

Complexation of Samarium Ion with Poly(acrylic Acid) Grafted onto Polyethylene by Radiation-Induced Method

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Synopsis

Acrylic acid was graft-polymerized onto polyethylene powder by preirradiation method. The grafted powder (PE-*g*-AA) rapidly adsorbed Sm³⁺ ion in high efficiency. The poly(acrylic acid) grafted to the surface region of PE acted as an effective chelating site for the relatively large Sm ion. The complex formation constant of Sm ion with PE-*g*-AA was much larger than those of Sm ion with poly(acrylic acid) and propionic acid and of Cu²⁺ ion with PE-*g*-AA.

INTRODUCTION

It is interesting to prepare a chelating resin with complexation ability for rare earth metal ions, because in recent years many developments have been seen in the application of rare earth elements.^{1,2} Furthermore, the complexation behavior of rare earth metal ions has been known to be similar to that of actinide ions: Rare earth metal ions are good model of radioactive actinide ions such as americium and curium ion, because the latter ions are radioactive and contain chemically similar rare earth metal elements as their fission products.³ The complex formation constants of rare earth metal ions in aqueous solution have been reported and are relatively large with the ligands having carboxylic group.^{4,5} From this view point, the complexation with poly(acrylic acid) (PAA) and the PAA grafted on polyethylene (PE) was studied in this paper, using samarium ion (Sm³⁺) as the example of rare earth metal ions.

Crosslinked poly(acrylic acid)s have been known to form stable complexes with transition metal ions, but they often adsorbed the metal ions slowly due to the relatively low diffusion rate of ions at the inside of the polymer. It is assumed for rare earth metal ions that the adsorption rate is much suppressed because of their larger ion radius. Thus, in this study, the PAA ligand was combined to the surface region of the trunk PE powder by radiation-induced polymerization. This PAA-grafted powder (PE-*g*-AA) is expected to form the Sm complex rapidly and effectively because of its well solvated PAA-graft chain, although PE-*g*-AA is easily separated from the solution.

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EXPERIMENTAL

Materials. PAA was obtained by radical polymerization of acrylic acid (mol weight = 8×10^5). Commercially available PE powder (32–48 mesh, Sholex 6050, Showa Denko Co.) and poly(isobutylene oxide) (PIBO) powder (Nippon Carbide Co.) were used as trunk polymers. Special grade samarium nitrate and cupric nitrate were used. 2,7-Bis(2-arsenophenylazo)-1,8-dihydroxy-naphthalene-3,6-disulfonic acid (arsenazo III) of analytical grade (Dote) was used as colorimetric reagent for Sm ion. Acrylic acid and Mohr's salt were reagent grade.

Irradiation and Grafting Procedure. The PE powder (10 g) was irradiated at -78°C by being passed under the electron beams of a cascade type accelerator (Dynamitron IEA 3000-25-2, Radiation Dynamics, Ltd.) operating at beam energy of 2 MeV. Immediately after the irradiation, the powder was immersed in the aqueous monomer solution which was prepared from 50% acrylic acid and 0.25% Mohr's salt. The reaction was carried out under nitrogen atmosphere at 30°C . Grafted powder was taken out from the monomer solution, washed with water and 0.1*N* hydrochloric acid, and extracted with hot water using a Soxhlet apparatus. The amount of grafted PAA was taken to be equal to the measured increase in weight, and the degree of grafting was defined as a ratio of the weight increase to the initial PE weight.

Molecular Weight of the Grafted PAA. As trunk polymer, the PIBO powder was used. The crystallinity of PIBO (ca. 70%, reported by the manufacture) was quite near that of PE (65%). The PIBO trunk polymer was decomposed in perchloric acid at room temperature.⁶ After the complete decomposition of PIBO (24 h), the perchloric acid solution was poured into acetone. Only the PAA branch was precipitated. Molecular weight of the isolated PAA was estimated by viscometric measurement.

Adsorption of Metal Ions on PE-*g*-AA. A batch type equilibration procedure was used to determine the Sm and Cu ion amount uptaken from aqueous solution by the PE-*g*-AA powder. The pH value was kept constant with 0.1*N* $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$ buffer solution. The two phases, which consisted of the powder and ion solution, were shaken at room temperature for 24 h. After shaking, the two phases were separated, and the ion amount in the supernatant solution was determined. The Sm ion amount was determined by colorimetry with arsenazo III. The Cu ion amount was measured with atomic absorption spectrometer (Shimadzu AA 640-01). The ion amount in the supernatant subtracted from the amount initially added gave the amount of ion adsorbed on the powder.

Complex Formation Constants. All titrations were carried out in the way reported by Gold and Gregor⁷ and by us⁸ under nitrogen atmosphere using distilled CO_2 -free water. Hydrogen ion activities were determined with a glass electrode and TOA HM-15A type pH meter. Concentration of hydrogen ion was calculated from the hydrogen ion activities assuming that the hydrogen ion activity coefficient was the same as the mean activity coefficient of the supporting electrolyte (0.1*M* sodium nitrate). Acid-base equilibrium of the polymer was not rapidly attained, so that the pH value

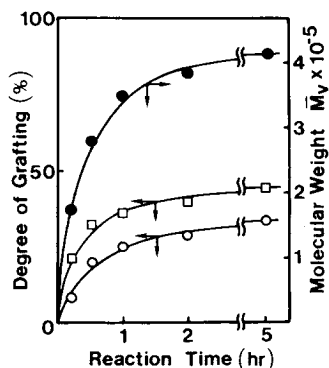


Fig. 1. Synthesis of PE-*g*-AA under the constant irradiation dose; 3 Mrad irradiated; grafted on PE (□) and PIBO (○,●).

of the solution was read after 1 h and 12 h of titration for PAA and PE-*g*-AA, respectively. Titration was repeated to check reproducibility.

EPMA Measurement. The ion distribution within the powder was measured with a electron probe X-ray microanalyzer (EPMA) (JEOL JXA-733).

RESULTS AND DISCUSSION

Figures 1 and 2 show influence of the irradiation dose and of the duration of the post-graft polymerization on the degree of grafting and the molecular weight of the PAA chain. The degree of grafting and the molecular weight increased with the reaction time under the constant irradiation dose (Fig. 1). On the other hand, the degree of grafting increased with the irradiation dose for the definite reaction time, although the molecular weight of the graft chain remained constant (Fig. 2). It is known that concentration of the radicals in irradiated polymers increased with dose at first and after a certain dose reached a saturated value.⁹ The result in Figure 2 agreed with this behavior of radiation induced polymerization. Anyhow, it is concluded that the molecular weight of the graft chain depends on the reaction time and the number of it on the irradiation dose. The desired PE-*g*-AA was

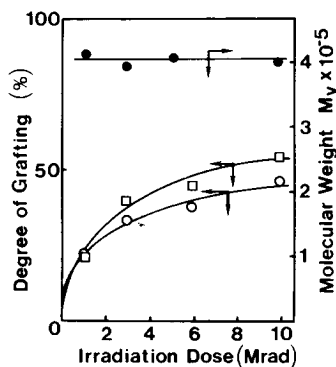


Fig. 2. Synthesis of PE-*g*-AA with the definite reaction time; 5 h reacted, grafted on PE (□) and PIBO (○,●).

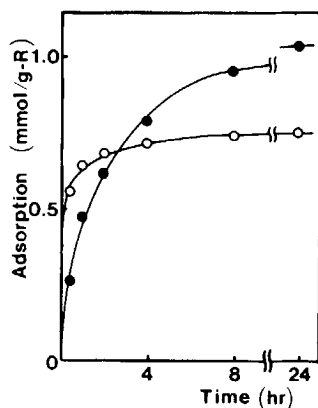


Fig. 3. Adsorption of Sm^{3+} with PE-g-AA powder; in pH 5.5 $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$ buffer; [ligand]/[metal] = 1; (○) Sm^{3+} ; (●) Cu^{2+} .

prepared by changing the polymerization conditions and provided to the following study.

The time curve of Sm ion adsorption on PE-g-AA is shown in Figure 3, with that of the Cu ion adsorption. The adsorption rate of Sm ion was larger than that of Cu ion and the main adsorption was completed within 1 h, although the saturated amount of the adsorption was larger for Cu ion. It is considered that Sm ion is adsorbed onto the grafted PAA in the surface region of the powder and complexation of trivalent Sm ion with the well solvated PAA chain proceeds relatively fast.

The adsorbed powder was easily regenerated with dilute hydrochloric acid for 2 h. The desorbed amount of ions agreed with the adsorbed amount.

Figure 4 shows the adsorption yield of Sm and Cu ion from the solution containing each ion. Sm ion is relatively well uptaken at lower pH region,

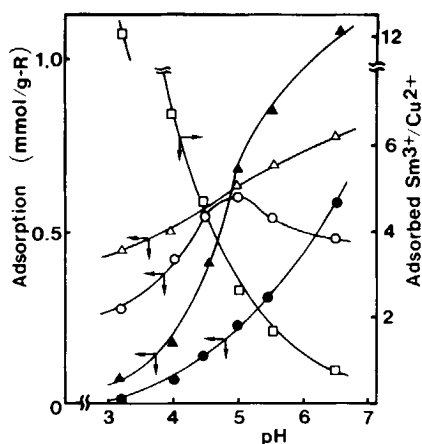


Fig. 4. Adsorption of Sm^{3+} and Cu^{2+} from the solution containing each ion, Sm^{3+} (Δ) and Cu^{2+} (\blacktriangle), and from the solution containing both Sm^{3+} and Cu^{2+} , Sm^{3+} (○) and Cu^{2+} (●).

while the adsorption amount of Cu ion increases with pH and overcomes that of Sm ion at higher pH region. Figure 4 also shows the same tendency for the adsorption from the solution containing both the equivalent ions, except that the Cu ion adsorption is suppressed even at a higher pH region. This result suggests that the complex formation constants of PE-*g*-AA with Sm ion is much larger than that with Cu although the number of adsorption site is larger for Cu ion. Anyhow, below pH 5 the ratio of ion adsorption capacity (Sm/Cu) for PE-*g*-AA is large enough to uptake Sm ion preferentially from the ion mixture solution. The separation of Sm and Cu ion was demonstrated by using a column (1 × 50 cm) packed with the PE-*g*-AA powder. After the packed column was conditioned with alkaline solution, equivalent mixture of Sm and Cu ion was adsorbed and eluted with 0.1N KCl-HCl buffer solution (pH 2.0); Sm and Cu ion were effectively separated.

The complex formation constants of PE-*g*-AA with Sm ion were determined by the modified Bjerrum method reported by Gregor.¹⁰ The calculated formation curves for the PE-*g*-AA-, PAA-, and propionic acid-Sm complexes are shown in Figure 5 with those for the corresponding Cu complexes, where \bar{n} is the average number of the complexed carboxylate groups per metal ion and [LH] is the concentration of carboxylic acid group. The formation curves of the polymer-Sm complexes, especially of PE-*g*-AA-Sm, are situated at lower carboxylic acid concentration, indicating that the Sm complexation proceeds easily for the polymeric carboxylic acids. The formation curves of PE-*g*-AA- and PAA-Sm appear to extrapolate to a maximum coordination number of 2, indicating the formation of Sm(carboxylate)₂.

Successive formation constants k_i and overall formation constants β_n ($= \prod_{i=1}^n k_i$) for the complexation of Sm and Cu ion are summarized in Table I. It is found that k_i and β_n for PE-*g*-AA are larger than those for PAA and much larger than those for the low molecular carboxylic acid. This phe-

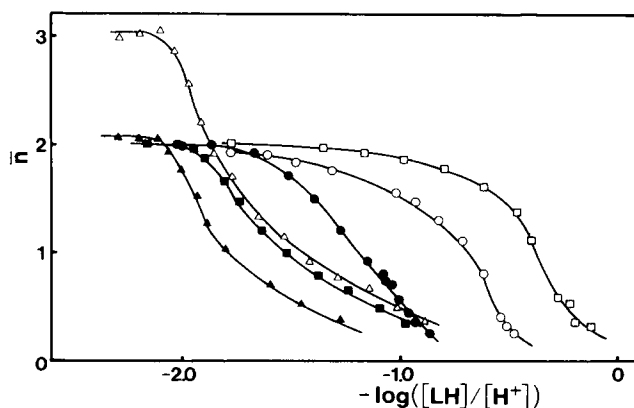


Fig. 5. Formation curves for the Sm complexes with PE-*g*-AA, PAA and propionic acid; Sm³⁺: (○) PE-*g*-AA; (□) PAA; (△) propionic acid; Cu²⁺: (●) PE-*g*-AA; (■) PAA; (▲) propionic acid.

TABLE I
Complexation Constants of Rare Earth Metal Ions with PE-*g*-AA and PAA

Ligand	Metal	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_n$
PE- <i>g</i> -AA	Sm ³⁺	6.2	5.9	—	12.1
	Cu ²⁺	5.9	5.2	—	11.1
PAA	Sm ³⁺	5.7	5.4	—	11.1
	Eu ³⁺	5.7	5.2	—	10.9
	Pr ³⁺	5.6	5.2	—	10.8
	Cu ²⁺	4.8	4.2	—	8.9
	Ni ²⁺	3.9	3.4	—	7.2
	Co ²⁺	3.7	3.1	—	6.8
Propionic acid	Sm ³⁺	3.9	3.2	2.9	10.0
	Eu ³⁺	3.8	3.2	2.9	9.9
	Pr ³⁺	3.7	3.1	2.9	9.7
	Cu ²⁺	3.4	2.9	—	6.4

nomenon is general with the polymer complex system, and can be explained by the assumption that the concentration of ligands is higher in the polymer domain, especially in the surface domain of the grafted polymer. Therefore, once the metal ion is attached to one group on the polymer chain, the other ligands coordinate more readily. k_i and β_2 for the Sm complexation are larger than those for the Cu ion: PE-*g*-AA forms a more stable complex with Sm ion than with Cu ion. The question still remained in Table I as to why the maximum coordination number is 2 for the trivalent Sm ion complex with PE-*g*-AA and PAA. It was assumed that the PAA chain could not easily form the Sm(carboxylate)₃ complex with its three carboxylic group due to the steric hindrance of the polymer chain and large Sm ion: The coordination chemistry of PAA-Sm will be reported in the following paper.¹¹

Figure 6 shows distribution of the adsorbed metal ions within the PE-*g*-AA powder measured by the X-ray microanalyzer. This indicates that Sm ion was adsorbed mainly on the surface region of the powder, although Cu

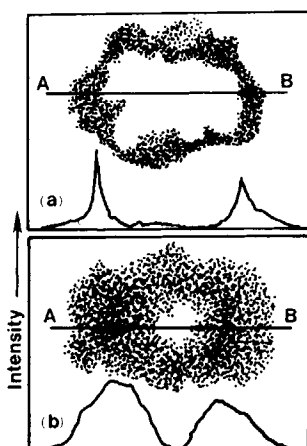


Fig. 6. Distribution of the adsorbed Sm³⁺ (a) and Cu²⁺ (b) within the PE-*g*-AA powder measured by EPMA.

ion was onto the inner region. It is considered that relatively large Sm ion is complexed only with the grafted PAA chain in the surface region, but, on the other hand, Cu ion is able to diffuse and complex into the inner region of the powder. This difference in the complexation site for Sm and Cu ion causes the difference in the adsorption rate and capacity shown in Figures 3 and 4. This consideration is supported by Figure 6: the ion distribution within the powder uptaken from the Sm-Cu mixture solution. At pH 3.3, Sm ion is adsorbed well in the surface region of the powder, and the Sm adsorption suppressed the Cu ion adsorption. On the contrary, at pH 6.5, Cu ion is able to diffuse into the inner region and more adsorbed than Sm ion is; this agrees with the result in Figure 4. PE-*g*-AA forms the complexes with Sm ion efficiently by the grafted PAA chain in the surface region.

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