

Visible Dichroism of the Poly(ethylene Terephthalate)-Disperse Dye System at High Temperatures

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Synopsis

The dichroic behavior of PET film dyed at 70°C with Disperse Red 17 or Disperse Yellow 7 was investigated in the temperature range 20–200°C with a view to studying the changes in amorphous region of PET at high temperatures. The dichroic orientation factor D versus temperature plot is expressed by a straight line with negative slope; two breaks appear at 80 (T_g) and 120°C. So long as the amorphous structure does not change irreversibly, the values of D change reversibly with the temperature. Hence, if a change in D after heating is observed at room temperature, it is evidence that an irreversible change occurred in the amorphous structure during the heating. The break at 120°C is a new amorphous transition point of PET existing along with T_g , although the T_g can hardly be observed after the cold crystallization; some phenomena reported in the literature are proposed as evidence.

INTRODUCTION

Visible dichroism can be used effectively to determine the degree of orientation of the amorphous region of polymer, especially, the region contributing to dyeing. Many studies have been performed on many different polymers, for example, cellulose,¹⁻⁷ poly(vinyl alcohol),^{4,6,8-10} polyacrylonitrile,^{11,12} poly(ethylene terephthalate),^{13,14} Nylon 66,¹⁵ and polypropylene.¹⁶

In the previous paper,¹⁴ one of the present authors dyed poly(ethylene terephthalate) filament with Disperse Red 17; the fiber was stretched and then heated in water at 50–170°C. The change in the thermal contraction S and the dichroic orientation D of the filament was studied. It was found that the two relations, the reciprocal absolute temperature of thermal treatment $1/T$ versus $\log S$ and $1/T$ versus D , could be expressed by straight lines, each with three breaks at nearly equal temperatures of 80, 140, and 150°C as shown in Figure 1 (reproduced from the previous paper¹⁴), while the degree of x-ray orientation was kept constant during the thermal contraction. It was concluded that the thermal contraction is caused principally by disorientation of amorphous chains, provided the dichroic

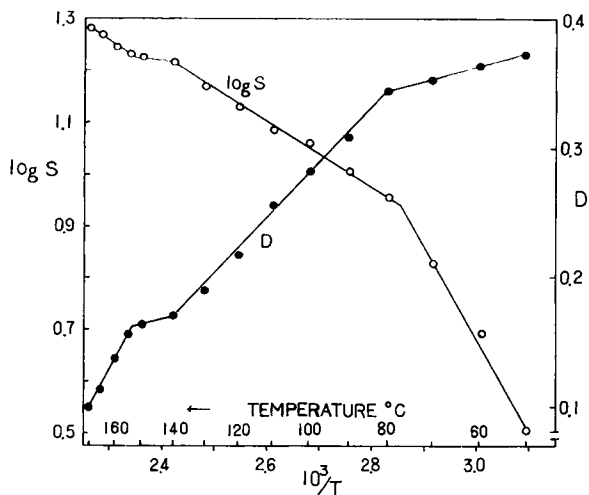


Fig. 1. Plot of dichroism D and logarithm of per cent shrinkage S of a PET filament against the reciprocal absolute temperature of treatment.

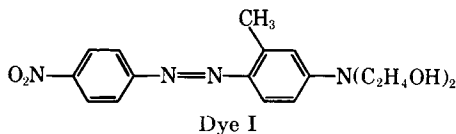
orientation measured at room temperature indicates accurately the orientation of amorphous chain which resulted from the heating. But consideration must also be given to the fact that disperse dye molecules diffuse out from a dyed film or fiber and actually sublime in vacuum at high temperature. There may be a contention that the dye molecules which combined definitely with the polymer chains at room temperature dissociate from the polymer chains at high temperatures and the dichroic value of the cooled specimen is now irrelevant to the actual amorphous orientation since the dissociated dye molecules do not return to the original state of combination. This problem has never been studied, however, so we measured the dichroism of dyed poly(ethylene terephthalate) film at several temperatures during repeated heating and cooling cycles to determine whether the values of dichroism change reversibly or not.

EXPERIMENTAL

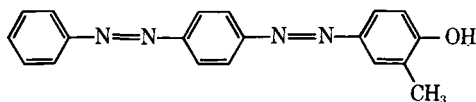
Preparation of Specimens

A poly(ethylene terephthalate) film (PET) supplied by Teijin Ltd. was used. Its thickness was about 50μ and nearly completely isotropic and amorphous. Specimens were cut out from this sample and dyed with dye I or II at 70°C for 20 hr.

C.I. Disperse Red 17:



C.I. Disperse Yellow 7:



Dye II

The dyed specimens, 6×3 cm., were stretched monoaxially to various degrees v in water at 68°C at a rate of $40\%/min$. Other undyed specimens were stretched in a similar way, annealed with the restraint to constant length in an oil bath at 190°C for 5 min and then dyed at 130°C for 90 min.

Measurement of Dichroism

When the intensities of a beam of plane-polarized light transmitted through the dyed film and the reference film are designated as I and I_0 , respectively, the absorbance K is expressed by eq. (1), where α is the extinction coefficient, c is the concentration of the dye, and d is the thickness of the film.

$$I/I_0 = 10^{-\alpha cd} = 10^{-K} \quad (1)$$

Equations (2) and (3) are special cases of eq. (1),

$$I_{||}/I_0 = 10^{-K_{||}} \quad (2)$$

$$I_{\perp}/I_0 = 10^{-K_{\perp}} \quad (3)$$

where the subscripts $||$ and \perp denote that the electric vector of light is parallel and perpendicular, respectively, to the direction of stretching of the specimen. Orientation factor D , a measure of the degree of orientation of the segments absorbing dye molecules is given by eq. (4).

$$D = (K_{||} - K_{\perp})/(K_{||} + 2K_{\perp}) \quad (4)$$

The value of D of an ideally oriented specimen is designated D_0 ; the degree of orientation f_D of a specimen is given by equation (5).

$$f_D = D/D_0 \quad (5)$$

The f_D value differs, in general, from f_x , the degree of crystalline orientation, or f_a , the degree of amorphous orientation. In accordance with our studies, it was found in the case of a dyed, and subsequently stretched specimen, $f_D = f_a$, but when the specimen is thermally contracted or relaxed freely, $f_D < f_a < f_x$. The value of D_0 of the dye I or II is about 0.7 and 1, respectively, but only the change in D was studied at this time. The determination of the exact value of D_0 is now in progress.

The values of $K_{||}$ and K_{\perp} were measured in the same way as in the earlier study.⁷ In the present study a spectrophotometer equipped with a specially prepared heating cell was used instead of an ordinary glass cell, so that the specimen may be heated to measure the dichroism at high tem-

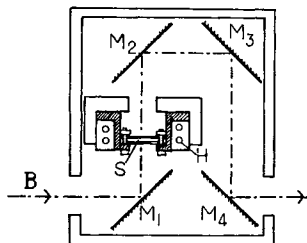


Fig. 2. Diagrammatic illustration of heating cell: (S) specimen film between cover-slips; (H) heater; (M_1 – M_4) metal mirrors; (B) incident beam (monochromatic and horizontally polarized light).

peratures. Figure 2 is a schematic diagram of the cell, in which M_1 – M_4 are four metal mirrors and S the specimen. A beam of plane-polarized light B, the electric vector of which is perpendicular to the paper, was passed through the cell by reflecting on mirrors M_1 – M_4 in such a way that the electric vector is always parallel to the surfaces of the mirrors. The specimen was rotated in its plane to obtain K_{\parallel} and K_{\perp} . To heat the specimen, it was placed in a casket with a heating element H. The temperature was measured and controlled by electric means.

In the previous experiments conducted at room temperature, a specimen was placed in a glass cell containing tricresyl phosphate to minimize the reflection and scattering of light on the film surface, but since liquid cannot be used in the heating cell, measurements taken with the heating cell may be less accurate than the previous measurements. Therefore, each specimen was measured two times, once with an ordinary glass cell and once with the heating cell at room temperature with the use of monochromatic light of different wavelengths (longer than $410\text{ m}\mu$). The corresponding values were plotted in Figure 3. The result shows that all points are on a line with an inclination of 45° and passing through the origin. It is confirmed, therefore, that the expected inaccuracy is negligibly small.

RESULTS

The spectra of PET film dyed with dye II were measured at different temperatures (Fig. 4). The specimens are monoaxially oriented, so the absorbance as the value of the isotropic state, is expressed by $K_{\text{iso}} = (K_{\parallel} + 2K_{\perp})/3$. The maximum absorbance is found at about $400\text{ m}\mu$ at 25°C . However, the spectrum shifts gradually toward shorter wavelength and at the same time lowers as the temperature is elevated. These changes are reversible, and when the specimen is cooled to 25°C the spectrum agrees with the original one within experimental error. It is shown, therefore, that this dye is stable at least up to 170°C . The shift of the spectrum toward shorter wavelength seems to be due to the decreasing interaction between the dye molecules and the substrate molecules with an increase in temperature.

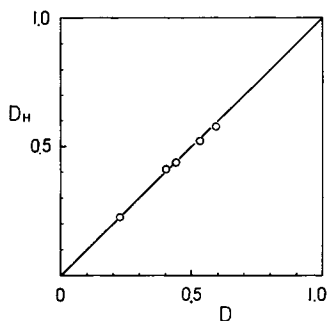


Fig. 3. Comparison between values of D obtained by usual method (D) and that obtained at room temperature with a heating cell (D_H).

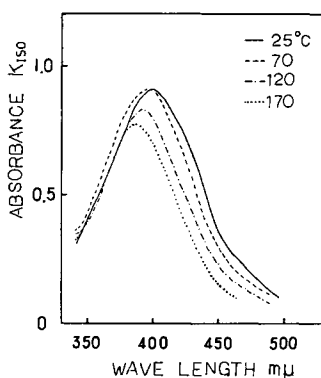


Fig. 4. Spectra of Disperse Yellow 7 in poly(ethylene terephthalate) film at different temperatures. $K_{iso} = (K_{\parallel} + 2K_{\perp})/3$.

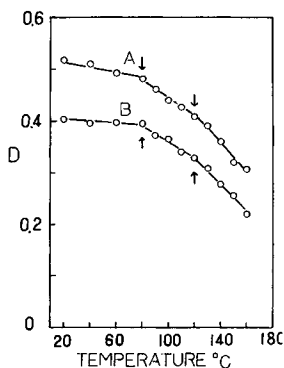


Fig. 5. Change in D of a dyed specimen with temperature: (A) dyed with Disperse Yellow 7; (B) dyed with Disperse Red 17.

Figure 5 is a plot of the dichroic orientation $D = f_D D_0$ versus temperature for two specimens A and B dyed with dyes II and I, respectively, and stretched under the same conditions. Each relation is expressed by a straight line with two breaks at 80 and 120°C. On plotting the value of D

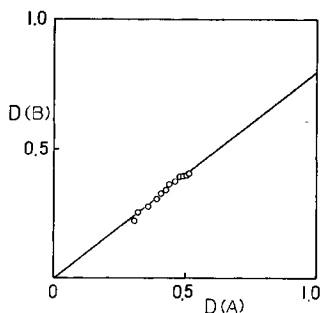


Fig. 6. Relation between the values of D of specimens A and B of Figure 5.

of two specimens in Figure 5 at the corresponding temperatures, the points fall on a line passing through the origin (Fig. 6). This suggests that there is a difference between the values of D_0 , which is characteristic of the chemical structure of dye molecule, but there is no difference between the values of f_D , the degree of amorphous orientation. Hence, the two breaks mean abrupt changes in f_D . Dye II with the larger D_0 is used mainly hereafter.

Figure 7 indicates the successively measured D of a dyed specimen C, which was drawn in water at 68°C ($\nu = 4.7$), during heating up to 160°C and cooling process to room temperature. As in Figure 5, two breaks, at 80 and 120°C are shown on the heating curve. As is known, the former temperature is the glass transition T_g of PET. At the temperature below T_g the structure is frozen and D decreases only slightly, while at temperatures above T_g , microbrownian motion of the amorphous chains begins and brings about a decrease in f_D . The break at 120°C can be explained as the result of the onset of another sort of microbrownian motion with a higher

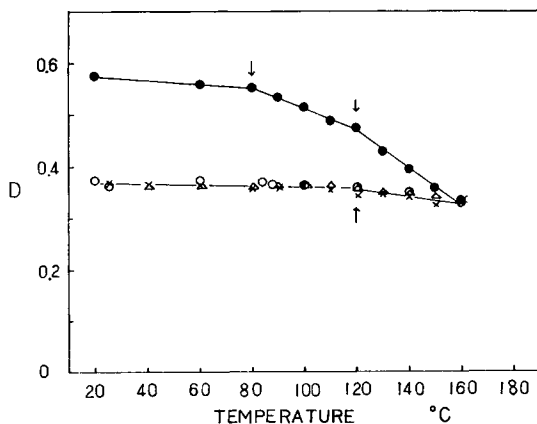


Fig. 7. Change in the value of D with temperature during heating and cooling cycles repeated between 20 and 160°C : (●) first heating; (○) first cooling; (×) second heating; (△) second cooling.

activation energy, which induces the so-called cold crystallization and further disorders the amorphous region remaining uncrystallized. This is reflected on a steeper lowering of D . The change in the microstructure caused by the cold crystallization is irreversible, so the D versus temperature relation in the cooling process is different from that in the heating process. But the secondary heating and cooling processes are unchanged and coincide completely with the first cooling process, provided the maximum temperature of the specimen is not elevated above 160°C . It is noteworthy that the 120°C break always appears on these reversible cycles. This leads us to the conclusion that 120°C is another amorphous transition point.

Similar experiments were carried out on two specimens, D and E ($\nu = 4.5$), which had been heat-treated in a taut condition for 5 min at 190 and 200°C , respectively. The results are shown in Figure 8; D and E have

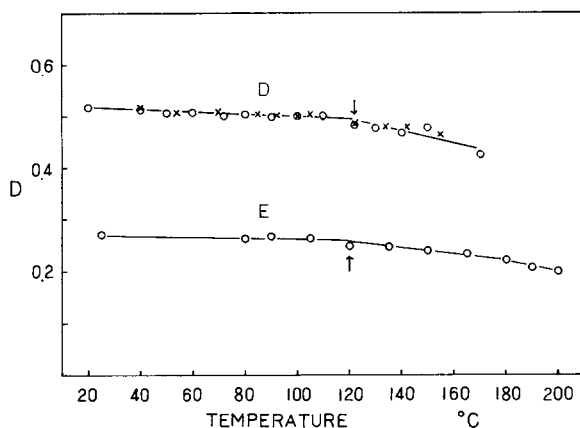


Fig. 8. Change in the value of D with temperature during a heating (\circ) and cooling (\times) cycle. Sample D, stretched at 57°C , $4.5\times$; heat treatment at 190°C , 5 min; dyed at 130°C , 90 min. Sample E, stretched at 68°C , $4.5\times$; heat treatment at 200°C , 5 min; dyed at 130°C , 90 min.

been stretched at 57 and 68°C , respectively, so f_D of the former, and consequently D , is higher than that of the latter. The changes in D with temperature are reversible in all cases, and the transition point of 120°C appears clearly, since the temperatures of measurement are always below the temperature of heat treatment.

For all the specimens A-E heated above 120°C T_g is barely evident (as observed above), but there is some evidence that T_g does not shift to merge with the 120°C transition but that the latter is a separate amorphous transition existing along with T_g as discussed below. The disappearance of the 80°C transition is only apparent; it is considered that the amorphous chain is greatly restricted by the many crystallites developed over 120°C . The crystallinity, calculated from the density, of specimens C, D, and E

is 27, 58, and 53%, respectively. Above 120°C. the amorphous chains acquire sufficient energy to overcome this restriction, and segmental motion with longer sequences occurs.

In order to study the effects of crystallization which occurs during the changes in D , a heating and cooling cycle was repeated three times on specimen F, with the highest temperatures gradually being raised to 90, 100, and 130°C on successive cycles. As shown in Figure 9, in the first

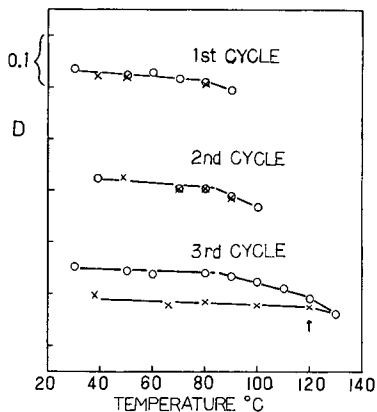


Fig. 9. Change in D of specimen F during three heating (O) and cooling (X) cycles. Specimen dyed with Disperse Red 17. Plots of each cycle are shifted vertically for clarity.

and second cycles (the maximum temperatures being 90 and 100°C., respectively) D changes reversibly and the transition at 80°C appears clearly; in the third cycle, however, where the maximum temperature is 130°C, the heating and cooling processes are different, and the transition at 80°C can no longer be observed, although the 120°C transition appears.

DISCUSSION

It can be concluded generally from the experiments described above that the dichroism developed by disperse dyes changes reversibly with temperature, so the dye molecules seem to return to the original state of combination, which is defined by the structures of polymer and dye molecules, even if the dye molecules may be detached slightly by thermal oscillation from the polymer chains at high temperatures. Hence the changes in D , measured at room temperature, of specimens heat-treated at high temperature, of specimens heat-treated at high temperatures indicate actually the change in the amorphous orientation occurring during the heat treatment.

The decrease in D with the elevation of temperature is shown to have resulted from the thermal oscillation of dye molecules around their combined position to the polymer chain at room temperature as well as the increased microbrownian motion of the polymer segments combined with dye mole-

cules. Of course, at temperatures above T_g the latter effect must be larger than the former.

The amorphous transition at 120°C is found clearly in this study. In fact, Hellwege et al.¹⁷ have also pointed out two breaks at 80 and 120°C in dilatometry, and Fujino et al.¹⁸ also observed two peaks at about 90 and 120°C in the $\tan \delta$ versus temperature plot of terylene at 2.4×10^{-2} cps. These authors have not given any explanation for the 120°C transition. According to our view, the cold crystallization of PET occurs at 110–120°C because the amorphous chain segments have sufficient energy at this temperature to overcome restrictions which prevent the cold crystallization below this temperature. Even above 120°C, however, a fraction of the segments remain uncrystallized, because they are not in a suitable position to be incorporated in the lattice although they too have sufficient energy. Therefore, a new thermal motion with higher activation energy begins, always within the amorphous region of the polymer, even after heating above the cold crystallization temperature, since the restriction is overcome at slightly higher temperature than the temperature of cold crystallization. This sort of motion ceases reversibly as the temperature is lowered and appears as the 120°C transition. Hence the transition can be observed in various fashions. Recently in our laboratory the same transition was found in addition to T_g in the diffusion of disperse dyes in PET and creep behavior of PET filament. These observations will be reported elsewhere in the near future.

An apparent contradiction would seem to exist with respect to Figure 1, in which no transition seems to exist at 120°C. The reason is perhaps that the PET sample (monofilament) in Figure 1 was heated without constraint in water at 50–170°C. The experimental conditions may thus produce a considerably different result from that of the present study. In the former case the amorphous chains are free to contract and disorient extremely at T_g so that the detection of the 120°C transition, actually lowered to some degree by water, becomes very difficult. An experiment recently carried out under similar conditions but in the absence of water exhibits a barely detectable break at 120°C with plotting of very many points.

The 140°C break is likely to be another transition in addition to that at 120°C. However, a clear explanation of the breaks at 140 and 150°C in Figure 1 is difficult at present and future study is necessary. We have observed frequently a transition on a dilatometric curve or shrinkage curve of PET at about 150°C.

The effect of absorbed dye on the transition temperature is negligible, according to an above-mentioned study on transition temperature obtained from diffusion velocity of dispersed dye in PET.

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