Chinese Chemical Letters Vol. 16, No. 9, pp 1193-1196, 2005 1193
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Adsorption Properties of Polystyrene-supported Chelating Resins Containing Heterocyclic Functional Groups

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Abstract: A series of new chelating resins with incorporating heterocyclic functional groups: pyridine, thiadizole, benzothizole into macroporous chloromethylated polystyrene were synthesized *via* hydrophilic spacer arm of polyethylene glycol containing sulfur. These chelating resins were found to show high adsorption capacities for Ag^{+}, Hg^{2+}, Au^{3+} and Pd^{2+}, and the presence of spacer arm can enhance adsorption ability due to increase the hydrophilicity of the chelating resins.

Keywords: Chelating resins, heterocyclic functional groups, spacer arm, adsorption, metal ions.

Chelating resins containing heterocyclic functional groups show high affinity for noble metal ions, some of them have been designed anchoring heterocycles onto solid supports[1,2]. The earlier studies were on the resins containing imidazolylazo[3] and benzimidazolylazo[4,5] functions in a polystyrene bed for the separation of Hg^{2+}, Ag^{+}, and Pd^{2+} metal ions. The recent literature reported that the introduction of spacer arm between functional group and polymeric matrix can enhance the hydrophilicity of the chelating resin and increase the adsorption capacity[6]. In this paper, we report the synthesis and adsorption properties of a series of chelating resins with incorporating heterocyclic functional groups: 2-aminopyridine (AP), 2-amino-5-methylthio-1,3,4-thiadizole (AMTZ), 2-amino-5-ethyl-1,3,4-thiadizole (AETZ), 2-mercaptobenzothiazole (MBZ) into macroporous chloromethylated polystyrene *via* resins with hydrophilic spacer arm containing sulfur.

Experimental

IR spectra were measured on Nicolet MAGNA-IR550 spectrophotometer. Elemental analysis was performed on a Zlementar Variozl III analyzer. Atomic adsorption was measured on GBC-932 AAS spectrograph.

PS-SH, PS-DEG, PS-TEG were synthesized according to the literature method[6,7]. PS-DEG or PS-TEG was then suspended in pyridine, after cooling, benzene sulfonyl chloride was dropped in, the reaction was allowed to proceed for 24 h at room

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temperature. After extraction with ethanol and removal the solvent in vacuum, PS-DEG-Bs, PS-TEG-Bs were obtained. Compounds **1a-d, 2a-d** were synthesized in the similar method. A suspension of PS-DEG-Bs or PS-TEG-Bs prepared above with the reagents(such as AP, AMTZ, AETZ and MBZ), K_2CO_3 in DMF was stirred for 24 h at 85℃. After filtration and washing with water, ethanol, successively the residue was dried under vacuum, **1a-d, 2a-d** were obtained.

Result and Discussion

The structures of the precursors and polymers **1a-d, 2a-d** were characterized by IR and elemental analysis. The IR of PS-SH showed the SH band at 2557 cm^{-1}. The characteristic peak of OH at 1072 cm^{-1} in the IR spectra of PS-DEG, PS-TEG indicated that the polyethylene glycol was successfully introduced into the polymers. In the spectra of PS-DEG-Bs, PS-TEG-Bs, existed the characteristic absorbance peaks of at 1196 cm^{-1}, 1187 cm^{-1}. In the IR spectra of polymers **1a-d**, **2a-d**, the characteristic peaks of benzene sulfonate were disappeared, and the new peaks of the absorbance of C-N appeared at 1213 cm^{-1}, which demonstrated the heterocyclic functional groups had been introduced into polymeric matrix.

Scheme 1

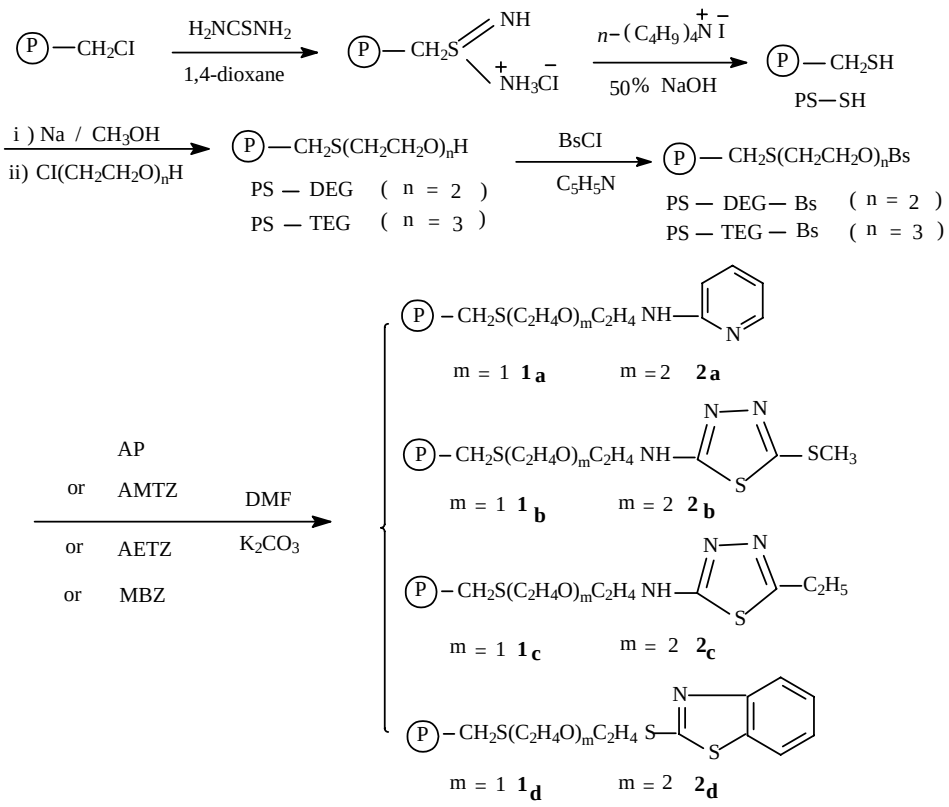

Table 2 showed that the polymers **1a-d**, **2a-d** showed high adsorption capacities for Ag^{+}, Hg^{2+}, Au^{3+}, Pd^{2+} than that for Zn^{2+}, Cu^{2+}, Pb^{2+}. The results are in according with the characteristic of heterocyclic functional group which is easily to bind the soft metal ions. As can be seen in **Table 2**, the different heterocyclic functional groups towards the investigated metal ions followed the order: pyridine $\geqslant$ thiadizole $>$ benzothiazole. Among the three heterocyclic functional groups, the benzothiazole has the lowest adsorption capacity, due to its high hydrophobicity.

Comparing with the adsorption capacities of the polymers **1a-d**, the polymers **2a-d** have higher adsorption capacities for Ag^{+}, Hg^{2+}, Au^{3+} and Pd^{2+}, which indicated the length of the hydrophilic spacer arm with sulfur has the important effect on the adsorption capacity, because the reaction between the functional group and metal ion is effected by the diffusion of the metal ion into the polymer, the high hydrophobicty of polymer makes the metal ions to interact with the functional groups of the polymers difficultly. Introduction of hydrophilic spacer arm can enhance the hydrophilicity of the ligand and so increase the capacity of polymer.

Table 1 Elemental analysis data, functional group concentrations of resins

Compd.	%C	%H	%N	%S	f.g.con(mmol/g)
PS-SH	73.17	6.724	0.477	16.92	5.12
PS-DEG	66.65	7.142	0.310	12.54	3.97
PS-TEG	65.79	7.353	0.254	11.20	3.87
1a	66.92	6.805	2.262	9.024	0.74
2a	63.60	6.791	1.177	10.95	0.43
1b	66.18	6.653	2.231	11.05	0.57
2b	63.47	6.764	1.521	11.78	0.38
1c	66.10	6.694	2.139	10.37	0.54
2c	63.80	6.832	1.400	11.31	0.35
1d	64.34	5.731	3.522	19.62	3.67
2d	63.75	6.080	2.593	17.51	2.56

According to the method described in literature[8]; 50 mg polymer was added to 20 mL of 2×10^{-3}mol/L solution of metal ions, then the solution was shaked for 24 h at 25℃. After filteration, the concentrations of Au^{3+}, Pd^{2+} were determined by means of atomic absorption spectrophotometer, the concentrations of other metal ions were determined by titration method with EDTA. The adsorption capacities were calculated by formula $Q=(C_0-C)V/W$.

Table 2 Adsorption capacities of polymers **1a-d, 2a-d** towards metal ions (mmol/g[a])

Ions	**1a**	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**
Zn^{2+}	0.31	0.25	0.10	0.40	0.30	0.26	0.30	0.15
Cu^{2+}	0.1	0.30	0.23	0.03	0.33	0.13	0	0.13
Pb^{2+}	0.19	0	0.06	0.24	0.83	0.83	0.70	0.18
Ag^{+}	1.32	1.70	1.32	0.38	1.32	1.27	1.71	0.73
Hg^{2+}	1.33	1.52	1.52	1.33	1.93	1.88	2.08	0.79
Au^{3+}	2.00	2.14	2.21	1.72	2.20	2.25	2.31	1.74
Pd^{2+}	1.61	1.40	1.12	0.26	1.77	0.93	1.44	0.37

Ackonwledgment

The authors are grateful to the financial support by the Postdoctoral Science Foundation of China (No. 2003034330), the Science Foundation for mid-youth elite of Shangdong Province, the Natural Science Foundation of Shangdong Province (No. Q99B15) and the National Natural Science Foundation of China (No.2906008)

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Received 15 November, 2004