

Polymerization of Surface-Active Monomers.

III. Polymer Encapsulation of Silica Gel Particles by Aqueous Polymerization of Quaternary Salt of Dimethylaminoethyl Methacrylate with Lauryl Bromide

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Synopsis

Polymer encapsulation of silica gel particles (SiO_2) by aqueous, radical polymerization of a cationic, surface-active monomer, quaternary salt of dimethylaminoethyl methacrylate with lauryl bromide, in the presence of the solid was investigated. The polymerization gave the polymer encapsulating the solid particles ("C-polymer"), though accompanied by the formation of that suspended in form of latex ("L-polymer"). The proportion of C-polymer in the products increased with increasing the amount of SiO_2 at a constant monomer concentration and only C-polymer was formed under the conditions where the feed ratio of monomer to SiO_2 is about 0.13 or lower by weight. Increasing the monomer concentration in feed increased slightly the ratio of C-polymer to SiO_2 . The results obtained here suggest that C-polymer is mainly formed through the polymerization of monomer adsorbed on the solid surface. An electron micrograph of the polymer-encapsulated SiO_2 revealed that the solid particles are uniformly encapsulated with the resulting polymer.

INTRODUCTION

Inorganic solid particles are often used as fillers or pigments in organic polymers. In such heterogeneous systems, the surface of solid substances is usually modified to improve an interaction between the solids and the surrounding polymeric medium. Polymerization of vinyl monomers on the surface of inorganic solid particles has been noted as a method to modify the surface property of solids¹ or to prepare the composite materials.²⁻⁴ Although radiation-induced polymerization has been shown to be effective for growth of a polymer film on the solid surface from vapor phase of monomer,^{5,6} the polymerization in solvent medium, especially in water, is preferable for polymer encapsulation because it can be easily handled by suspension polymerization equipment. Such a polymer encapsulation method in aqueous system has been developed: the suspension polymerization of methyl methacrylate (MMA) with sodium bisulfite as initiator in the presence of various inorganic solids²⁻⁴ and the polymerization of styrene (ST) solubilized in the layer of hydroxypropyl cellulose adsorbed onto SiO_2 by coacervation.⁷ Here, we will report a new polymer encapsulation method based on the aqueous polymerization of a cationic, surface-active monomer.

It is known that surface-active agents, especially cationic ones, are well adsorbed on the surface of inorganic solids from the aqueous solution, though dependent on the charge density of solid surface and pH of the medium.⁸ Therefore, aqueous polymerization of a cationic, surface-active monomer in the presence of solid particles can be expected to afford the polymer-encapsulated solid. In such a system, the monomer will be required to have a high polymerizability in addition to a strong adsorptive property so that the polymerization of the adsorbed monomer can precede the concurrent desorption. The polymerization of a series of cationic, surface-active monomers, obtained by the quaternization of dimethylaminoethyl methacrylate with higher alkyl bromides, has been found to exhibit a high polymerizability at a micellar state,⁹⁻¹² and hence the monomer molecules arrayed in the adsorbed layer on the solid surface may be fixed by polymerization, resulting in the formation of a polymer on the surface.

The present paper deals with aqueous polymerization of a cationic, lauryl bromide salt of dimethylaminoethyl methacrylate in the presence of silica gel (SiO_2), which bears a negative surface charge in aqueous medium owing to a low isoelectric point,¹³ in order to encapsulate the solid particles with the resulting polymer.

EXPERIMENTAL

Reagents

A cationic amphiphilic monomer used here was prepared by the reaction of dimethylaminoethyl methacrylate with *n*-lauryl bromide according to the procedure described earlier,⁹ which exhibits a critical micelle concentration at $6.02 \times 10^{-3} \text{ mol L}^{-1}$ at 25°C.^{9,10}

Water was deionized until a specific conductivity of $1 \times 10^{-6} \Omega^{-1}$ or lower was reached, and then it was doubly distilled under nitrogen atmosphere.

Potassium persulfate (KPS) and 2,2'-azobis(2-aminodino propane)dihydrochloride (AIBA), reagent grade from Wako Pure Chemicals Industries, Ltd. (Wako), were employed as received. 2,2'-Azobisisobutyronitrile (AIBN) from Wako was purified by recrystallization from methanol, followed by reprecipitation using a benzene-petroleum ether system to obtain a fine powdered form.

Silica gel particles (SiO_2 , for chromatography) from Wako were sieved to 150-200 mesh, washed with distilled water, and dried at 100°C in vacuum. The specific surface area determined by BET method with nitrogen was 483.

Measurement of the Amount of Cationic Monomer Adsorbed onto SiO_2

Known amounts of SiO_2 were added to the monomer solution in water at a given concentration. The mixture was shaken in the thermostated bath at 50°C for definite periods of time. A portion of the solution was drawn out, followed by titration with sodium tetraphenyl borate, to determine the equilibrium concentration of monomer in bulk phase¹⁴ and then the amount of monomer adsorbed on the solid was calculated. There was no variation in the

amount of adsorbed monomer with time after 1–24 h and hence the amount adsorbed after 6 h was taken as that at equilibrium.

Polymerization

The polymerization was carried out in a 50 mL flask under nitrogen atmosphere with stirring. Known amounts of solid were placed in the flask and the solution containing given amounts of monomer and initiator in 25 mL of water was added. The polymerization was conducted at a monomer concentration below 8 wt %, because the polymerization at a higher monomer concentration affords the polymer precipitating from the solution, which cannot be separated from the polymer-encapsulated solid. The mixture was degassed by freeze–thaw technique and then allowed to proceed polymerization with stirring at 50°C. After a definite period of time, a small amount of water-soluble inhibitor, nitrosophenylhydroxylamine ammonium salt (Cupferon), was added to the mixture to stop the polymerization, and then the mixture was centrifuged at 4000 rpm. The precipitate was washed with distilled water, followed by centrifugation. The procedure was repeated several times until the unreacted monomer was no longer eluted. The resulting precipitate was dried in a vacuum oven at 50°C and the weight of polymer formed on the solid surface (shown hereinafter as “C-polymer”) was calculated by subtracting the weight of solid from that of the product containing solid. On the other hand, to a somewhat opaque supernatant solution was added a 5 wt % aqueous solution of sodium bromide to precipitate the polymer dispersed in the form of latex. The salted-out polymer was filtered and dried in vacuum. The polymer obtained by the treatment was denoted hereinafter as “L-polymer.”

Soxhlet equipment was used for the extraction of polymer from the encapsulated solid with chloroform.

Electron micrographs were obtained using a Hitachi S-415 scanning electron microscopy. Ionetching was carried out at 5 mA in vacuum.

RESULTS AND DISCUSSION

Adsorption of Cationic Monomer onto SiO₂ from Aqueous Solution

The adsorption isotherm of the monomer onto SiO₂ is depicted in Figure 1, where the monomer concentration on the abscissa is expressed in the feed concentration rather than the equilibrium concentration so that one can know the amount of adsorbed monomer under the polymerization conditions. In general, the adsorption of ionic surfactants on the oppositely charged surface levels off above a critical micelle concentration (cmc).¹⁵ However, for the present system there is an appreciable increase in the adsorption even above the cmc and the adsorption is saturated at a concentration relatively higher than the cmc for the monomer. This is probably attributed to a highly porous structure of SiO₂ used here.

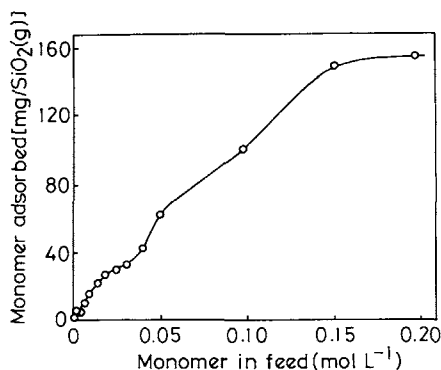


Fig. 1. Adsorption isotherm of cationic monomer on SiO_2 from the aqueous solution at 50°C . SiO_2 , 400 mg; monomer solution, 20 mL.

Polymerization of Cationic Monomer in the Presence of SiO_2

Polymerization of the cationic monomer in the presence of SiO_2 in aqueous system was carried out using three kinds of radical initiator: oil-soluble AIBN and water-soluble, anionic KPS, and cationic AIBA (see Table I). The polymerization with AIBN and AIBA affords the adsorbed polymer, "C-polymer," though accompanied by the formation of polymer dispersed in the form of latex, "L-polymer." Furthermore, no adsorption of L-polymer onto SiO_2 was observed under the present conditions. AIBA is the most effective of the initiators used here for the formation of C-polymer. On the other hand, KPS fails to initiate the polymerization in the presence of SiO_2 , though L-polymer is almost quantitatively formed in the absence of the solid (see Table III). Such a lack of polymerizability with KPS was also observed for the polymerization systems involving other solids such as titanium oxide and alumina. However, when a hydrophobic vinyl monomer such as ST or MMA, which is solubilized into an adsorbed layer of the cationic monomer on the solid surface, is added as a comonomer to the polymerization system using KPS as initiator, the copolymerization takes place and the solid is effectively encapsulated with the resulting copolymer.¹⁶ KPS forms a hydrophobic, complex salt

TABLE I
Polymerization of Cationic Monomer in the Presence of SiO_2
with Various Initiators^a

Initiator ^b	SiO_2 (g)	Yield (%)			C-polymer (g)
		C-polymer	L-polymer	Total	SiO_2 (g)
KPS	0.10	0.0	0.0	0.0	0.00
KPS	0.50	0.0	0.0	0.0	0.00
AIBN	0.50	2.4	87.4	89.8	0.02
AIBA	0.50	10.2	78.8	89.0	0.10

^a Monomer, 0.51 g (1.25 mmol); SiO_2 , 150–200 mesh; water, 25 mL; initiator, 4 mol % to monomer; time, 24 h; temp, 50°C .

^b KPS, potassium persulfate; AIBN = 2,2'-azobisisobutyronitrile; AIBA = 2,2'-azobis(2-amidinopropane) dihydrochloride.

TABLE II
Effect of Monomer Concentration on the Polymerization of
Cationic Monomer with AIBA in the Presence of SiO₂^a

Monomer (g)	Monomer (g)		Yield (%)			C-polymer (g)
	SiO ₂ (g)		C-polymer	L-polymer	Total	SiO ₂ (g)
0.51	1.0		10.2	78.8	89.0	0.10
1.02	2.0		6.2	82.5	88.7	0.13
1.52	3.0		4.8	91.7	96.5	0.15

^aSiO₂ (150–200 mesh), 0.50 g; AIBA, 4 mol % to monomer; water, 25 mL; time, 24 h; temp, 50°C.

with the cationic monomer, being deposited on the solid surface because of low solubility in water. Therefore, KPS is not decomposed to an inactive species, but the complex salt is probably occluded in hydrophobic sites on the solid surface where the initiator becomes nonoperative.

Table II shows results on the effect of monomer concentration on the polymerization with AIBA in the presence of SiO₂. The amount of C-polymer gradually increases with increasing the monomer concentration, though the yield, represented in %, decreases. Such dependence appears to correspond to the variation in the amount of adsorbed monomer with concentration shown in Figure I. The ration of C-polymer to SiO₂ at the highest monomer concentration in Table II is approximately equal to the amount of the monomer adsorbed at saturation. However, at lower monomer concentration in feed the ratio of C-polymer to SiO₂ slightly exceeds the amount of adsorbed monomer. Thus, the formation of C-polymer could be caused to some extent by the propagating species deposited on the solid surface, though C-polymer is formed mainly through the polymerization of the monomer adsorbed on the surface.

The results of polymerization in the presence of a varying amount of SiO₂ are presented in Table III. Although there is little variation in total polymer yield, the proportion of C-polymer in the products relatively increases with increasing the amount of SiO₂ and the selective formation of C-polymer is achieved under the conditions where the feed ratio of monomer to SiO₂ is 0.13 or lower by weight. Furthermore, the ratio of C-polymer to SiO₂ exhibits an

TABLE III
Effect of Amount of SiO₂ on the Polymerization of Cationic Monomer
with AIBA in the Presence of SiO₂^a

SiO ₂ (g)	Monomer (g)		Yield (%)			C-polymer (g)
	SiO ₂ (g)		C-polymer	L-polymer	Total	SiO ₂ (g)
0.0	—		—	99.9	99.9	—
0.5	1.00		10.2	78.8	89.0	0.10
2.0	0.25		38.1	49.0	87.1	0.10
3.0	0.17		78.9	13.3	84.2	0.12
4.0	0.13		84.3	0.0	84.3	0.11

^aMonomer, 0.51 g (1.25 mmol); SiO₂, 150–200 mesh; AIBA, 4 mol % to monomer; water, 25 mL; time, 24 h; temp, 50°C.

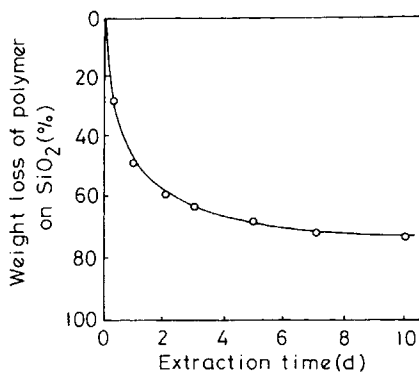


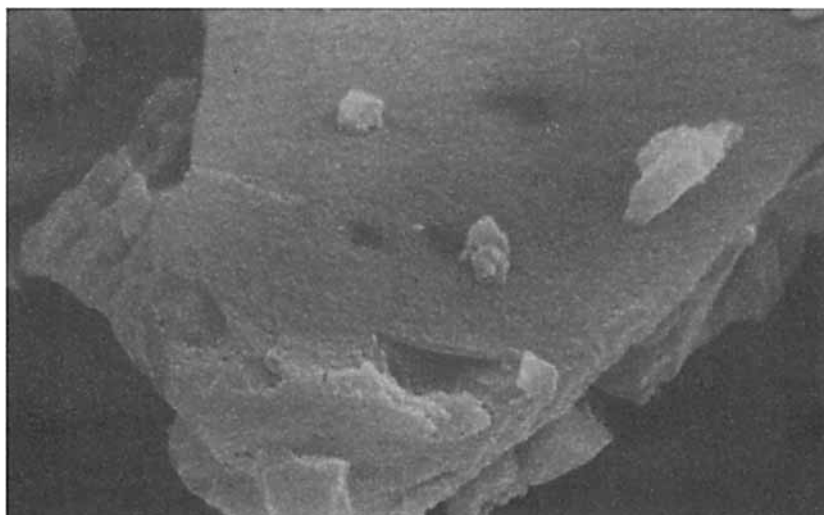
Fig. 2. Soxhlet extraction of polymer from encapsulated solid with chloroform. The encapsulated solid containing 15 wt % polymer was used.

approximately constant value in the range of present experiments, which is close to the amount of adsorbed monomer. The result also indicates that the polymerization of the adsorbed monomer gives most of the C-polymer.

The polymer-encapsulated solid particles obtained here are free-flowing and show an appearance similar to that of raw particles. Figure 2 shows a variation in the amount of residual polymer on the solid with extraction time for the encapsulated solid containing 15 wt % polymer. The unextractable polymer amounts to ca. 27%, which appears to be fixed tightly on the surface of solid particles.

Observation with Electron Microscopy

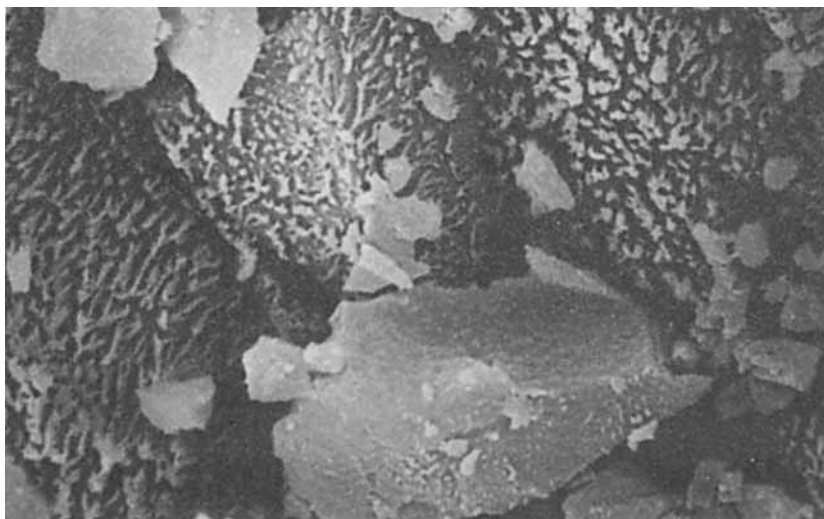
The electron micrographs of raw silica particles and polymer-encapsulated particles are represented in Figures 3(a) and (b), respectively. The ion-etched specimen was used for the polymer-encapsulated solid because only ambigu-



(a)

x 5000

Fig. 3. Electron micrographs of raw silica particles (a) and polymer-encapsulated particles containing 15 wt % polymer (b).



(b)

x 5000

Fig. 3. (Continued from the previous page.)

ous evidence on the encapsulation was obtained in the micrograph of the intact, encapsulated solid. Micrograph (b) explicitly demonstrates that the polymer, which looks like a "lawn," is uniformly formed on the surface of solid particles. Small pieces of solid particles appear to slightly increase during polymerization. Some breaking of solid particles could be caused by stirring, because of brittleness owing to the highly porous structure of the solid. Furthermore, dyeing with aqueous solution of methylene blue showed more evidence of uniform formation of the polymer on the solid particles. The raw solid was readily dyed, while little dyeing was observed for the encapsulated solid.

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