Infrared Refractive Indices of Some Oriented Polymers†

C. J. Henniker

Centre D'Etude des Matières Plastiques, Paris, France. *Received October 5, 1972*

ABSTRACT: The measurement of the infrared refractive index raises a problem whenever it is required to know the true absorbances in an anisotropic film placed obliquely to the incident radiation. This occurs in the determination of orientation of biaxially drawn films. A case in point is a study of oriented polyacrylonitrile, in which doubt concerning the refractive index led to results of doubtful value. We have used interferometric and reflection methods to measure refractive indices in polarized infrared, parallel and perpendicular to the orientation direction, in polyacrylonitrile, poly(vinyl alcohol), and polyamide 6. Each shows pleochroic absorptions, but up to about 1500 cm^{-1} the two indices are the same and may be used in orientation studies.

In the measurement of infrared absorbances in several directions in an anisotropic material, a problem is often raised by the determination of the refractive indices. A case of practical interest is the study of the degree of molecular orientation, in the three coordinate directions, in biaxially oriented films. Use is made of the relationship between orientation and pleochroism, but values of the refractive indices in the three directions are then needed in order to find the true optical paths in a film placed obliquely to the incident radiation, and hence the true absorbances.

It is to be expected that a considerable anisotropy of refractive index will be found in highly pleochroic polymers, since it is well known that complex changes in the index accompany absorption. This would be particularly marked in polyacrylonitrile, a structurally simple polymer in which the zig-zag (TTTT) conformation of the syndiotactic configuration predominates.[1] The principal transition moments, due to the nitrile and methylene groups, lie at 90° to the chain direction, and their high dichroic ratios are bound to lead to anisotropic refractive indices. Thus in a study of biaxially oriented polyacrylonitrile,[2] the final results seemed to be jeopardized because of uncertainty in the indices in the three directions. In the absence of direct measurements, a single calculated average value of refractive index was applied at two wavelengths and various orientations, in apparent contradiction with the phenomenon of pleochroism.

We have undertaken a preliminary survey of the refractive indices of some oriented polymers, hoping to justify the use of an average value and if not, to provide a base for a more satisfactory exploitation of absorbance measurements of biaxially oriented films.

Experimental Section

Because of the opacity of polymers in the infrared region, the usual techniques in the visible are unsuitable. Interferometric methods are valid in spectral regions of low absorbance, while in the neighborhood of absorption peaks, reflection methods alone are applicable. We have used both techniques, as has been done for nonoriented polymers[3,4] using one as a check on the other.

The interferometric method involves recording spectra, as free as possible from absorption and reflection effects, of the sinusoidal variations in intensity due to interference between reflected and direct ways in a parallel-faced film. The equation describing them is

$$2nl \cos \theta = 10^4 \frac{K}{\nu}$$

where K is an ordinal number, and the frequency ν is expressed in cm^{-1}. Recording on a linear frequency scale is extremely convenient.

Since K is not directly available, use is made of the equation:

$$\frac{K}{\nu} = \frac{\Delta K}{\Delta \nu}$$

involving the frequency difference and the K count over a spectral range in which n does not vary. Average values of n are then calculated from K/ν. The somewhat delicate operation of assigning K values to individual interference maxima has not been attempted in this survey.

The reflection method is based on the relations between n and the reflection coefficient R

$$n = \frac{1 + R^{1/2}}{1 - R^{1/2}}$$

$$R = \left(\frac{n - 1}{n + 1}\right)^2$$

Absolute values of R are dependent on the state of the surface, but a single n value from interferometry may be used in conjunction with the reflection spectrum from an imperfect surface to given n values at neighboring wavelengths. This is particularly valuable in estimating the refractive index at absorption peaks. The reflection spectrum must not be encumbered by absorption or interference effects.

The recording of pure interference and reflection spectra from polymer films requires the judicious use of reference beam compensation in a double-beam spectrometer.

Results

Polyacrylonitrile. The pure polymer being exceptionally difficult to draw, we gladly accepted a gift of material containing a few per cent of copolymer, offered by the Rhône Poulenc Textile Co. Films were prepared from dimethylformamide solution, dried at room temperature for a day, and drawn uniaxially at 170° at about 5%/min to a draw ratio of 3:1.

Refractive indices obtained by the $\Delta\nu/\Delta K$ method in two transparent spectral zones were found to be the same in the parallel and perpendicular directions, within experimental error: 3970–3370 cm^{-1}, n = 1.46; 2200–1750 cm^{-1}, n = 1.51. A measurement on nonoriented material gave at 1000–640 cm^{-1}, n = 1.55. We consider the precision to be ±1%.

Reflection spectra, recorded both in the parallel and perpendicular directions, show that the value of 1.46 may be used for the methylene antisymmetric moment at 2940 cm^{-1} in either direction while the index at the nitrile peak (2230 cm^{-1}) is somewhat sensitive to the absorption and descends to about 1.42 at the reflection minimum (2250 cm^{-1}) and rises to about 1.46 at the absorption

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(1) R. Yamadera, M. Tadokoro, and S. Murahashi, *J. Chem. Phys.*, 41, 1233 (1964).

(2) L. E. Wolfram, J. G. Grasselli, and J. L. Koenig, *Appl. Spectrosc.*, 24, 263 (1970).

(3) P. Chevalier, P. Dubois, and C. J. Henniker, "Methodes Physiques d'Analyse," Paris, 1966, p 237.

(4) C. J. Henniker, "Infrared Spectrometry of Industrial Polymers," Academic Press, London, 1967, p 100.

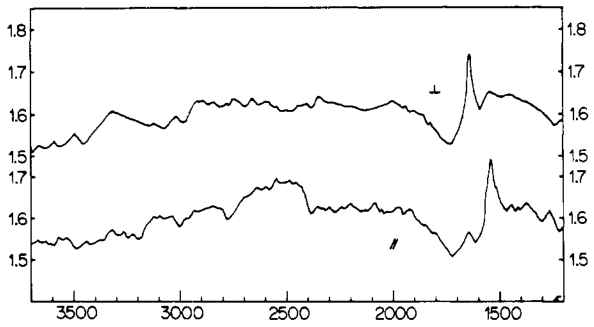

Figure 1.

peak. Both these observations refer to the (stronger) perpendicular transition moment. The parallel moment would give rise to less variation.

Poly(vinyl alcohol). The film examined was the Cipoviol, made by the Rhône Poulenc Co. This material is thought to be plasticized. It was drawn at 20 and 100°, at 500%/min, to a ratio of 3:1. It was clamped in a specially designed sample holder before release from the jaws. The most reliable index measurements, made at 2400-1800 cm^{-1}, show little difference between the parallel and perpendicular directions. An average value of 1.70 was calculated. The reflection spectra show that the index varied between 1.63 and 1.77 within the zone 4000-1200 cm^{-1}. At lower frequencies numerous absorptions made measurements unreliable. The reflection spectra show that the index varies little until it rises sharply between 500 and 440 cm^{-1}.

Polyamide 6. This material, showing several markedly dichroic absorptions, was chosen for its excellent drawing behavior. Films were drawn at 20° to a ratio of 7:1. The average value of the index, by the $\Delta K/\Delta\nu$ method, in the 2500-1800-cm^{-1} zone, was 1.62 both for the parallel and perpendicular directions.

Figure 1 shows the perpendicular and parallel refractive indices in this frequency region, together with perturbations accompanying the absorption peaks at 1660 and 1580 cm^{-1}. As might be expected from the presence of dichroic peaks in the 1700-1100-cm^{-1} zone, most absorbing strongly in the parallel direction, the indices in the 1000-800-cm^{-1} zone were not equal; parallel 1.79, perpendicular 1.72.

These values are in fair agreement with the value of 1.82 found for an amorphous peak at 1140 cm^{-1} [5] in polyamide 6-6, but higher than the reported value of 1.44 for a crystalline peak at 936 cm^{-1} in this polymer. The latter value is surprising in view of the rather flat reflection spectrum for polyamide 6-6 in the 1200-800-cm^{-1} zone,[4] which would signify a rather constant index over this range.

Conclusions

Even for a highly dichroic polymer such as polyacrylonitrile, the use of a single value of refractive index determined at a wavelength of low opacity would be a useful approximation. We believe our average value of 1.51 to be reliable for such use within ±5%, the reported value of 1.8[2] being too high by about 20%. For finer work it is necessary to make index measurements at the frequency of the absorption maximum, in at least two of the ordinate directions, making all associated absorption measurements at carefully calibrated wavelengths. No reliance can be placed on index measurements in the visible spectrum, the pleochroic infrared absorptions having a cumulative effect progressing toward lower frequencies.

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(5) J. L. Koenig and M. Itoga, *Appl. Spectrosc.*, **25**, 355 (1971).

Optical Rotatory Dispersion of Polypeptides and Proteins in the near-Infrared Region†

S. Yu. Venyaminov and Yu. N. Chirgadze*

Institute of Protein Research, Academy of Sciences of the USSR,
Poustchino, Moscow Region, USSR. *Received October 6, 1972*

ABSTRACT: It has been shown for polypeptides that the value of the ir term of optical activity which depends on the conformation of the polypeptide chain can be determined by ORD in the near-infrared region. This term corresponds to the sum of rotatory powers of optically active vibrational transitions. For the random state of this value is equal to zero, for the α-helical state, though small, it exceeds the error of measurement and for the β form it is higher by almost an order than for the α-helical state. Measurements carried out for a number of globular proteins with a known structure show a high sensitivity of the method. It is possible to detect the β conformation of three to five residues in a molecule consisting of 100-200 amino acid residues. The possibility of using the method for studies of protein structures is discussed.

Optical rotatory dispersion (ORD) of polypeptides and proteins in the ultraviolet and visible regions greatly depends on their conformations. ORD in these regions is accounted for by the interaction of light with the electronic transitions of the peptide group. In principle, the existence of optical activity of the vibrational transitions is not excluded, although at present the possibility of this is shown only theoretically.[1] Indirectly the optical activity of the vibrational transitions must be reflected in the rotatory dispersion in the near-infrared region and this was shown in measurements for crystal quartz.[2,3] On this basis an attempt was made to investigate ORD in the near-infrared region for polypeptides in different conformations.[4,5]

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† This paper is one of the group presented at the 10th Prague IUPAC Microsymposium on Macromolecules, August 28-31, 1972.

(1) C. W. Deutsche and A. Moscowitz, *J. Chem. Phys.*, **49**, 3257 (1968).

(2) T. M. Lowry and C. P. Snow, *Proc. Roy. Soc., Ser. A*, 127, 271 (1930).

(3) S. Yu. Venyaminov and Yu. N. Chirgadze, *Opt. Spectrosko.*, 23, 813 (1967).

(4) Yu. N. Chirgadze, S. Yu. Venyaminov, V. M. Lobachev, *Biopolymers*, **10**, 809 (1971).

(5) E. V. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).