

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Models for Polyesterification Kinetics. III. Preliminary Studies on the Catalysis by Titanium(IV) Tetraalkoxides

Alain Fradet^a; Ernest Marechal^a

^a Laboratoire de Synthèse Macromoléculaire, Université P. et M. Curie, Paris, France

To cite this Article Fradet, Alain and Marechal, Ernest(1982) 'Models for Polyesterification Kinetics. III. Preliminary Studies on the Catalysis by Titanium(IV) Tetraalkoxides', *Journal of Macromolecular Science, Part A*, 17: 5, 881 – 891

To link to this Article: DOI: 10.1080/00222338208063278

URL: <http://dx.doi.org/10.1080/00222338208063278>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Models for Polyesterification Kinetics. III. Preliminary Studies on the Catalysis by Titanium(IV) Tetraalkoxides

ALAIN FRADET and ERNEST MARECHAL

Laboratoire de Synthèse Macromoléculaire
Université P. et M. Curie
75005 Paris, France

ABSTRACT

The catalytic behavior of tetrabutoxytitanium in polyesterification between diacids and diols is studied with the help of two model reactions. One is the esterification between two monofunctional oligomers. The second is the reaction of 1-octadecanol with octadecanoic acid either in octadecanyl octadecanoate or in an excess of octadecanol. The behavior of this catalyst is complex since it depends on the reaction medium. A decrease of the vacuum and an increase of the acid concentration lead to poor catalytic efficiency which is also observed when the reaction is carried out in a hydrophilic medium such as polyoxyethylene. When the alcohol is in excess, the catalyst is much more efficient and experimental results fit with a zero overall order, although deviations are observed at the highest conversions. The existence of a complex between carboxyl groups and titanium is postulated.

INTRODUCTION

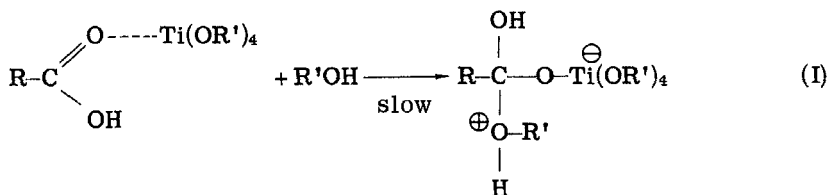
The use of tetraalkoxytitaniums as catalysts for the polyesterification between diacids and diols is claimed in many patents. However, there is a complete lack of information on the reaction mechanisms.

In previous work [1] we reported the beginning of a kinetic study on the catalysis of esterification by tetrabutoxytitanium. The reactional medium was either an equimolecular mixture of 1-octadecanol and octadecanoic acid or a mixture of an α, ω -dicarboxy poly(hexamethylene adipate) and an α, ω -dihydroxy poly(oxyethylene) which are models for high temperature polyesterifications. It appeared that the behavior of this catalyst is complex.

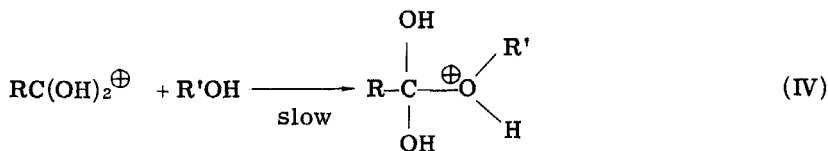
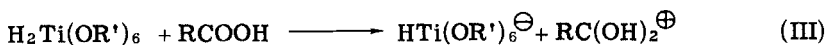
The present work is devoted to the study of the influence of the reaction medium on the behavior of the catalyst. It consists of the study of the reaction of 1-octadecanol and octadecanoic acid either in 1-octadecanyl octadecanoate or in an excess of 1-octadecanol at concentrations ranging from 0.5 to 0.07 eq/kg and with various ratios of the reactants.

BIBLIOGRAPHIC STUDY

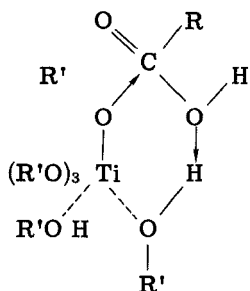
Bolotina and Kutsenko [2-4] found the same order in catalyst, acid, and alcohol:1. They suggested the following determining step:



Sorokina and Barshtein [5] found 1 and 1/2 for the orders in acid and alcohol, respectively, but did not determine the order in catalyst. Their determining step was



Sapunov et al. [6, 7] reported order 1 for acid, catalyst, and alcohol, respectively, and suggested the following intermediary complex:



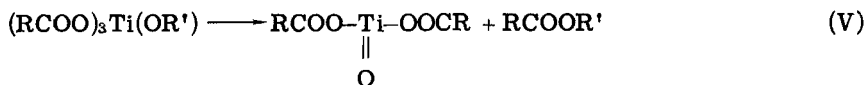
These results and mechanisms differ from each other and from ours.

In fact, the catalytic properties of $\text{Ti}(\text{OBU})_4$ largely depend on the reaction medium since it can readily react with many chemical species. The most important chemical reactions which can change the catalytic properties of titanium tetraalkoxides are the following:

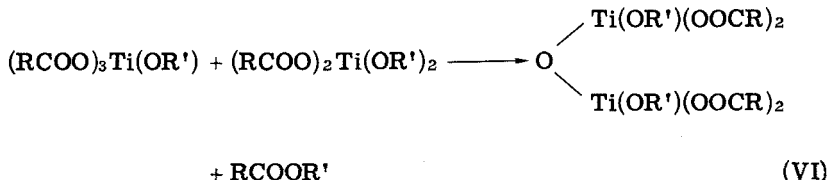
Hydrolysis, readily occurring and leading to the formation of titanoxanes whose degree of polycondensation depends on the water content of the medium.

Exchange with higher alcohols.

Reactions with carboxylic acids which can be followed by the degradation of the acid derivatives [8-13]:



or



These side reactions have a great influence on the catalytic behavior of tetrabutoxytitanium. In this work we show that they are responsible for the complex behavior of this catalyst and we determine suitable experimental conditions for an accurate study of the catalytic mechanism.

EXPERIMENTAL

Reactants and Catalyst

1-Octadecanol and octadecanoic acid (Fluka A.G., puriss. grade) were used without further purification.

1-Octadecanyl octadecanoate was prepared and purified according to Ref. 15, and ω -carboxy and ω -hydroxy polyoxyethylenes according to Ref. 16.

Tetrabutoxytitanium (Merck) was distilled (140-150°C/0.1 torr) under dry nitrogen and dissolved in pure dry dichloromethane (50 g/L). Amounts of catalyst were delivered from a calibrated microsyringe.

Procedure

Apparatus, procedure, measurements, and treatment of experimental data have been described in the first parts of this series [14, 15]. A noncatalyzed parallel reaction was always taken into account [15].

The initial concentration of carboxy groups is $x_0 = 0.5$ eq/kg in the absence of another specification.

RESULTS

As previously mentioned [14], alcoholysis, ester interchange, and acidolysis do not interfere with the main reaction. Hydrolysis can be disregarded as shown in specific experiments. The evaporation of reactants, oxidation, and decarboxylation were found to be negligible under our experimental conditions.

Reaction between ω -Hydroxy Polyoxyethylene
($\text{CH}_3\text{O}-\text{POE}-\text{OH}$) and ω -Carboxy Polyoxyethylene
($\text{CH}_3\text{O}-\text{POE}-\text{O}-\text{CH}_2-\text{COOH}$) ($M_n \approx 1000$)

The reaction between these two oligomers did not lead to a satisfactory fit of experimental data with a determined kinetic law. The best fit was found for an overall order close to 2.5. This is presumably due to the hydrophilicity of polyoxyethylene which retains reaction water and therefore favors the hydrolysis of the catalyst. In consequence, it is not surprising that only low values of rate constants are obtained.

TABLE 1. Reaction of 1-Octadecanol and Octadecanoic Acid in Octadecanyl Octadecanoate at 165.9°C, 14 torr, [TBT] = 2.69×10^{-3} mol/kg. Values of Best Fitting Overall Orders Obtained for Runs Carried Out with Various Initial Concentrations of Reactants

Run	x_0 (eq/kg)	p_{\max}	d
1	1.6	0.88	1
2	0.5	0.81	2
3	0.15	0.60	2 or 2.5

Reaction between 1-Octadecanol and Octadecanoic Acid in 1-Octadecanyl Octadecanoate (C36 ester)

Effect of Initial Concentrations of Reactants

Three runs (1, 2, 3) were carried out at 165.9°C, 14 torr, [TBT] = 2.69×10^{-3} mol/kg, and with various concentrations of reactants. From Table 1 and Fig. 1 it appears that the overall order changes continuously with the extent of reaction. The most reasonable explanation is, in our opinion, a decrease of catalytic activity with increasing extent of reaction. This decrease is not due to a slow destruction or evaporation of catalyst between the beginning and the end of the reaction, since the plots of the different runs fit. It is more probable that when the catalyst is introduced into the reaction mixture it becomes condensed (formation of titanoxanes) and that its degree of condensation changes continuously with the nature of the medium and therefore with the extent of reaction.

Effect of Catalyst Concentration

In order to determine whether the catalyst is associated or not, we carried out experiments with various catalyst concentrations and pressures at 165.9°C (Table 2, Runs 2, 4, 5).

A second-order rate equation fits the experimental data very well. However, when the conversion is above 75%, a decrease of reaction rate is observed as in Runs 1, 2, and 3. It can be observed that the reaction rate depends very little on catalyst concentration. This would seem to indicate that the catalyst is aggregated and that only the external part of the particles is efficient.

Effect of Pressure

Table 2 (Runs 2 and 4) shows a large decrease of rate constants with increasing pressure. This can be explained by the hydrolysis of the catalyst, since water concentration increases with increasing

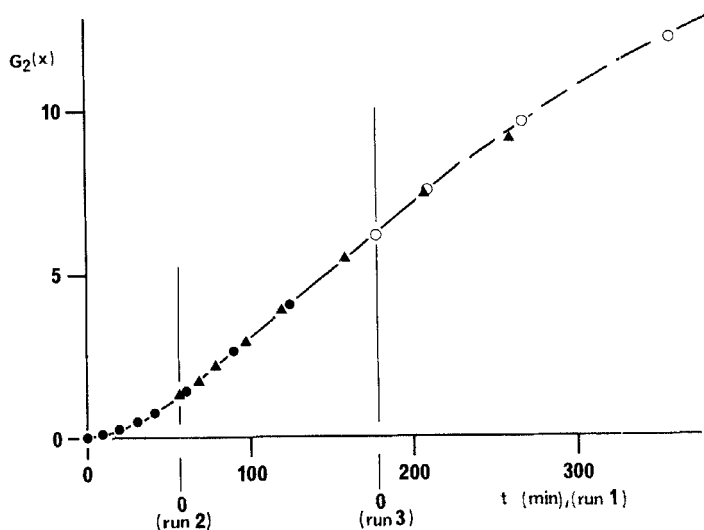


FIG. 1. Reaction of 1-octadecanol and octadecanoic acid in octadecanyl octadecanoate (Runs 2 and 3) and without solvent (Run 1) at 165.9°C , 14 torr, $[\text{TBT}] = 2.69 \times 10^{-3}$ mol/kg. Tentative second-order plots: (\bullet) Run 1, (\blacktriangle) Run 2, (\circ) Run 3.

TABLE 2. Reaction of 1-Octadecanol and Octadecanoic Acid in Octadecanyl Octadecanoate at 165°C , $r = 1$. Values of 2nd Order Rate Constants

Run	T ($^{\circ}\text{C}$)	P (torr)	$[\text{TBT}]$ (mol/ kg) $\times 10^3$	k^2 ($\text{kg}\cdot\text{eq}^{-1}\text{s}^{-1}$) $\times 10^4$
4	165.9	100	2.69	2.06
2	165.9	14	2.69	7.06
5	165.9	14	5.29	7.12
6	181.7	14	2.69	15.0

pressure. This decrease cannot be due to ester hydrolysis since it was shown [14] that at atmospheric pressure ester hydrolysis can be neglected.

Effect of Temperature

Table 2 (Runs 5 and 6) shows that the rate constant increases with increasing temperature. If it can be assumed that this increase depends only on the thermodynamic properties of the reaction, and not

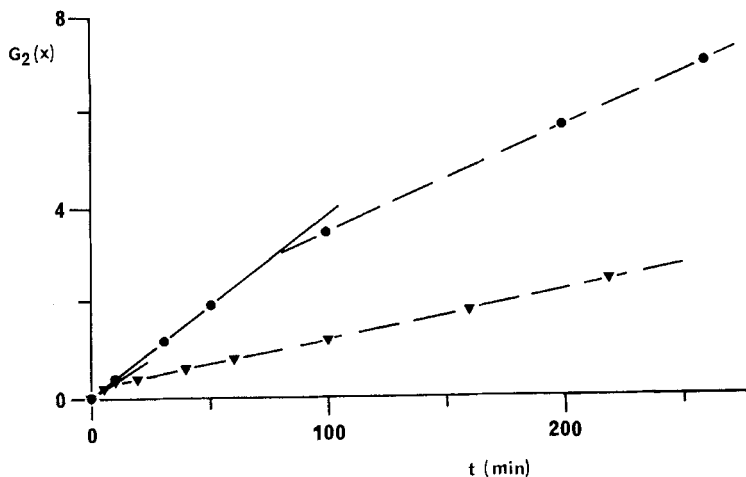


FIG. 2. Reaction of 1-octadecanol and octadecanoic acid in a 90/10 (weight) mixture of octadecanyl octadecanoate and α,ω -dimethoxy polyoxyethylene ($\bar{M}_n \approx 950$). 165.9°C , $r = 1$, $[\text{TBT}] = 3.18 \times 10^{-3}$ mol/kg.

on a decrease of hydrolysis contribution, the following activation parameters can be obtained:

$$\Delta H^\ddagger = 80 \text{ kJ/mol}, \quad \Delta S^\ddagger = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

In consequence, the catalytic effect would result in an increase of activation entropy.

Effect of the Addition of 10% α,ω -Dimethoxy Polyoxyethylene

The reactions are carried out in the following conditions: $r = 1$, 165.9°C , $[\text{TBT}] = 3.18 \times 10^{-3}$ mol/kg. Data of Runs 7 (14 torr) and 8 (100 torr) do not fit with the integrals of a simple rate equation. Plots of 2nd order integration are reported in Fig. 2.

Three observations can be made:

1. Initial rate constants are 25% lower than those obtained in pure octadecanyl octadecanoate.
2. The rate constant can increase up to three times its initial value when the pressure decreases from 100 to 14 torr.
3. There is an immediate strong decrease in the reaction rate when the extent of reaction is above 0.5. In the case of octadecanyl octadecanoate, this decrease occurs only above 0.75.

This very probably results from an increase of the hydrolysis of the catalyst due to an increase of the hydrophilicity of the reaction medium.

Effect of the Presence of an Excess of Acid

The experimental conditions are 14 torr, 165.9°C, $[TBT] = 2.69 \times 10^{-3}$ mol/kg, $r = 0.5$. As above, the experimental data do not fit with any simple rate equation integral. A strong decrease in the reaction rate occurs at a high extent of reaction.

Effect of an Excess of Alcohol

The experimental conditions are the following: 165.9°C, 14 torr, $r = 4$ and 7.

Reaction rates in Runs 8 ($[TBT] = 2.69 \times 10^{-3}$ mol/kg, $r = 4$, $x_0 = 0.29$ eq/kg) and 9 ($[TBT] = 0.587 \times 10^{-3}$ mol/kg, $r = 4$, $x_0 = 0.29$ eq/kg) are far above those obtained at stoichiometry or in an excess of acid. When the reaction is carried out in octadecanol (Run 10, $[TBT] = 0.587 \times 10^{-3}$ mol/kg), the reaction is once again faster than in Runs 8 and 9.

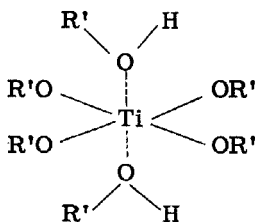
When the last data points are not taken into account (conversion below 65% in Run 9 and below 85% in Run 10), the reaction rate is proportional to the time. This fits with a zero-order rate equation (Fig. 3).

Moreover, a comparison of reaction rates obtained in the initial stages of the reaction for Runs 9 and 8 shows that order in catalyst is higher (≈ 0.65) when $r = 4$ (excess of alcohol) than when $r = 1$ (≈ 0). This shows that when there is an excess of alcohol, the catalyst is stabilized.

DISCUSSION

The catalytic behavior of tetrabutoxytitanium (TBT) is complex and apparently depends on the composition of the medium where it is used.

As soon as TBT is introduced, its butoxy groups interchange with the species present in the medium. When alcohol is in excess, the catalyst is in a favorable neighborhood since titanium can be complexed by two molecules of alcohol:



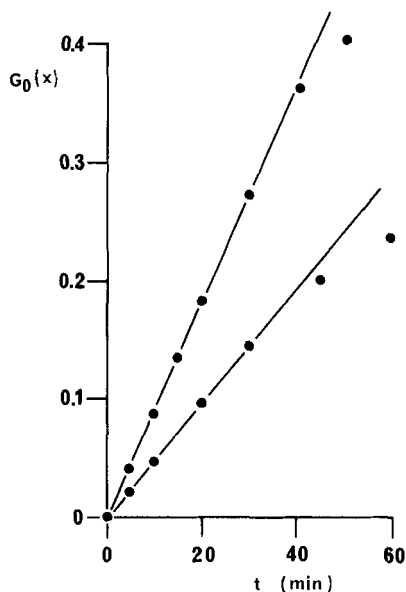
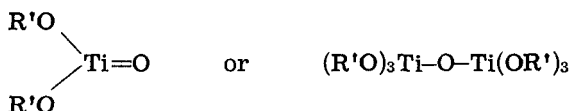


FIG. 3. Reaction of 1-octadecanol and octadecanoic acid in octadecanyl octadecanoate (Run 9) and in 1-octadecanol (Run 10). 165.9°C , 14 torr $[\text{TBT}] = 0.587 \times 10^{-3}$ mol/kg. Zero-order plots.

When an excess of acid is present, formation of condensed species takes place:

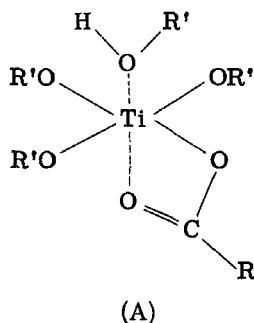


These forms have a catalytic efficiency which is probably lower than that of the noncondensed species.

When both water and TBT are present in sufficient quantities, hydrolysis occurs and condensed species are formed. These condensed species can even exist as colloids or aggregates which would explain the very low dependence of reaction rate on catalyst concentration.

Infrared study [1] of TBT in the presence of carboxylic acids showed a strong interaction between carboxyl groups and titanium. Carboxyl absorption of acid (near 1700 cm^{-1}) disappears entirely and is replaced by two other absorptions at 1560 and 1450 cm^{-1} . Such absorptions were found for tetrabutoxytitanium-terephthalic

acid interactions [17]. These observations fit with a catalytic complex which could be



If the formation of Complex A is rapid and followed by a slow intramolecular reaction of carboxy and alkoxy groups, the overall order should be zero.

In conclusion, we can say that we pointed out the influence of side reactions (acidolysis and hydrolysis of catalyst) on catalytic behavior of tetrabutoxytitanium. This is not mentioned in any of the work found in the literature. To obtain more information on the catalytic behavior of TBT, we have undertaken two research studies:

1. Study of the kinetics of the esterification catalyzed by TBT in media unfavorable to side reactions.
2. Determination and study of the effective catalytic species.

SYMBOLS

x, x_0	carboxyl group content (eq/kg) at times t (s) and 0
d	overall order
k_d	rate constant for a d -th overall order ($\text{kg}^{d-1} \cdot \text{eq}^{1-d} \cdot \text{s}^{-1}$)
$F_d(x)$	undefined integral corresponding to a d -th overall order rate equation
$G_d(x) =$	$F_d(x) - F_d(x_0)$
r	initial ratio of hydroxyl group concentration to carboxyl group concentration

T	temperature (K, unless °C is specified)
ΔS^\ddagger , ΔH^\ddagger	entropy and enthalpy of activation
p_{\max}	maximum extent of reaction

REFERENCES

- [1] A. Fradet and E. Marechal, Eur. Polym. J., **14**, 761 (1978).
- [2] L. M. Bolotina, E. G. Maksimenko, and A. I. Kutsenko, Plast. Massy, **7**, 13 (1973).
- [3] L. M. Bolotina, E. G. Maksimenko, and A. I. Kutsenko, Khim. Promst. (Moscow), **7**, 499 (1975).
- [4] A. I. Kutsenko, L. M. Bolotina, and S. D. Soinov, Plast. Massy, **1**, 23 (1971).
- [5] I. A. Sorokina and R. S. Barshtein, Ibid., **9**, 24 (1975).
- [6] N. N. Lebedev, V. N. Sapunov, and G. M. Lemman, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., **16**(11), 1762 (1973).
- [7] V. N. Sapunov, G. M. Lemman, and N. N. Lebedev, Ibid., **19**(5), 696 (1973).
- [8] K. C. Pande and R. C. Mehrotra, Z. Anorg. Allg. Chem., **290**, 87 (1957).
- [9] K. C. Pande and R. C. Mehrotra, Ibid., **290**, 95 (1957).
- [10] K. C. Pande and R. C. Mehrotra, Ibid., **291**, 97 (1957).
- [11] K. C. Pande and R. C. Mehrotra, J. Prakt. Chem., **5**, 101 (1957).
- [12] I. D. Varma and R. C. Mehrotra, Ibid., **8**, 235 (1959).
- [13] D. M. Puri and R. C. Mehrotra, J. Indian Chem. Soc., **39**, 447 (1962).
- [14] A. Fradet and E. Marechal, J. Polym. Sci., Polym. Chem. Ed., **19**, 2905 (1981).
- [15] A. Fradet and E. Marechal, J. Macromol. Sci.-Chem., **A17**(5), 859 (1982).
- [16] A. Fradet and E. Marechal, Polym. Bull., **4**, 205 (1981).
- [17] N. Yoshino and T. Yoshino, Kogyo Kagaku Zasshi, **74**, 1673 (1971).

Accepted by editor March 17, 1981

Received for publication April 7, 1981