# Studies on the Drawing of Polyamide Fibers.   VI. Effect of Drawing on the Dye Diffusion Parallel to the Fiber Axis

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## Synopsis

The diffusion rate of an acidic dye (vylene Fast Blue 2P) into polycaproamide fibers along the direction parallel to the fiber axis (longitudinal diffusion rate) was obtained by measuring the dye penetration distance from a cross section of the sample fiber embedded in an acrylic resin. The following results were obtained. The longitudinal diffusion constant decreases monotonically with increasing draw ratio. The difference between the lateral dye diffusion constant and the longitudinal dye diffusion constant passes through a maximum near a draw ratio of 2. The activation energy for the longitudinal dye diffusion increases monotonically with draw ratio.

## INTRODUCTION

It is generally considered that the rate of diffusion of dye into a polymer decreases with the increase in its orientation. In the previous paper of this series,[1] however, the authors reported that with increasing draw ratio the diffusion constant for the dye–nylon 6 system increases in the initial stage of drawing, passes a minimum near a draw ratio of 1.6, and then decreases. This result is for diffusion of dye along the direction normal to the fiber axis (lateral diffusion). No studies have ever been made on the diffusion of the dye into the fiber along the direction parallel to the axis (longitudinal diffusion). It thus seems worthwhile to investigate the longitudinal diffusion of dye into nylon 6 and to compare the results with those of the lateral diffusion, in order to elucidate the structural changes of nylon with the drawing. In the present paper, the longitudinal diffusion constants of an acidic dye into nylon 6 fibers of various draw ratios were measured and compared with the lateral diffusion constants obtained in the previous paper.

## EXPERIMENTAL

### Samples

The samples used were nylon 6 monofilaments which had been drawn immediately after spinning (draw ratio range 1.0 ~ 5.2). The procedure
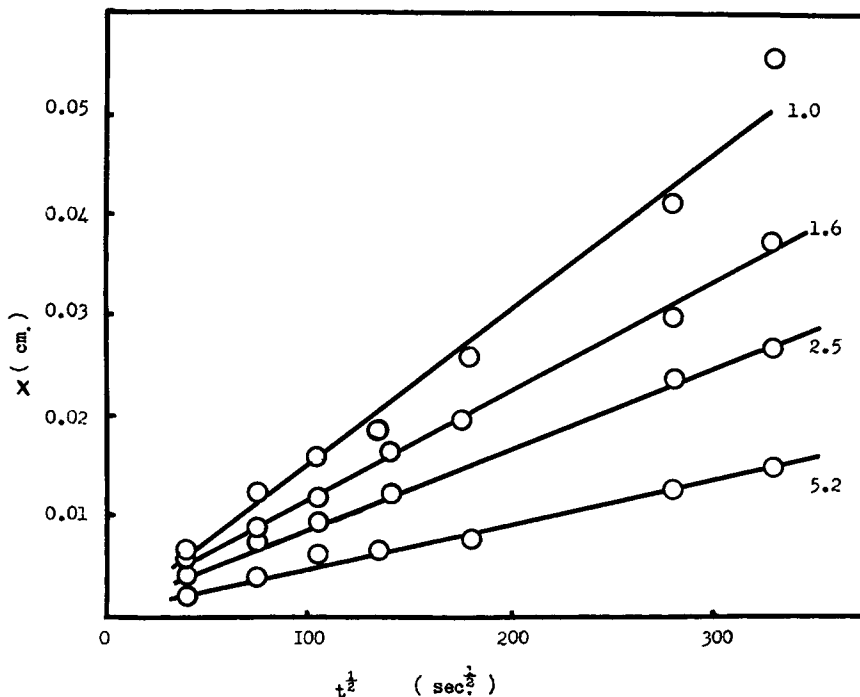
Fig. 1. Relation between time of dyeing and dye-penetration distance $x$ at a dyeing temperature of 80°C. Numbers in the graph show the draw ratios of the samples.

for their preparation is just the same as that used to prepare samples of group I in the previous paper.[1,2] They were cut to small pieces (about 2 cm. in length), each of which was put into a capsule (diameter 8 mm., length 24 mm.). Then, the capsule was filled with a viscous prepolymer of methyl methacrylate (2 parts) and $n$-butyl methacrylate (8 parts) which contained 0.1 part of benzoyl peroxide as a polymerization initiator, and heated at 60°C. for 6 hr. to complete the polymerization. The polymerized solid piece, including the nylon fiber sample, was cut perpendicular to the axis of the fiber, so that an end of the sample fiber appeared in the cut surface.

## Measurement of Dye Diffusion Constant

The apparatus and conditions of dyeing are exactly the same as those used in the previous work.[1] Several methacrylic resin-embedded samples were put into the dyeing bath (Xylene Fast Blue 2P) and taken out of the bath one after another at definite intervals. The methacrylic resin was dissolved away from the nylon with chloroform and then the dyed end of the sample fiber was examined under a microscope to measure the distance of dye penetration from the cut end. The boundary of dye in the sample was a
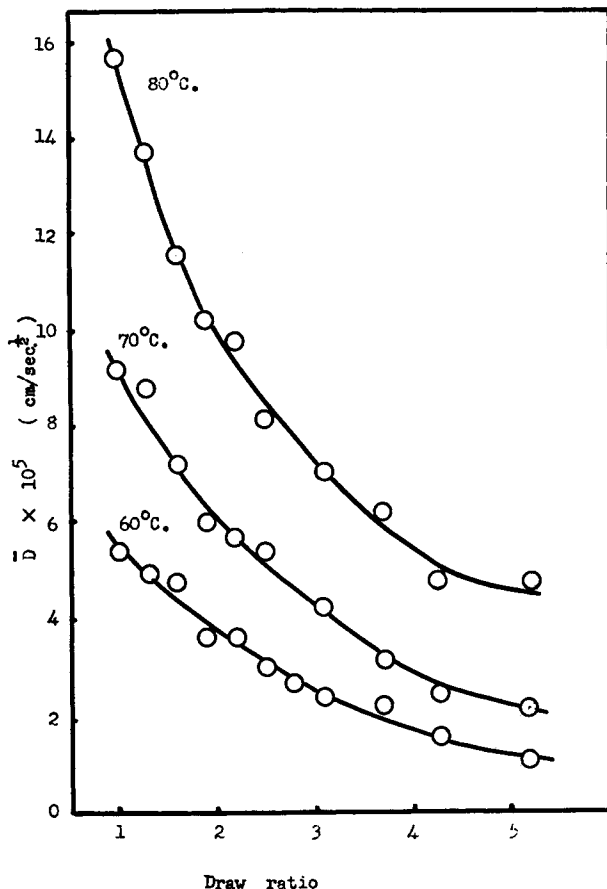
Fig. 2. Change of dye-penetration constant $\bar{D}$ with draw ratio.

clear plane parallel to the cut surface.    Preliminary tests confirmed that the methacrylic resin was not stained with the used dye.    The dye-penetration constant $\bar{D}$ was calculated from the slope of dye-penetration distance versus square root of time by using Kramer's equation.[3]    The activation energy was calculated from the Arrhenius plot of dye-penetration constant against the reciprocal absolute temperature of the dyeing bath.    At least two runs were carried out for each sample.

## RESULTS AND DISCUSSION

### Rate of Diffusion

   The dye-penetration distance $x$ was plotted against the square root of time of dyeing $t^{1/2}$.    Typical results are shown in Figure 1, which show good linearity between $x$ and $t^{1/2}$.    The dye-penetration constant $\bar{D}$ was calculated from the slope of the linear line, and the values obtained are listed in Table I.    As shown in Figure 2, $\bar{D}$ decreases monotonically with the draw ratio of the sample.    Figure 3 is a plot of $\bar{D}$ against the birefringence,
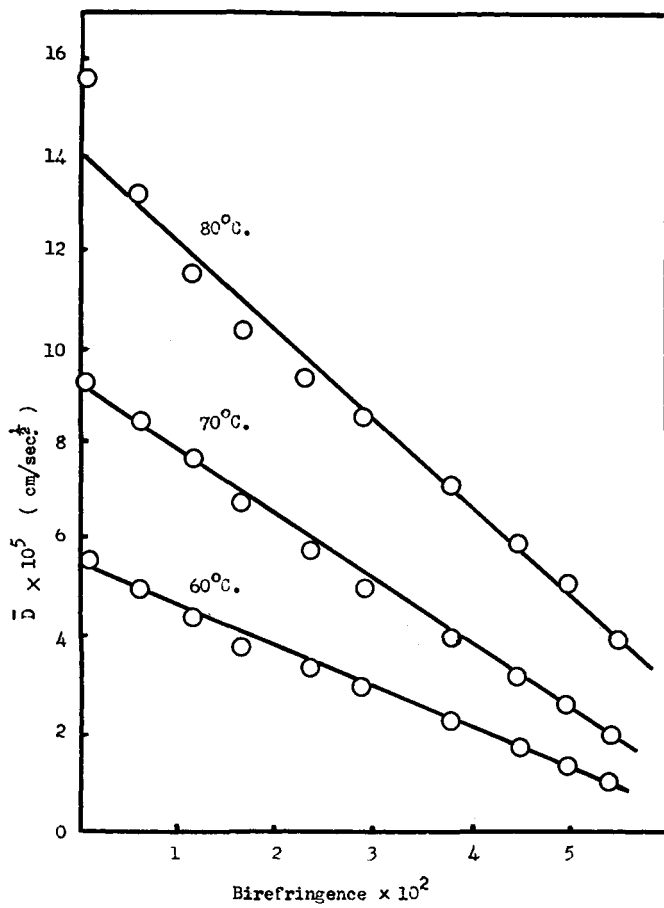
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Fig. 3. $\bar{D}$ vs. birefringence.

TABLE I
Dye-Penetration Constants, Dye-Diffusion Constants, and Activation Energies for Dye Diffusion

| Draw ratio | Penetration constant $\bar{D} \times 10_5$, cm./sec.$^{1/2}$ | | | Diffusion constant $D \times 10^{10}$, cm²./sec. | | | Activation energy, $E$, kcal./ mole |
|---|---|---|---|---|---|---|---|
| | 60°C. | 70°C. | 80°C. | 60°C. | 70°C. | 80°C. | |
| 1.0 | 5.6 | 9.3 | 15.7 | 15.6 | 43.2 | 123.3 | 23.4 |
| 1.3 | 5.0 | 8.4 | 13.1 | 12.5 | 35.2 | 85.6 | 24.4 |
| 1.6 | 4.4 | 7.7 | 11.6 | 9.7 | 29.6 | 67.1 | 23.6 |
| 1.9 | 3.8 | 6.6 | 10.4 | 7.2 | 21.7 | 54.0 | 24.0 |
| 2.2 | 3.4 | 5.8 | 9.5 | 5.8 | 16.8 | 45.1 | 24.8 |
| 2.5 | 3.0 | 5.1 | 8.5 | 4.5 | 13.0 | 36.0 | 24.8 |
| 3.1 | 2.3 | 4.0 | 7.1 | 2.6 | 8.0 | 25.2 | 26.6 |
| 3.7 | 1.8 | 3.2 | 6.0 | 1.6 | 5.1 | 18.0 | 28.2 |
| 4.3 | 1.4 | 2.6 | 5.1 | 0.98 | 3.4 | 13.0 | 30.6 |
| 5.2 | 1.1 | 2.1 | 4.0 | 0.61 | 2.2 | 8.0 | 32.0 |
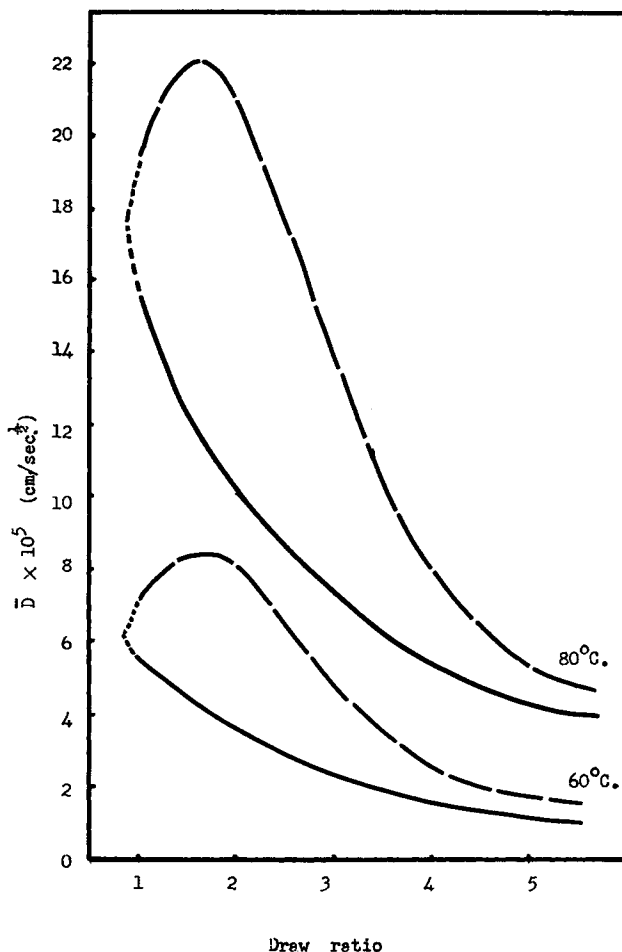
Fig. 4. Change of $D_\perp$ and $D_{||}$ with draw ratio: (———) $\bar{D}_{||}$; (– –) $\bar{D}_\perp$.

which shows that $\bar{D}$ decreases linearly with the birefringence. It is evident that the penetration constant for the longitudinal dye diffusion ($\bar{D}_{||}$) changes with the draw ratio or the birefringence in a quite different way than that for the lateral dye diffusion ($\bar{D}_\perp$); that is, the $\bar{D}_{||}$ decreases mono-tonically with the draw ratio, while $\bar{D}_\perp$ increases in the low draw ratio range, passes through a maximum, and then decreases with increasing draw ratio. Figure 4 shows distinctly the difference between these two penetration constants.

Since the rate of dye diffusion into a polymer is thought to depend on the disorder or the instability in the amorphous structure of polymer,[4] the difference between $\bar{D}_\perp$ and $\bar{D}_{||}$ might be regarded as a measure of the difference of structural disorder between the lateral and the longitudinal directions. For the undrawn sample, $\bar{D}_\perp$ must be equal to $\bar{D}_{||}$, but there is a small difference between them, probably because even the undrawn
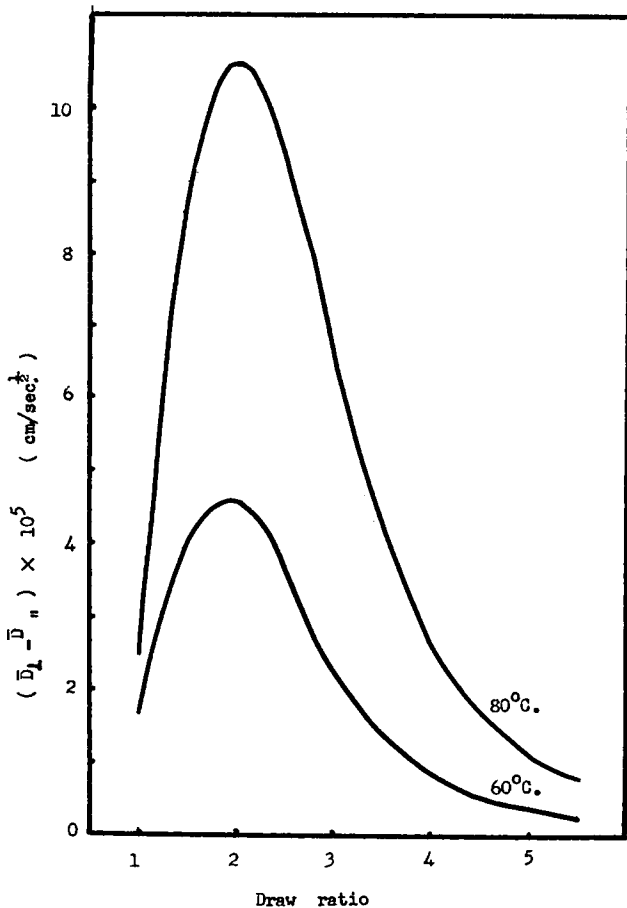
Fig. 5. $(\bar{D}_\perp - \bar{D}_\parallel)$ vs. draw ratio.

sample is not completely isotropic. The difference, $\bar{D}_\perp - \bar{D}_\parallel$, increases in the initial stage of drawing, shows a maximum near a draw ratio of 2 and then decreases, as the draw ratio increases (Fig. 5). However, $\bar{D}_\perp$ and $\bar{D}_\parallel$ themselves change considerably with the orientation of the sample, in other words, they are influenced both by the disorder of the amorphous region and the orientation of polymer. Therefore, $\bar{D}_\perp - \bar{D}_\parallel$ includes both effects (disorder and orientation), and may not be a strict measure for the difference in degree of order between the two directions only. Now, we define the value, $(\bar{D}_\perp - \bar{D}_\parallel)/\bar{D}_\parallel$, as another measure for the difference in disorder. As mentioned above and shown in Figure 3, $\bar{D}_\parallel$ decrease linearly with the birefringence (orientation) of the sample, so that it may be regarded as a property solely dependent on the orientation of sample. Therefore, $(\bar{D}_\perp - \bar{D}_\parallel)/\bar{D}_\parallel$ is a more suitable parameter to indicate the extent of structural disorder of the polymer in the lateral direction compared to that in the longitudinal direction. This value, as shown in Figure 6, is almost independent of the dyeing temperature. It
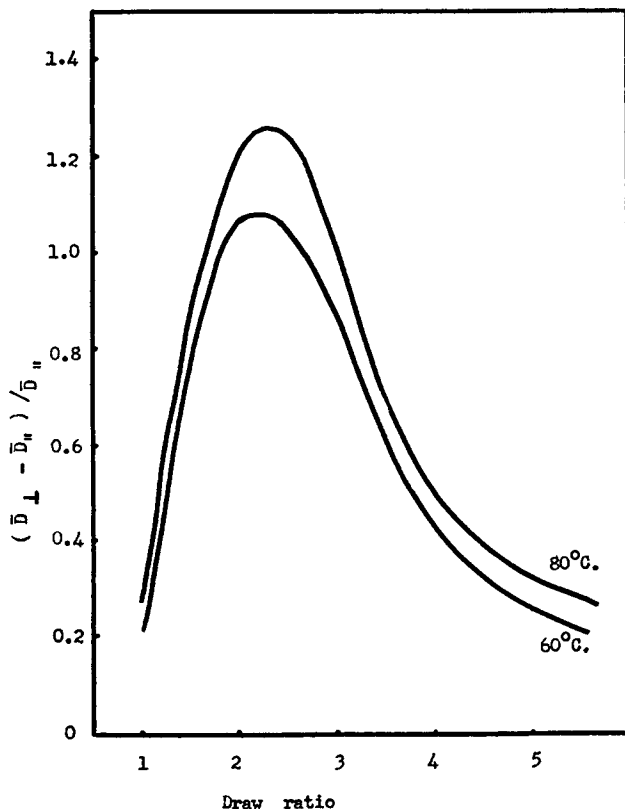
Fig. 6. $(\bar{D}_\perp - \bar{D}_{||})/\bar{D}_{||}$ vs. draw ratio.

has a maximum value between the draw ratios of 2 and 2.5, where the lateral disorder of the fiber is most marked. This draw ratio for the maximum $(\bar{D}_\perp - \bar{D}_{||})/\bar{D}_{||}$ coincides with that obtained for some other properties (e.g., strength and longitudinal swelling). It seemed odd that the dye-penetration constant $\bar{D}_\perp$ reached a maximum at a rather low draw ratio (about 1.6)[1], while other properties were at a maximum at a higher draw ratio (between 2 and 3). This can be explained, if we use $(\bar{D}_\perp - \bar{D}_{||})/\bar{D}_{||}$, instead of $\bar{D}_\perp$ itself as a measure of lateral disorder.

### Activation Energy and Entropy of Dye Diffusion

The activation energy for the dye diffusion was obtained from the slope of an Arrhenius plot of $\bar{D}$ against $1/T$ (shown in Fig. 7), by using the following equations;

$$D = D_0 e^{-E/RT} \tag{1}$$

or

$$\bar{D}^2 = \bar{D}_0{}^2 e^{-E/RT} \tag{2}$$

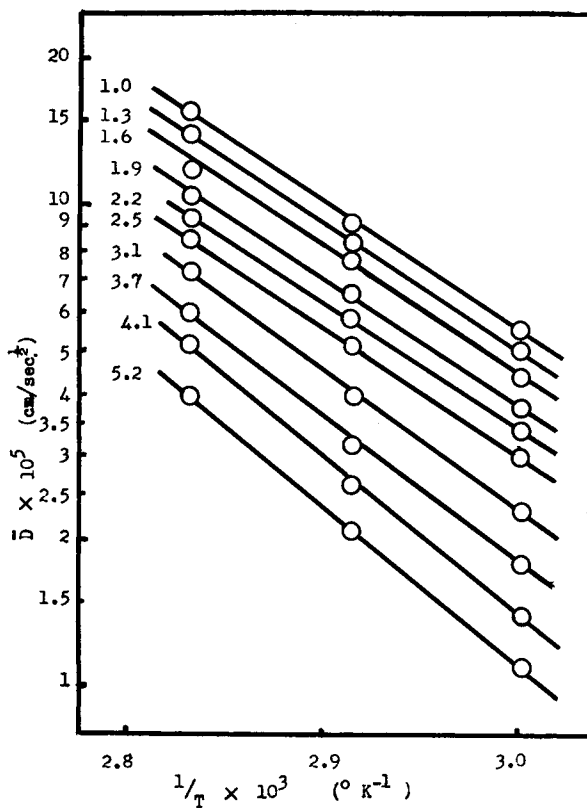$$\log \bar{D} = \log \bar{D}_0 - 0.434(E/2)/RT \tag{3}$$

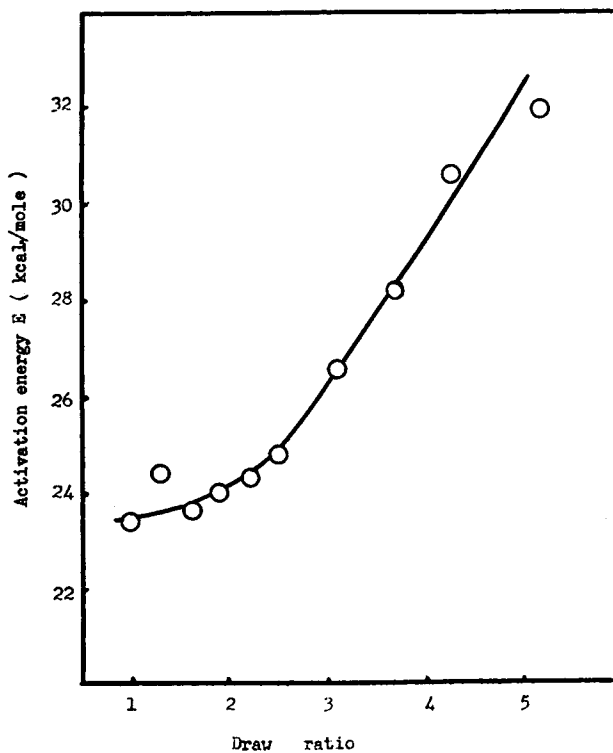Fig. 7. Arrhenius plot of $\bar{D}$. Numbers in the graph show the draw ratios of the samples.



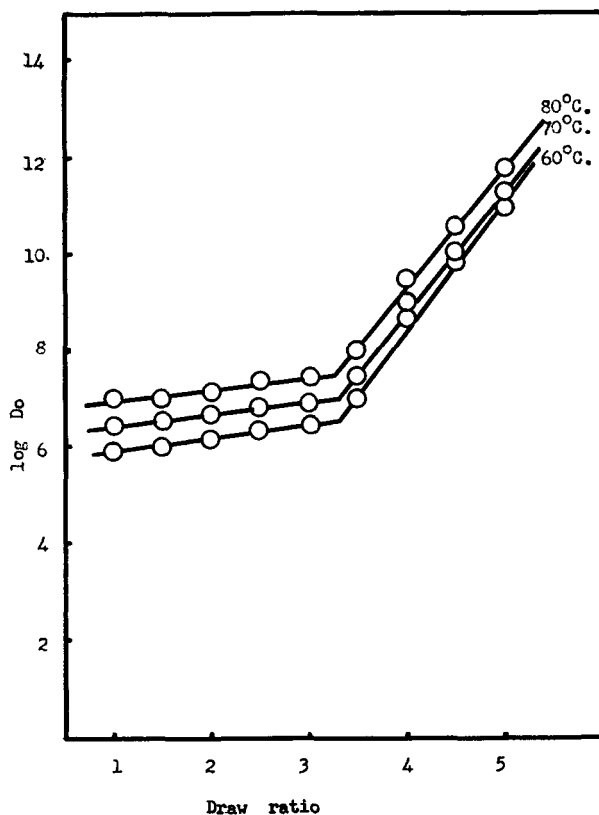Fig. 8. Change of activation energy with draw ratio.

Fig. 9. Log $D_0$ vs. draw ratio.

The results are shown in Figure 8 and listed on Table I. The activation energy for the longitudinal dye diffusion increases monotonically with the draw ratio of the sample, while that for the lateral diffusion decreases slightly in the low draw ratio range. This indicates that the structure, especially of amorphous region observed from the axial direction becomes more and more compact, as the draw ratio increases.

Log $D_0$ in eq. (3), which corresponds to the activation entropy for dye diffusion, was calculated, and results are shown in Figure 9. It is noticeable that the draw ratio–log $D_0$ curve has an inflection point at a draw ratio 3.5, above which the slope of the curve becomes much steeper than that below this draw ratio. This is probably because the structure changes from an intermediate, metastable state to a stable, compact one for a drawn fiber near a draw ratio of 3.5. It is probable that the transition from a folded structure to a fringed micelle structure is completed near this value of draw ratio.

## CONCLUSION

The longitudinal diffusion of an acidic dye into polycaproamide fibers was studied by using a unique experimental procedure. The results were compared with those for the lateral diffusion obtained in the previous work.

It was confirmed that the polymer structure viewed from the lateral direction is most unstable in the draw ratio between 2 and 2.5, while the structure viewed from the longitudinal direction becomes more and more stable with increasing draw ratio.

## References

1. Takagi, Y., and H. Hattori, *J. Appl. Polymer Sci.*, **9**, 2167 (1965).
2. Takagi, Y., and H. Hattori, *J. Appl. Polymer Sci.*, **9**, 2177 (1965).
3. Kramer, B., *Melliand Textilber.*, **35**, 518 (1954).
4. Kanetsuna, H., and N. Murase, *Sen-i Kogyo Shikensho Hokoku*, No. **57**, 97 (1961).

## Résumé

On a obtenu la vitesse de diffusion d'un colorant acide (bleu vylène rapide 2P) dans des fibres de polycaproamide le long d'une direction parallèle à l'axe de la fibre (vitesse de diffusion longitudinale) par des mesures de la distance de pénétration au départ d'une section transversale d'un échantillon de fibre enveloppée dans de la résine acrylique. On a obtenu les résultats suivants. La constante de diffusion longitudinale diminue de façon continue avec l'augmentation du rapport d'étirement. La différence entre la constante de diffusion latérale de la couleur et la constante de diffusion longitudinale passe par un maximum proche d'un rapport d'éntirement égal à 2. L'énergie d'activation de la diffusion longitudinale de la couleur augmente de façon continue avec le rapport d'étirement.

## Zusammenfassung

Die Diffusionsgeschwindigkeit eines sauren Farbstoffs (Vylen Fast Blue 2P) in Polycaproamidfasern in der Richtung parallel zur Faserachse (longitudinale Diffusionsgeschwindigkeit) wurde durch Messung der Eindringtiefe des Farbstoffes an einem in ein Acrylharz eingebetteten Querschnitt der Faserprobe erhalten. Folgende Ergebnisse wurden erhalten: Die longitudinale Diffusionskonstante nimmt mit zunehmendem Dehnungsverhältnis monoton ab. Der Unterschied zwischen der seitlichen Farbstoffdiffusionskonstante geht in der Nöhe des Dehnungsverhältnisses 2 durch ein Maximum. Die Aktivierungsenergie der longitudinalen Farbstoffdiffusion nimmt mit dem Dehnungsverhältnis monoton zu.