Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Kinetic Study on Models of the Noncatalyzed Reaction Between α, ω -Dicarboxypolyamide-11 and α, ω -Dihydroxypolyoxyalkylenes

Pascale Laporte[a]; Alain Fradet[a]; Ernest Maréchal[a]
[a] Laboratoire de Synthèse Macromoléculaire, C. N. R. S. U. A. 24 Université P. et M. Curie 12 Rue Cuvier, Paris, France

To cite this Article Laporte, Pascale , Fradet, Alain and Maréchal, Ernest(1987) 'Kinetic Study on Models of the Noncatalyzed Reaction Between α, ω -Dicarboxypolyamide-11 and α, ω -Dihydroxypolyoxyalkylenes', Journal of Macromolecular Science, Part A, 24: 11, 1269 — 1287

To link to this Article: DOI: 10.1080/00222338708076945

URL: http://dx.doi.org/10.1080/00222338708076945

J. MACROMOL. SCI.—CHEM., A24(11), pp. 1269-1287 (1987)

KINETIC STUDY ON MODELS OF THE NONCATALYZED REACTION BETWEEN α,ω-DICARBOXYPOLYAMIDE-11 AND α,ω-DIHYDROXYPOLYOXYALKYLENES

PASCALE LAPORTE, ALAIN FRADET, and ERNEST MARÉCHAL*

Laboratoire de Synthèse Macromoléculaire
C.N.R.S. U.A. 24
Université P. et M. Curie
12 Rue Cuvier, F-75005 Paris, France

ABSTRACT

The kinetics of the noncatalyzed reaction between α,ω-dicarboxypolyamide-11 and α,ω-dihydroxypolyoxyalkylenes is investigated by using the reactions of 11-dodecylamidoundecanoic acid with 1-dodecanol, 2-tridecanol, α-dodecyl-ω-hydroxypolyoxyethylene or α-dodecyl-ω-hydroxypolyoxypropylene as models. Kinetic data fit a 3rd overall order (2 in acid and 1 in alcohol). Rate constants and activation parameters are determined and compared.

INTRODUCTION

Copolymers with polyether and polyamide blocks have been the subject of growing interest as thermoplastic elastomers [1]. They are manufactured by reacting incompatible α,ω-dihydroxypolyethers and α,ω-dicarboxypolyamides. The kinetics and mechanisms of these polyesterifications are not well known due to the phase separation which takes place in the early stages of the process

---

*To whom correspondence should be addressed.

and to the lack of knowledge about the influence of the amide groups on the mechanism of polyesterification in the bulk.

Kinetic data obtained in the bulk can be interpreted only when the concentration of reactive groups is low [2-7]. Concentrations can then be approximated as activities, and the polarity of the medium remains constant throughout the reaction. This is why Flory [2-5], studying the polyesterification of diacids and diols, took into consideration only the experimental results obtained with conversions above 80%. The use of reactive oligomers is another method of studying bulk polycondensation kinetics. With these macromolecular systems, the concentrations of reactive groups are relatively low. What is more, reactions can be carried out under nonstoichiometric conditions, which allows the determination of the order in each reactant.

The present article includes the following parts:

1. Kinetic study of model monoesterifications carried out in the bulk. The models are 11-dodecylamidoundecanoic acid (DAUA), $CH_3-(CH_2)_{10}-CO-NH-(CH_2)_{10}-COOH$, which is the simplest model for α,ω-dicarboxypolyamide-11, and monohydroxy compounds of different molecular weights which are the models for α,ω-dihydroxypolyethers: 1-dodecanol, 2-tridecanol, α-dodecyl-ω-hydroxypolyoxyethylene (POE-OH) and α-dodecyl-ω-hydroxypolyoxypropylene (POP-OH).
2. Kinetic study of the diesterification of α-dodecyl-ω-carboxypolyamide-11 (PA11-COOH) with POE-OH or POP-OH and comparison of the results with those for the polyesterification of α,ω-dicarboxypolyamide-11 (PA11-diCOOH) with α,ω-dihydroxypolyoxyethylene (POE-diOH).

EXPERIMENTAL

Apparatus

The reactor was equipped with two thermocouples (regulation and monitoring), nitrogen inlet and outlet, a sampling outlet, and a magnetic stirrer. Temperature was controlled by a system including a heating jacket and a P.I.D. regulation operated by a thermocouple plunged in the reaction medium (residual temperature fluctuations, ±0.1°C; accuracy: ±0.1°C).

Reactants

1-Dodecanol (Fluka, puriss. grade), α-dodecyl-ω-hydroxypolyoxyethylenes (POE-OH, $\bar{M}_n$ = 370 (Janssen) and $\bar{M}_n$ = 1280 (Merck), [OH] = 2.673 and

0.776 mol/kg, respectively), α-dodecyl-ω-hydroxypolyoxypropylene (POP-OH, $\bar{M}_n$ = 1520 (Atochem), [OH] = 0.656 mol/kg), α,ω-dihydroxypolyoxyethylene (POE-diOH, $\bar{M}_n$ = 1100 (Hoechst), [OH] = 1.818 mol/kg) were used without further purification.

2-Tridecanol, prepared by reducing 2-tridecanone with $NaBH_4$, followed by distillation under reduced pressure (112°C, 4 torr), was characterized by ^1H and ^{13}C NMR, IR spectroscopy, GPC, and gas chromatography (purity $\geqslant$ 99.5%).

The preparation and characterization of DAUA, $CH_3-(CH_2)_{10}-[CO-NH-(CH_2)_{10}]_n-COOH$ (n = 1) has already been described [8]. It was useless to separate the compound with n = 1 (mp = 101°C) as DAUA undergoes a polycondensation equilibrium when heated. The DAUA used in this study was a mixture of oligomers, mainly n = 1 and 2, with traces of n = 3 ([COOH] = 2.373 mol/kg, n = 1.155). α-Dodecyl-ω-carboxypolyamide-11 (PA11-COOH, $\bar{M}_n$ = 1080, [COOH] = 0.926 mol/kg) and α,ω-dicarboxypolyamide-11 (PA11-diCOOH, $\bar{M}_n$ = 920, [COOH] = 2.174 mol/kg) were supplied by Atochem.

Procedure

The reactions were carried out at atmospheric pressure with DAUA and at 14 torr with the carboxypolyamides. A mixture of the hydroxy compound and of the carboxy compound (~20 g) was purged with oxygen-free nitrogen and heated to the reaction temperature. The time was t = 0 when thermal equilibrium was attained and the first sample withdrawn. Since no solvent was used for the reactions, the initial carboxyl group concentration x_i was determined by the choice of the stoichiometric ratio: ~ 0.5 mol/kg when hydroxyl groups are in excess, to ~ 1.7 mol/kg when there is an excess of carboxyl groups. The final extent of reaction was at least 55%, corresponding to ~10 data points.

Samples were withdrawn at predetermined times and titrated. Titrations were carried out under nitrogen with a Mettler DL 40 RC potentiometric titrator and alcoholic potassium hydroxide (0.06 mol/L) at room temperature. Samples were dissolved in a chloroform/ethanol mixture (1/1 vol). In the case of the experiments carried out on polyamides, samples were dissolved in boiling benzyl alcohol and titrated at room temperature. A blank titration was carried out. Free dodecanoic acid was converted to its ethyl ester by a 2-h reaction at 90°C in DMF with a twofold molar excess of *N,N*-diethylacetamide and titrated by gas chromatography using a OV 17/WAW-DMCS Chromosorb column, after establishing a calibration curve.

Calculations and Notations

An Intel iSBC 86/05 based microcomputer with Fortran-86 programs was used for the treatment of experimental data. Corrections account for the release of condensation water, and they are included in the programs for the kinetic calculations. The following notations are used:

x, x_0, x_i	carboxyl content (mol/kg) at times t (s), $t = 0$ (first sample), and before reaction, respectively
b	algebraic value of the excess hydroxyl group concentration (mol/kg)
m	order in carboxyl groups
n	order in hydroxyl groups
d	overall order ($d = m + n$)
r	initial molar ratio of hydroxyl groups to carboxyl groups
k_d or $k_{m,n}$	rate constant for a dth or a (m,n) order test ($\mathrm{kg}^{d-1} \cdot \mathrm{mol}^{1-d} \cdot \mathrm{s}^{-1}$)
I_d or $I_{m,n}$	correlation coefficient for a dth or (m,n) order test
S_d or $S_{m,n}$	standard deviation of the regression line slope of $G_d(x)$ or $G_{m,n}(x)$ vs time (calculated as a percentage)
$p_{\max}$	maximum extent of reaction
C^*	concentration unit (mol/kg)
ΔH^*, ΔS^*	enthalpy and entropy of activation (kJ/mol and $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

RESULTS

The Problem of Side Reactions

As the reactants are monofunctional, alcoholysis, acidolysis, and ester interchange do not interfere with the main reaction because they give back the reactive groups. The hydrolysis of ester bonds must be taken into account as initial alcohol and acid are formed back; moreover, water may hydrolyze DAUA into dodecanoic acid and 11-aminoundecanoic acid. However, the contribution of hydrolysis is negligible under our experimental conditions since the kinetic data for the DAUA/1-dodecanol reaction are not changed when water (0.2 mol/kg) is added to the reaction mixture after each sampling. In the same way, evaporation, oxidation, and decarboxylation of reactants are negligible when the reaction temperature is under 240°C.

The existence of a polycondensation equilibrium between amide and acid groups [8] is important. Although it does not alter the concentration of reactive groups, it changes the nature of the carboxylic species:

$$\text{D–(U)}_m\text{–COOH} + \text{D–(U)}_{m-n}\text{–COOH} \rightleftharpoons \text{D–COOH} + \text{D–(U)}_n\text{–COOH}$$

where D = $CH_3–(CH_2)_{10}–$ (n = 1, . . .) and U = $–CO–NH–(CH_2)_{10}–$, n=1, . . . (m = 1, . . ., n).

It is impossible to avoid the formation of free dodecanoic acid as soon as DAUA is heated. However, kinetic analysis showed that dodecanoic acid reactivity is close to that of the carboxylic end groups of the initial oligomers, which justifies the choice of DAUA as model. Moreover, the molar ratio of free dodecanoic acid to the total amount of carboxylic groups is below 0.06. All these observations show that the formation of free dodecanoic acid does not modify the kinetic data.

Determination of Orders in Each Reactant

The general rate equation

$$-dx/dt = k_{m,n}x^m(x+b)^n \tag{1}$$

is numerically integrated; m and n are varied between -0.5 and +3.2 in 0.1 steps with $m + n \leqslant 3.2$.

For each data point $x(t)$, the values of the integrals

$$G_{m,n}(x) = \int_{x_0}^{x} \frac{dx}{x^m(x+b)^n} \tag{2}$$

are calculated, and for each (m,n) a linear regression of $G_{m,n}(x)$ against time is carried out. The correlation coefficient $I_{m,n}$ and the standard deviation $S_{m,n}$ of the regression line slope are used to determine the best fit.

When the reaction is carried out under stoichiometric conditions (r = 1, b = 0), only the overall order $d = m + n$ can be determined. However, when the reaction is carried out under nonstoichiometric conditions (i.e., excess alcohol, $b > 0$), it is possible to determine m and n, provided the extent of reaction is >70% and the error of titration is low (<1%). When these conditions are not fulfilled, the position of the best fit (minimum of $S_{m,n}$) in the (m,n) plane is not limited to one point but to a straight line. Experiments with various molar ratios must then be carried out to determine the position of the best fit at the intersection of the corresponding best fit straight lines in the (m,n) plane (accuracy: $\Delta m = \Delta n = \pm 0.2$); (see Fig. 6, for example). If no intersection can be found, the Rate Equation (1) is not suitable for the process under consideration, and the corresponding mechanism must be rejected.

Determination of Activation Parameters

Activation parameters were obtained from the classical relation:

$$k_d = \frac{kT}{h}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right)(C^*)^{1-d} \qquad (3)$$

by least-square fitting of $-R \ln (hk_d)/kT$ versus $1/T$.

Reaction of DAUA with 1-Dodecanol

A series of experiments was carried out at various temperatures and under atmospheric pressure in the presence of an excess of alcohol (Fig. 1 and Table 1).

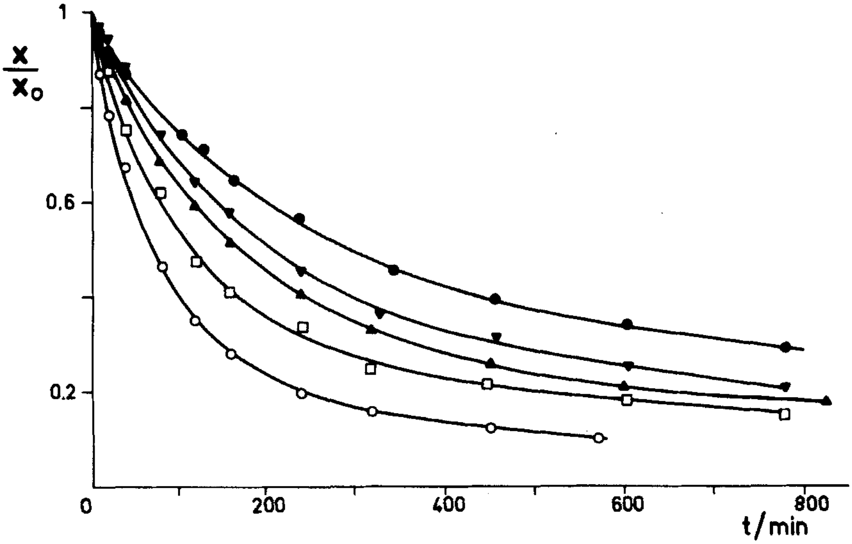


FIG. 1. Esterification of DAUA in 1-dodecanol at various temperatures. Variations of x/x_0 versus time. (○) 190°C, (□) 180°C, (▲) 170°C, (▼) 160°C, (●) 150°C.

TABLE 1. Esterification of DAUA in 1-Dodecanol. Values of Experimental Parameters

T, °C	r	p_{max}, %	x'_i, mol/kg
190	9.31	91	0.461
180	10.8	87	0.409
170	11.6	84	0.386
160	9.31	81	0.461
150	8.99	72	0.474

Satisfactory values of correlation coefficients are obtained only for the following pairs of integer or half-integer orders in acid and in alcohol: (2,1), (1.5,1.5), (2,0.5), (1.5,1). Table 2 and Fig. 2 show that (1.5,1.5) and (1.5,1) must be rejected whereas both (2,1) and (2,0.5) fit the experimental data satisfactorily since the standard deviation S is much lower (~1.5% instead of 4%). A reaction carried out under stoichiometric conditions (190°C, $r = 0.998$, $p_{max} = 77\%$, $x_0 = 1.58$ mol/kg) shows that the overall order $d = 2.5$ must be rejected (Fig. 3). Thus the process is 2nd order in acid and first order in alcohol ($(m,n) = (2,1)$). Moreover, Table 3 shows that the rate constants obtained for the (2,1) pair (excess of alcohol) and for overall order 3 (stoichiometry) are close to each other. The rate of carboxyl group consumption is given by

$$dx/dt = k_{2,1}\,[\mathrm{COOH}]^2\,[\mathrm{OH}]. \tag{4}$$

The calculation of activation parameters from the rate constants reported in Table 2 give the following results:

$$\Delta H^* = 64 \pm 1 \text{ kJ/mol},$$

$$\Delta S^* = -180 \pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Reaction of DAUA with 2-Tridecanol

A series of experiments was carried out at various temperatures and under atmospheric pressure in the presence of an excess of alcohol (Fig. 4, Table 4). The reaction rates are lower than those of the preceding system, and the maxi-

TABLE 2. Esterification of DAUA in 1-Dodecanol. Values of $k_{m,n}$ and of $S_{m,n}$ for Various (m,n) Pairs of Orders of Reaction[a]

	m,n							
	2,1		1.5,1.5		2,0.5		1.5,1	
T, °C	$k_{m,n} \times 10^4$	$S_{m,n}$	$k_{m,n} \times 10^4$	$S_{m,n}$	$k_{m,n} \times 10^4$	$S_{m,n}$	$k_{m,n} \times 10^4$	$S_{m,n}$
190	1.85	1.3	0.276	4.1	3.67	1.2	0.549	4.2
180	1.00	1.2	0.154	4.5	2.03	1.2	0.314	4.7
170	0.703	1.1	0.120	3.3	1.45	1.1	0.246	3.4
160	0.535	1.7	0.107	2.3	1.07	1.6	0.215	2.5
150	0.314	0.9	0.073	2.4	0.630	0.9	0.146	2.5

[a] Units: $k_{m,n}$, $\mathrm{kg}^{d-1} \cdot \mathrm{mol}^{1-d} \cdot \mathrm{s}^{-1}$; $S_{m,n}$, %.

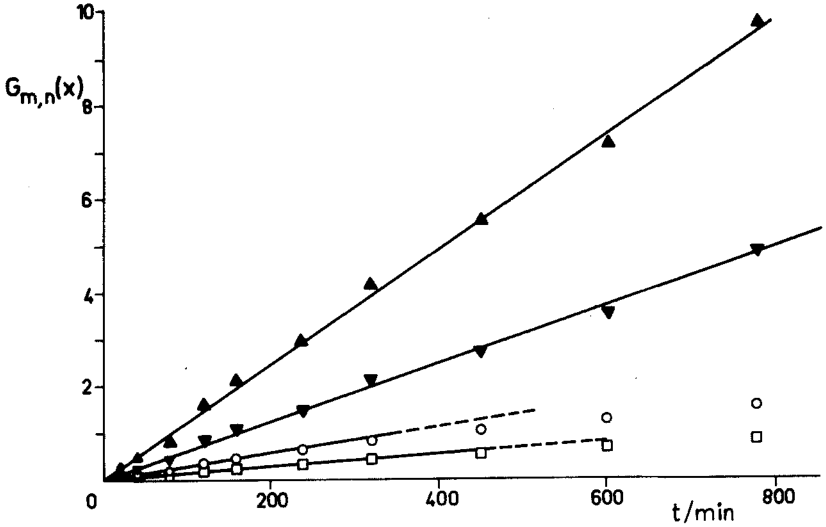


FIG. 2. Esterification of DAUA in 1-dodecanol at 180°C. Variations of integrals $G_{m,n}(x)$ versus time for various orders in acid and in alcohol. (m,n): □ (1.5,1.5); ○ (1.5,1); ▼(2,1); ▲(2,0.5).

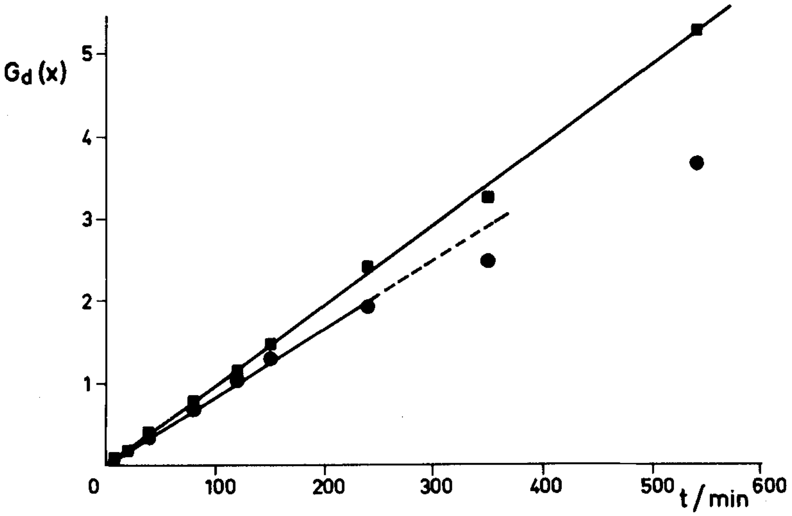


FIG. 3. Esterification of DAUA with 1-dodecanol under stoichiometric conditions at 190°C. Variations of integrals $G_d(x)$ versus time for (■) overall order 3 and (●) overall order 2.5.

TABLE 3. Esterification of DAUA with 1-Dodecanol at 190°C in an Excess of Alcohol or at Stoichiometry. Comparison of the Rate Constants and of Their Standard Deviations for Different Orders in Acid and in Alcohol[a]

	$r = 9.31$			$r = 0.998$	
(m,n)	$k_{m,n} \times 10^4$	$S_{m,n}$	d	$k_d \times 10^4$	$S_{m,n}$
(2,1)	1.85	1.3	3	1.60	1.2
(1.5,1.5)	0.276	4.1			
(2,0.5)	3.67	1.2	2.5	1.11	3.3
(1.5,1)	0.549	4.2			

[a] Units: $k_{m,n}$, $\mathrm{kg}^{d-1} \cdot \mathrm{mol}^{1-d} \cdot \mathrm{s}^{-1}$; $S_{m,n}$, %.

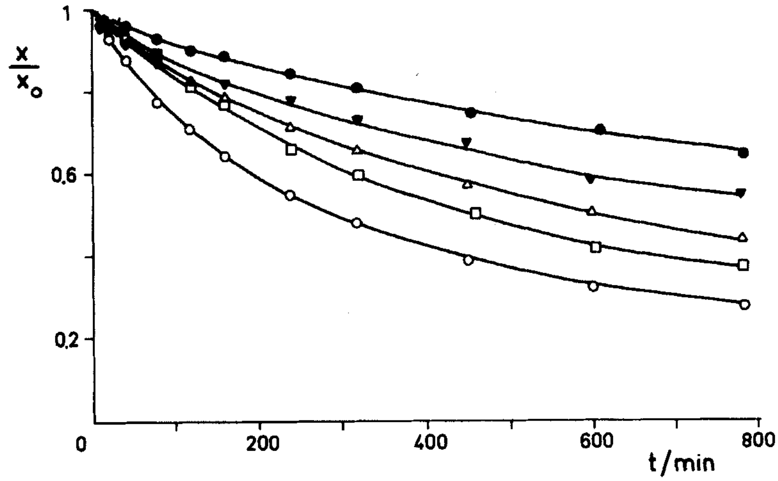


FIG. 4. Esterification of DAUA in 2-tridecanol at various temperatures. Variations of x/x_0 versus time. (○) 190°C, (□) 180°C, (△) 170°C, (▼) 160°C, (●) 150°C.

TABLE 4. Esterification of DAUA in 2-Tridecanol

T, °C	r	p_{max}, %	x_i, mol/kg
190	6.03	74	0.609
180	7.03	64	0.547
170	6.39	58	0.584
160	6.40	47	0.590
150	6.28	37	0.594

mum extent of reaction p_{max}, for the experiments carried out at 150 and 160°C is also low. Thus, any pair (m,n) can fit the experimental data. At 170, 180, and 190°C the following pairs of orders fit the experimental data: (2.1), (1.5,1.5), (2,0.5), (1.5,1) (Table 5). However, the experiment carried out at the stoichiometric ratio (190°C, $r = 0.998$, $p_{max} = 77\%$, $x_0 = 1.53$ mol/kg) shows that the 3rd order fits the experimental data better than the 2.5 order and that k_3 and $k_{2,1}$ are very close (Table 6). The rate of carboxyl group consumption is given by Eq. (4).

The activation parameters calculated from the rate constants in Table 7 are

$$\Delta H^* = 66.5 \pm 1 \text{ kJ/mol},$$

$$\Delta S^* = -190 \pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Reaction of DAUA with α-Dodecyl-ω-carboxypolyoxyethylene of $\bar{M}_n$ = 370 (POE-OH 370)

A series of experiments was carried out under atmospheric pressure in an excess of alcohol (Fig. 5) at various temperatures and at 180°C with various stoichiometric ratios (Table 8). A number of pairs of orders in acid and in alcohol fit the experimental data; in each case the best fit (minimum of standard deviation $S_{m,n}$ on $k_{m,n}$) is located on a straight line in the (m,n) plane. For experiments carried out at various stoichiometric ratios, the slopes of these straight lines are different, and the intersection occurs for $(m,n) = (1.7,0.8)$ (Fig. 6), indicating an order in alcohol close to 1 and an order in acid which could be either 1.5 or 2. According to our previous results on the kinetics of the esterification between hydroxy- and carboxypolyoxyethylenes

TABLE 5. Esterification of DAUA in 2-Tridecanol[a]

	m,n							
	2,1		1.5,1.5		2,0.5		1.5,1	
T, °C	$k_{m,n} \times 10^4$	$S_{m,n}$	$k_{m,n} \times 10^4$	$S_{m,n}$	$k_{m,n} \times 10^4$	$S_{m,n}$	$k_{m,n} \times 10^4$	$S_{m,n}$
190	0.317	1.1	0.089	1.6	0.581	0.9	0.163	1.8
180	0.204	1.9	0.0591	1.7	0.389	1.8	0.113	1.8
170	0.145	1.1	0.0461	1.1	0.272	0.97	0.086	1.0

TABLE 6. Esterification of DAUA with 2-Tridecanol at 190°C in an Excess of Alcohol or at Stoichiometry. Comparison of the Values of Rate Constants and of Standard Deviations on Rate Constants for Different Orders in Acid and in Alcohol[a]

	$r = 6.03$			$r = 0.998$	
(m,n)	$k_{m,n} \times 10^4$	$S_{m,n}$	d	$k_d \times 10^4$	$S_{m,n}$
(2,1)	0.317	1.1	3	0.378	0.6
(1.5,1.5)	0.089	1.6			
(2,0.5)	0.581	0.9	2.5	0.356	2.1
(1.5,1)	0.163	1.8			

[a] Units: $k_{m,n}$, $\mathrm{kg}^{d-1} \cdot \mathrm{mol}^{1-d} \cdot \mathrm{s}^{-1}$; $S_{m,n}$, %.

TABLE 7. Esterification of DAUA in 2-Tridecanol. Rate Constants Obtained at Various Temperatures for Order 2 in Acid and 1 in Alcohol

T, °C	$k_{2,1} (\mathrm{mol}^{-2} \cdot \mathrm{kg}^2 \cdot \mathrm{s}^{-1}) \times 10^4$
150	0.0560
160	0.0881
170	0.145
180	0.204
190	0.317

TABLE 9. Esterification of DAUA in POE-OH 370. Rate Constants for Order 2 in Acid and 1 in Alcohol[a]

T, °C	$k_{2,1}$(mol^{-2}·kg^2·s^{-1}) X 10^4
150	0.164
160	0.315
170	0.460
180	0.710[b]
190	1.16

[a] For experimental conditions, see Table 8.
[b] $r = 3.95$.

TABLE 10. Esterification of DAUA with POP-OH at Stoichiometric Ratio of Reactants. Rate Constants for Overall Order 3

T, °C	k_3(mol^{-2}·kg^2·s^{-1}) X 10^4
180	0.619
200	1.43
220	3.12

data obtained here. From Table 10 the following values of activation parameters are obtained

$$\Delta H^* = 70 \pm 1 \text{ kJ/mol},$$

$$\Delta S^* = -170 \pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Reactions Involving α-Dodecyl-ω-carboxypolyamide-11 of $\bar{M}_n$ = 1080 (PA11-COOH)

Due to phase separation, no kinetic study could be carried out with POP-OH as alcohol.

With POE-OH 1280, the medium remains homogeneous and the 3rd order rate constant, $k_3 = 1.41 \times 10^{-4}$ mol$^{-2}\cdot$kg$^2\cdot$s^{-1}, obtained for the stoichiometric reaction ($x_0 = 0.48$ mol/kg), at 190°C, is close to that obtained at the same conditions for POE-OH 370 ($k_3 = 1.16 \times 10^{-4}$ mol$^{-2}\cdot$kg$^2\cdot$s^{-1}). This shows that both model compounds of low molecular weight ($\bar{M}_n = 370$) and oligomers ($\bar{M}_n \approx 1000$ to 2000) have a similar behavior.

Reaction between α,ω-Dicarboxypolyamide-11 (PA11-diCOOH, $\bar{M}_n$ = 920) and α,ω-Dihydroxypolyoxyethylene (POE-diOH, $\bar{M}_n$ = 1100)

The reaction is carried out at reduced pressure (14 torr) and at a stoichiometric ratio of the reactants, i.e., under experimental conditions close to those of industry. In order to avoid the formation of high molecular weight compounds which would cause high viscosity of the reaction medium, the reaction is not carried out above 55% conversion. Assuming that overall order is 3, as above, the rate constants in Table 11 give the following activation parameters, of the same order of magnitude as those obtained previously:

$$\Delta H^* \approx 70 \text{ kJ/mol},$$

$$\Delta S^* \approx -180 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

DISCUSSION

The low molecular weight amido acid DAUA behaves in the same way as any carboxylic acid. When low molecular weight models are replaced by functional oligomers, the behavior of the system is the same. The values of the activation enthalpy obtained with oligomers are slightly higher than those obtained with the model compounds. On the other hand, there are no significant

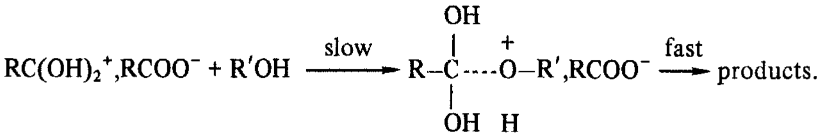
TABLE 11. Esterification between PA11-diCOOH and POE-diOH under 14 torr. Rate Constants for Overall Order 3

T, °C	k_3(mol$^{-2}\cdot$kg$^2\cdot$s^{-1}) $\times 10^4$
200	1.10
220	2.29

changes in the activation entropy, showing that interactions between backbones and reactive groups do not significantly affect the kinetics.

Orders of 2 in acid and 1 in alcohol have been obtained by Flory [2-5], Hamann and Solomon [6], and Fradet and Maréchal [7] for esterifications and polyesterifications in the bulk. An $A_{AC}2$ reaction scheme, in Ingold's classification [9], was proposed. This supposes that 1) ion pairs are not dissociated, and 2) the predominant acid species is free RCOOH:

$$2RCOOH \rightleftharpoons RC(OH)_2^+,RCOO^-$$



$$RC(OH)_2^+,RCOO^- + R'OH \xrightarrow{\text{slow}} R{-}\overset{OH}{\underset{OH}{C}}\cdots\overset{+}{\underset{H}{O}}{-}R',RCOO^- \xrightarrow{\text{fast}} \text{products.}$$

Even when an increased basicity of alcohol makes the following equilibrium preponderant,

$$RCOOH + R'OH \xrightleftharpoons{K'} RCOO^-,R'(OH)_2^+,$$

The corresponding nondissociated ion pair is not involved in kinetic calculations. The rate of acid consumption is

$$v = k[RC(OH)_2^+,RCOO^-]\,[R'OH] = kK\,[RCOOH]^2_{\text{free}}\,[R'OH]_{\text{free}}.$$

If we assume that ion-pair concentrations are negligible with regard to the total reactant concentrations, then

$$v = kK\,[RCOOH]^2_{\text{measured}}\,[R'OH]_{\text{measured}},$$

which fits our experimental data.

REFERENCES

[1] G. Deleens, P. Foy, and E. Maréchal, *Eur. Polym. J., 13,* 337, 343, 353 (1977).

[2] P. J. Flory, *J. Am. Chem. Soc., 58,* 1877 (1936).

[3] P. J. Flory, *Ibid., 59,* 466 (1937).

[4] P. J. Flory, *Ibid., 61,* 3334 (1939).
[5] P. J. Flory, *Ibid., 62,* 2261 (1940).
[6] S. D. Hamann, D. H. Solomon, and J. D. Swift, *J. Macromol. Sci.–Chem., A2,* 153 (1968).
[7] A. Fradet and E. Maréchal, *J. Polym. Sci., Polym. Chem. Ed., 19,* 2905 (1981).
[8] P. Laporte, A. Fradet, and E. Maréchal, *Polym. Bull., 13,* 385 (1985).
[9] C. K. Ingold, in *Structure and Mechanisms in Organic Chemistry,* 2nd ed., Cornell University Press, Ithaca, New York, 1969, pp. 1129-1131.

Received December 29, 1986
Revision received March 4, 1987