Dichroism of an Ideally Oriented Polymer Chain

YASUJI KOBAYASHI, SABURO OKAJIMA, and
KAZUO NAKAYAMA, *Faculty of Technology, Tokyo Metropolitan
University, Tokyo, Japan*

Synopsis

Visible dichroism can be utilized as a measure of the degree of orientation of an amorphous region in a polymer. But the relations between dichroism and states of dyes in polymer must be elucidated before dichroism can be used more widely as a reliable means for study of amorphous orientation. To calculate the orientation factor for visible dichroism, it is necessary to decide the dichroism of an ideally oriented polymer chain. For this purpose, a single crystal of Congo Red was prepared and the dichroic spectrum of the crystal was measured. It was found that the dichroism of the Congo Red molecule itself is unity in a suitable wavelength region. As a result, a simple means for the treatment of dichroic spectra was given. The angle between the polymer chain axis and the principal axis of the absorbed dye molecule was discussed.

Introduction

When a cellulose or a poly(vinyl alcohol) fiber is dyed with a dichroic dye such as Congo Red, the dye molecules are absorbed parallel to the amorphous chain segments of the polymer, and consequently dichroism develops if the polymer is anisotropic. This phenomenon can be utilized as a measure of the degree of orientation of the amorphous region. But the relations between dichroism and states of dyes in polymer must be elucidated, before dichroism can be used more widely as a reliable means for study of amorphous orientation.

When $D_{\parallel}$ and $D_{\perp}$ in eqs. (1) and (2) are the absorbance of the dyed polymer for polarized light vibrating parallel and perpendicular to the orientation axis, respectively.

$$10^{-D_{\parallel}} = I_{\parallel}/I_0 \tag{1}$$

$$10^{-D_{\perp}} = I_{\perp}/I_0 \tag{2}$$

$$D = D_{\parallel}/D_{\perp} \tag{3}$$

where $I_{\parallel}/I_0$ and $I_{\perp}/I_0$ are the fraction of the polarized light transmitted through the dyed polymer, and D is dichroic ratio.

Dichroism is defined by f_D:

$$f_D = (D_{\parallel} - D_{\perp})/(D_{\parallel} + 2D_{\perp})$$
$$= (D - 1)/(D + 2) \tag{4}$$

and dichroism f_D is related closely to the orientation factor f in the terms of P. H. Hermans:[1]

$$f = f_D/f_D{}^0 \tag{5}$$

where $f_D{}^0$ is the dichroism for ideally oriented polymer. $f_D{}^0$ is the product of the dichroism f_{Dye} of the dye molecule and the orientation factor f_θ of the dye molecule, which is related to the angle θ between polymer chain axis and the principal axis of the absorbed dye molecule.

$$f_D{}^0 = f_{Dye} f_\theta \tag{6}$$

$$f_\theta = (3 \cos^2 \theta - 1)/2 \tag{7}$$

Experimental

A direct method for determining the dichroism of dye molecule f_{Dye} is to measure the dichroic spectrum of a single crystal of dyestuff. Mitchell reported that Congo Red crystallized in thin plates under suitable conditions and that the crystal showed a strong dichroism.[2] However, the dichroic spectrum of a single crystal of Congo Red has not yet been reported.

The Congo Red crystal was prepared by the method of Mitchell,[1] and the dichroism was measured as follows. The potassium salt of Congo Red was crystallized by adding potassium chloride or potassium bromide to a dilute hot solution of the purified dyestuff. The temperature of the solution was kept in the range of 95–98°C.

At the boiling temperature, Congo Red crystallized in thin plates which were broken easily by the bubbling motion of solution; on the other hand,
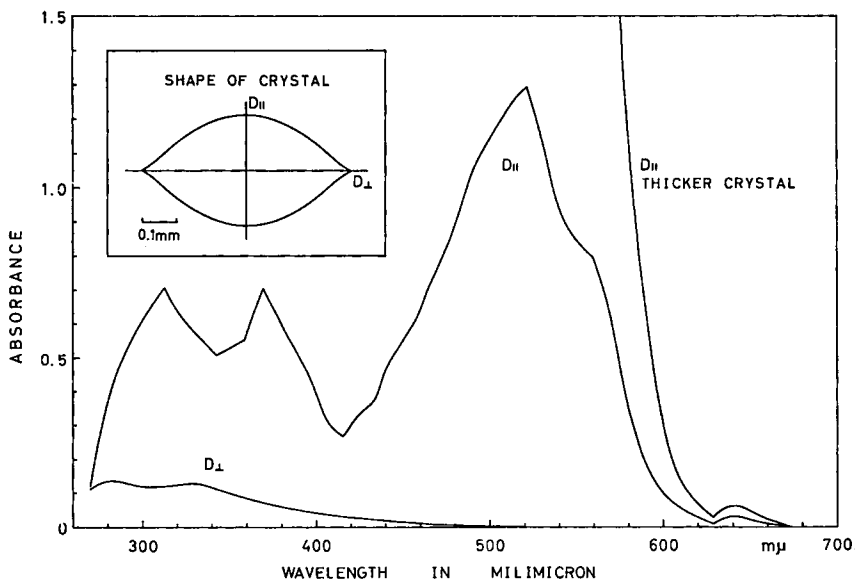

Fig. 1. Shape and dichroic spectrum of Congo Red single crystal.

at a temperature below 95°C. the crystals were rather thick and of low dichroism. The sodium salt of Congo Red has a tendency to coagulate, so it is very difficult to prepare crystals in large size.

The dichroic spectrum of the leaflet crystals prepared at 95–98°C. was measured in a 5% potassium chloride solution with an Olympus micro-spectroscope photometer, MSP-A IV. The dichroic spectrum is shown in Figure 1.

Results and Discussion

When the incident light is polarized parallel to the direction of the transition moment of the dye molecule, the absorbance of the crystal is maximum. As the direction of the maximum absorbance or the transition moment is parallel to line shown as $D_\parallel$ in the schematic diagram of the shape of the crystal (Fig. 1, inset), the long axis of the dye molecule must be lying along this line. In the perpendicular direction, very weak absorbance is observed in the ultraviolet region which tails off up to 500 mμ. In the region 500–650 mμ, there is no absorbance in the perpendicular direction.

A small peak is observed near 640 mμ on the $D_\parallel$ curve in Figure 1. A similar peak was found at 620 mμ in a spectrum of a concentrated aqueous solution of Congo Red as shown in Figure 2,[3] while in the spectrum of Congo Red solution in ethanol or pyridine there is no peak in this wave-length region.
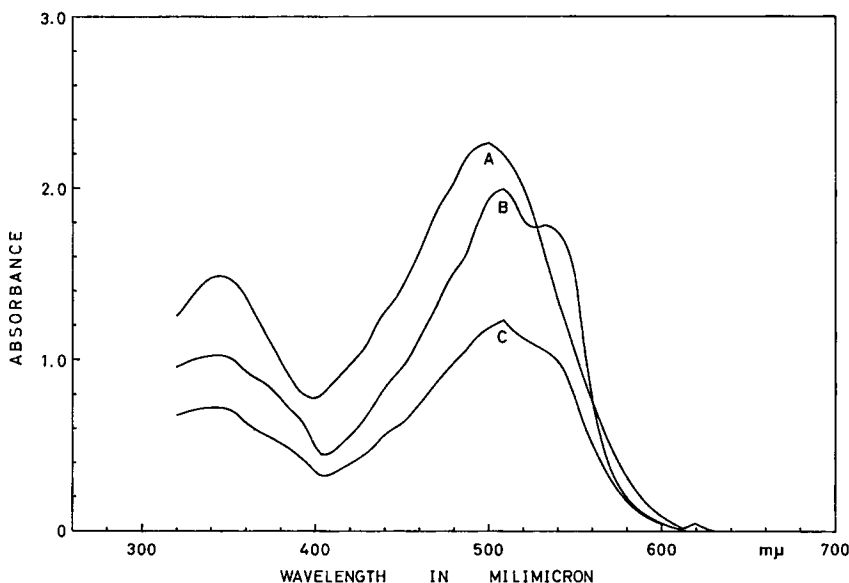

Fig. 2. Spectra of (A) aqueous solution of Congo red; (B) poly(vinyl alcohol) film dyed with Congo Red in dry state; (C) poly(vinyl alcohol) film dyed with Congo Red in swollen state.

Also a cellophane or a poly(vinyl alcohol) film dyed with Congo Red failed to show such a peak, even when the dye concentration was sufficiently high, as (Fig. 3) when a poly(vinyl alcohol) film was prepared from a polymer solution containing 1.20 g. Congo Red per gram polymer and the film was subjected to 3× stretching and, in another experiment, cellophane was dyed with saturated Congo Red solution at the boiling temperature till the dye content in cellophane reached on 22%.

Because dye molecules disperse in a unimolecular state in ethanol or pyridine aqueous solutions and the spectra do not show a peak, it may be concluded that the small peak in the spectrum of the crystal or concentrated
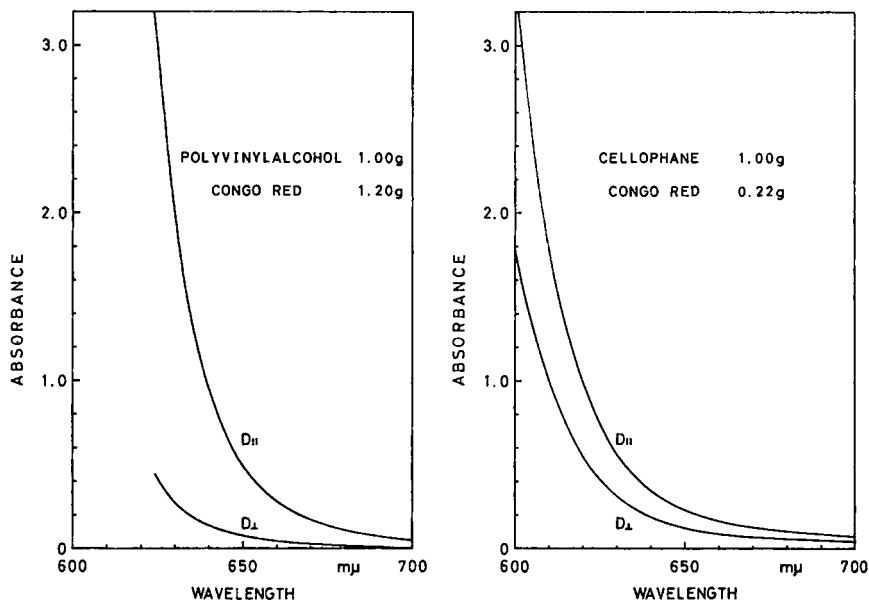

Fig. 3. Dichroic spectrum of a cellophane or a poly(vinyl alcohol) film dyed with Congo Red. Both the films lack a peak in the tailing region.

aqueous solutions is related to the associated dye molecules, and that the dye molecules exist in a more highly dispersed state, possibly a unimolecular state, in the polymers, too.

In the spectra of poly(vinyl alcohol) films containing Congo Red, the relative height of the shoulder or peak at 540 mμ varies according to the moisture content in the polymer. In Figure 2, curve B was obtained in the dry state in monochlorobenzene and curve C in the swollen state in a 1% potassium chloride solution. The shape of the shoulder of curve C is similar to the spectrum of the single crystal measured in a 5% potassium chloride solution.

In the near-ultraviolet region, the spectra of Congo Red in aqueous solution and in poly(vinyl alcohol) films have a peak at about 350 mμ. In the spectrum of the Congo Red crystal, this peak splits into two peaks
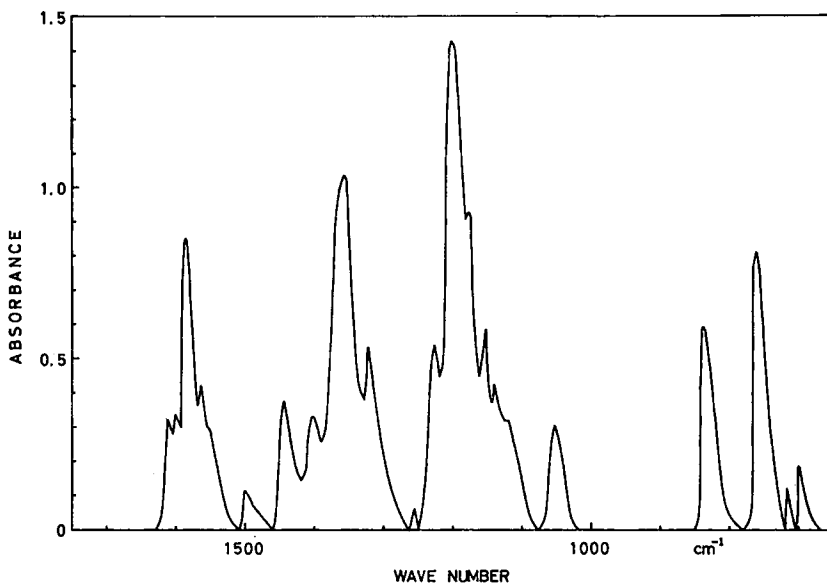
Fig. 4. Infrared spectrum of specimen on which the incident light is perpendicular to the plane of the Congo Red crystal leaflet.
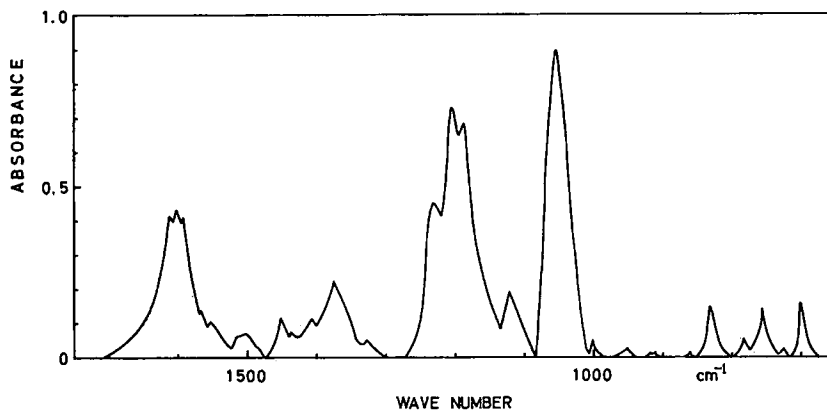

Fig. 5. Ordinary infrared spectrum of powdered Congo Red in a potassium bromide disk.

313 and 370 mμ as a result of the interaction among naphthalene rings lying side by side in the crystal.

As mentioned above, the long axis of the dye molecule lies parallel to the shorter dimension of the leaflet crystal.   The direction or the inclination of the benzene and naphthalene rings in the crystal can be determined by the infrared absorption.

When a drop of suspension of the thin leaflet crystals in a potassium chloride solution was laid on a silver chloride plate and the water removed, the planes of the crystals became parallel to the silver chloride plate, and

only the direction of the long axes of the crystals was random. The spectrum of the infrared absorption of this specimen is shown in Figure 4. For comparison, Figure 5 shows an ordinary spectrum of powdered Congo Red in a potassium bromide disk. In the latter case, the direction of all axes of dye molecules is perfectly random. In Figure 4, the absorbance at 1051 cm.$^{-1}$ is weaker than those at 832 and 755 cm.$^{-1}$, but the relative absorbances are reversed in Figure 5.

The absorption band at 1051 cm.$^{-1}$ is assigned to the symmetric stretching vibration of sulfonic acid and its direction of transition moment is in the plane of naphthalene ring. The absorption bands of 832 and 755 cm.$^{-1}$ are assigned to aromatic C—H out-of-plane bending vibrations, the band at 832 cm.$^{-1}$ being due to the vibration of the benzene ring and that at 755 cm.$^{-1}$ to the naphthalene ring.

These facts lead to the conclusion that the planes of the benzene and naphthalene rings are perpendicular to the plane of the Congo Red leaflet crystal and the aromatic rings are standing side by side. Interactions between the aromatic rings may play a role in this arrangement.

The dichroic spectrum of the crystal in Figure 1 shows no perpendicular absorption in the visible light region. As this direction corresponds to the out-of-plane vibration of the aromatic ring, the absence of absorbance in the visible light region is reasonable.

The absorption spectrum in the direction which contains the aromatic ring and is perpendicular to the long axis of the dye molecule is not yet known, but it is unlikely to have an absorption band in the visible light region, as highly oriented cellulose or poly(vinyl alcohol) fiber dyed with Congo Red has very high dichroic ratio which is constant regardless of wavelength in the region longer than 500 mμ. If the spectrum in the direction perpendicular to the long axis of dye molecule has an absorption band in this region, it can be determined only from the change in dichroic ratio near the absorption peak.

When both of the perpendicular directions show no absorbance, the dichroism of the dye molecule itself is unity. In this case, the dichroic ratio D is constant regardless of wavelength, and the dichroism f_D can be calculated on this dichroic ratio by eq. (4).

On the other hand, the dichroism for an ideally oriented polymer $f_D{}^0$ is equal to f_θ as long as dichroism of dye molecule itself is unity, and $f_D{}^0$ or f_θ is estimated by the dichroism of the highly oriented polymer of known degree of orientation as determined by other methods. When f_θ is given, the angle of inclination between the polymer chain axis and the direction of the transition moment of dye molecule is calculated by eq. (7).

One type of cellulose fiber, ramie, showed $f_D = 0.89 = 1/1.124$ after the correction of the spiral angle 5°.[4,5] P. H. Hermans and Heikens reported a nearly equal value 1/1.13 for highly oriented rayon.[5,6]

$$f_D/f_X = 1/1.13 = 0.885$$

where f_X is the x-ray orientation factor.

Smirnov measured the dichroic spectrum of poly(vinyl alcohol) film dyed with Congo Red and reported that parallel and perpendicular absorbances were $D_\parallel = 1.820$, $D_\perp = 0.070$ at 535 mμ when the film was stretched 4.2 times its original length.[8] Dichroism was calculated by eq. (4) as $f_D = 0.89$. Provided that the sample is perfectly oriented,

$$f_\theta = (3 \cos^2 \theta - 1)/2 = 0.89$$
$$\theta = 15°$$

Smirnov accepted this value and concluded that the Congo Red molecule is absorbed to the poly(vinyl alcohol) segment through two NH_2 groups in the *trans*-position, as the angle between the line connecting the two N atoms and the long axis of the Congo Red molecule is 15°.

According to Zollinger,[9] the energy difference between the *cis* and *trans* types is only 1/40 of the thermal energy at room temperature, so the existence of an equal amount of the two types may be considered. If Smirnov's view is allowed, it is better to consider that half of the absorbed Congo Red molecules is absorbed completely parallel to poly(vinyl alcohol) molecules, while the rest is inclined by 15°. Then f_D of the former molecules is 1.00 and that of the latter type is 0.89, and the mean value is 0.945.

For the maximum dichroism of poly(vinyl alcohol) dyed with Congo Red, a still greater value 0.95–0.96 instead of 0.89 was found for a poly(vinyl alcohol) fiber of the highest orientation which had been heat-treated after the stretching.[4,5]

As the stretched specimen is not perfectly oriented at all times, the real value of dichroism for an ideally oriented polymer is 0.96–1.0, and it is perhaps nearly equal to unity. Provided that the maximum dichroism is unity, the direction of the transition moment of dye molecule is parallel to the polymer segments, and the measured dichroism f_D is equal to the orientation factor f in terms of P. H. Hermans.

In general, however the angle of inclination between polymers and dye molecules may differ for each polymer and dyestuff.

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Résumé

Le dichroïsme visible peut être utilisé comme mesure du degré d'orientation de régions amorphes dans un polymère. Mais les relations entre le dichroïsme et l'état des colorants dans le polymère doivent être élucidées avant que le dichroïsme puisse être utilisé large-

ment comme méthode d'étude de l'orientation amorphe. En vue de calculer le facteur d'orientation, dans le dichroïsme visible, il est nécessaire de déterminer le dichroïsme pour des chaînes polymériques orientées idéalement. A cet effet, un monocristal de rouge congo a été préparé et spectre dichroïque du cristal a été mesuré. On a trouvé que le dichroïsme de la molécule de rouge congo elle-même était unitaire dans une région de longueur d'onde adéquate Une méthode simple pour utiliser les spectres de dichroïsme est ainsi mise au point. L'angle entre l'axe de la chaîne polymérique et l'axe principale de la molécule de colorant absorbé est discuté.

Zusammenfassung

Dichroismus im Sichtbaren kann als Mass für den Orientierungsgrad der amorphen Bereiche in Polymeren verwendet werden. Es müssen aber die Beziehunger zwischen Dichroismus und dem Zustand der Farbstoffe im Polymeren aufgeklärt werden, bevor der Dichroismus in grösserem Umfang als verlässliches Mittel zur Untersuchung der Amorphorientierung herangezogen werden kann. Um den Orientierungsfaktor für den Dichroismus im Sichtbaren zu berechnen, ist es notwendig den Dichroismus für eine ideal orientierte Polymerkette zu kennen. Zu diesem Zweck wurde ein Kongorot-Einkristall hergestellt und das dichroitische Kristallspektrum gemessen; es wurde gefunden, dass der Dichroismus des Kongorotmoleküls selbst in einem geeigneten Wellenlängenbereich gleich eins ist. Als Ergebnis wird ein einfaches Mittel zur Behandlung der dichroitischen Spektren angegeben. Der Winkel zwischen der Achse der Polymerkette und der Hauptkette der absorbierten Farbstoffmoleküle wurde diskutert.