$$\frac{1}{Y} \propto \frac{1}{R} = \frac{1 + K_T \bar{A}}{k_i K_S \bar{B}} \frac{1}{[C_8H_8]} + \frac{K_S - K_T}{k_i K_S \bar{B}} \qquad (7)$$

Registry No. TTB, 5593-70-4; styrene, 100-42-5; polystyrene, 28325-75-9.

References and Notes

(1) Ishihara, N.; Kuramoto, M.; Uoi, M. Eur. Pat. Appl. 210615, 1987; *Chem. Abstr.* **1987**, *106*, 177084p.
(2) Grassi, A.; Pellecchia, C.; Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *19*, 2465.
(3) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277.
(4) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
(5) Zambelli, A.; Pellecchia, C.; Oliva, L.; Shimin, H. *Chinese J. Polym. Sci.* **1988**, *6*, 365.
(6) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035.
(7) Unpublished data from our laboratories.

Electron-Transfer Reaction of Macromolecular Cobalt(III) Complex with $[Ru(NH_3)_6]^{2+}$. Effect of Microenvironment Occupied by Polymer Backbone

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ABSTRACT: The rates and kinetic parameters of the electron-transfer reaction of the polymer-bound Co(III) complex *cis*-$[Co(en)_2PVP(N_3)]^{2+}$ (PVP = poly(4-vinylpyridine), en = ethylenediamine) with $[Ru(NH_3)_6]^{2+}$ were determined in aqueous solutions of sodium perchlorate and sodium chloride and a water–ethanol mixture at pH 2. The electron-transfer rate of the polymer–metal complex was found to be very sensitive to the type of dissolved anion at a given ionic strength. Higher reactivity of the polymer–metal complex in perchlorate solution than in chloride solution may be ascribed to partial dehydration of the pendant Co(III) moieties and the $[Ru(NH_3)_6]^{2+}$ ions in the microenvironment of the polymer backbone. The lower activation enthalpy of the electron-transfer reaction seems to be attributable to the higher reactivity of the polymer–metal complex in perchlorate solution.

Despite the considerable experimental and theoretical studies of electron-transfer reactions of common metal complexes, there are few data on those of synthetic macromolecule–metal complexes.[1-7] Aquochromium(II) reduction of polypeptide–amminecobalt(III) complex, obtained by reaction of aquopentaamminecobalt(III) perchlorate with poly(glutamic acid), has been reported.[1,2] The results of detailed investigation suggested that there may be two parallel reactions: the faster and slower processes ascribed to the reduction of acidotetraamminecobalt(III) and (carboxylato)aquotetraamminecobalt(III), respectively.[2] The results of kinetic studies on the redox reactions of polycation-bound Co(III) complexes and anionic iron(II) complexes indicated that the most important factor governing the rate is Coulombic interaction.[3-7]

Investigation of the electron-transfer reactions of polycationic macromolecule–metal complexes with positively charged low molecular weight metal complexes are important since the results of such investigations would confer a wider understanding of the factors that govern the rate of electron-transfer of macromolecule–metal complexes. We report here the electron-transfer reaction of a polycationic macromolecule Co(III) complex, *cis*-$[Co(en)_2PVP(N_3)]^{2+}$ (en = ethylenediamine and PVP = poly(4-vinylpyridine)), with $[Ru(NH_3)_6]^{2+}$. We have found that (i) the repulsive force between the polycation of the Co(III) complex and $[Ru(NH_3)_6]^{2+}$ ion is not an important factor in controlling the reaction rate and (ii) the reaction rate is very sensitive to the type of dissolved anions in the polymer complex system.

Experimental Section

General Procedures. Poly(4-vinylpyridines) (PVP) having a degree of polymerization (Pn) of 98 and 19 were used as the polymeric ligands. Partially quarternized poly(4-vinylpyridine), quarternized by ethyl bromide (QPVP), was prepared by the reaction of the PVP of Pn = 98 with ethyl bromide in ethanol. $[Ru(NH_3)_6]Br_2{\cdot}6H_2O$ was prepared and analyzed according to the published procedure.[8] The method of preparation of *cis*-$[Co(en)_2PVP(N_3)]Cl_2$ and *cis*-$[Co(en)_2Py(N_3)]Cl_2$ (Py = pyridine)[9,10] has been described in the literatures cited. Degrees of coordination (x) of the Co(III) complexes for the $[Co(en)_2PVP(N_3)]Cl_2$ prepared were 0.39 for the PVP of Pn = 98 and 0.47 for the PVP of Pn = 19. The concentration of the polmer-bound Co(III) complex is represented by that of the monomeric Co(III) unit. Viscosity measurements were carried out in aqueous solutions with an Ubbelode type viscometer at (25 ± 0.1) °C. A solution of $[Ru(NH_3)_6]^{2+}$ was prepared by reduction of $[Ru(NH_3)_6]Br_3$ solution with amalgamized zinc. Concentrations of the Ru(II) were determined by reduction of a standard solution of $[Co(NH_3)_5]Cl_2$.

Kinetic Experiments. Rates of electron transfer were measured in dilute acid solutions at pH 2.0. Values of pH and ionic strength in the reaction solutions were adjusted with hydrochloric acid and sodium chloride or perchloric acid and sodium perchlorate. The former and latter cases will hereafter be described simply as a "chloride system" and a "perchlorate system", respectively. The reaction was initiated by mixing the solutions of Co(III) with those of Ru(II) by using a mixing apparatus (Union Gikken MX 7). All the reactions were followed with the Ru(II) in large excess, as required for pseudo-first-order kinetics. The initial concentration of the Co(III) and Ru(II) were 2.5×10^{-4} and $(2.5\text{–}6.0) \times 10^{-3}$ M, respectively. Reactions were followed by disappearence of the Co(III) absorption in the 510-nm region using a Hitachi Model 320 recording spectrometer. The second-order rate constants (k) were obtained from the slopes of the log $(A_t - A_\infty)$ vs reaction time plots where A_t and A_∞ are the absorbances at time t and after all the Co(III) had been reduced to Co(II), respectively.

Results and Discussion

The chemical structure and analytical data of *cis*-$[Co(en)_2PVP(N_3)]Cl_2{\cdot}nH_2O$ are shown in Figure 1 and Table I, respectively. Otherwise noted, the polymer Co(III)–PVP complex having the PVP with a degree of polymerization of 98 was used for the experiments. *cis*-$[Co(en)_2Py(N_3)]Cl_2$ was used as the corresponding low molecular weight ana-

Table I
Analytical Data of *cis*-[Co(en)$_2$(N$_3$)L]Cl$_2$•*n*H$_2$O (L = PVP and Py)

L	Pn	x[a]	n[b]	found (calcd), % H	found (calcd), % C	found (calcd), % N	composition[c] o	composition[c] p
PVP	98	0.39	6	6.62 (6.91)	40.02 (39.47)	19.99 (19.98)	0.39	0.61
PVP	19	0.47	6	6.28 (6.93)	36.38 (36.40)	20.90 (20.49)	0.47	0.53
Py				6.36 (6.40)	25.72 (25.42)	26.98 (26.47)		

[a] Degree of coordination. [b] Number of hydrated water molecules. [c] See Figure 1.

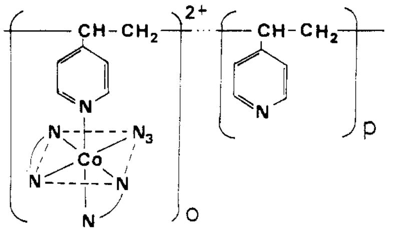

Figure 1. Chemical structure of *cis*-[Co(en)$_2$PVP(N$_3$)]$^{2+}$.

logue. Molecular absorptivities of *cis*-[Co(en)$_2$PVP(N$_3$)]Cl$_2$ and *cis*-[Co(en)$_2$Py(N$_3$)]Cl$_2$ were 298 ± 5 M^{-1} cm^{-1} (λ_{max}, 512 ± 2 nm) and 297 M^{-1} cm^{-1} (λ_{max}, 514 nm), respectively. The cis configurations of these complexes were ascertained by means of an IR spectrum from the sharp splitting of the –CH$_2$ rocking bands (870–900 cm^{-1}) of the coordinated ethylenediamine.[11]

For all the reactions, a linear correlation between log ($A_t - A_\infty$) and the reaction time was observed over at least 2 half-lives. Furthermore, a linear relationship between the pseudo-first-order rate constant and the [Ru(II)] was found to hold under the conditions employed. The results suggest that the rates of the electron-transfer reactions of the polymer and low molecular weight metal complexes are first-order with respect to the [Co(III)] and the [Ru(II)], respectively, and the interaction between neighboring groups on the polymer chains is not such an important factor in governing the reaction rate.

It was an interesting experimental evidence that the rate constant for the reduction of the polycationic [Co(en)$_2$PVP(N$_3$)]$^{2+}$ by [Ru(NH$_3$)$_6$]$^{2+}$ was fairly greater than that of the corresponding low molecular weight model system in perchlorate solution whereas the rate constant for the polymer system in chloride solution was smaller than that of the low molecular weight system at pH 2.0, I = 0.08, and 25 °C: the second-order rate constants in the perchlorate system were (6.9 ± 0.9) M^{-1} s^{-1} for the PVP complex and (1.9 ± 0.1) M^{-1} s^{-1} for the pyridine complex. Unfortunately, a kinetic run for the pyridine complex in perchlorate solution at $I > 0.08$ could not be obtained due to precipitation of the complex.

A reactivity of the polymer complex higher than that of the corresponding low molecular weight analogue in the perchlorate solution was actually unexpected because we had anticipated that the rate of the polymer complex would be smaller than that of the low molecular weight complex; the Coulombic repulsion force between the polycationic Co(III) complex moiety and the Ru(II) dication had been expected to be greater than that between [Co(en)$_2$Py(N$_3$)]$^{2+}$ and [Ru(NH$_3$)$_6$]$^{2+}$ because the Co(III) moieties are more closely bound to the polymer chain than to each other.

Dependences of the rate on the concentration of sodium perchlorate and sodium chloride are shown in Figure 2. In the perchlorate system, the reduction rate of the polymer complex increases sharply with concentration of added sodium perchlorate, [NaClO$_4$]$_{add}$, whereas the rate for the low molecular weight complex increases moderately with [NaClO$_4$]$_{add}$. The sharp increase in the rate for the polymer complex could not be attributed to the primary salt effect expressed by Brønsted–Debye–Hückel equation

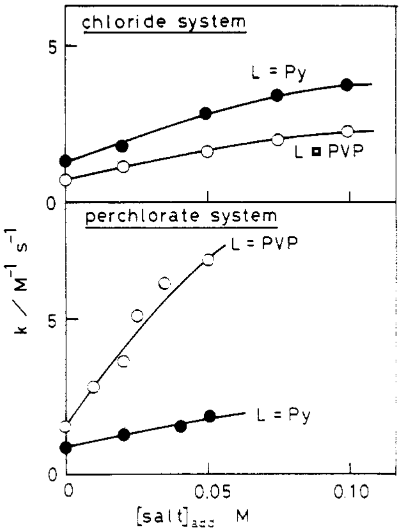

Figure 2. Dependence of the rate constant for the reductions of *cis*-[Co(en)$_2$L(N$_3$)]$^{2+}$ (L = PVP or Py) on the concentration of added salt at pH 2.0 and 25 °C. The ionic strength at [salt]$_{add}$ = 0 is 0.04.

$$\log k = \log k_0 + 1.02 Z_1 Z_2 \sqrt{I} / (1 + \sqrt{I}) \qquad (1)$$

where k and k_0 are the rate constant at ionic strength I and $I \rightarrow 0$, respectively, and Z_1 and Z_2 are the charges on the reactants. For the low molecular weight perchlorate and chloride systems the plots of log k versus $I^{1/2}/(1 + I^{1/2})$ give straight lines with slopes of 4.4 ± 0.2 and 4.2 ± 0.3, respectively. These values are very close to the theoretical value of 4.1, indicating that the influence of the salt concentration for the low molecular weight system in both solutions is to be ascribed to a primary salt effect.

For the polymer system, the rate dependence on $I^{1/2}/(1 + I^{1/2})$ in the chloride system fits satisfactorily eq 1; i.e., the value of the straight line was 4.4 ± 0.3 although the rate constant at a given added chloride concentration is slightly smaller than those of the corresponding low molecular weight model complex (Figure 2).

On the other hand, the value of the slope (9.4 ± 0.7) for the polymer system in the perchlorate solution is much greater than the theoretical value, suggesting that the reactivity of the polymer Co(III) complex in the microenvironment occupied by the polymer chain is sensitive to the type of dissolved anion. Such a special salt effect could be explained as due to a change in the physicochemical properties of the polymer domain upon replacing the dissolved salt.

In order to examine the effect of the concentration of chloride or perchlorate ions on the conformational change of the Co(III) polymer chain, the dependence of the viscosity of the aqueous polymer solution on the concentration of sodium perchlorate or sodium chloride was measured; the results are presented in Figure 3. The decreasing tendency of the reduced viscosity, η_{sp}/C, where

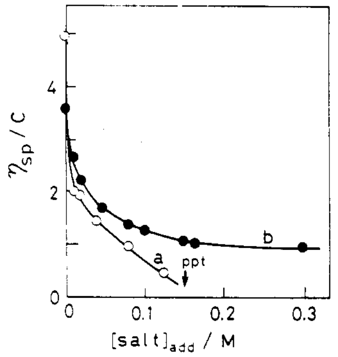

Figure 3. Variation of reduced viscosity of *cis*-$[Co(en)_2PVP(N_3)]^{2+}$ with the concentration of added salt at pH 2.0 and 25 °C: (a) perchlorate solution, (b) chloride solution.

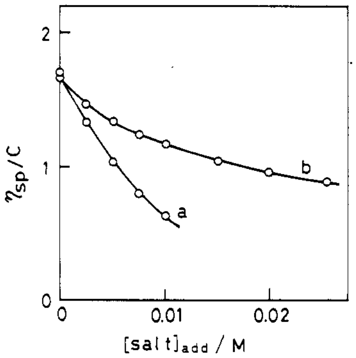

Figure 4. Variation of reduced viscosity of QPVP (Pn = 98) with the concentration of added salt at pH 2.0 and 25 °C: (a) perchlorate solution, (b) chloride solution.

Table II
Rate Constants for the Reductions of *cis*-$[Co(en)_2L(N_3)]^{2+}$ by $[Ru(NH_3)_6]^{2+}$ in Various Salt Solutions at $[salt]_{add}$ = 0.100 M, pH 2 ($HClO_4$), and 25 °C[a]

salt	k, M^{-1} s^{-1} L = Py	k, M^{-1} s^{-1} L = PVP
none	0.89 ± 0.03	1.42 ± 0.01
LiCl	3.37 ± 0.13	3.32 ± 0.07
NaCl	3.71 ± 0.42	3.34 ± 0.03
NaBr	3.85 ± 0.09	4.73 ± 0.40
$NaClO_4$	*b*	11.0 ± 0.22

[a] Values of Pn and x for the Co(III)–PVP complex are 19 and 0.47, respectively. [b] No data was obtained because the pyridine complex was precipitated under the conditions employed.

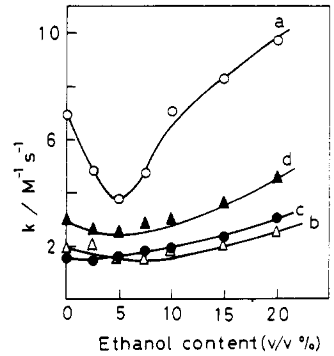

Figure 5. Dependence of the rate constant for the reductions of *cis*-$[Co(en)_2L(N_3)]^{2+}$ (L = PVP or Py) on ethanol content at I = 0.08, pH 2.0, and 25 °C: (a) L = PVP in perchlorate solution, (b) L = Py in perchlorate solution, (c) L = PVP in chloride solution, (d) L = Py in chloride solution.

η_{sp} and C are the specific viscosity and the concentration of the polymer (g dL^{-1}), respectively, was found to be more drastic in the perchlorate solution. That is, the degree of shrinkage of the polymer backbone is appreciably greater in the percholrate solution at a given concentration of added salt. A large number of positively charged Co(III) complexes and protonated pyridine moieties are localized in the polymer domain: the pK_a of PVP is about 5.[12] The higher degree of shrinkage in the perchlorate solution is probably to be ascribed to enhancement of dehydration of the pendant Co(III) complex moieties and/or that of the protonated pyridine rings as the result of accumulation of perchlorate ions in the polymer domain.

In order to estimate the conformational change of the protonated PVP with addition of sodium perchlorate or sodium chloride, partially quarternized poly(4-vinylpyridine) (QPVP) was used instead of the protonated PVP since the PVP was difficult to dissolve in an aqueous solution under the experimental conditions. Plots of the reduced viscosity of the QPVP solution versus salt concentration are presented in Figure 4. The results clearly indicate that the shrinkage of the QPVP chain occurs by shielding of the positive charges on the quarternized pyridine moieties by the counterion; the shrinkage is more pronounced in the perchlorate solution than in the chloride solution. This also seems to indicate that the protonated pyridine groups on the Co(III)–PVP chains are also associated with the counterions and tend to cause shrinkage of the polymer chain.

The effect of the charge in the dielectric constant in the polymer domain due to shrinkage of the polymer backbone caused by the addition of perchlorate ions may not be appropriate as an explanation of the rate enhancement in the perchlorate system. If the effect of dielectric constant is a major factor controlling the rate, the rate should be decreased upon increasing the salt concentration since the repulsive force between the Co(III) moiety and $[Ru(NH_3)_6]^{2+}$ would be increased with increasing $[ClO_4^-]$. This was contrary to the observed results. Therefore, it may be presumed that the predominant factor in enhancing the rate is a decrease in degree of hydration of the Co(III) moieties and $[Ru(NH_3)_6]^{2+}$ ions due to association of these with such bulky counteranions as perchlorate.

It is expected that the degree of hydration of the positively charged species such as $[Co(en)_2PVP(N_3)]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ will decrease with an increase in the bulkiness of the counteranion. Actually, the results shown in Table II show the reactivity increases in the order Cl^-, Br^-, and ClO_4^-. This seems to indicate that higher reactivity of the polymer complex in perchlorate solution is mainly to be ascribed to the larger size of the perchlorate ion. Unfortunately, the rate in sodium iodide solution could not be determined due to irregular spectral change of the reaction mixture, probably due to oxidation of the iodide ions.

The effect of the concentration of organic solvent on the reduction rate was examined in aqueous ethanol solution. The results are presented in Figure 5. For the low molecular weight analogue, a slight decrease in the rate was observed both in the chloride and perchlorate solutions below ca. 5% ethanol content and the rate then tended to increase with increasing concentration of ethanol. A slight decrease in the rate in the low-concentration range of the organic solvent would be ascribed to a decrease in the dielectric constant of the medium. The increase in the rate at higher ethanol content than ca. 5% both in perchlorate and chloride solutions may be caused by increasing dehydration of the reactant species, the Co(III) and Ru(II), with increase in the content of the organic solvent.

For the polymer complex, the rate profile in aqueous ethanol with chloride is almost the same shape as those

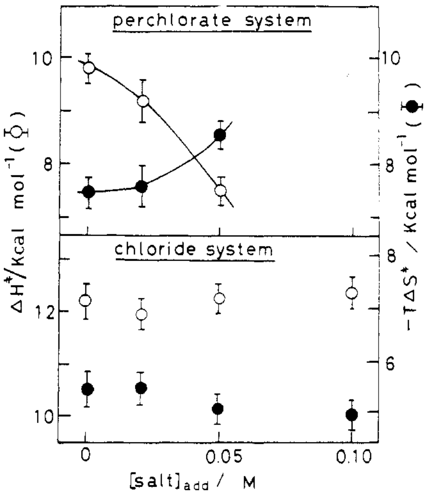

Figure 6. Dependences of $\Delta H^{\ddagger}$ (○) and $-T\Delta S^{\ddagger}$ (●) on the concentration of added salt for the reduction of *cis*-$[Co(en)_2PVP(N_3)]^{2+}$ at pH 2.0 and 25 °C.

of the low molecular weight analogue in chloride and perchlorate systems. However, in the perchlorate system, both the initial decrease in the rate and the enhancement of the rate at higher concentration range of ethanol are more drastic than those of the low molecular weight system, suggesting some special salt effect for the polymer system in perchlorate solution. It is presumed from the results obtained that, for the polymer complex in the perchlorate system, the positively charged species of the Co(III) and Ru(II) in the polymer domain are associated with perchlorate ions and, thus, dehydration of both reactive species occurs progressively, leading to enhancement of the reaction rate with increasing concentration of perchlorate ions.

For the polymer system, another characteristic feature was observed in the perchlorate system; i.e., a distinct decrease in the activation enthalpy of the electron transfer was found to occur with increase in the concentration of added sodium perchlorate, whereas no apparent decrease in the activation enthalpy was observed for the polymer complex in the chloride system as well as for the low molecular weight analogue both in perchlorate and chloride systems (Figure 6). These observations suggest that the rate enhancement for the polymer complex in sodium perchlorate solution is essentially attributable to decrease in activation enthalpy.

A tentative explanation for the smaller activation enthalpy for the reduction of the polymer complex in perchlorate solution is that larger destabilization of the ground state of the Co(III) and Ru(II) dications occurs than in the activated complex, which has four positive charges, due to different degrees of dehydration of these species.

In the local environment occupied by the synthetic polymer–metal complexes, several important effects affecting the reaction rate would be anticipated. These are, for example, effect of electrostatic[5] and hydrophobic[6] interactions, stabilization of coordinatively unsaturated complex species[13-15] interactions of the neighboring groups[7], effect of local distribution of the reactive species, and effect of conformational arrangement of the polymer chain.[16] In addition to these, it was clarified that, for the electron-transfer reactions of the polycation-bound Co(III) with $[Ru(NH_3)_6]^{2+}$, enormous rate enhancement occurred in aqueous solution at higher concentration of perchlorate due to a kind of special salt effect.

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Registry No. $NaClO_4$, 7601-89-0; LiCl, 7447-41-8; NaBr, 7647-15-6; NaCl, 7647-14-5; H_3CCH_2OH, 64-17-5; $[Ru(NH_3)_3]Br_2$, 16446-58-5.

References and Notes

(1) Kopple, K. D.; Svatos, G. S. *J. Am. Chem. Soc.* **1960**, *82*, 3227.
(2) Kopple, K. D.; Miller, R. R. *Inorg. Chem.* **1963**, *2*, 1204.
(3) Kurimura, Y.; Yamada, K.; Kaneko, M.; Tsuchida, E. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 3521.
(4) Kurimura, Y.; Sekine, I.; Tsuchida, E.; Karino, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1823.
(5) Tsuchida, E.; Karino, Y.; Nishide, H.; Kurimura, Y. *Makromol. Chem.* **1974**, *175*, 161.
(6) Tsuchida, E.; Shigehara, K.; Kurimura, Y. *J. Polym. Sci.* **1975**, *13*, 1475.
(7) Kurimura, Y.; Takato, K.; Takeda, M.; Ohtsuka, N. *J. Phys. Chem.* **1985**, *89*, 1023.
(8) Lever, F. N.; Powell, A. R. *J. Chem. Soc. A* **1969**, 1477.
(9) Tsuchida, E.; Karino, Y.; Takahashi, H.; Kurimura, Y.; Imai, K. *Nippon Kagaku Kaishi* **1972**, *12*, 2420.
(10) Staple, P. J.; Tobe, M. L. *J. Phys. Chem.* **1960**, *64*, 4821.
(11) Boldwin, J. *J. Chem. Soc.* **1965**, 4369.
(12) Kurimura, Y.; Takato, K. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 841.
(13) Kurimura, Y.; Uchino, Y.; Ohta, F.; Saito, C.; Koide, M.; Tsuchida, E. *Polym. J. (Tokyo)* **1981**, *31*, 247.
(14) Kurimura, Y.; Takagi, Y.; Tsuchida, E. *J. Macromol. Sci., Chem.* **1987**, *A24*, 419.
(15) Hirai, H.; Hara, S.; Komiyama, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 109.
(16) Kurimura, Y.; Takato, K.; Takeda, M.; Ohtsuka, N. *J. Phys. Chem.* **1985**, *89*, 1027.