Steam and Heat Setting of Nylon 6 Fiber. X. Effect of Heat Setting on Diffusion of Dyestuff into Nylon 6 Fiber*

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Synopsis

The degree of penetration, the diffusion constant, and the uptake of dyestuffs of different molecular sizes were measured in undrawn and drawn nylon 6 filament, heat-set under various conditions in order to determine the pore structure in the amorphous regions. Unset and dry-heat-set nylon 6 can be penetrated only with difficulty by the dyestuffs having molecular lengths above about 30 and 25 A., respectively. The apparent diffusion coefficients and molecular weight of dyestuffs are approximately hyperbolic. The relations are considerably different, depending on the degree of drawing and conditions of the heat setting. Further, the relations among molecular size, amount of absorbed dyestuffs, and fraction of amorphous region capable of being penetrated by dyestuff are discussed with reference to the lateral-order distribution of nylon 6, as evaluated from the accessibility to D_2O vapor.

1. INTRODUCTION

The physical properties of nylon 6 fiber have been improved by being melt-spun and subsequently subjected to drawing and heat setting.[1] Such processes have a great effect on dyeability, which depends on the state of amorphous region and its ability to be penetrated by dyestuff.[2] The cause of this effect has been considered from various points of view.[3]

In general, heat setting is accompanied by an increase of crystallinity. However, steam setting has a different effect on dyeability and other properties of nylon 6 from that of dry heat setting. To explain the differences, a change in molecular packing in the amorphous region as a result of heat setting, i.e., "loose packing" for steam-setting and "close packing" for dry heat setting, has been proposed.[4] Though the state of packing in the amorphous region might not be defined at a position and a time in space in polymer according to micro Brownian movement of polymer molecules, the average pore size and its distribution may be assumed in a model.[5]

The effect of heat setting on dyeability may be explained by the difference in pore size distribution, but the estimation of this distribution is difficult on the basis of experiments. However, the average pore size capable of

being easily penetrated by dyestuff may be investigated by the diffusion of dyestuffs having different size molecules.

The relation between the molecular weight of dyestuff and the diffusion coefficient has previously been reported.[6] The diffusion of dyestuff into fiber is governed by many factors, such as the affinity of dyestuff for fiber, the fine structure of the fiber, and the aggregation of dyestuff, so that a relation between the diffusion coefficient and the fine fiber structure must be evaluated under such conditions since as many other factors as possible may be neglected.

In a study of the pore size of Keratin,[7] the penetration of alcohols of different molecular sizes was examined. The diffusion of a few dyestuffs in nylon has also been discussed on the basis of the change produced in the fine structure by heat setting.[8]

In this paper, the change produced in the state of the amorphous region by heat setting is further investigated on the basis of the diffusion coefficient of dyestuffs.

2. EXPERIMENTAL

Materials

Experiments for the penetration and the diffusion coefficient were carried out on drawn nylon 6 gut (draw ratio 3.0) of 10,000 den. and the corresponding undrawn nylon. The samples were heat-set under the following conditions: dry heat setting was carried out in nitrogen at 170°C. for 1 hr. at constant length (under tension); steam setting was carried out in saturated steam at 130°C. for 1 hr. in the relaxed state.

Experiments on the absorption of dyestuff were carried out on the drawn nylon 6 filaments which were heat-set under the same conditions as described above for 30 min.

Nylon 6 film of 60 μ thickness was used to investigate the aggregation of dyestuff in the film.

Dyestuffs

As shown in Table I, direct, acid, and disperse dyestuffs of commercial grade were used. In particular, direct dyestuffs which had proportional relation between molecular weight and length were selected.

Measurement of the Penetration

Direct dyestuff was used. Drawn nylon 6 gut, unset or subjected to dry heat setting and steam setting, was dyed for 24 hr. in a dyebath containing sodium acetate (5.5 g./l.) and acetic acid (2.5 g./l.), buffered to pH 4.7 and dyestuff (5% o.w.f.). The liquor ratio was 1:100; the temperature was 100°C.

The distance the dyestuff penetrated into the fiber was measured by means of a micrometer.

Measurement of the Diffusion Coefficient

The dyeing with direct, acid, and disperse dyestuff was carried out on the undrawn and the drawn nylon 6 gut subjected to heat setting under the same conditions as described above, except that an infinite dyebath was used. After a given dyeing time, the diffused distance was measured by means of a micrometer and the apparent diffusion coefficient was calculated by the equation used by Kramer[9] for dyeing of nylon:

$$D = \bar{x}^2/2t$$

where D is the apparent diffusion coefficient, $\bar{x}$ is the mean distance diffused, and t is the time.

Investigation of the Aggregation of Dyestuff

Nylon 6 film was dyed with the direct dyestuff (Sumilight Supra Brown G) having the longest molecular length used in this experiment, under the same conditions as described for measurement of the diffusion coefficient. The optical absorption spectra of the films dyed in various concentrations were recorded spectrophotometrically, while the amount of dyestuff absorbed by the films was estimated colorimetrically after the films were dissolved in formic acid. The applicability of the Lambert-Beer law for the dyestuff in the dyed film was investigated, and the wavelength of maximum absorption and the shape of the spectra were compared.

Measurement of the Amount of Dyestuff Absorbed

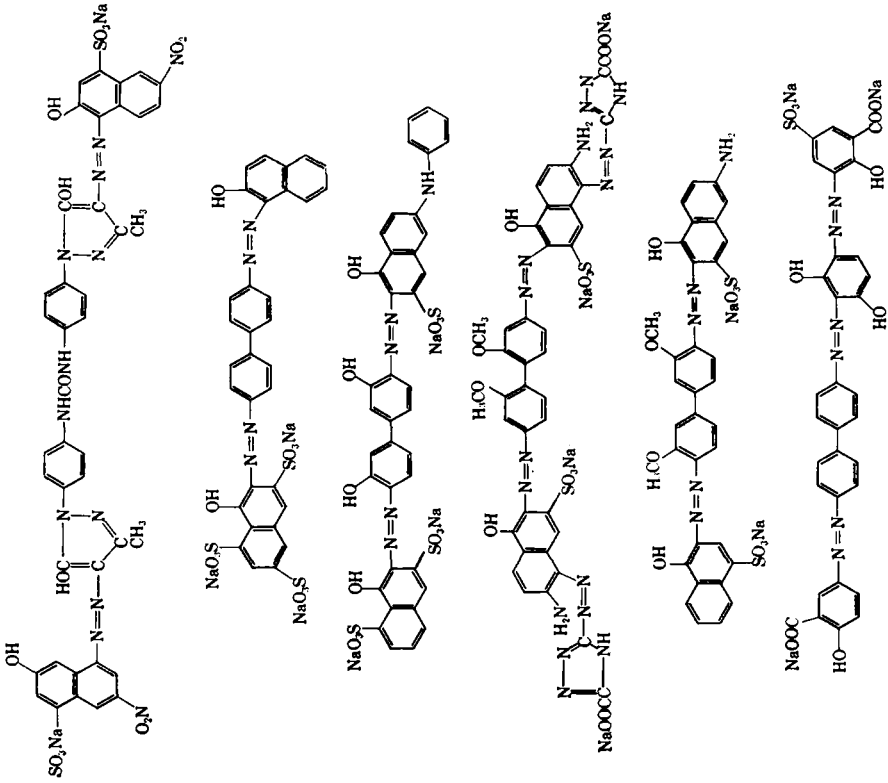Unset, dry-heat-set, and steam-set nylon 6 fibers were dyed with direct, acid, or disperse dyestuff for 48 hr. under the same conditons as described above, except that an infinite dyebath was used. The amount of dyestuff absorbed was estimated colorimetically by means of a photoelectric absorptiometer after 200 mg. of dyed fiber was dissolved in 500 ml. of formic acid.

3. RESULTS AND DISCUSSION

Results obtained on the penetration of direct dyestuffs of different molecular sizes into nylon 6 gut are shown in Figure 1, in which the length of the dyestuff molecule is plotted versus the diffused distance after 24 hr. dyeing. Dyestuffs used were commercial direct dyestuffs of known chemical formulas. The relation between molecular weight and length for these dyes are plotted in Figure 2. Owing to impurities in the commercial dyestuffs, the diffusion front was often indefinite and showed a few different colors, and thus the measured distances of the penetration seem to be in irregular disorder. However, in Figure 1 appears that the distance of penetration into the unset or dry-heat-set samples tends to decrease with increasing molecular length of dyestuff, and a marked decrease occurs at about 30 A. for the former and about 25 A. for the latter. With the
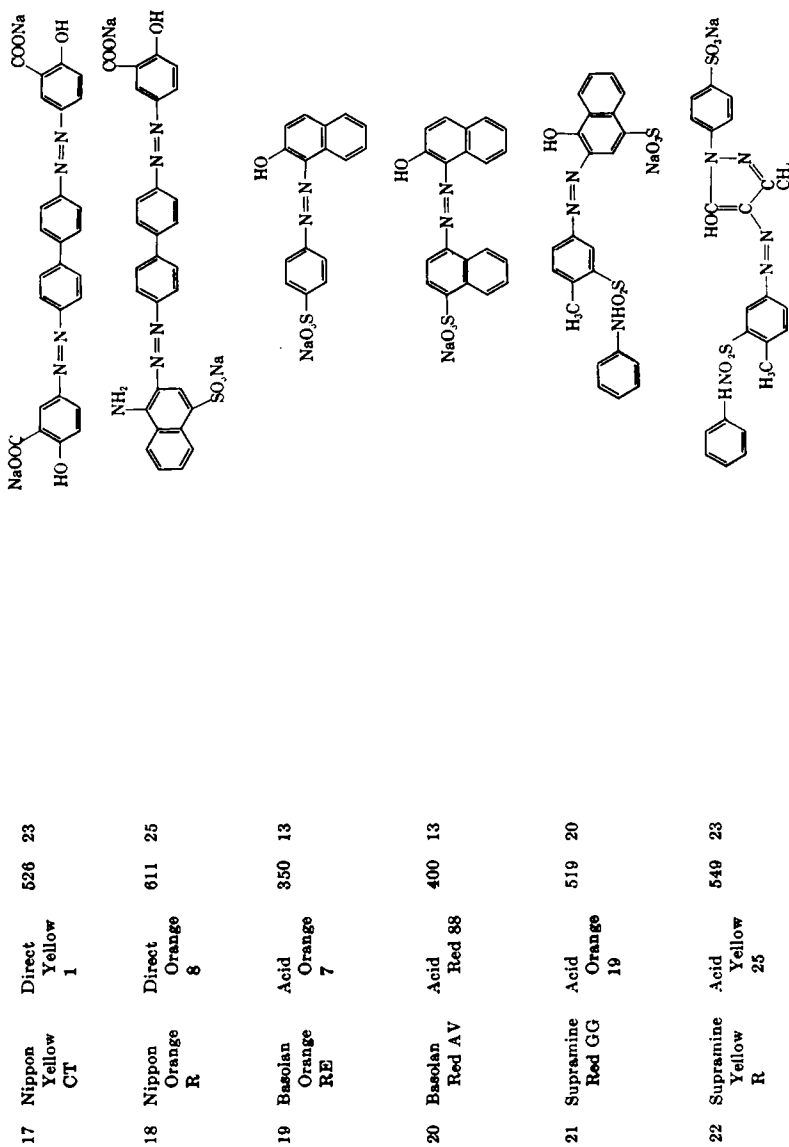
TABLE I

Molecular Structure of Dyestuffs Used

No.	Dyestuff	C.I. designation	Molecular weight	Molecular length, A.	Chemical constitution of dyestuff
1	Chlorazol Yellow 6GS	Direct Yellow 8	663	26	
2	Solar Yellow BG	Direct Yellow 28	680	25	
3	Benzo Cuprol Yellow GRL	Direct Yellow 33	1054	37	
4	Durazol Orange 4R	Direct Orange 87	343	13	
5	Benzo Purprine 4BKX	Direct Red 2	725	25	
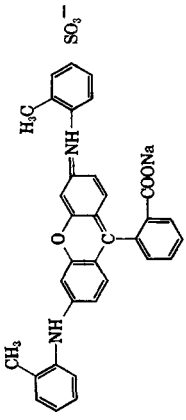
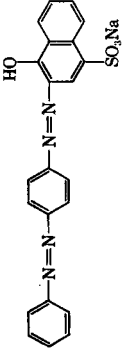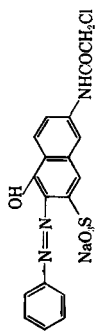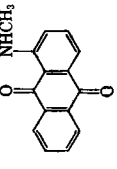| 6 | Benzo Cuprol Red RL | Direct Red 173 | 1038 | 34 |
7	Kayaku Direct Violet LN	Direct Violet 22	801	26
8	Sirius Supra Blue FBGL	Direct Blue 98	923	28
9	Benzo Cuprol Navy Blue RL	Direct Blue 150	1110	34
10	Kayaku Direct Copper Blue 2B	Direct Blue 151	773	26
11	Benzo Cuprol Brown NL	Direct Brown 173	764	29

TABLE I (continued)

No.	Dyestuff	C.I. designation	Molecular weight	Molecular length, A.	Chemical constitution of dyestuff
12	Solar Black G	Direct Black 19	839	32	
13	Sirius Black L	Direct Black 51	643	20	
14	Coprantine Black RLL	Direct Black 91	902	28	
15	Chlorantine Fast Yellow 4GLL	Direct Yellow 44	634	28	
16	Sumilight Supra Brown G	Direct Brown 106	1300	50	

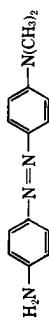| No.	Name		C.I.	
17	Nippon Yellow CT	Direct Yellow 1	526	23
18	Nippon Orange R	Direct Orange 8	611	25
19	Basolan Orange RE	Acid Orange 7	350	13
20	Basolan Red AV	Acid Red 88	400	13
21	Supramine Red GG	Acid Orange 19	519	20
22	Supramine Yellow R	Acid Yellow 25	549	23

TABLE I (continued)

No.	Dyestuff	C.I. designation	Molecular weight	Molecular length, A.	Chemical constitution of dyestuff
23	Cyanine Fast Violet 2B	Acid Violet 9	612	20	
24	Coomassie Red G	Acid Red 116	454	19	
25	Supramine Orange R	Acid Orange 30	441	16	
26	Amacel Red VI-X	Disperse Red 9	237	12	
27	Celliton Fast Orange GR	Disperse Orange 3	242	13	
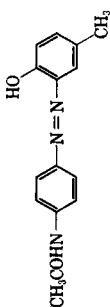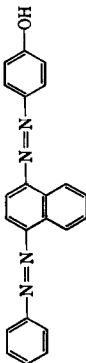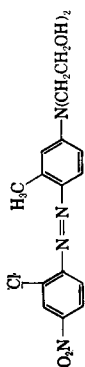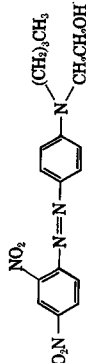
No.	Name	C.I. Name	Structure		
28	Supracet Diazo Black A	Disperse Black 3	270	15	$H_2N-\!\!\bigcirc\!\!-N=N-\!\!\bigcirc\!\!-N=N-\!\!\bigcirc\!\!-N(CH_3)_2$
29	Celliton Fast Yellow G	Disperse Yellow 3	299	15	$CH_3COHN-\!\!\bigcirc\!\!-N=N-\!\!\bigcirc\!\!$ (HO, CH$_3$ substituents)
30	Amacel Golden 1	Disperse Orange 18	352	18	(naphthalene $N=N$ azo, $-OH$)
31	Celliton Fast Rubine 3B	Disperse Red 5	378	18	$O_2N-\!\!\bigcirc\!\!-N=N-\!\!\bigcirc\!\!-N(CH_2CH_2OH)_2$ (Cl, H$_3$C substituents)
32	Celliton Red Violet RR	Disperse Violet 12	387	18	$O_2N-\!\!\bigcirc\!\!-N=N-\!\!\bigcirc\!\!-N\!\!<\!\!{}^{(CH_2)_3CH_3}_{CH_2CH_2OH}$ (NO$_2$ substituent)
33	p-Amino-azobenzene	Solvent Yellow 1	197	12	$-\!\!\bigcirc\!\!-N=N-\!\!\bigcirc\!\!-NH_2$

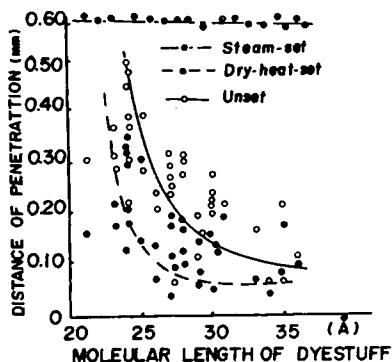Fig. 1. Relation between penetration and molecular length of various dyestuffs (drawn sample).
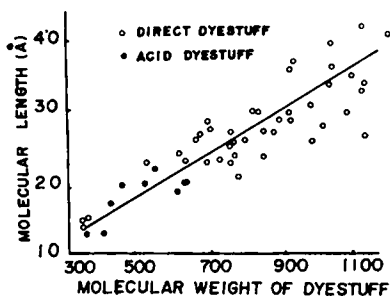

Fig. 2. Relation between molecular weight and length of various dyestuffs.

sample subjected to steam-setting, all dyestuff used penetrated to the center of the sample.   These distinct differences in the penetration among the samples may in this model be attributed to differences in the pore structure in the amorphous region of the samples.

Penetration into the sample subjected to steam setting takes place very easily in spite of the increase in crystallinity.[4]   This apparent inconsistency is evident in accord with the concept of "loose packing" in the amorphous region, which we have proposed.[4]   On the basis of the differences in penetration, the pore size in the amorphous region is the largest in the samples subjected to steam setting, is intermediate in the unset sample, and is smallest in the sample subjected to dry heat setting.

The difference of the pore size between the unset and dry-heat-set sample is not so great as that between the unset and the steam-set sample.   With the dry-heat-set and unset samples, pores above 25 A. and 30 A.; respectively, are considered to be very few, and with the steam-set sample there would be very few pores larger than 35 A.

These differences of the pore size were further investigated by the diffusion coefficient.   Estimation of the diffusion coefficient was carried by a method similar to that used by Boulton and Morton[10] in estimation of the diffusion coefficient of vat dyestuff into viscose rayon.   The value

estimated by this method is considered to be proportional to the diffusion coefficient and expressed as a relative diffusion coefficient.

This method affords a quick and convenient one of characterizing many dyestuffs. Kramer[9] used this method to investigate the diffusion coefficient of acid and disperse dyestuffs into nylon. We also adopted this method in order to investigate the diffusion coefficient. Dyestuffs which showed a definite diffusion front and a proportional relation between molecular weight and length were used.

The diffusion coefficient may be governed by the aggregation of dyestuff present in the substrate and affinity of dyestuff to substrate. The former was investigated by application of the Lambert-Beer law to nylon 6 film dyed in several different concentrations. The result with Sumilight Supra Brown G, which has the longest molecular length, the longest conjugation, and greatest ease of aggregation[11] of any dye used in this experiment is shown in Figure 3. The relation between the amount of dyestuff absorbed and the optical density of the films is a straight line through origin. Also
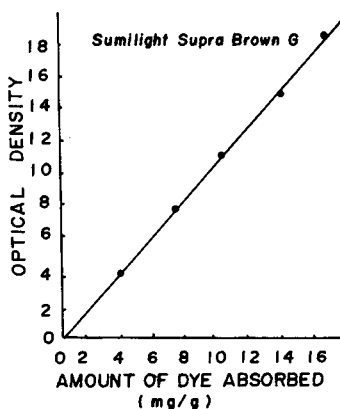

Fig. 3. Optical density of nylon 6 film containing various amounts of dyestuffs.

there was no change in shape of the absorption curve of the dyestuff. Therefore, it is concluded that the dyestuff on the film obeys the Lambert-Beer law and is present in a monomolecular state, especially at the diffusion front, where concentration of the dyestuff is low. As a measure of the affinity, the HLB (Hydrophile and Syophile Balance) value of the dyestuffs was calculated.[12] It is reported that when the HLB of a dyestuff is close to that of a fiber, the affinity and also the diffusion of the dyestuff to the fiber is good.[14] As shown in Figure 4, there is no definite relation between the apparent diffusion coefficient and HLB of the dyestuff. On the basis of the effects of the aggregation and the affinity on the diffusion coefficient as described above, the diffusion coefficient can be regarded as a measure of the packing state in the amorphous region. As an example of calculation of the diffusion coefficient, the diffusion of Benzo Cuprol Red RL into the undrawn and the drawn sample is shown in Figures 5 and 6, respectively.

After dyeing, the gut was cut into sections and the diffused distance was measured by means of a micrometer. On plotting the square of this diffused distance against the time, a straight line is obtained. Half of the slope of the line gives the apparent diffusion coefficient. This shows that there is no difference among the diffusion coefficients at the different dyeing times.
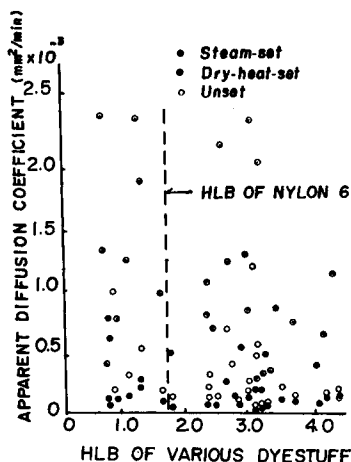

Fig. 4. Relation between apparent diffusion coefficient and HLB of various dyestuffs.

The apparent diffusion coefficients obtained for dyestuffs having different molecular weights are shown in Table II. The results were plotted against molecular weight as shown in Figures 7 and 8. Figure 7, which shows the relation between the apparent diffusion coefficient of direct dyestuffs into the undrawn samples and molecular weight, gives approximately hyperbolic relations. The apparent diffusion coefficients are found to be dependent on heat setting and the differences are especially large in the diffusion of dyestuffs having low molecular weight. With dry-heat-setting and unset samples, the apparent diffusion coefficient of dyestuffs having molecular weights above about 750 and 850, respectively, are approximately constant; with steam setting a constant value is approached at a molecular weight greater than 1000. As seen in Figure 2, molecular weights of about 750, 850, and 1000, correspond to molecular lengths of 25, 30, and 35 A., respectively. These results agree with those arrived at in the penetration studies. Figure 8 shows relations between the apparent diffusion coefficient of direct and disperse dyestuffs into the drawn samples and molecular weight.

These relations also give approximately hyperbolic curves in agreement with the case of the undrawn samples. The molecular size of the dyestuff, which then diffuses only with difficulty, is slightly smaller in the drawn sample than in the undrawn sample. Disperse dyestuffs do not obey the hyperbolic relations. This deviation may be attributed to the hydrophobic
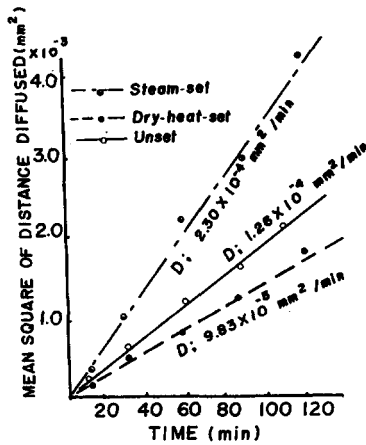
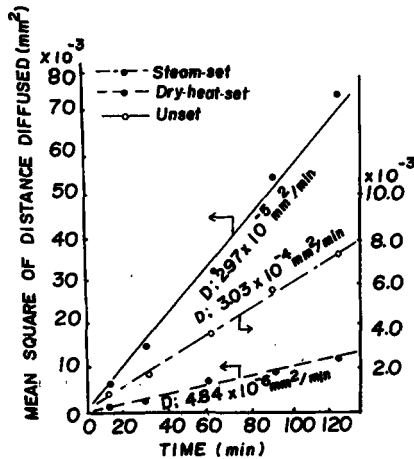Fig. 5. Diffusion of Benzo Cuprol Red RL into nylon 6 (undrawn sample).

Fig. 6. Diffusion of Benzo Cuprol Red RL into nylon 6 (drawn sample).

character of disperse dyestuff in contrast to direct and acid dyestuffs having a sulfonic group and to the influence of the surface-active agent contained in the commercial dyestuff used. As seen in Figures 7 and 8 and Table II, the apparent diffusion coefficient in the undrawn, unset sample is greater than that in the drawn, unset sample. This is explained by the increase of crystallinity with drawing.[15] The apparent diffusion coefficient in the drawn, dry-heat-set sample is very small in comparison with that in the undrawn sample subjected to the same heat-setting treatment, while the apparent diffusion coefficient in the drawn, steam-set sample is either close to or slightly larger than that in the undrawn sample subjected to the same steam-setting treatment. The difference in influence of heat-setting on the apparent diffusion coefficient in the drawn and the undrawn sample may be attributed to the difference in conditions of heat setting and the

TABLE II

Apparent Diffusion Coefficients and Amounts of Dyestuff in Nylon Treated under Various Conditions

Dyestuff[a]	Apparent diffusion coefficient, mm.²/min.						Amount of dyestuff absorbed after 48 hr. dyeing, mmole/g.		
	Unset		Dry-heat-set		Steam-set		Unset	Dry-heat-set	Steam-set
	Undrawn	Drawn	Undrawn	Drawn	Undrawn	Drawn			
1	4.68×10^{-4}	1.68×10^{-4}	3.81×10^{-4}	5.39×10^{-6}	8.29×10^{-4}	9.78×10^{-4}	—	—	—
2	2.92×10^{-4}	6.04×10^{-5}	2.11×10^{-4}	1.87×10^{-6}	5.70×10^{-4}	6.43×10^{-4}	0.0811	0.0615	0.0991
3	4.08×10^{-4}	1.06×10^{-4}	2.83×10^{-4}	3.89×10^{-6}	8.36×10^{-4}	1.07×10^{-3}	—	—	—
4	1.02×10^{-4}	1.46×10^{-5}	5.92×10^{-5}	2.35×10^{-6}	2.20×10^{-4}	2.83×10^{-4}	0.0428	0.0303	0.0628
5	2.32×10^{-4}	5.60×10^{-5}	1.61×10^{-4}	1.55×10^{-6}	4.29×10^{-4}	5.27×10^{-4}	—	—	—
6	1.26×10^{-4}	2.97×10^{-5}	9.83×10^{-5}	4.84×10^{-6}	1.70×10^{-4}	3.03×10^{-4}	0.126	0.0852	0.168
7	2.14×10^{-4}	9.25×10^{-5}	1.57×10^{-4}	3.44×10^{-6}	5.32×10^{-4}	6.02×10^{-4}	0.0346	0.0302	0.0420
8	—	—	—	—	—	—	0.0338	0.0229	0.0484
9	—	—	—	—	—	—	0.0261	0.0193	0.0359
10	—	—	—	—	—	—	0.0632	0.0442	0.0850
11	1.32×10^{-4}	1.91×10^{-5}	8.06×10^{-5}	7.39×10^{-6}	3.17×10^{-4}	3.27×10^{-4}	—	—	—
12	1.34×10^{-4}	2.63×10^{-5}	8.50×10^{-5}	6.70×10^{-6}	3.26×10^{-4}	3.16×10^{-4}	0.286	0.277	0.384
13	2.34×10^{-4}	9.30×10^{-5}	1.80×10^{-4}	3.68×10^{-5}	5.75×10^{-4}	7.25×10^{-4}	—	—	—
14	1.30×10^{-4}	2.19×10^{-5}	8.76×10^{-5}	4.31×10^{-6}	2.58×10^{-4}	2.75×10^{-4}	—	—	—
15	4.68×10^{-4}	1.57×10^{-4}	3.92×10^{-4}	4.53×10^{-5}	9.99×10^{-4}	8.33×10^{-4}	0.107	0.0855	0.152
16	—	6.38×10^{-5}	—	4.08×10^{-6}	—	5.42×10^{-4}	0.0412	0.0349	0.0575
17	1.43×10^{-3}	5.09×10^{-4}	9.28×10^{-4}	1.81×10^{-5}	2.07×10^{-3}	2.35×10^{-3}	0.148	0.119	0.177
18	—	1.66×10^{-4}	—	7.03×10^{-5}	—	8.25×10^{-4}	—	—	—

19	—	1.17×10^{-3}	—	4.25×10^{-4}	—	3.75×10^{-3}	—	—	—
20	—	6.41×10^{-4}	—	2.15×10^{-4}	—	2.17×10^{-3}	0.147	0.109	0.180
21	—	3.70×10^{-4}	—	9.87×10^{-5}	—	1.21×10^{-3}	0.0561	0.0409	0.0779
22	—	2.32×10^{-4}	—	1.25×10^{-4}	—	1.29×10^{-3}	0.0528	0.0402	0.0809
23	—	7.76×10^{-5}	—	2.43×10^{-5}	—	4.70×10^{-4}	0.0453	0.0298	0.0671
24	—	2.74×10^{-4}	—	9.81×10^{-5}	—	1.05×10^{-3}	—	—	—
25	—	4.35×10^{-4}	—	1.92×10^{-4}	—	2.02×10^{-3}	—	—	—
26	—	4.97×10^{-4}	—	1.86×10^{-4}	—	2.40×10^{-3}	0.293	0.234	0.345
27	—	1.33×10^{-3}	—	7.71×10^{-4}	—	2.43×10^{-3}	0.198	0.165	0.207
28	—	1.03×10^{-3}	—	5.91×10^{-4}	—	4.27×10^{-3}	0.180	0.171	0.204
29	—	5.04×10^{-4}	—	2.47×10^{-4}	—	1.88×10^{-3}	0.237	0.183	0.242
30	—	1.00×10^{-4}	—	3.67×10^{-5}	—	3.94×10^{-4}	—	—	—
31	—	2.73×10^{-4}	—	1.15×10^{-4}	—	1.26×10^{-3}	—	—	—
32	—	1.89×10^{-4}	—	8.02×10^{-5}	—	7.87×10^{-4}	—	—	—
33	—	—	—	—	—	—	0.426	0.350	0.418

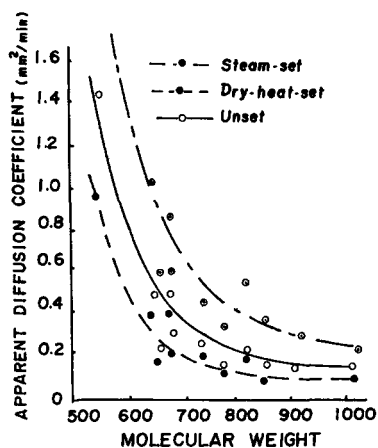a Number corresponds to dyestuffs listed in Table I.

Fig. 7. Relation between apparent diffusion coefficient and molecular weight of various dyestuffs (undrawn sample).
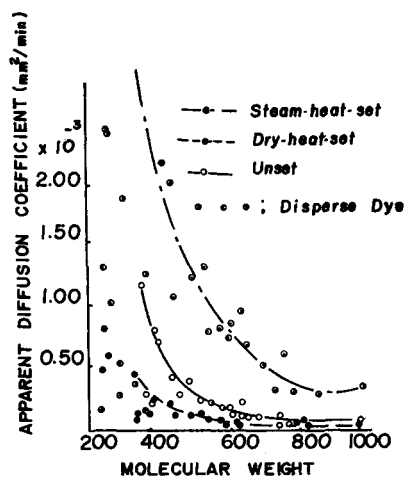

Fig. 8. Relation between apparent diffusion coefficient and molecular weight of various dyestuffs (drawn sample).

essentially different effect of both heat settings on the amorphous region. Since dry heat setting was carried out under tension, disordering of molecular orientation would not take place, but an increase of crystallinity and close packing in the amorphous region would take place. Steam setting, on the other hand, was carried out in the relaxed state, so that increase of crystallinity, disordering of molecular orientation, and loose packing in amorphous region would take place.

Then, we considered the mechanism of heat setting. The effect of heat setting is the formation of new stable interchain bonds among chain molecules which have been broken by the heat energy introduced. This

thermal energy added to the system must be greater than the interchain bonding energy.   However, the presence of a swelling agent, such as water, makes possible this heat-setting effect with less heat energy than in the absence of swelling agent, owing to relaxation of the molecular chain in the presence of swelling.   When heat energy is introduced in the absence of a swelling agent, hydrogen bonds between amide groups of adjacent chain molecules and other interchain bonds are broken up into an equivalent level corresponding to the amount of heat energy introduced.   These chain molecules will bond again in the stress-free state at a lower thermodynamic energy level, and this leads to closer packing than before heat setting. However, if water molecules take part in heat setting, as is the case in steam setting, the new bonding of chain molecules activated and loosened by heat energy will be prevented by that part containing water molecules, or the looser molecular structure will be set in the formation of hydrogen bonds between fiber and water.   The amorphous region of the fiber thus treated will show looser packing compared to the state before the treatment.   Therefore, the fact that the apparent diffusion coefficient in the drawn sample subjected to dry heat setting is very small in comparison with that in the dry-heat-set, undrawn sample, may be a consequence of a much larger effect of close packing in the drawn sample than that in the undrawn one.   The fact that the apparent diffusion coefficient in the drawn, steam-set sample, on the other hand, is either close to or slightly larger than that in the similarly treated undrawn one may be explained on the basis of the three following factors.

First, the highly oriented drawn sample decreases its molecular orientation as the result of steam setting.   Second, loose packing in the amorphous region with steam setting may be different in the drawn and the undrawn sample.   When the drawn fiber, which has a high degree of molecular orientation along the fiber axis and much internal strain, i.e., higher energy and lower entropy, is subjected to steam setting, looser packing may take place.   Third, the increase of crystallinity in the undrawn sample with heat setting is greater than that in the drawn one.   When heat energy is introduced, it causes polymer chains parallel to the fiber axis to move and to increase the crystallinity in three dimensions.   However those polymer chains constrained by drawing to orient parallel to the fiber axis may not crystallize and pack in all directions; the random or less oriented polymer chains in the undrawn sample, on the other hand, can crystallize in any direction, so that a tendency to crystallize may be greater in the undrawn sample than in the drawn one.   A similar phenomenon is shown by the greater increase of crystallinity in the samples heat-set under a tension state than those heat-set in the relaxed state.[16]

The discussion in the present paper is based on a string model which consists of continuous change from crystalline state to random and has lateral-order distribution between the states.   Recently, the concept of a lamellar structure which consists of folded long molecular chain has been introduced.[17]   However, in drawn samples not all parts are regarded as

consisting of such lamellae, and even if such a structure is present in our polymers, the results discussed for the string model are not invalidated.

The relation between the diffusion coefficient and molecular weight will now be considered and a quantitative expression for the effect of heat setting on the diffusion coefficient derived.

As is seen in Figures 7 and 8, a linear relation between the inverse apparent diffusion coefficient and molecular weight is expected. For a direct dyestuff, there is an approximate linear relation, as shown in Figures 9 and 10, which may be represented by the equation:

$$M = a (1/D) + b \qquad (1)$$

where M is molecular weight (proportional to molecular length in this experiment), D is the apparent diffusion coefficient, and a and b are con-
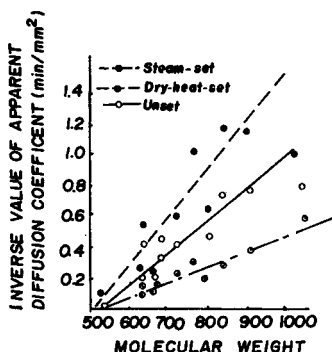

Fig. 9. Relation between inverse apparent diffusion coefficient and molecular weight of various dyestuffs (undrawn sample).
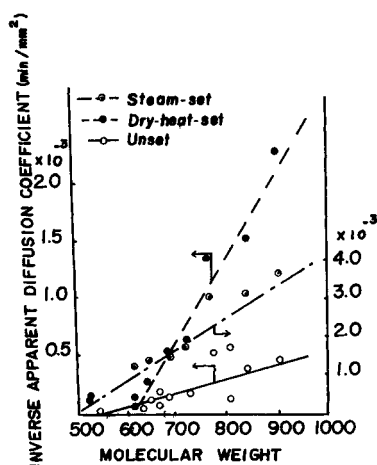

Fig. 10. Relation between inverse apparent diffusion coefficient and molecular weight of various dyestuffs (drawn sample).

stants.   Constants a and b were calculated by the method of least squares from plots of M against $1/D$ as shown in Table III.

The greater the value of a, the more easily diffusion of dyestuff takes place.   Constant a may be regarded as a semiquantitative measure of the effect of heat setting; it decreases in order of steam setting, no setting, and dry heat setting, both in the undrawn and the drawn sample.   Constant a in the drawn, steam-set sample is somewhat larger than that in the undrawn sample subjected to the same heat-setting treatment and is much larger than that in the other samples.   These differences of the samples are discussed above.

TABLE III
Correlation between Apparent Diffusion Coefficient and
Molecular Weight of Dyestuff

Sample treatment	Constant a[a]		Constant b[a]	
	Undrawn	Drawn	Undrawn	Drawn
Unset	0.049	0.0081	510	533
Dry-heat-set	0.030	0.0014	531	612
Steam-set	0.098	0.113	530	484

[a] See eq. (1).

We now consider the equation of Stokes-Einstein which is derived statistically from diffusion and precipitation phenomena, and is expressed as follows:

$$D = KT/6\pi\eta R \qquad (2)$$

where D is the diffusion coefficient, K is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium, and R is the radius of molecules which diffuse or precipitate.

In this experiment, the factors other than D, R, and η are regarded as constant, and direct dyestuffs having a proportional relation between molecular weight and length were used.   If the radius R in the eq. (2) corresponds to length of dyestuff and η is regarded as the resistance of the fiber to the diffusion of dyestuff, then $M = K/\eta D$, where K is a constant.   If it is assumed, from comparison of eqs. (1) and (2), that constant a in eq. (1) corresponds to K/η in eq. (2), then constant a may be considered a measure of the ease with which the dyestuff diffuses.   However, the experimental eq. (1) contains constant b.   This inconsistency between eqs. (1) and (2) may be attributed to a deviation from the theoretical relationship for the diffusion and the precipitation of cubic molecules without interaction with each other.   Dyestuff cannot be regarded as cubic form, and further R, corresponding molecular length of the dyestuff, may not be proportional to molecular weight in this experiment.   Although there is not complete correspondence of eqs. (1) and (2), constant a in the former is assumed to be related to the resistance of the substrate to

the diffusion of dyestuff, and it is reasonable to regard a as a measure of the effect on the amorphous region of heat setting.

The experimental equation, eq. (1), is applicable to the diffusion of direct dyestuff, but not of acid dyestuff. We now consider from another point of view, the relation between the apparent diffusion coefficient and molecular weight of dyestuff. Plotting the inverse molecular weight of dyestuff against the logarithm of the apparent diffusion coefficient, yields a linear relation, as shown in Figures 11 and 12. Considering this relationship from thermodynamic point of view, eq. (11) below is derived. The derivation has been previously discussed by Yoshida.[13]
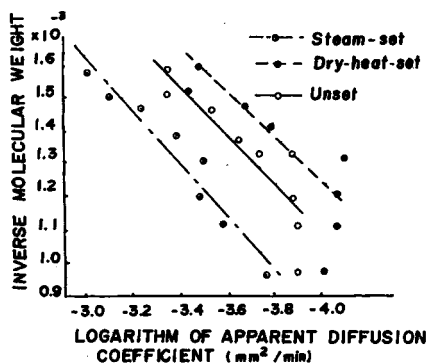

Fig. 11. Relation between inverse molecular weight and logarithm of apparent diffusion coefficient of various dyestuffs (undrawn sample).
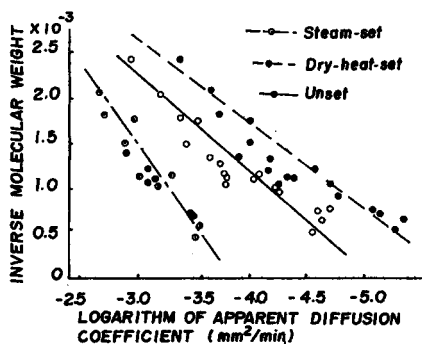

Fig. 12. Relation between inverse molecular weight and logarithm of apparent diffusion coefficient of various dyestuffs (drawn sample).

Dyestuff diffusible into substrate is required to have an activation energy E. The apparent diffusion coefficient D at an absolute temperature T is

$$D = D_0 e^{-E/RT} \tag{3}$$

where D_0 is a constant and R is a gas constant.

The logarithm of eq. (3) is then

$$-RT \ln D_T = E - T (R \ln D_0) \tag{4}$$

The activation entropy of the diffusion is shown in terms of $R \ln D_0$ from the eq. (4), while the activation energy of the diffusion is shown in eq. (5).

$$E = \sum_{n=1}^{p} D_n + mD' \tag{5}$$

The first term on the right-hand side of the eq. (5) represents the sum of various forces of interaction among chain molecules, i.e., the forces based on orientation, induction, dispersion, hydrogen bonding, coulombic force, etc., give rise to formation of p pairs of bonds between dyestuff and fiber, which have a bond energy of D_n. $\sum_{n=1}^{p} D_n$ is related to heat energy of dyeing ΔH^0 as follows:

$$- \Delta H^0 \doteqdot \sum_{n=1}^{p} D_n \tag{6}$$

The second term on the right-hand side of eq. (5) shows the sum of forces of interchain bonds broken owing to diffusion of dyestuffs. In this case, the number of bonds is m and the bond energy is D'.

When mD' approaches zero in eqs. (5) and (6), i.e., when the pore size of the substrate is large enough in comparison with the size of dyestuff, eq. (7) results:

$$E \doteqdot - \Delta H^0 \tag{7}$$

On the other hand, as is known from the relations between activation energy and activation entropy of chemical reaction, relation between heat and entropy of solution, and relation between bonding energy and entropy, there is a linear relation called the compensation effect of energy ΔH^0 and entropy ΔS^0. This linear relation is also known in dyeing and may be expressed by eq. (8):

$$\Delta S^0 = a\Delta H^0 + b \tag{8}$$

where a and b are constants.

As the activation entropy of diffusion shows the mobility of the dyestuff in substrate, a dyestuff having a smaller molecular volume gives larger activation entropy of diffusion and vice versa. If it is assumed that activation entropy of the diffusion is inversely proportional to the molecular volume of the dyestuff in some regions, eq. (9) holds:

$$\Delta S^0 = a'(1/M) + b' \tag{9}$$

where a' and b' are constants. The molecular weight M of the dyestuff is used in eq. (9) rather than molecular volume, because in this experiment

a proportional relation between molecular length and weight is assumed. By substituting eqs. (7–9) into eq. (4), eq. (10) is obtained:

$$-RT \ln D_T \doteq \frac{b}{a} - \frac{b'}{a} + b'T - \left(\frac{a'}{a} - Ta'\right)\frac{1}{M} \tag{10}$$

If temperature is constant, then

$$\log D_T \doteq (A/M) + B \tag{11}$$

where A and B are constants.

Therefore, the relationship between the apparent diffusion coefficient and inverse molecular weight of dyestuffs may be explained. Equation (11) is especially applicable for samples subjected to steam setting. This shows that the pore size in the steam-set samples is very large and that eq. (7) is reasonable.

On the basis of the above, the pore size in the amorphous region of nylon subjected to heat setting is now considered in relation to the diffusion coefficient of dyestuff for pores of such a size as to permit diffusion only with difficulty. Investigation of the distribution of each pore size is required to measure the absorbed amount of dyestuff; the model considered is as follows. The pore sizes $a_1 > a_2 > a_3 \ldots$, where these integers, are assumed to have the distribution $n_1, n_2, n_3, \ldots$, respectively. When dyestuffs having the same density and molecular weight $m_1 > m_2 > m_3 \ldots$, where these are proportional to molecular dimensions just sufficient to enter the pores $a_1 > a_2 > a_3 \ldots$ respectively, are used, the amounts of these dyes absorbed are assumed to be $w_1 > w_2 > w_3 \ldots$ grams. If the pores which are larger than the molecular dimensions of the dyestuff are filled completely with the dyestuff, the relation between the absorbed amount of dyestuff and the distribution of the pores is as follows: the number of pores n_1 corresponding to size a_1 is given by $n_1 = w_1/m_1$; the number of pores n_2 corresponding to size a_2 is $n_2 = (w_2 - w_1)/m_2$; the number of pores n_3 corresponding to size a_3 is $n_3 = (w_3 - w_1)/m_3$, etc. Further, the number of pores corresponding to each size is derived from the same equation. Practically, it is difficult to decide the distribution of the pore size because dyestuffs may not have the same density and not fill the pores in the fiber completely; moreover, it may be impossible to assume the existence of a definite number of pores among polymer chains which are always changing as a result of micro-Brownian movement. Thus in this experiment, the amounts of dyestuffs of various molecular sizes absorbed by the samples subjected to heat setting was measured, and their relations are discussed with reference to the change of the fine structure as a result of heat setting.[18] After 48 hr. dyeing, equilibrium may not be attained, depending on the different diffusion rate of each dye, so that the actual equilibrium values of dyestuff absorbed may be somewhat different from the values obtained. Figure 13 shows a general tendency of the amount of dyestuff absorbed at equilibrium. It is apparent that the amount of dyestuff absorbed increases with decreasing of molecular weight of the dyestuff. This relation shows an increase of the region
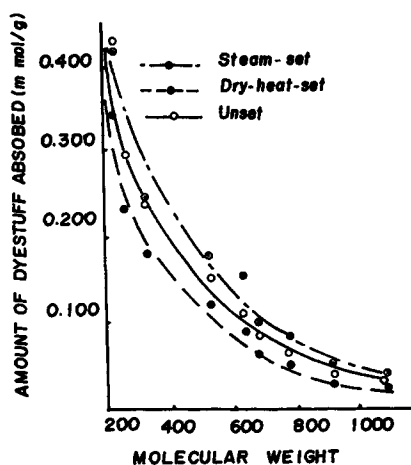
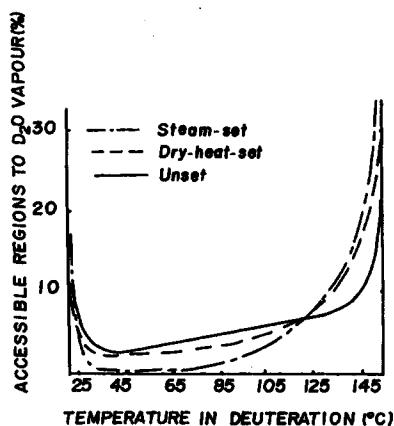Fig. 13. Relation between molecular weight and amount of absorbed dyestuffs (after 24 hr. dyeing).

Fig. 14. Lateral-order distribution of variously heat-set nylon 6.

capable of being penetrated by dyestuff and an increase of the amount of dyestuff absorbed even in the same pore, with decreasing molecular size of the dyestuff.

Except for p-aminoazobenzene, which has the smallest molecular size, the amount of dyestuffs absorbed on the samples subjected to heat setting decreases in the order: steam setting > no setting > dry heat setting. The amount of p-aminoazobenzene absorbed is the largest in unset samples and then least in dry-heat-samples. This difference from other dyestuffs is explained by the variation in lateral-order distribution of heat-set nylon 6 as shown in Figure 14, which shows the change of fraction of the amorphous region penetrated by D₂O vapor in nylon film with increasing temperature. The region capable of being penetrated at lower temperatures

may correspond to the loosely packed portions of the amorphous region. In the steam-set sample, most of the material is either loosely or closely packed with little intermediate.

The dry-heat-set sample has a smaller amount of the distribution in the loosely packed region and much in the regions of intermediate and high density. The sample unset has an intermediate amount of dense material relative to the steam-set and the dry-heat-set samples and has less in the loosely packed region and much in the region of intermediate packing. If this model of the distribution is maintained during dyeing, dyestuffs having a larger molecular size can dye only the loose regions in the fiber, while dyestuffs having a smaller molecular size can further penetrate the closely packed region. The amount of dyestuff absorbed is considered to correspond to the integral value of the region accessible to D_2O from 25°C. to a certain temperature. As seen in Figure 14 at one temperature this integral value for the steam-set sample becomes smaller than that in the unset sample. If the dyestuff can penetrate a denser region than that corresponding to the above temperature, the amount of dyestuff absorbed by the steam-set sample may become smaller than that absorbed by the unset sample. This is the case for the amount of p-aminoazobenzene absorbed by the steam-set and unset samples.

Further, the amount of a dyestuff smaller than p-aminoazobenzene absorbed by the steam-set sample would become smaller than that absorbed by the sample subjected to dry heat setting. This will be a subject to be examined in future.

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Résumé

On a mesuré le degré de pénétration, la constante de diffusion et le pouvoir de fixation de matières colorantes possédant des dimensions moléculaires différentes, sur un fil de nylon-6 étiré et non-étiré et chauffé sous différentes conditions afin d'obtenir une structure poreuse dans la région amorphe. Le nylon-6 non-chauffé et chauffé à sec est difficilement pénétré par les colorants ayant une longueur moléculaire supérieure à environ 30 A. et 25 A. respectivement. Les coefficients apparents de diffusion et le poids moléculaire des colorants sont approximativement dans une relation hyperbolique. Les relations en fonction du degré d'étirement et/ou du chauffage sont considérablement différentes. De plus on a discuté de la relation entre la grandeur moléculaire, la quantité de colorant absorbé et la fraction de région amorphe capable d'être pénétrée par le colorant en fonction de la distribution de l'ordre latéral du nylon-6, évalué à partir de l'accessibilité vis-à-vis de la vapeur de D_2O.

Zusammenfassung

Der Eindringungsgrad, die Diffusionskonstante und die Aufnahme von Farbstoffen mit verschiedener Molekülgrösse werden an ungereckten und gereckten Nylon-6-Fasern gemessen, die Zur Erzielung einer Porenstruktur im amorphen Bereich unter verschiedenen Bedingungen hitzebehandelt wurden. In nickt-hitzebehandeltes und trockenhitzebehandeltes Nylon-6 dringen Farbstoffe mit einer Moleküllänge oberhalf etwa 30 A. bzw. 25 A. nur schwer ein. Die scheinbaren Diffusionskoeffizienten und Molekulargewichte von Farbstoffen stehen angenähert in einer hyperbolischen Beziehung. Die Beziehungen weisen je nach dem Reckungs- und Hitzebehandlungsgrad beträchtliche Unterschiede auf. Weiters wird die Beziehung zwischen Molekülgrösse, Menge des absorbierten Farbstoffs und Bruchteil an amorphem, für das Eindringen von Farbstoff zugänglichem Bereich in Hinblick auf die aus der Zugänglichkeit für D_2O-Dampf ermittelten Verteilung der seitlichen Ordnung von Nylon 6 diskutiert.