

## Diffusion of Water and Caprolactam in Nylon 6 Melts

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### Synopsis

The diffusions of both caprolactam and water from nylon 6 melts have been measured using a semiinfinite geometry. The process involving diffusion and chemical reaction was analyzed utilizing Higbie's penetration model and known kinetic data. The caprolactam and water diffusion coefficients are, respectively,  $8 \times 10^{-8}$  and  $2.5 \times 10^{-4}$  cm<sup>2</sup>/sec. Using the data, molecular weight profiles were obtained for both semiinfinite and cylindrical geometries as a function of melt depth and time.

### INTRODUCTION

Recently we discussed the optimization of the water-initiated polymerization of caprolactam for a number of idealized processes.<sup>1,2</sup> The results favored a two-stage process entailing plug flow. Polymerization to a high conversion at a high initial water concentration characterized the first stage, whereas rapid removal of water and attainment of a final molecular weight by condensation between endgroups were the principal features of the second stage. In analyzing the considered process, both temperature and water concentration were identified as the main process variables, and it was recognized that the actual performance may considerably be affected by a number of operational parameters. Among these, the rate of water removal in the second stage appeared to be of particular significance because of its direct effect on the rate of the subsequent polycondensation and thus the total reaction time. Since the removal of water from the polymer is obviously governed by mass transfer rates, this study has been concerned primarily with the diffusion of water in the polymer melt. In addition, consideration has also been given to parameters related to the mass transport of caprolactam which is always present in appreciable amounts because of the polymer-monomer equilibrium. The removal of caprolactam from the equilibrium polymer does not affect the rates of conversion and polycondensation but is important for continuous integrated operations.

In this paper, we shall report on investigations designed to estimate diffusion coefficients for both water and caprolactam in melts of nylon 6

equilibrium polymers. Computations will be presented for a number of simple processes to assess the significance of the results of this study.

### MATHEMATICAL DEVELOPMENT

A main criterion for selecting approaches for the treatment of the problem considered in this study has been the accommodation of reequilibrium reactions, occurring as a direct consequence of the polymerization equilibrium. It is known that the reactions governing the polymerization of caprolactam are reversible and that caprolactam and water are principal components of the corresponding polymerization equilibrium. Their removal affects, therefore, both composition and molecular weight of the polymer. This equilibrium has been well investigated, and the three main reactions, (1) ring opening, (2) condensation, and (3) addition, are listed in Table I.

The process considered here is an unsteady-state operation involving simultaneous diffusion and reaction. Several kinetic theories dealing with simultaneous diffusion and reaction have been developed.<sup>3-8</sup> The most widely used one is the penetration theory of Higbee.<sup>9</sup> This model was considered most suitable for analyzing the experimental data of the present study. To write the corresponding mathematical expressions, it was assumed that: (1) the surface of the melt-gas interface was quiet and uniform; (2) transport occurred by one-dimensional, isothermal molecular diffusion; (3) factors such as hydrogen bonding were insignificant; (4) diffusion of polymer chains was much slower than that of water and caprolactam; (5) diffusion coefficients were independent of polymer molecular weight; and (6) diffusion coefficients of water and caprolactam were mutually independent.

TABLE I

|   | EQUILIBRIUM REACTIONS<br>( $K_i = k_i / k_i'$ )   | $\log K = \Delta S/4.574 - \Delta H/(4.574T)$ |                    |
|---|---|---|--------------------|
|   |   | $\Delta H$ (cal./mole)                        | $\Delta S$ (e. u.) |
| 1 | $\underbrace{\text{HN}-(\text{CH}_2)_5-\text{C}=\text{O}}_M + \text{H}_2\text{O} \xrightleftharpoons[k_i']{k_i} \text{H}_2\text{N}-(\text{CH}_2)_5-\text{COOH}$   | 2114.2  | -7.87              |
| 2 | $\begin{array}{c} \text{H}[\text{HN}-(\text{CH}_2)_5-\text{C}=\text{O}]_m\text{OH} + \text{H}[\text{HN}-(\text{CH}_2)_5-\text{C}=\text{O}]_n\text{OH} \xrightleftharpoons[k_2']{k_2} \text{H}[\text{HN}-(\text{CH}_2)_5-\text{C}=\text{O}]_{n+m}\text{OH} + \text{H}_2\text{O} \\ \text{---COOH} + \text{H}_2\text{N} \text{---} \xrightleftharpoons[k_2']{k_2} \text{---CONH} \text{---} + \text{H}_2\text{O} \\ c \qquad \qquad \qquad a \qquad \qquad \qquad z \qquad \qquad \qquad w \end{array}$ | -6140.4                                       | 0.93               |
| 3 | $\begin{array}{c} \text{HO}[\text{O}=\text{C}-(\text{CH}_2)_5-\text{NH}]_n\text{H} + \text{O}=\text{C}-(\text{CH}_2)_5-\text{NH} \xrightleftharpoons[k_3']{k_3} \text{HO}[\text{O}=\text{C}-(\text{CH}_2)_5-\text{NH}]_{n+1}\text{H} \\ \text{---NH}_2 + M \xrightleftharpoons[k_3']{k_3} S_{n+1} \\ a \qquad \qquad M \qquad \qquad \qquad S_{n+1} \end{array}$  | -4028.3                                       | -6.95              |

TABLE II

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$$r_M = -(k_1^o + k_1^c [s] m_o) \left( [M][W] m_o - \frac{[s_1]}{K_1} \right) - (k_3^o + k_3^c [s] m_o) \left( [M][s] m_o - \frac{[s] - [s_1]}{K_3} \right)$$

$$r_w = m_o (k_2^o + k_2^c [s] m_o) \left( [s]^2 - [W] \frac{1 - [s] - [M]}{K_2} \right) - (k_1^o - k_1^c [s] m_o) \left( [M][W] m_o - \frac{[s_1]}{K_1} \right)$$

$$r_{s_1} = (k_1^o + k_1^c [s] m_o) \left( [M][W] m_o - \frac{[s_1]}{K_1} \right) - 2 m_o (k_2^o + k_2^c [s] m_o) \left( [s][s_1] - [W] \frac{[s] - [s_1]}{K_2} \right) - (k_3^o + k_3^c [s] m_o) \left( [M] m_o - \frac{[s_1]}{K_3} \right)$$

$$m_o = 10^3 \left[ 113.16 + 18.016 ([W]_e + [s]_e) \right]^{-1} \quad (\text{moles/kg})$$


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The relevant differential equations can now be written as

$$\frac{\partial [w]}{\partial t} = D_w \left\{ \frac{\partial^2 [w]}{\partial x^2} + \frac{\lambda}{x} \frac{\partial [w]}{\partial x} \right\} + r_w \quad (1)$$

$$\frac{\partial [M]}{\partial t} = D_M \left\{ \frac{\partial^2 [M]}{\partial x^2} + \frac{\lambda}{x} \frac{\partial [M]}{\partial x} \right\} + r_M \quad (2)$$

$$\frac{d[s]}{dt} = -r_w \quad (3)$$

$$\frac{d[s_1]}{dt} = r_{s_1} \quad (4)$$

In these equations  $[M]$  = caprolactam concentration, dimensionless;  $[w]$  = water concentration, moles/mole of caprolactam;  $[s_1]$  = amino-caproic acid concentration, moles/mole of caprolactam;  $[s]$  = polymer chain concentration, moles/mole of caprolactam;  $x$  = distance in the direction of diffusion, cm;  $t$  = time, hr;  $r_w$ ,  $r_M$ ,  $r_{s_1}$  = rate of production of respective species through chemical reactions, moles/hr;  $D_M$ ,  $D_w$  = diffusion coefficients of caprolactam and water, cm<sup>2</sup>/hr; and  $\lambda$  = geometric factor, dimensionless. Expressions for  $r_M$ ,  $r_w$ , and  $r_s$  are given in Table II.

Equations (1) through (4) form a system of nonlinear equations that are solved conveniently by assuming that (a) the melt is initially under equilibrium, and (b) the interfacial water and caprolactam concentrations  $[w]_{if}$  and  $[M]_{if}$  are held constant. The boundary conditions are:

(i) For a semiinfinite geometry ( $\lambda = 0$ ):

$$[w] = [w]_e, [M] = [M]_e, [s] = [s]_e, [s_1] = [s_1]_e$$

$$\text{at } t = 0, x \geq 0 \text{ and at } t > 0, x = \infty$$

where the subscript  $e$  refers to equilibrium concentrations.

$$[w] = [w]_{if}, [M] = [M]_{if} \quad \text{at } t > 0, x = 0.$$

(ii) For a plane sheet ( $\lambda = 0$ ), a cylinder ( $\lambda = 1$ ) or a sphere ( $\lambda = 2$ ):

$$[w] = [w]_e, [M] = [M]_e, [s] = [s]_e, [s_1] = [s_1]_e \quad \text{at } t = 0, 0 \leq x \leq x_0$$

$$[w] = [w]_{if}, [M] = [M]_{if} \quad \text{at } t > 0, x = 0$$

$$\frac{\partial [w]}{\partial x} = \frac{\partial [M]}{\partial x} = \frac{\partial [s]}{\partial x} = \frac{\partial [s_1]}{\partial x} = 0 \quad \text{at } t > 0, x = x_0.$$

The rates of desorption of water and caprolactam through the melt-gas interface at time  $t$  are given by

$$N_w = D_w \left( \frac{\partial [w]}{\partial x} \right)_{x=0} \quad (5)$$

$$N_M = D_M \left( \frac{\partial [M]}{\partial x} \right)_{x=0} \quad (6)$$

The average desorption rates over a given time interval ( $t_1, t_2$ ) are given by

$$\bar{N}_w = \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} N_w dt \quad (7)$$

$$\bar{N}_M = \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} N_M dt. \quad (8)$$

The net water diffusion rate at depth  $x$  is given by

$$\begin{aligned} \frac{\partial [w_a]}{\partial t} &= D_w \left( \frac{\partial [w]}{\partial x} \right)_x - D_w \left( \frac{\partial [w]}{\partial x} \right)_{x+\Delta x} \\ &= -D_w \left\{ \frac{\partial^2 [w]}{\partial x^2} + \frac{\lambda}{x} \frac{\partial [w]}{\partial x} \right\} \\ &= -\frac{\partial [w]}{\partial t} - \frac{\partial [s]}{\partial t}. \end{aligned} \quad (9)$$

Using the boundary conditions  $[w_a] = 0$ ,  $[w] = [w]_e$ ,  $[s] = [s]_e$  at  $t = 0$ , we get the expression for the amount of water diffusing out of the melt at any  $x$  and  $t$  as

$$\begin{aligned} [w_a] &= [w]_e + [s]_e - [w] - [s] \\ &= [w]_0 - [w] - [s] \end{aligned} \quad (10)$$

where  $[w]_0 = [w]_e + [s]_e$  is the amount of water used in obtaining the equilibrium polymer at  $t = 0$ .

The expression for the net rate of caprolactam diffusion is obtained in an analogous manner:

$$\frac{\partial [M_a]}{\partial t} = -D_M \left\{ \frac{\partial^2 [M]}{\partial x^2} + \frac{\lambda}{x} \frac{\partial [M]}{\partial x} \right\}$$

whence

$$[M_d] = -D_M \left( \frac{\partial^2}{\partial x^2} + \frac{\lambda}{x} \frac{\partial}{\partial x} \right) \int_0^t [M_d] dt \quad (11)$$

and  $M_d$  = concentration of monomer diffused out of volume element.

The average degree of polymerization is given according to the relation

$$\bar{P}_n = \frac{1 - [M] - [M_d]}{[s]}$$

Since  $[M_d] \ll [M]$ , the approximate expression

$$\bar{P}_n = \frac{1 - [M]}{[s]} \quad (12)$$

will be adequate in most instances.

In applying the data to geometries other than semiinfinite ones, it is often convenient to evaluate average quantities of the polymeric material. At any time  $t$ , these are given<sup>13</sup> as

$$[\bar{w}] = \frac{\lambda + 1}{x_0^{\lambda+1}} \int_0^{x_0} [w] x^\lambda dx \quad (13)$$

$$[\bar{s}] = \frac{\lambda + 1}{x_0^{\lambda+1}} \int_0^{x_0} [s] x^\lambda dx \quad (14)$$

$$[\bar{M}] = \frac{\lambda + 1}{x_0^{\lambda+1}} \int_0^x [M] x^\lambda dx. \quad (15)$$

The average degree of polymerization may be computed again from the simplified relationship

$$\bar{P}_n = \frac{1 - [\bar{M}]}{[\bar{s}]} \quad (16)$$

### SOLUTION

The nonlinear eqs. (1) through (4) were solved numerically, using known kinetic parameters. The parameters used in the present work have been summarized in Table III. Solutions for the various reactor geometries were obtained by using algorithms derived by Secor and Beutler.<sup>10</sup> Calculations were carried out in an IBM 370/50 computer.

TABLE III  
Rate Constants<sup>a,1</sup>

| $k_i^0$ , kg $\times$ mole <sup>-1</sup> $\times$ hr <sup>-1</sup><br>$k_i^c$ , kg <sup>2</sup> $\times$ mole <sup>-2</sup> $\times$ hr <sup>-1</sup> | A                   | E, cal/mole |
|---|---------------------|-------------|
| $k_1^0$   | 16.94 $\times 10^6$ | 21,040      |
| $k_1^c$   | 41.06 $\times 10^6$ | 18,753      |
| $k_2^0$   | 86.87 $\times 10^6$ | 22,550      |
| $k_2^c$   | 23.37 $\times 10^9$ | 20,674      |
| $k_3^0$   | 26.20 $\times 10^8$ | 21,269      |
| $k_3^c$   | 23.72 $\times 10^9$ | 20,400      |

<sup>a</sup>  $\log k = \log A - E/(4.574T)$ .

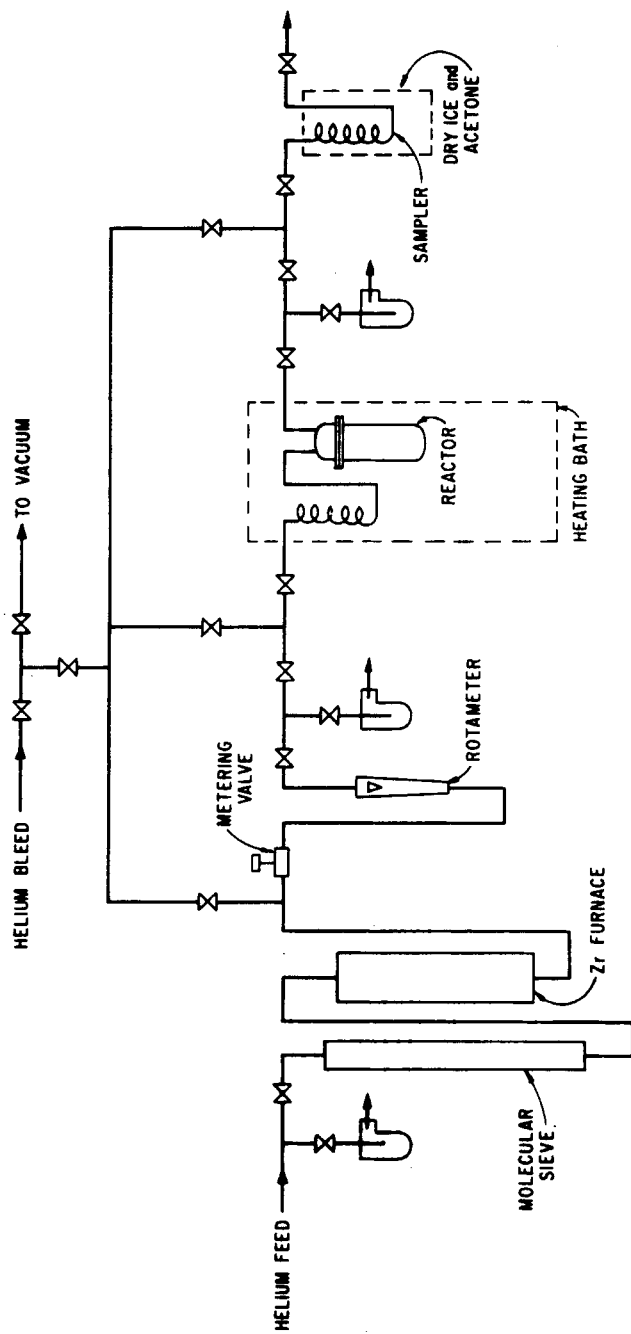


Fig. 1. Schematic diagram of equipment.

## EXPERIMENTAL

## Apparatus and Procedures

Both process and reactor were designed to approximate as closely as possible a semiinfinite medium since the required boundary conditions could be most easily realized with this geometry. The equipment flow sheet and reactor details are shown in Figures 1 and 2, respectively. All parts of the system that were in contact with water and caprolactam were made of stainless steel. Helium was used as an inert carrier gas; it was purified from any traces of water or oxygen by passing it through molecular sieves and heated zirconium sponge. A constant flow rate was maintained with aid of a metering valve. Preheating of the helium by passing it through a heated coil afforded isothermal operation.

In order to obtain the equilibrium polymer, water and caprolactam were placed into the reactor while maintaining a helium atmosphere. The system was then closed and heated for about 20 hr to  $265^{\circ} \pm 1^{\circ}\text{C}$ . The amount of the material in the reactor corresponded to a melt depth of about 7 cm. At the end of the polymerization period the reactor was depressurized, and a stream of helium was passed through the system at a constant rate of  $150 \pm 2 \text{ cm}^3/\text{min}$ . It was assumed that at these conditions constant interfacial concentrations with respect to water,  $[w]_{if}$ , and caprolactam,  $[M]_{if}$ , would be maintained. The exit gas was fed into U-tube traps cooled in a Dry Ice-acetone mixture. The concentrations of the condensed water and caprolactam were determined gas chromatographically at definite intervals.

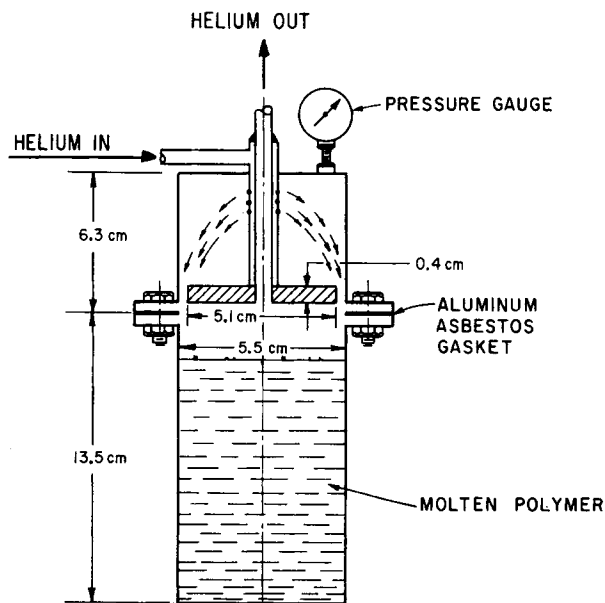


Fig. 2. Reactor detail.

Condensation in connecting lines was prevented by heating them with electrical tapes. At the end of the diffusion experiment, the reactor was immersed into ice water to quench the polymer, which was then cut into thin parallel slices, which were then analyzed to determine the molecular weight and composition profiles. To eliminate errors due to nonuniform quenching, the central core of the samples was discarded.

### Analysis of the Polymer

The composition of the polymer was determined by hot water extraction. The extractable fraction consisted mainly of caprolactam. In addition, it also contained some linear and cyclic oligomers. The number-average degree of polymerization was estimated from the viscosity of polymer solutions in *m*-cresol as described earlier.<sup>11</sup>

### EXPERIMENTAL DATA

Average diffusion rates for water and caprolactam as determined from the composition of the gas phase are summarized in Table IV.

Data on the composition and molecular weight profiles as functions of time are listed in Table V.

TABLE IV  
Results of vapor analysis<sup>a</sup>

| Sample no. | Time, hr | Average diffusion rates, mg/hr |            | $\frac{N_w}{N_M}$ |
|------------|----------|--------------------------------|------------|-------------------|
|            |          | Area $N_w$                     | Area $N_M$ |                   |
| 1          | 0.40     | 25.6                           | 4.00       | 6.4               |
| 2          | 0.42     | 78.0                           | 26.60      | 2.93              |
| 3          | 1.00     | 47.0                           | 5.80       | 8.10              |
| 4          | 1.70     | 66.2                           | 10.92      | 6.06              |
| 5          | 2.87     | 7.20                           | 1.08       | 6.6               |
| 6          | 3.07     | 22.80                          | 2.04       | 11.1              |
| 7          | 3.79     | 16.17                          | 0.64       | 25.26             |
| 8          | 4.12     | 7.92                           | 5.15       | 1.5               |
| 9          | 5.15     | 26.50                          | 3.72       | 7.1               |
| 10         | 6.12     | 15.94                          | 2.32       | 6.8               |

<sup>a</sup>  $A$  = Area of diffusion = 0.238 cm<sup>2</sup>.

### EVALUATION OF EXPERIMENTAL DATA

The estimation of the diffusion parameters necessitated some trial-and-error operations. Plots of  $(AN)_t$  versus time and  $\bar{P}_n$  versus melt depths were made using the data listed in Tables IV and V. Taking into account an assumed content of 3% of water-soluble oligomers, the surface monomer concentration  $[M]_{if}$  was estimated to  $3 \pm 0.5\%$  by extrapolation of the measured extractable contents from various melt depths to the surface. The unknown parameters  $[w]_{if}$ ,  $D_w$ , and  $D_w/D_M$  were then used in the trial-and-error procedures to find the best fit for the



TABLE V  
Analysis of Molecular Weight Gradient

| Sample no.                       | Slice thickness, mm | Av. distance from melt surface, mm | % Extractables | $\frac{[\eta]sp}{c}$ | $P_n$ |
|----------------------------------|---------------------|------------------------------------|----------------|----------------------|-------|
| (A) Diffusion Time $t = 1.10$ hr |                     |                                    |                |                      |       |
| 1                                | 2.5                 | 1.3                                | ...            | 1.93                 | 230   |
| 2                                | 3.5                 | 4.3                                | 9.28           | 1.86                 | 220   |
| 3                                | 3                   | 7.5                                | 11.77          | 1.79                 | 204   |
| 4                                | 3                   | 10.5                               | 12.0           | 1.79                 | 204   |
| 5                                | 3.5                 | 13.7                               | 11.9           | 1.76                 | 203   |
| 6                                | 3.5                 | 17.2                               | 12.0           | 1.74                 | 202   |
| (B) Diffusion time $t = 3.94$ hr |                     |                                    |                |                      |       |
| 1                                | 8                   | 4                                  | 8.48           | 2.46                 | 310   |
| 2                                | 3.5                 | 9.8                                | 12.3           | 2.19                 | 268   |
| 3                                | 4                   | 13.5                               | 11.9           | 11.92                | 230   |
| 4                                | 2                   | 16.5                               | 11.92          | 1.94                 | 234   |
| 5                                | 2.5                 | 18.8                               | 12.0           | 1.81                 | 212   |
| 6                                | 2.0                 | 21.0                               | 12.15          | 1.77                 | 207   |
| 7                                | 2.0                 | 23.0                               | 12.3           | 1.68                 | 195   |
| 8                                | 3.5                 | 29.3                               | ...            | 1.82                 | 214   |
| 9                                | 7.5                 | 45.8                               | 12.2           | 1.63                 | 188   |
| (C) Diffusion Time $t = 6.17$ hr |                     |                                    |                |                      |       |
| 1                                | 1.5                 | 0.8                                | ...            | 2.97                 | 400   |
| 2                                | 2.5                 | 2.7                                | 8.0            | 2.96                 | 390   |
| 3                                | 3.5                 | 5.7                                | 10.15          | 2.41                 | 305   |
| 4                                | 3.0                 | 9.0                                | 12.1           | 2.16                 | 265   |
| 5                                | 3.0                 | 12.0                               | 12.1           | 2.08                 | 250   |
| 6                                | 3.5                 | 15.2                               | 12.3           | 1.95                 | 236   |
| 7                                | 4.0                 | 19.0                               | 12.5           | 2.02                 | 245   |
| 8                                | 5.0                 | 28.5                               | 12.8           | 1.85                 | 215   |
| 9                                | 3.5                 | 37.8                               | 13.0           | 1.78                 | 206   |
| 10                               | 4.5                 | 45.8                               | 13.4           | 1.78                 | 206   |
| 11                               | 11.0                | 57.0                               | 13.2           | 1.71                 | 195   |

plotted data. The values listed below for the considered quantities correspond to the solid lines shown in Figures 3 and 4 (the symbols in these figures represent the experimental data):

$$D_w = (2.5 \pm 0.5) \times 10^{-4} \text{ cm}^2/\text{sec}$$

$$D_M = 8 \times 10^{-8} \text{ cm}^2/\text{sec} \text{ (average value; extreme values were } 1 \times 10^{-8} \text{ and } 15 \times 10^{-8} \text{ cm}^2/\text{sec)}$$

$$[w]_{if} = 0.0016 \pm 0.0002 \text{ mole/mole of caprolactam}$$

$$[M]_{if} = 0.03 \pm 0.005$$

Assuming a constant partial pressure at the melt-gas interface, an overall mass transfer coefficient  $k_t^m$  may in a first approximation be estimated

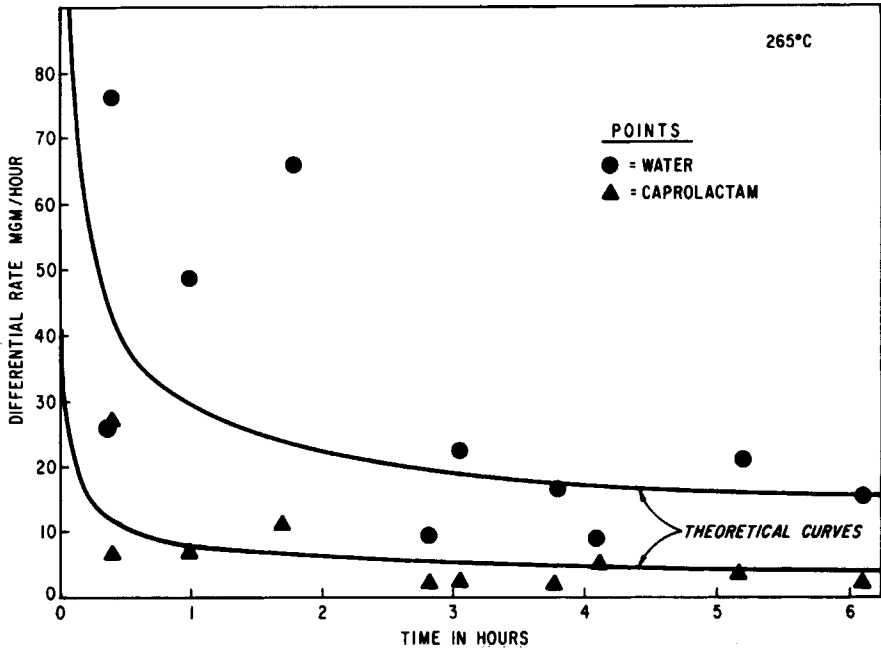


Fig. 3. Evolution rates of water and caprolactam as function of time.

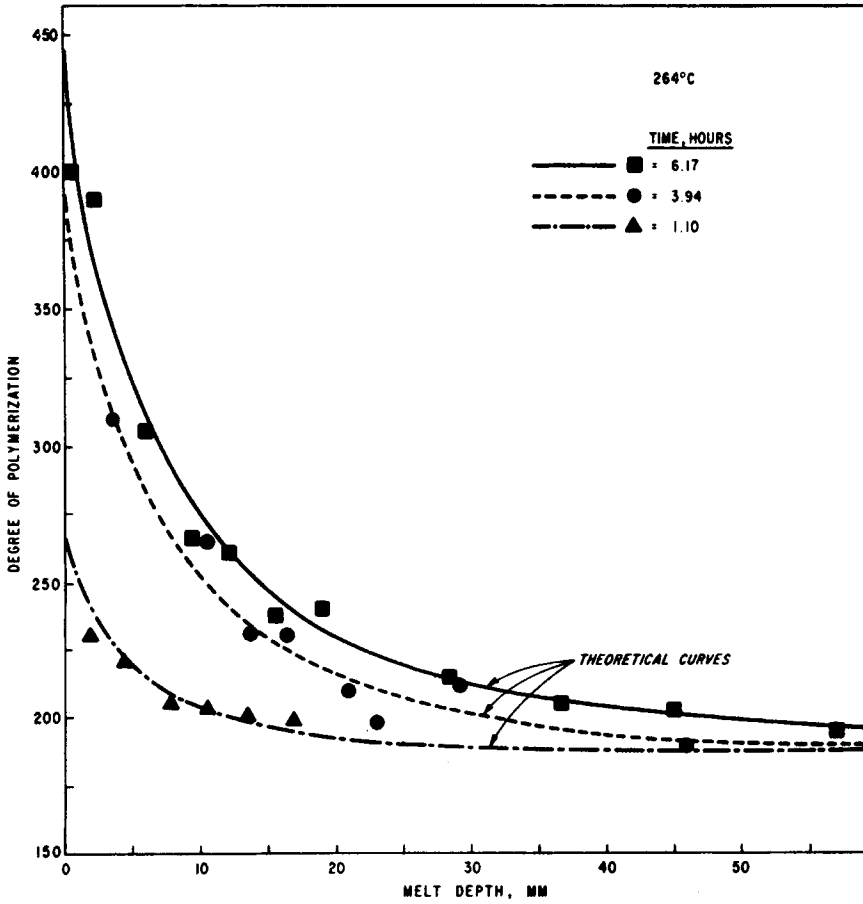


Fig. 4. Molecular weight as function of melt depth.

from the simple relationship  $N_i = k_i^m p_i$ , where  $p_i$  is the corresponding partial pressure. For the conditions and the reactor geometry employed in this study, values for  $k_w^m$  and  $k_M^m$  of 0.15 and 0.59 g cm<sup>-2</sup> hr<sup>-1</sup> atm<sup>-1</sup>, respectively, were obtained from plots of  $N_i$  versus  $p_i$ .

DISCUSSION

Examination of the results shows that the diffusion of water out of the melt is very rapid and appears to be governed primarily by the boundary

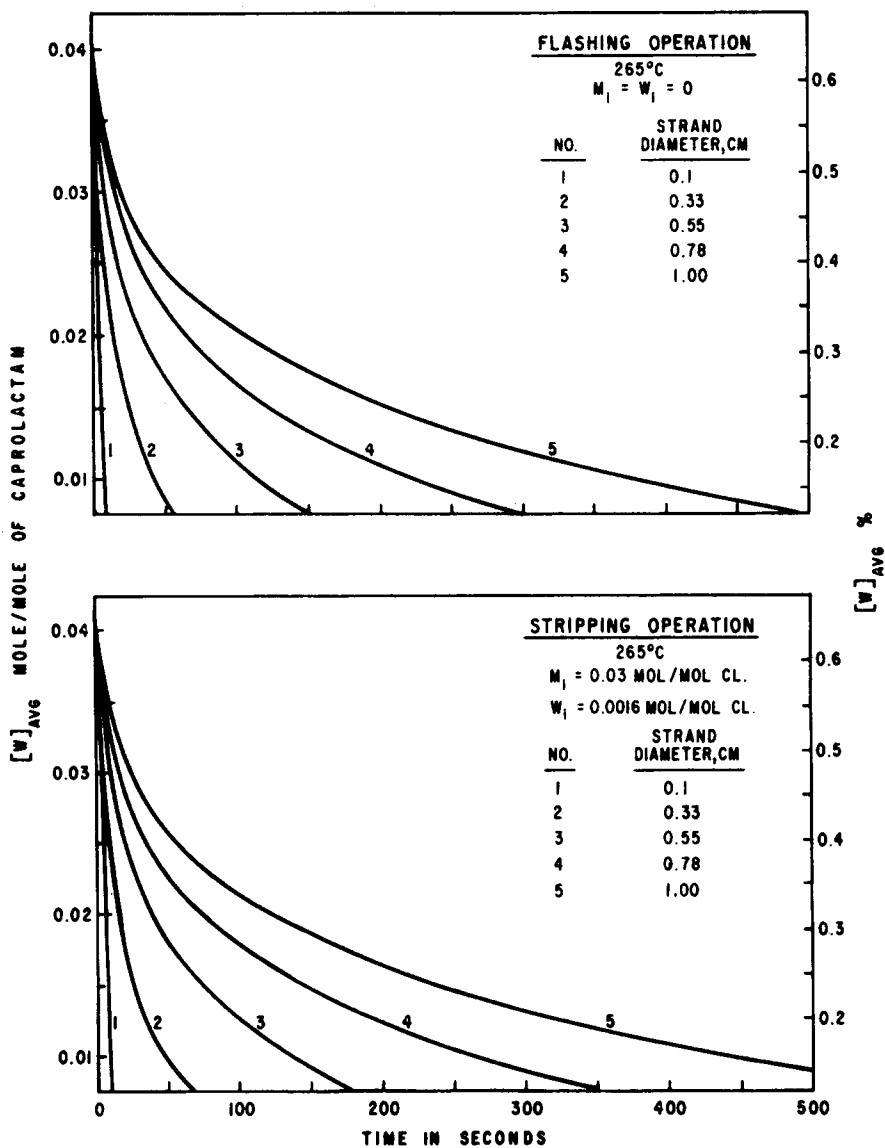


Fig. 5. Changes in average water concentrations in cylindrical geometrics, as a function of time.

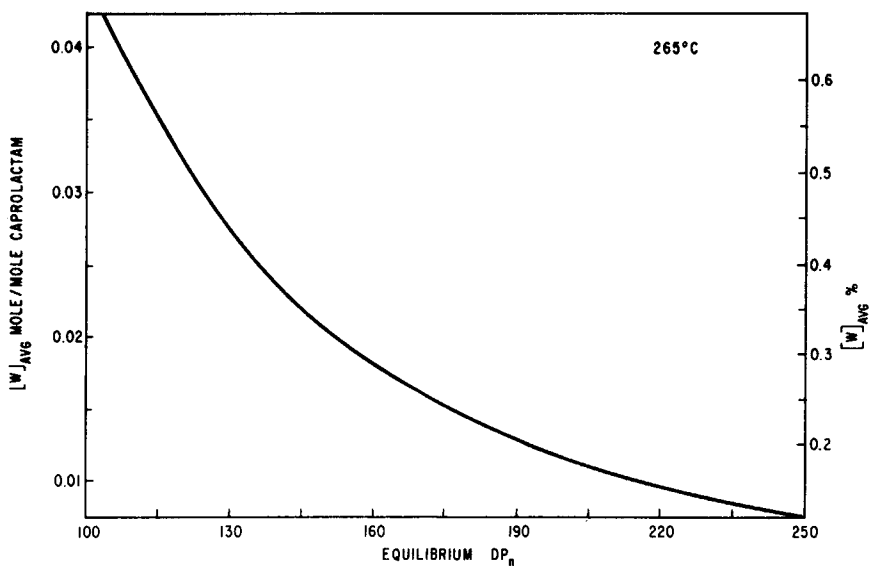


Fig. 6. Average equilibrium water concentrations as a function of degree of polymerization.

condition for the melt surface rather than the extent and rate of surface generation. These boundary conditions themselves are controlled by the respective modes of operation which may be characterized by the use of steam pressure, inert gas flow, or vacuum.

A rather different situation, however, prevails with respect to the caprolactam in the equilibrium polymer. Due to the low value of  $D_M$ , the rate at which caprolactam evaporates from the polymer melt depends mainly upon the surface area and thus on the rate of surface regeneration. Processes characterized by the direct vaporization of caprolactam from the polymer melt require therefore more sophisticated operations and equipment than the more conventional ones in which the unreacted monomer is removed from the quenched polymer by hot water extraction.

To demonstrate an application of the results of this study, the  $D_w$ ,  $D_M$ ,  $[w]_{if}$ , and  $[M]_{if}$  values listed above were used to calculate the rates of water removal isothermally at 265°C from a long, circular cylinder assuming exclusively radial diffusion. Considering an equilibrium polymer having a molecular weight of 12,000 ( $\bar{P}_n = 106$ ), the change in the average water concentration was calculated according to eq. (13) for the case that this polymer were suddenly subjected to either a stream of dry, inert gas (stripping) or vacuum (flashing). The boundary conditions for the former were taken from our experimental data, whereas limiting values were assumed for the vacuum operation. The results are shown in Figure 5.

It can be seen that for the considered polymer, the average water concentration can be reduced to about 25% in less than 10 sec for strands as thick as 0.1 cm. If the polymerization is then to be continued in a closed

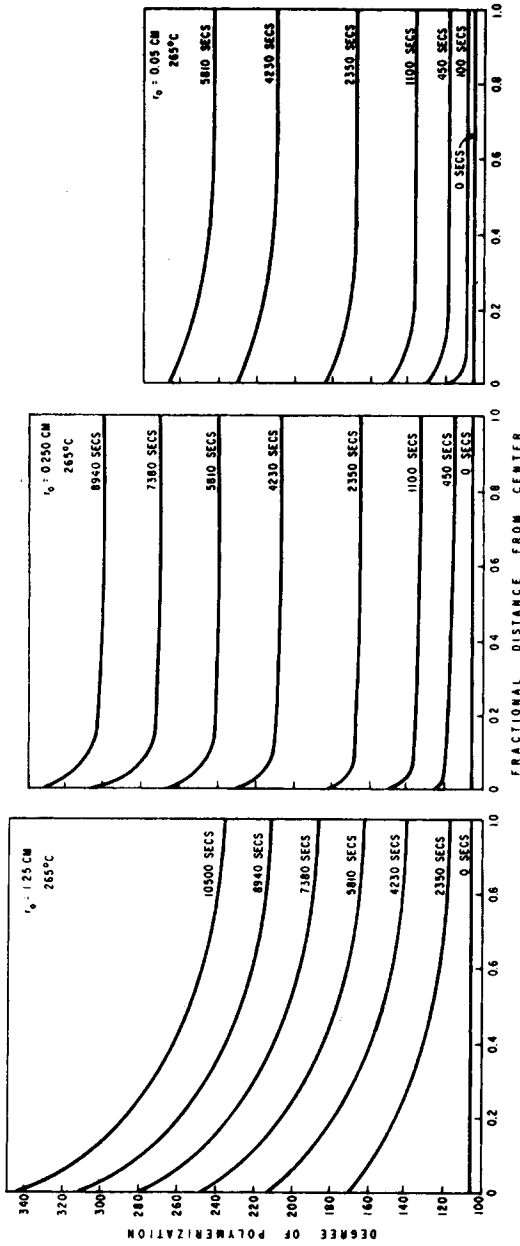


Fig. 7. Molecular weight profiles for cylindrical geometries in flashing operation  $\{[w]_{ir} = 0 \text{ for } t > 0\}$ , as a function of  $t$  and  $x$ .

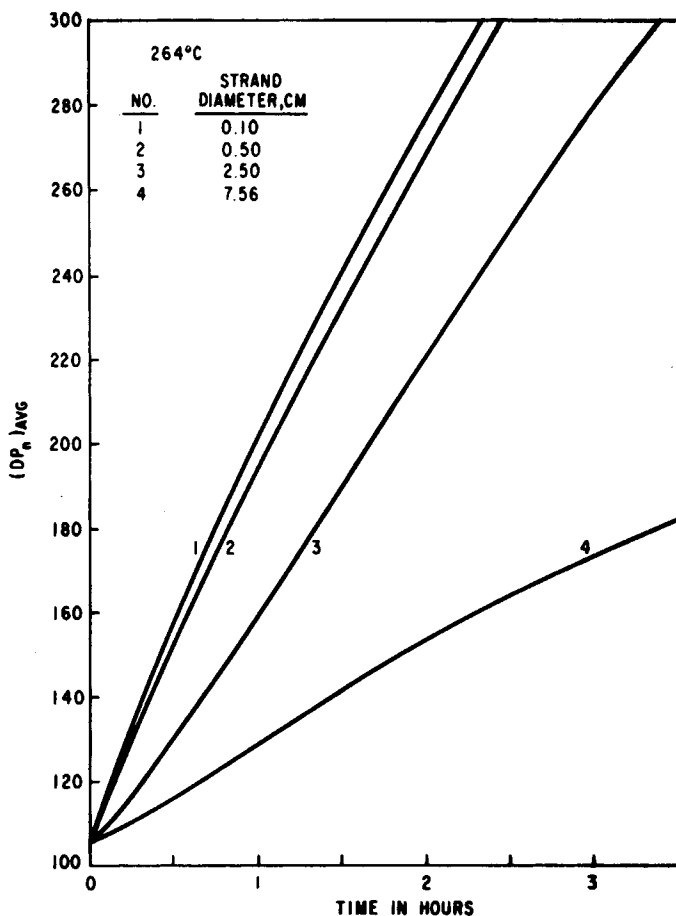


Fig. 8. Increase of the average molecular weight as a function of reaction time for cylindrical geometry.

system, the average degree of polymerization of the resulting equilibrium polymer will then according to Figure 6 be in excess of 200. The relationship pertaining to Figure 6 has been reported elsewhere.<sup>12</sup>

The molecular weight profiles for different strand diameters as a function of time are shown in Figure 7. This figure shows that at low strand diameters, the molecular weights are rather uniform, and little or no mixing would be required in any postcondensation stage. The change in the average degree of polymerization as a function of time and strand diameter is shown in Figure 8. The graphs in this figure reflect also the effect of mixing (surface regeneration) in an operating stage that is characterized by simultaneous polycondensation and water removal. For this case, the respective strand radii approximate average film thicknesses generated in the process.

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