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Notes

Determination of Molecular Spatial Orientation on Polymeric Surfaces Using Internal Total Reflection Infrared Dichroism

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Introduction

In recent years, rapid developments in fields like biomaterials, polymer processing etc., have underlined the need to develop techniques which probe only the surface properties and not the bulk properties.[1] One such technique is internal total reflection or attenuated total reflection (ATR)-FTIR. Its potential to extract information from the first few microns of the surface has been proven and reviewed extensively.[2,3] This technique which was first developed simultaneously and independently by J. Fahrenfort and N. J. Harrick had certain unique features which led to some artifactual errors and errors in interpretation. Chief among these were (a) the problem of irreproducible contact area between the sample and the crystal, (b) the fact that the observed frequencies are shifted slightly from those observed in transmission FTIR, and (c) the fact that the relative intensities between two distant wavenumbers can be quite different from that observed in the case of transmission FTIR. While a and c can be quite a problem in quantitative studies, b is important in studies involving comparisons with known transmission FTIR spectra as in the identification of chemical species at the surface. These problems have now been resolved to a large extent for most applications by correction methods arising from an understanding of the mechanism responsible and the use of band-ratioing methods.[3]

However, the use of ATR-FTIR dichroism for the specific application of the determination of spatial molecular orientation has been beset with practical difficulties which do not allow an accurate measurement[4] except in the case of polypropylene.[5,6] The problem arises from the fact that during dichroic measurement using ATR-FTIR one needs to rotate the sample which involves undoing the clamp holding the sample to the crystal, rotating the sample, and redoing the clamp. This invariably leads to substantial changes in the contact area and hence changes in the contact area dependent reflectivities. The usual strategies to overcome this problem have been as follows: (1) The first method is to identify a reference absorption band which does not show dichroism upon an orientation process and to use that to normalize all the dichroic bands for a given contact. The problem with this is that it is extremely difficult to determine such a reference band. (2) The second method has been to design a special sample holder that can be rotated as a whole instead of having to rotate the sample separately.[7,8] This does improve results, but the assumption that the two different paths taken by the IR beam before and after rotation yield the same contact area has been demonstrated to be incorrect.[9] This has been speculated to be probably due the directionality of surface roughness. (3) The third method is a method specific to polypropylene which utilizes the fortuitous occurrence of dipoles parallel and perpendicular to the major chain axis where the chain is assumed to have cylindrical symmetry.[4-6] This method is quite successful in polypropylene but is not useful in other polymers.

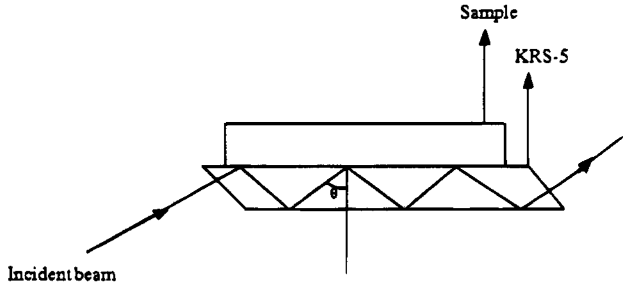

Figure 1. Schematic view of the plane of incidence and the arrangement of the sample and the internal reflection element.

The method developed herein, on the other hand, involves using a specific linear combination of the absorption of the dichroic band in the two polarizations in order to normalize the absorption of the dichroic band in each polarization. This works because the specific linear combination is known from the theory of ATR-IR dichroism to be only a function of the contact area and not a function of the direction of the orientation with respect to the plane of incidence. This method now needs only the identification of one dichroic band of interest in the polymer and no other information. Nothing is assumed about the structure of the polymer or symmetry along the chain axis. Furthermore, the experimental setup is now the same as the conventional setup used for ATR-IR. Hence, this method can be now universally applied to the surfaces of all materials showing infrared dichroism with the usual ATR-FTIR setup!

Theoretical Development

The first thorough theoretical treatment for the application of ATR-IR to the quantitative determination of molecular orientation was given by Flournoy and Schaffers in 1966.[10] According to their treatment (as described by Mirabella[4]), the practical experiment would be done as follows provided all the assumptions of the theory[10,11] are met. A flat sample is placed against the internal reflection element (crystal), with the surface of interest facing the crystal. (A typical arrangement of the crystal and sample is illustrated in Figure 1.) IR spectra are obtained under four different configurations.

Configuration 1. Here the sample is placed along the crystal such that the direction of orientation (x) is perpendicular to the plane of incidence. The incident beam is a TE wave (i.e., the electric vector is perpendicular to the plane of incidence). This is shown in Figure 2a. The corresponding equation for the reflec-

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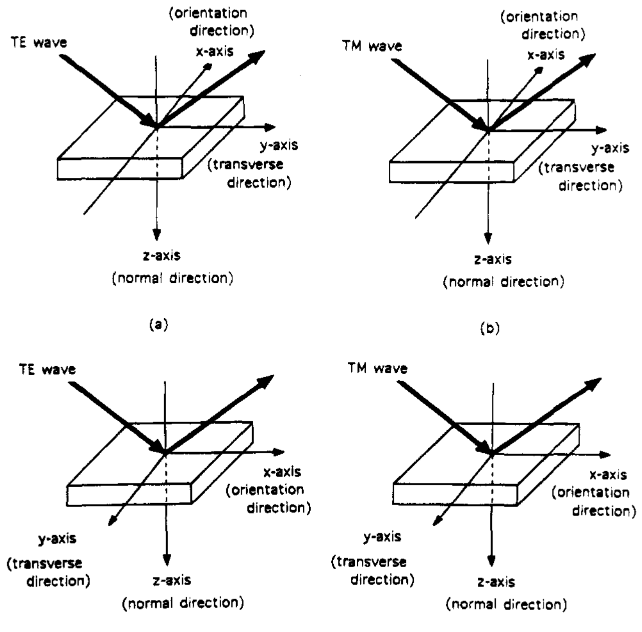

(a) (b) (c) (d)

Figure 2. Four different configurations under which IR spectra are obtained for a typical dichroic measurement using the ATR-FTIR (adapted from ref 4).

tivity, R, is given as

$$\ln R_x^{\mathrm{TE}} = -\alpha k_x \tag{1}$$

where k_i is the attenuation index along the i-axis ($i = x,y,z$) and α is given as

$$\alpha = \frac{4n_{21}^2}{\tan\theta[1 - n_{21}^2/\sin^2\theta]^{1/2}[(1 - n_{21})^2]} \tag{2}$$

Here, θ is the angle of incidence defined as the angle of the incident beam to the normal and n_{21} is the ratio of n_2 to n_1 (n is the refractive index and subscript 1 is for the crystal and 2 for the sample).

Configuration 2. The sample is in the same position, but the polarizer is rotated through 90°. Hence, the incident beam is now a TM wave (i.e., the electric vector is in the plane of incidence). This configuration is shown in Figure 2b. The corresponding equation is

$$\ln R_x^{\mathrm{TM}} = -\beta k_y - \gamma k_z \tag{3}$$

where the y-axis is the transverse direction, the z-axis is perpendicular to the plane of the surface, and β and γ are defined as follows:

$$\beta = \frac{4n_{21}^2[1 - n_{21}^2/\sin^2\theta]}{\tan\theta[1 - n_{21}^2/\sin^2\theta]^{1/2}[(1 - n_{21}^2/\sin^2\theta + n_{21}^4\cot^2\theta)]} \tag{4}$$

$$\gamma = \frac{4n_{21}^2}{\tan\theta[1 - n_{21}^2/\sin^2\theta]^{1/2}[(1 - n_{21}^2/\sin^2\theta + n_{21}^4\cot^2\theta)]} \tag{5}$$

Configuration 3. The sample is now rotated through 90°, and the incident beam is a TE wave (Figure 2c). The relevant equation is

$$\ln R_y^{\mathrm{TE}} = -\alpha k_y \tag{6}$$

Configuration 4. The polarizer is again rotated through 90° (Figure 2d). The corresponding equation then is

$$\ln R_y^{\mathrm{TM}} = -\beta k_x - \gamma k_z \tag{7}$$

For the purpose of this analysis, we shall deal with absorbances, A. The absorbances for small absorbance can be extracted from the reflectivities, R, as follows:

$$\ln R = \ln(1 - A) = (2.303)\log(1 - A) = (2.303)(-A) \tag{8}$$

We shall also distinguish between absorbance with a dependence on the contact area (as depicted by a) and absorbance independent of the contact area (as depicted by A). It is clear that a is the actual measured quantity, whereas A is the quantity for which the theory by Flournoy and Schaffers applies. We shall also assume that a and A are interrelated by the equation

$$a = A(S/S_{\mathrm{ref}})^n \tag{9}$$

where S is the contact area for a particular experiment and S_{ref} is a reference surface area which is just used as a normalizing factor. The power n is an unknown constant. This form is assumed because it is fairly general and can be used to illustrate the dependence of a on the contact area. Hence, the effect of changing contact areas on rotating the sample is likely to be seen due to a change in S.

Rewriting eqs 1, 3, 6, and 7 in terms of a

$$a_x^{\mathrm{TE}} = (2.303)\alpha k_x[S_x/S_{\mathrm{ref}}]^n \tag{10}$$

$$a_x^{\mathrm{TM}} = (2.303)(\beta k_y + \gamma k_z)[S_x/S_{\mathrm{ref}}]^n \tag{11}$$

$$a_y^{\mathrm{TE}} = (2.303)\alpha k_y[S_y/S_{\mathrm{ref}}]^n \tag{12}$$

$$a_y^{\mathrm{TM}} = (2.303)(\beta k_x + \gamma k_z)[S_y/S_{\mathrm{ref}}]^n \tag{13}$$

It is clear that the equations above cannot be used directly to evaluate the attenuation indices due to the differences in contact area between configurations 1 and 2 on one side and configurations 3 and 4 on the other (S_x is not equal to S_y). The difference in contact areas can arise due to either (a) differences in contact pressure or (b) differences in contact areas due to the directionality of the surface texture. Hence, it is necessary to ratio these equations with a quantity which has the same dependence on the contact area but no dependence on the orientation of the sample. Solutions in the past have attempted to either (a) identify a band which does not show dichroism and use it for band ratioing[12] or (b) try to eliminate the contact area difference due to possible differences in contact pressure by either strictly controlling the torque used to tighten the clamp[13] or rotating the crystal and sample as a whole instead of rotating the sample alone.[7,8] The former suffers from the difficulty in identifying nondichroic bands, whereas the latter suffers from a neglect of contact area changes due to the directionality of the surface texture.

The solution to this dilemma is as follows. It can be seen that the following linear combinations of the measured absorbance are independent of the orientation:

$$\beta a_x^{\mathrm{TE}} + \alpha a_x^{\mathrm{TM}} = (2.303)[\alpha\beta(k_x + k_y) + \alpha\gamma k_z][S_x/S_{\mathrm{ref}}]^n \qquad (14)$$

$$\beta a_y^{\mathrm{TE}} + \alpha a_y^{\mathrm{TM}} = (2.303)[\alpha\beta(k_x + k_y) + \alpha\gamma k_z][S_y/S_{\mathrm{ref}}]^n \qquad (15)$$

To simplify the equations, let us define the following:

$$a_x^{\mathrm{LC}} = \beta a_x^{\mathrm{TE}} + \alpha a_x^{\mathrm{TM}} = (2.303)\Delta(S_x/S_{\mathrm{ref}})^n \qquad (16)$$

$$a_y^{\mathrm{LC}} = \beta a_y^{\mathrm{TE}} + \alpha a_y^{\mathrm{TM}} = (2.303)\Delta(S_y/S_{\mathrm{ref}})^n \qquad (17)$$

$$\Delta = [\alpha\beta(k_x + k_y) + \alpha\gamma k_z] \qquad (18)$$

Now dividing eqs 10 and 11 by eq 16 and dividing eqs 12 and 13 by eq 17, we get

$$a_x^{\mathrm{TE}}/a_x^{\mathrm{LC}} = \alpha(k_x/\Delta) \qquad (19)$$

$$a_x^{\mathrm{TM}}/a_x^{\mathrm{LC}} = \beta(k_y/\Delta) + \gamma(k_z/\Delta) \qquad (20)$$

$$a_y^{\mathrm{TE}}/a_y^{\mathrm{LC}} = \alpha(k_y/\Delta) \qquad (21)$$

$$a_y^{\mathrm{TM}}/a_y^{\mathrm{LC}} = \beta(k_x/\Delta) + \gamma(k_z/\Delta) \qquad (22)$$

Three out of these four equations can be solved to get k_x/Δ, k_y/Δ, and k_z/Δ, which can then be used to get the dichroic ratio in each plane. For example, the dichroic ratio in the xy plane would be given by

$$D_{xy} = \frac{(k_x)}{(k_y)} = \frac{(k_x/\Delta)}{(k_y/\Delta)} = \frac{[a_x^{\mathrm{TE}}/a_x^{\mathrm{LC}}]}{[a_y^{\mathrm{TE}}/a_y^{\mathrm{LC}}]} = \frac{\left[1 + \left(\frac{\alpha}{\beta}\right)\left(\frac{a_y^{\mathrm{TM}}}{a_y^{\mathrm{TE}}}\right)\right]}{\left[1 + \left(\frac{\alpha}{\beta}\right)\left(\frac{a_x^{\mathrm{TM}}}{a_x^{\mathrm{TE}}}\right)\right]} \qquad (23)$$

The dichroic ratio can then be correlated to the orientation function, f_{xy}, of the chains as follows:

$$f_{xy} = \frac{(D_{xy} - 1)(D_0 + 2)}{(D_{xy} + 2)(D_0 - 1)} \qquad (24)$$

where D_0 is given by

$$D_0 = 2\cot^2\sigma \qquad (25)$$

σ is the angle between the chain axis and the transition moment vector for the vibration.

Discussion

As already discussed, the procedure developed above has some distinct advantages over the methods used in the past. To illustrate its use and results derived thereby, the data of Mirabella[9] on polypropylene sheets ($n = 1.5$) using a double-cut internal reflection element have been used here. The element was a KRS-5 element ($n = 2.38$), and the angle of incidence was 45°. Table 1 lists the bands studied, assignments, the observed absorbances in each of the four configurations, and dichroic ratios calculated assuming no differences in the contact area (called method 1 hereafter) and calculated by the procedure developed above (called method 2 hereafter) for samples at several different elongation ratios. The dichroic ratios are plotted against the elongation percent for the two methods in Figures 3 and 4.

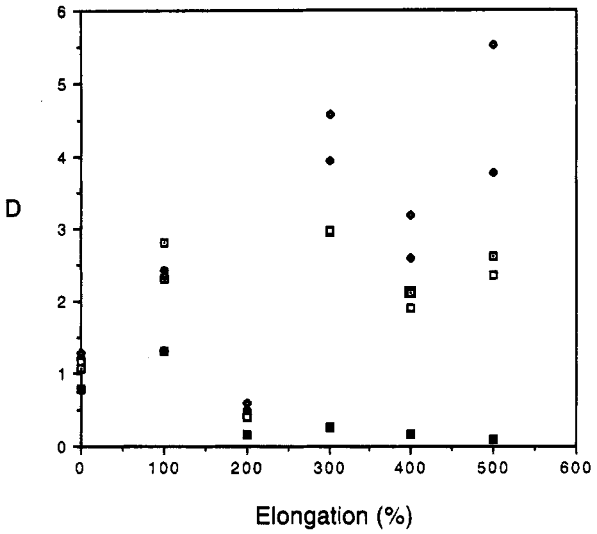

Figure 3. Dichroic ratio for various bands calculated using method 1 (ref 9). The symbols represent the following bands: (⊡) 1167, (◆) 998, (□) 973, (◇) 841, (■) 809 cm^{-1}.

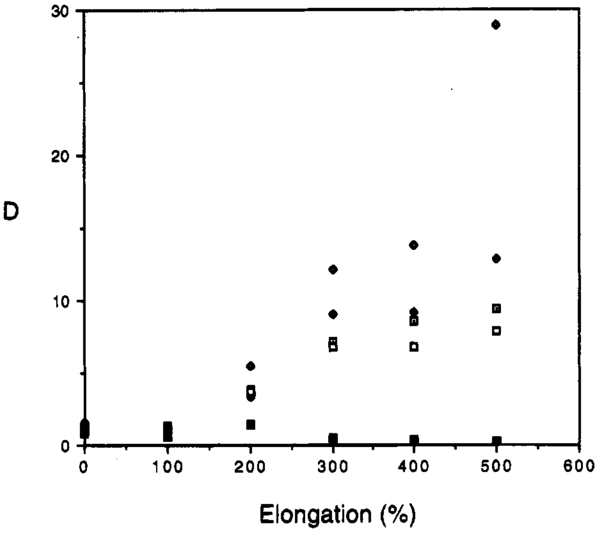

Figure 4. Dichroic ratio for various bands calculated using method 2. The symbols are the same as in Figure 3.

The most striking differences in Figures 3 and 4 are (a) the erratic behavior of the dichroic ratio when calculated using method 1 as opposed to the relatively smooth changes in the dichroic ratio when calculated using method 2 and (b) the underestimation of the dichroic ratio by method 1 in comparison to method 2. One interesting aspect that shows up now, with the dichroic ratios of the bands representing transition moments in the direction of the chain axis calculated by method 2, is the fact that the dichroic ratio remains nearly constant or decreases slightly during the first 100% elongation. Since this is consistently seen in all the bands, it could indicate that insignificant orientation is occurring in the early stages or that some initial anisotropy in the 0% sample is being destroyed in the first 100% elongation. However, in the absence of greater detail on how the experiment was conducted (especially the possible directionality of processing, the direction of elongation, and the direction assigned as the x-axis to the 0% sample), it shall be inappropriate to conclude anything. Yet another interesting observa-

Table 1. Absorbance Values and Calculated Dichroic Ratios for Polypropylene Sheets Measured on a Rotatable KRS-5, 45° Internal Reflection Element (Data from References 4 and 9)

		a				*D*	
band (1/cm)	elongation (%)	config 1	config 2	config 3	config 4	method 1	method 2
1167	isotropic	0.053	0.051	0.064	0.067	0.828	1.083
	0	0.165	0.161	0.155	0.194	1.065	1.267
	100	0.16	0.138	0.057	0.063	2.807	1.264
	200	0.033	0.014	0.081	0.143	0.407	3.787
	300	0.219	0.049	0.074	0.143	2.959	7.088
	400	0.155	0.035	0.073	0.172	2.123	8.535
	500	0.155	0.026	0.059	0.122	2.627	9.457
998	isotropic	0.065	0.069	0.077	0.082	0.844	1.003
	0	0.196	0.184	0.162	0.228	1.210	1.471
	100	0.194	0.166	0.08	0.076	2.425	1.103
	200	0.052	0.023	0.102	0.165	0.510	3.354
	300	0.304	0.057	0.077	0.167	3.948	9.106
	400	0.207	0.042	0.08	0.186	2.588	9.167
	500	0.216	0.028	0.057	0.134	3.789	12.906
973	isotropic	0.076	0.076	0.095	0.096	0.800	1.010
	0	0.216	0.209	0.185	0.248	1.168	1.364
	100	0.213	0.198	0.092	0.094	2.315	1.093
	200	0.051	0.02	0.126	0.205	0.405	3.750
	300	0.319	0.073	0.107	0.201	2.981	6.773
	400	0.215	0.055	0.113	0.235	1.903	6.832
	500	0.222	0.043	0.094	0.18	2.362	7.868
841	isotropic	0.101	0.068	0.084	0.093	1.202	1.594
	0	0.229	0.215	0.178	0.256	1.287	1.501
	100	0.224	0.179	0.095	0.086	2.358	1.124
	200	0.066	0.018	0.109	0.189	0.606	5.432
	300	0.35	0.05	0.076	0.18	4.605	12.140
	400	0.246	0.033	0.077	0.199	3.195	13.823
	500	0.254	0.015	0.046	0.152	5.522	28.980
809	isotropic	0.042	0.035	0.042	0.047	1.000	1.321
	0	0.08	0.107	0.101	0.119	0.792	0.886
	100	0.074	0.12	0.056	0.053	1.321	0.598
	200	0.015	0.015	0.09	0.13	0.167	1.421
	300	0.032	0.09	0.121	0.148	0.264	0.446
	400	0.02	0.078	0.119	0.187	0.168	0.412
	500	0.013	0.053	0.127	0.138	0.102	0.277

tion is the clear reduction in the sensitivity of the dichroic ratios of the 1167 and 973 cm^{-1} bands after 300% elongation. It becomes quite clear that the sensitivity of the dichroic ratio to elongation is the best for the bands at 998 and 841 cm^{-1}, which show almost linear increases in the dichroic ratio with elongation with a reasonably large slope.

The differences in the results from the two methods also underline the need to reassess information derived in the past (from calculations using method 1) about differences or the lack of differences between the polymer surface and the bulk during shear or elongation processes, differences in the orientation of chains in the amorphous and crystalline regions, etc.

In the special case of polypropylene, the fact that the chain is cylindrically symmetric and that the bands at 841 and 809 cm^{-1} represent transition moments parallel and perpendicular, respectively, to the chain axis allows the calculation of the orientation factor by an indirect method (called method 3 hereafter) described by Mirabella.[5,6] In this method, the ratio of the absorbance at 841 to 809 cm^{-1} is used to calculate P_x, the fraction of chains oriented with the major chain (helix) axis parallel to the orientation direction (x). P_x is then used to calculate the orientation function, f_{xy}.

$$P_x = \frac{[a_{841}/a_{809}]_x^{\mathrm{TE}}}{[4 + [a_{841}/a_{809}]_x^{\mathrm{TE}}]} \tag{26}$$

$$f_{xy} = \frac{(3P_x - 1)}{2} \tag{27}$$

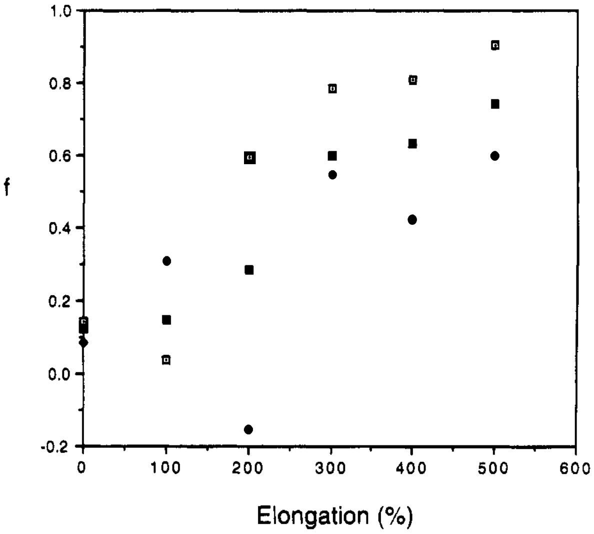

Figure 5. Comparison of the calculated values of the orientation function on the plane of the surface by methods 1 (◆), 2 (◘), and 3 (■) for the band 841 cm^{-1} (and 809 cm^{-1}).

This method has been demonstrated to give results consistent with bulk orientation measurements by X-ray diffraction and polarized refractometry.[4] However, this method is not universally applicable, and a model structure of the molecules is assumed.

Figure 5 plots f_{xy} calculated from each of the methods for various elongation percents. f_{xy} calculated from the different methods vary, though the trend is the same. In particular, method 1 gives erratic results, whereas methods 2 and 3 give smoothly increasing plots. Method

3 gives values of f which are less than those predicted by method 2. This could be due to the simplifying assumptions about the polymer structure in method 3. More experiments are required to ascertain the reason for this difference. In particular, comparison of the above results with those of another method measuring f only at the surface and not in the bulk would be particularly useful.

In conclusion, the band ratioing method introduced here can be an extremely useful tool for the quantitative measurements of molecular orientation in the first few microns of the surface of any polymer showing dichroic IR bands.

Summary

A simple arithmetic procedure was developed so as to be able to band-ratio dichroic measurements from simple attenuated total reflection (ATR)-IR spectroscopy to measure the surface molecular orientation of any polymer showing dichroism. This development eliminates the need to get a reproducible contact area or a reference band which does not show dichroism upon drawing. This method is universally applicable to any material showing dichroic IR bands. No assumptions are made regarding the structure of the sample in order to calculate the dichroic ratio. Furthermore, no special attachments are required for the dichroic measurements.

The discrepancies between the results from this method and those from the methods used in the past underscore the need to reassess past studies on changes in molecular orientation, crystallinity, and conformations with increasing elongation of the polymer.

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