The Influence of Polymer and Dye Characteristics on Diffusion in Nylon 66

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Synopsis

A study has been carried out of the relationship between polymer orientation and dyeing behavior using a specially prepared range of nylon 66 samples varying only in orientation and five dyes normally showing varying degrees of sensitivity to physical variations in nylon. Integral diffusion coefficients have been calculated using Crank's finite dyebath equation from appropriate rate of dyeing data. Evidence has been produced which suggests that except with dyes of low molecular weight, i.e., dyes insensitive to physical variations in the nylon, a diffusional interaction between diffusing dye molecules exists which leads to a variation in the concentration dependence of the diffusion coefficient with fiber orientation. The length of the diffusing dye ion has been shown to be of decisive importance in this interaction.

INTRODUCTION

The study of the correlation between the dyeing behavior of polymers and their physical characteristics is at the same time very important and very difficult. While it is clearly understood that the rate of diffusion of a dye molecule through a matrix of polymer molecules will be affected by the physical arrangement of the polymer chains, it is also known that the diffusion will be affected by numerous other factors which normally cannot be isolated. The availability of a special collection of nylon 66 yarns all spun specially from a single batch of polymer to a constant denier but with different draw ratios presented the opportunity for a valuable and possibly unique comparative study of the effect of molecular orientation on dyeing kinetics in aqueous dyebaths.

EXPERIMENTAL

Materials

Peters and Turner[1] have reported a series of dyes with dyeing behavior on nylon yarns which reveal varying sensitivity to physical differences in the nylon structure. From this series, five dyes were selected to provide a range of behavior from "insensitive" to "very sensitive." The five dyes that follow are described with relevant molecular dimensions based on Courtauld's models.

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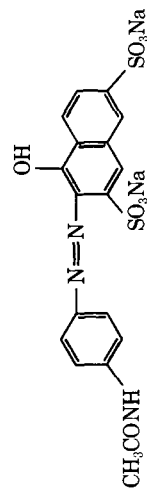
C.I. Acid Red 37 ("*Slightly Sensitive*")
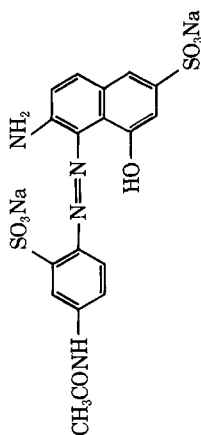
Length	1.86 nm
Width	0.96 nm
Height	0.83 nm
Volume (1)	1.48 nm^3
Volume (2)	1.40 nm^3
Area	1.79 nm^2
Mol. wt.	524

(Volume 1 = length × width × height; volume 2 = $\pi/4$ × length × width^2)

C.I. Acid Orange 10 ("*Relatively Insensitive*")
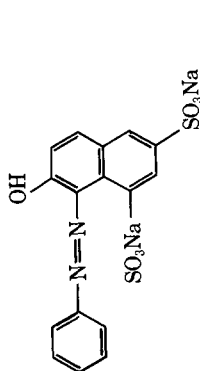
Length	1.55 nm
Width	1.00 nm
Height	0.60 nm
Volume (1)	0.94 nm^3
Volume (2)	1.25 nm^3
Area	1.55 nm^2
Mol. wt.	451

C.I. Acid Red 7 ("*Moderately Sensitive*")

Length	1.98 nm
Width	0.94 nm
Height	0.61 nm
Volume (1)	1.15 nm^3
Volume (2)	1.37 nm^3
Area	1.88 nm^2
Mol. wt.	509

C.I. Acid Blue 25 ("Sensitive")
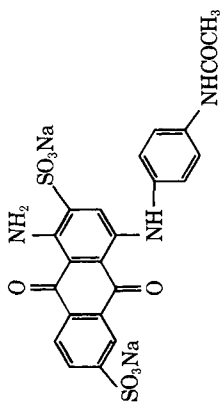
Length	1.98
Width	1.14 nm
Height	0.61 nm
Volume (1)	1.38 nm^3
Volume (2)	2.02 nm^3
Area	2.25 nm^2
Mol. wt	575

C.I. Direct Blue 71 ("Very Sensitive")
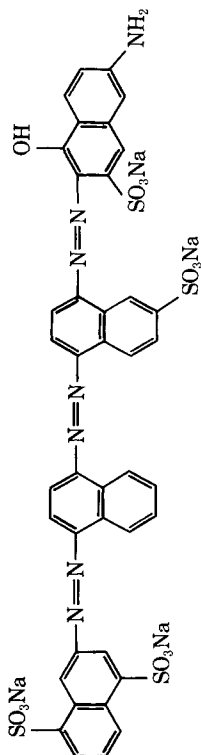
Length	3.07 (3.20) nm
Width	1.37 (1.44) nm
Height	0.52 (0.61) nm
Volume (1)	2.20 (2.81) nm^3
Volume (2)	4.51 (4.18) nm^3
Area	4.20 (4.59) nm^2
Mol. wt.	1029

TABLE I
The Physical Characteristics of the Yarns

Code number	Draw ratio	Sonic modulus, $\times 10^9$ dynes/cm^2	Birefringence	Contraction in aqueous phenol, %	X-Ray orientation factor, radians
250	2.91	62.50	0.0500	11.96	0.478
252	2.99	66.10	0.0511	12.79	0.449
254	3.08	66.50	0.0510	13.56	0.419
256	3.17	69.85	0.0527	14.81	0.408
257	3.27	71.15	0.0527	14.35	0.401
258	3.36	72.45	0.0541	16.03	0.386
259	3.46	75.00	0.0531	16.83	0.339
260	3.61	74.35	0.0550	17.00	0.339

This dye has two stereo isomers. The figures in parentheses refer to the second stereo isomer.

The yarns were 40 denier with an amine endgroup content of 41.1 ± 0.40 meq/kg and a density in m-nitrotoluene of 1.160 ± 0.002, and were supplied by Monsanto Co., Textiles Division.

The other characteristics of the yarns are shown in Table I. The code numbers are identifiers and have no other significance.

X-Ray diffraction photographs showed no significant variation in crystallinity, thus confirming the density data. Over the range of draw ratios, no significant chain unfolding had occurred in the process of producing increasing orientation.

X-Ray diffraction, sonic modulus, and birefringence data were all provided by Monsanto Co., Textiles Division. X-Ray diffraction results were obtained by standard procedures. Sonic modulus values were calculated from data produced using a pulse propagation meter (H. M. Morgan Co., Chicago). Birefringence values were obtained with the use of a polarizing microscope fitted with a Berek compensator.

Density values were obtained by the method of Black and Dole[2] based on flotation in m-nitrotoluene. Contraction data were obtained by the method of Munden and Palmer.[3]

Methods

The dyes were purified by dissolution in dimethylformamide and precipitation in acetone to remove unwanted electrolyte followed by recrystallization from aqueous alcohol. Elemental analysis showed the samples used for experiment to be 97–99% pure. The yarns were carefully scoured before use to remove finishing or other agents present. The nylon was scoured for 15 min at 90°C in a solution containing 10% (o.w.f.) of Lissapol N (ICI) and 2% (o.w.f.) of sodium carbonate. After thorough rinsing in distilled water, the samples were extracted for 6 hr each with carbon tetrachloride, ethanol, and diethyl ether in Soxhlet extraction units.

The existence of a relationship between fiber orientation and dyeing behavior was checked by a "competitive" dyeing; 0.1 g of each nylon sample was added to a dyebath containing 0.5% (on total weight of fiber) of C.I. Direct Blue 71 and 3% (o.w.f.) of ammonium acetate. The temperature was raised to 100°C over 30 min with mild agitation to ensure uniformity and maintained at that temperature for 1 hr. The dyed samples were rinsed and dried. The color content of each sample was determined by pyridine extraction and spectrophotometric estimation. The distribution of dye between the samples was then calculated.

Titration curves were prepared on a "standard" nylon 66 yarn for each of the five test dyes. The dyebath pH was set using Britton and Robinson's Universal Buffer at an ionic strength of $0.12M$, which was found to give excellent pH control over long periods of time. In each case the amount of dye present initially equaled twice that equivalent to the amine endgroup content of the nylon; 1 g of the fiber was dyed with a liquor ratio of 80:1. Dyeing temperature was 90°C. For all the dyes except C.I. Direct Blue 71, 24 hr sufficed for equilibration; for that dye, 48 hr was required. Checks were carried out for dye decomposition during the dyeing time. None was found. The use of the standard nylon 66 yarn arose because of the limited quantity of the special yarns. It was considered that the titration curves would not be unduly affected by orientation differences. Later results appeared to justify this assumption as the selected pH values for producing electrostatic saturation did in fact produce this condition with all five dyes on all eight fibers. Electrostatic saturation is defined as equality of the amine endgroup content of the polymer and the adsorbed dye ion concentration expressed as g-equivalent kg^{-1}.

Rate of dyeing experiments were carried out using an initial amount of dye equivalent to twice the amine endgroup content of the nylon. The pH was selected from the titration curve so that at equilibrium the adsorbed dye content of the nylon would be just equivalent to the amine endgroup content. Dyeing was carried out at 90°C using a liquor ratio of 80:1.

The dyebaths were stirred by a variable-speed reciprocating motor. The stirring speed was standardized at a level which gave violent agitation of the dyebath without tangling. The dyebath was sampled using a specially designed automatic dyebath sampler.[4] The device gave very precise sampling of the dyebath at predetermined times enabling rate of dyeing curves to be produced. The samples taken were very small (0.1 ml), thus minimizing disturbance of the system. The exhaustion of the dyebath was calculated from spectrophotometric measurements.

RESULTS AND DISCUSSION

The extent of the data on to the nylon yarns enables a comparison to be made between the different methods of describing fiber orientation. If
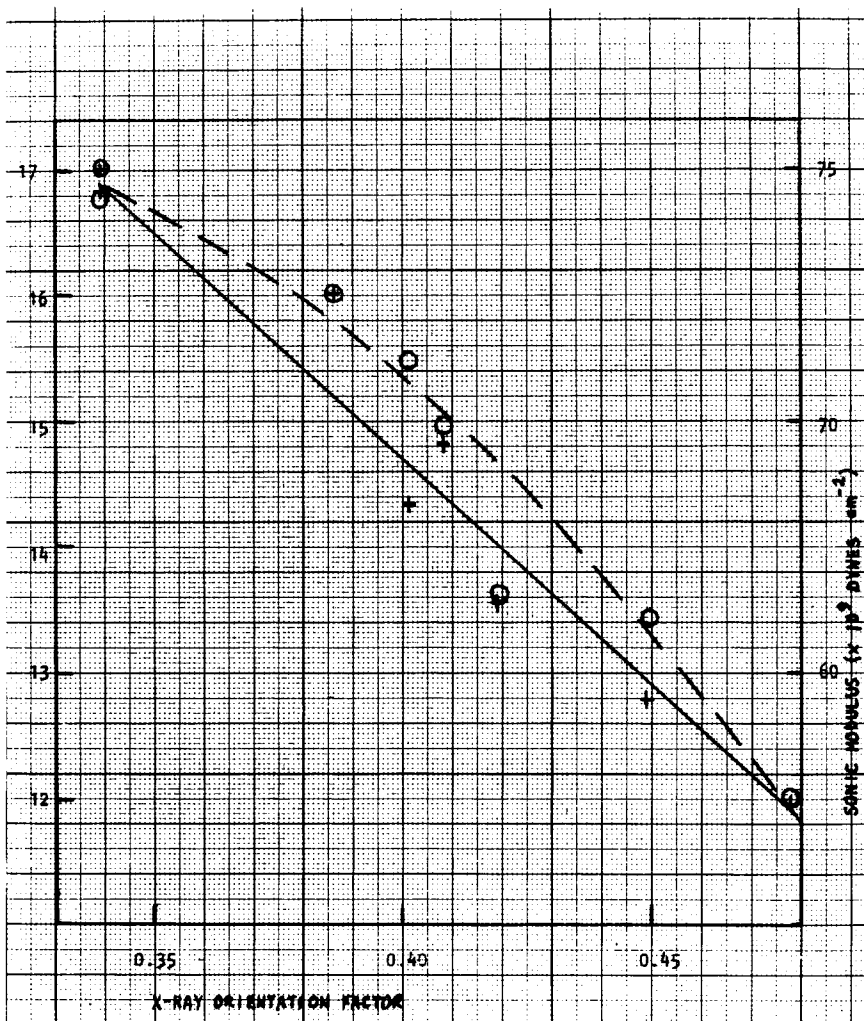
Fig. 1. Correlation between x-ray orientation factors and (a) contraction in aqueous phenol solution and (b) sonic modulus (b is shown as the broken line).

the x-ray orientation factor is taken as the standard truly representing the order in the fibers, it is found to correlate very well with the contraction in aqueous phenol and moderately well with the sonic modulus (see Fig. 1). The birefringence data give considerable scatter when plotted graphically and are not reliable. Clearly the contraction data produced by the method of Munden and Palmer[3] provide a very accessible way of assessing polymer orientation on nylon 66.

The relationship between orientation and dyeing behavior is well illustrated by the "competitive" dyeing experiment as shown in Figure 2. Here, dyeing behavior is shown in terms of dye uptake relative to the most oriented sample.
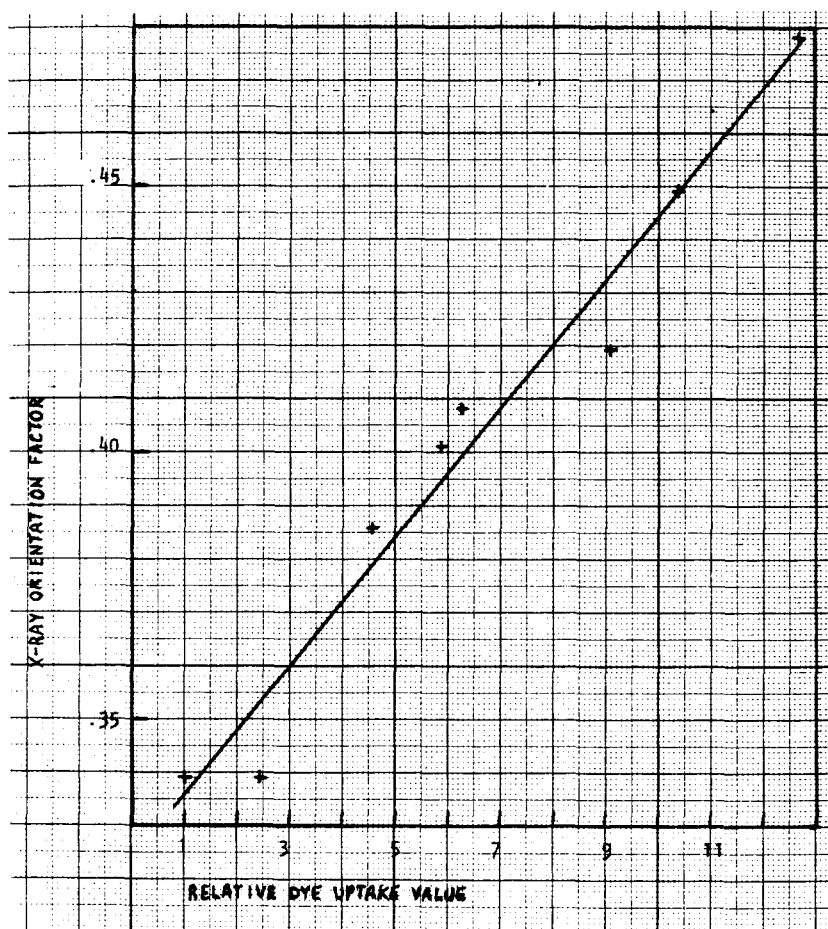
Fig. 2. Correlation between x-ray orientation factors and relative dye uptake (C.I. Direct Blue 37).

From the rate of dyeing data, integral diffusion coefficients have been calculated using Crank's equation[5] for diffusion into infinite cylinders in a finite dyebath, viz.,

$$\frac{C_t}{C_\infty} = 1 - \sum_1^n \frac{4a(1+a)}{4(1+a)+(aq_n)^2} \exp(-q_n Dt/r^2) \qquad (1)$$

in which C_t and C_∞ are the amounts of dye adsorbed at time t and at equilibrium, a equals $(1-E)/E$ where E is the fractional dyebath exhaustion at equilibrium, and $q_{1,2...n}$ are functions dependent upon E; D is the diffusion coefficient and r is the cylinder radius. Equation (1) has been solved graphically by producing plots of C_t/C_∞ against Dt/r^2 using values of q_n from Crank's tables of q_n versus a.[5] Real values of C_t/C_∞ can be substituted into the graph to give the associated values of Dt/r^2 so that D could be calculated using the known values of t and r. The relationships

between the integral diffusion coefficient and the dye uptake expressed as
the degree of electrostatic saturation, θ, take the expected form illustrated
in Figure 3 (θ is defined as the ratio of the adsorbed dye concentration
expressed in g· equivalents· kg^{-1} to the amine endgroup content of the
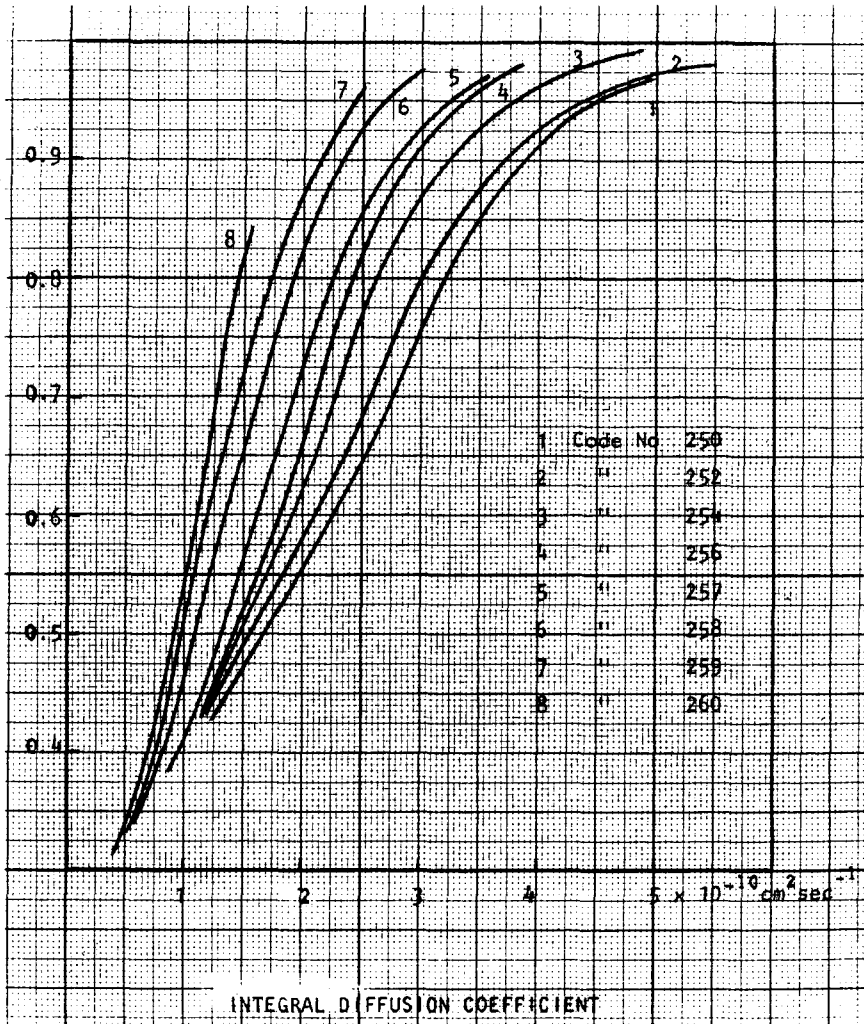nylon expressed in the same units).

Fig. 3. Relationship between the integral diffusion coefficient and θ for C.I. Acid Red 7
(pH $= 3.30$; $a = 1.079$).

From curves of the type shown in Figure 3, it is possible to deduce rela-
tionships between fiber orientation or dyestuff characteristics and diffu-
sional behavior at a given value of θ. For such comparative purposes,
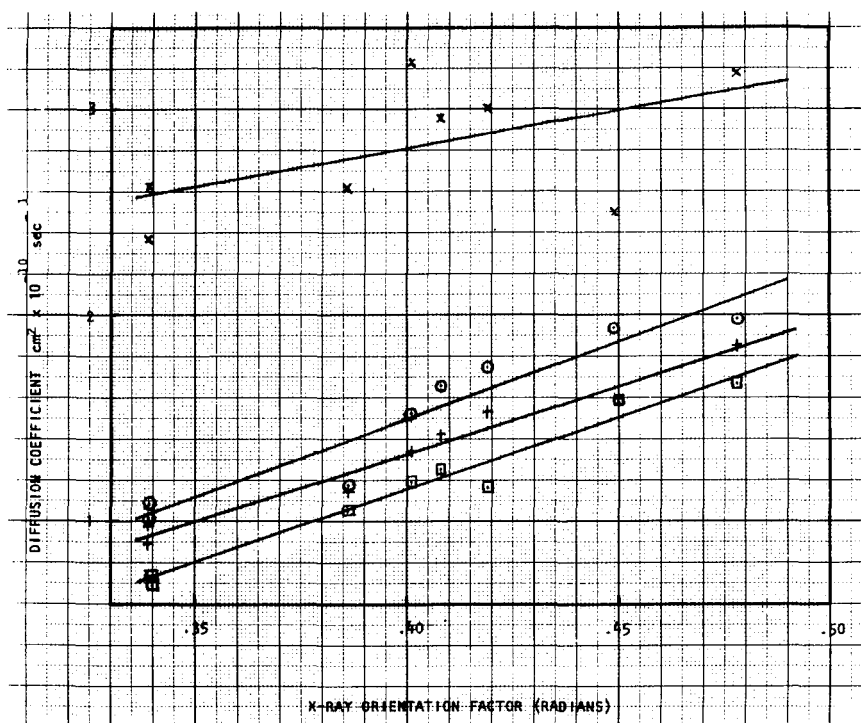a value of $\theta = 0.6$ was selected. The relationship between the diffusion

Fig. 4. Relationship between the integral diffusion coefficient and the x-ray orientation factor at $\theta = 0.6$ for dyes 1–4: ($\times$) C.I. Acid Orange 10; ($\odot$) C.I. Acid Red 7; ($+$) C.I. Acid Red 37; ($\square$) C.I. Acid Blue 23.

coefficient and the x-ray orientation factor is shown in Figure 4 for the first four dyes.

The behavior of C.I. Direct Blue 71 at $\theta = 0.6$ was markedly different from the other dyes, as shown in Figure 5.

The data of Figures 4 and 5 suggest that the dyes under examination fall into three types. The first, C.I. Acid Orange 10, diffuses very rapidly through all the nylon samples and is relatively unimpeded by the polymer network. Thus, the concentration dependence of its diffusion coefficient will depend upon electrostatic and affinity factors as discussed elsewhere,[6,7] and within limits the degree of orientation of the polymer will be unimportant. In this respect, its behavior is similar to the dye C.I. Acid Red 18 studied by Hopper et al.[6] and reported by Peters and Turner as "relatively insensitive" to physical variations in the polymer.[1]

The second type is exemplified by C.I. Acid Reds 7 and 37 and C.I. Acid Blue 23. These are dimensionally similar, all being larger than C.I. Acid Orange 10 and show some dependence on polymer orientation as far as their diffusion coefficients are concerned. With these dyes it is noticeable that the sensitivity of the diffusion coefficient to polymer orientation increases with θ as exemplified by Fig 3. With the polymer of highest
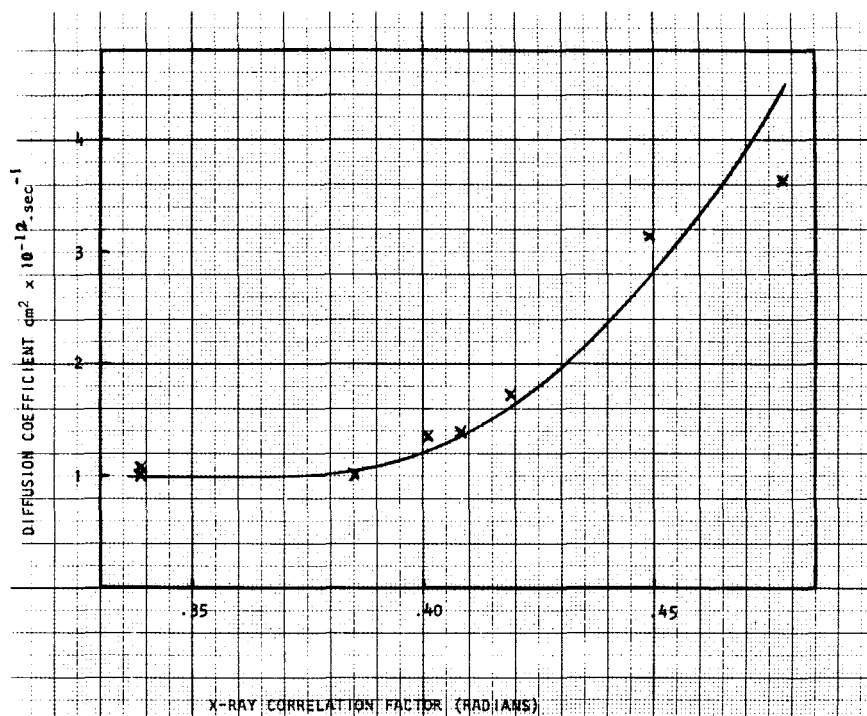
Fig. 5. Relationship between the integral diffusion coefficient and the x-ray orientation
factor $\theta = 0.6$ for C.I. Direct Blue 71.

orientation, moreover, the diffusion coefficient varies much less than that
with the least orientation. Thus, with these dyes the electrostatic and
affinity factors conditioning diffusion are joined by a new factor which
has increasing importance as the polymer orientation increases.

The effect is shown in a sharper form with the dye of the third type,
C.I. Direct Blue 71. As shown in Figure 5, the diffusion coefficient, al-
ready much lower in the least oriented samples than is the case with the
other dyes by two orders of magnitude, falls with increased orientation
to a constant value with six out of eight of the nylon samples studied.

The effects are consistent with a cross-coefficient characteristic of a dye–
dye diffusional interaction when the larger dye molecules are present.
The rate of movement of small ions through nylon polymer has been shown[7,8]
to be governed primarily by electrostatic or fixed charge effects. Al-
though the polymer matrix must offer some constraint to diffusion in all
cases, the diffusional "gaps" caused by thermal motion of the polymer mole-
cules appear to be sufficiently rapidly created to avoid any significant
variation in the probability of diffusion with concentration of the diffusing
species. All the concentration dependence of diffusion in such a case can
be ascribed to the probability of a diffusing ion being restrained by a fixed
charge in the polymer. The behavior of small dye molecules is also con-

sistent with this model so that the theoretical treatment due to McGregor and Peters[6] works well with the kind of dye which may be classed as "relatively insensitive" in its dyeing behavior as far as physical variations in the polymer are concerned. C.I. Acid Orange 10 appears to fall into this category giving rapid diffusion which is relatively little affected by the orientation of the nylon polymer. However, this is evidently no longer so with larger dye molecules of the size of C.I. Acid Red 7 or larger on nylon fibers within the orientation range under consideration.

It will be noticed that the cross section of the dyes used in the present investigation varies relatively little and bears no relation to diffusional behavior. Clearly, the important dimensional parameter is the length of the dyeing molecule, and it is clear that this will determine the time which the molecule will take to make a diffusional step. If the molecules are considered as passing through a plane in which diffusional gaps appear, then the rate of diffusion will depend upon both the probability of a molecule being close to a gap when it appears and the time for which it occupies the gap. When the rate of appearance of gaps is large and the diffusing molecule is small, then the diffusion of each molecule may be treated as being independent. However, as the polymer structure becomes more ordered, the rate of appearance of suitable gaps in our conceptual plane must diminish with eventually an effect on the rate of diffusion. The same effect will be found if the molecular size (particularly the length) of the diffusing molecule is increased. A situation can be readily envisaged in which a combination of factors leads to a permanent occupation of diffusional gaps in the plane so that the diffusion coefficient becomes independent of concentration. The development of this situation appears to take the form of a diffusional interaction between the diffusing molecules analogous to the problems of fat men waiting to squeeze through a narrow door.

This view of the diffusional process is supported by tracer diffusion studies[9] which will be reported in a further paper.

References

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