

Dichroism of Poly(ethylene Terephthalate)- Disperse Dye System

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Synopsis

As an approach to the basic study on the orientation behavior of amorphous region, the dichroic orientation factor, D , of poly(ethylene terephthalate), PET, fiber or film dyed with disperse dyes was investigated in relation to Δn , birefringence of the crystalline and amorphous regions, and Δn_a , birefringence of the amorphous region. It was found that D versus Δn plot belonged to a linear relationship passing through the origin but breaking slightly toward the D axis at $\Delta n \simeq 0.14$, while D versus Δn_a plot was expressed by a straight line passing similarly through the origin but with no break. D_0 , the value of D at the ideal parallel orientation, was obtained by extrapolating the latter plot of the samples stretched with no relaxation: 1.00 and 0.73 for the PET-C.I. Disperse Yellow 7 and PET-C.I. Disperse Red 17 systems respectively. When the sample had been relaxed, the D versus Δn_a was also linear; however, D_0 's obtained were smaller than the above mentioned respective values. Even in these cases D for Disperse Yellow 7 versus the corresponding D for Disperse Red 17 belonged to a linear relationship with the slope 1:0.73.

As the result it was concluded that the transition moment of molecule of C.I. Disperse Yellow 7 coincided with the molecular axis and the dye molecule combined parallel to PET chain, while as to C.I. Disperse Red 17 any definite conclusion could not be determined. However, in the both cases the mode of combination of dye molecules with PET is definite and kept unchanged during stretching and heating.

INTRODUCTION

The degree of dichroic orientation f_D for the uniaxially oriented polymer is expressed¹⁻³ by

$$D = (K_{\parallel} - K_{\perp}) / (K_{\parallel} + 2K_{\perp}) \quad (1)$$

$$f_D = D/D_0 \quad (2)$$

$$= 1 - [3/2 \cdot \langle \sin^2 \theta \rangle] \quad (3)$$

$$D_0 = [1 - (3/2 \cdot \sin^2 \alpha)][1 - (3/2 \cdot \sin^2 \beta)] \quad (4)$$

where K_{\parallel} and K_{\perp} are absorbancies for polarized light vibrating parallel and perpendicularly, respectively, to the stretching direction Z , θ , is the inclination angle of the polymer unit to Z , α is the angle between the axis

of polymer unit and combined dye molecule, and β is the angle between the axis of dye molecule and the direction of transition moment.

The D_0 value of Congo Red is equal to 1, as already reported.⁴ Hence, f_D of polymers dyed with Congo Red, such as cellulose,⁵ poly(vinyl alcohol)^{2,5} and polyacrylonitrile,^{6,7} have been evaluated easily and effectively. Congo Red, however, cannot be used for hydrophobic polymers, of which most of the present-day synthetic fibers are composed. Instead, disperse dyes are available for these hydrophobic fibers; however, few basic studies have been carried out on the dichroism developed by disperse dyes and the D_0 value has never been known. Consequently, f_D cannot be evaluated and we must be contented with change in D . The subject of this paper is to study the relation between the dichroism developed by disperse dyes and amorphous orientation of poly(ethylene terephthalate) fiber or film and to determine the D_0 value as an approach to the evaluation of f_D .

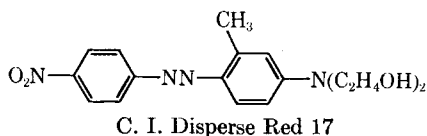
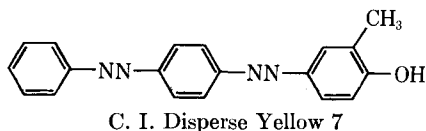
EXPERIMENTAL

Sample

A PET monofilament, F, and three PET films, A, B, and C, were used as samples. They were undrawn samples and were nearly isotropic and amorphous according to x-ray study. The diameter of the monofilament was about 400 μ . Respective thicknesses of films A, B, and C were 50, 50, and 100 μ . The samples were supplied by Teijin Ltd. (B, C, and F) and Toyo Rayon Co. Ltd. (A).

Dyeing

The samples were dyed from aqueous solution of C. I. Disperse Yellow 7 (Y-7) and/or C. I. Disperse Red 17 (R-17) with (for monofilament) or without (for films) using phenol as carrier (3%) under the conditions listed in Table I.



The monofilament was so thick that more than 40 hr of dyeing was necessary to obtain a homogeneously dyed cross section. It was confirmed, however, that the value of $K_{||}/K_{\perp}$ of the monofilament with ring-dyed cross section was independent of the thickness of the dyed layer. Hence, homogeneous dyeing was not always necessary. Dyed monofilament was

TABLE I
Conditions of Sample Preparation

Sample no.	Dyeing	Temp. of stretching, °C	Heat treatment
A-1	70°C, 20 hr	70	—
A-2 ^a	70°C, 20 hr	70	190°C, 10 min
B-1	90°C, 2 hr	100	—
C-1	70°C, 24 hr	80	—
C-2 ^b	120°C, 1.5 hr	65	190°C, 10 min
F-1	70°C, 24 hr	65–100	—
F-2	70°C, 24 hr	70	—

^a Dyeing, stretching, and heat treatment.

^b Stretching, heat treatment, and dyeing.

treated with hot water (70°C) for 4 hr and further with ordinary room-temperature water for 15 days or aqueous acetone to extract the phenol contained within the sample. But complete extraction was not certain, and the complete extraction of carrier is not always necessary for the purpose of study with monofilament.

As already reported¹⁸ D of the cellulose–Congo Red system increases steeply when the dye concentration in the cellulose is extremely low, even when the effect of stray light is corrected. Hence the PET sample was carefully dyed to such extent that the value of D was independent of the dye concentration. It was observed that the dye dependency was slight in the case of PET compared with that in the cellulose system.

Stretching

A dyed monofilament and a reference monofilament that had been treated similarly but not dyed were mounted to a stretching machine side by side and both monofilaments were stretched together to various extents, v , in water at desired temperatures. A dyed film, 6 cm long and 3 cm wide, was stretched similarly. The rate of stretching was 40%/min. Uniaxial stretching of broad film often brings about biaxial orientation; however, in the present study uniaxial orientation always resulted, as shown in Figure 1, where n_{ps} was nearly equal to n_{ss} . Here, n_{ps} is the refractive index per-

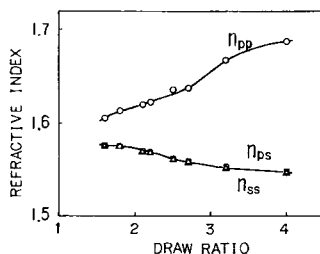


Fig. 1. Variation of refractive indices n_{pp} , n_{ps} , and n_{ss} with draw ratio v , for PET film stretched monoaxially at 70°C: (○) n_{pp} ; (□) n_{ps} ; (△) n_{ss} .

pendicular to the stretching direction but parallel to the film surface and n_{ss} is that parallel to the normal. They were measured with an Abbé refractometer.^{8,9}

Heat treatment of film was carried out isometrically after drying the film in a desiccator for 24 hr.

Measurement of Dichroism

Absorbancies of filament and film were measured at room temperature in the same way as in the earlier study.^{4,5,10} In the case of filament, correction was made for stray light. No correction is necessary for film sample.

For the measurement of K_{\parallel} or K_{\perp} , a filament or film treated exactly in the same manner as in the sample but undyed was used as reference.

Density

Density d was measured by the density gradient column method in a mixture of carbon tetrachloride and *n*-heptane at 20°C. Crystalline fraction in volume, X_v , was calculated as follows:

$$d = d_c X_v + d_a(1 - X_v) \quad (5)$$

Here, 1.455 g/cm³ and 1.335 g/cm³ were taken for the crystalline density d_c , and amorphous density d_a , respectively.^{11,12}

Birefringence

Birefringence, Δn , was measured by means of the retardation method. The degree of overall orientation, f_0 , is then given by

$$f_0 = (\Delta n / \Delta n_c^0)(d_c / d) \quad (6)$$

where Δn_c^0 is the intrinsic birefringence of PET crystal, for which 0.2165 was used.¹³

Degree of Crystalline Orientation

The degree of crystalline orientation, f_c , was evaluated after Wilchinsky's principle.¹⁴ For this purpose azimuthal scanings of (100) and (010) reflections were carried out with a Geigerflex (Rigaku Denki), from which $\langle \cos^2 \varphi_{100} \rangle$ and $\langle \cos^2 \varphi_{010} \rangle$ were evaluated by subtracting the amorphous contribution. Here, φ_{100} and φ_{010} are angles between the direction of stretching and the normals to the respective planes.

Degree of Amorphous Orientation

The degree of amorphous orientation, f_a , was estimated from the following expressions:

$$\Delta n = \Delta n_c X_v + \Delta n_a(1 - X_v) \quad (7)$$

$$\Delta n_c = \Delta n_c^0 f_c \quad (8)$$

$$\Delta n_a = \Delta n_a^0 f_a \quad (9)$$

where Δn_a^0 is the intrinsic birefringence value of the ideal parallel oriented amorphous phase.

RESULTS

The D versus Δn relation of filament stretched at different temperatures is shown in Figure 2. The dyed monofilament which was stretched at 90°C suffered the extraction treatment, but it was omitted from the other three samples. All the relations are of similar type and the breaks appear at nearly the same value of Δn , 0.14. The slope of the linear plot in the range of Δn higher than 0.14 decreases as the temperature of stretching is elevated, except for the 65°C plot. This exception may have resulted from the stretching below the glass transition temperature.

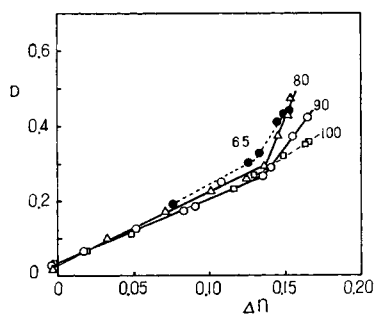


Fig. 2. Plot of dichroism, $D = (K_{\parallel} - K_{\perp}) / (K_{\parallel} + 2K_{\perp})$, of PET monofilament (F-1) dyed with R-17 against total birefringence Δn . Temperatures of stretching: (●) 65°C ; (Δ) 80°C ; (○) 90°C ; (□) 100°C .

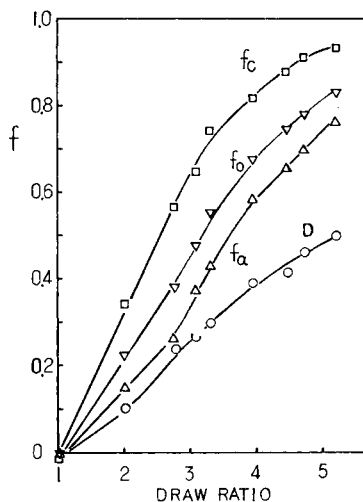


Fig. 3. Degree of orientation f vs. draw ratio for PET monofilament (F-2): (□) degree of crystalline orientation, f_c ; (∇) degree of overall orientation, f_o ; (Δ) degree of amorphous orientation, f_a ; (○) dichroism, D (R-17).

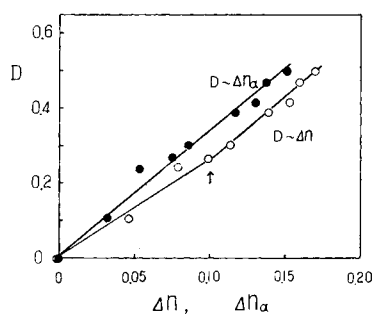


Fig. 4. Plot of dichroism D against total birefringence Δn (O), and against birefringence of amorphous region Δn_a (●).

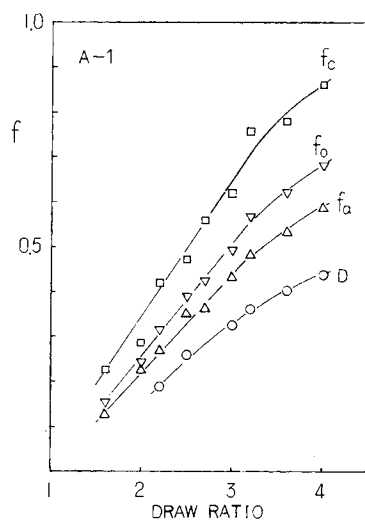


Fig. 5. Degree of orientation vs. draw ratio for sample A-1 (R-17).

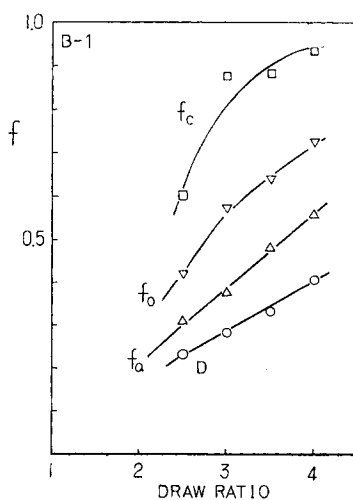


Fig. 6. Degree of orientation vs. draw ratio for sample B-1 (R-17).

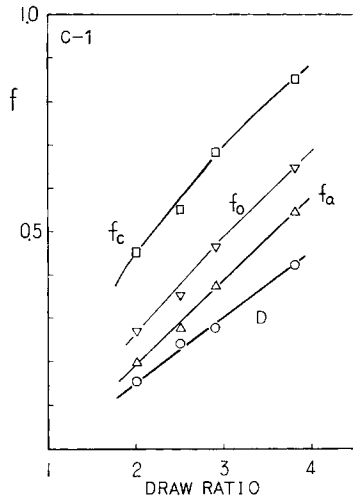


Fig. 7. Degree of orientation vs. draw ratio for sample C-1 (R-17).

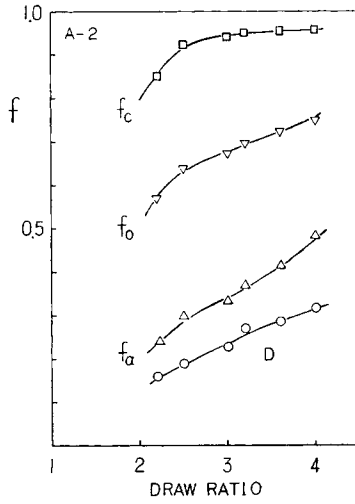


Fig. 8. Degree of orientation vs. draw ratio for sample A-2 (R-17).

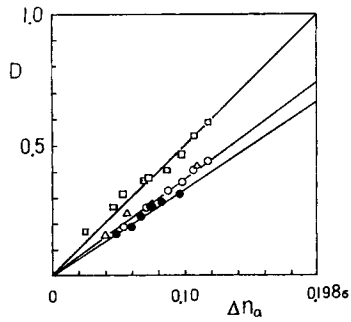


Fig. 9. Plot of D against Δn_a and extrapolation of D to $\Delta n_a = 0.1986$ for: (\square) A-1 (Y-7); (\circ) A-1 (R-17); (Δ) C-1 (R-17); (\bullet) A-2 (R-17).

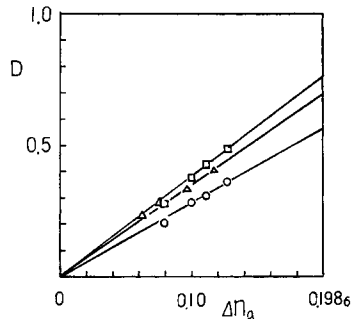


Fig. 10. Plot of D against Δn_a and extrapolation of D to $\Delta n_a = 0.1986$ for: (\square) C-2 (Y-7); (\circ) C-2 (R-17); (\triangle) B-1 (R-17).

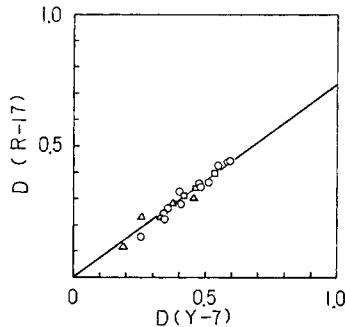


Fig. 11. Plot of D for R-17 vs. D for Y-7: (\circ) dyed and drawn; (\triangle) dyed, drawn, and heat treated; (\square) drawn, heat treated, and dyed.

In order to obtain the D versus Δn_a plot, the degree of overall orientation, f_0 , was divided into the degree of crystalline orientation, f_c , and degree of amorphous orientation, f_a , as usual. Figure 3 is an example (F-2) in which the carrier was extracted with 50% aqueous acetone at room temperature followed by treatment with water at 70°C. Within the experimental range the relation $f_c > f_0 > f_a$ holds good, indicating that the crystalline region orientates more prominently. The D versus Δn plot is of similar type to those in Figure 2, while the D versus Δn_a plot is a straight line without break in it, as seen in Figure 4.

Various film samples exhibit similar behavior as shown in Figures 5 to 8 and Figures 9 to 10, i.e., the crystalline region orientates higher than the amorphous region and the plots D versus Δn_a are linear without exception.

The value of D at the ideal parallel orientation may possibly be obtained by extrapolating these plots to $\Delta n_a = 0.1986$ and the actually obtained value, designated by D_∞ , is 1.00 for Y-7 (A-1) and 0.73 for R-17 (A-1 and C-1), as can be seen in Figure 9. In the case of A-2, B-1, and C-2, which suffered heating at higher temperature during the sample preparations, the D_∞ are smaller than those of A-1 and C-1, although the D is similarly in linear relation to Δn_a for each of the three (Fig. 10). These values of D_∞

are listed in Table II, which contains also the value of F-2 obtained from the plot in Figure 4.

The slope of the plot D versus Δn_a varies, and consequently D_∞ differs considerably according to the samples; but when the values of D for Y-7 are plotted against the corresponding D for R-17 on each sample, all the

TABLE II
Values of D_∞

Sample no.	Disperse Red 17 (R-17)	Disperse Yellow 7 (Y-7)
A-1	0.73	1.0
A-2	0.67	—
B-1	0.70	—
C-1	0.73	—
F-2	0.67	—
C-2	0.56	0.76

points fall on one and the same line passing through the origin independent of the history of the sample, as Figure 11 indicates. From this relationship, the ratio of D of the two dyes on PET is obtained to be 0.73. This value coincides with the ratio of D_∞ obtained above from A-1 and C-1.

DISCUSSION

The dye molecules cannot penetrate into the crystalline region; they are absorbed only in the amorphous phase. Hence it is generally considered that dichroism developed by dyed polymer is relevant to the amorphous orientation. This is evident from the linear relationship between D and Δn_a passing through the origin, as shown in the preceding section. Therefore, when f_c is not equal to f_a , as is the ordinary case, plotting of D against Δn is not reasonable; D should be plotted against Δn_a .

Patterson and Ward¹⁵ studied dichroism of PET filaments prepared by extruding and stretching the molten polymer-dye blend (an acid anthraquinone dye modified from Carbolan Green G). They found a linear relationship between D and Δn , but with a break toward the Δn axis, contrary to the result of the present paper. They attributed the break to the abrupt increase in crystallinity, which was indicated by the sharp x-ray reflections characteristic of crystalline PET at draw ratio higher than 3.42. The explanation cannot be applied to our case.

The cause of breaking is generally attributed to an abrupt change in (1) the ratio of f_c to f_a and/or (2) the ratio of crystalline to amorphous fractions. It seems reasonable, judging from the direction of breaking, that in the case of Patterson and Ward the phenomenon may be attributed to cause (2), while in our case it should be caused by (1). This is clearly seen in Figure 12, which is replotted from Figure 3. The break in Figure 4 appears at $\Delta n = 0.10$, which corresponds with $f_a = 0.37$, the break of the plot in

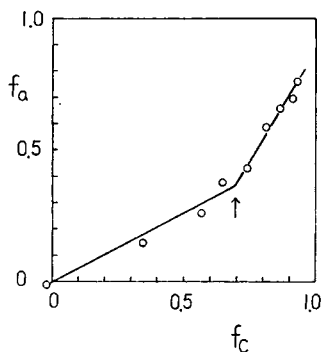


Fig. 12. Plot of f_a vs. f_c , replotted from Figure 3.

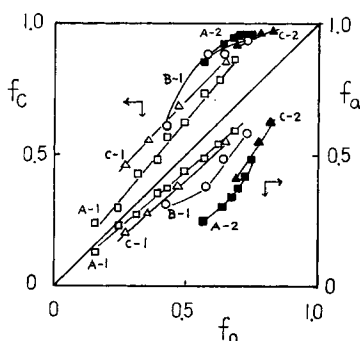


Fig. 13. Comparison between f_0 and f_c or f_a , for various samples.

Figure 12 as indicated by an arrow. As to the change in crystallinity, so much increase in density cannot be observed from Figure 14.

When f_c and f_a of various samples are plotted against the corresponding f_0 , as in Figure 13, f_c (f_a) becomes higher (lower) in the order from A-1 to A-2 through C-1, B-1, and C-2. This order agrees well with the order of maximum temperatures during the sample preparations such as stretching and heat treatment (Table I), or with the order of crystallinity (Fig. 14). This order is considered, therefore, to be caused by larger relaxation or slower orientation of polymer chains within the amorphous region at high temperatures. In the case of A-2, further crystallization yielded higher orientation of crystallizable chains and disorientation of noncrystallizable chains likely occurred during the heat treatment at 190°C under isometric condition.

The phenomenon is reflected in the slope of the plot D versus Δn_a , i.e., the slope and consequently D_∞ are smaller in A-2, B-1, and C-2 than in A-1 and C-1. However, if a sample is divided into two parts and one is dyed with Y-7 and the other with R-17 and the two D 's, designated by $D(Y-7)$ and $D(R-17)$, respectively, are compared, the ratio $[D(R-17)]/[D(Y-7)]$ is 0.73 and independent of the degree of orientation and history of the sample,

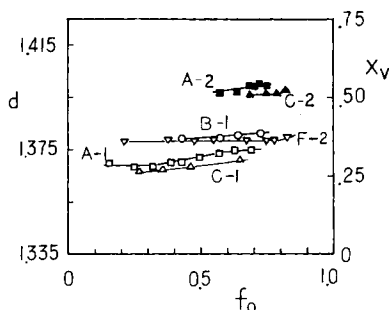


Fig. 14. Comparison between density d and f_0 , for various samples.

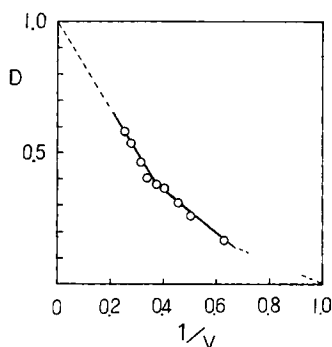


Fig. 15. Plot of D vs. $1/v$ for A-1 dyed with Y-7. D attains to 1 when $1/v$ is extrapolated to 0.

as indicated by Figure 11. These phenomena lead to the following consideration:

(1) The distribution of lateral order exists in the amorphous region and dye molecules do not distribute homogeneously throughout the entire amorphous region, but exist only within the region of the lowest lateral order, as suggested by Kanetsuna and Murase.¹⁶

(2) Relaxation and disordering of polymer chains start preferentially in the region of the lowest lateral order, hence D decreases sensitively as the sample is treated at high temperature. The change within the lowest-ordered region reflects only slightly in Δn_a , expressing the orientation of overall amorphous region; and therefore the correspondence between D and Δn_a is lost [see statement (6) below]. This gives rise to a decrease in slope of the plot D versus Δn_a and a drop in D_∞ (Table II).

(3) Dye molecules combine with polymer chains by a definite geometric relation and the angle α is kept unchanged during deformation and heat treatment. According to our recent study¹⁰ on dichroism of PET-disperse dye system at various temperatures, D decreases slightly as the temperature is elevated, and this change is reversible unless the temperature is raised above the highest temperature that the sample has experienced.

(4) The decrease in D or D_∞ shown in Figures 9 and 10 is attributable to the disorientation of polymer chains being combined with dye molecules, i.e., to the increase in θ in eq. (3). Then, according to eq. (2), the ratio $[D(\text{R-17})]/[D(\text{Y-7})]$ is equal to the ratio of the D_0 's of the two dyes, 0.73:1, because θ is a constant for each pair of specimens. This is clearly seen in Figure 11.

(5) Only when the sample has been stretched while suppressing relaxation of polymer chains, D_∞ is expected to be equal to D_0 . A-1 in Figure 9 seems to be this case, because the D_∞ takes the value 1, the maximum value of D theoretically possible. Then, from the similarity of condition of sample preparation A-1 and C-1, $D_\infty = 0.73$ obtained for R-17 can be considered to be equal to D_0 of this dye.

It is interesting to note that Y-7 takes $D_0 = 1$ also on polypropylene.¹⁷ However, generally speaking, the angles α and β in eq. (4) may be a function of chemical structure of polymer unit, although this problem has not yet been studied.

An investigation is added to lend support to the conclusion concerned with $D_0 = 1$ for Y-7. Some properties of uniaxially stretched filament or film are a linear function of v^{-1} for v larger than a certain critical value. This is true of D , as shown in Figure 15, and D attains 1 when v^{-1} is extrapolated to 0.

(6) When filament or film is stretched while suppressing relaxation, all polymer chains within the amorphous region orientate uniformly and the value of θ of amorphous chains seems to be independent of their lateral order. In such a case, D corresponds closely with Δn_a . Then the degree of dichroic orientation, $f_D = D/D_0$, can be compared with the degree of amorphous orientation evaluated by the combined birefringence-x-ray method or infrared method.

As a result it is concluded that D_0 of Y-7 and R-17 is 1 and 0.73, respectively. The angles α and β of the former dye (Y-7) are 0, while for the latter any definite information cannot be obtained. Three cases may be possible: (1) $\alpha = 0, \beta \neq 0$, (2) $\alpha \neq 0, \beta = 0$, and (3) $\alpha \neq 0, \beta \neq 0$. Further study is necessary to conclude which of the three is true.

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