

Preparation of Crosslinked Poly(styrene-*g*-N-carboxyalkylated Ethylenimine) as Chelating Resin

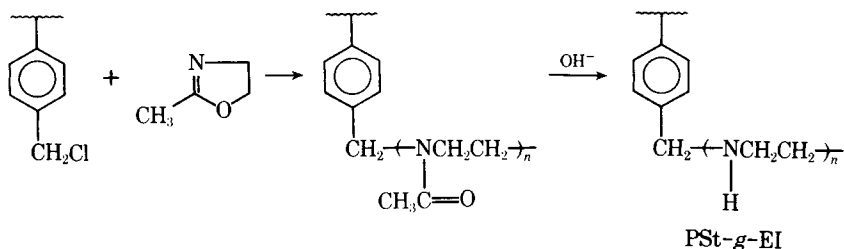
TAKEO SAEGUSA, SHIRO KOBAYASHI, and AKIRA YAMADA,
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

Synopsis

Carboxymethyl and ethyl groups were introduced into crosslinked poly(styrene-*g*-ethylenimine) (PSt-*g*-EI), consisting of a crosslinked polystyrene backbone with linear polyethylenimine branches, by the reaction of PSt-*g*-EI with monochloroacetic acid and β -chloropropionic acid. Carboxyethylation was also performed by reaction of the PSt-*g*-EI with acrylic acid. The extent of the reaction was determined by the change in the nitrogen content of the resin. The adsorption of metal ions such as Cu^{2+} , Cd^{2+} , Hg^{2+} , Ni^{2+} , and Ca^{2+} by carboxyalkylated PSt-*g*-EI was examined. With the introduction of carboxyalkyl groups, the adsorption capacity for metal ions (per gram of resin) decreased, whereas the affinity of the resin for these ions increased.

INTRODUCTION

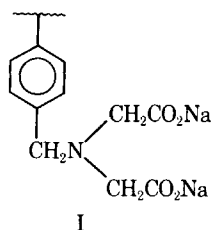
Recently, we reported the preparation of poly(styrene-*g*-ethylenimine) (PSt-*g*-EI) containing the linear structure of polyethylenimine. It was prepared by the graft polymerization of 2-methyl-2-oxazoline onto chloromethylated polystyrene (noncrosslinked or crosslinked) and by the subsequent hydrolysis of the graft copolymer¹:



Crosslinked PSt-*g*-EI was quite effective for the adsorption of heavy metal ions such as Cu^{2+} , Hg^{2+} , and Cd^{2+} . However, the resin could not be used for the adsorption of metal ions which do not form stable amine complexes, because the site for coordinating metal ions in PSt-*g*-EI is the secondary amino group.

It is well known that the carboxymethylation of amines produces effective chelating agents such as EDTA. Indeed, prior to the present study, Amberlite IR-4B and IR-45, two polyamine-type anion exchange resins, had been carboxymethylated by condensation with monochloroacetic acid.² Aminated PSt prepared by the reaction of chloromethylated PSt with ethylenediamine,

diethylenetriamine, or triethylenetetramine had been carboxymethylated.³ Crosslinked poly(N-carboxyalkylethylenimines) had been prepared by the copolymerization of 1-aziridinealkanoic acid esters and β,β' -di-(1-aziridinyl)diethylbenzene.⁴ Furthermore, an iminodiacetic acid-type resin (I) had been obtained by Okawara et al.⁵:



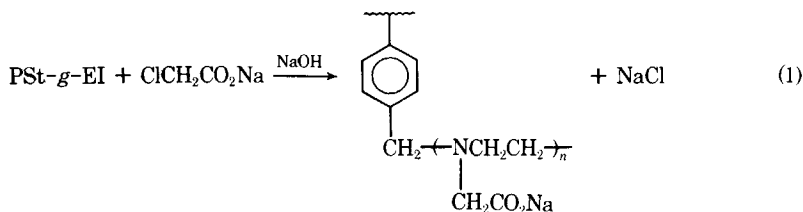
The chelation of metal ions by resin I is analogous to their chelation by EDTA. It is claimed that resin I adsorbs metal ions more effectively than other resins because of their chelation through nitrogen and oxygen atoms. Because of this adsorption advantage, it was considered worthwhile to introduce carboxyalkyl groups into PSt-*g*-EI in order to explore a new type of chelating resin. The present paper describes the preparation of crosslinked poly(styrene-*g*-N-carboxymethylethylenimine) and poly(styrene-*g*-N-carboxyethylethylenimine) and their chelating properties with several metal ions.

RESULTS AND DISCUSSION

In this paper, crosslinked poly(styrene-*g*-ethylenimine) (PSt-*g*-EI) was employed as the parent polymer in all cases. Three kinds of PSt-*g*-EI (A, B, and C) were employed (see experimental section).

Carboxymethylation of PSt-*g*-EI

PSt-*g*-EI was carboxymethylated by condensation with monochloroacetic acid under alkaline conditions:



As the reaction between PSt-*g*-EI and ClCH₂CO₂Na proceeded, the pH of the system gradually decreased. The system was then made alkaline with excess sodium hydroxide, and the reaction was allowed to continue until the pH of the system remained constant. The conditions employed and the results obtained are shown in Table I. Degree of substitution and the CO₂Na content were calculated based on the difference in the nitrogen content between the starting PSt-*g*-EI and the product. The determination of the CO₂Na content by pH titration was very difficult because the system was heterogeneous. The titration curve varied monotonously and the endpoint could not be resolved. It has been

TABLE I
Carboxymethylation and Carboxyethylation of PST-*g*-EI

Sample ^a	Kind of PST- <i>g</i> -EI, ^b g	Reagent	Reagent/ EI unit, molar ratio	Time at 70°, hr	Yield, g	N in the product, %	CO ₂ Na content, mmole/g	Degree of substi- tution, %
CM1	A (1.10)	ClCH ₂ CO ₂ H	10.1	33 ^c	1.64	9.14	5.11	94.2
CM2	B (3.51)	ClCH ₂ CO ₂ H	23.9	70 ^c	3.11	11.03	5.90	108.3
CM3	C (4.03)	ClCH ₂ CO ₂ H	1.43	30 ^d	5.60	15.00	3.42	47.4
CE1	C (2.09)	ClCH ₂ CH ₂ CO ₂ H	1.42	30 ^d	2.96	14.15	3.34	49.2
CE2	C (4.11)	CH ₂ =CHCO ₂ H	1.12	20 ^e	7.06	12.46	4.22	70.4
CE3	C (3.04)	CH ₂ =CHCO ₂ H	1.12	20	—	11.16	4.88	91.0

^a CM and CE mean carboxymethylation and carboxyethylation, respectively.

^b (a); EI unit content = 9.17 mmole/g, degree of hydrolysis = 83.1%, $\bar{D.P.}$ of the grafted EI unit = 4.3; (b); 10.30 mmole/g, 69.1%, 15.9; and (c); 9.92 mmole/g, 67.3%, 15.9.

^c Under weak alkaline conditions.

^d 7 hr under acidic conditions and 23 hr under weak alkaline conditions.

^e At 60°C.

reported that the carboxyl groups in a crosslinked polystyrene cannot be satisfactorily determined by titration.⁶

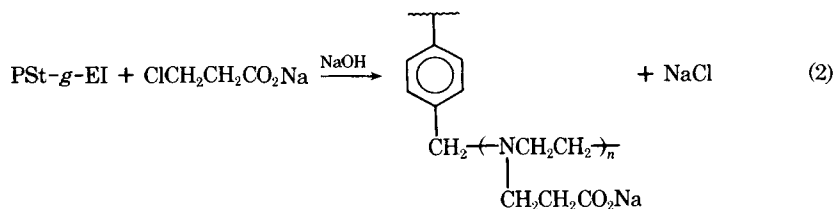
In the preparation of sample CM2, PST-*g*-EI was treated with a 10 molar excess of monochloroacetic acid for 35 hr, followed by repeated washing with water. The procedure was repeated. The extent of reaction exceeded 100%, i.e., 108.3%. A value greater than 100% may be explained as follows: (1) the acetyl group, present in the starting PST-*g*-EI due to incomplete hydrolysis, was further hydrolyzed and carboxymethylated under the above conditions; and/or (2) a fraction of the amino groups was quaternized. Using a slight excess of monochloroacetic acid, the degree of substitution was low because of a side reaction, i.e., hydrolysis of monochloroacetic acid (sample CM3).

The IR spectrum (KBr pellet) of the carboxymethylated PST-*g*-EI (sample CM3) showed two new absorption bands at 1550 and 1400 cm⁻¹ due to the carboxylate anion [Fig. 1(b)]. The characteristic band at 1130 cm⁻¹ of ν_{N-C} assigned to the crystalline polyethylenimine unit⁷ almost disappeared, most likely due to the decreased crystallinity introduced by the carboxymethylation.

Carboxyethylation of PST-*g*-EI

The carboxyethylation was carried out by two methods. The first (method I) used β -chloropropionic acid as a condensation reagent in the same manner as monochloroacetic acid was used for the carboxymethylation. In the second method (method II), the carboxyethylation was accomplished under a nitrogen atmosphere by the Michael addition of the N—H to acrylic acid in ethanol containing a small amount of 2,6-di-*tert*-butyl-*p*-cresol as a radical inhibitor:

Method I



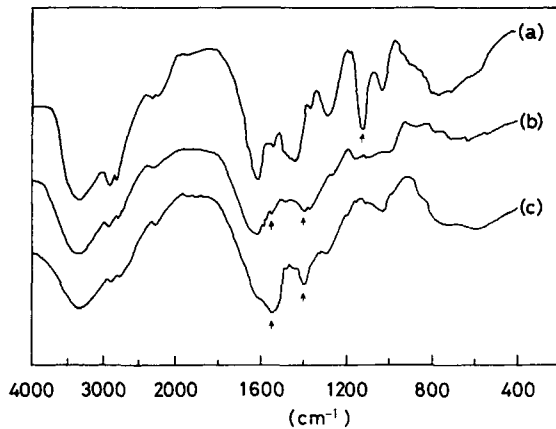
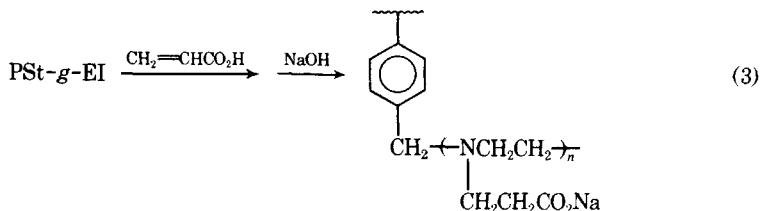


Fig. 1. Infrared spectra of polymers: (a) PSt-*g*-EI (C); (b) CM3; (c) CE2.

Method II



The product was isolated and converted to the Na salt by washing with an aqueous NaOH solution. The results are also listed in Table I. The extent of the reaction and the CO₂Na content were calculated as described above. The second method gave better results for the carboxyethylation.

The IR spectrum (KBr pellet) of sample CE2 revealed two clear absorption bands at 1550 and 1400 cm⁻¹. These are due to the carboxylate anion group [Fig. 1(c)].

Adsorption of Metal Ions by the Resins (Batch Method)

The adsorption of Cu²⁺, Cd²⁺, Hg²⁺, Ni²⁺, and Ca²⁺ was carried out in H₂O at 30°C for 72 hr, although the adsorption actually reached saturation within about 48 hr. The effect of pH on the adsorption of these metal ions by carboxymethylated and carboxyethylated PSt-*g*-EI is shown in Figures 2 and 3, respectively. The extent of adsorption was Hg²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺ > Ca²⁺ at pH 6 with both resins. The dependence on pH of the adsorption was larger with carboxyethylated PSt-*g*-EI than with carboxymethylated PSt-*g*-EI. This may be due to the smaller stability constant of β-carboxylamine chelate than that of α-carboxylamine chelate.⁸⁻¹⁰

By introducing carboxyalkyl groups into PSt-*g*-EI, a new type of chelating resin which adsorbs Ca²⁺ has now been prepared, whereas PSt-*g*-EI exhibits little adsorption capacity for Ca²⁺. The capacity for Ca²⁺ is related to the CO₂Na content as shown in Figure 2 (samples CM2 and CM3) and Figure 3 (samples CE2 and CE1). In Figures 2 and 3, the capacity noted for Hg²⁺, Cu²⁺, Cd²⁺, and Ni²⁺ includes the adsorption by secondary amino residues which have not been

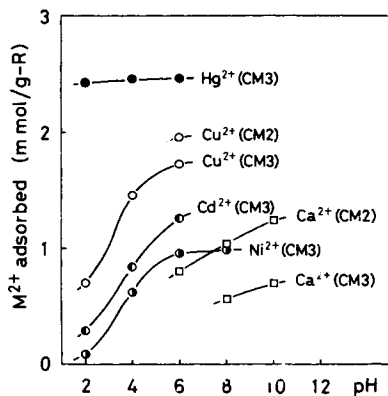


Fig. 2. Effect of pH on the adsorption of metal ions by carboxymethylated resin: resin (0.25 g) in 50 ml aqueous metal ion solution (0.025 mole/l.), 30°C for 72 hr.

carboxyalkylated. In the case of Ca^{2+} , the adsorption capacity is obviously due only to carboxyl groups. At pH 10, 1 mole Ca^{2+} is captured by 4.7 (CM2) and 3.2 (CE2) moles aminoacid groups, respectively (Figs. 2 and 3).

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

The adsorption and elution experiments of Cu^{2+} with CM3, CE3, and PST-g-EI (C) were carried out using the column method; the results are graphically presented in Figures 4 and 5. The column experiment with PST-g-EI has been described in a previous paper.¹ Copper leakage with CM3 was lowest, and that with PST-g-EI was greatest. Therefore, resins having higher apparent affinities for metal ions than the PST-g-EI resin can be obtained by introducing carboxyl groups, although the adsorption capacity (per gram of resin) becomes smaller; e.g., for Cu^{2+} the capacity is 3.85 and 2.88 mmole/g-R with PST-g-EI (C) and

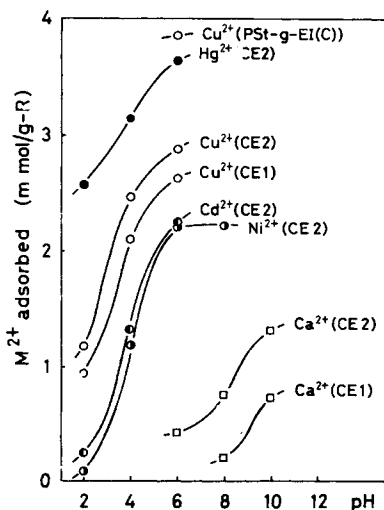


Fig. 3. Effect of pH on the adsorption of metal ions by carboxyethylated resin: resin (0.25 g) in 50 ml aqueous metal ion solution (0.025 mole/l.), 30°C for 72 hr.

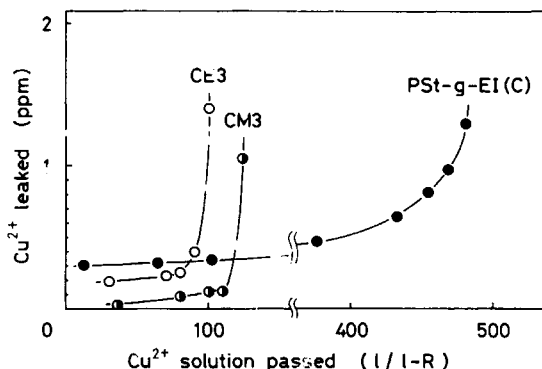


Fig. 4. Adsorption of Cu^{2+} by column method. Aqueous Cu^{2+} solution (32.0 ppm, pH 4.4) was passed through a column packed with 5 ml resin at a flow rate of SV 10.

CE2 at pH 6, respectively (Fig. 3). The pale yellow resins of CM3 or CE3 turn blue on complexation with Cu^{2+} and decolorize completely when a 1N HCl solution is passed through the column. Complete recovery of Cu^{2+} is achieved as shown in Figure 5. Furthermore, the adsorption-desorption procedures can be repeated.

EXPERIMENTAL

Materials

Commercial monochloroacetic and β -chloropropionic acids were used without further purification. Acrylic acid and EtOH were dried and distilled under nitrogen atmosphere.

Preparation of crosslinked PSt-g-EI was carried out according to the method described previously,¹ in which chloromethylated polystyrene (85.1% ring substitution) crosslinked with 3% divinylbenzene was used. Three graft copolymers were prepared: A (EI unit content = 9.17 mmole/g, degree of hydrolysis = 83.1%, $\overline{\text{D.P.}}$ of the grafted part = 4.3); B (10.30 mmole/g, 69.1%, 15.9); and C (9.92 mmole/g, 67.3%, 15.9).

Carboxymethylation of PSt-g-EI

A typical experiment (preparation of sample CM1) proceeded as follows: A mixture of 1.10 g PSt-g-EI (A), 9.64 g monochloroacetic acid, and 30 ml water was heated at 70°C under alkaline condition (pH 8–10) using NaOH until the pH of the system remained constant. The product was isolated by filtration and washed with water. When the effluent was neutral, the product was washed with methanol and diethyl ether, and then dried *in vacuo* at 70°C to a constant weight of 1.64 g. The detailed reaction conditions of the additional experiments may be found in Table I.

Carboxyethylation of PSt-g-EI

Method I. A mixture of 2.09 g PSt-g-EI (C), 3.19 g β -chloropropionic acid, and 15 ml water was heated at 70°C for 7 hr with gentle shaking. Further, the

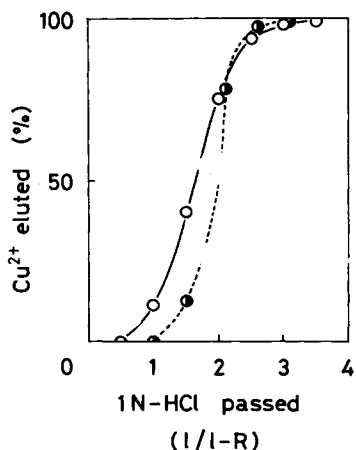


Fig. 5. Elution of the adsorbed Cu^{2+} with aqueous 1N HCl (flow rate = SV 2): (●) CM3 (adsorbed Cu^{2+} = 0.33 mmole); (○) CE3 (adsorbed Cu^{2+} = 0.23 mmole).

mixture was heated at the same temperature keeping the pH of the system in the range of 8–10 by adding 6N NaOH into the mixture. After 23 hr, no decrease in the pH was observed. The product was treated as described above. The yield was 2.96 g.

Method II. PSt-g-EI (C) (4.11 g) and 2,6-di-*tert*-butyl-*p*-cresol (0.06 g) were placed in a 100-ml flask equipped with a reflux condenser and a three-way cock. After the atmosphere in the flask was replaced with nitrogen, 22 ml EtOH and 3.1 ml acrylic acid were added to the flask. The mixture was kept at room temperature for a day so that the PSt-g-EI could be swollen sufficiently and then heated at 60°C for 20 hr with gentle shaking. The product was isolated by filtration and washed with MeOH, treated with aq. NaOH, and then washed with water until the washings became neutral. After drying at 70°C *in vacuo*, the product weighed 7.06 g.

Adsorption of Metal Ions by the Resins (Batch Method)

As metal salts, commercial $\text{Cu}(\text{NO}_3)_2$, HgCl_2 , CdCl_2 , NiCl_2 , and CaCl_2 were used without further purification. More details of the procedure have been described in the previous paper.¹

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

Resin of CM3, CE3, or PSt-g-EI (C) (5 ml in the wet state) was packed in a column with an 8-mm internal diameter. The height of the resin column was about 10 cm. An aqueous solution of Cu^{2+} (concentration of 32.0 ppm, pH 4.4) was allowed to flow through the column at a flow rate of space velocity (SV) 10. The effluent solution was sampled every 10 ml, and the Cu^{2+} concentration was determined by the method described in the previous paper.¹

After the adsorption experiment, the column was washed with 30 ml water. An eluting agent (1N HCl aq.) was passed through the column at a flow rate of SV 2. The Cu^{2+} content in every 2.5 ml of eluate was determined by chelometry.

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