

Synthesis of Polystyrene-Supported Dithiocarbamates and Their Complexation with Metal Ions

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ABSTRACT: The derivatives of 2%-divinylbenzene (DVB)-crosslinked polystyrene resins with *N*-ethylaminodithiocarbamate, *N*-ethanolaminodithiocarbamate, and *N*-*t*-butylamino-dithiocarbamate groups were prepared. The amine functionality was introduced to the acetylated polystyrene to give the imine-supported resins which were reduced by using NaBH₄ and then converted to the respective dithiocarbamates by reaction with carbon disulfide under alkaline conditions. The structure of the functionalized resins was confirmed by FTIR and elemental analysis. The ability of these polystyrene-dithiocarbamate resins to form complexes with Hg(II), Pb(II), and Cd(II) ions was found to be highest with Hg(II), followed by Pb(II), and then Cd(II). A

general increase in the ability to complex with metal ions was observed from the dithiocarbamate resin derived from *N*-*t*-butylamino polystyrene to those derived from *N*-ethylamino polystyrene and *N*-ethanolamino polystyrene. The complexation level and preference among ions of these dithiocarbamate resins depends on the structures of their functional groups. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 218–225, 2004

Key words: polystyrene; chelating agent; imine; dithiocarbamate-metal complexes; adsorption of metal ions; metal-polymer complexes

INTRODUCTION

Metal complexation behavior of polymer-supported ligands is critical to their use as analytical reagents and catalysts, and in applications related to pollution control.^{1,2} Chelating resins and water-soluble chelating polymers have been used for the selective removal and recovery of heavy metal ions from drinking and industrial water.³

Dithiocarbamates form a group of sulfur-containing ligands which have applications in many analytical and biological fields.^{4–6} They have been widely used for the collection of heavy metal ions from aqueous solutions, with the notable exception of alkali and alkaline earth metal ions.^{7,8} Many sulfur-containing chelators display strong affinities for certain transition and heavy metals [e.g., Cd(II), Pb(II), Hg(II)], as well as for some of the organometallic derivatives of these metals.^{9–13} Dithiocarbamates are known to form complexes of very high thermodynamic stability with several heavy metal ions, especially with Hg(II).^{12,14,15} It has been reported that only some noble metals form chelates of this type with similar or even higher thermodynamic stability.^{7,12,16} In addition to this, the substitution of Hg(II) for other metal ions in the form of

dithiocarbamate complex are reported to be extremely fast and quantitative for a number of metal ions (e.g., Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn).¹⁷

The present study is concerned with the synthesis of dithiocarbamates supported on functionalized polystyrene crosslinked with 2% divinylbenzene. Dithiocarbamates obtained from primary amines are less stable¹⁸ than those obtained from secondary amines which are fairly chemically stable under acidic conditions in the absence of oxidizing agents. Therefore, dithiocarbamates derived from secondary amine moieties were employed. Dithiocarbamates are difficult to prepare in pure form.¹⁹ Thus, these chelating groups were generated in the last synthetic step because of the simplified isolation of the macromolecular products. The complexation of these polystyrene-supported dithiocarbamates with Hg(II), Cd(II), and Pb(II) ions from aqueous solutions are investigated.

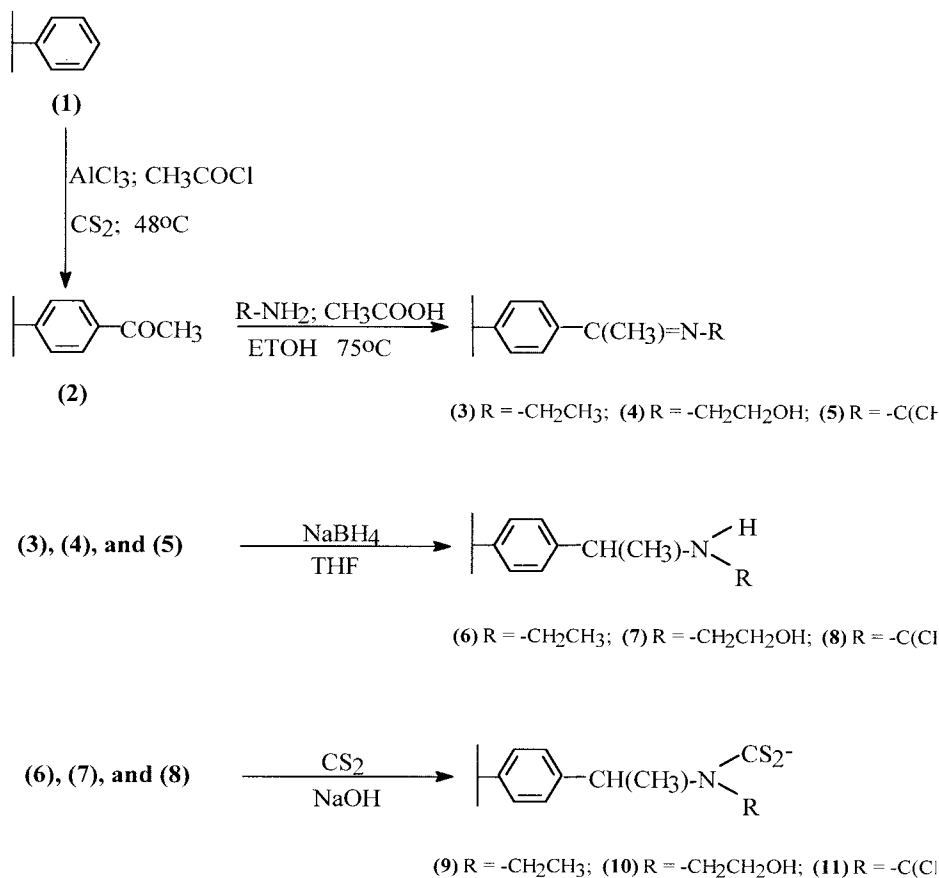
EXPERIMENTAL

Materials

Acetyl chloride (98%), carbon disulfide (CS₂) (99%), glacial acetic acid, ethanol (99%), hydrogen chloride (HCl), mercury acetate, sodium acetate (anhydrous), sodium hydroxide, sodium borohydride, tetrahydrofuran (THF), methanol, and 2% divinylbenzene polystyrene (DVB) beads, from Fisher Scientific (Pittsburgh, PA), as well as aluminum trichloride (99.9%), ethanolamine (EAA) (99%), ethylamine (EA), and *tert*-

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Scheme 1 Synthesis of dithiocarbamate chelators.

butyl amine (TBA), from Sigma Aldrich (St. Louis, MO), were used without further purification. Standard metal ion solutions were prepared with mercury nitrate, lead nitrate, and cadmium chloride, provided by Fisher Scientific.

Synthesis of polystyrene dithiocarbamates

The dithiocarbamate resins were synthesized from 2% DVB-crosslinked polystyrene in four reactions illustrated in Scheme 1. The dithiocarbamate functions were introduced in the acetylated polystyrene by the reaction of acetyl groups with selected amines. The secondary amino groups were formed on the resin by a reduction of the imine groups and then the resulting products were treated by carbon disulfide in alkaline solution to give the dithiocarbamate-supported polystyrene.

Acetylated polystyrene

Polystyrene (10.0 g; 96.0 mmol) was dissolved in 100 mL of carbon disulfide and slowly added to a three-necked flask containing carbon disulfide (50 mL), aluminum trichloride (25.0 g; 192.0 mmol), and

acetyl chloride (14.0 mL; 192.0 mmol) and was equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was allowed to reflux at 48°C in an oil bath for 2 h. The excess carbon disulfide was distilled out, and the semisolid mixture was added into 400 mL of ice-cold HCl (1.0M) to decompose the ketone- AlCl_3 complex. The product, which turned to a pale-yellow solid, was filtered and washed with NaOH (1.0M) and water several times, and then dried at 60°C under vacuum overnight. The weight of the product obtained was 13.12 g (93.5% yield).

Reaction with amine

The acetylated polystyrene (2.0g; 13.68 mmol) was swollen in 50 mL of ethanol for 15 min. Acetic acid (1.0 mL) and one of the primary amines [EA (3.10 mL; 54.72 mmol); EAA (3.31 mL); TBA (5.75 mL)] were added and the mixture was refluxed at 75°C for 24 h. The reaction mixture was filtered and subsequently washed with water, HCl (0.1M), water, and finally with methanol. The functionalized resins prepared from the reaction of EA, EAA, and TBA were designated as **3**, **4**, and **5**, respectively,

(Scheme 1) and were allowed to dry in a vacuum oven at 60°C overnight.

Reduction with Schiff base

Each of the imine resins (1.0 g) was swollen in 20 mL of THF in a Teflon-capped vial with vigorous stirring. The reaction mixture was placed in an ice bath to cool before adding NaBH₄ (1.0 g). The reaction mixture was stirred at room temperature and then filtered and washed several times with water to remove the excess NaBH₄ and then with methanol to yield the amine resins **6**, **7**, and **8**.

Dithiocarbamate (DTC) resins

The amino-functional polystyrene was suspended in 10 mL of 1.0M NaOH solution. The pH of the solution was measured to be between 10 and 12; 15.0 mL of 0.1M carbon disulfide solution in THF was added drop-wise to the reaction mixture and allowed to stir for 24 h at room temperature. Each of the products **9**, **10**, and **11** was filtered and washed several times with water, methanol, and finally with a 0.1M sodium acetate solution (pH = 8.0). The product was then air-dried.

Structural analysis

The infrared absorption spectrum of the resins in the form of pressed KBr pellets was obtained on a Perkin-Elmer 1600 series Fourier transform infrared (FTIR) spectrometer. The elemental analysis of oxygen, nitrogen, and sulfur contents in the acetylated, imine, and dithiocarbamate resins, respectively, were determined by Midwest Microlabs.

Complexation with metal ions

The functionalized resins were dried under vacuum at 60°C for 24 h before the complexation experiments. The resins were placed in 25 mL of a 25-ppm metal ion solution with constant stirring at 30°C. The concentration of the ions in the solution at specific time intervals was detected by using a Perkin-Elmer 2100 atomic adsorption spectrometer. The amount of absorbed ions, A (mg ion/g resin), of the functionalized resins were calculated as

$$A_t = \frac{V(C_i - C_t)}{W} \quad (1)$$

where A_t is the complexation capacity of the functional resin (mg/g); C_i and C_t are the concentrations (mg/L) initially and at a specific time, respectively; V

is the volume (L) of the aqueous ion solution, and W is the weight (g) of the functionalized resins.

RESULTS AND DISCUSSIONS

Structural confirmation of functional fibers

The dithiocarbamate functions were introduced in the acetylated polystyrene by a three-step reaction. The first step involves the incorporation of the amino groups at the end of the acetyl group by reacting PS-COCH₃ with EAA, EA, and TBA in ethanol, a good swelling solvent for PS, at 75°C in an oil bath for 24 h. Reduction of the imino group allowed the introduction of the dithiocarbamate chelators into the resin.

In Figure 1(a), the spectrum of the starting material polystyrene **1**, has peaks due to the C—H stretching vibration between 3200 and 2800 cm⁻¹. The peaks at 1600 and 1493 cm⁻¹ are assigned to the C=C stretching in the aromatic ring. The acetylated polystyrene **2** is characterized by a strong carbonyl absorption at 1682 cm⁻¹. Following the reaction with selected amines, the structure of all three imine-reacted resins was confirmed by FTIR measurements [Fig. 1(b)]. The imino polystyrene resins **3**, **4**, **5** exhibited strong absorption bands at 1667 cm⁻¹, which is due to the C=N stretch of the imine group. Resin **4** also showed a broad band centered at 3440 cm⁻¹ that is due to the —OH stretch of the terminal group. The imine-functional resins were converted to the corresponding dithiocarbamates **9**, **10**, and **11** by first a reduction of the imine, followed by a reaction with carbon disulfide in alkaline solution. The introduction of the dithiocarbamate groups into the resins is characterized by the disappearance of the absorption at 1667 cm⁻¹, the C=N stretch. The dithiocarbamate resins showed absorptions mainly in two regions. The absorption bands in the region ~ 1500 cm⁻¹ is associated with the thioureide vibration and is attributed to the C—N vibration of the CS₂—NR₂ bond. A second IR spectral region between 1070 and 1000 cm⁻¹ is associated with the CSS vibration [Fig. 1(c)].

The structure of the 2% DVB-crosslinked polystyrene resins containing the acetylated, imine, and dithiocarbamate functional groups are also confirmed by elemental analysis (Table I). The elemental contents of oxygen, nitrogen, and sulfur give the percentage of conversion of functional groups in the acetylated, imine, and dithiocarbamate polystyrene resins, respectively. The percentage of conversions for the resins were normalized to 100% (based on the original polystyrene) (Table I).

The molar content of acetylated styrene units C_A (mol/g) in the acetylated polystyrene resin can be calculated as

$$C_A = \frac{(A/M_{PS})X}{(A/M_{PS}(1-X)M_{PS} + (A/M_{PS})XM_{APS}} \quad (2)$$

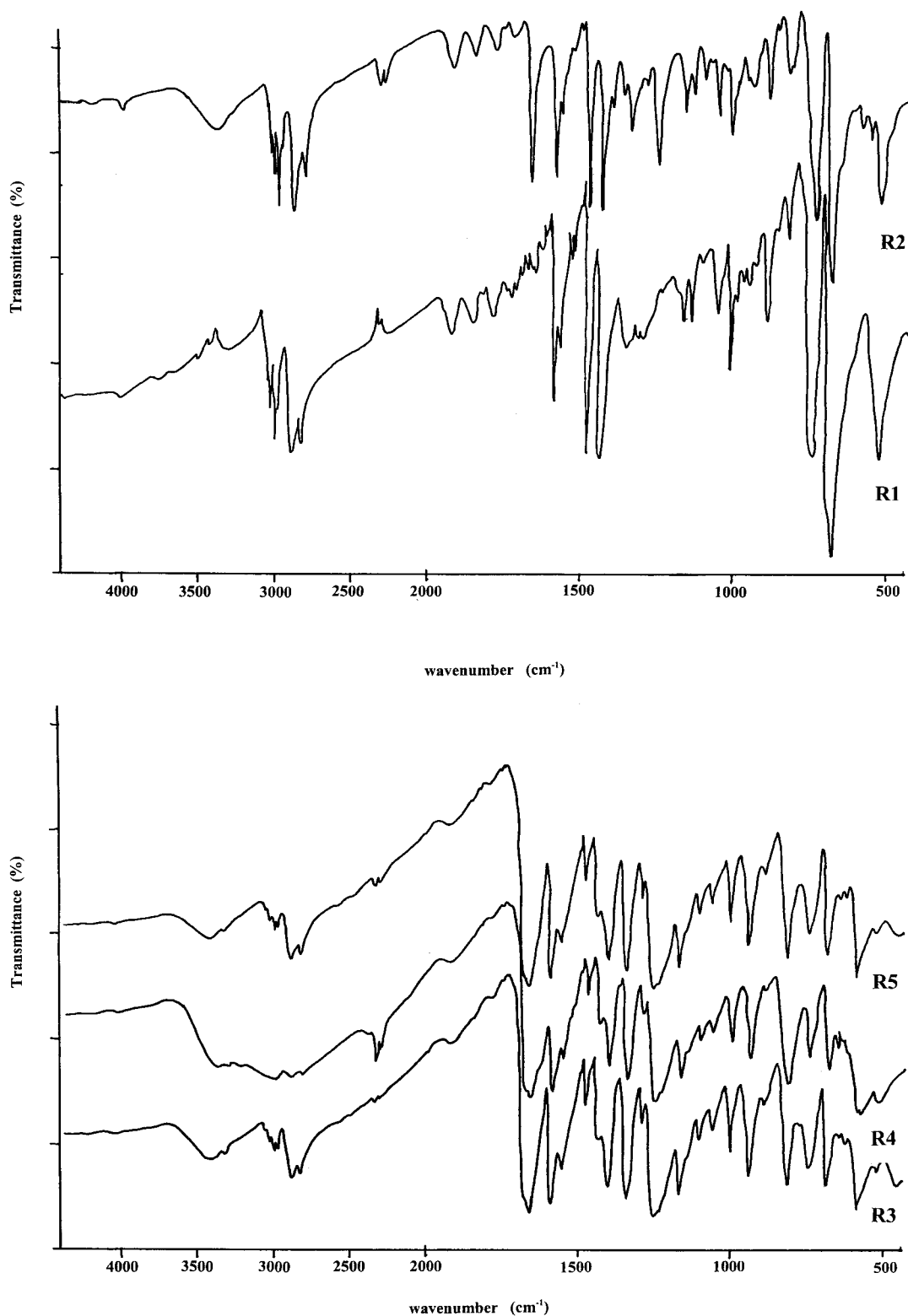


Figure 1 FTIR spectra of the polystyrene and functionalized PS: (a) 1, 2% DVB-crosslinked polystyrene; 2, acetylated polystyrene; (b) 3, 4, 5; (c) 9, 10, 11.

where A is grams of polystyrene resin used; M_{PS} is the molecular weight of styrene units; M_{APS} is the molecular weight of acetylated styrene unit; and X

is conversion of styrene units to acetylated styrene units in the resin (mol %). Equation (2) can be simplified to

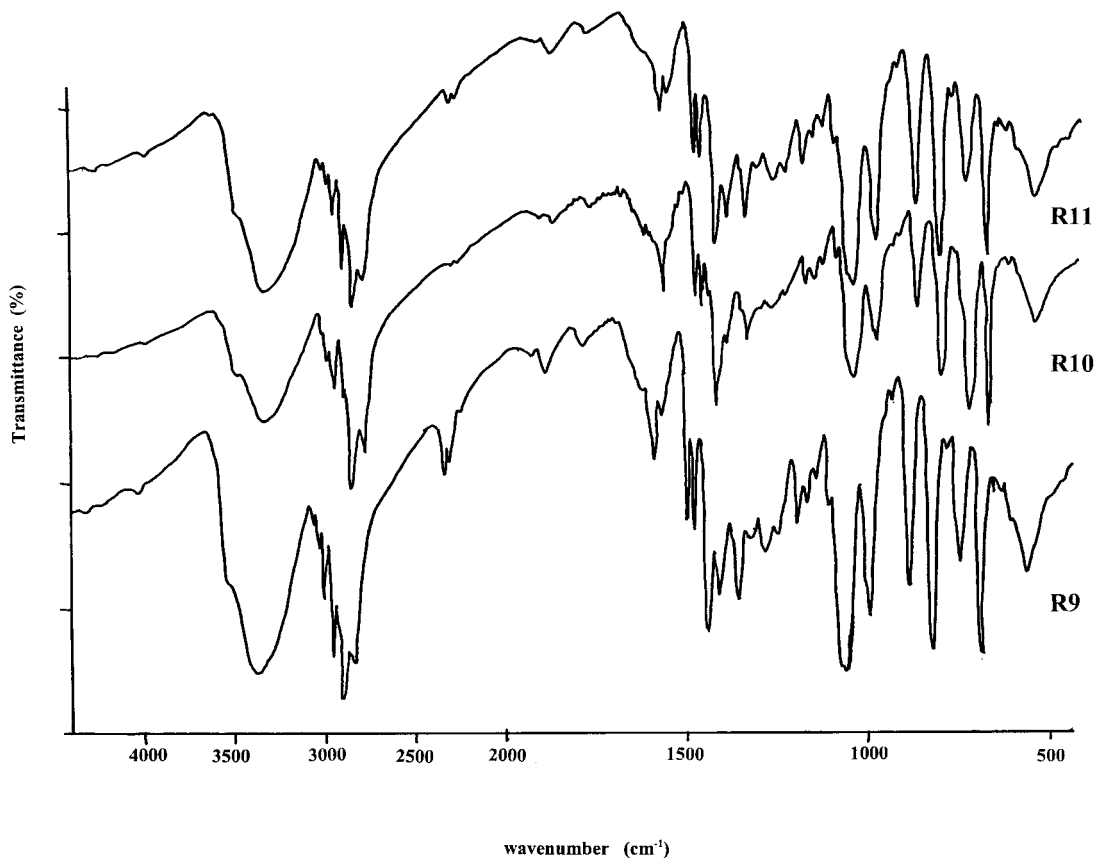


Figure 1 (Continued)

$$C_A = \frac{X}{(1 - X)M_{PS} + XM_{APS}} \quad (3)$$

Because each acetylated styrene resin has only one oxygen atom, then C_A is equal to the mole content of oxygen (mol/g) obtained from elemental analysis. Then from eq. (2), X can be calculated.

The molar content of imine styrene units C_B (mol/g) in imine polystyrene resin can be calculated as

$$C_B = \frac{C_A B Y}{(B - B C_A M_{APS}) + (1 - Y) C_A B M_{APS} + C_A B Y M_{IPS}} \quad (4)$$

TABLE I
Structures of Resins

Resin	Elemental analysis			Conversion (mol %)		
	O (%)	N (%)	S (%)	Acetylation	Imination	DTC
2	10.58	—	—	87.34	—	—
3	—	6.44	—	—	69.3	—
4	—	6.62	—	—	86.4	—
5	—	6.58	—	—	83.7	—
9	—	—	11.08	—	—	35.6
10	—	—	11.84	—	—	40.2
11	—	—	11.96	—	—	—

where B is grams of acetylated polystyrene used; M_{PS} is the molecular weight of styrene units; M_{APS} is the molecular weight of acetylated styrene units; M_{IPS} is the molecular weight of imino styrene units; and Y is the conversion of the acetylated styrene units to imine styrene unit in resin (mol %). Equation (4) can be simplified further to give

$$C_B = \frac{C_A Y}{1 + Y C_A (M_{IPS} - M_{APS})} \quad (5)$$

Because each imine styrene resin has only one nitrogen, the C_B equals the mole content of nitrogen (mol/g) obtained from elemental analysis. Y is then calculated from eq. (5).

The molar content of dithiocarbamate units C_D (mol/g) in the dithiocarbamate polystyrene resin was calculated as

$$C_D = \frac{C_B D Z}{(D - D C_B M_{IPS}) + C_B D (1 - Z) M_{IPS} + C_B D Z M_{DPS}} \quad (6)$$

where D is grams of imine polystyrene used; M_{IPS} is the molecular weight of imine styrene unit; and M_{DPS}

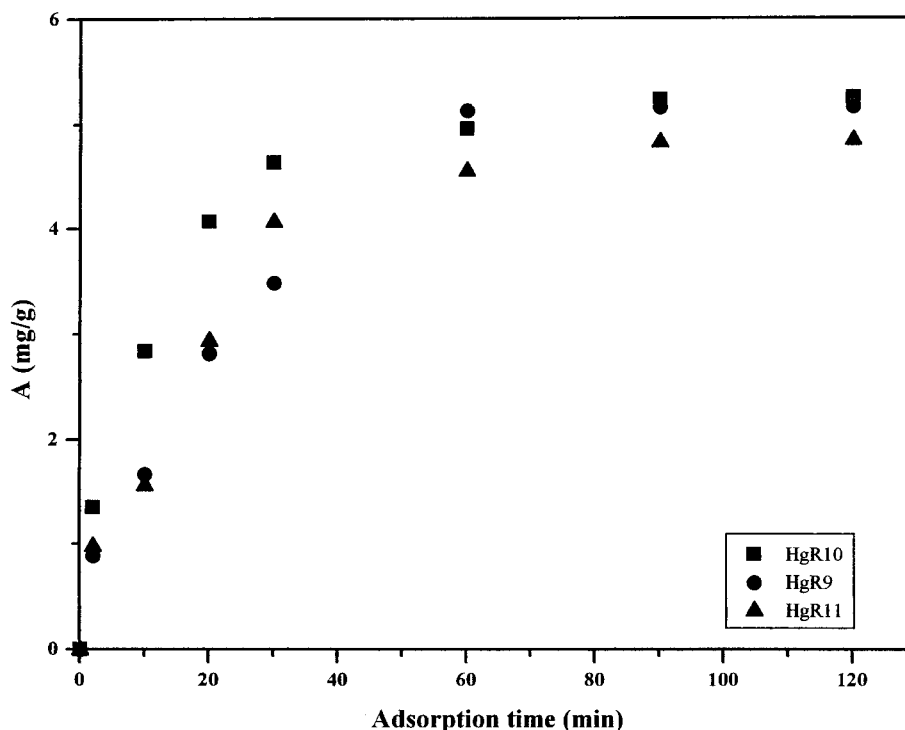


Figure 2 Complexation of Hg(II) ion on dithiocarbamates functionalized PS (30°C, 25 ppm): (●, 9; ■, 10; ▲, 11).

is the molecular weight of dithiocarbamate styrene units. Equation (6) can be simplified as

$$C_D = \frac{Z}{(1/C_B - M_{IPS}) + (1 - Z)M_{IPS} + ZM_{DPS}} \quad (7)$$

Because each dithiocarbamate styrene resin has two sulfur atoms, C_D is calculated by dividing the elemental content of sulfur by 2. Z can be calculated from eq. (7).

Complexation with metal ions

The complexation behavior of these polystyrene-supported dithiocarbamate resins toward Hg(II), Pb(II), and Cd(II) ion was investigated. Metal ion complexation on each of the dithiocarbamate resins occurred quickly upon immersion and reaches equilibrium within 30 min. The high rate of complexation at the low temperature (30°C) and ionic concentration (25 ppm) appears to be very promising.

Figure 2 shows the complexation of Hg(II) ions on dithiocarbamate resins 9, 10, and 11. During the initial 20 min, the Hg(II) ion complexation rate on dithiocarbamate resin 10 was higher than those observed for 9 and 11. After 60 min, Hg(II) complexation on product 11 became lower than 9 and 10, which are similar. This could be due to the steric hindrance of the bulky tertiary group, which can cause a hindrance in the complexing ability of the

metal ion. Overall, these DTC resins show a high affinity for mercuric ion.

The ability of resins 9, 10, and 11 to complex with Pb(II) ion shows consistently decreasing order of 10 > 9 > 11 (Fig. 3). This higher complexation on 10 may be due to the electron donor atom in the —OH terminal group and its higher hydrophilicity. 11 forms the lowest amount of complex because of steric hindrance of its end group.

The complexation of Cd(II) ions on the DTC resins occurred more gradually than Hg(II) ion during the first 30 min (Fig. 4). The complexation continued to increase but did not reach equilibrium within 60 min. The Cd(II) uptake by 10 is again more remarkable than those by 9 and 11 resins which adsorbed similarly.

The ability of all the polymeric dithiocarbamates to complex with metal ions was found to be much higher for Hg(II) than for Pb(II) and Cd(II). There was a general increase in the complexing ability observed going from the dithiocarbamate resin 11 derived from *N-t*-butylamino polystyrene to the dithiocarbamate resins 9 and 10 derived from *N*-ethylamino polystyrene and *N*-ethanolamino polystyrene, respectively. The 9 and 11 dithiocarbamate resins adsorbed the metal ion at similar rates.

The metal ion intake for dithiocarbamate resin 11 was less compared to resins 9 and 10 for each of the metal ions. This could be due to the steric hindrance of

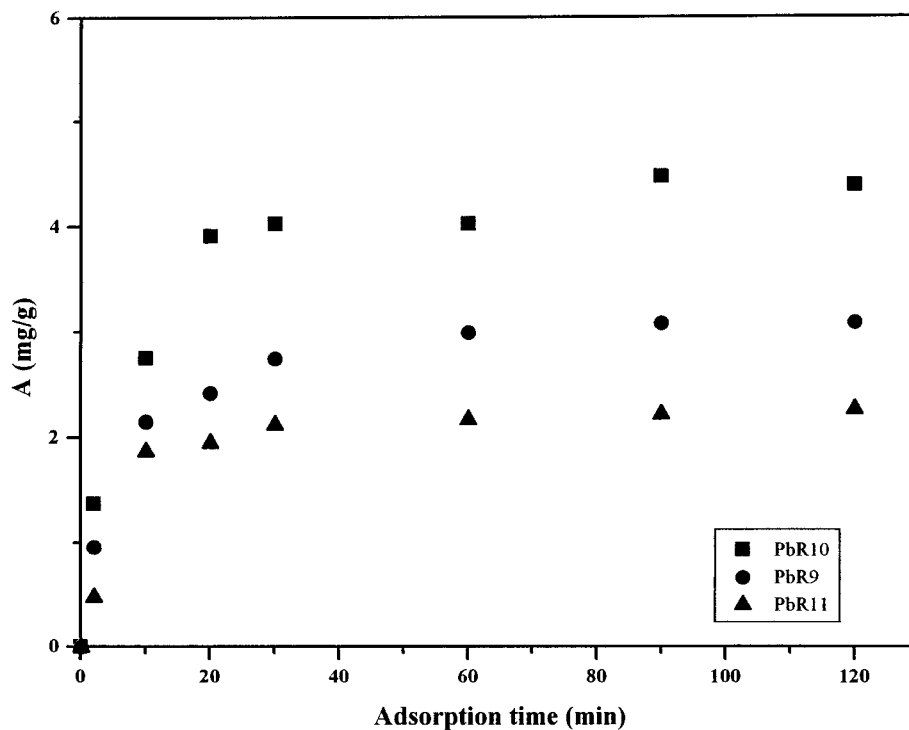


Figure 3 Complexation of Pb(II) ion on dithiocarbamates functionalized PS (30°C, 25 ppm): (●, 9; ■, 10; ▲, 11).

the bulky tertiary group in 11, which may have caused a reduction in the complexing ability of the metal ions. The ability to complex with metal ions follows a general order of Hg(II) > Pb(II) > Cd(II).

CONCLUSION

Chelating resins containing dithiocarbamate groups were synthesized and characterized for their capacity

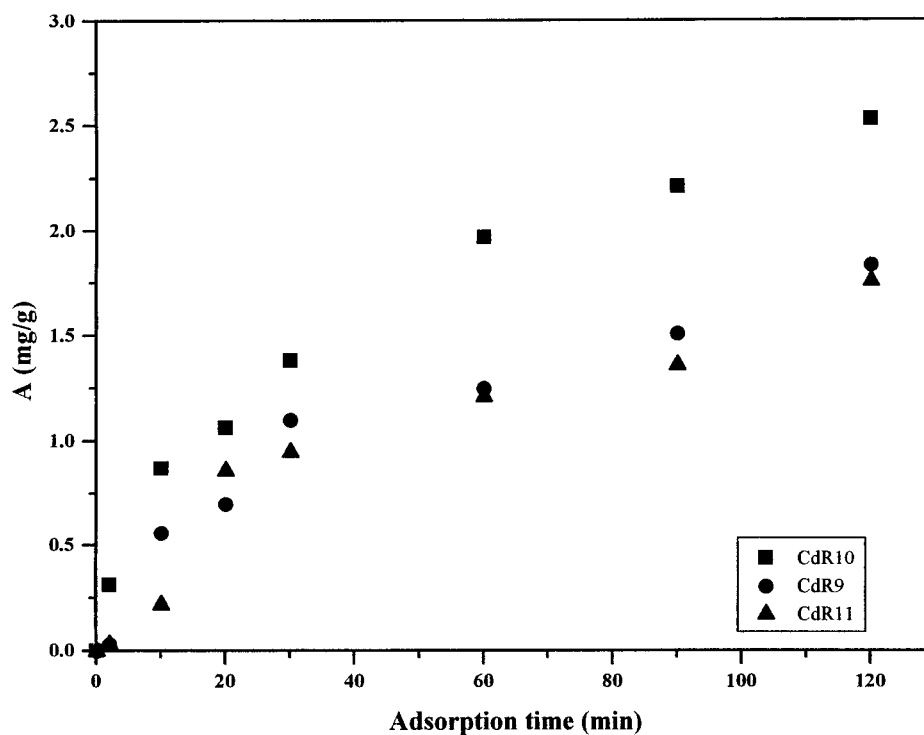


Figure 4 Complexation of Cd(II) ion on dithiocarbamates functionalized PS (30°C, 25 ppm): (●, 9; ■, 10; ▲, 11).

to adsorb heavy metal ions from aqueous medium. The imine functionality was first introduced to the crosslinked polystyrene resin by reacting the acetylated polystyrene with selected amines. These imine-functionalized polystyrene resins were converted to the respective dithiocarbamates by reduction of the imine group, followed by the reaction with carbon disulfide in the presence of alkali.

The metal complexation ability of the resulting insoluble polystyrene-dithiocarbamates was investigated toward Hg(II), Pb(II), and Cd(II) ions. The dithiocarbamate resin derived from *N*-ethanolamino polystyrene **10** showed a remarkable effect toward Hg(II) ion compared to that of Pb(II) and Cd(II). There was general decreasing metal complexation from the DTC resins derived from *N*-ethanolamino polystyrene **10** to those derived from *N*-ethylamino polystyrene **9** and *N*-*t*-butylamino polystyrene **11**. This could be due to the higher hydrophilicity of **10** than **9** and **11**. The electron donating nature of the —OH terminal group on the ligand of **10** also enhances the ionic complexation. The metal ion intake for dithiocarbamate resin **11** was less compared to **9** and **10**. This could be due to the steric hindrance of the bulky tertiary group, which may have caused a reduction in the complexing ability of the metal ions. The trend for these dithiocarbamate resins to form complexes with metal ions is in the descending order of Hg(II) \gg Pb(II) $>$ Cd(II). This investigation on the synthesis of the different polystyrene-supported dithiocarbamates and their complexation behavior indicates that the incorporation of dif-

ferent end-group structures in the ligands can impart unique characteristics to their abilities to form complexation with metal ions.

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