confirm our earlier observations that, in the methyl methacrylate-imide system the imide itself is more ready to copolymerize. In consequence, this leads to a considerable enrichment of the copolymer in methyl methacrylate in comparison with the initial mixture of the comonomers. If, additionally we take into consideration the low solubility of the imide in methyl methacrylate it is necessary to classify it as a factor which is of limited use in modifying methyl methacrylate. Alternatively, *N*-iso-BMI can, in a relatively broader range of concentrations, copolymerize in the mass form with styrene. The reactivity ratios observed indicate that in the copolymerization of styrene *N*-iso-BMI the reaction of mass radicals with the imide ($r_1 < 0$, $r_2 > 0$) will be facilitated. This results in enrichment of the copolymer in *N*-iso-BMI in comparison with the initial mixture of the comonomers. If we take into consideration the fact that the presence of heterocyclic imide units in the chain of a copolymer gives the copolymer on the whole, better properties. Looking at its thermal resistance, we must estimate *N*-iso-BMI as positive modifying factor for polystyrene.

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Macroinorganics: 8.* Chelation of copper(II) ion with some new poly(amido-amines)

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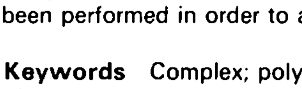
The effect on Cu(II) complexing ability of the number (n) of methylenic groups between aminic nitrogens has been studied for two classes of poly (amido-amines). In order to better elucidate the mechanism of complex formation, low molecular weight models of the polymers have also been studied. The complexing abilities of polymers and models are very similar and decrease by increasing n. Indeed compounds with $n=4$ fail to form complexes in aqueous solution. Some viscosimetric titrations have been performed in order to ascertain possible conformational transitions upon complexation.

Keywords Complex; poly(amido-amines); chelation; copper ion; viscometric titration; nitrogen

INTRODUCTION

We have recently studied the basicity[1] and complexing ability[2] of a new class of linear amino polymers: poly(amido-amines) in aqueous solution. We recall that these polymers look like non-macromolecular bases towards protonation and complex formation allowing the determination of 'sharp' thermodynamic properties[3]. As part of a comprehensive research programme designed to give a better insight into the reasons for the unusual behaviour of poly(amido-amines) we have recently studied the effect on stepwise protonation of the length of the aliphatic chain between the amino groups present in the monomeric unit[4]. In order to better ascertain specific effects due to the macromolecularity we have also studied a set of non-macromolecular model compounds.

Pn



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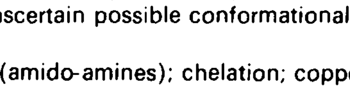

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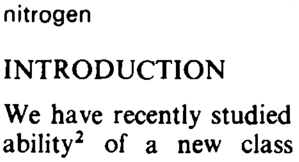

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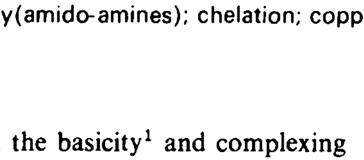

The aim of the present work is to widen the above study to the complex-formation behaviour, by reporting some results on the coordinating abilities towards copper(II) of poly(amido-amines), as a function of the length of the aliphatic chain within the monomeric units. The study has been carried out by potentiometric, spectrophotometric and viscosimetry techniques, and the conformational transitions upon complexation have been analyzed.

EXPERIMENTAL

Materials

The synthesis of polymers and the corresponding models have been previously reported[4].

CO_2-free NaOH solutions were prepared, stored and standardized as described elsewhere[5]. Stock solutions of 0.1 M NaCl were prepared from sodium chloride (C.Erba, ACS grade) without further purification and used as the ionic medium for potentiometric and viscosimetric measurements.

Emf measurements

Potentiometric titrations were carried out using a digital PHM-84 Radiometer 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. All the titration operations (the amount of the titrant

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* Part 7 is ref. 4

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liquid to add step-by-step, the total amount of titrant to add, the number of mV voltage readings at each step) were all programmed by a Rockwell minicomputer, and all the data the medium of the output voltages read at each step, the number of readings and the millilitre of titrant added, were automatically recorded. For each determination the cell, thermostatted at 25°C, was filled with $\sim 100\ \mathrm{cm}^3$ of 0.1 mol dm^{-3} NaCl solution, containing the poly(amido-amine), or the model compound, hydrochloric acid and $CuCl_2$ in a known amount. The solution was titrated with NaOH solution dispensed from a Metrohm Multidosimat piston burette graduated in hundredths of a millilitre under CO_2-free nitrogen. The experimental details are reported in *Table 1*. The program Miniquad 76-A used to calculate the stability constants has been previously described[6].

Table 1 Experimental details of the potentiometric measurements at 25°C in 0.1 M NaCl

Ligand	Curve	Initial amount mmol			Number of points
		L	Cu^{2+}	H^+	
P_3	1	0.2288	0.0464	0.5460	71
	2	0.2183	0.1271	0.5493	24
	3	0.1870	0.0431	0.5458	53
	4	0.2173	0.0527	0.5461	46
M_3	1	0.2512	0.0353	0.5724	52
	2	0.2467	0.0539	0.5732	56
	3	0.2679	0.0499	0.5720	53

Spectrophotometric measurements

Electronic spectra were recorded at 25°C on a Perkin-Elmer 200 spectrophotometer using 1-cm silica cells.

Viscosity measurements

The viscosity measurements were performed at 25°C with a Cannon Ubbelohde 50/E/998 having a flow time of 210 s for aqueous 0.1 M NaCl connected with a viscosity timer. Corrections for kinetic energy and rate of shear were found to be negligible. Pure CO_2-free water was used throughout, and the solutions were used immediately after preparation. The solutions were titrated with a 0.1 M NaOH solution, added through a Metrohm Dosimat E415 automatic piston burette. At least two complete titrations were carried out for each polymer. The salt concentration was 100 times larger than that of the polymer, and the ratio Cu(II)/polymer was about 1/3.

RESULTS AND DISCUSSION

Stability constants and electronic spectra

The coordinating abilities both of polymers and models with respect to Copper(II) ion in aqueous solution are summarized in *Table 2*. As for the other poly(amido-amines) previously studied, 'sharp' stability constants have been determined. CuL complexes (where the polymeric ligand 'L' denotes the repeating unit of the polymer) were in evidence in aqueous solution only for P_2, M_2, P_3, M_3, P_2P, M_2P. For the other studied

Table 2 Spectrophotometric data and solubility constants of copper (II) complexes with poly(amido-amines) and their non macromolecular models at 25°C in 0.1 M NaCl

Ligand (L)	Ability to form Cu^{2+} complexes in aqueous solution	Reaction	Stability constants[a]	Electronic spectra[b] ($10^3\ \mathrm{cm}^{-1}$)
P_2[c]	Yes	$Cu^{2+} + L \rightleftarrows CuL^{2+}$	8.96	14.8(174)
		$CuL^{2+} + OH^- \rightleftarrows Cu(OH)L^+$	5.52	
P_3	Yes	$Cu^{2+} + L \rightleftarrows CuL^{2+}$	5.36(2)	14.9(169)
		$CuL^{2+} + OH^- \rightleftarrows Cu(OH)L^+$	5.14(8)	
		$CuL^{2+} + 2OH^- \rightleftarrows Cu(OH)_2L$	10.25(5)	
P_4	No	–	–	–
M_2[c]	Yes	$CuL^{2+} + L \rightleftarrows CuL^{2+}$	9.10	14.8(176)
		$CuL^{2+} + 2OH^- \rightleftarrows Cu(OH)_2L$	8.40	
M_3	Yes	$Cu^{2+} + L \rightleftarrows CuL^{2+}$	6.45(2)	14.9(169)
		$CuL^{2+} + OH^- \rightleftarrows Cu(OH)L^+$	5.09(7)	
		$CuL^{2+} + 2OH^- \rightleftarrows Cu(OH)_2L$	9.90(6)	
M_4	No	–	–	–
P_2P[c]	Yes	$Cu^{2+} + L \rightleftarrows CuL^{2+}$	8.47	14.2(135)
		$CuL^{2+} + OH^- \rightleftarrows Cu(OH)L^+$	6.12	
P_3P	No	–	–	–
P_4P	No	–	–	–
M_2P[c]	Yes	$Cu^{2+} + L \rightleftarrows CuL^{2+}$	8.61	14.1(125)
		$CuL^{2+} + OH^- \rightleftarrows Cu(OH)_2L$	5.7	
		$CuL + 2OH^- \rightleftarrows Cu(OH)_2L$	8.7	
M_3P	No	–	–	–
M_4P	No	–	–	–

[a] Estimated standard deviations are given in parentheses

[b] The molar absorption coefficients ($\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$) are given in parentheses

[c] Ref. 2

compounds, insoluble hydroxides precipitate prior to the formation of a significant amount of CuL. These results show that increasing the chelating ring size from five (P_2,M_2 and P_2P,M_2P) to six, leads to a distinct reduction in the CuL complex stability (P_3, M_3) or even to the inability to chelate Copper(II) to give stable complexes (P_3P, M_3P). Ligands which would form seven membered chelate rings (P_4, M_4 and P_4P, M_4P) do not give stable complexes. This general behaviour is well documented for primary and secondary diamines. For instance the stability of CuL complexes decreases in going from ethylenediamine to propylenediamine and the following term of the series, putrescine, does not chelate to Copper(II) to give stable complexes in solution[7]. Less information is available for tertiary amines: *N*,*N*,*N*′,*N*′-tetramethylethylendiamine forms a CuL complex[8] but no evidence has been found for the formation of complexes by longer tertiary amines[7]. The reduction in the stability of CuL complexes increasing the chelating ring size has been related to the strain experienced by rings with more than 5 terms[9] and the same would also apply in the present case.

The different behaviour of P_3, M_3 and P_3P, M_3P (the former two compounds form stable CuL complexes while the latter two do not) indicate that unsymmetrically substituted diamines (P_3P, M_3P) have lower stability constants than their symmetrically substituted analogues. This result is perfectly in accord with those obtained for low molecular weight diamines. For instance *N*,*N*-dimethyl or *N*,*N*-diethyl ethylenediamine (unsymmetrically substituted) show lower stability constants than *N*,*N*′-dimethyl or *N*,*N*′-diethyl ethylenediamine(symmetrically substituted)[10]. This effect is probably due to the higher strains of the bulky substituents at the same nitrogen when the unsymmetrically substituted compounds are compelled to assume a conformation that is able to coordinate the metal ion. However, a further effect probably operates in the case of the present compounds studied here. In fact, besides the amino groups, the carbonyl groups probably also participate in the complexation in symmetrically substituted compounds[11], while this is not the case for unsymmetrically substituted compounds due to higher steric hindrances (see *Figure 1*).

As in the case of protonation constants[4] and of other poly(amido-amines)[2] the CuL stability constant of the model M_3 is slightly higher than that of the polymer P_3; this is presumably to be related to different entropy effects[1b].

Both Cu(OH)L and $Cu(OH)_2L$ complexes have been found for M_3 and P_3. The stability constants for Cu(OH)L are slightly lower than those obtained for $n=2$, (P_2), suggesting a larger distortion of the complex increasing the size of the chelate ring. The stability constant for the addition of a second group OH is nearly the same as for the first OH group: this suggests complete independence between the two groups. The electronic spectra of the two CuL complexes (P_3 polymer and M_3 model) are similar. They are consistent with an octahedral tetragonally-distorted structure having as chromophore group CuO_4N_2.[12] The fact that the electronic data of polymer and model are quite similar is in agreement with the substantial independence of the monomeric units of the polymer in the complexation.

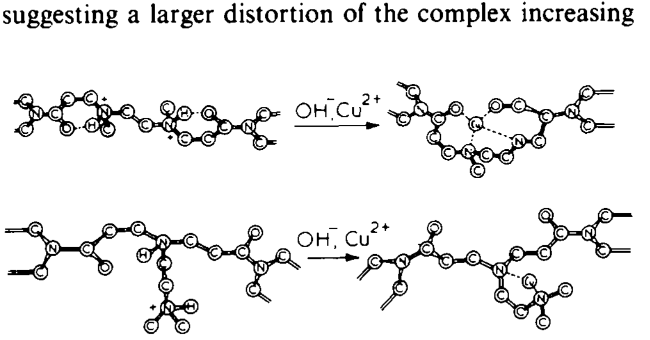

Figure 1 Available conformations of the polymers P_2 and P_2P in the di-protonated form and after the complex formation reaction

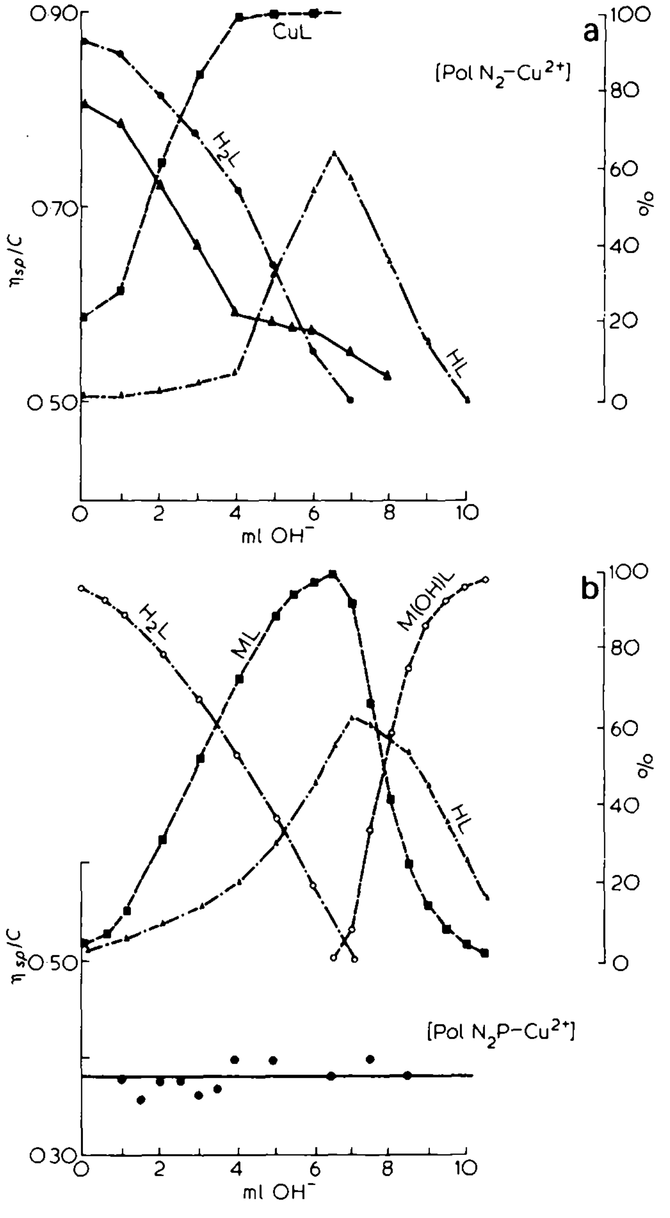

Figure 2 Variation of the viscosity η_{sp}/C (solid lines) and distribution curves (broken lines) vs. millilitres of OH^- added for the two systems Cu–P_2 (a) and Cu–P_2P. (b) For the lines not containing metal, the percentage is relative to total ligand; for the lines containing metal, the percentage is relative to total metal

Viscosimetric titrations

The η_{sp} *C*'s of P_2 and P_2P at various degrees of neutralization are shown in *Figure 2* together with the corresponding distribution curves. An analogous titration for polymer P_3 has not been performed because of the early precipitation of the hydroxide compound. The viscosimetric titrations were performed at the same concentrations as the potentiometric curves.

It may be observed that in other linear polymer P_2 the viscosity monotically decreases upon increasing the pH. Inspection of the superimposed distribution curves show that the decrease of η_{sp}/C is extremely large until the formation of the complex CuL is complete, it then remains nearly constant until complete deprotonation of the ligand; the second slight jump corresponds to the maximum of the HL species and is due to a conformational transition[4].

On the contrary, in the case of the 'branched' polymer P_2P, the corresponding plot (*Figure 2*) does not show any noticeable variations of η_{sp}/C over the whole range.

The independence of the viscosity from the pH and the degree of complexation for polymer P_2P is unusual and is probably due to the fact that the conformational transitions involved in the protonation[4] or complex formation only regard side substituents and do not alter the characteristics of the main chain substantially (*Figure 2*).

CONCLUSION

It has been shown that the lengthening of the aliphatic chain connecting the aminic nitrogens of a monomeric unit strongly reduces the complexing abilities of poly(amido-amines). The basic groups belonging to the different monomeric units remain independent as sharp basicity and stability constants have been obtained. Furthermore, we have again found a close similarity between poly(amido-amines) and their low molecular weight models.

However, significant (and different for isomeric polymers) conformational transitions are connected with the protonation and complex formation. These conformational transitions clearly regard each single monomeric unit, but in the case of the linear polymers the coordination of Cu(II) occurs on the main chain, while, in the case of unsymmetric polymers, the coordination only involves side groups. Hence only in the first case will these conformational transitions affect the properties of the whole macromolecule. This indeed is the case because the joints between different monomeric units (diacylpiperazinic rings) are always very rigid, so that freezing of all the monomeric units in a given conformation results in a freezing of the whole macromolecule.

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