

Simulation of Reversible Nylon-66 Polymerization in Homogeneous Continuous-Flow Stirred Tank Reactors

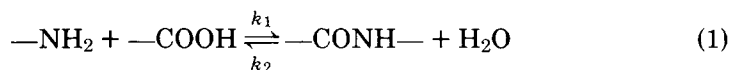
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Synopsis

Experimental data of Ogata¹ has been curve-fitted to obtain the forward and reverse rate constants for nylon-66 polymerization. Its molecular weight distribution (MWD) has been simulated in homogeneous continuous-flow stirred tank reactors (HCSTR) for 11 h of residence time when the reaction mass is very close to equilibrium. The set of algebraic equations have been solved using Brown's algorithm,² which was found to be more efficient compared to the Gauss-Jordan techniques of solution. The MWD thus obtained is compared with our earlier simulation of the molecular weight distribution from batch reactors³ and was found to differ significantly. In HCSTR, the weight fraction distribution does not undergo a maximum and the polydispersity index ρ of the polymer formed is much higher than that obtained from batch reactors. The number and weight average of the polymer formed in HCSTR is found to be significantly lower.

INTRODUCTION

The polymerization of nylon-66 from its salt can be written in terms of the reaction between functional groups as



where the rate constants, k_1 and k_2 , are associated with functional groups. These have been measured by Ogata¹ and correlated with the water concentration $[W]$ in the reaction mass. On careful examination of the experimental data,³ it was noted that the forward rate constant k_1 could be taken as dependent on $[W]$ in the reaction mass, whereas the equilibrium constant K is a function of the initial water concentration $[W]_0$ only. In view of this, the empirical correlations of k_1 and K have been developed with $[W]$ and $[W]_0$, respectively, as parameters and are given in Table I.

Very little has been reported on the simulation of condensation polymerization in HCSTRs in spite of its industrial and theoretical importance. Kilson and Biesenberger have studied the irreversible condensation polymerization in HCSTRs and calculated the molecular weight distribution (MWD).^{4,5} On comparison with the Flory's most probable distribution, they find it to have much higher polydispersity index. The effect of segregation has been studied by Tadmire and Biesenberger,⁶ and the problem of startup, the effect of periodic feed, and the CSTR optimization have been considered in Refs. 7, 8, and 9. In all cases studied, the reaction kinetics was assumed to be irreversible. In nylon-6

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TABLE I
Rate Constants for Nylon-66 Polymerization

Forward rate constant ^a (L/mol·h)				
$\log_{10}k_1 = 13.1/[W]^{0.025} - 4830/T$				
Equilibrium constant ^b				
$K = \exp \{a - b [W]_0\} = k_2/k_1$				
<i>a</i> and <i>b</i> are constants given by:				
<i>T</i> (°C)	200	210	220	
[<i>W</i>] ₀ < 3.4:	<i>a</i>	6.17	6.25	6.28
	<i>b</i>	0.22	0.23	0.24
[<i>W</i>] ₀ ≥ 3.4:	<i>a</i>	5.21	5.35	5.41
	<i>b</i>	0.01	0.0083	0.01

^a See Ref. 1; [*W*] concn water in reaction mass at any time (mol) water/mol fundamental units.

^b See Ref. 3.

polymerization, reactor sequencing of HCSTRs and flow reactors have been analyzed,^{9,10} but in these works, after making several simplifying assumptions, the MWD equations have been combined to give moments and the polydispersity index as a function of time. For several practical systems, the equal reactivity hypothesis does not hold,¹²⁻¹⁴ and for these systems MWD calculations for irreversible kinetics have been made.^{15,16}

The difficulties of numerical calculations of the molecular weight distribution for HCSTRs for reversible kinetics arises because the nonlinear algebraic equations governing the concentrations of different species are interconnected through the rate expression. In view of this, all these must be solved simultaneously. In this paper, the empirical expressions of k_1 and K for nylon-66 have been used to simulate the reversible polymerization in homogeneous continuous-flow, stirred tank reactors. To find the MWD, a set of algebraic equations must be solved simultaneously and Brown's numerical technique² has been used to find it.

In our earlier work of batch reactor simulation of nylon-66,³ we found that the MWD differed slightly from that given by Flory and, for higher oligomers, the deviation was as high as 10%. In this work, the MWD obtained in HCSTR has been compared with those for batch reactors, and it was found that, in the former, the polymer obtained had lower average molecular weights but has high polydispersity. The effect of the reverse reaction is found to reduce the polydispersity from the values for the irreversible polymerization without considerably affecting the average molecular weight. The temperature of polymerization and the initial water content [W]₀ are two important parameters, and a sensitivity analysis has been carried out to determine their effects upon the polymer formed in HCSTRs.

EQUATIONS FOR THE MWD FOR HOMOGENEOUS CONTINUOUS-FLOW STIRRED TANK REACTOR

If S_n and S_m are two polymer molecules of chain lengths n and m , respectively, the reaction between them can be written as

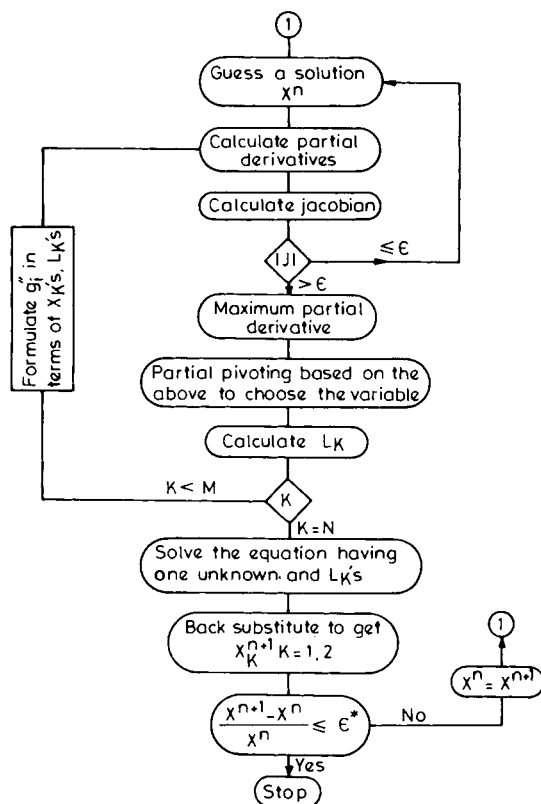
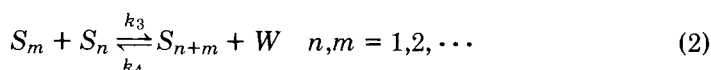


Fig. 1. Flow chart of the Brown's algorithm for solution of nonlinear algebraic equations.



where W represents a water molecule liberated on formation of a bond between S_n and S_m . The rate constants k_3 and k_4 can be written in terms of the reactivity of functional groups as follows: Since S_n and S_m each have one COOH group and one NH_2 group and can react in two distinct ways, k_3 is equal to $2k_1$. Similarly S_{n+m} has $(n + m - 1)$ reacted bonds with which W can react, and k_4 must therefore be equal to $(n + m - 1)k_2$.¹⁷ In terms of these, the rate of formation, r_1 , of S_1 for a batch reactor is given by

$$r_1 = -2k_1[S_1] \sum_{n=1}^{\infty} [S_n] + 2k_2[W] \sum_{n=2}^{\infty} [S_n] \quad (3)$$

where the square brackets stand for the concentration of the species. Similarly the rate of formation, r_m , of S_m is given by

$$r_m = -2k_1[S_m] \sum_{n=1}^{\infty} [S_n] + k_1 \sum_{n=1}^{m-1} [S_n][S_{m-n}] - k_2(m-1)[S_m][W] + 2k_2[W] \sum_{n=m+1}^{\infty} [S_n], \quad m \geq 2 \quad (4)$$

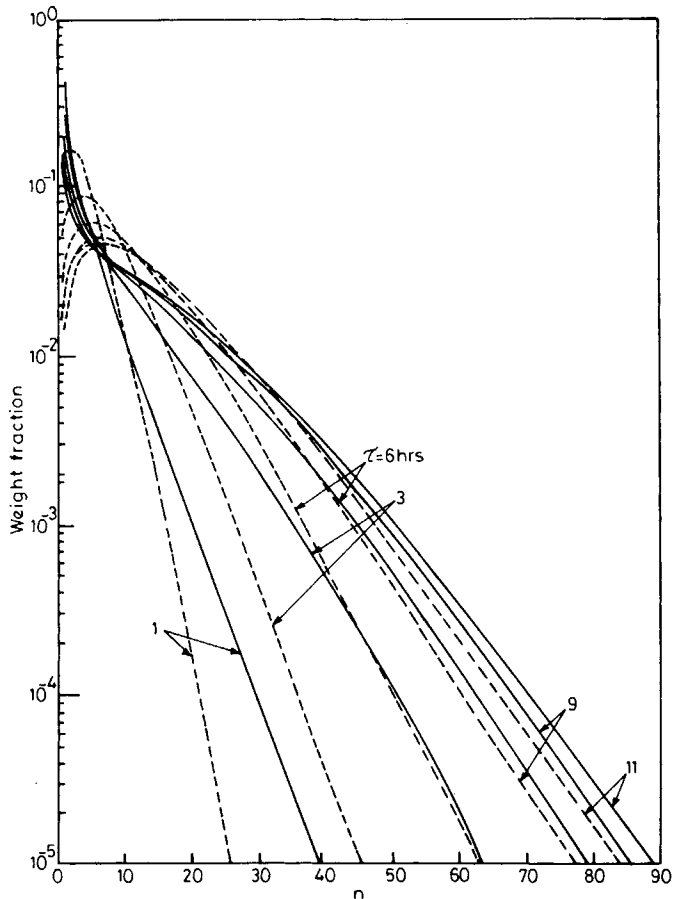


Fig. 2. Weight fraction distribution at different residence times of HCSTR: $[W]_0 = 1.0$; $[T] = 200^\circ\text{C}$; (---) batch reactor; (—) HCSTR.

Mass balance equations for different species for HCSTRs are therefore given by

$$[S_1] = [S_1]_0 - r_1\tau \quad (5a)$$

$$[S_m] = r_m\tau, \quad m \geq 2 \quad (5b)$$

where τ is the average residence time of the reactor and $[S_1]_0$ is the concentration of the monomer in the inlet stream. The set of algebraic equations in eq. (5) is interconnected and must be numerically solved simultaneously to obtain the desired MWD. The water concentration in the reaction mass is obtained from the stoichiometry.

BROWN'S NUMERICAL TECHNIQUE FOR SOLUTION OF ALGEBRAIC EQUATIONS

The mass balance equations of different species must be solved simultaneously and are highly nonlinear due to the reaction rate terms. They can in principle

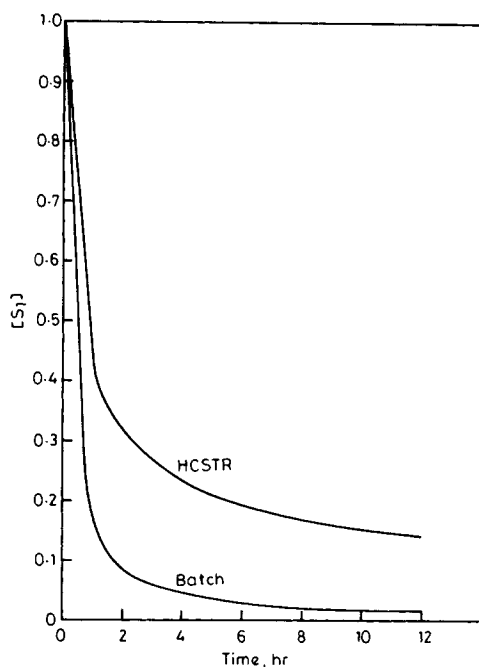


Fig. 3. Monomer concentration for batch and HCSTR vs. residence time: $T = 200^{\circ}\text{C}$; $[W]_0 = 1.0$.

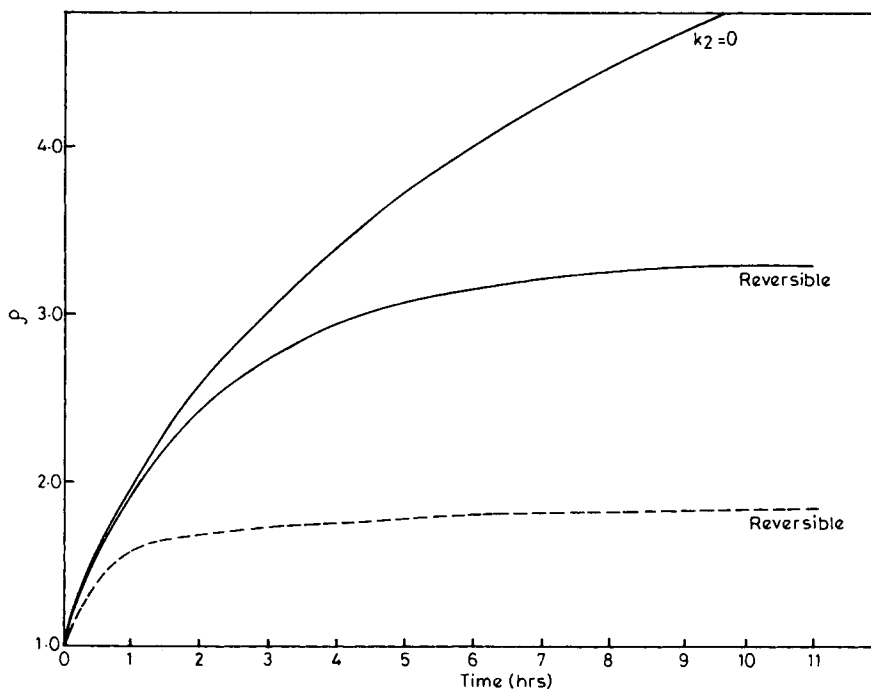


Fig. 4. Polydispersity index of the polymer formed vs. residence time for HCSTR: $[W]_0 = 1.0$; $T = 200^{\circ}\text{C}$; (- - -) batch; (—) HCSTR.

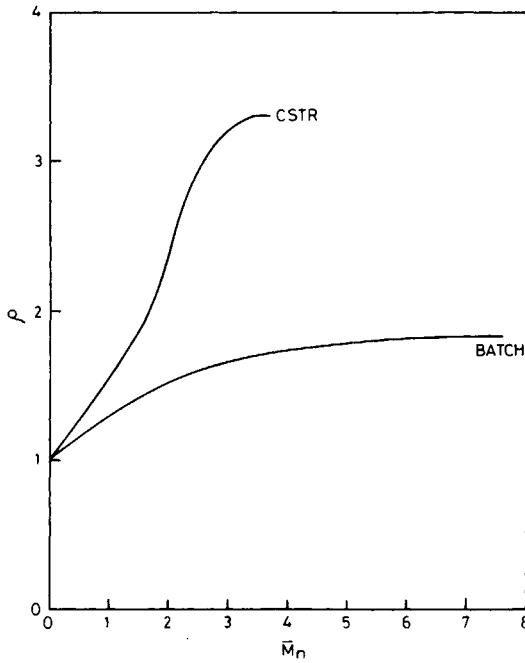


Fig. 5. ρ vs. number average molecular weight of the polymer: $T = 200^\circ\text{C}$; $[W]_0 = 1.0$.

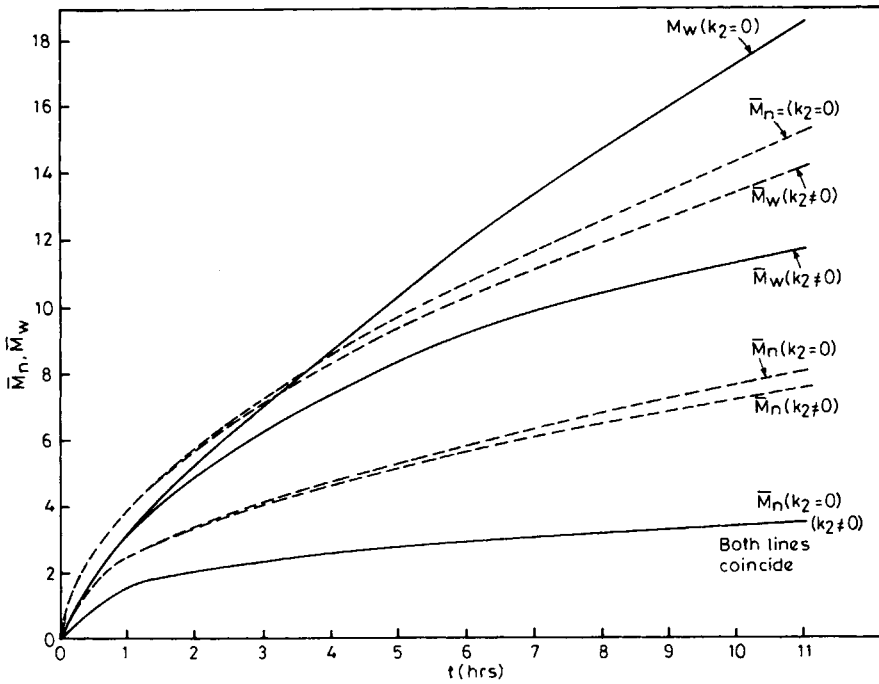


Fig. 6. \bar{M}_n and \bar{M}_w vs. HCSTR residence times: $T = 200^\circ\text{C}$; $[W]_0 = 1.0$; (—) HCSTR; (---) batch.

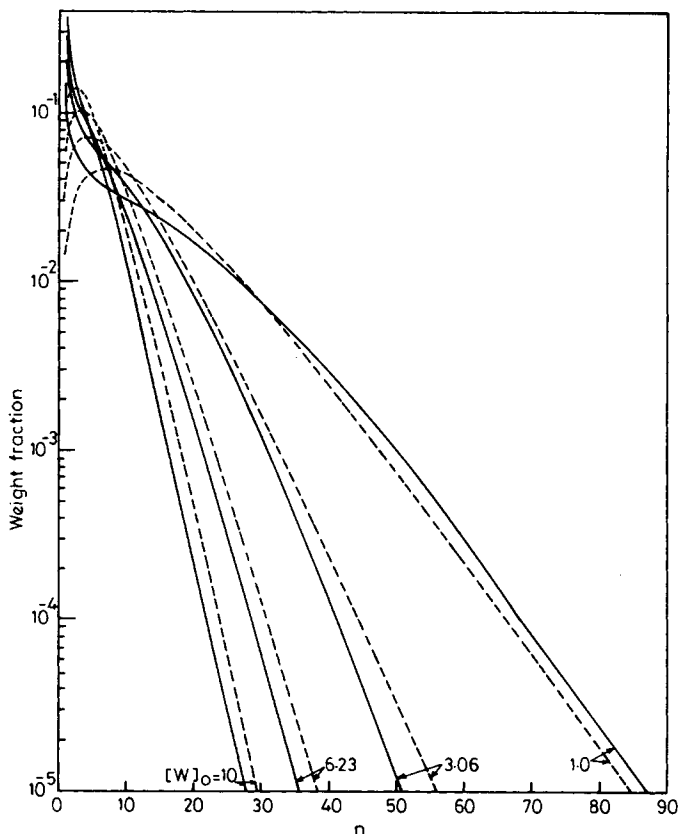


Fig. 7. Effect of initial water content $[W]_0$ on the weight fraction distribution of nylon 66 at $\tau = 11$ h, $T = 200^\circ\text{C}$: (—) HCSTR; (---) batch.

be solved using Gauss–Jordan technique in which one must provide the Jacobian matrix which consists of partial derivatives of the algebraic equations with respect to all independent variables and an initial guess solution of these must be provided which should be very close to the actual values. Deriving the Jacobian matrix for large number of equations, which one would normally come across in the calculation of MWD, is extremely cumbersome whereas providing a good initial guess for a given residence time τ is always a problem.

The flow chart of Brown's technique is given in Figure 1, and this algorithm overcomes both these difficulties as follows: The computer program has a built-in subroutine which generates the necessary partial derivatives, and the algebraic equations are solved sequentially in contrast to the Gauss–Jordan technique, in which they are solved simultaneously. In this regard Brown's algorithm is more efficient.

For small residence times, the solution for a batch reactor is expected to be close to that for an HCSTR. With this in mind, the MWD for the batch reactor of residence time 1 h (available from Ref. 3) was used as the initial guess for the MWD calculations for an HCSTR of the same residence time. The residence time for the HCSTR is then increased by 30 min ($\equiv \Delta\tau$), and the MWD previously calculated served as the initial guess for calculation of MWD for present τ .

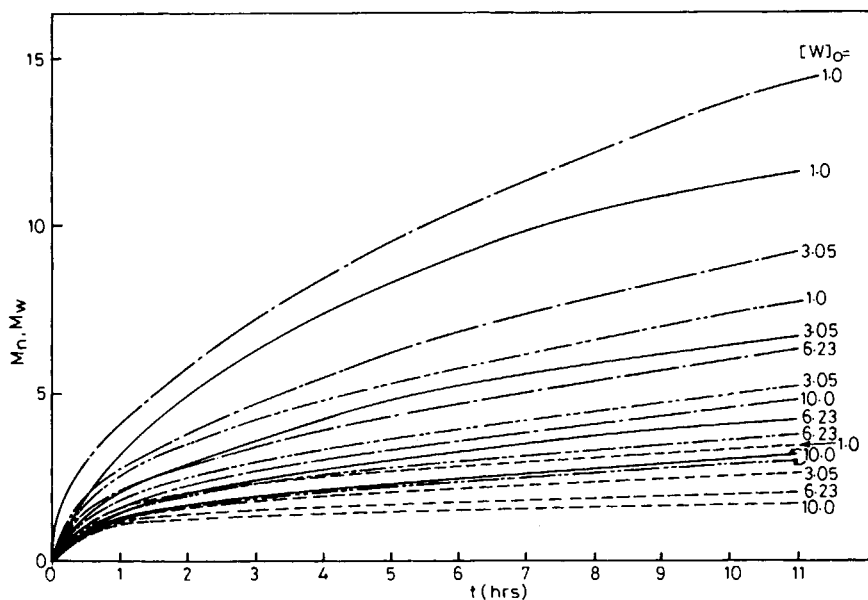


Fig. 8. Effect of $[W]_0$ and \bar{M}_n [(--·) batch; (—) CSTR and \bar{M}_n [(---) batch; (-·-·) CSTR] as a function of HCSTR residence time, $T = 200^\circ\text{C}$.

Whenever the final solution was not obtained in specified number of iterations, $\Delta\tau$ was reduced to 15 min, and results were then found to converge. To minimize the truncation error, the number of equations to be solved were increased by 10 whenever the concentration of the polymer molecule of the highest molecular weight became more than 10^{-6} . This way the residence time of an HCSTR was increased up to 11 h, and the MWD calculated as a function of τ . Since the total number of repeat units in the reaction mass should remain constant, this was checked for all calculations and even after 11 h of polymerization, it was found to be within 1% of the initial value.

RESULTS AND DISCUSSION

The weight fraction distribution (WFD) of nylon-66 polymer with reversible kinetics has been calculated for an HCSTR and has been plotted in Figure 2 with residence time as parameter. On the same diagram, the corresponding results for batch reactors have been given. As seen from the figure, the MWD curves do not undergo a maximum for any residence time. In Figure 3 the monomer conversion for HCSTR has been plotted as a function of τ and found to be considerably lower than those for batch reactors. In Figure 4, the polydispersity ρ has been plotted as a function of time. The curve marked $k_2 = 0$ gives the results for the irreversible polymerization of nylon-66, and it is seen that it continues to increase as τ is increased. In contrast to this, for the reversible polymerization, the curve reaches an asymptotic value of about 3.1. However, ρ for batch reactors approaches asymptotically the value of 2 for irreversible polymerization and the value of 1.8 for reversible polymerization. To bring out the difference in the performance of batch and HCSTRs, in Figure 5, ρ has been

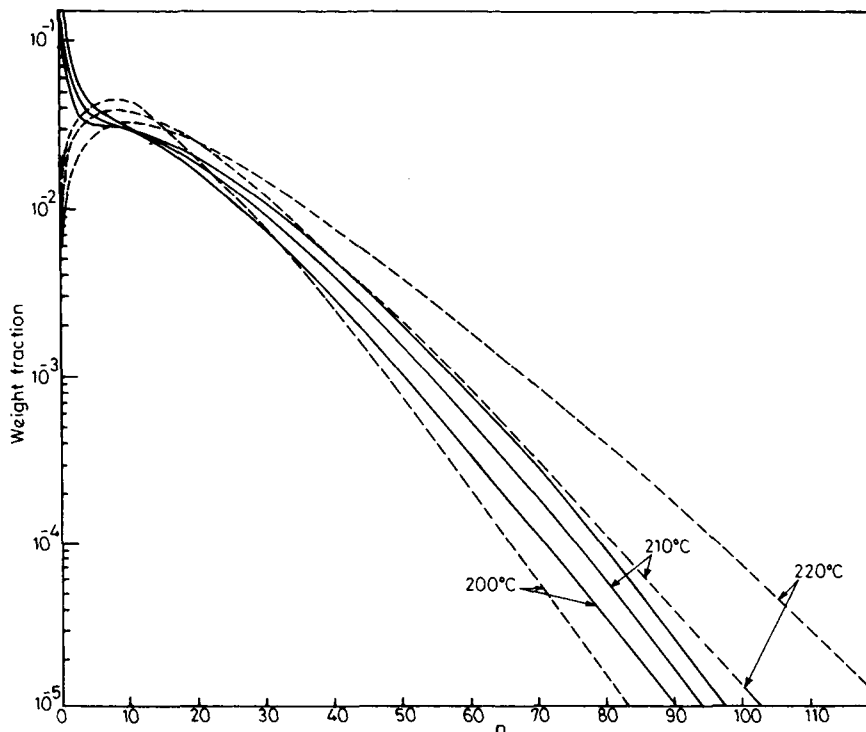


Fig. 9. Effect of temperature on the weight fraction distribution of nylon 66 at $\tau = 11$ hr, $[W]_0 = 1.0$: (—) CSTR; (---) batch.

plotted as a function of \bar{M}_n . For the latter, ρ increases sharply to the value of 3.1.

In Figure 6, the number average \bar{M}_n and weight average \bar{M}_w molecular weights for both batch reactors and HCSTRs have been plotted. \bar{M}_w for the reversible case is found to be lower than the corresponding batch reactor results, but for the irreversible case it is considerably higher.

In the polymerization of nylon-66, the initial water content $[W]_0$ and the temperature appear to be important parameters, and in Figures 7 and 8 the former has been examined. In Figure 7, the weight fraction distribution has been plotted for $\tau = 11$ h. As $[W]_0$ is increased from a value of 1, the distribution curves become sharper and sharper compared to those for batch reactors. In Figure 8, \bar{M}_n and \bar{M}_w have been plotted with $[W]_0$ as parameter. Results for batch reactors are always larger, and, for both reactors, the curves quickly approach the asymptotic value which becomes smaller and smaller as $[W]_0$ is increased.

In Figures 9 and 10, the effect of temperature of polymerization of nylon-66 has been examined. The weight fraction distributions have been calculated at 200°C, 210°C, and 220°C and plotted in Figure 9, and the polymer formed appears to be extremely sensitive to the temperature T . In Figure 10, \bar{M}_n and \bar{M}_w vs. time have been plotted for different T . For an HCSTR, \bar{M}_n is found to be relatively insensitive to T compared to the dependence of \bar{M}_w . The \bar{M}_w and \bar{M}_n

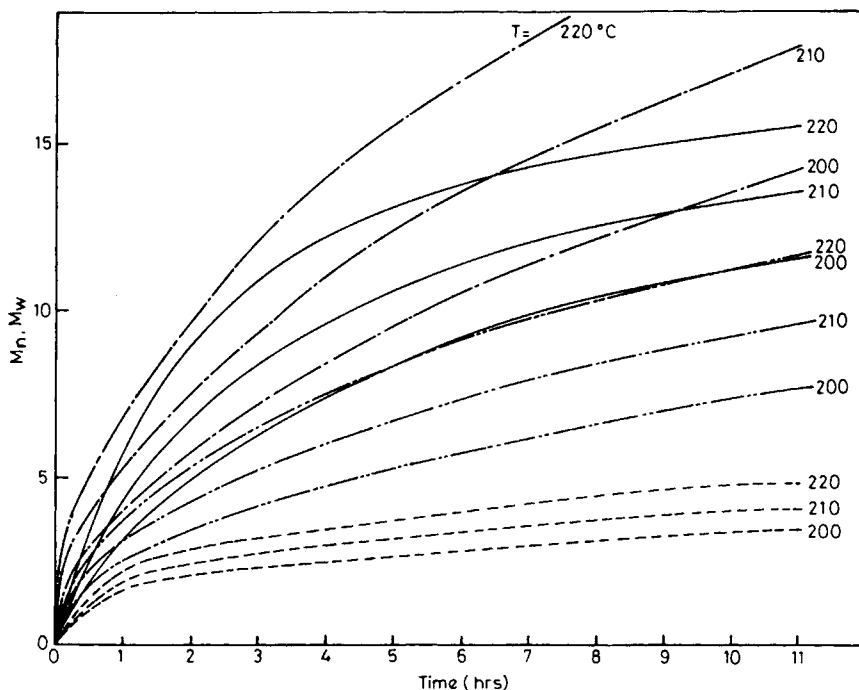


Fig. 10. Effect of temperature on \bar{M}_w [(---) batch; (---) CSTR] and \bar{M}_n [(---) batch; (---) CSTR] vs. reactor residence time.

curves for batch reactors are found to be always higher than those for HCSTR, even though the polydispersity index for the latter is always larger. With the increase in temperature, ρ for HCSTR is found to increase monotonically.

CONCLUSIONS

Nylon-66 polymerization has been simulated for HCSTR up to 11 h of residence time. The MWD of polymer formed in HCSTR differs significantly from the one obtained in a batch reactor with same residence time. In the former, the polymer has smaller number average and weight average molecular weights, but it is much more polydispersed.

The initial water content $[W]_0$ and the temperature T of polymerization are found to be extremely important parameters. $[W]_0$ not only lowers \bar{M}_n and \bar{M}_w but reduces the polydispersity index also. In contrast to this, increasing T has the opposite effect.

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