

Algorithm for Computation of Molecular Weight Distribution and Its Moments in Reversible Step-Growth Polymerization in Batch Reactors

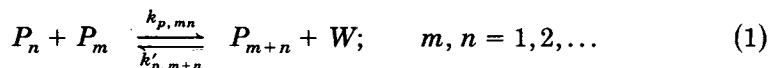
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Synopsis

The differential equations governing the molecular weight distribution (MWD) in step-growth polymerization are coupled and nonlinear and a large number of them must be solved simultaneously to keep the truncation error low. In this work, these equations have been decoupled so that they can be solved sequentially. The solution of these is independent of the truncation error and there is considerable saving of computation time. To demonstrate the efficiency of the algorithm, the formation of polyethylene terephthalate (PET) in batch reactors with ethylene glycol evaporating has been analyzed. The feed to the reactor is taken as polymer with its oligomers present according to the Flory's distribution. The effect of pressure and temperature of the reactor on the progress of polymerization has been modelled and evaluated. The amount of ethylene glycol distilled, the concentrations of the first five oligomers Q_1 to Q_5 , the number average chain length, and the polydispersity index of the polymer have been determined. It is shown that the reduced pressure and increased temperature reduce the concentration of the condensation product in the reaction mass, thus pushing the polymerization in the forward direction. Lastly the CPU time on Dec 1090 using this algorithm is only 0.40 s compared to about 10 min for similar computations using other existing methods.

INTRODUCTION

Step-growth polymerization occurs whenever the starting monomer has reacting functional groups on it.¹⁻⁶ If the monomer is bifunctional in nature, the resulting polymer is linear, whereas if it has more than two functional groups, the polymer is either branched or a network in structure. The step-growth polymerization of bifunctional monomers, denoted as ARB, where A and B are reacting functional groups, can be schematically written as:



Above, p_m and p_n are polymer molecules having m and n repeat units and W represents the condensation product. The $k_{p,mn}$ and $k'_{p,m+n}$ are the forward and the reverse rate constants which are in general chain length dependent.

The forward and the reverse rate constants in eq. (1) are usually complex functions of the chain length of the polymer molecules. Based on experimental results of Bhide and Sudborough⁷ on the esterification of aliphatic acids in presence of excess ethanol, Flory was the first to propose the equal reactivity hypothesis^{8,9} where $k_{p,mn}$ and $k'_{p,m+n}$ are assumed to be independent of the

chain lengths m and n . Mathematical results on polymerization in batch reactors, based on the equal reactivity hypothesis, have been extensively tested experimentally.¹⁰⁻¹⁴ The discrepancy between them has been explained in the literature either by assuming the chain length-dependent^{14,15} reactivity or the functional group-dependent reactivity.¹⁶ Even though step-growth polymerization in the reaction-controlled region was considerably more complex, the kinetic model based on the equal reactivity hypothesis is an extremely good approximation.

The reaction engineering of step-growth polymerization has recently been reviewed in the literature.¹⁷⁻¹⁹ A systematic analysis of irreversible polymerization of ARB monomers in batch reactors were presented in which the mole balance equations for various species were written. A Z-transform or a Laplace transform function was defined and various mole balance relations for various molecular species were combined into a single one to give the rate of generation of these functions. In these analyses, a kinetic approach has been taken to analyze the reactor performance.^{20,21} Probabilistic arguments have been forwarded by Flory and it has been shown the molecular weight distribution (MWD) in batch reactors is the most probable distribution.¹

For reversible polymerization, Flory and Tobolsky have shown through statistical arguments that the molecular weight distribution continues to be the most probable distribution. Subsequent numerical computations^{22,23} as well as the analytical development of Kilksen²⁰ both show that the kinetic approach gives the same result as long as the feed to the batch reactor is monomer. Deviations are found if the feed is a mixture of higher oligomers. Step-growth polymerization can be carried out in reactors other than batch reactors. Among the various possible reactor geometries which has found popularity in industries, are homogeneous continuous flow stirred tank reactors (HCSTRs). These analyses are particularly suited when a kinetic approach to analysis is adopted.

The major difficulty of solving the MWD of reversible ARB polymerization computationally lies in the fact that the chain growth step consists of infinite elementary reactions as written in Eq. (1). The various mole balance relations for batch reactors are highly nonlinear differential equations which are coupled with each other.

Computer calculations of the MWD of ARB polymerization have been performed by several workers and are found to require considerable computation time for the following reasons. It is not possible to define infinity on a computer and therefore one takes a large number of equations (say N_c) such that the total number of species count remains the same as the starting value. Any deviation between the two is called the truncation error and is kept to a minimum by continuously increasing N_c . A normal strategy of computation is to increase N_c by 10 whenever the concentration of the last species increases beyond a certain minimum value (about 10^{-8}).

It can be easily seen that the total number of species increases with increasing conversion and by the time 90% conversion is reached, one normally requires about 500 species to obtain meaningful solution. One of the ways to overcome this computational problem and the approach recommended in the literature, is to derive the moment generation equations from the mole balance relation governing the MWD. The i -th moment, λ_i , of a distribution

of p_m is defined as

$$\lambda_i = \sum_{m=1}^{\infty} m^i [P_m] \quad i = 0, 1, 2, \dots \quad (2)$$

where $[]$ refers to the concentration of the species. Among these moments, the first three are important: the zeroth moment, λ_0 , refers to the total moles of the species, the first moment, λ_1 , refers to the total species count, and λ_2 gives a measure of the breadth of the distribution. λ_1 is time invariant, but the generation relation for λ_2 involves λ_3 and that for λ_3 involves λ_4 , and so on. It is thus seen that the hierarchy of moments can be broken by assuming a suitable form of MWD which is close to the exact MWD form.

It is thus seen that determining the MWD of the polymer formed as well as their moments from the moment generation relations are both difficult tasks. In practice one would like to determine the concentration of the first few oligomers and the first three moments of the distribution.

In this work, we have decoupled the differential equations governing the MWD and we can now solve these exactly independent of the truncation error. We have subsequently determined the moment generation relations and solved them using a suitable relation to break the hierarchy of moments. We have demonstrated this algorithm on the polyethylene terephthalate formation in batch reactor from which ethylene glycol is flashing. We assumed the feed to consist of polymers which are initially present in accordance with Flory's distribution. We have simulated the industrial process in which high vacuum is applied by developing a simple model which determines the amount of condensation product (ethylene glycol) evaporated. We have computed the concentrations of the first five oligomers' three moments of the distribution the number average chain length, and the polydispersity index under different reactor pressures and temperatures.

KINETIC MODEL

We have already pointed out that the equal reactivity hypothesis, originally proposed by Flory, is a good representation of step-growth polymerization. The kinetic model can then be written as

$$k_{p, mn} = 2k_p; \quad m \neq n, m, n = 1, 2, \dots \quad (3a)$$

$$= k_p; \quad m = n, m = 1, 2, \dots \quad (3b)$$

$$k'_{p, m} = k'_p; \quad m = 2, 3, \dots \quad (3c)$$

It is assumed that the feed to the batch reactors consists of $[P_n]_0$, $n = 1, 2, 3, \dots$. It is observed that P_1 is consumed in the forward reaction whenever it reacts with any species of the reaction mass whereas it is formed in the reverse step whenever a P_n ($n \geq 2$) reacts with W at sites near its two ends. Similarly, a molecular species P_n is formed when a P_r ($r < n$) reacts with a P_{n-r} in the forward step or a P_i ($i > n$) reacts with W . A molecule of P_n is removed whenever it reacts with any other molecule or any of its bonds

reacts with W by the reverse reaction. These mole balance equations for the batch reactors can then be written in the dimensionless form as follows:

$$\frac{dP_1}{dt} = -2P_1P + 2\beta W \sum_{i=2}^{\infty} P_i \quad (4a)$$

$$\frac{dP_n}{dt} = -2P_nP + \sum_{r=1}^{n-1} P_r P_{n-r} + 2\beta W \sum_{i=n+1}^{\infty} P_i - \beta(n-1)P_n \quad n \geq 2 \quad (4b)$$

where

$$\lambda_{10} = \sum_{n=1}^{\infty} n[P_n]_0 \quad (5a)$$

$$P_n = [P_n]/\lambda_{10}; \quad n = 1, 2, \dots \quad (5b)$$

$$P_{n0} = \frac{[P_n]_0}{\lambda_{10}}; \quad n = 1, 2, \dots \quad (5c)$$

$$P = \sum_{n=1}^{\infty} P_n \quad (5d)$$

$$P_0 = \sum_{n=1}^{\infty} [P_n]_0 \quad (5e)$$

$$t = k_p \lambda_{10} t' \quad (5f)$$

$$\beta = k'_p/k_p \quad (5g)$$

$$W = [W]/\lambda_{10} \quad (5h)$$

$$W_0 = [W]_0/\lambda_{10} \quad (5i)$$

Above t' is the actual time and t the dimensionless time. The parameter β is the inverse of the equilibrium constant. The initial conditions are

$$\text{At } t = 0, P_i = P_{i0}, i = 1, 2, \dots \quad (6)$$

It is possible to determine the differential equation governing P by adding Eq. (4) for all n to obtain

$$\begin{aligned} \frac{dP}{dt} &= -2P \sum_{n=1}^{\infty} P_n + \sum_{n=2}^{\infty} \sum_{r=1}^{n-1} P_r P_{n-r} + 2\beta W \sum_{n=1}^{\infty} \sum_{i=n+1}^{\infty} P_i - \beta \sum_{n=2}^{\infty} (n-1)P_n \\ &= -P^2 + \beta W \sum_{n=2}^{\infty} (n-1)P_n \end{aligned} \quad (7)$$

It is further observed that the total repeat count, RC, defined as

$$RC = \sum_{n=1}^{\infty} nP_n \tag{8}$$

is indeed time invariant. This implies RC is the same as that charged to the reactor, initially, that is, for all time t , $RC = 1$. Therefore,

$$\sum_{n=2}^{\infty} (n - 1)P_n = \sum_{n=1}^{\infty} nP_n - \sum_{n=1}^{\infty} P_n = (1 - P) \tag{9}$$

we define conversion p_A as

$$p_A = (1 - P/P_0) \tag{10}$$

If whatever condensation product W formed during polymerization is kept within the reactor, then the stoichiometry gives

$$W = W_0 + (P_0 - P) \tag{11}$$

In terms of these, the differential equation governing conversion p_A is given by

$$\begin{aligned} \frac{dp_A}{dt} &= -(1 - p_A)^2 + \beta p_A^2 \\ \text{at } t = 0, p_A &= 0 \end{aligned} \tag{12}$$

MOLECULAR WEIGHT DISTRIBUTION

To obtain the MWD of the polymer, we observe that

$$\sum_{i=n+1}^{\infty} P_i = P - P_n - \sum_{i=1}^{n-1} P_i \tag{13}$$

Equation (4) under this transformation becomes

$$\frac{dP_1}{dt} = -2P_1(P + \beta W) + 2\beta WP \tag{14a}$$

$$\frac{dP_n}{dt} = -P_n\{2P + \beta W(n + 1)\} + \left\{ \sum_{r=1}^{n-1} P_r P_{n-r} + 2\beta W \left(P - \sum_{i=1}^{n-1} P_i \right) \right\} \tag{14b}$$

at

$$t = 0, P_i = P_{i0}, i = 1, 2, \dots \tag{14c}$$

Let us define variable ϕ_{n-1} and Z_n as

$$\Phi_{n-1} = \sum_{r=1}^{n-1} P_r P_{n-r} + 2\beta W \left(P - \sum_{i=1}^{n-1} P_i \right) \tag{15a}$$

$$Z_n = P_{n0} \exp \left\{ - \int_0^t [2P + \beta W(n + 1)] dt \right\} \tag{15b}$$

In terms of these Eq. (16) reduces to

$$\frac{dZ_n}{dt} = \Phi_{n-1} \exp \left\{ - \int [2P + \beta W(n+1)] dt \right\} \quad (16)$$

which gives

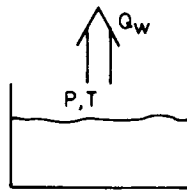
$$Z_n = \int_0^t \Phi_{n-1} \exp \left\{ - \int [2P + \beta W(n+1)] dt \right\} \quad (17)$$

The mole balance equation given in (16) is important for the following two reasons. Suppose it is decided to solve the concentrations of, say, the first ten species. The differential equations written in Eq. (4) require the entire MWD to be computed. As opposed to this, in the form written in Eq. (16), one can just solve for these ten species all the way up to the equilibrium conversion, without worrying about truncation error as was necessary in the earlier form.

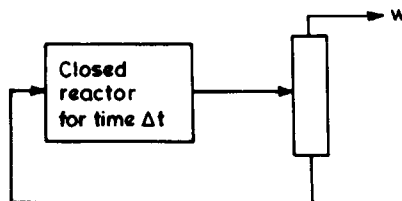
The second biggest advantage of the mole balance relations written in the form given in Eq. (14) is that one can in principle determine the MWD analytically. One first solves for P_1 ; after this is done, ϕ_1 is found using Eq. (16) and Z_1 by integrating Eq. (17). Once P_2 is known, P_3 can be found and so on. The analytical form of the MWD can be seen to be extremely complex and in the following, the advantages of the numerical integration is demonstrated.

VAPOR LIQUID MODEL OF THE BATCH REACTOR

In Figure 1(a), a batch reactor is shown in which the condensation product is shown evaporating. To be able to find the amount evaporated, we assume



(a)



(b)

Fig. 1. Model for the computation of MWD in batch reactors with condensation product distilling from it: (a) batch reactor; (b) scheme of computation.

that the vapor and the liquid are in equilibrium. The mole balance relation for the condensation product is given by

$$\frac{dW}{dt} = P^2 - \beta W(1 - P) - Q_w \quad (18)$$

assuming that the entire reaction mass is at the uniform concentration. If it is further assumed that the polymer cannot be evaporated and the vapor liquid equilibrium is governed by simple Roul't's law, then

$$P_r = P_r^*(T) \frac{W}{W + P} \quad (19)$$

Above P_r is the pressure applied on the reactor, $P_r^*(T)$ is the vapor pressure of the condensation products, and W is the uniform concentration of condensation product in the reactor. Eq. (19) can be rearranged to give the equilibrium concentration of the condensation product, W_{eq} , as

$$W_{eq} = P \frac{A_{eq}^*}{1 - A_{eq}^*} \quad (20a)$$

where

$$A_{eq}^* = \frac{P_r}{P_r^*(T)} \quad (20b)$$

If A_{eq}^* is greater than or equal to 1, it would mean that the vapor pressure of the condensation product is lower than the applied pressure and W would not evaporate from the reaction. In this case $Q_w = 0$ in Eq. (18), W would accumulate in the reactor and its concentration would be given by the stoichiometric relation in Eq. (11).

The amount of the condensation product distilled due to evaporation can be found using the computation scheme given in Figure 16. In this figure, by "closed reactor," it is meant that the condensation product is not allowed to escape. The total time of polymerization is divided into small increments, Δt . Equation (18) is integrated for time Δt using the usual fourth-order Runge Kutta method and then the reaction is flashed in a column [governed by Eq. (20)]. The polymer is recycled to the reactor for further polymerization and in this way the final time of polymerization is reached. The method outlined here is valid even when monomer P_1 can evaporate, in which case Eq. (19) has to be rewritten for the ternary mixture.

EXPRESSION FOR THE SECOND MOMENT OF DISTRIBUTION

From the definition of the second moment given in Eq. (2) and the mole balance relations given in Eq. (4), one has

$$\begin{aligned} \frac{d\lambda_2}{dt} = & -2P \sum_{n=1}^{\infty} n^2 P_n + \sum_{n=2}^{\infty} n^2 \sum_{r=1}^{n-1} P_r P_{n-r} \\ & + 2\beta W \sum_{n=1}^{\infty} n^2 \sum_{j=n+1}^{\infty} P_j - \sum_{n=1}^{\infty} n^2 (n-1) P_n \end{aligned} \quad (21)$$

It is further observed that

$$\sum_{n=1}^{\infty} n^2 \sum_{m=n+1}^{\infty} P_m = \sum_{n=1}^{\infty} \frac{2n^3 - 3n^2 + n}{6} P_n$$

$$= \frac{2\lambda_3 - 3\lambda_2 + \lambda_1}{6} \tag{22a}$$

$$\sum_{n=2}^{\infty} n^2 \sum_{m=1}^{n-1} P_m P_{n-m} = \sum_{n=1}^{\infty} P_n \sum_{m=1}^{\infty} (m+n)^2 P_m$$

$$= 2\lambda_2\lambda_0 + 2\lambda_1^2 \tag{22b}$$

which gives

$$\frac{d\lambda_2}{dt} = 2\lambda_1^2 + \frac{\beta W}{3} \{2\lambda_3 - 3\lambda_2 + \lambda_1 - 3\lambda_3 + 3\lambda_2\}$$

$$= 2\lambda_1^2 + \frac{\beta W}{3} \{\lambda_1 - \lambda_3\} \tag{23}$$

The moment closure approximation that we have used earlier¹⁹⁻²⁵ and found

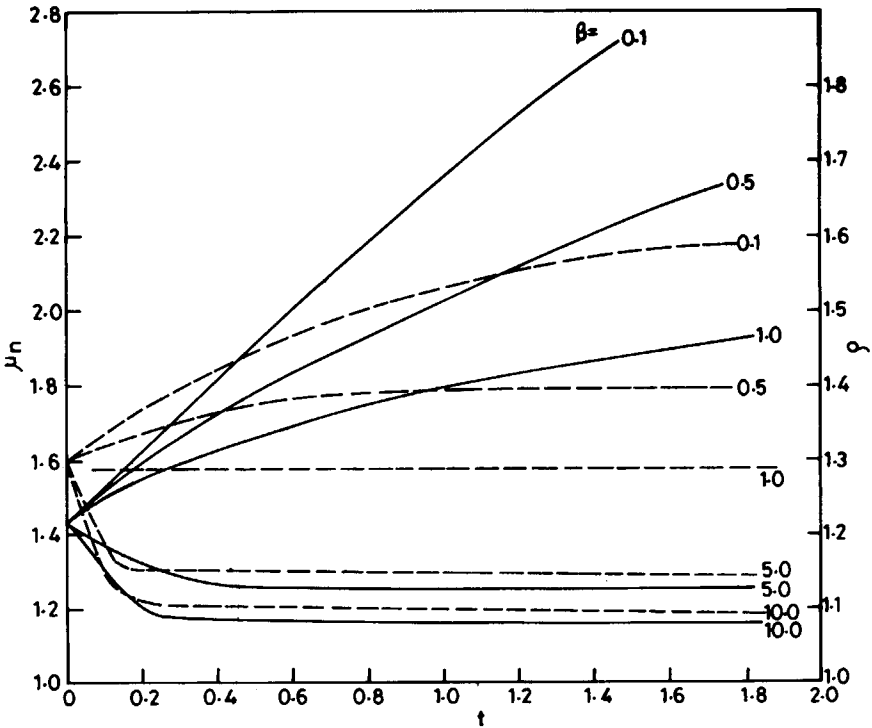


Fig. 2. μ_n (—) and ρ (---) versus time of polymerization for various $\beta \cdot \mu_{n_0} = 1.43, \rho_0 = 1.30$.

to give results within 2% of the exact solution is the following

$$\lambda_3 = \frac{\lambda_2(2\lambda_2\lambda_0 - \lambda_1^2)}{\lambda_1\lambda_0} \tag{24}$$

RESULTS AND DISCUSSION

To test the computational algorithm presented in this paper, we assumed an arbitrary feed to the reactor consisting 0.1 mol/liter of condensation product *W*. It was further assumed that the polymer portion of the feed was a set of oligomers whose concentrations are governed by the following relation

$$\frac{P_{i0}}{\sum_i [P_i]_0} = (1 - P_{A0})^2 P_{A0}^{i-1} \tag{21}$$

where P_{A0} is the conversion of functional groups and is taken as 0.3 for all computations. Expressions for the zeroth moments (which is the same as P) are given in Eq. (7). The first moment is time invariant and therefore need not be solved.

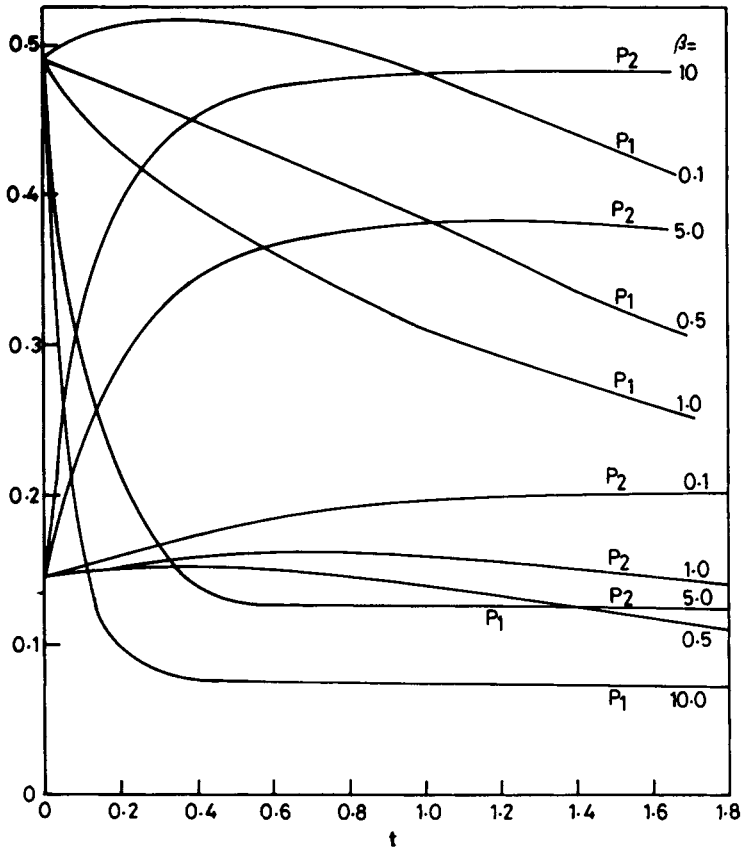


Fig. 3. Concentrations of P_1 and P_2 species versus time for various β . $P_{10} = 0.49$, $P_{20} = 0.143$.

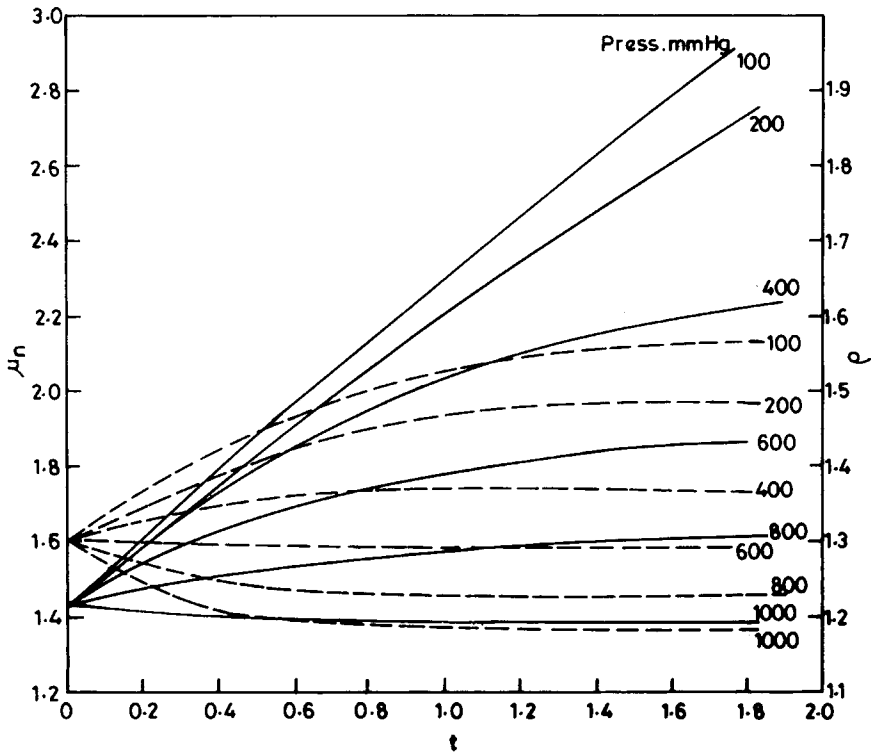


Fig. 4. Effect of reactor pressure on μ_n (—) and ρ (---) of polyethylene terephthalate polymer. $\mu_{n0} = 1.43$, $\rho_0 = 1.30$. $T = 500^\circ \text{K}$, $\beta = 2.0$.

In the computation of MWD when the equations are solved simultaneously, as it has already been explained, one starts with a large number of equations to keep the truncation error within limits. This was necessary because the MWD equations written in the form as in Eq. (4) are coupled. These have been decoupled in Eq. (14) and, in this form, once P is known P_1 can be calculated uniquely without knowing P_2 , P_3 , etc. This follows for P_1 and so on. It is thus seen that one can calculate the concentration of any number of oligomers without solving the entire MWD. Practically, the entire MWD is never needed and the concentration of only a few species are sufficient. In addition, the sequential computation does not take more than 0.40 CPU seconds on Dec 1090. As opposed to this, the simultaneous solution of the MWD may take as much as 10 CPU minutes for the same conversion.

For the computations of Figures 2 to 7, we arbitrarily decided to compute λ_0 , λ_2 , P_1 , P_2 , P_3 , P_4 , and P_5 which constitutes seven differential equations only. We varied Δt starting from a very large value of 0.1 and found that for $\Delta t \leq 0.01$, the numerical results were independent of Δt . In view of this, Δt was chosen to be 0.01 in generating all the results of this paper. We have generated Figures 2 and 3 for various value of β as follows. We have fixed A_{eq}^* in Eq. (20) at 0.5 and plotted the number average chain length μ_n and the polydispersity index ρ . The value of μ_n and ρ for feed, μ_{n0} and ρ_0 , can be computed as 1.43 and 1.30, respectively. The average chain length μ_n for short times rises but for large times, it approaches the equilibrium value which

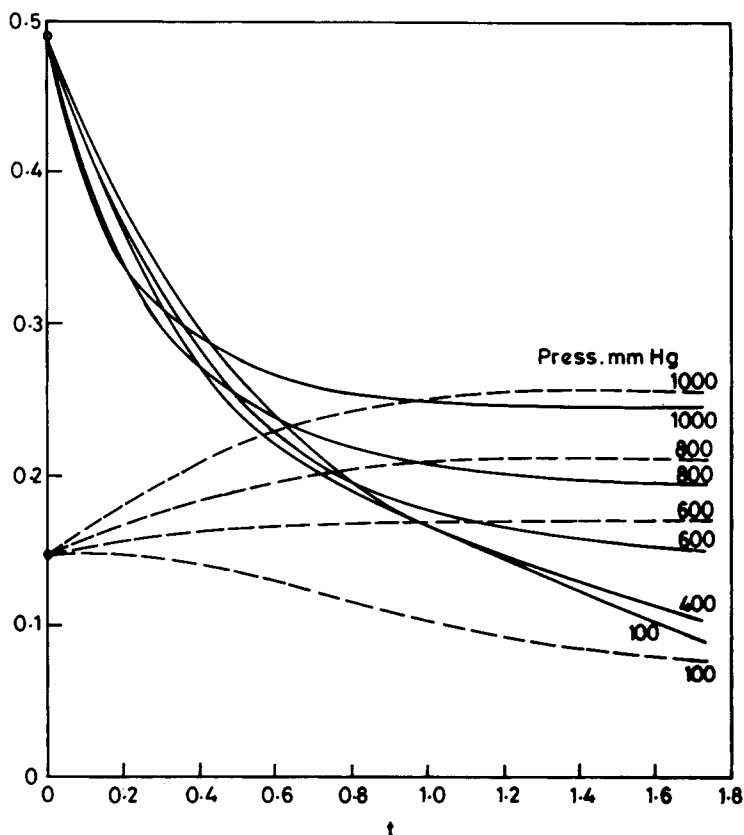


Fig. 5. Effect of reactor pressure on concentrations of P_1 (—) and P_2 (---). $P_{10} = 0.49$, $P_{20} = 0.143$, $T = 500^\circ \text{K}$.

depends upon β only. For β larger than 5, there is essentially depolymerization and the final value of μ_n is completely determined by β . The same effect is observed in the polydispersity index. Whenever there is depolymerization, the final polymer is less polydispersed giving lower ρ as seen in Figure 2.

In Figure 3 the concentration of P_1 and P_2 species have been plotted. For large β and large dimensionless time, the reaction mass appears to have settled on the equilibrium as P_1 as well as P_2 both appear to have attained the asymptotic levels. Since the equilibrium demands that P_2 be present in larger quantity, most of P_1 has depleted to form P_2 as seen. However, for $\beta < 5$, the reaction mass is far from equilibrium because P_1 and P_2 are both getting depleted even for $t = 2.0$ as apparent from their downward trends.

The formation of polyethylene terephthalate (PET) starting from its monomer dimethyl terephthalate (DMT) is industrially carried out in two stages.²⁶⁻³² In the first stage, DMT is reacted with ethylene glycol (called transesterification stage) in which the end methyl groups are removed and there is a capping of both its ends predominantly forming bishydroxyethyl terephthalate (BHET). The polymerization of BHET is called the polycondensation stage, and it is known that there are several side reactions occurring in addition to the main step-growth polymerization. These side reactions have

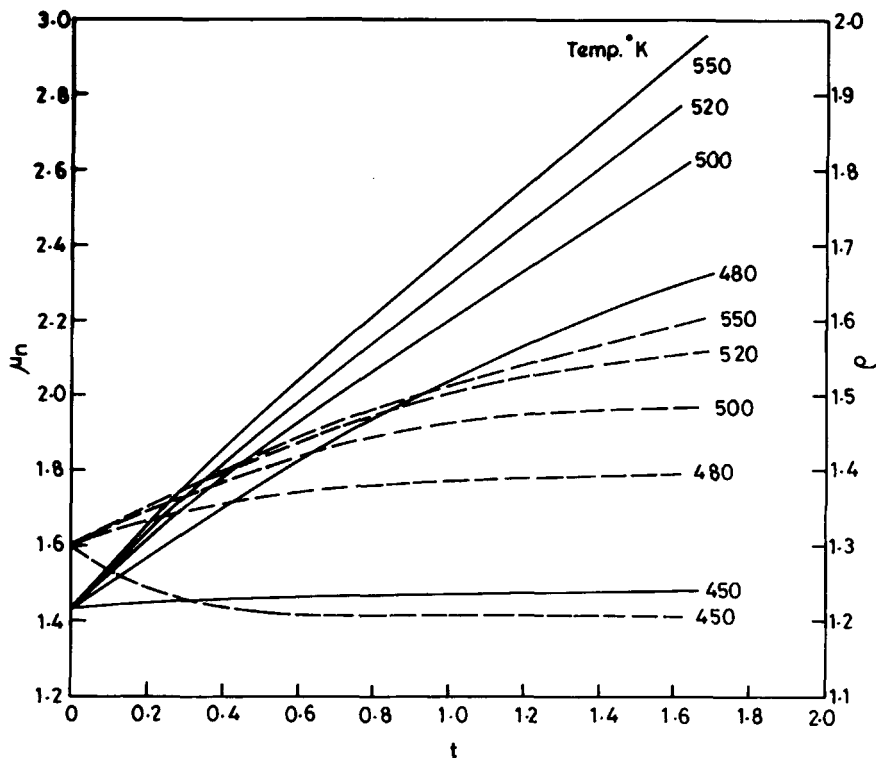


Fig. 6. Effect of reactor temperature on μ_n (—) and ρ (---) of PET polymer. $P = 200$ mmHg, $\beta = 2.0$.

been simulated for the batch reactors as well as HCSTRs.²⁶⁻³¹ Using this kinetic model we have earlier carried out the optimization of batch reactors.²⁸⁻³⁰ In these, we found that even though the side reactions are extremely important in accounting for the side products, the molecular weight of the polymer is determined by the step-growth step which can be represented by Eq. (1). We further assume that polymer does not get into the vapor phase and Eq. (20) holds. The polymerization of BHET has the equilibrium constant of 0.5 and is independent of temperature.³² This implies that $\beta = 2$ and, in generating Figures 4 to 7 we have kept β unchanged. The vapor pressure of ethylene glycol is presented in Ried et al.³³ and is curve-fitted by an Antoine equation of the following form³³

$$\ln P_r^*(T) = 20.2501 - \frac{6022.18}{T - 28.25} \quad (22)$$

Above $P_r^*(T)$ is in mmHg, while T is the temperature in °K.

In Figures 4 and 5, we have fixed the reaction temperature as 500 °K and varied the reactor pressure systematically from 100 to 1000 mmHg. The vapor pressure of ethylene glycol at this temperature is about 1100 mmHg and if the pressure is more than this, evidently there is no evaporation of ethylene glycol (EG), but for pressure less than this, the distillation of EG occurs almost

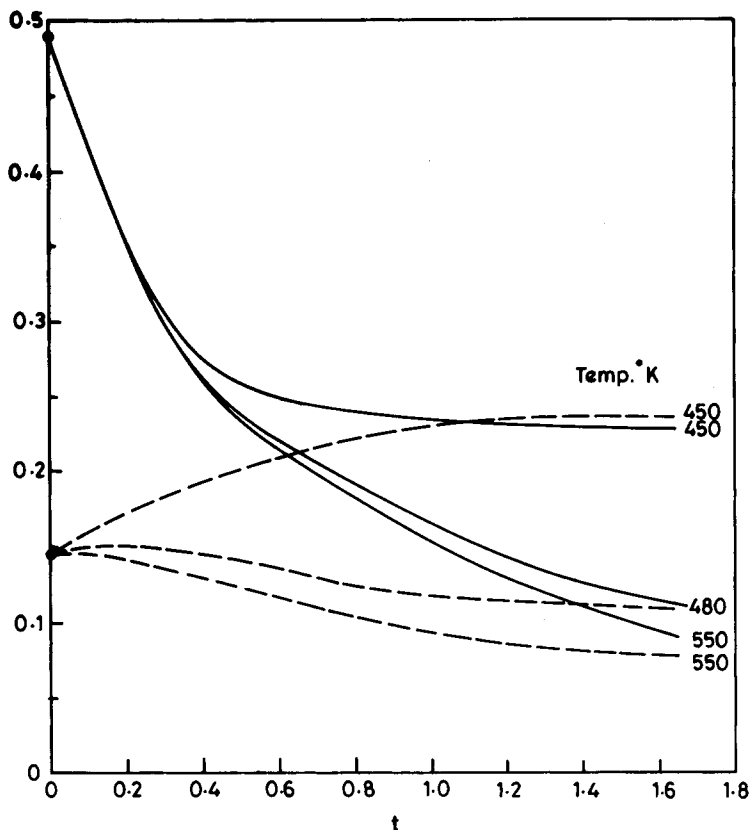


Fig. 7. Effect of reactor temperature on concentrations of P_1 (—) and P_2 (- - -). $P = 200$ mmHg, $\beta = 2.0$.

immediately. For low pressures (up to 200 mmHg), μ_n and ρ both rise for the time of polymerization studied, however for large pressures, the reaction mass appears to reach equilibrium. Polymerization at 600 and 800 mmHg is interesting in the sense that even though μ_n rise, the polymer becomes less polydispersed from the starting material. In Figure 5, concentrations of P_1 and P_2 have been plotted. As expected, for lower pressures higher oligomers are formed preferentially, which means that both P_1 and P_2 deplete very fast. However, for larger pressures, concentrations of both P_1 and P_2 rise, as is seen in Figure 5.

The polycondensation stage of the PET polymer formation is one of the few systems in which the forward and the reverse steps are equally affected leaving the equilibrium constant unchanged. In Figures 6 and 7, the reactor temperature has been changed systematically. Since temperature does not affect the equilibrium constant, β for all these runs remain at 2. As vapor pressure of ethylene glycol increases with temperature, the net effect of T is to lower A_{eq}^* which in turns lowers the EG content of the reaction mass. The polymerization proceeds closer to the irreversible case leading to continuous

increase of μ_n and ρ with time of polymerization, as seen in Figure 6. However, for lower temperatures (e.g., 450°) the MWD of the polymer becomes narrower even though μ_n increases only slightly. The behavior of P_1 and P_2 in Figure 7 is similar to that in Figure 5. For larger temperatures, the reaction mass is far from equilibrium and concentrations of both P_1 and P_2 fall due to their reactions, giving higher oligomers. However, for lower temperatures they approach an asymptotic level, which is determined by the equilibrium of the reaction mass.

CONCLUSIONS

The computation of the MWD of step-growth polymerization in batch reactors required a large number of differential equations to be numerically solved simultaneously. This was necessary to keep the truncation error within specified bounds.

In this work the differential equations governing the MWD have been decoupled and these have been arranged in a possible analytical solution. In view of the complexity, a convenient algorithm of computations has been developed which gives the concentrations of any number of molecular species, the number average chain length, and the polydispersity index of the polymer formed. The CPU time taken for the sequential computation is only 0.4 s as opposed to about 10 min for simultaneous solutions on a Dec 1090. In addition, the MWD results obtained from the algorithm developed in this work is independent of the truncation error.

The polyethylene terephthalate formation in the poly-condensation step has been solved using the method outlined in this work. The first five oligomers P_1 to P_5 , the number average chain length μ_n , and the polydispersity index ρ of the polymer, have been determined. The effects of temperature and pressure of the batch reactor on the properties of the polymer have been determined.

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