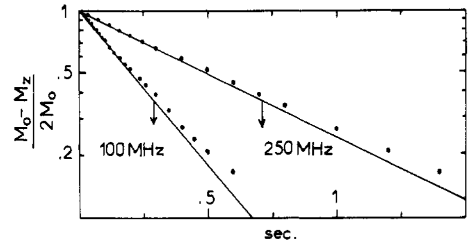

Figure 5. Semilogarithmic plots of typical longitudinal magnetization recovery curves of H_3 at 284 K for the two frequencies. The solid lines are the tangents at $t = 0$, and the vertical arrows indicate the value of T_1.

The influence of the cross relaxation on the determination of the proton relaxation times has been examined in our preceding work of P4VP[3] by simulating the recovery of the longitudinal magnetizations of Hα, Hβ, and H_3 taking account for the eight nearest neighbor protons. The conformation of the $P4VPD^+$ being not essentially different from that of P4VP, the conclusions of this previous work may be extended to the present one. As expected from other studies[11,12] it was found that the direction of the deviation of $\log[(M_0 - M_z)/2M_0]$ vs. t from the tangent at $t = 0$ changes from one branch of the $T_1 = f(T^{-1})$ curve to the other canceling out near the minimum (more exactly at $\tau_R \simeq 1.12\ \omega_H^{-1}$ for an isotropic motion). The error introduced by this deviation increases with the spectrometer frequency and may be important, exceeding 20% for correlation times longer than 5×10^{-9} s, i.e., below 250 K for the polymers under study. In the range of temperatures investigated here, this possible cause of error in the determination of T_1 was reduced as far as possible by measuring carefully the initial slope of $\log[(M_0 - M_z)/2M_0]$ vs. t in a time interval less than 30% of the estimated value of T_1 as shown in Figure 5. The problems raised by the cross relaxation make it more essential to support the interpretation of proton relaxation experiments by ^{13}C T_1 measurements where this effect is removed by noise decoupling of protons.

Acknowledgments. The authors are greatly indebted to Dr. Buu Ban for his help in conformational calculations and for fruitful discussions.

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Oligomeric *N*-(Phenylcarbamoyl)ethylenimine for Highly Specific Absorption of Mercury(II) and Copper(II) Ions[1]

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ABSTRACT: Poly[1-(*N*-phenylcarbamoyl)aziridine] $(CH_2CH_2N(CONHPh))_n$ ($\overline{DP}$ ca. 8) was found to show highly specific affinity for Hg^{2+} and Cu^{2+} as compared with Co^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions at pH 6–8. Absorbed ions can be removed by simply immersing in 1 N HCl solution at 32 °C. Laser Raman and IR studies showed that the Cu^{2+} ion is strongly interacting with the carbonyl oxygen atoms and weakly with nitrogen atoms. Selectivity of Hg^{2+} and Cu^{2+} ions from binary ion systems was shown to be high enough as expected from the single metal ion systems. The absorption specificity is considerably different from the ureanized polyEI, a branched higher molecular weight analogue of the poly(NPCA), and from poly[1-(*N*-methylcarbamoyl)aziridine]. Conformational requirement with regularly ordered CONHPh side group is suggested to be responsible for developing high absorption specificity, in which the phenyl group plays an important role.

We have reported a new synthetic route for oligomers of *N*-carbamoylethylenimine with a narrow molecular weight distribution (DP ca. 8) of type $(CH_2CH_2N(CONHPh))_n$ directly from 1-(*N*-phenylcarbamoyl)aziridine (NPCA).[2] The polymer showed significant specificities in the absorption of a variety of S=O or P=O compounds.[3] The specificity in absorption is probably assisted by the conformational change of the poly(NPCA) in the presence of the guest molecules, when considered the properties of related polymers of type $(CH_2CH_2N(COR))_n$ studied by several research groups.[4–7] It seems of value that the synthetic noncross-linked oligomeric compound possesses this kind of specificity in affinity for small molecules, because the host molecules must have special structural characteristics to accommodate the guest molecules in definite proportions.

Chemical property of an oligomeric compound with intermediate DP differs largely from its monomer or oligomers with smaller DP and from its high polymer. Important features of a functional oligomeric compound with intermediate DP are as follows: The oligomeric compound has enough chain atoms to keep its functional groups unseparable. The functional groups can be gathered intramolecularly to increase the functionality concentration. If the freedom in the molecule is restricted to some extent by the chemical bonds involved,

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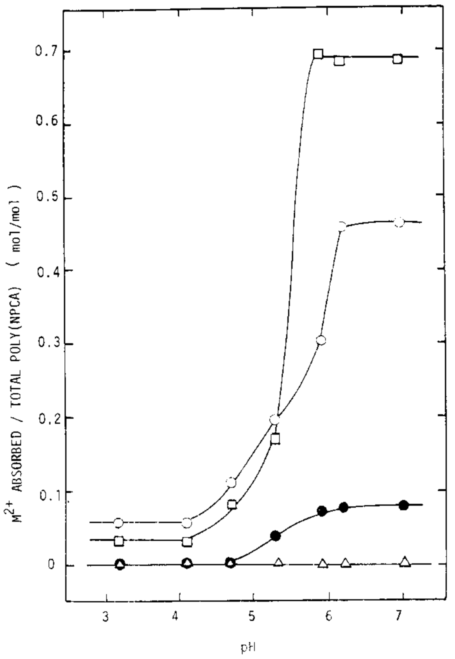

Figure 1. Absorption of several divalent metal ions to "freed poly(NPCA)", pH dependence: (□) Hg^{2+}; (○) Cu^{2+}; (●) Ni^{2+}; and (△) Co^{2+}, Zn^{2+}, and Cd^{2+}. Absorption conditions: Poly(NPCA), 0.02 monomer unit M; metal ion, 0.016 M; temperature, 32.0 °C; time, 24 h; absorption state, poly(NPCA) was suspended in an aqueous solution of a metal ion buffered by NaOAc–AcOH–NaCl.

numbers of the conformation will be reduced to result in development of some specific affinity.

The previous finding of the specificity in affinity for the S=O or P=O compounds encouraged the investigation of the affinity of the oligomeric poly(NPCA) for some metal ions. In this study we chose divalent metal ions, since these have been extensively used for modification studies[8] of metalloenzymes, metalloproteins and their model compounds, and polymer chelate studies.[9] Further, comparison of the affinities of the poly(NPCA) with other polymer systems may demonstrate some aspects of the chemical characteristics of the oligomeric poly(NPCA) in the affinity behaviors.

We found that the poly(NPCA) shows higher specific affinity for Hg^{2+} and Cu^{2+} ions than for other divalent metal ions studied. The binding state was investigated by vibration spectroscopies, and the amount of the Cu^{2+} ion absorbed into the oligomer was estimated by studying the absorption behavior. Selective absorption of Hg^{2+} and Cu^{2+} ions from the binary systems including Ni^{2+}, Co^{2+}, Cd^{2+}, or Zn^{2+} was found to be effective. The affinity for the divalent ions for the poly(NPCA) is significantly different from that of the branched higher molecular weight analogue derived from commercial polyethylenimine and phenyl isocyanate.

Results and Discussion

The poly[1-(*N*-phenylcarbamoyl)aziridine] (poly(NPCA)) was prepared from 1-(*N*-phenylcarbamoyl)aziridine (NPCA) directly by its ring-opening polymerization with Et_2SO_4. Since the polymer adsorbs Et_2SO_4 molecules even after being washed, it was treated with an aqueous NH_4OH solution followed by elution through an Amberlite-400 column to remove the Et_2SO_4 from the polymer.[2] The "freed" poly(NPCA) thus obtained was shown to have the same chemical structure of $(CH_2CH_2N(CONHPh))_n$ as the untreated sample and was almost free from the Et_2SO_4 (S content 0.09%, which is almost equivalent to the blank value of S analysis).[2,3]

The "freed polymer" was finely pulverized and suspended at 32 °C in water containing a divalent metal acetate: $Hg(OAc)_2$, $Cu(OAc)_2$, $Ni(OAc)_2$, $Co(OAc)_2$, $Zn(OAc)_2$, or $Cd(OAc)_2$. The pH value of the aqueous solution was varied by adding a buffer solution of NaOAc–AcOH–NaCl mixture. The pH range of the experiments was limited to pH 3–7 at which no precipitation of metal hydroxide occurs. The amount of the metal ions bound was determined titrimetrically with EDTA solution for the aqueous phase after careful separation of the poly(NPCA).

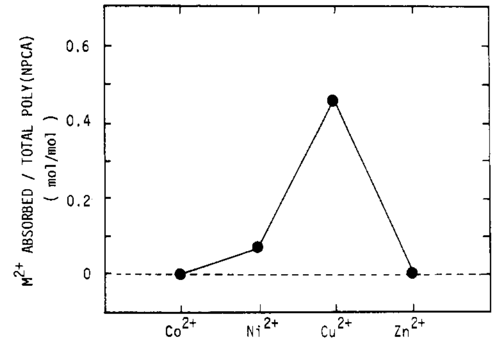

Figure 2. Irving-Williams plot in the absorptivity of poly(NPCA) for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions.

Table I
Recovery of Metal Ions from Poly(NPCA)[a]

	Recovery, %		
M^{2+}	12 h	24 h	48 h
Hg^{2+}	42	81	93
Cu^{2+}	35	82	89
Ni^{2+}			78

[a] Metal containing poly(NPCA) (7×10^{-3} monomer unit mol/L) was suspended in 1 N aqueous HCl solution at 32 °C.

The results of absorption behavior at different pH for these divalent metal ions in 24 h (Figure 1) indicate that (i) the poly(NPCA) absorbs Hg^{2+} and Cu^{2+} strongly, Ni^{2+} slightly, and others (Co^{2+}, Zn^{2+}, and Cd^{2+}) hardly, (ii) amounts of the metal ions absorbed depend largely upon the pH of the system, and (iii) effective absorption of Hg^{2+} and Cu^{2+} occurs at a pH range of 6–8. The order in the affinity at pH 6.22 for the metal ions of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} follows the Irving–Williams order of stability[10] as shown in Figure 2 and also follows the order of stability for EDTA coordination compounds as they appear in the literature:[11a] $Hg^{2+} > Cu^{2+} > Ni^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+}$. This indicates that the fundamental aspect of affinity of the poly(NPCA) for the divalent metal ions is not unusual as compared with a majority of coordination systems already reported.[11b]

By simply immersing in the aqueous 1 N HCl solution at 32 °C for 48 h, the metal ions absorbed can be removed from the polymer. The time dependences of desorption of the Hg^{2+}, Cu^{2+}, and Ni^{2+} ions are shown in Table I. The rate of desorption under this condition is nearly identical order as the case of absorption. The time dependences of absorption of Hg^{2+} and Cu^{2+} at pH 6.22 at 32 °C (Figure 3) show that the absorption occurs gradually and equilibrates after approximately 30 h.

The similarity of the poly(NPCA) to a low molecular weight ligand can be supported by the following studies of chemical nature of the absorbed state. Comparison of the laser Raman spectra of the "freed" with the Cu^{2+}-absorbed poly(NPCA)'s (Figure 4) indicates that considerable changes occur in the amide-I, -II, and -III frequencies: broadening, triplication, and low-wave number shift of the amide-I band due to absorption of the Cu^{2+} ion were apparent, and low-wave number shift of the amide-II band was observed. The change in the amide-III

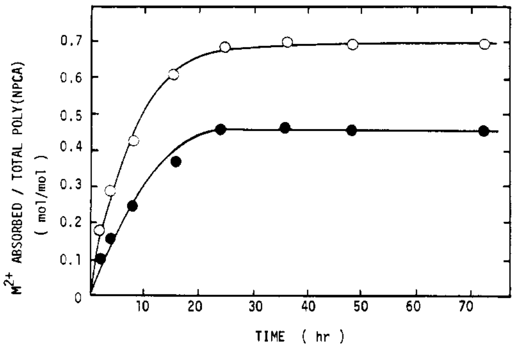

Figure 3. Time dependence of absorption equilibration for Hg^{2+} and Cu^{2+} ions. Absorption conditions: "freed poly(NPCA)", 0.02 monomer unit M; metal ion, 0.016 M; temperature, 32.0 °C; pH, 6.22; absorption state, suspension.

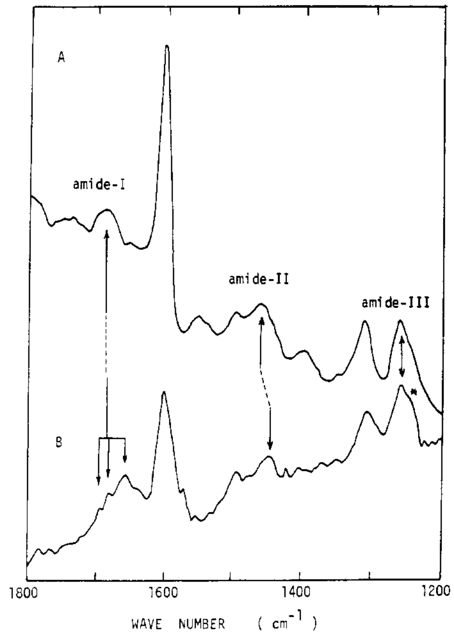

Figure 4. Laser Raman spectra of the "freed poly(NPCA)" (A) and Cu^{2+} absorbed poly(NPCA) (B). Operated at laser power of 230–240 mW at 514.5 nm. Interference filter was placed before the sample to remove plasma lines. The photon counting system was equipped. Recording conditions: sample state, powdery; spectral split width, 2 cm^{-1}; slit height, 5.2 mm; sampling time, 0.2 s; repeat times, 16; sensitivity, 2 × 100 pA full scale.

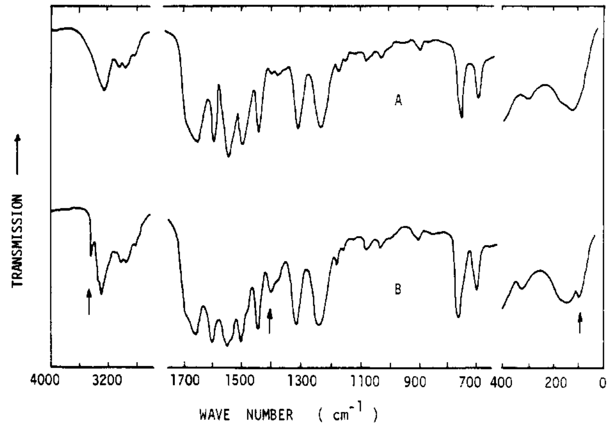

Figure 5. IR spectra of the "freed poly(NPCA)" (A) and Cu^{2+} absorbed poly(NPCA) (B); KBr disks.

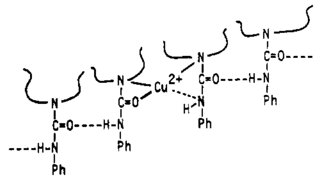

Figure 6. A possible model of absorbed state of Cu^{2+} ion in the poly(NPCA). The dark line shows stronger interaction and the dashed lines show weaker interaction.

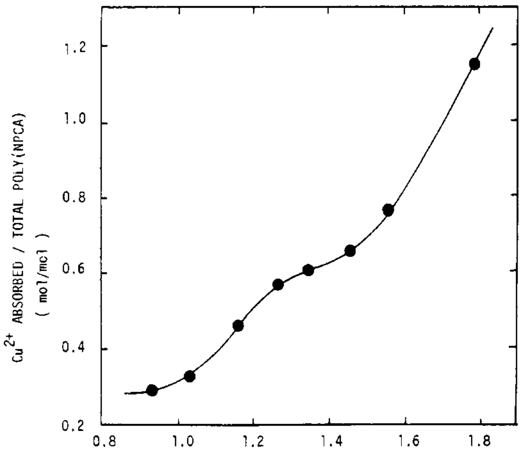

Figure 7. Absorption isotherm of the Cu^{2+} ion to the "freed poly(NPCA)". Absorption conditions: poly(NPCA), 0.02 monomer unit M; temperature, 32.0 °C; time, 24 h; pH, 6.22; absorption state, suspension.

band was less prominent, but the increase in the intensity of the shoulder band marked by an asterisk exceeds that for a blend sample prepared by mixing of the poly(NPCA) with $Cu(OAc)_2$ in powdery states. The laser Raman results suggest a strong interaction between a Cu^{2+} ion and the carbonyl oxygen atom in the poly(NPCA).

Comparison of the IR spectra of the "freed" with the Cu^{2+}-absorbed poly(NPCA)'s over a range of IR to far-IR regions (Figure 5) indicates that the new bands occur at 3450, 1400, and 95 cm^{-1}. The band at 3450 cm^{-1} corresponds to dissociation of the N–H hydrogen bond, and the band at 95 cm^{-1} can be due to ν_{CuO} or ν_{NCuN} frequencies.

From the spectroscopic results, we can depict the most probable model of the interaction between the poly(NPCA) and the Cu^{2+} ion as shown in Figure 6. It seems reasonable that a Cu^{2+} ion dissociates a CO- - -H–N hydrogen bond to result in an interaction with the carbonyl oxygen, which is almost comparable to a chemical bond, and less strong interactions with some nitrogen atoms. Thus, the absorption of the Cu^{2+} ion by the poly(NPCA) is not simple inclusion of the Cu^{2+} ion in the entanglement of the poly(NPCA) molecules nor interaction due to van der Waals forces.

This chemical state of the Cu^{2+} ion in the poly(NPCA) may explain why our system follows the Irving–Williams stability order or its generalized form but other cross-linked systems do not. The stability order, in general, is observed for the systems in which metal ions are chemically bound, while spatial distribution is a major factor for incorporation of the metal ions in the cross-linked systems.

Absorption Behavior of Cu^{2+} Ion in the Oligomer. A feature of absorption of the Cu^{2+} ion is illustrated in Figure 7 as a function of log [free Cu^{2+}], where a hump in the curve is observed. This curve appears to indicate that the absorption occurs in at least three steps. This impression was found to be improper by the following analysis.

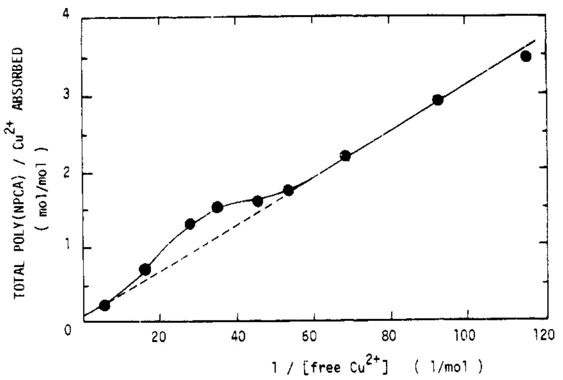

Figure 8. Plot of eq 3 for absorption of Cu^{2+} ion to the "freed poly(NPCA)". Absorption conditions: the same as those described in Figure 7.

In order to obtain the absorption information in some detail, the absorption process was analyzed by means of the Langmuir type equation for the following system:

$$\text{oligomer} + M^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{oligomer–}M^{2+}$$

From

$$dw/dt = k_1c(w_s - w) - k_2w = 0$$

it follows

$$1/w = k_1/k_2w_sc + 1/w_s \quad (1)$$

where, w is the amount of the absorbed species (oligomer–M^{2+}), w_s is the amount of the absorbed species at saturation, c is an equilibrium concentration of the free metal ion, and k_1 and k_2 are the rate constants of absorption and desorption, respectively. Since the apparent equilibrium constant of the system can be represented as:

$$K_{app} = [\text{oligomer–}M^{2+}]/[\text{oligomer}] \cdot [M^{2+}]$$

then,

$$K_{app} = w/(w_s - w)c \quad (2)$$

From eq 1 and 2, the following relation can be derived:

$$1/w = 1/Kw_sc + 1/w_s \quad (3)$$

When plotted (mol of total oligomer)/(mol of absorbed Cu^{2+} ion)(w) vs. 1/[Cu^{2+} free](1/c), we obtained a curve as shown in Figure 8. This curve consists of a linear plot (intervened by a dashed line) and a hump at the range of 1/[Cu^{2+} free] being 15–60 L/mol. This observation indicates that the net absorption behavior can basically be represented by a single process, superimposed by an abnormal absorption which appears in the hump portion. We suggest that the hump can be due to the faster absorption process on the surface of the oligomer and that the slower and linear absorption is due to the absorption into the interior of the polymer. A temporary slowdown of the absorption can be attributed to the repulsion between Cu^{2+} ions already absorbed on the surface and coming ones, preventing further absorption until the molecular rearrangement of the poly(NPCA) is attained.

The amount of the saturated absorption (w_s) calculated from the intercept of the linear relation was extrapolated as 8 Cu^{2+} ions per molecule of the poly(NPCA), corresponding to one Cu^{2+} ion per monomer unit of the oligomer. The results indicate that the poly(NPCA) can absorb, at infinitely high Cu^{2+} concentration, one Cu^{2+} ion per monomeric unit if all are ideal. At the highest Cu^{2+} ion concentration studied, we observed about half of the ideal value being practical.

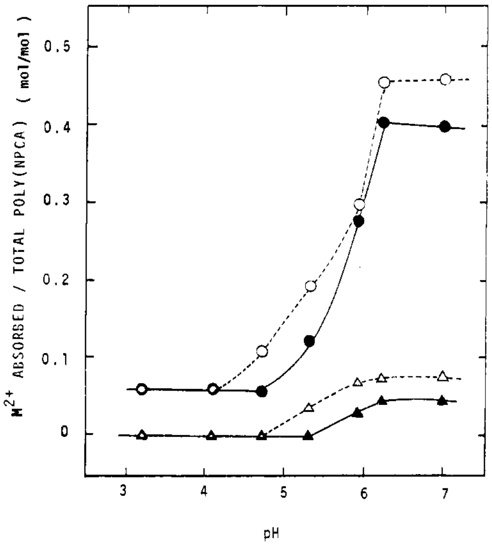

Figure 9. Selective absorption of the Cu^{2+}–Ni^{2+} binary ion system: ●, Cu^{2+} ion absorption in the binary system; ▲, Ni^{2+} ion absorption in the binary system; ○, Cu^{2+} ion absorption in the Cu^{2+} alone system; and △, Ni^{2+} ion absorption in the Ni^{2+} system. Absorption conditions: "freed poly(NPCA)", 0.02 monomer unit M; metal ions, 0.016 M, respectively; temperature, 32.0 °C; time, 24 h; absorption state, suspension.

Table II
Absorption Selectivity of Poly(NPCA) for Cu^{2+} and Hg^{2+} Ions from Binary Mixtures[a]

M_1^{2+}	M_2^{2+}	Selectivity[b] %
Cu^{2+}	Ni^{2+}	91
Cu^{2+}	Cd^{2+}	100
Cu^{2+}	Zn^{2+}	100
Hg^{2+}	Ni^{2+}	94
Hg^{2+}	Cd^{2+}	100
Hg^{2+}	Zn^{2+}	100

[a] Absorption conditions: poly(NPCA), 2×10^{-2} unit M; metal ions, 1.6×10^{-2} mol/L; pH 6.22; temperature, 32 °C; time, 24 h.
[b] Defined by percent absorption of M_1^{2+} in total absorbed metal ions (M_1^{2+} + M_2^{2+}).

Selective Absorption of Cu^{2+} or Hg^{2+} Ions from Binary Ion Mixtures. "Freed poly(NPCA)" was suspended at 32 °C for 24 h in an aqueous solution containing equal amounts of two kinds of metal ion: Cu^{2+}–Ni^{2+}, Cu^{2+}–Cd^{2+}, Cu^{2+}–Zn^{2+}, Hg^{2+}–Ni^{2+}, Hg^{2+}–Cd^{2+}, and Hg^{2+}–Zn^{2+}. The absorptivity was determined by observing the concentration of two ions in the aqueous phase in a given system with EDTA chelatemetry. Absorption selectivity of the poly(NPCA) for the Cu^{2+} and Hg^{2+} ions at pH 6.22 was excellent in these binary systems as shown in Table II.

The values in the Table II are shown by the percent absorbed amount of the Cu^{2+} and Hg^{2+} ion (M_1^{2+}) in the total absorbed amount of two ions in a given system (M_1^{2+} + M_2^{2+}). In the Cu^{2+}–Cd^{2+}, Cu^{2+}–Zn^{2+}, Hg^{2+}–Cd^{2+}, and Hg^{2+}–Zn^{2+} systems, the Cu^{2+} and Hg^{2+} ions were absorbed in the poly(NPCA) exclusively, and even in the Ni^{2+} systems, the absorption selectivity exceeds 90% for Cu^{2+} and Hg^{2+}.

The absorption in the binary systems is almost parallel to the absorption behaviors of individual metal ions, which are illustrated in Figure 1. Comparison of a Cu^{2+}–Ni^{2+} binary system with the Cu^{2+} and Ni^{2+} systems for the function of pH is shown in Figure 9. The absorbed amounts of the Cu^{2+} and Ni^{2+} ions somewhat decrease in the binary systems, compared

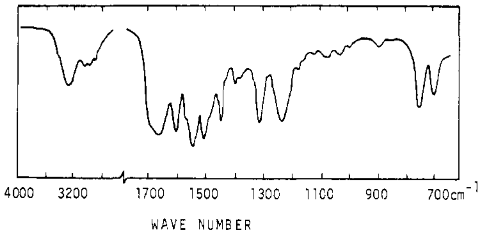

Figure 10. IR spectra of ureanized polyEI used for the absorption experiment. Ether insoluble, THF soluble, and acetone insoluble fraction; KBr disk.

with the single systems, but their relative selectivities are retained for the pH 5–7 range. Thus, we can conclude that the effect of the coexisting ion is not significant for the selective absorption on the metal ions and that the selectivity for two kinds of metal ion can be predicted from the results of affinities obtained in the single ion systems.

High selectivity for metal ion absorption by low molecular weight ligands has been known.[12] For the polymer chelating reagent, considerably higher selectivity was recently attained with some specially designed imino-diacetate modified styrene–divinylbenzene resins, in which Cu^{2+} and Ag^{+} ions were strongly absorbed compared with Zn^{2+}, Cd^{2+}, and Co^{2+} ions.[13] Another example of Cu^{2+} ion selectivity was observed with polyvinylpyridine cross-linked under a Cu^{2+} template. The results show that the cross-linked resin absorbs a 6–9 times larger amount of Cu^{2+} ion than Co^{2+}, Zn^{2+}, and Cd^{2+} ions (Cu^{2+} 52%, Co^{2+} 6%, Zn^{2+} 8%, and Cd^{2+} 9%).[14] The selectivities of Hg^{2+} and Cu^{2+} ions from Co^{2+}, Zn^{2+}, and Cd^{2+} ions in the oligomeric poly(NPCA) are unexpectedly high when it is considered that the matrix is not as specifically designed as in the cases of the precedents.

The absorptivity of the poly(NPCA) for the metal ions is predominantly due to the strength of the chemical interaction forming a bond to resist against dissociation of the metal ions from the bound field conformation. It is highly possible that the weakly interacting metal ions are rejected at the surface of the poly(NPCA) because of regularly situated binding sites in this oligomer. Hence, we suggest that at least two factors, i.e., stability constant in the complex formation and conformational requirement, participate cooperatively in the poly(NPCA) to result in a high preference for Hg^{2+} and Cu^{2+} absorptions.

Absorption Behavior of Ureanized Commercial Polyethylenimine. Ureanized polyethylenimine (polyEI) was obtained from the reaction of phenyl isocyanate with a commercial polyEI with branching (tertiary N:secondary N = 1:2) (mol wt, 30 000–100 000). The IR spectrum of the ureanized polyEI fractionated (Figure 10) resembles that of the "freed" poly(NPCA), showing the similarity in the chemical constitutions except for branching.

The absorptivity of the ureanized polyEI at pH 6.22 is somewhat specific. However, it is remarkably different from the "freed" poly(NPCA) as shown in Table III. The former polymer has affinity in the decreasing order of $Co^{2+} > Hg^{2+} > Cd^{2+} > Cu^{2+}, Ni^{2+}, Zn^{2+}$, derived from the stability orders mentioned above. The most striking result is that the ureanized polyEI has no affinity for Cu^{2+} ion and only weak affinity for Hg^{2+} ion. This indicates that the major factor for absorptivity in this polymer is not the chemically binding process as observed for the poly(NPCA). Probably a cage effect is a predominating factor in this case.

Since polyEI has relatively strong affinity for Cu^{2+} ion,[15] the unreacted $-NH-CH_2CH_2-$ unit in the ureanized polyEI cannot operate as a major factor to cause the difference between affinities of the ureanized polyEI and the poly(NPCA).

Table III
Absorption of Divalent Metal Ions to Ureanized Polyethylenimine and "Freed" Poly(NPCA)[a]

	M^{2+} absorbed (mmol/g-polymer)	
M^{2+}	Ureanized PEI	"Freed" poly(NPCA)
Co^{2+}	0.221	None
Ni^{2+}	None	0.054
Cu^{2+}	None	0.349
Zn^{2+}	None	None
Cd^{2+}	0.066	None
Hg^{2+}	0.107	0.521

[a] Absorption conditions: polymer 3.28 g/L; M^{2+} 0.016 M; pH 6.22; temperature, 32.0 °C; time, 24 h. Other factors are identical and are described in Figure 1.

The most probable interpretation of this difference in the ureanized polyEI from the poly(NPCA) may be a diversity in the ligand molecular circumstances in which metal ions are incorporated. Irregularly occurring branching would cause a variety of spacing and electronic states in the ureanized polyEI to result in less significant absorption specificity. The regular structure in the poly(NPCA) oligomer, in turn, appears to provide a structural situation suitable for giving rise to higher specificity. The structural problem would be associated with the conformational requirement, and more work is needed for further development of the specifically functionalized oligomers.

Related Systems. In an experiment using poly[1-(*N*-methylcarbamoyl)aziridine] in which the carbamoylmethyl group is substituted for the carbamoylphenyl group in the poly(NPCA), we found that the affinity for the Cu^{2+} ion is much less than that of poly(NPCA). In the former case, $Cu(OH)_2$-like (maybe an aquo complex of Cu ion) precipitates were formed at pH 5.9–7.0 instead of a polymer–Cu^{2+} adduct (see the Experimental Section). This suggests that the metal binding site in the poly(NPCA) is constituted under participation of the phenyl group. This suggestion is partially supported by the observation that a relatively strong Cotton effect occurs at a wavelength of the phenyl transition in the ORD of (+)-poly-[(*S*)-1-(*N*-phenylcarbamoyl)-2-methylaziridine].[16]

Other related polymeric materials already reported include a resin with cyclic urea units derived by pyrolysis of poly(*tert*-butyl-*N*-vinyl carbamate),[17] a cross-linked polymer from polyEI with tolylene 2,4-diisocyanate,[18] and a normal type urea polymer derived from *N*,*N*-diaminopiperazine with methylenebis(4-phenyl isothiocyanate).[19] The characteristic metal ion affinities for these polymers are considerably different from our results, and no structural generalization is yet possible.

Experimental Section

Materials. Poly[1-(*N*-phenylcarbamoyl)aziridine] (poly(NPCA)) was prepared by ring-opening polymerization of 1-(*N*-phenylcarbamoyl)aziridine with Et_2SO_4 as described in the preceding paper.[2] Removal of the Et_2SO_4 by treatment with an Amberlite-400 column gave poly(NPCA) free from Et_2SO_4 ("freed polymer" (S content 0.09%)).[2,3]

Poly[1-(*N*-methylcarbamoyl)aziridine] ([η] 0.05 in water at 34.8 °C) was prepared similarly, the THF-insoluble fraction was collected, and the Et_2SO_4 adsorbed was removed as described before.[2]

Polyethylenimine (polyEI) was ureanized with phenyl isocyanate in benzene.[20] Five grams of the polyEI was dehydrated azeotropically with benzene, and the resulting polyEI was suspended in benzene (30 mL). Then 20 g of phenyl isocyanate in 30 mL of benzene was added under cooling. The product was fractionated and a fraction which is ether insoluble, THF soluble, and acetone insoluble was used after confirming its IR spectra to be reasonable for the structure

$(CH_2CH_2N(CONHPh))_n$. Other fractions were not used because of the IR spectra being complicated and seemed to contain unreacted $-CH_2CH_2NH-$ units to a larger extent. The reasonable fraction was of higher molecular weight ($[\eta]$ 0.07 dL/g in DMF at 34.5 °C) compared to the poly(NPCA) ($[\eta]$ 0.04 dL/g in the same condition): yield, 45%. The fraction probably contains branching since the original polyEI contained tertiary N and secondary N in a ratio of 1:2; in addition there was no guarantee that 100% of the secondary and primary nitrogen atoms were ureanized.

PolyEI was ureanized with MeNCO similarly, and a fraction which is a THF insoluble, benzene insoluble, and water soluble fraction was used, after the IR spectra of the product was confirmed to be reasonable for the desired structure: yield, 40%, $[\eta]$ 0.3 dL/g in water at 34.8 °C.

Metal acetates, acetic acid, sodium chloride, and other analytical grade reagents were used for the metal absorption experiments.

Metal Ion Absorption Experiments. $Hg(OAc)_2$, $Cu(OAc)_2$, $Ni(OAc)_2$, $Cd(OAc)_2$, $Zn(OAc)_2$, and $Co(OAc)_2$ were dissolved in an aqueous buffer solution of NaOAc–AcOH–NaCl whose pH was preadjusted in a range of pH 3–8. In the pH range no precipitation of methyl hydroxides occurs. To the metal acetate solutions a given amount of the "freed poly(NPCA)" pulverized (~100 mesh) was suspended at a given temperature. After a given time, the polymer was separated by centrifugation and it was washed by the same buffer solution several times. The aqueous phases were combined and titrated by EDTA chelatemetry.[21] The indicators used were pyrocatechol violet for Cu^{2+} and Co^{2+}, murexide for Ni^{2+}, eriochrome black T for Cd^{2+} and Zn^{2+}, and xylenol orange for Hg^{2+}. The absorbed amount of the M^{2+} ion was determined from the difference between the amounts of the metal ions added and remaining.

Selective Absorption Experiments with Binary Metal Ions. The procedures were identical with the case of absorption of single ions. For a Cu^{2+}–Ni^{2+} system, the total metal ions were titrated by EDTA chelatemetry by using pyrocatechol violet as indicator, then the Ni^{2+} ion was determined as dimethylglyoximenickel salt. For Cu^{2+}–Cd^{2+} and Cu^{2+}–Zn^{2+} binary systems, the total amounts of the ions were determined first, then the Cu^{2+} ion was masked with KCN for titration of the Cd^{2+} or Zn^{2+} ion by EDTA chelatemetry. For Hg^{2+}-containing binary systems, the Hg^{2+} ion was first determined as HgS by using ammonium sulfide, then the remainding aqueous phases were titrated by EDTA chelatemetry.

Absorption of Metal Ions by Poly[1-(N-methylcarbamoyl)-aziridine]. In an aqueous solution of poly[1-(*N*-methylcarbamoyl)-aziridine] the $Cu(OAc)_2$ compound was dissolved under buffered condition at room temperature. After several hours blue precipitates gradually increased at pH 5.9–7.0. The amounts of the precipitates formed for 54 h at various pH values for a given molar ratio of monomeric unit in the polymer to Cu^{2+} ion added were as follows: pH 7.00, polymer unit/Cu^{2+} ratio 3.9 mol/mol, yield of the precipitate 18%; pH 6.22, 4.1 mol/mol, 15%; pH 5.90, 4.5 mol/mol, 6%; and pH 5.30, 4.5 mol/mol, 0%. The IR spectrum of the precipitates resembles largely that of $Cu(OH)_2$, but four bands were observed between the 700- and 900-cm^{-1} region with relatively strong intensities. The corresponding four bands in $Cu(OH)_2$ spectra are weaker and observable in a higher frequency region (800–1100 cm^{-1}). Elemental analysis of the precipitates showed that only very little organic moiety was involved (C 1.18%, H 2.15%, N 0.56%). The precipitates seem to be mainly a kind of aquo complex of an inorganic copper compound, since $Cu(OH)_2$ does not precipitate at that pH range and two of the characteristic frequencies due to aquo complex of Cu (887 and 855 cm^{-1})[22] are nearly the same as those of the blue precipitate. The polyEI ureanized by methyl isocyanate did not form any precipitates in the same procedure.

Experimental procedures and metal analyses for the cases of ureanized polyEI's were identical with those for the poly(NPCA).

Apparatus. IR spectra were recorded with a Hitachi Model EPI-2 and Hitachi Model FIS-3 type spectrometers. Laser Raman spectra were recorded with a Nihon Bunko Model J 0002 spectrometer. An Ubbelohde type viscometer was used to determine $[\eta]$ values of the polymers.

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