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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Holló, J. , László, E. and Toth, M.(1970) 'Effect of the Properties of Polyelectrolytes on Their Catalytic Behavior. I', *Journal of Macromolecular Science, Part A*, 4: 5, 1215 – 1221

**To link to this Article:** DOI: 10.1080/00222337008061014

**URL:** <http://dx.doi.org/10.1080/00222337008061014>

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## Effect of the Properties of Polyelectrolytes on Their Catalytic Behavior. I

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### SUMMARY

The hydrolysis-catalyzing effect in starch hydrolysis of soluble copolymeric acids prepared from mixtures of acrylic acid and acrylamide of various ratios was investigated in experiments carried out with acrylic acid: acrylamide copolymers in ratios of 10:5, 10:2, and 10:1 at temperatures of 100, 105, 110, 115, and 120°C at an initial pH value of 3.2. A mean value of 32,610 cal/mole was obtained, on calculating the activation energies from the initial reaction rates. This is in fair agreement with the data observed in the hydrolyses conducted with other acids.

The degradation of starch has been in the center of interest of the kinetic investigations of a number of research workers or research teams for several decades. Of the various methods of degradation, decomposition by acids and by enzymes had been the subject of the most detailed investigations because of their industrial significance.

Our research team has spent fifteen years doing starch investigations. In the course of this work, a number of our results have been reported in respect to the acidic and enzymatic hydrolysis of starch and of its components, and to the mechanism of reaction of the formation of various by-products [1-4].

Up to the present, experiments with hydrolysis by acids had been carried out both by us and by other authors mainly by means of mineral acids in spite of the fact that in order to solve a number of problems the investigation of the catalytic effect in a homogeneous phase of soluble polymeric acids, and particularly of polymeric acids also carrying various vicinal groups, would be quite reasonable. The mechanism of hydrolysis may be affected in a decisive way by the nature and solution conformation of a polymeric acid substituted to various degrees, or by the character and location of the substituents within the polymer chain itself. The examination of the hydrolysis-catalyzing effect of polyfunctional compounds of that type is also justified by the fact that in this way there is a possibility of finding some correlations between the mechanism of acidic and enzymatic hydrolysis.

Though the specificity of enzymatic hydrolysis and its extremely high catalytic activity offer appreciable advantages, with the exception of a few cases, the instability of the enzymes against heat, pH, and chemical agents is actually a great disadvantage. In recent times, reports of experiments carried out with so-called "enzyme-models" [5-7] have been published in steadily increasing numbers. In these experiments, groups which presumably play some role in a given enzymatic process are introduced by way of synthesis into polymeric chains of various types. By means of groups of that type, on the one hand, a deeper knowledge of the mechanism of enzymatic degradation and, on the other hand, the detection of groups is possible, the formation of which may result in a stability higher than that of enzymes, besides a specific and high catalytic activity similar to that of enzymes.

Our investigations started with copolymeric acids and was aimed mainly at the completion of the results attained in the field of acidic hydrolysis. However, by advancing in this way, we found it possible to develop macromolecules that carry functional groups similar to those present in the enzymes hydrolyzing or synthesizing starch and which are suitable for use in investigations undertaken to clarify the groups and the steric conditions required to attain maximum catalytic effects. Polyacrylic acid and polyacrylamide copolymers were chosen as proton carriers in our hydrolysis experiments, and they were prepared as follows.

To purified diluted acrylic acid freed of stabilizer, acrylamide was added at weight ratios of 10:1, 10:2, and 10:5 referred to acrylic acid, then the mixture was subjected to polymerization for 15 min at 60°C in the presence of ammonium persulfate. The copolymer obtained, which contained 9.1, 15.7, and 33.3% of acrylamide, was purified by dialysis

with distilled water. The purified products showed, respectively, a limiting viscosity of 2, 3.2, and 1.2 at 20°C in an aqueous solution.

The hydrolysis experiments were carried out with starch samples made by Merck, transferred to ampoules, and the ampoules placed in a liquid paraffin bath thermostated at 100, 105, 110, 115, and 120°C. The initial pH value of the reaction was adjusted at 20°C to 3.2 by diluting the copolymer (the lowest adjustable value for every copolymer after the dissolution of starch).\* The degree of starch conversion was followed by the iron(III) cyanide method [8]. Both during their preparation and their processing, the samples were cooled to a temperature between 0 and +2°C. Cooling during processing appeared to be of importance since it was necessary to remove the copolymer by centrifugation at pH 0.5 immediately after withdrawal of samples in order to eliminate the interfering effect of the copolymer in the determination of terminal groups. This latter procedure has been carried out only after neutralization.

Though the acidic hydrolysis of starch has been proved to take place as a first-order reaction, in the above-described case the conversion curve pointed to a fractional order only. This is due to the fact that, in parallel to the effect of heating hydrolysis, an imide-formation reaction occurs [9], during which an amide group reacts with a vicinal carboxyl group within the chain or with another carboxyl group in a favorable position. The reaction proved to be proton-consuming. This was followed by measurement of the pH value of consecutively withdrawn samples. As an example, the conversion curves of hydrolysis experiments with a copolymer at a 10:1 ratio are presented in Fig. 1, while the changes in pH values occurring during hydrolysis are shown by Fig. 2. Imide formation, though it modified the shape of the conversion curve during hydrolysis, did not interfere with the determination of the thermodynamical characteristics of hydrolysis when this was combined with the determination of the initial reaction rates.

At the beginning of hydrolysis ( $\tau = 0$ ), the initial rate constants ( $k_0$ ) can be determined either by means of the initial slope tangents of the conversion curve or on the basis of the initial slope angle of the curves  $\ln [1/(\tau - p)]$  plotted against time. In Fig. 3 the initial rate constants plotted against the ratios of acrylic acid to acrylamide within the copolymer are presented.

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\*pH measurements were made with a Radiometer instrument with an accuracy of  $\pm 0.02$ . After adjusting the pH, the copolymer content of the solutions was 0.51 g/100 ml for the catalyser with 9.1% amide content (10:1), whereas with 16.6% (10:2) the content was 0.76 g/100 ml and for 33.3% (10:5) it was 1.03 g/100 ml.

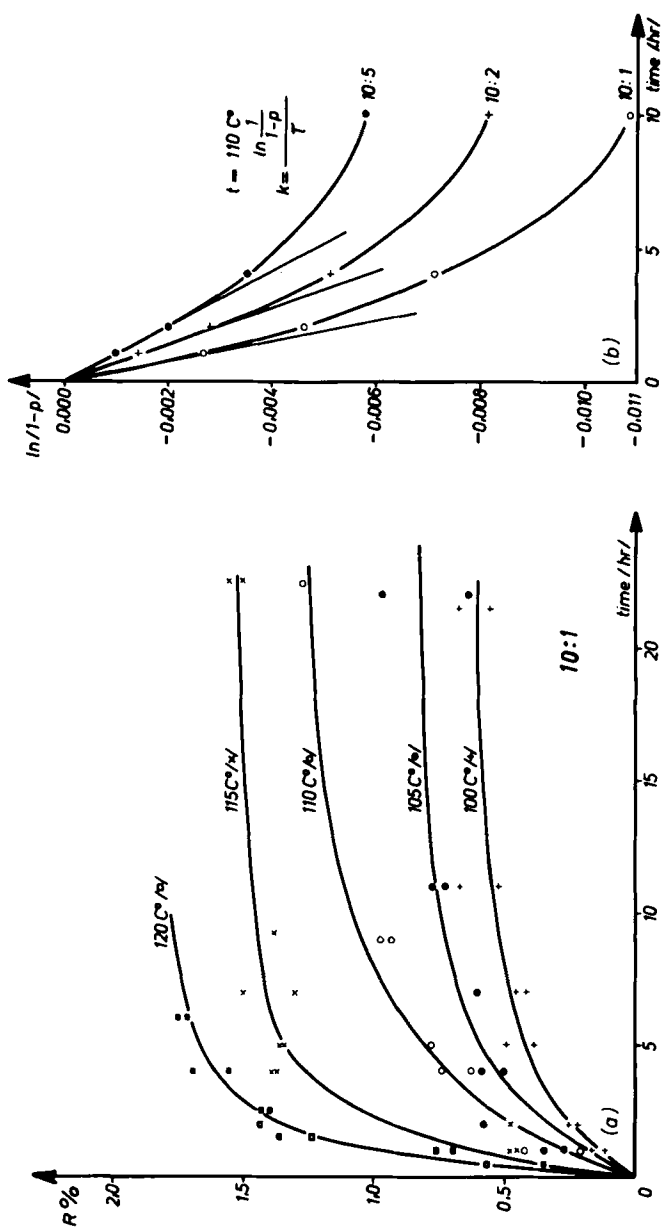


Fig. 1. Left: Time curves of starch conversion (R%). Right: Determination of initial hydrolysis rate constants ( $k_0$ ).

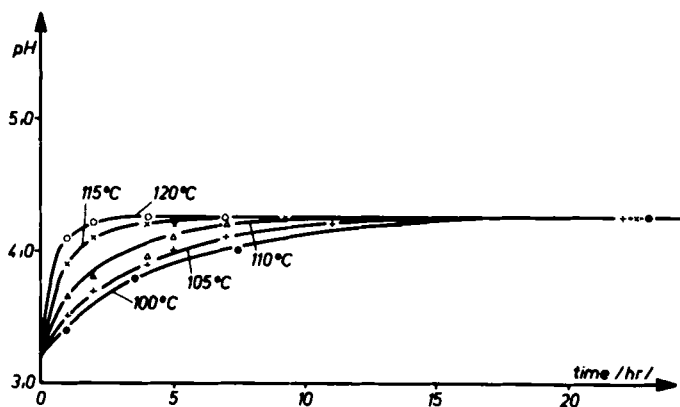


Fig. 2. Changes in the pH of a 10:1 ratio copolymer as a function of time and temperature.

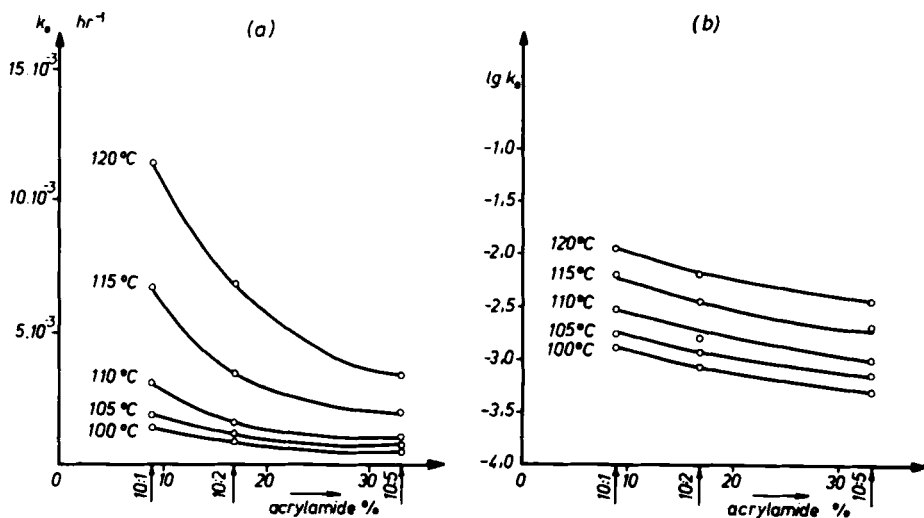


Fig. 3. Changes of the initial hydrolysis rate constant (left) and of its logarithm (right) as functions of the acrylic acid: acrylamide ratio.

Since these are initial rate constants, the effect of imide groups cannot manifest itself. Consequently, the shape of the curves is defined only by the presence of the amide groups and by the temperature.

It can be seen in Fig. 3 that the logarithmical values of the reaction rates

alter at an identical ratio in the copolymers of various mixture ratios. Thus, no dependence of the values of activation energy on the amide ratios can be expected. On plotting the temperature dependence of the reaction rates in the hydrolysis experiments conducted with various copolymers, straight lines were obtained for parallel runs (Fig. 4). The activation energies calculated from the slope angles of these straight lines were as follows: 32,500 cal/mole for a copolymer with a 10:1 ratio of acrylic acid to acrylamide; 32,350 cal/mole for a copolymer with a 10:2 ratio, and 32,980 cal/mole for a copolymer with a 10:5 ratio, i.e., a mean value of 32,610 cal/mole, in fair agreement with the data obtained in our experiments with other

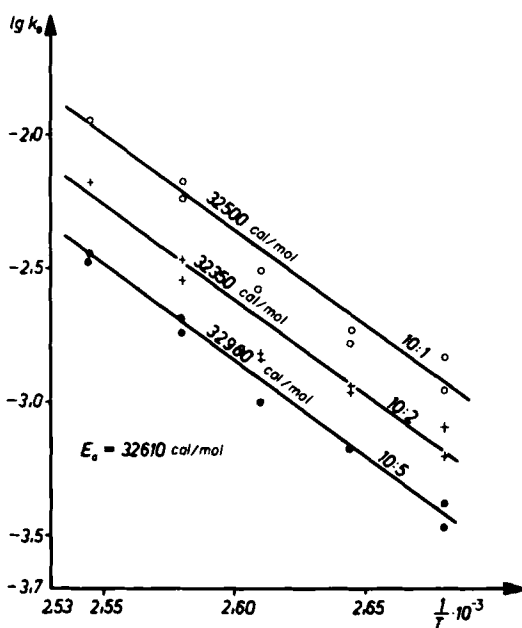


Fig. 4. Temperature dependence of the initial hydrolysis rate constant.

acids and with the data of other authors obtained in experiments with mineral acids.

The activation energy obtained for the hydrolysis of glucosidic bonds was identical with all three copolymers, but increasing the amide content decreased the hydrolysis catalyzing effect of the copolymer. This might be due to the fact that protons of neighboring carboxyl groups are bound, or shadowed by the amide groups, so to say, which may be considered as

an initial step in imide formation (Fig. 5). Hydrogen ions bound in this way are not involved in the hydrolysis of glucosidic bonds, and this shows itself in the lower values of measured hydrolysis rate constants.

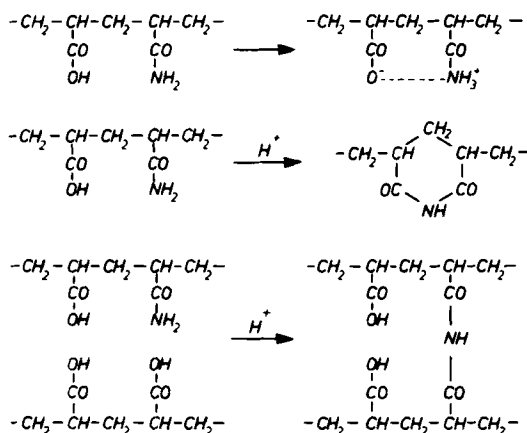


Fig. 5. Conversion of amide  $\rightarrow$  imide resulting from increasing the pH.

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