Modeling of Poly(ethylene Terephthalate) Reactors. IX. Solid State Polycondensation Process*

K. RAVINDRANATH and R. A. MASHELKAR, *Polymer Science and Engineering Group, Chemical Engineering Division, National Chemical Laboratory, Pune-411 008, India*

Synopsis

A mathematical model for simulation of industrial process of solid state polycondensation of poly(ethylene terephthalate) (PET) has been developed. The model eliminates errors evident in the earlier models by proper formulation. The model results have been validated by experimental data in the literature. It enables prediction of the influence of particle shape, size, temperature, etc. on the polycondensation process correctly in all different regimes of operation, apart from bringing out the importance of gas-side resistance, influence of carrier gas, etc. for the first time.

INTRODUCTION

This work is a continuation of our earlier work[1-4] pertaining to the modeling of industrial reactors used in the poly(ethylene terephthalate) (PET) manufacture. PET is extensively used in the form of staple and filament, fiber, film, etc. Recently PET has found widespread acceptance for soft drink and beverage bottles. PET is produced as per its end use application. For example, PET of number average molecular weight of 15,000–25,000 is suitable only for textile applications whereas, for injection or blow molding applications, the number average molecular weight should be more than 30,000.

The common commercial practice of producing textile-grade PET involves the process of melt polycondensation carried out usually at around 285°C. The preparation of injection or blow molding grade PET by melt polycondensation route is associated with technical difficulties. The rate of thermal degradation at the melt polycondensation temperature usually employed is so high that if any further increase in reaction temperature or time is made, then the degradation of PET dominates the main polycondensation reaction. In fact, the molecular weight of PET [as reflected by change in intrinsic viscosity (IV) in Fig. 1] decreases and the polymer quality suffers due to an increase in the concentration of side products.

For preparing PET, which has molecular weight greater than 20,000, solid state polycondensation is generally preferred. The solid state polycondensation is carried out by heating the solid low molecular weight PET below its crystalline melting point but above its glass transition temperature. The process is carried out at approximately 200–240°C. Under these conditions,
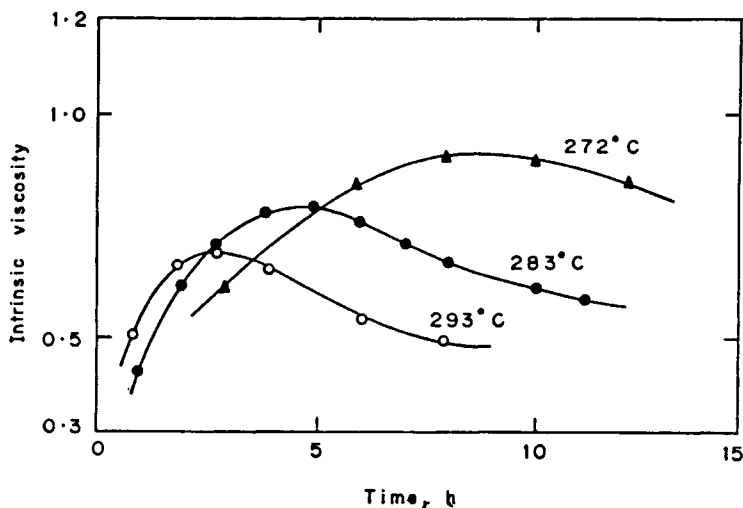
Fig. 1. Effect of temperature on the melt polycondensation rate.[5]

the polymer end groups are sufficiently mobilized for reaction to take place. The reaction byproducts are removed by allowing a flow of inert gas or by maintaining reduced pressure. The main polycondensation reaction is an equilibrium reaction and the byproduct ethylene glycol (EG) is removed so that the forward reaction will be favored:

$$2E \rightleftharpoons Z + EG \tag{1}$$
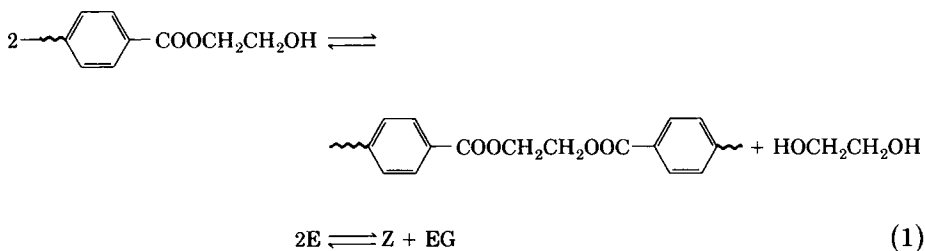
The polycondensation rate depends on both chemical and physical processes, and the possible rate determining steps are

1. A reversible chemical reaction
2. Diffusion of the volatile reaction products (predominantly EG) in the solid polymer
3. Diffusion of the volatile reaction products from the surface of the polymer to the inert gas.

Depending on the process and operating variables, the polycondensation rate is controlled by one or more of these steps. It is important to examine the controlling mechanism of solid state polycondensation process not only for optimizing the process parameters but also for improving the product quality.

Many experimental investigations on solid state polycondensation have been reported in the literature and diverse models have been used by various authors. For example, Chang[6] interpreted his data using a diffusion controlled
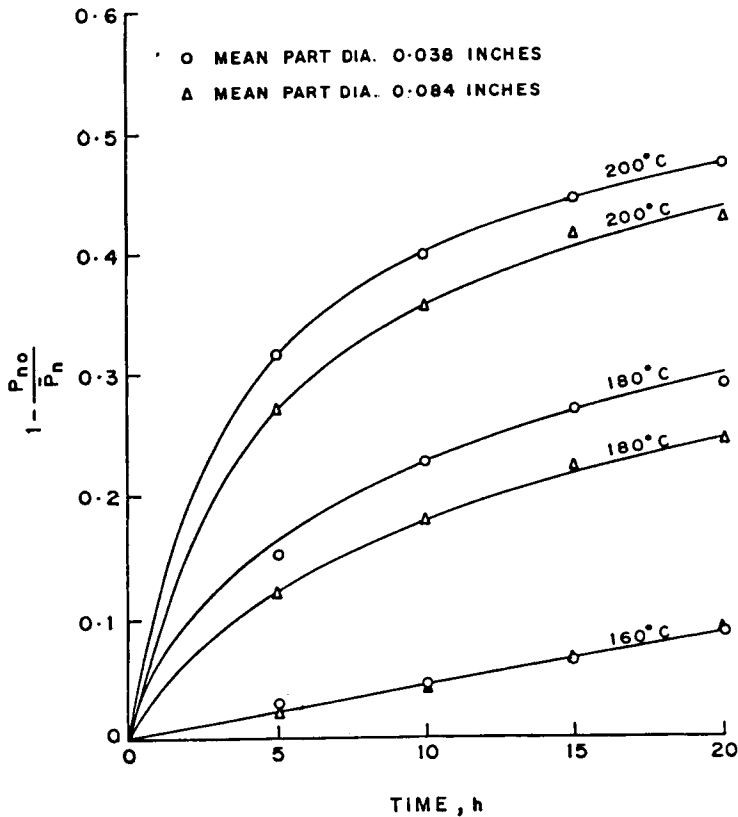
Fig. 2. Effect of temperature and particle size on DP.[8]

model, whereas Schaaf et al.[7] and Chen et al.[8] analyzed their data using a purely kinetic model. Recently Chen and Chen[9] analyzed the solid state polycondensation process taking into account the diffusion of end groups in a purely kinetic model. Jabarin and Lafgren[10] developed empirical equations relating final molecular weight and reaction time for specified catalyst and polymer systems.

The existing models appear to have a number of lacuna. For instance, the variation of molecular weight (see Fig. 2) observed by Chen et al.[8] for a set of operating conditions cannot be explained, if one assumes that the process is purely kinetically controlled. Indeed, the models developed by Chen et al.[8] and Chang[6] contain fundamental errors as can be seen from the following arguments. They assumed that the diffusion of EG through the solid polymer is the rate-controlling step. Then the mass balance for EG in a polymerizing particle was written as

$$\frac{\partial g}{\partial t} = D\frac{\partial^2 g}{\partial x^2} \qquad (2)$$

$$g = g_0, \qquad t = 0 \qquad (3)$$

$$g = g_s, \qquad x = x_0 \qquad (4)$$

and

$$T = \int D(t)\, dt \tag{5}$$

Here g and D are the concentration and the diffusivity of EG, respectively. t is the reaction time and x is the distance in the direction of diffusion. The above equation (2) considers only the diffusion of the initially present EG (g_0) and not that of EG that is formed due to the polycondensation reaction (1). In fact, the contribution of EG formed as a result of polycondensation reaction is significant and taking its presence into account will affect the model predictions significantly. Indeed, *no* analytical solutions become possible, as soon as this complexity is taken into account, as we shall show later.

Our objective is to provide a comprehensive mathematical analysis of the solid state polycondensation process occurring in a single solid particle of arbitrary shape (viz., sphere, cylinder, plane sheet, and cube). We will present the limiting cases of purely kinetically controlled, diffusion-controlled and furthermore consider the intermediate case, where both the influences determine the polycondensation process. Additionally, we will also provide analysis for the case where gas-side resistance assumes importance in solid state polycondensation. Our endeavor is to provide a mathematical analysis, which will lead to suitable criteria for data analysis as well as recommendations for design strategies. As a result of our analysis, we will also explain rationally some hitherto unexplained phenomena, such as the influence of inert gas on the progress of polycondensation.

MODEL DEVELOPMENT FOR SOLID STATE POLYCONDENSATION PROCESS

In our earlier work on modeling of the melt polycondensation process, we have considered the total network of reaction scheme consisting of main polycondensation reactions due to transesterification and esterification, and a number of side reactions.[11] In solid state polycondensation process only the polymer end groups are sufficiently mobilized and the mobility of polymer chain is very low. In addition, the rate of PET degradation decreases by an order of magnitude due to low temperatures employed. For calculating the order of magnitude changes that occur in these processes the rate constants obtained from melt polycondensation data[12] can be used, even though these are not strictly applicable to the solid state polycondensation process. One then sees that the polycondensation rate decreases by six times, when the temperature is decreased from 285 to 230°C, whereas the degradation of diester group decreases by 40 times for the same temperature drop. Therefore, only the polycondensation reactions due to transesterification and esterification reactions need only be considered for modeling the solid state polycondensation process. If the concentration of acid end groups is rather small, then the polycondensation due to esterification reactions need not be taken into account.

In the present paper, solid state polycondensation is examined by considering the unsteady state diffusion of EG in a polymer particle and the main polycondensation reaction [eq. (1)]. This represents a binary system, viz.,

diffusion of EG in polymer with an additional complexity involving the main polycondensation reaction. The mass transfer process is assumed to be isothermal and the diffusion process is of Fickean type. It is further assumed that the partial specific volumes are independent of composition so that there is no volume change as mixing. Hence mean volume average velocities vanish. With these assumptions the 1-dimensional unsteady state diffusion process can be described by the following[10, 11]

$$\frac{\partial g}{\partial t} = D\left[\frac{\partial^2 g}{\partial x^2} + \frac{\lambda}{x}\frac{\partial g}{\partial x}\right] + k\left(e^2 - \frac{4gz}{K}\right) \tag{6}$$

At very low concentration of EG, the mutual diffusion coefficient (D) is equal to the self-diffusion coefficient of EG[15] and this is used in eq. (6). The mass density of polymer is uniform through out the particle. However, the concentration of polymer end groups changes due to the polycondensation reaction and the time rate of change can be represented as

$$\frac{\partial e}{\partial t} = -2k\left(e^2 - \frac{4gz}{K}\right) \tag{7}$$

and

$$z = z_0 + (e_0 - e)/2 = 1 - e/2 \tag{8}$$

where $\lambda = 0$ for a plane sheet, 1 for a cylinder, and 2 for a sphere. Note that in eqs. (6)–(8) e and z are the concentration of hydroxyl end groups and diester groups, respectively. The subscript 0 indicates the initial concentration. K and k are the equilibrium and forward rate constants. The boundary conditions for eqs. (6) and (7) are

$$g = g_0, \quad e = e_0, \quad z = z_0, \quad t = 0, \quad 0 < x < x_0 \tag{9}$$

$$g = g_s, \quad \frac{\partial e}{\partial x} = 0, \quad \frac{\partial z}{\partial x} = 0, \quad t > 0, \quad x = x_0 \tag{10}$$

or

$$-D\frac{\partial g}{\partial x} = k_g(g - g_b), \quad \frac{\partial e}{\partial x} = 0, \quad \frac{\partial z}{\partial x} = 0, \tag{11}$$

$$\frac{\partial g}{\partial x} = 0, \quad \frac{\partial e}{\partial x} = 0, \quad \frac{\partial z}{\partial x} = 0, \quad t > 0, \quad x = 0 \tag{12}$$

Here g_s and g_b are the concentration of EG at the gas–solid interface and in the bulk inert gas phase, k_g is the gas phase mass transfer coefficient, and x_0 is the particle size. For polycondensation occuring in a cubic particle, the

following material balance equations are valid:

$$\frac{\partial g}{\partial t} = D\left[\frac{\partial^2 g}{\partial x_1^2} + \frac{\partial^2 g}{\partial x_2^2} + \frac{\partial^2 g}{\partial x_3^2}\right] + k\left(e^2 - \frac{4zg}{K}\right) \tag{13}$$

$$\frac{\partial e}{\partial t} = -2k\left(e^2 - \frac{4zg}{K}\right) \tag{14}$$

$$z = z_0 + (e_0 - e)/2 = 1 - e/2 \tag{15}$$

x_1, x_2, and x_3 represent the distance in x, y, and z coordinates. The relevant boundary conditions are

$$g = g_0, \quad e = e_0, \quad z = z_0, \quad t = 0, \quad -x_0 \le x_i \le x_0 \tag{16}$$

$$g = g_s, \quad \frac{\partial e}{\partial x_i} = 0, \quad \frac{\partial z}{\partial x_i} = 0, \quad t > 0, \quad x_i = \pm x_0 \tag{17}$$

or

$$-D\frac{\partial g}{\partial x} = k_g(g - g_b), \quad \frac{\partial e}{\partial x_i} = 0, \quad \frac{\partial z}{\partial x_i} = 0, \quad t > 0, \quad x_i = \pm x_0 \tag{18}$$

$$\frac{\partial g}{\partial x_i} = 0, \quad \frac{\partial e}{\partial x_i} = 0, \quad \frac{\partial z}{\partial x_i} = 0, \quad t > 0, \quad x_i = 0 \tag{19}$$

where $i = 1, 2, 3$. Generally solid state polycondensation is carried out under very high vacuum or under high inert gas flow rate. Under these conditions, the mass transfer resistance in the gaseous phase may be neglected and the concentration of EG (g_s) at the surface of the particle can be assumed to be finite as shown in boundary conditions (10) and (17). However, under certain operating conditions, gas side mass transfer resistance can play an important role. In such cases, eqs. (11) and (18) will have to be employed and solutions obtained accordingly. Three limiting cases of eqs. (6) and (12) can be discussed.

Case 1. Reaction Rate-Controlled Process

If the diffusion of EG is rapid compared to the rate of chemical reaction, then the concentration of EG can be assumed to be nearly zero throughout the particle. Then eq. (7) reduces to

$$\frac{de}{dt} = -2ke^2 \tag{20}$$

Integrating eq. (20) and expressing e in terms of degree of polymerization

(DP), we get

$$P_n = P_{n0} + 4kt \tag{21}$$

where $P_n = 2/e$ (by definition) and P_{n0} is the initial DP. Equation (21) shows that plots of DP vs. time should be linear and DP should be independent of particle size. This trend is demonstrated in Figure 2 for the solid state polycondensation data obtained at 160°C. DP is now a function of the following variables:

$$P_n = f(t, P_{n0}, k) \tag{22}$$

Case 2. Diffusion-Controlled Process

When the rate of polycondensation reaction is much faster than the diffusion of EG, the rate is controlled by the diffusion of EG. Then the reaction can be assumed to be at equilibrium at all points and the following equilibrium relation holds:

$$e^2 = 4gz/K \tag{23}$$

By combining eqs. (6) and (7), we get

$$\frac{\partial g}{\partial t} = D\left[\frac{\partial^2 g}{\partial x^2} + \frac{\lambda}{x}\frac{\partial g}{\partial x}\right] - \frac{1}{2}\frac{\partial e}{\partial t} \tag{24}$$

Substituting the derivative of eq. (23) in (24) and rearranging the resulting expression, we obtain

$$\left(1 + \frac{1}{2\sqrt{Kg}}\right)\frac{\partial g}{\partial t} = D\left[\frac{\partial^2 g}{\partial x^2} + \frac{\lambda}{x}\frac{\partial g}{\partial x}\right] \tag{25}$$

Chen et al.[8] and Chang[6] used eq. (24) without considering the contribution of the term on the right hand side, viz., $-\frac{1}{2}\partial e/\partial t$. Their omission implied that the contribution of EG formed due to polycondensation reaction was not taken into account. We can easily show that the contribution of $1/2\sqrt{Kg}$ (which can be of the order of 100) in eq. (25) arising out of the term $-\frac{1}{2}\partial e/\partial t$ is important and cannot be neglected. We now express eq. (25) in terms of DP which is directly measurable. Substituting $e = 2/P_n$ in eq. (23) and using eq. (8), we obtain

$$g = \frac{K}{P_n(P_n - 1)} = \frac{K}{P_n^2} = \frac{K}{P_{n0}^2}\eta, \qquad P_n \gg 1 \tag{26}$$

where

$$\eta = P_{n0}^2/P_n^2 \tag{27}$$

Substituting eq. (26) in (25) and assuming $P_{n0}/2K \gg 1$, we get

$$\frac{\partial \eta}{\partial \Theta} = \sqrt{\eta} \left(\frac{\partial^2 \eta}{\partial \xi^2} + \frac{\lambda}{\xi} \frac{\partial \eta}{\partial \xi} \right) \tag{28}$$

where

$$\Theta = \frac{2K}{P_{n0}x_0^2} \int_0^t D \, dt \tag{29}$$

$$\xi = x/x_0 \tag{30}$$

The relevant boundary conditions (9)–(12) reduce to

$$\eta = 1, \qquad 0 < \xi < 1, \qquad \Theta = 0 \tag{31}$$

$$\eta = \eta_s, \qquad \xi = 1, \qquad \Theta > 0 \tag{32}$$

or

$$-\frac{\partial \eta}{\partial \xi} = \Phi \left(\eta - \frac{P_{n0}^2}{K} g_b \right), \qquad \xi = 1, \qquad \Theta > 0 \tag{33}$$

$$\frac{\partial \eta}{\partial \xi} = 0, \qquad \xi = 0, \qquad \Theta \geq 0 \tag{34}$$

where $\Phi = k_g x_0/D$. The average degree of polymerization is given by

$$\frac{P_{n0}}{\overline{P}_n} = (\lambda + 1) \int_0^1 \eta^{0.5} \xi^\lambda \, d\xi \tag{35}$$

Equation (29) assumes that the diffusivity is a function of reaction time, since the polymer starts crystallizing as it builds up its molecular weight. The nonuniform profile of the molecular weight within the particle implies variation in crystallinity as a function of distance from the interface of the particle. Thus diffusivity is not only time-dependent but also position-dependent. As a first approximation we have considered only the time dependence of diffusivity in this work. However, the model can be extended when diffusivity is a function of time and position. Such refinements will require backup of more detailed data.

For polycondensation occurring in a cubic particle, the following equation (34) is derived by following a procedure used in the derivation of eq. (28).

$$\frac{\partial \eta}{\partial \Theta} = \sqrt{\eta} \left[\frac{\partial^2 \eta}{\partial \xi_1^2} + \frac{\partial^2 \eta}{\partial \xi_2^2} + \frac{\partial^2 \eta}{\partial \xi_3^2} \right] \tag{36}$$

$$\eta = 1, \qquad 0 < \xi_i < 1, \qquad \Theta = 0 \tag{37}$$

$$\eta = \eta_s, \qquad \xi_i = 1, \qquad \Theta > 0 \tag{38}$$

or

$$-\frac{\partial \eta}{\partial \xi} = \Phi\left(\eta - \frac{P_{n0}^2}{K}g_b\right), \qquad \xi_i = 1, \qquad \Theta > 0 \tag{39}$$

$$\frac{\partial \eta}{\partial \xi_i} = 0, \qquad \xi_i = 0, \qquad \Theta \geq 0 \tag{40}$$

where

$$\xi_i = x_i/x_0, \qquad i = 1, 2, 3$$

The average degree of polymerization $(\bar{P}_n)$ is given by

$$\frac{P_{n0}}{\bar{P}_n} = \int_0^1 \int_0^1 \int_0^1 \eta^{0.5} \, d\xi_1 \, d\xi_2 \, d\xi_3 \tag{41}$$

Equations (28)–(35) were solved by using the Crank–Nicholson method.[16] Because of the nonlinear terms appearing in eq. (28), integration was carried out iteratively at each step, until consistent values were obtained. For solving eqs. (36)–(41), the method suggested by Brian[17] was used. DP is now a function of the following variables:

$$\bar{P}_n = f(t, P_{n0}, x_0, K, D) \tag{42}$$

DP now depends on two physicochemical parameters (viz., K and D) compared to the dependence on a single parameter k in the reaction-rate-controlled process.

Case 3. Process Controlled by Diffusion and Reaction Rate

Under certain operating conditions the polycondensation rate is determined by the rate of reaction as well as by the diffusion of EG. Expressing eqs. (6)–(12) in the nondimensionalized form

$$\frac{\partial g}{\partial \Theta^*} = \left(\frac{\partial^2 g}{\partial \xi^*} + \frac{\lambda}{\xi^*}\frac{\partial g}{\partial \xi^*}\right) + e^2 - \frac{4g(1 - e/2)}{K} \tag{43}$$

$$\frac{\partial e}{\partial \Theta^*} = -2\left[e^2 - \frac{4g(1 - e/2)}{K}\right] \tag{44}$$

where

$$\Theta^* = kz_0 t \tag{45}$$

$$\xi^* = \sqrt{\frac{kz_0}{D}}\, x \tag{46}$$

The relevant boundary conditions are

$$g = g_0, \quad e = e_0, \quad \Theta^* = 0, \quad 0 < \xi^* < \xi_0^* \tag{47}$$

$$g = g_s, \quad \frac{\partial e}{\partial \xi^*} = 0, \quad \Theta^* > 0, \quad \xi = \xi_0 \tag{48}$$

$$\frac{\partial g}{\partial \xi^*} = 0, \quad \frac{\partial e}{\partial \xi^*} = 0, \quad \Theta^* > 0, \quad \xi = 0 \tag{49}$$

The average degree of polymerization is given by

$$\frac{2}{\overline{P}_n} = \frac{(\lambda + 1)}{\xi_0^{\lambda+1}} \int_0^{\xi_0} e \xi^\lambda \, d\xi \tag{50}$$

Equations (41)–(50) were solved numerically for various process and operating variables using Crank–Nicolson method.[16] DP is now function of three physicochemical parameters (viz., k, K, and D) and generally we find that

$$\overline{P}_n = f(t, P_{n0}, x_0, k, K, D) \tag{51}$$

DISCERNING THE CONTROLLING MECHANISM

It is important to discern *a priori* the controlling mechanism for analyzing the solid state polycondensation data. In the case of reaction-rate-controlled process, the rate of diffusion of EG is rapid as compared to the rate of chemical reaction. Mathematically this means

$$k \ll \frac{D}{x_0^2} \tag{52}$$

The dependence of various process and operating variables on the controlling mechanism is shown in Table I. This could be used as an approximate guide for discerning the operative mechanism.

TABLE I
Dependence of Various Process and Operating Variables on the Controlling Mechanism in the Absence of Gas Phase Resistance

No.	Controlling mechanism	Particle size (x_0)	Temperature	Catalyst concentration (k)
1	Reaction rate	No	Yes	Yes
2	Diffusion within the polymer particle	Yes (strong influence)	Yes	No
3	Diffusion and reaction rate	Yes (weak influence)	Yes	Yes

RESULTS AND DISCUSSION

Depending on the process and operating conditions, solid state polycondensation rate will be determined by one of the limiting cases discussed in the foregoing. We shall now present the model results for all the limiting cases. The limited solid state polycondensation data available in the open literature are analyzed assuming that we are able to judge the rate controlling step *a priori* based on the considerations described in the foregoing.

Case 1. Reaction-Rate Controlled Solid State Polycondensation

DP can be easily calculated using eq. (21) once the value of k is known. For the data presented in Figure 2 for 160°C, DP is found to be independent of particle size. Hence the process can be assumed to be controlled by reaction rate alone and eq. (21) can be applied. Rearranging eq. (21), we get

$$1 - \frac{P_{n0}}{P_n} = \frac{4kt/P_{n0}}{1 + 4kt/P_{n0}} \tag{53}$$

$$= \frac{4kt}{P_{n0}} \qquad \text{for} \quad \frac{kt}{P_{n0}} \ll 1 \tag{54}$$

Applying eq. (54) for the data presented in Figure 2, the value of k/P_{n0} at 160°C is 1.172×10^{-3} h^{-1}. The exact value of P_{n0} is not provided in Ref. 8. Assuming that $P_{n0} = 100$, the value of k will be $0.1172 \left(\text{mol} / \hexagon \right)^{-1} h^{-1}$.

It is interesting to compare this value with that obtainable from the reported data in the literature on melt polycondensation. The data reported by Yokoyama et al.[12] indicate an activation energy of 18.5 kcal/mol based on the data obtained in the temperature range 275–285°C. Extrapolation of these data to 160°C gives a value of $0.117 \left(\text{mol} / \hexagon \right)^{-1} h^{-1}$, which is surprisingly close to the value of $0.1172 \left(\text{mol} / \hexagon \right)^{-1} h^{-1}$ deduced earlier.

However, we cannot draw any firm conclusions on the basis of such an agreement which may well be fictitious.

Case 2. Diffusion-Controlled Solid State Polycondensation

Finite Gas Side Resistance

There are instances when for fixed process and operating conditions, the number average molecular weight that can be obtained in solid state polycondensation process is known to depend on the inert gas flow rate as shown in Figure 3. This shows that, at small gas flow rates, the gas side resistance plays an important role. Recently Chang et al.[18] showed that the solid state
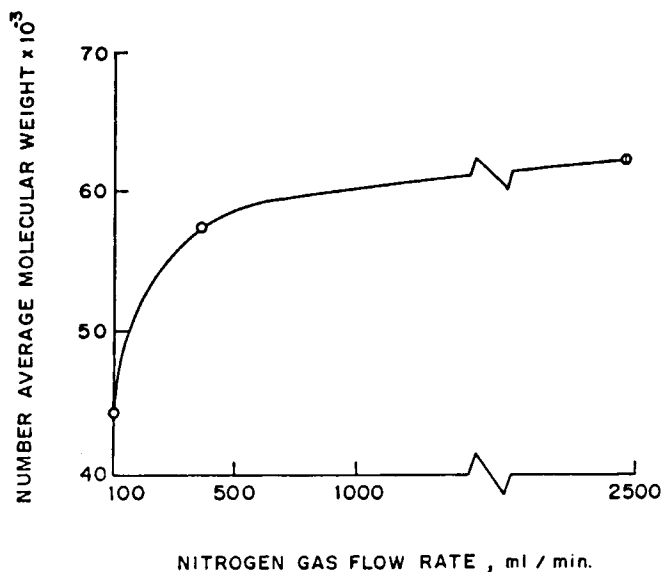
Fig. 3. Effect of nitrogen gas flow rate on solid state polycondensation.[20]

polycondensation process is also affected by the stirring rate. This is also due to the presence of gas side resistance.

It is important to examine the influence of gas side resistance quantitatively and these results are given in Figure 4 for various values of Φ ($= k_g x_0/D$), which is a parameter indicative of gas side resistance. When Φ is small, gas side resistance is maximum and vice versa. Values of $\Phi \gg 1$ imply that there
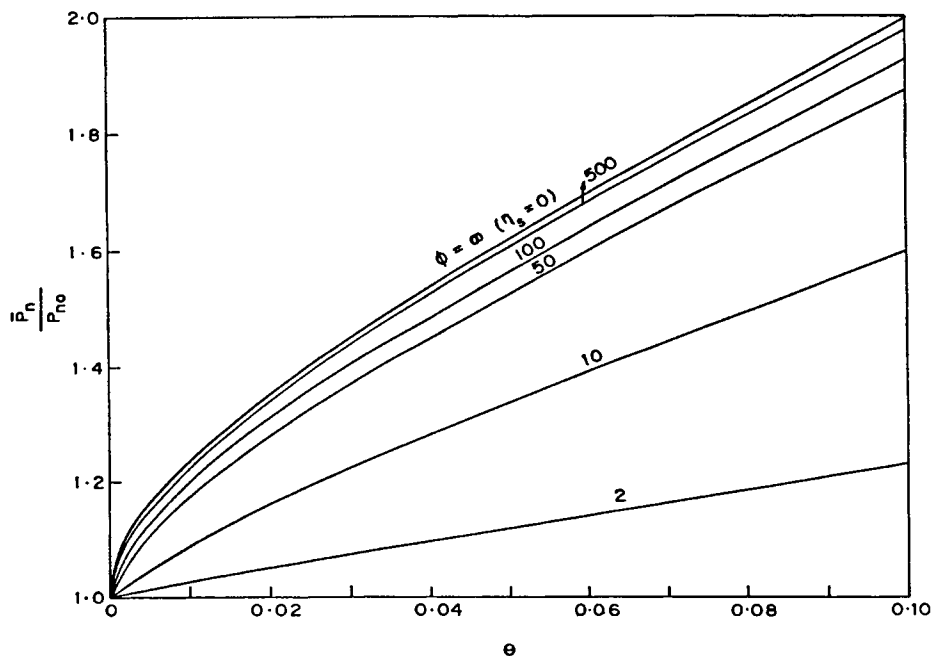

Fig. 4. Influence of Φ on DP (case 2, $g_b = 0$, $\lambda = 2$).

are no concentration gradients in the gas phase and therefore, with increase in Φ, DP will increase too. For $\Phi > 500$, the final DP is the same as that obtained in the case when $\eta_s = 0$.

The range of particle sizes encountered in solid state polycondensation is 0.01–0.3 cm. No information on the gas-side mass-transfer coefficient is available for the devices that are generally used in solid state polycondensation. However, it is reasonable to assume values in the range of 10^{-2}–10^{-1} cm/s. This implies that we will encounter a range of Φ between 10 and 10^4, and especially in the lower range, gas side resistance will tend to influence the progress of polycondensation significantly (see Fig. 4).

No Gas Side Resistance

Figure 5 shows the influence of particle geometry on DP for diffusion-controlled solid state polycondensation process. DP is always found to be maximum for polycondensation occurring in spherical particles and it is minimum for flat film type of particles. This is mainly due to interfacial area considerations. For example, when x_0 is fixed, the interfacial area per unit volume is $3/x_0$ for spherical particles, $2/x_0$ for cylindrical particles, and $1/x_0$ for film type of particles. Therefore, not only does the particle size but also the particle shape influences the final DP. The DP obtained in a cubic particle is approximately the same as can be obtained in spherical particles since the interfacial areas are equal.

For the model results presented in Figure 5, we assumed that the value of η_s at gas–solid interface is nearly zero. However, under certain operating conditions, η_s can be finite, depending upon the applied vacuum and inert gas flow rate. The influence η_s on DP for solid state polycondensation occurring in
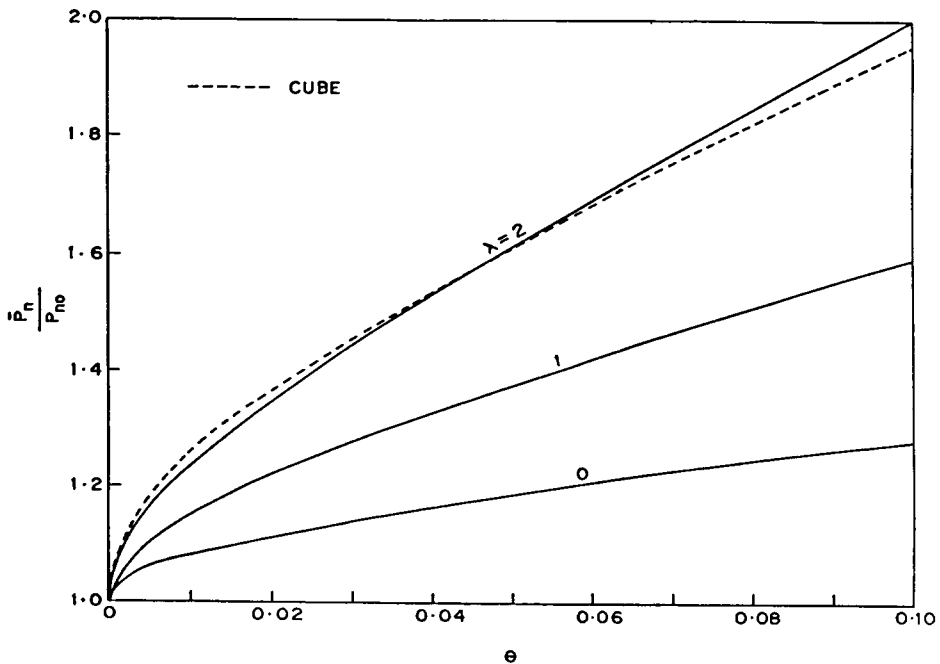

Fig. 5.   Effect of particle geometry on DP (case 2; $\lambda_s = 0$).

TABLE II
Influence of Finite Surface Concentration (η_s) on DP ($\lambda = 2$)

Θ	$\overline{P}_n/P_{n0}$			
	$\eta_s = 0$	$\eta_s = 0.001$	$\eta_s = 0.01$	$\eta_s = 0.1$
0	1.000	1.000	1.000	1.000
0.01	1.236	1.233	1.227	1.193
0.02	1.348	1.345	1.337	1.282
0.03	1.445	1.440	1.431	1.357
0.05	1.616	1.610	1.595	1.481
0.7	1.773	1.767	1.742	1.590
0.10	1.996	1.988	1.953	1.733

spherical particles is shown in Table II. As expected, DP decreases with an increase in η_s values. Therefore, it is important to operate solid state polycondensation under high vacuum or under high inert gas flow rate, so that η_s is small at gas–solid interface.

As pointed out earlier, the analysis of Chang[6] is in error. Therefore, we have analyzed the experimental data of Chang. For doing so, we need to know the controlling mechanism. His data show only the dependence on the particle size. In such cases the process can be either diffusion-controlled or it can be controlled by both diffusion and chemical reaction. We assume a priori that the process is diffusion-controlled. Again we assume that the gas phase resistance is negligible and the concentration of EG at the gas–solid interface is nearly zero.

By knowing the initial and final DP values, the corresponding values of Θ can be obtained from Figure 5 for different reaction times. Here Θ is given by

$$\Theta = \frac{2K}{P_{n0}x_0^2} \int D \, dt \tag{55}$$

In eq. (55), K (assumed to be 0.5 in this work) P_{n0}, and x_0 are constant and do not vary with time. The diffusivity of EG (D), depends on the crystallinity which can change with time. Then plots of Θ vs. $\int D \, dt$ should be linear, if the assumption of process controlled by diffusion mechanism is valid. Chang[6] showed that the crystallization rate is rapid in the beginning and thereafter increases slowly. For major part of the solid state polycondensation process, the crystallinity can be assumed to be constant for polycondensation occuring in the case of large particles. Therefore D can be assumed to be approximately constant. Then plots of Θ vs. t should be linear. The deduced values of Θ from the experimental data of Chang[6] are shown in Figure 6 and 7. For most of the data, the linear relationship is valid. The values of D calculated from the slope of these plots are tabulated in Table III. An activation energy for diffusion of EG is found to be 31.26 kcal/mol from the Arrhenius plot (Fig. 8). It is important to note that the diffusivity values obtained from Chang's data are independent of the particle size he has used, lending further credence to the deductions made by us.

The values of D obtained here are of the order of 10^{-6} cm^2/s whereas Chang[6] deduced the diffusivity values of the order of 10^{-9} cm^2/s. Because of
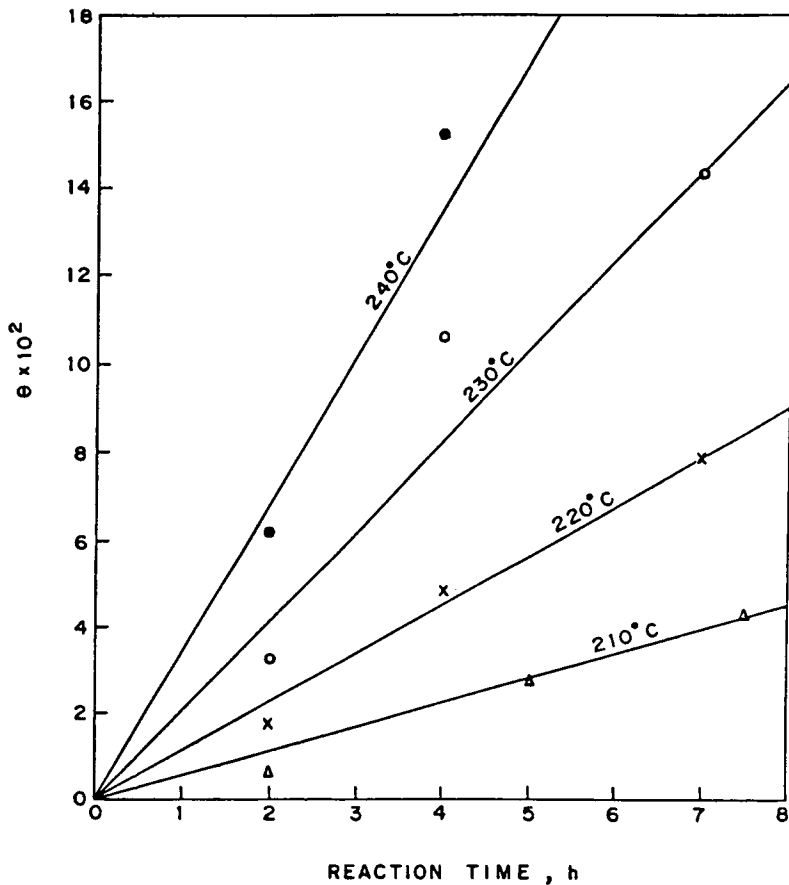
Fig. 6. Values of θ deduced from Chang's data (Ref. 6, Fig. 1, particle size = 1/16 in. cube).

the fundamental errors in Chang's analysis mentioned in the foregoing, the diffusivity values obtained by him are not correct. It is important to emphasize that the order of magnitude of diffusivity value of EG obtained in this work is comparable to the order of magnitude of diffusivity of water (= 10^{-6} cm^2/s) at 200°C in PET obtained by Whitehead.[19]

It is interesting to note that there is reported evidence in the literature that the polycondensation rate also depends on the type of inert gas used in the solid state polycondensation process.[13] The role of inert gas for solid state polycondensation will have to be understood clearly, since it is likely to have major implications in terms of the process performance. Lichen[20] found that the number average molecular weight of PET varied with the type of inert gas used. For example, the number average molecular weights of PET obtained with nitrogen, carbon dioxide, and helium were 58,000, 81,000, and 90,000, respectively, when all other conditions such as flow rate, temperature, etc. were kept constant. There are two possible ways in which the inert gas could have influenced. First is due to the change of gas side resistance with different gases. The gas-side mass-transfer coefficient (k_g) increases with an increase in the flow rate and the gas phase diffusivity. Since the flow rate was kept
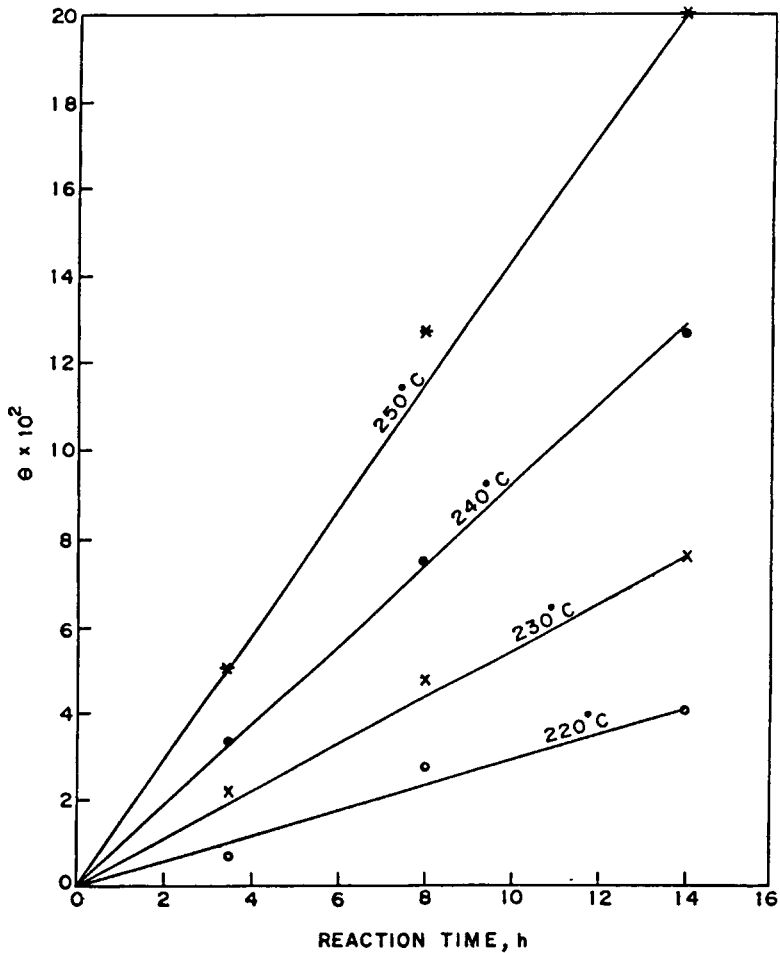
Fig. 7. Values of θ deduced from Chang's data (Ref. 6, Fig. 1, particle size = 1/8 in. cube).

TABLE III
Values of Diffusivity of EG in PET Obtained from Chang's Data[6]

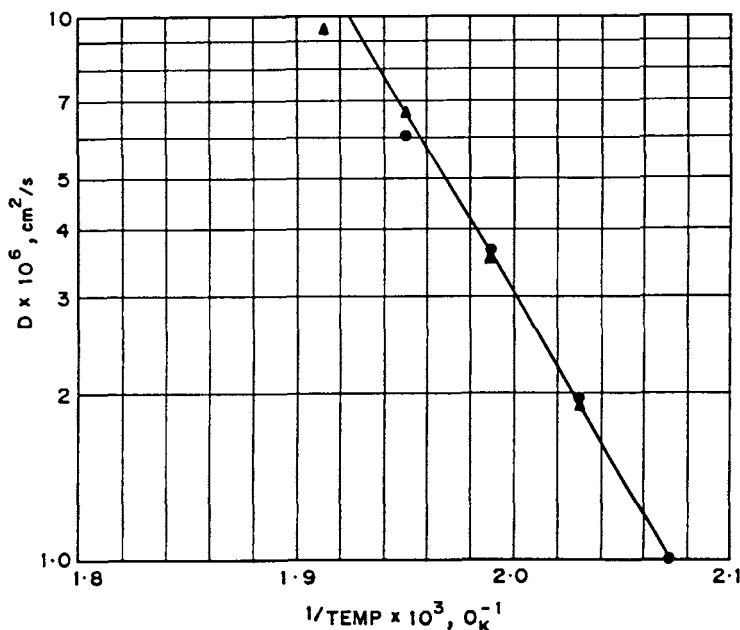| Temp (°C)	Particle size (cm)	$(DK/P_{n0}x_0^2) \times 10^7$ (cm^2/s)	$D \times 10^6$ (cm^2/s)
210	0.1588	7.870	0.99
220	0.1588	0.1567	1.97
	0.3175	3.968	1.90
230	0.1588	0.287	3.60
	0.3175	7.440	3.56
240	0.1588	0.467	6.00
	0.3175	13.890	6.65
250	0.3175	19.84	9.50

Fig. 8.   Arrhenius plot for diffusivity of EG. Particle size: ($\times$) 0.3175 cm; ($\bigcirc$) 0.1588 cm.

constant, k_g can be influenced only due to the changes in gas-phase diffusivities of EG in nitrogen, carbon dioxide, and helium. These have been calculated by using Fuller–Schettla–Gidding equation (Ref. 21, eq. 2.20). The gas phase diffusivities of EG in nitrogen, carbon dioxide, and helium were found to be 0.278, 0.203, and 0.749 cm^2/s, respectively. The data show that the diffusivity of EG in carbon dioxide is approximately the same as that of EG in nitrogen. This means that the gas side resistance will be practically the same in both these cases (see Fig. 4). On the other hand, the rise of molecular weight with carbon dioxide as an inert gas is higher than that with nitrogen. This implies that the observed influence on polycondensation cannot be explained in terms of the gas side resistance alone.

It is well known that exposure of polymer to liquid or vapor induces crystallization.[22] There are reports[23] on solubilization of gases in polymers that can induce a plasticization effect. Any attendant changes in free volume will alter the molecular diffusivity of EG and therefore will alter the process of desorption of EG. In the solid state polycondensation process, absorption of inert gas occurs simultaneously with the desorption of EG. Such cases have been analyzed by Vrentas et al.[24] and Ravindranath and Mashelkar[25] and the process of desorption is shown to be enhanced considerably when such complications are taken into account. It is not unlikely that these considerations are responsible for the change of DP observed in the rate of polycondensation process.

The above data as well as its analysis presented by us points towards the possibility of using a strategy of conducting solid state polycondensation by using alternative carrier gases such as carbon dioxide with some advantage.
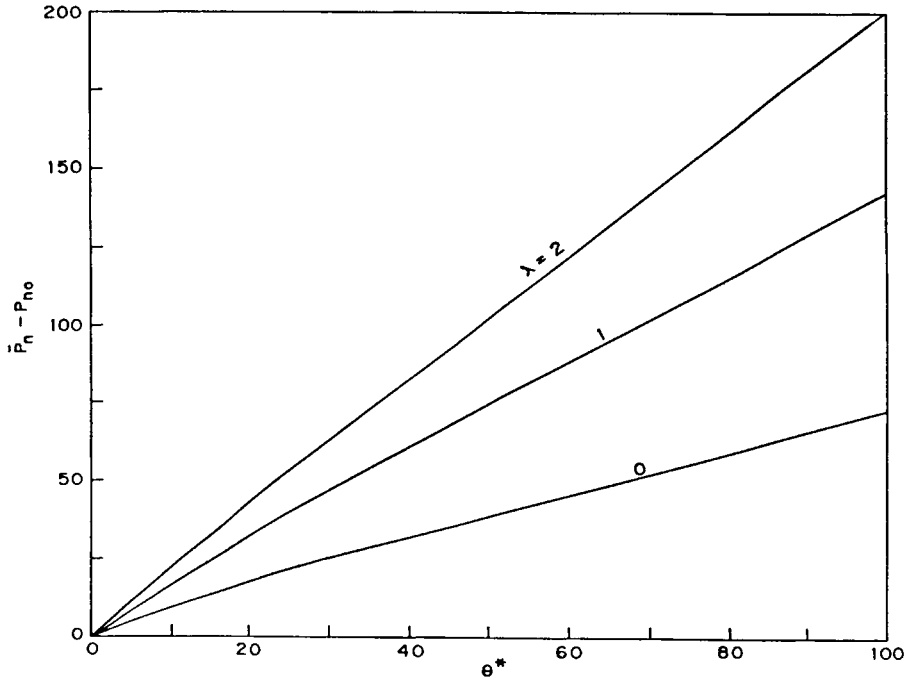
Fig. 9. Influence of particle geometry on DP (case 3, $g_s = 0$, $K = 0.5$, $P_{n0} = 100$, $\xi_0^* = 1.0$).
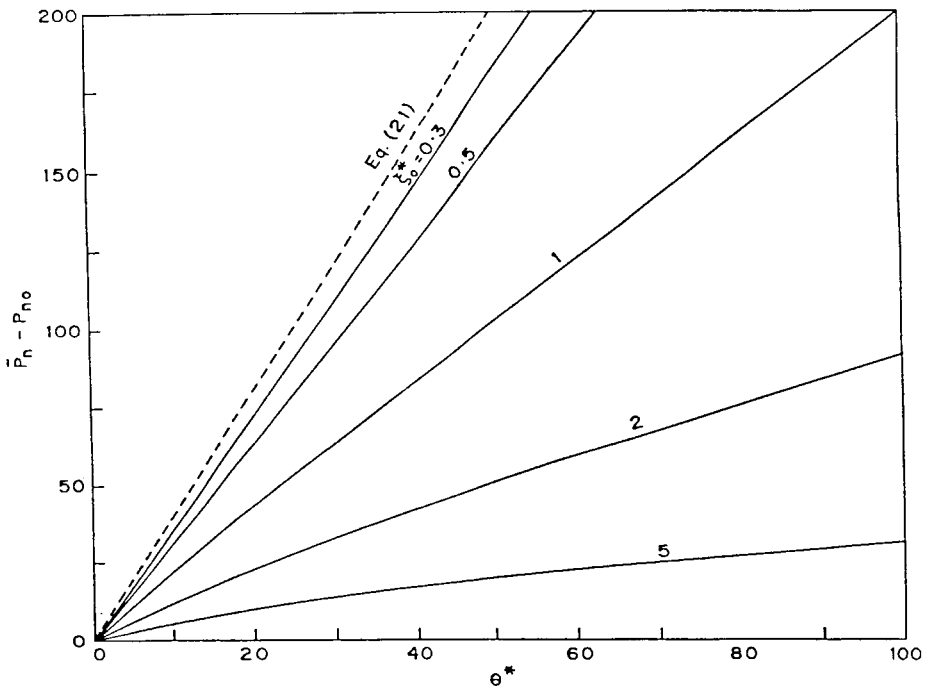

Fig. 10. Influence of particle size on DP (case 3, $g_s = 0$, $K = 0.5$, $P_{n0} = 100$, $\lambda = 2$).
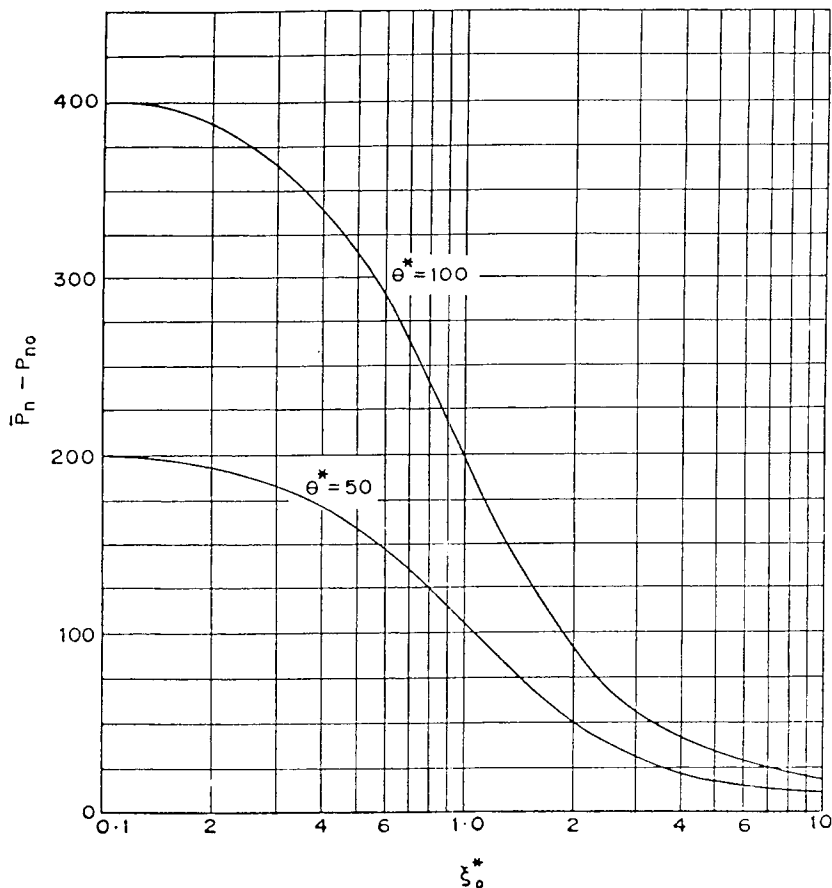
Fig. 11. Influence of particle size on DP for fixed reaction times (case 3, $g_s = 0$, $K = 0.5$, $P_{n0} = 100$, $\lambda = 2$).

Case 3. Process Controlled by Diffusion and Reaction Rate

The influence of particle geometry on DP is shown in Figure 9. In this case also DP is maximum for the spherical geometry as compared to all other geometries. The influence of particle size is shown in Figure 10. For comparison, the DP values obtained by eq. (21) for reaction rate controlled process are also presented in Figure 10. The rate of DP rise is very small for $\xi_0^* > 5$ and it increases as ξ_0^* decreases. For very low values of ξ_0^* the process approaches the reaction-rate-controlled mechanism. This can be clearly seen in Figure 11 where DP is plotted as a function of particle size for different reaction times. Figure 11 shows that if $\xi_0^* < 0.2$, solid state polycondensation is controlled by the rate of reaction and, for $\xi_0^* > 5$, the process approaches diffusion-con- trolled mechanism. For an intermediate range of ξ_0^* values, the process is controlled by both diffusion and reaction rate.

CONCLUSIONS

A mathematical model has been developed for the process of solid state polycondensation of PET in the range of operating and process variables

normally encountered in industrial practice. The deficiencies and errors in the earlier models have been eliminated in this model. The model distinguishes different regimes of operation, and provides quantitative criteria for differentiating these. The model is validated on the basis of the experimental data reported in the literature. Apart from bringing out the importance of particle shape, size, temperature, vacuum, etc., the model also provides, for the first time, quantitative means of ascertaining the importance of gas side resistance. Some hitherto unexplained phenomena, such as influence of carrier gas on the rate of polycondensation, have also been explained. Although the model specifically discusses PET polycondensation, it can also be used for analyzing solid state polycondensation of poly(butylene terephthalate), nylon 6, nylon 66, etc.

The development of the present model also raises interesting issues. The model can be improved by including crystallization kinetics and its attendant influence on the rate of diffusion of EG. Our present understanding of kinetics of multitude of main and side reactions in solid state is rather inadequate and that is another area of investigation and incorporation in the present model. The influence of local nonisothermality due to the crystallization is likely to be negligible and further refinements need not be sought in that direction. However, the influence of the dissolution of the carrier gas on modifying the desorption process of EG and the crystallization kinetics are extremely interesting. The present model can be improved substantially as our understanding in these areas improves.

APPENDIX: NOMENCLATURE

D	ethylene glycol diffusivity (cm^2/s)
e	hydroxyl end group concentration $\left(\text{mol} \middle/ \hexagon \right)$
f	function as defined in eqs. (22), (42), and (51)
g	concentration of ethylene glycol $\left(\text{mol} \middle/ \hexagon \right)$
k	polycondensation rate constant $\left[\left(\text{mol} \middle/ \hexagon \right)^{-1} s^{-1} \right]$
k_g	gas-side mass transfer coefficient (cm/s)
K	equilibrium constant
P_n	degree of polymerization
P_{n0}	initial degree of polymerization
$\overline{P}_n$	average degree of polymerization
t	reaction time (s)
T	$= \int D \, dt$
x	distance in the direction of diffusion (cm)
x_0	particle size (cm) (in the case of cube particle size is $2x_0$)
x_1, x_2, x_3	distance in x, y, and z directions
z	concentration of diester groups $\left(\text{mol} \middle/ \hexagon \right)$

Greek symbols

η $\quad= P_{n0}^2/P_n^2$

Θ $\quad$ as defined in eq. (29)

Θ^* $\quad$ as defined in eq. (45)

λ $\quad$ geometry parameter

Φ $\quad= k_g x_0/D$

ξ $\quad= x/x_0$

ξ^* $\quad$ as defined in eq. (46)

Subscripts

0 $\quad$ initial values

s $\quad$ values at the surface of the particle

b $\quad$ bulk gas phase

References

1. K. Ravindranath and R. A. Mashelkar, *J. Appl. Polym. Sci.*, **27**, 2625 (1982).
2. K. Ravindranath and R. A. Mashelkar, *Polym. Eng. Sci.*, **22**, 628 (1982).
3. K. Ravindranath and R. A. Mashelkar, *Chem. Eng. Sci.*, **41**, 2197 (1986).
4. K. Ravindranath and R. A. Mashelkar, *Chem. Eng. Sci.*, **41**, 2969 (1986).
5. K. Tomita, *Polymer*, **14**, 50 (1973).
6. T. M. Chang, *Polym. Eng. Sci.*, **10**, 364 (1970).
7. E. Schaaf, H. Zimmermann, W. Dietzel, and P. Lohmann, *Acta. Polym.*, **32**, 250 (1981).
8. F. C. Chen, R. G. Griskey, and G. H. Beyer, *AIChE J.*, **15**, 680 (1969).
9. S. Chen and F. Chen, *J. Polym. Sci. Polym. Chem. Ed.*, **25**, 533 (1987).
10. S. A. Jabarin and E. A. Lofgren, *J. Appl. Polym. Sci.*, **32**, 5315 (1986).
11. K. Ravindranath and R. A. Mashelkar, *AIChE J.*, **30**, 415 (1984).
12. H. Yokoyama, J. Sano, T. Chijiiwa, and R. Kajiya, *J. Jpn. Petrol. Inst.*, **21**(4), 271 (1978).
13. R. M. Secor, *AIChE J.*, **15**, 861 (1969).
14. P. J. Hoftyzer, *Appl. Polym. Symp.*, **26**, 34 (1975).
15. J. S. Vrentas and J. L. Duda, *Encyclopedia of Polymer Science and Technology*, Vol. 5, Wiley, New York, 1986, p. 37.
16. B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, Wiley, New York, 1969.
17. P. L. T. Brian, *AIChE J.*, **7**, 367 (1961).
18. S. Chang, M. Sheu, and S. Chen, *J. Appl. Polym. Sci.*, **28**, 3289 (1983).
19. B. D. Whitehead, *Ind. Eng. Chem. Process Des. Dev.*, **16**, 341 (1977).
20. H. Lichen, *J. Macromol. Sci. Phys.*, **B1**(4), 801 (1967).
21. T. K. Sherwood, P. L. Figford, and C. R. Wilke, *Mass Transfer*, McGraw-Hill, New York, 1975.
22. R. P. Kambour and C. L. Gruner, *J. Polym. Sci. Polym. Phys. Ed.*, **16**, 703 (1978).
23. J. S. Chiou, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 2633 (1985).
24. J. S. Vrentas, J. L. Duda, and H. C. Ling, *J. Appl. Polym. Sci.*, **30**, 4499 (1985).
25. K. Ravindranath and R. A. Mashelkar, *Chem. Eng. Sci.*, **47**, 429 (1988).