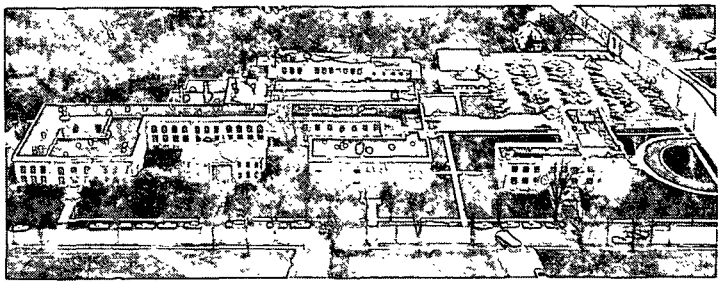

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THE EFFECTS OF OXYGEN AND ANTHRAQUINONE ON THE ALKALINE DEPOLYMERIZATION OF AMYLOSE*+

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The influence of oxygen and anthraquinone on the alkaline (1.0M NaOH) degradation of amylose was investigated at 80° and 100°. Yields and molecular weight distributions (MWD) were determined as functions of reaction time. In the absence of oxygen, extensive end-wise depolymerization (peeling) occurred, with levelling-off yields of 55 and 35%, respectively, at 80° and 100°. This corresponded to peeling lengths of 290 and 400 glucose units, indicating that the stabilization reaction (stopping) is relatively more important at the lower temperature. During the reaction, the amylose MWD continually shifted toward lower values until the levelling-off yield was reached. Thus, the "single-chain" theory of degradation is not valid. Oxygen induced random cleavage of the polymer chain, but enhanced a stopping reaction so that the average peeling length was estimated to be only 20-30 glucose units at 100°. Similarly, addition of 5% anthraquinone (w/w, amylose basis) drastically reduced peeling losses, but caused severe random cleavage of the amylose.

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Zusammenfassung

Der Einfluß von Sauerstoff und Anthrachinon auf den alkalischen (1.0 m NaOH) Abbau von Amylose wurde bei 80° und 100° untersucht. Ausbeuten und Molekulargewichtsverteilung wurden als Funktion der Reaktionszeit bestimmt. In Abwesenheit von Sauerstoff trat eine starke, an den Endgruppen ansetzende, stufenweise Abbaureaktion mit Ausbeutegrenzwerten von 55% bei 80° und 35% bei 100° ein. Das entsprach einem stufenweisen Abbau von 290 beziehungsweise 400 Glucoseeinheiten und deutet darauf hin, daß die Stabilisierungsreaktion bei niedrigerer Temperatur relativ mehr Bedeutung hat. Während der Reaktion zeigte die Molekulargewichtsverteilung der Amylose einen kontinuierlichen Trend zu niedereren Werten bis die Grenzausbeute erreicht war. Deshalb ist die Einzelketten-Abbautheorie nicht zutreffend. Die Gegenwart von Sauerstoff löste statistisch ungeordnete Polymerkettenspaltung aus, begünstigte aber die Stabilisierungsreaktion, sodaß die mittleren Verluste durch stufenweisen Abbau bei 100° mit nur 20 bis 30 Glucoseeinheiten abgeschätzt wurden. Ähnlich verringerte die Zugabe von 5% Anthrachinon (Gew./Gew. Amylose) die Verluste durch stufenweisen Abbau drastisch, verstärkte jedoch die statistisch ungeordnete Kettenspaltung der Amylose.

INTRODUCTION

It is commonly agreed that polysaccharides depolymerize in alkali by step-wise "peeling" of monomers from the reducing end, and by random internal chain cleavage. A simultaneous, competing mechanism ("stopping") stabilizes the reducing end against further peeling. The relative importance of these reactions depends not only on alkali concentration and temperature, but also on the presence of other reactants. These concepts have been thoroughly reviewed by Meller[1] and more recently by Sjöström[2].

All details of the mechanisms of these reactions are not known. Recent studies[3-5] have resulted in new hypotheses, such as the inaccessibility mechanism for "physical stopping"[3] and the single chain theory of degradation.[5] Areas of conflicting evidence remain and call for continued efforts to evaluate the validity of the classical theory and its more recent modifications.

In addition to this fundamental interest, these reactions also have great economic importance. A thorough understanding of the basic chemistry involved is essential in the optimization of new industrial processes. Innovations such as oxygen bleaching and anthraquinone-catalyzed pulping encourage further research on the behavior of cellulose and related polysaccharides in alkaline environments.

In this study, the effects of molecular oxygen and anthraquinone (AQ) on the alkaline depolymerization of amylose were investigated. Amylose was chosen as the substrate because it is alkali-soluble. Thus, the extent of degradation would be attributable only to chemical reactions and not be influenced by physical factors such as swelling and crystallinity.

EXPERIMENTAL

Materials

Potato amylose (Aldrich Chemical Co.) was fractionated to remove impurities and the shorter polysaccharide molecules. The material was dissolved in dimethylsulfoxide (5% amylose w/v) and filtered through a glass filter. Ethanol was used to fractionally precipitate the amylose from the filtrate.[6,7] Traces of solvents were removed from the amylose by Soxhlet extraction with anhydrous ether and by vacuum drying. ^{13}C-Nmr spectra of the purified amylose were essentially identical with amylose spectra in the literature.[8] Exclusion chromatography showed that the amylose molecular weight distribution was nearly symmetrical and bell-shaped (Fig. 1, graph X). The number- and weight-average degrees of polymerization (DP) were estimated to be 630 and 2220, respectively.[9]

[Figure 1 here]

Traces of metal impurities were removed from the sodium hydroxide by extraction with phenyl-2-pyridyl ketoxime.[10]

Water used in the reactions was triply distilled.[11]

Degradation Procedures

Amylose degradations were performed in a Teflon-lined steel reactor equipped with a magnetic stirrer, a chromel-constantan thermocouple probe, and an air-tight Teflon capsule attached to the gas pressurization port. The reagents were prepared and placed in the reactor under a nitrogen atmosphere. The amylose (1% w/v, alkali basis) was held in the Teflon capsule until the 1.0M NaOH solution had reached the desired temperature. Pressurization of the reactor [total pressure ca. 165 psia (1.14 MPa)]

released the amylose into the alkali to start the reaction. Details about the reactor design and operation can be found elsewhere.[9] Anaerobic, alkaline degradation conditions were created by pressurizing the reactor with nitrogen. The reactor was pressurized with oxygen for oxygen-alkali reactions. Anthraquinone (5% w/w, amylose basis), when used, was added to the alkali in the reactor.

The reactions were monitored for up to 20 hours, but the main part of the degradation occurred during the first 5-7 hours. Most samples were taken during this early reaction period. Samples were withdrawn through a Teflon sampling line which had a cooling coil in an ice bath for primary quenching and were neutralized with 2.2M hydrochloric acid. Samples used for amylose yield measurements (1.0 mL) were acidified further (HCl) for hydrolysis. Samples taken to recover the partially degraded amylose (15-20 mL) were neutralized and poured into ethanol (150-200 mL) to precipitate the polymer. To prevent hornification upon drying, the precipitated amylose was washed with absolute ethanol and anhydrous ether, and then dried under vacuum.

Analytical Methods

Yield

The concentration of amylose in solution was measured as glucose after total hydrolysis in 0.6M HCl at about 120°. The concentration of glucose was determined by an enzymatic method (Method 15-UV, Sigma Chemical Co.). Spectrophotometric measurements were made on a Perkin Elmer 576 ST instrument. This method was considerably more rapid and at least as accurate as alternative procedures to measure amylose concentration.[9]

Molecular Weight Distribution

Percarbanilates of amylose samples (100-200 mg) were prepared using phenyl isocyanate (18 mL) in anhydrous pyridine (90 mL) by a procedure adapted from Schroeder et al.[12] Tetrahydrofuran solutions of the carbanilates (0.25% w/v) with an internal reference, methyl N-phenylcarbamate, were analyzed on Styragel columns (Waters Associates) having nominal permeability ranges of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} cm, and capable of resolving polymers in the molecular weight range of 1×10^3 to $> 2 \times 10^7$. Freshly prepared tetrahydrofuran[13] was used as the elution solvent at a flow rate of 2.0 cm^3/min. The spectrophotometric detector was operated at 235 nm.

The Styragel columns were calibrated by the universal technique[14,15] using eleven "monodisperse" polystyrene standards with molecular weights from 2.1×10^3 to 3.6×10^6. Mark-Houwink constants, K and α, used in the calibration were 9.06×10^{-4} cm^3 g^{-1} and 0.92, respectively, for amylose tricarbanilate in dioxane[16], since data for tetrahydrofuran is not available, and 1.8×10^{-2} cm^3 g^{-1} and 0.74, respectively, for polystyrene.[17] The chromatograms were evaluated numerically by computer[9,12], providing number-, viscosity-, and weight-average DP values and plots of normalized molecular weight distributions.

RESULTS AND DISCUSSION

Degradation in Alkali

Several investigations of the degradation of amylose in oxygen-free alkali are described in the literature.[4,5,18,20,21] Similar reactions from this study are summarized in Fig. 2 (A and B). For reactions at 80° and 100°, the yield losses levelled off at ca. 45 and 65%, respectively,

after a few hours reaction time. The residual $\overline{DP}_n$, i.e., the number-average degree of polymerization of the partially degraded amylose expressed as a percentage of the original $\overline{DP}_n$, decreased at approximately the same rate as the yield. This indicates that random alkaline cleavage of the amylose chains was not important under anaerobic conditions at these temperatures.

[Figure 2 here]

Representative molecular weight distributions of the alkaline reaction at 80° are shown in Fig. 1. A significant shift in the molecular weight distribution toward lower values occurred during the first hours of the reaction. Only a minor shift occurred in the distribution after the levelling-off yield was reached. This is consistent with the classical theory of polysaccharide degradation,[1,2] which predicts that at some point the 3-deoxy-hexonic (metasaccharinic) or 2-C-methyl-glyceric acid end groups,[2] will form, thereby terminating the peeling reaction.

The Effect of Temperature on the Stopping Reaction

When amylose degraded only by the peeling reaction, the average number of glucose monomers lost per amylose molecule (peeling length) could be calculated as the product of the levelling-off yield and the original $\overline{DP}_n$. The peeling lengths were 290 and 400 units at 80 and 100°, respectively. Thus, the stopping reaction is relatively more important at lower temperatures. Reanalysis of data from an earlier study,[18] is consistent with this finding.

The levelling-off yield losses were significantly larger than those reported by Lai for amylose.[18] The difference, which was larger at 100° than at 80°, can reasonably be attributed to the manner in which the

reactions were conducted. In the earlier study,[18] the amylose was dissolved in the alkali at room temperature and the solution was heated to the reaction temperature. Since the heat-up period was short relative to the total degradation time, it was assumed that reactions taking place prior to reaching the reaction temperature were negligible. In this study the alkali and amylose were not mixed until the desired temperature was reached. Since the stopping reaction is relatively more important at lower temperatures, proportionately more end-group stabilization would take place during the heating-up period than at the higher reaction temperature. Consequently, the yield loss would be smaller if the reactants were mixed before the reaction temperature was reached.

The negative temperature dependence of the amylose stopping reaction (relative to the peeling reaction) conflicts with a report that the relative temperature effect for the chemical stopping reaction in the alkaline degradation of hydrocellulose is positive.[3] This contradiction cannot be resolved at this time, but the conclusion from the hydrocellulose study, based on a kinetic model assuming both physical and chemical stopping reactions, has been criticized.[19]

The Single Chain Theory

Measurement of the molecular weight distribution of the amylose as the degradations progressed allowed a direct test of the validity of the single chain theory of degradation, which was developed by Ziderman and Bel-Ayche[5,21,22] as an extension of the kinetic model of Lai and Sarkanen.[4,18]

According to this theory ionization and elimination of the initial reducing end glucose unit would be slow and rate determining, while the peeling of subsequent glucose units would be extremely fast (ca. 10^3 times faster). Thus, once peeling was initiated, it would proceed through the entire molecule ("total unzipping"). Amylose chains would either remain unaffected or be completely converted to acid degradation products. A corollary of the theory is that during alkaline degradation of amylose the molecular weight distribution of the residual polysaccharide would remain unchanged.

Different modes of alkaline degradation of polysaccharides can be identified by plotting the yield versus residual $\overline{DP}_n$ (Fig. 3A). Depolymerizations from peeling, random chain cleavage, or the single chain mechanism would fall in areas which are clearly separated from each other. Analyses of reactions from this study are shown in Fig. 3B. The anaerobic reactions designated N-80 and N-100 are consistent with classical peeling-type degradation, but not with the single chain theory. This, in conjunction with the continuous shift in the amylose molecular weight distribution toward lower values (Fig. 1), leads to the conclusion that the single chain theory is not a viable description of alkaline degradation of amylose.

[Figure 3A and 3B here]

However, low DP polysaccharides could potentially degrade in a way resembling the single chain theory. The classical peeling reaction would approach the single chain theory if the original $\overline{DP}_n$ ($\overline{DP}_{n,o}$) of the polysaccharide was of the same order as the peeling chain length. The first

hypothesis about single chain-type depolymerization[22] was based on alkaline degradation of an amylo-dextrin of DP 130.

Degradation in Oxygen-Alkali

Figures 2C and 2D show the yield and residual $\overline{DP}_n$ for amylose reactions in oxygen-alkali at 80° and 100°. The yield losses were much smaller than for the reactions under nitrogen atmosphere. In fact, at 80° there was no significant loss of amylose for 5 hours (Fig. 2C). This was not, however, an induction period, such as those often encountered in oxygen-alkali systems,[23] since the $\overline{DP}_n$ dropped continuously from the start of the reaction. The oxygen-alkali degradations designated 0-80 and 0-100 are plotted in Fig. 3B. Their position relative to the anaerobic, alkaline reactions (N-80 and N-100) and to the characteristic areas of Fig. 3A shows how oxygen enhances the stabilization of reducing end groups and also brings about significant internal chain cleavage. Thus, the behavior of amylose parallels that of cellulosic pulps during oxygen delignification; i.e., relatively high yield but low viscosity and strength.

Estimation of Peeling Length

Figures 2C, 2D, and 3B show that at 100° in oxygen-alkali both peeling and chain cleavage contribute to the depolymerization, while at 80° only chain cleavage is important. This presents a possibility to estimate the average chain length lost via peeling at 100°.

The rate constant for chain cleavage at 80° was calculated according to Equation (1), which is applicable to exclusive random chain cleavage depolymerization.[24,25]

$$1/\overline{DP}_{n,t} - 1/\overline{DP}_{n,o} = k_{cc} * t \qquad (1)$$

By plotting the inverse of experimentally determined $\overline{DP}_n$ values versus reaction time (Fig. 4, Table 1), the rate constant for chain cleavage at 80° was calculated to be 6.08×10^{-8} s^{-1} (Fig. 4, line CC80). McCloskey[26] estimated the activation energy for glycosidic bond cleavage in oxygen-alkali to be 21 kcal mol^{-1} under conditions similar to those used in this work. This activation energy was used to estimate that the rate of amylose chain cleavage at 100° was 5.0 times faster than at 80°, corresponding to a rate constant of 30.4×10^{-8} s^{-1} (Fig. 4, line CC100). The experimentally determined $\overline{DP}_n$ values for degradation at 100° (Table 1) are plotted with their linear approximation (line T100) in Fig. 4. The actual $\overline{DP}_n$ values were significantly lower than predicted solely on the basis of chain cleavage. This difference represents the peeling contribution to the depolymerization and can be interpreted as the average length of each chain lost via peeling. The peeling length was 20-30 monomer units (Table 1), which is only 5-10% of the peeling length in anaerobic alkali. Such a relatively short peeling length is consistent with the small yield loss in the oxygen-alkali reactions (Fig. 2A and 2B) and agrees also with the estimate of Malinen and Sjöström[27] that the peeling length for hydrocellulose at 120° in oxygen-alkali is of the order of 10-50 glucose units. The agreement between reactions of amylose and hydrocellulose suggests that physical structure may have a subordinate influence on the degradation rate of the polysaccharide, and supports the assumption[28] that differences in degradation between α- and β-linked saccharides in oxygen-alkali systems are small.

[Figure 4 and Table 1 here]

Oxidation of Internal Glucose Monomers

Based on their studies of degradations of monomeric glucosides in oxygen-alkali, Ericsson et al.[29] and Malinen and Sjöström[28] have proposed dicarboxylic acid and carboxy-furanoside structures as potential products of oxygen-alkali reactions of polysaccharides. The presence of such groups in oxygen-alkali treated polyglucans has, however, not been verified. In this study, amylose recovered after extensive degradation was analyzed by ^{13}C-nmr and gave a spectrum practically identical with that of the starting material and of the amylose spectra in the literature.[8] However, signals for the reducing end group carbon atoms of an amylose with $\overline{DP}_n$ of 18 were barely distinguishable, indicating that functions appearing less frequently than on approximately every 20th glucose unit could not be expected to be seen in the spectrum.

Nevertheless, peripheral evidence indicated that oxidative modifications of the amylose were occurring. Under anaerobic conditions, the amylose concentration in the liquor, as determined from the absorbance of the amylose-iodine complex,[4] agreed with the primary determination by enzymatic assay of glucose after total hydrolysis. In the case of degradation under oxygen at 100°, however, the iodine analysis gave a much lower value, and the discrepancy increased with reaction time. The error is not primarily due to the oxygen-induced DP reduction, since amylose yields at similar DP levels in anaerobic cooks were accurately determined by the iodine complexing method. Similar observations about the influence of molecular oxygen during the alkaline degradation on the iodine binding capacity of the reacted amylose were made by Hollo, Szejtli and Laszlo,[20] but they did not speculate about possible causes.

The blue amylose-iodine complex is characterized as a regular, helical structure[30] in which polyiodide ions (I_5^-)[31] are captured inside the helices. The formation of the complex depends on the DP of the amylose. The iodine-binding capacity of amylose is essentially the same for all DP values greater than 100, but below that it decreases rapidly with DP and is nil for amyloses of DP less than 30.[32] Thus, one possible explanation for the comparatively low complexing tendency of oxygen-alkali degraded amylose is that molecular oxygen introduces disruptions in the polysaccharide chain by forming dicarboxylic acid or carboxyfuranoid moieties from anhydroglucose units. The oxidized groups would alter the flexibility of the amylose chain, which in turn would prevent long range order in the helices. The amylose complex is envisioned as normally existing as a deformed helix (i.e., a wormlike coil),[32] while the disruptions introduced by the oxygen in alkali in essence would transform the complex to the structure of the interrupted helix model.[32] The effective DP, i.e., the distance between such kinks of altered chain stiffness, might well be as low as 30, when no complex would form, while the true DP of the oxidized amylose could be of the order of 300-500. The number of oxidized internal glucose units would be small compared to the number of normal monomers, which would explain why it was not possible to find spectrometric evidence for their presence.

Degradation in Alkali with Anthraquinone (AQ)

The effectiveness with which AQ and related compounds catalyze alkaline pulping of wood is well documented.[33-35] The rates of delignification and carbohydrate stabilization are accelerated relative to

AQ-free conditions. It is frequently assumed that AQ provides this increased selectivity by creating a redox system in which AQ is reduced to anthrahydroquinone (AHQ) by carbohydrate end group oxidation, and then AHQ is reoxidized to AQ during lignin fragmentation.

Studies of alkaline degradation of carbohydrate model compounds in the presence of AQ have been inconclusive in their attempts to clarify the details of the reaction mechanism. Cotton cellulose was reported to be stabilized by AQ,[36] while hydrocellulose under the same conditions was not.[36] Cellobiose was not stabilized by AQ (or its soluble sulfonate) in anaerobic alkali[37,38] but with oxygen in alkali, AQ caused very effective stabilization.[37] In contrast, AQ had no beneficial effects upon oxygen-alkali treatment of pulp[39] or wood meal.[40]

Pulps derived from soda-AQ cooks often have slightly lower viscosities than AQ-free reference pulps.[38,41] This has been attributed to increased stabilization and retention of hemicellulose.

The effects of AQ on alkaline degradation of a soluble polysaccharide have not been reported. In this study, AQ (5% w/w, amylose basis) was used in alkaline reactions under both nitrogen and oxygen at 100°. The amount of AQ was considerably larger than the 0.1-0.25% (wood basis) often used in pulping experiments.[33] This dosage was chosen to emphasize the effect of AQ, especially under anaerobic conditions, where AQ was expected to be rapidly consumed, without any possibility of becoming reoxidized to its active form by lignin moieties.

Effect of AQ in Anaerobic Reactions

The ability of AQ to stabilize amylose against peeling yield loss under nitrogen is apparent in Fig. 2E. Greater than 80% of the amylose lost in alkali (Fig. 2B) is retained by the addition of AQ. In addition, the yield loss is even smaller than that resulting from the AQ-free oxygen-alkali reaction (Fig. 2D).

It is interesting to note that the residual $\overline{DP}_n$ falls faster than the yield. This is evidence for random chain cleavage caused by the addition of AQ.[42] Even limited similar AQ-induced chain cleavage during wood pulping could explain observed drops in soda-AQ pulp viscosities. However, the effect on cellulose in pulps would be expected to be much smaller than that on amylose (Fig. 2E), due to the heterogeneity of the lignified cellulosic systems.

The mechanism of oxidative alkaline chain cleavage of polyglucans is not well understood. Figures 2D and 2E are nearly superimposable, indicating that oxygen and AQ have very similar effects on the alkaline depolymerization of amylose. Possibly both reagents generate common intermediates which are necessary for the cleavage of the chain.

In anaerobic AQ-alkali cooks, the red color of the liquor is qualitative evidence that AQ has been reduced by the carbohydrate to form soluble AHQ ions. It was found that the red color vanished after the first hour of reaction after which the liquor remained pale yellow. AQ is known to react readily with products from alkaline degradation of carbohydrates.[36,38] The disappearance of the red color indicates that anthrahydroquinone is also able to react with such compounds.

Effect of AQ in Oxygen-alkali Reactions

AQ had a less pronounced influence on the amylose degradation under oxygen pressure. The liquor remained clear and colorless as under other oxygen-alkali reactions. Reduced, colored forms of AQ were apparently reoxidized immediately by the oxygen, since none of the liquor samples showed any red color. Various peroxides are formed in this reaction[43] and may have been present in sufficient concentration to contribute to the amylose degradation.

The amylose yield curves for the oxygen-alkali reactions with and without AQ (Fig. 2D and 2F) are very similar. This does not mean, however, that AQ does not give additional stabilization of end groups under oxygen. Throughout the reaction, the residual $\overline{DP}_n$ was lower when AQ was present, indicating that the chain cleavage reaction was significantly faster. Thus, there must be a proportionately greater number of reducing ends available to the peeling reaction, and a relatively higher yield loss should be expected. The fact that the yield loss instead was slightly lower shows that the AQ does enhance end group oxidation under these conditions. The average chain length lost via peeling can be roughly estimated. During the first couple of hours of the reactions, the residual $\overline{DP}_n$ of the AQ-oxygen-alkali reaction (Fig. 2F) is only about one half of the residual $\overline{DP}_n$ of the AQ-free oxygen-alkali reaction (Fig. 1D). However, the amylose yields are about the same. Thus the peeling length under oxygen with added AQ must be about one half of that in the absence of AQ (i.e., 10-15 units), to compensate for the approximately double number of sites available for peeling. This positive effect is small relative to the detrimental chain cleavage caused by AQ, and the results support

reports[39,40] that AQ should not be expected to have any beneficial influence on an oxygen-alkali delignification process.

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TABLE I

Estimation of Average Peeling Lengths in Oxygen-alkali Reactions (See Figure 4)

Reaction Time, hours	Experimental $\overline{DP}_n$		Calculated $\overline{DP}_n$		Peeling Length (CC100-T100)
	80°C	100°C	T100[a]	CC100	
0.00	630	630	nd	nd	nd
0.25	568	nd	nd	nd	nd
0.50	nd	376	445	469	24
1.0	nd	298	344	374	30
1.5	515	nd	280	310	30
2.0	nd	244	237	265	28
3.0	465	195	180	206	26
5.0	381	124	122	142	20
7.0	284	91	92	109	17

[a]Linear approximation of experimental $\overline{DP}_n$ (100°C) data.
nd, not determined.

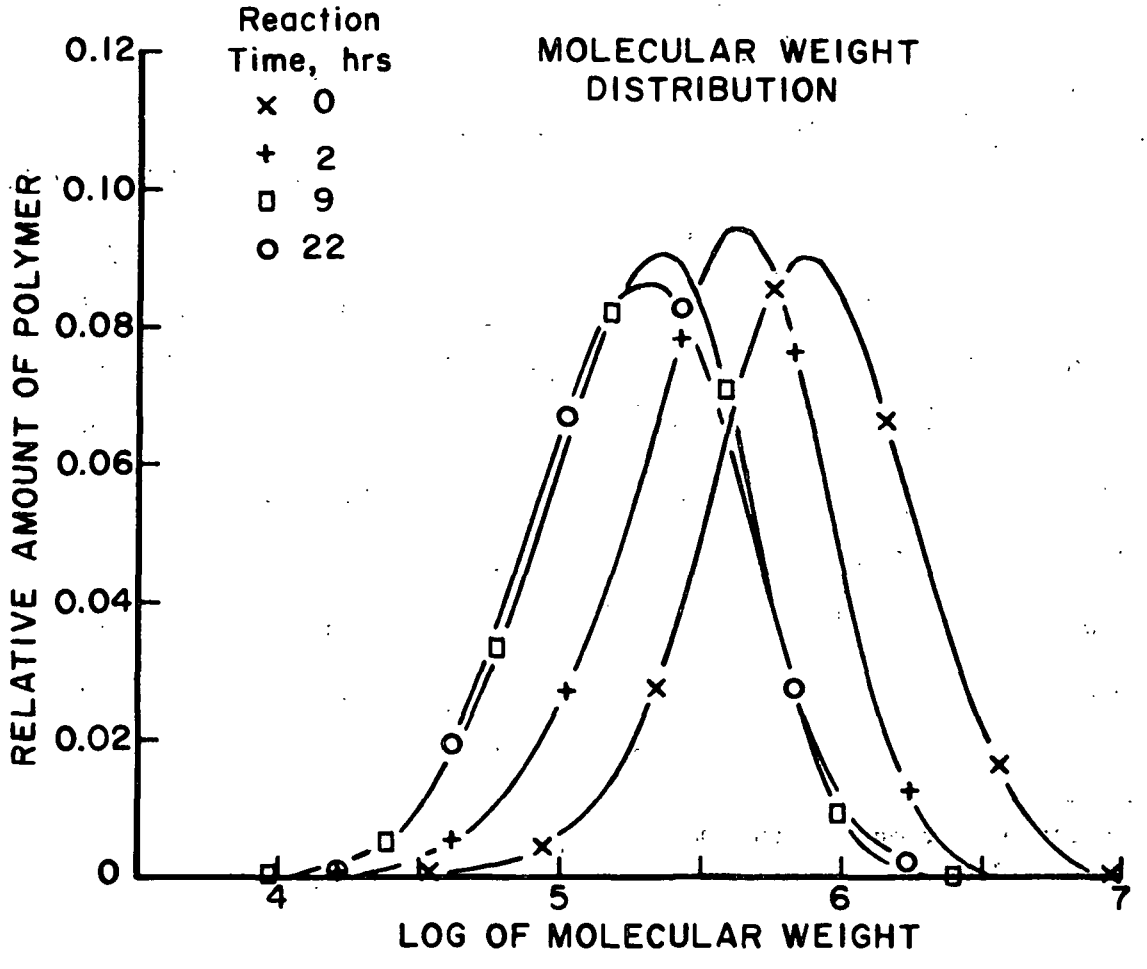

Figure 1. Changes in the molecular weight distribution of amylose during alkaline degradation in 1.0M NaOH at 80°.

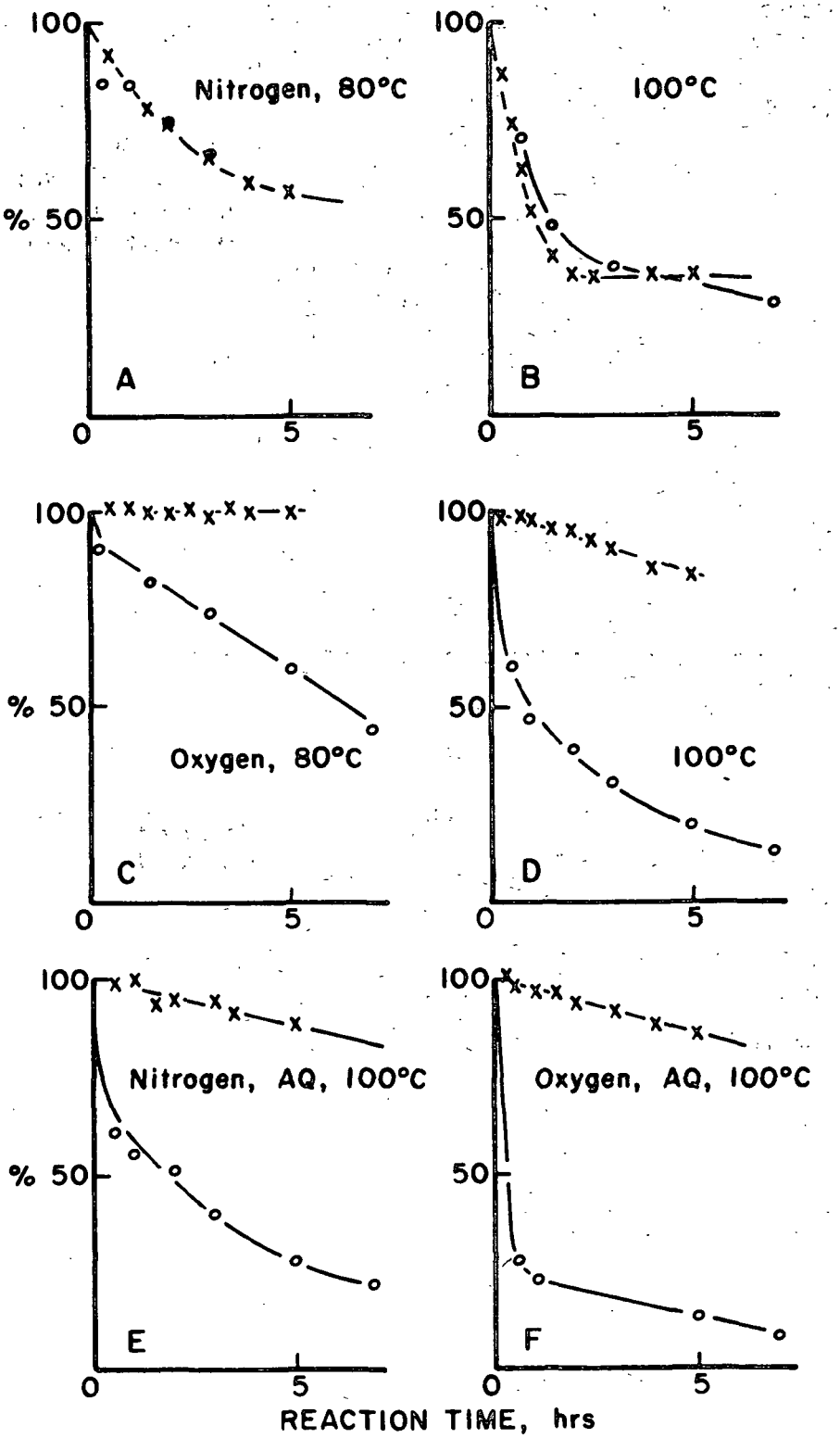

Figure 2.

A-F. Amylose yield (X) and residual $\overline{DP}_n$ (◎) as functions of reaction time under different conditions of alkaline degradation (1.0M NaOH)

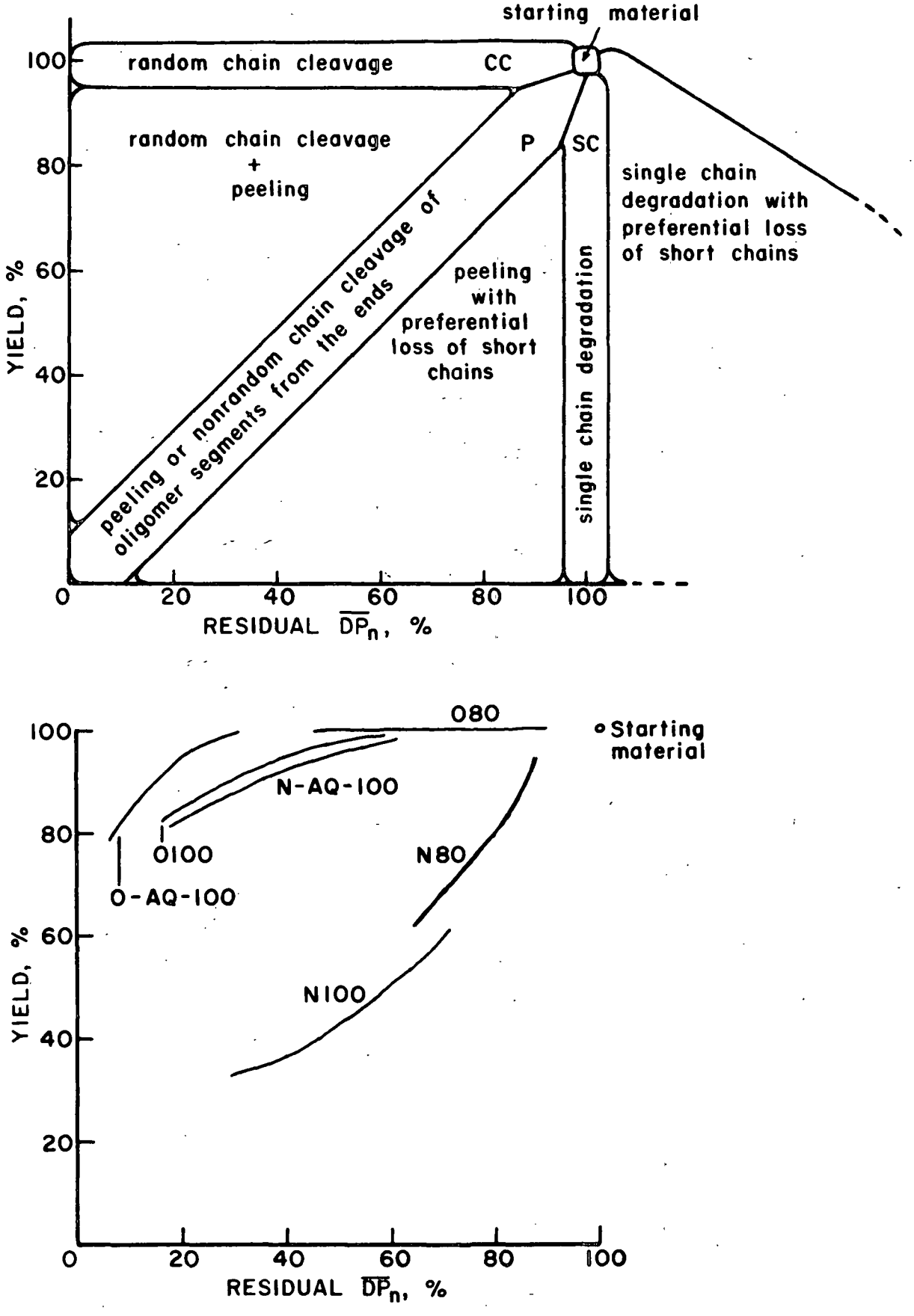

Figure 3. Amylose yield versus residual $\overline{DP}_n$:

A. Areas representing various modes of degradation
B. Alkaline depolymerization of amylose (N, nitrogen atmosphere; O, oxygen atmosphere, AQ, anthraquinone additive; and 80 or 100 are the reaction temperatures).

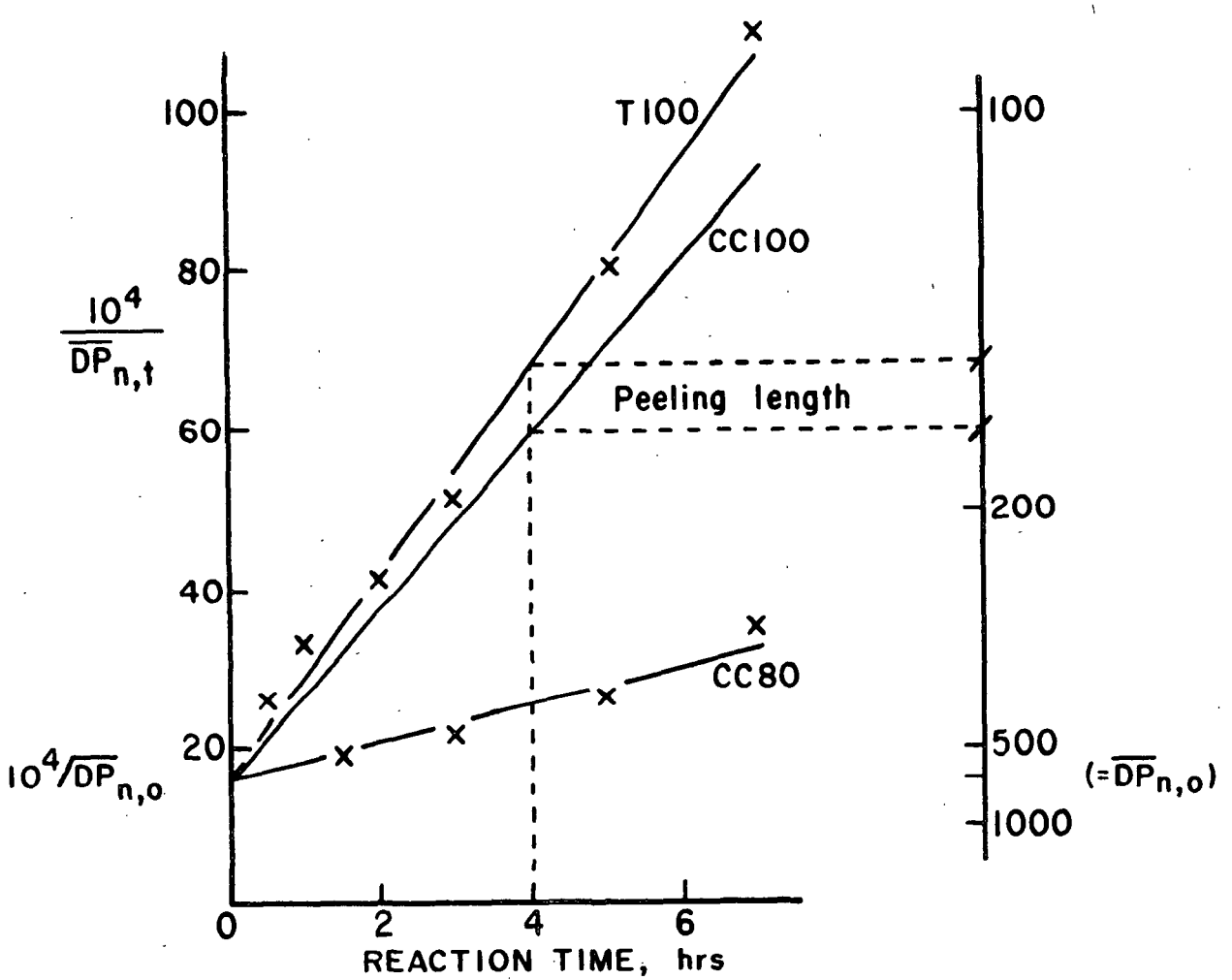

Figure 4. The inverse of $\overline{DP}_n$ of amylose degraded in oxygen-alkali as functions of reaction time.

$\overline{DP}_{n,o}$ - number average DP of starting material (= 630).
CC80 - observed depolymerization at 80°.
CC100 - calculated chain cleavage depolymerization at 100°.
T100 - linear approximation of observed depolymerization at 100°.