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Macro Inorganics V*.
Basicity and Complexing Ability of a New Class of Poly(amido-amines) with Tertiary Amino Groups Present both in the Main Chain and as Side Substituent

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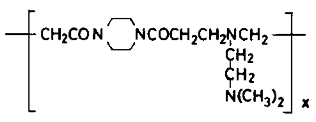
The basicity and Cu(II) ion complexing ability of a poly(amido-amine) carrying two tertiary amino groups in its repeating unit, one in the main chain and one as side substituent, have been studied in aqueous solution by potentiometric, calorimetric and spectrophotometric techniques. Contrary to most polymeric acids and bases, but according to the previously studied poly(amido-amines), whose amino groups were all present in the main chain, the new polymer exhibits 'sharp' constants, i.e. *its constants do not depend on the ionization degree of the whole macromolecule. This peculiar behaviour was found in both the protonation and in complex formation processes.*

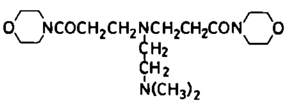
Introduction

It is well known that the protonation and complex formation of macromolecular ligands is usually a very complicated process, involving functional groups belonging to different monomeric units. In previous papers [1–5] we have reported some unusual results obtained on studying the protonation and complex formation behaviour of some polymers having a poly(amido-amine) structure and carrying tertiary amino groups regularly arranged along the macromolecular chain. In particular, the aminic nitrogens of each monomeric unit of these polymers behave independently on those of the other units, leading to basicity constants which in turn do not depend on the ionization degree of the whole macromolecule.

At this point, we thought it interesting to investigate if the position of the aminic nitrogens in poly(amido-amines) could influence this behaviour. On this respect, we report here some results on the basicity and Cu^{2+} complex ability of a poly(amido-amine) (I) having the same general structure of the previously reported ones, but carrying additional amino groups in the side chains. A parallel study has been performed on a low molecular weight model (II) having essentially the same structure of the monomeric unit of the polymer



I



II

The above studies have been carried out by a number of different physico-chemical techniques, including potentiometry, calorimetry and electronic spectroscopy.

Experimental

Synthesis

The syntheses of both polymer and model have been performed as previously reported [6].

EMF Measurements

Potentiometric titrations were carried out using an Ag/AgCl reference electrode, an Orion 91-01 glass electrode and a salt bridge containing 0.1 *M* NaCl solution. For each determination of protonation

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*Part IV is reference 3.

TABLE I. Experimental Details of the Potentiometric Measurements at 25 °C in 0.1 *M* NaCl.

Reaction	Curve	Initial conc. of L ($M \times 10^3$)	Initial conc. of Cu(II) ($M \times 10^3$)	Range $-\log [H^+]$	Number of Points
Polymer I + H^+	A	2.993		9.9–2.5	60
	B	0.612		9.3–2.7	53
	C	6.156		10.1–2.5	36
Polymer I + Cu^{2+}	A	6.151	1.525	9.2–2.8	39
	B	4.930	0.827	9.4–2.7	41
	C	3.136	0.573	9.5–2.6	35
Model II + H^+	A	2.589		9.5–2.5	49
	B	2.382		10.0–2.6	49
	C	4.630		10.0–2.4	49
Model II + Cu^{2+}	A	5.330	1.439	9.2–2.8	36
	B	4.747	0.962	9.2–3.0	31
	C	4.076	0.508	9.6–3.4	33

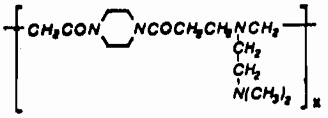
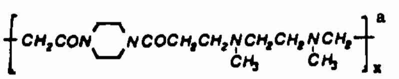
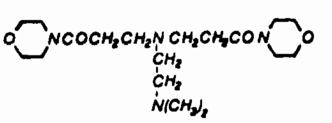
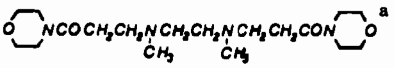
TABLE II. Experimental Details of Microcalorimetric Measurements at 25 °C in 0.1 *M NaCl.*

Reaction	V_H[a] μmol s^{-1}	V_L[a] μmol s^{-1}	R[b] μl s^{-1}	Q[c] μcal s^{-1}
Polymer I + H^+				
	0.02723	0.02598	6.770	0.2012
	0.02723	0.01301	5.080	0.1810
	0.01927	0.00855	3.388	0.1227
	0.01927	0.01713	5.086	0.1436
	0.03800	0.00855	5.038	0.1312
	0.03800	0.01713	6.736	0.2308
	0.09583	0.01713	11.831	0.2545
	0.09583	0.00855	10.133	0.1270
	0.01927	0.04303	10.208	0.1485
	0.03800	0.04303	11.831	0.2860
Model II + H^+				
	0.01967	0.00925	3.383	0.1272
	0.01967	0.01848	5.073	0.1554
	0.01967	0.04653	10.208	0.1450
	0.09889	0.04653	10.133	0.1333
	0.00983	0.00925	3.383	0.0748
	0.01972	0.00925	5.080	0.1247
	0.04944	0.00925	10.183	0.1352
	0.00983	0.01848	5.073	0.0729
	0.01972	0.01848	6.770	0.1448
	0.04944	0.01848	16.953	0.2664

[a] Total flow rate of the acid and compound. [b] Total flow rate. [c] Heat flow corrected for dilution.

constants the cell was thermostatted at 25 °C and filled with 100 ml of 0.1 *M* NaCl solution containing a known amount of amine. For the determination of stability constants the cell, at the same temperature, was filled with ≅100 ml of 0.1 *M* NaCl solution containing a known amount of ligand and of copper(II) nitrate solution. In both cases, the solutions were titrated with a 0.1 *M* hydrochloric acid solution, added by a Metrohm Dosimat E 415 automatic piston burette under CO_2 free nitrogen. The program Miniquad 76A which was used to calculate the constants, has been described elsewhere [7].

TABLE III. Basicity of Poly(amido-amines) and Their Corresponding Non Macromolecular Models at 25 °C in 0.1 *M* NaCl.

		log K[b]	$-\Delta H°$ [b] kcal mol^{-1}	$\Delta S°$ [b] cal K^{-1} mol^{-1}
I		8.87 (1)	7.05 (12)	16.9 (4)
		4.10 (2)	7.09 (21)	−5.0 (9)
III		8.09	7.35	12.4
		4.54	6.09	0.3
II		9.05 (1)	6.92 (18)	18.2 (6)
		4.35 (2)	6.91 (21)	−3.3 (7)
IV		8.248	7.34	13.1
		4.80	6.05	1.7

[a] Ref. 2. [b] The values in parentheses are the standard deviations.

The protonation constants and the experimentally measured ionic product of water were held constant during the calculation of the complex formation constants. Details of the potentiometric titrations are reported in Table I.

Calorimetric Measurements

Calorimetric measurements were carried out with an LKB 10700-1 Flow calorimeter. The output voltages were recorded using a Keithley 153 Microvoltmeter. The enthalpies of protonation were obtained using the mixed cell: the titrant (HCl) and the solution of amine were introduced into the calorimeter at constant flow rate by two Perfusor continuous infusion pumps. The enthalpy of formation of H_2O, obtained in the same experimental condition by mixing HCl with an excess of NaOH, was 13.34 kcal mol^{-1}, in good agreement with the accepted value [8]. Numerical analysis of the data was handled by means of a previously described computer program [9]. Experimental details of calorimetric measurements are reported in Table II.

Electronic Spectra

Absorption spectra were recorded at room temperature with a Cary model 14 spectrophotometer using 1 cm silica cells.

Results and Discussion

Protonation

As for the previously studied poly(amido-amines), 'sharp' basicity constants have been obtained in the case of I. Moreover the number of basicity constants is equal to that of the aminic nitrogens present in the repeating unit. This apparently demonstrates that the position of the nitrogen atoms in poly(amido-amines) either in the main chain or as side substituents, is irrelevant as far as their protonation behaviour is concerned. The basicity constants relative to the protonation of I and II are reported in Table III. Both protonation constants of polymer I are similar to those of its non macromolecular model II. However, the model is little more basic, as already found for all poly(amido-amines) [1, 3]. By comparing the basicity constants obtained in the case of I and II with those of the isomeric polymer III and model IV containing both tertiary amino groups in the main chain (Table III) we observe that the log K_1 s of the former compounds are higher. Besides, the logK_1 of model I is quite similar to that of N,N,N′,N′-tetramethylethylenediamine [10], diminished for the statistical effect. On the contrary, the logK_2's of I and II are lower than those of III and IV. This is probably due to the presence, in the former compounds, of two basicity depressing carbonyl groups in β position (Table III). On the basis of our results we think that the mechanisms of protonation involves the following steps:

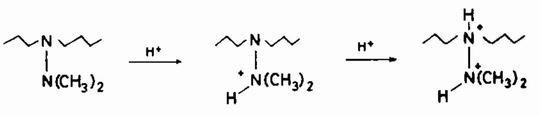


TABLE IV. Cu(II) Complexes with Poly(amido-amines) and Their Non Macromolecular Models.

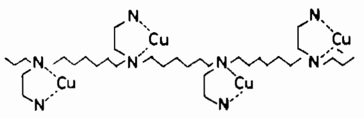
System	Stability Constants and Electronic Spectra		
	Complexes[a]	Stability Constants[b]	Electronic Spectra[c]
Polymer I + Cu^{2+}	CuL	8.47 (5)	14.2 (135)
	Cu(OH)L	6.1 (1)	
Model II + Cu^{2+}	CuL	8.61 (5)	14.4 (125)
	Cu(OH)L	5.7 (8)	
	$Cu(OH)_2L$	8.7 (9)	
Polymer III + Cu^{2+} [d]	CuL	8.96 (10)	14.8 (174)
	Cu(OH)L	5.52 (25)	
Model IV + Cu^{2+} [d]	CuL	9.10 (7)	14.8 (176)
	Cu(OH)L	[e]	
	$Cu(OH)_2L$	8.40 (13)	

[a] L (for polymer) means the repeating unit. [b] The values in parentheses are the standard deviations. [c] The values in parentheses are the molar extinction coefficients. [d] Reference 4. [e] Evidence of its formation in aqueous solution.

The enthalpy values for both I and II are quite similar. Hence, the difference in their basicity constants is due to the entropy value. This behaviour is similar to that already observed in other previously studied poly(amido-amines), and their non macromolecular models [11]. The lower entropy gain of the polymer in each protonation step is presumably due to a greater loss of conformational freedom. The first protonation enthalpies of I and II are lower than those of III and IV. This is not surprising, since, as a rule, unsymmetrically substituted amines exhibit lower $|\Delta H_1^\circ|$'s than those of symmetric amines of corresponding structure [12]. The enthalpy value relative to the second protonation step is in all cases similar to the first one ($|\Delta H_2^\circ| \cong |\Delta H_1^\circ|$), and this trend, observed in N,N-diethylethylenediamine too, can be explained by considering both the different solvation degree and the 'freezing' of the bulky alkyl groups into fixed orientations upon protonation [9]. As a matter of fact, the entropy values of I and II are lower than those of the 'linear' compounds III and IV.

Cu(II) Complex Formation

Both polymer I and model II give complexes with Copper(II) ion in aqueous solution. Complexes with general formula CuL (where in the case of the polymeric ligand 'L' means the repeating unit of the polymer) were evidenced in aqueous solution. Some hydroxo species were also found. The stability constants of all these complexes are reported in Table IV. As in the case of protonation constants, the CuL stability constant of model II is slightly higher than that of polymer I. Moreover, the constants of I and II are lower than those of III and IV (Table IV). This result is perfectly coherent with those obtained for low molecular weight diamines. The unsymmetrically substituted ones, such as N,N-dimethyl- or N,N-diethylethylenediamine, always show lower stability constants than their symmetrically substituted analogues, such as N,N'-dimethyl- or N,N'-diethylethylenediamine [9]. This effect may be due to the higher strains of the bulky substituents to the same nitrogen, when the unsymmetrically substituted compounds are compelled to assume a conformation able to coordinate the metal ion. The electronic spectra of the two CuL complexes (polymer and model) are similar. They are consistent with an octahedral tetragonally distorted structure having as chromophore group CuO_4N_2. The maximum is equal to that observed for the complex Cu(NNN'N'-tetramethylethylenediamine)$^{2+}$ in aqueous solution [13]; the higher value of ϵ may be explained by an increase in the polarizability of the donor atom caused by bulker alkyl groups. This behaviour agrees with that already observed in some NN'-dimethyl- and NN'-diethylethylenediamine complexes [14]. The fact that the electronic data of polymer and model are quite similar means that interactions between nitrogens belonging to different monomeric units are not present in the polymer. Therefore a schematic picture of the Copper(II) complex may be as follows:



Previously a linear relationship between the maxima of the electronic spectra in aqueous solution for Cu^{2+} polyamine complexes and the enthalpy values relative to their complex formation has been found [15]. The above results suggest that, as in the protonation, the slight difference between the stability constants of Cu(II) complex with I and II is mainly due to entropy effect.

As far as the hydrolysis reaction is concerned, both ligands form a Cu(OH)L complex in solution, but only model II forms the $Cu(OH)_2L$ species. This agrees with the results previously reported for other poly(amido-amines) and their corresponding non macromolecular models, where the numer of hydroxy species is larger in the case of non polymeric ligands [4]. The stability constants are virtually the same as those obtained with the isomeric ligands III and IV having both basic nitrogens in the main chain. This means that the stability of the hydroxo complexes does not depend on the steric effects of the polyamine bound to the metal ion. This seems to suggest that the complexes Cu(OH)L and $Cu(OH)_2L$ have a square planar structure in solution, since this is the only structure in which there is no steric interference from the ligand [16].

Conclusions

It has been shown that it is possible to obtain *sharp* basicity and stability constants for a poly(amido-amine) having additional amino groups in the side substituents. This indicates that in the poly(amido-amines) the basic groups belonging to different monomeric units behave independently of their position. Furthermore, we have always found a close similarity between poly(amido-amines) and their low molecular weight models. In other words, in this class of polymers the effect of the macromolecularity is small. In order to better ascertain the structural reason of this unusual feature, further studies with purposely tailored polyamines are presently in progress.

Acknowledgement

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