Effects of Conformational Transition on Electron-Transfer Reaction between Poly(methacrylic acid-*co*-styrenesulfonic acid)-Bound Co(III) Complexes and Fe(edta)²⁻ in Aqueous Solution

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ABSTRACT: Three Co(III) complex-containing poly(methacrylic acid-*co*-styrenesulfonic acid)s (CoPMASs) with different copolymerization ratios were synthesized, and the effects of conformational transition on electron-transfer reaction between CoPMAS and Fe(edta)²⁻ (edta = ethylenediamine-*N,N,N',N'*-tetraacetic acid) were investigated. The conformation of CoPMAS varied with the ratio of residues having negative charge as carboxylate and styrenesulfonate on one polymer chain (α'). The α' -induced conformational transition of CoPMAS was similar to that of PMAS as the parent polymer. In electron-transfer reactions, the degree of reduction of Co(III) complex by Fe(edta)²⁻ depended on α' . This dependence is explained by the decrease of shield effect: the Co(III) complex surrounded in polymer backbone was exposed to the aqueous phase by the α' -induced conformational transition. The rates for the electron-transfer reactions of CoPMASs with Fe(edta)²⁻ increased with increasing α' . The increase was attributed to a lowering of negative charge density around the Co(III) complex by the α' -conformational transition.

KEY WORDS Conformational Transition / Electron-Transfer Reaction / Luminescence Probe /

A number of experimental approaches has been used to obtain the relationship between electron-transfer rate and the distance separating redox sites. One approach includes measurement of intramolecular electron-transfer rate in synthetic system where two redox sites are separated by a rigid bridging group or a spacer of various length.^{1–3} In another approach, electron-transfer rates, in which depend exponentially on the distance separating the two redox sites, are analyzed by considering electronic coupling between donor and acceptor molecules as well as the nuclear factor.^{4–6} The third approach, of particular importance in biological systems, is based on different protein conformations. Conformational changes afford a mechanism for controlling electron-transfer rates; they lead to directional electron-transfer under suitable conditions.⁷

Poly(methacrylic acid) (PMA) reveals a unique conformational transition with changing pH.^{8–11} At low pH, PMA has a compact coil structure. With increasing pH, the carboxylic acid groups of PMA dissociate and simultaneously are exposed to bulk aqueous phase. Consequently, PMA forms a micelle-like structure in which methyl groups are gathered by hydrophobic interaction. At high pH, PMA has an expanded structure by electrostatic repulsion among carboxylate residues. That is to say, PMA has three conformations in aqueous solution. Investigation on the electron-transfer reaction of PMA-bound Co(III) complex (CoPMA) with Fe(edta)²⁻ revealed that both the rate and degree of reduction of Co(III) complex depend significantly on the conformation of the polymer backbone.¹¹ Further, the conformational transition of poly(methacrylic acid-*co*-styrenesulfonic acid) (PMAS) with changing the ratio of residues having negative charge as carboxylate and styrenesulfonate on one polymer chain (α') has also been investigated. Each PMAS-8 (SS = 8 mol%) and PMAS-

16 (SS = 16 mol%) may have four conformations in aqueous solution.¹² Namely, polymers having four conformations in aqueous solution are obtained by the introduction of styrenesulfonic acid to PMA.

The present paper reports the synthesis of Co(III) complex-containing poly(methacrylic acid-*co*-styrenesulfonic acid)s (CoPMASs) with different copolymerization ratios and the effects of the conformational transition of polymer on electron-transfer reaction between CoPMASs and Fe(edta)²⁻ were studied.

EXPERIMENTAL

Materials

Methacrylic acid (MA) was purified by distillation under reduced pressure. Sodium styrenesulfonate (NaSS) and 2,2'-azobis(isobutyronitrile) (AIBN) were recrystallized from distilled water and methanol, respectively. Tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate (Ru(bpy)₃Cl₂·6H₂O) was prepared and purified by the method described elsewhere.¹³ Ammonium iron(II) sulfate hexahydrate, (NH₄)₂Fe(SO₄)₂·6H₂O, and Na₂EDTA were purified by recrystallization from water. PMAS-8, PMAS-16, and PMAS-43 as the parent polymer were prepared and purified according to the reported procedure.¹² Co(III) complex-containing poly(methacrylic acid-*co*-styrenesulfonic acid)s (CoPMASs) were prepared as follows: PMAS was dissolved in double distilled water and the solution was adjusted to about pH = 7.4. The *trans*-[Co(en)₂Cl₂]Cl (en = ethylenediamine)¹⁴ in double distilled water adjusted to about pH = 7.4, which immediately isomerizes to *cis*-[Co(en)₂(OH₂)₂]³⁺, was added slowly to aqueous PMAS with stirring. The resulting solution was heated to 50°C for 5 h with stirring. After being filtered, the hot solution was evaporated to about 150 ml. The solution was dialyzed in dilute

hydrochloric acid of pH 2 with cellulose tube (Nacalai Tesque Inc., M.W. cut-off 8000) for 2 days at room temperature. The dialyzed solution was evaporated to an appropriate volume under reduced pressure at 40–45°C and stored in the refrigerator. The degree of coordination of Co(III) complex in CoPMASs were determined by elemental analysis.

Measurements

Acid dissociation constant (pK_a) and n of CoPMAS-8, CoPMAS-16, and CoPMAS-43 were determined by potentiometric titration using a modified Henderson–Hasselbach equation.¹⁵ Sample solutions were adjusted to 10^{-3} mol dm⁻³ on the basis of the unit concentration of the carboxy group. The ionic strength of solution was adjusted to 0.06 with NaCl. Titration was carried out using 0.1 mol dm⁻³ NaOH aqueous solution at 25°C under an argon atmosphere on a Horiba M-13 pH meter. The luminescence spectra of Ru(bpy)₃²⁺ were recorded on a HITACHI 150-60 spectrofluorometer using 10 mm quartz cell. Viscosity was measured using a Ubbelohde viscometer at 25°C. Electronic spectra were recorded on a HITACHI-330 spectrophotometer. The apparent rate constants, k_{app} , were determined from the slope of the straight line in plots of $\ln(A_t - A_\infty)$ versus reaction time t , where A_t and A_∞ are the absorbance at 500 nm corresponding to Co^{III}PMAS at t and after the reaction is complete. The degree of reduction of Co(III) complex was calculated from eq 1:

$$\text{degree of reduction} = ([\text{Co(III)}]_0 - [\text{Co(III)}]_\infty) / [\text{Co(III)}]_0 \quad (1)$$

In all measurements, dioxygen in sample solution was removed by bubbling argon for 20 minutes.

RESULTS AND DISCUSSION

The structure of CoPMAS together with the degree of coordination of Co(III) is illustrated in Scheme 1.

Complexes	x	y	z	DC*
CoPMAS-8	1	28	3	0.032
CoPMAS-16	1	27	5	0.030
CoPMAS-43	1	28	21	0.020

* DC, degree of coordination.

Scheme 1. Chemical structures of CoPMAS.

Table I. pK_a and n for CoPMAS-8, CoPMAS-16, and CoPMAS-43

	pK_a	n
CoPMAS-8	6.64 ± 0.02	1.80 ± 0.04
CoPMAS-16	6.67 ± 0.03	1.62 ± 0.02
CoPMAS-43	6.75 ± 0.01	1.68 ± 0.03

pK_a and n were obtained from the intercept and slope of the straight line of pH versus $\log [(1 - \alpha)/\alpha]$ plots using a modified Henderson–Hasselbach equation:

$$\text{pH} = pK_a - n \log [(1 - \alpha)/\alpha] \quad (2)$$

where n is indication of the effects of neighboring groups on dissociation of proton and α is the degree of dissociation of the carboxy group on the polymer chains. pK_a and n are summarized in Table I. The degree of dissociation of carboxy group was calculated from eq 2 in each pH. The ratio of residue having negative charge on one polymer chain is for α' ; $\alpha' = \alpha y + z$, where y and z are the values shown in the Scheme.

Viscosity Studies

Dependence of the reduced viscosity (η_{sp}/c) of aqueous solution of CoPMAS-8, CoPMAS-16, and CoPMAS-43 on α' is shown in Figure 1. This figure represents that viscosity of CoPMAS-8 and CoPMAS-16 solution changed in two steps with increasing α' . The first viscosity change was observed when the carboxy group was slightly dissociated ($\alpha' \approx 0.08$ – 0.10 for CoPMAS-8 and $\alpha' \approx 0.16$ – 0.18 for CoPMAS-16), and the second change occurred over 0.4 of α' . Viscosity after the first viscosity change ($\alpha' = 0.10$ for CoPMAS-8 and $\alpha' = 0.18$ for CoPMAS-16) was almost constant up to $\alpha' = 0.4$ in which the second viscosity change started. This indicates that CoPMAS-8 and CoPMAS-16 retain their compact structures until 0.4 of α' , and are transformed to expanded structures at the second viscosity change over 0.4 of α' .

CoPMAS-43 reveals one viscosity change corresponding to a conformational transition from a compact structure to an expanded one. The behavior of α' -dependent viscosity for CoPMASs, as illustrated in Figure 2, is almost similar to that for PMAS-8, PMAS-16, and PMAS-43 of parent polymers.¹² These observations led us to conclude that CoPMAS-8 and CoPMAS-16 possess two conformational transitions, and CoPMAS-43 has one conformational transition with varying α' . The three conformations of CoPMAS-8 and CoPMAS-16 are compact coil, a carboxy group-dissociating compact, and expanded structures.

Luminescence Studies

In order to obtain further information about local conformations and physicochemical environments of the micro-domain of the polymer metal complexes, the effects of changing of α' on the relative intensity and

Figure 1. Dependence of reduced viscosity (η_{sp}/c) on α' in CoPMAS-8 (○), CoPMAS-16 (□), and CoPMAS-43 (△).

Figure 2. Dependence of relative luminescence intensity (I/I_0) (A) and maximum wavelength ($\lambda_{\max}$) of luminescence spectrum (B) for the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ on α' in CoPMAS-8 (○), CoPMAS-16 (□), and CoPMAS-43 (△).

the maximum wavelength ($\lambda_{\max}$) of the $\text{Ru}(\text{bpy})_3^{2+}$ luminescence spectra were investigated in aqueous CoPMAS solutions. Relative luminescence intensity is defined as I/I_0 , where I and I_0 are luminescence intensity of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence and absence of CoPMAS.

Figures 2A and 2B show that I/I_0 for CoPMAS-8 and CoPMAS-16 increases through a maximum at $\alpha' \approx 0.20$, and then decreases with increasing α' . The variation of I/I_0 corresponds to that of $\lambda_{\max}$. Such luminescence behavior has been reported for PMA⁹ and PMAS¹². In aqueous PMAS-8 and PMAS-16 solutions at $\alpha' \approx 0.20$, the $\text{Ru}(\text{bpy})_3^{2+}$ species were incorporated into a hydrophobic micelle-like domain by cooperative interactions caused by electrostatic and hydrophobic effects. The incorporation of $\text{Ru}(\text{bpy})_3^{2+}$ species results in enhancement of I/I_0 and blue shift of $\lambda_{\max}$ (Figure 2B). In the range of $\alpha' < 0.20$, the polymer backbone changes from a compact to compact micelle-like conformation with increasing α' . For CoPMAS-43, the luminescence intensity decreased slightly with increasing α' , whereas $\lambda_{\max}$ is constant. $\text{Ru}(\text{bpy})_3^{2+}$ species are restricted on polymer backbone of CoPMAS-43 by strong electrostatic interaction with SS segment, and these quenching reactions of the restricted $\text{Ru}(\text{bpy})_3^{2+}$ species by Co(III) complex depend on flexibility of the polymer chain. The flexibility of polymer chains of CoPMAS-43 increases with increasing α' because of the conformational transition from a compact to expanded structure. Consequently, luminescence intensity decreases due to the quenching reaction. These results indicate that CoPMAS is characterized by the α' -induced conformational transition which is similar to PMAS-8, PMAS-16, and PMAS-43 of parent polymers.

Figure 3. Dependence of degree of reduction of Co(III) complex residue by $\text{Fe}(\text{edta})^{2-}$ (R_{co}) on α' in CoPMAS-8 (○), CoPMAS-16 (□), and CoPMAS-43 (△).

Electron-Transfer Reaction

When $\text{Fe}(\text{edta})^{2-}$ is added to the CoPMAS solution, an electron-transfer from $\text{Fe}(\text{edta})^{2-}$ to CoPMAS takes place as expressed by eq 3:

Generated $\text{Co}^{\text{II}}\text{PMAS}$ would dissociate into component species without edta.

One markedly characteristic feature in the electron-transfer reaction is that all Co(III) complex residues are hardly reduced even in the presence of excess reducing agent, because the polymer chain forming compact conformation shields Co(III) center from the reducing agent. In contrast, the corresponding low-molecular-weight Co(III) complex, $\text{cis}[\text{Co}(\text{en})_2(\text{OH}_2)(\text{O}_2\text{CCH}_2\text{C}-\text{H}_3)]^{2+}$, is completely reduced under similar conditions. No absorption spectral change in the pH range under the experimental conditions was seen.

The degree of reduction of Co(III) complex, referred to as R_{co} , was examined. Figure 3 shows the dependence of R_{co} on α' in $\text{Fe}(\text{edta})^{2-}$ /CoPMAS. R_{co} for CoPMAS-8 and CoPMAS-16 changed in two steps with increase in α' . At low α' ($\alpha' = 0.08$ for CoPMAS-8; $\alpha' = 0.16$ for CoPMAS-16), only a small amount of Co(III) complex was reduced by $\text{Fe}(\text{edta})^{2-}$. With slightly increasing α' , R_{co} increased sharply in the α' range corresponding to the first viscosity change. Finally, R_{co} reached 100% at high α' in all systems. The α' -dependence of R_{co} is similar to that of the reduced viscosity, suggesting that the environment of Co(III) residues is changed by conformational transition. The CoPMASs have two kinds of Co(III) complexes on the polymer chains, a reactive and unreactive complexes. The former exposed to the aqueous bulk phase is attacked by $\text{Fe}(\text{edta})^{2-}$, and the latter protected by polymer chains is hardly attacked by $\text{Fe}(\text{edta})^{2-}$.

The CoPMAS-8 caused conformational transition in the α' range of 0.08 to 0.10, during which time the SS segments surrounded in polymer domain were exposed to the aqueous phase. Consequently, R_{co} increased sharply from 40 to 70%. This indicates that the conformational transition brings about not only exposure of the SS segments but also that of the Co(III) complex to the bulk solution, because counter ions of the Co(III) complex are SS segments. R_{co} is constant in the α' range of 0.10 to 0.30, in which the conformational transition into a compact micelle-like structure occurs, indicating that the environment of the Co(III) complex hardly

Figure 4. Dependence of reaction rate for electron-transfer reaction between Co(III) complex residue and $\text{Fe}(\text{edta})^{2-}$ on α' in CoPMAS-8 (○), CoPMAS-16 (□), and CoPMAS-43 (△).

changes. A sharp increase of R_{∞} from 70 to over 90% was observed at 0.35 of α' . This is the reason why the remaining Co(III) complex in polymer domain is exposed to the aqueous phase by a conformational transition from a compact structure to an expanded one.

R_{∞} of CoPMAS-43 is constant in the α' range of 0.43 to 0.65, and increases above 0.65 of α' . It is noteworthy that the R_{∞} of CoPMAS-43 is 75%, though CoPMAS-43 forms a compact structure at 0.43 of α' . This indicates that 75% of Co(III) complex segments in CoPMAS-43 holding the compact structure is exposed to the aqueous phase. It is clear that the surrounded Co(III) complex is exposed to the aqueous phase by conformational transition from the compact to expanded structure.

For CoPMAS-16, the α' -dependence of R_{∞} similar to CoPMAS-8 was obtained, but R_{∞} was smaller than for CoPMAS-8 until 0.50 of α' . This indicates that most of the Co(III) complex is incorporated into the CoPMAS-16 domain and prevents $\text{Fe}(\text{edta})^{2-}$ from attacking until 0.50 of α' , and then the Co(III) complex segments are exposed to the aqueous phase at high α' . This can be explained by differences in the hydrophobicity of the micelle-like domain. We previously reported that hydrophilicity in the micelle-like domain of CoPMAS-8 is stronger than that of CoPMAS-16.¹² Therefore, the hydrophilic Co(III) complex on CoPMAS-8 may be hardly incorporated into the micelle-like domain, compared with CoPMAS-16. Thus R_{∞} may be small due to the incorporation of Co(III) complex on CoPMAS-16 into polymer domain.

The initial rates of electron-transfer reaction between CoPMASs and $\text{Fe}(\text{edta})^{2-}$ were analyzed under pseudo first-order conditions with respect to $\text{Fe}(\text{edta})^{2-}$. Figure 4 shows the dependence of the initial rate for electron-transfer reaction for CoPMAS and $\text{Fe}(\text{edta})^{2-}$ on α' . Unique α' -dependence was observed for three systems. The initial rate for CoPMAS-8/ $\text{Fe}(\text{edta})^{2-}$ was almost constant until about 0.30 of α' , and increased with α' . This indicates that the initial rate hardly changes in the compact state as a compact coil, carboxy group-dissociating compact, or compact micelle-like structure, and increases with conformational transition from the compact to expanded state. For CoPMAS-16, the initial rate was constant in α' range until about 0.45, and then increased at above 0.45 of α' . These results led us conclude that the rate for the electron-transfer reaction is determined by not only the shield effect but also steric hindrance caused by bulky of the vicinity of Co(III)

complex residues. With increasing α' , the shield effect and steric hindrance by polymer backbone are reduced because the polymer chain expands. Consequently, the initial rate increases. α' -dependence of the rate for CoPMAS-43 can be explained by the interpretation given for CoPMAS-8 and CoPMAS-16. The initial rates for CoPMAS-8 and CoPMAS-16 increased over 0.30 of α' and over 0.45 of α' , respectively. This was similar to that of reduced viscosity. The initial rates for CoPMAS-8 and CoPMAS-16 increased over α' where second viscosity change occurred. These results indicate that the initial rate increased when the conformational transition from a compact to expanded structure occurred. Namely, the initial rate for electron-transfer reaction would be determined by the shield effect and steric hindrance.

In conclusion, CoPMASs cause the α' -induced conformational transition similar to PMAS of the corresponding parent polymer in aqueous solution. In particular, CoPMAS-8 and CoPMAS-16 revealed four conformations, compact, carboxy group-dissociating compact, micelle-like, and expanded structures. In electron-transfer reaction between CoPMAS and $\text{Fe}(\text{edta})^{2-}$, the degree of reduction of the Co(III) complex by $\text{Fe}(\text{edta})^{2-}$ significantly depends on α' . This is the reason why the Co(III) complex surrounded by polymer backbone are exposed to the aqueous bulk phase by the α' -induced conformational transition. The degree of reduction of the Co(III) complex depends on the shield effect by polymer backbone. The α' -dependence of the initial rates for the electron-transfer indicates that the initial rate are influenced by the electrostatic effect between the charge in the vicinity of the Co(III) complex and $\text{Fe}(\text{edta})^{2-}$. The initial rate and degree of reduction for the Co(III) complex in the electron-transfer reaction are determined by conformation of parent polymer, which is affected by α' and the conformational structure.

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