Electron paramagnetic resonance investigations of the effect of hydrophilic and flexible crosslinking on the coordination structures of copper complexes of triethyleneglycol dimethacrylate-crosslinked aminopolyacrylamides

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(Received 24 February 1993; revised 29 March 1993)

Copper(II) complexation of amino functions supported on triethyleneglycol dimethacrylate-crosslinked polyacrylamides in varying structural environments was investigated. The electron parametic resonance spectrum is used to probe the coordination structure and the nature of the Cu–N bond of the derived aminopolyacrylamide–Cu(II) complexes. The extent of the hydrophilic and flexible crosslinking agent in the macromolecular matrix has a significant effect on the coordination structure of the complexes.

(Keywords: e.p.r.; crosslinking; coordination)

Introduction

In a crosslinked polymer-supported ligand the ligand function is only an infinitesimal part of the insoluble macromolecular support. Hence its interaction with metal ions is decided by a number of factors characteristic of the polymer support, such as the nature of the polymer matrix, molecular character and extent of crosslinking, separation of the ligand function from the insoluble support and hydrophilic/hydrophobic balance[1–5]. Studies have been reported[6,7] on the dependence of the extent of crosslinking and separation of the ligand from the polymer matrix on the coordination structures of the Cu(II) complexes of polymer-supported ligands. The present paper describes the synthesis of polyacrylamides with 2–20 mol% of triethyleneglycol dimethacrylate (TEGDMA) crosslinks, transamidation with excess ethylenediamine to the corresponding poly(*N*-2-aminoethylacrylamide)s, complexation with Cu(II) ions and electron paramagnetic resonance (e.p.r.) studies to delineate the dependence of the hydrophilic and flexible crosslinking on coordination structures of the Cu(II) complexes.

Experimental

General. All the reagents were of certified ACS reagent grade. The copper sulfate used was the purest available sample (Merck). The e.p.r. spectra were recorded on a Varian E-12 spectrometer at room temperature.

Preparation of TEGDMA-crosslinked polyacrylamides. TEGDMA-crosslinked polyacrylamides were prepared by free radical solution polymerization of the monomers in ethanol. For the preparation of 2% TEGDMA-crosslinked polymer, 100 mg potassium persulfate was dissolved in ethanol (100 ml) at 70°C. The monomer mixture containing acrylamide (20.87 g) and TEGDMA (1.72 g) was added to this and heated with stirring until the polymer precipitated. At this stage the polymerization corresponded to approximately 65% conversion of monomers. Water (100 ml) was added and the contents were filtered, washed several times with water and methanol and dried in an oven at 80°C. Polymers with 4, 5, 10, 15 and 20 mol% of TEGDMA 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. The gel was washed with water to remove NaCl, then washed 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 deionized 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. A sample (200 mg) of each 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 and washed with distilled water to remove uncomplexed metal ions. The concentrations of Cu(II) salt solutions were determined by iodometry employing standard procedures[8]. The complexation studies were carried out in triplicate.

Results and discussion

Preparation of TEGDMA-crosslinked polyacrylamides. Polyacrylamides with 2–20 mol% of TEGDMA crosslinks were prepared by the solution polymerization of the monomers in ethanol at 70°C using potassium persulfate as the initiator (*Scheme 1*). It is possible that some unreacted double bonds exist in the TEGDMA-crosslinked polyacrylamides as the pendant unreacted double bond originating from the crosslinking agent. This possibility is indicated in *Scheme 1*.

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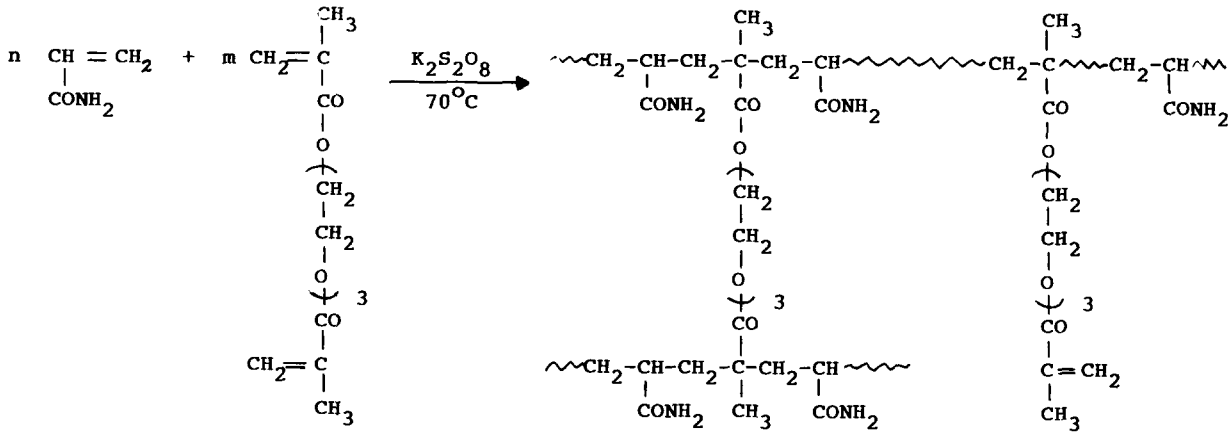
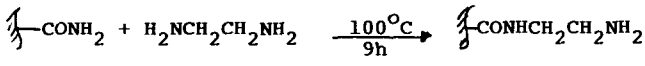


Scheme 1 Preparation of TEGDMA-crosslinked polyacrylamides



Scheme 2 Transamidation of TEGDMA-crosslinked polyacrylamides

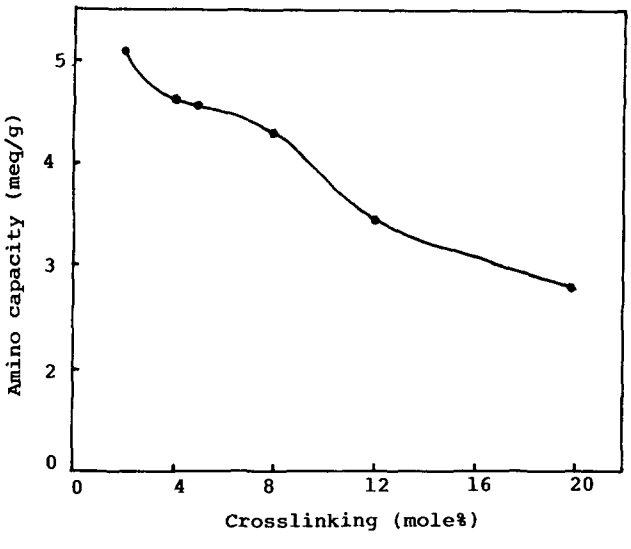


Figure 1 Amino capacity *versus* extent of TEGDMA crosslinking

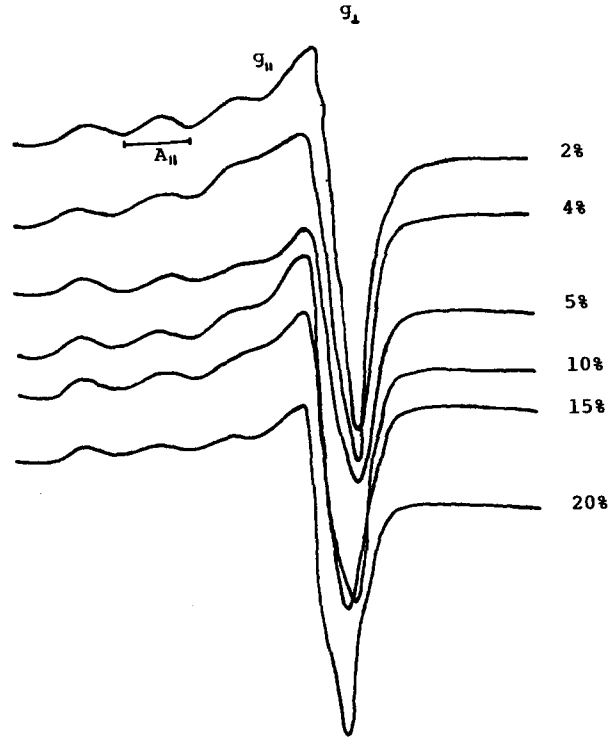


Figure 2 E.p.r. spectra of Cu(II) complexes of aminopolyacrylamides with varying extent of TEGDMA crosslinking

Preparation of TEGDMA-crosslinked poly(N-*2-aminoethylacrylamide*)*s.* Transamidation of crosslinked polyacrylamides with excess ethylenediamine afforded the corresponding aminopolyacrylamides (*Scheme 2*). The amino functions were detected by semiquantitative ninhydrin reaction and estimated by acid treatment[9,10]. The capacities of the amino resins decrease with increasing crosslinking, as expected[11] (*Figure 1*). The amino capacity is defined as the number of millimoles of amino groups per gram of the resin. The decrease in amino capacity with increasing crosslinking is small. This arises from the increased availability of amide groups owing to the flexible and polar nature of the crosslinks for polar transamidation with ethylenediamine (*Scheme 2* and *Figure 1*).

Cu(II) complexation of poly(N-*2-aminoethylacrylamide*)*s.* The Cu(II) intakes (in meq g^{-1}) by the different amino resins are: 2% (2.24), 4% (2.39), 5% (2.11), 10% (1.75), 12% (1.70), 15% (1.61), 20% (1.56). The standard deviations in the Cu(II) complexation are less than 1%. The decrease in Cu(II) intake is similar to the decrease in amino capacity.

E.p.r. spectra. The e.p.r. spectra of the various Cu(II) complexes at room temperature are given in *Figure 2*. They showed a distinct change with the extent of TEGDMA crosslinking and are clearly anisotropic at room temperature. This is the case only when the Cu(II) ion is directly attached to a polymeric ligand[12]. Such coordination is able to immobilize the Cu(II) ion and leads to anisotropic e.p.r. spectra at room temperature, at which low molecular weight species exhibit isotropic features. These spectra are characteristic of the tetragonal or almost tetragonal Cu(II) complexes with dx^2-y^2 ground state[13] (*Figure 2*).

The e.p.r. data of the various Cu(II) complexes are given in *Table 1*. The *g* and *A* values for the tetragonal Cu(II) complexes depend on the ligand donors bound to the metal ion. Increasing the bound nitrogens (from one

Table 1 E.p.r. data of Cu(II) complexes of aminopolyacrylamides with 2–20 mol% of TEGDMA crosslinking

TEGDMA (mol%)	$g_{\|}$	$g_{\perp}$	$A_{\|}$	$A_{\perp}$	α^2_{Cu}
2	2.2543	2.0542	162	39.1667	0.7647
4	2.2543	2.0599	161	42.6667	0.7643
5	2.2435	2.0543	159	40.000	0.7564
10	2.2431	2.0530	161	38.6667	0.7502
15	2.2331	2.0484	162	42.000	0.7495
20	2.2311	2.0595	167	40.000	0.7576

to four) leads to a distinct decrease of $g_{\|}$ and an increase of $A_{\|}$ (refs 14, 15). In the systems investigated, the amino resins may involve both the amino and amide nitrogens to coordinate metal ions[14]. However, in the present complexation process the coordination sites are amino nitrogens only (*Table 1*).

Values of $g_{\|}$ less than 2.3 suggest the covalent nature of the Cu–N bond[16]. Even though the values are in the same range, variation of the values with the extent of crosslinking is observed. The number of nitrogens coordinated depends on the availability of the ligands in the polymer support. With increasing TEGDMA crosslinking, the $g_{\|}$ values decrease and the $A_{\|}$ values increase until a certain limit of crosslinking is reached, after which this trend is reversed. Thus in the low-crosslinked system, ligands are readily available owing to the hydrophilic and flexible nature of the crosslinks, while in the highly crosslinked systems, the ligand functions are located on the surface of the polymer support owing to the steric effect originating from the high degree of crosslinking.

The bonding parameter (α^2_{Cu}) of the Cu(II) complexes, which is a measure of the in-plane σ-bonding of the Cu–N bond, was calculated by the expression given by Kivelson and Nieman[16]. The expression is based on the copper hyperfine tensor A:

$$\alpha^2_{Cu} = -[A_{\|}/0.036 + (g_{\|} - 2.002) + (g_{\perp} - 2.002)3/7 + 0.04]$$

Although the α^2_{Cu} values of the complexes are in the same range, they decrease with increasing crosslinking reaching a minimum at 10–15%, and increase thereafter. Thus the low and highly crosslinked systems have a greater number of complexed nitrogens because of the increased availability of ligands resulting from low crosslinking and the high concentration of ligands on the surface of highly crosslinked systems. With increasing crosslinking (2–10%) the number of nitrogen donors decreases from four, which is evident from the α^2_{Cu} values. After 15% crosslinking, the α^2_{Cu} again increases owing to the increased number of nitrogens on the surface of the highly crosslinked systems. A similar decrease in thermal stability with increasing crosslinking until a particular level of crosslinking, after which thermal stability increases, has been reported[17]. Complexation usually leads to the formation of stable ring structures with increased thermal stability[18]. With decreasing number of coordinated nitrogens, ring formation decreases with a corresponding decrease in thermal stability. α^2_{Cu} is inversely proportional to the covalency of the Cu–N bond. Thus the covalency of the copper complexes with 10 and 15% crosslinks is higher than the other systems. The steric effect developed in the system with moderate crosslinking (10–15%) prevents the formation of stable ring structures. In the highly crosslinked system, the ligand functions are concentrated on the surface, making them easily available. The geometry of the complex varies with the microenvironments around the ligand functions, which is decided by the extent of crosslinking in the polymer support.

The α^2_{Cu} value and the extent of crosslinking (C) fit into the general equation for a cubic polynomial of the type

$$\alpha^2_{Cu} = a + bC + cC^2 + dC^3$$

The specific equation for this is

$$0.7672 + 7.4688 \times 10^{-4}C - 3.7840 \times 10^{-4}C^2 + 1.5956 \times 10^{-5}C^3 = \alpha^2_{Cu}$$

The curve tends to take the shape of a parabola within the experimental limits. The experimental values of the 2 and 4% crosslinked systems are in agreement with the theoretical values obtained from this equation.

Conclusion

These investigations on the synthesis of poly(*N*-2-aminoethylacrylamide)s with varying extents of TEGDMA crosslinks and their complexation with Cu(II) ions reveal that the binding of Cu(II) ion depends on the crosslinking in the polyacrylamide support. The e.p.r. spectra indicate the almost tetragonal geometry of the Cu(II) complexes. The covalency of the Cu–N bond varies with the extent of crosslinking in the polymer support.

Acknowledgements

The authors thank the Material Research Centre (MRC), Indian Institute of Science (IISc), Bangalore, for the e.p.r. spectral analyses. The University Grants Commission, New Delhi, is thanked for the award of a Fellowship under the Faculty Improvement Programme to L. J.

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