proper energy calculations is required.

The differences between geometries of the isolated chain and of the crystal model are small, as may be observed by comparing data reported in Table II with data reported in Table I (skew* model), but this does not reduce, in our opinion, the importance of taking into account simultaneously both intra- and intermolecular interactions in the packing refinement process applied to a flexible model. First of all the energy difference between model B and C is small enough (0.3 kcal/mol) to be easily influenced even by small changes in the model adopted. Second, we think the flexibility of the model to be very important in determining the path of the minimization process, since it allows for smoothing asperities on the energy hypersurface.

A number of calculations, performed in the region of the absolute minimum, ensures its uniqueness and confirms the preeminent role played by side methyl groups in determining the packing features of the polymer crystal; main-chain atoms undergo less critical interactions and are particularly insensitive to displacements along the *b* direction.

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Registry No. ITPP, 29191-23-9.

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(10) This work had just been completed when we became aware of a very recent article by R. A. Sorensen, W. B. Lian, and R. H. Boyd (*Macromolecules* **1988**, *21*, 194) who propose a method for predicting polymer crystal structures accounting for both *intra-* and *inter*molecular energy. Although differing in the choice of the independent variables, their method shares with ours the use of *simultaneous* minimization of all energy contributions without arbitrary geometrical assumptions.

Chelating Ability of Poly(vinylamine): Effects of Polyamine Structure on Chelation

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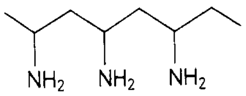
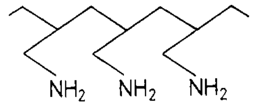
ABSTRACT: Chelating properties of poly(vinylamine) (PVAm) possessing the amino group linked directly to the main chain have been examined quantitatively for various heavy metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. Potentiometric titrations were performed and analyzed according to the modified Bjerrum method to give successive and overall stability constants, k_n and K_n, respectively. Two PVAm samples of different molecular weight were used for the chelate formation. The chelating ability of PVAm was compared with that of a polyamine, poly(allylamine) (PAAm), having one methylene group between the amino group and the main chain. The structural difference of PVAm and PAAm was shown from the dependency of the reduced viscosity on the pH value in the range of ionic strength $\mu < 1.0$. The difference in molecular weight of PVAm does not effect the chelate formation with heavy metal ions. From the K_n values, the chelating ability of PVAm was approximately 10–50 times less than that of PAAm for metal ions examined. Continuous variation analysis of the PVAm–Cu^{2+} complex examined by spectrophotometry revealed that the most stable complex is formed at $[PVAm]/[Cu^{2+}] = 4.0$.

Introduction

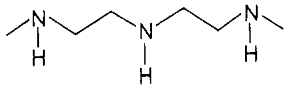
Polyamines form chelating complexes with various heavy metal ions. Recently, we have reported quantitative investigations on the chelating abilities of polyamines, linear and branched poly(ethylenimines) (LPEI and BPEI, respectively),[1] and poly(allylamine) (PAAm).[2] These three polymeric amines provide very good polymer ligands having different structures; i.e., LPEI has chelating sites only in the main chain,[3] BPEI in both the main and side chains,[4,5] and PAAm only in the side chain.[6] On the other hand, poly(vinylamine) (PVAm) has only primary amino groups linked directly to the main chain. These four polyamines constitute a full set of polymer samples having different chelating sites due to the different microstructures. In a previous paper,[1] chelating properties of LPEI and BPEI have been studied to examine the influence of the microstructural difference of PEI (i.e., linear and branched structure) on the chelate formation. In this paper, the chelating ability of PVAm with various metal ions has been evaluated quantitatively by the determination of successive and overall stability constants with a potentiometric titration method and compared with that of PAAm. It is very significant that the chelating ability of four polyamines having different microstructures is evaluated on the basis of stability constants obtained by the same procedure in similar measurement conditions.[1,2] Relevant to the present study, chelation between PVAm



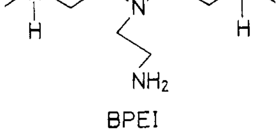
PVAm



PAAm



LPEI



BPEI

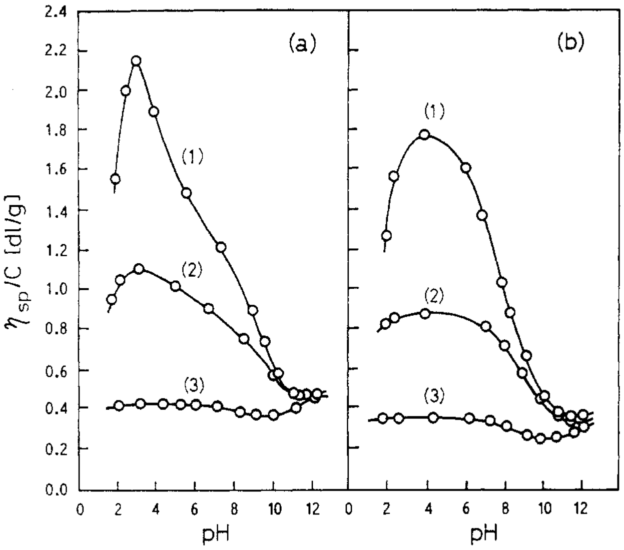


Figure 1. (a) η_{sp}/C–pH relationships of PVAm-1·HCl at 25 °C in water: $C = 0.54$ g/dL; μ = (1) 0.01, (2) 0.1, (3) 1.0 mol/L (KCl). (b) η_{sp}/C–pH relationships of PAAm·HCl (M_w = 10000) at 25 °C in water: $C = 0.61$ g/dL; μ = (1) 0.01, (2) 0.1, (3) 1.0 mol/L (KCl).

and Cu^{2+} was once examined in connection with the polymerization catalyst activity of PVAm–Cu^{2+} complexes.[7]

Results and Discussion

Viscosity Behavior. Figure 1 shows the relationship between the reduced viscosity (η_{sp}/C, dL/g) and pH for aqueous solutions of PVAm (Figure 1a) and PAAm (Figure 1b) with various ionic strengths (μ = 0.01, 0.1, and 1.0 mol/L of KCl). The viscosity behaviors of both samples are almost similar over the wide range pH 2–12 in the case of μ = 1.0. As the ionic strength decreases, however, the effect of structural difference of the viscosity is observed around pH 2–5: a relatively steep peak appears for the PVAm sample at pH ~3 in the cases of μ = 0.1 and 0.01, whereas the peak of PAAm is broad around pH 4. For the PVAm sample, the degree of neutralization is zero around pH 3; i.e., all the amino groups attached to the polymer chain are protonated. Thus, polymer chains take the most stretched structure in this pH region because of the electrostatic repulsion among neighboring ammonium groups. On the other hand, in the region of pH >3, the value of reduced viscosity decreased gradually since the repulsion is relaxed and the flexibility of chain is enhanced due to the neutralization of ammonium groups. The behaviors of reduced viscosity observed around pH 2–5 for both samples reflect the difference of the degree of chain flexibility: with respect to the pH change, the response of the electrostatic repulsion among neighboring ammonium groups for PAAm is less sensitive than for PVAm, since PAAm has one methylene group between the main chain and the amino group.

Titrations. To determine stability constants of PVAm with several heavy metal ions, a potentiometric titration method has been employed. Figure 2 shows typical titration curves of a PVAm·HCl aqueous solution with a 0.1 N NaOH aqueous solution in the absence and presence of Cu^{2+} ions ($CuCl_2$). The ionic strength μ = 1.0 mol/L was kept constant with a neutral salt, KCl. From curve 1, it is apparent that PVAm·HCl behaves as a monobasic acid. As the metal ion concentration increased, the titration curves shifted downward due to the chelate formation of Cu^{2+} ion to nitrogen atoms of PVAm. For curve 5, the titration mixture began to precipitate in the region of pH >5.

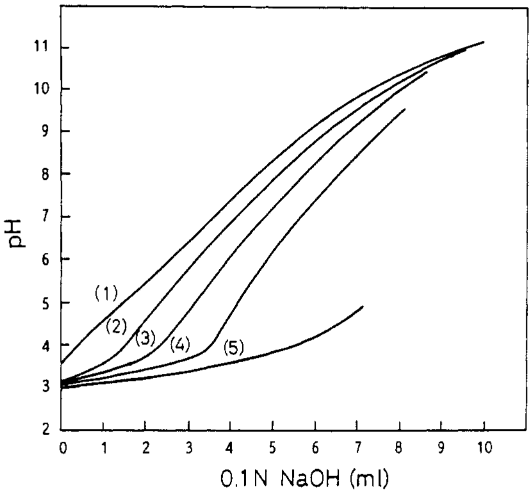


Figure 2. Titration curves of PVAm-1·HCl ([PVAm-1·HCl] = 0.02 mol/L; 50 mL of μ = 1.0 mol/L (KCl) at 25 °C) with 0.1 N NaOH in the presence of Cu^{2+} at concentrations of (1) 0, (2) 5.0×10^{-4}, (3) 1.0×10^{-3}, (4) 1.6×10^{-3}, and (5) 4.0×10^{-3} mol/L.

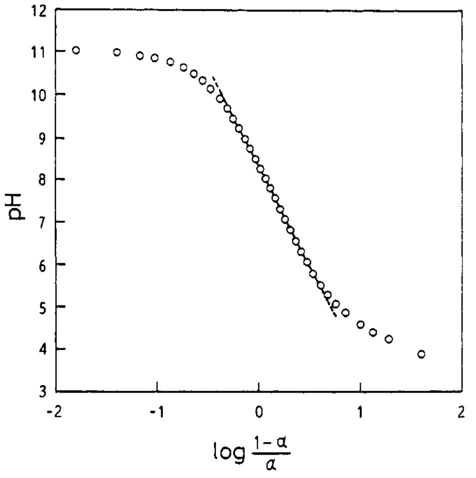


Figure 3. Plots of eq 3.

Figure 3 shows the so-called Henderson–Hasselbalch plots of the simple neutralization curve 1 of Figure 2, whose equation is expressed as follows

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

where α is the degree of neutralization, K_a is the average dissociation constant, and m is a constant. PVAm has two inflection points as observed in Figure 3. The m value can be obtained from the slope of plots at an α value range between 0.2 and 0.6. The m values of PVAm and PAAm are listed in Table I. PVAm takes m values of about 5.34 and 5.35, depending on the molecular weight, which are much larger than that of PAAm. It should be noted that PVAm has almost the same m value as LPEI (m = 5.3). It is considered that the m value is a measure of electrostatic interactions of neighboring groups on the chain.[8,9] From the results of Table I, it is obvious that PVAm is a polymer ligand showing relatively strong interactions in neighboring ammonium groups on the polymer chain in comparison with PAAm (m = 1.85). Considering the chelate formation between polymer ligands and metal ions achieved by the competitive reaction of both proton and metal ions to the nitrogen atoms, this difference in the m values of polyamines is also expected to affect the chelating ability with metal ions.

In addition, the degree of protonation of PVAm and PAAm is given in Table I. Both samples reached 100% degree of protonation. On the contrary, it was impossible

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

polyamines	molec wt $\times 10^3$	deg of protontn, %	pK_a	m (valid α range)
PVAm-1	10[a]	100	8.49	5.34 ($0.2 < \alpha < 0.6$)
PVAm-80	800[a]	100	8.59	5.35 ($0.2 < \alpha < 0.6$)
PAAm[b]	10	100	9.67	1.85 ($0.1 < \alpha < 0.7$)

[a] The number-average molecular weight determined according to ref 10. [b] Taken from ref 2.

to achieve 100% protonation of BPEI, and the degree of protonation hardly exceeded 75% even in the highly acidic conditions of pH 2.[10–13] In the previous paper,[1] 70% degree of protonation was reported for BPEI and LPEI. It is reasonable to assume from these results that the nature of coordination site affects significantly the protonation of polyamine: PVAm having ligands only in the side chain is of greater advantage for protonation than the case having in the main chain LPEI and BPEI, in spite of the same chemical formula of $(C_2H_5N)_n$ for these three polyamines.

Stability Constants for Chelate Formation. The chelating ability of PVAm has been evaluated according to the modified Bjerrum method.[14] The average number of ligands bound per metal ion present in all forms ($\bar{n}$) is expressed as a function of the free ligand concentration to give the formation curve of the system. For the present systems, $\bar{n}$ is defined as

$$\bar{n} = \frac{[\mathrm{PVAm_t}] - [\mathrm{PVAm}] - [\mathrm{PVAm{\cdot}H^+}]}{[\mathrm{metal_t}]} \qquad (2)$$

where $[\mathrm{PVAm_t}]$ denotes the total unit concentration of PVAm, [PVAm] that of free PVAm, $[\mathrm{PVAm{\cdot}H^+}]$ that of the protonated PVAm ion, and $[\mathrm{metal_t}]$ that of the metal. In eq 2, $[\mathrm{PVAm{\cdot}H^+}]$ can be determined by the following material balance and the electroneutrality requirement:

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

It was also shown empirically that over a wide range, the titration of PVAm could be expressed as

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

where z is the ratio of charged to uncharged groups on the polymer chain and m is the Henderson–Hasselbalch slope in the absence of added metal salt. It was reported by many investigators that eq 4 will hold empirically for polyelectrolytes such as poly(vinylimidazole),[15] poly(vinylpyridine),[16] and branched poly(ethylenimine).[17] In a simple titration, $[\mathrm{PVAm{\cdot}H^+}] = [\mathrm{PVAm_t}] - [\mathrm{PVAm}]$ and z becomes $[\mathrm{PVAm{\cdot}H^+}]/[\mathrm{PVAm}]$. Equation 4 thus takes the form

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

The equation is then solved for the only unknown [PVAm] through an iterative procedure. Values of [PVAm] and $[\mathrm{PVAm{\cdot}H^+}]$ are determined by eq 3 and 5, and $\bar{n}$ can be obtained by introducing these values to eq 2. Plots of $\bar{n}$ versus p[PVAm] give a formation curve (Figure 4), from which a successive stability constant k_n is determined

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

Thus, the overall stability constant K_N is given by

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

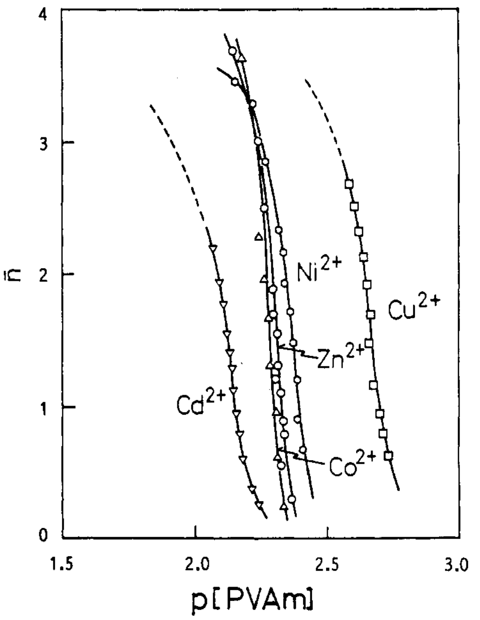


Figure 4. Formation curves for PVAm complex with five metal ions.

Table II
Stability Constants of PVAm and PAAm for Heavy Metal Ions at 25 °C, μ = 1.0 mol/L (KCl)

polyamines	metal ions	log k_1	log k_2	log k_3	log k_4	log K_4
PVAm-1	Co^{b+}	2.31	2.29	2.27	2.24	9.11
PVAm-1	Ni^{2+}	2.41	2.36	2.32	2.11	9.20
PVAm-1	Cu^{2+}	2.72	2.65	2.58	2.40[b]	10.35[b]
PVAm-1	Zn^{2+}	2.21	2.28	2.25	2.21	9.05
PVAm-1	Cd^{2+}	2.18	2.10	2.05[b]	1.80[b]	8.15[b]
PVAm-80	Co^{2+}	2.33	2.30	2.27	2.21	9.11
PVAm-80	Ni^{2+}	2.44	2.39	2.33	2.23	9.39
PVAm-80	Cu^{2+}	2.75	2.70	2.65	2.43[b]	10.53[b]
PVAm-80	Zn^{2+}	2.35	2.30	2.26	2.05[b]	8.96[b]
PVAm-80	Cd^{2+}	2.20	2.13	2.04[b]	1.78[b]	8.13[b]
PAAm[a]	Ni^{2+}	2.72	2.59	2.48	2.22	10.0
PAAm[a]	Cu^{2+}	3.75	3.57	3.04	1.5[b]	11.9[b]
PAAm[a]	Zn^{2+}	3.08	2.92	2.51	2.2[b]	10.7[b]
PAAm[a]	Cd^{2+}	2.71	2.46	2.08	1.9[b]	9.2[b]

[a] Taken from ref 2. [b] These values are obtained by the extrapolation of the respective formation curve.

Table II shows values of stability constants of two PVAm samples for five heavy metal ions obtained by the above procedure. For comparison, data of PAAm for four metal ions are also sited.[2] The overall stability constants, K_4 values, of the two PVAm samples are almost the same for the respective metal ions in spite of a large difference in molecular weight. For LPEI and BPEI, similar results were reported: over a wide range of degree of polymerization, K_4 values are not changed in the polyamine of linear and branched structure.[1] This means that K_4 values are not influenced by the molecular weight of polyamine. For Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} ions, the K_4 values of PVAm are approximately 10–50 times less than those of PAAm. This is probably due to the entropically unfavorable situation of PVAm as ligand for metal ion complexes, since it has coordinating amino groups linked directly to the main chain.

In the previous paper,[1] it was shown that the microstructure of the polymer is much less operative in complex formation for LPEI and BPEI having the linear and branched structures in comparison with corresponding amines of lower molecular weight: the K_4 values indicate that the Cu^{2+} complexes (planar) of both polyamines are 10 times more stable than the Zn^{2+} complexes (tetrahe-

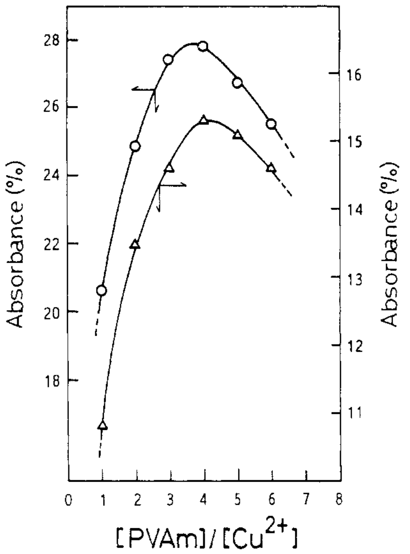


Figure 5. Continuous variation analysis of the PVAm–Cu^{2+} complexes measured at 580 nm with μ = 0.2 mol/L (KCl) at 25 °C. Measurement condition: [PVAm-1·HCl] = 0.05 mol/L at pH 3.8 (○); [PVAm-80·HCl] = 0.02 mol/L at pH 3.9 (△).

dral). However, the microstructure of corresponding model compounds, triethylentetramine (trien) and 2,2′,2″-triaminotriethylamine (tren), is very sensitive in complex formation; the stability difference given by K_4 values between Cu^{2+} and Zn^{2+} complexes is $10^{8.3}$ for trien and $10^{4.1}$ for tren, respectively. In the case of PVAm and PAAm (Table II) the stability difference in the K_4 values between both metal complexes is only $10^{1.3}$, which is understood in the framework of polyamine ligands.

Continuous Variation Analysis. The coordination number of the metal ion complex on PVAm was confirmed by the continuous variation method.[18] Figure 5 indicates the result of a continuous variation analysis of the PVAm–Cu^{2+} complex system measured around 580 nm at the total concentration of 0.05 (PVAm-1) and 0.02 mol/L (PVAm-80). The maximum absorbance of visible spectra was measured at pH 3.8–3.9 for each ratio of [PVAm]/[Cu^{2+}] since the PVAm–Cu^{2+} complex is only soluble at pH <4.0. The maximum is observed at the ratio of [PVAm]/[Cu^{2+}] = 4.0 in both cases, indicating that PVAm forms the most stable complexes with Cu^{2+} having four coordinating amino groups.

Experimental Sections

Materials. Two PVAm·HCl samples prepared by radical polymerization of *N*-vinylformamide followed by acidic hydrolysis[19] were supplied from Mitsubishi Kasei Co., Tokyo. The ^{1}H NMR spectrum of PVAm·HCl showed no signal due to formyl proton (δ 8.1); the amount of *N*-formyl group in PVAm·HCl was less than 1%, if any. The η_{sp}/C values of the two samples were 0.33 and 3.23, respectively, measured in 1 N NaCl aqueous solution with C = 0.1 g/dL, and the number-average molecular weights of these samples are estimated as 1.0×10^4 and 8.0×10^5, respectively, according to the calculation manner of ref 10. All the heavy metal salts, $CuCl_2$, $NiCl_2$, $CoCl_2$, $ZnCl_2$, and $CdCl_2$, were commercial reagents, which were employed without further purification.

Measurements. The reduced viscosities of polymer solution were measured with an Ubbelohde viscometer at various pH values at 25 °C with μ = 1.0 mol/L (KCl). Potentiometric titration was carried out by using a Toa HM-20E pH meter under Ar. All measurements were performed under Co_2-free condition. Visible spectra were recorded on a Shimadzu UV-200 spectrophotometer using a 0.01 mol/L of $CuCl_2$ aqueous solution as a reference sample at room temperature.

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Registry No. Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-48-4; Zn, 7440-66-6; Cd, 7440-43-9.

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