The Influence of Molecular Weight of Acid Dyes on the Yield Stress of Dyed Nylon Monofilament

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Synopsis

The yield stress of nylon filament dyed with several acid dyes has been determined as a function of dye content and the molecular weight of acid dyes. The nylon filament dyed with acid dye has greater yield stress than undyed one. The relation between the increment of the yield stress (f) due to the adsorption of acid dye and the dye content (C) in the filament can be expressed by parameters A and B as $\log f = A \log(C - C_0) + B$, where C_0 is the dye content under which no contribution to the yield stress is observed and C_0 depends on the number of sulfonic groups in acid dye. It is found that these parameters A and B are expressed by M (the difference between the molecular weight of acid dye and the weight of SO_3Na groups in it) as $A = 1 - 100/M$, $B = k_1 M^{k_2}$, where k_1 and k_2 are the constants which depend on the parent chemical structure of dyes. The parameters A and B are expected to give available informations as to the physical state of adsorbed dye on nylon filament.

INTRODUCTION

In general, polymeric substances drawn by the cold-drawing process have two kinds of yield point near 20% and 2% elongation. The former is called the first-order yield point, and the latter, the second-order one.[1] The second-order yield point is the point at which plastic deformation starts to take place. This plastic deformation results from a breaking of bonds and their reforming new positions. That is, the yield stress has enough potential energy to overcome molecular forces and allow the molecules to slip over from one equilibrium position to another when stress is applied.[2,3]

The nylon filament dyed with acid dyes has greater secondary yield stress than the undyed one.[4] From the results of previous investigations,[5] it is considered that the increase in the yield stress due to the adsorption of acid dyes, and this increase reflects the physicochemical state of adsorbed dye on nylon filament. It is a help to investigate the relation between the increment of the yield stress and the type or nature of acid dye in studying the molecular considerations of the yield stress and the physicochemical state of adsorbed dye on nylon filament.

The present work, being concerned with the effect of various acid dyes on the yield stress of nylon filament, proposes certain relation between molecular weight of acid dyes and the yield stress.

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TABLE I
Structure of Dyes

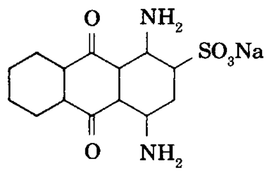
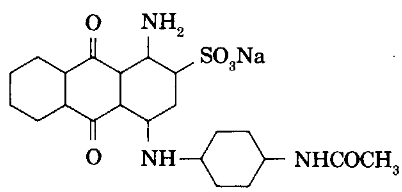
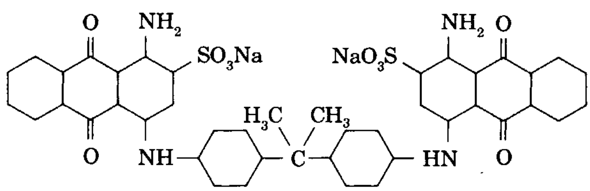
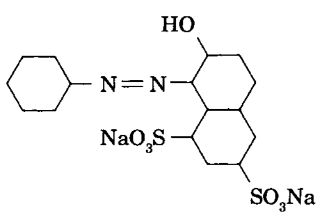
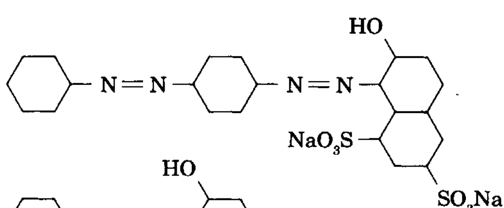
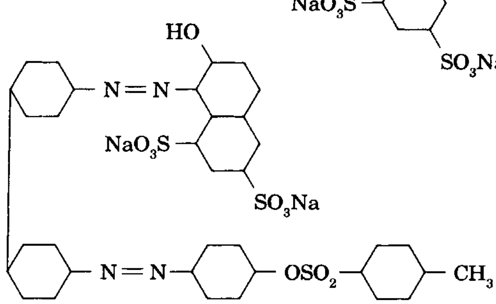
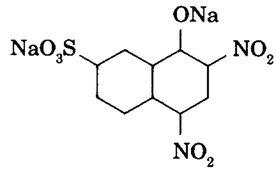
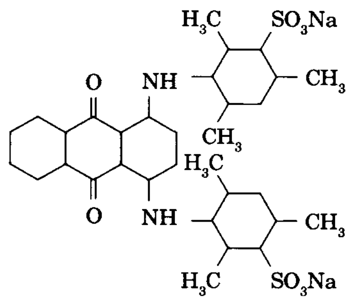
Dye	Structure
Acid Nylon Fast Violet 6B	
CI Acid Blue 40	
CI Acid Blue 127	
CI Acid Orange 10	
CI Acid Red 73	
CI Acid Red 85	

TABLE I
(*Continued from the previous page.*)

Dye	Structure
CI Acid Yellow 1	
CI Acid Blue 80	

EXPERIMENTAL

Materials

Nylon Filament. Drawn nylon 6 monofilament 0.15 mm in diameter supplied by Toray Co., Ltd. was used. Each sample was scoured in pure water in the presence of nonionic surfactant (0.1%) and sodium carbonate (0.07%) for 30 min at 60°C. After scouring, it was washed thoroughly in cold water and heat-set in water for 2 h at 110°C.

Dyestuff. The dyes used in this work are shown in Table I. They are CI Acid Yellow 1, CI Acid Blue 80, and two kinds of related series of dyes, one of which has 1,4-diaminoanthraquinone-2-sulphonic acid (sodium salt) as a skeletal structure and the other has aniline→ 2-naphthol-6,8-disulphonic acid (sodium salt). Pure samples of these dyes were obtained by purification of seven commercial dyes and one synthesized (Acid Nylon Fast Violet 6B). The method was as follows: the dyes were dissolved in pure water followed by hot filtering and filtrate was salted out with sodium acetate twice. The pure specimen was obtained for colorimetric determination by crystallizing several times from an ethanol–water (1:1) solution. All the dyes were checked by paper chromatography which revealed no colored impurities. The molecular extinction coefficients of these dyes are shown in Table II.

Method

Dyeing Conditions. Nylon 6, about 1.15 g, was dyed for 5 h at 100°C using a 200:1.15 liquor–goods ratio. It was dyed in the presence of a buffer solution to give pHs of 1.4 or 2.2 (20°C). In a previous paper,[5] the effect of the pH of the dye bath on the yield stress was investigated, and the yield stress was independent of four pH values (1.4, 2.0, 3.19, and 4.5). Therefore, in this work pH 1.4 was mainly selected because it gave the widest dye

TABLE II
The Molecular Extinction Coefficients of Dyes[a]

Dye	Molecular weight Na-salt	Measurement wave length (nm)	Molecular extinction coefficient
Acid Nylon Fast Violet 6 B	340	565	1.23×10^4
CI Acid Blue 40	473	620	1.29×10^4
CI Acid Blue 127	872	615	2.06×10^4
CI Acid Orange 10	452	480	2.21×10^4
CI Acid Red 73	556	510	3.90×10^4
CI Acid Red 85	802	510	4.27×10^4
CI Acid Yellow 1	358	430	2.09×10^4
CI Acid Blue 80	678	625	2.22×10^4

[a] In water.

content range among the four pH values. The total number of amino groups after blank dyeing under the same conditions used for dyeing was 3.87×10^{-5} eq/g dry fiber. Dye concentration in the dye bath was from 5.65×10^{-5} to 7.03×10^{-2} mol/L and the dye content was from 2.74×10^{-5} to 14.70×10^{-5} eq/g dry fiber. In order to determine the effect of the dyes on the yield stress of nylon filament, blank dyeing was carried out as a reference under the same conditions used for dyeing. Although maybe a blank dyeing cannot take account of the reductions in internal pH in the nylon that are likely to occur when the fiber becomes overdyed at low pH, we used ordinary blank dyeing as a reference in order to exclude the factors except dyes affecting the yield stress as great as possible.

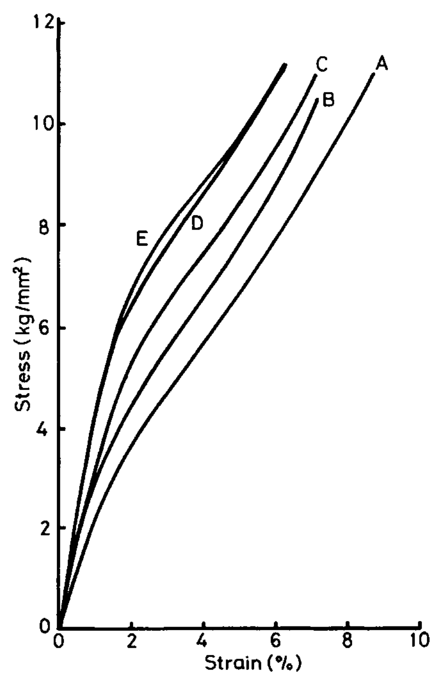


Fig. 1. Initial part of stress–strain curves of nylon filament dyed with CI Acid Blue 127 (20°C, 65% RH, 0.8/min rate of extention). Dye content (mol/kg): (A) undyed; (B) 0.0310; (C) 0.0660; (D) 0.0991; (E) 0.1241.

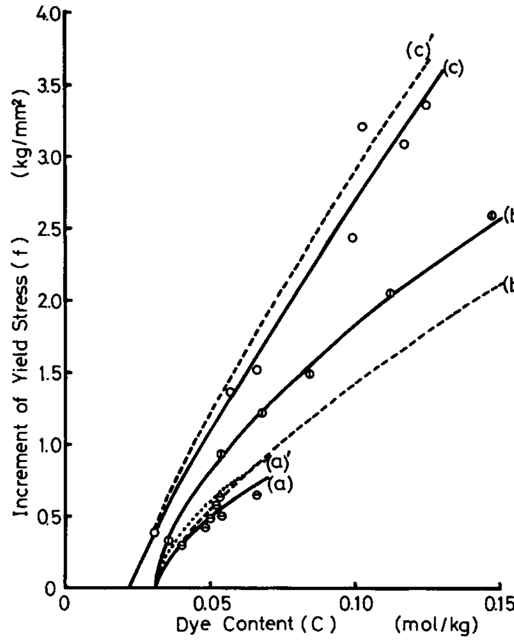


Fig. 2. The increment of the yield stress of nylon filament due to the adsorption of acid dyes: (⊖, ⦶, ○), experimental data for Acid Nylon Fast Violet 6B(a), CI Acid Blue 40(b), and CI Acid Blue 127(c), respectively; (—) (calculated from eq. (2); (· · ·, - - -) calculated from eq. (8).

The dye content on the filament was determined through colorimetric analysis by dissolving 0.05 g or 0.1 g of dyed nylon filament in 80% formic acid (seven dyes) or 80% sulfuric acid (CI Acid Blue 127).

Determination of Yield Stress. An autograph S-100 (Shimazu Co.) and 500-g load cell (Toyo Baldwin Co.) were used for measurement of the yield stress. Samples were kept at 20°C under 63 $\pm$ 3% RH for 24 h before tensile

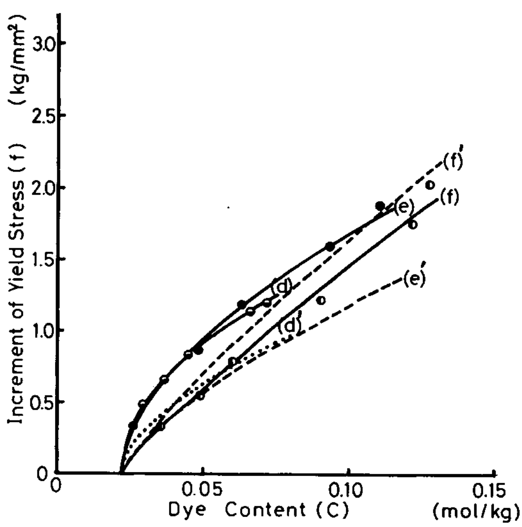


Fig. 3. The increment of the yield stress of nylon filament due to the adsorption of acid dyes: (◒, ●, ◐) experimental data for CI Acid Orange 10(d). CI Acid Red 73(e), and CI Acid Red 85(f), respectively; (—) calculated from eq. (2); (· · ·, - - -) calculated from eq. (9).

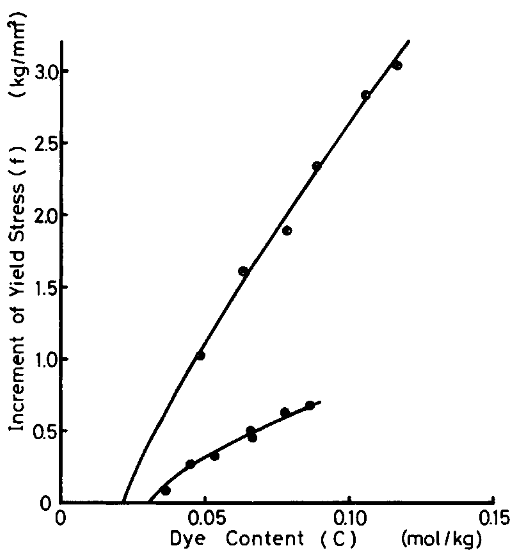


Fig. 4. The increment of the yield stress of nylon filament due to the adsorption of acid dyes: (●, ⊗) experimental data for CI Acid Yellow I and CI Acid Blue 80, respectively; (—) calculated from eq. (2).

tests. A rate of traverse was 200 mm/min and an effective test length was 25 cm. The stress–strain curve was measured and the second-order yield point was defined using the method recommended by Kawaguchi.[1,4] In order to keep the error at a minimum, the tensile tests for dyed nylon filament and blank dyed one were measured in turns. The temperature and humidity were 20.5 $\pm$ 0.25°C and 63 $\pm$ 3% RH, respectively. Ten tests were made on each sample at the above conditions. The error was at most $\pm$ 0.15, at minimum $\pm$ 0.03, and the mean error was $\pm$ 0.085 kg/mm^2.

RESULTS AND DISCUSSION

The Effect of Adsorbed Dye on the Yield Stress

The initial part of the typical stress–strain curves of nylon 6 filament dyed with CI Acid Blue 127 is shown in Figure 1. The secondary yield stress was determined at about 1.7% elongation, and the values of it varied from 3.21 to 6.19 kg/mm^2. Figure 1 shows that the yield stress evidently increases with increase in the dye content. Similar results were obtained with the other seven dyes. In order to estimate the effect of the dyes on the yield stress of nylon filament, the difference (f) of the yield stress between dyed filament and blank dyed one is given as a function of the dye content (C) in Figures 2–4. In this work, mono- and dibasic dyes were applied to nylon filament and the points (C_0), where the curves of the former dyes and the latter ones intersected the abscissa were about 0.031 and 0.022 mol/kg, respectively.

The mechanism of acid dyeing of nylon can be divided into two parts, the adsorption taking place on the terminal amine groups in nylon and the overdyeing taking place on the amide groups in it.[6] The dyeing properties are influenced by the number of sulfonic groups in dyes.[7,8] In the previous

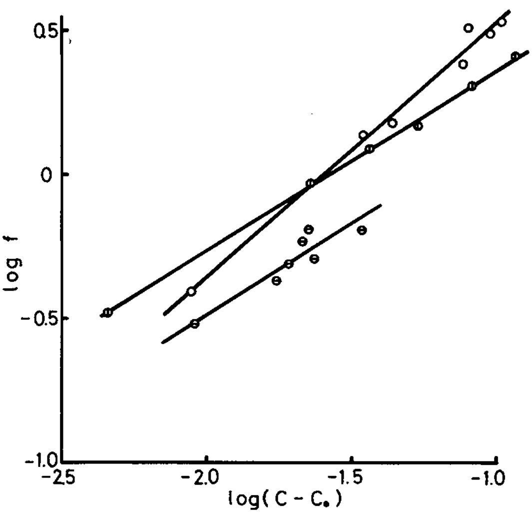


Fig. 5. The relation between log f and log(C − C_0). f is the difference between the yield stress of dyed filament and that of blank-dyed one, C the total dye content, and C_0 the dye content where the curves of Figure 2 intersect the abscissa axis. The values C_0 of CI Acid Blue 127 (○) and the others [(⊖) Acid Nylon Fast Violet 6B; (⦶) CI Acid Blue 40] are 0.022 and 0.031 mol/kg, respectively.

paper,[5] the dye contents of mono-, di-, and tribasic dyes saturated all the amine groups of nylon filament were 0.036, 0.019, and 0.012 mol/kg, respectively. These values coincide with the values of C_0 in the present work fairly well, and it can be concluded that the dye content adsorbed on the amine groups contributes little to the increase in the yield stress of nylon

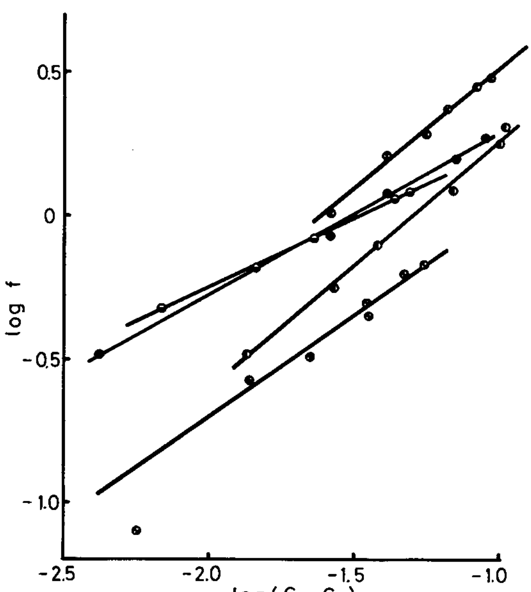


Fig. 6. The relation between log f and log (C − C_0). The values C_0 of CI Acid Yellow 1 (⊗) and the others [(◒) CI Acid Orange 10; (●) CI Acid Red 73; (◐) CI Acid Red 85; ⦸ CI Acid Blue 80] are 0.031 and 0.022 mol/kg, respectively.

filament. That is, the increase in the yield stress can be attributed to the dye content in the region of overdyeing.

The logarithm of the increment of the yield stress ($\log f$) is plotted against the logarithm of dye content [$\log (C - C_0)$] in Figures 5 and 6. The relations are linear and expressed as

$$\log f = A \log(C - C_0) + B \tag{1}$$

where A and B are constants whose values depend on the dye species. C_0 is the dye content, whose value is given above, under which the dye shows no contribution to the yield stress of nylon filament.

In Figures 5 and 6 each dye has different values for the slope and the intercept. The values of the slope A and the intercept B obtained by a least squares method are summarized in Table III. By rearrangement, eq. (1) leads to

$$f = 10^B (C - C_0)^A \tag{2}$$

A comparison of eq. (2) (solid curves) and experimental results (circle points) is given in Figures 2–4, from which it can be seen that quite good agreement between eq. (2) and experimental results is obtained.

The Relation between the Molecular Weight and the Constants A and B

It is said that the strength of attachment of the dye to the polymer chains tends to increase as dye size increases.[9] Derbyshire et al.[10] emphasized the importance of nonpolar forces in the overdyeing of the nylon fiber with acid dye. Therefore, it is plausible that the effect of adsorbed dyes on the yield stress also increases as dye size increases. In fact, anthraquinone dyes (CI Acid Blue 127, CI Acid Blue 40, and Acid Nylon Fast Violet 6B) used

TABLE III
Values of Slope A and Intercept B[a]

Dye	Molecular weight	A	B
Acid Nylon Fast Violet 6 B	340 (237)	0.635 ± 0.317	0.781 ± 0.542
CI Acid Orange 10	452 (246)	0.476 ± 0.042	0.703 ± 0.071
CI Acid Yellow 1	358 (255)	0.704 ± 0.200	0.711 ± 0.304
CI Acid Red 73	556 (350)	0.562 ± 0.071	0.849 ± 0.113
CI Acid Blue 40	473 (370)	0.629 ± 0.039	0.992 ± 0.060
CI Acid Blue 80	678 (472)	0.846 ± 0.121	1.359 ± 0.154
CI Acid Red 85	802 (596)	0.865 ± 0.082	1.123 ± 0.112
CI Acid Blue 127	872 (666)	0.889 ± 0.120	1.416 ± 0.162

[a] The 95% confidence intervals for the values A and B are given in this table.

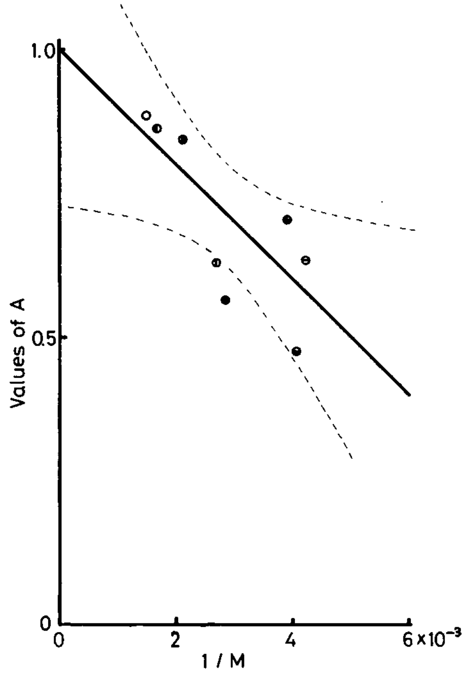


Fig. 7. The relation between slope A and M. M is the difference between the molecular weight of acid dye and the weight of SO_3Na groups in it. The 95% confidence interval for the values of A is given by dashed curves: (⊖) Acid Nylon Fast Violet 6B; (⦶) CI Acid Blue 40; (○) CI Acid Blue 127; (◒) CI Acid Orange 10; (●) CI Acid Red 73; (◐) CI Acid Red 85; ⊖ CI Acid Yellow 1; ⊗ CI Acid Blue 80.

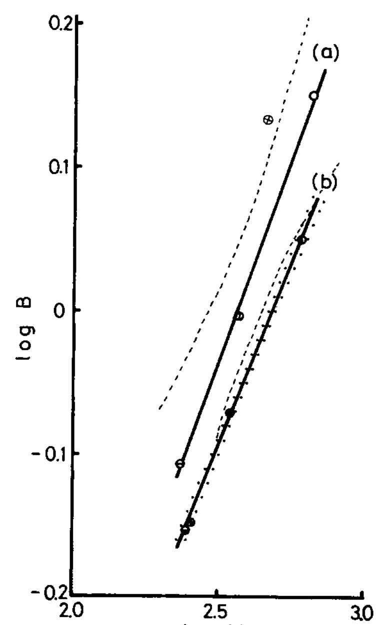


Fig. 8. The relation between intercept B and M. Straight lines (a) and (b) correspond to eqs. (4) and (6), respectively. The 95% confidence intervals for the values of log B are given by dashed and dotted curves for straight lines (a) and (b), respectively. Symbols are the same as Figure 7.

in this work appear to have greater effect on the yield stress as dye size increases, but with azo dyes (CI Acid Orange 10, CI Acid Red 73, and CI Acid Red 85) the effect is not clear.

It is found in this work that the parameters A and B are related to dye size. The values in parentheses (M) in the column for the molecular weight in Table III are the differences between the molecular weight of dyes and the weight of SO_3Na groups in the respective dyes. Table III shows that with a few exceptions both A and B tend to increase with the increase in M rather than the increase in the molecular weight. Three dyes used in the previous paper,[5] which have identical parent chemical structure and differ only in the number of sulfonic groups, give nearly equal values for A (0.720) and B (1.140) when determining the parameters A and B by the present method. From these results, it is considered that the values of A and B are characterized by the addition of polymer chains and not by the sulfonic groups. The sulfonic groups take part in determining the values of C_0 and have little effect on the values of A and B.

The relation between A and M is given in Figure 7, where A is approximately linear to the reciprocal of M and can be expressed as

$$A = 1 - 100/M \tag{3}$$

The maximum value of A is 1.0. If each dye disperses in monomolecular state and attaches to nylon filament in the same direction, the effect of dye on the yield stress is proportional to the dye content, that is, A must be equal to 1.0. The values of A obtained in this work are less than 1.0. Since acid dye should attach to nylon filament in monomolecular state, it is considered that the dye orientation to the fiber axis is not uniform. In Figure 7, the values of A increase with increase in M, and, therefore, it can be said that the effect of dye on the yield stress depends more greatly on the dye content as M increases. It is presumable that the probability of the dye orientation in nylon filament might become more uniform as M increases.

On the other hand, the relation between the intercept B and M is shown in Figure 8. Concerning with the dyes having the same parent chemical structure, the logarithm of B is linearly related to the logarithm of M. With the anthraquinone dyes used in this work, the relation between the two is expressed as

$$\log B = 0.575 \log M - 1.476 \tag{4}$$

or

$$B = 0.0334M^{0.575} \tag{5}$$

With azo dyes it is expressed as

$$\log B = 0.519 \log M - 1.391 \tag{6}$$

or

$$B = 0.0406M^{0.519} \tag{7}$$

Since the value of B is thus related to M, that is, B increases due to the addition of the molecular chains, it can be said that various groups in a dye molecule take part in the yield stress of nylon filament.

The Relation between the Yield Stress and Molecular Weight

The increment of the yield stress of nylon filament due to the adsorption of acid dye is approximately expressed by M as in the following equations: with anthraquinone dyes

$$f = (1.08)^{M^{0.575}} (C - C_0)^{(1 - 100/M)} \tag{8}$$

with azo dyes

$$f = (1.10)^{M^{0.519}} (C - C_0)^{(1 - 100/M)} \tag{9}$$

Over the dye content range $0 < (C - C_0) < 1$, the value of $(1.08)^{M^{0.575}}$ or $(1.10)^{M^{0.519}}$ becomes larger but the value of $(C - C_0)^{(1 - 100/M)}$ becomes lower as M increases. Both the terms have the opposite effect on the yield stress with the increase in M. Therefore, the relation between the yield stress and M varies with the dye content and the value of M. In some cases the yield stress becomes larger, and in other cases it becomes lower or remains almost unchanged as M increases.

A comparison of the experimental increment of the yield stress (circle points) and calculated one from eqs. (8) and (9) (dotted or dashed curves) is given in Figures 2–4. The agreement between the experimental and the calculated one is fair. These equations reveal that the increment of the yield stress can be approximately calculated from the molecular weight and the number of sulfonic groups in acid dyes.

CONCLUSIONS

The effect of adsorbed acid dyes on the yield stress of nylon filament is expressed as

$$f = 10^B (C - C_0)^A$$

where the parameters A and B are expressed by M as

$$A = 1 - 100/M, \qquad B = k_1 M^{k_2}$$

These equations mean that the increment of the yield stress (f) due to the adsorption of dye depends on the dye content (C), the difference (M) between the molecular weight and the weight of SO_3Na groups in acid dye, and the dye content (C_0) which depends on the number of SO_3Na groups.

From the relation between A and M, it is found that the effect of dye on the yield stress depends more greatly on the dye content as M increases, and it is assumed that the probability of the dye orientation might become more uniform as M increases. From the relation between B and M, it is found that the additional molecular chains take part in the yield stress of nylon filament.

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