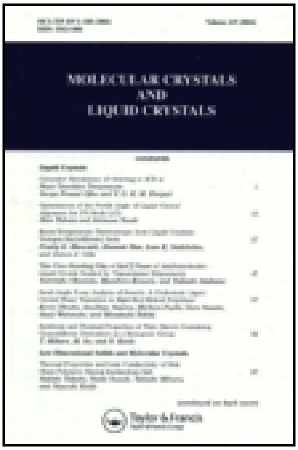

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Correlation Between Order Parameter of Liquid Crystal Mixture and Dichroic Ratio of its Guest-Host System

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CORRELATION BETWEEN ORDER PARAMETER OF LIQUID CRYSTAL MIXTURE AND DICHROIC RATIO OF ITS GUEST-HOST SYSTEM

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Good correlation was found between the order parameter S of liquid crystal (LC) host-mixture and the dichroic ratio of its guest-host system. We investigated temperature dependence of the S value of several LC substances, focusing on its index β. The index β was determined by measuring the temperature dependence of refractive index. LC substances with a cyano terminal group have smaller β values than those with an alkoxy or a fluoro-substituted terminal. This means that the S value is expected to be larger for the cyano substances than the alkoxy or fluoro substances at a fixed reduced-temperature. There exists good correlation between the calculated S value of a host LC mixture and the measured dichroic ratio of its guest-host system. This enables us to design highly ordered LC mixtures for high contrast guest-host LC displays based on β values of LC substances.

Keywords: dichroic ratio; guest-host; liquid crystal; order parameter

1. INTRODUCTION

The application field of liquid crystal displays (LCDs) has been expanding. Currently the demand of LCDs for mobile applications is increasing drastically. In this application field, reduction of power consumption is strongly required for the displays since they operate from batteries. From this point of view, reflective LCDs are very attractive compared with transmissive ones.

Guest-host (G-H) LCDs, in which dichroic dyes and a host LC mixture are used, are promising candidates for a reflective LCD. G-H LCDs have a feature of high brightness, but a disadvantage of poor contrast ratio compared with other LCDs, such as the single polarizer twisted-nematic LCD.

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An increase in the orientational order of dichroic dye molecules is effective to get a higher contrast ratio.

Although the investigation of dichroic dye itself is very active [1,2], host LC mixtures have not been studied so deeply from the point of increasing the orientational order of contained dye molecules. We will discuss the influence of the chemical structure of the LC molecules on the order parameter S in order to design advanced LC materials featuring large S values.

2. MEASUREMENT METHOD OF ORDER PARAMETER OF HOST LC MIXTURE AND ITS TEMPERATURE DEPENDENCE

Several methods have been proposed for the measurement of the order parameter of LC materials. They are classified into microscopic and macroscopic methods and are listed in Table 1 [3].

In LCDs, the orientation of LC molecules is controlled by an applied voltage for adjustment of the intensity of transmissive or reflective light. Macroscopic properties, optical and dielectric ones, of LC materials are related to the contrast ratio of LCDs. Comparing to these two properties, measuring value of optical anisotropy is about 10 times more precise than that of dielectric anisotropy. Therefore optical anisotropy measurement method is considered to be most suitable for investigation the relationship between the S value and the contrast ratio of LCD.

The following equation was proposed for the temperature dependence of refractive index of LC material [4],

$$\frac{n_e^2 - n_o^2}{\bar{n}^2 - 1} = \frac{\Delta\alpha}{\alpha} S(T) \left(\bar{n}^2 = \frac{n_e^2 + 2n_o^2}{3} \right)$$

with n_e: refractive index corresponding to extraordinary ray

n_o: refractive index corresponding to ordinary ray

α: electronic polarizability of LC molecule

$\Delta\alpha$: anisotropy of electronic polarizability

T: temperature.

TABLE I Measurement Method of Order Parameter

Microscopic method	Macroscopic method
NMR	Optical anisotropy
IR spectroscopy	Dielectric anisotropy
Raman spectroscopy	Diamagnetic anisotropy
X-ray spectroscopy	

Furthermore, the following simple relation was proposed between the temperature dependence of S and nematic-isotropic phase-change temperature, T_{NI} [5],

$$S(T) = \left(1 - \frac{T}{T_{NI}}\right)^{\beta}$$

By combining the above two equations, β value can be obtained by measuring the temperature dependence of refractive index of LC material. In other words, the temperature dependence of S is determined by β and T_{NI}. Calculation results are shown in Figure 1. As shown in Figure 1, β of LC1 is smaller than LC2, although both LC1 and LC2 have the same T_{NI}, 100°C. Comparing the order parameter at 20°C, LC1 has a larger value than LC2. Regarding LC1 and LC3, they have the same β value, 0.16, but T_{NI} value of LC1 is larger by 30°C than that of LC3. LC1 shows a larger S value than LC3 because of its higher T_{NI}. From these results, it is clear that small β and high T_{NI} are effective for a high order parameter of LC host mixture.

3. EXPERIMENTAL RESULTS AND DISCUSSION

In order to design LC mixtures with small β values, it is necessary to know the β values of the single LC substances. For this purpose, we have investigated chemical-structure dependence of β by focusing on the influence of

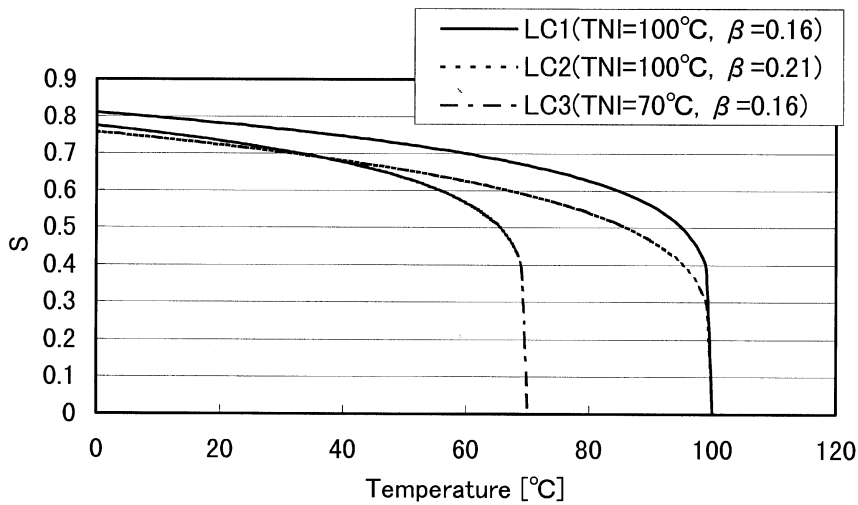
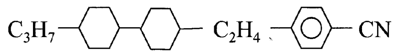
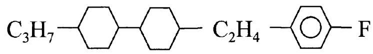
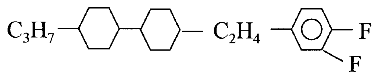
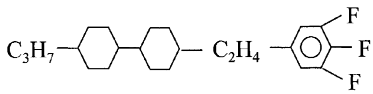
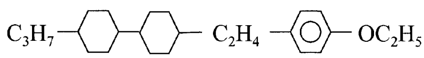


FIGURE 1 Temperature dependence of order parameter S.

TABLE II Chemical Structure of Experimental Materials

Acronym	Chemical structure
ECCP-3N	
ECCP-3F	
ECCP-3F.F	
ECCP-3F.F.F	
ECCP-3O2	

the terminal group of the LC substance. Materials studied are listed in Table II. Their core structures are fixed at (2-(4-cyclohexylcyclohexyl) ethyl)benzene. Their alkyl chain length is also fixed at propane, and the opposite terminal is either cyano, fluoro (mono, di and tri) or ethoxy. Samples for characterization by their β value are prepared by mixing each LC single substance into a standard LC mixture, ZLI-3086, in concentration of 15 mol%. Physical properties of ZLI-3086 are given in Table III, and as can be seen its dielectric anisotropy is nearly 0. The temperature dependence of the refractive index was measured at 589 nm, providing calculation of β values using the above formula and refractive indexes measured at fixed five reduced temperatures.

The β values obtained from the samples are shown in Figure 2. The cyano-substituted material, ECCP-3N, has the smallest value among the LC substances. It is also shown that fluoro-substituted LC substances exhibit a reciprocal relation between the β value and the number of fluorine atoms. Moreover, the LC material having an ethoxy group (ECCP-302) has a similar β value to the trifluoro-substituted substance (ECCP-3F).

TABLE III Physical Properties of Nematic LC Mixture, ZLI-3086

T_{NI}[°C]	72.0
Optical anisotropy (589 nm, 20°C)	0.1131
Dielectric anisotropy (1 kHz, 20°C)	0.1

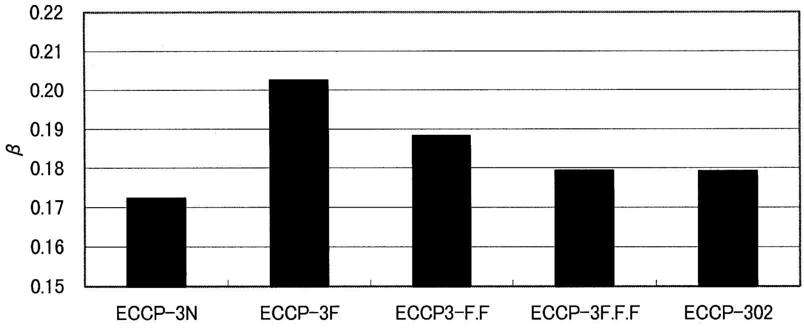


FIGURE 2 β values of LC substances (15 mol% in ZLI-3086).

As a result, the effectiveness of terminal group to reduce the β value of LC substances was obtained as follows:

(larger effect) cyano > ethoxy ≅ trifluoro > difluoro > monofluoro (smaller effect).

Regarding the contrast ratio of a display using guest-host system, high values are expected for systems composed of small-β LC substances.

G-H systems were prepared by adding 1 wt% of BDH-D35 (an anthraquinone dichroic dye) to the above samples. The dichroic ratio was measured at room temperature by using a homogeneously aligned cell with a gap of about 9 μm. Transmittance of linearly polarized light either parallel or perpendicular to the direction of rubbing of the cell was measured. The dichroic ratio D is defined as follows:

$$D = \frac{T_{\parallel} - T_{\perp}}{2T_{\perp} + T_{\parallel}},$$

where $T_{\parallel}$: transmittance of polarized light, parallel to the rubbing direction (at 550 nm)

$T_{\perp}$: transmittance of polarized light, perpendicular to the rubbing direction (at 550 nm).

The relation between measured D and S, which was calculated with β and T_{NI} values of a host LC material by using the mentioned equation, is shown in Figure 3. Good correlation between S (at 20°C) and D (at room temperature) has been found except for one material, ECCP-302. It is not easy to understand the exceptional case of ECCP-302 only from these experiments, but we believe that the alkoxyl chains disturb the orientation of BDH-D35 molecules and the dichroic ratio is decreased.

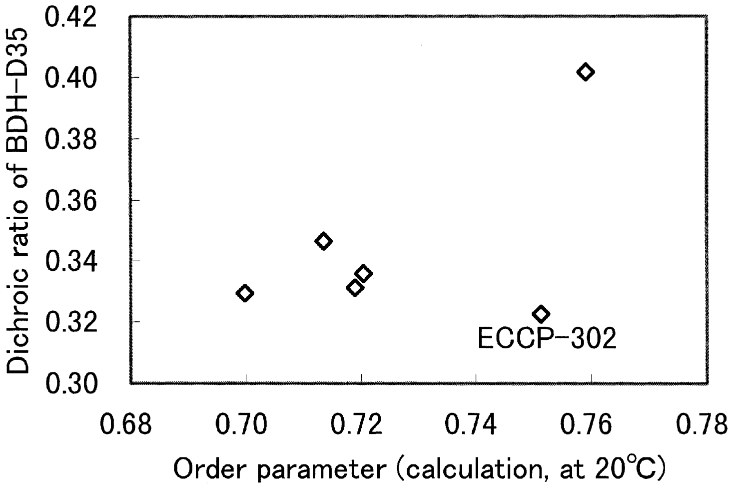


FIGURE 3 Relation between order parameter of LC host and dichroic ratio of dye.

As the next step, investigations were expanded to a simple LC mixture composed of only two substances in order to apply the obtained results to design LC host mixtures for a G-H system featuring a high contrast ratio.

ECCP-3N and ECCP-3F, which have quite different S values as shown in Figure 2, were selected as the components of a binary system for another set of experiments. The host LC mixture was prepared by mixing both LC substances into ZLI-3086 at an equal concentration (7.5 mol%). Its S value was calculated by measuring the temperature dependence of refractive index. Then its dichroic ratio was measured by the same method mentioned above after adding 1 wt% of BDH-D35. The results are shown in Figure 4. The *D* value was almost the average between ECCP-3N and ECCP-3F. On the other hand, the S value is slightly larger than the average of those of the two components. Judging from the level of correlation between S and *D* in Figure 3, however, it can be said that there seems to exist an additive property between the binary system and the two components, ECCP-3N and ECCP-3F. This idea can be applied not only to simple LC mixtures composed of two components but also to actual LC mixtures containing many more components. In other words, the S value of practical LC mixtures can also be estimated by the values of β and T_{NI} of the LC substances used. Furthermore, highly ordered LC mixtures can be designed to improve the contrast of G-H displays based on the data of β and T_{NI} of the LC components.

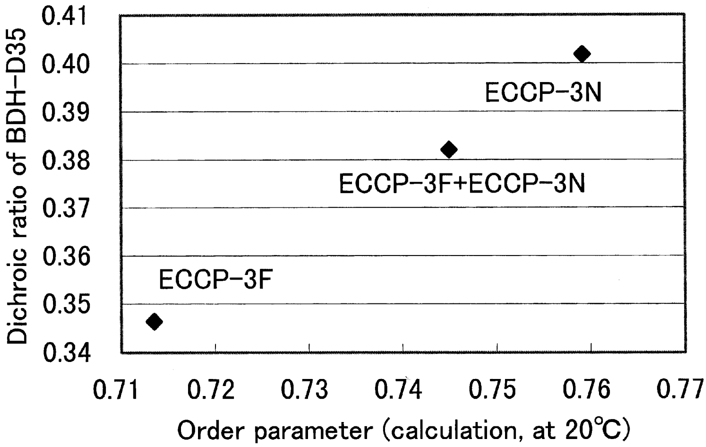


FIGURE 4 Relation between order parameter of host LC mixture and dichroic ratio.

4. CONCLUSION

The temperature dependence of order parameter S of a LC mixture is characterized by its index β and the nematic-isotropic phase temperature T_{NI}. The β value can be determined by the measurement of the temperature dependence of refractive index. Small β and large T_{NI} values are required to increase the order parameter according to the equation proposed in Ref. 5. We investigated the chemical-structure dependence of the β value by focusing on the influence of the terminal group of the LC substance. The effectiveness of a terminal group to reduce the β value was obtained experimentally as follows:

(larger effect) cyano > ethoxy $\cong$ trifluoro > difluoro > monofluoro (smaller effect).

The dichroic ratio *D* of a guest-host system was measured for several LC substances. Good correlation was found between S, which was calculated by the β value, and *D*. Two LC substances were selected to confirm the above relation with the binary system. An additive relationship was found between the two LC substances and the binary system not only for the S value of a LC mixture but also for the *D* value of its G-H system. This means that the S value of a LC mixture can be estimated by the values of β and T_{NI} of the LC components. Furthermore, highly ordered LC mixtures can be designed to improve the contrast of G-H displays based on those data of the LC components.

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