Induced Circular Dichroism from Cholesteric Polypeptide Films Doped with an Azobenzene Derivative

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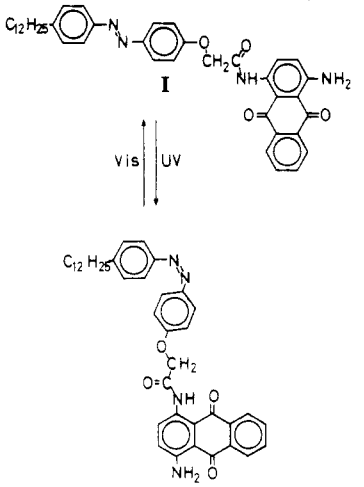
ABSTRACT: Induced circular dichroism (ICD) from thermotropic cholesteric films of poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamate) doped with an azobenzene derivative was studied. Optimum conditions for the ICD intensity were explored by varying the cholesteric pitch of the film and the content of the dodecyl groups x. The cholesteric pitch was varied by changing the annealing temperature of the film. The strongest ICD was observed when the polymer with $x = 0.63$ was annealed at 180 °C (cholesteric pitch = 6.7 μm). The ICD intensity vs inverse pitch plot was compared with theoretical curves calculated on the basis of Chandrasekhar's theory. The best fit was obtained when the birefringence Δn and the linear dichroism Δk were set to be 0.1 and (1.2–1.5) × 10^{-6}/nm, respectively.

One of the important characteristics of liquid-crystalline (LC) polymers is optical anisotropy. Induced circular dichroism (ICD) and optical rotation of cholesteric LC's have been used to characterize the mesophase.[1-12] Applications of ICD of cholesteric LC's to circular optical devices, optical filters,[13] and so on, have been proposed.[14,15] In previous reports, we have proposed a photorecording system that utilizes the ICD of dyes in polymer gels possessing a cholesteric LC order.[16,17] The system consisted of a polypeptide gel that is cross-linked under cholesteric conditions and a photochromic dichroic dye (I) that is doped in the LC gel. The photochromic dye undergoes a local orientational change of the dichroic dye unit (anthraquinonyl group) induced by the trans/cis photoisomerization of the azobenzene unit (Scheme I).[17]

Since the intensity and even the sign of ICD are sensitive to the orientation of doped dyes, the photocontrol of the orientation of the anthraquinone dye may change the ICD significantly. The dye-doped cholesteric gel is a potential system for a chiroptical photorecording, because the photochromic state can be detected by the ICD at the wavelength of the anthraquinone dye that is longer than the azobenzene absorption band; i.e., the photochromic state may be read out many times without affecting the original photochromic state. However, for the chiroptical system to be practically usable, the LC gel is too weak and too flexible. As a tough cholesteric system, thermotropic cholesteric polymers doped with the photochromic dye will be more promising. An additional advantage of the thermotropic polymers is that their cholesteric structure (cholesteric pitch) may be varied by changing the annealing temperature, and once an optimum structure is found, the structure may be stored for a long time at lower temperatures than the glass temperature.

Thermotropic cholesteric mesophases of polyglutamates carrying long alkyl chains have been developed.[18-22] The polypeptide LC films show uniform Grandjean textures (the cholesteric axis being perpendicular to the film surface) that exhibit a bright reflective color when the optical pitch is within the visible region. Furthermore, the pitch can be controlled by annealing the film at appropriate temperatures and can be immobilized by quenching the film rapidly below its glass temperature. Therefore, the thermotropic polypeptide LC film may be the best cholesteric media for producing and keeping strong ICD.

Scheme I



In this report, we describe attempts to optimize the LC structure to induce maximum ICD from thermotropic cholesteric LC films of poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamate) doped with the photochromic dichroic dye I.

Experimental Section

Materials. Synthesis of Poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamate). γ-Benzyl L-glutamate *N*-carboxyanhydride (NCA) (6.58 g, 2.5 × 10^{-2} mol) was polymerized with a $^1/_{250}$ equiv of *n*-hexylamine in dimethylformamide (70 mL). After 3 days the polymer solution was poured into ether to obtain poly(γ-benzyl L-glutamate) (PBLG). The crude polypeptide was redissolved in chloroform and precipitated with ether. The purified polymer was washed with ether and dried under vacuum (4.22 g, 77%). The molecular weight evaluated from viscosity measurement in dichloroacetic acid was 53 000 (degree of polymerization = 240). PBLG (3.5 g, 1.6 × 10^{-2} mol of monomer units) and dodecyl alcohol (89.3 g, 4.8 × 10^{-1} mol) were dissolved in dichloroethane (175 mL), and *p*-toluenesulfonic acid (5.25 g, 3.05 × 10^{-2} mol) was added. The mixture was heated at 60 °C. Aliquots were taken out after 30, 45, and 60 h, and each fraction was poured into ice-cooled methanol. The polymers precipitated were redissolved in chloroform and again poured into methanol. NMR analysis indicated that the dodecyl contents were 0.63,

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0.74, and 0.80 with respect to the glutamate unit, in increasing order of reaction time. In the following section, the polypeptides are named BD-63, BD-74, and BD-80, respectively. A copolypeptide with a dodecyl content of 0.44 was also prepared separately. The polypeptides showed a crystal to LC phase transition in the DSC thermogram. The transition temperatures were 100, 96, and 87 °C for BD-63, BD-74, and BD-80, respectively.

Preparation of Cholesteric Films with a Grandjean Texture. It is known that cholesteric LC's placed between a pair of flat plates take a Grandjean texture with the cholesteric axis perpendicular to the glass surface. Polypeptide LC's have a marked propensity to show this texture because of the long molecular axis of α-helices. Indeed, a clear reflective color originating from selective reflection has been observed.[20-22] The copolypeptide (0.01 g) and a guest dye (0.3 mol % with respect to the glutamate unit) were dissolved in chloroform (0.32 g). The solution was cast onto a flat plate and stored in a desiccator for 2 days. The desiccator was then evacuatd for 3 h at room temperature. The film formed was removed from the plate by immersing the plate in water and dried under vacuum. The film was placed on a quartz plate and heated on a hot stage (Mettler FP 80) above the crystal–LC transition temperature. The film was covered with a flat quartz plate and pressed at 100 °C to the desired thickness (30–60 μm). To obtain cholesteric films with different pitches, the above films were annealed at appropriate temperatures for 2 h or 15 h and quenched to room temperature.

The synthesis and conformation of the photochromic dichroic dye have been reported previously.[17]

Measurements. UV and CD measurements were made on a Hitachi 320 spectrometer and a Jasco J-500 spectropolarimeter, respectively. In some cases, the cholesteric film showed a biased CD baseline in a region where no absorption is expected. This may be attributed to the residual linear birefringence of the film and hampers true CD measurement by the accompanying residual linear dichroism.[23] The birefringence could be eliminated by further annealing the film to obtain a full cholesteric structure (Grandjean texture). The absence of linear dichroism was confirmed by the fact that the CD intensity did not change upon a rotation of the film around an axis parallel to the incident light.

Results and Discussion

Numerical Calculations of ICD from the Optical Theory of Chandrasekhar. Chandresekhar derived an optical theory for light passing through a cholesteric plate.[1] In his theory, a cholesteric plate is considered as a pile of linearly birefringent and linearly dichroic layers (quasi-nematic layers) that are arranged helically along a helix axis. The angle of two successive quasi-nematic layers is β. β is calculated from the pitch P by $2\pi p/P$, where p is the thickness of a single layer. P and β are positive for right-handed helices. The cholesteric film is assumed to be in a Grandjean texture; that is, the helix axis is normal to the film surface and the light travels along the axis. Under these conditions, the Jones matrix for a cholesteric plate consisting of m quasi-nematic layers is

$$\mathbf{J}_m = \mathbf{S}^m(\mathbf{G}\mathbf{S}^{-1})^m \tag{1}$$

$$\mathbf{S} = \begin{bmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{bmatrix} \tag{2}$$

$$\mathbf{G} = \exp(-k)\begin{bmatrix} \exp(i\gamma) & 0 \\ 0 & \exp(-i\gamma) \end{bmatrix} \tag{3}$$

where k is an average absorption coefficient of a quasi-nematic layer and $\hat{\gamma}$ is a complex function of linear birefringence Δn and linear dichroism Δk of the quasi-nematic layer.

$$\hat{\gamma} = \pi\Delta np/\lambda - i\Delta kp/2 \tag{4}$$

Chandrasekhar showed that J_m can be factored into Jones matrices representing rotation around an azimuthal angle ψ, a rotator $\mathbf{R}$, a circular dichroic plate $\mathbf{\Sigma}$, a retarder $\mathbf{\Phi}$, and a linear dichroic plate $\mathbf{K}$.[2]

$$\mathbf{J}_m = \exp(-km)\mathbf{\Psi}\mathbf{R}\mathbf{\Sigma}\mathbf{\Phi}\mathbf{K}\mathbf{\Psi}^{-1} \tag{5}$$

The elements of each Jones matrix have been formulated in Chandrasekhar's paper.[1] For numerical calculation, however, it is easier to use the original equation (1). The number of layers m is calculated from $m = d/p$, where d and p are the thickness of the film and that of a single layer, respectively. The Jones vectors of transmitted light when the incident light is left- and right-circularly polarized (R-cpl, L-cpl) are

$$\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \left(1/\sqrt{2}\right)\mathbf{J}_m\begin{bmatrix} 1 \\ i \end{bmatrix} \quad \text{(for R-cpl)} \tag{6}$$

$$\begin{bmatrix} B_1 \\ B_2 \end{bmatrix} = \left(1/\sqrt{2}\right)\mathbf{J}_m\begin{bmatrix} 1 \\ -i \end{bmatrix} \quad \text{(for L-cpl)} \tag{7}$$

ICD is calculated from a difference of transmitted intensities for left-circularly polarized light and right-circularly polarized light.

$$I_R = |A_1|^2 + |A_2|^2, \quad I_L = |B_1|^2 + |B_2|^2 \tag{8}$$

$$\psi = 32.98 \log (I_R/I_L) \quad \text{(degree)} \tag{9}$$

The parameters needed to calculate ICD intensity are the birefringence Δn, the linear dichroism Δk, the absorption coefficient k, the pitch P, and the total thickness d. As a standard set of parameters, the following values were employed: $\Delta n = 0.1$, $k = 2 \times 10^{-5}$/nm, $\Delta k = 1.2 \times 10^{-6}$/nm, $d = 50$ μm, and $\lambda = 350$ nm. These values were determined to reproduce experimental ICD intensities, as described below. The thickness of a single layer p was somewhat arbitrarily taken to be 10 nm. The ICD intensity was found to be insensitive to the thickness at least over the range between 5 and 50 nm.

Figures 1 and 2 show theoretical ICD intensities calculated as functions of the inverse pitch P^{-1} for the different total thicknesses d. The ICD profiles show complicated patterns for thin samples of $d < 10$ μm (Figure 1). When the sample becomes thicker, the complicated pattern disappears (Figure 2). The magnitude of the maximum and minimum ICD intensities increased linearly with the total thickness, but the inverse pitches that give the optimum ICD are unchanged ($P^{-1} = 0.00012$ nm^{-1} or $P = 8.3$ μm). Although it cannot be demonstrated analytically, numerical calculations indicated that the ICD

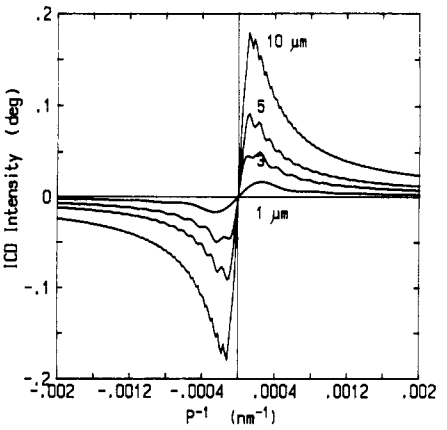


Figure 1. Theoretical ICD intensity plotted against inverse pitch P^{-1} for cholesteric polymer films of different thicknesses d, as indicated in the figure. Other parameters are: $\Delta n = 0.1$, $k = 2 \times 10^{-5}$/nm, $\Delta k = 1.2 \times 10^{-6}$/nm, and $\lambda = 350$ nm.

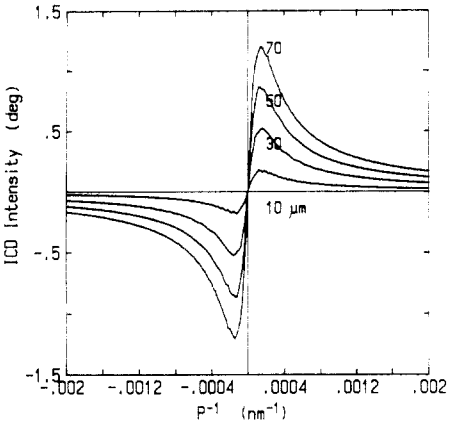


Figure 2. Same as Figure 1 for d = 10–70 μm.

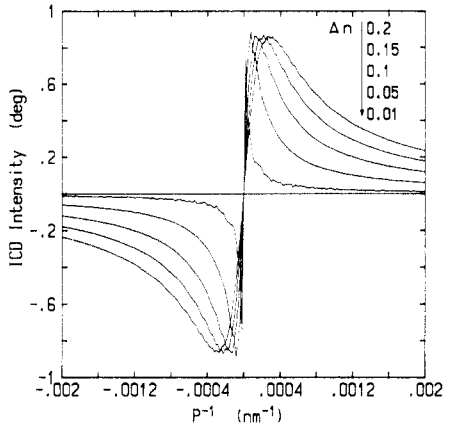


Figure 3. Theoretical ICD intensity plotted against inverse pitch P^{-1} for various cholesteric films of different layer birefringences Δn. Other parameters are d = 50 μm, $k = 2 \times 10^{-5}$/nm, $\Delta k = 1.2 \times 10^{-6}$/nm, and λ = 350 nm.

intensity is a linear function of the linear dichroism per unit thickness Δk and of the concentration of the dye molecules (k and Δk are varied keeping the $\Delta k/k$ ratio constant). The linear dependence of ICD intensity against the thickness and the dye concentration ensures that the ICD intensities of different samples with different dye concentrations and with different thicknesses can be compared with each other after the ICD intensity is normalized by the total amount of doped dyes, which can be evaluated by absorption spectroscopy.

Figure 3 shows the ICD vs inverse pitch plots theoretically calculated for various linear birefringence Δn over the range from 0.01 to 0.2. Contrary to the cases of varying the thickness of varying Δk or k, the maximum ICD values are insensitive to Δn, but the inverse pitch that gives the maximum ICD becomes larger when the birefringence becomes larger. This suggests that the Δn value can be determined from the optimum pitch that is experimentally observed.

ICD from the Photochromic Dye I Doped in Thermotropic Cholesteric Polymer Films. The photochromic dye I tends to orient itself in LC media with its dodecyl chain and the *trans*-azobenzene unit parallel to the molecular axis or, in the present case, parallel to the helical polypeptide chains.[17] A molecular model study indicated that the anthraquinone unit is oriented perpendicular to the azobenzene unit.[17] Since the transition moment of the *trans*-azobenzene group is parallel to the line connecting the centers of the two benzene rings[24] and that of the anthraquinone group is parallel to the long axis,[25] the parallel arrangement of the dye I in right-handed cholesteric LC will induce positive ICD at the absorption band

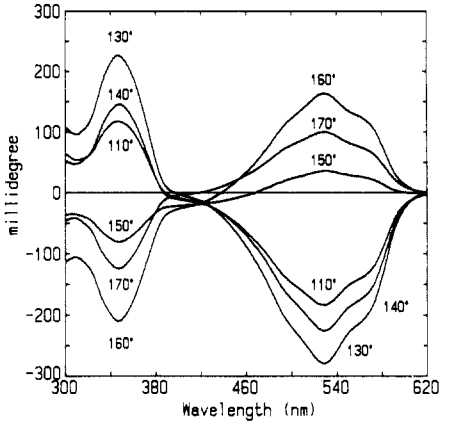


Figure 4. Experimental ICD spectra of a BD-74 film doped with 0.3 mol % of the dichroic dye I annealed at various temperatures for 2 h. The spectra were measured at room temperature. The ICD intensities are normalized to show a unit absorbance at 350 nm.

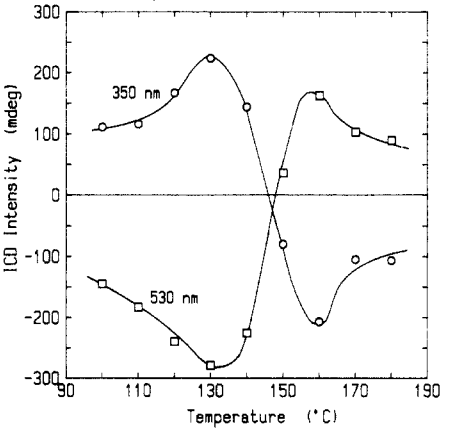


Figure 5. ICD intensity of BD-74 film with 0.3 mol % of the dichroic dye I plotted against the annealing temperature. The ICD intensities are normalized to show a unit absorbance at 350 nm.

of the azobenzene group and negative ICD at the anthraquinone absorption band.[1-5] The same molecular arrangement in left-handed cholesteric LC will induce ICD's of opposite signs.

The ICD spectra of the BD-74 polypeptide film doped with 0.3 mol % of I are shown in Figure 4. Since the ICD intensity also depends on the thickness of the sample, which becomes smaller at high temperatures, the observed ICD intensity was divided by the absorption of the azobenzene unit at 350 nm. The normalization of the ICD spectra was carried out also for other samples containing different amounts of the doped dyes. Therefore, the ICD intensities in Figure 4 and other figures are the normalized values for samples that show A_{350} = 1.0. This procedure is justified by the linear dependence of ICD intensity on the sample thickness and on the dye concentration, as described in the theoretical section.

As expected from the molecular structure, the azobenzene absorption band shows positive ICD and the anthraquinone band shows negative ICD below 150 °C. Above 150 °C, the signs of both ICD peaks were reversed, indicating a reversal of the cholesteric screw sense from right-handed to left-handed. The apparently complex temperature dependence in Figure 4 becomes simple when the ICD peak intensities are plotted against temperature as shown in Figure 5. The reversal of cholesteric screw sense is clearly seen in the figure. From the midpoint of the transition, the nematic temperature was determined to be 147 °C. Similar experiments were carried out using

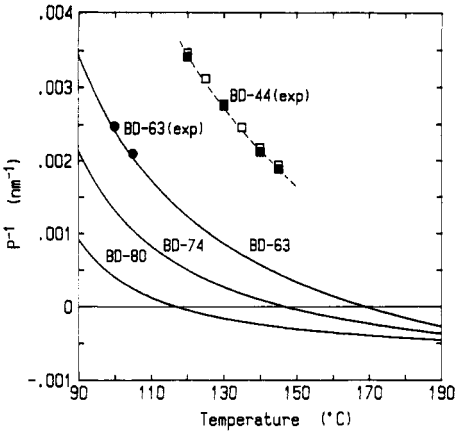


Figure 6. Inverse pitch P^{-1} plotted against temperature. Filled squares are the experimental values for BD-44 films measured from CD reflection spectroscopy using the equation $\lambda = nP$, $n = 1.51$. Open squares are those for BD-44 films doped with 3 mol % of azobenzene. Filled circles are the experimental values for BD-63. Lines are calculated values using eq 8.

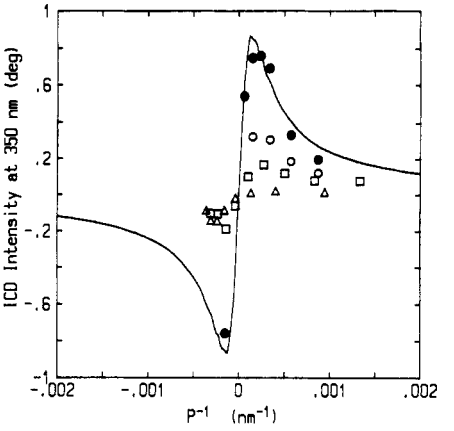


Figure 7. ICD intensity at 350 nm plotted against inverse pitch for BD-63 (○), BD-74 (□), and BD-80 (△) doped with 0.3 mol % of I and annealed for 2 h. The ICD intensities are normalized to show $A_{350} = 1$. Filled circles are those for BD-63 films annealed for 15 h at each temperature. Solid line is a calculated curve with $\Delta n = 0.1$, $k = 2 \times 10^{-5}$/nm, $\Delta k = 1.2 \times 10^{-6}$/nm, and $d = 50$ μm.

BD-63 and BD-80 as the cholesteric hosts. All three polypeptide films showed a right-handed cholesteric screw sense at lower temperatures and a left-handed sense at higher temperatures. The nematic temperatures were 169 °C for BD-63 and 117 °C for BD-80.

Estimation of Cholesteric Pitch. To compare the experimental results with the theoretical calculations, the temperature dependence of the ICD intensity must be converted to the pitch dependence. From a detailed study on the temperature dependence of the cholesteric pitch for poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamate) films of different contents of dodecyl groups, an empirical equation relating the pitch P with temperature T (K) has been reported.[22]

$$P^{-1} = P_0^{-1}(T_N - T)/(T - T_c) \qquad (10)$$

T_N is the nematic temperature (K) where the ICD disappears. P_0 and T_c are adjustable parameters to fit the equation to experimental data. From the data shown in Figure 4 in ref 22, P_0^{-1} (nm^{-1}) and T_c (K) were estimated to be 1.8×10^{-3} and 322 for BD-63, 1.1×10^{-3} and 334 for BD-74, and 7.6×10^{-4} and 341 for BD-80, respectively. The inverse pitches P^{-1} calculated as functions of temperatures for the three polypeptides are shown in Figure 6.

Unfortunately, the pitches of the present polypeptide film fell in a range that cannot be measured by the spectroscopic technique. Therefore, a direct test of the calculated data could not be made, except for two points for BD-63 that were determined from the reflective peaks in CD spectroscopy. The two points lie on the calculated line. In the same figure, the inverse pitch for BD-44 is also shown (solid squares). In this case, the nematic temperature was higher than 200 °C and consequently the comparison with the equation could not be made. The open squares in the figure are the observed pitch of BD-44 samples doped with 3 mol % of azobenzene. It is evident that a small amount of doped dyes does not affect the cholesteric pitch. In the following experiment, the amount of the dyes is 0.3 mol %, so the effect must be even smaller.

ICD Intensity vs Inverse Pitch. On the basis of the above relation, the annealing temperature was converted to the inverse pitch, and the ICD intensities were plotted against the inverse pitch for the three cholesteric hosts. Results are shown in Figure 7 for ICD peaks of azobenzene units (350 nm) and in Figure 8 for anthraquinone peaks (530 nm). Among the three cholesteric polymers, BD-63

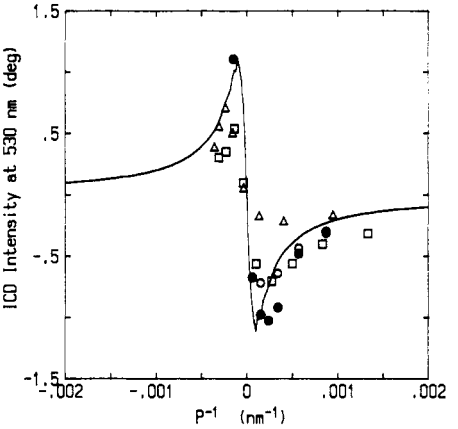


Figure 8. ICD intensity at 530 nm plotted against inverse pitch for BD-63 (○), BD-74 (□), and BD-80 (△) doped with 0.3 mol % of I and annealed for 2 h. The ICD intensities are normalized to show $A_{530} = 1$. Filled circles are those for BD-63 films annealed for 15 h at each temperature. Solid line is a calculated curve with $\Delta n = 0.1$, $k = 2 \times 10^{-5}$/nm, $\Delta k = 1.5 \times 10^{-6}$/nm, and $d = 50$ μm.

induced the most intense ICD. The ICD intensities shown by open circles, open squares, and open triangles are for BD-63, BD-74, and BD-80 samples, respectively, annealed at the corresponding temperatures for 2 h. It has been reported that for polypeptides of the degree of polymerization 250, 2 h is enough to reach an equilibrium cholesteric structure.[20] However, when the sample was further annealed for 15 h at each temperature, the ICD intensity increased significantly (solid circles). This suggests that the reorientation of the dichroic dye I requires further annealing after the cholesteric order has been attained. No further increase of the ICD intensity was observed after annealing for more than 15 h.

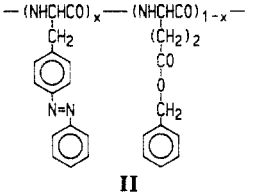
The order of the ICD intensity after annealing for 2 h, BD-80 < BD-74 < BD-63, may reflect the intrinsic propensity of each cholesteric film for the ordering of the doped dyes. Presumably, the increased amount of dodecyl groups increased free spaces for the rotational motions of the dye molecules, resulting in the decrease of the Δk value.

The ICD intensities at the absorption band of the anthraquinone unit were also plotted against inverse pitch in Figure 8. In this figure, the ICD intensities are normalized by the absorbance of the anthraquinone unit at 530 nm, so the ICD intensities are apparently larger than those of the azobenzene unit shown in Figure 7.

In the above experiment, the maximum ICD at 350 nm (ψ = +760 mdeg/(unit absorbance)) was observed for a BD-63 film doped with 0.3 mol % of I when the film was annealed at 155 °C for 15 h. Under these conditions the film shows a right-handed cholesteric structure with a pitch P of +6.7 μm. The minimum ICD at 350 nm (ψ = −760 mdeg/(unit absorbance)) was observed for the same sample when it was annealed at 180 °C for 15 h to attain a left-handed cholesteric structure with P = −6.7 μm.

Simulation of the ICD vs Inverse Pitch Plot. The parameters that may reproduce the experimental ICD vs P^{-1} plot for the dye-doped BD-63 polypeptide film of 50-μm thickness annealed for 15 h were determined through the following procedure. As described above, the optimum pitch almost solely depends on the layer birefringence Δn. The Δn value that reproduces the experimental pitch for the maximum ICD (P = 6.7 μm) was 0.1 ± 0.02. The birefringence is much larger than the values previously suggested (0.02–0.03).[15] The ICD intensity after normalization by the absorbance is a linear function of Δk = (k parallel to the molecular axis) − (k perpendicular to the molecular axis). The Δk value that reproduces the maximum ICD of the azobenzene unit (±760 mdeg when A_{350nm} = 1) was 1.2 × 10^{-6}/nm. The Δk value to fit the maximum ICD of the anthraquinone unit (±1100 mdeg when A_{530nm} = 1) was 1.5 × 10^{-6}/nm. Finally, the total absorbance (1.0) of the cholesteric film of 50-μm thickness is attained by setting k = 2 × 10^{-5}/nm. It should be noted that the two adjustable parameters, Δn and Δk, can be determined independently from the optimum pitch and the maximum ICD intensity, respectively.

The theoretical curves are plotted against inverse pitch in Figures 7 and 8 as solid lines. The agreement between the theoretical curves and the experimental plots is satisfactory. The anisotropic factor $\Delta k/k$ was 6 × 10^{-2} for the azobenzene unit and 7.5 × 10^{-2} for the anthraquinone unit. These values correspond to dichroic ratios k(parallel)/k(perpendicular) 1.062 and 1.078, respectively. The anisotropic factor is smaller in magnitude than the value estimated for azobenzene groups covalently attached to poly(γ-benzyl L-glutamate) through a single methylene spacer (II), $\Delta k/k$ = −0.384.[16] The ordering of azobenzene and other chromophores in LC polymers may be much more improved when they are covalently linked to polypeptide main chains through shortest spacers.



II

Conclusions

ICD from dye-doped cholesteric films was investigated theoretically and experimentally. Theory predicted a linear dependence of the ICD intensity on the thickness, the linear dichroism, and the concentration of doped dyes. Therefore, the magnitude of the ICD from samples of different thickness and of different dye concentrations can be compared by normalization with the total amount of dyes or with the absorbance at the dye absorption band. The linear birefringence did not affect the maximum ICD intensity markedly but changed the optimum cholesteric pitch that gives the maximum ICD. The ICD vs inverse pitch profiles were measured on cholesteric polypeptide films doped with an azobenzene derivative I. The best fit to the experimental ICD profile was attained when Δn = 0.1, k = 2 × 10^{-5}/nm, and Δk = 1.2 × 10^{-6}/nm at 350 nm and 1.5 × 10^{-6} at 530 nm.

Acknowledgment. We appreciate Professor Hideo Takezoe of the Department of Organic and Polymeric Materials, Tokyo Institute of Technology, for helping us to understand the optical theory of cholesteric LC's.

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