[CONTRIBUTION FROM AMILAN DEPARTMENT, TOYO RAYON COMPANY, NAGOYA]

Studies on Synthetic Polyamides. XVIII.[1]   On Hydrolysis of Polycapramide

BY KOHEI HOSHINO AND MASAMOTO WATANABE

Assuming that the molecular weight distribution of polycapramide is a Flory equilibrium distribution, the hydrolysis mechanism of polycapramide in 50% sulfuric acid was studied by viscosity measurement data using Montroll depolymerization equation. The Staudinger viscosity equation is not applicable to polycapramide, and the Sakurada-Houwink general viscosity equation holds; the following result was obtained: $[\eta] = (M_o/K)^{\frac{1}{a}} \Gamma\left(2 + \frac{1}{a}\right) / [-\ln p \ (1 - \alpha)]^{\frac{1}{a}}$ and the first order velocity constant is

(a) $dB/dt = -\lambda B$

	30°	40°	50°
$\lambda (10^{-4}\,\text{hr.}^{-1})$	4.98	8.15	29.4

(b) $\lambda t = \ln p + A/[\eta]t$

	30°	40°	50°
$\lambda (10^{-4}\,\text{hr.}^{-1})$	4.47	11.28	36.18

Introduction

The theoretical treatment of depolymerization of the linear condensation polymer was solved previously by Montroll and Simha,[2] and in a simpler fashion, by Sakurada and Okamura.[3] Matthes[4] measured the rate of hydrolysis of polycapramide in 40% sulfuric acid at 50°. The degree of polymerization decreases in accordance with a first-order splitting of amide linkage over the entire range investigated from $\bar{x}_n = 220$ to 6. But Montroll and Simha,[2] Sakurada,[3] and Matthes[4] assumed that all bonds connecting monomeric units in the homogeneous system of the same molecular weight have the same probability of being broken regardless of their position in a given polymer in which they are found. Such a homogeneous system is difficult to prepare, so one must often be satisfied with more or less heterogeneous mixtures. Montroll[5] obtained the theoretical equation of depolymerization in a polydisperse system of long chain molecules. We used this Montroll depolymerization equation, and the hydrolysis mechanism of polycapramide in 50% sulfuric acid at 30°, 40° and 50° was studied kinetically. The aim of this paper is to establish the general law of degradation of high polymers in a polydisperse system taking polycapramide as an example.

Experimental and Results

The material for measurement was cold-drawn fiber spun from the melt of polycapramide which had been prepared by polyamidation of ε-caprolactam. Its number-average degree of polymerization was 143. The polymer was fractionated into

(1) K. Hoshino and H. Yumoto, Paper XVII, J. Chem. Soc. Japan, 70, 104 (1949).

(2) E. Montroll and R. Simha, J. Chem. Phys., 8, 721 (1940).

(3) I. Sakurada and S. Okamura, Z. physik. Chem., A187, 289 (1940).

(4) A. Matthes, J. prakt. Chem., 162, 245 (1943).

(5) E. Montroll, THIS JOURNAL, 63, 1215 (1941); Montroll leaves out α and n_{x+1}, at the right side in (13a) and (13b), respectively. And the term of (13a) is $y \le k$.

6 cuts in a phenol-water, two-liquid phase system at 70°.[6] Viscosity of the fractionated materials in 50% sulfuric acid was measured in Ostwald viscometers.

Generally, number-average molecular weight $\bar{M}_n$ and intrinsic viscosity $[\eta]$ are related by the Sakurada-Houwink equation of the form

$$\bar{M}_n = K[\eta]^a \qquad (1)^7$$

where K and α are constants. Data shown in Table I are the results of the viscosity measurement in 50% sulfuric acid.

TABLE I

RESULTS OF THE VISCOSITY MEASUREMENT IN 50% SULFURIC ACID

Sample Fraction	M_n	Intrinsic viscosity in 50% sulfuric acid 30°	40°	50°
1	3,793	0.222	0.307	0.275
2	4,471	.353	.343	.304
3	7,067	.392	.378	.396
4	8,165	.433	.353	.417
5	9,704	.441	.417	.421
6	10,700	.631	. . .	. . .

M_n in Table I were determined from equation $(1)'$ in m-cresol

$$\bar{M}_n = 10,400 \ [\eta]^{1.61} \qquad (1)'\ 6$$

Constants K and α in equation (1) in 50% sulfuric acid were calculated by the least square method from the data shown in Table I. Its result is given in Table II.

As an example of the depolymerization reaction, hydrolysis in 50% sulfuric acid at 30°, 40° and 50° was followed by viscosity measurements. Relative viscosity was measured by Ostwald viscometers

(6) K. Hoshino and M. Watanabe, J. Chem. Soc. Japan, 70, 24 (1949).

(7) The reciprocal of a corresponds to a' in $[\eta] = K'\bar{M}_n^{a'}$. Accordingly it is not surprising that values of a in Table I are greater than unity. An equation of the form of (1) is only generally applicable when the viscosity average molecular weight is employed, but we regard $\bar{M}_n$ equal to $\bar{M}_v$ for sharp fractions.

TABLE II

VALUES OF K AND a IN THE SAKURADA-HOUWINK EQUATION
(1) IN 50% SULFURIC ACID

	30°	40°	50°
K	19,200	22,500	25,800
a	1.10	1.25	1.38

and specific viscosity extrapolated to $c = 0$ from graphs constructed from the formula

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (2)$$

where k is 0.31, 0.33 and 0.34 at 30, 40 and 50°, respectively. The results are shown in Table III.

TABLE III

THE RESULT OF VISCOSITY MEASUREMENTS AND THE DEG-
RADATION CONSTANTS CALCULATED FROM (8) AND (10)

At 30°

t, hr.	$[\eta]$	$1 - \alpha$	$\lambda \times 10^4$
0	0.644	1	...
10	.36	0.9908	9.27
14	.311	.9890	7.88
21	.331	.9877	5.89
27	.296	.9862	5.12
38	.275	.9843	4.17
47	.257	.9824	3.77
53	.246	.9811	3.64
62	.222	.9777	3.62
71	.219	.9772	3.25
83	.197	.9735	3.24
		Average	4.98

At 40°

0	0.597	1	...
5	.392	0.9941	11.90
8	.310	.9887	11.30
20	.245	.9816	9.29
32	.204	.9748	7.96
48	.164	.9636	7.71
56	.151	.9605	7.13
66	.141	.9548	7.00
72	.138	.9532	6.65
80	.131	.9501	6.47
90	.125	.9465	6.09
		Average	8.15

At 50°

0	0.570	1	...
2	.385	0.9931	34.7
4	.310	.9873	31.8
6	.250	.9797	33.9
9	.208	.9718	31.8
13	.174	.9618	29.9
21	.153	.9519	23.4
26	.128	.9365	25.2
29	.121	.9303	24.9
		Average	29.4

Equations on Depolymerizations.—It has been shown from statistical consideration of condensation polymerization that the molecular size distribution in linear condensation polymers containing equal numbers of the two co-reacting functional groups (e.g., NH_2 and $COOH$) is given by[8]

$$N_x = Np^{x-1}(1 - p) \qquad (3)$$

where N_x is the number of molecules composed of

(8) P. J. Flory, THIS JOURNAL, **58**, 1877 (1936).

x monomer units, N is the total number of molecules and p is the extent of reaction, i.e., the fraction of the functional groups which have condensed. Montroll[5] calculated the molecular weight distribution in the case where the bonds of all chains in the mixture at any given time are equally accessible to reaction independent of both their position in a chain and the length of their parent chains. If x is the degree of polymerization before hydrolysis, y is the degree of polymerization after hydrolysis, and α is the degree of depolymerization, the Montroll equation reduces to

$$N_y(\alpha) = N[1 - p(1 - \alpha)]^2[p(1 - \alpha)]^{y-1} \qquad (4)$$

When the Staudinger viscosity equation is generally applicable, viscosity average molecular weight $\overline{M}_v$ is equal to weight average molecular weight $\overline{M}_w$. But if the Sakurada-Houwink general equation (1) is applicable

$$\overline{M}_v = \left(\sum_i N_i M_i^{1+(1/a)} \Big/ \sum_i N_i M_i \right)^a \qquad (5)$$

and

$$[\eta] = (M_0/K)^{1/a} \bar{x}_v^{1/a} \qquad (6)$$
$$M_v = \bar{x}_v M_0$$

therefore

$$[\eta] = (M_0/K)^{1/a}(\Sigma N_x x)^{1+1/a}/(\Sigma N_x x) \qquad (6')$$

The total number of molecules before hydrolysis N is given by $N = \Sigma x N_x$ if the molecular distribution of polycapramide is a Flory equilibrium distribution (3)

$$\Sigma N_x x^{1+\frac{1}{a}} = N(1 - p)^2 \Sigma p^{x-1} x^{1+\frac{1}{a}}$$

$$= N(1 - p)^2 p^{-1} \int_0^\infty x^{1+\frac{1}{a}} e^{-(-\ln p)x} dx$$

$$= N(1 - p)^2 p^{-1} \Gamma\left(2 + \frac{1}{a}\right) \Big/ (-\ln p)^{2+}$$

From (6'), the viscosity before hydrolysis is expressed by the equation

$$[\eta]_0 = (M_0/K)^{\frac{1}{a}} \Gamma\left(2 + \frac{1}{a}\right) \Big/ (-\ln p)^{\frac{1}{a}}$$

Similarly the viscosity after hydrolysis may be expressed by the equation

$$[\eta]^* = (M_0/K)^{\frac{1}{a}} \Gamma\left(2 + \frac{1}{a}\right) \Big/ [-\ln p(1 - \alpha)]^{\frac{1}{a}} \qquad (7)$$

therefore

$$[\eta]^*/[\eta]_0 = [\ln p/\ln p(1 - p)]^{\frac{1}{a}} \qquad (8)$$

As the extent of reaction p is 0.9904, the number of unbroken bonds $(1 - \alpha)$ divided by the total number of bonds in the undegraded system, is calculated by (8). To express the time dependence of α, we shall assume that the rate of depolymerization is proportional to the number of unbroken bonds

$$dB/dt = -\lambda B \qquad (9)$$

where B is the number of unbroken bonds at time t and λ is the degradation constant. Integration of (9) gives

$$\lambda = -\ln(1 - \alpha)/t \qquad (10)$$

The degradation constants calculated from (8) and (10) using the experimental results are given in the 4th column in Table III. These degradation constants are apt to decrease as the hydrolysis
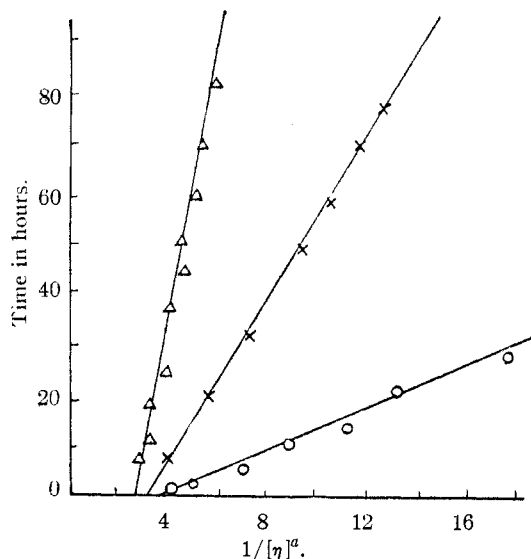
Fig. 1.—Plot of $1/[\eta]^a$ vs. t: $-\triangle-\triangle-\triangle$, 30°; $-X-X-X$, 40°; $-O-O-O$, 50°.

progresses, but they are nearly constant. Moreover if we put in (7)

$$\left[(M_0/K)^{\frac{1}{a}}\ \Gamma\!\left(2 + \frac{1}{a}\right)\right]^a = A \ (\text{a const.}) \qquad (11)$$

and introduce (10), we get

$$\lambda t = A/[\eta]^{*a} + \ln p \qquad (12)$$

This equation should give a straight line by plotting $1/[\eta]^{*a}$ against t. The experimental data for the relation between t and $1/[\eta]^{*a}$, plotted in Fig. 1, show a linear relationship within the experimental error.

The values of A were calculated from (11) by use of the experimental values of K and a. A/λ was calculated from the slope of the straight line in Fig. 1. The values of λ from these relations, as is shown in Table IV, almost agree with the values of λ in the 4th column in Table III.

TABLE IV

Temp., °C.	A	A/λ	$\lambda \times 10^4$
30	0.0115	25.70	4.47
40	.00957	8.50	11.28
50	.00827	2.29	36.18

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL COLLEGE]

Factors Affecting the Rate of Hydrolysis of Ketimines

BY J. B. CULBERTSON

Earlier work on the preparation of ketimines (references 1, 2 and 4) has indicated wide variation in the ease of their hydrolysis to the corresponding ketones. Certain structural relations have appeared to be connected with this variation in rate of hydrolysis. It has been the purpose of this study to investigate some of these structural influences. To this end variously substituted diphenyl ketimine hydrochlorides have been prepared—their rates of hydrolysis, ultraviolet absorption spectra and ionization of the free ketimines as bases determined. Two types of substituent effects have appeared to be established; (1) a tautomerism and/or resonance, and (2) steric hindrance. Two other intramolecular factors suggested from earlier work on ketimines, and analogous compounds, have been considered. They are: (1) the relative negativity of the radicals attached to the carbimino group, and (2) strength of the free ketimines as bases. From the data of this report there is only meager evidence for the operation of any such factors.

This report represents an investigation of the rates of hydrolysis of variously substituted diphenyl ketimines—as hydrochloride salts in dilute aqueous solution—to their corresponding ketones. The general reaction is: $[\text{R-C}(=\text{NH}_2)\text{-R}_1]^+\text{Cl}^- + \text{HOH} \rightarrow \text{R-CO-R}_1 + \text{NH}_4{}^+\text{Cl}^-$.

A number of reports has indicated wide variation in the rate of this hydrolysis with structural differences. The early work of Moureu and Mignonac[1] pointed out that diaryl ketimines were more stable toward hydrolysis than the alkyl aryl ketimines. They were unable to prepare dialkyl ketimines. Later work[2] revealed striking effects of other structural differences.[3] Especially the

work of Hoesch[4] on the preparation of polyhydroxy diphenyl ketones by way of intermediate ketimines has suggested the latter as much more stable toward hydrolysis than the unsubstituted diphenyl ketimine.

To gain some idea of the structural relations involved, measurements have been made on the rates of hydrolysis and ionization constants as bases of a selected group of substituted diphenyl ketimines. Table I lists these data. Large variations in rates of hydrolysis are evident.

Two factors have appeared to play significant roles in affecting this sensitiveness of ketimines toward hydrolysis: (1) a ketimine–enamine tautomerism and/or resonance, (2) steric hindrance (ortho-effect).

(1) The imine-enamine tautomerism has been suggested by the early work of Collie[5] and of Best

(1) C. Moureu and G. Mignonac, Compt. rend., 156, 1801 (1913); 169, 237 (1919); 170, 936 (1920); Ann. Chim., [9] 14, 322 (1920).

(2) P. Bruylants, Bull. sci. acad. roy. Belg., [5] 8, 7 (1922); Bull. soc. chim. Belg., 32, 307 (1923); L. Bary, ibid., 31, 397 (1922); De Boosere, ibid., 32, 26 (1923); R. Breckpot, ibid., 32, 386 (1923); and M. Jaspers, ibid., 34, 182 (1925).

(3) The extraordinarily stable ethyl cyclopropyl ketimine hydrochloride reported by DeBoosere was shown by Cloke to be the isomeric 2-ethylpyrroline salt (J. B. Cloke, THIS JOURNAL, 51, 1174 (1929)).

(4) K. Hoesch, Ber., 48, 1122 (1915); K. Hoesch and T. V. Zarzecki, ibid., 50, 462 (1917).

(5) J. N. Collie, J. Chem. Soc. 71, 299-311 (1897).