Formation of poly(butylene terephthalate): growing reactions studied by model molecules

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The growing reactions in the formation of poly(butylene terephthalate) have been studied from a kinetic viewpoint with the aid of model molecules. The dependence of the reaction rates on temperature and on the presence of a catalyst (titanium tetrabutylate) and/or of benzoic acid, which shows an inhibition effect, are discussed. A coordinative reaction mechanism is suggested.

INTRODUCTION

The reactions taking place during the formation of poly(butylene terephthalate) have been investigated[1-4]. Recently, we have extended this research with the aid of model molecules: 4-hydroxybutyl benzoate was chosen as 'monomer', 1,4-butylene dibenzoate as 'polymer'. The model system can adequately be used to study the kinetics of polycondensation reactions. The following set of reactions was considered:

$$2\,C_6H_5{-}COO(CH_2)_4OH \rightleftharpoons HO(CH_2)_4OH + C_6H_5{-}COO(CH_2)_4OCO{-}C_6H_5 \quad (1)$$

$$C_6H_5{-}COO(CH_2)_4OH \rightarrow C_6H_5COOH + (CH_2)_4O \quad (2)$$

$$HO(CH_2)_4OH \rightarrow H_2O + (CH_2)_4O \quad (3)$$

$$C_6H_5{-}COO(CH_2)_4OH + C_6H_5COOH \rightleftharpoons H_2O + C_6H_5{-}COO(CH_2)_4OCO{-}C_6H_5 \quad (4)$$

$$HO(CH_2)_4OH + C_6H_5COOH \rightleftharpoons H_2O + C_6H_5{-}COO(CH_2)_4OH \quad (5)$$

$$C_6H_5{-}COO(CH_2)_4OCO{-}C_6H_5 \rightarrow C_6H_5COOH + CH_2{=}CH(CH_2)_2OCO{-}C_6H_5 \quad (6)$$

$$C_6H_5{-}COO(CH_2)_2CH{=}CH_2 \rightarrow C_6H_5COOH + CH_2{=}CH{-}CH{=}CH_2 \quad (7)$$

where, in addition to the main reaction (1) and to the 'useful' reactions (4) and (5), we can recognise the 'undesired' reactions, leading to lower yields and to products of poorer quality. Among these reactions, the formation of tetrahydrofuran (2), (3), and thermal degradation, which brings about a decrease in molecular weight and an increase in the number of carboxyl groups (6), (7), are readily noted.

Here, we take into account the reactions (1), (4) and (5), which have been examined in the temperature range 150° to 190°C, both in the presence and in the absence of titanium tetrabutylate, a widely used polycondensation catalyst.

EXPERIMENTAL

4-Hydroxybutyl benzoate (HBB)

Benzoyl chloride (1 mol) was added dropwise to a solution of 1,4-butanediol (4 mol) in anhydrous pyridine (1.1 mol) in a flask equipped with a magnetic stirrer. Stirring was continued for several hours at room temperature. The reaction mixture was extracted with $CHCl_3$, repeatedly washed with water, and dried over anhydrous sodium sulphate. The mixture was evaporated to dryness in a rotoevaporator and the crude product was twice distilled at reduced pressure (Kp_{3mm}159°–162°C). It was characterized by ^1H n.m.r., i.r., *HP*-l.c. and benzoic acid titration.

1,4-butylene dibenzoate (BDB)

A solution of 1,4-butanediol (1 mol) in ether was added dropwise to a solution of benzoyl chloride (2.2 mol) and pyridine (2.1 mol) in a flask equipped with a magnetic stirrer. Stirring was continued for several hours at room temperature. The mixture was extracted with chloroform as described above for 4-hydroxybutyl benzoate, and butanediol dibenzoate was recovered by repeated crystallization. The product was characterized by the techniques already mentioned.

Reagent grade anhydrous benzoic acid (BA) was used as supplied by Merck; 1,4-butanediol (BD) and titanium tetrabutylate were commercial products: they were distilled at reduced pressure before use.

For kinetic and equilibrium experiments homogeneous samples were introduced into glass tubes (6 mm internal diameter) in a dry box. They were weighted and sealed under a reduced pressure of nitrogen, and then placed in a constant temperature (± 0.1°C) oil bath.

After appropriate time intervals, the tubes were removed and quenched in an ice bath. They were broken and the mixtures dissolved in a suitable solvent.

HP-l.c. analysis

Measurements were carried out on a Perkin–Elmer Series 2 *HP*-l.c. instrument, equipped with a LC-65T u.v. detector fixed at 254 nm. A ODS-HC SIL-X-1 0,26 × 25 cm column was employed. Samples were dissolved in weighed amounts of an acetonitrile/naphthalene solution, and eluted with a mixture of acetonitrile and water (40/60 by vol) at 1.0 ml min^{-1} flow rate; the temperature of the column was kept at 45°C. Under such conditions benzoic acid, 4-hydroxybutyl benzoate, naphthalene (used as internal standard) and butanediol dibenzoate were eluted in about 10 min. The amounts of 4-hydroxybutyl benzoate and butanediol dibenzoate were measured by the internal standard calibration method.

Titrations

Benzoic acid content could not be evaluated by *HP*-l.c., because of unsatisfactory analytical reproducibility. It was determined by titration with an alcoholic solution of NaOH (phenol red as indicator).

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RESULTS AND DISCUSSION

Figure 1 collects the results for the formation of 'polymer' BDB (reaction 1). In the temperature range examined the reaction does not take place to a significant extent in the catalyst-free samples, but occurs at a measurable rate when catalyst is present. It can be noted that the addition of small amounts of benzoic acid brings about a slight rate increase in the absence of $Ti(OBu)_4$, but shows a strong inhibiting effect in the presence of the catalyst. An analogous effect has been described for the reaction between model molecules of poly(ethylene terephthalate) catalysed by compounds of lead, zinc and magnesium[5].

Under our operating conditions the reaction clearly tends to equilibrium. The limiting concentration of BDB is practically independent of the temperature: this is consistent with the fact that the reaction enthalpy is negligibly small. It is also increased by the presence of benzoic acid.

Secondary reactions (2), (3), (6) and (7) were found elsewhere[1] to be slower than (1) by some orders of magnitude, provided that catalyst was present and temperature was not too high; under these conditions reaction (1) may be assumed to be reversible and unperturbed by other processes.

If we assume that direct and reverse reaction (1) are both second order in their respective reagents, we obtain:

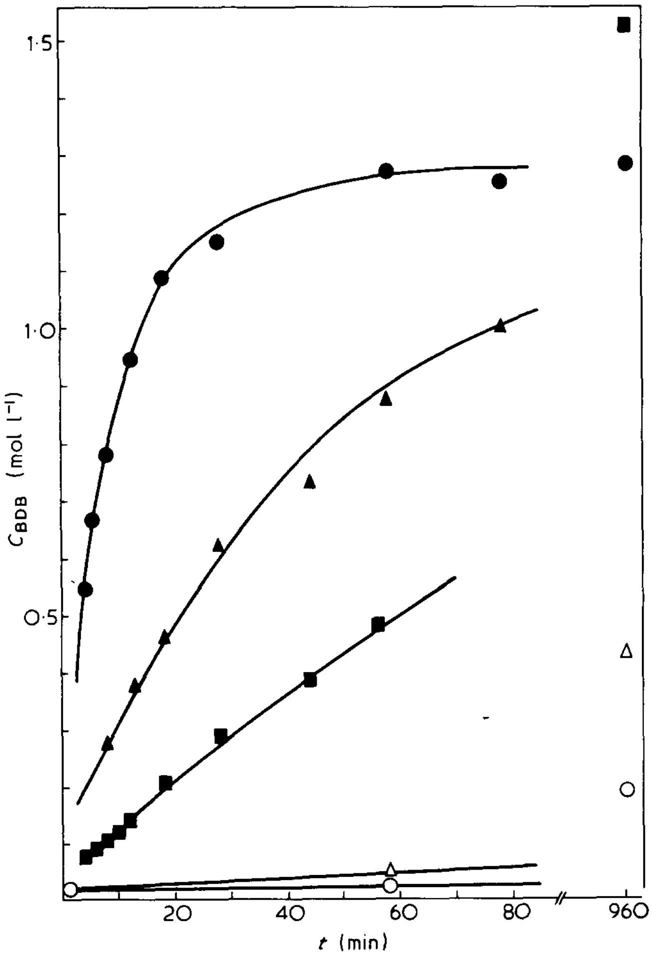


Figure 1 Formation of BDB at 167°C with catalyst ($Ti(OBu)_4$, 2.25×10^{-1} g kg^{-1}): ●, from HBB; ▲, from HBB + BA 1.5 mol %; ■, from HBB + BA 21.5 mol %. Without catalyst: ○, from HBB; △, from HBB + BA 1.5 mol %

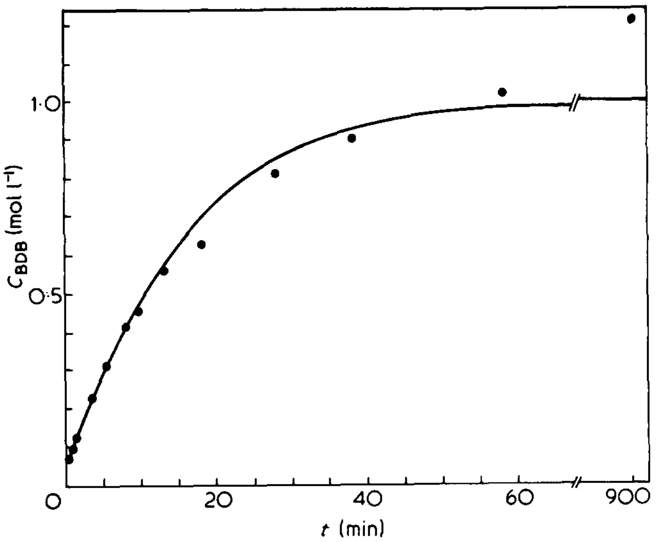


Figure 2 Formation of BDB (reaction 1): ●, experimental data obtained at 150°C in the presence of $Ti(OBu)_4$ (2.25×10^{-1} g kg^{-1}) compared with the calculated curve (——)

$$-\frac{1}{2}\frac{d[HBB]}{dt}=\frac{d[BDB]}{dt}=k_1[HBB]^2-k_1'[BDB][BD]$$

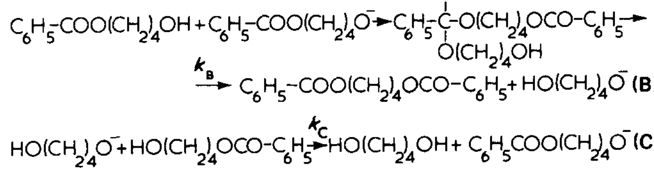
k_1 and k_1' are the rate constants for the direct and reverse processes, respectively.

This kinetic equation has been integrated (see Appendix) and the results are given in *Figure 2*, where the experimental data describing the formation of BDB at 150°C in the presence of the catalyst are shown along with the curve obtained using the mathematical treatment. The agreement is good, at least until the reaction approaches equilibrium; the asymptotic value of the experimental BDB concentration is somewhat higher than the calculated one. This may be explained as being due to the formation of small amounts of benzoic acid from reactions (2) and (3), since benzoic acid, in the presence of the catalyst increases the maximum attainable BDB concentration, despite its negative effect on the rate (see *Figure 1*).

The order of reaction over a wide temperature range has been determined for the catalyst with the aim of interpreting the mechanism of the catalysed reaction (1). This mechanism is generally described in the literature in terms of coordination[6-9] of the transition metal to the carbonyl group, or alternatively of basic catalysis[10-11].

In *Figure 3* the logarithm of the initial rate of formation of BDB from HBB is plotted *versus* the logarithm of the catalyst concentration. We obtain a reaction order of 0.9 over the whole temperature range (between 150° and 200°C).

With regard to the mechanism of basic catalysis, if we assume, in accordance with the literature, that the catalyst reacts with HBB and replaces completely or in part the butoxy groups (this is reasonable, in view of their concentration ratio), the following steps may be suggested:



$$-\overset{|}{\underset{|}{Ti}}-O(CH_2)_4OCO-C_6H_5 \overset{k_A}{\rightleftharpoons} -\overset{|}{\underset{|}{Ti}}^{+} + C_6H_5COO(CH_2)_4O^- \quad (A)$$

$$C_6H_5-COO(CH_2)_4OH + C_6H_5-COO(CH_2)_4O^- \rightarrow C_6H_5-\overset{O^-}{\underset{O(CH_2)_4OH}{\overset{|}{\underset{|}{C}}}}-O(CH_2)_4OCO-C_6H_5 \xrightarrow{k_B} C_6H_5-COO(CH_2)_4OCO-C_6H_5 + HO(CH_2)_4O^- \quad (B)$$

$$HO(CH_2)_4O^- + HO(CH_2)_4OCO-C_6H_5 \xrightarrow{k_C} HO(CH_2)_4OH + C_6H_5COO(CH_2)_4O^- \quad (C)$$

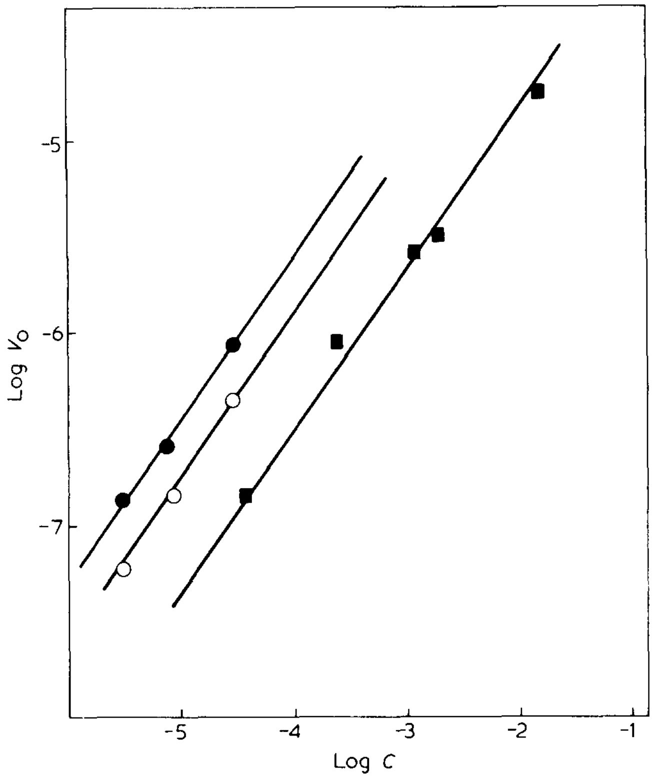


Figure 3 Dependence of the initial rates of reaction (1) at different temperatures on the catalyst (Ti(OBu)$_4$) concentration: ■, T = 150°C; ○, T = 200°C; ●, T = 220°C

Step (A) can be always considered as an equilibrium; steps (B) and (C) may be assumed to be initially irreversible, because of the high concentration of HBB and the lacking of BDB. If we put $k_B \ll k_C$, which is reasonable, the steady state condition may be applied to the BD^- ion: its concentration will always be low, and negligible in comparison with that of the HBB^- ion. Therefore

$$[HBB^-] \cong [Ti^+]$$

and

$$K_A = \frac{[Ti^+][HBB^-]}{[Cat]}$$

Consequently:

$$K_A = \frac{[HBB^-]^2}{[Cat]_0 - [HBB^-]};$$

Since the value of K_A is presumably low, $[HBB^-]$ is negligibly small in comparison with [Cat], so that:

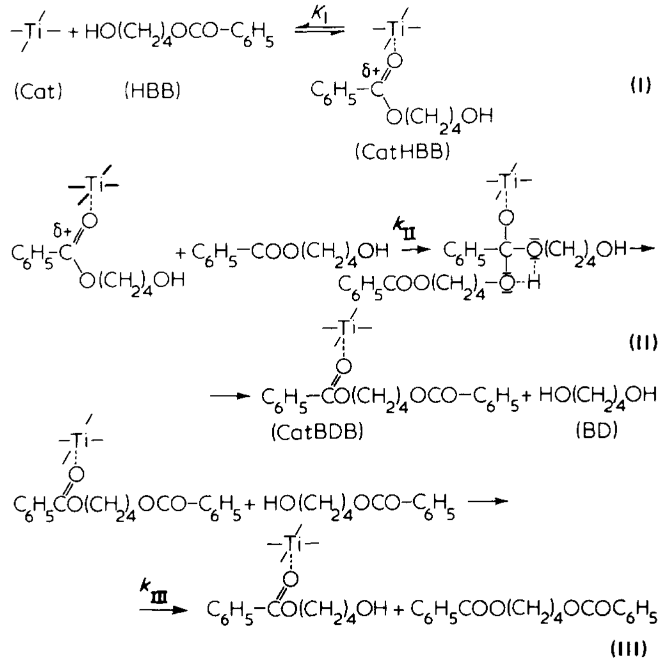
$$K_A = \frac{[HBB^-]^2}{[Cat]_0}; \quad [HBB^-] = (K_A[Cat]_0)^{1/2}$$

Therefore, the rate of formation of BBB will be

$$\frac{d[BDB]}{dt} = k_B[HBB][HBB^-] = k_B\, K_A^{1/2}[Cat]_0^{1/2}[HBB]$$

Hence, under the initial conditions, the reaction should be first order with respect to HBB and of order 0.5 with respect to the catalyst.

If the mechanism of catalysis should involve a coordination at the titanium atom, the following mechanism may be considered:



Step (I) can be assumed to be an equilibrium reaction, whereas steps (II) and (III) can be taken as being initially irreversible, because of the high concentration of HBB and the deficiency of BDB and BD. If we suppose $k_{II} \ll k_{III}$, the steady state condition leads to:

$$k_{II}[CatHBB][HBB] = k_{III}[CatBDB][HBB]$$

$$[CatBDB] = \frac{k_{II}}{k_{III}}[CatHBB]$$

and:

$$K_I = \frac{[CatHBB]}{[Cat][HBB]}$$

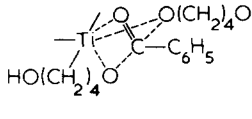
$$[CatHBB] = K_I[Cat][HBB]$$

$$[CatBDB] = K_I\frac{k_{II}}{k_{III}}[Cat][HBB]$$

The rate of formation of BDB will be:

$$\frac{d[BDB]}{dt} = k_{III}[CatBDB][HBB] = K_I k_{II}[Cat][HBB]^2$$

Under the initial conditions the reaction should be second order with respect to HBB and first order with respect to the catalyst. If we assume that the catalyst has replaced the butoxy groups completely or in part (as already postulated for basic catalysis) almost the same results are obtained. In this case a reactive intermediate might be drawn as follows:



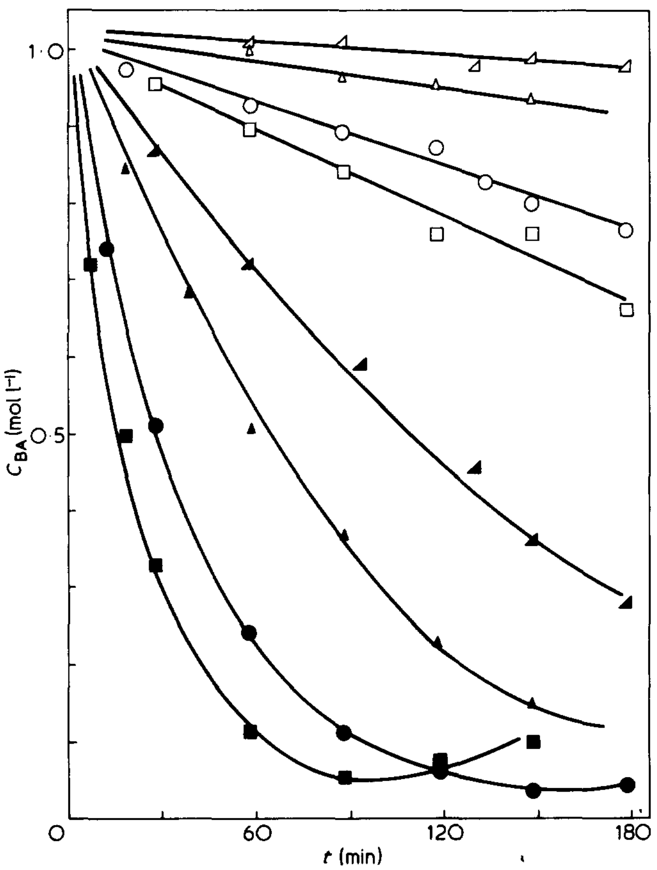


Figure 4 Reaction of BA with BD (reaction 5) at different temperatures. With catalyst (Ti(OBu)$_4$, 2.25 x 10^{-1} g kg^{-1}): ◢, T = 158°C; ▲, T = 167°C; ●, T = 180°C; ■, T = 190°C. Without catalyst: ◿, T = 158°C; △, T = 167°C; ○, T = 180°C; □, T = 190°C

The inhibiting effect of benzoic acid can easily be explained, in the case of basic catalysis, as arising from the decrease in alcoxy ion concentration. Mechanisms involving coordination of the Ti atom to the carbonyl group can also account for this effect, by formation of more stable adducts. The second interpretation is also consistent with the observation that even in the presence of big amounts of benzoic acid Ti(OBu)$_4$ shows measurable catalytic activity in reaction (1) as well as in (4) and (5); this is shown in *Figures 4* and *5*, where it appears that these reactions tend to equilibrium. The increase in the acid concentration after some time at high temperatures may be explained as arising mainly from secondary reaction (2).

A coordinative mechanism thus seems to be the preferable explanation of experimental results, although some contribution from basic catalysis cannot be ruled out completely.

Because of the simultaneous occurrence of (1), partly inhibited by benzoic acid, we were not able to develop an overall kinetic scheme. However, an apparent kinetic constant for reaction (4) can be obtained from the initial slopes, by assuming that the reaction is of the first order with respect to each reagent. Reaction (5) was treated in the same way.

In *Table 1* some of the results for fixed catalyst concentrations are shown. It appears that the kinetic constant for the forward reaction (1) is greater than that of the forward reaction (4) by about one order of magnitude. Moreover, the reactivity of the OH groups in HBB towards benzoic acid is the same as in BD.

The activation energies obtained from the data of *Figures 4, 5* and *6* are reported in *Table 1*. Reactions (4)

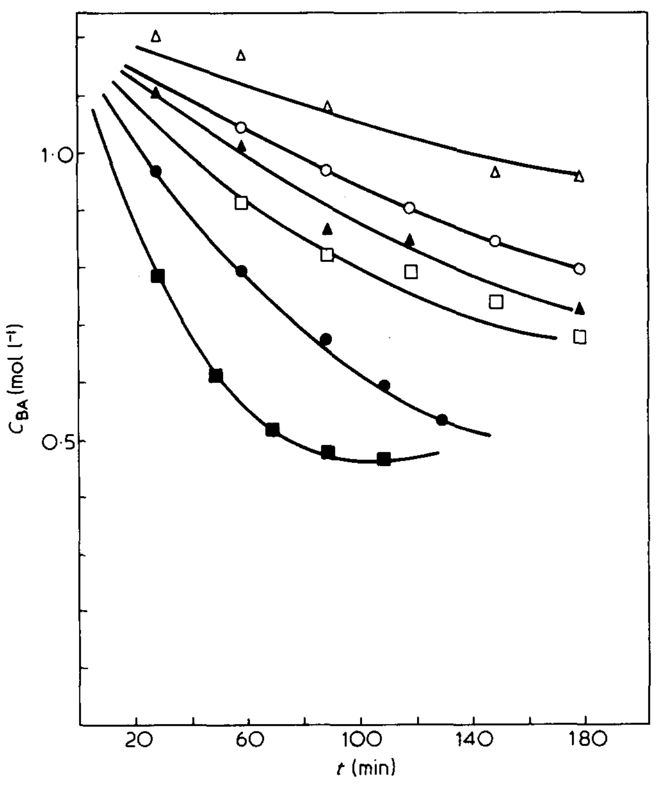


Figure 5 Reaction of BA with HBB (reaction 4) at different temperatures. With catalyst (Ti(OBu)$_4$, 2.25 x 10^{-1} g kg^{-1}): ▲, T = 167°C; ●, T = 180°C; ■, T = 190°C. Without catalyst: △, T = 167°C; ○, T = 180°C; □, T = 190°C

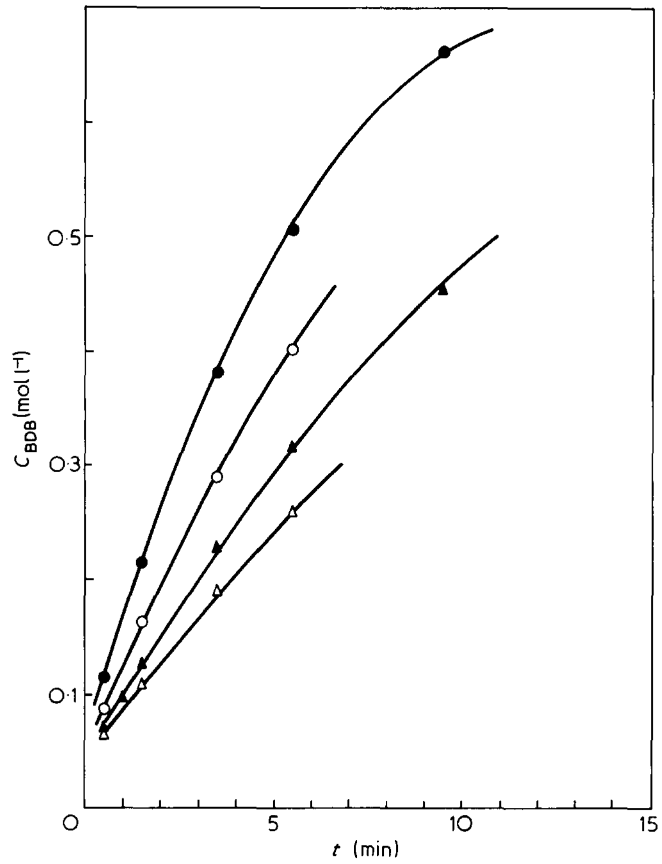


Figure 6 Formation of BDB from HBB with Ti(OBu)$_4$ as catalyst (2.25 x 10^{-1} g kg^{-1}) at different temperatures: △, T = 145°C; ▲, T = 150°C; ○, T = 158°C; ●, T = 167°C

Table 1 Constant rate values at 167°C and characteristic constants of Arrhenius equation for reactions (1), (4) and (5)

Reaction	K* at 167°C ($l\ mol^{-1}\ s^{-1}$) x 10^6	*A** ($l\ mol^{-1}\ s^{-1}$)	E_a ($kcal\ mol^{-1}$)
(1)	68	1.25	11.2
(4)	9.8	5.15 x 10^{11}	33.7
(5)	10	2.28 x 10^6	22.9

* Including catalyst concentration

and (5) show activation energies higher than for reaction (1), and may become important at higher temperatures.

CONCLUSIONS

In the main propagation reaction (1) the catalytic effect of $Ti(OBu)_4$ is inhibited by benzoic acid. Consequently, in the formation of poly(butylene terephthalate) the concentration of the carboxyl end groups in the reaction mixture deserves special attention.

The reaction is more likely to follow a coordinative mechanism than an ionic path.

A temperature increase enhances the relative importance of reactions (4) and (5) (direct esterification).

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APPENDIX

The material balance for reaction (1) may be written:

$$[HBB] = [HBB]_0 - 2([BDB] - [BDB]_0)$$

$$[BD] = [BD]_0 + [BDB] - [BDB]_0$$

where the subscript 0 refers to initial concentrations.

The kinetic equation for reaction (1) then becomes:

$$\frac{d[BDB]}{dt} = k_1\left[[HBB]_0 - 2([BDB] - [BDB]_0)\right]^2 - k'_1\left[[BD]_0 + ([BDB] - [BDB]_0)\right][BDB]$$

This can easily be integrated, and the result may be put into the form:

$$[BDB] = A_1 \frac{(1 + \frac{A_2}{A_1}\beta \exp(-\alpha k_1 t)}{1 + \beta \exp(-\alpha k_1 t)}$$

where

$$A_1 = \frac{4([HBB]_0 + 2[BDB]_0) - \frac{k'_1}{k_1}([BDB]_0 - [BD]_0) - \alpha}{-2\left(\frac{k'_1}{k_1} - 4\right)}$$

$$A_2 = \frac{4([HBB]_0 + 2[BDB]_0) - \frac{k'_1}{k_1}([BDB]_0 - [BD]_0) + \alpha}{-2\left(\frac{k'_1}{k_1} - 4\right)}$$

$$\beta = \frac{A_1 - [BDB]_0}{[BDB]_0 - A_2}$$

$$\alpha = \left[\left\{4([HBB]_0 + 2[BDB]_0) - \frac{k'_1}{k_1}([BDB]_0 - [BD]_0)\right\}^2 + 4\left(\frac{k'_1}{k_1} - 4\right)([HBB]_0 + 2[BDB]_0)^2\right]^{1/2}$$

k_1 was obtained from the initial slopes at 150°C, in the absence of the reverse reaction (see *Figure 6*), whereas k'_1 was evaluated by trial-and-error method. The following values, at a catalyst concentration of 2.25×10^{-1} g/kg were obtained: $k_1 = 3.6 \times 10^{-5}\ l\ mol^{-1}\ s^{-1}$; $k'_1 = 3.7 \times 10^{-6}\ l\ mol^{-1}\ s^{-1}$.