The Simulation of Hydrolytic Polymerization of ε-Caprolactam in Various Reactors: A Simulation Model for the Tubular Reactor with Heat Exchanger and Its Numerical Solution

KAZUO TAI, YOSHIHIRO ARAI, and TAKASHI TAGAWA, *Research and Development Center Unitika Ltd., 23 Kozakura, Uji, Kyoto, 611 Japan*

Synopsis

A concrete simulation model which deals with the hydrolytic polymerization of ε-caprolactam (CL) in the tubular reactor (TR) with the heat exchangers (HEx's) was described, and a method for its numerical solution was presented. The numerical calculations were carried out for 13 cases, where the position and number of the HEx's in the TR were varied. The effects of the HEx on the distribution of the temperature in the TR and of the characteristic data of the polymerization (the concentration of CL and number average degree of polymerization) in the TR and at the outlet of the TR were investigated. The results suggested that the HEx positioned at the upper half of the TR and the HEx positioned at the lower half of the TR are effective to narrow the temperature distribution in the TR and to produce the polymer product with narrower molecular weight distribution, respectively.

INTRODUCTION

In the preceding paper,[1] the concrete simulation models dealing with the hydrolytic polymerization of ε-caprolactam (CL) in the various reactors used in the industry were reported. As an extension of the previous study, the simulation model of the polymerization in the tubular reactor (TR) with the heat exchangers (HEx's) is dealt with in this work.

Several patents[2] have claimed the utilization of the HEx for the TR with respect to the polymerization. So far as we know, however, no publication has appeared in which the experimental and/or theoretical interpretations of the polymerization in the TR with the HEx's are reported.

The objectives of this paper are (1) to give a concrete mathematical simulation model which represents the polymerization in the TR with the HEx's, (2) to clarify the effects of the HEx's on the temperature distribution in the TR and on the distribution of the characteristic data of the polymerization such as the concentration of CL (i.e., the yield) and the number average degree of polymerization (P_N) in the TR and at the outlet of the TR, and (3) to predict the position and number of the HEx's in the TR which are preferable for improving the performance of the TR.

SIMULATION MODEL AND NUMERICAL CALCULATION

Chemistry of the polymerization. The mechanism and kinetics of the hydrolytic polymerization of CL are summarized in Table I.[3,4] The polymerization

CCC 0021-8995/83/082527-14$02.40

TABLE I
Mechanism and Kinetics[3,4]

Equilibrium reactions

1. Ring opening: $CL + H_2O \rightleftharpoons ACA$ (1)
                           $ x \quad\;\; w \qquad z$

2. Polycondensation: $P_n + P_m \rightleftharpoons P_{n+m} + H_2O$
                         $-\!-NH_2 + HOCO-\!- \rightleftharpoons -\!-NHCO-\!- + H_2O$ (2)
                         $y \qquad\;\; y \qquad\quad x_0 - x - y \quad w$

3. Polyaddition: $CL + P_n \rightleftharpoons P_{n+1}$
                         $CL + H_2N-\!- \rightleftharpoons H_2N-\!-$ (3)
                         $x \quad\;\; y \qquad\quad y - z$

Rate equations

$$dx/dt = -k_1[x(w_0 - y) - z/K_1] - k_3[xy - (y - z)/K_3] \tag{4}$$

$$dy/dt = k_1[x(w_0 - y) - z/K_1] - k_2[y^2 - (x_0 - x - y)(w_0 - y)/K_2] \tag{5}$$

$$dz/dt = k_1[x(w_0 - y) - z/K_1] - 2k_2[yz - (y - z)(w_0 - y)/K_2]$$
$$\quad -k_3(xz - z/K_3) \tag{6}$$

Rate constants and equilibrium constants

$$k_i = k_i^0 + k_i^c y \qquad\qquad (i = 1, 2, 3) \tag{7}$$

$$k_i^j = A_i^j \exp[-E_i^j/(RT)] \qquad (j = 0, c) \tag{8}$$

$$K_i = \exp[(S_i - H_i/T)/R] \tag{9}$$

can be characterized by the following equilibrium reactions: (1) ring opening reaction of CL, (2) polycondensation between the end groups (EG), and (3) polyaddition reaction of CL. The cyclic oligomer formation[5] was neglected in this work, since the fraction of the reaction heat generated by this reaction is negligibly small. Equations (4)–(6) listed in the table are the rate equations derived from the reaction mechanism, where x, y, z, and w are the concentrations of CL, EG, ϵ-aminocaproic acid (ACA), and water, respectively. k_i is the rate constant. K_i $(= k_i/k_i')$ is the equilibrium constant.

Those three reactions have been accepted to be catalyzed by the carboxyl end group, so that the rate constant k_i can be expressed as eq. (7). All the constants depend on temperature T (°K) for which the Arrhenius relation can be assumed, and the equilibrium constants are expressed as a function of T [cf. eqs. (8) and (9)]. The values of the kinetic constants such as the frequency factor A_i^j and activation energy E_i^j and the thermodynamic constants such as the enthalpy H_i and entropy S_i are listed in Table II.[6]

Tubular reactor with heat exchanger. As reported in the preceding paper,[1] the temperature distribution in a tubular reactor (TR) can be obtained by solving the heat diffusion equation [eqs. (10) and (11)] given in Table III, where eq. (11) is the finite difference approximation of eq. (10). v is the mean linear flow rate, α is the heat diffusion coefficient, c_p is the specific heat, and Q_R is the sum of the reaction heat. The TR has the cylindrical symmetry, so that the coordinate system (r, s) shown in Figure 1 can be defined. The division j $(j = 1, 2, \ldots, M)$ of the radius along the r-direction corresponds to the polymerization time (t) if the laminar flow is assumed, and the division i $(i = 1, 2, \ldots, N)$ in the flow $(s$-$)$ direction correspond to that of the residence time (τ). The (i, j) volume element can be signified by the ith plate and jth stream. The mean kinetic data at the outlet of the ith plate $\overline{X}(i)$ is given by the integration of eq. (12). Here $X(t)$ is the kinetic data at time t (i.e., the solution of the set of the rate equations listed in Table I) and $E(\tau, t)$ is the density distribution function of the TR. In this

TABLE II
Kinetic Constants and Thermodynamic Constants[6,a]

i^b	A_i^0	E_i^0	A_i^c	E_i^c	S_i	H_i
1	5.9874×10^5	1.9980×10^4	4.3075×10^7	1.8806×10^4	-7.8846×10^0	1.9180×10^3
2	1.8942×10^{10}	2.3271×10^4	1.2114×10^{10}	2.0670×10^4	9.4374×10^{-1}	-5.9458×10^3
3	2.8558×10^9	2.2845×10^4	1.6377×10^{10}	2.0107×10^4	-6.9457×10^0	-4.0438×10^3

[a] Dimensions: A^0 (kg·mol^{-1}·h^{-1}); A^c (kg^2·mol^{-2}·h^{-1}); E (cal·mol^{-1}); S (eu); H (cal·mol^{-1}).
[b] $i=1$, ring opening of CL; $i=2$, polycondensation; $i=3$, polyaddition of CL.

TABLE III
Basic Equations for the TR with the HEx's

Heat diffusion equation

$$v(\partial T/\partial s) = \alpha[\partial^2 T/\partial r^2 + (1/r)(\partial T/\partial r)] + Q_R \tag{10}$$

$$(v/\Delta s)(T_{i+1,j} - T_{ij}) = (\alpha/\Delta r^2)(T_{i,j+1} - 2T_{ij} + T_{i,j-1})$$
$$+ (\alpha/r\Delta r)(T_{i,j+1} - T_{ij}) - (1/c_p)\sum_l (H_l \Delta X_l/\Delta t) \tag{11}$$

Outlet mean characteristic data

$$\overline{X}(i) = \int X(t)E(\tau, t)\,dt = \sum_j^M X(i,j)E(i,j)\Delta t_j \tag{12}$$

$$E(\tau, t) = \tau^2/(2t^3) \tag{13}$$

Heat transfer equations for HEx

$$Q_T = h_{oa}A_{f,j}(\Delta T)_{am} = w_j c_p(T_{f,j}^{in} - T_{f,j}^o) \tag{14}$$

$$h_{oa} = 2.02(\lambda/D')[(\omega_j c_p F)/(\lambda n_j L')]^{1/3}(\mu/\mu')^{0.14} \tag{15}$$

$$(\Delta T)_{am} = 0.5(\Delta T_{f,j}^{in} + \Delta T_{f,j}^o) = 0.5(T_{f,j}^{in} + T_{f,j}^o - 2T^m) \tag{16}$$

work, the laminar flow was assumed, so that the E has the expression of eq. (13). The plate to which no HEx is located can be dealt with by eqs. (11) and (12).

Here we deal with the simulation model for the HEx. A schematic representation of the TR with one HEx is shown in Figure 1, where L/N and D are the divided length and diameter of the TR and L' and D' are the length and diameter of the HEx. The total length of this reactor is $L' + (N - 1)L/N$, while that of the reference TR is L. T^{in}, T^o and T^m are the temperature (°C) of the input reactant, output reactant, and heat transfer medium of the HEx, respectively. In the figure, the ith plate is the HEx with n fine tubes. A set of the basic equations to express the performance of the HEx can be given by eqs. (14)–(16) listed in Table III. Equation (14) is the well-known heat transfer equation applicable to the fine tube. The nomenclature of the variables and constants are as follows; Q_T is the heat to be transferred; h_{oa} is the overall heat transfer coefficient; A is the contact surface area; ω is the mass flow rate; λ is the heat conductivity; μ is the viscosity of the reactant at T; μ' is the viscosity of the reactant at T^m; f ($f = 1, 2, \ldots, F$) signifies the division of the HEx in its flow direction. The flow in each fine tube of the HEx was assumed to be the plug flow for simplification, although it is also to be approximated by the laminar flow. The mean linear flow rate in each tube was determined so that the mean mass flow rate at the outlet of the $(i - 1)$th plate is equal to that at the inlet of the $(i + 1)$th plate.

The simulation calculation for the TR with the HEx's requires us to solve the heat diffusion equation [eq. (10) or (11)] and the heat transfer equation [eqs. (14)–(16)] together with the set of the rate equations [eqs. (4)–(6)] and the equation of the reactor performance [eqs. (12) and (13)].

Numerical calculation. The set of the rate equations [eqs. (4)–(6)] listed in Table I was solved numerically using the Runge–Kutta–Gill integration scheme. The integration of eq. (12) was carried out by the well-known integration scheme. Equation (11) was solved according to the numerical method, details of which were reported in the Refs. 1 and 7. The TR was divided in the equal parts (of residence time) of $1/12$ along the s-direction (i.e., $i = 1, 2, \ldots, 12$) and in the equal parts of $1/9$ along the radius (r-) direction (i.e., $j = 1, 2, \ldots, 9$).
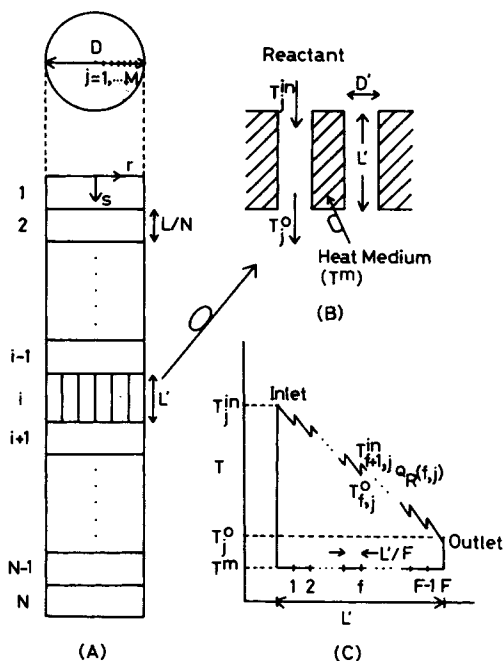
Fig. 1. Schematic representation of the TR with the HEx's. (A) and (B) show the definition of the coordinate, variables, and constants for the TR and HEx (cf. text). (C) is the representation of the algorithm for solving the HEx, where the ordinate is the temperature, the abscissa is the length (L') of the HEx, and Q_R (f, j), for example, is the reaction heat at the fth division of the HEx in the jth stream of the TR.

The resultant solution gave the temperature distribution for the plates without the HEx.

A set of the temperatures at the outlet of the HEx can be obtained by solving the set of equations [eqs. (14)–(16)] according to the scheme of the algorithm shown in Figure 1(C). The distance from the inlet to the outlet of the HEx is divided in the equal parts of $\frac{1}{5}$ (i.e., $f = 1, 2, \ldots, 5$) and the iteration calculation between eqs. (14)–(16) to obtain a consistent solution of the outlet temperatures was carried out for each division. The consecutive process from the first division to the final (fifth) division gives a set of the temperatures at the outlet of the HEx.

All the calculations in this report were carried out with a HITAC 8250 Computer.

Assumptions for the numerical calculations. So far as we know, no publication including a patent article which has the experimental results suitable for confirming those of the simulation calculations exists. Therefore, the following model reactor system and polymerization conditions were assumed for a set of the numerical computations, which were transferred from the preceding paper[1] and patent article[8] with a little alteration but have no experimental background with respect to the introduction of the HEx's.

The postulated reactor is a part of the combination reactor[1] with no recycle of the polymeric reactant. The dimensions of the TR with the HEx's are as

follows; $D = 0.90$ m, L/N ($= L/12$) $= 1.0$ m, $D' = 0.0317$ m, $L' = 3.535$ m (determined so as $\tau = 2$ h at the HEx), and $n = 228$.

The polymerization conditions for the TR with the HEx's are as follows: (1) the characteristic data of the reactant input into the TR are [CL] = 4.10 mol·kg^{-1}, [EG] = 0.091 mol·kg^{-1}, and the concentration of the free water [FW] = 0.649 mol·kg^{-1}; (2) the temperatures of the input reactant, jacket of the TR, and HEx's are 260°C; (3) the parameter δ, which is an expression of the behavior of the water removal at the top of the TR and is defined as $1 -$ [effective water]/[FW] is 0.94; (4) 80% of the reaction heat generated at the first plate ($i = 1$) is removed by the stripping operation of N_2 gas; (5) the mean linear flow rate (v) of the reactant in the TR is 0.5 m·h^{-1}, so that the mean residence time (τ) is 24 h.

In the actual calculations, the following constants and computational simplifications were used; $\alpha = \lambda/(c_p \rho)$ (m^2·h^{-1}); $\lambda = 0.21$ (kcal·m^{-1}·h^{-1}·°C^{-1})[9]; $\rho = 1.1238 - 0.566 \times 10^{-3}\ T$ (g·cm^{-3}, T °C)[10]; $c_p = 0.5 + 5.0 \times 10^{-4}\ T$ (kcal·kg^{-1}·°C^{-1}, T °C)[11]; to save the computer memory, the mean kinetic data at the outlet of the (i, j) volume element were used for the initial values of the ($i + 1$, j) volume element, since this is valid when the division (j) is fine enough; the reaction heat Q_R of eqs. (10) and (11) was approximated by $Q_R = (-1/c_p) \cdot H_3 \Delta[\text{CL}]/\Delta t$, since the Δ[CL] term due to the polyaddition reaction of CL is the majority of the heat.

RESULTS AND DISCUSSION

Calculated results. The numerical calculations were carried out for 13 cases of the TR with the HEx's. The positions of the HEx's are listed in the Table IV. Two examples of the detailed calculated results corresponding to the case 1 (the control, without the HEx) and case 3 (with the HEx at fifth plate) are shown in Table VA and Table VB. The upper thirds of the tables are the calculated temperature distribution (a set of the T_{ij}'s, $i \times j = 108$) in the TR. The notation J means the jacket. The intermediate thirds and lower thirds of the tables correspond to the distribution of the CL concentration and that of the P_N in the TR, respectively, where $\bar{X}(i)$ signifies the mean kinetic data at the outlet of the ith plate.

In Table IV, a summary of the results of the calculations for 13 cases are given; viz., the temperature data in the TR consisting of the maximum temperature ($T_{\max}$), arithmetic mean value ($\langle T \rangle$) for 108 temperature data, and standard deviation (σ) for the data, the characteristic data, x (= [CL]) and P_N, at the outlet of the TR consisting of each maximum value, minimum value, range (the difference in value between the maximum and minimum), and mean kinetic data defined by eq. (12).

Effect of HEx on the temperature distribution. The upper thirds of Table VA and Table VB demonstrate the detailed temperature data in the TR without the HEx and with the HEx, respectively. In comparison with these two sets of the data, it is found that the HEx remarkably affects the temperature distribution in the TR. Figures 2 and 3 are the graphic expression of the maximum temperature in each plate plotted against the plate number and traced by the solid line. In the figures, the broken line indicates the position of the HEx and shows the drop of the maximum temperature by the heat exchange. The numbers denoted by #1, #2, etc., correspond to the case number listed in Table IV.

TABLE IV
Results of Calculations for Various Cases of the TR with the HEx's[a]

Case no.	Positions of HEx's (i)		Temperature in the TR			x_{max}	x_{min}	Characteristic data at the outlet of the TR					
			T_{max}	$\langle T \rangle$[b]	σ[c]			$R(x)$[d]	$\bar{x}$[e]	P_N^{max}	P_N^{min}	$R(P_N)$[d]	$\bar{P}_N$[e]
1	...	...	272.9	267.4	3.75	0.850	0.731	0.119	0.793	198.3	187.7	10.6	191.6
2	3	...	266.7	263.2	1.97	0.887	0.725	0.162	0.799	199.5	191.5	8.0	195.0
3	5	...	269.0	262.5	2.30	0.889	0.722	0.167	0.796	200.0	193.9	6.1	197.0
4	7	...	271.0	263.2	3.44	0.874	0.721	0.153	0.788	200.2	195.5	4.7	198.0
5	9	...	272.1	264.5	4.11	0.859	0.721	0.138	0.783	200.3	195.8	4.5	198.2
6	11	...	272.7	265.9	4.23	0.853	0.722	0.131	0.788	200.3	193.4	6.9	196.6
7	3	5	265.2	261.8	1.32	0.914	0.723	0.191	0.808	199.9	193.0	6.9	196.4
8	3	7	265.2	261.5	1.33	0.915	0.721	0.194	0.806	200.2	194.3	5.9	197.4
9	3	9	265.4	261.8	1.73	0.907	0.721	0.186	0.803	200.3	195.0	5.3	197.9
10	3	11	266.3	262.5	1.99	0.899	0.721	0.178	0.802	200.3	194.2	6.1	197.4
11	5	7	269.0	262.0	2.46	0.904	0.721	0.183	0.801	200.2	194.7	5.5	197.6
12	5	9	269.0	261.9	2.49	0.903	0.721	0.182	0.800	200.3	195.3	5.0	198.1
13	5	11	269.0	262.2	2.44	0.900	0.721	0.179	0.800	200.3	195.1	5.2	198.0

[a] Dimensions: T(°C), x (= [CL]) (mol·kg^{-1}).
[b] Arithmetic mean temperature in the TR (108 temperature data).
[c] Standard deviation for 108 data.
[d] Range of the data; $R(X) = X_{max} - X_{min}$.
[e] Outlet mean kinetic data defined by eq. (12) in Table III.

TABLE V(A)
Temperature Distribution and Detailed Kinetic Data in the TR without the HEx

Temperature (°C)

i\j	1	2	3	4	5	6	7	8	9	J
1	261.7	261.4	261.2	261.0	260.8	260.7	260.7	260.6	260.4	260.0
2	265.2	265.0	264.8	264.6	264.4	264.3	264.0	263.4	261.7	260.0
3	267.4	267.2	267.0	266.8	266.6	266.4	265.8	264.5	262.1	260.0
4	269.0	268.8	268.6	268.4	268.1	267.7	266.8	264.8	262.2	260.0
5	270.1	270.0	269.8	269.5	269.2	268.5	267.2	264.9	262.3	260.0
6	271.0	270.9	270.6	270.3	269.8	268.9	267.3	264.9	262.3	260.0
7	271.7	271.5	271.3	270.9	270.2	269.1	267.3	264.8	262.2	260.0
8	272.1	272.0	271.7	271.2	270.5	269.2	267.2	264.7	262.2	260.0
9	272.4	272.3	272.0	271.5	270.6	269.2	267.1	264.6	262.2	260.0
10	272.7	272.5	272.2	271.6	270.6	269.1	266.9	264.5	262.2	260.0
11	272.8	272.7	272.3	271.6	270.5	268.9	266.8	264.4	262.1	260.0
12	272.9	272.7	272.3	271.6	270.5	268.8	266.7	264.3	262.1	260.0

Concentration of CL (mol·kg^{-1})

	1	2	3	4	5	6	7	8	9	$\bar{X}(i)$
1	2.69	2.68	2.63	2.58	2.48	2.34	2.13	1.78	1.05	2.31
2	2.13	2.11	2.06	2.01	1.91	1.77	1.57	1.25	0.78	1.76
3	1.78	1.77	1.72	1.67	1.58	1.44	1.26	1.00	0.74	1.45
4	1.53	1.52	1.48	1.42	1.34	1.22	1.06	0.87	0.73	1.24

TABLE V(A). *(Continued from the previous page.)*

										$\overline{X}(i)$
5	1.35	1.33	1.29	1.24	1.17	1.07	0.94	0.80	0.73	1.10
6	1.20	1.19	1.16	1.11	1.05	0.96	0.86	0.77	0.73	1.00
7	1.09	1.08	1.05	1.02	0.96	0.89	0.82	0.76	0.73	0.93
8	1.01	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.73	0.88
9	0.95	0.94	0.92	0.90	0.86	0.82	0.78	0.75	0.73	0.84
10	0.91	0.90	0.88	0.86	0.83	0.80	0.77	0.75	0.73	0.82
11	0.87	0.87	0.85	0.84	0.82	0.79	0.77	0.74	0.73	0.80
12	0.85	0.85	0.83	0.82	0.80	0.78	0.76	0.74	0.73	0.79

Number average degree of polymerization (P_N)

										$\overline{X}(i)$
1	102.1	102.8	105.1	108.1	113.2	121.3	134.4	156.6	191.5	123.5
2	135.2	136.0	138.8	142.4	148.3	156.8	168.5	183.4	198.1	155.9
3	156.2	157.0	159.5	162.7	167.5	173.8	181.7	190.7	198.4	172.1
4	168.8	169.4	171.4	173.8	177.4	181.9	187.3	193.4	198.3	180.4
5	176.1	176.6	178.2	180.0	182.6	185.9	190.0	194.7	198.3	184.9
6	180.4	180.9	182.1	183.5	185.5	188.2	191.5	195.3	198.2	187.4
7	183.1	183.5	184.4	185.6	187.3	189.5	192.4	195.6	198.2	188.9
8	184.8	185.1	186.0	187.0	188.4	190.4	193.0	195.8	198.2	189.9
9	186.0	186.3	187.0	187.9	189.2	191.0	193.4	195.9	198.2	190.6
10	186.8	187.0	187.6	188.5	189.7	191.4	193.6	196.1	198.3	191.0
11	187.3	187.6	188.1	188.9	190.1	191.8	193.9	196.2	198.3	191.4
12	187.7	187.9	188.5	189.2	190.4	192.0	194.1	196.3	198.3	191.6

TABLE V(B)
Temperature Distribution and Detailed Kinetic Data in the TR with the HEx at Fifth Plate

$i \backslash j$	1	2	3	4	5	6	7	8	9	J
					Temperature (°C)					
1	261.7	261.4	261.2	261.0	260.8	260.7	260.7	260.6	260.4	260.0
2	265.2	265.0	264.8	264.6	264.4	264.3	264.0	263.4	261.7	260.0
3	267.4	267.2	267.0	266.8	266.6	266.4	265.8	264.5	262.1	260.0
4	269.0	268.8	268.6	268.4	268.1	267.7	266.8	264.8	262.2	260.0
5	260.3	260.3	260.3	260.3	260.2	260.2	260.1	260.1	259.8	260.0
6	261.1	261.1	261.1	261.0	260.9	260.8	260.6	260.3	260.1	260.0
7	261.7	261.7	261.7	261.6	261.5	261.2	260.9	260.5	260.2	260.0
8	262.2	262.2	262.2	262.0	261.9	261.6	261.1	260.6	260.3	260.0
9	262.7	262.6	262.5	262.4	262.1	261.8	261.2	260.7	260.3	260.0
10	263.0	263.0	262.8	262.7	262.4	261.9	261.3	260.8	260.3	260.0
11	263.3	263.2	263.1	262.9	262.5	262.0	261.4	260.8	260.4	260.0
12	263.5	263.4	263.3	263.0	262.6	262.0	261.4	260.8	260.4	260.0
				Concentration of CL (mol·kg^{-1})						$\bar{X}(i)$
1	2.69	2.68	2.63	2.58	2.48	2.34	2.13	1.78	1.05	2.31
2	2.13	2.11	2.06	2.01	1.91	1.77	1.57	1.25	0.78	1.76
3	1.78	1.77	1.72	1.67	1.58	1.44	1.26	1.00	0.74	1.45
4	1.53	1.52	1.48	1.42	1.34	1.22	1.06	0.87	0.73	1.24

TABLE V(B).   (Continued from the previous page.)

i										$\overline{X}(i)$
5	1.41	1.40	1.36	1.31	1.23	1.11	0.97	0.82	0.73	1.16
6	1.27	1.26	1.22	1.17	1.10	1.00	0.89	0.77	0.72	1.04
7	1.17	1.16	1.13	1.08	1.02	0.93	0.83	0.75	0.72	0.97
8	1.09	1.08	1.05	1.01	0.95	0.88	0.80	0.74	0.72	0.91
9	1.02	1.01	0.99	0.95	0.90	0.84	0.77	0.73	0.72	0.87
10	0.97	0.96	0.93	0.90	0.86	0.81	0.76	0.73	0.72	0.84
11	0.93	0.92	0.89	0.87	0.83	0.79	0.75	0.73	0.72	0.81
12	0.89	0.88	0.86	0.84	0.81	0.77	0.74	0.73	0.72	0.80

Number average degree of polymerization (P_N)

| i										$\overline{X}(i)$
1	102.1	102.8	105.1	108.1	113.2	121.3	134.4	156.6	191.5	123.5
2	135.2	136.0	138.8	142.4	148.3	156.8	168.5	183.4	198.1	155.9
3	156.2	157.0	159.5	162.7	167.5	173.8	181.7	190.7	198.4	172.1
4	168.8	169.4	171.4	173.8	177.4	181.9	187.3	193.4	198.3	180.4
5	174.9	175.5	177.1	179.3	182.4	186.3	190.9	195.9	199.3	184.5
6	181.8	182.4	183.8	185.7	188.4	191.7	195.3	198.7	200.3	190.2
7	186.1	186.5	187.8	189.4	191.6	194.2	197.0	199.3	200.2	192.9
8	188.9	189.3	190.3	191.7	193.5	195.6	197.8	199.5	200.1	194.4
9	190.9	191.2	192.1	193.2	194.7	196.5	198.2	199.6	200.1	195.5
10	192.2	192.5	193.3	194.2	195.5	197.0	198.5	199.6	200.1	196.1
11	193.2	193.5	194.1	194.9	196.1	197.4	198.7	199.6	200.0	196.6
12	193.9	194.2	194.7	195.5	196.5	197.6	198.8	199.6	200.0	197.0
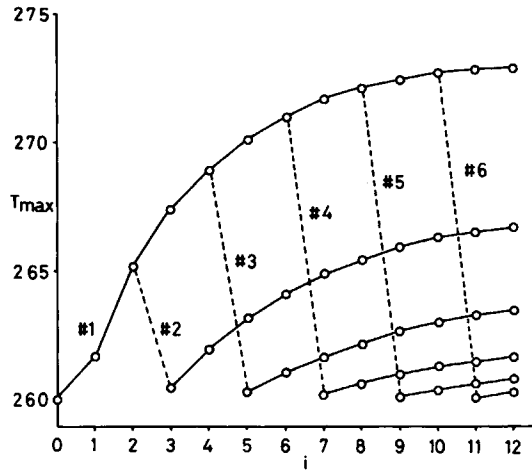
Fig. 2. Graphic representation of the maximum temperature profile in the TR with one HEx. The maximum temperature in each plate of the TR was plotted by the open circle against the plate number (i) and traced by the solid line. The trace by the broken line indicates the position of the HEx in the TR. The number denoted by (#) such as # 1, # 2, etc., in the figure corresponds to the case number listed in Table IV.

Figure 2 covers the TR's without and with one HEx (cases 1–6), and Figure 3 covers the TR's with two HEx's (cases 7–10). From these two figures, it is evident that the maximum temperature in the TR can be controlled by introducing one or two HEx's. The TR's with two HEx's (cases 7–9) are found to be more preferable to reduce the maximum temperature in each plate of the TR.

From the temperature data for each case listed in Table IV, it is found that the arithmetic mean temperature in the TR and its standard deviation could be interpreted as a function of the position and/or number of the HEx's in the
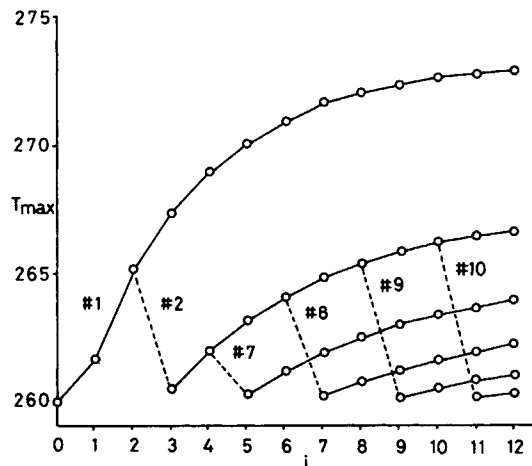
Fig. 3. Graphic representation of the maximum temperature profile in the TR with two HEx's. The maximum temperature in each plate of the TR was plotted by the open circle against the plate number (i) and traced by the solid line. The trace by the broken line indicates the position of the HEx in the TR. The number denoted by (#) such as # 7, # 8, etc., in the figure corresponds to the case number listed in Table IV.
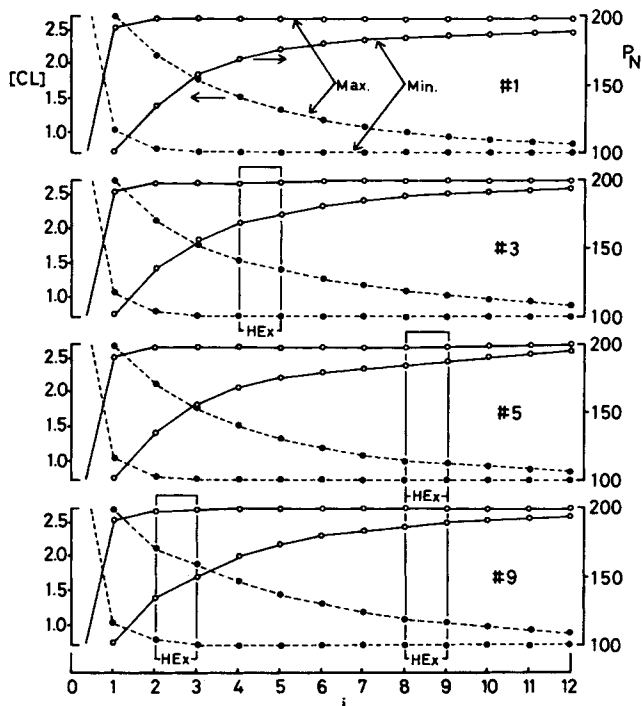
Fig. 4. Graphic representation of the profiles of the maximum and minimum characteristic data of the polymerization in the TR with the HEx's, where the data in each plate are plotted against the plate number (i) of the TR. The graphs shown by the open circle and solid line and by the closed circle and broken line correspond to the number average degree of polymerization and CL concentration, respectively. The number denoted by ($\#$) in the figure signifies the case number listed in Table IV. The positions of the HEx's are directly shown in the figure.

TR. From the point of view of the standard deviation which is a measure of the unevenness of the temperature in the TR, the cases 2 and 3 (with one HEx) and cases 7–13 (with two HEx's) are preferable, so that at least one HEx positioned at the upper half of the TR (e.g., at i = 3, 4, or 5) is to be recommended. Based upon those temperature data, it is strongly suggested that the mean temperature and its standard deviation can be controlled by changing the position and number of the HEx's.

Effect of HEx on the yield. The yield of the polymerization can be evaluated from the concentration data of CL, so that the CL concentration is dealt with in this section. The intermediate thirds of Table VA and Table VB demonstrate the distribution of the CL concentration in the TR. Comparing these two sets of the data, a slight influence of the HEx is found on the distribution of the CL concentration in the TR. The similar fact can also be seen in Figure 4, where the maximum concentration of CL (the upper graph) and minimum concentration of CL (the lower graph) in each plate were plotted against the plate number (i) by the closed circle and traced by the broken line.

The concentration data of CL at the outlet of the TR listed in Table IV suggest that the effect of the HEx is to increase the range of the CL concentration (i.e., the unevenness in the CL concentration) and the mean value in most cases. Although this effect is not advantageous for the polymerization in the industry,

the amount of the deviation from the control (the case 1) is as slight as the experimental measurement of the CL concentration by the gas chromatographic method could distinguish it with some difficulty.

Effect of HEx on the degree of polymerization. The lower thirds of Tables VA and VB demonstrate the detailed distribution of the number average degree of polymerization (P_N) in the TR's. From the tables, the considerable influence of the HEx is recognized on the distribution of the P_N in the TR.

Figure 4 is the schematic representation of the maximum P_N value (the upper graph) and minimum P_N value (the lower graph) in each plate, which is plotted against the plate number by the open circle and traced by the solid line. It is clear that the cases 3, 5, and 9 have the narrower differences in value between the maximum P_N and minimum P_N graphs than that of the control (the case 1).

The calculated data of the P_N at the outlet of the TR listed in Table IV also suggest that the HEx is very effective in reducing the range defined by $P_N^{max} - P_N^{min}$ and that the narrower range is established by setting the HEx at the lower half of the TR (e.g., at $i = 7, 8$, or 9). It should be pointed out here that the range has a close relation with the molecular weight distribution of the outlet polymer product and with reducing the range, the molecular weight distribution converges to a certain distribution which is to be described by the Schultz–Zimm distribution function.[12]

Conclusive remarks. The simulation model and its algorithm for the numerical calculation presented in this report were well proved to be very effective for elucidating the performance of the TR with the HEx's. From the present investigations for 13 cases of the TR with the HEx's, the following conclusions were derived; (1) the HEx at the upper half of the TR is advantageous for narrowing the temperature distribution in the TR; (2) the HEx at the lower half of the TR is advantageous for narrowing the molecular weight distribution of the outlet polymer; (3) the HEx has a slight adverse influence on the outlet yield. Experimental verification by the plants is expected in future.

References

1. K. Tai, Y. Arai, and T. Tagawa, *J. Appl. Polym. Sci.*, **27**, 731 (1982).
2. BASF, Jpn. Kokoku Tokkyo Koho 45-23952 (1970); Toray, Jpn. Kokoku Tokkyo Koho, 48-3916 (1973); Toyoboseki, Jpn. Kokoku Tokkyo Koho, 48-37152 (1973); Toyoboseki, Jpn. Kokoku Tokkyo Koho, 49-6198 (1974); Toyoboseki, Jpn. Kokoku Tokkyo Koho, 49-26314 (1974); Toyoboseki, Jpn. Kokoku Tokkyo Koho, 49-37705 (1974).
3. K. Tai, H. Teranishi, Y. Arai, and T. Tagawa, *J. Appl. Polym. Sci.*, **24**, 211 (1979).
4. H. K. Reimschuessel, *J. Polym. Sci., Macromol. Rev.*, **12**, 65 (1977).
5. Y. Arai, K. Tai, H. Teranishi, and T. Tagawa, *Polymer*, **22**, 273 (1981).
6. K. Tai, H. Teranishi, Y. Arai, and T. Tagawa, *J. Appl. Polym. Sci.*, **25**, 77 (1980).
7. Y. Murakami and D. Miura, *Kagaku Kogaku*, **28**, 601 (1964).
8. Unitika, Jpn. Kokoku Tokkyo Koho 49-38113 (1974).
9. *Encyclopedia of Chemical Technology*, H. F. Mark, Ed., 2nd ed., Wiley, New York, 1968, Vol. 16, p. 32.
10. P. Cefelin, J. Trekoval, and Z. Drbalek, *Collect. Czech. Chem. Commun.*, **24**, 2890 (1959).
11. I. Hamana, *Seni no Keisei to Kozo no Hatsugen*, The Society of Fiber Science and Technology, Ed., Kagakudojin, Kyoto, 1969, Chap. 5, p. 123.
12. K. Tai, Y. Arai, H. Teranishi, and T. Tagawa, *J. Appl. Polym. Sci.*, **25**, 1789 (1980).