Supramolecular Structure of Polypeptides in Concentrated Solutions and Films. III. Inhomogeneous Twisting of Cholesteric Mesophase as Clarified from Multiple-Order Light-Scattering Maxima

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ABSTRACT: We investigated the twisted structure in the cholesteric liquid crystals in which the directors $\mathbf{n}$ (parallel to axes of α -helical molecules of polypeptides) are helicoidally twisted about the helical axis. We propose here that this twisting occurs, in general, nonlinearly or inhomogeneously with displacement along the helical axis for the poly(γ -benzyl L-glutamate) systems studied in this work, in contrast to a picture of 'linear twisting' appearing in earlier literature on the cholesteric liquid crystals. The inhomogeneous twisting in the cholesterics is exhibited most spectacularly in the multiple-order scattering maxima of a laser-light. The deviation from the homogeneous twisting was studied as a function of cell thickness, solvent, polymer concentration, temperature, and aging; the results indicate that the inhomogeneous twisting of the directors is a general phenomenon in the lyotropic liquid crystal system studied in this work. We present a theory for elastic light scattering from the cholesteric mesophase having inhomogeneously twisted structure.

KEY WORDS Cholesteric Liquid Crystal / Poly(γ -benzyl L-glutamate) /
Light Scattering / Cholesteric Twisted Structure / Inhomogeneous Twisting /
Homogeneous Twisting / Director / Multiple-Order Diffraction /

We explored elastic light scattering from the cholesteric mesophase of poly(γ -benzyl L-glutamate) (PBLG) in helicogenic solvents.^{1–3} We found that at a small momentum transfer vector $\mathbf{q}$ ($|\mathbf{q}| = (4\pi/\lambda) \sin(\theta/2)$ where λ is the wavelength of light in medium and θ is the scattering angle), the scattering (designated as 'rod-like scattering') depends on the dimensions and shape of the cholesteric domain^{2,3} in which the helical axes of the cholesteric, twisted structure (oriented normal to the director $\mathbf{n}$) have correlated orientation (see Figure 9). At large $\mathbf{q}$ where $q \sim 1/S$ (S being one-half the cholesteric pitch P , the distance over which the director makes a complete rotation) the scattering

(designated as 'cholesteric scattering') reflects the internal structure of the cholesteric domain, i.e., a periodic variation of the orientation correlation of the director $\mathbf{n}$ or the optical axis $\mathbf{d}$ in the twisted structure.³ The 'cholesteric scattering' reaches a maximum intensity at q_m or θ_m satisfying Bragg's equation,

$$2S \sin(\theta_m/2) = \lambda, \quad \text{or} \quad q_m = 2\pi/S \quad (1)$$

We found two sources of anomalies in the elastic scattering patterns: (i) an anomaly in the azimuthal angle (μ) dependence of the depolarized pattern^{1–3} and (ii) an anomaly in the presence of *multiple-order scattering maxima*. The former anomaly is attributed to the effect of form optical rotation⁴ on the depolarized light scattering patterns. That is, an extraordinary large optical rotatory power of the cholesteric twisted structure distorts μ -dependencies of the depolarized patterns, the manner of distortion being shown to determine the sign of the

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optical rotatory power of the cholesterics, *i.e.*, the sense of cholesteric twisting.^{1,3} The latter anomaly is considered in the present investigation.

We show that the homogenous twisting of the director, *i.e.*, $\omega_{12}(z)$ as given by eq 2 and as appeared in earlier literatures,⁵ gives rise to a single scattering maximum only and that the inhomogeneous twisting of the director is essential to account for the multiple-order diffraction.

$$\omega_{12}(z) = (\pi/S)z \quad (2)$$

where $\omega_{12}(z)$ is a relative twist angle of the two directors separated by a distance z along the helical axis $\hat{z}_1$.

In Section of EXPERIMENTAL EVIDENCES ON MULTIPLE-ORDER SCATTERING MAXIMA we shall investigate experimental evidence for the multiple order scattering maxima as a function of the thickness of the cell used to enclose the specimen, solvent, concentration of polymer, temperature, and aging. All the results indicate that inhomogeneous twisting is a general phenomenon existing in the lyotropic liquid crystals studied in this work. In Section of SCATTERING THEORY we give a theoretical interpretation for the multiple-order scattering maxima from an inhomogeneously twisted cholesteric domain. It becomes evident that relative peak-height of the higher-order scattering is associated with inhomogeneity of the twisting.

TEST SPECIMENS AND APPARATUS

PBLG specimens were prepared by polymerizing *N*-carboxyanhydride of γ -benzyl L-glutamate in a mixture of dioxane-dichloromethane (1:1, v/v) with triethylamine as an initiator. The polymers were further fractionated to have a heterogeneity index (M_w/M_n) approximately equal to 1.3 from gel-permeation chromatography (GPC) measured on a dimethylformamide solution. From viscosity measurements in dichloroacetic acid at 25°C, the PBLG specimens used in this work have molecular weights of 1.06×10^5 .

The PBLG specimen was dissolved in helicogenic solvents such as *m*-cresol, dioxane, and 1,1, 2,2-tetrachloroethane (TCE). Solutions of various concentrations were enclosed in a glass cell of 10 mm diameter and of thickness ranging from 0.18 to 2 mm as described in a previous paper.³ Great care was taken to prevent the solvents from leaking.

Temperature was regulated within $\pm 0.25^\circ\text{C}$ and the scattering patterns were taken with the apparatus described in detail in the previous paper.³

EXPERIMENTAL EVIDENCES ON MULTIPLE-ORDER SCATTERING MAXIMA

Figure 1 shows typical cholesteric scattering patterns under H_V and V_V polarization conditions from 12.1 wt% TCE solution of PBLG at 35°C.⁶ The bottom two patterns were obtained with a shorter exposure time, in comparison with the upper two patterns, in order to resolve the zero-order scattering and the first-order scattering maximum. The H_V and V_V patterns manifest upto the fourth-order scattering maxima, each maximum reflecting a single spacing S , *i.e.*, a half of the cholesteric pitch P ,

$$2S \sin(\theta_{m,n}/2) = n\lambda, \quad \text{or} \quad q_{m,n} = n(2\pi/S) \quad (3)$$

where n is an integer, *i.e.*, the order of scattering maximum.

The dependencies of the scattering patterns with azimuthal angle μ are somewhat distorted in that the H_V pattern does not show a regular, four-fold symmetry with intensity maxima at odd multiples of $\mu = 45^\circ$, and the V_V pattern does not show a regular, two-fold symmetry with intensity maxima at equator, *i.e.*, $\mu = 90^\circ$ and 270° . The origin of the distortion is attributed to optical activity and/or macroscopic orientation of the cholesteric domains.^{1-3,7} In this particular case, the pattern is distorted primarily by macroscopic orientation.¹⁰

The multiple-order diffraction as a manifestation of the inhomogeneous twisting was investigated as a function of thickness of the sample cell, solvent, concentration, temperature, and aging. The results are described in following sections.

1. Effect of Cell Thickness

Figures 2 and 3 show the effect of cell thickness on the multiple-order diffraction and the cholesteric spacing S , respectively, for 19.5 wt% *m*-cresol solution of PBLG. It can be seen that there is no significant effect of cell thickness on either the multiple-order diffraction or spacing S for the thicknesses considered in this studies. Thus, the multiple-order diffraction is an inherent property to the cholesterics, and not an artifact due to the effect of

Figure 1. Typical H_V and V_V light scattering patterns from 12.1 wt% TCE solution of PBLG at 35°C. The bottom two patterns were taken with a shorter exposure time than the upper two patterns.

the cell wall. The results shown hereafter were obtained with a cell 1 mm in thickness.

2. Effect of Solvent

Figure 4 shows the effect of solvent on the multiple-order diffraction from the cholesteric. The results indicate that multiple-order diffraction is commonly found for solvents which form a cholesteric mesophase. The number of diffraction rings is determined mainly by the size of the cholesteric domain and regularity of the cholesteric pitch which are functions of solvent, concentration, and temperature.

3. Effect of Concentration

Figure 5 shows the effect of polymer concentration on the multiple-order diffraction of TCE solutions of PBLG.

Multiple diffraction is commonly observed at concentrations where the cholesterics are formed. The number of multiple diffraction rings seems to depend on the concentration.

4. Effect of Temperature

Figure 6 shows the effect of temperature on the multiple-order diffraction for a 11.1 wt% TCE solution of PBLG under the H_H polarization condition (both polarizer and analyzer oriented horizontally). As discussed in our previous paper,³ the cholesteric pitch increases, *i.e.*, q_m or θ_m shifts to smaller angles with increasing temperature. The temperature T_N , at which the pitch diverges to infinity, is about 60°C for this system. The multiple-order diffraction varies with temperature. The general trend is that higher order diffractions tend to smear and bury in the enhanced background diffuse scattering with increasing temperature. The background scattering is attributed to thermal diffuse scattering (TDS) from the cholesterics *i.e.*, the scattering associated with random disorders in the twist angle and in the spacing due to thermal motions.

5. Effect of Aging

Figure 7 shows the effect of aging on the multiple-

order diffractions under H_V and V_V polarization conditions for a 12.1 wt% TCE solution of PBLG. The patterns were taken as a function of time after the solution was enclosed in the cell. In the early

stage, only first-order diffraction is observable but higher-order diffractions come about with time. Figure 8 shows the effect of aging on the spacing S as measured from q_m or θ_m for 11.1 and 12.1 wt%

Figure 2. Effect of cell thickness on the multiple-order diffraction from 19.5 wt% *m*-cresol solution of PBLG. H_V scattering.

Figure 3. Effect of cell thickness on the half cholesteric pitch S from 19.5 wt% m -cresol solution of PBLG.

H_V 25°C

Figure 4. Effect of solvent on the multiple-order diffraction from the cholesterics. H_V scattering.

TCE solutions of PBLG. It is seen that the system tends to reach equilibrium after several days. The time required for equilibration is dependent on the concentration. Thus the multiple-order diffractions are observed in the equilibrium state.

The initial decrease in S with time as seen in Figure 8 may be due to a shear deformation to which the solution is subjected when enclosed in the cell with an injector. The absence of higher-order diffractions at the initial stage is primarily due to broadening of the line profiles resulting from distribution of the pitch S and the small size of the 'cholesteric domain.' These effects are described in Section of SCATTERING THEORY.

SCATTERING THEORY

1. Model

Figure 9(a) shows a model for calculating the scattering function from a single cholesteric domain of cylindrical shape having radius R and length L oriented randomly in three-dimensional space. $0x_1y_1z_1$ is the coordinate fixed to the apparatus and $0xyz$ is the one fixed to the cholesteric domain where z_1 and z are the coordinates parallel to the vertical direction of the apparatus and to the helical axis of the twisted structure, respectively. The orientation of the cholesteric domain is specified by the

PBLG-TCE

Figure 5. Effect of polymer concentration on the multiple-order diffraction for TCE solutions. H_V scattering.

PBLG-TCE 11.1 wt%

Figure 6. Effect of temperature on the multiple-order diffraction from 11.1 wt% TCE solution. H_H scattering.

orientation of the helical axis (the unit vector $\hat{z}$) with respect to the $0x_1y_1z_1$, *i.e.*, by α and Ω . The unit vectors s_0 and s' are parallel to the propagation directions of the incident and scattered beams, respectively. The scattering intensity is recorded as a function of the scattering vector $q = (q, \mu) =$

(θ, μ) where μ is the azimuthal angle

$$q = (2\pi/\lambda)(s' - s_0) \quad (4)$$

The internal structure of the cholesteric domain is shown in Figure 9(b) in which the α -helical molecules are twisted about $\hat{z}$; l is the intermolecular

Figure 7. Effect of aging on the multiple-order diffraction for 12.1 wt% TCE solution of PBLG. Top: H_V scattering, Bottom: V_V scattering. Each pattern was taken as a function of time after the solution was enclosed in the cell.

Figure 8. Effect of aging on the half cholesteric pitch S for 11.1 and 12.1 wt% TCE solutions.

Figure 9. (a) Model of a cylindrical cholesteric domain of radius R and length L at a given orientation $\hat{z}$ (a unit vector parallel to the helical axis) and (b) of an internal, twisted structure. $0x_1y_1z_1$ is the coordinate fixed to the apparatus where $0z_1$ is in a vertical direction, and $0xyz$ is the coordinate fixed to the helical axis. $\mathbf{n}$ is the director, i.e., a unit vector parallel to α -helical molecule, ω is the twist angle of the director, ω_{12} is the relative twist angle of the two directors separated by a distance $z = |z_1 - z_2|$, and l is the intermolecular distance.

distance, $\mathbf{n}_1$ and $\mathbf{n}_2$ are the directors (unit vectors parallel to the molecular axes) at z_1 and z_2 , respectively, and ω_1 and ω_2 are the twist angles of the directors at the planes z_1 and z_2 , respectively. We assume that $(\mathbf{n} \cdot \hat{z}) = 0$.¹¹

2. Elastic Scattering Function

A) General Equation. The elastic scattering amplitude E_{Ab} under the given polarization condition A_B , where A and B designate the polarization directions of the analyzer and the polarizer used in the scattering experiments (H_V , V_V , V_H , H_H polar-

izations being usually used), is given, in the context of the Born and Fraunhofer approximation, as,

$$E_{Ab}(\mathbf{q}; \hat{z}) = C_1 \int_{\mathbf{r} \in \mathcal{D}} d\mathbf{r} (\mathbf{M}_B \cdot \mathbf{O}_A)_r \exp(-i\mathbf{q} \cdot \mathbf{r}) \quad (5a)$$

$$= C_1 \int_{(\infty)} d\mathbf{r} \sigma(\mathbf{r}) (\mathbf{M}_B \cdot \mathbf{O}_A)_r \exp(-i\mathbf{q} \cdot \mathbf{r}) \quad (5b)$$

where C_1 is a constant related to absolute scattered intensity, $\mathbf{M}_B$ the induced dipole moment at $\mathbf{r}$ under a given polarization condition B , and $\mathbf{O}_A$ is a unit vector along the analyzer, $\int_{\mathbf{r} \in \mathcal{D}} d\mathbf{r}$ designates the

volume integration over the cholesteric domain $\mathcal{D}$, and $\int_{(\infty)} d\mathbf{r}$ designates the volume integration over all real space. $\sigma(\mathbf{r})$ is the shape function of the cholesteric domain defined by,

$$\sigma(\mathbf{r}) = \begin{cases} 1 & \text{for } \mathbf{r} \in \mathcal{D} \\ 0 & \text{for } \mathbf{r} \notin \mathcal{D} \end{cases} \quad (6)$$

From eq 5 the scattered intensity $I_{Ab}(\mathbf{q}; \hat{\mathbf{z}})$ for a domain having a given orientation $\hat{\mathbf{z}}$ is given by

$$I_{Ab}(\mathbf{q}; \hat{\mathbf{z}}) = C_2 \int_{(\infty)} d\mathbf{r} \hat{\sigma}^2(\mathbf{r}) \langle (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_1} (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_2} \rangle_r \exp(-i\mathbf{q} \cdot \mathbf{r}) \quad (7)$$

where

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

$$\hat{\sigma}^2(\mathbf{r}) = \int d\mathbf{u} \sigma(\mathbf{u}) \sigma(\mathbf{r} + \mathbf{u}) \quad (8)$$

and $\langle \rangle_r$ designates an average of the product for a given displacement vector $\mathbf{r}$, i.e.,

$$\langle (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_1} (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_2} \rangle_r = \int_{(\infty)} d\mathbf{r}_1 (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_1} (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_1 + \mathbf{r}} \quad (9)$$

This average depends on the *spatial orientation correlation* of the two directors separated by a displacement vector $\mathbf{r}$. Equation 7 is rewritten as,

$$I_{Ab}(\mathbf{q}; \hat{\mathbf{z}}) = C_2 \mathcal{F}\{\hat{\sigma}^2(\mathbf{r})\} \mathcal{F}\{\langle (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_1} (\mathbf{M}_B \cdot \mathbf{O}_A)_{r_2} \rangle_r\} \quad (10)$$

where $\mathcal{F}\{g(\mathbf{r})\}$ designates a Fourier transform of the function $g(\mathbf{r})$,

$$\mathcal{F}\{g(\mathbf{r})\} = \int d\mathbf{r} g(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) \quad (11)$$

and $\widehat{g \circ h}$ designates a convolution product,

$$\widehat{g \circ h}(x) = \int d\mathbf{u} g(\mathbf{u}) h(x - \mathbf{u}) \quad (12)$$

The term $\mathcal{F}\{\hat{\sigma}^2\}$ is the scattering intensity from the domain as a whole (a *spape factor*) and $\mathcal{F}\{\langle \rangle_r\}$ is the scattering intensity from the cholesteric, twisted structure.

B) Scattering from Twisted Structure. The in-

duced dipole moment at $\mathbf{r}$ is given by,

$$\mathbf{M}(\mathbf{r}) = E_0 \delta \{[\mathbf{e} \cdot \mathbf{n}(\mathbf{r})] \mathbf{n}(\mathbf{r}) + p(\mathbf{r}) \mathbf{e}\} \quad (13)$$

where E_0 is the electric field strength of the incident beam, $\mathbf{e}$ is a unit vector along the polarization direction of the incident beam, $\mathbf{n}(\mathbf{r})$ is the director at $\mathbf{r}$, and $p(\mathbf{r})$ is given by,

$$p(\mathbf{r}) = (\alpha_2 - \alpha_s)/\delta, \quad \delta = \alpha_1 - \alpha_2 \quad (14)$$

where the scattering element is assumed to have uniaxial anisotropy with polarizabilities α_1 and α_2 parallel and perpendicular to $\mathbf{n}$, and α_s is the polarizability of the medium surrounding the domain. Under H_V polarization at small q ,

$$\mathbf{e} = \hat{\mathbf{z}}_1, \quad \mathbf{O}_H = \hat{\mathbf{y}}_1 \quad (15)$$

Thus $(\mathbf{M} \cdot \mathbf{O})_{H_V}$ is given by

$$(\mathbf{M} \cdot \mathbf{O})_{H_V} = E_0 \delta (\mathbf{n} \cdot \hat{\mathbf{z}}_1) (\mathbf{n} \cdot \hat{\mathbf{y}}_1) \quad (16)$$

where $\hat{\mathbf{y}}_1$ and $\hat{\mathbf{z}}_1$ are the unit vectors along y_1 and z_1 axes, respectively.

$$\begin{aligned} \mathbf{n} = & (\sin \omega \sin \Omega + \cos \omega \cos \alpha \cos \Omega) \hat{\mathbf{x}}_1 \\ & + (\cos \omega \cos \alpha \sin \Omega - \sin \omega \cos \Omega) \hat{\mathbf{y}}_1 \\ & - \cos \omega \sin \alpha \hat{\mathbf{z}}_1 \end{aligned} \quad (17)$$

It should be noted that the twist angle of the director ω is a function of z only and that the anisotropy δ can be treated as a constant value in our analysis since the scale over which the fluctuations of δ occur (i.e., order of intermolecular distance) is much shorter than the wavelength of light.

From eq 16 and 17, it follows that

$$\begin{aligned} \langle (\mathbf{M}_V \cdot \mathbf{O}_H)_{r_1} (\mathbf{M}_V \cdot \mathbf{O}_H)_{r_2} \rangle_r &= \frac{1}{16} E_0^2 \delta^2 \{ \sin^2 2\alpha \\ &\times \sin^2 \Omega \langle (1 + \cos 2\omega_1)(1 + \cos 2\omega_2) \rangle_r \\ &- \sin 2\alpha \sin \alpha \sin 2\Omega \langle (1 + \cos 2\omega_1) \sin 2\omega_2 \rangle_r \\ &+ \langle (1 + \cos 2\omega_2) \sin 2\omega_1 \rangle_r \} \\ &+ 4 \sin^2 \alpha \cos^2 \Omega \langle \sin 2\omega_1 \sin 2\omega_2 \rangle_r \} \end{aligned} \quad (18)$$

Since the arguments in the angular bracket depend only on $z = |z_1 - z_2|$, it can be shown that the spatial correlation $C(\mathbf{r}) \equiv \langle \cos 2\omega_1 \cos 2\omega_2 \rangle_r$ can be written,

$$C(\mathbf{r}) = \langle \cos 2\omega_1 \cos 2\omega_2 \rangle_z = C(z)$$

Since $\omega_2 = \omega_1 + \omega_{12}$ it follows that

$$C(z) = \langle \cos^2 2\omega_1 \cos 2\omega_{12} \rangle_z - \frac{1}{2} \langle \sin 4\omega_1 \sin 2\omega_{12} \rangle_z \quad (19)$$

where $\omega_{12}(z)$ is a relative twist angle of the two directors separated by a distance z and is assumed to be a function of z , only, but not ω_1 . Noting that

$$\langle \cos^2 2\omega_1 \rangle = 1/2, \quad \langle \sin 4\omega_1 \rangle = 0$$

one obtains

$$C(r) = C(z) = (1/2)g(z)$$

where

$$g(z) \equiv \langle \cos 2\omega_{12} \rangle_z \quad (20)$$

is the spatial correlation function of the twisting which decays from unity at $z=0$ toward zero with increasing z . Calculating other terms in eq 18, it follows that

$$\begin{aligned} & \langle (\mathbf{M}_V \cdot \mathbf{O}_H)_{r_1} (\mathbf{M}_V \cdot \mathbf{O}_H)_{r_2} \rangle_r \\ &= \frac{1}{16} E_0^2 \delta^2 \left\{ \left[1 + \frac{1}{2} g(z) \right] \sin^2 2\alpha \sin^2 \Omega \right. \\ & \quad \left. + 2g(z) \sin^2 \alpha \cos^2 \Omega \right\} \quad (21) \end{aligned}$$

Now we shall calculate the Fourier transform of eq 21. From the definition,

$$\begin{aligned} \mathbf{q} &= \frac{2\pi}{\lambda} [(1 - \cos \theta) \hat{x}_1 - \sin \theta \sin \mu \hat{y}_1 - \sin \theta \cos \mu \hat{z}_1] \\ &= q_x \hat{x} + q_y \hat{y} + q_z \hat{z} \quad (22) \end{aligned}$$

The relation between $(\hat{x}, \hat{y}, \hat{z})$ and $(\hat{x}_1, \hat{y}_1, \hat{z}_1)$ is obtained by a coordinate transformation matrix $T = T(\alpha, \Omega)$. Thus

$$\begin{aligned} & \mathcal{F} \left\{ 1 + \frac{1}{2} g(z) \right\} \\ &= \int_{-\infty}^{\infty} dz \left[1 + \frac{1}{2} g(z) \right] \exp(-iq_z z) \\ & \quad \times \iint_{-\infty}^{\infty} dx dy \exp[-i(q_x x + q_y y)] \\ &= \delta(q_x, q_y, q_z) + \frac{1}{2} \delta(q_x, q_y) \int_{-\infty}^{\infty} dz g(z) \\ & \quad \times \exp(-iq_z z) = \delta(q_x, q_y) \left[\delta(q_z) + \frac{1}{2} \mathcal{J}(q_z) \right] \quad (23) \end{aligned}$$

where $\delta(q)$ is the Dirac's delta function, and

$$\mathcal{J}(q_z) \equiv \int_{-\infty}^{\infty} dz g(z) \exp(-iq_z z) \quad (24)$$

Consequently,

$$\begin{aligned} & \mathcal{F} \{ \langle (\mathbf{M}_V \cdot \mathbf{O}_H)_{r_1} (\mathbf{M}_V \cdot \mathbf{O}_H)_{r_2} \rangle_r \} \\ &= \frac{1}{16} E_0^2 \delta^2 \delta(q_x, q_y) \left\{ \left[\delta(q_z) + \frac{1}{2} \mathcal{J}(q_z) \right] \right. \\ & \quad \times \sin^2 2\alpha \sin^2 \Omega \\ & \quad \left. + 2\mathcal{J}(q_z) \sin^2 \alpha \cos^2 \Omega \right\} \quad (25) \end{aligned}$$

where

$$\begin{aligned} q_x &= q \left[\sin \frac{\theta}{2} \cos \alpha \cos \Omega \right. \\ & \quad \left. + \cos \frac{\theta}{2} (\cos \mu \sin \alpha - \sin \mu \cos \alpha \sin \Omega) \right] \\ q_y &= -q \left[\sin \frac{\theta}{2} + \cos \frac{\theta}{2} \sin \mu \cos \Omega \right] \\ q_z &= q \left[\sin \frac{\theta}{2} \sin \alpha \cos \Omega \right. \\ & \quad \left. - \cos \frac{\theta}{2} (\cos \mu \cos \alpha + \sin \mu \sin \alpha \sin \Omega) \right] \\ q &= \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \end{aligned}$$

C) Shape Factor.

$$\begin{aligned} |\Sigma(\mathbf{q}, \hat{z})|^2 &\equiv \int_{(\infty)}^2 \mathbf{dr} \hat{\sigma}^2(\mathbf{r}) \exp[-i(\mathbf{q} \cdot \mathbf{r})] \\ &= \left| \int_{\mathbf{r} \in \mathcal{Q}} \mathbf{dr} \exp[-i(\mathbf{q} \cdot \mathbf{r})] \right|^2 \\ &= \left| \int_{-L/2}^{L/2} dz \exp[-iq_z z] \int dx dy \right. \\ & \quad \left. \exp[-i(q_x x + q_y y)] \right|^2 \\ &= L^2 j_0^2(q_z L/2) \left| \int_0^R \rho d\rho \int_0^{2\pi} d\phi \right. \\ & \quad \left. \exp[-i\rho(q_x \cos \phi + q_y \sin \phi)] \right|^2 \\ &= 4V^2 j_0^2(q_z L/2) J_1^2([q_x^2 + q_y^2]^{1/2} R) \\ & \quad \times [q_x^2 + q_y^2]^{-1} R^{-2} \quad (26) \end{aligned}$$

where V is the volume of the cylindrical domain, j_0 is the zeroth order spherical Bessel function of the first kind, and J_1 is 1st order Bessel function of the first kind.

D) *Average Scattering Intensity $I_{H_v}(q)$:*

The average scattering intensity under H_v polarization is given by,

$$I_{H_v}(q) = \frac{1}{4\pi} \int_0^\pi d\alpha \sin \alpha \int_0^{2\pi} d\Omega I_{H_v}(q; \hat{z}) \quad (27)$$

for random orientation of the cholesteric domain. It may be worth while to consider a simplified case where the cholesteric domains are oriented randomly in two-dimensional space $0y_1z_1$ (i.e., a case of $\Omega = 90^\circ$) to gain a physical insight into eq 27. In this case, q_x , q_y , and q_z are slightly simplified, at small θ , as,

$$\begin{aligned} q_x &= q \sin(\alpha - \mu) \\ q_y &= -q \sin(\theta/2) \\ q_z &= -q \cos(\alpha - \mu) \end{aligned} \quad (28)$$

From eq 10, 25, 26, and 28 the scattering from a single oriented domain is given by

$$\begin{aligned} I_{H_v}(q; \hat{z}) &= K \sin^2 2\alpha \left\{ \left| \sum(q; \hat{z}) \right|^2 + \frac{1}{2} \frac{J_1^2(qR \sin(\alpha - \mu))}{[qR \sin(\alpha - \mu)]^2} \right. \\ &\quad \left. \times \left[j_0^2 \left(\frac{qL}{2} \cos(\alpha - \mu) \right) \mathcal{J}(q \cos(\alpha - \mu)) \right] \right\} \quad (29) \end{aligned}$$

where K is a constant related to absolute intensity. The first term on right hand side of eq 29 is the scattering from a cholesteric domain as a whole. Note that it has an optical anisotropy so that the domain oriented at a given α is weighted by the factor $\sin^2 2\alpha$. The second term is associated with the internal twisted structure.

We can simplify eq 29 by noting that the lateral dimension R is much larger than λ in real system; R/λ is at least greater than 10 and is of the order of 100 in many cases. If this is the case,

$$\begin{aligned} J_1^2(qR \sin(\alpha - \mu)) / [qR \sin(\alpha - \mu)]^2 \\ \longrightarrow \delta(\alpha - \mu) \end{aligned} \quad (30)$$

for $q \neq 0$. In this case, the average intensity is simply given from eq 27, 29, and 30 by,

$$\begin{aligned} I_{H_v}(q) &= \frac{1}{2\pi} \int_0^{2\pi} d\alpha I_{H_v}(q; \hat{z}) \\ &= K \sin^2 2\mu (I_{H_v}^b + I_{H_v}^d) \end{aligned} \quad (31)$$

where

$$I_{H_v}^b(q) = j_0^2(qL/2)$$

$$I_{H_v}^d(q) = \frac{1}{2} j_0^2(qL/2) \widehat{\mathcal{J}}(q)$$

$$\mathcal{J}(q) = \mathcal{F}\{g\} = \int_{-\infty}^{\infty} dz g(z) \exp(-iqz) \quad (32)$$

where $I_{H_v}^b$ is the small-angle diffuse scattering due to the cholesteric domain as a whole. The size distribution of the domain gives rise to $I_{H_v}^b$ which monotonically decreases with q . $I_{H_v}^d$ gives rise to the 'cholesteric scattering' with maximum at q_m as given by eq 1 or 3, the maximum being attributed to the function $\mathcal{J}(q)$. The optical anisotropy of the cholesterics gives rise to H_v scattering with maximum intensities at odd multiples of $\mu = 45^\circ$. If the cholesterics are embedded in an optically active medium, this μ -dependence is disturbed by the effect of optical rotation on the scattering as described in our previous papers.^{2,3}

3. Homogeneous Twisting

For *homogeneous twisting* in which a relative twist angle ω_{12} of the two directors varies linearly with the distance z as described by eq 2, the spatial correlation function $g(z)$ of the twist angle is given by,

$$g(z) = \langle \cos 2\omega_{12} \rangle_z = \cos(2\pi/S)z \quad (33)$$

Thus $\mathcal{J}(q)$ in eq 32 is given,

$$\mathcal{J}(q) = \frac{1}{2} \left[\delta\left(q + \frac{2\pi}{S}\right) + \delta\left(q - \frac{2\pi}{S}\right) \right] \quad (34)$$

Thus the 'cholesteric scattering' $I_{H_v}^d(q)$ is given, from eq 32 and 34, by,

$$I_{H_v}^d(q) = \frac{1}{4} \left\{ j_0^2 \left(\left[q + \frac{2\pi}{S} \right] \frac{L}{2} \right) + j_0^2 \left(\left[q - \frac{2\pi}{S} \right] \frac{L}{2} \right) \right\} \quad (35)$$

From eq 34 the homogeneous twisting gives the first-order diffraction at scattering vector $\pm 2\pi/S$ satisfying the Bragg's equation 1. The line profile is determined by the domain size L , i.e.,

$$j_0^2 \left(\left[q - \frac{2\pi}{S} \right] \frac{L}{2} \right) = 1 - \frac{1}{3} \left[\left(q - \frac{2\pi}{S} \right) \frac{L}{2} \right]^2 + \dots$$

$$\simeq \exp \left\{ -\frac{(q-2\pi/S)^2}{2\sigma^2} \right\}, \quad \sigma = \sqrt{6}/L \quad (36)$$

The larger the L , the smaller the standard deviation σ , and consequently the shaper the profile.

4. Random Disorders Superposed on the Homogeneous Twisting

We consider here a random disorder $\Delta\omega_{12}(z)$ superposed on the linear twisting $\omega_{12}^0(z)$, i.e.,

$$\omega_{12}(z) = \omega_{12}^0(z) + \Delta\omega_{12}(z) \quad (37)$$

$$\omega_{12}^0(z) = (\pi/S)z$$

In this case, $g(z)$ is given by

$$g(z) = \langle \cos 2\omega_{12} \rangle_z \quad (38)$$

$$= \cos 2\omega_{12}^0(z) \langle \cos 2\Delta\omega_{12} \rangle_z$$

It should be noted that in eq 38 $\langle \sin 2\Delta\omega_{12} \rangle_z = 0$ since positive and negative values of $\Delta\omega_{12}$ are equally probable.

$\langle \cos 2\Delta\omega_{12} \rangle_z$ is the spatial correlation function for the fluctuations in the twist angle and can be easily calculated on the basis of a random stochastic process with n steps and 'step length' δ_l where δ_l is the uncertainty (or fluctuation) in the relative twist angles of the two directors separated by an intermolecular distance l (see Figure 9b). Thus

$$\delta_l \equiv \Delta\omega_{12}(l) \quad (39)$$

$$n \equiv z/l \quad (40)$$

The probability $P(\Delta\omega_{12})$ that the two directors separated by a distance z have the fluctuations $\Delta\omega_{12}$ in the relative twist angle is given by the one-dimensional stochastic problem,

$$P(\Delta\omega_{12}) \sim \exp(-\Delta\omega_{12}^2/2n\delta_l^2) \quad (41)$$

Therefore

$$\begin{aligned} \langle \cos 2\Delta\omega_{12} \rangle_z &= \int_{-\infty}^{\infty} d\Delta\omega_{12} \cos(2\Delta\omega_{12}) P(\Delta\omega_{12}) / \\ &\quad \int_{-\infty}^{\infty} d\Delta\omega_{12} P(\Delta\omega_{12}) \\ &= \exp(-2n\delta_l^2) = \exp(-|z|/a) \end{aligned} \quad (42)$$

where a is the correlation distance defined by

$$a \equiv l/2\delta_l^2 \quad (43)$$

From eq 32, 38, and 42, $\mathcal{J}(q)$ is given by

$$\begin{aligned} \mathcal{J}(q) &= \mathcal{F}\{\cos 2\omega_{12}^0(z) \langle \cos 2\Delta\omega_{12} \rangle_z\} \\ &= \mathcal{J}_0(q) \widehat{\mathcal{F}}\{\langle \cos 2\Delta\omega_{12} \rangle_z\} \end{aligned} \quad (44)$$

where $\mathcal{J}_0(q)$ is identical to $\mathcal{J}(q)$ in eq 34 and

$$\widehat{\mathcal{F}}\{\langle \cos 2\Delta\omega_{12} \rangle_z\} = 2 \frac{1/a}{(1/a)^2 + q^2} \quad (45)$$

From eq 44 and 45, it follows that

$$\mathcal{J}(q) = \frac{1/a}{1/a^2 + (q+2\pi/S)^2} + \frac{1/a}{1/a^2 + (q-2\pi/S)^2} \quad (46)$$

Thus $\mathcal{J}(q)$ is given by a Lorentzian with FWHM = $2/a$ and maxima at $\pm 2\pi/S$.

The random disorders thus give a broad first-order diffraction only, the breadth being associated with δ_l^2/l .

5. Inhomogeneous Twisting

From the preceding discussion in sections 3 and 4 it is evident that having non-random disorders in the twist angle or inhomogeneous twisting is essential in order to account for the multiple-order diffraction. The inhomogeneity may be described by a Fourier expansion of the correlation function $g(z)$ as in eq 47 in which the coefficients of the higher-order harmonics are associated with the non-linearity of the twisting,

$$\begin{aligned} g(z) = \langle \cos 2\omega_{12} \rangle_z &= \sum_{n=0}^{\infty} a_n \cos(2n\pi/S)z \\ \sum_{n=0}^{\infty} a_n &= 1 \end{aligned} \quad (47)$$

The normalization condition is necessary since $g(z=0)=1$. Equation 47 satisfies a periodicity $g(z)=g(z+S)$ and symmetry, $g(z)=g(-z)$. Substituting eq 47 into eq 32,

$$\mathcal{J}(q) = \frac{1}{2} \sum_{n=0}^{\infty} a_n \{ \delta(q+2n\pi/S) + \delta(q-2n\pi/S) \} \quad (48)$$

and

$$\begin{aligned} I_{H_v}^d(q) &= \frac{1}{4} \sin^2 2\mu \sum_{n=0}^{\infty} a_n \left\{ j_0^2 \left(\left[q + \frac{2n}{S} \right] \frac{L}{2} \right) \right. \\ &\quad \left. + j_0^2 \left(\left[q - \frac{2n}{S} \right] \frac{L}{2} \right) \right\} \end{aligned} \quad (49)$$

Thus the 'cholesteric scattering' becomes maximum at $q=q_m$ satisfying eq 3. Inhomogeneous twisting which may be stabilized by the presence of acoustic

phonons in the cholesterics can thus account for the multiple-order diffraction.

From eq 49, the m -th order scattering maximum is given by,

$$I_{H_v}^d(q_m) = (\text{constant}) a_m \sin^2 2\mu$$

thus,

$$I_{H_v}^d(q_m)/I_{H_v}^d(q_{m+1}) = a_m/a_{m+1} \quad (m \neq 0) \quad (50)$$

Figure 10. Results of numerical calculations for $I_{H_v}^d(q)$ (solid curve) and for $I_{H_v}^b(q)$ (broken curve) at $\mu=45^\circ$ for $R \gg \lambda$ and $L/S=4$. $a_1 : a_2 : a_3 : a_4 = 1 : 0.4 : 0.1 : 0.01$. The correlation function $g(z)$ is calculated for the homogeneous twisting (broken curve) and for the inhomogeneous twisting with the Fourier coefficients a_i 's as given above. The distance D corresponds to $P (=2S)$.

Consequently one can estimate the Fourier coefficient a_m from the maximum intensities of the 'cholesteric scattering.'

DISCUSSION

Figures 10 and 12 show some results of numerical calculations for $I_{H_v}^d(q)$ (solid curve) and $I_{H_v}^b(q)$ (broken curve) at $\mu=45^\circ$ for the case of $R \gg \lambda$ and $L/S=4$. Figure 10 was obtained where $a_1 : a_2 : a_3 : a_4 = 1 : 0.4 : 0.1 : 0.01$. Both the background scattering $I_{H_v}^b$ and the 'cholesteric scat-

Figure 11. Measured angular dependence of H_v scattering intensity for 12.1 wt% TCE solution with θ^* , the scattering angle in the medium (measured with a photomultiplier system). Open circles: measured profile, solid curve, $I_{H_v}^b$; broken curve, $I_{H_v}^d$.

Figure 12. Calculated $I_{H_v}^d$ at $\mu=45^\circ$ for $R \gg \lambda$, $L/S=4$, and for inhomogeneous twisting with $a_1 : a_2 : a_3 : a_4 = 1 : 0.16 : 0.016 : 0.0016$, and calculated $g(z)$ for homogeneous twisting (broken curve) and for inhomogeneous twisting (solid curve) with the coefficients a_i 's as given above. $D \equiv P = 2S$.

tering' $I_{H_v}^d$ have a number of scattering maxima with a spacing Δq between them much smaller than that between the multiple-order scattering ($\Delta q_m = 2\pi/S$). This spacing Δq can be predicted from $j_0^2(qL/2)$, i.e.,

$$\Delta q = 2\pi/L \quad (51)$$

The fine modulation (with the spacing Δq) is one origin of "speckling" of the laser-light scattering patterns, arising from intraparticle interference of the cholesteric domain. This speckling is modified by the interparticle interference of the different cholesteric domains, resulting essentially in the observed speckled patterns.

The maximum intensity of $I_{H_v}^d$ occurs at q_m satisfying eq 3, and the relative peak-height satisfies the relation given by eq 50. Figure 10 also includes the spatial correlation function $g(z)$ as predicted from the assumed values of the Fourier coefficients. The solid and broken curves correspond to the case of the inhomogeneous twisting and homogeneous twisting, respectively.

Figure 11 shows the measured angular dependence of H_v scattering intensity for 12.1 wt% TCE solution with θ^* , the scattering angle in the medium. The measured profile as marked by open circles are resolved into $I_{H_v}^b$ as drawn by the solid curve and $I_{H_v}^d$ as drawn by broken curve. Although the assessment of $I_{H_v}^b$ involves some uncertainty, $I_{H_v}^d$ is seen to have maximum intensity at q_m satisfying eq 3, and the relative height of each maximum is 1:0.16:0.016:0.0016. Figure 12 shows calculated $I_{H_v}^d$ and $g(z)$ for the Fourier coefficients $a_1:a_2:a_3:a_4 = 1:0.16:0.016:0.0016$ corresponding to the experimental results shown in Figure 11.

Thus, from the measured scattering profile one can estimate inhomogeneity or nonlinearity in the twisting of the directors in the cholesteric liquid crystals. The nonlinearity for the TCE sys-

tem may be accompanied by excess free energy relative to the homogeneously twisted system which, however, may be stabilized by thermal energy, i.e., through the presence of *acoustic phonons*.

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10. This is because the H_v pattern is nearly identical to the V_H pattern.
11. It is conceivable that the orientation of the directors has spatial fluctuations with respect to the cholesteric axis $\hat{z}$. This fluctuations, however, give only a minor effect on our conclusion, unless the fluctuations occur periodically with z . Such special fluctuations are, of course, highly improbable, but the fluctuations should be more or less random. This random fluctuations generally broaden the line profiles of the multiple-order scattering maxima.