# Molecular weight distributions for reversible nylon-6 polymerizations in batch reactors

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The reversible polymerization of nylon-6 including ring opening, polycondensation, polyaddition and cyclization reactions as well as the reaction with monofunctional acids, has been modelled. Molecular weight distributions and their moments have been obtained for various initial conditions and at two temperatures, 235° and 265°C, for a batch reactor. The cyclic oligomer concentrations have also been computed. It is found that even though the cyclization step has little influence on the monomer conversion, it does affect the molecular weight distribution and its moments.

## INTRODUCTION

Previous simulations[1-10] of the industrially important polymerization of caprolactam have accounted for the ring-opening, polycondensation and polyaddition reactions. These have been reviewed by Reimschuessel[11]. However, these studies are restricted to obtaining the time variation of the conversion of the lactam[8-11], the number-[8-11] and weight-average[8] chain lengths and the polydispersity index[8]. No attempt has been made to obtain the molecular weight distribution of the polymer formed. In addition, except for the simplified and empirical studies of Mochizuki and Ito[9,10], most of the simulations ignore the formation of cyclic oligomers. The latter is important because the presence of cyclic oligomers, even though in small quantities, causes problems in the spinning process. Here, the formation of cyclic oligomers has been modelled and included in the mass balance equations for each species. These equations are integrated to give the conversion of the lactam, the molecular weight distribution (*MWD*) and its moments for the polymer formed, and the amounts of cyclic oligomers formed, as a function of time and for various initial conditions.

## FORMULATION

The kinetic scheme shown in *Table* 1 is a comination of that of Tirrell *et al.*[8] with the cyclization reaction used by Mochizuki and Ito[9,10]. The rate constants $k_1$ to $k_5$ are associated with *functional groups*. Thus, for example, the forward reaction between the *molecular species* $S_n$ and $S_m$ is associated with a rate constant $2k_2$ and that between $S_n$ and $A_m$ by $k_a$. For reactions between two identical molecules, e.g. $S_n$ and $S_n$, a factor of one-half is necessary in the rate constant to prevent the counting of molecular collisions twice, as used earlier by Kumar, Gupta and coworkers[12-17].

Accounting for the reverse reactions is slightly involved because of the various possibilities for the reactions, as for example, between $S_{n+m}$ and W (*Table* 1). A rate constant $2k'_2$ is associated with the formation of $S_i$ and $S_{n+m-i}$ because there are two –CONH– sites on a molecule of $S_{n+m}$ at which water can react to give these two products (except for one of the reactions shown in *Table* 1, where only one site is available). The reaction between W and $A_{n+m}$, however, gives different products when water attacks the $i$th and the $(n+m-i)$th –CONH– sites. In the reverse reaction of the polyaddition step, there is a single –CONH– site on $S_{n+1}$ which can react with the amine end of the molecule to give $S_n$ and the cyclic monomer, and thus the rate constant associated with this is $k'_3$. In the reaction between $C_n$ and W, there are $n$ sites on $C_n$ at which water can react and the rate constant is taken as $nk'_5$.

The mass balance equations for the various species for an isothermal batch reactor from which there is no removal or addition of the condensation product, water, during the course of the reaction, are given in *Table* 2. These equations are more general than earlier work and the commonly used approximation[8,11] of $[S_2] \simeq [S_1]$ (square brackets denote concentrations) is not used. When these equations were summed up appropriately after neglecting reactions (4) and (5) of *Table* 1, it was found that they reduced to the expressions of Reimschessel[5,11] for $d[M]/dt$,

$$d \sum_{n=1}^{\infty} [S_n]/dt$$

and $d[S_1]/dt$.

### *Rate and equilibrium constants*

The rate constants, $k_1$, $k_2$ and $k_3$, are a function of the acid end-group concentrations[5,11] (in moles $kg^{-1}$ mixture):

$$k_i = k_i^0 + k_i^c \sum_{n=1}^{\infty} ([A_n] + (S_n]) \qquad i = 1, 2, 3 \tag{2}$$

The coefficients $k_i^0$ and $k_i^c$ are expressed in terms of Arrhenius parameters and the values are listed by Reimschuessel[5,11]. Similarly, the equilibrium constants $k_1$, $k_2$ and $k_3$ (defined in terms of functional groups and equal to $k_1/k'_1$, $k_2/k'_2$ and $k_3/k'_3$, respectively) can be

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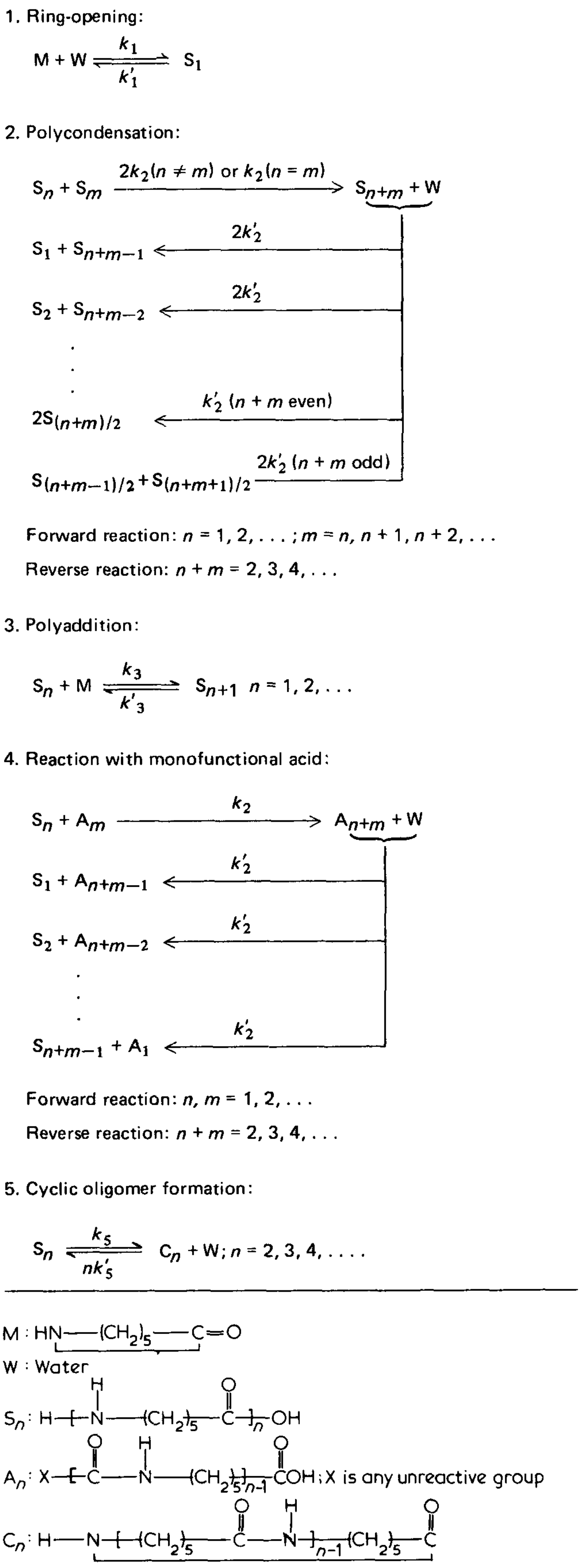
*Table 1* Kinetic scheme for nylon-6 polymerization



1. Ring-opening:

$$M + W \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} S_1$$

2. Polycondensation:

$$S_n + S_m \xrightarrow{2k_2(n \neq m) \text{ or } k_2(n = m)} \underbrace{S_{n+m} + W}$$

$$S_1 + S_{n+m-1} \xleftarrow{2k_2'}$$

$$S_2 + S_{n+m-2} \xleftarrow{2k_2'}$$

$$\vdots$$

$$2S_{(n+m)/2} \xleftarrow{k_2' \,(n+m \text{ even})}$$

$$S_{(n+m-1)/2} + S_{(n+m+1)/2} \xleftarrow{2k_2' \,(n+m \text{ odd})}$$

Forward reaction: $n = 1, 2, \ldots ; m = n, n+1, n+2, \ldots$

Reverse reaction: $n + m = 2, 3, 4, \ldots$

3. Polyaddition:

$$S_n + M \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} S_{n+1} \quad n = 1, 2, \ldots$$

4. Reaction with monofunctional acid:

$$S_n + A_m \xrightarrow{k_2} \underbrace{A_{n+m} + W}$$

$$S_1 + A_{n+m-1} \xleftarrow{k_2'}$$

$$S_2 + A_{n+m-2} \xleftarrow{k_2'}$$

$$\vdots$$

$$S_{n+m-1} + A_1 \xleftarrow{k_2'}$$

Forward reaction: $n, m = 1, 2, \ldots$

Reverse reaction: $n + m = 2, 3, 4, \ldots$

5. Cyclic oligomer formation:

$$S_n \underset{nk_5'}{\overset{k_5}{\rightleftharpoons}} C_n + W; n = 2, 3, 4, \ldots .$$

M : $HN-(CH_2)_5-C=O$

W : Water

$S_n$: $H-[\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}]_n-OH$

$A_n$: $X-[\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_5]_{n-1}\overset{O}{\overset{\|}{C}}OH$ ; X is any unreactive group

$C_n$: $H-N-[(CH_2)_5-\overset{O}{\overset{\|}{C}}-\overset{H}{N}]_{n-1}(CH_2)_5-\overset{O}{\overset{\|}{C}}$

obtained at any temperature using the corresponding standard-state enthalpy and entropy changes for the reactions[5,11].

Data for the formation of the cyclic oligomers are not as readily available. Mochizuki and Ito[9,10] have modelled this step using several approximations and have computed the rate constants from their experimental work using a non-linear parameter estimation technique. But the rate constants are not reported for proprietory reasons. In the absence of this information, $k_5$ and $k_5'$ are treated as parameters in our simulation study. Rough estimates of $k_5$ may be obtained by focussing attention on the reactions on a molecular level. The forward reaction in step 5 (*Table 1*) involves two steps: (i) the diffusion of the $-NH_2$ end-group on a molecule of $S_n$ to within close proximity of the $-CONH-$ group at the other end of the molecule and (ii) the chemical attack. The first of these two steps requires intramolecular backbone rotations and thus depends on the flexibility of the chain[12] (steric hindrance, etc.) as well as the chain length. The larger the chain length, the easier it is for the two ends of the molecule to come together and the more rapid is the diffusion step. Thus, $k_5$ should increase from a value of $k_1'$ (which represents the maximum chain stiffness for $S_1$) to an upper limit of $k_2$ (which characterizes the absence of intramolecular chain motions — it being the rate of reaction of an $-NH_2$ group on one molecule with a $-CONH-$ on another), as the chain length, $n$, increases. In this study, $k_5$ will be taken as a constant between zero and $k_2$ independent of chain length.

In order to get rough estimates of the equilibrium constant $K_5(\equiv k_5/k_5')$, the following reaction studied by Andrews *et al.*[18] is used of:

$$S_n \rightleftharpoons S_{n-m} + C_m \tag{3}$$

The forward step in this reaction is associated with the reaction between the end $-NH_2$ group on a molecule of $S_n$ with a $-CONH-$ group somewhere inside the same molecule. Since this requires similar molecular motions as the forward reaction in step 5 (*Table* 1), the forward step in equation (3) may be associated with $k_5$. The reverse step in equation (3) represents the attack on any of the $m$ $-CONH-$ groups of $C_m$ by the end-group of $S_{n-m}$. As a first approximation, the rate constant for this can be written as $mk_5'$ where $k_5'$ rigorously represents the rate constant for the reaction between a water molecule and a $-CONH-$ group on $C_m$. These approximations are not a drawback of this work since both $K_5$ and $k_5$ are taken as parameters and the approximations are used only to obtain starting values for simulation runs. Indeed, simulation results presented later show that the conversion of the caprolactam and the *MWD* of the polymer formed is relatively insensitive to the value of $K_5$ and that only the amount of cyclic oligomer formed is sensitive to the value chosen for $K_5$.

Andrews *et al.*[18] have defined the equilibrium constant, $K^A_{5,m}$ for the reaction in equation (3) in terms of functional groups, as follows:

$$K^A_{5,m} \equiv \frac{[S_{n-m}][C_m]}{[S_n]} \simeq [C_m] = \frac{k_5}{mk_5'} \tag{4}$$

and have presented data (*Table* 3) on $K^A_{5,m}$ as a function of temperature for $m$ up to 6. Values of $K^A_{5,m}$ beyond $m = 6$ are

*Table 2* Mass balance equation for an isothermal batch nylon-6 reactor

$$\frac{d[M]}{dt} = -k_1[M][W] + k'_1[S_1] - k_3[M]\sum_{n=1}^{\infty}[S_n] + k'_3\sum_{n=1}^{\infty}[S_{n+1}] \qquad \text{(a)}$$

$$\frac{d[W]}{dt} = -k_1[M][W] + k'_1[S_1] + k_2\sum_{n=2}^{\infty}\sum_{m=1}^{n-1}[S_{n-m}][S_m] - k'_2[W]\sum_{n=2}^{\infty}(n-1)[S_n] + k_2\sum_{n=2}^{\infty}\sum_{m=1}^{n-1}[S_{n-m}][A_m]$$

$$-k'_2[W]\sum_{n=2}^{\infty}(n-1)[A_n] + k_5\sum_{n=2}^{\infty}[S_n] - k'_5[W]\sum_{n=2}^{\infty}n[C_n] \qquad \text{(b)}$$

$$\frac{d[S_1]}{dt} = k_1[M][W] - k'_1[S_1] - 2k_2[S_1]\sum_{n=1}^{\infty}[S_n] + 2k'_2[W]\sum_{n=2}^{\infty}[S_n] - k_3[S_1][M] + k'_3[S_2] - k_2[S_1]\sum_{n=1}^{\infty}[A_n]$$

$$+k'_2[W]\sum_{n=2}^{\infty}[A_n] \qquad \text{(c)}$$

$$\frac{d[S_n]}{dt} = -2k_2[S_n]\sum_{m=1}^{\infty}[S_m] + k_2\sum_{m=1}^{n-1}[S_m][S_{n-m}] - k'_2[W](n-1)[S_n] + 2k'_2[W]\sum_{m=1}^{\infty}[S_{n+m}] - k_3[M][S_n] + k_3[M][S_{n-1}]$$

$$-k'_3[S_n] + k'_3[S_{n+1}] - k_2[S_n]\sum_{m=1}^{\infty}[A_m] + k'_2[W]\sum_{m=1}^{\infty}[A_{n+m}] - k_5[S_n] + k'_5[W]\,n[C_n]\,;\; n = 2, 3, 4, \ldots \qquad \text{(d)}$$

$$\frac{d[A_1]}{dt} = -k_2[A_1]\sum_{n=1}^{\infty}[S_n] + k'_2[W]\sum_{n=2}^{\infty}[A_n] \qquad \text{(e)}$$

$$\frac{d[A_n]}{dt} = -k_2[A_n]\sum_{m=1}^{\infty}[S_m] + k_2\sum_{m=1}^{n-1}[A_m][S_{n-m}] - k'_2[W](n-1)[A_n] + k'_2[W]\sum_{m=1}^{\infty}[A_{n+m}]\,;\; n = 2, 3, 4, \ldots \qquad \text{(f)}$$

$$\frac{d[C_n]}{dt} = k_5[S_n] - nk'_5[W][C_n]\,;\; n = 2, 3, 4, \qquad \text{(g)}$$

not available. Moreover, since $K^{A}_{5_m}$ is defined in terms of molecular species instead of in terms of functional groups it is not expected to attain an asymptotic value with increasing $m$. Here, we used the equilibrium constant $K_5$ ($\equiv k_5/k'_5$) defined in terms of functional groups. It is expected that as for the case of rate constants[19], $K_5$ will attain an asymptotic value as $n$ increases. A constant value of $K_5$ of 0.06 mol kg$^{-1}$ at 235°C and 0.08 mol kg$^{-1}$ at 265°C was chosen (so that $K_5/3$ matched the experimental value of $K^{A}_{5,3}$)[9,10] for simulation purposes. A comparison of $K_5/m$ with $K^{A}_{5_m}$ (*Table 3*) shows that a better assumption for $K_5$ would have been a decreasing function of $m$ for $K_5$ for the first few oligomers, followed by a constant value beyond some value of $m$. However, such multiparameter models must await experimental data on the cyclization step.

### *Simulation procedure*

The Runge–Kutta–Gill[20] method was tried to solve for the *MWD* and other properties of interest as a function of time with a value of $\Delta t$ of 1/1000 h. Such a small value of $\Delta t$ took too much computer time and had to be increased to a value of about 1/60 to 1/30 h for $T = 235$°C and 1/150 h for $T = 265$°C, depending on the initial concentrations of acid and water. However, at these values of $\Delta t$, several of the $[C_n]$ came out to be negative because of the highly negative values of $(d[C_n]/dt)\Delta t$ compared with $[C_n]$. To surmount this problem, it was decided to mix the Runge–Kutta–Gill technique with an analytical solution for $[C_n]$ in any interval $t_1 \leqslant t \leqslant t_1 + \Delta t$, assuming $[S_n]$ and $[W]$ constant over this small period of time, while integrating for $[C_n]$. The equation used was:

$$[C_n]_t = \frac{k_5[S_n]}{nk'_5[W]} - \left\{\frac{k_5[S_n]}{nk'_5[W]} - [C_n]_{t_1}\right\}\exp\{-nk'_5[W](t-t_1)\} \tag{5}$$

Results obtained by this method matched extremely well with the *MWD*s obtained using only the Runge–Kutta–Gill (RKG) method and a $\Delta t$ of 1/1000 h, for one set of conditions. An alternate method of reducing the interval of integration when the concentrations become negative was tried but was abandoned since it took more computer time and yielded results which were comparable with the method discussed above. A reduction of $\Delta t$ below the values used for a few typical runs did not alter the results much when the modified RKG technique was employed. A check on the programme was to compute the total concentration of $-(CH_2)_5-$ groups (present in various $S_n$, $A_n$, $C_n$ and M) at any time and match it with the initial values (only on $A_1$ and M). This check came out to within 1% in the worst case at $T=235$°C and 3% at $T=265$°C.

In the computer program, approximately 250 equations for $S_n$, 200 equations for $A_n$ (unless $[A_1]_0=0$) and 80 equations for $C_n$ were first used for solution for the 235°C runs. After every hour of polymerization time, the number of equations was increased by approximately 80 for $S_n$, 80 for $A_n$ and 25 for $C_n$ till a polymerization time of about 12 h, after which the number of equations was not increased any further. For the 265°C run, 450 equations for $S_n$, 450 for $A_n$ and 200 for $C_n$ were taken initially and these were increased by 8, 8 and 8 for $S_n$, $A_n$ and $C_n$, respectively, after every 1/2 h of polymerization time. Such a procedure was essential because of the reversible nature of the reactions, to give a good check on the $-(CH_2)_5-$ group balance. The computation time for a typical run at 235°C, up to a polymerization time of 16 h, was 4 h on a DEC 1090, most of this time on the computer being used in the final stage of polymerization.

*Table 3* Comparison of computed values of $K_5/m$ with experimental values of $K^A_{5m}$ for various $m$

| | 235°C, $K_5$ = 0.06 mol kg$^{-1}$ (assumed) | | 265°C, $K_5$ = 0.08 mol kg$^{-1}$ (assumed) | |
|---|---|---|---|---|
| $m$ | $K_5/m$ | $K^A_{5m}$ (experimental) | $K_5/m$ | $K^A_{5m}$ (experimental) |
| 2 | 0.03 | 0.0448 | 0.04 | 0.0553 |
| 3 | 0.02 | 0.0199 | 0.026 | 0.0264 |
| 4 | 0.015 | 0.0112 | 0.02 | 0.015 |
| 5 | 0.012 | 0.0069 | 0.016 | 0.0091 |
| 6 | 0.01 | 0.0045 | 0.013 | 0.0055 |

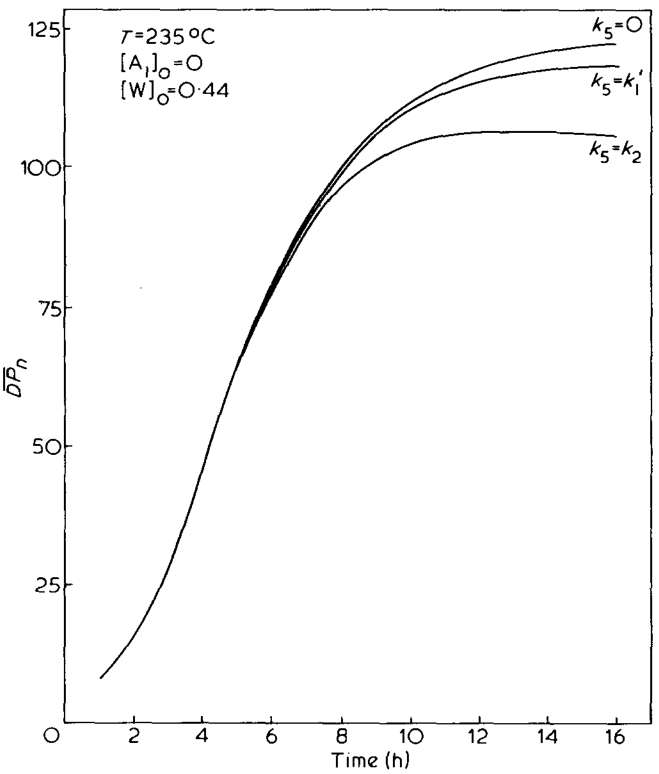


*Figure 1* $\overline{DP}_n$ vs. time using three different values of $k_5$

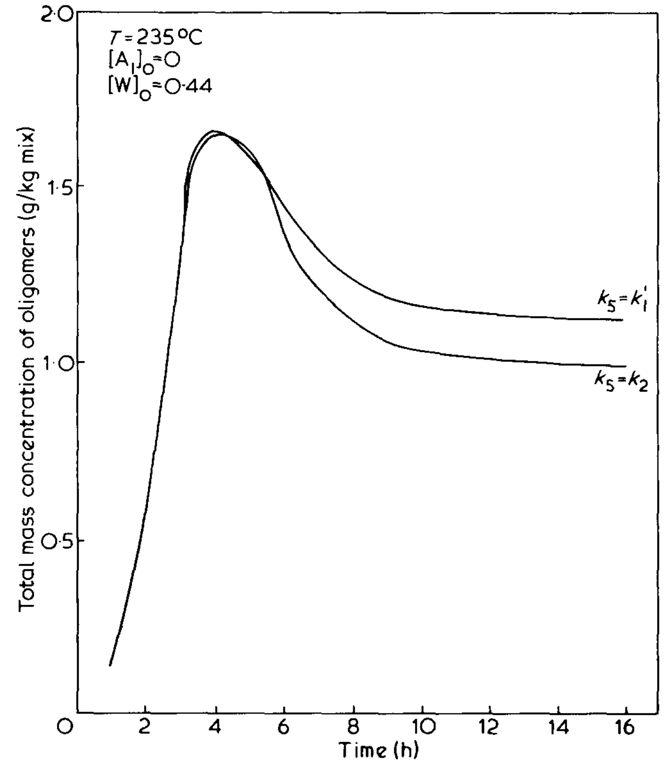


*Figure 2* Mass concentration of cyclic oligomers for different values of $k_5$

## RESULTS AND DISCUSSION

Simulations were carried out at 220°C with $k_5=0$ (i.e., no cyclization) and results were found to be close to those of Tirrell *et al.*[8]. Since these workers had already found that their simulation results compared well with experimental data of Hermans *et al.*[2], we proceeded with parametric studies using out model. Similar simulations at 235°C with $k_5=0$ compared well with results of Reimschuessel[11].

Simulation at 235°C using $K_5=0.06$ mol kg$^{-1}$ and 3 values of $k_5$ of zero (no cyclization), $k_1$ and $k_2$ (highest value) were carried out to study the effect of varying $k_5$. During this parametric study, the initial concentrations of the monofunctional acid, caprolactam and water were taken as 0, 8.8 and 0.44 mol kg$^{-1}$, respectively. These concentrations are typical of those chosen by Tirrell *et al.*[8] and correspond to run *C* of the experimental work of Hermans *et al.*[2] It was found that the conversion of the caprolactam was not affected considerably by $k_5$ (after 15 h, the caprolactam conversions were 92.16, 92.2 and 92.5% for $k_5 = 0, k_1$ and $k_2$). However, the number-average degree of polymerization, $\bar{D}\bar{P}_n$

$$\left[ \equiv \sum_{n=1}^{\infty} \{n([\mathrm{A}_n]+[\mathrm{S}_n])\} / \sum_{n=1}^{\infty} ([\mathrm{A}_n]+[\mathrm{S}_n]) \right]$$

is significantly influenced by $k_5$. *Figure* 1 shows that $\bar{D}\bar{P}_n$ reduces by about 5% and 15% (for 16 h) as $k_5$ is increased from 0 to $k_1$ and $k_2$, respectively. Neglecting the cyclization reaction, as done by earlier workers, is thus not fully justified. It is possible that if $\bar{D}\bar{P}_n$ is defined to include the cyclic oligomers as well, the change in $\bar{D}\bar{P}_n$ with $k_5$ may be less but since the cyclic oligomers are extracted by hot water, the $\bar{D}\bar{P}_n$ as defined above has more physical relevance. *Figure* 2 shows the effect of $k_5$ on the total mass of cyclic oligomers

$$= \sum_{n=2}^{\infty} 113n[\mathrm{C}_n].$$

There is a maximum in these curves at ~ 3–4 h after which the cyclic oligomer concentration decreases as the reverse step of the cyclization reaction becomes important. The larger the value of $k_5$, the larger is the value of $k'_5$ since $K_5$ is assumed constant and because the reverse reaction is associated with a rate constant $nk'_5$, a higher $k_5$ leads to a lower final oligomer concentration. The *MWD*s at different times are shown in *Figure 3* and *4* for the 3 values of $k_5$. At polymerization times of below 5 h, there is little difference in the *MWD*s for the 3 values of $k_5$. At larger times, an increase in $k_5$ from 0 to $k_2$ shows two phenomena; a shift in the curves to lower values of $n$ and the small difference in the *MWD*s at polymerization times of 10 and 15 h at high $k_5$. All theses are consistent with the behaviour of $\bar{D}\bar{P}_n$ shown in *Figure* 1. It may be emphasized that previous work[8,11] on caprolactam polymerization yielded only the first 3 (zeroth, first and second) moments of *MWD* and not the entire distribution. The approximation of $[\mathrm{S}_1] \simeq [\mathrm{S}_2]$ used by earlier workers[8] is observed from *Figures* 3 and 4 to be in error, though its effect on the final results is marginal.

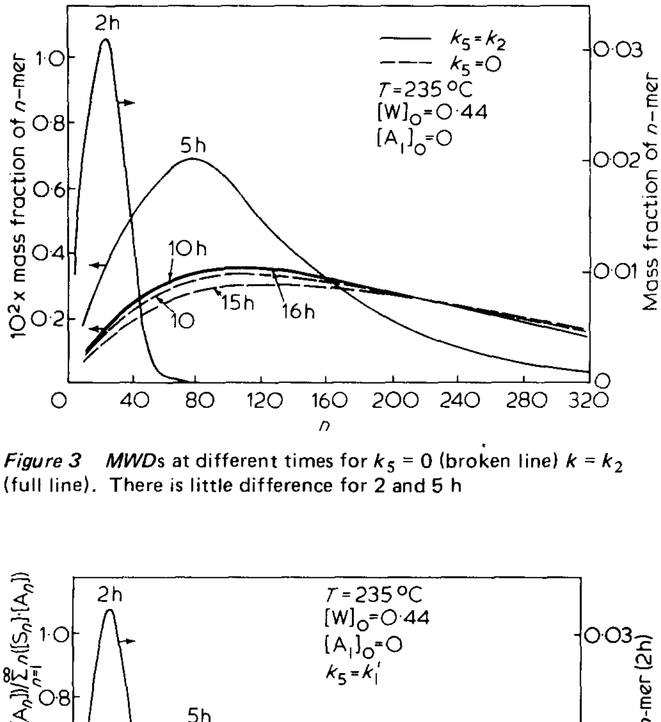


*Figure 3* *MWD*s at different times for $k_5$ = 0 (broken line) $k$ = $k_2$ (full line). There is little difference for 2 and 5 h

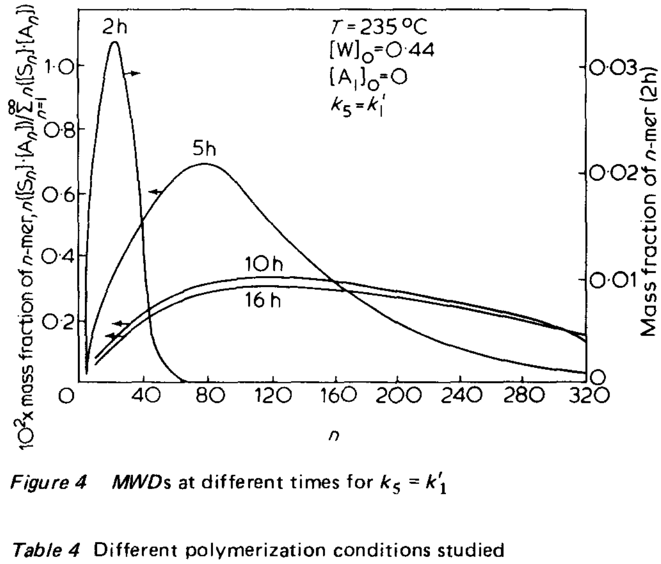


*Figure 4* *MWD*s at different times for $k_5$ = $k'_1$

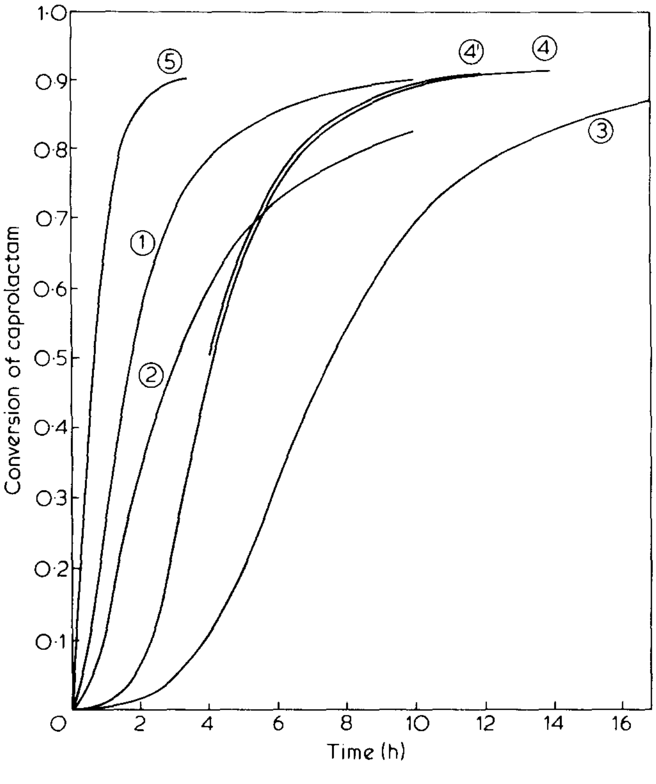


*Figure 5* Conversion as a function of time for the various conditions given in *Table 4*. Case numbers indicated, $k_5$ = $k'_1$

*Table 4* Different polymerization conditions studied

| | $k_5 = k'_1$ | | | | | |
|---|---|---|---|---|---|---|
| | Case 1 | Case 2 | Case 3 | Case 4 | Case 4′ | Case 5 |
| Temperature (°C) | 235 | 235 | 235 | 235 | 235 | 265 |
| $[\mathrm{W}]_0$ (mol kg$^{-1}$) | 0.44 | 0.22 | 0.22 | 0.44 | 0.44 | 0.44 |
| $[\mathrm{A}_1]_0$ (mol kg$^{-1}$) | 0.088 | 0.088 | 0 | 0 | 0 | 0.088 |
| $K_5$ (mol kg$^{-1}$) | 0.06 | 0.06 | 0.06 | 0.06 | 0.12 | 0.08 |

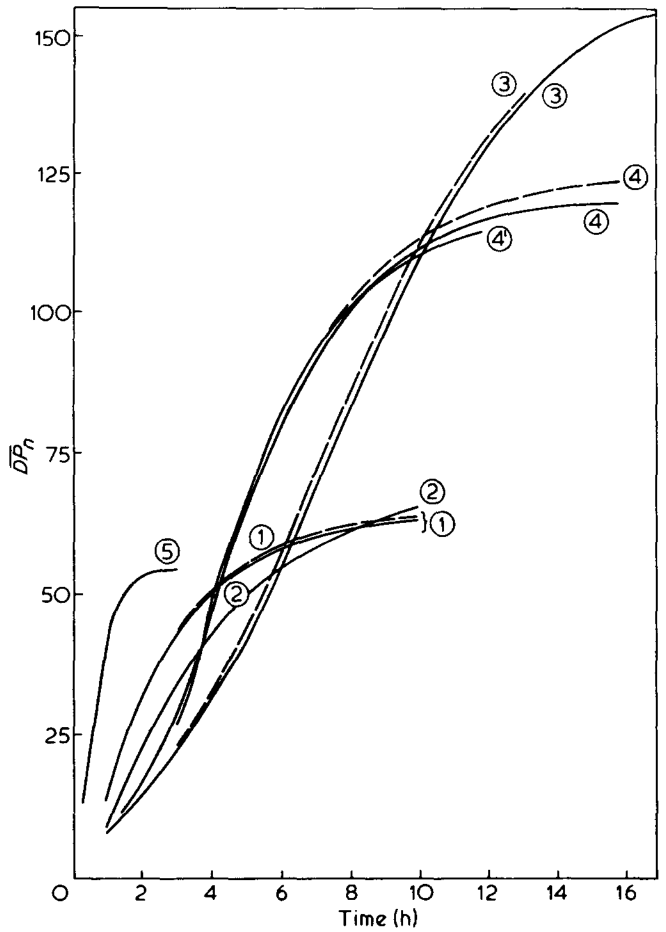


*Figure 6* $\overline{DP}_n$ vs. time for the various conditions of *Table 4*. Solid lines $k_5 = k'_1$. Case numbers indicated. Broken lines show corresponding values with $k_5 = 0$ (no cyclization) for a few of the cases

Having studied the parametric sensitivity of the results to $k_5$, the effect of varying the polymerization conditions was taken up with $k_5$ chosen as the intermediate value of $k'_1$. Four conditions were chosen at 235°C and one at a higher temperature of 265°C to discover the effect of varying water and monofunctional acid concentrations. These conditions are given in *Table* 4. One run was also made (case 4') with a higher value of $K_5$ of 0.12 mol kg$^{-1}$ to study the effect of varying this parameter. *Figure* 5 shows the conversion of caprolactam as a function of time for these various cases. The conversion is found to be insensitive to the value of $K_5$ and also the value of $k_5$ (as discussed earlier). It is observed from *Figure* 5 that as $[W]_0$ is increased, the lactam is consumed faster due to the enhanced rate of the ring-opening reaction. The effect is even more pronounced in the presence of monofunctional acid for two reasons: the presence of the latter consumes the $S_n$ and thus drives the ring-opening step in the forward direction and secondly, the reaction with monofunctional acid produces water. The trends are similar to those observed by Tirrell *et al.*[8] and Reimschuessel[11].

At a higher temperature, again, the conversion is more rapid. *Figure* 6 shows the $\bar{DP}_n$ as a function of time for the various cases. The dotted lines show values in the absence of the cyclization step (i.e. $k_5 = 0$) for some of the conditions. The presence of more water and monofunctional acid leads to lower final values of $\bar{DP}_n$. Again, the trends are similar to the results of earlier workers but the values of $\bar{DP}_n$ become lower by about 5% due to the inclusion of the cyclization reaction in our model. A choice of a still higher value of $k_5$ would lead to a further decrease in the $\bar{DP}_n$, as was found in *Figure* 1. An increase in $K_5$ (runs 4 and 4') is found to influence $\bar{DP}_n$ insignificantly. Increasing the temperature also reduces the final $\bar{DP}_n$ though it hastens the conversion of the caprolac-

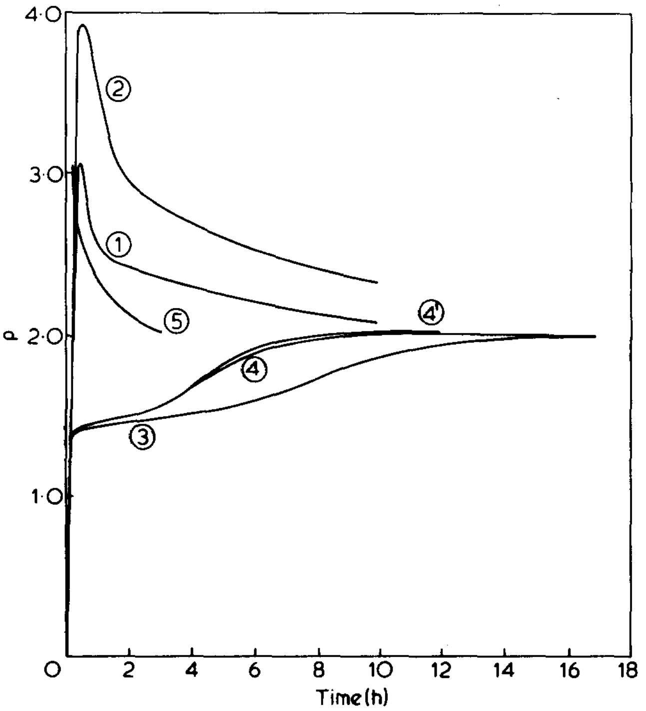


*Figure 7* Polydispersity index as a function of time for the various cases shown in *Table 4*. $k_5 = k'_1$

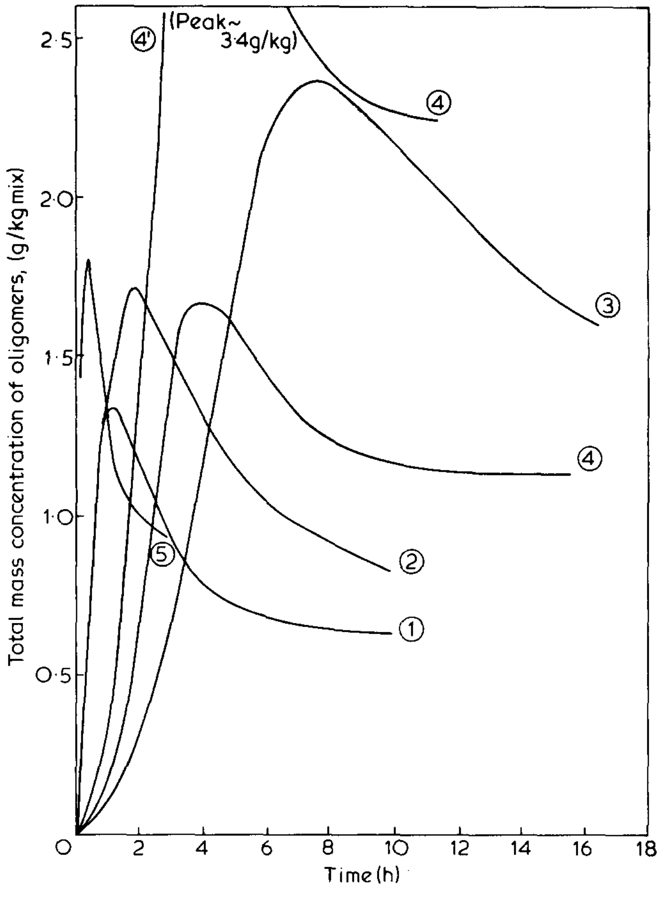


*Figure 8* Total mass concentration of oligomers as a function of time for the conditions of *Table 4*

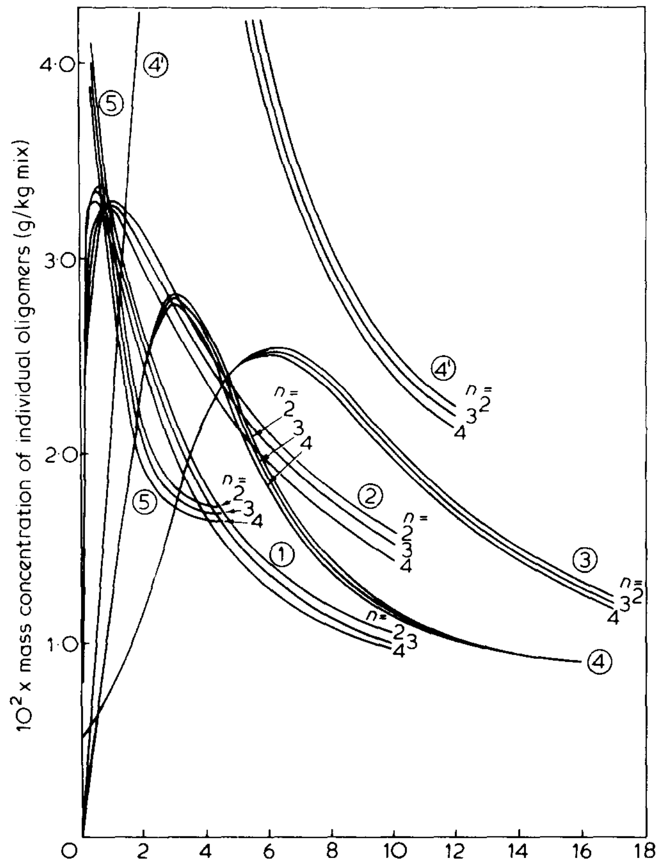


*Figure 9* Concentrations of the first few cyclic oligomers as a function of time

tam. *Figure* 7 depicts the polydispersity index, $\rho$, of the polymer formed (including both $S_n$ and $A_n$). The polydispersity index rises to a peak value larger than 2 when monofunctional acid is present and thereafter decreases asymptotically to a value of 2, typical of condensation polymerizations. Such a maximum is not observed in the absence of monofunctional acid. There is little effect when $k_5$ is changed on the values of $\rho$. Similar peaks were observed by Tirrell *et al.*[8] in the presence of acids, at 220°C. *Figure 8* is a plot of the total oligomer concentration. The final oligomer concentration decreases as the initial water concentration increases, due to the enhanced rates of the reverse reaction of the cylization step. The effect of increasing the initial monofunctional acid is to lower the final oligomer concentration. This is because the reaction of $A_n$ with $S_m$ competes with the cyclization step. The increase in the value of $K_5$ at constant $k_5$ implies a lower rate for the reverse reaction of equation (5) of *Table* 1 and thus gives considerably higher amounts of the cyclic oligomer. Thus it is seen that oligomer formation is highly sensitive to the value of $K_5$, event though this parameter has little effect on the *MWD* of the polymer formed. Similarly, an increase in temperature leads to a faster approach to equilibrium concentrations of the oligomer. *Figure* 9 shows the concentrations of $C_2$, $C_3$ and $C_4$ as functions of time for the various cases. The peak and the other trends are similar to those observed in *Figure* 8. It is interesting to observe that the total cyclic oligomer concentration is almost 100 times that of $C_2$, $C_3$ or $C_4$, in contrast with the model of Mochizuki and Ito[9,10] who obtain the total cyclic oligomer concentration as three times that of $C_3$. *Figure* 10 compares the *MWD*s for the various cases at 235°C. The general conclusions drawn from these curves are similar to what can be inferred from *Figures* 6 and 7. The *MWD* for low times (not shown in *Figure* 10) is much broader in the presence of monofucntional acid than in its absence.

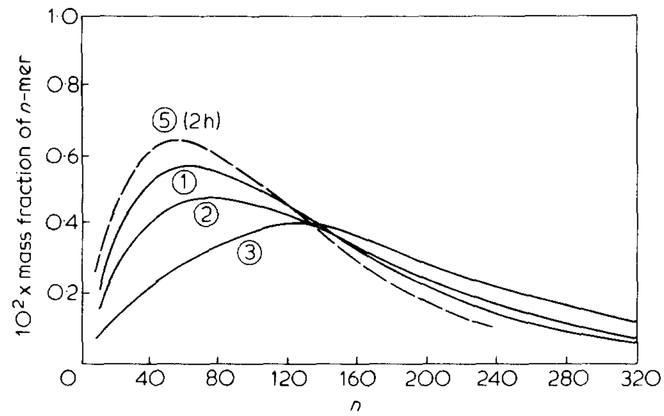


*Figure 10* *MWD*s for cases 1, 2, 3 for polymerization times of 10 h and for case 5 for 2 h

## CONCLUSIONS

Molecular weight distributions and cyclic oligomer formation have been obtained for reversible nylon-6 polymerizations under different polymerization conditions. Due to a lack of experimental data, the forward rate constant of the cyclization step, $k_5$, and the equilbrium constant for this reaction, $K_5$, have been treated as parameters. The conversion of caprolactam and the *MWD* of the polymer formed is relatively insensitive to the values of $K_5$ whereas the concentration of cyclic oligomers depends significantly upon it: $k_5$ influences $\bar{DP}_n$ more significantly.

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