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Surface Grafting onto Barium Sulfate: Polymerization of Acrylamide Initiated by the System Consisting of Alcoholic Hydroxyl Groups on the Surface and Ceric Ion

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SURFACE GRAFTING ONTO BARIUM SULFATE: POLYMERIZATION OF ACRYLAMIDE INITIATED BY THE SYSTEM CONSISTING OF ALCOHOLIC HYDROXYL GROUPS ON THE SURFACE AND CERIC ION

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ABSTRACT

To modify the surface of barium sulfate, the grafting of polymers onto the surface by the polymerization of acrylamide (AAm) initiated by the system consisting of ceric ion and alcoholic hydroxyl groups on the surface was investigated. Barium sulfate modified by 12-hydroxystearate ($\text{BaSO}_4\text{-HS}$) was prepared by the reaction of barium chloride with sodium sulfate containing a small amount of sodium 12-hydroxystearate. The presence of 12-hydroxystearate groups on the BaSO_4 surface was confirmed by XPS analysis and infrared spectra. It was found that the graft polymerization of AAm is initiated by the system consisting of ceric ion and $\text{BaSO}_4\text{-HS}$ to give poly(AAm)-grafted BaSO_4 . This indicated that the grafted polymer chains are propagated from surface radicals formed by the redox reaction of ceric ion with 12-hydroxystearate groups on the surface. The polymerization rate (R_p) of AAm initiated by the redox system was given by

$$R_p = k[\text{AAm}][\text{Ce(IV)}][\text{BaSO}_4\text{-HS}]$$

where k is constant, $[\text{AAm}]$ is AAm concentration, $[\text{Ce(IV)}]$ is ceric ion concentration, and $[\text{BaSO}_4\text{-HS}]$ is $\text{BaSO}_4\text{-HS}$ concentration. The result suggested that in such an initiating system, the unimolecular termination

of growing polymer radicals from the surface of BaSO_4 proceeds preferentially. Furthermore, by grafting of poly(AAm) onto the BaSO_4 -HS surface, the wettability of the surface was found to turn from hydrophobic to hydrophilic.

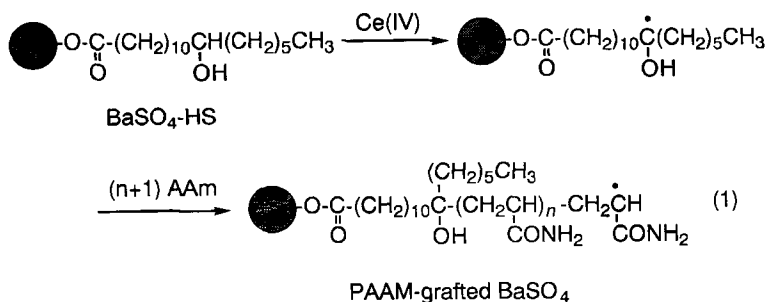
INTRODUCTION

In a series of papers we reported the grafting of polymers onto inorganic powder surfaces by the polymerization of various monomers initiated by initiating groups introduced onto these surfaces [1-3]. For instance, radical [4-6], cationic [7], and anionic [8] graft polymerizations onto a silica surface were successfully initiated by azo and peroxyester, acylium perchlorate, and potassium carboxylate groups introduced onto a surface, respectively. Furthermore, the redox graft polymerizations of vinyl monomers onto carbon black and silica surfaces are also initiated by a system consisting of ceric ion and alcoholic hydroxyl groups introduced onto these surfaces [9, 10].

By grafting polymers onto inorganic powder surfaces, the dispersibility of the powder in solvents and in polymer matrices was remarkably improved [1-3]. This is due to the fact that the grafted polymer chains on the surface interfere with the aggregation of particles and increase the wettability with dispersing solvents and polymer matrices.

On the other hand, the preparation of 12-hydroxystearate-modified barium sulfate by the reaction of barium chloride with sodium sulfate containing a small amount of sodium hydroxystearate was reported by Kotani et al. [11].

Therefore, in the present paper the grafting of poly(AAm) onto a barium sulfate surface by the redox graft polymerization of AAm initiated by a system consisting of ceric ion and 12-hydroxystearate groups on the surface was investigated (Eq. 1):



EXPERIMENTAL

Materials

Guaranteed reagent-grade barium chloride and sodium sulfate obtained from Kanto Chemical Ind. Co., Ltd., Japan, were used without further purification. 12-Hydroxystearic acid obtained from Kanto Chemical Ind. Co. Ltd., Japan, and

sodium lauryl sulfate obtained from Wako Pure Chemical Ind. Co., Ltd., Japan, were also used without further purification.

Sodium 12-hydroxystearate was prepared by the neutralization of 12-hydroxystearic acid with sodium hydroxide in methanol at 85°C.

Acrylamide (AAM) was recrystallized from benzene, sublimed under reduced pressure, and stored in a desiccator. Guaranteed reagent-grade ceric ammonium nitrate and nitric acid were used without further purification.

Preparation of Barium Sulfate Modified by 12-Hydroxystearate

Barium sulfate modified by 12-hydroxystearate (BaSO₄-HS) was prepared by the reaction of barium chloride with sodium sulfate containing a small amount of sodium 12-hydroxystearate according to the method of Kotani et al. [11]. A typical example is as follows. Into a flask that contained a 150 cm³ aqueous solution of 21.9 g (0.105 mol) of barium chloride, 100 cm³ aqueous solution of 14.2 g (0.10 mol) of sodium sulfate containing 0.80 g (0.1 mmol) of sodium 12-hydroxystearate was added under stirring. The reaction was conducted at 85°C for 1 hour. The precipitate formed was filtered, washed repeatedly with pure water and methanol, and dried in vacuo at 100°C for 24 hours.

Graft Polymerization of Acrylamide

Into a 100 cm³ flask, 0.50 g barium sulfate, 0.05 g sodium lauryl sulfate, and 9.0 cm³ of a 4.7 mol/dm³ aqueous solution of AAm were charged. After deaeration of the mixture by bubbling nitrogen, 1.0 cm³ of 0.2 mol/dm³ solution of ceric ammonium nitrate in 1 N nitric acid was added. The polymerization was conducted at 40°C with stirring by a magnetic stirrer under nitrogen.

After the reaction, the content of the flask was poured into an excess of acetone to precipitate the polymer containing barium sulfate. The conversion was determined by

$$\text{conversion (\%)} = \frac{\text{precipitate (g)} - \text{barium sulfate (g)}}{\text{AAm charged (g)}} \times 100$$

Percentage of Grafting

In order to isolate poly(AAm)-grafted barium sulfate, the product was dispersed in water and the dispersion was centrifuged at 1.0×10^4 rpm until the barium sulfate precipitated completely. Subsequently, the supernatant solution was removed and the precipitated barium sulfate was dispersed in water again and centrifuged. The procedures were repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting was calculated by

$$\text{grafting (\%)} = \frac{\text{poly(AAm) grafted (g)}}{\text{barium sulfate charge (g)}} \times 100$$

Wettability of Poly(AAm)-Grafted Barium Sulfate

The wettability of poly(AAm)-grafted barium sulfate surface was estimated by the penetrating rate of water through a column packed with modified BaSO₄. A

typical example is as follows. Into a glass column (inside diameter: 2 mm), 0.3 g poly(AAm)-grafted BaSO_4 (or $\text{BaSO}_4\text{-HS}$) was packed and water was added from the top of the column. Then the penetrating rate of water through the column was determined.

Instruments for IR and XPS Analysis

The infrared spectra of polymer-grafted and ungrafted barium sulfate were recorded on a Hitachi Infrared Spectrophotometer, Model 270-30, using KBr pellets. A Kratos X-ray Photoelectron Spectrometer, Model XSAM-800, was used for the surface analysis of modified barium sulfate.

RESULTS AND DISCUSSION

Preparation of Barium Sulfate Modified by 12-Hydroxystearate

Kotani et al. reported that barium sulfate modified by 12-hydroxystearate is readily prepared by the reaction of barium chloride with sodium sulfate containing a small amount of sodium 12-hydroxystearate [11]. Therefore, barium sulfate modified by 12-hydroxystearate ($\text{BaSO}_4\text{-HS}$) was prepared according to the above method. Figure 1 shows the infrared spectra of unmodified BaSO_4 and $\text{BaSO}_4\text{-HS}$. The infrared spectra of $\text{BaSO}_4\text{-HS}$ shows absorptions at 2928, 2856, 1440, and 1404 cm^{-1} , characteristic of methylene and methyl groups.

Table 1 shows the results of surface analysis of $\text{BaSO}_4\text{-HS}$ and unmodified BaSO_4 by XPS. The presence of carbon on the surface of $\text{BaSO}_4\text{-HS}$ was confirmed by the results, which are different from those of unmodified BaSO_4 . The atomic percent of carbon of $\text{BaSO}_4\text{-HS}$ is high in comparison with that of sulfur. This indicates the localization of 12-hydroxystearate groups on the BaSO_4 surface.

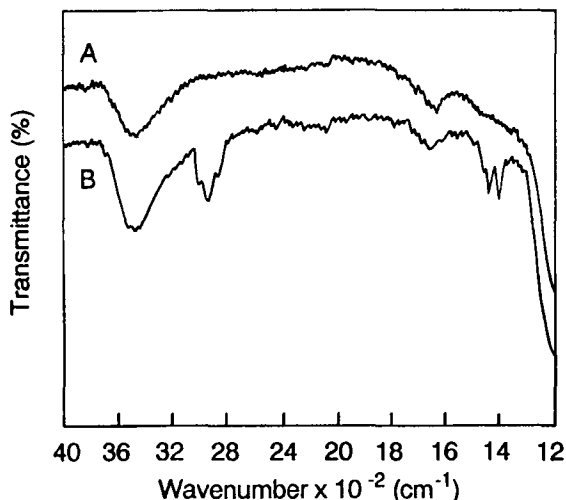


FIG. 1. Infrared spectra of (A) unmodified BaSO_4 and (B) BaSO_4 modified by 12-hydroxystearate.

TABLE 1. Surface Analysis of Barium Sulfate Modified with 12-Hydroxystearate by XPS

Element		Content, atomic %	
		Unmodified BaSO ₄	BaSO ₄ -HS
Carbon	C _{1s}	1.0	16.0
Oxygen	O _{1s}	73.2	52.2
Sulfur	S _{2p}	8.3	19.0
Barium	Ba _{3d}	17.5	12.8

The average particle sizes of unmodified BaSO₄ and BaSO₄-HS were determined to be 1.0 and 0.3 μm, respectively, by SEM. This indicates that sodium 12-hydroxystearate interferes with the growth of barium sulfate crystals [11].

Initiation of Polymerization by Ceric Ion/BaSO₄-HS System

It is well known that polymerizations of vinyl monomers are initiated by system consisting of ceric ion and a reducing agent such as alcohols [12], aldehydes [13], and amines [14]. Ceric ion/alcohol systems have been used for the graft polymerization of vinyl monomers to polymers having hydroxyl groups [15].

We reported that the redox graft polymerization of vinyl monomers onto carbon black and a silica surface is initiated by a system consisting of ceric ion and alcoholic hydroxyl groups introduced onto these surfaces [9, 10]. In the polymerization, grafted polymer chains were propagated from the surface radicals formed by the redox reaction of surface alcoholic hydroxyl groups with ceric ions.

Therefore, the graft polymerization of AAm initiated by a system consisting of ceric ion and BaSO₄-HS was investigated. The results are shown in Table 2. In the polymerization, sodium lauryl sulfate was added to the reaction system to improve the surface wettability of BaSO₄-HS to water (reaction solvent).

TABLE 2. Polymerization of AAm Initiated by the Redox System Consisting of BaSO₄-HS and Ceric Ion^a

BaSO ₄	Ce(IV) solution, ^b cm ³	Conversion, %	Grafting, %
None	—	0	—
None	1.0	12.1	—
Unmodified	—	0	—
Unmodified	1.0	22.8	0
BaSO ₄ -HS	—	0	—
BaSO ₄ -HS	1.0	38.6	4.6

^aBaSO₄-HS, 0.50 g; AAm aqueous solution (4.7 mol/dm³), 9.0 cm³; sodium lauryl sulfate, 0.05 g; 40°C; 5 hours.

^b0.20 mol/dm³ in 1 N HNO₃ solution.

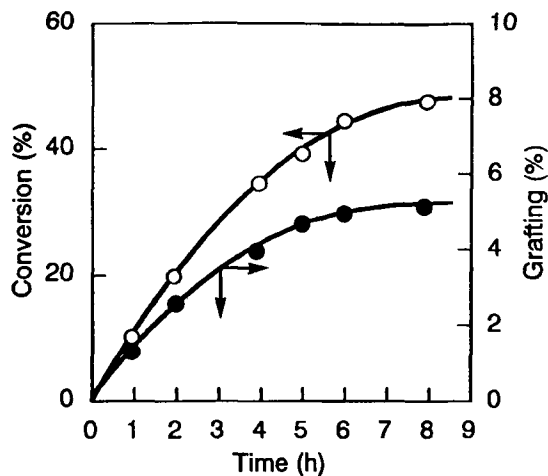


FIG. 2. Graft polymerization of AAm initiated by the system consisting of BaSO_4 -HS and ceric ion. BaSO_4 -HS, 0.50 g; AAm aqueous solution (4.7 mol/dm^3), 9.0 cm^3 ; Ce(IV) solution (0.20 mol/dm^3 in 1 N HNO_3 solution), 1.0 cm^3 ; sodium lauryl sulfate, 0.05 g; 40°C .

As shown in Table 2, the polymerization of AAm was initiated by ceric ion alone, but the rate of the polymerization was small. In the absence of ceric ion, BaSO_4 -HS had no ability to initiate polymerization. Polymerization of AAm was found to be initiated by a system consisting of BaSO_4 -HS and ceric ion. A system consisting of unmodified BaSO_4 and ceric ion had the ability to initiate polymerization, but the polymerization rate of the system was considerably smaller than that using BaSO_4 -HS.

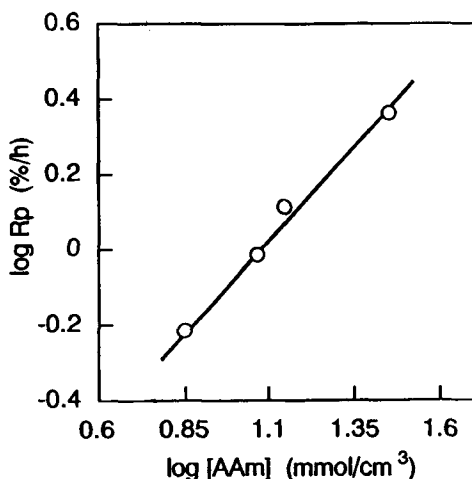


FIG. 3. Relationship between polymerization rate (R_p) and AAm concentration ($[\text{AAm}]$). Polymerization conditions are given in Fig. 2.

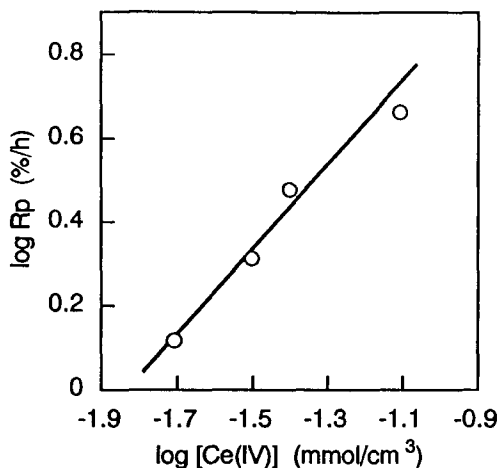


FIG. 4. Relationship between polymerization rate (R_p) and ceric ion concentration ($[Ce(IV)]$). Polymerization conditions are given in Fig. 2.

On the other hand, although poly(AAm) was grafted onto the surface of $BaSO_4$ -HS, no grafting of polymers onto unmodified $BaSO_4$ was observed. These results indicate that in a system consisting of ceric ion and $BaSO_4$ -HS, polymerization is initiated by the surface radicals formed by the redox reaction of alcoholic hydroxyl groups on $BaSO_4$ -HS with ceric ion, and grafted polymer chains are propagated from the surface (Eq. 1).

In the system of unmodified $BaSO_4$, polymerization is initiated by sulfate anion radicals formed by electron transfer from the sulfate anion to the ceric ion

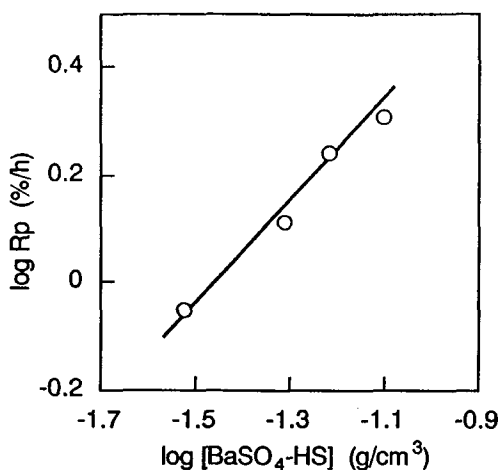


FIG. 5. Relationship between polymerization rate (R_p) and $BaSO_4$ -HS concentration ($[BaSO_4$ -HS]). Polymerization conditions are given in Fig. 2.

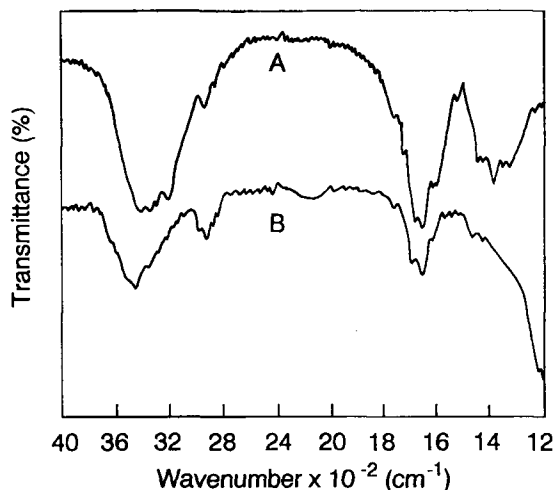


FIG. 6. Infrared spectra of (A) poly(AAm) and (B) poly(AAM)-grafted BaSO_4 .

because the system consisting of sodium sulfate and ceric ion has the ability to initiate the radical polymerization of AAm [16].

Figure 2 shows time-conversion and time-grafting curves in the polymerization of AAm initiated by a system consisting of BaSO_4 -HS and ceric ion. The percentage of grafting of poly(AAm) onto the surface increased with time up to 6 hours. This may be due to blocking of surface functional groups by grafted polymer chains.

Effect of the Concentration of Monomer, Ceric Ion, and BaSO_4 -HS on the Polymerization Rate

The effect of monomer concentration ($[\text{AAm}]$) on the polymerization rate (R_p) initiated by a system consisting of BaSO_4 -HS and ceric ion was investigated. The result is shown in Fig. 3, which clearly shows that the polymerization rate is directly proportional to the monomer concentration.

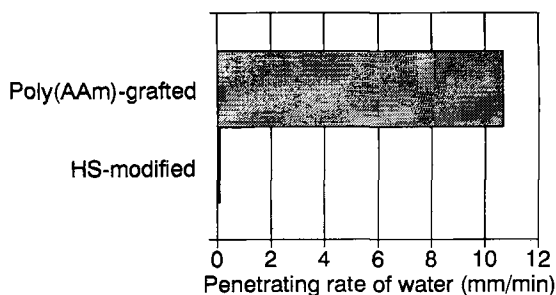


FIG. 7. Penetrating rate of water through the column packed with BaSO_4 -HS and poly(AAm)-grafted BaSO_4 .

The relationship between R_p and ceric ion concentration ($[Ce(IV)]$) was determined under constant concentrations of monomer and $BaSO_4$ -HS (Fig. 4). Figure 4 shows that the polymerization rate has a first order dependence on the ceric ion concentration.

Figure 5 shows the effect of $BaSO_4$ -HS concentration ($[BaSO_4$ -HS]) on the polymerization rate. It was found that the polymerization rate also has a first order dependence on the $BaSO_4$ -HS concentration.

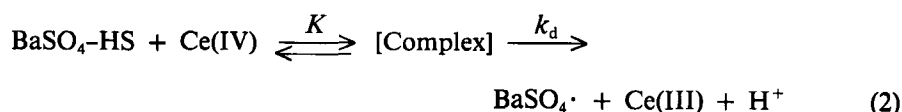
Therefore, the polymerization rate of AAm initiated by a system consisting of $BaSO_4$ -HS and ceric ion was found to be given by

$$R_p = k[AAm][Ce(IV)][BaSO_4\text{-HS}]$$

Mechanism of Initiation

The following reaction mechanism is suggested by the above results.

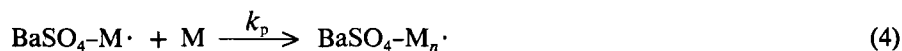
Primary radical formation:



Initiation:



Propagation:



Unimolecular termination:



By applying the steady-state principle to the active intermediates, the following equation was derived:

$$R_p = K \frac{k_p k_d}{k_t} [AAm][Ce(IV)][BaSO_4\text{-HS}]$$

The experimental results agree with the above equations. These results suggest that the unimolecular termination of growing polymer radicals from the surface of $BaSO_4$ preferentially proceeded in the initiating system. The same tendency was observed in radical graft polymerization initiated by azo and peroxide groups introduced onto a powder surface [4, 17]. This may be due to the fact that the bimolecular termination of polymer radicals is inhibited because the growing polymer radicals on the surface are fixed on the solid (powder) surface.

Characterization of Poly(AAm)-Grafted $BaSO_4$

Figure 6 shows the infrared spectra of poly(AAm) and poly(AAm)-grafted $BaSO_4$. The infrared spectra of poly(AAm)-grafted $BaSO_4$ exhibits absorptions at 1670 and 1640 cm^{-1} , characteristic of the amide bond of poly(AAm).

Although BaSO₄-HS powder floated on water because of the hydrophobic nature of the surface, poly(AAm)-grafted BaSO₄ readily disperses in water.

The penetrating rate of water through a column packed with poly(AAm)-grafted BaSO₄ was compared with that of BaSO₄-HS. As shown in Fig. 7, water readily penetrated through a column packed with poly(AAm)-grafted BaSO₄ but scarcely penetrates through a column packed with BaSO₄-HS.

These results indicate that by grafting poly(AAm) onto a BaSO₄-HS surface, the wettability of the surface changes from hydrophobic to hydrophilic.

CONCLUSIONS

1. BaSO₄ modified by alcoholic hydroxyl groups was obtained by reaction of barium chloride with sodium sulfate containing a small amount of sodium 12-hydroxystearate.
2. The redox graft polymerization of AAm was successfully initiated by a system consisting of ceric ion and BaSO₄-HS to give poly(AAm)-grafted BaSO₄.
3. By grafting poly(AAm) onto the BaSO₄-HS surface, the wettability of the surface changed from hydrophobic to hydrophilic.

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