Modelling of Poly(ethylene Terephthalate) Reactors. III. A Semibatch Prepolymerization Process*

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Synopsis

A mathematical modelling of a semibatch prepolymerization process has been undertaken. Prepolymerization conducted at constant temperature and pressure and with a predetermined variation in temperature and pressure has been studied. Influence of DMT and TPA addition during prepolymerization has also been examined. The focus has been on investigation of the influence of processing and operational variables on productivity and side product formation, which controls product quality. The results of this investigation (which are applicable only up to DP $\simeq$ to 30) are borne out by the limited experimental data available in the literature. Important pragmatic implications of the results of the work in terms of design and operation of prepolymerization reactors have been emphasized.

INTRODUCTION

With an objective to analyze and model the entire process of production of poly(ethylene terephthalate) (PET), we have launched a major modelling program. The first two contributions in this series[1,2] provided models of a semibatch ester interchange reactor and a continuous transesterification process. The objective was to examine the influence of process and operational variables on productivity and byproduct formation. As a continuation of this effort, we will analyze the problem of modelling a semibatch prepolymerization reactor. Again, the influence of pertinent process and operational variables will be examined in depth, and the results will be analyzed from the point of view of offering a mechanistic explanation of the trends observed as well as from the potential industrial significance of these results. Certain ideas, which are not commonly practiced industrially, will also be examined to see as to whether there is a possibility of an improvement in productivity and reduction in side products and therefore improvement in product quality on implementation of these ideas.

Although some experimental laboratory investigations have appeared on the determination of the details of the kinetics of the main and side reactions which occur during polymerization of bis(2-hydroxyethyl) terephthalate (BHET) to PET, there are practically no previous studies in the literature which have attempted to model a prepolymerization reactor, with the possible exception of Ault and Mellichamp.[3] However, these authors have not modelled the process in the range of industrial interest. The emphasis in their work was more on investigating parametric sensitivity. Further, the important problem of side product formation, which is so vital for product quality was not examined at all.

It needs to be emphasized here that due to the complexities of diffusional transport effects which appear at higher degree of polymerization (DP), the present work is confined to examining the implications of an ideal kinetic model in the lower range of DP. For reasons to be discussed later, the results of this investigation may be considered to be valid up to a DP of 30 only.

SEMIBATCH PREPOLYMERIZATION PROCESS

A process flow diagram for semibatch prepolymerization is shown in Figure 1. The prepolymer coming from ester interchange reactor contains mainly BHET and its linear oligomers, and it is passed on to the prepolymerization reactor. In industrial practice, the temperature of the semibatch reactor is increased from approximately 240°C to approximately 290°C, and at the same time vacuum is applied slowly. It is always advantageous to work under low operating pressures from the beginning of the reaction to suppress the reverse reactions. If high vacuum were to be applied right in the beginning of the reaction, then a part of low molecular weight polymer species will go along with ethylene glycol (EG) vapor and it may block the vacuum line. Due to this operational constraint, an optimal pressure cycle is necessary for smooth running of the plant. The vapors coming out of the reactor contain mainly EG and small quantities of diethylene glycol (DEG), water, and ketones.

It is an industrial practice to carry out the entire polymerization in a single reactor. In the final stages of polymerization (DP > 50), extremely viscous mass has to be handled; therefore, an agitation system which is suitable for this range is usually employed throughout. Helical screw or ribbon agitators are most commonly used. The details of agitation system will not be considered to be significant in this part of prepolymerization where the DP rises from about 1 to 30. However, for higher DP values it could be of considerable importance. The detailed considerations in the region of high DP have been discussed critically by Ravindranath and Mashelkar.[4] Before developing an ideal kinetic model, it is desirable to discuss carefully the key assumption concerning the role of diffusional limitations, which have been neglected in the prepolymerization process analysis presented here.
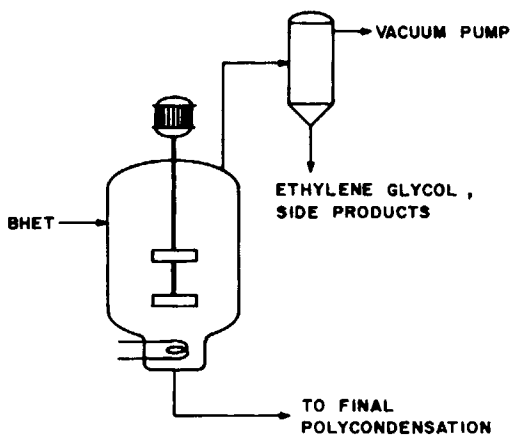

Fig. 1. A semibatch prepolymerization process.

As will be seen later, the main reaction involves an equilibrium polycondensation which is accompanied by the rate of removal of volatile ethylene glycol from the molten mass. Some authors (Hoftyzer and Vankrevelen,[5] Hoftyzer,[6] and Secor[7]) have attempted to model the later stages of polycondensation (especially over DP of 50) and showed that diffusional limitations do play an important role in this region. Indeed, considerations for design of a polycondensation reactor are completely different in this region. It is conceivable that, during prepolymerization when DP is built up from a value of about 1 to 30, such diffusional limitations will not play an important role. An approximate idea of the possible role of diffusional limitations can be obtained if a completely comprehensive model which includes diffusional effects were to be built up for the entire process of polymerization from DP of about 1 to over 100. However, this is an extremely formidable task, and therefore we have preferred to model the initial stages of polycondensation separately. However, the relative effect of diffusional limitations can be seen at least qualitatively from the following discussion.

Whenever processes where a chemical reaction is accompanied by diffusion effects occur, the role of diffusional factors becomes unimportant when the following inequality is satisfied:

rate of chemical reaction $\ll$ rate of mass transfer

Expressing it in terms of kinetic constants and mass transfer coefficients, the inequality could be expressed as
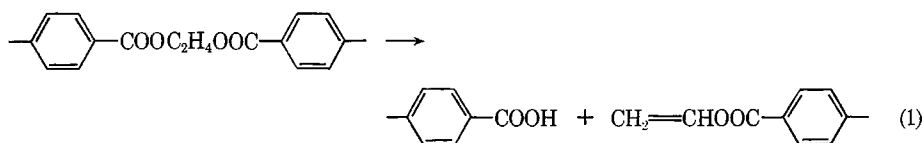
$$k_1' \ll k_L \mathbf{a}$$

Here k_1' can be considered as an equivalent polycondensation rate constant.[5] k_L is the mass transfer coefficient, and $\mathbf{a}$ is the interfacial area per unit volume. $k_L \mathbf{a}$ depends strongly on hydrodynamics, and, for standard configuration, empirical correlations are available for calculating the values of $k_L \mathbf{a}$ in the case of low surface area-high speed agitation (see, for instance, Mashelkar[8]). In view of the fact that rather unconventional large-surface-area, low-speed agitation systems such as helical ribbon and helical screws are commonly used in semibatch prepolymerizations, it is not possible to evaluate the approximate order of magnitude of $k_L \mathbf{a}$. However, reported observations on prepolymerization in the literature[9] indicate that during the start of prepolymerization the polymerizing mass resembles a boiling liquid. Therefore, a reasonably high value of $k_L \mathbf{a}$ may be expected, at least in the initial stages of prepolymerization. Approximate calculations indicate that $k_L \mathbf{a}$ would be of the order of $10^{-2}\,\mathrm{s}^{-1}$. k_1' values, on the other hand, would be of the order of $10^{-3}\,\mathrm{s}^{-1}$. It thus appears that, at least in the initial stages of polycondensation (say up to DP of 30), the influence of diffusional factors may not be significant. The results of this work should therefore be considered to be valid only up to DP of 30, even though the results are presented up to DP of 50.
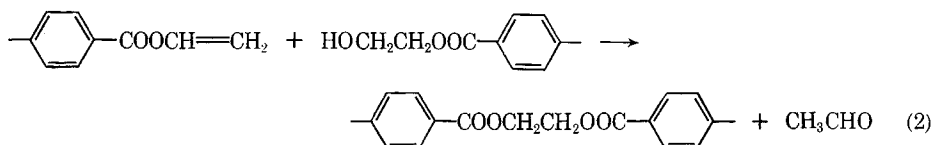
REACTION SCHEME

Various reactions occur in the prepolymerization process. These consist of the main polycondensation reaction and also side reactions forming side products such as acetaldehyde, DEG, and water. Ravindranath and Mashelkar[1,2] have

discussed in detail the above reactions while modelling the semi-batch ester interchange reactor and the continuous transesterification process. Apart from these reactions, one needs to include ester interchange and transesterification reactions in the modelling of prepolymerization stage. This facilitates a study of the effect of unreacted methyl end groups left in the ester interchange reactor on the prepolymerization process. In addition to the above side reactions, the other important side reactions in the prepolymerization process are:
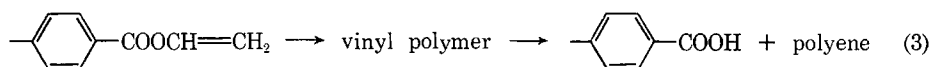
1. Degradation of diester group:

$$\text{—}\langle\bigcirc\rangle\text{—COOC}_2\text{H}_4\text{OOC—}\langle\bigcirc\rangle\text{—} \quad \longrightarrow$$

$$\text{—}\langle\bigcirc\rangle\text{—COOH} + \text{CH}_2\text{=CHOOC—}\langle\bigcirc\rangle\text{—} \quad (1)$$

2. Polycondensation reaction of vinyl end groups:

$$\text{—}\langle\bigcirc\rangle\text{—COOCH=CH}_2 + \text{HOCH}_2\text{CH}_2\text{OOC—}\langle\bigcirc\rangle\text{—} \quad \longrightarrow$$

$$\text{—}\langle\bigcirc\rangle\text{—COOCH}_2\text{CH}_2\text{OOC—}\langle\bigcirc\rangle\text{—} + \text{CH}_3\text{CHO} \quad (2)$$

As long as free hydroxyl end groups exist in the polymer, broken polymer links will be formed. When most of the hydroxyl end groups have been consumed, DP will begin to fall. The vinyl end groups formed in (1) will react further to give a complex mixture:

$$\text{—}\langle\bigcirc\rangle\text{—COOCH=CH}_2 \longrightarrow \text{vinyl polymer} \longrightarrow \text{—}\langle\bigcirc\rangle\text{—COOH} + \text{polyene} \quad (3)$$

Cyclic oligomers (mainly the trimer) are also formed during polycondensation reaction. The mechanism for the formation of cyclic oligomers in the melt is probably the intramolecular reaction by the action of hydroxyl end groups to the ester linkages.[10] The mechanism is shown below:

$$(4)$$
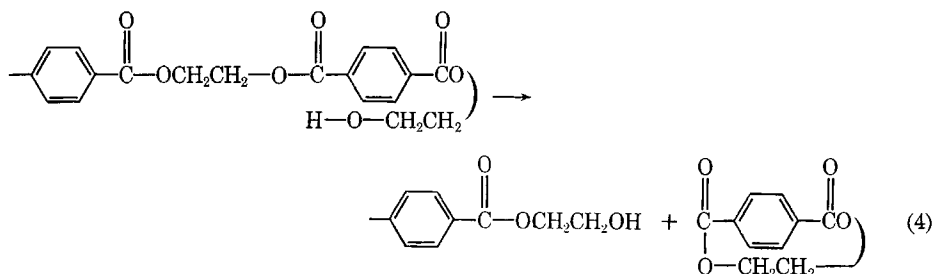
The mechanistic details of formation of such cyclic products are becoming clearer only in recent years, and, therefore, there are no comprehensive kinetic studies published so far. We shall, therefore, not consider reactions (3) and (4) in this model.

A summary of various reactions considered in the present model is given below.

The symbols used are explained in Table I. Reaction schemes presented here can also be used to study the effect of terephthalic acid (TPA) addition to the reaction mass.
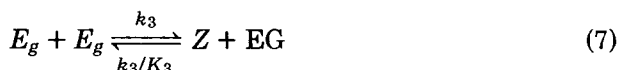
Ester interchange reaction:

$$E_m + EG \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} E_g + M \qquad (5)$$

Transesterification reaction:

$$E_m + E_g \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} Z + M \qquad (6)$$

Polycondensation reaction:

$$E_g + E_g \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} Z + EG \qquad (7)$$

Side reactions forming acetaldehyde, DEG, and acid end groups:

$$E_g \overset{k_4}{\rightarrow} E_c + A \qquad (8)$$

$$E_g + EG \overset{k_5}{\rightarrow} E_c + DEG \qquad (9)$$

$$E_g + E_g \overset{k_6}{\rightarrow} E_c + E_{DEG} \qquad (10)$$

Esterification reactions:

$$E_c + EG \underset{k_7/K_4}{\overset{k_7}{\rightleftharpoons}} E_g + W \qquad (11)$$

$$E_c + E_g \underset{k_8/K_5}{\overset{k_8}{\rightleftharpoons}} Z + W \qquad (12)$$

Degradation reaction of diester groups:

$$Z \overset{k_9}{\rightarrow} E_c + E_v \qquad (13)$$

TABLE I
Explanation of Symbols

E_m	$\text{\textasciitilde}C_6H_4-COOCH_3$	Methyl ester end group
E_g	$\text{\textasciitilde}C_6H_4-COOC_2H_4OH$	Hydroxyethyl ester end group
Z	$\text{\textasciitilde}C_6H_4-COOC_2H_4OOC-C_6H_4\text{\textasciitilde}$	Diester group
E_c	$\text{\textasciitilde}C_6H_4-COOH$	Acid end group
E_{DEG}	$\text{\textasciitilde}C_6H_4-COOC_2H_4OC_2H_4OH$	DEG ester end group
E_v	$\text{\textasciitilde}C_6H_4-COOCH=CH_2$	Vinyl ester end group
EG	HOC_2H_4OH	Ethylene/glycol
M	CH_3OH	Methanol
W	H_2O	Water
DEG	$HOC_2H_4OC_2H_4OH$	Diethylene glycol
A	CH_3CHO	Acetaldehyde
$\text{\textasciitilde}$		Polymer chain
⬡	$-OC-$⬡$-COOCH_2CH_2O-$	Repeating unit

TABLE II
Kinetic Parameters Used in the Present Work

Reaction	Ester inter-change eq. (5)	Trans-esteri-fication eq. (6)	Poly-conden-sation eq. (7)	Acetal-dehyde formation eq. (8)	DEG formation eqs. (9), (10)	Esteri-fication reaction eq. (11)	Esteri-fication reaction eq. (12)	Diester group degradation eq. (13)
Activation energy (kcal/mol)	15.0	15.0	18.5	29.8	29.8	17.6	17.6	37.8
Frequency factor (L/mol·min)	4.0×10^4	2.0×10^4	6.8×10^5	4.16×10^7 [a]	4.16×10^7	1.04×10^6	1.04×10^6	3.6×10^{9a}
Equilibrium constant	0.3	0.15	0.5	—	—	2.5	1.25	—

[a] Units are min^{-1}.

Polycondensation of vinyl end groups:

$$E_g + E_v \xrightarrow{k_3} Z + A \tag{14}$$

MATHEMATICAL MODEL FOR A SEMIBATCH PREPOLYMERIZATION PROCESS

The reaction mixture of prepolymerization process contains mainly EG, DEG, water, and linear polymer molecules having methyl, hydroxyl, vinyl, and acid end groups. Assuming that the reactivity of functional groups does not depend on the polymer chain length, material balance equations for an ideal semibatch reactor can be written as follows:

$$\frac{1}{V}\frac{de_m}{dt} = -R_1 - R_2 \tag{15}$$

$$\frac{1}{V}\frac{de_g}{dt} = R_1 - R_2 - 2R_3 - R_4 - R_5 - R_6 + R_7 - R_8 - R_{10} \tag{16}$$

$$\frac{1}{V}\frac{dg}{dt} = -R_1 + R_3 - R_7 - Q_G(t) \tag{17}$$

$$\frac{1}{V}\frac{dz}{dt} = R_2 + R_3 + R_8 - R_9 + R_{10} \tag{18}$$

$$\frac{1}{V}\frac{de_c}{dt} = R_4 + R_5 + R_6 - R_7 - R_8 + R_9 \tag{19}$$

$$\frac{1}{V}\frac{dw}{dt} = R_7 + R_8 - Q_W(t) \tag{20}$$

$$\frac{1}{V}\frac{dg^*}{dt} = R_5 + R_6 \tag{21}$$

$$\frac{1}{V}\frac{de_v}{dt} = R_9 - R_{10} \tag{22}$$

$$\frac{1}{V}\frac{dm}{dt} = R_1 + R_2 \tag{23}$$

$$\frac{1}{V}\frac{da}{dt} = R_4 + R_{10} \tag{24}$$

Here $e_m, e_g, z, e_c, w, e_v, m$, and a represent the number of moles of the respective species shown in Table I (with capital letters). g and g^* are the number of moles of EG and DEG, respectively. V is the volume of the reaction mixture. $Q_G(t)$ and $Q_W(t)$ represent EG and water flow rates at any instant of time t. R_1–R_{10} represent the reaction rates. Assuming that order and molecularity of the reactions are the same, reaction rates for reactions (5)–(14) can be written as follows:

$$R_1 = k_1(2e_m g - e_g m/K_1)/V^2 \tag{25}$$

$$R_2 = k_2(e_m e_g - 2zm/K_2)/V^2 \tag{26}$$

$$R_3 = k_3(e_g{}^2 - 4zg/K_3)/V^2 \tag{27}$$

$$R_4 = k_4 e_g/V \tag{28}$$

$$R_5 = 2k_5 e_g g / V^2 \tag{29}$$

$$R_6 = k_6 e_g{}^2 / V^2 \tag{30}$$

$$R_7 = k_7 (2 e_c g - e_g w / K_4) / V^2 \tag{31}$$

$$R_8 = k_8 (e_c e_g - 2 z w / K_5) / V^2 \tag{32}$$

$$R_9 = k_9 z / V \tag{33}$$

$$R_{10} = k_3 e_v e_g / V^2 \tag{34}$$

Note that reactions (5)–(7), (9)–(12), and (14) are second order and (8) and (13) are first order. k_1–k_9 are functions of concentration and the type of the catalyst used. The terminal vinyl end groups behave like hydroxyl end groups, so that the rate constant for (7) and (14) are assumed to be equal.[11] The vapor pressure of acetaldehyde and methanol at prepolymerization temperature is very high, and, hence, while writing material balance equations (23) and (24), it is assumed that acetaldehyde and methanol leave the reaction mixture as soon as it is formed. Therefore, the concentration of methanol in the reaction mixture will be zero. In the present work also, the total content of DEG is calculated on the basis of eq. (21), and therefore material balance equations for free DEG and incorporated DEG in the polymer chain have not been written separately. Since the reactivity of DEG and E_{DEG} is assumed to be the same as that of EG and E_g, the rate of disappearance of EG by reaction (9) is not included in eq. (17), and the disappearance of E_g by reaction (10) is considered only once in eq. (16).

Equations (15)–(24) were suitably nondimensionalized. All concentrations were normalized by using the initial number of moles of repeating units. Since the nondimensionalized governing equations were too complex to yield analytical solutions, they were solved numerically by using the modified fourth-order Runge–Kutta and Gill method. For solving eqs. (15)–(24), concentration of the volatile species in the reaction mixture is calculated by a flash distillation process, assuming a quasisteady state approximation. The material balance equations for each volatile species concentration for a flash tank is written separately. Assuming that Raoult's law is valid for the volatile species, the concentration of volatile species in the reaction mass and its flow rate in the vapor phase is calculated. Here acetaldehyde and methanol are considered as noncondensables and polymer molecules as nonvolatiles. If the vapor liquid equilibria are nonideal, then the concentration of volatile species in the liquid will be less as compared to that predicted by an ideal system. In view of this, the present analysis may be considered to give a conservative estimate of the prepolymerization process.

Flash calculations are done only when the sum of the partial pressures developed by all the volatile species was greater than the reactor pressure. The details of the flash distillation process calculation procedure have been already reported by Ravindranath and Mashelkar.[1]

It may be noted that the effect of increase in the catalyst concentration because of decrease in the volume of the reaction mixture is also considered in the numerical computation procedure. Assuming that the density of the reaction mixture is not changing appreciably, the volume of the reaction mixture is given by

$$\frac{V}{V_0} = 1 - \frac{\text{amount of volatiles removed}}{\text{initial mass}} \tag{35}$$

Here V_0 is the initial volume of the reaction mixture. The objective now is to solve the governing equations to obtain the following information:

1. DP as a function of time.

2. The amount of side products such as acid end groups, vinyl end groups, DEG, acetaldehyde, and water formed as a function of time. Concentrations of side products are expressed in mol/⬡ .

In order to obtain the above information, we need the following information:

1. Kinetic parameters k_1–k_9 as functions of catalyst type and concentration.

2. Equilibrium constants, viz., K_1–K_5.

3. Vapor pressure data of EG and water.

Kinetic and Equilibrium Parameter Values

The values of ester interchange rate constant (k_1) and transesterification rate constant (k_2) are already reported in our previous investigations.[1] It may be noted here that common transesterification catalysts (such as zinc or manganese acetate) are poisoned by very small amounts of acid end groups.[12] In fact, acid-end-group formation is significant at the end of the transesterification process and in the beginning of the polycondensation reaction. Therefore, k_1 and k_2 values in the prepolymerization process will be somewhat less compared to those in the transesterification process.

Rate constants for reactions (7)–(14) are deduced from the available data in the literature[11] for Sb_2O_3 catalyst. Here it is assumed that the rate constants k_3, k_7, and k_8 are linearly proportional to the catalyst concentration. It may be remarked here that there is some uncertainty in the literature about the polycondensation rate constant k_3. We shall discuss this point briefly.

Stevenson[13] pointed out that the observation of extremely high rates in thin layers compared to rates exhibited in the presence of reverse reaction may not be due to complete suppression of the reverse reaction, but it may be due to volatile component (EG) inactivating the catalyst. Stevenson[13] observed that improved efficiency of removal of the volatile component by decreasing melt thickness improves the activity of the catalyst and thus increases the observed rate.

Using the model system glycoldibenzoate—EG—glycol—monobenzoate, Hovenkamp[12] showed that hydroxyl groups deactivate the Sb_2O_3 catalyst and the activity increases, as the hydroxyl group concentration decreases. In the present analysis also, we have studied the effect of increasing catalytic activity of Sb_2O_3 as hydroxyl end group concentration decreases. The following relationship is deduced from the Hovenkamp's[12] experimental analysis:

$$k_3 = k_{3,0} \frac{1 + 0.9132\,DP}{1 + 0.9132\,DP_0} \tag{36}$$

where $k_{3,0}$ is the polycondensation rate constant for initial degree of polymerization (DP_0). It can be seen that as per this kinetic model, the polycondensation rate constant increases by 10 times when DP changes from 1.5 to 25.

The equilibrium constants, viz., K_1–K_5 reported in our previous work[1,2] will be used in the present work also.
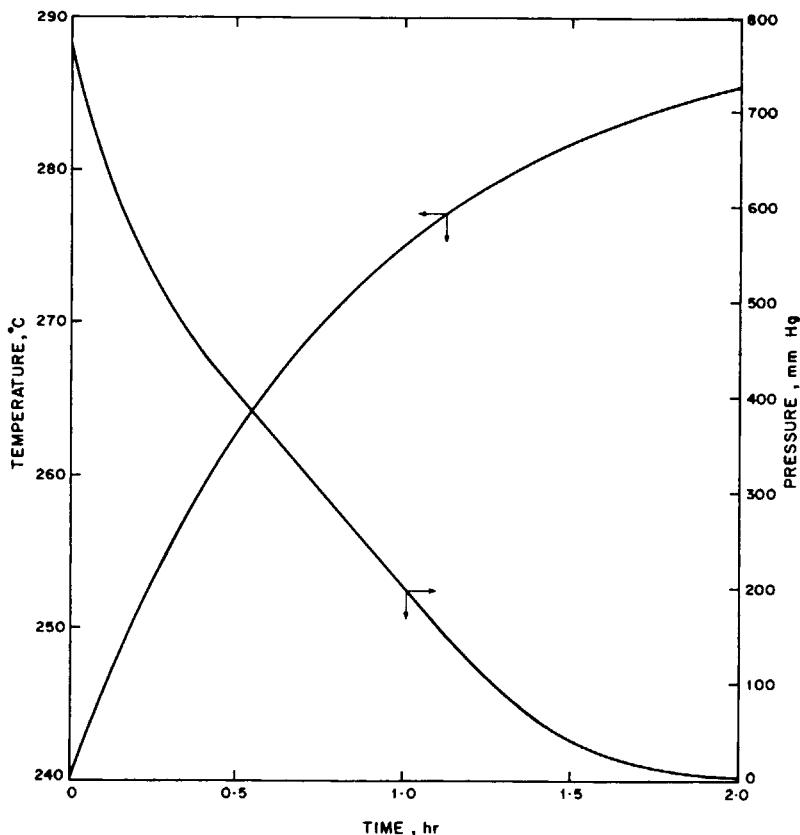
Fig. 2. Temperature and pressure program.

Vapor Pressure Data

The vapor pressure data for water were obtained from Perry[14] and correlated by using an equation of the following type for the temperature range of 240–290°C:

$$\log P^*_W \ (\text{mm}) = 8.064103 - 1757.853/(239.726 + T) \tag{37}$$

The following equation[15] was used for calculating the vapor pressure of EG:

$$\log P^*_G \ (\text{mm}) = 21.61 - 3729/(273 + T) - 4.042 \log (T + 273) \tag{38}$$

Operating and Process Variables Used in This Work

In view of the large number of process and operational variables, numerical calculations were done only for a specific set of values of these variables, which pertained as closely as possible to the industrial practice. Note that, in order to assess clearly the influence of temperature and pressure, we have also performed calculations at constant values of these variables. A summary of the range of variables is given below:

initial degree of polymerization = 1.5
catalyst concentration (Sb$_2$O$_3$) = 0.025, 0.05 (wt %)
temperature = 240, 260, 280 (°C)

$$\text{pressure} = 20, 50, 200 \text{ (mm)}$$
$$\text{reaction time} = 2 \text{ (h)}$$

The feed for prepolymerization process is assumed to have the following species concentrations (nondimensionalized with respect to the number of moles of repeating units):

$$\text{hydroxyl end groups} = 1.332$$
$$\text{diester groups} = 0.334$$
$$\text{EG concentration} = 0.302$$

Further, it is assumed that the feed is in physical equilibrium with vapor at atmospheric pressure.

As indicated earlier, the industrial practice is to vary the temperature and pressure with time in a predetermined manner. Although a number of such programs are possible, we chose the following program which is quite representative of common industrial practice:

$$T = 290 - 50e^{-1.2\theta} \tag{39}$$

$$P_T = 760(e^{-1.8587\theta} + 1.776\theta^2 - 1.2527\theta^3) \tag{40}$$

Here T is the temperature (°C), P_T is the reactor pressure (mm Hg), and θ is time
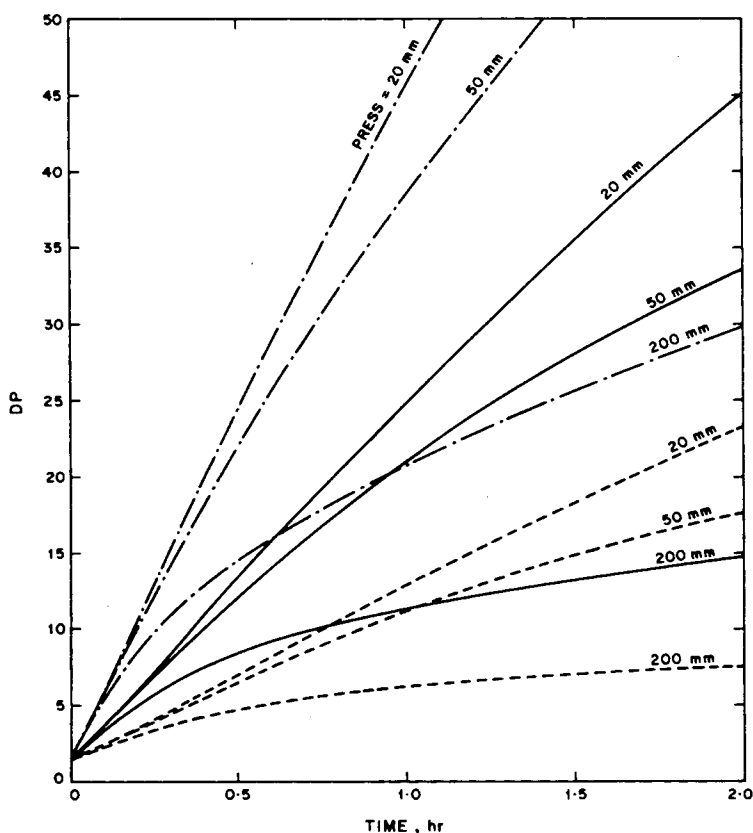
Fig. 3. Effect of temperature and pressure on DP: (- - -) 240°C; (——) 260°C; (—·—·) 280°C.
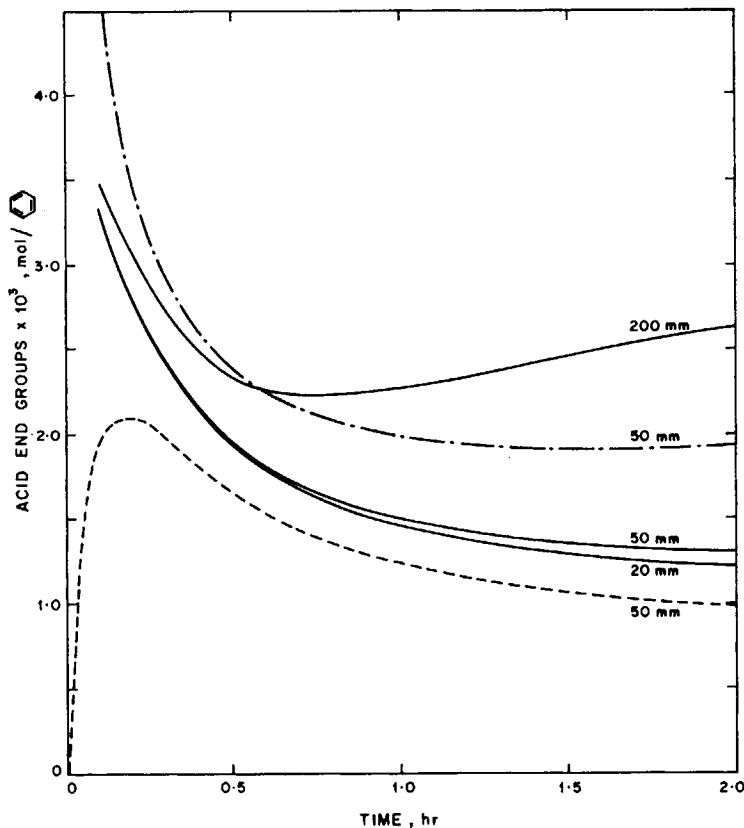
Fig. 4. Effect of temperature and pressure on acid end-group formation:　(- - -) 240°C; (——) 260°C; (—·——·) 280°C.

(h).　The manner in which temperature and pressure actually change with time as per the above program can be seen in Figure 2.　Thus the temperature is increased from about 240°C to about 285°C in 2 h, whereas the pressure is reduced from 760 mm Hg to 1 mm Hg in the same time.

RESULTS AND DISCUSSION

The mathematical model developed in the foregoing was used to predict the performance of semibatch prepolymerization reactor for various operating and process variables.　It may be noted later that the predictions are in agreement with the experimental observation of various investigators[16,17] and also some results available from industrial practice.　Results are presented for the following four cases.

1.　Constant temperature and pressure operation.

2.　Operation with predetermined temperature and pressure programs.

3.　Influence of dimethyl terephthalate (DMT) and TPA addition under conditions specified in 2 above.

4.　Sensitivity of the computed numerical results to the assumed degradation and esterification rate constants for conditions specified in 2 above.

We shall now analyze each of these cases systematically.

Constant Temperature and Pressure

The effect of temperature and pressure on DP is shown in Figure 3. The rate of rise of DP increases as the temperature is increased. It is interesting to observe that at high pressures (for instance, 200 mm) DP reaches a plateau, and, unless the pressure is decreased, the DP rise is not appreciable. This is obviously due to the reverse reaction [see eq. (7)], which is favored at high EG concentration in the melt builtup at higher pressures. For constant temperature of 280°C and pressure of 200 mm, the initial rate of rise of DP is very high, but in the end the rate reduces.

Figure 4 shows the effect of temperature and pressure on acid-end-group formation rate. Initially, the rise in acid-end-group concentration is very rapid. Because of high initial concentration of hydroxyl end groups [see eqs. (8), (9), and (10)], the temperature has a significant effect on the rate of formation of acid end groups in the beginning. Subsequently, the acid end groups are consumed by the esterification reactions. After a certain time, the rate of generation is equal to the rate of consumption, and there is no further decrease in the acid end
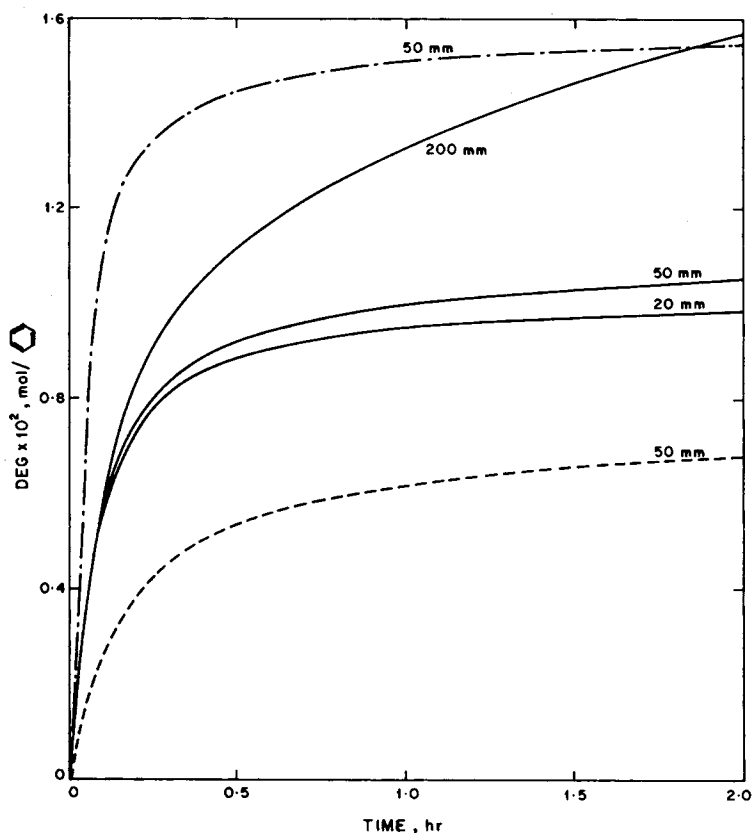

Fig. 5. Effect of temperature and pressure on DEG formation: (- - -) 240°C; (——) 260°C; (—·—·—·) 280°C.
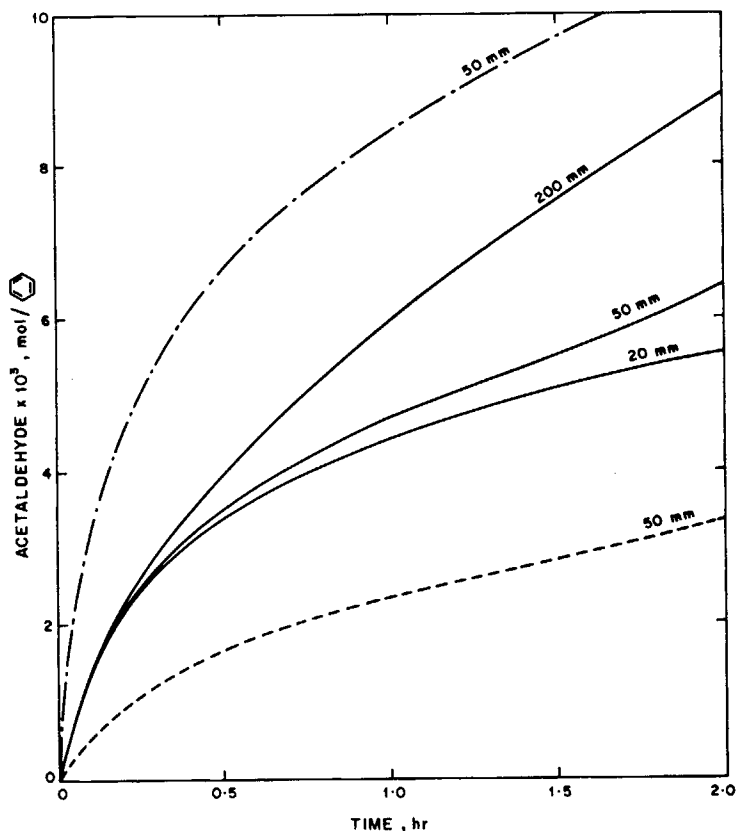
Fig. 6. Effect of temperature and pressure on acetaldehyde formation: (- - -) 240°C; (——) 260°C; (—·—·) 280°C.

group concentration.   It is conceivable that at longer times, the acid end groups again will increase, because the concentration of hydroxyl end groups is very low and hence the acid end group consumption rate will decrease compared to the formation rate.

The findings in this work are substantiated by the work of Cefelin and Malek,[16] who studied polycondensation of BHET in an inert solvent such as 1-methyl naphthalene.   In their experimental observations, it was found that acid-end-group concentration increased very fast initially because of hydroxyl-end-group degradation and then the acid end groups decreased rapidly because of the es-terification reactions.   But in the later stages again acid end groups increased because of the degradation of polymer repeating units.   Obviously, there is no quantitative comparison possible, because the process being modelled here is a melt polycondensation.   The qualitative similarity in the trends, however, is decidedly significant.

Figure 4 also shows the effect of pressure on acid-end-group formation.   For high pressures the acid-end-group formation rate is high compared to that at low pressures.   The concentration of acid end groups formed is practically the same for 20 mm and 50 mm pressures up to about 45 min, but, in the end, acid-end-group concentration is smaller for 20 mm pressure compared to that at a
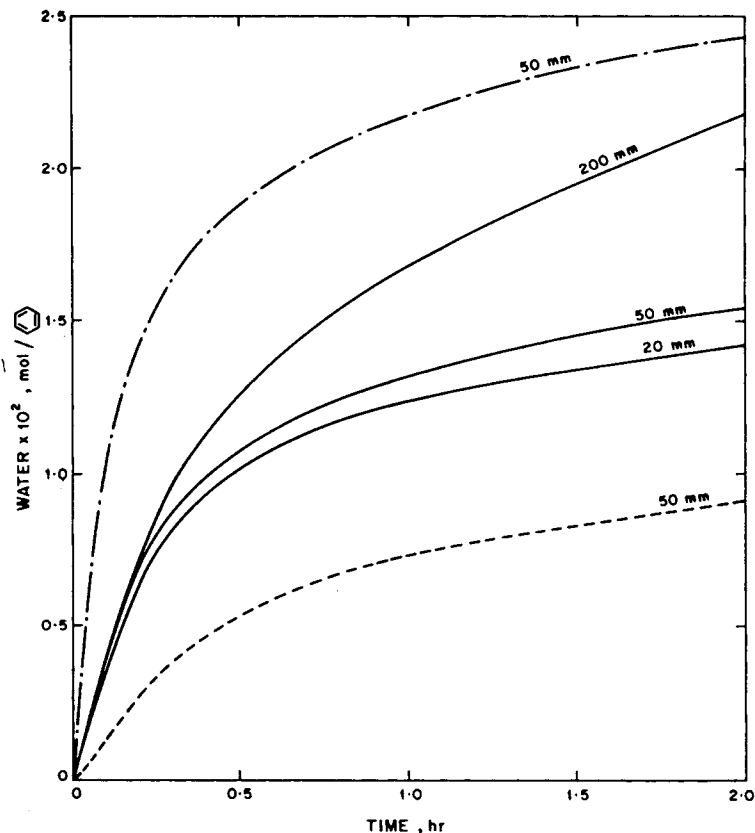
Fig. 7. Effect of temperature and pressure on water formation: (- - -) 240°C; (———) 260°C; (—·—·) 280°C.

pressure of 50 mm. This implies that pressure has a significant effect especially in the latter stages of the reaction. Unless the pressure is reduced, the acid-end-group concentration will increase continuously. By decreasing the pressure, hydroxyl end groups are consumed fast, and hence the degradation reaction rate will be less.

Figure 5 shows the manner in which DEG formation rate changes. As the temperature is increased, the rate of DEG formation increases, especially in the beginning. After certain time, the DEG formed reaches a plateau depending on the temperature of the reaction. DEG is formed mainly because of the presence of hydroxyl end groups. The rate of DEG formation at higher DP values is less because of low concentrations of hydroxyl end groups. Similarly the effect of pressure is shown in Figure 5. As the pressure is decreased, the DEG formation rate is also decreased.

The influence of temperature and pressure on the formation of acetaldehyde and water is shown in Figures 6 and 7. It is seen that, with increase in either temperature or pressure or both, concentration of these two side products increases continuously. Figure 8 shows the effect of temperature and pressure on vinyl-end-group formation. As the temperature is increased, the vinyl-end-group formation rate increases. It is interesting to note that vinyl-end-group
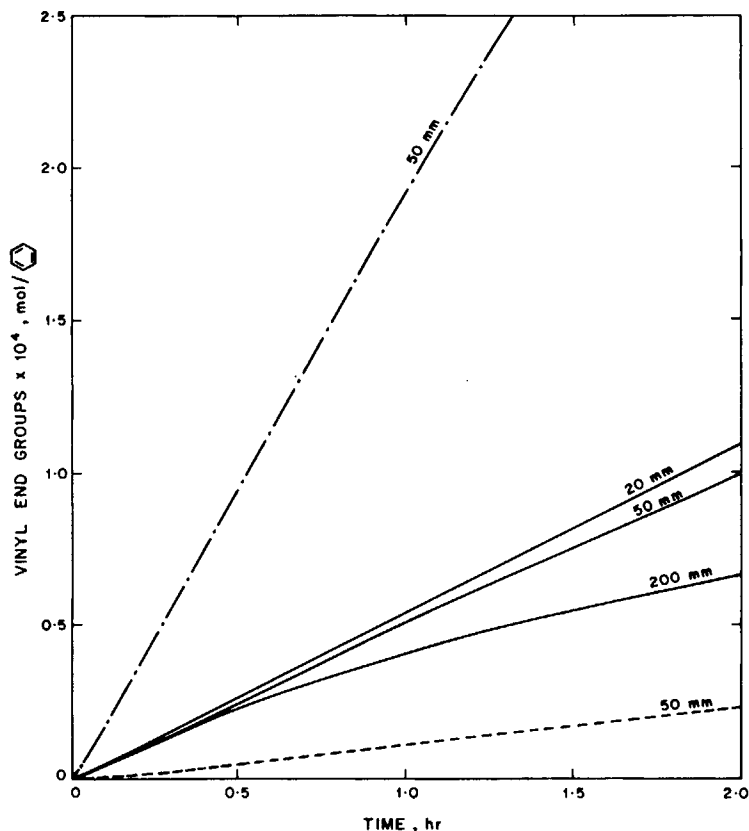
Fig. 8. Effect of temperature and pressure on vinyl end-group formation: (- - -) 240°C; (——) 260°C; (—·—·) 280°C.

concentration increases as the pressure is decreased. Vinyl end groups are formed because of degradation of diester groups. Therefore, as the DP increases, the vinyl-end-group formation rate also increases.

Figure 9 shows the effect of Sb_2O_3 catalyst concentration for 0.025 wt % and 0.05 wt %. The rate constants k_3–k_9 will be twice as much for 0.05% catalyst concentration as compared to that for 0.025%. The DP rises fast as the catalyst concentration is increased. It may be remarked here that in industrial practice it is not desirable to continuously increase Sb_2O_3 concentration, since the side products formation rate also increases and a grey color is imparted to the product.

Although it is not an industrial practice to run the prepolymerization process at either a constant temperature or a constant pressure, the data presented in Figures 3–9 give us valuable information concerning the role of these two variables. It may be generally concluded that, mainly from the point of view of minimizing byproducts, it is desirable to start the reaction at a low enough temperature and then increase the temperature slowly and reduce the pressure at the same time. It may be remarked here that higher temperatures do lead to higher rates of DP rise, but this is also accompanied by significant side product formation. High vacuum plays a key role in increasing the DP and therefore a combination of moderate temperature and high vacuum is always desirable.
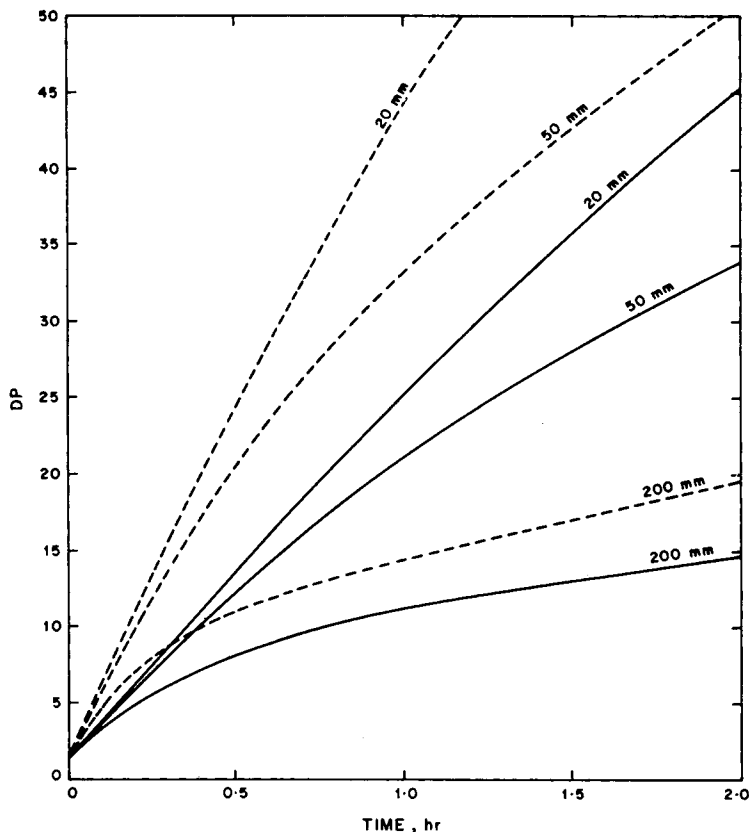
Fig. 9. Effect of catalyst concentration on DP: (- - -) 0.05%; (——) 0.025%; temp = 260°C.

Temperature and Pressure Program

Figure 10 shows the effect of temperature and pressure programs [specified in eqs. (39) and (40) and depicted in Fig. 2] on the rate of change of DP. Initially, the rise in DP is small but as the time proceeds, the rise in DP is fast. For example, DP reaches a value of 25.46 in 1.5 h for the temperature and pressure program used here, whereas DP reaches a value of 35.44 in 1.5 h for a constant temperature of 260°C and pressure of 20 mm. Figure 11 shows the acid-end-group and DEG formation rate, and Figure 12 shows the acetaldehyde formation rate for the temperature and pressure program. The trends are similar to those observed in the constant temperature and pressure cases examined in the foregoing.

Addition of DMT and TPA

The effect of DMT addition during the start of the prepolymerization process on DP build up is shown in Figure 10. The main objective of studying the effect of DMT addition is to see as to whether unreacted DMT in the ester interchange reactor will have any effect on DP buildup and also on the side-product formation. It is observed that for 5–10 wt % DMT addition, the rate of rise in DP is small as compared to the process without addition of DMT. This can be readily
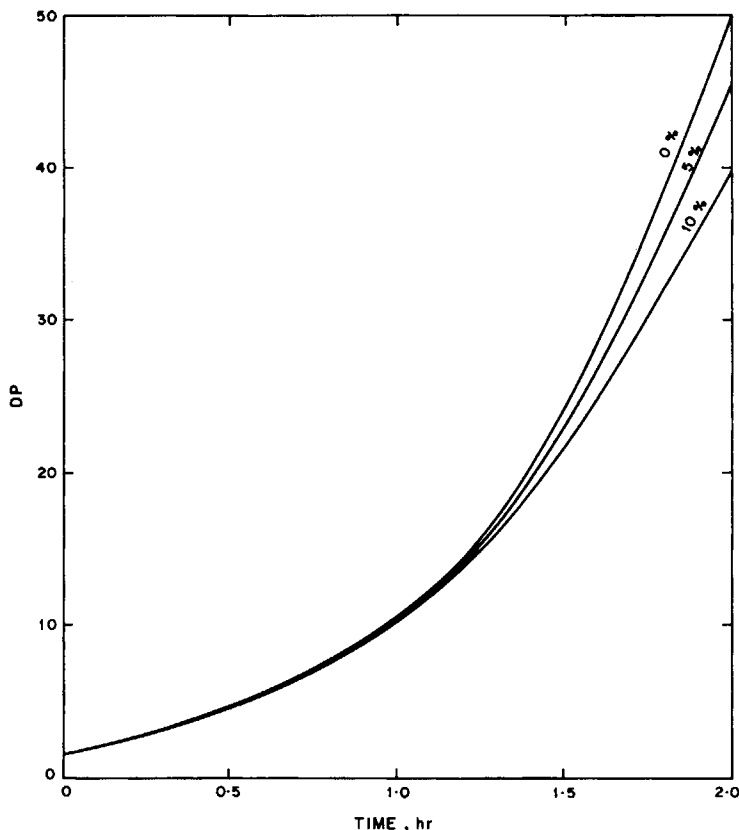
Fig. 10. Effect of DMT addition on DP. Temperature and pressure programs as per Figure 2.

explained. At low EG concentration, methyl end groups are consumed only by the transesterification reaction. If the polycondensation reaction is faster than transesterification reaction, hydroxyl end groups will be consumed fast by the polycondensation reaction before they have an opportunity of reacting with the hydroxyl end groups. Hence DP obtained with DMT addition will be less as long as the transesterification rate constant is less than the polycondensation rate constant. Ault and Mellichamp[3] also found that the unreacted methyl end groups in the polycondensation reaction can decrease the DP if the transesterification rate constant is less than the polycondensation rate constant. These authors, however, did not study the important aspect of side-product formation. We find interestingly enough that the side products formed are less when DMT is added. The effect of DMT addition on DEG and acid end groups formation rate is shown in Figure 12. It is seen that when DMT is added, the acid-end-group concentration decreases. This can be easily explained since, in the presence of DMT, hydroxyl end groups will react with methyl end groups, thereby reducing the effective hydroxyl-end-group concentration for degradation reaction. Similar behavior is observed with regard to DEG formation. The influence of DMT addition on acetaldehyde formation rate is shown in Figure 12. As DMT concentration increases, the acetaldehyde formation rate decreases.

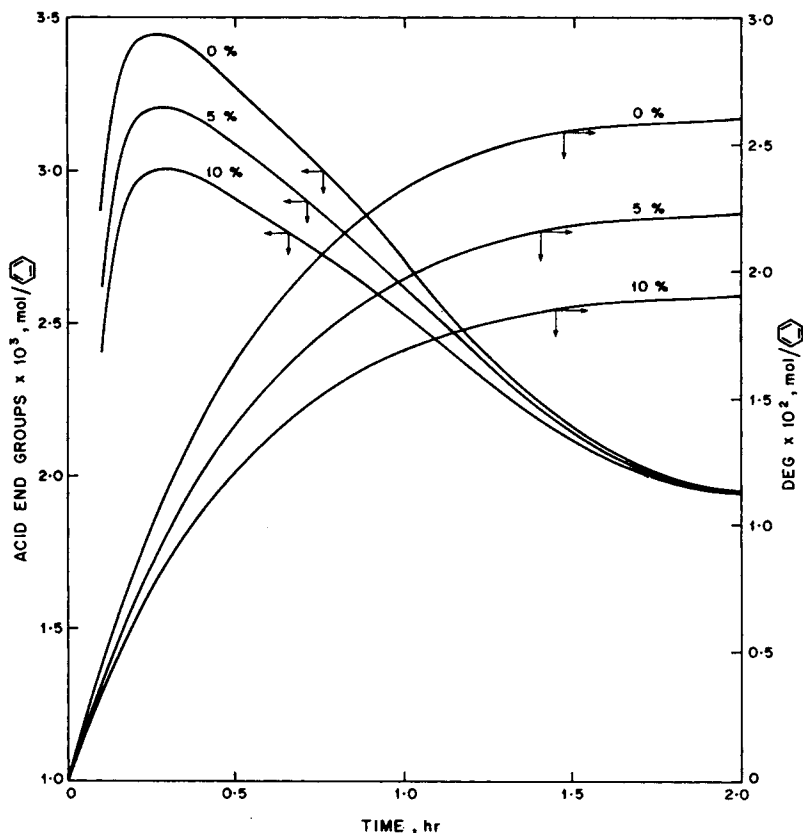The effect of TPA addition on DP is shown in Figure 13. In the beginning,

Fig. 11. Effect of DMT addition on acid end-group and DEG formation. Temperature and pressure programs as per Figure 2.

there is a slight increase in DP for higher concentrations of TPA and in the later stages of the reaction, DP decreases slightly as the initial concentration of TPA increases. This can be again explained as follows. In the beginning, acid-end-group concentration is very high, and, therefore, the esterification reaction is faster than the polycondensation reaction wherein hydroxyl end groups are consumed mainly by esterification reactions. After a reaction time of 2 h, DP value obtained for 10% TPA addition process is 49.06 compared to a value of 50 for the process without addition of TPA. If the concentration of TPA is too high, then, in the later stages, the acid-end-group concentration will be greater than the hydroxyl-end-group concentration. Hence DP will continuously decrease after a particular level of initial TPA concentration. The inherent assumption in the above analysis is that 10% TPA is completely soluble in the molten BHET. This is a fair assumption, as can be seen from the data presented by Baranova and Kremer.[18]

Figure 14 shows the effect of TPA addition on acid-end-group concentration profile. In the beginning, acid end groups are consumed very fast and reach a plateau. This is seen to be the case for all the cases considered here. The findings in this work are substantiated by the work of Cefelin and Malek,[16] who studied the effect of 2-hydroxyethyl hydrogen terephthalate addition on the
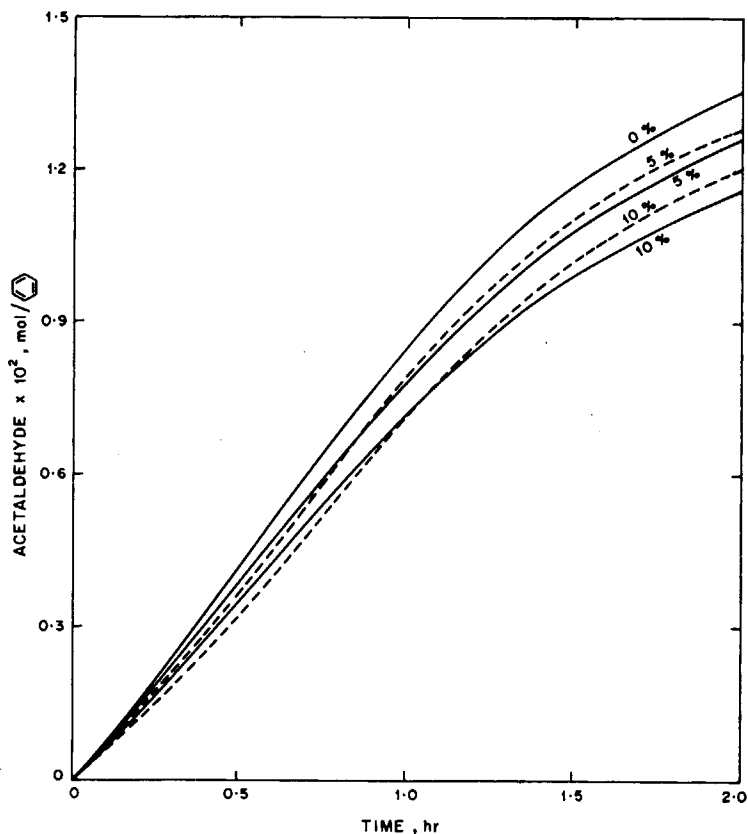
Fig. 12. Effect of DMT and TPA addition on acetaldehyde formation. Temperature and pressure programs as per Figure 2: (——) DMT; (- - -) TPA.

polycondensation of BHET. The trends obtained by these authors are qualitatively similar to the trends observed in this work. In fact, Cefelin and Malek[16] find that the acid-end-group concentration decreases very rapidly in the beginning of the reaction and reaches a plateau. Since hydroxyl end groups are consumed very fast in the beginning of the reaction, acetaldehyde and DEG formation rates decrease as the amount of TPA that is added increases. These trends are shown in Figures 12 and 14. The amount of side products formed for obtaining DP of 30 using different process and operating variables is shown in Table III. It is interesting to note that even for the temperature and pressure program considered here, the side products are high compared to the values for constant temperature of 280°C and pressure of 20 mm and time taken to reach DP of 30 is also high for the prescribed temperature and pressure program. Therefore, pressure plays an important role in increasing DP rather rapidly and at the same time reducing the side-production formation.

   The implications of DMT and TPA addition from a process angle are rather interesting and warrant a discussion. As can be seen, the addition of DMT helps in reducing the side products, but the rate of buildup of DP is also reduced. Additionally, the generation of methanol and its handling under vacuum could be a process constraint. It is seen that TPA addition is decidedly beneficial from
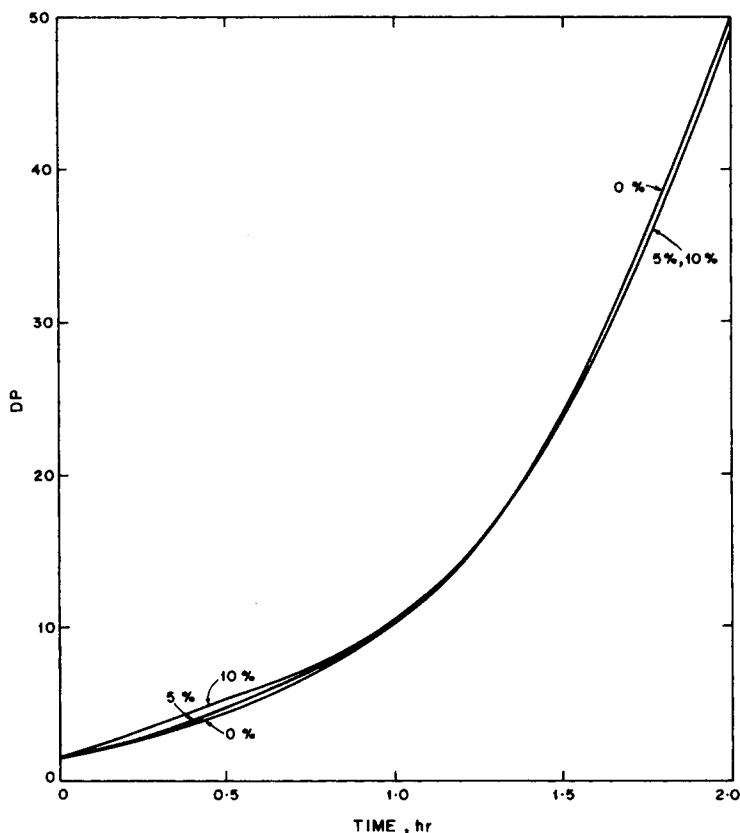
Fig. 13. Effect of TPA addition on DP.   Temperature and pressure programs as per Figure 2.

the point of view of both improvement in productivity as well as product quality. However, the extent of the addition of TPA will have to be restricted since the water of esterification generated will have to be removed in the vacuum system, which is designed to handle predominantly EG, and in the final stage of poly-condensation it may limit the DP buildup.   It may be remarked here that there is an interesting observation reported in the literature[17] that TPA addition during polycondensation (especially in the later stages) is helpful in terms of the im-provement of productivity and product quality.

Parametric Sensitivity

   The computations in the foregoing pertain to the specific set of rate constants outlined in the foregoing.   Since some uncertainty would exist in terms of the exact knowledge of rate constants, it is desirable to examine the parametric sensitivity insofar as the progress of polymerization and side product formation is concerned.
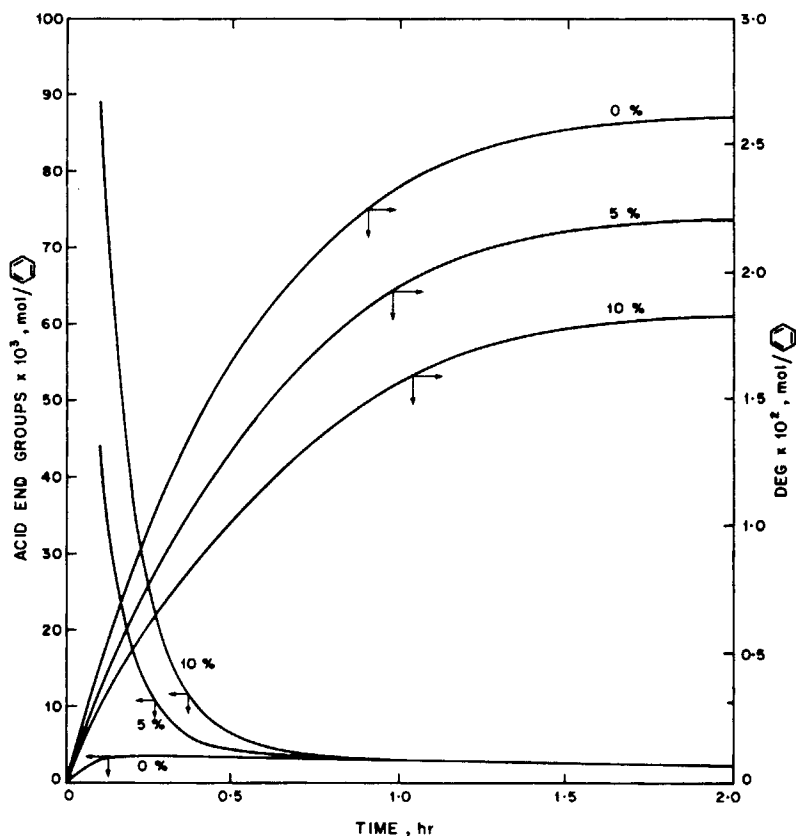   In order to examine these, we considered the following four cases:

Fig. 14. Effect of TPA addition on acid end-group and DEG formation. Temperature and pressure programs as per Figure 2.

Case I

This case pertains to the rate constants taken from Table II, which have been used throughout this investigation.

Case II

In this case, the focus is on the degradation reactions represented in (8), (9), and (10). The values of rate constants k_4, k_5, and k_6 are taken to be half of the values considered in case I.

Case III

In this case, the esterification reaction rate constants k_7 and k_8 are taken as half of the values considered in case I.

TABLE III
Comparison of Side Products Formed for Obtaining DP of 30

| System	Catalyst concn (wt %)	Temp (°C)	Pressure (mm Hg)	Reaction time (h)	DEG × 10²	Side products formed (mol/ benzene ring)			
						acetaldehyde (× 10³)	acid and groups (× 10³)	Water (× 10²)	Vinyl end groups (× 10⁴)
Feed (DP = 1.5)	0.025	280	20	0.70	1.42	7.18	2.08	1.94	1.37
Feed (DP = 1.5)	0.025	260	20	1.30	0.96	4.89	1.33	1.32	0.69
Feed (DP = 1.5)	0.025	programed as per Fig. 2	programed as per Fig. 2	1.65	2.58	12.5	2.05	3.64	1.69
Feed (DP = 1.5 + 10% TPA)	0.025	programed as per Fig. 2	programed as per Fig. 2	1.65	1.80	10.8	2.05	29.10	1.50
Feed (DP = 1.5 + 10% DMT)	0.025	programed as per Fig. 2	programed as per Fig. 2	1.75	1.89	11.1	1.99	2.81	1.98
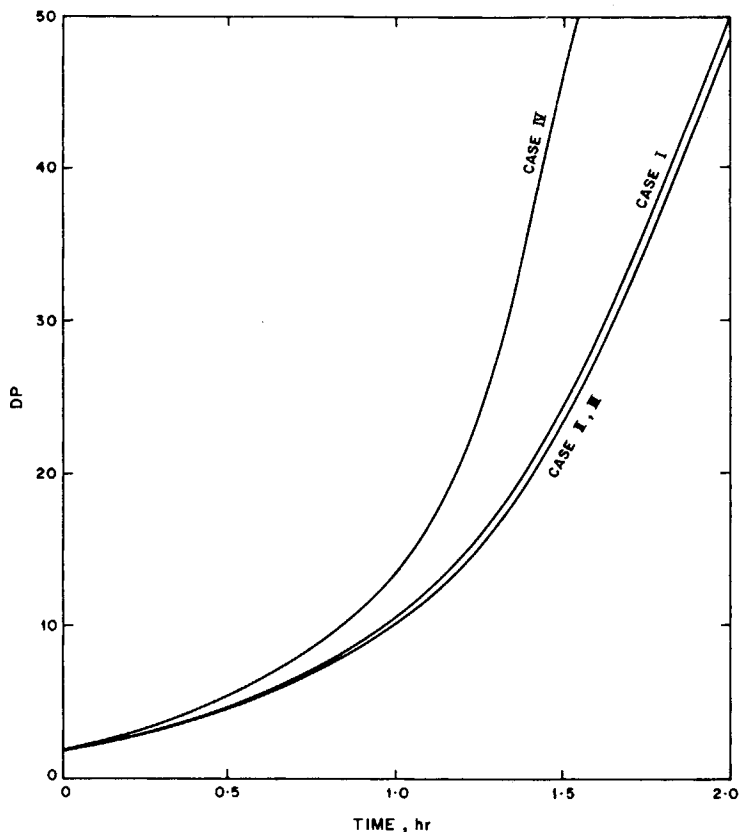
Fig. 15. Sensitivity of numerical results to the assumed kinetic constants on DP. Temperature and pressure programs as per Figure 2.

Case IV

This pertains to the case where the polycondensation rate constant depends on the hydroxyl-end-group concentration and increases with it, as per the discussion earlier. The functional dependence of this rate constant k_3 was taken to be the same as in eq. (36).

Figures 15–18 clearly show the influence of the above parametric variation on both DP and on side-product formation. It is readily seen from Figure 15 that, in spite of the variation in rate constants, the progress of polymerization is predicted to be practically the same as when cases I, II, and III are considered. On the other hand, (as will be intuitively obvious) when case IV is considered, DP rise is much faster in comparison to cases I, II, and III. The role of parametric variation on side-product formation can be seen in Figures 16–18. Depending on the values of degradation and esterification rate constants chosen, byproduct formation can show significant differences. For instance, Figure 16 shows that the acid-end-group formation is much more in case III as compared to case I. Since the esterification rate constant is less, the acid end groups formed because of the degradation reaction react at a much slower rate.

It is rather interesting to note that in case I, DP increases faster because of the side reactions compared to case II, where degradation rate constants are lower.
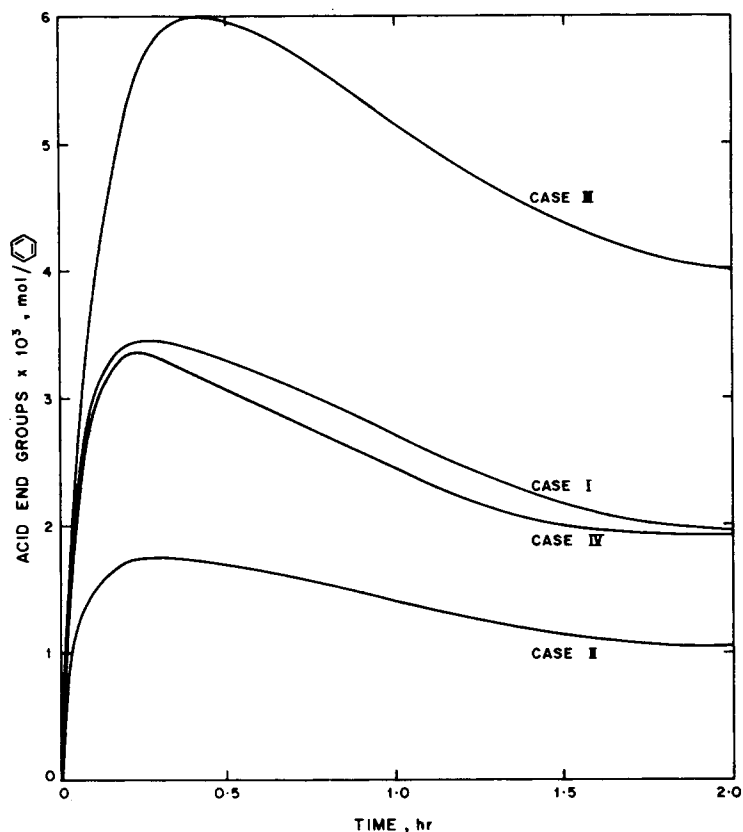
Fig. 16. Sensitivity of numerical results to the assumed kinetic constants on acid end-group formation. Temperature and pressure programs as per Figure 2.

This apparently surprising observation can be explained when it is realized that the rate constant for esterification reaction is about 2–3 times greater than polycondensation reaction. We have also performed numerical computations to show that the results are rather insensitive to the degradation of diester groups rate constant (k_9).

CONCLUDING REMARKS

In the present work, we have undertaken mathematical modelling of a semi-batch prepolymerization process. Due to the limitations outlined in the foregoing, the results of modelling are applicable only up to DP of approximately 30. The influence of the key process and operational variables on productivity and side-product formation, which controls the product quality, has been carefully examined. The modelling has been carried out in the range of process and operational variables which are as close to the industrial practice as possible. It is hoped that the results of the investigations would have an important bearing on both the analysis of prepolymerization processes and also on the design of prepolymerization reactors.
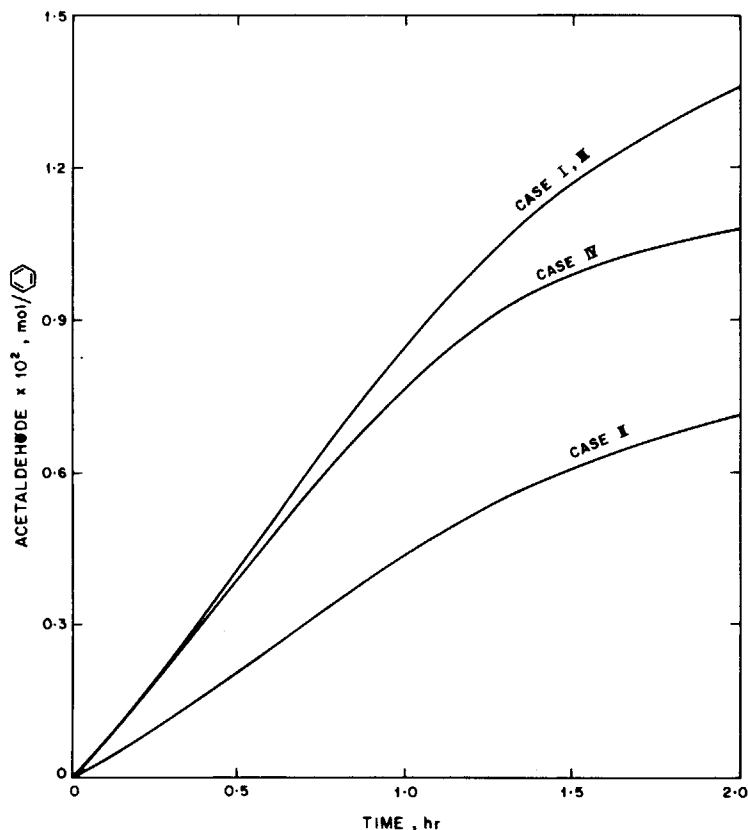
Fig. 17. Sensitivity of numerical results to the assumed kinetic constants on acetaldehyde formation. Temperature and pressure programs as per Figure 2.

NOMENCLATURE

|	
a	number of moles of acetaldehyde
$\mathbf{a}$	interfacial area per unit volume (cm^{-1})
e_m, e_g, e_c, e_v	number of moles of methyl, hydroxyl, acid and vinyl end groups, respectively
g	number of moles of ethylene glycol
g^*	number of moles of diethylene glycol
k_L	mass transfer coefficient (cm/s)
k_1'	an equivalent first-order polycondensation rate constant (s^{-1})
k_1–k_3, k_5–k_8	second-order rate constants (L/mol·min)
k_4, k_9	first-order rate constants (min^{-1})
$k_{3,0}$	initial polycondensation rate constant, (L/mol·min)
K_1–K_5	equilibrium constants
m	number of moles of methanol
P_T	total pressure (mm Hg)
P_G^*, P_W^*	vapor pressures of ethylene glycol and water (mm Hg)
$Q_G(t), Q_W(t)$	flow rates of ethylene glycol and water (mol/min)
R_1–R_{10}	reaction rates (mol/L·min)
t	time
T	temperature (°C)
V_0	initial volume of the reaction mixture (L)
V	volume of the reaction mixture at any time t (L)
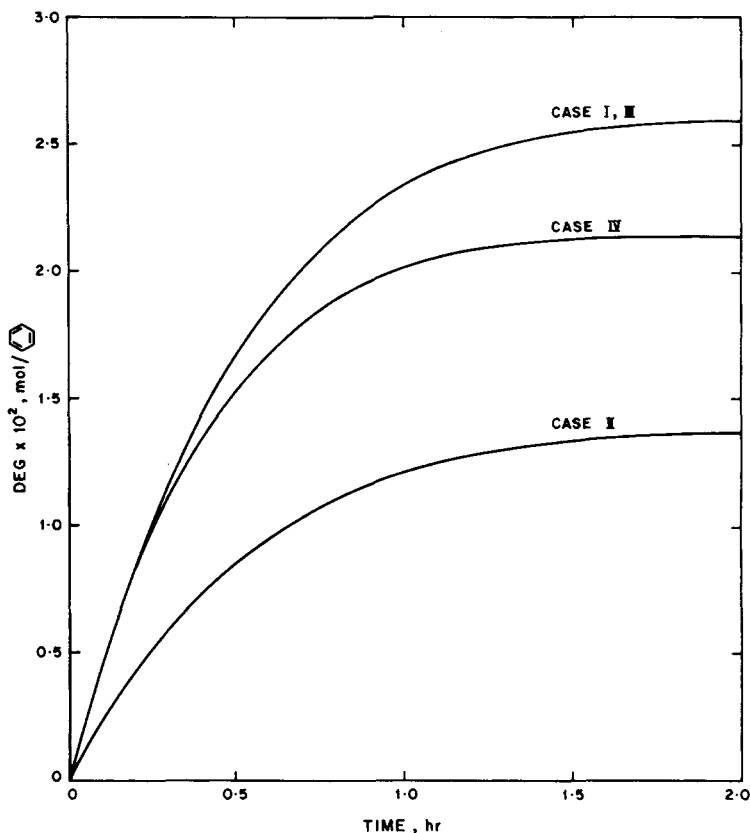
Fig. 18. Sensitivity of numerical results to the assumed kinetic constants on DEG formation. Temperature and pressure programs as per Figure 2.

w	number of moles of water
z	number of moles of diester groups
θ	time (h)

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