Modelling of Reversible Poly(ethylene Terephthalate) Reactors

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Synopsis

The second stage of batch poly(ethylene terephthalate) (PET) reactor with bis(2-hydroxyethyl) terephthalate (BHET) as the feed has been simulated. In this stage, the overall polymerization is not diffusion limited and is known to be a complex reaction. In this work it has been assumed to consist of polycondensation, reaction with monofunctional compounds (cetyl alcohol), redistribution, and cyclization reactions. The forward and reverse steps of each of these have been modelled in terms of the rate constants involving functional groups and the reacted bonds. The equations for the calculation of the molecular weight distribution (MWD) in batch reactors have been written and solved numerically. The MWD reported in this work is assumed to include the monofunctional products only, and, for the case where ethylene glycol is not removed from the reaction mass, it was found to be unaffected by the choice of the redistribution rate constant (k_r). Since the removal of ethylene glycol is not mass transfer controlled, its concentration in the reaction mass is assumed be given by the vapor–liquid equilibrium existing at the pressure applied on the reactor. In this work, the level of ethylene glycol concentration, y_g ($\equiv [G]/[P_1]_0$), has been taken as a parameter, and, on application of vacuum, the MWD results were found to vary with k_r with the sensitivity increasing with y_g. It was then shown that the importance of the redistribution reaction is enhanced when the cyclization reaction also occurs. The effect of vacuum on the performance of the reactor has been studied by varying y_g. For y_g less than 0.01, the change in the MWD of the polymer becomes very small. The effects of polymerization temperature and initial concentration of monofunctional compounds on MWD were found to be small.

INTRODUCTION

Polyesters of high molecular weight (fiber spinning grade) from dimethyl terephthalate (DMT) are commercially manufactured in three stages.[1] In the first stage, an ester interchange reaction between DMT and ethylene glycol is carried out in the molar ratio of 1:2 and the main product of this reaction is bis(2-hydroxyethyl) terephthalate which serves as the monomer for the second stage.[2-4] In the second stage, this is polymerized almost to equilibrium conditions under vacuum. The final stage of polymerization is mass transfer controlled and is carried out in special wiped-film reactors.[5] It is at this stage that a high molecular weight polyester is obtained which can be spun into fibers.

In the second stage, most of the monomer is polymerized in the presence of a catalyst to enhance the rate of polymerization and a monofunctional compound like cetyl alcohol is added to control the molecular weight of polymer formed.[6] The final polymer consists of bifunctional polyester molecules (P_n), polyester molecules capped with the monofunctional compound (MF_n) and cyclic polymers (C_n), where the subscript n in P_n, MF_n, and C_n refers to the chain length. In addition to the main reactions forming these, Tomita[7] observes that, at high

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temperatures of polymerization, there is a degradation of polymer due to chain scission. The different reactions occurring in the reactor have been summarized in Table I, and, as can be seen, the overall kinetics of the formation of polyesters is a complex one.

The equilibrium of the polycondensation reaction alone has been studied by Challa,[4] and it was found to be independent of temperature. This has also been confirmed by Fontana.[8] These studies were made in sealed tubes, and equilibrium was assumed to be attained after 36 h of reaction.

The kinetics of the reversible polycondensation step was studied by Challa. The forward rate of polymerization is known to be affected by several catalysts, and the wide variation of the effect of the latter on the forward rate constant is given in Ref. 9. The study of this reaction by Tomita[7] is of more recent origin and is worth mentioning here. The polycondensation was carried out at temperatures above 280°C under very high vacuum and the number-average molecular weight of the forward polymer, $\overline{M}_n$ (or the degree of polymerization, $\overline{DP}$) was measured as a function of time. On plotting $\overline{DP}$ vs. time, $\overline{DP}$ was found to undergo a maximum after about 5 h of polymerization, corresponding to a value of $\overline{DP}$ of about 100. This means that the conversion p (in the Carother's equation) is about 99% and so the overall reaction must necessarily by mass transfer controlled.[1,5,9,10–15] The fall in the average molecular weight of the polymer was explained through the inactivation of polymer molecules due to bond breakage at high temperatuares, and Tomita proposed a model equation giving $1/(\overline{DP})$ as a function of time. In view of the mathematical complexities, he evaluated two empirical constants from his experimental data which are not the rate constants for the polycondensation and the chain scission steps. They, however, represent some measure of these rate constants.

The redistribution reaction occurs between a reaction bond and an OH group at the end of another polymer molecule as follows:
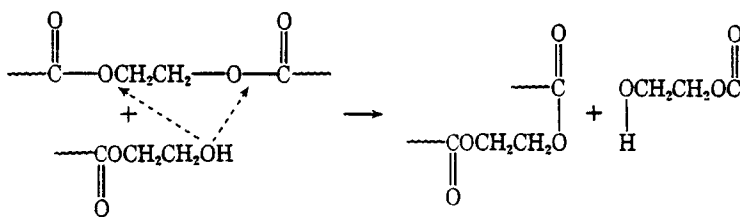

This reaction has been called ester interchange by Flory.[16] In Table I, the reverse reaction has not been shown because it is not independent and can be written as a linear combination of the forward redistribution reactions. Challa[4] has studied this reaction and has evaluated the rate constant by monitoring the concentration of the monomer in the reaction mass.

The cyclization equilibrium in polyethylene terephthalate has been studied by several workers.[17–19] In these studies, polymer of high molecular weight was sealed in a glass tube, and, after sufficient time had elapsed, the concentration of cyclic compounds was determined either through gel permeation chromatography[17] or through fractionation.[18] The equilibrium constant of the following reaction.
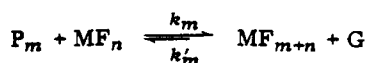
$$P_m \overset{K_c}{\rightleftharpoons} C_x + p_{m-x} \qquad (2)$$

TABLE I
Different Reactions Occurring in Polyester Formations

1. Polycondensation
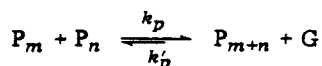
$$P_m + P_n \underset{k_p'}{\overset{k_p}{\rightleftharpoons}} P_{m+n} + G$$

2. Reaction with monofunctional compounds

$$P_m + MF_n \underset{k_m'}{\overset{k_m}{\rightleftharpoons}} MF_{m+n} + G$$

3. Redistribution

$$P_m + P_n \xrightarrow{k_r} P_{m+n-r} + P_r$$

4. Cyclization

$$P_n \underset{nk_c'}{\overset{k_c}{\rightleftharpoons}} C_n + G, \; n > 2$$
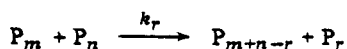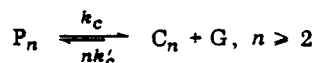
5. Degradation reactions

   (a) Thermal chain scission

   $$P_m \xrightarrow{heat} Z_r + Z'_{m-r}$$

   (b) Vinyl end reactions

   $$Z_n + P_n \rightleftharpoons P_{n+r} + CH_3CHO$$

   $$Z_r + G \rightleftharpoons P_r + CH_3CHO$$

   $$Z_r + H_2O \rightleftharpoons Z'_r + CH_3CHO$$

   $$Z_r \xrightarrow{heat} X + CO_2$$
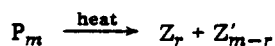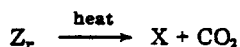
   (c) Carbonyl end reactions

   $$Z'_r \xrightarrow{heat} X' + CO_2$$

P_n:

MF_1: ; MF_n:

C_n:

Z_n:

Z'_n:

X:

X':
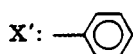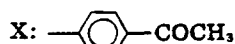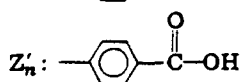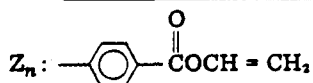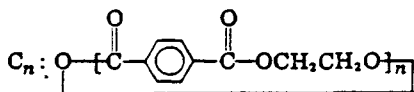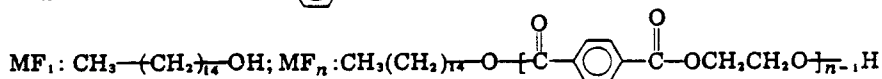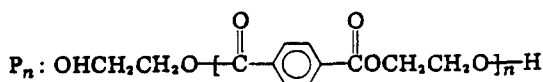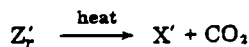
was determined. This information is not expected to be directly applicable to second stage reactors, because the molecular weight of the final polymer is always small. In addition to this, there is a considerable amount of ethylene glycol in the reaction mass with which C_x can react through the reverse reaction in eq. (2). As a first approximation, therefore, the cyclic compounds are assumed to interact with ethylene glycol only, as follows:

$$P_m \rightleftharpoons C_m + G \qquad (3)$$

as shown in Table I.

Ault and Mellichamp[20,21] have studied the transesterification reaction of dimethyl terephthalate in PET formation in semibatch reactors with constant removal of ethylene glycol and found out concentrations of various functional groups in the reaction mass. Ravindranath and Mashelkar have considered a more generalized kinetic scheme, including side reactions like acetaldehyde and diethylene glycol formations for first[22-24] and second stage[25-28] of PET formation and solved for various functional group concentrations in semibatch and continuous flow stirred tank reactors.

In these studies,[22-26] only the concentration of various functional groups were given, and it was not possible to determine the molecular weight distribution of the polymer formed. In the present work, the kinetic scheme consisting of polycondensation, redistribution, reaction with monofunctional compounds, and cyclization reaction has been used and equations for the molecular weight distribution carefully established. The polycondensation is assumed to be uncatalyzed, and the experimental rate constants of Challa[2-4] have been used. The results can, however, be easily modified by suitably changing the rate constants in cases of catalyzed polymerization. As we found in our earlier simulation of nylon-6,[29,30] nylon-66,[31] and phenol–formaldehyde reactors (novolac[32,33] or resole type[34,35]), the MWD results cannot be represented by Flory's most probable distribution.[36,37] The various parameters that are important in polyester formation in commercial reactors have been identified in this work, and a sensitivity analysis has been carried out to isolate the important ones. Ravindranath and Mashelkar[22-25] in their work have clearly shown that the effect of diffusion in the removal of the condensation product (ethylene glycol) becomes important only after the average molecular weight $(\overline{DP})$ of the polymer in the reaction mass is beyond 30. Since, in the second stage, only about 90% conversion is reached, the effect of the application of vacuum can be simulated by assuming a low and uniform glycol concentration corresponding to the vacuum applied on the reaction mass.

KINETIC MODEL

In the following discussion, the rate of formation of molecule P_n from the several reaction steps given in Table I is individually considered and analyzed.

Polycondensation Step

P_n in the batch reactor is formed either when P_r $(r < n)$ reacts with P_{n-r} through the forward reaction or any molecule P_m $(m > n)$ reacts with ethylene glycol (G) through the reverse reaction. P_n is depleted when it reacts with P_i,

$i = 1$ to ∞ through the forward reaction or reacts with G through the reverse reaction. Thus, the rate of formation of P_n by this step, $\dot{P}_{n,I}$, is given by

$$\dot{P}_{n,I} = -4k_p[P_n] \sum_{m=1}^{\infty} [P_m] + \frac{1}{2}(4k_p) \sum_{r=1}^{n-1} [P_r][P_{n-r}]$$

$$- 2k_p'[G](n-1)[P_n] + 4k_p'[G] \sum_{i=n+1}^{\infty} [P_i] \quad (4)$$

where k_p is the forward rate constant involving the functional group and k_p' is the reverse rate constant involving G and the reacted bond. The factor of 4 in the first term appears because P_m and P_n can react in four ways, the extra factor of 1/2 in the second term is because of the symmetry in the summation $\sum_{r=1}^{n-1}$ $[P_r][P_{n-r}]$, the factor of $(n-1)$ in the third term because there are $(n-1)$ reacted bonds on P_n, and the factor of 4 in the fourth term because a given G molecule can react in two ways at two possible sites on P_i. The rate of formation of P_1, $\dot{P}_{1,I}$, however is given by

$$\dot{P}_{1,I} = -4k_p[P_1] \sum_{m=1}^{\infty} [P_m] + 4k_p'[G] \sum_{i=2}^{\infty} [P_i] \quad (5)$$

### Step Involving the Reaction with Monofunctional Compounds

P_n is depleted when it reacts with any MF_i. $i = 1$ to ∞ through the forward reaction whereas it is formed when an MF_j ($j \geq n + 1$) reacts with G through the reverse reaction. In other words, the rate of formation of P_n, $\dot{P}_{n,II}$ is given by

$$\dot{P}_{n,II} = -2k_m[P_n] \sum_{m=1}^{\infty} [MF_m] + 2k_m'[G] \sum_{m=n+1}^{\infty} [MF_m] \quad (6)$$

The monofunctional compounds MF_i are expected to react similarly as P_i because they differ only in terms of the end group substitution.[27-31] In view of this, in this work k_m and k_m' have been taken to be equal to k_p and k_p'.

Redistribution Step

As shown in eq. (1), the redistribution reaction is the interaction of the reacted bond with the functional group, OH of another polymer molecule. In view of this, not only P_m and P_n can undergo the redistribution reaction, but P_m, MF_n, and C_j can also undergo a reaction through this mechanism. Since the concentrations of monofunctional and cyclic compounds in the reaction mass are expected to be small, only P_m and P_n have been assumed to interact in this way. Symbolically, this can be written as

$$P_m + P_n \rightarrow P_{m-r} + P_{n+r} \quad (7)$$
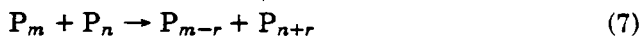
where r can take any value except $r = m - n$. For this value of r, the reactant and products become the same, and therefore this reaction should be properly excluded in the mass balance. However, when $m = n$, r can take any nonzero value.

Keeping this characteristic of reaction in mind, all possible reactions between molecular species P_x and P_y are written. For example, P_1 cannot react with P_1

and P_2. If P_3 reacts with P_3, molecular species that can be formed are P_1 and P_5 and P_3 and P_4. Similarly, when P_3 reacts with P_4, the molecular specied that can be formed are P_1 and P_6 and P_2 and P_5. After carrying out this exercise, the various reactions that lead to the formation of a given polymer molecule (say P_n) are collected.. For example, P_4 is formed when P_1 reacts with either P_5, P_6, P_7, ··· . This exercise shows that a given molecule P_x can be formed in two distinct ways:

(a) by a process of elimination in which a reacted bond of a molecule P_m having chain length greater than x undergoes a redistribution reaction, such that $m - r = x$;

(b) by a process of combination in which a molecule P_n having chain length less than x combines with a part of a chain of the other molecule, such that $n + r = x$.

It is further observed that a given polymer molecule P_n is eliminated in two distinct ways: (a) by the reaction of $n - 1$ bonds of P_n with the OH groups of any of the polymer molecules and (b) by the reaction of the two OH groups of P_n with any of the reacted bonds of any other polymer molecule.

To decide over the reactivity of reaction (7), the reaction of OH groups of P_3 with the various sites of P_5 are considered as an example. The molecular structure of P_5 is
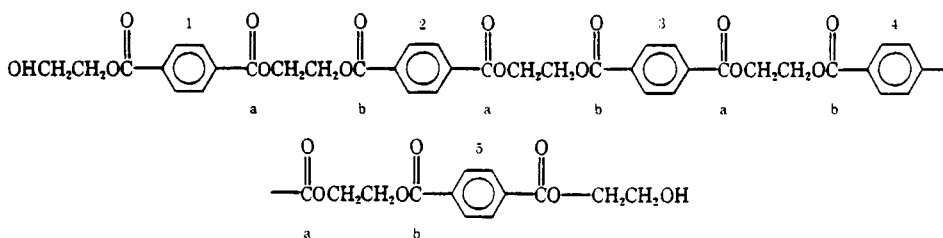
Evidently the redistribution reaction can occur at sites ①a and b to ④a and b. It the reaction occurs at ①a, two P_4 are formed, and, if it occurs at ①b, P_1 and P_7 are formed. Similarly, P_3, P_5 and P_2, P_6 are found due to reactions at ②a and

TABLE II
Various Rate Parameters Used in the Simulation[a]

Temp (°C)	$(k_p$ (L/mol·h)	R_1	R_2	R_3	R_4	R_5	R_6
254	0.047 (exptl)	2.13 (exptl)	1.00	2.13	0.1	0.21	2.55 (exptl)
260	0.054 (exptl)	2.37 (exptl)	1.00	2.37	0.1	0.24	3.17 (exptl)
282	0.114 (exptl)	2.63 (exptl)	1.00	2.63	0.1	0.26	4.78 (exptl)
300	0.229	2.71	1.00	2.71	0.1	0.27	5.75

[a] $\ln k_p = -22.00/1.987/T \times 10^3 + 17.85$ L/mo·h;
$\ln k_p' = -23.00/1.987/T \times 10^3 + 19.724$ L/mo·h;
$\ln k_r = -30.88/1.987/T \times 10^3 + 27.397$ L/mol·h;
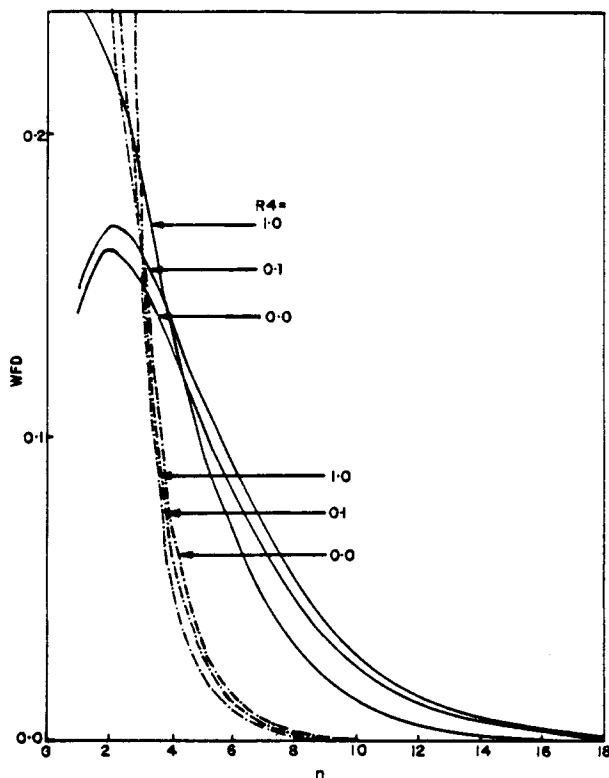k_p, k_p', and k_r have been taken from Challa.[2–4]

Fig. 1. Effect of cyclization rate constant (R_4) upon the weight fraction distribution given by eq. (29). R_1–R_3 and R_6 are evaluated at 282°C: $R_1 = 2.631$, $R_2 = 1.0$, $R_3 = 2.631$, $R_6 = 4.781$, $Y_{MF_{10}} = 0.01$, $\theta = 1.0$. (– · – ·) closed; (——) $y_g = 0.001$.

②b, P_2, P_6 and P_3, P_5 with reactions at ③a and ③b and P_1, P_7 and $2P_4$ with reactions at ④a and ④b. It can thus be seen that there are two sites on P_5 which through redistribution give P_1, two sites which give P_2, two sites which give P_3, and so on. If k_r is the rate constant involving an OH group and a reacted bond, the overall reactivity of P_3 and P_5 would therefore be $2 \times 2\,k_r$ or $4\,k_r$ because P_3 has two OH groups which can participate in the redistribution reaction.

Using the method outlined above, the net rate of formation of P_1, P_2, P_3, etc. through the redistribution reaction has been written and has been ultimately generalized as

$$\dot{P}_{1,III} = -4k_r[P_1] \sum_{x=2}^{\infty} (x-1)[P_x] + 4k_r \left(\sum_{y=1}^{\infty} [P_y] \right) \left(\sum_{x=2}^{\infty} [P_x] \right) \qquad (8)$$

$$\dot{P}_{n,III} = -4k_r(n-1)[P_n] \sum_{x=1}^{\infty} [P_x] - 4k_r[P_n] \sum_{x=2}^{\infty} (x-1)[P_x]$$

$$+ 4k_r \left(\sum_{y=1}^{\infty} [P_y] \right) \left(\sum_{x=n+1}^{\infty} [P_x] \right) + 4k_r \sum_{y=1}^{n-1} \sum_{x=n-y+1}^{\infty} [P_x][P_y] \quad (9)$$

In eq. (9), the first term accounts for the reaction of $n-1$ bonds of P_n with any OH groups in the reaction mass, and the second term gives the reaction of the OH group of P_n with any polymer molecule through redistribution. The third
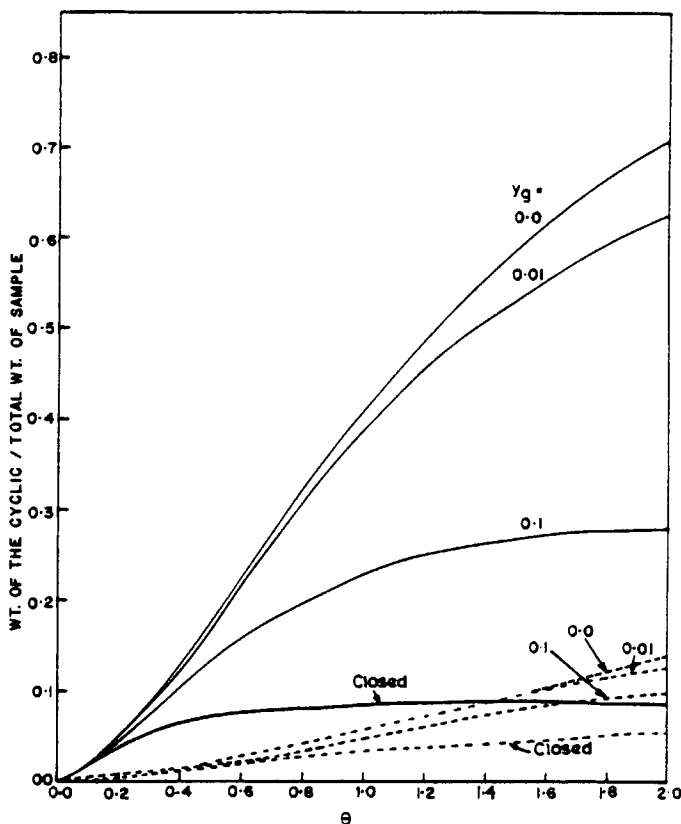
Fig. 2. Effect of R_4 and the level of vacuum measured by y_g on the weight fraction of cyclic compounds. R_1–R_3 and R_6 are evaluated at 282°C: $R_1 = 2.631, R_2 = 1.0, R_3 = 2.631, R_6 = 4.781, y_{MF_{10}}$ $= 0.01$. R_4: (——) 1.0; (---) 0.01.

term accounts for the formation of P_n by the process of elimination, and the fourth term gives the formation of P_n through the process of combination. Challa has derived the formation of P_1 through the redistribution and is the same as eq. (8). On examination of eq. (1), it is found that in the redistribution reaction, the following must be true:

(a) the total number of polymer molecules should not change;

(b) the total count of benzene rings (in PET polymerization) must remain constant.

This would mean that

$$\sum_{i=1}^{\infty} \dot{P}_{i,\mathrm{III}} = 0 \tag{10}$$

and

$$\sum_{i=1}^{\infty} i\dot{P}_{i,\mathrm{III}} = 0 \tag{11}$$

To check if this is true for eqs. (8) and (9), one has

$$\sum_{i=1}^{\infty} \dot{P}_{i,\mathrm{III}} = -4k_r \left(\sum_{m=1}^{\infty} [P_m] \right) \left\{ \sum_{n=2}^{\infty} (n-1)[P_n] \right\}$$

$$- 4k_r \left(\sum_{m=1}^{\infty} P_m \right) \left(\sum_{n=2}^{\infty} (n-1)[P_n] \right) + 4k_r \left(\sum_{y=1}^{\infty} [P_y] \right) \left(\sum_{n=1}^{\infty} \sum_{x=n+1}^{\infty} [P_x] \right)$$
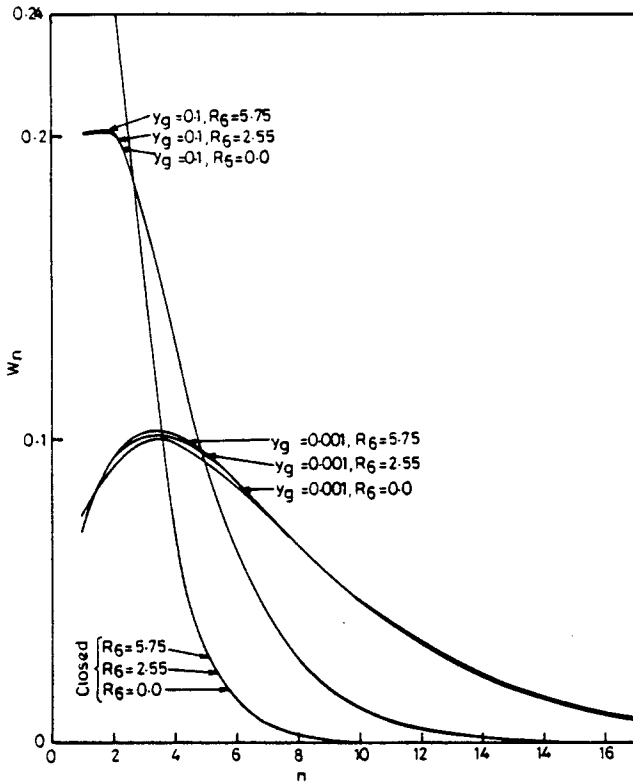
Fig. 3. Effect of redistribution rate constant (R_6) and the level of vacuum measured by y_g on weight fraction distribution given by eq. (29). $R_1 = 2.631, R_2 = 1.0, R_3 = 2.631, R_4 = 0.1, R_5 = 0.263, y_{MF_{10}} = 0.01, [MF_1]_0 = 0.01, x = 1.8.$

$$+ 4k_r \sum_{n=2}^{\infty} \sum_{y=1}^{n-1} \sum_{x=(n-y+1)}^{\infty} [P_x][P_y] \quad (12)$$

But

$$\sum_{n=1}^{\infty} \sum_{m=n+1}^{\infty} [P_m] = \sum_{n=1}^{\infty} (n-1)[P_n] \quad (13)$$

and

$$\sum_{n=2}^{\infty} \sum_{y=1}^{n-1} \sum_{x=n-y+1}^{\infty} [P_x][P_y] = \left(\sum_{y=1}^{\infty} [P_y]\right)\left(\sum_{x=2}^{\infty} (x-1)[P_x]\right) \quad (14)$$

These relations can be checked through term-by-term expansion of the summations, and, on substitution of these in eq. (12), $\sum_{i=1}^{\infty} \dot{P}_{i,III}$ is found to be zero. Similarly $\sum_{i=1}^{\infty} i \dot{P}_{i,III}$ can be shown to be zero using the following relations:

$$2 \sum_{n=1}^{\infty} n \sum_{y=1}^{n-1} \sum_{x=n-y+1}^{\infty} [P_x][P_y] = 2 \sum_{n=1}^{\infty} n \sum_{m=1}^{\infty} \sum_{r=1}^{n-1} [P_r][P_{m+n-r}]$$

$$= 2 \sum_{n=1}^{\infty} n[P_n] \sum_{j=2}^{\infty} (j-1)[P_j] + \left(\sum_{j=1}^{\infty} [P_j]\right)\left(\sum_{n=2}^{\infty} n(n-1)[P_n]\right) \quad (15)$$

and

$$\left(\sum_{j=1}^{\infty} [P_j]\right)\left(\sum_{n=2}^{\infty} n(n-1)[P_n]\right) = 2 \left(\sum_{n=1}^{\infty} P_n\right)\left(\sum_{n=1}^{\infty} n \sum_{j=n+1}^{\infty} [P_j]\right) \quad (16)$$
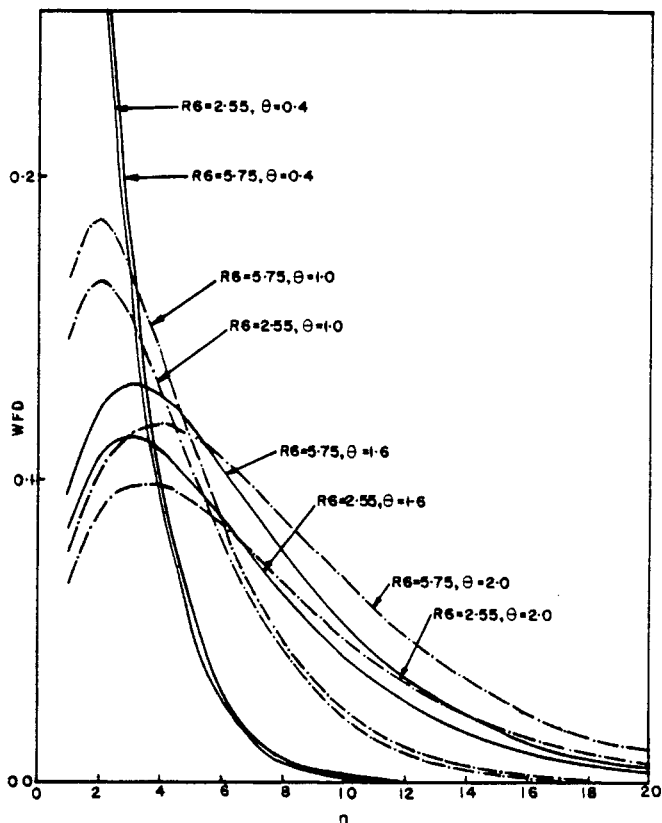
Fig. 4. Effect of R_6 on the WFD at different times of polymerization. $R_1 = 2.631$, $R_2 = 1.0$, $R_3 = 2.631$, $R_4 = 0.1$, $R_5 = 0.263$, $y_g = 0.001$, $y_{MF_{10}} = 0.01$.

Equations (10) and (11) imply that the number-average molecular weight of the polymer is not affected by the redistribution step as reported by Flory.[16]

Cyclization Step

P_n is depleted when the two end groups of the polymer chain interact to form C_n. The forward rate constant k_c is a first-order constant and is a product of the second-order rate constant k_p and the "mutual concentration" of chain ends of the same molecule given by

$$k_c = k_p (3/2\pi \langle r^2 \rangle^{3/2}/N_{avo} \tag{17}$$

where $\langle r^2 \rangle^{1/2}$ is the radius of gyration of the chain and N_{avo} is the Avogadro number.[38,39] In the absence of information on the radius of gyration of the polymer at the reaction conditions, k_c cannot be estimated from the knowledge of k_p alone. In view of this, (k_c/k_p) in this study has been taken as an adjustable parameter such that the total amount of cyclic compound formed in the reaction mass does not increase beyond about 5%. In the reverse reaction, ethylene glycol (G) can react at any of the reacted bonds of C_n. Therefore, if k_c' is the rate constant involving the reaction between an OH group of ethylene glycol and one of the reacted bonds of C_n, the rate constant for the reaction between G and C_n will be $2nk_c'$. Therefore, the rate of formation of P_n due to this step, $\dot{P}_{n,\text{IV}}$, is given by
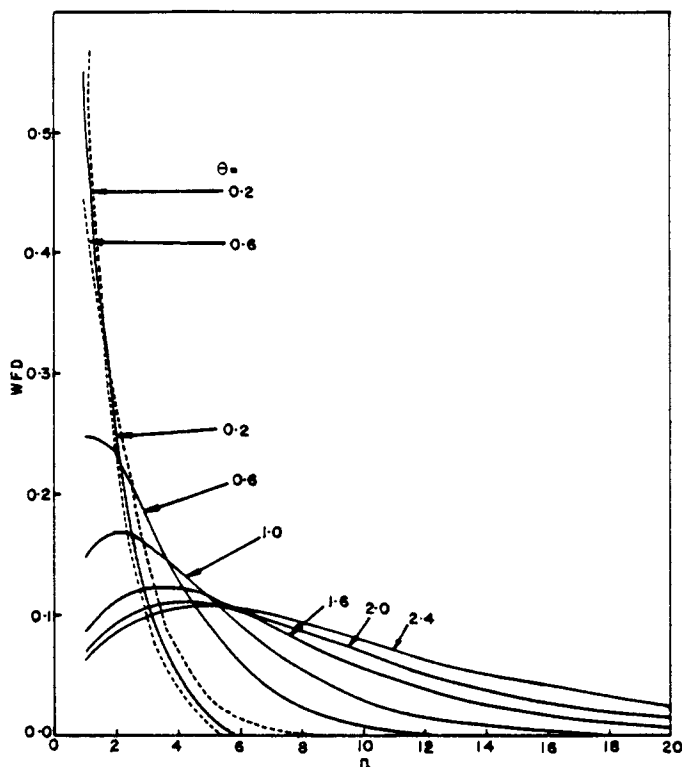
Fig. 5. Weight fraction distribution at high vacuum (y_g = 0.001) and reversible polymerization at 282°C at various times. R_1 = 2.631, R_2 = 1.0, R_3 = 2.631, R_4 = 0.1, R_5 = 0.263, R_6 = 4.781, $y_{MF_{10}}$ = 0.01. (——) y_g = 0.001; (---) closed.

$$\dot{P}_{n,IV} = -k_c[P_n] + 2nk_c'[G][C_n], \quad n \geqslant 2 \tag{18}$$

Since the reverse cyclization reaction rate constant involves the reaction between a reacted bond and ethylene glycol, as a first approximation, k_c' can be approximated as equal to k_p'. This would mean that $k_c'/k_p = k_p'/k_p$.

With this analysis, one can write the balance equation for all the species in the batch reactor, and these are given below

$$\frac{d[P_1]}{dt} = -4k_p[P_1] \sum_{i=1}^{\infty} [P_i] + 4k_p'[G] \sum_{i=2}^{\infty} [P_i] - 2k_m[P_1] \sum_{i=1}^{\infty} [MF_i]$$

$$+ 2k_m'[G] \sum_{i=2}^{\infty} [MF_i] - 4k_r[P_1] \sum_{i=2}^{\infty} (i-1)[P_i] + 4k_r \left(\sum_{y=1}^{\infty} [P_y] \right) \sum_{x=2}^{\infty} [P_x] \tag{19}$$

$$\frac{d[P_n]}{dt} = -4k_p[P_n] \sum_{m=1}^{\infty} [P_m] + 2k_p \sum_{m=1}^{n-1} [P_m][P_{n-m}] - 2k_p'(n-1)[G][P_n]$$

$$+ 4k_p'[G] \sum_{m=n+1}^{\infty} [P_m] - 2k_m[P_n] \sum_{m=1}^{\infty} [MF_m] + 2k_m'[G] \sum_{m=n+1}^{\infty} [MF_m]$$

$$-4k_r(n-1)[P_n] \sum_{m=1}^{\infty} [P_m] - 4k_r[P_n] \sum_{m=2}^{\infty} (m-1)[P_m]$$

$$+4k_r \left(\sum_{y=1}^{\infty} [P_y] \right) \left(\sum_{x=n+1}^{\infty} [P_x] \right) + 4k_r \sum_{y=1}^{n-1} \sum_{x=(n-y+1)}^{\infty} [P_x][P_y]$$
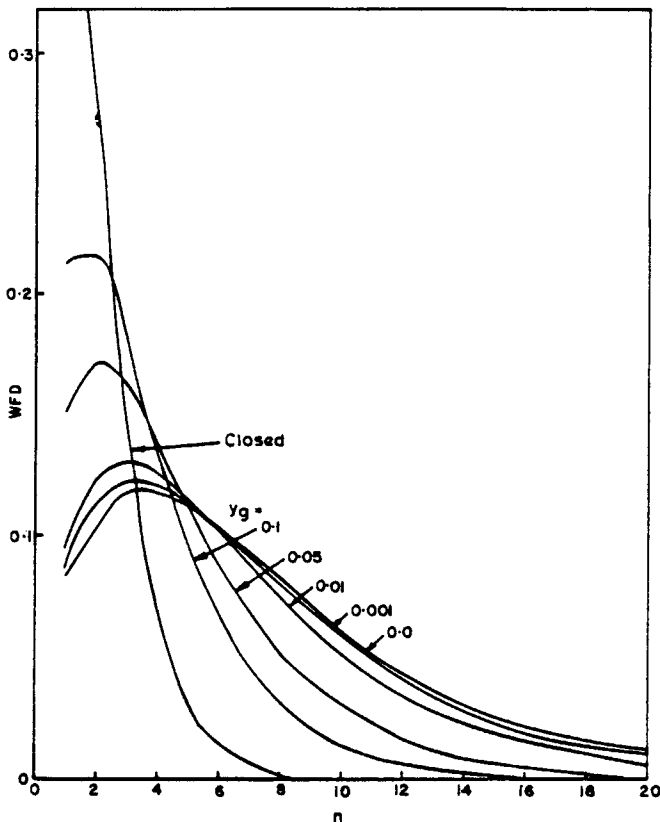
Fig. 6. Effect of level of vacuum on the WFD of the polymer formed at $\theta = 1.6$. $R_1 = 2.631$, $R_2 = 1.0$, $R_3 = 2.631$, $R_4 = 0.1$, $R_5 = 0.263$, and $R_6 = 4.781$, $y_{MF_{10}} = 0.01$.

$$+2k'_c n[C_n][G] - k_c[P_n] \qquad \text{for } n \geq 2 \qquad (20)$$

$$\frac{d[MF_1]}{dt} = -2k_m[MF_1] \sum_{m=1}^{\infty} [MP_m] + 2k'_m[G] \sum_{m=2}^{\infty} [MF_m] \qquad (21)$$

$$\frac{d[MF_n]}{dt} = -2k_m[MF_n] \sum_{m=1}^{\infty} [P_m] + 2k_m \sum_{m=1}^{n-1} [MF_m][P_{n-m}]$$

$$-2k'_m (n-1)[G][MF_n] + 2k'_m[G] \sum_{m=n+1}^{\infty} [MF_m], \qquad n \geq 2 \qquad (22)$$

$$\frac{d[C_n]}{dt} = k_c[P_n] - 2nk'_c[C_n][G] \qquad n \geq 2 \qquad (23)$$

When ethylene glycol is not removed from the reaction mass, as in sealed tube experiments, the total OH⁻ group concentration is found to remain constant, i.e.,

$$2[G] + 2 \sum_{i=1}^{\infty} [P_i] + \sum_{i=1}^{\infty} [MF_i] = 2[P_1]_0 + [MF_1]_0 \qquad (24)$$

where $[P_1]_0$ and $[MF_1]_0$ refer to the initial concentrations. This relation is used to obtain [G] as a function of time. To solve eqs. (18)–(23) numerically, the following dimensionless terms are defined:

$$R_1 = k'_p/k_p \qquad (25a)$$
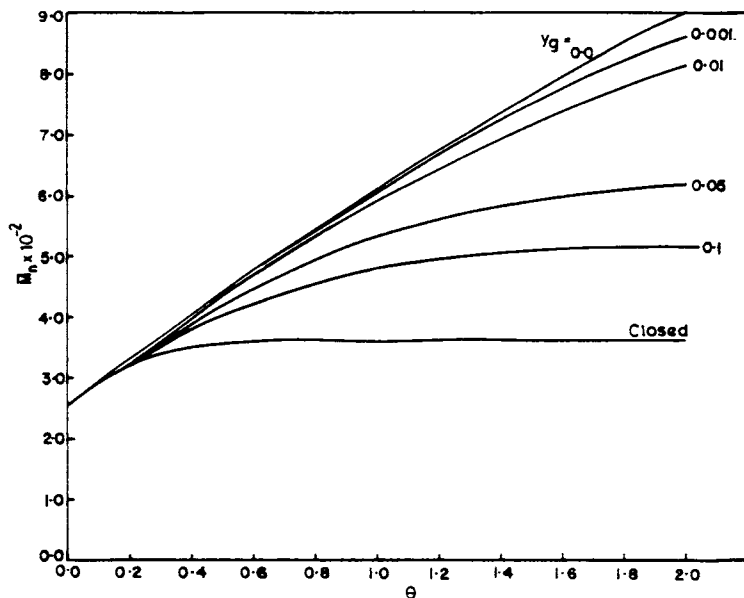
Fig. 7. Number average molecular weight of the polymer as a function of θ. $R_1 = 2.631, R_2 = 1.0,$ $R_3 = 2.631, R_4 = 0.1, R_5 = 0.263,$ and $R_6 = 4.781, y_{MF_{10}} = 0.01.$

$$R_2 = k_m/k_p \tag{25b}$$

$$R_3 = k'_m/k_p \tag{25c}$$

$$R_4 = k_c [P_1]_0/k_p \tag{25d}$$

$$R_5 = k'_c/k_p \tag{25e}$$

$$R_6 = k_r/k_p \tag{25f}$$

$$\theta = k_p [P_1]_0 t \tag{25g}$$

$$y_g = [G]/[P_1]_0 \tag{25h}$$
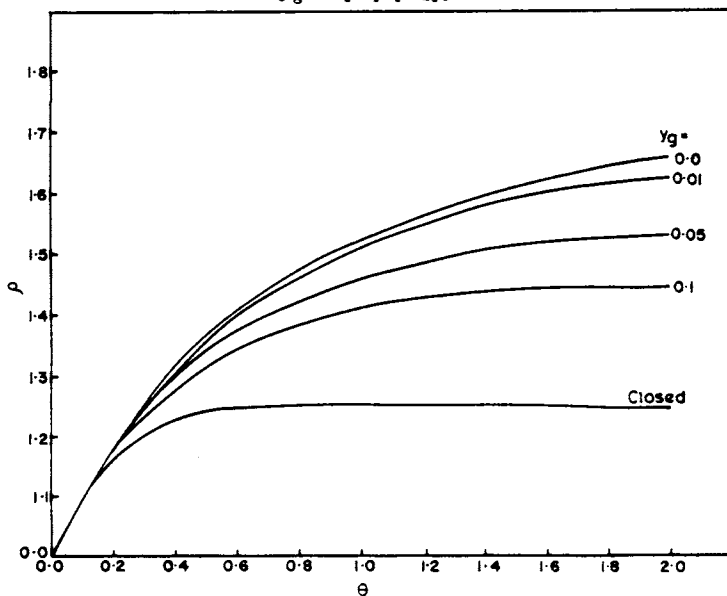
Fig. 8. Polydispersity index ρ of the polymer as a function of θ. $R_1 = 2.631, R_2 = 1.0, R_3 = 2.61,$ $R_4 = 0.1, R_5 = 0.263,$ and $R_6 = 4.781, y_{MF_{10}} = 0.01.$
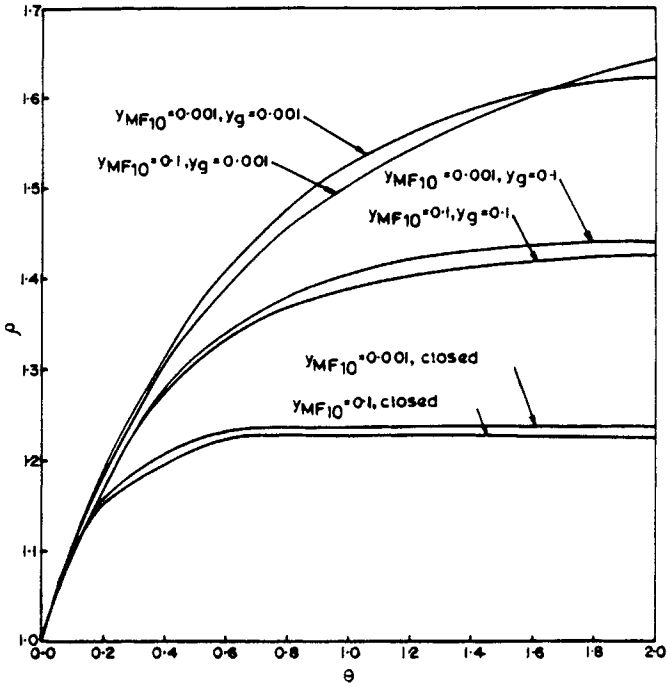
Fig. 9. Effect of initial concentration of cetyl alcohol on at 282°C.

$$y_{P_i} = [P_i]/[P_1]_0, \quad i = 1,2,\cdots \tag{25i}$$

$$y_{MF_i} = [MF_i]/[P_1]_0, \quad i = 1,2,\cdots \tag{25j}$$

$$y_{C_i} = [C_i]/[P_1]_0, \quad i = 2,3,\cdots \tag{25k}$$

Fig. 10. Effect of temperature on polydispersity index ρ of the polymer. $y_{MF_{10}} = 0.01$.

The rate constants of Challa,[2-4] which have been evaluated in sealed tube experiments, have been used in this work and are summarized in Table II. The monofunctional compounds are assumed to react exactly as P_i. Since the rate constants $k_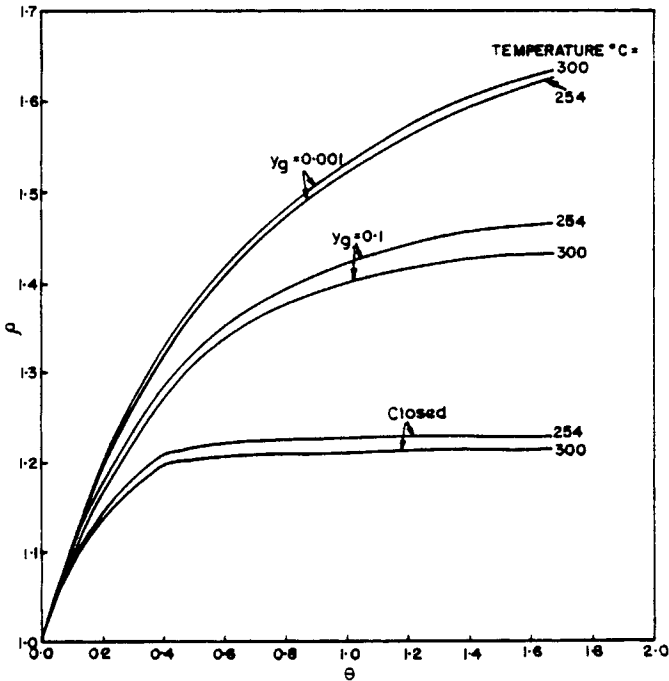c$ and k'_c are not known experimentally, these have been treated as parameters. Their values have been adjusted such that, even in the worst condition of polymerization, the total amount of cyclic compounds does not exceed more than 5–6% by weight.

Lastly, in any commercial system, the cyclic compounds are always extracted because these cause problem in spinning yarns. In view of this, in calculating weight fraction distribution (WFD), only the polymer and monofunctional compounds are considered. Therefore, at a given time

$$MFD_i = \frac{WP_i + WMF_i}{\sum_{i=1}^{\infty} (WP_i + WMF_i)} \qquad (26)$$

where WP_i and WMF_i are the weights of P_i and MF_i in the reaction mass.

RESULTS AND DISCUSSION

Equations (19)–(23) have been solved on a DEC 1090 computer using the Runge–Kutta method of the fourth order. The increment size $\Delta\theta$ was adjusted to obtain a stable solution, and $\Delta\theta = 10^{-3}$ was found to be suitable. There were several checks made on the computer programme. By setting R_1–R_6 equal to zero, eqs. (19)–(23) reduce to the case of irreversible AB type polymerization of bis(2-hydroxyethyl) terephthalate for which an analytical solution exists. The numerical solution was found to match with the analytical one exactly. Next, the computations were made for large times for reversible polymerization (with no removal of ethylene glycol) with $R_2 = R_3 = R_4 = R_5 = R_6 = 0$. The values of R_1 used was that given by Challa. The MWD was found to change negligibly after $\theta = 1.5$, and the total conversion at this time was found to match with the experimental values in sealed tubes.[4-6] Finally, a phenyl ring count was made in all computations, and the agreement with the initial value was within 1% in all cases.

In Figure 1, the effect of changing the cyclization rate constant on the weight fraction distribution of P_i (WFD) is shown. If a high vacuum is applied to the batch reactor, whatever ethylene glycol is formed through polymerization is instantaneously removed, and results for such a system could be calculated by setting $y_g = 0$ in eqs. (19)–(23). When ethylene glycol is not removed from the reactor, as in sealed tube experiments, eqs. (19)–(23) are solved with y_g determined by the stoichiometry of polymerization, and we have labelled such results as "closed." For "closed" polymerization, the WFD becomes slightly sharper as R_4 is increased from 0 to 1, without affecting significantly the total amount of cyclic compounds as seen in Figure 2. For "open" polymerization (i.e., $y_g = 0$ in the reaction mass), however, the effect of R_4 is large as seen in Figure 2. The fraction of cyclic compounds is as high as 75% for $R_4 = 1$ and the maximum in the WFD curve for $R_4 = 0$ in Figure 1 disappears when R_4 is made equal to 1. For $R_4 = 0.1$ and θ as large 2, the total amount of cyclic compounds, as seen in Figure 2, does not increase beyond 6% even for "open" polymerization, and therefore this value of R_4 has been used in subsequent runs.

The effect of the redistribution constant, R_6 (or k_r) is shown in Figure 3. Under the usual range of the temperature of polymerization (i.e., 254–300°C), k_r varies between 2.55 and 5.75. In generating the WFD of P_i, the other parameters were evaluated at 282°C. For "closed" polymerization [i.e., y_g given by eq. (24)], the variation of k_r (or R_6) is found to have a negligible effect upon the molecular weight distribution. Flory states that if the redistribution reaction proceeds under conditions which do not permit further polymerization, each species will be formed at a rate equal to its destruction. This would mean that the redistribution reaction, if at all, should contribute to the MWD (or WFD) for small times of polymerization. In the case of closed polymerization, the MWD results were not found to be affected even for short times for the range of R_6 studied. Since the removal of ethylene glycol is not mass transfer controlled, on application of vacuum, the concentration of ethylene glycol falls to the level determined by the thermodynamic equilibrium at the pressure applied. As increasing vacuum gives lower y_g, in Figure 3, we have treated y_g as a parameter and plotted WFD for various values of R_6 and y_g. To show that the effect of R_6 and y_g on the MWD does not vanish with time, in Figure 4, the weight fraction distribution for R_6 = 2.55 and 5.75 at different times have been plotted. The difference between the two curves at a given time increases as the residence time of the reactor is increased. It has been argued that for irreversible polycondensation alone (i.e., in the absence of redistribution and cyclization), the MWD in batch reactors is given by Flory's most probable molecular weight distribution.[16] Since redistribution reaction tends to drive the reaction mass towards the latter,[14] it is therefore expected that R_6 should have no effect upon the MWD in irreversible polymerization. To isolate the effect observed in Figures 3 and 4, R_4 was set equal to zero (i.e., no cyclization), and the MWD was calculated for different y_g and R_6. Results were found to be negligibly affected, which means that the redistribution reaction step should be included whenever cyclization reaction occurs in the reaction mass. In view of this, using experimental rate constants of Table II, the MWD obtained for "open" polycondensation (with cyclization and redistribution) has been shown in Figure 5 with θ as parameter. The results have also been compared with those for "closed" polymerization.

In Figure 6, the effect of vacuum has been examined. The curve for y_g corresponds to the case of open polymerization. For y_g less than 0.1, the MWD undergoes a maximum, and, with reducing y_g (or increasing degree of vacuum), the curves become broader and broader. In Figures 7 and 8, the number average molecular weight and the polydispersity index ρ, respectively, have been plotted as a function of the dimensionless time θ. Examination of Figure 6–8 reveals that the MWD, number-average molecular weight, and polydispersity index all change very significantly till y_g falls up to the values of 0.01. Beyond this value, the changes are very small and curves are close to those for "open" polymerization.

In Figure 9, the effect of initial concentration of monofunctional compounds (cetyl alcohol) y_{MF_1} on the resultant polymer has been examined. For reversible polymerization, the effect on ρ is small and on application of vacuum, the ρ vs. θ curves shift upwards, but, for y_g = 0.001, the curves cross each other at large times. It may be recalled that a smaller y_{MF_1} gives a larger value of $\Sigma_{i=1}^{\infty} [P_i]$ or average chain length of P_i. On the other hand, increased $\Sigma [P_i]$ in the reaction

mass and a high vacuum level increase the contribution of the cyclization reaction, thus lowering ρ for large θ, as seen in Figure 9.

In Figure 10, the temperature of the reaction mass has been varied and the polydispersity plotted as a function of time of polymerization. On the application of vacuum, the curves simply shift upwards.

CONCLUSIONS

The second stage of commercial PET reactors is known to be very complex. In this work, the overall polymerization process is assumed to consist of redistribution, reaction with monofunctional compound (cetyl alcohol) and cyclization reactions in addition to the usual polycondensation step. The reactions have been modelled in terms of the rate constants involving functional groups and reacted bonds for each of these reactions, and mass balance equations for polymer P_n, monofunctional compound MF_n, and cyclic compound C_n have been written. The experimental rate constants k_p, k'_p, and k_r of Challa have been used. MF_n have been assumed to behave kinetically the same as P_n, and k_m and k'_m have been taken as equal to k_p and k'_p. R_4 has been taken as a parameter and adjusted to give the total amount of cyclic compounds in any numerical run not exceeding about 5%.

With the rate constants decided above, the effects of the redistribution rate constant upon the MWD of the polymer has been studied. When polymerization is carried out under the condition that G is not allowed to escape, as in sealed tube experiments, R_6 is found to have no effect upon the MWD of the polymer formed. However, on the application of vacuum, the MWD is found to be affected by the choices of R_6, and their sensitivity to R_6 is found to increase with increasing degree of vacuum. It is further shown that R_6 is important when the cyclization reaction occurs in the reaction mass. When R_4 is equated to zero, R_6 has been found to have no effect on the molecular weight distribution.

On the application of vacuum, the ethylene glycol extent in the reaction mass reduces; to study its effect, y_g has been treated as a parameter, and variations in the MWD of the polymer have been calculated. The curves are first drastically affected but for y_g less than 0.01 change slowly, ultimately approaching the irreversible results.

The usual temperature of polymerization lies in the range of 254–300°C, and, in this range for reversible polymerizations, the effect is small. On the application of vacuum, the polydispersity index of the polymer is found to increase. Similarly, the choice of initial concentration of monofunctional compounds has small effect upon the MWD of the polymer.

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