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Complexation of Terbium Ion with the Copolymer of Acrylic Acid and Acrylamide Grafted onto Polyethylene

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ABSTRACT

Acrylic acid (AA) and acrylamide (AAm) were graft copolymerized onto polyethylene powder by the preirradiation method. The PE powder grafted with both AA and AAm (PE-g-(AA-co-AAm)) rapidly adsorbed Tb ion with an efficiency higher than did PE powder grafted with AA (PE-g-AA). The complex formation constant of Tb ion with PE-g-(AA-co-AAm) was larger than that with PE-g-AA because the introduction of the acrylamide part decreased the steric hindrance for complexation between Tb and the carboxyl group of the graft chains. Tb ion was efficiently separated from transition metal ions, such as Co, upon passage of a solution through a column packed with PE-g-(AA-co-AAm).

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INTRODUCTION

The synthesis of chelating resins to be used for separating radioactive actinide ions such as americium and curium is of great interest [1, 2]. However, few studies involving polymers with complexation ability for actinide ions have been reported. As the complexation behavior of rare earth metal ions is known to be similar to that of actinide ions [3], the complexation of rare earth metal ions is a good model of that for radioactive actinide ions, which are not as easy to handle.

Previously the authors reported the complexation of Sm ion with poly(acrylic acid) grafted onto polyethylene powder [5]. Although that polymer rapidly and efficiently adsorbed Sm ions, the maximum coordination number was only 2 for trivalent Sm ion due to steric hindrance between the grafted chain and the relatively large Sm ion. In this paper the copolymer of acrylic acid with acrylamide was grafted onto polyethylene powder (PE-g-(AA-co-AAm)) in order to decrease the steric hindrance mentioned above. The complexation of the powder with Tb ion was compared with that of PE-g-AA and Tb ion because the hydrophilic acrylamide residue was expected to promote the complexation behavior of the AA residue.

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EXPERIMENTAL

Materials

Commercially available PE powder (Hizex A-105083, Mitsui Petrochemical Co.) and poly(isobutylene oxide) (PIBO) powder (Nippon Carbide Co.) were used as trunk polymers for grafting. Acrylic acid (AA) and acrylamide (AAm) were purified by common methods. Special grade terbium nitrate and cobalt nitrate were used. 2,7-Bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo III) of analytical grade (Dotite) was used as a colorimetric reagent for Tb ion.

Preparation of PE-g-(AA-co-AAm)

PE powder was irradiated at -78°C by passing it under the electron beam of a cascade-type accelerator (Dynamitron IEA 3000-25-2, Radiation Dynamics Ltd.) operating at a beam energy of 2 MeV. Immediately after irradiation, the powder was immersed in the solution of AA and AAm. The reaction was carried out under nitrogen. The reacted powder was removed from the monomer solution, washed with methanol, and extracted with hot water for 16 h with a Soxhlet extraction apparatus. The degree of grafting was determined as the weight increase to initial PE weight ratio, and the composition of the graft chain was obtained by elemental analysis, as shown in Table 1.

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TABLE 1. Preparation of the Graft Polymers

Resin No.	AAm mole fraction in the monomer solution	Temperature, °C	Time, h	Degree of grafting, %	AAm mole fraction in the graft chain	AAm mole in resin, mmol/g	AA mole in resin, mmol/g
1	0.75	70	2	64	0.63	3.43	2.03
2	0.75	70	0.25	35	0.70	4.04	1.73
3	0	40	21	35	0	0	3.60
4	0.15	70	2	25	0.30	0.87	1.95

Molecular Weight of the Graft Chain

PIBO powder was used as the trunk polymer to estimate the molecular weight of the graft chain, because PIBO was decomposable with perchloric acid and the behavior of the graft polymerization of PIBO was similar to that of PE [5]. About 5 g of the PIBO trunk polymer was decomposed in 100 mL of perchloric acid at room temperature for 2 days. After the decomposition of PIBO, only the graft chain was separated by pouring into acetone. The apparent molecular weight of the graft chain was estimated by viscometric measurement.

Adsorption of Tb Ion on PE-g-(AA-co-AAm)

A batch-type equilibration procedure was used to determine the Tb ion taken up from 50 mL of solution by PE-g-(AA-co-AAm) and PIBO-g-AA powders (AA residue, 1 mmol). The pH value of the solution was kept constant with Clark-Lubs buffer. The powder was immersed in a buffer solution and conditioned for 1 day. The Tb ion solution was then added and the mixture was shaken for 5 h at room temperature. At fixed times the Tb ion amount in the supernatant was measured by colorimetry with Arsenazo III. The amount of Tb ion adsorbed on the powder was determined by subtracting the final amount from that initially present in solution.

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EPMA Measurement

The distribution of graft chain within the powder was estimated from the distribution of K ion with an electron probe x-ray microanalyzer (EPMA) (JEOL JXA-733) after the powder had been refluxed in aqueous KOH for 16 h. The Tb ion distribution within the powder was also measured by EPMA.

Separation of Tb Ion by a Column Method

The PE-g-(AA-co-AAm) powder (2 g) was packed in a column (0.5 cm diameter × 20 cm) and was conditioned with distilled water. A solution containing Tb and Co ions was placed on the top of the column and the sorbed ion mixture was subsequently eluted with water, pH 5.5 buffer solution, pH 4.0 buffer solution, and 1 N hydrochloric acid. The eluted ions were monitored by colorimetry or with an atomic absorption spectrometer (Shimadzu AA 640-01).

RESULTS AND DISCUSSION

Figure 1 shows the adsorption yield of Tb ion on the PE-g-(AA-co-AAm) powders. The adsorption yield increases sigmoidally with the pH value of the solution, and the ion is taken up in ~90% yield at pH 5-7. This pH dependence of adsorption corresponds to the dissociation of the acrylic acid residue in the graft polymer. Midpoints of the adsorption curves appear at ~pH 4.3, and the slope increases with the AAm residue of the graft chain.

The rate curves of Tb ion adsorption on PE-g-(AA-co-AAm) are shown in Fig. 2. The adsorption rate with the powder (No. 2) of high acrylamide content is several times larger than those of the others. The equilibrium degree of adsorption with No. 2 is also larger than those of the others. No. 3, which contains only AA graft chain, has

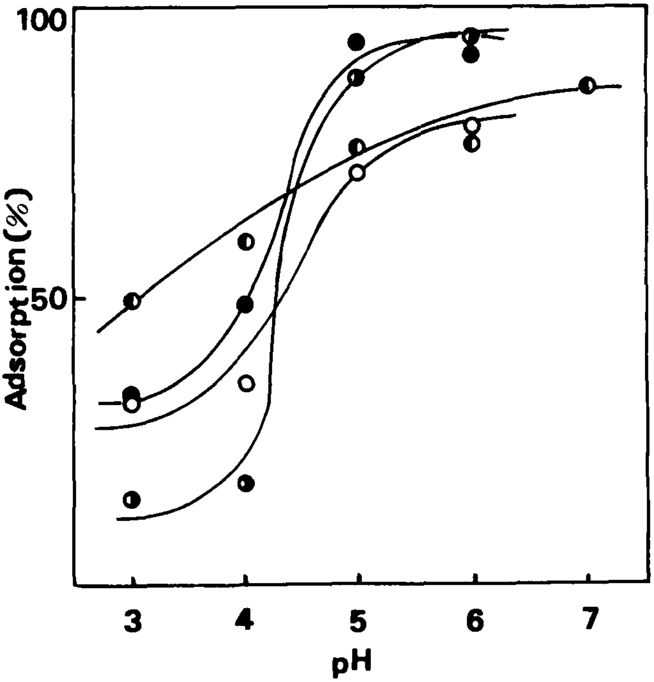

FIG. 1. Effect of pH on the adsorption of Tb^{3+}; $[Tb^{3+}]$ = 0.1 mM, [AA residue]/$[Tb^{3+}]$ = 10, (○) No. 1; (◑) No. 2; (◐) No. 3; (●) No. 4.

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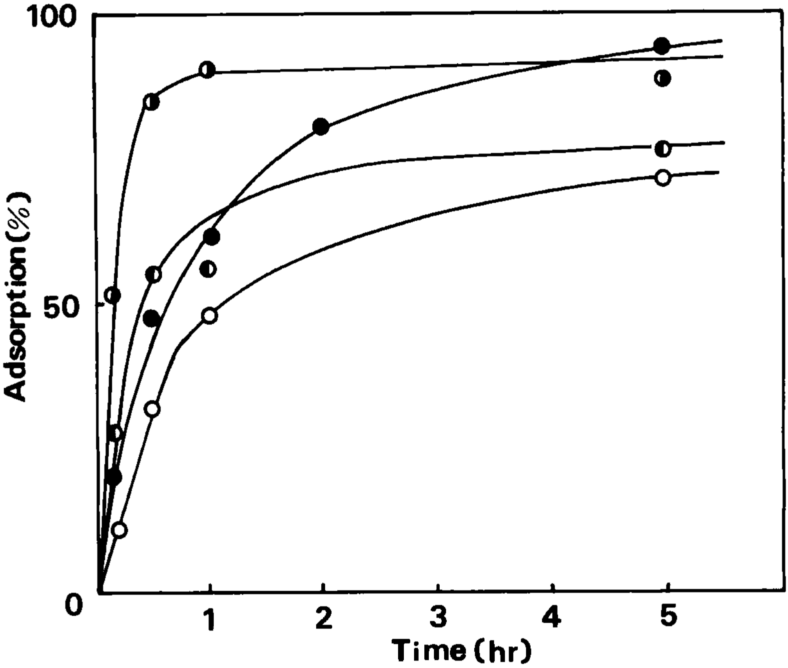

FIG. 2. Complexation between the graft polymers and Tb^{3+}; $[Tb^{3+}] = 0.1$ mM; [AA residue]/$[Tb^{3+}] = 10$; pH 5.0, (○) No. 1; (◑) No. 2; (◐) No. 3; (●) No. 4.

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the lowest adsorption rate except for No. 1, which has a graft chain of higher molecular weight. On the other hand, No. 4 which has a lower AAm residue content shows an intermediate adsorption rate. The equilibrium adsorption in a long run is virtually the same as that of No. 2. It was previously reported that the AAm residue in the copolymer of AA and AAm has no ability to form a complex with Tb ion [6]. The hydrophilic property introduced by the AAm residue to the graft chain is considered responsible for enhancing the diffusion of Tb ion into the powder as well as the resultant increase in both the adsorption rate and the equilibrium amount.

Figure 3 shows the influence of the molecular weight of the PAA graft chain and the grafting density of the PAA chain on the Tb ion adsorption with PIBO-g-AA. The adsorption yield of Tb ion increases with the PAA chain, which can be explained by a higher concentration of the ligand in the grafted polymer. That is, once the metal ion is attached to one ligand in the graft chain, the other coordinates more easily. On the other hand, the adsorption yield of Tb ion on PIBO-g-

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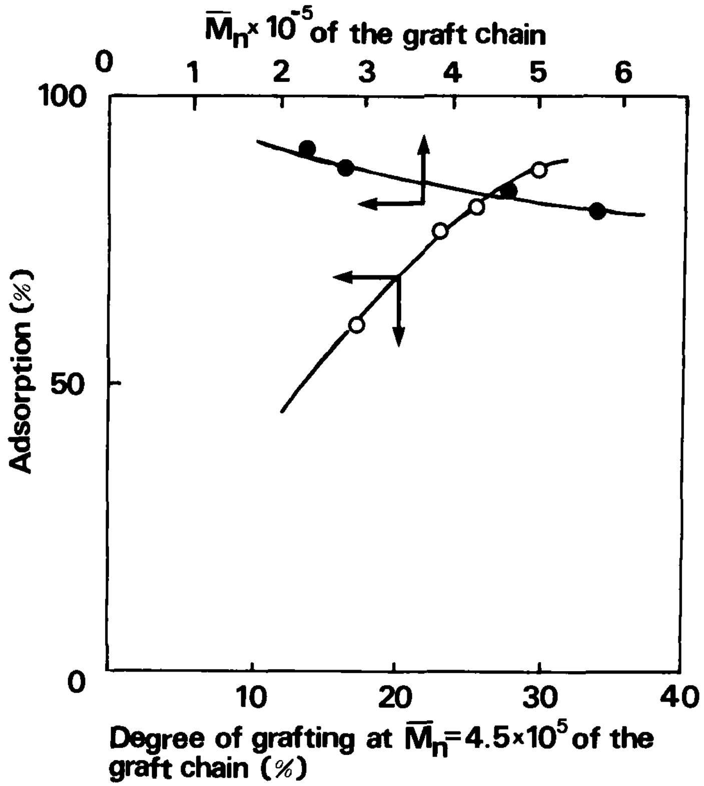

FIG. 3. Effect of the graft chain on adsorption.

AA decreases with the molecular weight of the PAA chain. It is supposed that the lower mobility of the higher molecular weight chain reduces the complexation ability.

The complex formation constant of Tb ion with PE-g-(AA-co-AAm) was determined. The adsorption curve given in Fig. 4 appeared to be Langmuir's type, and the stability constant K of the Tb complex and the saturated adsorption amount of Tb were evaluated for the complexes by fitting Langmuir's equation

$$\frac{c}{a} = \frac{1}{KA_s} + \frac{c}{A_s}, \qquad (1)$$

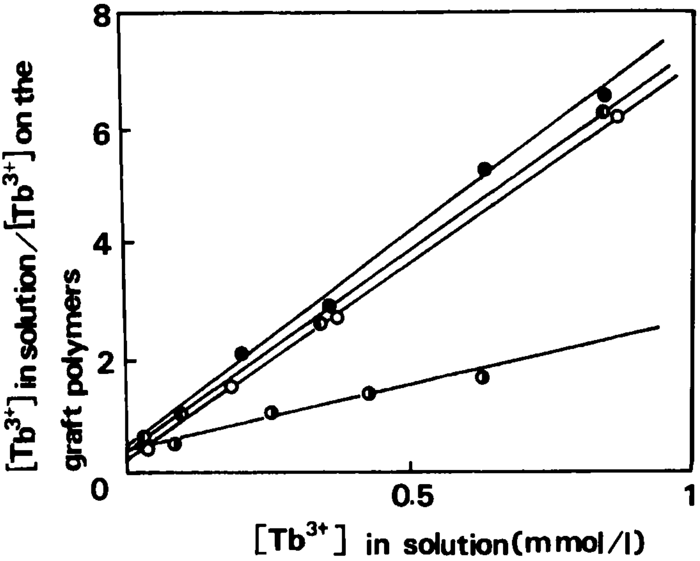

FIG. 4. Adsorption behavior of Tb^{3+} on the graft polymers; [AA residue] = 1 mM constant; pH 5.0. (○) No. 1; (◑) No. 2; (◐) No. 3; (●) No. 4.

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where A_s is a constant value which corresponds to the saturated adsorption amount, c is the concentration of unadsorbed Tb ion, K is the stability constant, and a is the quantity adsorbed. These values are given in Table 2. While A_s decreases with the content of AAm, K for Tb-PE-g-(AA-co-AAm) increases with AAm content, which supports the result that Tb ion is complexed by PE-g-(AA-co-AAm) more efficiently than PE-g-AA.

The distribution of the adsorbed metal ions such as K ion and Tb ion within the PE-g-(AA-co-AAm) powder was measured by EPMA, as shown in Fig. 5. The distribution of K ion corresponds to the distribution of the acrylic acid residue of the graft chain, which is homogeneously distributed within the powder. Figure 5(b) shows that Tb ion is adsorbed into the inner region of the powder, especially for the PE-g-(AA-co-AAm) powder, the hydrophilicity of which is increased with the co-grafting.

The separation of Tb and Co ion was demonstrated by using a column with the PE-g-(AA-co-AAm) powder. As shown in Fig. 6, only Co ion was eluted with the pH 5.5 solution. Tb ion was not eluted until a concentrated HCl solution (1 N) was used. This result indicates that PE-g-(AA-co-AAm) has the ability to separate Tb ion and Co ion completely.

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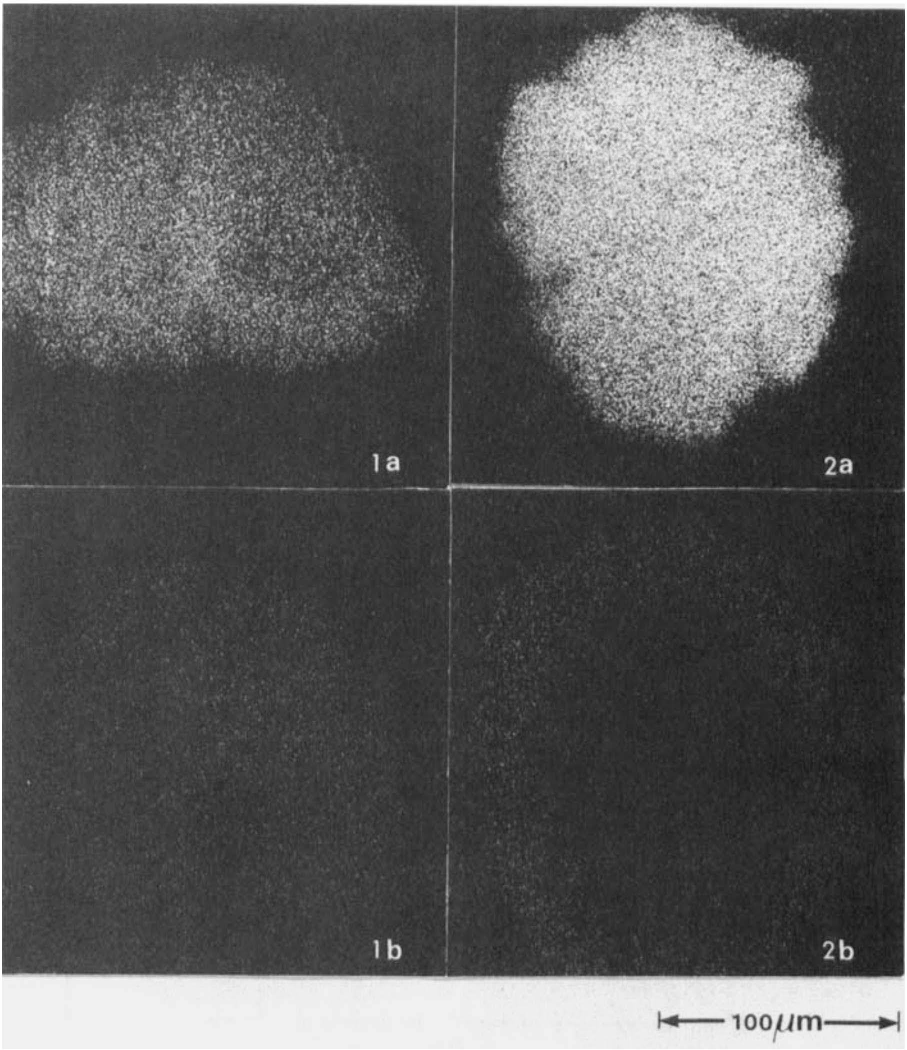

FIG. 5. Distribution of Tb^{3+} in the graft polymers; (1) No. 2, (2) No. 3, (a) K^+, (b) Tb^{3+}.

TABLE 2. Stability Constant of the PE-g-(AA-co-AAm) Complex with Tb^{3+} (log K) and Saturated Amount of Adsorption (A_s)

	Graft polymer			
	1	2	3	4
log K (L/mol)	4.52	4.36	3.32	3.86
A_s (mol/unit mol)	0.15	0.13	0.38	0.17

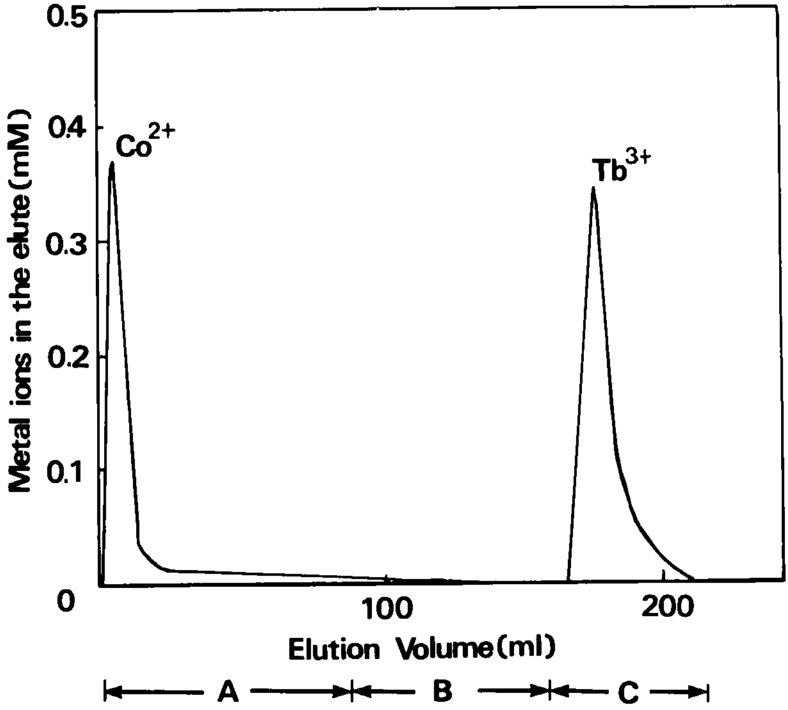

FIG. 6. Separation of Tb^{3+} from the mixture of Tb^{3+} and Co^{2+} solution with the column (0.5 cm diameter × 20 cm) packed with PE-g-(AA-co-AAm) (No. 2). A: pH 5.5 buffer solution. B: pH 4.0. C: 1 N HCl.

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It is concluded that the PE-g-(AA-co-AAm) powder with a degree of grafting of ~35% and an acrylamide content in the graft chain of ~ 70% adsorbs Tb ion most efficiently.

ACKNOWLEDGMENT

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