New developments in macroinorganics – the thermodynamics of basic polymers

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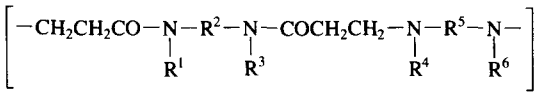
(Received 18 October 1984)

The protonation and complex formation of some basic polymers have been studied in aqueous solution by potentiometric, calorimetric, spectrophotometric and viscosimetric techniques. Specific methods for the treatment of either 'sharp' or 'apparent' thermodynamic functions in polyelectrolyte bearing one or two basic groups in the repeating unit have been developed. The results are related to structure features and presence of various types of chemical function besides the aminic function.

(Keywords: polymeric amines; poly(amido-amine)s; poly(β-aminosulphone)s; poly(β-aminoketone)s; poly(γ-amino-alcohol)s; poly(1,4-piperazinediyl-1-oxotrimethylene); poly[1-(1-piperazinyl carbonyl)ethylene]; poly{1-[(4-methyl-1-piperazinyl)-carbonyl]ethylene}; polyelectrolytes; basicity constants; protonation enthalpies; calculation methods; heavy metal ion complexes)

INTRODUCTION

In previous papers we have studied the synthesis and the physico-chemical behaviour of a family of water-soluble polymers having a regular sequence of aminic and amidic groups along the macromolecular chain[1-8]:



Poly(amido-amine)s may act as heavy metal ion complexing agents in aqueous solution. Complexes have well defined stoichiometries, in particular one metal ion is coordinated to each repeating unit[9,10]. We have found these polymers exhibit 'real' basicity and stability constants, i.e. the basicity and stability constants of each repeating unit are independent of the overall protonation or complexation degree of the whole macromolecule. By virtue of this unusual behaviour the poly(amido-amine)s look like small molecules.

Because of the similarity with some branches of 'classical' inorganic chemistry, these studies are known as 'macroinorganics'[11-14]. As a further development in macroinorganics we have modified the monomeric unit of poly(amido-amine)s in several respects. For example we have substituted the bis-acrylamidic moiety with others having minor size and stiffness[15], or synthesized poly(amido-amine)s bearing aminic groups as side substituents[16,17] (*Table 1*). We have also investigated the effect of carboxyl groups as side substituents in a poly(amido-aminic) structure[18].

In the case of P_3, P_4 and P_5 we have also studied the behaviour towards complexation. Calculation programs purposely written by us were used for the computation of basicity, stability constants and protonation enthalpies.

The aim of this paper is to relate the polyelectrolyte behaviour to the structural characteristics of this series of polymers.

SYNTHESIS

The polymers studied in this work (*Table 1*) have been synthesized according to two different mechanisms: an ionic and a radical one.

The ionic polymerization, that has been followed in the synthesis of the polymers P_1–P_8 is based on the polyaddition by a Michael-type mechanism of bis-secondary amines or amino acids to symmetric difunctional compounds containing activated vinylic groups such as divinylketones[1,9] divinylsulphones[15] or bis-acrylamides[1-4]. The reaction takes place readily in water or alcohols at room temperature and without added catalysts. Aprotic solvents are not recommended if high molecular weight products have to be obtained.

Polymer P_2 is obtained by reducing polymer P_1 in the presence of $LiAlH_4$ in suspension, in refluxing THF[20]. The synthesis of the polymers of the series P_4–P_8 has been carried out in the presence of an equimolecular quantity of NEt_3 to avoid the presence of the zwitterionic form of the ω-aminoacids[21]. The polymer P_9 is synthesized by polyaddition of *N*-acryloylpiperazine obtained *in situ* by acidic removal of the triphenylmethyl group from the corresponding *N*-acryloyl-*N'*-triphenylmethylpiperazine. The radical polymerization has been followed in the synthesis of the polymers with polyvinylic structure bearing the aminic group as side substituents, i.e. P_{10} and P_{11}[16,17,22].

The first polymer was prepared by the radical polymerization of the corresponding monomer 1-acryloyl-4-methyl-piperazine (which was obtained by reaction of acryloyl chloride with *N*-methylpiperazine and in the presence of 2,2'-azoisobutyronitrile (AIBN) as initiator), organic peroxides being liable to react with the tertiary amino group present in this monomer. The synthesis of the polymer P_{11} was instead preceded by the protection of one aminic group of piperazine by the triphenylmethyl group to avoid the self-polyaddition of the monoacylated

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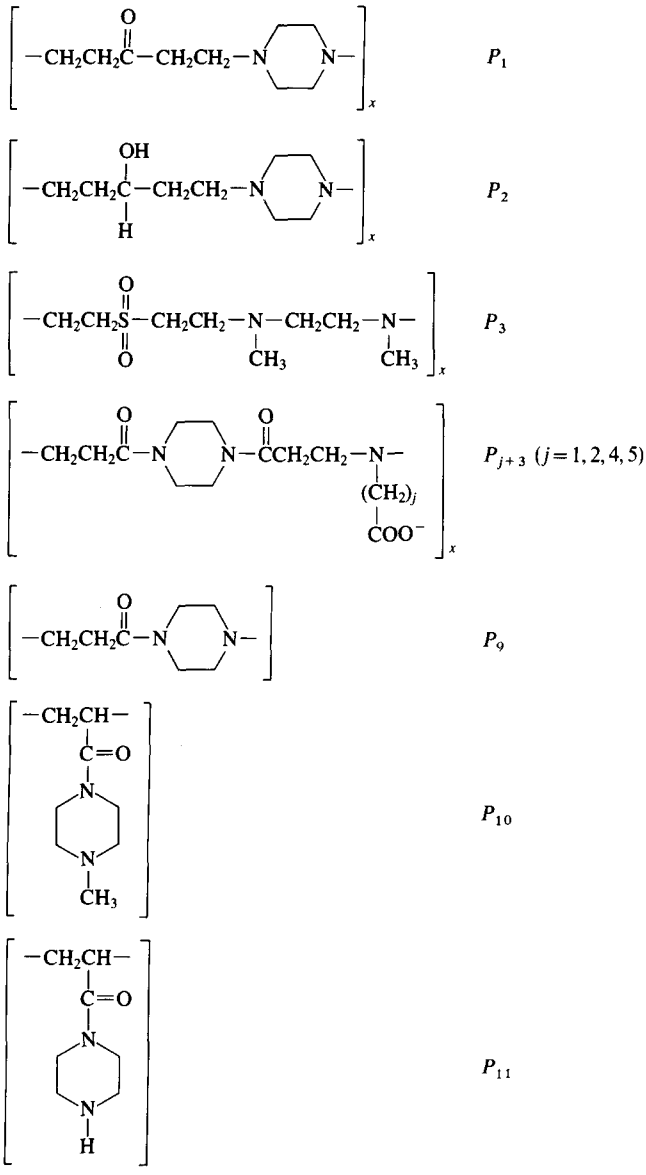
Table 1 Structures of the basic polymers



intermediate with a Michael-type mechanism. After polymerization (performed in benzene or toluene solution by a radical initiator), the triphenylmethyl groups were quantitatively removed from this polymer with hydrochloric acid in aqueous 1,4-dioxane and the product was finally transformed in the free aminic form by treating with a strongly basic anion-exchange resin[17].

METHOD OF CALCULATION

Basicity constants

The computation of the basicity constants from potentiometric data was performed by using the program APPARK previously described[15]. This program, written in Basic, utilizes as input the volume (in ml) of titrant added at each step and the corresponding output voltages together with the analytical data. When more than one basic group is present in each monomeric unit, the computation is possible if the stepwise protonation constant K_i differs by at least 2 orders of magnitude from K_{i-1} so that the ith step can be considered independent from the others and the monomeric unit can be treated as a monoprotic base. Log K_i is computed at each pH value by the well-known Henderson–Hasselbach equation:

$$\log K_i = \mathrm{pH} + \log[\alpha/(1-\alpha)]$$

where α is the degree of ionization $\alpha = [\mathrm{LH}_i]/C_L$, and L the repeating unit of the polymer. As the situation at each point of the titration is equivalent to a buffer solution of LH_i and LH_{i-1}, the concentration of LH_i can be calculated by the formula[23]

$$[\mathrm{LH}_i] = C_{H^+} - [H^+] + [OH^-] + C_L \delta_{OH}$$

by using $-C_{H^+} = C_{OH^-}$ and $\delta_{OH} = 1$ when the titrant is a base and $\delta_{OH} = 0$ when the titrant is an acid.

In the case of typical polyelectrolytes the trend of pK_i as a function of α is described by the modified Henderson–Hasselbach equation:

$$\mathrm{pH} = \log K_i^\circ + n \log(1-\alpha)/\alpha$$

or

$$\log K_i = \log K_i^\circ + (n-1)\log(1-\alpha)/\alpha$$

where $\log K_i^\circ = \mathrm{pH}$ at $\alpha = 0.5$ and $n = 1$ in the case of sharp basicity constants. A linear regression of pH vs. $\log[(1-\alpha)/\alpha]$ in the α-range 0.1–0.8 gives $\log K_i$ and n as the intercept and the slope respectively. The program also gives the standard deviations of the two parameters, the confidence limit of n with a probability of 99% and the correlation coefficient R. The program APPARK has been tested with reference to the MINIQUAD program[24] using several compounds with sharp basicity constants.

Protonation enthalpies

In the case of apparent basicity constants the protonation enthalpies have been calculated by means of the program APPARQ[15], written in Basic, which utilizes as input the heats of a whole calorimetric titration together with the value of the constant and the analytical data. This program can be utilized in a pH-range where only one protonation equilibrium is present and gives as output the value of ΔH_i° for each point by means of the formula:

$$\Delta_{p,q} = \Delta_{dil} + \Delta_w + ([\mathrm{LH}_i]_q - [\mathrm{LH}_i]_p)\,\Delta H_i^\circ$$

where $\Delta_{p,q}$ is the difference of the heats at points p, q, Δ_{dil} is the corresponding difference of dilution heats, Δ_w is the heat due to the formation of water and the concentrations at the points p, q are determined from the value of the apparent basicity constant. In the case of sharp protonation enthalpies it has also been used with another program[15] (FITH) that can take into account more than one protonation equilibrium at a time, by means of the equation:

$$\Delta_{p,q} = \Delta_{dil} + \Delta_w + \sum_{i=1}^{N_T} ([\mathrm{LH}_i]_q - [\mathrm{LH}_i]_p)\Delta H_i^\circ$$

where N_T is the number of different species and the set of the N_T equation is solved for N measured points ($N > N_T$) by the least squares method which also gives the standard deviation σ_i as the square root of the diagonal elements of the variance–covariance matrix. The concentrations are calculated from the mass balance equations by using the Newton–Raphson method[25].

Stability constants

The program used to evaluate the stability constants of polymer metal ion complexes from potentiometric data[18] takes into account the variation of the protonation constants according to the modified Henderson–Hasselbach equation (see above). In particular it calculates the basicity constants for each value of observed pH by means of this equation considering as input the values of log K° and n. Using the basicity constants calculated in such a way and the stability constant to be refined, together with the analytical data, a system of mass balance equations is solved for each titration point by the Newton–Raphson method, giving the equilibrium concentrations of all the species present in solution and in particular a calculated value of pH (pH_{calc}). The program refines the stability constant of the species considered in respect to the previous point by choosing as titre parameter the pH and solving[26] iteratively the equation:

$$pH_{obs} = pH_{calc} + (\partial pH/\partial \beta)\,\Delta\beta \qquad (1)$$

in the form:

$$\Delta\beta = (pH_{obs} - pH_{calc}) \Big/ \frac{\partial pH}{\partial \beta}$$

where β is the stability constant to be refined and the derivate is evaluated numerically. This means that the program iteratively varies β until the difference between the calculated pH and the pH measured by the potentiometer is less than 0.01.

Particular attention has to be paid to the fact in equation 1 that the divergence between pH_{obs} and pH_{calc} is exclusively attributed to a wrong value of the stability constant β and this is possible by virtue of the fact that the basicity constant can be exactly evaluated point by point in the way described above. If it had not been exactly their value, it would have provoked a much more remarkable variation on pH than that induced by the stability constant, and equation 1 would not have been valid. The convergence of this procedure is usually very rapid and the results compare very well in the case of 'sharp' stability constants with those obtained by the program SUPERQUAD[27]*. In fact the values of log β in this case show an oscillatory behaviour around a mean value, the divergence being within the experimental error.

EXPERIMENTAL

Synthesis

All the polymers studied in this paper have been synthesized as previously described[15-17,19,21].

EMF measurements

Potentiometric measurements were performed according to a previously described procedure, using a digital PHM-84 radiometer potentiometer, an Ag/AgCl reference electrode, an Orion 91-01-00 glass electrode, and a salt bridge containing a 0.1 M NaCl solution[7].

The potentiometric and titration apparatus were automatically governed by a Rockwell AIM 65 microcomputer. All the potentiometric titrations were carried out at 25°C in 0.1 M NaCl.

The basicity constants were computed for each titration by the APPARK program (see calculation method) operating on the Rainbow 100 Minicomputer purchased by Digital Eq.

Calorimetric measurements

Calorimetric titrations were performed using a Tronac Model 1250 Calorimeter operating both in the Isoperibol or Isothermal mode using 50 ml or 25 ml reaction vessel respectively[15].

Titrations were performed either by adding HCl to the solutions of the polymer in 0.1 M NaCl or by adding NaOH to a solution of polymer hydrochlorides. The titrant solutions were delivered through a Gilmont buret driven by a synchronous motor. All calorimetric titrations were carried out at 25°C in 0.1 M NaCl and governed by a North Star CCP 930 computer connected to the instrument

The enthalpy values were computed by the APPARQ or FITH programs as described above (see calculation method).

Viscosity measurements

The viscosity measurements were performed with a Cannon Ubbelohde 50E 988 viscosimeter having a flow time of 210 s for aqueous 0.1 M NaCl at 25°C.

Spectrophotometric measurements

The electronic spectra were recorded at 25°C on a Perkin-Elmer 320 spectrophotometer using 1 cm silica cells.

RESULTS AND DISCUSSION

Protonation

The basicity constants of *Table 2* refer to the protonation of the aminic nitrogens. The protonation of the amidic nitrogens of the polymers occurs in a very low pH region (pH < 2), which was not reached in our titrations.

The values of the intrinsic protonation constants (log K°) are in agreement with those already found in the corresponding amines with low molecular weight[28]. As a matter of fact the secondary amino groups present in polymer P_{11} are more basic than the tertiary ones of P_9 and P_{10}. On the other hand, the basicity constant of P_{10} is higher than that of P_9. This may be explained by the fact that the tertiary amino groups of P_9 belong to the macromolecular chain, and consequently, each of them is affected by the $-I$ effect of the carbonyl groups of both the unit to which it belongs and the neighbouring one.

As shown in *Table 2*, with the exception of the second basicity constant of P_3, n is always > 1, therefore, in all cases, log K_i linearly decreases by increasing the overall degree of protonation of the macromolecule. In fact, the approach of the incoming proton becomes more and more difficult as the overall positive charge of the whole macromolecule increases.

This process occurs gradually and therefore, a conformational change at a specific α value can be excluded. By considering the polymers with two aminic nitrogens in the repeating unit (P_1, P_2, P_3) the following trends are observed[15]. In general the n_1 value is higher than that of n_2. Such an effect can be explained by considering that the conformational freedom of the macromolecule decreases

* Details available from Professor R. Barbucci.

Table 2 Basicity constants of polymeric amines at 25°C in 0.1 M NaCl

Polymer	Reaction	$\log K^{\circ a}$	n^a
P_1	$L + H^+ \rightleftharpoons LH^+$	9.09	2.64
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	3.71	2.12
P_2	$L + H^+ \rightleftharpoons LH^+$	7.64	1.35
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	3.33	1.31
P_3	$L + H^+ \rightleftharpoons LH^+$	6.28	1.36
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	2.46	0.92
P_9	$L + H^+ \rightleftharpoons LH^+$	5.89	1.21
P_{10}	$L + H^+ \rightleftharpoons LH^+$	6.09	1.27
P_{11}	$L + H^+ \rightleftharpoons LH^+$	7.13	1.40

[a] $\log K_i = \log K_i + (n-1)\log(1-\alpha)/\alpha$

upon protonation, so that during the second protonation step the different monomeric units can interact with each other less effectively than in the first one. We can also observe that both the n values for the polymer P_1 are higher than the ones relative to the polymers P_2 and P_3 so that, while both the basicity constants of P_1 are undoubtedly apparent, in the last cases they can be considered on the borderline between sharp and apparent. This behaviour can be explained by the greater shielding effectiveness of the CH–OH and the SO_2 groups with respect to the C=O. This is probably related to the large size of the sulphonic group and of the strong hydration of the secondary alcoholic group[29].

The polymers P_9, P_{10} and P_{11} carrying only one aminic nitrogen in the main chain or as side substituent, show a polyelectrolyte behaviour. By comparing these results with those found in the previously studied poly(amido-amine)s, derived from bis-acryloyl-piperazine and showing 'sharp' basicity constants, we can suppose that for P_9 the reduced size of the shielding group is responsible of the interaction between neighbouring amino units, while for P_{10} and P_{11} the flexible polyvinylic chain of the polymer permits a cooperation between the monomeric units.

In the case of P_{11} the relatively high n value can be ascribed to a further interaction via spatial approaching of vicinal secondary aminic nitrogens[17]. This does not occur in the case of P_{10} because of the steric hindrance of the methyl groups.

In *Table 3* the potentiometric results of the poly(amido-amine)s carrying carboxylate groups as side substituents are reported[18]. This family of polymeric amino acids shows a polyelectrolyte behaviour towards protonation. The log K_1 values, corresponding to the protonation equilibrium of the aminic nitrogens, sensibly increase passing from P_4 to P_5, and then remain constant along the series up to P_7. Log K_2 values relative to the carboxylate group increase with the lengthening of the aliphatic chain between the nitrogen and carboxylate groups, and the basicity constants determined are very close to the corresponding values obtained for simple ω-amino-acids[28]. In the case of polymeric aminoacids both the n values are >1 and practically similar along the whole series. In the second protonation step of P_4 an anomalous n value has been found, indicating that the accessibility of proton to $-COO^-$ groups increases with the protonation degree of the whole macromolecule. This is not in agreement with a typical polyelectrolyte behaviour and cannot be simply explained if compared with the homologous series studied in this work.

In this case a polyelectrolyte behaviour has been found even in the presence of diacylpiperazine as shielding group, unlike that previously reported for poly(amido-amine)s. This means that the shielding effectiveness of this group is decreased by the presence of the charged carboxylate groups as side substituents. They are probably responsible of an internal charge neutralization occurring when the polymer is in the zwitterionic form and creating a strain force that partially removes the stiffness of the shielding groups.

In order to ascertain if the variation of the basicity constants with α is due to an enthalpic or entropic effect a calorimetric study has been performed for all the above basic polymers. The results are reported in *Table 4*[15,30]. They are in close agreement with those found for the corresponding non-macromolecular models[15]. Only the ΔH_2° value in P_5 is anomalous when compared to that derived from simple β-alanine[31]. This result was confirmed by the non-macromolecular model purposely synthesized. With the exception of the second protonation step of P_1 and of P_{10}, P_{11} the enthalpies of protonation do not depend on α. This means that the protonation process involves the basic sites only in their microenvironment without altering the neighbouring units.

On the grounds of these results, the variation of the basicity constants with α depends mainly on a variation of ΔS°. The ΔH_2° of P_1 decreases with α till $\alpha = 0.5$ and then remains almost constant[15].

It is interesting to note the behaviour of the polymeric amines of polyvinylic structure P_{10} and P_{11}. In particular the enthalpy change of P_{11} gradually increase with α till $\alpha = 0.5$ and then sharply decrease[17]. This peculiar behaviour, similar to simple amino polymers, such as PVA[32], may be explained by the formation of hydrogen bonds between a protonated nitrogen and the unprotonated nitrogen of a neighbouring unit via a spatial approach.

This process proceeds until $\alpha = 0.5$ when all units are engaged. At $\alpha > 0.5$ the hydrogen bonded structure is then destroyed by further addition of H^+ leading to a decrease of ΔH°.

In the case of P_{10}, ΔH° linearly increases with α. This trend can be explained by considering that the compact coil conformation, assumed by the macromolecule as a consequence of the hydrophobic nature of the polyvinylic chain and the N-methyl groups, breaks down upon protonation leading to an easier accessibility of proton to the residual basic amino groups. No hydrogen bond can be formed owing to the steric repulsion of the methyl groups.

Table 3 Basicity constants of polymeric aminoacids at 25°C in 0.1 M NaCl

Polymer	Reaction	$\log K^{\circ a}$	n^a
P_4	$L^- + H^+ \rightleftharpoons LH^\pm$	8.30	1.07
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	2.01	0.80
P_5	$L^- + H^+ \rightleftharpoons LH^\pm$	8.52	1.14
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	3.57	1.23
P_7	$L^- + H^+ \rightleftharpoons LH^\pm$	8.47	1.10
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	4.21	1.12
P_8	$L^- + H^+ \rightleftharpoons LH^\pm$	8.50	1.16
	$LH^\pm + H^+ \rightleftharpoons LH_2^+$	4.28	1.08

[a] $\log K_i = \log K_i + (n-1)\log(1-\alpha)/\alpha$

Table 4 Thermodynamic values of protonation of the polymers at 25°C in 0.1 M NaCl

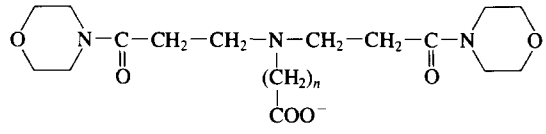
Polymer	Reaction	$-\Delta G^{\circ}$ [a] (kcal mol^{-1})	$-\Delta H^{\circ}$ (kcal mol^{-1})	ΔS° [a] (cal mol^{-1} K^{-1})
P_1	$L + H^+ \rightleftharpoons LH^+$	12.40	$\simeq 6$	[c]
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	5.06	3.8[a]	4.2
P_2	$L + H^+ \rightleftharpoons LH^+$	10.42	5.76	15.6
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	4.54	3.88	2.2
P_3	$L + H^+ \rightleftharpoons LH^+$	8.56	6.49	6.95
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	3.35[b]	2.06[a]	4.4
P_4	$L^- + H^+ \rightleftharpoons LH^{\pm}$	11.32	7.62	12.4
	$LH^{\pm} + H^+ \rightleftharpoons LH_2^+$	2.74	0.60	7.2
P_5	$L^- + H^+ \rightleftharpoons LH^{\pm}$	11.62	8.64	10.0
	$LH^{\pm} H^+ \rightleftharpoons LH_2^+$	4.87	2.57	7.7
P_7	$L^- + H^+ \rightleftharpoons LH^{\pm}$	11.55	8.83	9.1
	$LH^{\pm} + H^+ \rightleftharpoons LH_2^+$	5.74	0.26	18.4
P_8	$L^- + H^+ \rightleftharpoons LH^{\pm}$	11.59	9.17	8.1
	$LH^{\pm} + H^+ \rightleftharpoons LH_2^+$	5.84	0.07	19.4
P_9	$L + H^+ \rightleftharpoons LH^+$	8.03	5.74	7.7
P_{10}	$L + H^+ \rightleftharpoons LH^+$	8.30	6.78[a]	5.1
P_{11}	$L + H^+ \rightleftharpoons LH^+$	9.72	9.29[a]	1.4

[a] Calculated at $\alpha = 0.5$
[b] 'Sharp' free energies
[c] Not possible to calculate owing to its limited water solubility in the form of free base

Table 5 Stability constants and electronic spectra of Cu^{2+} complexes of polymeric ligands and their non-macromolecular models at 25°C in 0.1 M NaCl

Compound	Reaction	pH-range	log β	ε[a] (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)
P_4	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	2.5–4.0	9.0–8.3	32(2)	735
P_5	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	4.2–6.5	6.8–5.9	44(2)	735
M_1[b]	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	2.3–3.8	9.98(2)[b]	36(1)	730
M_2[b]	$L^- + Cu^{2+} \rightleftharpoons CuL^+$	3.3–7.6	6.05(6)[b]	50(1)	740

[a] Molar absorption coefficients (values in parentheses are the standard deviations)
[b] M_n ($n = 1, 2$):



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Obtained by SUPERQUAD Program (values in parentheses are the standard deviations)

Complex formation

The coordinating ability of the whole series of polymers with respect to copper(II) ion has been investigated in aqueous solution. Only polymeric diamine P_3 and polymeric aminoacids P_4 and P_5 are able to form Cu(II) complexes in aqueous solution[18]. These results are not unexpected since it is well known that tertiary monoamines and *N,N'*-disubstitituted piperazines usually do not give stable complexes in aqueous solution. Besides, in the homologous series of the ω-aminoacids only glycine and β-alanine give complex formation under these conditions. The coordinating ability of these polymers has been studied by potentiometric, spectrophotometric and viscosimetric techniques.

In the case of P_3 polymer a spectrophotometric investigation has shown a dependence of λ_{max} on pH, meaning that the structure and/or the kind of the complex is not constant. We can suppose that the conformation of the polymer influences in some way the number of coordinating groups around the Cu^{2+} ion and the possibility of coordination of the SO_2 group.

In the case of P_4 and P_5 polymers, the equilibrium constants relative to the Cu^{2+} complex formation could be calculated by taking into account the dependence of the protonation constants on pH via the Henderson–Hasselbach equation. By choosing the pH region in which only CuL^+ species is present, it was possible to evaluate its stability constant for each titration point[18]. The results are given in *Table 5* and *Figure 1*. As we can see, the stability constants for both P_4 and P_5 decrease with pH. At pH > 7 for P_5 and at pH > 4 for P_4, the stability constants of the CuL^+ species do not follow a regular trend. This means that beyond this point, new complex species are probably formed and therefore the computation cannot be carried out. The values of the $Cu(P_4)^+$ stability constant are always higher than those of $Cu(P_5)^+$ consistently with what happens in the case of the corresponding ω-aminoacids glycine and β-alanine and of the non-macromolecular compounds purposely synthesized by us (see *Table 5*). This indicates that chelation occurs between the carboxyl and the amino group. On the other hand, no appreciable conformational

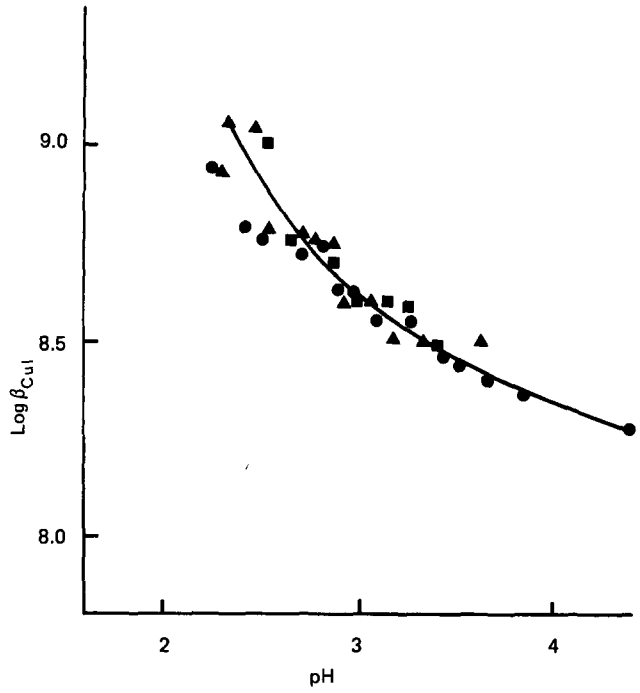

Figure 1 Variation of the $Cu(P_4)^+$ stability constant vs. pH at different (●, 1/1; ■, 1/2; ▲, 1/3) polymer/Cu^{2+} molar ratio

variation seems to occur during complex formation as shown by viscosimetric and spectrophotometric measurements.

CONCLUSIONS

By comparing the results obtained in this work for the protonation equilibria, we can conclude that a polyelectrolyte behaviour is due to the nature of the shielding group, even if a considerable effect is exerted by the position of ionic groups, either in the macromolecular chain, or as side substituent.

In the case of polymers with a polyvinylic structure the presence of the pendant charged groups separated by a short aliphatic chain makes a spatial approach between groups belonging to neighbouring units possible.

In the case of polymeric aminoacids, on the contrary, even if the shielding group is the most effective between all those examined so far, the possibility of interaction is attributable to the presence of opposite charges that evidently create an internal strain force competitive with stiffness of the bis-acryloyl-piperazine group. In fact, in the case of poly(amido-amine)s bearing the same shielding group, no polyelectrolyte behaviour has ever been found even if an aminic or polar (–OH) group was inserted as side substituent[33]. Only the polymer bearing two coordinating groups, placed at a suitable distance and not constricted into a rigid structure, for each monomeric unit are able to give copper(II) complexes in aqueous solutions. This means that the metal ion cannot be coordinated to groups belonging to different monomeric units.

In the case of P_3 the Cu^{2+} complex continuously varies its stereochemistry as shown by the spectrophotometric measurements. In the case of P_4 and P_5 the spectrophotometric results suggest that chelation occurs between the amino and the carboxylate group[18].

It is interesting to note that a dependence of log β on pH is clarified indicating that the interaction between different monomeric units, that has been found in the protonation process, is present in complex formation too. In particular we have found that the approach of the Cu^{2+} ion becomes more and more difficult as the pH increases.

However, several aspects of this problem have still to be investigated, for example the dependence of log β on the percentage of metal bound and the role played by the ratio between polymer and metal ion.

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