Synthesis and Separation Properties for Cu(II)-Ni(II) of Macroporous Crosslinked Polystyrene-Supported Triethylenetetramine Resin Using Cu(II) as Template

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ABSTRACT: A new method for preparing a novel macroporous chelating resin that has good adsorption capability for Cu(II) and high selectivity for it with the coexistence of Ni(II) was introduced in this article. First, the aminated resin (PS-TETA) was synthesized by the reaction of crosslinked macroporous chloromethylated polystyrene with triethylenetetramine. Subsequently, PS-TETA was coordinated with Cu(II) and then PS-TETA-Cu was obtained. After the crosslinking reaction of PS-TETA-Cu with epoxy chloropropane, the adsorbed Cu(II) was removed by chlorhydric acid, and then the target resin-Cu(II) template triethylenetetramine crosslinked polystyrene resin was obtained. The selectively sorption tests for Cu(II) showed that the sorption capacity was as high as 1.6 mmol/g and the selectivity coefficient $\alpha_{Cu(II)/Ni(II)}$ could reach to 9.06 with the coexistence of Ni(II). SEM and nitrogen adsorption at 77 K methods were used to characterize the porous structure of the resin. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 963–967, 2007

Key words: macroporous polymers; polyamides; templates; selectivity; adsorption

INTRODUCTION

It is well-known that chelating resins with complex ligands containing nitrogen especially polyamine have excellent sorption selectivity for heavy metal ions due to the strong affinity between nitrogen atom and these metal ions. So, they were widely used in the purification of the industrial effluent containing heavy metal ions.[1–11] The sorption of these chelating resins for metal ions was nonselective, so they can only be used in treating industrial effluent rather than in separating one kind of metal ion from another one.

Recently, the ''metal ion-templated method'' was used to prepare novel chelating resins possessing special selectivity for specific metal ions.[12] The common

synthesis process is as follows: first, the monomers react with the metal ions to form coordination compound. Subsequently, the coordination compound was polymerized and crosslinked. Finally, the metal ions were removed from the polymeric matrix and the novel resin was obtained. We have prepared several chitosan resins using Cu(II) and Ni(II) as template, and studied their capabilities for metal ions such as Cu(II), Ni(II), and Co(II).[13–15] The results showed that the resins had better sorption capabilities for both Cu(II) and Ni(II) than the nontemplate ones, while the sorption selectivity for the two metal ions was unsatisfactory (the selectivity coefficients were less than 2). Ramazan and coworkers prepared a reactively fibrous adsorbent by graft copolymerization of methacrylic acid (MAA)/acrylamide (AAm) monomer mixture onto poly(ethylene terephthalate) (PET) fiber.[16] The competitive adsorption tests verified that the selectivity coefficient $\alpha_{Cu(II)/Ni(II)}$ of the reactive fiber was 4.10 and the sorption capacity for Cu(II) was only about 0.2 mmol/g. He and his coworkers prepared some novel chelating resins containing polyethylene polyamine using Cu(II) and Ni(II) as template ions.[17] They found that the resins had good sorption and separation capabilities for Cu(II) and Ni(II). But the resins they obtained were breakable and their mechanical stability was poor.[17,18]

According to the reports on the syntheses of chelating resins by metal ion-templated method, most of them are gel-type resins but macroporous ones. However, macroporous-chelating resins can adsorb metal
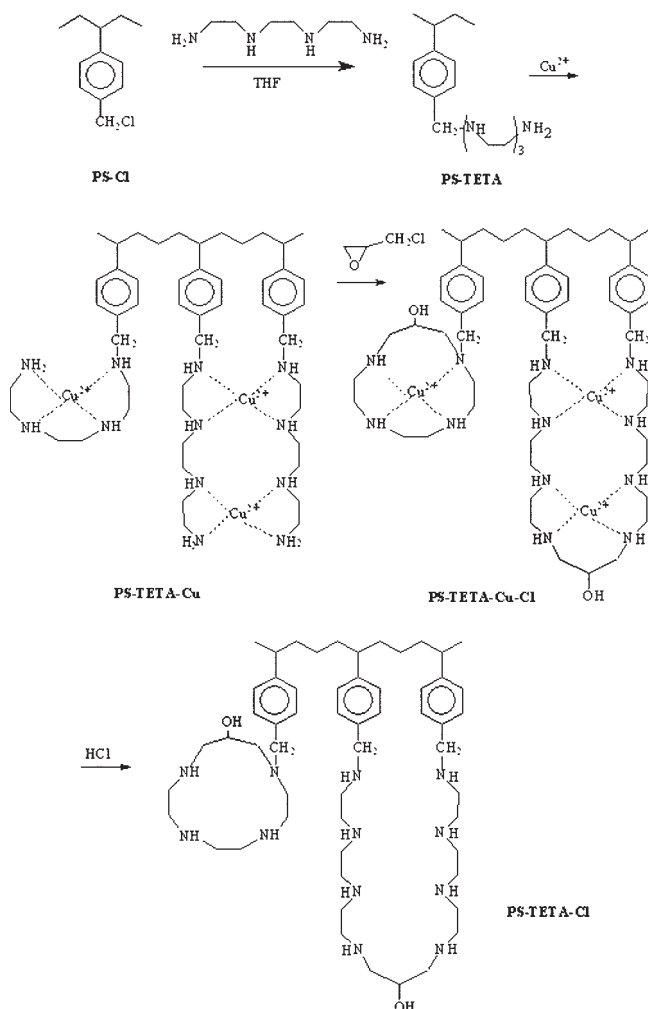
Figure 1 The structure and synthesis route of PS-TETA-Cl resin.

ions more efficiently because the existence of macropores would provide convenient diffusion channels for metal ions into the interior of the resins when they are used in sorption of metal ions in aqueous solution. It is a pity that chelating resins with macro pores can hardly be prepared by traditional metal ion-templated method. To obtain chelating resin with macropores using metal ions as template, we tried preparing it by the reaction of triethylenetetramine-Cu^{2+} complex with macroporous chloromethylated polystyrene (PS-Cl), which is the ideal polymeric matrix that often used to prepare novel cheating resins because of its stable mechanical property, but we failed. It is mainly because of the bulky size and strong hydrophilicity of triethylenetetramine-Cu^{2+} complex, which makes it difficult to diffuse into the matrix of hydrophobic PS-Cl to react with —Cl.

In this article, we developed a new method for preparing a novel chelating resin that has good adsorption capability for Cu(II) and high selectivity for it with the coexistence of Ni(II). First, the macroporous PS-Cl was reacted with triethylenetetramine, and then

aminated resin was obtained. Subsequently, the aminated resin coordinated with Cu(II). After the aminated resin-Cu(II) complex crosslinked with epoxy chloropropane, the adsorbed Cu(II) was removed by chlorhydric acid and then the target resin, triethylenetetramine crosslinked polystyrene resin using Cu(II) as template, was obtained. The selectively sorption tests for Cu(II) showed that the sorption capacity was as high as 1.6 mmol/g and the selectivity coefficient $\alpha_{Cu(II)/Ni(II)}$ could reach to 9.06 with the coexistence of Ni(II).

EXPERIMENTAL

Materials and instruments

Commercial macroporous chloromethylpolystyrene beads (chlorobeads, PS-Cl), chlorine content 19.85%, BET surface area 31.86 m^2/g, and BJH desorption average pore diameter 36.66 nm were purchased from Chemical Factory of Nankai University, Tianjing, China. Triethylenetetramine and other reagents were analytical-grade chemical products and used without any further purification. Aqueous solutions containing metal ions at various concentrations (10^{-2} to $10^{-3}M$) were prepared from metal salts and controlled by titration with a standard EDTA solution.

Infrared spectra were recorded on a Nicolet MAGNA-IR 550 (series II) spectrophotometer; test conditions: potassium bromide pellets, scanning 32 times, and resolution are 4 cm^{-1}. The data were treated with Thermo Nicolet OMNIC32 software of version 6.0a. The shapes and surface morphology of the resins were examined on a scanning electron microscope (SEM), JSF5600LV, JEOL. Porous structures of the resins were characterized using an automatic physisorption analyzer ASAP 2020 by BET and BJH methods through N_2 adsorption at 77 K.

Synthesis of the resins

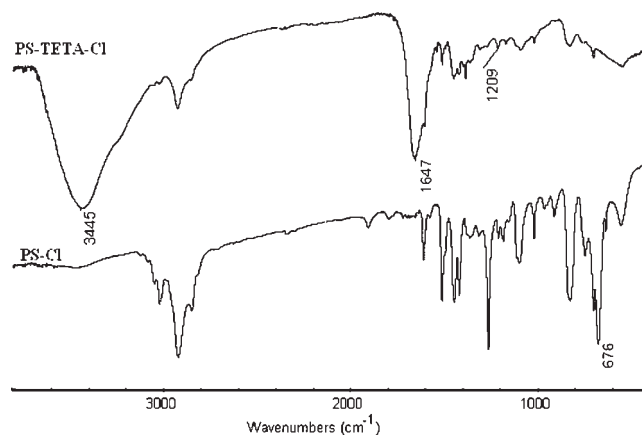The synthesis route of the resins was shown in Figure 1.

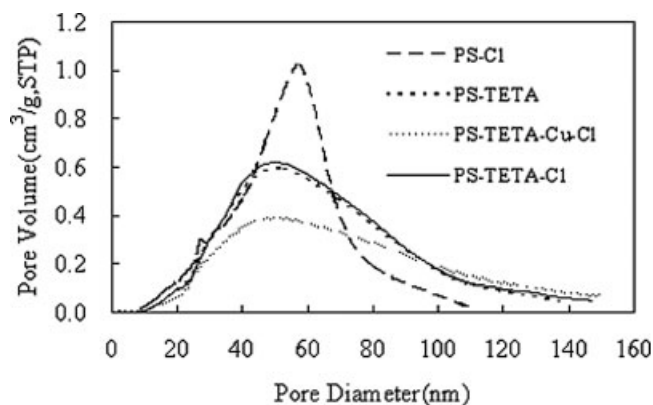**Figure 2** The IR spectra of PS-Cl and PS-TETA-Cl resin.

Figure 3 BJH desorption pore size distributions of the resins.

Fifteeen grams of PS-Cl beads were swollen in 100 mL of tetrahydrofuran in a three-necked flask for more than 18 h, and then 100 mL of triethylenetetramine was added. In ice-water bath, the mixture was stirred for 1.5 h, and then the temperature was raised to 15°C. After 22 h, the temperature was raised to 25°C and the mixture became pasty. At 48°C, 50 mL of tetrahydrofuran and 4 g of NaOH were added, and the mixture was refluxed for 22 h. Then the product was filtered off, washed with distilled water and ethanol, and then moved to a Soxhlet's extraction apparatus for reflux-extraction in 95% ethanol for 24 h. Finally, the product was dried under vacuum at 50°C over 48 h. The product was abbreviated to PS-TETA in this article. According to the results of elemental analysis, the content of functional group was calculated to be 3.1 mmol/g.[19]

One gram of PS-TETA was added in 50 mL of 0.02 mol/L CuSO$_4$ aqueous solution, and the mixture was shaken at room temperature for 48 h. Then the resin was filtered off, washed with distilled water, and dried under vacuum. The product obtained was abbreviated to PS-TETA-Cu in this article. In the crosslinking reaction, 1.5 mmol of epoxy chloropropane was used. After that, the resin was moved to 10% dilute hydrochloric acid and shaken for 8 h. Then the resin was filtered off, washed with distilled water, and dried under vacuum at 50°C over 48 h. The product was abbreviated to PS-TETA-Cl in this article.

Sorption experiments

In a thermostat-cum-shaking assembly, batch adsorption experiments were carried out by shaking 0.05 g of resin with 20 mL of an aqueous solution of metal ions of the desired concentration, pH, and temperature in 50 mL Pyrex glass tube. At predetermined time intervals, the solutions in the specified tubes were separated from the adsorbent. The concentration of metal ions was decided by titration method. The adsorption amounts were calculated according to the following eq. (1)

$$Q = \frac{(C_0 - C)V}{W} \tag{1}$$

where Q is the adsorption amount, mmol/g; C_0 and C, the initial and concentrations of metal ions in solution when the contact time is t, respectively, mmol/mL; V, the volume, mL; W, the weight of resin beads, g.

RESULTS AND DISCUSSION

FTIR characterization

The FTIR spectra of PS-Cl and PS-TETA-Cl were shown in Figure 2.

When compared with the curve of PS-Cl, the characteristic peak of C—Cl at 676 cm^{-1} weakened apparently in the curve of PS-TETA-Cl, and a series of new peaks involved appeared at 3445, 1647, and 1209 cm^{-1} corresponding to the stretching vibration of O—H and N—H bonds, the bending vibration of N—H bone and the stretching vibration of C—O bond, which indicated that the group of TETA had been introduced successfully into polymeric matrix and the crosslinking reaction had occurred.

Porous structure of the resins

The porous structure parameters of the resins were obtained by nitrogen adsorption–desorption experiment at 77 K. The BJH desorption pore size distributions of the resins were shown in Figure 3. As illustrated in Figure 3, mesopores and macropores were dominant for all resins. After the reaction of PS-Cl with TETA, the pore size distribution of the resin was broadened as could be seen from the curve of PS-TETA, that is, the amount of

TABLE I
Porous Structure Parameters of the Resins

Resins	BET surface area (m^2/g)	BJH desorption average pore diameter (nm)	BJH desorption cumulative volume of pores (cm^3/g)[a]
PS-Cl	31.68	39.59	0.32
PS-TETA	31.42	39.16	0.31
PS-TETA-Cu-Cl	28.90	35.29	0.24
PS-TETA-Cl	36.29	38.74	0.33

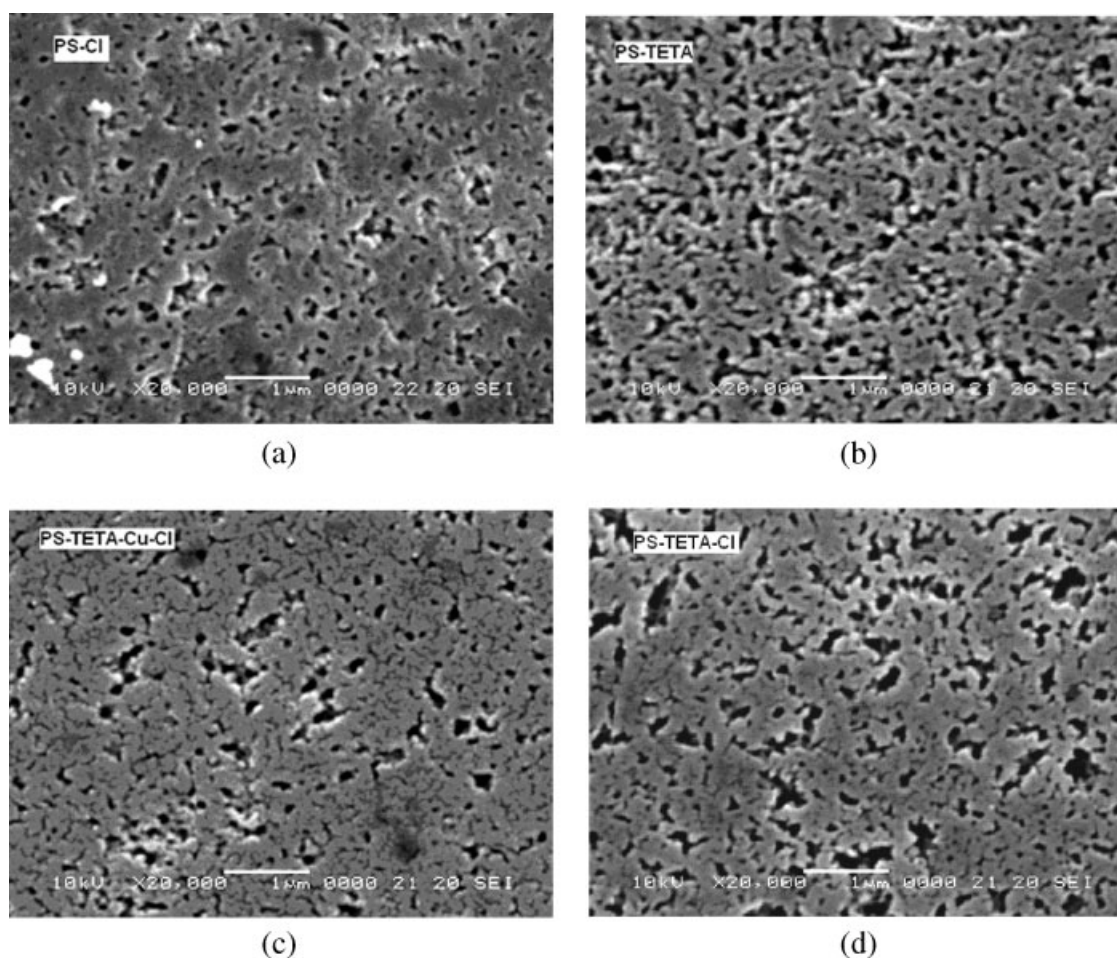[a] The total volume of pores between 1.7 nm and 300 nm diameter.

Figure 4 The SEM images of PS-Cl, PS-TETA, PS-TETA-Cu-Cl, and PS-TETA-Cl resins.

the pores between 40 and 70 nm decreased and the amount of those between 70 and 150 nm increased remarkably. It was probably because of these pores, which collapsed before the reaction reopened after the polar groups, TETA were introduced into the polymer matrix. When PS-TETA adsorbed Cu(II) ions and was crosslinked by epoxy chloropropane, the amount of the pores of the resin decreased obviously (see the curve of PS-TETA-Cu-Cl) because of the crosslinking reaction. Once the Cu(II) ions were removed from the resin, the amount of the pores increased again (see the curve of PS-TETA-Cl), which was caused by the disappearance of the Cu(II)-complex. The porous structure parameters of the resins were summarized in Table I.

SEM observation

The SEM images in Figure 4 visually showed the morphological differences of the surface of the resins. Except PS-TETA-Cu-Cl, the other resins had abundant pores distributing on the surface, which was in accordance with the results of porous structure analysis. The existence of macropores would provide convenient diffusion channels for metal ions into the interior of the resin when it was used in sorption of metal ions in aqueous solution.

Separation properties of PS-TETA-Cl for Cu(II)-Ni(II)

The sorption kinetics curves of PS-TETA-Cl for Cu(II)-Ni(II) were shown in Figure 5. It is obvious that the
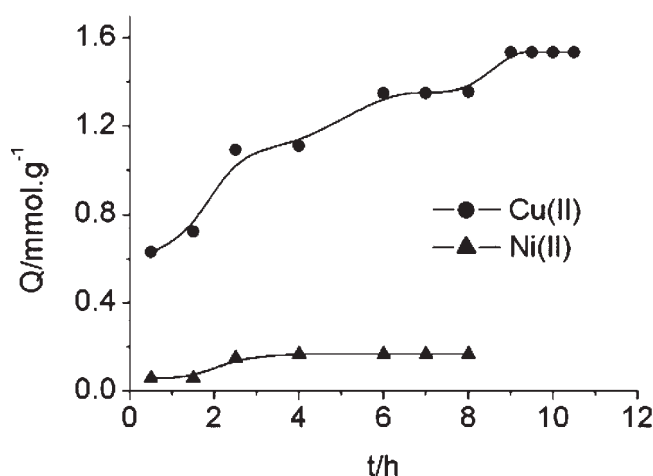

Figure 5 The sorption kinetics of PS-TETA-Cl for Cu(II)-Ni(II) solution (25°C, [Cu(II)] = 0.0135 mol/L, [Ni(II)] = 0.0157 mol/L, pH = 4.5).
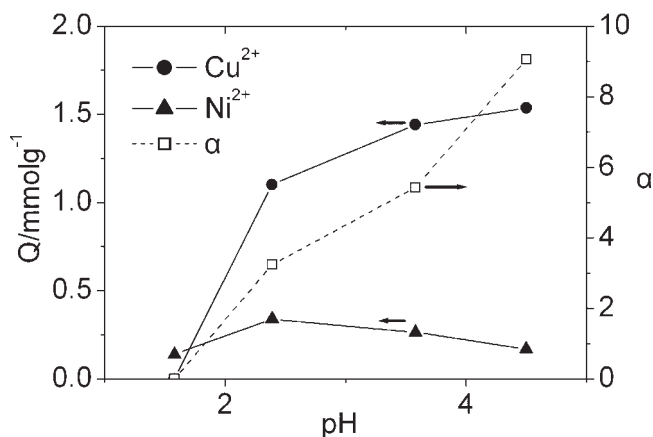
Figure 6 The pH effect on the sorption of PS-TETA-Cl for Cu(II)-Ni(II) solution (25°C, [Cu(II)] = 0.0135 mol/L, [Ni(II)] = 0.0157 mol/L).

sorption capability of PS-TETA-Cl for Cu(II) was much better than for Ni(II), and the selectivity coefficient $\alpha_{Cu(II)/Ni(II)}$ was calculated to be 9.06. Also, it should be noticed that the sorption capacities of PS-TETA-Cl for Cu(II) and Ni(II) were both gradually increased with the prolonging time. Shortly after 3 h, the sorption for Ni(II) achieved equilibrium and the amount of sorption was only 0.2 mmol/g. Contrastively, the sorption equilibrium for Cu(II) was established after 9 h, and the amount of sorption was as high as 1.6 mmol/g. All the above facts showed that PS-TETA-Cl had strong sorption capability for Cu(II), and it could separate Cu(II) from Cu(II)-Ni(II) aqueous solution efficiently.

**pH effect on the sorption of PS-TETA-Cl
for Cu(II)-Ni(II)**

Figure 6 showed the pH effect on the sorption of PS-TETA-Cl for Cu(II)-Ni(II). The studied pH range was from 1.0 to 4.6. No results at pH > 4.5 were given because Cu(II) would deposit at higher pH value. From Figure 6, it could be seen that Cu(II) could hardly be adsorbed by the resin when pH < 2. With the increasing pH value, the amount of sorption for Cu(II) increased gradually. For Ni(II), the amount of sorption at pH = 2.4 was a little higher than the others. When pH > 2, the amounts of sorption for Ni(II) were far smaller than those of Cu(II). The selectivity coeffi-

cient $\alpha_{Cu(II)/Ni(II)}$ also increased with the increasing pH value and became the highest when pH was 4.5.

CONCLUSIONS

A new method for preparing a novel macroporous chelating resin that has good adsorption capability for Cu(II) and high selectivity for it with the coexistence of Ni(II) was introduced in this article. Porous structure analysis and SEM of the resin showed that mesopores and macropores were dominant for it. The selectively sorption tests for Cu(II) showed that the sorption capacity was as high as 1.6 mmol/g, and the selectivity coefficient $\alpha_{Cu(II)/Ni(II)}$ could reach to 9.06 with the coexistence of Ni(II). The $\alpha_{Cu(II)/Ni(II)}$ increased with the increasing pH value and became the highest when pH was 4.5.

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