

Chelating Resin: Pyridine Derivatives Attached to Poly(styrene) Beads with Spacer Group

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Synopsis

The pyridine derivatives were combined to poly(styrene) beads with spacer groups or a graft chain. These spacer-type and graft-type pyridine beads formed their Cu complexes with high rates and large stability constants; they act as an effective chelating resin. The pyridine residues were more mobile due to the spacer group and the graft chain, compared with the poly(4-vinylpyridine) powder.

INTRODUCTION

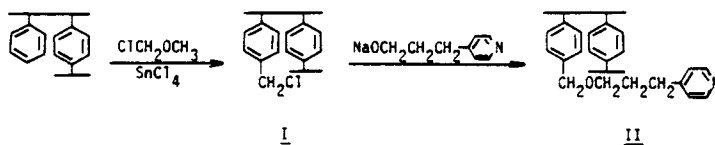
Various types of ligands have been introduced into a network poly(styrene) to use as chelating resins. Although such chelating resins take up transition-metal ions in high yield from aqueous solutions, they often adsorb metal ions very slowly due to the steric hindrance of polymer matrixes and due to the lower activity of the ligands situated at the inside of resins.¹

In order to improve these points, we synthesized in this paper the pyridine derivatives which were bound to poly(styrene) beads with spacer groups or a graft chain. Oligo(ethylene oxide) and the copolymer with 1-vinylpyrrolidone were selected as the spacer group and as the graft chain for the use in water. The pyridine-ligand parts of these poly(styrene) beads are expected to be well solvated just as in a homogeneous solution, although they are very easily separated from the solution. The complexation behavior with Cu ion was studied.

EXPERIMENTAL

Synthesis of Pyridine Beads

The spacer-type pyridine beads (II) were synthesized as follows (Scheme 1). 10 g of the poly(styrene) beads crosslinked with 20 mol % divinylbenzene (200–400 mesh) was chloromethylated in chloromethylmethylether (100 mL) with stannic chloride (3.0 g) (caution: chloromethylmethylether has carcinogenic properties). 13.3 g of the chloromethylated beads (I, degree of chloromethylation



Scheme 1.

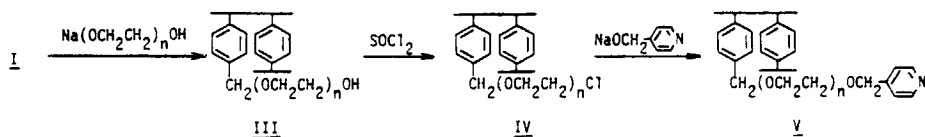
tion: see Table I) was added to the 100-mL dimethylformamide (DMF) solution containing 6 g of sodium hydride (55%) and 18.8 g of 4-hydroxypropylpyridine, and the mixture was stirred for 1 day under nitrogen atmosphere at 50°C. The modified beads were filtered out and washed with methanol and water. Yield: 19.4 g. Elemental analysis and degree of pyridination: see Table I. IR: $\nu_{\text{C-O-C}} = 1095 \text{ cm}^{-1}$.

To obtain the pyridine-ligand having a long spacer group (Scheme 2, V), oligo(ethyleneoxide) was attached to the chloromethylated poly(styrene) beads. 10 g of the chloromethylated beads I was added to the 100-mL DMF solution containing sodium hydride (5 g) and oligo(ethyleneoxide) ($\bar{M}_n = 1000, 200 \text{ g}$), and the mixture was stirred for 2 days at 60°C. The resulting beads (III) were collected by filtration, washed successively with water, methanol, and benzene, and finally washed with benzene using a Soxhlet apparatus for 2 days. Yield: 32.6 g. Elemental analysis and degree of hydroxylation: see Table I. IR: $\nu_{\text{C-O-C}} = 1095 \text{ cm}^{-1}$, $\nu_{\text{O-H}} = 3790 \text{ cm}^{-1}$. The end hydroxyl group was substituted with chloride (IV) by refluxing with thionyl chloride (100 mL). Yield: 32.9 g. Elemental analysis and degree of chlorination: see Table I. 4-Hydroxymethylpyridine (4 g) was attached in a similar manner as mentioned above (V). Yield: 33.5 g. Elemental analysis and degree of pyridination: see Table I.

Long spacer-type bipyridine beads (VI) were synthesized as follows (Scheme 3). 10 g of III was stirred in the 300-mL DMF solution of sodium hydride (0.4 g) for 3 h. 13.7 g of 4-chloromethyl-4'-methyl-2,2'-bipyridine was added to this mixture and kept at 40°C for 2 days. Yield: 10.5 g. Elemental analysis and degree of bipyridination: see Table I.

The graft-type pyridine beads (VIII) were obtained as follows (Scheme 4). 10 g of the 20 mol % crosslinked poly(styrene) beads (200–400 mesh) were isopropylated with isopropyl chloride (13 mL) and aluminum chloride (3.5 g) in 200 mL nitrobenzene at 35°C for 1 day.² Elemental analysis and degree of isopropylation: see Table I. 11.0 g of the isopropylated beads (VII) was added to 200 mL of nitrobenzene solution containing 2.75 g of benzoyl peroxide, and the mixture was stirred under oxygen atmosphere at 80°C for 12 h to yield 11.8 g of peroxidated beads.² The content of the peroxide group was determined by iodometric titration. Degree of peroxidation: 12 mol %. Using this peroxide (2 g) as the initiator of radical polymerization, 4-vinylpyridine (8 mL) and 1-vinylpyrrolidone (30 mL) were graft-copolymerized from the surface of these modified poly(styrene) beads *in vacuo* at 60°C for 8 h. After polymerization, the beads were filtered out and washed with benzene, methanol, and water repeatedly. Finally the beads were washed with methanol using a Soxhlet apparatus for 2 days. Yield: 6.3 g. Elemental analysis and degree of pyridination: see Table I. IR: $\nu_{\text{C=O}} = 1660 \text{ cm}^{-1}$.

Poly(4-vinylpyridine) powders (IX) (Scheme 5) were obtained by the bulk copolymerization of 4-vinylpyridine (20 mL) and divinylbenzene (55%, 12 or 1



Scheme 2.

TABLE I
 Elemental Analysis of the Pyridine Beads

Beads	Elemental analysis: found (calcd)				Degree of function- alization (%) ^a	mmol of pyridine unit per g beads
	C (%)	H (%)	N (%)	Cl (%)		
I ^b	75.8 (75.4)	6.0 (6.3)	—	18.3 (18.3)	75 ^c	—
II ^b	81.1 (81.4)	7.5 (7.4)	4.2 (4.2)	2.2 (2.2)	62 ^d	3.0
III ^b	61.9 (61.6)	7.9 (8.4)	—	2.5 (3.0)	33 ^e	—
IV ^b	60.3 (60.8)	8.5 (8.3)	—	5.5 (5.5)	29 ^f	—
V ^b	62.2 (61.9)	8.2 (8.3)	0.5 (0.5)	3.1 (4.0)	19 ^d	0.36
VI ^b	61.9 (61.9)	8.2 (8.2)	0.7 (0.7)	2.3 (2.8)	13 ^g	0.50
VII ^b	91.5 (91.7)	8.3 (8.3)	—	—	26 ^h	—
VIII ^b	78.2 (78.4)	7.5 (7.7)	8.9 (8.9)	—	35 ^d	3.2
IX ^b	83.2 (82.9)	6.1 (6.9)	10.2 (10.2)	—	80 ^d	7.3
IX ⁱ	80.1 (80.3)	6.6 (6.7)	13.0 (13.0)	—	98 ^d	9.3
X ^j	70.3 (70.5)	7.4 (7.5)	12.8 (12.8)	—	40 ^d	3.7

^a Unit mol %.

^b Copolymer of 4-vinylpyridine and 20 mol % divinylbenzene.

^c Degree of chloromethylation based on the Cl content.

^d Degree of pyridination based on the N content.

^e Degree of hydroxylation based on both the Cl content and the increase in weight.

^f Degree of chlorination based on the Cl contents.

^g Degree of bipyridination based on the N content.

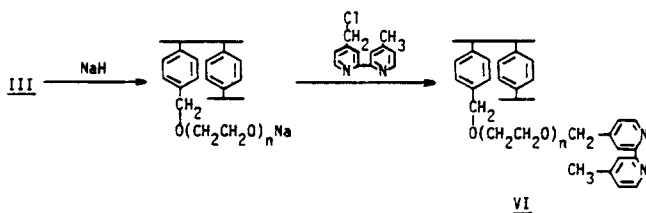
^h Degree of isopropylation based on the increase in weight.

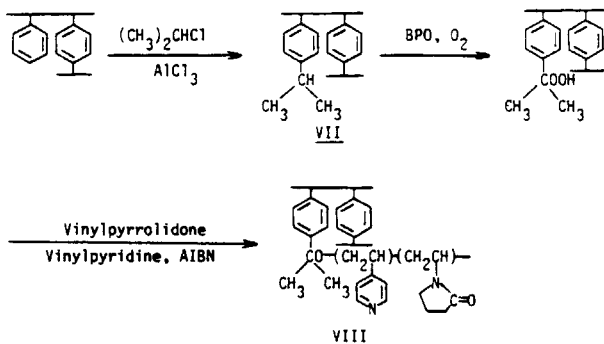
ⁱ Copolymer of 4-vinylpyridine and 2 mol % divinylbenzene.

^j Copolymer of 4-vinylpyridine and 1-vinylpyrrolidone.

mL) with azobisisobutyronitrile (AIBN, 0.2 g) at 60°C for 6 h. The resin obtained was crushed to 200–400 mesh powder and washed with methanol. Copolymer of 4-vinylpyridine and 1-vinylpyrrolidone (4-vinylpyridine residue: 40 mol %, $\bar{M}_n = 12,000$) (X) was also used as a soluble analogue of VIII.

The composition of these pyridine beads was determined by the elemental analysis and the weight change of polymer beads are given in Table I.



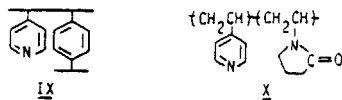


Scheme 4.

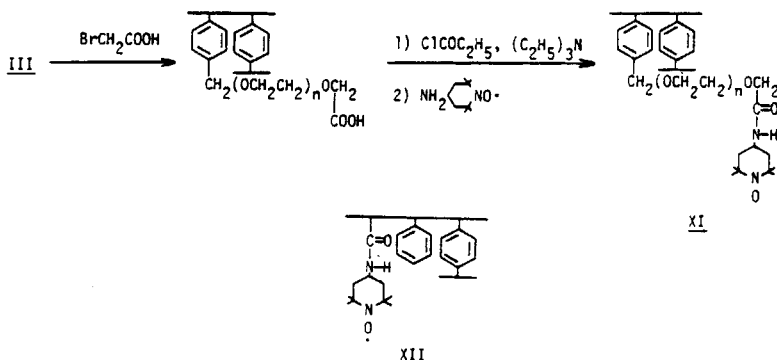
Synthesis of Spin-Labeled Beads

The spin-labeled model compound of the long spacer-type beads (XI) were synthesized as follows (Scheme 6). The poly(styrene) beads with oligo(ethyleneoxide) III (1.5 g) was refluxed with bromoacetic acid (3 g) in 30 mL ethylacetate for 8 h. The beads obtained were stirred in the 10-mL DMF solution containing chloroethylformate (0.5 mL) and triethylamine (0.5 mL) at -5°C for 2 h. Then, the 5-ml DMF solution of 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl³ (0.05 g) was added to the mixture and stirred at room temperature for 8 h. The beads were filtered out and washed with benzene and methanol repeatedly. The obtained spin-labeled beads were further washed enough with hot methanol to remove completely the unreacted 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl.

The spin-labeled model compound of the poly(4-vinylpyridine) powder (XII) was synthesized as follows. The copoly(styrene-acrylic acid) powder was obtained by the bulk copolymerization of styrene (1.5 g), acrylic acid (0.04 g), and divinylbenzene (55%, 0.5 mL) with AIBN (0.003 g) at 60°C for 12 h. The obtained powder (200–400 mesh) was reacted with 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl in a manner similar to that mentioned above.



Scheme 5.



Scheme 6.

Adsorption of Cu Ion on the Beads

A batch type equilibration procedure⁴ was used to determine the Cu(II) ion uptaken from solution by the beads. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was used as cupric salt. The pH value of the system was kept constant by a 0.1M $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$ buffer. The two phases were shaken on a mechanical shaker at room temperature for 12 h. After shaking, the two phases were separated, and the supernatant solution was titrated with EDTA. The amount of Cu ion in the supernatant subtracted from the amount initially added gave the amount of Cu ion adsorbed on the resin. Adsorption by the soluble copolymer X was measured by dialysis.

ESR Measurement

The ESR spectra of the Cu complexes and of the spin-labeled beads were measured on JEOL FE-3X.

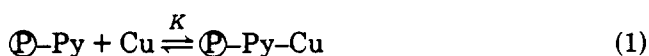
RESULTS AND DISCUSSION

The compositions of the spacer-type and graft-type pyridine beads were listed in Table I. Warshawsky et al.⁵ and Fujita et al.⁶ have reported that the cross-linking by two hydroxyl groups of oligo(ethyleneoxide) took place in the preparation of III. But the elemental analysis data in Table I show that the cross-linking reaction was not predominant under this preparative condition, probably due to the relatively high molecular weight of oligo(ethyleneoxide).

Examples of the electromicroscopic photographs were shown in Figure 1. Poly(styrene) beads ($\phi = \text{ca. } 70 \mu$) were expanded to 120–130 μ after the graft polymerization [Fig. 1 (a),(b)]. The graft beads VIII looked like wrinkled ones, and the complexation with Cu ion changed the wrinkled surface to the smooth one [Fig. 1 (c),(d)]. This suggested that the grafted pyridine chain was rearranged and shrunk by the Cu complexation. The same photographic result was obtained for the long spacer-type pyridine beads V.

Metal ions were very rapidly complexed to the pyridine residues of the spacer-type and graft-type beads, when the beads were dipped into a solution containing metal ions. The apparent rate constant of the Cu complex formation k was estimated by the decrease curve of Cu ion in the supernatant solution (Table II). The k values of the spacer-type and graft-type pyridine beads were much larger than that of the poly(4-vinylpyridine) powder IX. The largest k value was observed for the long spacer-type beads. These result suggests that the pyridine-ligand parts are well solvated and move easily with the spacer groups.

The adsorption curves given in Figure 2 appeared to be a Langmuir type and the stability constant K of the Cu complex and the saturated adsorption amount of Cu ion were evaluated by fitting Langmuir's equation, (2):



(K in L/mol, Py = pyridine groups of the beads)

$$\frac{c}{a} = \frac{1}{K \cdot A_s} + \frac{1}{A_s} \cdot c \quad (2)$$

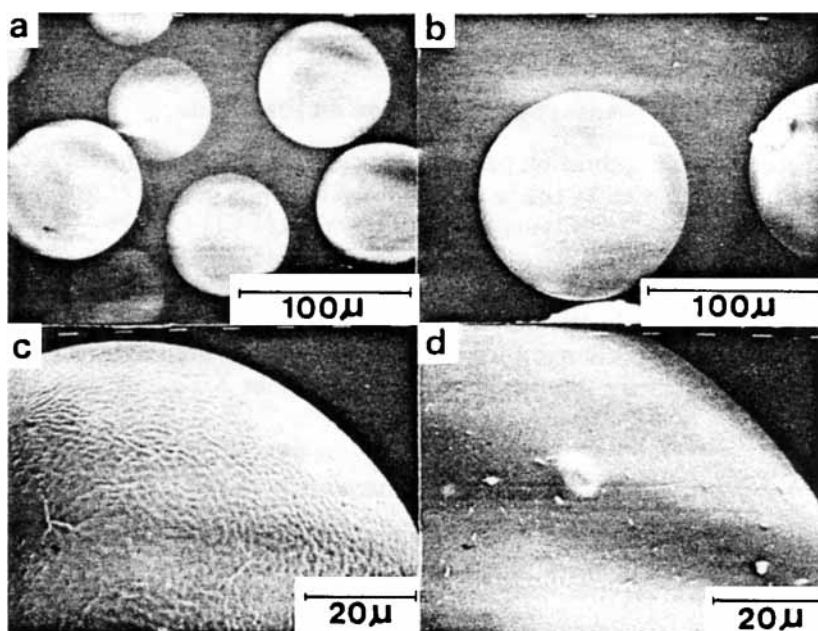


Fig. 1. Electromicroscopic photographs (SEM) of the pyridien beads; (a) poly(styrene) beads; (b) graft-type beads; VIII; (c) VIII; (d) Cu complex of VIII.

where A_s is a constant value which corresponds to the saturated adsorption amount, c is the concentration of Cu ion, K is the stability constant, and a is the quantity of adsorption. They are summarized in Table II with those of the Cu-pyridine complex.

The stability constant K of the Cu-copoly(4-vinylpyridine-1-vinylpyrrolidone) (X) complex was about four times as large as that of the Cu-pyridine complex. Furthermore, the K values in the pyridine beads system were 1 or 2 orders of magnitude greater than in the homogeneous copolymer system, which indicates that the pyridine beads uptake Cu ion from solution in a high efficiency. This

TABLE II
Apparent Rate Constant of Cu Complex Formation (k), Stability Constant of Cu Complex (K), and Saturated Amount of Cu Adsorption (A_s)

Pyridine beads	$k \times 10^4$ (s^{-1})	K ($L \cdot mol^{-1}$)	A_s	
			($mol \cdot unit \ mol^{-1}$) ^a	($mg \cdot g^{-1}$) ^b
Spacer type (II)	7.2	2500	0.15	8.3
Long spacer type (V)	16	3400	0.17	20
Long spacer type bipyridine (VI)	11	4700	0.18	40
Graft type (VIII)	10	9100	0.37	23
Poly(4-vinylpyridine)(IX)	<0.1	— ^c	— ^c	— ^c
Copoly(4-vinylpyridine-1-vinylpyrrolidone)(X) ^d	—	132	—	—
Pyridine	—	3.2	—	—

^a Mole ratio of Cu ion per pyridine residue of the beads.

^b Cu ion (mg) per 1 g of the beads.

^c Adsorption amount of Cu ion on the powder (IX) was small within experimental error.

^d Soluble, noncrosslinked polymer.

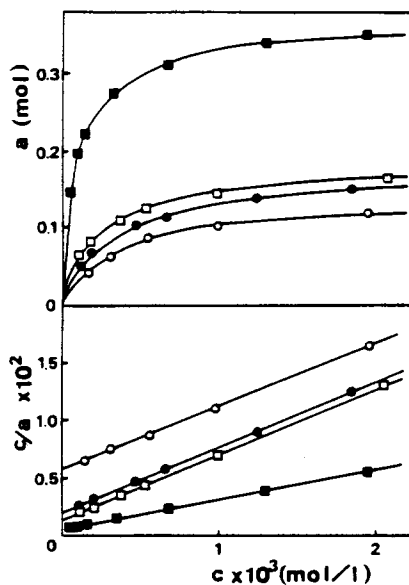


Fig. 2. Adsorption behavior of Cu ion on the pyridine beads; [pyridine residue] = 0.01 mol/L const.; pH 5.5; (O) II; (●) V; (■) VI; (□) VIII. c is Cu ion in solution (mol/L); a is Cu ion adsorbed on the beads (mol).

phenomenon appears to be general with the polymer complex system,^{7,8} and can be explained by the assumption that the concentration of ligand is higher in the polymer domain, especially in the surface domain of the pyridine beads. So that, once the metal ion is attached to one ligand group on the beads surface, other ligands coordinate more readily. The large K values for VI and VIII indicate that very stable Cu complexes are formed with the graft-type pyridine beads and with the long spacer-type bipyridine beads, probably due to chelate effect.

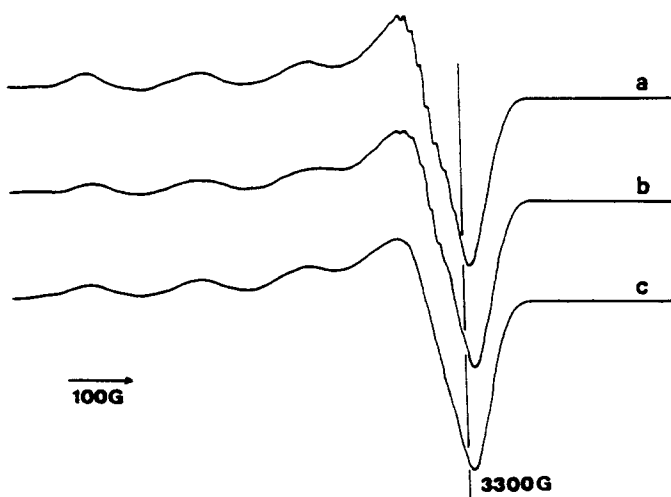


Fig. 3. ESR spectra of the Cu complexes on the pyridine beads; [pyridine residue]/[Cu] = 10, in pH 5.5 $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$ buffer, at 77°K; (a) VIII; (b) V; (c) IX crosslinked with 2 mol % divinylbenzen.

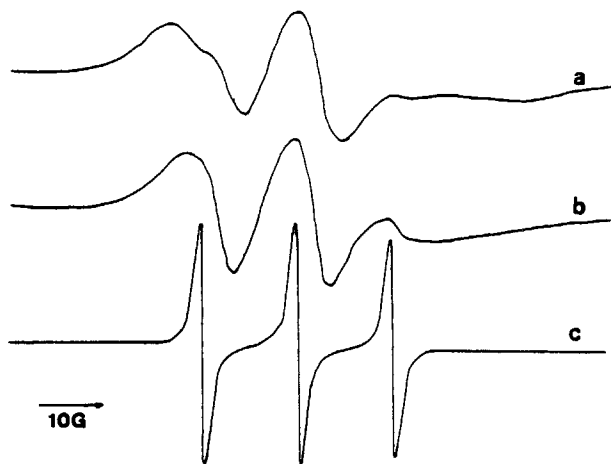


Fig. 4. ESR spectra of the spin-labeled beads; in pH 5.5 buffer, at room temperature; (a) XII; (b) XI; (c) 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl.

Table II also gives the A_s value in the molar ratio of Cu ion per the pyridine residue of the beads. If the Cu ion forms a tetradentate complex, $\text{Cu}(\text{pyridine residue})_4$ or $\text{Cu}(\text{bipyridine residue})_2$, the value of A_s becomes 0.25 (0.5 for VI). The A_s values in Table II show that one third of the pyridine residues in all beads cannot coordinate to Cu ion. Conformational rearrangement of the pyridine-ligand parts to form the Cu complex is assumed to be still difficult, although the pyridine residues are bound to poly(styrene) supporter with the spacer or graft group.

The A_s values per 1 g of the beads showed that the graft-type pyridine beads adsorbed Cu ion in high efficiency. As discussed above from the complexation rate and stability constant of the Cu complex, it is concluded that the long-spacer type bipyridine beads VI and the graft-type pyridine beads VIII act as a good chelating resin caused by their flexible spacer groups.

The ESR study on the Cu complex supported the good effect of the long spacer-group and the graft chain. The ESR parameters from Figure 3 ($g_{\perp} = 2.070$, $g_{\parallel} = 2.242$, $A_{\parallel} = 150$ G) showed that the coordination structure of these Cu complexes was square planar one in the pyridine beads. The ESR signals were clearly split for the Cu complexes of V and VIII, compared with that of IX. This means that the pyridine residues of the long spacer-type V and the graft-type VIII can complete the complexation with Cu ion while the pyridine residues of IX are immobilized and do not strongly coordinate to the Cu ion.

The ESR spectra of the spin-labeled beads (XI and XII) were shown in Figure 4. This absorption is based on the rotational motion of the spin-label piperidine-oxyl, which is considered to be corresponding to the mobility of the pyridine residue bound to the beads. The spin label attached to the terminus of the oligo(ethyleneoxide) spacer on the beads [Fig. 4(b)] exhibited a narrower line spectrum⁹ than was observed with the spin-labeled beads XII [Fig. 4(a)]. This result also supported that the pyridine residue of the long-spacer beads was more mobile and has a good affinity with solvent.

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