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### Kinetic Study on Models of the Tetrabutqxyzirconium-Catalyzed Reaction Between $\alpha, \omega$ -Dicarboxypolyamide-11 and $\alpha, \omega$ -Dihydroxypolyoxyethylene

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# KINETIC STUDY ON MODELS OF THE TETRABUTOXYZIRCONIUM-CATALYZED REACTION BETWEEN $\alpha, \omega$ -DICARBOXYPOLYAMIDE-11 AND $\alpha, \omega$ -DIHYDROXPOLYOXYETHYLENE

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## ABSTRACT

The kinetics of the tetrabutoxyzirconium-catalyzed esterifications between 11-dodecylamideundecanoic acid and 1-dodecanol, 2-tridecanol,  $\alpha$ -dodecyl- $\omega$ -hydroxypolyoxyethylene are studied and compared to that of  $\alpha, \omega$ -dicarboxypolyamide-11 and  $\alpha, \omega$ -dihydroxypolyoxyethylene. The reaction with 2-tridecanol is characterized by an autoacceleration phenomenon. In the other cases the reaction rate is not greatly affected by catalyst concentration. An explanation involving the formation of catalyst condensates at the very beginning of the reaction is put forward.

## INTRODUCTION

In a preceding article [1] we studied the noncatalyzed esterifications between dicarboxypolyamide-11 and dihydroxypolyoxyalkylenes in the bulk using low molecular weight models and functional oligomers. This is a third-

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order reaction, with low rate constants, exactly like classical solution esterifications. The use of a catalyst is, therefore, required to obtain polyamide block polyethers of high molecular weight. In previous studies we analyzed the catalytic behavior of titanium and zirconium alkoxides [2-6], which are known to be efficient polyesterification catalysts. In the present article we study the block polycondensation of  $\alpha,\omega$ -dicarboxyoligoamides and  $\alpha,\omega$ -dihydroxypolyethers, in the bulk, using the following model esterifications and polyesterifications:

(1) 11-Dodecylamidoundecanoic acid (DAUA),  $\text{CH}_3-(\text{CH}_2)_{10}-\text{CO}-\text{NH}-(\text{CH}_2)_{10}-\text{COOH}$ , with 1-dodecanol, 2-tridecanol,  $\alpha$ -dodecyl- $\omega$ -hydroxypolyoxyethylene ( $\bar{M}_n = 370$ ; POE-OH 370)

(2)  $\alpha,\omega$ -Dicarboxypolyamide-11 ( $\bar{M}_n = 920$ ; PA11-COOH) with  $\alpha,\omega$ -dihydroxypolyoxyethylene ( $\bar{M}_n = 1100$ ; POE-diOH).

Reactions (1) were studied at atmospheric pressure and Reaction (2) under 14 torr, i.e., under experimental conditions close to those of industry.

## EXPERIMENTAL

Chemicals, experimental techniques, and notations are described in a preceding article [1]. Data treatment is described in Refs. 1 and 6. The parallel nuncatalyzed esterification is always taken into account. [Zr] is the concentration in tetrabutoxyzirconium ( $\text{Zr}(\text{OBu})_4, \text{BuOH}$ ) added to the reaction medium (mmol/kg).

## RESULTS

### Reaction between 11-Dodecylamidoundecanoic Acid (DAUA) and 1-Dodecanol

#### Influence of Initial Acid Concentration

Two experiments were carried out at  $180^\circ\text{C}$  under atmospheric pressure with different initial acid concentrations  $x_i$  and similar catalyst concentrations ( $x_i = 0.478$  mol/kg,  $[\text{Zr}] = 1.76$  mmol/kg, and  $x_i = 0.251$  mol/kg,  $[\text{Zr}] = 1.81$  mmol/kg). Figure 1 shows that the two kinetic plots can be superimposed by translation, showing that a change in  $x_i$  does not affect catalytic activity.

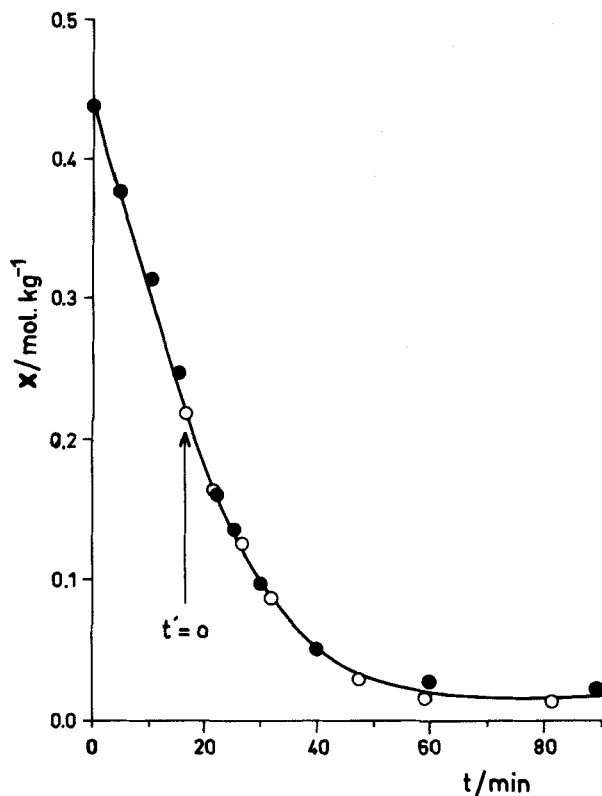


FIG. 1. Esterification of DAUA in 1-dodecanol in the presence of  $Zr(OBu)_4$  at different initial carboxyl group concentrations  $x_i$  ( $180^\circ\text{C}$ , atmospheric pressure).  $x_i$ ,  $[Zr]$  (mmol/kg): (●) 0.478, 1.76; (○) (after translation  $t = t + 16.5$  along  $t$ -axis) 0.251, 1.81.

#### Influence of Acid Addition after Completion of the Reaction

To determine whether the catalytic activity changes during the course of a polyesterification, we carried out a two-step experiment at  $180^\circ\text{C}$  under atmospheric pressure. In the first step,  $x_i = 0.485$  mol/kg and  $[Zr] = 0.615$  mmol/kg. After complete esterification of the carboxyl groups, the reaction medium contains 0.485 mol/kg of ester and 3.81 mol/kg of alcohol. The second step consists of the addition of DAUA (0.501 mol/kg) and results in a

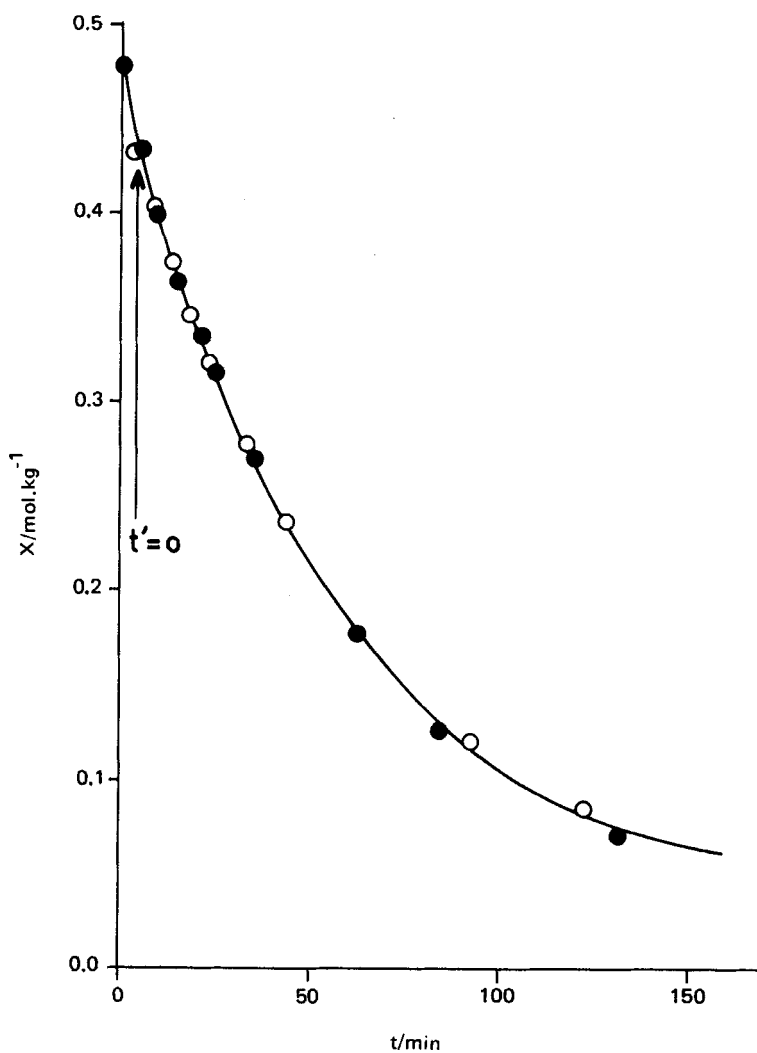


FIG. 2. Esterification of DAUA in 1-dodecanol in the presence of  $\text{Zr}(\text{OBU})_4$  ( $180^\circ\text{C}$ , atmospheric pressure). (●) Fresh DAUA ( $0.501 \text{ mol/kg}$ ) was added after completion of the preceding run. Catalyst concentration after addition:  $[\text{Zr}] = 0.488 \text{ mmol/kg}$ . (○) Reference experiment ( $x_i = 0.466 \text{ mol/kg}$ ,  $[\text{Zr}] = 0.439 \text{ mmol/kg}$ ).

catalyst concentration equal to 0.488 mmol/kg. The corresponding kinetic plot (Fig. 2) can be superimposed, by a translation along the  $t$ -axis, upon the plot for a reference experiment ( $x_i = 0.466$  mol/kg;  $[Zr] = 0.439$  mmol/kg). The same slope  $dx/dt$  always corresponds to the same carboxyl group concentration in both plots, showing that the activity of the catalyst is not modified during the course of the experiment.

#### Influence of Catalyst Concentration

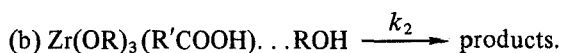
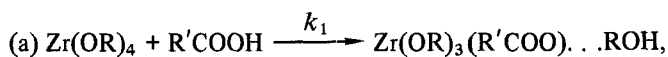
The results of a series of experiments carried out at 180°C under atmospheric pressure with various catalyst concentrations (Table 1) are reported in Fig. 3. This shows that there is no autoacceleration phenomenon analogous to that observed in the case of the  $Zr(OBu)_4$ -catalyzed esterification of octadecanoic acid in 1-octadecanol [4].

The variation of  $x = [COOH]$  with respect to time is analyzed by taking into account one or the other of the two following hypotheses:

(1) Kinetic data fit the following rate equation:

$$-dx/dt = k_{m,n} [COOH]^m [OH]^n.$$

(2) Parallel reactions take place:



Reactions (a) and (b) correspond to a differential equation system which, for given values of  $k_1$  and  $k_2$ , can be solved by Runge-Kutta's method. The  $k_1$  and  $k_2$  values are optimized by a procedure described in Ref. 6.

None of the kinetic schemes fits the experimental data satisfactorily. The best results are obtained for a very low order in acid ( $m \approx 0$ ). This fits our preceding results [4] on the catalysis by  $Zr(OBu)_4$ , where it was assumed that side reactions of the catalyst (such as  $2 \begin{array}{c} | \\ -Zr-OR \\ | \end{array} + H_2O \rightarrow \begin{array}{c} | \\ -Zr-O- \\ | \end{array} Zr + 2ROH$ ) interfere with a zero-order kinetic step.

#### Reaction between 11-Dodecylamidoundecanoic Acid (DAUA) and Tridecanol-2

Experimental parameters and results are reported in Table 2 and Figs. 4 and 5. These show that, as in the case of the  $Zr(OBu)_4$ -catalyzed reaction of

TABLE 1. Esterification of DAUA in 1-Dodecanol (180°C, atmospheric pressure)

Experiment	$x_i$ , mol/kg	[Zr], mmol/kg
1	0.466	0.439
2	0.462	1.44
3	0.478	1.76
4	0.411	2.52

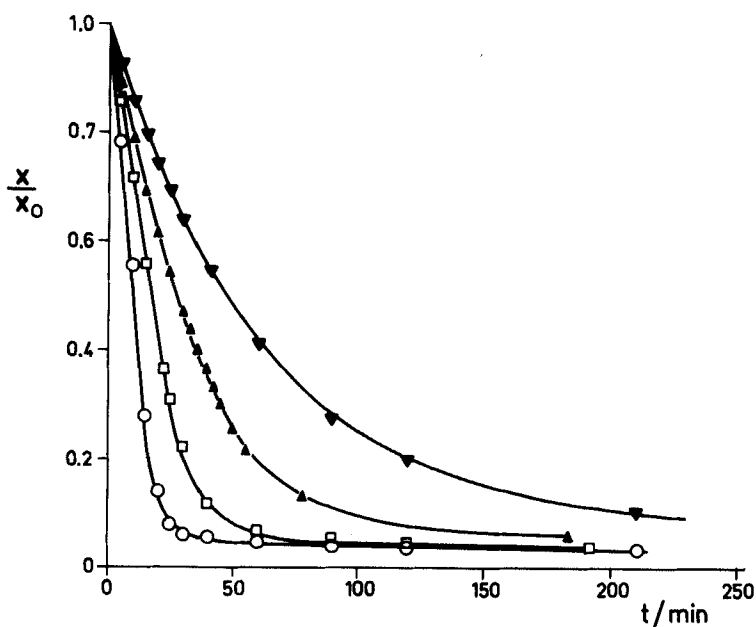


FIG. 3. Esterification of DAUA in 1-dodecanol in the presence of  $Zr(OBu)_4$  (180°C, atmospheric pressure). [Zr] (mmol/kg): ( $\blacktriangledown$ ) 0.439, ( $\blacktriangle$ ) 1.44, ( $\square$ ) 1.76, ( $\circ$ ) 2.52. (See Table 1.)

TABLE 2. Esterification of DAUA in 2-Tridecanol at Atmospheric Pressure

Experiment	$x_i$ , mol/kg	$[Zr]$ , mmol/kg	$T$ , °C
5	0.486	0.541	180
6	0.485	1.32	180
7	0.485	2.87	180
8	0.488	4.27	180
9	0.424	3.64	190

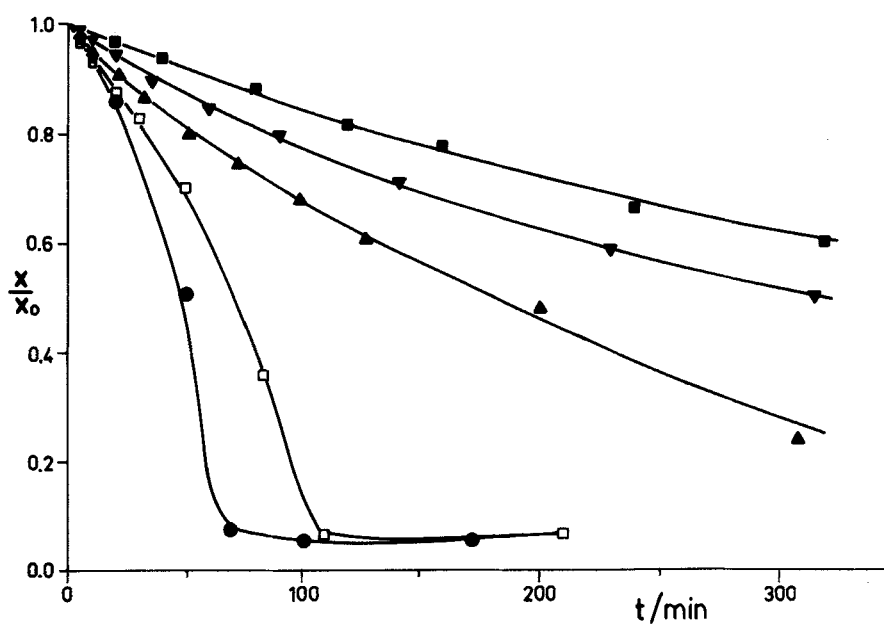


FIG. 4. Esterification of DAUA in 2-tridecanol (180°C, atmospheric pressure).  $[Zr]$  (mmol/kg): (■) 0, (▼) 0.541, (▲) 1.32, (□) 2.87, (●) 4.27.



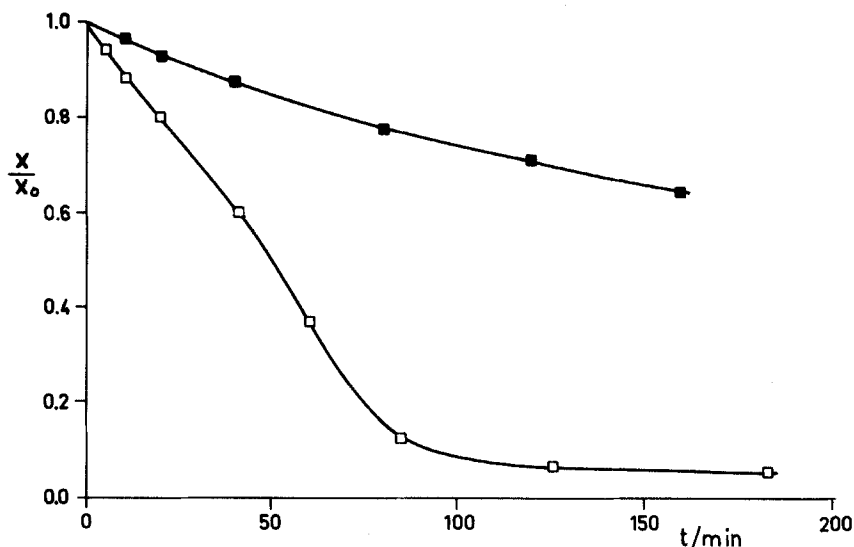


FIG. 5. Esterification of DAUA in 2-tridecanol (190°C, atmospheric pressure). [Zr] (mmol/kg): (■) 0, (□) 3.64.

octadecanol with octadecanoic acid [5], autoacceleration contributes to the kinetics, particularly for the reactions carried out at high catalyst concentrations (Exp. 7-9). Autoacceleration can be explained by the cleavage, in the presence of esterification water and acid, of catalyst condensates formed immediately after the introduction of the catalyst, i.e., when its local concentrations are still high. This cleavage increases the number of accessible  $-Zr-OR$  groups and thus enhance the catalytic effect. As the extent of cleavage cannot be quantified precisely, no kinetic calculation can be carried out.

#### Reaction between 11-Dodecylamidoundecanoic acid (DAUA) and $\alpha$ -dodecyl- $\omega$ -hydroxypolyoxyethylene ( $\bar{M}_n = 370$ ; POE-OH 370)

Experimental parameters and results are reported in Table 3 and Figs. 6-8. No catalytic effect is observed when the catalyst concentration is below 2.5 mmol/kg, at least in our experimental conditions. In fact, the rates of the non-catalyzed and of the catalyzed reactions are of the same magnitude. Figure 8 shows clearly that catalytic efficiency is not proportional to catalyst concen-

TABLE 3. Esterification of DAUA in POE-OH 370 at Atmospheric Pressure

$T, ^\circ\text{C}$	$x_i, \text{mol/kg}$	$[\text{Zr}], \text{mmol/kg}$
180	0.459	0.686
180	0.453	0.986
180	0.453	1.71
180	0.457	1.92
180	0.457	2.42
180	0.449	4.29
180	0.454	6.77
190	0.453	2.41
240	0.454	3.58
240	0.456	5.00
240	0.453	5.74
240	0.451	6.70

tration as the shape of the curves corresponding to  $[\text{Zr}]$  (mmol/kg) = 3.58 and 5.00, on the one hand, and 5.74 and 6.70, on the other, are similar. This rather unusual behavior could also be explained by the formation of catalyst condensates.

**Reaction between  $\alpha,\omega$ -Dicarboxypolyamide-11 ( $\bar{M}_n = 1080$ ; PA11-diCOOH) and  $\alpha,\omega$ -Dihydroxypolyoxyethylene ( $\bar{M}_n = 1100$ ; POE-diOH)**

A series of stoichiometric reactions was carried out at  $240^\circ\text{C}$  under 14 torr with various catalyst concentrations (Table 4). To avoid diffusion control of the kinetics, the extent of reaction was kept below 80%, thus limiting any increase in viscosity of the medium. The results (Fig. 9) show a catalytic effect when  $[\text{Zr}] > 0.4$  mmol/kg. This threshold concentration is lower than that for the DAUA/POE-OH 370 system, probably because the lower polyoxyethylene concentration of the medium limits the formation of catalyst condensates at the very beginning of the reaction.

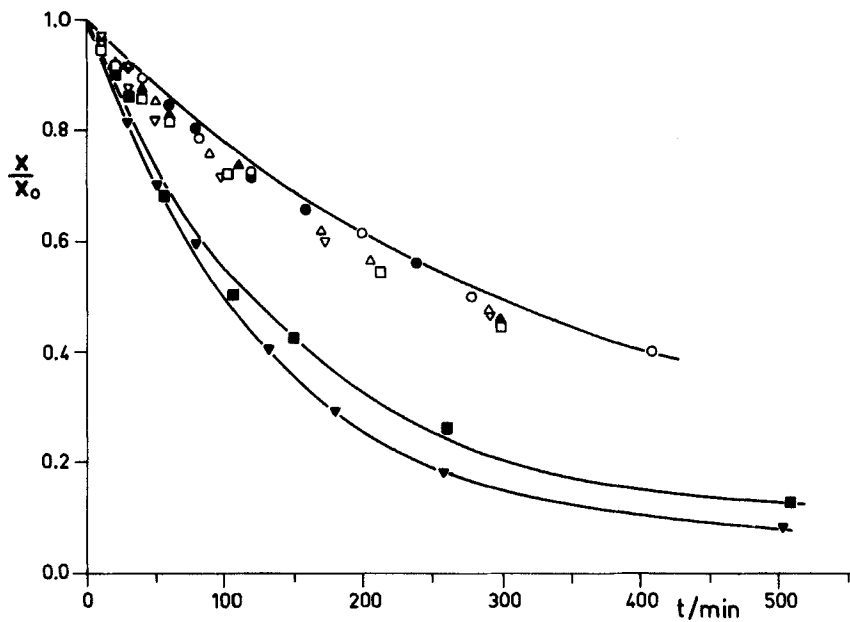


FIG. 6. Esterification of DAUA in POE-OH 370 (180°C, atmospheric pressure). [Zr] (mmol/kg): (○) 0, (△) 0.686, (□) 0.986, (▽) 1.71, (●) 2.42, (■) 4.29, (▼) 6.77.

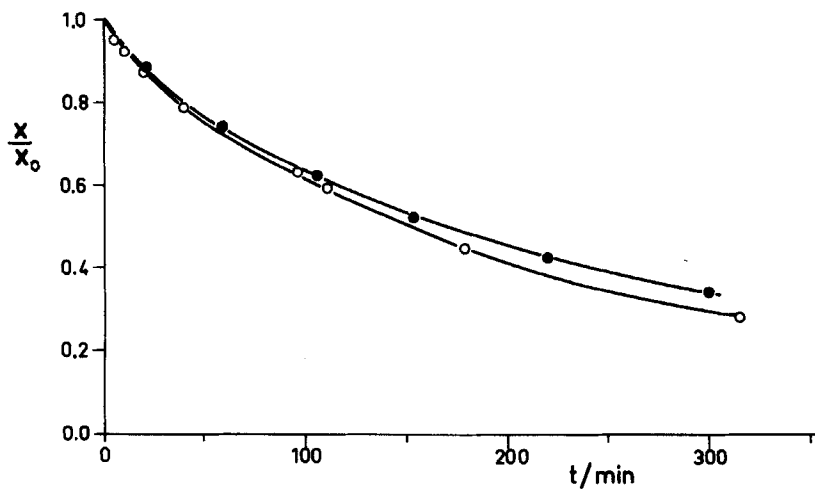


FIG. 7. Esterification of DAUA in POE-OH 370 (190°C, atmospheric pressure). (●) No catalyst, (○) [Zr] = 2.41 mmol/kg.

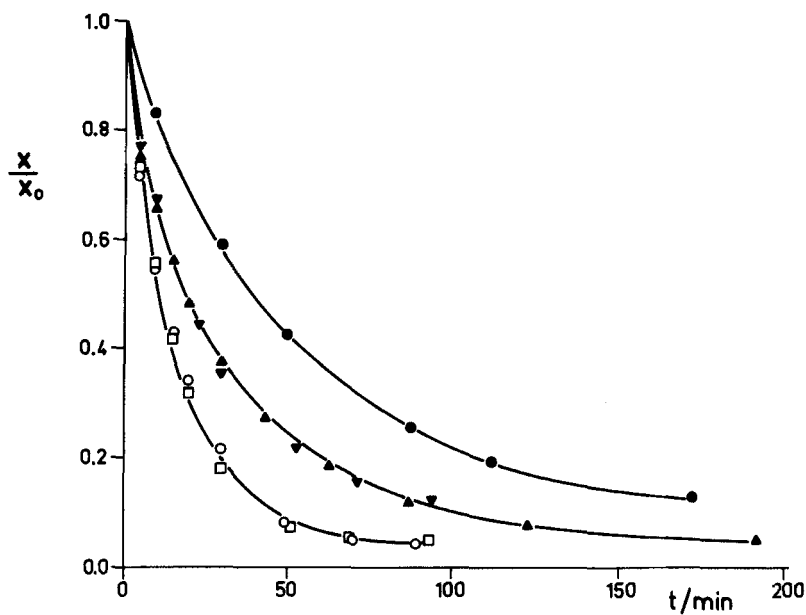


FIG. 8. Esterification of DAUA in POE-OH 370 (240°C, atmospheric pressure). [Zr] (mmol/kg): (●) 0, (▲) 3.58, (▼) 5.00, (□) 5.74, (○) 6.70.

TABLE 4. Polyesterification of PA11-diCOOH with POE-diOH (14 torr, 240°C)

$x_i$ , mol/kg	[Zr], mmol/kg
0.994	0.408
0.993	1.41
0.994	2.50

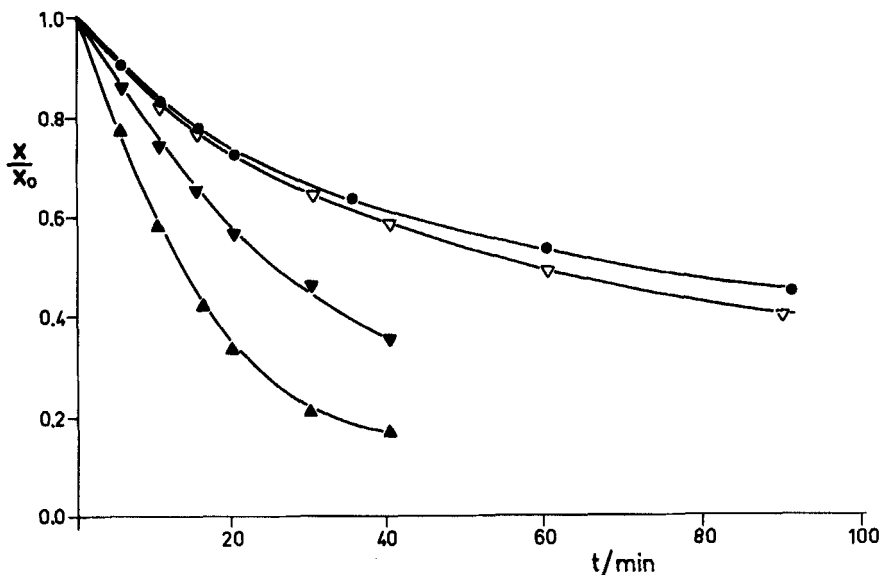


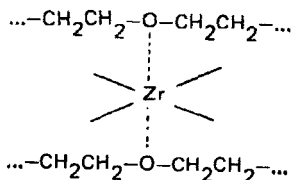
FIG. 9. Polyesterification of PA11-diCOOH with POE-diOH (240°C, 14 torr). [Zr] (mmol/kg): (●) 0, (▽) 0.408, (▼) 1.41, (▲) 2.50.

## DISCUSSION

The tetrabutoxyzirconium-catalyzed esterification or polyesterification of carboxylic compounds containing amide groups is similar to that of the aliphatic long-chain carboxylic acids or carboxylic oligoesters. Depending on the reaction medium, it is characterized by either an acceleration or a low dependence of the reaction rate on catalyst concentration. The reaction rate decreases greatly when the aliphatic alcohol is replaced by a functional polyoxyethylene.

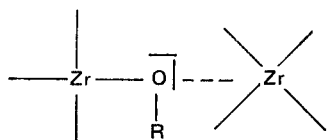
The low dependence of the catalytic effect on the catalyst concentration may be explained in two ways:

- (1) Oxygen atoms of polyoxyethylene coordinate to the zirconium alkoxide:

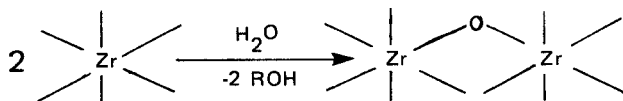


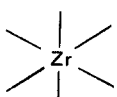
This decreases the exchange capability of Zr—OR groups shown by Fradet et al. [4, 5] to play a determining role in the catalytic activity. However, due to the very low amount of catalyst in the reaction medium, this cannot account for the strong catalytic effect observed when the catalyst concentration is above its threshold value. This led us to propose another explanation.

(2) As soon as the zirconium alkoxide is introduced in the reaction medium, its butoxy groups are exchanged with the R—O— or R—CO—O— groups present in the medium. It can also coordinate with alcohol, acid, or other zirconium alkoxide molecules,



resulting in hexa (or higher) coordination of zirconium. It is generally accepted [7] that, in dilute solutions, such metallic alkoxides are associated by coordination. However, in the presence of water, such associations can transform into condensed structures,



where  is a nonassociated catalyst molecule. This decreases the num-

ber of active sites from 6 to 5 per catalyst molecule. However, such a reaction can extend to the formation of organometallic chains with a condensation degree higher than 2. In these chains, zirconium atoms have 4 active sites, with the exception of end atoms which have 5. Thus two nonassociated and three associated catalyst molecules have the same number of active sites: 12. The polycondensation of the catalyst is not linear but can develop in different directions. However, only the surface of the catalyst condensed structure is accessible to the reactants. Thus, when the condensation degree increases, the catalyst efficiency depends mainly on the number and on the size of the condensed structures.

The presence of the catalyst condensed structure accounts for both the low dependence of catalytic efficiency on the catalyst concentration and the auto-acceleration, provided the catalyst condensation is a reversible process due to the possible hydrolysis.

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