Some Optical Properties of Cellulose Hydrate

Saburo OKAJIMA, Yasuji KOBAYASHI and Tetsuya KIKUCHI

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In the preceding paper⁽¹⁾ a linear relation between the intrinsic double refraction Γ and the dichroic orientation f_D of a fibre was derived as follows:

$$f_D=\frac{K_{\parallel}-K_{\perp}}{K_{\parallel}+2K_{\perp}}=\frac{k_{\parallel}-k_{\perp}}{k_{\parallel}+2k_{\perp}}\cdot\frac{\Gamma}{\Gamma_{\infty}} \qquad (1)$$

As is well known f_O, i.e. Γ/Γ_{∞}, indicates the orientation of the total molecules, while f_D mainly indicates that of the amorphous region. As to the orientations of the crystalline and amorphous regions, the former is higher than the latter according to the general views⁽²⁾ at present. The above relation (1) was obtained on the tacit assumption of an equal orientation degrees in the crystalline and amorphous regions, but the linear relation is also expected even when the two regions have different orientation degrees, if f_O and f_D are always in proportion. This proportional constant being C, (1) becomes

$$f_D=((k_{\parallel}-k_{\perp})/(k_{\parallel}+2k_{\perp})\cdot C\cdot\Gamma/\Gamma_{\infty}, \quad C\leqq 1.$$

In the range of the constancy of C, Γ/f_D is directly proportional to Γ_{∞}. As Γ_{∞} of a certain polymer changes with its crystallinity, Γ/f_D may possibly be a measure of the crystallinity of the polymer.

It is known that the crystallinity of a regenerated cellulose fibre is kept constant during the deformation. Accordingly a linear relation is expected between its f_D and Γ when C is also kept constant and it is actually confirmed experimentally as below. Then Γ_{∞} of the hydrate cellulose may be estimated from the experimental relation (1).

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1) Y. Kobayashi and S. Okajima, This Bulletin, **27**, 471 (1954).

2) P. H. Hermans, "Contribution to the Physics of Cellulose Fibre, 1946; J. M. Preston and P. C. Tsien, *J. S. D. C.*, **66**, 361 (1950), etc.

A. Measurements of Γ and f_D of the Fixed Specimens

(1) Preparation of the Anisotropic Filaments.—A sample of the absorbent cotton on the market was purified by extracting with a boiling 1% NaOH solution and dissolved in a cuprammonium solution, from which cellulose was coagulated into an isotropic filament and regenerated as described previously.3)

This isotropic filament of cellulose hydrate was stretched to various degrees, v, but in Exp. II the decoppering was carried out after being stretched to v which was calculated from the residual dry length relative to the isotropic dry state.

(2) Measurements of Γ and f_D.—The filaments were fixed to the frames as described previously4) and Γ and f_D were measured with D-line.

An appropriate mixture of tricresylphosphate and dibutylphthalate was used as the mountant. The refractive index was 1.54, which is equal to n_{iso}5) of the cellulose hydrate.

The dyeing was made with a 1% solution of Kongo red in 50% C_2H_5OH-H_2O and it was carefully controlled so that $K_{\parallel}$ did not go over 0.6 in any case.

Exp. I. A fresh and undried isotropic filament of cellulose was stretched and treated in succession as follows and used for the measurement of f_D.

(a) Dyed with Kongo red.
(b) Stretched to v in water at room temperature.
(c) Air-dried.
(d) Relaxed in water at room temperature.
(e) Air-dried again.

The filament was not allowed to shrink during the treatments (a)-(c) but it was free in (d) and (e). The specimen for Γ was prepared in the same way but a 50% C_2H_5OH-H_2O was used in (a) instead of the dye solution.

In Figs. 1 and 2 Γ and f_D are plotted against v and in Fig. 3 Γ against f_D. According to the figures Γ and f_D increase almost linearly with v and Γ-f_D is also linear as the theoretical relation (1) requires.

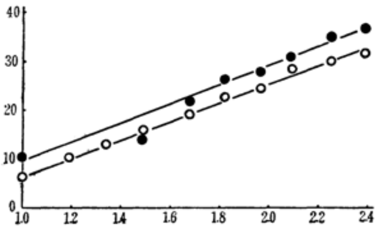

Fig. 1.
○ before Mercerization.
● after Mercerization.

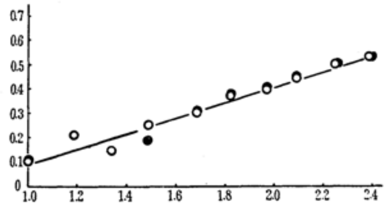

Fig. 2.
○ before Mercerization.
● after Mercerization.

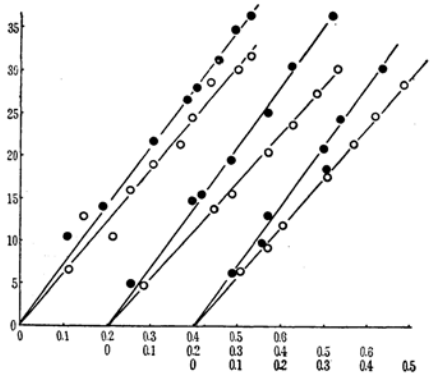

Fig. 3.
○ before Mercerization.
● after Mercerization.

The specimens used for the above measurements were then washed free from the mountant, mercerized with an 18% NaOH solution at room temperature, regenerated by pouring into a boiling 0.5% acetic acid solution, washed thoroughly and again observed. Of course in these treatments the longitudinal shrinkage was prohibited, otherwise they would shrink and disorientate. As shown in Figs. 1-3, Γ increases after the mercerization, but f_D remains almost unchanged. Both measures are also in a linear relation but the slope grows steeper.

Exp. II. In this experiment an isotropic filament, which was not yet decoppered was stretched in a 5% NaOH solution and then regenerated, washed, and treated as in (c)-(e) of the preceding experiment. The specimens for f_D were dyed after fixing to the frame, while those for Γ were treated, of course, with a 50% C_2H_5OH aq. solution.

In order to observe the effect of the mercerization, separate specimens were mercerized in this case as they were fixed to the frames and then dyed or treated with the 50% C_2H_5OH-H_2O solution. In other words, the mercerization was given to the undyed specimens. Fig. 3 indicates that the result is similar to the above: the linear relation of Γ-f_D holds good and the slope increases after the mercerization also in this case.

Exp. III. The isotropic filament used in the above experiment was decoppered and then stretched as in Exp. I. But the undyed specimens were mercerized as in Exp. II. A similar result is obtained as shown in Fig. 3.

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3) S. Okajima and S. Hayama, This Bulletin, **27**, 61 (1954).

4) S. Okajima and Y. Kobayashi, This Bulletin, **25**, 268 (1952); S. Okajima, Y. Kobayashi and R. Yamada, ibid,, **26**, 235 (1953).

5) S. Okajima, *J. Soc. Chem. Ind. Japan*, **49**, 128 (1946); P. H. Hermans, "Contribution to the Physics of Cellulose Fibre", 1946.

B. Measurements of Γ and f_D of the Relaxed Specimens

In the foregoing measurements each specimen was treated in the fixed state to a frame. Now the measurements of Γ and f_D were carried out in the relaxed state. The specimens were cut into the pieces of 3-4 mm lengths after the treatments (a)-(e) mentioned below, and they were inserted into a thin-walled glass capillary in a line and dried at 60°C under the high vacuum (<0.001 mm Hg) as shown in Fig. 4, when one drop of the mountant was also placed in the capillary near the open end. After the specimens were dried completely they were mounted. For this purpose the capillary was bent slightly down at the rubber connection, then the mountant streamed down along the inner wall of the capillary and dipped the specimens. The capillary was closed by melting near the open end. $K_{\parallel}$, $K_{\perp}$ and Γ of the specimens in the closed capillary were measured as usual but from the outside of the capillary. Therefore the last drying and the measurements were carried out in the relaxed state in this case as compared with the treatments in A.

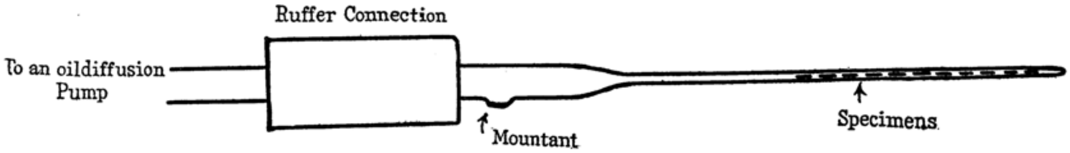

Fig. 4.

The stretching of the isotropic cellulose filament which was prepared as in A was carried out successively in the following order.

(a) Stretched in water at room temperature.
(b) Boiled in water.
(c) In Exp. IV, air-dried at room temperature. In Exps. V and VI, oven-dried at 100°C.
(d) Relaxed in boiling water.
(e) Air-dried again under no tension.

In these treatments (b) and (c) were carried out under tension, while (d) and (e) were carried out in the free state as described in each experiment.

Hg-line filtered through a Mazda's filtere VG1A was used for the following measurement of f_D. Of course the green light is absorbed so much by Kongo red, that the specimens must be dyed very lightly, otherwise $K_{\parallel}$ goes over 0.6. Then the specimens are, on the contrary, so transparent for Na-line, that the same dyed specimens can be used for the measurement of Γ. In Fig. 5 the points ● and ○ are the observed values of the dyed and undyed specimens respectively which show clearly that the effect of the dyeing is negligible. So the same specimens were used for the measurements of Γ and f_D in Exps. V and VI. Of course for this purpose the specimens must be dyed under the conditions which do not cause any disorientation due to swelling and contraction and the condition was accomplished by using the 50% C_2H_5OH aq. solution as the dyeing medium at room temperature.

A small discontinuity can be seen in the early stage of the deformation in Fig. 5, which was already pointed out previously.[6]

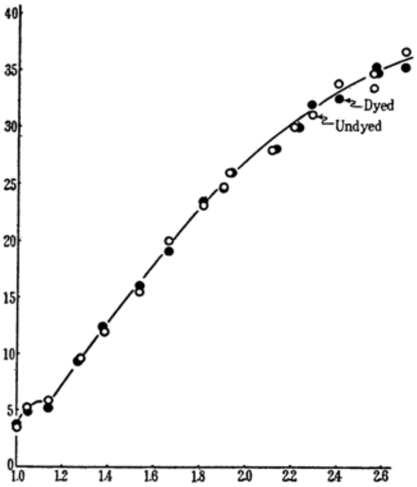

Fig. 5.

Exp. IV. Each specimen was cut into two parts, one of which was dyed with Kongo red as before to measure f_D, while the other half was used for the measurement of Γ after being treated with the alcohol solution. The relation between Γ and f_D is shown in Fig. 6.

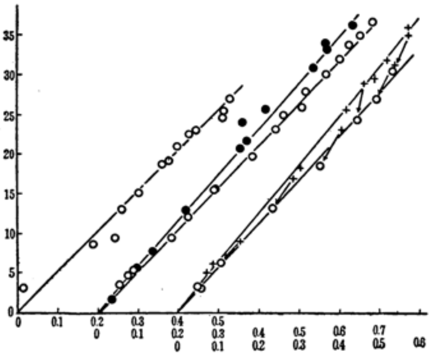

Fig. 6.

○ before Mercerization.
● after Mercerization.

Exp. V. Γ of the unmercerized and mercerized specimens were measured at first and after being dyed, again Γ and f_D were measured. The results

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[6] S. Okajima and Y. Kobayashi, This Bulletin **24**. 85 (1951).

are similar to the above. The mercerization was carried out under tension to avoid the shrinking of the anisotropic filament.

Exp. VI. A part of the specimens were dyed, air-dried, fixed to the frame, vacuum-dried and $K_{\parallel}$, $K_{\perp}$ and Γ were measured as mentioned in A, except that the same dyed specimens were used for both measurements (VIa). These specimens were cut into pieces after 10 days' vacuum-drying and relaxing in boiling water and again observed in the free state (VIb). As shown in Fig. 6, the slope of the line Γ-f_D becomes less steep by this relaxation, although the linear relation holds goods also in this case.

C. Discussion

All the experimental results prove that a linear relation holds good between Γ and f_D as the theory requires. But the slope θ of the line is not necessarily constant and changes from case to case as shown in the acompanying table. In order to analyze the causes of this fluctuation, the following effects are considered:

(1) The mercerization increases the slop in all cases.

(2) Among Exps. I, II, III and VIa, where the specimens were observed in the fixed state, θ in Exp. II is 56-57$\times 10^{-3}$ and slightly smaller than the others. This is because the filament was decoppered under the stretched state. It is interesting to note that this θ increases also to the equal level of 70$\times 10^{-3}$ after mercerization.

		$\theta.10^3$	
Exp. No.	State of the specimen	Before merc.	After merc.
I	Fixed to the frame	60—62	69—70.5
II	" "	55.5—57	70—71.5
III	" "	58—59.5	70.5
IV	Relaxed	50	—
V	"	52	58
VIa	Fixed to the frame	60—61	—
VIb	Relaxed	55	—

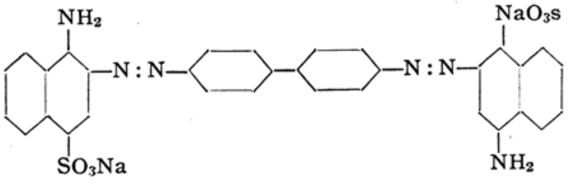
(3) θ in Exps. I, III and VIa are also larger than those in Exps. IV, V and VIb. This seems to be related to the fact that the specimens in the former experiments are dried and observed in the fixed states, while in the latter cases they are in the relaxed states.

Now we consider the meaning of this θ. If the orientation degrees in the crystalline and amorphous regions of a fibre are not different from each other as assumed in the calculation of (1), the linear relation between Γ and f_D means at once the correctness of the formula (1). Then the inclination is equal to

$\Gamma_{\infty} \div \frac{k_{\parallel} - k_{\perp}}{k_{\parallel} + 2k_{\perp}}$ and the fluctuation of this value is nothing but the variation of Γ_{∞}. Γ_{∞} increases generally with the crystallinity, so the value of Γ_{∞} indicates quantitatively the relative amount of the crystalline region. So the constancy of Γ_{∞} through a series of the varying v is a new support for the specimens of view[7] that the crystallinity is kept constant during the stretching of the cellulose fibre.

As to the absolute value of Γ_{∞}, the authors[8] obtained 62.4$\times 10^{-3}$, while P. H. Hermans[5] 55$\times 10^{-3}$, J. M. Preston[9] 54$\times 10^{-3}$ and A. Frey-Wyssling[10] 49$\times 10^{-3}$. These estimations contain some assumptions and the above θ appears to be very valuable for criticising these values of Γ_{∞}, but the problem is not so simple. The inclination θ is

$\Gamma_{\infty} \div \frac{C \cdot (k_{\parallel} - k_{\perp})}{k_{\parallel} + 2k_{\perp}}$ and knowledge of C or $(k_{\parallel} - k_{\perp})/(k_{\parallel} + 2k_{\perp})$ is necessary for this purpose, but it is yet poor. The term $(k_{\parallel} - k_{\perp})/(k_{\parallel} + 2k_{\perp})$ is 1 and 0.89 according to Preston's view[11] and the authors' old data respectively, but our latest data show the possibility of a still greater value 0.96. This value was found repeatedly when a polyvinylalcohol fibre of the highest orientation which had been heat-treated after the highest stretching was observed. Considering that the real filament must fall short of the ideally parallel orientation and further that the ordinary polyvinylalcohol sample on the market contains some irregularities in the structure, then $(k_{\parallel} - k_{\perp})/(k_{\parallel} + 2k_{\perp})$ of the ideal filament must be still greater than 0.96. But if Kongo red molecule has the structure



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[7] e. g. H. R. Kruyt, "Colloid Science" II, p. 55, 613 (1949).

[8] K. Atsuki and S. Okajima, *J. Soc. Chem. Ind. Japan*, **40**, 360B (1937).

[9] J. M. Preston, *Trans. Faraday Soc.*, **29**, 65 (1933).

[10] A. Frey-Wyssling, *Helv. Chim. Acta*, **22**, 981 (1939).

[11] J. M. Preston and P. C. Tsien, *J. S. D. C.*, **66**, 361 (1950).

and this molecule orientates parallel to a cellulose molecule by means of two NH_2-groups, then $(k_{\parallel}-k_{\perp})/(k_{\parallel}+2k_{\perp})$ may be smaller than 1 because the line connecting the two NH_2-groups is not parallel to the direction of the diazo groups. After all the value can be considered to exist between 1 and 0.96 and it is approximated to 1 in the following discussion.

Now Γ_{∞} are 60×10^{-3} and 50–55×10^{-3} according to the states of the specimens and nearly coincide with the hitherto obtained data by the present authors and the others mentioned above, then C can be considered to be nearly equal to 1 and θ is directly equal to Γ_{∞}. If C is much smaller than 1, Γ_{∞} must also be smaller. This means that the orientation degree of the amorphous region is not especially lower than that of the crystalline region, provided, of course, the dichroism can indicate the orientation of the amorphous region only. But another concept is also possible. Because a simple estimation of $(K_{\parallel}+2K_{\perp})$ from the present degree of dyeing shows that about one molecule of Kongo red is absorbed to 10,000 glucose residues and such small quantities of the dye molecules are not necessarily considered to be absorbed only in the amorphous region but also on the surfaces of the crystallites where the orientations are more or less higher; in other words, the dye molecules seem to be distributed uniformly in the filament. Then C can be equal to 1.

The selective indication of the orientation in the amorphous region may occur only when the more intense dyeing was made and the absorbtion becomes decisively predominant in the amorphous region.

A similar linear relation between Γ and f_D can be seen also in the case of a polyvinylalcohol filament till $f_D=0.89$ or 0.96 as will be described in a separate report. In the case of the cellulose filament the line Γ-f_D is interrupted at $f_D=0.6$ by the breakdown of the sample. Of course it can not be decided at present which of the views is true, but it can be said that f_D is equivalent to f_O.

From these points of view the change of θ can be explained directly by the concept of the change in Γ_{∞} and, therefore, the change in crystallinity as below:

(1) The mercerization followed by the hot-regeneration must be considered to increase the relative amount of the crystalline region. This confirms the result of Hermans,[12] who found it by means of the X-ray method. According to him the crystallinity increases by about 10% after the mercerization and our Γ_{∞} increases also by the same amount.

(2) The crystallinity of the filament decoppered under tension is slightly lower than that regenerated in the free state. The cause may be that a too excessive strain appears in the filament due to the deswelling at the decoppering process. This strain is released when it is mercerized and the crystallinity increases to the normal level. Therefore the value of Γ_{∞} is equal to 70×10^{-3}, irrespective of the slightly lower value of the original Γ_{∞} in Exp. II.

(3) As is often mentioned, the relaxed specimens give the smaller value of Γ_{∞}. The effect of the relaxation may appear principally in the last drying operation. The filament highly dried under tension may cause the crystallization of the metastable portion, among which the smaller or more unstable crystals are destroyed again when the filament is treated in boiling water in the free state. And this recrystallization appears to become more stable if the filament has been dried at a higher temperature and for a longer period because Γ_{∞} increases in the order IV to VIb (excepting VIa). They were relaxed similarly in boiling water after air-drying (IV), oven-drying for 1 hr. (V) and oven-drying followed by vacuum-drying for 10 days (VIb) and the larger portion of the crystals appears to survive after the relaxation in the above order.

Therefore the fluctuations observed in the hitherto obtained values of Γ_{∞} by the different authors may be related to the small fluctuation of the crystallinity due to the slight difference in the conditions under which the specimens were treated.

(4) The mercerization was carried out before and after the dyeing in Exps. III and I respectively but Γ_{∞} increases by the equal amount and arrived at the equal level after the treatment in both cases. Therefore such a crystallization is thought not to be disturbed by the dye molecules. This is very interesting when it is considered that the crystallization of a polyvinylalcohol filament due to heating is fairly disturbed by the dye molecules absorbed as will be reported in a separate paper.

Faculty of Engineering,
Tokyo Metropolitan
University, Tokyo

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[12] P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **6**, 533 (1951).