Effect of the Nature of the Crosslinking Agent on the Metal-Ion Complexation Characteristics of 4 Mol % DVB- and NNMBA-Crosslinked Polyacrylamide-Supported Glycines

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ABSTRACT: Metal-ion complexation behavior of glycine functions supported on divinyl-benzene (DVB)- and N,N'-methylene bisacrylamide (NNMBA)-crosslinked polyacrylamide was carried out toward Co(II), Ni(II), Cu(II), and Zn(II) ions. The polymeric ligands and the derived metal complexes were characterized by IR, UV, and EPR spectra and by SEM. The metal-ion complexation of the rigid DVB-crosslinked system is lower than that of the semirigid NNMBA-crosslinked system. The glycine ligands renervated after the desorption of the metal ions showed an unusual specificity toward the desorbed metal ion. The low degree of crosslinking makes the desorption process simple and shows fast rebinding kinetics. The metal-ion-desorbed polymeric ligands would have *pocket*s or *holes* characteristic of the desorbed metal ion, resulting in its specific rebinding. The rigidity of the crosslinking also determines the kinetics of metal-ion rebinding. The specificity and selectivity characteristics of the crosslinked polymeric ligand was found to be increased as the crosslinking agent changes from semirigid NNMBA to rigid and hydrophobic DVB. Thus, copper-desorbed resins showed an increased specificity toward copper ions and selectively binds copper ions from a mixture of copper and cobalt ions. The metal-ion specificity and selectivity characteristics of the metal-ion-desorbed system is exploited for the concentration of desorbed metal ions from a mixture of metal ions. The resin is amenable for a continuous process and can be regenerated several times. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3432–3444, 1999

Key words: polymer–metal complex; nature of crosslinking; polyacrylamide-supported; metal-ion specificity

INTRODUCTION

The syntheses of crosslinked polymers with chelating groups have received considerable attention in recent years for easy, rapid, and inexpensive metal-ion separation and concentration.[1–3]

The conventional chelating ligands suffer mainly from two shortcomings, namely, slow metal-ion uptake and lack of selectivity toward a particular metal ion. Several criteria are important in the design of chelating polymers with substantial stability for the selective concentration of metal ions: specific and fast binding of the metal ions as well as the recyclability/reuse of the crosslinked chelating polymeric ligands. The increased specificity and selectivity originates from the macromolecular characteristics and extent of crosslinking, the hydrophilic/hydrophobic balance of the macromolecular matrix, the structure of the attached li-

gand function, and the stability constant of the resulting polymer–metal complex.[4−6] To overcome the limitations of metal-ion chelating polymeric ligands, new metal-ion complexing polymers with improved specific and selective complexing properties were developed using molecular imprinting.[7] These systems retain their precise coordination geometry of the resulting desorbed metal ions, leading to its specific rebinding.

The present article describes the successful design of two low-crosslinked systems based on polyacrylamides for the selective concentration of the metal ions desorbed from the polymer support. The effect of the semirigid and polar N,N'-methylene bisacrylamide (NNMBA) and rigid and hydrophobic divinylbenzene (DVB) crosslinking agents on the metal-ion specificity and selectivity characteristics of polyacrylamide-supported glycine ligands is illustrated. The characterization of the polymeric ligands and its metal complexes, optimization of the complexation conditions, effect of pH dependence on metal-ion binding and rebinding, kinetics of metal ion binding, and rebinding and investigation of the specific and selective metal-ion binding are also described.

EXPERIMENTAL

Materials and Methods

All reagents were of certified ACS reagent grade. The metal salts used were cobalt chloride, nickel sulfate, copper sulfate, and zinc sulfate. The UV-vis spectra were recorded on a Shimadzu 160-A spectrometer. The FTIR spectra were recorded on a Bruker IFS-55 spectrometer using KBr pellets. The EPR spectra were recorded on a Varian E-12 spectrometer. SEM photographs were taken using a Hitachi S-2400 instrument.

Transamidation of Polyacrylamides with Sodium Salt of Glycine

Crosslinked polyacrylamide (10 g) was heated with excess sodium salt of glycine [glycine (20 g) and NaOH (10.64 g) in water (50 mL)] at 100°C for 20 h. The reaction mixture was poured into water containing crushed ice. The functionalized polymers were collected by filtration, Soxhletted using methanol and acetone, and dried in an oven at 50°C.

Estimation of Carboxyl Capacity

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

Metal-ion Complexation of 4 Mol % NNMBA- and DVB-crosslinked Polyacrylamide-supported Glycines: General Procedure

The crosslinked carboxylate polymers (100 mg) were stirred with a metal salt solution (0.05N, 50 mL) for 24 h. The complexed resins were collected by filtration and washed to remove uncomplexed metal ions. The concentrations of Co(II), Ni(II), and Cu(II) solutions were followed by UV-vis spectrometry, and of Zn(II), by the complexometric method.

Effect of pH Dependence on Metal-ion Binding and Rebinding

To different sets of crosslinked carboxylate polymers (100 mg), metal salt solutions at different pH were added and stirred. At 0.05N concentration, the natural pH's for different metal salt solutions are Co(II) = 5.1, Ni(II) = 5.8, Cu(II) = 5.1, and Zn(II) = 4.8. The metal-ion binding was carried out in a thermostated shaker for 24 h. The uncomplexed metal ions were washed using distilled water and analyzed using UV-vis spectrometry. The same experiment was repeated for the metal-ion-desorbed systems.

Swelling Studies of 4 Mol % DVB- and NNMBA-crosslinked Polyacrylamides, Polyacrylamide-supported Glycines, and Cu(II) Complexes: General Procedure

Two hundred milligrams of each of the different polymers was equilibrated with 50 mL distilled water for 48 h. The swollen resins were collected by filtration, adhering traces of water were removed by wiping with blotting paper, and the swollen weight was determined. The samples were dried in a vacuum and weighed.

Desorption of Complexed Metal Ions: General Procedure

The complexed metal ions were desorbed using H_2SO_4 (0.2N) and the acid-treated resins were washed with distilled water to remove the unreacted H_2SO_4 and neutralized using dilute NaOH (0.2N) and again washed with distilled water to remove alkali.

$$\text{—CONH}_2 + 2\text{HNCH}_2\text{COO}^-\text{Na}^+ \xrightarrow[\text{20 h}]{100\,^{\circ}\text{C}} \text{—CONHCH}_2\text{COO}^-\text{Na}^+$$

Scheme 1   Synthesis of crosslinked polyacrylamide-supported gycines.

Rebinding of Metal Ions: General Procedure

The neutralized, metal-ion-desorbed resins were treated with solutions of the desorbed metal ion (0.05N, 50 mL) and other metal ions and the extent of the complexation was followed by UV-vis spectrometry for the Co(II), Ni(II), and Cu(II) ions and by complexometric titration against EDTA for the Zn(II) ion.

Kinetics of Metal-ion Binding and Rebinding: General Procedure

To different sets of crosslinked resins (100 mg), a copper sulfate solution (0.05N, 50 mL) was added and shaken in a thermostat for different time intervals at 30 and 40°C. The metal-ion binding was followed by UV-vis spectrometry. The same was repeated for metal-ion rebinding.

Selectivity Studies: General Procedure

To each of the metal-ion-desorbed polymers, a mixture of the metal ions: $CuSO_4 \cdot 5H_2O$ (50 mL) + $CoCl_2 \cdot 6H_2O$ (50 mL); and $CuSO_4 \cdot 5H_2O$ (50 mL) + $NiSO_4 \cdot 6H_2O$ (50 mL), was added and stirred for 24 h. The amount of different metal ions complexed was estimated by multicomponent UV-vis spectrometry.

RESULTS AND DISCUSSION

Preparation of 4 Mol % DVB- and NNMBA-crosslinked Polyacrylamide-supported Glycines

Polyacrylamides crosslinked with DVB and NNMBA (4 mol %) were prepared by free-radical solution polymerization as reported earlier.[8] Glycine functions were incorporated into crosslinked poyacrylamides by transamidation with excess sodium salt of glycine as represented in Scheme 1.

The carboxyl capacities of the resulting polymers were determined by alkali titration and found to be 3.05 and 4.65 mmol/g for the DVB- and NNMBA-crosslinked systems, respectively. The higher carboxyl capacity of the NNMBA-crosslinked system is obvious. The less rigidity and polarity of the NNMBA-crosslinking favors

the polar transamidation with the sodium salt of glycine.

Metal-ion Complexation Studies and Metal-ion Rebinding Studies of Metal-ion-desorbed Systems: Effect of the Nature of the Crosslinking Agent

The metal-ion complexations of the glycine functions in different structural environments were investigated toward Co(II), Ni(II), Cu(II), and Zn(II) ions. The insoluble polymeric ligand on treatment with the metal salt solution resulted in the formation of an insoluble polymer–metal complex. The original metal-ion complexations at their natural pH are given in Figure 1. To investigate the specificity characteristics of metal-ion-desorbed resins, the complexed metal ions were desorbed using 0.2N H_2SO_4 and the acid-treated polymeric ligands after neutralization were subjected to their own desorbed metal ion and other metal ions. From the results, it was found that the metal-ion-desorbed resins specifically bind the desorbed metal ion rather than other metal ions as shown in Table I. On metal-ion desorption, certain *cavities* or *pockets* developed, which are the coordination geometry of the desorbed metal ion. If these cavities remained as such during the rebinding, experimental conditions would favor the specific binding of the desorbed metal ion.
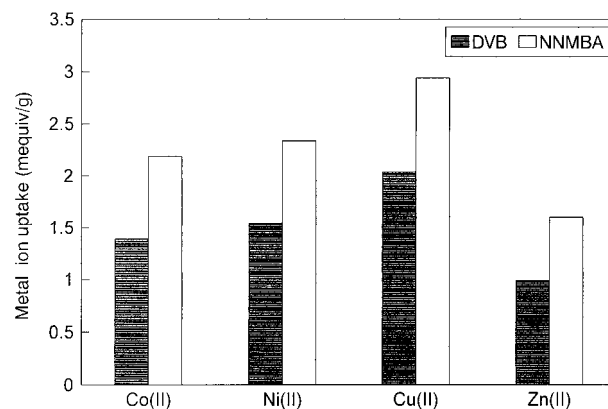

Figure 1   Metal-ion complexation of 4 mol % DVB- and NNMBA-crosslinked polyacrylamide-supported glycines.

Table I Metal-ion Specificity Studies of 4 mol % DVB- and NNMBA-crosslinked Polyacrylamide-supported Glycines

Crosslinking Agent	Desorbed Metal Ion	Metal-ion Uptake on Rebinding[a] (mequiv/g)				Original Metal-ion Uptake (mequiv/g)
		Co(II)	Ni(II)	Cu(II)	Zn(II)	
DVB	Co(II)	1.38 ± 0.019 (99.2%)	0.81 ± 0.016 (52.6%)	1.19 ± 0.015 (58.3%)	0.48 ± 0.011 (48.5%)	1.39
DVB	Ni(II)	0.84 ± 0.010 (60.4%)	1.53 ± 0.012 (98.9%)	1.14 ± 0.014 (55.8%)	0.57 ± 0.017 (56.4%)	1.54
DVB	Cu(II)	0.77 ± 0.012 (55.4%)	0.81 ± 0.012 (52.5%)	2.03 ± 0.010 (99.5%)	1.04 ± 0.012 (51.6%)	2.04
DVB	Zn(II)	0.71 ± 0.012 (51.0%)	0.65 ± 0.014 (42.2)	0.92 ± 0.016 (45.1%)	0.97 ± 0.017 (98.2%)	0.99
NNMBA	Co(II)	2.15 ± 0.015 (98.2%)	1.23 ± 0.010 (52.3%)	1.30 ± 0.013 (44.2%)	1.09 ± 0.014 (68.1%)	2.19
NNMBA	Ni(II)	1.50 ± 0.013 (68.4%)	2.31 ± 0.013 (98.3%)	2.00 ± 0.014 (68.0%)	1.50 ± 0.019 (93.5%)	2.34
NNMBA	Cu(II)	1.20 ± 0.013 (55.0%)	1.50 ± 0.017 (64.2%)	2.93 ± 0.016 (99.7%)	1.21 ± 0.017 (75.2%)	2.94
NNMBA	Zn(II)	1.01 ± 0.012 (46.0%)	1.61 ± 0.016 (68.8%)	2.06 ± 0.012 (70.6%)	1.60 ± 0.018 (98.6%)	1.60

[a] Average of three experiments; values in parentheses show the percentage of metal uptake.

Whereas if the polymer was subjected to vigorous stirring, upsetting the coordination geometry left by the desorbed metal ion, there is no specific rebinding of the desorbed metal ion. The specific metal-ion complexation of the polymeric ligands depends on the stability of the coordination geometry left by the desorbed metal ion. This, in turn, depends on the mechanical stability of the polymer support, which depends on the nature of the monomers and the crosslinking agent and the degree of the crosslinking. The optimization of the specificity and selectivity on tailoring the best conformation by adjusting the nature and degree of crosslinking was reported.[9,10] From the results of the specificity studies, it is clear that the DVB-crosslinked system has the highest specificity, that is, it showed higher specificity for its own desorbed metal ion than for other metal ions. This specific binding occurred as a result of the rigid and hydrophobic nature of the polymer backbone to keep the *cavities* of the original metal ion without any deformation in the aqueous media. It is possible to maintain the stable geometry of the desorbed metal ion with increasing rigidity of the polymer support (Scheme 2). Compared to the rigid and hydrophobic DVB-crosslinked system, the semirigid and hydrophilic NNMBA-crosslinked system gave lower specificity.

Characterization

FTIR Spectra

The IR spectra of the DVB- and NNMBA-crosslinked polyacrylamides showed the characteristic absorptions of the amide —NH and C=O at 3500 and 1658 cm^{-1}, respectively. The absorption of the aromatic ring in the DVB crosslinking and the secondary amide group in the NNMBA crosslinking were observed at 800 and 1570–1500 cm^{-1}, respectively. In the functionalized polymer, the carboxylate group absorbs strongly at 1673 cm^{-1}. During complexation, the carboxylate group shifts from 1673 to 1640 cm^{-1}, indicating complexation with the metal ion.

UV-vis Spectra

The structure and geometry of a polymer metal complex is largely determined by the microenvironment of the polymer domain. The UV-vis spectra of the Co(II), Ni(II), and Cu(II) complexes of 4 mol % NNMBA-crosslinked polyacrylamide-sup-
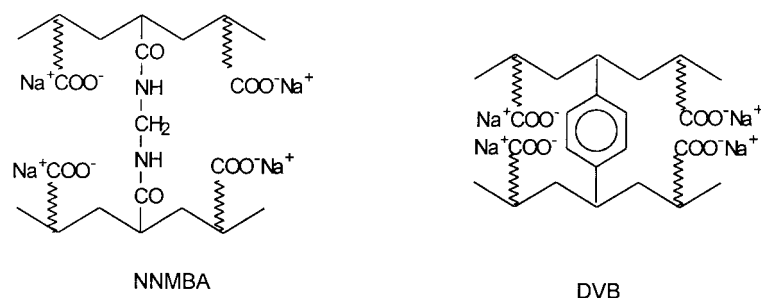
Scheme 2   Relative rigidity and flexibility of the crosslinking agents.

ported glycines are given in Figure 2. In the DVB- and NNMBA-crosslinked systems, the Co(II) complex exhibits bands in the regions 9623–9685 cm^{-1} and 18,315–19,083 cm^{-1} due to $^4T_{1g}$ (F) − $^4T_{2g}$ (F) (γ_1) and $^4T_{1g}$ (F) − $^4T_{1g}$ (P) (γ_3) transitions of an octahedral geometry. In polymer-anchored Ni(II) complexes, there are three spin-allowed transitions, $^3A_{2g}$ − $^3T_{1g}$ (P), 13,531–15,174 cm^{-1}, $^3A_{2g}$ − $^3T_{1g}$ (F), 24,752–25,062 cm^{-1} and $^3A_{2g}$ − $^3T_{2g}$ (P), 33,222–33,225 cm^{-1}, suggesting near octahedral geometry. Due to Jahn–Teller distortions, the d^9 configuration of the Cu(II) complexed polymer, a tetragonal structure is obtained. xy–x^2—y^2 and xz, yz–x^2–y^2 transitions occur as the axial bond is lengthening and the xy–x^2—y^2 transition shifts to the blue region. The tetragonal Cu(II) complex is expected to show the transition $^2B_{1g}$ − $^2A_1$, $^2B_{1g}$ − $^2B_{2g}$, and $^2B_{1g}$ − $^2B_{2g}$, but bands due to these transitions overlap to give one broad band as represented in Figure 2. The broad band observed in the region 19,721–20,010 cm^{-1} indicates tetragonal-type symmetry for the Cu(II) complex. In the polymer-anchored Zn(II) complex, the spectra obtained are ligand related and no d–d transitions occur. Therefore, it would have a tetrahedral geometry.
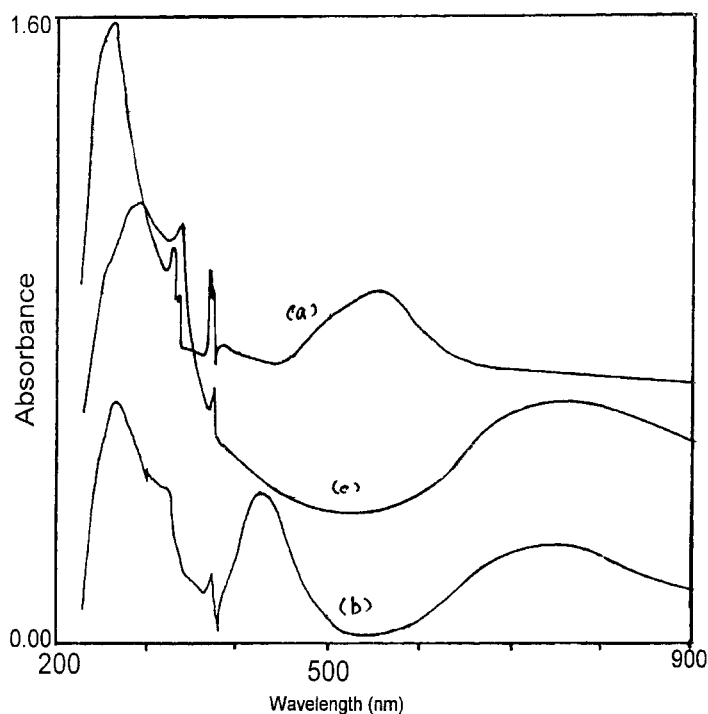

Figure 2   UV-vis spectra of 4 mol % NNMBA-crosslinked polyacrylamide-supported glycine: (a) cobalt, (b) nickel, and (c) copper complexes.

Table II   EPR Parameters of 4 mol % DVB- and NNMBA-crosslinked Polyacrylamide-supported Glycine–Cu(II) Complexes

Crosslinking Agent	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	α^2 Cu
DVB	2.4912	2.0932	176	54	0.7895
NNMBA	2.4448	2.0953	172	62	0.7834

EPR Spectra

DVB, 4 mol %,- and NNMBA-crosslinked polyacrylamide-supported glycine Cu(II) complexes were also characterized by EPR spectroscopy. The EPR spectral pattern of the paramagnetic Cu(II) complex was influenced by the number of coordinating ligands as well as by the geometry of the complex.[11,12] The g values of Cu(II) complex of polymeric ligands indicate tetragonal-type symmetry about the Cu(II) ion. The values of $g_\parallel > g_\perp$ and $A_\parallel > A_\perp$ indicates the presence of an unpaired electron in the dx^2–y^2 orbitals.[13] The EPR spectrum is clearly anisotropic, which can be the case in which the metal ions bonded directly to the polymeric ligand. The bonding parameter α^2 Cu, which is a measure of the covalency of the in-plane σ-bonding of the ligand group with the coordinating metal ion, was calculated by the expression given by Kivelson and Neimen.[14] The expression is based on the copper hyperfine factor $A_\parallel$ as

$$\alpha^2 \text{ Cu} = -(A_\parallel/0.36) + (g_\parallel - 2.002)$$
$$+ 3/7(g_\perp - 2.002) + 0.04$$

The EPR parameters of 4 mol % DVB- and NNMBA-crosslinked polyacrylamide-supported glycine-Cu(II) complexes are given in Table II.

Scanning Electron Microscopy (SEM)

SEM is the most widely used technique to study the shape, size, morphology, and porosity of polymers.[15–17] The change in the surface morphology of the polymeric ligand on metal-ion complexation was investigated using this technique.

In the present study, SEM was used to probe the change in morphological features of the DVB- and NNMBA-crosslinked polyacrylamide-supported glycines on Cu(II) complexation [Fig. 3(a,b)]. The SEMs of uncomplexed resins have smooth surfaces. The voids/channels present in the crosslinked polymer matrix are responsible for the swelling of the polymer and the complexation of the active sites buried within the three-dimensional crosslinked polymer matrix.

A comparison of the SEM patterns of the DVB- and NNMBA-crosslinked systems indicated that the surface of the DVB-crosslinked system is rougher than that of the NNMBA-crosslinked resin. This could arise from the change in morphology arising from the hydrophobic and rigid nature of the DVB crosslinks. But in the complexed resin, the voids/channels present in the uncomplexed resin are absent and the surface becomes rough and rigid. This is from the contraction of the polymer matrix by the cooperative contribution of the ligands for complexation with the Cu(II) ion.

pH Dependence on Metal-ion Binding

The metal-ion complexation of polymeric ligands is highly dependent on the equilibrium pH of the medium.[18,19] The pH dependence of metal-ion complexation is widely used for the selective separation of metal ions from a mixture of metal ions. In the present study, since most of the metal ions are prone to precipitation at higher pH, investigations were limited to those pH values where precipitation was just prevented. Use of buffer solutions for adjusting the pH was avoided due to the undesirable results from the coordination of the ionic species with metal ions.[20] The effect of pH dependence on the complexation of various metal ions with the DVB- and NNMBA-crosslinked (4 mol %) polyacrylamide-supported glycines are given in Figure 4(a,b).

The results of the pH studies revealed that at lower pH values the nonionic bonding mechanism (e.g., hydrogen bonding) occurs and this hydrogen bonding lowers the metal-ion binding. Since the dissociation of the carboxyl group will be favored in the alkaline pH region, high metal-ion binding should take place at higher pH values. Similar observations were reported in the binding of ZrO_2 by polyacrylamide.[21] The results indicate that the optimum pH for different metal ions are Co(II): 5.4, Cu(II): 5.4, Ni(II): 6.1, and Zn(II): 5.6.

pH Dependence on Metal-ion Rebinding

To investigate the pH dependence on metal-ion rebinding, the complexation of 4 mol % DVB- and NNMBA-crosslinked metal-ion-desorbed polyacrylamide-supported glycine systems was carried out at different pH values. But the pH has no
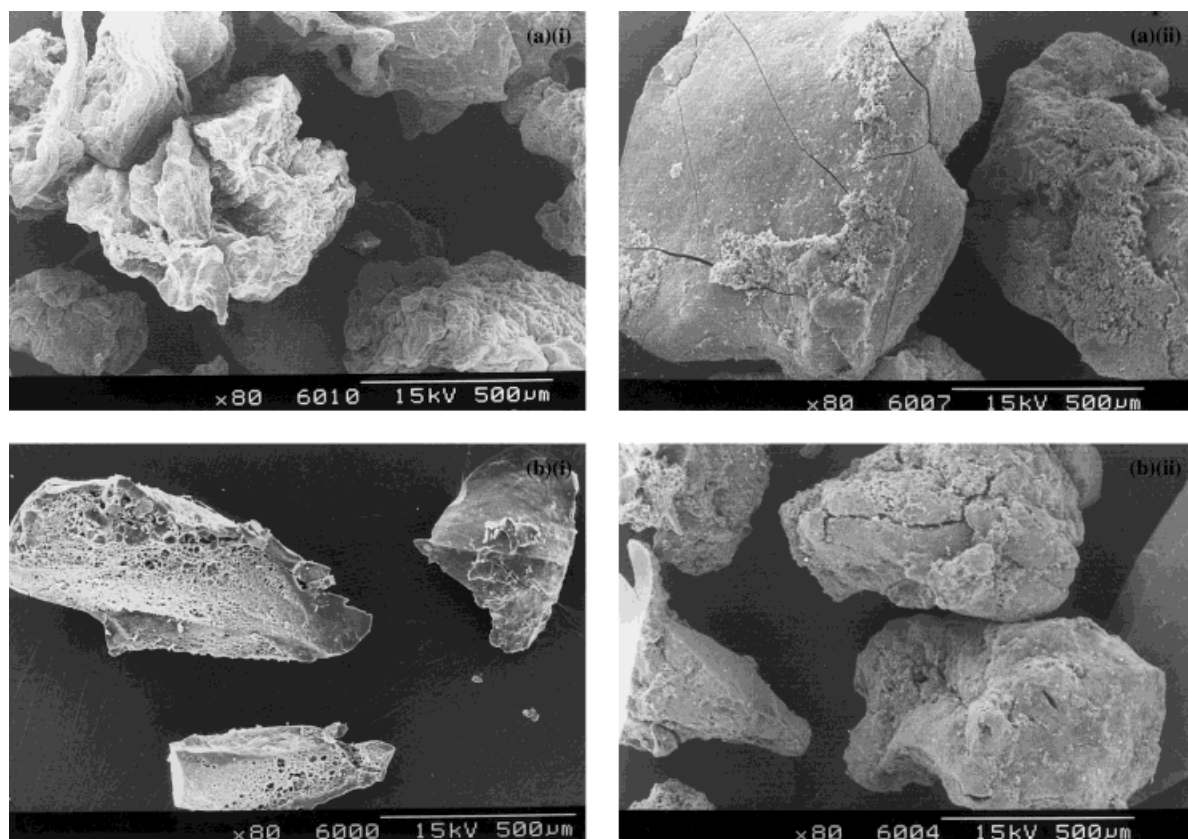
Figure 3   (a) SEM of (i) 4 mol % DVB-crosslinked polyacrylamide-supported glycine and (ii) Cu(II) complex. (b) SEM of (i) 4 mol % NNMBA-crosslinked polyacrylamide-supported glycine and (ii) Cu(II) complex.

significant effect on metal-ion rebinding. This points to the fact that the specific metal-ion rebinding is solely determined by the *memory* of the fixed geometry kept in the three-dimensional polymer matrix. But pH has a definite role in the initial metal-ion binding of the polymeric ligand. However, in the rebinding of metal ions by the metal-ion-desorbed systems, no considerable difference was noted with varying pH, suggesting that the rebinding is independent of the pH of the metal salt solution [Fig. 5(a,b)].

Swelling Studies of 4 Mol % DVB- and NNMBA-crosslinked Polyacrylamides, Polyacrylamide-supported Glycines, and Cu (II) Complexes

For a crosslinked polymer, the extent of swelling depends on the solvent–polymer interaction which is determined not only by the nature of the solvent and polymer matrix but also by the active groups introduced into the polymer matrix. The presence of hydrophobic/hydrophilic crosslinking

agents would lead to the formation of crosslinked systems with varying solvation and swelling characteristics. In the present study, the extent of swelling of the polymer in water is represented as the equilibrium water content (EWC), which is expressed as

$$EWC = \frac{\text{weight of wet resin} - \text{weight of dry resin}}{\text{weight of wet resin}} \times 100$$

To investigate the nature of the crosslinking agent on the swelling equilibria of the polyacrylamide-supported systems in water, the EWC (%) was calculated for 4 mol % DVB- and NNMBA-crosslinked polyacrylamides, functionalized resins, and their metal complexes. In the case of hydrophobic DVB-crosslinked systems, the EWC values are very low. In the NNMBA-crosslinked system, the polar and flexible nature of the crosslinking agent favors swelling more than does
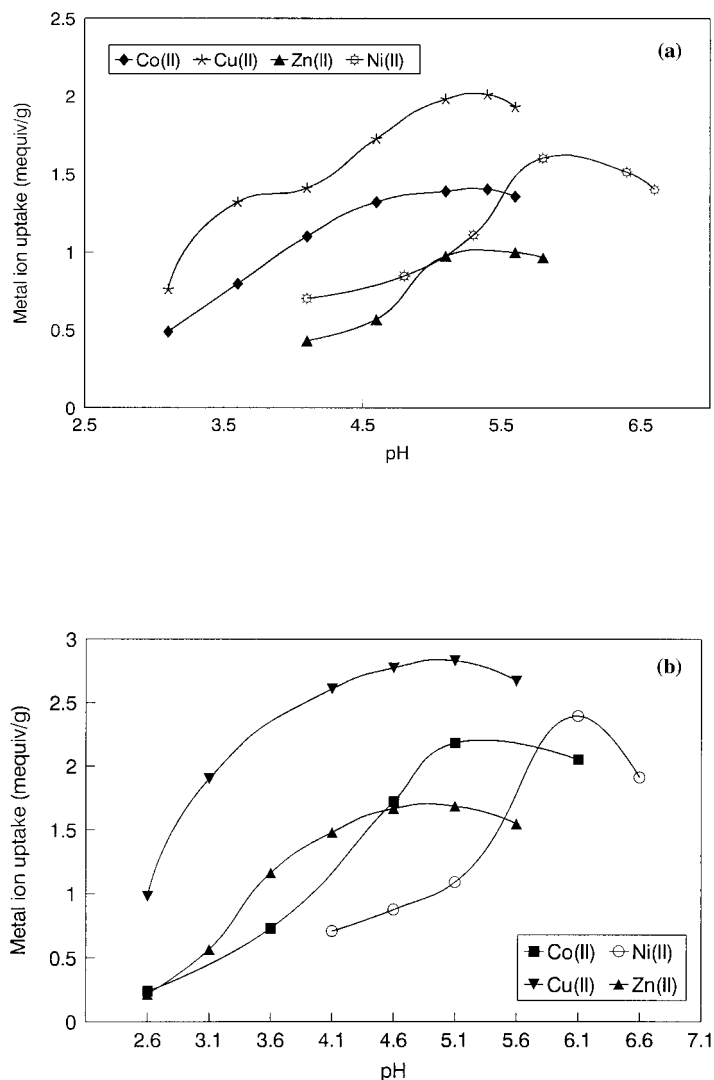
Figure 4 pH dependence on the metal ion binding of 4 mol % (a) DVB- and (b) NNMBA-crosslinked polyacrylamide-supported glycines.

the rigid and hydrophobic DVB-crosslinked system as represented in Figure 6. The polyacrylamide-supported glycine ligands showed higher swelling compared to the unfunctionalized polymer due to increase in the polarity of the system by the presence of more polar functional groups. In the metal-ion complexed state, the ligand groups are less amenable for binding with water, and, hence, the reduction in the EWC values is understandable. Moreover, metal-ion complexation acts as additional crosslinking, leading to strong chain contraction, eventually resulting in decreased swelling of the polymer.[22]

Time-course of Metal-ion Binding and Rebinding

The nature of the polymer backbone and the degree of the crosslinking has a significant effect on the kinetics of metal-ion complexation.[23] If a polymeric ligand is highly selective and has sufficient sorptive capacity but has a poor kinetics property, its application for the concentration of metal ions is proved ineffective, especially in the separation of metal ions.[24]

To follow the time-course and kinetics of Cu(II) ion binding and rebinding, 4 mol % DVB- and NNMBA-crosslinked polyacrylamide-supported glycines with a 200–400 mesh size were selected. A definite amount of the insoluble ligands was equilibrated with the Cu(II) salt solution (0.05N) in a thermostatically controlled system and the amount of the Cu(II) ion bound was followed at regular intervals of time. Figure 7 shows the time-course of Cu(II) binding by 4 mol % DVB- and NNMBA-crosslinked polyacrylamide-sup-
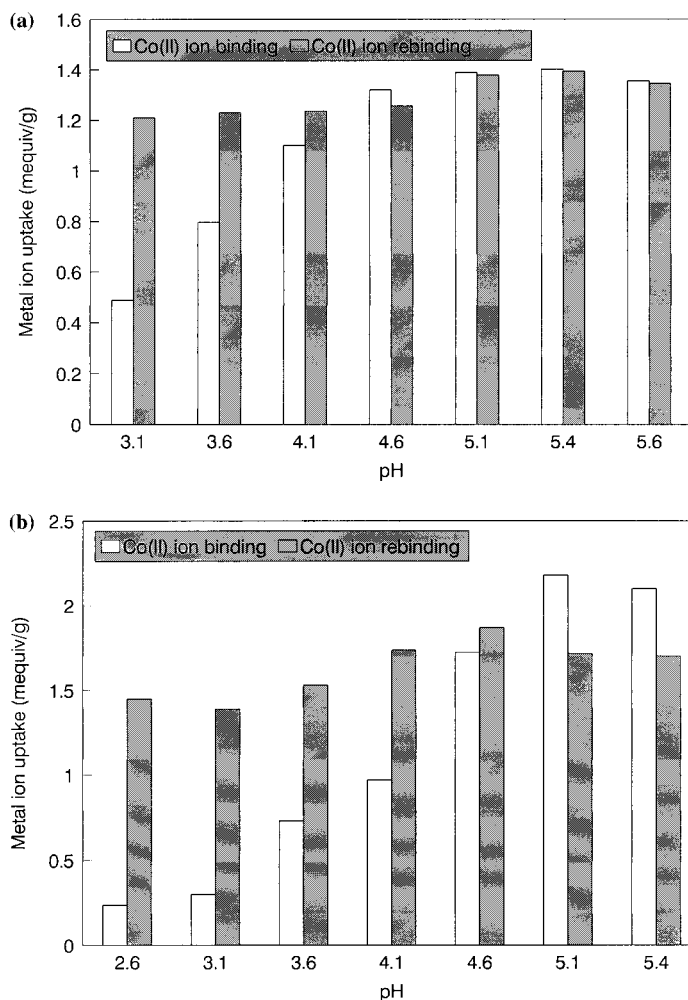
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Figure 5 pH dependence on the Cu(II) ion rebinding of 4 mol % (a) DVB-crosslinked and (b) NNMBA-crosslinked polyacrylamide-supported glycines.

ported glycines. The time required for the original Cu(II)-ion complexation by the DVB- and NNMBA-crosslinked systems was 2.5 and 2 h, respectively. During metal-ion complexation, the ligand groups in the crosslinked polymers would undergo certain rearrangement to a conformation favorable for coordination with the metal ion. The time required for the original complexation is higher for the rigid and hydrophobic DVB-crosslinked system than for the NNMBA-crosslinked system, whereas, for rebinding, it requires only 1 and 1.25 h, respectively, with a $t_{1/2}$ of 0.5 and 0.75 h for the DVB- and NNMBA-crosslinked systems. This indicates a favorable stable geometry kept in the metal-ion-desorbed polymer, resulting in its fast rebinding. The stability of this geometry is higher in the rigid DVB-crosslinked system, making the rebinding process fast.

Kinetics of Metal-ion Binding and Rebinding

The kinetics of Cu(II) ion binding by the 4 mol % DVB- and NNMBA-crosslinked systems was followed by equilibrating the polymeric ligands with Cu(II) salt solutions at 304 and 313 K for varying time intervals. The kinetic plots for the Cu(II) binding and rebinding by the 4 mol % NNMBA-crosslinked systems are given in Figures 8 (a,b), respectively.

The kinetics was found to be first order. Table III shows a comparison of the kinetic parameters calculated by the Arrhenius equation. On comparing the DVB- and NNMBA-crosslinked systems, the lower rigidity and polarity of NNMBA crosslinks makes the complexation processes easier with less activation energy for the original complexation than that of the rigid and hydropho-
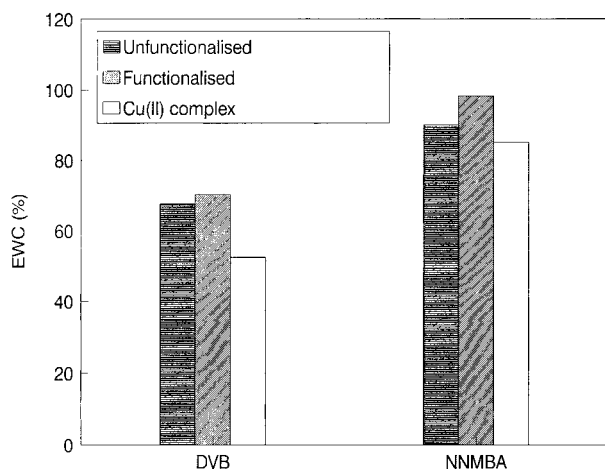
Figure 6 Swelling studies of 4 mol % DVB- and NNMBA-crosslinked polyacrylamide-supported glycines.

Figure 8 Kinetic curves for the Cu(II) binding of 4 mol % NNMBA-crosslinked polyacrylamide-supported glycines.

bic DVB-crosslinked system. The higher activation energy required for the initial complexation is for the adjustment of the macromolecular chains from their normal position for creating the required geometry for the complexed metal ions. The higher energy required in the DVB-crosslinked system is for more rearrangement of the more rigid polymer chains for the metal-ion complexation. For rebinding of the desorbed metal ion, the activation energy required for the DVB-crosslinked polyacrylamide system is much less. Compared to the NNMBA-crosslinked system, in
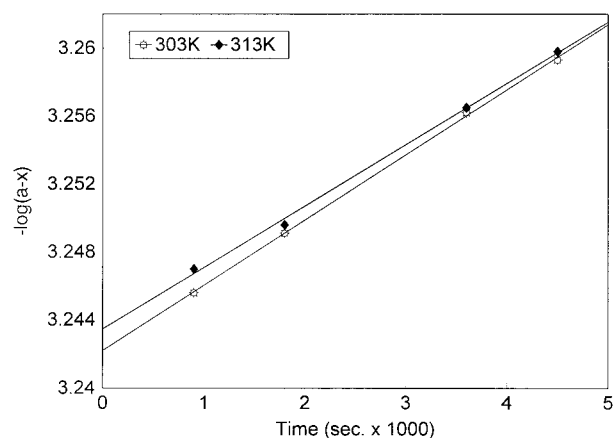
the DVB-crosslinked system, the coordination geometry left by the desorbed metal ion is more stabilized, requiring less activation energy for rebinding.

Metal-ion Selectivity Studies

To investigate the selectivity characteristics of metal-ion-desorbed polyacrylamide-supported glycine ligands, competitive rebinding experiments were carried out with pairs of metal ions. On metal-ion desorption, certain cavities are sculpt by the desorbed metal ion developed, and on re-
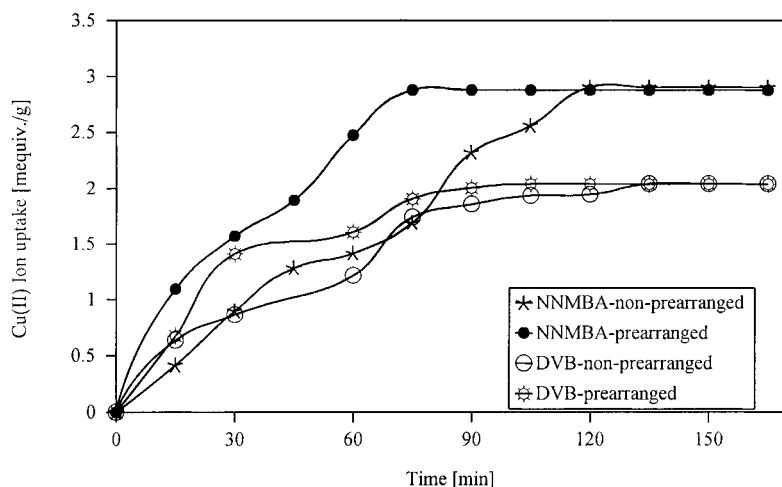

Figure 7 Time-course of Cu(II) ion binding of 4 mol % DVB- and NNMBA-crosslinked polyacrylamide-supported glycines.
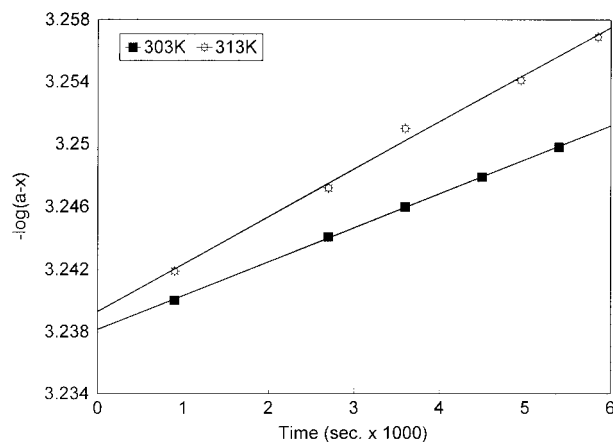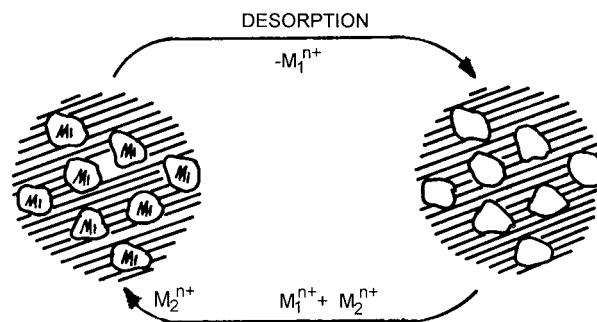
Figure 9. Kinetic curves for the Cu(II) rebinding of 4 mol % NNMBA-crosslinked Cu(II)-desorbed polyacryl-amide-supported glycines.

Scheme 3 Selective rebinding of metal ions.

binding from a mixture of metal ions, they selectively bind the desorbed metal ion from a mixture of metal ions as represented in Scheme 3. The results of the selectivity studies of the two crosslinked systems and their metal-ion-desorbed systems are given in Table IV. For the original polymer, that is, the polymer without metal-ion desorption, no selectivity was observed. The metal-ion-desorbed system remembers the coordination geometry of the desorbed metal ion. If this geometry is not disturbed during the rebinding experimental conditions, the metal-ion-desorbed systems selectively rebind the desorbed metal ions rather than other metal ions. The *memory* of the developed systems can be exemplified by comparing the selectivity characteristics of the original and the metal-ion-desorbed systems. From the results, it was found that the original poly-

meric ligand showed no selectivity toward either of the metal ions and this was a strong indication of the formation of specific cavities on metal-ion desorption. On metal-ion desorption, the cavities formed by the rigid DVB-crosslinked system were kept more stable than in the semirigid NNMBA-crosslinked system. The Cu(II)-ion-desorbed systems specifically and selectively rebind Cu(II) ions from a mixture of Cu(II) and Co(II) ions. With other pairs of metal ions, even though selectivity for the desorbed metal ions was observed, a complete separation was not possible (Fig. 10). This specific concentration of Cu(II) ions from a Cu(II)—Co(II) mixture arises from the differences in the geometries and the size differences between the two ions. Thus, specificity of these systems could be exploited for the specific concentration of metal ions which vary in their coordination behavior.

CONCLUSIONS

The foregoing investigations of the metal complexation behavior of lightly crosslinked polyacrylamide-supported glycine ligands revealed the development of a lightly crosslinked polymeric metal-ion specific system with high selectivity. The observed trend in complexation was Cu(II) > Ni(II) > Co(II) > Zn(II). The polymeric ligands and the metal complexes were characterized by their typical IR absorptions and UV-vis and EPR spectra. The morphology of the polymeric ligands changed on metal-ion complexation. The kinetics of metal-ion complexation was found to be first order. The activation energy required for rebinding was much less compared to the initial complexation. Even though the initial complexation is

Table III   Comparison of the Kinetic Parameters for the Cu(II) Binding and Rebinding by 4 mol % DVB- and NNMBA-crosslinked Polyacrylamides

Polymeric System	ΔE (kJ/mol)	ΔS (J)	A (s^{-1})
DVB			
Cu(II) binding	41.69	−202.40	1.53×10^{-2}
Cu(II) rebinding	2.81	−146.83	3.91×10^{-2}
NNMBA			
Cu(II) binding	32.20	−206.24	1.72×10^{-2}
Cu(II) rebinding	3.31	−159.38	3.30×10^{-2}

Table IV   Summary of Selectivity Studies of 4 mol % NNMBA- and DVB-crosslinked Polyacrylamide-supported Glycines (Original and Metal-ion-desorbed Systems)

Crosslinking Agent	Original Metal Ion	Rebinding Pair of Metal Ions	Metal-ion Complexation of Desorbed System from the Mixture	Original Complexation (mequiv/g)
NNMBA	Co(II)	Co(II) + Cu(II)	Co(II) = 1.78, Cu(II) = 1.19	2.19
	Ni(II)	Cu(II) + Ni(II)	Cu(II) = 1.069, Ni(II) = 1.42	2.34
	Cu(II)	Cu(II) + Co(II)	Co(II) = 0.00, Cu(II) = 2.83	2.94
	Cu(II)	Cu(II) + Ni(II)	Cu(II) = 1.89, Ni(II) = 1.03	2.94
Original polymer	Nil	Cu(II) + Co(II)	Co(II) = 0.89, Cu(II) = 2.07	—
	Nil	Cu(II) + Ni(II)	Cu(II) = 1.51, Ni(II) = 1.46	—
DVB	Co(II)	Co(II) + Cu(II)	Co(II) = 0.98, Cu(II) = 1.19	1.40
	Ni(II)	Cu(II) + Ni(II)	Cu(II) = 1.06, Ni(II) = 0.90	1.55
	Cu(II)	Cu(II) + Co(II)	Co(II) = 0.00, Cu(II) = 1.97	2.04
	Cu(II)	Cu(II) + Ni(II)	Cu(II) = 1.07, Ni(II) = 0.92	2.04
Original polymer	Nil	Cu(II) + Co(II)	Co(II) = 1.45, Cu(II) = 0.64	—
	Nil	Cu(II) + Ni(II)	Cu(II) = 1.61, Ni(II) = 0.46	—

pH-dependent, metal-ion rebinding is independent of the pH. The metal-ion-desorbed systems showed specificity and selectivity toward the desorbed metal ions. Complete separation of Cu(II) ions could be achieved with the Cu(II)-desorbed system from a mixture of copper and cobalt ions. The specificity and selectivity characteristics are higher for the rigid DVB-crosslinked system. Thus, the rigidity of the polymer support has an effect in enhancing the selectivity of the metal-ion-desorbed systems.
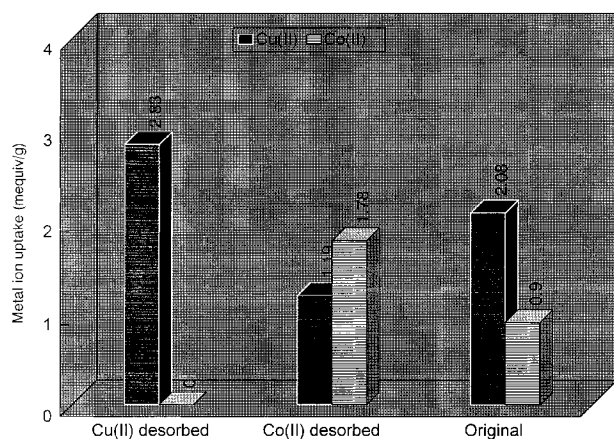

Figure 10   Selective Cu(II) ion rebinding of 4 mol % NNMBA-crosslinked Cu(II)-desorbed, Co(II)-desorbed, and original polyacrylamide-supported glycines.

REFERENCES

1. Warshawsky, A. In Synthesis and Separations Using Functional Polymers; Sherrington, D. C.; Hodge, P., Eds.; Wiley: Chichester, 1987; p 325.
2. Ciardelli, E.; Tsuchida, E. In Macromolecular Metal Complexes; Wohrle, D.; Ed.; Springer: Berlin, 1996.
3. Kaneko, M.; Tsuchida, E. Macromol Rev 1981, 16, 397.
4. Mathew, B.; Pillai, V. N. R. Polymer 1993, 34, 2650.
5. Lindsay, D.; Sherrington, D. C.; Greig, J. A.; Hancock, R. D. React Polym 1990, 12, 59.
6. Green, R. B.; Hancock, R. D. Hydrometallurgy 1981, 6, 351.
7. Tsukagoshi, K.; Yu, K. Y.; Maeda, M.; Takagi, M.; Miyajama, T. Bull Chem Soc Jpn 1995, 68, 3095.
8. Mathew, B.; Pillai, V. N. R. Angew Makromol Chem 1993, 208, 1.
9. Mathew, B.; V. Pillai, N. R. Polym. Int 1992, 28, 201.
10. Sherrington, D. C. Makromol Chem Macomol Symp 1993, 70/71, 303.
11. Froncicz, W.; Hyde, J. S. J Chem Phys 1980, 73, 3123.
12. Gersman, H. R.; Swalen, J. D. J Chem Phys 1962, 36, 3211.
13. Baranca, M.; Micerea, G.; Dessi, A.; Koztowski, H. J Chem Soc Dalton Trans 1989, 1283.

14. Kivelson, D.; Nieman, R. J Chem. Phys 1961, 35, 149.
15. Tomoi, M.; Oda, H.; Kaikuchi, H. Makromol Chem Rapid Commun 1987, 8, 339.
16. Kun, K. A.; Kunin, R. J Polym Sci Polym Chem 1968, 7, 2689.
17. Guyot, A. Pure Appl Chem 60, 365, 1988.
18. Janes, L.; Morcellet, J.; Delperte, M. M.; Morcellet, H. Eur Polym J 1992, 28, 185.
19. Lieser, K. H.; Kurbouy, M.; Thybusch, B. Angew Macromol Chem 1987, 152, 69.
20. Egawa, H.; Nonaka, T. J Appl Polym Sci 1986, 311, 677.
21. Chong, P.; Curthoys, G. J Appl Polym Sci 1979, 123, 1565.
22. Quin, F. X.; Kampt, E.; Symyth, G.; Mc Briety, V. J. Macromolecules 1988, 21, 3191.
23. Mathew, B.; Madhusudanan, P. M.; Pillai, V. N. R. J Macromol Sci Chem A 1995, 32, 1781.
24. Effendiev, A. A.; Kabanov, V. A. J Appl Polym Sci 1979, 24, 259.