Electro-optical properties of polymer dispersed liquid crystal materials

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Polymer dispersed liquid crystal (PDLC) materials based on poly(polyethyleneglycol methacrylate) are prepared by ultraviolet light induced polymerization. Microphase structure of PDLC films is observed by scanning electron microscopy. It reveals that reversed morphology type PDLC is obtained. The liquid crystal (LC) is a continuous phase and fills up the irregular space of the polymer network. A comprehensive investigation is performed on the electro-optical properties of PDLC films. The light scattering and transmittance properties of PDLC films are studied. The effects of LC domain size, light wavelength, applied voltage, frequency, temperature, incident angle, and film thickness on electro-optical properties of PDLC films are discussed. The results show that size and shape of LC domain seriously affect the electro-optical properties of PDLC film. © *1996 American Institute of Physics.* [S0021-8979(96)09315-2]

I. INTRODUCTION

Polymer dispersed liquid crystal (PDLC) materials have been interestingly studied as electro-optical display materials during the last few years since they can be switched electrically from a light scattering state to a transparent state without polarizers and alignment layers. PDLC films are of considerable potential for displays and light control applications.[1,2]

Liquid crystal (LC) in PDLC materials could be separately or continuously dispersed in polymer matrix. The former type is regarded as droplet type PDLC in which LC forms spherical droplets of micrometer to submicrometer sizes. In the latter type of PDLC which is referred to as reversed morphology type, a three dimensional polymer network is filled up with LC. Recent research found that the reversed morphology type PDLC had low saturation voltage and was highly transparent in a field-on condition.[2]

In a field-off condition, normal mode PDLC film is opaque because of the light scattering caused by the refractive index mismatch between LC and polymer.[3] When the electric field is applied, the film becomes transparent because the alignment of LC molecules is parallel to the electric field and the ordinary refractive index of the LC matches the refractive index of the polymer.[4,5]

Polymerization induced phase separation is often used to prepare PDLC films since it generally forms droplets with identical size distribution and density. The mixture of monomer and LC is homogeneous. As polymerization processes, the LC separates as a distinct microphase because of the increasing miscibility gap between LC and polymer.[1] When the polymerization system consists of the monomers with light-induced polymerization ability, the objective microphase structure of PDLC is possible to be obtained by controlling the polymerization optically.[1]

The electro-optical properties of PDLC are affected by the inherent properties of the LC such as dielectric anisotropy, viscosity and elastic constant, the shape, size,[6,7] and structure of the LC domains,[8] the interface and compatibility of LC and polymer, and the electric field conditions.[4]

Although PDLC has superiority when compared to LC, PDLC also has drawbacks. The polydispersity in the size of LC domains makes PDLC have high saturation voltage and high value of slope characteristic. These limit the applications of PDLC. Therefore, much attention is paid to improve these properties.

In this paper, our study is devoted to the electro-optical properties of PDLC films prepared from poly(polyethyleneglycol methacrylate). The results show that PDLC films have good slope characteristic. The light scattering of the PDLC films under different electric field driving conditions is investigated. The effects of LC content, microstructure, incident light wavelength, temperature, incident angle, and film thickness on electro-optical properties of PDLC are also discussed.

II. EXPERIMENT

PDLC films were prepared with ultraviolet (uv) curable macromonomer (polyethyleneglycol methacrylate) and nematic LC mixture (main composition: E7 from BDH). A series of polyethyleneglycol methacrylate was synthesized by the ester reaction of polyethyleneglycol with methacryl chloride. The lab-synthesized macromonomers (20–50 wt % of the total weight) and a small amount of photoinitiator were added to the LC. Then the homogeneous mixture was sandwiched between two transparent conducting glass plates and polymerized under uv light irradiation. The value of the refractive index of the polymer was adjusted to be equal or close to the ordinary refractive index of the LC. The film thickness was controlled by 7–25 μm spacers. The exact value of the film thickness was determined by the mass of PDLC material on the unit area.

The structure of PDLC film was observed by a scanning electron microscopy (SEM). The samples were soaked in methanol to remove the LC and then baked in a vacuum-desiccator, thus the LC domains appeared as holes in the SEM micrographs. The electro-optical properties of PDLC

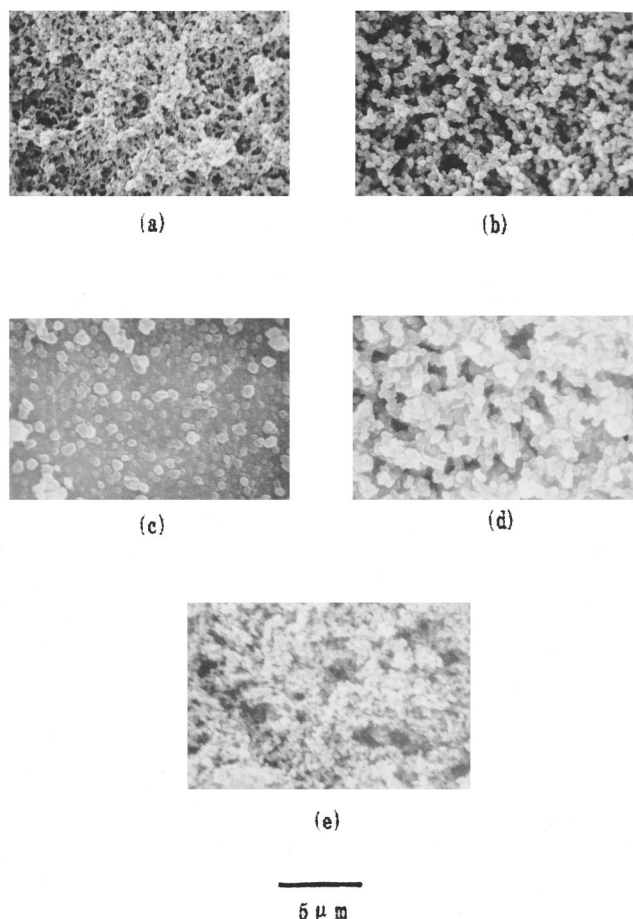[a]Author to whom correspondence should be addressed; Electronic mail: pcym@DMSE.MSE.ustc.edu.cn

FIG. 1. SEM micrographs of PDLC films with different LC content: (a) 50 wt %, (b) 60 wt %, (c) 65 wt %, (d) 70 wt %, and (e) 80 wt %.
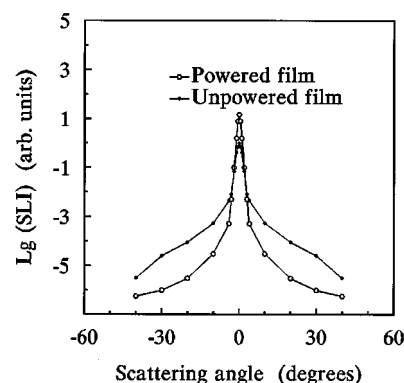

FIG. 2. The dependence of scattering light intensity on scattering angle for both powered and unpowered PDLC film with 65 wt % LC content. The data of powered film were measured under an applied rms field of 8 V (f=1 KHz).

films were studied by a photo-electric photometry with a collection angle which was less than 1°. Light source was a He–Ne laser. The electric field was applied using a function generator. Transmittance of the PDLC film was measured by pressing the PDLC film close to the photometry. Thus photometry can detect almost all light that transmits the film. The light scattering of PDLC films in dependence of light wavelength was measured by ultraviolet–visible spectroscopy. The distribution of scattering light intensity was measured for fixed incident angle θ and the scattering angle δ was varied. Measurements of incident angular dependent contrast ratio were performed with the detector at δ=0° and θ was varied. Unless otherwise mentioned, film thickness was 7 μm, measurements were carried out at 25 °C.

III. RESULTS AND DISCUSSION

Microphase structure in PDLC films with different LC content was studied by SEM. LC domains were holes on the SEM micrographs because of the treatment of the samples with methanol. The PDLC has reversed morphology. As shown in Fig. 1, a three dimensional polymer network was formed and submicrometer-size polymer particles are connected with each other. The LC is a continuous phase and fills up the irregular space of the polymer network. The reversed morphology type PDLC can be generally obtained

when LC content of the film is relatively high and the interaction between polymer and LC is not very strong.

The sizes of the LC domains vary from 0.3 to 3.0 μm as shown in Figs. 1(a)–1(e). In general, LC domain size increases with increasing LC content. In the film with 50 wt % LC content, the LC domains are relatively small, 0.3 μm in diameter [Fig. 1(a)]. Large LC domains: 3.0 μm were obtained for the film with 80 wt % LC content [Fig. 1(e)]. However, in the film with 65 wt % LC content [Fig. 1(c)], the LC domain size is difficult to define since most of the polymer particles are not connected with each other. In spite of the variation of LC domain sizes, the difference between polymer particle sizes is not so obvious as on the SEM micrographs. Polymer particle size also increases with increasing LC content. However, when LC content is 80 wt %, polymer particles become small instead and the interface between polymer and LC is not clear [Fig. 1(e)].

We measured the scattering light intensity (SLI) at varied scattering angles for 7 μm PDLC film in which LC content was 65 wt %. The incident light was perpendicular to the PDLC film. Figure 2 shows the angular distribution for SLI for both powered and unpowered PDLC film. If the electric field is turned on, the PDLC film becomes transparent. Through the powered film, the direction of the light changes very slightly. As a result, SLI curve is peaked near δ=0° and decreases abruptly for increasing δ; when the field is turned off, the PDLC film strongly scatters the incident light and the film becomes opaque. SLI curve decreases gradually for increasing δ. In contrast to the results obtained from powered PDLC film, the SLI of unpowered film is lower in the range of narrow angle near 0°, but higher in other angles. The SLI curve is symmetric about δ=0°.

Previously, electro-optical property of PDLC was often represented by transmittance or the function of transmittance to show the difference between powered and unpowered film. In fact, because electro-optical property of PDLC is not the twisted nematic effect as in nematic LC, but the light scattering effect, the transmittance of PDLC film includes regular transmittance T_r and diffuse transmittance T_d
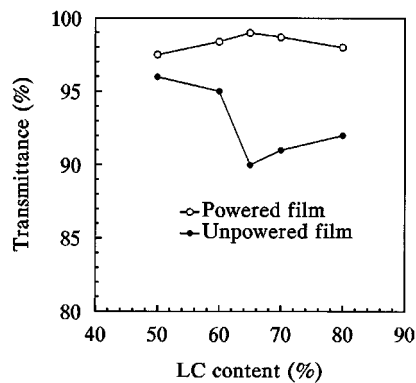
$$T=T_r+T_d. \tag{1}$$

FIG. 3. Transmittance versus LC content for both powered and unpowered PDLC films. The data of powered films were measured under corresponding saturation voltage for each film (f=1 KHz). All data have been corrected for reflection losses at glass–air interface.

FIG. 5. Ultraviolet–visible spectroscopy of unpowered PDLC films with different LC content. (a) 50 wt %, (b) 60 wt % (c) 65 wt %, (d) 70 wt %, and (e) 80 wt %. The collection angle of the spectroscopy was about 5°.

We have studied the transmittance of PDLC films with different LC content. Our observations suggest that if the transmittance value is corrected for reflection losses at glass–air interface, the transmittance of the unpowered film is considerably high, $\geq$90%, and approaches the transmittance of the powered film as shown in Fig. 3. The transmittance of the unpowered PDLC film is mainly diffuse transmittance. The light scattering of unpowered film is a forward scattering.[5] The light absorbed or reflected by the film is very little. In contrast, the transmittance of the powered PDLC film is mainly regular transmittance which makes the film highly transparent.

In order to express the light scattering of PDLC film, we define contrast ratio (CR) to characterize the difference between the two states.

$$CR = I_{on}/I_{off}, \tag{2}$$

where I_{on} and I_{off} are scattering light intensity of powered and unpowered PDLC film at δ=0°, respectively. Although the value of CR is obtained by only measuring SLI at δ=0°, it reflects the extent of light scattering because CR increases with the increasing diffuse transmittance of unpowered film, and diffuse transmittance increases with increasing extent of light scattering.
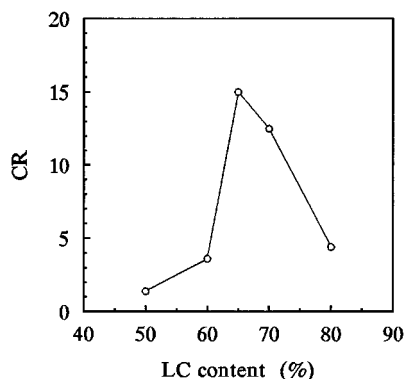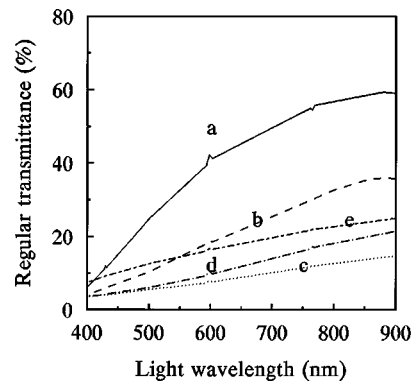

FIG. 4. Contrast ratio as a function of LC content. The PDLC films were driven by corresponding saturation voltage of each film (f=1 KHz). The collection angle was less than 1°.

As shown in Fig. 4, CR increases with increasing LC content, reaches a maximum at 65 wt % and then decreases with further increasing LC content. Comparing Fig. 4 with Fig. 1, it would be found that LC content which determines the microstructure of films has indispensable effect on the electro-optical properties of PDLC films. A high value of CR can be obtained when the microstructure of film is appropriate.

PDLC is an optically soft, anisotropic object. The treatment for light scattering of a random dispersion of aligned nematic LC in a polymer network is based on the anomalous diffraction approximation for droplets larger than the wavelength of light, and the Rayleigh–Gans approximation for droplets smaller than the wavelength of light.[5,9] The light scattering is strongest when the particle diameter is equal to the incident light wavelength.[10] However, in the PDLC films we prepared, the LC domains are not spherical. They are not only irregular but also link each other. The polymer particles are quasi-spherical when LC content is between 60 and 70 wt % [Figs. 1(b), 1(c), and 1(d)], and are irregular when LC content is 50 and 80 wt % [Figs. 1(a) and 1(e)]. Since LC domain size, shape, and density are not identical in each film, the light scattering of PDLC films is not strongly dependent on the incident light wavelength as shown in Fig. 5. Figure 5 is the ultraviolet–visible spectroscopy of unpowered PDLC films with different LC content. Ultraviolet–visible spectroscopy detected the light at δ=0° as regular transmittance. The collection angle of ultraviolet–visible spectroscopy is larger than that of the photometry, so the transmittance value in spectroscopy is not equal to the transmittance in other experiments. However, the spectroscopy is a useful means of comparing the light scattering of different films. The light scattering of all films in which LC content is between 50 and 80 wt % decreases with increasing light wavelength. Comparing with other films, the film containing 65 wt % LC is of strongest light scattering when incident light wavelength ranges from 430 to 900 nm.

Figure 6 shows the influence of electric field and temperature on CR of the PDLC film. The degree of field induced director alignment in the LC domains depends on the inherent properties of PDLC material and strength of the
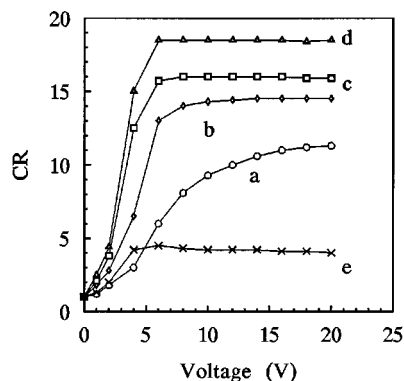
FIG. 6. Contrast ratio of PDLC film with 65 wt % LC content as a function of applied voltage at different temperatures. (a) 5 °C, (b) 20 °C, (c) 35 °C, (d) 45 °C, and (e) 50 °C. The collection angle was less than 1°.

FIG. 8. Contrast ratio as a function of electric field frequency. The PDLC film with 65 wt % LC content was driven by an applied rms field of 8 V. The collection angle was less than 1°.

external field. CR increases with increasing applied voltage, reaches a maximum and then maintains the constant value.

The threshold voltage V_{10} and the saturation voltage V_{90} are defined as applied voltages required to achieve 10% and 90% of the maximum CR, respectively. The slope characteristic λ is given by

$$\lambda = V_{90}/V_{10}. \qquad (3)$$

Slope characteristic of PDLC is not as sharp as that of LC because of the polydispersity in the size of LC domains.

We calculated λ value of PDLC film at different temperatures and the data are shown in Fig. 7. The result shows the great effect of temperature on λ. The film is easier to be driven at higher temperature under same electric field. This is the reason why V_{10} and V_{90} decrease with the increasing temperature. Our experiments demonstrate that V_{90} depends more strongly on temperature. Therefore, λ decreases with increasing temperature. When temperature was higher than 45 °C, the unpowered PDLC film became transparent because the compatibility of LC and polymer increased with increasing temperature, thus the error of measurement became larger and the change of λ was irregular.

The electro-optical property of PDLC film was investigated under different driving field frequencies. Figure 8 shows that CR of PDLC film increases with increasing fre-
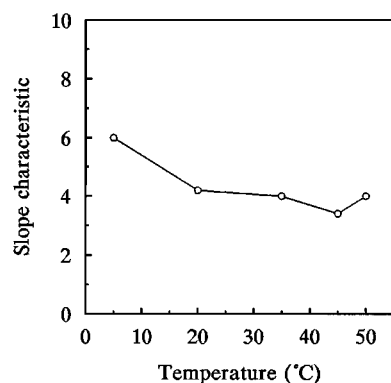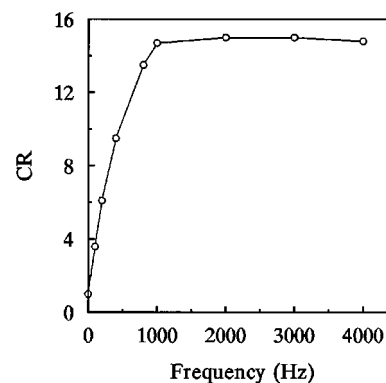
quency, reaches a maximum at 1000 Hz. It is well known when a PDLC film is driven by a low-frequency electric field, the actual field that appears across the LC domains gets strongly masked by the space-charge build-up at the polymer-LC interface due to their different electrical conductivities.[4] The space-charge build-up decreases with increasing frequency and the electric field appearing across the LC domains increases. This leads to an increase in the CR and it attains a maximum at the frequency without the build-up of space-charge. If frequency increases further, the value of CR will not change.

We focused our attention on the relation between CR and incident angle θ in Fig. 9. In this experiment, the film was rotated around an axis orthogonal to the direction of the incident light. As shown in Fig. 9, a minimum value of CR is obtained at $\theta=0°$. Although the refractive index mismatch increases with the increasing incident angle, CR increases with increasing angle because larger incident angle causes the light to cross thicker PDLC material. The latter is a decisive effect on the CR curve. The light path length l as a function of the incident angle θ is given by

$$l = d_0/\cos \theta. \qquad (4)$$

FIG. 7. The dependence of slope characteristic on temperature for PDLC film with 65 wt % LC content.
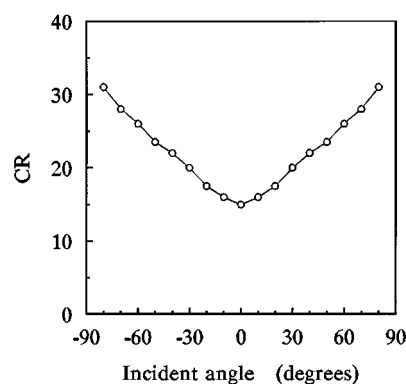

FIG. 9. The dependence of contrast ratio on incident angle. The PDLC film with 65 wt % LC content was driven by an applied rms field of 8 V (f=1 KHz). The collection angle was less than 1°.
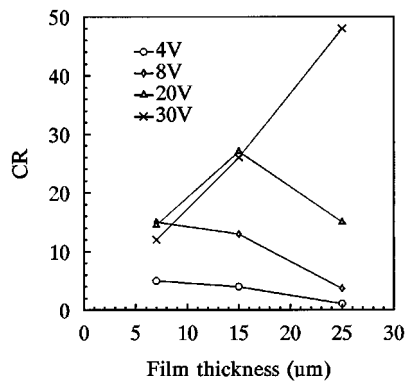
FIG. 10. Contrast ratio as a function of film thickness at various voltages (f=1 KHz) for PDLC films with 65 wt % LC content. The collection angle was less than 1°.

In Eq. (4) d_0 is the film thickness. However, the clarity of powered films will depend on the refractive index mismatch between polymer and LC. That is, although CR is higher at larger θ, the clarity of powered film decreases with increasing θ because the perfect refractive index match between LC and polymer can only be obtained when the incident light is perpendicular to the film.

Film thickness is an important factor influencing the CR value. From Fig. 10, it is found that CR of thin film is higher than that of thick film when applying low voltage. On the contrary, CR of thick film is higher than that of thin film when applying high voltage. Saturation voltage of PDLC increases with increasing film thickness because the voltage applied on per unit thickness decreases with increasing film thickness when applying same field. Applying corresponding saturation voltage, CR increases with increasing film thickness. Theoretical approximant of CR as a function of film thickness is given by

$$CR_2 = CR_1^{d_2/d_1}, \tag{5}$$

where CR_1 and CR_2 are contrast ratio of PDLC films with thickness d_1 and d_2, respectively. In our experiments, CR

value does not closely agree with theory because of effects such as refraction at glass-air interface and transition layer between glass and PDLC material.[2]

IV. CONCLUSIONS

The light scattering and transmittance properties of both powered and unpowered PDLC films were studied. The transmittance of PDLC film is high even in unpowered state because of the diffuse transmittance. The result of scattering light intensity distribution versus scattering angle δ shows that scattering light intensity near δ=0° of powered film is higher than that of unpowered film. In contrast, scattering light intensity at other δ of powered film is lower than that of unpowered film. Electro-optical property of PDLC film can be clearly represented by contrast ratio. LC domain size and microstructure of the film strongly affect the light scattering properties. We have also found that the light scattering of PDLC film strongly depended on external electric field. PDLC film with suitable LC domain size and microstructure exhibits good electro-optical properties for 0°–60° viewing angle at 5–45 °C temperature.

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