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EPR investigations of the influence of *N,N'*-methylene-bis-acrylamide (NNMBA) crosslinks on the coordination structure of Cu(II) complexes of poly(*N*-2-aminoethylacrylamide)s

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SUMMARY

The coordination structures of Cu(II) complexes of amino functions supported on polyacrylamides with varying extents of NNMBA-crosslinks were followed by EPR techniques. The geometry of the Cu(II) complexes changes with increasing crosslinking. The covalency of the Cu-N bond also depends on the extent of the NNMBA-crosslinking in the polymer-support.

INTRODUCTION

The study of the interdependence of the reactivity of the polymeric ligands with the metal ions and the fine molecular structure of the polymers has been a subject of contemporary interest(1-3). The nature of the polymer backbone, molecular character and extent of crosslinking and the separation of the ligand function from the three-dimensional macromolecular matrix have a significant effect on the interaction with the metal ions and the coordination structures of the resulting polymer-metal complexes(4,5). The structures of the polymer-metal complexes showed a distortion with the extent of crosslinking in the polymer-support(6). In this paper, we report the synthesis of polyacrylamides with 2-20 mole% of NNMBA-crosslinks, transamidation with ethylenediamine to afford the amino resin, complexation with Cu(II) ions and EPR studies on the dependence of the extent of the semi-rigid and hydrophilic NNMBA-crosslinking on the coordination structures of the Cu(II) complexes.

EXPERIMENTAL

General

All the reagents were of certified ACS reagent grade. The copper sulphate used was the purest available (Merck). The EPR spectra were recorded on a Varian E-12 spectrometer at room temperature and liquid nitrogen temperature.

Preparation of NNMBA-crosslinked polyacrylamides

NNMBA-crosslinked polyacrylamides were prepared by free radical solution polymerization of the monomers in water. For the preparation of the 2% NNMBA-crosslinked polymer, 100 mg $K_2S_2O_8$ was dissolved in deionised water (100 ml) at 80 ^{o}C. The monomer mixture containing acrylamide (14.0 g) and NNMBA (0.64 g) was

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added and heated with stirring until the polymer got precipitated. Water (100 ml) was added and the contents heated at 80°C for 20 min. The lumps of the polymer were filtered, washed several times with water and methanol and dried in an oven at 80°C. Polymers with 4, 8, 12 and 20 mole% of NNMBA-crosslinks were prepared by varying the compositions of the monomers in the feed.

Preparation of poly(N-2-aminoethylacrylamide)s

Ethylenediamine (20 ml) was added to polyacrylamide (2 g) with stirring. The mixture was heated at 100°C for 9 h. The reaction mixture was poured into water (250 ml) containing crushed ice. The resin was filtered, washed several times with NaCl solution (0.1 M) until the filtrate was free from ethylenediamine as indicated by the absence of blue colouration with ninhydrin reagent. The gel was washed with water to remove NaCl and with methanol and dried at 70°C.

Estimation of resin amine content

Aminopolyacrylamide (100 mg) was equilibrated with HCl (0.2 N, 10 ml) with stirring for 24 h. The resin samples were filtered, washed with deionised water to remove unreacted HCl and the filtrate was titrated against NaOH (0.2 N) to a phenolphthalein end point.

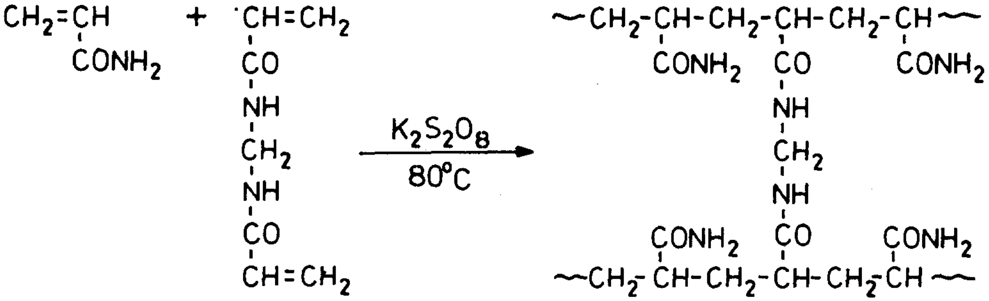
Complexation of Cu(II) with poly(N-2-aminoethylacrylamide)s

200 mg each of the amino resin was equilibrated by stirring with excess Cu(II) salt solution (0.03 N, 50 ml) for 24 h at its natural pH. The complexed resins were collected by filtration, washed with distilled water to remove uncomplexed metal ions. The concentrations of Cu(II) solutions were estimated by iodometry.

RESULTS AND DISCUSSION

Preparation of NNMBA-crosslinked polyacrylamides

Polyacrylamides with 2-20 mole% of NNMBA-crosslinks were prepared by the solution polymerisation of the monomers in water at 80°C using potassium persulphate as the initiator as represented in scheme 1. With increasing amount of the

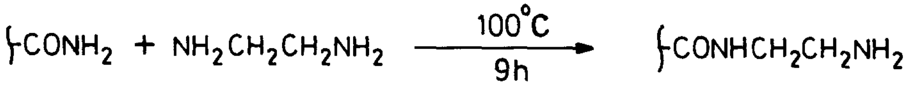


Scheme 1. Preparation of NNMBA-crosslinked polyacrylamides

crosslinking agent, the rigidity as well as the swelling properties of the resins also varied.

Preparation of poly(N-2-aminoethylacrylamide)s

Transamidation of polyacrylamides of varying extents of NNMBA-crosslinks with excess ethylenediamine resulted in aminopolyacrylamides (Scheme 2). The amino functions were detected by the semiquantitative nihydrin reaction (7). The resins developed deep blue colour with ninhydrin reagent. The amino groups were estimated by equilibrating a definite amount of the resin with known concentration of excess HCl and estimating the unreacted acid by alkali titration. The capacities of the various resins are given in Fig. 1. The amino capacity increases with increasing crosslinking, reaches a maximum at 8% crosslinking and decreased further. An increased reactivity was observed in the case of NNMBA-crosslinked polyacrylamides with crosslinking in the range 8-10% (8).



$$\text{-}CONH_2 + NH_2CH_2CH_2NH_2 \xrightarrow[9h]{100^{\circ}C} \text{-}CONHCH_2CH_2NH_2$$

Scheme 2. Preparation of poly(N-2-aminoethylacrylamide)s

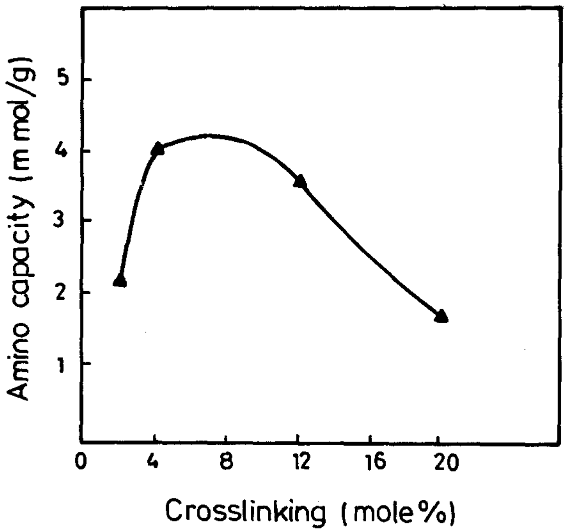


Fig.1. Dependence of NNMBA-crosslinking on transamidation.

Cu(II) complexation of poly(N-2-aminoethylacrylamide)s

The Cu(II) intake (in mg/g) by the different crosslinked (mole%) amino resins are: 2% (114 mg), 4% (183 mg), 8% (200 mg), 12% (133 mg) and 20% (107 mg). The Cu(II) intake also increases with imcreasing crosslinking, reached a maximum at 8% and decreased thereafter as observed in the case of the variation of amino capacity with crosslinking.

EPR spectra

EPR spectra of magnetically dilute Cu(II) complexes (40 mg Cu(II)/g of resin) at room temperature and at liquid nitrogen temperature are given in Fig. 2. The spectra obtained at low temperature are of better resolution than those obtained at room temperature. The spectra showed some difference with the variation in the content of crosslinking. The spectra are

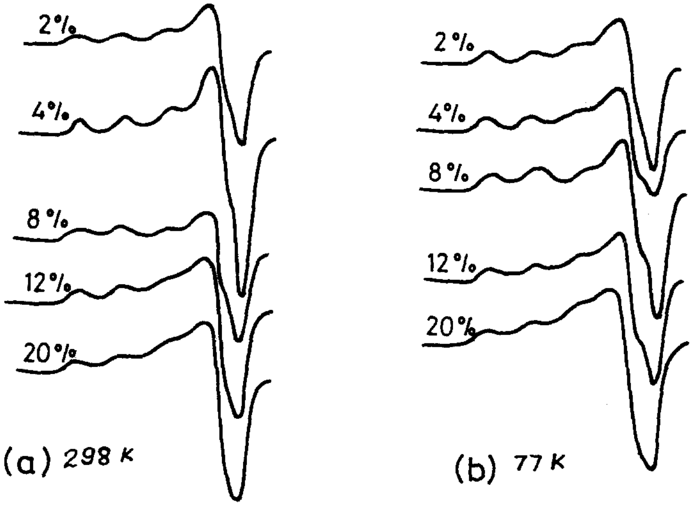


Fig.2. EPR spectra of Cu(II) complexes of aminopolyacrylamides

Table 1. EPR data of Cu(II) complexes with varying extents of NNMBA-crosslinks at room temperatures and (at liquid nitrogen temperature).

NNMBA (mole %)	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	α^2 Cu
2	2.2548	2.0542	160	40.000	0.7596
	(2.2690)	(2.0562)	(163)	(36.667)	(0.7858)
4	2.2485	2.0477	160	37.667	0.7505
	(2.2623)	(2.0674)	(164)	(41.667)	(0.7810)
8	2.2525	2.0562	154	41.333	0.7415
	(2.2485)	(2.0529)	(165)	(43.333)	(0.7667)
12	2.2439	2.0542	164	41.333	0.7599
	(2.2602)	(2.0634)	(164)	(41.667)	(0.7801)
20	2.2431	2.0595	165	41.000	0.7640
	(2.2659)	(2.0694)	(164)	(45.000)	(0.7883)

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

clearly anisotropic at room temperature which can be the case only when the metal ions are bound directly to the polymeric ligand (9). The EPR parameters of the different complexes are given in Table 1.

The EPR values are in agreement with the tetragonal geometry of the Cu(II) complexes (10). The EPR parameters indicate the presence of unpaired electrons in the $d_{x^2-y^2}$ orbital. The values of $g_{\parallel} \leqslant 2.3$ suggests the covalent nature of the Cu-N bond. Even though the values are in the same range, there is some variation in the values with the extent of crosslinking. The number of nitrogens complexed depends on the availability of the ligands in the polymer-support. Thus 8% crosslinked system has a lower number of nitrogen atoms coordinated because of the decreased availability of amino groups by the uniform distribution of NNMBA-crosslinks. In the low-crosslinked systems, the ligands are easily available by the cooperative contribution of randomly distributed ligands. While for the highly crosslinked systems, the functional groups are concentrated on the surface of the polymer matrix making them more accessible. But the complexes of these systems have some strain in the coordination geometry created by the extent of crosslinking as well as the microenvironments created around the ligand functions. In the present study, the resins may involve both the amide and amine nitrogens to coordinate metal ions. The possibility of amide coordination is facilitated only at higher pH. Thus in the studied systems the anchoring sites are amino nitrogens which are distinctly more basic than the amide nitrogens.

The bonding parameter, (α^2Cu) of the Cu(II) complexes, which is a measure of the covalency of the inplane σ-bonding of the Cu-N bond was calculated by the expression given by Kivelson and Neiman (11). The expression is based on the copper-hyperfine tensor $A_{\parallel}$ as

$$\alpha^2\mathrm{Cu} = -(A_{\parallel}/0.036) + (g_{\parallel}-2.002) + 3/7(g_{\perp}-2.002) + 0.04$$

Even though the α^2Cu of the complexes are in the same range, the values decreases with increasing crosslinking, reached a minimum at 8% and increased thereafter. The low and high crosslinked systems have a higher number of nitrogens complexed because of the increased availability by low-crosslinking and high concentration of ligands on the surface of highly crosslinked systems. With decreasing nitrogen donors (3N-1N), the α^2-Cu decreases slightly. But for 4N complex, a lowering of the α^2Cu is reported (12). The possibility of 4N cmplex in the 8% crosslinked system is less because of the incrased strain in the polymer-support developed by the uniform distribution of crosslinks. This is also confirmed from the low thermal stability of the Cu(II) complex of 8% crosslinking (13). The α^2Cu is inversely proportional to the covalency of the Cu-N bond. Thus the covalency of the Cu complexes of 8% crosslinking is higher than the other crosslinked systems. It has been reported that the reactivity and complexation of NNMBA-crosslinked systems reaches a maximum at 8% crosslinking (8). The increase in the $g_{\parallel}$ value of the 2% crosslinked system is because of the multi-transamidation, which leads to additional crosslinking and lower capacity. The 12% and 20% crosslinked systems have the active sites mainly on the surface of the polymer-support. Similar trends have been observed in the change of thermal stability of Cu(II) complexes with 2-20 mole% of NNMBA-crosslinks (13). Usually the thermal stabilities of polymer-metal complexes are higher than the uncomplexed resins (14). This arises from the additional stability gained by the development of stable ring structures in the polymer-support and it depends on the availability of the amino functions. The steric effect developed by the uniform crosslinking prevents the formation of stable ring structures in the 8% crosslinked system. Thus in the Cu(II) complexes of aminopolyacrylamides with 2-20 mole% of NNMBA-crosslinks, the geometry of the complex varies with the availability of the ligands, which is decided by the extent of crosslinking in the polymer-support.

CONCLUSION

The foregoing investigations on the preparation of aminopolyacrylamides, their complexation with Cu(II) and the EPR characterization of the Cu(II) complexes with varying extents of NNMBA-crosslinks revealed that the binding of Cu(II) ions with the amino functions in polyacrylamide-supports depends on the extent of the crosslinking in the three-dimensional polymer-support. The EPR spectra indicates almost tetragonal geometry of the Cu(II) complexes. The covalency of the Cu-N bond varies with the extent of the crosslinking in the polymer-support.

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