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**CHEMICAL PROCESS SYSTEMS
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Catalyzed by Tetrabutyl Titanate

by

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Kinetics of Transesterification of Dimethyl Terephthalate With 1,4-Butanediol Catalyzed by Tetrabutyl Titanate

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Synopsis

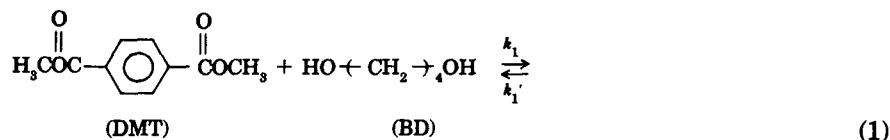
The kinetics of tetrabutyl titanate catalyzed transesterification of dimethyl terephthalate (DMT) with 1,4-butanediol (BD) is investigated. Detailed analysis of experimental data indicates that equal reactivity hypothesis for functional groups is valid for [BD]/[DMT] molar ratios greater than 2 up to 75% conversion. Effects of reaction temperature and catalyst concentration are also discussed.

INTRODUCTION

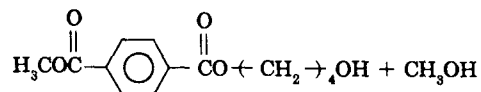
In recent years, there has been reported a remarkable progress in the development of new polymeric materials which exhibit superior performances over the conventional plastic materials in many engineering applications. A family of elastomers and reinforced plastics based on thermoplastic polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) is the fastest growing with an average annual growth rate of 14–18%.^{1–4} These new thermoplastics offer some very special combinations of properties—wide ranges of flexural moduli, hardness, toughness, abrasion resistance, heat and chemical resistances. Moreover, these materials are suitable for mass production of parts by high speed injection molding and extrusion processes.

Poly(ether ester) (PEE) is one of the most important new members of high performance engineering resins. PEE is the random block copolymer prepared by step growth melt polymerization of poly(ether terephthalate) and thermoplastic polyester precursors (e.g., PBT) in the presence of metal acetate catalyst. The first step of the polymerization is the transesterification of methyl ester groups of dimethyl terephthalate (DMT) with 1,4-butanediol (BD) and poly(ether glycol). The subsequent low pressure polymerization is carried out at 250–350°C. In order to tailor the polymer properties through improved reactor control, a deepened understanding of the reaction kinetics at each reaction stage is required.

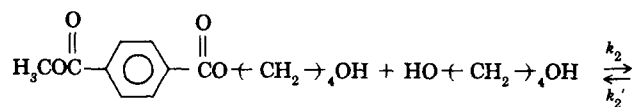
At the transesterification stage, the following main reactions occur in the presence of metal acetate catalyst:



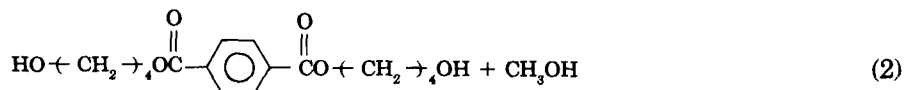
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(monohydroxybutylterephthalate, MHBT)

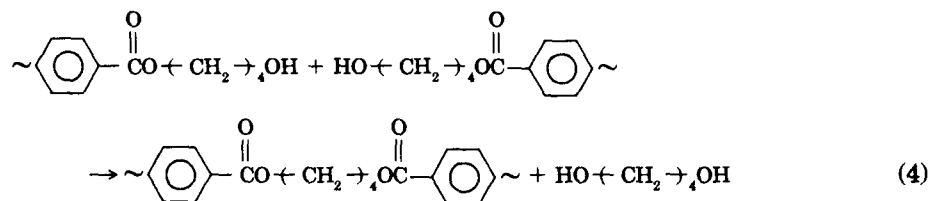
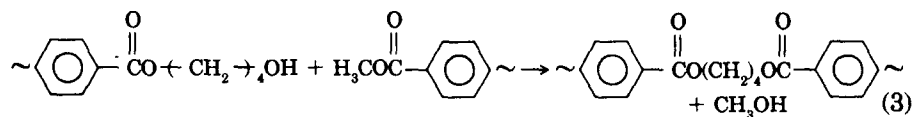


(MHBT)



(bishydroxybutylterephthalate, BHBT)

In addition to these reactions, the following oligomerization reactions may also occur:



It has been reported that for the transesterification of DMT with *ethylene glycol* (EG) in PET process, oligomerizations do not occur up to about 88% conversion when excess EG is used (i.e., EG/DMT > 2).⁵⁻⁹ As shown above, the transesterification reaction is essentially reversible reaction; however, the reaction can be promoted forward by removing methanol continuously from the reaction mixture. One of the issues in analyzing the kinetics of transesterification of DMT with diol (e.g., EG) is whether the reactive functional groups on various intermediates and reactants have equal reactivities. Although Peebles and Wagner⁶ report that the second step rate constants of the zinc-acetate-catalyzed transesterification of DMT with EG to produce bishydroxyethylterephthalate (BHET) is about three times greater than the rate constant of the first step, several other investigators^{5,7-10} report that methyl ester groups on DMT and MHET are equally reactive.

Unfortunately, there is a dearth of open literature on the kinetics of transesterification and polymerization of PBT and poly(ether ester) block copolymerization. In the following sections, we shall analyze the kinetics of tetrabutyltitanate-catalyzed transesterification of DMT with BD through

experimentation and kinetic modeling. Later papers in this series will deal with transesterification of DMT with poly(ether glycol) and low pressure block copolycondensation of PBT and polyether.

EXPERIMENTAL

Predetermined amount of DMT (Aldrich Chemical Co.) and 1,4-butanediol (BD) (Aldrich Chemical Co.) were weighed and added to a 125-mL glass reactor. Tetrabutyl titanate (Aldrich Chemical Co.) catalyst was mixed with 3 mL of pure BD and injected to the reactor containing molten DMT and BD. Upon addition of catalyst solution, methanol vapor evolved from the reactor almost immediately. The reaction was carried out under nitrogen atmosphere. A Vigreux distillation column was attached to the reactor in order to distill off the reaction byproduct, methanol. The column was maintained at approximately 100–120°C throughout the reaction. The methanol vapor was condensed and collected in a graduate cylinder, and the rate of methanol evolution was used to monitor the progress of transesterification. The standard reaction condition was as follows: temperature = 200°C, catalyst concentration = 3×10^{-4} mol/mol DMT, [BD]/[DMT] = 3 (mol ratio). All the experiments were duplicated to confirm the consistency of the data obtained, and the reproducibility was excellent.

RESULTS AND DISCUSSION

The three major parameters controlling the transesterification reaction are the [BD]/[DMT] mole ratio, temperature, and catalyst concentration. Although zinc acetate is widely used for the transesterification of DMT with ethylene glycol in the poly(ethylene terephthalate) (PET) process, our test of zinc acetate and tetrabutyl titanate indicates that the latter is the more efficient transesterification catalyst for the DMT–BD system.¹¹ Figure 1 shows the effect of [BD]/[DMT] molar ratio on the conversion of methylester group of DMT. Note that the reaction rate becomes slower with increase in [BD]/[DMT] ratio. Here, the conversion was estimated from the amount of methanol generated by the reaction. Gas chromatography analysis [with 20% Carbowax, 20M on Chrom-p 80/100 mesh] of the collected liquid indicated that the amount of BD in the condensates was negligibly small during the whole reaction period. The conversion levels off at about 90% conversion, probably due to the enhanced reverse reaction at high conversion of methyl ester groups. The reaction temperature has also a pronounced impact on the transesterification rate as indicated in Figure 2. The effect of catalyst concentration is illustrated in Figure 3. The catalyst concentrations chosen here are comparable with industrial reaction conditions. Note that the reaction rate is quite sensitive to the change in catalyst concentration. It has been observed that when nonuniform distribution of catalyst occurred in the reaction mixture due to inefficient mixing or rapid catalyst injection, vigorous evaporation of methanol took place, resulting in temperature fluctuation and entrainment of DMT and butanediol vapor to the distillation column.

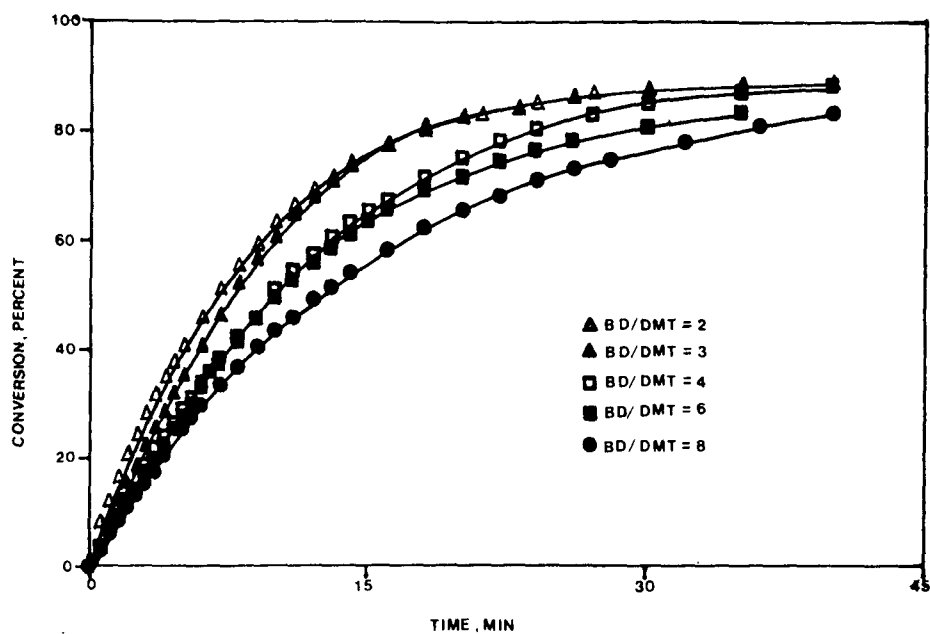


Fig. 1. Effect of different [BD]/[DMT] mole ratios on the conversion of methyl ester groups, 200°C, $[Ti[O(CH_2)_3CH_3]_4]/[DMT] = 3 \times 10^{-4}$: (Δ) 2; (\blacktriangle) 3; (\square) 4; (\blacksquare) 6; (\bullet) 8.

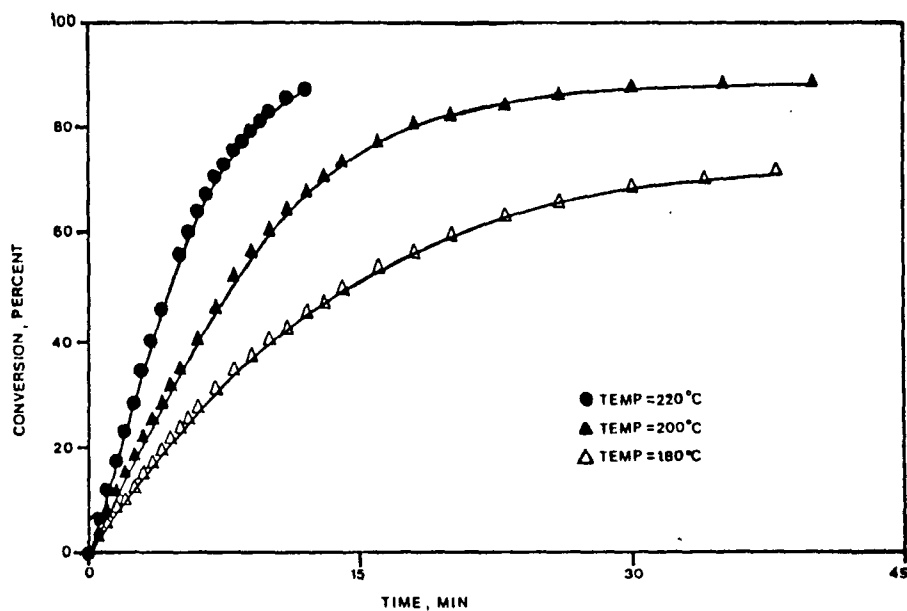


Fig. 2. Effect of different reaction temperatures ($^{\circ}C$) on the conversion of methyl ester groups: $[BD]/[DMT] = 3.0$, $[Ti[O(CH_2)_3CH_3]_4]/[DMT] = 3 \times 10^{-4}$: (\bullet) 220; (\blacktriangle) 200; (Δ) 180.

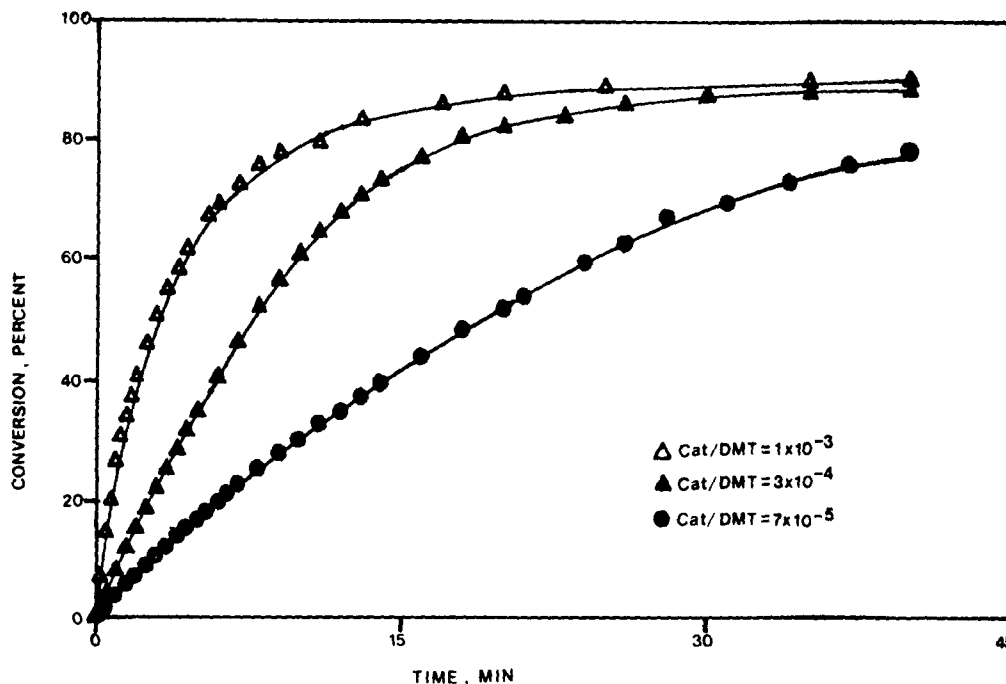


Fig. 3. Effect of catalyst concentration on the conversion of methyl ester groups, $[BD]/[DMT] = 3.0$, $T = 200^\circ\text{C}$. $[Cat]/[DMT]$: (Δ) 1×10^{-3} ; (\blacktriangle) 3×10^{-4} ; (\bullet) 7×10^{-5} .

DETERMINATION OF KINETIC PARAMETERS

Molecular Species Model

The two prominent reactions (1) and (2) may be written as follows in a simplified form:



where A is the DMT, B the 1,4-butanediol, C the monohydroxybutyl terephthalate (MHBT), D the methanol, and E the bishydroxybutyl terephthalate (BHBT). Here, the reverse reactions have been ignored based on the assumption that methanol is removed efficiently from the reaction mixture. Also ignored are side reactions and oligomerization. Then, the rate expressions for both reactions take the form

$$r_1 \triangleq \frac{1}{V} \frac{d\xi_1}{dt} = k_1 \frac{n^* n_A n_B}{V V V} \quad (7)$$

$$r_2 \triangleq \frac{1}{V} \frac{d\xi_2}{dt} = k_2 \frac{n^* n_B n_C}{V V V} \quad (8)$$

where ξ_1 and ξ_2 represent the extent of reaction of (5) and (6), respectively.

V is the volume of reaction mixture, n^* the number of moles of catalyst, and n_j the number of moles of species j .

The rate expressions for the change in the number of moles of A (DMT) and C (MHBT) are represented by

$$\frac{1}{V} \frac{dn_A}{dt} = -k_1 \frac{n^* n_A n_B}{V V V} \quad (9)$$

$$\frac{1}{V} \frac{dn_C}{dt} = k_1 \frac{n^* n_A n_B}{V V V} - k_2 \frac{n^* n_B n_C}{V V V} \quad (10)$$

Note that the effective catalyst concentration (n^*/V) varies during the reaction due to the decrease in reaction volume. By assuming equal reactivities for the methyl ester groups of A and C (i.e., $k_1 = 2k_2$), one can simplify eqs. (9) and (10) as follows:

$$\frac{dn_C}{dn_A} = -1 + \frac{1}{2} \left(\frac{n_C}{n_A} \right) \quad (11)$$

Upon integration of eq. (11), we obtain

$$n_C = 2n_A \left[\left(\frac{n_{A0}}{n_A} \right)^{1/2} - 1 \right] \quad (12)$$

Now, from the mass balances of DMT, BD, and methanol

$$n_{A0} = n_A + n_C + n_E \quad (13)$$

$$n_{B0} = n_B + n_C + 2n_E \quad (14)$$

$$n_D = n_{B0} - n_B \quad (15)$$

we obtain

$$n_B = n_{B0} - n_D \quad (16)$$

$$n_C = 2(n_{A0} - n_A) - n_D \quad (17)$$

$$n_E = n_A - n_{A0} + n_D \quad (18)$$

From eqs. (12) and (17) we get

$$n_A = \frac{(2n_{A0} - n_D)^2}{4n_{A0}} \quad (19)$$

Here, n_{A0} and n_{B0} represent initial number of moles of A and B, respectively. Since the rate of transesterification is estimated from the rate of methanol (D) evolution, the following equation is useful to describe the rate of reaction:

$$\frac{dn_D}{dt} = k_1 \frac{n^*}{V^2} (n_A n_B + 0.5 n_B n_C) \quad (20)$$

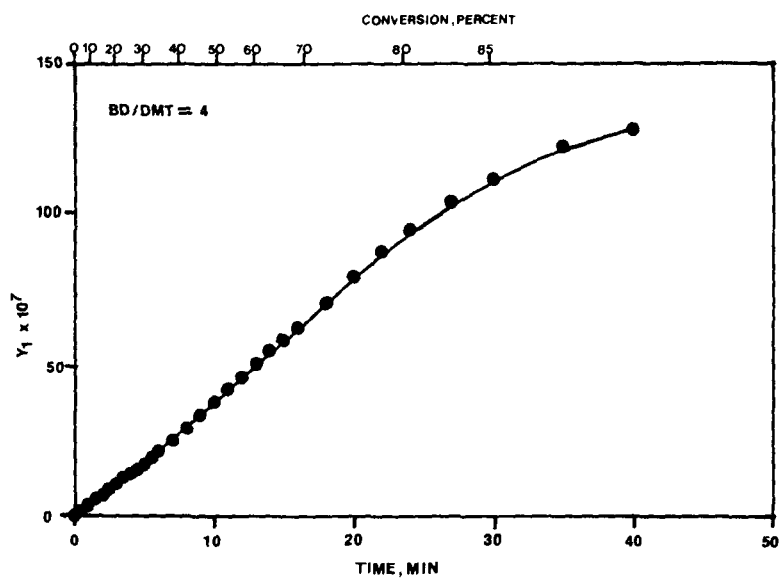
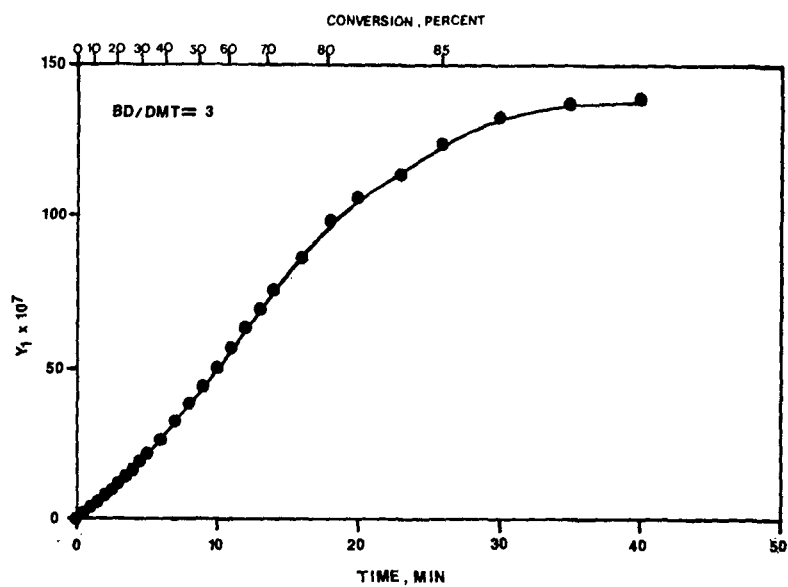


Fig. 4. (Continued from previous page.)

Here, the volume of reaction mixture is given by

$$V = V_0 - n_D/\rho_D \quad (21)$$

where V_0 is the initial reactor volume and ρ_D the molar density of methanol. Then, the volume of methanol collected is $V_D = n_D/\rho_D$. Therefore, after integrating eq. (20), we obtain

$$Y_1 = \int_0^{V_D} \left(\rho_D (V_0 - V_D)^2 \left[n^* \left(\frac{(2n_{A0} - \rho_D V_D)^2}{4n_{A0}} (n_{B0} - \rho_D V_D) \right) + \frac{1}{2} (n_{B0} - \rho_D V_D) \left[2 \left(n_{A0} - \frac{(2n_{A0} - \rho_D V_D)^2}{4n_{A0}} \right) - \rho_D V_D \right] \right] \right) dV_D = k_1 t \quad (22)$$

Experimental data for different values of [BD]/[DMT] ratio shown in Figure 1 have been tested with eq. (22) and the results are shown in Figure 4. Note that the model fits the experimental data very well up to about 75% conversion for high [BD]/[DMT] ratios; however, a considerable deviation from the model occurs even at lower conversion level when the [BD]/[DMT] ratio is small. Reaction rate constants (k_1 and k_2) estimated from eq. (22) are given in Table I. Comparison with kinetic constants for *zinc-acetate*-catalyzed transesterification of DMT with *ethylene glycol* (i.e., $k_1 = 3.4 \times 10^7$ mL²/mol² min, $k_2 = 1.65 \times 10^7$ mL²/mol² min at 200°C¹⁰) indicates that the transesterification of DMT with 1,4-butanediol is faster than the former when tetrabutyltitanate catalyst is used.

Optimal Parameter Search Method

In the molecular species model described above, it was assumed that reactivities of all methyl ester groups on A and C are equal. In this section, the two rate constants for the transesterification of DMT with 1,4-butanediol

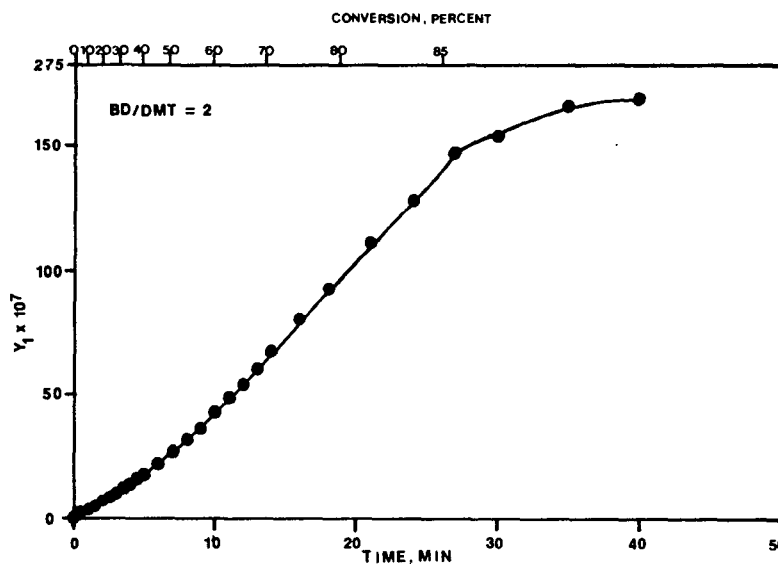


Fig. 4. Test of equal reactivity hypothesis (molecular species model): $T = 200^\circ\text{C}$, $[\text{Ti}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4]/[\text{DMT}] = 3 \times 10^{-4}$.

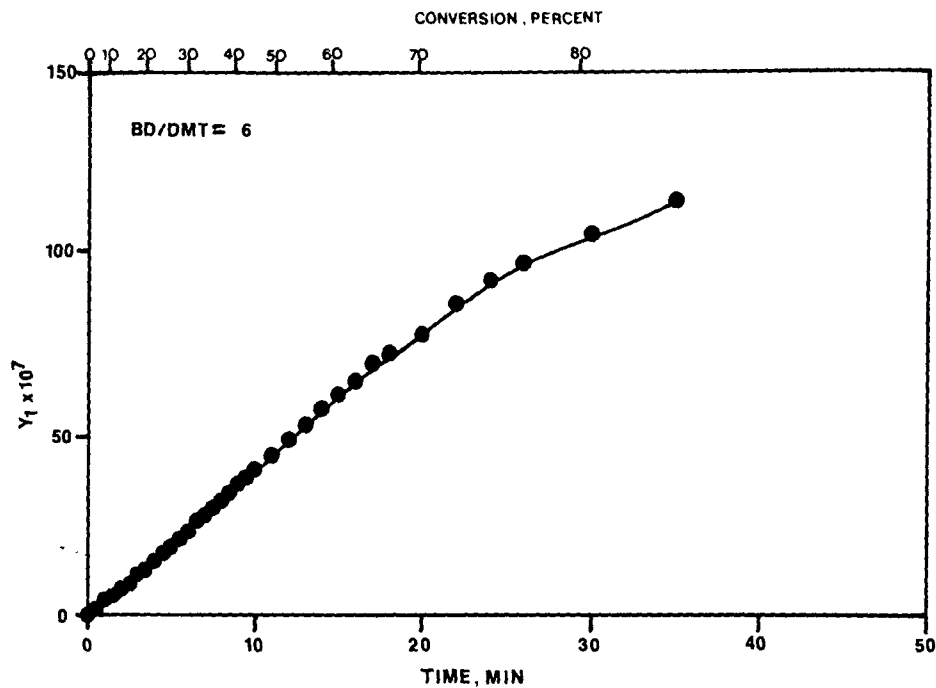


Fig. 4. (Continued from previous page.)

(BD) will be determined without invoking the equal reactivity hypothesis. Using eqs. (7) and (8), one obtains

$$\frac{dV_D}{dt} = \frac{k_1 n^* n_A n_B + k_2 n^* n_B n_C}{\rho_D (V_0 - n_D / \rho_D)^2} \quad (23)$$

where V_D denotes the volume of methanol evolved (i.e., $V_D = n_D / \rho_D$). n_A , n_B , n_C , and n_D can be rewritten in terms of ξ_1 and ξ_2 as follows:

$$\begin{aligned} n_A &= n_{A0} - \xi_1 \\ n_B &= n_{B0} - \xi_1 - \xi_2 \\ n_C &= \xi_1 - \xi_2 \\ n_D &= \xi_1 + \xi_2 \end{aligned} \quad (24)$$

TABLE I
Kinetic Parameters by the Molecular Species Model^a

[BD]/[DMT] (mol/mol)	k_1 (mL ² /mol ² min)	k_2^b (mL ² /mol ² min)	Range of % conversion chosen for computation
2	5.7×10^7	2.8×10^7	63
3	4.6×10^7	2.3×10^7	60
4	4.0×10^7	2.0×10^7	75
6	4.1×10^7	2.0×10^7	72

^a Temperature = 200°C, catalyst/DMT = 3.0×10^{-4} (mol/mol).

^b $k_2 = k_1/2$.

Then eqs. (7), (8), and (23) become

$$\frac{d\xi_1}{dt} = \Gamma k_1 n^* (n_{A0} - \xi_1)(n_{B0} - \xi_1 - \xi_2) \quad (25)$$

$$\frac{d\xi_2}{dt} = \Gamma k_2 n^* (n_{B0} - \xi_1 - \xi_2)(\xi_1 - \xi_2) \quad (26)$$

$$\begin{aligned} \frac{dV_D}{dt} = \frac{\Gamma}{\rho_D} [k_1 n^* (n_{A0} - \xi_1)(n_{B0} - \xi_1 - \xi_2) \\ + k_2 n^* (n_{B0} - \xi_1 - \xi_2)(\xi_1 - \xi_2)] \end{aligned} \quad (27)$$

where

$$\Gamma \equiv [V_0 - (\xi_1 + \xi_2)/\rho_D]^{-2}$$

During the early reaction period (i.e., $t \simeq 0$), we may assume that the second reaction [eq. (6)] does not proceed to a considerable extent. Thus, eq. (27) can be simplified to the following form:

$$\left. \frac{dV_D}{dt} \right|_{t=0} = \frac{k_1 n^* n_{A0} n_{B0}}{\rho_D V_0^2} \quad (28)$$

Thus, one can estimate k_1 by extrapolating V_D vs. time curve to $t = 0$. Table II shows the values of the rate constant k_1 for different [BD]/[DMT] ratios. Note that k_1 values in Table II agree quite well with those k_1 values determined by molecular species model. With average value of k_1 (i.e., $k_1 = 4.28 \times 10^7$ mL²/mol² min), the second rate constant k_2 has been estimated for various reaction conditions by a modified multivariable simplex search technique, in which the following objective function was minimized:

$$P = \sum_i (V_D - V_{D,\text{exp}})^2 \quad (29)$$

where $V_{D,\text{exp}}$ denotes the volume of methanol measured experimentally. The details of the computational procedure can be found in Ref. 11. Note that for [BD]/[DMT] > 2, estimated values of k_2 (in third column of Table

TABLE II
Kinetic Parameters Determined by Optimal Search Method

[BD]/[DMT] (mol/mol)	k_1 ($t=0$) (mL ² /mol ² min)	k_2^a (mL ² /mol ² min)	k_2^b (mL ² /mol ² min)
2	5.5×10^7	4.95×10^7	
3	3.8×10^7	1.45×10^7	2.01×10^7
4	3.8×10^7	1.55×10^7	1.87×10^7
6	4.0×10^7	1.84×10^7	2.27×10^7
Avg.	4.28×10^7	2.45×10^7	2.05×10^7

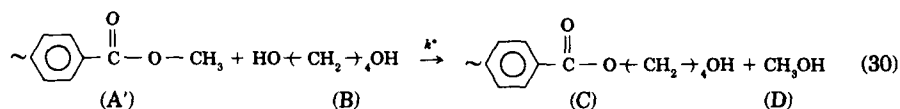
^a $k_1 = 4.28 \times 10^7$ was used.

^b $k_1 = 3.87 \times 10^7$ (average of k_1 's for [BD]/[DMT] = 3, 4, 6) was used.

II) are essentially constant; however, the predicted value of k_2 for low [BD]/[DMT] ratio (e.g., 2) is considerably higher than others. It has been well known that, in catalytic transesterification of DMT with diols, some side reactions and oligomerizations may occur when the [BD]/[DMT] ratio is low. Therefore, we reestimated k_2 using the data obtained for [BD]/[DMT] ≥ 3 , and the result is shown in the fourth column of Table II. Note that k_1 and k_2 estimated by the optimal search technique are in good agreement with those obtained by the molecular species model, in which the equal reactivity hypothesis was employed (cf. Table I).

Functional Group Model

Since the transesterification is the reaction between the methyl ester group and hydroxyl group, one may view the reaction as follows:



The rate equation is thus given by

$$\frac{d\xi^*}{dt} = k^* \frac{n^*(n_{A0} - \xi^*)(n_{B0} - \xi^*)}{V^2} \quad (31)$$

Let us define the fractional conversion of methyl ester group (A') as

$$f_A \triangleq \frac{n_{A0} - n_A}{n_{A0}} \quad (32)$$

Then, eq. (31) can be rewritten as follows:

$$\frac{df_A}{dt} = k^* \frac{n^* n_{B0} (1 - f_A) [1 - (n_{A0}/n_{B0}) f_A]}{[V_0 - (n_{A0}/\rho_D) f_A]^2} \quad (33)$$

Upon integration,

$$\begin{aligned} Y_2 = & \frac{V_0^2}{n_{B0} n^*} \left(\frac{1}{1 - \gamma} \ln \left(\frac{1 - \gamma f_A}{1 - f_A} \right) - \frac{2n_{A0}}{V_0^2 \rho_D (1 - \gamma)} \right. \\ & \left. \left[-\ln(1 - f_A) + \frac{1}{\gamma} \ln(1 - \gamma f_A) \right] + \left(\frac{n_{A0}}{V_0^2 \rho_D} \right)^2 \right. \\ & \left. \left[\frac{1}{(1 - \gamma)(1 - f_A)} - \frac{1}{1 - \gamma} + \frac{1}{(1 - \gamma)^2} \left[-\frac{1}{\gamma} \ln(1 - \gamma f_A) \right. \right. \right. \\ & \left. \left. \left. + (2 - \gamma) \ln(1 - f_A) \right] \right] \right) = k^* t \end{aligned} \quad (34)$$

where

$$\gamma \equiv n_{A0}/n_{B0}$$

Figure 5 shows the test result of eq. (34) for the experimental data. Again, the linearity becomes poor at high conversion, particularly for low [BD]/[DMT] ratios. The average value of k^* is $2.28 \times 10^7 \text{ mL}^2/\text{mol}^2 \text{ min}$, which is very close to the k_2 values obtained from (B) and (C). This indicates that methyl ester groups on DMT and MHBT have equal reactivities for [BD]/[DMT] > 2 and up to about 75% conversion with tetrabutyl titanate as a catalyst.

The composition of the reaction mixture during the transesterification has been calculated and is illustrated graphically in Figure 6. It is interesting to note that even at high conversion (e.g., 80%) of methyl ester groups, a substantial amount of partially transesterified DMT (MHBT) exists in the

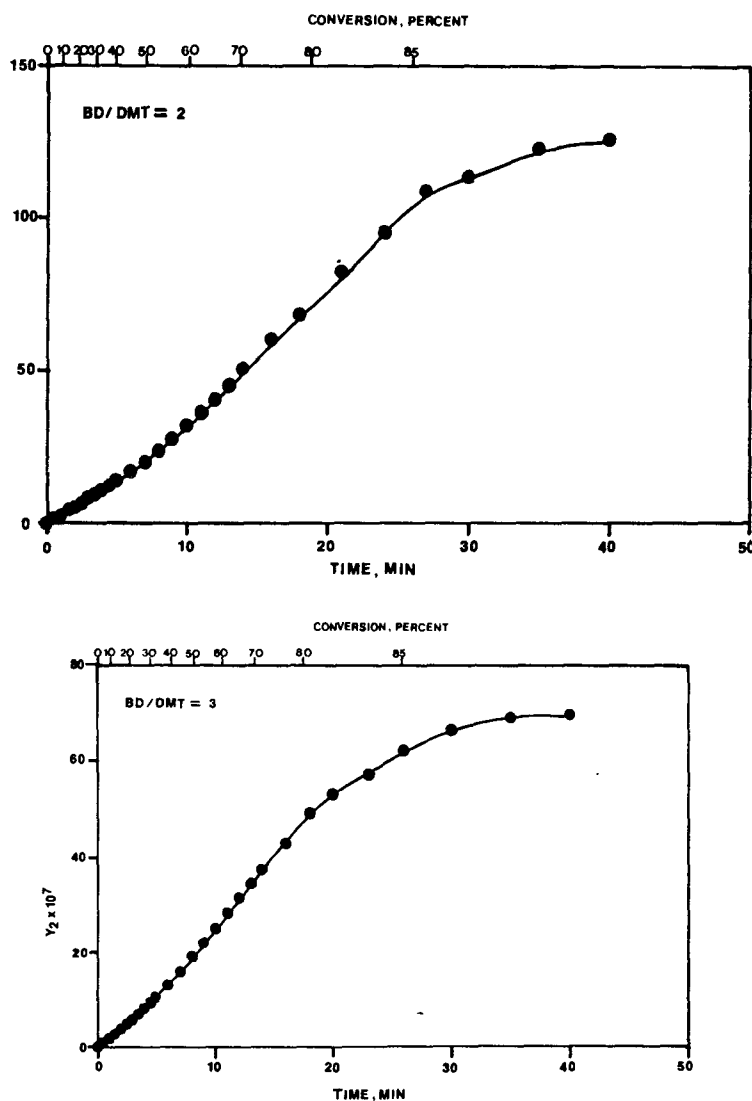


Fig. 5. Test of functional group model [eq. (34)]: $T = 200^\circ\text{C}$, $[\text{Ti}(\text{OCH}_2)_3\text{CH}_3]_0/[\text{DMT}] = 3 \times 10^{-4}$.

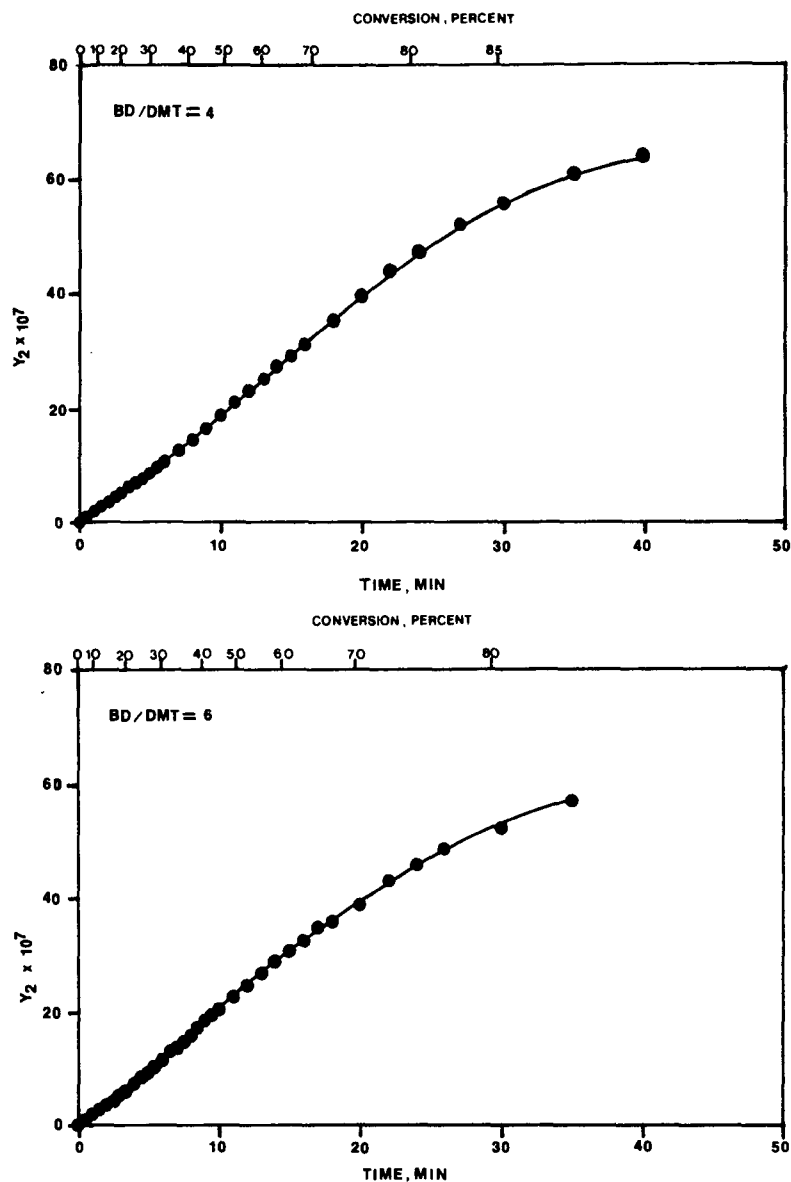


Fig. 5. (Continued).

reaction mixture. Thus, in order to obtain high conversion of DMT to BHBT, the transesterification should be conducted more than 60 min.

The temperature dependency of the rate constants is illustrated in Figure 7. From this Arrhenius plot, the following rate expressions have been obtained:

$$k_1 = 6.22 \times 10^{11} \exp(-9140/RT) \text{ (mL}^2/\text{mol}^2 \text{ min)} \quad (35)$$

$$k_2 = 3.18 \times 10^{11} \exp(-9140/RT) \text{ (mL}^2/\text{mol}^2 \text{ min)} \quad (36)$$

where the activation energies are in cal/mol.

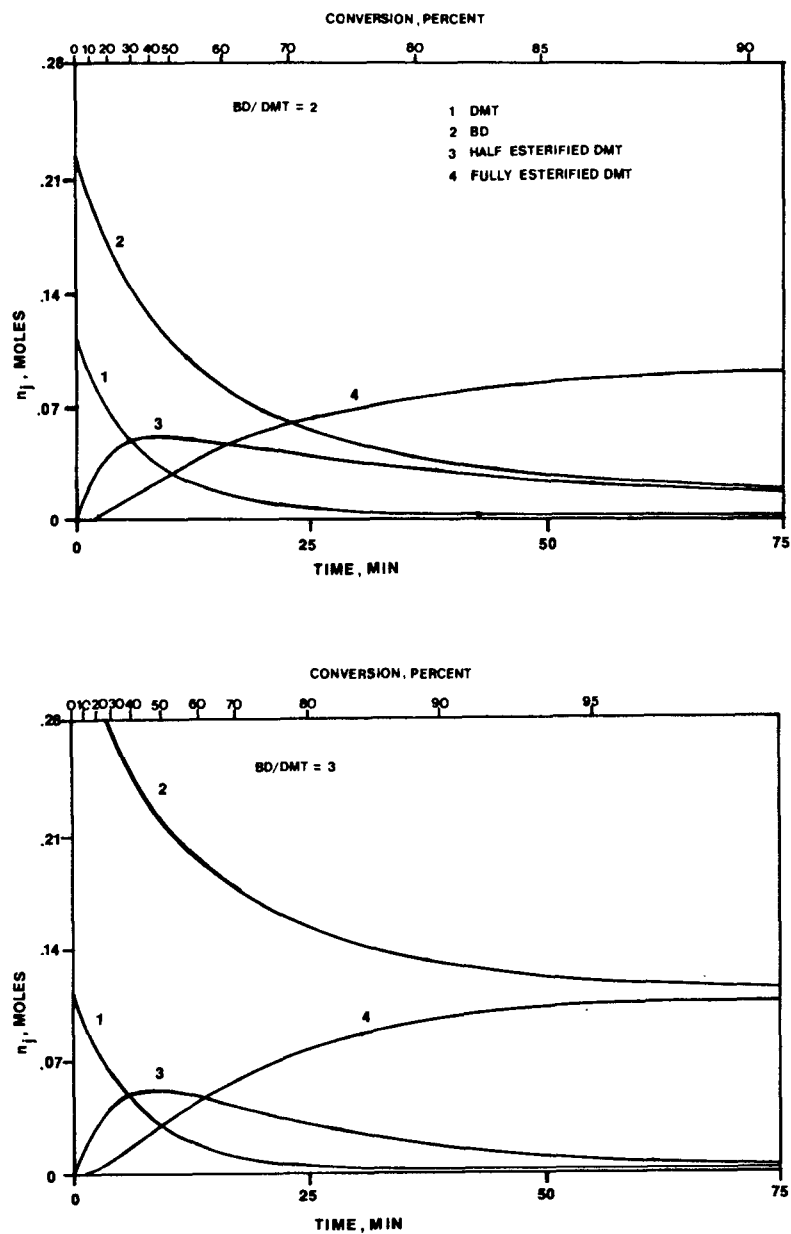


Fig. 6. Effect of $[BD]/[DMT]$ ratio on the product distribution of transesterification reaction: $T = 200^\circ\text{C}$, $k_1 = 4 \times 10^7$, $k_2 = 2 \times 10^7$: (1) DMT; (2) BD; (3) half-esterified DMT; (4) fully esterified DMT.

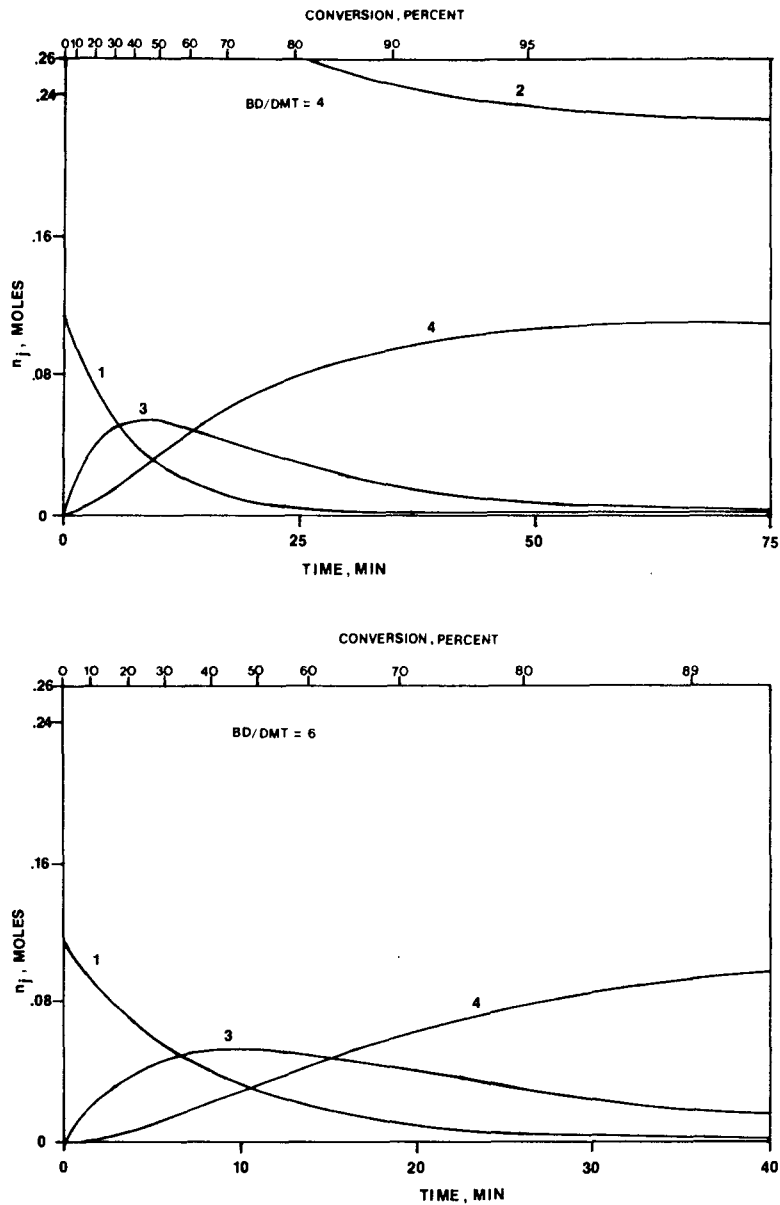


Fig. 6. (Continued from previous page.)

CONCLUDING REMARKS

The kinetics of semibatch transesterification of dimethylterephthalate with 1,4-butanediol in the presence of tetrabutyl titanate catalyst was studied at 180–220°C. Three different methods were used to estimate the transesterification rate constants, and the equal reactivity hypothesis was found to be valid for the reaction system when excess 1,4-butanediol was used

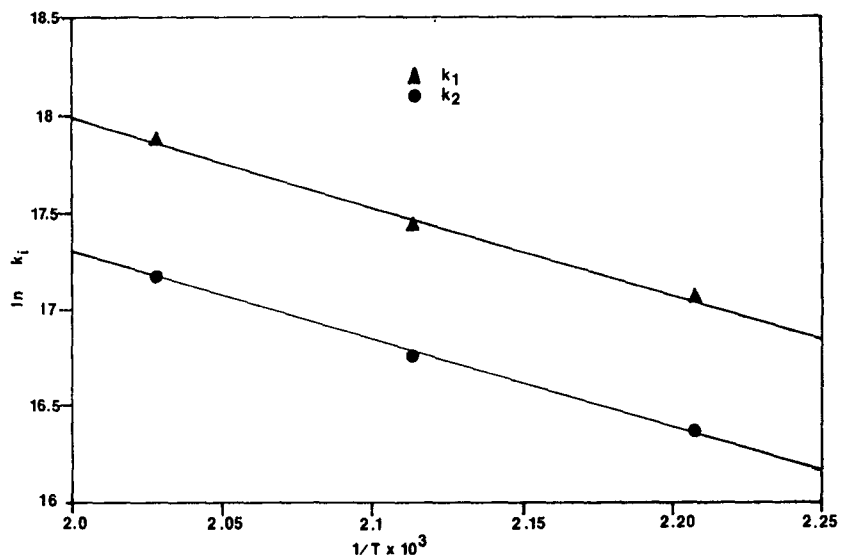


Fig. 7. Arrhenius plots for rate constants k_1 and k_2 (●), $[BD]/[DMT] = 3.0$, $[Ti(OCH_2)_3]_4/[DMT] = 3 \times 10^{-4}$.

(i.e., $[BD]/[DMT] > 2$). The conversion of methyl ester groups was also strongly influenced by reaction temperature and catalyst concentration.

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