

Graft Polymerization of Acrylamide from Ultrafine Silica Particles by Use of a Redox System Consisting of Cerium Ion and Reducing Groups on the Surface

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ABSTRACT: Radical graft polymerization from ultrafine silica surface was investigated. A redox system consisting of ceric ion and the silica particles carrying reducing groups, such as alcoholic hydroxyl, amino, and mercapto groups, was capable of initiating the radical polymerization of acrylamide (AAM). The introduction of alcoholic hydroxyl groups onto the surface was achieved by the treatment of the silica with 3-glycidoxypropyltrimethoxysilane in acidic condition in water. Amino or mercapto groups were introduced onto the silica by reactions of surface silanol groups with 3-aminopropyltriethoxysilane or 3-mercaptoethyltrimethoxysilane, respectively. The initiating ability of the redox system changed, depending on the reducing groups on the silica surface, in the following order: alcoholic hydroxyl group < amino group < mercapto group. In the above redox polymerization, polyacrylamide was grafted onto the silica based on the propagation of the polymer from the radicals formed by the reaction of ceric ion with alcoholic hydroxyl, amino, or mercapto groups. The percentage of grafting onto the silica reached about 25%. The silica obtained from the redox graft polymerization gave a stable colloidal dispersion in water.

KEY WORDS Ultrafine Particle / Silica / Radical Grafting / Redox Polymerization / Cerium Ion / Acrylamide / Silane Coupling Agent / Colloidal Dispersion /

In the preceding paper, we reported the grafting of poly(propylene glycol) onto an ultrafine ferrite particle by the reaction of hydroxyl groups on the surface with isocyanate-capped poly(propylene glycol).¹ The percentage of grafting, however, was less than 15%. As described in the review paper, it is required to initiate the graft polymerization from an active site (initiating group) introduced onto a particle surface to obtain polymer-grafted carbon black with a higher percentage of grafting.² For instance, in the anionic ring-opening polymerization of β -propiolactone (PL) initiated by potassium carboxylate groups on

carbon black, the percentage of grafting of poly-PL increased to about 100%.³

We succeeded in the radical graft polymerization of water-soluble vinyl monomers onto carbon black initiated by a redox system consisting of ceric ions and alcoholic hydroxyl groups on the surface.^{4,5} In the redox polymerization of acrylamide (AAM), poly-AAM was effectively grafted from carbon black based on the propagation of the polymer from radicals formed by the reaction of ceric ions with alcoholic hydroxyl groups.

In the present paper, we report the graft polymerization of AAM from an ultrafine silica

methanol for 24 h and dried *in vacuo*.

Polymerization Procedures

Into a flask, 0.50 g of silica and 9.0 cm³ of 4.7 mol dm⁻³ aqueous solution of AAm were charged. After deaeration of the mixture by bubbling nitrogen, 1.0 cm³ of 0.2 mol dm⁻³ solution of ceric ammonium nitrate in 1 mol dm⁻³ nitric acid was added. The polymerization was conducted at 30°C with stirring by a magnetic stirrer under dry nitrogen. After the reaction, the reaction mixture was poured into a large excess of acetone to precipitate the polymer containing silica and the product was dried *in vacuo* at 45°C. The conversion was determined by the following equation:

$$\text{Conversion (\%)} = \frac{\text{Precipitate (g)} - \text{Silica (g)}}{\text{AAm used (g)}} \times 100$$

Percentage of Grafting of Poly-AAm

To isolate poly-AAm-grafted silica, the product was dispersed in distilled water and the dispersion was centrifuged at 3.0×10^3 rpm until silica particles precipitated completely. The silica precipitated was dispersed again in water and centrifuged. The procedure was repeated until no polymer was detected in the supernatant solution. The percentage of grafting onto the surface was calculated by the following equation:

$$\text{Percentage of grafting (\%)} = \frac{\text{Poly-AAm grafted (g)}}{\text{Silica used (g)}} \times 100$$

Stability of Dispersion of Poly-AAm-Grafted Silica

Poly-AAm-grafted silica (0.30 g) was dispersed in 100 cm³ of distilled water with a magnetic stirrer and the dispersion was allowed to stand at room temperature. After a definite time, 5.0 cm³ of dispersion liquid was taken out with a pipette and the content of silica dispersed was determined. The stability of dispersion was determined by the following equation:

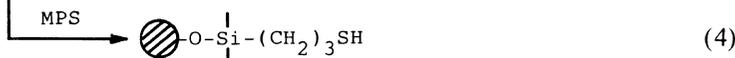
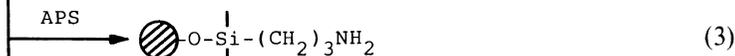
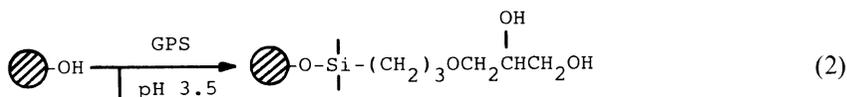
$$\text{Stability of dispersion (\%)} = \frac{\text{Silica dispersed after standing (g)}}{\text{Silica dispersed before standing (g)}} \times 100$$

RESULTS AND DISCUSSION

Introduction of Alcoholic Hydroxyl, Amino, or Mercapto Groups onto the Silica Surface

Introduction of alcoholic hydroxyl groups onto the silica surface was achieved by hydrolysis of the glycidoxy group introduced by the coupling of GPS (eq 2). It has been reported that mildly acidic conditions (pH = 3.5) used in coupling of GPS to silica are sufficient to convert the glycidoxy group to alcoholic hydroxyl group during the coupling reaction.⁸

Amino or mercapto groups can be introduced onto the silica surface by reaction of their silanol groups with APS or MPS, respectively (eq 3 and 4).



The amounts of alcoholic hydroxyl, amino, and mercapto groups introduced onto the surface were determined by elemental (carbon) analysis. The results are shown in Table I. The amount of alcoholic hydroxyl groups on the surface was estimated based on the assumption that a glycidoxo group produces two alcoholic hydroxyl groups (primary and secondary alcohol) (eq 2).

Table I clearly shows that alcoholic hydroxyl, amino, or mercapto groups can be introduced onto the silica surface. The amounts of functional groups decreased in the following order: alcoholic hydroxyl group > amino group > mercapto group. Particularly, GPS was found to have high reactivity toward

silanol groups on the silica surface under the acidic reaction conditions.

Initiation by a Redox System Consisting of Ceric Ions and Silica Carrying Alcoholic Hydroxyl Groups

It has been reported that vinyl polymerizations are initiated by ceric ions in combination with organic reducing agents such as alcohols,^{9,10} amines,¹¹ and thiols.¹² A redox system, particularly, ceric ion/alcohol system, has been used for the grafting of vinyl monomers onto poly(vinyl alcohol) and starch.¹³

The polymerization of AAm was carried out by a redox system consisting of ceric ions and silica carrying alcoholic hydroxyl groups (Silica-R-OH) under various conditions. The results are shown in Table II.

The polymerization of AAm in the absence of ceric ions was not initiated by either untreated silica (No. 2) or Silica-R-OH alone (No. 4). The system consisting of ceric ions and untreated silica has no ability to initiate the polymerization (No. 3), because the conversion of the system is almost equal to that of ceric ions alone (No. 1).

On the contrary, the polymerization of AAm was found to proceed in the coexistence of ceric ions and Silica-R-OH (No. 5). These results suggest that the radical formed by the redox reaction of ceric ions with alcoholic hydroxyl groups on Silica-R-OH initiates the polymerization.

Initiating Activity of a Redox System Consisting of Ceric Ions and Silica Carrying Reducing Groups

The effects of reducing groups on the initiating activity of redox polymerization for AAm were investigated.

Figure 1 shows the time conversion curves of the polymerization of AAm initiated by a redox system consisting of ceric ions and silica carrying reducing groups (Silica-R-OH, Silica-R-NH₂, and Silica-R-SH). This indicates that the polymerization was initiated by Silica-R-

Table I. Hydroxyl, amino, or mercapto groups introduced onto the surface of ultrafine particles

Silica	Silane coupling agent fixed ^a	Reducing groups ^b
	meq g ⁻¹	meq g ⁻¹
Silica-R-OH	0.36	0.72
Silica-R-NH ₂	0.31	0.31
Silica-R-SH	0.26	0.26

^a Determined by elemental (carbon) analysis.

^b The amount of hydroxy groups was estimated based on the assumption that a glycidoxo group produces two hydroxy groups.

Table II. Polymerization of AAm under various conditions

No.	Silica	Ce ⁴⁺ soln. ^a	Conversion ^b
		cm ³	%
1	None	1.0	5.0
2	Untreated	—	0
3	Untreated	1.0	4.9
4	Silica-R-OH	—	0
5	Silica-R-OH	1.0	9.5

^a 0.2 mol dm⁻³ of ceric ammonium nitrate solution in 1.0 mol dm⁻³ nitric acid.

^b Silica, 0.50 g; AAm aqueous solution (4.7 mol dm⁻³), 9.0 cm³; 30°C; 24 h.

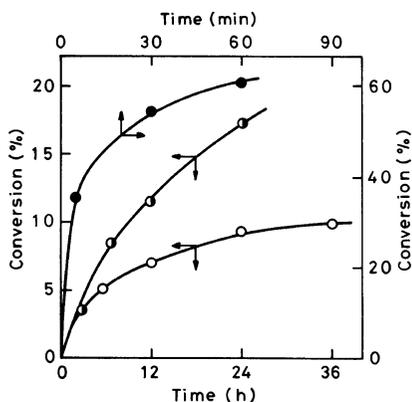


Figure 1. Polymerization of AAm initiated by a redox system consisting of ceric ion and reducing groups on silica surface. Silica, 0.50 g; AAm aqueous solution (4.7 mol dm^{-3}), 9.0 cm^3 ; Ce^{4+} solution, 1.0 cm^3 ; 30°C . (●), Silica-R-SH; (◐), Silica-R-NH₂; (○), Silica-R-OH.

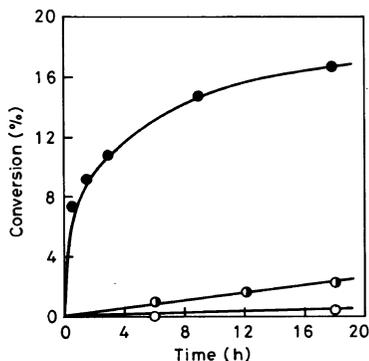


Figure 2. Polymerization of AAm initiated by a redox system consisting of ceric ion and Silica-R-NH₂ or Silica-R-SH at 10°C . Polymerization conditions are given in Figure 1. (●), Silica-R-SH; (◐), Silica-R-NH₂; (○), Silica-R-OH.

NH₂ and Silica-R-SH in combination with ceric ions as well as Silica-R-OH.

Based on the above results, it is concluded that the polymerization of AAm is initiated by a redox system consisting of ceric ion and reducing groups on the silica.

It is interesting that, in spite of the low content of mercapto groups, a redox system consisting of ceric ions and Silica-R-SH has very high activity for initiation. Figure 2 shows

the results of the polymerization of AAm initiated by a redox system consisting of ceric ion and Silica-R-OH, Silica-R-NH₂, and Silica-R-SH at 10°C . The redox system consisting of ceric ion and Silica-R-SH was found to have high initiating activity even at 10°C .

On the contrary, in spite of its higher content of hydroxyl groups, the system of Silica-R-OH scarcely had initiating ability of the polymerization at 10°C . Therefore, it is concluded that the initiating activity of reducing groups on silica surface decreases in the following order: mercapto group > amino group > alcoholic hydroxyl group.

It is reported that in redox polymerization using RCH₂OH and ceric ion, polymerization is initiated by both carbon (RCHOH) and oxygen radical (RCH₂O·).¹³ Although little is known about the mechanism of initiation by a redox system consisting of ceric ion and amines or thiols, the difference in the initiating activity of these redox systems is due to the reducing activity of these groups.

The bond energy of C-H (O-H), N-H, and S-H bond gave a clue for estimating the reducing activity of these groups. The bond energy of these groups is known to decrease in the following order: C-H (O-H) > N-H > S-H.¹⁴ However, further detailed investigation on the oxidation-reduction potentials of these reducing groups is required to estimate the reducing activity more exactly.

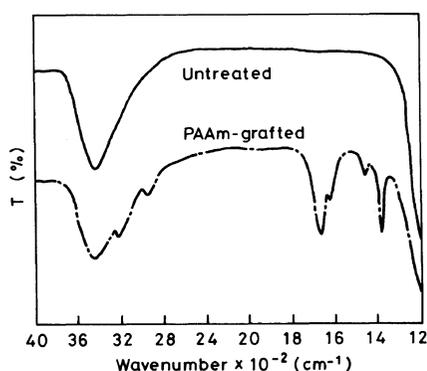
Proof of Grafting onto Silica

To assess the grafting of poly-AAm from the silica, the percentage of grafting was determined. The results are summarized in Table III. As shown in Table III, the percentage of grafting onto Silica-R-OH, Silica-R-NH₂, and Silica-R-SH reached 10–24%. To evaluate the adsorption of poly-AAm onto the silica, the silica was mixed with poly-AAm in water at 30°C for 20 h. The amount of the polymer remaining on the surface after the washing with water was determined to be 2.5%. This value is much less than that of the polymer

Table III. Percentage of grafting of poly-AAm from silica surface^a

Silica	Time	Conversion	Percentage of grafting
	h	%	%
Untreated	24	4.9	0
Silica-R-OH	24	9.5	10.5
Silica-R-NH ₂	24	17.0	23.9
Silica-R-SH	0.08	36.0	24.3

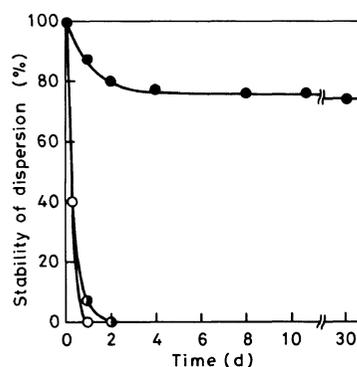
^a Polymerization conditions are given in Table II.

**Figure 3.** IR spectra of ungrafted and poly-AAm-grafted silica.

grafted onto the silica surface. During the polymerization in the coexistence of untreated silica and ceric ions, no grafting of poly-AAm was observed.

Therefore, it is concluded that poly-AAm is grafted from the silica based on the propagation of the polymer from the radical formed on the surface. The redox graft polymerization is accompanied by the formation of ungrafted poly-AAm. This may be due to a chain transfer reaction of growing polymer radical.

Figure 3 shows the IR spectra of untreated and poly-AAm-grafted silica. In the IR spectra of poly-AAm-grafted silica, a new absorption at 1668 cm^{-1} , characteristic of amide bond of poly-AAm, and an absorption at 3190 cm^{-1} , corresponding to stretching of the N-H bond,

**Figure 4.** Stability of dispersion of poly-AAm-grafted silica in water at room temperature. (●), PAAm-grafted silica; (●), PAAm-adsorbed silica; (○), ungrafted silica.

were observed. On the other hand, the IR spectra of silica, which was washed with water after adsorption of poly-AAm, was the same that of an untreated one. These results also indicate that poly-AAm is grafted onto the surface of silica.

Stability of Dispersion of Poly-AAm-Grafted Silica

The dispersibility of poly-AAm-grafted silica in water was compared with that of untreated and poly-AAm-adsorbed ones. The results are shown in Figure 4.

Although untreated silica precipitated completely within 1 day, poly-AAm-grafted silica gave a stable colloidal dispersion in water. The stability of dispersion of silica was scarcely improved by adsorption of poly-AAm onto the surface. These results suggest that poly-AAm chains grafted onto the silica surface interfere with the aggregation of silica particles. Accordingly, the dispersibility of the silica in water was remarkably improved by grafting of poly-AAm onto the surface.

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