Effect of Nonrandom Polymer Chain Orientation in the Thickness Direction on Infrared Absorption Measurements

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ABSTRACT: The dependence of infrared band intensities on the amount of preferential polymer chain orientation normal to the plane of the film in polymer samples has been calculated. The effect of tilting the sample in the incident beam has also been derived. These theoretical results dictate a simple infrared method of determining the amount of preferential chain orientation and a procedure for minimizing the effects of orientation on the band intensities. The theoretical predictions have been confirmed by measurements on solution cast films of poly(ethylene oxide) of varying molecular weight.

In the spectroscopic characterization of many polymeric systems, quantitative infrared measurements are often made on films prepared by solvent casting, cold pressing, or compression molding.[1,2] It has been common knowledge that random orientation of the polymer chains in the plane of the film is required for accurate measurements. However, in the compression molding and solvent casting methods of preparing polymer films, a preferred orientation of the chains perpendicular to the film surface may be introduced. The influence of this preferred orientation on measured absorbance of parallel and perpendicular bands for crystalline *n*-parafins has been recognized by Snyder.[3] Krimm and Liang[4] utilized the change in intensity with angle of tilt to show preferential orientation of benzene rings in polyethylene terephthalate (PET).

If the sample contains polymer molecules preferentially oriented normal to the surface of the film, and the film is tilted about an axis normal to the direction of the light, the measured absorbance depends on the angle of tilt. In addition to the normal increase in absorbance which would be expected for an increasing amount of sample in the path of the beam, parallel and perpendicular bands, *i.e.*, bands for which the transition moments are aligned predominantly parallel and perpendicular to the polymer chain axis, show different behaviors. The ratio of the absorbance of a parallel band to a perpendicular band increases as the angle of the tilt increases.

It is our intention to demonstrate the effects of this preferred orientation on infrared band ratios of polymer samples, and to report a simple method using unpolarized radiation for obtaining an idea of the percentage orientation normal to the plane of the film. The measured absorbances can be corrected for effects due to preferred orientation by making measurements at several angles of tilt and extrapolating to an angle of 54°44′, where effects due to orientation disappear. Such corrections are required in order to obtain accurate structural information from the infrared spectra of thin films.

Theory

The infrared spectrum of a helical polymer contains infrared bands with inherent polarization properties perpendicular or parallel to the axis of the helix.[1] Radiation of oriented samples with linearly polarized infrared light can quickly and easily establish the nature of this polarization for most bands.[1] When the polymer chains are randomly oriented with respect to an unpolarized infrared beam, the measured absorbance depends only on the path length and the extinction coefficient. If orientation is introduced, the absorbance also depends on the degree of alignment of the transition moment with the electric vector of the polarized infrared radiation.[4]

Liang and Krimm[4] have shown the dependence of the measured absorbance on the alignment of the dipoles for specific orientations, and as a function of the angle of tilt from the vertical.

We shall, however, assume that the classical definition of parallel and perpendicular bands as being those bands which arise from transition moment vectors perfectly aligned, parallel, and perpendicular to the helix axis is strictly applicable.

Polymer molecules will be considered to be cylinders, the degree of orientation in any sample being represented by the number of cylinders concentrated along each of the three mutually perpendicular directions. We shall initially consider systems in which molecules are oriented in only one direction, and then extend our arguments to the case when preferential though not complete orientation is present. The systems to be discussed are illustrated in Figure 1.

Any individual transition moment vector $\vec{M}$ may be resolved with respect to the coordinates of the helix. Thus

$$\vec{M} = \vec{M}_t + \vec{M}_a + \vec{M}_c \tag{1}$$

where $\vec{M}_a$ is the component of the transition moment vector perpendicular to the helix axis, and $\vec{M}_c$ is the component parallel to the helix axis. The terminology $\vec{M}_{ax}$, $\vec{M}_{ay}$, and $\vec{M}_{az}$ to be used subsequently applies to

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(1) R. Zbinden, "Infrared Spectroscopy of High Polymers," Academic Press, New York, N. Y. 1964.

(2) J. L. Koenig, in "Applied Infrared Spectroscopy," D. Kendall, Ed., Rheinhold Publishing Corp., New York, N. Y., 1960.

(3) R. G. Snyder, *J. Chem. Phys.*, **42**, 1744 (1959).

(4) C. Y. Liang and S. Krimm, *ibid.*, **27**, 327 (1957).

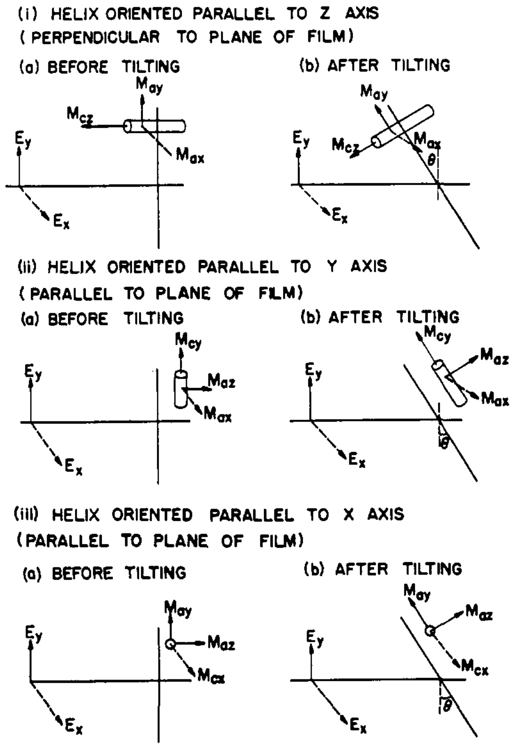

Figure 1. Coordinate system based on coordinates of the helix.

the alignment of the helix with respect to the cartesian coordinates of the film.

1. Helices Oriented Normal to Plane of Film. For this orientation, the specific absorbance of any band of wavelength λ can be calculated (eq 2). If the hel-

$$\alpha_\lambda = k|E_xM_{ax}|^2 + k|E_yM_{ay}|^2 \tag{2}$$

ices are random in the x–y plane, $M_{ax} = M_{ay}$, and so

$$\alpha_\lambda = 2k|E_xM_{ax}|^2 \tag{3}$$

This indicates that only perpendicularly polarized bands should appear in the spectra.

When a sample containing helices oriented normal to the plane of the film is tilted about the x axis by an angle θ (Figure 1(ib)) the specific absorbance becomes

$$\alpha_\lambda = k|E_xM_{ax}|^2 + k|E_yM_{ay}\cos\theta|^2 + k|E_yM_{cz}\sin\theta|^2 \tag{4}$$

Since $M_{ax} = M_{ay}$, this can be expressed as eq 5. A

$$\alpha_\lambda = k|E_xM_{ax}|^2(1 + \cos^2\theta) + k|E_xM_{cz}|^2\sin^2\theta \tag{5}$$

parallel band, which we will designate λ_1, has no M_a components, only M_c components. Therefore the dependence of the specific absorbance on the tilt angle is given by eq 6. This result can be obtained from the

$$\alpha_1^{\parallel} = k_1|E_xM_{cz}|^2\sin^2\theta \tag{6}$$

work of Liang and Krimm.[4] Similarly, a perpendicular band, which we will designate λ_2, has no M_c component, only M_a components, and so its dependence on the tilt angle is

$$\alpha_2^{\perp} = k_2|E_xM_{ax}|^2(1 + \cos^2\theta) \tag{7}$$

The ratio of the specific absorbances of a parallel and perpendicular band for the helix orientation normal to the film is

$$R_{12}^{\theta} = \frac{\alpha_1^{\parallel}}{\alpha_2^{\perp}} = K_{12}\frac{\sin^2\theta}{1 + \cos^2\theta} \tag{8}$$

which is dependent on the tilt angle. It is to be remembered that the ratio for randomly oriented samples was independent of the tilt angle.

2. Helices Oriented Parallel to the Plane of the Film. In a similar manner by considering the orientations in Figures 1(iib) and 1(iiib), it can be shown that the specific absorbance for this orientation of helices (assuming random orientation within the plane) is

$$\alpha_\lambda = k|E_xM_{ax}|^2[(\sin^2\theta) + 2] + k|E_xM_{cz}|^2(1 + \cos^2\theta) \tag{9}$$

The ratio (R) of the specific absorbances as a function of tilt angle becomes

$$R_{12}^{\theta} = \frac{\alpha_1^{\parallel}}{\alpha_2^{\perp}} = K_{12}\frac{1 + \cos^2\theta}{(\sin^2\theta) + 2} \tag{10}$$

Here the dependence is functionally different from the results in eq 8.

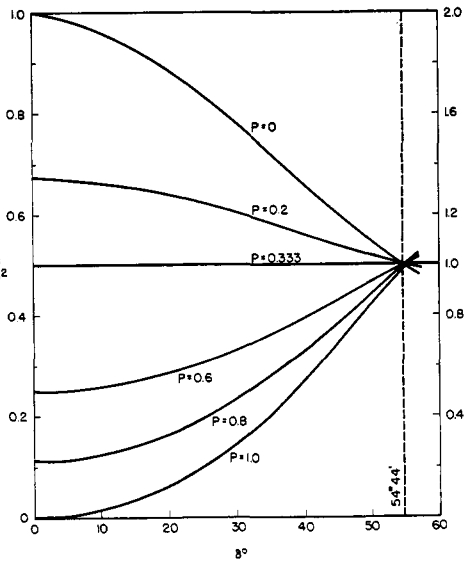

Figure 2. Variation of R with δ° for unpolarized light.

The above derivations give the ratio of the specific absorbances of a parallel band to a perpendicular band for the two extreme cases of helices being aligned either all perpendicular to the film or all in the plane of the film. No allowance has been made for preferred orientation, say in the z direction, or also for the refractive index of the film. The latter is a simple correction and can be shown merely to involve the substitution of the angle of refraction δ for the angle of tilt θ.

3. Helices Oriented Preferentially Normal to the Plane of the Film. Unfortunately, we seldom encounter circumstances of perfect orientation perpendicular or parallel to the surface of the film but rather some intermediate case. However, the intermediate case of preferred but not prefect orientation can be obtained by forming the proper linear combination of the functions representing the absorbance behavior of the perfectly oriented states. That is, the absorbance behavior of any helix in the system upon tilting the sample can be represented by considering the fraction of its absorbance in the direction perpendicular to the surface of the film to have the same functional dependence on tilting as the state of perfect orientation. Similarly the absorbance of the remaining portion of the helix can be considered to have the functional dependence on tilting found for the perfect orientation of this type. Since the spectrometer records the sum of the behavior of all helices in the sample, we can define P as the fraction of the absorbances in the sample projected on the z axis or equivalently, and the matter of interest here, the fraction of molecules having preferential orientation perpendicular to the plane of the film. Then if the molecules are randomly aligned in the xy plane, the fraction along the x axis is equal to the fraction along the y axis which is $(1 - P)/2$.

The total absorbance of any band is therefore given by

$$A_\lambda = P\{|E_yM_{cz}\sin\delta|^2 + |E_yM_{ay}\cos\delta|^2 + |E_xM_{ax}|^2\} + \frac{1-P}{2}\{|E_yM_{cy}\cos\delta|^2 + |E_yM_{az}\sin\delta|^2 + |E_xM_{ax}|^2 + \frac{1-P}{2}\{|E_xM_{cx}|^2 + |E_yM_{ay}\cos\delta|^2 + |E_yM_{az}\sin\delta|^2\} \quad (11)$$

For a parallel band, where all components of M_a are zero, this will reduce to eq 12, and similarly for a perpendicular band, where all components of M_c are zero

$$A_1^{\parallel} = k_1|E_xM_{cx}|^2\left\{P(\sin^2\delta) + \left(\frac{1-P}{2}\right) \times [(\cos^2\delta) + 1]\right\} \quad (12)$$

$$A_2^{\perp} = k_2|E_xM_{ax}|^2\left\{P[(\cos^2\delta) + 1] + \left(\frac{1+P}{2}\right) \times [(\sin^2\delta) + 2]\right\} \quad (13)$$

The ratio of a parallel band to a perpendicular band for unpolarized light is therefore given by

$$R_{12}^{\delta} = K_{12}\left\{\frac{P(\sin^2\delta) + \left(\frac{1-P}{2}\right)[(\cos^2\delta) + 1]}{P[(\cos^2\delta) + 1] + \left(\frac{1-P}{2}\right)[(\sin^2\delta) + 2]}\right\} \quad (14)$$

If light polarized in the y direction is used and the film is rotated about the x axis, the ratio $\alpha_1^{\parallel}/\alpha_2^{\perp} = Q_{12}^{\delta}$ can be shown to be

$$Q_{12}^{\delta} = K_{12}\left\{\frac{P(\sin^2\delta) + \left(\frac{1-P}{2}\right)\cos^2\delta}{P[(\cos^2\delta) + 1] + \left(\frac{1-P}{2}\right)\sin^2\delta}\right\} \quad (15)$$

The results are plotted in Figures 2 and 3. It will be noticed that for unpolarized light, the function $R(\delta)$ becomes independent of orientation at the one angle of refraction δ approximately 54°. Zbinden[1] has shown that, if the transition moment vector makes an angle of 54°44′ with the helix axis no dichroism will be observed for such a band, since its intensity in any polarization direction is the same.

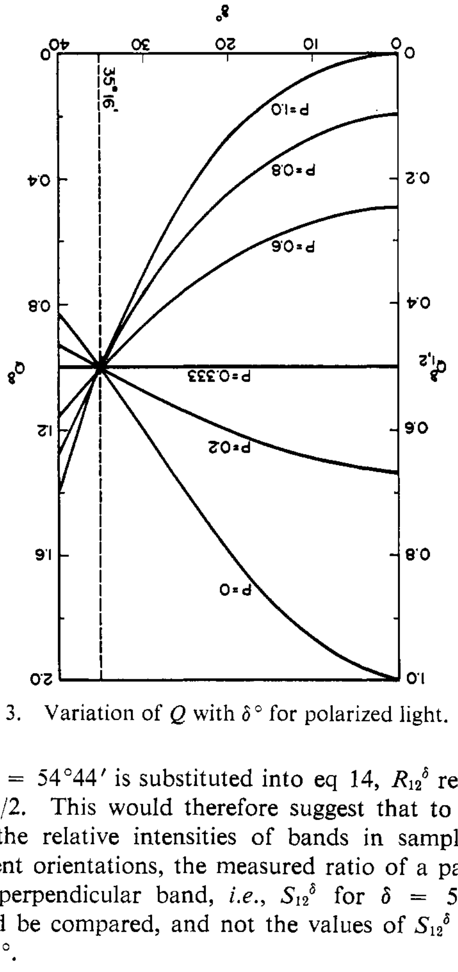

Figure 3. Variation of Q with $\delta°$ for polarized light.

If $\delta = 54°44'$ is substituted into eq 14, R_{12}^{δ} reduces to $K_{12}/2$. This would therefore suggest that to compare the relative intensities of bands in samples of different orientations, the measured ratio of a parallel to a perpendicular band, *i.e.*, S_{12}^{δ} for $\delta = 54°44'$ should be compared, and not the values of S_{12}^{δ} when $\delta = 0°$.

The theoretical results will now be compared with experimental results for chloroform cast films of poly(ethylene oxides) of varying molecular weights. This comparison of the measured dependence of $\alpha_1^{\parallel}/\alpha_2^{\perp}$-($S_{12}^{\delta}$) with δ, with the calculated dependence of R_{12}^{δ} with δ, gives a simple measure of the degree of any preferred orientation of chains perpendicular to a polymer film.

R_{12}^{δ} and S_{12}^{δ} should both be normalized so that they are unity at 54°44′. These normalized ratios, R^{δ} and S^{δ}, are obtained by dividing R_{12}^{δ} and S_{12}^{δ} by their respective values at $\delta = 54°44'$.

It is our intention to obtain an estimate of the amount of orientation of polymer chains normal to the plane of the film by simply tilting the sample, irradiated by nonpolarized light, and comparing the plot of S^{δ} against δ, with the theoretical plot of R^{δ} against δ.

Experimental Section

Chloroform cast films of low molecular weight poly(ethylene oxide) were believed to exhibit preferential orientation perpendicular to the plane of the film.

Before a quantitative measurement could be made, it was necessary to obtain a value for the refractive index (n) of poly(ethylene oxide) in order to determine the value of the angle of refraction δ associated with the measured angle of tilt θ.

Preparation of Samples. Chloroform cast films of poly(ethylene, oxide) of varying molecular weight were prepared by depositing solution on rolled silver chloride plates and allowing the solvent to evaporate. The resultant film was then sandwiched between silver chloride plates by cold pressing to provide a sample which could be melted and otherwise thermally treated without change in its physical dimensions. The silver chloride appeared to provide some insulation from the heat of the beam for the low molecular weight samples.

Spectra were run in a Perkin-Elmer 521 at room temperature, using wire grid polarizers, and the tilting mechanism described by Koenig, Cornell, and Witenhafer.[5]

Determination of Refractive Index. The ratio $A_{1339}^{\parallel}/A_{1355}^{\perp} = S_{12}^{\delta}$ for chloroform cast films of high molecular weight Polyox W.S.R. 301 was found to be independent of the angle of tilt, and also of the direction of polarization of the incident radiation. $A_{1339}^{\parallel}$ is the measured absorbance of the parallel band at 1339 cm^{-1}. $A_{1355}^{\perp}$ is the measured absorbance of the perpendicular band at 1355 cm^{-1}.

This high molecular weight sample was therefore concluded to be perfectly random, enabling the refractive index n for polyethylene oxide to be calculated from the ratio

$$n = \frac{\sin \theta}{\sin [\cos^{-1} (A^{\circ}/A^{\theta})]}$$

where θ is the angle of tilt, A^0 is the measured absorbance at 0° tilt, and A^{θ} the absorbance at θ°. n was determined for $\theta = 45°$ for the bands at both 1355 and 1339 cm^{-1}. The values of δ corresponding to the measured angle θ were then calculated.

As a check on the method, the value of $A_{1339}^{\parallel}$ was calculated for various angles of refraction by a variety of methods, and these values were compared with the experimentally observed quantities. The results are shown in Table I. $(A_{1339}^{\parallel})_{\text{obsd}}$ is the experimentally obtained value; $(A_{1339}^{\parallel})_{\delta}$ is the value of $A_{1339}^{\parallel}$, calculated to allow for the change in path length due to the refractive index of the film; and $(A_{1339}^{\parallel})_{\theta}$ is the value of $A_{1339}^{\parallel}$, assuming the beam goes straight through the sample. It can be seen that the values for $(A_{1339}^{\parallel})_{\delta}$ show quite good agreement with the experimentally determined value $(A_{1339}^{\parallel})_{\text{obsd}}$.

Table I
Variation of $A_{1339}^{\parallel}$ with Different Calculations of Film Thickness

θ	δ°	$(A_{1339}^{\parallel})_{\text{obsd}}$	$(A_{1339}^{\parallel})_{\delta}$	$(A_{1339}^{\parallel})_{\theta}$
0	0	0.299	0.289	0.299
15	11.5	0.316	0.305	0.309
30	23	0.332	0.321	0.345
45	34	0.352	0.352	0.422

Results

The observed ratios $A_{1339}^{\parallel}/A_{1355}^{\perp}$ were plotted against both θ and δ, for unpolarized light (S_{12}^{δ}) and polarized light (T_{12}^{δ}) for Carbowax 1540. The observed ratios were then normalized. Figure 4 shows the plots of S_{12}^{θ} against θ, and S_{12}^{δ} against δ for unpolarized light, and T_{12}^{θ} against θ and T_{12}^{δ} against δ for polarized light. This figure may then be compared with Figures 2 and 3 to obtain an estimate of the orientation normal to the plane of the film.

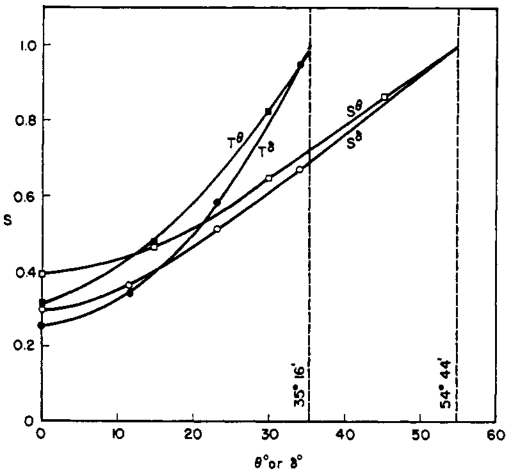

Figure 4. Variation of S or T with θ° or δ° for Carbowax 1540: ○, W.S.R. 301; □, Carbowax 1540.

Figure 5 shows the results for S^{δ} *vs.* δ for chloroform cast films of polyethylene oxides of varying molecular weights as designed by Union Carbide.

It will be noticed that W.S.R. 301 is clearly random ($P = 0.333$). Carbowax 6000 is about 40% oriented in the z direction while Carbowax 4000 and 1540 are between 60 and 80% oriented in the z direction.

Although it is not intended to discuss the crystallization of poly(ethylene oxide) at this point, it would seem appropriate to suggest that these results could be explaned on the basis of crystallization of the lower molecular weight samples in extended chains, normal to the plane of the substrate.

The corrected values for samples of different molecular weights are shown in Table II. It can be clearly

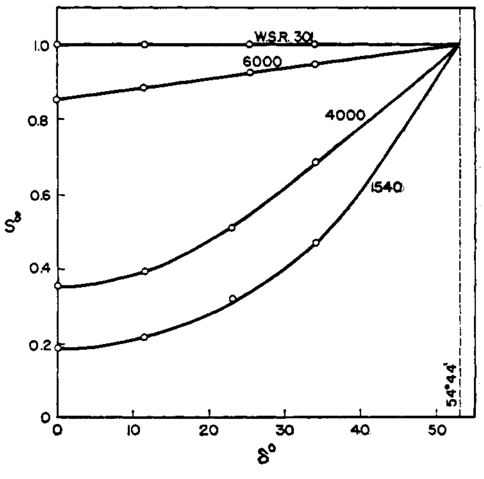

Figure 5. Variation of S^{δ} with δ° for different molecular weight poly(ethylene oxides): ○, W.S.R. 301; □, Carbowax 1540.

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[5] J. L. Koenig, D. Witenhafer, and S. W. Cornell, *J. Polym. Sci., Part A-2*, 5, 301 (1967).

TABLE II
VARIATION OF S_{12}^{δ} WITH δ

Mol wt	$S_{12}^{\delta}(\delta = 0°)$	$S_{12}^{\delta}(\delta = 54°44')$
1540	0.44	1.80
4000	0.51	1.50
6000	1.15	1.40
W.S.R. 301	2.74	2.74

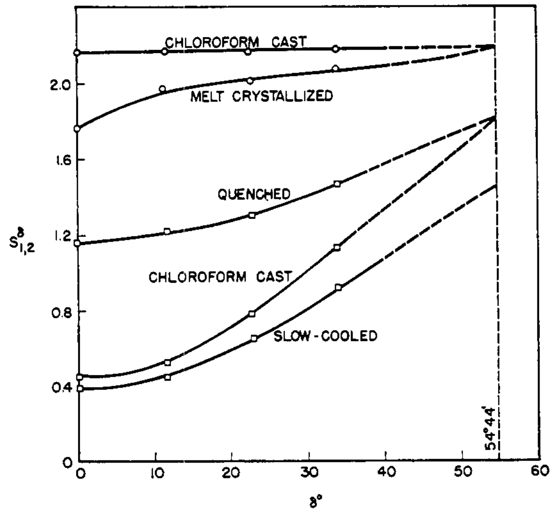

Figure 6. Effect of thermal treatment on S_{12}^{δ} vs. δ°: ○, W.S.R. 301; □, Carbowax 1540.

seen that if the ratio of absorbances at 0° tilt had been used, as might have been logically done, considerable errors would have been introduced.

The effect of different thermal treatments on the ratio of a parallel to a perpendicular band may also be demonstrated by consideration of Carbowax 1540. Figure 6 shows the relationship between S_{12}^{δ} and δ for various samples of Carbowax 1540 and high molecular weight Polyox W.S.R. 301. It can be seen that although the quenched sample and the chloroform cast films show different orientations, S^{δ} is approximately the same in both cases. However, for the slow-cooled sample, although it has approximately the same S^0 as the chloroform cast film, S^{δ} differs considerably between the two preparations.

The samples used for W.S.R. 301 were both self-supporting films, the melt-crystallized film being pressed at 100°. It can be seen that a certain amount of orientation is introduced into the sample by this method of preparation.

These results show that all results previously obtained from infrared studies on solution cast and compression-molded films may be a trifle suspect, as the inherent orientation introduced into the sample by its initial preparation may influence measured absorbances considerably.

Nomenclature

α_{λ}	Specific absorbance of a band, wavelength λ
$\vec{E}$	Electric vector of incident radiation
$\vec{M}_{\lambda}$	Transition moment vector of band λ
M_x, M_y, M_z	Components of transition moment vector
$\alpha_{\lambda}^{\theta}$	Specific absorbance of band λ, with the film tilted at an angle of θ
A_{λ}	Measured absorbance of band λ
$\vec{M}_a$, $\vec{M}_c$	Transition moment vectors for the E and A modes, respectively.
R	Ratio of any pair of bands
R_{12}^{θ}	Ratio of any pair of bands, wavelength λ_1 and λ_2, at an angle of tilt θ
Q	Ratio of any pair of bands when polarized light is used
$\alpha_1^{\parallel}$	Specific absorbance of a parallel band, wavelength λ_1
$\alpha_2^{\perp}$	Specific absorbance of a perpendicular band, wavelength λ_2
δ	Angle of refraction
Q_{12}^{δ}	$\alpha_1^{\parallel}/\alpha_2^{\perp}$ for polarized light
R_e^{δ}	R_{12}^{δ} when $\delta° = 54°44'$
R^{δ}	$R_{12}^{\delta}/R_e^{\delta}$
S_{β}^{α}	Measured ratio of absorbance of any two bands, when α and β can be replaced by any index already mentioned
T_{β}^{α}	Measured ratio of absorbance of any two bands, using polarized light