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Electrooptical Properties of Diacrylate Based Polymer Network Stabilized Ferroelectric Liquid Crystals

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Polymer network stabilized ferroelectric liquid crystals were produced by mixing a ferroelectric liquid crystal with a small amount of photo-cross-linkable diacrylate monomer and in situ polymerization of the monomer in homogeneously aligned ferroelectric liquid crystal environment. The addition of the diacrylate monomer into the ferroelectric liquid crystal causes dramatic reduction in spontaneous polarization and decrease in response speed. The formation of diacrylate polymer network in the ferroelectric liquid crystal can improve the response speed. The V-shape switching can be achieved by properly increasing the amount of polymer network.

Keywords: diacrylate; polymer network; polymer network stabilized ferroelectric liquid crystal; V-shape switching

INTRODUCTION

Polymer network stabilized liquid crystals (PNSLCs) are two phase composites which consist of a low molar mass liquid crystal and at least one polymer component [1–4]. In the most common way, PNSLCs can be produced by mixing a liquid crystal with a small amount of cross-linkable monomer and in situ polymerization of the monomer to form a solid polymer network in the liquid crystal. These materials have attracted considerable attention because of their great potential in display applications and scientific interests.

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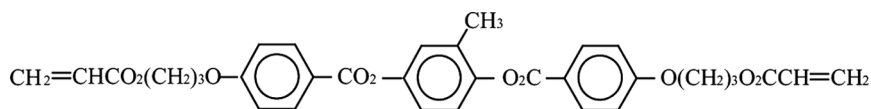
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In recent years, ferroelectric liquid crystals (FLCs) have been used with the aims to produce polymer stabilized liquid crystals with better electrooptical performance. The formation of a solid state polymer network in a FLC can promote many interesting features. For example, phase transition behavior of the liquid crystal host is affected by the embedded polymer network [5]. The rate of the polymerization will influence the spontaneous polarization [6,7]. With proper polymers and under suitable polymerization conditions, the polymer network formed can stabilize various optical states of the FLC to achieve either a thresholdless V-shape switching mode, which can be used for creating analog grey scale, or a bistable switching mode for passive addressing devices [8–11]. PNSFLCs also draw much attention as candidates for flexible displays that can be applied to smart cards or e-paper with very low power consumption [12–14]. The electrooptic behavior of the FLC can be modified by the formation of the polymer network [15,16]. It has been reported that the electrooptical characteristics of PNSFLC depends on the polymer density [17].

Recently, we have produced diacrylate based PNSFLCs, and examined the effect of the polymer network on the FLC host. In this article, we demonstrate that the embedded polymer network can strongly affect the spontaneous polarization of the FLC host. We report that the effects of polymer network on electrooptical properties of the PNSFLCs. We also show that the V-shape switching can be realized when proper amount of polymer is added into the FLC host.

EXPERIMENTAL

In the present studies, the diacrylate monomer used was mesogenic RM257 (Merck). The chemical structure and the phase sequence of the monomer are shown in Figure 1. The monomer was doped with 2 wt% of Irgacure 907 (Ciba Geigy) before it was added into the liquid crystal, this provides free radicals when irradiated with UV light that induce polymerisation of the reactive monomer.



Transition temperature: C 70 N 126 I

FIGURE 1 Chemical structure of RM257.

The nonreactive liquid crystal used in the present studies was a commercial ferroelectric liquid crystal Felix015/100 (Hoechst) whose phase sequence is given as follows

$$C(<0) \text{ Sc}^* 73.6 \text{ S}_A 84.8 \text{ N}^* 87.5. \text{ I.}$$

A small amount, ≤ 5 wt%, of RM257 was added into the FLC, and the mixture was stirred at an elevated temperature to form a uniform solution. Cells used for PNSFLC samples were made using ITO glass plates with their inner surfaces coated with unidirectionally rubbed polyimide alignment layer. The thickness of the cells was $5 \mu\text{m}$. Samples were made by injecting the FLC/monomer mixture into cells by capillary action at an elevated temperature when the mixture was in isotropic phase. The samples were then carefully cooled down to room temperature to achieve a homogeneous alignment of the composite mixture. The polymerization of the monomer in the homogeneously aligned environment was initiated using 365 nm wavelength UV radiation emitted from a medium pressure mercury lamp (Phillips 93136E). The UV intensity on the surface of the sample was 10 mW/cm^2 . The UV dosage for the curing was fixed at 30 J/cm^2 for all samples. During the polymerization of the monomer, the sample temperature was kept at 30°C where the liquid crystal host was in the Sc^* phase. The temperature of the sample was controlled using a Linkam TMS93 temperature system.

The textures of the materials, both LC/monomer mixture and PNLCS, were observed by means of optical microscopy. The texture observation was performed using an Olympus CH-2 polarizing microscope.

The spontaneous polarization was measured utilizing the current reversal method [18].

RESULTS AND DISCUSSION

Figure 2 shows a photomicrograph of a PNSFLC when the sample is heated to an elevated temperature at which the FLC is in isotropic state. The appearance of the white stripes in the picture results from the light leakage from the polymer stems. When the sample was rotated, the appearance of the stripes became black and white alternatively. This indicates that the polymer stems are of optical anisotropy. The optical anisotropy is attributed to a molecular ordering in the stems.

When evaluating the influence of diacrylate on the ferroelectricity of the FLC, two cases, with diacrylate in monomeric and polymeric forms, respectively, were considered. Figure 3(a) shows the variation of the spontaneous polarization with temperatures for the



FIGURE 2 Photomicrograph showing optical anisotropy of polymer network in the FLC. The sample was heated to 95°C where the FLC host was in isotropic state. The appearance of the white stripes in the picture results from the light leakage from the polymer stems.

Felix015-100/RM257 mixtures. As can be seen, the addition of RM257 in the FLC causes the reduction of the spontaneous polarization P_s . It is noticed that the reduction of P_s is not linearly proportional to the concentration of the monomer. This suggests that the reduction of the P_s cannot simply be attributed to the delusion of the FLC by the addition of the monomer. The ferroelectricity in the liquid crystal results from the existence of a transverse dipole moment which originates from the asymmetric distribution of electron density in the vicinity of various sites of the molecules. We believe that the added monomers may change the profile of the distribution of the dipole moments. As a result a huge reduction in P_s occurs. After the UV curing, the P_s increases dramatically, however, it cannot reach the value of the pure FLC.

Figure 3(b) shows the dependence of spontaneous polarization on the amount of RM257 for the samples at 30°C. At the temperature, the spontaneous polarization of the pure FLC is 32 nC/cm². The addition of a small amount, < 5 wt%, of RM257 causes the value of P_s drops below 13 nC/cm². The spontaneous polarization is increased after the polymerization of the monomers. It can be seen that in both cases in which RM257 existing in monomeric and polymeric form, respectively, increasing the amount of RM257 results in the decrease in the spontaneous polarization. There are several phenomena which are responsible for the decrease in P_s for PNSFLCs. Here we consider empirically the effect

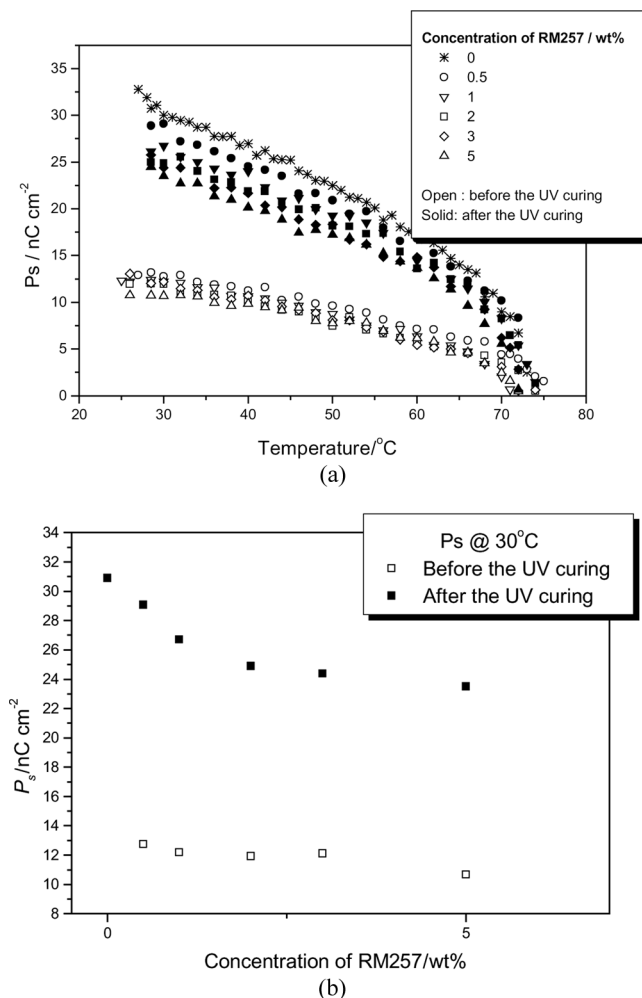


FIGURE 3 (a) Spontaneous polarization vs. temperature for Felix015-100/RM257 systems. (b) Spontaneous polarization as a function of concentration of RM257. The samples are kept at 30 $^{\circ}\text{C}$ during the measurement.

of the changes in the density of the dipoles on the spontaneous polarization. At least two aspects can be considered, the existence of a polymer network reduces the number of dipoles in a unit volume, and the surface anchoring effect of the polymer stems further reduces the number of dipoles that can respond to an external field. As a result, the number of active dipoles that can respond to an external field is reduced leading to the decrease in the spontaneous polarization.

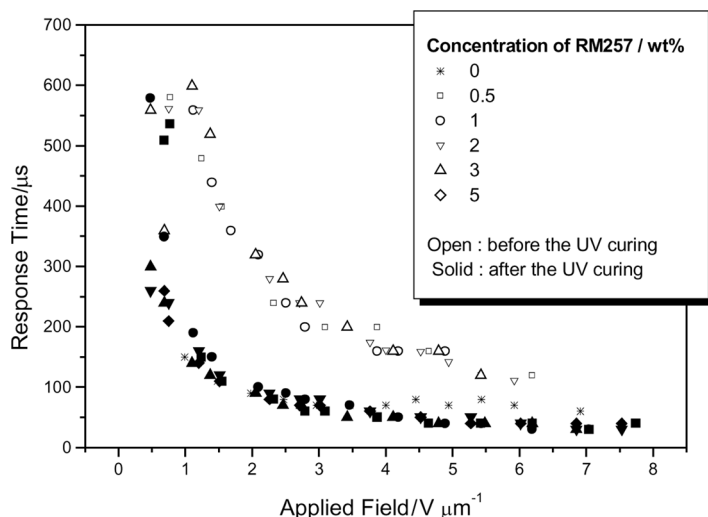


FIGURE 4 Response time against external electric field for Felix015-100/RM257 systems.

Figure 4 shows the response time of the PNSFLC against applied field for different concentrations of RM257. The response time increases upon the addition of the monomer. The increase in response time of the mixtures may result from the existence of the monomers as an impurity in the FLC, which may hinder the motion of the LC molecules in the electric field. The response times of the materials decrease as the external field increases, and become saturated when the applied field is large enough. For FLC/monomer mixtures the response times will be saturated when the applied field reaches $4\text{V}/\mu\text{m}$, whereas the saturation field for FLC/polymer network systems is about $2\text{V}/\mu\text{m}$.

After the UV curing and the formation of the polymer network in the FLC, the response times drop dramatically. As illustrated in Figure 5, when the amount of polymer network is small, e.g. $\leq 5\text{ wt\%}$, the response times of the PNSFLCs are nearly independent of concentration of the diacrylate polymer network. It can be seen that the existence of a diacrylate-based polymer network can reduce the response time. The reduction in the response time in the existence of a diacrylate-based polymer network is an interesting phenomenon, which is still not well understood. In order to explain this phenomenon it is necessary to investigate the behavior of the dipoles in the polymer network environment.

The characteristics of the optical response of the PNSFLCs to an external field are illustrated in Figure 6. The sample made using

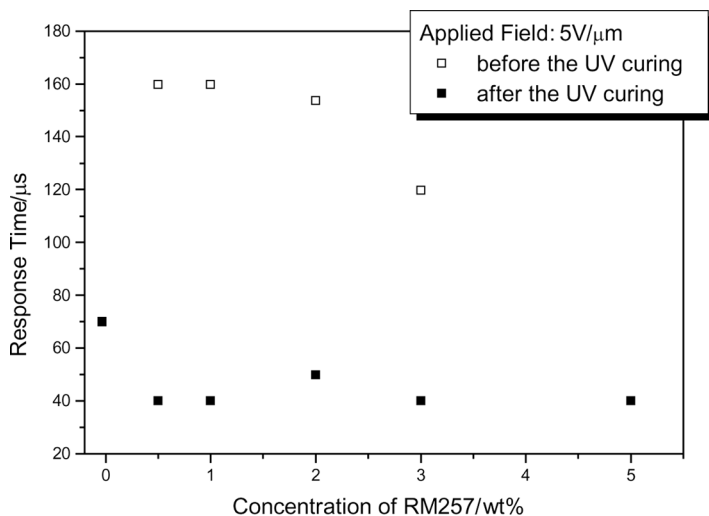


FIGURE 5 Response time vs. concentration of RM257 for Felix015-100/RM257 systems when the samples are driven by a $5\text{V}/\mu\text{m}$ field.

pure FLC shows a bistable switching, and possesses a good light transmittance. The light transmittance decreases when there is a diacrylate polymer network, and is further reduced as the amount of

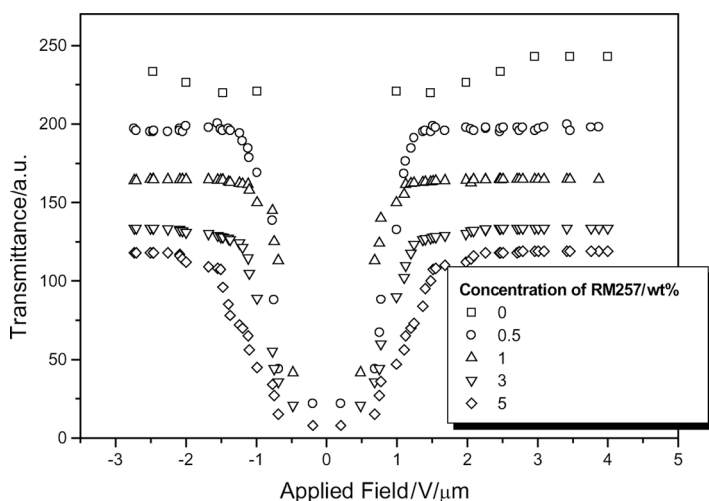


FIGURE 6 Optic transmittance against applied field for diacrylate-based PNSFLCs. The saturation field is shifted to a higher value as the amount of polymer network increases.

the polymer network increases. When considering the electrooptical switching behavior of the PNSFLCs, two parameters, the threshold field and the saturation field, were evaluated. The threshold field is the field required to drive FLC molecules to switch from one optical state to another, and the saturation field is the value of the applied field that corresponds to the saturated optical response of the PNSFLC device. It was observed that all samples could be switched by a very low voltage, and it seems that the threshold field is not affected by the embedded polymer network. However, the existence of the polymer network can delay the saturation state and reduce the steepness of the optical transmission-electrical field (OE) curve. As the amount of polymer network increases, the saturation field is shifted to a higher value and the steepness of the OE curve is further reduced. When the concentration of polymer network is increased to 5 wt%, a very distinct and nearly thresholdless V-shape switching characteristic is achieved (c.f. Fig. 6).

CONCLUSION REMARKS

We have produced PNSFLCs by in situ polymerization of a small amount of photo-cross-linkable diacrylate in a FLC. Both the spontaneous polarization and the switching speed of the ferroelectric liquid crystal are reduced upon the addition of the monomer, and further decrease when the concentration of the monomer is increased. It is believed that the significant reduction in the spontaneous polarization is not only caused by the decrease in the number of dipoles due to the addition of the monomer, and other mechanisms must be involved. After the UV curing of the sample and the formation of a polymer network in the FLC, the spontaneous polarization of the FLC host is increased. However, it cannot be recovered to the value of the pure FLC due to the effect of the polymer network stabilization. The PNSFLCs possess better electrooptical response to an external electric field compared to the pure FLC. The materials also exhibit thresholdless V-shape electrooptical switching when a proper amount of the polymer network is embedded in the FLC.

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