

Electro-optical Properties of Liquid Crystal Molecules in the Induced Isotropic state by Polymer Network

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Electric field-induced birefringence behavior was investigated for composites composed of low-molecular-weight nematic liquid crystals (LCs) and poly(ethylene-co-methylacrylate-co-glycidylmethacrylate) which exhibits good miscibility with LCs. The electro-optical properties (mainly, Kerr effect) of the composites were measured in an isotropic phase induced by coexisting with a polymer network (polymer-induced isotropic state). The magnitude of Kerr constant of composites at the temperature exhibiting Kerr effect was 30~50% lower than that of corresponding LCs, regardless of the miscibility between LCs and polymer. This decrease in the Kerr constant could be accounted for by the restriction of the response of LC due to the anchoring from polymers. The electro-optical properties of the composites having good miscibility exhibited the Kerr effect according to the Landau-de Gennes theory. On the other hand, the electro-optical properties of the composites having relatively poor miscibility deviated from Kerr law near the isotropic-nematic phase transition temperature. Such composites exhibited spontaneous birefringence at zero electric field, indicating a nematic-like nano-structure due to the polymer network in induced-isotropic phase.

Key words: Kerr effect, liquid crystal, polymer, composite, miscibility

1. INTRODUCTION

Recently, the organic materials with large optical nonlinearities have received much attention from the viewpoints such as the variety of processing and material design and a cost. The Kerr effect is a kind of nonlinear optical effect and is caused by an electric field induced-orientation of permanent molecular dipoles, or that of induced molecular dipoles polarizability, in the material [1-3]. The anomalously large Kerr effect is observed in liquid crystals (LCs) heated to just above the nematic-isotropic phase transition temperature due to the nematic-like fluctuations embeded within the isotropic matrix. In this temperature range, though the magnitude of Kerr constant is more than 100 times in comparison with nitrobenzene [4-7], the large temperature dependence of birefringence makes practical use difficult.

The goal of this research is to form and control the nematic-like fluctuations in isotropic matrix by the introduction of the three-dimensional network structure using the polymer and so on. The large birefringence caused by electric field and the insensitive temperature dependence are expected to be simultaneously achieved by controlling the size of fluctuations. Though some literatures about Kerr effect of the polymer / LC composites are available [8-12], there are a few reports about the composite material having the polymer network structure in LCs [13-15].

In this study, we investigate the electro-optical properties (mainly, Kerr effect) of the composites composed of LCs and a polymer showing good miscibility, at an isotropic phase induced by polymer network (induced isotropic state). This paper presents the result that the electro-optical properties of polymer / LC composites varied depending on the kind of the LC, and the discussion about the nematic-like nano-structure induced by polymer network in the composites in isotropic phase.

2. THEORY

The Kerr law is given by [16]:

$$\Delta n = \lambda K E^2 \quad (1)$$

where Δn is the induced birefringence, K the Kerr constant, E the applied electric field, and λ the probe wavelength.

The Kerr constant of LCs in an isotropic phase diverges as the temperature decreases to the temperature T^* which is a critical temperature where the coherence length of nematic-like order diverges infinitely, actually slightly below the nematic-isotropic transition temperature. This phenomenon is accounted for by the considerable contribution of nematic-like fluctuations of order parameter in the isotropic phase. This contribution can be calculated by the Landau-de Gennes theory[17].

Field E induces the orientational order [18]

$$Q(E) = \rho \Delta \varepsilon E^2 / 12 \pi a_0 (T - T^*) \quad (2)$$

where ρ is the number density of molecules and a_0 is the parameter of the Landau expansion. On the other hand, the field-induced birefringence Δn is given by

$$\Delta n = \Delta n_0 Q(E) \quad (3)$$

where Δn_0 is the birefringence of the perfectly aligned liquid crystal. Therefore, from eqs. (1) - (3) the Kerr constant can be expressed as follows:

$$K = a / (T - T^*) \quad (4)$$

where a is the constant.

3. EXPERIMENTAL PROCEDURE

The structures of the liquid crystals used in this study are shown in Figure 1. The samples studied were 7CB, F-1, the mixtures of these compounds and the composites with polymer using them. The constitutions of the samples were shown in Table 1. The composites were prepared by dissolving the poly(ethylene-co-methylacrylate-co-glycidylmethacrylate)(PEMA-GMA, Aldrich) into LCs at an isotropic phase. The isotropic-nematic phase transition temperature (T_{IN}) for the samples was determined by differential scanning calorimetry (DSC) with the cooling rates of 5 K min^{-1} . The miscibility between a polymer and nematic LCs was evaluated by the difference in T_{IN} of LCs ($T_{IN(LC)}$) and composites ($T_{IN(comp.)}$). The parameter of this difference is expressed by ΔT ($\Delta T = T_{IN(LC)} - T_{IN(comp.)}$).

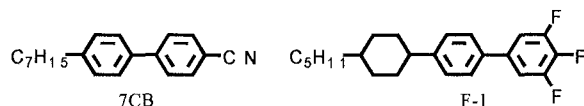


Figure 1. Structural formulae of liquid crystals.

Table 1. Constitutions of liquid crystals and composites

| LC- | 1 | 2 | 3 | 4 | 5 | 6 |
|--|-----|----|----|----|----|----|
| Molar ratio of 7CB(%) | 100 | 80 | 60 | 40 | 20 | 0 |
| Comp.- | 1 | 2 | 3 | 4 | 5 | 6 |
| Weight ratio of PEMA-GMA(%) in composite | 10 | 10 | 10 | 10 | 10 | 10 |
| Molar ratio of 7CB(%) in LC | 100 | 80 | 60 | 40 | 20 | 0 |

Figure 2 shows the schematic diagram of experimental set-up for measuring birefringence induced by an electric field. The samples were contained in Kerr cells consisting of polished aluminum electrodes of 10mm path length and 0.5mm electrode separation. The temperature of the Kerr cell was controlled ($\pm 0.1 \text{ K}$) in a water bath by a proportional integral differential (PID) controller. An ac electric voltage from 0 to 210V supplied by the power amplifier and function generator was applied between the electrodes in the cell. The transmitted light intensity through the cell placed

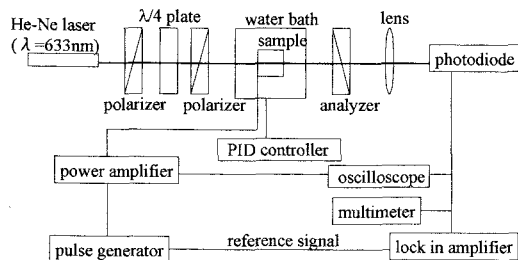


Figure 2. Experimental set up for birefringence measurement.

between crossed Nicoles was detected by a photodiode. The second harmonic component of the output ac signal from the photodiode was detected by a lock-in amplifier because the magnitude of electric field-induced birefringence based on the Kerr effect is proportional to E^2 , that is, a sin wave signal with doubled frequency, 2ω , is generated when a sinusoidal ac electric voltage with a frequency of ω was applied. All measurements were taken with a fundamental drive frequency of 1kHz and a signal response of 2kHz.

The change in output intensity due to optical retardation generated by an applied electric field was measured. Output intensity I_{out} is expressed by eq. (5)

$$I_{out} = I_{in} \sin^2(\phi/2) \quad (5)$$

where I_{in} is input intensity and ϕ is retardation.

The change in birefringence Δn is calculated from eq. (6)

$$\phi = 2\pi \Delta n L / \lambda \quad (6)$$

where L is the length of the light path.

The values of Kerr constant (K) were determined from the plots of induced birefringence with respect to the square of electric field, and T^* was given by the temperature with an intercept on the temperature axis in the linear plots of the reciprocal of K with temperature. The values a of composites were calculated using the Kerr constants and T^* in the temperature range exhibiting Kerr effect. Therefore the obtained value of a of Comp.-1 may have errors because the temperature range exhibiting Kerr effect was narrow within the measurement temperature, and all the parameters using Kerr constant for example T^* and a on the Comp.-2 could not be calculated because the temperature range exhibiting Kerr effect was far from T_{IN} .

The values of spontaneous birefringence at zero electric field were also measured.

4. RESULTS AND DISCUSSION

4.1. Phase diagram

Figure 3 shows 7CB/F-1 ratio dependence of T_{IN} and ΔT . As molar fraction of 7CB increased, both $T_{IN(LC)}$ and ΔT decreased. This decrease in ΔT indicates that as the molar fraction of 7CB increased, the miscibility between a PEMA-GMA and LCs became poorer.

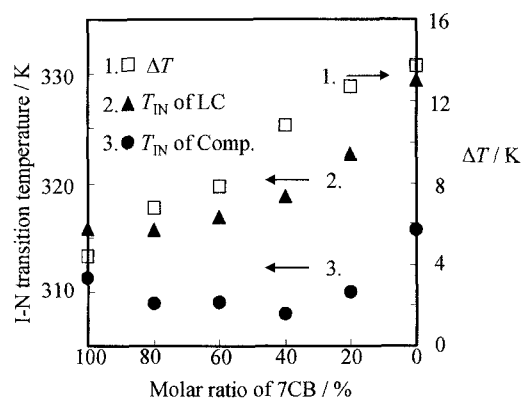


Figure 3. Phase diagram of LCs and composites.

4.2. Electro-optical properties

Figure 4 shows the plots for the reciprocal of Kerr constant as a function of temperature ($T - T^*$) about all

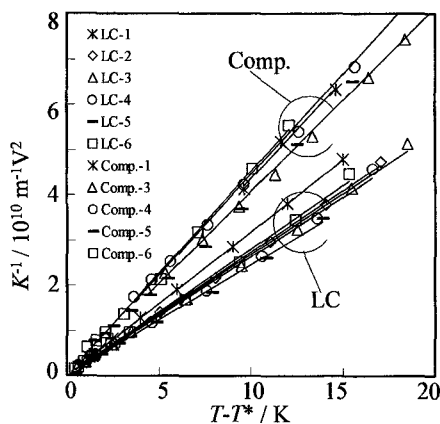


Figure 4. Reciprocal of Kerr constant as a function of temperature ($T-T^*$).

LCs and Comp.1, 3-6. As for all LCs and the Comp.5 and 6 containing less than 20mol% of 7CB in LC, the plots were in good accordance with the Landau-de Gennes theory in a whole temperature range in isotropic phase. From these results, polymer networks in the Comp.-5 and 6 might be dissolved homogeneously in induced isotropic phase due to their good miscibility between the polymer and LCs.

Figure 5 shows the values of a calculated from the slope of the plots in Figure 4. Compared with LCs, the value of a for F-1 was larger than that of 7CB, and the LC mixtures exhibited larger value than compounds. The values of a for composites were 30~50% lower than LCs, and in comparison among the composites, the values of a were nearly equal to one another. Therefore, the polymer greatly contributed to decreasing values of a in the composites, but no correlation with the miscibility was observed in the temperature range exhibiting Kerr effect. The decrease in the values of a for composites had been observed in previous works [13-15], and could be accounted for by the restriction of the response of LC

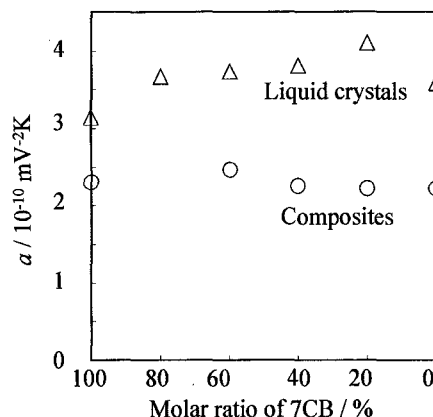


Figure 5. Concentration dependence of the value of ' a '

due to the anchoring from polymers.

Figure 6 shows the plots for the induced birefringence as a function of the square of electric field about Comp.-1, 3-6. Interestingly, the Comp.1, 3 and 4 containing 7CB more than 40mol% in LC deviated from the Kerr law near the temperature T^* . That is, the plots of the induced birefringence with the square of electric field were not linear at high electric field (Figure 6(a)-c)). These results imply the formation of heterogeneous structures in the Comp.1, 3 and 4 due to their relatively poor miscibility in induced isotropic phase in contrast to the discussion about the homogeneous structure of Comp.-5 and 6 from Figure 4.

4.3. Spontaneous birefringence at zero electric field

Spontaneous birefringence appeared near the temperature T^* in specified composites even at zero electric field. Figure 7 shows the plots for birefringence of Comp.-1, 3-6 as a function of the temperature ($T-T^*$). The Comp.-1, 3 and 4 containing 7CB more than 40mol% in LC exhibited a remarkable increase in birefringence near T^* , though the Comp.-5 and 6 didn't,

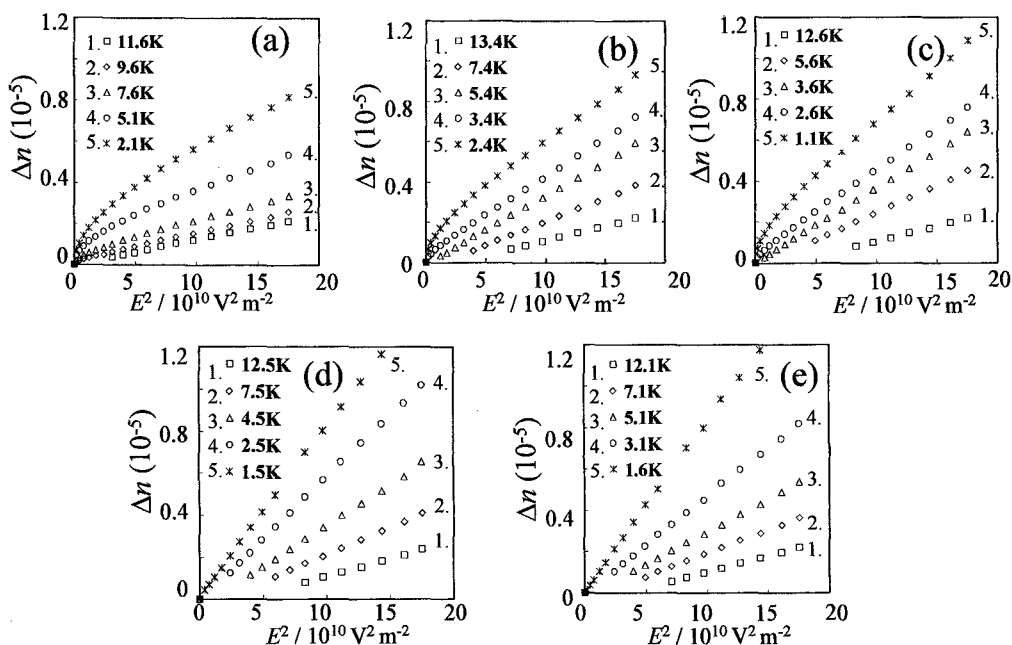


Figure 6. Induced birefringence of composites as a function of E^2 .

(a)Comp.-1, (b)Comp.-3, (c)Comp.-4, (d)Comp.-5, (e)Comp.-6. The temperature in figures is the value of $T-T^*$.

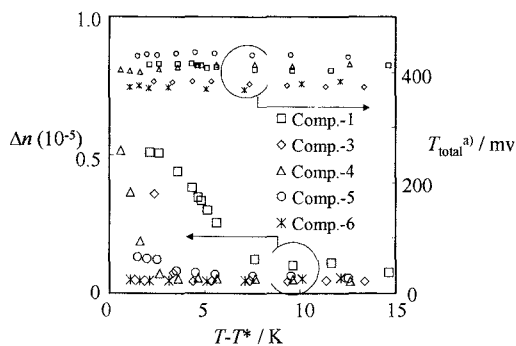


Figure 7. Spontaneous birefringence and total output intensities (T_{total}) at zero field.

a) T_{total} is the total output intensity of signals sent from the photodiode at zero field, which shows the optical intensity through the samples.

and the starting temperatures that birefringence increased were higher as the concentration of 7CB were increased except the Comp.-2 (no data). It is noticeable that the composites exhibiting spontaneous birefringence had deviated from the Kerr law near the temperature T^* as shown in Figure 6.

The spontaneous birefringence might be caused by the formation of nematic-like nano-structure due to the polymer network in an induced isotropic state. The reasons for this hypothesis are follows;

- 1) As shown in Figure 7, the total output intensity corresponding to transparency of the sample was not decreased so much for each sample even near the temperature T^* , that is, no macroscopic structure should be existed.
- 2) The birefringence at zero field indicates that there should be an orientational order exhibiting optical anisotropy.

To sustain the hypothesis, further structural studies are necessary.

4.4. Saturating behavior of induced birefringence

Figure 8 shows the plots for induced birefringence and spontaneous birefringence of Comp.-4 as a function of the reciprocal of temperature ($T-T^*$). From eqs. (1) and (4), though the plots should be linear in the isotropic phase, the birefringence of Comp.-4 was saturated as the spontaneous birefringence increased. If the nematic-like nano-fluctuation induced by polymer network had been formed, the fluctuation sizes could have been limited and this saturation behavior could have been caused.

5. CONCLUSIONS

In this study, we investigated the electro-optical properties (mainly, Kerr effect) of the composites composed of a LC and a polymer which has relatively good miscibility with the LC at an isotropic state induced by polymer network (induced isotropic state). The electro-optical properties of polymer / LC composites varied dependent on the kind of the LC, that is to say, the composites having good miscibility exhibit Kerr effect according to the Landau-de Gennes theory. On the other hand, the composites having relatively poor miscibility deviated from the Kerr law. Such materials exhibited spontaneous birefringence at zero field. The spontaneous birefringence and electro optical properties could be accounted for by the

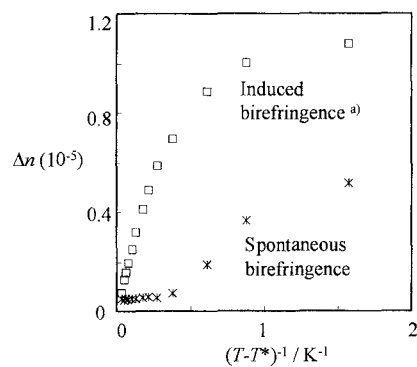


Figure 8. Birefringence plots as a function of $T-T^*$ (Comp.-4). a) Measured at $E=4 \times 10^5$ V/m

hypothesis that the nematic-like nano-structure formed in the isotropic phase due to the polymer network.

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