Transition Metal Complexes of Polymeric Amino Ligands Derived from Triethyleneglycol Dimethacrylate Crosslinked Polyacrylamides

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SYNOPSIS

Amino functions were incorporated into triethyleneglycol dimethacrylate (TEGDMA)-crosslinked (2–20 mol %) polyacrylamides by transamidation with ethylenediamine. The complexation of these polymeric ligands with the amino function in different structural environments was investigated toward Cr(III), Mn(II), Fe(III), Cu(II), Cd(II), and Pb(II) ions. The metal ion intake decreased with the extent of the crosslinking and followed the order Cu(II) > Cr(III) > Mn(II) > Fe(III) > Pb(II) > Cd(II). The pH dependence of complexation and distribution coefficient; time course and kinetics of complexation; swelling properties of the uncomplexed and complexed resins in water; recyclability; infrared (IR) spectra; electron paramagnetic resonance; ultraviolet visibility; magnetic susceptibility; and thermogravimetric and scanning electron microscopy studies were carried out. The kinetics of complexation was found to be first order. The swelling of the complexed resins is lower than that of the uncomplexed resins. Complexation resulted in the lowering of the IR absorption of the amino ligands. The IR data of the TEGDMA-crosslinked polyacrylamide amine and the corresponding Cr(III) complex reveals that the metal is coordinated with the ligand through the amino nitrogen. The SO_4^- is also coordinated. The number of coordinated nitrogen atoms varies as the hydrophilicity and flexibility of the polymer change with the crosslinking. Thus spectral and magnetic studies suggest a distorted octahedral geometry for Cu(II) complexes, octahedral geometry of the d^3 system for Cr(III), and d^5 high-spin octahedral geometry for Fe(III) and Mn(II) complexes. The thermal stabilities of the complexed resins increase with increase in the metal content. Surface morphology of the polymeric ligand changes on complexation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The study of the interdependence of attached species' reactivity on macromolecular characteristics is immensely significant in the chemistry of functional polymers.[1-3] In a polymer-supported ligand, the ligand function is only an infinitesimal part of the three-dimensional macromolecular matrix. The characteristics of the macromolecular supports (such as the nature of the monomers, the molecular character and extent of crosslinking, separation of the ligand function from the solid polymer support, and the hydrophilic/hydrophobic balance) are decisive in dictating the reactivity/complexation ability of polymer-supported ligands.[4-8] Amino resins are widely used as complexing agents for the collection of metal ions from aqueous solution.[9-11] The hydrophilic nature of the polymer support is an important factor in the collection of metal ions from aqueous solution. This can be achieved by selecting hydrophilic monomers or by the introduction of hydrophilic crosslinking agents which contain oligoethyleneglycol units, which form the subject matter for this paper.

Table I   Preparation of TEGDMA-crosslinked Polyacrylamides

| TEGDMA (mol %)	Wt of Acrylamide (g)	Wt of TEGDMA (g)	Yield (g)
2	20.87	1.62	20.00
4	20.43	3.24	21.47
8	19.59	6.48	24.95
12	18.74	9.72	26.20
20	17.04	16.20	22.24

EXPERIMENTAL

General

All the reagents were of certified ACS grade. The purest available metal salts $K_2SO_4Cr_2(SO_4)_3 24H_2O$, $CuSO_4$, $FeCl_3$, $MnSO_4$, $Pb(NO_3)_2$, and $CdCl_2$ were used to prepare metal ion solutions. The infrared (IR) spectra were recorded on a Shimadzu 470 IR spectrophotometer; ultraviolet (UV) spectra on a Shimadzu-UV 160A UV-visible spectrophotometer; and thermogravimetric (TG) curves on a Delta-Series TGA-7 thermal analyzer at a heating rate of $20°C$ min^{-1} under nitrogen atmosphere.

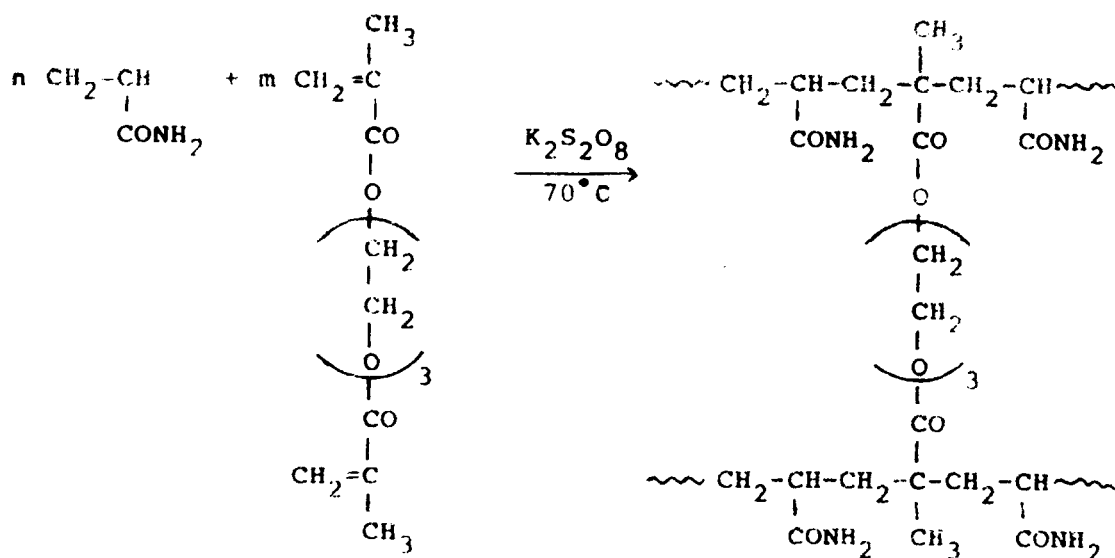### Synthesis of TEGDMA-crosslinked Polyacrylamides

For the preparation of 2 mol % triethyleneglycol dimethacrylate (TEGDMA)-crosslinked polyacrylamide, acrylamide (20.87 g in 20 mL water) and
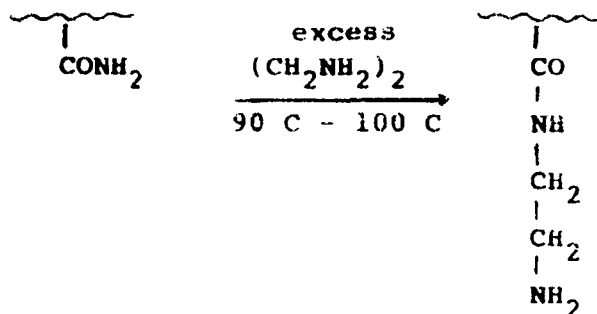
Scheme 2   Transamidation of TEGDMA-crosslinked polyacrylamides.

TEGDMA (1.716 g or 1.572 mL) were added with stirring to ethanol (100 mL) containing $K_2S_2O_8$ (100 mg), at $70°C$.[12] Heating and stirring were continued until the polymer precipitated. Water (100 mL) was added and heating continued for 1 h to complete the polymerization. The polymer was filtered, washed with water and methanol, and dried at $70°C$. Poly-acrylamides with 4, 8, 12, and 20 mol % of TEGDMA crosslinks were prepared by varying the mol % of the monomers in the feed (Table I).

Preparation of Poly(N-2-aminoethylacrylamides)

Polyacrylamide (10 g) was added in small portions to well-stirred ethylenediamine (100 mL). The mixture was refluxed at $90-100°C$ for 9 h. The reaction mixture after transamidation was poured into water (1 L) containing crushed ice. The resin was filtered and washed with NaCl solution ($1M$) until the filtrate was free from ethylenediamine, as indicated

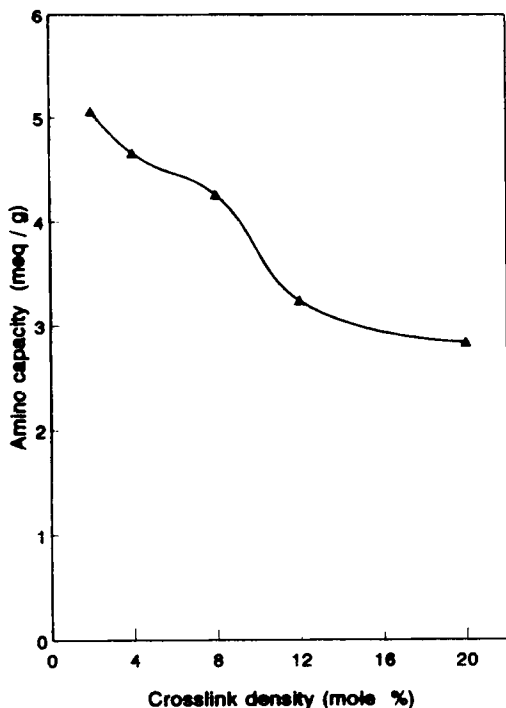**Scheme 1**   Preparation of TEGDMA-crosslinked polyacrylamides.

Figure 1 Amino capacity versus extent of TEGDMA crosslinking.

by the absence of any blue coloration with ninhydrin reagent. The gel was washed with distilled water to remove chloride ions. The resin was washed with methanol and dried in vacuum.

The amino resin (100 mg) was neutralized by equilibration with HCl ($0.2N$, 10 mL) for 9 h under stirring. The resin samples were filtered and washed. The filtrate together with washings were titrated against NaOH ($0.2N$) to a phenolphthalein end point.

Complexation of Amino Resin with Metal Ions

The complexation of the resin with varying extents of TEGDMA crosslinks was carried out toward
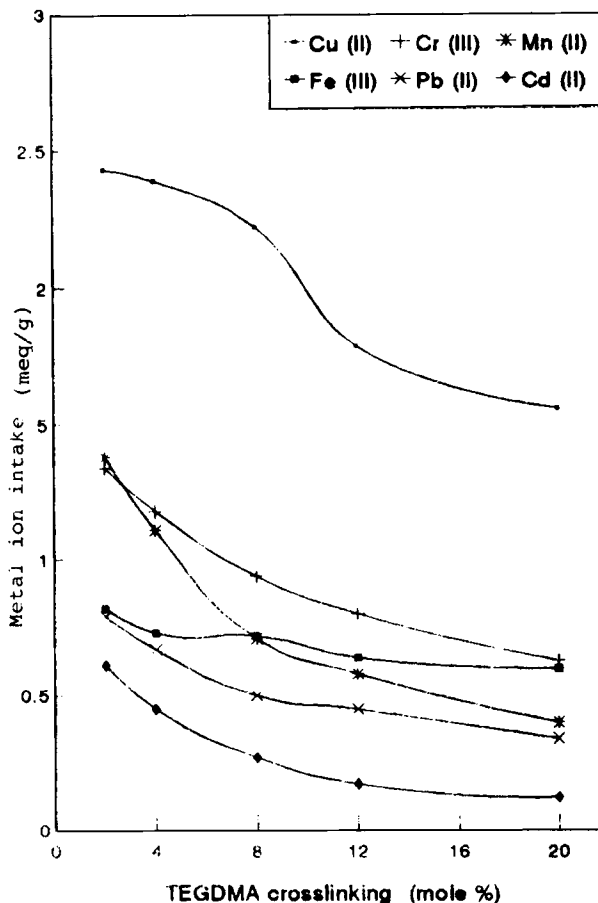

Figure 2 Metal ion intake versus extent of TEGDMA crosslinking.

Cr(III), Mn(II), Fe(III), Cu(II), Cd(II), and Pb(II) ions by the batch equilibration method. One hundred mg each of the resin samples was stirred with a definite concentration of excess metal salt solution (5 $\times 10^{-3}M$, 80 mL) for 9 h. The concentrations of the metal ions before and after complexations were estimated: Pb(II) and Cd(II) were estimated by complexometry using xylenol orange as indicator; and Cr(III), Mn(II), and Fe(III) by spectrophotometry

Table II Metal Ion Intake by TEGDMA-crosslinked Aminopolyacrylamides

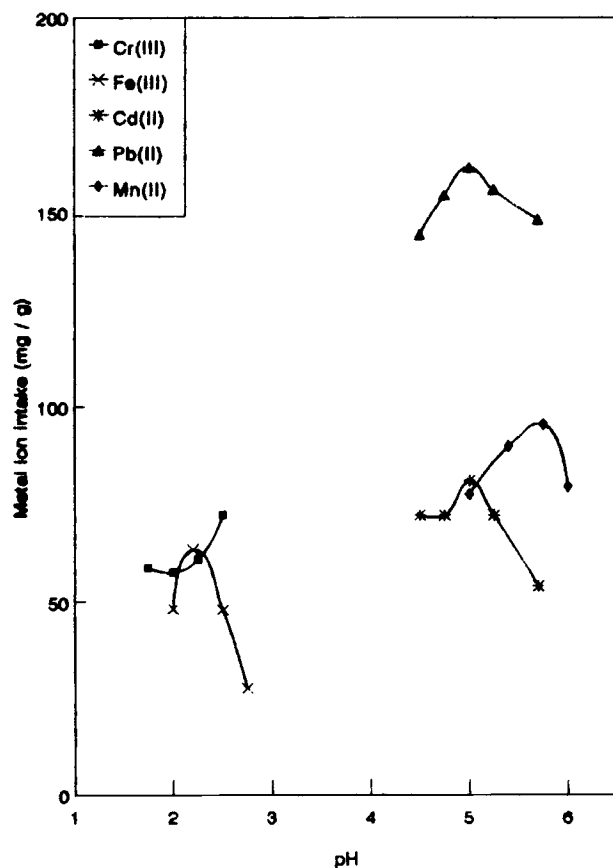| TEGDMA (mol %)	Metal Ion Intake (meq/g)					
	Cu (II)	Cr (III)	Mn (II)	Fe (III)	Pb (II)	Cd (II)
2	2.43	1.34	1.38	0.82	0.79	0.61
4	2.39	1.18	1.11	0.73	0.67	0.45
8	2.39	0.94	0.71	0.72	0.50	0.27
12	1.79	0.80	0.58	0.64	0.45	0.17
20	1.56	0.63	0.40	0.60	0.34	0.12

Figure 3 Metal intake of 2% TEGDMA-crosslinked polymeric ligand versus pH.

at 575, 544, and 299 nm respectively.[13,14] For estimation by spectrophotometric method, different solutions of $K_2SO_4Cr_2(SO_4)_324H_2O$ having concentrations 0.01, 0.25, 0.5, 0.75, and $1M$ were prepared. One mL of each of these solutions was taken for the UV-visible measurements and the corresponding absorptions were measured. A graph was plotted with concentration against absorption. From this standard curve, the concentration of unknown

chromium salt solution was obtained by measuring the absorbance. In a similar manner, standard curves for Mn(II) and Fe(III) ions were also plotted with concentration against absorption.

pH Measurements

The metal ion intake of the resin was studied as a function of pH to determine the optimum pH for maximum complexation. The pH of the metal ion solution was adjusted by adding dilute HCl or NaOH. The use of buffer solutions for the control of pH will cause undesirable results due to the coordination of the ligand species of the buffer solution.[15] The amino resin (100 mg) was added to the metal salt solution (80 mL) of definite pH and kept for complexation by stirring for 9 h. The metal ion concentrations before and after complexation were estimated.

Distribution Coefficient

The amino resin (100 mg) was equilibrated with metal solution (80 mL) of definite pH and kept for complexation by stirring for 9 h. The metal ion concentrations before and after complexation were estimated. From these two values the distribution coefficient (K_d) was calculated.[16] With 4% TEGDMA resin, the distribution coefficients were estimated toward Cr(III), Mn(II), Fe(III), Cd(II), and Pb(II) ions.

Time Course of Complexation

Batch studies were carried out with 4% TEGDMA-crosslinked amino resin to determine the optimum duration necessary for maximum complexation. One hundred sixty mL each of Cr(III), Pb(II), Cd(II), Mn(II), and Fe(III) solutions (0.2 mg/mL concentration) were mixed with amino resin (100 mg) and

Table III   pH Dependence of Complexation and Distribution Coefficient (K_d)

	Cr (III)			Mn (II)			Fe (III)			Pb (II)			Cd (II)	
pH	Metal Intake (mg/g)	K_d	pH	Metal Intake (mg/g)	K_d	pH	Metal Intake (mg/g)	K_d	pH	Metal Intake (mg/g)	K_d	pH	Metal Intake (mg/g)	K_d
1.75	56.80	256.75	5.0	77.5	1126	2.0	48.2	288	4.5	144.8	4219	45.0	72.14	432
2.0	57.52	261.09	5.4	89.92	1687	2.2	63.37	420	4.75	151.87	7121	4.75	72.14	432
2.25	57.84	263.0	5.75	95.52	2063	2.25	47.99	248	5.0	159.46	12904	5.0	81.0	521
2.5	67.84	358.39	6.0	79.52	1189	2.5	29.66	162	5.25	151.87	7607	5.25	72.14	432
									5.7	148.07	5081	5.4	54.11	284
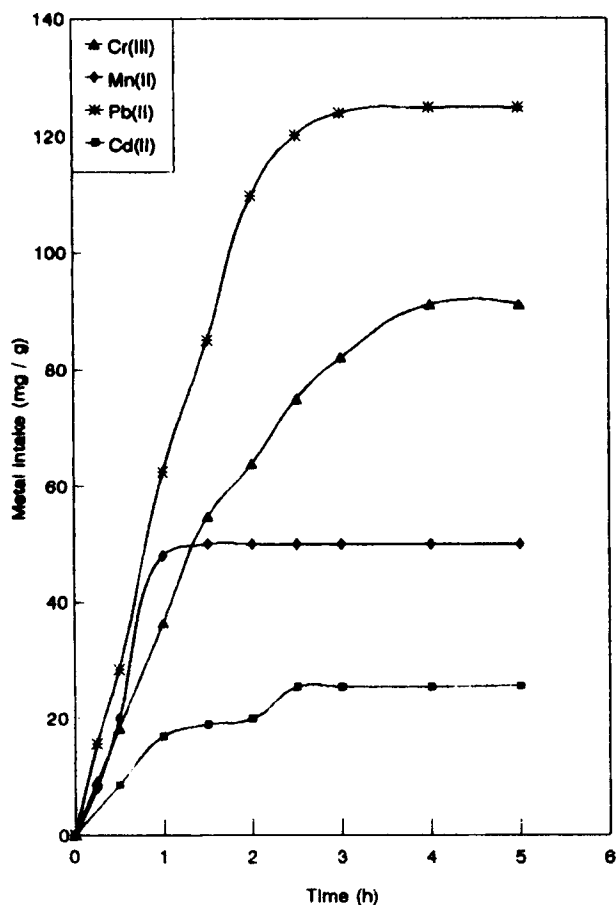
Figure 4 Time course of complexation of 4% TEGDMA-crosslinked aminopolyacrylamide.

Table IV Recyclability of 4% TEGDMA-crosslinked Polyacrylamide Amines

Metal Ions	Number of Cycles (mg/g)			
	1	2	3	4
Cu (II)	154.00	153.00	152.50	152.25
Cr (III)	69.00	68.00	67.00	66.00
Fe (III)	45.00	43.00	42.00	42.50
Mn (II)	75.00	74.75	74.50	74.00
Cd (II)	68.00	67.00	66.00	65.50
Pb (II)	164.00	163.75	163.50	163.25

Recyclability of Complexed Resin

The 4% TEGDMA-crosslinked amino complexes (200 mg) were stirred with HCl (15 mL, 2N) for desorption of Mn(II), Pb(II), and Cd(II); and with H_2SO_4 (15 mL, 2N) for desorption of Fe(III) and Cr(III) ions. The desorbed metal ions were collected and estimated. The resin after the acid treatment
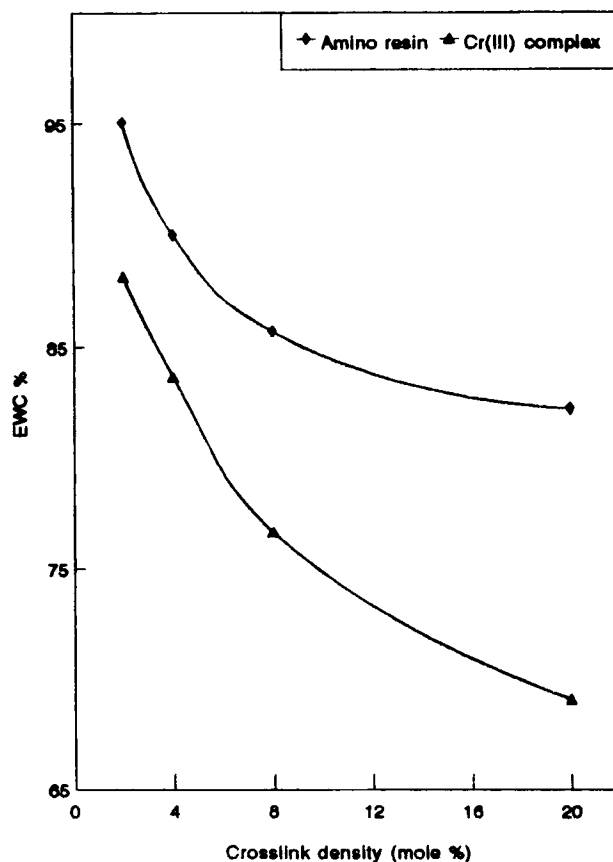
stirred. At regular intervals, aliquots were withdrawn from the test solution and estimated.

Swelling Studies

The TEGDMA-crosslinked amino resin (500 mg) was equilibrated with distilled water (30 mL) for 48 h. The swollen resins were collected by filtration, adhering traces of water were removed by pressing with filter paper, and the resin was weighed. The swollen resins were dried under vacuum for 48 h and weighed. In the case of complexed resins, 500 mg each of the samples was equilibrated with 160 mL Cr(III) salt solution containing 32 mg Cr(III) and swelling measurements were similarly carried out after washing. From the swollen and dried weights of the samples, the equilibrium water content (EWC) was calculated using the expression.

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

Figure 5 Equilibrium water content versus extent of TEGDMA crosslinking in aminopolyacrylamides and Cr(III) complexes.
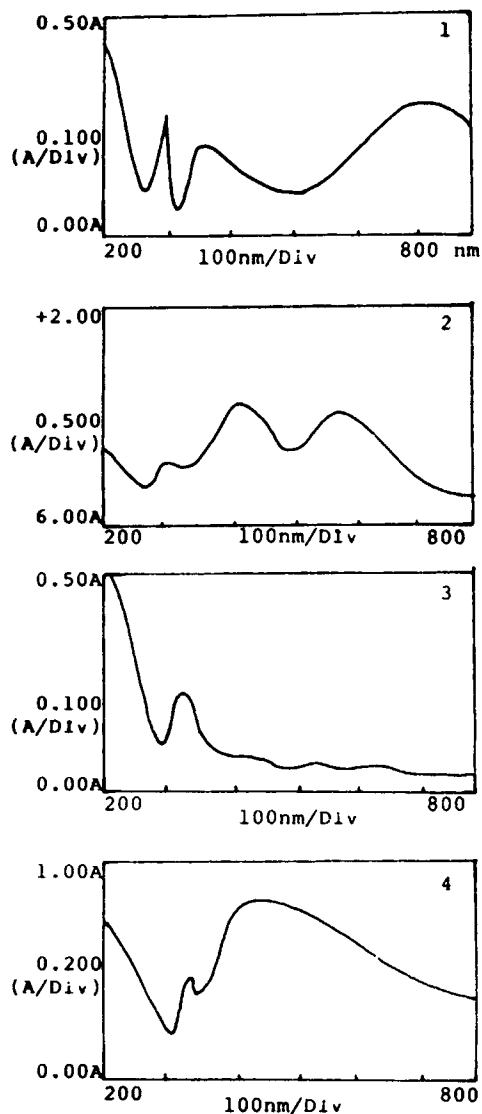
Figure 6 UV-visible spectrum of 4% TEGDMA-cross-linked polyacrylamide amino: (1) Cu(II), (2) Cr(III), (3) Fe(III), (4) Mn(II) complexes.

was neutralized with dilute NaOH, washed with distilled water, and again subjected to complexation.

RESULTS AND DISCUSSION

Polyacrylamides with 2 to 20 mol % of TEGDMA crosslinks were prepared by the solution polymerization of the monomers in ethanol at 70°C using potassium persulphate as the initiator (Scheme 1). The compositions of the monomers and crosslinking agent used for polymerization are given in Table I.
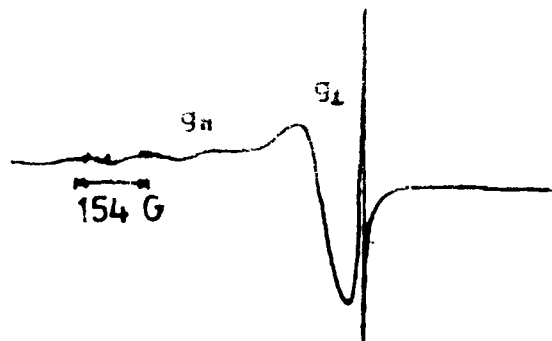

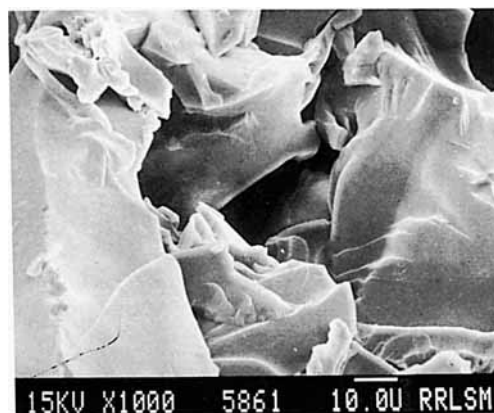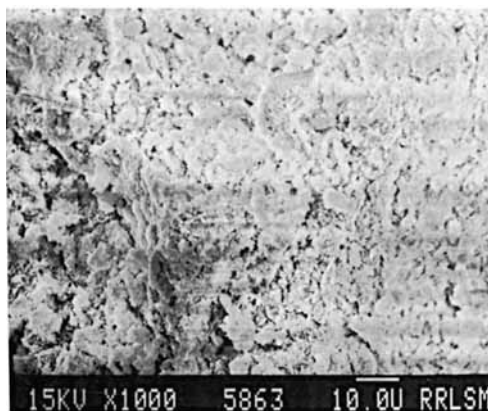**Figure 7** Epr spectrum of Cu(II) complex of amino polyacrylamide with 8% TEGDMA crosslinking.

Preparation of Poly(N-2-aminoethylacrylamides)

Amino functions were incorporated into TEGDMA-crosslinked polyacrylamides by transamidation with excess ethylenediamine at 100°C (Scheme 2).

(a)

(b)

Figure 8 Scanning electron patterns of (a) 2% TEGDMA-crosslinked polyacrylamide amine, (b) corresponding Cu(II) complex.
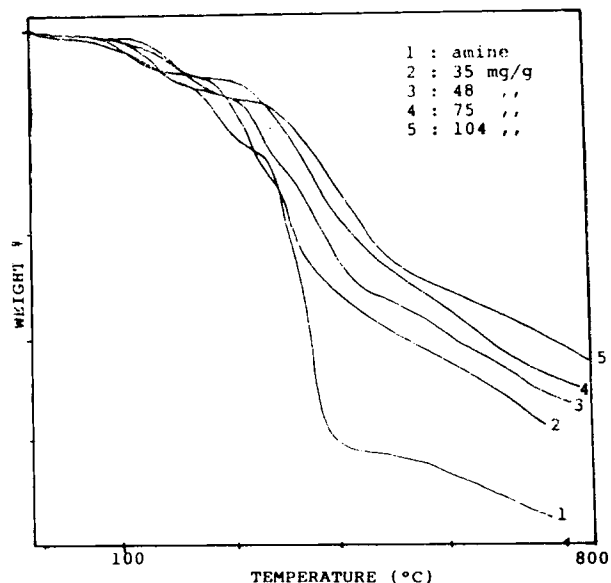
Figure 9 TG curves of 2% TEGDMA-crosslinked amino polyacrylamide and Cr(III) complexes with varying amounts of complexed metal ions.

The amino functions were detected by the semiquantitative ninhydrin reaction; the resins developed a deep blue color with ninhydrin reagent.[17] The amino functions were estimated by equilibrating a definite amount of the resin with a known concentration of excess hydrochloric acid and estimating the unreacted acid. The variation of amino capacity with crosslinking in the case of the different resins is represented in Figure 1. With increasing crosslinking the amino capacity decreases. Thus the 2% crosslinked resin has the maximum capacity of 5.06 mmol/g, and the 20% crosslinked system has the minimum (2.84 mmol/g). The reduction in capacity with increased crosslinking is expected because of the reduced availability of the reactive sites buried within the crosslinks for transamidation.[18]

Polymeric systems with oligoethyleneglycol crosslinking units show a higher capacity toward amino functions.[19] This could arise from the favorable microenvironment created by the polar and flexible oligoethyleneglycol units in the crosslinking agent for the polar transamidation reaction. The reduction in capacity with increasing crosslinking is also less in this case.

Complexation of Aminopolyacrylamides. Effect of the Extent of TEGDMA Crosslinking

The complexation of aminated derivatives of polyacrylamide with the amino functions in different structural environments was investigated toward Cr(III), Mn(II), Fe(III), Cu(II), Cd(II), and Pb(II) by the batch equilibration method. The metal ion intake by the different resins is given in Table II.

The metal ion intake decreases with increased crosslinking. As in the case of amino capacity, the metal ion intake is maximum for the 2% crosslinked system and minimum for the 20% (Fig. 2).

pH Dependence of Complexation and Distribution Coefficient

In order to investigate the optimum pH for maximum complexation, batch studies were carried out at varying pH. The pH dependence of complexation was studied for the regions above and below the natural pH of the metal salts solution in aqueous medium. In all cases the upper limit was just below the precipitation. The optimum pH for complexation of different metal ions were 5 for Cu(II), Cd(II), and Pb(II); 5.75 for Mn(II); 2.2 for Fe(III); and 2.5 for Cr(III) (Fig. 3 and Table III). The distribution coefficient (K_d) at different pH were calculated, using the equation

Table V Phenomenological Data of the Thermal Decomposition of TEGDMA-crosslinked Polyacrylamides and Complexes with Varying Extents of Cr (III)

Crosslinking	Resin/Complex	Decomposition Temperature in TG Curves (K)		Peak Temperature in DTG (K)	Mass Loss (%)
		T_i	T_f	T_s	
TEGDMA	Amine (mg/g)	558	843	668	30
	(1) 35	593	782	666	25
	(2) 48	578	763	671	22
	(3) 75	555	702	695	21
	(4) 104	612	675	658	20

Table VI   Kinetic Data on the Thermal Decomposition of 2% TEGDMA-crosslinked
Aminopolyacrylamide with Varying Extents of Complexed Cr (III) Ions

Resin/Complex	Equation 1				Equation 2			
	E (kJ/mole)	A (s^{-1})	ΔS (J)	γ	E (kJ/mole)	A (s^{-1})	ΔS (J)	γ
Amine	72.75	3.16	−259.44	0.9955	73.16	5.71	−254.53	0.9995
(1) 35 mg/g	81.27	9.42	−248.75	0.9984	81.69	17.10	−244.95	0.9982
(2) 48 mg/g	95.29	1.73×10^2	−166.84	0.9933	95.66	3.09×10^2	−220.99	0.9933
(3) 75 mg/g	98.55	4.84×10^2	−217.30	0.9913	98.99	8.77×10^2	−212.36	0.9914
(4) 104 mg/g	109.44	3.30×10^3	−201.28	0.9973	109.87	5.97×10^3	−196.36	0.9973

$$K_d = \frac{\text{Wt. of metal ion on the resin (mg)} / \text{Wt. of the resin (g)}}{\text{Wt. of metal ion in solution (mg)} / \text{Volume of solution (cm}^3)}$$

The K_d values at maximum pH were in the order Pb(II) > Mn(II) > Fe(III) > Cd(II) > Cr(III). The distribution coefficient gives the ratio of the amount of metal ion adsorbed by 1 g of the resin to the amount of metal ion remained in 1 cm³ of the solution. The K_d value of Pb(II) is very high compared to those of other metal ions. Hence Pb(II) is preferentially complexed by the resin in the presence of other metal ions and can be pre-concentrated. The metal ion intake and distribution coefficients are highly pH-dependent.

Time Course and Kinetics of Complexation

In order to follow the relative performance of the resin, the time course of the complexation of 4% TEGDMA-crosslinked amino resin with Pb(II), Cd(II), Fe(III), Cr(III), and Mn(II) were followed by the change in concentration of the metal salt solution at regular intervals (Fig. 4). The Mn(II) complexation was complete in 1.5 h, Cd(II) required 2.5 h, Pb(II) 3 h, and Cr(III) 4 h. The hydrophilic and flexible nature of the polymer support makes the complexation much easier.

The complexation of a crosslinked polymer-supported ligand with metal ions in aqueous medium is heterogeneous in nature, since it is a solid–solution reaction. The kinetics of Cr(III) complexation by 2% TEGDMA-crosslinked aminated derivatives of polyacrylamide were followed at 301 K and 311 K at regular intervals. The rates of reaction fit into the first-order kinetics. The plot of $-\log(a - x)$ against time t is a straight line. The rate constants at the higher temperature were found to be higher than those at the lower temperature. The kinetic

parameters of complexation were calculated from the Arrehenius equation:

$$\log k = \log A - E/RT$$

The entropy of activation was calculated using the equation:

$$e^{\Delta S^*/R} = Ah/KT$$

The kinetic parameters are: Activation energy $(E) = 58.429$ kJ/mole; Arrhenius parameter $(A) = 2.02 \times 10^4 \text{ J}^{-1}$; and entropy of activation $(\Delta S^*) = -2.36 \text{ s}^{-1}$.

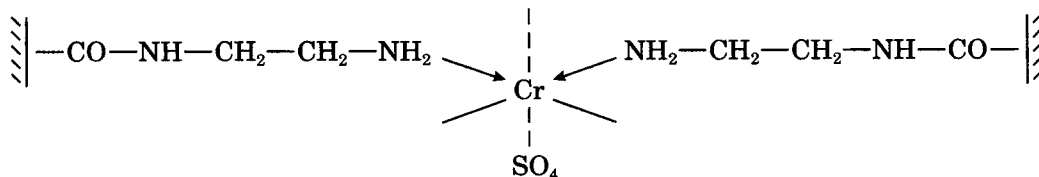## Recyclability of the Complexed Resins

The possibility of recycling the various complexes was investigated in the case of 4% TEGDMA-crosslinked resin (Table IV). Thus the complexed Mn(II), Pb(II), Cd(II), and Cu(II) can be desorbed using 2N HCl, and Cr(III), and Fe(III) by 2N H_2SO_4. On recycling, the desorbed resin complexed almost the same amount of metal ion even after four cycles. This points to the possibility of reusing the complexed resin several times.

Swelling Characteristics

The introduction of a hydrophilic crosslinking agent into a polymer system increases the complexation of the polymer in a polar environment over the same system with a hydrophobic crosslinking agent.[20] The EWC of the various amino resins and their Cr(III) complexes with the same amount of Cr(III) (64 mg/ g) were followed. The EWCs of the uncomplexed resins are in the range 82% to 95% (Fig. 5). The hydrophilic nature of the crosslinks made the solvation much easier, resulting in increased swelling in water. The reduction in swelling with increasing

crosslinking is much less because of the presence of increasing amounts of the hydrophilic and flexible TEGDMA crosslinks.

The $EWCs$ of complexed resins (88% to 77%) are lower than those of the corresponding uncomplexed resins (95% to 82%). This reduction arises from the introduction of additional crosslinks on complexation with metal ions.[21] In the complexation of polymeric ligands with metal ions, the macromolecular chains coil more tightly by crosslinking with metal ions. This reduction of $EWCs$ is higher in low crosslinked systems. In lightly crosslinked systems, the polymer chain can undergo extensive swelling from the increased diffusion of water molecules into the loose networks. The complexation of the amino groups in this highly swollen polymer-support will result in contraction, with low water uptake. With increased crosslinking the presence of consecutive crosslinking points makes the diffusion difficult, thereby decreasing the swelling. Hence the reduction in swelling by complexation is less in the highly crosslinked systems.

IR Spectra

The IR spectra of the crosslinked polyacrylamide showed the characteristic absorption peaks of amide, ester, and ether, at 3400 cm^{-1} (NH_2), 1680 cm^{-1} (amide), and 1700 cm^{-1}. Transamidation resulted in the development of a secondary amide group at 1445 cm^{-1}. The amino group absorption at 3500 cm^{-1} appeared much broader by extensive hydrogen bonding. In the Cr(III) complex, the absorption appeared sharp at 3500 cm^{-1} and lowered to 3450 cm^{-1} on complexation. The NH stretching frequencies of Cu(II) complexes are lower than those of free amines.[22] The peak at 1110 cm^{-1} is intense after complexation because of the coordinated sulphate in the Cr(III) complex.[23] The IR data of the TEGDMA-crosslinked polyacrylamide amine and the corresponding Cr(III) complex reveal that the metal is coordinated with the ligand through the amino nitrogen. The SO_4^{-} is also coordinated. So the possible structure of the complex is

The number of coordinated nitrogen atoms varies as the hydrophilicity and the flexibility of the polymer changes with the crosslinking.

Electronic Spectra

The UV-visible spectral studies of 4% TEGDMA-complexes were performed (Fig. 6). Cu(II) complex showed λ max at 13,793 cm^{-1} corresponding to $^2B_{1g} \rightarrow {}^2E_g$ transition in distorted octahedral geometry.[24] Cr(III), Fe(III), and Mn(II) complexes showed transitions of octahedral geometry, with absorption maxima at 17,094 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{2g}$) (F) and 23,829 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{1g}$) (F) for Cr(III) complex; 15,552 cm^{-1} ($^6A_{1g} \rightarrow {}^4T_{1g}$) (G), 17,213 cm^{-1} ($^6A_{1g} \rightarrow {}^4T_{2g}$) (G), and 21,978 cm^{-1} ($^6A_{1g} \rightarrow {}^4E_g$) (G) for Fe(III) complex; and a broad band between 20,000–25,000 cm^{-1} which is supposed to be the combination of $^6A_{1g} \rightarrow {}^4T_{2g}$ (G), and $^6A_{1g} \rightarrow {}^4E_g$ (G) for Mn(II) complex.[25]

EPR Spectrum

The electron paramagnetic resonance (EPR) spectrum of the Cu(II) complex of amino polyacrylamide with 8% TEGDMA crosslinking is given in Figure 7. The EPR parameters suggested the distorted octahedral geometry for the Cu(II) complex[26] ($g_{||}$ = 2.2694, $g_{\perp}$ = 2.0584, $A_{||}$ = 154, $A_{\perp}$ = 35). The α^2Cu which is a measure of the inplane σ bonding of the Cu—N bond was calculated using the expression given by Kivelson and Neiman and was found to be 0.7593.[27] This, together with the value of $g_{||}$ < 2.3, suggests the covalent nature of the Cu—N bond.

Magnetic Moment

The magnetic susceptibilities of 2% TEGDMA-crosslinked polyacrylamide-supported amino complexes were determined by the Gouy method using Hg[Co(NCS)$_4$] as the standard. The diamagnetic corrections were computed using Pascal's constants.[28] The Cu(II) complex exhibits an effective magnetic moment of 1.76 BM. The magnetic moment of single Cu(II) complexes generally occur in the range 1.75–2.2 BM regardless of the stereochemistry.[29] For Cr(III) complex the observed magnetic moment is 4.00 BM, which is also in agreement with the spin-only magnetic moment of the d^3 spin-

free arrangement.[30] The room-temperature magnetic moments 5.47 BM and 4.39 BM for Fe(III) and Mn(II) complexes, respectively, are slightly less than the theoretical value of 5.92 BM for d^5 high-spin octahedral complexes.[31] This may be because of the distortions in the geometry of these complexes due to the microenvironments in the polymer backbone.

Scanning Electron Microscopy

The change in morphology of polymeric ligands with complexation was investigated by scanning electron microscopy. The scanning electron micrographs (SEM) of the 2% crosslinked amino resin and the corresponding Cr(III) complex are given in Figure 8. The SEM of the uncomplexed amino resins have smooth surfaces with few of the voids and channels which are responsible for the swelling and reactivity of the active sites buried within the polymer matrix. In the Cr(III) complexed resin, the morphology is entirely different from that in the corresponding uncomplexed amino ligand. The voids disappeared on complexation due to the contraction of the polymer matrix by metal complexation. The surface becomes rough, resulting from the rearrangement of the already-orderly macromolecular chains for complexation.

Thermogravimetric Studies

The thermogravimetric (TG) curves of the 2% TEGDMA-crosslinked amino polyacrylamides and Cr(III) complexes with varying amounts of complexed metal ions are given in Figure 9.

With increasing metal content, the thermal stability of the polymer increases. The curve showed three stages of decomposition. The first decomposition stage is due to the removal of adsorbed/coordinated solvent molecules. The second stage is the decomposition of amides and noncoordinated amino groups in the polymer matrix. The third stage is the major decomposition stage and is used for kinetic analysis of the TG curves. The phenomenological data for this stage are given in Table V. The differential[32] and approximation methods[33] [eqs. (1) and (2), below] are used for the kinetic analysis of the TG curves by the least square method:

$$\log g(\alpha)/T^2 = \log[AR/\phi E(1 - 2RT/E)]$$
$$- E/2.303RT \quad (1)$$

$$\log g(\alpha)/T^{1.921503} = \log[AE/\phi R] + 8.68703$$
$$- 1.921503 \log E - 0.120394(E/T) \quad (2)$$

The kinetic data and the correlation coefficient (γ) of the thermal decomposition are given in Table VI. With increasing Cr(III) complexation, the thermal stability gradually increases. Thus the fully Cr(III)-complexed system has the highest activation energy for decomposition. The increased thermal stabilities of the complexes arise from the formation of stable ring-structured complexes.[34] The change in thermal stabilities of metal complexes with the variables of the polymer-support have been reported.[35] The entropies of decomposition of the complexes are more positive than the uncomplexed system. This results from the distortion of the polymer chains from their normal position on complexation.

CONCLUSION

The foregoing investigations of the complexation and characterization of the polyacrylamide–amine–metal complexes reveal the dependence of the extent of TEGDMA crosslinking on the metal ion intake and physicochemical properties of the derived metal complexes. The metal ion intake decreases with increased crosslinking. The complexed resins can be recycled up to four times. The swelling characteristics of the complexes are lower than the amino resins and the swelling decreases with increased crosslinking. The spectral and magnetic studies suggest distorted octahedral geometry with one unpaired electron for Cu(II) complexes, three electrons for Cr(III) complexes, and d^5 high-spin octahedral geometry for Fe(III) and Mn(II) complexes. The thermal stabilities of the Cr(III) complexes vary with increasing metal content in the polymer matrix. The scanning electron micrograph of the 2% TEGDMA-crosslinked amino resin shows a smooth surface with voids and channels. The corresponding Cr(III) complex has a comparatively rough surface.

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