클로로메틸폴리스티렌의 高分子反應에 關한 硏究(Ⅲ)
—에틸렌디아민 리간드형 및 아미노메틸히드록시 퀴놀린형 킬레이트 수지의 합성—

朴壽永 · 洪性一

서울大學校 工科大學 纖維工學科

(1982년 7월 15일 접수)

Studies on the Polymer Reaction of Chloromethyl Polystyrene (Ⅲ)
—Preparation of Ethylenediamine Ligand Type and Aminomethylhydroxyquinoline Type Chelate Resins—

Soo Young Park and Sung Il Hong

Department of Textile Engineering, College of Engineering,
Seoul National University, Seoul, Korea

(Received July 15, 1982)

요약 : 표준적인 분산중합법으로 구(球)형의 Styrene-Divinylbenzene 가교 공중합 bead를 얻었다. 이러한 불용성의 polystyrene bead들을 ZnCl₂의 존재하에서 chloromethyl methyl ether와 고분자 반응시켜 chloromethylated polystrene bead를 얻었다. 또한 chloromethylstyrene 단량체의 단독중합 혹은 chloromethylstyrene과 styrene, divinylbenzene의 共重合에 의해서도 불용성의 chloromethylated polystyrene bead를 직접 얻을 수 있었다. 이렇게 얻은 다양한 종류의 chloromethylated polystyrene bead와 ethylenediamine을 DMF/water上에서 반응시켜 diamine배위자 형의 킬레이트 수지를 얻고 그의 Cu²⁺에 대한 흡착능을 batch equilibration法에 의해 pH 5에서 측정하였다. 또한 chloromethyl基와 diamine의 反應에 있어서의 site-Site interaction을 chloromethylated polystyrene의 chloromethyl基 치환도 및 중합체의 가교도와 관련지어 검토하였다. Aminomethylhydroxyquinoline배위자 型의 chelate수지는 diamine배위자 型의 chelate 수지를 5-chloromethyl-8-hydroxy quinoline hydrochloride로 N-alkylation시켜 얻었다.

ABSTRACT : Insoluble styrene-divinylbenzene copolymer beads were obtained by the standard suspension polymerization techniques. These beads were chloromethylated with chloromethyl methyl ether in the presence of anhydrous zinc chloride. Altern-

atively, chloromethylated polystyrene beads were prepared by the homopolymerization reaction of chloromethylstyrene monomer, or by the copolymerization reaction of chloromethylstyrene with styrene and divinylbenzene. Thus obtained chloromethylated polystyrenes were reacted with ethylenediamine in DMF/water solution to obtain diamine ligand type chelate resins. In the reaction of chloromethyl group with ethylenediamine, site-site interactions were investigated. Cu^{2+} chelation capacity was determined by the batch equilibration method at pH 5. In addition, aminomethylhydroxyquinoline type chelate resin was prepared by the N-alkylation of diamine ligand type chelate resin with 5-chloromethyl-8-hydroxyquinoline hydrochloride.

1. INTRODUCTION

Insoluble macromolecular polystyrene beads are drawing attention in all fields of research where recycle of reagent, catalyst, or ligand is essential and where facile separation between reactants and products is required. They are used as supports for ion-exchange processes[1], solid phase peptide syntheses[2], organic syntheses[3], catalysts[4], selective separation of metal ions[5] and solvent impregnated resin (SIR) preparation[6].

In the preparation of the effective chelation ion-exchange resins, these insoluble polystyrene beads were transformed into the polyamine ligand type chelate resins, using the reactivity of the chloromethyl group of chloromethylated polystyrene (CMPS) beads[3,9,10,11].

Up to now, a lot of research was focused on the modification of polystyrene beads containing polyamine type chelate ligands. Kobayashiet al[8]. prepared highly effective Hg^{2+} binding chelate resin containing thiuram disulfide groups by the polymeric reaction of the ethylenediamine ligand type resin with carbon disulfide. Saegusa et al.[9,10]. prepared polystyrene beads containing polyethyleneimine ligands by the ring-opening graft copolymerization of 2-methyl-2-oxazoline onto the CMPS beads[9], and further modified their metal chelating properties by carboxyalkylation[9], mercaptoethylation[10]

and dithiocarboxylation[10].

The authors are interested in the polymer reaction of the CMPS beads with ethylenediamine (EN) and their further modification by the alkylation with 5-chloromethyl-8-hydroxyquinoline hydrochloride.

In this work, solvent expandable and macroreticular polystyrene beads were prepared by the standard suspension polymerization of the styrene-divinylbenzene mixture[7].

CMPS beads were prepared by the reaction of the various polystyrene beads with chloromethyl methyl ether (CME) in the presence of anhydrous zinc chloride, where the chloromethylation degree was controlled by varying the concentration of the added catalyst. Alternatively we prepared CMPS beads by the autocrosslinking homopolymerization of chloromethylstyrene monomer or by the ternary copolymerization of styrene-divinylbenzene-chloromethylstyrene.

The polymeric reaction of these CMPS's with ethylenediamine was carried out in dimethyl formamide (DMF)/water solution to introduce the bidentate ethylenediamine chelate ligand into the preformed insoluble polymer beads. From the chlorine and nitrogen contents of the resins (II) and (III), site-site interactions (double coupling; path b) were studied (Scheme 1).

On the other hand, we noticed the fact that
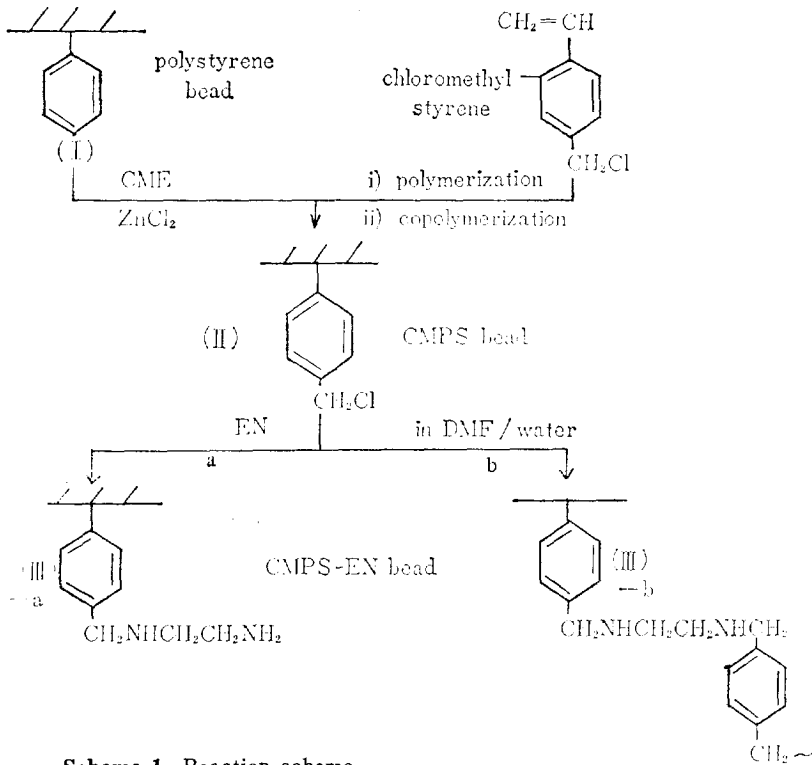
Scheme 1. Reaction scheme

8-hydroxyquinoline (IV) is an effective chelating agent for metal complexation[12]. To introduce the chelate ligand (IV) into the CMPS-EN (III) bead (IV) was transformed into 5-chloromethyl-8-hydroxyquinoline hydrochloride (5-CHL) according to the method described by Burckhalter et al.[13]. Reaction of (III) with 5-CHL in aqueous medium resulted in the aminomethylhydroxyquinoline type chelate resin (VI) (Scheme 2).

Then, Cu²⁺ chelation capacities of the above (III) and (VI) type beads were investigated.

2. EXPERIMENTAL

2-1. Bead polymerization

Commercial monomers such as styrene (St), divinylbenzene (DVB) and chloromethylstyrene (CMS) were freed from phenolic inhibitors by shaking with 5% sodium hydroxide solution. After washing with distilled water, these were dehydrated with barium oxide, and distilled under vacuum. The destabilized monomers were stored in a refrigerator. Just before the polymerization, these were redistilled under reduced pressure. (b.p. St; 52°C/28mmHg, DVB: 76.5–78°C/8mmHg, CMS;72°C/2mmHg.)

St-DVB solvent expandable bead (R-), St-DVB macroreticular bead (MP), chloromethylstyrene homopolymer bead (HCMS) and St-DVB-CMS ternary copolymer bead (TCMS) were obtained as 25-60 mesh particle size by the standard suspension polymerization techniques.

A1-l three-necked flask equipped with stirrer (with revolution indicator), thermometer, reflux condenser and nitrogen gas inlet tube was charged with 450ml water. It was refluxed for an hour under nitrogen bubbling. As a suspe-

nsion stabilizer 0.75g polyvinyl alcohol (PVA) was added and dissolved at 50°C. To this solution was added with constant stirring a freshly prepared solution of benzoyl peroxide (BPO) in the comonomer solutions detailed in Tables I, II, III and IV. A suspension of fine monomer droplets in water was obtained. Particle size was controlled by the step-by-step increase of the revolution speed. Passing a slow stream of nitrogen continuously, the temperature was elevated to 90°C. At this constant temperature, stirring was continued for more than 8hours at the fixed revolution speed.

After cooling the mixture, supernatant liquid was decanted. Obtained insoluble polymer beads were washed with hot water, methanol, dioxane and were finally slurried in methanol for 2 hours. Then the beads were filtered and vacuum dried at 50°C overnight.

To determine the swelling ratio (S.R.) in nonaqueous solvents, 30-40 ml portion of the dried beads were placed in a 100ml graduated cylinder. The volume(Vd) was read with an accuracy of ±0.5ml. The beads were then covered with solvent up to the 100ml mark. After 3 hours, the bed height of the beads were read again (Vs). The swelling ratio was estimated as Vs/Vd.

Table I. Composition and conditions for the polymerization of R-type polystyrene (PSt) beads.

Resin	St (ml)	DVB (ml)	% cross-linking	BPO (g)	Temp. (°C)	Time (hr)
R-1	80	1	1.25	0.50	90±2	9
R-2	75	3	3.90	0.50	90±2	9
R-3	75	6	7.50	0.50	90±2	9
R-4	70	8.4	10.8	0.50	90±2	9
R-5	70	12	14.8	0.50	90±2	9

Table II. Polymerization of MP type PSt bead.

Resin	St (ml)	DVB (ml)	% cross-linking	n-hexane (ml)	BPO (g)	water (ml)	PVA (g)	Temp. (°C)	Time (hr)
MP	24	6	20.2	42	0.5	400	0.75	87	16
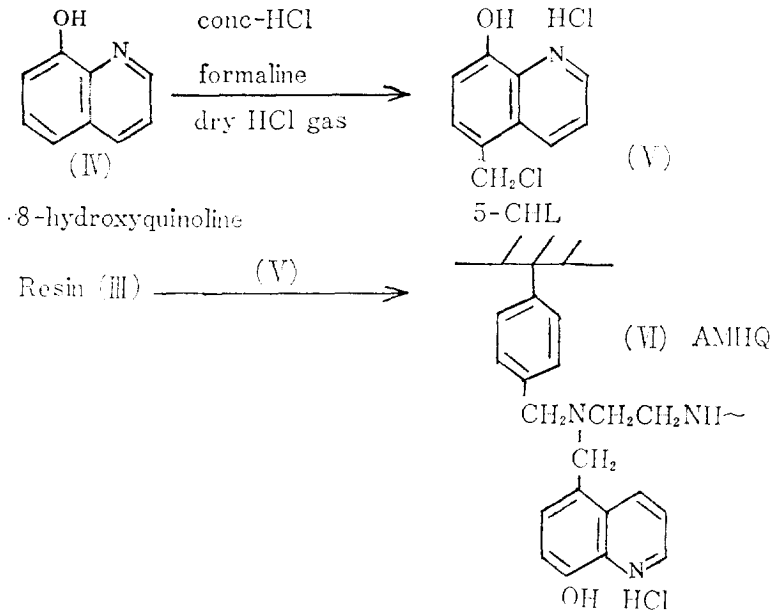
Scheme 2. Alkylation of resin (III) with H5-CL.

2-2 Chloromethylation of the polystyrene beads

R- and MP type polystyrene beads (25-60 mesh particle size) were chloromethylated with chloromethyl methyl ether in the presence of the anhydrous zinc chloride. As a diluent we chose dichloroethane (DCE) for all the chloromethylation reactions.

Various types of the polystyrene beads were collected and weighed for the chloromethylation reaction. These beads were swollen in dichloroethane at room temperature. Then chloromethyl methyl ether was added and the reaction mixture was stirred for 30 minutes. Anhydrous

Table Ⅲ. Homopolymerization of CMS.

Resin	CMS (ml)	BPO (g)	PVA (g)	Water (ml)	Temp. (°C)	Time (hr)
HCMS	8	0.05	0.08	50	82	8.7

Table Ⅳ. Ternary copolymerization of St-DVB-CMS.

Resin	St (ml)	DVB (ml)	CMS (ml)	BPO (g)	PVA (g)	Temp. (°C)	Time (hr)
TCMS	11.5	4	30	0.33	0.50	82	8.7

zinc chloride was added portionwise with constant stirring over 40 minutes. Heat was slowly supplied and the temperature was elevated to 50°C. At this constant temperature reaction was continued for 2.5 hours. Chloromethylation reaction was stopped by the addition of water into the reaction mixture. Resulting beads were washed with methanol, dichloroethane, dioxane, dioxane/water (3:1), water and methanol, and then the beads were vacuum dried at 60°C overnight. Details of the chloromethylation conditions are given in Table V.

Thus obtained chloromethylated polystyrene beads were characterized by IR (KBr method), and the chloromethylation degrees of the CMPS beads were determined by the chlorine content analysis.

Chlorine contents of the various CMPS's (obtained by the chloromethylation of the PSt beads or by the suspension polymerization of the CMS monomer) were analyzed by the combustion method using Modified Combustion Flask. 5-10 mg portion of the sample was accurately weighed and wrapped with a filter paper. Into the Combustion Flask 5ml distilled

Table Ⅴ. Reaction conditions for the chloromethylation of PSt beads

CMPS's (product)	PSt (g)	CME (ml)	DCE (ml)	ZnCl₂ (g)	Temp.
CMPS-1-A	R-1 (15.9)	30	130	7.65	50±2°C
CMPS-1-B	R-1 (3.0)	3.8	27	0.57	50±2°C
CMPS-1-C	R-1 (3.0)	3.8	27	0.19	50±2°C
CMPS-1-D	R-1 (3.0)	3.8	27	0.09	50±2°C
CMPS-1-E	R-1 (10.6)	20	90	2.0	r.t.*
CMPS-2	R-2 (15.9)	30	90	7.65	50±2°C
CMPS-3	R-3 (15.9)	30	90	7.65	50±2°C
CMPS-4	R-4 (15.9)	30	90	7.65	50±2°C
CMPS-MP-A	MP (9.0)	28	100	7.0	50±2°C**
CMPS-MP-B	MP (2.0)	2.53	18	0.38	50±2°C
CMPS-MP-C	MP (2.0)	2.53	18	2.12	50±2°C
CMPS-MP-D	MP (2.0)	2.53	18	0.06	50±0°C

*r.t.; room temperature
** ; exceptionally 8 hour reaction.

water and 0.5ml pure H_2O_2 (28%) was added. Then oxygen was allowed to flow into the Combustion Flask from the oxygen-bomb for ten seconds. Then combustion was immediately performed. After 30 minutes, the combustion gas was fully absorbed in hydrogen peroxide as Cl^- form. By the addition of 1-2 drops of bromophenol blue, pH was optimized between 2-3. Then Cl^- ion was titrated by 0.005N Hg $(NO_3)_2$ using diphenylcarbazone as an indicator. At the end point of the titration, color changed from yellowish to violet. Chlorine contents of the sample was calculated as follows[14].

$$Cl(\%) = \frac{0.005N\ Hg(NO_3)_2(ml) \times 0.1773}{sample\ weight} \times 100$$

2--2. Amination of CMP's with ethylene-diamine

All the CMPS beads which were obtained by the homopolymerization of chloromethylstyrene (HCMS), by the ternary copolymerization of CMS-St-DVB (TCMS) and by the chloromethylation of PSt beads (CMPS-and CMPS-MP) were sieved and 25-60 mesh size beads were collected.

Sieved CMPS beads (7g) were added to the DMF/water (34ml/10ml) solution. After 30 minutes, about ten-fold excess of the ethylenediamine (ca. 27ml) was added. The reaction mixture was stirred for 4 hours at constant temperature of 60°C. Resulting CMPS-EN (III) beads were recovered by filtration and washed with dioxane, water and methanol. It was dried at 60°C in vacuum. They were characterized by IR, chlorine content analysis and nitrogen content analysis.

To determine the nitrogen contents of the various CMPS-EN(III) beads, Kjeldahl process was utilized.

500-600 mg portion of the sample was accurately weighed and wrapped with filter paper.

This sample was placed in the Kjeldahl digestion flask containing 10ml of 98% sulfuric acid and 1.0g of potassium sulfate/copper sulfate (9 : 1 on weight basis). Then, this CMPS-EN sample was digested over an open flame for several hours. After digestion, above digestion product was transferred into the kjeldahl apparatus and neutralized by 30% NaOH solution using the bromocresol green/methyl red as an indicator. On heating the neutralized sample solution, ammonia gas was evolved. This ammonia gas immediately reacted with water vapor, then it was caught by 25 ml of 0.1N NaOH solution. By this titration of the remaining 0.1 N NaOH, nitrogen contents of the CMPS-EN beads could be calculated.

$$N(\%) = \frac{(0.1NH_2SO_4^* \times Xfa) - (0.1N\ NaOH^{**}}{sample\ weight\ (mg)}$$

$$\frac{Xfb) \times 1.4}{} \times 100$$

where * ; (ml)
　　　** ; 25ml was used.
　　　fa ; correction factor of 0.1 N H_2SO_4
　　　fb ; correction factor of 0.1 N NaOH

2-3. Chloromethylation of 8-hydroxyquinoline

7, 3g(0, 05mole) of 8-hydroxyquinoline (IV) was completely dissolved in 8ml of conc-HCl/8 ml (0, 05mole) of 37% formaldehyde. The reaction mixture was treated with dry HCl gas for 90 minutes[13]. As the reaction proceeded, yellow precipitates were formed in the reaction mixture. After 90 minutes HCl gas treatment, yellow solid was collected on a glass filter and dried in a vacuum desiccator over $CaCl_2$ for several days. Resulting powder (V) was analyzed by IR and chlorine contents analysis. Melting point was determined with the micro

melting point apparatus and DTA.

2-5. Preparation of aminomethylhydroxy quinoline (AMHQ) type chelate resin

3g of 5-CHL(V) was completely dissolved in 60ml water. Then, 3g of CMPS-EN beads were added to this solution. They were stirred at room temperature for 1 hour and at 60°C for additional 4 hours.

Resulting beads were washed with water, dioxane, chloroform, methanol and ether. They were finally Soxlet extracted with methanol for a day. The beads were filtered and dried in vaccum. Thus obtained AMHO resin was analyzed by the chlorine content analysis.

2-6. Metal chelation experiment

0, 30g of the resin (III)'s and (VI)'s was added to the 200ml erlenmeyer flask containing 50ml of 0, 025M cupric sulfate solution adjusted to pH 5 with the Clark-Lub's buffer solution[15]. Then they were shaken occasionally at room temperature for 72 hours. At appropriate time intervals small aliquots of the supernatant liquid was titrated with 0, 001M ethylenediamine tetraacetic acid (EDTA) solution using 1-(2-pyridylazo)-2-naphthol (PAN) as an indicator at pH 5[16]. At the end point of the titration PAN showed color change from red to yellow. Then Cu^{2+} concentration in the solution was calculated from the quantities of the used EDPA. From this value Cu^{2+} chelation capacity of the resin was to be calculated.

The Clark-Lub's buffer solution and 0.025M cupric sulfate solution were prepared as follows;

(a) Preparation of the Clark-Lub's buffer solution (pH5); 0.2M potassium biphthalate 500ml was mixed with 0.2N NaOH 238.5ml.

(b) Preparation of the 0.025M $CuSO_4 \cdot 5H_2O$ solution 3.121g of $CuSO_4 \cdot 5H_2O$ was dissolved in 500ml of the Clark-Lub's buffer solution.

3. RESULTS AND DISCUSSON

3-1. Polymerization

By the suspension polymerization of styrene-divinylbenzene mixture, various polystyrene resins can be obtained in the forms of solvent expandable bead, macroreticular bead and popcorn polymers[17]. Recently, Davankov et al.[25] prepared "macronet isoporous gels" through cross-linking of dissolved linear polystyrene by the difunctional monomeric reagents. More recently, Negre et al.[23] prepared "autocross-linking isoporous polystyrene resins" by the copolymerization of styrene and chloromethylstyrene.

The polystyrene resins which are used most often in the various fields of application shown in the introduction part are spherical beads of solvent expandable type (R—), and macroreticular type (MP) polystyrene resin.

As shown in Table VI, R-type PSt beads show different swelling ratios depending on their degree of crosslinking. The swelling ratio in organic solvents increased as the degree of cross-linking was lowered. In R-type beads swelling is the main factor determining the reactivity of the bead.

Macroreticular polystyrene (MP) was prepared by the addition of appropriate quantities of non-solvating diluent (n-hexane) to the monomer solution of styrene and divinylbenzene.

Table VI. Swelling ratios (Vs/Vd) of R—type PSt beads

Resin	Vs/Vd	
	in dioxane	in pyridine
R—1	6.37	5.45
R—2	3.0	2.93
R—3	1.24	2.24
R—4	1.10	1.3
R—5	1.03	1.08

The quantities of n-hexane, styrene and divinylbenzene shown in Table Ⅱ satisfies the monomer feed ratio (fm) for the macroporisity described by Sedrel and Dejong[23].

Though it's physical properties (e.g. pore size, pore volume and surface area) were not examined, it's opaque appearance in contrast to the transparent nature of the R—type beads and it's low density (0.4) revealed the macroreticular nature of the prepared MP bead. So this polymer was used as supports for the functionalization reactions.

In the homopolymerization of CMS, it is known that autocross-linking occurs[24]. The HCMS bead was insoluble in the various solvents of polystyrene, and the chlorine content of the insoluble HCMS was only 17.6% (theoretical chlorine content is 23% in the absence of autocross-linking). HCMS showed fairly high swelling ratios in dioxane and pyridine (Table Ⅳ). When St, DVB and CMS were copolymerized, the chlorine content of the terpolymer was 14.6%. IR spectra of HCMS and TCMS showed a sharp absorption at 1270cm^{-1} characteristic of chloromethyl group (Fig.1).

3-2. Chloromethylation

The process of chloromethylation is an important intermediate stage in the production of anion-exchange resins of varying basicity. In the chloromthyleation reaction of PSt bead with chloromethy methyl ether in the presence of a Friedel-Crafts catalyst such as ZnCl$_2$, the occurrence of additional cross-linking by the methylene bridging is a common feature. This methylene bridging reduces the degree of functionality and the solvent swelling ratios.

To reduce undesirable methylene bridging, Frechet[17] carried out the chloromethylation in a mixture of chloroform or carbon tetrachloride and chloromethyl methyl ether. Similarly, we

Table Ⅶ. Results of the chloromethylation of the R-type PSt beads.

Resin	Chlorine contents		Vs/Vd	
	(%)	(meq Cl/ g-R*)	in dioxane	in pyridine
CMPS-1-A	22.5	6.34	3.76	4.12
CMPS-1-B	16.9	4.76	—	—
CMPS-1-C	11.3	3.18	—	—
CMPS-1-D	9.02	2.54	—	—
CMPS-1-E	8.0	2.25	—	—
CMPS-2	20.8	5.83	2.45	1.85
CMPS-3	15.2	4.28	2.30	1.20
CMPS-4	14.5	4.08	2.21	1.00

* ; resin

Table Ⅷ. Results of the chloromethylation of MP type PSt beads.

Resin	Chlorine contents	
	(%)	meq Cl/g-R
CMPS-MP-A	16.5	4.65
CMPS-MP-B	5.38	1.52
CMPS-MP-C	4.71	1.33
CMPS-MP-D	5.13	1.45

chose dichloroethane (DCE) as a diluent, because DCE is a good swelling agent for the PSt beads. As Table Ⅶ and Ⅷ show, high degree of chloromethylation was obtained by this method. Initial maximum swelling of the PSt beads in DCE reduced the possibility of methylene bridging since a fully swollen matrix reacted much faster with chloromethyl methyl ether and was less prone to intramolecular reactions.

The degree of chloromethylation was controlled by varying the catalyst concentration (Table Ⅶ). Chlorine contents of the CMPS increased as the amount of the added catalyst was increased. In the case of R—type PSt beads, the degree of chloromethylation increased as the degree of swelling was lowered.

All the CMPS beads showed similar absorption bands in IR spectra. Their degree of chloromethylation and the intensity of the peak

at 1270cm⁻¹ showed some dependencies. Though their quantitative relationships were not investigated, they showed a general trend. As the degree of chloromethylation increased, relative peak height at 1270cm⁻¹ also increased.

3-3. Preparation of the ethylenediamine ligand type chelate resin

Ethylenediamine (EN) is a bidentate chelate

ligand which can be attached to the CMPS beads by the reaction of primary amino group of the ligand with the chloromethyl functionality of the resin. In this reaction, because of the fact that EN is a symmetrical bifunctional reagent and the chloromethylation degree of the resin is fairly high, the possibility of site-site interactions exist. Though we used 10 molar-excess EN, the occurrence of the double coupling (path b; Scheme 1) was observed (Table X).

As Table X shows, site-site interaction increased as the functionalization (chloromethylation) of the CMPS increased. Highly chloromethylated CMPS-1-A (22.5% Cl) showed 100% double coupling but CMPS-1-E (9%Cl) showed virtually single coupling.

Table IX. Results of the HCMS and TCMS polymerization

Resin	Chlorine contents		Vs/Vd	
	(%)	(meq Cl/g-R)	in dioxane	in pyridine
HCMS	17.6	4.96	—	4.5
TCMS	14.6	4.11	2.14	2.5

Table X. Results of the ethylenediamination of the CMPS-1-'s

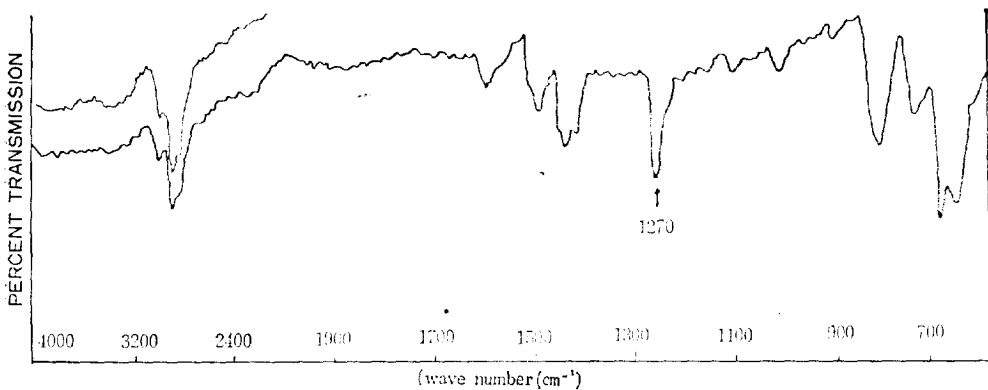| Resin	Chlorine contents		Nitrogen contents		S.R.	% double	Cu²⁺capacity
	(%)	(meq/g-R)	(%)	(meq/g-R)	in pyridine	coupling	(meq/g-R)
CMPS-1-A-EN	2.4	0.68	7.93	5.60	1.54	100	1.13
CMPS-1-B-EN	2.81	0.79	5.90	4.21	—	83	0.47
CMPS-1-C-EN	2.08	0.59	4.00	2.86	—	81.1	0.37
CMPS-1-D-EN	2.17	0.61	4.47	3.19	—	21	0.42
CMPS-1-E-EN	2.45	0.69	4.09	2.92	—	6.8	0.35

Fig. 1. IR spectrum of CMPS-2

Table XI. Results of the ethylenediamination of the other CMPS-'s

Resin	Chlorine contents		Nitrogen contents		S.R.	% double	Cu²⁺ capacity
	(%)	(meq/g-R)	(%)	(meq/g-R)	in pyridine	coupling	(meq/g-R)
CMPS-2-EN	3.8	1.07	6.98	4.99	1.31	93.2	0.73
CMPS-3-EN	3.2	0.90	5.96	4.26	—	54.0	0.50
CMPS-4-EN	4.7	1.32	5.44	3.89	1.11	42.0	0.38

Table XII. Results of the ethylenediamination of the HCMS and TCMS

Resin	Chlorine contents		Nitrogen contents		S.R.	% double	Cu²⁺ capacity
	(%)	(meq/g-R)	(%)	(meq/g-R)	in pyridine	coupling	(meq/g-R)
HCMS-EN	2.4	0.68	6.38	4.56	—	88	0.62
TCMS-EN	1.91	0.54	5.23	3.74	—	91	0.38

Table XIII. Results of the ethylenediamination of the CMPS-MP-beads

Resin	Chlorine contents		Nitrogen contents		% double	Cu²⁺ capacity
	(%)	(meq/g-R)	(%)	(meq/g-R)	coupling	(meq/g-R)
CMPS-MP-A-EN	3.32	0.94	5.65	3.98	85.4	1.13
CMPS-MP-B-EN	1.31	0.37	2.78	1.99	15.6	0.60
CMPS-MP-C-EN	1.07	0.30	3.08	2.0	3	0.38
CMPS-MP-D-EN	1.53	0.43	2.37	1.69	20.7	0.42

The ethylenediamination results of the other CMPS beads and the Cu²⁺ chelation capacities of the beads are shown in Tables XI, XII and XIII.

Comparing the % double coupling data of CMPS-1-A-EN, CMPS-2-EN, CMPS-3-EN and CMPS-4-EN, it can be concluded that site-site interactions increase as the degree of cross-linking decreases. i.e. Highly swellable beads prefer double coupling in DMF-water solution. This is the consistent results with the general characteristics of site-site interaction described by Farral et al.[18], who studied site-site interactions in the reaction of CMPS beads with butanedithiol.

Cu²⁺ chelation capacity of the various EN ligand type PSt beads at pH 5 is shown in Tables X, XI, XII and XIII. From the data it

can be shown that CMPS-1-A-EN and CMPS-MP-EN absorb Cu²⁺ ions most effectively.

3—4. Preliminary studies on the syntheses of aminomethylhydroxyquinoline type chelate resin

8-Hydroxyquinoline (IV) is an effective bidentate chelate ligand for Cu, Co, Ni, Zn, Au and UO₂²⁺ extraction. To introduce this ligand into the CMPS-EN (III) bead for the modification of the chelation behavior of (III), we transformed (IV) into the reactive form. Chloromethylation of (IV) was performed by the method of Burckalter[13]. Resulting 5-CHL has not been analyzed by spectroscopic methods or elemental analyzed up to the present. Only it's melting point was reported. We tried to analyze 5-CHL by the chlorine content analysis. 5-CHL
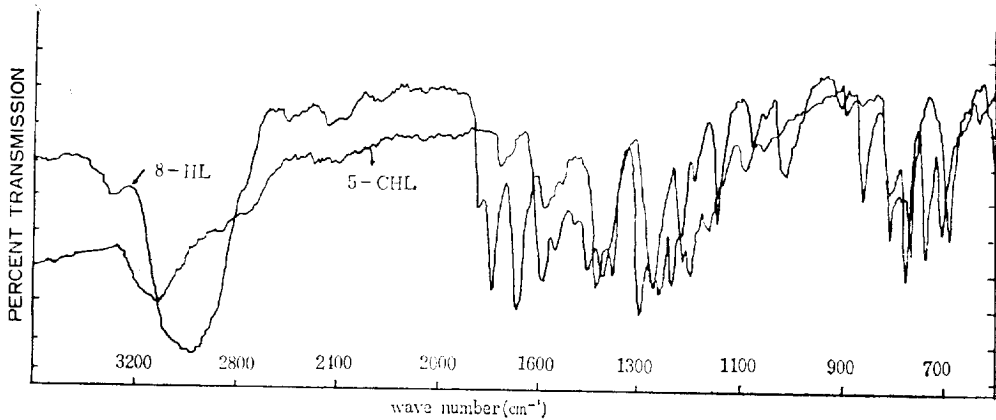
Figure 2. IR spectra of 8-hydroxyquinoline (8-HL) and 5-CHL.

showed 28–31% chlorine (calc. 30.9%), 225–230°C melting range (lit.[20] 225°C). IR spectra of 5-CHL show significant difference from(Ⅳ). Though (Ⅳ) was insoluble in water, 5-CHL was completely dissolved in water.

The reactions of 5-CHL has not so much been investigated. Warshawsky[20] used this compound in nitrobenzene solution for the Friedel-Crafts alkylation of polystyrene. 5-CHL was investigated in the reactions with polyaminostyrene in aqueous medium[21], or with cellulose in an aqueous medium[22] only by a few Russian chemists.

We tried to examine the polymeric reaction of CMPS-1-A-EN and CMPS-2-EN with 5-CHL in aqueous medium. Though IR spectra of the reaction products did'nt show clear difference from CMPS-EN due to the complexity of the peaks, the high increases in the chlorine content and weight reveal the possibility of the reaction shown in Scheme 2. The obtained resin was yellow color characteristic of the 5-CHL. Cu^{2+} chelation capacity of the AMHQ's are given in Table XIV.

As the Cu^{2+} adsorption increased, the color

Table XIV. Reaction of CMPS-EN with 5-CHL

Resin	Chlorine (%)	Weight increase (g)	Cu^{2+} capacity (meq/g-R)
AMHQ-1*	14.23	0.4	1.00
AMHQ-2**	11.43	0.3	0.73

* ; Reaction product of CMPS-1-A-EN with 5-CHL

** ; Reaction product of CMPS-2-EN with 5-CHL

Table XV. Cu^{2+} chelation of AMHQ-1 and CMPS-1-A-EN

Resin	Resin type	Cu^{2+} (meq/g-R)			
		2hr	24hr	46hr	72hr
CMPS-1-A-EN	(Ⅱ)	0.25	0.42	0.92	1.13
AMHQ-1	(Ⅵ)	0.25	0.67	1.00	1.00

of the CMPS-1-A-EN turned to deeper blue, but AMHQ resin which was originally yellow turned to green.

From the adsorption rate study shown in Table Ⅺ, it can be said that Cu^{2+} adsorption capacity was reduced by the alkylation of CMPS-EN with 5-CHL, but the adsorption rate increased

At this stage of investigation, the reaction

of CMPS-EN with 5-CHL is not fully underst-ood, but it was shown that the Cu²⁺ adsorption behavior of the AMHQ resin deviated from the CMPS-EN beads.

4. CONCLUSIONS

CMPS-EN and AMHQ chelate resins were synthesized and their Cu²⁺ chelation capacities were investigated. From the experimental results, this paper came to the following conclusions.

1. In the chloromethylation of the polystyrene beads, dichloroethane was an effective diluent for the preparation of the highly chloromethylated polystyrene bead.

2. In the ethylenediamination of the CMPS beads. site-site interactions predominantly existed in the case of the resins whose degree of chloromethylation was high and degree of cross-linking was low.

3. Cu²⁺ adsorption capacity of the aminated PSt (CMPS-EN) varied depending on the nitrogen contents and the nature of the cross-linking. High nitrogen contents and low degree of cross-linking yielded high Cu²⁺ capacity.

4. By the N-alkylation of the CMPS-EN bead with 5-CHL, yellow bead (AMHQ) was obtained. Total capacity for Cu²⁺ was slightly decreased by this reaction but the adsorption rate was increased.

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