optical response were successfully prepared and its mechanism was elucidated by dielectric analyses and light scattering measurements. From the results of the dielectric analyses of the (polymer/LC) composite, the nematic directors in the composites were found to have a tendency to align in a parallel direction to the electrode substrates. The application of an electric voltage around 1~3 V put the alignment of the nematic directors into disorder and enhanced light scattering. This could be a possible mechanism for the steep electro-optical response of the (polymer/LC) composite systems. Key words: (Polymer/LC) composite films, electro-optical response, dielectric property, light scattering

1. INTRODUCTION

Because of their potential in industrial applications such as flexible and large dimensional displays, there has been a growing interest in the (polymer/liquid crystal) composite systems.¹⁾⁻³⁾ (Polymer/liquid crystal) composites are composed of a continuous LC phase embedded in a three-dimensional network of a polymer matrix. The composites have been known since the 1980s to show remarkable light switching between the light-scattering state and the light-transmitting one upon the removal and application of an electric field, respectively. The light-scattering and transmitting states of the composites are induced by the macroscopically random orientation and unidirectional one of liquid crystal directors embedded in the three-dimensional polymer networks, respectively. Since the LC possesses a large birefringence in general, the spatial distortion of LC directors on the order of sub- μm induced by the complicated polymer network formations is particularly supposed to be an important origin for the light scattering in addition to the mismatch of refractive indices between polymer and LC. The electro-optical properties of the composites strongly depend on their morphology, which is very sensitive to the preparing conditions. It has been found

by the authors that the (polymer/LC) composite prepared by photo-polymerizing monoacrylate and divinylether dissolved in the liquid crystals exhibited excellent electro-optical properties such as low voltage driving and high steepness of the electro-optical response, that is, the slope of the light transmittance-voltage curve.

The steepness of electro-optical response is one of the important factors for the composite to utilize as the passive matrix electrode display device. However, the mechanism causing a steep electro-optical response has not been clarified. In this paper, we investigated the relationship between steepness of the electro-optical response for (polymer/LC) composite systems and the electric field-induced realignment behavior of the nematic directors in LC domains was elucidated based on the light scattering and dielectric properties.

2. EXPERIMENTAL SECTION

2.1 Materials

The liquid crystal mixture, MJ991807 (1807), used in this study was supplied from the Merck Co. 3,5,5-trimethyl hexylacrylate (TMHA) used as mono-functional monomer and 1,6-hexanediol divinyl ether (HDDVE) used as

bi-functional monomers (cross-linker) were purchased from Aldrich. Diisopropyl fumarate (DiPF) and diethyl fumarate (DEtF) were supplied by NOF Co. 2,2-dimethoxy-2-phenylacetophenon (DMPAP) from Aldrich was used as a photo-initiator.

2.2 Preparation for the (polymer/LC) composite systems

A liquid crystal mixture, TMHA, HDDVE, the fumarate monomer and photo initiator were mixed thoroughly and then injected into the cell consisting of a pair of indium/tin oxide (ITO) coated glass plate. The cell gap was maintained to be 13 μm with a spacer. The filled cell with the mixture solution was then irradiated with ultra violet (UV) light from a Xenon lamp at 303 K. The intensity of the UV light was 15 mWcm^{-1} measured at 365 nm. In this study, three types of the composite were used as listed in Table 1.

Table 1 The types of the composite used in this study.

Type	Monomers	LC
(a)	TMHA/HDDVE	1807
(b)	TMHA/HDDVE/DEtF	1807
(c)	TMHA/HDDVE/DiPF	1807

2.3 Electro-optical measurement

The electro-optical measurements were carried out by the experimental setup schematically shown in Fig. 1. A He-Ne laser (wavelength of 632.8 nm) was used as incident light. External ac electric fields were applied across the cell. The transmitted light intensity through the cell without any polarizer was measured with photodiode under the application of an ac electric field.

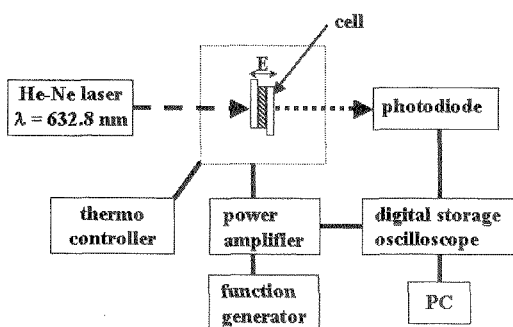


Fig. 1 Experimental setup for measuring electro-optical property.

2.4 Light scattering measurement

The linearly polarized He-Ne laser through a polarizer was incident on the sample cell upon application of an ac electric field. The scattered light passing through the sample was projected onto a screen through an analyzer. When the polarization directions of the polarizer and analyzer are crossed and parallel, the observed scatterings are called H_v and V_v , respectively. The intensity profile of light scattering was measured by the polymer film dynamic structure analyzer (Dyna-3000, Otsuka Electronics Co., Ltd).

2.5 Dielectric measurements

In order to investigate the electric field-induced orientational behavior of the liquid crystal molecular alignment, dielectric constant was evaluated for the composites. The oscillation amplitude dependence of an electric capacitance of the cell was measured.

3. RESULTS AND DISCUSSION

3.1 Morphology

Fig.2 shows the scanning confocal laser micrographs for the (polymer/LC: 20/80 wt%) composite system in which the polymer network was prepared from the monomer mixture of (TMHA/HDDVE: 2/1 mol%) (a), (TMHA/HDDVE/DEtF: 1.2/1.0/0.8 mol%) (b), (TMHA/HDDVE/DiPF: 1.2/1.0/0.8 mol%) (c). The mesh size of the polymer network in the composite including fumarate monomer, DEtF or DiPF, was larger compared with the composite including no fumarate monomer. It is known that the polymerization reactivity of fumarate monomers is lower than that of acrylate monomers. The slower polymerization in a polymerization-induced phase separation system generally results in larger dimension of phase-separated domains. Therefore, it is reasonable to consider that the difference in the morphology of the polymer network shown in Fig. 2 should be due to the difference in polymerization rate of the monomers in each composite.

3.2 Electro-optical property

Fig.3 shows the transmitted light intensity upon application of electric field for (TMHA/HDDVE/fumarate/LC) composites system. In composite (a), the initial light transmitted intensity without external electric field T_0 was 4 %. The saturated light transmitted intensity T_{100} was 91 %. The V_{10} voltage that is the electric voltage at the transmittance of $((T_{100}-T_0) \times 0.1 + T_0)$ was 3 V_{rms} . In the composite (b) including DEtF, 1 % of T_0 , 97 % of T_{100} , and 4

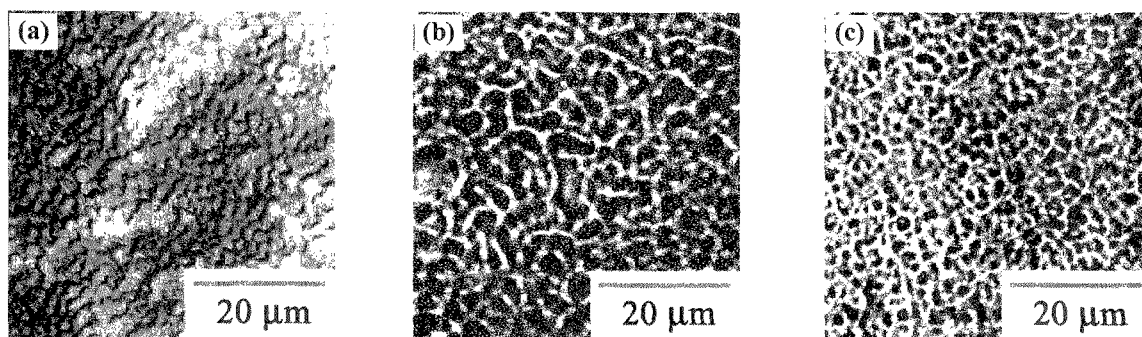


Fig. 2 The scanning confocal micrographs for (TMHA/fumarate/HDDVE/1807) composite systems.

V_{rms} of V_{10} . The composite (c) including DiPF showed 10% of T_0 , 91% of T_{100} , and $3 V_{rms}$ of V_{10} . Both the composites (b) and (c) are able to be driven by a low voltage. This result suggested that the addition of fumarate monomer in the composites enlarged the mesh size of the polymer network. The larger mesh size of the polymer network allows easier electric field-induced realignment of the LC molecules embedded in the polymer network.

The magnitude of the steepness (V_{80}/V_{10}) was about 1.5 in the composite (b), which is steeper switching curve compared to other two composites (a) and (c). The reason why the composite (b) shows the steep electro-optical response will be discussed later.

3.3 Light scattering properties

Fig.4 shows the scattered light intensities at the scattering angle of 5 or 13 degree upon application of electric field for the composites. The Hv scattering is originated from optically anisotropic objects, in this study, nematic domains. The change in the scattering intensity was very small upon an application of electric voltage of 0-6 V_{rms} , 0-2 V_{rms} and 0-3 V_{rms} for the composites (a), (b) and (c), respectively. With increasing electric voltage further, the scattering intensity was decreased. The intensity of Hv scattering depends on the birefringence of nematic domains. When an external electric field was applied, the nematic directors reoriented to the direction parallel to the electric field, that is perpendicular to the substrate surface. Therefore, the effective birefringence of nematic domains for light incident along the substrate normal was decreased with increasing electric voltage, resulting in the decrease in the intensity of Hv scattering upon application of a high electric field. In the case of Vv scattering, the composite (b) including DEtF showed the maximum of the scattered intensity at the electric voltage of 3 V_{rms} . Such the maximum of light scattering induced by application of an electric field was not observed in the composites (a) and (c). Generally, Vv scattering is caused by the spatial heterogeneity of reflective indices. A larger heterogeneity in the orientation of the nematic directors might be induced by application of low electric fields.

3.4 Dielectric properties

The dielectric constant of the (polymer/LC) composite is dependent on the orientation of the LC because of the dielectric anisotropy between parallel and perpendicular to the directors. Therefore, the dielectric analysis is useful method to evaluate the orientation of nematic directors induced by application of electric field. Fig.6 shows the applied ac electric field dependence of the dielectric constant for the composites. Since the LC used in this has a positive dielectric anisotropy, an increase in the dielectric constant corresponds to the reorientation of the LC directors along the direction of an electric field. From the comparison between the onset voltages for increasing transmittance in Fig. 4 and dielectric constant in Fig. 6, the LC molecules began to reorient to the direction of electric field while the light transmittance was still low. This result indicates that the reorientation of LC directors in a low electric voltage did not contribute to the decrease in the light scattering of the composites. Especially in the case of the composite (b) which showed a steep electro-optical response as shown in Fig. 4, though the dielectric constant was increasing remarkably upon 2-4 V_{rms} , the intensity of the light scattering exhibited

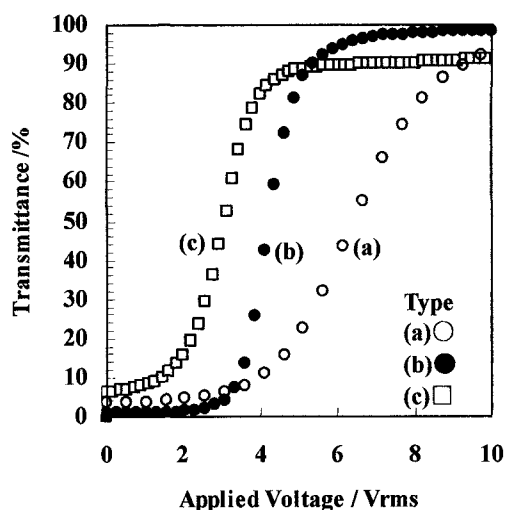


Fig.3 Applied voltage dependence for the light transmittance of (TMHA/fumarate/HDDVE/1807) composite systems.

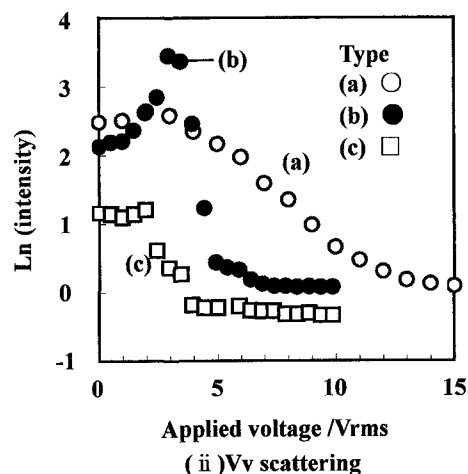
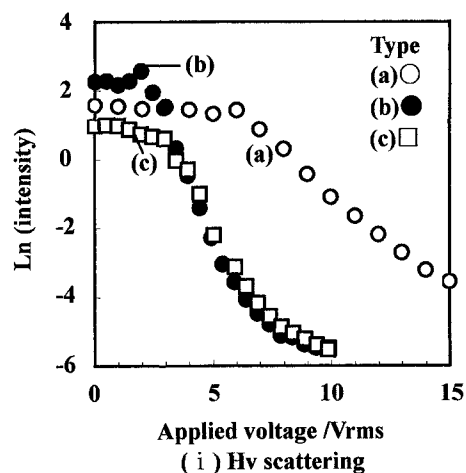


Fig.4 Applied voltage dependence of the Vv and Hv light scatterings for (TMHA/fumarate/HDDVE/1807) composite systems.

the large maximum as shown in Fig. 5. This phenomenon is difficult to be explained by a proposed mechanism of the electro-optical effect of (polymer/LC) composites so far. In

order to clarify a cause of this anomalous phenomenon, the initial orientation of LC directors was analyzed based on the dielectric measurements. The dielectric constant of the (polymer/LC) composite system ϵ_{comp} can be adequately approximated by equation (1).

$$\frac{1}{\epsilon_{comp}} = \frac{w}{\epsilon_{LC}} + \frac{1-w}{\epsilon_{polymer}} \quad (1)$$

where ϵ_{LC} is the dielectric constant of LC, $\epsilon_{polymer}$ is dielectric constant of the matrix polymer, and w is weight fraction of LC. When the alignment of LC molecules is three-dimensionally random, the dielectric constant of LC ϵ_{random} can be calculated by equation (2) using $\epsilon_{\parallel}=15.6$ and $\epsilon_{\perp}=4.8$, which are dielectric constants for an electric field applied parallel and perpendicular to the director, respectively.

$$\epsilon_{LC,random} = \frac{1}{3}(2\epsilon_{\perp} + \epsilon_{\parallel}) \quad (2)$$

Then the dielectric constants of the composite (b) in which the LC alignment is random, parallel to an electric field and perpendicular to the electric field are calculated to be $\epsilon_{comp,random} = 7.4$ and $\epsilon_{comp,\parallel} = 11$, $\epsilon_{comp,\perp} = 4.9$, respectively. At the zero electric fields, the value of dielectric constant of the composite (b) was lower than calculated $\epsilon_{comp,random}$ suggesting that the alignment of the LC directors was biased in favor of being parallel the substrate surface. In the other two composites, the dielectric constants at zero electric fields were both higher than $\epsilon_{comp,random}$. The LC directors in the composites (a) and (c) had a tendency to align the direction perpendicular to the substrate surface.

3.5 A possible mechanism of the steep electro-optical response

It is very important to make a through investigation into the cause of the steep electro-optical response of the composite (b). As shown in the section 3.4, the initial distribution of LC directors has a slight planar alignment bias (Fig. 7(a)). Therefore, the spatial heterogeneity of refractive indices which gives rise to light scattering is small in the depth direction of the composite. When a relatively low electric voltage is applied, the fraction of the LC directors having larger polar angle with respect to the substrate surface (out-of-plane angle) increases as shown in Fig. 7(b) because the LC has a positive dielectric anisotropy. Then, the spatial heterogeneity of the refractive indices in the composite increases in the depth direction, resulting in an increase in the light scattering intensity as shown in Fig. 5. This suppresses a rise of the light transmittance, which usually increases according to an increase in an electric voltage. An application of a higher electric voltage imposes a uniform orientation of the LC directors along the electric field, that is, the substrate normal as shown in Fig. 7(c), then the light transmittance increases because the refractive indices becomes uniform spatially. The electric field-induced light scattering in a low voltage region seems to play an important role for the steep electro-optical response.

4. CONCLUSIONS

The mechanism of steep electro-optical property for (TMHA/HDDVE/fumarate/LC) composite system was investigated by light scattering measurements and dielectric analyses. Addition of a fumarate monomer had an effect to give an increase in the polymer network mesh size, resulting

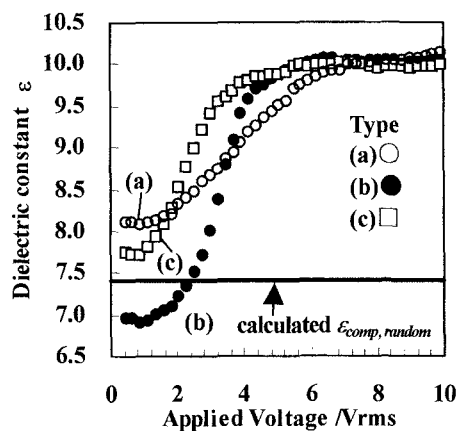
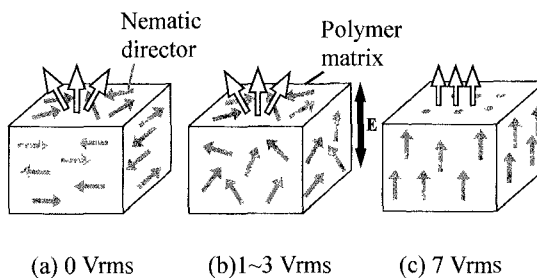


Fig.6 Applied voltage dependence of the dielectric constant for (TMHA/HDDVE/fumarate/LC) composite systems.



(a) 0 Vrms (b) 1~3 Vrms (c) 7 Vrms
Fig.7 The reorientation model of nematic directors at each driving voltage

in a low voltage driving of the light scattering-light transmitting switching of the composites. Particularly, the composite including DETF showed a remarkably steep electro-optical response. While the lower electric fields 1~3 Vrms was applied, the light scattering intensity was enhanced rather than the initial (zero-voltage) state. This process could serve an important role for appearing a steep electro-optical response.

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