

Polyelectrolyte Effect and Conformational Transition in a Restricted Polyacid Structure

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Synopsis

In a polyacid consisting of polyacrylic acid attached to a polyamide matrix, marked effects in equilibrium acid-base characteristics are observed, attributable to a hindered polyelectrolyte structure. In the presence of neutral electrolyte, the very high values found for pK_a drop sharply. A break in the Henderson-Hasselbalch curve indicates a conformational transition at $\alpha = 0.55$ which is deferred to 0.95 by the presence of neutral electrolyte.

INTRODUCTION

Various aspects of hydrogen ion equilibria of polyelectrolytes such as poly(acrylic acid) (PAA) have been reported by several authors.¹⁻⁴ More recently, the potentiometric titration of poly(methacrylic acid) (PMA) with several hydroxides was described by Wojtczak.⁵ Discontinuities in the slope of Henderson-Hasselbalch curves, described also by others,^{6,11} were found by this worker to be strongly affected by the nature of the hydroxide used and the presence of neutral electrolyte.

In the cases cited, the polybasic acid studied was a homopolymer, soluble in water, and hence free to assume the conformation of lowest energy by movement of the functional groups and the polymer chain.

In the present work, titration characteristics were obtained for a polyacrylic acid structure held in a highly constrained configuration. The material used was a radiation graft copolymer of acrylic acid on a nylon 66 backbone. In the procedure utilized in the preparation of this copolymer, acrylic acid is permitted to diffuse to equilibrium into the nylon 66 fiber.^{7,8} After exposure to ionizing radiation, the resulting copolymer consists of nylon 66 carrying grafted side chains of homopolymerized acrylic acid.^{7,8} The acidic functionality, therefore, may be considered to be polyacrylic acid held primarily in the less-ordered regions of a polyamide matrix. Distinct effects, attributable to such a hindered structure, are reported here.

EXPERIMENTAL

Samples of nylon 66 fiber (0.500 g), containing approximately 2 meq/g of graft-copolymerized acrylic acid, were cut into 2-mm lengths and stirred very rapidly under nitrogen in 500 ml of boiled distilled water. Titration with 0.001M KOH was carried out at $50^\circ \pm 0.2^\circ\text{C}$. Readings to the nearest 0.001 pH unit were taken on a Beckmann Research pH Meter, using a combination electrode. Initial difficulties with meter instability appeared due in part to capacitance effects and were minimized by placing large grounded metal sheets between the operator and the experimental setup. Equilibrium was assumed when a reading changed less than 0.002 units over a 2-min period.

DISCUSSION

The continuous decrease in apparent acid strength of a polymeric acid as it is neutralized is generally attributed to the polyelectrolyte effect,^{9,10} a result of the development of increasingly large charges on the polymer with consequent increases in the work required to remove successive protons. In accordance with this concept, the KOH titration for the insoluble graft copolymer of acrylic acid and nylon 66 indicates an acidity strikingly lower than that reported³ for soluble PAA (Fig. 1).

The titration characteristics of polymer acids have been shown to be affected markedly by the nature of the hydroxide cation used.^{3,5} In the present work, the apparent acidity of the acrylic acid-nylon graft copolymer was found to increase to a marked degree (Fig. 1) when calcium hydroxide, rather than potassium hydroxide, was used as titrant. Both the smaller radius of the calcium ion and its divalent character would be expected to facilitate the process of neutralization, with less energy expended in the formation of the negatively charged carboxylate groups.¹¹

The strong polyelectrolyte effect manifested by the confined polyacrylic acid of the graft copolymer should be suppressed even more effectively by the addition of a neutral electrolyte such as potassium chloride.^{3,5}

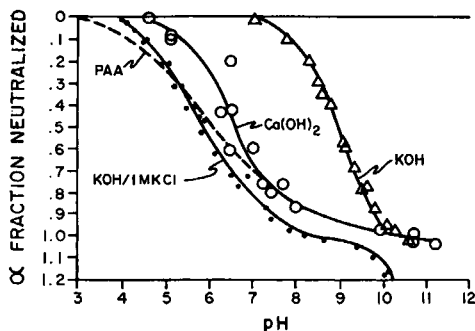


Fig. 1. Titration of acrylic acid nylon graft copolymer at 50°C with KOH, KOH with 1M KCl, and $\text{Ca}(\text{OH})_2$. PAA (data points omitted) is included for comparison.

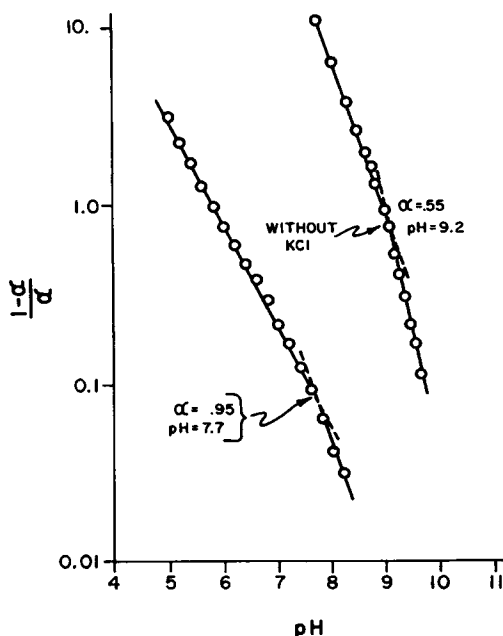


Fig. 2. Henderson-Hasselbalch plot of KOH titration at 50°C with and without 1M KCl.

Shielding of the carboxylate anions would lead to a neutralization curve characteristic of a much stronger acid. Such a curve was found for the graft copolymer (Fig. 1).

When the appropriate logarithmic function of the degree of neutralization (α) is plotted against the pH for PAA, the resulting Henderson-Hasselbalch curve (Fig. 2) is a straight line with a slope of 2.2.¹¹ With PMA, on the other hand, a discontinuity appears, breaking the curve into two linear segments. It has been postulated⁴ that the methyl groups on the PMA chain interfere with the uncoiling or other rearrangement as the anionic charges develop until some critical pH is reached, whereupon a marked change in configuration occurs, with an accompanying change in titration characteristics.

Restraining the movement of the functional groups or of the chain itself by a low degree of crosslinking might be expected to delay the occurrence of this conformational transition until a larger fraction of the acid groups has been neutralized. Such an effect, however, has not been reported. No breaks were found in the Henderson-Hasselbalch curves for a crosslinked ion exchange resin¹² nor for PAA and PMA, which are crosslinked to various degrees.

With the graft copolymer of acrylic acid on nylon reported here, a distinct effect attributable to a moderate level of restraint on the polyelectrolyte system is seen. In the absence of added neutral electrolyte, a transition is seen to occur (Fig. 2) at pH 9.2, when the polymer is slightly over half neutralized ($\alpha = 0.55$).

TABLE I
Henderson-Hasselbalch Parameters at 50°C

KCl Concn.	pK_a^a	Slope n	Transition	
			pH	α
	9.0	1.2	9.2	0.55
	9.1	0.7		
0.004M	7.5		8.4	0.75
1.0M	5.8	1.7	7.7	0.95
	6.5	1.2		

* Values of pK_a are given for each of the two straight-line segments found; these were obtained by extrapolation to $\alpha = 0.5$.

In the presence of a significant amount of neutral electrolyte (1M KCl), however, the repulsion between the developing anionic groups is so minimized that the transition is not seen until neutralization is nearly complete ($\alpha = 0.95$). Data derived from these curves is collected in Table I.

It appears, then, that the graft copolymer of acrylic acid on nylon 66 represents an example of an anionic polyelectrolyte held in a restraining matrix, but held less rigidly than in crosslinked structures, so that a conformational transition is possible under sufficient dislocating force.

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