

Heavy Metal Ion Adsorbents Having Thioamide Groups

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Synopsis

Polyhydrazides are prepared by condensation of cyanuric chloride with dihydrazides of dibasic carboxylic acids and are sulfurized with phosphorus pentasulfide. Copolymers of acrylamide and dimethylacrylamide with divinylbenzene are also sulfurized with phosphorus pentasulfide. The sulfurized polymers adsorb mercuric ion. In order to incorporate thiocarbamide groups into a polymer matrix, methylthioureas are condensed with polyethylenimine. The reactions are carried out in the solid state or in aqueous solution. In the former, water is distilled off from the solidified mixture of the reactants; in the latter, methylthiourea and polyethylenimine are allowed to react in the presence of sulfuric acid. The products are good mercuric ion adsorbents.

INTRODUCTION

Heavy metal ions dissolved in water are one of the worst pollutants of the environment and have caused disasters in many countries. Drainage should be freed of heavy metals such as mercury, cadmium, chromium, and copper as far as possible. Adsorption by synthetic polymers can reduce the concentration of heavy metal ions to a lower level than any other method can. It is an important challenge for polymer chemists to develop new scavengers for heavy metal ions. In fact, many attempts have been made to create complexing polymers.¹

Some heavy metal ions, for example, mercuric, mercurous, and methylmercuric ions, are typical soft acids and form stable complexes with soft bases containing bivalent sulfur. In a previous paper,² heavy metal ion scavengers containing bivalent sulfur were prepared from polyethylenimine, cyanuric chloride, and thiourea. They have advantageous chemical properties but are produced only in the form of powder or flakes. In the present paper, heavy metal ion adsorbents are obtained in the form of beads, which would be more suitable for column operations than powder or flakes.

EXPERIMENTAL

Synthesis of Sulfurized Polyhydrazides

In 67 ml dioxane 2.46 g cyanuric chloride was dissolved and 3.89 g finely pulverized isophthalic dihydrazide was added. After agitation at 70°C for 1 hr, 1.6 g sodium hydroxide in 8 ml water was added dropwise and the reaction was continued for 4 hr. Polymer was collected on a glass filter, washed with water and then with methanol, and dried under vacuum. The yield of beads larger than 100 mesh was 2.78 g. The polymer was sulfurized by refluxing 1.5 g of it with 12 g phosphorus pentasulfide in 55 ml pyridine and heating the reaction

TABLE I
 Sulfurized Polyhydrazide

Dihydrazide	Removal, %
Carbodihydrazide	100
<i>i</i> -Phthalic dihydrazide	99.995
Adipoyl dihydrazide	99
Thiocarbonyldihydrazide	99.6

mixture with water at 70°C for 2 hr. The polymer was collected on a glass filter and washed with water and methanol. Heating with pyridine and water was repeated twice. The pulverized product was removed by decantation. Yield of beads was 0.94 g. Poly(adipoyl dihydrazide) and polycarbonyldihydrazide were sulfurized similarly.

Sulfurized Copolymers of Acrylamides

Copolymers of acrylamide (AAM) and *N,N*-dimethylacrylamide (DMAA) with divinylbenzene were prepared by radical copolymerization under nitrogen atmosphere. Graft copolymers of AAM and DMAA on polypropylene (PP) film are obtained by simultaneous irradiation of γ -rays from ^{60}Co . These copolymers were sulfurized in a similar way as described above.

Synthesis of Methylolthioureas

Methylolthiourea (MTU) and dimethylthiourea (DMTU) were prepared according to Pollak.³ As DMTU was difficult to be isolated from aqueous solution because of high solubility, in some cases a reaction mixture of thiourea with formalin was used for the subsequent reactions without isolation and purification. The reaction mixture gave the same results as pure DMTU.

Dimethylolthylenethiourea was synthesized as follows.⁴ A quantity of 20.4 g ethylenethiourea was dissolved at 45°C in 40 ml formalin adjusted to pH 5.6. The solution was kept at the temperature for 15 min, then water was distilled off under reduced pressure and the residue was solidified in a refrigerator. The product was washed with cold ethanol and tetrahydrofuran and dried. Recrystallization from ethanol gave 14.1 g white crystal, mp 89–90°C.

ANAL. Calcd. for $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2\text{S}$: C, 37.02%; H, 6.21%; N, 17.27%. Found: C, 37.01%; H, 6.31%; N, 17.35%.

Dimethylol compounds of *N,N'*-diethylthiourea and thiosemicarbazide could not be isolated. A reaction mixture with formalin adjusted to pH 5.3–5.7 was used for the reaction with polyethylenimine.

TABLE II

Polyacrylamide	Removal, %
AAM-DVB	99.99
AAM-graft PP	98
DMAA-DVB	100
DMAA-graft PP	99.5

Reaction of Methylolthioureas with Cellulose

Methylolthioureas dissolved in 6 ml water were reacted with 3 g of cellulose powder at 65°C for 1 hr, and then water was distilled off at 100°C by a rotary pump. The products were washed with water and methanol and dried under vacuum.

Reaction of DMTU with Polyethylenimine (PEI)

PEI was supplied as 30% aqueous solution by Nippon Catalyst Chemical Industry Co. Ltd. The degree of polymerization is about 10^3 . The ratio of primary, secondary, and tertiary amines is 1:2:1. DMTU was condensed with PEI by solid-state reaction or aqueous solution reaction.

Solid-state reaction was, for example, carried out as follows. After 3.42 g thiourea was dissolved in 7.1 ml 35% formalin at 45°C, the solution was kept at the temperature for 15 min. The solution was mixed up with 10 ml PEI solution. The mixture was solidified within a few minutes, and a small amount of water came out. After the water was filtered off, the residue was heated at 70°C for 5 hr under evacuation. The product was washed with water and methanol and dried under vacuum. Yield was 6.98 g. The product was pulverized, and beads of 50–80 mesh were used for the evaluation to scavenge heavy metal ion.

An example of the aqueous solution reaction is as follows. A solution of 2.04 g DMTU in 4 ml water was mixed with the solution of 5 ml PEI diluted with 15 ml water and 0.45 ml of sulfuric acid. The mixture was stirred at 70°C for 4 hr. Solid product was collected on a glass filter, washed with water and methanol, and dried under vacuum. Yield was 2.21 g. Beads of 30–50 mesh were collected by sieving. Paper indicators showed that the pH changed from about 8 at the beginning of the aqueous solution reaction to about 3 at the end.

Evaluation of Ability to Scavenge Mercuric Ion

After 30 ml of 10 ppm mercuric ion solution containing 1% sodium chloride (pH 4) was shaken with 150 mg adsorbents overnight, the concentration of mercuric ion was determined by atomic absorption spectroscopy. The lower limit of detection is 0.1 ppb. The percentage of mercuric ion removed from aqueous solution is taken as a measure of the scavenging ability.

RESULTS AND DISCUSSION

Sulfurization of Polymers with Phosphorus Pentasulfide

Polymeric beads are obtained by condensation of cyanuric chloride with dihydrazides of dibasic carboxylic acids. Polymers are insoluble in such ordinary solvents as pyridine, hexamethylphosphoramide, dimethylformamide, alcohol, and water. The polyhydrazides are sulfurized by the reaction with phosphorus

TABLE III
Cellulose Treated with Methylolthioureas

Run No.	DMTU, g	MTU, g	Cellulose, g	Catalyst	Temperature, °C	Time, hr	Yield, g	Removal, %
1	3.06	—	3	—	100	5	2.93	99.97
2	—	1.06	3	HCl	100	6	3.14	99.9
3	—	1.59	3	NaOH	100	4	3.27	94
4	2.04	—	3	HCl	100	4	4.37	89
5	2.72 ^a	—	3	HCl	65	19	3.69	98
6	3.06	—	3 ^b	—	100	4	4.47	96
7	3.06	—	3 ^c	—	100	4	3.87	99.98
8	2.43 ^d	—	3	—	100	4	3.61	16

^a Reaction in aqueous suspension.

^b Aminoethylcellulose instead of cellulose.

^c Cellulose-polyethylenimine graft copolymer instead of cellulose.

^d Dimethylolmethylenurea instead of DMTU.

TABLE IV
Adsorbents by Solid-State Reaction

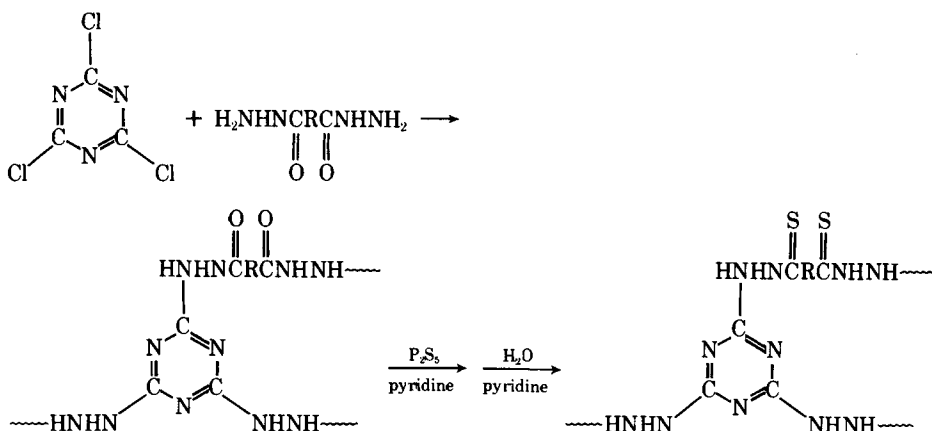
Run No.	Reactant		Reaction		Yield, g	Properties		
	PEI, ml	TU, g	Temperature, °C	Time, hr		Size, mesh	Removal, %	pH
1	10	2.28	80	9	5.55	50-80	99.7	8.3
2	10	3.42	70	5	6.98	50-80	99.8	7.7
3	5	1.55 ^a	70	5	2.32	50-80	99.7	9.1
4	5	1.55 ^b	60	8.5	2.85	30-50	97	7.5
5	5	1.80 ^c	70	5	2.00	30-50	95	7.3
[1]							99.97	3.6
[2]							99.99	4.7

^a Diethylthiourea instead of thiourea.

^b Thiosemicarbazide instead of thiourea.

^c Dimethylolurea in 5 ml water.

pentasulfide and subsequent hydrolysis:



In the sulfurization of polyhydrazides with phosphorus pentasulfide, degradation of polymers is minimized by application of pyridine as solvent.⁵ Therefore, pyridine was used in the present work. As shown in Table I, sulfurized polyhydrazides remove mercuric ion from aqueous solution.

Copolymers of AAM and DMAA with DVB and graft copolymers onto PP film were also sulfurized with phosphorus pentasulfide. Vibrational absorption of amide carbonyl disappeared on sulfurization. Results of mercuric ion absorption are shown in Table II. While copolymers with DVB absorb mercuric ion very well, absorption by graft copolymer is unsatisfactory. This could be attributable to the smaller surface area of graft copolymers than that of beads. From this point of view, grafting onto polypropylene fiber would give more favorable results. Polymers sulfurized with phosphorus pentasulfide are good scavengers for mercuric ion in aqueous solution, but yield of products is too small compared with quantities of starting materials. The polymers are not stable enough, as can be seen from the color change in the course of a few months. During sulfurization and subsequent hydrolysis, much hydrogen sulfide is evolved as by-product. The pyridine, which is used as solvent, has a disagreeable odor. This implies that the process is not recommended from an environmental point of view.

Use of Methylolthioureas

Because sulfurization of preformed polymers with phosphorus pentasulfide has been found to be undesirable, functional sulfur compounds are used to incorporate bivalent sulfur into polymers. Thiocarbamide polymers are prepared by reaction of methylolthioureas with the active hydrogen in the polymers.

Methylolureas are finishing agents for cellulose, and their crease-proofing effect is attributable to crosslinking cellulose molecules. Analogous to methylolureas, reaction of methylolthioureas with cellulose powder has been attempted, and products were examined for mercuric ion adsorption. Results are shown in Table III. Although cellulose loses several percent of its weight during the reaction procedure and vacuum drying, a considerable increase in weight is observed in some runs. Adsorption is low in run 4, where weight increase is large.

TABLE V
Adsorbents by Aqueous Solution Reaction

Run No.	Reactant		TU, g	Reactant		Reaction		Yield, g	Size, mesh	Properties	
	PEI, ml	H ₂ O, ml		H ₂ SO ₄ , ml	F, ml	H ₂ O, ml	Temperature, °C			Time, hr	Removal, %
1	5	20	0.5	2.5	7	70	5	2.22	30-50	99.97	3.6
2	5	15	0.45	—	4	70	4	2.21	50-80	100	3.7
3	5	20	0.6	2.5	7	70	19	2.08	30-50	99.98	4.3
4	10	50	0	5	5	70	19	3.78	20-50	99.98	3.7
5	5	10	0.45	—	3	70	3	0.89	—	99	7.5
6				commercial adsorbent A					30-50	99.7	3.6
7				commercial adsorbent B						99.97	4.1
8				commercial adsorbent C						95	3.6
										99.8	5.6

^a Dimethylolthiourea instead of thiourea.

^b Dimethylolthylenethiourea instead of thiourea.

Products whose weight increase is small adsorb mercuric ion well (nos. 1 and 2). As their sulfur content is low, adsorption capacity should be low. Results are unsatisfactory, except for no. 7, where cellulose-polyethylenimine graft copolymer is used instead of cellulose. Both weight increase and adsorption are high.

As reaction between cellulose-polyethylenimine graft copolymer and DMTU yielded a favorable product, polyethylenimine was reacted with DMTU to obtain mercuric ion adsorbents. They are insoluble in all solvents examined because of crosslinking with thiourea. The reaction can be shown schematically as follows:

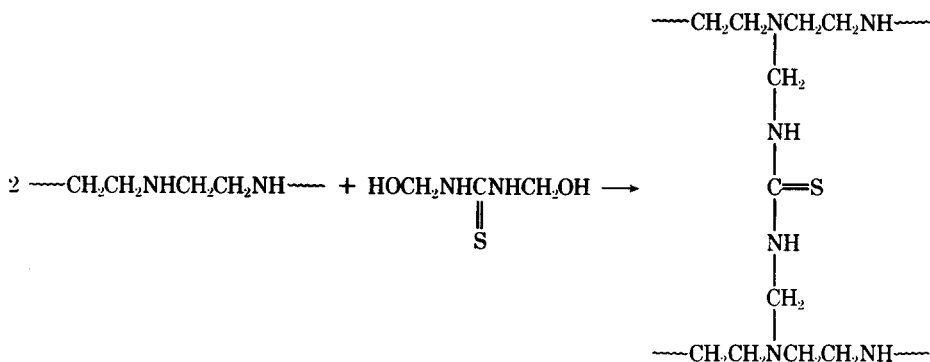
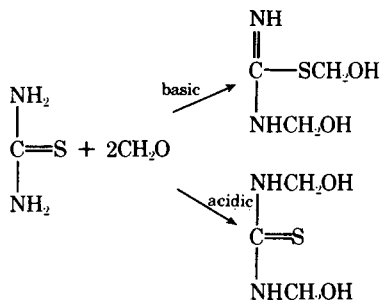


Table IV shows the adsorption of mercuric ion with polymers obtained by solid-state reaction. Removal of mercuric ion is fairly good, but the pH value increased considerably after the solution was shaken with the adsorbents. Therefore, they were washed with 1*N* hydrochloric acid, and removal of mercuric ion was then tried. As shown with [1] and [2], the change in pH value is small and removal of mercuric ion is improved markedly. As polymer crosslinked by means of dimethylolurea adsorbs only 95% of mercuric ion, the thiocarbamide group plays an important role in the adsorption of mercuric ion.

Adsorbents were also prepared by aqueous solution reaction of PEI with methylolthioureas. Table V shows removal of mercuric ion by these adsorbents. They have satisfactory ability to scavenge mercuric ion, and changes in pH are small. When the pH was adjusted with formic acid instead of sulfuric acid, no crosslinked product was precipitated. Sulfuric acid is assumed to work as dehydration catalyst. Without addition of any acid, an insoluble product is obtained from a basic solution, but the product is inferior in adsorbing mercuric ion. Thiourea reacts with formaldehyde at the sulfur atom in basic solutions, and *N,N'*-dimethylolthiourea is obtained from acidic solutions³:



Because the pH of formalin is about 3 due to stabilization by formic acid, N,N'-dimethylolthiourea is obtained. But it is isomerized to N,S-dimethylolthiourea on heating in basic solutions. As polyethylenimine solution is strongly basic, acid is necessary to hinder N,N'-dimethylolthiourea from isomerizing. Washing with acid does not improve the adsorbent which is obtained in the absence of sulfuric acid. The ability to scavenge mercuric ion corresponds well with the sensitivity to the $\text{NaN}_3\text{-I}_2$ test.⁶ This suggests that the effective structure is an S-H group or thiocarbamide group which readily isomerizes to an S-H type.

Commercial adsorbents were examined by the same procedure that was applied to the present adsorbents. Results are shown in the last three lines of Table V. Polymer A is the reaction product of crosslinked amine polymer with carbon disulfide. Polymer B is assumed to have an aminocarboxylic acid as functional group. Polymer C is prepared by the reaction of thiourea, phenol, and formaldehyde. It is apparent that the present adsorbents have excellent performances.

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References

1. T. Saegusa, S. Kobayashi, K. Hayashi, and A. Yamada, *Polym. J.*, **10**, 403 (1978); L. R. Melby, *J. Am. Chem. Soc.*, **97**, 4044 (1975).
2. K. Kaeriyama, T. Rokusha, and K. Naomi, *J. Appl. Polym. Sci.*, **22**, 3075 (1978).
3. F. Pollak, *Mod. Plast.*, **16**, 45, 74, 76 (1939).
4. M. Kato, R. Murase, and S. Yamamoto, *Bull. Text. Res. Inst. Jpn. Government*, **60**, 71 (1961).
5. A. H. Frazer and W. P. Fitzgerald, *J. Polym. Sci. C*, **24**, 25 (1968).
6. F. Fiegl, *Spot Test*, Vol. 2, Elsevier-Maruzen, Amsterdam, 1961, p. 242.

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