EFFECT OF ORIENTATION OF THE OPTICAL AXIS OF A BIREFRINGENT MATERIAL ON BIREFRINGENCE VALUES

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The formalism of Mueller's matrices has been used to determine the effect of orientation of the fast axis of an elliptical retarder replacing a birefringent medium with optical activity on the intensity of the transmitted light in two experimental arrangements. A relationship allowing the determination of retardation values for a general position of the fast axis on Poincaré's sphere has been derived and relation between the linear, circular and elliptical retarder has been determined.

Measurements of the molecular orientation of materials are important from both the theoretical and practical standpoints. The dependence of orientation on parameters such as temperature, time, degree of swelling *etc.* allows a deeper insight into the molecular behaviour of materials. Orientation considerably affects mechanical, optical, electrical and other properties of polymers. Molecular orientation influences birefringence values; the sign and magnitude of birefringence depend on the structure of the material[1]. The birefringence method can be employed for studying materials exhibiting birefringence as a consequence of their anisotropy, and also compounds in which birefringence appears only as a result of external effects (mechanical tensile or compressive stress, orientation due to electromagnetic or hydrodynamic field *etc.*)

The method outlined in this paper is an attempt to solve the problem of mutual orientation of a polarizer, analyzer and a principal direction of a birefringent material (fast direction) on the intensity of light transmitted through a system exhibiting linear and circular birefringence.

THEORETICAL

If light passes through a birefringent medium, a phase difference (optical retardation) arises between the two polarization vectors. Let us regard the birefringent uniaxial medium as an elliptical retarder (compensator) and determine the relationship between birefringence in the case of a general position of the elliptical retarder and the measured intensity of polarized light transmitted in two experimental arrangements. We shall use the formalism of Mueller's matrices[2] characterizing each optical element of the experimental arrangement by a matrix of the 4×4 type, and determine the explicit form of the matrix for the elliptical retarder. The phenomenological form of the matrix for the elliptical retarder will serve as a basis[2]. Substitution and a simple rearrangement gives

$$\mathbf{W} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 + (\boldsymbol{M}^2 - \boldsymbol{C}^2 - \boldsymbol{S}^2 - 1)\sin^2 \Delta/2 & 2\boldsymbol{MC}\sin^2(\Delta/2) + \boldsymbol{S}\sin\Delta & -2\boldsymbol{MS}\sin^2(\Delta/2) - \boldsymbol{C}\sin\Delta \\ 0 & 2\boldsymbol{MC}\sin^2(\Delta/2) - \boldsymbol{S}\sin\Delta & 1 - (\boldsymbol{M}^2 - \boldsymbol{C}^2 + \boldsymbol{S}^2 + 1)\sin^2\Delta/2 & \boldsymbol{M}\sin\Delta - \boldsymbol{CS}\sin^2\Delta/2 \\ 0 & -2\boldsymbol{MS}\sin^2(\Delta/2) + \boldsymbol{C}\sin\Delta & -\boldsymbol{M}\sin\Delta - \boldsymbol{CS}\sin^2\Delta/2 & 1 - (\boldsymbol{M}^2 + \boldsymbol{C}^2 - \boldsymbol{S}^2 + 1)\sin^2\Delta/2 \end{pmatrix} \quad (1)$$

$\boldsymbol{M}$, $\boldsymbol{C}$, $\boldsymbol{S}$ are Stokes' parameters of the normalized fast eigenvector of the retarder, Δ is retardation in rads or degrees. Explicit relationships for the elements w_{ik} of the matrix of the elliptical retarder are obtained by using relationships for the elements of the $\boldsymbol{S}$ vector and angles λ, ω characterizing the position of the representing point on Poincaré's sphere[2]

$$\boldsymbol{M} = \cos 2\omega \cos 2\lambda\,, \quad \boldsymbol{C} = \cos 2\omega \sin 2\lambda\,, \quad \boldsymbol{S} = \sin 2\omega\,. \quad (2)$$

One should bear in mind that this choice (Fig. 1) of the position of the retarder on Poincaré's sphere affects the retardation value Δ. The specific retardation of the elliptical retarder is determined by the sum of contributions of linear and circular birefringence. The total retardation of two mutually orthogonal elliptically polarized waves can be written as[3]

$$\Delta = d(4a^2 + b^2)^{1/2}\,, \quad (3)$$

where d is thickness of the birefringent medium, $a = (\pi/\lambda_0)(n_+ - n_-)$; n_+, n_- are refractive indices of the right and left circularly polarized waves, $b = (2\pi/\lambda_0)\,.\,(n_{01} - n_{02})$; n_{01}, n_{02} are refractive indices of the ordinary and extraordinary beam respectively, and λ_0 is the light wavelength.

If the elliptical retarder is situated in a position characterized by the angles λ, 2ω (Fig. 1) between crossed polarizes, *i.e.* polarizers $\mathbf{P}(\alpha)$ with the orientation angle α (angle between the transmitting direction of the polarizer and the horizontal axis) and the analyzer $\mathbf{A}(\beta)$ with the orientation angle $\beta = \alpha + 90$, we obtain, by applying the relationship characterizing this experimental arrangement[4],

$$\boldsymbol{S}' = \mathbf{A}(\alpha + 90)\,\mathbf{W}(\lambda, \omega, \Delta)\,\mathbf{P}(\alpha)\,\boldsymbol{S}\,. \quad (4)$$

It holds then for the intensity $I'_{\perp}$ (first component of Stokes' vector)

$$I'_{\perp} = (I_0/4)\left[1 - \mathbf{w}_{22}C_2^2 - (\mathbf{w}_{23} + \mathbf{w}_{32})\, S_2C_2 - \mathbf{w}_{33}S_2^2\right], \tag{5}$$

where $\mathbf{w}_{ik}$ are components of the matrix of the elliptical retarder $\mathbf{W}$, $S_2 = \sin 2\alpha$, $C_2 = \cos 2\alpha$. In a similar way we shall determine the intensity $I'_{\parallel}$ of light transmitted by the system with the polarizer and the analyzer situated parallel to each other, *i.e.* for the arrangement

$$\mathbf{S}' = \mathbf{A}(\alpha)\, \mathbf{W}(\lambda, \omega, \Delta)\, \mathbf{P}(\alpha)\, \mathbf{S}\,. \tag{6}$$

By substituting into relationship (*6*) we obtain

$$I'_{\parallel} = (I_0/4)\left[1 + \mathbf{w}_{22}C_2^2 + (\mathbf{w}_{23} + \mathbf{w}_{32})\, S_2C_2 + \mathbf{w}_{33}S_2^2\right]. \tag{7}$$

If we choose vertical position of the input polarizer, *i.e.* position $\alpha = 90°$, we have in Eq. (*5*) $C_2^2 = 1$, $S_2^2 = 0$, and for the intensity of light transmitted by the system we obtain

$$I'_{\perp,\mathrm{v}} = (I_0/4)\,(1 - \mathbf{w}_{22})\,. \tag{8}$$

Substitution of relationships (*1*) and (*2*) into (*8*) and simple rearrangements give

$$I'_{\perp,\mathrm{v}} = (I_0/4)\sin^2(\Delta/2)\left[2 - \cos^2 2\omega(\cos 4\lambda + 1)\right]. \tag{9}$$

Similarly, substitution of Eqs (*1*) and (*2*) into Eq. (*7*) gives for the intensity $I'_{\parallel}$ of light transmitted with parallel polarizers

$$I'_{\parallel,\mathrm{v}} = (I_0/4)\left[2\cos^2(\Delta/2) + \sin^2(\Delta/2)\cos^2 2\omega(\cos 4\lambda + 1)\right]. \tag{10}$$

DISCUSSION

Relationships (*9*) and (*10*) determine the intensity of light transmitted by a system consisting of the polarizer, elliptical retarder, analyzer for a parallel and a perpendicular position of the polarizer and the analyzer. The position of the input polarizer is vertical, *i.e.* in the direction of the *y*-axis. In the case of a general position of the optical elements used it is necessary to apply relationships (*5*) and (*7*) and to rearrange them in a similar way. The total dependence of $I'_{\perp,\mathrm{v}}$ on the position of the fast axis is shown in Fig. 2. Let us notice the extreme values of the expression $I'_{\perp,\mathrm{v}}$ as a function of λ. If the fast axis lies in a plane perpendicular to the incident radiation ($\omega = 0$), a minimum appears at the position $\lambda = 0$, and $I'_{\perp,\mathrm{v}} = 0$. In this position the elliptical retarder is reduced to a linear one, with its eigenvector in positions **H** and **V**. At the same time, in Eq. (3) $a = 0$, and the measured retardation $\Delta = b$. Birefringence is then suitably measured at a position $\lambda = \pi/4$, *i.e.* a position with the fast axis bisecting the angle between the crossed polarizers. For this position $I'_{\perp,V}$ is maximum. If we want to measure retardation by changing the position of the retarder as a fixed position of crossed polarizers, it follows from Eq. (9) that the suitable positions are those symmetrical around the angle $\pi/8$, *i.e.* positions $(\pi/8) + \varepsilon$ and $(\pi/8) - \varepsilon$. If the intensities measured in these positions are denoted by i_1, i_2,

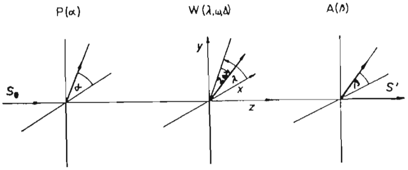

FIG. 1

Schematic View of the Experimental Arrangement

$\boldsymbol{S}_0$ Stokes' vector of incident light, $\boldsymbol{P}(\alpha)$ polarizer with the transmitting direction at an angle α with the horizontal axis, elliptical retarder $\boldsymbol{W}(\lambda, \omega, \Delta)$, λ is the angle between the fast axis of the retarder and the horizontal axis in a plane perpendicular to the incident beam in the direction $\boldsymbol{S}_0$, 2ω is the angle of deviation of the fast axis of the retarder from a plane perpendicular to $\boldsymbol{S}_0$, analyzer $\boldsymbol{A}(\beta)$ with the transmitting direction at an angle β with the horizontal axis.

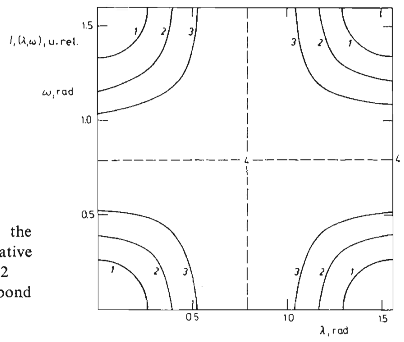

FIG. 2

Dependence of the Intensity $I_{\perp,V}$ on the Orientation of the Fast Axis in Relative Units of the Constant $A = (I_0/4) \sin^2 \Delta/2$

Curves of the same intensity correspond to *1* 0·5 A, *2* 1·0 A, *3* 1·5 A, *4* 2 A.

we have $(i_1 + i_2) = (I_0/4) \sin^2 \Delta/2$ irrespective of the absolute magnitude of ε. If the fast axis is oriented in the direction of light propagation, the elliptical retarder behaves as a circular retarder and rotates the plane of linearly polarized light depending on the magnitude of Δ. In this position in Eq. (3) $b = 0$, and the measured retardation is $\Delta = 2a$. It also follows from the relationships derived above that certain arrangements of the linear retarder may act similarly to the elliptical retarder. Let us consider *e.g.* a linear retarder at a small angle $\pm\alpha$ with the horizontal axis, which corresponds to the distribution of the orientation of the optical axes of the system in the orientating field around the axis of this field. We shall obtain for the intensity of light transmitted through the system $I'_{\perp,\mathrm{V}}(\alpha, \omega = 0) = 2I_0\alpha^2 \sin^2 \Delta/2$. Relationship (9) gives, for an elliptical retarder with a small deviation of the fast axis from the plane perpendicular to the incident light, $I'_{\perp,\mathrm{V}}(\lambda = 0, \omega) = 2I_0\omega^2 \,.\, \sin^2 \Delta/2$. Consequently, the fact that the intensity is non-zero for various orientations of the retarder does not allow conclusions about the ellipticity of the retarder without a preliminary examination of the exact orientation of the fast axis. If the ellipticity is defined as $\eta = \mathrm{tg}\,|\omega|$, the comparison with Eq. (2) gives $\mathbf{S} = (2\eta) : (1 + \eta^2)$. By using this relationship between the normalized Stokes' parameter S and ellipticity, we obtain identical relationships for the matrix of the elliptical retarder (1) and for that of the optically active medium as given by Grečušnikov and coworkers[5]. The substitution of a generally birefringent medium with an elliptical retarder for the characterization of the transmission behaviour is also justified by the finding that the total effect of the medium on the retardation of the polarized light can be reflected by shifting of the representing point determining the position of the fast eigenvector of the retarder, regardless of the fact that from the structure viewpoint partial retardations occur on many structural units, because the resulting effect of partial motions of this point can be represented by a single change from the initial to the final position.

It should be pointed out, in conclusion, that the above calculations were carried out for ideal optical elements polarizers), and do not include the effect of the boundary with different refractive indices (phase changes due to multiple boundary reflexions).

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