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Preliminary Analysis of the Electronic Absorption Spectrum of a Solute in a Biaxially-Stretched Polymer Film

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A biaxially-stretched film method has been proposed and applied for the analysis of the electronic absorption spectrum of a solute embedded in a biaxially-stretched polymer film to demonstrate its usefulness. The intrinsic absorbance change of the solute on biaxial stretching was measured by a ratio (R_{bi}) of the molar absorptivity (ε_b) of the solute in the biaxially-stretched film to that (ε_i) in the nonstretched isotropic film. This $R_{bi}(=\varepsilon_b/\varepsilon_i)$ spectrum was expressed in terms of three orientation factors for three molecular axes of the solute and three absorption components (three-dimensional reduced spectra) purely polarized along the three molecular axes. Problems inherent in this method are discussed by analyzing the R_{bi} spectra of spherical, disk-like, and rod-like molecules. An approximate estimate of the three-dimensional reduced spectra of a rod-like molecule (pinacyanol, 1-ethyl-2-[3-(1-ethyl-2(1*H*)-quinolinylidene)-1-propenyl]quinolinium iodide) was obtained by an analysis of its R_{bi} spectrum by use of orientation factors with the aid of a uniaxially-stretched film method formulated by the use of an orientational distribution function.

It has been well established by several groups that the polarization of an electronic absorption band of a symmetric solute molecule can be determined by a uniaxially-stretched film technique, i.e., by an analysis of the polarized absorption spectra ($A_{/\!/}$ and $A_\perp$) of the solute molecules embedded in a uniaxially-stretched polymer film.[1-19] In general, the absorption spectrum of a symmetric molecule consists of three absorption components (A_z, A_y, A_x), which are purely polarized along the three molecular axes (long axis z, short axis y, out-of-plane axis x), i.e., three-dimensional reduced spectra. It has been shown that the spectrum of a molecule with a C_2 axis in an isotropic film can be decomposed into two absorption components (two-dimensional reduced spectra), which are polarized parallel and perpendicular to the C_2 axis, by the use of only two measured spectra, $A_{/\!/}$ and $A_\perp$, in some special cases as follows:[1,2] (1) If one of the three absorption components vanishes throughout the spectral region, the other two absorption components can be obtained. (2) For a disk-shaped molecule, the spectrum can be reduced to the in-plane (A_z+A_y) and out-of-plane (A_x) polarized absorption components. (3) For a rod-shaped molecule, the spectrum can be reduced to two absorption components polarized parallel (A_z) and perpendicular (A_y+A_x) to the z axis. (The analytical procedures to obtain the two-dimensional reduced spectra in these special cases by the Tanizaki model[7,8] are given in Appendix I, where the procedure given in Refs. 7 and 8 is extended to include the out-of-plane polarized absorption component A_x explicitly.) For many planar molecules with a C_2-axis, A_x is negligible and the uniaxially-stretched film method can determine A_z and A_y. Except for disk-shaped molecules, it is difficult to resolve A_x, which is overlapped by A_z and/or A_y, by the uniaxially-stretched film technique alone.[1,20]

It was pointed out that three-dimensional reduced spectra can be obtained if at least three independent spectra are available experimentally.[1,2] That is, a third independent spectrum is needed in addition to the measured spectra $A_{/\!/}$ and $A_\perp$ for the determination of three-dimensional reduced spectra. In this paper, we propose that the biaxially-stretched film technique can provide this third independent spectrum. Problems inherent in this technique are discussed by analyzing the spectra of spherical, disk-like, and rod-like molecules in the biaxially-stretched film by the use of orientation factors similar to those used in the TEM model.[1,2,4] As a preliminary study for demonstrating the usefulness of the biaxially-stretched film technique coupled with the uniaxially-stretched film technique, three orientation factors of a rod-like molecule (pinacyanol, PC; 1-ethyl-2-[3-(1-ethyl-2(1*H*)-quinolinylidene)-1-propenyl]quinolinium iodide) in the biaxially-stretched film and the three-dimensional reduced spectra of PC were estimated by a tentative coupling of two theories for the biaxially and uniaxially-stretched film techniques. In this tentative coupling, the theory for the biaxially-stretched film technique was formulated differently from that for the uniaxially-stretched film technique; the former was formulated after the TEM model and the latter by the Tanizaki model. Despite some objections[1,10,13] to the Tanizaki model, we believe that this model is approximately valid if the out-of-plane polarized absorption

component is properly included in the procedure to get two-dimensional reduced spectra as described in Appendix I. Our criticisms of these objections are offered in Appendix II.

Theoretical

Spectral Intensity Change of a Solute Embedded in a Biaxially-Stretched Polymer Film. For synchronous biaxial stretching of a polymer film in the Z- and Y-directions, we consider the orientational model in which the molecular planes of the solute molecules gradually become parallel to the ZY-plane (film plane), as illustrated in Fig. 1a, with an increase in the magnitude of biaxial stretching. It is reasonable to consider that, on biaxial stretching, the molecular long axis (z) of a solute approaches parallel to the film plane to a greater extent than the molecular short axis (y), the molecular out-of-plane axis (x) approaching normal to the film plane. Following this orientational model, together with the condition that the light beam enters normal to the film plane, the intensity of the out-of-plane polarized absorption band of the solute will become smaller on biaxial stretching, while that of the in-plane polarized band larger. As an experimental measure for these intensity changes, we define the experimental absorbance ratio of the measured absorbance (A_b) in the biaxially-stretched film to that (A_i) in the nonstretched film as $(R_{bi})_{exp}$. Since $A_b=\varepsilon_b c t_b$ and $A_i=\varepsilon_i c t_i$, c being the concentration of the solute in the film, it can be shown that

$$(R_{bi})_{exp}=A_b/A_i=\varepsilon_b t_b/\varepsilon_i t_i=kR_{bi}, \tag{1}$$

where

$$R_{bi}=\varepsilon_b/\varepsilon_i=\langle\mu^2\rangle_b/\langle\mu^2\rangle_i, \tag{2}$$

$$k=t_b/t_i. \tag{3}$$

In these equations, ε is the molar absorptivity, t is the thickness of the film, μ is the transition moment, and the subscript b or i stands for the value in the biaxially-stretched or nonstretched film. The symbol $\langle\ \rangle_b$ stands for an average over all the solute molecules which are anisotropically oriented in the biaxially-stretched film, and $\langle\ \rangle_i$ is an average over all solute molecules isotropically distributed in the nonstretched film. It is evident from the definition (Eq. (2)) that R_{bi} measures the intrinsic absorbance change, which is calibrated for the change in the film thickness and depends only on the orientation of solute molecules embedded in a biaxially-stretched film.

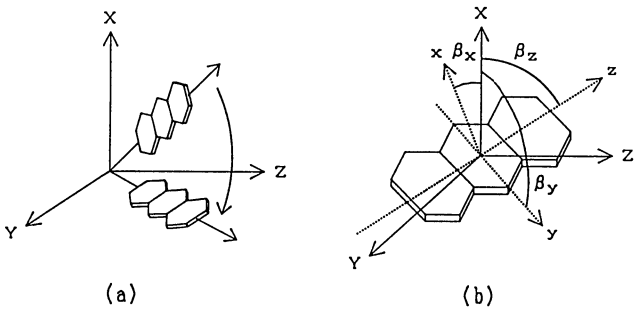

Fig. 1. (a): Orientational model of the solute molecule on biaxial stretching of the polymer film. (b): The relation between the coordinates (z,y,x) fixed to the solute molecule and those (Z,Y,X) fixed on the film.

Expression of R_{bi} in Terms of Orientation Factors. We define the orientation factors, which represent the averaged degrees of anisotropic orientations of three molecular axes (z,y,x) of solute molecules in the biaxially-stretched film, as

$$K_u=\langle\sin^2\beta_u\rangle_b \quad (u=z,y,x), \tag{4}$$

leading to the following relation,

$$K_z+K_y+K_x=2. \tag{5}$$

Here, z(long axis), y(short axis), and x(out-of-plane axis) are the coordinates fixed to the solute molecule, and Z, Y, and X (perpendicular to the film plane) on the film, their mutual relations being illustrated in Fig. 1b; β_u is the angle between the X- and u-axes. According to the orientational model considered here, the following relation also holds,

$$1\geqslant K_z\geqslant K_y\geqslant K_x\geqslant 0. \tag{6}$$

The magnitude of the averaged absorbance, which is detected by the unpolarized light propagating in the X-direction, for the solute molecules embedded in the biaxially-stretched film is expressed as

$$\langle A\rangle_b=K_zA_z+K_yA_y+K_xA_x. \tag{7}$$

Substituting $K_z=K_y=K_x=2/3$, which applies to the isotropic distribution of solute molecules in the nonstretched film, into Eq. 7, we obtain the following expression for $\langle A\rangle_i$,

$$\langle A\rangle_i=(2/3)(A_z+A_y+A_x). \tag{8}$$

Thus, R_{bi} is expressed from Eqs. 2, 7, and 8 as

$$R_{bi}=(3/2)(K_zA_z+K_yA_y+K_xA_x)/(A_z+A_y+A_x). \tag{9}$$

Therefore, R_{bi} depends on A_u ($u=z,y,x$) and K_u ($u=z,y,x$). This means that, since the A_u values depend on the degree of biaxial stretching, R_{bi} depends on the relative magnitudes of three A_u components and on the biaxial stretching ratio (R_{sb}) of the film. It can be understood by an examination of the expression for R_{bi} in Eq. 9 that R_{bi} takes a maximum value of 1.5 and a minimum of 0; the maximum value will be observed for the long-axis or in-plane polarized band when the molecular long axes or the molecular planes of all solute molecules are aligned parallel to the film plane in a biaxially-stretched film ($K_z=1$ or $K_z=K_y=1$), and the minimum for the out-of-plane polarized band when the molecular planes of all solute molecules are aligned parallel to the film plane ($K_x=0$).

Now we consider the behavior of R_{bi} in the whole spectral region under a constant value of R_{sb} for a particular solute. In this case, since the orientation factors are constant, the variation of R_{bi} in the whole

spectral region depends only on the relative magnitudes of A_u. This dependence is classified into three cases according to the geometrical shape of the solute molecule as follows.

Spherical Molecule: In this case, it follows that $A_z=A_y=A_x$ and $K_z=K_y=K_x=2/3$. These relations together with Eq. 9 result in the fact that R_{bi} is constant (=1) in the whole spectral region.

Disk-Shaped Molecule: Since $K_z=K_y$, R_{bi} is expressed as

$$R_{bi}=(3/2)\,[K_z(A_z+A_y)+K_xA_x]/(A_z+A_y+A_x). \quad (10)$$

The inclination of the disk (zy-plane) to the ZY-plane on biaxial stretching of the film yields the relation $K_z>K_x$. Coupled with this relation, Eq. 10 predicts that R_{bi} becomes smaller with an increasing ratio of the out-of-plane polarized absorption component (A_x) to the in-plane polarized component (A_z+A_y). Therefore, in the case of a disk-shaped molecule, we can qualitatively predict that a larger fraction of A_x exists in the spectral region with a smaller value of R_{bi}.

Molecule of General Shape: In this case (hereafter, a molecule of general shape means a molecule of symmetrical shape other than spherical, disk-like, and rod-like molecules), K_z, K_y, and K_x satisfy the relation $K_z>K_y>K_x$. Therefore, R_{bi} becomes smaller not only on an increasing ratio of $A_x/(A_z+A_y)$ but also on that of A_y/A_z. In the latter ratio, the fraction of A_x is considered to be constant. Thus, in contrast to the disk-shaped molecule, there is no simple criterion for predicting the fraction of A_x from the relative magnitudes of the R_{bi} values.

Determination of the Orientation Factors of a Solute in the Biaxially-Stretched Film. Orientation factors are determined in different ways depending on the shapes of the solute molecules as described below with special emphasis on a rod-shaped molecule.

Molecule of General Shape: If there exists a u-band that is purely polarized along the molecular $u(=z,y,x)$-axis, the orientation factor K_u is evaluated by Eq. 11, which is derived by a substitution of zero for the two absorption components other than A_u into Eq. 9.

$$K_u=(2/3)R_{bi}(\lambda_u). \quad (11)$$

In this equation, $R_{bi}(\lambda_u)$ stands for the R_{bi} value at the band position (λ_u) of the u-band. In general, therefore, all three orientation factors can be evaluated from Eqs. 11 and 5 if there exist two separate bands which are purely polarized along different molecular axes.

Disk-Shaped Molecule: In the case of a disk-shaped molecule, all the orientation factors can be determined only if there exists a single band which is purely in-plane or out-of-plane polarized, by substitution of the R_{bi} value at the position of this band for $R_{bi}(\lambda_u)$ in Eq. 11 and by the use of Eq. 5 with $K_z=K_y$.

Rod-Shaped Molecule: In the special case of a rod-like molecule, there are two ways to evaluate the orientation factors with the aid of a uniaxially-stretched film method formulated by the Tanizaki model:

(1) All three orientational factors can be evaluated approximately if, for example, a z-band and an in-plane polarized band with no contribution of A_x are assumed to exist at λ_z and λ_{zy}, respectively. According to this assumption, the R_{bi} value at λ_{zy} is expressed as Eq. 12, which is obtained by substitution of $A_x=0$ into Eq. 9,

$$R_{bi}(\lambda_{zy})=(3/2)\,[K_z+K_y(A_y/A_z)]/[1+(A_y/A_z)]. \quad (12)$$

As described in Case 2 of Appendix I, the A_y/A_z value at λ_{zy} for a rod-shaped molecule is obtained approximately by the uniaxially-stretched film method as $A_y/A_z=\tan^2\theta$ (here A_x is assumed to be zero), where θ is the orientation angle at λ_{zy}. Substituting the A_y/A_z value thus obtained and the K_z value evaluated from the $R_{bi}(\lambda_z)$ value for the z-band by use of Eq. 11 into Eq. 12, we obtain an approximate value of K_y, an approximate value of K_x also being obtained from Eq. 5.

(2) As an approximate evaluation of the orientation factors for a rod-like molecule, one can also evaluate an "apparent" orientation factor K' defined, for example,

$$K_yA_y+K_xA_x=K'(A_y+A_x). \quad (13).$$

It is evident from this definition that K' obeys the inequality $K_y>K'>K_x$ and K' approaches K_x as A_x increases. By use of Eq. 13, Eq. 9 can be rearranged as

$$R_{bi}(\lambda)=[K_z+K'(\lambda)(A_y+A_x)/A_z]/[1+(A_y+A_x)/A_z]. \quad (14)$$

If only a pure z-band is assumed to exist, the K' value at any $\lambda(K'(\lambda))$ is evaluated by substitution of the $R_{bi}(\lambda)$ value, the K_z value obtained from the R_{bi} value for the z-band, and the approximate $(A_y+A_x)/A_z$ value ($=\tan^2\theta$) obtained from the uniaxially-stretched film method (see Case 2 in Appendix I) into Eq. 14. The K_y value satisfies

$$K_z>K_y>K'(\lambda). \quad (15)$$

This inequality for K_y, together with Eq. 5, yields the following inequality for K_x,

$$2-2K_z>K_x>2-K_z-K'(\lambda). \quad (16)$$

Analytical Procedure to Obtain Three-Dimensional Reduced Spectra. If the values of the three orientation factors for solute molecules in the biaxially-stretched film are estimated as described above, the three-dimensional reduced spectra are obtained by the biaxially-stretched film method in a different way depending on the molecular shape of the solute as described below.

Disk-Shaped Molecule: As described in Case 1 in Appendix I, the spectrum (A_i) for a disk-shaped molecule can be reduced to the in-plane (A_z+A_y) and out-of-plane (A_x) polarized absorption components by the uniaxially-stretched film technique.[21–23] A similar reduction of the spectrum is also possible by the biaxially-stretched film method as follows. Eq. 10 is rearranged as

$$R_{bi}=(3/2)[K_z+K_xA_x/(A_z+A_y)]/[1+A_x/(A_z+A_y)]. \quad (10')$$

Substitution of the R_{bi} value at any λ and estimated values of K_z and K_y into Eq. 10′ yields the $A_x/(A_z+A_y)$ value at λ, thus enabling reduction of the spectrum (A_i) of a disk-shaped molecule to A_z+A_y and A_x.

Rod-Shaped Molecule: For a rod-like molecule, A_x and A_y have equivalent uniaxis-orientational behavior and, hence, can not be reduced separately only by the uniaxially-stretched film technique (cf. Appendix I, Case 2). This reduction, however, can be accomplished by a tentative coupling of the biaxially- and uniaxially-stretched film methods as follows. Eq. 9 is rearranged as

$$R_{bi}=(3/2)[K_z+K_y(A_y+A_x)/A_z - (K_y-K_x)(A_x/A_z)]/[1+(A_y+A_x)/A_z]. \quad (9')$$

In this equation, the $(A_y+A_x)/A_z$ value can be obtained from the uniaxially-stretched film method (cf. Appendix I, Case 2). As already described, there are two kinds of values to be assigned to the orientation factors in Eq. 9′. One is the approximate values obtained from Eq. 12 and the other is those given in the forms of the inequalities given in Eqs. 15 and 16. Substitution of the R_{bi} value obtained from the biaxially-stretched film technique into Eq. 9′ yields, therefore, two kinds of values of A_x/A_z. Solving the values of $(A_y+A_x)/A_z$ and A_x/A_z along with $A_z+A_y+A_x=A_i$ as simultaneous equations, one can obtain estimates of the three-dimensional reduced spectra (A_z,A_y,A_x); either as approximate values or as inequalities.

Molecule of General Shape: In order to obtain three-dimensional reduced spectra for a molecule of general shape, the relation between the orientation of solute molecules in the biaxially-stretched film and that in the uniaxially-stretched film must be clarified. This relation will be presented in a forthcoming paper.

Experimental

Commercial crystal violet (CV) and pinacyanol (PC) were purified by recrystallization from water and ethanol, respectively. Tris(1,10-phenanthroline)iron(II) chloride (TPI) was synthesized and recrystallized from water. The structures are shown in Fig. 2. The polymer films used were prepared from commercial poly(vinyl alcohol) (PVA) powder (degree of polymerization=1500) as described previously.[7]

The polymer films were stretched biaxially as shown schematically in Fig. 3a. Four sheet-holders were placed at the shaded areas and expanded radially, as indicated by the arrows, at constant temperature (about 80 °C). When four points with their distances of a_0 and b_0 marked on the non-stretched film were changed to the points with their distances of a_1 and b_1 on biaxial stretching (Fig. 3b), the biaxial stretching ratio R_{sb} was defined as $R_{sb}=(a_1/a_0+b_1/b_0)/2$. The upper limit of R_{sb} was about 2.3. The spectra of the non-stretched (A_i) and biaxially-stretched (A_b) sample films were calibrated by use of nonstretched and biaxially-stretched reference films, respectively. The polarized absorption spectra, $A_{/\!/}$ and $A_\perp$, which represent the absorbances measured by the polarized lights whose electric vectors were parallel and perpendicular to the uniaxial stretching direction of the film, respectively, were measured by the uniaxially-stretched film technique as described previously.[7,8] All the spectra were measured on a Shimadzu UV-360 spectrophotometer equipped with a Rochon-type polarizer.

Results and Discussion

Spherical Molecule (TPI). Figure 4a shows the polarized absorption ($A_{/\!/}$ and $A_\perp$) and $R_d(=A_{/\!/}/A_\perp)$ spectra of TPI in the visible region obtained by the uniaxially-stretched film technique. It can be seen that the R_d values were almost unity in the whole spectral region. The R_d values were also shown to be independent of the uniaxial stretching ratio (R_s) of the film, as shown in Fig. 5. Figure 4b shows the A_b, A_i, and $(R_{bi})_{exp}$ spectra of TPI obtained by the biaxially-stretched film technique. The $(R_{bi})_{exp}$ values were almost constant in the whole spectral region. These

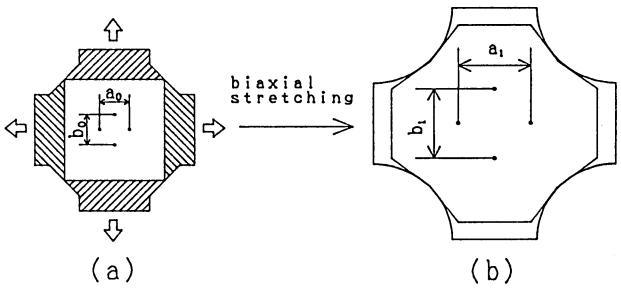

Fig. 3. Deformation of a polymer film on biaxial stretching. (a): the film before the stretching, (b): the film after the biaxial stretching performed synchronously in the directions indicated by the arrows.

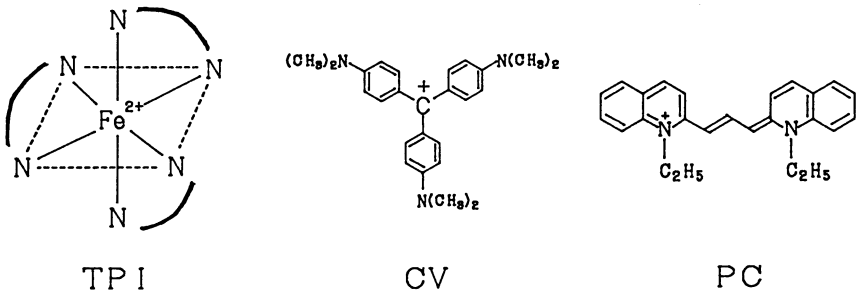

Fig. 2. Molecular structures of TPI, CV, and PC.

experimental findings demonstrate that the TPI molecule is optically isotropic or spherical in shape, as expected from the molecular structure of TPI shown in Fig. 2.

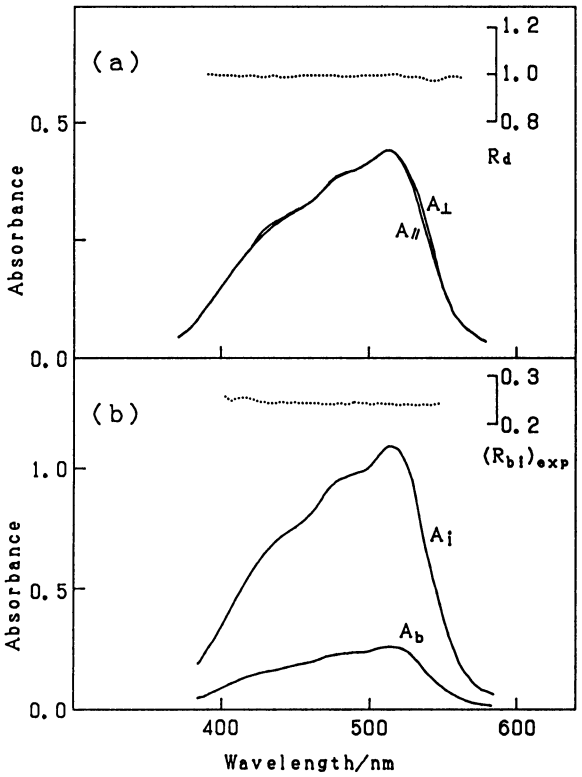

Fig. 4. Observed spectra for TPI obtained by (a): uniaxial stretching (R_s=9.0), (b): biaxial stretching (R_{sb}=2.1).

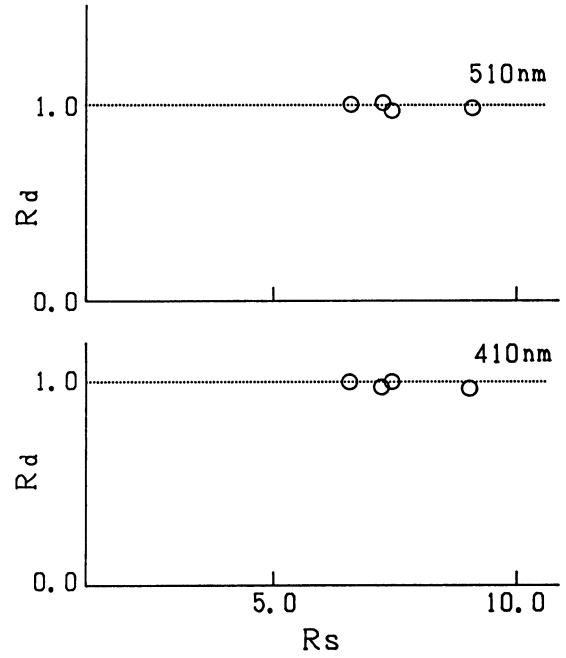

Fig. 5. Dependence of R_d (at 510 and 410 nm) for TPI on R_s.

For such a spherical molecule as TPI, the R_{bi} value should be nearly unity. This and Eq. 1 yield the relation $(R_{bi})_{exp}=k=t_b/t_i$. If the film maintains a constant volume during biaxial stretching, the surface area at the middle part is expected to be multiplied by R_{sb}^2 and the thickness by $1/R_{sb}^2$ after biaxial stretching. For the TPI molecule, therefore, both $(R_{bi})_{exp}$ and t_b/t_i are expected to be equal to $1/R_{sb}^2$. These expectations are verified experimentally in Figs. 6 and 7. Since R_{sb} can be measured with greater precision than t_b or t_i, the

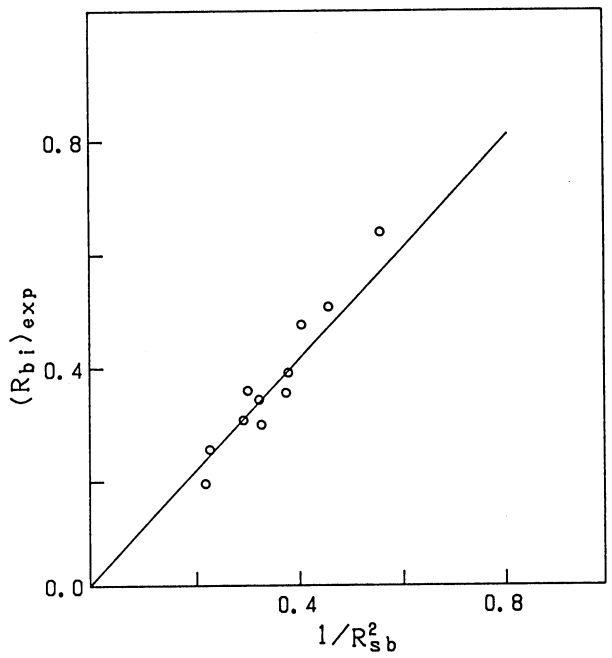

Fig. 6. Plots of $(R_{bi})_{exp}$ for TPI against $1/R_{sb}^2$, showing $(R_{bi})_{exp}\simeq 1/R_{sb}^2$.

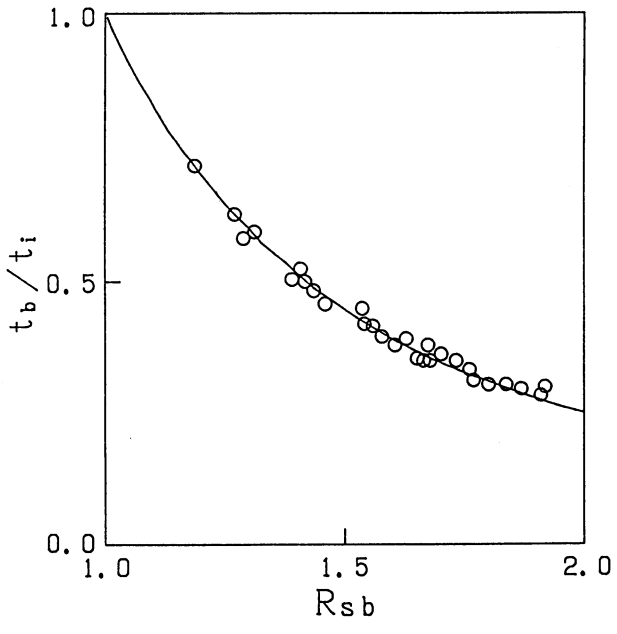

Fig. 7. Plots of t_b/t_i against R_{sb}, showing $t_b/t_i=1/R_{sb}^2$.

following practical relation (1'), derived from Eq. 1 and the relation $k=t_b/t_i=1/R_{sb}^2$ verified in Fig. 7, is used for a nonspherical solute molecule to obtain the R_{bi} value from the $(R_{bi})_{exp}$ value.

$$R_{bi}=(R_{bi})_{exp}R_{sb}^2. \quad (1')$$

Disk-Shaped Molecule (CV). The CV molecule is shaped like a disk, and its π-π^* transition band contains A_x because the three benzene moieties are not coplanar. Figures 8a and 8b show the $A_{/\!/}$, $A_\perp$ and R_d spectra of CV in the uniaxially-stretched film and the A_b, A_i, and R_{bi} spectra of CV in the biaxially-stretched film, respectively. The ratio of A_x to A_z+A_y determined for a disk-shaped molecule by the uniaxially-stretched film method is given by (cf. Appendix I, Case 1)

$$A_x/(A_z+A_y)=(2-R_{d\infty})2R_{d\infty}.$$

As the R_d value decreases, the $R_{d\infty}$ value (>0) decreases (note that $1>T>0$; see Appendix I) and the $A_x/(A_z+A_y)$ value increases. In other words, the R_d value decreases with an increasing ratio of A_x to A_z+A_y. This is the same tendency as that of the R_{bi} value predicted from Eq. 10 or 10'. Therefore, the R_d and R_{bi} spectra for a disk-shaped molecule are expected to exhibit the same contour. This expectation is verified experimentally for CV; the contour of the R_{bi} spectrum in Fig. 8b is similar to that of the R_d spectrum in Fig. 8a except for some details.

Rod-Shaped Molecule (PC). While the PC molecule is assumed to be oriented like a rod-shaped molecule in the uniaxially-stretched film,[24] we will demonstrate in the following that the PC molecule is oriented biaxially like a planar molecule with a rectangular shape in a biaxially-stretched film. This demonstration can be made if the orientation factors of the molecular short-axis (K_y) and the out-of-plane axis (K_x), which should be equivalent if only the molecular long-axis is oriented uniaxially like a rod-shaped molecule, are shown to be inequivalent.

Of the two ways to evaluate the orientation factors for a rod-shaped molecule described in the Theoretical section, the second one is easier to handle and more efficient in elucidating the uncertain nature of the evaluated K values than the first one. Thus, the second method is used here.

Figures 9a and 9b show the R_d spectrum of PC in the uniaxially-stretched film and the R_{bi} spectrum in the biaxially-stretched film, respectively, in the 270—450 nm region. The 385 nm band, indicated by arrow 1, is now assumed to be a pure z-band, because this band has the largest R_d value (Fig. 9a). The orientation angle θ, the angle between the uniaxial orientation axis and the transition moment, for this pure z-band is evaluated to be 0° according to a quantitative analysis of linear dichroism proposed by Tanizaki.[6] This means that the uniaxial orientation axis coincides with the molecular long-axis (z) and the $(A_y+A_x)/A_z$ value is given by $\tan^2\theta$ (cf. Appendix I, case 2). The substitution of the

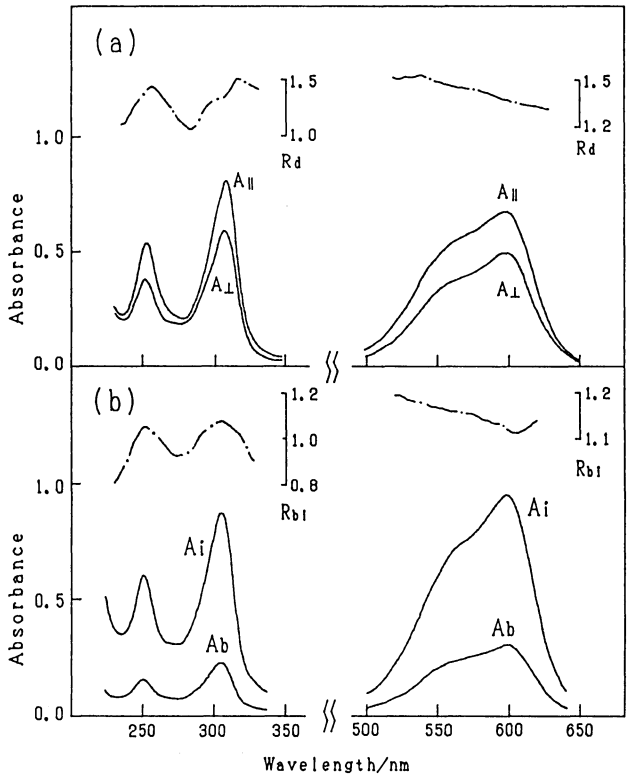

Fig. 8. Observed spectra for CV obtained by (a): uniaxial stretching (R_s=6.3 (left), 6.2 (right)), (b): biaxial stretching (R_{sb}=2.1 (left), 1.9 (right)).

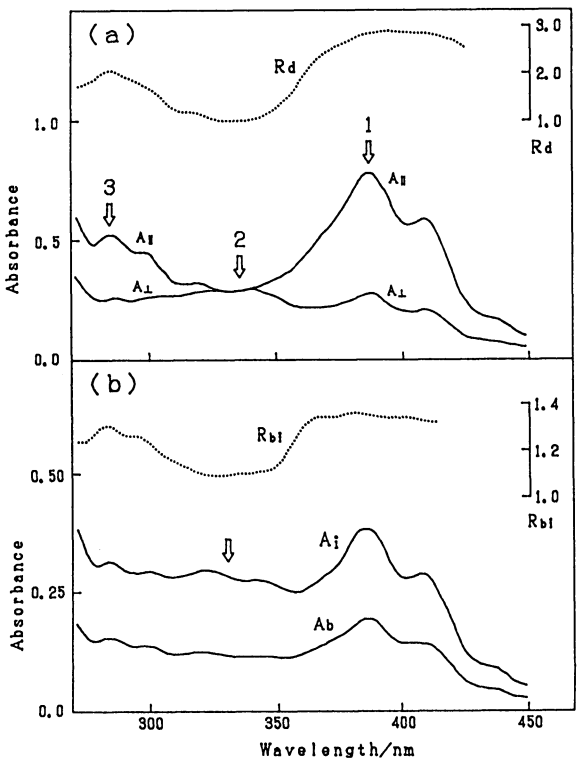

Fig. 9. Observed spectra for PC in the 270—450 nm region obtained by (a): uniaxial stretching (R_s=2.3), (b): biaxial stretching (R_{sb}=1.6).

R_{bi} value (=1.35; Fig. 9b) for the 385 nm band into Eq. 11 yields K_z=0.9.

We are now ready to evaluate the $K'(\lambda)$ value using Eq. 14. The R_d spectrum in Fig. 9a shows a minimum at 330 nm (arrow 2) and a second peak at 285 nm (arrow 3), the corresponding θ values being 55° and 25°, respectively. The substitution of $(A_y+A_x)/A_z=\tan^2 25°$, K_z=0.9 and R_{bi} (285 nm)=1.3; or $(A_y+A_x)/A_z=\tan^2 55°$, K_z=0.9 and R_{bi} (330 nm)=1.1 into Eq. 14 yields K'(285 nm)=0.71 or K'(330 nm)=0.65. Since the K_y value must be larger than any $K'(\lambda)$ value, K_y is larger than K'(285 nm)=0.71, resulting in the following inequality for K_y according to Eq. 15.

$$0.9 > K_y > 0.71. \quad (15')$$

This inequality for K_y yields the inequality for K_x shown below according to Eq. 16.

$$0.2 < K_x < 0.39. \quad (16')$$

These inequalities for K_y and K_x clearly show that K_y and K_x are inequivalent, ie., K_y is larger than K_x ($K_z > K_y > K_x$), demonstrating that the PC molecule is oriented biaxially, the biaxial orientation axes being the z- and y-axes, like a planar molecule with a rectangular shape in the biaxially-stretched film.

Since two quinoline moieties of the PC molecule deviate from coplanarity,[25] the π-π^* absorption spectrum of PC is expected to contain A_x. The A_i absorption at the arrow (330 nm) in Fig. 9b is considered to contain the largest fraction of A_x because both the R_d and R_{bi} values show minima at 330 nm. Substitution of the R_{bi}(330 nm) value (=1.1), the K_z value (=0.9), and the inequalities for K_y (Eq. 15′) and K_x (Eq. 16′) into Eq. 9′ yields the percentage of A_x(330 nm) contained in A_i(330 nm) along with those of A_y(330 nm) and A_z(330 nm) as follows.

$$24\% > A_x(330\text{ nm}) > 4\%;\ 57\% < A_y(330\text{ m}) < 77\%;$$
$$A_z(330\text{ nm}) = 19\%.$$

The substitution of the $R_{bi}(\lambda)$ value at any wavelength λ yields a similar estimation of the fractions of $A_x(\lambda)$, $A_y(\lambda)$, and $A_z(\lambda)$ contained in $A_i(\lambda)$.

Thus, the nonunified coupling of the biaxially- and uniaxially-stretched film methods tentatively proposed in this paper proved to yield an approximate estimation of the three-dimensional reduced spectra of PC. This estimation, though approximate, may be effective enough to demonstrate the usefulness of the biaxially-stretched film technique coupled with the uniaxially-stretched film technique. A unified theory, formulated by the use of an orientational distribution function of solute molecules as an extension of Tanizaki's theory,[6] of the biaxially- and uniaxially-stretched film techniques will be proposed in a forthcoming paper to form a self-consistent estimation of the three-dimensional reduced spectra for a molecule of general shape.

Appendix I

The conventional procedure to get the two-dimensional reduced spectra described in Refs. 7 and 8 is extended to include the out-of-plane polarized absorption component (A_x) explicitly, assuming that the uniaxial orientation axis, not coinciding with the molecular long-axis (z), of the solute molecule is in the molecular plane (zy plane). That is, for infinite uniaxial stretching ($R_s=\infty$), $A_{//\infty}$, $A_{\perp\infty}$, and $R_{d\infty}$ are expressed including A_x as follows: $A_{//\infty}=A_z\cos^2\psi+A_y\sin^2\psi$; $A_{\perp\infty}=(A_z\sin^2\psi+A_y\cos^2\psi+A_x)/2$ (ψ is the angle between the z-axis and the uniaxial orientaion axis); $R_{d\infty}=A_{//\infty}/A_{\perp\infty}=[A_z\cos^2\psi+A_y\sin^2\psi]/[(A_z\sin^2\psi+A_y\cos^2\psi+A_x)/2]$. This expression for $R_{d\infty}$ is referred to as $R_{d\infty}(\psi)$ in the following descriptions. (A similar expression for $R_{d\infty}$ was proposed by the use of the orientation factor K_z by Thulstrup and Michl.[1]) The $R_{d\infty}$ value is obtained from the R_d and R_s values as $R_{d\infty}=[2(T-1)+R_d(T+1)]/[R_d(T-1)+2T]$, where $T=[R_s^2/(R_s^2-1)][1-(R_s^2-1)^{-1/2}\tan^{-1}(R_s^2-1)^{1/2}]$.

Case 1. For a disk-shaped molecule, the z- and y-axes are equivalent and ψ is considered to be 45°. The substitution of ψ=45° into $R_{d\infty}(\psi)$ leads to the relation $R_{d\infty}/2=(A_z+A_y)/(A_z+A_y+2A_x)$. Solving this equation and the equation of $A_z+A_y+A_x=A_i$ simultaneously, we can reduce the spectrum (A_i) of a disk-shaped molecule in a nonstretched film to the in-plane (A_z+A_y) and out-of-plane (A_x) polarized absorption components as follows.

$$A_z+A_y=[2R_{d\infty}/(2+R_{d\infty})]A_i;$$
$$A_x=[(2-R_{d\infty})/(2+R_{d\infty})]A_i.$$

Case 2. For a rod-shaped molecule, the uniaxial orientation axis coincides with the z-axis and ψ is equal to 0°. The substitution of ψ=0° into $R_{d\infty}(\psi)$ leads to the relation $R_{d\infty}=2A_z/(A_y+A_x)$. Therefore, the following equation is derived (see Ref. 7 for the derivation of the second equality).

$$(A_y+A_x)/A_z=2/R_{d\infty}=\tan^2\theta,$$

where θ is the orientation angle, i.e., the angle between the transition moment and the uniaxial orientation axis. Thus, A_i is reduced to the A_z and (A_y+A_x) components.

Appendix II

The objections to the Tanizaki model are concerned with the validity of the orientational distribution function and with that of the procedure to get two-dimensional reduced spectra. The former objection seems to arise mainly from a misunderstanding of the orientation axis in the Tanizaki model. The actual orientation of a solute in the uniaxially-stretched film depends on the shape or molecular structrue of the solute molecule and on the nature of the polymer film used. Two orientation mechanisms are considered for solute molecules embedded in a uniaxially-stretched polymer film: (1) The solute molecules are bonded with a unique orientation (hence the molecular orientation axis is unique) to the polymer substrate, and the molecules are oriented together with the polymer substrate. (2) The solute molecules are oriented by intermolecular interaction with the polymer substrate.

When mechanism (1) is dominant, a molecule of any shape should behave as a rod-like molucule. In this case, therefore, the orientational behavior of solute molecules can be expressed by a one-parameter model; the orientational distribution function proposed by Tanizaki[6] can be applied to a

solute molecule of any shape. The orientation of the molecules embedded in the PVA film is considered to obey mechanism (1), because the PVA molecule is very polar and interacts strongly with the solute molecules. This argument may be supported by the following experimental fact. The dichroic behavior of the sample film prepared by uniaxial stretching after dyeing is the same as that of the film prepared by dyeing after uniaxial stretching.[26]

On the other hand, when mechanism (2) is dominant, the Tanizaki model may still be valid for solute molecules other than rod-like molecules; the Tanizaki model can account for the difference in the three orientation factors in the TEM model by taking a unique direction of the orientation axis in the molecular frame.

The Tanizaki model assumes that the orientational distribution function of the orientation axes fixed to the solute molecules is identical to that of the unit vectors fixed to the polymer substrate, i.e., that the orientation axis of the solute molecule responds without retardation to the orientation of the unit vector of the polymer substrate. This assumption might not be generally valid, and the microscopic stretch ratio effective for the solute might not always be the same as the macroscopic one of the polymer substrate. This is one of the unsolved problems in the Tanizaki model.

There are two assumptions included in the procedure to obtain two-dimensional reduced spectra. Firstly, the orientation axis of the solute molecule is assumed to be aligned exactly along the stretching direction at infinite stretching. We consider this assumption to be approximately valid. The criticism of Thulstrup and Michl on this first assumption[1] seems to be unfounded. They claim that Tanizaki's theory[6] will produce incorrect orientation angles, which are the angles made by the transition moments and the orientation axis, unless a special constraint (relation 28 in Ref. 1) derived from the first assumption is fulfilled. This claim has no basis because the orientation angles are calculated without the first assumption by Tanizaki's theory; the first assumption is adopted merely to obtain reduced spectra and is not related to the calculation of orientation angles.

Secondly, the orientation axis is assumed to be in the molecular plane. This assumption is not generally valid; the orientation axis must make a finite angle with the molecular plane in order to consider the orientation factor for the out-of-plane axis of the solute molecule. This limitation of the second assumption may yield some error in the two-dimensional reduced spectra obtained by the Tanizaki model.

In a unified theory of the biaxially- and uniaxially-stretched film techniques to be proposed in a forthcoming paper, none of the three orientation axes need to be assumed to be in the molecular plane and, therefore, the resulting three-dimensional reduced spectra may be more reliable than those derived from the nonunified coupling of two stretched film methods tentatively proposed in this paper.

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