Polymer Bulletin 26, 603–610 (1991)

**Polymer Bulletin**

# Divinylbenzene-crosslinked polyacrylamide-supported dithiocarbamates as metal complexing agents

**Beena Mathew and V. N. Rajasekharan Pillai***

School of Chemical Sciences, Mahatma Gandhi University, Kottayam – 686 631, Kerala, India

## SUMMARY

Dithiocarbamate (DTC) functions were incorporated into divinylbenzene-crosslinked (2-20 mole %) polyacrylamides by a two-step polymer-analogous reaction. The complexations of these resins with DTC functions in different structural environments were investigated towards Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) by batch equilibration technique. The metal ion intake decreased with the extent of the DVB content in the order Hg(II) >> Cu(II) > Zn(II) > Ni(II) > Co(II). The time-course on complexation, swelling behaviours of the uncomplexed and complexed resins, recyclability, IR and thermogravimetric characterisation of the complexes were carried out. The swelling of the resins decreased on complexation with metal ions and the thermal stability increased.

## INTRODUCTION

The study of the metal complexation behaviour of polymer-supported ligands is of significant relevance in various branches of chemistry(1,2). The complexation of a polymer-supported ligand is influenced by the characteristics of the macromolecular matrix like the nature and extent of the crosslinking agent, nature of the polymer-backbone and separation of the ligand function from the polymer matrix(3-5). The study of the interdependence of these factors on the reactivity of the attached functional groups form the basis of tailor-made functional and speciality polymers(6-8). DTC ligands are widely used complexing agents for the collection of metal ions from aqueous solutions(9). This paper describes the complexation behaviour of DTC functions supported on polyacrylamides with 2-20 mole% of divinylbenzene crosslinks and their characterisation. The DTC functions were incorporated by a two-step polymer-analogous reaction involving (i) transamidation of polyacrylamides with ethylenediamine to aminopolyacrylamides and (ii) dithiocarbamylation of the aminopolyacryl-amides with carbon disulphide and alkali. The complexation behaviour of these ligand functions occuring in different macromolecular structural environments was investigated towards Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions. The time-dependence on complexation, swelling studies, possibility of recycling of the complexed resins, IR characterization of the complexes and thermogravimetric studies are reported here.

---

*To whom offprint requests should be sent

## EXPERIMENTAL

### 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. Thermograms were recorded on a Delta Series TGA-7 Thermal Analyser at a heating rate of 20°C/min under nitrogen atmosphere.

### Synthesis of divinylbenzene(DVB)-crosslinked polyacrylamides

Divinylbenzene-crosslinked polyacrylamides were prepared by free radical solution polymerization. For the preparation of the 2% DVB-crosslinked polymer, acrylamide(20.9 g) and divinylbenzene (1.3 g) were dissolved in ethanol (100 ml). Benzoyl peroxide (200 mg) was added and the mixture was heated with stirring at 70°C for 4h. The polymer formed was collected by filtration, washed with water, ethanol, benzene and methanol and dried at 70°C. Polyacrylamides with 4, 8, 12 and 20 mole% of DVB-crosslinks were prepared by varying the mole% of the monomers.

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

Ethylenediamine (100 ml) was added to polyacrylamide (10 g) with stirring. The mixture was heated at 100°C for 9h. The reaction mixture 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 blue colouration with ninhydrin reagent. The gel was washed with water to remove NaCl and with MeOH and dried at 70°C.

### Estimation of resin amine content

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

### Dithiocarbamylation of poly(N-2-aminoethylacrylamide)s

Poly(N-2-aminoethylacrylamide) (5 g) was suspended in a five-fold molar excess (calculated on the basis of amino capacity) of $CS_2$ and NaOH in water (50 ml) and shaken in mechanical shaker for 9h. The resin was collected by filtration, washed with water till the washings were free from NaOH and finally with MeOH and dried in vacuum.

### Complexation of metal ions with dithiocarbamate resins

The complexations of DTC resins with varying extents of DVB-crosslinks were carried out with Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions by batch equilibration method. 200 mg each of the resin samples was stirred with definite concentration of excess metal salt solution (0.01 N, 50 ml) for 24h. The complexed resins were collected by filtration, washed with distilled water to remove uncomplexed metal ions. The concentrations of the metal salt solutions 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.

### Time-course of complexation

Batch studies were carried out with 500 mg of 4% DVB-crosslinked DTC resin in order to arrive at the optimum period necessary for maximum complexation. Cu(II), Ni(II), Zn(II), and Co(II) solutions (100 ml each) were added to the DTC resins and stirred. At regular intervals, 2 ml aliquots were withdrawn from the test solution and estimated.

### Recyclability of the complexed dithiocarbamate resin

Cu(II) complexed DTC resin (4% crosslinked, 1 g) was stirred with $HNO_3$ (3 N, 15 ml) for 2h. The desorbed metal ion was collected by washing with distilled water and estimated iodometrically. The resin after the treatment with $HNO_3$ was washed with dilute NaOH and water and again subjected to dithiocarbamylation and complexation.

### Swelling studies of dithiocarbamate resins and Cu(II) complexes

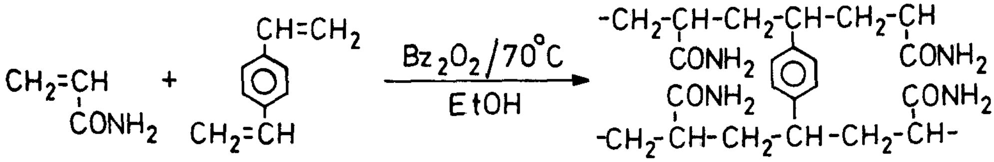
500 mg each of the DTC resin was equilibrated with 30 ml distilled water for 4 days. The swollen resins were collected by filtration, adhering traces of water were removed by pressing with filter paper and weighed. The swollen resins were dried in vacuum for 24h and weighed. In the case of complxed resins, 500 mg each of the samples was equilibrated with 30 ml Cu(II) salt solution containing 55 mg Cu(II) and the swelling measurements were similarly carried out after washing. From the swollen and dry weights of the samples, the equilibrium water content (EWC) was calculated using the expression.

$$\text{EWC} = \frac{\text{Wt. of swollen resin} - \text{Wt. of dry resin}}{\text{Wt. of swollen resin}} \times 100$$

## RESULTS AND DISCUSSION

### Synthesis of divinylbenzene (DVB)-crosslinked polyacrylamides

Polyacrylamides with 2-20 mole% of DVB crosslinks were prepared by the solution polymerization of the monomers in ethanol at 70°C using benzoyl peroxide as initiator (Scheme 1). When the mole% of the the hydrophobic and rigid DVB-crosslinks increased, the rigidity as well as the swelling of the resin in water also varied.



**Scheme 1.** Preparation of DVB-crosslinked polyacrylamide

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

Transamidation of the crosslinked polyacrylamides with excess ethylenediamine at 100°C afforded poly(N-2-aminoethylacrylamide)s (Scheme 2). With ethylenediamine there is the possibility of multitransamidation. The amino functions were detected by the semiquantitative ninhydrin reaction (10). The resins developed a deep blue colour with ninhydrin reagent. The amino groups were estimated by equilibrating a definite amount of the resin with known concentration of excess HCl and estimating the unreacted acid by alkali titration. The capacities of the various amino resins are given in Figure 1. The amino capacity decreased with increasing mole% of the DVB-crosslinks because of the decreased availability of the amide groups buried within the rigid and hydrophobic networks. Thus the amino capacity of the 20% crosslink resin is only 0.5 mmol/g whereas the 2 % crosslinked resin has the highest capacity of 3.52 mmol/g.

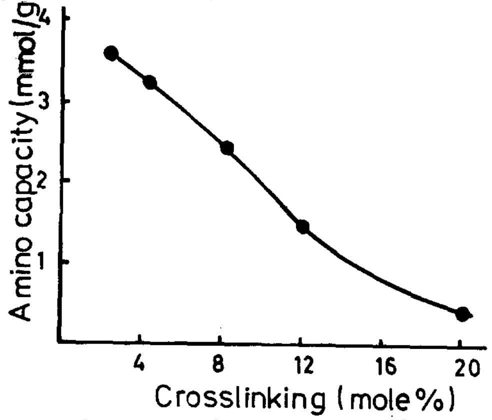
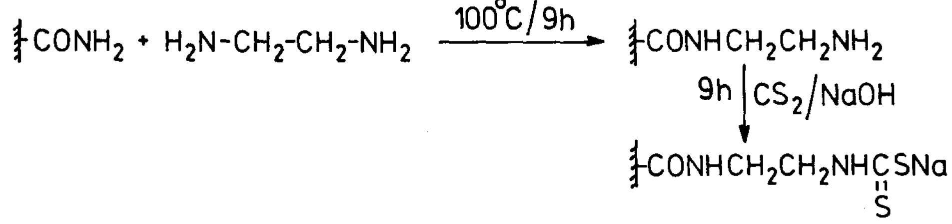


**Fig.1.** Dependence of transamidation on crosslinking

Dithiocarbamylation of poly(N-2-aminoethylacrylamide)s

Amino polyacrylamides with varying extents of DVB-crosslinks were converted to the corresponding DTC by treatment with five-fold molar excess of $CS_2$ in aqueous medium(Scheme 2). The dithiocarbamylation was found to be complete from the negative ninhydrin reaction.



**Scheme 2.** Incorporation of amino and DTC functions in DVB-crosslinked polyacrylamides

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

The complexations of the DTC functions supported on polyacrylamides in different structural environments were investigated towards Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions by batch equilibration technique. The metal ion intakes of the various resins are given

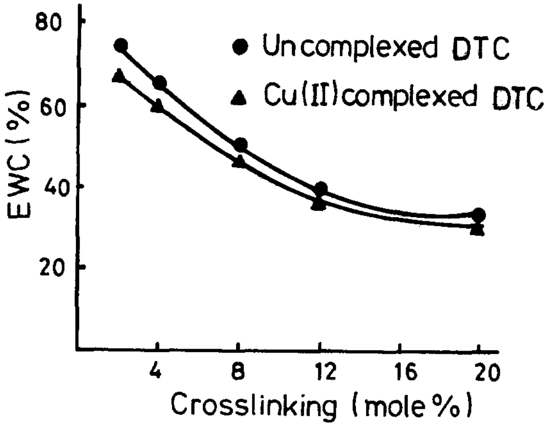


**Fig.2.** EWCs of the uncomplexed and Cu(II)-complexed DTC resins

polymer matrix. The EWCs of the uncomplexed resins were in the range 33-74% but the complexed resins with 110 mg Cu(II)/g of the resins had a lower EWC in the range 30-68% (Fig.2). The decrease in EWC with complexation is due to the introduction of additional crosslinks by complexation with metal ions. This decrease is higher in the low-crosslinked systems and lower for the high-crosslinked systems. In lightly crosslinked systems the polymer chains can undergo extensive swelling than a tightly crosslinked system. The complexation of a lightly crosslinked resin makes the polymer chain more compact by the cooperative contribution of randomly distributed ligands to the metal ions and this decreases with increasing crosslinking because of the increased rigidity of the polymer-support.

## Infra-red spectra

The infra-red spectra of the polymer-supported DTCs and their complexes showed absorptions characteristics of amides, DTCs and metal-ligand bonds. The C=0 and NH absorptions of the amide group occur at 1690 and 3400 cm$^{-1}$ respectively. The DTCs showed absorptions mainly in three regions: The peak in the region 1550-1450 cm$^{-1}$ is associated with thioureide vibration and is attributed to the C-N vibration of the CS$_2$-NR$_2$ bond (14), a peak in the range 1050-950 cm$^{-1}$ is characteristic of the DTC complexes and is attributed to the (CSS) vibration. In the metal complexes, this peak is broadened and showed a splitting of 20 cm$^{-1}$ indicating the bidentate coordination of the -CS$_2$ group (11). The IR spectral region between 400 and 200 cm$^{-1}$ is associated with the M-S translational vibrations (15). In the case of the Cu(II) complexes of the polymeric ligands these peaks occur in the regions 370-340 cm$^{-1}$ and 260-240 cm$^{-1}$. For Ni(II) complexes the Ni-S translational vibrations are in the region 390-380, 340 and 240 cm$^{-1}$.

## Thermogravimeric Studies

The TG curves of the 4% DVB-crosslinked DTC resin and its various metal complexes showed decompositions in three steps (Fig. 3). The first step decompositions were in the range 34-213°C with mass losses in the range 3-16% which may be assumed as due to the liberation of absorbed or coordinated water molecules present in the complexes.

**Table 1.** Metal ion-intakes of polyacrylamide-supported dithiocarbamates of varying extents of DVB crosslinks

| DVB | Metal ion intake (mg/g) | | | | |
|---|---|---|---|---|---|
| (mole%) | Co(II) | Ni(II) | Cu(II) | Zn(II) | Hg(II) |
| 2 | 51 | 66 | 128 | 117 | 890 |
| 4 | 47 | 52 | 102 | 72 | 756 |
| 8 | 38 | 45 | 83 | 41 | 655 |
| 12 | 20 | 37 | 52 | 39 | 409 |
| 20 | 10 | -- | 9 | -- | 130 |

in Table 1. When the yellow DTC resin was treated with solutions of coloured metal salt solution, the resin turned dark. But the amino resin retained the colour of the metal salt solution evenafter complexation. This colour change in DTC resins can be taken as a measure of the conversion of the amino resins to the DTCs. A metal ion can be complexed by the one or more DTC ligands depending on the proximity of the ligands in the polymer matrix(11).

For all the metal ions, the complexation is maximum for the 2% crosslinked system and decreases further with increasing crosslinking. This observation is similar to the decrease in ligand concentration with the DVB content. DTCs generally complex heavy metal ions(9). The Hg(II) complexation of the DTC is very high and is in the range 890-130 mg/g of resin. The observed trend in complexation is Hg(II) >> Cu(II)> Zn(II) > Ni(II) > Co(II). This trend is typical of DTCs(12). The complexation of the 20% crosslinked resin for Ni(II) and Zn(II) was negligible.

## Time-course of complexation

In order to get a measure of the relative performance of the resin in kinetic terms, the complexations of Co(II), Ni(II), Cu(II) and Zn(II) were followed by the change in the concentrations of the metal salt solutions at regular intervals of time. In the case of 4% DVB-crosslinked resin, maximum Cu(II) complexation was achieved in 1h. For Ni(II) and Co(II) ions the time required for maximum complexation was 0.75h whereas Zn(II) required 1.25h.

## Recyclability of the complexed resin

The recyclability of the DTC resin was investigated for the Cu(II) complex of the 4% crosslinked resin. The resin with 103 mg Cu(II)/g of the resin on treatment with 3 N $HNO_3$, desorbed Cu(II) quantitatively. The acid-treated resin was neutralised and again subjected to dithiocarbamylation and complexation. The resin complexed 62 mg Cu(II) compared to an original intake of 103 mg. This is due to the acid-catalysed decomposition of dithiocarbamates to the protonated amine and carbondisulfide (13).

## Swelling characteristics

The EWCs of the DTC resins decreased with increasing crosslinking because of the increasing hydrophobicity and rigidity of the

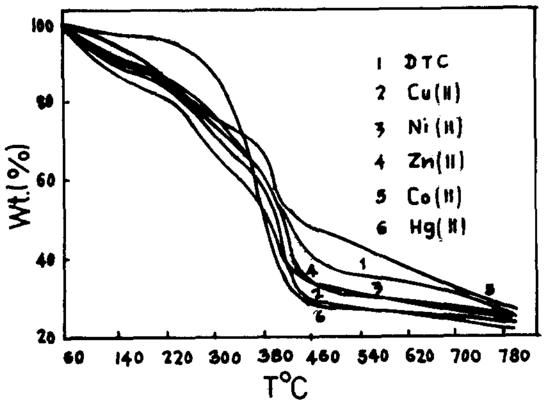


**Fig.3.** TG curves of uncomplexed and complexed DTC resins

The second step decompositions were in the range 168-263°C with mass losses between 10-19%. This step consists of two stages which are due to the decompositions of the unfunctionalised amide groups and free ligands. The last step is the major decomposition and is shifted by the incorporation of metal ions. For the uncomplexed dithiocarbamate resin this step occurs in two stages whereas for the metal complexes this occurs in a single stage.

The kinetic parameters of decompositions are calculated by integral and approximation methods using equations [1] and [2] (16,17). The activation energies of decomposition, Arrhenius parameters and the entropy of activation are calculated using the least square method. The kinetic parameters and the correlation coefficients are given in Table 2.

**Table 2.** Kinetic data of the thermal decompositions of 4% DVB-cross-linked polyacrylamide-supported DTC and its metal complexes

| Resin/ | Equation [1] / Equation [2] | | | |
|---|---|---|---|---|
| Complex | E KJ $\text{mole}^{-1}$ | A $\text{Sec}^{-1}$ | $\Delta$S J $\text{mole}^{-1}$ | r |
| DTC | 67.6842 | 10.8341 | -232.1600 | 0.9989 |
| | 68.1970 | 5.9360 | -237.1632 | 0.9989 |
| Cu(II) | 110.1226 | $1.3338 \times 10^{3}$ | -192.0495 | 0.9870 |
| | 110.4513 | $2.3679 \times 10^{3}$ | -187.2797 | 0.9869 |
| Ni(II) | 112.0448 | $6.1243 \times 10^{3}$ | -179.4380 | 0.9992 |
| | 112.4504 | $1.1016 \times 10^{4}$ | -174.5561 | 0.9993 |
| Zn(II) | 125.0597 | $2.5844 \times 10^{4}$ | -167.4654 | 0.9982 |
| | 125.5055 | $4.6829 \times 10^{4}$ | -162.5224 | 0.9983 |
| Co(II) | 125.7571 | $4.4482 \times 10^{4}$ | -162.7567 | 0.9967 |
| | 125.4068 | $7.0529 \times 10^{4}$ | -158.9224 | 0.9945 |
| Hg(II) | 97.5101 | $4.2015 \times 10^{2}$ | -201.1426 | 0.9934 |
| | 97.9257 | $7.5772 \times 10^{2}$ | -196.2390 | 0.9935 |

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

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

The thermal stability of the DTC resin is increased by complexation. Complexation with metal ions results in the formation of stable ring structures of additional stability (18). With DTCs the formation of ring structures is more favoured because of the bidentate coordination of the DTC group (18). The activation energies decreased in the order Co(II) > Zn(II) > Ni(II) > Cu(II) > Hg(II) > uncomplexed resin. The residue left in each case is the corresponding metallic sulphide.

The entropies of the uncomplexed resin and the metal complexes are negative showing the ordered structure of the polymer support. The entropies of the complexes are higher than the uncomplexed resin pointing to the distortion of the ordered structure of the polymer-support for complexation with metal ion.

## ACKNOWLEDGEMENTS

The Regional Sophisticated Instrumentation Centre (RSIC), IIT, Madras is thanked for the spectral analysis and Catalysis Division, IIT, Madras for the thermal analysis. The authors thank Prof. P.M. Madhusudanan for detailed discussion and help in the interpretation of the thermal data of the polymer-metal complexes.

## REFERENCES

1. A. Warshawsky, in "Syntheses and Separations using Functional Polymers", ed. by D.C. Sherrington and P. Hodge, J. Wiley and Sons, Chichester, 325 (1988).
2. M. Kaneko and E. Tsuchida, Macromol. Rev. **16**, 397 (1981)
3. H. Nishide, N. Shimidzu and E. Tsuchida, J. Appl. Polym. Sci., **27**, 4161 (1982)
4. K.M. Saldadze, V.D. Kopilova and G.D. Asambadze, "Ionic Exchange and Ionites", Moscow, 251 (1967)
5. R.S. Drago and J.H. Gaul, Inorg. Chem. **18**, 2019 (1979)
6. K.S. Devaky, B.K. George and V.N.R. Pillai, Ind. J. Chem. **29A**, 1045 (1990)
7. B.K. George and V.N.R. Pillai, J. Polym. Sci. Polym. Chem. Ed. **28**, 2585 (1990)
8. K. Sreekumar and V.N.R. Pillai, J. Appl. Polym. Sci. **37**, 2109 (1989)
9. J.F. Dingman Jr, K.M. Gloss, E.A. Milano and S. Siggia, Anal. Chem. **46**, 774 (1974)
10. V.K. Sarin, S.B.H. Kent, J.P. Tam and R.B. Merrifield, Anal. Bio. Chem. **117**, 147 (1981)
11. P.C.H. Mitchel and M.G. Taylor, Polyhedron, **1**, 225 (1982)
12. K. Hitarni, Y. Onishi and T. Nakayama, J. Appl. Polym. Sci. **26**, 1475 (1981)
13. A. Hulanicki, Talanta **14**, 1371 (1967)
14. D. Coucouvanis, Prog. Inorg. Chem. **11**, 233 (1970)
15. I. Ojima, T. Onishi, T. Iwamoto, N. Inamoto and K. Tamaru, Inorg. Nucl. Chem. Lett. **6**, 65 (1970)
16. A.W. Coats and J.P. Redfern, Nature **201**, 68 (1964)
17. P.M. Madhusudanan, K. Krishnan and K.N. Ninan, Thermochim. Acta **97**, 189 (1986)
18. A.Z. El-Sonbati and M.A. Diab, Polym. Deg. and Stab. **22**, 295 (1988)

Accepted May 20, 1991 S