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Spectroscopic study (u.v.–visible and electron paramagnetic resonance) of the interactions between synthetic polycarboxylates and copper ions

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The interactions of poly(methacrylic acid) (PMA), poly(acrylic acid) (PAA) and a copolymer of acrylamide and acrylic acid (CAMAA) with copper (II) ions in aqueous solutions were studied by electron paramagnetic resonance (e.p.r.) spectroscopy as a function of the degree of neutralization α. A procedure for decomposition of the e.p.r. spectra was developed in order to evaluate the fraction of free copper and bound copper ions. When a loss of the e.p.r. signal intensity is observed in the solutions containing polymer with respect to the one of the reference copper salt solutions without polymer, this effect is attributed to the formation of a binuclear polymer/copper complex (copper: carboxylates, 2/4), inactive in e.p.r. The complex visible in e.p.r. is assumed to be mononuclear (copper: carboxylates, 1/2). This indicates that the main PMA/copper complex is binuclear. PAA and copper interactions lead to both bi- and mono-nuclear complexes, but this last species is preponderant at the higher α values. In the case of CAMAA of lower charge density and where the charges are quenched, only a mononuclear complex was found. The constants of formation of the mono- and bi-nuclear complexes were evaluated by assuming that the system was ruled by a series of equilibrium laws: copper hydrolysis, polymer ionization and polymer/copper complexation. The peculiar behaviour for PAA may be explained by considering that the constant of formation for the binuclear complex decreases when the intramolecular monomer concentration is lowered by the chain expansion. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Numerous studies have already been devoted to the interactions between poly(methacrylic acid) (PMA) or poly(acrylic acid) (PAA) and copper ions[1–9]. The methods mainly used were potentiometry, viscosimetry, ultraviolet (u.v.)–visible spectroscopy and dialysis equilibrium. There is clear evidence of formation of complexes resulting from the interactions between the different species of copper (II) ions and the carboxylic functions. The nature and amount of such complexes are strongly dependent on the pH. In the case of PMA, which was probably the most extensively studied, it has been suggested that the PMA–Cu^{2+} complexes imply two carboxylic functions per copper ion in a broad range of pH. Nevertheless, Mandel and Leyte[1,2] concluded from u.v.–visible and infra-red (i.r.) investigations that the complex is binuclear (two copper ions per complex) at low pH and mononuclear at higher pH. This hypothesis is partially based on the particular behaviour of PMA, which exhibits a conformational transition when its degree of neutralization increases. At low pH, its conformation is compact and the chain dimensions

are intermediate between that of a globule without solvent and that of a statistical coil. It is assumed that the high segment density associated with this conformation favours the formation of a binuclear complex. For a degree of neutralization higher than a value around 0.4, but which depends on the polymer concentration, the conformation is that of a strongly charged polyelectrolyte: a very expanded coil or a worm-like chain. Under these latter conditions, the electrostatic repulsions between the ionized carboxylate groups result in a dissociation of the binuclear complex, which is replaced by a mononuclear one.

The interactions of PAA with copper are described in the same terms, but no clear characterization of the complexes for both polymers have been obtained through u.v.–visible spectroscopy[8,9]. Moreover, it appeared interesting to establish the role played by the presence of the methyl group in the PMA monomer on these interactions.

PMA and PAA are two polymers whose charge density can be varied by changing the pH, and for partial neutralization, the charges have not well fixed positions along the chain but may organize themselves in order to favour the formation of complexes with cationic species (annealed charges). On the other hand,

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copolymers of acrylamide and acrylic acid (CAMAA) are polymers where the charge distribution, at neutral pH, is determined by their method of preparation (quenched charges). It is indeed well known that the distribution of the acrylic acid units is regular, sequential or Bernouillan, if the polymers are prepared by alkaline hydrolysis, acid hydrolysis or copolymerization, respectively[10-12]. Then, one can expect that this restriction in the charge freedom can have some consequences on the nature of the carboxylate–copper complexes, and this aspect has never been considered up to now. Several studies have shown that the monomer distribution has a dramatic effect on the stability of these copolymers towards calcium[13,14].

Also, electron paramagnetic resonance (e.p.r.) spectroscopy was extensively used to study the formation of complexes between paramagnetic ions and low molecular weight ligands[15-17]. The studies of polymer–copper interactions are scarce despite the potentialities of this technique and most of them were performed on solid solutions (frozen or desiccated samples) for which the high signal resolution makes the interpretation easy[18-20]. Nevertheless, some attempts have been made to characterize by e.p.r. the copper–polycarboxylate complexes and to propose quantitative interpretation of the spectra[5,21,22].

The aim of this work is to present the results of an u.v.–visible and e.p.r. investigation of aqueous solutions of PAA, PMA and CAMAA in the presence of copper salts as a function of pH. The e.p.r. results will be discussed in terms of complexation equilibria.

EXPERIMENTAL

Samples

The PMA sample was prepared by radical polymerization in water at 70°C, using potassium persulfate as initiator and quaternized mercaptoethylbutylamine $(HS-CH_2-CH_2-NH_2(Bu)^+Cl^-)$ as transfer agent. The polymer under its acid form was lyophilized. A first purification was carried out by triple precipitation in ether from a solution in methanol. Non-negligible amounts of sulfur (1%), nitrogen (0.3%) and chlorine (1%) were still present after this treatment, as measured by elemental analysis. Further purification was achieved by dialysis and ion exchange (cationic resins from Merck), which reduced the percentages of these elements down to 0.2, 0.09 and 0, respectively, close to the values estimated from the number average molecular weight of the sample and assuming the presence of a mercapto-ethylbutylamine at one end of the chain.

The sample was characterized by size exclusion chromatography either in aqueous medium [using a mixture of water and acetonitrile (4/1 v/v) and double detection: refractometry and small angle light scattering detection; Chromatix apparatus] or in tetrahydrofuran (refractometric and multi-angle light scattering detection) after esterification performed according to the method described in ref. 23. The weight average molecular weight M_w was found to be 58 000 and 54 000 from the two methods, respectively. The polydispersity index was approximately 2. The PAA sample was purchased from Aldrich. Its molecular weight was 250 000.

The CAMAA sample was prepared by Rhône-Poulenc Industries by radical polymerization at high pH[24]. The weight average molecular weight measured by static light scattering was found to be close to 5×10^6. The molar fraction of acrylic acid (τ) was determined by elemental analysis, potentiometric titration and ^{13}C nuclear magnetic resonance; τ was 0.27 ± 0.01.

U.v.–visible spectroscopy

Two spectrophotometers were used: Shimadzu UV 240 and Shimadzu UV-2100 PC. The cells had an optical pathlength of 10 mm for the range of wavelengths between 400 and 850 nm, and of 1 mm for the range between 190 and 400 nm.

E.p.r. spectroscopy

The e.p.r. spectra were recorded at room temperature with a Jeol JES-RE 2X spectrometer equipped with an ES-UCX 2 cylindrical cavity, using an aqueous sample flat cell. The irradiation power (40 mW), magnetic field modulation amplitude (0.5 mT) and frequency (100 kHz) were set to avoid signal saturation and were kept constant. The data treatments (smoothing, decomposition and double integration) were performed with Jeol 'espit 330, 01 521 version' software.

Preparation of the solutions

Polymers under their acid form were solubilized in pure water at a concentration of $2c_p$. After gentle stirring for several hours, the polymer solution was mixed with an equal volume of copper nitrate solution. Aliquots of sodium hydroxide were then added in order to modify the neutralization degree of the polymer. The degree of neutralization α is given with respect to the polymer: $\alpha = [NaOH]/c_{pM}$ where [NaOH] is the molarity of Na^+, and c_{pM} is the molar concentration of carboxylic groups. The pH of the solution was measured for each addition of NaOH.

RESULTS

E.p.r. study

Solutions of $(NO_3)_2Cu$. The spectra of the ionic species $Cu(H_2O)_6^{2+}$ (2.5 mM) in their frozen state, in the presence of 20% (w/w) glycerol to prevent ice demixing (138 K, anisotropic spectrum, $g// = 2.4198$ and $g\perp = 2.083$) and under its free state in solution at room temperature (isotropic spectrum, $g_{iso} = 2.1948$) are given in *Figures 1a* and *1b*, respectively. They were obtained at the pH (3.6) of the solution when $Cu(H_2O)_6^{2+}$ was the predominant species.

When copper is neutralized by addition of NaOH, hydrolysis reactions take place and lead mainly to the formation of a dimer species $Cu_2(OH)_2(H_2O)_{10}$[25]. *Figure 2* represents the variation of the area of the spectra (normalized by that obtained before neutralization) *versus* pH as well as the variation of the fraction of $Cu(H_2O)_6^{2+}$ and $Cu_2(OH)_2(H_2O)_{10}$. The shape of the signal does not change, but the area dramatically drops when the fraction of mononuclear species decreases, which means that it is the only species 'visible' in e.p.r., as already shown[26].

System PMA–CU. In *Figure 3* is depicted a typical spectrum obtained with the system PMA–CU. It has two components: the first one corresponds to the species $Cu(H_2O)_6^{2+}$, called 'free copper', and a second one which is shifted towards higher field values. We attribute this component to a copper species which interacts with the
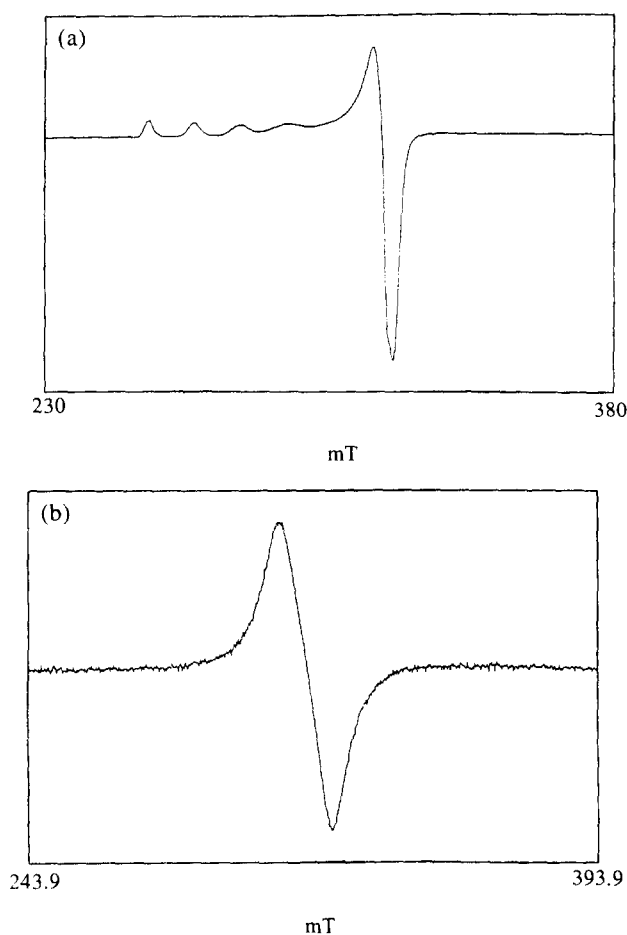
Figure 1 (a) Anisotropic e.p.r. spectrum of the species $Cu(H_2O)_6^{2+}$ obtained at 138 K in water with glycerol (20% w/w); (b) isotropic e.p.r. spectrum of the species $Cu(H_2O)_6^{2+}$ obtained at room temperature in water
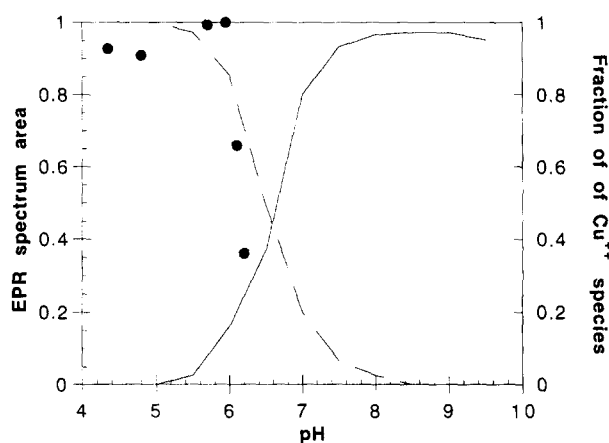

Figure 3 Example of spectrum obtained with (1) the system PMA/Cu; contributions of the (2) free Cu and (3) bound Cu as calculated from deconvolution procedure

Figure 2 Variation of the e.p.r. signal area *versus* pH for a $Cu(NO_3)_2$ (1.5 mM) solution (O) and calculated fraction of $Cu(H_2O)_6^{2+}$ (- -) and $Cu_2(OH)_2(H_2O)_{10}^{2+}$ (-)

polymer and is 'visible' in e.p.r.; it will be called 'bound copper'.

One adjusts the PMA–Cu spectrum and that of the corresponding $Cu(NO_3)_2$ solution (at the same concentration and at its own pH) through an adjustable factor, in the range where the free copper component is preponderant. One obtains the fraction of free copper and, by subtraction, the fraction of bound copper, visible
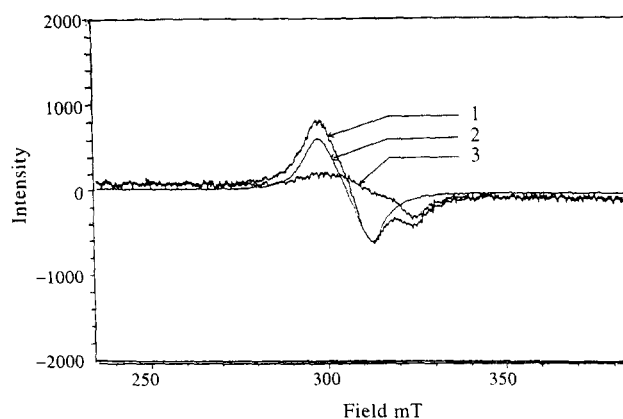
in e.p.r. The apparent g value of the slightly anisotropic spectra corresponding to this species is $g_{app} = 2.067$.

Figure 4 shows the evolution of the relative total spectra area (normalized to that obtained before neutralization) within the degree of neutralization α of the polymer for a given composition of the system. The total area decreases dramatically when α increases, while at higher α value the total spectrum is very close to that of 'bound copper'. At pH 4, the signal is 25% that of the corresponding $Cu(NO_3)_2$ solution and this cannot be attributed to the hydrolysis of the free copper (see *Figures 5* and *2*). There is clearly a loss of signal which suggests that the polymer–copper interactions lead to the formation of a species inactive in e.p.r. Thus, it seems reasonable to distinguish in the PMA–Cu solutions three different sorts of copper: (1) free copper, (2) bound copper visible in e.p.r., and (3) bound copper inactive in e.p.r. Leyte *et al.*[4] have proposed the following model for the PMA–copper interactions on the basis of u.v.–visible and i.r. measurements:

- At low pH a binuclear complex is formed implying two copper ions for four carboxylate ligands. Its structure has a D_{4h} symmetry and the two remaining water molecules are on the C4 axis.
- At high pH, there is dissociation of the binuclear complexes into mononuclear ones, which implies one copper ion per two carboxylates. This effect is attributed to the chain expansion which favours the hydration of the chain. Water molecules can hinder the formation of the binuclear species because of their strong coordination strength[6].

It is known that in the copper–carboxylate binuclear complexes, the coupling between the spins tend to be antiferromagnetic[27], leading to a loss of e.p.r. signal intensity. In such compounds, the coupling of the unpaired electrons on the copper ions gives rise to a singlet ground state with a triple state lying only a few $kJ\,mol^{-1}$ above it. The latter state could be populated at higher temperature, the compounds becoming paramagnetic. An increase of the temperature enhances the e.p.r. signal intensity.

We have, therefore, performed some experiments at varying temperatures, for the system PMA–copper ($c_{pM} = 24$ mM, $c_{Cu} = 2.5$ mM, $\alpha = 0.3$), for which all the copper ions appear to be bound. Raising the temperature to 339 K, the signal intensity does not
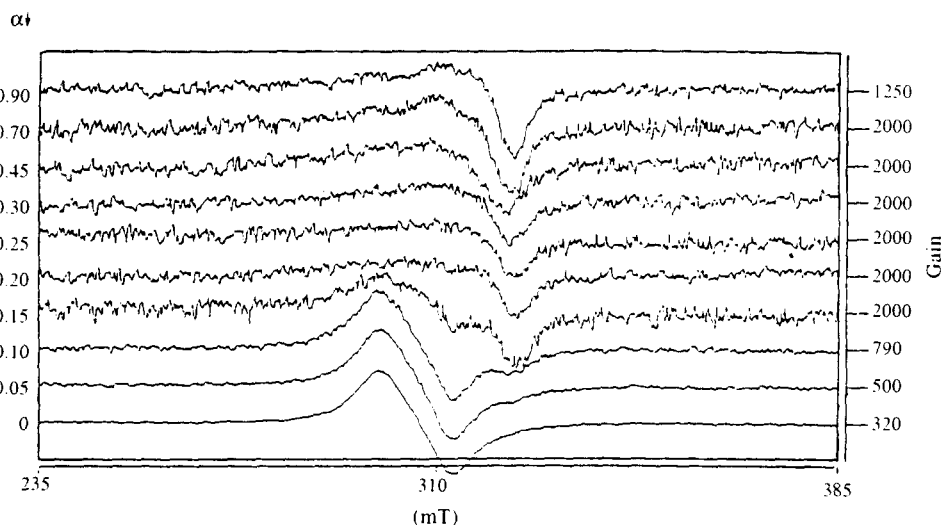
Figure 4 Evolution of the e.p.r. spectra as a function of α for the system PMA/Cu (c_{pM} = 24 mM; c_{Cu} = 1.5 mM) (room temperature)

increase, but decreases according to the Curie law, behaviour characteristic of a paramagnetic system. This suggests that the species (2) is not a binuclear complex, but more likely a mononuclear one. We have depicted in *Figure 6* the spectrum of the same system obtained at 138 K, which is characteristic of mononuclear species.

Table 1 reports the apparent $g//$ and $g\perp$ values for copper solutions in the presence or absence of the polymer. One can see that, in the presence of the polymer, the $g//$ value at $\alpha = 0$ is close to that obtained for the pure copper solution. This indicates that the main part of the copper is free in solution, behaviour which is observed also at room temperature. Also, this spectrum is characterized by a hyperfine line width larger than the one observed at $\alpha = 0.3$. This could be attributed to dipolar interactions between the non-complexed paramagnetic centres, which demix partially with ice when the system is frozen. The spectrum obtained at $\alpha = 0.3$ is characteristic of mononuclear species in interaction with the polymer, which provokes the shift of $g//$ and $g\perp$ to smaller values than at $\alpha = 0$.

The e.p.r. characteristics of the PMA–Cu system are consistent with the presence of free copper and of two kinds of complexes: the complex (2) mononuclear and 'visible' in e.p.r., and the complex (3) binuclear, inactive in e.p.r. We would like to discuss how the fractions of these copper species vary as a function of α or pH and of the copper concentration.

Figure 7 shows the results obtained for the PMA–Cu system at two different copper concentrations, for the same c_{pM} = 24 mM. When the results are plotted as a function of pH, no differences between the two values of c_{Cu} are observed. The fraction of free copper decreases up to pH 5 where it becomes negligible. Simultaneously, the fraction of bound copper (species visible in e.p.r.) slightly increases and reaches a plateau at approximately 15% for pH > 5 while the inactive species is preponderant over the whole range of pH. This suggests that PMA interacts with copper ions mainly through the formation of the binuclear complex, results in disagreement with the model of Leyte *et al.*[4] who have proposed the dissociation of this species at the higher pH. *Figure 8* shows that the variations of the free copper *versus* α are shifted to the high α values, for the higher copper concentration, as expected.
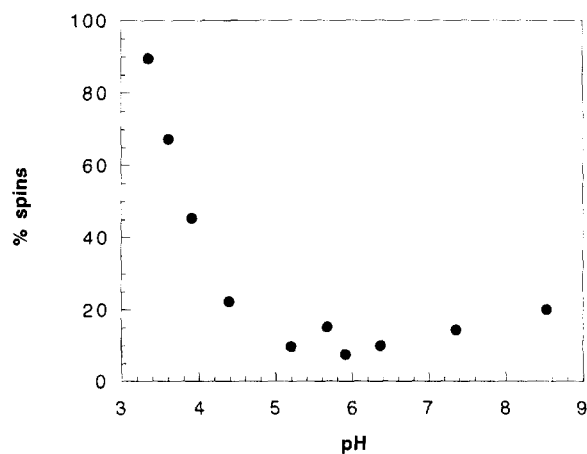

Figure 5 Variation of the area of the e.p.r. signal *versus* pH for the system PMA/Cu (c_{pM} = 24 mM; c_{Cu} = 1.5 mM) (room temperature)
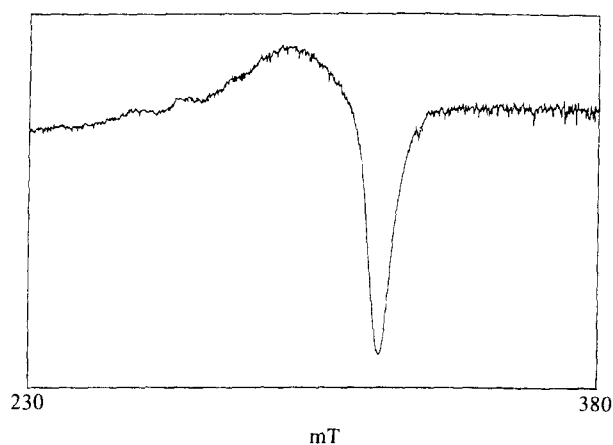

Figure 6 E.p.r. spectrum of a solution of PMACu at $\alpha = 0.3$ and T = 138 K

Systems PAA/Cu and CAMAA/Cu. The systems PAA/Cu (c_{pM} = 24 mM, c_{Cu} = 1.5 mM) and CAMAA/Cu (c_{pM} = 7.5 mM, c_{Cu} = 1.0 mM) were studied by e.p.r. under the same conditions and they behave very differently compared to the PMA/Cu system (the polymer concentration for CAMAA was taken lower than

Table 1 E.p.r. parameters for Cu(II) ion under various conditions of pH and temperature

Solution	$g_{//}$	$g_{\perp}$
PMA + Cu ($\alpha' = 0$)	2.413	2.114
PMA + Cu ($\alpha' = 0.3$)	2.383	2.080
Cu(NO₃)₂ (+20% glycerol) ($T = 105$ K)	2.420	2.083
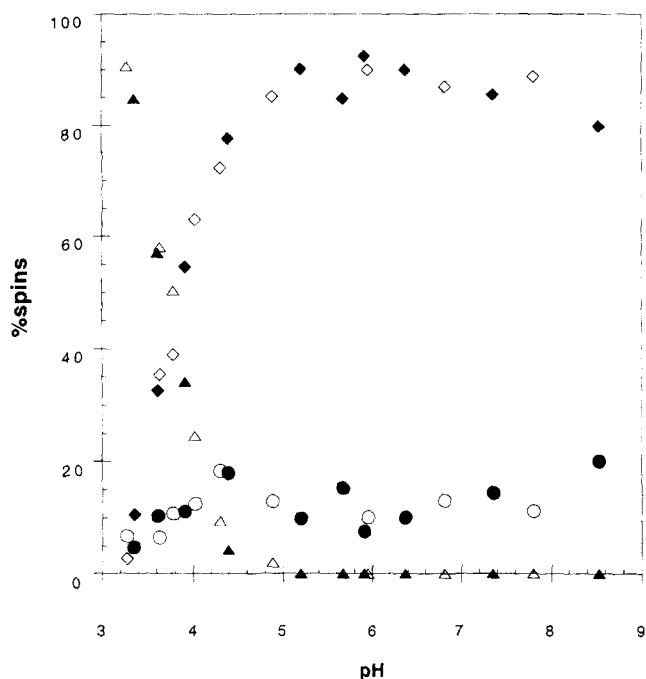
Figure 7 Evolution of the different species of Cu *versus* pH for the system PMA/Cu ($c_{pM} = 24$ mM): free Cu (triangles); bound copper visible in e.p.r. (circles), bound Cu inactive in e.p.r. (diamonds). $c_{Cu} = 1.5$ mM (full symbols); $c_{Cu} = 3$ mM (open symbols)
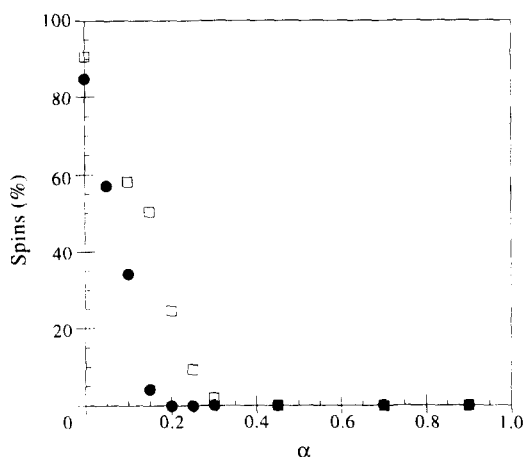
Figure 8 Variation of the fraction of free Cu in the system PMA/Cu *versus* α ($c_{pM} = 24$ mM). $c_{Cu} = 1.5$ mM (●); $c_{Cu} = 3$ mM (squares)

for PAA and PMA due to its high molecular weight and the high viscosity of the aqueous solutions). A first difference concerns the variation with pH or α of the relative total area of the spectra (normalized as previously).

While in the case of PMA, the total area of the spectra decreases continuously, a minimum is observed for PAA at pH 4.5 and for pH 7 the totality of the area is recovered (*Figure 9*).

For CAMAA (*Figure 9*), the area of the spectra is constant up to pH 6 and one can assume that the decrease for pH > 6 is only due to the hydrolysis of the copper. The shape of the signal corresponding to the bound copper is more isotropic than in the case of PMA and does not vary over the whole range of pH ($g_{app} = 2.1429$). One can conclude that the interactions between the CAMAA sample and the copper ions do not lead to the formation of a binuclear complex. The loss over a large range of pH seems to be a characteristic of the PMA–copper system.

Figures 10a and *10b* show the variations of the fraction of the different copper species for PAA and CAMAA as a function of α. In the case of CAMAA, the free copper fraction tends to 0 for a relatively high value of α and that of the mononuclear species passes through a maximum. Due to the low charge density of this polymer, it could be that the totality of the copper is not bound by the polymer, and the residual free ions are transformed at high pH into the dimeric ionic species, which are inactive in EPR or copper hydroxide. It is worthwhile to mention that a precipitate is observed in this pH range. The initial slope of the PAA curve is comparable with that of PMA and more negative compared to that of CAMAA, but at higher pH, there is a complete disappearance of the binuclear complexes.

It is, then, interesting to mention that the behaviour observed with PAA seems to be exactly that predicted in the model of Leyte *et al.*[4] (binuclear complex at low pH and mononuclear one at higher pH) while, in the case of PMA, the binuclear complex remains stable up to high pH.

U.v.–visible spectroscopy

1) Solutions of $Cu(NO_3)_2$. The aqueous solutions of copper (II) have two absorptions peaks at 795 and 230 nm.
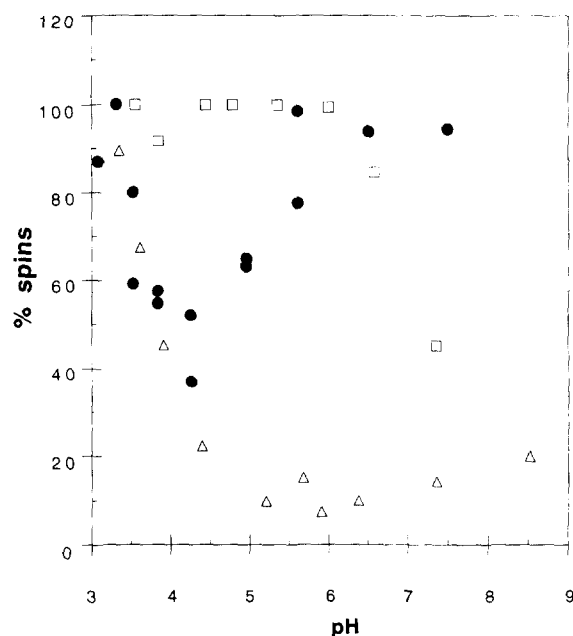
Figure 9 Evolution of the area of the e.p.r. signal for three systems: PMA/copper ($c_{pM} = 24$ mM, $c_{Cu} = 1.5$ mM) (triangles); PAA/Cu ($c_{pM} = 24$ mM, $c_{Cu} = 1.5$ mM) (circles); CAMAA/Cu ($c_{pM} = 7.5$ mM, $c_{Cu} = 1$ mM) (squares)
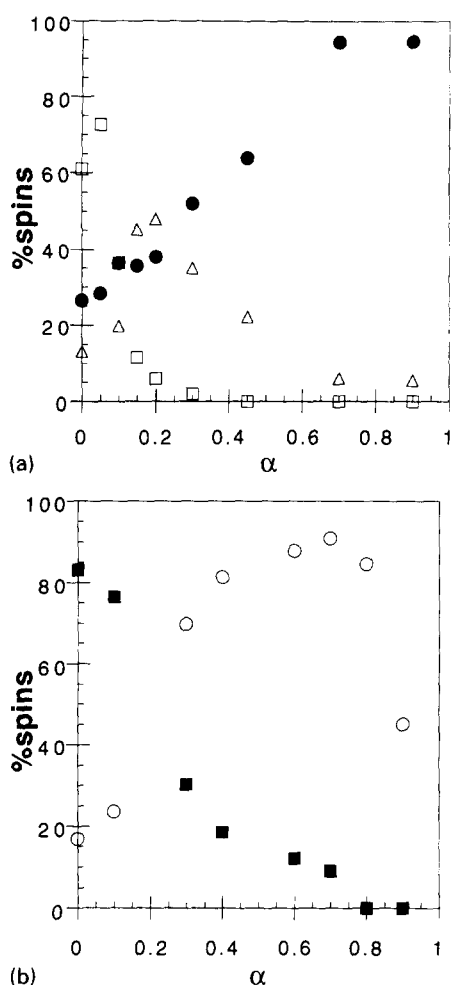
Figure 10 Variation of the different Cu species with α: (a) system PAA/Cu ($c_{pM} = 24\,mM$, $c_{Cu} = 1.5\,mM$): free Cu (squares), bound Cu visible in e.p.r. (circles), bound Cu inactive in e.p.r. (triangles); (b) system CAMAA/Cu ($c_{pM} = 7.5\,mM$, $c_{Cu} = 1\,mM$): free Cu (squares), bound Cu visible in e.p.r. (circles)

2) Polymer/Cu systems. The polymer solutions free of copper absorb only in the u.v. region, at 215 nm.

In the system PMA/Cu, the formation of complexes leads to the appearance of three peaks which are modified according to the α value, as shown in *Figure 11*: a peak at 265 nm in the u.v. region, a shoulder at 375 nm and a peak at 685 nm in the visible region. In the three cases the intensity passes through a maximum at $\alpha = 0.2$. This is in agreement with the literature data[1,3,4,7]. The presence of a shoulder at 375 nm was attributed by Leyte *et al.*[4] to the formation of the binuclear complex, a hypothesis consistent with a very low value of the magnetic moment in the PMA/Cu solutions. Nevertheless, there is some controversy about the assignment of this shoulder[6,28-33].

The maxima in the α dependence of the intensities was explained by the dissociation of the binuclear complex, which was assumed to have an higher absorption coefficient than the mononuclear one. Indeed, complementary i.r. measurements have shown that the number of carboxylate groups per copper in the complexes does not decrease when the intensity of the u.v.–visible peak decreases, which means that no copper hydroxide is formed[5].

The spectra obtained with the system PAA/Cu are qualitatively similar to those observed with PMA,
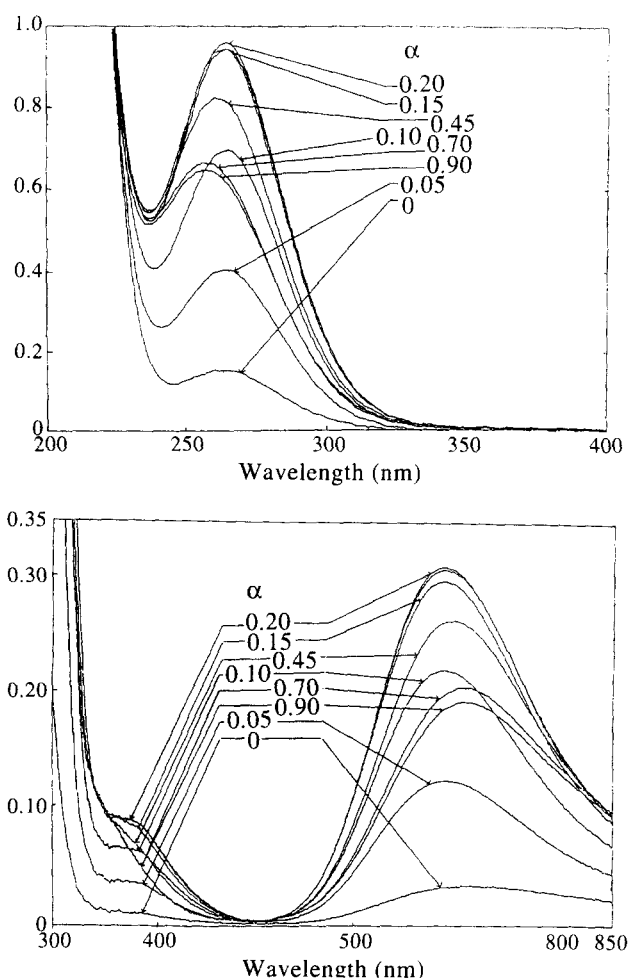

Figure 11 U.v. and visible spectra of the systems PMA/Cu ($c_{pM} = 24\,mM$, $c_{Cu} = 1.5\,mM$) as a function of α

according to previous data[9,10]. In the case of CAMAA in the presence of copper, the shoulder at 375 nm is absent, which confirms that the binuclear complex is not formed. In *Figures 12a–12c*, we compare the α dependence of the peaks and the shoulder for different systems. The results are reminiscent of those of the e.p.r. study. Indeed, the intensity of the shoulder at 375 nm passes through a maximum, and the shoulder almost disappears at $\alpha = 0.8$ for PAA, while it decreases slightly for PMA after the maximum. This confirms that the binuclear complex is dissociated for PAA when the chain expansion is high, but that it persists in the case of PMA. The same observations can be made for the u.v. and visible peaks. In the case of CAMAA, a continuous increase in the absorbance is observed in the u.v. and visible region.

This spectroscopic study confirms qualitatively the previous literature data. Nevertheless, as with the e.p.r. study, it demonstrates the great difference between polymers according to their chemical composition and charge parameter.

Comparison between e.p.r. and u.v.–visible results

In order to check the consistency between the two sets of results (e.p.r. and u.v.–visible), one can plot the absorbance at the maximum of the u.v.–visible peaks as a function of the fraction of the three different copper species, determined by e.p.r.
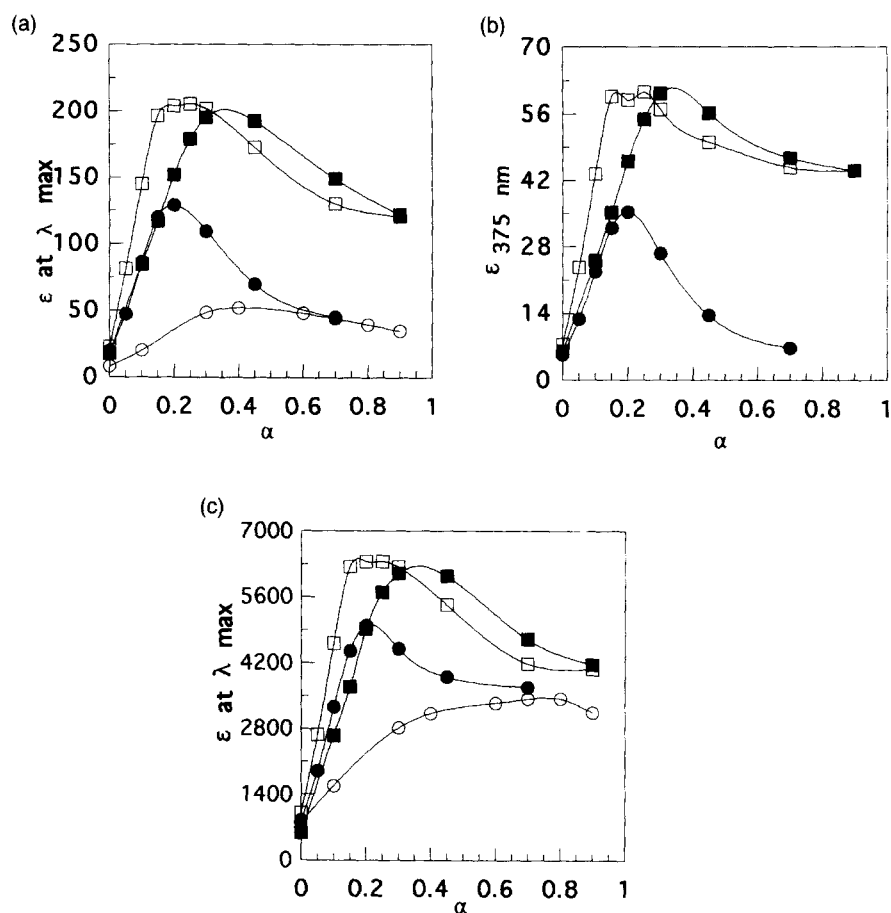
Figure 12 Variations of the extinction coefficients in u.v.–visible spectra *versus* α for different systems: PMA/Cu ($c_{pM} = 24\,mM$, $c_{Cu} = 1.5\,mM$) (open squares); PMA/Cu ($c_{pM} = 24\,mM$, $c_{Cu} = 3\,mM$) (full squares); PAA/Cu ($c_{pM} = 24\,mM$, $c_{Cu} = 1.5\,mM$) (full circles); CAMAA/Cu ($c_{pM} = 7.5\,mM$, $c_{Cu} = 1\,mM$) (open circles)

For CAMAA, the absorbance at 254 nm, A_{254} varies linearly with the fraction of bound copper (visible in e.p.r.) if one excepts the high α range, as shown by *Figure 13a*. The same observation was made for the peak at 730 nm. This clearly demonstrates that the same complex (the mononuclear one) is responsible for the u.v.–visible absorption and the e.p.r. for α values up to 0.8. From the value of the molar extinction coefficient of free copper (u.v.–visible spectra of copper nitrate solutions) and the fractions of free and bound copper (e.p.r.), the value of the molar extinction coefficient of the mononuclear complex can be evaluated; one finds for instance at 730 nm.

$$\varepsilon_{730}^{Bound\ Cu\,(2)} = 54\,mol^{-1}\,cm^{-1}$$

For PAA, the absorbance at 375 nm is a linear function of the fraction of bound copper inactive in e.p.r. (*Figure 13c*). This result confirms that the shoulder is only due to the binuclear complex. At 254 nm, the absorbance passes through a maximum at $\alpha = 0.2$ (*Figure 13b*) when 45% of the bound copper is visible in e.p.r. The maximum is due to the fact that both complexes absorb at this wavelength. At high pH, only the mononuclear complex is present and it is possible to calculate its extinction coefficient. The value found for 710 nm is

$$\varepsilon_{710}^{Bound\ Cu\,(2)} = 46\,mol^{-1}\,cm^{-1}$$

a value close to that previously determined in the case of CAMAA. At lower pH, if one knows the fraction of each

complex and that of free copper, the extinction coefficient of the binuclear complex can also be easily obtained:

$$\varepsilon_{710}^{Bound\ Cu\,(3)} = 255\,mol^{-1}\,cm^{-1}$$

For PMA, *Figure 13c* shows that the absorbance at 375 nm follows the same variation *versus* the fraction of the inactive species as for PAA for the same copper concentration. However, there is no direct correlation between the u.v. band and the fraction of bound copper 'visible' in e.p.r. (*Figure 13d*). The species which contribute to the u.v. or visible absorption are not the same as those which are visible in e.p.r. By comparison with the PAA case, the relative proportion of mono- and binuclear complexes is different; the binuclear one is preponderant and this explains why the average extinction coefficient is much higher for PMA.

DISCUSSION

Nature of the complexes

This set of spectroscopic results confirms the formation of bi- and mono-nuclear complexes in aqueous solutions of polycarboxylates in the presence of copper ions. Nevertheless, the systematic comparison of different systems under the same experimental conditions and with the same techniques allows us to give further information on the relationship between the nature of the complex and the characteristics of the polymer.
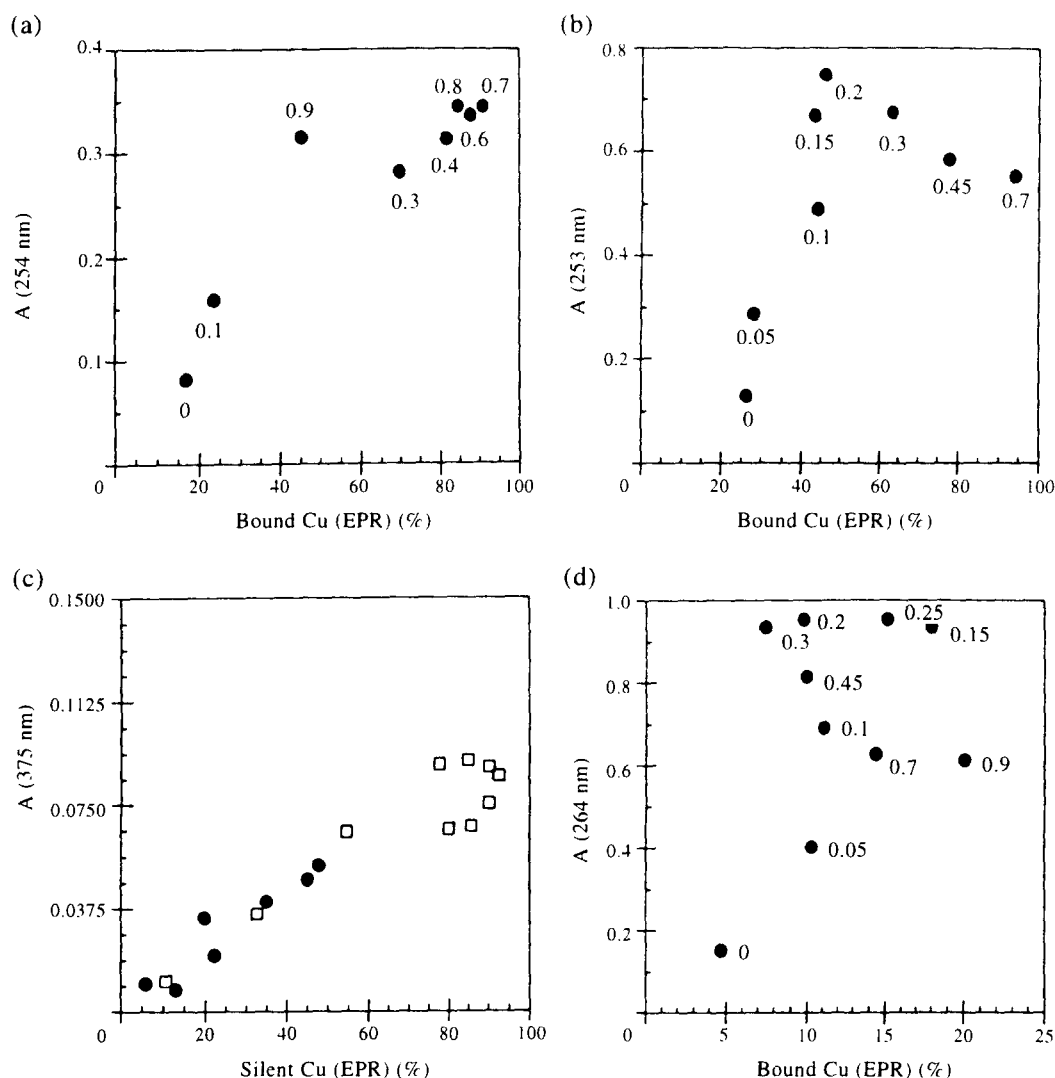
Figure 13 Comparison between u.v.–visible and e.p.r. results: (a) correlation between absorbance at 254 nm and the fraction of bound Cu visible in e.p.r. for the CAMAA/Cu system; (b) correlation between absorbance at 253 nm and the fraction of bound Cu visible in e.p.r. for the PAA/Cu system; (c) correlation between absorbance at 375 nm and the fraction of bound Cu inactive in e.p.r. for the PAA/Cu system; (d) no correlation between absorbance at 254 nm and the fraction of bound Cu visible in e.p.r. for the PMA/Cu system

It clearly appears that the binuclear complexes cannot form when the ionizable groups are far away along the chain. In the case of the weakly charged polyelectrolyte, CAMAA, the charges, even at complete ionization, are separated by two acrylamide units and only the mononuclear complex is observed. One can assume that the sequentiality of the monomer distribution must play an important role and, probably, for polymers prepared by acid hydrolysis which leads to acrylic acid sequences, the binuclear complexes may form.

The formation of binuclear complexes seems, then, to be the prerogative of polymers with a high density of ionizable monomers. Moreover, the very significant differences between the behaviours of PMA and PAA illustrate the importance of the hydrophobic character of the chain. There is a correlation between the ability of PMA to exhibit a compact structure at low pH and its interaction with copper through mainly a binuclear complex. These observations lead us to make some hypothesis on the formation of this binuclear complex.

In the case of the mononuclear complex, the fact that it is observed for CAMAA and PAA as well means that

it can imply two carboxylate groups separated along the chain.

For the binuclear complex, it requires a high density of ionizable groups. We can eliminate the model represented in *Figure 14a* where its formation should imply four groups far away along the chain, and the results obtained with CAMAA suggest that pairs of adjacent groups must be implied. The complex may be formed by association of two carboxylate pairs belonging to different chains (*Figure 14b*); but in another work[34,35], we have shown through light scattering measurements that, at least in the dilute regime, the addition of copper ions to PMA solutions does not induce aggregation. One may imagine that, as represented in *Figure 14c*, the complex is made of four adjacent carboxylate groups, but, due to the chain rigidity, this seems improbable. The last and, in our opinion, the most satisfactory hypothesis assumes that the complex is formed through the association of two copper ions with two pairs of adjacent carboxylate groups as schematized in *Figure 14d*. The local chain folding responsible for the compact conformation of PMA at low pH may also favour the
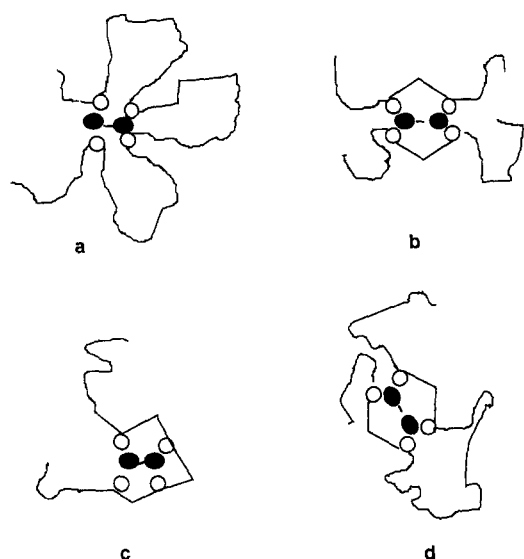
Figure 14 Schemes of possible structures of the binuclear complex

formation of a binuclear complex at low pH and stabilizes it up to high pH.

Evaluation of the complexation constants

In simple terms of equilibria between the different species in solution, the system is ruled by three sets of equilibria.

(a) The hydrolysis equilibria of the $Cu(H_2O)_6^{2+}$ ion:

$$x M^{2+} + y H_2O \rightarrow M_x(OH)_y^{(2x-y)} + y H^+ \qquad (1)$$
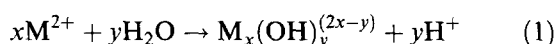
with associated formation constants:

$$K_{xy} = \frac{[M_x(OH)_y^{(2x-y)+}][H^+]^y}{[M^{2+}]^x} \qquad (2)$$

The constants are $K_{11} = 10^{-8}$ mol, $K_{12} = 10^{-17.3}$ mol^2, $K_{13} = 10^{-27.8}$ mol^3, $K_{14} = 10^{-39.63}$ mol^4 and $K_{22} = 10^{-10.36}$ mol and the solubility product of $Cu(H_2O)_6^{2+}$ is[25,27,36-38]

$$K_s = [Cu^{2+}][OH^-]^2 = 10^{-19.36} \text{ mol}^3 \qquad (3)$$

(b) The acid–base equilibrium of the carboxylate groups:

$$K_a = \frac{[COO^-][H^+]}{[COOH]} \qquad (4)$$

It is well known that the pK_a of a polyacid is not a true constant as in the case of low molecular weight acids, but is an increasing function of the degree of neutralization[39]. This effect has already been extensively studied for PAA and CAMAA[40-42]. However, the case of PMA is rather more complicated due to the conformational transition, which results in a discontinuous variation of pK_a[43-48].

(c) The equilibria of the formation of the mono- and binuclear complexes:

$$K_{pCu1} = \frac{[COO_2Cu]}{[COO^-]^2[Cu^{2+}]} \qquad (5)$$

$$K_{pCu2} = \frac{[COO_4Cu_2]}{[COO^-]^4[Cu^{2+}]^2} \qquad (6)$$

This gives a set of three equations to solve:

$$[Cu^{2+}]\left[1 + \frac{K_{11}}{[H^+]} + \frac{K_{12}}{[H^+]^2} + K_{pCu1}[COO^-]^2\right]$$
$$+ [Cu^{2+}]^2\left[2\frac{K_{22}}{[H^+]^2} + 2K_{pCu2}[COO^-]^4\right] = c_{Cu} \qquad (7)$$

$$[COO^-]\left[1 + \frac{H^+}{K_a}\right] + 2K_{pCu1}[COO^-]^2[Cu^{2+}]$$
$$+ 4K_{pCu2}[COO^-]^4[Cu^{2+}]^2 = c_{pM} \qquad (8)$$

$$[COO^-] + \frac{10^{-14}}{[H^+]} + 2c_{Cu} - \alpha c_{pM} - [H^+] - [Cu^{2+}]$$
$$\times \left[2 + \frac{K_1}{[H^+]} + 2K_{22}\frac{[Cu^{2+}]}{[H^+]^2}\right] = 0 \qquad (9)$$

We will start with the following hypotheses:

(i) only neutral complexes can be formed;
(ii) the polyelectrolyte effect is neglected, the charges being assumed to be uniformly distributed in the solution;
(iii) the pK_a value was kept constant and equal to that of PMA at $\alpha = 0$ (5.2)—this is justified at least up to the complete complexation of the available copper, since the ionization of the polymer remains rather low.

Let us note that the same results should be obtained if one considers that the binuclear complex was formed by the interaction between four carboxylate groups and a binuclear hydrolysed copper ion instead of two mononuclear ions, as implied in equation (6). Moreover, we assume that:

- CAMAA forms only mononuclear species with copper, which means that $K_{pCu2} \ll K_{pCu1} = 0$;
- PMA forms mainly binuclear species with copper, which means that $K_{pCu1} \ll K_{pCu2} = 0$.

Table 2 shows that the experimental fractions of free copper are comparable to those calculated if one uses $K_{pCu1} = 2 \times 10^6$ mol^{-2} for CAMAA. The agreement between calculation and experiment is then rather good.

The results obtained for PMA are given in *Figures 15* and *16*. It can be seen that for two different compositions of the system, the value of $K_{pCu2} = 10^{17}$ allows one to fit correctly the experimental variations of the fraction of free copper *versus* α. Moreover, in all these experiments the pH was measured and *Figure 16* shows that the best

Table 2 Comparison between the experimental (exp.) and the calculated (calc.) values of the fraction of free Cu *versus* the ionization degree, α, in the system CAMAA–Cu. Constant of the equilibrium, equation (5), taken as $K_{pCu1} = 2 \times 10^6$

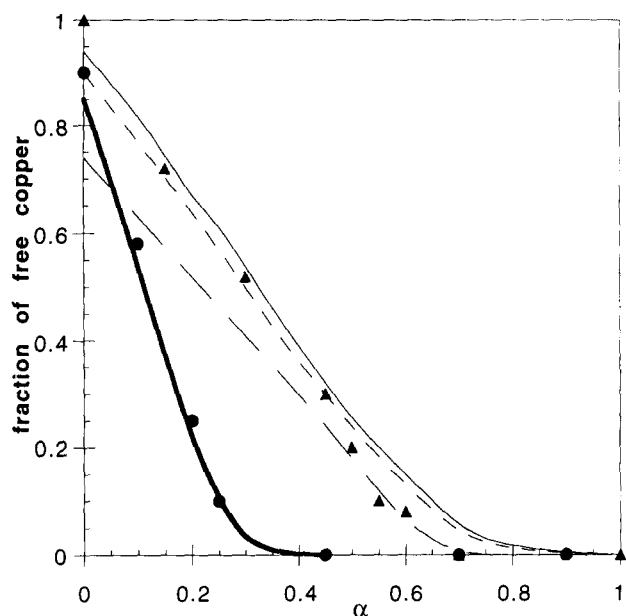|	α						
	0	0.1	0.3	0.4	0.6	0.7	0.8
Exp.	0.84	0.76	0.30	0.17	0.12	0.09	0
Calc.	0.95	0.77	0.34	0.20	0.06	0.04	0.03

Figure 15 Comparison between the experimental and calculated values of the fraction of free Cu *versus* ionization degree for the system PMA/copper: $c_{pM} = 24$ mM, $c_{Cu} = 3$ mM: experimental points (full circles), calculated curve (———); $c_{pM} = 8$ mM, $c_{Cu} = 2.5$ mM: experimental points (full triangles), curves calculated for $K_{pCu2} = 10^{17}$ (full line), $K_{pCu2} = 10^{18}$ (- - -) and $K_{pCu2} = 10^{20}$ (-- -- --)
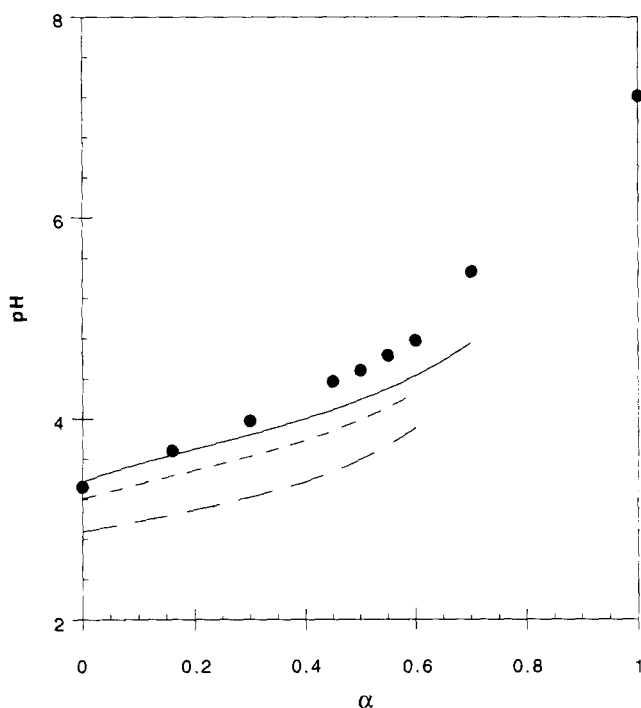

Figure 16 Comparison between the experimental and calculated pH *versus* ionization degree for the system PMA/Cu: $c_{pM} = 8$ mM, $c_{Cu} = 2.5$ mM: experimental points (full circles); curves calculated for $K_{pCu2} = 10^{17}$ (full line); $K_{pCu2} = 10^{18}$ (- - -) and $K_{pCu2} = 10^{20}$ (- - -- - --)

fit of the pH variation is also obtained for this value of K_{pCu2}. At higher values of α, hypothesis (iii) is no longer correct; the pK_a is much higher than 5.2 and the calculation underestimates the pH. Thus, for these two simplest systems, we can conclude that a rather rough set of equilibrium laws permits one to predict the fractions of each species, at least to a first approximation.

As demonstrated above, the case of PAA seems to be much more complicated; indeed, the coexistence of the two types of complexes (mono- and bi-nuclear ones) may be taken into account by considering all the terms given in equations (7)–(9). However, if the constants K_{pCu1} and K_{pCu2} are kept constant when α varies, it is not possible to explain the maximum in the variation of the fraction of binuclear complexes for $\alpha = 0.2$, since the fractions of both the mono- and bi-nuclear species are expected to increase with α. In order to overcome this difficulty, one has to consider the schemes of *Figure 14*. According to the hypothesis of Leyte *et al.*[4] the probability of formation of the binuclear complexes decreases when the chain expansion increases. This can be understood from our model 'd' (*Figure 14*) by considering that this complexation requires a high segment density favouring the intramolecular contacts. Thus, the concentration that one must introduce in equation (6) is no longer the average concentration of carboxylate groups, but their true intramolecular concentration, which may be evaluated from

$$\frac{[COO^-]_\alpha}{[COO^-]_0} \propto \frac{R_{g0}^3}{R_{g\alpha}^3} \qquad (10)$$

where $[COO^-]_\alpha$ and $[COO^-]_0$ are the intramolecular concentrations of COO^- groups for ionization at α and 0, respectively, and $R_{g\alpha}$ and R_{g0} are the corresponding radii of gyration of the macromolecular coil. From a fundamental point of view, it is well known that the electrostatic repulsions between the charges have short and long range contributions and result both in an increase of the persistence length and of the excluded volume, as described by Odijk and Houwaart[49], Fixman and Skolnick[50] and Reed and Reed[51]. In the case of copolymers of the CAMAA type, the experimental variations of the chain dimensions with α, measured by light scattering and viscosimetry, have been explained by taking into account these two effects[51]. An empirical expression for the variation of R_g with α, in good agreement with the theoretical predictions, was obtained [equation (32) of ref. 52] and can be transformed into

$$\frac{R_{g\alpha}}{R_{g0}} = \left[1 + 1.67\frac{\alpha^{0.5}}{c_{pM}^{0.5}}\right] = c_\alpha \qquad (11)$$

for a polyion in the absence of salt. Due to the similarity of the skeletons of CAMAA and PAA, the electrostatic effects must be very close for both polymers, as shown through several experimental observations[53–57]. For $\alpha = 0$, we had to solve equations (7)–(9); $K_{pCu2} = 10^{17}$ and $K_{pCu1} = 2 \times 10^6$ were the values obtained for PMA and CAMAA, respectively. For the higher α values, K_{pCu2} was then divided by c_α^3, α being increased by very small increments. The aim of such a calculation was not to obtain a quantitative fit of the experimental results, due to the crude approximations used, but to check if the original idea was reasonable. *Figure 17* shows the calculated values for the fractions of free copper and of copper involved in the mono- and bi-nuclear complexes. The decrease in the free copper concentration is quite close to that obtained experimentally and the model predicts correctly the features of the two other variations (*Figure 17* compared to *Figure 10a*). However, different results would be obtained, taking into account the increase in pK_a.
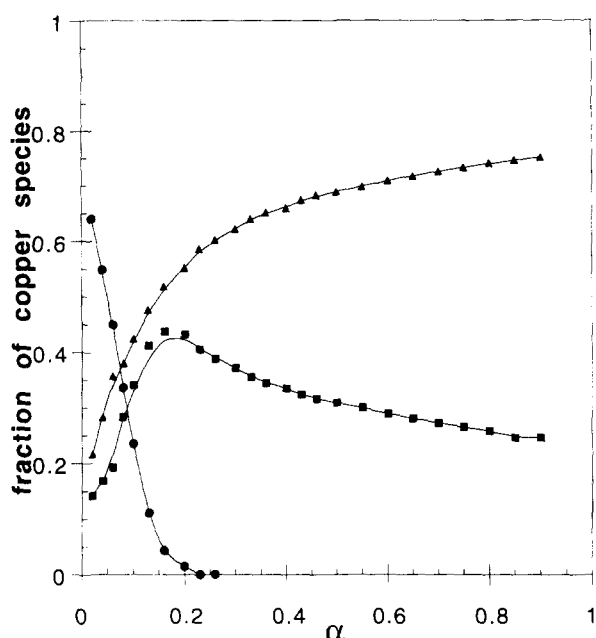
Figure 17 Calculated variations of the free Cu (circles), Cu in mononuclear complexes (triangles) and in binuclear complexes (squares) with α for the PAA/Cu system

To correct the constant of formation of the binuclear complex by a factor depending on the intramolecular concentration and to keep constant that of the mononuclear species is consistent with our complexation model. Indeed, if the mononuclear complexes are mainly formed between adjacent carboxylate groups, no α dependence of K_{pCu1} is expected. For PMA, the results can be adjusted with a constant value of K_{pCu2} and this suggests that the formation of binuclear species does not depend on the average intramolecular segment density, but more likely on the ability of the chain to fold around two copper ions.

CONCLUSION

The set of results presented in this work allows us to progress in the description of the interactions between copper ions and polycarboxylates. The formation of both bi- and mono-nuclear complexes are clearly confirmed by the e.p.r. measurements, and the u.v.–visible study provides a set of data consistent with the interpretation of the e.p.r. results. We show that the model already proposed by Leyte et al.[4] for PMA applies very well to PAA and we propose to explain the disappearance of the binuclear complexes at high values of the ionization degree by an intramolecular segment density effect. In contrast, the binuclear complexes remain preponderant over the whole range of pH in the case of PMA. This difference must be related to the capacity of PMA to form a compact structure at a low ionization degree. In this respect, since it is known that the conformation of PMA is strongly dependent on its tacticity, it should be of great interest to perform a spectroscopic study of PMA samples of various tacticities in the presence of copper. The behaviour of the acrylamide–acrylic acid copolymers compared to that of PMA and PAA in the same range of low charge density suggests that the average number of charges inside the coil is not the only driving force for the formation of

binuclear complexes, but that it requires an annealing of the charges as in the cases of PMA or PAA, while in the copolymers the charges are quenched. Thus, one can expect that the fraction of such complexes will vary with the distribution of the acrylic units along the chain, and an interesting complementary study should consist in checking the influence of the method of preparation of CAMAA copolymers on their interaction with copper. Also, one can question if the binuclear complexation is a prerogative of copper or if it may be observed with other divalent cations.

ACKNOWLEDGEMENTS

REFERENCES

1. Mandel, M. and Leyte, J. C., *J. Polym. Sci., Part A*, 1964, **2**, 3771.
2. Mandel, M. and Leyte, J. C., *J. Polym. Sci., Part A*, 1964, **2**, 2883.
3. Kotliar, A. M. and Morawetz, H., *J. Am. Chem. Soc.*, 1955, **77**, 3692.
4. Leyte, J. C., Zuiderweg, L. H. and van Reisen, M., *J. Phys. Chem.*, 1968, **72**, 1127.
5. Want, L., Mémoire de fin d'étude, Université catholique de Louvain, Belgium, 1993.
6. Kato, M., Jonassen, H. B. and Fanning, J. C., *Chem. Rev.*, 1964, **64**, 99.
7. Marinsky, J. A. and Anspach, W. M., *J. Phys. Chem.*, 1975, **79**, 439.
8. Wall, T. F. and Gill, S. J., *J. Phys. Chem.*, 1954, **58**, 1128.
9. Yamaoka, K. and Masujima, T., *Bull. Chem. Soc. Japan*, 1979, **52**, 1819.
10. Truong, N. D., Galin, J. C., François, J. and Pham, Q. T., *Polymer*, 1986, **27**, 459.
11. Truong, N. D., Galin, J. C., François, J. and Pham, Q. T., *Polymer*, 1986, **27**, 467.
12. Kheradmand, H., François, J. and Plazanet, V., *Polymer*, 1988, **29**, 860.
13. Truong, N. D., Galin, J. C., François, J. and Pham, Q. T., *Polym. Commun.*, 1984, **25**, 208.
14. Truong, N. D. and François, J., *Solid–Liquid Interactions in Porous Media*, Technip, Paris, 1985, **42**, 251.
15. Boas, J. F., Pilbrow, J. R. and Smith, T. D., *ESR of Copper in Biological Systems*.
16. Malkin, R. and Malmström, B. G., *Adv. in Enzymol. and Related Areas of Mol. Biol.*, 1970, **33**, 177.
17. Smith, T. D., *Coord. Chem. Rev.*, 1974, **13**, 173.
18. Rex, G. C. and Schlick, S., *J. Phys. Chem.*, 1985, **89**, 3598.
19. Rex, G. C. and Schlick, S., *Polymer*, 1987, **28**, 2134.
20. Artyushin, A. M., Przhevalskaya, L. K., Epishina, G. P. and Shvets, V., *Russian J. Phys. Chem.*, 1990, **64**, 560.
21. Van Custem, P., Gillet, C., Mestdagh, M. and Rouxhet, P. G., *Solid–Liquid Interactions in Porous Media*, Technip, Paris, 1985, **42**, 171.
22. Debongnie, P., Mestdagh, M. and Rinaudo, M., *Carbohyd. Res.* 1987, **170**, 137.
23. Blumstein, R., Murphy, G., Blumstein, A. and Waterson, A. C., *Polym. Letters*, 1973, **11**, 21.
24. Boutin, J. and Contat, S., Rhône Poulenc Ind., French Patent No. 249 217, 1980.
25. Baes, C. F. and Mesmer, R. E., *The Hydrolysis of Cations*. Wiley-Interscience, New York, 1976, 496 pp.
26. Wertz, J. L., Thesis, Université Catholique Louvain, Belgium, 1981, 130 pp.
27. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*. Wiley-Interscience, New York, 1980, 1396 pp.

28. Dubicki, L., Harris, C. M., Kokot, E. and Martin, R. L., *Inorg. Chem.*, 1966, **5**, 93.
29. Melnik, M., Macaskova, L. and Mrozinsky, J., *Polyhedron*, 1988, **7**, 1745.
30. Figgis, B. N. and Martin, D. J., *Inorg. Chem.*, 1966, **5**, 100.
31. Edmonson, B. J. and Lever, A. B. P., *Inorg. Chem.*, 1965, **4**, 1608.
32. Newton, W. J., Oldham, C. and Tabner, B. J., *J.C.S., Dalton*, 1980, 1379.
33. Tsuchida, R. and Yamada, S., *Nature*, 1955, **176**, 1171.
34. Heitz, C., Thesis, University Louis Pasteur, Strasbourg, France, 1996.
35. François, J., Heitz, C. and Duval, M., *Polymer* (in preparation).
36. Ohtaki, H., *Inorg. Chem.*, 1968, **7**, 1205.
37. Perrin, D. D., *J. Chem. Soc.*, 1960, **3**, 189.
38. Kakihana, H., Amaya, T. and Maeda, M., *Bull. Chem. Soc. Japan*, 1970, **43**, 3155.
39. Mandel, M., in *Polyelectrolytes in Encyclopedia of Polymer Science and Engineering*, Vol. 11, 2nd edn, ed. N. M. Bikales, C. G. Overberger and G. Menges, John Wiley, New York, 1988, 829 pp..
40. Mandel, M., *Eur. Polym. J.*, 1970, **6**, 807.
41. Truong, N. D., Medjahdi, G., Sarazin, D. and François, J., *Polym. Bull.*, 1990, **24**, 101.
42. El Brhami, K., Rawiso, M. and François, J., *Eur. Polym. J.*, 1993, **22**, 1531.

43. Katchalsky, A., *J. Polym. Sci.*, 1951, **7**, 393.
44. Arnold, R. and Overbeek, J. T., *Rec. Trav. Chim.*, 1950, **69**, 192.
45. Leyte, J. C. and Mandel, M., *J. Polym. Sci.*, Part A, 1964, **2**, 1879.
46. Mandel, M. and Stadhouter, M. G., *Makromol. Chem.*, 1964, **80**, 141.
47. Liquori, A. M., Barone, G., Crescenzi, V., Quadrifoglio, F. and Vittigliano, V., *J. Macromol. Chem.*, 1966, **1**, 291.
48. Crescenzi, V., *Adv. Polym. Sci.*, 1968, **5**, 5388.
49. Odijk, T. and Houwaart, A. C., *J. Polym. Sci., Polym. Phys. Ed.*, 1978, **16**, 627.
50. Fixman, M. and Skilnick, J., *Macromolecules*, 1978, **11**, 863.
51. Reed, C. E. and Reed, W. F., *J. Chem. Phys.*, 1990, **92**, 6916.
52. Reed, W. F., Ghosh, S., Medjahdi, G. and François, J., *Macromolecules*, 1991, **24**, 6189.
53. Schwartz, T. and François, J., *Makromol. Chem.*, 1981, **182**, 2757.
54. Kulkarni, R. A. and Gundiah, S., *Makromol. Chem.*, 1984, **185**, 957–967; 969–982; 983–989.
55. Kowblansky, M. and Zema, P., *Macromolecules*, 1981, **14**, 1448–1451.
56. Noda, I., Tsuge, T. and Nagasawa, M., *J. Phys. Chem.*, 1970, **74**, 710.
57. Kheradmand, H., Thesis, Louis Pasteur University, Strasbourg, France, 1987.