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Preparation of Chelating Resins Containing a Pair of Neighboring Carboxylic Acid Groups and the Adsorption Characteristics for Heavy Metal Ions

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Abstract: For the functional enhancement of chelating resins containing carboxylic acids, copolymer beads were prepared by suspension polymerization of styrene (St), methyl methacrylate (MMA), and divinylbenzene (DVB) in the presence of toluene as diluent. The phenyl rings of the beads were directly chloromethylated, and the carboxylic ester groups of the beads were converted into hydroxymethyl groups by reduction followed by chlorination to give chloromethyl groups, respectively. The chelating resins containing a pair of neighboring carboxylic acid groups (NCAGs) were obtained by the alkylation of chloromethyl groups in copolymer beads with diethyl malonate in the presence of sodium hydride followed by hydrolysis using aqueous alkali solution. Accordingly, the structural effects of the resins on the adsorption of heavy metal ions were investigated. Poly(St-*co*-DVB)-based chelating resin containing NCAGs showed adsorption abilities toward heavy metal ions like Pb^{2+}, Cd^{2+}, and Cu^{2+}, whereas poly(MMA-*co*-DVB)-based chelating resin containing NCAGs showed adsorption abilities toward heavy metal ions like Cu^{2+}, Cd^{2+}, and Co^{2+}. On the other hand, poly(St-*co*-MMA-*co*-DVB)-based chelating resin containing NCAGs showed adsorption abilities toward heavy metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, and Cu^{2+}: a synergistic effect on the adsorption of heavy metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+}, and Co^{2+} was observed. The adsorption ability of poly(St-*co*-MMA-*co*-DVB)-based chelating resin among three kinds of chelating resins was relatively good.

Keywords: Chelating resin, bead, carboxylic acid, adsorption, heavy metal ion

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INTRODUCTION

Bead-typed resins have been applied as a supporting polymer in the form of a porous cross-linked resin or a macro-reticular resin. Macro-reticular resin beads containing chelating groups have been utilized in the separation, isolation, and purification of metal ions and/or small molecules (1–3). There have been many studies to introduce chelating groups into a supporting polymer to capture a peculiar metal ion very selectively. Most studies performed until now have been aimed at getting good chelating groups (4–10). Among them, the weak acid-typed cation exchange resins have been prepared by hydrolysis of cross-linked poly(acrylate)s under caustic conditions. Most of the chelating resins containing carboxylic acid groups have been utilized as dispersing agents, and partially applied as bleaching agents together with amino groups (11–14). For the enhancement of the adsorption capacity toward divalent metal ions like Ca^{2+} and Mg^{2+}, studies on the chemical modification of the resins containing carboxylic ester groups have been found to be effective (15, 16). Also, the chelating ability of carboxylic acid groups toward multivalent ions such as Cu^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, and Fe^{2+} have been found (17–21). For more introduction of carboxylic acid groups into poly(St-*co*-DVB)-based chelating resins, iminodiacetic acid groups as chelating groups had been utilized: the metal-chelated polymer could be regenerated 10 times by acid leaching without losing its original reactivity, which was suitable for removal of Ca^{2+} and Mg^{2+} ions to supply soft water (22, 23). A spacer effect among pendant chelating groups consisted in a polymer backbone have been recognized as an important factor for metal ion chelation (24, 26, 27, 28). In relation to this, studies on the improvement of adsorption ability through the arrangements of iminodiacetic acid- or malonic acid-pendant groups have not been observed yet. Thus, further improvement on designing the effective structural arrangement of neighboring carboxylic acid groups (NCAGs) consisted in a polymer backbone is of interest.

In this study, two different kinds of short/long malonic acid pendant groups were added to a chelating polymer backbone. A zigzag arrangement made by two different kinds of malonic acid pendant groups was designed for the optimization of adsorptivity toward heavy metal ions of chelating resins: benzene structure from St was used as spacer of malonic acid pendant groups. That is, for the improvement of adsorptivity toward heavy metal ions of NCAGs, three kinds of copolymer beads such as poly(St-*co*-DVB), poly(MMA-*co*-DVB), and poly(St-*co*-MMA-*co*-DVB) were prepared as base polymers. Accordingly, the phenyl rings and carboxylic ester groups of the beads were chloromethylated, respectively. The chelating resins containing NCAGs were obtained through hydrolysis after the alkylation of the beads with diethyl malonate. The effects of the chemical and physical structure of all the resins prepared for the adsorption of heavy metal ions were also were investigated.

EXPERIMENTAL

Materials and Apparatus

Lead(II) nitrate, mercury(II) chloride, copper(II) chloride, cadmium(II) nitrate, nickel(II) chloride, cobalt(II) nitrate hexahydrate, chromium(III) nitrate, sodium borohydride, zinc chloride, chloromethyl methyl ether (CMME), sodium hydride, diethyl malonate (DEM), and sodium hydroxide were purchased from Aldrich Chemical Company and used without further purification. Styrene (St), methyl methacrylate (MMA), divinylbenzene (DVB), thionyl chloride, pyridine, *N*,*N*′-dimethylaniline, and solvents were also purchased from Aldrich Chemical Company and used after fresh distillation under nitrogen atmosphere.

The structure of chelating resins was confirmed by a Bio-rad Digilab FTS-165 Fourier-Transform Infrared Spectrometer (FT-IR). Each elemental composition was measured with a Fisons 1108 Elemental Analyzer (EA) and partially supported by chlorine analysis (25). The quantitative analysis of heavy metal ions was performed by using a Perkin-Elmer 2380 Atomic Absorption Spectrometer (AAS) for Hg^{2+} and a Jobin-Yvon Ultima-C Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) for other heavy metal ions.

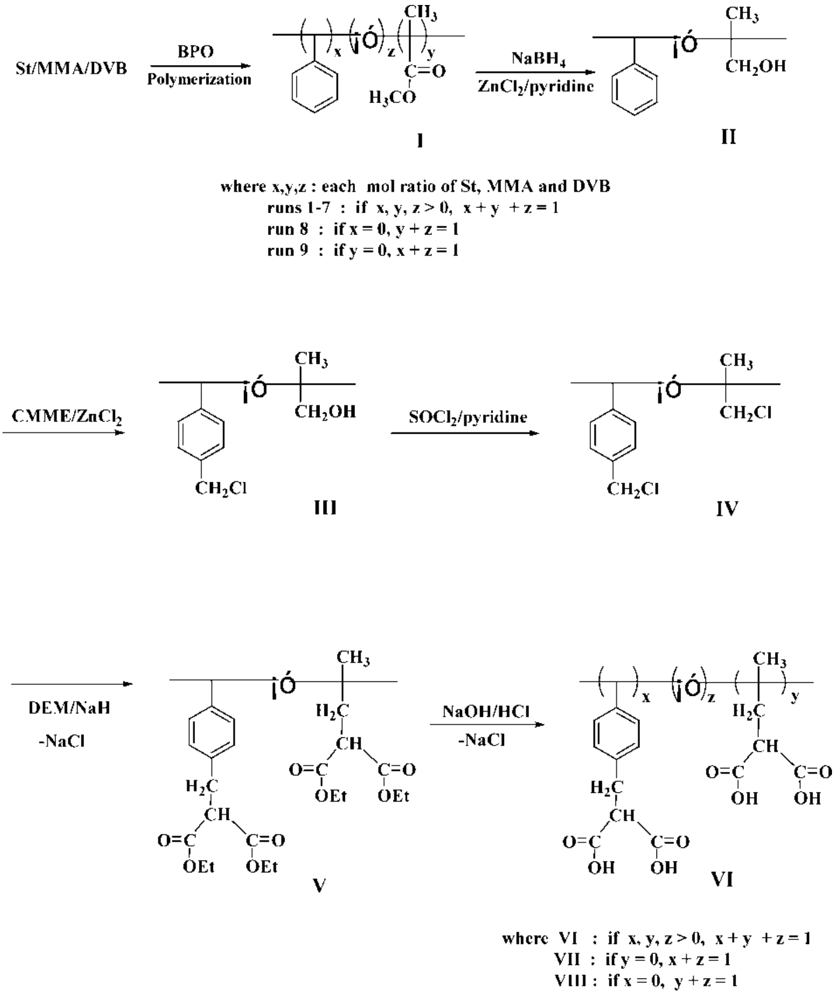
Preparation of Macro-Reticular Chelating Resin (Scheme 1, VI)

Preparation of Copolymer Beads **I** (Table 1, run 3)

Macro-reticular copolymer beads were prepared by suspension polymerization of styrene (17.056 g, 0.164 mol), methyl methacrylate (9.151 g, 0.092 mol), and divinylbenzene (7.995 g, 0.062 mol) in the presence of toluene (3.42 g) as diluent at 80°C for 8 h. The beads were filtered off, washed with water and with a mixture of methanol/water (1 : 1) and finally methanol. After drying under vacuo at 60°C for 48 h, copolymer **I** (40–90 mesh; 33.463 g; yield 97.84 wt.%; 5.22 meq g^{-1} O) was obtained.

Preparation of a Resin Containing Hydroxyl Groups **II** (Table 2, run 3)

A mixture of the copolymer bead **I** (24.254 g), sodium borohydride (2.873 g, 0.076 mol), zinc chloride (10.357 g, 0.076 mol), and *N*,*N*′-dimethylaniline (9.196 g, 0.076 mol) in tetrahydrofuran (150 mL) was refluxed for 2 h. The reaction mixture was poured into a mixture of ice-cold 10 wt.% of aqueous ammonium chloride and chloroform (100 mL each), blended with, and then filtered off. The filtered resin was washed with acetone, water, and finally methanol. After drying under vacuo at 60°C for 48 h, a resin containing



where x,y,z : each mol ratio of St, MMA and DVB
runs 1-7 : if x, y, z > 0, x + y + z = 1
run 8 : if x = 0, y + z = 1
run 9 : if y = 0, x + z = 1

where VI : if x, y, z > 0, x + y + z = 1
VII : if y = 0, x + z = 1
VIII : if x = 0, y + z = 1

Scheme 1. Preparation of chelating resins containing a pair of carboxylic acid groups.

hydroxyl groups **II** (23.581 g; conversion 38.00 mol%; 4.34 meq g^{-1} O) was obtained.

Preparation of a Chloromethylated Resin III (Table 3, run 3)

The resin **II** (17.006 g) above-prepared was suspended into a mixture of chloromethyl methyl ether (23.40 g, 0.291 mol) and 1,2-dichloroethane (142.39 g) in the presence of zinc chloride (8.503 g, 0.062 mol) at 45°C for 5 h. The reaction mixture was poured into ice water and then filtered off. The filtered resin was successively washed with acetone, diethyl ether, and

Table 1. Copolymer beads **I** obtained from styrene, methyl methacrylate, and divinylbenzene

	Feed				Product **I**				
	Composition[a,b] (mol)			Oxygen content[b] (meq/g-resin)	Yield (wt.%)	Composition[a,c] (mol)			Oxygen content[c] (meq/g-resin)
Run	St	MMA	DVB			St	MMA	DVB	
1	1.000	0.143	0.284	1.84	98.56	1.000	0.137	0.288 (24.13)[d]	1.77
2	1.000	0.281	0.311	3.26	98.44	1.000	0.275	0.316 (23.80)	3.19
3	1.000	0.558	0.375	5.35	97.84	1.000	0.542	0.382 (23.89)	5.22
4	1.000	0.843	0.444	6.85	97.83	1.000	0.798	0.446 (23.97)	6.60
5	1.000	1.091	0.510	7.81	96.71	1.000	1.023	0.516 (24.54)	7.48
6	1.000	1.310	0.549	8.55	96.66	1.000	1.253	0.560 (24.10)	8.30
7	1.000	1.678	0.627	10.18	95.64	1.000	1.618	0.650 (24.12)	9.24
8	—	1.000	0.245	15.17	95.76	—	1.000	0.260 (25.26)	14.95
9	1.000	0.076	0.260	1.05	98.77	1.000	0.074	0.264 (23.55)	1.02

[a] St: styrene units, MMA: methyl methacrylate units, and DVB: divinylbenzene units.

[b] Calculated from the raw materials feed composition.

[c] Calculated by elemental analysis.

[d] Calculated from the difference in weight before and after the reaction (wt.% is given in brackets).

Table 2. Preparation of copolymer beads **II** containing hydroxyl groups by reduction of ester groups

	Feed **I**				Product **II**					
	Composition[a,b] (mol)					Composition[a,b] (mol)				
Run	St	MMA	DVB	Oxygen content[b] (meq/g-resin)	Swelling ratio[c]	St	HMMA	DVB	Oxygen content[b] (meq/g-resin)	Conversion (mol%)
1	1.000	0.137	0.288	1.77	1.08	1.000	0.048	0.288 (23.34)[d]	1.47	35.04
2	1.000	0.275	0.316	3.19	1.09	1.000	0.101	0.316 (24.20)	2.64	36.73
3	1.000	0.542	0.382	5.22	1.08	1.000	0.206	0.382 (24.57)	4.34	38.00
4	1.000	0.798	0.446	6.60	1.09	1.000	0.312	0.446 (24.88)	5.51	39.10
5	1.000	1.023	0.516	7.48	1.10	1.000	0.449	0.516 (25.72)	6.12	43.89
6	1.000	1.253	0.560	8.30	1.11	1.000	0.603	0.560 (25.52)	6.67	48.12
7	1.000	1.618	0.650	9.24	1.12	1.000	0.823	0.650 (25.82)	7.37	50.87
8	—	1.000	0.260	14.95	1.13	—	0.535	0.270 (29.22)	12.20	53.50
9	1.000	0.074	0.264	1.02	1.09	1.000	0.026	0.264 (23.67)	0.84	35.14

[a] St: styrene units, MMA: methyl methacrylate units, DVB: divinylbenzene units, and HMMA: structural units containing hydroxyl groups obtained from modification of MMA.

[b] Calculated by elemental analysis.

[c] Measured after immersed in THF.

[d] Calculated from the difference in weight before and after the reaction (wt.% is given in brackets).

Table 3. Preparation of copolymer beads **III** by chloromethylation

	Feed **II**		Product **III**					
	Composition[a,b] (mol)			Composition[a,b] (mol)				
Run	St	DVB	Swelling ratio[c]	St	Cl-St	DVB	Chlorine content[b] (meq/g-resin)	Conversion (mol%)
1	1.000	0.288 (23.34)[d]	1.10	0.490	0.510	0.288 (22.51)[e]	3.07	51.0
2	1.000	0.316 (24.20)	1.10	0.452	0.548	0.316 (22.47)	2.99	54.8
3	1.000	0.382 (24.57)	1.11	0.380	0.620	0.382 (22.86)	2.85	62.0
4	1.000	0.446 (24.88)	1.12	0.333	0.667	0.446 (23.25)	2.67	66.7
5	1.000	0.516 (25.72)	1.13	0.317	0.683	0.516 (24.17)	2.46	68.3
6	1.000	0.560 (25.52)	1.15	0.353	0.647	0.560 (24.18)	2.15	64.7
7	1.000	0.650 (25.82)	1.16	0.402	0.598	0.650 (24.71)	1.75	59.8
8	—	0.270 (29.22)	1.18	—	0.004[f]	0.266 (28.74)	0.03	0.4
9	1.000	0.264 (23.67)	1.10	0.508	0.492	0.264 (21.85)	3.13	49.2

[a] Compositions directly related to the chloromethylation; St: styrene units and DVB: divinylbenzene units. Structural units existed in copolymer beads **III**; St: styrene units, Cl-St: chlorinated styrene units, and DVB: divinylbenzene units.

[b] Calculated by elemental analysis and chlorine analysis.

[c] Measured after immersed in 1,2-dichloroethane.

[d] wt.% is given in brackets.

[e] Calculated from the difference in weight before and after the reaction (wt.% is given in brackets).

[f] Concentration of chlorinated divinylbenzene units.

methanol. After drying under vacuo at 60°C for 48 h, a chloromethylated resin **III** (18.284 g; conversion 62.0 mol%; 2.85 meq g^{-1} Cl) was obtained.

Preparation of a Resin by Converting Hydroxyl Groups into Chlorine Groups **IV** (Table 4, run 3)

The resin **III** (17.075 g) above-prepared was swelled in benzene (34.87 g) for 30 min and a mixture of pyridine (6.34 g, 0.140 mol) and thionyl chloride (8.23 g, 0.069 mol) was added dropwisely over 10 min, and then stirred at 0°C for 2 h under nitrogen atmosphere. The product was washed with acetone, diethyl ether, and methanol, and then dried under vacuo at 60°C for 48 h to afford a resin **IV** (17.340 g; conversion 72.82 mol%; 3.49 meq g^{-1} Cl).

Preparation of a Resin Containing a Pair of Neighboring Carboxylic Ester Groups **V** (Table 5, run 3)

The resin **IV** (14.212 g) above-prepared was swelled in *N*,*N*′-dimethylformamide (DMF, 512.34 g) containing sodium hydride (5.116 g, 0.213 mol) for 30 min. To the swelled resin **IV** was dropwisely added diethyl malonate (39.794 g, 0.249 mol) in DMF (219.58 g) over 1 h, and then stirred at 80°C for 72 h. The reaction mixture was poured into ice water and filtered off, washing with a mixture of acetone and methanol. After drying under vacuo at 60°C for 48 h, a resin **V** (16.339 g; conversion 30.00 mol%; 2.06 meq g^{-1} Cl; 6.56 meq g^{-1} O) containing a pair of neighboring carboxylic ester groups was obtained.

Preparation of a Resin Containing a Pair of Neighboring Carboxylic Acid Groups **VI** (Tables 6 and 7, run 3 each)

The resin **V** (14.458 g) above-prepared was hydrolyzed by 5 *N* NaOH solution (150 mL) at 90°C for 24 h. The resin was filtered off, washed with 1 *N* hydrochloric acid solution, and finally plenty of water until the washed water became neutral. After drying under vacuo at 60°C for 48 h, a resin **VI** (13.668 g; conversion 94.73 mol%; 3.65 meq g^{-1} COOH) containing a pair of neighboring carboxylic acid groups was obtained.

Measurement of Swelling Ratios (6, 24)

For the measurement of swelling ratios, the chelating resin **VI** (0.1–0.5 g) was immersed in each of organic solvents and water in a 10 mL measuring cylinder at room temperature for 24 h. The swelling ratio of the resin was calculated by

Table 4. Preparation of copolymer beads **IV** by chlorination

	Feed[a,b] **III**			Product[a,b] **IV**					
	Composition (mol)		DVB content (wt.%)	Swelling ratio[c]	Composition (mol)		DVB content[d] (wt.%)	Chlorine content (wt.%)	Conversion (mol%)
Run	Cl-St	HMMA			Cl-St	Cl-MMA			
1	0.510	0.048	22.51	1.07	0.510	0.032	22.43	3.24	66.67
2	0.548	0.101	22.47	1.08	0.548	0.070	22.27	3.35	69.31
3	0.620	0.206	22.86	1.09	0.620	0.150	22.51	3.49	72.82
4	0.667	0.312	23.25	1.10	0.667	0.231	22.86	3.54	74.04
5	0.683	0.449	24.17	1.10	0.683	0.346	23.62	3.62	77.06
6	0.647	0.603	24.18	1.11	0.647	0.481	23.49	3.64	79.77
7	0.598	0.823	24.71	1.12	0.598	0.680	23.84	3.60	82.62
8	0.004[e]	0.535	28.74	1.13	0.004[e]	0.449[f]	26.88	3.52	83.93
9	0.492	0.026	21.85	1.07	0.492	0.015	21.81	3.22	57.69

[a] Compositions directly related to the chlorination; Cl-St: chlorinated styrene units, HMMA: structural units containing hydroxyl groups obtained from modification of MMA, and DVB: divinylbenzene units. Structural units existed in copolymer beads **IV**; Cl-St: chlorinated styrene units, Cl-MMA: MMA-modified structural units obtained by converting hydroxyl groups into chlorine groups, and DVB: divinylbenzene units.

[b] Calculated by elemental analysis and chlorine analysis.

[c] Measured after immersed in benzene.

[d] Calculated from the difference in weight before and after the reaction.

[e] Concentration of chlorinated divinylbenzene units.

[f] Concentration of chlorinated methyl methacrylate units.

Table 5. Preparation of copolymer beads **V** by the reaction with diethyl malonate

	Feed **IV**			Product **V**					
	Composition[a,b] (mol)				Composition[a,b] (mol)				
Run	Cl-St	Cl-MMA	DVB content (wt.%)	Swelling ratio[c]	DEM	DVB content[d] (wt.%)	Chlorine content[b] (meq/g-resin)	Oxygen content[b] (meq/g-resin)	Conversion (mol%)
1	0.510	0.032	22.43	1.09	0.164	19.62	1.98	4.45	30.26
2	0.548	0.070	22.27	1.10	0.191	19.37	2.01	5.38	30.91
3	0.620	0.150	22.51	1.09	0.231	19.57	2.06	6.56	30.00
4	0.667	0.231	22.86	1.10	0.269	19.88	2.15	7.30	29.96
5	0.683	0.346	23.62	1.09	0.308	20.52	2.20	7.60	29.93
6	0.647	0.481	23.49	1.10	0.339	20.42	2.21	7.79	30.05
7	0.598	0.680	23.84	1.10	0.383	20.88	2.19	8.06	30.21
8	0.004[e]	0.449	26.88	1.10	0.137	23.79	2.17	10.76	30.24
9	0.492	0.015	21.81	1.09	0.154	18.98	1.95	3.99	30.37

[a] Compositions directly related to the reaction; Cl-St: chlorinated styrene units, Cl-MMA: MMA-modified structural units obtained by converting hydroxyl groups into chlorine groups, and DVB: divinylbenzene units. Structural units existed in copolymer beads **V**; DEM: diethyl malonate units, and DVB: divinylbenzene units.

[b] Calculated by elemental analysis and chlorine analysis.

[c] Measured after immersed in benzene.

[d] Calculated from the difference in weight before and after the reaction.

[e] Concentration of chlorinated divinylbenzene units.

Table 6. Preparation copolymer beads **VI** by hydrolysis of diethyl malonate units

	Feed[a,b] **V**			Product[a,b] **VI**						
	Composition (mol)				Composition (mol)					
Run	DEM	DVB content (wt.%)	Oxygen content (meq/g-resinl)	Swelling ratio[c]	St	MMA	MLA	DVB content[d] (wt.%)	Oxygen content (meq/g-resinl)	Conversion (mol%)
1	0.164	22.43	4.45	1.04	0.149	0.009	0.155	20.56	4.66	94.61
2	0.191	22.27	5.38	1.04	0.160	0.020	0.180	21.92	5.65	94.40
3	0.231	22.51	6.56	1.04	0.176	0.043	0.219	20.71	6.94	94.73
4	0.269	22.86	7.30	1.05	0.189	0.066	0.255	20.90	7.68	94.88
5	0.308	23.62	7.60	1.04	0.194	0.099	0.293	21.60	8.00	94.97
6	0.339	23.49	7.79	1.05	0.185	0.137	0.322	21.51	8.21	95.11
7	0.383	23.84	8.06	1.05	0.172	0.193	0.365	21.99	8.49	95.34
8	0.137	26.88	10.76	1.04	0.001	0.129	0.130	20.44	12.54	94.98
9	0.154	21.81	3.99	1.04	0.142	0.005	0.147	19.99	4.20	95.21

[a] Compositions directly related to the hydrolysis of copolymer beads **V**; DEM: diethyl malonate units and DVB: divinylbenzene units. Structural units existed in copolymer beads **VI**; St: styrene units, MMA: methyl methacrylate units, MLA: malonic acid units, and DVB: divinylbenzene units.

[b] Calculated by elemental analysis and chlorine analysis.

[c] Measured after immersed in water.

[d] Calculated from the difference in weight before and after the reaction.

Table 7. Adsorption ability for heavy metal ions of chelating resins **VI** containing a pair of neighboring carboxylic acid groups

	Chelating resin[a,b] **VI**					Adsorptivity[d] (mg/g-resin)						
	Composition (mol)											
Run	St	MMA (MA)	MLA (BA)	DVB content (wt.%)	Carboxylic acid content[c] (meq/g-resin)	Pb^{2+}	Hg^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Cr^{3+}
1	0.146	0.009	0.155	20.56	3.42	28.21	23.12	23.44	26.49	6.40	20.36	0.00
2	0.160	0.020	0.180	21.92	3.56	40.79	28.92	24.51	34.41	8.52	25.74	2.01
3	0.176	0.043	0.219	20.71	3.65	52.21	40.26	25.73	43.00	9.60	31.82	2.25
4	0.189	0.066	0.255	20.90	3.68	47.37	36.43	24.48	46.88	10.56	29.85	2.10
5	0.194	0.099	0.293	21.60	3.77	35.74	24.59	23.21	32.61	9.57	23.63	2.07
6	0.185	0.137	0.322	21.51	3.81	29.58	22.48	22.91	26.74	7.43	19.28	1.14
7	0.172	0.193	0.365	21.99	3.80	23.01	21.25	22.74	19.27	7.38	17.26	1.07
8[e]	0.001	0.129	0.130	20.44	6.21	14.56	9.62	22.47	17.19	4.16	16.07	0.00
9[f]	0.142	0.147	0.005	19.99	3.41	24.52	18.36	20.44	22.48	4.27	16.40	0.00
10[g]		(0.203)	(0.107)	20.07	6.14	17.71	12.23	23.02	24.43	5.37	18.22	0.00

[a] Structural units existed in chelating resins **VI**; St: styrene units, MMA: methyl methacrylate units, MLA: malonic acid units, MA: methylacrylate units, BA: butylacrylate units, and DVB: divinylbenzene units.

[b] Calculated by elemental analysis and chlorine analysis.

[c] IEC values caused by only sodium salts of carboxylic acid groups in the beads containing a pair of neighboring carboxylic groups.

[d] Resin 0.2 g, 20 mL of each metal solution (pH 5.0), 20°C, 28 h.

[e] Chelating resin **VII** shown in Scheme 1.

[f] Chelating resin **VIII** shown in Scheme 1.

[g] Hydrolyzed poly(MA-*co*-BA-*co*-DVB) obtained by the same method mentioned in USP 4614751 (11).

using the following equation:

$$\text{Swelling ratio} = \frac{\text{Volume of wet resin}\,(\text{cm}^3)}{\text{Volume of dry resin}\,(\text{cm}^3)}$$

Measurement of Ion Exchange Capacities for Chelating Resins VI (24, 25)

The experiments for the calculation of ion exchange capacity (IEC) were carried out by adding 0.2 g of each resin to 40 mL of 0.1 N caustic soda solution containing 5% of sodium chloride solution and stirred the mixture at 20°C for 24 h. After this, 20 mL of the supernatant solution in the mixture was selected and titrated by 0.1 N hydrochloric acid solution. The IECs were calculated using the following equation

$$\text{Capacity}\ (\text{meq}\cdot\text{g}^{-1}\ \text{resin}) = \frac{(50 \times C_{NaOH}) - 2.5(C_{HCl} \times V_{HCl})}{\text{Weight of resin} \times \text{wt.\% of dried resin/100}}$$

where C_{NaOH} is the normality of NaOH, C_{HCl} is the normality of HCl, and V_{HCl} is the quantity of HCl (in mL)

Measurement of Adsorption Capacities toward Heavy Metal Ions (24, 26, 27, 28)

The adsorption experiments were carried out by adding 0.2 g of each sample of chelating resins **VI** to 20 mL (pH 5) of aqueous metal ion (each of Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, and Co^{2+}) solution (1000 ppm each), aqueous Ni^{2+} solution (750 ppm), and aqueous Cr^{3+} solution (500 ppm). The mixture was stirred at 20°C for 28 h and the resin was separated by filtration. The concentration of the residual ions in supernatant solution was measured by AAS and ICP-AES. Each adsorption capacity toward heavy metal ions of the resins was calculated from measured values.

RESULTS AND DISCUSSION

Preparation and Properties of Chelating Resins Containing Carboxylic Acid Groups

The resins with spacer units among pendant chelating groups were more accessible for the adsorption of heavy metal ions than those without spacers, and the intervals between a pair of neighboring chelating groups

(NCAGs) had been also controlled for the effective adsorption of heavy metal ions (24, 26, 27, 28). In this study, the chelating resins containing NCAGs as pendant chelating groups were prepared as shown in Scheme 1. The structures of NCAGs had been designed to get good chelation through a pair access mechanism (24, 29).

Preparation of Copolymer Beads **I**

Copolymer beads were prepared varying the concentration of styrene (St) and methyl methacylate (MMA) for a given concentration of divinylbenzene (DVB) in the presence of toluene as a diluent. Although the reactive ratios ($\gamma_{St} = 0.52$, $\gamma_{MMA} = 0.46$) between St and MMA in the copolymerization were very similar (30), the yields in the copolymerization slightly decreased with increase of mol ratio of MMA to St for a given concentration of DVB due to the affinity of MMA to water compared to St and DVB: a copolymer **I** (Table 1, run 8) produced by copolymerization of MMA with DVB was the lowest yield. On the other hand, it was presumed that each of the mol ratios of MMA to St existed in the core/shell side of a copolymer bead prepared by suspension copolymerization was somewhat different due to the affinity of MMA to water compared to St and DVB. For the design of new resin structure with cross-linking spacers, it was necessary to control rigidity inside and outside of bead-typed polymers. Cross-linked copolymers must be rigid enough to withstand collapse and must have sufficient space enough to allow metal ions toward the chelation. In the presence of the copolymers, these two kinds of factors are always competitive (31). When 23 wt.% of DVB as cross-linked agent and 10 wt.% of toluene as diluent were used for copolymerization., cross-linked copolymers were balanced between rigidity enough to withstand collapse and sufficient sorption of metal ions for chelation.

Preparation of Copolymer Beads **III** & **IV** Containing Two Kinds of Structurally Different Chloromethylated Groups

Carboxylic ester groups in the resins derived from MMA were reduced to the corresponding hydroxymethyl groups in good yields by refluxing sodium borohydride in the presence of zinc chloride in *N*,*N*′-dimethylaniline and tetrahydrofuran (THF) (32–34). THF was a poor solvent for St/DVB units existed in copolymer beads, whereas it was a good solvent for used reduction reagents (32–34). It was considered that THF was a good dispersing agent for the reagents. In spite of the poor affinity to the beads of THF, the reduction of carboxylic ester groups existed in the poly(St-*co*-DVB)-based or poly(St-*co*-MMA-*co*-DVB)-based beads in THF gave the best yield: solvents such as diethyl ether, dioxane, THF, and ethanol were applied by separated experiments. The conversions of copolymer beads **I** to copolymer beads **II** gradually increased with increase of MMA units existed in the beads **I** as shown in Table 2. The swelling ratios of the beads **II** slightly also increased with increase of the quantity of MMA component in the beads **II** as shown in Table 2.

There were two different kinds of chloromethyl groups in copolymer beads **II** as shown in Scheme 1. The chloromethylation of phenyl rings in copolymer beads **II** were directly conducted using chloromethyl methyl ether (CMME) in the presence of zinc chloride. The chloromethylation of the carboxylic ester groups in the bead **II** were conducted by reduction using sodium borohydride to give hydroxylmethylated groups, which were subsequently chlorinated using thionyl chloride. When the chlorination for the hydroxyl groups existed in the beads **II** was carried out in advance, the chlorination for the phenyl rings existed in the beads **II** brought about a lot of cross-linking reactions as a side reaction, due to the existence of a lot of chloromethylated groups in the presence of zinc chloride. Also, in the preferential chlorination to phenyl rings existed in copolymer beads **II**, the reaction yields progressively increased in the early chlorination stage and reached a maximum value (Table 2, run 9) at 45°C for 5 h, decreasing with increase of reaction time as shown in Figure 1. It was considered that the decrease of yields was caused by the inter- or intramolecular cross-linked reactions between chloromethylated groups and phenyl rings (35, 36). The cross-linked reactions in the chloromethylation could be inhibited by using polystyrene containing small quantity of MMA (37, 38). The reaction yield of the chloromethylation of poly(St-*co*-MMA-*co*-DVB) with CMME in the presence of zinc chloride was higher than from the chloromethylation of poly(St-*co*-DVB) without MMA component (Table 1, run 9), and reached a

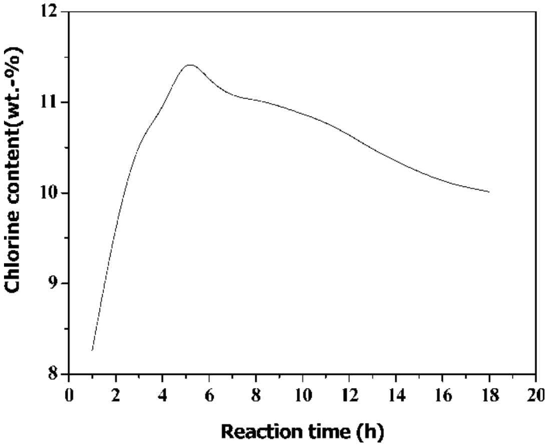


Figure 1. Dependence of chlorine content upon reaction temperature in the chloromethylation of poly(St-*co*-MMA-*co*-DVB)-based copolymer beads (Table 4, run 9) containing a small quantity of MMA component at 45°C.

maximum value at 45°C for 4.2 h. If MMA component contained in copolymer beads **II** increased in Table 1, the phenyl rings as reaction sites for chloromethylation decreased. Nevertheless, the conversions in the chloromethylation of the bead **II** preferably increased due to the affinity of chlorinating agents to MMA component as well as the cross-linked reaction inhibited by MMA component as shown in Table 3 (30, 37, 38). The chlorinated DVB component was also obtained from the chlorination (Table 3, run 8) of poly(MMA-*co*-DVB) using CMME in the presence of zinc chloride, which was confirmed by measuring a slight increase of chlorine content. Chlorinations at temperatures above 60°C brought about low conversions caused by a lot of cross-linking reactions. The weight ratio of cross-linked component contained in copolymer beads **III** slightly decreased with the increase in weight of reactants after chloromethylated. The swelling ratios of the beads **III** in 1,2-dichloroethane slightly increased with increase of the quantity of MMA component. On the other hand, as shown in Scheme 1, the transformation of hydoxymethylated groups contained in copolymer beads **III** into chloromethylated groups contained in copolymer beads **IV** was conducted using thionyl chloride in benzene, and the results were summarized in Table 4. The conversions gradually increased with increase of hydoxymethylated groups existed in the beads **III**. The copolymer beads **III** were partially swelled in hydrophobic solvents like benzene, toluene, cyclohexane, and methylcyclohexane, whereas they were fully dispersed in hydrophilic solvents like thionyl chloride, chloroform, and DMF. It was considered that the accessibility of thionyl chloride to copolymer beads **III** in the chlorination was greater than that of hydrophobic solvents to the beads **III**. But it was more affirmative to utilize non-polar solvents as swelling agents of copolymer beads III in the chlorination. By separated experiments, it was also found that the conversions in the transformations using non-polar solvents like benzene and cyclohexane were better than those using polar solvents like chloroform and DMF (39). As mentioned, the weight ratio of cross-linked components contained in copolymer beads **III** slightly decreased with the increase in weight of reactants after chloromethylated. Even though both the content of chloromethylated groups and the component mol ratio of MMA to St contained in the beads **IV** increased, the swelling ratios in benzene did not nearly change, due to the poor affinity of benzene to both MMA component and chloromethylated groups.

Preparation of Chelating Resins Containing a Pair of Neighboring Carboxylic Acid Groups **VI**

The alkylation of chloromethylated groups in copolymer beads **IV** with diethyl malonate was carried out in the presence of sodium hydride-DMF solution as shown in Scheme 1 (40). The alkylations, in spite of using two kinds of structurally different chloromethylated groups, showed similar conversions as shown in Table 5. It was considered that there was no selectivity for the alkylation of diethyl malonate toward two kinds of structurally different chloromethylated groups: the conversions of alkylation were not so good, due to the poor penetration effect of diethyl malonate-benzene solution toward the inside of copolymer beads **IV**, which could be confirmed in comparison with each content of elements like C, H, O before and after the alkylated. There were not differences in the swelling ratios of copolymer beads **V** to benzene. In the same manner, the weight ratio of cross-linked component contained in the beads **V** slightly decreased with the increase in weight of reactants after alkylation. On the other hand, the hydrolysis of copolymer beads **V** gave poor conversions in strong acidic media, whereas good conversions in strong alkali media, due to good hydrophilic property of carboxylic acid sodium salts. Thus, the hydrolysis of the beads **V** was carried out under aqueous alkali solution as shown in Table 6: in spite of taking two kinds of structurally different alkylating sites, all the hydrolyses showed good conversions. After all, it was considered that there was no selectivity in the hydrolysis causing two kinds of alkylated sites existed in copolymer beads **V**. The chelating resins **VI** after hydrolyzed was evidenced by IR spectra in Fig. 2(F); the peaks of (B): C–O(CH_2OH) at 1069 cm^{-1} and (C): C–Cl at 671 cm^{-1} were newly created, whereas the peaks of (D): C–Cl at 675 cm^{-1}, (E): C–O at 1230 cm^{-1}, and (F): OH at 3400 cm^{-1} appeared to be strengthened.

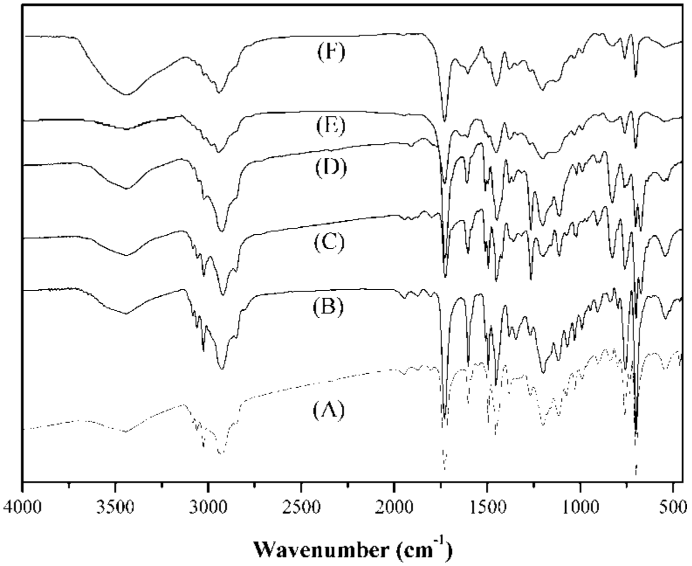


Figure 2. IR spectra of chelating resins: (A) **I** (Table 1, run 2), (B) **II** (Table 2, run 3), (C) **III** (Table 3, run 3), (D) **IV** (Table 4, run 3), (E) **V** (Table 5, run 3) and (F) **VI** (Table 6, run 3).

Evaluation for Improved Chelating Resins

The adsorption capacities for heavy metal ions on chelating resins containing NCAGs at pH 5 were investigated as shown in Table 7. The pH of aqueous metal ion solution was adjusted by adding 10% aqueous solution of HCl, 0.5% aqueous solution of HCl, finally 0.1% aqueous solution of HCl. In the adsorption experiments of heavy metal ions, the concentration of each aqueous metal ion solution was determined by considering the values lower than the solubility of each metal ion at 20°C. The adsorption capacities of chelating resins containing carboxylic acid groups toward heavy metal ions have been known very low (41). The chelating capacities of the carboxylic acid groups toward multivalent ions such as Cu^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, and Fe^{2} have been reported (17–20). Also, the metal ion adsorption capacities of poly(acrylic acid-*co*-acrylamide) for Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Pb^{2+} except of Hg^{2+} have been studied (42, 43). Nevertheless, chelating resins **VI** containing NCAGs prepared in this study showed the good adsorption capacity toward Hg^{2+} as shown in Table 7 (run 3). The chelating resins **VI** observed from run 1 to run 7 of Table 7 showed similar IEC values based on similar cross-linked contents. In the evaluation of chelating resins, poly(St-*co*-DVB)-based chelating resins **VII** containing NCAGs showed adsorption abilities toward heavy metal ions like Pb^{2+}, Cd^{2+}, and Cu^{2+} (Table 7, run 9), whereas poly(MMA-*co*-DVB)-based chelating resins **VIII** containing NCAGs showed adsorption abilities toward heavy metal ions like Cu^{2+}, Cd^{2+}, and Co^{2+} (Table 7, run 8). And poly(St-*co*-MMA-*co*-DVB)-based chelating resins **VI** containing NCAGs showed adsorption abilities toward heavy metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, and Cu^{2+} (Table 7, run 3): a synergistic effect resulted in the adsorption of heavy metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+}, and Co^{2+}. Table 7 showed that it was very worth optimizing the mol ratio of MMA to St when copolymer beads **I** were polymerized (31). The adsorption abilities of poly(St-*co*-MMA-*co*-DVB)-based chelating resins (Table 7, run 3) compared to chelating resins (Table 7, run 8 & 9) as mentioned as well as hydrolyzed poly(MA-*co*-BA-*co*-DVB) (Table 7, run 10) were relatively good. But all the chelating resins showed poor adsorptivity toward Ni^{2+} and Cr^{3+}. Figure 3 showed the adsorbed quantity toward Pb^{2+} and Hg^{2+} of three kinds of chelating resins containing NCAGs mentioned as a function of pH. The quantity increased gradually with increasing of pH value after passing by pH 3: a synergistic effect for the adsorption quantity in the pH range of 3 to 6 was also observed. In addition, the effect of metal ion uptake upon the mol ratio of MMA to St consisted in poly(St-*co*-MMA-*co*-DVB)-based chelating resins **VI** containing NCAGs at pH 5 was investigated as shown in Fig. 4: when the mol ratio of MMA to St in the preparation of copolymer beads **I** was 0.25, the adsorption capacities of the resins **VI** toward Pb^{2+}, Cd^{2+}, Hg^{2+}, and Co^{2+} reached a maximum value in each and showed a tendency to decrease gradually before and after the mol ratio. In addition, Table 8 showed the adsorption capacities after 10 adsorption-elution

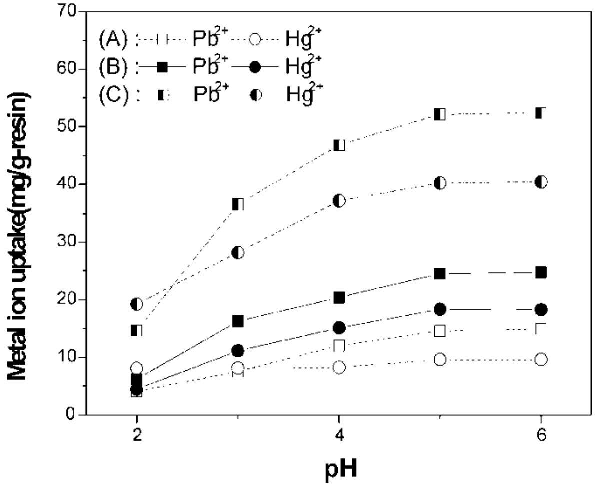


Figure 3. Effect of pH upon the adsorptivity toward Pb^{2+} and Hg^{2+} of three kinds of chelating resins containing a pair of neighboring carboxylic acid groups: (A) Poly(MMA-*co*-DVB)-based chelating resin **VII** (Table 7, run 8), (B) Poly(St-*co*-DVB)-based chelating resin **VIII** (Table 7, run 9) and (C) Poly(St-*co*-MMA-*co*-DVB)-based chelating resin **VI** (Table 7, run 3).

cycles for the reutilization of chelating resins **VI**; the elution of each metal ion was accomplished by using 1 M caustic soda or HCl solution at 25°C for 24 h. It was observed that all the chelating resins containing NCAGs could be regenerated without loosing its original performance during the reutilization.

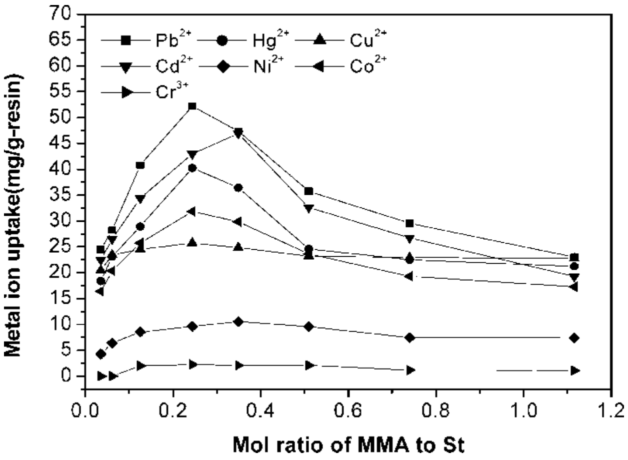


Figure 4. Effect of metal ion uptake upon the mol ratio of MMA to St existed in poly(St-*co*-MMA-*co*-DVB)-based chelating resins **VI** (Table 7, run 1∼7, 9) containing a pair of neighboring carboxylic acid groups at pH 5.

Table 8. Adsorption ability for heavy metal ions of reutilized chelating resins **VI** containing a pair of neighboring carboxylic acid groups

	Chelating resin[a,b] **VI** reutilized 10 times					Adsorptivity[d] (mg/g-resin)						
	Composition (mol)			DVB content (wt.%)	Carboxylic acid content[c] (meq/g-resin)							
Run	St	MMA	MLA			Pb^{2+}	Hg^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Cr^{3+}
1	0.146	0.009	0.155	20.56	3.42	28.19	23.10	23.42	26.46	6.39	20.34	0.00
2	0.160	0.020	0.180	21.92	3.56	40.73	28.90	24.50	34.40	8.52	25.73	2.00
3	0.176	0.043	0.219	20.71	3.65	52.20	40.25	25.73	43.02	9.60	31.80	2.24
4	0.189	0.066	0.255	20.90	3.67	47.33	36.37	24.44	46.82	10.50	29.80	2.09
5	0.194	0.099	0.293	21.60	3.77	35.71	24.58	23.21	32.59	9.56	23.62	2.05
6	0.185	0.137	0.322	21.51	3.80	29.55	22.45	22.88	26.72	7.42	19.25	1.12
7	0.172	0.193	0.365	21.99	3.80	23.00	21.24	22.72	19.27	7.38	17.24	1.06
8[e]	0.001	0.129	0.130	20.44	6.20	14.54	9.60	22.42	17.18	4.15	16.05	0.00
9[f]	0.142	0.005	0.147	19.99	3.41	24.51	18.34	20.42	22.47	4.27	16.39	0.00

[a] Structural units existed in reutilized chelating resins **VI**; St: styrene units, MMA: methyl methacrylate units, MLA: malonic acid units, and DVB: divinylbenzene units.

[b] Calculated by elemental analysis and chlorine analysis.

[c] IEC values caused by only sodium salts of carboxylic acid groups in the beads containing a pair of neighboring carboxylic groups.

[d] Resin 0.2 g, 20 mL of each metal solution (pH 5.0), 20°C, 28 h.

[e] Chelating resin **VII** shown in Scheme 1.

[f] Chelating resin **VIII** shown in Scheme 1.

CONCLUSION

Poly(St-*co*-DVB)-based chelating resins containing a pair of neighboring carboxylic acid groups (NCAGs) showed adsorption abilities toward heavy metal ions like Pb^{2+}, Cd^{2+}, and Cu^{2+}, whereas poly(MMA-*co*-DVB)-based chelating resins containing NCAGs showed adsorption abilities toward heavy metal ions like Cu^{2+}, Cd^{2+}, and Co^{2+}. Moreover, poly(St-*co*-MMA-*co*-DVB)-based chelating resins containing NCAGs showed adsorption abilities toward heavy metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, and Cu^{2+}: a synergistic effect in the adsorption of heavy metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+}, and Co^{2+}. The adsorption ability of poly(St-*co*-MMA-*co*-DVB)-based chelating resin among three kinds of chelating resins gave the best results. The ability could be optimized by controlling the mol ratio of MMA to St when a based resin was polymerized.

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