

Models for the formation of poly(butylene terephthalate): effect of water on the kinetics of the titanium tetrabutylate-catalysed reactions: 3.

F. Pilati, A. Munari, P. Manaresi and V. Bonora

Istituto Chimico, Facoltà di Ingegneria, Università di Bologna, Viale Risorgimento 2, 40136 Bologna, Italy

(Received 1 November 1984; revised 23 January 1985)

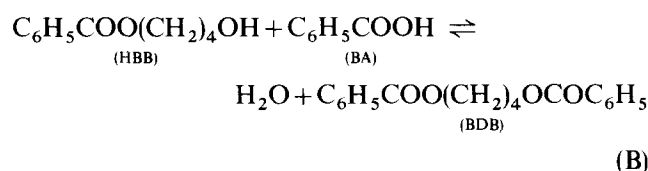
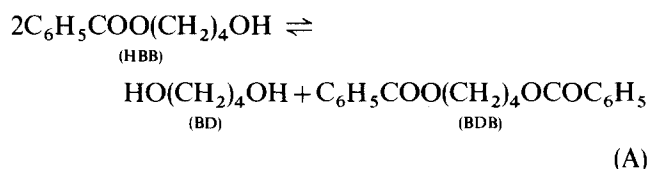
In an effort to investigate the mechanism of catalysis of titanium tetrabutoxide on the polycondensation of poly(butylene terephthalate), alcoholysis and hydrolysis reactions were studied with the aid of model molecules. The retarding effect of water has also been taken into account. Appropriate kinetic equations are derived and discussed and the results compared with experimental data obtained at different molar ratios of reactants.

(Keywords: poly(butylene terephthalate); alcoholysis; hydrolysis; kinetics; titanium tetrabutylate; catalysis)

INTRODUCTION

In previous studies¹⁻⁴ some of the reactions taking place during the formation of poly(butylene terephthalate) have been investigated with the aid of monofunctional model molecules. 4-Hydroxybutyl benzoate (HBB) was chosen as a model for the hydroxyl end-groups, 1,4-butylene dibenzoate (BDB) as a model for the polymer, and benzoic acid (BA) as a model for the carboxyl end-groups. Titanium tetrabutylate, Ti(OBu)₄, was used as the catalyst.

Among the reactions examined, particular attention was paid to those leading to polymer growth by ester interchange and direct esterification:



It appeared that reactions (A) and (B), in the temperature range 150°C–200°C, are both catalysed by Ti(OBu)₄. However, it was also found that the activity of Ti(OBu)₄ is partially inhibited by benzoic acid.

The kinetic equations derived from the proposed reaction mechanism were found to be in good agreement with the experimental data. Since water is often present as an impurity in the reaction system, we thought it interesting to study its effect on the catalytic system. Due to the high solubility of water in 1,4-butanediol (BD), the reverse reactions to (A) and (B) (i.e. the alcoholysis and hydrolysis of BDB) particularly were studied.

Experiments were carried out on BD/BDB mixtures, with and without Ti(OBu)₄, in the presence and absence of water, at 167°C and without solvent. Under these conditions, and for low conversions, side and forward reactions can be neglected.

EXPERIMENTAL

4-Hydroxybutyl benzoate and 1,4-butylene dibenzoate were synthesized as reported previously². 1,4-Butanediol and titanium tetrabutylate were commercial products and they were distilled at reduced pressure before use. Commercial BD contained about 1500 ppm of water: this amount was reduced to about 200 ppm by drying BD over molecular sieves (4 Å).

In previous papers we have described how kinetic experiments were performed⁵ and how HBB, BDB and BA were analysed⁴.

RESULTS AND DISCUSSION

The results pertaining to the reverse reaction to (A), at 167°C, are shown in *Figure 1*, for different initial ratios of BDB/BD. It appears that the catalytic effect of Ti(OBu)₄ on the glycolysis reaction is very strong and that the contribution of the uncatalysed reaction to the initial rate is negligible for all the BDB/BD ratios.

In *Figure 2* the results obtained for the reverse reaction to (A) are shown, when different amounts of water were added initially. The strong inhibiting effect of the water should be noted. A similar effect was observed in a test made starting from HBB (forward reaction (A)).

This behaviour cannot be ascribed to any BA formed by hydrolysis, as BA was found only in a very low concentration ($< 10^{-2} \text{ mol} \times \text{l}^{-1}$) even after a long time of reaction. Since the amount of water added to BD and BDB was always larger than that of Ti(OBu)₄ for two or more orders of magnitude, the inhibiting effect of water

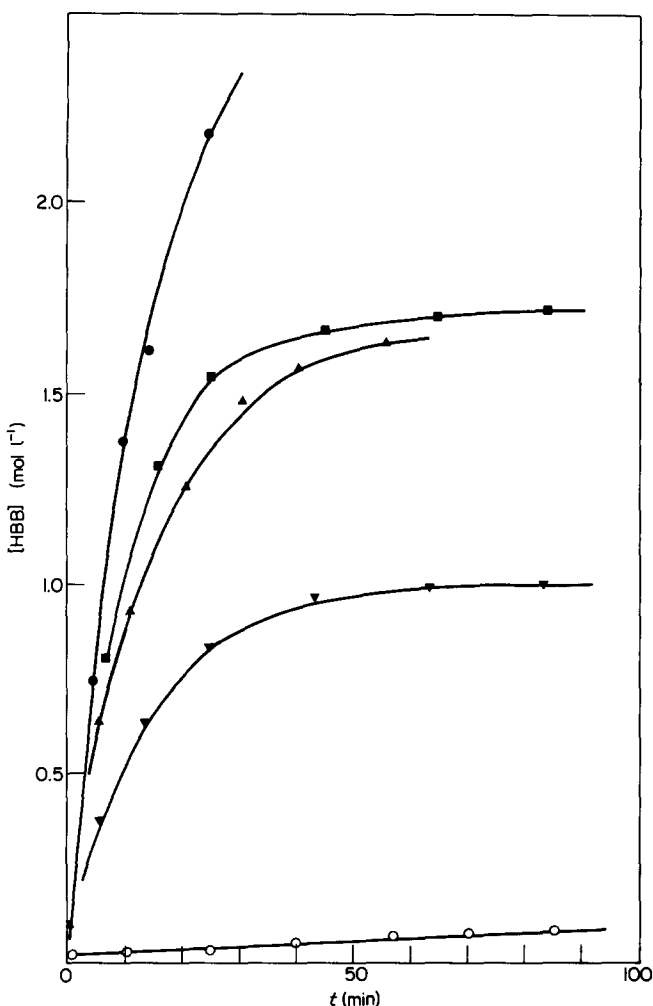


Figure 1 Formation of HBB at 167°C starting from different ratios $[BDB]_0/[BD]_0$ in the presence of $Ti(OBu)_4$ ($\approx 6.6 \times 10^{-4} \text{ mol l}^{-1}$): (■) $[BDB]_0/[BD]_0 = 0.116$, (●) $[BDB]_0/[BD]_0 = 0.752$, (▲) $[BDB]_0/[BD]_0 = 3.12$, (▼) $[BDB]_0/[BD]_0 = 5.78$, and without catalyst: (○) $[BDB]_0/[BD]_0 = 0.77$

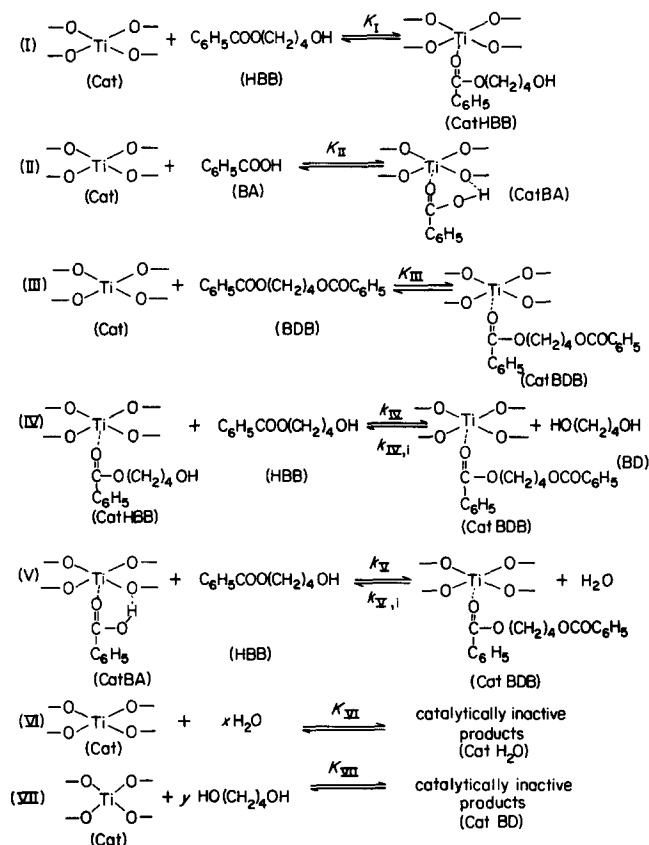
may be ascribed to an incomplete reaction with $Ti(OBu)_4$ owing to either kinetic or equilibrium factors. To gain a deeper insight into this latter aspect, we performed the following experiment. A large amount of water and $Ti(OBu)_4$ were added to BD and heated at 167°C for 100 min. This mixture was then cooled and BDB was added to it until the concentration of a previous run was reached for all substances (BDB, BD, $Ti(OBu)_4$ and water). Then the mixture was heated at 167°C and samples were withdrawn at different times. The results are reported in Figure 3. It can be seen that the data fit the curve obtained in the previous run quite well. This experiment suggests that kinetic factors must be excluded, and the main effect of the reaction of water with the Ti catalyst is an equilibrium between the active catalyst, water and the catalytically not-active Ti compounds.

In order to consider the effect of water, another reaction (VI) must be added to the reaction scheme previously reported⁴.

From the slope of the experimental curves, the initial rate was obtained. In trying to fit the experimental data, in the absence of water, with the equation for the disappearance of BDB derived from the kinetic scheme, we found different results with different initial BDB/BD ratios.

Only if we suppose that BD interacts with $Ti(OBu)_4$, i.e. we introduce in the above scheme a further reaction (VII), we can succeed in the fitting of the initial slopes with the kinetic equations for all the BDB/BD ratios.

The complete scheme resulting is:



According to a previous study⁴ we supposed that, under these experimental conditions, the effective catalyst (Cat) is not autoassociated and that some of its butoxy groups have been replaced by other alcoxide groups. Furthermore (Cat H₂O) and (Cat BD) are considered simply catalytically as inactive products.

Steps I, II, III, VI and VII are assumed to be fast equilibrium reactions, whereas the other steps are assumed to be slower, with kinetic constants $k_{IV,i}$ and $k_{V,i}$ respectively. Forward reactions IV and V can be neglected under our experimental conditions (zero initial concentration of HBB and BA).

The material balance for catalyst, HBB, BA and BDB previously reported⁴, must be modified as follows for the above scheme:

$$[\text{Cat}]_0 = [\text{Cat}] + [\text{Cat HBB}] + [\text{Cat BA}] + [\text{Cat BDB}] + [\text{Cat BD}] + [\text{Cat H}_2\text{O}] \quad (1)$$

$$[\text{HBB}]_0 + 2[\text{BDB}]_0 + [\text{BA}]_0 = [\text{HBB}] + 2[\text{BDB}] + [\text{BA}] \quad (2)$$

$$[\text{BDB}]_0 - [\text{H}_2\text{O}]_0 - [\text{BD}]_0 = [\text{BDB}] - [\text{BD}] - [\text{H}_2\text{O}] \quad (3)$$

$$[\text{BA}]_0 + [\text{H}_2\text{O}]_0 = [\text{BA}] + [\text{H}_2\text{O}] \quad (4)$$

under the previous assumptions of neglecting [Cat HBB], [Cat BA], [Cat BDB], [Cat BD] and [Cat H₂O] in equations (2), (3) and (4).

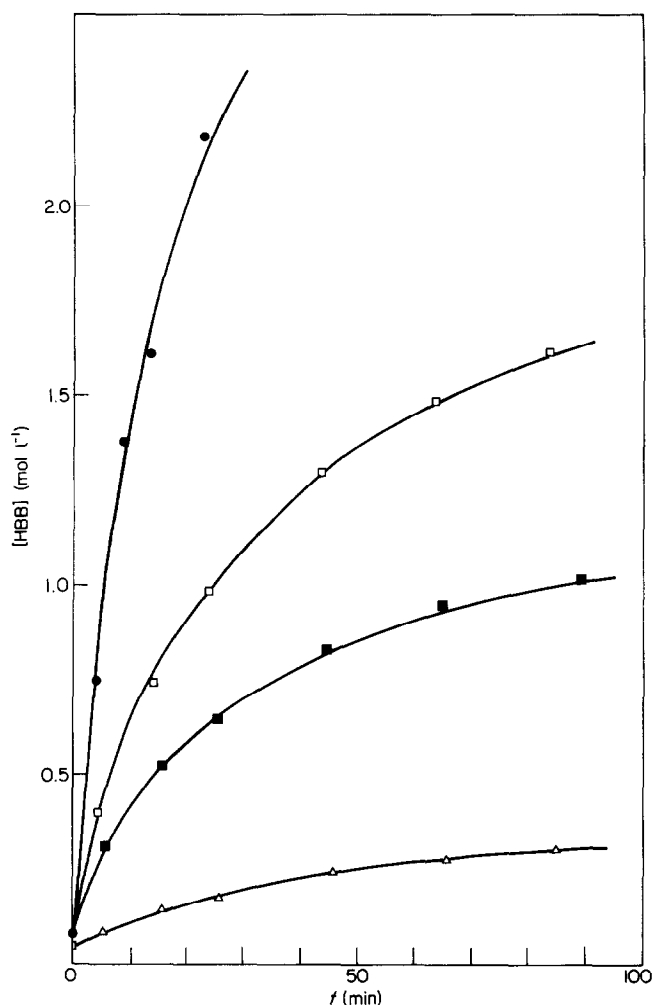


Figure 2 Formation of HBB at 167°C starting from BDB and BD ($[\text{BDB}]_0/[\text{BD}]_0 \approx 0.75$) with different concentrations of H_2O initially added, in the presence of $\text{Ti}(\text{OBu})_4$: (●) $[\text{H}_2\text{O}]_0 = 0.0$, (□) $[\text{H}_2\text{O}]_0 = 0.11$, (■) $[\text{H}_2\text{O}]_0 = 0.16$, (△) $[\text{H}_2\text{O}]_0 = 0.32 \text{ mol l}^{-1}$

From equations (3) and (4) it follows:

$$\frac{d[\text{BDB}]}{dt} = \frac{d[\text{BD}]}{dt} + \frac{d[\text{H}_2\text{O}]}{dt} \quad (5)$$

$$\frac{d[\text{BA}]}{dt} = -\frac{d[\text{H}_2\text{O}]}{dt} \quad (6)$$

Moreover, from the kinetic scheme and neglecting forward reactions for steps IV and V because of our experimental conditions, we obtain:

$$\begin{aligned} \frac{d[\text{BD}]}{dt} &= -k_{\text{IV},i}[\text{BD}][\text{Cat BDB}] \\ &= -k_{\text{IV},i}K_{\text{III}}[\text{BD}][\text{Cat}][\text{BDB}] \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{d[\text{H}_2\text{O}]}{dt} &= -k_{\text{V},i}[\text{H}_2\text{O}][\text{Cat BDB}] \\ &= -k_{\text{V},i}K_{\text{III}}[\text{H}_2\text{O}][\text{Cat}][\text{BDB}] \end{aligned} \quad (8)$$

(it must be emphasized here that a mistake appeared in equation (7) of our previous paper⁴; it should be read as $(d[\text{BD}]/dt) = k_{\text{IV}}[\text{HBB}][\text{Cat HBB}]$).

From equation (1) and from the equilibrium constants for steps I, II, III, VI and VII, it follows that:

$$\begin{aligned} [\text{Cat}]_0 &= K_{\text{I}}[\text{Cat}][\text{HBB}] + K_{\text{II}}[\text{Cat}][\text{BA}] \\ &\quad + K_{\text{III}}[\text{Cat}][\text{BDB}] + K_{\text{VI}}[\text{Cat}][\text{H}_2\text{O}]^x \\ &\quad + K_{\text{VII}}[\text{Cat}][\text{BD}]^y \end{aligned} \quad (9)$$

Finally, substituting equations (7), (8) and (9) in equations (5) and (6), we obtain for the initial reaction rates:

$$\left(-\frac{d[\text{BDB}]}{dt}\right) = \frac{K_{\text{III}}[\text{Cat}]_0[\text{BDB}]_0(k_{\text{IV},i}[\text{BD}]_0 + k_{\text{V},i}[\text{H}_2\text{O}]_0)}{1 + K_{\text{III}}[\text{BDB}]_0 + K_{\text{VI}}[\text{H}_2\text{O}]_0^x + K_{\text{VII}}[\text{BD}]_0^y} \quad (10)$$

$$\left(\frac{d[\text{BA}]}{dt}\right) = \frac{K_{\text{III}}k_{\text{V},i}[\text{Cat}]_0[\text{BDB}]_0[\text{H}_2\text{O}]_0}{1 + K_{\text{III}}[\text{BDB}]_0 + K_{\text{VI}}[\text{H}_2\text{O}]_0^x + K_{\text{VII}}[\text{BD}]_0^y} \quad (11)$$

considering $[\text{HBB}]_0 = [\text{BA}]_0 = 0$, as under our experimental conditions, and neglecting the contributions of the uncatalysed reactions.

From the experimental data of initial rates at different BDB/BD/ H_2O initial ratios we were able to calculate the constants that appear in equations (10) and (11) previously not evaluated. The experimental initial slopes fit well with the calculated ones from equation (10) for all BDB/BD/ H_2O ratios when x and y in steps VI and VII (and in equations (10) and (11) of the scheme are 2.5 and 0.5 respectively).

The values of the kinetic and equilibrium constants are reported in Table 1.

In Table 2 the experimental initial rates are compared with the values calculated by introducing the data from Table 1 into equation (10) where quite good agreement is found.

The effects of BD and H_2O on Ti alcoxides seems to be more complex than those of HBB, BA and BDB, as suggested by the values derived for the exponents x and y .

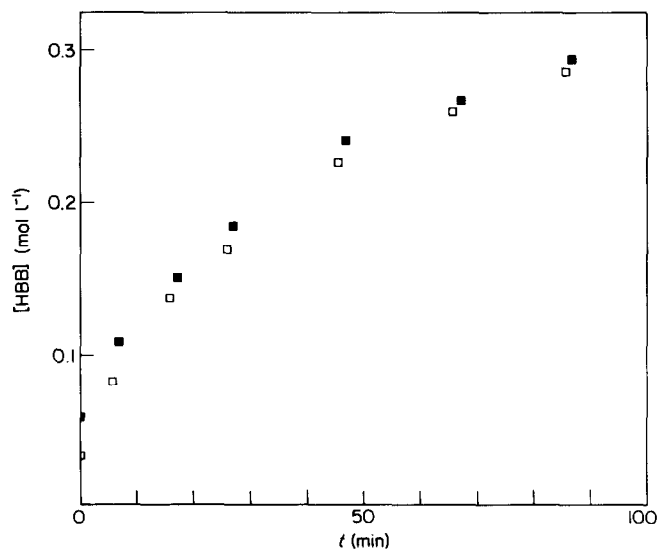


Figure 3 Formation of HBB at 167°C starting from BDB, BD and H_2O ($[\text{BDB}]_0/[\text{BD}]_0 = 0.69$, $[\text{H}_2\text{O}]_0 = 0.32 \text{ mol l}^{-1}$) (□), and in the same conditions, but obtained by adding BDB to a mixture of BD, $\text{Ti}(\text{OBu})_4$ and H_2O previously heated for 100 min at 167°C (■)

Table 1 Values of the kinetic and equilibrium constants at 167°C

K_{III} ($l \times$ mol^{-1})	K_{VI} ($l^{2.5} \times$ $mol^{-2.5}$)	K_{VII} ($l^{0.5} \times$ $mol^{-0.5}$)	$k_{IV,i}$ ($l \times$ $mol^{-1} s^{-1}$)	$k_{V,i}$ ($l \times$ $mol^{-1} s^{-1}$)
0.16	1100	1.1	5.0	0.8

Table 2 Experimental and calculated initial rates of BDB disappearance at 167°C with different initial BD and BDB concentrations with and without water added and in the presence of $Ti(OBu)_4$ ($\approx 6.6 \times 10^{-4} mol l^{-1}$)

[BD] ₀ ($mol l^{-1}$)	[BDB] ₀ ($mol l^{-1}$)	[H ₂ O] ₀ ($mol l^{-1}$)	- (d[BDB]/dt) × 10 ⁴ ($mol l^{-1} s^{-1}$)	
			Experimental	Calculated
3.18	2.39	—	11.5	12.0
0.98	3.06	—	6.0	6.1
0.55	3.18	—	4.0	3.9
8.03	0.93	—	9.7	9.1
3.18	2.38	0.11	5.2	4.8
3.18	2.38	0.16	2.5	2.6
3.34	2.32	0.32	0.6	0.6

At present we cannot suggest a detailed mechanism to account for the values of x and y : tentatively we may suppose that the reactions of Ti alcoxides with water and or BD lead to catalytically inactive compounds, in equilibrium with active catalyst. It must be emphasized that the strong difference between the equilibrium constants K_{VI} and K_{VII} , and between x and y , suggests a different mechanism of interaction of BD and H₂O with Ti.

CONCLUSIONS

We have studied the reaction between BDB and BD at 167°C in the presence and in the absence of water, with the aim of attaining a better understanding of the catalytic activity of the titanium alcoxides.

We have found that the reaction scheme must take into account interactions of water and BD with Ti catalyst to explain the experimental results.

The inhibiting effect of water was particularly strong leading to catalytically inactive products in equilibrium with the catalyst.

The equations derived from the scheme enable us to calculate values of initial rates in quite good agreement with the experimental data for different BDB/BD/H₂O initial ratios.

ACKNOWLEDGEMENTS

This work is supported by the financial aid from the Consiglio Nazionale delle Ricerche (CNR), Progetto Finalizzato 'Chimica Fine e Secondaria'.

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