

Preparation and Chelating Properties of Mercaptoethylated and Dithiocarboxylated Poly(styrene-*g*-ethylenimine)

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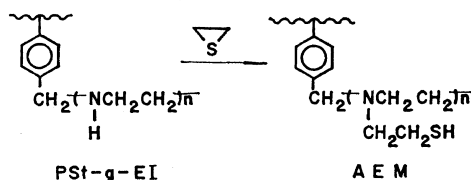
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ABSTRACT: Sulfur atom-containing functional groups were introduced into poly(styrene-*g*-ethylenimine) (PSt-*g*-EI) consisting of a cross-linked polystyrene backbone and linear polyethylenimine branches by reactions with ethylene sulfide (ES) and with carbon disulfide which produced new chelating resins of the aminoethylmercaptan type (AEM) and diethyldithiocarbamate type (DTC), respectively. In the mercaptoethylation of PSt-*g*-EI with ES, the amount of sulfur atom in the SH group was about 65% for all sulfur atoms introduced and the SH group in the polymer was more stable toward oxidation in the atmosphere than monomeric aminomercaptans. AEM was found to form stable complexes with heavy metal ions and quite effective for the adsorption of Hg²⁺. The Cu(II) complex with AEM was pale yellow in acidic and blue in nonacidic media. The extent of dithiocarboxylation with carbon disulfide was about 66%. DTC was less stable in acidic media, whereas the Cu(II) complex was not readily decomposed with 1*N*-HCl. The order of the adsorption capacities of these three resins was PSt-*g*-EI > AEM > DTC.

KEY WORDS Poly(styrene-*g*-ethylenimine) / Mercaptoethylation / Ethylene Sulfide / Dithiocarboxylation / Carbon Disulfide / Chelating Resin /

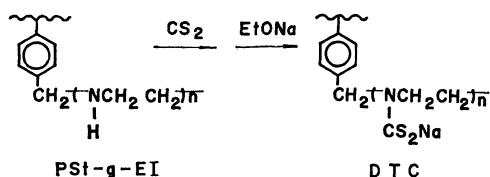
In a previous paper¹ we reported the preparation and application of cross-linked poly(styrene-*g*-ethylenimine) (PSt-*g*-EI) (as chelating resins) having linear polyethylenimine blocks. Further, PSt-*g*-EI was carboxyalkylated.² PSt-*g*-EI was found to form chelates with metal ions such as Hg²⁺, Cu²⁺, Cd²⁺, Ni²⁺, and Co²⁺ by nitrogen atoms. On the other hand, carboxyalkylated PSt-*g*-EI adsorbed metal ions more compactly by chelation through the action of nitrogen and oxygen atoms.

This paper describes the derivation from PSt-*g*-EI to two types of chelating resins containing nitrogen and sulfur atoms as the coordinating sites to metal ions. The first one is an aminoethylmercaptan resin (AEM) from the mercaptoethylation of PSt-*g*-EI. Snyder, *et al.*,³ prepared aminomercaptans by the reaction of amines with olefin sulfides, and the mercaptoethylation of polyethylenimine was already performed with a highly branched sample of polyethylenimine.⁴ However,



the chelating properties of mercaptoethylated polyethylenimine have not been described. Yamaguchi, *et al.*,⁵ reported that β-aminoethylmercaptan was a good masking agent for Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Hg²⁺ in chelatometric titrations. Therefore, AEM is interesting as a new chelating resin with a chelation by nitrogen and sulfur atoms.

The second one is the reaction of PSt-*g*-EI with carbon disulfide leading to the formation of dithiocarbamate resin (DTC). It is well known that a secondary amine gives dithiocarbamates by treating with carbon disulfide;^{6,7} therefore, PSt-*g*-EI will also react with carbon disulfide as shown below. Dithiocarbamates are useful complexing



agents and have been used in an analytical chemistry.⁸ These facts have prompted us to prepare DTC by treating PS-g-EI with carbon disulfide.

This paper also describes the chelating properties of AEM and DTC with metal ions such as Cu^{2+} and Hg^{2+} .

RESULTS AND DISCUSSION

Mercaptoethylation of PS-g-EI

The mercaptoethylation of PS-g-EI was carried out in ethanol, dioxane, or bulk. On addition of ES to PS-g-EI, the system became exothermic, especially in bulk. The system was heated to 80°C for 30 hr in order to complete the reaction. The results are shown in Table I. PS-g-EI swelled to a greater extent in ethanol than in dioxane, so the extent of the reaction (the sulfur content in the product) was higher with the former. Some sulfur atoms were not present in the form of SH group because of the polymerization of ES (eq 1)³ and the air oxidation of SH group producing disulfide (eq 2). The SH group was 65% and 52% of all sulfur atoms, respectively, in those cases of treatment

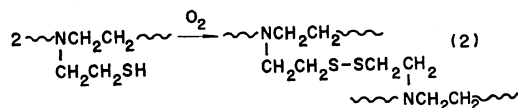
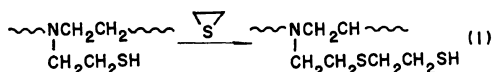


Table I. Mercaptoethylation of PS-g-EI^a

No.	PS-g-EI, ^b g	Solvent ml	ES, g	Yield g	% ^c	S content, ^d mmol/g	SH group, ^e mmol/g
AEM1	0.56	Ethanol (2.5)	0.33	0.86	91	6.18	3.74
AEM2	0.51	Bulk	0.30	0.81	100	6.46	3.33
AEM3	0.55	Dioxane (2.0)	0.32	0.85	94	5.60	3.65
AEM4	4.60	Ethanol (30)	2.75	7.31	98	6.15	4.00

^a 80°C for 30 hr.

^b EI unit content, 9.92 mmol/g.

^c Based on ES.

^d By elemental analysis.

^e By titration.

with and without solvent. But the total sulfur content was highest in the bulk reaction. This result can be understood if it is assumed that ES polymerization occurred more readily without solvent because of an increase in the concentration of ES.

The IR spectrum (KBr disk) of mercaptoethylated PS-g-EI (sample AEM1) shows the appearance of a new absorption at 1190 cm^{-1} of $\nu_{\text{N-C}}$ due to a tertiary amino group through a decrease in absorption at 1130 cm^{-1} of $\nu_{\text{N-C}}$ owing to the secondary amino group in polyethylenimine.⁹ In addition, two new weak absorptions appeared at 721 and 672 cm^{-1} which were assignable to $\nu_{\text{C-S}}$ (Figure 1b).

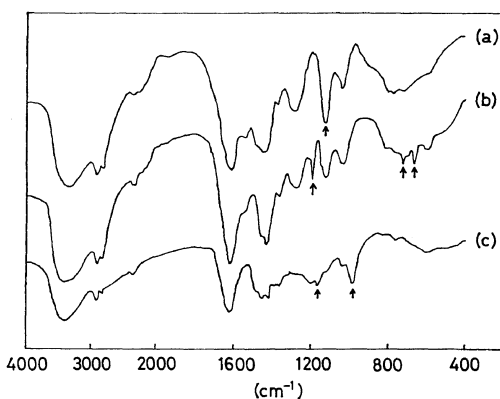
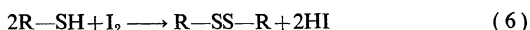
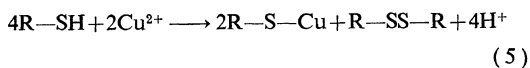
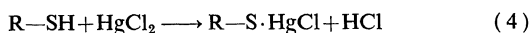
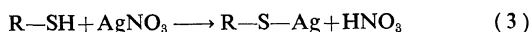


Figure 1. IR spectra (KBr disk) of (a) PS-g-EI, (b) mercaptoethylated PS-g-EI, (sample AEM1), and (c) dithiocarboxylated PS-g-EI (sample DTC).

Determination of the SH Group in AEM

AEM is not soluble in any solvent because of its cross-linked structure. Therefore, it is preferable to determine the SH group by a back titration using

an excess of a reagent which reacts selectively with the SH group in a heterogeneous system. The fundamental reactions used to determine SH residue are as follows.¹⁰ In this study, PS-*g*-EI



was also found to consume I₂, though it did not contain any SH groups. This is probably due to physical adsorption. Thus, the method based on eq 6 was not suitable for the determination of SH groups in AEM. According to method which uses metal salts (eq 3–5), the amino groups in AEM will also form complexes with these metal ions. But the amine complex of Ag⁺ is known to be less stable. For example, the stability constants of triethylenetetramine complexes with Ag(I), Hg(II), and Cu(II) are 7.7, 25.26, and 20.4, respectively.¹¹ Therefore, in a strong acidic condition Ag⁺ will react exclusively with the SH group. AEM was subjected to a reaction with AgNO₃ at a pH below 0.1 in the dark at 30°C for 72 hr, and the quantity of Ag⁺ adsorbed (mmol/g) was calculated. The results are shown in the last column of Table I. Under the same conditions, PS-*g*-EI adsorbed 0.02 mmol/g of Ag⁺, which was less than the limit of experimental error. Accordingly, the quantity of Ag⁺ (gram atom) adsorbed was taken to be equal to the content of the SH group (in moles).

Stability of the SH Group in Air

It was reported that the primary mercapto groups prepared from ES and secondary amines were less stable than simple unsubstituted mercaptans in air.³ Therefore, the SH group in AEM was also assumed to be less stable in air. AEM4 (dried or

Table II. Stability of the SH group in AEM toward oxidation in the atmosphere^a

Time (month)	0	1 ^b	3 ^b	2 ^c
SH (mmol/g)	4.00	4.01	3.95	3.88

^a AEM4 was allowed to stand at room temperature in contact with the air. After a fixed period of time, the SH content was determined.

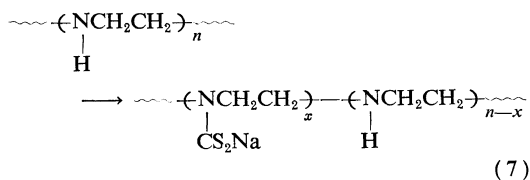
^b Dry AEM4 was used.

^c AEM4 swollen with water was used.

swollen with water) was allowed to stand at room temperature in air. After a specified period of time, the SH group content was determined. The results are shown in Table II. The content of SH group in AEM decreased only slightly in the time allotted. It seems that the SH group in AEM is more stable since the aminomercapto groups are included in cross-linked PST.

Dithiocarboxylation of PS-*g*-EI

PS-*g*-EI was allowed to react with excess carbon disulfide in ethanol. As the reaction proceeded, the pale yellow resin turned yellow. Dithiocarboxylated PS-*g*-EI was obtained as a sodium salt by treating with sodium ethoxide after the reaction. The IR spectrum (KBr pellet) of the sample showed absorptions at 1155 and 980 cm⁻¹ due to ν_{C=S} and ν_{N-C=S}, respectively. The characteristic band at 1130 cm⁻¹ of ν_{N-C} assigned to crystalline polyethylenimine blocks⁹ nearly disappeared probably because of a decrease in crystallinity by dithiocarboxylation. The content of the CS₂Na group and the extent of the reaction were estimated by the difference in nitrogen content between that of the original PS-*g*-EI and that of the product, assuming there was no side reaction. Even if a by-product of sodium xanthate had been



present, it would have been removed by washing with ethanol. Thus, the CS₂-Na content and the extent of reaction yield (100*x*/*n*) were 3.60 mmol/g and 65.7%, respectively.

Adsorption of Metal Ions with AEM and DTC (Batch Method)

The adsorption experiment was carried out at 30°C for 72 hr. It had been established that the adsorption actually reached saturation within about 48 hr.

The effect of pH on the adsorption of Cu²⁺, Cd²⁺, and Hg²⁺ with AEM4 is shown in Figure 2. The adsorption capacity includes both the capacity of mercaptoamine chelate (or mercaptide) and that of simple amine chelate. Since the former is more stable, even in acidic medium, the pH dependence

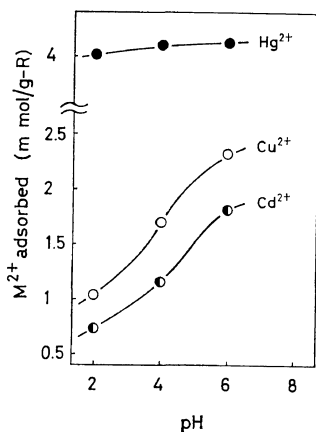
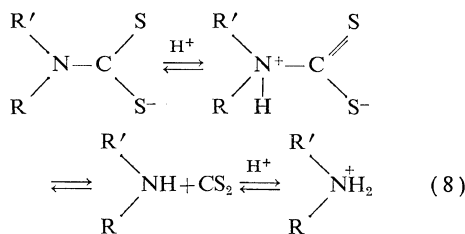


Figure 2. Effect of pH on the adsorption of metal ions with AEM4; resin (0.25 g) in 50 ml of metal ion solution (0.025 mol/l), 30°C for 72 hr.

of this capacity seems to be due primarily to the latter. Anyway, the adsorption of Hg^{2+} was much higher, *i. e.*, $\text{Hg}^{2+} \gg \text{Cu}^{2+} > \text{Cd}^{2+}$, by mercaptoethylation. In the case of PS-*g*-EI, the selectivity was $\text{Hg}^{2+}(4.79) > \text{Cu}^{2+}(4.57) > \text{Cd}^{2+}(3.76)$, where the values in parentheses are the adsorption capacity (mmol/g) at pH 6.¹

When DTC (yellow resin) was treated with Cd^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , and Ni^{2+} , all systems except Cd^{2+} turned dark brown. The Cd^{2+} system was yellow. Since the color of PS-*g*-EI—metal complexes is similar to those of amine complexes, (for example, Cu(II) complex is blue), the color change of DTC is taken to show that PS-*g*-EI was definitely dithiocarboxylated with carbon disulfide.

In acidic media, DTC was less stable and it decomposed to give carbon disulfide and the starting polymer. It is reported that dithiocarbamate ion is protonated in an acidic solution and decomposed subsequently into carbon disulfide and the protonated amine according to the following scheme.⁸



The decomposition is favored when the pH of the medium is lower than the $\text{p}K_a$ for the $\text{R}'\text{RNH}_2^+$ ion.⁸ The $\text{p}K_a$ of a conjugate acid of linear PEI is probably lower than 10, as the $\text{p}K_a$ for Et_2NH_2^+ is 10.11. Therefore, DTC will be unstable when the pH of the medium is lower than 10. But heavy metal ions usually form hydroxides and precipitate at pH 10. Therefore, the adsorption experiments were carried out in moderate acidic conditions. The results are shown in Table III. The order of adsorption capacity was $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$, which agreed with the stability constants for dithiocarbamate complexes.⁸

Table III. Adsorption of metal ions with DTC (Batch method)^a

Metal ion	Hg^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
pH	5.5	5.5	5.5	6.5	6.5
Adsorption capacity, mmol/g	1.44	0.91	0.28	0.29	0.31

^a Experimental conditions; resin (0.25 g) in 50 ml of metal ion (0.025 mol/l) solution, 30°C for 72 hr.

Adsorption and Elution by a Column Method

The adsorption and elution experiments of Cu^{2+} and Ni^{2+} with AEM4 and DTC were carried out using a column method. The results are shown in Figures 3 and 4. The adsorption capacity itself (mol/l of resin) became smaller by the mercaptoethylation and by the dithiocarboxylation. But the level of the quantity of Cu^{2+} , leaking at the bottom of the column, with PS-*g*-

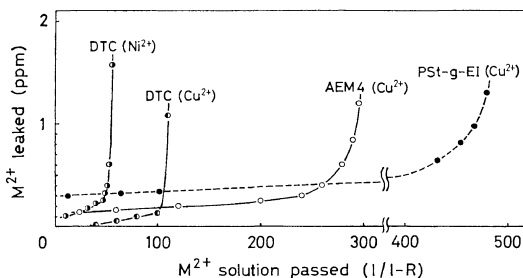


Figure 3. Adsorption of metal ions by the column method: O, ●, and ●, a Cu^{2+} solution (32.0 ppm, pH 4.4) was passed through a column packed with 5 ml of resin at a flow rate of SV 10; ●, a Ni^{2+} solution (29.4 ppm, pH 6.2) was passed through a column packed with 4.5 ml of DTC at a flow rate of SV 11.

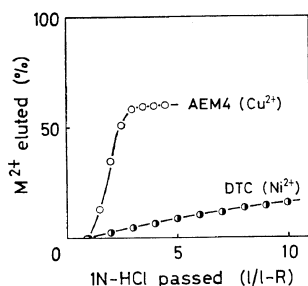


Figure 4. Elution of the adsorbed metal ions with 1 *N*-HCl: ○, AEM4 (adsorbed Cu²⁺ = 47.3 mg, flow rate = SV2; ●, DTC (adsorbed Ni²⁺ = 10.2 mg, flow rate = SV3).

EI (0.30–0.40 ppm), AEM4 (0.15–0.2 ppm), and DTC (~0.15 ppm) decreased in this order. The lower level of Cu²⁺ leaking indicates the higher stability of the Cu(II) complex with the respective resin.

By passing a 1-*N* HCl solution through the column, the Cu²⁺ complexed with PS-*g*-EI was recovered completely.¹ But the recoveries of Cu²⁺ with AEM4 and DTC were 60% and about 0%, respectively. In the AEM4 column, the recovered Cu²⁺ is probably due to the complexed one with only nitrogen atoms. The pale yellow resin of AEM4 turned to blue by complexation with Cu²⁺ and it was decolorized by passing 1-*N* HCl solution. The resin in the column turned blue again under neutral or alkaline conditions by washing the column with water or with NaOH aqueous solution. By passing the 1-*N* HCl solution through the column again, the resin decolorized again. However, no more Cu²⁺ was recovered. It may be concluded that the Cu²⁺ complexed with sulfur and nitrogen atoms cannot be liberated with 1-*N* HCl and the complex itself is pale yellow in acidic media and blue in nonacidic media.

In the DTC column, the Cu²⁺ adsorbed was not recovered with 1-*N* HCl, but the Ni²⁺ was gradually liberated with the evolution of carbon disulfide.

These results suggest that introducing sulfur atom-containing functional groups into PS-*g*-EI produced chelating resins which formed more stable complexes. But it was not possible to repeat the adsorption–desorption procedures.

EXPERIMENTAL

Materials

ES was prepared according to the literature,¹² and redistilled under nitrogen. Commercial reagents of carbon disulfide and all solvents were distilled under nitrogen. Cross-linked PS-*g*-EI was prepared by the graft polymerization of 2-methyl-2-oxazoline onto chloromethylated polystyrene (cross-linked) followed by the hydrolysis of the graft copolymer as reported previously.¹ The EI unit content was 9.92 mmol/g (degree of hydrolysis = 67.3%), and the \overline{DP} of the grafted part was 15.9.

Mercaptoethylation of PS-*g*-EI

A typical experiment (No. AEM4) is given as follows. PS-*g*-EI (4.60 g, NH = 45.7 mmol) was placed in a 150-ml ampoule under nitrogen. After 30 ml of ethanol were added into the ampoule, the mixture was kept at room temperature for a day so that PS-*g*-EI could become swollen sufficiently. ES (2.75 g, 45.7 mmol) was added into the mixture, then the ampoule was sealed after the system was degassed. After the mixture was shaken at 80°C for 30 hr, the resin was isolated by filtration, and washed with nitrogen-treated ethanol, and dried *in vacuo* at 70°C to give 7.31 g. The product (AEM4) was stored under nitrogen.

Dithiocarboxylation of PS-*g*-EI

After the PS-*g*-EI (3.10 g) swelled in 20 ml of ethanol in a 100-ml flask under nitrogen for a day at room temperature, 3.5 ml of carbon disulfide were added to the flask and the mixture was heated at 60°C for 23 hr. A sodium ethoxide solution (0.5 g of sodium metal and 20 ml of ethanol) was added, and the mixture was allowed to stand at room temperature for a day. The resin was isolated by filtration and washed with ethanol until the washings became neutral, followed by washings with toluene and with diethyl ether, and then, dried *in vacuo* at 70°C to a constant weight of 4.63 g.

Determination of the SH Group in AEM

About 0.25 g of AEM was weighed out into a 100-ml Erlenmeyer flask, to which 0.1-*N* AgNO₃ aqueous solution (25 ml) and 2-*N* HNO₃ (25 ml) were added. The mixture was allowed to stand in the dark at 30°C for 72 hr with occasional shaking.

The Ag^+ concentration of the supernatant solution was determined by thiocyanate titration. The SH group content was calculated from the consumption of Ag^+ .

Adsorption of Metal Ions with the Resins (Batch Method)

Commercial reagents of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, HgCl_2 , $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were used without further purification. Metal salts were dissolved in Clark Lubs' buffer solution in order to keep the pH constant during the adsorption experiment. The adsorption capacity for the metal ion (mmol/g-Resin) was estimated in a way similar to the method for determination of the SH group. The metal-ion concentration was assayed by chelatometry with EDTA.

Adsorption and Elution of Cu^{2+} and Ni^{2+} by a Column Method

A column packed with AEM4 or DTC (5 ml in the wet state) in a glass tube (8 mm of internal diameter) was prepared for these experiments. The details of the procedure have been described previously.^{1,2} The concentration of Ni^{2+} effluent solution was determined as follows. A mixture of the sample solution (5.0 ml) and 0.2 ml of bromine-saturated water solution were placed in a 10 ml volumetric flask, to which a 14% ammonia aqueous solution was added until the bromine color disappeared; also three drops of excess ammonia solution were added. Then, 1.0 ml of a 0.1% dimethylglyoxime ethanol solution was added to the flask and the mixture was diluted to the mark with water. The absorbance at 444 nm¹³ after 5 min from the addition of the bromine

solution was used to determine the concentration of Ni^{2+} .

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