Graft Polymerization of Vinyl Monomers by Peroxyester Groups Introduced onto the Surface of Inorganic Ultrafine Particles

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ABSTRACT: The radical graft polymerization of vinyl monomers from inorganic ultrafine particles, such as silica, titanium oxide, and ferrite, initiated by peroxyester groups introduced onto their surfaces was investigated. The introduction of peroxyester groups onto the ultrafine particles was achieved by reactions of hydroperoxide with acid anhydride groups, introduced by the reaction of hydroxyl groups on the surface with 4-trimethoxysilyltetrahydrophthalic anhydride. The amounts of diisopropylbenzene peroxyester groups introduced onto ultrafine silica, titanium oxide, and ferrite were determined to be 0.11, 0.07, and 0.05 mmol g^{-1}, respectively. The polymerization of vinyl monomers, such as methyl methacrylate (MMA) and styrene, or copolymerization of divinyl ether with maleic anhydride was initiated by peroxyester groups introduced onto ultrafine particles. During the polymerization, the corresponding polymer was effectively grafted onto these surfaces through the propagation of the polymer from the surface radicals formed by decomposition of the peroxyester groups; the percentage of grafting was 45—50%. Furthermore, the rate of the polymerization was found to be accelerated by the addition of reducing agents to the polymerization system. Polymer-grafted ultrafine particles gave a stable colloidal dispersion in organic solvent for grafted polymer.

KEY WORDS   Inorganic Ultrafine Particles / Surface Grafting / Silica / Titanium Oxide / Ferrite / Peroxyester Group / 4-Trimethoxysilyltetrahydrophthalic Anhydride / Redox Initiation / Dispersibility /

The grafting of polymers onto inorganic ultrafine particles was widely investigated to improve surface properties.[1,2] We succeeded in the surface grafting of inorganic ultrafine particles, such as silica, titanium oxide, and ferrite, by the polymerization of various monomers initiated by initiating groups introduced onto these surfaces.[2]

For example, potassium carboxylate groups introduced onto inorganic ultrafine particles were capable of initiating the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides and polyester was grafted onto the surface through the propagation of the polymer from the surface.[3] In addition, the radical polymerization of vinyl monomers was initiated by azo groups introduced onto inorganic ultrafine particles to give polymer-grafted particles.[4]

In previous paper, we succeeded in the introduction of peroxide groups onto an ultrafine silica surface by the reaction of surface chlorosilyl groups with hydroperoxide.[5,6] The silica having peroxide groups has ability to initiate the radical polymerization of methyl methacrylate (MMA). In the polymerization, poly(MMA) was grafted onto silica surface through the propagation of polymer from surface radicals formed by the thermal decomposition of peroxide groups.

In the present paper, the introduction of peroxyester groups onto inorganic ultrafine

particles, such as silica, titanium oxide, and ferrite, by the reaction of surface acid anhydride groups with hydroperoxide (eq 1), and

the graft polymerization of vinyl monomers initiated by the peroxyester groups were investigated (eq 2). Furthermore, the effects of

$$
\text{1} + \text{HOO-R} \longrightarrow \qquad (1)
$$

$$
\text{2} + \text{n } CH_2{=}CH \xrightarrow[-CO_2]{\Delta} \qquad (2)
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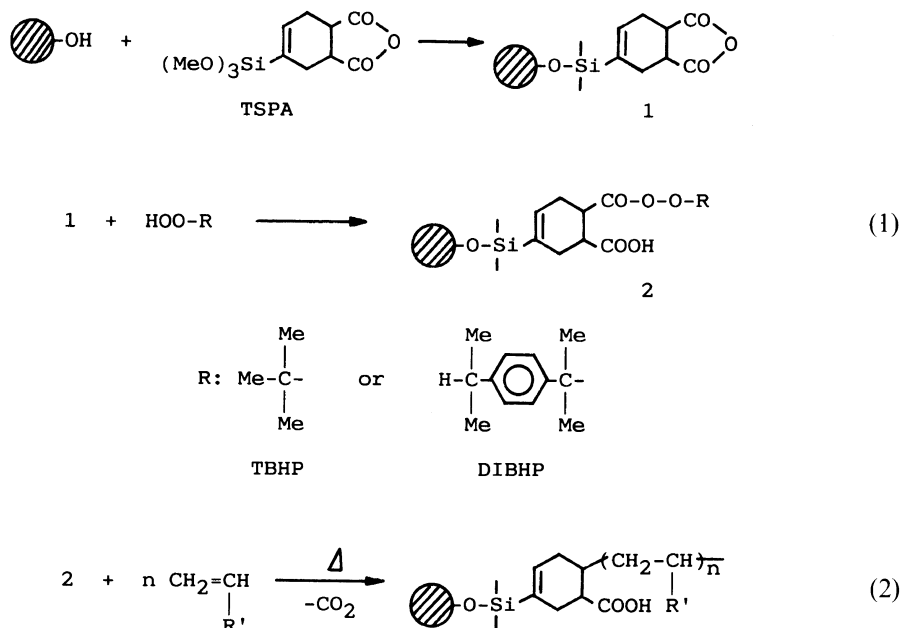
reducing agents such as amines and iron(II) ion on the graft polymerization were examined. The stability of polymer-grafted inorganic ultrafine particle dispersion in solvents is also discussed.

EXPERIMENTAL

Materials

Ultrafine silica, titanium oxide, and ferrite used were Aerosil 200 (Nippon Aerosil Co., Japan), STT-30 (Titan Kogyo K.K., Japan), and ultrafine nickel zinc ferrite (Sumitomo Cement Co., Ltd., Japan), respectively. The BET specific surface area, particle size, and the content of hydroxyl groups on the surface of these ultrafine particles are summarized in Table I.

Hydroxyl group content was determined by measuring volumetrically the amount of ethane evolved by the reaction with triethylaluminum. The ultrafine particles were dried *in*

vacuo at 110°C before use.

Methyl methacrylate (MMA) was washed with dilute alkali solution, dried over sodium sulfate, and distilled twice under reduced pressure. Styrene was also washed with dilute alkali solution, dried over barium oxide, and distilled twice under reduced pressure. Acrylonitrile (AN) was distilled twice beofore use. *N*-Vinylcarbazole (NVC) was recrystallized from hexane and dried *in vacuo* at room temperature. Divinyl ether obtained from NOK Co., Ltd., Japan, was distilled before use. Maleic anhydride was purified by distillation under reduced pressure.

4-Trimethoxysilyltetrahydrophthalic anhydride (TSPA) obtained from Nissan Chemical Ind. Ltd., Japan, was used without further purification. *tert*-Butyl hydroperoxide (TBHP) and diisopropylbenzene hydroperoxide (DIBHP) were obtained from Nippon Oil and Fats Co., Ltd., Japan, and used without further purification.

Table I. Properties of ultrafine silica, titanium oxide, and ferrite

Ultrafine particle	BET surface area	Particle size	OH group
	$m^2 g^{-1}$	nm	$mmol\, g^{-1}$
Silica[a]	200	16	1.37
Titanium oxide[b]	90–150	120	0.77
Ferrite[c]	110	15	0.50

[a] Aerosil 200 (Nippon Aerosil Co., Japan).
[b] STT-30 (Titan Kogyo K.K., Japan).
[c] Nickel zinc ferrite (Sumitomo Cement Co., Ltd., Japan).

Toluene, benzene, dioxane, and tetrahydrofuran (THF) were refluxed over sodium and distilled twice before use. N,N-Dimethylaniline was dried over sodium hydroxide and distilled. Iron(II) sulfate was used without further purification. All other reagents and solvents were used after ordinary purification.

Introduction of Acid Anhydride Groups onto the Surface of Ultrafine Particles

The introduction of acid anhydride groups onto the surface of inorganic ultrafine particles was achieved by reactions of hydroxyl groups on the surface with TSPA. The procedures were described in detail in the preceding paper.[3]

Introduction of Peroxyester Groups onto Ultrafine Particles

The introduction of peroxyester groups onto ultrafine particles was achieved by reactions of acid anhydride groups on the surface with TBHP or DIBHP. A typical example is as follows. Into a 100 cm³ flask that contained 2.0 g of ultrafine particle having acid anhydride groups and 30.0 cm³ dioxane, 5.0 cm³ of DIBHP were added and the reaction mixture was stirred with a magnetic stirrer under dry nitrogen at 20°C in the dark. After the reaction for 8 h, the resulting ultrafine particles were washed with methanol repeatedly and dried in vacuo at room temperature. The treated

ultrafine particles were stored in vacuo in a refrigerator.

Determination of Peroxyester Groups on Ultrafine Particles

Into a Erlenmeyer flask that contained 0.2 g of ultrafine particles having peroxyester groups and 10.0 cm³ of acetic anhydride, 0.5 g of potassium iodide were added and the mixture was stirred with a magnetic stirrer for 20 min. Then isolated iodide was titrated with 0.1 mol dm⁻³ sodium hyposulfite using starch as an indicator.[7]

Polymerization Procedures

Into a polymerization tube, 0.30 g of ultrafine silica and 10.0 cm³ of MMA were charged. The tube was cooled in a liquid nitrogen bath, thawed three times with nitrogen, and sealed. Polymerization was conducted at 70°C with shaking. After a definite time, the reaction mixture was poured into a large excess of methanol and the precipitate was dried in vacuo at 40°C. The conversion was determined by the following equation:

Conversion (%)

$$= \frac{\text{Product (g)} - \text{Ultrafine silica (g)}}{\text{Monomer used (g)}} \times 100$$

Percentage of Grafting and Grafting Efficiency

The product was dispersed in a solvent for the polymer and the dispersion was centrifuged at 1.0×10^4 rpm until ultrafine particles precipitated completely. The ultrafine particles were extracted with THF using Soxhlet apparatus until no polymer was eluted in the refluxing solvent. The percentage of grafting and grafting efficiency was calculated as follows:

$$\text{Grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Ultrafine silica used (g)}} \times 100$$

Grafting efficiency (%)

$$= \frac{\text{Polymer grafted (\%)}}{\text{Total polymer formed (g)}} \times 100$$

The amount of grafted-polymer was determined from the increment in weight of ultrafine particles after the graft polymerization.

Dispersibility of Poly(MMA)-Grafted Silica Dispersions in THF

The stability of poly(MMA)-grafted silica dispersions in THF was estimated from the content of silica particles in the dispersion after standing at room temperature as shown in the following equation. The detailed procedures were described in the previous paper.[4]

$$\text{Content of silica in dispersion } (\%) = \frac{A}{B} \times 100$$

A, silica in dispersed phase $(g\,cm^{-3})$

B, silica in initial dispersion $(g\,cm^{-3})$

RESULTS AND DISCUSSION

Introduction of Peroxyester Groups onto Ultrafine Particles

In the preceduing paper, we reported that peroxide groups can be introduced onto silica surface by reactions of hydroperoxides with chlorosilyl groups introduced onto the surface.[5,6] The introduction of peroxide groups onto ultrafine ferrite, however, was unsuccessful, because chlorination of the ferrite surface hardly proceeded.

We achieved the introduction of acid anhydride groups onto inorganic ultrafine particles, such as silica, ferrite, and titanium oxide, and the grafting onto these surfaces by reactions of acid anhydride groups with hydroxyl- or amino-terminated polymers.[8]

Therefore, the introduction of peroxyester groups onto inorganic ultrafine particles by the reaction of acid anhydride groups on the surface with hydroperoxide was examined. The introduction of acid anhydride groups onto inorganic ultrafine particles was carried out by reactions of hydroxyl groups on the surface with TSPA. Table II shows the amount

Table II. Functional group content of treated ultrafine particles

Ultrafine particle	Acid anhydride group	Peroxyester group	R^a
	$mmol\,g^{-1}$	$mmol\,g^{-1}$	
Silica	0.96	0.11	0.11
Titanium oxide	0.47	0.07	0.15
Ferrite	0.31	0.05	0.16

[a] The ratio of acid anhydride groups on ultrafine particles that reacted with hydroperoxide.

of diisopropylbenzene peroxyester groups introduced onto inorganic ultrafine particles by the raction of acid anhydride groups on the surface with DIBHP.

As shown in Table II, peroxyester groups were found successfully introduced onto these ultrafine particles. The results indicate that only 11—16% of acid anhydride groups react with DIBHP. No increase in peroxyester group content of these ultrafine particles was observed even if the treating time was extended to 24 h. Therefore, the low conversion of acid anhydride groups is considered to be due to the low reactivity of acid anhydride groups to hydroperoxides.

tert-Butyl peroxyester groups were also introduced onto these ultrafine particles by use of TBHP instead of DIBHP.

Initiating Activity of Peroxyester Groups Introduced onto Silica Surface

The polymerization of MMA was carried out in the presence of silica having diisopropylbenzene peroxyester (Silica–CO–OO–DIB) or tert-butyl peroxyester groups (Silica–CO–OO–tBu) at 70°C and the initiating activity of the peroxyester groups on the surface was examined. The results are shown in Table III.

As shown in Table III, although the polymerization of MMA initiated even in the absence of initiator, the rate of the polymerization was small. The conversion of MMA in the presence of untreated silica and TSPA-

Table III. Polymerization of MMA in the presence of various treated silicas[a]

Silica	Conversion/%	Grafting/%
None	1.2	—
Untreated	1.3	0
DIBHP-treated[b]	1.3	0
Silica-Anhydride	1.1	0
Silica–CO–OO–DIB	3.2	38.1
Silica–CO–OO–tBu	3.0	25.8

[a] Silica, 0.30 g; MMA, 10.0 cm^3; 70°C; 9 h.
[b] Untreated silica was treated with DIBHP in dioxane and washed with methanol after treatment.

treated silica (Silica-Anhydride) was almost equal to that in the absence of silica. This indicates that untreated and TSPA-treated silica have no ability to initiate the polymerization. But in the presence of silica having diisopropylbenzene peroxyester and *tert*-butyl peroxyester groups, polymerization was found to be initiated.

To evaluate the effects of DIBHP adsorbed on the silica surface during the introduction reaction of peroxyester groups, the initiating activity of DIBHP-treated silica, prepared by the treatment of untreated silica with DIBHP in dioxane followed by the washing with methanol after the treatment, was compared with that of untreated silica. Table III clearly shows that DIBHP-treated silica has no ability to initiate the polymerization. This suggests that DIBHP adsorbed on the silica surface during the introduction reaction of peroxyester groups can be removed completely by washing with methanol after treatment.

Effect of Temperature on the Polymerization

Figure 1 shows the effect of temperature on the polymerization of MMA initiated by Silica–CO–OO–DIB.

Although thermal polymerization proceeded even in the presence of untreated silica, the rate of the polymerization in the presence of Silica–CO–OO–DIB was much larger than that in the presence of untreated silica. Fur-
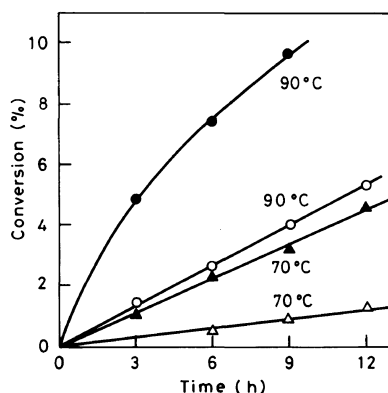

Figure 1. Polymerization of MMA initiated by Silica–CO–OO–DIB. Silica, 0.30 g; MMA, 10.0 cm^3. (●,▲), in the presence of Silica–CO–OO–DIB; (○,△), in the presence of untreated silica.
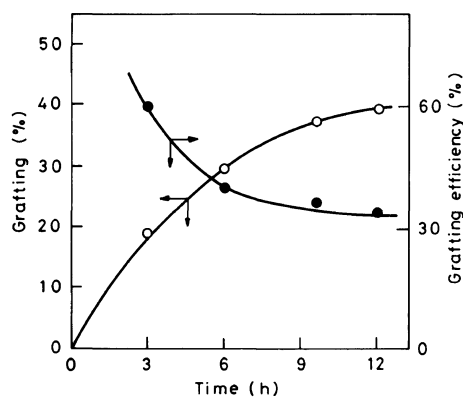

Figure 2. Percentage of grafting and grafting efficiency of poly(MMA) onto Silica–CO–OO–DIB at 70°C. Polymerization conditions are given in Figure 1.

thermore, the rate of the polymerization increased with polymerization temperature. This indicates that the decomposition of peroxyester groups is accelerated at higher temperature.

Although the amounts of peroxyester groups introduced onto silica were less than those of peroxide groups, the rate of the polymerization initiated by peroxyester groups was larger than that initiated by peroxide groups.[6] This may be due to lower decomposition temperature of peroxyester than that of peroxide.

Proof of Grafting onto Silica Surface

Figure 2 shows the relationship between polymerization time and percentage of grafting of poly(MMA) onto silica surface obtained from the polymerization at 70°C shown in Figure 1.

It is apparent that poly(MMA) is grafted onto silica surface and percentage of grafting reached about 60% at 70°C after 12 h.

Grafting efficiency was high at the initial stage of the polymerization, but gradually decreased with a progress of the polymerization. These results indicate that although the polymer propagates from surface radical formed by the decomposition of the peroxyester groups, ungrafted polymer was preferentially formed with progress of the polymerization.

Based on the above results, it is concluded that the graft polymerization is initiated by surface radicals on silica formed by the thermal decomposition of peroxyester groups introduced onto the surface to give polymergrafted silica.

Grafting onto Various Ultrafine Particles

In analogy with silica, untreated titanium oxide and ferrite failed to initiate the polymerization of MMA from titanium oxide and ferrite by use of diisopropylbenzene peroxyester groups introduced onto these surfaces as initiator was examined. The results are shown in Table IV.

As shown in Table IV, it is apparent that peroxyester groups on titanium oxide and ferrite also have ability to initiate polymerization of vinyl monomers. Therefore, the graft polymerization of MMA and poly(MMA) is effectively grafted onto these surfaces. The percentage of grafting onto these particles tends to increase with an increase in peroxyester group content of the surfaces.

Grafting of Various Polymers onto Silica Surface

The grafting of polystyrene, poly(AN), and poly(NVC) onto silica was carried out by the

Table IV. Graft polymerization of MMA initiated by peroxyester groups introduced onto ultrafine particles[a]

Ultrafine particle	Peroxyester group	Conversion	Grafting
	mmol g^{-1}	%	%
Silica	0.11	3.2	38.1
Titanium oxide	0.07	3.3	35.2
Ferrite	0.05	3.7	32.9

[a] Ultrafine particles, 0.30 g; MMA, 10.0 cm^3; 70°C; 9 h.

Table V. Graft polymerization of several monomers initiated by peroxyester groups introduced onto silica surface

Vinyl monomer	Time/%	Conversion/%	Grafting/%
MMA[a]	9	3.2	38.1
AN[a]	12	5.0	21.4
Styrene[a]	9	4.5	25.0
NVC[b]	9	3.2	28.6

[a] Silica, 0.30 g; monomer, 10.0 cm^3; 70°C.
[b] Silica, 0.30 g, NVC, 3.0 g; dioxane, 10.0 cm^3; 70°C.

polymerization of the corresponding monomers using diisopropylbenzene peroxyester groups on the surface as initiator. The results are shown in Table V.

The peroxyester groups introduced onto silica have ability to initiate the polymerization of various vinyl monomers to give polymergrafted silica.

The grafting of copolymer of divinyl ether with maleic anhydride, known to be a biologically active polymer,[9,10] onto ferrite surface by the copolymerization initiated by peroxyester groups introduced onto the surface (Ferrite–CO–OO–DIB) was examined. Figure 3 shows time vs. conversion and time vs. percentage of grafting of the copolymer onto ferrite.

It was found that the copolymerization of divinyl ether with maleic anhydride is also initiated by peroxyester groups on ferrite surface and the corresponding copolymer can be grafted onto ferrite surface.
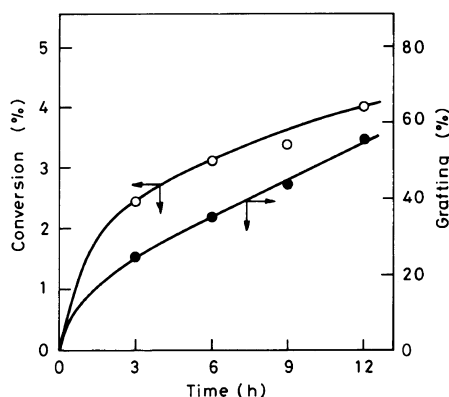
Figure 3. Copolymerization of divinyl ether with maleic anhydride initiated by Ferrite–CO–OO–DIB. Ferrite–CO–OO–DIB, 0.30 g; divinyl ether, 0.01 mol; maleic anhydride, 0.02 mol; 70°C.
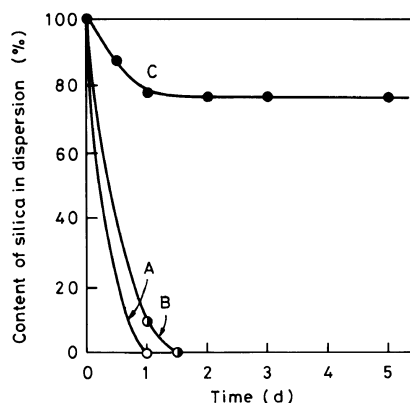

Figure 4. Stability of dispersion of (A) untreated silica, (B) poly(MMA)-adsorbed silica, and (C) poly(MMA)-grafted silica in THF at room temperature.

Table VI. Effects of reducing agents on the graft polymerization of MMA initiated by peroxyester groups on silica[a]

Reducing agent	Temperature	Conversion	Grafting
	°C	%	%
None	50	1.4	Trace
None	70	3.2	38.1
N,N-Dimethylaniline	50	11.6	5.0
N,N-Dimethylaniline	70	22.7	25.0
Iron(II) ion[b]	70	14.1	20.4

[a] Silica–CO–OO–DIB, 0.30 g, MMA, reducing agent, 0.04 cm³; 10.0 cm³; 9 h.
[b] Aqueous solution of FeSO₄ (5.0%).

Effect of Reducing Agent on the Graft Polymerization

It is well known that the decomposition of peroxides and peroxyesters accelerated by the addition of reducing agent such as amines and iron(II) ion. Therefore, the redox graft polymerization of MMA initiated by the system consisting of diisopropylbenzene peroxyester group on silica and N,N-dimethylaniline or iron(II) ion was examined. The results are summarized in Table VI.

As shown in Table VI, the rate of the polymerization was accelerated by the addition of N,N-dimethylaniline and iron(II) ion. The percentage of grafting, however, was scarcely affected by the addition of these reducing agents. This is explained as follows. Although the initiating sites on the surface increase in the presence of these reducing agents, the molecular weight of grafted polymer chain is considered to be reduced because of the preferential chain transfer reaction of growing polymer radical. The molecular weight of ungrafted polymer in the above redox systems was found to be smaller than that in the absence of reducing agent.[11]

Dispersibility of Poly(MMA)-Grafted Silica Dispersion

The stability of poly(MMA)-grafted silica dispersion in THF was compared with that of untreated silica and poly(MMA)-adsorbed-silica. The results are shown in Figure 4.

Untreated silica precipitated completely after 1 day. The stability of the dispersion of poly(MMA)-adsorbed silica, prepared by the mixing of silica with poly(MMA) in dioxane followed by the extraction with THF, was scarcely improved. The poly(MMA)-grafted silica was found to produce a stable colloidal dispersion in THF. Accordingly, the dispersi-

bility of silica was remarkably improved by grafting of the polymer onto the surface.

CONCLUSIONS

1. The introduction of peroxyester groups onto inorganic ultrafine particles was sucessfully achieved by the reaction of hydroperoxide with acid anhydride groups introduced onto these surfaces.

2. The polymerization of vinyl monomers was initiated by peroxyester groups introduced onto inorganic ultrafine particles and the corresponding polymer was effectively grafted from these surfaces.

3. The rate of graft polymerization initiated by surface peroxyester groups on the particles was accelerated by addition of reducing agent.

4. Polymer-grafted ultrafine particles gave a stable colloidal dispersion in organic solvents for the grafted polymer.

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