$$R_1 = Da_I \exp\left[\gamma_I\left(1 - \frac{1}{T}\right)\right]$$

$$R_2 = Da_p\left(\frac{2f}{Da_T}\right)^{1/2} \exp\left[\gamma\left(1 - \frac{1}{T}\right)\right] M$$

We now introduce the following deviation variables:

$$x_1 = I - I_s; \quad x_2 = M - M_s; \quad x_3 = T - T_3; \quad U = I_o - I_{os}$$

and linearize the system around the steady state. If the control variabile U is related to the polymerization temperature x_3 in the form of Eq. 19

$$U = -K_c \cdot x_3 \tag{A4}$$

the characteristic equation of system (Eq. A4), in the Laplace domain, is in the form:

$$(s + 1)(s^2 + As + B) = 0 \tag{A5}$$

It is simple to verify that the term A does not contain the controller gain K_c. This term is equal to:

$$A = D_{aI} \exp\left[\gamma_I\left(1 - \frac{1}{T_s}\right)\right] + (T_s - T_o) \times \left[\frac{1}{M_s} - \frac{\gamma}{T_s^2} - \frac{1}{2}\frac{\gamma_I}{T_s^2}\right] + 2 \tag{A6}$$

When $A < 0$, the system is always unstable because Eq. A5 has always a positive root. The value of T_s for which $A = 0$ defines the minimum light-off temperature that is the critical value under which the reactor is always closed-loop unstable, for any choice of the controller parameters. In the reference conditions (Table 1), this temperature is equal to 137°C for initiator #10 and to 158°C for initiator #12. From an analysis of Eq. A6 it is noted that, for a given initiator, the minimum light-off temperature is decreased only by increasing the input temperature T_o.

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van der Molen Th. J., and A. Koenen, "Effect of Process conditions on 'light off' temperature and consumption of 16 initiators, as determined from high pressure radical polymerization of ethylene," 7th Colloquium of Chem. Reac. Eng., Novara, Italy (1981).

Finishing Stages of PET Synthesis: a Comprehensive Model

A comprehensive mathematical model for the finishing stages of polyethylene terephthalate (PET) synthesis is developed. The model takes into account the variables which have significant influences on polymerization but have not been hitherto taken into account, e.g., changing interfacial concentration and the presence of side reactions. The model is applicable to industrial polymerizations, and the predictions agree well with the literature and with certain pilot-plant and commercial data.

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SCOPE

During the manufacture of polyethylene terephthalate, a complex series of reactions accompanies the main polycondensation reaction. Apart from playing an important role in controlling the product quality (such as fiber color, dyeability and stability), these side reactions also modify the progress of polymerization. The modelling problem, however, is formidable due to the coupling of the diffusional and kinetic phenomena occurring in the final stages.

There have been some efforts to model this process in the past. However, in all these cases, simple approximations, such as the neglect of the presence of side reactions and assumption of constant interfacial concentration, have been made. Such simplified analyses, although valuable from the point of view of providing first insights, are not directly pertinent as far as the industrial reactor operations are concerned. A need to develop a more comprehensive model which avoids these deficiencies was felt. Since PET is a large-tonnage polymer, any insight into the complex interactions in the finishing stages leading to improved methods of design, productivity, and product quality control is extremely useful.

CONCLUSIONS AND SIGNIFICANCE

A comprehensive model incorporating the major side reactions that occur during the PET formation and also accounting for the continuous change of the interfacial concentration of the volatile species was developed. An approximate numerical technique was devised to calculate the interfacial concentration.

The influence of important process and operational variables, such as pressure, temperature, mixing and film thickness (equivalent to the reciprocal of specific interfacial area), was examined; the trends predicted by the model were successfully compared with the available experimental and industrial data. Some novel and "unobvious" predictions emerged from the

analysis: 1. the degree of polymerization actually rises faster in the presence of side reactions; and 2. the compensation of the effect of nonideal mixing with the presence of side reactions could ensure a linear DP rise curve.

The comprehensive model not only explains certain hitherto unexplained anomalies, but also provides useful conclusions from the point of view of industrial PET reactor analysis and design. Additionally, certain computational techniques developed in this work are of general interest in other polycondensation reactions (nylons, polybutylene terephthalate, etc.) as in the general problem of desorption with reaction.

INTRODUCTION

Polyethylene terephthalate (PET) is a major polymer with applications in both fiber and engineering plastic industry. Its manufacture involves the transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) or esterification of terephthalic acid (TPA) with EG followed by the polycondensation of bis(2-hydroxyethyl) terephthalate. The finishing stages of polycondensation where the degree of polymerization (DP) rises from about 30 to about 100 poses challenging modelling problems due to the coupling of the diffusional and kinetic phenomena.

There have been many efforts on the modelling of transesterification, esterification and prepolymerization reactors (Ravindranath and Mashelkar, 1981, 1982a, 1982b, 1982c, 1982d). As regards the finishing stages of polycondensation, some of the notable contributions are by Secor (1969), Hoftyzer and Van Krevelen (1968), Hoftyzer (1975), Ault and Mellichamp (1972), Amon and Denson (1980), Gupta et al. (1982), and Ravindranath and Mashelkar (1982e). In all these cases simple models based on the so-called "penetration theory approximations" have been developed.

Such simple models simulate conditions which do not exactly pertain to industrial reactor operations. For instance, it is well known that the interfacial concentration of volatile species changes as the reactions proceed. However, almost all the above authors assume the interfacial concentration to be either zero or they hold it at a fixed value. Further, PET formation is accompanied by a large number of complex side reactions which critically control the product quality. These have been always neglected previously. We shall show subsequently that such approximations could lead to gross errors.

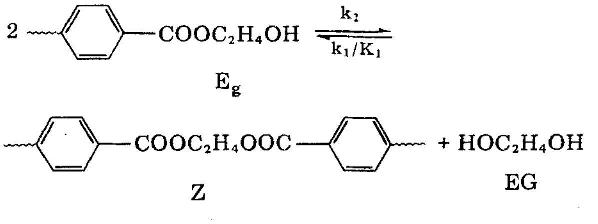
In this work, we shall develop a model for the finishing stages of polycondensation which simulates conditions as close to the industrial practice as possible. This will appear to be the first comprehensive model, which relaxes many of the unduly restrictive assumptions. The results obtained by us give an interesting insight into many complex interactions and provide important clues for industrial reactor analysis, design and operation.

MATHEMATICAL MODEL

Polycondensation Reactions

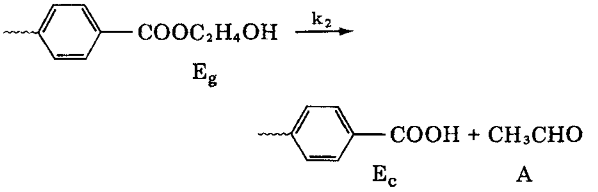
The following reactions occur during the finishing stages of polycondensation:

1. *Polycondensation reactions through ester interchange*



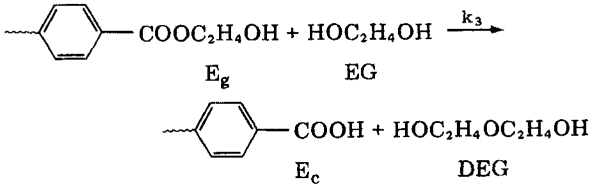
(1)

2. *Acetaldehyde formation*

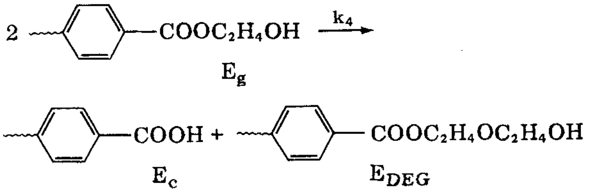


(2)

3. *Diethyleneglycol (DEG) formation*

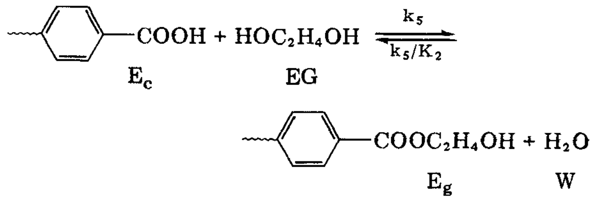


(3)

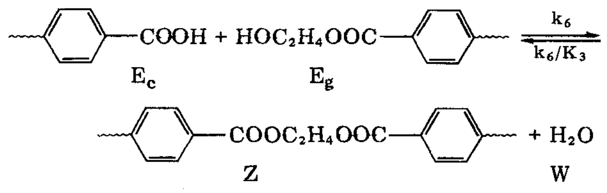


(4)

4. *Water formation*

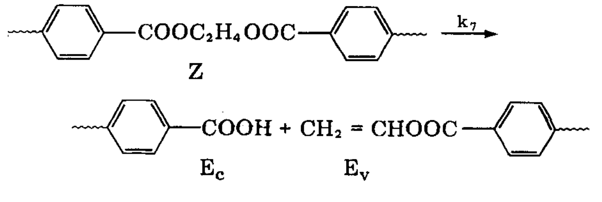


(5)



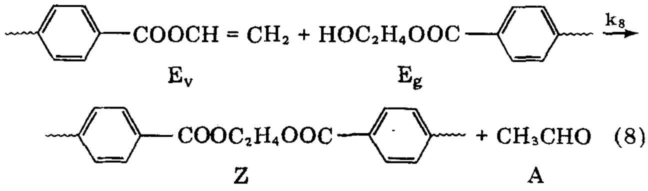
(6)

5. *Degradation of diester end group*



(7)

6. *Polycondensation reaction of vinyl end group*



(8)

In the above k_1–k_8 are pertinent reaction rate constants and K_1, K_2 and K_3 are equilibrium constants.

Model development

The details of the thin-film devices used for PET manufacture in commercial practice have been given by Ravindranath and Mashelkar (1982e).

As a simplification, we shall assume that polycondensation occurs in a thin film of a finite thickness L placed on a solid impermeable surface with a free interface. The reaction mixture in the final stages of polycondensation contains volatile species, such as EG, water and DEG, and nonvolatile linear polymer molecules having hydroxyl, acid and vinyl end groups. Due to the bulkier size of the polymeric species in comparison to the volatile species, we shall assume that the molecular diffusivity of these is much smaller in comparison to that of the volatile species

$$\frac{D_{E_g}}{D_G} = \frac{D_{E_c}}{D_G} = \frac{D_{E_v}}{D_G} = 0 \tag{9}$$

We will further use the well accepted equal reactivity hypothesis (Flory, 1953).

The mass balance equations for individual species can be written as follows:

$$\frac{\partial g}{\partial t} = D_G \frac{\partial^2 g}{\partial x^2} + R_1 - R_5 \tag{10}$$

$$\frac{\partial w}{\partial t} = D_W \frac{\partial^2 w}{\partial x^2} + R_5 + R_6 \tag{11}$$

$$\frac{\partial e_g}{\partial t} = -2R_1 - R_2 - R_3 - R_4 + R_5 - R_6 - R_8 \tag{12}$$

$$\frac{\partial z}{\partial t} = R_1 + R_6 - R_7 + R_8 \tag{13}$$

$$\frac{\partial e_c}{\partial t} = R_2 + R_3 + R_4 - R_5 - R_6 + R_7 \tag{14}$$

$$\frac{\partial e_v}{\partial t} = R_7 - R_8 \tag{15}$$

$$\frac{\partial g^*}{\partial t} = R_3 + R_4 \tag{16}$$

$$\frac{\partial a}{\partial t} = R_2 + R_8 \tag{17}$$

$R_1 - R_8$ are reaction rates for reactions represented in Eqs. 1–8, and kinetic studies in the literatuare suggest the rate expressions of the following form:

$$R_1 = k_1(e_g^2 - 4zg/K_1) \tag{18}$$

$$R_2 = k_2 e_g \tag{19}$$

$$R_3 = 2k_3 e_g g \tag{20}$$

$$R_4 = k_4 e_g^2 \tag{21}$$

$$R_5 = k_5(2e_c g - e_g w/K_2) \tag{22}$$

$$R_6 = k_6(e_c e_g - 2zw/K_3) \tag{23}$$

$$R_7 = k_7 z \tag{24}$$

$$R_8 = k_8 e_v e_g \tag{25}$$

Here, g, w, e_g, z, e_c, e_v and a represent the concentration of the species as shown in Eqs. 1–8 with capital letters. g^* represents the concentration of DEG. The following additional approximations have been introduced in writing the above equations.

- The vapor pressure of acetaldehyde is very high at the polycondensation temperature. We shall therefore assume that acetaldehyde is instantly removed as soon as it is formed.
- There are two reactions by which the formation of DEG can be accounted for. (See Eq. 3 and 4.)

In the present work the total content of DEG (free DEG and DEG incorporated in the polymer chain) is calculated and therefore the material balance equations for the DEG and incorporated DEG in the polymer chain have not been written separately. However, the reactivity of EG is assumed to be the same as that of DEG and the rate of disappearance of EG by reaction 3 is not included in Eq. 10 and E_g disappearance by reaction 4 is considered only once in Eq. 12.

Boundary conditions for solution of Eqs. 10–25 are given by:

$$\begin{array}{lll} e_g = e_{go} & g = g_o & \\ e_c = e_{co} & w = w_o & t = 0, \quad 0 \le x \le L \\ e_v = e_{vo} & g^* = g^*_o & \\ z = z_o & & \end{array} \tag{26}$$

$$g = g_i, \quad w = w_i, \quad \frac{\partial e_g}{\partial x} = \frac{\partial e_c}{\partial x} = \frac{\partial e_v}{\partial x} = 0, \quad x = 0, \quad t > 0 \tag{27}$$

$$\frac{\partial g}{\partial x} = 0, \quad \frac{\partial w}{\partial x} = 0, \quad \frac{\partial e_g}{\partial x} = \frac{e_c}{\partial x} = \frac{\partial e_v}{\partial x} = 0, \quad x = L, \quad t > 0 \tag{28}$$

Here subscript o indicates the initial concentration of the respective species. g_i and w_i are interfacial concentration of EG and water. The average species concentration is obtained by the integration,

$$\bar{e}_g(t) = \frac{1}{L}\int_0^L e_g(t,x)dx \tag{29}$$

Similarly the expression for the average concentration of the other species could be written. The average DP over the film can be shown to be given by

$$P_n(t) = 1 + \frac{2\bar{z}}{\bar{e}_g + \bar{e}_c + \bar{e}_v} \tag{30}$$

Development of a Method of Calculation of Interfacial Concentration

As the reaction proceeds, DP increases and the interfacial concentration of EG and water changes continuously. Our model, unlike all the previous simplified models, takes into account this change in the species concentration at the interface.

We use an approximate procedure to obtain the interfacial concentration. This is done by considering that at an instant the number of moles of the product produced due to the reaction should be equal to the amount retained in the liquid at equilibrium and the amount leaving the system at the interface. Such considerations suggest that instantaneously *at the interface* the following material and component balances apply

$$f = d + b \tag{31}$$

$$f x_g = d y_g + g_i \tag{32}$$

$$f x_w = d y_w + w_i \tag{33}$$

$$1 = y_g + y_w + y_a \tag{34}$$

Here, f represents the total number of moles produced as a result of the reaction in a short time interval at the interface, b represents the number of moles retained in the liquid at equilibrium and d represents the number of moles leaving the liquid. x_g and x_w rep-

TABLE 1. KINETIC PARAMETERS USED IN THIS WORK

Reaction	Polycondensation Eq. 1	Acetaldehyde formation Eq. 2	DEG formation Eqs. 3 and 4	Esterification Eq. 5	Esterification Eq. 6	Diester Group Degradation Eq. 7	Polycondensation of Vinyl End Group Eq. 8
Activation Energy, kcal/mol	18.5	29.8	29.8	17.6	17.6	37.8	18.5
Frequency Factor, L/mol·min	1.36×10^6	8.32×10^7*	8.32×10^7	2.08×10^6	2.08×10^6	7.2×10^9*	1.36×10^6
Equilibrium Constant	0.5	—	—	2.5	1.25		—

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* min^{-1}

resent the mole fractions of EG and water, respectively. y_g, y_w and y_a represent the mole fractions of EG, water and acetaldehyde leaving in the vapor phase, respectively.

Assuming that physical equilibrium prevails at the interface, vapor phase composition of EG and water could be calculated by using Flory-Huggins theory (Flory, 1953) as

$$y_g = \frac{P_g}{P_T} \frac{g_i M_g}{M} e^1 + \chi \tag{35}$$

$$y_w = \frac{P_w}{P_T} \frac{w_i M_w}{M} e^1 + \chi \tag{36}$$

Here χ is the polymer-solvent interaction parameter (approximated as 0.5 in the present work). $g_i M_g/M$ and $w_i M_w/M$ are the volume fractions of EG and water in the polymer melt. We assume that the specific gravity of the polymer and the solvent is approximately unity.

For calculating the mole fraction of acetaldehyde in the vapour phase, we need to know the molar fluxes of EG, water and acetaldehyde from the polymer melt interface. In principle, these could be calculated by considering EG and water desorption rates which at any instant of time t are given as

$$N_g = D_G \left.\frac{\partial g}{\partial x}\right|_{x=0} \tag{37}$$

$$N_w = D_W \left.\frac{\partial w}{\partial x}\right|_{x=0} \tag{38}$$

These equations were impracticable to use especially when the gradients were steep resulting in large truncation errors. Hence the values of N_g and N_w were calculated by using the procedure suggested by Amon and Denson (1980) as

$$N_g = \frac{1}{L} \int_0^L [(e_g + e_v + z + g^* + a)_t - (e_g + z + g^* + g + e_v + a)_{t+\Delta t}] dx \tag{39}$$

$$N_w = \frac{1}{L} \int_0^L [(e_c + w + a - e_v - g^*)_t - (e_c + w + a - e_v - g^*)_{t+\Delta t}] dx \tag{40}$$

The above equations essentially represent the balance on total number of moles of species and the decrease in this amount is due to the amount lost by diffusion.

The knowledge of molar flux of EG and water in the vapour phase is necessary for calculating g_i and w_i and vice versa (Eqs. 31–40). An iteration procedure was therefore developed. The fluxes of EG and water at time t were used for calculating the mole fractions of acetaldehyde (y_a). Using Eqs. 31–36 the interfacial concentrations were calculated at time $t + \Delta t$. This assumption saved a considerable amount of computer time. Equations 31–34 amount to adopting an "effective flash" procedure. Only when the sum of the partial pressures of the volatile species was greater than the reactor pressure, "flashing" was supposed to occur, otherwise there was no flux of EG and water out of the film.

The vapor pressure data for water were obtained from Perry (1973) as:

$$\log P_w = 10.14889 - \frac{1{,}721.355}{T + 245} \tag{41}$$

Where T is in °C and the vapor pressure of EG is taken as (Fontana, 1968).

$$\log P_g = 23.73483 - \frac{3{,}729}{T + 273} - 4.042 \log(T + 273) \tag{42}$$

The kinetic data for the reaction networks indicated in the foregoing were obtained (or approximated) from the reported information in the literature (Table 1) (Ravindranath and Mashelkar, 1981, 1982b, 1982d). The feed for final stages of polycondensation process was assumed to have the following species concentration (nondimensionalized with respect to the number of moles of repeating units)

Hydroxyl end groups (e_{go})	$= 0.10$
Diester groups (z_o)	$= 0.95$
EG concentration (g_o)	$= 1.32 \times 10^{-3}$

Numerical Procedure

Equations 10–40 were nondimensionalized as

$$\theta = k_1 \xi(0) t \tag{43}$$

$$y = x\sqrt{k_1 \xi(0)/D_G} \tag{44}$$

Here $\xi(0)$ is the initial benzene ring concentration. Concentration terms, rate constants and diffusivities were nondimensionalized with respect to $\xi(0)$, k_1 and D_G respectively.

The dimensionless mass balance equations were solved by using an implicit finite difference procedure (Crank-Nicolson method). Note that Eqs. 10 and 11 cannot be solved independently because of the EG and water concentration terms which appear in both these equations. We adopted the procedure suggested by Secor (1967) for tackling this problem. While solving Eq. 10 at time $t + \Delta t$; the values of w at time t were used and the new concentration profile of g was used in solving Eq. 11. This procedure helps in reducing the computation time considerably.

RESULTS AND DISCUSSION

The accuracy of the numerical results obtained in this work was checked by comparing the results of the analysis with that presented by Secor (1969), who considered only the main reaction given by Eq. 1. The agreement between our numerical results and that of Secor was excellent.

There is some uncertainty in the kinetic data on polycondensation. Therefore, the parametric sensitivity was examined rather critically. It was seen that the model results are not very sensitive

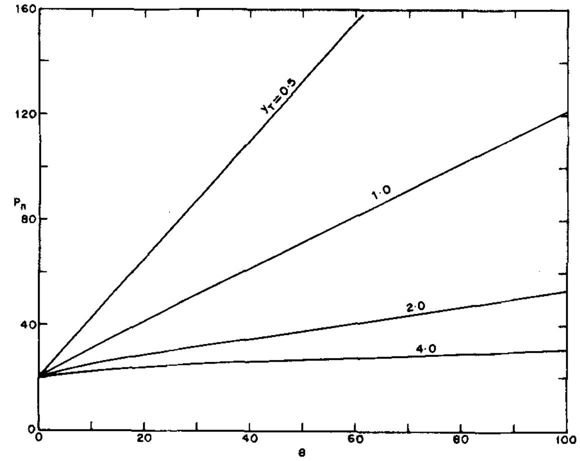

Figure 1. Effect of film thickness on DP (without side reactions). P_T = 0, Temp. = 553 K.

to certain kinetic parameters such as k_5, k_6, k_7 and k_8, etc., but they are very sensitive to the equilibrium constants, especially to K_1.

We shall now examine the numerical results obtained in this work with a view to understand the influence of process and operational variables in the finishing stages of polycondensation reaction.

Influence of Film Thickness

Figure 1 shows $P_n(\theta)$ curves for various values of normalized film thickness. As is to be intuitively expected in a mass-transfer-dominated process such as this, an increase in the normalized film thickness (equivalent to a reduction in the specific interfacial area) leads to a reduction in the rate of DP rise. Interestingly enough, in the absence of side reactions, the progress of polymerization in very thin films leads to linear P_n (θ) curves, whereas at higher film thicknesses, these are curved.

This trend is borne out at least qualitatively by comparison with some of the studies reported in the literature (Rafler et al., 1973; Rafler et al., 1979). In Figure 2 we have shown the experimental data obtained by Rafler et al. Both the trends predicted above have been verified.

Influence of Pressure

The effect of pressure is shown in Figure 3 in the presence and absence of side reactions. Reduction in reactor pressure helps in increasing the DP. This (rather obvious) conclusion supports the industrial practice of operating the reactor at as low a pressure as possible. The curve for $P_T = 0$ is linear and DP appears to increase continuously. When P_T is finite (as considered in this work) there is an equilibrium value of DP that is reached. Figure 4 shows some data from an industrial reactor, which was operated in a semibatch mode. The finishing stages were operated at a fixed vacuum level. The asymptotic levelling-off of P_n (time) curve is readily seen. Note that many of the prior model results in the literature have been obtained with the assumption of $P_T = 0$; they are clearly unrealistic, since they do not predict the industrial reactor behavior properly.

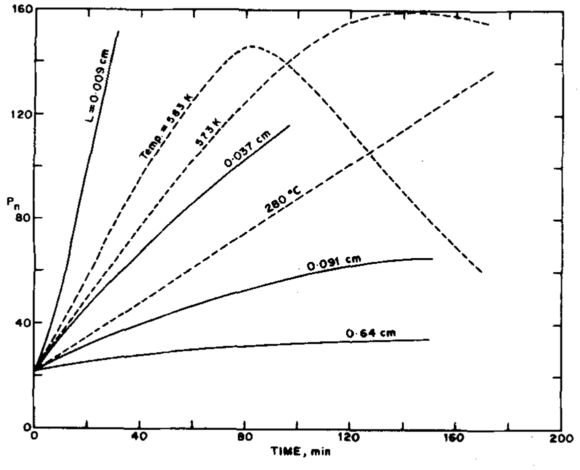

Figure 2. Experimental data (—) Table 1, Rafler et al. (1979), (- - -) Figure 3, Rafler et al. (1973).

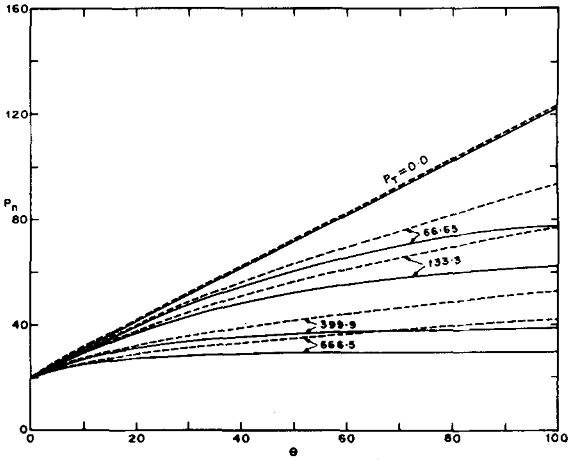

Figure 3. Effect of pressure on DP with side reactions (- - -), without side reaction (—); y_T = 1, Temp. = 553 K.

The equilibrium value of DP for finite values of P_T can be approximately calculated as follows. In the absence of side reactions, total pressure is equal to the partial pressure of EG.

$$P_T = P_g \frac{gM_g}{M} e^{1+x} \tag{45}$$

When chemical equilibrium prevails in the system, we have

$$g = \frac{K_1 e_g^2}{4z} \tag{46}$$

and

$$P_n = 1 + \frac{2z}{e_g} \tag{47}$$

Using Eq. 45–47, we get

$$P_n = 1 + \sqrt{\frac{P_g K_1 M_g}{P_T M} e^{1+x}} \tag{48}$$

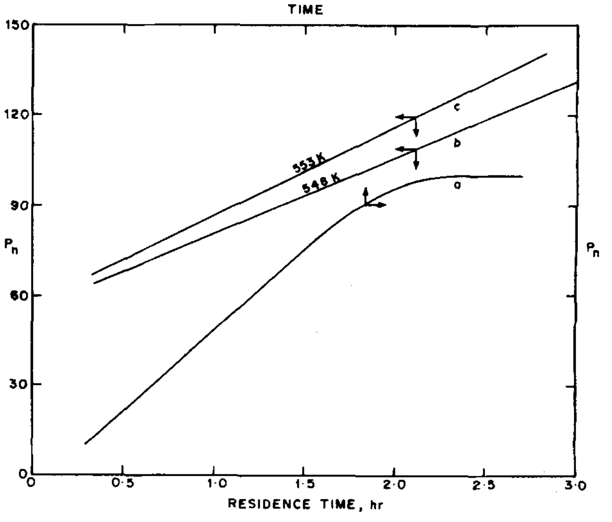

Figure 4. DP rise as a function of time. Commercial semibatch plant data (a); pilot-plant data (*b,c*) (Yokoyama et al., 1979).

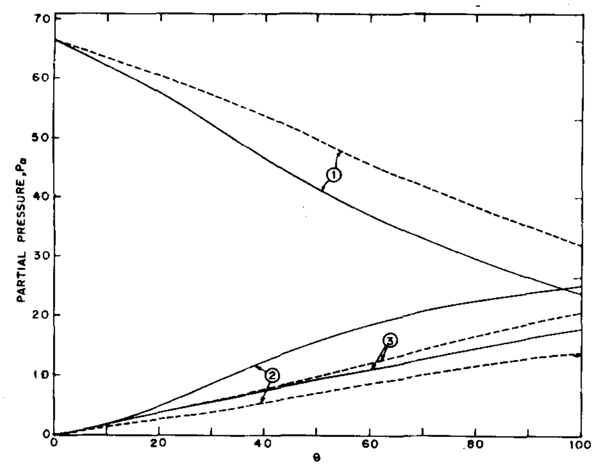

Figure 5. Effect of mixing on the partial pressures of EG, water and acetaldehyde. No mixing (—), mixing (- - -); P_T = 66.65, y_T = 1, Temp. = 553 K, N = 50; 1, EG; 2, water; 3, acetaldehyde.

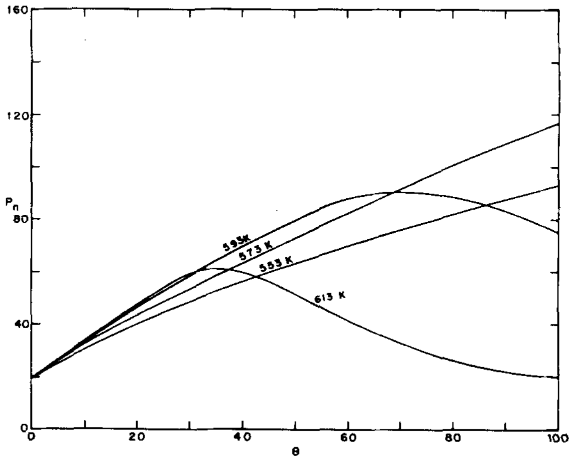

Figure 6. Effect of temperature of DP. P_T = 66.65, y_T = 1.

Influence of Side Reactions

The most remarkable deduction emanating from the present work is that in the presence of side reactions the DP rise is higher in comparison to the case where the side reactions are not present (Figure 3). The increase in DP can be because of two reasons. In the presence of side reactions the acid end groups, acetaldehyde and water are formed. The polycondensation reaction rate (k_6) through esterification is 2–3 times higher than that via polycondensation through ester interchange reaction (k_1). Therefore the acid end groups formed (Eq. 6) will react faster compared to the hydroxyl end groups. Hence DP rises faster in the presence of side reactions.

The second reason for increasing DP is sought through the partial pressure considerations. When there are no side reactions, the partial pressure of EG is equal to the reactor pressure, whereas in the presence of side reactions partial pressure of EG is reduced considerably, because of the contribution of volatiles such as water and acetaldehyde. This is verified by examination of Figure 5, where we have shown the effective partial pressure of EG (and also other volatile components) as a function of time in the presence and absence of mixing.

Revealing observations also result when the case $P_T = 0$ is considered. In this case, the effect of esterification reaction on DP profile is small, compared to the other cases (Figure 3). Therefore, the esterification reaction in the present model has a negligible effect on the DP profile, and the side reactions have a favourable effect in increasing DP, when P_T is finite. The effect of DEG and vinyl end groups on DP is negligible since in our work, the reactivities of DEG and vinyl end group are assumed to be equal to that of EG and E_g.

Our observations on the interesting influence of side products substantiate the views expressed by Hoftyzer (1975), who observed that the contribution of side products cannot be neglected at high DP values while calculating the equilibrium relationships. The computations presented by us highlight the difficulties in such measurements.

Figure 4 shows some interesting observations from an industrial semibatch reactor operation (curve a). Also shown in Figure 4 (curves b and c) are some data from a continuous pilot plant (Yokoyama, 1979). In both these cases, curves for DP rise have been shown to be linear. Such observations had led the previous workers (for example, Hoftyzer, 1975; Ravindranath and Mashelkar, 1982e) to believe that simple models of the kind proposed in their work might explain such data. A closer scrutiny of the data analysed by Ravindranath and Mashelkar (1982e) for a continuous reactor shows that finite mixing is predicted to cause a curvature in the DP rise curve. Such mixing effect must have undoubtedly existed in the continuous pilot plant data shown by Figure 4 (curves b and c) and therefore the curves should have been nonlinear. Why are the resulting DP rise curves still linear then? No satisfactory answer to this perplexing problem was provided by Ravindranath and Mashelkar, but this anomaly can be explained for the first time now. It seems that a significant number of side reactions do occur in such systems making the DP rise curve tend towards linearity, as predicted by our present model. It appears *prima facie* that the effect of nonideal mixing on the DP rise curve was perhaps more or less compensated by the inevitable presence of the side reactions.

Influence of Temperature

Figure 6 illustrates the influence of temperature. Although increasing the temperature helps in increasing DP, after a temperature of 573 K is reached, DP starts decreasing. The acid end groups and vinyl end groups formed can react with hydroxyl end groups and the chain builds up continuously. As DP increases the hydroxyl end group concentration decreases. At high temperatures the acid and vinyl end group formation rate is high as compared to its consumption rate (Eq. 4–8); as a result, there is a fall in DP. Our computations are supported by the data reported in the literature, Figure 2. The present calculations also indirectly support the currently used practice of operating range of 553–563 K in industry.

Influence of Mixing

It is of interest to understand the influence of periodic mixing on the progress of polymerization. We computed two cases. In the first case the film was unmixed during the course of reaction whereas in the second case the film was mixed 50 times for the same period (θ = 100). At the end of each mixing operations, the average species concentration was evaluated by averaging over the length of the film. This average concentration provided the starting concentration for the next mixing operation.

As shown in Figure 7, the periodic mixing obviously helps in

TABLE 2. EFFECT OF MIXING ON *DP*
TEMP. = 553 K; P_T = 66.65

No. of Contacts (θ = 100) N	$y_T = 1$ DP Without Side Reactions	$y_T = 1$ DP With Side Reactions	$y_T = 2$ DP Without Side Reactions	$y_T = 2$ DP With Side Reactions
0	79.72	93.45	53.48	52.68
10	85.00	97.21	61.40	66.34
50	86.62	99.85	67.49	72.75

TABLE 3. EFFECT OF MIXING ON SIDE PRODUCTS FORMATION
TEMP. = 553 K, P_T = 66.65

No. of Contacts in θ = 100	y_T = 2.0						y_T = 1					
	Acetal-dehyde $\times 10^3$	DEG $\times 10^4$	Vinyl Ends $\times 10^4$	Acid Ends $\times 10^3$	Water $\times 10^3$	EG $\times 10^2$	Acetal-dehyde $\times 10^3$	DEG $\times 10^4$	Vinyl Ends $\times 10^4$	Acid Ends $\times 10^3$	Water $\times 10^3$	EG $\times 10^2$
0	4.15	7.82	5.90	1.78	3.71	2.90	3.07	3.81	9.00	1.42	2.92	3.85
10	3.82	6.32	6.69	1.47	3.63	3.32	3.00	3.57	9.21	1.14	3.12	3.88
50	3.61	5.46	7.30	1.62	3.24	3.50	2.92	3.33	9.45	1.16	3.03	3.92

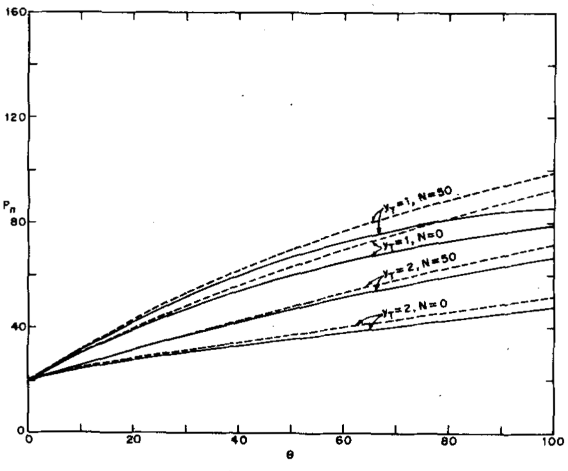

Figure 7. Effect of mixing on DP. With side reactions (- - -), without side reactions (—); P_T = 66.65, Temp. = 553 K.

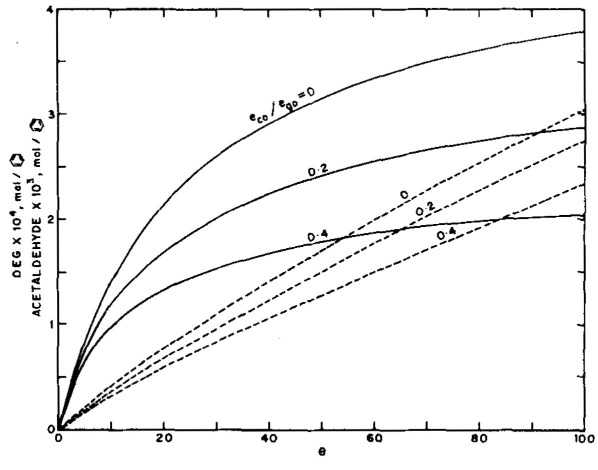

Figure 9. Effect of TPA addition on DEG (—) and acetaldehyde (- - -) formation rate. (Conditions are the same as in Figure 8).

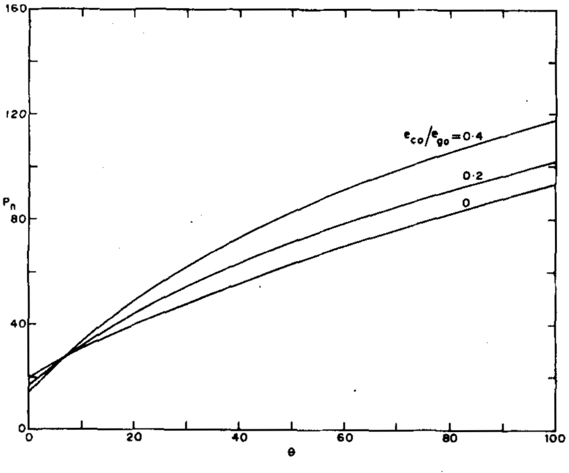

Figure 8. Effect of TPA addition on DP. P_T = 66.65, y_T = 1, Temp. = 553 K.

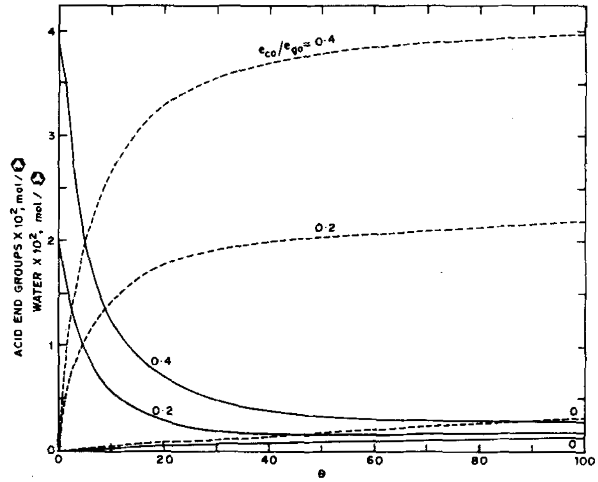

Figure 10. Effect of TPA addition on acid end groups (—) and water (- - -) formation rate. (Conditions are the same as in Figure 8).

increasing DP rise. For thicker films, mixing has a more profound effect, Tables 2 and 3. The formation of side products seems to generally decrease when the film is mixed periodically. This observation has an important consequence in reactor operation.

Industrial reactors are operated in a semibatch manner (use helical screws or ribbons). Due to a large hydrostatic head, the bulk of the polymer melt is in chemical equilibrium, and the reaction proceeds only within a short distance of the free interface, where a sufficient driving force for desorption exists. (Note that the vacuum levels used are 13.33 Pa). The circulation provided by the agitator helps bring fresh fluid to the interface where a continuous surface renewal takes place. Our model shows that an opportunity to increase this periodic mixing is helpful from both improved productivity and product quality point of view. The observations reported by Yokoyama (1978) support this contention.

Similar role of mixing is likely to prevail in reactors operated in a continuous manner, where mechanical devices with thin-film generators are used.

Influence of TPA Addition

It has been recommended in the literature (Chegolya et al., 1979) during the finishing stages polycondensation/TPA addition helps increase the DP and improving the quality of the fibre. We believe that this method has also been used in industrial practice. Using the present model, the effect of TPA addition on DP and on the side products was examined, Figures 8 to 10.

The model indeed shows that the addition of TPA helps increase the DP, although due to the addition of low molecular weight compound to the high molecular weight product there is a slight decrease in DP in the beginning. Interestingly the formation of DEG and acetaldehyde decreases, Figure 9, on TPA addition. This observation may be valuable from the point of view of product quality improvement in industrial practice.

CONCLUDING REMARKS

The present model approximates some of the limiting cases of industrial reactor operations rather directly. Thus, for instance, in a semibatch polycondensation reactor, if the rate of mixing is kept at a relatively low level, the model results for deep stagnant films will represent such an operation rather closely. Similarly, afrer the end of polycondensation cycle in an industrial semibatch reactor, the PET melt is drained for casting by applying nitrogen pressure. The potential degradation occurring in a deep melt pool may also be closely simulated by our model. An operating semibatch reactor, where there is adequate mixing and circulation could be simulated by superimposing a surface renewal mechanism, which is governed by the agitation process. Similarly the model could be a starting basis for development of a model for typical continuous polycondensation reactors which use multidisks as film generating devices. Considering the intradisk and interdisk interaction, an axially-dispersed plug flow model with an exchange of fluid with the stagnant zone could be built, with the model parameters linked directly to the reactor details. We would like to emphasize that the problems of molecular weight distribution in PET reactors is an equally important one (Ravindranath and Mashelkar, 1983) and its calculation in the framming of a complete model incorporating such complexities pose formidable numerical difficulties.

The present model is rather specific to the PET synthesis. However, the methodology developed can be rather straightforwardly employed in the case of other polycondensations which involve reversible reactions and formation of volatile side products. Directly relevant examples are synthesis of polybutylene terephthalate, Nylon-6, etc. The side products in such cases invariably control the product quality and, as shown in this work, they may also have some "unobvious" effects on productivity.

NOTATION

a = concentration of acetaldehyde, mol/L
b = number of mol of the product in the liquid phase
d = number of mol of the product in the vapor phase
$D_{E_g}, D_{E_c}, D_{E_v}, D_G, D_W$ = difusivity of hydroxyl end group, acid end group, vinyl end group, EG and water respectively, cm^2/min
e_c, e_g, e_v = concentration of acid, hydroxyl and vinyl end groups, respectively, mol/L
f = total number of moles produced as a result of reaction (Eq. 37) at the interface
g = concentration of EG, mol/L
g^* = concentration of DEG, mol/L
$k_1, k_3 - k_6, k_8$ = second order rate constants, L/mol·min
k_2, k_7 = first order rate constants, min^{-1}
$K_1 - K_3$ = equilibrium constants
L = film thickness, cm
M_g, M_w, M = molecular weights of EG, water and repeating unit respectively, kg/mol
N = number of times film is mixed in $\theta = 100$
N_g, N_w = molar flux of EG and water respectively, mol/cm^2·min
P_n = degree of polymerization
P_g, P_w = vapor pressure of EG and water, Pa
P_T = reactor pressure, Pa
$R_1 - R_8$ = reaction rates as defined in Eqs. 18–25
t = time, min
T = temperature, K
w = concentration of water, mol/L
x = film thickness from the interface, cm
x_g, x_w = mole fraction of EG and water as defined in Eqs. 32–33
y = dimensionless film thickness (Eq. 44)
y_T = $L\sqrt{k_1 \, \xi(\theta)/D_G}$
y_g, y_w, y_a = mol fraction of EG, water and acetaldehyde in the vapor phase (Eqs. 32–34)
z = concentration of diester groups, mol/L

Greek Letters

χ = polymer-solvent interaction parameter
θ = dimensionless time as defined in Eq. 43

Subscripts

o = initial concentration
i = interfacial concentration

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