

Effect of the Nature of Crosslinking Agent on the Unusual Metal Ion Specificity and Selectivity of *N,N*-bis(2-aminoethyl)polyacrylamide

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ABSTRACT: Metal ion desorbed crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides showed enhanced specificity for the desorbed metal ion, and these polymers selectively rebind the desorbed metal ion from a mixture of metal ions. For this, polyacrylamide with 8 mol % divinylbenzene (DVB) and *N,N'*-methylene-bisacrylamide (NNMBA) crosslinking were prepared by solution polymerization. Diethylenetriamino functions were incorporated into the polymers by polymer analogous reactions. The complexing ability of the amino polymers were investigated toward various transition metal ions like Co(II), Ni(II), Cu(II), and Zn(II). Polymeric ligand and metal complexes were characterized by various spectral methods. The removal of the metal ion from the polymer

matrix resulted in a memory for the desorbed metal ion. On rebinding, these polymers specifically rebind the desorbed metal ion and from a mixture of metal ions, it showed selectivity to the desorbed metal ion. Thus, the Cu(II) desorbed polymer specifically and selectively rebind Cu(II) ion from a mixture of Cu(II) and other metal ion. This selectivity is higher in the rigid DVB-crosslinked system, resulting from the high rigidity of the crosslinked matrix compared to the semirigid NNMBA-crosslinked system. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2017–2022, 2008

Key words: metal–polymer complexes; crosslinking; selectivity

INTRODUCTION

During recent years, there has been a growing interest in metal ion selective chelating polymers.^{1–4} This interest originates from their possible applications in analytical chemistry, metal processing, waste-water treatment,^{4,5} and in solving problems in environmental chemistry.⁶ Demands on the properties of these polymers include high capacity, high selectivity, and fast kinetics.⁷ Most of the commercial chelating polymers show a high capacity but has poor selectivity. Now a days, the development of polymers with improved selectivity has been initiated.^{8–10} We have observed the unusual specific rebinding of a metal ion desorbed amino functionalized polyacrylamide for its desorbed metal ion, unless the coordination geometry is not destroyed.¹¹

The present article describes the synthesis of polymers with unusual metal ion specificity and selectivity. For this, divinylbenzene (DVB)- and *N,N'*-methylene-bisacrylamide (NNMBA)-crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides were synthesized and complexed with Co(II), Ni(II), Cu(II), and Zn(II) ions. Characterization of the polymeric ligand

and metal complexes, pH dependence on metal ion complexation, recyclability, specificity, and selectivity are detailed.

EXPERIMENTAL

General

All the polymers in the present investigation were synthesized in the laboratory and were characterized. Acrylamide, NNMBA were purchased from SRL, Mumbai and DVB from Aldrich, Germany. All other low-molecular weight compounds used were commercially available and were purified by literature procedures unless otherwise specified. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer using KBr pellets. UV–vis spectra were recorded on a Shimadzu UV-1700 spectrometer. EPR spectra were recorded at X band at 303 K with a Varian E-12 spectrometer at RSIC, IIT, Mumbai.

Preparation of 8 mol % DVB- and NNMBA-crosslinked polyacrylamides

DVB was washed with sodium hydroxide solution (1%) and water to remove the inhibitor. Acrylamide (9.80 g) and DVB (3.15 g) were dissolved in ethanol (70 mL). Benzoylperoxide (100 mg) was added to the solution and it was heated on a water bath with

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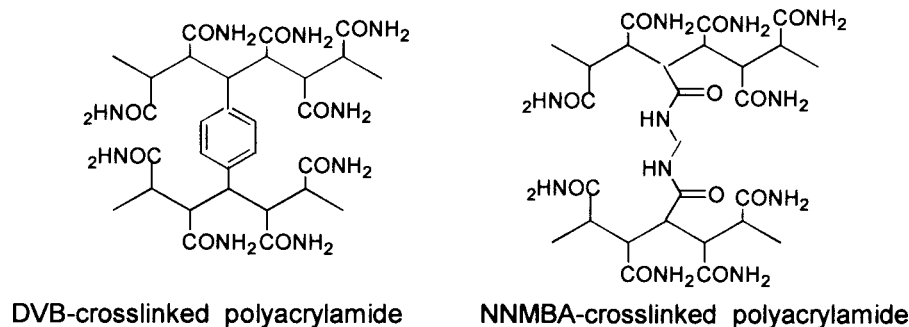


Figure 1 DVB- and NNMBA-crosslinked polyacrylamides.

stirring at 80°C. Heating and stirring were continued until the polymer got precipitated. The polymer was collected by filtration, washed several times with water, ethanol, benzene, and methanol. The polymer was dried in an oven at 50°C. NNMBA-crosslinked polyacrylamide was prepared by the same procedure by mixing acrylamide (13.91 g) and NNMBA (0.61 g) in water at 80°C using potassium persulphate (100 mg) as the initiator. The DVB- and NNMBA-crosslinked polymers were obtained in 86 and 95%, respectively.

Preparation of *N,N*-bis(2-aminoethyl) polyacrylamide

Crosslinked polyacrylamide (11.00 g) was swelled in dioxane and stirred with the Schiff base of salicylaldehyde and diethylenetriamine for about 24 h at 90°C. The polymer was washed with water and Soxhlet extracted with dioxane. The Schiff base anchored polymer (8 g) was swelled in dioxane and stirred with 6M HCl (100 mL) at 60°C for 24 h. Salicylaldehyde was liberated as an oil on hydrolysis. The hydrochloride form of the polymer was filtered off and washed with methanol. The free diethylenetriamino polymer was obtained by treatment with 2M NaOH followed by water until the washings were alkali free. To estimate the amino functions, the amino polymer (100 mg) was stirred with 0.2N HCl for 5 h. The polymer was filtered and the filtrate together with the washings were collected. Excess HCl was titrated against standard alkali using phenolphthalein indicator.

Complexation of metal ions with *N,N*-bis(2-aminoethyl)polyacrylamide

Polymer ligand (50 mg) was stirred with 20-mL metal salt solution (0.05N) at its natural pH. The metal ion intake of the polymeric ligand was obtained from the determination of the concentration of the metal salt solutions before and after complexation by spectrophotometric method.

pH dependence on metal ion binding

The pH of the metal ion solution was adjusted by the dropwise addition of 1M HCl or 1M NaOH as shown by a pH meter. The polymer (50 mg) was mixed with 20 mL of the metal salt solution of definite pH and kept for complexation. The amount of metal ion present in the filtrate was estimated.

Recyclability of complexed polymers

The polymer-metal complex (50 mg) was washed several times with 2N HCl for desorption. The desorbed ions were collected by washing with distilled water and estimated after the neutralization. The polymer after the acid treatment was washed with dilute NaOH and distilled water, and again subjected to complexation. The process was repeated four times.

Specificity studies of metal ion desorbed polymers

The metal ion desorbed polymers were treated with solutions of the desorbed metal ion as well as solutions of other metal ions, and the amount of metal ion complexed were estimated as described earlier.

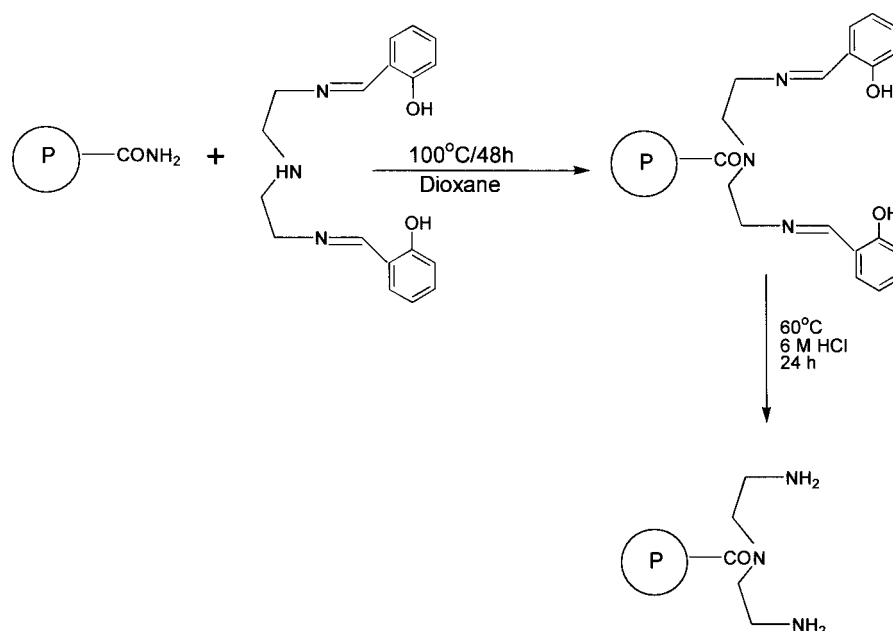
Selectivity studies of complexed polymers

To each of the metal ion desorbed polymer, mixture of metal ion: (0.05N) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (20 mL) + $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (20 mL); and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (20 mL) + $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (20 mL) were added and stirred for 6 h. The amount of different metal ions complexed was estimated by titrimetric methods.

RESULTS AND DISCUSSION

Synthesis of DVB- and NNMBA-crosslinked polyacrylamides

DVB- and NNMBA-crosslinked polyacrylamides were prepared by solution polymerization of the monomers in ethanol/water at 80°C (Fig. 1). The



Scheme 1 DVB- and NNMBA-crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides.

introduction of hydrophobic DVB crosslinks impart rigidity and hydrophobicity to the hydrophilic polyacrylamide, while NNMBA crosslinks give flexibility and hydrophilicity to the polymer.

Preparation of *N,N*-bis(2-aminoethyl)polyacrylamides

The crosslinked polyacrylamides were converted to the corresponding *N,N*-bis(2-aminoethyl)polyacrylamide by the *N*-alkylation of the salicylaldehyde-diethylenetriamine Schiff base at the secondary amino group followed by the hydrolysis at the azomethine site (Scheme 1). The functional group capacities were estimated from the equivalent of acid (Table I). The amino capacity of the hydrophilic and semirigid NNMBA-crosslinked system is higher than the rigid and hydrophobic DVB-crosslinked system.

Metal ion complexation of crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides

The complexations of diethylenetriamino functions were investigated toward Co(II), Ni(II), Cu(II), and Zn(II) ions at their natural pH by batch equilibration method (Table I). The decrease in concentration of

the metal ion solution was determined by spectrophotometric methods. The metal ion intake followed the order: Cu(II) > Co(II) > Ni(II) > Zn(II). As observed in the amino capacity, the metal intake by the NNMBA-crosslinked system is higher than the DVB-crosslinked system.

Characterization

The crosslinked polyacrylamides, functionalized polymers, and the metal complexes were characterized by IR, UV-vis, and EPR spectra.

IR spectra

The IR spectra of the crosslinked polymers showed the characteristic absorptions of amide carbonyl and C–N stretching of the amide group at 1660 and 1445 cm^{-1} , respectively. The aromatic ring of the DVB crosslinking is observed at 800 cm^{-1} . The secondary amide group of NNMBA crosslinking was observed at 1500–1590 cm^{-1} . N–H stretching was observed at 3500 cm^{-1} . The N–H stretching frequencies of the metal complexes were lower than the free amines. Upon coordination, N–H bond is weakened and the N–H stretching frequencies were

TABLE I
Metal Ion Complexation of Crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides

Crosslinking (8 mol %)	Amino capacity (mmol/g)	Metal ion intake (mequiv/g)			
		Co(II)	Ni(II)	Cu(II)	Zn(II)
DVB	3.12	2.67	2.53	2.71	2.19
NNMBA	3.79	3.12	2.93	3.46	2.34

TABLE II
EPR Parameters of the Cu(II) Complexes of DVB- and NNMBA-Crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides

Crosslinking	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	$\alpha^2\text{Cu}$	G
DVB	2.195	2.0452	35	11.67	0.4452	4.3
NNMBA	2.185	2.0451	45	15	0.4632	4.1

lowered in the complexes. The M—N stretchings were observed in the region $400\text{--}500\text{ cm}^{-1}$.¹²

UV-vis spectra

Electronic spectra provide an accurate and simple method for determining geometry around the transition metal ion in the complexes of the chelating polymers.¹³ Ni(II) complexes anchored on NNMBA-crosslinked system showed three bands due to the spin allowed transitions corresponding to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{2g}$ in the region $13,477$, $14,492$, and $24,630\text{ cm}^{-1}$ in a near octahedral field.¹⁴ The absorption maxima for the Cu(II) complexes at $13,227\text{ cm}^{-1}$ is assignable to ${}^2T_{2g} \rightarrow {}^2E_g$ transition. Because of Jahn–Teller distortions, the d^9 configuration of the Cu(II) ion complexed polymer, a tetragonal structure is obtained. $xy \rightarrow x^2 - y^2$ and $xz, yz \rightarrow x^2 - y^2$ transitions occur as the action bond lengthens and $xy \rightarrow x^2 - y^2$ shifts to blue region.

EPR spectra

The EPR parameters of the DVB- and NNMBA-crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides are given in Table II. The results suggest tetragonal symmetry about Cu(II) ion.¹⁵ The EPR data show that $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$ are indicative of the presence of the unpaired electron on the $dx^2 - y^2$ orbital.¹⁶ $g_{\parallel} < 2.3$ indicates covalent character of Cu—N bond. The calculated G values are larger than 4 showing that there is negligible interaction between Cu—Cu centers and these complexes are mononuclear.¹⁷ The bonding parameter $\alpha^2\text{Cu}$ that describe the fraction of

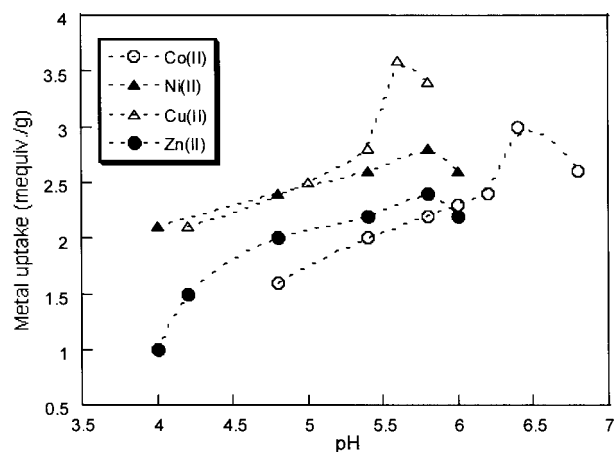


Figure 2 pH dependence on metal ion intake by *N,N*-bis(2-aminoethyl)polyacrylamide.

d orbitals used for in-plane bonding were also calculated and found that there is appreciable covalent character for the bond between the metal and the ligand.¹⁸

Influence of equilibrium pH on metal ion intake by *N,N*-bis(2-aminoethyl)polyacrylamides

The chelation of metal ion by a polymeric ligand is highly dependent on the equilibrium pH of the medium. The pH dependence on the metal ion complexation of *N,N*-bis(2-aminoethyl)polyacrylamides were studied by batch technique. Since most of the metal ions are prone to precipitation at high pH, investigations were limited to those values of pH where precipitation is just prevented. The amount of Zn(II) complexed by *N,N*-bis(2-aminoethyl)polyacrylamide was very low, probably due to the tridentate nature of the polymeric ligand and the tetrahedral geometry of the Zn(II) complex. The results show that the maximum complexation of Cu(II) takes place at pH = 5.51 and that of Co(II) at pH = 6.3. The optimum pH for Ni(II) and Zn(II) are 5.57 and 4.74, respectively (Fig. 2). The optimum pH is independent of the nature of the crosslinking agent.

TABLE III
Recycling of DVB- and NNMBA-Crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides

Crosslinking agent (8 mol %)	Number of cycles	Metal ion uptake (mequiv./g)			
		Cu(II)	Ni(II)	Co(II)	Zn(II)
DVB	1	2.71	2.53	2.67	1.97
	2	2.71	2.53	2.66	1.93
	3	2.70	2.51	2.66	1.93
	4	2.70	2.48	2.64	1.93
NNMBA	1	3.46	2.96	3.12	2.34
	2	3.43	2.93	3.10	2.31
	3	3.43	2.89	3.07	2.27
	4	3.39	2.89	3.07	2.27

TABLE IV
Recyclability Studies of Crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides With Vigorous Stirring

Crosslinking agent	Number of cycles	Cu(II) uptake (mequiv/g)
DVB	1	2.24
	2	1.62
NNMBA	1	2.82
	2	1.93

Recyclability of metal complexes of *N,N*-bis(2-aminoethyl)polyacrylamides

The most important advantage of chelating polymers is their reuse after a particular process. The recycling of the neutralized, acid-treated polymer was repeated four times and the results are given in Table III. The retention of the initial capacity even after four cycles of repeated operations suggests that the polymer can be used several times without reduction in capacity. Under the conditions of recyclability studies, when the polymeric ligand was subjected to vigorous stirring, the amount of metal ion rebound was lower than initial amount (Table IV). This is due to the disruption of the orientation of the ligands for coordination with the metal ion.

Metal ion rebinding studies of metal ion desorbed systems

In the metal ion complexation of polymer-supported ligands, the polymer chains undergo some sort of rearrangement from their normal position for creating an optimum coordination geometry for metal ion complexation and in the rebinding experimental conditions, if this geometry is not disturbed, the metal ion desorbed polymers would have certain holes or pockets left by the desorbed metal ions. These holes or pockets have an unusual memory for the desorbed metal ion resulting in its specific rebinding. This specific rebinding depends on the stability of the polymer support. This depends on the nature of

the polymer backbone and nature and degree of crosslinking in the polymer support.

To investigate the specific complexing ability of metal ion desorbed *N,N*-bis(2-aminoethyl)polyacrylamide-metal complexes, the complexed metal ions were desorbed using dilute hydrochloric acid. The acid treated, neutralized polymeric ligands were treated with desorbed metal ions and other metal ions. On metal ion desorption, the tendency of the metal ion desorbed systems to complex with other metal ions is poor compared to their initial complexation. This supports the maintenance of the coordination geometry of the desorbed metal ion that is not suitable for the guest metal ion. Thus, specific rebinding arises from the difference in the coordination geometries as well as the difference in size between the desorbed metal ion and other guest metal ions.

In the DVB- and NNMBA-crosslinked polyacrylamide-supported amines, the metal ion desorbed systems rebind the desorbed metal ions quantitatively (Table V). From the results of the specificity studies, it is clear that the DVB-crosslinked system has the highest specificity. This specific binding occurred as a result of the rigid and hydrophobic nature of the polymer back bone to keep the "cavities" of the original metal ion without any deformation. Specificity of the rigid and hydrophobic DVB-crosslinked system is higher than the semirigid and hydrophilic NNMBA-crosslinked system.

Metal ion selectivity studies of *N,N*-bis(2-aminoethyl)polyacrylamides

To investigate the selectivity characteristics of metal ion desorbed DVB- and NNMBA-crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides, competitive rebinding experiments were carried out with pairs of metal ions at its natural pH. All the metal ion desorbed systems showed a higher selectivity toward the desorbed metal ion from a mixture of metal ions (Table VI). The size of the metal ion and the difference in the coordination

TABLE V
Metal Ion Specificity Studies of DVB- and NNMBA-Crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides

Crosslinking	Desorbed metal ion	Metal ion intake (mequiv/g)			
		Cu(II)	Ni(II)	Co(II)	Zn(II)
DVB	Cu(II)	2.67 _(2.68)	0.15	0.50	0.81
	Ni(II)	0.30	2.53 _(2.55)	0.67	0.41
	Co(II)	0.50	0.77	2.66 _(2.67)	0.29
	Zn(II)	0.74	0.14	0.16	1.96 _(1.97)
NNMBA	Cu(II)	3.43 _(3.46)	0.20	0.70	1.10
	Ni(II)	0.67	2.93 _(2.96)	0.34	0.51
	Co(II)	0.44	0.08	3.12 _(3.16)	0.67
	Zn(II)	1.22	0.56	1.30	2.34 _(2.37)

TABLE VI
Summary of Selectivity Studies

Crosslinking agent	Desorbed metal ion	Rebinding pair of metal ion	Complexation from mixture (mequiv/g)	Original complexation (mequiv/g)
DVB	Cu(II)	Co(II) + Cu(II)	Co(II) = 0.0 Cu(II) = 2.44	2.68
	Cu(II)	Ni(II) + Cu(II)	Ni(II) = 0.32 Cu(II) = 2.20	2.68
	Ni(II)	Cu(II) + Ni(II)	Cu(II) = 0.42 Ni(II) = 1.93	2.53
	Co(II)	Co(II) + Cu(II)	Co(II) = 2.32 Cu(II) = 0.10	2.66
NNMBA	Cu(II)	Co(II) + Cu(II)	Co(II) = 0.01 Cu(II) = 3.24	3.46
	Cu(II)	Ni(II) + Cu(II)	Ni(II) = 0.56 Cu(II) = 2.70	3.46
	Ni(II)	Cu(II) + Ni(II)	Cu(II) = 0.76 Ni(II) = 1.84	2.96
	Co(II)	Co(II) + Cu(II)	Co(II) = 2.86 Cu(II) = 0.14	3.16

geometry of the various polymer–metal complexes are decisive in dictating this selectivity.

The selectivity studies of the Co(II), Ni(II), and Cu(II)-desorbed DVB- and NNMBA-crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides were carried out with Co(II)-Cu(II); Cu(II)-Ni(II); Cu(II)-Co(II); and Ni(II)-Cu(II) pairs of metal ions. In all these cases, the metal ion desorbed polymers showed a higher selectivity for its desorbed metal ion. This selectivity is higher for the Cu(II)- and Co(II)-desorbed systems for a Cu(II)-Co(II) mixture than the Ni(II)-desorbed system for a Cu(II)-Ni(II) mixture. Even though both crosslinked systems showed enhanced specificity and selectivity, rigid DVB-crosslinked system has higher specificity and selectivity. This originates from the rigidity of the crosslinked support for maintaining the coordination geometry.

CONCLUSION

Systematic investigations on the correlation between the variables of structural parameters of a macromolecular matrix and the metal ion complexation of the incorporated ligands are very useful in the design of metal ion specific and selective polymers. The metal uptake of DVB- and NNMBA-crosslinked *N,N*-bis(2-aminoethyl)polyacrylamides depends on the nature of crosslinking. The polymeric ligands and metal complexes were characterized by IR, UV–vis, and EPR spectral analysis. The metal ion complexation depends on the pH of the medium. The metal ion desorbed polymers specifically rebind the desorbed metal ion. The specificity of the metal ion-desorbed systems could be made use of for the selective concentration of the metal ion from a mixture. The spec-

ificity and selectivity of the metal ion desorbed systems depend on the nature of crosslinking agent. Thus, these investigations help to design the development of better and efficient metal ion selective polymeric systems, which exclusively rebind the desorbed metal ion from a mixture of metal ions.

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