Polymer Bulletin 17, 119–125 (1987)

Polymer Bulletin

Effect of the complexation with copper(II) on the hydrodynamic behaviour of some polyelectrolytes

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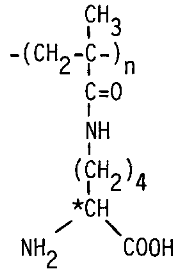
Summary

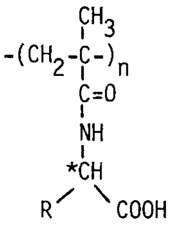
The complex formation between copper and a number of polyelectrolytes derived from amino-acids was studied by viscosimetry. It was concluded that the complexes involving two side chains of the polymer form between two neighbouring side chains of the same polymeric chain. The effect of copper on the viscosity of the polymer solutions was thus accounted for mainly by changes in the net charge of the polymer and changes in the electrostatic interactions.

Introduction

In previous papers (1-5) was reported the potentiometric and spectroscopic study of the complexation of copper (II) with some polyelectrolytes derived from natural amino-acids. The polyelectrolytes under study were poly(N methacryloyl-L-alanine) (PNMA) (1,2), poly(N-methacryloyl-L-aspartic acid) (PNMAS) (3), poly(N-methacryloyl-L-glutamic acid) (PNMG) (3), poly(N-methacryloyl-L-asparagine) (PNMAsn) (4) and poly(N-methacryloyl-L-lysine) (PNML) (5).



PNML



R=CH_3	PNMA
R=CH_2COOH	PNMAS
R=$(CH_2)_2COOH$	PNMG
R=CH_2-CO-NH_2	PNMAsn

In all cases, complexes involving two side chains of the polymer were evidenced, especially at high pH. With PNMA, PNMG, PNMAS and PNMAsn, these complexes are formed by deprotonation of the amide nitrogens of two side

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chains (1-4). With PNML, the 2:1 complex is glycine-like i.e. involves only the terminal α amino and carboxyl groups (5).

As spectroscopic methods do not give any information on the conformation of the polyelectrolyte-metal complexes, we have undertaken a viscosimetric study in order to distinguish between intra and intermolecular complex formation.

Experimental

Samples PNMA, PNMG, PNMAS, PNMAsn and PNML were synthesized according to methods described elsewhere (5,6). Copper perchlorate $Cu(ClO_4)_2$, $6H_2O$ (Fluka) was used as the metal ion source. Copper solutions were standardized by ion exchange on a I.R. 120 Amberlite resin, followed by an acid-base titration of the resulting $HClO_4$ solution.

Solutions with molar ratio R ([ligand]/[metal]) ranging from 1.7 to 15 were investigated.

Viscosity measurements were carried out with a Fica "Viscomatic" apparatus equipped with an Ubbelhode type viscosimeter, at 25 ± 0.01°C.

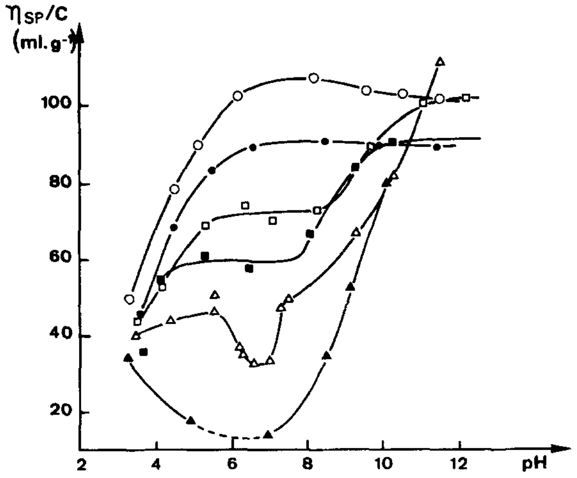
The concentration of the ligand was 3-5 10^{-3} mole.l^{-1}.

Results and discussion

The complex formation between a polyelectrolyte and the metal ion has many effects. Complex formation decreases the net charge of the polymer. Thus, the electrostatic repulsions are reduced and the viscosity decreases. Intramolecular

Figure 1

Reduced viscosity of PNMA-Cu solutions as a function of pH, in 0.1 M $NaClO_4$.
(○) no copper ; (□) R=5 ; (■) R=3.8 ; (△) R=2.8 ; (▲) R=1.7 ; (•) R=4 with Ca^{++}.
[PNMA] = 4.3 10^{-3} mole.l^{-1}
(- - -) : précipitation



complexation collapses the macromolecules and decreases the viscosity whereas intramolecular complexation increases the apparent molecular weight and increases the viscosity. In most cases, the hydrodynamic behaviour is the result of all these contributions. In our case, the concentration range used is lower than the critical concentration c* beyond which the macromolecules can interpenetrate. Thus the intermolecular complexation is not likely to occur (7) and complex formation is expected to induced a decrease of the viscosity.

Figure 1 shows the reduced viscosity of PNMA-Cu mixtures as a function of pH at different R values. In the absence of copper, the viscosimetric behaviour of PNMA is typical of that of a polyelectrolyte despite the presence of a ionic background. Even at low pH, the reduced viscosity is rather high due to auto-ionization. It increases strongly from pH 3 to 7 when the carboxyl groups ionize. Beyond pH 7, the viscosity decreases slightly when excess of titrant is added.

For all R values, the addition of copper drastically reduces the viscosity especially at high copper concentration (low R values) and even at low pH. In some cases (ex: R=1.7 pH 5-7) the net charge is very low and the polymeric complex precipitates. Such results were reported for other polyelectrolytes as poly(acrylic acid) (8), poly(vinylamine) (9), partially quaternized poly(vinylpyridine) (10) or poly(glutamic acid) (11). At R=5 and 3.8, the viscosity increases during the ionization of the carboxyl groups, but less than without copper because the formation of a complex between copper and two carboxylate groups reduces the overall charge. (The net charge for two repeat units is zero instead of -2). The plateau at pH 5-8 can be explained by the formation of the second complex involving one peptide nitrogen (net charge zero) (1,2). At higher

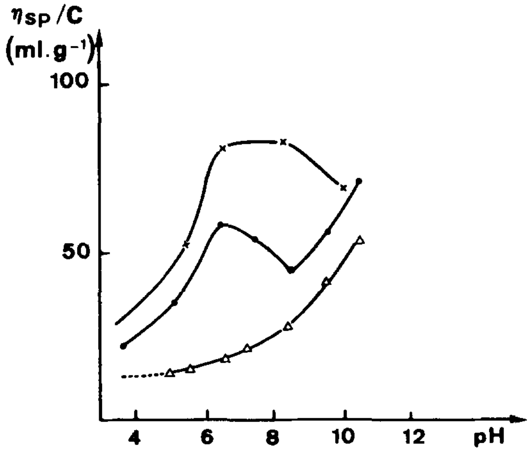
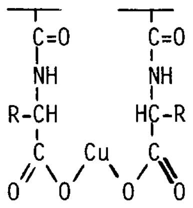


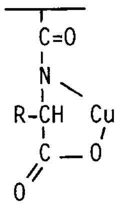
Figure 2

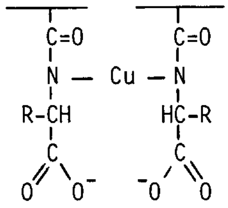
Reduced viscosity of PNMAsn-Cu solutions as a function of pH in 0.1 M $NaClO_4$.
(×) no copper ; (•) R=10 ; (△) R=5.
[PNMAsn] = 3.8 10^{-3} mole.l^{-1}
(----) : precipitation

pH a third complex is formed between one copper and two peptide nitrogens of two side chains, and the copper-carboxylate bonds are broken thus increasing the electrostatic interactions and the viscosity.

The fact that the reduced viscosity at high pH is nearly the same than in absence of copper suggests that two neighbouring side chains are involved in complex formation in agreement with a previous work (12). At lower R values, the formation of the second complex is more important and the viscosity strongly decreases around pH 7, at which the formation of this complex is maximum (1,2).


Complex 1


Complex 2


Complex 3

With calcium, only the first complex is formed. The deprotonation of the peptide nitrogen (second complex) cannot occur and the viscosity decrease is much less.

Results obtained with the PNMAsn-Cu system (figure 2) are very similar and may be explained in the same way.

The case of PNMG and PNMAs is different. These two polymers contain two carboxyl groups in each side chain and the first complex mentioned above between one copper and two carboxylates may also form inside one side chain,

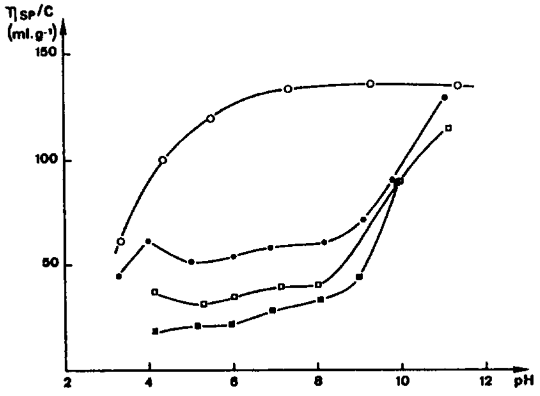


Figure 3

Reduced viscosity of PNMG-Cu solutions as a function of pH in 0.1 M $NaClO_4$.
(○) no copper ; (•) R=6 ;
(□) R=4 ; (■) R=3

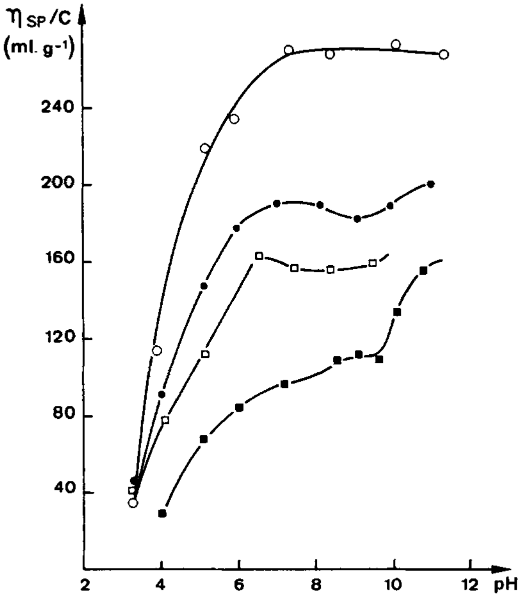
with formation of a eight or seven membered chelate, respectively. This chelate competes with the intramolecular complex which may also form, as for PNMA or PNMAsn. With PNMG (figure 3), the viscosity at low pH decreases in the presence of copper as for PNMA and PNMAsn indicating a complex between two side chains. This is not surprising since eight membered rings are not very stable. In the intermediate pH range, the formation of the second complex does not result in a strong drop of the viscosity since in that case, this complex is charged. Beyond pH 8, the viscosity increases again up to values obtained in the absence of copper, indicating the complete liberation of the carboxylate groups as for PNMA and PNMAsn.

The viscosimetric behaviour of PNMAs is different. At low pH, the addition of copper does not change the viscosity except at very low R values. In the high pH range, the viscosity is much lower than in the absence of copper. This clearly indicates that some carboxylates groups remain involved in a complex which is a seven membered stable chelate (3).

It may thus be concluded that for the above polyelectrolytes, the formation of the complexes occurs between two neighbouring side chains. At high pH all the carboxylate groups are released from the complex, except for PNMAs where the seven membered chelate formed with two carboxylates groups of the same side

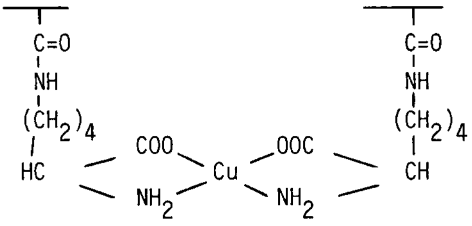
Figure 4

Reduced viscosity of PNMAs-Cu solutions as a function of pH in 0.1 M $NaClO_4$.
(○) no copper ; (●) R=8 ; (□) R=4 ; (■) R=3



chain is stable enough, thus decreasing the overall charge of the complex, even at high pH.

PNML is a polyampholyte with a net charge of zero per residue between pH 4 and 9. Above pH 9 the deprotonation of the NH_3^+ group creates a net charge of -1 per residue and the viscosity increases strongly even in the presence of 0.1 M $NaClO_4$ (figure 5). On addition of copper, a 2:1 PNML-Cu complex involving two side chains is formed with a net charge of zero (5). The variation of the charge is sufficient to explain the viscosity drop. The complex probably forms between two neighbouring side chains because collapsing of the polymer would result in a more drastic viscosity drop.



2:1 complex

Thus it is concluded that, for all the polymer under study, neighbouring side chains are involved in complex formation. This is in agreement with the results of previous works which have shown that the tacticity of the polymer is of importance in the process of complex formation (12-14).

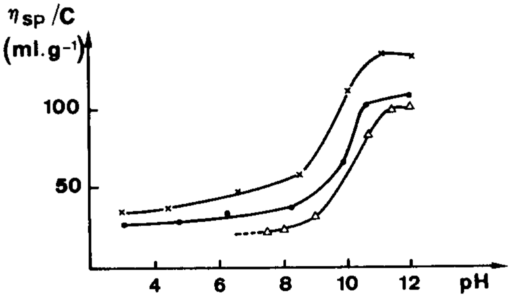


Figure 5

Reduced viscosity of PNML-Cu solutions as a function of pH.

0.1 M $NaClO_4$; (×) no copper ; (●) R=15^4; (△) R=7.

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Accepted December 9, 1986 C