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Preparation and Properties of a Macroreticular Resin Containing Thiohydantoinyl Groups

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A new macroreticular polystyrene resin containing thiohydantoinyl groups was prepared by the cyclization of thioureido resin derived from DL-alanine and isothiocyanate resin. Hg(II) showed the highest adsorption on the resin at the range above pH 1, while the adsorption of Cd(II), Co(II), Cu(II), Mg(II), Ni(II) and Zn(II) depend on the pH values. This resin was stable in the solutions below pH 10. Adsorption and elution behavior of Hg(II) was also investigated by a column experiment.

Although ion exchange resins containing various functional groups have been widely investigated, adsorption characteristics of the resins are not satisfactorily selective for the metal ions. It is well known that the thiohydantoins form the stable complexes with several heavy metal ions.[2-4] Majority of the metal complexes of thiohydantoins are colorless and insoluble in organic solvents. Therefore, in spite of the interesting compounds, thiohydantoins have been of a little value as analytical reagent for the metal ions except for the few cases.[5,6] However, it is expected that the above disadvantages may be negligible by introducing to a polymer matrix as functional group. This paper concerns with the synthesis and basic properties of a new resin having thiohydantoinyl groups.

Results and Discussion

Preparation of Resin

In this work, macroreticular (MR) type resin was selected for the polymer matrix because it has large surface area and porosity and possesses more outstanding characteristics in physical stability and reactivity than the gel type.[7-9] A series of resin modification was carried out according to the pathway shown in Chart 1.

The data of elementary analyses and the infrared (IR) spectra of resins (I—VI) are given in Table I and Fig. 1, respectively. Nitrogen content of III was approximately equal to the calculated value based on the chlorine content of II, and the presence of residual chlorine in III was negligibly small. In addition the IR spectrum showed a strong absorption at 2139 cm^{-1} due to the azide group. In a preliminary experiment for the preparation of IV, triphenylphosphine was used in the reaction, but resulting product showed the presence of small amounts of unreacted azide group in the IR spectrum. It is considered that the steric hindrance may contributes to this reaction. Consequently, trimethyl phosphite, which

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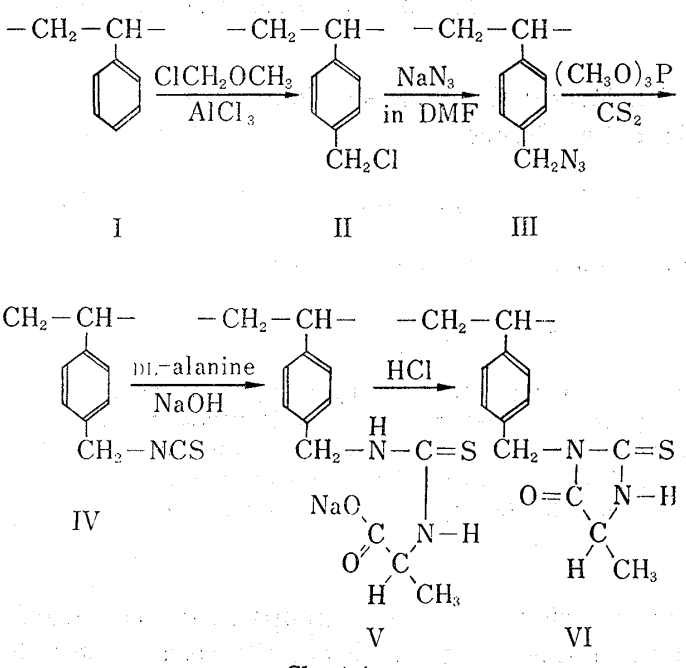

Chart 1

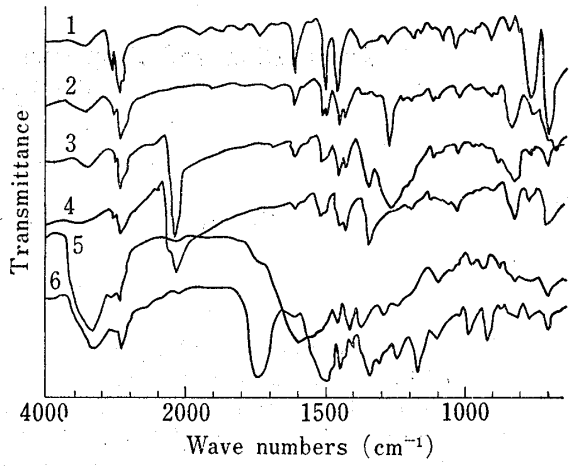

Fig. 1. Infrared Spectra of Resins (in KBr Disks)

1: resin I, 2: resin II, 3: resin III, 4: resin IV, 5: resin V, 6: resin VI

Table I. Elementary Analyses of Resins

Resins	Cl (%)	N (%)	S (%)	Functional group[a] (mmol/g)
II	18.2	—	—	5.1
III	0	20.9(20.9)	—	5.0(5.0)
IV	—	6.2(6.4)	14.8(14.8)	4.5(4.6)
V[b]	—	7.1(8.5)	8.2(9.7)	2.5(3.0)
VI	0	8.9(9.7)	10.8(11.1)	3.2(3.4)

a) calculated value from elementary analyses (mean value)
b) Na content, 5.8% (7.0%)
Values in parentheses indicate the calculated values based on the Cl content of II.

was smaller molecule than triphenyl phosphine, was used and IV was obtained in a satisfactory yield. The analytical data of sulfur and nitrogen of IV agreed with the calculated values, and the IR spectrum showed a strong characteristic peak at 2100 cm^{-1} due to the isothiocyanate group. As this peak is confusing with that of azide group (2139 cm^{-1}), the absence of azide group in IV was confirmed by the IR spectrum of reaction product of IV with ammonia. Thioureido resin thus obtained showed no absorption peak in the region of 1700 to 2400 cm^{-1}. The isothiocyanate (NCS) content of IV determined by using ethyl glycinate according to Dowling[10] was 4.5 mmol/g and this approximated to the calculated value of 4.6 mmol/g.

It is known that the thiohydantoins derived from glycine are easily autoxidized to corresponding bis-form in alkaline media.[5,11] Therefore, we attempted preparation of 5-substituted-2-thiohydantoinyl resin having resistance to autoxidation and V was prepared by using DL-alanine. The IR spectrum of V exhibited characteristic absorption of imino and carbonyl groups, but the data of elementary analyses of nitrogen, sulfur and sodium suggested that the product was contaminated by small amounts of impurities. Without further purification, VI was prepared by heating of V in dioxane containing hydrochloric acid. The IR spectrum of VI showed the shift of absorption peak ($\nu_{C=O}$), from 1600 to 1745 cm^{-1}, due to the cyclization of V.[11,12]

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Stability of VI

This was investigated by comparison of the IR spectra. The IR spectra of resin samples which were treated with various buffer, acid and alkaline solutions were measured. It was stable for a week in 6M HCl and buffer solutions below pH 10. However, it was easily decomposed in strong alkaline solutions and afforded thioureido resin V almost quantitatively by standing 72 hr in 1M NaOH solution at room temperature. From these facts, it is understandable that this resin can withstand for the use under the usual chromatographic conditions.

Adsorption Characteristics of Metal Ions on VI

Adsorption of some metal ions such as Cd(II), Co(II), Cu(II), Hg(II), Mg(II), Ni(II) and Zn(II) were examined as a preliminary experiment. A relation between shaking time and adsorbed amounts of metal ions at pH 5 was shown in Fig. 2. Twenty four hr was found to be adequate for the establishment of equilibrium in the case of dry resin. Moreover, adsorption amounts of metal ions at various pH values were determined. As is shown in Fig. 3 the order of adsorption of metal ions in acidic region is Hg(II)>Cu(II)>Cd(II)>Zn(II)>Co(II), Ni(II)>Mg(II) and this tendancy is analogous to that of the Irving-Williams series of the stability of chelates with divalent metal ions. As this resin shows strong affinity for soft metal ions, the selectivity for metal ions may be affected by the sulfur atom, soft ligand. Thioureido resin V is also expected for chelate formation, however thioureido group is easily converted into thiohydantoin ring by the treatment in acidic media. Accordingly, the adsorption characteristics of V, intermediate of VI, were not examined.

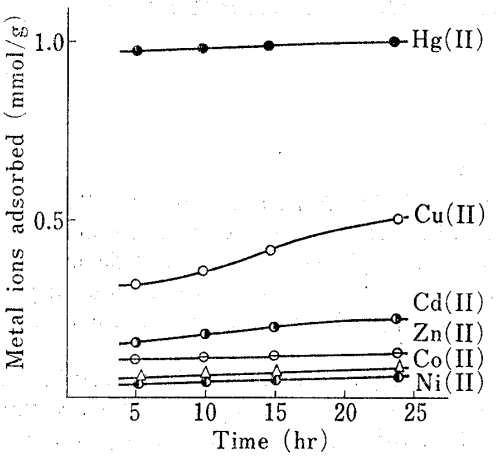

Fig. 2. Effect of Shaking Time on the Adsorption of Metal Ions (pH: 5.0)

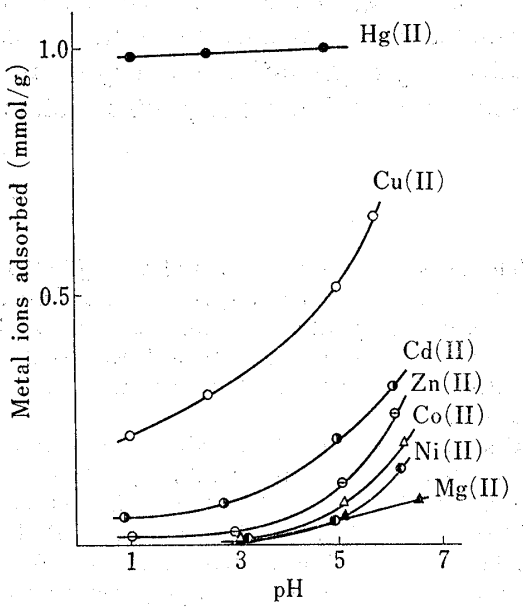

Fig. 3. Effect of pH on the Adsorption of Metal Ions (shaking time: 24 hr)

Since the resin VI showed strong affinity for Hg(II) as indicated above, the adsorption behavior of Hg(II) was further investigated by varying the concentration of Hg(II) at constant amount of resin. As is shown in Fig. 4, Hg(II) is almost quantitatively adsorbed on the resin up to a quarter of the resin capacity and then adsorption rate is gradually decreasing with increasing of the amounts of Hg(II) added. In the case of the total volume of solution is 50 ml, the amounts of Hg(II) adsorbed become nearly constant (about 1.9 mmol/g). Although it is difficult to determine the exact molar ratio of Hg(II) and the resin, the complex of Hg(II) with the resin is presumably a mixture of 1: 1 and 1: 2 complexes because the value, 1.9 mmol/g, is greater than the half value of the resin capacity (3.2 mmol/g).

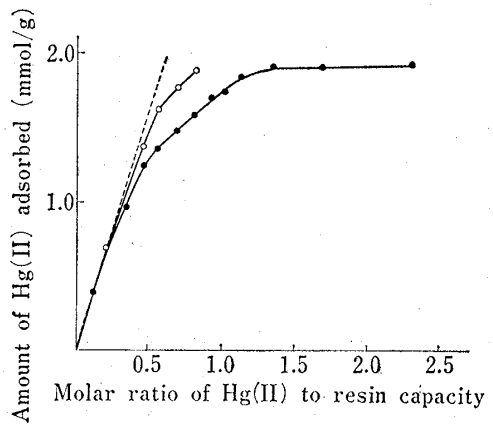

Fig. 4. Adsorption Characteristics of Hg(II) on Resin VI (shaking time: 24 hr)

—●—: Volume of Hg(II) is 50 ml.
—○—: Volume of Hg(II) is 10 ml.
——: amount of Hg(II) added

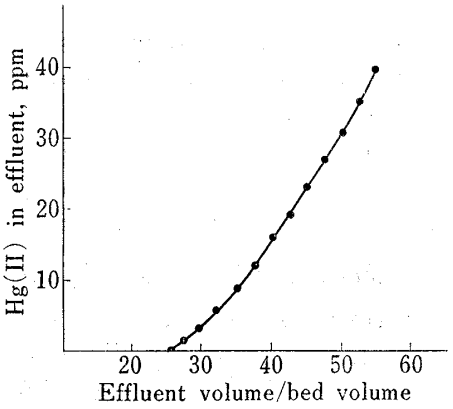

Fig. 5. Break-through Curve of Resin VI for Hg(II)

column: 1×11.5 cm, feed: Hg(II) in 0.1 M HCl(1 mg/ml), flow rate: 3 ml/min (SV 20)

Adsorption and elution of Hg(II) were examined by column operation. As is shown in Fig. 5, leaks of Hg(II) from the column are scarecely observed until the ratio of effluent volume to bed volume becomes 25 at a space velocity of 20. On the other hand, the elution of Hg(II) adsorbed on the column was carried out with 0.1M HCl containing 10% thiourea, and 85% of Hg(II) was recovered in 100 ml of the eluate. The advantage of proposed resin VI, compared to conventional resins, is high selectivity for Hg(II). This resin is applicable repeatedly by regeneration and may be useful for the removal or concentration of Hg(II) from the solution containing many other metal ions.

Experimental

The IR spectra were measured on a JASCO DS-301 spectrophotometer in KBr disks. The metal ion solutions used were prepared by reagent grade nitrate, sulfate and chloride in water to produce solutions which were approximately 0.1 M, and were standardized by titration with ethylenediaminetetraacetic acid (EDTA). In the case of column study, $^{203}HgCl_2$ was used as a tracer. The buffer systems were as follows: pH 1—2, 0.2 M HCl–0.2 M KCl; pH 3—6, 0.2M acetic acid–0.2 M sodium acetate; pH 7—8, 0.2 M ammonium acetate–0.2 M acetic acid.

Resin I——Styrene (127.5 ml) and 50% divinylbenzene solution (22.5 ml) were polymerized in the presence of 150 ml of isooctane and 2.25 g of benzoyl peroxide as the method described by Egawa, *et al.*[9] The dry resin was sieved and a 35—100 mesh fraction was collected. White spherical resin (125 g) was obtained.

Resin II—Resin I (80 g) was chloromethylated with chloromethyl methyl ether (320 ml), anhydrous $AlCl_3$ (90 g) and 80 ml of tetrachloroethane at 0—5° by the usual method. The yield was 99 g.

Resin III——This resin was prepared by a modified method for poly(vinyl chloride)[13] being applied. Resin II (98 g) was swelled in 300 ml of dimethylformamide (DMF) for 30 min, then sodium azide (52 g) and additional DMF (100 ml) were added to this mixture with stirring. The mixture was heated at 70° for 20 hr with continuous stirring, and then solid phase was filtered and washed with water and methanol. The yield was 100 g.

Resin IV——Resin III (96 g) was added to a mixture of carbon disulfide (192 ml) and tetrahydrofurane (192 ml). After had been stirred for 30 min, freshly distilled trimethyl phosphite (109 ml) was added to this mixture, and the mixture was heated at 35° for 24 hr with stirring under a nitrogen stream. The solid was filtered and washed with methanol, water and dioxane, successively, and was dried in a vaccum. The yield was 104.5 g.

Resin V——Resin IV (40 g) was swelled in 200 ml of dioxane for 30 min at room temperature. To the mixture was added a solution of 30.5 g of DL-alanine dissolved in 60 ml of 5 M NaOH aqueous solution and 140 ml of dioxane. The mixture was heated at 55° for 10 hr with stirring, and then stood over night at room

13) M. Takeishi and M. Okawara, *Polymer Letters*, 7, 201 (1969).

temperature. The solid was filtered and washed with water, dioxane and methanol, and was dried. The yield was 65 g.

Resin VI——The resin V(56 g) was swelled in 170 ml of dioxane for 30 min at room temperature. To the mixture was added 240 ml of 1 M HCl and refluxed for 3 hr. The resin thus obtained was filtered, and washed with large amounts of water until the washings become neutral, and was dried in a vaccum. The pale yellow resin (47 g) was obtained.

Adsorption of Metal Ions on Resin VI——Determinations of the amounts of metal ions adsorbed were carried out as follows: To a glass-stoppered test tube were added 0.100 g of the dry VI, 9 ml of a buffer solution and 1 ml of 0.1 M metal ion solution, then the mixture was shaken at room temperature. After had been shaken for a definite time, the resin was filtered and the amounts of metal ion presented in filtrate was determined by chelatometry with EDTA.

Adsorption and Elution of Hg(II) by Column Operation——A column (1×11.5 cm) containing 4 g of VI was equilibrated with 0.1 M HCl and then 500 ml of Hg(II) solution, which was prepared by dissolving 0.68 g of $HgCl_2$ in 0.1 M HCl, was passed over the adsorbent at a flow rate of 3 ml/min. The amounts of Hg(II) in the each 5 ml of effluents were determined by scintillation counting. After the column had been washed with 100 ml of 0.1 M HCl, adsorbed Hg(II) was eluted with 0.1 M HCl containing 10% thiourea.