Kinetics for Unidirectional Endwise Chain Depolymerizations. Experiments with Amylose in Aqueous Alkaline Solutions*

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Synopsis

A kinetic model for the unidirectional endwise chain-propagated depolymerization of a linear polymer is described in terms of three pseudo-first-order rate constants: k_1 for the unzipping itself; k_2 for termination through the formation of stable endgroups; and k_3 for termination through complete degradation of polymer chains. It is shown that the calculated zip length, $\nu = k_1/(k_2 + k_3)$, will decrease as the initial substrate D.P. is reduced. For the dimer, a maximum value of $\nu = 1$ is expected. During the anaerobic degradation of potato amylose in aqueous alkaline solutions, k_1 decreases and k_2 increases in value as the initial amylose concentration is raised. As a result, quantitative depolymerization occurs at low substrate concentrations, while at raised starch levels an alkali-stable residue is formed. It is proposed that intermolecular association between polymer chains causes these kinetic differences. For amylose, the constants k_1, k_2, and k_3 are approximately related by the ratio 1000:1:1 or 1000:0:1; and for the homologous disaccharide, the ratio is 10:1:10. The relevance of these findings to the kinetics of cellulose decomposition in aqueous alkali is discussed.

INTRODUCTION

The alkaline degradation of 1,4-glucans below 100°C proceeds by a chain-propagated endwise depolymerization (the beta-alkoxycarbonyl elimination reaction, or "peeling" or "unzipping" process), releasing mainly saccharinic acids, and chain termination occurs due to the formation of alkali-stable endgroups (SEG), for example, *meta*-saccharinate residues. The homogeneous degradation kinetics for amylose were studied by Lai and Sarkanen[2] at various alkalinities while preserving a constant ratio between the initial concentrations of amylose and sodium hydroxide. We here describe the effect on the rate constants of varying the amylose concentration at constant pH. In order to account for the experimental findings in cases of complete degradation, it has been useful to modify the original kinetic theory[2] by reinterpreting the nature of the chain termination process.

The anomalous difference noted[2] between zip lengths (degradable chain length) for disaccharides and for amylose is tentatively accounted for on the basis of the observations here reported.

* A preliminary report was presented at the 40th Meeting of the Israel Chemical Society held in Haifa in 1970.[1]

Journal of Applied Polymer Science, Vol. 22, 1151–1158 (1978)

0021-8995/78/0022-1151$1.00

THEORY

The treatment given by Lai and Sarkanen[2] for amylose is here generalized for any linear polymer undergoing unidirectional endwise chain depolymerization, and it is modified so as to account for complete degradation of polymer chains. The original symbols and definitions[2] are retained whenever possible.

Evaluating the Rate Constants for Polymers

Let us consider a linear homopolymer comprising monomer units G with an initial number-average degree of polymerization of $n + 1$ and with a reactive endgroup G_r. The propagation reaction proceeds as follows:

$$(G)_n \cdot G_r \xrightarrow{k_1} (G)_{n-1} \cdot G_r + G_e$$

where G_e is an eliminated G unit. Chain termination may occur both by SEG formation ("chemical termination"),

$$(G)_n \cdot G_r \xrightarrow{k_2} (G)_n \cdot SEG$$

or by complete depolymerization of chains ("physical termination")

$$(G)_n \cdot G_r \xrightarrow{k_3} G_r + nG_e$$

The pseudo-first-order rate constants k_1, k_2, and k_3 are defined as follows:

$$d[G_e]/dt = k_1[G_r] = dL/dt \tag{1}$$

$$d[SEG]/dt = k_2[G_r] \tag{2}$$

$$d[N]/dt = k_3[G_r]$$

where L is the base mole fraction eliminated in propagation after time t, N is the number of completely degraded chains, and the square parentheses indicate mole fractions.

Since $[G_r]$ remains unaffected by the propagation reaction, eq. (1), it is possible also to write

$$-d[G_r]/dt = k_2[G_r] + k_3[G_r] = k_t[G_r]$$

where k_t is the total rate constant for chain termination. Consequently, $k_t = k_2 + k_3$.

As shown by Haas, Hrutfiord, and Sarkanen,[3] the magnitude of k_t may be obtained by determining the fraction of depolymerized substrate, L, as a function of time and using eq. 3:

$$k_t = \frac{\ln [L_\infty/(L_\infty - L)]}{t} \tag{3}$$

where L_∞ is the value of L after infinite reaction time. Furthermore, the propagation constant k_1 may be evaluated[3] by measuring the initial content of reactive endgroups, $[G_r]_0$, and using eq. (4),

$$k_1 = L_\infty \cdot k_t \cdot \frac{1}{[G_r]_0} = L_\infty \cdot k_t \cdot (n + 1) \tag{4}$$

Now, the rate constant for unzipping of entire chains, k_3, is given by relationship (5)*:

$$k_3 = k_1 \cdot n^{-1} \tag{5}$$

Substitution of eq. (4) for k_1 in (5) yields

$$k_3 = L_\infty \cdot k_t \cdot (n + 1)n^{-1} \tag{6}$$

which becomes expression (7) at $n \gg 1$:

$$k_3 = L_\infty \cdot k_t \tag{7}$$

The rate constant for SEG formation, k_2, is evaluated with relationship (8):

$$k_2 = k_t - k_3 \tag{8}$$

Substitution of eq. (6) for k_3 in (8) yields

$$k_2 = k_t[1 - L_\infty(n + 1)n^{-1}] \tag{9}$$

which becomes expression (10) at $n \gg 1$:

$$k_2 = k_t \cdot (1 - L_\infty) \tag{10}$$

In contrast to this result, the original treatment published by Lai and Sarkanen[2] uses the following expression for k_2:

$$k_2 = \ln[L_\infty/(L_\infty - L)]/t \tag{11}$$

Equation (11) yields a finite value for k_2 even when $L_\infty = 1$, i.e., when no SEG is formed and the value of k_2 must be zero! This anomaly is avoided in the present treatment.

It follows from eq. (7) that

$$L_\infty = k_3/k_t = k_3/(k_2 + k_3) \tag{12}$$

Substitution of expression (5) for k_3 in (12) yields, after rearrangement,

$$L_\infty = k_1/(n \cdot k_2 + k_1) \tag{13}$$

Relationship (13) predicts that the fraction of polymer eliminated, L_∞, should decrease when substrates of higher initial D.P. are depolymerized.

* It has been commented that eq. (5), and the subsequent equations derived from it, are incorrect if the rate of termination through complete degradation of polymer chains (k_3) is a time-variable process, being zero during the initial phase of degradation and increasing during the terminal phases of this process, in a manner dependent on the molecular weight distribution. It is therefore necessary to clarify here that our other studies of hydrocelluloses[15] have provided experimental evidence that complete degradation of entire polymer chains in alkali occurs in a rapid chain-propagated depolymerization (rate constant k_3) that is initiated by a rate-limiting scission of the glucosidic linkage at the reducing terminal of the intact polysaccharide molecule. Consequently, the molecular weight remains unaltered during the degradation. For these reasons we have here adopted expression (5) for k_3, which is independent of the time variable. We consider this a valid kinetic framework for treating endwise polysaccharide depolymerizations in alkali.

Rate Constants in the Case of Dimers

When the substrate is a dimer, n has the value of unity. Consequently, eqs. (4), (6), and (9) become respectively eqs. (14)–(16):

$$k_1 = 2L_\infty \cdot k_t \tag{14}$$

$$k_3 = 2L_\infty \cdot k_t \tag{15}$$

$$k_2 = (1 - 2L_\infty)k_t \tag{16}$$

Zip Length

The degradable chain length, or zip length, ν is defined[4,5] by expression (17):

$$\nu = k_1/k_t = k_1/(k_2 + k_3) \tag{17}$$

Substitution of expression (5) for k_3 in this equation and rearrangement yields

$$\nu = [(k_2/k_1) + (1/n)]^{-1} \tag{18}$$

According to (18), ν is determined by the kinetic parameters k_1 and k_2 only when $n > (k_1/k_2)$. However, when $n < (k_1/k_2)$, ν becomes independent of the ratio k_2/k_1 and is determined by the D.P. of the substrate. Therefore, values for the zip length of unidirectional, endwise depolymerizations are of ambiguous significance, since in some cases ν will depend on molecular size while in others, on the ratio of rate constants.

Equation (18) thus requires that the magnitude of ν decrease with decrease in the initial chain length n of the substrate. This result corresponds, of course, to the significance which one intuitively attaches to a concept bearing the name "degradable chain length." However, this conclusion cannot be derived from a kinetic theory for unidirectional, endwise depolymerization that is not based on a clear distinction between k_2 and k_t, as is made above. Thus, Lai and Sarkanen[2] postulated that k_2 and k_t are equivalent. They were accordingly constrained to consider low ν values for cellobiose to be "in profound disagreement with the current (amylose) data, suggesting that projections made on the basis of disaccharide studies are, for some reason, uncertain."

This point is illustrated more strikingly when expression (4) for k_1 is substituted in eq. (17) to yield

$$\nu = L_\infty(n + 1) \tag{19}$$

For the limiting case of the dimer, the maximum value that is permitted for L_∞ is 0.5. Therefore, according to (19), the zip length of a dimer ($n = 1$) has a maximum theoretical magnitude of unity, as is expected by intuitive considerations.

Analogy with Thermal Degradations

It is of interest to note that the kinetic model described above is analogous in many respects to the behavior of[5] poly(methyl methacrylate) and poly(α-methylstyrene) during thermal degradation.

RESULTS

Aqueous alkaline solutions of potato amylose starch fraction were heated under nitrogen at 98°C for 20 hr, and the amount of substrate that had decomposed was estimated spectrometrically using iodine reagent. The extent of degradation was found to depend on the initial amylose concentration (Table I). At the lower polymer concentrations, quantitative depolymerization occurred in media of alkalinity up to 1*N* sodium hydroxide. The fact that no alkali-stable residue remained proved that the original amylose was free of SEG. Thence, two conclusions can be drawn. First, the theoretical eq. (5) (viz., $k_3 = k_1 \cdot n^{-1}$) is indeed valid and applicable to the experimental data obtained. Furthermore, it follows that the alkali-stable residue remaining at higher initial amylose concentrations is due to formation of SEG during the depolymerization, as is required by the theory.

In order to ascertain the nature of the concentration dependence of the reactions involved, the kinetics of amylose degradation were determined at alkalinities of $10^{-4}M$ and $0.1M$. When the substrate concentration is varied, the rate constants for unzipping and for SEG formation (viz., k_1 and k_2) change, as is illustrated in Table II. As the initial amylose level is raised at constant alkalinity, k_1 decreases and k_2 increases in value. Since the pseudo-first-order rate constants are concentration dependent, the reactions are not strictly first order in amylose. This conclusion may necessitate a reevaluation of the kinetic pattern presented for this system by Lai and Sarkanen.[2]

For purposes of comparison, therefore, the rate constants as defined in the theory were also calculated from the experimental data previously reported in

TABLE I
Dependence of Degradation on Amylose Concentration

Sodium hydroxide, *M*	Amylose degraded after 20 hr at 98°C, %			
	0.01%[a]	0.04%	0.2%	0.5%
0.02	—	100	—	—
0.1	—	100	68	52
0.3	100	—	88	76
0.5	100	100	90	80
1.0	100	78	80	54

[a] Initial amylose concentration.

TABLE II
Kinetics of Alkaline Degradation of Amylose at 98°C

Sodium hydroxide, *M*	Amylose		L_∞	k_t, hr^{-1}	k_1, hr^{-1}	k_2, hr^{-1}	k_3, hr^{-1}
	%	$M \times 10^6$					
10^{-4}	0.04	2.4	1.0	0.10	105	0	0.10
10^{-4}	1.0	59	0.46	0.070[a]	34	0.038	0.032
10^{-1}	0.04	2.4	1.0	0.40	420	0	0.40
10^{-1}	0.2	12	1.0	0.28	294	0	0.28
10^{-1}	0.5	29	0.51	0.51[b]	272	0.25	0.26

[a] Yellowing data gave $k_t = 0.058\ hr^{-1}$.
[b] Yellowing data gave $k_t = 0.46\ hr^{-1}$.

studies of amylose,[2] maltose,[6] and cellobiose[6] (see Tables III and IV). (The data of Lindberg, Theander and Uddegard[7] on cellobiose degradation in 20m*M* sodium hydroxide turned out to be in error in their later studies (private communication to K. V. Sarkanen). Consequently, they have been omitted from Table IV.)

Considering Tables II and III together, it appears that in the case of amylose, values for the rate constants k_1, k_2, and k_3 are respectively interrelated by a ratio of the orders of magnitude 1000:1:1 or 1000:0:1. For maltose, however, the ratio k_1:k_2 is of the order of 10:1 (Table IV). Despite an a priori independence of D.P., the ratio k_1:k_2 is thus much smaller for the disaccharide than for the polymer. This difference is due to the comparatively low k_1 values found for maltose and cellobiose, which, by analogy with the amylose data (Table I), may be tentatively ascribed to the relatively high concentrations of disaccharide in the systems that have been hitherto examined.

TABLE III
Kinetics of Alkaline Degradation of Amylose[a]

Temperature, °C	Sodium hydroxide, *M*	Amylose,[b] *M*	L_∞	k_t, hr^{-1}	k_1, hr^{-1}	k_2, hr^{-1}	k_3, hr^{-1}
56	1.25	1.1×10^{-4}	0.21	0.035	8.5	0.028	0.0073
78	1.25	1.1×10^{-4}	0.25	0.23	66	0.17	0.058
87	1.25	1.1×10^{-4}	0.28	0.58	186	0.42	0.16
100	10^{-3}	10^{-7}	1.0	0.14	166	0	0.14
100	10^{-2}	10^{-6}	1.0	0.27	310	0	0.27
100	10^{-1}	10^{-5}	1.0	0.35	403	0	0.35
100	0.33	3.5×10^{-5}	0.82	0.42	397	0.076	0.34
100	0.5	5.4×10^{-5}	0.53	0.61	373	0.29	0.32
100	1.0	1.1×10^{-4}	0.45	0.81	420	0.45	0.36
100	1.25	1.1×10^{-4}	0.32	1.0	372	0.69	0.32
100	1.66	1.8×10^{-4}	0.40	0.92	427	0.55	0.37
100	5.0	5.35×10^{-4}	0.40	0.92	427	0.55	0.37
118	1.25	1.1×10^{-4}	0.35	3.68	1487	2.39	1.29

[a] Calculated from experimental data in reference 2.
[b] D.P. 1154 ($[\eta]$ = 1.56 dl/g).

TABLE IV
Degradation Kinetics for Disaccharides (0.7m*M*) in 5m*M* Sodium Hydroxide at 74°C[a]

	Maltose	Cellobiose
L_∞	0.48	0.50
k_t,[b] hr^{-1}	3.4 ± 0.0	2.5 ± 0.1
k_1, hr^{-1}	3.2	2.5
k_2, hr^{-1}	0.13	0.03

[a] Values in table are calculated from the experimental data in reference 6.
[b] Calculated by least-squares method, with standard error.

DISCUSSION

As the concentration of amylose in dilute aqueous solutions is increased, intermolecular entanglement occurs between polymer chains. This conclusion follows, inter alia, from the theoretical explanation given[8] for the positive dependence[9] of the viscosity number on amylose concentration. Molecular aggregation of this kind will tend to reduce the entropy (freedom of motion) of the individual chain and of the activated complex to a similar level.[10] If the entropy of activation is as a result more negative at a higher amylose concentration, the reaction rate for unzipping will then be slower.[11] In other words, k_1 decreases in magnitude owing to molecular immobilization.

This study is pertinent to the treatment of data obtained for the heterogeneous degradation of celluloses in alkali. First, the kinetic model adopted in the case of cellulose should take into account the possibility of complete dissolution of individual molecular chains by the peeling process. Second, SEG formation is expected to occur on cellulose in those mildly alkaline media in which amylose exhibits a finite value for k_2 at elevated substrate concentrations (Table II). Indeed, one would expect that effects accompanying intermolecular association, which are here invoked in order to rationalize the behavior of amylose at high concentrations, may be enhanced in the case of solid cellulose fibers in aqueous suspension leading to a lower value of the ratio k_1:k_2 than in the case of a dissolved substrate.

EXPERIMENTAL

Potato amylose starch fraction was the product of AVEBE, Holland, with a limiting viscosity number of 1.42 dl/g (D.P. 1050) in 1*N* potassium hydroxide and a Blue Value[12] of 1.35. Amylose was dissolved in aqueous sodium hydroxide (0.5 or 1.0*N*) under Matheson prepurified nitrogen with magnetic stirring and diluted to obtain the required concentration. The $10^{-4}M$ alkalinity was a buffer (pH 9.85) prepared by adding aqueous sodium hydrogen carbonate (5%, four volumes) to a 5% solution of amylose in sodium hydroxide (1*N*, one volume). After spurging with the inert gas, aliquots (5–6 ml) were sealed in 20-ml test tubes and immersed in a boiling water both (98°C) for the required time interval.

After rapid cooling, the yellowing absorbance[13] of the solution (A) was measured at 288 nm, and the undegraded amylose was estimated with iodine reagent,[12] using a Perkin-Elmer 450 spectrophotometer.

The values for k_t were calculated graphically from the Blue Value data, according to eq. (3). L_∞ values were chosen[2] so as to give the most rectilinear plots. Some runs were also monitored by yellowing,[13] in which case k_t was obtained using eq. (20), which is equivalent to relationship (3):

$$k_t = \ln[A_\infty/(A_\infty - A)]/t \tag{20}$$

The D.P. of amylose was calculated from the limiting viscosity number in accordance with the equation[14]

$$\text{D.P.} = 7.4[\eta]$$

The authors gratefully appreciate the interest and encouragement given by the Director of the Institute, Professor M. Lewin. Dr. A. Knoll is thanked for his cooperation in computing the least-squares statistics of the disaccharide data.

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Received October 5, 1976
Revised February 4, 1977