

# Macroporous Chelating Resins Incorporating Heterocyclic Functional Groups via Hydrophilic PEG Spacer Arms. I. Synthesis and Characterization

Chunnuan Ji,<sup>1</sup> Rongjun Qu,<sup>1</sup> Changmei Sun,<sup>1,2</sup> Chunhua Wang,<sup>1</sup> Qiang Xu,<sup>1</sup> Yanzhi Sun,<sup>1</sup> Chunxian Li,<sup>1</sup> Shuhua Guo<sup>1</sup>

<sup>1</sup>School of Chemistry & Materials Science, Yantai Normal University, Yantai 264025, China

<sup>2</sup>School of Materials Science & Engineering, Tianjin University, Tianjin 300072, China

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**ABSTRACT:** A series of novel chelating resins were synthesized by incorporating heterocyclic functional groups such as 2-aminopyridine (AP), 2-amino-5-methylthio-1,3,4-thiadiazole (AMTZ), 2-amino-5-ethyl-1,3,4-thiadiazole (AETZ), and 2-mercaptobenzothiazole (MBZ) into macroporous crosslinked polystyrene via a hydrophilic spacer arm of polyethylene glycol containing sulfur. Structures of the above-mentioned resins were

characterized by elemental analysis, Fourier transform-infrared spectra (FTIR), ASAP-2020 surface area and porosity analyzer, and scanning electron microscopy (SEM). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3220–3227, 2007

**Key words:** chelating resins; heterocyclic functional groups; spacer arm; synthesis; characterization

## INTRODUCTION

It is well known that chelating resins with covalently bonded functional groups containing nitrogen and sulfur atoms possess excellent adsorption and selectivity properties for metal ions, especially for noble metal ions.<sup>1–6</sup> Heterocyclic functional groups<sup>7–18</sup> including pyridine, imidazole, thiazole, pyrazole, etc., show high affinity for gold, palladium, silver, and mercury. Earlier reports<sup>19–21</sup> have shown the usefulness of the chelating resins anchoring heterocyclic functional groups to a solid support in a polymer matrix for the separation of  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ , and  $\text{Pd}^{2+}$

in trace quantities from geological, medicinal, and environmental samples.

The reaction between the functional group and the metal ion, and the diffusion of metal ions into the interior of the resin, play a key role for chelating resins in adsorbing metal ions. The hydrophobicity of the chelating resins with S-donor centers or heterocyclic ligands sometimes make it difficult for metal ions to diffuse and interact with functional groups.

The recent literature shows that the introduction of a spacer arm can enhance the hydrophilicity and steric flexibility of the polymeric ligand and so increase the adsorption capacity of the chelating resin.<sup>22–25</sup>

Considering the above, we designed some novel chelating resins by incorporating such heterocyclic functional groups as 2-aminopyridine (AP), 2-mercaptobenzothiazole (MBZ), 2-amino-5-ethyl-1,3,4-thiadiazole (AETZ), and 2-amino-5-methylthio-1,3,4-thiadiazole (AMTZ) into macroporous crosslinked polystyrene via a hydrophilic spacer arm of polyethylene glycol containing sulfur. Their structures were characterized by infrared spectra and elementary analysis. Their surface morphology and surface area analysis were also determined.

## EXPERIMENTAL

### Materials

Commercial macroporous polychloromethylstyrene-co-divinylbenzene beads (PS-Cl), with a degree of crosslinking 10% DVB, chlorine content 19.85%, BET surface area 31.85 m<sup>2</sup>/g, BJH desorption cumulative

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

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volume of pores  $0.31 \text{ cm}^3/\text{g}$ , BJH desorption average pore width  $366 \text{ \AA}$ , was obtained from Chemical Factory of Nankai University of China. AMTZ, AETZ, 2-(2-chloroethoxy) ethanol, and 2-[2-(2-chloroethoxy) ethoxyl] ethanol were purchased from Aldrich Chemical (Milwaukee, WI) and used as received. AP, MBZ, benzenesulfonyl chloride (BsCl), tetrabutyl ammonium iodide, thiourea, methanol, tetrahydrofuran (THF), dioxane and other solvents were of reagent grade quality and used without any purification.

### Equipment

The contents of S and N elementary analyses were performed by an Elementar Analysensysteme Varioel made in Germany. The infrared spectra were recorded on a Nicolet MAGNA-IR550 (series II) spectrometer. The BET surface area, pore volume, and average pore diameter were determined by an ASAP-2020 Surface Area and Porosity Analyzer (Micromeritics, Atlanta, GA). The surface morphology of the precursors and resins 1–8 were examined with a scanning electron microscope (SEM), JSF5610LV (JEOL Tokyo, Japan).

### Synthesis of precursors and resins 1–8

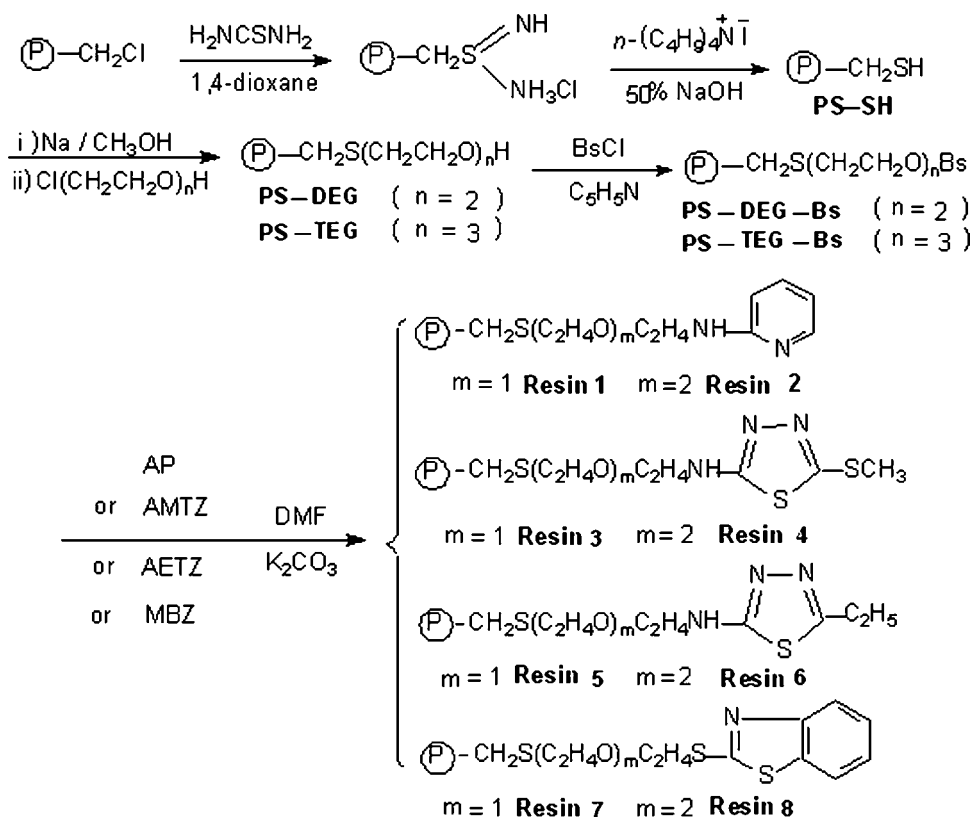
The synthetic route of the precursors and resins 1–8 is shown in Scheme 1.

### Synthesis of PS-SH

PS-Cl (10 g,  $\sim 55.9 \text{ mmol Cl}$ ) and thiourea (17 g) were suspended in dioxane/ethanol (4:11, 50 mL) and the reaction was stirred at  $85^\circ\text{C}$  for 1 h. The resin was then washed with distilled water and benzene to remove all excess soluble reagents and by-products. After this washing the resin was suspended in benzene (120 mL) and a solution of 0.16 g of tetrabutyl ammonium iodide in 8 mL of distilled water and 6 g sodium hydroxide was added. The mixture was then refluxed under a nitrogen atmosphere for 48 h. After filtration the resin was washed with THF, water, and methanol. Then the resin was moved to a Soxhlet's extraction apparatus for reflux-extraction in 95% ethanol for 4 h and finally was dried under vacuum at  $50^\circ\text{C}$  for 48 h. 9.76 g of PS-SH was obtained. Anal. found (%): C 73.17, H 6.72, S 16.92. IR (KBr,  $\text{cm}^{-1}$ ): 3019 w, 2920 s, 2851 m, 2557 w, 1608 m, 1509 m, 1448 m, 1421 m, 827 m, 761 m, 567 w.

### Synthesis of PS-DEG

Small pieces of sodium metal (0.75 g) were slowly added to a mixture of methanol (20 mL) and dioxane (20 mL). When all of the sodium had undergone reaction, PS-SH (4.0 g,  $\sim 20.5 \text{ mmol SH}$ ) prepared as above was added and the suspension was shaken at room temperature overnight. 2-(2-chloroethoxy)ethanol (5 g,



Scheme 1 Synthetic route of precursors and resins 1–8.

40.1 mmol) was then added and the reaction was stirred at 50°C for 24 h. The resin was filtered and washed with water and ethanol. The procedure for purification of the resin was similar to that of PS-SH. 4.92 g of PS-DEG was obtained. Anal. found (%): C 66.65, H 7.14, S 12.54. IR (KBr,  $\text{cm}^{-1}$ ): 3433 s, 3021 w, 2919 s, 2861 m, 1609 w, 1509 m, 1451 m, 1421 m, 1117 s, 1072 m, 830 m, 762 m, 701 w, 564 w.

#### Synthesis of PS-TEG

The reaction involved 5.0 g ( $\sim 25.5$  mmol SH) of PS-SH, 0.77 g of sodium, 7.2 g of 2-[2-(2-chloroethoxy)ethoxy] ethanol, 20 mL of ethanol, and 20 mL of dioxide. The procedure for synthesis and purification of product was similar to that of PS-DEG. 7.35 g of PS-TEG was obtained. Anal. found (%): C 65.79, H 7.35, S 11.20. IR (KBr,  $\text{cm}^{-1}$ ): 3433 s, 3022 w, 2919 s, 2869 m, 1606 w, 1509 m, 1451 m, 1421 m, 1109 s, 1071 m, 828 m, 761 m, 702 w, 564 w.

#### Synthesis of PS-DEG-Bs

PS-DEG (4.3 g,  $\sim 17.1$  mmol OH) was suspended in pyridine (100 mL) and the mixture was cooled in an ice-water bath. With stirring, 9 mL of BsCl was added dropwise over 0.5 h. After the addition, the mixture was stirred at room temperature for 24 h. The procedure for purification of the product was similar to that of PS-SH. 5.02 g of PS-DEG-Bs was obtained. Anal. found (%): C 64.17, H 6.46, S 11.93. IR (KBr,  $\text{cm}^{-1}$ ): 3021 w, 2919 s, 2860 m, 1607 w, 1508 m, 1448 m, 1423 m, 1188 s, 1123 s, 829 w, 757 w, 689 w, 613 m, 564 w.

#### Synthesis of PS-TEG-Bs

The reaction involved 5.06 g ( $\sim 19.6$  mmol OH) of PS-TEG, 10 mL of BsCl, and 100 mL of pyridine. The procedure for synthesis and purification of product was similar to that of PS-DEG-Bs. 6.23 g of PS-TEG-Bs was obtained. Anal. found (%): C 63.23, H 6.64, S 12.15. IR (KBr,  $\text{cm}^{-1}$ ): 3022 w, 2920 s, 2868 m, 1607 w, 1509 m, 1488 m, 1423 m, 1188 s, 1128 s, 827 w, 757 w, 689 w, 617 m, 564 w.

#### Synthesis of resin 1

Under a nitrogen atmosphere, PS-DEG-Bs (1.5 g,  $\sim 3.08$  mmol  $\text{phSO}_3$ ), AP (0.52 g), and  $\text{K}_2\text{CO}_3$  (0.23 g) were suspended in 80 mL of DMF. The mixture was stirred at 85°C for 24 h. After filtration and washing with water and ethanol, the product was moved to a Soxhlet's extraction apparatus for reflux-extraction in ethanol for 4 h and then was dried under vacuum at 50°C for 48 h. 1.39 g of product was obtained. Anal. found (%): C 66.92, H 6.81, N 2.26, S 9.02. IR (KBr,

$\text{cm}^{-1}$ ): 3431 s, 3022 w, 2921 s, 2861 m, 1604 m, 1509 m, 1450 m, 1421 m, 1214 m, 1112 m, 826 w, 765 w, 701 w, 613 w, 563 w.

#### Synthesis of resin 2

The reaction involved 1.0 g ( $\sim 1.90$  mmol  $\text{phSO}_3$ ) of PS-TEG-Bs, 0.32 g of AP, 0.15 g of  $\text{K}_2\text{CO}_3$ , and 80 mL of DMF. The reactant mixture was stirred for 24 h at 80°C. The procedure for purification of product was similar to that of resin 1. 0.85 g of product was obtained. Anal. found (%): C 63.60, H 6.79, N 1.18, S 10.95. IR (KBr,  $\text{cm}^{-1}$ ): 3432 s, 3021 w, 2919 s, 2865 m, 1605 m, 1508 m, 1446 m, 1422 m, 1212 m, 1110 s, 828 w, 759 w, 699 w, 614 w, 564 w.

#### Synthesis of resin 3

The reaction involved 1.20 g ( $\sim 2.46$  mmol  $\text{phSO}_3$ ) of PS-DEG-Bs, 0.65 g of AMTZ, 0.20 g of  $\text{K}_2\text{CO}_3$ , and 80 mL of DMF. The reactant mixture was stirred for 24 h at 80°C. The procedure for purification of product was similar to that of resin 1. 0.95 g of product was obtained. Anal. found (%): C 66.10, H 6.69, N 2.14, S 10.37. IR (KBr,  $\text{cm}^{-1}$ ): 3432 s, 3021 w, 2919 s, 2857 m, 1605 m, 1509 m, 1445 m, 1421 m, 1214 m, 1120 s, 825 m, 758 w, 700 w, 613 w, 563 w.

#### Synthesis of resin 4

The reaction involved 1.50 g ( $\sim 2.85$  mmol  $\text{phSO}_3$ ) of PS-TEG-Bs, 0.75 g of AMTZ, 0.23 g of  $\text{K}_2\text{CO}_3$ , and 80 mL of DMF. The reactant mixture was stirred for 24 h at 80°C. The procedure for purification of product was similar to that of resin 1. 1.34 g of product was obtained. Anal. found (%): C 63.80, H 6.83, N 1.40, S 11.31. IR (KBr,  $\text{cm}^{-1}$ ): 3448 s, 3021 w, 2918 s, 2864 m, 1605 m, 1509 m, 1448 m, 1421 m, 1213 m, 1109 s, 827 m, 758 w, 701 w, 613 w, 563 w.

#### Synthesis of resin 5

The reaction involved 1.20 g ( $\sim 2.46$  mmol  $\text{phSO}_3$ ) of PS-DEG-Bs, 0.57 g of AETZ, 0.20 g of  $\text{K}_2\text{CO}_3$ , and 80 mL of DMF. The reactant mixture was stirred for 24 h at 80°C. The procedure for purification of product was similar to that of resin 1. 0.97 g of product was obtained. Anal. found (%): C 66.18, H 6.65, N 2.23, S 11.05. IR (KBr,  $\text{cm}^{-1}$ ): 3440 s, 3021 w, 2921 s, 2858 m, 1614 m, 1509 m, 1445 m, 1423 m, 1213 m, 1121 m, 826 m, 758 w, 700 w, 613 w, 564 w.

#### Synthesis of resin 6

The reaction involved 1.50 g ( $\sim 2.85$  mmol  $\text{phSO}_3$ ) of PS-TEG-Bs, 0.66 g of AETZ, 0.23 g of  $\text{K}_2\text{CO}_3$ , and

80 mL of DMF. The reactant mixture was stirred for 24 h at 80°C. The procedure for purification of product was similar to that of resin 1. 1.32 g of product was obtained. Anal. found (%): C 63.47, H 6.76, N 1.52, S 11.78. IR (KBr,  $\text{cm}^{-1}$ ): 3443 s, 3022 w, 2920 m, 2867 m, 1605 m, 1509 m, 1449 m, 1422 m, 1213 m, 1110 s, 829 w, 758 w, 701 w, 615 w, 564 w.

#### Synthesis of resin 7

The reaction involved 1.14 g ( $\sim 2.34$  mmol  $\text{phSO}_3$ ) of PS-DEG-Bs, 0.70 g of MBZ, 0.19 g of  $\text{K}_2\text{CO}_3$ , and 80 mL of DMF. The reactant mixture was stirred for 24 h at 80°C. The procedure for purification of product was similar to that of resin 1. 1.27 g of product was obtained. Anal. found (%): C 64.34, H 5.73, N 3.52, S 19.62. IR (KBr,  $\text{cm}^{-1}$ ): 3442 s, 3021 w, 2919 s, 2854 m, 1605 m, 1508 m, 1457 s, 1426 s, 1107 s, 995 s, 825 w, 758 s, 703w, 563w.

#### Synthesis of resin 8

The reaction involved 1.50 g ( $\sim 2.85$  mmol  $\text{phSO}_3$ ) of PS-TEG-Bs, 0.86 g of MBZ, 0.23 g of  $\text{K}_2\text{CO}_3$ , and 80 mL of DMF. The reactant mixture was stirred for 24 h at 80°C. The procedure for purification of product was similar to that of resin 1. 1.61 g of product was obtained. Anal. found (%): C 63.75, H 6.08, N 2.59, S 17.51. IR (KBr,  $\text{cm}^{-1}$ ): 3441 s, 3022 w, 2919 s, 2863 m,

1605 m, 1509 m, 1456 s, 1427 s, 1108 s, 995 s, 829 w, 758 s, 703 w, 562 w.

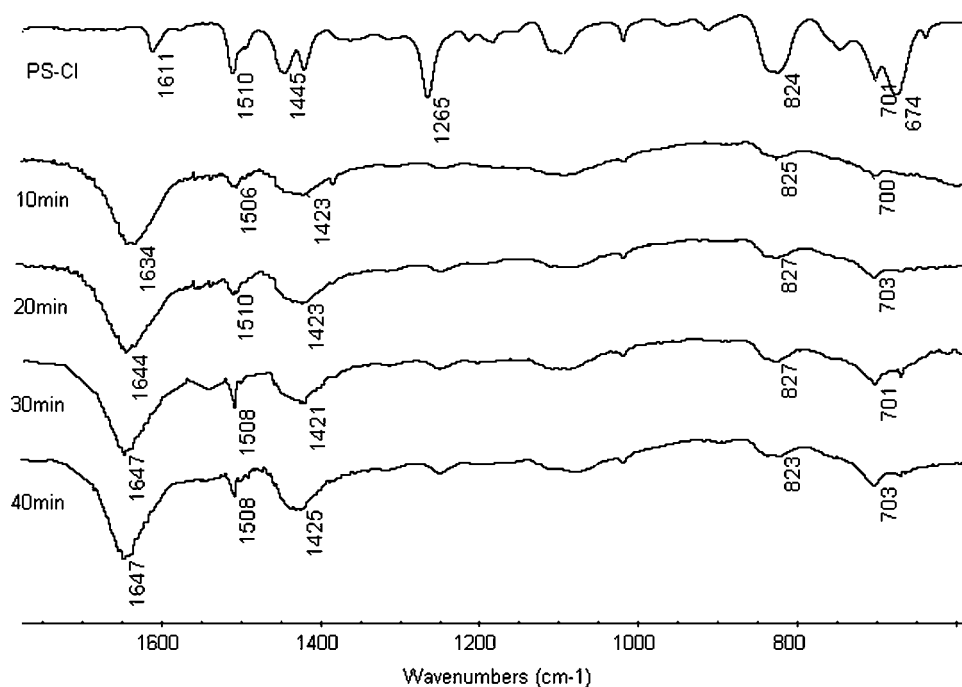
## RESULTS AND DISCUSSION

### Synthesis and characterization of the precursors and resins 1–8

#### Synthesis and FTIR characterization of PS-SH

PS-SH was commonly synthesized by a two-step reaction. That is, PS-Cl was first reacted with thiourea, then hydrolyzed by NaOH aqueous solution. Frechet et al.<sup>26</sup> reported that the first-step reaction should be carried out under refluxing conditions for 48 h using THF/ethanol (3.5:1) as solvent. Our research showed that accomplishing the above reaction needed only 10 min if dioxane/ethanol (4:1) was used as solvent. A possible explanation for this is that: 1) the boiling point of the dioxane/ethanol solution is higher than that of THF/ethanol, which would allow the reaction to be carried out at higher temperature; and 2) dioxane had a better swelling property for PS-Cl and a better soluble property for thiourea than THF, and this made thiourea easily enter into the polymer matrix and then react with C-Cl in PS-Cl.

The entire reaction process could be monitored by the FTIR method. Figure 1 shows that when the reaction was carried out for 10 min the characteristic peaks PS-Cl at  $674\text{ cm}^{-1}$  and  $1265\text{ cm}^{-1}$  of the C-Cl bond<sup>27</sup> almost disappeared completely, meaning that the substitute reaction was accomplished at this time.



**Figure 1** FTIR spectra of the intermediates in the reaction process of PS-Cl with thiourea at different reaction times.

In our work the reaction was kept for 1 h to ensure that the reaction was carried out completely.

#### Synthesis and characterization of PS-DEG and PS-TEG

PS-DEG and PS-TEG were synthesized according to the literature method.<sup>21</sup> PS-DEG and PS-TEG were characterized by the presence of a strong absorption band at 1117  $\text{cm}^{-1}$  (1109  $\text{cm}^{-1}$ ) corresponding to C—O stretching, and by the band at 1072  $\text{cm}^{-1}$  (or 1071  $\text{cm}^{-1}$ ) belonging to the flexural vibration of the —OH group.

In this work, to ensure that the reaction could be carried out completely, the molar ratio of —SH/Na/C1C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH (or C1C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH) of 1:1.5:2 was adopted. However, according to the data of the elementary analysis the percent conversions of the —SH group in PS-SH were only 77.53% and 75.59%, respectively. The probable reason for this was that steric hindrance had arisen by the newly introduced groups (C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH or C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH) and seriously affected further diffusion of reactant into the internal matrix of polymer.

#### Synthesis and characterization of PS-DEG-Bs and PS-TEG-Bs

Recently, we reported the synthesis of poly[4-vinylbenzyl (2-benzenesulfonateethyl)] sulfide (PSMP),<sup>28</sup> which had a similar structure to the PS-DEG and PS-TEG resins. In this study, a similar reaction condition described in the above-mentioned reaction was adopted for the sulfonation of PS-DEG and PS-TEG. The experimental results show that the percent conversions of the —OH group in PS-DEG and PS-TEG (calculated according to the elemental analysis sulfur content) were only 72.8% and 69.0%, which were far lower than that of the PSMP resin. From this it could be assumed that the length of the spacer arm between the —OH group and polymeric matrix had a significant effect on the percent conversion of the —OH group. A steric hindrance arising by a longer spacer arm might make it more difficult for the reaction reagents to arrive at the active site.

The structures of PS-DEG-Bs and PS-TEG-Bs were confirmed by the weakened absorption bands at 1072  $\text{cm}^{-1}$ , 1071  $\text{cm}^{-1}$  in their IR spectra. Furthermore, the presence of the strong absorption bands at 1188  $\text{cm}^{-1}$  (stretching in the —SO<sub>2</sub>— group), 613, 617  $\text{cm}^{-1}$  (bending in the —SO<sub>2</sub>— group) suggested that the phSO<sub>3</sub><sup>−</sup> group had been introduced successfully into the polymer matrix.

#### Synthesis and characterization of resins 1–8

The structures of resins 1–6 were characterized by the presence of new absorption peaks at 1212–1214  $\text{cm}^{-1}$

corresponding to C—N stretching and by the weakened strong bands at 1188  $\text{cm}^{-1}$ , which suggest that the heterocyclic functional groups (AP, AETZ, and AMTZ) were introduced into polymeric matrix. Also, it could be noted that there were still weak absorption peaks of the —SO<sub>2</sub>— group at 613–615  $\text{cm}^{-1}$  in the IR spectra of resins 1–6, indicating that there were some phSO<sub>3</sub><sup>−</sup> groups that had not been substituted by the heterocyclic functional groups.

During the synthesis of resins 7 and 8, their structures were confirmed by the weakened absorption bands at 1188  $\text{cm}^{-1}$ , 613  $\text{cm}^{-1}$  belonging to the —SO<sub>2</sub>— group, and by the presence of strong bands at 1457  $\text{cm}^{-1}$ , 1427  $\text{cm}^{-1}$ , and 995  $\text{cm}^{-1}$  corresponding to the skeletal vibration of MBZ.

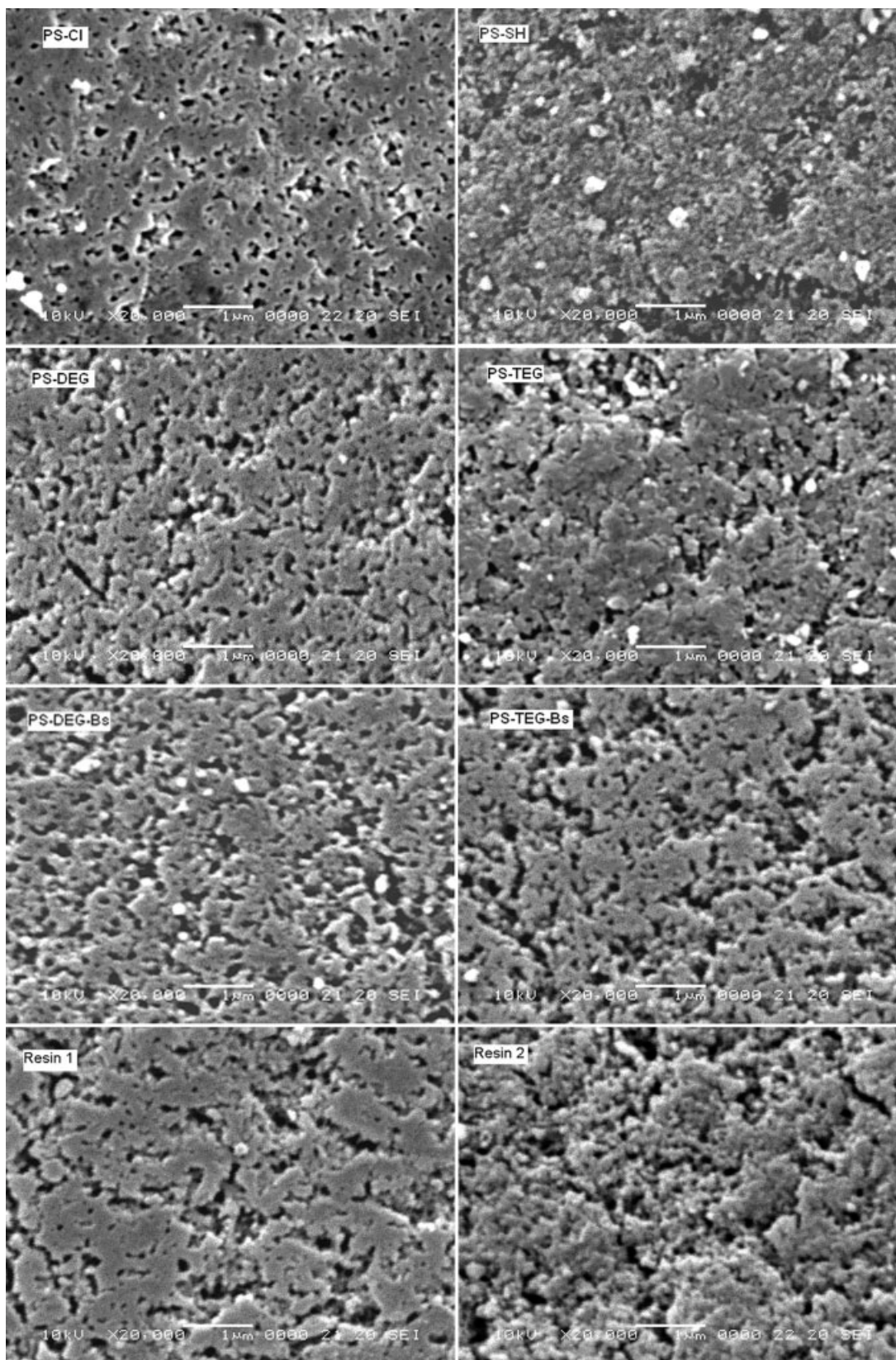
From Table I we note that: 1) compared with resins 1–6, the percent conversion of the functional groups of resins 7 and 8 were 92.44% and 66.1%, respectively, which were much higher. A reasonable explanation for this was that the mechanism of the reaction of PS-DEG-Bs or PS-TEG-Bs with reagents such as AP, AETZ, AMTZ, and MBZ belonged to the S<sub>N</sub>2 mechanism. In general, the nucleophilicity of nucleophile had a significant effect on the nucleophilic substitution reaction. Because the —SH in MBZ was acidic, under basic conditions MBZ could exist in the form of an anion, the nucleophilicity of the S atom was stronger than that of the N atom, so the reaction of MBZ with PS-DEG-Bs or PS-TEG-Bs was easier. As a result, the yields of resins 7 and 8 were higher than those of resins 1–6. 2) The contents of the functional group in resins 1, 3, 5, and 7 were higher than their analogs resins 2, 4, 6, and 8, respectively. Apparently, the length of the spacer arm had a significant effect on the content of the functional group.

**TABLE I**  
Functional Group Capacity and Percent Conversion of Functional Group Resins 1–8

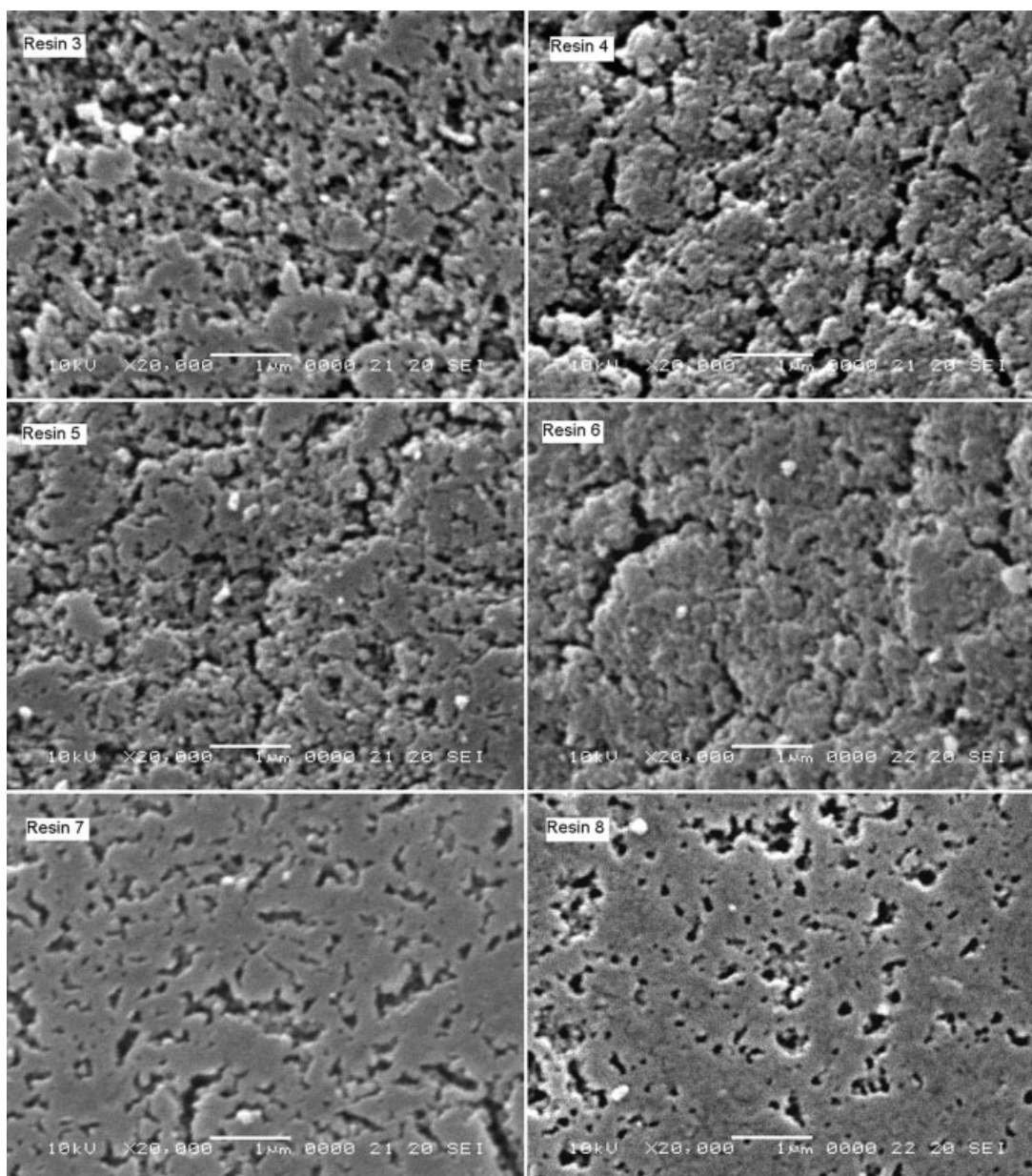
Resins	Functional group capacity <sup>a</sup> (mmol FG/g)	Percent conversion of functional group <sup>b</sup>
Resin 1	0.74	18.63
Resin 2	0.43	11.22
Resin 3	0.57	14.36
Resin 4	0.38	9.82
Resin 5	0.54	13.60
Resin 6	0.35	8.94
Resin 7	3.67	92.44
Resin 8	2.56	66.1

<sup>a</sup> Functional group capacity and percent conversion of functional group were calculated from the sulfur or nitrogen content of resins 1–8.

<sup>b</sup> Percent conversion of the functional group was calculated from the functional group capacity of resin and divided by the content of phSO<sub>3</sub><sup>−</sup> group present in corresponding PS-DEG-Bs or PS-TEG-Bs.



**Figure 2** SEM images of the precursors and resins 1–8.



**Figure 2** (Continued from the previous page)

#### SEM observation of the precursors and resins 1–8

The macroporous structure of chelating resin was of utmost importance in the application for adsorption. The existence of macropores would provide convenient diffusion channels for metal ions into the interior of resins. To observe the surface morphology of the precursors and resins 1–8, micrographs of the gold-coated samples were taken with an SEM and the images are shown in Figure 2. Obviously, there were abundant pores distributed on the surface of the precursors and resins 1–8, which indicated that the macroporous structure of PS-Cl had not been damaged after the reaction with thiurea, NaOH aqueous solution,

benzenesulfonyl chloride, and further with the heterocyclic functional groups.

#### Analysis of pre structures of the precursors and resins 1–8

The BET surface area, BJH desorption cumulative volume of pores, and BJH desorption average pore width of resins 1–8 were determined by the BET method. The results are listed in Table II. From these data we found that resins 1–8 had a similar BET surface area, average pore width, and pore volume due to the similarity of their structures. The range of BJH average

**TABLE II**  
**Data of the Surface Area and Average Pore Diameter of Resins 1–8**

Resins	BET surface area (m <sup>2</sup> /g)	BJH desorption cumulative volume of pores (cm <sup>3</sup> /g)	BJH desorption average pore width (Å)
Resin 1	28.61	0.29	376
Resin 2	23.50	0.28	482
Resin 3	27.37	0.22	380
Resin 4	22.00	0.28	478
Resin 5	29.62	0.19	385
Resin 6	24.16	0.28	476
Resin 7	28.89	0.23	370
Resin 8	21.54	0.26	469

pore width was 370–482 Å, which agrees with the results from SEM observation. As shown in Table II for resins 1–8, a decrease of BET surface area and BJH pore volume was observed compared with the initial material (PS-Cl). This phenomenon might be attributed to some pores being blocked up after crosslinking in the reaction, which resulted in a decreased amount of nitrogen adsorbed in polymeric matrix, thus lowering the BET surface area and BJH pore volume. On the other hand, when the BJH average pore width of resins 1–8 were compared with PS-Cl, an increase was observed. In addition, it was also observed that BJH average pore width and BJH pore volume in resins 2, 4, 6, and 8 were higher than their analogs resins 1, 3, 5, and 7, respectively. This was probably due to the introduction of strong polar groups (C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>) into the weakly polar polystyrene matrix. The difference of polarity in polymeric matrix would result in a repellant, thus increasing BJH average pore width and BJH pore volume, especially in resins containing the longer spacer arm (C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>).

## CONCLUSIONS

Eight macroporous chelating resins incorporating heterocyclic functional groups (such as 2-aminopyridine, 2-amino-5-methylthio-1,3,4-thiadiazole, 2-amino-5-ethyl-1,3,4-thiadiazole, and 2-mercaptobenzothiazole) were synthesized via the hydrophilic spacer arm of polyethylene glycol containing sulfur. Their structures were characterized by FTIR and elemental analysis. The functional group capacities of resins 1–8 were 0.74, 0.43, 0.57, 0.38, 0.54, 0.35, 3.67, 2.56 mmol/g, respectively. In addition, the results of SEM show that

resins 1–8 and the precursors had macroporous structures. The introduction of a spacer arm and the length of the hydrophilic spacer arm might increase BJH average pore width and BJH pore volume. These experimental results indicate that the new resins synthesized here are worth studying further. We are investigating the adsorption properties of resins 1–8 for other metal ions, as well as the selectivity of the resins toward heavy and noble metal ions.

## References

- Chen, Y. Y.; Yuan, X. Z. *React Polym* 1994, 23, 165.
- Shah, R.; Devi, S. *Talanta* 1998, 45, 1089.
- Chen, Y. Y.; Chen, X. W. *J Macromol Sci Chem* 1998, A25, 1443.
- Chen, Y. Y.; Cai, G. P.; Wang, N. D. *J Macromol Sci Chem* 1990, A27, 1321.
- Polakovicova J.; Medved, J.; Stresko, V.; Kubokova, J.; Celkova, A. *Anal Chim Acta* 1996, 320, 145.
- Moyers, E. M.; Fritz, J. S. *Anal Chem* 1976, 48, 1117.
- Nishikawa, H.; Tsuchida, E. *J Phys Chem* 1975, 79, 2072.
- Chen, Y. Y.; Lu, B. X.; Chen, X. W. *J Macromol Sci Chem* 1988, A25, 1443.
- Wang, X. T.; Chen, W. Z.; He, B. L. *Chem J Chin Univ* 1987, 8, 81.
- Dong, S. H.; Liu, F.; Hu, Y. H. *Chem J Chin Univ* 1990, 5, 511.
- Collman, J. P.; Reed, G. A. *J Am Chem Soc* 1973, 95, 2048.
- Collman, J. P.; Gagne, R. R.; Kouba, J.; Lausberg-Wahren, H. *J Am Chem Soc* 1974, 96, 6800.
- Gold, D. H.; Gregar, H. P. *J Phys Chem* 1960, 64, 1464.
- Drago, R. S.; Gout, J. H. *Inorg Chem* 1979, 18, 2019.
- Chen, Y. Y.; Zhaol, Y. *React Funct Polym* 2003, 55, 89.
- Chen, Y. Y.; Liang, C.; Chao, Y. *React Funct Polym* 1998, 36, 51.
- Pramanik, S.; Dhara, P. K.; Chattopadhyay, P. *Talanta* 2004, 63, 485.
- Qu, R. J.; Wang, C. H.; Sun, C. M.; Ji, C. N. *J Appl Polym Sci* 2004, 92, 1646.
- Chattopadhyay, P.; Sinha, C.; Fresenius, D. K. *J Anal Chem* 1997, 357, 368.
- Das, D.; Das, A. K.; Sinha, C. *Talanta* 1999, 48, 1013.
- Baumann, T. F.; Reynolds, J. G.; Fox, G. A. *React Funct Polym* 2000, 44, 111.
- Zuo, G.; Muhammen, M. *React Polym* 1995, 24, 165.
- Kumagai, H.; Inoue, Y.; Yokoyama, T.; Suzuki, T. M.; Suzuki, T. *Anal Chem* 1998, 70, 1970.
- Sanchez, J. M.; Hidalgo, M.; Valiente, M.; Salvado, V. *J Polym Sci A Polym Chem* 2000, 38, 269.
- Bourdelande, J. L.; Campa, C.; Font, J.; de March, P. *Eur Polym J* 1989, 25, 197.
- Frechet, J. M. J.; de Smet, M. D.; Farrall, M. J. *Polymer* 1979, 20, 675.
- Chen, Y. Y.; Yuan, X. Z. *React Polym* 1994, 23, 165.
- Qu, R. J.; Wang, C. H.; Sun, C. M.; Ji, C. N.; Sun, X. Y.; Chen, G. X. *J Appl Polym Sci* 2005, 95, 1558.