Polymer Bulletin 26, 231–235 (1991)

Polymer Bulletin

Electron paramagnetic resonance evidence for direct co-ordination of copper(II) ions by acrylic resins containing amine groups

Julia Jezierska[1], Henryk Kozłowski[1,*], Bozena N. Kolarz[2], and Andrzej Trochimczuk[2]

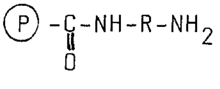
[1]Institute of Chemistry, University, F. Joliot-Curie 14, PL-50-383 Wroclaw, Poland
[2]Institute of Organic and Polymer Technology, Technical University, PL-50-370 Wroclaw, Poland

SUMMARY

E.p.r. and absorption spectra were used to indicate the formation of the complexes between copper(II) ions and acrylic resins containing oligoamines bound via amide bonds to acrylate units. The number of bound nitrogen atoms depends on the length of the amine chain attached to acrylamide unit.

INTRODUCTION

The sorption of copper(II) ions by acrylic resins containing different amine units bound to acryl unit via amide bond has been estimated by the spectrophotometric method which could evaluate the amount of metal ion removed from the solution after addition of solid state polymer. The performed studies have shown the relationships between the amount of sorbed metal and the length of an amine chain, anion exchange capacity and the degree of the crosslinking |1|. The direct indication of the formation of the chemical bonding of metal ions with components of solid state polymer is a rather difficult task and could not be obtained on the basis of the earlier study. The methods applied to low molecular weight soluble complexes are in most cases unreliable in the study of totally insoluble resins. However, we have decided to apply the electron paramagnetic resonance (e.p.r.) spectroscopy to investigate the copper(II) ion co-ordination to series of the following acrylic resins:



$$\text{Ⓟ}-\underset{\underset{O}{\|}}{C}-NH-R-NH_2$$

where: R is absent (20-HYDR), R = $-CH_2CH_2-$ (20-ETDA),
R = $-CH_2CH_2NHCH_2CH_2-$ (20-DETA) or (B-DETA),
R = $-CH_2CH_2NHCH_2CH_2NHCH_2CH_2-$ (20-TETA).

EXPERIMENTAL

The acrylic resins are derived from acrylonitrile-divinylbenzene copolymer containing 20 wt.% of DVB (20) or acrylonitrile-butyl acrylate-divinylbenzene copolymer (B) which were obtained according to earlier described procedure |2|. Aminolysis of these copolymers was carried out using hydrazine (HYDR), ethylenediamine (ETDA), diethylenetriamine (DETA), triethylenetetramine (TETA) according to |3|.

---

*To whom offprint requests should be sent

E.p.r. spectra were measured on a RADIOPAN SE type X-band spectrometer. Electronic reflectance spectra were recorded on a BECKMAN UV 5240 instrument.

The e.p.r. measurements were performed:

1. for Cu(II)-polymer complexes in dry state prepared at pH 5,
2. for freshly prepared at different pH Cu(II)-polymer systems in swollen state, separated from the suspension of 0.3 g of acrylic resins in 3 cm^3 of a Cu(II) solution,
3. after 3 days from the preparation of the Cu(II)-polymer samples and 1 day after pH adjustment.

RESULTS AND DISCUSSION

The e.p.r. spectra obtained at higher pH values for the studied systems are distinctly different than that of Cu(II) aquaion (Fig.1).It clearly indicates the formation of direct metal polymer bond. These spectra are already anisotropic at room temperature which can be the case only when metal ion is directly bound to polymeric ligand. Such co-ordination is able to immobilize copper(II) ions |4| and to lead to anisotropic e.p.r. spectra at room temperature at which low molecular weight species exhibit the isotropic features. These spectra are characteristic for tetragonal or almost tetragonal Cu(II) complexes having $d_{x^2-y^2}$ ground state.

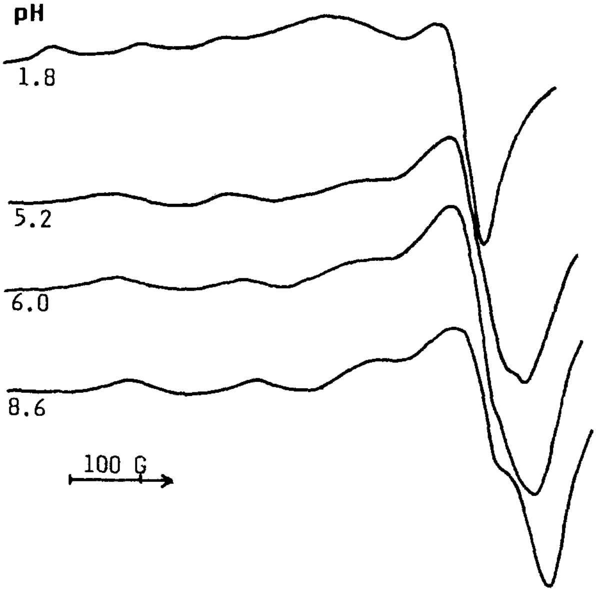


Figure 1. E.p.r. spectra of Cu(II)-B-DETA complexes as a function of pH measured at 77 K.

It should be mentioned, however, that the spectra obtained at low temperature are of much better resolution than those recorded at room temperature. The reasonable resolutions of the spectra recorded at room temperature is obtained only for Cu(II)-2O-TETA system for the samples prepared at pH 6 or higher.

The e.p.r. spectra of the Cu(II)-20-TETA complex in dry state with parameters $A_{\parallel}$=175 cm^{-1} and $g_{\parallel}$=2.217 differ from those found for freshly prepared water containing samples. Therefore, the most valuable e.p.r. spectra for the interpretation of the formed complexes were those recorded for freshly prepared samples at 77 K and their parameters have been used in the further discussion.

The highest intensity and the best resolution of the obtained spectra is observed in the case of the Cu(II)-20-TETA complexes as the 20-TETA polymer has the highest copper sorption capacity among the systems studied |1|. On the other hand the complexation of Cu(II) by 20-HYDR and 20-ETDA results in similar e.p.r. spectra of rather poor resolution and low intensity although the amount of Cu(II) ions sorbed by these polymers is different. This may be associated with comparable ion-exchange capacity of both these polymers which is much lower than that found for the others.

There is rather small dependence of the e.p.r. spectra on the counter anions and on the concentration of Cu(II) ions in the stock solutions to which the polymer was added.

The degree of the spectra variation when compared to the Cu(II) aquaion spectrum depends strongly on pH and on the chain length of the ligands. The changes in the spectrum starts at lower pH for the longer chains and thus, for Cu(II)-20-HYDR and Cu(II)-20-ETDA the transformation of aquaion spectrum into the spectrum typical for the complex starts at pH about 5, for Cu(II)-20-DETA and Cu(II)-B-DETA systems at pH about 4, while for Cu(II)-20-TETA system at pH about 3 (Table 1).

Table 1. EPR parameters of the copper(II)-polymer complexes as a function of pH at 77 K.

	Cu-20-HYDR		Cu-20-ETDA		Cu-20-DETA		Cu-B-DETA		Cu-20-TETA	
pH	$A_{\parallel}$	$g_{\parallel}$	$A_{\parallel}$	$g_{\parallel}$	$A_{\parallel}$	$g_{\parallel}$	$A_{\parallel}$	$g_{\parallel}$	$A_{\parallel}$	$g_{\parallel}$
3									177	2.231[a]
4					170	2.24	175	2.26	190	2.231
5	175	2.25	175	2.25	178	2.243[a]	175	2.256[a]	194	2.233
6	178	2.25[a]	176	2.26[a]	184	2.253	182	2.252	194	2.220
7	177	2.25	176	2.26	186	2.238	187	2.245	196	2.223
8	178	2.25	176	2.25	188	2.245[b]	189	2.237	196	2.224
9			176	2.26			191	2.229[b]	196	2.218[c]

Parameters $A_{\parallel}$ are given in $10^{-4} cm^{-1}$ units.

[a] 2N species, [b] 3N species, [c] 4N species.

It is well established that the $g_{\parallel}$ and $A_{\parallel}$ values for the tetragonal Cu(II) complexes depends on the ligand donors bound to metal ion. The higher number of bound nitrogens (1 to 4) leads to distinct decrease of $g_{\parallel}$ and the increase of $A_{\parallel}$ values |5,6|. In the studied cases the acrylic resins may involve both the amine and amide nitrogens to co-ordinate metal ion. The possibility of the amide co-ordination is facilitated by higher pH as well as by formation of the chelate ring simultaneously with the adjacent amino nitrogen |6,7|. Thus, in the studied systems the anchoring sites are the amino nitrogens which are distinctly more basic than the amide nitrogens.

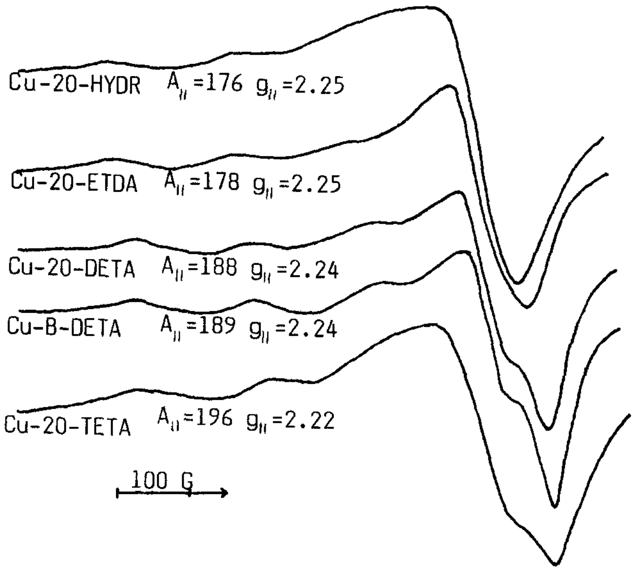


Figure 2. E.p.r. spectra of the Cu(II)-polymer complexes prepared at pH about 8 and measured at 77 K. Parameters $A_{\parallel}$ are given in 10^{-4}cm^{-1} units.

It is evident from the spectra collected in Fig.2 that there are three different sets of e.p.r. parameters corresponding to the formed Cu(II)-polymer complexes at pH close to 8. The spectra indicate different co-ordination modes resulting from the different number of nitrogen atoms (characteristic increase of $A_{\parallel}$) bound to copper(II) ion. The comparison to earlier works suggests that the number of nitrogens involved in metal ion co-ordination is four for Cu(II)-20-TETA, three for Cu(II)-20-DETA and Cu(II)-B-DETA, and two for Cu(II)-20-ETDA and Cu(II)-20-HYDR systems. This suggestion obtained from the e.p.r. spectra is supported by the d-d transition energy. The related bond occurs at 650 nm for Cu(II)-20-TETA and at 730 nm for Cu(II)-20-DETA. These d-d transition energies indicate clearly the stronger ligand field in the former system complex (i.e. the higher number of nitrogens bound to metal ion |6,7|) than in the latter case.

The maximum number of nitrogen atoms bound to metal ion (except 20-HYDR) corresponds to the length of amine chain bound to polymer. It does not depend, however, on metal binding ability (4 equatorial nitrogens). This fact can suggests that each metal ion interacts with one amine chain only. In the case of 20-HYDR polymer, the involvement of two independent ligand units to one copper(II) ion. Additionally, the metal ion co-ordination to one amino unit may be favoured as the result of the fact that only 15 % of acrylic moieties bind the amine chain via amide bond and only these fragments can interact with metal ions.

CONCLUSIONS

Oligo-amine ligands bound to acrylic resins via amine bond may form effective complexes with copper(II) ions via direct co-ordination through amino or amide nitrogens. This bond formation may be reliably followed by e.p.r. spectra measurements.

REFERENCES

1. A.Trochimczuk, B.N.Kolarz and M.Wojaczyńska, Reactive Polym., 7, 197 (1988).
2. M.Wojaczyńska and B.N.Kolarz, J.Chromatogr., 358, 189 (1986).
3. E.S.Dragan, C.Luca and I.Petrariu, Rom.Patent, 70,119 (1980).
4. M.Branca, G.Micera, A.Dessi and H.Kozłowski, J.Chem.Soc. Dalton Trans., 1283 (1989).
5. J.Peisach and W.E.Blumberg, Arch.Biochem.Biophys., 165, 691 (1974).
6. G.Formicka-Kozłowska, H.Kozłowski and B.Jeżowska-Trzebiatowska, Inorg.Chim.Acta, 25, 1 (1977).
7. H.Sigel and R.B.Martin, Chem.Rev. 82, 385 (1982).

Accepted February 22, 1991 C