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

The Kinetics and Mechanism of Esterification and Polyesterification Reactions

S. D. Hamann[a]; D. H. Solomon[b]; Jean D. Swift[b]
[a] Division of Applied Chemistry, C.S.I.R.O., Melbourne, Australia [b] Division of Applied Mineralogy, C.S.I.R.O., Melbourne, Australia

To cite this Article Hamann, S. D. , Solomon, D. H. and Swift, Jean D.(1968) 'The Kinetics and Mechanism of Esterification and Polyesterification Reactions', Journal of Macromolecular Science, Part A, 2: 1, 153 — 174
To link to this Article: DOI: 10.1080/00222336808053354
URL: http://dx.doi.org/10.1080/00222336808053354

J. MACROMOL. SCI.—CHEM., A2(1), pp. 153-174, Jan., 1968

The Kinetics and Mechanism of Esterification and Polyesterification Reactions

S. D. HAMANN
Division of Applied Chemistry
and
D. H. SOLOMON and JEAN D. SWIFT
Division of Applied Mineralogy
C.S.I.R.O.
Melbourne, Australia

Summary

The conditions under which previous kinetic measurements have been carried out on esterification and polyesterification reactions have been examined in relation to the significance of the conclusions reached. It is suggested that only in the later stages of the reactions are conditions achieved which yield sensible kinetic results.

Experiments have been designed to obtain more accurate kinetic data than have previously been available for the later stages of reaction. The results establish that the overall kinetic order of both esterifications and polyesterifications is third order. Reactions in which the molar ratios of the initial reactants have been varied indicate that esterifications are second order in carboxyl and first order in hydroxyl group concentrations. Acid-catalyzed reactions have also been studied. A mechanism consistent with the results is proposed.

Kinetic studies of the reaction between an alcohol and an acid under conditions such that water of reaction is removed rapidly are of particular importance to polymer science; the kinetic order of the reaction is a necessary prerequisite to assigning a mechanism to the reaction, and a comparison of the kinetics of esterification and polyesterification reactions is the basis on which the concept of equal reactivity of functional groups irrespective of molecular size has been developed.

Flory [1] studied the kinetics of esterification and polyesterification and concluded that both reactions obeyed third-order kinetics in the later stages of reaction (80–93%). He proposed that the reaction was second order in acid and first order in alcohol and that it involved a trimolecular reaction between two carboxyl groups and one hydroxyl group [2].

Many other investigations into polyesterification reactions have been carried out and a variety of conclusions have been reached regarding the kinetic order and hence the mechanism of the reactions [3–7]. However, in most cases the experimental results have been similar and the disparity of conclusions has arisen from the different ways in which the results have been interpreted. For example, the results reported by Flory have been interpreted as supporting a third-order [1], a second-order [8], a second-order followed by a third-order [8], and more recently a $2\frac{1}{2}$-order [3] reaction. A number of other recent studies have led to the conclusion that, in the absence of added catalyst, esterifications and polyesterifications are $2\frac{1}{2}$-order reactions [4, 5, 7].

Much of this controversy has arisen from failure to appreciate the complexity of kinetics under the conditions usually encountered in esterification and polyesterification reactions. These are generally carried out in the absence of solvent and consequently the reactants themselves function as the solvent. Initially the medium is an equimolar mixture of alcohol and acid, whereas at complete reaction it is an ester. In kinetic studies such a large change in polarity would not normally be considered acceptable. Moreover, because the initial mixture is very concentrated, it is likely to be thermodynamically nonideal in the sense that the activities of the two reactants may not be simply proportional to their concentrations. In these conditions a kinetic analysis based on concentrations can be misleading and may, for example, yield rate equations that have apparent fractional orders instead of integral ones. For these reasons we believe that significant kinetic results can only be obtained in the later stages of reaction, when the acid and alcohol can be regarded as forming a dilute and relatively ideal solution in the product [ester or low molecular weight polyester]. Although Flory was evidently aware of this limitation [1], it is one that has been overlooked by later workers.

There is another important reason for concentrating on the later stages of reaction in experiments designed to compare polyesterifications with simple esterifications. If the reactivity of functional groups in a polyesterification were to change with the degree of polymerization or with the viscosity of the medium, the effect would be most apparent in the later stages and would appear as a progressive deviation of the reaction kinetics from those of a simple esterification. In many of the kinetic comparisons that have been made, the starting materials in the polyesterification have had lower molecular weights that the acid and alcohol used in the simple esterification, so that noticeable deviations could only be expected to occur late in the reactions. For example, in a comparison of the esterification of lauryl alcohol–lauric acid mixtures with the polyesterification of diethylene glycol and adipic acid [1], the molecular weights of the initial reactants in the esterification are about 200, whereas in the polyesterification the average molecular weight only reaches that value after 35% reaction.

Unfortunately, there are experimental difficulties in making accurate kinetic measurements toward the end of a reaction and the problem is especially serious in esterifications. In the absence of an added catalyst an esterification is usually slow, and to attain an acceptable rate of reaction it is necessary to use high temperatures. Also to study the kinetics satisfactorily it is desirable to avoid the reverse reaction of hydrolysis by removing the water that is formed, by passing a stream of dry nitrogen through the mixture. In these conditions there is some unavoidable loss of the volatile reactants in the early stages of reaction [1, 3] and for that reason their concentrations become uncertain in the later stages.

In the present work we have approached the study of the kinetics of esterification by choosing reaction conditions that avoid or minimize the problems discussed above. Instead of starting with an equimolar mixture of the pure acid and alcohol, we have used a solution of these in their ester. For example, to study the esterification of lauryl alcohol with lauric acid we synthesized lauryl laurate and used this as the solvent for the reaction. The initial concentrations were chosen so that our kinetic analysis began at a point corresponding to 80% reaction in the system used by Flory [1], Tang and Yao [3] and others [4–7]. Similarly, with polyesterification reactions, a low molecular weight polymer was prepared under mild conditions and this was then used in kinetic studies at a higher temperature. Once again the initial concentration of unreacted hydroxyl and carboxyl groups corresponded to 80% reaction on other workers' scales.

EXPERIMENTAL

Materials

Lauric acid was recrystallized from ethanol and had a melting point of 42–44°C. Titration with alkali gave calculated purity of 99.4%. Lauryl alcohol was "puriss" grade, specified as >99% pure, with a melting point of 22–23°C. Diethylene glycol was distilled under reduced pressure, and had a boiling point of 75°C at 1 mm Hg. The hydroxyl value was 1051 mg of KOH/g (calculated hydroxyl value 1057). Decamethylene glycol was recrystallized from ethylene dichloride and had a melting point of 72°C. The hydroxyl value was 640 mg of KOH/g (calculated hydroxyl value 644). Adipic acid was recrystallized from ethanol and had a melting point of 151–153°C. Titration with alkali gave a calculated purity of 99.9%.

Lauryl laurate was prepared by refluxing, for 18 hr, a mixture of lauryl alcohol (1.0 mole), lauric acid (1.05 moles) and toluene (10 wt. %). Water was removed continuously in a Dean and Stark water separator. The reaction mixture was fractionally distilled and the fraction boiling at 185–188°C, at 0.6 mm Hg, collected. The maximum acid content, estimated from titration with alkali, was 0.05%.

The polyesters with a low average molecular weight were prepared as follows: equimolar amounts of the diol and dibasic acid were heated with toluene (approx. 30 wt. %) under reflux at about 120°C and the water of reaction removed in a Dean and Stark water separator until 60–65% of the carboxyl groups had been esterified The toluene was removed by stripping under reduced pressure. The polyesters gave the following analytical results, which indicate that losses, if any, during their preparation are negligible: poly (diethylene glycol–adipic acid)—acid value found 257, hydroxyl value found 254, hydroxyl value calculated 257, saponification value found 219, saponification value calculated 216. Poly(decamethylene glycol–adipic acid)—acid value found 160, hydroxyl value found 159, hydroxyl value calculated 160, saponification value found 211, saponification value calculated 214.

Procedure and Apparatus Used for Kinetic Measurements

Reactions were carried out in a 750-ml flanged-top flask fitted with a constant-speed stirrer (300 rpm), a nitrogen gas inlet, a sampling device, a thermometer, and a condenser. The gas flow rate was about 60 cc/min. The flask and contents were placed in a constant-temperature (±0.1°C) oil bath and samples of about 2 g were withdrawn at intervals and cooled rapidly. The carboxyl content was measured by titration of accurately weighed samples with alkali. All measurements were made in duplicate. The initial weight of the ester or polyester loaded into the flask was about 250 g. This quantity was necessary to minimize temperature fluctuations which can result when the weight of samples removed is significant compared with the total weight of reactants. Sample sizes and the normality of the alkali used for titration were selected so that acceptable titers were obtained.

The polyesters used for the kinetic studies had an initial degree of polymerization of 60–65%. They were further polymerized for a short time at the reaction temperature, and kinetic analysis was begun when 80% of the original carboxyl groups had been esterified. In the simple esterification experiments the temperature uncertainty was minimized by preheating the components. For example, a mixture of lauryl laurate and lauryl alcohol was preheated to a temperature slightly above that required for the kinetic run, and preheated lauric acid was then added to start the reaction.

The kinetic runs were discontinued if monomeric compounds (lauryl alcohol, lauric acid, diethylene glycol, etc.) were detected in the condenser.

In acid catalyzed reactions, the p-toluene sulfonic acid was added when the other reactants had reached the reaction temperature.

The results are listed in Table 1-4.

ANALYSIS OF RESULTS

The symbols used in this section are defined as follows:

a = initial concentration of acid groups [COOH]

b = initial concentration of hydroxyl groups [OH]

t = time of reaction

x = concentration of ester groups at the time t

$a-x$ = concentration of acid groups at the time t

$b-x$ = concentration of hydroxyl groups at the time t

n = order of reaction

k_n = rate constant for reaction

Uncatalyzed Reactions

The term "uncatalyzed" is to be understood here to mean that the reactions were carried out in the absence of added acid catalyst.

The results for equimolar ($a = b$) esterifications [Tables 1 (a), (b); 3 (a), (b); 4 (a), (b)] were analyzed using the general rate formula

$$(n - 1)k_n t = \frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}} \qquad (1)$$

for $n > 1$, and the usual first-order formula for $n = 1$. It was found that the data could only be fitted properly by the equation for a third-order reaction, $n = 3$; values of $n = 1, 2, 2.5$, and 4 all gave pronounced deviations from straight lines. The third order plots are shown in Figs. 1, 6, and 7.

Having established that the overall kinetics were third order, we examined nonequimolar mixtures ($a \neq b$) to determine the order

TABLE 1. Reaction of Lauryl Alcohol (b = 0.200 mole) with Lauric Acid (a = 0.200 mole) in Lauryl Laurate (0.800 mole)

(a) Temp. 195°C		(b) Temp. 163°C		(c) Temp. 163°C Catalyzed by p-toluene sulfonic acid (0.004 mole)	
Time, min	Percentage reaction	Time, min	Percentage reaction	Time, min	Percentage reaction
0	0	0	0	0	0
15	6.20	30	5.48	5	36.7
30	8.50	60	9.82	10	59.7
60	18.5	120	18.1	15	69.4
120	33.1	180	23.8	20	74.3
180	40.7	240	27.1	25	78.0
240	44.7	300	32.4	35	83.5
300	49.7	360	35.2	44	86.5
360	53.6	420	38.0	50	88.0
420	57.0	480	40.7	60	89.8
480	59.7	540	42.3	70	90.9
555	61.6	600	44.6		
600	62.9	720	48.0		
660	64.6	840	50.1		
780	66.9	960	53.2		
900	69.2	1080	54.8		
1080	71.6	1200	57.5		
1320	74.1	1380	59.8		
1620	76.6	1560	61.7		

TABLE 2. Reaction of Lauryl Alcohol with Lauric Acid in Lauryl Laurate at 195°C Using Various Initial Ratios of Acid to Alcohol[a]

(a)		(b)		(c)	
$\frac{a}{b} = 0.50$		$\frac{a}{b} = 2.0$		$\frac{a}{b} = 0.112$	
Time, min	Percentage reaction	Time, min	Percentage reaction	Time, min	Percentage reaction
0	0	0	0	0	0
10	2.6	10	5.0	4	12.0
30	19.4	30	11.2	10	38.7
60	35.4	70	26.9	16	51.8
120	49.3	130	41.9	22	60.0
170	59.1	190	49.3	30	67.8
240	66.2	240	54.4	38	71.9
300	70.2	320	64.4	48	76.4
365	74.6	420	69.4	70	83.3
420	77.5	510	75.0		
530	80.8	630	80.0		

[a] In reactions (a), (b) and (c) the initial amount of acid was 0.2 mole in each case; the amount of alcohol was 0.4, 0.1, and 1.78 mole; and the amount of lauryl laurate was 0.699, 0.851 and 0 mole, respectively.

TABLE 3. Further Polymerization of Poly(1:10 decanediol-adipate)[a] of Calculated Average Molecular Weight 640[b]

(a) Temp. 190°C		(b) Temp. 161°C		(c) Temp. 161°C Catalyzed by p-toluene sulfonic acid (0.004 mole per mole of polymer)	
Time, min	Percentage reaction	Time, min	Percentage reaction	Time, min	Percentage reaction
0	0	0	0	0	0
30	20.6	20	9.1	5	34.6
60	39.0	40	16.0	10	54.7
90	50.2	100	31.6	15	65.5
150	61.2	150	41.1	20	70.8
225	66.8	210	47.9	30	77.9
300	71.5	270	52.5	40	82.9
370	74.4	330	57.0	50	85.7
465	77.2	390	60.0	60	87.9
510	78.2	450	62.6	75	90.1
550	78.8	510	64.6	90	91.5
600	79.6	550	65.5	105	92.6
660	80.6	700	69.2	120	93.6
730	81.7	840	71.9		
800	82.5	880	72.4		
		1060	74.8		
		1200	76.2		
		1320	77.2		

[a] This polymer was prepared under mild conditions and was characterized prior to use.

[b] This corresponds to 82.0% esterification of the original carboxyl groups.

TABLE 4. Further Polymerization of Poly(diethylene glycol-adipate)[a] of Calculated Average Molecular Weight 565[b]

(a) Temp. 190°C		(b) Temp. 161°C	
Time, min	Percentage reaction	Time, min	Percentage reaction
0	0	0	0
30	16.9	17	5.2
60	22.7	30	9.0
120	31.6	60	12.4
180	42.9	90	19.2
240	46.3	120	23.0
360	54.1	180	30.0
480	59.2	240	36.4
600	62.7	300	40.2
720	65.5	405	46.1
840	67.9	540	51.3
960	69.7	660	55.0
		780	58.0
		975	61.9
		1140	64.2

[a] This polymer was prepared under mild conditions and was characterized prior to use.

[b] This corresponds to 80.0% esterification of the original carboxyl groups.

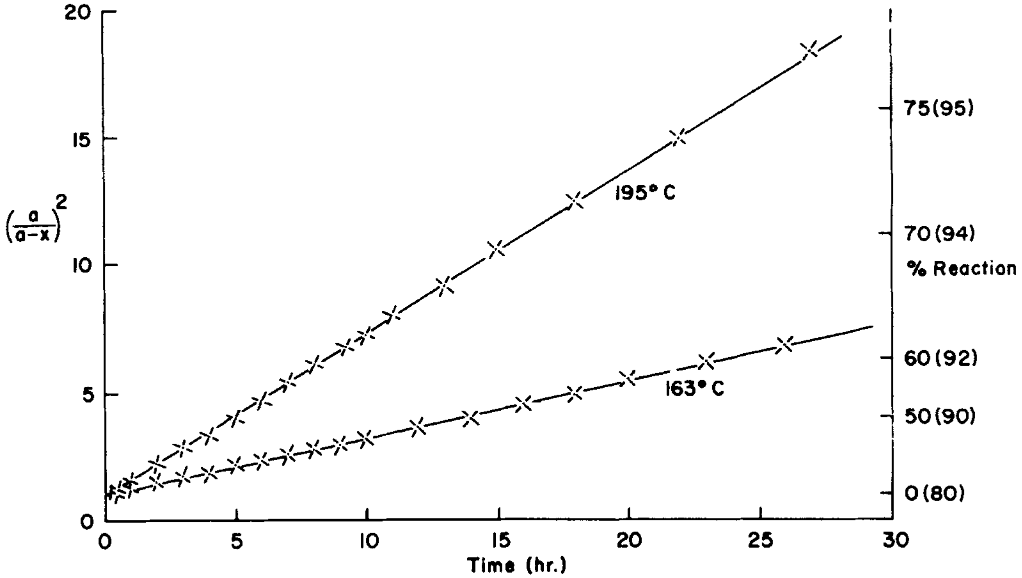

FIG. 1. Reaction of lauryl alcohol (0.200 mole) with lauric acid (0.200 mile) in lauryl laurate (0.800 mole) at 195 and 163°C. The numbers in parentheses denote the corresponding percentages of reaction in the systems studied by Flory [1] and others [3–7].

with respect to each component. As Figs. 2–4 show, the data of Table 2 can be fitted closely by the relation

$$\ln\left(\frac{a-x}{b-x}\right) - \left(\frac{a-b}{a-x}\right) = k_3(a-b)^2 t + \ln\frac{a}{b} - \frac{a-b}{a} \tag{2}$$

obtaining by integrating

$$\frac{dx}{dt} = k_3(a-x)^2(b-x) \tag{3}$$

The analogous relation based on

$$\frac{dx}{dt} = k_3'(a-x)(b-x)^2 \tag{4}$$

failed badly. In addition, the values of k_3 derived from (2) were almost unchanged when the ratio a/b was changed from 2 to $\frac{1}{2}$

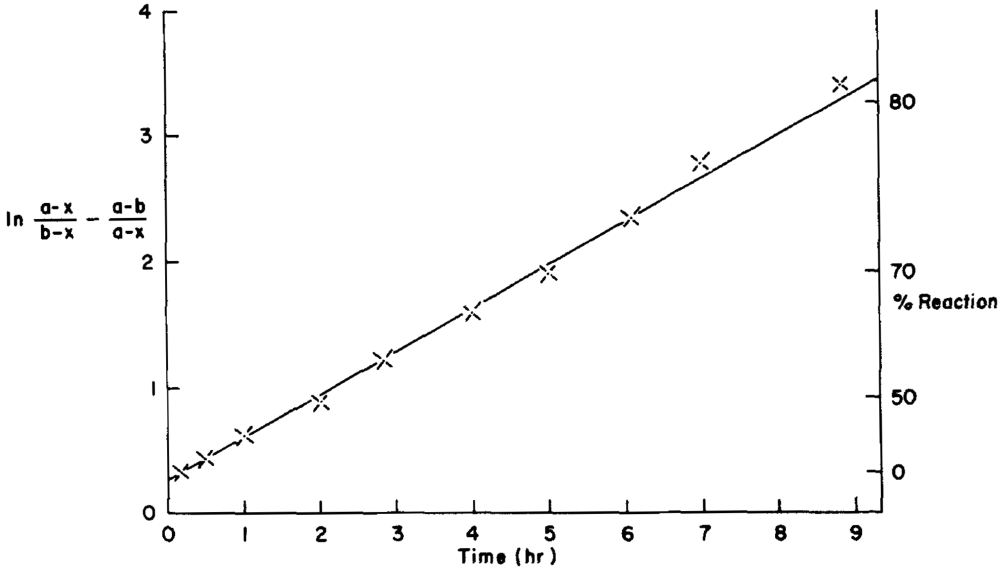

FIG. 2. Reaction of lauryl alcohol (0.400 mole) with lauric acid (0.200 mole) in lauryl laurate (0.699 mole) at 195°C.

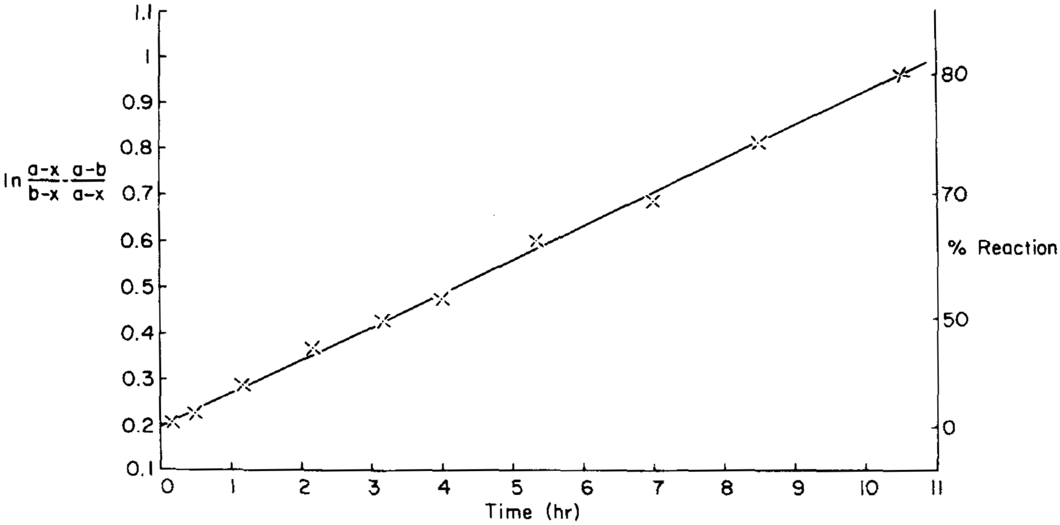

FIG. 3. Reaction of lauryl alcohol (0.100 mole) with lauric acid (0.200 mole) in lauryl laurate (0.851 mole) at 195°C.

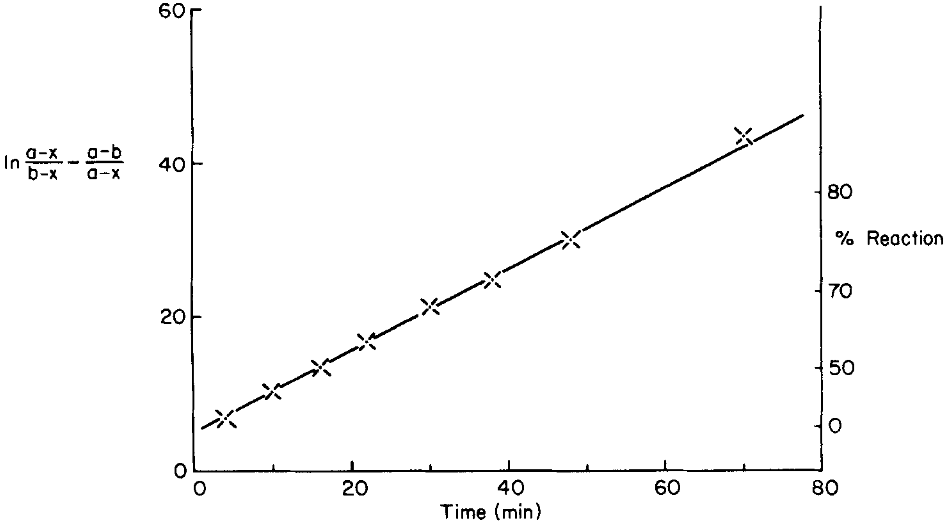

FIG. 4. Reaction of lauryl alcohol (1.78 moles) with lauric acid (0.200 mole) at 195°C.

(cf. Table 5). These results prove that the reaction is of the second order in acid groups and of the first order in hydroxyl groups.

Catalyzed Reactions

The results for acid-catalyzed reactions [Table 1 (c), 3 (c)] were analyzed by a general method that allowed for the occurrence of simultaneous uncatalyzed reactions. Following Flory [1], we assumed the catalyzed reaction to be a second-order one and the uncatalyzed reaction to be a third-order one. For an equimolar mixture the total rate of reaction is then

$$\frac{dx}{dt} = k_3(a-x)^3 + k_2(a-x)^2 \qquad (5)$$

where k_2 is a function of the concentration of added catalyst, but not of time. Integration gives

$$k_2t = \frac{k_3}{k_2}\ln\left[\frac{a-x}{k_3(a-x)+k_2}\,\frac{k_3a+k_2}{a}\right] - \frac{1}{a} + \frac{1}{a-x} \qquad (6)$$

In applying this equation we first obtained an approximate value for k_2 by treating the reaction as if it were a pure second-order

TABLE 5. Rate Constants for Esterification and Polyesterification

System	See Table	Temp., °C	k_3, equiv.^{2}/kg^2 min
Uncatalyzed Reactions			
Lauryl alcohol–lauric acid–lauryl laurate			
[COOH]/[OH] = 1	1(a)	195[a]	0.0183
[COOH]/[OH] = 1	1(b)	163[a]	0.0064
[COOH]/[OH] = 0.5	2(a)	195	0.0197
[COOH]/[OH] = 2	2(b)	195	0.0168
Lauryl alcohol–lauric acid			
[COOH]/[OH] = 0.112	2(c)	195	0.0288
1,10-Decanediol adipate			
	3(a)	190[b]	0.0131
	3(b)	161[b]	0.0045
Diethylene glycol adipate			
	4(a)	190[c]	0.0021[d]
	4(b)	161[c]	0.0012[d]
Acid-Catalyzed Reactions			k_2[e]
Lauryl alcohol–lauric acid–lauryl laurate			
[COOH]/[OH] = 1	1(c)	163	0.272
1,10-Decanediol adipate			
	3(c)	161	0.097

[a] Activation energy = 12.9 kcal/mole.

[b] Activation energy = 14.2 kcal/mole.

[c] Activation energy = 7.6 kcal/mole.

[d] We consider these results less accurate than the rest because kinetic studies on the same reaction catalyzed by p-toluene sulfonic acid have indicated that the functional groups in low molecular weight polymers of diethylene glycol–adipic acid do not conform to the concept of equal reactivity, irrespective of molecular size [8,9].

[e] In equiv./kg min.

one and then combined this value with the value of k_3 derived from independent measurements made at the same temperature in the absence of an added catalyst [Tables 1 (b), (c); (b), (c)]. It emerged that the first term in (6) was, in fact, insignificant in comparison with the last two and that the reaction could justifiably be treated as a simple second-order one. The second-order plots are shown in Figs. 5 and 8.

Table 5 lists the individual rate constants.

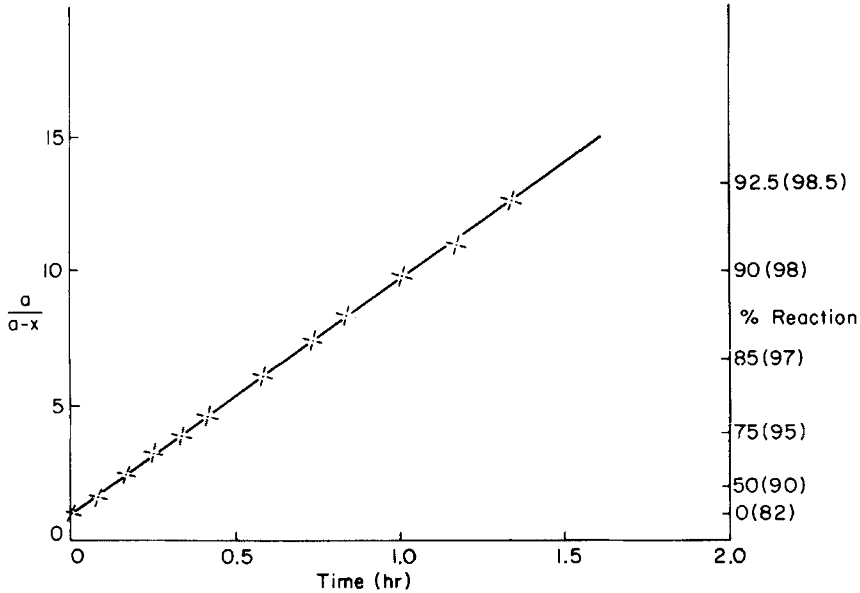

FIG. 5. Reaction of lauryl alcohol (0.200 mole) with lauric acid (0.200 mile) in lauryl laurate (0.800 mole) at 163°C in the presence of p-toluene sulphonic acid (0.004 mole). The numbers in parentheses denote the corresponding percentages of reaction in the systems studied by Flory [1] and others [3-7].

DISCUSSION

Our results show that simple esterification and polyesterification reactions are of the same kinetic order. In the absence of an

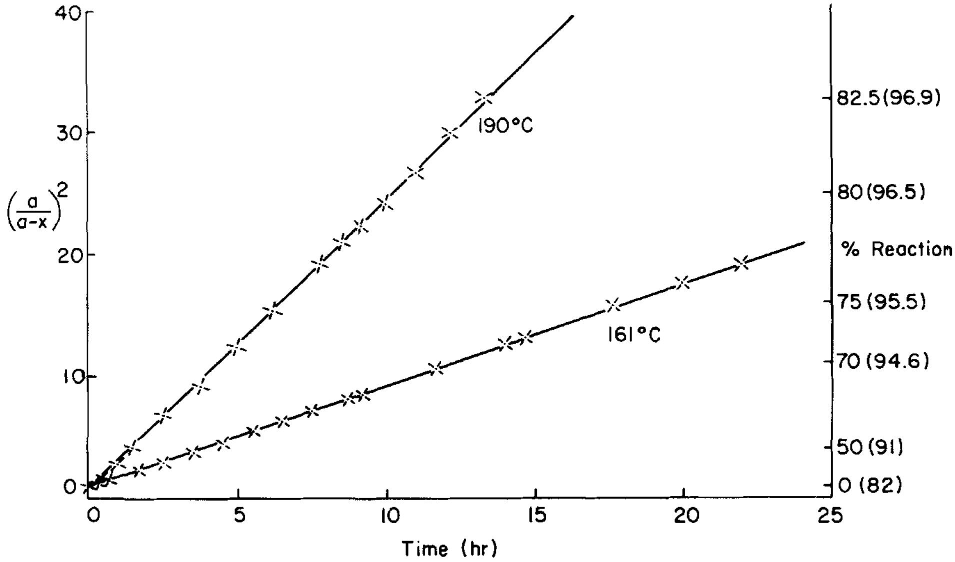

FIG. 6. Further polymerization of poly(1:10 decane diol-adipate) of calculated average molecular weight 640. The numbers in parentheses denote the corresponding percentages of reaction in the systems studied by Flory [1] and others [3-7].

added catalyst (Figs. 1, 6, and 7) they both follow third-order kinetics:

$$\text{rate} \propto [\text{RCOOH}]^2[\text{R'OH}]$$

and in the presence of a catalyst (Figs. 5 and 8) they obey second-order kinetics:

$$\text{rate} \propto [\text{RCOOH}][\text{R'OH}]$$

Our findings are in complete agreement with those of Flory [1, 2] for the later stages of the reactions that he studied.

The experiments on the polyesterification of decamethylene glycol with adipic acid were continued until 96.9% of the initial carboxyl group had reacted, whereas Flory's measurements stopped at 92.7%. Our final mixture was therefore much more viscous and had a much higher molecular weight than Flory's. Nevertheless the reaction still obeyed third-order kinetics (Fig. 6) and this result provides powerful support for the concept that the reactivity of a functional group is independent of the size of the molecule to

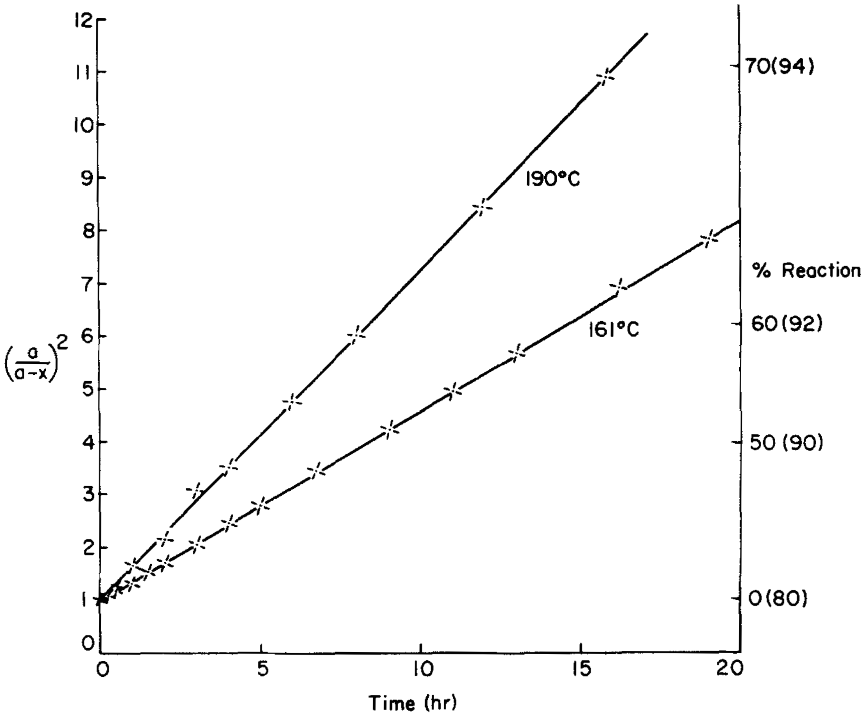

FIG. 7. Further polymerization of poly(diethylene glycol–adipate) of calculated average molecular weight 565. The numbers in parentheses denote the corresponding percentages of reaction in the systems studied by Flory [1] and others [3–7].

which it is attached [9]. We might add that although other authors have suggested that uncatalyzed polyesterification reactions obey second-order [8] and $2\frac{1}{2}$-order [3-7] kinetics, they have not challenged the concept of equal reactivity, since they have assumed or claimed that simple esterifications have similar kinetics. For linear systems such as we have studied here, the kinetic evidence is therefore consistent with the idea that functional group activity is independent of molecular size, although deviations from the rule have been observed in more highly functional systems and in the early stages of some diethylene glycol reactions [10, 11].

Now that their kinetics are established, it is worthwhile to consider the detailed mechanisms of these reactions. Day and Ingold [12] and Ingold [13] have classified the possible mechanisms of esterification and hydrolysis in acidic systems and we shall use

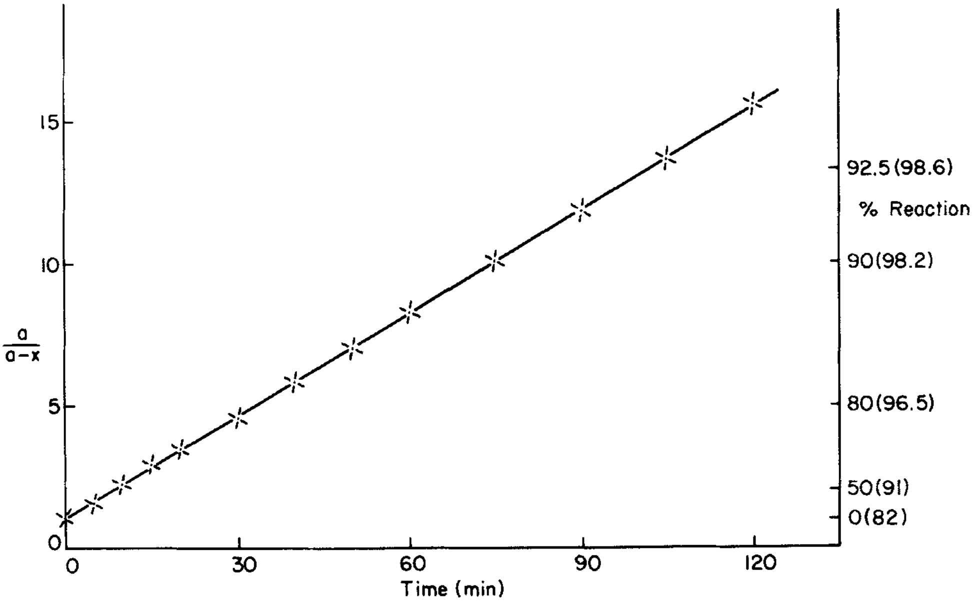

FIG. 8. Further polymerization at 161°C of poly(1:10 decane diol–adipate) of calculated average molecular weight 640 in the presence of p-toluene sulfonic acid (0.004 mole). The numbers in parentheses denote the corresponding percentages of reaction in the systems studied by Flory [1] and others [3–7].

their notation in this discussion. The unimolecular $A_{AC}1$ and $A_{AL}1$ mechanisms can be ruled out by the observed high-order kinetics and by the fact that the reactants are not of the kind that readily form carbonium or acylium ions. Of the two possible bimolecular mechanisms, the $A_{AL}2$ has never been observed [13] and there is no reason to suppose that it operates in the present systems. We therefore consider that the reactions occur by the common $A_{AC}2$ mechanism, in which the rate-determining step is

$$RCOOH_2^+ + R'OH \longrightarrow RCOOHR'^+ + H_2O \tag{7}$$

In the absence of an added catalyst the oxonium ions $RCOOH_2^+$ are formed by autoprotolysis of the carboxylic acid:

$$2RCOOH \rightleftharpoons RCOO^- + RCOOH_2^+ \tag{8}$$

where, in a medium of low dielectric constant, the ions will be largely associated as ion pairs. From arguments that are presented in the Appendix, we conclude that the slow step is the attack of ion pairs on an alcohol group:

$$(RCOO^- \cdots RCOOH_2^+)_{\text{ion pair}} + R'OH \xrightarrow{\text{slow}}$$

$$(RCOO^- \cdots RCOOHR'^+)_{\text{ion pair}} + H_2O \xrightarrow{\text{fast}}$$

$$RCOOR' + RCOOH + H_2O \qquad (9)$$

In the presence of a strong acid catalyst AH the oxonium ions are formed by the proton transfer:

$$AH + RCOOH \rightleftharpoons A^- + RCOOH_2^+ \qquad (10)$$

and the slow step is

$$(A^- \cdots RCOOH_2^+)_{\text{ion pair}} + R'OH \xrightarrow{\text{slow}}$$

$$(A^- \cdots RCOOHR'^+)_{\text{ion pair}} + H_2O \xrightarrow{\text{fast}}$$

$$RCOOR' + AH + H_2O \qquad (11)$$

These mechanisms are consistent with the kinetics and, chemically, they are very reasonable ones.

Acknowledgments

We are indebted to Dr. J. E. Lane for deriving formula (6) and to Mr. R. Grace for his help in some of the measurements.

APPENDIX

An Examination of Possible Reaction Mechanisms

As explained in the text, we presume that the reactions follow Ingold's $A_{AC}2$ mechanism [13], in which the slow step is the bimolecular reaction

$$RCOOH_2^+ + R'OH \longrightarrow RCOOHR'^+ + H_2O \qquad (12)$$

so that

$$\text{rate} \propto [RCOOH_2^+][R'OH] \qquad (13)$$

where the species $RCOOH_2^+$ may be either a free ion or the component of an ion pair.

Uncatalyzed Reactions

In the absence of an added catalyst, the source of the oxonium ions is the autoprotolysis equilibrium

$$2RCOOH \rightleftharpoons RCOO^- + RCOOH_2^+ \tag{14}$$

$$K_1 = \frac{[RCOO^-][RCOOH_2^+]}{[RCOOH]^2} \tag{15}$$

which occurs simultaneously with protonation of the alcohol groups

$$RCOOH + R'OH \rightleftharpoons RCOO^- + R'OH_2^+ \tag{16}$$

$$K_2 = \frac{[RCOO^-][R'OH_2^+]}{[RCOOH][R'OH]} \tag{17}$$

The extent of both protonations is extremely small in media of low dielectric constant, so that the concentrations of RCOOH and R'OH are effectively equal to the total concentrations of acid and alcohol $[RCOOH]_t$ and $[R'OH]_t$. Since alcohols are much stronger proton acceptors than acids, the equilibrium (16) must predominate and we assume here that $[R'OH_2^+] \gg [RCOOH_2^+]$.

Case 1. If the ions were unassociated, then, for electrical neutrality,

$$[RCOO^-] \approx [R'OH_2^+] \approx (K_2[RCOOH]_t[R'OH]_t)^{1/2} \tag{18}$$

$$[RCOOH_2^+] \approx \frac{K_1[RCOOH]_t^{1.5}}{K_2^{1/2}[R'OH]_t^{1/2}} \tag{19}$$

Hence, from (13), the kinetics would be

$$\text{rate} \propto [RCOOH]_t^{1.5}[R'OH]_t^{1/2} \tag{20}$$

This is, the reaction would be a second-order one, in disagreement with the experiments.

Case 2. On the other hand, if the ions produced in (14) and (16) were completely associated as ion pairs, the concentration of $(RCOO^- \cdots RCOOH_2^+)_{\text{ion pair}}$ would be independent of the equilibrium (16) and, from (14) would be simply proportional to $[RCOOH]_t^2$. The kinetics would then be

$$\text{rate} \propto [RCOOH]_t^2[R'OH]_t$$

in agreement with the experiments.

Catalyzed Reactions

There is evidence [14] that p-toluene sulphonic acid is only very slightly ionized in a carboxylic acid medium, so we may justifiably assume that the proton transfer reactions

$$AH + RCOOH \rightleftharpoons A^- + RCOOH_2^+ \qquad (21)$$

$$K_3 = \frac{[A^-][RCOOH_2^+]}{[AH][RCOOH]} \qquad (22)$$

$$AH + R'OH \rightleftharpoons A^- + R'OH_2^+ \qquad (23)$$

$$K_4 = \frac{[A^-][R'OH_2^+]}{[AH][R'OH]} \qquad (24)$$

occur to only a small degree and that [RCOOH] and [R'OH] may be written $[RCOOH]_t$ and $[R'OH]_t$. Again it can be assumed that the equilibrium (23) predominates.

Case 1. If the ions were free, then for electrical neutrality

$$[A^-] \approx [R'OH_2^+] \approx (K_4[AH][R'OH]_t)^{1/2} \qquad (25)$$

$$[RCOOH_2^+] \approx \frac{K_3[AH]^{1/2}[RCOOH]_t}{K_4^{1/2}[R'OH]_t^{1/2}} \qquad (26)$$

Hence, from (13), at constant [AH],

$$\text{rate} \propto [RCOOH][R'OH]^{1/2} \qquad (27)$$

in disagreement with the experiments.

Case 2. If the ions were associated, the concentration of ion pairs containing the protonated acid would be given by

$$[(A^- \cdots RCOOH_2^+)\text{ion pair}] \propto [AH][RCOOH]_t \qquad (28)$$

and the kinetics at constant [AH] would be

$$\text{rate} \propto [RCOOH][R'OH] \qquad (29)$$

in agreement with the experiments.

We conclude that both the uncatalyzed and catalyzed reactions proceed through the reaction of R'OH with $RCOOH_2^+$ ions in the form of ion pairs. We have no direct information on ion-pair formation under the conditions of our reactions, at high temperatures and low values of dielectric constant (ϵ). But Fuoss's theory [15] predicts an association constant of 4 × 10^9 kg/mole at 190°C, $\epsilon = 5$, for ions whose charge centers are 5 Å apart, and that may be a realistic value for our system. It certainly suggests that our suppositions are reasonable.

REFERENCES

[1] P. J. Flory, *J. Am. Chem. Soc.*, **61**, 3334 (1939).
[2] P. J. Flory, *J. Am. Chem. Soc.*, **59**, 466 (1937).
[3] Au-Chin Tang and Kuo-Sui Yao, *J. Polymer Sci.*, **35**, 219 (1959).
[4] C. Y. Huang, Y. Simono, and T. Onizuka, *Chem. High Polymers Japan*, **23** (254), 408 (1966); *Polymer Previews*, **2**, 307 (1966).
[5] I. Vansco-Szmercsanyi and E. Makay-Bödi, *Polymer Previews*, **2**, 611 (1966).
[6] S. V. Vinogradova, V. V. Korshak, and Yu. I. Korzenova, *Polymer Sci. USSR*, **7**, 2242 (1965).
[7] M. Imoto, C. Huang, J. Hashizumo, S. Sano, and K. Amamuja, *J. Japan. Chem. Soc. Ind. Chem. Sect.*, **63**, 1807 (1960).
[8] M. Davies, *Research (London)*, **2**, 544 (1949).
[9] P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithica, N.Y., 1953, p. 102.
[10] M. T. Pope and R. J. P. Williams, *J. Chem. Soc.*, 1959, 3579.
[11] D. H. Solomon, B. C. Loft, and Jean D. Swift, *J. Appl. Polymer Sci.*, **11**, 1593 (1967).
[12] J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).
[13] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Bell, London, 1953, Chap. XIV.
[14] I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).
[15] R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

Accepted by editor November 14, 1967
Submitted for publication December 6, 1967

Zusammenfassung

Die Bedingungen bei welchen frühere kinetische Messungen von Esterifikations und Polyesterifikationsreaktionen ausgeführt wurden, sind in Bezug auf die Bedeutung der dabei erzielten Schlüsse untersucht worden. Es wird darauf hingewiesen, dass nur in den letzten Phasen der Reaktion Bedingungen vorherrschen, die sinnvolle kinetische Ergebnisse ergeben.

Experimente wurden entwickelt, die es erlauben, genauere kinetische Daten für die späteren Phasen der Reaktion zu erhalten als sie je vorher verfügbar waren. Die Ergebnisse ergeben, dass die Esterifizierung als auch die Polyesterifizierung summarisch gesehen nach dritter Ordung verlaufen. Bei Reaktionen in welchen die molaren Verhältnisse der Ausgangsmaterialien variiert wurden, ergab sich eine Abhängigkeit zweiter Ordung in Bezug auf die Carboxylgruppenkonzentration und erster Ordnung in Bezug auf die Hydroxylgruppenkonzentration. Säure-katalysierte Reaktionen wurden ebenfalls untersucht. Ein mit diesen Resultaten übereinstimmender Mechanismus wird angegeben.

Résumé

On a examiné les conditions dans lesquelles on a fait précedement des mesures cinétiques des réactions d'esterification et de polyesterification par rapport à la signification des conclusions obtenues. On a suggèré que c'est uniquement dans les derniéres étapes de ces réactions qu'on parvient aux conditions donnant des résultats cinétiques raisonables.

On a mis au point des experiénces afin d'obtenir des données cinétiques plus precises que ces disponsibles anterieurement pour les derniérs stades de la réaction. Les résultats prouvent que l'ordre global cinétique de l'esterification et de la polyesterification est de 3me ordre. Les réactions dans lesquelles on a varié les taux molaires des réactifs de départ indiquent que l'esterification est du 2me ordre par rapport au carboxyle et de Ier ordre en relation aux concentrations du groupe hydroxyle. On a aussi étudié les réactions acido-catalysées. On propose un mécanisme en accord avec les résultats.