

Simulation of Molecular Weight Distribution and Cyclic Oligomer Formation in the Polymerization of Nylon 6

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Synopsis

The reversible polymerization of nylon 6 including ring opening, polycondensation, polyaddition, and cyclization reactions as well as the reaction with monofunctional acids was simulated for an isothermal batch reactor at 235°C. The cyclic oligomer concentrations, the molecular weight distributions, and its moments have been computed using a chain length-dependent equilibrium constant for the cyclization reaction. Even though the cyclization step does not influence the monomer conversion considerably, it does effect the molecular weight distribution and its moments.

INTRODUCTION

Even though nylon 6 is commercially an important polymer, only a few studies are available on the modeling, simulation, and optimization of its polymerization. These studies have considered ring opening, polycondensation, and polyaddition reactions¹⁻¹³ and are restricted to obtaining the time variation of the conversion of the lactam,⁸⁻¹³ the number-^{8,11-13} and weight-average⁸ chain lengths, and the polydispersity index.⁸ Also, except for the studies of Mochizuki and Ito,^{11,12} which are highly simplified and empirical, most of the studies ignore the formation of cyclic oligomers. This reaction is important because the formation of cyclic oligomers causes trouble in the spinning processes, and these must be removed by an energy-intensive extraction process with hot water. Moreover, Gupta et al.¹⁴ have shown recently, using a simple kinetic model for the cyclization reaction, that the formation of cyclic oligomers influences the number-average chain length and the molecular weight distribution (MWD) of the formed polymer substantially, though its effect on the conversion is not as great.

In this study, a more realistic kinetic model for the formation of cyclic oligomers is chosen, in which the equilibrium constant is a function of the chain length. Such a scheme has been suggested by Andrews et al.¹⁵ and Stockmayer and Jacobson.¹⁶ This is incorporated in the kinetic scheme, and mass balance equations for each species in the reaction mass are solved numerically to obtain the variation of the MWD, its moments, and the concentration of the various cyclic oligomers as a function of time.

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FORMULATION

The kinetic scheme used in this study is shown in Table I. It is a combination of the reactions given by Tirrell et al.⁸ and the cyclization reaction suggested by Andrews et al.¹⁵ and Stockmayer and Jacobson.¹⁶ This cyclization reaction differs from that used by Mochizuki and Ito^{11,12} and has been selected for study since a considerable amount of experimental information on the equilibrium constant of the reaction is available. In contrast, data are not available for the equilibrium constant associated with the cyclization step used by Mochizuki and Ito due to proprietary reasons; and, at best, a parametric study is possible with it.¹⁴

The rate constants k_1 , k_2 , k_3 , k'_1 , k'_2 , and k'_3 shown in Table I are associated with the reaction of *functional groups* and are therefore, identical with those of Reimschuessel¹³ who wrote mass balance equations in terms of functional group concentrations, e.g., [—COOH], [—NH₂], [—CONH—], etc. (square brackets indicate concentration). In writing mass balance equations for *molecular species*, e.g., S_n , A_n , etc., proper accounting of the number of reacting functional groups must be made. Thus, in the reaction between S_n and S_m , there are two possibilities: the —COOH of S_n may react with the —NH₂ of S_m and the —COOH of S_m may react with the —NH₂ of S_n , and the forward reaction between S_n and S_m should be associated with a rate constant $2k_2$. If n and m are equal a factor of $1/2$ is necessary in the rate constant to prevent counting of molecular collisions twice as discussed extensively by Kumar and Gupta¹⁷ and used in their earlier studies on the simulation of condensation polymerizations violating the equal reactivity hypothesis¹⁸⁻²⁰ and the modeling of novolac-type phenol-formaldehyde polymerization.²¹ Similarly, since only one —NH₂ on S_n can react with the —COOH on A_m , the corresponding forward rate constant will be k_2 . And since the —NH₂ end group of S_n can react with any of the m —CONH— groups of the cyclic C_m , the forward rate constant for reaction (3) in Table I will be mk_3 . In doing this, it is assumed that the constants depend only on the functional groups and not the units to which they are attached.

Accounting for the reverse reactions is slightly more involved because of the existence of several possibilities. The reactions between S_{n+m} and W are given in Table I. A rate constant $2k'_2$ is associated with the reaction of S_i and S_{n+m-i} because there are two —CONH— sites on S_{n+m} at which water can react to give the two products (except for one of the reactions shown in Table I 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; and the various possibilities are again shown in Table I. In the reverse reactions of the third step (polyaddition and cyclization), the —NH₂ end group of S_{n+m} can attack any of the $n+m-1$ —CONH— groups on itself to give several products shown in Table I. The rate constants or these will be different and will depend on the size of the cyclic oligomer, C_i , formed. These are thus written as $k'_3(i)$. No such chain-length dependence is expected for the forward rate constant.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 II. Further, when our equations were summed up appropriately after neglecting reactions (4) and the cyclization steps of Table I, it was found that they reduced to the expressions

of Reimschuessel¹³ for $d[M]/dt$, $d \sum_{n=1}^{\infty} [S_n]/dt$, and $d[S_1]/dt$. The mass balance equations given in Table II are more detailed and general than earlier work, and the commonly used approximation^{8,13} of $[S_2] \simeq [S_1]$ is not made.

The Rate Constants

As given by Reimschuessel,^{5,13} the rate constants are a function of the acid end group concentration (in g-mol/kg mixture)

$$k_i = k_i^0 + k_i^c \sum_{n=1}^{\infty} ([A_n] + [S_n]) \quad (1)$$

where k_i and k_i^0 have units of kg/mol-h, and k_i^c have units of kg²/mol-h. The individual coefficients k_i^0 and k_i^c are functions of temperature and are expressed in terms of Arrhenius parameters A^* and E :

$$\log k = \log A^* - \frac{E}{4.574T} \quad (2)$$

where T is the absolute temperature in K. Values of A^* for k_1^0 , k_1^c , k_2^0 , k_2^c , k_3^0 , and k_3^c are 1.694×10^6 , 4.106×10^7 , 8.687×10^9 , 2.337×10^{10} , 2.620×10^9 , and 2.372×10^{10} and those of E (cal/mol) are 21,040, 18,753, 22,550, 20,674, 21,269, and 20,400, respectively.^{5,13} Also, the equilibrium constants K_1 , K_2 , and $K_3(1)$ [defined in terms of functional groups and equal to k_1/k_1' , k_2/k_2' , and $k_3/k_3'(1)$], respectively, are available as functions of the absolute temperature (K) as

$$\log K_i = \frac{\Delta S_i}{4.574} - \frac{\Delta H_i}{4.574T} \quad (3)$$

The values^{5,13} of ΔS_i (e.u.) for K_1 , K_2 , and $K_3(1)$, respectively, are -7.87 , 0.93 , and -6.95 ; whereas those of ΔH_i (cal/mol) are 2114.2, -6140.4 , and -4028.3 , respectively. These values of the rate and equilibrium constants have also been used earlier by Mochizuki and Ito^{11,12} and by Tirrell et al.⁸ and have recently been found to explain satisfactorily extensive experimental data of Tai et al.^{9,10} on caprolactam and carboxyl end group concentrations.

Andrews et al.¹⁵ and Stockmayer and Jacobson¹⁶ have obtained the equilibrium constants $K_A(n)$ for the cyclization reaction



as

$$K_A(n) = \frac{[S_m][C_n]}{[S_{n+m}]} \simeq [C_n] \quad n = 2, 3, \dots \quad (5)$$

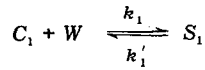
and have reported $K_A(n)$ computed from equilibrium values of $[C_n]$ as a function of temperature for n up to 6. Values of $K_A(n)$ beyond $n = 6$ are not given. Their values of $K_A(n)$ at a temperature of 235°C can be curve-fitted by the following empirical equation:

$$K_A(n) = \frac{0.1692}{n^2} \text{ (g-mol/kg) at } 235^\circ\text{C} \quad n = 2, 3, \dots \quad (6)$$

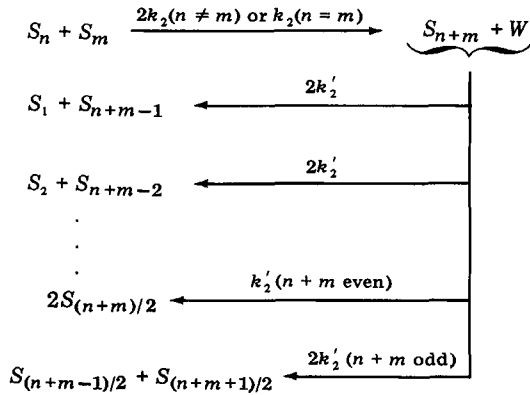
The relationship between $K_A(n)$ and the equilibrium constant $K_3(n) [= k_3/k_3'(n)$, $n = 2, 3, \dots$] used in the present model is difficult to deduce exactly. At equi-

TABLE I
The Kinetic Scheme for Nylon 6 Polymerization^a

1. Ring-Opening



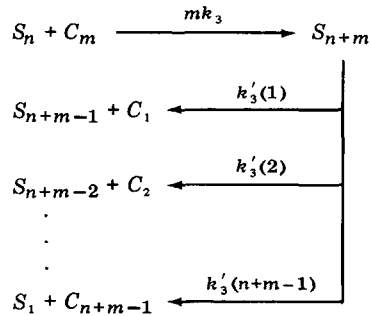
2. Polycondensation



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

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

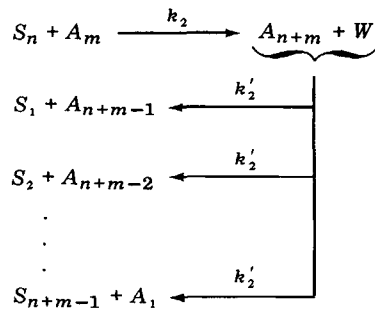
3. Polyaddition and Cyclization



Forward reaction, $n, m = 1, 2, \dots$

Reverse reaction, $n + m = 2, 3, \dots$

4. Reaction with Monofunctional Acid



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

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

^a See footnote a to Table II.

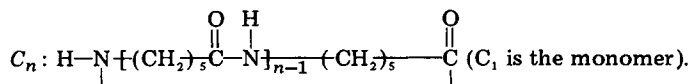
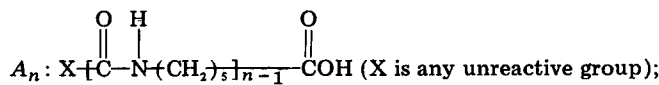
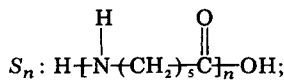
librium, eq. (g) of Table II gives, on equating $d[C_n]/dt$ to zero:

$$\frac{nk_3}{k'_3(n)} = nK_3(n) = \frac{\sum_{m=1}^{\infty} [S_{n+m}]}{[C_n] \sum_{m=1}^{\infty} [S_m]} \simeq \frac{1}{[C_n]} = \frac{1}{K_A(n)} \quad (7)$$

TABLE II
Mass Balance Equations for an Isothermal Batch Nylon 6 Reactor^a

$\frac{d[C_1]}{dt} = -k_1[C_1][W] + k'_1[S_1] - k_3[C_1] \sum_{n=1}^{\infty} [S_n] + k'_3(1) \sum_{n=1}^{\infty} [S_{n+1}]$	(a)
$\frac{d[W]}{dt} = -k_1[C_1][W] + k'_1[S_1] + k_2 \sum_{n=2}^{\infty} \sum_{m=1}^{n-1} [S_{n-m}][S_m]$ $-k'_2[W] \sum_{n=2}^{\infty} (n-1)[S_n] + k_2 \sum_{n=2}^{\infty} \sum_{m=1}^{n-1} [S_{n-m}][A_m] - k'_2[W] \sum_{n=2}^{\infty} (n-1)[A_n]$	(b)
$\frac{d[S_1]}{dt} = k_1[C_1][W] - k'_1[S_1] - 2k_2[S_1] \sum_{n=1}^{\infty} [S_n] + 2k'_2[W] \sum_{n=2}^{\infty} [S_n]$ $-k_3[S_1] \sum_{n=1}^{\infty} n[C_n] + \sum_{n=1}^{\infty} [S_{n+1}]k'_3(n) - k_2[S_1] \sum_{n=1}^{\infty} [A_n] + k'_2[W] \sum_{n=2}^{\infty} [A_n]$	(c)
$\frac{d[S_n]}{dt} = -2k_2[S_n] \sum_{m=1}^{\infty} [S_m] + k_2 \sum_{m=1}^{n-1} [S_m][S_{n-m}] - k'_2[W](n-1)[S_n]$ $+ 2k'_2[W] \sum_{m=1}^{\infty} [S_{n+m}] - k_3[S_n] \sum_{m=1}^{\infty} m[C_m] + k_3 \sum_{m=1}^{n-1} (n-m)[S_m][C_{n-m}]$ $- [S_n] \sum_{m=1}^{n-1} k'_3(m) + \sum_{m=1}^{\infty} k'_3(m)[S_{n+m}] - k_2[S_n] \sum_{m=1}^{\infty} [A_m] + k'_2[W] \sum_{m=1}^{\infty} [A_{n+m}] \quad n = 2, 3, 4, \dots$	(d)
$\frac{d[A_1]}{dt} = -k_2[A_1] \sum_{n=1}^{\infty} [S_n] + k'_2[W] \sum_{n=2}^{\infty} [A_n]$	(e)
$\frac{d[A_n]}{dt} = -k_2[A_n] \sum_{m=1}^{\infty} [S_m] + k_2 \sum_{m=1}^{n-1} [A_m][S_{n-m}] - k'_2[W](n-1)[A_n]$ $+ k'_2[W] \sum_{m=1}^{\infty} [A_{n+m}] \quad n = 2, 3, 4, \dots$	(f)
$\frac{d[C_n]}{dt} = -k_3n[C_n] \sum_{m=1}^{\infty} [S_m] + \sum_{m=1}^{\infty} k'_3(n)[S_{n+m}] \quad n = 2, 3, 4, \dots$	(g)

^a Legend: W: Water;



where an approximation similar to that made by Andrews et al.¹⁵ has been made to cancel out $\sum_{m=1}^{\infty}[S_{n+m}]$ and $\sum_{m=1}^{\infty}[S_m]$ at equilibrium. Thus, from eq. (6) and (7), we obtain

$$K_3(n) \equiv \frac{k_3}{k'_3(n)} = \frac{1}{nK_A(n)} = \frac{n}{0.1692} \text{ at } 235^\circ\text{C} \quad n = 2, 3, \dots \quad (8)$$

The chain length dependence of $K_3(n)$ is the most significant difference between the present study and our earlier work.¹⁴

THE SIMULATION PROCEDURE

The Runge-Kutta-Gill²² method was used to solve for the MWD and other variables of interest as a function of time with a value of Δt of 1/60 h. Some preliminary trials using a Δt of 1/1000 h gave similar results. A check made on the program was to compute the total concentration of $\text{-(CH}_2\text{)}_5$ groups present on various S_n , A_n , and C_n at any time and match it with the initial value (only A_1 and C_1). This check came out to within 0.5%. In the computer program, approximately 250 equations for S_n and A_n (unless $[A]_0 = 0$) and 200 equations for C_n (i.e., equations for S_1 to S_{250} , A_1 to A_{250} , and C_1 to C_{200}) were first used for solution. After every hour of polymerization time, the number of equations was increased by approximately 80 for each of these. Such a procedure was essential because of the reversible nature of the reactions to give a good check on the $\text{-(CH}_2\text{)}_5$ group balance. The computation time for a typical run up to a polymerization time of 8 h was 5 h on a DEC 1090, most of this time on the computer being used in the final stages of polymerization.

Some preliminary runs were made at 220°C neglecting the cyclization steps (but accounting for the polyaddition step corresponding to $m = 1$ in reaction three of Table I), and the monomer conversion and the degree of polymerization were found to be close to those of Tirrell et al.⁸ who used a generating function technique. Since the simulations of Tirrell et al. compared very well with the experimental runs of Hermans et al.,² this confirms at least some parts of our model and computations. It may be added that there is very little experimental work reported in the literature on the formation of cyclic oligomers and the MWD of the polymer formed with which to compare our results.

RESULTS AND DISCUSSION

Two simulations were carried out at 235°C taking the initial concentration of caprolactam as 8.8 g-mol/kg mixture. In run 1, the initial water concentration was taken as 0.44 g-mol/kg, a value very close to that of run C of Hermans et al.² and that of monofunctional acid as zero. In run 2, the water concentration was taken at a lower value of 0.22 g-mol/kg (which corresponds to average values present in several industrial VK-type reactors),^{13,23} and $[A]_0$ was taken as 0.088 g-mol/kg. Figure 1 shows the conversion of the caprolactam as a function of time along with results obtained¹⁴ by neglecting the cyclization reaction. It is thus observed that cyclization has little effect on the conversion of caprolactam.

Figure 2 shows the number-average degree of polymerization, $DP_n \{ \equiv \sum_{n=1}^{\infty} n([A_n] + [S_n]) / \sum_{n=1}^{\infty} ([A_n] + [S_n]) \}$ as a function of time. Results of run 1 without

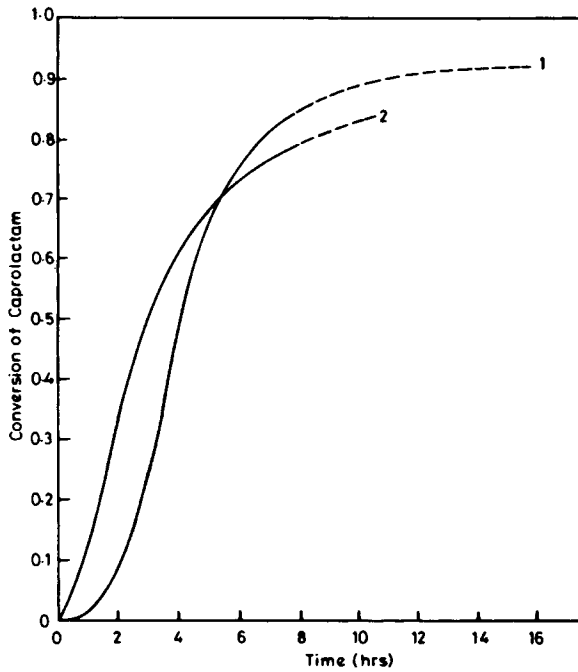


Fig. 1. Conversion as a function of time for runs 1 and 2. Solid line: this work; dotted line: ref. 14 (no cyclization).

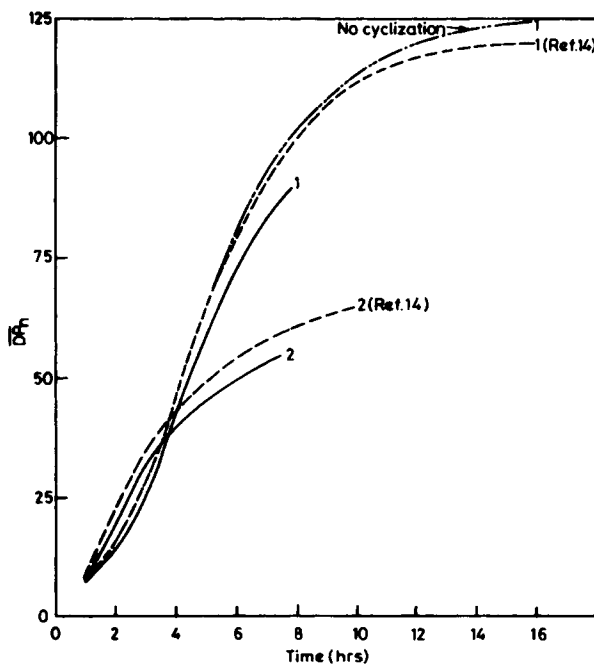


Fig. 2. Number-average degree of polymerization as function of time. Solid line: this work; dotted line: ref. 14 ($k_5 = k'_1$, $K_5 = 0.06$ mol/kg); (---) run 1 without cyclization.

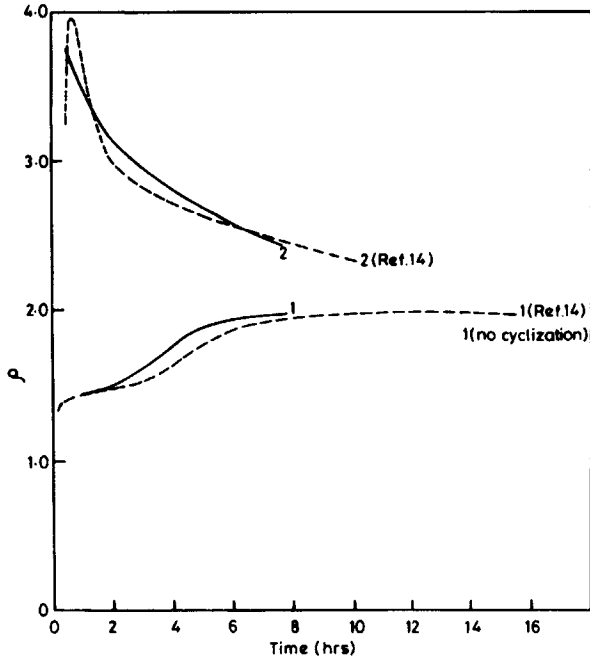


Fig. 3. Polydispersity index as function of time. Results of ref. 14 shown by dotted lines. Run 1 (without cyclization) is identical with run 1 of ref. 14.

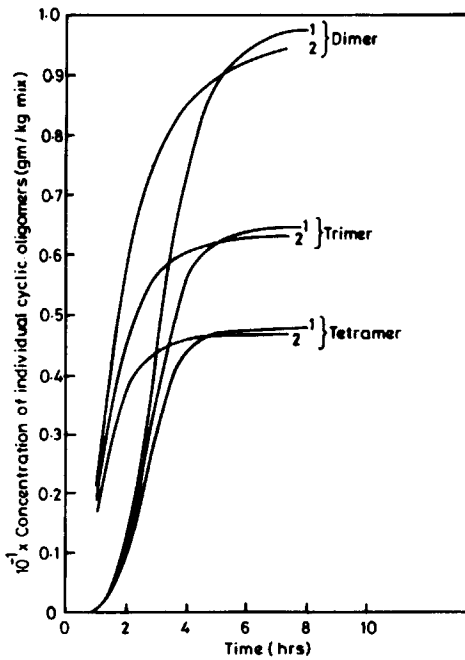


Fig. 4. Weight percent of the first few cyclic oligomers (dimer, trimer, and tetramer).

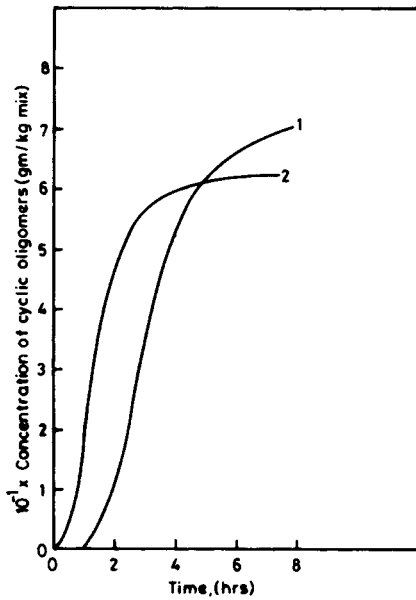


Fig. 5. Total cyclic oligomer content as function of time.

cyclization are shown for comparison, and it is observed that \overline{DP}_n depends significantly on the cyclization reaction. Also shown in Figure 2 are results from our previous study¹⁴ in which, instead of the cyclization reactions shown in Table I, the following reactions proposed by Mochizuki and Ito^{11,12} were used:

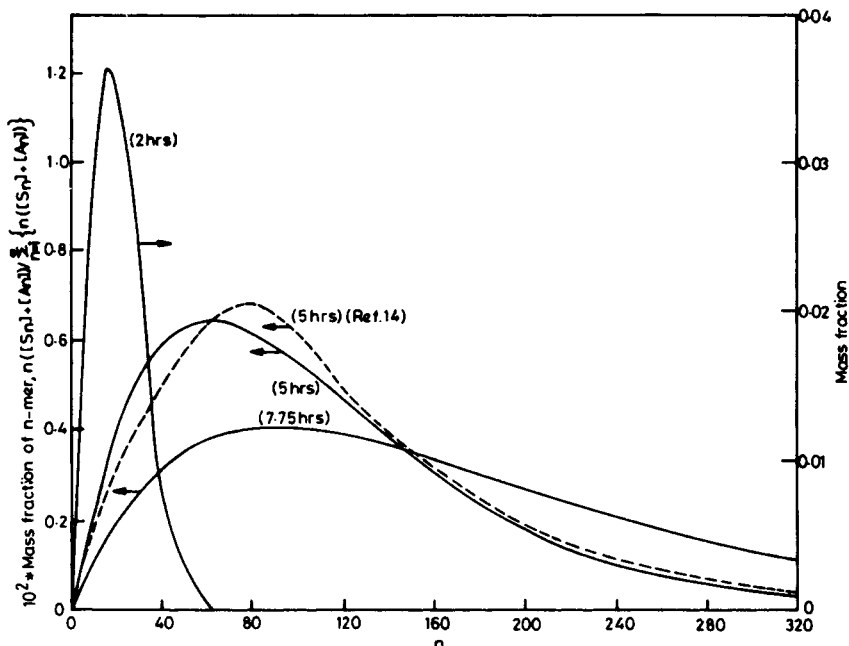
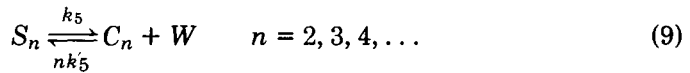


Fig. 6. MWD at three different polymerization times for run 1. Dotted curve shows corresponding results of ref. 14 ($k_5 = k'_1$, $K_5 = 0.06$ mol/kg).

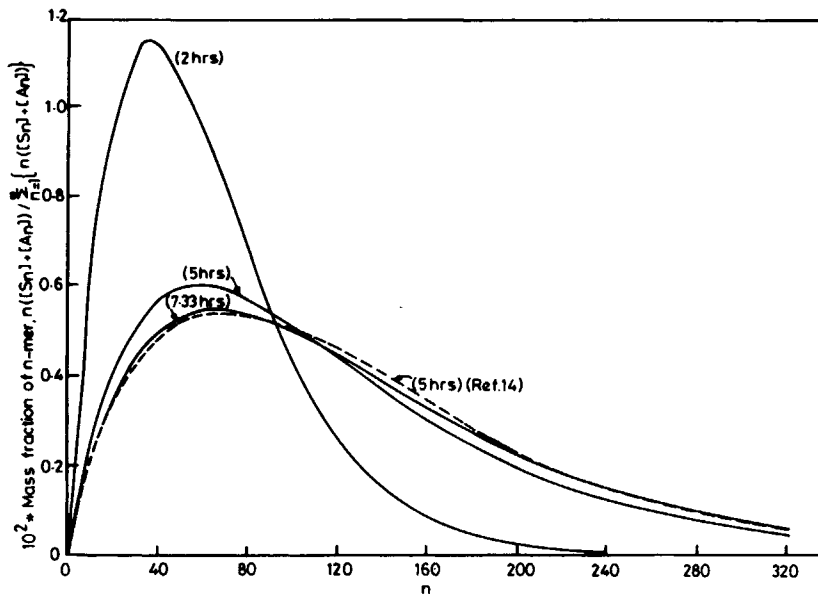


Fig. 7. MWDs for run 2. Dotted curve: ref. 14 ($k_5 = k'_1$, $K_5 = 0.06$ mol/kg).

The rate constant k_5 and the equilibrium constant $K_5 (\equiv k_5/k'_5)$ were treated as parameters because of lack of experimental information. The \overline{DP}_n obtained in the present study are observed to be lower than those obtained earlier using the "reasonable" values of $k_5 = k'_1$ and $K_5 = 0.06$ mol/kg.¹⁴ The effect of the cyclization reactions on the polydispersity index ρ is seen to be small from Figure 3. In addition, there is very little difference between the values of ρ in the present work and those obtained earlier.¹⁴ The sharp peak observed for run 2 is characteristic of nylon 6 polymerized in the presence of monofunctional acid and has been observed earlier by Tirrell et al.⁸

Figures 4 and 5 show the concentrations of the first few cyclic oligomers as well as the total cyclic oligomer content (in weight percent) for runs 1 and 2. These results differ most significantly from those obtained using the earlier kinetic model of cyclization.¹⁴ The total cyclic oligomer content is observed to be about 6% for run 2, which represents conditions typically encountered in industrial reactors. The values reported for commercial polymerizations are 3–4%.^{11–13} Minor variations may be made in the constant used for $K_3(n)$ in eq. (8) to obtain a better match between simulation results and experimental values. In the previous work,¹⁴ the cyclic oligomer concentration obtained using reasonable values of k_5 and K_5 was an order of magnitude lower (approximately 0.2 wt%). The concentration-vs.-time plots (Fig. 4) for the individual cyclic oligomers do not show any peak, which seems to be consistent with some experimental results shown by Mochizuki and Ito.^{11,12} Thus, the present kinetic scheme using a chain length-dependent equilibrium constant for the cyclization reaction is superior to the earlier kinetic model.

Figures 6 and 7 show the MWDs at different times for runs 1 and 2, respectively. The results are found to be significantly different from that reported in reference 14, the trends being similar to those predicted from results on \overline{DP}_n and ρ .

A comparison of the various curves for runs 1 and 2 as well as earlier results reveals that as the initial water concentration $[W]_0$ is reduced (corresponding to higher vacuums being applied), the conversion of the caprolactam is slowed down, but as $[A]_0$ is increased, the conversion is speeded up. Figure 1 shows that the latter effect predominates over the former. Increasing the value of $[A]_0$ or $[W]_0$ reduces the \overline{DP}_n , the effect of $[A]_0$ being again more pronounced. Reducing $[W]_0$ or $[A]_0$ also gives lower oligomer content. An optimal value of $[W]_0$ and $[A]_0$ is thus indicated for rapid conversion with controlled values of \overline{DP}_n and low cyclic oligomer content.

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