

Applied Macroinorganics. IV. Effect of the Crosslinking Agent on Protonation, and Metal Ions Complexing Abilities, of Ion Exchange Resins with Poly(amido–Amine) Structure

M. PESAVENTO and T. SOLDI, *Istituto di Chimica Generale de Inorganica dell'Università, 27100 Pavia, Italy*, P. FERRUTI, *Istituto di Chimica degli Intermedi dell'Università, 40186 Bologna, Italy*, and R. BARBUCCI and M. BENVENUTI, *Istituto di Chimica Generale dell'Università, 53100 Siena, Italy*

Synopsis

Two classes of resins, having a poly(amido–amine) structure, have been synthesized. The basicity constants and the complexing abilities toward copper (II) and nickel (II) ions have been investigated by potentiometric techniques. The influence of the nature of the crosslinking agent on the basicities and the complexing abilities has been studied.

INTRODUCTION

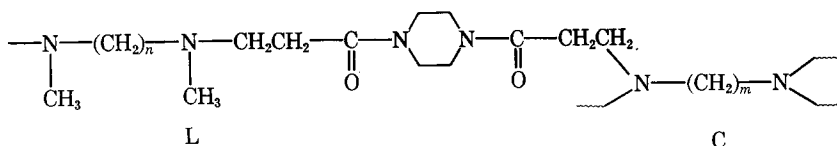
The protonation and heavy metal ions complexing ability of a series of tertiary amino polymers of poly(amido–amine) structure, either in a linear (i.e., water soluble)^{1,2} or in a crosslinked form^{3,4} have been recently studied.

A peculiar feature of these polymers is that, in both forms, their repeating units behave independently, i.e., the protonation and complex formation behavior of each unit does not depend on the protonation or complexation degree of the whole macromolecule. As a consequence “sharp” thermodynamic functions could be determined.^{2,5}

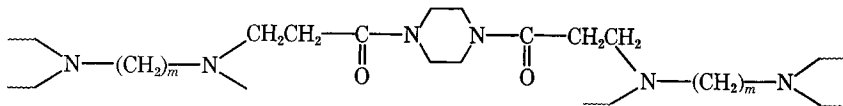
As a rule, the basicity constants and the complexing abilities of the polymers in a crosslinked form were found to be similar to those obtained with the linear polymers.³ Some differences, however, were observed, and were attributed to the presence in the resin of the crosslinking units, which also contained tertiary amino groups.

Therefore, we thought it interesting to study the influence of the nature of the crosslinking agent on the basicities and complexing abilities of some poly(amido–amine) ion–exchange resins.

Two groups of resins have been prepared and studied. In the first group, the tertiary amino groups belong partly to the crosslinking agents (C), and partly to linear segments (L). In the second group, all the aminic groups belong to the crosslinking agents. The general structure of the resins of the first group is



where the ratio L:C = 3:1 (mol/mol) and n, m can be $n = 2, m = 2$ (RN_2C_2), $n = 4, m = 2$ (RN_2LLC_2), $n = 2, m = 4$ (RN_2C_4), $n = 4, m = 4$ (RN_2LLC_4). The structure of resins of the second group is



where $m = 2$ (RC_2) or $m = 4$ (RC_4).

EXPERIMENTAL

Materials. Resin RN_2C_2 has been prepared by polyaddition of a mixture of N,N' -dimethylethylenediamine (0.55 g; 0.0062 mol) and ethylenediamine (0.12 g; 0.0020 mol) to 1,4-bisacryloylpiperazine (2.0 g; 0.010 mol) in turn prepared as previously described.⁶ The reaction has been performed in water (5 mL) at room temperature and under inert atmosphere. After standing 7 days, the reaction mixture, which settled into a hard gel, was finely triturated and repeatedly washed with distilled water, and finally dried under high vacuum at room temperature. The yield was practically quantitative.

Resin RN_2LLC_2 was prepared in the same way, by substituting an equivalent quantity of N,N' -dimethylputrescine for N,N' -dimethylethylene diamine.

Analogously, resin RN_2C_4 was prepared by substituting 1,4-diaminobutane for ethylenediamine and resin RN_2LLC_4 , by substituting both N,N' -dimethylputrescine and 1,4-diaminobutane for N,N' -dimethylethylenediamine and ethylenediamine, respectively, in the recipe given for RN_2C_2 .

Resin RC_2 was prepared in the same way, starting from ethylenediamine (0.30 g; 0.0050 mol) and 1,4-bisacryloylpiperazine (2.0 g; 0.010 mol). Resin RC_4 was prepared as RC_2 by substituting 1,4-diaminobutane for ethylenediamine.

IR Spectra. IR spectra were obtained by using a Perkin-Elmer 597 spectrophotometer.

Stability of the Resins. The stability of the resins in aqueous media at various pH's (0,7,12) has been verified by letting them stand in these media for 15 days,

TABLE I
Effects of Crosslinking on Swelling of Poly(amido-Amine) Resins^a

Resins	H_2O	Swelling ^b			
		0.1M NaCl, pH = 1.5	0.1M NaCl, pH = 9	0.1M (CH_3COO^- / CH_3COOH), pH = 5.4	1M (CH_3COO^- / CH_3COOH), pH = 5.4
RC_2	17	17	15	17	16
RN_2C_2	24	23	22	27	25
RN_2LLC_2	31	29	28	34	27
RC_4	18	14	15	18	16
RN_2C_4	28	25	23	29	22
RN_2LLC_4	31	29	28	33	26

^a 6.5 mm ϕ column filled with 100 mg resin in form of small particles (mesh 25).

^b Height of the column (mm).

when neutralizing them, washing them with water, and drying them. No significant weight losses were observed. Moreover, the IR spectra of the resins (KBr pellets) were unchanged.

Swelling. The swelling of the resins in water and in saline solution at various pH's has been measured by determining the increase in height of columns 6.5 mm in diameter and containing 100 mg of dry resin. The results are given in Table I.

Potentiometric Measurements and Complexing Abilities. The protonation of the resins have been studied by the potentiometric method as previously described.³ Experimental details are given in Table II. The titration curves¹ indicate the following protonation stoichiometries: in RN_2C_2 both the aminic nitrogens of L and one aminic nitrogen of C are protonated; in RN_2LLC_2 both the aminic nitrogens of C (besides those of L) are protonated; in RN_2C_4 and RN_2LLC_4 , as previously reported, both the aminic nitrogens of L are protonated, but the aminic nitrogens of C are protonated only in the latter; both the aminic nitrogens undergo protonation, both in RC_2 and RC_4 . The calculation method and symbols have been reported in a previous paper.⁷ It may be observed that the protonation kinetics are very slow in all cases but especially so in RC_2 and RC_4 . The time necessary to obtain a stable potential value is about 1–3 h. This leads to much uncertainty in the determination of the constants. The reactions of complex formation with Cu^{2+} and Ni^{2+} have been performed in batch and in 1M acetate buffer in the pH range 3–6.5. The amount of metal ions present in solution have been determined polarographically on small aliquots (0.1–0.5 mL); after each determination the amount of ion absorbed by the resin has been checked after elution with 0.1M HCl. The complexation reaction is very slow in the case of Ni^{2+} , for instance, while with RN_2C_2 the equilibrium is reached after about 24 h. The adsorption of Cu^{2+} and Ni^{2+} on different resins as a function of time is given in Figure 1.

RESULTS AND DISCUSSION

Swelling. The heights of the columns of the various resins prepared in different buffer solutions, as described in the Experimental part, are given in Table

TABLE II
Experimental Details of Potentiometric Measurements in 0.1 mol/dm³ NaCl and at 25°C

Reaction	Concn L (mmol/gR)	Concn C (mmol/gR)	Curve	g resin	V (mL)	pH range	Number of points	Capacity towards H ⁺ ion (meq H ⁺ / g resin)
$RC_2 + H^+$	0	2.2321	1	0.0483	30.14	10.6– 2.3	19	4.48
			2	0.0483	30.74	2.3–11.1	13	
$RN_2C_2 + H^+$	2.3152	0.7717	1	0.0754	20.75	11.4– 1.8	10	5.48
			2	0.0731	21.81	1.8–11.8	12	
$RN_2LLC_2 + H^+$	2.1749	0.7250	1	0.0474	30.30	10.9– 2.5	18	5.65
			2	0.0474	30.63	2.5–11.0	22	
			3	0.1248	20.87	10.9– 2.2	12	
			4	0.1248	22.02	2.5–10.8	12	
$RC_4 + H^+$	0	2.1008	1	0.0485	30.60	2.4–10.8	15	4.13
			2	0.0485	32.01	10.4– 2.5	11	

TABLE III
Basicity of Resins and Polymers in 0.1 mol/dm³ NaCl at 25°C

System no.	Resin	log K ₁ [†]	log K ₂ [‡]	log K ₃ [§]	log K ₄ [¶]
1		~7.5	~3.2		
2		7.8(5) L	4.2(6) L	6.2(6) C	
3		8.9(1) L	7.7(1) L	5.7(1) C	~3 C
4		~8.5	~6.5		

5 ^b		7.74(10) L	4.78(10) L		
6 ^b		8.58(10) L	7.44(7) L	6.20(10) C	~3.0 C
1	<p style="text-align: center;">RN₂C₄</p> <p style="text-align: center;">Polymer^c</p>	8.09	4.54		
2		8.715	7.689		

^a The values in parentheses are the standard deviations.

^b Ref. 4.

^c Ref. 5.

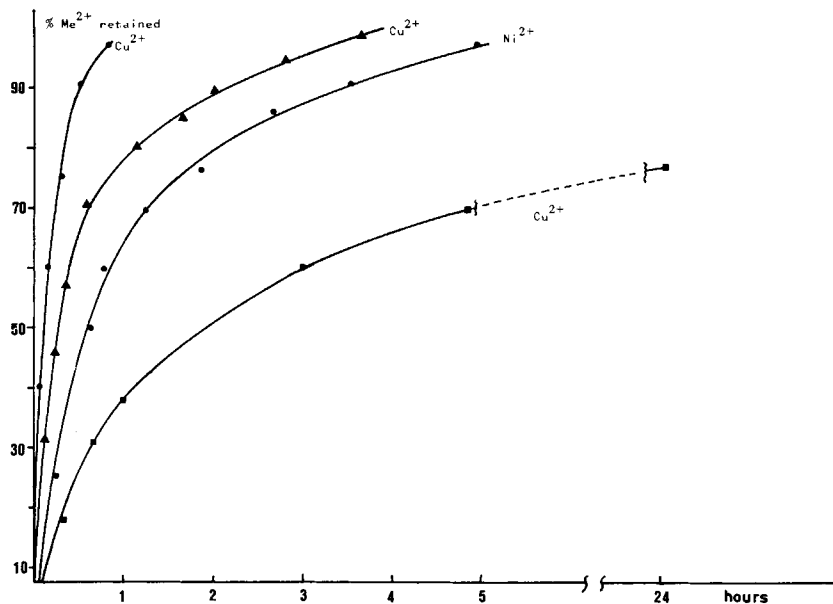


Fig. 1. Cu^{2+} and Ni^{2+} fixation on resins RN_2C_4 (\bullet), RN_2C_2 (\blacktriangle), and RC_2 (\blacksquare) as a function of time.

I. It may be noted that the pH has little effect on swelling. As expected, resins RC_2 and RC_4 swell to a minor degree with respect to the other ones, owing to their more tightly crosslinked structure. On the other hand, resin RN_2C_2 swells considerably less than RN_2LLC_2 and RN_2C_4 less than RN_2LLC_4 . These differences may be due to the less flexible structure of the linear part of RN_2C_2 and RN_2C_4 . By comparing RN_2C_2 with RN_2C_4 and RN_2LLC_2 with RN_2LLC_4 it may be concluded that the different length of the crosslinking agents has negligible effect on swelling.

Protonation Constants. The protonation constants of the resins are reported in Table III. As in other resins previously studied,^{3,7} these constants must be considered as "real," at least for the resins in which a linear portion is present (see below). In all cases, the constants relative to the linear portion of the resins are very close to those of the corresponding linear polymers⁵ (Table III). This means that neither the nature of the crosslinking agent nor the crosslinking itself significantly affects the basicity of the aminic nitrogens present in the linear part. On the other hand, by comparing the protonation constants relative to the crosslinking units in resins RN_2C_2 and RN_2LLC_2 with those of RC_2 , it would appear that in these resins the basicity of the crosslinking units is considerably lower when an already protonated linear portion is present. It may be observed, however, that we cannot establish, at present, if the protonation constants of RC_2 and RC_4 are "real" or "apparent," owing to the experimental difficulties connected with the very slow kinetics of protonation of these results. However, a nonmacromolecular model of RC_4 gave the values $\log K_1 = 8.34$ and $\log K_2 = 7.16^3$; these values are in agreement with those of the resin (Table III).

Complexation Behavior. The exchange capacity of the resins is reported in Table IV. Only the resins RC_2 , RN_2C_2 , RN_2LLC_2 , and RN_2C_4 are able to

TABLE IV
Ion Exchange Capacities of Poly(amido-Amine) Resins

Resin	Capacity found ^a (mg atoms/g resin)	Theory capacity (mg atoms/g resin)
RC ₂	2.1	2.96
RN ₂ C ₂	2.9	2.96
RN ₂ LLC ₂	0.7	0.74
RC ₄	b	
RN ₂ C ₄	2.4	2.22
RN ₂ LLC ₄	b	

^a Determined by Ni²⁺ (pH = 6.8) and Cu²⁺ (pH = 5.8) ion uptake.

^b No evidence of complexation.

adsorb metal ions from aqueous solutions, while the resins RC₄ and RN₂LLC₄ are not. By considering the structure of the resins, only those containing two tertiary nitrogens connected by two methylene groups are capable of bonding the metal ions. This is due to the possibility of forming a five-membered chelate ring with Cu²⁺ or Ni²⁺ ion. It is well known that this kind of ring forms the most stable complexes in solution. Considering the exchange capacity of the resins, we observe that it increases in the order

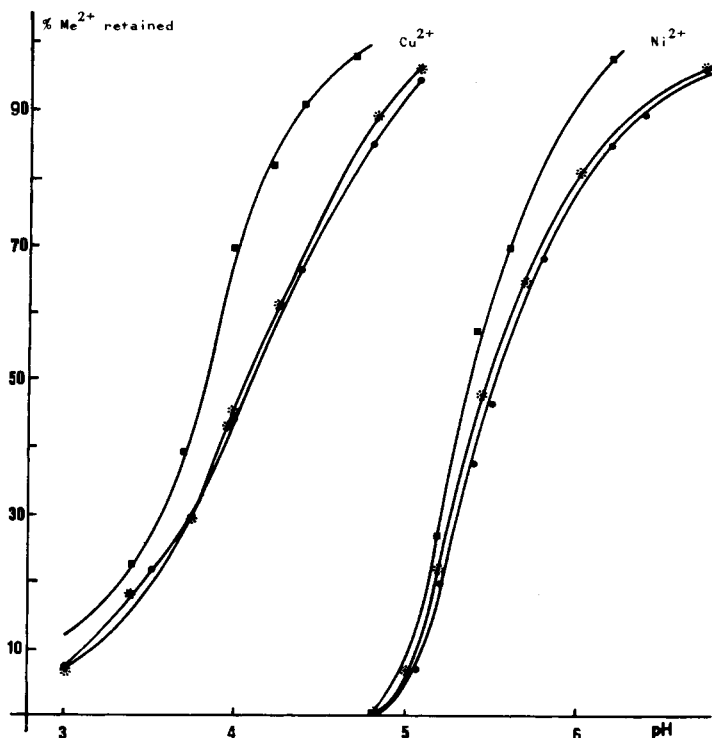
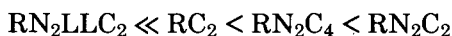


Fig. 2. Plot of the percentage of metal ion Cu²⁺ or Ni²⁺ retained in the resins RN₂C₄ (●), RN₂C₂ (*), and RN₂LLC₂ (■) against pH.

i.e., the resins RN_2C_2 with the greatest complexing power shows, in its structure, the best coordinating group in both the linear portion and the crosslinking agent, both of them having the skeleton of the ethylenediamine molecule.

The resin has been synthesized with a 1/4 ratio of crosslinking agent and a 3/4 ratio of linear polymer; therefore, the substitution of the crosslinking agent C_2 with another, C_4 , incapable of forming complexes (see RC_4 in Table IV), lowers the metal loading capacity to about 1/4 and the substitution of the linear part N_2 with N_2LL , incapable of forming complexes² (see also RN_2LLC_4 in Table IV) lowers the metal loading capacity to about 3/4.

Figure 2 shows the amount of metal ion retained in the different resins at various pH values. It may be observed that the elution conditions are sharply different for the two ions, but there is no remarkable difference between the resins RN_2C_4 , RN_2C_2 , and RN_2LLC_2 (the curves of resins RN_2C_2 and RN_2C_4 are practically superimposed). The curve of the resin RC_2 has not been reported due to the slowness of the kinetics of complexation (Fig. 1), in fact the recovery of adsorbed metal ions is not quantitative, even after 4 days.

The kinetics follows this trend:



This order, which is opposite to that found for the complexation capacity, can be explained with the different accessibility to the active sites for the different tightness of the net work of the resins.

This work has been supported by the Progetto Finalizzato del CNR Chimica Fine e Secondaria.

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Received January 20, 1983

Accepted April 18, 1983