

Analytical Solution of Reversible Step Growth Polymerization in Semibatch Reactors

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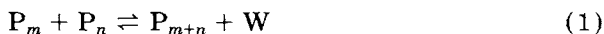
Synopsis

We have developed an analytical solution of reversible step growth polymerization in semibatch reactor with condensation product flashing. We have shown that the MWD of the polymer formed has Flory distribution, unaffected by flashing of condensation product, if the feed to the reactor is either pure monomer or has most probable MWD. We have determined analytical expression for the time when the evaporation of condensation product starts. Assuming the vapor liquid equilibrium (VLE) is given by Raoult's law (as well as the Flory-Huggins relation) we have determined the number and weight average chain lengths. We have subsequently analyzed the polycondensation step of the formation of polyethylene terephthalate and determined the effect of temperature and pressure on the course of polymerization.

INTRODUCTION

Polymerization can occur either by chain growth or by step growth mechanism.¹⁻⁷ In the latter there are reacting functional groups on polymer molecules which lead to their chain growth on chemical reaction. If the functionality of the starting monomer is 2, the polymer formed has a linear structure because of the following reasons. All molecules in the reaction mass, whether monomer or polymer, have two unreacted functional groups situated at chain ends. This implies that the growth of molecules can occur only in one direction, thus giving linear molecular structure.

In this paper we consider the analysis of step growth polymerization of bifunctional ARB monomer, where A and B are the reacting functional groups. Like all other reactions in nature, this is also reversible and can be schematically represented as⁸⁻¹⁰



In this P_m represents polymer chain having m repeat units and W , the condensation product formed in the chemical reaction of functional groups A and B. Above $k_{m,n}$ and k'_{m+n} are the forward and the reverse rate constants respectively and their subscripts (m , n and $m+n$) denote that they are dependent upon the chain lengths of the reacting species. Since the forward reaction involves macromolecules P_m and P_n , $k_{m,n}$ depends on both m and n while the reverse reaction depends upon $(m+n)$.

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In the celebrated work, based on the experimental work of Bhide and Sudborough,¹¹ Flory proposed equal reactivity hypothesis^{12,13} in which the forward and reverse rate constants, $k_{m,n}$ and k'_{m+n} were assumed to be independent of m and n . Recently experimental works^{14,15} have been reported where it has been shown that this is a gross simplification. Under θ -conditions, the rate constant versus chain length n has an S-shaped dependence. In the literature this has been modeled by the unequal reactivity of monomer.¹⁵⁻¹⁹

Step growth polymerization is either carried out batchwise in a vessel or continuously in suitable continuous reactors.^{1,4,5} The latter have either the geometry of a stirred vessel (modeled as continuous flow stirred tank reactor) or a long tube (modeled as plug flow reactors) through which the reacting fluid is continuously pumped. The main goal of these reactors is to form polymer of high molecular weight, which means that the polymerization must be carried out to high conversion. However, due to reversibility of eq. (1), overall polymerization is limited by equilibrium, which means that a high vacuum must be applied to the reactor to remove condensation product W in order to obtain the desired polymer.²⁰⁻²⁵ Reactors from which the condensation product is continuously flashing are called semibatch reactors. In this study, we undertake an analysis of them because of their industrial importance.

The original analysis of Flory for step growth polymerization assumed equal reactivity hypothesis. Using statistical arguments he solved the molecular weight distribution (MWD) of polymer formed in batch reactors (i.e., reactors in which there is no flashing of W). There have been several analyses of MWD of polymer in industrial reactors, but most of these assume polymerization to be irreversible in order to simplify the mathematical analysis.²⁶⁻³¹ A kinetic approach has been taken and for a given reactor mole balance relations for various oligomeric species have been written. A Z-transform or a Laplace transform function is defined and the infinite mole balance equations are combined into a single one using this. In this way, an analytical solution of the MWD of the polymer has been found. Abraham³⁰ has addressed the problem of reversible step growth polymerization in semibatch reactors. Assuming monomer as feed, no change in density of the reaction mass, and the vapor-liquid equilibrium given by Raoult's law from the beginning of polymerization, he assumes the Flory-Schultz distribution for the MWD of the polymer. He defines a Flory-Schultz parameter, which he solves numerically. It may be recognized that flashing in an industrial reactor starts after some time of polymerization and it is desirable to know this time a priori.

When vacuum is applied to a semibatch reactor, the condensation product begins to boil out of the reaction mass. The modeling of flashing of W from semibatch reactors has been attempted in the literature.³²⁻³⁶ In these analyses, the diffusional resistance of the reaction is assumed to be zero. In addition, the escaping vapor is assumed to be in thermodynamic equilibrium with the reaction mass. This leads to mole balance relations as a set of differential equations, while thermodynamic equilibrium as an algebraic inequality. These could be solved numerically only and have been described in the literature in complete detail.

Computer calculations of the MWD of ARB polymerization have been found to be difficult and time consuming. This is because the set of nonlinear ordinary differential equations governing it are coupled and must be solved simulta-

neously. We arbitrarily choose a large number of equations (say N_c) such that the concentration of P_{N_c} oligomer is negligibly small. We keep increasing N_c whenever the concentration of P_{N_c} increases beyond some minimum value (say 10^{-8}). In our earlier work we have found that N_c increases very sharply with conversion and, as a result, computations slow down considerably and the truncation error begins to build up with increasing time of polymerization. One of the ways to overcome this computational problem is to derive moment generation relations from the MWD equations.^{23,36} On doing this, it is found that the relation for the i th moment of MWD involves higher moments and these can be found only after suitable moment closure approximation.

In this paper we present an analysis of the general problem reversible step growth polymerization in semibatch reactor. We have recognized the change in volume of the reaction mass due to flashing and polymerization. We then modeled the flashing of the condensation product and developed a complete analytical solution of the MWD and moments of the polymer formed. We have shown that no matter what the history of polymerization, at equilibrium, the formed polymer has most probable distribution. We recognize that the flashing of the condensation product starts after certain time of polymerization and this depends upon the reactor pressure. We have found this time analytically as a function of reactor temperature and pressure and subsequently derived an analytical expression for the moles of condensation product flashed and the average chain length of the polymer formed. We also show that if the feed to the semibatch reactor is either pure monomer or oligomers having Flory's distribution, the flashing of the condensation product does not change the distribution. We subsequently solved the problem of polymerization of polyethylene terephthalate and compared our results with those available in the literature.

THEORY

A schematic diagram of a semibatch reactor carrying out reversible step growth polymerization is shown in Figure 1. Depending upon the volatility of components of the reaction mass, there is a flashing of the vapor stream shown in the figure. In the analysis presented in this work, we assume only monomer P_1 and condensation product W vaporize and are present in the vapor phase at concentrations governed by vapor-liquid equilibrium. This assumption is made here to keep the analysis simple but can be easily extended for cases where higher oligomers also vaporize.

In all semibatch reactors, monomer in the vapor phase is condensed in a suitable separator and recycled because of its high costs. It is assumed that the reactor is operating isothermally with its total pressure as P_T . The volume of the liquid phase of the reactor, V , changes with time as flashing of W and P_1 occurs, and we account for its time dependence in this analysis as follows. We define p_n as the total moles of species P_n ($n = 1, 2, \dots$) and w as moles of W in the liquid phase. The mole balance relations of these on the control volume shown in Figure 1 are given by

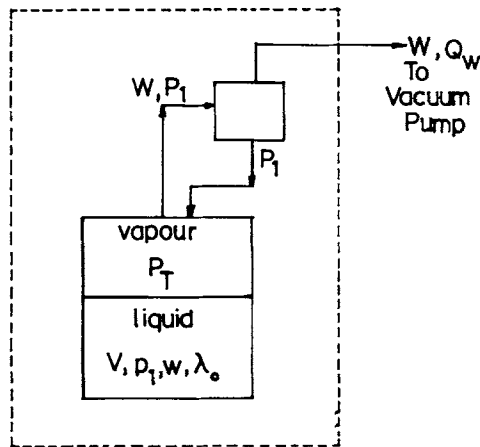


Fig. 1. Schematic diagram of a semibatch reactor with monomer and condensation product evaporating. S = separator; W = condensation product; P_1 = monomer; P_T = reactor pressure; Q_w = instantaneous rate of evaporation of W ; V = volume of reaction mass in the liquid phase; p_1, w, λ_0 = no. of moles of monomer P_1 , condensation product W and the polymer respectively in the reaction mass.

$$dp_1/dt = [-2k_f p_1 \lambda_0 + 2k_r w \sum_{r=2}^{\infty} p_r] / V \quad (2a)$$

$$dp_n/dt = [-2k_f p_n \lambda_0 + k_f \sum_{r=1}^{n-1} p_r p_{n-r} - k_r w (n-1) p_n + 2k_r w \sum_{r=n+1}^{\infty} p_r] / V, \quad n \geq 2 \quad (2b)$$

$$dw/dt = [k_f \lambda_0^2 - k_r w (\lambda_1 - \lambda_0)] / V - Q_w \quad (2c)$$

where k_f and k_r are the forward and reverse rate constants (assuming equal reactivity hypothesis) and λ_0 and λ_1 , are the zeroth and first moments which are defined as

$$\lambda_0 = \sum_{n=1}^{\infty} p_n, \quad \lambda_1 = \sum_{n=1}^{\infty} n p_n \quad (3)$$

The zeroth moment λ_0 gives the total moles of polymer at any time whereas λ_1 the total count of repeat units which will be shown to be time invariant a little later on. Let us assume that the feed to the semibatch reactor is pure monomer, i.e.,

$$\text{at } t = 0: \quad p_1 = p_{10}, \quad p_n = 0 \quad \text{for } n \geq 2 \quad (4)$$

In order to solve for the molecular weight distribution (MWD) of the polymer, we must know the volume V of the liquid phase of the reactor and the rate of vaporization, Q_w . The volume V is given by

$$dV/dt = -v_W Q_W \quad (5)$$

where v_W is the molar volume of the condensation product W. Subsequently, we assume vapor liquid equilibrium given by the Raoult's law as

$$\frac{(P_{p1}^0 p_1 + P_W^0 w)}{(\lambda_0 + w) P_T} = 1 \quad (6)$$

Equations (2), (5), and (6) specify the MWD of the polymer formed and must be solved simultaneously for the analytical solution that follows.

Equations (2a) and (2b) are suitably added to determine the generation relation of the zeroth moment λ_0 and first moment λ_1 as

$$d\lambda_0/dt = -[k_f \lambda_0^2 - k_r w (\lambda_1 - \lambda_0)]/V \quad (7a)$$

$$\begin{aligned} V d\lambda_1/dt = & -2k_f \lambda_1 \lambda_0 + k_f \sum_{n=2}^{\infty} \sum_{r=1}^{n-1} n p_r p_{n-r} - k_r w \left(\sum_{n=2}^{\infty} n^2 p_n - \sum_{n=2}^{\infty} n p_n \right) \\ & + 2k_r w \sum_{n=2}^{\infty} \sum_{r=n+1}^{\infty} n p_r \\ = & -2k_f \lambda_1 \lambda_0 + 2k_f \lambda_1 \lambda_0 - k_r w (\lambda_2 - \lambda_1) + k_r w (\lambda_2 - \lambda_1) = 0 \end{aligned} \quad (7b)$$

Equation [7(b)] implies that the first moment λ_1 is time invariant. Equations [7(a)] and [2(c)] give

$$d(w + \lambda_0)/dt = -Q_W \quad (8)$$

which on substitution in eq. (5) yields

$$V - V_0 = -v_W \{ (w_0 + p_{10}) - (w + \lambda_0) \} \quad (9)$$

Herein, w_0 is the moles of condensation product in the liquid phase having total volume V_0 at time $t = 0$.

We propose the MWD of the polymer to be of the same form as the Flory distribution

$$p_n = x(t)y(t)^{n-1} \quad (10)$$

where $x(t)$ and $y(t)$ are independent of the chain length n . On direct substitution of eq. (10) in eqs. [2(a)] and [2(b)] it is seen that it satisfies the mole balance relation no matter what the concentration of W is. If the starting feed is either pure monomer or has its MWD governed by a relation similar to eq. (10), then the form of MWD remains unaffected by flashing. The $x(t)$ and $y(t)$ in eq. (10) however are not independent because of the invariance of λ_1 , or,

$$\sum p_n = x/(1-y) = \lambda_0 \quad (11a)$$

$$\sum np_n = x/(1-y)^2 = p_{10} \quad (11b)$$

These give

$$y(t) = 1 - (\lambda_0/p_{10}) \quad (12a)$$

$$x(t) = (\lambda_0^2/p_{10}) \quad (12b)$$

We rewrite the vapor liquid equilibrium in eq. (6) as

$$w = \frac{P_T \lambda_0 - P_{P_1}^0 p_1}{P_W^0 - P_T} \quad (13)$$

However, eq. (10) gives p_1 as $x(t)$ or λ_0^2/p_{10} [see eq. (12)], which on substituting in the above relation gives

$$\begin{aligned} w &= \{P_T/(P_W^0 - P_T)\} \lambda_0 - \{P_{P_1}^0/(P_W^0 - P_T)\} \lambda_0^2 \\ &= (a_1 \lambda_0 - a_2 \lambda_0^2) \end{aligned} \quad (14)$$

Between eqs. (9) and (14), it is thus possible to obtain an explicit relation between V and P as

$$V = b_0 + b_1 \lambda_0 - b_2 \lambda_0^2 \quad (15a)$$

where

$$b_0 = V_0 - v_W(w_0 + p_{10}) \quad (15b)$$

$$b_1 = v_W(a_1 + 1) \quad (15c)$$

$$b_2 = v_W a_2 \quad (15d)$$

We can now substitute eq. (14) for w and eq. (15) for V in eq. [7(a)] to obtain

$$(b_0 + b_1 \lambda_0 - b_2 \lambda_0^2) d\lambda_0/dt = -k_f \lambda_0^2 + k_r(\lambda_{10} - \lambda_0)(a_1 \lambda_0 - a_2 \lambda_0^2) \quad (16)$$

This can be integrated with the initial condition that at $t = 0$ λ_{10} is the same as p_{10} and the final result can be derived as

$$\begin{aligned} A_1 \ln(\lambda_0/\lambda_{00}) + A_2 \ln[(\lambda_0 - d_1)/(\lambda_{00} - d_1)] \\ - A_3 \ln[(\lambda_0 - d_2)/(\lambda_{00} - d_2)] = t \end{aligned} \quad (17)$$

where

$$g_1 = k_r a_2 \quad (18a)$$

$$g_2 = k_f + \lambda_{10} k_r a_2 + k_r a_1 \quad (18b)$$

$$g_3 = k_r a_1 \lambda_{10} \quad (18c)$$

$$d_1 = \{ [g_2 + (g_2^2 - 4g_1g_3)^{0.5}] / 2g_1 \} \quad (18d)$$

$$d_2 = \{ [g_2 - (g_2^2 - 4g_1g_3)^{0.5}] / 2g_1 \} \quad (18e)$$

$$A_1 = b_0 / (d_1 d_2 g_1) \quad (18f)$$

$$A_2 = (b_0 + b_1 d_1 - b_2 d_1^2) / [d_1 g_1 (d_1 - d_2)] \quad (18g)$$

$$A_3 = (b_0 + b_1 d_2 - b_2 d_2^2) / [g_1 d_2 (d_1 - d_2)] \quad (18h)$$

When monomer P_1 has very low volatility and only water flashes,

$$w = P_T \lambda_0 / (P_W^0 - P_T) = a_1 \lambda_0 \quad (19a)$$

$$V_0 = b_0 + b_1 \lambda_0 \quad (19b)$$

Equation (16) then becomes

$$(b_0 + b_1 \lambda_0) d\lambda_0 / dt = -k_f \lambda_0^2 + k_r (\lambda_{10} - \lambda_0) a_1 \lambda_0 \quad (20)$$

which can be integrated to

$$A_4 \ln(\lambda_0 / \lambda_{00}) - (A_5 / g_4) \ln[(g_4 \lambda_0 - g_5) / (g_4 \lambda_{00} - g_5)] = t \quad (21)$$

where

$$g_5 = g_3 \quad (22a)$$

$$g_4 = k_f + k_r a_1 \quad (22b)$$

$$A_4 = b_0 / g_5 \quad (22c)$$

$$A_5 = (g_4 b_0 + b_1 g_5) / g_5 \quad (22d)$$

CLOSED REACTORS

When the condensation product is not allowed to escape from the reactor, Q_w in eq. [2(c)] is zero and according to eq. (5), the volume of the liquid phase of the reactor is time invariant. It is now possible to write the mole balance relations in concentrations of oligomers as follows

$$\frac{dC_1}{dt} = -2k_p C_1 \lambda_0^* + 2k_r C_w (\lambda_0^* - C_1) \quad (23a)$$

$$\frac{dC_n}{dt} = -2k_f C_n \lambda_0^* + k_f \sum_{r=1}^{n-1} C_r C_{n-r} + 2k_r C_w \sum_{r=n+1}^{\infty} C_r - k_r C_w (n-1) C_n \quad (23b)$$

$$\frac{dC_w}{dt} = k_f \lambda_0^{*2} - k_r C_w (\lambda_1^* - \lambda_0^*) \quad (23c)$$

where C_n (for $n = 1, 2, \dots$) represent concentration of species P_n and λ_0^* and λ_1^* zeroth and first moments in terms of concentration unit defined as

$$\lambda_0^* = \sum_{n=1} C_n \quad (24a)$$

$$\lambda_1^* = \sum_{n=1} n C_n \quad (24b)$$

The feed to the batch reactor is once again to be pure monomer, in which case

$$\text{at } t = 0 \quad C_1 = C_{10} \quad (25a)$$

$$C_n = 0 \quad n \geq 2 \quad (25b)$$

We proceed similarly to propose the form of MWD as

$$C_n = x_c(t) y_c(t)^{n-1} \quad (26)$$

which satisfies the MWD relations in eq. (23) and the initial conditions in eq. (25). Since the distribution has time invariant first moment λ_1^* ($= C_{10}$) and the zeroth moment λ_0^* , x_c and y_c in eq. (26) can be written in terms of them as

$$x_c = \lambda_0^{*2} / \lambda_1^* \quad (27a)$$

$$y_c = 1 - \lambda_0^* / C_{10} \quad (27b)$$

The generation relation for the zeroth moment, λ_0^* , can be derived from eq. (23) as

$$\frac{d\lambda_0^*}{dt} = -k_f \lambda_0^{*2} + k_r C_w (C_{10} - \lambda_0^*) \quad (28)$$

For closed reactors, $Q_w = 0$, consequently eq. (8) yields

$$C_w = (C_{w0} + C_{10}) - \lambda_0^* \quad (29)$$

where C_{w0} is the concentration of the condensation product W in the feed which need not be zero. On eliminating C_w in eq. (28), one has

$$\frac{d\lambda_0^*}{dt} = -k_f \lambda_0^{*2} + k_r (C_{W0} + C_{10} - \lambda_0^*) (C_{10} - \lambda_0^*) \quad (30)$$

This can be easily integrated to get λ_0^* as

$$q/q_0 = \exp(-\delta t) \quad (31)$$

where

$$m_0 = k_r (C_{W0} + C_{10}) C_{10} \quad (32a)$$

$$m_1 = k_r (C_{W0} + 2C_{10}) \quad (32b)$$

$$m_2 = (k_f - k_r) \quad (32c)$$

$$\delta = (m_1^2 + 4m_0 m_2)^{1/2} \quad (32d)$$

$$q = \frac{2m_2 \lambda_0^* + m_1 - \delta}{2m_2 \lambda_0^* + m_1 + \delta} \quad (32e)$$

$$q_0 = \frac{2m_2 C_{10} + m_1 - \delta}{2m_2 C_{10} + m_1 + \delta} \quad (32f)$$

EQUILIBRIUM POLYMERIZATION

Let us assume that the concentration of oligomer P_n at equilibrium in the reaction mass is C_{ne} . If C_{We} is the concentration of the condensation product at equilibrium, eq. (23) is written as

$$\frac{dC_{ne}}{dt} = -2k_f C_{ne} \lambda_0^* + k_f \sum_{r=1}^{n-1} C_{re} C_{(n-r)e} + 2k_r C_{We} \sum_{r=n+1}^{\infty} C_{re} - k_r C_{We} (n-1) C_{ne} = 0 \quad (33)$$

The form of the MWD remains to be the same as eq. (26) as

$$C_{ne} = x_{ce} y_{ce}^{n-1} \quad (34)$$

where x_{ce} and y_{ce} are parameters defined for the equilibrium and

$$x_{ce} = \lambda_{0e}^* / C_{10} \quad (35a)$$

$$y_{ce} = 1 - \lambda_{0e}^* / C_{10} \quad (35b)$$

If eq. (34) is substituted in eq. (33), we find that in order to satisfy it exactly, one must have

$$x_{ce} = \beta C_{we} y_{ce} \quad (36a)$$

where

$$\beta = k_r / k_f \quad (36b)$$

This specifies the entire MWD of the polymer.

RESULTS AND DISCUSSION

Let us consider that certain moles of a monomer (say p_{10}) are mixed with some moles (say w_0) of condensation product before the mixture is charged to the reactor. As long as the constraint of vapor-liquid equilibrium [given in eq. (6)] is not satisfied, there is no flashing of W and P_1 and it behaves like a closed reactor. During polymerization w increases and λ_0 goes down and there is a time when the condensation product begins to evaporate. The time when this occurs can be easily determined by first finding the intersection point of eq. (6) and (29). When there is no flashing, according to eq. (5), the volume of the reaction mass is constant and as a consequence eq. (29) can be rewritten as

$$\lambda_0 + w = w_0 + \lambda_{00} \quad (37)$$

Depending on whether monomer is flashing or not, we have 2 situations. When only W is evaporating, eq. (19) holds for thermodynamic equilibrium and the intersection point is given by

$$\lambda_0^{c1} = \frac{w_0 + \lambda_0}{(1 + a_1)} \quad (38)$$

In this, superscript c1 stands for this situation (called case 1). This is now substituted either in eq. (21) or (31). When P_1 as well as W evaporate (called case 2), eq. (37) is used to eliminate w from eq. (13) and λ_0^{c2} for this situation is determined from

$$\lambda_0^{c2} = \frac{(a_1 + 1) - \sqrt{(a_1 + 1)^2 - 4a_2(w_0 + \lambda_0)}}{2a_2} \quad (39)$$

This is once again substituted in eq. (17) to get the time of transition.

In order to demonstrate the efficiency of solution developed in this paper, we have reexamined the analysis semibatch reactor given in Ref. 33. For specified final stage, the time of transition, t_{tr} , is first determined by using eq. (38) [or eq. (39)] and eqs. (31) [or eq. (17)] and after that, the time of polymerization. We have compared our results with those found numerically using the technique of Ref. 33. We have found exactly the same result and our method has the advantage of being simple and can be adapted on any programmable calculator.

In the following, we now examine the sensitivity of design of the semibatch reactor to various reaction parameters.

Theoretically, the time of transition, t_{tr} , is expected to depend upon the reactor pressure and β . We have varied β from 0.1 to 3 and have found that it is relatively insensitive to it. However, reactor pressure has profound effect on t_{tr} as seen in Figure 2. As the reactor pressure is reduced, the transition time falls almost linearly. We have shown t_{tr} for the case when P_1 and W both flash in this figure by dotted line and find that for a given reactor pressure it is lower for this case. This is observed because of the additional term due to the monomer concentration in the vapor-liquid equilibrium relation eq. (6).

From the knowledge of λ_0 in the reaction mass, it is possible to compute number average chain length μ_n defined as

$$\mu_n = \lambda_1/\lambda_0 \quad (40)$$

Since the molecular weight distribution (MWD) is given by the Flory's relation in eq. (10), the polydispersity index, PDI, is equal to

$$PDI = \mu_w/\mu_n = 1 + p_{FG} \quad (41a)$$

where

$$p_{FG} = (1 - \lambda_0/p_{10}) \quad (41b)$$

$$\mu_w = \lambda_2/\lambda_1 \quad (41c)$$

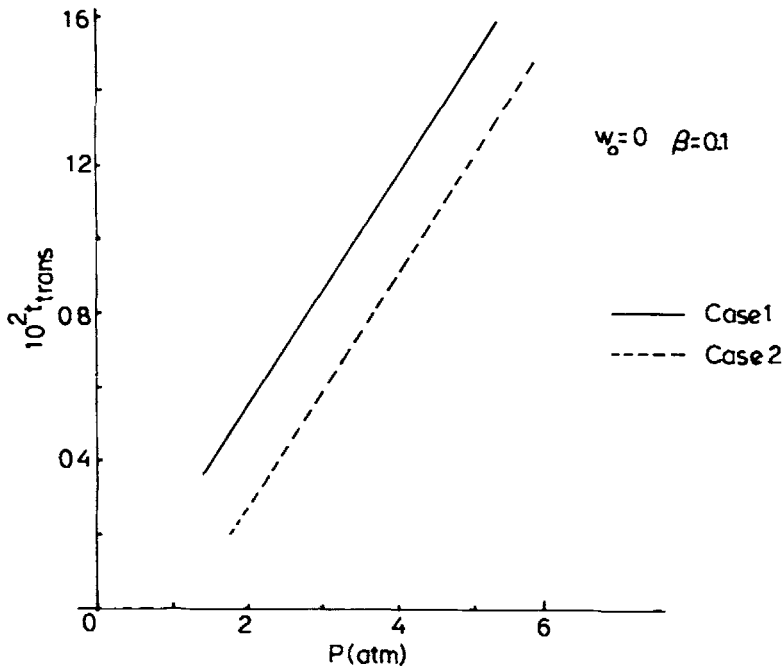


Fig. 2. Time of start of evaporation versus reactor pressure for case 1 and case 2.

Above p_{FG} represents the conversion of functional groups. Evidently the maximum value of p_{FG} is unity which means that PDI is limited to a maximum value of 2, as expected. The μ_n versus time of polymerization in semibatch reactor has been plotted in Figure 3. It is found to rise quickly for short times, but for longer time spans, it is limited by the equilibrium. In this figure the effect of β has been examined and it is found that as β is increased, the asymptotic value of μ_n falls. This is because smaller conversions are attained for larger β leading to smaller μ_n .

The instantaneous evaporation of the condensation product, Q_w can be easily derived from eq. (5)

$$Q_w = - (1/v_w) dV/dt \quad (42)$$

where dV/dt is found from eq. (15) as

$$dV/dt = b_1 R_p - 2b_2 \lambda_0 R_p \quad (43a)$$

$$R_p = -\lambda_0^2 + \beta w (\lambda_1 - \lambda_0) \quad (43b)$$

In Figure 4, instantaneous Q_w has been evaluated as a function of time. It is found to be very large for short times which progressively reduces in mag-

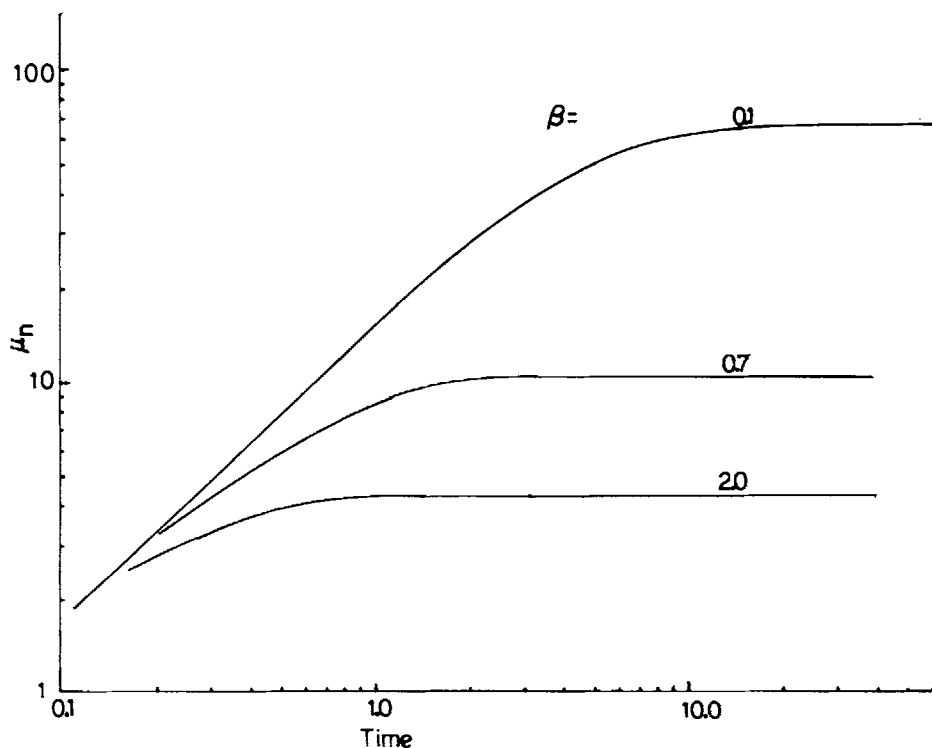


Fig. 3. Average chain length μ_n versus time of polymerization with β as parameter at $P_T = 5.0$ atm for case 1.

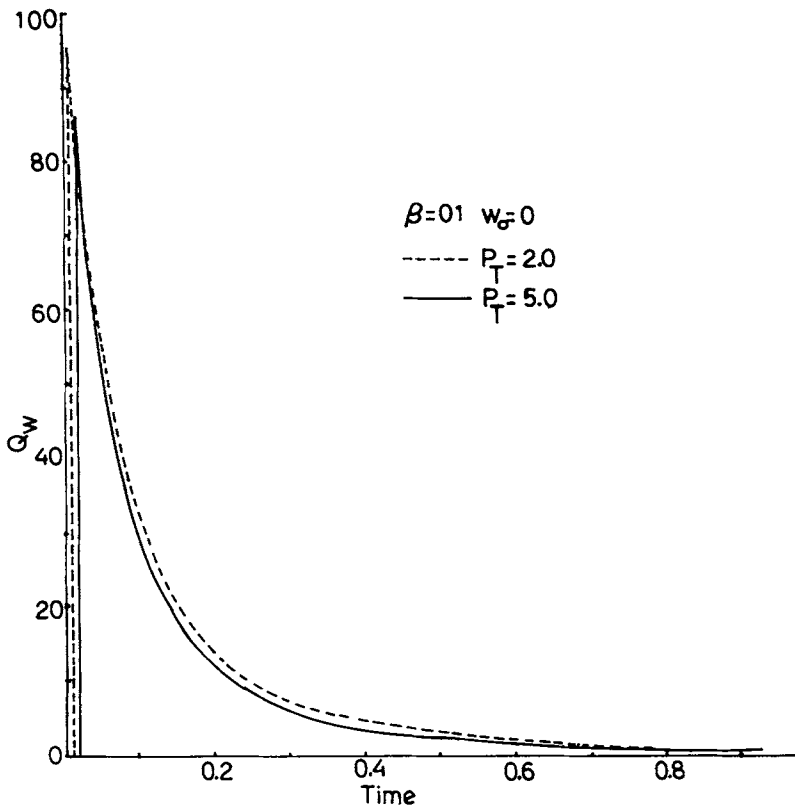


Fig. 4. Rate of evaporation Q_w versus time of polymerization for different reactor pressure for case 2.

nitude. Evidently at the reaction equilibrium, polymerization stops and Q_w is zero. In this figure we have examined the effect of reducing reactor pressure. We find that flashing starts earlier and the initial value of Q_w is higher. Also the case of only W flashing shows an earlier transition and a higher peak of Q_w than the case when both P_1 and W flash.

The development presented in the text of this paper assumes Raoult's law for the vapor liquid equilibrium. It is well known that a more realistic representation of this for polymer solution is the Flory-Huggins relation. The difference between the two theories lies in the fact that there is an empirical parameter χ characterizing the polymer solvent system. For this case, the scheme of the solution remains unchanged and results are given in the Appendix. In Figure 5, we have treated χ as a parameter and plotted μ_n versus time of polymerization. For given β , as χ is increased, the moles of condensation product W in the reaction mass decreases, which increases the average chain length of the polymer.

Lastly we have undertaken an analysis of the formation of polyethylene terephthalate (PET) from bishydroxyethyl terephthalate (BHET) in semibatch reactors. If the formation of side products is neglected, the polymerization mechanism can be written as in eq. (1). For this system, the value of parameter

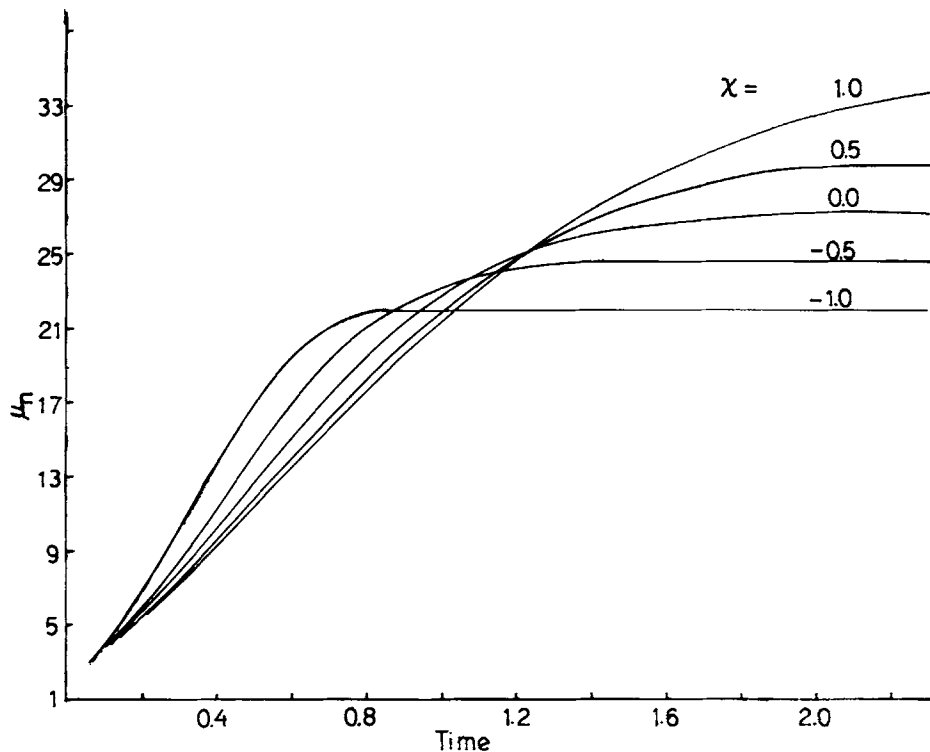


Fig. 5. Effect of χ on average chain length versus time of polymerization at $\beta = 0.1$, $P_T = 5.0$.

β is 2 and is independent of temperature. The effect of varying reaction temperature, T , alters the vapor pressure of the condensation product W . The results have been summarized in Figure 6. As T is increased, vapor pressure of ethylene glycol increases, as a result of which the time of flashing and the value of W decreases which leads to higher μ_n .

CONCLUSIONS

We have developed an analytical solution for reversible step growth polymerization carried out in semibatch reactors. It has been assumed that polymer evaporates along with condensation product. Analytical expression for the time when flashing starts has been obtained employing both the idealized Raoult's law as well as the more realistic Flory-Huggin's relation for the vapor liquid equilibrium. Expression for the MWD of the polymer formed has been obtained, and it has been shown that this remains unaffected by evaporation if the feed to the reactor is either a pure monomer or it is the product from a preceding batch reactor. Transcendental relationship between the polymer concentration and time of polymerization has been derived. The results match perfectly with those obtained by numerical schemes presented in the previous literature. A sensitivity analysis with respect to kinetic parameter β and reactor operating conditions has been carried out. Subsequently, we have analyzed the industrial

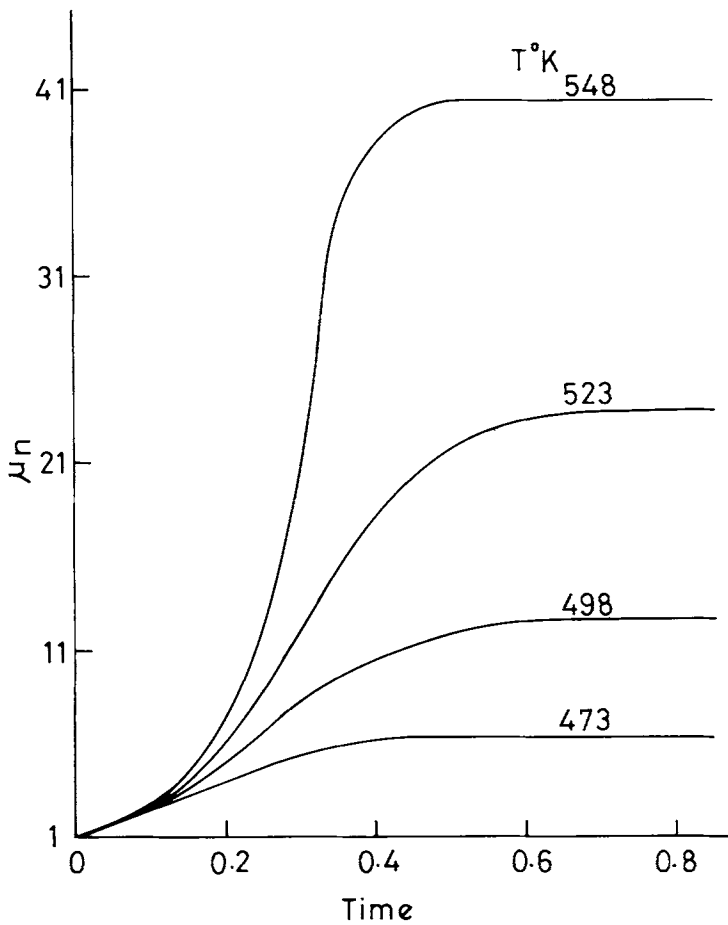


Fig. 6. Effect of reactor temperature on average chain length versus time of polymerization for PET formation at $P_T = 66$ mm Hg, $\beta = 2.0$.

example of PET formation in a semibatch reactor and have examined the effect of temperature and pressure.

APPENDIX: SEMIBATCH REACTOR ANALYSIS USING THE FLORY-HUGGINS RELATION

The vapor-liquid equilibrium relation for monomer P_1 and condensation product W flashing is given by

$$\left(\frac{P_1 v_{P_1}}{V} \frac{P_{P_1}^0}{P_T} + \frac{w v_w}{V} \frac{P_W^0}{P_T} \right) \exp(1 + \chi) = 1 \quad (44)$$

where P_T is the total pressure in the reactor, V is the volume of reaction mass, $P_{P_1}^0$ and P_W^0 are vapor pressures, v_{P_1} and v_w are specific molar volumes of P_1 and W , respectively, and χ is the Flory-Huggins parameter.

Approach similar to that employed for Result's law vapor liquid equilibrium is adopted here to determine w and V in terms of λ_0 alone. Rewriting eq. (44) for w we get

$$w = [P_T V \exp - (1 + \chi) - P_{P_1, v_{P_1}, P_1}^0] / (v_W P_W^0) \quad (45)$$

Substituting this relation in eq. (9), we get a quadratic expression for V , analogous to eq. (15)

$$V = b_{0F} + b_{1F} \lambda_0 - b_{2F} \lambda_0^2 \quad (46a)$$

where

$$b_{0F} = [V_0 - v_W(w_0 + \lambda_{00})] / [1 - P_T \exp - (1 + \chi) / P_w^0] \quad (46b)$$

$$b_{1F} = v_w / [1 - P_T \exp - (1 + \chi) / P_w^0] \quad (46c)$$

$$b_{2F} = \frac{v_{P_1} P_{P_1}^0}{P_{10} P_w^0} / [1 - P_T \exp - (1 + \chi) / P_w^0] \quad (46d)$$

Substituting eq. 46 (a) back in eq. (45) we get a quadratic expression for w , analogous to eq. (14)

$$w = c_{0F} + c_{1F} \lambda_0 - c_{2F} \lambda_0^2 \quad (47a)$$

where

$$c_{0F} = \frac{P_T \exp[-(1 + \chi)] b_{0F}}{v_W P_W^0} \quad (47b)$$

$$c_{1F} = \frac{P_T \exp[-(1 + \chi)] b_{1F}}{v_W P_W^0} \quad (47c)$$

and

$$c_{2F} = [P_T \exp[-(1 + \chi)] b_{2F} + v_{P_1} P_{P_1}^0 / P_{10}] / (v_W P_W^0) \quad (47d)$$

Substituting eq. (46a) for V and eq. (47a) for w in the rate expression [eq. (7a)] for λ_0 , one obtains

$$(b_{0F} + b_{1F} \lambda_0 - b_{2F} \lambda_0^2) d\lambda_0 / dt = d_{0F} - d_{1F} \lambda_0 - d_{2F} \lambda_0^2 + d_{3F} \lambda_0^3 \quad (48a)$$

where

$$d_{0F} = k_r \lambda_{10} c_{0F} \quad (48b)$$

$$d_{1F} = k_r (c_{1F} \lambda_{10} + c_{0F}) \quad (48c)$$

$$d_{2F} = (k_f + k_r \lambda_{10} c_{2F} + k_r c_{1F}) \quad (48d)$$

$$d_{3F} = k_r c_{2F} \quad (48e)$$

Equation (48) can also be used for the case when only condensation product flashes, then the terms accounting for $P_{P_1}^0$, the vapor pressure of monomer P_1 , have to be discounted, that is,

$$b_{2F} = c_{2F} = d_{3F} = 0 \quad (49)$$

Integrating eq. (48a) for the simpler case of only condensation product flashing, taking account of eq. (50), one obtains

$$A_{1F} \ln \left(\frac{\lambda_0 - e_{1F}}{\lambda_{00} - e_{1F}} \right) + A_{2F} \ln \left(\frac{\lambda_0 - e_{2F}}{\lambda_{00} - e_{2F}} \right) = -d_{2F} t \quad (50)$$

where

$$e_{1F} = -[d_{1F} + (d_{1F}^2 + 4d_{0F}d_{2F})^{1/2}]/2d_{2F} \quad (51a)$$

$$e_{2F} = -[d_{1F} - (d_{1F}^2 + 4d_{0F}d_{2F})^{1/2}]/2d_{2F} \quad (51b)$$

$$A_{1F} = (b_{0F} + b_{1F}e_{1F})/(e_{1F} - e_{2F}) \quad (51c)$$

$$A_{2F} = -(b_{0F} + b_{1F}e_{1F})/(e_{1F} - e_{2F}) \quad (51d)$$

For the other case, when both P_1 and W are flashing the roots of the cubic expression on the right hand-side of eq. (51a) can be obtained and hence a similar approach is adopted for obtaining time versus λ_0 .

The transition from closed reactor operation to semibatch reactor operation (i.e., when flashing starts) is obtained by substituting

$$w = w_0 + \lambda_{00} - \lambda_0 \quad (52a)$$

$$V = V_0 \quad (52b)$$

$$p_1 = \lambda_0^2/P_{10} \quad (52c)$$

in eq. (44), giving a quadratic in λ_0

$$a_F \lambda_0^2 - b_F \lambda_0 + c_F = 0 \quad (53a)$$

where

$$a_F = v_{P_1} P_{P_1}^0 / p_{10} \quad (53b)$$

$$b_F = v_W P_W^0 \quad (53c)$$

$$c_F = (w_0 + \lambda_{00}) v_W P_W^0 - P_T \exp - (1 + \chi) \quad (53d)$$

The transition λ_0 is the feasible root of this quadratic equation

$$\lambda_{0,ir} = \frac{b_F + \sqrt{b_F^2 - 4a_F c_F}}{2a_F} \quad (54)$$

The transition time corresponding to this value of λ_0 is obtained by substituting $\lambda_{0,ir}$ in eq. (50).

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