

Preparation, Characterization, and Metal Binding Behavior of Novel Chelating Resins Containing Sulfur and Polyamine

Rongjun Qu,^{1,2} Chunhua Wang,¹ Chunnuan Ji,¹ Changmei Sun,^{1,2} Xiangrong Sun,¹ Guoxiang Cheng²

¹School of Chemistry and Materials Science, Yantai Normal University, Yantai, 264025, People's Republic of China

²School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

Received 1 May 2004; accepted 30 August 2004

DOI 10.1002/app.21370

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Several kinds of polyamine-type chelating resins containing sulfide were synthesized by the reaction of polyamines, such as ethanolamine (EA), ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA), with poly[4-vinylbenzyl (2-benzenesulfonate ethyl) sulfide] (PSMP), which was itself prepared by the reaction of poly[4-vinylbenzyl (2-hydroxyethyl) sulfide] (PSME) with benzenesulfonal chloride in pyridine solution. Factors affecting syntheses of PSMP, such as solvents, reaction temperature and time, and ratio of reactants, were investigated. Structures of the above resins were confirmed

by FTIR and elemental analysis. Their surface morphology and pore structures were observed on a SEM and determined by the BET method, respectively. Adsorption experiments showed that these resins exhibit better adsorption selectivity for noble metal ions and Hg(II) than other heavy ones. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1558–1565, 2005

Key words: chelating resins; polyamines; poly[4-vinylbenzyl (2-benzenesulfonate ethyl) sulfide]; synthesis; adsorption

INTRODUCTION

It is well known that chelating resins with complex ligands containing nitrogen have excellent sorption selectivity for divalent transition metal cations due to the strong affinity between the nitrogen atom and these metal ions. Examples of such complex ligands mainly include ethylenediamine, diethylenetriamine, triethylenetetramine, etc., polyamines, guanidyl group, and aminopyridine.^{1–5} Chelating resins with polyamine, were prepared generally through the reaction of crosslinked polymers containing active chloride such as chloromethylated polystyrene⁷ and polyvinyl chloride^{7,8} with polyamine. Compared to chlorine-containing polymers, sulfonate-containing ones have much higher reaction activity. Its reaction with polyamine is carried out under mild conditions such as at room or lower temperature. To the contrary, the reactions of chlorine-containing polymers with amines must be carried out under heating conditions such as 40 – 60°C or a still higher temperature. Recently, several kinds of chelating resins with polyamines have been synthesized based on phenol–formaldehyde res-

ins by the author and his coworkers,⁹ and their sorption properties for Ag(I), Cu(II), Pb(II), Ni(II), and Zn(II) were also investigated.

Sulfur, a member of the third period, having low-lying empty 3d orbitals, exhibits markedly different bonding properties compared to nitrogen. It has been proven that chelating resins containing sulfur have excellent adsorption selectivity for such noble metals as gold, silver, palladium, platinum, etc.^{7,10,11} To augment the adsorption capacity and selectivity of chelating resin for noble metal, many efforts have been made to introduce the sulfide structure into polymeric matrices in recent years.^{12–15} In this work, we synthesized four kinds of novel chelating resins containing sulfur and nitrogen by means of introducing first a sulfur atom, then polyamines into a cross-linked polystyrene structure. The effects of synthetic conditions such as reaction time, reaction temperature, and ratio of reactants etc, on reaction were investigated. Also the adsorption properties of these resins for several kinds of metal ions were studied.

EXPERIMENTAL

Materials

Poly[4-vinylbenzyl (2-hydroxyethyl) sulfide] (PSME) was prepared under phase-transfer catalyzed conditions according to our previous work:¹⁶ content of

Correspondence to: R. Qu (rongjunqu@sohu.com or qurongjun@eyou.com).

functional groups ($-\text{OH}$) was $4.95 \text{ mmol} \cdot \text{g}^{-1}$. Benzenesulfonal chloride, ethanolamine (EA), ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) were purchased from Aldrich Chemical Co. Before using, pyridine was redistilled after being dried over potassium hydrate.

Equipment

Infrared spectra were recorded on a Nicolet MAGNA-IR 550 (series II) spectrophotometer; test conditions: potassium bromide pellets, scanning 32 times, resolution 4 cm^{-1} . The data were treated with Thermo Nicolet Corporation OMNIC32 software, version 6.0a. Elemental analysis was performed by a Perkin-Elmer Model 1106 Elemental Analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT). The shapes and surface morphology of the resins were examined on a scanning electron microscope (SEM), JSF5610LV, JEOL. The BET surface area (m^2/g), BET average pore diameter (\AA), and pore volume in the dry state (cm^3/g) were determined by the BET method from low-temperature nitrogen adsorption isotherms (ASAP Micromeritics 2000, Version 2.02) at 77 K using a high-vacuum volumetric apparatus. The samples were degassed at $100^\circ\text{C}/1 \text{ mPa}$ for 3 h. The concentration of metal ion was measured on a GBC-932 atomic absorption spectrophotometer (AAS) made in Australia.

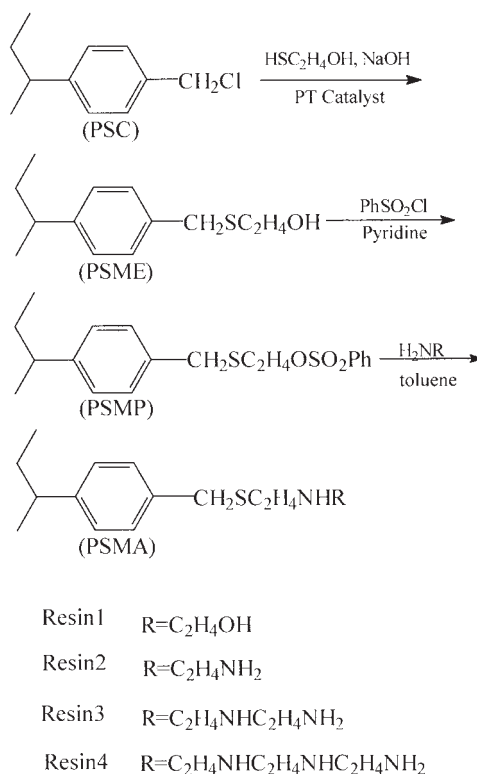
Preparation of chelating resins

Synthetic route

The structures and synthetic routes of Resin 1–Resin 4 are described in Scheme 1.

Preparation of PSMP (typical synthesis)

Under a nitrogen atmosphere, a suspension of 6.0 g of PSME (ca. 28 mmol OH) and 80 ml of pyridine was stirred at room temperature (about 15°C) for 4 h to swell sufficiently, and then 15 g of benzenesulfonal chloride (ca. 78 mmol) was added dropwise into the mixture in a bath of ice-water (about 0°C). After the procedure of adding benzenesulfonal chloride was completed, the reactant mixture was stirred for a further 17 h at room temperature. The polymeric beads then were filtered off and washed with ethanol, distilled water, acetone, and, finally, methanol. The product was transferred to a Soxhlet extraction apparatus for reflux-extraction in 95% ethanol for 10 h and then was dried under vacuum at 50°C over 48 h. 9.47 g of product was obtained. The yield, calculated according to the results of elemental analysis, was 92.8% and the content of phSO_3^- in PSMP was $2.7 \text{ mmol} \cdot \text{g}^{-1}$.



Scheme 1

Preparation of resin 1

In a nitrogen atmosphere, a mixture of 1 g of PSMP, 10 ml of toluene, and 10 ml of EA was stirred at 10°C for 12 h and at room temperature for another 12 h. The product was then filtered and washed with methanol, ethanol, distilled water, 1% hydrochloric acid aqueous solution, distilled water, 2% sodium hydrate, and, finally, distilled water. The product was moved to the Soxhlet extraction apparatus for reflux-extraction in 95% ethanol for 14 h and then was dried under vacuum at 50°C over 48 h. Approximately 0.74 g of product was obtained.

Preparation of resin 2

The reaction involved 1.01 g of PSMP, 10 ml toluene, and 10 ml of EDA. The reactant mixture was stirred for 12 h at 10°C and for 2 h at 25°C . The procedure of purification of product was similar to that of Resin 1. 0.73 g of product was obtained, N content was 9.9%.

Preparation of resin 3

The reaction involved 1.058 g of PSMP, 10 ml of toluene, and 10 ml of DETA. The reactant mixture was stirred for 12 h at 10°C and for another 2 h at 25°C . The purification procedure of product was similar to that

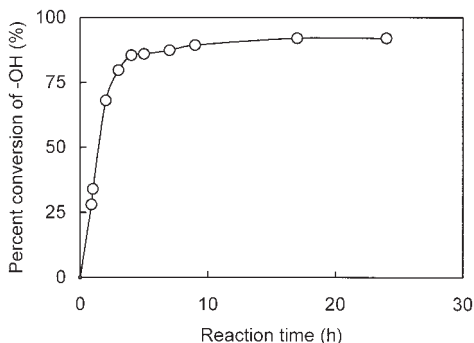


Figure 1 The effect of reaction time on percent conversion of —OH.

of Resin 1. 0.87 g of product was obtained. N content of resin was 11.99%.

Preparation of resin 4

The reaction involved 2.07 g of PSMP, 20 ml of toluene, and 20 ml of TETA. The reactant mixture was stirred for 20 h at 10°C and for 2 h at 25°C. The purification procedure of product was similar to that of Resin 1. 1.81 g of product was obtained. The N content of resin was 13.5%.

The adsorption properties of resins 1–4

Adsorption experiments were made to determine the properties of Resins 1–4 for 10 kinds of metal ions. A typical procedure was as follows: 50-ml Pyrex glass tubes were prepared with the desired amounts of reagent solution and were placed in a thermostat-cum-shaking assembly. At 25°C, a known amount resin (0.05 g) was added into each tube, and the mixed solutions were mechanically shaken. After 24 h, the solutions in the specified tubes were separated from the adsorbent and the concentrations of Cd(II), Zn(II), Pb(II), Cu(II), Hg(II), Pt(IV), Au(III), Pd(II), and Ag(I)

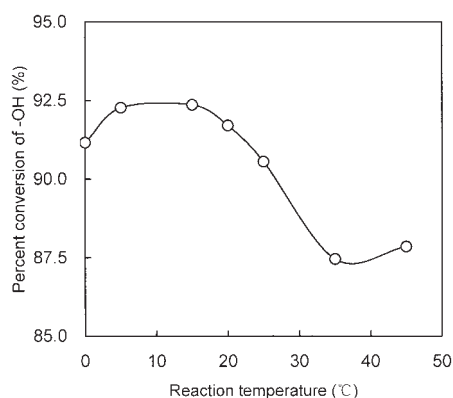
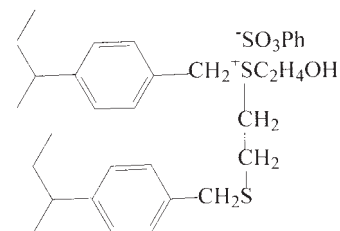


Figure 2 The effect of reaction temperature on the percent conversion of —OH.



Scheme 2

were determined by means of AAS. The adsorption amounts were calculated according to the eq. (1):

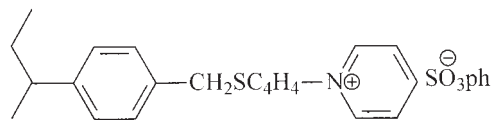
$$Q = \frac{(C_0 - C)V}{W} \quad (1)$$

where Q is the adsorption amount (mmol/g); C_0 and C are the initial and final concentrations of metal ions in solution (mmol/ml); V is the volume (ml); and W is the dry weight of resin (g).

RESULTS AND DISCUSSION

The evaluation of the reaction progress

The progress of reaction of PSME with benzenesulfonate chloride could be evaluated by monitoring the changes of percent conversion of hydroxyl groups. In general, the percent conversion of hydroxyl groups could be calculated by determining the content of residual hydroxyl groups in resin after reaction. There have been several methods to determine content of hydroxyl groups in polymer. Of these, the most popular is the “acetic anhydride–pyridine reflux” method described in Gong and Shi.¹⁷ However, in this experiment, according to the results of FTIR, we found that the hydroxyl group in PSME resin couldn’t react completely with acetic anhydride whenever the reaction conditions were changed: residual hydroxyl groups remained in the resin after reaction. This would seriously affect the calculated results of percent conversion of hydroxyl groups. For this reason, the percent conversions of hydroxyl groups in this paper were calculated according to the changes of S content before and after reaction, and the S content was measured by means of element analysis.



Scheme 3

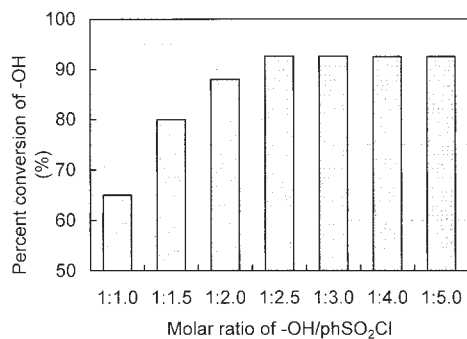


Figure 3 The effect of ratio of reactants on percent conversion of —OH.

Preparation of PSMP

Selection of solvents

The synthesis of tosylated polystyrene having diethylene glycols by using carbon tetrachloride as solvent at a refluxed temperature has been reported in the literature.¹⁸ The synthesis of PEG-tosylate by using methylene chloride as solvent at 0°C has also been reported.¹⁹ The experimental conditions for synthesis of PSMP were determined to use carbon tetrachloride or methylene chloride as solvents, pyridine as catalyst

(molar ratio of —OH : phSO₃ : pyridine = 1 : 5 : 5), temperature 0 ≈ 5 °C, reaction time 10 h. However, the results showed that the experimental yields were unsatisfactory and the percent conversions of hydroxyl group were only 70–78%. Similar results were also obtained when other solvents with different polarities such as benzene, tetrahydrofuran, and dioxane, were used. The experiment also revealed that the increase of polarities of solvents was slightly beneficial to the reaction. However, if the reaction was carried out in the presence of a large excess pyridine (here pyridine was both catalysis and solvent), the percent conversion of hydroxyl groups increased significantly and reached more than 90%. A reasonable explanation for this was that, although solvents carbon tetrachloride, methylene chloride, benzene, tetrahydrofuran, and dioxane had good swelling properties for PSMP resin, which made phSO₂Cl enter easily into polymer matrix and react with —OH, these solvents could not dissolve effectively the pyridine hydrochlorate, formed in the reaction as a side product of the reaction, and completely transport rapidly outside of the polymer matrix. Pyridine hydrochlorate staying in the interior of resin matrix would obstruct the diffusion channel of phSO₂Cl further into the resin. With prolonged reaction time, the appearance of more and more sus-

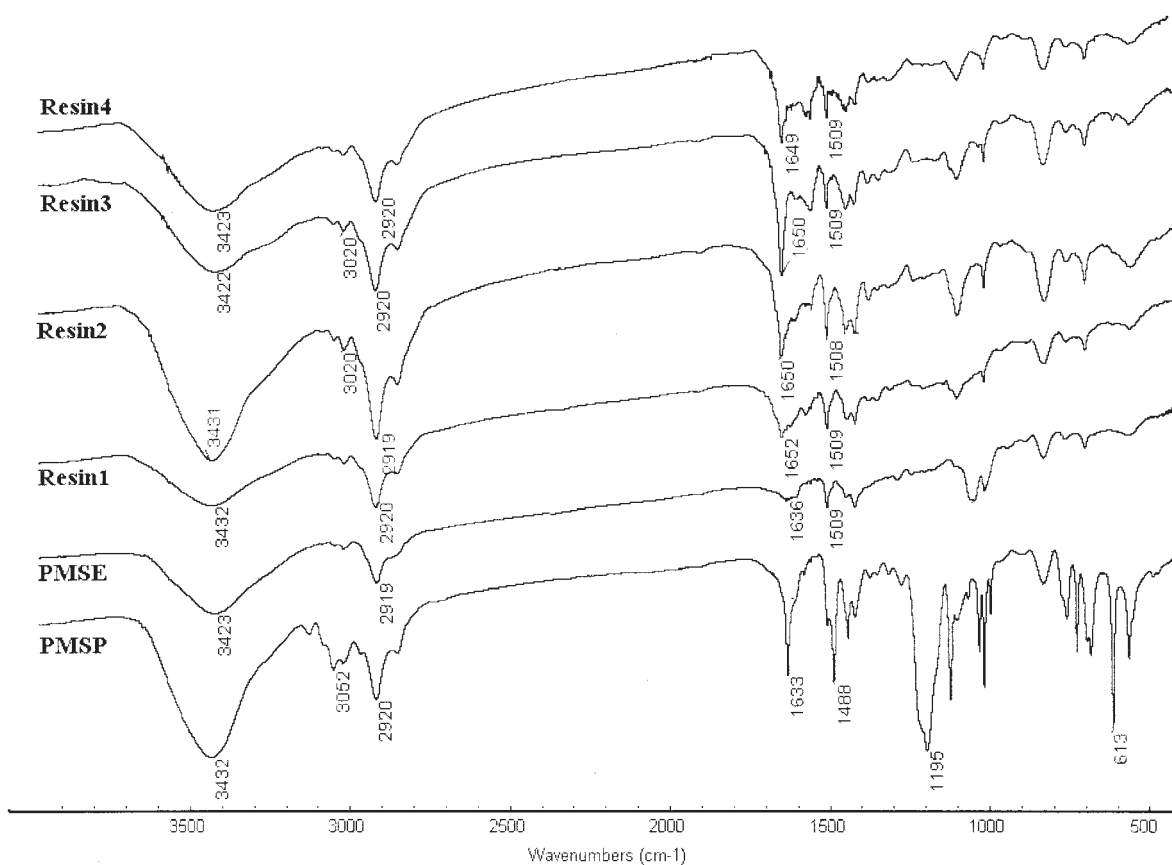


Figure 4 The FTIR spectra of PMSE, PSMP, and Resins 1–4.

TABLE I
Data of Elemental Analysis, Functional Contents, and Cross-linking Degree of Resins

Resins	Functional group	N% content (theoretical value)	Content of functional group ($\text{mmol} \cdot \text{g}^{-1}$)	Crosslinking degree (%) ^a
Resin 1	$-\text{NHC}_2\text{H}_4\text{OH}$	5.12 (5.14)	3.64	—
Resin 2	$-\text{NHC}_2\text{H}_4\text{NH}_2$	9.90 (10.31)	3.53	5.1
Resin 3	$-\text{NH}(\text{C}_2\text{H}_4\text{NH})_2\text{H}$	11.99 (12.76)	2.85	12.9
Resin 4	$-\text{NH}(\text{C}_2\text{H}_4\text{NH})_3\text{H}$	13.50 (15.60)	2.41	21.2

^a Cross-linking degree means the molar proportion of functional group cross-linked in the total functional group taken part in the substitution reaction.

pendent substance in the solvents could prove the poor solvency of these solvents for pyridine hydrochlorate. But a similar phenomenon couldn't be observed with pyridine as solvent, implying the good solvency of pyridine to its hydrochlorate salt. The timely transportation of pyridine hydrochlorate, from the interior to the exterior of the resin matrix, would guarantee the reaction to go smoothly. So, pyridine was finally chosen as the solvent in synthesis of PSMP.

Effect of reaction time

Reaction time is a significant factor in a reaction process. Under the conditions using pyridine as solvent, 10°C , $-\text{OH} : \text{phSO}_3 = 1 : 5$ (molar ratio), the effect of reaction time, on the percent conversion of hydroxyl groups, was investigated, and the results are shown in Figure 1. From Figure 1 it can be seen that the reaction proceeded very quickly in the initial period of reac-

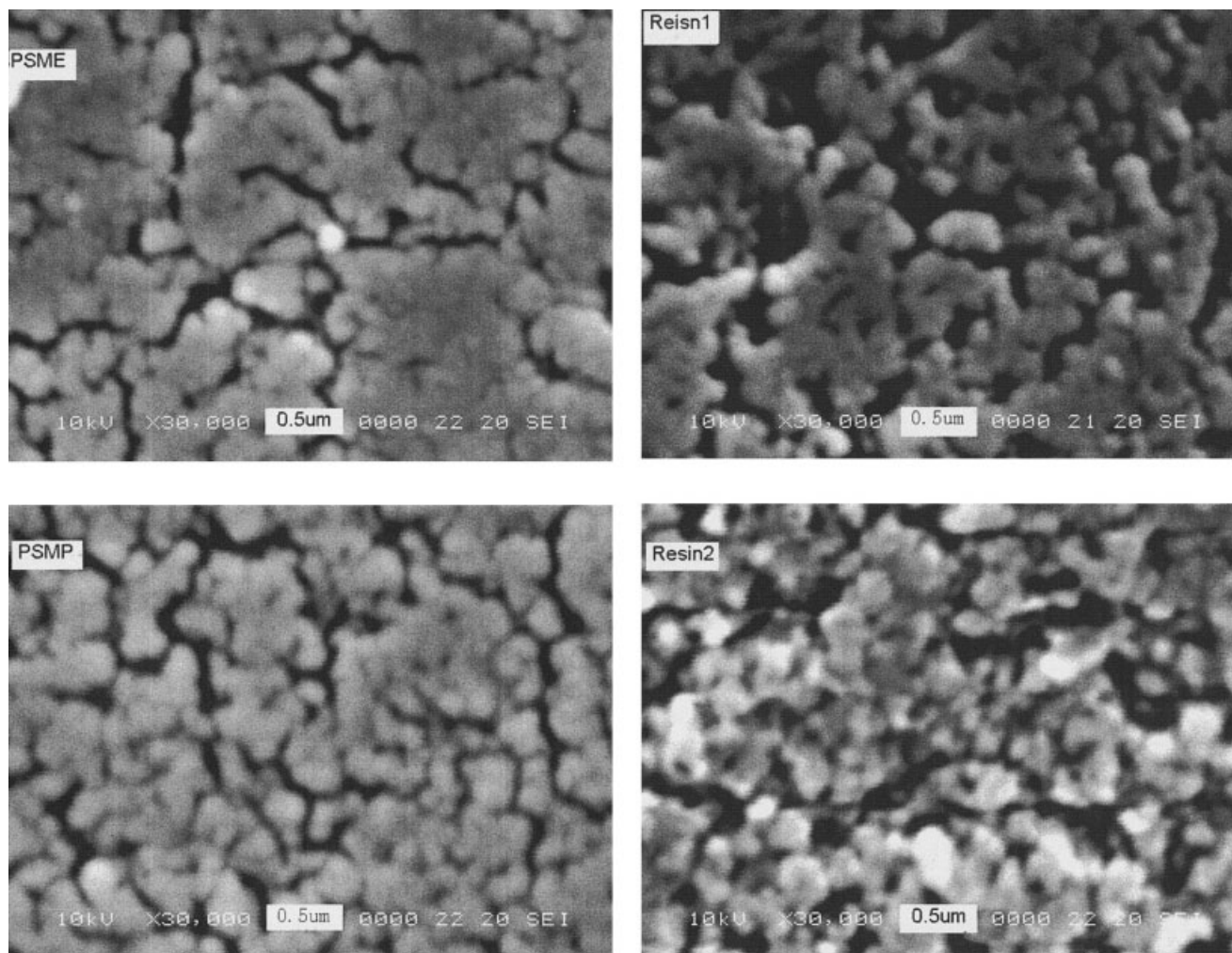


Figure 5 The SEM images of PSME, PSMP, and Resins 1–4.

tion. The percent conversion of hydroxyl groups was as high as 85.5% when the reaction time was 4 h. When the reaction time was 17 h, the percent conversion of hydroxyl groups reached 92%, with no distinct change thereafter. It should be noticed that the hydroxyl groups in PSME were not converted completely into benzenesulphonate after reaction with benzenesulfonyl chloride; the peak characteristic absorption of —OH at 3432cm^{-1} in the FTIR spectra of PSMP also proved this conclusion. There were two possible explanations of these experimental facts: 1) the reaction rate was to some extent limited by the diffusion rate of the reactant (benzenesulfonyl chloride) to the active sites in the polymer matrix, in addition to the rate of the inherent reaction at the active sites. At the beginning, the most accessible reactive sites were involved in the reaction; therefore diffusion limitations were less significant to affect the overall reaction rate. For prolonged reaction time, the less accessible sites would be involved also, and diffusion limitations significantly affected the overall reaction rate. Therefore, the overall reaction rate decreased as the reaction con-

version increased. 2) The formation of considerable benzenesulphonates generated steric hindrance, which affected seriously further diffusion of reactant into the internal matrix of polymer.

Effect of reaction temperature

When the reaction time was fixed at 17 h, the effect of reaction temperature on the percent conversion of hydroxyl groups was also investigated under similar conditions, pyridine as solvent and $\text{—OH} : \text{phSO}_3 = 1 : 5$ (molar ratio). The results are shown in Figure 2, which shows that, when the reaction temperature was kept between 5 and 15°C , the percent conversion of hydroxyl groups could reach as high as 92.4%; when the reaction temperature was lower than 5°C or higher than 20°C , especially under the condition of more than 25°C , the percent conversion of hydroxyl groups decreased. This was probably because at the lower reaction temperature, the reaction rate between —OH and benzenesulfonyl chloride was too slow; on the other hand, when the reaction temperature was higher, overly quick formation of benzenesulphonate on the external layer of polymeric beads obstructs the diffusing channels for benzenesulfonyl chloride further into the polymeric matrix. The other probable reason for this was that the higher temperature was beneficial to the formation of structures as follows (Scheme 2): Considering the high reaction activity of benzenesulphonate, we didn't study the reaction, in the case of temperatures of more than 45°C , further to avoid the formation of alkyl pyridinium as described in Scheme 3.

Effect of ratio of reactants

Generally, the ratio of reactants would be a significant factor affecting reaction. In this work, the effect of molar ratio, between hydroxyl group and benzenesulfonyl chloride ($\text{—OH}/\text{phSO}_2\text{Cl}$) on the reaction was investigated within the range of $1 : 1.0 - 1 : 5.0$ at 10°C . The results are shown in Figure 3 and demonstrate that, when the ratio of $\text{—OH}/\text{phSO}_2\text{Cl}$ was within $1 : 1.0 - 1 : 2.5$, the percent conversion of hydroxyl groups increased with the increase of proportion of phSO_2Cl , and when the ratio was within $1 : 2.5 - 1 : 5.0$, the percent conversion of hydroxyl group was almost unchanged. A molar ratio of $\text{—OH}/\text{phSO}_2\text{Cl}$ of $1 : 2.5$ was regarded as optimum. To ensure that the reaction was carried out completely, the ratio of $1 : 3.0$ was adopted in the following synthetic reaction process.

Preparation of resins 1-4

Generally, nitrogen-containing chelating resins are prepared through the reactions of chlorine-containing polymers with polyamines while heating. Compared to chlorine-containing compounds (e.g., PSC), ben-

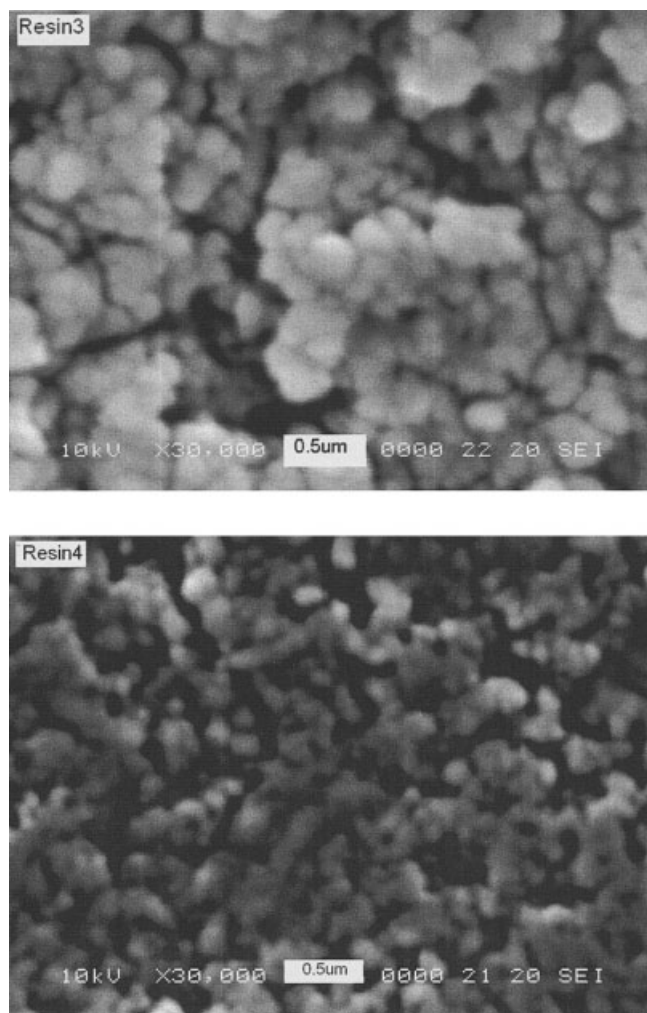


Figure 5 (Continued)

zenesulfonate compounds have higher reaction activity because the benzenesulfonate group is a more mobile group than chlorine in the reaction of nucleophilic substitution, so the reaction of benzenesulfonate-containing polymers with polyamines can be carried out at a lower temperature. In this work, we found that the reaction of PSMP with amines could be carried out smoothly at 10–25°C and the chelating resins 1–4 could be obtained under this condition when the amines were EA, EDA, DETA, and TETA, respectively.

Assuming that the benzene sulfonate groups in PSMP were substituted completely with amine groups after the reaction was finished (this assumption can be regarded as reasonable from the FTIR spectra in Fig. 4), the contents of functional groups and crosslinking degrees of amines could be calculated according to the N% of elemental analysis. The results are listed in Table I.

From Table I, some conclusions can be drawn: 1) the N% content of Resin 1 was almost equal to the theoretical N% content, implying that the substitution reaction was carried out completely and few cross-linking products were generated in the process of substitution; 2) the difference between the measured and the theoretical value of N% increased with the increase of the length of polyamine chain. This resulted from internal cross-linking of polyamine. The longer the chain of the functional group was, the more the number of nitrogen atoms functional groups it contained, and the easier the cross-linking reaction was carried out. It can be found from the experiment that an atmosphere of inactive gas was necessary to this reaction even if this reaction was carried out under mild conditions, otherwise, the product would be dark colored. This was probably because benzenesulfonic acid generated from the substitution reaction catalyzed the oxidization of amines by oxygen in the air.

Characterization of resins

The structures of Resins 1–4 and starting materials were characterized by means of FTIR. The results are shown in Figure 1. Comparing the spectrum of PMSP with PSME, it can be seen that a series of new absorption peaks at 1195 and 613 cm⁻¹, representing the characteristic absorption peaks of phSO₃⁻, appeared after reaction of PSME with benzenesulfonal chloride, indicating that phSO₃⁻ groups were introduced successfully into the structure of PMSP; this result accorded with the desired structure of PMSP. Also, it should be noted that there was still a strong absorption peak of —OH at 3400 cm⁻¹ in the structure of PMSP, indicating that there were some —OH groups that had not reacted with benzenesulfonal chloride. From the spectra of Resins 1–4, it was easy to observe that the characteristic absorption peaks of phSO₃⁻ disappeared

TABLE II
The Pore Surface Area, Pore Volume, and Pore Diameter

Resin	BET surface area (m ² /g)	Volume (cm ³ /g)	BET average pore diameter (Å)
PSME	21	0.16	303
PSMP	22	0.16	332
Resin 1	21	0.18	335
Resin 2	24	0.20	342
Resin 3	27	0.23	340
Resin 4	27	0.21	344

after the reaction of PMSP with different polyamines, indicating that the substitution reaction was carried out very completely.

The SEM observations of resins

To observe the surface morphology of the PSME, PSMP, and Resins 1–4, scanning electron micrographs of the gold-coated samples were taken with a SEM. The images are shown in Figure 5. It is clearly seen that there are abundant pores distributed on the surface of PSMP and Resins 1–4, implying that the macroporous structures of PSME resin had not been damaged after the reaction with benzenesulfonyl chloride and further with polyamines. The existence of macropores would provide convenient diffusion channels for metal ions into the interior of resins when these resins are used in adsorption of metal ions in aqueous solution.

The analysis of pore structures of resins

The BET surface area, pore volume, and BET average pore diameters of PSME, PSMP, and Resins 1–4 in the dry state, were determined by the BET method. The results are shown in Table II which reveals that the Resins 1–4 have similar BET surface area, BET average diameter, and volume due to their similarity of structures. The range of BET average diameters is from 335 to 344 Å, indicating that these resins are macroporous: this agrees with the results from SEM observation. It is notable that both the BET average pore diameters and surface areas of Resins 1–4 increased compared with PSMP and PSME. This is probably due to internal amine-cross-linking, resulting in the increase of surface area, and the introduction of strong polar polyamine groups into the weakly polar polystyrene matrix, resulting in a crystalline. By change of the polymeric matrix.

The adsorption properties of resins 1–4 for metal ions

Figure 6 shows the saturated adsorption capacities of Resins 1–4 for Cd(II), Zn(II), Pb(II), Cu(II), Hg(II),

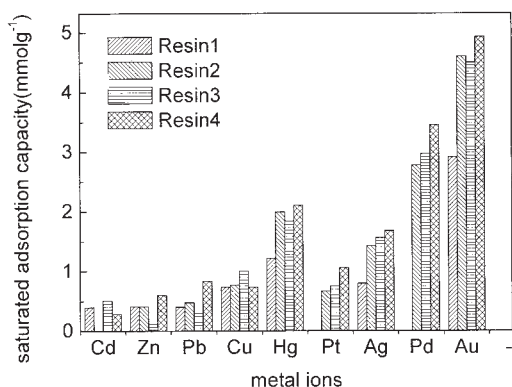


Figure 6 The saturated adsorption capacities of Resins 1–4 for metal ions.

Pt(IV), Au(III), Pd(II), and Ag(I). Obviously, the adsorption capacity of these resins for noble metal ions [Pt(IV), Au(III), Pd(II), Ag(I)] was higher than that of heavy metal ions [Cd(II), Zn(II), Pb(II), Cu(II)] except for Hg(II). Generally, it can be concluded that, for the four kinds of noble metal ions, the order of adsorption capacity of Resins 1–4 was as follows: Resin 4 > Resin 3 > Resin 2 > Resin 1, but, for the five kinds of heavy metal ions studied, a similar rule couldn't be found. This implies that the increase of length of polyamine chain was beneficial to the adsorption of chelating resin for noble metal ions.

CONCLUSION

Under mild conditions, four kinds of polyamine-type chelating resins with sulfide and ethanolamine (Resin 1), ethylenediamine (Resin 2), diethylenetriamine (Resin 3), and triethylenetetramine (Resin 4) were synthesized and their structures were characterized by FTIR and elemental analysis. The SEM observation and analysis of pore structure showed that the resins prepared, and their intermediates had macroporous structures. The intermediate PSMP was prepared in a yield of 92% by the reaction of PSME with benzenesulfonate chloride in the presence of an excess amount

of pyridine. The adsorption properties of these resins, for Cd(II), Zn(II), Pb(II), Cu(II), Hg(II), Pt(IV), Au(III), Pd(II), and Ag(I), were studied and the results revealed that these resins exhibit better adsorption selectivity for noble metal ions than heavy ones.

The authors are grateful for the financial support by the Postdoctoral Science Foundation of China (No.2003034330), the Nature Science Foundation of Shandong Province (No. Q99B15), and the National Nature Science Foundation of China (No. 29906008).

References

1. Navarro, R. R.; Sumi, K.; Fujii, N.; Matsumura, M. *Water Res* 1996, 30, 2488.
2. Delacour, M. I.; Gailiez, E.; Bacaut, M.; Morcelle, M. *J Appl Polym Sci* 1999, 73, 899.
3. Ridvan, S.; Ali, T.; Adli, D. *J Appl Polym Sci* 2002, 83, 2467.
4. Bozena, N. K.; Orola, Jermakowicz-Bartkowiak; Andrzej, W. T.; Wieslaw A. *React Funct Polym* 1999, 42, 213.
5. Chen, Y. Y.; Lu, B. X.; Chen, X. W. *J Macromol Sci Chem* 1988, A25, 1443.
6. Chen, Y. Y.; Yuan, X. Z. *React Polym* 1994, 23, 165.
7. Chang, X. J.; Luo, X. Y.; Su, Z. X.; Zhao, X. B.; Lu, Y. H. *Chem J Chin Univ* 1988, 9, 574.
8. Chang, X. J.; Su, Z. X.; Zhan, G. Y.; Luo, X. Y.; Xu, Z. *Acta Chim Sinica* 1990, 48, 157.
9. Qu, R. J.; Liu, C. P.; Ruan, W. J.; Sun, L.; and Liu, Q. J. *Chin J Mater Res* 1999, 13, 51.
10. Chen, Y. Y.; Cai, G. P.; Wang, N. D. *J Macromol Sci Chem* 1990, A27, 1321.
11. Grote, M.; Schumacher, U. *React Funct Polym* 1997, 35, 179.
12. Dong, S. H.; Hu, Y. H.; Zhao, Y. M.; Zhang, W. H.; Xu, Y. W. *J Wuhan Univ (Natural Sci Ed)* 1995, 41, 161.
13. Xu, Y. W.; Li, H. P.; Dong, S. H. *J Wuhan Univ (Natural Sci Ed)* 1995, 41, 401.
14. Ni, C. H.; Xu, Y. W. *Huaxue Shiji* 1992, 14, 153.
15. Xu, Y. W.; Li, J.; Dong, S. H. *Acta Polym Sinica* 1993, 5, 576.
16. Qu, R. J.; Cheng, G. X.; Ji, C. N.; Wang, C. H. *Environ Chem* 2003, 22, 284.
17. Gong, Y. B.; Shi, A. F.; *Handbook of Synthetic Resin and Plastics*; Science and Technology Press of Shanghai: Shanghai, 2000; p 413.
18. Kong, B. C.; Masao, T. *J Polym Sci, Part A: Polym Chem*, 1992, 30, 1089.
19. Harris, J. M.; Struck, E. C.; Mateven Paley M. G. *J Polym Sci, Part A: Polym Chem Ed* 1984, 22, 341.