# Analysis of the Potentiometric Titration Curves of Some Polyacids Using Polymeric Subunits†

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ABSTRACT: The potentiometric titration curves of a series of polyelectrolytes have been analyzed by considering oligomeric subunits containing eight monomeric units. In each case, the eight distinct and successive ionization constants have been calculated and discussed in relation with the structural features of the polymer (tacticity, nature of the side chain, conformation). In the cases where a two-state conformational transition occurs, the population distribution among the various deprotonation states of the subunits was calculated according to the method of Strauss and found to be bimodal.

## Introduction

In a previous paper,[1] we studied the formation of the complexes between a metal ion and the polymeric ligand poly(*N*-methacryloyl-L-lysine) (PLL), a poly(methacrylic acid) derivative with $CONHCH(COOH)(CH_2)_4NH_2$ as a side chain. For this purpose and as a preliminary step, it was necessary to determine the protonation constants of the polymeric ligand in the absence of the metal ion. It was found that the titration curve of PLL could be successfully simulated by using only three or four distinct p*K* values, i.e., considering PLL as a dimeric species having two $NH_2$ and two COOH functions. This result was attributed to the polyampholytic nature of PLL over most of its titration curve. In most cases, for example, for pure polyacids, a greater number of successive ionization constants is necessary to account for the titration curve and laborious calculations are necessary to determine these constants.

A few years ago, Strauss[2,3] introduced a novel method for the analysis of the potentiometric titration curves of these polymers in terms of successive ionization constants of a suitably sized subunit (oligomeric subunit) of the polymer chain. This method allows the resolution of the subunits into species that differ in their degree of dissociation, and the distribution of the population of these species can be obtained over the pH range of the titration. The numbers obtained by this method should be used for comparison purposes between different polymers only.

Synthetic water-soluble polyelectrolytes may be divided into two classes: (i) those undergoing a normal molecular expansion upon ionization and (ii) those undergoing a conformational transition between a random conformation typical of class (i) and a compact conformation resulting from the balance between hydrophobic cohesive forces and electrostatic interactions. Poly(methacrylic acid) (PMA) (4) and copolymers of maleic acid and alkyl vinyl ethers (5) are typical examples of this behavior. In the second case, the population distribution curve appeared to be bimodal, whereas in the first case, a single-peaked distribution was obtained.[2,6]

In order to generalize these results to other polyelectrolytes, we have used the method of Strauss to analyze the potentiometric titration curves of a series of polymers and copolymers that differ in tacticity, nature of the side chain, number of ionizable functions per side chain and conformation. For this purpose, subunits containing eight repeat units of the polymer were considered and the successive p*K* values were computed. In cases where a conformational transition occurs, the distribution of the different deprotonation states was established.

† This paper is dedicated to the memory of the late Prof. Michel Wozniak.

## Theory

According to Strauss,[2] an entity $AH_N$ is chosen as a polyacid subunit containing $N$ acidic groups. The dissociation of this entity is described by the overall reaction:

$$AH_N \rightarrow AH_{N-i}^{-i} + iH^+ \qquad 1 < i < N \tag{1}$$

If the concentration of simple added salt is constant and high enough, the activity coefficients may be considered as constant and the overall dissociation constants may be defined by the relations:

$$\beta_i = aH^{+i}(AH_{N-i}^{-i})/(AH_N) \qquad 0 < i < N \tag{2}$$

The stepwise ionization constants, $K_i$, are defined by the relation:

$$K_i = \beta_i/\beta_{i-1} \tag{3}$$

The mole fraction of the polyacid species with $i$ dissociated protons, $x_i$, is defined by the expression

$$x_i = (AH_{N-i}^{-i})/\sum_{j=0}^{N}(AH_{N-j}^{-j}) \qquad 0 < i < N \tag{4}$$

which leads to

$$x_i = \beta_i h^i/\sum_{j=0}^{N}\beta_j h^j \qquad 0 < i < N \tag{5}$$

by using eq 2 ($h$ represents the reciprocal value of $(H^+)$).

The complexity of the titrations curve requires a value of $N$ that is not too small.[3] The minimum value of $N$ depends on the nature of the polymer. After a few trials we chose $N = 8$, which may account for all the titration curves, thus allowing a direct comparison between all our samples and the results of the literature.[2,6]

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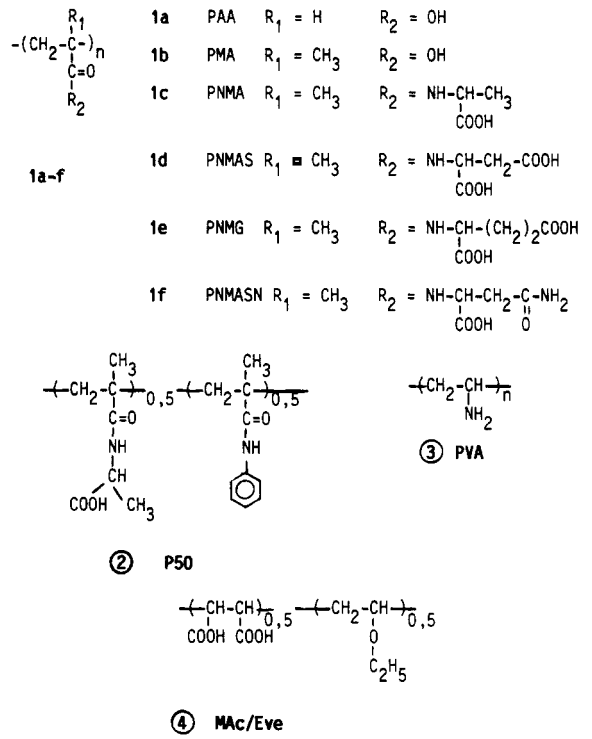


**Figure 1.** Chemical structures of the polymers under study.

## Experimental Section

**Materials.** Polymers whose chemical structures are given in Figure 1 were used in this work. Samples **1a–f** are derived from poly(acrylic acid) or poly(methacrylic acid). Sample **2** is a copolymer containing 50 mol % of the *N*-methacryloyl-L-alanine residue and 50 mol % of the *N*-phenylmethacrylamide residue. Sample **3** is poly(vinylamine), and sample **4** is an alternating copolymer of maleic acid and ethyl vinyl ether.

Poly(acrylic acid) (**1a**-PAA) was prepared by free-radical polymerization of acrylic acid in dioxane at 60 °C[7] ($\bar{M}_n$ = 20 000).

Syndiotactic poly(methacrylic acid) (**1b**-sPMA) was obtained from the free-radical polymerization of methacrylic acid in aqueous solution, at 50 °C, pH 10, using $K_2S_2O_8$ as initiator[8] ($\bar{M}_w$ = 80 000).

Isotactic poly(methacrylic acid) (**1b**-iPMA) was prepared from the anionic polymerization of methyl methacrylate initiated by $AlLiH_4$ in diethyl ether at −70 °C,[9] followed by a hydrolysis in concentrated sulfuric acid[10] ($\bar{M}_w$ = 13 000).

Samples **1c–f** (PNMA, PNMAS, PNMG, PNMASN) resulted from the radical polymerization of the corresponding monomers obtained from the reaction between acryloyl chloride and an amino acid[11–13] ($\bar{M}_w \sim$ 150 000). Copolymer **2** (P50) was obtained in the same way[14] ($\bar{M}_w$ = 80 000).

Copolymer **4** (MAc/EVE) was prepared by an alternating radical copolymerization of maleic anhydride and ethyl vinyl ether followed by alkaline hydrolysis[15] ($\bar{M}_w$ = 100 000).

Polymer **3** (PVA) was prepared by a radical polymerization of *N*-vinyl *tert*-butyl carbamate followed by a solvolysis with HCl in ethanol[16,17] ($\bar{M}_w$ = 155 000).

**Potentiometric Titrations.** The potentiometric data (added volume of sodium hydroxide, pH of the solution) were collected by using the automated titration system described elsewhere.[18] Added volumes and pH were measured to a precision of $10^{-4}$ cm$^3$ and $10^{-3}$ pH unit, respectively. The studies were carried out at 25 °C in a 0.1 M sodium perchlorate medium and under purified nitrogen. The glass electrode was standardized in the concentration scale with perchloric acid in the presence of 0.1 M sodium perchlorate.

Titrations of perchloric acid ($2 \times 10^{-3}$ M) with sodium hydroxide (0.25 M) were performed periodically in order to check the parameters of the measuring cell (zero shift, sensitivity), the ionic product of water, and relevant data for the titrant (total concentration of the sodium ion and of the carbonate). The carbon dioxide evolution coefficient was fixed at $3 \times 10^{-4}$ to take into account the transformation of the hydrogenocarbonate ion in acidic medium. The liquid-junction potentials were always negligible.

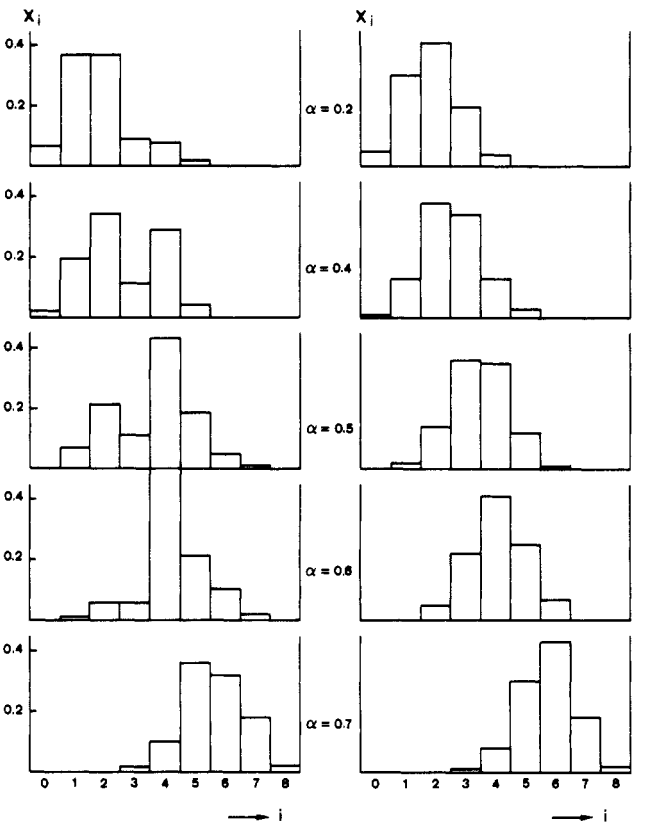


**Figure 2.** Plots of the species distribution (mole fraction $x_i$ versus the number of dissociated protons $i$) at different degrees of ionization. Left: P50. Right: PNMA.

The experimental data were processed as in earlier studies by use of the MUPROT multiparametric refinement program in order to derive the ionization constants of the polymers.[19]

## Results and Discussion

Among the polymers described in Figure 1, most take a random conformation whatever the extent of dissociation. Only samples **1b** and **2** have a compact conformation at low $\alpha$ values. The species population distribution ($x_i$ versus $i$) was determined for all these samples in the following way: first the pH corresponding to a given $\alpha$ value is obtained from the titration curve and thus the $h$ value ($1/(H^+)$). Then the $\beta_i$ and $\beta_j$ values are calculated from data of Figures 3–8 using eq 3. Finally, $x_i$ is obtained from eq 5. The same calculation is done for other $\alpha$ values. Figure 2 shows the species population distribution at different values of PNMA (**1c**) and P50 (**2**). For PNMA, the distribution is unimodal and the maximum shifts gradually to higher values of $i$ with an increasing degree of ionization. On the contrary, P50 exhibits a bimodal distribution with a minimum at $i$ = 3. This is consistent with a two-state conformational distribution. This means that each subunit can be either in the compact conformation ($i < 3$) or in the random conformation ($i > 3$). It appears from Figure 2 that the conformational transition of P50 is more pronounced than that of PMA[6] in agreement with the reported values of the standard Gibbs free energy of conformational transition: 2.05[20,21] and 0.46[22] kJ/mol, respectively.

Figures 3–5 show the effect of ionic strength and tacticity on the ionization behavior of PAA (**1a**) and PMA (**1b**).

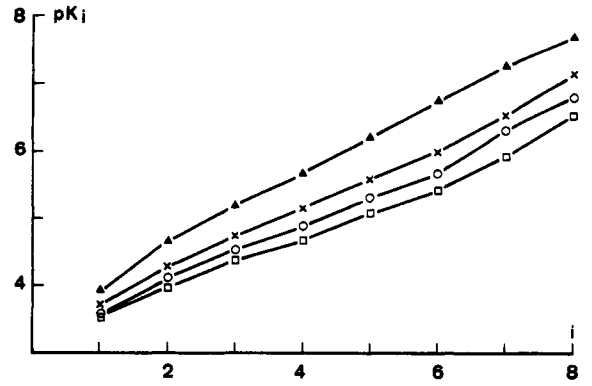


**Figure 3.** Stepwise ionization constants p$K_i$ as a function of $i$ ($N$ = 8) for PAA. Ionic strength of $NaClO_4$: 0.02 M (▲); 0.1 M (×); 0.2 M (○); 0.5 M (□).

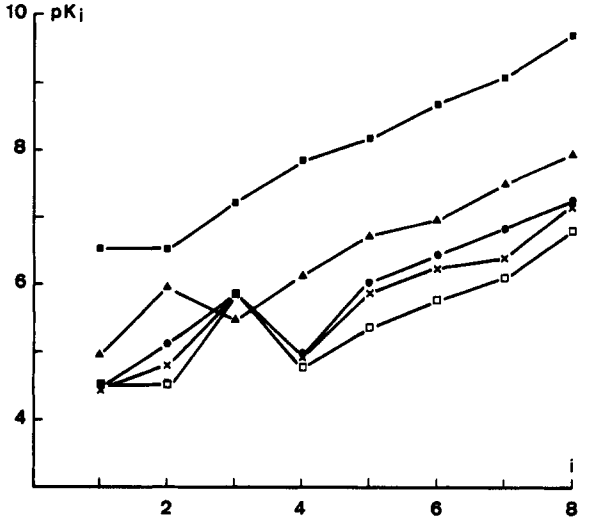


**Figure 4.** Stepwise ionization constants p$K_i$ as a function of $i$ ($N$ = 8) for syndiotactic PMA. No added salt (■). Ionic strength of $NaClO_4$: 0.02 M (▲); 0.1 M (●); 0.2 M (×); 0.5 M (□).

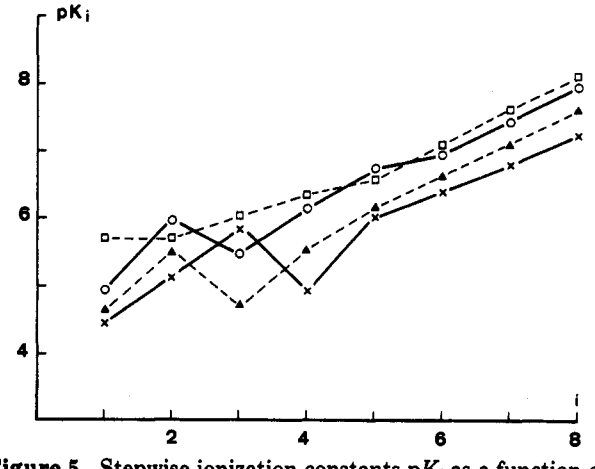


**Figure 5.** Stepwise ionization constants p$K_i$ as a function of $i$ ($N$ = 8). For syndiotactic PMA. Ionic strength of $NaClO_4$: 0.02 M (○); 0.1 M (×). For isotactic PMA. Ionic strength of $NaClO_4$: 0.02 M (□); 0.1 M (▲).

For PAA, as no conformational transition occurs, the p$K_i$ value increases monotonously because of the electrostatic interactions. Addition of a neutral salt induces a decrease of the p$K_i$ especially at high $i$ values. Nevertheless, this effect also exists even at $i$ = 1 due to the autodissociation of PAA.

For syndiotactic PMA, the conformational transition is evidenced by a strong increases of the p$K_i$ value between $i$ = 2 and 3 due to the close vicinity of the carboxyl groups

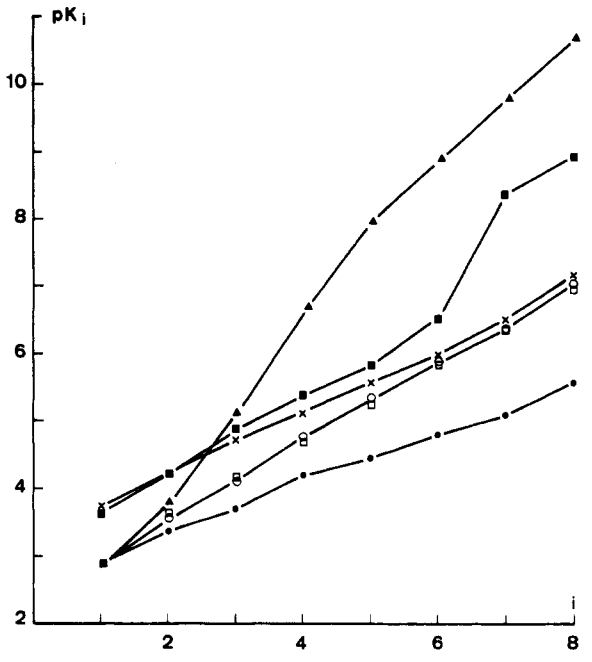


**Figure 6.** Stepwise ionization constants p$K_i$ as a function of $i$ (N = 8). Ionic strength of $NaClO_4$ = 0.1 M: PVA (▲); PNMASN (■); PAA (×); PNMAS (○); PNMG (□); PNMA (●).

in the compact conformation. When electrostatic interaction overcome the cohesive forces, the p$K_i$ suddenly decreases upon unfolding of the structure then increases again by increase of the average charge. The p$K_2$ value is very sensitive to ionic strength.

The conformational transition occurs in the same range for $I$ = 0.1–0.5 and is shifted toward lower $i$ values when the ionic strength decreases. At the same time all the p$K_i$ values increase.

The effect of tacticity is shown in Figure 5. At constant ionic strength, the conformational transition occurs more rapidly for the isotactic sample of PMA because, in this case, the electrostatic interactions are maximum. The p$K_i$ values are also higher at each $i$ value. For iPMA in 0.02 M $NaClO_4$, the compact conformation is very unstable and has completely disappeared at $i$ = 2.

Figure 6 shows the effect of the chain length and of the presence of an added group, ionizable or not, in the side chain of the repeat unit. In PNMA, the ionizable group is further away from the main chain, and thus from other groups, compared to PAA. The p$K_i$'s of PNMA are always lower than those of PAA, and the difference increases on increasing $i$.

When two carboxyl groups are present in the side chain, as in PNMG or PNMAS, the situation is intermediate: at low $i$ values, only the first carboxyl group of each side chain is ionized (in the model molecule p$K_1$ = 2.18 or 1.94 and p$K_2$ = 4.18 or 3.71, respectively[23]). In this case, PNMG and PNMAS behave as PNMA. At high $i$ values, the two carboxyl groups of each side chain ionize and both polymers behave as PAA because the distance between the two carboxyl groups is nearly the same as in PAA: two or three intermediate carbon atoms in PNMAS and PNMG, three in PAA, against nine in PNMA.

PNMASN should have the same p$K_1$ value as PNMA, based on their related structure. In fact, PNMASN has a higher value. This is due to the formation of hydrogen bonds between the carboxyl group and the primary amide group in one or two vicinal side chains.

In the case of PVA, p$K_i$ increases regularly but very steeply. For this sample, the electrostatic interactions

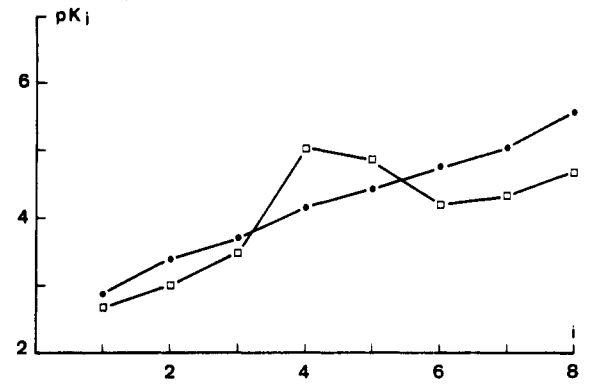


**Figure 7.** Stepwise ionization constants $pK_i$ as a function of $i$ ($N = 8$). Ionic strength of $NaClO_4$ = 0.1 M: PNMA (●); P50 (□).

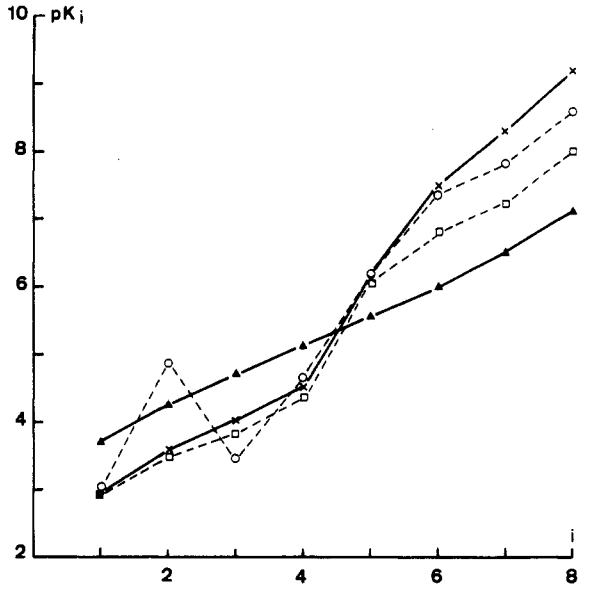


**Figure 8.** Stepwise ionization constants $pK_i$ as a function of $i$ ($N = 8$). Ionic strength of $NaClO_4$ = 0.1 M: PAA (▲); Mac/EVE (×); Mac/MVE (□) (ref 2); Mac/BVE (○) (ref 2).

are very strong because the positive charges are located very close to the main chain.

P50 (polymer 2 in Figure 1) is a random copolymer of the analogue of PNMA and of *N*-phenylmethacrylamide. The incorporation of this aromatic hydrophobic residue has many effects:

(1) The average distance between charges is decreased, which should decrease the $pK$ values.

(2) The local dielectric constant decreases, which should increase the electrostatic repulsions.

(3) In addition, this copolymer has a very tight compact conformation at low $\alpha$ values.[20,21]

Figure 7 shows that the "dilution" effect is predominant since the $pK_i$ values of P50 are lower than those of PNMA except for $i = 4$ and 5 where the conformational transition occurs.

Figure 8 presents results obtained with copolymers of maleic acid with alkyl vinyl ethers of various chain length.

For Mac/EVE (maleic acid/ethyl vinyl ether), no conformational transition exists. The first four values of $pK$ are lower than that of PAA by a "dilution effect," but then $pK$ suddenly increases when the second acid group ionizes. The curve thus reflects the two-step ionization of this polymer.

On the same figure are reported results obtained by Strauss et al.[2] with the lower and upper analogue of Mac/EVE with a methyl and butyl side chains (Mac/MVE and Mac/BVE, respectively). Both copolymers present the two-step ionization with an additional change for Mac/BVE at low $i$ values corresponding to its conformational transition.

The results presented in this paper show that the method proposed by Strauss and co-workers[2] may be successfully applied to polymers and copolymers having different structures. The effect of side-chain length, density of charge, tacticity, and ionic strength are clearly shown in the evolution of the successive ionization constants $pK_i$. Conformational transitions can also be demonstrated by this method.

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**Registry No.** **1a** (homopolymer), 9003-01-4; **1b** (syndiotactic homopolymer), 25750-36-1; **1b** (isotactic homopolymer), 25068-55-7; **1c** (homopolymer), 77349-79-2; **1d** (homopolymer), 108417-17-0; **1e** (homopolymer), 107709-62-6; **1f** (homopolymer), 105502-49-6; **2** (copolymer), 77349-80-5; $NaClO_4$, 7601-89-0.