Polymer Journal, Vol. 4, No. 4, pp 452—459 (1973)

Light-Scattering Patterns from Random Assembly of Anisotropic Rod-like Structures with their Principal Optic Axes Oriented in Cylindrical Symmetry with Respect to their Own Rod Axes*

Yukinobu MURAKAMI, Norio HAYASHI,** Takeji HASHIMOTO, and Hiromichi KAWAI***

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

(Received September 14, 1972)

ABSTRACT: Polarized light scattering from systems having random assembly of anisotropic fibrils with finite length L and infinitely thin thickness were theoretically calculated. The calculations were carried out for the fibrils randomly oriented in three-dimensional space. As for orientation of optic axes within the fibrils, two types of fibrils were considered; one in which the orientation of the optic axes is fixed in a plane within the fibril and the other in which the orientation is cylindrically symmetric around the fibril axis. Differences in the scattering patterns from two types of the fibrils were discussed. By comparing the scatterings from two types of the fibrils with experimental scattering patterns, it is suggested that the fibrils which show maximum H_V scattering intensities at azimuthal angles $\mu=0°$ and $90°$ must be the former type of the fibrils. However for the fibrils which show maximum H_V scattering intensity at $\mu=45°$, a unique determination of the types of the fibrils seems to be difficult by light-scattering method alone.

KEY WORDS Polarized Light Scattering / Anisotropic Fibrils / Anisotropic Rods / Cylindrically Symmetric Anisotropy /

The scattering patterns which do not exhibit the characteristics typical to spherulitic scattering[2] have been occasionally observed in crystalline polymer films such as poly(tetrafluoroethylene),[3] poly(chlorotrifluoroethylene),[4] amylose,[5] water soluble hydroxypropylcellulose,[6] native cellulose,[7] and collagen.[1,8] The scatterings called as "rod-like scattering" have been shown to arise from textures of nonspherulitic but random assembly of anisotropic fibrils.

In a previous paper,[1] scattering patterns from the unoriented denatured collagen films were theoretically explained in terms of a random assembly of optically anisotropic rod-like structure. Figure 1 shows the previous model used to describe the anisotropic fibrillar scattering entity oriented randomly in three-dimensional space. In the

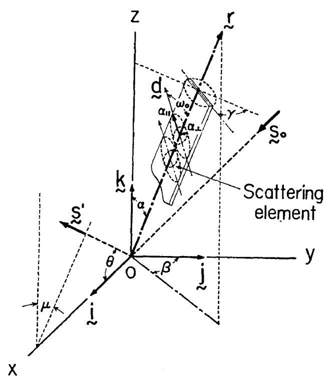

Figure 1. Model of an anisotropic rod for Model A fibrils.[1] Model B fibrils have cylindrically symmetric orientation of the optic axis, *i.e.*, randomly varying γ within the fibrils.

* This work may be considered to be a supplement of the previous paper of ref 1.

** Present address: *The Central Research Laboratories, Mitsubishi Chemical Industries, Inc., Hisamoto-Kamoi-cho, Kawasaki, Japan.*

*** To whom correspondence should be sent.

model the orientation of the optic axis which is designated as a unit vector **d** was assumed to be constant within the fibrils, so that the polar angle ω_0 and azimuthal angle γ were kept constant. In case of the collagen films the optic axis direction may be considered to be parallel to the tropocollagen molecules.[9] The fibrils were assumed to have finite length of L but infinitely thin lateral dimensions.

In this paper, we shall treat the scattering from a supplementary system to the previous model in which the fibrils have cylindrically symmetric optical anisotropy, *i.e.*, a system in which γ is randomly varying within the fibrils. The new model which shall be designated as "fibrils of Model B" for conveniences of further descriptions differs only in the manner of the orientation of the optic axes from the previous model[1] which shall be designated as "fibrils of Model A." Differences in scattering patterns from two systems, the models A and B, were analyzed for a better understanding of the rod-like scattering.

Such fibrils of the model B may be found when (i) the fibrils are composed of a stack of hellically twisted chain molecules parallel to the fibrillar axes with twisting periode short compared with the wavelength of visible light, when (ii) the fibrils are composed of more elementary fibrils arranged cylindrically symmetrically around their fibrillar axes, or when (iii) the fibrils themselves are twisted around their fibrillar axes with twisting period which is irregular or short compared with wavelength of the visible light like the radial fibrils of nonringed spherulites.

CALCULATIONS

As in the previous Model A,[1] the fibrils are assumed to be composed of uniaxially anisotropic scattering elements with polarizabilities $\alpha_{/\!/}$ and $\alpha_{\perp}$ along and perpendicular to the optic axis, respectively. Angles α and β are the orientation angles of the fibril with respect to Cartesian coordinate $O\text{-}XYZ$ where the OX and OZ axes are set parallel to a unit vector $\mathbf{s}_0$ parallel to propagation direction of incident beam and vertical direction of the photographic system, respectively. The scattered beam parallel to a unit vector $\mathbf{s}'$ is observed as a function of scattering angle θ and azimuthal angle μ as well as polarization conditions of experiments; V_V scattering in which both polarizer and analyzer are set in the vertical direction and H_V scattering in which the polarizer and analyzer are set in vertical and horizontal directions, respectively.[3]

Amplitude of scattering from the fibril is given, according to Rayleigh—Gans theory,[10] by

$$E=C\int_{-L/2}^{L/2}(\mathbf{M}\cdot\mathbf{O})\cos[k(\mathbf{r}\cdot\mathbf{s})]\,\mathrm{d}r \qquad (1)$$

where **M** and **O** are induced dipole moment and a unit vector parallel to the polarization direction of the analyzer set perpendicular to OX axis and in between the sample and the photographic plate to record the scattering patterns. The scattering vector **s** is defined as $\mathbf{s}=\mathbf{s}_0-\mathbf{s}'$ and **r** is a vector along the fibrillar axis.

For the system with random assembly of the fibrils in which interfibrillar interferences of the scattered light can be ignored, average scattered intensity is given by

$$I=K\int_0^{2\pi}\int_0^{\pi}E^2\sin\alpha\,\mathrm{d}\alpha\,\mathrm{d}\beta \qquad (2)$$

As before we shall assume that the fibril is homogeneous so that the effective induced dipole moment under a given polarization condition is independent of r. Consequently

$$E^2=C^2(\mathbf{M}\cdot\mathbf{O})^2\left[\int_{-L/2}^{L/2}\cos[k(\mathbf{r}\cdot\mathbf{s})]\,\mathrm{d}r\right]^2 \qquad (3)$$

The integration can be readily carried out as shown in a previous paper.[1] In a more general case in which there is optical heterogeneities within the fibrils, $(\mathbf{M}\cdot\mathbf{O})$ depends upon r, and the calculations become more complex, the effect of which shall be discussed elsewhere.[11] It is also assumed that the fibrils are identical with respect to their size. The effect of the size distribution on the scattering shall be also discussed elsewhere.[11]

The effective induced dipole moment is obtained by evaluating the components of the incident field $\mathbf{E}_0=(E_{0x}, E_{0y}, E_{0z})$ along the principal axes of the polarizability ellipsoid of the scattering element $(\mathbf{Q}^t\mathbf{E}_0)$ and by evaluating the components of the induced dipole moment thus calculated $(\boldsymbol{\alpha}\mathbf{Q}^t\mathbf{E}_0)$ along the polarization direction of the analyzer $(\mathbf{Q}\boldsymbol{\alpha}\mathbf{Q}^t\mathbf{E}_0)$. Thus if matrix of an orthogonal coordinate transformation between $O\text{-}XYZ$ system and the principal axes of the scattering element is given by $\mathbf{Q}$, and for vertically polarized incident beam in which $\mathbf{E}_0=(0, 0, E_0)$, the induced dipole moment under H_V and V_V polarizations are given by

$$(\mathbf{M}\cdot\mathbf{O})_{H_V}=\mathbf{Q}\boldsymbol{\alpha}\mathbf{Q}^t\begin{pmatrix}0\\0\\E_0\end{pmatrix}\cdot\mathbf{j} \qquad (4)$$

$$(\mathbf{M}\cdot\mathbf{O})_{V_V}=\mathbf{Q}\boldsymbol{\alpha}\mathbf{Q}^t\begin{pmatrix}0\\0\\E_0\end{pmatrix}\cdot\mathbf{k} \qquad (5)$$

where $\mathbf{j}$ and $\mathbf{k}$ are the unit vectors parallel to OY and OZ axes, and $\boldsymbol{\alpha}$ is a polarizability tensor along the principal axes given by

$$\boldsymbol{\alpha}=\begin{pmatrix}b_t & 0 & 0\\0 & b_t & 0\\0 & 0 & b_r\end{pmatrix} \qquad (6)$$

$\mathbf{Q}^t$ is a transposed matrix of $\mathbf{Q}$. b_t and b_r are defined as $b_t=\alpha_\perp-\alpha_s$, and $b_r=\alpha_{/\!/}-\alpha_s$ where α_s is polarizability of medium surrounding the fibril as in a previous paper.[1]

The transformation matrix $\mathbf{Q}$ is obviously given by a product of orthogonal matrices of coordinate transformations.

$$\mathbf{Q}=\mathbf{Q}_1\mathbf{Q}_2 \qquad (7)$$

where $\mathbf{Q}_1$ and $\mathbf{Q}_2$ are given by

$$\mathbf{Q}_1=\begin{pmatrix}\cos\alpha\sin\beta, & -\cos\beta, & \sin\alpha\sin\beta\\ \cos\alpha\cos\beta, & \sin\beta, & \sin\alpha\cos\beta\\ -\sin\alpha, & 0, & \cos\alpha\end{pmatrix} \qquad (7a)$$

$$\mathbf{Q}_2=\begin{pmatrix}\cos\omega_0\cos\gamma, & -\sin\gamma, & \sin\omega_0\cos\gamma\\ \cos\omega_0\sin\gamma, & \cos\gamma, & \sin\omega_0\sin\gamma\\ -\sin\omega_0, & 0, & \cos\omega_0\end{pmatrix} \qquad (7b)$$

Now from eq 4 to 7, it follows that

$$\begin{aligned}(\mathbf{M}\cdot\mathbf{O})_{H_V} &=(b_r-b_t)E_0[(\cos^2\omega_0\\ &\quad-\sin^2\omega_0\cos^2\gamma)\sin\alpha\cos\alpha\cos\beta\\ &\quad+\sin\omega_0\cos\omega_0\cos\gamma(\cos^2\alpha-\sin^2\alpha)\cos\beta\\ &\quad-\sin^2\omega_0\sin\gamma\cos\delta\sin\alpha\sin\beta\\ &\quad+\sin\omega_0\cos\omega_0\sin\gamma\cos\alpha\sin\beta] \qquad (8)\end{aligned}$$

$$\begin{aligned}(\mathbf{M}\cdot\mathbf{O})_{V_V} &=(b_r-b_t)E_0[(\cos^2\omega_0-\sin^2\omega_0\cos^2\gamma)\cos^2\alpha\\ &\quad+\sin^2\omega_0\cos^2\gamma\\ &\quad-2\sin\omega_0\cos\omega_0\cos\gamma\sin\alpha\cos\alpha]+b_tE_0 \qquad (9)\end{aligned}$$

The effect of the orientations of optic axes on the light scattering can be seen in eq 8 and 9.

For the fibrils of the Model B in which γ is varying randomly with constant angle ω_0, only an average of the effective induced dipole moment with respect to γ contributes to the scattering, so that it follows that

$$\begin{aligned}&\langle(\mathbf{M}\cdot\mathbf{O})_{H_V}\rangle_{av}\\ &=(b_r-b_t)E_0\left[\frac{3\cos^2\omega_0-1}{2}\right]\sin\alpha\cos\alpha\cos\beta \qquad (10)\end{aligned}$$

and

$$\begin{aligned}&\langle(\mathbf{M}\cdot\mathbf{O})_{V_V}\rangle_{av}\\ &=(b_r-b_t)E_0\left\{\left[\frac{3\cos^2\omega_0-1}{2}\right]\cos^2\alpha\right.\\ &\quad\left.+\frac{1}{2}\sin^2\omega_0\right\}+b_tE_0 \qquad (11)\end{aligned}$$

Consequently the average values of $\langle(\mathbf{M}\cdot\mathbf{O})_{H_V}\rangle_{av}^2$ and $\langle(\mathbf{M}\cdot\mathbf{O})_{V_V}\rangle_{av}^2$ should be used for $(\mathbf{M}\cdot\mathbf{O})^2$ in eq 2 and 3 in order to calculate the H_V aud V_V scatterings from the fibrils, respectively. From eq 10 it is expected that the value of ω_0 affects only the absolute intensity of H_V scattering but not the relative intensity distributions, while from eq 11 both the absolute intensity and the relative intensity distributions are affected by the value of ω_0 for the V_V scattering.

On the other hand, for the fibrils of the Model A, the orientation of optic axes is fixed to a particular value of γ within the fibrils, but the fibrils as a whole are randomly rotated around their axes to result in randomly varying γ in macroscopic scale. In this case the intensity of scattering from the fibril depends upon $\langle(\mathbf{M}\cdot\mathbf{O})_{H_V}^2\rangle_{av}$ and $\langle(\mathbf{M}\cdot\mathbf{O})_{V_V}^2\rangle_{av}$. Thus average H_V and V_V intensities over all volumes of γ for the fibril oriented in a given direction specified α and β in space are given by substituting $\langle(\mathbf{M}\cdot\mathbf{O})_{H_V}^2\rangle_{av}$ and $\langle(\mathbf{M}\cdot\mathbf{O})_{V_V}^2\rangle_{av}$ into $(\mathbf{M}\cdot\mathbf{O})^2$ in eq 3. From eq 8 and 9, it follows that

$$\begin{aligned}&\langle(\mathbf{M}\cdot\mathbf{O})_{H_V}^2\rangle_{av}\\ &=(b_r-b_t)^2E_0^2\{[\cos^4\omega_0-\cos^2\omega_0\sin^2\omega_0\\ &\quad+(\tfrac{3}{8})\sin^4\omega_0]\sin^2\alpha\cos^2\alpha\cos^2\beta\\ &\quad+(\tfrac{1}{2})\sin^2\omega_0\cos^2\omega_0\cos^2 2\alpha\cos^2\beta\\ &\quad+(\tfrac{1}{8})\sin^4\omega_0\sin^2\alpha\sin^2\beta\\ &\quad+(\tfrac{1}{2})\sin^2\omega_0\cos^2\omega_0\cos^2\alpha\sin^2\beta\} \qquad (12)\end{aligned}$$

$$\begin{aligned}\langle(\mathbf{M}\cdot\mathbf{O})^2_{V_V}\rangle_{av} &= (b_r-b_t)^2E_0{}^2\{[\cos^4\omega_0-\sin^2\omega_0\cos^2\omega_0 \\ &+(\tfrac{3}{8})\sin^4\omega_0]\cos^4\alpha+(\tfrac{3}{8})\sin^4\omega_0 \\ &+2\sin^2\omega_0\cos^2\omega_0\sin^2\alpha\cos^2\alpha \\ &+[\cos^2\omega_0-(\tfrac{3}{4})\sin^2\omega_0]\cos^2\alpha\sin^2\omega_0\} \\ &+2(b_r-b_t)b_tE_0{}^2\left[\left(\frac{3\cos^2\omega_0-1}{2}\right)\cos^2\alpha\right. \\ &\left.+(\tfrac{1}{2})\sin^2\omega_0\right]+b_t{}^2E_0{}^2 \end{aligned} \quad (13)$$

Consequently, in contrast to the scattering from the Model B fibrils both the absolute intensities and the relative intensity distributions of H_V and V_V scatterings depend upon the angle ω_0 as previously reported for the fibrils of the Model A.[1]

From eq 2 to 7, 10, and 11, H_V and V_V scattered intensities for the fibrils of the Model B can be calculated.

$$\begin{aligned}I_{H_V} &= (1/16)K^2\pi^2L^2(b_r-b_t)^2[P_2(\cos\omega_0)]^2 \\ &\times[(35A-30B+3C)\cos^4(\theta/2)\sin^2\mu\cos^2\mu \\ &-(5A-6B+C)\cos^2(\theta/2)+(A-2B+C)] \end{aligned} \quad (14)$$

$$\begin{aligned}I_{V_V} &= (1/16)K^2\pi^2L^2(b_r-b_t)^2\{[P_2(\cos\omega_0)]^2 \\ &\times[(35A-30B+3C)\cos^4(\theta/2)\cos^4\mu \\ &-6(5A-6B+C)\cos^2(\theta/2)\cos^2\mu \\ &+3(A-2B+C)]+8P_2(\cos\omega_0)[(\tfrac{1}{2})\sin^2\omega_0+p] \\ &\times[(3B-C)\cos^2(\theta/2)\cos^2\mu-(B-C)] \\ &+8[(\tfrac{1}{2})\sin^2\omega_0+p]^2C\} \end{aligned} \quad (15)$$

where the quantities, p, A, B, and C are defined in a similar way as in a previous paper.[1]

$$p=(\alpha_\perp-\alpha_s)/(\alpha_{/\!/}-\alpha_\perp) \quad (16)$$

$$A=\frac{1}{3U^2}-\left(\frac{2U^2-1}{4U^5}\right)\sin 2U-\frac{1}{2U^4}\cos(2U) \quad (17)$$

$$B=\frac{1}{U^2}-\frac{1}{2U^3}\sin 2U \quad (18)$$

$$C=\frac{2}{U}S_i(2U)-\frac{1}{U^2}+\frac{1}{U^2}\cos(2U) \quad (19)$$

$$U=(2\pi/\lambda')L\sin(\theta/2) \quad (20)$$

$P_2(X)$ is the second order Legendre function defined by $P_2(X)=(3X^2-1)/2$, and $S_i(U)$ is the sine function defined by

$$S_i(U)=\int_0^U(\sin X)/X\,\mathrm{d}X\,.$$

λ' is wavelength of light in the medium, and the constant K related to the absolute intensity is identical to that in a previous paper.

As expected from eq 14, the intensity distributions of the H_V scattering with respect to θ depend only upon length L of the fibrils and have a four fold symmetry with respect to the azimuthal angle μ. The H_V scattering depends only upon P_2 $(\cos\omega_0)$ in contrast to that of the previous model, Model A which depends also upon P_4 $(\cos\omega_0)$, the fourth order Legendre function as discussed in eq 6 of ref 1. Moreover, the angle ω_0 affects only the absolute intensity, which is very much in contrast to the scattering from the fibrils of the Model A in which ω_0 affects also the angular distributions with respect to μ, as discussed in detail in eq 6 of ref 1.

On the other hand, V_V scattering intensity distributions depend upon the angle ω_0 as well as the length L as seen in eq 15. As in the previous case, V_V scattering is composed of the terms with circular symmetry, two-fold and four-fold symmetries with respect to μ. A difference of V_V scatterings from two types of fibrils, the Model A and the Model B, may be seen by comparing eq 15 with eq 7 of ref 1. The scattering from the fibrils of the Model B depends only upon P_2 term, while that from the fibrils of the Model A depends upon P_4 term as well.

The length of the fibrils of the Model B can be estimated by utilizing H_V scattering intensity distributions with respect to θ at $\mu=0°$ and $\mu=45°$ (eq 14),

$$\begin{aligned}&(I_{H_V})_{\mu=45°}-(I_{H_V})_{\mu=0°} \\ &=K_3[P_2(\cos\omega_0)]^2(35A-30B+3C)\end{aligned} \quad (21)$$

From eq 21 which is valid for small θ, the length of the fibrils is determined by using the relationship

$$U_{max}=4.80=(2\pi L/\lambda')\sin(\theta_{max}/2) \quad (22)$$

The relationship is exactly identical to that for the Model A.[1]

NUMERICAL CALCULATIONS

The results of numerical calculations are shown in Figures 2, 4, and 5 for Model B. The calculations were carried out for a value of L specified by $L/\lambda'=40$ as in the previous calculations for the Model A.

Figure 2 shows the result of H_V scattering for a particular value of ω_0 for which P_2 (cos ω_0) becomes unity. The angular dependences of the H_V pattern are independent of ω_0. The absolute intensity of the pattern is maximum for $\omega_0=0°$ and becomes zero at ω_0 satisfying $P_2(\cos \omega_0)=0$ as which the fibrils become optically isotropic.

The effect of ω_0 on the H_V patterns is markedly different from that on the H_V patterns for the Model A as shown in Figure 3 (cited from Figure 9 of ref 1) in which the H_V patterns were shown

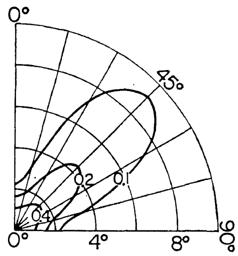

Figure 2. H_V scattering pattern from the fibrils of Model B.

to exhibit ×-type scattering with maximum intensities at odd multiples of $\mu=45°$ for ω_0 from 0° to 30°33′, (+)-type scattering with maximum intensities at $\mu=\pm 0°$ and $\pm 90°$ for ω_0 from 30°33′ to 70°07′ and the ×-type scattering for ω_0 from 70°07′ to 90°.

In contrast to the H_V scattering, the angular dependences of the V_V scattering depend upon ω_0 even for Model B as shown in Figures 4 and 5 for the value of $p=-0.27$ and 0.0, respectively, in which the patterns for the Model A and B are drawn by broken and solid lines, respectively.

The patterns drawn by the broken lines are identical to those shown in Figures 10 and 11 in a previous paper.[1] The differences of V_V patterns for Model A and Model B are due to the differences in the relative contribution of orientation and density fluctuations, so that the differences become smaller for values of p for which the density contributions become larger.

Values listed in brackets (a, b) beneath each scattering patterns are those indicating relative

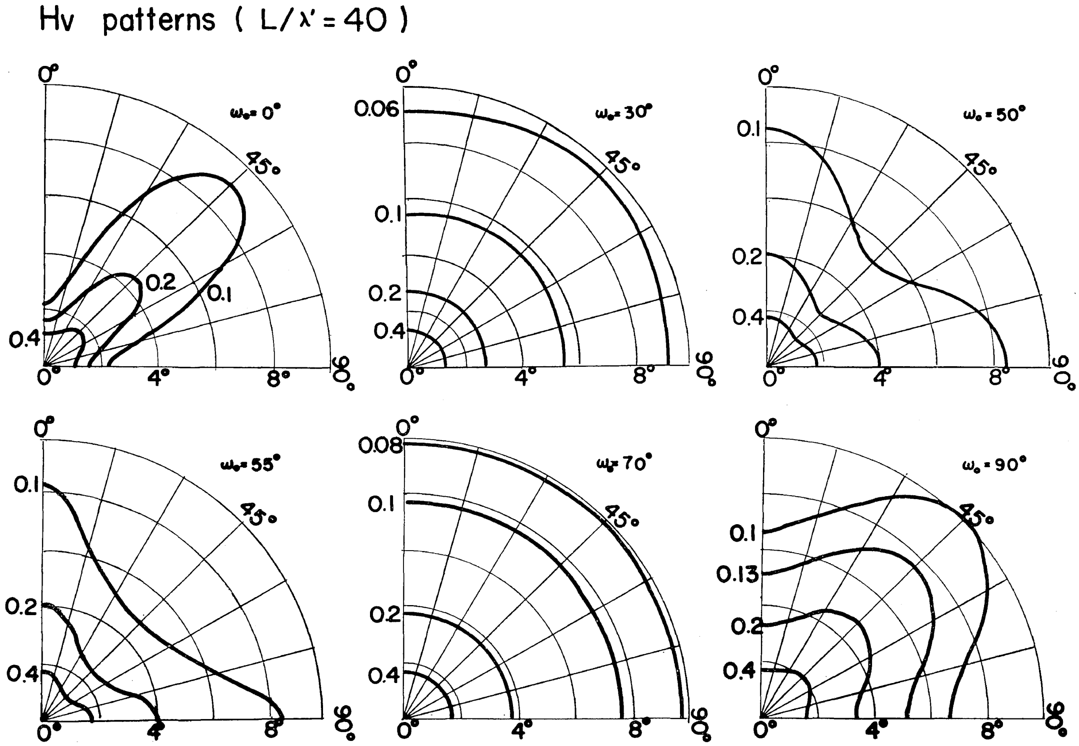

Figure 3. H_V scattering patterns from the fibrils of Model A for various values of ω_0. The patterns are identical to those of Figure 9 of ref 1.

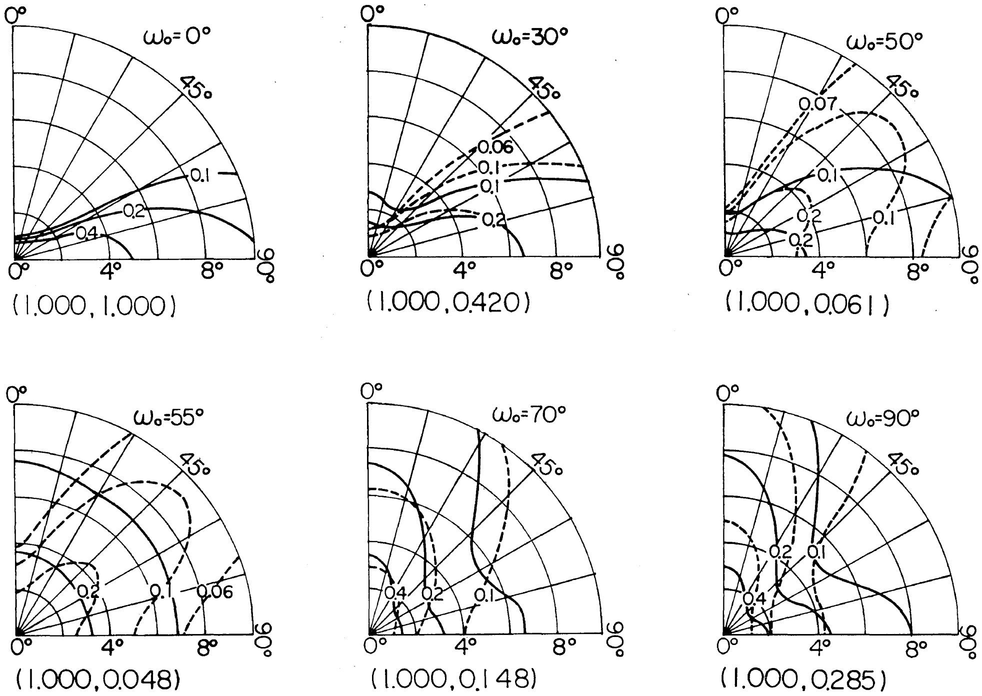

Figure 4. V_V scattering patterns from the fibrils of Model A (broken lines) and Model B (solid lines) for $p=-0.27$ and for various values of ω_0.

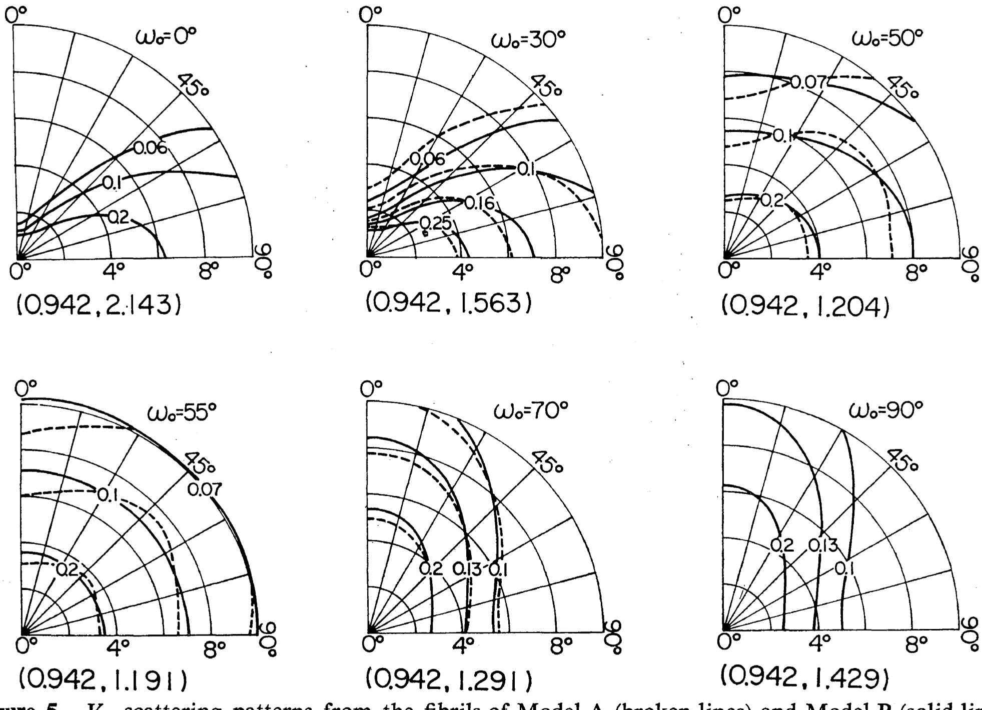

Figure 5. V_V scattering patterns from the fibrils of Model A (broken lines) and Model B (solid lines) for $p=0$ and for various values of ω_0.

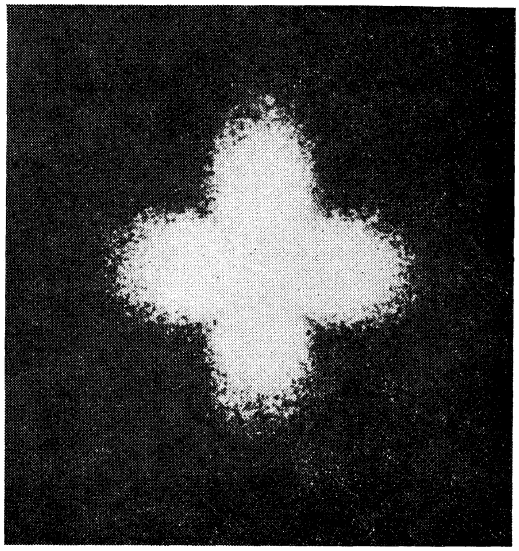

Figure 6. H_V scattering patterns from RC-1 collagen films.

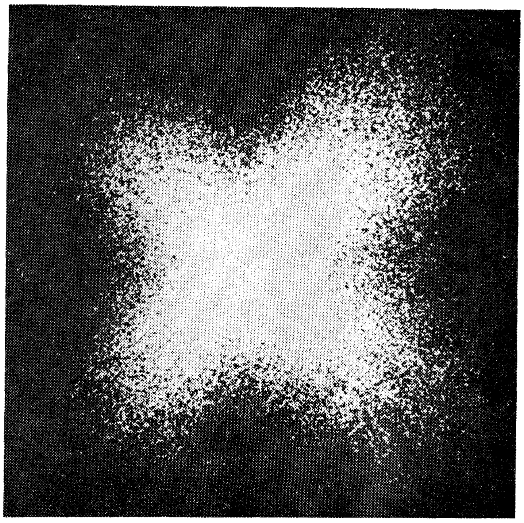

Figure 7. H_V scattering patterns from the poly(tetrafluorethylene) films.

intensity changes upon changing the values of ω_0 for models, A and B, respectively when intensity levels of the V_V pattern for $\omega_0=0°$ and $p=-0.27$ are chosen as unity.

In Figure 6, H_V scattering pattern is shown for the denatured collagen films previously studied.[1] By comparing Figures 2 and 3 with Figure 6, the +-type scattering must be interpreted as arising from the fibrils of Model A rather than those of Model B. Consequently, for any fibrils which give the (+)-type scatterings the optic axes must be essentially oriented in a special plane of the fibrils, keeping γ constant within the fibrils and ω_0 constant between 30°33′ and 70°07′.

Thus in case of the collagen films, the tropocollagen molecules, the chain axes of which are parallel to the optic axes may be considered to be stacked side-by-side with a polar angle ω_0 in the range of about 30°33′ to 70°07′ with respect to the fibrilar axes as in the fibrils of Model A rather than being stacked cylindrically symmetrically around the fibrilar axes as in the fibrils of Model B.

In Figure 7, the ×-type H_V scattering is shown for poly(tetrafluoroethylene) films. The films were made by heat treating the dispersion for 2 hr at 412°C and subsequent natural cooling to room temperature.

The ×-type scattering pattern may arise either from the fibrils of Model A with the polar angle ω_0 in the range characteristic to the scattering or from the fibrils of Model B, so that the problem arises as to the proper choice of models. Although there are small differences in the angular dependences of H_V and V_V scattering from the fibrils of Models A and B, the differences are modified by other factors such as sized distribution, internal heterogeneities and finite lateral dimensions of the fibrils.[12,13] Consequently, in this case it is not feasible to determine uniquely the model from light scattering experiment alone. The determination of the model from V_V scattering experiments requires a knowledge of α_s which is usually difficult to obtain.

CONCLUSIONS

H_V and V_V light scatterings from systems with two types of anisotropic fibrils are compared. In fibrils of type A, the principal optic axis is oriented in a special plane of the fibril indicated by azimuthal angle γ and with constant polar angle ω_0 (Figure 1), while in fibrils of type B, the optic axis orients cylindrically symmetrically around the fibril axis. By comparing the calculated results for the models with experimental patterns, it is shown that the previously observed (+)-type H_V scatterings from the collagen films and from other crystalline polymer films must be scatterings from type A fibrils. This may indicate, in case of the collagen films, that the tropocollagen molecules constituting the fibrils are packed parallel to the others with polar angle ω_0 in a range about 30°33′ to 70°07′ in a special plane of the fibrils. However for the fibrils which give the $\times$-type H_V scattering patterns it is difficult to select a proper model by light-scattering experiment alone.

REFERENCES

1. M. Moritani, N. Hayashi, A. Utsuo, and H. Kawai, *Polymer J.*, **2**, 74 (1971).
2. R. S. Stein and M. B. Rhodes, *J. Appl. Phys.*, **31**, 1873 (1960).
3. M. B. Rhodes and R. S. Stein, *ibid.*, **39**, 4903 (1968).
4. N. Hayashi, Y. Murakami, M. Moritani, T. Hashimoto and H. Kawai, *Polymer J.* in press.
5. J. Borch, R. Muggli, A. Sarko, and R. H. Marchessault, *J. Appl. Phys.*, **42**, 4570 (1971).
6. R. J. Samuels, *J. Polym. Sci., Part A-2*, **7**, 1197 (1969),
7. J. Borch and R. H. Marchessault, *ibid.*, *Part C*, **28**, 153 (1969).
8. J. C. W. Chien and E. P. Chang, to be published.
9. A. Rich and F. H. C. Crick, *J. Mol. Biol.*, **3**, 483 (1961).
10. H. C. van de Hulst, "Light Scattering by Small Particles", John Wiley and Sons, Inc., New York, N. Y., 1957.
11. T. Hashimoto, N. Hayashi, Y. Murakami and H. Kawai, to be submitted to *Polymer J.*
12. N. Hayashi and H. Kawai, *ibid.*, **3**, 140 (1972).
13. M. Matsuo, S. Nomura, T. Hashimoto and H. Kawai, to be submitted to *Polymer J.*