

# Kinetic and Catalytic Aspects of the Formation of Poly(ethylene terephthalate) (PET) Investigated with Model Molecules

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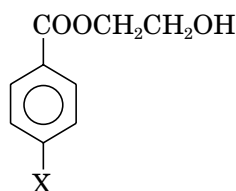
**ABSTRACT:** Kinetic and catalytic aspects of the formation of poly(ethylene terephthalate) (PET) have been studied in this work using model molecules such as 2-hydroxyethyl 4-methylbenzoate (MP), 2-hydroxyethyl 4-benzoate (MB), and 2-(hydroxyethyl 4-methylbenzoate) 4-methylbenzoate (DP), synthesized and purified in our laboratories. The methods to obtain these molecules have been described in detail. Many kinetic runs have been performed using different catalysts, such as compounds of Sb, Ti, Zr, Al, Mo (VI), Mn, Zn, Sn (IV), and Ge. We have made kinetic runs on some catalysts under different operative conditions to evaluate the effect of catalyst concentration and temperature on the reaction rate. We have observed that a second-order kinetic law is suitable for both condensation and reverse reaction. All kinetic runs have been interpreted and kinetic parameters determined. Activity can depend on catalyst concentration in a different way for each type of catalyst. Bivalent metals activity is affected by the presence of a substituent in the aromatic ring, unlike tri- and tetravalent metals. Suggestions on the reaction mechanisms conclude the work. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2423–2433, 1998

**Key words:** poly(ethylene terephthalate); bis(hydroxyethyl)terephthalate; model reactions; kinetics; catalysis

## INTRODUCTION

In the production of high molecular weight poly(ethylene terephthalate) (PET) by the polycondensation of bis(2-hydroxyethyl)terephthalate (BHET), the presence of a catalyst is essential. Despite the large number of papers and reviews published in the literature on the kinetic and catalytic aspects of the formation of PET,<sup>1–23</sup> the mechanism of the reaction in the presence of different metals is still the object of controversial interpretations owing to difficulties in the kinetic treatment of polycondensation. Some authors<sup>2,3,5,12,17</sup> have made attempts to correlate the kinetic data obtained in the presence of different

metals by drawing plots of the activities as functions of the metals acidity, usually obtaining volcano-shaped curves. Recently, we have shown<sup>17</sup> that such curves must be considered with caution if catalytic activities depend on the catalyst concentration, in a different way for each catalyst, and if the activation energies are different. To simplify the comparison of the kinetic and catalytic behavior of different metals in the BHET polycondensation we have studied the reaction that occurs using model molecules of the following type:



(1)

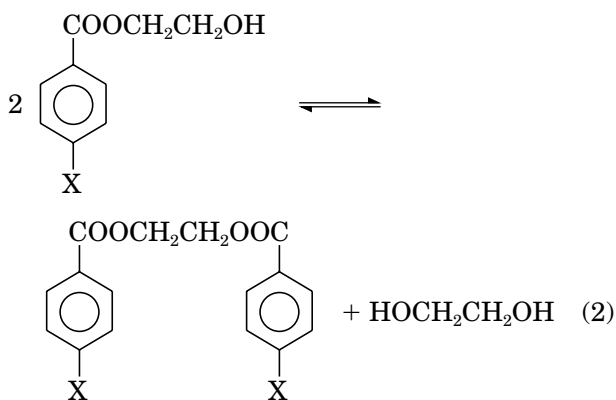
where X = CH<sub>3</sub>, H

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prepared and purified in our laboratories.

The reaction studied is:



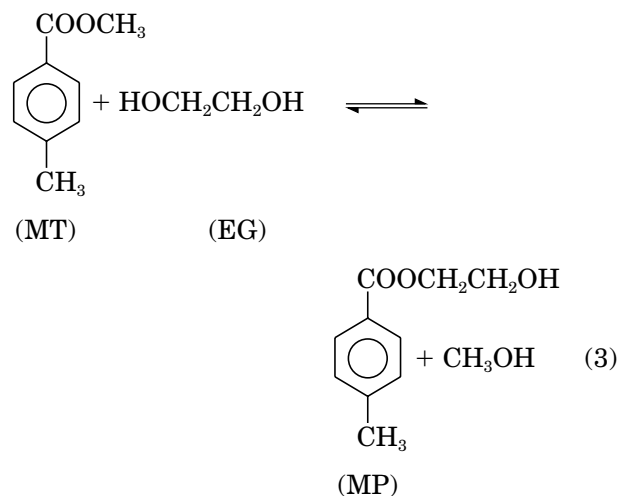
which is a similar reaction occurring in the BHET polycondensation but stopped at the formation of only the dimer. It must be pointed out the kinetic behavior could be strongly affected by the nature of the substituent X, as observed in a previous work<sup>17</sup> for transesterification. However, we have observed the activity of bivalent metal catalysts is greatly affected by the substituent X. On the contrary, the activity is poorly affected in the presence of tri- or tetravalent metals such as Sb or Ti. This allows us to conclude the use of model molecules is particularly useful to study the behavior of tri- and tetravalent metals, which are the most commonly used in polycondensation.<sup>2,12,18,19,21</sup> To study the behavior of bivalent metals it is opportune to use a model molecule in which X has the same influence on the reaction rate of the BHET terminal group —COOCH<sub>2</sub>CH<sub>2</sub>OH. In this article we have studied the equilibrium reaction (2) in both directions, that is, from the 2-hydroxyethyl 4-methylbenzoate (MP) or 2-hydroxyethyl 4-benzoate (MB) and from the dimer 2(-hydroxyethyl 4-methylbenzoate) 4-methylbenzoate (DP) in the presence of ethyleneglycol (EG). The reaction has been studied in the presence of different catalysts based on Sb, Ti, Zr, Al, Mo (VI), Mn, Zn, Sn (IV), and Ge. The results obtained have been compared. Kinetic aspects have been deepened in particular for Sb- and Ti-based catalysts to also evaluate the effect of temperature and the difference between the kinetic parameters obtained with the model molecules, considered in this article, and the ones reported by the literature on the BHET polycondensation.<sup>2,12,18</sup>

## EXPERIMENTAL SECTION

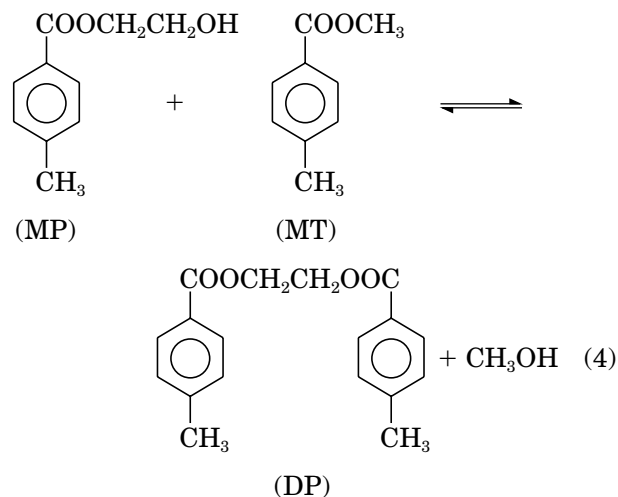
### Preparation of the Reagents

The reagents used are not commercially available; thus, they have been prepared and purified in our laboratories.

To prepare MP and DP, we have made, first of all, the transesterification of the 2-methoxy 4-methylbenzoate (MT) with ethyleneglycol (EG) in the presence of cadmium acetate as a catalyst:



The reaction was performed in a well-mixed jacketed stainless steel reactor. The temperature of the reaction was kept at 190°C, by recirculating a thermostatted oil. The methanol produced as a consequence of the reaction was distilled off to shift to the right the reaction equilibrium. Together with reaction (3), also the formation of the dimer DP occurs:



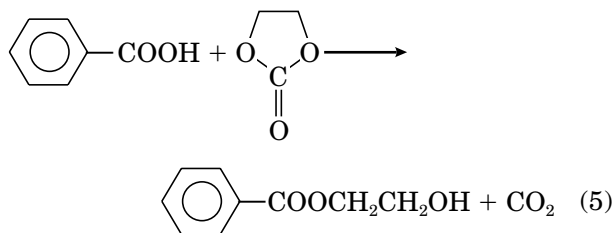
The amount of MP and DP, respectively produced, largely depends on the initial ratio of the reagents MT/EG. As we are interested in the production of both the compounds, the initial ratio of the reagent MT to the reagent EG is 1/4 when we are interested to have a good yield of MP and  $MT/EG = 4$  when the formation of DP must be favored.

In the first case 400 g of MT were introduced in the reactor, at a temperature of 190°C, together with 660 g of EG and  $8 \times 10^{-3}$  mol/L of cadmium acetate (2.3 g). Three hours later, the conversion of MP was 98%. The mixture obtained contains MT, EG, and DP. To eliminate DP the mixture was treated with ethylether three times. Ethylether dissolves MP and MT in preference, while DP and EG are poorly soluble in this solvent. The ether solution was then treated twice with distilled water to eliminate EG and the catalyst, and three times with a NaCl saturated water solution to reduce the amount of MP in the ether solution. The ether solution was then cooled at 4–5°C to eliminate residual quantities of DP dissolved by crystallization. At last, the ether solution containing MP was first treated with anhydrous  $Na_2SO_4$ , filtered, and then vaporized by a rotavapor.

We have obtained 320 g of MP with 98.5% of purity determined by gaschromatography (66% of yield).

To prepare the dimer DP, 400 g of MT were introduced in the reactor, at a temperature of 190°C, with 41 g of EG and  $8 \times 10^{-3}$  mol/L (0.8 g) of cadmium acetate. Four hours later, the MT conversion was 98%. The reaction mixture was filtered under vacuum. The solid obtained was purified washing it five times with distilled water and five times with ethylether. So we obtained about 100 g of DP with 98% of purity and 50% of yield.

The other test molecule, 2-hydroxyethyl 4-benzoate (MB) has been prepared by the following reaction:



In a 2-L four-necked vessel equipped with a

stirrer and a reflux condenser were introduced 250 g of benzoic acid, 649 g of ethylencarbonate, and 11 g of KI. The reaction was followed both by observing the evolution in time of  $CO_2$  and by analyzing samples withdrawn at different times by gaschromatography.

The reaction mixture frozen at room temperature was treated with 1.4 L of ethylether. Then five extractions with 700  $cm^3$  of an aqueous solution of 5% of  $NaHCO_3$  are made. The ether solution has been treated three times with a saturated solution of NaCl in water, dried with anhydrous  $Na_2SO_4$ , filtered, and concentrated by a rotavapor. The product obtained was distilled twice at low pressure in an apparatus equipped with a Vigreux column. 187 g of MB with 99% of purity determined by gaschromatography were obtained, equivalent to 55% of yield. The melting points of the product prepared, determined by a DSC (Differential Scanning Calorimetry) were, respectively, 116°C for DP, 37°C for MB, and 40°C for MP.

#### Apparatus, Methods, and Other Reagents

The condensation reactions have been made in a magnetically stirred glass reactor. The jacketed reactor was kept isothermal by recirculating a thermostatted oil at the desired temperature in the range of 182–215°C. The reaction was made by introducing a known amount of both the reagents, usually about 20 g, and the catalyst kept in the concentration range of  $3 \times 10^{-5}$  to  $4 \times 10^{-2}$  mol/L. The concentrations of catalysts are calculated in regard to the initial volume. All the catalysts are completely homogeneous with reactants at the reaction temperatures. The reactions were followed for about 7 h by withdrawing small samples of the reaction mixtures at different times. Withdrawn samples were analyzed by gaschromatography injecting a solution of those samples in dichloromethane (0.05 g of sample in 4  $cm^3$  of  $CH_2Cl_2$ ) into a HP1 column of the Crompack Co. (25 m in length, 0.32 mm i.d., containing 100% of dimethylpolysiloxane gum). FID was used as a detector. The temperature of the oven was gradually increased by an opportune program from 35 to 280°C.

The glycolysis of DP has been performed in the same reactor using about 20 g of DP and 4.4 g of EG, corresponding to a molar ratio DP/EG of 1. The concentration of the catalyst has been taken similar to the one used in the direct reaction of condensation. DP was introduced in the reactor

**Table I List of the Kinetic Runs Performed on 2-Hydroxyethyl 4-Methylbenzoate (MP) with Related Operative Conditions, Kinetic, and Equilibrium Constants**

Run	Catalyst	Metal Concentration 10 <sup>3</sup> (mol/L)	$k$ 10 <sup>4</sup> (L mol <sup>-1</sup> min <sup>-1</sup> )	$K_e$	$T$ (°C)
1	Sb <sub>2</sub> O <sub>3</sub>	44.2	4.9	0.18	202
2	Sb <sub>2</sub> O <sub>3</sub>	5.00	3.6	0.24	212
3	Sb <sub>2</sub> O <sub>3</sub>	5.00	3.6	0.19	207
4	Sb <sub>2</sub> O <sub>3</sub>	5.00	3.6	0.18	202
5	Sb <sub>2</sub> O <sub>3</sub>	5.00	0.62	0.17	182
6	Sb <sub>2</sub> O <sub>3</sub>	2.20	2.9	0.18	202
7	Sb <sub>2</sub> O <sub>3</sub>	0.34	2.1	0.24	212
8	Sb <sub>2</sub> O <sub>3</sub>	0.34	2.1	0.18	202
9	Sb <sub>2</sub> O <sub>3</sub>	0.34	0.42	0.17	182
10	Ti(OBut) <sub>4</sub>	19.1	9.2	0.18	202
11	Ti(OBut) <sub>4</sub>	4.85	11	0.24	212
12	Ti(OBut) <sub>4</sub>	4.85	11	0.18	202
13	Ti(OBut) <sub>4</sub>	4.85	1.5	0.17	182
14	Ti(OBut) <sub>4</sub>	0.16	6.2	0.18	202
15	Zr(OBut) <sub>4</sub>	1.90	0.77	0.18	202
16	Zr(OCH <sub>2</sub> CH <sub>2</sub> OOC— $\phi$ —CH <sub>3</sub> ) <sub>4</sub>	2.05	0.77	0.18	202
17	Zr(OCH <sub>2</sub> CH <sub>2</sub> OOC— $\phi$ —CH <sub>3</sub> ) <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub> (1 : 1)	2.10	0.77	0.18	202
18	Sb <sub>2</sub> O <sub>3</sub> + Zn(Ac) <sub>2</sub> + Co(Ac) <sub>2</sub>	5.10	3.9	0.18	202
19	Al(isoPrO) <sub>3</sub>	1.90	1.3	0.18	202
20	Al(isoPrO) <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> (1 : 1)	1.90	1.35	0.18	202
21	Al(isoPrO) <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> (1 : 0.5)	1.90	1.3	0.18	202
22	Mn(Ac) <sub>2</sub>	5.12	1.1	0.18	202
23	Zn(Ac) <sub>2</sub>	5.00	2.5	0.18	202
24	Mo(acac) <sub>6</sub>	43.8	13	0.18	202
25	Mo(acac) <sub>6</sub>	11.0	5.7	0.18	202
26	Mo(acac) <sub>6</sub>	5.00	5.0	0.18	202
27	Mo(acac) <sub>6</sub>	0.324	1.2	0.18	202

and heated at the reaction temperature, then glycol containing the catalyst dissolved was added. The reaction was followed for more than 3 h by withdrawing and analyzing samples of the reacting mixtures at different times.

All the catalysts and commercially available reagents used have been furnished by the Aldrich Co. (Milwaukee, WI).

## RESULTS AND DISCUSSION

Kinetic data have been collected with the reference to reaction (2) using either the reagent MB or MP, while glycolysis has been studied only for DP.

The runs performed on MP with different types of catalysts are summarized in Table I, together with the adopted experimental conditions concerning temperature and catalyst concentrations.

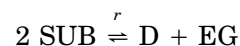
The runs performed on MB in the presence of different catalysts at different temperatures and catalyst concentrations are collected in Table II, while the kinetic runs made for the glycolysis of DP are reported in Table III. The kinetic runs of MP and MB condensation have been made determining the composition of the reaction mixtures, withdrawn from the reactor at different times, by gaschromatography and calculating the molar conversion of the reagent used. The conversions obtained were then arranged in a plot, as a function of time and in Figures 1 and 2 we report, as examples, the conversions obtained for, respectively, MP and MB in the presence of Sb<sub>2</sub>O<sub>3</sub>, as a catalyst. As it can be seen, the conversion increases in time until it reaches the equilibrium value. To define the equilibrium position best, we have made runs starting from MP for the condensation and from DP for the reverse reaction of glycolysis at the same temperature, and in the

**Table II List of the Kinetic Runs Performed on 2-Hydroxyethyl 4-Benzoate (MB) with Related Operative Conditions, Kinetic, and Equilibrium Constants**

Run	Catalyst	Metal Concentration 10 <sup>3</sup> (mol/L)	$k$ 10 <sup>4</sup> (L min <sup>-1</sup> min <sup>-1</sup> )	$K_e$	$T$ (°C)
1	Sb <sub>2</sub> O <sub>3</sub>	4.80	3.3	0.24	205
2	Sb <sub>2</sub> O <sub>3</sub>	2.39	3.3	0.25	215
3	Sb <sub>2</sub> O <sub>3</sub>	2.41	3.2	0.24	205
4	Sb <sub>2</sub> O <sub>3</sub>	2.39	1.2	0.22	190
5	Sb <sub>2</sub> O <sub>3</sub>	2.00	2.8	0.24	205
6	Sb <sub>2</sub> O <sub>3</sub>	0.808	0.93	0.24	205
7	Sb <sub>2</sub> O <sub>3</sub>	0.46	0.80	0.24	205
8	Ti(isoPrO) <sub>4</sub>	0.16	6.0	0.24	205
9	Ti(isoPrO) <sub>4</sub>	0.03	18	0.24	205
10	Ti(isoPrO) <sub>4</sub>	0.0032	5.2	0.24	205
11	Ti(isoPrO) <sub>4</sub>	0.0016	5.1	0.24	205
12	Zr(PrO) <sub>4</sub>	0.154	0.77	0.24	205
13	Al(secButO) <sub>3</sub>	0.201	0.38	0.24	205
14	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SnO	1.25	20	0.24	205
15	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SnO	0.59	8.2	0.24	205
16	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SnO	0.30	9.9	0.24	205
17	GeO <sub>2</sub>	3.14	0.39	0.24	205
18	GeO <sub>2</sub>	1.85	1.2	0.24	205
19	GeO <sub>2</sub>	1.43	0.50	0.24	205
20	Zn(Ac) <sub>2</sub>	5.00	7.5	0.24	205

presence of Sb<sub>2</sub>O<sub>3</sub>, as a catalyst in the same amount. The results obtained are reported in Figure 3, as evolution with the time of the ratio [DP]/([DP]+[MP]) for both the forward and the reverse reaction. The two reactions seem to converge at a unique value of the considered ratio corresponding to the equilibrium composition. Therefore, equilibrium constants can be determined by runs of this type and are then confirmed by the final conversion in runs such as the ones reported in Figures 1 and 2.

All kinetic runs can be interpreted by assuming a second-order kinetic law for both the condensation and the glycolysis:



Thus, the evolution in time of the composition of the reacting mixture can be evaluated solving the following system of differential equations:

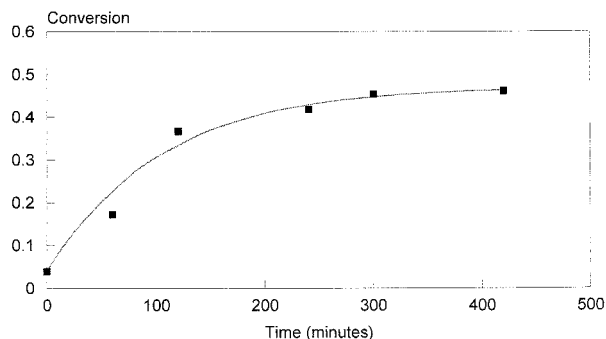
$$\frac{d[\text{SUB}]}{dt} = -2r$$

$$\frac{d[\text{D}]}{dt} = r$$

$$\frac{d[\text{EG}]}{dt} = r$$

**Table III List of the Kinetic Runs Performed on 2-(Hydroxyethyl 4-Methylbenzoate) 4-Methylbenzoate (DP) with Related Operative Conditions, Kinetic, and Equilibrium Constants**

Run	Catalyst	Catalyst Concentration 10 <sup>3</sup> (mol/L)	$k$ 10 <sup>4</sup> (L mol <sup>-1</sup> min <sup>-1</sup> )	$K_e$	$T$ (°C)
1	Sb <sub>2</sub> O <sub>3</sub>	5.00	3.9	0.17	202
2	Ti(OBut) <sub>4</sub>	0.16	6.1	0.17	202



**Figure 1** Simulation of a kinetic run performed on 2-hydroxyethyl 4-methylbenzoate (MP) with  $\text{Sb}_2\text{O}_3$  as a catalyst.

where  $\text{SUB} = \text{MP}$  or  $\text{MB}$  and  $\text{D} = \text{DP}$  or  $\text{DB}$ , while:

$$r = k[\text{SUB}]^2 \left( 1 - \frac{[\text{D}] * [\text{EG}]}{K_e [\text{SUB}]^2} \right) \quad (1)$$

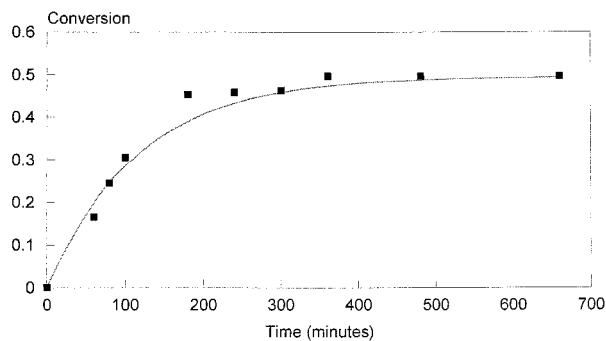
where  $k$  is the kinetic constant of the forward reaction and  $K_e$  the equilibrium constant of the reaction. It is simple to write  $r$  as a function of the conversion

$$x = \frac{2[\text{D}]}{[\text{SUB}]_0}$$

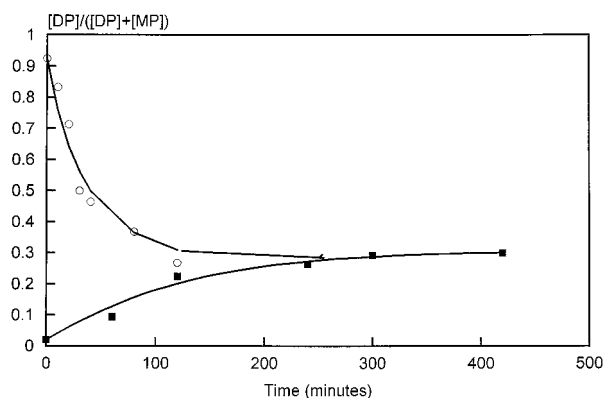
( $[\text{SUB}]_0$  being the initial concentration of the reagent MP or MB):

$$r = \left( \frac{4k(1-x)^2}{x^2} - \frac{k}{K_e} \right) x^2 \frac{[\text{SUB}]_0^2}{4} \quad (2)$$

Consequently:



**Figure 2** Simulation of a kinetic run performed on 2-hydroxyethyl 4-benzoate (MB) with  $\text{Sb}_2\text{O}_3$  as a catalyst.



**Figure 3** Comparison between two kinetic runs respectively performed with 2-hydroxyethyl 4-methylbenzoate (MP = ■) and 2(-hydroxyethyl 4-methylbenzoate) 4-methylbenzoate (DP = ▲) with  $\text{Sb}_2\text{O}_3$  as a catalyst.

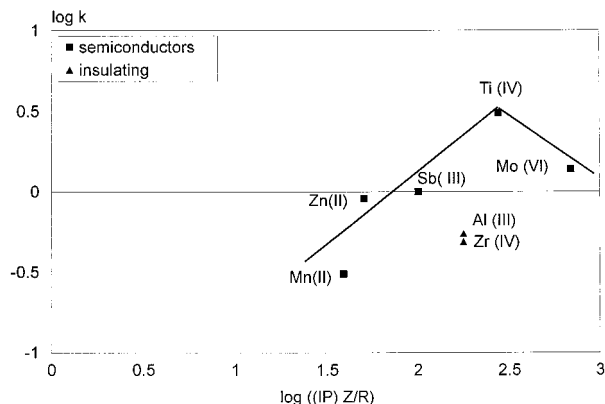
$$\frac{dx}{dt} = \left( \frac{4k(1-x)^2}{x^2} - \frac{k}{K_e} \right) x^2 \frac{[\text{SUB}]_0}{2} \quad (3)$$

From the experimental data of conversion vs. time as the ones reported in Figures 1 and 2, it is possible to evaluate  $k$  by mathematical regression analysis.  $K_e$  has been experimentally determined by runs such as the ones reported in Figure 3 and confirmed by comparing runs performed with different catalysts at the same temperature. We have observed fitting experimental data that the assumption of a second-order law is correct (see curves reported in Figs. 1, 2, 3, 7, 8, and 9) in agreement with the findings reported by the literature on the model reactions of condensation of benzoic acid monofunctional esters.<sup>19-22</sup>

We have never observed byproducts with the exception of the runs performed with MP for more than seven hours in the presence of  $\text{Sb}_2\text{O}_3$  as a catalyst. However, the amount of byproducts obtained was less than 0.5%, so we have neglected their formation.

The kinetic and equilibrium constants determined for the different runs performed are reported in Tables I, II, and III, and are related to the runs made, respectively, with MP, MB, and DP. In the case of MP, we have made runs in the presence of different metals. For the three metals Ti, Sb, and Mo, we have also made runs in the presence of different catalyst concentrations.

The kinetic constants obtained for the runs performed with different metals at the same concentration of about  $5 \times 10^{-3}$  mol/L have been ar-



**Figure 4** Volcano-shaped curve of all catalysts kinetic constants as a function of metal acidities for 2-hydroxyethyl 4-methylbenzoate (MP) as a reagent.

ranged in a plot (Fig. 4) reporting the activity expressed as  $\log k$  as a function of the catalyst acidity. The metal acidity has been determined as a linear combination of three parameters: the ionization potential (IP), the radius of the cation (R), and the valence of the cation (Z), as suggested by Chung.<sup>2</sup>

As it can be seen, the trend obtained is a volcano-shaped curve, similar to the one obtained for the BHET polycondensation reported in the literature.<sup>12,15</sup> The low activities shown by Al- and Zr-based catalysts are also in agreement with the literature findings because two volcano-shaped curves are normally reported with two different activity levels: a higher one for the metals giving oxides that are semiconductors, and another for the metals giving insulating oxides. However, these volcano-shaped curves must be considered with caution because comparing the activities shown by Ti, Sb, and Mo at different catalyst concentrations, linear trends with different slopes have been obtained for the  $\log k$  as a function of the  $\log [\text{Me}]$  (Fig. 5). The average order of the reaction with respect to the catalyst concentration resulted 0.2 for the antimony, 0.5 for molybdenum and 0.09 for titanium. This fact suggests volcano-shaped curves for activities, as functions of the catalyst acidities cannot be considered useful to a general use.

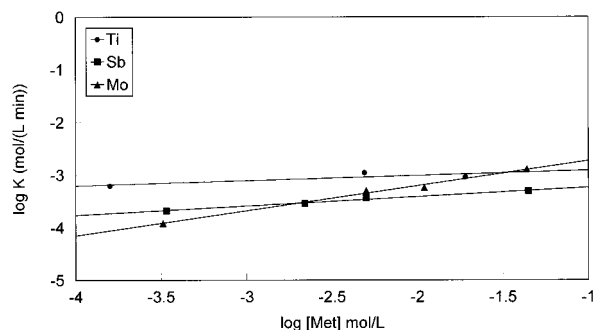
Another important conclusion can be reached by observing the results reported in Figure 5. In the case of Ti, the reaction rate remains high also at very low catalyst concentrations. This fact can be interpreted by considering titanium glycoxide forms oligomers<sup>11</sup> with a molecular weight dependent on the catalyst concentration. Probably the

number of active sites remains almost constant as a consequence of the change of the molecular size with dilution. Observing titanium is still active at very low concentrations gives a useful suggestion on the possibility to use this metal for industrial applications in the BHET polycondensation.<sup>24</sup>

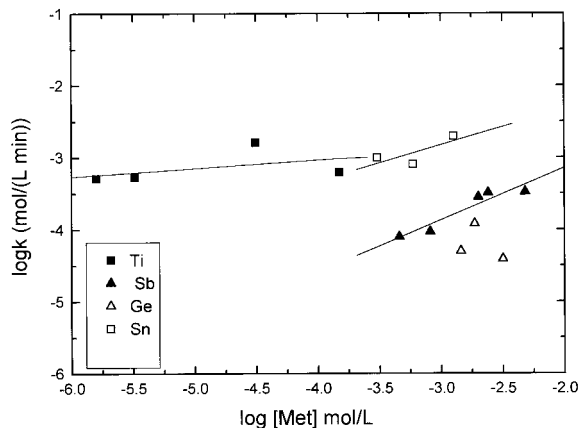
The kinetic runs with MB, reported in Table II, have been made in the presence of different catalysts such as: Sb, Ti, Zr, Al, Sn, Ge, and Zn compounds. In the case of Sb, Ti, Ge, and Sn, runs have been made by using different concentrations of the catalyst. In the case of Sb, runs have also been made at different temperatures. Kinetic constants have been determined in the same way described before for the runs performed on MP, while equilibrium constants have been determined by the conversion values reached in equilibrium conditions. The values of the kinetic and equilibrium constants obtained are reported in Table II.

By considering the effect of the catalyst concentration on the kinetic constants, we have observed a different behavior for each catalyst again, as can be seen in Figure 6, in which  $\log k$  is reported as a function of the log of the catalyst concentration. Linear correlations have also been obtained in these cases with the exclusion of  $\text{GeO}_2$ , probably because this catalyst is not completely soluble in the reaction mixtures.

It is interesting to compare runs performed at the same temperature and catalyst concentration for, respectively, MB and MP. This comparison related to the  $\text{Zn}(\text{CH}_3\text{COO})_2$  catalyst is reported in Figure 7. As it can be seen, activity is decreased by the presence of a methyl group in the *para* position. The effect of the substituent result was negligible for, respectively,  $\text{Sb}_2\text{O}_3$  and  $\text{Ti}(\text{OR})_4$ , as it can be seen in Figures 8 and 9, respectively.



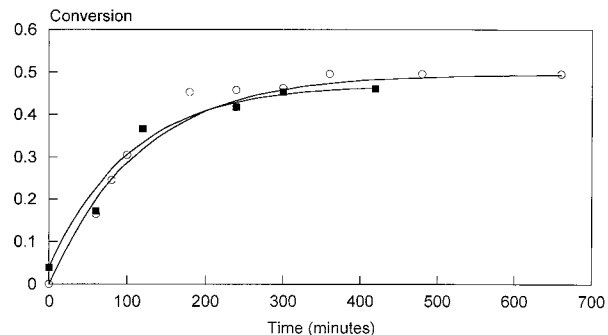
**Figure 5** The trend of kinetic constants vs. catalyst concentration for Ti, Sb, and Mo, with MP as a reagent.



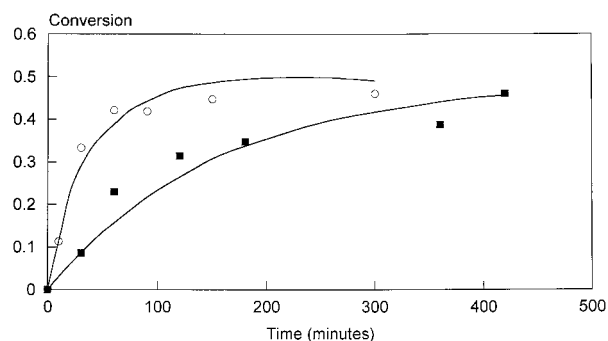
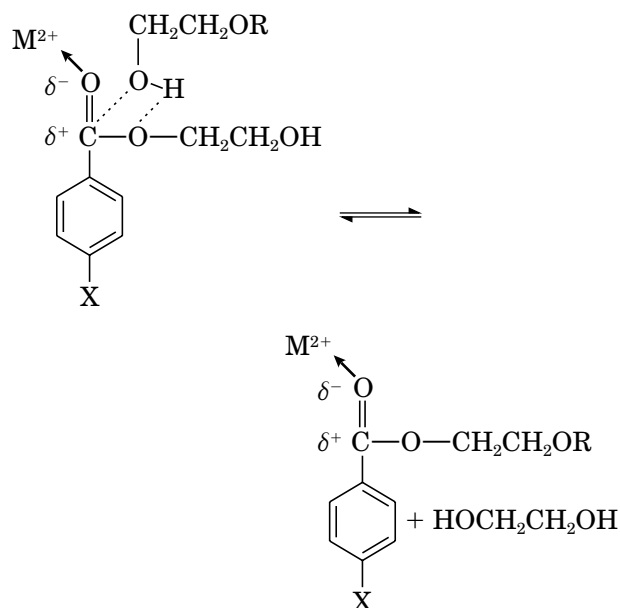
**Figure 6** The trend of kinetic constants vs. catalyst concentration for Ti, Sb, Sn, and Ge, with MB as a reagent.

This suggests that the mechanism of the reaction is different in the case of bivalent catalysts such as  $\text{Zn}(\text{Ac})_2$  and tri- or tetravalent ones (e.g.,  $\text{Sb}_2\text{O}_3$  and  $\text{Ti}(\text{OR})_4$ ). Moreover, as the same difference in the behavior has been observed and explained for the transesterification of the methylesters having different *para*-substituents with EG,<sup>17</sup> the mechanism of condensation is probably very similar to that of transesterification. On the other hand, the suggestion of the existence of an analogy between the mechanism of DMT transesterification and that of BHET polycondensation has been already proposed by other authors in the literature,<sup>1,2,12</sup> even though different mechanisms are proposed to justify the analogy.

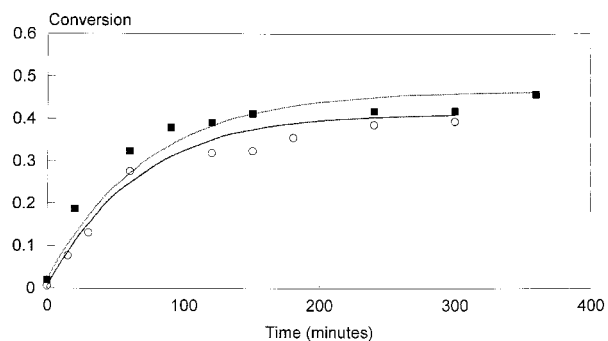
According to the same authors<sup>1,13</sup> bivalent metal catalysts attack the carbonylic oxygen in the following way:



**Figure 8** Comparison between two kinetic runs respectively performed with 2-hydroxyethyl 4-methylbenzoate (MP = ■) and 2-hydroxyethyl 4-benzoate (MB = ▲) with  $\text{Sb}_2\text{O}_3$  as a catalyst.



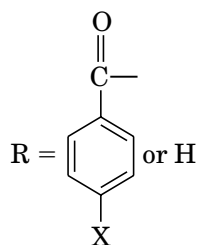
**Figure 7** Comparison between two kinetic runs respectively performed with 2-hydroxyethyl 4-methylbenzoate (MP = ■) and 2-hydroxyethyl 4-benzoate (MB = ▲) with  $\text{Zn}(\text{Ac})_2$  as a catalyst.



**Figure 9** Comparison between two kinetic runs respectively performed with 2-hydroxyethyl 4-methylbenzoate (MP = ■) and 2-hydroxyethyl 4-benzoate (MB = ▲) with  $\text{Ti}(\text{OBut})_4$  as a catalyst.

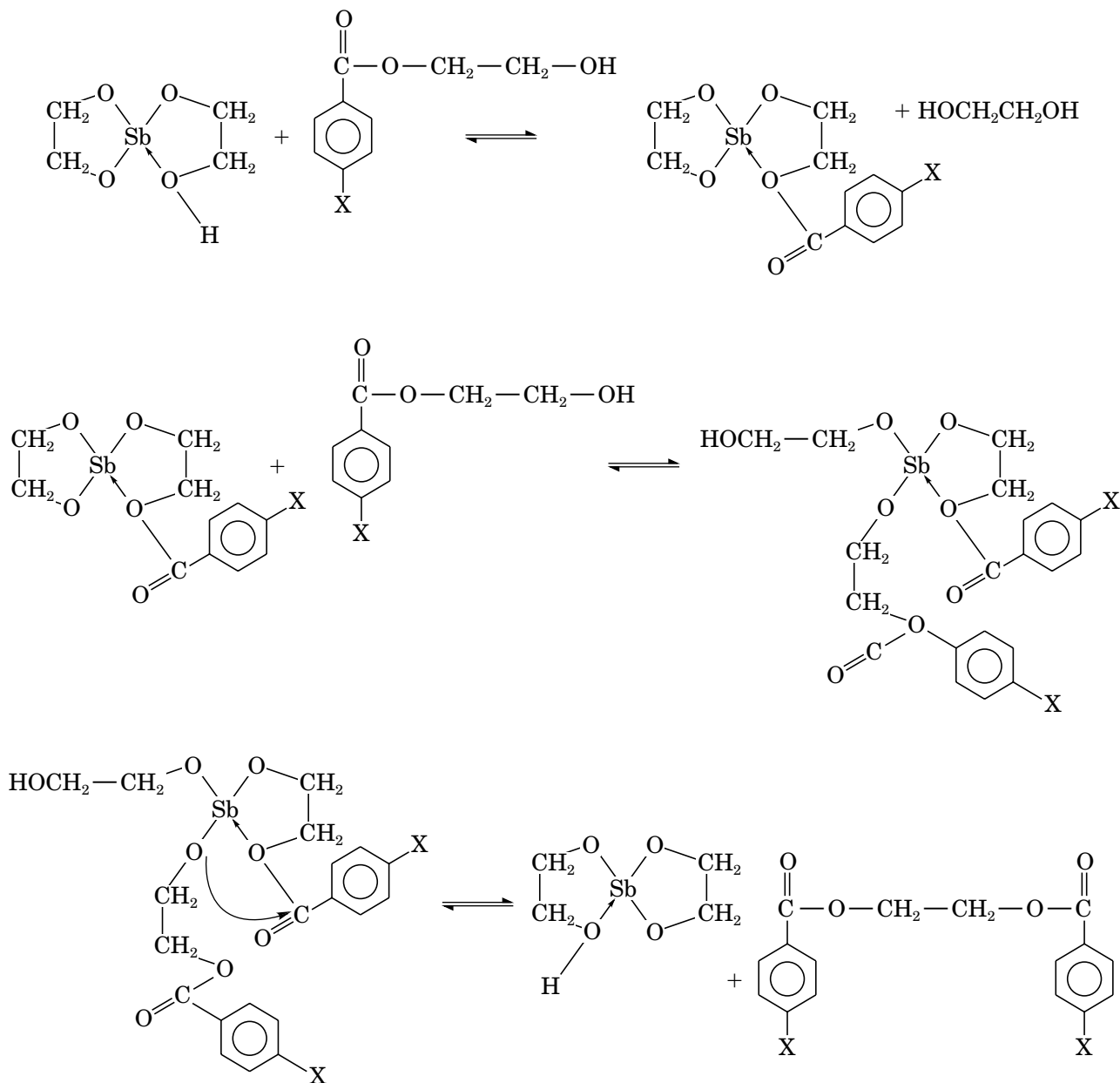


with

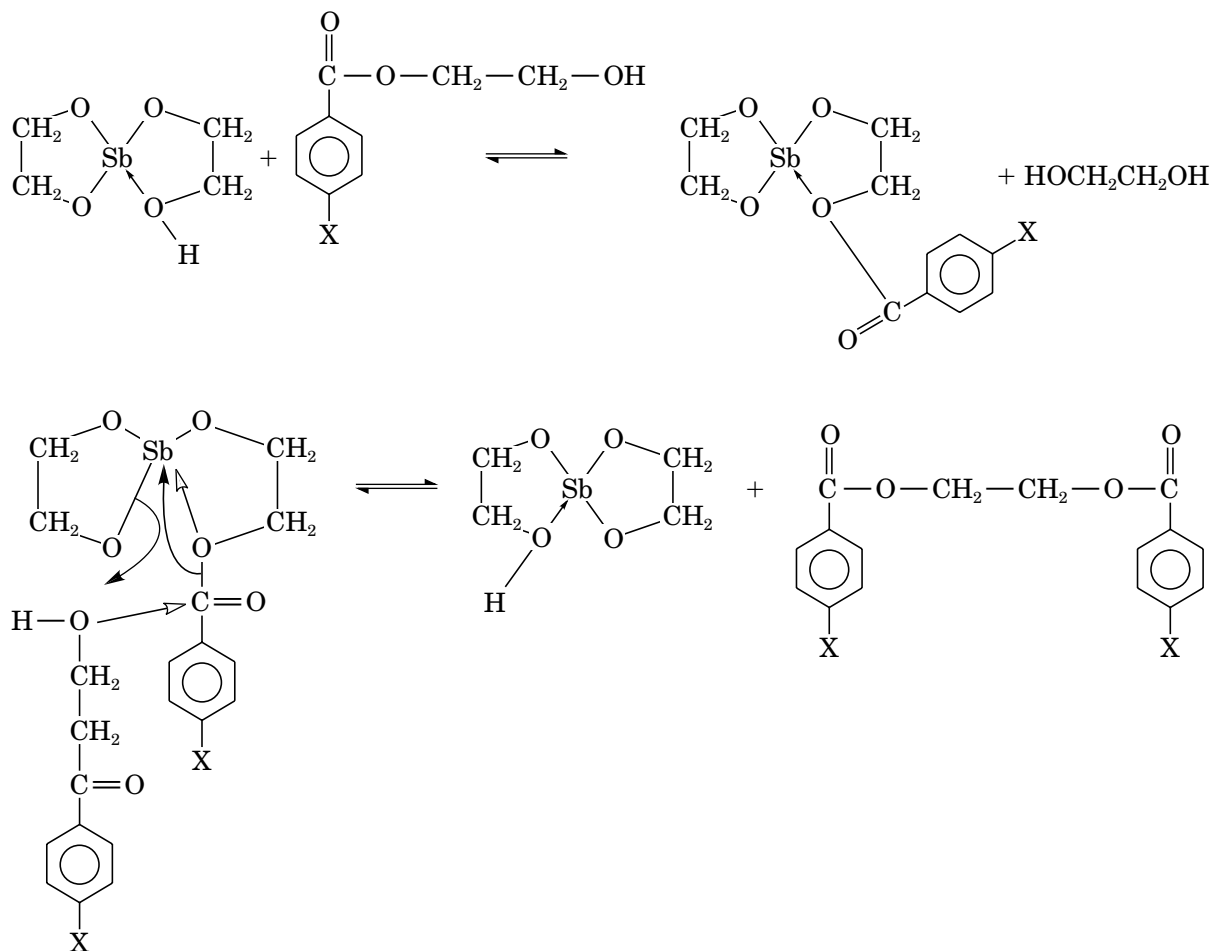


and X = H or CH<sub>3</sub>, and favor a successive nucleo-

philic attack of a glyoxide oxygen to the carboxylic carbon atom. In this case, the metal has a strong inductive effect and influences the resonance of the aromatic ring. For this reason *para* substituent strongly affects the performances of the catalyst, as shown in a previous article.<sup>17</sup> On the contrary, tri- and tetravalent metals are coordinated to the acyclic oxygen, and this favors the nucleophilic attack to carbon from the alkoxide coordinated to the metal,<sup>1,14,15</sup> in a three-step mechanism:



where X = H or CH<sub>3</sub>.



Also possible is a two-step mechanism:

These catalysts have a low effect on the resonance of the molecule and their performances are not affected by the presence of *para* substituents.

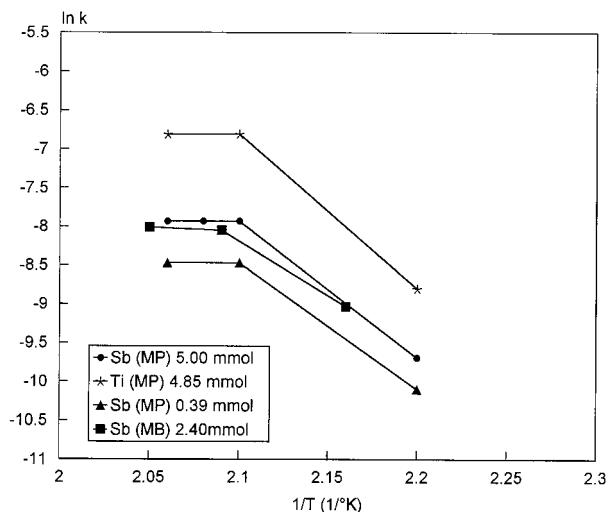
Chung<sup>2</sup> proposed a different mechanism where the activities are related to the strength of the bond between the metal ion and the carbonylic oxygen, both in DMT transesterification and BHET condensation, and the difference is only due to the difference in the basicity of the carbonylic oxygen. This mechanism, however, cannot explain the effect on the activity of the substituent in the *para* position in the model molecules.

Kinetic runs have been made for both MP and MB, at different temperatures in the presence of Sb<sub>2</sub>O<sub>3</sub> and for MP in the presence of Ti(OR)<sub>4</sub>. The results obtained are compared in Figure 10, where all the data have been arranged in an Arrhenius plot. As it can be seen, the trend is the same in all the cases considered. Besides, other authors reported for BHET polycondensation a similar trend<sup>18</sup>

without giving any explanation of the observed behavior according to a reaction mechanism. The change observed for the apparent activation energy from a value  $\geq 15.5$  kcal/mol to about 0 can be explained only assuming the change of the rate-determining step in the reaction mechanism.

## CONCLUSIONS

The kinetic study of the MP and MB condensation reaction in the presence of different catalysts has shown that reaction rates are affected by the catalyst concentration in different ways. Therefore, the volcano shaped curves for the activity as a function of the metal acidity reported by various authors give only qualitative information on the comparison of catalyst performances. The activity of bivalent metals (e.g., zinc) is affected by aromatic substituent such as the *para*-methyl group



**Figure 10** An Arrhenius type plot for the runs performed on MB and MP, respectively, at different temperatures.

in MP when compared with MB. Tri- and tetravalent catalysts are poorly affected by the presence of substituents. This behavior has already been observed for the transesterification reaction, also was studied using model molecules, as reported in a recent work.<sup>17</sup> This fact suggests that the mechanisms of the two reactions, transesterification and condensation, are similar in agreement with other authors, suggesting DMT transesterification and BHET polycondensation have the same mechanism.<sup>1,2,12</sup> We can recognize two mechanisms: the one related to the action of the bivalent metal catalysts, and the other one to the action of tri- and tetravalent metal catalysts. In the former, the metal would attack the carbonylic oxygen favoring the nucleophilic attack of the carboxylic carbon. In the latter, the metal is coordinated to the terminal part of the molecule, that is, to both the acyclic oxygen and the terminal hydroxy group. Bivalent metals are involved and affect the resonance of the molecule, while this does not occur in the case of tri- and tetravalent catalysts. For these reasons bivalent metals are optimal for transesterification and tri- and tetravalent catalysts for polycondensation. We have shown that titanium-based catalysts could be used at very low levels of concentration without losing efficiency. The behavior of Sb and Ti catalysts, changing the temperature in the condensation reaction, is similar and reveals a complex mechanism in which a change in the rate determining step occurs.

And last, we have demonstrated that the use of model molecules is useful to a better interpreta-

tion of the kinetic and catalytic aspects of the BHET polycondensation.

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