Studies on Sublimation of Disperse Dye out of Dyed Polymers. II. Rate of Sublimation and Amorphous Transition of Polypropylene

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Synopsis

The diffusion coefficient D of disperse dyes through unmodified polypropylene (dyed at 120° and 137°C) was measured at 50°–160°C in the dry system. The diffusion transition points indicated by the breaks in the log D versus $1/T$ °K were obtained at about 70°, 90°, and 115°C. The 70° and 115°C transitions are in good accordance with the transition temperature of smectic into monoclinic phase and with the temperature of abrupt change in lattice expansion of monoclinic crystal, respectively. These phenomena were explained on the basis of the intimate correspondence between amorphous and crystalline transitions, as expressed by one of us for poly(ethylene terephthalate). The 115°C transition was confirmed by the same sort of diffusion transition occurring, expectedly, at 83°C in the case of polyethylene, an abrupt increase in lattice expansion of which had been found at about 80°C. The diffusion transitions were also confirmed by dilatometry and shrinkage measurement. The 90°C transition has never been reported and it cannot be explained at present.

INTRODUCTION

In the preceding papers, one of the authors reported that apparent activation energy for diffusion of disperse dye in poly(ethylene terephthalate) (PET) change abruptly at three temperatures between T_g and 200°C and that the amorphous transition points indicated by these temperatures corresponded with the crystalline transition points reported in literatures by other authors.

Although the information on the transitions above T_g is extremely important for high-temperature dyeing, such studies have not been reported except one carried out recently by Duda and Vrentas[2] on amorphous polystyrene.

Hence in the present paper the diffusion behavior of disperse dyes in polypropylene (PP) was studied in order to confirm the view concerning the intimate correspondence between the amorphous and the crystalline transitions on PET. PP appears to be a suitable material for this purpose because the crystalline transitions have been well studied by many workers.

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EXPERIMENTAL

Sample

Three samples, A, B, and C, were mainly used. Sample A was undrawn isotactic PP film supplied by Chisso Corporation; its tacticity was 95% and molecular weight was 220,000. Sample B was commercially available PP filament (Mitsubishi Rayon Co., 3 × 30 den.). Before use, sample B was soaped, rinsed with water, and air dried. Part of B was annealed without restriction at 160°C for 1 hr under nitrogen atmosphere and was designated as sample C.

Also used were an undrawn film of linear polyethylene (sample E), (Hizex of Mitsui Petrochemical Ind. Ltd.) and a drawn (8.5X) film of similar type polyethylene (sample F) (Staflon E-615 of Furukawa Chemical Ind. Ltd.); E and F were 175 and 19 μ thick, respectively. Before use, E and F were preheated at 100°C in water and at 130°C in air, respectively.

Dyeing

Disperse Yellow 7 (Y-7) (C.I.) and two other dyes, I and II, being prepared and supplied for this study through the courtesy of Hodogaya Chemical Ind. Ltd., were used.
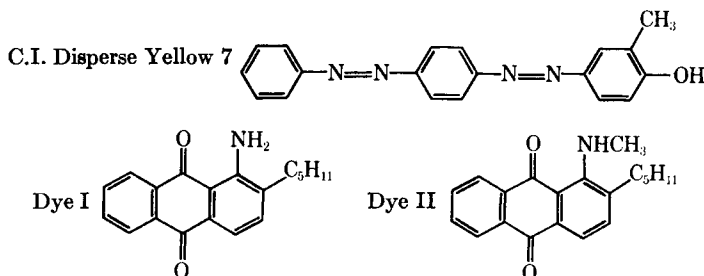
A high-temperature dyeing machine, Tumblet (Toa Seiki Ltd., Japan), was used for dyeing as previously described[1] under the conditions summarized in Table I. Dyed filament and film were rinsed with 50% aqueous acetone and an aqueous solution of Disper-TL (0.5%), respectively, in order to remove the dye adsorbed on the surface of the dyed samples. The dye was stripped from the dyed sample with monochlorobenzene and the amount of dye was estimated photometrically.

Sublimation of Dye Out of the Dyed Sample

Sublimation of dye out of dyed sample and its determination were carried out similarly as in the preceding paper. It was confirmed that the dyes used suffered no thermal decomposition during the sublimation procedure. Figure 1 shows that the absorption spectra of fractions 1 and 2 of Y-7, which sublimed during the first 3 min and the next successive 8 min, respectively, are in perfect agreement with each other. Similar results were obtained for dyes I and II.

TABLE I
Dyeing Condition[a]

Sample	Weight of sample, g	Dye	Amount of dye, g	Amount of Disper. TL,[b] g	Time of dyeing, min	Temp. of dyeing, °C
A	10	Y-7	0.15	0	90	120, 137
		I	0.06	0.5	90	120
		II	0.04	0.5	90	120
B	2.0	Y-7	0.3	0	120	120
		I	0.1	1.0	120	120
C	2.0	Y-7	0.3	0	120	120
E	2.5	I	0.23	2	120	100
F	3.1	I	0.55	4	180	115

[a] Volume of dye bath 100 ml.
[b] Anionic surface active agent, registered trade name of Meisei Chemical Works, Ltd., Japan.
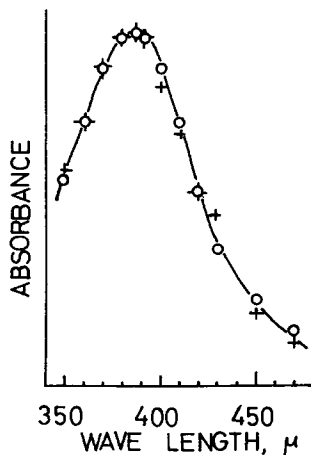

Fig. 1. Absorption spectra of fractions 1 and 2 of Y-7 sublimed during first 3 min and next 8 min. Respective amounts of fractions 1 and 2 are 7.9% and 42% of the total amount of dye contained in the sample: (+) fraction 1; (O) fraction 2.

As is well known, the diffusion constant of disperse dye in a hydrophobic polymer is concentration independent. This is the case in the present polymers as shown in Figure 2, where the slopes of the $M_t/M\infty$-versus-$t^{1/2}$ plots are independent of the initial dye concentration of polymer within the experimental error. Here M_t and $M\infty$ are the amounts of dye sublimed during the periods of t min and $t = \infty$, respectively. $M\infty$ was practically equal to the dye content of specimen.

Calculation of Diffusion Constant D

The diffusion constant D in cm²/min was calculated from eq. (1),[3] where A is the surface area of sample in cm²/g, d is the density of sample in
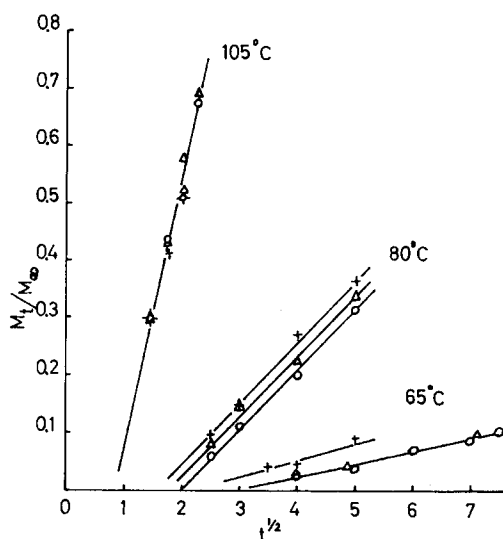
Fig. 2. M_t/M_∞ vs. $t^{1/2}$ for samples of various dye II contents. Amount of dye per mg of polymer: (+) 6.43 mg; (Δ) 14.7 mg; (O) 22.7 mg.

g/cm³, and t is the time of sublimation in min. The thickness of sample A was 760 μ, and the radii of samples B and C were 10.0 and 12.6 μ, respectively.

$$M_t/M_\infty = 2Ad(Dt/\pi)^{1/2}. \tag{1}$$

Thermal Shrinkage

Thermal shrinkage S of sample B was followed by heating in air at the rate of 0.7°C/min. Three runs were performed by changing the weight hanging from the lower end of a yarn (30 filaments) at three levels, 0.184, 0.339, and 0.684 g. S is expressed by $(L_0 - L)/L_0$, where L is the length at temperature T°C and L_0 is the initial length.

Dilatometry

Dilatometry was carried out as described previously. The rate of heating was 0.7°C/min. The samples used were film A, as received, and crystallized at 135°C for 28 hr after melt pressing at 200°C.

Degree of Orientation

The overall degree of orientation, f_0, and the degree of crystalline orientation, f_c, were measured by means of retardation and x-ray methods,[4] respectively. Degree of amorphous orientation f_a was evaluated from

$$\Delta n = \Delta n_c^0 f_c X + \Delta n_a^0 f_a (1 - X) \tag{2}$$

where Δn, Δn_c^0, and Δn_a^0 are birefringence of sample, intrinsic birefringence of crystalline region, and intrinsic birefringence of amorphous region, re-
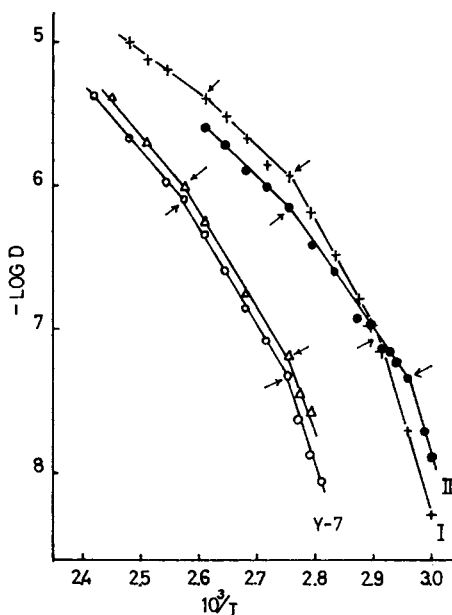
Fig. 3. Log D vs $1/T°$K for dyes Y-7, I, and II through sample A: (O) dyed at 120°C; (△) dyed at 137°C.

spectively. The value[5] of Δn_c^0 is 0.0415 and of Δn_a^0, $0.0415 d_a/d_c$, where d_a and d_c are the amorphous and crystalline densities, 0.870[6] and 0.936[7] g/cm^{3}, respectively. The crystalline fraction X in eq. (2) was evaluated from

$$d = d_c X + d_a (1 - X) \tag{3}$$

and the density of sample d was measured by a density gradient tube composed of ethanol and water.

RESULTS

Diffusion Constant

The diffusion constants of the three dyes in samples A, B, and C observed at various temperatures T are plotted against the reciprocals of the absolute temperatures of diffusion in Figures 3 to 6. Each plot is composed of three or four intersecting lines the slopes of which progressively decrease as the temperature is elevated. The values of D for dyes I and II are nearly equal to each other but they are larger than the value for Y-7 by about one to two logarithmic units in A (Fig. 3) and B (Fig. 6). This is reasonable because dyes I and II are akin to each other in molecular size and shape but smaller than Y-7. In Figure 3, two plots for samples A dyed with Y-7 at 120° and 137°C are close to each other; slightly larger values of D for the latter seems to be due to its more loosely packed struc-
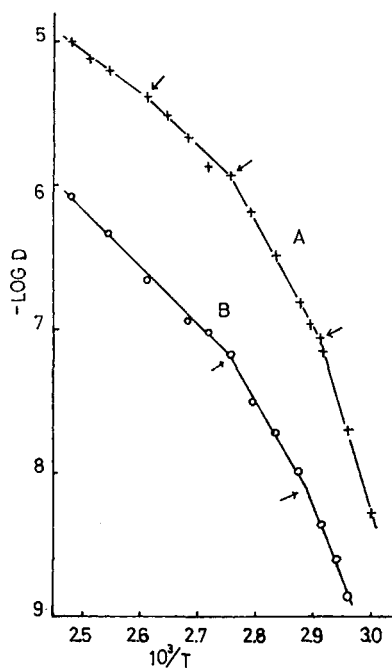
Fig. 4. Log D vs. $1/T°K$ for dye I through samples A and B.

ture of the amorphous region brought about by dyeing at the higher temperature. A similar relationship can be seen between samples B and C (Fig. 5). In this case the larger diffusion constant for sample C results from the annealing at 160°C. It can be seen in Figures 4 and 5 that the dyes diffuse more easily in sample A than in B or C, probably because of the unoriented structure of sample A.

Temperatures at the breaks $(T_{dt}, i = 1, 2, 3)$ indicated by arrows in these plots are listed in Table II. It is clearly seen that three transitions

TABLE II
Transition Temperature T^a_{di} Read from Plot log D vs. $1/T^a$

Dye	Sample A			Sample B			Sample C		
	$i = 1$	2	3	$i = 1$	2	3	$i = 1$	2	3
Y-7		90	115		90	140		90	130
		90[b]	115[b]						
I	72.5	90	110	70	90				
II	65	90							

[a] Values shown are °C.
[b] Read from plot for sample A dyed at 137°C.

appear at 65°–72.5°C (T_{d1}), 90°C (T_{d2}), and 110°–115°C (T_{d3}). T_{d1} and T_{d2} do not vary so much with the samples and dyes. However, T_{d3}
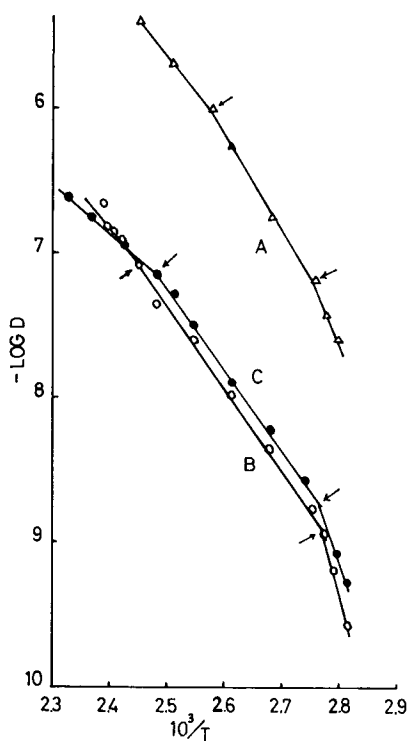
Fig. 5. Log D vs. $1/T^\circ$K for dye Y-7 through samples A, B, and C.

is considerably higher in samples B and C than in A. We will discuss this point later.

The apparent activation energies, ΔE_i $(i = 1\text{–}4)$, obtained from these log D-versus-$1/T$ plots are shown in Table III, where suffix numbers 1 to

TABLE III
Apparent Activation Energy for Diffusion

Sample	Dye	ΔE_1, kcal/mole	ΔE_2, kcal/mole	ΔE_3, kcal/mole	ΔE_4, kcal/mole
A	Y-7		56.5	32.0	21.6
	I	55.0	35.0	17.5	12.2
	II	59.5	26.6	17.0	
B	Y-7		54.0	25.3	21.2
	I	55.0	33.8	18.2	
C	Y-7		48.5	25.5	14.7

4 denote the regions below T_{d1}, $T_{d1}\text{–}T_{d2}$, $T_{d2}\text{–}T_{d3}$, and above T_{d3}, respectively. The value of ΔE_i decreases as i increases for any sample; but it does not change so much among samples A, B and C when the comparison is made for the same dyes. The apparent activation energy
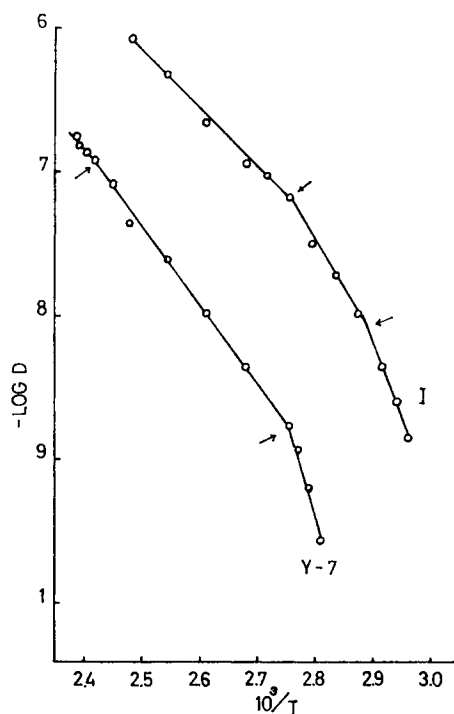
Fig. 6. Log D vs. $1/T°K$ for dye Y-7 and I through sample B.

for dye Y-7 is larger than those for the other two dyes. The tendency resembles that observed in samples E and F (Table VI). It is noteworthy that the value of D is much larger and ΔE is slightly smaller compared to those for PET[1] at the corresponding temperature.

Dilatometry

Temperatures at the breaks in volume-versus-temperature plots, T_{vi}, are summarized in Table IV. A dilatometer was heated up to 145°C in the

TABLE IV
Comparison of Transition Points Obtained by Various Methods

Method	Transition point, °C			
	$i = 0$	$i = 1$	$i = 2$	$i = 3$
Diffusion		65–72	90	110–115, 130, 140
Shrinkage		60–67	84–93	140–141
Dilatometry				
First run	40–44	63	84–86	115–116
Second run	37–41	68–70	90	115–119

first run and the second run was started again at room temperature. The table shows that the breaks (the second run) appear at 37°–41°C (T_{v0}),
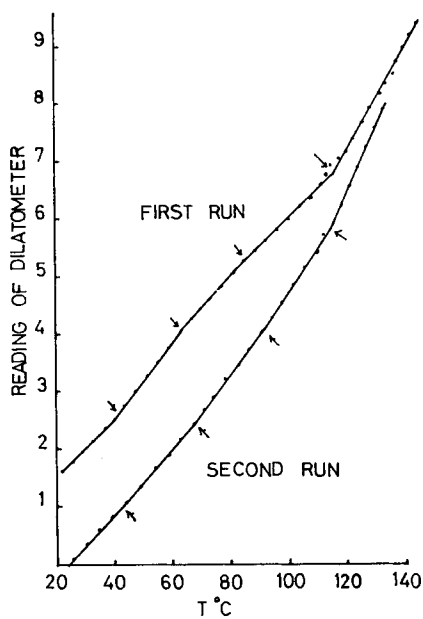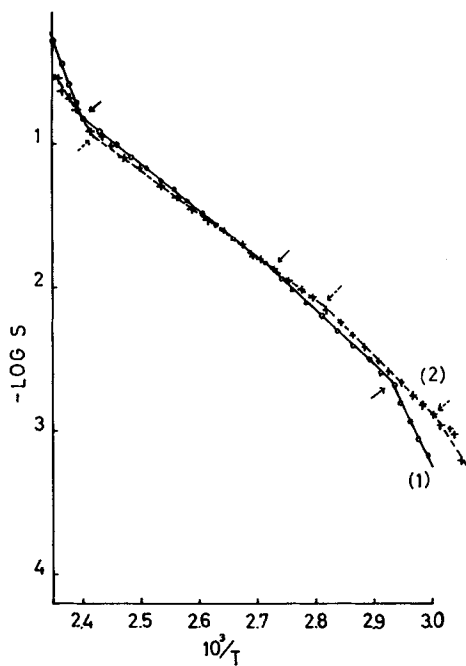
Fig. 7. Dilatometry for sample A.

Fig. 8. Log S vs. $1/T$ °K for sample B.   Suspended weight: (1) 0.684 g; (2) 0.184 g.

68°–70°C (T_{v1}), 90°C (T_{v2}), and 115°–119°C (T_{v3}).   Figure 7 is a typical example of the dilatometries.

The dilatometry shows the considerable volume increase at T_{v0} and the volume decrease at T_{v1} and T_{v2} in the first run as already pointed out by Minami et al.,[3] while in the second run no more volume decrease is observed.   Therefore, it can be considered that the smectica crystal melts at T_{v0} and recrystallizes into the monoclinic system at T_{v1} as Minami et al. suggested.   The break at 90°C (T_{v2}) has never been reported and its interpretation is not clear at present.

Thermal Shrinkage

One of the present authors has shown that the log S-versus-$1/T$ plot is composed of straight lines intersecting at the transition points and this plot is capable of detecting the thermal change of fine structure in the case of PET[9] and polyacrylonitrile.[10]   The plot for sample B shows the breaks at 68°–70°C (T_{s1}), 84°–93°C (T_{s2}), and 131°–140°C (T_{s3}), as seen in Figure 8.   These T_{si} are in good accordance with T_{di} and T_{vi} as shown in Table IV. T_{si} shifts slightly toward the high temperature side with increase in hanging weight.   The plots obtained under the weights 0.184 and 0.684 g are shown in Figure 8.

DISCUSSION

Dye molecules generally combine with substrate in the amorphous region and they diffuse through the amorphous region.   Therefore, an abrupt change in ΔE at a certain temperature suggests that some change occurs in segmental motion of the amorphous region at that temperature. Comparing the transition temperatures obtained by the various methods, there is a good correspondence among T_{di}, T_{vi}, and T_{si} as can be seen in Table IV.

A few papers have described the transition points of PP above T_g. Kishi et al.[11] and Minami et al.[8] found a tan δ peak at about 50°C, which intensified with increase in amount of smectic fraction, and Kishi et al. proposed that the transition of smectic into monoclinic crystal occurred at about 50°C.   However, Minami et al., based on their dilatometric study, concluded that this phase transformation proceeds in two steps, i.e., smectic → amorphous and amorphous → monoclinic transformations. According to these authors, premelting of the smectic crystal occurs at about 30° to 50°C.   Kawai et al.[12] reported an increase in thermal expansion coefficient of $(hk0)$ spacing of smectic crystal at this temperature range.

The next high transition temperature appears at about 70°C.   Wyckoff,[13] Jambrich and Diacik,[14] Krämer, and Helf[15] and Flocke[16] reported that the smectic phase is transformed into the monoclinic system at about this temperature.

X-Ray study has shown an increase in thermal expansion coefficient of PP monoclinic crystals at 115°C. The corresponding change appears also in the infrared spectrum.[17]

T_{d1} and T_{d3} in the present study seem to accord well with the 70°C and 115°C transitions mentioned above, respectively. The 40°C transition was not studied by diffusion experiment because sublimation of the dyes used was too slow to be measured accurately at such a low temperature range. It is believed that the transition can be detected when a substance with higher vapor pressure such as p-nitroaniline or azobenzene is used instead of the disperse dyes. The shrinkage of sample B was so small at that temperature range that it could hardly be measured with sufficient accuracy to detect the 40°C transition.

According to the literature, these transitions relate to the change of the molecular motion in the crystalline phase, while T_d must relate to transitions in the amorphous phase. Hence, it is considered that the mode of segmental motion in the amorphous phase in close co-operation with that in the crystalline phase.

The dyed samples, which have been heated at 120°C, are already monoclinic crystalline matter, while still exhibiting the 70°C transition. This is similar to the phenomena reported in the case of PET[1] and it can be explained reasonably in a similar manner, as follows. When amorphous PP is heated to 70°C or higher, the chain segments get sufficient thermal energy to overcome the restriction which prevents the crystallization into monoclinic system below this temperature. Even above 70°C, however, a fraction of the amorphous segments remains uncrystallized because they are not in a suitable position to be incorporated into the lattice although they too have sufficient energy. When the polymer crystallized into monoclinic matter is again heated above 70°C, this sort of segmental motion with higher activation energy begins at 70°C, always within the amorphous region but without further crystallization, and energy dissipation is observed always at 70°C as the amorphous transition.

Another sort of illustration is necessary for the 115°C transition. It is known that the thermal expansion coefficient of the lattice spacing of monoclinic PP increases abruptly at 115°C.[12,17] Hence it is considered that the amorphous segments are free of restriction imposed by the crystallites, and new energy dissipation is reflected in diffusion, volume increase, shrinkage, and dynamic mechanical behavior at this temperature as an amorphous transition. This is the case of film A, T_{d3} of which corresponds well with the crystalline transition at 115°C (α_c). In the cases of samples B and C, the T_{d3} are 140°C and 130°C, respectively, which are considerably higher than 115°C. However, the abrupt increase in the thermal expansion coefficient of the lattice spacing still occurs at 115°C even in these samples, as is shown in Figure 9. The spacing in the figure is not yet exactly corrected, but it is sufficient to indicate the b eak at 115°C. The (130) spacing is omitted from the figure because it has been confirmed that it expands in a similar manner. The correspondence of
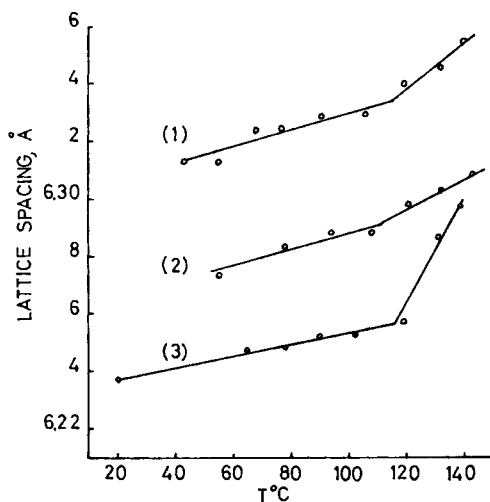
Fig. 9. Lattice spacing (110) of monoclinic polypropylene crystals at various temperatures: (1) sample C; (2) sample A; (3) sample B (see Table V).

T_{d3} and α_c is not true for these samples of high orientation. The reason may be that the segments in the amorphous region within highly oriented samples suffer so large a restriction from the crystallites that the T_{d3} deviates from 115°C and shifts toward higher temperatures to obtain a sufficient energy for being free from the restriction and exhibiting the transition. The deviation becomes larger with increase in amorphous orientation, as Table V shows. T_{d3} is linearly related to f_a within the

TABLE V
Relation Between T_{d3} and f_a

Sample	f_a	T_c,[a] °C	T_{d3}, °C
Film A	0.0	114	115
Filament annealed at 160°C	0.30	111	130
Filament dyed at 120°C	0.49	116	140

[a] Temperature at break in plot of lattice spacing of monoclinic PP crystal versus temperature.

TABLE VI
Apparent Activation Energy of Diffusion of Dye I
Through Polyethylene

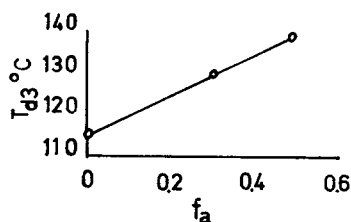|	Sample E	Sample F
Transition point, °C	83	92
ΔE, kcal/mole		
{Below transition pt.	31.6	49.4
{Above transition pt.	11.4	18.3

Fig. 10. Plot of T_{d3} vs. f_a.

experimental range, as shown in Figure 10.   The smaller f_a value and lower T_{d3} value of the filament annealed at 160°C than the corresponding values of the filament dyed at 120°C are due to the more loosely packed structure of the amorphous region of the former as a result of the high-temperature annealing, as repeatedly mentioned.

Recently Nishijima and Masai[18] and Gondo and Utsunomiya[19] studied the diffusion of antioxidants in PP and found the breaks in the log D-versus-$1/T$ plot at 120°C and 60° to 70°C, respectively.

If the above explanation for the 115°C transition is correct, a break is expected at about 80°C in the log D-versus-$1/T$ plot in the case of polyethylene, because the crystalline transition relevant to the lattice expansion has been observed at about 80°C for polyethylene.[20]   Experimental results met this expectation, as shown in Figure 11.   Similarly to the case of PP, the transition point of the stretched sample F is slightly higher than that of the undrawn sample E.
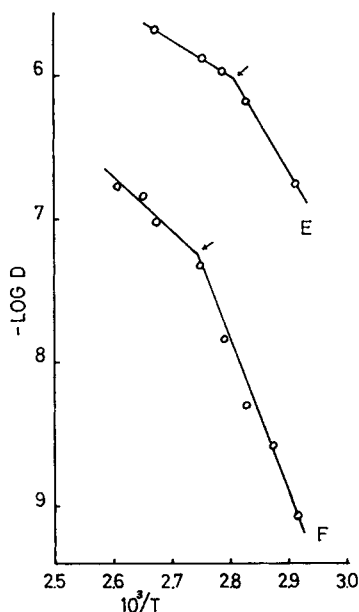

Fig. 11. Log D vs. $1/T°K$ for polyethylene samples E and F.   E is unoriented, F is oriented.

The 90°C transition was definitely observed by the various experiments carried out in the present study, although it has never been reported. It can, therefore, be considered to be a new transition point. Further study is necessary for this.

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