

acids in general may alter the activity of an enzyme by causing the rupture of intramolecular hydrogen bonds in the enzyme protein. The results of such bond breaking may be the arising

of modified forms of the enzyme with more internal degrees of freedom, possessing less catalytic activity.

NEW YORK, N. Y.

RECEIVED SEPTEMBER 27, 1939

[CONTRIBUTION FROM THE BASIC SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

## Kinetics of Polyesterification: A Study of the Effects of Molecular Weight and Viscosity on Reaction Rate<sup>1</sup>

BY PAUL J. FLORY

### Introduction

Investigators in the field of macromolecular chemistry have been prone to attribute the apparent sluggishness of some polymer reactions either to an inherent diminished reactivity of large molecules, or to the high viscosity of the reaction medium. Various arguments have been advanced in an effort to show theoretically that increase in size of the molecule and increase in viscosity should decrease reactivity.<sup>2,3</sup> However, no direct experimental evidence has been advanced to prove even the existence of an effect of either molecular weight or viscosity on reactivity of polymer molecules.

The problem of the effect of viscosity on reaction rate of liquid phase reactions in general has been the subject of frequent discussion,<sup>4</sup> but again conclusive experimental evidence does not seem to be available. Moelwyn-Hughes<sup>5</sup> has concluded that the rate of collision between solute and solvent molecules should increase proportionally with viscosity and, hence, the rate of a reaction between solute and solvent should be proportional to viscosity also. More recently Rabinowitch and Wood<sup>6</sup> have shown with exceptional clarity that one should expect no effect of viscosity on reaction rate, except at very high viscosities (very low rates of diffusion) or when a large fraction of collisions leads to reaction.

The study of the kinetics of a condensation polymerization offers a splendid opportunity to

observe the effects of molecular weight and viscosity on reaction rate. Both molecular weight and viscosity increase continuously as such reactions proceed. It should be possible, therefore, to observe the effects of molecular weight and viscosity on reaction rate, if such effects exist.

The present investigation has been primarily concerned with the kinetics of polyesterification reactions between glycols and dibasic acids. The kinetics of several esterifications involving monofunctional reactants have been investigated also, in order that the polyesterification reactions could be compared with similar reactions in which neither molecular weight nor viscosity underwent appreciable change. All of these reactions have been followed by titration of the total free carboxyl in samples removed from the reaction mixture at suitable intervals.

In contrast to monofunctional esterification where there are only two species of reactants, many species of molecules are present during polyesterification. Any one of these species bearing an hydroxyl group may react with any other bearing a carboxyl; the product of this reaction may react with another molecule, etc. Many reactions are occurring simultaneously: *i. e.*, monomers react with monomers, dimers, trimers, etc., dimers react with monomers, dimers, trimers, etc., trimers react with monomers, etc., etc. A complete kinetic analysis, treating each of these reactions individually, is obviously hopeless. All of these reactions, however, are chemically identical, and their rates may differ only in so far as reactivity is affected by molecular weight. Instead of attempting to unravel the maze of individual reactions, one may consider merely the reaction of all functional groups, disregarding the size of the molecule to which each group is attached. If, as usually has been supposed, reac-

(1) A portion of this work was included in a paper presented before the Organic Plastics Section, Paint and Varnish Division of the American Chemical Society at the Boston Meeting, September 14, 1939.

(2) C. E. H. Bawn, *Trans. Faraday Soc.*, **32**, 178 (1936).

(3) H. Dostal, *Monatsh.*, **67**, 63 (1935); **70**, 409 (1937); H. Mark, *Nature*, **140**, 8 (1937).

(4) See E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Univ. Press., New York, N. Y., 1933, p. 51.

(5) Reference 4, pp. 19, 159 *et. seq.*

(6) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936).

tivity decreases with increase in size of the molecule, then the ratio of the rate of polyesterification to the rate of a simple esterification at the same degree of reaction should decrease as the reactions progress. The results presented below show that polyesterification and esterification reactions follow identical courses.

### Experimental

**Materials.**—Diethylene glycol, lauryl alcohol, adipic acid, lauric acid, and caproic acid were obtained from the Eastman Kodak Company. Decamethylene glycol, which had been prepared by hydrogenation of diethyl sebacate, was obtained from the University of Illinois. The diethylene glycol was carefully fractionated through a carborundum packed column. The boiling point was practically constant throughout almost the entire distillation, 129.5 to 130.0° at 10.5 mm. A center cut was retained for use. Decamethylene glycol was treated with boiling 5% aqueous caustic to remove unreduced ester, then recrystallized three times from ethylene dichloride. The final product had a freezing point of 71.9 ( $\pm 0.1$ )°. Lauryl alcohol, freezing at 21.9 ( $\pm 0.1$ )°, was used without further purification.

Adipic acid was recrystallized from conductivity water; m. p. 151.5°; neutral equivalent 72.9, 73.0; calcd. 73.07. Caproic acid, neutral equivalent 117.6, calcd. 116.2, and lauric acid, neutral equivalent 200.6, 200.9, calcd. 200.3, were used with no further purification.

**Apparatus and Procedure.**—The apparatus consisted of a Pyrex reaction bulb of about 50 cc. capacity sealed to the bottom of a 15-mm. tube about 25 cm. long. Through a stopper at the top of this tube a pipet was inserted. The pipet was used to remove samples, and also for admitting a slow stream of nitrogen through the reaction mixture in order to facilitate removal of water. The effluent stream of nitrogen and water vapor passed through a 12-mm. tube sealed to the vertical tube just below its upper end. This side tube sloped upward at about 45° from horizontal for about 30 cm., and then led downward to a dry-ice trap. With the apparatus designed in this way loss of glycol was minimized by condensation in the side arm, followed by its return to the reaction mixture. Glycol is lost more readily during the early stages of the reaction; later on nearly all glycol molecules have reacted at one end or the other (or both) and hence are no longer volatile.

The reaction bulb and adjacent tubing were carefully cleaned before each experiment. This is especially important since esterification is an acid catalyzed reaction, and hence is sensitive to traces of acids or bases.

Equivalent quantities of glycol (or alcohol) and acid were placed in the reaction bulb which was then sealed onto the vertical tube. The reaction bulb and several cm. of the vertical tube above were heated with a vapor-bath, which remained within 0.2° of constant temperature throughout any one experiment. Liquids used in the vapor-bath were toluene boiling at 109°, phenetole at 166°, and *m*-cresol, 202°. From time to time samples were removed, weighed and titrated (at 20–25°) with 0.1 *N* alcoholic potassium hydroxide, using phenolphthalein indicator. High molecular weight samples, which tended

to dissolve slowly, were dissolved in hot chloroform, cooled and then titrated. The end-point was very sharp.

Reactions catalyzed with *p*-toluenesulfonic acid were carried out in the same manner except that, due to the lower temperature, 109°, it was necessary to reduce the pressure to about 200 mm. in order to ensure rapid removal of water.

### Experimental Results

From the neutral equivalent determined by titration one can calculate both the extent of reaction *p*, *i. e.*, the ratio of the number of ester groups to the number of ester plus free carboxyl groups, and the degree of polymerization *DP*, which is defined as the average number of glycol and dibasic acid residues per molecule. The number of free carboxyl groups will equal the number of molecules, provided that equivalent amounts of glycol and dibasic acid are used and that the only reaction occurring is intermolecular esterification. When these conditions are fulfilled the neutral equivalent must be equal, therefore, to the average molecular weight, and

$$DP = \frac{\text{neut. equiv.} - 18}{\text{mean segment weight}} = 1/(1 - p) \quad (1)$$

where the mean segment weight is half the molecular weight of the structural unit —ORO—COR'CO— of the polymer.

As Goldschmidt<sup>7</sup> has shown, esterification reactions are hydrogen ion catalyzed. In the absence of a strong acid catalyst a second molecule of the carboxylic acid undergoing esterification must function as catalyst. Therefore, the reaction rate is proportional to the hydroxyl concentration and to the square of the carboxyl concentration. When hydroxyl and carboxyl groups are present in equal numbers, the process becomes a third order reaction,<sup>8</sup> for which

$$2kt = 1/C^2 - 1/C_0^2 \quad (2)$$

where *k* is the velocity constant, *C* is the concentration of unreacted groups at time *t*, and *C*<sub>0</sub> is the initial concentration. If one neglects the effect on concentration of the decrease in volume due to loss of water, this equation may be replaced by

$$2C_0^2kt = 1/(1 - p)^2 - 1 \quad (3)$$

with which the data presented below will be compared. The error arising from the use of (3) rather than (2) is appreciable only during the

(7) H. Goldschmidt and co-workers, *Z. physik. Chem.*, **60**, 728 (1907); **70**, 627 (1910); **81**, 30 (1913); *Ber.*, **29**, 2208 (1896). See also Hinshelwood and co-workers, *Trans. Faraday Soc.*, **30**, 935, 1145 (1934); *J. Chem. Soc.*, 593 (1939).

(8) P. J. Flory, *THIS JOURNAL*, **59**, 466 (1937).

first part of the polymerization, which is of minor interest here.

TABLE I  
DIETHYLENE GLYCOL-ADIPIC ACID AT 166°

<i>t</i> in min.	Neutral equiv.	<i>p</i>	<i>DP</i>	$1/(1-p)^2$
6	143.3	.01379	1.160	1.346
12	161.5	.2470	1.328	1.761
23	189.0	.3675	1.581	2.50
37	233.0	.4975	1.990	3.96
59	293.0	.6080	2.55	6.47
88	363.5	.6865	3.19	10.18
129	451	.7513	4.02	16.16
170	532	.7894	4.75	22.6
203	606	.8161	5.44	29.6
235	673	.8349	6.06	36.7
270	738	.8500	6.67	44.4
321	832	.8672	7.53	56.7
397	947	.8837	8.60	73.8
488	1072	.8974	9.75	95.0
596	1198	.9084	10.92	119.0
690	1309	.9163	11.94	142.5
793	1404	.9220	12.82	164.0
900	1507	.9273	13.77	189.5
1008	1569	.9303	14.33	206
1147	1691	.9354	15.48	239
1370	1835	.9405	16.81	283
1606	1973	.9447	18.08	327

Data from two typical experiments are given in Tables I and II. Extents of reaction and *DP*'s have been calculated using (1). In Figs. 1 and 2,  $1/(1-p)^2$  is plotted against *t* for the reaction of

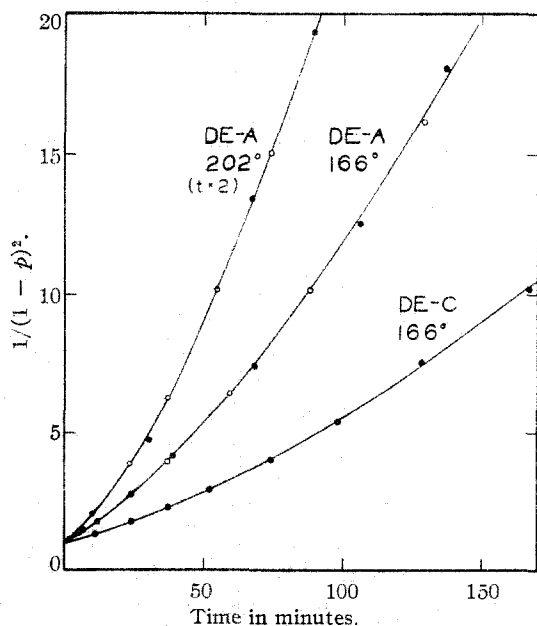


Fig. 1.—Diethylene glycol-adipic acid (DE-A) and diethylene glycol-caproic acid (DE-C) reactions during initial stages. Time values at 202° have been multiplied by two.

TABLE II  
LAURYL ALCOHOL-ADIPIC ACID REACTION AT 202°

<i>t</i> in min.	Neutral equiv.	<i>p</i>	$1/(1-p)^2$
4	344.5	0.2609	1.83
15	532	.5307	4.53
28	742	.6669	9.01
43	955	.7425	15.08
65	1227	.8004	25.1
91	1525	.8400	39.0
116	1772	.8624	52.7
148	2050	.8812	70.9
183	2330	.8957	91.8
226	2581	.9059	112.9
267	2840	.9145	136.9
322	3105	.9219	163.8
378	3365	.9279	192.3

diethylene glycol with adipic acid at 166 and 202°, and of the same glycol with caproic acid at 166°. It has been necessary to use two graphs having different scales in order to show effectively the entire course of the reaction. Dots and circles are used to distinguish data obtained in different experiments. The agreement between two such sets of points indicates the reproducibility. Data from the reactions of decamethylene glycol with adipic acid, lauryl alcohol with adipic acid, and lauryl alcohol with lauric acid are shown in Fig. 3.

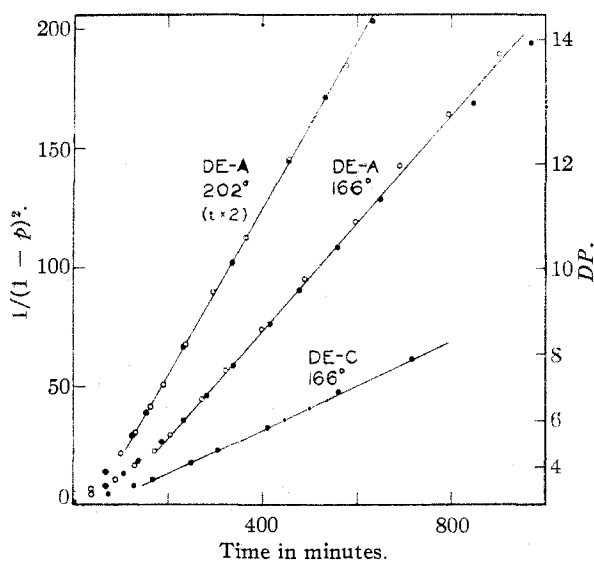


Fig. 2.—Diethylene glycol-adipic acid (DE-A) and diethylene glycol-caproic acid (DE-C) reaction including later stages of the reactions. Time values at 202° have been multiplied by two.

During the portion of the reaction shown in Fig. 1 the relationship between  $1/(1-p)^2$  and *t* is definitely not linear, in disagreement with the

third order equation (3). However, at the larger extents of reaction included in Figs. 2 and 3 the data do approach this linear relationship. Straight lines have been drawn through the points in these two figures in order to show clearly the range over which  $1/(1-p)^2$  is approximately linear with  $t$ . Attempts to fit the data to an equation for a reaction of lower order have not been successful; although such equations offer somewhat better agreement within a limited range during the early portion of the reaction, they fail completely at higher extents of reaction.

In the case of the diethylene glycol-caproic acid reaction, reliable data could not be obtained beyond the range given in Fig. 2, due to excessive loss of the comparatively volatile caproic acid. With diethylene glycol and adipic acid at extents of reaction somewhat beyond those covered in Fig. 2 the points fell consistently below the extrapolation of the straight lines shown in the figure. This is attributed to the effect of the inevitable slight loss of the glycol by volatilization. Small losses of one reactant are of no consequence except at large extents of reaction where the concentration of unreacted functional groups is so low that a small deficiency of one functional group produces an appreciable reduction in rate. This deviation sets in at a much later stage in the reaction of decamethylene glycol with adipic acid, since this glycol is less volatile.

Careful examination of the data presented in the figures fails to reveal any significant dissimilarities between polyesterification and esterification. The courses which they follow are so similar that their points may be made to follow approximately the same curve by merely multiplying all time values for one of them by a suitable factor.

Velocity constants for the esterifications and polyesterifications included in this investigation are given in Table III. These have been evaluated, using (3), from the slopes of the straight lines in Figs. 2 and 3.<sup>9</sup> The velocity constants fall into two groups, those for reactions of diethylene glycol and ethylene glycol being lower than those for decamethylene glycol and lauryl alcohol. Between polyesterifications and ester-

(9) The velocity constant for the ethylene glycol-adipic acid reaction could not be determined accurately due to the volatility of this glycol. The experimental data have not been included here.

fications within each group there are no important differences in the values of the velocity constants. The lower rates of the esterifications compared with polyesterification (see Fig. 3) are due merely to the diluting effect of the larger proportion of hydrocarbon chain in the esterification reactions which have been studied.

These velocity constants are some ten to twenty times larger than those calculated from Fairclough and Hinshelwood's<sup>10</sup> data for esterification of dilute solutions of various aliphatic

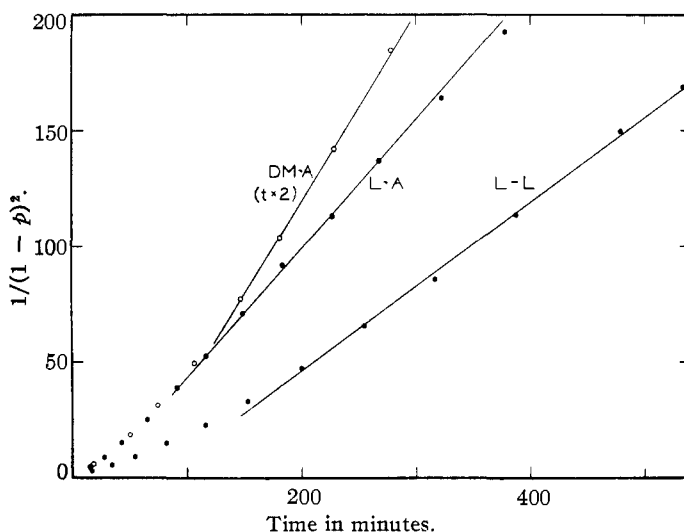


Fig. 3.—Decamethylene glycol-adipic acid (DM-A), lauryl alcohol-adipic acid (L-A), and lauryl alcohol-lauric acid (L-L) reactions at 202°.

acids in ethanol. The energy of activation, 13 kcal., calculated from rates of the diethylene glycol-adipic acid reaction at 166 and at 202°, is slightly less than the value, 15.0 kcal., obtained by these authors for esterifications in ethanol.

TABLE III

VELOCITY CONSTANTS FOR POLYESTERIFICATION AND ESTERIFICATION

Reaction	$k \times 10^{-3}$ at 202° in (equiv./1000 g.) <sup>-2</sup> min. <sup>-1</sup>
$\text{HO}-(\text{CH}_2)_8-\text{O}-(\text{CH}_2)_8-\text{OH} + \text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	0.41
$\text{HO}-(\text{CH}_2)_8-\text{O}-(\text{CH}_2)_8-\text{OH} + \text{H}-(\text{CH}_2)_8-\text{COOH}$	0.35
$\text{HO}-(\text{CH}_2)_8-\text{OH} + \text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	~0.5
$\text{HO}-(\text{CH}_2)_{10}-\text{OH} + \text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	1.63
$\text{H}-(\text{CH}_2)_{12}-\text{OH} + \text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	1.57
$\text{H}-(\text{CH}_2)_{12}-\text{OH} + \text{H}-(\text{CH}_2)_{11}-\text{COOH}$	2.5

Over the portions of the polyesterifications shown in Figs. 2 and 3 the molecular weight increases about fourteen-fold. In this range the viscosity increased from about 0.015 to 0.30 poise,

(10) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 593 (1939).

in the diethylene glycol-adipic acid reaction. In the esterification reactions the viscosity remains practically constant, at about 0.01 poise, except for a probable slight decrease. The polyesterification reaction is unaffected, therefore, by increase in viscosity, as well as by increase in molecular weight, within the range investigated.

Several experiments on the reaction of diethylene glycol with adipic acid catalyzed by a small amount of *p*-toluenesulfonic acid (0.004 mole per mole of glycol) have been carried out at 109°. These should be second order, according to the results of numerous researches<sup>7</sup> on acid catalyzed esterifications. For a second order reaction,  $1/(1 - p)$  increases linearly with time. In striking similarity to the reaction in the absence of added catalyst, the slope of  $1/(1 - p)$  plotted against  $t$  (see Fig. 4) increases at first, but becomes constant later on. Even as far as *DP* 90 no tendency of the slope to decrease, as would occur if reactivity decreased as the average molecular weight increases, has been observed. The viscosity increase accompanying this increase in molecular weight is over two thousand-fold.

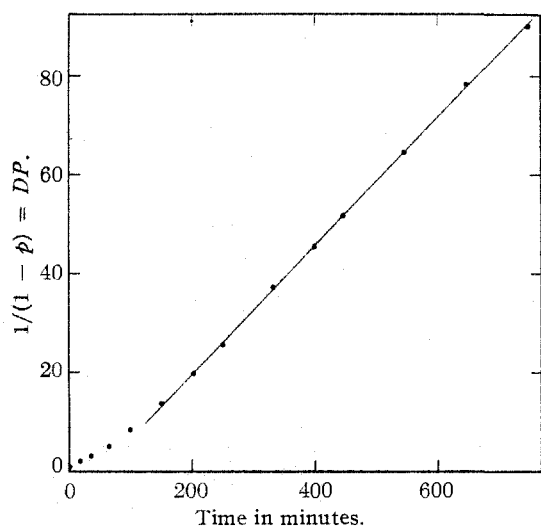


Fig. 4.—Diethylene glycol-adipic acid reaction at 109° catalyzed by 0.4 mole per cent. of *p*-toluenesulfonic acid.

It has been suggested in the past that the rate of polyester formation is governed by the rate at which moisture formed in the reaction escapes from the molten polymer.<sup>11</sup> Recently Schulz<sup>12</sup> has offered a detailed analysis of polyesterification based on the assumption that this is the rate

controlling process. In order to test this assumption, diethylene glycol and adipic acid were heated (without catalyst) at 166° under reduced pressure (about 200 mm.), instead of at atmospheric pressure as in other experiments. More efficient removal of moisture resulting from this reduction in pressure should have brought about an increase in the rate of reaction, if the escape of water were the rate determining step. The data obtained in this experiment are given in Table IV.

TABLE IV  
REACTION OF DIETHYLENE GLYCOL WITH ADIPIC ACID UNDER REDUCED PRESSURE AT 166°

$t$ , n min.	$p$	$t$ interpolated from expts. at 1 atm.
6.5	0.1535	6
23.5	.3947	23
55	.5927	55
84	.6793	84
135	.7633	137
176	.7983	176

That the reaction velocity is not affected by the reduction in pressure is shown in the table by a comparison of time values with those for the same extent of reaction interpolated from the curve in Fig. 1.<sup>13</sup> The rate must be controlled by factors inherent in the mechanism of the reaction, and not by escape of moisture as Schulz has assumed.

Obviously it is necessary to provide adequate means for escape of water formed in the reaction; otherwise the occurrence of the reverse reaction, hydrolysis, would set up an equilibrium and further polymerization would cease. According to the usual practice, which was followed essentially here, a stream of gas bubbled through the polyester is used to provide for escape of water. Only a very gentle gas stream is required to maintain the normal rate, which cannot be exceeded by increasing the rate of bubbling.

The slow rate of advancement of polyesterification when the average molecular weight becomes large, sometimes attributed in the past to a low reactivity of large molecules or to the difficulty of removing moisture, is a consequence of the kinetic order (third) of the reaction. The rate, being proportional to the third power of the concentration of unreacted functional groups, decreases rapidly as the extent of reaction increases.

(13) The experiment at reduced pressure from which the data in Table IV were taken was not extended to large extents of reaction. The excessive loss of glycol under these conditions might have vitiated results at larger extents of reaction.

(11) See, for example, W. H. Carothers, *Chem. Rev.*, **8**, 367 (1931).  
(12) G. V. Schulz, *Z. physik. Chem.*, **A182**, 127 (1938).

Although initially the reaction is rapid, a very long time is required for close approach to complete reaction, which is essential for attainment of high molecular weight.

### Discussion

The failure of the reaction to adhere to the third order equation (3) during the first stages of the reaction is difficult to explain. A part of this deviation can be attributed to the decrease in volume due to loss of water (*i. e.*, to the error arising from the use of (3) rather than (2)). This will not account for the entire deviation, however.

Inasmuch as esterification is catalyzed by hydrogen ions (or hydrogen donors, *i. e.*, acids), it probably is sensitive to the nature of the reaction medium. For example, the change in dielectric constant which occurs as hydroxyl and carboxyl groups are converted to ester may influence the reaction rate. In dilute solutions, which have been used almost exclusively in previous work on esterification, the change in properties of the reaction medium as the esterification progresses is inappreciable. If the process is sensitive to changes in the reaction medium, then in the present experiments deviation from third order may be expected, except at large extents of reaction where one is dealing with a dilute solution of functional groups.

The above discussion has been presented merely as a possible explanation for the peculiar course of the reaction. Whatever the cause of this behavior may be, it is typical of both polyesterification and esterification. The fact of primary importance to this investigation is their similarity, in spite of the high molecular weight and viscosity attained in the former.

Bawn<sup>2,14</sup> has attempted to show, on the basis of the transition state method developed by Eyring<sup>15</sup> for the treatment of reaction velocity from a statistical mechanical point of view, that reactivity should decrease continually as size of the molecule increases. According to the transition state method<sup>15</sup>

$$k = K^* (k'T/h) \quad (4)$$

where  $k$  is the velocity constant,  $k'$  is Boltzmann's constant,  $T$  is the absolute temperature,  $h$  is Planck's constant and  $K^*$  is the constant for the equilibrium between normal molecules and activated complexes.

$$K^* = (F_{ab}^*/F_a F_b) \exp(-E_0/k'T) \quad (5)$$

(14) See also reference 3.

(15) H. Eyring, *J. Chem. Phys.*, **3**, 107, 492 (1935).

where  $(F_{ab}^*/F_a F_b)$  is the ratio of the partition function for the activated complex to the product of the partition functions for the reactants, and  $E_0$  is the activation energy at the absolute zero. Evans and Polanyi<sup>16</sup> have shown that the partition function factor  $F_{ab}^*/F_a F_b$  must be smaller for the recombination of radicals (*e. g.*,  $\text{CH}_3$ ) than for the recombination of atoms (*e. g.*, H). Bawn considers that this decrease in "steric factor" will continue indefinitely as the complexity of the molecule increases. Thus, in the vinyl type of polymerizations, in which a polymer molecule bearing a free radical adds on monomers consecutively, he concludes that the rate should decrease with each successive addition of monomer, the rate finally approaching zero when the polymer molecule becomes very large.

An increase in complexity of one of the reacting molecules modifies both  $F_{ab}^*$  and the product  $F_a F_b$ . Unless the increase in complexity involves modification at a point in the molecule very close to the functional group, both  $F_{ab}^*$  and  $F_a F_b$  will be altered by virtually identical factors for the added degrees of freedom. The structure in the immediate vicinity of the functional group of a polymer molecule is independent of its degree of polymerization. Hence, contrary to Bawn's conclusion, no decrease in rate of polymerization due to a decrease in the partition function factor with increasing length of the molecule should be expected.

Rabinowitch and Wood<sup>6</sup> have shown convincingly that the actual collision rate in the liquid phase is not affected appreciably by changes in viscosity, although the rate of diffusion is materially decreased. Even if the frequency of collision is decreased by low mobility of large polymer molecules, the duration of collisions must be proportionately increased. Hence, the concentration of molecules in the collided state cannot be affected by either molecular size or viscosity. Consequently, the rate of reaction should be independent of these factors.

The same conclusion follows directly from the transition state method, since the activated complex is in thermodynamic equilibrium with the reactants; the concentration of activated complexes will not be affected by changes in mobility, unless the mobility is too low to maintain their equilibrium concentration.

(16) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935). See also C. E. H. Bawn, *ibid.*, **31**, 1536 (1935).

Rabinowitch and Wood<sup>6,17</sup> have pointed out that at sufficiently high viscosities the rate of diffusion will become too slow to maintain the "equilibrium" number of pairs of reactants adjacent to each other in the liquid (*i. e.*, within colliding distance of each other). Diffusion, rather than the passage of molecules through the activated state, becomes the rate controlling step when such viscosities are reached, and the rate will no longer be independent of molecular size and viscosity. For most reactions (those with very low values of  $E_0$  excepted) extremely high viscosities would be required to effect a perceptible decrease in rate.

Some time ago the author published equations<sup>13</sup> for calculating the numbers of molecules of various sizes in a linear condensation polymer. The validity of these equations rested entirely on the postulate, presented at that time without experimental proof, that the functional groups of all molecules, regardless of size, are equally reactive. Dostal<sup>19</sup> objected to the size distribution equations on the grounds that this postulate could not possibly be valid. The present investigation furnishes proof that this postulate is correct. The quantities of molecules of various sizes in a linear condensation polymer can be determined reliably,

(17) See also E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1223 (1937).

(18) P. J. Flory, *This Journal*, **58**, 1877 (1936).

(19) H. Dostal, *Monaish.*, **70**, 324 (1937).

therefore, by simple calculation using the distribution equations referred to above.

### Summary

1. The kinetics of two polyesterifications, diethylene glycol-adipic acid, and decamethylene glycol-adipic acid, have been compared with several non-polymer forming esterifications, diethylene glycol-caproic acid, lauryl alcohol-adipic acid, and lauryl alcohol-lauric acid. Preliminary experimental data on the reaction of diethylene glycol with adipic acid catalyzed by *p*-toluenesulfonic acid have been presented also.

2. As the reactions proceed (in the absence of catalyst) the course followed corresponds to a continuous increase in kinetic order, becoming approximately third order at large extents of reaction.

3. Polyesterification and esterification follow similar courses, from which it has been concluded that reaction rate is not affected by either increase in molecular weight or the concurrent increase in viscosity.

4. This conclusion has been shown to be in agreement with theory, contrary to previous theoretical deductions.

5. The slow rate of polyesterification when the average molecular weight is large is due to the third order character of esterification.

CINCINNATI, OHIO

RECEIVED SEPTEMBER 30, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

## Acetometallates. II. Acetozincate

BY ALEXANDER LEHRMAN AND PHILIP SKELL

It has been shown<sup>2a</sup> that the solubility of metal hydroxides in aqueous solutions of alkali metal hydroxides can best be explained as the formation of hydroxyl complex ions.  $M(OH)_2$ , for example, may dissolve to give  $M(OH)_4^{2-}$ . In the case of zinc, Goudriaan<sup>1</sup> isolated as a solid phase the compound  $Na_2O \cdot ZnO \cdot 4H_2O$  which was formerly thought to be  $Na_2ZnO_2 \cdot 4H_2O$ , but which according to the complex ion hypothesis could also be written as  $Na_2Zn(OH)_4 \cdot 2H_2O$ . More recently, Scholder and co-workers<sup>2</sup> have isolated a mono-

and a disodium zincate in both the anhydrous and hydrated condition. On the basis of the ease of removal of water from these compounds it was concluded by Scholder that they were  $NaZn(OH)_3$  and  $Na_2Zn(OH)_4$ , respectively, and their hydrates, rather than the various hydrates of  $NaHZnO_2$  and  $Na_2ZnO_2$ . Subsequently Brintzinger and Wallach<sup>3</sup> showed from the rate of diffusion of zincate ions through a cellophane membrane that their ionic weight is consistent with the formula  $Zn_2(OH)_8^{4-}$ . More light could be thrown on the question if the system  $NaOH-Zn(OH)_2$  could be shown to be a simple binary system with com-

(1) Goudriaan, *Rec. trav. chim.*, **39**, 505 (1920).

(2) (a) R. Scholder, *Z. angew. Chem.*, **46**, 509 (1933); (b) R. Scholder and H. Weber, *Z. anorg. allgem. Chem.*, **215**, 355 (1933);

(c) R. Scholder and G. Hendrich, *ibid.*, **241**, 76 (1939).

(3) H. Brintzinger and J. Wallach, *Z. angew. Chem.*, **47**, 61 (1934).