

Metal Chelating Resins by Condensation of Ethylene Diamine with *p*-Dichloromethyl Benzene

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SYNOPSIS

Polycondensation of ethylene diamine with *p*-dichloromethyl benzene in different molar ratios (0.8–1.5) gives mostly crosslinked polymers. These resinous polymers are water-compatible and have moderate swelling ability (swelling rate 1.6–20) in water depending on the pH of the solutions. The free amine state of the resinous polymers are capable of chelating with various transition-metal ions such as Cu(II), Ni(II), Co(II), Cd(II), and Zn(II), even in very low concentrations. Due to rapid complexation, high metal binding capacity, and ease of regenerability, these resins can be useful for the removal and recovery of transition-metal ions from water solutions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, there appears to have been a considerable interest in metal uptake by polymeric chelating ligands for recovery or removal of metal ions from water solutions. Crosslinked polymers possessing ligating groups are promising materials for the purification of water, metal processing, etc., due to their ease of separation.

Many reviews cover recent attempts to incorporate many different chelating groups into various natural and synthetic polymer networks.^{1,2} Complexation parameters of polymeric ligands are governed by the nature of the polymeric backbone, crosslinking density, nature of the ligand, and its accessibility in the polymer matrix. The main criteria for a good chelating polymer is a high metal binding ability with a high interaction rate and regenerability without losing its original activity.

Metal-binding ability depends on the nature of the ligating groups. The complexation rate depends on accessibility in the polymer matrix and density of the crosslinking, which are called the matrix effect. To overcome the difficulties in the access in the polymer matrix, the ligands with spacer chains were demonstrated to be very useful in many cases.³

Regenerability is an important criterion for reuse of the polymeric ligand. Regeneration is generally carried out by acid washing causing decomplexation. During leaching (acid treatment), polymers bearing hydrolyzable groups such as amide and esters may undergo hydrolysis. For this reason, a polymer carrying hydrolyzable or easily oxidized or reduced groups is not suitable even though it has the ability of fast complexation.

On the other hand, variation of the hydrophil–lipophil balance of the chelating structure during complexation is another important factor affecting the intrinsic activity of the sorbent. If the chelation proceeds via deprotonation of the ligating groups, generally, neutral metal complexes form on the polymer. Generally, neutral complexation causes a considerable enhancement of lipophilicity and a reduction of hydrophilicity.⁴

In such systems, complexation with metal ions proceeds until such a point that the hydrophil–lipophil balance does not permit any further complexation. Thereafter, the system becomes inactive and many ligating groups remain unreacted.

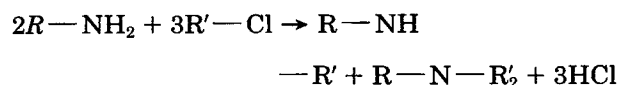
In the case of the formation of charged complexes (outer-sphere complexes), due to the polarity of the charged complexes, the hydrophilicity is not reduced and the water compatibility continues to a further extent of complexation. From this standpoint, polymers carrying all amine ligating groups seem to satisfy the above requirements. Also, there is an ad-

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ditional advantage of these polymers in that they bind not only metal cations but also their counterions by forming cationic complexes. This point is especially important for a complete purification.

In the present study, we prepared crosslinked polymers by a simple condensation of ethylene diamine with *p*-dichloromethyl benzene (DMB). The reaction is reasonably fast and a crosslinked polymer forms in a few minutes. Depending on the ratio and concentration of the two components, the crosslinking density and swelling degree of the resulting resin can be changed.

The reaction of amines with alkyl halogenides is known as the Hoffmann alkylation reaction. However, this reaction gives a mixture of secondary and tertiary amines:



Due to the difficulty of separation of the reaction products, Hoffmann alkylation of amines has found only little attention in preparative organic chemistry. On the other hand, interaction of low molecular weight diamines with dihalogenides tends to give cyclic products rather than polymers.⁵ For instance, ethylenediamine reacts with 1,2-dichloroethane and 2,2'-dichloroethyl ether to give piperazine and 2-ethylaminomorpholine, respectively.

Furthermore, in the presence of transition-metal ions, suitable dihalogenides with diamines form cyclic tetramines, called cyclams. This reaction is referred to as metal template macrocyclization.⁶

To avoid any cyclization, in the present study, *p*-dichloromethyl benzene (DMB) was used as the dihalogenide component in which the cyclization tendency was sterically hindered. In this reaction, DMB acts also as a crosslinking agent and a light yellow powder is obtained. In the study, swelling characteristics, metal uptake from aqua solutions, and regenerability conditions of the resulting resin were investigated.

EXPERIMENTAL

All the chemicals were analytical-grade chemical products (Fluka). They were used without any further purification.

Preparation of the Polymer

A required amount of DMB was dissolved in 10 mL DMF. While stirring at room temperature 1.0 mL

(15.0 mmol), ethylenediamine (EDA) was added to the above solution. A light yellow polymer precipitated in a few minutes. The mixture was heated at 60–70°C for 1 h and poured into 50 mL of 0.1 M HCl solution to remove soluble low molecular weight fragments.

After filtration, the polymer was dispersed in 100 mL of 2 M KOH solution. The free amine form of the polymer was filtered and washed with an excess of water and dried at 40°C for 24 h. Similarly, a series of polyamines composed of different molar ratios DMB/EDA: 0.8, 1.1, 1.25, and 1.5, was prepared with the yields of 82.7, 89.5, 91.6, and 96.0%, respectively.

Estimation of Accessible Amine Contents

The resin (DMB/EDA: 1.1), 0.5 g, was placed in a flask and 20 mL of 5 M HCl solution was added. The mixture was left overnight, while stirring. The excess of unreacted acid was titrated with 0.1 M NaOH solution in the presence of phenolphthalein as an indicator. The accessible amine content was calculated as 6.51 mmol NH₂/g resin.

Swelling Experiments

The swelling of the resin samples was found by the following procedure: Two identical circular pellets (250 mg) with a diameter of 1 cm and thickness of 3.4 mm are prepared by an IR pellet sampler. Each pellet is placed in a sintered glass funnel which is in a 100 mL volume of a glass bottle containing 50 mL tampon solution (pH 1.3 and 5.6). The bottle is sealed to prevent any CO₂ uptake which might cause shifts in pH. The pellets are allowed to stand in contact with the solution for 5 weeks at room temperature. From time to time, the glass funnels are taken out, filtered by suction, and weighed. The swelling ratios (w/w_0) found were recorded as a function of time (Fig. 1).

Metal-uptake Experiments

Simple batch kinetic experiments for metal sorptions were performed as follows: A 0.5 g sample of polyamine resin (with DMB/EDA: 1 : 1), was soaked into a 50 mL solution of one of the metal ions in 2.9×10^{-2} M concentrations, at a constant pH (4.4) which is adjusted by a tampon solution. The mixture was stirred gently and at appropriate times aliquots (1.0 mL) of the solution were transferred through filter paper into volumetric flasks, by means of a pipette. Sample solutions were made up

to 50 mL and metal contents were assayed by electrothermal-atomic absorption spectrometry (ET-AAS). Metal-sorption kinetics of the resin for different metal ions were pictured as shown in Figure 2.

Loading Capacity of the Resin for Various Metal Ions

To estimate maximum metal-binding capacities, 0.5 g of the resin sample (DMB/EDA: 1 : 1) was contacted with a 50 mL solution of the metal ion in a 0.2 M concentration, which is sevenfold in excess of the theoretical amount. The mixture was stirred for 30 min and filtered. The filtrate and washings were combined and diluted to 250 mL in a volumetric flask. Nonsorbed metal concentrations of these solutions were assayed by ET-AAS. The resulting metal loading data were tabulated as shown in Table I.

pH-Dependence of the Metal Uptakes

To investigate the pH dependence of the metal sorptions, 50 mL of each metal-ion solution ($2.9 \times 10^{-2} M$) at different constant pH's were interacted with 0.5 g resin (DMB/EDA: 1.1) for 30 min. The

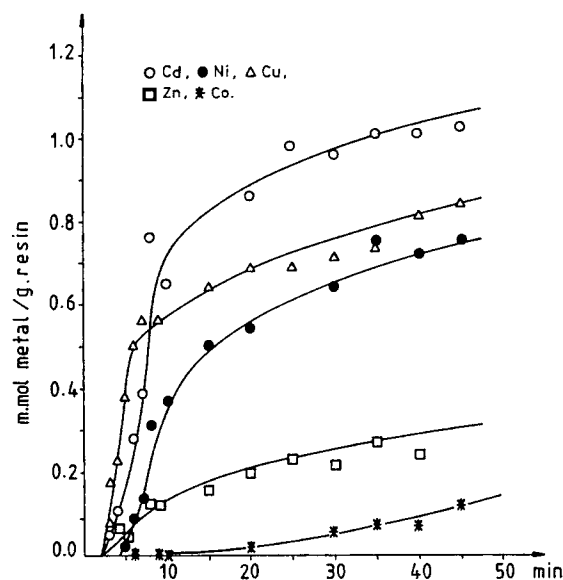


Figure 2 Metal-sorption kinetics of the resin (DMB/EDA: 1.1).

pH values (1.2, 3.8, 4.4, 5.6) were chosen below 6.5 so that none of the metal hydroxide precipitates.

The mixtures were filtered and washed with water. Metal contents of the filtrates were determined by ET-AAS. The pH dependence of the metal sorptions for various metal ions is depicted in Figure 3.

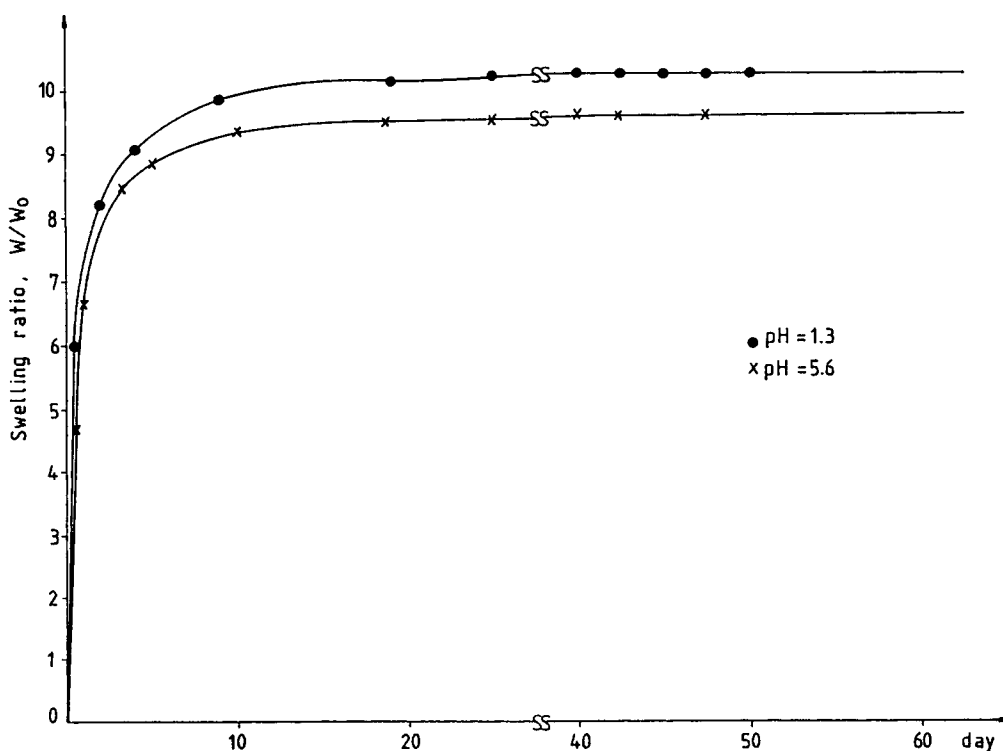


Figure 1 pH dependence swelling of the resin (DMB/EDA: 1.1).

Regeneration of the Resin

Regeneration of the resin samples loaded with metal ions was performed by interaction of concentrated HCl solutions (0.8M) for 3 h. This concentration is sufficient for elution of the sorbed metal ions. The higher acid concentrations cause the reducing of the metal-binding capacities in the next use. After filtration, the stripped metal contents of the filtrates were determined by the ET-AAS method. The amounts of stripped and absorbed metal ions were compared as shown in Table I.

The hydrochloride form of the resin was treated with 2M concentrations of 50 mL KOH solution for 30 min. The resulting free amine form of the resin was filtered, washed with an excess of water, and dried.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Resin

Interaction of EDA with DMB in DMF gives an insoluble white resin in a few minutes at room temperature. At different molar ratios of the components, insoluble resin always forms. However, here, the excess of DMB is expected to act as a crosslinker. This is because of the fact that the basicity of tertiary amines is higher than those of secondary ones. After filtration, the hydrochloride form of the resins can be transformed into the free amine state by a simple treatment with aqua alkali (Scheme 1).

In the IR spectra (with KBr disk) of the resulting resin, N—H stretching and bending vibrations are observed at 3300 and 1580 cm^{-1} . The swelling characteristics of the resins were followed in tampon solutions at different pH values. The pH-dependent swelling of the resins is shown in Figure 1. In acid solutions, the swelling rates and ratios are always higher than those in alkaline solutions, due to higher

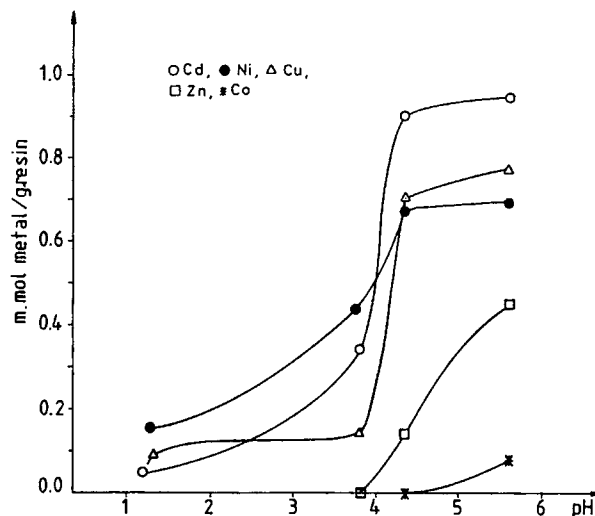


Figure 3 pH dependence of metal sorptions of the resin (DMB/EDA: 1.1).

dissociation of ionized amine groups. This is in accordance with the polyelectrolyte gel behavior.⁷

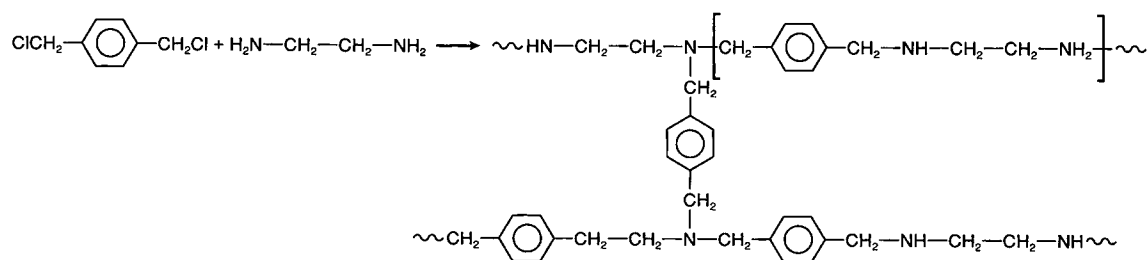
Metal Sorption

Metal-sorption experiments indicated that the resin studied shows a maximum loading capacity toward the Co(II) ion of 4.60 mmol/g resin (Table I). To find the intrinsic activity of the resin, ligating amine groups were determined by treating with hydrochloric acid and back-titration of the excess acid with NaOH solution. In this way, the accessible amine content was found to be 6.51 mmol per g resin. This amount is 56% of the theoretical amine content.

Taking into account the free amine groups, the number of amine groups coordinated with one metal ion was calculated to be in the 1.4–3 range for all metal ions. In ideal conditions, four or six amine groups coordinate with one metal ion, giving square planar, tetrahedral, or octahedral arrangements

Table I Metal Sorption Characteristics of the Polymer (DMB/EDA: 1 : 1)

	Accessible Amine Content (mmol/g resin)	Amine Content (mmol/g resin)	Max Loading (mmol metal/g resin)	pH	Stripped Metal Ion (mmol/g resin)	Amine (mmol)/ Metal (mmol)
Cu(II)	6.51	11.6	2.45	4	2.43	2.66
Ni(II)	6.51	11.6	2.51	5.7	2.40	2.60
Co(II)	6.51	11.6	4.60	6.9	4.52	1.41
Cd(II)	6.51	11.6	3.81	5	3.84	1.70
Zn(II)	6.51	11.6	2.20	5.5	2.14	2.96



Scheme 1 Polymerization of EDA and DMB.

around the metal ion. Since five-membered rings are the most stable, formation of five-membered metal chelates is most favored thermodynamically. In the case of 4- and 6-coordination, two and three five-membered rings must be formed, respectively. Tetracoordination results in two six-membered chelate rings. This might be either by intermolecular or intramolecular complexation. In the former case, the central metal ion locates between two polymer chains. However, this is difficult in crosslinked polymers due to less flexibility of the polymer chains.

Whereas in the latter case complexation requires the folding of polymer chains, rigidity of our polymer does not easily permit such a folding. For these reasons, tetracoordination is the uppermost limit for all transition-metal ions. Indeed, in the study, the number of coordinated amine groups per metal ion was found to be in the 1.4–3 range, which is consistent with the above prediction.

On the other hand, the lower limit of coordinated amines should be 2. Because once a metal ion coordinates with an amine group, the neighboring amine group must also be involved in the coordination. However, the Co(II) ion is ruled out because 1.41 mol of free amine groups is being incorporated into complexation with 1 mol of the Co(II) ion. Presumably, this is because of the precipitation of $\text{CoCl}(\text{OH})$ or $\text{Co}(\text{OH})_2$ in microholes of the resin. Indeed, when the polymeric resin is directly interacted with the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution, the pH of the mixture becomes 6.9, which is higher than those for the other metal ions and this pH is in the precipitation range of Co(II) basic hydroxides.

Structurally, these polymer-metal complexes must be outer-sphere complexes in which metal ions form cationic complexes, as depicted in Scheme 2. Being cationic complexes, these complexes must bear counteranions, chloride or hydroxide anions. To prove the presence of chloride counterions, the metal-sorbed resin was treated with a 0.05 M HNO_3 solution and AgNO_3 was added to the filtered solution. Precipitation of AgCl clearly indicates that chloride ions take part in outer-sphere complexation

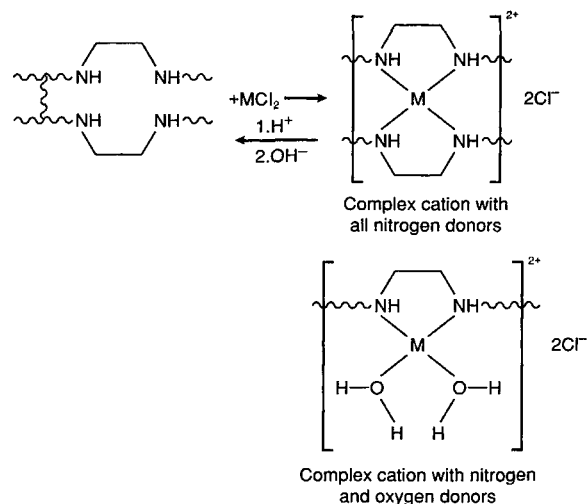
as counterions. This reveals that not only metal ions but also their counterions are being complexed by the resin, in accordance with those for low molecular weight amine ligands.

We also investigated the kinetics of metal sorptions. For this purpose, dilute metal solutions ($2.9 \times 10^{-2} \text{ M}$) which are equivalent to one-fourth of amine groups were interacted with resin samples at pH 4.4, which is adjusted by the tampon solution. This pH value was deliberately chosen so not to precipitate hydroxides of the metal ions. Kinetic data shows that Cd(II) uptake is faster than those of other metals. Also, the pH dependence of metal sorptions is in accordance with the kinetic data. When pH is above 4, the order of metal uptake follows as $\text{Cd} > \text{Cu} > \text{Ni} > \text{Zn} > \text{Co}$. From Figure 3, it is clearly shown that in the acidic region sorption of metal ions are drastically low. Obviously, this can easily be attributed to the cationic complex formation which is lower in acidic media.

Stripping of Metal Ions and Regeneration of the Resin

Decomplexation of metal ions from the loaded samples was carried out by hydrochloric acid (0.8 M). In the case of Cu, Ni, and Co, decomplexation can be followed visually by the disappearance of the characteristic colors of the polymer-metal complexes.

Three hours of interaction time with 0.8 M hydrochloric acid is enough for a complete stripping and the amounts of the stripping metal ions are almost the same with the sorbed amounts in the experimental error limits (Table I). A simple washing with 1 M NaOH solution followed with water is enough for the regeneration of the resin. But when the stripping is performed by using more concentrated HCl solutions (2 M), we observed that the metal-sorption capacity of the regenerated resins reduces drastically to about one-fifth of the original value.



Scheme 2 Cationic polymer-metal complexes with counteranions.

The reason for this result is unclear yet. Probably, the loss of the activity can be attributed to an acid-catalyzed heterocondensation reaction through phenyl rings in high acid concentrations. So, during regeneration, acid concentration should be kept below 1 *M* to avoid an activity loss. Probably this point is the only limitation in the use of this resin.

In conclusion, this amine resin presented has capabilities of high metal uptakes and regenerabilities. More important than these, it acts not only as a cation binder but also as an anion binder. In this way, cations and anions of transition-metal

salts are removed and this provides a complete cleaning up of aqua solutions. Moreover, since DMB itself is prepared from *p*-xylene and chlorine which are cheap, this resin might be of interest for the scale up.

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