

## A method for calculating order parameter and determining orientation direction on polarized molecules in organic–inorganic hybrid film

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Molecular orientation in organic–inorganic hybrid films has attracted considerable attention for application in functional materials. When molecules are oriented in a certain direction in such films, optical, mechanical, or electrical anisotropy appears [1, 2]. These films can also be used as templates for aligned pores [3–7].

Various methods, such as optical absorption and electrical conductivity, can determine orientation direction by measuring the properties parallel and perpendicular to the direction. Polarized IR measurement is one such method [8]. In this method, when a molecule has a functional group parallel or perpendicular to the molecular long axis, the group's absorption coefficient for polarized light differs from that in the sample direction. If there is a uniaxial group that absorbs IR, the IR absorbance will be highest when the polarized direction is identical to the group's expansion and contraction directions. When the polarizing plate or the sample is rotated, the absorbance will change.

If the orientation direction is perpendicular to the surface, the anisotropy of absorbance is not observed when incident polarized light is perpendicular to the face. In such a case, when the sample is tilted against the light, optical anisotropy is observed.

If the orientation direction is tilted from the perpendicular direction, the optical anisotropy is changed from the observing direction. The orientation direction can be obtained from measurements of several sets of absorbance ratios from several directions. This paper discusses the method of calculating the order parameter and determining the orientation direction.

For the theoretical calculation, we consider a uniaxial orientation of molecules here. The order parameter,  $S$ , is expressed as

$$S = \frac{1}{2}(3 \langle \cos^2 \theta \rangle - 1). \quad (1)$$

Here,  $\theta$  is the angle between each molecular axis and the orientation vector, and  $\langle \rangle$  denotes the mean value. The  $\langle \cos^2 \theta \rangle$  value is represented by molecular axis distribution  $f(\theta)$ ,

$$\langle \cos^2 \theta \rangle = \frac{\int_0^\pi f(\theta) \cdot \cos^2 \theta \cdot 2\pi \sin \theta d\theta}{4\pi}. \quad (2)$$

When all molecules are ordered in the same direction,  $S$  becomes 1. If the molecular directions are totally random,  $f(\theta) = 1$  and  $\langle \cos^2 \theta \rangle = 1/3$ , then  $S$  becomes 0. When  $S$  is not zero, IR dichromatism will appear. The absorbance of polarized IR for a bond parallel to the molecular long axis becomes an index of orientation.

Let's consider a sample coordination  $xyz$  and molecular coordination  $XYZ$ . The sample plane for film shape is  $yz$  in this case. When the distribution of molecular axes tends to turn in the  $X$  direction as shown in Fig. 1, the distribution can be represented as an ellipsoid, like a rugby ball, as shown in Fig. 2. When the long axis is  $X$ , the ellipsoid can be expressed as

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$$(X/a)^2 + Y^2 + Z^2 = c^2.$$

Here,  $a$  is the long radius and  $c$  is a constant. Length  $r$ , from the center to a point on the ellipsoid surface, represents the relative probability that the molecular axis points in the direction. The ellipsoid can be represented by polar coordinates with  $r$ ,  $\theta$ , and  $\phi$ , as shown in Fig. 2. Since  $X = r \cos \theta$ ,  $Y = r \sin \theta \cos \phi$ ,  $Z = r \sin \theta \sin \phi$ , and  $\sqrt{(Y^2 + Z^2)} = r \sin \theta$ ,

$$(r/a)^2 \cos^2 \theta + r^2 \sin^2 \theta = c^2$$

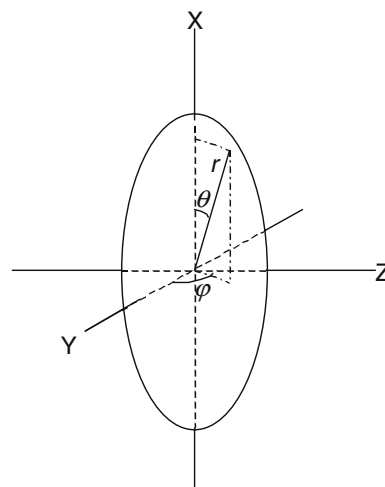
and the relative probability  $r$  is

$$r = \frac{ac}{\sqrt{\cos^2 \theta + a^2 \sin^2 \theta}}.$$

In case the mean molecular axis,  $X$ , is parallel to the  $y$  axis, the intensity of the absorbance of polarized IR,  $I$ , becomes proportional to the mean square of each component. Hence  $I_y$  is expressed as

$$\begin{aligned} I_y &= k \langle r \cos^2 \theta \rangle / \langle r \rangle \\ &= k \cdot \frac{\int_0^\pi r \cos^2 \theta \cdot 2\pi \sin \theta d\theta}{4\pi} \cdot \frac{1}{\langle r \rangle} \\ &= \frac{k}{2} \cdot \int_0^\pi \frac{ac}{\sqrt{\cos^2 \theta + a^2 \sin^2 \theta}} \cos^2 \theta \sin \theta d\theta \cdot \frac{1}{\langle r \rangle} \end{aligned} \tag{3}$$

here  $k$  is a constant.  $I_z$ , the component perpendicular to the  $X$  direction, becomes



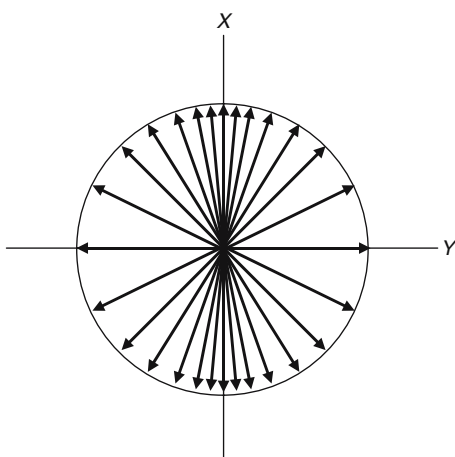
**Fig. 2** The relative probability distribution of the direction of molecular axes shown in Fig. 1. The ellipsoid is represented by polar coordinates with  $r$ ,  $\theta$ , and  $\phi$ . Length  $r$  represents the relative probability that the molecular axis points in the direction

$$\begin{aligned} I_z &= k \langle r(\sin \theta \sin \phi)^2 \rangle / \langle r \rangle \\ &= k \cdot \frac{\int_0^{2\pi} \int_0^\pi r \sin^2 \theta \cdot \cos^2 \phi \cdot 2\pi \sin \theta d\theta d\phi}{2\pi \cdot 4\pi} \cdot \frac{1}{\langle r \rangle} \\ &= \frac{k}{4\pi} \cdot \int_0^{2\pi} \cos^2 \phi d\phi \int_0^\pi r \sin^2 \theta \cdot \sin \theta d\theta \cdot \frac{1}{\langle r \rangle} \\ &= \frac{k}{4\pi} \cdot \pi \int_0^\pi r \sin^2 \theta \cdot \sin \theta d\theta \cdot \frac{1}{\langle r \rangle} \\ &= \frac{k}{4} \cdot \int_0^\pi \frac{ac}{\sqrt{\cos^2 \theta + a^2 \sin^2 \theta}} (1 - \cos^2 \theta) \sin \theta d\theta \cdot \frac{1}{\langle r \rangle}. \end{aligned} \tag{4}$$

From (3), (4), and (1), the intensity ratio of the absorbance of polarized IR,  $I_y/I_z$ , becomes

$$\frac{I_y}{I_z} = \frac{\langle \cos^2 \theta \rangle}{\langle \sin^2 \theta \cdot \sin^2 \phi \rangle} = \frac{\langle \cos^2 \theta \rangle}{(1 - \langle \cos^2 \theta \rangle)/2} = \frac{1 + 2S}{1 - S}. \tag{5}$$

When the mean molecular axis,  $X$ , is perpendicular to the  $yz$  plane, the intensity ratio of the absorbance of polarized IR,  $I_y/I_z$ , becomes unity and dichromatism cannot be observed. Here, let's consider  $x'y'z'$  coordination, which is based on the polarized light. If the sample is tilted from incident light with angle  $\eta$  on the  $xy$  plane, the absorbance observed from the  $y'$  direction becomes



**Fig. 1** Distribution scheme of molecular axes for partially uniaxially oriented material. The  $z$  axis is perpendicular to the figure and is equivalent to the  $y$  axis in this case

$$I_{y'} = k[\cos^2 \eta(1 - \langle \cos^2 \theta \rangle)/2 + \sin^2 \eta \langle \cos^2 \theta \rangle] \tag{6}$$

if the refractive index in the film is unity. When the refractive index of the film is  $n$ , the angle,  $\eta$ , between the  $x$  axis and the incident light in the film is represented as

$$\sin \eta = \sin \eta' / n,$$

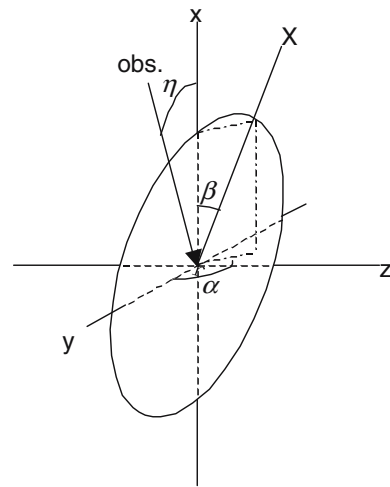
where  $\eta'$  is the tilt angle of the film and  $\eta$  contains the modification of the refractive index,  $n$ . Then

$$\begin{aligned} \frac{I_{y'}}{I_{z'}} &= \frac{\cos^2 \eta \cdot (1 - \langle \cos^2 \theta \rangle)/2 + \sin^2 \eta \cdot \langle \cos^2 \theta \rangle}{(1 - \langle \cos^2 \theta \rangle)/2} \\ &= \frac{\cos^2 \eta - \cos^2 \eta \langle \cos^2 \theta \rangle + 2 \sin^2 \eta \cdot \langle \cos^2 \theta \rangle}{(1 - \langle \cos^2 \theta \rangle)} \\ &= \frac{\cos^2 \eta - 3 \cos^2 \eta \langle \cos^2 \theta \rangle + 2 \langle \cos^2 \theta \rangle}{(1 - \langle \cos^2 \theta \rangle)} \\ &= \frac{1 + 2S - 3S \cos^2 \eta}{1 - S}. \end{aligned} \tag{7}$$

If the  $X$  direction is tilted from the  $x$  axis with angle  $\beta$  in the direction shown in Fig. 3, the point

$$\begin{pmatrix} X_1 \\ Y_1 \\ Z_1 \end{pmatrix} = \begin{pmatrix} \cos \theta_1 \\ \sin \theta_1 \cos \varphi_1 \\ \sin \theta_1 \sin \varphi_1 \end{pmatrix} \text{ on the } XYZ \text{ coordinate}$$

can be represented on the  $xyz$  coordinate as



**Fig. 3** The case of tilted direction of  $X$  from the  $x$  axis with angle  $\beta$ . The tilt direction  $\alpha$  represents the rotated angle in polar coordinates.  $\eta$  denotes the observed direction for the polarized light

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & \sin \alpha \\ 0 & -\sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} \cos \beta & -\sin \beta & 0 \\ \sin \beta & \cos \beta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X_1 \\ Y_1 \\ Z_1 \end{pmatrix}.$$

When this tilted ellipsoid is observed from  $\eta$  direction on the  $xy$  plane, the point is expressed as

$$\begin{pmatrix} x'_1 \\ y'_1 \\ z'_1 \end{pmatrix} = \begin{pmatrix} \cos \eta & -\sin \eta & 0 \\ \sin \eta & \cos \eta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}.$$

In such a case,  $I_{z'}$  becomes

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$$\begin{aligned} I_{z'} &= k \langle rz'^2 \rangle / \langle r \rangle \\ &= \frac{k}{4\pi} \int_0^\pi \int_0^{2\pi} rz'^2 \sin \theta d\varphi d\theta \cdot \frac{1}{\langle r \rangle} \\ &= \frac{k}{4\pi} \int_0^\pi \int_0^{2\pi} r[-\sin \alpha(\sin \beta \cos \theta + \cos \beta \sin \theta \cos \varphi) + \cos \alpha \sin \theta \sin \varphi]^2 \sin \theta d\varphi d\theta \cdot \frac{1}{\langle r \rangle} \\ &= \frac{k}{4} \int_0^\pi r(2 \sin^2 \alpha \sin^2 \beta \cos^2 \theta + \sin^2 \alpha \cos^2 \beta \sin^2 \theta + \cos^2 \alpha \sin^2 \theta) \sin \theta d\theta \cdot \frac{1}{\langle r \rangle} \\ &= \frac{k}{4} \int_0^\pi r[2 \sin^2 \alpha \sin^2 \beta \cos^2 \theta + (\sin^2 \alpha \cos^2 \beta + \cos^2 \alpha) \sin^2 \theta] \sin \theta d\theta \cdot \frac{1}{\langle r \rangle} \\ &= k[\sin^2 \alpha \sin^2 \beta \langle \cos^2 \theta \rangle + (1 - \sin^2 \alpha \sin^2 \beta) \langle \sin^2 \theta \sin^2 \varphi \rangle]. \end{aligned} \tag{8}$$


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and  $I_{y'}$  becomes

$$\begin{aligned}
 I_{y'} &= k \langle ry'^2 \rangle / \langle r \rangle = \frac{k}{4\pi} \int_0^\pi \int_0^{2\pi} ry'^2 \sin \theta d\varphi d\theta \cdot \frac{1}{\langle r \rangle} = \frac{k}{4\pi} \int_0^\pi \int_0^{2\pi} r [\sin \eta (\cos \beta \cos \theta - \sin \beta \sin \theta \cos \varphi) \\
 &\quad + \cos \eta \{ \cos \alpha (\sin \beta \cos \theta + \cos \beta \sin \theta \cos \varphi) + \sin \alpha \sin \theta \sin \varphi \}]^2 \sin \theta d\varphi d\theta \cdot \frac{1}{\langle r \rangle} \\
 &= \frac{k}{4} \int_0^\pi r [2 \sin^2 \eta \cos^2 \beta \cos^2 \theta + \sin^2 \eta \sin^2 \beta \sin^2 \theta + 4 \sin \eta \cos \eta \cos \alpha \sin \beta \cos \beta \cos^2 \theta - 2 \sin \eta \cos \eta \cos \alpha \sin \beta \cos \beta \sin^2 \theta \\
 &\quad + 2 \cos^2 \eta \cos^2 \alpha \sin^2 \beta \cos^2 \theta + \cos^2 \eta \cos^2 \alpha \cos^2 \beta \sin^2 \theta + \cos^2 \eta \sin^2 \alpha \sin^2 \theta] \sin \theta d\theta \cdot \frac{1}{\langle r \rangle} \\
 &= \frac{k}{4} \int_0^\pi r [2 (\sin \eta \cos \beta + \cos \eta \cos \alpha \sin \beta)^2 \cos^2 \theta + \{ (\sin \eta \sin \beta - \cos \eta \cos \alpha \cos \beta)^2 + \cos^2 \eta \sin^2 \alpha \} \sin^2 \theta] \sin \theta d\theta \cdot \frac{1}{\langle r \rangle} \\
 &= k [(\sin \eta \cos \beta + \cos \eta \cos \alpha \sin \beta)^2 \langle \cos^2 \theta \rangle + \{ (\sin \eta \sin \beta - \cos \eta \cos \alpha \cos \beta)^2 + \cos^2 \eta \sin^2 \alpha \} \langle \sin^2 \theta \sin^2 \varphi \rangle]
 \end{aligned} \tag{9}$$

The intensity ratio,  $R$ , becomes

$$\begin{aligned}
 \frac{I_y}{I_z} \equiv R &= \frac{(\sin \eta \cos \beta + \cos \eta \cos \alpha \sin \beta)^2 \cdot \langle \cos^2 \theta \rangle + \{ (\sin \eta \sin \beta - \cos \eta \cos \alpha \cos \beta)^2 + \cos^2 \eta \sin^2 \alpha \} \cdot (1 - \langle \cos^2 \theta \rangle) / 2}{\sin^2 \alpha \sin^2 \beta \langle \cos^2 \theta \rangle + (1 - \sin^2 \alpha \sin^2 \beta) (1 - \langle \cos^2 \theta \rangle) / 2} \\
 &= \frac{\{ 3 (\sin \eta \cos \beta + \cos \eta \cos \alpha \sin \beta)^2 - 1 \} \cdot \langle \cos^2 \theta \rangle + \{ (\sin \eta \sin \beta \cos \alpha - \cos \eta \cos \beta)^2 + \sin^2 \alpha \sin^2 \beta \}}{(3 \sin^2 \alpha \sin^2 \beta - 1) \langle \cos^2 \theta \rangle + (1 - \sin^2 \alpha \sin^2 \beta)}
 \end{aligned} \tag{10}$$

and then,

$$\langle \cos^2 \theta \rangle = \frac{R(1 - \sin^2 \alpha \sin^2 \beta) - (\cos \eta \cos \beta - \sin \eta \cos \alpha \sin \beta)^2 - \sin^2 \alpha \sin^2 \beta}{R(1 - 3 \sin^2 \alpha \sin^2 \beta) + 3(\sin \eta \cos \beta + \cos \eta \cos \alpha \sin \beta)^2 - 1}. \tag{11}$$

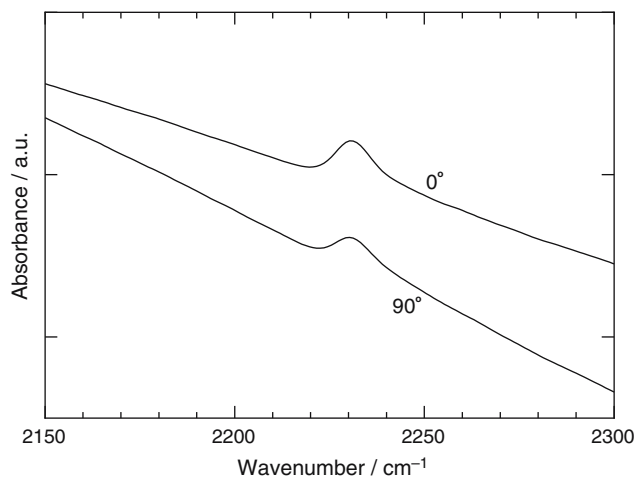
From equation (1),

$$S = \frac{R - 1}{R(1 - 3 \sin^2 \alpha \sin^2 \beta) + 3(\sin \eta \cos \beta + \cos \eta \cos \alpha \sin \beta)^2 - 1}. \tag{12}$$

**Table 1** Example of molecular orientation by magnetic field

		$\alpha'-\eta'$ / degree						$S$	$\beta$	$\alpha$
		0–0	0–30	0–50	180–30	90–30	45–0			
A	Exptl.	1.00	1.03	1.30	1.03	1.02	1.00	0.22	–11.5	101.1
	Calc.	0.97	1.09	1.23	1.05	1.02	0.99			
B	Exptl.	1.48	1.40	1.15	1.31	0.63	0.91	0.16	80.4	173.6
	Calc.	1.52	1.40	1.29	1.52	0.66	0.91			

The magnetic field was applied to the normal of the surface for sample A and was horizontally parallel to the surface for B. Peak ratios were measured with several sample rotation angles,  $\alpha'$ , and sample tilt angles,  $\eta'$ , as shown in the table. The first line for each sample shows the experimental peak ratios, and the second line shows the calculated ratios from obtained  $\alpha$ ,  $\beta$ , and order parameter  $S$



**Fig. 4** An example of polarized IR measurement results. The tilt angle  $\eta$  was  $30^\circ$ . The polarized light of  $0^\circ$  faces the  $xy$  plane and that of  $90^\circ$  faces the  $xz$  plane. The intensity ratio,  $R$ , of the absorbance of polarized IR,  $I_y/I_z$ , was calculated from each peak height.  $R$  was 1.40 in this case

$\alpha$  can be changed to  $\alpha + \alpha'$  by rotating the sample on its face.  $S$ ,  $\alpha$ , and  $\beta$  are calculated from several sets of  $R$ ,  $\eta'$ , and  $\alpha'$  by the nonlinear least squares method.

To confirm the theoretical calculation, liquid crystals for oriented molecules were introduced in silica-based films by the sol-gel method [9]. p-cyanophenyl-p-(nonyl)benzoate was used for the molecule. Sol composition and preparation were described elsewhere [9]. A silicon single crystal substrate was dipped in the sol in a magnetic field at 1.3 T. The polarized IR peak for the cyano group at  $2,230\text{ cm}^{-1}$  was measured with FT-IR (JASCO, FT/IR-660) in a vacuum. In this apparatus, the sample arrangement against the IR light could be changed: It could be tilted against the incident light or rotated on the sample plane. The absorption peak ratios for the polarized light parallel and perpendicular to the tilt direction were recorded for several sets of tilt and rotation angles.

Figure 4 shows an example of polarized IR measurement. The peak ratio was calculated from the absorption peak height. Table 1 shows the results of the polarized IR measurement. Sample A was prepared by applying the magnetic field perpendicular to the substrate, and sample B was prepared by applying that parallel to the surface. Sample B was set parallel to the applied field direction at IR measurement to be  $\alpha' = 0$ . The refractive index was measured by an ellipsometer (J. A. Woollam, VASE) and was about 1.48 at 600 nm. If the dispersion of refractive indices in this film was similar to that in silica, the value would be 1.40 at  $4.5\ \mu\text{m}$  IR light. From this value, the incident angles,  $\eta$ , were calculated to be  $21$  and  $33^\circ$  when the tilt angles,  $\eta'$ , were  $30$  and  $50^\circ$ , respectively. The first line for each sample shows the experimental peak ratios and the  $\alpha$ ,  $\beta$ , and  $S$  values obtained from parameter fitting. The second lines are ratios calculated from these  $\alpha$ ,  $\beta$ , and  $S$  values.

On sample A,  $\beta$  was expected to be 0 if the molecules were oriented in the magnetic field direction which was applied perpendicular to the surface. On sample B,  $\beta$  and  $\alpha$  would be  $90$  and  $0$  (or  $180$ ) degrees. From Table 1, it can be seen that the experimental values were in good agreement with the expected values. This means that the organic molecules in the silica-based film were oriented to the magnetic field direction and that the calculation was valid for obtaining the orientation direction.

The calculation discussed here is limited to uniaxial distribution of the molecular orientation. If the distribution has  $\phi$  dependence in polar coordination, the calculation will be more complicated. Such a discrepancy would be observed when orientation domains formed in a sample.

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