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Rate Characteristics for the Reaction of Carboxyl-Modified Polyamide with Potassium Hydroxide

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Synopsis

Nylon 66 fiber, carrying 2.0 meq/g of carboxyl groups from radiation grafting of acrylic acid, was found to display chemical kinetics strongly first order with respect to the potassium hydroxide. The apparent rate constant k' remains nearly unchanged as the initial bath pH is varied from 8.3 to 10.5. At this point, the value of k' drops sharply, and continues to drop as the initial pH is increased. This discontinuity is attributed to a previously reported morphological transition indicated by a break in titration data at the corresponding equilibrium point of pH 9.2.

INTRODUCTION

The reaction characteristics of polyelectrolytes have long been a subject of interest, in part because of the fundamental aspects of intramolecular group interactions involved, in part because of their potential relevance to biological systems.[1]

Much of the work in this area has dealt with polyacids which are quite soluble in water and which therefore possess a high degree of chain mobility in solution.[2–9] Among those studying solid resins, Selegny and co-workers[10,11] have reported minima in volume as certain resins were titrated.

The material studied in the present work was a graft copolymer of acrylic acid on a polyamide (nylon 66) backbone. The acid was permitted to diffuse to equilibrium in the polyamide; exposure to ionizing radiation resulted in the formation of nylon 66 carrying grafted side chains of homopolymerized acrylic acid.

Previous work with this type of fiber, reported by us,[12] showed a distinct discontinuity in equilibrium acid-base characteristics. This was attributed to the effects of the hindered structure resulting from the formation of the hydrophilic polyacid on the solid polyamide backbone.

The work reported here examines the rate properties of this heterogenous structure, and presents further evidence of a morphological discontinuity in such a system.

EXPERIMENTAL

Fibers of nylon 66, graft copolymerized with acrylic acid according to the method described by Magel et al.[13,14] were treated with 1*N* HCl at room tem-

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perature for 6 h, to assure complete conversion to the acid form. These were rinsed repeatedly with distilled water until no change in pH of the wash could be observed. The fibers were cut into short segments (1 mm or less) for the rate studies reported here. An acid content of 2.0 (meq/g) of fiber was found by electrometric titration to equilibrium.

For each kinetic run, 0.5 g of chopped fiber, conditioned at 65% RH and 25°C for at least 24 h, was dropped into 500 mL of potassium hydroxide solution of specified initial pH, rapidly stirred under flowing nitrogen, and maintained at 25°C. The change in pH was recorded, either continuously or at intervals of 0.25–0.50 min, using a Beckman Research pH meter with combination electrode.

DISCUSSION

A series of 26 runs was made, using a wide range of initial base concentrations (pH 8.3–11.5). A typical curve is shown in Figure 1. When plotted appropriately, the entire family showed excellent first-order rate characteristics with respect to the potassium hydroxide concentration. Several representative curves are shown in Figure 2. Adherence to first-order kinetics was found for 60–95% of the complete reaction; over 80% was found for most runs.

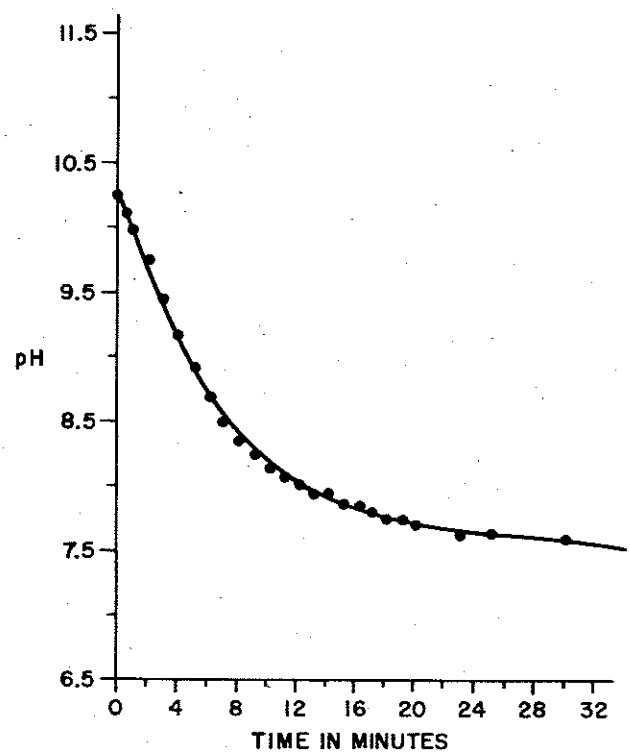

Fig. 1. Reaction rate KOH with grafted fiber.

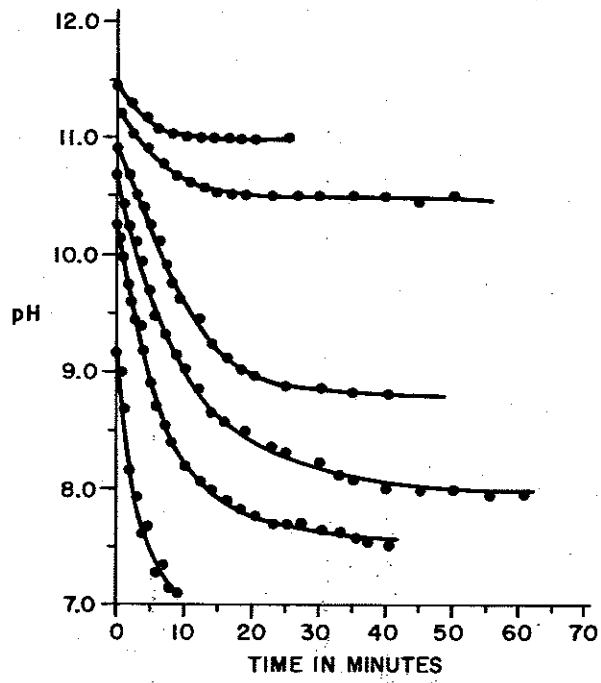

Fig. 2. Effect of initial pH on rate.

The reaction involved here, between a carboxylic acid and potassium hydroxide, is clearly first order with respect to each reactant and second order overall. For such a reaction to appear first order with respect to the potassium hydroxide, in the circumstances under which we measured it, it is necessary that the concentration of the carboxylic acid remain essentially constant for the observed period of the reaction. Usually, this condition exists when one reactant is present in such large amounts that the change in its concentration over the course of the observed reaction is not significant.

At the low end of the pH range used in this work, the total amount of carboxyl groups present did indeed exceed the total amount of hydroxyl groups present (at pH 8, 0.0005 meq of base, compared to 1.0 meq of acid) at the beginning of the reaction. However, in the more concentrated solutions of base, the total number of carboxyl groups was less than the number of hydroxyl (at pH 12, 1.0 meq of carboxyls, 5.0 meq of potassium hydroxide).

It should be noted, however, that observations on the rate law applicable to a given reaction generally assume a uniform distribution of the reactants throughout the reaction volume. In the present case, however, it is probable that the acid groups present are collected in localized regions. In fact, the method used to prepare the graft fiber, involving initial diffusion of acrylic acid into the nylon 66, would be expected to lead to a high concentration of the acid in those regions within the fiber most accessible to the diffusing material. Subsequent polymerization and grafting of the acrylic acid would then result

in formation of a copolymer with polyacid highly localized in these regions. The present rate data, therefore, supports the picture of a polymer acid in a matrix of the polyamide.

A quite unexpected effect of the initial base concentration on the apparent first-order rate constant (k') was found when the values for $1/k'$ were plotted against the initial pH of the solution. For a wide range of pH values, k' and its reciprocal remained essentially unchanged, as solutions initially more basic were used, up to an initial pH of 10.5. Beyond this point, the value of k' decreased, and continued to do so with successively higher initial basicities (Fig. 3).

Thus, for lower initial base concentrations, the initial pH has no effect on the apparent rate constant, and presumably no effect on the structure of the polyacid. The distinct change in rate characteristics which occurs with the solution initially at pH 10.6, strongly suggests a change in the morphological structure of the polymer. At successively higher initial basicities, the structure appears to be modified still further, in a progressive but unidentified manner.

Correlation of these observations with the equilibrium data reported earlier[12] were made by comparing the initial pH of several runs made in the present study, with the pH values obtained when another set of runs were carried to equilibrium. Some of the resulting data are given in Table I.

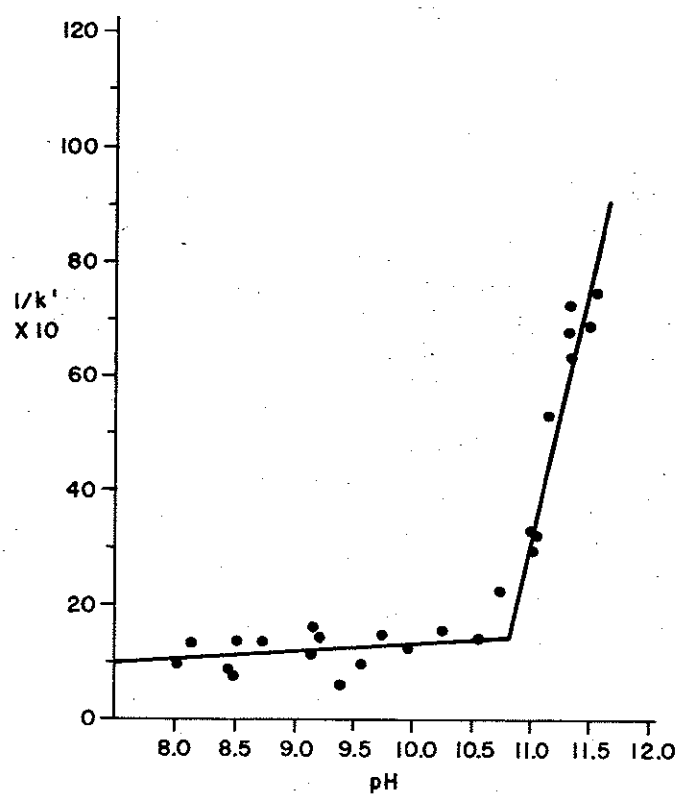

Fig. 3. Change in $1/k'$ vs. pH.

TABLE I
Comparison of Initial and Final pH Values

Initial pH	Final pH
8.4	6.3
9.2	7.1
9.7	7.8
10.8	8.9

It will be seen that the reaction mixture initially at pH 10.8 (the discontinuity point noted in the present study) finally reaches pH 8.9, very near the value, 9.2, reported by us for the discontinuity point observed under equilibrium conditions.

It appears, then, that both the data obtained earlier under equilibrium conditions and the kinetic data reported here reveal related discontinuities. A morphological transition of the polyacid structure brought about by immersion in a solution having the critical pH appears to bring about a structure which establishes both the rate properties of the system and its equilibrium characteristics. The nature of the transition has not been elucidated.

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