

Electrically and Thermally Modulated Optical Properties of Polymer Dispersed Chiral Liquid Crystal

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The polymer dispersed chiral liquid crystals (PDCLCs) film was fabricated by photopolymerization induced phase separation (PIPS) of chiral liquid crystal (CLC)/polymerizable monomers/photoinitiator composites. The effects of the electrical and thermal modulation on optical rotation properties of PDCLCs film were investigated. The microsized liquid crystal droplets were resulted from the rapid polymerization of trifunctional monomers. The effects of the electrically and thermally modulated on realignment of liquid crystal director were investigated. It was found that the intensity of electric and thermal field influenced the alignment of liquid crystal droplets' director on PDCLCs film, and the electro-optical properties of the composites were affected accordingly. The principle of free energy minimum was used for explaining the change of optical rotation and transmittance of PDCLCs film with applying the voltage to the film. The dispersion and sizes of liquid crystal droplets were described by polarizing optical microscope (POM). POLYM. COMPOS., 00:000-000, 2010. © 2009 Society of Plastics Engineers

INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) film consists of liquid crystal (LC) material which dispersed within a polymer matrix. PDLC films are potentially used for a variety of electro-optical applications, including switchable windows, flexible large-area displays, reflection/transmittance gratings [1–4], and are used for laser emission or modulation. PDLCs films are formed by exposing a photosensitized mixture of prepolymerizable monomer/LCs/photoinitiator to be cured by ultra-

violet source. The monomers and LCs are chosen to be miscible with each other and form initial homogeneous syrup. However, the miscibility of LCs is reduced with the polymer to be formed in the syrup. As the polymer network growing, the phase is separated into interpenetrating domains which are constitutive of polymer-rich and LCs-rich domains. The LCs-rich domains consist of randomly oriented director in micrometer-sized LCs droplets [5–8]. In addition, droplets size, density, distribution, and geometry are essentially governed by the density of LCs and the functional monomer in the mixture of PDLCs composites. So, the density of LCs is a key to optimize the overall performance of PDLCs films. The director of the LCs droplets and the optical properties of the films are strongly dependent on the parameters, such as curing parameters, viscosity of polymer, structure of the polymer, electric field, and temperature [9–12].

To prepare the PDLCs film, the following methods are used [5, 13–16]. First, a technique known as solvent-induced phase separation (SIPS) produces liquid crystals droplet in which the sizes were determined by the rate of solvent evaporation. In SIPS process, both the polymeric matrix and the liquid crystals are dissolved in a solvent solution. Second, polymerization-induced phase separation (PIPS) cures the prepolymer with either heat- or light-initiated polymerization. The curing of polymer matrix process forces the liquid crystals out of the polymer, and phase separation between the polymer matrix and the liquid crystal occurs.

The phase separation and formation of LCs droplets are influenced by density of LCs and functional group of cross-linking in mixture. In this article, one PDCLCs film was fabricated by the ultraviolet (UV)-light-induced polymerization of photosensitive mixture of chiral LCs/photopolymerizable monomers. The effects of the electrical and thermal modulation on the optical rotation properties of PDCLCs film were studied. The principle of free energy minimum was used for explaining the change of optical property of PDCLCs film to which applied voltage and thermal field.

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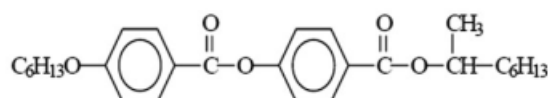
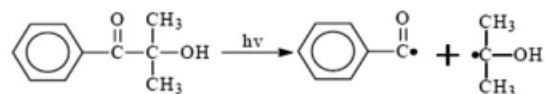
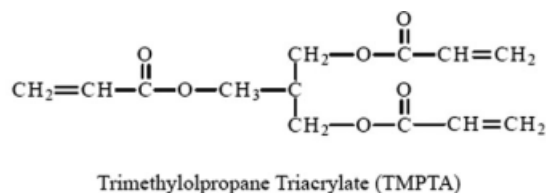


FIG. 1. The structure and properties for monomer TMPTA, photoinitiator 1173, chiral agent S-811, and nematic liquid crystal.

EXPERIMENTS

Materials

Our composites of the PDCLCs film was a solution of the monomer trimethylolpropane triacrylate (TMPTA) and the photoinitiator 1173 (Tianjin Tianjiao chemical company), and the chiral liquid crystals (CLCs) was a mixture for S-811 and 76G9700 (Shijiazhuang SLICHEM material company). Trimethylolpropane triacrylate (TMPTA) is a transparency liquid and refractive index is 1.4723. Nematic liquid crystal 76G9700 is a eutectic mixture of cyanobiphenyl and cyanoterphenyl ($n_0 = 1.49$, $\Delta n = 0.15$, $T_{N-I} = 122^\circ\text{C}$). Mixture was achieved by heating to the clearing point (T_{N-I}) of chiral liquid crystal (The clearing point of mixture S-811 and 76G9700 is $T_{N-I} = 103.6^\circ\text{C}$) and stirring for several hours. The structure of TMPTA, 1173 and S-811 were shown in Fig. 1.

Apparatus

The optical rotation of PDCLCs film was investigated with the change of electric and thermal field by Polarimeter (PerkinElmer Model 341). The alternating current voltage (sine wave, 50 Hz) and temperature controller (calibrate at 0.01°C) were used for experiment. The curves of optical rotation and transmittance were obtained under the change of electric and thermal field which were applied to the PDCLCs film. The morphology of the PDCLCs film was explored by polarizing optical microscope (POM, A Leica Germany DMRX).

The Preparation of PDCLCs Film

A 12- μm thick aluminum foil was used as the spacer between two indium-tin-oxide (ITO) substrates. The cell

was sealed by cured epoxy resin when the spacer was fixed. The aluminum foil was drawn out from the cell to escaping short-circuit of the upper and lower ITO substrates. The syrup of sample was injected in two ITO-coated glass substrate by capillarity at about 80°C and cooled to room temperature. The ratio of different component was shown in Table 1. The distance of the sample was 1 m from the UV light. Then the mixture was irradiated by UV light (1 KW) for 3 min at room temperature, and polymer network was formed from the polymerization of the photopolymerizable monomer in the composites. The polymerization of the TMPTA was occurred by irradiation of UV light. Thus, the PDCLCs film was prepared.

Observation of the Morphology in the PDCLCs Film

The sizes and dispersion of LCs droplets are important factors to influence the optical properties of PDCLCs film. The trifunctional group of monomer TMPTA was suitable for giving rapid polymerization and then microsized-CLCs droplets were obtained. The observation of the microstructure of the polymer network and CLCs droplets textures in the film were carried out by POM (A Leica Germany DMRX). To observe the morphology, the PDCLCs film was separated from the ITO coating glasses, and dipped in methanol for 24 h at room temperature, so that the LCs molecules were extracted. The PDCLCs film was dried in vacuum.

Electrically and Thermally Modulated Optical Rotation Measurements

Optical rotation of the PDCLCs film was measured under the modulation of electrical and thermal field by a setup which was schematically shown in Fig. 2. A collimated beam of polarized Na light (598 nm) was used for an incident light source. The optical rotation of the PDCLCs film was measured in the wavelength of 598 nm by Polarimeter (PerkinElmer Model 341). The curves of optical rotation were described with the change of electric and thermal field which were applied to the PDCLCs film.

Electrically and Thermally Modulated Transmittance Measurements

The transmittance of the PDCLCs film was measured under the modulation of electric and thermal field by Polarimeter (PerkinElmer Model 341). The sine wave

TABLE 1. Summary of PDCLCs mixture with different component ratios.

Mixture	76G9700	S-811	TMPTA	1173
	45%	0.3%	46%	8.7%

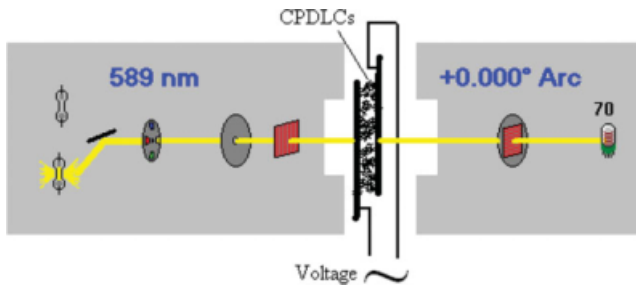


FIG. 2. The sketch map of setup. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

voltage was used for driving PDCLCs film with 50 Hz. The temperature controller was used for changing the thermal field, which was applied to PDCLCs film (calibrate at 0.01°C).

RESULTS AND DISCUSSIONS

The Morphology of PDCLCs Film

Clearly phase-separated morphologies of periodic polymer-rich domains and LCs-rich domains could be observed by observation of POM for the formed PDCLCs film. In Fig. 3, POM pictures of the samples were shown for polymer-rich and LCs-rich domains. The morphology of the dispersed LCs droplets depends on a number of factors, such as the materials which are used for forming the film, the composition, and, in particular, on the details of the film formation procedure. In PIPS, the trifunctional group of monomer and CLCs were chosen to be miscible with each other forming an initial homogeneous mixture. However, the miscibility of CLCs was reduced with the polymer to be formed under the exposure of ultraviolet light. As the polymer network grows, the phase separates into interpenetrating domains of polymer-rich and CLCs-rich domains. The trifunctional group of monomer

TMPTA was suitable for giving rapid polymerization and then microsized-CLCs droplets were obtained. The trifunctional group of monomer was rapidly polymerized and did not allow the CLCs to coalesce in sufficient time. To form microsized-CLCs droplets, we could accelerate the speed of polymerization with the increasing of the functional group of photosensitive monomer.

The POM micrograph of the CLCs droplets was shown in Fig. 3a with the fingerprint texture at room temperature. The liquid crystals droplets grew into fingerprint texture with the twist force of chiral agent S-811 under the cooling temperature. The rapid polymerization of photosensitive monomer with three acrylic functional groups forced the chiral liquid crystal out of the polymer matrix, and the chiral liquid crystal did not have enough time to grow into larger droplets. In the end, the PDCLCs film was obtained with uniform chiral fingerprint droplets which dispersed in polymer matrix at micrometer sized. The size of liquid crystals droplets was close to 5 μm as shown in Fig. 3b. The chiral liquid crystals droplets were etched from polymer matrix with black cave and the bright bubbles were an unetched chiral liquid crystal in polymer matrix.

Electrically and Thermally Modulated Optical Rotation of the PDCLCs Film

The chiral phase, due to its helical arrangement of molecules, exhibits some unique optical properties. The most striking is the so-called selective reflection, where circularly polarized light of a specific handedness and wavelength is reflected. We consider the propagation of light in a helical medium in a bit more detail by following the description of de Vries [17]. He solved the Maxwell equations for light propagating along the helix axis of a continuously twisted birefringent medium and obtained an expression for the optical rotation φ (radians unit length) as a function of wavelength λ [17]:

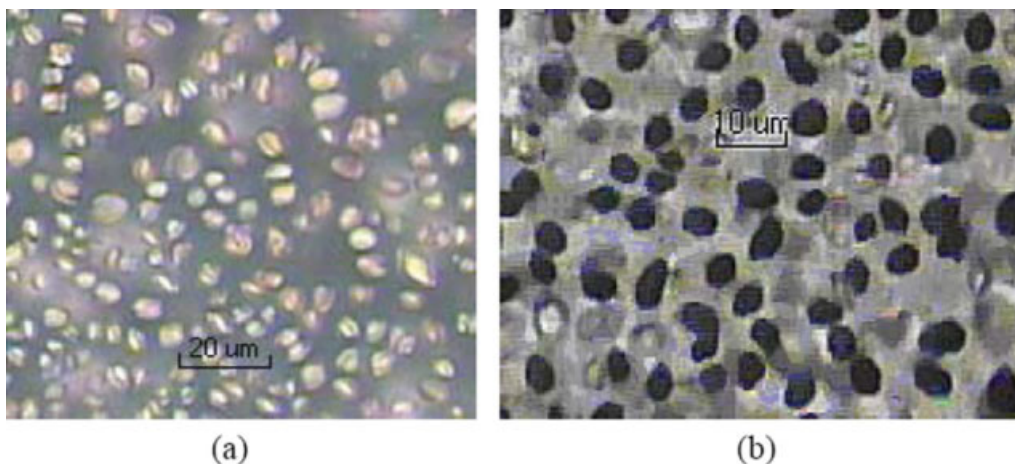


FIG. 3. The photograph of the PDCLCs film (a) with polarized light ($\times 200$); (b) with unpolarized light ($\times 500$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

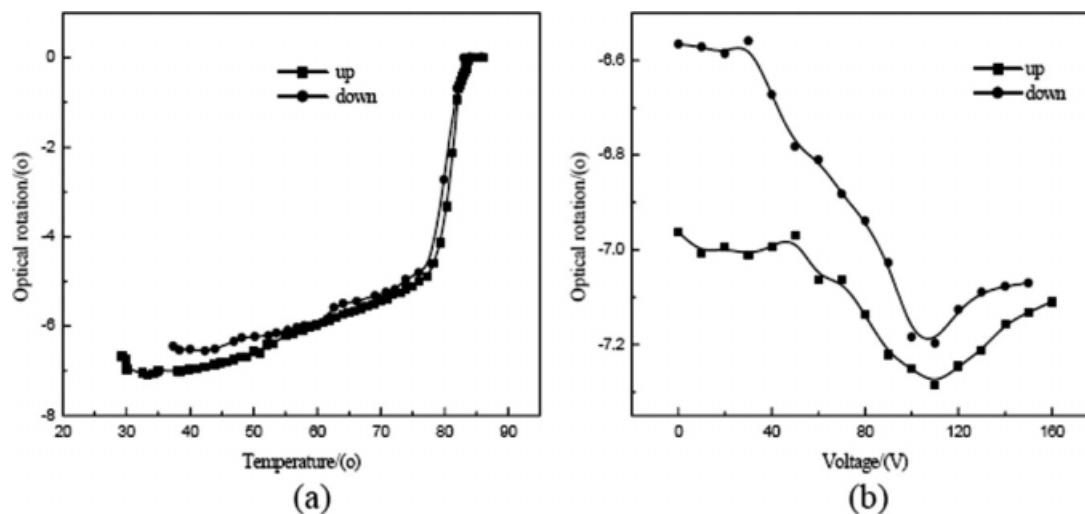


FIG. 4. The curves of optical rotation, (a) temperature; (b) voltage changed.

$$\varphi = \frac{\pi \Delta n^2 P}{4\lambda^2} \times \frac{1}{1 - (\lambda/\lambda_0)^2} \quad (1)$$

where Δn is the birefringence of a quasi-nematic layer, P is the chiral pitch and $\lambda_0 = nP$ is the wavelength of selective reflection (n is the average index of refraction of a quasi-nematic layer). Equation is valid in the regime $\lambda \approx P$ and is derived under the following simplifying assumption: (1) molecular optical activity is neglected; (2) the material is nonabsorbing; (3) only nonferromagnetic materials are considered; and (4) the sample dimension is infinite. Note that the optical rotation diverges and changes the sign [17] when $\lambda = \lambda_0$ holds.

As the expression of optical rotation φ , the wavelength λ was fixed at the 598 nm (Na light), and the optical rotation was determined by helical pitch and selective reflection wavelength $\lambda_0 = nP$. As shown in Fig. 4a, the optical rotation of PDCLCs film was left handed helix. The selective reflection wavelength λ_0 was smaller than the wavelength (598 nm) of light source according to the Eq. 1. The change of optical rotation of PDCLCs film was determined by the pitch of chiral liquid crystal P and selective reflection wavelength λ_0 . The pitch of chiral liquid crystals was sensitive to the applied temperature. The chiral liquid crystals pitch and selective wavelength were shortened under the increase of temperature which was applied to the PDCLCs film. The change of intensity of $(\frac{\lambda}{\lambda_0})^2 = (\frac{\lambda}{nP})^2$ was more rapid than the pitch of chiral LCs and the change of tendency of optical rotation φ was determined by $(\frac{\lambda}{\lambda_0})^2 = (\frac{\lambda}{nP})^2$. The optical rotation was decreased since the pitch of chiral liquid crystal was shortened when the applied temperature was increased.

On the basis of the aforementioned discussion, we concluded that, the optical rotation of chiral liquid crystal was decreased with the increase of the applied temperature. The result of experiment was consistent with the theory of Eq. 1 as shown in Fig. 4a. The optical rotation

of PDCLCs film was diminished or increased with elevation and reduction of the temperature which was applied to the chiral liquid crystal.

The effect of applied voltage on the optical rotation of PDCLCs film was not decreased but also increased under the elevation of voltage, which could be observed in Fig. 4b. The increased optical rotation of PDCLCs film was determined by pitch of chiral liquid crystal which was lengthened with the influence of voltage according to Eq. 1. The realignment or alignment of a chiral liquid crystal director in an applied electric, in the purely dielectric interaction picture, results from the system's tendency to minimize its total free energy [18]. This process can be described by the free-energy minimum process. The total free energy of the system is given by Eq. 2 [18],

$$F_{\text{total}} = \frac{1}{2} \int dz \left[K_2 \left(\frac{\partial \phi}{\partial z} - q_0 \right)^2 - \Delta \varepsilon E^2 \sin^2 \phi \right] \quad (2)$$

where K_2 is the elastic constant, $q_0 = 2\pi/p_0$, E is the applied electric field, $\Delta \varepsilon$ is the anisotropies in the dielectric constant $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$. We can see that the total free energy is minimized with the electric field increased. The influence of voltage on chiral liquid crystal is that, the director axis tends to align parallel to the field for positive dielectric anisotropies, and normal to the field for negative dielectric anisotropies. In chirals, however, the realignment of the director axis in the direction of the applied field will naturally affect the helical structure. For $E < E_{\text{th}}$ (E_{th} is threshold electric field which applied to PDCLCs film), the variation of P with E is well approximated by the expressions [18]:

$$P = P_0 \left[1 + \frac{(\Delta \varepsilon)^2 P_0^4 E^4}{32(2\pi)^4 K_2^2} + \dots \right] \quad (3)$$

Here it should be noted that the preceding treatment of field-induced pitch changes assumes that the chiral liquids

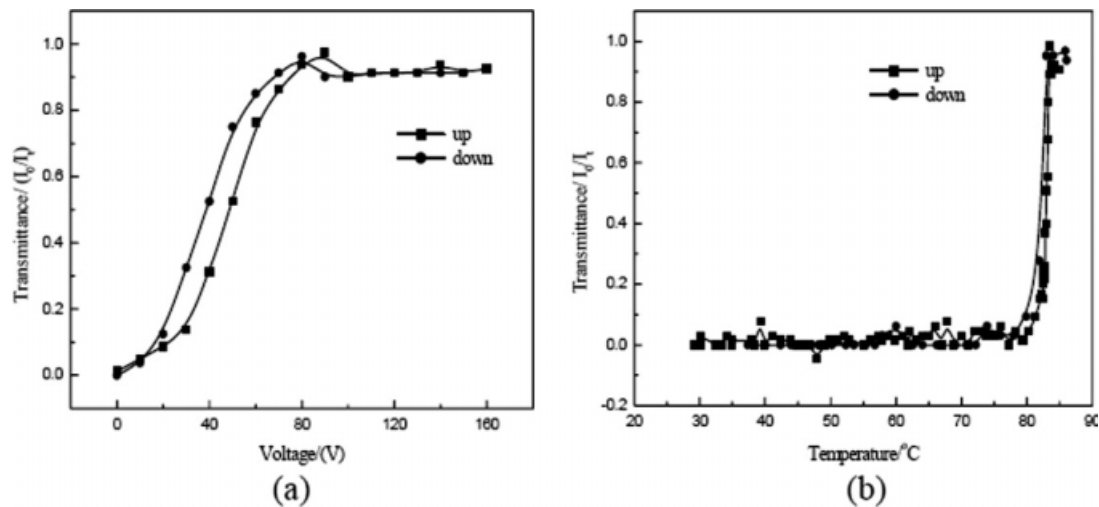


FIG. 5. The curves of transmittance of CPDCLCS film, (a) voltage; (b) temperature changed.

crystal cell is thick and in an initially ideally twisted arrangement, and there is negligible influence from the cell walls. The pitch of chiral liquid crystal depends on average orientation of CLCs directors, which is determined by the balance between electric and elastic torque. As shown in Eq. 3, the pitch of chiral liquid crystals was lengthened with increase of applied voltage and the optical rotation was increased. The tendency of optical rotation was determined by the pitch of chiral liquid crystals, and the optical rotation was increased with the growing of pitch. The result of experiment was consistent with the theory of optical rotation expression with the applied voltage.

As discussed earlier, the optical rotation φ was sensitively changed by thermally modulated than electric field. We had obtained the best effect of the modulation of the temperature on the PDCLCs film, when it was used for polarizer.

Electrically and Thermally Modulated Transmittance of the PDCLCs Film

It should be mentioned that the transmittance of PDCLCs film is an important optical property to influence its application under the applied electric and thermal field. In a certain frequency range, molecular orientation cannot follow a superposed electric polarity change, and the transmittance output varies in a fashion of simple monotonic asymptote [18]. The transmittance of powered film depends on average orientation of LC directors, which is determined by the balance between electric and elastic torque. The elastic torques consists of splay, twist, and bends deformations and depends on the director configuration [19].

The threshold voltage (V_{th}) is defined that the voltage when transmittance reached at 10% maximum. The higher

field requirement of film with low LCs loading is consonant with general trends reported by others [20, 21] and is predictable from the polymer-LC series model [20]. For comparable droplet size bipolar configuration, which occurs in most cases, V_{th} is substantially less than in alphabet configuration [12, 22, 23], as given by

$$V_{th} = \frac{d}{3a} \left(\frac{\rho_P}{\rho_{LC}} + 2 \right) \left(\frac{K(l^2 - 1)}{\epsilon_0 \Delta \epsilon} \right)^{1/2} \quad (4)$$

where d , a , ρ , K , and l represent film thickness, major dimension, resistivity, elastic constant, and aspect ratio, respectively. With larger sections of the polymer-LC interfacial area V_{th} become smaller, leading to smaller total interfacial energy requirement for director alignment.

The change of transmittance of PDCLCs film as a function of applied voltage was shown in Fig. 5a. The transmittances of PDCLCs film was slowly increased when the applied voltage was below the threshold voltage $V_{th} = 20$ V, and was dramatically increased with the voltage exceed threshold voltage $V_{th} = 20$ V. The transmittance of PDCLCs film reached the maximum when the voltage was 85 V and did not change when the voltage was elevated continuously. The threshold and driving voltage were too larger than most reasonably working PDCLCs. The morphology of PDCLCs films are important parameter to influence on the threshold and driving voltage [24, 25]. From the aforementioned analysis, it was found that the size of CLCs droplets was too small to decrease the threshold and driving voltage. The interfacial tension of CLCs droplets and polymer matrix was enhanced with decreasing the size of CLCs droplets. The threshold and driving voltage were increased by the influence of enhanced interfacial tension. The optimization of sizes of CLCs droplets is an effective method to lower the threshold and driving voltage. To lower the threshold and driving voltage, it is important to reduce

the interfacial tension between CLCs droplets and polymer matrix by doped suitable surfactants. The effect of surfactant on performance of PDLCs film will be talked in next research. The transmittance was decreased when the voltage stepped-down and slowly decreased when the voltage beneath 15 V. Because of the competition of electric and elastic torque, the director did not immediately realign along the direction of electric field and showed a hysteresis ring when the voltage rose and fell.

As shown in Fig. 5a, the director was realigned and parallelized along the direction of applied voltage, and the transmittance was increased or decreased with the voltage rose and fell. The threshold voltage is $V_{th} = 20$ V. As discussed in Fig. 4b, the pitch of the helical structure would be lengthened and shown “untwisting” phenomenon with the director was realigned along the direction of applied voltage.

The effect of voltage on transmittance of PDCLCs film is more important to switch from off-state to an on-state. In the field-off state, surface anchoring causes a nonuniform director field in the droplets, the film scatters light due to the mismatch between the effective refractive index of the LCs n_{eff} and the refractive index of the polymer n_p . In the field-on state, the director is aligned along the field direction, $n_{eff} = n_o$, and for normally incident light the film becomes transparent if the ordinary refractive index of the LCs n_o is equal to n_p .

The effect of temperature on the transmittance of PDCLCs was shown in Fig. 5b. The transmittance of PDCLCs film was invariant when the voltage below 75°C and dramatically increased at adjacent of 80°C. The analysis of the phenomenon was that the scattering was increased when the pitch of CLCs was shorten and the molecular movement was accelerated with the temperature elevated. However, when the temperature reaches at adjacent of temperature 80°C, the CLCs droplets show an isotropy and optical transparent state.

CONCLUSIONS

We have presented the preparation, the electric field and thermal field modulated optical property of the micrometer-sized PDCLCs film. Micrometer-sized droplets of chiral liquid crystal were fabricated by rapid polymerization of trifunctional group of monomer. Micrometer-sized fingerprint texture of chiral liquid crystal droplets were dispersed in polymer matrix in room temperature.

The optical rotation and transmittance of PDCLCs film was measured by Polarimeter (PerkinElmer Model 341). The change of optical properties of PDCLCs film was explained by the principle of free energy minimum under the influence of voltage which was applied to the film. The threshold electric field of PDCLCs film was gotten in the experiment was $E_{th} = 2$ V/ μ m.

In conclusion, we have demonstrated that good optical rotation and transmittance with the change of electric and thermal field which were applied to the PDCLCs film

which the micrometer-sized CLCs droplets were dispersed in polymer matrix. The optical rotation and transmittance of PDCLCs film were potentially used for polarizer and switchable windows, respectively.

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