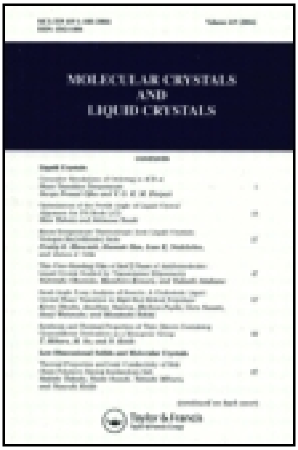

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Optical Properties of Diffusion-Type Cholesteric Liquid Crystalline Polymer Film

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In the application of cholesteric liquid crystal (CLC) polymer film to mono-color polarizers, diffusive reflection is preferred rather than mirror reflection at the point of visibility. This led us to develop a diffusion-type CLC (D-CLC) film. The newly developed D-CLC film exhibits high circular dichroism with bright color reflection that can be observed from almost all directions. The layer structure of the D-CLC film was directly confirmed by analysis with transmission electron microscopy (TEM). It was found that the diffusive property and polarization of the reflected light are mainly affected by the layer structure of the D-CLC.

Keywords: cholesteric liquid crystal; polymer film; diffusive reflection; TEM; layer structure; mono-color polarizer

INTRODUCTION

It is well known that short-pitch cholesteric liquid crystals (CLCs) have unique optical properties[1]. Their main characteristic is the selective reflection of circularly polarized light. If the cholesteric layer of CLC film is in the planar orientation, the helical axes are perpendicular to the film surface, and the reflected light is observed only at the point where the reflection angle is equal to the angle of the incident light. In this case, the characteristics of the reflection are the same as those of a mirror. We have already commercialized this planar oriented CLC polymer film [2] [3] and call this type of CLC polymer film the "mirror type."

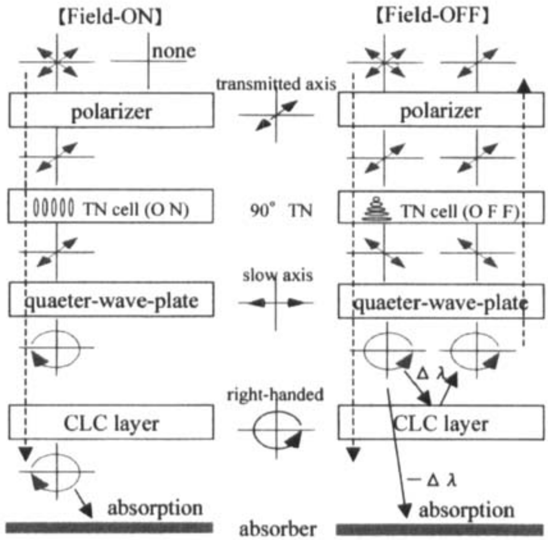


FIGURE 1 The schematic view of the display device
: liner polarized light :circular polarized light
Slow axis of quarter-wave plate makes at 45° angle with the transmitted axis of polarizer. Δ λ and - Δ λ refer to light falling inside and outside of cholesteric reflection band.

CLC films have been applied to mono-color polarizers for TN and STN displays of the reflection type, which have the additional feature of a uniquely bright background color [4]. A schematic view of the display device is shown in Figure 1. This device consists of a polarizer, TN cell, quarter-wave retardation plate, and right-handed CLC film. The left and right drawings in the figure refer to the field-on and field-off states. In the field-on state, no light reaches the observer from the display, while in the field-off state the observer sees the characteristic reflection color of the CLC. These functions of the CLC film are made possible by the property that circularly polarized light is selectively reflected. However, in spite of the positive reception of the mirror-type CLC film's uniquely bright color and high polarization efficiency, it was pointed out that the direct reflection on the film surface impaired its visibility.

We intended to overcome this drawback by developing a technique which gives a diffusive property without spoiling the optical properties characteristic of CLC films. The use of additional elements such as diffusion film was avoided because that would increase the cost and complicate the manufacturing process.

We noticed that the CLC film has a high diffusion level before the heat annealing (nonaligned state) and turned into the mirror type after the annealing. Our approach was to search for intermediate states that might have both diffusive and CLC characteristics in the course of the alignment process. In this report, we will discuss how the diffusive property and reflection properties of CLC films are affected by the CLC layer structure.

RESULTS AND DISCUSSION

Samples

In this research, we employed a thermotropic liquid crystalline polymer of the main chain type. A thin film was prepared on an alignment substrate by spin-coating a polymer solution and drying it on a hotplate. The alignment of the polymer film was accomplished by heat treatment at a temperature at which the polymer is in liquid crystal phase. After the treatment, the film was cooled down to room temperature to fix the alignment structure for evaluation. In this report, the film surface which had contact with air during the annealing is called the "air surface," while the opposite surface on the substrate is called the "substrate surface."

Diffusive property of D-CLC film

CLC film has a high diffusion level before annealing (nonaligned state) and becomes the mirror type after annealing. This fact inspired us to investigate intermediate states in the heat treatment. We prepared four films of different diffusion levels by controlling the conditions of heat treatment. The thickness of the CLC layer was made the same for all samples, and the diffusion level was controlled by the length of time at elevated temperature.

We defined a new optical parameter called the "diffusion ratio" for making quantitative evaluations of the diffusive reflection properties. To determine the diffusion ratio, the values of Rd (the diffusive reflection rate) and Rt (the total ray reflection rate) were measured based on the d/8 law. A Minolta CM3500d optical color meter was used for the measurement. As shown in equation (1), the diffusion ratio D is determined by Rd/Rt. When the diffusion level of the reflected light increases,

$$D = Rd\ /\ Rt \times 100 \quad (\%) \tag{1}$$

the value of D increases. The measurement results for D of the four samples are shown in Table 1. The order of diffusion level of the reflected light by visual observation was a < b < c < d, which corresponded well to the order of D.

The spatial distribution of the reflected light was determined with an EZ Contrast spatial photometer, wherein the incident light was set to30° inclined from perpendicular to the film surface. The results of the measurement of each sample are shown in Figure 2. It was found that the angle of the reflective direction spreads out when the diffusion ratios increase. CLC film which has a wide reflective angle, such as sample d,

TABLE 1 Diffusion ratio (D) of different diffusion levels

Sample	a	b	c	d
D (%)	8	28	53	77

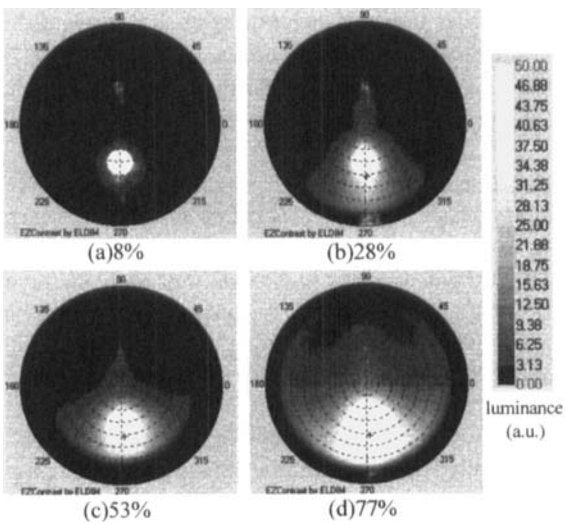


FIGURE 2 The spatial distribution of reflective light
A specular reflective point is (30° , 270°). As indicated color approach white, luminescence is higher, but excluded 10° radius region around the specular reflective point.

is called D-CLC film. These results suggest that the visibility performance of D-CLC film is superior to that of the conventional mirror type in applications to mono-color polarizers.

Relationship of diffusive property to polarization of reflected light

We made a detailed study of the effect of the diffusive state on the polarization of the reflected light because an increase in the diffusive property might impair the high circular dichroism of the CLC. We measured the polarizing coefficient P, which is defined by equation (2):

$$P = (Tl - Tr)/(Tl + Tr) \times 100\ (\%) \qquad (2)$$

where Tl and Tr are the transmittance of left- and right-handed circular polarized light, respectively. The spectrum of transmittance of right-handed circular polarized light (T) and the calculated polarizing coefficient (P) are shown in Figure 3. Although the polarizing coefficient generally depends on the number of twists [4], the influence can almost be

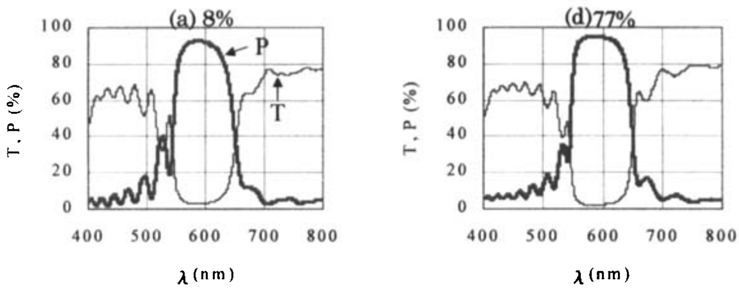


FIGURE 3 Transmittance of right-handed polarized light(T) and polarizing coefficient(P).

ignored because these samples were prepared so that the thickness and the pitch of the twist were almost the same. T in the reflection band hardly changes, indicating that the properties of selective reflection are preserved in the case of D-CLC films. Moreover, P for the light of selective reflection exceeds 90% for both samples, indicating that they are suitable for use as reflective polarizers [5]. From these results it was confirmed that the optical properties characteristic of CLC are preserved in D-CLC film.

Relationship of CLC structure to diffusive property

As mentioned above, it was found that D-CLC has superior visibility without damaging other the distinctive optical characteristics of CLCs. In order to discuss the relationship of the optical properties to the alignment structure of D-CLC, cross-sections of CLCs (samples a to d) were observed with transmission electron microscopy (TEM). With careful observation of the typical TEM images shown in Figure 4, it was found

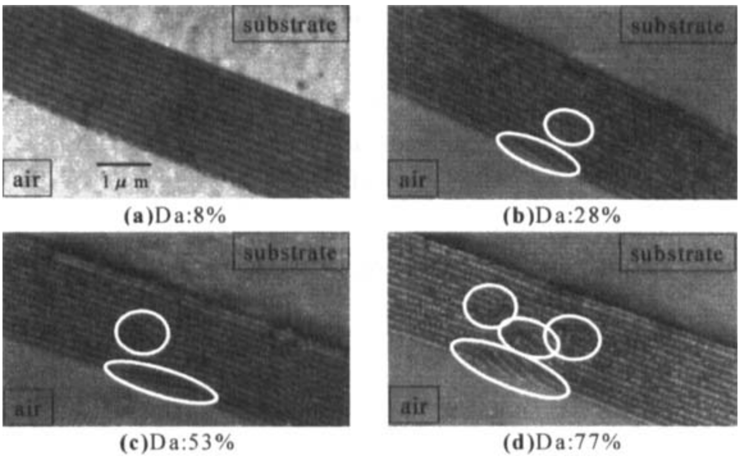


FIGURE 4 Photographs of cross sections of CLC (○: Waving structure)

that there are wave-shaped structures around the disclination. We named the structure as the waving structure. The structure is maldistributed in the air surface side while it was never observed on the substrate surface. It seemed that the existence of the waving structure and disclination affected the diffusive characteristics. From Figure 4, spatial density of the disclinations was evaluated and it was classified into three categories, i.e., inside the layer, on the air surface, and on the substrate surface as shown in Table 2. Here, the disclination density is defined as the number of disclinations per 10 μ m width of the film. The diffusion ratios measured on both surfaces and the polarizing coefficient for the light of selective reflection are also shown in Table 2. The spatial densities inside the layer and on the air surface are proportional to the diffusion ratio. On the other hand, the diffusion ratio on the substrate surface was nearly equal to that of the mirror type. In contrast, the diffusion ratio is related to the spatial

TABLE 2 Diffusion ratio and disclination density

Sample	diffusion ratio (%) air surface	diffusion ratio (%) substrate surface	polarizing coefficient (%)	disclination density[1)] in layer	disclination density[1)] on air surface	disclination density[1)] on substrate surface
a	8	4	93	0	0	0
b	28	8	95	0.9	0	1.0
c	53	13	95	2.3	0	1.7
d	77	16	93	3.8	0	3.9

1) The disclination density is defined as the number of disclinations per 10 μ m width of the film.

density of the waving structure and disclination points, and diffusive characteristics predominate on the air surface.

Considering these results, it seemed that the simple scattering process caused by the disclinations is difficult to be applied to explain these results because of the following reasons;

1. Diffusion ratios on both surfaces are not equal,
2. The disclination points are too small to scatter visible light,
3. Scattering process may not result in such high polarization as 90%.

We inferred that the shape of the waving structure affects the diffusive characteristics. Estimated mechanism is shown in Figure 5.

Generally it is said that the selective reflection of CLC is a kind of the Brag's reflection, so interference along the helical axis causes the selective reflection. In this mean, the helical axis is a propagation axis of light. Thus a direction of reflective light is determined by the direction of the helical axis. In the case of D-CLC, the waving structure maldistributed in the air surface side bends the helical axis so that the helical axes point in various directions in the air surface. The randomness of the directions of the

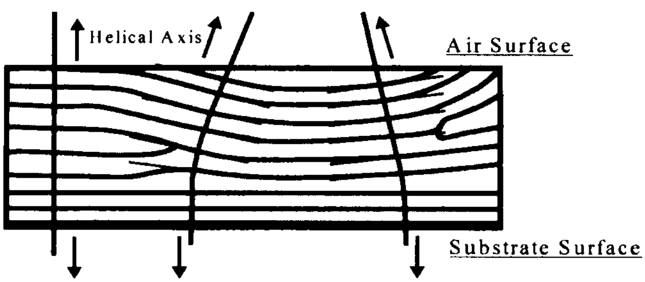


FIGURE 5 The mechanism of diffusive reflection estimated

helical axes is the origin of the diffusive reflection. In the substrate surface, the waving structure doesn't exist and the helical axes are uniformly parallel to the normal axis so that incident light reflects specularly.

Considering that visible light ranges about from 0.4 μm to 0.8 μm in wavelength, the radius of curvature of the bended helical axis is possible to be regarded being gently enough. Visible light can be propagated along the axis without any energy loss. Thus D-CLC can reflect as bright as mirror type.

Relationship of CLC structure to polarization coefficient of reflected light

Here, the relationship between the alignment structure and the polarizing coefficient of the D-CLC is discussed. Every maximum polarization coefficient shown in Figure 3 is above 90%, while the diffusion ratios of samples a to d are widely varied from 8% to 77%. This raises the question of why the polarization coefficient is not affected by the diffusion ratio, that is, the waving structure.

To answer this question, the time courses of the alignment process were examined. In Figure 6, the diffusion ratio and polarization coefficient are shown relative to the annealing time. From Figure 6, it was found that the polarization coefficient is saturated within several dozen seconds while the diffusion ratio shows a gradual decrease over a few minutes. It was also found that the diffusion ratio changes as a convex curve while the polarization coefficient rapidly increases within the first minute. It would be very informative to compare states that have the same diffusion ratio and different polarization coefficients. TEM images of samples at 5 and 75 seconds were taken for this purpose and are shown in Figure 7 together with a sample at 40 seconds, which represents the maximum diffusion ratio. In Table 3 are summarized the diffusion ratio polarization coefficient and the spatial density of the waving structure and disclination points. The layer structure of sample g with higher polarizing coefficient showed an almost mono domain structure. The layer structure of sample e with lower polarizing coefficient was an aggregate with many micro domain CLC structures of about one pitch.

From these observations, it was concluded that the origins of the diffusive properties of samples e and g are different. In the case of sample e, the normal scattering process determines the diffusion ratio, while in the case of sample g the diffusion ratio is determined by the bent helical axes. In sample f, the micro domain CLC in sample e grew into a larger domain with several pitches.

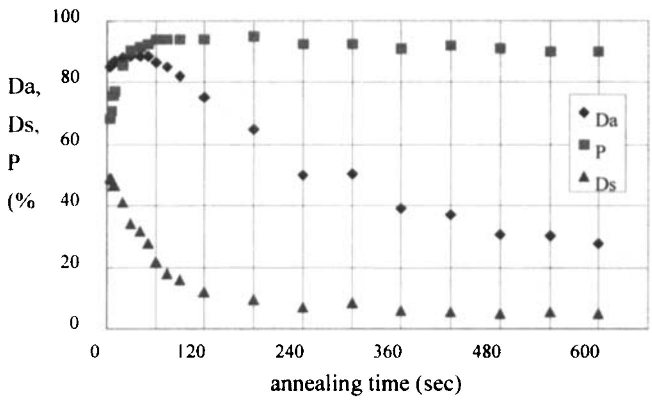
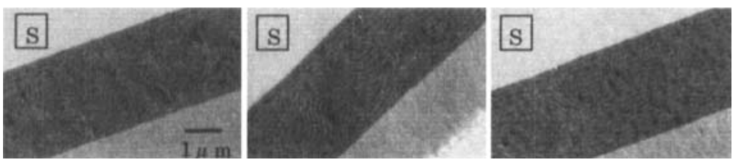


FIGURE 6 Annealing time dependence of diffusion ratio on air surface (Da), substrate surface (Ds) and polarizing coefficiency(P).



(e)5s (f)40s (g)75s

FIGURE 7 Photographs of cross sections of CLC S: sbsurate side

TABLE 3 Diffusion ratio and disclination density

Annealing time (sec)	diffusion ratio (%)		polarizing coefficient (%)	disclination density		
	air surface	Substrate surface		in layer	on air surface	on substrate surface
5 (e)	85	48	75	U.C.*	9.6	0
40 (f)	89	32	92	29.7	10.9	0
75 (g)	85	18	94	11.3	8.9	0

*Uncountable

Consequently, it can be concluded that the polarization coefficient of D-CLC depends on number of pitches in CLC domains, which is observed as stripes in TEM images. This conclusion is also supported by the generally accepted fact that the polarization coefficient of the cholesteric layer improves proportionately as the thickness of the layer increases [4].

On the other hand, as shown in Table 3, the spatial density of the waving structure and disclination points has little effect on the polarization coefficient. The layer structure of CLC is formed more quickly than the dissolving of the waving structure, so D-CLC with a high polarization coefficient is created.

CONCLUSION

The visibility of CLC film was greatly improved in the newly developed D-CLC film, which exhibits diffusive reflection with high circular dichroism.

The layer structure of the D-CLC film was confirmed directly by analyses with TEM. We concluded that the randomness of the waving structure of the CLC layer determines the degree of the diffusive property. It was found that the polarization coefficient depends on number of pitches in CLC domains, which is formed more quickly than the dissolution of the waving structure, so D-CLC with a high polarization coefficient was created.

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