

## Studies on the Drawing of Polyamide Fibers. III. Change of Dye-Diffusion Behavior into Polyamide Fibers with Drawing

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### Synopsis

The diffusion constants of an acidic dye (Xylene Fast Blue P) into nylon 6 monofilaments of various draw ratios have been measured at several temperatures by measuring the distance of dye penetration into the cross-sections of the sample. The results are as follows. The diffusion coefficient of dye increases, reaches a maximum at a draw ratio near 1.6, and then decreases as the draw ratio increases. The activation energy of dye diffusion obtained from the temperature dependence of dye diffusion coefficient remains nearly constant in the initial and middle stages of drawing and increases above a draw ratio of about 3, as the draw ratio increases. The change in the polymer structure during drawing is discussed on the basis of these results.

In the previous papers in this series,<sup>1,2</sup> the dependence of some physical properties on the draw ratio of nylon 6 monofilaments was studied, and it was suggested that the fine structure of the polymer would become most unstable at an intermediate stage of drawing (draw ratio of about 2), since, near this draw ratio, peculiarities of some properties, such as tensile strength and shrinkage in boiling water, have been observed.

In this paper, we discuss the influence of drawing on the diffusion behavior of an acidic dye into nylon 6 monofilaments. Although several studies have been made on this subject,<sup>3-5</sup> all the samples used in these studies were multifilament yarns which are considered to be largely oriented even in the undrawn states. Therefore, from these results we could not get exact information on the initial stage of drawing. Moreover, attention had not been given especially to the dye diffusion at low degree of orientation. Therefore, we carried out experiments on dyeing of nylon 6 monofilaments which had negligibly small birefringences in their undrawn states, in order to investigate the effect of orientation in the initial stage of drawing. The activation energy as well as the coefficient of dye diffusion was measured for the samples of various draw ratios.

### EXPERIMENTAL

#### Samples

**Group I.** Undrawn nylon monofilament (about 1300 den.), prepared under the same conditions as in the previous papers,<sup>1,2</sup> were drawn to var-

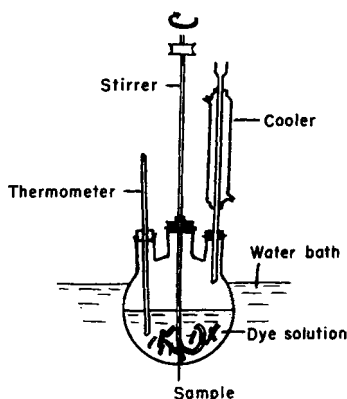


Fig. 1. Apparatus for dyeing experiments.

ious draw ratios in the water at 90°C. immediately after melt spinning. The drawing speed was 26 m./min.

**Group II.** The same undrawn monofilament as that used for group I was drawn several weeks after it had been melt-spun. The drawing speed was 5 m./min., and the temperature of the drawing bath was 90°C.

**Group III.** The undrawn sample of group I was heat-treated at 180°C. for 30 sec. in a hot air bath and then drawn to various draw ratios, the drawing was carried out under the same condition as for group II.

### Method of Experiments

The dyeing was carried out with the apparatus shown in Figure 1, under the following conditions.

The composition of dyeing solution was dye (Xylene Fast Blue P\*), 0.1% (by weight); acetic acid, 0.05% (by weight); solvent, water; pH of the solution at 25°C., 5.75

The volume of the dyeing solution was 200 ml.; the sample (about 2 cm.) ca. 0.1 g.; dyeing was carried out at temperatures of 40, 50, 60, 70, and 80°C.

A piece of each sample was taken out from the dyeing bath at a definite time after the experiment had been started, the ring-dyed section was examined under a microscope, and the distance of dye penetration was measured. According to Kramer,<sup>6</sup> the dye diffusion constant  $D$  is given by eq. (1):

$$D = X^2/2t \quad (1)$$

or

$$X = (2D t)^{1/2}$$

where  $X$  is the distance of dye penetration and  $t$  the time of dyeing. In our experiments,  $X$  was plotted against  $\sqrt{t}$ , and  $\sqrt{2D} = \bar{D}$ , obtained from this relation, was used in the discussion of the results. We call this

\* Commercial dye was used after having been dried. The molecular weight of this dye is about 500.

value the dye penetration constant, according to Yoshida and Hirota.<sup>7</sup> No measurable decrease in the concentration of dye in the solution was observed during dyeing, because of the small quantity of sample used compared with that of the dye used.

## RESULTS

### Effect of Drawing on Dye Diffusion Velocity

A good linear relationship exists between the distance of dye penetration and the square root of time in each run. Typical results are shown in

TABLE I  
Dye Penetration Constants at 60°C.

| Draw ratio | $\bar{D} \times 10^8, \text{ cm.}/\text{sec.}^{1/2a}$ |          |           |
|------------|---|----------|-----------|
|            | Group I   | Group II | Group III |
| 1.0        | 7.2   | 6.5      | 8.2       |
| 1.3        | 8.0   | 8.7      | 10.2      |
| 1.6        | 8.4   | 8.9      | 9.4       |
| 1.9        | 7.9   | 8.5      | 7.2       |
| 2.2        | 7.3   | 8.0      | 6.4       |
| 2.5        | 7.1   | 6.8      | 4.8       |
| 2.8        | 5.6   | 6.0      | 5.2       |
| 3.1        | 5.1   | 5.1      | 3.8       |
| 3.4        | 3.4   | 3.5      | 2.7       |
| 3.7        | 3.0   | 3.0      | 2.2       |
| 4.0        | 2.4   | 2.7      | 1.5       |
| 4.3        | 2.1   | 1.4      | 1.3       |
| 4.6        | 1.8   | 1.1      | 1.5       |
| 4.9        | 1.8   | 1.3      | 1.1       |
| 5.2        | 1.7   | 0.9      | 1.0       |

\* Each value is a mean value of more than 2 runs.

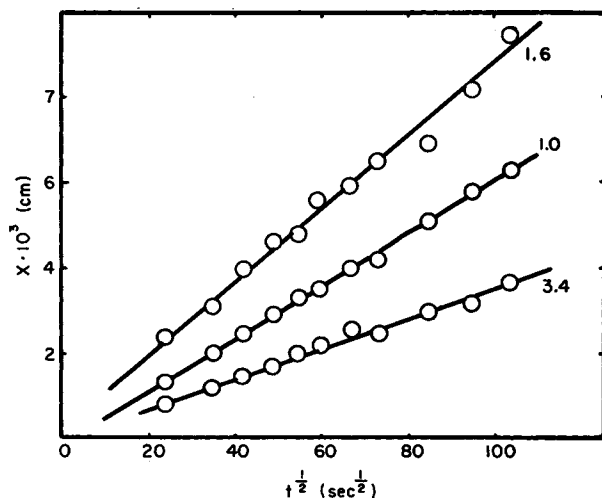


Fig. 2. Distance of dye penetration  $X$  for samples of group I vs. square root of time,  $t^{1/2}$  for samples of various draw ratios.

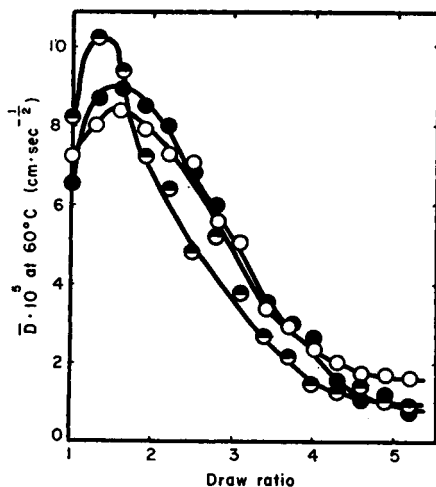


Fig. 3. Dye penetration constant  $\bar{D}$  vs. draw ratio: (O) group I; (●) group II; (◐) group III.

Figure 2. The dye penetration constants  $\bar{D}$  of all samples at 60°C., obtained from the tangents of these linear lines, are given in Table I and Figure 3.

In every group of samples,  $\bar{D}$  (and therefore the diffusion constant) increases, passes through a maximum at a low draw ratio, and then decreases, as the draw ratio increases. In the initial stage of drawing, the velocity of dye diffusion is greater for the heat-treated samples than for the untreated samples, but in the range of draw ratio higher than 2, the decrease of velocity with the draw ratio is more marked for the treated samples. No marked difference in diffusion rate was observed between group I and II.

#### Effect of Drawing on Activation Energy of Dye Diffusion

Between the absolute temperature of dyeing,  $T$ , and the coefficient of dye diffusion  $D$  there is a relation expressed by eqs. (2):

$$\ln D = \ln D_0 - E/RT$$

or

$$\log D = \log D_0 - 0.434E/RT \quad (2)$$

where  $T$  is absolute temperature,  $E$  is the activation energy of dye diffusion, and  $R$  is the gas constant. Putting the relation,  $\bar{D} = \sqrt{2D}$ , into eq. (2), we get the following relation:

$$\log \bar{D} = \log \bar{D}_0 - 0.434 (E/2)/RT \quad (3)$$

Therefore, we can obtain the activation energy from the tangent of the plot of  $\log \bar{D}$  versus  $1/T$  by using eq. (3).

$\bar{D}$  values were measured at several temperatures for each sample.  $\log \bar{D}$  proved to be a linear relation of  $1/T$ , as shown in Figure 4. The values of

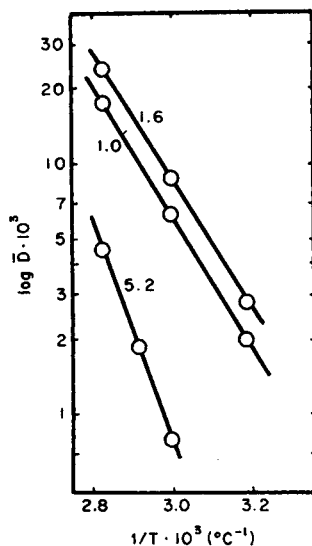


Fig. 4. Plot of  $\log D$  vs.  $1/T$  for samples drawn to draw ratios of 1.0, 1.6, and 5.2.

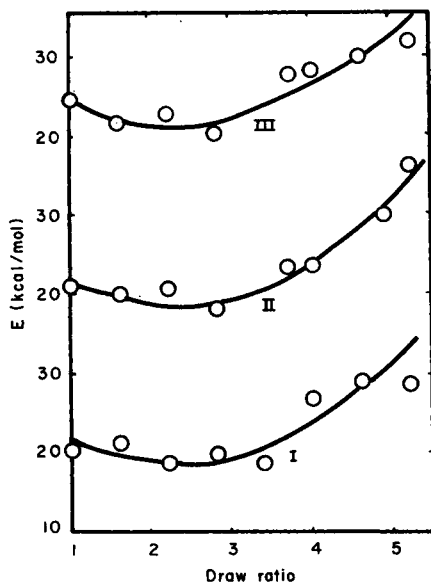


Fig. 5. Plot of activation energy vs. draw ratio for groups I, II, and III.

activation energies obtained by this method are given in Table II and Figure 5.

This figure indicates that the activation energy increases from about 20 to about 35 kcal./mole as a result of drawing. Although the difference in the activation energy is small between these three groups of samples, the activation energy for group III seems to be slightly higher than for the others. In the initial stage of drawing, the activation energy decreases

TABLE II  
Activation Energy of Dye Diffusion

| Draw ratio | <i>E</i> , kcal./mole |          |           |
|------------|-----------------------|----------|-----------|
|            | Group I               | Group II | Group III |
| 1.0        | 20.2                  | 20.8     | 24.6      |
| 1.6        | 21.3                  | 20.0     | 21.4      |
| 2.2        | 18.6                  | 20.6     | 22.8      |
| 2.8        | 19.9                  | 18.2     | 20.0      |
| 3.4        | 18.5                  | —        | —         |
| 3.7        | —                     | 23.5     | 27.9      |
| 4.0        | 26.8                  | 23.4     | 27.9      |
| 4.6        | 29.0                  | —        | 30.0      |
| 4.9        | —                     | 29.7     | —         |
| 5.2        | 28.5                  | 36.2     | 31.9      |

slightly as the draw ratio increases for every group of samples. The energy of activation begins to increase markedly with the draw ratio at the draw ratio near 3.

## DISCUSSION

### Diffusion Velocity

An interesting phenomenon which was observed for every group of samples is that the diffusion velocity of dye into the samples increases with the draw ratio in the initial stage of drawing. Munden et al.<sup>3</sup> and Shimizu et al.<sup>4</sup> reported that the diffusion coefficients of acidic dyestuff into nylon 66 and nylon 6, respectively, monotonously decreased with the draw ratio; they did not find such a maximum of diffusion velocity at a low draw ratio.

The following factors may be considered as reasons for the difference between our results and those of other authors: (a) Munden et al. and Shimizu et al. did not study the dye diffusion behavior for samples having draw ratios lower than 2; (b) samples used by these authors are thought to have been considerably oriented even in their undrawn states. For example, the birefringence of the undrawn nylon 66 filament yarn used by Munden et al. was  $18 \times 10^{-3}$ , a value which is nearly equal to that of our sample of draw ratio about 1.5. Although the orientation during spinning and that induced by drawing may not be of the same kind, both kinds of orientation would have a similar influence on the diffusion behavior of dye molecule into the polymer.

Now, let us consider the reasons why the velocity of dye diffusion increases with draw ratio in the initial stage of drawing. The following reasons would be possible: (a) change in the crystallinity; (b) breaking of the crystallites; (c) change in the secondary network structure; (d) distortion of orientation.

For every group of samples, the diffusion velocity increases with draw ratio in the initial stage of drawing, whether the density of the sample in-

creases with the draw ratio (in case of group I or II) or not (in case of group III).<sup>2</sup> Therefore, the maximum of diffusion velocity in the initial stage of drawing cannot be attributed to the change of crystallinity of the sample during drawing.

It has been shown by means of small-angle x-ray diffraction analysis that the size of crystallites in a nylon fiber is decreased by drawing or stretching the fiber.<sup>8,9</sup> Therefore, the decrease in size of crystallite might suggest that the breaking of the crystallites was induced by drawing. The rupture of the crystallites would cause the growth or increase of the defects between the crystallites where dye molecules can penetrate more easily. Since it is thought that the higher the crystallinity of an undrawn sample, the more the defects which have grown during drawing, the diffusion velocity for the sample of group III becomes the greatest in the initial stage of drawing.

The secondary network structure in the polymer is deformed by drawing, and the breakage of knots in the deformed network makes the diffusion of dye easier. We believe the knots of the secondary network structure to be entangled parts or pseudocrystalline parts in the polymer.

Since the velocity of dye diffusion into the polymer is thought to depend not on the quantity but on the nature of the amorphous regions, i.e., on the mobility of the segments between the knots in the amorphous regions, the mechanism mentioned above is highly probable.

At any rate, both mechanisms are based on the concept of instability of the microstructure of the polymer in the initial stage of drawing and subsequent gradual restabilization on drawing it further.

### Activation Energy of Diffusion

Although many studies have been made of the effect of heat treatments or of swelling agents on the activation energy of dye diffusion into the polymer, almost no reports have been published concerning the effect of drawing on the activation energy.

The activation energy of dye diffusion into nylon 6, as shown in Figure 5, exhibits a draw ratio dependence which is a little different from that of the rate of dye diffusion on the draw ratio. The activation energy is kept nearly constant or decreases slightly below the draw ratio of 3 and then it begins to increase with the draw ratio from the ratio of about 3, while the velocity of diffusion increases in the initial stage of drawing, reaches a maximum, and then decreases as the draw ratio increases.

The sudden increase in the activation energy near a draw ratio of 3 implies a change in the mechanism of drawing, but some other properties (shrinkage in boiling water, tensile strength etc.) exhibited a peculiarity near a draw ratio of 2.<sup>1,2</sup> This might be explained in terms of the stabilization of the structure by orientation and a decrease in stability of the structure due to the destruction of the undrawn network by the drawing, which becomes most marked at an intermediate stage of drawing, probably at a draw ratio near 2. Every property of the variously drawn samples is decided by the sum of these two effects. For a certain property the effect of

stabilization is more pronounced than the other effect, with the result that the minimum or maximum of the property appears at a lower draw ratio than that of another property for which the effect of unstabilization is stronger than the other effect.

The activation energy does not increase with the draw ratio in the range of draw ratio from 1.6 to about 3, where the decrease in the diffusion velocity with the draw ratio is quite considerable. Qualitatively, the fact that the diffusion velocity  $D$  decreases without any marked change in the activation energy  $E$  means that the entropy term  $\log D_0$  in eq. (2) decreases. Therefore, in this range of draw ratio, the polymer structure seems to be changed by drawing in such a way that the diffusion of the dye is entropically prevented. In other words, the polymer structure is changed by the drawing to a state in which the molecule of diffusing dye partly loses its degree of freedom in the activated state of diffusion. This is probably so

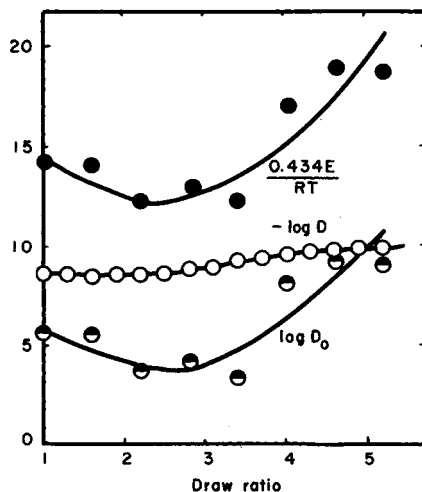


Fig. 6. Dependence of  $D_0$ ,  $D$ , and  $E$  on draw ratio for samples of group I.

because, in the activated state, it is necessary for the dye molecule to be oriented in a certain direction when the polymer is oriented. In the range of draw ratio of 1.6–3, however, the diffusion is not energetically hindered and, therefore, it is expected that the intermolecular forces in the amorphous region are not so strong. At draw ratios higher than 3, the total degree of orientation of the polymer molecule increases only slightly with the draw ratio, but the degree of orientation in the amorphous regions seems to increase further, the configuration of these molecules then becomes highly oriented by drawing the polymer to a higher draw ratio. A new kind of network structure is thus gradually formed between the polymer molecules in the amorphous region. In other words, a stable structure for a drawn polymer begins to be completed from the draw ratio near 3, with the result that the activation energy begins to increase with the draw ratio.



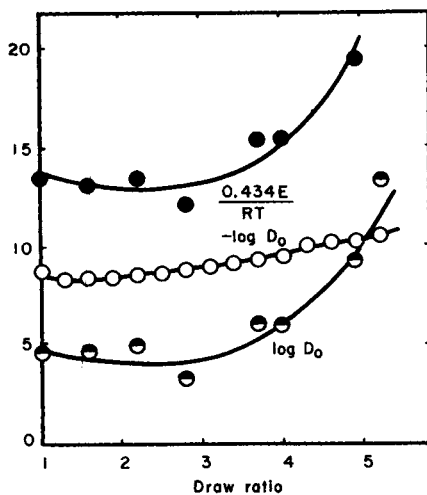


Fig. 7. Dependence of  $D_0$ ,  $D$ , and  $E$  on draw ratio for samples of group II

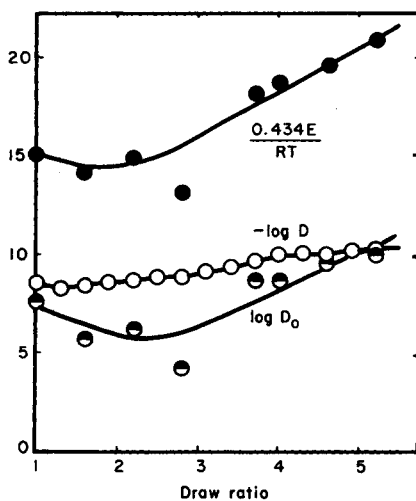


Fig. 8. Dependence of  $D_0$ ,  $D$ , and  $E$  on draw ratio for samples of group III.

Quantitatively, the entropy term,  $\log \bar{D}_0$ , and the energy term  $0.434E/RT$  can be calculated individually from the obtained data by using eq. (3). The calculated values are shown in Figures 6–8. Unfortunately, the data for activation energy are not sufficiently accurate compared with  $\bar{D}$  to permit us to discuss the change of  $\log \bar{D}_0$  with the draw ratio, especially in the range of low draw ratios.

### CONCLUSIONS

We have investigated the dependence of the behavior of dye diffusion into nylon 6 on the draw ratio and have found that the coefficient of dye

diffusion reaches a maximum in the initial stage of drawing and the activation energy begins to increase with the draw ratio near this ratio of 3. From these facts, it was suggested that the structure of the polymer becomes unstable in the intermediate stage of drawing.

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### Résumé

Les constantes de diffusion d'un colorant acide (xylène Fast Blue P) à l'intérieur de monofilaments de nylon 6 de différents rapports d'étirement ont été mesurées à plusieurs températures, en mesurant la distance de pénétration du colorant sur la section transversale de l'échantillon. Les résultats sont: le coefficient de diffusion du colorant augmente, atteint un maximum pour un rapport d'étirement situé aux environs de 1,6 et puis diminue lorsque le rapport d'étirement augmente. L'énergie d'activation de la diffusion du colorant obtenue à partir de la dépendance du coefficient de diffusion du colorant vis-à-vis de la température demeure pratiquement constante au début de l'étirement et pour un étirement moyen et augmente au-dessus d'un rapport d'étirement d'environ 3 lorsque le rapport d'étirement augmente. Sur la base de ces résultats les auteurs discutent du changement de structure du polymère pendant l'étirage.

### Zusammenfassung

Die Diffusionskonstanten eines sauren Farbstoffs (Xylen Fast Blue P) in Nylon 6-Einzelfäden von verschiedenem Dehnungsverhältnis wurde bei mehreren Temperaturen durch Messung der Eindringtiefe des Farbstoffs auf dem Querschnitt der Probe bestimmt. Folgende Ergebnisse wurden erhalten: der Diffusionskoeffizient des Farbstoffs steigt zunächst an, erreicht bei einem Dehnungsverhältnis um 1,6 ein Maximum und nimmt dann mit steigendem Dehnungsverhältnis ab. Die aus der Temperaturabhängigkeit des Farbstoffdiffusionskoeffizienten erhaltene Aktivierungsenergie der Farbstoffdiffusion bleibt im Anfangs- und Mittelstadium der Dehnung konstant und nimmt oberhalb eines Dehnungsverhältnisses von etwa 3 mit steigendem Dehnungsverhältnis zu. Die Änderung der Polymerstruktur während der Dehnung wird auf Grundlage der Ergebnisse diskutiert.

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