A Procedure for the Accurate Measurement of Infrared Dichroism of Oriented Film*

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INTRODUCTION

In previous publications of this laboratory,[1-4] the relationship between the orientation of polymer molecules in films and the optical properties of these films has been discussed. For amorphous polymers, two optical methods are available for characterizing orientation: the measuring of birefringence and of infrared dichroism. The birefringence method is experimentally simple and precise, but has the disadvantage that only two experimental quantities, Δ_x and Δ_z, may be determined for a general three-dimensional orientation. Four or five orientation functions are necessary in order to characterize the state of orientation. Obviously, all five functions cannot be uniquely determined from two experimentally determined quantities. On the other hand, the infrared dichroism method is, at least in principle, capable of determining the individual orientation functions provided that a sufficient number of assignable absorption bands of the proper type exist.[4] The method has the disadvantage that, as ordinarily measured, infrared dichroism cannot be determined very accurately, especially at low degrees of orientation. One usually measures the absorbency using polarized infrared radiation with the polarization direction oriented first vertically and then horizontally in two separate experiments, and one then determines the ratio or difference between the two quantities obtained. Usually the difference between the two absorbencies is small compared with their magnitudes. If the difference may be obtained directly, as is done in an interferometric birefringence measurement where one determines the difference in the two refractive indices without determining them individually, then a much more precise measurement is possible.

Recently, a method for doing this has been described by Marrinan,[5] which utilizes a double-beam spectrometer (Fig. 1). Two polarizers are used, one in the reference beam and the other in the sample beam. One of the polarizers is oriented in the horizontal direction and the other in the vertical direction. The sample is placed in front of the entrance slit of the spectrometer after the two beams come together. If the sample is not dichroic, the reference and sample beams transmitted through the sample will be of identical intensity and there will be no signal recorded by the spectrometer. The spectrometer responds only to a difference in the transmittances of the two beams. Marrinan reports that by using this technique it is possible to increase the precision of measurement of dichroism by over a hundred fold. In this paper, an alternative method of directly measuring the dichroism, by use of a single-beam spectrometer, is reported.
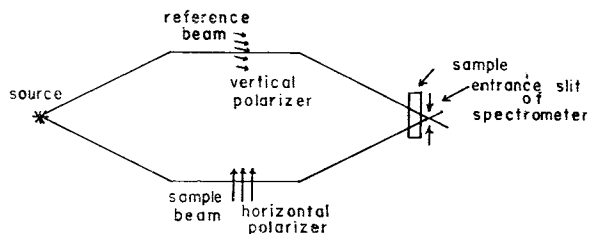

Fig. 1. Marrinan's method for determining dichroism by use of a double-beam spectrometer.

THE ROTATING POLARIZER METHOD

The method which is proposed for direct measurement of dichroism requires a single-beam spectrometer. This instrument utilizes the chopped beam principle, in which the beam is ordinarily interrupted by a rotating chopper which modulates the beam at a frequency of the order of 13 cycles/sec. The beam, after passing through the sample, falls on a detector, the output of which goes through an a.c. amplifier tuned to respond to the chopping
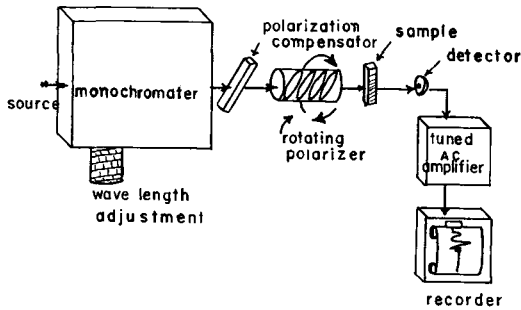
Fig. 2. The rotating polarizer single-beam spectrometer.

frequency. Any constant signal coming from the thermocouple will not be amplified. The spectrometer is modified as indicated in Figure 2. The beam chopper is removed. The infrared beam which emerges from the monochromator is usually slightly polarized because of asymmetry of the optics of the spectrometer. This polarization is compensated by introducing a polarizing plate of selenium or silver chloride which may be tilted with respect to the beam, at an adjustable angle, to control its reflectance for the two components of polarization. The beam then passes through a polarizer which is made to rotate by a motor about an axis coincident with the beam at a frequency equal to half the chopping frequency of the spectrometer. It then passes through the sample and to the detector. Since the detector is a tuned a.c. amplifier, it will respond only to variations in the intensity produced by rotation of the polarizer. With the sample removed, the polarization compensating plate is tilted to such an angle that the output from the amplifier is nil. This indicates that the beam emerging from the compensator is unpolarized, so that there is no variation in intensity with rotation of the rotating polarizer. If such a beam is now passed through a sample which is not dichroic, the absorption will be independent of the rotation of the polarizer, so there will still be no response from the amplifier. However, with a dichroic sample, the absorption depends upon the angle of the polarizer and will consequently vary with its rotation. The amplitude of the alternating current response will then depend upon the difference between the principal absorbencies of the sample, and will be a direct measure of the dichroism of the sample. There is no particular advantage to using a double-beam system since, with this arrangement, the only response detected will be one which will vary with the rotation of the polarizer. Such will not be the case with atmospheric absorption, etc., so that compensation for this is not

necessary. The rotation frequency is chosen to be half the chopping frequency because a minimum in absorption will occur every 180° rotation of the polarizer, and two minima are observed per rotation.

MATHEMATICAL ANALYSIS

Let the angle θ designate the angle between the direction of maximum transmittance of the rotating polarizer and the vertical direction (Fig. 3). Let
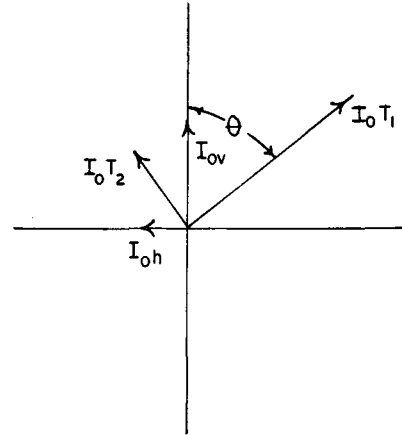

Fig. 3. Resolution of the polarized components of the infrared beam by the rotating polarizer.

T_1 be the transmittance of the polarizer in this direction of maximum transmittance and T_2 the transmittance in a direction perpendicular to this. If I_0 is the intensity of the incident unpolarized light emerging from the compensator, the intensities of the polarized components in the 1 and 2 directions emerging from the rotating polarizer will be given by

$$I_{01} = T_1 I_0 \tag{1}$$

$$I_{02} = T_2 I_0 \tag{2}$$

The vertical and horizontal components of the polarized beam emerging from the rotating polarizer will then be given by

$$I_{0v} = I_0 \left[T_1 \cos^2 \theta + T_2 \sin^2 \theta\right] \tag{3}$$

$$I_{0h} = I_0 \left[T_1 \sin^2 \theta + T_2 \cos^2 \theta\right] \tag{4}$$

If A_o and A_h are the vertical and horizontal absorbencies of the sample, the intensity of the beam transmitted by the sample in the vertical and horizontal direction will be given by

$$I_{tv} = I_0 (1-A_v) \left[T_1 \cos^2 \theta + T_2 \sin^2 \theta\right] \tag{5}$$

$$I_{th} = I_0 (1-A_h) \left[T_1 \sin^2 \theta + T_2 \cos^2 \theta\right] \tag{6}$$

The total transmitted intensity I_t is given by the sum of the transmitted horizontal and vertical components in the equation

$$I_t = I_{tv} + I_{th} = I_0 [(1-A_v)(T_1 \cos^2 \theta + T_2 \sin^2 \theta)$$

$$+ (1-A_h) (T_1 \sin^2 \theta + T_2 \cos^2 \theta)]$$

$$= I_0 [(1-A_v)T_2 + (1 - A_h)T_1 + 1/2 (T_1 - T_2)$$

$$+ [1/2 I_0 (T_1 - T_2)(A_h - A_v)] \cos 2\theta \quad (7)$$

This reduces to $I_t = [I_0 (T_1 - T_2)(A_h - A_v)/2] \cos 2 \omega t$

where

$$K = I_0 [(1-A_v)T_2 + (1-A_h)T_1 + 1/2 (T_1 - T_2)]$$

$$\theta = \omega t$$

$$\omega = 2\pi\nu$$

Here ω is the angular velocity of rotation t, the time in seconds; ν the number of rotations of the polarizer per second. K is a constant component of the transmitted intensity, independent of time, which will not be detected by the amplifier. Therefore, the response of the amplifier will be given by

$$R_\lambda = C_\omega \tau [I_0 (T_1 - T_2)(A_h - A_v)/2]$$

$$= B_\lambda |(A_h - A_v)_\lambda|^2$$

where

$$B_\lambda = C_\omega \tau [I_0(T_1 - T_2)/2] \quad (9)$$

C_ω is a constant which relates the intensity of the light falling on the detector to the reading of the meter (or recorder) driven by the amplifier. It is a function, of course, of ω, the frequency of chopping or of rotation of polarizer. τ is a transmittance constant which corrects for the absorption by windows and atmospheric constituents in the beam path of the radiation. The quantities C_ω, τ, $I_0 T_1$, and T_2 will be independent of the dichroism of the sample and will be a constant at a given wave length. Consequently, these are grouped together in the composite constant B_λ in eq. (9). If B_λ is known, then the difference in absorbencies $(A_h - A_v)$ may be determined by dividing the recorder response R by β_λ. This constant B_λ may be determined experimentally by determining the instrument response for a sample of known dichroism. The dichroism of a second polarizer of known transmittance at the particular wave length may be used. It is essential, of course, that the detector and amplifier be linear so that B_λ does not depend on $(A_h - A_v)$. In practice one would need to determine R_λ for the sample and R_λ for the apparatus. By dividing R_λ

by B_λ one would obtain a spectrum of $A_h - A_v$. This would be a spectrum containing only the dichroic bands of the sample with a height dependent upon the difference between their principal absorbencies. It should be noted that the absolute value of $(A_h - A_v)$ appears in eq. (9). One cannot determine from the instrument response whether A_h or A_v is bigger; this must be determined in a separate experiment. The perpendicular dichroism would be given by

$$D_\perp = A_h/A_v = [(A_h - A_v)/A_v] + 1 \quad (10)$$

which reduces to

$$D_\perp = 1 \pm (R_\lambda/D_\lambda)/A_v \quad (11)$$

The A_v required by this equation would be determined in an independent experiment by use of a conventional spectrometer with a vertically oriented polarizer.

Similarly, with the use of the equation for A_u,

$$A_u = A_v + A_h \quad (12)$$

equations for (A_h/A_v) and (A_v/A_u), which are required for determination of orientation functions, may be obtained:

$$A_h/A_u = 1/[2 + (R_\lambda/B_\lambda)/A_h] \quad (13)$$

$$A_v/A_u = 1/[2 + (R_\lambda/B_\lambda)/A_v] \quad (14)$$

References

1. Stein, R. S., and F. H. Norris, *J. Polymer Sci.*, **21**, 381 (1956).
2. Stein, R. S., *J. Polymer Sci.*, **31**, 327, 335 (1958).
3. Stein, R. S., ONR Technical Report No. 21, Contract Nonr 2151(00), Project NR 356-378, Univ. of Mass, "The Specification of Biaxial Orientation," August 8, 1960.
4. Stein, R. S., ONR Technical Report No. 22, Contract Nonr 2151(00), Project NR 356-378, Univ. of Mass. "The Optical Properties of Oriented Polystyrene," August 15, 1960.
5. Marrinan, H. J., private communication.

Synopsis

A method is described for measuring directly the infrared dichroism spectrum of a film by use of a single-beam spectrometer. The method involves modulating the beam passing through the sample with a rotating polarizer rather than with a chopper. The a.c. response of a detector is then proportional to the difference between the principal absorbencies of the sample.

Résumé

On décrit une méthode pour mesurer directement le spectre de dichroïsme infra-rouge d'un film en utilisant un spectromètre à un seul faisceau. La méthode comprend une variation du faisceau passant par l'échantillon, variation à

l'aide d'un polariseur rotatif plutôt qu'à l'aide d'un interrupteur à répétitions. La résponse d'un détecteur est alors proportionnelle à la différence entre les absorptions principales de l'échantillon.

Zusammenfassung

Eine Methode zur direkten Messung des Dichroismus im Infrarotspektrum eines Films mit einem Einzelstrahlspektrometer wird beschrieben. Die Methode verwendet einen rotierenden Polarisator zur Modulation des durch die Probe gehenden Strahles anstelle eines Zerhackers. Der Wechselstromausschalg eines Detektors ist dann der Differenz zwischen den Hauptabsorptionen der Probe proportional.