Macro-inorganics. Part 6.† Protonation and Complex Formation of a New Series of Polymers whose Repeating Units behave Independently

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The protonation and copper(II) complex formation of some new polymers with a poly(amido-amine) structure has been studied in aqueous solution by potentiometric, calorimetric, and spectroscopic techniques. The polymers are characterized by the fact that no ring structures are present along the main chain between tertiary amino-groups of different units. The results indicate that the monomeric units of this new family of poly(amido-amines) behave independently towards both protonation and complex formation. Comparison with previously studied poly(amido-amines) shows that the presence of linear diamide moieties in place of 1,4-diacylpiperazine rings [as in the previously studied poly(amido-amines)] has a slight influence on the protonation constants, although differences may be observed in the thermodynamic functions $\Delta H^\ominus$ and $\Delta S^\ominus$. Significant differences are observed in copper(II) complex formation.

IT is well known that, due to co-operative effects between different repeating units, the behaviour of polyelectrolytes towards both protonation and complex formation must be described through the ' apparent ' thermodynamic functions of an average group carried by the polyelectrolyte.[1-3] Recently, however, we have found that some water-soluble regular polymers, having a poly(amido-amine) structure,[4] show an unusual behaviour since their monomeric units behave independently towards both protonation [5-7] and complex formation with heavy-metal ions.[8,9] As a consequence, the behaviour of these polymers is similar to that of small molecules, for which the precise site of protonation and ' sharp ' thermodynamic functions may be determined. The first two series of poly(amido-amines) studied by us (hereafter referred to as ' rigid ') contained tertiary amino-groups only in the main chain [5-9] or also as side substituents,[10,11] and amide moieties derived from 1,4-bis(acryloyl)piperazine, *i.e.* containing a ring structure. The structures of the ' rigid ' poly(amido-amines) already studied are shown in Figure 1.

TABLE 1

Thermodynamic functions for the stepwise protonation of ' rigid ' and ' flexible ' poly(amido-amines) at 25 °C in 0.1 mol dm^{-3} NaCl *

Polymer	log K	$-\Delta G^\ominus$/kcal mol^{-1}	$-\Delta H^\ominus$/kcal mol^{-1}	$\Delta S^\ominus$/cal K^{-1} mol^{-1}	Ref.
L^1	7.79(2)	10.62(3)	8.26(7)	7.9(3)	5, 6
L^7	7.81(1)	10.65(1)	8.23(10)	8.1(3)	This work
L^2	8.09(3)	11.03(4)	7.35(12)	12.3(6)	5, 6
	4.54(9)	6.19(12)	6.09(11)	0.3(7)	
L^8	8.09(1)	11.03(1)	7.20(9)	12.8(3)	This work
	4.53(3)	6.18(4)	5.40(11)	2.6(6)	
L^4	7.01(1)	9.56(1)	5.71(9)	13.3(3)	6, 18
	2.98(4)	4.06(5)	5.24(9)	$-3.9(4)$	
L^9	6.94(1)	9.46(1)	5.21(11)	14.3(4)	This work
	3.08(2)	4.20(3)	3.63(10)	1.7(4)	
L^5	8.87(1)	12.10(1)	7.05(12)	16.9(4)	10, 11
	4.10(2)	5.59(3)	7.09(9)	$-5.0(4)$	
L^{10}	8.78(1)	11.97(1)	6.89(10)	17.1(3)	This work
	3.89(2)	5.30(3)	6.98(10)	$-5.6(7)$	

* The values in parentheses are the estimated standard deviations of the last significant figure.

In a previous paper [5] we suggested that the presence of a ring structure between the tertiary amino-groups belonging to different units might play a role in determining the unusual behaviour of ' rigid ' poly(amido-amines). In order to verify this hypothesis we have now synthesized and studied a new series of poly(amido-amines) (hereafter referred to as ' flexible ') derived from 3,5-bis(acryloyl)-3,5-diazaoctane, *i.e.* without ring structures in the amide moieties. The structures of these polymers are also shown in Figure 1.

EXPERIMENTAL

Materials.—3,5-Bis(acryloyl)-3,5-diazaoctane was prepared as previously described.[12]

Compound L^7 was obtained by mixing in aqueous solutions equimolecular quantities of the above bis(acrylamide) and $NMeH_2$. The concentrations were *ca.* 1 mol dm^{-3} in both reagents. The reaction mixture was allowed to stand at room temperature for *ca.* 3 days, it was then evaporated to dryness *in vacuo*. The gummy residue was dissolved in dichloromethane and reprecipitated with an excess of dry

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† Part 5 is reference 11.

diethyl ether. The product was then dried under high vacuum to constant weight. Yield: 90% (Found: C, 60.9; H, 10.1; N, 16.2. Calc. for $C_{13}H_{25}N_3O_2$: C, 61.15; H, 9.85; N, 16.45%); intrinsic viscosity [η] ($CHCl_3$, 30 °C) = 0.1 dl g^{-1}.

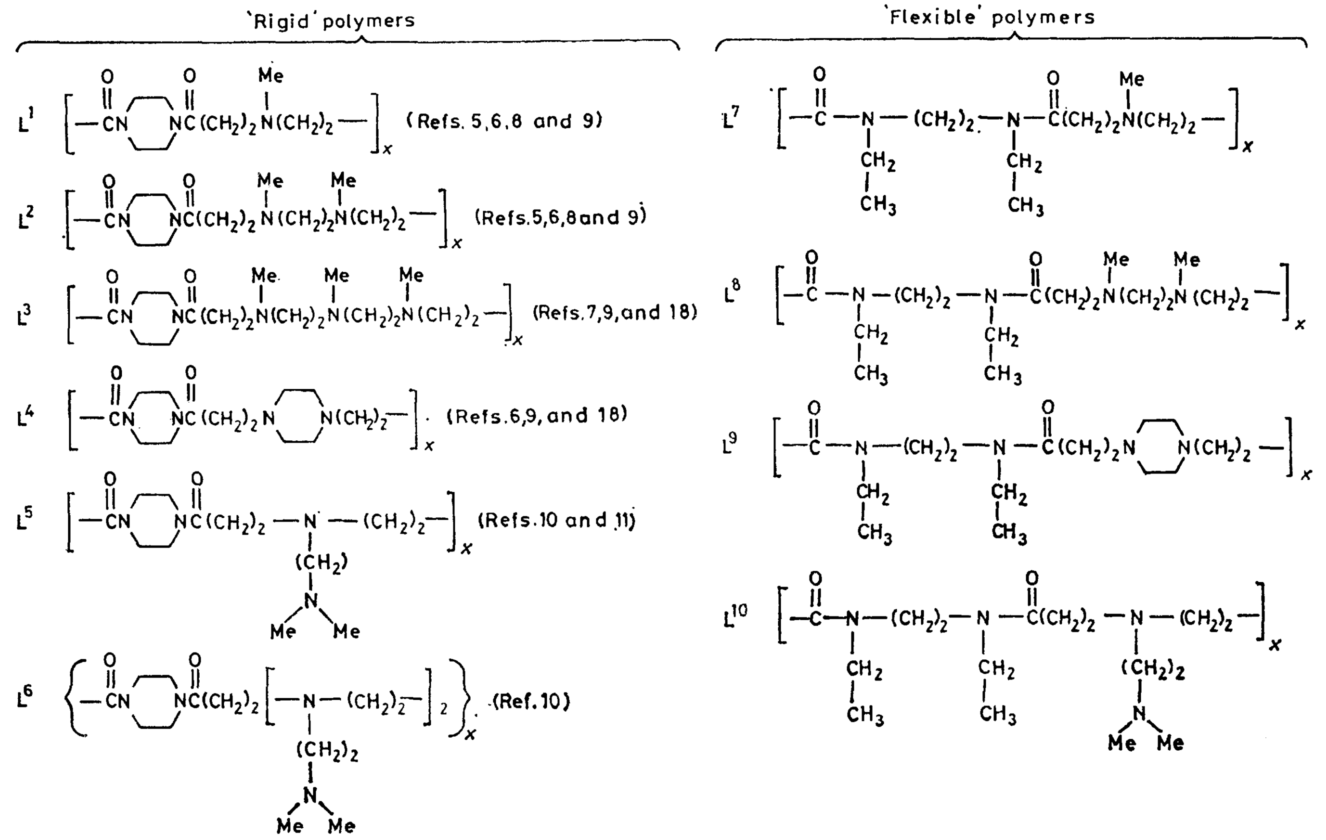

Figure 1 Structures of ' rigid ' and ' flexible ' poly(amido-amines)

Compound L^8 was obtained in exactly the same way by substituting 2,4-diazahexane for $NMeH_2$. Yield: *ca.* 90% (Found: C, 61.2; H, 10.5; N, 17.7. Calc. for $C_{16}H_{32}N_4O_2$: C, 61.5; H, 10.3; N, 17.95%); [η] ($CHCl_3$, 30 °C) = 0.20 dl g^{-1}.

Compounds L^9 and L^{10} were obtained in the same way by using piperazine or (2-dimethylamino)ethylamine. Yields were similar [Found: C, 61.8; H, 9.8; N, 18.3. Calc. for $C_{16}H_{30}N_4O_2$ (L^9): C, 61.9; H, 9.75; N, 18.05%]; [η] ($CHCl_3$, 30 °C) = 0.26 dl g^{-1} [Found: C, 61.3; H, 10.7; N, 17.7. Calc. for $C_{16}H_{32}N_4O_2$(L^{10}): C, 61.5; H, 10.3; N, 17.95%]; [η] ($CHCl_3$, 30 °C) = 0.12 dl g^{-1}.

None of the ' flexible ' poly(amido-amines), unlike most of the ' rigid ' ones,[12] would crystallize. In a pure state they are amorphous rubbers soluble in water, chloroform, dichloromethane, and lower alcohols, but insoluble in diethyl ether and aliphatic hydrocarbons.

*Methods.—E.m.f. measurements.** Potentiometric titrations were carried out using a digital potentiometer, an Ag–AgCl reference electrode, an Orion 91–01–00 glass electrode, and a salt bridge containing 0.1 mol dm^{-3} NaCl solution. The output voltages (mV) were automatically recorded using an alphanumeric printer Printina Gay. For each determination the cell, thermostatted at 25 °C, was filled with *ca.* 100 cm^3 of 0.1 mol dm^{-3} NaCl solution, containing a known amount of poly(amido-amine). The solution was titrated with 0.1 mol dm^{-3} hydrochloric acid solution added through a Metrohm Dosimat E 415 automatic piston burette under CO_2-free nitrogen. The program MINIQUAD used to calculate basicity and stability constants has been previously described.[13]

*Calorimetric measurements.** These were made with an LKB 10 700-1 flow calorimeter. The output voltages were recorded using a Keithley 153 microvoltmeter. The titrant (HCl) and the solution of the polymer were introduced into the calorimeter at a constant velocity by two Perfusor continuous infusion pumps. The enthalpy of formation of H_2O, obtained under the same experimental conditions by mixing HCl with an excess of Na[OH], was 13.34 kcal mol^{-1},† in good agreement with the accepted value.[14, 15] Numerical analysis of the data was handled by a purpose-written program.

Spectrophotometric measurements. Electronic spectra were recorded at 25 °C on a Beckman DK-A spectrometer using 1-cm silica cells. Reflectance spectra were obtained by a method analogous to that reported by Venanzi and co-workers.[16]

RESULTS AND DISCUSSION

Protonation.—The basicity constants and the enthalpy values of ' flexible ' poly(amido-amines) are reported in Table 1, together with the corresponding $\Delta S^{\ominus}$ values.

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* Listing of both experimental details and the final computer output maybe obtained from the authors on request.

† Throughout this paper: 1 cal = 4.184 J.

For comparison purposes, the thermodynamic functions previously found for the ' rigid ' poly(amido-amines) are given in the same Table.

In the case of ' flexible ' poly(amido-amines) ' sharp ' basicity constants and protonation enthalpies were obtained in aqueous solution. The number of basicity constants is equal to the number of amino-nitrogens present in the repeating units. Attempts to increase the number of basicity constants were rejected by the computer.

It may be observed that the thermodynamic functions of ' flexible ' poly(amido-amines) are generally similar to those of the corresponding ' rigid ' ones. In general, the protonation enthalpies decrease with the number of amino-nitrogens present in the repeating unit, due to inductive effects.[17,18]

In the first protonation step all the thermodynamic functions are equal for corresponding polymers of both classes, when considering the estimated standard deviations. In the second step, however, some differences are observed, except for L^5 and L^9. The largest difference in the thermodynamic functions is observed for polymers L^4 and L^9, derived from piperazine, where $|\Delta(\Delta H_2^\circ)| = 1.61$ and $|\Delta(\Delta S_2^\circ)| = 5.6$. It is interesting to note that the values relative to the ' flexible ' polymer are very similar to those previously determined for the non-macromolecular model[6,18] of the ' rigid ' polymer ($-\Delta H_1^\circ = 5.50$ kcal mol^{-1}, $\Delta S_1^\circ = 14.1$ cal K^{-1} mol^{-1}; $-\Delta H_2^\circ = 4.00$ kcal mol^{-1}, $\Delta S_2^\circ = 1.6$ cal K^{-1} mol^{-1}). This is further proof that the behaviour of the highly cyclized polymer L^9 is anomalous among poly(amido-amines).[18] A smaller, but significant, difference is also observed in the case of L^2 and L^8, where $|\Delta(\Delta H_2^\circ)| = 0.69$ and $|\Delta(\Delta S_2^\circ)| = 2.3$. This may be explained by considering that these polymers tend to assume a rod-like structure, when fully protonated, due to the possibility of hydrogen-bond formation between the ' onium ' ions and the carbonyl groups.[19] Thus, a rod-like conformation is favoured when there are equal numbers of protonated nitrogens and carbonyl groups, and when both belong to the main chain, as in L^2,L^8 and L^4,L^9, but not in L^5,L^{10} and L^1,L^7. Furthermore, a rod-like conformation is more likely to occur when ring structures are present in the main chain, as in ' rigid ' poly(amido-amines). A possible rod-like conformation for the polymer L^2 after the second protonation step (the most stable one, according to preliminary computations[19] performed by the PCILO method[20]) is shown in Figure 2.

TABLE 2

Spectrophotometric data and stability constants of copper(II) complexes with ' rigid ' and ' flexible ' poly(amido-amines) in aqueous solution at 25 °C

Ligand	Complexing reaction	log β [a]	Electronic spectra [b]/ 10^3 cm^{-1}
L^2 [c]	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	8.96 (10)	14.8 (174)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	5.52 (25)	
L^8	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	8.72 (5)	14.9 (220)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	6.39 (14)	
L^5 [d]	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	8.47 (5)	14.2 (135)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	6.1 (1)	
L^{10}	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	8.03 (2)	14.4 (145)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	6.08 (4)	

[a] Estimated standard deviations are given in parentheses. [b] The molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] Ref. 9. [d] Ref. 11.

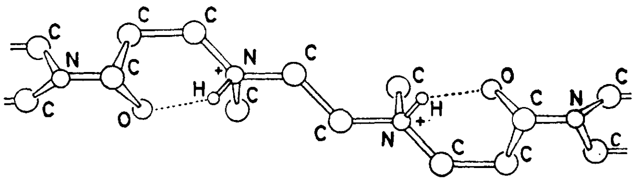

FIGURE 2 Possible rod-like conformation for the polymer L^2 after the second protonation

Copper(II) *Complex Formation.*—The ability of ' flexible ' poly(amido-amines) to complex with copper(II) is similar to that of the corresponding ' rigid ' ones (Table 2). The polymer L^7 does not form any copper(II) complex in aqueous solution, as its ' rigid ' counterpart does. This is obviously related to the fact that only one tertiary amino-group is present in the repeating unit of both polymers and there are no co-operative effects between different units belonging to the same or to different macromolecules. For the latter reason, the polymers L^4 and L^9 do not form complexes in aqueous solution either, since their tertiary amino-groups are joined in a piperazine ring, which doesn't easily adapt to a conformation able to complex the metal ion. On the other hand, polymers L^8 and L^{10} do form the same copper(II) complexes in aqueous solution as their ' rigid ' counterparts, *i.e.* CuE and Cu(OH)E (where E means the repeating unit of the polymer). The stability constants of CuE complexes are slightly lower in the case of ' flexible ' poly(amido-amines). The latter polymers give rise to electronic spectra in aqueous solution, the maxima of which are slightly shifted to higher frequencies with molar absorption coefficients which are significantly greater (Table 2).

Conclusions.—From the above results the following conclusions may be drawn. Firstly, the presence of cyclic or linear structures between the tertiary amino-groups belonging to different repeating units has only a slight influence on the protonation constants, although in some instances differences may be observed in the thermodynamic functions ΔH° and ΔS°. Secondly, when the basic nitrogens are co-ordinated to a larger doubly charged ion, such as copper(II), significant differences are observed between the two series of polymers.

In any case, even the ' flexible ' poly(amido-amines) behave towards both protonation and complex formation in a way which may be regarded as exceptional in the polymeric domain.

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REFERENCES

[1] H. Morawetz, 'Macromolecules in Solution,' 2nd edn., Wiley–Interscience, New York, 1975, pp. 344 and 369.

[2] S. L. Davydova and N. A. Plate, *Co-ordination Chem. Rev.*, 1975, **16**, 195.

[3] V. Crescenzi, F. Quadrifoglio, and F. Debben, *J. Polymer Sci., Part A*-**2**, *Polymer Phys.*, 1972, **10**, 337.

[4] F. Danusso and P. Ferruti, *Polymer*, 1970, **11**, 88.

[5] R. Barbucci, P. Ferruti, C. Improta, M. Delfini, A. L.Segre, and F. Conti, *Polymer*, 1978, **19**, 1329.

[6] R. Barbucci, P. Ferruti, M. Micheloni, M. Delfini, A. L. Segre, and F. Conti, *Polymer*, 1980, **21**, 81.

[7] R. Barbucci, P. Ferruti, C. Improta, M. La Torraca, L. Oliva, and M. C. Tanzi, *Polymer*, 1979, **20**, 1298.

[8] R. Barbucci, V. Barone, and P. Ferruti, *Atti Accad. naz. Lincei, Rend. Classe Sci.*, 1978, **64**, 481.

[9] R. Barbucci, V. Barone, P. Ferruti, and M. Delfini, *J.C.S. Dalton*, 1980, 253.

[10] R. Barbucci and P. Ferruti, *Polymer*, 1979, **9**, 1061.

[11] P. Ferruti, L. Oliva, R. Barbucci, and M. C. Tanzi, *Inorg. Chim. Acta*, 1980, **41**, 25.

[12] F. Danusso, P. Ferruti, and G. Ferroni, *Chimica e Industria*, 1967, **45**, 453.

[13] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

[14] J. D. Hole, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605; C. E. Vanderzee and J. A. Swanson, *ibid.*, p. 2608; L. Sacconi, P. Paoletti, and M. Ciampolini, *Ricerca sci.*, 1959, **29**, 2412.

[15] J. J. Christensen, L. D. Hansen, and R. M. Izatt, 'Handbook of Proton Ionization Heats and related Thermodynamic Quantities,' Wiley–Interscience, New York, 1976.

[16] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.

[17] R. Barbucci and V. Barone, *J. Solution Chem.*, 1979, **8**, 427 and refs. therein.

[18] R. Barbucci, V. Barone, P. Ferruti, and L. Oliva, *J. Polymer Sci.*, in the press.

[19] V. Barone, unpublished work.

[20] J. P. Malrieu, in 'Modern Theoretical Chemistry,' ed. G. Segal, Plenum Press, New York, 1977, vol. 7, pp. 69—103 and refs. therein.