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CROSSLINKED POLYSTYRENE-SUPPORTED DITHIOCARBAMATES AS METAL COMPLEXING AGENTS

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Abstract—Dithiocarbamate functions were introduced into divinylbenzene (DVB)-crosslinked polystyrene matrices in different structural environments and their complexation behaviour with various metal ions was investigated. The reactions involved introduction of the amino functionality into the polystyrene matrix through a number of different heterogeneous amination procedures. These aminopolystyrene derivatives which contain the amino functions in different steric environments were converted to the respective dithiocarbamates by reaction with carbondisulphide in the presence of alkali. The metal complexing ability of the resulting insoluble polystyrene-dithiocarbamates was investigated towards Fe(III), Ni(II), Cu(II) and Zn(II) ions. The structural factors characteristic of the polymer matrix like the molecular character and extent of crosslinking were found to exert influence on the metal complexing ability. The spectral characterization and the relative thermal stabilities of the complexes were also investigated.

INTRODUCTION

The study of the metal complexation behaviour of polymer-supported ligands is of importance in a number of fields like catalysis, metal ion separation and in bioinorganic chemistry [1–3]. The most important advantages of polymeric ligands are their easy recovery and reuse after a particular process. The investigation of the polymer–metal complexes is also fundamentally important. The organic polymer-support can induce specific control over the catalytic and complexing ability of the ligands depending upon the structural variants in and around the macromolecular matrix. The crosslink density, nature of the crosslinks, separation of the ligand functions from the three dimensional crosslinked matrix and other microenvironmental factors like the presence of functional groups in the viscinity, precise stereochemistry and the hydrophilic–hydrophobic balance of the polymer matrix can affect the overall selectivity and specificity of the complexation [4–7].

The present study is concerned with the synthesis and characterization of the metal complexes of dithiocarbamate functions supported on crosslinked polystyrene-supports with a view to analysing the effects of some of the above structural parameters characteristic of the polymer matrix. The polymeric dithiocarbamates are of practical importance in complexation of heavy metal ions and in catalysis [8–11]. Metalfix® and Dithiochel are two commercially available dithiocarbamate resins used for separation of metal ions (Fluka, 63983). Here we selected crosslinked polystyrene as the polymer matrix in view of its ease of functionalization and the possibility of introducing the various structural parameters in a relatively well-defined manner.

Commercially available standard polystyrene samples (Fluka, Switzerland) with 1–20 mol% of DVB crosslinks were employed for these investigations. Infrared spectra were recorded on a Perkin–Elmer 283 IR spectrometer using KBr pellets. ESR spectra were taken on a Varian E-12 instrument at room temperature. TG curves were recorded on a Delta Series TGA 7 Thermal Analyser at a heating rate of 20°/min in nitrogen atmosphere.

Chloromethylation of DVB-crosslinked polystyrenes: general procedure [12]

Crosslinked polystyrene (1–20 mol% DVB-crosslinked, 8 g) was allowed to swell in dichloromethane (40 ml). Stannic chloride (7 g) was added to the well-stirred suspension of the polymer beads containing chloromethyl methyl ether (25 ml) at 0° (CAUTION: suspected carcinogen!). The temperature was allowed to rise to room temperature during a period of 1 hr. The mixture was stirred for 55 hr. The resin was collected by filtration, washed with dioxane–water (1 : 1), water, dioxane–water–HCl (1 : 1 : 1), methanol, drained and dried in vacuum. The extent of chloromethylation was followed by estimation of chlorine by Volhard's method (Table 1). Additional crosslinking via methylene bridges is also possible in the chloromethylation reaction.

*Preparation of aminomethyl polystyrene (**2**)*

A mixture of chloromethylpolystyrene (2% DVB-crosslinked, 4.2 mmol Cl/g, 10 g), hexamethylenetetramine (11.8 g, 84 mmol) and KI (13.9 g, 84 mmol) in DMF (200 ml) was heated with stirring at 100° for 10 hr. The suspension was poured into water and stirred for 30 min, the resin was filtered, washed with 6 N HCl and water. It was then stirred with a solution of NaOH (10 g, 150 ml) for 2 hr, filtered, washed several times with water and methanol and dried under vacuum to afford the aminomethyl resin (**2**). The analytical data are given in Table 1.

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Table 1. Elemental analysis data and capacity of amino resins

Resin	N (%)	Cl (%)	Amino capacity (mmol/g)	Conversion (%)
2	3.92	0.81	3.95	94
3	2.10	1.40	2.98	71
4	8.56	0.62	3.86	92
5	8.41	0.61	3.95	94
6	3.81	0.49	2.94	70
7	3.73	0.32	2.31	55

Preparation of N-ethylaminomethyl polystyrene (3)

Chloromethyl polystyrene (2% DVB-crosslinked, 4.2 mmol Cl/g, 5 g) was allowed to swell in dichloromethane (25 ml) for 2 hr. Dry ethylamine gas was passed through the suspension for 4 hr and the suspension was shaken in a mechanical shaker for 3 hr. The resin was collected by filtration, washed with dichloromethane, ethanol, water and ethanol and dried in vacuum. The amino capacity and other analytical data are given in Table 1.

Aminofunctional polystyrene resins by treatment with excess diamines (4) and (5)

Chloromethylpolystyrene resins (1–20 mol% DVB-crosslinked, 3 g) was allowed to swell in dioxane (15 ml). To this suspension, a five-fold molar excess of diamine (ethylenediamine/hexamethylenediamine) and pyridine (based on chlorine capacity) were added and heated under reflux for 6 hr. The resin was collected by filtration, washed with water, water–dioxane (1 : 1) and methanol and dried in vacuum.

Aminofunctional polystyrene resins by treatment with limited amount of diamines (6) and (7)

Chloromethyl polystyrene (2% DVB-crosslinked, 4.2 mmol Cl/g, 3 g) was allowed to swell in dioxane (15 ml). Ethylenediamine or hexamethylenediamine (6.65 mmol) and pyridine (13 mmol) were added and heated under reflux for 6 hr. The resin was washed and collected as described earlier (Analytical data: Table 1).

Preparation of dithiocarbamate resins (8)–(13)

Aminofunctional polystyrene (3 g) was allowed to swell in dioxane 7 ml. NaOH (3 g, in 25 ml H_2O) and CS_2 (3 g) was added and stirred until the reaction mixture turned dark red (6 hr). The resin was collected by filtration, washed with water, methanol and dried under vacuum.

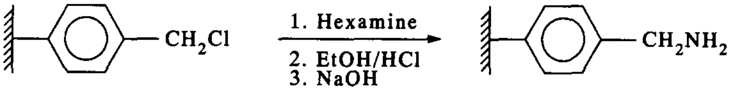
Preparation of low-molecular sodium 1,6-bis(dithiocarbamato) hexane and sodium 1,2-bis(dithiocarbamato) ethane [13]

Carbondisulfide (20 g, 260 mmol) was added over a period of 1 hr to 1,6-hexanediamine (15 g, 130 mmol) and NaOH (10.4 g, 260 mmol) in water (25 ml). The reaction mixture was stirred for a further 15 hr. The precipitated product was filtered, washed with acetone and dried.

Sodium 1,2-bis(dithiocarbamato)ethane was also prepared as described above starting from ethylenediamine.

Complexation of the dithiocarbamate resins: general procedure

200 mg each of the crosslinked polystyrene-supported dithiocarbamate resin was stirred with known concentration of aqueous metal salt solution (0.03 N) at its natural pH. The complexed resin was collected by filtration and washed with water to remove the uncomplexed metal ions. The concentrations of metal salt solutions were determined by



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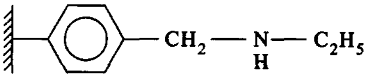

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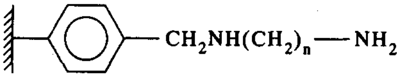
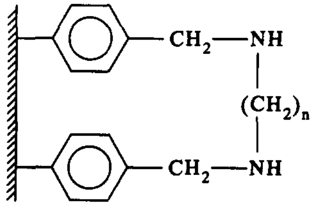
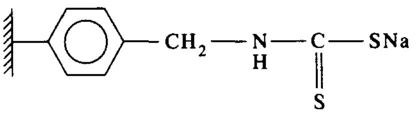


(4) n = 2 ; (5) n = 6



(6) n = 2 ; (7) n = 6



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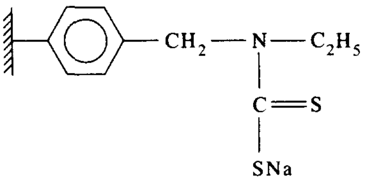

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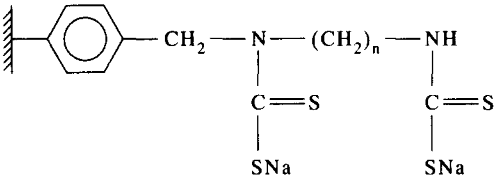
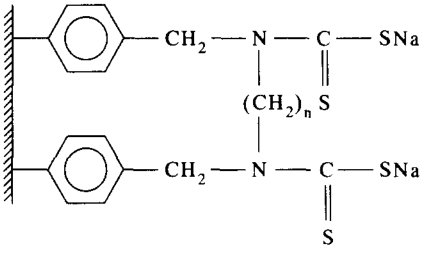


(10) n = 2 ; **(11)** n = 6



(12) n = 2 ; **(13)** n = 6

volumetric and colorimetric methods: Cu(II) by iodometry, Ni(II) and Zn(II) by complexometry and Fe(III) by colorimetry.

RESULTS AND DISCUSSION

Synthesis of polystyrene-supported dithiocarbamates

Crosslinked polystyrene resins with the amino groups in different structural environments were prepared starting from chloromethyl polystyrene resins. Primary amino groups were introduced by a one-step reaction involving treatment with hexamethylene tetramine. Resin with a secondary amino function directly attached to the polymer matrix was obtained by treating with ethylamine. Ethylenediamino- and hexamethylenediamino-methyl polystyrene resins were prepared by the reaction of a five-fold molar excess of the diamine with the chloromethyl polystyrene. Even when sufficient excess diamines is used there is still possibility of bridging in **4** and **5** to some extent. Reaction of the chloromethyl polystyrene resin with limited amount of the diamines gave the amino functional polystyrene resins of the type **6** and **7** respectively. These resins are different from the amino resins **4** and **5** in that they contained mainly the secondary amino groups of which the dithiocarbamates are more stable than the primary dithiocarbamates. The complete bridging by amines is not guaranteed in the preparation of **6** and **7**.

The amino functions were detected by the semi-quantitative ninhydrin reaction [14] and characterized by i.r. absorptions at 3400 and 3500 cm^{-1} The elemental analysis and the chlorine estimation suggested the 94–96% conversion except the amino resins obtained by treatment with limited amount of diamines in which there is only 70–75% conversion (Table 1). The possibility of the quarternization of the pyridine ring at the chloromethyl groups does not arise here because of the increased basicity of the reaction medium due to the presence of excess ethylenediamine.

The amino functional resins were converted to the corresponding dithiocarbamates (**8**–**13**) by reaction with carbondisulphide and alkali. The negative ninhydrin reaction and the sulphur contents of the various dithiocarbamates supports the quantitative conversion of amines to dithiocarbamates (Table 1). The dithiocarbamate resins gave characteristic i.r. absorptions at 3400 (NH), 1440 (C—N) and 930 cm^{-1} (C—S).

Complexation of metal ions with the dithiocarbamate resins

The complexation behaviour of low-molecular weight alkyl dithiocarbamates is well-documented [15, 16]. The polystyrene-supported dithiocarbamates in the present study were observed to undergo complexation with Cu(II), Ni(II), Zn(II) and Fe(III) ions at room temperature on treatment with aqueous solution of the metal salt at its natural pH. The complexing ability of all the polymeric dithiocarbamates was found to be much greater for Cu(II) than other metal ions. A general increase in the complexing ability was observed on going from the dithiocarbamate resin **8** derived from aminomethyl polystyrene to the dithiocarbamate resins **9**, **10** and **11** derived from *N*-ethylaminomethyl polystyrene, ethylenediaminomethyl polystyrene and hexamethylenediaminomethyl polystyrene respectively. For the dithiocarbamate resins **12** and **13** also the complexation was higher than that of the resin **8** in the case of Cu(II). However the extent of increase was not that predominant as was observed for the resins **10** and **11**. The metal ion intake for the dithiocarbamate resin **8** was observed to be in the range 0.03–0.16 meq/g. No specific metal ion selectivity was observable for this dithiocarbamate resin. The extent of complexation of the secondary dithiocarbamate is much higher than the primary dithiocarbamates [15]. The complexation of the dithiocarbamate resin which contains only secondary ligand functions **9** was found to be higher than those with primary dithiocarbamate functions even though the extent of functionalization is less (Table 2). The metal ion intake for the dithiocarbamate resin **11** was less compared to the resin **10** even though the primary dithiocarbamate function in the former is at a longer distance from the crosslinked polymer matrix. This could arise from the decreased concentration of the ligand functions by crosslinking during functionalization.

In reactions of functional groups attached to crosslinked polymer matrices it should be expected that the reactivity increases with increasing separation from the polymer backbone [17–19]. The presence of a spacer group between the polymer matrix and the ligand function influences the complexation with the metal ion [20]. The reduced complexation of the resin **11** compared to the resin **10** may be explained as follows: the secondary dithiocarbamate functions in both the resins are in the same structural environment. Contribution to complexation by the primary dithiocarbamate function which is relatively far from the polymer matrix in the case of the resin **11** is lower. This is also evident in the comparatively very low metal ion intake for the dithiocarbamate resin **8** which does not have any secondary dithiocarbamate function. Thus it can be reasonably assumed that the role of the crosslinked matrix in reducing the complexing ability is not very much observable due to the fact that almost the entire complexation arises from the secondary dithiocarbamate functions.

Table 2. Metal ion intakes of polystyrene-supported dithiocarbamates

Dithio resin	Metal ion intake (meq./g)			
	Cu(II)	Ni(II)	Zn(II)	Fe(III)
8	0.16	0.15	0.12	0.03
9	0.79	0.24	0.29	0.14
10	1.30	0.37	0.46	0.08
11	0.76	0.17	0.18	0.14
12	0.60	0.03	0.06	0.03
13	0.35	0.02	0.02	0.05

Table 3. Elemental analysis data of the various Cu(II) complexes

Resin	N (%)	S (%)	Cu(II)
8	3.27	6.27	2.3
9	1.87	6.53	5.0
10	5.49	12.47	8.2
11	5.62	9.61	4.8
12	2.54	8.41	3.8
13	2.91	7.63	2.2

In the case of the dithiocarbamate resins **12** and **13** which were derived from chloromethyl polystyrene by treatment with limited quantity of the diamines, the complexation was found to be almost half that of the corresponding resins prepared by treatment with excess diamines. The reduction in metal intake observed in the hexamethylenediamino-derived resin **11** compared to the corresponding ethylenediamino-derived resin **10** was also observable in the case of the resins **12** and **13** prepared by treatment with limited amount of the diamines.

A comparison of the elemental analysis values of the functionalized 2% DVB-crosslinked polystyrene-supported dithiocarbamates and their Cu(II) complexes suggests that approximately one dithiocarbamate ligand is complexed by one copper (Table 3). This is only an average since a metal ion can be complexed by one or more ligands depending on the availability of the ligands in the insoluble polymer matrix [21]. In the case of these Cu(II) complexes, the steric effect in the polymer-support is the reason for the 1:1 metal–ligand ratio.

Effect of the extent of crosslinking on complexation

The dependence of the extent of crosslinking on complexation of the dithiocarbamate resins derived from ethylenediaminomethyl polystyrene with 1, 2, 4 and 20 mol% of DVB crosslinking was investigated towards different metal ions. With increasing crosslink density complexation decreases [22, 23]. The values of metal ion intake by the different resins are given in Fig. 1. The significant effect of the extent of crosslinking on complexation is observable here. For the 1% crosslinked resin, the functionalization is maximum and for the highly crosslinked systems, the functionalization is less on account of the reduced availability of the reactive sites. In highly crosslinked systems the rigidity of the polymer backbone is higher

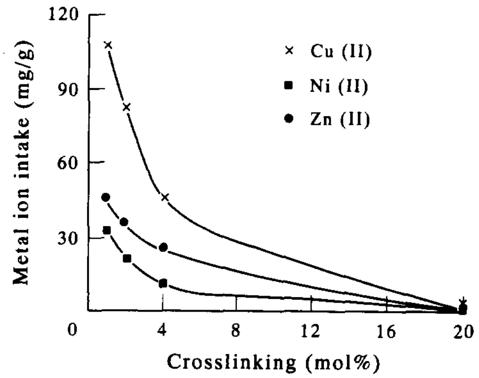


Fig. 1. Effect of the extent of DVB crosslinking on metal ion intake.

Table 4. Thermal decomposition of Cu(II) and Ni(II) complexes of polystyrene-supported dithiocarbamates

Resin	Metal ion	Weight loss at different temperatures (%)					
		100°	200°	300°	400°	500°	600°
8	Cu^{2+}	5.5	8.3	14.5	45.5	71.0	96.6
	Ni^{2+}	1.4	3.4	7.6	15.9	57.2	66.2
9	Cu^{2+}	6.2	7.6	18.6	64.8	94.5	—
	Ni^{2+}	2.8	4.8	9.0	27.6	54.5	67.6
10	Cu^{2+}	6.9	9.7	22.1	29.0	52.4	58.6
	Ni^{2+}	5.5	9.0	15.2	22.8	57.2	62.1
12	Cu^{2+}	7.6	11.7	24.8	31.7	64.1	68.3
	Ni^{2+}	6.2	11.7	20.0	28.1	63.5	68.3

and the reaction sites are buried within the crosslinks [24, 25]. This effect increases with increasing crosslinking leading to reduced functionalization and complexation. Even though the 1% crosslinked resin showed maximum complexation, handling of this resin was difficult due to the extensive swelling and reduced mechanical stability of the resin beads.

Infrared and EPR spectra

By analogy with low molecular weight species $RNHCS_2^-$, the band occurring at 1460 cm^{-1} and a strong band at 965 cm^{-1} in the i.r. spectra of the polymeric dithiocarbamates have been assigned to $\nu(NCS_2)$ and $\nu(CNC) + \nu(CS_2)$ vibrations. In the spectra of the metal complexes, the band occurring at 1480 cm^{-1} moved to higher frequencies and the lower band at 965 cm^{-1} broadened and showed a splitting of $< 20\ cm^{-1}$ indicating the bidentate coordination mode of the CS_2 group [26]. The bands observed in the region 352–384 and 240–260 cm^{-1} have been assigned to ν(M–S) vibration by comparison with low molecular weight complexes.

The EPR spectrum of a metal complex reflects its coordination structure, the interaction between the spin of the central metal ion and the coordinating ligand. The $g\|$, $g_\perp$, $A\|$ and $A\perp$ of the Cu(II) complex of the dithiocarbamate resin **10** are 2.3, 2.1, 140 and 26.7 **G** respectively. These values are in agreement with a square-planar geometry of the copper complex.

Thermal decomposition behaviour

The details of the thermal decompositions of the Cu(II) and Ni(II) complexes are given in Table 4. For all the complexes the weight loss up to 150° is due to the elimination of absorbed solvent molecules. Except for the complex derived from the resin (**12**), the weight loss at different temperature ranges for the decomposition of the Ni(II) complexes are lower than the corresponding Cu(II) complexes. This indicates a higher thermal stability for the Ni(II) complexes. Except for the Cu(II) complexes of the resins **8** and **9** the decompositions were incomplete even at 650°.

CONCLUSION

The foregoing investigations on the syntheses of different polystyrene-supported dithiocarbamates and their complexation behaviour indicate that the incorporation of the ligand function in a crosslinked macromolecular matrix can impart unique characteristics to their complexation pattern. The extent of the DVB crossliking has a significant effect on its functionalization and complexation.

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