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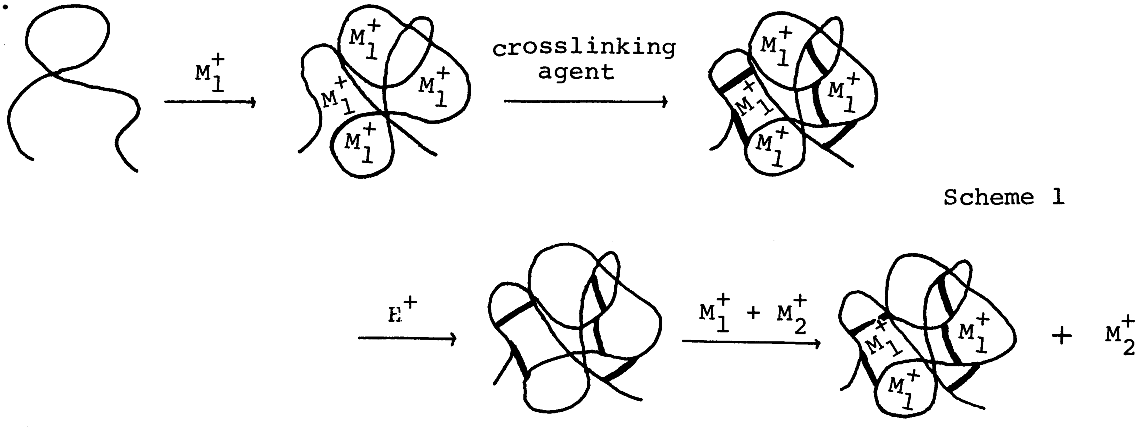
SELECTIVE ADSORPTION OF METAL IONS ON CROSSLINKED POLY(VINYLPYRIDINE) RESIN PREPARED WITH A METAL ION AS A TEMPLATE

Hiroyuki NISHIDE, Jichio DEGUCHI, and Eishun TSUCHIDA
Department of Polymer Chemistry, Waseda University,
Nishiohkubo, Shinjuku-ku, Tokyo 160

A new chelate resin was prepared by crosslinking poly(4-vinylpyridine) with a metal ion (Cu^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Hg^{2+}) as a template. The resin comparatively adsorbed the metal ion which was used as a template. The stability constants of the copper complexes with the resins were measured.

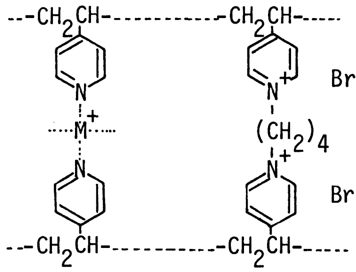
A metal ion is added to the solution of a polymer-ligand, such as poly(ethyleneimine), poly(vinylpyridine), poly(vinylalcohol), and poly(acrylic acid), and then the polymer-metal complex is rapidly formed. As has been reported previously[1,2], polymer-metal complexes show following two features; (1) a polymer-ligand is markedly contracted because of an intra-polymer chelation, and a polymer complex takes very compact form, (2) the stability constants of a polymer complex are about three or four orders of magnitude larger than those of a monomeric analogous complex. This is due to the successive increment of the stepwise formation constants in a polymer complex, in contrast to a monomeric complex. It is also an important feature that the shape and the stability of a polymer complex depend on the metal ion species.

Thus one previously makes the complex between a polymer-ligand and a metal ion (M_1), and after then, the polymer-ligand is crosslinked by adding a crosslinking agent to the polymer complex solution (Scheme 1). After that, the metal ion M_1 is removed by treating the resin with acid. In this resin, if the polymer-ligand chain is maintained at the best conformation for the metal ion M_1, which is used as a template, it is expected that the resin will preferentially form the complex with the metal ion M_1, when the resin is soaked into the solution containing various metal ions.



Scheme 1

In this letter, we report the new chelate resins which were produced by the template method as mentioned above and which selectively adsorbed a metal ion. Although crosslinked polymer-ligands, e.g. crosslinked poly(ethyleneimine)[3,4], are well known to uptake metal ions in a high efficiency, never before has the approach to produce the resin with selective binding ability for a metal ion been made. Poly(4-vinylpyridine)(PVP) was used as a polymer-ligand and was crosslinked with a metal ion as template by three different methods; alkylation of PVP by 1,4-dibromobutane, formation of the polymer complex between partially-quaternized PVP and poly(styrene sulfonate), and polymerization of 4-vinylpyridine-divinylbenzene with a metal ion.



Scheme 2

Crosslinking reaction of the PVP-metal complex by 1,4-dibromobutane(DB) is listed in Table 1. We selected four metal ions as template ions; four-coordinate square planar copper ion, six-coordinate octahedral iron and cobalt ion, and four-coordinate tetrahedral zinc ion. The PVP complex solutions were green, brown, pink, or white, respectively. PVP was crosslinked by alkylation of pyridine groups in PVP with DB to yield insoluble PVP resins of which free pyridines were utilized to coordinate metal ions(Scheme 2). The resins were washed with methanol and hydrochloric acid repeatedly in order to remove uncrosslinked PVP and the metal ion used as a template. And then, the resins were washed with dilute alkaline and distilled water repeatedly. The dried resin was ground and the 100-150 mesh size was used in all the metal uptake studies presented. The percentage of the quaternized pyridine unit in the resin(Q%) was determined from the ratio of absorption at 1600 cm^{-1}(due to pyridine group) to the absorption at 1640 cm^{-1}(due to quaternized pyridine group) of IR spectra. The percentage of crosslinking was caluculated by using the C/N ratio of elemental analysis. The percentage of quaternization was 30-40%, and the percentage of crosslinking was about 10%, in all resins.

Table 1 Crosslinking Reaction of the PVP-metal Complexes by 1,4-dibromobutane(DB)

Templates	Coordination Number	$[M^+]/[PVP]$	Crosslinked PVP	
			Quaternization	Crosslinking
–	–	–	36 %	12 %
Cu^{2+}	4	0.10	37	11
Fe^{3+}	6	0.067	33	12
Co^{2+}	6	0.067	35	11
Zn^{2+}	4	0.10	30	10

[PVP]=1 M, Degree of polymerization of PVP=122, [DB]/[PVP]=0.3, solvent : methanol, 55°C, 50 hrs, A batch type equilibration procedure was used to determine the metal uptake from solution by the resin. Throughout this study, 0.001 mol of $\bar{\mathrm{N}}$*) in the resin was placed in a 200-ml flask, to which were added the aqueous solutions 100 ml of 0.001 M metal ions ([metal ion]/[$\bar{\mathrm{N}}$]=1/10). The pH value of the system was kept constant by 0.1 N CH_3COOH-CH_3COONa buffer. The two phases were shaken on a mechanical shaker at room temperature for 5 hrs. After shaking, the two phases were separated, and the supernatant solution was then analyzed for the metal ion, using atomic absorption spectrophotometry(JEOL JAA-7000). The amount of metal ion in the supernatant subtracted from the amount initially added gave the amount of metal ion adsorbed by the resin.

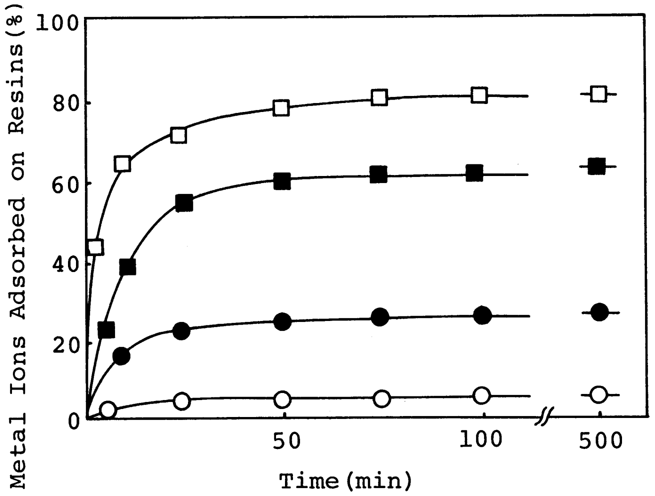


Fig.1 Complexation between Resins and Cu^{2+}, Fe^{3+}
$[M^+]$=0.001 M, $[\bar{N}]/[M^+]$=10, CH_3COOH-CH_3COONa buffer(Cu^{2+}:pH 5.5, Fe^{3+}: pH 5.0), □ :DBQP(Cu^{2+})~Cu^{2+}, ■ :DBQP(Fe^{3+})~Cu^{2+}, ○ :DBQP(Cu^{2+})~Fe^{3+}, ● : DBQP(Fe^{3+})~Fe^{3+},

Fig.1 shows the adsorption of metal ions on the PVP resins crosslinked with DB(abbreviated as DBQP) and the metal ion in blanket indicates the metal ion used as a template. One notices in Fig.1 that copper ion is adsorbed on DBQP(Cu^{2+}) more than on DBQP(Fe^{3+}). On the contrary, the amount of iron ion adsorbed on DBQP(Fe^{3+}) is larger than that on DBQP(Cu^{2+}). This adsorption behavior does not depend on the rate of adsorption but on the equilibrium amount of adsorption.

Table 2 Adsorption of Metal Ions on DBQP Resins

Resins	Adsorbed Metal Ions (%) Cu^{2+}	Fe^{3+}	Co^{2+}	Zn^{2+}
pH	5.5	5.0	5.5	6.2
DBQP(none)	65		9.9	13
DBQP(Cu^{2+})	77	4	9.6	14
DBQP(Fe^{3+})	59	25	5.6	22
DBQP(Co^{2+})	63		8.8	35
DBQP(Zn^{2+})	39		2.9	38

CH_3COOH-CH_3COONa buffer, [Metal ion]/[$\bar{\mathrm{N}}$]=1/10,

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*) $\bar{\mathrm{N}}$ is the unquaternized and coordinable vinylpyridine group in the resin.

Table 2 also shows that the DBQP resin comparatively adsorbs the metal ion used as a template. It is an important result that there is a difference among these DBQP resins in the binding ability of a metal ion in spite of these resins with the same chemical composition.

Under the constant amount of the resin, changing the concentration of copper ion, we determined the amount of the copper ion adsorption; the adsorption behavior was based on the Langmuir's type as shown in Fig.2. Then, the stability constant of the copper complex(K) and the saturated amount of copper ion adsorbed on the resin(As) were evaluated by fitting the Langmuir's equation and were listed in Table 3. The larger value of K is observed in DBQP(Cu^{2+}) which adsorbs copper ion in a high efficiency.

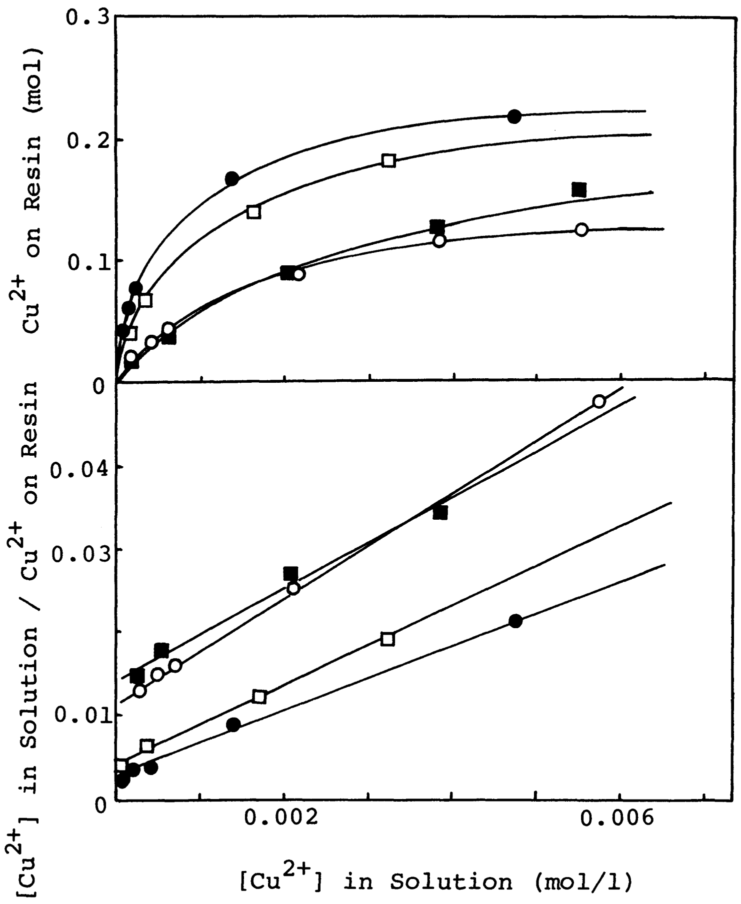

Fig.2 Adsorption Behavior of Cu^{2+} on DBQP Resins (Langmuir's Plots) $[\bar{N}]=0.01$ M Constant, CH_3COOH-CH_3COONa buffer pH 5.5, ○ :DBQP(none), ● :DBQP(Cu^{2+}), □ :DBQP(Co^{2+}), ■ :DBQP(Zn^{2+}),

Table 3 Stability Constant of Cu-DBQP Complexes(K) and Saturated Amount of Adsorption(As) (from Fig.2)

Resins (M^+ as template)	DBQP (none)	DBQP (Cu^{2+})	DBQP (Co^{2+})	DBQP (Zn^{2+})
$K\cdot 10^{-2}$(l/mol)	17	20	16	3.9
As(mol/unit mol)	0.20	0.22	0.20	0.19

CH_3COOH-CH_3COONa buffer, pH 5.5,

The visible absorption spectra of the Cu-DBQP complexes in a Nujol mull were measured with a high sensitive spectrophotometer(Union Giken SM-401). On the copper complex of DBQP(Cu^{2+}), the maximum of d-d absorption is observed at the shorter wavelength, 660 nm. This result agrees with the larger stability constant(K) of this resin(Table 3); it is suggested that the DBQP(Cu^{2+}) resin has the stronger ligand-field and that the conformation of the PVP chain in DBQP(Cu^{2+}) is maintained at the best conformation for copper ion.

Table 4 Absorption Spectra of the DBQP-Cu Complex

Cu Complex	DBQP(none)	DBQP(Cu^{2+})	DBQP(Fe^{3+})	DBQP(Co^{2+})	DBQP(Zn^{2+})
d-d Abs. λmax(nm)	680	660	675	670	680

The second method utilized in the preparation of the PVP resin is complex formation between partially-quaternized PVP(QP) and poly(styrene sulfonate)(PSS), i.e. the network polymer complex between a polycation and a polyanion[5]. A homogeneous solution of the QP-metal complex (CH_3COOH-CH_3COONa buffer solution, pH 5.0) was prepared by adding metal chloride 0.00625 mol to the solution 125 ml of 0.025 mol($\bar{N}$) QP. After then, to this solution the buffer solution 100 ml of 0.025 mol($-SO_3Na$) PSS was added dropwise, the QP-PSS resin was precipitated. The filtered resin was washed with dilute hydrochloric acid and distilled water repeatedly. Composition of the resin ($[-SO_3^-]_{PSS}/[-N^+]_{QP}$) was determined by elemental analysis.

Table 5 Adsorption of Metal Ions on QP-PSS

Resins	$[-SO_3^-]_{PSS}/[-N^+]_{QP}$	Adsorbed Metal Ions (%)				
		Cu^{2+}	Fe^{3+}	Co^{2+}	Zn^{2+}	Hg^{2+}
QP-PSS(none)	1.3	52	16	26	32	88
QP-PSS(Cu^{2+})	1.0	43	18	54	11	90
QP-PSS(Fe^{3+})	1.5	43	32	23	43	77
QP-PSS(Co^{2+})	1.2	41	26	51	27	84
QP-PSS(Zn^{2+})	0.8	43	6	0	9	76
QP-PSS(Hg^{2+})	0.5	34	5	11	14	84

CH_3COOH-CH_3COONa buffer(pH 5.0), $[\bar{N}]$ of QP=0.01 M, $[M^+]/[\bar{N}]=1/10$, Degree of polymerization of QP=122, Q% of QP=50, Molecular Weight of PSS=56000,

Adsorption of metal ions on QP-PSS resins was studied as above mentioned and was listed in Table 5. With a few exceptions, the QP-PSS resin relatively adsorbs the metal ion used as a template. QP-PSS is rapidly and easily formed, however, its crosslinking structure is partially destroyed with acid, which is a demerit of the template reaction in the QP-PSS system.

The third method to obtain the crosslinked PVP resin is the radical polymerization of 4-vinylpyridine-metal ion complex and divinylbenzene. 0.02 mol of metal acetate was dissolved in 0.12 mol 4-vinylpyridine, and 0.0435 mol styrene, 0.03 mol divinylbenzene, 0.0026 mol azobisisobutylonitrile and 17 ml methanol was added. This mixture was charged in a Pyrex tube and the tube was sealed under vac. The vinylpyridine-metal complex was polymerized by heating the sealed tube at 60°C for 8 hrs. The obtained resins(VP-DVB) were washed with methanol, dilute hydrochloric acid, and distilled water repeatedly. $Co(CH_3COO)_2$ and $Ni(CH_3COO)_2$ were used as a template because these metal salts hardly inhibited the radical polymerization of 4-vinylpyridine$^{6)}$. However, the obtained VP-DVB resins do not show the selectivity in the metal ion adsorption.

Table 6 Adsorption of Metal Ions on VP-DVB Resins

Resins	Solution	Adsorbed Metal Ions(%)	
		Co^{2+}	Ni^{2+}
VP-DVB(none)	CH_3OH	24	38
VP-DVB(Co^{2+})	CH_3OH	40	57
VP-DVB(Ni^{2+})	CH_3OH	43	63
VP-DVB(none)	CH_3COOH-	9	14
VP-DVB(Co^{2+})	CH_3COONa buffer	14	16
VP-DVB(Ni^{2+})	(pH 6.0)	10	19

$[\bar{N}]$=0.01 M, [Metal ion]/$[\bar{N}]$=1/10,

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