Cyclic Dithia/Diaza with Dual Schiff Base Linkage Functionalized Polymers for Heavy Metal Adsorption

Pradit Nutthanara,[1,2] Wittaya Ngeontae,[3] Apichat Imyim,[2] Thanapong Kreethadumrongdat[2]

[1]Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[2]Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[3]Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

ABSTRACT: Three new types of functionalized polystyrene-divinylbenzene resins containing two sulfur and two nitrogen atoms and four nitrogen atoms in cyclic form were prepared by using two lab-synthesized ligands; 2-[3-(2-amino ethylsulfanyl)-propylsulfanyl]-ethylamine (AEPE) and 2-[2-(2-amino-ethylsulfanyl)-ethylsulfanyl]-ethylamine (AEEE), and a commercial one; triethylenetetramine (TETA). Chloromethylated polystyrene-divinylbenzene copolymer (Cl-PS-DVB) was initially oxidized to aldehydic polystyrene-divinylbenzene (CHO-PS-DVB) with approximately 57% yield. CHO-PS-DVB was subsequently reacted with the ligands through dual Schiff base linkage. The products were named AEPE-PS-DVB, AEEE-PS-DVB and TETA-PS-DVB, respectively. The optimum coupling reaction times and temperatures were 6 h at 50°C for AEPE-PS-DVB, AEEE-PS-DVB and 6 h at room temperature for TETA-PS-DVB. The appropriate amount of the three ligands was 2.65 mmol/g CHO-PS-DVB corresponding to the mole ratio between the chelating ligand and aldehyde group of 1 : 2. All derivative resins were characterized by elemental analysis, thermogravimetry, FT-IR and FT-Raman spectroscopy and Ninhydrin test. The adsorption properties of the synthesized resins towards Pb(II), Cu(II), Cd(II), Zn(II), Ni(II), Co(II) and Cr(III) ions in aqueous solution were preliminarily investigated by batch method. AEPE-PS-DVB and AEEE-PS-DVB showed the same sorption behavior. Their selectivity order was Pb(II) > Zn(II) > Cu(II) > Cd(II) and no significant adsorption for Co(II), Ni(II), Cr(III) was observed. In addition, TETA-PS-DVB showed a selectivity toward only Pb(II). © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 801–809, 2010

Key words: chelating resin; heavy metals; extraction; Schiff base

INTRODUCTION

Functionalized polymers have a variety of chemical functional groups attached to the polymer backbone. They combine latent advantages of small molecules of functional groups and physical properties of polymers. They have been used in wide applications, such as catalysts, reagents in synthetic reaction, and separations.[1] In particular, they are used in solid phase extraction (SPE) for metal ions from water.[2–4] Polymeric sorbents, which are selective towards a specific metal ion, have been developed during the past several decades.[3] Most of these studies involved the hard-soft acid-base principle (HSAB) utilizing different donor sites of the chelating moiety. Indeed, geometry, flexibility and orientation of electron donor groups in molecules of chelating ligands are the main focus to control selectivity of metal adsorption.[5] The study using both principles—HSAB and geometry—will provide an attractive way to prepare a selective SPE adsorbent.[6] Although many types of polymers have been used as a polymeric solid sorbent, the most widely used solid support is polystyrene-divinylbenzene (PS-DVB) owing to its chemical and physical stability.[2,3]

There are two common methods in preparing chelating polymers. The first one involves physical sorption of chelating ligands onto polymers; the second method is covalent coupling of ligands to polymer backbones through a spacer arm. The latter approach is preferred due to absence of ligand leaching. Several articles on development of chelating polymers with different chelating ligands have been reported in the recent past. For example, acetylated PS-DVB was coupled with 1-hydrazinophthalazine, and its selectivity toward Fe(III) was observed.[7] Amberlite XAD-2 resins loaded with various chelating ligands for preconcentration of heavy metal ions in aqueous samples were developed. The studied ligands were, for example, pyrocatechol,[8]

chromotropic acid and thiosalicylic acid,[9] and Nitroso R salt (disodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate).[10] The study of macromolecules such as calix[4]arene-semicarbazone derivative covalently linked with commercially available Merrifield's resin for separation of La(III), Ce(III), Th(IV), and U(VI) from aqueous solution was reported.[11] The reaction of chloromethylated polystyrene with 2-mercapto ethanol yielded poly[4-vinylbenzyl-(2-hydroxyethyl)] sulfoxide (PVBSO) and poly[4-vinylbenzyl-(2-hydroxyethyl)] sulfone (PVBSO2). The results showed that PVBSO had good adsorption and selectivity for Au(III), Pd(II) and Cu(II), whereas PVBSO2 adsorbed only Cu(II).[12] Functionalized Amberlite XAD-4 resin using a coupling reaction with dibromosuccinic acid after acetylation was also synthesized for preconcentration and separation of U(VI).[13] XAD-4 bound to salen [N,N'-bis(salicylidene)ethylenediamine] by diazonium coupling reaction was studied for the separative concentration of Cu(II), Pb(II), and Bi(III) from an aqueous solution.[14] Recently, our research group reported the synthesis of benzothiazole-based PS-DVB for the extraction and preconcentration of Cd(II), Cu(II), and Pb(II) from aqueous solution,[15] and the synthesis of Amberlite XAD-2 with purpurin for the extraction of Cd(II), Cr(III), and Pb(II) from leachate of cement-based stabilized waste.[16]

From the literature, few chelating polymers based on both principles of HSAB and geometry were developed. In this context, our research aims to synthesize new chelating polymers containing 2N and 2S as donor atoms concerning the geometry of the chelating ligands. Furthermore, the synthesis of chelating polymers that have two Schiff-base groups and 2N atoms in ligand was also conducted. The metal ion adsorption property of synthetic polymers was tested with Pb(II), Cd(II), Cu(II), Zn(II), Ni(II), Co(II), and Cr(III) ions in aqueous solution.

EXPERIMENTAL METHOD

Apparatus

Nuclear magnetic resonance (NMR) spectrometer (Varian Mercury 400) was used for the characterization of the synthesized ligands. Infrared and Raman spectra were recorded on a Fourier transforms infrared (FTIR) spectrometer (Nicolet Impact 410) and a Fourier transforms Raman (FT-Raman) spectrometer (Perkin-Elmer Spectrum GX). A CHNS/O analyzer (Perkin-Elmer PE 2400 Series II) was used for elemental analysis. Thermogravimetric measurements were taken using a simultaneous thermal analyzer (Netzsch 409) at a heating rate of $10°C/min$ under nitrogen atmosphere. A flame atomic absorption spectrometer (Perkin-Elmer AAnalyst 100) was used for the deter-

Scheme 1 Synthesis of AEEE and AEPE ligands.

mination of metal concentrations using an air-acetylene flame. The pH measurements were made on digital pH meter (pH211 Hanna instruments).

Materials and reagents

The reagents used in the synthesis were chloromethylated styrene-divinylbenzene copolymer 1% crosslinked, 100–200 mesh, 4.42 mmol Cl/g (Aldrich), cysteamine hydrochloride (Fluka), 1,2-dibromoethane (Merck), 1,3-dibromopropane (Merck), sodium metal (Fluka), and ethanol absolute anhydrous (Mallinckrodt, Baker). All chemicals were used without further purification. Purified grade solvents such as 1,4-dioxane, dichloromethane, dimethyl sulfoxide, and methanol were used. Working metal solutions were freshly prepared by stepwise dilution of 1000 mg/L stock standard solution (BDH Laboratory Supplies). The pH of the solution was adjusted with 1% (v/v) HNO_3 and 1% (w/v) KOH. All solutions were prepared by using deionized water with resistance higher than 18 MΩ cm. All reagents were of analytical grade.

Preparation of chelating agents

Synthesis of 2-[3-(2-amino-ethylsulfanyl)-propylsulfanyl]-ethylamine (AEPE)

The synthesis procedure (Scheme 1) was adapted from Choudhury et al.[17] Sodium metal (1 g, 43 mmol) was dissolved in absolute ethanol (20 mL) and then cooled to 15°C. The cool solution was added to cysteamine hydrochloride (2.3 g, 20 mmol) and stirred for 15 min under nitrogen atmosphere. 1,3-Dibromopropane (1.0 mL, 9.8 mmol) was added and stirred for 4 h at 40°C. The mixture was evaporated and then sodium hydroxide (5 g in 15 mL water) was added. The solution was kept in a refrigerator overnight. The solution was extracted with dichloromethane and washed with water. The solution was evaporated by a rotary evaporator. The oily yellow product was obtained and characterized by ^{1}H-NMR, ^{13}C-NMR, and FTIR.

^{1}H-NMR δ in ppm: 1.77 (2H, t, $CH_2CH_2CH_2$, J = 7.02 Hz), 2.53 (8H, t, SCH_2, J = 6.24 Hz), 2.78 (4H, t, CH_2NH_2, J = 6.24 Hz).

^{13}C-NMR δ in ppm: 29.40 (1C, $CH_2\mathbf{C}H_2CH_2$), 30.46 (2C, $S\mathbf{C}H_2CH_2NH_2$), 36.18 (2C, $CH_2CH_2\mathbf{C}H_2S$), 41.02 (2C, $NH_2\mathbf{C}H_2CH_2$).

FTIR (KBr disk) in cm^{-1}: 3354–3280 (N—H stretching), 1592 (primary amine N—H bending), 1069 (primary amine C—N stretching), 2856–2915 (aliphatic C—H stretching), 1344 (aliphatic C—H bending).

Synthesis of 2-[2-(2-amino-ethylsulfanyl)-ethylsulfanyl]-ethylamine (AEEE)

This reaction was prepared by the same methodology as AEPE, but 1,3-dibromopropane was replaced with 1,2-dibromoethane (1.0 mL, 11.6 mmol), and cysteamine hydrochloride (2.7 g, 23.6 mmol) was used (Scheme 1). The oily yellow liquid was obtained and characterized by ^{1}H-NMR, ^{13}C-NMR, and FTIR.

^{1}H-NMR δ in ppm: 2.83 (4H, t, NH$_2$CH_2CH$_2$, J = 6.24 Hz), 2.67 (4H, s, SCH_2CH$_2$S), 2.60 (4H, t, SCH_2CH$_2$NH$_2$, J = 6.24 Hz).

^{13}C-NMR δ in ppm: 41.18 (2C, NH$_2$**C**H$_2$CH$_2$), 36.36 (2C, SCH$_2$**C**H$_2$S), 31.92 (2C, S**C**H$_2$CH$_2$NH$_2$).

FTIR (KBr disk) in cm^{-1}: 3349–3285 (primary amine N—H stretching), 1591 primary amine (N—H bending), 1072 (primary amine C—N stretching), 2907–2817 (aliphatic C—H stretching), 1452 (aliphatic C—H bending).

Preparation of resins

Aldehydic styrene-divinylbenzene copolymer (CHO-PS-DVB)

Chloromethylated styrene-divinylbenzene copolymer (Cl-PS-DVB, 5 g) was stirred in dimethyl sulfoxide (40 mL) and sodium bicarbonate (2.11 g) for 6 h at 155°C.[18] The resin was then filtered, washed with dimethyl sulfoxide, hot water, and dioxane-water (2 : 1), then rinsed with dioxane, acetone, ethanol, chloroform, and benzene. The resin was dried at 100°C under vacuum, labeled as CHO-PS-DVB (Scheme 2).

Preparation of functionalized resins; AEPE-PS-DVB, AEEE-PS-DVB, and TETA-PS-DVB

The CHO-PS-DVB (1 g) was swelled in dichloromethane (10 mL) for 1 h. AEPE (0.5131 g, 2.65 mmol) or AEEE (0.4761 g, 2.65 mmol) in 10 : 1 dichloromethane-acetonitrile (30 mL) or TETA (0.3860 g, 2.65 mmol) in dichloromethane (30 mL) was added dropwise over a period of 30–45 min using an addition funnel with constant stirring. The mixture was refluxed under N$_2$ for 2–6 h at room temperature and 50°C. The solid was filtered, washed thoroughly with methanol, dichloromethane, and vacuum dried, labeled as AEPE-PS-DVB, AEEE-PS-DVB, and TETA-PS-DVB, respectively (Scheme 2).
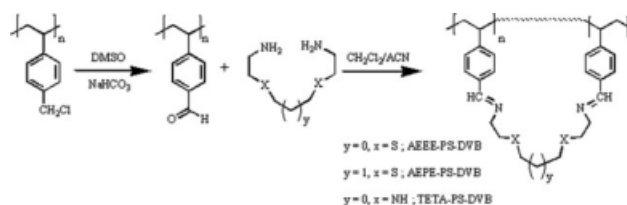
Scheme 2 Synthesis of polystyrene containing Schiff base.

Metal adsorption study

The study of metal adsorption of chelating resins was done in batch method. The effect of pH on metal adsorption was studied. An aliquot of Pb(II) solution (5 mg/L, 5.0 mL) was pipetted into a test tube after being adjusted its pH ranging from 1.0 to 7.0. TETA-PS-DVB, AEPE-PS-DVB, or AEEE-PS-DVB (0.050 ± 0.001 g) was added, and the mixture was shaken for 1 h to ensure the adsorption equilibrium. The solid resin was separated and the remaining amount of Pb(II) in the solutions was determined by flame atomic absorption spectrometry (FAAS). The studies of Zn(II), Ni(II), Cu(II), Cd(II), Co(II), and Cr(III) adsorption were performed in the same manner but their initial concentrations were 3, 1, 1.5, 2, 4, and 4 mg/L, respectively.

RESULTS AND DISCUSSION

Preparation of aldehydic polymer

Polystyrene-divinylbenzene with aldehyde functional groups (CHO-PS-DVB) has been first prepared by oxidizing chloromethylated PS-DVB (Cl-PS-DVB) with dimethyl sulfoxide and sodium bicarbonate. CHO-PS-DVB was characterized to investigate specifically the presence of aldehyde group. The FTIR spectrum of CHO-PS-DVB (Fig. 1) showed two important peaks that were significantly different from the spectrum of Cl-PS-DVB. These were an intense C=O absorption band at 1695 cm^{-1} and aldehydic C—H stretching absorption at 2718 cm^{-1}. However, the weak band of C—Cl stretching peak is ascribed to the remaining chloride groups appearing at 669–705 cm^{-1}. To estimate a yield of oxidation reaction, the aldehyde group on CHO-PS-DVB was transformed into oxime by reacting with excess hydroxylamine hydrochloride (0.3 g) in pyridine (5 mL) for 6 h at 90–100°C. Conversion of CHO-PS-DVB into its oxime (Oxime-PS-DVB) seemed to be quantitative because the FTIR spectrum of Oxime-PS-DVB did not show any C=O stretching absorption peak (Fig. 1-I). From the elemental analysis of Oxime-PS-DVB, it was shown that this resin contained 3.52% nitrogen content that corresponds to 2.51 mmol of aldehyde group/g resin. This indicated a yield of 57% for oxidation of Cl-PS-DVB.
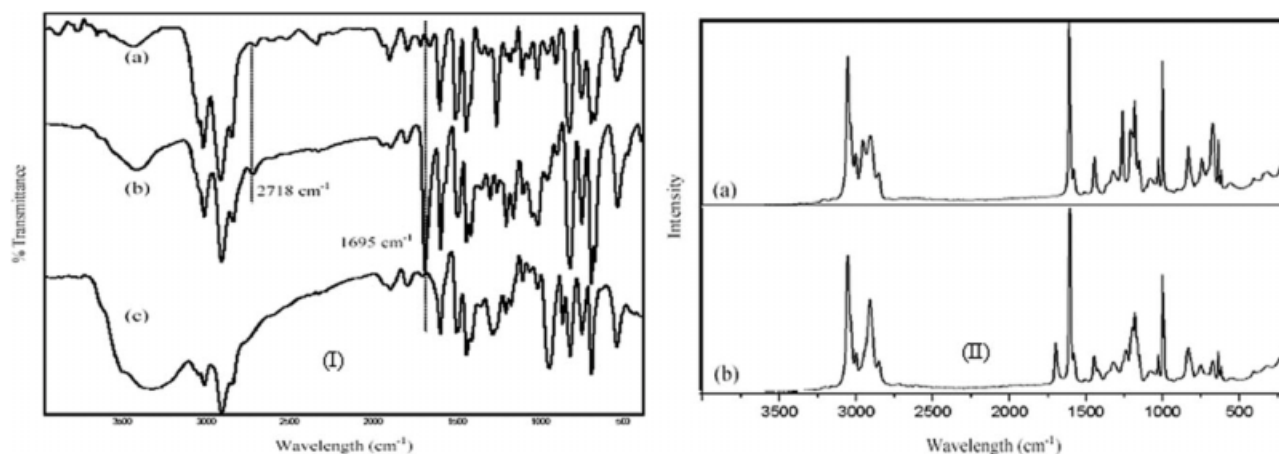
Figure 1 (I) FTIR spectra of (a) Cl-PS-DVB, (b) CHO-PS-DVB, and (c) Oxime-PS-DVB; and (II) FT-Raman spectra of (a) Cl-PS-DVB and (b) CHO-PS-DVB.

Raman spectra (Fig. 1-II) showed agreeable results to FTIR spectra. The important peak is C=O vibration at 1698 cm^{-1}; aldehydic C—H stretching scattering was observed as weak scattering at 2715 cm^{-1}; and the remaining C—Cl peaks with weak intensity at 636–673 cm^{-1}.

Preparation of PS-DVB containing Schiff-base ligands

The conditions of the reaction such as reaction times, amount of chelating ligands, and reaction temperature were studied. The progress of reaction was followed by FTIR spectroscopy. The reaction progress could be observed by the disappearance of the C=O absorption band at 1695 cm^{-1} and the appearance of a new C=N absorption band at 1645 cm^{-1}. The starting amount of chelating ligands was calculated by assuming that the yield of oxidation of Cl-PS-DVB was 100%, so the aldehyde group was obtained at 4.42 mmol/g resin. According to Scheme 2, the mole ratio between chelating ligand and aldehyde group should be 1 : 2. Thus, the minimum amount of chelating ligands of 2.21 mmol/g resin was required.

PS-DVB containing Schiff-base AEPE ligand, AEPE-PS-DVB

The reaction time was varied initially between 0 and 6 h at room temperature with 2.65 mmol AEPE/g resin (1.2 times of stoichiometrical amount). The intensity of the C=O absorption band decreased slightly with increasing reaction time from 2 to 6 h. The appropriate reaction time was chosen at 6 h to obtain a more complete reaction.

Subsequently, at the appropriate reaction time, the reaction was performed at room temperature and at 50°C with different amounts of AEPE (2.65, 3.32, 3.87, and 4.42 mmol/g resin). The experimental

results (Fig. 2) indicate that increasing in the amount of chelating ligand did not decrease the C=O absorption band significantly. When comparing non-refluxed and refluxed experiments, the intensity of C=O absorption band at 1695 cm^{-1} for each amount of AEPE decreased slightly (Fig. 2-II). In addition, there was no significant decrease in intensity of the C=O absorption band when the amount of ligand increased. Thus, 2.65 mmol AEPE/g resin were enough. However, the reaction was preferably refluxed for ensuring a complete reaction.

PS-DVB containing Schiff-base AEEE ligand, AEEE-PS-DVB

AEEE-PS-DVB was synthesized from the reaction between AEEE and CHO-PS-DVB. The reaction time was fixed at 6 h. The reaction condition was studied in the same manner as AEPE-PS-DVB. The appropriate amount of 2.65 mmol AEEE/g resin and reaction temperature at 50°C were achieved similar to AEPE-PS-DVB.

PS-DVB containing Schiff-base TETA ligand, TETA-PS-DVB

TETA-PS-DVB was synthesized from the reaction between TETA and CHO-PS-DVB. The reaction time at 6 h was chosen from the preparation of AEPE-PS-DVB. The studied parameters in the preparation of TETA-PS-DVB were the amount of TETA and the reaction temperature.

When increasing the starting amount of TETA, the FTIR spectra (Fig. 3) of the products did not differ. In addition, the overall FTIR spectra of the products synthesized at room temperature (Fig. 3-I) and at 50°C (Fig. 3-II) were not significantly different. In conclusion, the preparation of TETA-PS-DVB could be achieved with the amount of TETA at 2.65
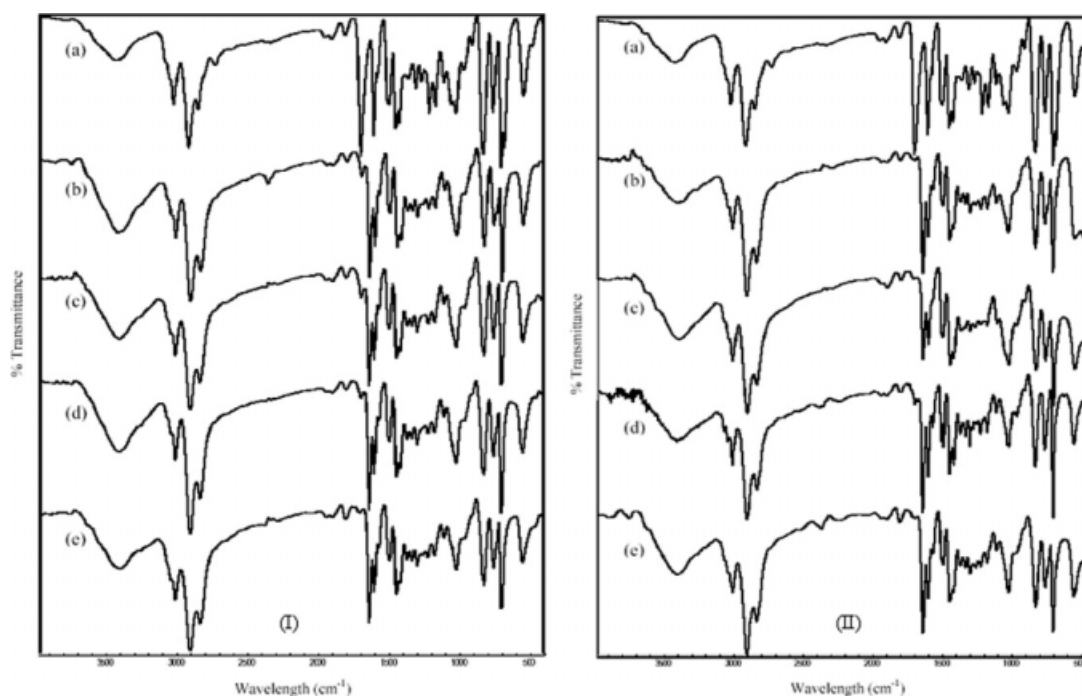
Figure 2 FTIR spectra of the reaction mixture of CHO-PS-DVB at (I) room temperature and (II) 50°C with different amounts of AEPE (a) 0, (b) 2.65, (c) 3.32, (d) 3.87, and (e) 4.42 mmol/g resin.

mmol/g resin and a reaction time for 6 h at room temperature.

Characterization of the synthesized resins

FT-Raman spectroscopy

Raman spectra of three chelating resins (Fig. 4) showed similar results as FTIR spectra. The spectra of all chelating resins were almost similar with the spectrum of CHO-PS-DVB, but there was the appear-

ance of important peaks such as C=N vibration at 1642 cm^{-1} and the disappearance of C=O stretching peak at 1698 cm^{-1}. However, there was some remaining chloromethyl group as observed by the weak intensity of C—Cl peak at 636 and 673 cm^{-1}.

Elemental and thermogravimetric analyses

The nitrogen contents of the AEEE-PS-DVB, AEPE-PS-DVB, and TETA-PS-DVB resins from elemental
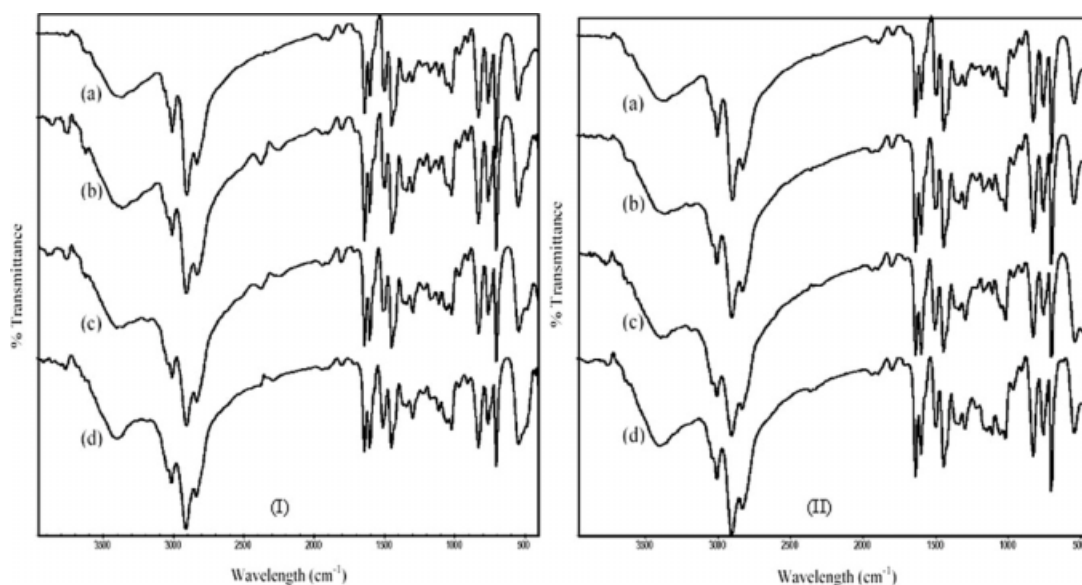

Figure 3 FTIR spectra of the reaction mixture of CHO-PS-DVB (I) at room temperature and (II) at 50°C with different amount of TETA (a) 2.65, (b) 3.32, (c) 3.87, and (d) 4.42 mmol/g resin.
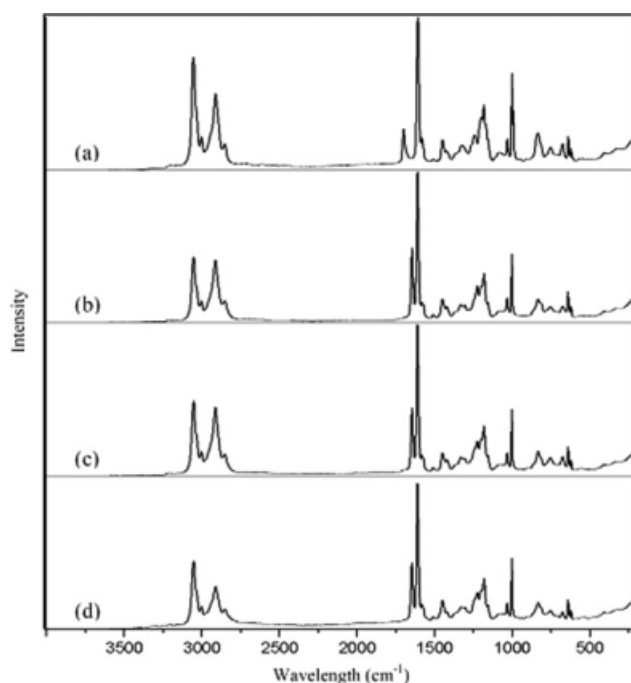
Figure 4 Raman spectra of (a) CHO-PS-DVB, (b) AEPE-PS-DVB, (c) AEEE-PS-DVB, and (d) TETA-PS-DVB.

analysis were 0.97, 1.31, 3.19 mmol/g, respectively. To investigate thermal stability of the synthesized chelating polymers, TGA measurements were applied. The TGA curves (Fig. 5) were similar to that of CHO-PS-DVB, but they showed lower weight loss. All chelating resins showed maximum weight loss in the region of $\sim$ 350–450 °C, which might be a degradation of polymeric backbone. From Figure 5, it was observed that the CHO-PS-DVB thermogram showed $\sim$ 8% weight loss in the region of 150–250°C. Although AEPE-PS-DVB and AEEE-PS-DVB thermograms showed a weight loss in the region of 240–310°C, the percentage weight loss of the former was 1% more than the latter. For TETA-PS-DVB, the weight loss in this region could not be observed. The thermograms indicated that the chelating resins were more thermally stable than CHO-PS-DVB.

Ninhydrin test

The Ninhydrin test is a rapid, simple, and sensitive method for the qualitative analysis of free-terminal amino groups.[19,20] The reaction is based upon the development of color between a free amino group and ninhydrin reagent (yellow solution). The Ninhydrin method was applied to detect the uncoupled terminal amine group of the chelating ligands. If there is any free primary amine, treatment with ninhydrin should result in a dramatic deep blue color; if not, the color would not change. The results showed that all synthesized chelating resin beads retained their original color and the solution was

brownish yellow. A control test was done in parallel using PS-DVB impregnated with the ligands, and a deep blue solution was observed. This finding confirms that the coupling of two terminal amine groups on the ligands with aldehydic moieties on the resins (Scheme 2) was complete.

Metal adsorption study

Adsorption behavior in different pHs

The metal adsorption property of the chelating resins was studied by batch method. The studied metal ions were Pb(II), Cu(II), Cd(II), Zn(II), Ni(II), Co(II), and Cr(III). The adsorption of metal ions with chelating ligand moiety onto the resins is based on chelation. The pH of the solution is one of the effect factors because most chelating ligands are a conjugated base of weak acid and have a very strong affinity for hydrogen ions. Thus, in this study, only the effect of solution pH was investigated. The initial pHs of metal ion solution varied from 1–7; higher pH was not performed due to precipitation of metal hydroxide. The results of metal adsorption are illustrated in Figure 6.

The Pb(II) sorption of all chelating resins increased when the pH of solutions increased. In acidic solution, donor N and S atoms in chelating moiety that act as electron donors might be protonated, resulting in positive charge and very low ability to bind with Pb(II) ion. When the pH of solution was increased, the donor sites were deprotonated, resulting in better binding ability toward Pb(II). However, at pH 3 and 4, TETA-PS-DVB could extract Pb(II) better than the other two chelating resins. Indeed, the Pb(II) ion is a borderline Lewis acid that prefers to bind with the N atom rather than the S atom.[21] At pH higher than 4, this phenomenon was not affected. The sorption behaviors of both AEPE-PS-DVB and AEEE-PS-
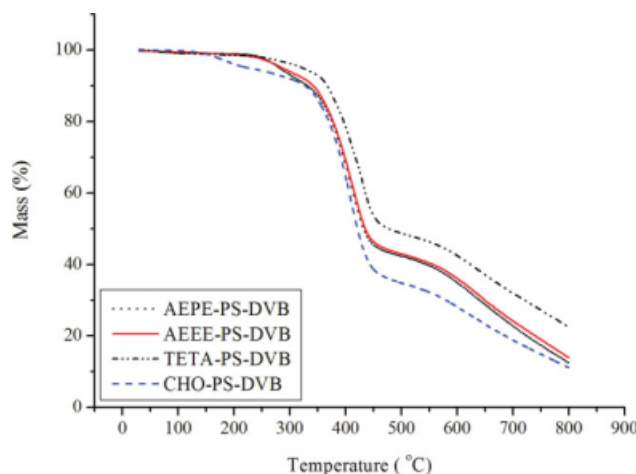

Figure 5 TGA thermograms of resins. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
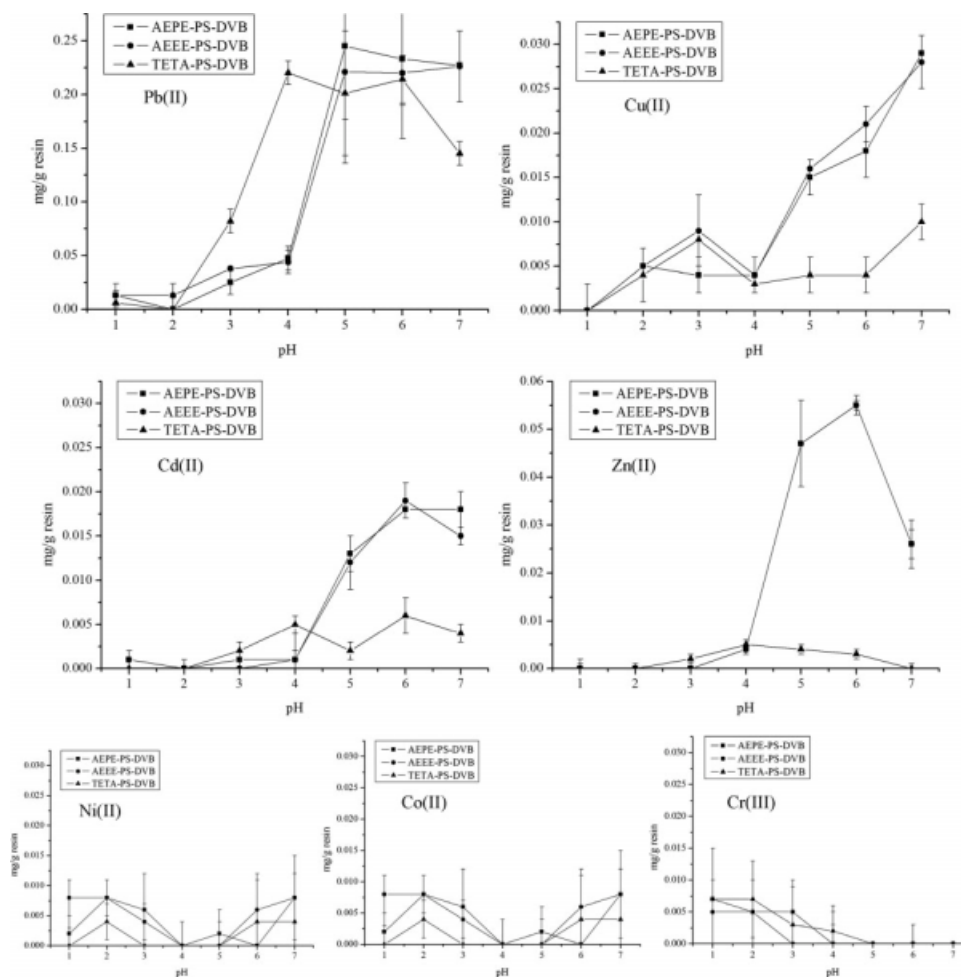
Figure 6 Effect of solution pH on metal ion sorption onto chelating resins ($n = 3$).

DVB were similar. The optimum pH values on Pb(II) sorption of AEPE-PS-DVB, AEEE-PS-DVB and TETA-PS-DVB were 5–7, 5–7, and 4–6, respectively.

The sorption of Cu(II) of all chelating resins, except TETA-PS-DVB, increased when the pH of the solutions increased. The effect of pH to the sorption of chelating resins could be discussed in the same manner as Pb(II) sorption. The trends of metal sorption of AEPE-PS-DVB and AEEE-PS-DVB were similar. The optimum pH values on Cu(II) sorption of AEPE-PS-DVB, AEEE-PS-DVB, and TETA-PS-DVB were 5–7, 5–7, and 7, respectively. The sorption behaviors of synthesized chelating polymers toward Cu(II) are probably due to the nature of N donor atoms in the ligand moiety in TETA-PS-DVB classified between borderline and hard ligand. Therefore, Cu(II), which is a borderline/soft cation, was not a preferable ion to be chelated.

The sorption behaviors of the three resins toward Cd(II) were similar to Cu(II) sorption. TETA-PS-DVB extracted Cd(II) in very low amounts, probably due to the fact that N donor atoms in TETA-PS-DVB are harder than S atoms. In addition, Cd(II) is a very

soft acid and thus would prefer softer S atoms. The optimum pH values on Cd(II) sorption of AEPE-PS-DVB and AEEE-PS-DVB were ~ 6–7.

The Zn(II) sorption behaviors of all the resins were similar to Cu(II) and Cd(II) sorption. TETA-PS-DVB adsorbed Zn(II) in a very low amount. The optimum pH values on Zn(II) sorption of AEPE-PS-DVB and AEEE-PS-DVB were the same at 5–6.

The extraction of Ni(II), Co(II), and Cr(III) were not significantly different upon the pH. The amounts of the metals extracted were low, or no extractions were observed. This might be explained by the fact that Ni(II) and Co(II) are borderline cation and possess affinity for oxygen and sulfur containing ligands. Meanwhile, Cr(III) is hard cation that could not be coordinated by the borderline and soft donor atoms in chelating ligand moiety.

Selectivity of resins

The principles of HSAB and geometry are used to describe the selectivity that depends on ionic or dipole-dipole interactions or complexation stability
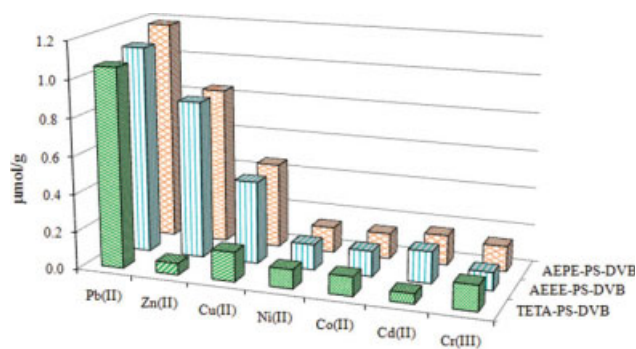
Figure 7 Maximum metal sorption of the resins. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

between the metal ions and the ligand moiety on the resins. Pb(II), Zn(II), Cu(II), Ni(II), and Co(II) ions are borderline cations that possess affinity for both hard and soft ligands. The hierarchy of softness is Pb(II) > Zn(II) > Cu(II) > Ni(II) > Co(II). By considering the types of donor atoms in chelating ligands, they can be classified as soft base (R2S) and borderline bases (C=N, R2NH). AEPE-PS-DVB and AEEE-PS-DVB have the same donor atoms (C=N and S), but the cavity size of AEPE-PS-DVB is slightly bigger and more flexible due to the propylene bridge between the two sulfur atoms. In addition, AEEE-PS-DVB and TETA-PS-DVB have nearly the same cavity size of the chelating ligand ring but differ in donor atoms. The soft Lewis base order could be AEPE-PS-DVB ∼ AEEE-PS-DVB > TETA-PS-DVB. These characteristics could be assumed to affect the selectivity of the resins toward metal ions. The proper metal ion should be coordinated by the proper chelating resin.[5] In this experiment, the selectivity of chelating resin could be estimated by observing the maximum metal sorption (in µmol/g resin) at optimum pH. The results are shown in Figure 7.

AEPE-PS-DVB and AEEE-PS-DVB showed similar sorption behavior. The order of maximum sorption capacity is Pb(II) > Zn(II) > Cu(II) > Cd(II). No significant extraction for Co(II), Ni(II), Cr(II) was observed. Indeed, the Pb(II) ion is the softest-borderline acid and it prefers soft-borderline ligands. By contrast, Cr(III) is a hard cation and does not prefer to bind with these chelating resins.

The difference in structure of TETA-PS-DVB and AEEE-PS-DVB is only two nitrogen atoms. TETA-PS-DVB shows the highest selectivity toward the Pb(II) ion, whereas it could not adsorb the other ions. This behavior is probably attributed to the appropriate ionic radius of Pb(II) ion that fits the cavity of the ligand. In this study, it can be remarked that the Pb(II) ion is only one ion that is not a transition metal ion. It shows the highest selectivity of all three resins and this might result from the strongest covalent or coordination bonds because of the most electronegative element.[21]

The possible chelate structure between metal ions and chelating resins is one in which metal ions would bind to the nitrogen and sulfur atoms of the chelating ligand moiety on the resins to form tetradentate metal complexes as shown in Figure 8.

CONCLUSIONS

Cyclic dithia (2S) and diaza (2N) with dual Schiff-base linkage functionalized polymeric resins were prepared by surface modification of aldehydic polystyrene-divinylbenzene (CHO-PS-DVB) with chelating ligands. Two chelating ligands; 2-[3-(2-amino-ethylsulfanyl)-propylsulfanyl]-ethylamine (AEPE) and 2-[2-(2-amino-ethylsulfanyl)-ethylsulfanyl]-ethylamine (AEEE), were synthesized through nucleophilic substitution reaction. Subsequently, AEPE, AEEE, and one commercially available ligand (triethylenetetramine (TETA)) were reacted with CHO-PS-DVB to prepare three chelating resins: AEPE-PS-DVB, AEEE-PS-DVB, and TETA-PS-DVB. The characterization by FTIR, FT-Raman, and TGA techniques as well as ninhydrin test confirmed the expected synthetic products. The synthesized resins were subject to metal adsorption study. The optimum pHs for metal sorption on the chelating resins were achieved. The sorption behavior of both AEPE-PS-DVB and AEEE-PS-DVB resins was similar. The selectivity order is Pb(II) > Zn(II) > Cu(II) > Cd(II),
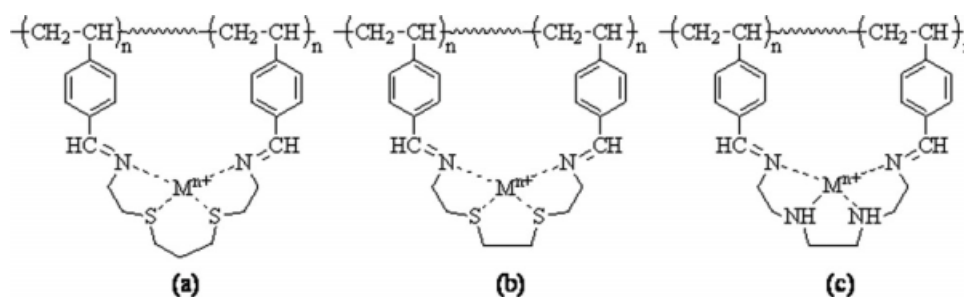

Figure 8 Proposed chelate structures of metal ions with (a) AEPE-PS-DVB, (b) AEEE-PS-DVB, and (c) TETA-PS-DVB.

Co(II), Ni(II), Cr(II). Further, TETA-PS-DVB showed a high selectivity toward Pb(II).

The success of this research can be attributed to Environmental Analysis Research Unit.

References

1. Akelah, A.; Moet, A. Functionalized Polymers and Their Applications; Chapman and Hall: London, 1990.
2. Leon-Gonzalez, M. E.; Perez-Arribas, L. V. J Chromatogr A 2003, 902, 3.
3. Camel, V. Spectrochim Acta B 2003, 58, 1177.
4. Lemos, V. A.; Teixeira, L. S. G.; Bezerra, M. A.; Costa, A. C. S.; Castro, J. T.; Cardoso, L. A. M.; Jesus, D. S.; Santos, E. S.; Baliza, P. X.; Santos, L. N. Appl Spectrosc Rev 2008, 43, 303.
5. Constable, E. C. Coordination Chemistry of Macrocyclic Compounds; Oxford University Press Inc.: New York, 1999.
6. Ngeontae, W.; Aeungmaitrepirom, W.; Tuntulani, T.; Imyim, A. Talanta 2009, 78, 1004.
7. Pathak, R.; Rao, G. N. Talanta 1997, 44, 1447.
8. Tewari, P. K.; Singh, A. K. Talanta 2001, 53, 823.
9. Tewari, P. K.; Singh, A. K. Talanta 2002, 56, 735.
10. Lemos, V. A.; Santos, J. S.; Nunes, L. S.; Carvalho, M. B.; Baliza, P. X.; Yamaki, R. T. Anal Chim Acta 2003, 494, 87.
11. Jain, V. K.; Handa, A.; Pandya, R.; Shrivastav, P.; Agrawal, Y. K. React Funct Polym 2002, 51, 101.
12. Qu, R.; Sun, C.; Wang, C.; Ji, C.; Sun, Y.; Guan, L.; Yu, M.; Cheng, G. Eur Polym J 2005, 41, 1525.
13. Meltida, P.; Sanghamitra, K.; Gladis, J. M.; Naidu, G. R. K.; Rao, T. P. Talanta 2005, 65, 192.
14. Kim, Y. S.; In, G.; Han, C. W.; Choi, J. M. Microchem J 2005, 80, 151.
15. Meesri, S.; Praphairaksit, N.; Imyim, A. Microchem J 2007, 87, 47.
16. Wongkaew, M.; Imyim, A.; Eamchan, P. J Hazard Mater 2008, 154, 739.
17. Choudhury, S. B.; Ray, D.; Chakravorty, A. Inorg Chem 1991, 30, 4354.
18. Frechet, J. M.; Schuerch, C. J Am Chem Soc 1971, 93, 492.
19. Kaiser, E.; Colescott, R. L.; Bossinger, C. D.; Cook, P. I. Anal Biochem 1970, 34, 595.
20. Kono, K.; Fukui, T.; Takagishi, T.; Sakurai, S.; Kojima, C. Polymer 2008, 49, 2832.
21. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. Advanced Inorganic Chemistry, 6th ed.; Wiley: New York, 1993.