

Metal complexation of crosslinked polyacrylamide-supported dithiocarbamates: Effect of the molecular character and extent of crosslinking on complexation

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Abstract. Dithiocarbamate functions were incorporated into different polyacrylamide matrices crosslinked with a flexible and hydrophilic crosslinking agent, tetraethyleneglycol diacrylate (TEGDA), and their complexation behaviours were investigated. Crosslinked polyacrylamides with varying extents of the tetrafunctional TEGDA crosslinks were prepared by free radical solution polymerization at 60°C using potassium persulphate as initiator in ethanol. The dithiocarbamate functionality was incorporated into these polyacrylamides by a two-step polymer-analogous reaction involving (i) *trans*-amidation with ethylenediamine and (ii) dithiocarbamylation of the aminopolyacrylamide with carbon disulphide and alkali. The complexations of dithiocarbamate with Cu(II), Ni(II), Zn(II), Co(II) and Hg(II) ions were followed under different conditions. The metal ion intake varied with the extent of the crosslinking agent and the observed trend in complexation is Hg(II) > Cu(II) > Zn(II) > Co(II) > Ni(II). The time-course of complexation, the possibility of recycling, swelling characteristics, and spectral and thermal analyses were carried out. The thermal stability increases upon complexation with metal ions.

Keywords. Polymer-metal complexes; crosslinked polyacrylamide support; dithiocarbamate metal complexes; thermal stability.

1. Introduction

The study of the metal complexation behaviour of polymeric ligands is of great significance in various branches of chemistry (Kaneko and Tsuchida 1981; Warshawsky 1988). In a polymer ligand, the structural environment of the ligand function is one of the key factors directing the complexation with metal ions. The structural factors characteristic of the macromolecular matrix like the nature and extent of crosslinking, hydrophilic/hydrophobic balance and the spacer between the ligand function and the polymer matrix influenced the complexation behaviour of polymeric ligands (Drago and Gaul 1979; Nishide *et al* 1982; Hirotsu *et al* 1987).

The progress made in the synthesis of polymers with widely varying properties permits one to obtain macromolecular systems with well-defined characteristics. The nature of the monomer, the chemical nature and extent of crosslinking agents, different experimental conditions of polymerisation and the method of polymerisation can be controlled to produce polymers of definite functional morphology and physicochemical

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characteristics (Egawa *et al* 1988). Chemical reactions for the introduction of functional groups in polymers and the functional group conversion in polymers are also dependent on the nature of the polymer backbone, molecular character and the extent of crosslinking, pore size and pore volume of the polymer particles and the separation of the functional groups from the polymer support (Sreekumar and Pillai 1987). Interdependence of the reactivity of functional groups and the fine molecular structure of polymers has been a subject of contemporary interest in the chemistry of functional and speciality polymers (Sreekumar and Pillai 1989; Devaky *et al* 1990; George and Pillai 1990; Jayakumari and Pillai 1991).

One of the most important and thoroughly studied classes of sulphur-containing ligands are dithiocarbamates (Coucovanis 1970, 1979). They have been used extensively in analytical and biological fields for the complexation of heavy metal ions (Magee and Hill 1985; Kojima *et al* 1987). The present paper describes the complexation behaviour of dithiocarbamate ligands supported on polyacrylamides crosslinked with varying extents of hydrophilic and flexible tetraethyleneglycol diacrylate (TEGDA) crosslinks. The complexations of the ligand functions supported on different structural environments, time-course of complexation, the swelling nature, recyclability of the complexed resin, spectral characterisation of the complexes and thermogravimetric studies are reported here.

2. Experimental

2.1 General

All the reagents were of certified ACS reagent grade. The purest available metal salts were used to prepare metal ion solutions. The IR spectra were recorded on a Perkin Elmer-983 IR Spectrophotometer and TG curves on a Delta Series TGA-7 Thermal Analyser at a heating rate of $20^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere. The scanning electron micrographs of the uncomplexed and complexed resins were recorded on a Cambridge Stereo Scan S-180 Scanning Electron Microscope.

2.2 Synthesis of tetraethyleneglycol diacrylate (TEGDA)-crosslinked polyacrylamides

For the preparation of the 2% crosslinked polyacrylamide, acrylamide (13.92 g) and tetraethyleneglycol diacrylate (1.21 g) were dissolved in ethanol (100 ml) at 70°C . This solution of the monomer mixture was purged with nitrogen gas for 10 min to remove the dissolved oxygen. Potassium persulphate (100 mg) was dissolved in water (5 ml) and added to the monomer mixture slowly with stirring. The mixture was heated with stirring on a water bath till the polymer got precipitated. Water (75 ml) was added and heated for 20 min at 80°C . The lumps were powdered, filtered, washed with water, ethanol and methanol and dried in an oven at 80°C . The relative amounts of the monomers for the different extents of crosslinking and the yields of the crosslinked polymers under these conditions are presented in table 1. The polymers could also be prepared in more or less the same yields on direct polymerization of the monomer mixture without degassing.

Table 1. Preparation of TEGDA-crosslinked polyacrylamides.

TEGDA (mole%)	Weight of monomers		yield (g)
	Acrylamide (g)	TEGDA (g)	
2	14.00	1.21	14.80
4	13.60	2.42	15.80
8	13.10	4.84	17.40
12	12.50	7.26	18.00
20	11.40	12.00	20.10

2.3 Transamidation of TEGDA-crosslinked polyacrylamides to the poly(*N*-2-aminoethylacrylamide)s

Ethylenediamine (100 ml) was added to crosslinked polyacrylamide (10 g) with stirring. The mixture was heated with stirring for 9 h at 100°C. This was poured into water (1 l) containing crushed ice. The resin was filtered, washed with NaCl solution (0.1 M) until the filtrate was free from ethylenediamine as indicated by the absence of any blue colouration with ninhydrin reagent. The gel was washed with water to remove NaCl and with methanol and dried at 70°C.

2.4 Determination of resin amine content

For the determination of the amino content of the different resins, 100 mg each of the resins were equilibrated with HCl (0.2 N, 10 ml) for 24 h with magnetic stirring. The resin samples were filtered, washed with distilled water to remove unreacted HCl and the filtrate was titrated with NaOH (0.2 N) to a phenolphthalein end point.

2.5 Dithiocarbamylation of poly(*N*-2-aminoethylacrylamide)s

The TEGDA-crosslinked amino resin (10 g) was suspended in a five-fold molar excess of carbondisulphide. Sodium hydroxide (five-fold excess in 50 ml water) was added and the whole shaken in a mechanical shaker for 9 h. The resin was collected by filtration, washed with water till the washings were free from sodium hydroxide, and finally washed with methanol and dried in vacuum.

2.6 Complexation of metal ions with dithiocarbamate resins

The complexation of the dithiocarbamate resins with varying amounts of TEGDA crosslinks was investigated towards Cu(II), Ni(II), Zn(II), Co(II) and Hg(II) ions by the batch equilibration method. 200 mg each of the resin samples were stirred with known concentrations (0.01 M) of excess metal salt solution for 24 h. The complexed resins were collected by filtration and washed with distilled water to remove uncomplexed metal ions. The concentrations of the uncomplexed metal ions were estimated by volumetric methods: Cu(II) by iodometry, Ni(II) and Zn(II) by

complexometry and Co(II) and Hg(II) by back titration using complexometric methods.

2.7 Time-course of complexation

To follow the time-dependence of metal ion intake by the resin, batch studies were carried out with 500 mg of 4% crosslinked dithiocarbamate resin. Metal salt solution (0.01 M, 100 ml) was added to the dithiocarbamate resin, which was stirred immediately after the addition. At regular intervals, a 2 ml solution was withdrawn from the test solution and estimated as detailed earlier.

2.8 Swelling studies of the resins and resin-Cu(II) complexes

500 mg each of the different resins were equilibrated with 30 ml distilled water for four days. The swollen resins were collected by filtration, adhering traces of water were removed by pressing with filter paper and the residue was weighed. The swollen resins were dried in vacuum for 24 h and again weighed. For the swelling studies of the Cu(II) complexes, 500 mg each of the resin were equilibrated with 30 ml Cu(II) salt solution containing 55 mg Cu(II) and swelling measurements were similarly carried out. From the swollen and dried weights of the samples, the equilibrium water content (EWC) was calculated using the expression

$$\text{EWC} = \frac{(\text{wt. of wet resin} - \text{wt. of dry resin})}{\text{wt. of wet resin}} \times 100$$

2.9 Recyclability of complexed resins

500 mg of the Cu(II) complexed dithiocarbamate resin (4% crosslinked) were stirred with HNO₃ (3 N, 15 ml) for 2 h. The desorbed Cu(II) was collected by washing with distilled water and estimated after neutralization. The resin left after the treatment with acid was washed with sodium hydroxide and distilled water and again subjected to dithiocarbamylation and complexation.

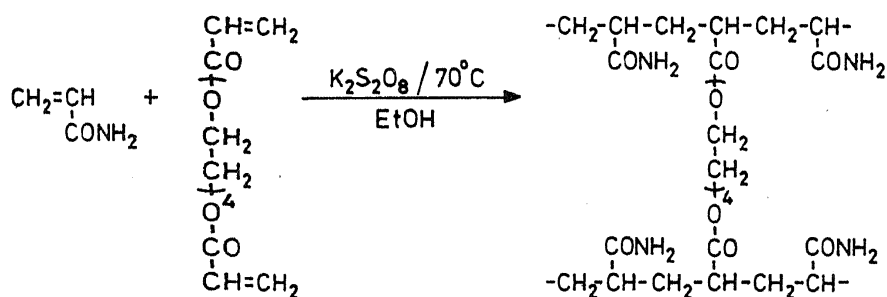
3. Results and discussion

3.1 Synthesis of TEGDA-crosslinked polyacrylamides

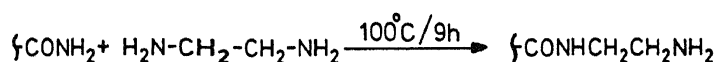
Polyacrylamides with 2–20 mole% of tetraethyleneglycoldiacrylate (TEGDA)-crosslinks were prepared by free-radical solution polymerization. The polymerization reaction was carried out in ethanol at 60°C using potassium persulphate as initiator. The polymerization reaction is depicted in scheme 1. When the mole percentages of the hydrophilic and flexible TEGDA-crosslinks increased from 2 to 20 the rigidity of the gels increased and the extent of swelling in water also varied.

3.2 Preparation of poly(N-2-aminoethylacrylamide)s

Polyacrylamides with varying extents of TEGDA-crosslinks were converted to the corresponding poly(N-2-aminoethylacrylamide)s by transamidation with ethylene-



Scheme 1. Preparation of TEGDA-crosslinked polyacrylamides.



Scheme 2. Transamidation of TEGDA-crosslinked polyacrylamides with ethylenediamine.

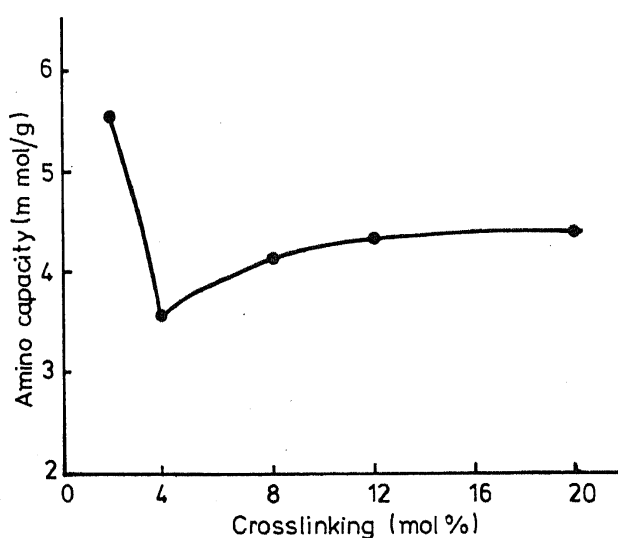


Figure 1. Dependence of transamidation on the extent of TEGDA-crosslinking.

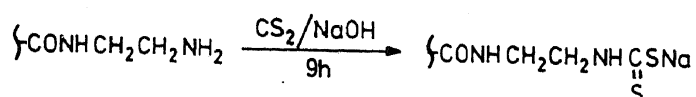
diamine at 100°C (scheme 2). Ethylenediamine itself was used as the solvent. With diamines, the possibility of multi amidation leads to additional crosslinking which lowers the swelling of the resins.

The amino functions were detected by the semiquantitative ninhydrin reaction (Spackman and Stein 1958) and estimated by equilibrating definite amounts of the amino resins with 0.2N HCl and estimating the unreacted acid by alkali titration. The variation of the amino capacities of the different resins with the extent of crosslinking is depicted in figure 1.

The amino capacity of the 2% crosslinked amino resin is higher, decreasing at 4% crosslinking and increasing further with the extent of the crosslinking agent. Generally the capacity decreases with the extent of the crosslinking agent because of the reduced availability of the reactive sites for the low molecular weight reagents. But for the oligoethyleneglycol diacrylate-crosslinked systems, the possibility of cleavage of the ester groups of the crosslinking agent in basic medium is reported (Egawa *et al* 1988). This results in the introduction of additional amino groups. Thus the increasing amino capacities after the 4% crosslinking arises from the aminolysis of the crosslinking ester linkages.

3.3 Preparation of poly(*N*-2-dithiocarbamatoethylacrylamide)s

Amino polyacrylamides with varying extents of TEGDA crosslinks were converted to the corresponding dithiocarbamates by treatment with five-fold molar excess (calculated on the basis of amino capacity) of carbon disulphide and sodium hydroxide in aqueous medium. The dithiocarbamylation is depicted in scheme 3. The reaction was found to be complete from the negative ninhydrin reaction.



Scheme 3. Dithiocarbamylation of amino polyacrylamides.

For comparing the different resins, the crosslinking density was assumed to be directly proportional to the mole% of the diacrylate crosslinking agent in the feed. But the possibility of the cleavage or the reformation of the diacrylate-crosslinks on transamidation, the chances of multi-transamidation leading to additional crosslinks and the dithiocarbamylation reaction could lead to changes in the extent of crosslinking in the polymeric ligands. The transamidation reaction also changes the hydrophilicity and the length of the crosslinking segment. This influences the swelling characteristics of the resin and hence its ability to chelate with the metal ions. In order to delineate these possible changes, the swelling characteristics of the acrylamide resins, the amino resins obtained after transamidation with ethylenediamine and methylamine and the dithiocarbamate resins were investigated. The equilibrium water content (EWC) values of the 2% and 4% crosslinked polyacrylamide and the derived amino resins by transamidation with ethylenediamine and methylamine followed the same trend. The resins obtained on transamidation with methylamine were found to be less swelling than the amino resins derived by transamidation with ethylenediamine. This is due to the absence of the polar amino groups on the resins. But the EWCs of the 8%, 12% and 20% crosslinked resins increased on transamidation. This arises from the cleavage of the ester linkages in the crosslinking agent. This view is supported by the observed increase in amino capacities of the resins. The amino capacity increases after 4% crosslinking and it increases with increasing in crosslinking in the polymer. The EWCs of the dithiocarbamate resins were found to be generally lower than the corresponding amino resins on account of the relatively decreased polarity and reduced compatibility of the dithiocarbamate resins in the aqueous medium. Complete cleavage of the crosslinking agent leading to the formation of the tetraethylene glycol in any detectable and quantifiable amount by GLC could not be observed.

3.4 Complexation of polyacrylamide-supported dithiocarbamates: Effect of the extent of crosslinking on complexation

The effect of the extent of crosslinking on complexation was investigated for Cu(II), Ni(II), Zn(II), Co(II) and Hg(II) ions. The metal ion intakes of the dithiocarbamates with 2 to 20 mole% of TEGDA crosslinks are given in table 2. When the yellow dithiocarbamate resin was treated with Cu(II), Ni(II) and Co(II) solutions, the colour turned dark. In the case of Zn(II) and Hg(II) the yellow colour of the dithiocarbamate resin lightened to white. For the amino complexes, the colours of the corresponding metal salts were retained even after complexation. This colour change

Table 2. Metal ion intakes of TEGDA-cross-linked polyacrylamide-supported dithiocarbamate resins.

TEGDA (mole%)	Metal ion intake mg/g (meq/g.)				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Hg(II)
2	48 (0.82)	108 (1.84)	154 (2.43)	117 (1.80)	1215 (6.06)
4	39 (0.66)	87 (1.48)	136 (2.14)	109 (1.67)	860 (4.29)
8	80 (1.36)	96 (1.64)	134 (2.11)	111 (1.70)	979 (4.88)
12	84 (1.43)	100 (1.70)	132 (2.08)	113 (1.73)	1007 (5.02)
20	88 (1.49)	102 (1.74)	130 (2.05)	115 (1.76)	1053 (5.09)

in dithiocarbamate resins can be taken as an approximate measure of the conversion of amino resins to the dithiocarbamates.

For all the metal ions investigated, complexation is highest at 2% crosslinking. Except Cu(II), the intakes of metal ions are lower at 4% crosslinking and gradually increase with increase in the TEGDA content. In the case of Cu(II), the complexation decreased with the increasing crosslinking without much variation. The higher complexation at 2% crosslinking is reasonable because of the lower content of the crosslinking agent and the increased availability of the ligands for complexation with metal ions. The lower complexation at 4% crosslinking is due to the low ligand concentration and the high content of the crosslinking agent which makes the diffusion of the metal ions through the matrix difficult. The unusual increase in complexation after 4% crosslinking originates from the contribution of ligands by the crosslinking agent and it increases with increasing amounts of the crosslinking agent. But there is no general trend in complexation in these cases (figure 2). For Ni(II), Zn(II) and Hg(II) the complexation was maximum for the 2% crosslinked system, decreased at 4%, increased further and reached a value nearly equal to that complexed by the 2% crosslinked resin. For Co(II), the complexation followed a similar manner but the Co(II) intake by the 20% crosslinked resin is higher than the 2% crosslinked system. The observation of a significantly lower uptake of Co(II) in 2% and 4% crosslinked resins compared to the corresponding highly crosslinked systems was reproducible. Generally, cobalt requires six sulphur atoms from the three dithiocarbamate groups for coordination in contrast to two dithiocarbamate groups for other metal ions.

The cobalt complexes contain mainly Co(III), whereas in the case of Ni(II) complexes the presence of both diamagnetic and paramagnetic species was shown (Mitchell and Taylor 1982). Co(III) dithiocarbamates are coordinated by six sulphur atoms and so the degree of reaction depends on the accessibility of the three dithiocarbamate groups for coordination, whereas the requirements of Ni(II), Cu(II), Zn(II) and Hg(II) are two dithiocarbamates. The simultaneous availability of the three dithiocarbamate groups for complexation could be more feasible in the case of the resins prepared with more than 4% crosslinking monomer in the feed, where greater cleavage of the crosslinking agent and hence greater capacity for the ligands was actually

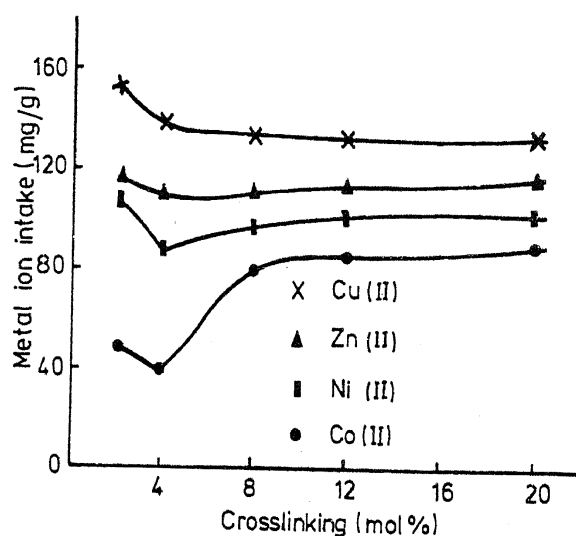


Figure 2. Dependence of complexation on the extent of TEGDA-crosslinking.

observed. However, a final conclusion in this case is possible only after the determination of the absolute values of the crosslink density in these cases. Hg(II) has the highest complexation of $860\text{--}1215\text{ mg g}^{-1}$ of the resin. The complexation was minimum for Co(II). The metal ion intake followed the order Hg(II) > Cu(II) > Zn > Ni(II) > Co(II). This trend is characteristic for the complexations of dithiocarbamates (Hitarni *et al* 1981). The chelating ability of sulphur-containing ligands to heavy metal ions is higher and is effective in the extraction of Hg(II). The chelating ability is in the order Hg(II) > Cu(II) > Cd(II) agreeing very well with the stability constants for dithiocarbamate complexes of these metal ions (Hulanicki 1967).

3.5 Time-course of complexation

The time-dependence on the complexations of Cu(II), Ni(II), Zn(II) and Co(II) was followed by the change in concentrations of the metal salt solutions at regular intervals of time. The time required for the complete complexation of the 4% crosslinked resin was followed. The maximum Cu(II) complexation was achieved in 1.5 h. For Ni(II) and Co(II) the time required for the maximum complexation was less than 0.5 h. But Zn(II) required 2 h for complete complexation. The results are depicted in figure 3. The reduced time required for the complete complexation appears to be due to the increased availability of the ligands for the metal ions caused by the flexible and hydrophilic nature of the crosslinks.

3.6 Swelling studies of the polymeric ligands and derived complexes

The swelling characteristics of the polyacrylamide-supported dithiocarbamates with TEGDA crosslinks and their Cu(II) complexes with $110\text{ mg Cu(II) g}^{-1}$ of the resin varied with the extent of the TEGDA content as shown in figure 4. The equilibrium water content (EWC) of the 2% crosslinked resin is higher and decreases with the TEGDA content. The high value of the EWC of the 2% crosslinked resin is due to the low content of the crosslinks which allows extreme swelling in water. But the decrease in swelling with increasing crosslinking is less than expected because of the

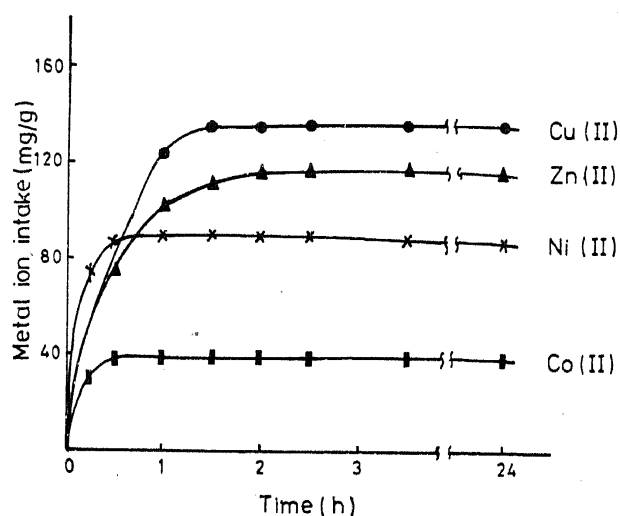


Figure 3. Time-dependence of complexation.

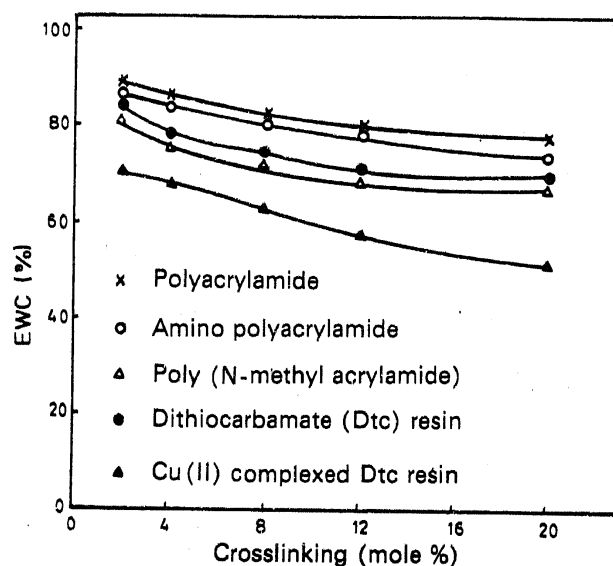


Figure 4. Equilibrium water contents of the uncomplexed and Cu(II) complexed resins.

cleavage of the ester groups of the crosslinking agent and it increases with increasing crosslinking.

In 2% and 4% crosslinked resins, the cleavage of the crosslinking is not observed from the EWC values. Thus the reduction in amino capacity and hence the metal intake could arise from the reduced availability of the amide groups for transamidation with increase in the crosslinking of 4% rather than the 2% crosslinked system. The higher amino capacity and hence higher complexation after 4% arises from the cleavage of the crosslinking points resulting in increased amino groups. A reduction in the extent of crosslinking can also enhance the possibility of interaction with the metal ions.

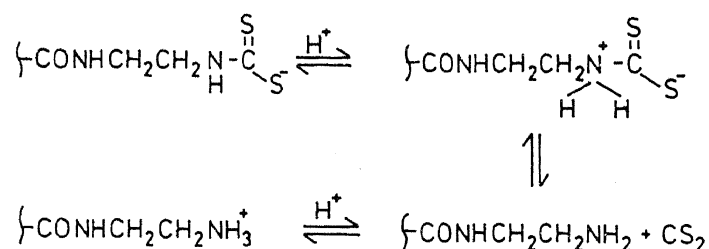
The water intake by the Cu(II) complexed resins is lower than the uncomplexed resin because of the introduction of additional crosslinks by intramolecular chelation with Cu(II). This reduction is much higher in the highly crosslinked systems because

of the tightening of the lightly packed polymer chains by the rupturing of the crosslinks during transamidation (Welleman *et al* 1981).

3.7 Recyclability of the complexed resin

The recyclability of the Cu(II) complexed dithiocarbamate resin was investigated for the 4% crosslinked resin. The resin with 136 mg Cu(II) intake on treatment with 3 N nitric acid desorbed Cu(II) quantitatively. The acid-treated resin after neutralization was again subjected to dithiocarbamylation and complexation. The resin complexed only 92 mg Cu(II) compared to an original intake of 136 mg of Cu(II).

It is reported that dithiocarbamate ion exists protonated in acid solution (Joris *et al* 1969). The protonated dithiocarbamate resin decomposed to give carbon disulfide and protonated amino polymer as represented in scheme 4.



Scheme 4. Acid-catalysed decomposition of dithiocarbamate resin.

3.8 Infra-red spectra

The infra-red spectra of the TEGDA-crosslinked dithiocarbamate resin showed absorptions characteristics of the ester groups of the crosslinking agent and of amide groups which may be the unfunctionally amide or amide linkages formed by the amination of the ester groups of the crosslinking agent. The characteristic peaks of the dithiocarbamates are in the following three regions: the peak in the region 1550–1450 cm^{-1} is associated with the $\nu(\text{C-N})$ vibration of the $\text{CS}_2\text{-NR}_2$ bond. In the case of the polyacrylamide-supported dithiocarbamate metal complexes this peak is seen around 1444 cm^{-1} . A second IR spectral region characteristic of the dithiocarbamate complexes is between 1050 and 950 cm^{-1} and this is associated with $\nu(\text{CSS})$ vibration (Coucouvanis 1970). In metal complexes of dithiocarbamates, this peak is broadened and shows a splitting of less than 20 cm^{-1} indicating bidentate coordination nature of the CS_2 groups (Mitchell and Taylor 1982). The IR spectral region between 400 and 200 cm^{-1} is associated with M-S translational vibrations in low molecular weight complexes (Ojima *et al* 1970). In the case of the Cu(II) complexes, Cu-S peaks are seen at 360 and 240 cm^{-1} . For the Ni(II) complexes, Ni-S translational vibrations are seen around 390–380 and 240 cm^{-1} . In this study IR spectral measurements were carried out only up to 200 cm^{-1} .

3.9 Thermogravimetric studies

The TG curves of the 2% TEGDA-crosslinked dithiocarbamate resin and its Cu(II), Ni(II), Zn(II), Co(II) and Hg(II) complexes showed three stages of decompositions (figure 5). The first stage decomposition is in the temperature range 34–176°C with

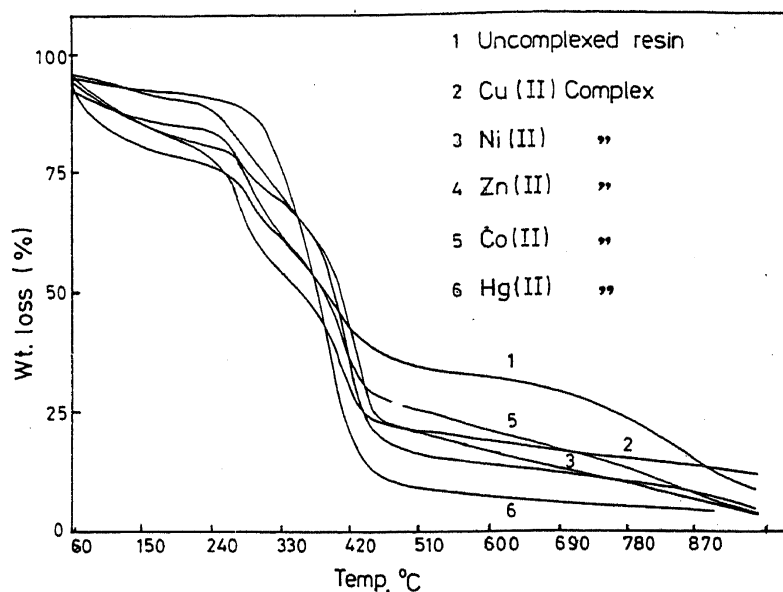


Figure 5. TG curves of 2% crosslinked dithiocarbamate resin and its metal complexes.

Table 3. Phenomenological data of the thermal decompositions of 2% TEGDA-crosslinked polyacrylamide-supported dithiocarbamate and its metal complexes.

Resin	Temp. range of decomposition in TG (K)		Peak temp. in DTG (K) T_s	Mass loss (%)
	T_i	T_f		
Dithiocarbamate	529	753	665	29
Cu(II)	569	759	679	34
Ni(II)	545	737	665	23
Zn(II)	525	789	667	50
Co(II)	561	745	667	24
Hg(II)	541	773	649	61

mass losses between 3 and 15%. This is due to the liberation of adsorbed or coordinated water molecules present in the complexes. The higher water content is due to the hydrophilic nature of the polymer-support as evidenced from the IR spectra. The second stage represents the slow decomposition of the free ligands. This stage occurs in the temperature range 136–296°C. The third stage is the major decomposition and is used for the kinetic analysis of the complexes and the phenomenological data of this stage for the various systems are given in table 3.

The energy of activation, the Arrhenius parameter and the entropy of activation are calculated using [1] (Coats and Redfern 1964) and [2] (Madhusudanan *et al* 1986) by the least squares method:

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\phi E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (1)$$

$$\ln \frac{g(\alpha)}{T^{1.921503}} = \ln \frac{AE}{\phi R} + 3.772050 - 1.921503 \ln E - 0.120394 \left(\frac{E}{T} \right) \quad (2)$$

Table 4. Kinetic data of the thermal decomposition of 2% TEGDA-crosslinked dithiocarbamate and its metal complexes.

Resin	Equation (1)				Equation (2)			
	<i>E</i> (kJ mol ⁻¹)	<i>A</i> (s ⁻¹)	ΔS (J mol ⁻¹)	<i>r</i>	<i>E</i> (KJ mol ⁻¹)	<i>A</i> (S ⁻¹)	ΔS (J mol ⁻¹)	<i>r</i>
Dithiocarbamate	110-6509	3.5572×10^3	-183-6209	0.9936	111-0858	6.4355×10^3	-178-6909	0.9937
Cu(II)	156-2403	1.1605×10^7	-116-5198	0.9918	156-6772	2.0979×10^7	-111-5963	0.9919
Ni(II)	119-7297	1.7688×10^4	-170-2837	0.9989	120-1652	3.1994×10^4	-165-3553	0.9989
Zn(II)	112-1783	2.4841×10^3	-186-6316	0.9993	112-6029	4.4850×10^3	-181-7185	0.9930
Co(II)	179-6545	1.9796×10^9	-073-6365	0.9966	180-0950	3.5785×10^9	-068-7109	0.9966
Hg(II)	123-1687	8.4406×10^4	-157-0859	0.9917	123-1688	1.5208×10^5	-165-4979	0.9918

The kinetic data and the correlation coefficients are given in table 4. The activation energies of the metal complexes are higher than the uncomplexed resin. The order of thermal stability is Co(II) > Cu(II) > Ni(II) > Zn(II) > Hg(II) > dithiocarbamate resin. This shows the additional thermal stability gained by complexation with metal ions by the formation of stable ring structures (Desai and Suthar 1986). A metal ion can be complexed by one, two or three dithiocarbamate ligands in the polymer support, depending on the coordination ability of the metal ion and the availability of the ligands. With dithiocarbamates the formation of ring structures of the metal complexes is more favoured because of the bidentate coordination mode of the CS₂ group (Mitchell and Taylor 1982). The entropies of the uncomplexed resin and the metal complexes are negative showing the ordered structure of the polymer-support. The entropies of the complexed resins is higher than the uncomplexed resin. The already ordered structures of the polymer chains are distorted by complexation with metal ions resulting in an increase in disorder.

3.10 Scanning electron microscopy

The scanning electron micrographs of the uncomplexed and complexed resins are given in figure 6. The surface of the uncomplexed resin appears rough and that of complexed resin seems smooth. This suggests higher strain energy regions on the surface of the uncomplexed resin. Complexation would occur in these regions which lowers the surface energy. Hence the surface gets smoothed in the complexed resin.

3.11 Conclusion and outlook

The foregoing studies on the preparation of macromolecular dithiocarbamates of varying specific microenvironments and their complexation behaviour with metal ions suggest a definite correlation between the molecular character and extent of crosslinking on ligand-metal ion interactions. The swelling nature of these gel-type polymers in water is dependent on the extent of the polar and flexible hydrophilic crosslinking agent, tetraethyleneglycol diacrylate, in the macromolecular matrix. The extent of functionalization with the ligand group is also dependent on the crosslink density. The recyclability of dithiocarbamate resin is not possible because of its liability to decomposition. The thermal stability increases by complexation with metal ions.

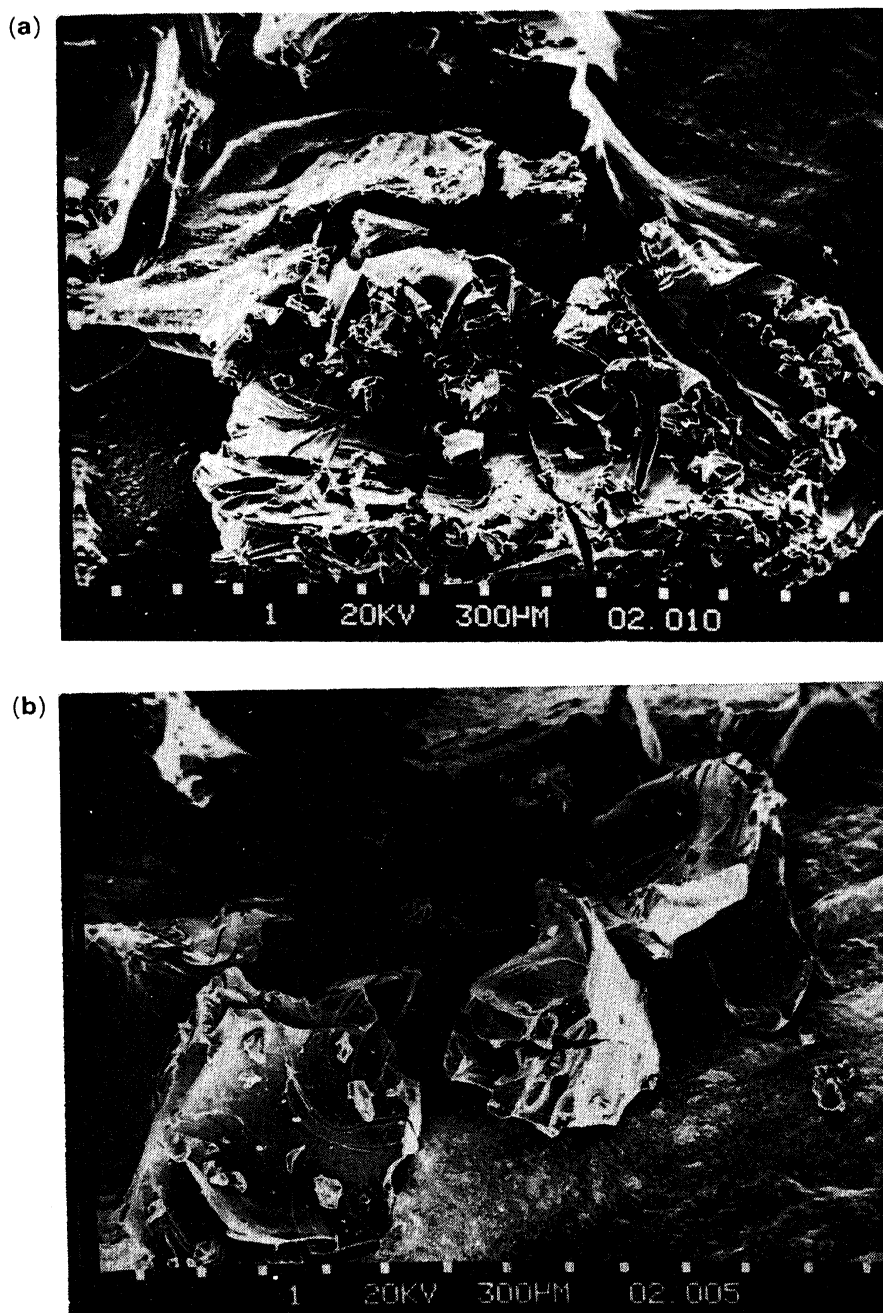


Figure 6. Scanning electron micrographs of (a) uncomplexed resin, and (b) Co(II) complexed resin.

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