PREFERENTIAL ABSORPTION OF DYE TO THE HIGHER ORDER AMORPHOUS REGION

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Synopsis

Dye dichroism can be used to determine the mean amorphous orientation. For this purpose, absorbed dyes must be dispersed uniformly in a whole amorphous region. This uniform dispersion may not always occur in all cases. When the oriented cellulose and polyvinyl alcohol films are dyed with direct dichroic dyes, small amounts of dye molecules are absorbed preferentially into the higher order region of the polymer chain. With an increase of amount, dye molecules disperse uniformly in the whole amorphous region and the observed dichroism approaches to the mean amorphous orientation. But, the dye molecule of longer length has a lower preferential absorption. The preferential absorption phenomena relates to the affinity of dye to polymer and to the steric hindrance of dye diffusion into the narrow gaps of the higher order polymer chains. The study of dichroism of polymer at low content values of the dichroic dye may be useful for obtaining information on the lateral order of amorphous polymer chains. Conversely, to determine the mean amorphous orientation, the lower concentration dyeing must be avoided.

INTRODUCTION

Dye dichroism is an important method for evaluation of the amorphous orientation. The relations between dye dichroism and states of dyes in polymer must be elucidated, before dichroism can be used more widely as a reliable means for the study of amorphous orientation. In most cases, the test polymer is dyed in the original state and then stretched in dye dichroism experiment. After the stretching, dye molecules may be dispersed uniformly in the whole amorphous region and the dichroism refers to the average orientation of the amorphous region. It cannot be, however, expected a priori that the dye molecules disperse uniformly in the whole amorphous region, when the polymers are dyed in the stretched state. It is not very likely that the dichroic dyes enter into the crystalline regions of polymer, but it may be possible that the dyes are absorbed on the surface of crystals, or that the dyes are preferentially absorbed by the well-oriented parts of the amorphous regions. In either case, the dichroism does not exactly refer to the average orientation of the amorphous. In this paper, the preferential absorption of dichroic dye molecules in the higher order region of polymer was studied. For the study of this phenomenon, cellulose and polyvinyl alcohol films and several dichroic dyes were used.

EXPERIMENTAL

Preparation of Polyvinyl alcohol Film

Polyvinyl alcohol (DP=1270) was dissolved in water at 80°C and the hot solution was cast on a glass plate. The film was treated in the following four steps:
(1) stretched to three times its original length in an atmosphere of relative humidity 95%, 20°C,
(2) heat-treated for two minutes in an oil bath of 205~210°C, keeping the stretched length constant,
(3) annealed for one minute in an oil bath in a free state at 227°C,
(4) boiled in a 1% sodium chloride water solution for 30 minutes.

The diffusion of dyes in polymer which was heat-set under the constant length is very slow, but after annealing at 227°C the polymer film was stable in 70°C water and accepted dye readily without any change in the polymer texture.

**Preparation of Cellulose Film**

Viscose made from linter pulp by the ordinary method was spread on a glass plate and coagulated into a xanthate film in an ammonium sulphate solution. The xanthate film was stretched up to twice its original length in a zine chloride solution. The cellulose xanthate of the stretched film was decomposed to cellulose by a 5% acetic acid. A stable oriented cellulose film was obtained after boiling in water.

**Determination of the Orientation**

The orientation factor $f_b$ of the b-axis of the polymer crystal was determined from azimuthal scanning of (101) and (10̅1) reflections, as it was confirmed that the specimens have monoaxial orientation. The degree of crystallinity was obtained from the diffraction pattern in the range of $2\theta$ from 15° to 25°. The total orientation factor $f_o$ of the polymer was determined from the birefringence. The intrinsic birefringence value of 0.055 was given by P.H.Hermans for the completely oriented regenerated cellulose. The relation between the crystal orientation and the birefringence corrected by the density was extrapolated up to perfect crystal orientation, resulting in value 0.0429 for the intrinsic birefringence of polyvinyl alcohol. The amorphous orientation $f_a$ was obtained by subtracting the crystal contribution from the total orientation from the birefringence.

**Measurement of Dichroism**

The cellulose and polyvinyl alcohol films were dyed at 70°C for 20 hours until dye absorption was at equilibrium. In the case of desorption of dye from the films, 50% ethanol water solution was used at room temperature. Measurement of absorbance was made by spectrophotometer with polarizer. When the parallel and perpendicular absorbances $K_\parallel$ and $K_\perp$ are plotted on a rectangular co-ordinate, measured values fall on a line passing through the origin regardless of the wavelength in the region of 540~700 m\(\mu\). The slope of the line is a mean dichroic ratio and dichroism can be calculated exactly by the mean dichroic ratio,

$$D = \frac{(R-1)}{(R+2)}$$
$$R = \frac{K_\parallel}{K_\perp}$$

where $D$ is dichroism and $R$ is dichroic ratio.

For the measurement of absorbances in dry state, a specimen was placed in a glass cell containing a mixed solution of tricresyl phosphate and dibutyl phthalate to minimize the reflection and scattering of light on the film surface. The mixed solution has the refractive index of 1.54 near the value of the cellulose and polyvinyl alcohol films. To measure the absorbance in swollen state, a specimen was placed in a glass cell containing water in which
1% sodium chloride was dissolved to prevent the diffusion of dye into water.

RESULTS and DISCUSSION

The annealed polyvinyl alcohol film can be easily dyed by Congo Red up to about 80 weight per cent per polymer as shown in Figure 1. Observed dichroism is differentiated into three ranges according to the amount of absorbed dye in the polymer: the first, i.e., 0%–10%; the second, 10%–20%; the third, 20%–80%. In the low content of dye, the dichroism is very high and gives nearly the equal orientation factor to that of the crystal region. The suggests that the small amount of dye is absorbed preferentially in higher order regions of polymer chain and then the dichroism decreases gradually with the additional increment of dye content. In the intermediate content from 10% to 20% in Figure 1, the dichroism has uniform value independently on the change in dye contents, and the dichroism in dry state coincides with the amorphous orientation which was obtained by subtracting the crystal contribution from the total orientation. This indicates that dye molecules are dispersed uniformly in the whole amorphous region in the intermediate dye content and thus the dichroism refers to the average orientation of the amorphous region.

When the polyvinyl alcohol film of the specimen was swollen, its length was increased by 39% along the axis of stretching and by 9% across this axis. The relation between the dichroic ratio in the dry state $R_d$ and that in the swollen state $R_w$ is given as follows,

$$\frac{R_d}{R_w} = \frac{2 \cot^2 \theta_d}{2 \cot^2 \theta_w} = \frac{(L_1/L_3)^2}{(L_1/L_4)^2} = \frac{(L_4/L_3)^2}{(L_4/L_1)^2} = \frac{(1.09)^2}{(1.39)^2} = 0.617$$

where $L_1$ and $L_3$ and dry length; $L_2$ and $L_4$ are swollen length; $L_1$ and $L_3$ are along the stretching axis; $L_2$ and $L_4$ are across this axis as shown in Figure 2.

On the basis of this relation, the dichroic ratio in the swollen state can be calculated from
the dichroic ratio in the dry state and the degree of swelling. The calculated dichroism agrees with the dichroism observed in the swollen state in the case of the low and intermediate dye content. But in the higher dye content of over 20\% in Figure 1, the dichroism observed in the swollen state is lower than that in the calculated one. This means that in this higher dye content, the orientation of dye molecules does not follow to the change in the orientation of the amorphous chain during the anisotropic swelling process, and the dye molecules are absorbed with a weak affinity in polymer. At the low dye content, the orientation factor from the dichroism is near that of the crystal orientation determined by X-ray. The crystal orientation is not changed in the dry state or the swollen state, though the dry and wet dichroism are different. Therefore the dye molecules may be absorbed preferentially in the higher order amorphous regions and are not on the surface of the crystal.

This preferential absorption phenomenon is not only specific in polyvinyl alcohol—Congo Red system, but also in the other polymer and dye systems. In Figure 3, the dichroism in the dry state of oriented cellulose films dyed with three dichroic dyes shows two regions of preferential absorption and of uniform dispersion. The three dichroic dyes used were Congo Red (C.I. 22120), Sky Blue FF (C.I. 24410), and Kayarus Blue G (C.I. 34200). The dichroism increases gradually with the decrease of the dye in polymer for dye content below 1.5\%. This increase of the dichroism is lower in the case of Kayarus Blue G than in the other cases. This may be related to the length of the dye molecule, for the longer dye molecule may not diffuse readily into the narrow gaps of polymer chains in the higher order regions. The dichroism shows same value in the range of dye content over 1.5\% for the three dyes, as

Fig. 2. The relation between the mean orientation angle $\theta$ and the macroscopic dimension of the polymer film during the swelling process, where the change of dichroism with swelling obeys the affine deformation. $L_1, L_4$: dry length, $L_2, L_4$: wet length, $L_1, L_2$: along stretching direction, $L_3, L_4$: perpendicular direction, $\theta_d, \theta_w$: orientation angles in dry and wet.

Fig. 3. Changes in dichroism in the dry state with uptake of dye for cellulose films. Two regions, i.e. preferential absorption and uniform dispersion regions, can be observed.
This dichroism coincides with the average amorphous orientation obtained by subtracting the crystal contribution from the total orientation. Therefore it appears that dye molecules disperse uniformly in the whole amorphous region of polymer in the range of dye content over 1.5%.

When the film of cellulose was swollen, the length was increased only 5% of the dye state along the axis of stretching and 46% along the axis perpendicular to stretching. If the swelling process is the affine deformation, the dichroism of the swollen state must be very low. This is not the case with cellulose, in spite of a good agreement with the polyvinyl alcohol film. The observed wet dichroism is near the dry dichroism and coincides with the dry value at the small content of dye, as shown in Figure 4.

The polyvinyl alcohol films were dyed with the three dichroic dyes, as used for cellulose, at a small content of dye. The dichroism by three dyes differs from one dye to another, as shown in Figure 5. A specimen dyed with Kayarus Blue G has an uniform dichroism and does not change at lower content of dyes, moreover the dichroism of dry state is close to the average amorphous orientation, obtained from the X-ray and birefringence methods. It may be explained by the same reason for the case of cellulose dyed with the same dye.
CONCLUSION

When the oriented cellulose and polyvinyl alcohol films are dyed with direct dichroic dyes, small amounts of dye molecules are absorbed preferentially into the higher order regions of the polymer chain. With the increase in content of absorbed dye, dye molecules are dispersed uniformly in the amorphous region and the observed dichroism approaches the average amorphous orientation. The shorter the length of dye molecules, the preferential absorption becomes remarkable. The preferential absorption relates to the affinity of the dye to the polymer and the steric hindrance of dye diffusion into the narrow gaps of higher order of polymer chains. The study of dichroism of polymer at low content of dye may provide the information on the lateral order of amorphous polymer chains. But, to get the mean amorphous orientation, low concentration dyeing must be avoided.

Reference