
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 62

SEPTEMBER 7, 1940

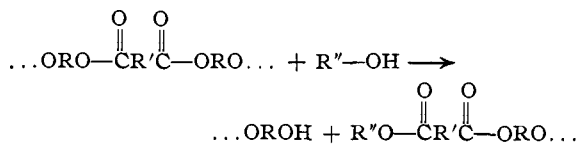
NUMBER 9

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

Kinetics of the Degradation of Polyesters by Alcohols¹

BY PAUL J. FLORY

In a kinetic study of polymer degradation there immediately arises the question whether certain inter-group linkages are preferentially ruptured; *e. g.*, whether rupture is more likely near the end of the chain than near the center. Kuhn, Freudenberg and co-workers² have shown that the degradation of cellulose proceeds essentially by hydrolysis of inter-glucoside linkages at random, except that end linkages react somewhat more rapidly. Results which corroborate this have been obtained by Wolfrom, Sowden and Lassetre³ on methylated cellulose. The author⁴ showed recently that in the synthesis of linear polyesters there is no effect of molecular weight on reactivity, *i. e.*, the reaction proceeds at random. In view of these results it was anticipated that the degradation of polyesters by ester interchange with alcohols



would proceed by random rupture of ester linkages in the polymer. Experiments reported here confirm this expectation.

(1) Presented before the Division of Physical and Inorganic Chemistry at the ninety-ninth meeting of the American Chemical Society, Cincinnati, Ohio, April 10, 1940.

(2) W. Kuhn, *Ber.*, **63**, 1503 (1930); K. Freudenberg, W. Kuhn, W. Durr, F. Bolz and G. Steinbrunn, *ibid.*, **63**, 1510 (1930); K. Freudenberg, *Trans. Faraday Soc.*, **32**, 74 (1936).

(3) M. L. Wolfrom, J. C. Sowden and E. N. Lassetre, *THIS JOURNAL*, **61**, 1072 (1939).

(4) P. J. Flory, *ibid.*, **61**, 3334 (1939).

The unique experimental method which has been devised is perhaps of more interest than the results which have been obtained. Recently it has been shown⁵ that the viscosity of a molten linear polyester is accurately represented as a function of the chain length (*i. e.*, the number of chain atoms in the molecule) by the relationship

$$\log \eta = A + CZ_w^{1/2} \quad (1)$$

where η is the viscosity, A and C are constants and Z_w is the *weight average* chain length defined by

$$Z_w = \sum w_x Z_x \quad (2)$$

where w_x and Z_x are the weight fraction and chain length, respectively, of the species composed of x structural units.⁶ As degradation proceeds, Z_w decreases. By measuring at suitable intervals the viscosity of a mixture of decamethylene adipate polyester and a small amount of decamethylene glycol, or lauryl alcohol, it has been possible to follow the decrease in Z_w with time. By assuming that the ester groups react at random it is possible to relate Z_w to the amount of glycol which has been assimilated by the polymer. The rate of consumption of glycol calculated in this way from the viscosity is in excellent agreement with a first order equation.

This method is well suited to the study of ester interchange, a reaction which evades conventional

(5) P. J. Flory, *ibid.*, **62**, 1057 (1940).

(6) The weight average chain length Z_w is not the average which would be obtained by conventional molecular weight determination methods (*e. g.*, cryoscopic, osmotic or end-group methods). The latter is the *number average* Z_n . See W. D. Lansing and E. O. Kraemer, *J. Phys. Chem.*, **39**, 153 (1935).

methods of analysis. It should be applicable also to a number of other interchange reactions involving polymers. It offers the advantages of unusual simplicity and sensitivity to very small amounts of reaction.

Experimental

Preparation of Polymers.—In order to exclude the possibility of polyesterification during the ester interchange experiments, polymers were prepared by allowing an excess of decamethylene glycol to react with adipic acid at 109° in the presence of a small amount of *p*-toluenesulfonic acid catalyst until the viscosity became constant. Since the resulting polymer had hydroxyl end-groups exclusively, there was no possibility for further esterification. Details of the method of preparation have been described previously.⁵

From viscosities of the polymers, determined at 109° by the method previously described,⁵ weight average chain lengths were calculated from

$$\log \eta_{109^\circ} = -1.435 + 0.1144 Z_w^{1/2} \quad (1')$$

The constants in this relationship have been established for decamethylene adipate polyesters having hydroxyl and carboxyl end-groups in equal numbers. The viscosity certainly is dependent to some extent upon the nature of the end-groups, but results which follow show that this effect is not sufficiently great to invalidate the use of (1'). This is probably the outstanding source of error, however. If a suitable method can be found for determining free hydroxyl in the polyester, it will be possible to evaluate experimentally the proper constants for (1) when applied to hydroxyl end-group polyesters.

Polymer A was prepared by heating adipic acid and decamethylene glycol of high purity,⁵ the latter in about 5.5% excess of the equivalent amount, at 109° in the presence of 0.10 equivalent per cent. of *p*-toluenesulfonic acid. The mixture was heated for a total of forty hours under a pressure of 200 mm.; a slow stream of nitrogen was passed through the polymer to facilitate removal of moisture. Beyond twenty-five hours the viscosity remained constant at 27.5 poises. From (1'), $Z_w = 631$; the ratio ρ^0 of glycol to adipic acid in the final polymer, calculated from Z_w using equation (7') (cf. *seq.*), is 1.0587. According to the amount of excess glycol used in the preparation, ρ^0 should have equalled about 1.055. As will be shown later, the number average chain length Z_n equals $Z_w/2$ to a close approximation. The number average molecular weight M_n is given by $15.80 \times Z_n$. Hence, for polymer A, $M_n \cong 5000$.

Polymer B was prepared without catalyst by heating a 5.5% excess of decamethylene glycol with adipic acid at 202° for fifty-five hours. At the end of this time the viscosity, 29.8 poises at 109°, was increasing very slowly. Further heating at this high temperature seemed inadvisable. From (1), $Z_w = 647$; $M_n = 5150$. A sample dissolved in chloroform yielded a neutral equivalent of 27,800; *i. e.*, the polymer possessed one carboxyl group per 5.5 molecules, or per 190 ester groups. The virtual impossibility of carrying this uncatalyzed reaction to completion is readily understood. Since the esterification process is catalyzed by a second carboxyl group, the rate, which de-

pends upon the *square* of the carboxyl concentration, decreases rapidly as completion of the esterification is approached. In the *p*-toluenesulfonic acid catalyzed reaction the rate depends upon the first power of the carboxyl concentration, and in the presence of an excess of hydroxyl groups practically all of the carboxyl groups may be esterified within a reasonable length of time.

Polymer C was prepared, following the procedure described for polymer A, using a 4.72% excess of the glycol and 0.08 equivalent per cent. of *p*-toluenesulfonic acid. After a total of sixty hours at 109°, the viscosity was 51.9 poises; $Z_w = 758$; $\rho^0 = 1.0486$; $M_n = 6000$. Based on the amount of excess glycol used, $\rho^0 = 1.0472$ and $Z_w = 781$. Although the difference between the calculated and observed quantities is no larger than might be attributed to loss of ingredient during the long time required for preparation, it is believed to be due to the end-group effect on the viscosity. An acid end-group polymer, prepared for use in another investigation, showed the opposite deviation between chain length calculated from viscosity and chain length determined by end-group titration, as would be expected according to this explanation.

The polymers were stored in desiccators after preparation in order to prevent degradation by atmospheric moisture.

Degradation Experiments.—About 3 g. of polymer and from 0.05 to 0.18 g. of decamethylene glycol, or lauryl alcohol, were weighed carefully and placed in a 15-mm. tube. This was sealed to a vertical tube through the upper end of which the viscometer was inserted. A stream of dry nitrogen through the viscometer served to mix polymer and glycol, or alcohol, after melting. Effluent nitrogen passed through an outlet tube near the upper end of the vertical tube. A temperature of 109.0° (± 0.2) was maintained by a toluene vapor-bath.

In some of the experiments *p*-toluenesulfonic acid catalyst was added to that already present in the polymer. An appropriate amount (0.30 to 1.74 cc.) of a 0.0269 *N* solution of catalyst in chloroform was introduced from a pipet into the tube prior to introduction of the polymer and glycol. The chloroform was then removed by evaporation.

At the beginning of an experiment several minutes were required before the reactants were completely melted and mixed together. Consequently, initial time values are uncertain by about \pm three minutes. Viscosities were measured at suitable intervals during the course of the reaction. Since the viscometer was not removed for cleaning between measurements, it was necessary to empty it slowly in order to minimize the drainage error.⁵ Tests showed this error to be seldom greater than 1%, which is not objectionable.

Theoretical Treatment

It has been shown in a previous publication⁷ that polyesters are formed by random esterification of the functional groups. If all of the carboxyl groups are esterified, then r defined by

$$r = \frac{[-\text{OCR}'\text{CO}-]}{[-\text{ORO}-]} \quad (3)$$

represents the probability that any particular

(7) P. J. Flory, *THIS JOURNAL*, **61**, 3334 (1939).

hydroxyl group has been esterified. The probability that any particular molecule selected at random will possess y glycol residues is given by

$$P_y = r^{y-1}(1-r) \quad (4)$$

Obviously P_y is equal to the mole fraction P_x of x -mer, which contains y glycol and $y-1$ adipic acid residues. Since $x = 2y - 1$

$$P_x = r^{(x-1)/2}(1-r) \quad (4')$$

where x is limited to odd integral values.

The chain length of an x -mer molecule is

$$Z_x = zx + \alpha \quad (5)$$

where z is the mean chain length of a glycol and an adipic acid residue ($z = 9$ for decamethylene adipate) and α represents an "end-group correction" equal to the chain length of the glycol molecule minus z . Taking the chain length of the glycol to be twelve atoms, $\alpha = 3$. Making the slight approximation that the molecular weight is proportional to Z_x , the weight fraction of x -mer is given by

$$w_x = (zx + \alpha)P_x / \Sigma(zx + \alpha)P_x \quad (6)$$

Substituting (4), (5), and (6) in equation (2), there is obtained for the weight average chain length

$$Z_w = \frac{\Sigma[z(2y-1) + \alpha]^2 r^{y-1} (1-r)}{\Sigma[z(2y-1) + \alpha] r^{y-1} (1-r)}$$

These summations, as well as those which follow, are over $y = 1$ to ∞ . Since

$$\begin{aligned} \Sigma y^2 r^{y-1} &= (1+r)/(1-r)^3 \\ \Sigma y r^{y-1} &= 1/(1-r)^2 \\ \Sigma r^{y-1} &= 1/(1-r) \end{aligned}$$

the above expression for Z_w becomes

$$Z_w = 2z \left(\frac{1+r}{1-r} \right) \left[\frac{2(1+r) - 2(1-\alpha/z)(1-r) + 1/2(1-\alpha/z)^2(1-r)^2}{(1+r)^2 + (\alpha/z)(1-r)^2} \right] \quad \text{ratio of acid to glycol residues}$$

Series expansion of the expression in brackets gives

$$Z_w = 2z \left(\frac{1+r}{1-r} \right) [1 - (1 - \alpha^2/z^2)(1-r)^2/8r + \dots] \quad (7)$$

In most of the experiments reported here $1-r$ was approximately 0.10, or less, at completion of the degradation. Taking $1-r = 0.10$ and $\alpha = 3$, the second term in the series in (7) equals 1.2×10^{-3} , and higher terms not included here amount to about 2×10^{-5} . To an approximation sufficiently exact for the purposes of the present paper we will take

$$Z_w = 2z(1+r)/(1-r) = 2z(\rho+1)/(\rho-1) \quad (7')$$

where $\rho = 1/r$. Similarly, it may be shown that the number average chain length Z_n , *i. e.*, the

average obtained by conventional molecular weight determination methods and defined by

$$Z_n = \Sigma Z_x P_x$$

is given by

$$Z_n = z(1+r)/(1-r) + \alpha \quad (8)$$

It is interesting to note that whereas the end-group correction α modifies the number average in proportion to the magnitude of α compared to Z_n , the weight average chain length as given by (7) is almost independent of α .

As decamethylene glycol is assimilated by the polymer through ester interchange, Z_w decreases. The manner in which Z_w depends upon the amount of glycol assimilated will be determined by the nature of the distribution of species produced by the degradation. If, for example, there is preferential reaction with ester groups near the chain ends, Z_w will be greater for a given amount of assimilation of glycol than if there is a preference for reaction with ester groups near the middle of the chain.

Let it be postulated that *the ester groups are attacked at random*. At a given stage in the degradation the distribution will be that which results from the random intermolecular esterification during synthesis followed by random degradation. It is at once evident that the resulting distribution is the same as would have been obtained by direct synthesis of the polymer using an excess of glycol equal to that included in the polymer at the given stage of degradation. That is, the distribution at any stage of the degradation may be represented by (4'), where r is the ratio of acid to glycol residues (including that assimilated by ester interchange) in the polymer.⁹ Hence, Z_w at any stage of the degradation is given by (7), provided that the ester groups along the chains are attacked at random as postulated above.

The discussion so far has been confined to the reaction of hydroxyls of the added glycol with ester groups. Hydroxyl groups at the ends of polymer chains also react with ester groups, and by such reactions a given size distribution conceivably could be altered. As will be shown in another paper, such reactions will not disturb the distribution (7) which represents the most

(9) This may be shown more rigorously by letting $1-r^0$ represent the value of $1-r$ prior to degradation, and $1-r'$ = (assimilated glycol)/(total glycol residues) at time t . Upon deriving a distribution function, one finds an expression equivalent to (4) with r replaced by $r'r^0$. From the definitions just given, $r'r^0 = r$ where r is defined as in the text above. Hence the resulting expression is identical with (4).

(8) See equation (30b), THIS JOURNAL, 58, 1877 (1936).

probable state. These inter-polymer interchanges do not alter Z_w and, therefore, may be disregarded in the present investigation. As soon as one or the other of the hydroxyls of a particular glycol molecule has reacted with an ester group, it has delivered its total potential contribution to the degradation and to the decrease in Z_w ; a reaction of the remaining free hydroxyl of this glycol residue is of no consequence.¹⁰ If the postulate of the preceding paragraph is not valid, these remarks will require modification, of course.

The above treatment is equally applicable to degradations by lauryl alcohol; in equation (7') $Z'_w = 2z \left\{ \frac{(\rho + 1)(\rho^\infty + 1) - (1 + \alpha/z)(\rho^\infty - \rho) [2 + \frac{1}{2}(\rho - 1)(1 - \alpha/z)]}{(\rho^\infty + 1)(\rho - 1)} \right\}$ for Z_w it is merely necessary to equate r (or $1/\rho$) to the ratio of adipic acid to glycol plus lauryl alcohol residues.

During the degradation, one measures the viscosity of a mixture of polymer and unassimilated decamethylene glycol (or lauryl alcohol). The viscosity of this mixture is less than the viscosity which the polymer would possess in the absence of the glycol. It will be shown below that (1') can be applied with sufficient accuracy to mixtures containing small amounts of glycol if, in place of Z_w for the polymer alone, one uses the weight average chain length Z'_w for the mixture of polymer plus glycol.

$$Z'_w = (1 - w_g)Z_w + w_g(z + \alpha)$$

where w_g is the weight fraction of unassimilated glycol. Recalling (7')

$$Z'_w = (1 - w_g)2z(\rho + 1)/(\rho - 1) + w_g(z + \alpha) \quad (9)$$

$$w_g = \frac{174.3(\rho^\infty - \rho)}{284.4 + 174.3(\rho^\infty - 1)} \quad (10)$$

where 174.3 is the molecular weight of decamethylene glycol, 284.4 is the molecular weight of one glycol plus one adipic acid residue ($-\text{ORO}-\text{OCR}'\text{CO}-$), and ρ^∞ is the value of ρ when assimilation of glycol is complete.

Values of ρ^∞ have been calculated from the initial weight fraction of added glycol w_g^0 and ρ^0 , using

$$\rho^\infty - \rho^0 = (0.6317 + \rho^0)w_g^0/(1 - w_g^0) \quad (11)$$

(10) Since the reaction of a glycol molecule with the ester group nearest the end of the chain releases another glycol molecule, it might appear that such reactions should not be included as assimilation reactions. However, it must be borne in mind that the initial polymer possesses monomeric glycol in amount given by (4'). One may picture two groups of glycol molecules, those "belonging to the polymer" and unassimilated glycol molecules. The lower the average molecular weight, the greater the amount of monomeric glycol which belongs to the polymer. The glycol released by reaction of unassimilated glycol with ester groups nearest chain ends will be just sufficient to bring about the necessary increase in monomeric glycol demanded by (4). Such reactions, therefore, are properly included as degradation reactions.

which follows from equation (10). Similarly, when lauryl alcohol was added to the polymer ρ^∞ has been calculated from

$$\rho^\infty - \rho^0 = (0.5906 + 0.936 \rho^0)w_a/(1 - w_a^0) \quad (11')$$

In this case ρ^∞ is the ratio of glycol plus lauryl alcohol to adipic acid residues in the mixture.

Instead of the correct expression (10) for w_g , the approximate expression

$$w_g \cong (\rho^\infty - \rho)(z + \alpha)/(\rho^\infty + 1)z \quad (10')$$

has been used in (9) in order to simplify subsequent relationships. Substituting (10') in (9)

Replacement of the quantity in brackets in the numerator of (12) by 2 introduces an error of only 0.1% when $\rho - 1 = 0.05$ and $\rho^\infty - \rho = 0.05$. Making this approximation and rearranging (12)

$$\rho^\infty - \rho = \frac{Z'_w(\rho^\infty - 1) - 2z(\rho^\infty + 1)}{Z'_w - 2z - 4z(1 + \alpha/z)/(\rho^\infty + 1)} \quad (13)$$

by means of which $\rho^\infty - \rho$, a quantity proportional to the concentration of unassimilated glycol, can be calculated from Z'_w .

TABLE I

Expt. no.	3	4
Glycol, g./polymer B, g.	0.0524	0.0271
$\rho^\infty - \rho^0$.0885	.0457
η_{109° at $t = 0$ in poises, by extrapolation	23.8	26.4
Initial Z'_w calcd. from η_{109°	604	623.5
Initial Z'_w calcd. from (11)	612	628.5

In Table I, Z'_w values calculated (using (1')) from the initial viscosities of mixtures of small amounts of decamethylene glycol and polymer are compared with the initial Z'_w 's calculated from (13). In the latter calculation ρ^∞ from equation (11) and $\rho = \rho^0$ have been used. Polymer B, which contained no catalyst, was used in these experiments. Degradation was so slow at 109° that the initial viscosity could be determined accurately by extrapolation (see Fig. 1). As comparison of the last two rows in Table I shows, the observed viscosities, and the Z'_w values calculated from them, are low. Apparently, the decrease in viscosity due to the presence of the glycol is somewhat greater than can be attributed to the decrease in weight average. The discrepancy is not large and it must decrease as the glycol is assimilated. Hence, equation (13) should yield sufficiently accurate values of $\rho^\infty - \rho$ throughout the course of the reaction.

The viscosity method for studying degradations

depends primarily upon equations (1) and (13). Through the use of the former, an empirical relationship, Z'_w can be calculated from the viscosity. As previously stated, this calculation of Z'_w for the hydroxyl terminated polymers from (1'), the constants of which were evaluated for polymers having hydroxyl and carboxyl end-groups in equal numbers, is probably the greatest source of error in the present investigation. Since ρ^0 is determined from the viscosity, and hence is subject to the same source of error, the effect on the final results will be compensated to some extent.

Equation (13) has been derived theoretically from the postulate that the degradation reaction attacks ester groups at random. By means of this equation, the concentration of unassimilated glycol may be calculated from Z'_w . Thus, the progress of the assimilation of the degrading agent, glycol or alcohol, may be followed by viscosity measurements.

Results

On the basis of the results of previous ester interchange investigations¹¹ and in analogy with esterification and ester hydrolysis kinetics, we may write the rate expression

$$-\frac{d[R''OH]}{dt} = \nu k [R''OH][\text{ester}][\text{catalyst}] \quad (14)$$

where $[R''OH]$ represents the molar concentration of *unassimilated* glycol or alcohol, k is the velocity constant, and ν is a factor equal to two when $R''OH$ is a glycol and to one when it is a monohydric alcohol. In this expression there is no differentiation between different ester groups; all are considered equally reactive. $[R''OH]$ is proportional to $\rho^\infty - \rho$. Since the concentrations of ester and catalyst remain unchanged throughout the reaction, the process obviously should be first order with respect to unassimilated $R''OH$; the integrated expression may be written

$$-\ln[(\rho^\infty - \rho)/(\rho^\infty - \rho^0)] = k't \quad (15)$$

where $k' = \nu k[\text{ester}][\text{catalyst}]$.

Typical results from one of the experiments, number 8, are presented in Table II. The lower curve in Fig. 1 has been plotted from the same data. The estimated catalyst (*p*-toluenesulfonic acid) concentration was 0.45×10^{-2} mmol. per g. of mixture (*cf. seq.*). In expt. 3, also

(11) G. B. Kolhatkar, *J. Chem. Soc.*, **107**, 921 (1915); W. A. Waters, *ibid.*, 1014 (1936); Z. H. Patel and H. E. Watson, *J. Indian Inst. Sci.*, **16A**, 55 (1938); B. Dasannacharya, *THIS JOURNAL*, **46**, 1627 (1924).

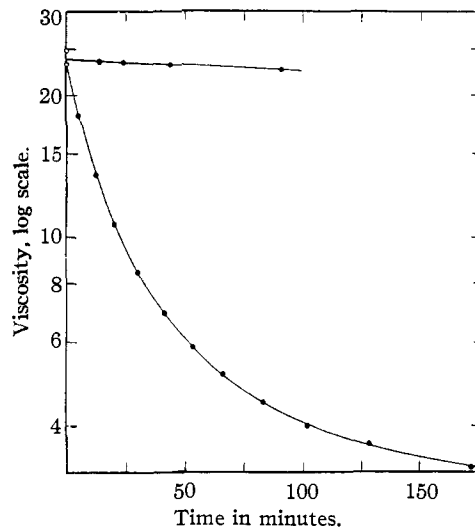


Fig. 1.—Viscosity *vs.* time at 109°: upper curve, in absence of added catalyst (expt. 3); lower curve in presence of *p*-toluenesulfonic acid catalyst (expt. 8). Open circles represent calculated initial values.

shown in Fig. 1 (see Table I), no *p*-toluenesulfonic acid was present. The very slow decrease in viscosity presumably was due to catalysis by the few carboxyl groups, 3.4×10^{-2} mmol./g., present in this polymer (B).

TABLE II

<i>t</i> , min.	η_{1090} , poises	Z'_w	$(\rho^\infty - \rho)/(\rho^\infty - \rho^0)$
5	18.12	554.2	0.935
12	13.56	503.6	.848
20	10.64	463.1	.764
30	8.43	425.8	.672
41	6.90	395.0	.579
53	5.85	370.5	.494
66	5.13	351.6	.420
83	4.47	332.3	.333
102	3.98	316.4	.253
128	3.65	304.8	.188
172	3.26	290.0	.097
253	3.04	281.0	.036
375	2.88	274.2	
500	2.89	274.6	

In Fig. 2 the values of $\log [(\rho^\infty - \rho)/(\rho^\infty - \rho^0)]$ from several experiments are plotted against *t*. In expt. 19 lauryl alcohol was used. In all cases the relationship is linear from 5 to 90% assimilation, in agreement with (15). It should be recalled that both (15) and (13), by means of which $\rho^\infty - \rho$ values have been calculated, rest upon the postulate that all ester groups are equally available for reaction regardless of the molecular weight of the chain molecule or of the location of the ester group within the chain. The results confirm this postulate.

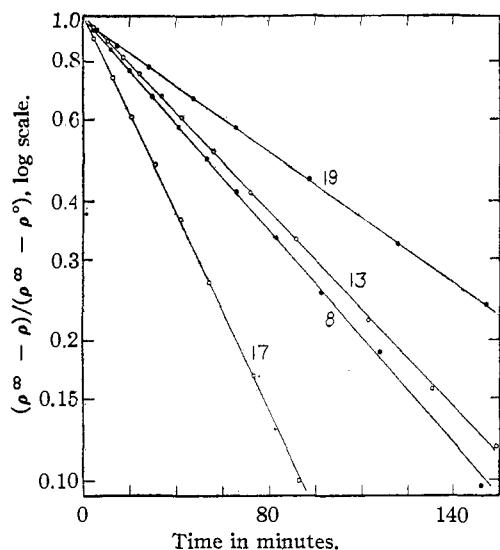


Fig. 2.—Log fraction of decamethylene glycol, or lauryl alcohol (expt. 19), assimilated vs. time at 109°.

Table III presents a summary of results. In the first six experiments listed polymer A was used; polymer C was used in the others. All experiments were carried out at $109.0 \pm 0.2^\circ$. Figures in column two indicate the amount of decamethylene glycol, or lauryl alcohol (expts. 10 and 19), added to the polymers. The amounts of *p*-toluenesulfonic acid added to the polymers are given in the third column. Both polymers A and C were prepared with the aid of the same catalyst, most of which was retained by the polymer. First order velocity constants k' in reciprocal minutes, evaluated graphically from plots such as are shown in Fig. 2, are given in the fourth column.

In the last two columns of Table III, Z_w^∞ calculated from ρ^∞ using equation (7') is compared with Z_w^∞ computed from the limiting constant value of the viscosity at completion of the process. The agreement is gratifying in view of the uncertainties pertaining to the application of (1') to hydroxyl group terminated polymers.

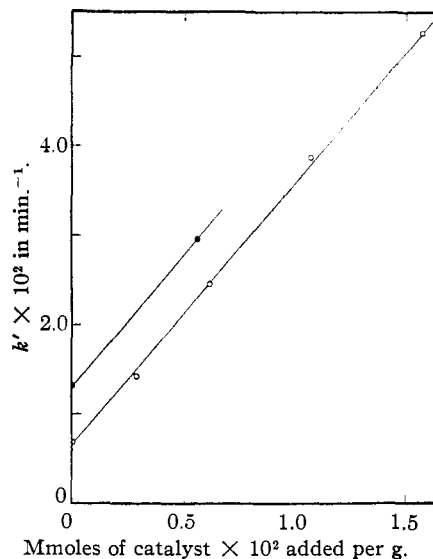


Fig. 3.—Rate of assimilation vs. quantity of catalyst added to polymer. Upper line, polymer A. Lower line, polymer C.

The Effect of Total Hydroxyl Concentration.—Considering the experiments in which no catalyst was added, it is apparent that k' decreases somewhat with increasing total hydroxyl concentration. Perhaps this effect is related in some way to the formation of $-R-OH_2^+$ ions; increasing the

TABLE III

Expt. ^a	$\rho^\infty - \rho^0$	Added catalyst, mmol./g. $\times 10^2$	$k' \times 10^2$, min. ⁻¹	Total catalyst, mmol./g. $\times 10^2$	k , (mmol./g.) ⁻² min. ⁻¹	Z_w^∞ (calcd.)	Z_w^∞ from viscosity
1	0.0469	0	1.51	0.462	0.247	359	
8	.0808	0	1.33	.453	.226	276	274
6	.0907	0	1.32	.451	.227	259	255
7	.0890	0.56	2.97	1.01	.228	262	258
5	.0510	.92	4.20	1.38	.231	347	348
10 (L)	.0570	.70	2.02	1.16	.266	329	324
12	.0440	0	0.815	0.233	.263	407	409
15	.0602	0	.685	.230	.226	349	
13	.1037	0	.615	.225	.212	254	255
16	.0643	0.285	1.42	.515	.209	337	337
17	.0670	.615	2.46	.84	.223	329	
18	.0612	1.07	3.88	1.30	.226	346	
14	.0614	1.57	5.27	1.80	.222	345	342
19 (L)	.0560	0	0.406	0.230	.268	362	362

^a Experiments in which polymers were degraded by lauryl alcohol are indicated by "(L)" after the experiment number in column one. In all other experiments decamethylene glycol was used.

hydroxyl concentration would diminish the hydrogen ion activity and, hence, decrease the rate of the acid catalyzed reaction. It will be noted that velocity constants for the lauryl alcohol reaction are somewhat larger than the others. When one takes into account the lower hydroxyl concentration in these experiments, the rates are found to fall in line with those for the decamethylene glycol reaction.

The Effect of Catalyst Concentration.—In Fig. 3, k' values are plotted against the amount of catalyst added to the polymer. The upper line is drawn through data from expts. 6 and 7 with polymer A; the lower set of results is from expts. 14 to 18, inclusive, with polymer C. In order to avoid effects of varying hydroxyl concentration, in each case experiments are compared in which $\rho^\infty - \rho^0$ was approximately the same. Over the range shown k' appears to be linear with the catalyst concentration, and both lines possess the same slope.¹²

Assuming that the straight lines in Fig. 3 extrapolate to zero *total* catalyst concentration at $k' = 0$, one obtains for the concentration of catalyst in polymers A and C (in the absence of added glycol) 0.475×10^{-2} and 0.239×10^{-2} mmol. per

(12) Proportionality between rate of ester interchange and catalyst concentration was observed by G. B. Kolhatkar and by W. A. Waters, ref. 11.

g., respectively.¹³ Total catalyst concentrations given in column five of Table III have been calculated from these values and the amounts of catalyst added to the mixture (column three). The velocity constants k , given in column six of Table III, have been obtained from k' using the ester and total catalyst concentrations given in the table.

Summary

A method for studying the kinetics of polymer degradations from viscosity measurements has been demonstrated. Results with degradations of decamethylene adipate polyesters by decamethylene glycol and by lauryl alcohol are in excellent agreement with theory based on the postulate that ester groups of the polymer molecules are attacked at random.

The method offers a simple means for studying the kinetics of ester interchange. In agreement with previous work, the rate of the reaction has been found to be proportional to the concentration of acid catalyst. The rate constants decrease somewhat with increasing hydroxyl group concentration.

(13) These values are appreciably less than those calculated from the amounts of catalyst used in preparation of the polymer; the latter values are 0.68×10^{-2} and 0.54×10^{-2} mmol./g., respectively. Apparently much of the catalyst is lost during the rather long time required to carry the preparation reaction to completion.

CINCINNATI, OHIO

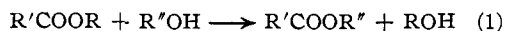
RECEIVED MAY 31, 1940

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

A Comparison of Esterification and Ester Interchange Kinetics

BY PAUL J. FLORY

The similarity between the mechanism of the interchange reaction between an ester and an alcohol



and the mechanism of esterification has been recognized for some time. Kolhatkar¹ pointed out that the rates of alcoholysis of esters and the rates of esterification of acids depend in a parallel manner upon the structure of the reactants. Esterification, hydrolysis and alcoholysis of esters are catalyzed by acids, and the latter two are catalyzed by bases as well. The recent investigation of Roberts and Urey² has shown

(1) G. B. Kolhatkar, *J. Chem. Soc.*, **107**, 921 (1915).

(2) I. Roberts and H. C. Urey, *THIS JOURNAL*, **61**, 2580, 2584 (1939).

that oxygen exchange between benzoic acid and water should be included in this group of similar reactions.

In comparison with esterification and the hydrolysis of esters, the kinetics of ester interchange reactions have received scant attention, which is probably due to the lack of suitable means by which the progress of such reactions can be followed. In the preceding paper³ it has been shown that ester interchange reactions with polyesters can be followed conveniently by viscosity measurements. The present paper presents a comparison of rate constants and activation energies for alcoholysis and for esterification, determined by application of the viscosity method.

(3) P. J. Flory, *ibid.*, **62**, 2255 (1940).