Effect of the Conformation of Polymer Chain on the Reduction Rate of Polyacrylatopentaamminecobalt(III) by Polymer-Bound Ferrous Chelates and the Excited State of Tris(Bipyridine)Ruthenium(Ii)

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ABSTRACT

Electron transfer reactions of $Co(NH_3)_5PAA$ (PAA = polyacrylic acid) with either the polyanionic polymer-bound ferrous chelate, $Fe^{II}P$-SS (P-SS = vinylbenzylaminediacetate-co-styrenesulfonate) or the uncharged polymer-bound ferrous chelate, $Fe^{II}P$-VPRo (P-VPRo = vinylbenzylaminediacetate-co-vinylpyrrolidone), and the $Ru(bpy)_3^{2+}$ photosensitized reduction of $Co(NH_3)_5PAA$ have been investigated in aqueous solutions at pH 5.4, $I = 0.06$ (I is ionic strength), and 25°C. For the ferrous chelate reductions, the second-order rate constants for Fe^{II}-PSS and $Fe^{II}P$-VPRo were almost equal to that for the corresponding nonpolymer-bound ferrous chelate, $Fe^{II}BDA$ (BDA = benzylaminediacetate). The results indicate that there is no appreciable steric hindrance due to the polymer chains of the polymer-bound ferrous chelates and that the effect of columbic repulsion force between the polyanion chains can be ignored for the reaction of $Co(NH_3)_5PAA$ with $Fe^{II}P$-SS. The results also suggest that there are two kinds of the pendant Co(III) species, "reactive"

and "inert." The inert Co(III) species are shielded by the polymer chains from attack of the Fe(II) chelates that are present in the bulk solutions. A similar reaction behavior was observed in the $Ru(bpy)_3^{2+}$ photosensitized reduction of $Co(NH_3)_5PAA$ at pH 5.4. For the Co(III) complex having an extremely few Co(III) complex moieties on the polymer chain, almost all of the Co(III) groups were hardly reduced by the excited state of $Ru(bpy)_3^{2+}$, and reverse quenching occurred due to binding of the $Ru(bpy)_3^{2+}$ to the polyacrylic acid chain of the polymer complex. On the other hand, for $Co(NH_3)_5PAA$ with a relatively large number of the Co(III) moieties on the polymer chain, lifetime measurements at a higher concentration of the $Ru(bpy)_3^{2+}$ showed a double-exponential fit, which suggests that there are two parallel decay processes. The fast and slow components mainly correspond to the decays: $Ru(bpy)_3^{2+}$ quenched by Co(III) and reverse quenching due to binding of $Ru(bpy)_3^{2+}$ into the compact polymer chains.

INTRODUCTION

In previous studies of the electron transfer reactions of synthetic polymer metal complexes, we were concerned with reactions of the polymer metal complexes in which the transition metal ions are coordinated to a high degree [1–6, 11].

The results of the reduction of the peptide-amminecobalt(III) complex by chromium(II) [7] suggested that there are two parallel reactions, a faster process and a slower process which are ascribed to the reduction of carboxylatoaquatetraamminecobalt(III) and carboxylatopentaaminecobalt(III), respectively [8].

The results of the kinetic studies on the electron transfer reactions of polycationic polymer-bound Co(III) complexes with iron(II) complex suggested that the most important factor governing the reaction rate is an electrostatic attraction force. Specifically, the rate is markedly enhanced by increasing the negative charges on the reductants [9].

For the reduction of cis-$Co(N_3)(en)_2PVP^{2+}$ (PVP = poly-4-vinylpyridine, en = ethylenediamine) by $Ru(NH_3)_6^{2+}$, no appreciable effect of electrostatic repulsion force between the reactants was observed. Furthermore, enhancement of the rate was found compared with that of the corresponding nonpolymeric system, cis-$Co(N_3)(en)_2Py^{2+}/Ru(NH_3)_6^{2+}$, in aqueous perchloric acid solution, which suggests that an important fac-

tor governing the reaction rate is the physicochemical behavior of the microheterogeneous regions of the polymer backbone, called domains [5].

However, almost nothing is known about the electron transfer reaction between synthetic macromolecule–metal complexes. It is our intention to study the effects of polymer chain conformation of macromolecule–metal complexes in which the metal ion has a low degree of coordination and where the effect of polymer chain conformation would be an important factor in determining the reaction rate.

In this report, kinetics of the electron transfer reactions between polyacrylatopentaamminecobalt(III), $Co(NH_3)_5PAA$ (where PAA = polyacrylic acid, and the charge on the polymer metal complex is omitted), and polymer-bound ferrous chelates, and, also, the $Ru(bpy)_3^{2+}$ photosensitized reduction of $Co(NH_3)_5PAA$, are investigated to clarify the effect of polymer conformation on the reaction rate.

EXPERIMENTAL

$[Co(NH_3)_5H_2O](ClO_4)_3$ was prepared and analyzed according to a published procedure [10]. Polyacrylic acid (MW 90,000, 25 wt% solution in water) was purchased from Aldrich Chemical Inc. Polyacrylatopentaamminecobalt(III) perchlorate, $[Co(NH_3)_5PAA](ClO_4)_2$ (Fig. 1), was prepared by ligand substitution reaction of $Co(NH_3)_5(H_2O)^{3+}$ with polyacrylic acid in an aqueous solution at ca. pH 3 and 60°C for 2–8 h. The degree of coordination was regulated by controlling the concentration of $[Co(NH_3)_5H_2O](ClO_4)_3$ and the reaction time in the reaction mixture. The
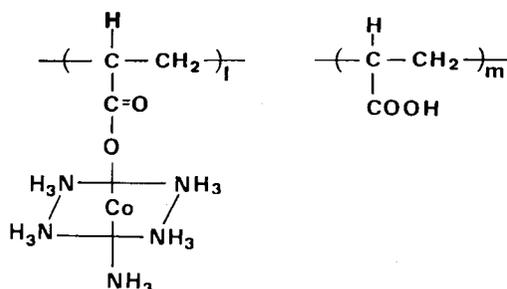

FIG. 1.   Chemical structure of $Co(NH_3)_5PAA$.

reaction mixture was dialyzed against pure water with cellulose dialyzer tubing (Nakarai Chemicals Inc., MW cutoff 8000) for 2 days. The dialyzed solution was evaporated to appropriate volume under reduced pressure in order to concentrate the Co(III). The resulting solution was then stored in the dark at ~10°C until use. $Co(NH_3)_5PAA$ with different degrees of coordination (X) were prepared, where X is defined as the number of moles of the Co(III) complex to the total acrylic acid residues on the polymer chain $[X = 1/(1 + m)$ in Fig. 1]. An aliquot of the solution was evaporated to dryness. The resulting filmy product was ground with a mortar and dried *in vacuo*. The powder obtained was not completely soluble in water, and it was only used for elemental analyses of C, H, and N. The degrees of coordination (X) in the prepared $Co(NH_3)_5PAA$ complexes were 0.010, 0.013, 0.021, 0.024, 0.048, and 0.12. $Co(NH_3)_5PAA$ with a greater degree of coordination than 0.12 could not be prepared since precipitation formed during the ligand substitution process. For the polymer systems, the concentration of the pentaaminecobalt(III) complex is represented by moles of the Co(III) complex moieties.

Molar absorptivity of the complex moieties in the polymers was determined to be 76 ± 2 M^{-1} cm^{-1} at λ_{max} of 502 nm, which was used for determination of the rate. The molar absorptivity at the other absorption maximum wavelength (~350 nm) was about 66 M^{-1} cm^{-1}. The molar absorptivity and the absorption maximum of $Co(NH_3)_5PAA$ at around 350 nm were dependent on the sample due to weak absorption of the polymer backbone. The molar absorptivities of the corresponding non-polymer Co(III) complex, $Co(NH_3)_5(C_3H_5COO)^{2+}$, at the absorption maxima were also determined to be 76 M^{-1} cm^{-1} at 502 nm and 66 M^{-1} cm^{-1} at 352 nm. It has been reported that the molar absorptivities of $Co(NH_3)_5(OAc)^{2+}$ at its absorption maxima of 503 and 358 nm are 71 and 60 M^{-1} cm^{-1}, respectively [12]. Ferrous chelates of the polymer-bound benzylaminediacetic acid, vinylbenzylaminediacetate-*co*-sodiumpolystyrenesulfonate (P-SS), and vinylbenzylaminediacetate-*co*-vinylpyrrolidone (P-VPRo) (Fig. 2) were prepared as described in a previous paper [11].

Acid dissociation constants, K_a, of polyacrylic acid were determined by means of a potentiometric titration using Horiba Model M-13 pH meter. Ionic strength (I) of the reaction solutions was adjusted by the addition of sodium perchlorate. Rates of electron transfer between $Co(NH_3)_5PAA$ and the ferrous chelates were measured in aqueous solution at pH 5.4, $I = 0.06$ (where I is ionic strength in $NaClO_4$), and 25°C.
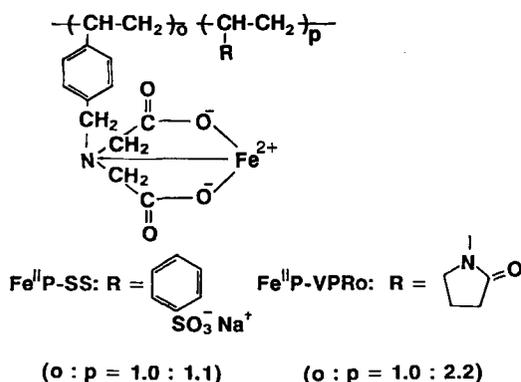
FIG. 2.   Chemical structure of $Fe^{II}P$-SS and $Fe^{II}P$-VPRo.

The reaction was initiated by mixing the solution of the Co(III) with that of ferrous chelate by using a mixing apparatus (Ohtsuka Denshi Model MX 7). The reactions were followed by the disappearance of the Co(III) absorption in the 502-nm region by using Hitachi Model 150-20 recording spectrophotometer.

The emission spectra of $Ru(bpy)_3^{2+}$ were obtained by using a 10 mm × 10 mm in a quartz cell on a Shimadzu RF-500 spectrofluorimeter and an excitation wavelength of 452 nm. A nanosecond fluorimeter (Horiba Model NAES-550) was used for the determination of the excited state lifetime of $Ru(bpy)_3^{2+}$. The pH of all the reaction solutions were adjusted by the addition of dilute perchloric acid or dilute sodium hydroxide solutions. The pH values of the reaction solution before and after the reaction remained constant within ±0.02 pH. All the solutions were pre-pared with deionized water, and all samples were deaerated by bubbling with argon.

RESULTS AND DISCUSSION

Electron-Transfer Reactions of Co(NH₃)₅PAA with Polymer-Bound Fe(II)-Chelates

Chemical structures of $Co(NH_3)_5PAA$ and the polymer-bound ferrous chelates are shown in Figs. 1 and 2, respectively.

The modified Henderson-Hasselbach equation [13] for the dissocia-
tion of polyelectrolytes is expressed by

$$pH = pK_a - n \log \{(1 - \alpha)/\alpha\} \tag{1}$$

where α is the degree of dissociation and the value of n, which lies
between 1 and 2, is a measure of the effect of neighboring groups on
dissociation. For PAA (MW = 90,000), the values of pK_a and n, which
were obtained by means of a potentiometric titration by using Eq. (1),
were 6.0 ± 0.1 and 2.0, respectively, at 25°C.

Electron transfer reactions of the polyanion-bound Co(III) complex,
$Co(NH_3)_5PAA$, with the polyanion-bound ferrous chelate have been in-
vestigated in aqueous solution at pH 5.4, I = 0.06, and 25°C. $Fe^{II}BDA$
was used for the corresponding nonpolymer analog. The reaction is rep-
resented by

$$Co(NH_3)_5PAA + Fe^{II}L \rightarrow Co(NH_3)_5PAA^{2+} + Fe^{III}L \tag{2}$$
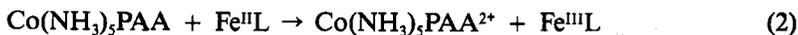
where L is P-SS, P-VPRo, and BDA.

An example of the spectral change for the reduction of
$Co(NH_3)_5PAA$ by $Fe^{II}P-SS$ is shown in Fig. 3. Similar spectral changes
were observed for $Fe^{II}P$-VPRo and $Fe^{II}BDA$ reductions.

Figure 4 represents the decay curves for the reduction of
$Co(NH_3)_5PAA$ by Fe(II)-chelates. It is striking that the Co(III) complex
moieties on the polymer chain could either not be reduced completely or
that some of them were reduced too slowly to determine the reduction
rate. Thus, the usual second-order plot did not fit all the reactions ob-
served, and the straight-line plots indicated the reactions went to only 20–
30% of completion.

The results seem to suggest that there are two kinds of Co(III) species
on the Co(III)-PAA chain, one of which is "reactive" and the other
"inert." The reactive species is in close contact with the aqueous phase
and, conversely, the "inert" species is protected by the polymer chain
from attack by $Fe^{II}L$ from the bulk solution.

The pH-induced phase transition of polymethacrylic acid, PMA, and
PAA was reported by Thomas et al. [14, 15]. Their data indicate that the
lifetime and the luminescence intensity of $Ru(bpy)_3^{2+}$ in PMA and PAA
solution show maxima at intermediate pH (pH 5). Furthermore, the
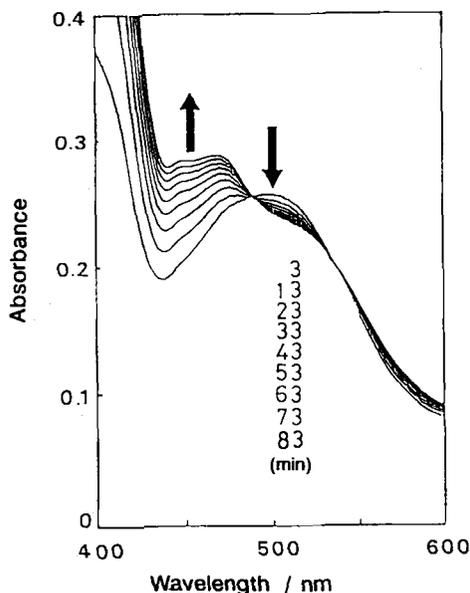probe exhibits a blue spectral shift compared to other pH. It was indicat-

FIG. 3.   Spectral change for the reduction of $Co(NH_3)_5PAA$ (X = 0.010) by $Fe^{II}P-SS$.

ed that these properties are due to binding of the $Ru(bpy)_3^{2+}$ into coiled or swollen PMA at around pH 5. The $Ru(bpy)_3^{2+}$ bound into coiled PMA was found to be shielded from attack by molecules from the aqueous phase. At high pH, $Ru(bpy)_3^{2+}$ is completely bound to the anionic stretched polymer, and it is in close contact with the aqueous phase, consistent with the observation that the photochemical properties of the probe are identical with those observed for the free complex in an aqueous phase [14].

In the present study, the fraction of the reactive Co(III) species, which is defined by the ratio of the concentration of reactive Co(III) to that of the total Co(III), is referred to the "reduction ratio" and represented by R_{Co}. For all cases, when second-order plots were modified with respect to the concentration of $Fe^{II}L$ and that of the "reactive" Co(III), fairly good straight lines were obtained for at least 90% of the reactions, as shown in Fig. 5. More specifically, the plots were modified by plotting the value of $\log(A_t - A_\infty)/(A_t - \beta)$, where A_t and A_∞ are the absorbances at time t
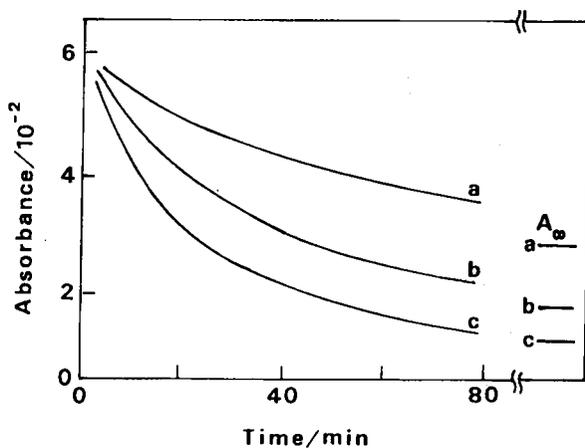
FIG. 4.   Decay curves for the reduction of $Co(NH_3)_5PAA$ (X = 0.021) by $Fe^{II}L$ at 502 nm. Reductants: (a) $Fe^{II}P$-VPRo, (b) $Fe^{II}P$-SS, (c) $Fe^{II}BDA$.

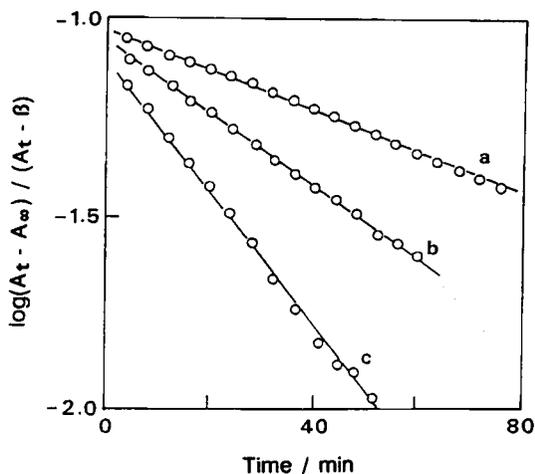FIG. 5.   Plots of log $(A_t - A_\infty)/(A_t - \beta)$ vs reaction time for the reduction of $Co(NH_3)_5PAA$ (X = 0.010) by $Fe^{II}L$. Reductants: (a) $Fe^{II}P$-SS, (b) $Fe^{II}BDA$, (c) $Fe^{II}P$-VPRo. $\beta = \epsilon_{Co(III)}\{[Co(III)]_t - [Fe(II)]_0\} + \epsilon_{Fe(III)} [Fe(II)]_0$.

and at reaction completion, respectively (Fig. 5), and β is given by Eq. (3), against the reaction time:

$$\beta = \epsilon_{Co(III)}\{[Cc(III)]_r - [Fe(II)]_0\} + \epsilon_{Fe(III)}[Fe(III)]_0 \tag{3}$$

where $\epsilon_{Co(III)}$ (76 M^{-1} cm^{-1} at 502 nm) and $\epsilon_{Fe(III)}$ (52 M^{-1} cm^{-1} at 502 nm) are the molar absorptivities of the Co(NH$_3$)$_5$PAA and Fe^{III}L, respectively, and [Co(III)]$_r$ is the concentration of reactive Co(III) which could be determined from the value of A_∞, and [Fe(II)]$_0$ is the initial concentration of Fe^{II}L.

The effect of the degree of coordination (X) on the rate constant (k) and the reduction ratio are shown in Figs. 6(A) and 6(B), respectively. Unfortunately, a detailed discussion of the effect of X on the rate constant is difficult, as the precision of the rate constants is insufficient to support such a discussion. Nevertheless, it is clear that the rate constants for the Fe^{II}P-SS and Fe^{II}P-VPRo reductions are not very much different from that of Fe^{II}BDA reduction in magnitude. This indicates that there is no appreciable effect of steric hindrance due to the polymer chains of the polymer-bound ferrous chelates on the rate constant. Furthermore, the effect of the columbic repulsion force between the polyanion chains was not observed for the reaction of Co(NH$_3$)$_5$PAA with Fe^{II}P-SS. Under the conditions employed, the polyanionic domains of Co(NH$_3$)$_5$PAA and Fe^{II}P-SS would be almost shielded by the counterions and, thus, the repulsion force between the polyanions is not strong. Therefore, no appreciable effect of electrostatic repulsion on free energy for the formation of the activated complex is apparent. It has been reported that about 60% of the anionic sites on the polymer chains are shielded by the counterions in an aqueous solution of 0.04 M sodium polyacrylate even in the absence of inert salt [16, 17].

Figure 6(A) indicates that the values of R_{Co} increase with an increase in the degree of coordination. Under the conditions employed, about 30% of the carboxylic acid groups on the PAA chains of the Co(NH$_3$)$_5$PAA are dissociated in the reaction mixture, assuming that the pK_a and n values of the polyacrylic acid chains of the Co(NH$_3$)$_5$PAA are equal to those of the PAA. It seems likely that a large number of carboxylate anions and carboxylic acid groups may be necessary to shield a Co(III) center from attack by Fe^{II}L from the aqueous phase [14, 15]. The concentration of the "shielded" Co(III) moieties on a Co(NH$_3$)$_5$PAA chain increase with an increasing number of $-$COOH and $-$COO$^-$ groups per one Co(III) complex moiety, i.e., the value of R_{Co} increases with an increase in X.
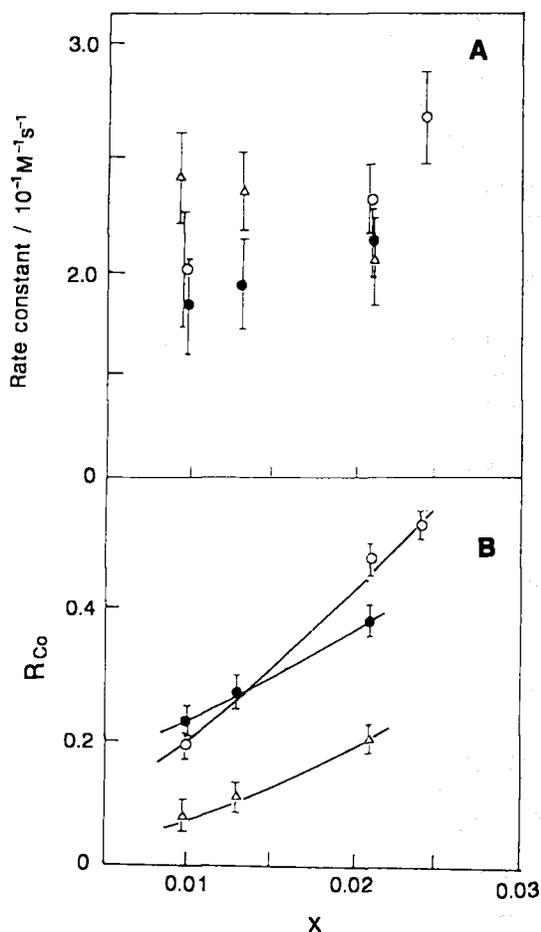
FIG. 6.   Effect of degree of coordination (X) on the rate constant (k) and that on the reduction ratio (R_{Co}) for the reaction of $Co(NH_3)_5PAA$ with $Fe^{II}L$. Reducing agent: ($\bigcirc$) $Fe^{II}P$-SS, ($\bullet$) $Fe^{II}BDA$, ($\triangle$) $Fe^{II}P$-VPRo.

The $Ru(bpy)_3^{2+}$ Photosensitized Electron Transfer Reaction of $Co(NH_3)_5PAA$ in Aqueous Solution

The effect of conformation of the polyanion chain of $Co(NH_3)_5PAA$ on the rate of the photosensitized electron transfer reaction was studied by means of both lifetime and steady-state luminescence intensity measurements.

In aqueous solution at pH 5.4, $Ru(bpy)_3^{2+}$ binds to the polymer chains of $Co(NH_3)_5PAA$. First, the binding constant of $Ru(bpy)_3^{2+}$ with PAA (MW 90,000), rather than with the polyacrylic acid chain of $Co(NH_3)_5PAA$ with a low X value, was estimated by means of luminescence intensity measurements. In aqueous $Ru(bpy)_3^{2+}/PAA$ solution, the luminescence intensity of $Ru(bpy)_3^{2+}$ increases with an increase in the concentration of PAA, as already reported by Thomas et al. [14].

The dependence of the relative luminescence intensity, I/I_0 (where I and I_0 are the luminescence intensities in the presence and absence of PAA, respectively), on the concentration of the PAA is shown in Fig. 7.
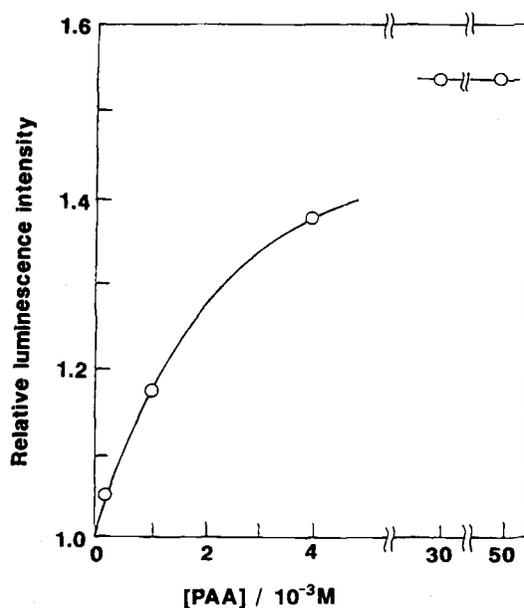

FIG. 7.   Dependence of relative luminescence intensity (I/I_0) on the concentration of the PAA at pH 5.4, $I = 0.06$, and 25°C.

When a large excess of PAA is present, the apparent binding constant, K_{app}, is expressed by

$$K_{app} = \frac{(I/I_0) - 1}{\{(I/I_0)_\infty - (I/I_0)\}[PAA]} \tag{4}$$

where $(I/I_0)_\infty$ is the saturation value of I/I_0, which was evaluated to be 1.54. Thus, the value of apparent binding constant can be calculated from the measurable parameters by using the above relation, i.e., from the slope of the straight line of the plot of $\{(I/I_0) - 1\}/\{(I/I_0)_\infty - (I/I_0)\}$ vs [PAA] as shown in Fig. 8. The value of K_{app} was estimated to be 570 $\pm$ 4 M^{-1} at pH 5.4, $I = 0.06$, and 25°C.

We estimated the approximate value of the fraction of the binding Ru(bpy)$_3^{2+}$ to the polymer chain of the Co(NH$_3$)$_5$PAA ($X = 0.010$) in a solution containing Co(NH$_3$)$_5$PAA by assuming that the binding constant of Ru(bpy)$_3^{2+}$ to the polyacrylic acid chain of the Co(NH$_3$)$_5$PAA is of the same order or one-order smaller than that of PAA since the degree of

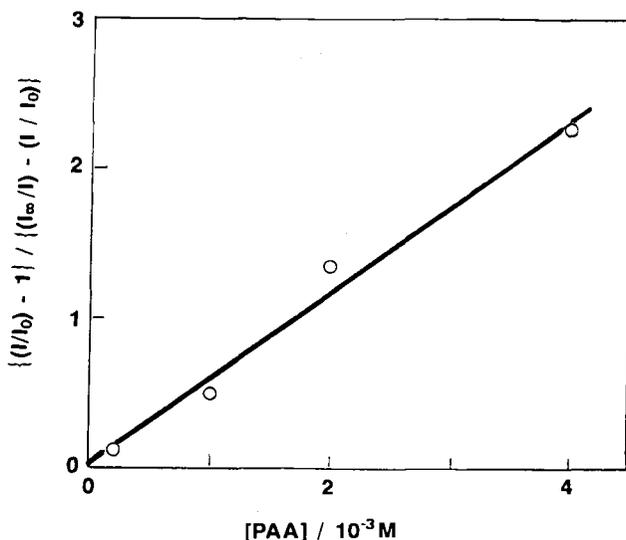FIG. 8.   Plot of $\{(I/I_0) - 1\}/\{(I/I_0)\infty - (I \neq I_0)\}$ versus the concentration of acrylic acid, [Ru(II)] = 2.0 × 10^{-5} M.

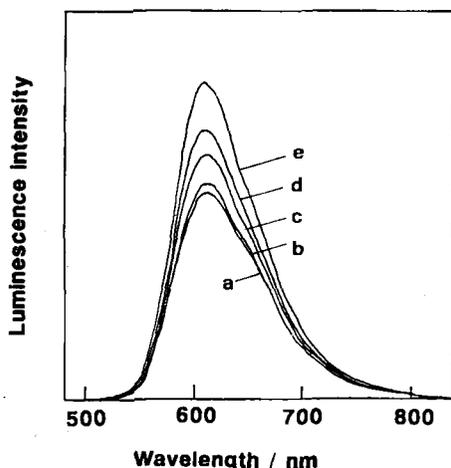**FIG. 9.**   Luminescence spectra of $Ru(bpy)_3^{2+}$ in aqueous $Co(NH_3)_5PAA$ ($X =$ 0.010) solutions at pH 5.4, $I = 0.06$, and 25°C. [PAA]/M: (a) 0, (b) 2.0×10^{-4}, (c) 1.0×10^{-3}, (d) 2.0×10^{-3}, (e) 3.0×10^{-2}.

coordination of $Co(NH_3)_5PAA$ is very small. Based on this assumption, almost all the $Ru(bpy)_3^{2+}$ ions were estimated to be bound to polymer chains under the present conditions.

The lifetime measurement involving $Co(NH_3)_5PAA$ ($X = 0.010$)/Ru-$(bpy)_3^{2+}$ indicated that a single-exponential fit of the time-dependent lifetime decay was observed at several concentrations of Co(III), 2.0×10^{-6} to $1.0 \times 10^{-3} M$ at [Ru(II)] $= 2.0 \times 10^{-5} M$ (see Fig. 11).

The luminescence spectra of $Ru(bpy)_3^{2+}$ in aqueous $Co(NH_3)_5PAA$ ($X = 0.010$) solution and the dependence of the lifetime on the concentration of the Co(III) are shown in Figs. 9 and 10, respectively. The result of the lifetime measurements shows that, for $Co(NH_3)_5PAA$ with a low X value, no distinct quenching behavior of the excited state of $Ru(bpy)_3^{2+}$ by Co(III) was observed, and, interestingly, the lifetime of the $*Ru(bpy)_3^{2+}$ increases with an increase in the concentration of the Co(III). The single exponential decay of the lifetime of $Ru(bpy)_3^{2+}$ in a solution of $Co(NH_3)_5PAA$ with a low degree of coordination may be ascribed to the very small fraction of the reactive species ($<5\%$) rather than to the inert species.

The results of steady-state luminescence intensity measurements are also shown in Figs. 9 and 10. Figure 9 shows that the dependence of I/I_0
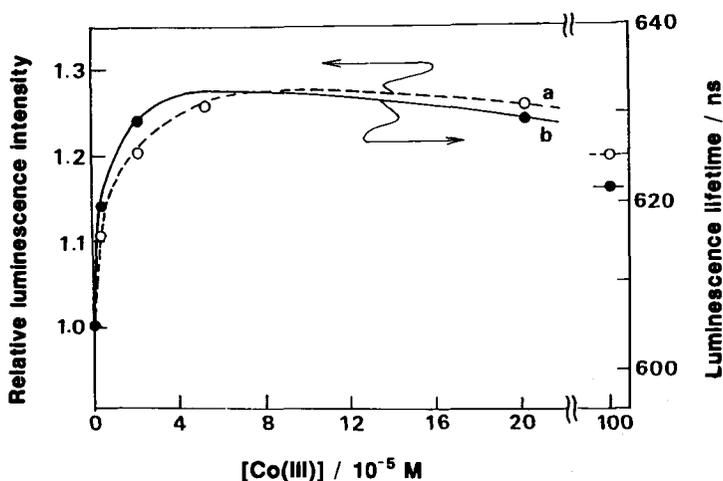
FIG. 10. Dependence of relative luminescence intensity (I/I_0) (a) on the life-time (τ) of the excited state of the $Ru(bpy)_3^{2+}$, and (b) on the concentration of the $Co(NH_3)_5PAA$ ($X = 0.010$) at pH 5.4, $I = 0.06$, 25°C, and [Ru(II)] = 2.0 × $10^{-5} M$.

on the Co(III) concentration is similar to that of the lifetime on [Co(III)]. An increase in the luminescence intensity and a slight blue shift are seen with increasing [PAA], as shown in Fig. 9.

The luminescence decay curves for $Co(NH_3)_5PAA$ with $X = 0.12$ are shown in Fig. 11. For $Co(NH_3)_5PAA$ with such a high degree of coordination, the kinetics follow a double-exponential decay:

$$I = I_0[\alpha \exp(-k_1 t) + (1 - \alpha) \exp(-k_2 t)] \qquad (5)$$

where k_1 and k_2 are the first-order rate constants for the fast and slow decay processes, respectively, and α is the fraction that decays with the rate constant k_1. The values of k_1, k_2, and α were 2.7 × $10^7 s^{-1}$, 2.3 × 10^6 s^{-1}, and 0.40, respectively, for $Co(NH_3)_5PAA$ ($X = 0.12$) at [Co(III)] = 2.0 × $10^{-4} M$. These results indicate that, for $Co(NH_3)_5PAA$ with $X = 0.12$, the amounts of nonshielded Co(III) moieties which are in close contact with the aqueous phase are at least above 40% of the total Co(III) at 2.0 × $10^{-4} M$.

Again, it was clear that almost all of the dissolved $Ru(bpy)_3^{2+}$ is bound to the polymer chains of $Co(NH_3)_5PAA$ with low X, and, for

Time / μs

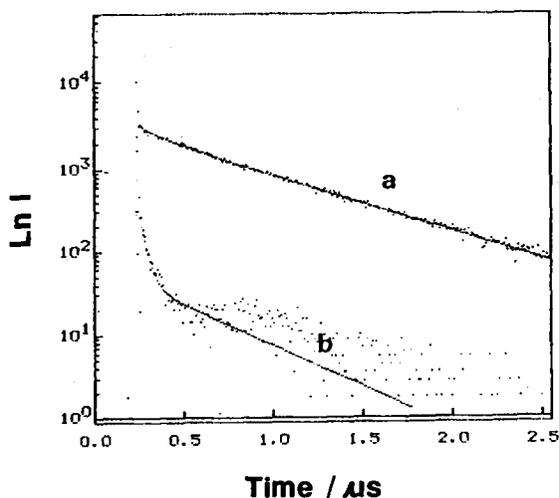FIG. 11.   Logarithmic luminescence intensity (ln I) vs time in aqueous Ru(bpy)$_3^{2+}$/Co(NH$_3$)$_5$PAA (X = 0.12) solutions at pH 5.4, I = 0.06, 25°C, and [Ru(bpy)$_3^{2+}$] = 2.0 × 10^{-3} M. [Co(III)]/M: (a) 2.0 × 10^{-6} M, (b) 2.0 × 10^{-4} M.

Co(NH$_3$)$_5$PAA with a relatively higher X, some part of the bound Ru-(bpy)$_3^{2+}$ ions are quenched effectively by the pendant Co(III) complex moieties.

The main feature of the luminescence behavior in Co(NH$_3$)$_5$PAA/Ru(bpy)$_3^{2+}$ may be explained as follows. If no appreciable quenching of the excited state of Ru(bpy)$_3^{2+}$ by Co(III) occurs, the value of I/I_0 would vary as shown in Fig. 12 (Curve a) since, at a low concentration of Co(III) in this pH region, the fraction of reverse quenching increases with increasing concentration of acrylic acid residues on the Co(NH$_3$)$_5$PAA chains, and at high [Co(III)], I/I_0 would reach a finite value because all the Ru(bpy)$_3^{2+}$ ions are bound to the polymer. On the other hand, if only static quenching of *Ru(bpy)$_3^{2+}$ occurred, the I/I_0 value would vary as shown in Fig. 12 (Curve b). Such a static quenching behavior of Ru-(bpy)$_3^{2+}$ has been observed for solutions containing anionic polyelectrolytes such as PMA and PAA [13]. In this case, the observed I/I_0 vs [Co(III)] curve should be the sum of a and b, as shown in Fig. 12 (Curve c). The shape of Curve c is similar to that of the observed one, indicating that the predominant feature of the luminescence behavior may be accounted for by this explanation.
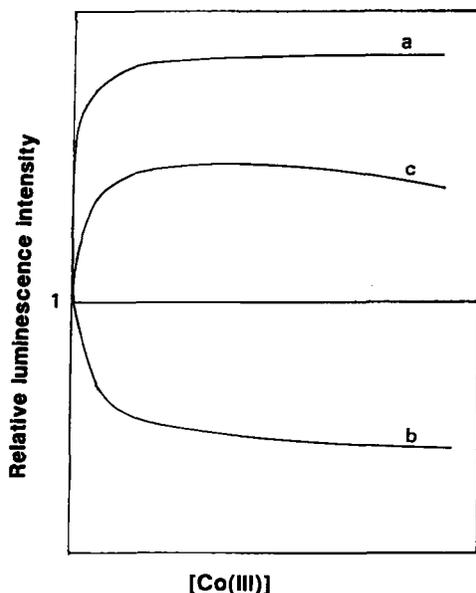
FIG. 12. Schematic representations of the dependence of the relative luminescence intensity (I/I_0) for reverse quenching (a), for static quenching by the Co(III) (b), and for the estimated observed I/I_0 (c). The obtained I/I_0 was estimated from the following relationship at a given concentration of Co(III):

$$(I/I_0)_{obs} = (I/I_0)_{rev} - (I/I_0)_q$$

where $(I/I_0)_{obs}$, $(I/I_0)_{rev}$, and $(I/I_0)_q$ are the values of (I/I_0) for the observed, the reverse quenching, and the quenching processes, respectively.

Comparison of the Kinetics of the Fe^{II}L and *Ru(bpy)$_3^{2+}$ Reductions

One of the remarkable differences between the reaction kinetics for the reduction of Co(NH$_3$)$_5$PAA with an extremely lower degree of coordination ($X = 0.010$) by noncharged and negatively charged ferrous chelates vs positively charged *Ru(bpy)$_3^{2+}$ is that at least some of the Co(III) complexes were reduced by Fe^{II}L whereas almost none of the Co(III) complexes were reduced by *Ru(bpy)$_3^{2+}$ under the conditions employed.

In the Co(NH$_3$)$_5$PAA ($X = 0.01$)/Ru(bpy)$_3^{2+}$ system, some part of

both the $Co(NH_3)_5PAA$ and $Ru(bpy)_3^{2+}$ moieties are shielded by the polymer chains from the bulk phase whereas only some part of $Co(NH_3)_5PAA$ moieties are shielded in the $Co(NH_3)_5PAA/Fe^{II}L$ system. These seem to reflect that almost all the Co(III) complexes moieties were hardly reduced by the excited state of the photosensitizer in the former system and some fraction of the Co(III) complex moieties were reduced in the latter system.

The luminescence behavior is affected by the degree of coordination of $Co(NH_3)_5PAA$. When the degree of coordination is extremely low, the Co(III) moieties could hardly be reduced by the excited state of $Ru(bpy)_3^{2+}$, and when that is relatively high, the Co(III) moieties could easily be reduced by the reductant.

Further studies on the effect of conformation of the polymer chains, especially the dynamic process of the electron transfer reactions of the macromolecule–metal complexes, are now in progress.

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