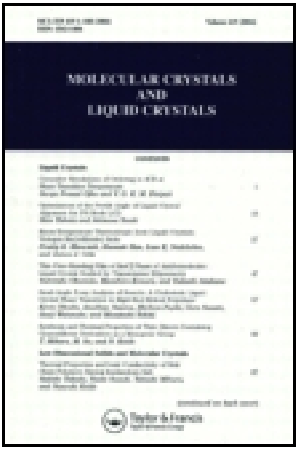

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Helical Sense and Pitch of Cholesteric Liquid Crystals

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Helical Sense and Pitch of Cholesteric Liquid Crystals

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The rotatory sense of a circularly polarized light transmitted through a cholesteric liquid crystal cell was studied by measuring the retardation of a birefringent plate placed upon the cell. Furthermore, the dependence of helical pitch on composition is described for various binary cholesteric and nematic–cholesteric mixtures. The helical sense of eleven cholesterics was determined by the experimental results. As a result, it is shown, for example, that cholesteryl chloride has a right-handed helical structure and cholesteryl propionate has a left-handed helical structure.

1 INTRODUCTION

Cholesteric liquid crystals† have a twisted structure, which is characterized by a helical pitch and a helical sense (right-handed or left-handed). The helical pitch can be varied by mixing cholesteric compounds,[1,2] or by adding nematic compound to a cholesteric compound.[3–5] Such cholesteric mixtures or pure cholesteric compounds have been known to selectively reflect one sense of circularly polarized component of incident light at a narrow wavelength band which matches the helical pitch of the compounds.[6] For normal incidence to the helical axis, the central wavelength (λ_0) of the selective reflection band is expressed by product of a mean refractive index (n) and a helical pitch (p), that is, $\lambda_0 = np$.

It has been well known that the dependence of $1/\lambda_0$ on composition in binary cholesteric mixtures follows a linear additive law,[3,7] as shown in

† The term "cholesteric liquid crystal" (or cholesteric compound) in this paper indicates derivatives of the cholesterol such as cholesteryl ester. We consider that chiral nematic compound is not included in this class, since the molecular structure and the properties of the mixtures are different from those of the derivatives of cholesterol.

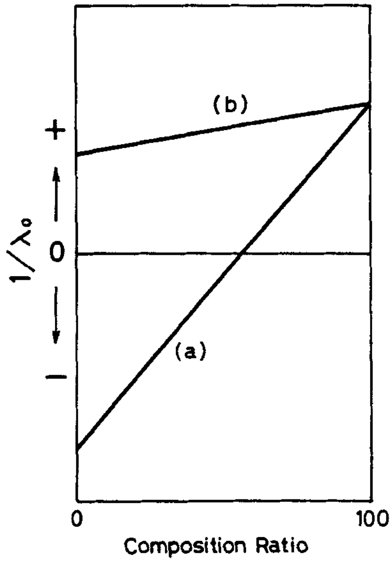


FIGURE 1 Schematic examples of composition dependence of $1/\lambda_0$ in binary cholesteric mixtures.

Figure 1. In this figure, the helical sense of cholesterics in the positive $1/\lambda_0$ region is opposite to that of cholesterics in the negative $1/\lambda_0$ region. As shown in Figure 1, the $1/\lambda_0$ vs. composition curve crosses a line of $1/\lambda_0 = 0$ in case of the binary mixtures of cholesterics having opposite helical sense each other (line (a) in Figure 1), while the curve does not cross the line in the case where the binary mixtures of cholesterics have the same helical sense with each other (line (b) in Figure 1). Furthermore, for nematic-cholesteric mixtures, various dependences of $1/\lambda_0$ on composition have been reported[8] as shown in Figure 2.

However, there is an ambiguous point for the helical sense, because two contradictory views have been reported on the helical sense of a cholesteric compound. For example, some workers have reported that cholesteryl chloride (CC) has a left-handed helical structure,[2,4,9] while others have reported that the compound has a right-handed structure.[8,10,11] We consider that the confusion has been caused mainly by some uncertain definitions of the circularly polarized light.

In this paper, therefore, the helical sense of cholesteric liquid crystals is re-examined in detail. First, the dependence of $1/\lambda_0$ on composition in various binary cholesteric mixtures and nematic-cholesteric mixtures are described by assuming that $1/\lambda_0$ of pure CC is positive. From these results, the sign of the $1/\lambda_0$ is determined for the mixtures and the pure cholesteric

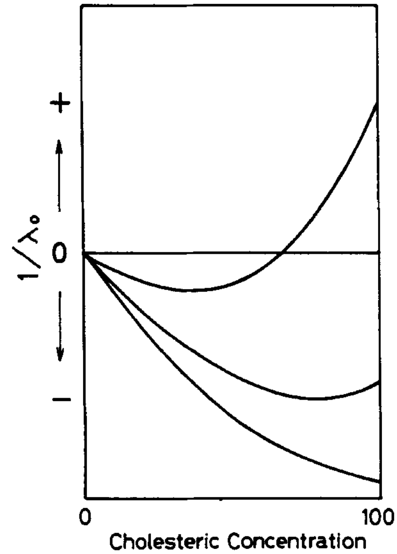


FIGURE 2 Schematic examples of composition dependence of $1/\lambda_0$ in nematic–cholesteric mixtures.

compounds. Next, the rotatory sense of transmitted circularly polarized light is measured for some mixed compounds with positive or negative $1/\lambda_0$, and then the relationship between the helical sense and the sign of $1/\lambda_0$ is clarified. Furthermore, the helical sense of many cholesteric compounds is determined from the results.

Concerning the relation between the characteristics of the selective reflection and the helical sense, Priestley's theory[12] in which the definition for circularly polarized light is given expressly is referred to.

2 EXPERIMENTS

The liquid crystals used in our experiments are shown in Table I. All nematic components and cholesteryl mercaptan (CMe) were synthesized in our laboratory. Other cholesteric compounds were commercially available, some of which were purified further by recrystallization from appropriate solvents, for the isotropic temperatures of these commercial materials were much lower than values given in the literature.[13]

The mixtures of these liquid crystals were sandwiched between two glass plates separated by a Mylar spacer, and the cell was placed in a sample holder, temperature of which could be controlled. The wavelength of selective reflection was determined by measuring the transmission or reflection

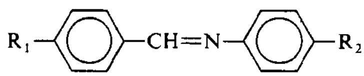
TABLE I

Liquid crystal substance used in the experiments
(a) Cholesteric liquid crystals

$C_{27}H_{45}$—R

R	Name	Abbreviation
OCOH	Cholesteryl formate	C F
$OCOCH_3$	Cholesteryl acetate	C A
$OCOC_2H_5$	Cholesteryl propionate	C P
$OCOC_4H_9$	Cholesteryl valerate	C V
$OCOC_6H_{13}$	Cholesteryl heptanoate	C H
$OCOC_8H_{17}$	Cholesteryl nonanoate	C N
$OCOC_{11}H_{23}$	Cholesteryl laurate	C L
$OCOC_{13}H_{27}$	Cholesteryl myristate	C My
Cl	Cholesteryl chloride	C C
Br	Cholesteryl bromide	C B
SH	Cholesteryl mercaptan	C Me

(b) Nematic liquid crystals



R_1	R_2	Name	Abbreviation
C_2H_5O	C_4H_9	*p*-ethoxybenzylidene-*p*'-*n*-butylaniline	EBBA
C_3H_7O	C_4H_9	*p*-*n*-propoxybenzylidene-*p*'-*n*-butylaniline	PBBA
$C_6H_{13}O$	C≡N	*p*-*n*-hexyloxybenzylidene-*p*'-aminobenzonitrile	HBAB

spectra.[3] The rotatory sense of circularly polarized light was determined by using a polarizing microscope and a Berek compensator. A detailed explanation of this method will be given later.

3 EXPERIMENTAL RESULTS

3.1 Dependence of selective reflection wavelength on composition for cholesteric mixtures

Figures 3 to 5 show the dependence of $1/\lambda_0$ on composition in various binary cholesteric mixtures. Figures 3 and 4 were plotted by assuming that the sign of $1/\lambda_0$ for CC is positive. Since the $1/\lambda_0$ vs. composition curves cross a line of $1/\lambda_0 = 0$ in all mixtures as shown in Figures 3 and 4, CC and the other component in each mixture have the opposite helical sense with each

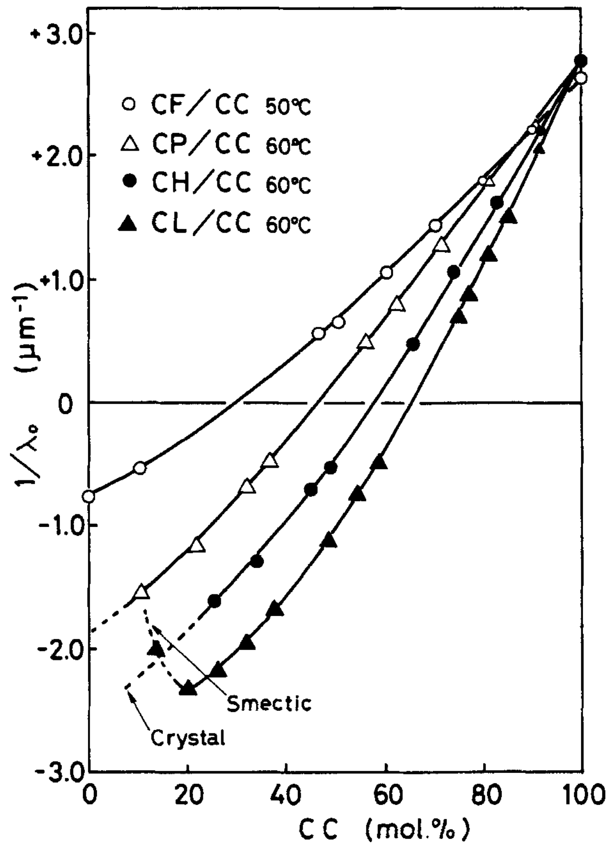


FIGURE 3 Composition dependence of $1/\lambda_0$ in binary cholesteric mixtures (I).

other. Figure 5 was plotted after determining the sign of $1/\lambda_0$ for CN from Figure 4. From the results shown in Figures 3 to 5, CB and CMe are concluded to have the same sense as CC, and other cholesteric compounds are concluded to have the sense opposite to CC. Figure 6 shows the dependence of $1/\lambda_0$ on composition in various nematic-cholesteric mixtures. The sign of $1/\lambda_0$ for these mixtures was determined on the basis of the definition of cholesteric compounds.

From the results mentioned above, cholesteric compounds are classified into two groups based on the sign of $1/\lambda_0$. The results are shown in Table II (A-group: $1/\lambda_0 > 0$, B-group: $1/\lambda_0 < 0$). This table also shows the sign in nematic–cholesteric mixtures.

In the next section, the correlation of the sign with the helical sense is clarified by measuring the transmitted circularly polarized light for some mixed compounds.

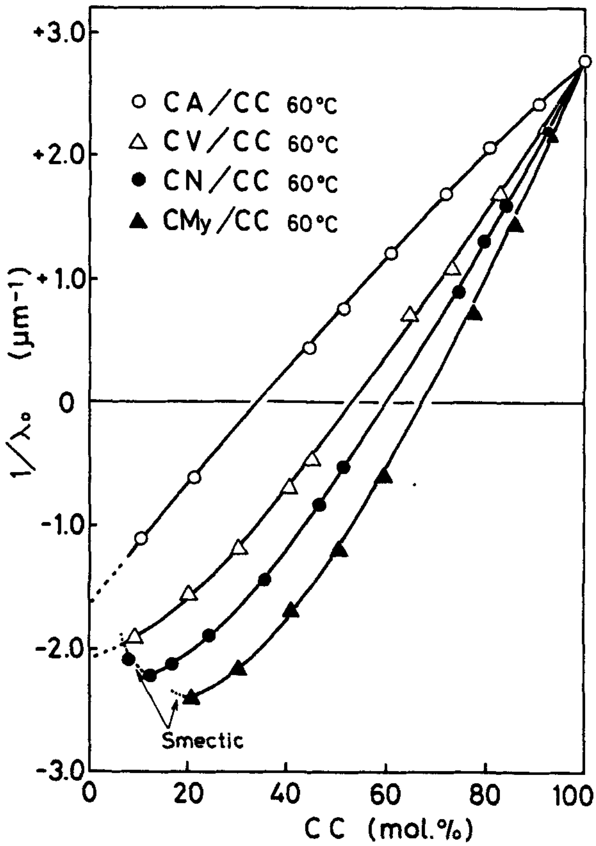


FIGURE 4 Composition dependence of $1/\lambda_0$ in binary cholesteric mixtures (II).

3.2 Determination of the helical sense

3.2.1 Experimental methods The rotatory sense of the circularly polarized light reflected by the selective reflection depends on the helical sense of cholesterics. The relation between the characteristics of selective reflection and the helical structure has been theoretically investigated by de Vries,[6] Chandrasekhar *et al.*[14] and by Priestley.[12] According to their studies, for example, a right-handed cholesteric liquid crystal selectively reflects the light wave of which the instantaneous spatial electric field pattern matches exactly with the cholesteric helix. Here, considering the temporal variation of the light wave which has the spatial right-handed electric field pattern, the electric vector of the light wave rotates clockwise at some fixed position, when viewed toward the light source.[12] Such a wave is commonly called a

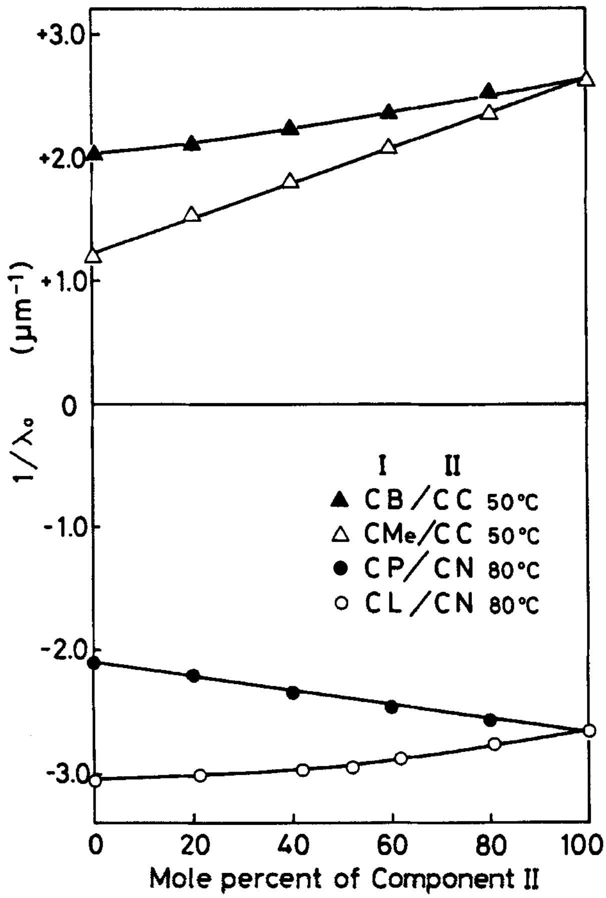


FIGURE 5 Composition dependence of $1/\lambda_0$ in binary cholesteric mixtures (III).

right circularly polarized light. Therefore, a right-handed (left-handed) cholesteric liquid crystal reflects a right (left) circularly polarized light, and transmits a left (right) circularly polarized light at the selective reflection band. In this section, the helical sense of cholesterics is determined from a comparison with the observation of the transmitted circularly polarized light and the principle mentioned above. An observation was made with the experimental arrangement shown in Figure 7.[15] The plate C is a Berek compensator. The plate is made of a crystal plate of Iceland spar and can be rotated around the X-axis. Since the refractive anisotropy for the normal incident light varies in accordance with the rotation angle, the plate can be used to a birefringent plate having desirable retardation. The X-component of the electric vectors of incident light is an ordinary ray component,

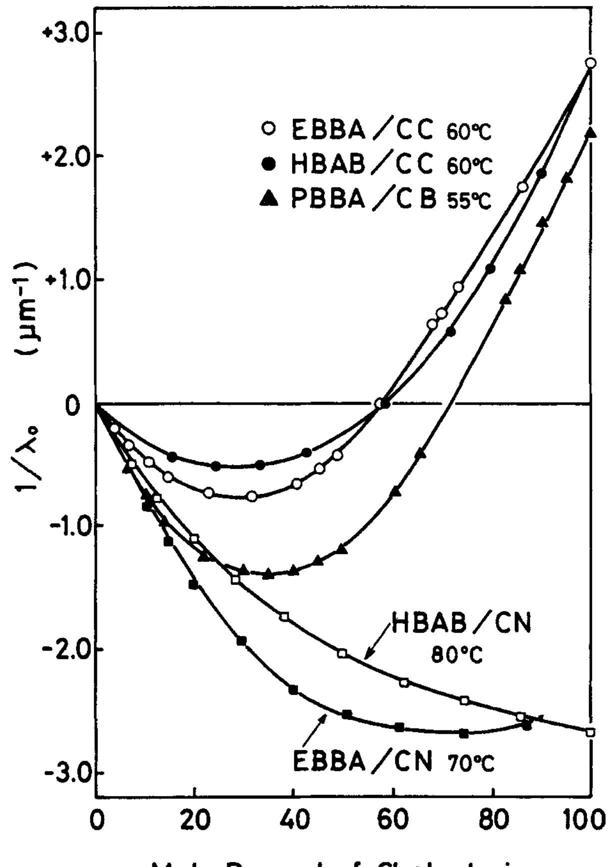


FIGURE 6 Examples of composition dependence of $1/\lambda_0$ in nematic–cholesteric mixtures.

and their Y-component is an extraordinary ray component in the compensator. The linear polarizer P is set parallel to the X-Y plane with its axis at 45° to the X-axis. When the light passes through the experimental arrangement, the polarized state of the transmitted light depends on the rotatory sense of the circularly polarized light passing through the liquid crystal cell as follows:

a) In the case where the right circularly polarized light is transmitted through the cell and is incident to the compensator.

Decomposing the electric vectors of the incident right circularly polarized light into an ordinary ray component (X-component in Figure 8) and an extraordinary ray component (Y-component in Figure 8), the two

TABLE II

Classification of cholesteric compounds based upon the helical sense. The helical sense of compounds in A group is different from that of compounds in B group.

A $(1/\lambda_0 > 0)$	B $(1/\lambda_0 < 0)$
Ch. chloride	Ch. formate
Ch. bromide	Ch. acetate
	Ch. propionate
Ch. mercaptan	Ch. valerate
	Ch. heptanoate
	Ch. nonanoate
	Ch. laurate
	Ch. myristate
EBBA/CC	EBBA/CC
(CC > 60 mol %)	(0 < CC < 60 mol %)
PBBA/CB	PBBA/CB
(CB > 70 mol %)	(0 < CB < 70 mol %)
	EBBA/CN
	(0 < CN ≦ 100 mol %)

components can be written respectively as follows:

$$E_x = A \cos \omega t, \qquad E_y = -A \sin \omega t. \tag{1}$$

Since a crystal of Iceland spar is an optically negative uniaxial crystal, the extraordinary ray passes through faster than the ordinary ray and there is a gradual separation in the phases of the two components. Hence, after the

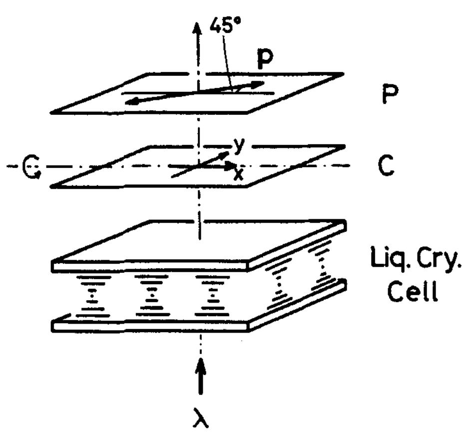


FIGURE 7 Schematic representation of the experimental arrangement of apparatus for the measurement of retardation.

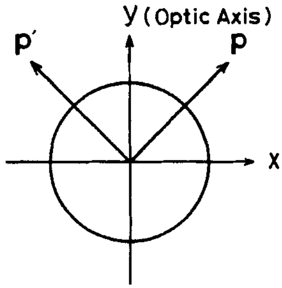


FIGURE 8 Co-ordinate system used in our discussions.

light has passed through the compensator, the two components can be written as follows:

$$E_x = A\cos(\omega t - \phi_0), \qquad (2)$$
$$E_y = -A\sin(\omega t - \phi_e) = -A\sin(\omega t - \phi_0 + \Delta\phi),$$

where $\Delta\phi = \phi_0 - \phi_e$ is the phase difference between the two components. In particular, when the phase difference is $\Delta\phi = 2n\pi + \pi/2 (n = 0, 1, 2, \ldots)$, the relation $E_x = -E_y$ is given, and the incident right circularly polarized light is transformed into the linearly polarized light with electric vector parallel to P' direction. Therefore, when the intensity of the transmitted ligh through a polarizer with its axis at P direction is observed, the light is completely extinguished. The retardation in the compensator R is described by the phase difference $\Delta\phi$ as follows:

$$R = \lambda/2\pi \cdot \Delta\phi, \qquad (3)$$

and the retardation in this condition is given as follows:

$$R = (n + 1/4)\lambda, \qquad (4)$$

where λ is the wavelength of the incident light.

b) In the case where the left circularly polarized light is transmitted through the cell and is incident to the compensator.

The electric vectors of the incident left circularly polarized light can be decomposed as follows:

$$E_x = A\cos\omega t, \qquad E_y = A\sin\omega t. \qquad (5)$$

Hence, from a discussion similar to that in a) mentioned above, after the light has passed through the compensator, the two components of the light is given respectively as follows:

$$E_x = A\cos(\omega t - \phi_0), \qquad E_y = A\sin(\omega t - \phi_0 + \Delta\phi). \qquad (6)$$

Since the relation $E_x = -E_y$ is given when $\Delta\phi = 2n\pi + 3\pi/2$ ($n = 0, 1, 2, \ldots$), the incident left circularly polarized light is transformed into the linearly polarized light with electric vector parallel to P' direction, and the transmitted light is completely extinguished. The retardation in this condition is given as follows:

$$R = (n + \tfrac{3}{4})\lambda. \tag{7}$$

As mentioned above, the retardation at the extinguished state is different in a) from b), hence the rotatory sense of the circularly polarized light transmitted through the cholesteric compound can be determined by measuring retardation. This method for determining the helical sense of cholesterics is characterized by a simple experimental arrangement with a polarizing microscope and a birefringent plate (a compensator).

3.2.2 Experimental results and discussion In the observation of the transmitted circularly polarized light, five mixed compounds shown in Figure 9 were selected from the mixtures shown in Figures 3 to 6. Table III shows the compounds, measuring temperature, the selective reflection wavelength band at the measuring temperature and the wavelength (λ_m) of the light source used for experiments, where the λ_m is adequately chosen within the value of the selective reflection wavelength band. These samples were selected by considering the following conditions necessary to the experiments: λ_0 is in the visible wavelength region and the variation of λ_0 with temperature is rather small. Since most of pure cholesteric compounds are monotropic and λ_0 of these compounds is in the ultraviolet wavelength region, pure cholesterics are difficult to use for such an optical observation in the visible region.

Figures 10 and 11 show the retardation in the extinguished state for each sample. Two solid lines in these figures show the curves calculated from

TABLE III

The composition and λ_0 of samples used and experimental conditions: Tm; measuring temperature, $(\lambda_0 - \Delta\lambda) \sim (\lambda_0 + \Delta\lambda)$; selective reflection wavelength band, λ_m; wavelength of the light source used for experiments.

No.	Compounds	Tm (°C)	$(\lambda_0 - \Delta\lambda) \sim (\lambda_0 + \Delta\lambda)$ (nm)	λ_m (nm)
S_1	$CP_{90}CC_{10}$	78	590 ~ 600	595
		73	605 ~ 617	611
S_2	$CP_{20}CC_{80}$	60	547 ~ 555	552
		50	589 ~ 601	595
S_3	$EBBA_{70}CN_{30}$	60	505 ~ 543	522
S_4	$PBBA_{65}CB_{35}$	57.5	698 ~ 742	720
S_5	$PBBA_5CB_{95}$	45	602 ~ 618	611
		55	544 ~ 552	552

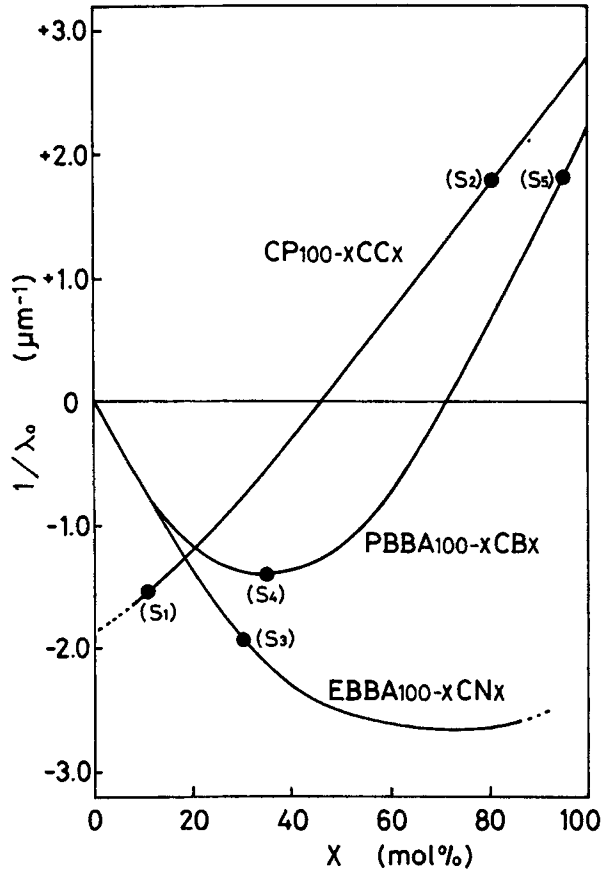


FIGURE 9 Samples used for the observation of transmitted circularly polarized light; S_1, S_2, S_3, S_4, and S_5.

$(n + \frac{1}{4})\lambda$ or $(n + \frac{3}{4})\lambda$. By comparing the measured value shown by black circles with the two lines, it is seen that the retardation in the extinguished state is $(n + \frac{1}{4})\lambda$ for S_1, S_3 and S_4 samples and is $(n + \frac{3}{4})\lambda$ for S_2 and S_5 samples. Therefore, the former samples are found to have the left-handed helical structure because the right circularly polarized light is transmitted through these samples, while the latter samples are found to have the right-handed helical structure because the left circularly polarized light is transmitted through these samples. Furthermore, concerning the sign of $1/\lambda_0$, the positive sign indicates the right-handed and the negative sign indicates the left-handed as shown in Figure 9. By comparing with the results obtained in Section 3.1, it is concluded that the cholesteric compounds in A-group

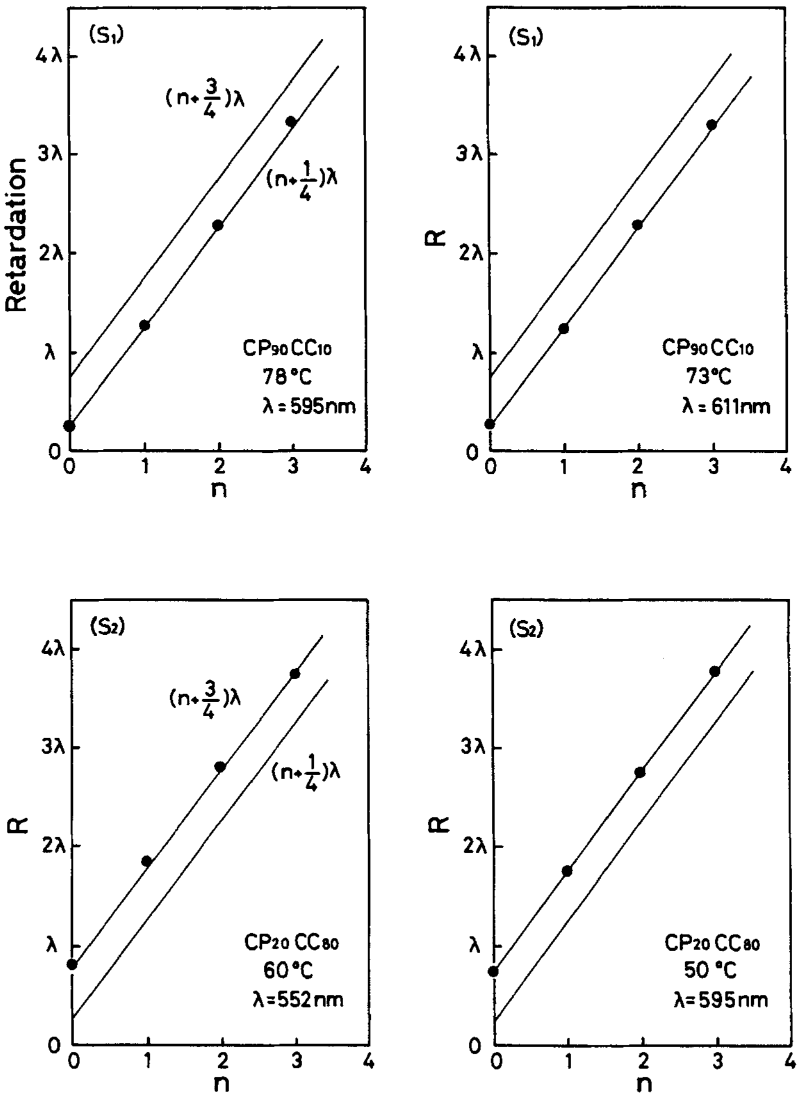


FIGURE 10 Retardation in the compensator when the intensity of light transmitted through polarizer is extinguished for samples S_1 and S_2. Solid lines show the curves calculated from $(n + \frac{1}{4})\lambda$ or $(n + \frac{3}{4})\lambda$ respectively.

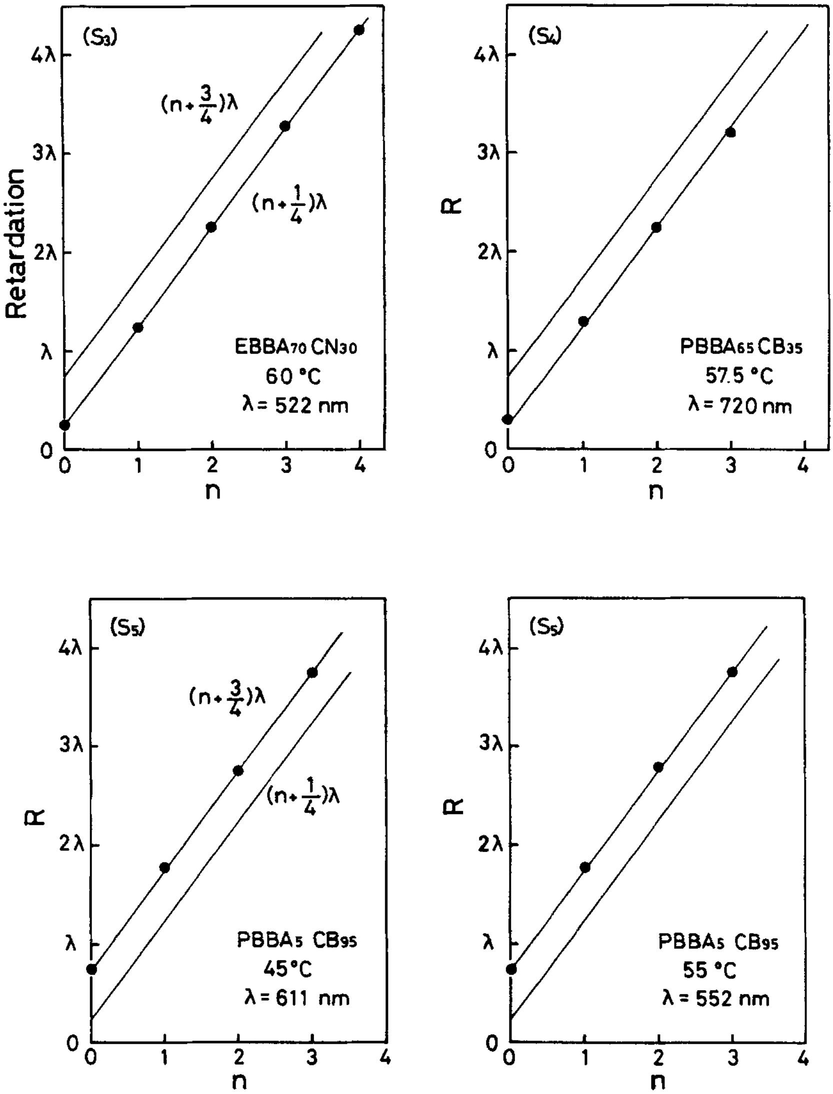


FIGURE 11 Retardation in the compensator when the intensity of light transmitted through polarizer is extinguished for samples S_3, S_4 and S_5.

have the right-handed helical structure and the cholesterics in B-group have the left-handed helical structure.

In addition to cholesteric compounds discussed in this paper, it can be seen that cholesteryl iodide, cholesteryl oleate and cholesteryl oleyl carbonate have the left-handed helical structure, while cholesteryl fluoride and cholesteryl 2-(2-ethoxyethoxy) ethyl carbonate have the right-handed helical structure by others' reports[2,15] and classification method similar to that in Section 3.1.

4 SUMMARY

The helical sense of cholesteric compounds was studied by observing the circularly polarized light under a microscope. By comparing the results with the composition dependence of the wavelength of selective reflection, we determined the helical sense of eleven cholesteric compounds. From the results obtained, it can be seen that cholesteryl halide compounds (for example, cholesteryl chloride) have the right-handed helical structure and cholesteryl fatty ester compounds (for example, cholesteryl propionate) have the left-handed helical structure.

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