

Visible Dichroism of Polypropylene-Disperse Dye System at High Temperatures

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Synopsis

The dichroism of polypropylene film dyed with C. I. Disperse Yellow 7 was investigated at various temperatures up to 160°C. The dichroic value D drops as the temperature is raised. So long as the amorphous structure does not change irreversibly, D changes reversibly with temperature. The experimental results agree qualitatively with those obtained on poly(ethylene terephthalate) in our previous paper, although the effect of temperature on the extent of the reversible change in D is larger in PP than in PET. The plot of D versus temperature exhibits breaks at 40°–50°C (T_0), 70°–80°C (T_1), and 115°–120°C (T_2). These temperatures agree with the transition points of polypropylene in the literature. From the change in the intrinsic dichroism D_0 with temperature, it is concluded that the decrease in D at high temperatures is due to the drop of D_0 caused by the disorientation of dye molecules in the amorphous region, while the amorphous polymer chain is not disoriented. Such a conclusion is supported by the fact that Δn of a heat-set specimen is kept constant during heating, in contrast to D .

INTRODUCTION

In the previous paper¹ the dichroic orientation behavior of poly(ethylene terephthalate) films, abbreviated PET films hereafter, dyed with disperse dyes was investigated at high temperatures, and some interesting phenomena had been reported. They were: (1) The dichroic orientation value decreases as the temperature is raised. However, the dichroic value returns to the original value reversibly when the temperature is lowered, unless the film is not heated above the highest temperature the film had experienced. (2) The relation between the dichroic orientation value and the temperature is expressed by straight lines with breaks at temperatures corresponding to T_0 and other transition temperatures of PET. The importance of these phenomena should be realized as the change in the dichroic orientation value is closely related to the change in the fine structure of PET, particularly in the low-ordered region.

In this paper, a similar study to that in the previous paper will be reported using polypropylene (PP) in order to confirm the conclusions made in the previous paper.

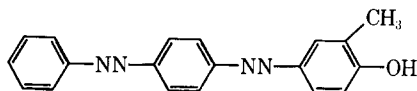
EXPERIMENTAL

Sample

The polypropylene films used here were supplied by Chisso Corporation. The film was about 110μ thick; it had an isotropic and smectic structure as determined by x-ray investigation. The viscosity-molecular weight (evaluated by using the equation of Kinsinger and Hughes²) and the tacticity (extracted with boiling *n*-heptane) were 29.5×10^4 and 94.9%, respectively.

Dyeing and Stretching

Dyeing was carried out at 120°C for 2 hr with C.I. Disperse Yellow 7 (C.I. 26090). The dyed film was stretched in the air at various temperatures.



C.I. Disperse Yellow 7

Dichroic Value D

The dichroic value D was calculated as previously^{1,3}:

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

where K_{\parallel} and K_{\perp} are absorbancies for polarized light vibrating parallel and perpendicularly, respectively, to the stretched direction of the film.

In order to measure the absorbance at a high temperature, the specimen room of a Hitachi photoelectric spectrophotometer, EPU-2A, was heated at the desired temperature by two specially equipped heaters, the temperature of which was controlled by circulating hot silicone oil through them, as shown in Figures 1 and 2.

The specimen was fixed on a metal frame to prevent it from thermal contraction. A film which underwent the same treatment as that of the specimen film, except for the dyeing treatment, was used for reference. The temperature of the specimen room, measured by a Thermistor, was taken as the temperature of the specimen.

The degree of the dichroic orientation f_D was expressed^{1,3} by eqs. (2) and (3):

$$f_D = (1 - \frac{3}{2} \cdot \langle \sin^2 \theta \rangle) = D/D_0 \quad (2)$$

$$D_0 = (1 - \frac{3}{2} \cdot \sin^2 \alpha)(1 - \frac{3}{2} \cdot \sin^2 \beta) \quad (3)$$

where θ is the inclination of polymer segment against the stretching direction, α is the angle between the polymer segment and the combined dye molecule, and β is the angle between the axis of the dye molecule and the direction of the transition moment. The intrinsic dichroism D_0

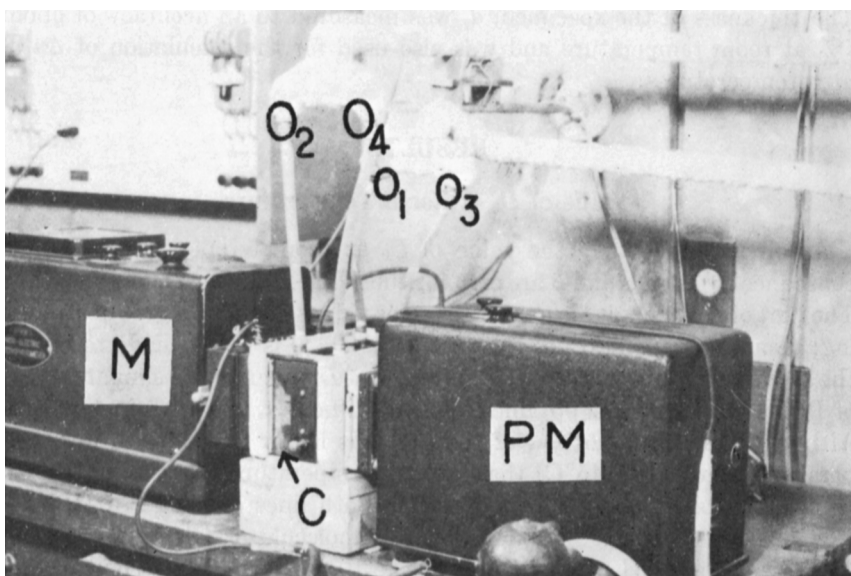


Fig. 1. Apparatus for measurement of dichroism at high temperatures: (M) monochromator; (PM) photomultiplier; (C) cell room; (O₁), (O₃) high-temperature oil inlet; (O₂), (O₄) oil outlet.

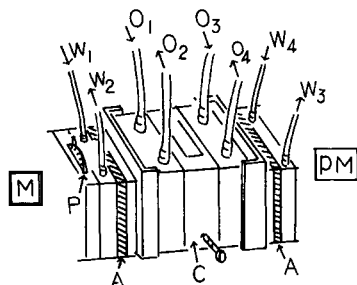


Fig. 2. Schematic diagram of apparatus for measurement of dichroism at high temperatures: (M) monochromator; (PM) photomultiplier; (C) cell room; (P) polarizer; (O₁), (O₃) high-temperature oil inlet; (O₂), (O₄) oil outlet; (W₁), (W₄) cooling water inlet; (W₂), (W₃) water outlet.

is the value which is obtained when the polymer segment is perfectly oriented parallel to the stretching direction. The value of D_0 is 1 when both α and β are zero.

Birefringence at High Temperatures

The retardation Γ of a film was measured by using an ordinary polarizing microscope equipped with a Berek compensator, a heating stage, and a sodium lamp as light source. The birefringence Δn was calculated from eq. (4):

$$\Delta n = \Gamma/d. \quad (4)$$

The thickness of the specimen, d , was measured to an accuracy of about 1% at room temperature and was also used for the calculation of Δn at high temperatures.

RESULTS

Value of D_0 at Room Temperature

As already reported,³ the value of D_0 at room temperature is 1, and consequently both α and β are zero for the PET-Disperse Yellow 7 system. The plot of D versus v^{-1} is linear for larger values of v , the degree of stretching; hence extrapolation of the plot to $v^{-1} = 0$ is easily made to obtain the D_0 value. In the case of PP, the plot of D versus v^{-1} is similar to that of PET, and $D_0 = 1$ is obtained without difficulty, as shown in Figure 3. Although the linear portion of the plot has larger D values in low-temperature stretching (145°C) than in high-temperature stretching (155°C), as usually observed on other polymers,¹ both lines converge to $D_0 = 1$. The phenomenon suggests that the long molecule of Disperse Yellow 7 combines in parallel with the axis of the PP segment. We shall discuss this point later in some detail.

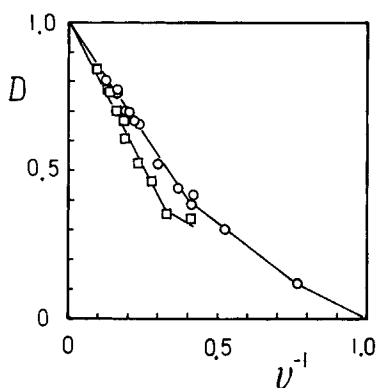


Fig. 3. Plot of D vs. v^{-1} for PP films dyed with Disperse Yellow 7. D attains to 1 when v^{-1} is extrapolated to zero. Temperatures of stretching: (O) 145°C; (□) 155°C.

A break can be seen in the plot of D versus v^{-1} in the case of 145°C stretching. This is because the deformation mechanism of PP changes abruptly around $v = 2.5$; the deformation is ascribed mainly to the unfolding of lamellar crystals in the higher stretching region, while in the low stretching region, plastic deformation of spherulites and destruction of spherulites and lamellar crystals into blocks are predominant, as discussed in the case of biaxial stretching.^{4,5} Hence the deformation mechanism is so complex in the latter region. The value of v at the break in this study accords with those reported on the biaxial stretching⁵ and uniaxial stretching samples of Baltá-Callejá and Peterlin.⁶

Change in Absorption Spectrum at High Temperatures

The absorption spectrum of Disperse Yellow 7 combines with PP shifts toward lower wavelengths as the temperature is raised and is restored to the original wavelength when the sample is cooled to room temperature. The extent of the shift of λ_{\max} , the wavelength of maximum absorbance, is compared in Figure 4 for three substrates, PET, PP, and cellulose triacetate. It is clearly seen that the shift in PP is the largest among the

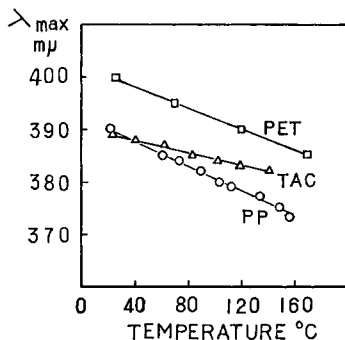


Fig. 4. Changes with temperature in λ_{\max} of spectra of Disperse Yellow 7 in polymer films: (□) PET; (Δ) TAC; (○) PP.

three. The shift suggests the weakening of the interaction between dye molecules and substrate at high temperatures. Therefore, the interaction between C.I. Disperse Yellow 7 and PP seems to be weaker compared with PET or cellulose triacetate. This is not unreasonable, because PP is nonpolar in contrast to PET and cellulose triacetate.

Reversible Change in D

A heating and cooling cycle was repeated four times on the same specimen, which had been stretched $4.5\times$ at 145°C , with the highest temperature being changed gradually to 60° , 100° , 140° , and 138°C . As seen in Figure 5, the values of D in the cooling processes of the first three cycles are slightly smaller than those in the corresponding heating processes, while in the fourth cycle the values of D in the cooling and heating processes agree with each other. This is because the highest temperature rose gradually in the first three cycles, and hence the last stage of each heating process brought about some irreversible changes in the fine structure. However, in the last cycle, the maximum temperature did not exceed that of the third cycle, and therefore there was no irreversible change in the fine structure.

A break, T_0 , appeared clearly in the first cycle, while in the other cycles two breaks could be observed at 70° – 80°C (T_1) and 115° – 120°C (T_3) instead of T_0 ; T_1 and T_3 became slightly higher as the cycling was repeated. The breaks are indicated by arrows in the figure.

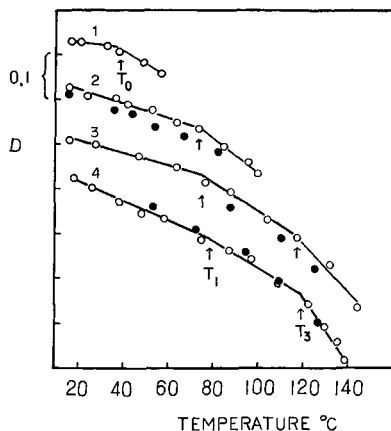


Fig. 5. Changes in D during four heating (O) and cooling (●) cycles. Plots of each cycle are shifted vertically for clarity.

D_0 at High Temperatures

A dyed film was melted in a press at 220°C , with subsequent quenching in water at 0°C . The obtained film was stretched at 150°C and heated in a taut condition at the same temperature for 10 min. The value of D of this sample decreased as the temperature was raised from room temperature, as shown in Figure 6. It is seen that the extent of this change in D is smaller compared with those of the samples which underwent no heat set after stretching.

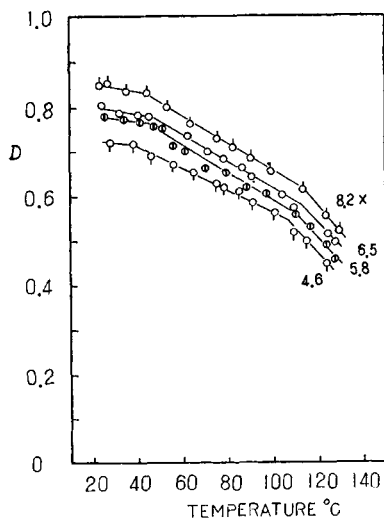


Fig. 6. Change in D with temperature. Specimens were dyed, quenched from melt, stretched at 150°C , and annealed at 150°C . Values of ν : (∇) 4.6; (\odot) 5.8; (\circ) 6.5; (δ) 8.2.

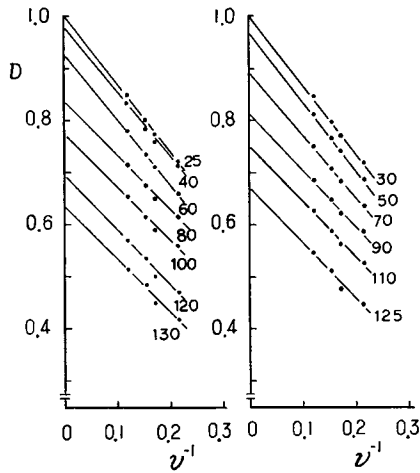


Fig. 7. Relation between D and ν^{-1} at various temperatures, replotted from Fig. 6. Arabic numeral in figure expresses temperature at which D was measured.

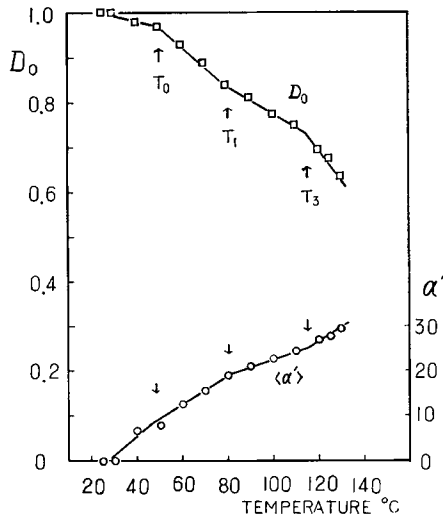


Fig. 8. Changes in D_0 and $\langle \alpha' \rangle$ with temperature.

In this sample only two breaks, T_0 and T_3 , are observed, and they shift slightly toward higher temperatures as ν becomes larger.

When the values of D at certain temperatures in Figure 6 are replotted against ν^{-1} , a group of linear relations are obtained, as shown in Figure 7, from which D_0 at various temperatures can be read by extrapolating to $\nu^{-1} = 0$. It is seen from Figure 8 that D_0 decreases gradually as the temperature increases; of course, D_0 at room temperature is 1, in agreement with the result shown in Figure 3. It is interesting to note that the three breaks, T_0 , T_1 , and T_3 , appear also in this plot.

Relation Between D and Δn at High Temperatures

A sample stretched $5\times$ at 130°C and cooled to room temperature was heat set at 160°C in a taut condition for 15 min. The values of D and Δn at various temperatures of this sample are given in Figure 9. The change in the value of D is similar to that previously described, while Δn remains constant throughout the temperature range of the experiments, which was kept below the setting temperature. The phenomenon may be explained by the fact that Δn expresses the overall orientation, while D expresses selectively the orientation of the small amount of low-ordered region.

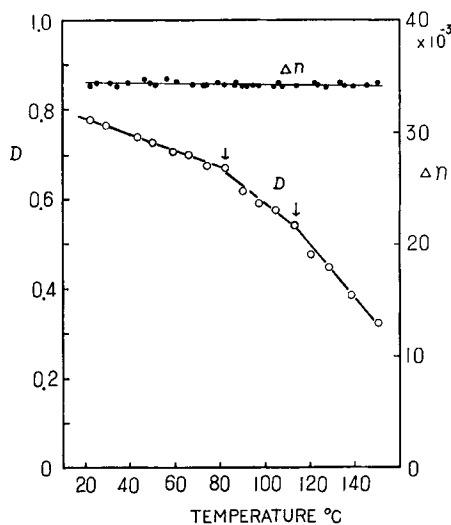


Fig. 9. Change in D and Δn with temperature. Specimen was dyed, stretched at 130°C $5\times$, and annealed at 160°C .

DISCUSSION

The experimental results described above agree qualitatively well with those reported on PET in the previous paper,¹ although the effect of temperature on the extent of the reversible change in D is larger in PP than in PET. This phenomenon is relevant to the fact that the comparison of D is made in the same temperature range without consideration for the existence of the great difference between T_g values of PP and PET. The three breaks in the plot of D versus temperature correspond to the transitions of PP, i.e., amorphous \rightarrow smectic, smectic \rightarrow monoclinic and lattice expansion point. This correspondence can be taken as evidence for the fact that D is affected by the thermal motion of substrate segments at high temperatures in addition to the dissociation of the combined dye molecules from the substrates. One of the present authors, Okajima,^{7,8} has suggested in separate papers that the mode of segmental motion within the amor-

phous region changes abruptly around the temperatures hitherto known as crystalline transition points.

Polypropylene has no specific sites where hydrogen bonding or electrostatic attraction can operate.⁹ Hence, the attraction force between PP and dyes is mainly of a nonpolar van der Waal's type, and consequently a long dye molecule such as Disperse Yellow 7 is considered to be adsorbed in parallel with the helical axis of PP.

Of course, the possibility that $D_0 = 1$ is obtained as a result of hydrodynamic interaction of dyes with the fully oriented amorphous region of the polymer may not be excluded by the results reported here alone. However, the possibility can be excluded, as the authors have found a good correspondence between the visible dichroism and the degree of amorphous orientation obtained from infrared dichroism in the same dye-polymer system through a wide range of orientation.¹⁰

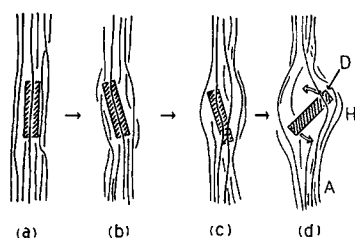


Fig. 10. Schematic illustration of a hole-dye system at various temperatures: (a) at room temperature; (b) \rightarrow (c) \rightarrow (d) at higher temperatures; (A) oriented amorphous; (D) dye molecule; (H) hole at high temperature.

The behavior of the parallel combination of this dye with substrate has been found in the case of the polar polymers, such as nylon 6, cellulose triacetate, and PET.¹¹ From the dichroic point of view, there may be no fundamental difference in the modes of dyeing among these polymers, including PP.

Further, the value of D changed reversibly with heating and cooling. This fact indicates that the dyes are not simply dissolved in the amorphous region of PP, but a considerable interaction force is acting between PP segments and dye molecules. This seems to support the above-mentioned consideration.

In the dyeing process, dye molecules diffuse into substrate by repeat jumping from a hole to a new adjacent hole. When the dyed sample is cooled to room temperature, the segments of substrate are nearly immobilized in a state where a dye molecule is locked in a hole in which the dye molecule combines parallel to the axes of the surrounding segments (Figs. 10 d \rightarrow 10 a). This is the reason why dichroism can indicate the orientation of the amorphous region of the substrate. It is considered from a statistical point of view that the locking state at room temperature does not change so much by stretching.

When a dyed film is again heated much above the T_g , the segments surrounding a dye molecule regain mobility to relax and form a hole containing a dye molecule (Figs. 10 a \rightarrow 10 b).

The hole expands gradually and tends to take a spherical shape with increasing temperature, since the segments gain increasing amounts of thermal energy and become more and more flexible. The change is conspicuous when the system passes through the transition points. The change is, therefore, a function of the free volume of the system.

The interaction between the dye molecules and the polymer segments weakens as the temperature increases, and the dye molecule locked in a hole gains increasing amounts of thermal energy. At the same time, the expansion of the hole toward a sphere affords room for the rotation and oscillation of the dye molecules locked in the hole. Therefore, D , which is given by the time and number-average orientation of the dye molecules, decreases as observed experimentally. This weakening of the interaction is reflected in the shifting of the absorption spectra in Figure 4. The hole shape and the interaction between the dye molecules and the substrates change reversibly as a function of temperature; hence the change in D is also reversible, and the transition points of substrate polymer are reflected in the D -versus-temperature plot through the change of hole shape, which is a function of flexibility of the segments.

Of course, a dye molecule would not always stay in the same hole at high temperatures but would jump into adjacent holes. However, the dye molecules seem not to diffuse so much, judging from the absence of a concentration gradient in the dyed sample.

This consideration can explain the smaller values of D_0 at higher temperatures and the appearance of the transitions even in the plot of D_0 versus temperature. As the percentage of the number of substrate segments which contribute to the formation of the holes is very small, the number of dye molecules which give dichroism is considerably smaller than the number of the segments which is usually kept unchanged during the dichroism measurements at high temperatures. Therefore, Δn , which expresses the average orientation of the whole segments, remains constant even if D changes, so long as the temperature does not exceed the highest temperature experienced by the system (Fig. 9).

When the ratio of D at any temperature on each plot in Figure 6 to D_0 at the corresponding temperature in Figure 8 is plotted against temperature ($v = \text{constant}$), this ratio D/D_0 stays constant below 110°C (Fig. 11). Thus, Figure 11 shows that the decrease in D at high temperatures is due to the decrease of D_0 caused by the disorientation of the packed dye molecules (Fig. 10), while the overall amorphous region is not disoriented.

When the mean orientation angle of dye molecules against the hole axis is expressed by $\langle\alpha'\rangle$, it can be calculated from eq. (3) using the values of D_0 in Figure 8. The value of $\langle\alpha'\rangle$ increases gradually as the temperature increases and amounts to 30 degrees at 140°C, as shown in Figure 8. Of course, β is 0 in this case.

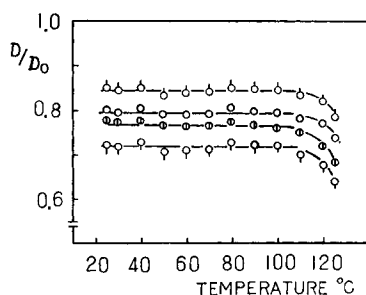


Fig. 11. Change in D/D_0 with temperature, replotted from Figs. 6 and 8. Values of ν : (○) 4.6; (⊖) 5.8; (○) 6.5; (⊖) 8.2.

Table I is added here in connection with the thermally changed hole shape. By using Bueche's theory,¹³ Kumis and Roteman¹² calculated the hole volume, $Q_{00} - V_{00}$, in the segments (the volume of which is V_{00}) for the diffusion of simple gas molecules through a copolymer of vinyl chloride and vinyl acetate. The method of the calculation of the hole volume by Kumis and Roteman was applied here to calculate the hole volume of PP from the rate of diffusion of Disperse Yellow 7 in unoriented PP.⁷ The application was possible because the disperse dyes bring about no swelling of PP and the diffusion is concentration independent. It is interesting to do such an application because the hole volumes have never been calculated before for such large molecules as Disperse Yellow 7. The hole volumes calculated are listed in Table I.

The values of $Q_{00} - V_{00}$ obtained seem reasonable for the molecular size of Disperse Yellow 7, and the ratio between $Q_{00} - V_{00}$ and V_{00} agrees with the values reported for simpler molecules.¹² Further, the activation energy of diffusion calculated as the product of $Q_{00} - V_{00}$ and the cohesion energy density of PP is also in agreement with the values observed above 90°C.

The decrease in $Q_{00} - V_{00}$ and the increase in $(Q_{00} - V_{00})/V_{00}$ with elevation in temperature seem to be evidence for the increased flexibility of PP segments and the more spherical shape of holes at higher temperatures, as already mentioned.

TABLE I
Calculation of Hole Size for the Diffusion of Disperse Yellow 7 Through PP at Different Temperatures

	70°-90°C	90°-110°C	Above 110°C
$V_{00}, 10^3 \text{ \AA}^3$	11.3	2.38	1.11
$Q_{00} - V_{00}, \text{ \AA}^3$	2180	635	360
$(Q_{00} - V_{00})/V_{00}$	0.19	0.27	0.33
Activation energy of diffusion, kcal/mole			
observed	57	32	22
calculated	115	34	19

So far, the hole shape has been assumed to be only a function of temperature. However, it is necessary to take into consideration the influence of the orientation of substrate upon the hole shape. The hole shape at high temperatures, where polymer chains are flexible, is thought to become more ellipsoidal as the draw ratio increases. Then, the D_0 read in Figure 7 is not always correct because the influence of stress was neglected there. That is to say, the value of D at lower (or higher) v in Figure 7 is slightly underestimated (or overestimated) compared with the value of D at higher (or lower) v . The value of D_0 obtained by extrapolation in Figure 7 under the condition of constant hole shape at any v should be slightly smaller than that shown in Figure 8. The extent of this overestimation is smaller for the lower temperature.

That the drop of D/D_0 begins at about 110°C is evidence that this overestimation of D_0 is not negligible above 110°C, and it is reasonable that this temperature range agrees with T_3 .

As to the amorphous transition points, T_0 (40°–44°C), T_1 (60°–70°C), T_2 (84°–90°C), and T_3 (110°–115°C) have been observed in the diffusion study.⁷ In the present study, only three transitions appeared, and they were designated as T_0 , T_1 , and T_3 following the designation made in the previous paper. However, it is not clear at present why T_0 or T_1 disappeared in some cases although T_3 appeared always and T_2 disappeared without exception. Further study is required to clarify this problem.

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