Graft Polymerization of Vinyl Monomers Initiated by Peroxycarbonate Groups Introduced onto Silica Surface by Michael Addition

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ABSTRACT: The introduction of peroxycarbonate groups onto a silica surface and the graft polymerization of vinyl monomers initiated by peroxycarbonate groups introduced onto a silica surface were investigated. The introduction of peroxycarbonate groups onto a silica surface was achieved by Michael addition of amino groups introduced onto the silica surface to *t*-butylperoxy-2-methacryloyloxyethylcarbonate (HEPO). The amount of peroxycarbonate groups was determined to be 0.17 mmol/g. The graft polymerization of various vinyl monomers such as styrene (St), *N*-vinyl-2-pyrrolidinone (NVPD), and 2-hydroxyethyl methacrylate (HEMA) was initiated by peroxycarbonate groups introduced onto the silica surface to give the corresponding polymer-grafted silicas. The percentage of poly(St)-grafting reached about 120% after 5 h. This means that 1.20 g of poly(St) is grafted onto 1.0 g of silica. The surface of poly(St)-grafted silica shows a hydrophobic nature, but the surfaces of poly(NVPD) and poly(HEMA)-grafted silica shows a hydrophilic nature. Furthermore, the poly(St)-grafted silica was found to give a stable colloidal dispersion in a good solvent for the grafted polymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1491–1497, 1999

Key words: graft polymerization; Michael addition; *t*-butylperoxy-2-methacryloy-loxyethylcarbonate; peroxycarbonate group; ultrafine silica

INTRODUCTION

The grafting of polymers onto inorganic ultrafine particles, such as silica and titanium oxide, is effective to improve the dispersibility in organic solvent and the compatibility in polymer matrix. In a series of articles, we reported the grafting of polymers onto these particles by the graft polymerization of vinyl monomers initiated by azo,¹ potassium carboxylate,² and acylium perchlorate³ groups introduced onto the surfaces. By these graft polymerizations, polymer-grafted ultrafine particles with a higher percentage of grafting were obtained because of the propagation of polymer chains from the particles surface.

The conjugate addition of a carbanion to acryl ester is commonly known as a Michael addition.³ Recently, the Michael addition was utilized in the preparation of polyamidoamine dendrimer by the following two processes: (1) Michael addition of ammonia or amines as initiator core to acryl ester, and (2) amidation of resulting ester moieties with an alkylene diamine.^{4,5} We have reported

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that the polyamidoamine dendrimer is grafted onto silica surface by the Michael addition of amino groups introduced onto silica surface to methyl acrylate and the amidation of resulting ester moieties with an alkylene diamine.⁶

On the other hand, vinyl polymers having pendant peroxycarbonate groups were easily synthesized by the copolymerization of vinyl monomers with *t*-butylperoxy-2-methacryloyloxyethylcarbonate (HEPO) and applied to synthesis of various graft copolymers.⁷ We have also reported that the polymer radicals formed by the decomposition of polymers having pendant peroxycarbonate groups, which were synthesized by the copolymerization of HEPO with vinyl monomers, were trapped by a carbon black surface to give the corresponding polymer-grafted carbon blacks.⁸

In the present article, the introduction of peroxycarbonate groups onto a silica surface by the Michael addition of amino groups previously introduced onto the silica surface to HEPO [Scheme 1(1)] and the radical graft polymerization of vinyl monomers initiated by peroxycarbonate groups introduced onto silica surface [Scheme 1(2)] were investigated.

EXPERIMENTAL

Materials

The ultrafine silica used was Aerosil 200 (Nippon Aerosil Co. Ltd., Japan; specific surface area, 200 m^2/g ; particle size, 16 nm; surface silanol group, 1.37 mmol/g). The silica was dried *in vacuo* at 110°C for 24 h before use.

 γ -Aminopropyltriethoxysilane (APS) obtained from Kanto Chemical Ind. Co., Japan, was used without further purification. A sample of *t*-butylperoxy-2-methacryloyloxyethylcarbonate (HEPO) obtained from Nippon Oil and Fats Co., Ltd., Japan, was used without further purification.

Styrene (St) was washed with 10% aqueous solution of sodium hydroxide and water, dried over calcium chloride, and distilled twice under reduced pressure. Methyl methacrylate (MMA) was washed with dilute aqueous solution of sodium hydrogen sulfite, dried over sodium sulfate, and distilled twice under reduced pressure. N-Vinyl-2-pyrroridinone (NVPD), glycidyl methacrylate (GMA), and 2-hydroxyethyl methacrylate (HEMA) were distilled before use. Toluene was washed with concentrated sulfuric acid, 5% aqueous solution of sodium hydroxide, and water, then dried over calcium chloride, refluxed over sodium, and distilled. Tetrahydrofuran (THF) was refluxed over sodium and distilled. All other reagents and solvents were used after ordinary purification.

Introduction of Amino Groups onto Silica Surface

The introduction of amino groups onto silica surface was achieved by the reaction of APS with silanol groups on silica surface. A typical example was as follows. Into a 300-mL flask equipped with a reflux condenser, 5.0 g of silica and 150 mL of 5% toluene solution of APS were charged. The mixture was refluxed for 8 h under stirring with a magnetic stirrer. After the reaction, the mixture was centrifuged, and the precipitate was extracted with THF for 24 h. The treated silica having amino groups (silica– NH_2) was stored in vacuo at 110°C.

Introduction of Peroxycarbonate Groups onto Silica Surface

The introduction of peroxycarbonate groups onto silica surface was achieved by the Michael addition of the amino groups introduced onto the silica surface to HEPO. A typical example was as follows. Into a 300-mL flask, 5.0 g of silica–NH₂, 1.1 g of HEPO, and 150 mL of methanol were charged. The mixture was stirred with a magnetic stirrer at 30°C for 24 h under dry nitrogen. After the reaction, the mixture was repeatedly washed with methanol and dried *in vacuo* at room temperature. The silica having peroxycarbonate groups (silica–HEPO) was stored in the dark below 0°C.

Determination of Peroxycarbonate Group Content of Silica

The amount of peroxycarbonate groups introduced onto the silica surface was determined by iodometry.⁹ A typical example is as follows. Into a 100-mL flask, 0.10 g of silica having peroxycarbonate groups, 0.20 g of potassium iodide, 10.0 mL of deaired water, and 1.0 mL of 0.5 mol L H_2SO_4 were charged. The mixture was stirred with a magnetic stirrer for 20 min, and isolated iodide was titrated with 0.1 mol L sodium hyposulfite using starch as an initiator.

Polymerization of Vinyl Monomer Initiated by Silica-HEPO

Into a glass tube, 0.30 g of silica and 80 mmol of vinyl monomer were charged. The tube was freeze-thawed three times and sealed under vacuum. The contents of the sealed tube were stirred with a magnetic stirrer at 100°C. After the polymerization, the content of the tube was poured into a large excess of precipitant for the polymer. The precipitate was filtered and dried *in vacuo* at 60°C. The conversion was calculated by the following equation:

Conversion (%)

$$= \frac{\text{product (g)} - \text{silica used (g)}}{\text{monomer used (g)}} \times 100$$

Percentage of Grafting and Grafting Efficiency

To isolate the polymer-grafted silica from the reaction mixture containing ungrafted polymer, the reaction product was dispersed in a solvent for polymer and the dispersion was centrifuged at 1.0 $\times 10^4$ rpm until the silica was precipitated completely. The silica precipitated was dispersed again, and the dispersion was centrifuged. The procedures were repeated until no more polymer was detected in the supernatant solution. Then, the resulting silica was dried *in vacuo* at 60°C. The percentage of grafting and grafting efficiency were calculated by the following equations:

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

Grafting efficiency (%)

 $= \frac{polymer \ grafted \ (g)}{total \ polymer \ formed \ (g)} \times \ 100$

Wettability of Polymer-Grafted Silica

The wettability of polymer-grafted silica surface was estimated by the penetrating rate of water through a column packed with polymer-grafted silica. A typical example is as follows. Into a glass column (inside diameter: 2.0 mm), 0.30 g of polymer-grafted silica was packed, and water was added from the top of the column. Then the penetrating rate of water through the column was determined.

Dispersibility of Poly(St)-Grafted Silica

The dispersibility of poly(St)-grafted silica in THF was estimated from the content of silica in the dispersion after standing at room temperature, as shown in the following equation. The detailed procedures were described in the previous article.¹⁰

Silica dispersed (%) =
$$\frac{A}{B} \times 100$$

where A is the silica in the dispersed phase after standing (g/mL) and B is the silica in the initial dispersion (g/mL).

RESULTS AND DISCUSSION

Introduction of Peroxycarbonate Groups onto Silica Surface

The introduction of peroxycarbonate groups onto silica surface by the Michael addition of amino



Figure 1 IR spectra of untreated silica and silica–HEPO.

groups introduced onto silica surface to HEPO was investigated. The introduction of amino groups onto silica surface was achieved by the treatment of silica with APS; in this study, silica having 0.90 mmol/g of amino groups was used.

It was found that peroxycarbonate groups are successfully introduced onto the silica surface by the reaction of HEPO with amino groups on the surface in methanol at 30°C for 24 h. The amount of peroxycarbonate groups introduced onto the surface by the reaction was determined to be 0.17 mmol g by iodometry.⁹ This indicates that about 18.9% of surface amino groups are reacted with HEPO. The efficiency of the Michael addition of surface amino groups to HEPO is almost same as that of methyl acrylate, as reported in the dendrimer grafting onto silica.⁶

Figure 1 shows the infrared (IR) spectra of untreated silica and silica–HEPO. The IR spectra of silica–HEPO shows new absorptions at about $1530-1710 \text{ cm}^{-1}$, which are characteristic of per-oxycarbonate moieties.

Based on the above results, it was concluded that peroxycarbonate groups were successfully introduced onto the silica surface by the Michael addition of amino groups on silica to HEPO.

Polymerization of St in the Presence of Silica–HEPO

The polymerization of St in the presence of silica– HEPO was examined. The results are shown in

Table IPolymerization of St Initiated bySilica-HEPO

Silica	Conversion (%)	Grafting (%)	
None	1.0	_	
Untreated	1.1	Trace	
Silica–HEPO	1.6	20.2	

Silica-HEPO, 0.30 g; St, 0.08 mol; 100°C; 0.5 h.

Table I. The thermal polymerization of St proceeded even in the absence of initiator. In the presence of untreated silica, the thermal polymerization of St was also initiated, but poly(St) was scarcely grafted onto the surface. On the contrary, in the presence of silica–HEPO, the polymerization of St was successfully initiated, and the poly(St)-grafted silica was obtained.

These results suggest that the polymerization of St was initiated by the surface radicals formed by the decomposition of peroxycarbonate groups introduced onto silica surface.

Figure 2 shows time versus the conversion curve and time versus the percentage of the grafting curve in the polymerization of St initiated by silica-HEPO. The percentage of grafting increased with progress of the polymerization and reached about 120% after 5 h. This means that 1.20 g of poly(St) is grafted onto 1.0 g of silica.

Figure 3 shows the relationship between grafting efficiency and conversion in the above polymerization. Grafting efficiency was high, about 50%, at the initial stage of the polymerization but



Figure 2 Polymerization of St initiated by silica– HEPO: Silica–HEPO, 0.30 g; St, 80 mmol; 100°C.



Figure 3 Relationship between conversion and grafting efficiency in the polymerization of St initiated by silica–HEPO: Silica–HEPO, 0.30 g; St, 80 mmol; 100°C.

gradually decreased with progress of the polymerization.

These results are explained as follows. The surface peroxycarbonate groups produce both surface radicals and fragment radicals, that is, the *t*-butoxy radical, as shown in Scheme 2. The former initiate graft polymerization from the surface, but the latter produce ungrafted polymer. Although the polymerization of St is started from surface radicals and fragment radicals at the initial stage of the polymerization, the formation of ungrafted polymer preferentially proceeds at the middle and the last stage of the polymerization because surface radicals and propagating radicals from the surface are blocked by grafted polymer chains and/or the chain transfer reaction from propagating radicals of grafted polymers occurs at the middle and the last stage of the polymerization.

Table IIPolymerization of Several VinylMonomers Initiated by Silica-HEPO

Monomer	Time (min)	Conversion (%)	Grafting (%)
MMA	60	20.5	18.0
GMA	30	12.3	17.5
HEMA	10	22.3	97.2
NVPD	30	74.1	29.8

Silica-HEPO, 0.30 g; monomer, 0.08 mol; 100°C.

Polymerizations of Various Vinyl Monomers Initiated by Silica–HEPO

Polymerizations of various vinyl monomers initiated by silica–HEPO were examined. As shown in Table II, it is apparent that the polymerizations of various vinyl monomers were initiated by silica– HEPO to give the corresponding polymer-grafted silicas.

Figure 4 shows the IR spectra of untreated silica, poly(HEMA)-grafted and poly(St)-grafted silica exhibited the absorptions at 3030 and 700 cm⁻¹, which are characteristic of a phenyl group. On the other hand, the IR spectrum of poly(HEMA)-grafted silica exhibited the absorption at 1750 cm⁻¹, which is characteristic of carbonyl group. These results clearly show the grafting of poly(St) and poly(HEMA) onto silica surface.

Based on the above results, it is concluded that the graft polymerizations of various vinyl monomers are initiated by surface radicals formed by the decomposition of peroxycarbonate groups introduced onto the silica surface to give the corresponding polymer-grafted silicas.



Scheme 2



 $\label{eq:Figure 4} Figure \ \ IR \ spectra \ of \ (a) \ untreated, \ (b) \ poly (HEMA) \ -grafted, \ and \ (c) \ poly (St) \ -grafted \ silica.$

Properties of Polymer-Grafted Silica

The dispersibility of poly(St)-grafted silica (grafting = 57.6%) in THF, which is a good solvent for poly(St), was compared with that of untreated silica. The results are shown in Figure 5. Untreated silica completely precipitated after 1 day. On the contrary, poly(St)-grafted silica gave a



stable colloidal dispersion in THF. This indicates that the grafted polymer chains interfere with the aggregation of silica particles.

Figure 6 shows the penetrating rate of water through a column packed with untreated, poly(St)-grafted, poly(NVPD)-grafted, and poly-(HEMA)-grafted silica. The results clearly show that the poly(St)-grafted silica surface shows a hydrophobic nature, but the surface of poly(N-VPD) and poly(HEMA)-grafted silica show an extremely hydrophilic nature. Therefore, it is concluded that the wettability of silica surface can be controlled by the grafting of polymers.



Figure 5 Dispersibility of poly(St)-grafted silica in THF at room temperature: (\bigcirc) untreated; (\bigcirc) poly(St)-grafted (grafting = 57.6%).

Figure 6 The penetrating rate of water through the column packed with polymer-grafted silica. Grafting equals (a) 80.4, (b) 29.8, and (c) 97.2%.

CONCLUSIONS

- 1. The introduction of peroxycarbonate groups onto the silica surface was successfully achieved by the Michael addition of amino groups introduced onto silica surface to HEPO.
- 2. The radical polymerization of vinyl monomers was initiated by peroxycarbonate groups introduced onto the silica surface to give the corresponding polymer-grafted silica.
- 3. The dispersibility of silica in a good solvent for the grafted polymer chains was remarkably improved by the grafting of polymers onto the surface.

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