

Reaction and Diffusion of Reactive Disperse Dye in Nylon 6

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Synopsis

The diffusion of a reactive disperse dye with a vinylsulfonyl group accompanied by simultaneous reaction with the amino end groups in nylon 6 was examined by the method of cylindrical film roll at 70°C and pH 2.2–8.0. The experimental diffusion profiles of the active and fixed species of the dye in nylon 6 were confirmed to be described by the diffusion equation accompanied by the chemical reaction with substrate taking the limited amount of the end groups into account, where the active species of dye were assumed to react only with the free base of amino end groups. The completion of the reaction with the amino end groups was observed in the first layer from the surface at pH 6.0–8.0. The value of diffusion coefficient was constant (8.0×10^{-10} cm²/s) at all the pH's. The product of the second-order rate constant, k_2 , of reaction of the dye and the dissociation constant, K_a , of the amino end groups was constant ($k_2 K_a = 4.0 \times 10^{-9}$ s⁻¹) at pH 2.2–8.0. The k_2 values of the reaction with various substrates for vinylsulfonyl and monochlorotriazinyl-reactive dyes were compared and the practical dyeing conditions were discussed.

INTRODUCTION

The reactions of reactive dyes with fiber are classified into two types, nucleophilic substitution and Michael addition.¹ This does not depend on the reactive sites of fiber but on the reactive groups of the reactive dyes. Reactive dyes for wool, silk, and nylon react with various kinds of functional groups in fiber. Extensive studies have been carried out so far to identify the side or end groups reacting with reactive dyes.^{2–11} Shore investigated the rate of reaction of a monochlorotriazinyl dye with water, alcohols, amines, and amino acids.¹² In spite of the complex relation between the reaction rate and pH of the solution, he concluded that the respective anions in the fiber, (i.e., OH⁻, RO⁻, RS⁻, etc.), reacted with the dye and that amines reacted as unprotonated base, even when the equilibrium was far on the side of corresponding protonated ions.¹³ Shore also showed that the apparent reactivity of wool was given by the sum of the reactivity of individual reactive site and that the amount of total adsorption was described by the diffusion equation accompanied by the pseudo-first-order reaction of the total reactivity by regarding wool as an infinite cylinder.¹⁴ The groups of thiolate ion, free amine, and hydroxide ion were estimate by Corbett to have an approximate reactivity ratio of 10⁴ : 10² : 1 for vinylsulfonyl dyes at 30°C.¹⁵

Since some of the groups are present only in small amounts, the completion of reaction with these groups will take place depending on the reaction time.

The real reactivity of protein fibers, therefore, is not a simple superposition of the individual reactive site except for the initial period of dyeing. However, as reactive dyes for protein fibers usually contain some sulfonic acid groups or anionic charges, they behave as an acid dye in the adsorption process. The adsorption is due to the salt formation between the anionic charges of reactive dye and the protonated amino side or end groups, though all the adsorption may not be the case. This salt formation may influence the acid-base equilibria of these amino groups.

On the other hand, the authors showed that the experimental diffusion profiles of active and fixed species of reactive dyes in cellulose were described by a diffusion equation accompanied by the pseudo-first-order reaction with cellulose, where the equation could be analytically solved.¹⁶⁻¹⁸

In the present paper, a reactive disperse dye with a vinylsulfonyl group is applied to nylon 6 which has only one kind of functional group. The terminal amino group undergoes an acid-base equilibrium and only the free base is expected to react with the dye.^{12,13,15} As this reactive dye is adsorbed by nylon 6 as a disperse dye, there is no salt formation between dye and terminal amino groups. Thus, the present system is one of the simplest models for the reactive dyeing of protein or polyamide fibers without ionic adsorption.

In the beginning, a diffusion equation accompanied by a chemical reaction with the amino end groups which undergo an acid-base equilibrium is derived. A numerical solution of the equations is obtained by the finite difference method. Then, the concentration profiles of active and fixed species in the substrate at various pH's are obtained by the method of cylindrical film roll. The values of diffusion coefficient, second-order rate constant of reaction, surface concentration, and dissociation constant of amino end groups are determined by comparing the experimental diffusion profiles of active and fixed species with the theoretical profiles of both the species.

THEORETICAL

Dissociation Equilibrium

It can be assumed that a dissociation equilibrium for the amino end groups of nylon (Ny-NH₂) is given by:

$$K_a = \frac{[\text{Ny-NH}_2][\text{H}^+]}{[\text{Ny-NH}_3^+]} \quad (1)$$

where the square brackets denote the concentration of the component in them and K_a is the acid dissociation constant. It is also assumed that since $[\text{H}^+]$ in the substrate is kept constant, the acid-base equilibrium of carboxyl end groups is independent on the dissociation equilibrium of amino end groups. Since the amount, S , of end groups available for reaction decreases with the progress of reaction of reactive dyes, Eq. (1) is again described by:

$$K_a = \frac{[\text{Ny-NH}_2][\text{H}^+]}{S - C^* - [\text{Ny-NH}_2]} \quad (2)$$

where C^* is the concentration of dye reacted with the amino end groups.

In the present study, as citric acid is added as the buffer solution to the dyebath, a quantity of acid adsorption on the amino end groups is inevitable. Though some acid is desorbed from the end groups with the progress of chemical reaction, the pH change in the substrate may be minimized by the buffering action of the weak acids added. Since the adsorption of aliphatic carboxylic acids on nylon is low compared with that of acid dyes,^{19,20} the effect of acid adsorption on the acid-base equilibrium of amino end groups may be small.

Reaction with Amino Groups

Although the acid-base equilibrium of amino end groups is far on the side of protonated amine in the neutral and acidic regions, the vinylsulfonyl groups of dye used are assumed to react only with the free base of amino end groups in nylon 6.

The rate of reaction for a vinylsulfonyl dye with the free base of amino groups is given by:

$$\frac{dC^*}{dt} = k_2[\text{Ny-NH}_2]C/V \quad (3)$$

$$= \frac{k_2(S - C^*)C}{V(1 + [\text{H}^+]/K_a)} \quad (4)$$

where k_2 is the rate constant of the reaction and V is the volume of aqueous solution in the substrate. When $[\text{H}^+]/K_a \gg 1$ as in the neutral or acidic region, Eq. (4) is approximated by:

$$\frac{dC^*}{dt} = \frac{k_2K_a(S - C^*)C}{V[\text{H}^+]} \quad (5)$$

Diffusion with Simultaneous Reaction

The diffusion coefficient, D , of disperse dye can be regarded to be constant in nylon. The diffusion equation accompanied by the chemical reaction, therefore, can be written as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial C^*}{\partial t} \quad (6)$$

The simultaneous differential Eqs. (4) and (6), must be solved under the initial and boundary conditions:

$$\begin{aligned} t = 0, \quad x > 0, \quad C = 0, \quad C^* = 0 \\ t > 0, \quad x = 0, \quad C = C_0 \\ t > 0, \quad x \rightarrow \infty, \quad C = 0 \end{aligned} \quad (7)$$

where the infinite dyebath conditions are postulated and C_0 denotes the surface concentration of active species. In order to use the finite-difference method,²¹ the following transformations were made:

$$\begin{aligned} Y &= C/C_0 \\ Z &= C^*/C_0 \\ \alpha &= C_0 k/V(1 + [H^+]/K_a) \\ \beta &= \Delta t/2 \\ \gamma &= D/(\Delta x)^2 \end{aligned} \quad (8)$$

where Δt is the difference of time and Δx the difference of distance.

The differential Eqs. (4) and (6) were converted into the difference equations by using the Crank-Nicolson method.²¹ In the numerical solution of partial differential equation by the finite-difference methods, the differential system is replaced by a matrix system. The general formula to be solved by the Gauss-Seidel method are given as follows:

$$Z_{i,j+1}^{(n+1)} = \left\{ \alpha\beta \left(\frac{S}{C_0} \right) (Y_{i,j+1}^{(n)} + Y_{i,j}) + (1 - \alpha\beta Y_{i,j}) Z_{i,j} \right\} / \left(1 + \alpha\beta Y_{i,j+1}^{(n)} \right) \quad (9)$$

$$\begin{aligned} Y_{i,j+1}^{(n+1)} &= \left[\beta\gamma (Y_{i-1,j+1}^{(n+1)} + Y_{i+1,j+1}^{(n)}) + \beta\gamma (Y_{i-1,j} - 2Y_{i,j} + Y_{i+1,j}) \right. \\ &\quad \left. + \left\{ 1 - \alpha\beta \left(\frac{S}{C_0} - Z_{i,j} \right) \right\} Y_{i,j} \right] / \left\{ 1 + 2\beta\gamma + \alpha\beta \left(\frac{S}{C_0} - Z_{i,j+1}^{(n+1)} \right) \right\} \end{aligned} \quad (10)$$

As the boundary condition (11) is always satisfied,

$$Y_{0,j+1}^{(n)} = 1 \quad (11)$$

the numerical calculations were made by the usual iteration using Eqs. (9), (10), and (11). The difference of t was taken as $t = 60$ s in the beginning and that of x was determined so as to satisfy the condition:

$$\Delta x = \epsilon/2l \quad (12)$$

$$\Delta t D/(\Delta x)^2 \doteq 0.5 \quad (13)$$

where ϵ is the thickness of a film and l is a natural number. The iteration was carried out to satisfy the following conditions:

$$|Y_{i,j+1}^{(n)} - Y_{i,j+1}^{(n-1)}| < 10^{-6} \quad (14)$$

$$|Z_{i,j+1}^{(n)} - Z_{i,j+1}^{(n-1)}| < 10^{-6} \quad (15)$$

The results were checked by comparing them with the results calculated with smaller differences.

In the method of cylindrical film roll, the concentrations of active and fixed species in the film are obtained as the mean concentration, \bar{C}_m , or the total adsorption of the m -th layer. The theoretical values of Y and Z for each layer were calculated as the mean concentrations by use of the Simpson's 1/3 rule and compared with the experimental values.

As Eq. (6) can be analytically solved when $k_2 = 0$, the numerical solutions for Eqs. (9) and (10) were checked by the comparison with the results of analytical solution.

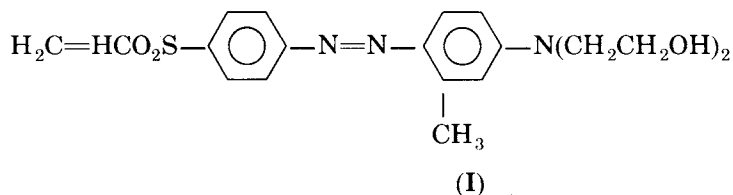
This treatment can be extended to the multicomponent system of reactive site such as wool fiber and it was reported elsewhere.²²

EXPERIMENTAL

Materials

Biaxially oriented nylon 6 film, Emblem, manufactured and supplied by Unitica Ltd. was used as the substrate. It was cut 4 cm wide and 55 cm long, scoured with hot water, and heat set at 95°C in water for 24 h. The film was wound so tightly on a glass tube ($\phi = 1.0$ cm) that there were no bubbles between the consecutive layers. The thickness of a film was $(2.72 \pm 0.02) \times 10^{-3}$ cm. The contents of amino and carboxyl groups were 4.64×10^{-2} and 4.50×10^{-2} mol/kg, respectively.

A reactive disperse dye [I] (m.p. 101°C), supplied by Mitsui Toatsu Chemicals, Inc., was used as penetrant.



The chemicals used were of reagent grade.

Diffusion Profiles

Experimental conditions were shown in Table I. The pH of the dye solution was adjusted by McIlvaine's buffer and measured at 70°C.

A cylindrical film roll was immersed in the dyebath for a prescribed time. After the diffusion, the layers from the surface were cut in half. The film cut

TABLE I
Experimental Conditions

Diffusion time (h)	2, 4, 8
pH	2.2, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0
Conc. of dye	0.01 g/dm ³
Temperature	70.0°C

off was washed in an acidic pyridine solution (formic acid : pyridine (90%) : water = 2 : 1 : 7)²³ at 70°C to extract the unfixed species. The optical densities of the respective layers of both the films were measured at the wavelength of maximum absorption of the dye by a UVIDEC-505 spectrophotometer (Japan Spectroscopic Co., Ltd.). Those of washed and unwashed films correspond to the mean concentration of fixed and total species on the films. From the difference between them, the mean concentration of active species was obtained. The concentration profiles of fixed and active species in the nylon 6 were calculated by the use of calibration curves prepared previously.

RESULTS AND DISCUSSION

Diffusion Profiles

The diffusion profiles of active and fixed species for the diffusion time of 4 h are shown in Figures 1–3. Though this penetrant shows a color change such as 4-aminoazobenzene and *N,N*-dimethylaminoazobenzene in the solution below pH 3.0,^{24–26} no change in the absorption spectra of the aqueous solution was

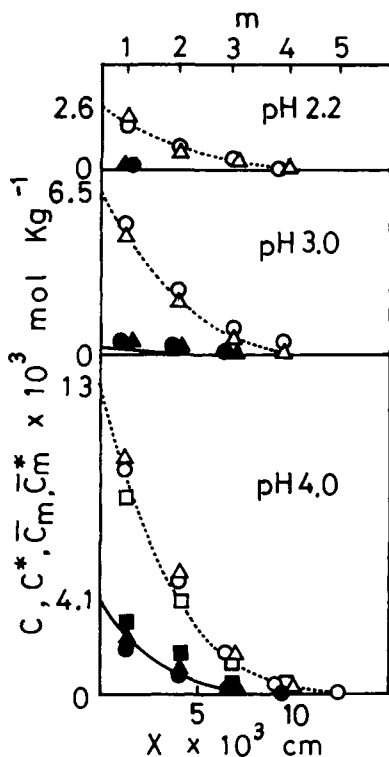


Fig. 1. Diffusion profiles of active (\circ , Δ , \square) and fixed species (\bullet , \blacktriangle , \blacksquare) of dye (I) in nylon 6 at 70°C, and at pH 2.2, 3.0, and 4.0 ($t = 240$ min). The theoretical profiles for active (----) and fixed (—) species are described as the relationship between C or C^* and x for $D = 8.0 \times 10^{-10}$ cm²/s, $k_2 = 40$ dm³/mol s, and $\text{p}K_a = 10.0$. The experimental data are plotted as the relationship between C_m or C_m^* and m . Three experiments were performed under the same conditions.

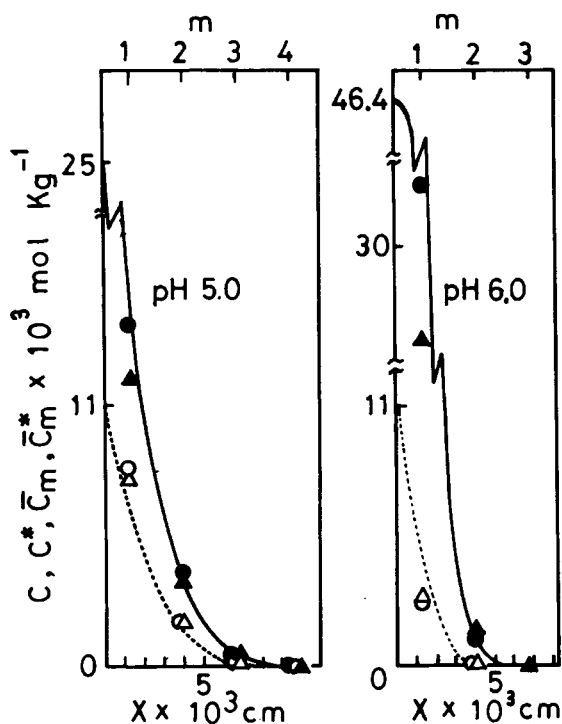


Fig. 2. Diffusion profiles of active and fixed species of dye (I) in nylon 6 at 70°C, and at pH 5.0 and 6.0 ($t = 240$ min). The theoretical curves and experimental plots were drawn by the same values of parameters and symbols as those in Fig. 1.

observed above pH 4.0. No change in the absorption spectra on the films dyed at pH 3.0 and 2.2 was observed when measured in the dry state and the absorption spectra in the wet state was not measured. The analyses of diffusion profiles, therefore, were mainly made over the pH range 4.0–6.0. The hydrolysis of vinylsulfonyl groups in the dyebath at 70°C was confirmed to be negligible below pH 8.0. The surface concentrations of active species over the pH range examined were constant during the diffusion experiment within the experimental errors.

The surface concentrations of active species below pH 4 decreased with a decrease in pH and those above pH 7 also decreased with an increase in pH. The former is due to the decrease in the concentration of unprotonated species, since the protonated species may have smaller affinity to the substrate at low pH, while the latter may be a usual phenomenon of disperse dyes because of an increase in the solubility. The surface concentrations of fixed species increased monotonically with an increase in pH and reached the saturation value above pH 6 within the diffusion time examined.

As in the case of the reactive dye-cellulose system,^{16,17} the penetration of active species into substrate decreased with an increase in pH (Figs. 2 and 3), since the apparent rate of reaction of vinylsulfonyl groups ($k_2[\text{Ny-NH}_2]/V$) increased by a factor of 10 for every one pH unit increase.

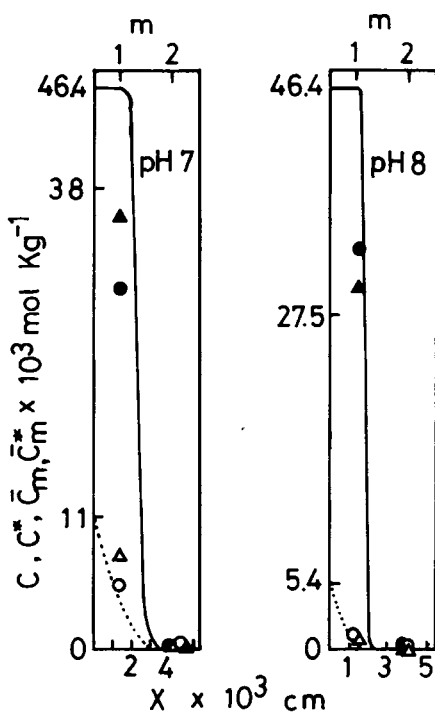


Fig. 3. Diffusion profiles of active and fixed species of dye (I) in nylon 6 at 70°C, and at pH 7.0 and 8.0 ($t = 240$ min). The theoretical curves and experimental plots were drawn by the same values of parameters and symbols as those in Fig. 1.

Reaction and Diffusion in Nylon 6

When the diffusion profiles for active and fixed species were obtained by more than two experiments at various pH levels, scattering of surface concentration, C_0 , was large but the reproducibility of the penetration distance was good. An attempt was made to find the common values of parameters k_2 , D , and K_a so as to fit the theoretical profiles for the fixed and active species with the experimental ones, \bar{C}_m^* or \bar{C}_m vs. m plots, by the use of Eqs. (9) and (10) (Figs. 1–3). The experimental profiles for the fixed and active species agreed well at pH 4.0, 5.0, and 6.0 with the theoretical ones for the common values of parameters as shown in Figures 1 and 2. The theoretical profiles at the other pH values were drawn with the same values of parameters. The values of parameters estimated are shown in Table II.

TABLE II
Values of Parameters Estimated ($t = 240$ min, 70°C)

pH	2.2	3.0	4.0	5.0	6.0	7.0	8.0
C_0 (mmol/kg)	2.6	6.5	13.0	11.0	11.0	11.0	5.4
C_0^* (mmol/kg)	0	0.2	4.1	25.0	46.4	46.4	46.4
D	8.0×10^{-10} (cm ² /s)						
$k_2 K_a$	4.0×10^{-9} (s ⁻¹)						

Since the values of C_0 at pH 7.0 and 8.0 could not be precisely determined by the extrapolation of experimental profiles, they were estimated so as to fit the experimental profiles of fixed species with the theoretical ones for the common values of parameters at pH 4.0–6.0. At pH 6.0, 7.0, and 8.0, where the completion of reaction with amino end groups were observed in the first layer, the smaller values of differences, Δx and Δt , were adopted to describe the steep change in the concentration of fixed species.

The theoretical mean concentrations of the first layer \bar{C}^* of fixed species at pH 7.0 and 8.0 agreed roughly with the experimental values (Fig. 3). The effect of protonation on the diffusion and reaction behaviors was not observed at pH 2.2 and 3.0, as the experimental profiles of the fixed and active species agreed well with the theoretical profiles described by the same values of parameters.

Although a decrease in the value of C_0 at high and low pH values is attributed to another reason, all the characteristic behaviors of reaction and diffusion could be described by the theoretical equations in the present study.

As mentioned before, it was confirmed by the present study that the adsorption of weak acid on the substrate gave no effect on the acid-base equilibrium of amino end groups.

Rate of Reaction of Vinylsulfonyl Dyes

The pK_a value of the amino end groups in nylon 6 was estimated to be 10 by McGregor and Harris,²⁷ and that of 5-aminocaproic acid was determined to be 9.5 at 70°C.²⁸ That is why Eq. (5) holds over all the pH range examined and a constant value of the product $k_2 K_a = 4.0 \times 10^{-9} \text{ s}^{-1}$ is obtained. The second-order rate constant of reaction, k_2 , with the amino end groups for this vinylsulfonyl reactive dye is determined to be 40 dm³/mol s, when the value of pK_a is regarded as 10.

The second- (k_2) and pseudo-first-order rate constants (k_1) of reaction for with various reactive substrates for the vinylsulfonyl reactive dyes are shown in Table III. Although the values of k_2 for various substrates are different from each other, the practical values of k_1 are prepared by adjusting the dyeing conditions. Thus, the value of k_1 with cellulose for vinylsulfonyl reactive dyes is of the order of 10 s⁻¹ at the temperature of practical dyeing.²⁸ As the ratio of [cell-O⁻]/[OH⁻] was estimated to be 20 at $I = 0.1$,²⁹⁻³¹ the value of k_2 could be determined.

The value of k_1 for the dye used in the present study at pH 5 is considerably smaller than those for the other cases in spite of the large value of k_2 . This is due to the small amount of amino end groups and to the large value of pK_a . In case of wool, however, since the large amount of side- and end-reactive groups whose pK_a value is smaller than 10 is contained in the wool fiber,²² many vinylsulfonyl reactive dyes are used for wool dyeing. Some of them are marketed as acid dye,³² because they have a practical value of k_1 even in acidic regions.

On the other hand, the practical dyeing conditions for reactive dyeing of cellulose are based on the large amount of [cell-O⁻] contained in the substrate and on the high alkalinity of the dyebath, in spite of the relatively small value of k_2 .

TABLE III
Pseudofirst- (k_1) and Second-Order Rate Constants (k_2)
of Reaction for Reactive Dyes

C. I. Reactive	Substrate (pK _a)	Temp. (°C)	k_2 (dm ³ /mol s)	k_1		Ref.
				Formula	(s ⁻¹) (at pH)	
Dye (I)	Nylon 6 (10)	70	40	$k_2[\text{Ny-NH}_2]/V$	2.3×10^{-3} (6.0)	—
Yellow 17 ^a			0.060		3.5×10^{-4} (10.78)	
Blue 19 ^b	Water ^c	60	0.046	$k_2[\text{OH}^-]$	5.3×10^{-4} (11.08)	33
Yellow 17			0.034		2.1×10^{-3} (10.5)	
Blue 19	Cellulose	60	0.027	$k_2[\text{cell-O}^-]^c$	9.2×10^{-4} (10.25)	27
	(10.8)	20	2.5×10^{-4}		1.5×10^{-6} (10.7)	
Red 3	<i>n</i> -Amylamine (10.1)	70	0.077	$k_2[\text{R-NH}_2]^d$	4.3×10^{-5} (8.96)	12
Red 3	Cellulose	80	1.2×10^{-3}	$k_2[\text{cell-O}^-]^c$	1.7×10^{-4} (10.4)	34

^a 7.88×10^{-3} mol/dm³.

^b 5.83×10^{-3} mol/dm³.

^c $K_w = 9.619 \times 10^{-14}$ (60°C), $K_w = 2.69 \times 10^{-13}$ (80°C).

The value of $[\text{cell-O}^-]/[\text{OH}^-]$ was assumed to be 20.²⁹

^d 7.6×10^{-3} mol/dm³.

The k_2 value for vinylsulfonyl dye are larger than those for monochlorotriazinyl dyes. The latter dyes have in general higher affinity than the former ones to prepare the practical dyeing conditions.

The ratio of k_2 values for water and cellulose was 1.75 for vinylsulfonyl dyes, Yellow 17 and Blue 19. It was estimated to be 1.5 for a monofluorotriazinyl dye.³⁵

APPENDIX: LIST OF SYMBOLS

C :	concentration of active species in nylon (mol/kg)
C^* :	concentration of fixed species in nylon (mol/kg)
C_o :	surface concentration of active species (mol/kg)
C_o^* :	surface concentration of fixed species (mol/kg)
\bar{C}_m :	mean concentration of active species in the m -th layer (mol/kg)
\bar{C}_m^* :	mean concentration of fixed species in the m -th layer (mol/kg)
D :	diffusion coefficient of active species (cm ² /s)
$[\text{H}^+]$:	hydrogen ion concentration (mol/dm ³)
k_1 :	pseudo-first-order rate constant of reaction (s ⁻¹)
k_2 :	second-order rate constant of reaction defined by Eq. (3) (dm ³ /mol s)
K_a :	dissociation constant of amino end groups in nylon (mol/dm ³)

l :	natural number
m :	number of layers
$[\text{Ny-NH}_2]$:	concentration of amino groups in nylon (mol/kg)
S :	amino end group content in nylon (4.64×10^{-2} mol/kg)
t :	time (s)
Δt :	difference of time (s)
V :	volume of aqueous solution in nylon ($0.08 \text{ dm}^3/\text{kg}$)
x :	distance (cm)
Δx :	difference of distance (cm)
$Y_{i,j}^{(n)}$:	$Y^{(n)}(ix, jt)$, defined by Eq. (10). Superscript (n) denotes the n -th iteration.
$Z_{i,j}^{(n)}$:	$Z^{(n)}(ix, jt)$, defined by Eq. (9). cf. Y
α, β, γ :	defined by Eq. (8)
ϵ :	thickness of a swollen film (2.72×10^{-3} cm)

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