Chelating Properties of Linear and Branched Poly(ethylenimines)

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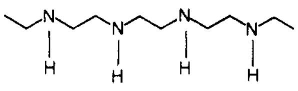
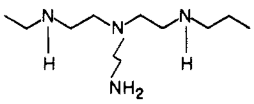
ABSTRACT: Chelating properties of linear and branched poly(ethylenimines) (LPEI and BPEI, respectively) have been studied quantitatively to examine the chelating ability of PEI having the different microstructures. Five PEI samples of various molecular weights (LPEI of 2900 and 1300, and BPEI of 100 000, 1800, and 600) were used for complexation with six heavy metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and UO_2^{2+}. First, characteristics of structural differences of LPEI and BPEI were observed from relationships between the viscosity and the pH value in water. Then, potentiometric titration was performed and analyzed according to the modified Bjerrum method to give successive and overall stability constants, k_n and K_n. From the K_n values, the chelating ability of LPEI was approximately 10 times less than that of BPEI for all cases except for UO_2^{2+}. The branched structure gave a more favorable complexation than the linear structure. The effect of the molecular weight on the chelating ability was small for both linear and branched structures. The microstructure of PEI had little influence on the chelating ability, in sharp contrast to tetramines of linear and branched structures that show a large difference in chelating ability. The Scatchard method was applied to determine formation constants ($\mathcal{K}_n$), k_n, and β_4. Continuous variation analysis revealed that the LPEI–Cu^{2+} system forms the most stable complex at [LPEI]/[Cu^{2+}] = 4.0.

Introduction

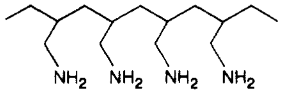
Amines form chelating complexes with various metal ions.[1] Poly(ethylenimine) (PEI) is a typical polymeric amine and is known to exist as a linear structure (LPEI)[2] or a branched structure (BPEI).[3,4] The structure of amines of low molecular weight has great influence on the stability of chelate formation with heavy metal ions.[5-8] Therefore, it is important to investigate the chelating abilities of the polymeric amines LPEI and BPEI quantitatively with respect to their structural differences. In very recent papers, we quantitatively studied the chelate formation of poly(allylamine) (PAA) with heavy metal ions,[9a] and PAA and BPEI have been used conveniently to prepare functionalized resins for the efficient recovery of uranium from sea water.[9]



LPEI



BPEI



PAA

LPEI has only secondary amino groups in the main chain. A commercial BPEI contains primary, secondary, and tertiary amino groups in a ratio of approximately 25%, 50%, and 25%, respectively.[4] PAA is a polymer having only primary amino groups as pendant.[10] These three polymeric amines provide very good polymer ligands of different structures, i.e., LPEI has chelation sites only in the main chain, BPEI in both the main and side chains, and PAA only in the side chain. In the present paper, the chelating abilities of LPEI and BPEI with several heavy metal ions have been evaluated quantitatively by the determination of successive and overall stability constants, k_n and K_n, respectively, with a potentiometric titration method.[11] It is to be noted that the chelate formation of BPEI with Cu^{2+} and Ni^{2+} ions was previously reported.[12]

Results and Discussion

Viscosity Behavior. Figure 1 indicates the relationship of the specific viscosity (η_{sp}/C, dL/g) of LPEI and BPEI in water as a function of pH of the aqueous solution in the presence of 1.0 mol/L KCl. The viscosity value of BPEI-18 (average molecular weight of 1800) is almost constant over the wide range of pH 2–11 in an aqueous solution containing chloride ions. This observation suggests that BPEI-18 does not cause the conformation change of polymer chains in aqueous solution probably due to a highly branched globular structure. Previously, Liu examined counteranion effects on the viscosity of protonated BPEI in water as a function of the degree of protonation.[13] The above behavior of BPEI-18 is similar to that observed by him for BPEI of higher molecular weight (30 000–40 000); the intrinsic viscosity of the BPEI sample stayed almost constant at $\eta_{sp}/C = 0.45–0.50$ over the range of the nominal stoichiometric degree of protonation, 0.0–2.0, in an aqueous solution containing 1.0 mol/L chloride ions.

On the other hand, the intrinsic viscosity of LPEI decreased with increasing pH and reached a minimum at around pH 6. A further increase in pH caused the viscosity to increase and finally reach a value of 0.31 at pH ~2.

At the lower pH range, LPEI is highly protonated and the polymer chain stretches due to electrostatic repulsion of ammonium groups causing an increase in viscosity. When the pH increases, the degree of protonation decreases and the opposing tendency to decrease the viscosity starts to operate. Such a tendency is mainly because the polymer tends to shrink from reduced solvation power for the protonated polymer in the presence of a higher concentration (1.0 mol/L) of KCl. The increase of the viscosity beyond pH ~7 is possibly due to the stretching of the polymer chain, which may be caused partly by repulsion between lone-pair electrons of nitrogen atoms in LPEI and anions of chloride and/or hydroxy in the medium. Another possibility causing the viscosity increase is polymer–polymer association at the higher pH range, which may be supported by the fact that LPEI starts to precipitate at pH ranges higher than ~9. However, the important point is that the viscosity–pH relationship shows a U-shaped profile clearly and indicates the specific

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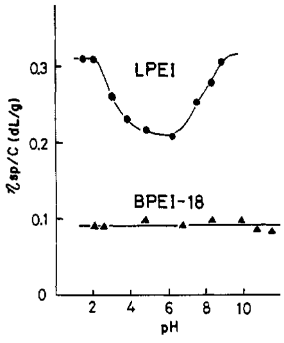


Figure 1. Dependence of the specific viscosity of LPEI and BPEI-18 (C = 0.86 g/dL) on the pH value in water in the presence of KCl (1.0 mol/L) at 24.5 °C.

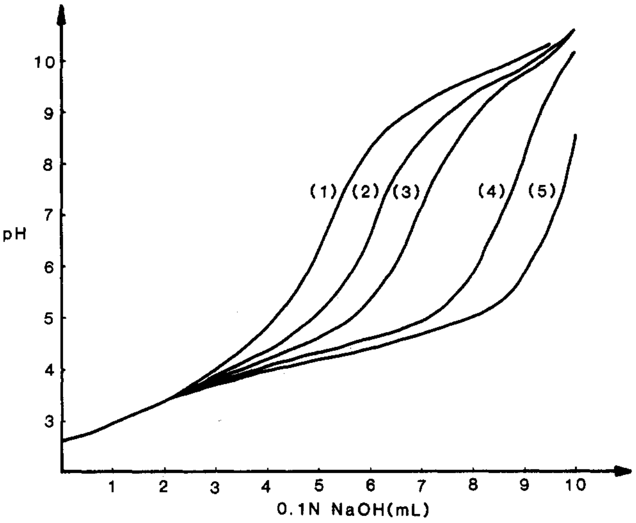


Figure 2. Titration curves of LPEI·HCl ([LPEI·HCl] = 2.00 × 10^{-2}mol/L; 50.0 mL of μ = 1.0 mol/L (KCl)) with 0.1 N NaOH in the presence of Ni^{2+} at concentrations of (1) 0; (2) 5.00 × 10^{-4}; (3) 1.00 × 10^{-3}; (4) 2.00 × 10^{-3}; (5) 4.00 × 10^{-3} mol/L.

character of the linear structure of LPEI chain.

Titrations. In order to determine stability constants of LPEI and BPEI with several heavy metal ions, a potentiometric titration method has been employed. Figure 2 shows typical titration curves of a LPEI·HCl aqueous solution with a 0.1 N NaOH aqueous solution in the absence and presence of Ni^{2+} ions ($NiCl_2$). The degree of polymerization ($\overline{DP}$) of LPEI employed is 67. The ionic strength μ = 1.0 mol/L was kept constant with neutral KCl throughout this work. The aqueous solution becomes more acidic with increasing amounts of Ni^{2+} ions because both protons and Ni^{2+} ions compete to bind with nitrogen atoms. It is clear from curve 1 that LPEI·HCl behaves as a monobasic acid. From the curve the equivalent point was obtained as pH 4.1 at which 70% of the nitrogen atoms are protonated.

On the basis of the simple neutralization curve 1 of Figure 2, the so-called Henderson–Hasselbalch plots were made according to

$$\mathrm{pH} = \mathrm{p}K_a - m \log \frac{1-\alpha}{\alpha} \qquad (1)$$

where α is the degree of neutralization, K_a is the average dissociation "constant", and m is the constant (Figure 3). It should be noted that plots of LPEI show two inflection points at α = 0.5 and 0.2. In the range of α values between 0.2 and 0.5, eq 1 is valid. The constants, pK_a and m, were obtained at the half-neutralization point (α = 0.5) and from the slope of the plot of eq 1. Two values pK_a = 8.74 and m = 5.3 were obtained.

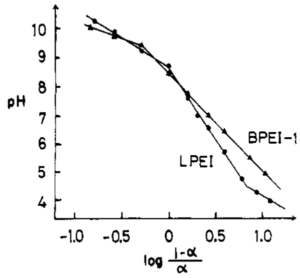


Figure 3. Plots of eq 1: LPEI (●) and BPEI-18 (▲).

Table I
Data from Simple Titration Curves for Seven Polyamines at 25 °C with μ = 1.0 mol/L (KCl)

polyamines	$\overline{DP}$	degree of protonation, %	pK_a	m value (valid α range)
LPEI	67	70	8.74	5.3 (0.2 < α < 0.5)
LPEI′	30	70	8.76	5.3 (0.2 < α < 0.5)
PEH[a]	5	80	8.99	4.5 (0.15 < α < 0.5)
BPEI-1000	2300	70	8.49	3.8 (α < 0.6)
BPEI-18	42	70	8.56	3.8 (α < 0.6)
BPEI-6	14	70	9.15	3.6 (α < 0.6)
BPEI[b]		66[b]	8.90[b]	2.5 (α < 0.5)[b]

[a] Pentaethylenehexamine. [b] Data from ref 12.

Similarly titrations were made for other polyamines such as PLEI′ ($\overline{DP}$ = 30), pentaethylenehexamine (PEH), BPEI-1000, BPEI-18, and BPEI-6. Table I summarizes values of $\overline{DP}$, the percentage of protonated nitrogen atoms, pK_a, and m values for these polyamines. All LPEI·HCl and BPEI·HCl behaved as a monobasic acid. Even PEH·HCl acted in a similar manner.

The upper three polyamines in Table I have linear structures. They displayed two inflection points in the plots of eq 1. It is striking that two LPEI samples take m values of 5.3, which is the highest ever obtained. PEH is also high; m = 4.5. On the other hand, the next three polyamines have highly branched structures and showed only one inflection point as observed previously with fairly high m values of 3.8, 3.8, and 3.6, respectively. The m value is virtually not influenced by $\overline{DP}$ and is compared with a reported value (m = 2.5)[12] as listed in the bottom line of Table I. Poly(acrylic acid)[14] and poly(allylamine)[9] exhibited m values of ~1.8 and 1.85, respectively. It is considered that the m value is a measure of electrostatic interactions of neighboring groups on the chain. In this respect LPEI is a polymer ligand showing interactions in neighboring ammonium groups on the polymer chain, which is the strongest case examined hitherto. BPEI is less strong in neighboring interactions but more than poly(acrylic acid) or poly(allylamine).

So far, protonation of BPEI has been studied by several groups with potentiometric titrations.[4,12,15,16] It was impossible to achieve 100% protonation of BPEI, and the degree of protonation hardly exceeded 75% even in the highly acidic conditions of ~pH 2. The previous paper described 66% protonation for BPEI,[12] but the 70% degree of protonation at the equivalent point best fits both BPEI and LPEI under the present titration conditions. PEH was 80% protonated (Table I). Calorimetric and potentiometric titrations of LPEI, on the other hand, have been performed to determine the thermodynamic parameters for proton ionization.[17]

Stability Constants of Chelate Formation. For evaluation of the chelating abilities of polyamines, stability constants were determined according to the modified Bjerrum method.[14] The average number of ligands bound

Table II
Stability Constants of LPEI and BPEI-18 for Six Heavy Metal Ions at 25 °C with μ = 1.0 mol/L (KCl)

polymers	metal salts	log k_1	log k_2	log k_3	log k_4	log K_3	log K_4
LPEI	$CoCl_2$	2.7	2.6	2.5	2.3		10.1
LPEI	$NiCl_2$	2.8	2.7	2.7	2.6		10.8
LPEI	$CuCl_2$	3.0	2.9	2.7	2.5		11.1
LPEI	$ZnCl_2$	2.7	2.6	2.5	(2.4)[a]	7.8	(10.2)[a]
LPEI	$CdCl_2$	2.6	2.6	2.5	(2.3)[a]	7.7	(10.0)[a]
LPEI	$UO_2(OAc)_2$	2.9	2.8	2.5	(2.2)[a]	8.3	(10.4)[a]
BPEI-18	$CoCl_2$	2.8	2.8	2.7	2.6		10.9
BPEI-18	$NiCl_2$	3.0	3.0	2.9	2.8		11.7[b]
BPEI-18	$CuCl_2$	3.4	3.3	3.2	2.2		12.1[b]
BPEI-18	$Cu(NO_3)_2$	3.5	3.4	3.3	2.6		12.8
BPEI-18	$ZnCl_2$	2.9	2.9	2.8	2.5		11.1
BPEI-18	$CdCl_2$	3.0	2.9	2.7	2.4		11.0
BPEI-18	$UO_2(OAc)_2$	2.9	2.8	2.7	(2.3)[a]	8.4	(10.7)[a]

[a] These are values obtained by extrapolation of the respective formation curve. [b] Thiele and Gronau[12] reported log K_4 values as 15.8 for BPEI–Ni^{2+} and 16.6 for BPEI–Cu^{2+}, respectively.

Table III
Effect of Degree of Polymerization ($\overline{DP}$) on Stability Constants of Polyamine–Ni^{2+} Complex Formations at 25 °C with μ = 1.0 mol/L (KCl)

polyamines	$\overline{DP}$	log k_1	log k_2	log k_3	log k_4	log K_4
LPEI	67	2.8	2.7	2.7	2.6	10.8
LPEI′	30	2.8	2.7	2.6	2.5	10.6
PEH	5	2.9	2.8	2.7	2.5	10.9
trien[a]	3					14.0[a]
BPEI-1000	2300	3.1	3.0	3.0	2.9	12.0
BPEI-18	42	3.0	3.0	2.9	2.8	11.7
BPEI-6	14	3.1	3.1	3.0	2.5	11.7
tren[b]	3					14.8[b]

[a] Triethylenetetramine; data at 20 °C with μ = 0.1 mol/L (KCl) from ref 5. [b] 2,2′,2″-Triaminotriethylamine; data at 20 °C with μ = 0.1 mol/L (KCl) from ref 6.

per metal ion, $\bar{n}$, is determined as a function of the free ligand concentration to give the formation function of the system. For the present systems, $\bar{n}$ is given as

$$\bar{n} = \frac{[\mathrm{PEI}]_t - [\mathrm{PEI}] - [\mathrm{PEI{\cdot}H^+}]}{[\mathrm{metal}]_t} \qquad (2)$$

where $[\mathrm{PEI}]_t$, [PEI], and $[\mathrm{PEI{\cdot}H^+}]$ denote the concentrations of the total base, the free base, and the protonated base groups, respectively, expressed in base moles per liter, and $[\mathrm{metal}]_t$ is the total metal concentration.

The following equation expresses the electroneutrality requirement:

$$[\mathrm{PEI{\cdot}H^+}] = [\mathrm{PEI}]_t(1 - \alpha) - [\mathrm{H^+}] + [\mathrm{OH^-}] \qquad (3)$$

In the case of a polyacid the acid dissociation "constant" is a function of the degree of chain charging. It was empirically shown that over a wide range of α the titration of PEI could be expressed as

$$K_a = \frac{[\mathrm{H^+}][\mathrm{PEI}]}{[\mathrm{PEI{\cdot}H^+}]}\left(\frac{1}{Z}\right)^{m-1} \qquad (4)$$

where Z is the ratio of charged to uncharged groups on the polymer chain and m is obtained from eq 1. Equation 4 is now transformed to the following:

$$K_a = \frac{[\mathrm{H^+}][\mathrm{PEI}]}{[\mathrm{PEI{\cdot}H^+}]}\left\{\frac{[\mathrm{PEI}]}{[\mathrm{PEI}]_t - [\mathrm{PEI}]}\right\}^{m-1} \qquad (5)$$

Plots of p[PEI] vs. $\bar{n}$ give a formation curve (Figure 4), from which a successive stability constant k_n is determined

$$\log k_n = -\log\,[\mathrm{PEI}]_{n=n-1/2} = \mathrm{p}[\mathrm{PEI}]_{n=n-1/2} \qquad (6)$$

Then, the overall stability constant K_N is given by

$$K_N = \prod_{n=1}^{N} k_n \qquad (7)$$

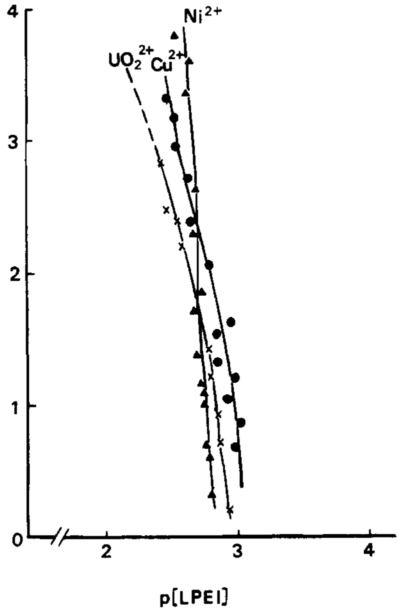


Figure 4. Formation curves for LPEI complexes with Ni^{2+}, Cu^{2+}, and UO_2^{2+}.

Table II shows values of stability constants obtained by the above procedures. In nine cases k_1–k_4 and K_4 values could be determined. However, the four systems LPEI–Zn^{2+}, -Cd^{2+}, and -UO_2^{2+} and BPEI–UO_2^{2+} did not give plots beyond $\bar{n}$ = 3.5 and hence k_4 was obtained by extraporation of the formation curve. As a source of metal ions, metal chlorides were normally used except for $Cu(NO_3)_2$ and $UO_2(OAc)_2$. It is known that the five metal ions except for uranyl ion (UO_2^{2+}) form the most stable complexes with the coordination number N = 4. Uranyl ion, however, is known to form stable quasi-planar hexacoordinated complexes,[18] and so the overall stability con-

Table IV
Comparison of Overall Stability Constant (K_4) between Polyamines and Model Compounds for Cu^{2+} and Zn^{2+} Complexes at 25 °C with μ = 1.0 mol/L (KCl)

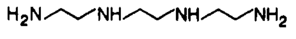
	log K_4 (Cu^{2+})	log K_4 (Zn^{2+})
LPEI	11.1	10.2
BPEI-18	12.1	11.1
trien	20.4[a]	12.1[a]
tren	18.8[b]	14.7[b]

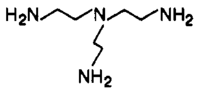
[a] Taken from ref 5; data at 20 °C with μ = 0.1 mol/L (KCl). [b] Taken from ref 6; data at 20 °C with μ = 0.1 mol/L (KCl).

stants ($K_4 = k_1k_2k_3k_4$) are taken as an important measure for comparison of these five heavy metal ions. With Co^{2+} Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, LPEI showed definitely less chelating stability with approximately 10 times the K_4 values as BPEI-18. With UO_2^{2+}, however, both LPEI and BPEI-18 exhibited comparative chelating ability reflected by the K_4 value.

Table III indicates effects of $\overline{DP}$ of polyamines on the chelate formation of Ni^{2+} with several polyamines. The upper four polyamines have a linear structure. It is noteworthy that over a wide range of $\overline{DP}$ (67, 30, and 5) overall stability constant K_4 values are almost constant at log $K_4 \sim 10.8$. Even a pentamer (PEH) showed similar behavior to LPEI. Three BPEI samples show almost constant K_4 values of log $K \sim 11.8$ in spite of a large difference in $\overline{DP}$ (2300, 42, and 14). Thus, K_4 values are not influenced by $\overline{DP}$ within a respective polyamine series with linear and branched structures, which can also be seen from examination of the m values in Table I. The Ni^{2+} complexes of the linear structure series are about 10 times less stable than those of the branched structure series.

As corresponding models of these two series, triethylenetetramine ("trien") and 2,2′,2″-triaminotriethylamine ("tren") were chosen and their K_4 values are also listed in Table III. Tren forms a more stable Ni^{2+} complex than trien. The chelating stability of Ni^{2+} with both model compounds is approximately 10^3 times larger in K_4 value than that with the polymeric analogues LPEI and BPEI, as shown in Figure 5.


trien


tren

These tendencies become greater when the K_4 values of Cu^{2+}–LPEI and –BPEI complexes are compared with those of Cu^{2+}–trien and –tren complexes (Table IV). It is well-known that Cu^{2+} forms stable complexes having a four-coordinate planar structure.[19] Therefore, the Cu^{2+} complex of trien should be more stable than that of tren. Nevertheless, LPEI forms less stable complexes with Cu^{2+} than BPEI. Cu^{2+} complexes of both model compounds are by far more stable than those of LPEI and BPEI. The stability difference in the K_4 value is $10^{9.3}$ for the linear polyamines and $10^{6.7}$ for the branched polyamines. Trien easily forms a planar Cu^{2+} complex. However, LPEI, an amine of "higher molecular weight", does not exhibit characteristics of a linear structure like trien. This is probably due to the entropically (sterically) unfavorable situation of LPEI as ligand for Cu^{2+} complexes, which demand a planar structure. Such an unfavorable situation can be noticed above for linear hexamine (PEH) in Ni^{2+} complexes. In BPEI, coordination sites are more readily available even for a planar complex than in LPEI. In turn, the most stable complexes of Zn^{2+} are of a tetrahedral structure,[19] with tren forming more stable complexes with Zn^{2+} than trien. PEI also shows the same tendency; the K_4 values indicate that BPEI-18 forms a 10 times more stable complex than LPEI.

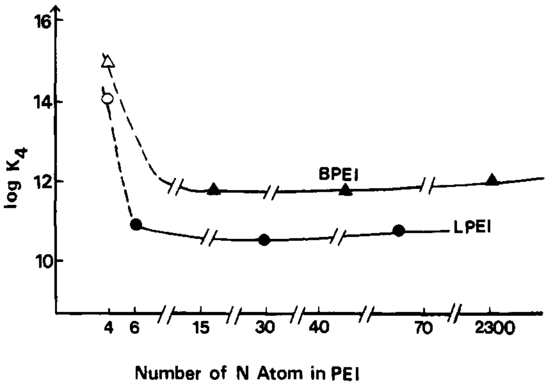


Figure 5. Relationships between number of nitrogen atom in PEI and log K_4 in complexation with Ni^{2+}. Plots of trien (○) and tren (△) (log K) from the literature.[5,6]

Chelate formation of trien and tren is very much affected by metal ions, which require coordination sites of specific configuration. Trien is the most striking case. It is a ligand favored for forming a complex with Cu^{2+} (planar) but less favored for a Zn^{2+} complex (tetrahedral). The stability difference given by K_4 values is $10^{8.3}$. Such a difference for tren between Cu^{2+} and Zn^{2+} complexes is less, i.e., $10^{4.1}$ given by K_4 values. In the case of polyamines, however, the K_4 values indicate that the Cu^{2+} complexes of both LPEI and BPEI-18 are only 10 times more stable than the Zn^{2+} complexes. Polymeric amines are much less sensitive ligands to form complexes demanding specific configuration, e.g., planar or tetrahedral.

The above observations indicate that for polymeric amines the microstructure of the polymer is not operative in complex formation. The coordination sites of the amino groups are present in concentrations too high on the polymer chain of LPEI or of BPEI, and each amino group is highly restricted for coordination to a metal ion because of strong neighboring interactions. This situation is more profound for LPEI since the coordination of an amino group in the main chain requires moving the main chain of the large polymer. In the case of BPEI, branched-chain amino groups are able to coordinate more readily to a metal ion without moving the larger main chain.

An attempt was made to obtain intrinsic formation constants $\mathcal{K}_n$ according to the Scatchard method.[20] The method was used for the first time by Edsall et al.[20a] for the analysis of imidazole complexes with Zn^{2+} and Cu^{2+}, by Liu and Gregor[20b] for poly(N-vinylimidazole) complexes with Zn^{2+} and Cu^{2+}, and by Nishikawa and Tsuchida[20c] for complexes of poly(vinylpyridine) derivatives with Cu^{2+}. Table V summarizes values of $\mathcal{K}_n$, k_n, and β_4 ($=k_1k_2k_3k_4$)

Table V
Intrinsic Formation Constants $\mathcal{K}_n$, k_n, and β_4 Values for Four PEI–Metal Ion Complexes

ligand metal ions	log $\mathcal{K}_1$	log k_1	log $\mathcal{K}_2$	log k_2	log $\mathcal{K}_3$	log k_3	log $\mathcal{K}_4$	log k_4	log β_4
LPEI–$NiCl_2$	1.7	2.3	2.1	2.3	3.1	2.9	3.5	2.9	10.4
BPEI-18–$NiCl_2$	2.1	2.7	2.5	2.7	3.3	3.1	3.7	3.1	11.6
BPEI-18–$ZnCl_2$	2.0	2.6	2.4	2.6	3.3	3.1	3.7	3.1	11.4
BPEI-18–$CdCl_2$	2.0	2.6	2.3	2.6	3.3	3.1	3.7	3.1	11.4

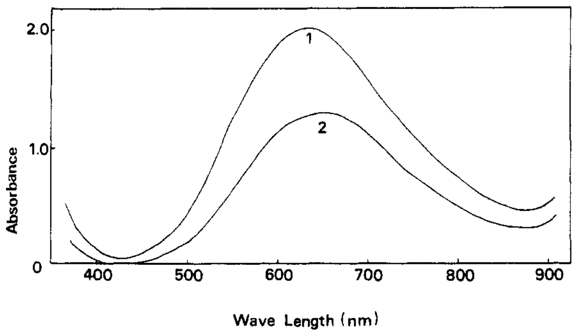


Figure 6. Visible spectra of LPEI–Cu^{2+} complex solutions. Measurement conditions: [LPEI] + [Cu^{2+}] = 6.57×10^{-2} mol/L, [LPEI]/[Cu^{2+}] = 4.0, and water as reference sample at pH 5.3 (curve 1) and at pH 2.3 (curve 2).

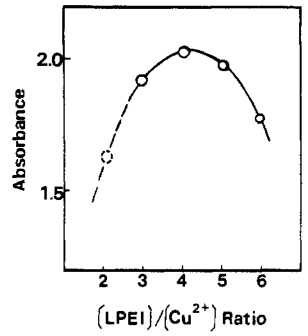


Figure 7. Continuous variation analysis of the LPEI–Cu^{2+} complexes measured at λ_{max} ~630 nm at pH 5.3. The value indicated with a broken circle was obtained at pH 4.2. Total concentrations; [LPEI] + [Cu^{2+}] = 6.57×10^{-2} mol/L.

for four PEI–metal ion complexes, all of which gave a satisfactory formation curves beyond $\bar{n}$ = 3.5, the N value being 4. Values of $\mathcal{K}_n$ were obtained from linear extraporation in the Scatchard plots. The following relationships hold: $\mathcal{K}_1 = k_1/4$, $\mathcal{K}_2 = 2k_2/3$, $\mathcal{K}_3 = 3k_3/2$, and $\mathcal{K}_4 = 4k_4$.[20c] The overall stability constant β_4 corresponds to K_4 obtained by the modified Bjerrum method with both values being very close. Therefore, so far as the overall stability constants is concerned, the values obtained by either method are valid. The successive stability constants obtained by the Scatchard method, on the other hand, seem better since the constants showed successive increments. This means that once the metal ion is coordinated on the one ligand site of the polymer chain, the next coordination comes more readily. These observations seem general characteristics for polymer ligands.[20b,c]

Continuous Variation Analysis. Figure 6 shows visible spectra of LPEI–Cu^{2+} complex solutions at two different pH values. The shape of the spectra is very similar to that previously reported for BPEI–Cu^{2+} complex solutions.[12] The LPEI–Cu^{2+} complex is only soluble in a lower pH range; i.e., [LPEI]/[Cu^{2+}] = 2 < pH ~4.5 and [LPEI]/[Cu^{2+}] ≥ 3 < pH ~6.5. The absorbance is very much dependent upon the pH value measured, and λ_{max} changes slightly with pH, 630 nm at pH 5.3 and 648 nm at pH 2.3.

Figure 7 exhibits the result of continuous variation analysis of the LPEI–Cu^{2+} complex system by comparing the absorption at λ_{max} around 630 nm measured at pH 5.3. The plot at [LPEI]/[Cu^{2+}] = 2.0 was obtained at pH 4.2 (λ_{max} = 638 nm). A maximum is observed in the ratio of [LPEI]/[Cu^{2+}] = 4.0, indicating that LPEI forms the most stable complexes with Cu^{2+} having four coordinating amino groups. This observation is similar to that for BPEI–Cu^{2+} complexes previously studied.[12]

Experimental Section

Materials. LPEI was prepared by the alkaline hydrolysis of poly(*N*-formylethylenimine), which was obtained by the cationic ring-opening polymerization of 2-oxazoline with methyl tosylate initiator.[2] The ^{1}H NMR spectrum (D_2O + DCl) of LPEI showed only a singlet at δ 3.0–3.6, and no signal due to formyl proton (δ 8.1) was observed; the amount of *N*-formyl group in LPEI was less than 1%, if any. Molecular weight was 2900 by vapor pressure osmometry (VPO) in $CHCl_3$ at 40 °C ($\overline{DP}$ = 67). The sample of LPEI′ was analogously prepared by starting from 2-methyl-2-oxazoline. The amount of *N*-acetyl group in LPEI′ was less than 1.5%. Molecular weight of LPEI′ was 1300 ($\overline{DP}$ = 30). BPEI-1000, -18, and -6 (the average molecular weights of 100 000, 1800, and 600, respectively) were obtained from Dow Chemical Co. and used after reprecipitation from ethanol (solvent)/*n*-hexane (nonsolvent) followed by drying in vacuo. Pentaethylenehexamine(PEH), triethylenetetramine (trien), and 2,2′,2″-triaminotriethylamine (tren) were purchased from Tokyo Kasei Co. and purified by distillation. All the heavy metal salts, $CoCl_2$, $NiCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $ZnCl_2$, $CdCl_2$, and $UO_2(CH_3CO_2)_2 \cdot 2H_2O$ (Merck Co.) were commercial reagents, which were employed without further purification.

Measurements. The specific viscosity of the polymer solutions was measured with an Ubbelohde viscometer at various pH values (24.5 °C, C = 0.86 g/dL with μ = 1.0 mol/L (KCl)). Potentiometric titration was carried out by using a Horiba M-8 Type pH Meter under N_2 using distilled, CO_2-free water. Visible spectra were recorded on a Hitachi Model 200-20 spectrophotometer.

Registry No. PEH, 4067-16-7; $CoCl_2$, 7646-79-9; $NiCl_2$, 7718-54-9; $CuCl_2$, 7447-39-4; $Cu(NO_3)_2$, 3251-23-8; $ZnCl_2$, 7646-85-7; $CdCl_2$, 10108-64-2; $UO_2(CH_3CO_2)_2$, 4067-16-7; aziridine homopolymer, 9002-98-6.

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