Simulation of reversible nylon-6,6 polymerization

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The forward and reverse rate constants for nylon-6,6 polymer formation have been determined through curve fitting of experimental data by Ogata[1]. The molecular weight distribution (*MWD*) in a batch reactor is simulated and determined numerically for up to eleven hours of reversible polymerization. The *MWD* obtained differs from Flory's distribution due to reversibility of the reaction. The deviation increases as the time of polymerization progresses. The polydispersity index increases asymptotically to a value of 1.8 in contrast with the value of 2 for irreversible polymerization. This asymptotic value is found to increase as the reaction temperature increases and reduce as the initial water content increases.

INTRODUCTION

The polymerization of nylon-6,6 from its salt can be written in terms of the reaction between functional groups as [2-4]

$$\_NH_2 + —COOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} —CONH— + H_2O \quad (1)$$

where k_1 and k_2 are the rate constants for the forward and reverse reactions associated with the functional groups. The formation of nylon-6,6 has been studied by Ogata who reports k_1 and the equilibrium constant, K, as a function of water concentration present in the reaction mass (in mol water/mol of fundamental units) and the temperature of polymerization. For short times, the polymerization can be approximated as irreversible, but as the time of reaction increases, the reversibility of equation (1) cannot be ignored irrespective of any vacuum level applied[4].

In this paper, an empirical expression of K has been developed from the experimental data of Ogata[1] (*Table 1*) and the molecular weight distribution (*MWD*) of nylon-6,6 in a batch reactor has been simulated for eleven hours of reversible polymerization with the final conversion very close to the equilibrium value. The *MWD* has been obtained numerically as a function of time and compared with Flory's distribution. The results are found to deviate as much as 10% for molecules of higher chain lengths at 200°C. The temperature and the initial water concentration of the reaction mass are two important parameters and a sensitivity analysis has been carried out to evaluate their effects upon the *MWD* under reversible polymerization.

Batch reactor equations for MWD

If S_n and S_m are two polymer molecules of chain lengths n and m respectively in the reaction mass, the polycondensation reaction in terms of these can be written as:

$$S_n + S_m \underset{k_4}{\overset{k_3}{\rightleftharpoons}} S_{n+m} + W; \qquad n, m = 1, 2, \ldots \quad (2)$$

where W represents a water molecule and k_3 and k_4 the forward and reverse rate constants associated with the molecular species shown in the above equation. These rate constants can be written in terms of the rate constants associated with functional groups, k_1 and k_2, as follows. Both S_n and S_m have one NH_2 and one COOH group and can react in two distinct ways which means that $k_3 = 2k_1$. Similarly in the reverse reaction of S_{n+m}, there are $(n+m-1)$ CONH– sites where the water molecule can react and therefore $k_4 = (n+m-1)k_2$. With this, the mass balance equation for S_n can be written. For S_1, it is:

$$\frac{d[S_1]}{dt} = -2k_1[S_1] \sum_{n=1}^{\prime} [S_n] + 2k_2[W] \sum_{n=2}^{\prime} [S_n] \quad (3)$$

Table 1 Rate constants for nylon-6,6 polymerization. (a) Forward rate constant[1] (in l/mol-h)

$$\log_{10} k_1 = \frac{13.1}{[W]^{0.025}} - \frac{4830}{T}$$

where $[W]$ is the concentration of water in the reaction mass in mol of water per mol of fundamental units. (b) Equilibrium constant

$$K = \mathrm{Exp}\{a - b[W]_0\}$$

where $[W]_0$ is the initial water concentration and a and b are constants which are given by:

(1) $[W]_0 < 3.4$

T°C	200	210	220
a	6.17	6.25	6.28
b	0.22	0.23	0.24

(2) $[W]_0 \geqslant 3.4$

T°C	200	210	220
a	5.207	5.35	5.41
b	0.01	0.0083	0.01

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Square brackets represent concentration. The factor of 2 in the last term in the above equation appears because the reaction of water with S_n can occur at either end of the molecule to give S_1 and S_{n-1}. In the forward step, the rate constant associated with the reaction between similar molecules, e.g. S_1 and S_1, is k_1 instead of $2k_1$ to avoid counting molecular collisions twice[3,5,6]. A similar balance on S_n leads to the following equation:

$$\frac{d[S_n]}{dt} =$$

$$\frac{1}{2}2k_1 \sum_{r=1}^{n-1} [S_r][S_{n-r}] - 2k_1[S_n] \sum_{m=1}^{\infty} [S_m] - (n-1)k_2[W][S_n]$$

$$+ 2k_2[W] \sum_{m=n+1}^{\infty} [S_m], \qquad n \geqslant 2 \tag{4}$$

Equations (3) and (4) can be summed over all values of n to find the variation of

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

as

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

$$-2k_1\left(\sum_{n=1}^{\infty} [S_n]\right)^2 + k_1 \sum_{n=2}^{\infty} \sum_{r=1}^{n-1} [S_{n-r}][S_r] - k_2[W]$$

$$\sum_{n=1}^{\infty} (n-1)[S_n] + 2k_2[W] \sum_{n=1}^{\infty} \sum_{m=n+1}^{\infty} [S_n] \tag{5}$$

Noting that:

$$\sum_{n=2}^{\infty} \sum_{r=1}^{n-1} [S_{n-r}][S_r] = \left(\sum_{n=1}^{\infty} [S_n]\right)^2 \tag{a}$$

and:

$$\sum_{n=1}^{\infty} \sum_{m=n+1}^{\infty} [S_n] = \sum_{n=1}^{\infty} (n-1)[S_n] \tag{6}$$

equation (5) reduces to:

$$\frac{d \sum_{n=1}^{\infty} [S_n]}{dt} = -k_1\left(\sum_{n=1}^{\infty} [S_n]\right) + k_2[W] \sum_{n=1}^{\infty} (n-1)[S_n] \tag{7}$$

On examination of the above equation, it is noted that:

$$\sum_{n=1}^{\infty} (n-1)[S_n]$$

is the total number of reacted functional groups and

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

the concentration of unreacted $-NH_2$ (or $-COOH$).

RESULTS AND DISCUSSION

Ref 1 has given an empirical equation for k_1 and graphical representation of K as a function of temperature, T, and water concentration, $[W]$, (in mol water/mol fundamental units) of the reaction mass at the time of polymerization. This is also confirmed in ref 2. In the initial simulation runs, the water concentration was determined at a given time by solving the differential mass balance equation for $[W]$ and k_1 and K evaluated at this value. A conversion of 90% was reached in 10 h for initial water concentration, $[W]_0 = 1$ and $T = 200°C$, whereas the experimental equilibrium conversion in sealed ampules at these conditions has been given to be 87%.

After checking the computer programme, the correlations for k_1 and K were examined more closely. To determine k_1, Ogata started with a known amount of water and monomer (nylon-6,6 salt) in sealed ampules and measured conversion as a function of time for ~2 h. Initial water concentration can be assumed to represent the average concentration in the reaction mass which, on examination of his experimental results, appears to be reasonable. The equilibrium constant, however, has been calculated from experimentally determined equilibrium conversions and correlated with $[W]_0$ in a plot even though the abscissa of this plot showed the equilibrium water concentration. This has been corrected in the empirical correlations developed in *Table 1* and K has been expressed as a function of $[W]_0$ instead of $[W]$. This would imply that K in any given simulation does not change with time.

Equations (3), (4) and (7) were solved on a DEC 1090 computer as a function of time using the Runge–Kutta method of 4th order for different values of n. The molar distribution (N_n) of the polymer formed was obtained for 11 h of actual polymerization and compared with that from the Flory's equation for *MWD* given by [7]:

$$\frac{N_{n,F}}{N_0} = (1-p)^2 p^{n-2} \tag{8}$$

where $N_{n,F}$ is the mol of polymer molecules of chain length, n, N_0 the mol of monomer at time $t = 0$ and p is the conversion of the monomer at the time selected. The ratio ($N_n/N_{n,F}$) is plotted as a function of n in *Figure 1*. This is

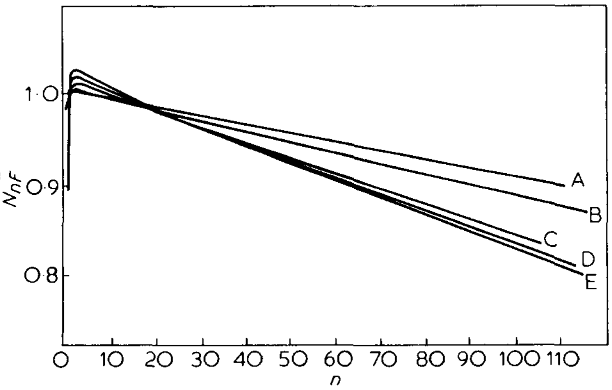

Figure 1 Percent deviation from Flory's distribution as a function of the time of polymerization for nylon-6,6. $[W]_0 = 1.0$, $T = 200°C$; t = (A) 1 h; (B) 2 h; (C) 5 h; (D) 8 h; (E) 11 h

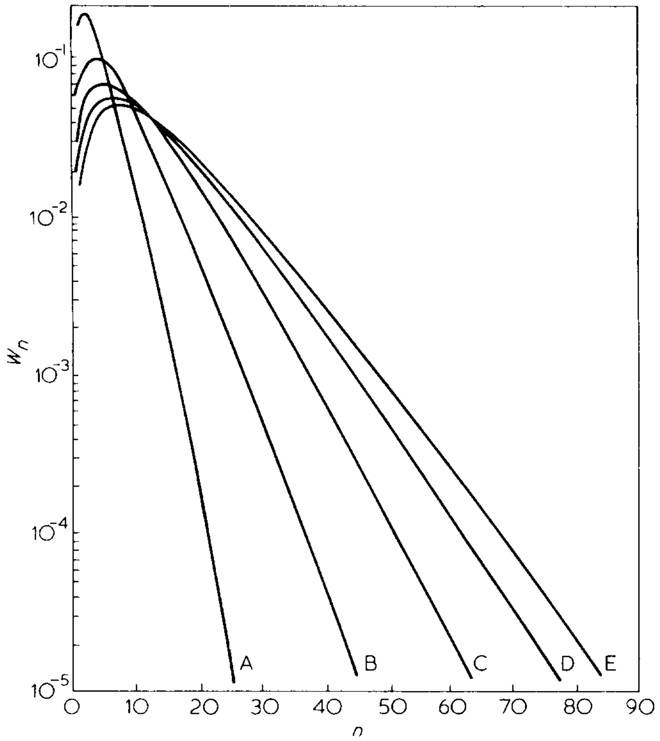

Figure 2 The weight distribution of nylon-6,6 as a function of time of polymerization. $[W]_0 = 1.0$, $T = 200°C$; t = (A) 1 h; (B) 3 h; (C) 6 h; (D) 9 h; (E) 11 h

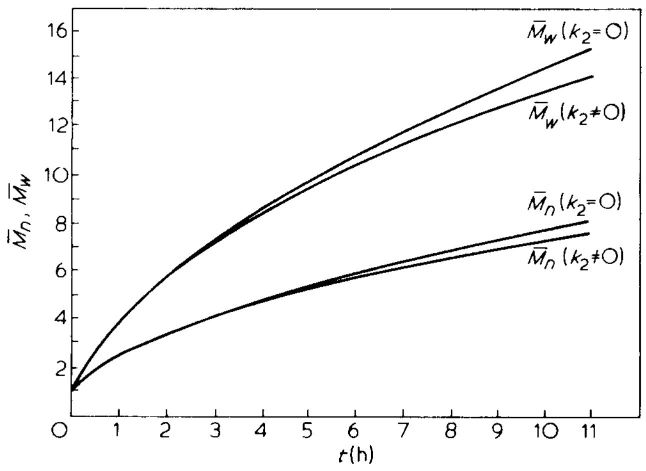

Figure 3 $\bar{M}_n$ and $\bar{M}_w$ of reversible nylon-6,6 polymerization as a function of time. In curves marked with $k_2 = 0$, the variation of forward rate constant k_1 is given in *Table 1* and k_2 is equated to zero. $[W]_0 = 1.0$, $T = 200°C$

always less than 1 for the monomer, (i.e. $n = 1$), undergoes a maximum at $n \sim 2$ and then falls monotonically for larger n as shown. As the time of polymerization increases, the rise and the subsequent fall become sharper.

In this simulation of the polymerization reactor, the rate constants for both the forward and reverse reactions are varying with time due to the change in the water concentration. To study whether this variation of rate constants with time was responsible for the deviation in *MWD* from equation (8), another run was made in which k_2 was set equal to zero. The ratio $(N_n/N_{n,F})$ for the irreversible case was found to be 1 for all n values and for all times (up to 11 h of simulated time) in confirmation of the theoretical analysis of Ray[8].

In *Figure 2*, the weight distribution of nylon-6,6 is plotted as a function of time. The weight distribution undergoes a maximum and becomes broader as the time of polymerization increases. In *Figure 3*, the number and wt average molecular weights, $\bar{M}_n$ and $\bar{M}_w$ have been plotted both for the irreversible, (rate constant k_1 given in *Table 1* with $k_2 = 0$) and reversible cases. From *Figure 3*, the polydispersity index, ρ, can be calculated as a function of time and is found to approach a value of 1.8 asymptotically for large times as opposed to the value of 2 for the irreversible case.

In *Figures 4–7*, the effects of initial water content, $[W]_0$ and the temperature of polymerization have been examined. As the initial water content is increased, the weight distribution becomes sharper with the corresponding

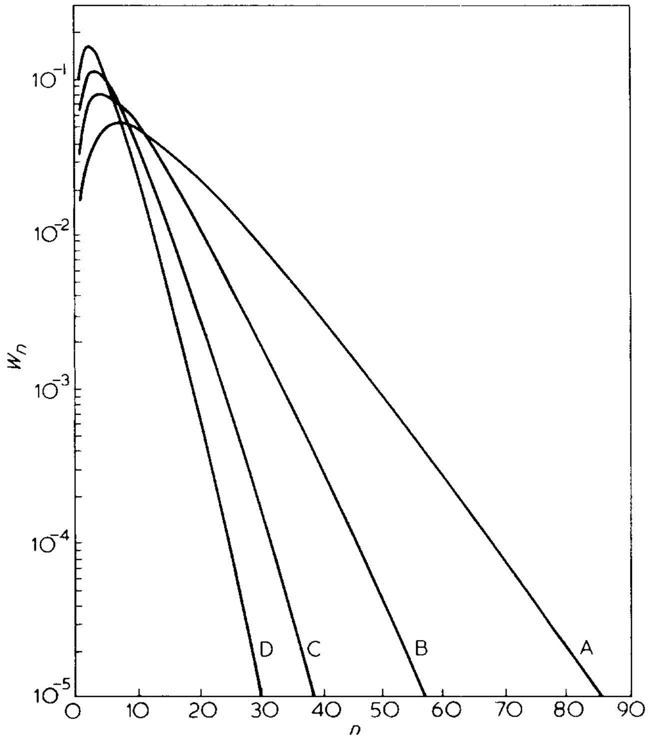

Figure 4 Effect of initial water concentration upon the weight distribution of nylon-6,6. $T = 200°C$, $t = 11$ h; $[W]_0$ = (A) 1; (B) 3.05; (C) 6.23; (D) 10

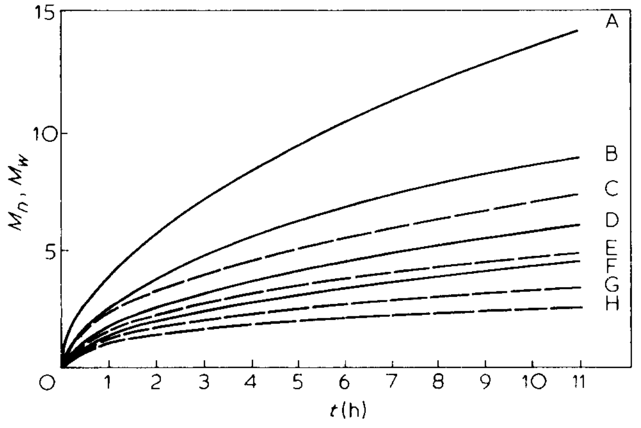

Figure 5 Effect of initial water concentration on $\bar{M}_n$ (— — —) and $\bar{M}_w$ (——). $T = 200°C$; $[W]_0$ = (A) 1.0; (B) 3.05; (C) 1.0; (D) 6.23; (E) 3.05; (F) 10.0; (G) 6.23; (H) 10.0

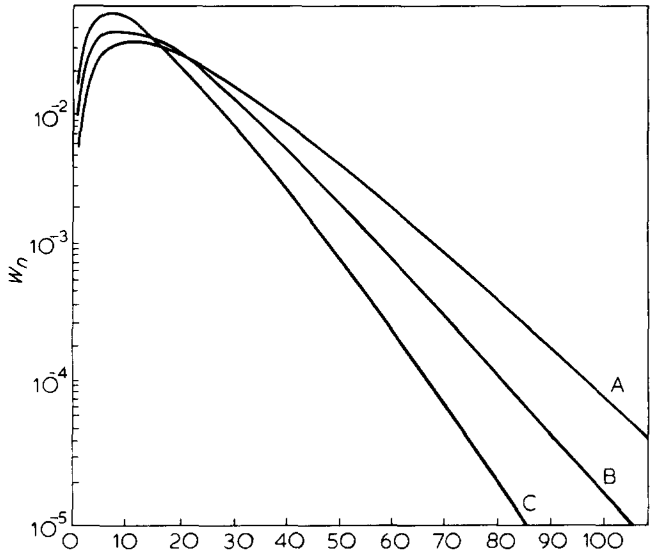

Figure 6 Effect of the temperature upon the weight distribution of nylon-6,6. $[W]_0 = 1.0$, $t = 11$ h; T = (A) 220°C; (B) 210°C; (C) 200°C

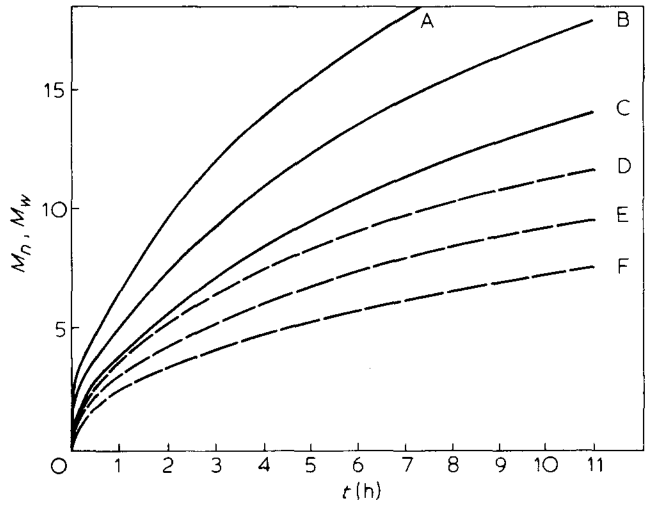

Figure 7 Effect of temperature on $\bar{M}_n$ (— — —) and $\bar{M}_w$ (——). $[W]_0 = 1.0$; T = (A), (D) 220°C; (B), (E) 210°C; (C), (F) 200°C

average *MWs* reducing as shown in *Figure 5*. This is because the reaction mass reaches the equilibrium faster with little monomer reacted. In *Figure 6* the *MWD* is found to be sensitive to the temperature of polymerization. The weight distribution curves broaden with corresponding average *MW* increasing with increasing temperature (*Figure 7*). The rate constants increase with temperature and higher conversions are reached for the same time of polymerization, which implies that the *MWD* must become broader.

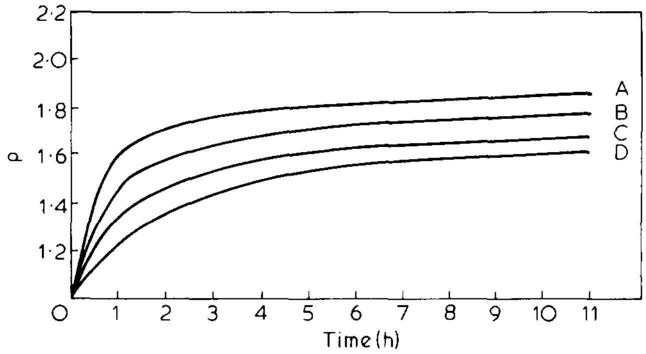

Figure 8 Effect of initial water concentration on ρ as a function of time. $T = 200$°C; $[W]_0$ = (A) 1.0; (B) 3.05; (C) 6.23; (D) 10.0

The effects of initial water content upon the polydispersity index have been examined in *Figure 8*. The plot of ρ *versus* time rises quickly at first, slowly approaching an asymptotic value. This asymptotic value is found to reduce with initial water content. There is a similar effect when the temperature of polymerization is increased as can be found from *Figure 7*. The asymptotic value increases as the temperature is increased.

CONCLUSIONS

The forward rate constant and the equilibrium constant for nylon-6,6 formation are known to depend upon the water content and the temperature of the reaction mass. These have been correlated empirically from the experimental data reported in the literature.

The reversible polymerization of nylon-6,6 has been simulated for a batch reactor and the *MWD* of the polymer formed determined numerically for 11 h of actual polymerization time. The calculated *MWD* is found to be completely described by Flory's distribution for the irreversible case, but a sizeable deviation from it exists when the reversible polymerization occurs.

In this reversible polymerization of nylon-6,6, the polydispersity index approaches a value of 1.8 asymptotically which decreases as the initial water content is increased, and increases as the temperature of polymerization is increased.

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