

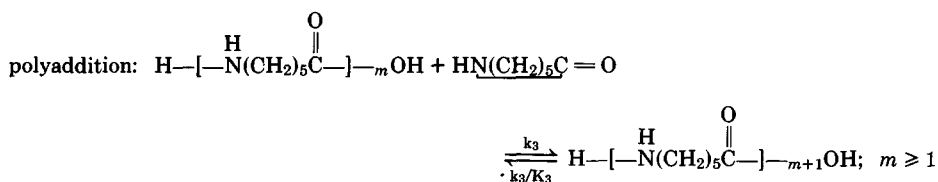
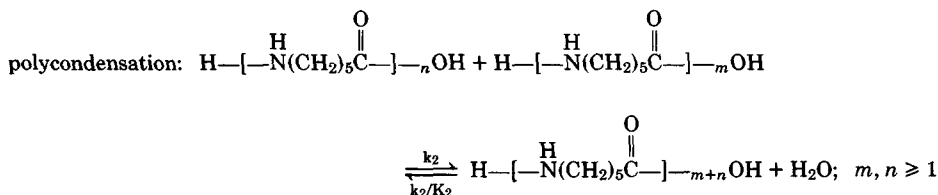
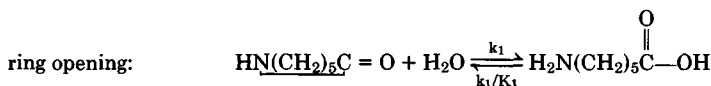
## Molecular Weight Distribution in Batch Hydrolytic Polymerization of Caprolactam

Nylon-6 is generally manufactured by the hydrolytic polymerization of  $\epsilon$ -caprolactam. While the kinetics of the polymerization processes have been widely investigated,<sup>1,2</sup> only one report<sup>3</sup> has been devoted to a study of the molecular weight distribution (MWD) of the resulting polymer. Gupta et al.<sup>3</sup> modeled batch polymerization of caprolactam by integrating balance equations for all polymer molecules having a dp of up to 300 and reported MWD. The equations used were similar to (1)–(3) listed in the next section except that they considered the presence of catalyzing acid and cyclic oligomer formation also. A maximum value for dp has to be assumed to integrate the equations due to their coupled nature, and it was assumed to be 300. However, the procedure employed by these workers is time consuming as it involves integration of 300 coupled nonlinear differential equations. Thus Gupta et al.<sup>3</sup> reported that the calculation took 4 h on a DEC-1090 Computer system to reach a batch time of 16 h. Clearly an alternate less time-consuming procedure is required for simulation of and dynamic studies on the reactor. Such a procedure would be useful in simulating continuous reactors as well. In the present work a less time-consuming method based on the work of Min<sup>4</sup> has been developed to model the batch hydrolytic polymerization of caprolactam.

### MODEL

#### Mechanism and Kinetics

Hermans et al.<sup>1</sup> and Kruissink et al.<sup>2</sup> showed that water-initiated polymerization of caprolactam is governed by a mechanism mainly comprising of three reversible reactions:



Other side reactions involving formation of cyclic oligomers have not been considered in this work. The rate equations for a batch reactor for the above reaction scheme can be written as follows:

$$\frac{dM}{dt} = k_1 \left( MW - \frac{S_1}{K_1} \right) - k_3 \left( M \sum_{n=1}^{\infty} S_n - \frac{\sum_{n=1}^{\infty} S_{n+1}}{K_3} \right) \quad (1)$$

$$\frac{dS_1}{dt} = k_1 \left( MW - \frac{S_1}{K_1} \right) - 2k_2 \left( S_1 \sum_{m=1}^{\infty} S_m - \frac{W \sum_{m=1}^{\infty} S_{m+1}}{K_2} \right) - k_3 \left( MS_1 - \frac{S_2}{K_3} \right) \quad (2)$$

$$\frac{dS_n}{dt} = k_2 \sum_{m=1}^{n-1} S_m S_{n-m} + 2 \frac{k_2}{K_2} W \sum_{m=n+1}^{\infty} S_m - 2k_2 S_n \sum_{m=1}^{\infty} S_m - \frac{k_2}{K_2} W(n-1)S_n + k_3 M(S_{n-1} - S_n) + \frac{k_3}{K_3} (S_{n+1} - S_n); \quad n \geq 2 \quad (3)$$

In the above equations  $M$ ,  $S_1$ ,  $S_n$  ( $n \geq 2$ ), and  $W$  are the concentrations (g mol/kg) of caprolactam, aminocaproic acid, linear  $n$ -mer, and water respectively. In deriving the above equations, besides making the usual assumptions, it has been assumed that all the amide bonds of a linear  $n$ -mer are equally accessible for the reverse reaction. These equations are different from those given by Tirrell et al.<sup>5</sup> However, they are consistent with those given by Hermans et al.,<sup>1</sup> Hoftyzer et al.,<sup>6</sup> and Reimschuessel<sup>7</sup> with respect to the definitions of equilibrium constants and concentrations of acid and amide groups as will be shown now. The acid group concentration  $C$  is given by

$$C = \sum_{n=1}^{\infty} S_n \quad \text{or} \quad \frac{dC}{dt} = \sum_{n=1}^{\infty} \frac{dS_n}{dt} \quad (4)$$

If eqs. (2) and (3) are substituted into the rhs of eq. (4), we obtain

$$\frac{dC}{dt} = k_1 \left( MW - \frac{S_1}{K_1} \right) - k_2 \left( C^2 - \frac{WZ}{K_2} \right) \quad (5)$$

and this is consistent with earlier results.<sup>1,6,7</sup> In the above,  $Z$  is the amide group concentration which is given by

$$Z = \sum_{n=1}^{\infty} (n-1)S_n \quad \text{or} \quad \frac{dZ}{dt} = \sum_{n=1}^{\infty} (n-1) \frac{dS_n}{dt} \quad (6)$$

Further, if eqs. (2) and (3) are substituted into the rhs of eq. (6), we get

$$\frac{dZ}{dt} = k_2 \left( C^2 - \frac{WZ}{K_2} \right) + k_3 \left[ MC - \frac{(C - S_1)}{K_3} \right] \quad (7)$$

which is also consistent with earlier results.<sup>1,6,7</sup> Moreover, according to the above equations,

$$K_1 = S_1/MW, \quad K_2 = WZ/C^2, \quad K_3 = (C - S_1)/MC$$

and these definitions are consistent with the ones given earlier.<sup>1,6,7</sup>

It should be noted here that integration of Eq. (3) for  $S_n$  requires a knowledge of  $S_{n+1}$ , showing the coupled nature of the equations.

### Generation of MWD

It is shown that smooth distributions can be represented by a finite number of moments, say  $N_{\max}$ , of the distribution. Keeping in view the more general orthogonal properties of Laguerre polynomials,  $L_n^\alpha$ , Min<sup>4</sup> suggested that any normalized MWD density function  $G(x)$  be represented as

$$G(x) = \frac{x^\alpha \exp(-x)}{\Gamma(\alpha + 1)} \sum_{n=0}^{N_{\max}} C_n^\alpha L_n^\alpha(x) \quad (8)$$

where  $C_n^\alpha$  are constants and  $\Gamma(\alpha + 1)$  is the gamma function. For rapid convergence Min<sup>4</sup> suggested that  $\alpha$  be selected such that  $C_1^\alpha$  and  $C_2^\alpha$  are zero. This implies the following relations, which were given by Min<sup>4</sup>:

$$\alpha = -1 + \frac{(\bar{G}_x^1)^2}{\bar{G}_x^2 - (\bar{G}_x^1)^2} = -1 + 1 / \frac{\bar{M}_v^2}{\bar{M}_v^1} \cdot \frac{\bar{M}_m^0}{\bar{M}_v^1} - 1 \quad (9)$$

$$v = \frac{\bar{M}_v^1}{(\alpha + 1) \bar{M}_v^0} \cdot x \quad (10)$$

$$\bar{M}_v^k = \bar{M}_v^0 \left[ \frac{\bar{M}_v^1}{(\alpha + 1) \bar{M}_v^0} \right]^k \bar{G}_x^k \quad (11)$$

$$M(v)dv = \bar{M}_v^0 G(x) dx \quad (12)$$

where  $\bar{G}_x^k$  is the  $k$ th moment of the normalized distribution and  $M(v)$  and  $\bar{M}_v^k$ , respectively, are the unnormalized MWD density function and its  $k$ th moment. Also from eq. (8) it follows that

$$C_n^\alpha = \sum_{j=0}^n \frac{(-1)^j \binom{n}{j} \Gamma(\alpha + 1)}{\Gamma(\alpha + j + 1)} \bar{G}_x^j \quad (13)$$

and that

$$\bar{G}_x^k = \frac{\Gamma(\alpha + k + 1)}{\Gamma(\alpha + 1)} + \frac{1}{\Gamma(\alpha + 1)} \sum_{n=3}^{N_{\max}} C_n^\alpha \sum_{j=0}^n \frac{(-1)^j \Gamma(\alpha + n + 1) \Gamma(\alpha + k + j + 1)}{\Gamma(\alpha + j + 1) \Gamma(n - j + 1) \Gamma(j + 1)} \quad (14)$$

Thus if  $N_{\max}$  number of moments of unnormalized MWD density function are available using eqs. (9), (11), (13), (8) and (12), the unnormalized MWD can be constructed. Further, using (13) and (14),  $\bar{G}_x^k$ , and in particular  $\bar{G}_x^{N_{\max}+1}$ , can also be computed.

### Formulation of Moment Equations

The  $k$ th moment of MWD,  $\bar{M}_v^k$ , can be defined as

$$\bar{M}_v^k = \sum_{v=1}^{\infty} v^k S_v \quad (15)$$

and hence

$$\frac{d\bar{M}_v^k}{dt} = \frac{dS_1}{dt} + \sum_{v=2}^{\infty} v^k \frac{dS_v}{dt} \quad (16)$$

Substituting eqs. (2) and (3) into the above, we get

$$\begin{aligned} \frac{d\bar{M}_v^k}{dt} &= k_1 \left( MW - \frac{S_1}{K_1} \right) + K_2 \sum_{x=1}^{k-1} \binom{k}{x} \bar{M}_v^x \bar{M}_v^{k-x} \\ &+ \frac{k_2}{K_2} W \left[ \frac{k-1}{k+1} (S_1 - \bar{M}_v^{k+1}) + \sum_{t=1}^{k/2 \text{ or } (k-1)/2} \frac{(-1)^{t+1}}{t} \binom{k}{2t-1} B_t \right. \\ &\times (\bar{M}_v^{k-2t+1} - S_1) \left. \right] + k_3 M \sum_{x=1}^k \binom{k}{x} \bar{M}_v^{k-x} + \frac{k_3}{K_3} \\ &\times \left[ \sum_{j=1}^k \binom{k}{j} (-1)^j \bar{M}_v^{k-j} + S_1 \right]; \quad k \geq 1 \end{aligned} \quad (17)$$

In the above the  $B_t$  are the Bernoulli numbers as defined by Jolley.<sup>8</sup> As expected, the calculation of each moment requires a value of the next higher moment. The above equations are also consistent with these given by Tai et al.<sup>9</sup> for the first and second moments.

### Calculation of MWD

The reaction rate constants  $k_1$ ,  $k_2$ , and  $k_3$  are written as

$$k_i = k_i^0 + k_i^1 C, \quad i = 1-3 \quad (18)$$

as all the three reactions are known to be catalyzed by carboxyl end groups. The particular numerical values used in this work are listed in Table I. These values have been selected to facilitate comparison with the results of Gupta et al.<sup>3</sup> and have been obtained from Reimschuessel.<sup>7</sup>

For the present work smooth distributions could be generated by selecting  $N_{\max}$  to be 5. Thus eqs. (17) were integrated for  $k = 1-5$ , generating the first five moments. By using eqs. (9), (11), (13), and (14)  $\bar{M}_v^6$  could be calculated from the first five moments and that value was used in integrating eq. (17).

The Runge-Kutta-Gill (RKG) technique<sup>10</sup> was used with a step size of 1/20 h. It was found that reducing the step size from 1/20 h to 1/100 h produced no significant changes in the results.

By the procedure already described, the MWD was constructed using the first five moments.

TABLE I  
Rate and Equilibrium Constants at 235°C

$i$	$k_i^0$ (kg · h <sup>-1</sup> · mol <sup>-1</sup> )	$k_i^1$ (kg <sup>2</sup> · h <sup>-1</sup> · mol <sup>-2</sup> )	$K_i$
1	1.491 × 10 <sup>-3</sup>	0.3489	2.34 × 10 <sup>-3</sup>
2	1.714	29.61	702.2
3	1.84	39.44	1.638

## RESULTS AND DISCUSSION

In all the calculations, it has been assumed that feed contains 0.44 mol of water for every 8.8 mol of caprolactam. These figures were chosen so that our results can be compared with those of Gupta et al.<sup>3</sup>

The fractional conversion of caprolactam, the number average molecular weight ( $M_n$ ), the weight average molecular weight ( $M_w$ ), and the polydispersity index (PDI) are plotted against batch time in Figure 1. The results of Gupta et al.<sup>3</sup> are also shown. As can be seen, the present results are in good agreement (maximum deviation being about 5%) with the exact results of Gupta et al.<sup>3</sup> In particular, the agreement on  $M_w$  is important in view of its relevance in calculation of viscosity and, consequently, transport processes in a continuous reactor.

As expected, the polydispersity index (PDI) reaches a limiting value of two typical of polycondensation reactions. Equations (1), (2), (5) and (7) can be integrated to obtain fractional conversion of caprolactam and  $M_n$  after using the approximation that  $S_2 \approx S_1$ .<sup>1,6</sup> Our results are in agreement with such results as well, although the comparison is not shown in the figure.

The five moments obtained by the procedure already indicated were used in the recovering the MWD. The MWD obtained is shown in Figure 2 along with the results of Gupta et al.<sup>3</sup> who reported the weight fraction of  $n$ -mer. Their results were converted to mole fraction and are shown in Figure 2. We chose to plot mole fraction vs.  $n$  since a plot of weight fraction of  $n$ -mer vs.  $n$  does not clearly bring out the deviation between our results and results of Gupta et al.<sup>3</sup> The MWD shows a maxima at some intermediate value of  $n$  whereas the exact results<sup>3</sup> indicate that the maximum should be present at  $n = 1$ . Tai et al.<sup>9</sup> integrated the first two moment equations assuming Schultz-Zimm distribution to be valid and employing it to calculate the third moment. Following this approach,

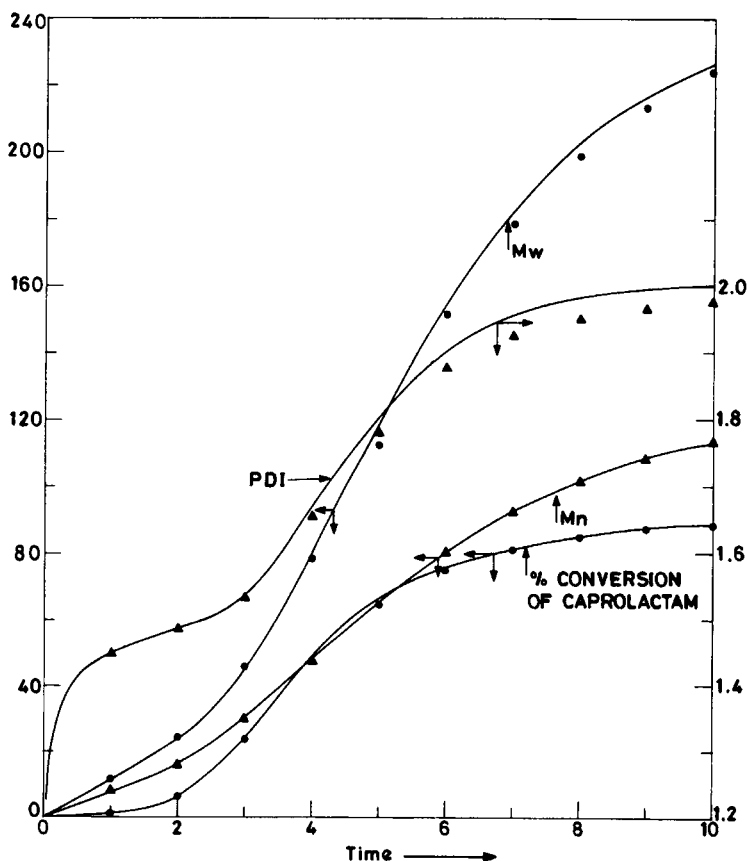


Fig. 1. Fractional conversion, weight and number average molecular weights and PDI vs. batch time. (—) Our results; (●,▲) results of Gupta et al.<sup>3</sup>

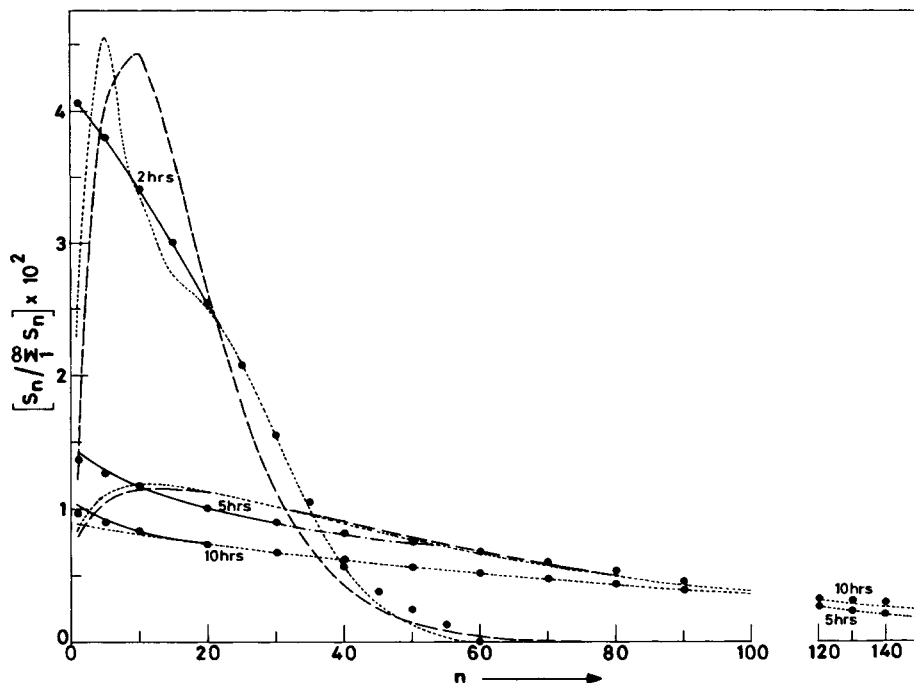


Fig. 2. MWD at different batch times. (---) Distribution from moments; (—) oligomer distribution from direct integration; (····) extrapolated; (●) computational results of Gupta et al.<sup>3</sup>; (----) distribution from the Tai et al.<sup>9</sup> approach.

the MWD (given by Schultz-Zimm distribution) was also obtained at  $t = 2$  h and  $t = 5$  h, using our kinetic parameters. These MWD also show a maxima at an intermediate value of  $n$  and are shown in Figure 2. The maxima at an intermediate value of  $n$  disappears as time of polymerization increases in both our results and results obtained using Tai's approach. Our results are in better agreement with the exact results at  $t = 2$  h. The disagreement between the exact results and our results as well as those obtained using Tai's approach decreases as time of polymerization increases. The discrepancy between the exact results and our results is also confined to about  $n \approx 35$ . The reason for the differences seem to arise from the fact that while  $L_n^\alpha(x) \rightarrow 0$  as  $x \rightarrow 0$ ,  $M(v)$  has a maximum as  $v \rightarrow 1$ . Thus the initial distribution is more "complex" in the sense that it would require a larger number of moments for its description. Increasing the number of moments beyond 5 did not lead to any better results, and they would not be increased beyond 10 due to numerical difficulties. The choice at this stage was either to split the distribution into two parts and try to compute them separately in terms of moments of the two distributions or to try to compute oligomer distribution by direct integration of eqs. (1), (2), and (3) and match this with the distribution calculated with the help of moments. The later approach was chosen here due to its simplicity. Oligomer distribution up to  $n = 30$  was obtained by direct integration using the formula  $S_{31} = (S_{21}/S_{20}) \cdot S_{30}$ . This was based on the hypothesis that Flory<sup>11</sup> distribution is a good first approximation. Again the RKG method with a step size of  $1/40$  h was employed. The resulting distributions match well with the exact results, as shown in Figure 2.

The integration of moment equations, monomer balance equation, the balance equations for oligomers of dp of up to 30, and the construction of MWD takes approximately 55 s on a DEC-1090 Computer system to reach a polymerization time of 16 h. Thus saving in time is considerable.

### CONCLUSIONS

A method for generating MWD in batch hydrolytic polymerization of caprolactam with the aid of few moments based on the procedures of Min<sup>4</sup> has been developed. The moment values compare to within 5% of the exact results. The agreement improves with increasing reaction time. There

was discrepancy between MWD generated with the aid of the few moments and the exact results. This could be eliminated only after the oligomer distribution was obtained by direct integration.

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