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Acid–Base and Metal Ion Complex Formation Properties of Polymers Containing Amino Acid Residues

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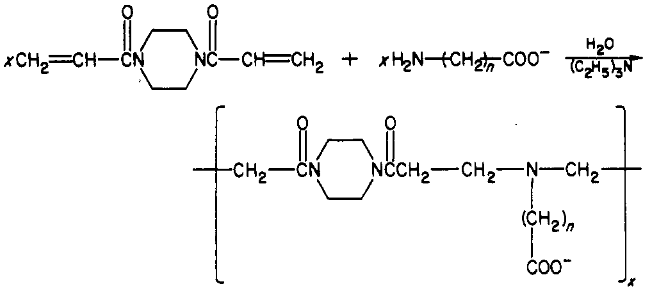
ABSTRACT: The basicity and Cu(II) ion complexation of polymers containing amino acid residues, carrying a tertiary amino group in the main chain and a carboxylic group as the side-chain substituent, have been studied in aqueous solution by potentiometric, viscosimetric, and spectrophotometric techniques. Both protonation constants of each polymer follow the modified Henderson–Hasselbach equation. The protonation of a given unit, with one exception, becomes more and more difficult as the degree of protonation of the whole macromolecule increases. A new method of computation for evaluating the stability constants of polymer–metal ion complexes from potentiometric data has been developed. The log β of the CuL^+ complex (L being the repeating unit of the polymers) decreases with increasing pH, even if the spectrophotometric parameters of the complex remain constant.

Introduction

The acid–base properties of polyelectrolytes have been extensively studied by potentiometric titration[1] and recently St. Pierre et al. proposed as a definition of the polyelectrolyte effect the difference in the apparent pK values at the extremes of the titration curve for a polyacid or polybase.[2] In other words, a polymer exhibiting a strong polyelectrolyte effect shows a large change in pK on going from the uncharged state to the charged state. On the contrary, two families of polyelectrolytes exhibit basicity constants that are independent of the overall degree of protonation of the macromolecule: poly(diazacrown ethers)[3] and poly(amido amines).[4] Both series show a bulky group in their structures (i.e., macrocycles or acryloylpiperazine ring), which shelter the positive charges on the protonated nitrogens. Also, no cooperative effects between nitrogen groups belonging to different units take place in complex formation; thus "real" stability constants could be obtained with these two series of ligands.

On the other hand, we have recently found that other amino polymers, which contain tertiary amino groups in the main chain, and are structurally related to poly(amido amines), for instance poly(β-amino sulfones)[5] and poly(β-amino ketones),[5] exhibit intermediate behavior between poly(amido amines) and "classical polyelectrolytes". As a further development of our studies on poly(amido amine) chemistry, we thought it interesting to investigate the protonation and Cu^{2+} complexation of polymeric amino acids having the structure of poly(amido amines) bearing carboxyl groups as side substituents, obtained by the polyaddition of ω-amino acids to 1,4-diacryloylpiperazine[6] according to a general synthetic route (Scheme I) for this class of polymers[7].

Scheme I



PAAA$_n$
$n = 1, 2, 4, 5$

It was immediately apparent that these new polyelectrolytes did not follow the pattern usually found in poly(amido amines), since the basicity and the complexing ability of the ionic groups of each unit did depend on the overall degree of protonation and complexation of the whole macromolecule. In order to study these polymers in solution, it was necessary to use a method of calculation different from those previously used in the case of poly(amido amines).[8] As far as protonation was concerned, a method had been already developed. However, the methods of calculation described in the literature[9] for determining the stability constants of metal ion complexes of polyelectrolytes whose repeating units do not behave independently were not entirely satisfactory, especially as a clear picture of the trend followed by these constants as a function of pH, in the case of polyelectrolytes whose basicity constants also depend on pH, was needed.

The aim of this paper is to report the synthesis of the above new family of polyampholytes, a new method of

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Table I
Protonation: Experimental Details of the Potentiometric Measurements at 25 °C in 0.1 M NaCl

reacn	α range	pH range	$T_L \times 10^3$,[a] mol	$T_H \times 10^3$,[b] mol	C_T,[c] mol dm^{-3}	points[d]
			PAAA$_1$			
$L^- + H^+ \rightleftharpoons LH^\mp$	0.79–0.21	7.70–9.14	0.4147	0.5727	−0.1288	19
	0.63–0.24	8.05–9.18	0.2847	0.8775	−0.1343	16
$LH^\mp + H^+ \rightleftharpoons LH_2^+$	0.14–0.44	2.61–2.08	0.3895	0.3895	0.5160	14
	0.20–0.44	2.46–2.11	0.3798	0.3798	0.5160	11
			PAAA$_2$			
$L^- + H^+ \rightleftharpoons LH^\mp$	0.75–0.21	8.01–9.18	0.3745	0.8761	−0.1535	34
	0.71–0.21	8.06–9.17	0.3626	0.7276	−0.1401	25
	0.73–0.21	8.03–9.16	0.3586	0.7344	−0.1393	28
$LH^\mp + H^+ \rightleftharpoons LH_2^+$	0.72–0.21	3.13–4.34	0.3745	0.8761	−0.1535	44
	0.72–0.22	3.04–4.23	0.3626	0.7276	−0.1401	40
	0.72–0.22	3.07–4.28	0.3586	0.7344	−0.1393	39
			PAAA$_4$			
$L^- + H^+ \rightleftharpoons LH^\mp$	0.79–0.21	7.85–9.12	0.3331	0.8313	−0.1528	33
	0.80–0.20	7.81–9.09	0.3031	0.8070	−0.1258	37
$LH^\mp + H^+ \rightleftharpoons LH_2^+$	0.79–0.21	3.59–4.90	0.3331	0.8313	−0.1528	37
	0.79–0.20	3.61–4.87	0.3031	0.8070	−0.1258	41
			PAAA$_5$			
$L^- + H^+ \rightleftharpoons LH^\mp$	0.72–0.22	8.02–9.11	0.3301	0.9067	−0.1393	27
	0.77–0.21	7.86–9.10	0.2289	0.5560	−0.1286	26
	0.74–0.28	7.96–8.97	0.2686	0.6326	−0.1399	17
$LH^\mp + H^+ \rightleftharpoons LH_2^+$	0.76–0.20	3.76–4.93	0.3301	0.9067	−0.1393	30
	0.80–0.21	3.64–4.87	0.2289	0.5560	−0.1286	30
	0.80–0.20	3.65–4.92	0.2686	0.6326	−0.1399	23

[a] Initial amount of ligand. [b] Initial amount of hydrogen ion. [c] Titrant concentration (negative values indicate titrations with NaOH). [d] Number of points from titration curve.

calculation for determining their complex stability constants, and their acid–base and complexing properties.

Experimental Section

Synthesis. Polymers. 1,4-Diacryloylpiperazine (5.0 g, 0.0258 mol), dissolved in water (10 mL), was added to an aqueous solution (10 mL) of the appropriate amino acid (0.0258 mol) and triethylamine (4.2 mL, 0.030 mol). The mixture was kept in an ice bath under an inert atmosphere for 0.5 h and then at room temperature for 7 days. After this time the solution was run on an Amberlite IRC 50 (C. Erba, ACS grade) column in order to eliminate $(C_2H_5)_3NH^+$ and then evaporated to a small volume in vacuo.

The polymer was finally recovered by diluting with a large excess of acetone, filtering, and drying to constant weight at room temperature (0.1 torr): PAAA$_1$ (from glycine), potentiometric purity 86%, $[\eta]_{H_2O}^{30^\circ C} = 0.12$ dL/g; PAAA$_2$ (from β-alanine), potentiometric purity 89%, $[\eta]_{H_2O/CH_3OH}^{30^\circ C} = 0.12$ dL/g; PAAA$_4$ (from δ-aminovalerianic acid), potentiometric purity 82%, $[\eta]_{H_2O}^{30^\circ C} = 0.18$ dL/g; PAAA$_5$ (from ϵ-aminocapronic acid), potentiometric purity 91%, $[\eta]_{H_2O}^{30^\circ C} = 0.17$ dL/g.

Models. The corresponding low molecular weight models MAAA$_1$ (from glycine) and MAAA$_2$ (from β-alanine) were synthesized in a similar way as previously reported,[4c] starting from the corresponding amino acids and *N*-acryloylmorpholine in a 1:2 molar ratio.

Emf Measurements. Potentiometric measurements were performed according to a previously described procedure,[4c] using a digital pHM-84 Radiometer potentiometer, an Ag/AgCl reference electrode, on Orion 91 01 00 glass electrode, and a salt bridge containing a 0.1 M NaCl solution. The potentiometric apparatus and titration apparatus were automatically controlled by a Rockwell AIM 65 minicomputer. All titrations were carried out in a constant-temperature cell at 25 °C. Presaturated nitrogen was kept over the surface of the cell to prevent carbon dioxide adsorption.

The basicity constants were determined by the addition of 0.1 N NaOH solution to an aqueous polymer solution containing a large excess of H^+. In the case of PAAA$_1$ the basicity constant relative to the carboxyl group was determined by the addition of 0.5 M HCl to an aqueous polymer solution. Formation constants for the Cu(II) complexes were determined by adding standard NaOH solution to an acidic solution containing a (1–3)/1 molar ratio of polymeric amino acid to copper nitrate. All polymer solutions were prepared immediately before use. At least two independent titrations were performed for each system. The experimental details are reported in Tables I and II.

Table II
Cu(II) Complex Formation: Experimental Details of the Potentiometric Measurements at 25 °C in 0.1 M NaCl

pH range	$T_L \times 10^3$,[a] mol	$T_M \times 10^3$,[b] mol	$T_H \times 10^3$,[c] mol	C_T,[d] mol dm^{-3}	points[e]
		PAAA$_1$			
2.3–4.4	0.2818	0.2995	0.8178	0.0871	24
2.5–3.4	0.2818	0.1184	0.5554	0.0871	16
2.3–3.6	0.2619	0.0873	0.8541	0.1340	20
		PAAA$_2$			
3.3–3.8	0.3536	0.1785	0.7285	0.0871	13
2.8–3.8	0.3354	0.1064	0.8484	0.1503	12
3.2–3.8	0.3337	0.3148	0.9087	0.1503	8
4.0–6.4	0.3536	0.1785	0.7285	0.0871	27
3.8–6.0	0.3354	0.1064	0.8484	0.1503	13
3.8–4.8	0.3337	0.3148	0.9087	0.1503	17

[a] Initial amount of ligand. [b] Initial amount of metal ion. [c] Initial amount of hydrogen ion. [d] NaOH titrant concentration. [e] Number of points from titration curve.

E° calibrations were performed before and after each titration. The concentration of hydrogen ions was calculated from the emf values (in mV) by means of the formula $[H^+] = \exp(E - E^\circ)/25.693$.

The basicity constants were computed for each titration by the APPARK program, as described elsewhere,[5a] operating on the Rainbow 100 minicomputer purchased from Digital Equipment Corp.

Viscosity Measurements. The viscosity measurements were performed with a Cannon Ubbelohde 50 E 988 viscosimeter having a flow time of 210 s for aqueous 0.1 M NaCl at 25 °C. Corrections for kinetics energy and rate of shear were found to be negligible.

A weighed amount of polymer (ca 0.100 g) was dissolved in 0.1 M NaCl, and an equimolecular quantity of 0.1 M NaOH was added in order to obtain an alkaline poymer solution (15-mL total volume). Pure CO_2-free water was used throughout, and the solutions were used immediately after preparation. The solutions were titrated with 0.1 M HCl. The percentages of the different ionic species present in solution were computed by means of the FITH program as described elsewhere.[5a]

In the case of complex formation, $PAAA_1$ or $PAAA_2$ solutions (ca. 0.100 g in 15 mL) were titrated with 0.1 M aqueous $Cu(NO_3)_2$ after pH adjustment at the lowest value reached in the protonation.

Spectrophotometric Measurements. The electronic spectra were recorded at 25 °C on a Perkin-Elmer 320 spectrophotometer using 1-cm^3 silica cells. Spectrophotometric titrations were performed in a similar way on either $PAAA_1$ or $PAAA_2$ complexes. A 0.03 M aqueous solution of the polymer was added with 0.1 M $Cu(NO_3)_2$ solution to obtain a polymer/Cu^{2+} ratio of 2/1. A 0.1 M HCl solution was added in order to adjust the pH to a value of 2.5. The titrations were carried out with 0.1 M NaOH solution. After each step the absorbances were measured and the ϵ values calculated by means of the species distribution given by the program FITH previously described.[5a] The same procedure was carried out with the corresponding nonmacromolecular models.

Other Reagents. CO_2-free NaOH solutions were prepared, stored, and standardized as described elsewhere.[10] Stock solutions of 0.1 M NaCl were prepared from sodium chloride (C. Erba, ACS grade) without further purification and were used as the ionic medium for the potentiometric, viscosimetric, and spectrophotometric measurements. Copper(II) nitrate solution was prepared with decarbonated water with a C. Erba RPE grade product. To prevent hydrolysis the solution was slightly acidified with nitric acid, and the acidity was determined potentiometrically. The titer of copper(II) solution was checked gravimetrically.[11]

Method of Computation

At each point of the titration curve an equilibrium is established among different species whose general formula is $H_pM_qL_r$ (charges are omitted for clarity and the OH ion is indicated by H^-). The concentration of $H_pM_qL_r$ is given by

$$[H_pM_qL_r] = \beta_{pqr}[H]^p[M]^q[L]^r \qquad (1)$$

where β_{pqr} is the formation constant of the species under consideration and [H], [M], and [L] are the concentrations at equilibrium of the hydrogen ion, of the free metal ion, and of the free ligand, respectively. For each point the mass balance equations (2)–(4) must hold, where C_M, C_L,

$$C_M = [M] + \sum_q \beta_{pqr}[H]^p[M]^q[L]^r \qquad (2)$$

$$C_L = [L] + \sum_r \beta_{pqr}[H]^p[M]^q[L]^r \qquad (3)$$

$$C_H = [H] + \sum_p \beta_{pqr}[H]^p[M]^q[L]^r \qquad (4)$$

and C_H are the analytical concentrations of the metal, ligand, and acid respectively, the sum being extended over all the species $H_pM_qL_r$ that are assumed to be present in solution. For a given value of the formation constants, the set of simultaneous equations (2)–(4) is solved for the unknowns [H], [L], and [M] at each titration point by the Newton–Raphson method.[12]

In the case of "sharp" stability constants, their refinement is then usually accomplished by the minimization of $U = \sum_i(y_i(\text{obsd}) - y_i(\text{calcd}))^2$, where y is a titer parameter.[8,13] In the case of polyelectrolytes, the "apparent" stability constants depend on pH[14] so that each titration point must be treated independently unless the functional dependence of the stability constants is known in advance. This is actually the case for protonation constants by using the generalized Henderson–Hasselbach equation

$$\log K = \log K^\circ + (n - 1) \log [(1 - \alpha)/\alpha] \qquad (5)$$

where stepwise constants are used, $\alpha = [LH_i]/C_L$ and, in the case of sharp constants, $n = 1$. This equation merely represents a convenient manner of representing the variation of log K with varying charge, but with its application the refinement of protonation constants can be performed by the standard methods with only minor modifications.

An analogous generalized expression is not known in the case of metal complexes, so that we have written a Basic program, which for each titration point refines the stability constant of the species with respect to the previous point by choosing as titer parameter the pH[15] and solving eq 6 iteratively

$$pH_{obsd} = pH_{calcd} + (\partial pH/\partial\beta)\Delta\beta \qquad (6)$$

in the form

$$\Delta\beta = (pH_{obsd} - pH_{calcd})/(\partial pH/\partial\beta) \qquad (7)$$

where the derivative is evaluated numerically. The convergence of the procedure is usually very rapid, and the results compare very well in the case of "sharp" constants with those obtained by the program MINIQUAD.[8]

Furthermore, a plot of the values of log β's computed at the different titration points shows an oscillatory behavior around a mean value for sharp constants, while the trend is monotonic in the case of "apparent" constants. This allows an unbiased discrimination between the two situations. All the programs were run on different microcomputers (Rainbow 100 Digital, Victor Harden, North Star) and are available on request. Whenever the relevant stability constants are "sharp", the determination of the absorbances of the different complexes can be performed with the previously described program FIT,[4e] which determines by a least-squares method any set of observables that are linear functions of the concentrations at the equilibrium. Both "sharp" and "apparent" protonation constants can be handled by the use in the latter case of the generalized Henderson–Hasselbach equation (5).

When the stability constants are "apparent" the same program has been used, but different values of the stability constants at the different titration points have been given to the computer by means of a previously determined curve of log β vs. pH.

Results and Discussion

Protonation Studies. Viscosimetric Measurements. The reduced viscosities η_{sp}/C (with C in g/dL) of all the polymeric amino acids studied plotted against the percentage of different ionic species present in aqueous solution steadily decrease to a critical value corresponding to the maximum formation of the L^-H^+ zwitterionic form. This phenomenon is more pronounced as the number of methylene groups between the amino and carboxyl groups decreases. After the minimum value has been reached, the viscosities remain constant up to and beyond the point of complete protonation of the polymers (Figure 1). This phenomenon is apparently due to a decrease of the size of the macromolecular coil on passing from the L^- to the L^-H^+ form due to an internal neutralization of charges.

In the second protonation step, the macromolecule only has a positive charge on the nitrogen group in the main chain due to the complete neutralization of the carboxyl group, and this does not induce any further change in the extension of the macroion. It may be observed that poly(amido amines) containing only one basic nitrogen per repeating unit in the main chain do not show viscosity changes on neutralization.[4c] In the case of polymeric amino acids, it is reasonable to hypothesize dipolar interactions between different units of the same macromolecule, leading to a more compact structure when passing from the L^- to an L^-H^+ form.[16] This effect is more pronounced with more hydrophilic, and hence more solvated and extended, structures. As proton uptake proceeds, even if the zwit-

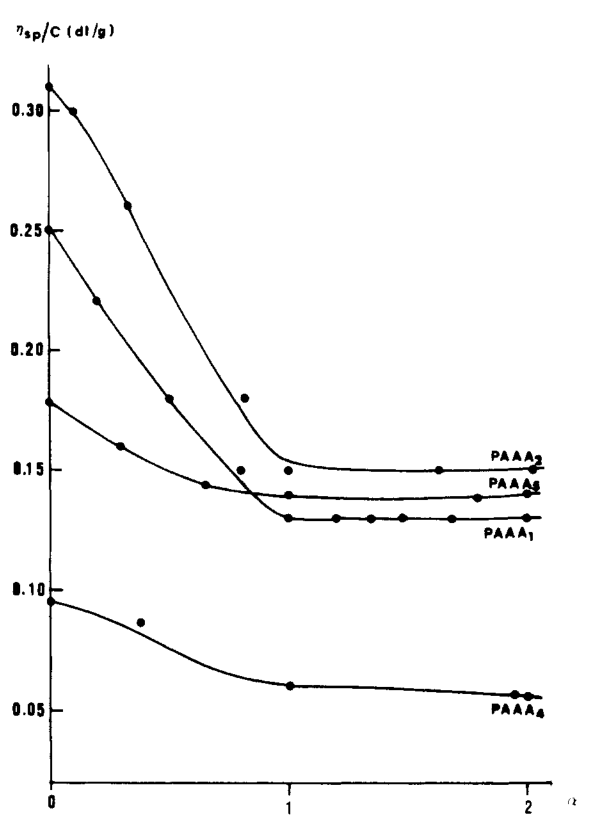


Figure 1. Variation of the reduced viscosity η_{sp}/C of polymeric amino acids PAAA$_n$ vs. the protonation degree α (α = 0, 100% L$^-$; α = 1, 100% LH$^\pm$; α = 2, 100% LH$_2^+$).

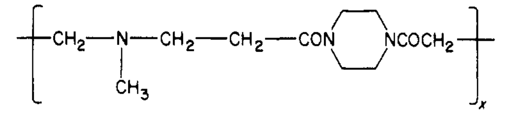
Table III
Basicity Constants of Polymeric Amino Acids at 25 °C in 0.1 M NaCl

compd	reacn	log $K^{\circ\ a,b}$	n^a
PAAA$_1$	$L^- + H^+ \rightleftharpoons LH^\pm$	8.30 (2)	1.07 (3)
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	2.01 (1)	0.80 (7)
PAAA$_2$	$L^- + H^+ \rightleftharpoons LH^\pm$	8.52 (2)	1.14 (2)
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	3.57 (4)	1.23 (1)
PAAA$_4$	$L^- + H^+ \rightleftharpoons LH^\pm$	8.47 (2)	1.10 (1)
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	4.21 (1)	1.12 (2)
PAAA$_5$	$L^- + H^+ = LH^\pm$	8.50 (1)	1.16 (1)
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	4.28 (1)	1.08 (1)

[a] The values in parentheses are standard deviations. [b] $\log K_i = \log K^\circ + (n - 1) \log [(1 - \alpha)/\alpha]$.

terionic state vanishes, this more compact structure is apparently retained. This is also not very easy to explain by considering that in some examples of amphoteric polyelectrolytes,[17] the reduced viscosity reaches a minimum at the isoelectric point. It may be observed, however, that the hydration shell of a carboxylate ion is bigger than that of a tertiary ammonium ion.[18] Consequently LH$_2^+$ is not equivalent in this respect to L$^-$, even if the absolute value of the net charge is equal.

Basicity Constants. The values of the protonation constants of all the polymers studied in the present work are reported in Table III. Both protonation constants of each polymer follow the modified Henderson–Hasselbach equation in the $0.2 < \alpha < 0.8$ region.[14] The log K_1 values, corresponding to the protonation equilibrium of the nitrogens, increase markedly on passing from PAAA$_1$ to PAAA$_2$ and then remain constant along the series to PAAA$_5$. The n values (see Method of Computation eq 5) pertaining to log K_1 are always >1 and are very similar in all cases, indicating that the protonation of a single basic nitrogen becomes more and more difficult as the degree of protonation (α) of the whole macromolecule increases. At the same time, a significant conformational change takes place, as indicated by viscosimetric measurements (see above). This behavior is different from that of poly(amido amines) having no carboxylate group as side substituent, such as, for instance



In this case, however, no major conformational changes take place upon protonation of the basic nitrogens, since no variations in viscosity are observed.[4c] In the case of polymeric amino acids, passing to a more compact structure brings the positive ions closer and closer, resulting in more difficult protonation of the uncharged groups. The almost constant value of n in all the polymeric amino acids considered strongly supports this point of view. The addition of the second proton to the polymeric amino acids in their zwitterionic form leads to the neutralization of the negative COO$^-$ charges. log K_2 values increase with the number of methylene groups between the nitrogen and COO$^-$ groups, and the basicity constants determined are very close to the corresponding values obtained for nonpolymeric amino acids.[19] With the exception of PAAA$_1$, the n values relative to log K_2 are >1 and decrease from PAAA$_2$ to PAAA$_5$, reaching a value very close to 1 for the last polymer. This means that the tendency of each carboxylate ion to take up a proton becomes less and less influenced by the overall negative charges of the whole macromolecule as its distance from the main chain increases. This is precisely what would be expected.

Contrary to the other polymeric amino acids considered, the n value of log K_2 of PAAA$_1$ is <1. This means that the approach of incoming protons to COO$^-$ groups becomes easier and easier as the degree of protonation of the whole macromolecule increases, i.e., as the number of negative charges decreases. Even though some similar cases have been described in the literature in the case of polymeric bases,[20] no simple explanation of the anomalous behavior of PAAA$_1$ with respect to the homologous polymeric amino acids described in this paper can be found. Further calorimetric and spectrophotometric work can elucidate whether different polymer conformations can explain the observed trend as a function of pH, as it has been previously invoked for some polymeric acids.[21]

Cu^{2+} Complex Formation Studies. Only PAAA$_1$ and PAAA$_2$ are able to form Cu^{2+} complexes in aqueous solution. The addition of Cu^{2+} to a solution of the other polymeric amino acids in their zwitterionic form causes a phase separation to occur, while at acidic pHs the solutions are not colored, showing no complex formation.

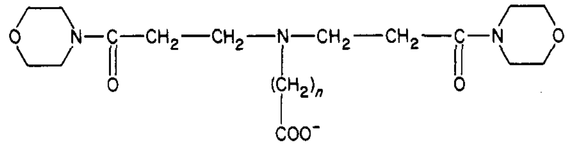
Viscosimetric Measurements. Viscosimetric measurements have been performed after adding increasing amounts of Cu^{2+} ions to aqueous solution of PAAA$_1$ and PAAA$_2$ in the pH ranges 3.4–2.0 and 4.1–3.5, respectively, i.e., after the minimum critical value has been reached (see above).

No significant changes in the viscosity on complexation have been observed. This indicates that no major conformational change takes place. It may be observed that complex formation induces a decrease in viscosity in the case of other poly(amido amines) previously described,[4i] when the coordinating nitrogen groups are placed on the main chain, but in the case of other "branched" poly(amido amines) no noticeable variation of η_{sp}/C has been noted.[4i] This behavior was explained by the fact that the conformational transitions involved in the complex formation only regard side substituents and do not alter substantially

Table IV
Stability Constants and Electronic Spectra of Cu^{2+} Complexes of Polymeric Ligands and Their Nonmacromolecular Models at 25 °C in 0.1 M NaCl

compd	reacn	pH range	log β	ε,[a] $dm^3\ mol^{-1}\ cm^{-1}$	λ_{max}, nm
$PAAA_1$	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	2.5–4.0	9.0–8.3	32	735
$PAAA_2$	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	4.0–6.4	6.5–5.8	53	745
	$L^- + H^+ + Cu^{2+} \rightleftharpoons CuHL^{2+}$	3.0–3.8	10.5	39	790
$MAAA_1$[b]	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	2.3–3.8	9.98 (2)[b]	36	730
$MAAA_2$[b]	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	2.8–7.6	6.05 (6)[b]	50	740
	$L^- + H^+ + Cu^{2+} \rightleftharpoons CuHL^{2+}$	2.8–7.6	10.8	35	785

[a] Molar absorption coefficients. [b] Obtained with the program SUPERQUAD (values in parentheses are the standard deviations).



the characteristics of the main chain.

Stability Constants. Several titration curves were carried out at different polymer/Cu^{2+} ratios. The equilibrium constants relative to the Cu^{2+} complex formation for each point of the titration curve were calculated by taking into account the dependence of log K's on pH via the Henderson–Hasselbach equation (see Method of Calculation). The calculation is valid only if the formation of a single complex species is considered. Therefore it was necessary to know the pH region in which it is formed. This was determined by analogy with the species formed at various pHs by nonmacromolecular models purposely synthesized, having a structure very similar to that of the repeating units of the polymers (Table IV). By analyzing the titration curves relative to the models using the program SUPERQUAD,[22] we deduced that two complex species, $CuHL^{2+}$ and CuL^+, are present with $MAAA_2$ and only the one species, CuL^+, with $MAAA_1$ (see Table IV). Subsequently by analyzing the corresponding titration curves of the Cu^{2+}–polymer systems with the program SUPERQUAD, we found that the same species are present, and we were able to obtain a rough idea of the pH regions in which they are formed and the average values of their stability constants. The presence of these Cu^{2+}–polymer complexes was also confirmed by the analysis of the EPR spectra.[23] By choosing the pH region in which only one species is present, we were able to evaluate its stability constant with our method of computation for each titration point. In the case of the Cu^{2+}–$PAAA_2$ system, the constant relative to the $Cu^{2+} + L^- + H^+ \rightleftharpoons CuHL^{2+}$ equilibrium was computed in the pH range ~3–4. For all three Cu^{2+}/polymer ratios this species is only present in small amounts in solution, reaching a maximum of about 20% with respect to total L for a ratio of 1/1, and its equilibrium constant appears to be independent of pH.

The stability constant of the CuL^+ species was computed at each pH value by assuming a "sharp" value for the $CuHL^{2+}$ species. It appears that the CuL^+ stability constant decreases regularly with pH; i.e., it is an "apparent" log β (Figure 3). The results are given in Table IV and Figures 2 and 3.

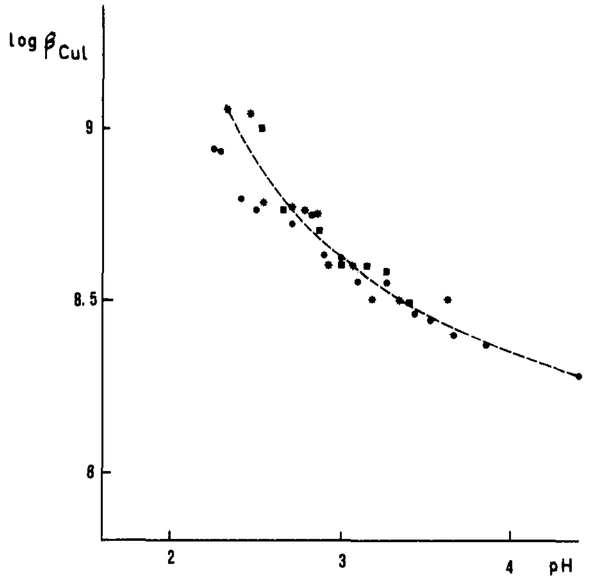


Figure 2. Variation of the $Cu(PAAA_1)^+$ stability constant vs. pH at different [(●) 1/1; (■) 2/1; (*) 3/1] polymer/Cu^{2+} molar ratios.

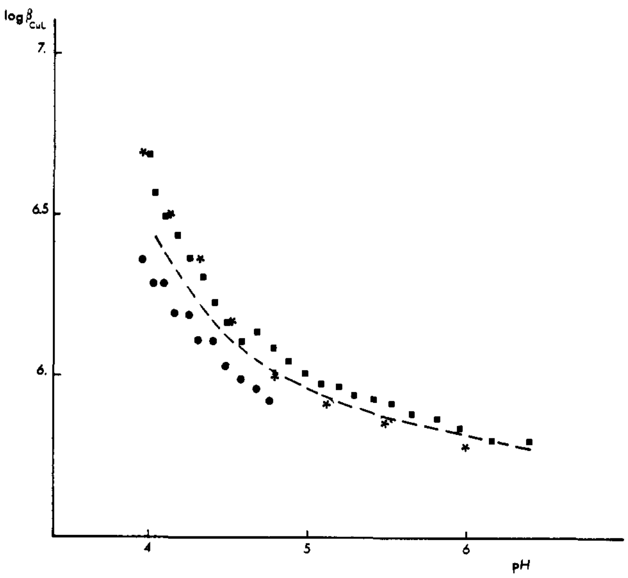


Figure 3. Variation of the $Cu(PAAA_2)^+$ stability constant vs. pH at different [(●) 1/1; (■) 2/1; (*) 3/1] polymer/Cu^{2+} molar ratios.

An analogous mathematical computation on the nonmacromolecular models in the same pH regions gives a fluctuation around 9.98, 10.80, and 6.05, which are the stability constants obtained respectively for the $CuMAAA_1^+$, $CuHMAAA_2^{2+}$, and $CuMAAA_2^+$ complexes obtained with the program SUPERQUAD.

The value of the apparent stability constant of $Cu(PAAA_1)^+$ is always higher than that of $Cu(PAAA_2)^+$, which is consistent with what happens in the case of the corresponding nonmacromolecular models and for glycine (log $\beta = 8.15$) and β-alanine (log $\beta = 7.04$).[24] This indicates that the chelation occurs between the carboxyl and the amino group. It is well-known that the formation of a six-membered chelate ring is less favored thermodynamically than the formation of a five-membered chelate ring. Thus the behavior of these polymers with respect to complex formation is close to that shown by the corresponding simple amino acids glycine and β-alanine.

Electronic Spectra. Electronic spectra of both $PAAA_1$ and $PAAA_2$ in the presence of Cu^{2+} ions at different pHs were measured (Table IV). In the case of the CuPAAA$_1^+$ complex, the position of the absorption maximum is not pH-dependent in the pH range considered for the calculation of the stability constant. Assuming for the concentration of the absorbing species CuPAAA$_1^+$ that obtained from its "apparent" stability constant at each pH, we found a constant value of ϵ that was very close to that of the corresponding complex of the nonmacromolecular model.

In the case of the PAAA$_2$ complexes, a shift in the absorption maximum from 790 nm for the CuHPAAA$_2^{2+}$ species to 740 nm for the CuPAAA$_2^+$ species is observed. The limiting spectrum of the protonated complex species was determined at low pH, and the ϵ value relative to CuPAAA$_2^+$ was computed by taking into account the absorbance of CuHPAAA$_2^{2+}$. In this case, too, a constant value of ϵ was obtained by assuming a variation of the CuPAAA$_2^+$ stability constant with pH. This value is again in agreement with that obtained for the corresponding nonmacromolecular model.

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Magnetic Effects on Photoinduced Emulsion Polymerization. Effects of Lanthanide Ion Addition

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ABSTRACT: Photoinduced emulsion polymerization of styrene with sodium dodecyl sulfate (SDS) as the surfactant and dibenzyl ketone (DBK) as an initiator was significantly prevented at 0 G in the presence of La^{3+}, Gd^{3+}, or Mg^{2+}. At 2000 G good yields of high molecular weight polystyrene were obtained in the presence of La^{3+} or Mg^{2+} but polymerization was significantly prevented in the presence of Gd^{3+}. These results are explained on the basis of a combination of salt effects on micellar structure and magnetic effects on the reactions of geminate triplet radicals in micelles. The presence of salts caused an increase in the size of micelles, which in turn resulted in a reduced efficiency of free-radical escape from the micelles, and the effect of magnetic field on photoinduced emulsion polymerization was counteracted by the presence of Gd^{3+}. The polymerization of methyl methacrylate was found to be unaffected by the addition of these ions in the absence or presence of external magnetic field.

Photoinduced emulsion polymerization provides the potential for combining the advantages of emulsion polymerization, such as the ease of production of high molecular weight polymers at relatively fast rates,[1] with those of the photoinitiation processes,[2] such as the formation of free radicals at low temperatures compared to those required for thermal initiation. The reaction of free radicals in micellar solutions have also been found to be influenced

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