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STUDY OF MODEL ESTERIFICATIONS AND OF POLYESTERIFICATIONS CATALYZED BY VARIOUS ORGANOMETALLIC DERIVATIVES—II. STUDY OF ESTERIFICATIONS AND POLYESTERIFICATIONS CATALYZED BY ZIRCONIUM DERIVATIVES

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Abstract—The esterification of octadecanoic acid in 1-octadecanol catalyzed by zirconium derivatives is studied. The catalytic efficiency does not depend on $[COOH]_0$ and does not change during the esterification. Reactions carried out at 760, 100 or 50 mmHg are characterized by autoacceleration which is not observed when pressure is 14 mmHg. The dependence of the catalytic efficiency on the nature of the zirconium ligands is studied as well as the behaviour of the system when water is added in various experimental conditions. The polycondensation of oligo (1,6-hexanediyl adipate) and of oligo (1,10-decanediyl adipate) is studied in the absence of catalyst or in the presence of tetrabutoxyzirconium.

INTRODUCTION

In Part I we studied model esterifications catalyzed by organometallic compounds, particularly titanium derivatives. We showed that the exchange between the reacting alcohol and the titanium ligands is an essential step before catalysis takes place. The mechanism very probably involves coordination between titanium and carbonyl groups. In this part we carry out a similar study with model esterifications and polyesterifications catalyzed by zirconium derivatives.

EXPERIMENTAL

All information on experimental techniques was given in Part I [1].

Oligomers were obtained by refluxing a toluene solution (20% wt) of diacid (1 mol) and of diol (1 mol); reaction water was eliminated through a Dean–Stark apparatus until 60% of carboxylic groups were esterified; toluene was distilled off under vacuum. End-group concentrations (mol; kg^{-1}): oligo(1,6-hexanediyl adipate): $[COOH] = 4.11 \pm 0.01$; $[OH] = 4.16 \pm 0.08$ oligo(1,10-decanediyl adipate): $[COOH] = 1.43 \pm 0.01$; $[OH] = 1.45 \pm 0.04$.

Notation: $Bu = -(CH_2)_3-CH_3$.

RESULTS AND DISCUSSIONS

(*A*) *Study of the Catalytic Activity of* $NaZr_2(OBu)_9$

We carried out several model esterifications using the following system: octadecanoic acid ($0.5\ mol\ kg^{-1}$) in 1-octadecanol at 165°C under 14 mmHg with various catalyst concentrations. The results showed that $Zr(OBu)_4$ and $NaZr_2(OBu)_9$ have the same activity, which is probably due to the fact that in the reaction medium $NaZr_2(OBu)_9$ is cleaved into NaOBu and $Zr(OBu)_4$. The same study was carried out under stoichiometric conditions: [octadecanol] = [octadecanoic acid], in the presence of either $Zr(OBu)_4$ or $NaZr_2(OBu)_9$ and led to the same conclusion. For this reason we limited our study to $Zr(OBu)_4$.

(*B*) *Kinetic Study of the Reaction of 1-Octadecanol with Octadecanoic Catalyzed by Tetrabutoxyzirconium*

Preliminary study

Two reactions were carried out with two values of $[COOH]_0$ (0.5 and $0.25\ mol\ kg^{-1}$) in the same experimental conditions (165°C; 14 mmHg; $[Zr(OBu)_4] = 0.902\ 10^{-3}\ mol\ kg^{-1}$). The corresponding plots (Fig. 1) can be superimposed by translation showing that the catalytic activity of $Zr(OBu)_4$ does not depend on $[COOH]_0$.

To discover any possible change in catalytic efficiency during an experiment, we carried out a two-step experiment. In the first step $[COOH]_0 = 0.5\ mol\ kg^{-1}$; $p = 14$ mmHg; $T = 165°C$; $Zr(OBu)_4 = 0.944.\ 10^{-3}\ mol\ kg^{-1}$. After complete acid conversion, the reaction medium contains $0.5\ mol\ kg^{-1}$ of ester and $2.69\ mol\ kg^{-1}$ of alcohol; $0.5\ mol\ kg^{-1}$ of acid is then added resulting in a catalyst concentration of $0.851\ 10^{-3}\ mol\ kg^{-1}$.

The corresponding kinetic plot can be superimposed on that of a reference experiment carried out under the same experimental conditions (Fig. 2). This shows that the activity of the catalyst did not decrease during the first step.

Influence of pressure

The kinetic plots for experiments carried out at 165°C under different N_2 pressures are reported in Fig. 3; reactions at 760, 100 or 50 mmHg are characterized by autoacceleration which is not observed when $p = 14$ mmHg or when the catalyst is $Ti(OBu)_4$ [1]. As this effect could be due to an impurity which might be eliminated when $p = 14$ mmHg but not

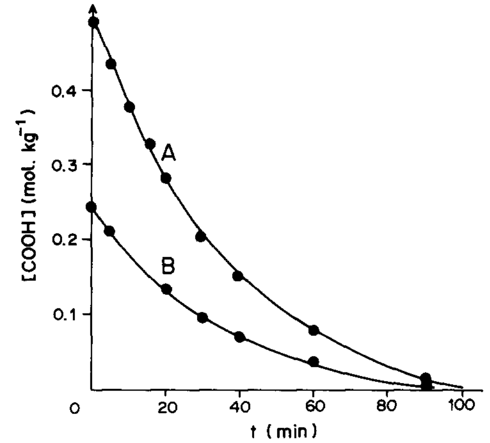


Fig. 1. Esterification of octadecanoic acid in 1-octadecanol (165°C; 14 mmHg); $[Zr(OBu)_4]_0 = 0.902\ 10^{-3}$ mol kg^{-1}. (A) $[COOH]_0 = 0.5$ mol kg^{-1}; (B) $[COOH]_0 = 0.25$ mol kg^{-1}.

when it is 50, 100 or 760 mmHg, we carried out a further experiment at 760 mmHg using reactants previously (and separately) heated at 165°C under 14 mmHg, in order to eliminate any possible volatile impurities. The corresponding kinetic plot was identical to that obtained from non-preheated reactants, showing that autoacceleration is not due to the presence of impurities in the reaction medium.

Influence of water

The residual amount of water in the reaction medium is higher at 760 mmHg than in other experiments since the rate of water elimination decreases with increasing pressure. To determine the influence of residual water, we carried out experiments at 14 mmHg introducing water (2.5 ml kg^{-1}) at timed intervals during which vacuum was broken with N_2. Figure 4 shows that water additions, at least after a certain time, result in an increase of the rate of reaction; water additions at the beginning of the reaction have apparently no effect.

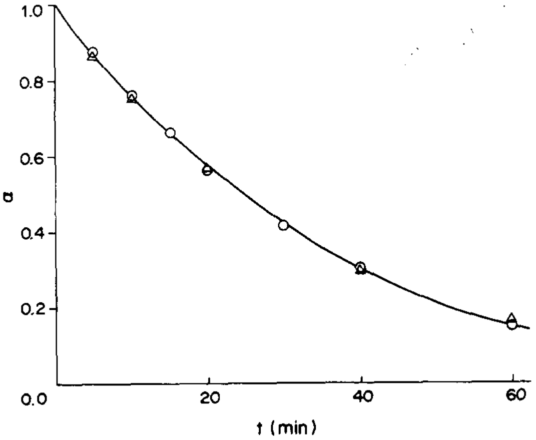


Fig. 2. Esterification of octadecanoic acid in 1-octadecanol (165°C, 14 mmHg). Variations of $\alpha = [COOH]/[COOH]_0$ with time. —△—: Fresh acid (0.5 mol kg^{-1}) was added after completion of a preceding run. Catalyst concentration after acid addition: $[Zr(OBu)_4] = 0.852\ 10^{-3}$ mol kg^{-1}; —○—: Reference experiment: $[COOH]_0 = 0.493$ mol kg^{-1}; $[Zr(OBu)_4] = 0.902\ 10^{-3}$ mol kg^{-1}.

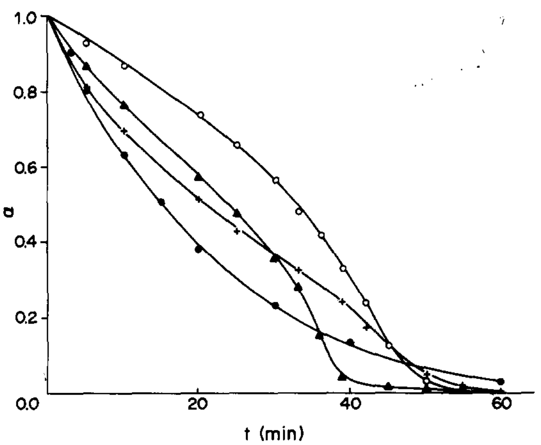


Fig. 3. Esterification of octadecanoic acid in octadecanol (165°C). Variation of $\alpha = [COOH]/[COOH]_0$ with time of reaction at various pressures. Pressure (mmHg): $[Zr(OBu)_4] \times 10^3$ (mol kg^{-1}); $[COOH]_0$ (mol kg^{-1}): —○—: 760; 1.88; 0.484; —▲—: 100; 1.85; 0.472; — + —: 50; 1.80; 0.489; —●—: 14; 1.89; 0.475.

The influence of water could be due to two phenomena:

- —local increase of the dielectric constant, as water is mainly localized in the neighbourhood of the polar end-groups;
- —association (or reaction) with the catalyst to produce species more active than the catalyst itself.

An experiment carried out in benzophenone did not bring about any conclusion as this solvent probably binds to the catalyst reactive sites, resulting in very low catalytic activity.

Influence of the initial acid concentration

Results reported in Fig. 5 (165°C; 760 mmHg; [Catalyst] = $1.88\ 10^{-3}$ mol kg^{-1}) were obtained with the following reaction mixtures (mol kg^{-1}) in 1-octadecanol:

a—$[COOH]_0 = 0.484$ (Plot A)
b—$[COOH]_0 = 0.25$; $[ester]_0 = 0.25$ (Plot B)
c—$[COOH]_0 = 0.25$ (Plot C).

Experiment b corresponds to experiment "a" at 50% conversion.

Figure 5 shows that the presence of ester groups has no influence on initial slopes as these are identical in experiments A, B and C. This also shows that the kinetics do not depend on carboxyl group concentration, thus the order in these groups is 0, which is contrary to what we observed when $p = 14$ mmHg.

Influence of the nature of zirconium ligands

Zirconium-2,4-pentanedionate $(Zr(acac)_2$. Two experiments were carried out at 165°C under 14 and 760 mmHg. Figure 6 shows that $Zr(acac)_2$ and $Zr(OBu)_4$ have the same activity, which is reasonable as acetylacetonyl and butoxy groups are exchanged with octadecanol to form $Zr[O(CH_2)_{17}CH_3]_4$.

Bis(isopropoxy) (p-*nitro* o-*phenlenedioxy*) *zirconium* $(Zr(O_2PhNO_2)(OiPr)_2$. The results for this

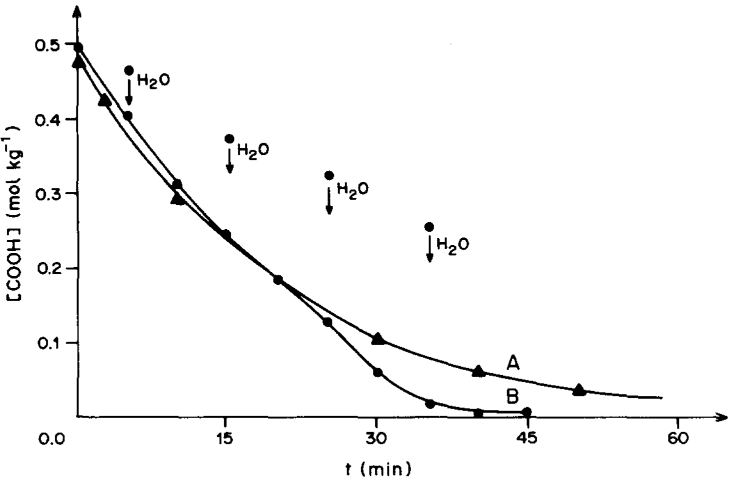


Fig. 4. Esterification of octadecanoic acid in 1-octadecanol (165°C; 14 mmHg); $[Zr(OBu)_4] = 1.88\ mol\ kg^{-1}$). A: No introduction of water; B: Introduction of water ($2.5\ ml\ kg^{-1}$) at $t = 5$, 15, 25 and 35 min.

catalyst are similar to those obtained with $Ti(O_2PhNO_2)(OiPr)_2$ [1]: the reaction is very slow and at 760 mmHg no autoacceleration is observed. This shows that no exchange is possible between these ligands and either octadecanol or water.

Study of the influence of water addition to an acid/catalyst mixture

Mehrotra [2] proposed the following reaction scheme to describe the reaction between tetraisoproproxyzirconium and octadecanoic acid.

$$2\,Zr(OiPr)_4(iPrOH) + 6\ RCOOH \longrightarrow 2\,Zr(OiPr)(OOCR)_3 + 8\,iPrOH$$

$$Zr(OiPr)(OOCR)_3 + RCOOH \xrightarrow{\text{slow}} Zr(OOCR)_4 + iPrOH$$

$$Zr(OiPr)(OOCR)_3 + Zr(OOCR)_4 \longrightarrow (RCOO)_3ZrOZr(OOCR)_3 + RCOOiPr$$

$$Zr(OiPr)(OOCR)_3 \xrightarrow{\text{heat}} (RCOO)_2Zr{=}O + RCOOiPr$$

It is reasonable to assume that, in our experimental conditions, tetraisoproproxyzirconium, in the presence of only acid RCOOH would give mainly $O{=}Zr(OOCR)_2$. To determine the influence of water on the products of these side reactions of the catalyst, we carried out the following experiments:

(a) a mixture of acid and $Zr(OBu)_4$ is stirred for 30 min at 165°C; alcohol is then added to obtain an acid concentration of $0.5\ mol \cdot kg^{-1}$ and kinetic determinations are carried out (Fig. 7; plot A);

(b) a mixture of acid, of $Zr(OBu)_4$ and of water ($7.5\ ml\ kg^{-1}$) is stirred for 30 min at 165°C then alcohol is added so that the concentration of acid is $0.5\ mol\ kg^{-1}$ and determinations are carried out (Fig. 7; plot B).

The reaction corresponding to plot A (no addition of water is much slower than that corresponding to plot B (addition of water).

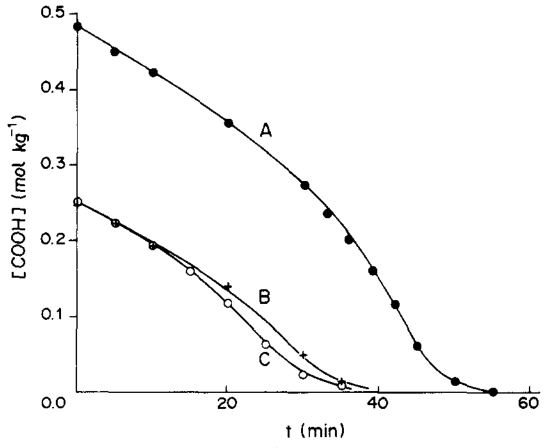


Fig. 5. Esterification of octadecanoic acid in 1-octadecanol (165°C; 760 mmHg); $[Zr(OBu)_4] = 1.88\ 10^{-3}\ mol\ kg^{-1}$). Influence of $[COOH]_0$: (A) $[COOH]_0 = 0.484\ mol\ kg^{-1}$; (B) $[COOH]_0 = 0.249\ mol\ kg^{-1}$, $[ester]_0 = 0.25\ mol\ kg^{-1}$; (C) $[COOH]_0 = 0.251\ mol\ kg^{-1}$.

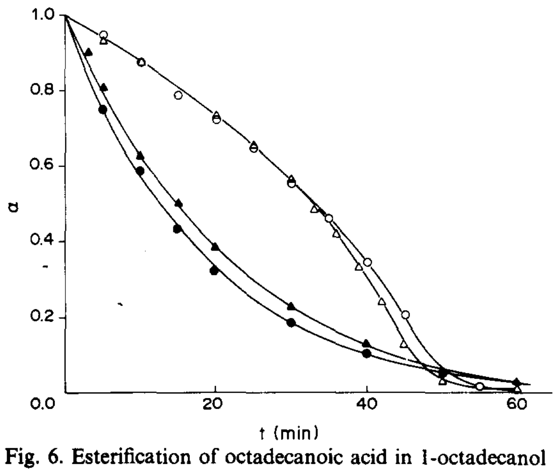


Fig. 6. Esterification of octadecanoic acid in 1-octadecanol (165°C). Pressure (mmHg); [catalyst] × 10^3 ($mol\ kg^{-1}$); $[COOH]_0$ ($mol\ kg^{-1}$): $Zr(OBu)_4$: —▲—: 14;1.89;0.475, —△—: 760;1.88;0.508; $Zr(acac)_2$: —●—: 14;1.78;0.475, —○—: 760;1.87;0.484.

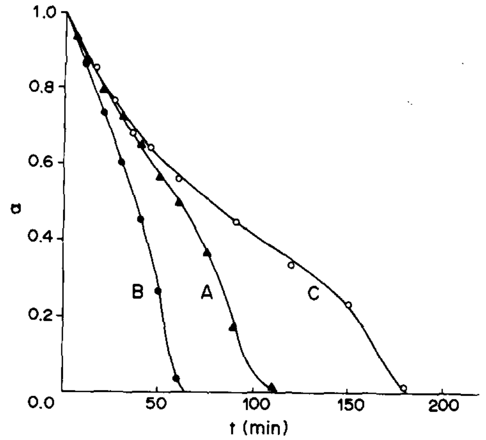
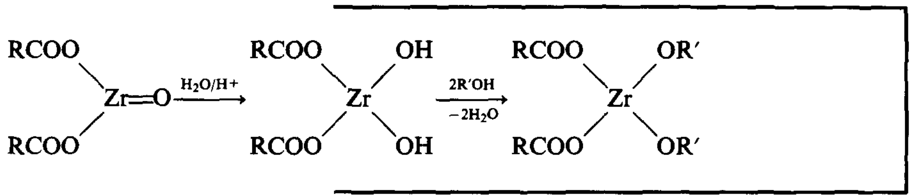


Fig. 7. Esterification of octadecanoic acid in 1-octadecanol (760 mmHg; 165°C). (A) Addition of 1-octadecanol after reaction (760 mmHg; 165°C; 30 min) between acid and $Zr(OBu)_4$. Concentrations after alcohol addition: $[Zr(OBu)_4]_0 = 2.08\ 10^{-3}$ mol kg^{-1}; $[COOH]_0 = 0.499$ mol kg^{-1}. (B) Addition of 1-octadecanol after reaction (760 mmHg; 165°C; 30 min) between acid, $Zr(OBu)_4$ and H_2O (7.5 ml kg^{-1}). Concentrations after alcohol addition: $[Zr(OBu)_4] = 2.02\ 10^{-3}$ mol kg^{-1}; $[COOH]_0 = 0.488$ mol kg^{-1}. (C) Addition of octadecanoic acid after reaction (760 mmHg; 165°C; 50 min) between octadecanol. $Zr(OBu)_4$ and H_2O (7.5 ml kg^{-1}). Concentrations after acid addition: $[Zr(OBu)_4]_0 = 0.202\ 10^{-3}$ mol kg^{-1}; $[COOH]_0 = 0.480$ mol kg^{-1}.

This could be explained by assuming that, in case "a", species such as $(RCOO)_2Zr{=}O$ are formed; this has a lower activity than $Zr(OBu)_4$ as the two sites occupied by the double bonded oxygen atom are no longer able to accept 1-octadecanol. However, after a certain time this less reactive species could possibly be hydrolyzed by the esterification water:



On the other hand, in case "b", the $Zr{=}O$ species might be hydrolyzed on formation as water is present at the very beginning of the reaction.

When fresh acid (0.5 mol kg^{-1}) is added after completion of the case "a" reaction and the kinetics studied, a plot is obtained which can be superimposed on curve B showing that, at the end of the reaction carried out in case "a", the catalytic activity had been completely regenerated by the slow action of esterification water. This backs up the assumption that the low activity of the catalyst in case "a" results from the formation of species such as $Zr{=}O$.

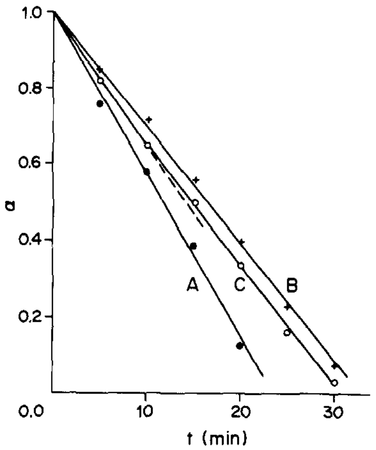


Fig. 8. Esterification of octadecanoic acid in 1-octadecanol. Addition of fresh acid (0.5 mol kg^{-1}) after the completion of a proceding run. Experimental conditions are given in Table 1.

Study of the influence of water addition to an alcohol/catalyst mixture

A mixture of octadecanol (2.5 mol kg^{-1}), catalyst (0.923 mol kg^{-1}) and water (7.5 ml kg^{-1}) was stirred for 50 min at 165°C; acid was then added and kinetic determinations carried out. The results (Fig. 7; Plot C) show that the reaction is very slow at the beginning then accelerating after 2.5 hr. This result can be partly explained by the formation of almost inactive species $Zr{=}O$ or $-Zr-O-Z_r-$ which are slowly hydrolyzed to reactive species in the presence of reaction water.

Study of the influence of acid addition after completion of the reaction

To determine whether the catalytic activity is maximal at the end of the reaction (165°C; 760 mmHg), we carried out several experiments adding acid (0.5 mol kg^{-1}) at the end of a kinetic run, after the completion of the esterification. The experimental conditions are given in Table 1 and the results in Fig. 8. Kinetic plots are straight lines showing that reaction rate does not depend on acid concentration.

Reaction rate in experiment A is higher than in experiment B; this fits experiment C where there is a decrease of the reaction rate when pressure is increased from 14 to 760 mmHg after 10 min.

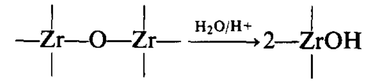
Table 1. Octadecanoic acid esterification in octadecanol (165°C). Addition of fresh acid to the reaction medium after completion of the first kinetic run

Experiment	$[COOH]_0$ 1st run	$[COOH]_0$ 2nd run	$[Zr(OBu)_4] \times 10^3$ (mol kg^{-1})	Pressure (mmHg)
A	0.538	0.489	2.71	14
B	0.517	0.471	2.40	760
C	0.547	0.484	2.18	0 to 10 nm: 14 10 to 30 mn:760

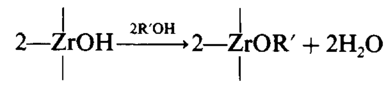
DISCUSSION

The phenomena relative to the esterifications can be explained by assuming that the catalyst is in condensate form. Condensates are either already present in the catalyst or formed very rapidly after its introduction by reaction with the esterification water.

The first part of the reaction carried out under 760 mmHg corresponds to the cleavage of these aggregates by the acid–water mixture; this increases the number of reactive sites:

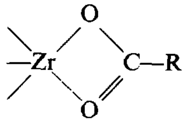


$$-\overset{|}{\underset{|}{Zr}}-O-\overset{|}{\underset{|}{Zr}}- \xrightarrow{H_2O/H^+} 2-\overset{|}{\underset{|}{Zr}}OH$$



$$2-\overset{|}{\underset{|}{Zr}}OH \xrightarrow{2R'OH} 2-\overset{|}{\underset{|}{Zr}}OR' + 2H_2O$$

At the end of the reaction, non-associated $Zr(OR)_4$ molecules are present in the reaction mixture and cannot be reassociated as they are dispersed in the bulk. This would explain the very high activity which is observed when fresh acid is added after completion of the reaction and the zero-order in carboxyl groups, in which case the reaction rate would depend only on the concentration of species such as:



(*C*) *Kinetic Study of Polycondensations Catalyzed by* $Zr(OBu)_4$

In Part I [1] and in parts (A) and (B) of this paper, studies were carried out in the presence of a high excess of alcohol; however as most polycondensations are carried out in stoichiometric conditions, it was necessary to test the possible catalysts with a stoichiometric model: $[\text{octadecanoic acid}]_0 = [\text{octadecanol}]_0 = 1.80\ \text{mol kg}^{-1}$; 165°C; 14 mmHg.

Our results show that $Zr(OBu)_4$ is more efficient than $Ti(OBu)_4$; consequently it was chosen as catalyst for the polycondensation studies.

Study of the polycondensation of oligo(1,6-hexanediyl adipate)

Non-catalyzed polycondensation. The results obtained at various temperatures and at 14 mmHg are reported in Table 2. It is reasonable to assume that the overall order is 3 which fits Fradet's results [3]. The rate-constants give the following activation parameters:

$$\Delta H^{\neq} = 47.3 \pm 0.1\ \text{kJ mol}^{-1};$$

$$\Delta S^{\neq} = 223 \pm 37\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$Zr(OBu)_4$ catalyzed polycondensation. The results (Fig. 9) show that high conversions are not obtained; the last part of the reaction is very slow; this is very probably due to the formation of 1,6-dihydroxyhexane (transesterification) which distills off at 14 mmHg; this destroys stoichiometry. To overcome this difficulty, we used a less volatile alcohol viz. 1,10-dihydroxydecane.

Table 2. Further polycondensation of oligo(1,6-hexanediyl adipate); 14 mmHg

Temperature (°C)	Overall order	$k(\text{kg}^2\ \text{mol}^{-2}\ \text{sec}^{-1}) \times 10^4$
165	2.8	0.422
185	2.95	0.943
205	3.1	1.36

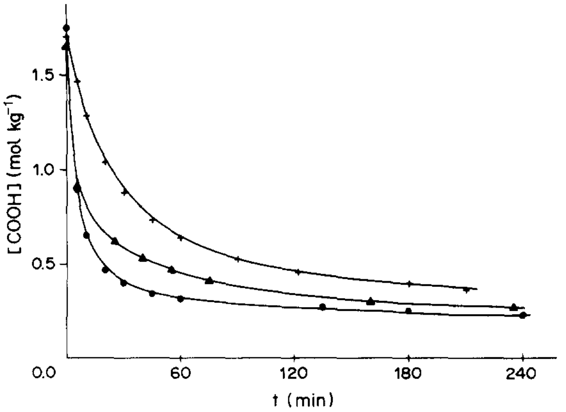


Fig. 9. Further polycondensation of oligo (1,6-hexanediyle adipate) (14 mmHg). Temperatures (°C); $[Zr(O\ Bu)_4] \times 10^3$ (mol kg^{-1}): —+—: 165; 2.25; —▲—: 185; 2.04; —●—: 205; 2.11.

Table 3. Further polycondensation of oligo(1,10-decanediyl adipate); 14 mmHg

Temperature (°C)	Overall order	$k(\text{kg}^2\ \text{mol}^{-2}\text{sec}^{-1}) \times 10^4$
165	2.75	0.725
185	2.75	0.1602
205	2.85	1.2829

Study of the polycondensation of oligo(1,10-decanediyl adipate)

Non-catalyzed polycondensation. The results obtained at various temperatures and at 14 mmHg are reported in Table 3. As in the case of oligo(1,6-hexanediyl adipate), it is reasonable to assume that the overall order is 3. The values of the rate constants give:

$$\Delta H^{\neq} = 55.6 \pm 0.1\ \text{kJ mol}^{-1}$$

$$\Delta S^{\neq} = 200 \pm 16\ \text{J mol}^{-1}\ \text{K}^{-1}$$

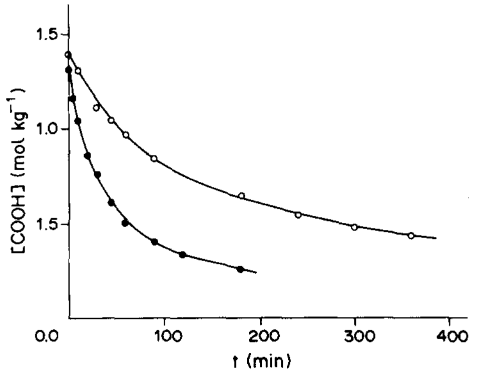


Fig. 10. Further polycondensation of oligo(1,10-decanediyl adipate) (165°C). Influence of pressure. Pressure (mmHg); $[Zr(O\ Bu)_4] \times 10^3$ (mol kg^{-1}): —○—: 760; 2.29; —●—: 14; 2.47.

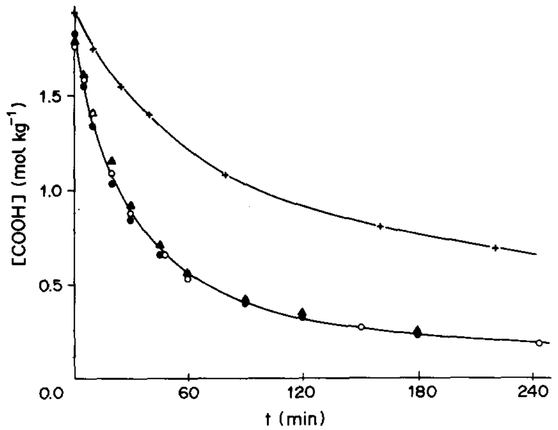


Fig. 11. Further polycondensation of oligo (1,10-decanediyle adipate) (165°C; 14 mmHg). Influence of catalyst concentration (mol kg^{-1}). [Zr(OBu)$_4$] 10^3 (mol kg^{-1}): —+—: 0; —▲—: 1.14; —○—: 1.61; —●—2.84.

Zr(OBu)$_4$ catalyzed polycondensation. The influence of pressure is shown in Fig. 10; the reaction rate is lower at 760 mmHg than at 14 mmHg; in addition, no autoacceleration is observed.

The results (Fig. 11) show that the concentration of catalyst has practically no influence; this could be explained by the existence, in the bulk of the reaction medium, of polar domains which are progressively saturated by catalyst molecules; when saturation point is reached, an increase in catalyst concentration has no effect. Another possible explanation is the formation of catalyst condensates of which only the surface is active thus limiting the influence of the catalyst concentration. These two assumptions are not independent as polar domains might contain catalyst condensates, acid and hydroxy end-groups.

The number of effective catalytic sites is in fact unknown and differs from that corresponding to the amount of catalyst introduced.

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