Copper(II) Complexes with Polymer Bound S-methyl-L-cysteine

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The interaction of N-methacryloyl-S-methyl-L-cysteine (SMC) homopolymer with copper(II) was studied by spectroscopic methods and viscosity measurements. The fact that the polymer chain brings several carboxylates close to each other leads to the formation of complex species of $Cu–(COO^-)_n$ type which are stable enough to enable metal ions to deprotonate the amide nitrogen and to form a $Cu(N^-, COO^-)$ complex.

In the basic pH region, the Cu–N bond undergoes a hydrolysis and in the main species existing in solution, the copper is still bound to carboxylate groups of the polymer.

Introduction

Our recent work on Pd(II) interaction with polymer-bound S-methyl-L-cysteine [1] has shown that amino acid bound to a polymer chain coordinates the metal ion with the same donor set [S, N] as that found in Pd(II) complexes with polymer-free S-methyl-L-cysteine [2, 3].

The immobilization of amino acid, however, may lead to different states of the polymer conformation, *e.g.*, due to formation of intramolecular loops in which the metal ion bridges two or more residues which are far from each other [1] or a different mechanism of the metal ion bindings [4]. The cupric ion interaction with S-methyl-L-cysteine may differ distinctly from that of Pd(II). The main difference derives from the fact that cupric ions would interact much less effectively with the thioether donor than Pd(II) ions [5, 6]. To establish such differences

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TABLE I. Circular Dichroism Data.

Homopolymer			Homopolymer/ $Cu(COO^- = 6)$		
pH	λ[nm]	Δε	pH	λ[nm]	Δε
5.1	216	+1.4	5.2	217	+1.45
	222	+1.35		222	+1.25
	247	−0.002		247	−0.12
				342	+0.06
				730	−0.17
				765	−0.20
6.2	214	+1.65	6.2	216	+1.45
	221	+1.5		222	+1.25
	247	−0.002		247	−0.12
				335	+0.05
				730	−0.13
				765	−0.15
7	215	+1.7	7.3	214	+1.6
	222	+1.6		222	+1.35
	247	−0.003		245	−0.11
				332	+0.03
				730	−0.13
				765	−0.10
9	216	+2.4	9	212	+1.70
	222	+1.7		222	+1.35
	247	−0.003		247	−0.04
11	216	+1.9	11	215	+1.6
	221	+1.65		221	+1.5
	247	−0.003		249	−0.03

we have studied the Cu(II) interaction with N-methacryloyl-S-methyl-L-cysteine homopolymer by spectroscopic methods and viscosity measurements.

Experimental

Poly/N-methacryloyl-methyl-L-cysteine (PNMSMC) was prepared according to the procedure described in a previous paper [1]. CD spectra were recorded on a Mark III Jobin-Yvon dichrograph in the 800–200 nm region with polymer concentration 6×10^{-3} mol/l. Absorption spectra were recorded on a Cary 219 spectrometer with copper concentration 10^{-3} mol/l. The Cu/COO^- molar ratios of 1/8, 1/6 and 1/4 were used for the studies. The Cu(II) concentration was used to calculate ϵ and $\Delta\epsilon$ values in the d–d region. For the other transitions both values were calculated assuming the polymer concentration. EPR spectra were recorded on a Varian E-109 spectrometer at 77 K in the X-band.
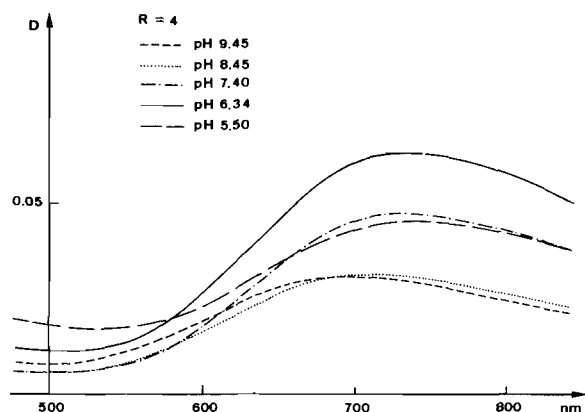
Fig. 1. Visible region of the electronic spectrum of PNMSMC: Cu(II) solutions.

Results and Discussion

The CD spectrum of metal-free homopolymer exhibits a weak Cotton effect at 246 nm and two strong positive bands at 222 and 212 nm (Table I). The 246 nm band increases its intensity when Cu(II) ions are added to the polymer containing solutions at pH 4.5–6.0. The complexation of cupric ions is also seen by formation of the d–d transition bands at 765 and 730 nm and a band at ~336 nm. The bands at 765 and 730 nm result from $B_{1g} \rightarrow B_{2g}(B)$ and $B_{1g} \rightarrow E_g(E)$ d–d transitions respectively and suggest complexation of cupric ion by N^- and COO^- donors of SMC residues. The 335 nm band assigned as a $N^- \rightarrow Cu(II)$ charge transfer transition [6] supports the coordination of an amide nitrogen to cupric ion in the 4.5–6.0 pH range.

The absorption spectrum exhibits a d–d transition at 740 nm (Fig. 1). It may also support 1N coordination. The slightly lower energy of the transition than expected [8, 9] may suggest the equilibrium of the 1N species with the complex in which Cu(II) is bound to carboxylate donors only [10].

The COO^- donor is known to be inefficient in promoting amide nitrogen deprotonation by cupric ions before metal ion hydrolysis [6]. Thus, the polymeric backbone stabilizes the Cu(II) carboxylate complex until the deprotonation of the amide nitrogen takes place. The Cotton effect around 250 nm sometimes assigned as a $COO^- \rightarrow Cu(II)$ charge transfer transition [11, 12] in the Cu(II) PNMSMC system seems to be an intraligand transition the value of which could be enhanced due to the more rigid structure of a ligand when bound to the metal ion.

The EPR spectra of the Cu(II) PNMSMC frozen solutions exhibit only a broad signal around g = 2 suggesting close proximity of metal ions bound to a polymeric matrix.

The increase of pH above 6.0 causes the disappearance of the complex transitions in the CD spectra.
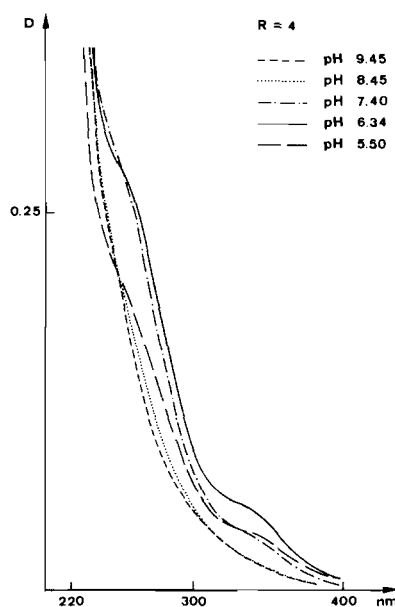

Fig. 2. U.V. region of the electronic spectrum of PNMSMC: Cu(II) solutions.

At pH 8 the Cu(II) PNMSMC solution spectra look like the spectra of the metal free homopolymer. In the absorption spectra the band at 340 nm vanishes (Fig. 2) and the d–d transition shifts slightly to higher energy and decreases distinctly its intensity. The same behaviour was observed during the hydrolysis of cupric ions with NaOH in the absence of polymer. It should be mentioned, however, that in the presence of homopolymer no precipitation of copper hydroxide takes place.

These results strongly suggest that at pH above 6, the species present in solution undergo partial hydrolysis. The hydrolysis of the $Cu-N^-$ bond leads to a decrease of ϵ of the d–d transition [8] and also increases distinctly the metal ion distance from optically active α carbon. It may lead to a dramatic decrease of the $\Delta\epsilon$ values, i.e. disappearance of the CD spectra of the complex species present in Cu(II) homopolymer solutions at pH > 6.

The complexation of copper by carboxylate groups of the polymer molecule is, however, very effective [4] and even partial hydrolysis of the species present in the studied solutions at pH around 6 does not decompose completely the copper polymer bindings. Thus, the lack of precipitation of copper hydroxide could indicate that at higher pH partially hydrolysed metal ion is still bound to the polymer carboxylate groups.

The viscosity measurements (Table II) seem to support the conclusion obtained from the spectroscopic results. The pH dependence of the polymer viscosity without and with cupric ions present in the solution shows that in both cases increase of pH increases the viscosity of the solutions. In the copper

TABLE II. Specific Viscosity (η_{sp}) for PNMSMC Polymer and its Complexes with Cu(II) Ions ((COOH) = 2 × 10^{-2} mol/l, R = 4).

pH	4.20	4.9	6.60	7.5	9	9.60	10.9
η_{sp} free PNMSMC	0.367		0.402			0.472	
η_{sp} Cu(II) complex		0.027	0.09	0.144	0.213		0.337

containing solutions, the viscosity increase is much more drastic but even at high pH it does not reach the values of the metal free polymer solutions. The very low viscosity observed at low pH for Cu(II) polymer solutions indicates that the polymr chain has a very compact structure caused by metal ion bound to residues apart from each other, most likely by COO^- donors. The dramatic increase of the viscosity with pH suggests strongly that some of the metal polymer bonds are hydrolyzed, *i.e.* $Cu-N^-$ (see above) as well as some of the $Cu-COO^-$ bonds. The latter bond breaking could have considerable impact on the polymer chain conformation leading to a more open structure and simultaneously to a higher viscosity of the copper polymer solutions. It should be mentioned here that in the Pd(II) PNMSMC solutions, viscosity was almost independent of pH since the Pd(II) complex with polymer bound SMC was stable over the whole pH range studied [1].

Conclusions

The immobilization of aminoacid residue on a polymer chain may change dramatically the equilibria between the coordinated species formed in solution as well as the coordination modes, compared to the aminoacid molecule.

The fact that the polymer chain brings several carboxylate groups close to each other allows the formation of the stable complex species in which Cu(II) binds two or more carboxylate groups. These species are stable enough to enable the metal ion to deprotonate the amide nitrogen and a $[N^-, COO^-]$ optically active complex is formed. In the basic pH region in which the Cu–N bond undergoes hydrolysis

the metal binding with carboxylate groups is still dominating in the partially hydrolyzed complexes. The latter conclusion seems to fit earlier findings about the very high stability of metal complexes with carboxylate containing polymers.

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