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ORIGINAL CONTRIBUTION

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Polymer modification of colloidal particles by spontaneous polymerization of surface active monomers

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Abstract Adsorption and spontaneous polymerization of head- or tail-type surface active monomers having long methylene chains on colloidal silica and δ-alumina were investigated. Both head-type and tail-type ammonium monomers on silica in chloroform or tetrahydrofuran had the maximum adsorption on the respective adsorption isotherm. Above the monomer concentration giving the maximum adsorption, it was observed that the monomer formed micelles or clusters in bulk solution with removal of adsorbed water molecules from the silica surface. At the monomer concentration giving the maximum adsorption, heating the silica suspension containing the monomer at 40°C or 60°C in tetrahydrofuran or chloroform solution resulted in spontaneous polymerization. The composite particles formed by polymerization were observed to have many spots consisting of polymer on the surface. Therefore, it is suggested that the monomers are concentrated by micelle-like aggregation on the silica surface and consecutively spontaneous polymerization takes place. Adsorption of an anion-type monomer having a carboxyl group on δ-alumina, which exhibited a positive ζ potential in neutral aqueous solution, was higher than that on colloidal silica, but did not spontaneously polymerize on alumina.

Key words Colloidal particles – Polymer modification – Surface active monomer – Spontaneous polymerization – Adsorption

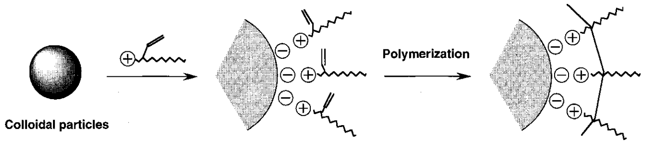
Introduction

Fabrication and controlling of physical and chemical properties on ultrafine particles give great hope for new developments in materials chemistry [1–3]. We have been functionalizing monodisperse inorganic colloidal particles, mostly silica, by polymer modification. If it is possible to control the surface potential or energy by modification of colloidal particles with polymer materials, the modified particles have the potential to assume the architecture of the composite particles; for instance two- or three-dimensional particle-arrayed substrates [2, 4–6].

So far, we have developed a convenient polymer modification of monodisperse colloidal silica particles using a polymeric coupling agent of trimethoxysilyl-terminated maleic anhydride-styrene copolymer [7, 8]. The modification led to the preparation of monodisperse and stable composite particles in acidic or basic conditions by the reaction of maleic anhydride moiety with diisocyanate, and the introduction of amino and carboxyl groups on the surface [9]. Further, binding of the secondary polymer to the poly(maleic anhydride-styrene)-modified silica successfully brought about control of the surface polarity [10]. However, application of the modification is limited to inorganic colloids having many hydroxyl groups, such as silica or titania, so it is necessary to exploit a new method to modify colloidal particles having fewer surface hydroxyl groups.

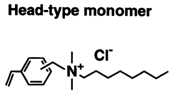
On the other hand, the fact that the formation of micelles or reversed micelles from surface active vinyl monomer induces polymerization without an initiator, i.e. “spontaneous polymerization, has recently received much attention [11–14]. In this regard, it has been reported that polymerization of vinyl monomer in suspensions containing fine inorganic particles such as porous silica gel or alumina and polymerizable surfactants with or without a radical initiator has led to encapsulation of the particles [15–18]. These methods are based on the formation of hydrophobic areas around the particles by adsorption of the surface active monomer through electrostatic interaction. Therefore, if the polymerizable surfactant were also effectively adsorbed on colloidal particles in a similar manner to those in the encapsulation of silica gel or alumina, surface modification of the colloid by polymerization could be possible. Moreover, if the surface active monomer having a long methylene chain could be efficiently adsorbed and aggregated via electrostatic interaction or hydrogen bonding on the surface of colloidal particles, polymerization would take place spontaneously, as shown in Scheme 1.

This paper describes the adsorption of head- or tail-type surface active monomers, HC-8, HC-10, HC-18, HC-18, HC-Ole, TC-10, TMC-10 and TA-10, on monodisperse colloidal silica or δ-alumina and surface modification by successive spontaneous polymerization.



Scheme 1 Schematic diagram of adsorption and spontaneous polymerization of the surface active monomer on colloidal particles

Head-type monomer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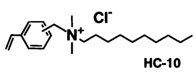
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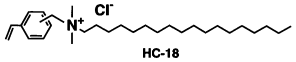
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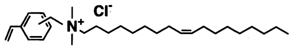
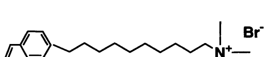
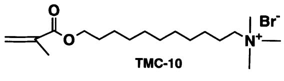
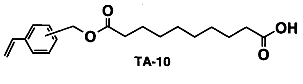

HC-Ole

Tail-type monomer


TC-10


TMC-10


TA-10

Experimental

Materials

Ethanolic suspensions of monodisperse colloidal silica, containing 23 wt% SiO_2 of 500 nm size, was kindly supplied by Catalysts & Chemicals, Japan. δ-Alumina (13 nm), having a specific surface area of 100 $m^2\ g^{-1}$, was supplied by Nippon Aerosil, Japan. Chloromethylstyrene (CMS), consisting of *meta* and *para* isomers, *p*-chlorostyrene and tertiary amines of *N*,*N*-dimethyl-1-octylamine, *N*,*N*-dimethyl-1-decylamine, *N*,*N*-dimethyl-1-octadecylamine and *N*,*N*-dimethyl-1-oleylamine were purchased from Tokyo Chemical Industry Co., Japan and used without further purification. Hydroxymethylstyrene was synthesized by the reaction of CMS with $AgNO_3$ [19].

Measurements

^1H NMR spectra were measured at a resonance frequency of 500 MHz on a JEOL JNM-A500. Infrared spectra were recorded by a diffuse reflectance method on a JEOL-JIR5500. Spectrophotometric absorption was measured on a JASCO V-520S. Scanning electron micrographs (SEM) were taken by a field emission-scanning electron microscope on a JEOL-JSM-6320F. Particle size distribution and the molecular weight of the polymerization product were measured using an argon laser by a dynamic and a static light-scattering method on an Ohtsuka DLS-700S, respectively. Thermal gravimetric analysis was carried out on a Shimadzu TA-50.

Synthesis of HC-8, HC-10, HC-18 and HC-Ole

These head-type monomers were synthesized by the reaction of CMS with the corresponding tertiary amine. A typical run was as follows. A mixture of 0.98 cm^3 CMS, 2.5 g *N*,*N*-dimethyl-1-octylamine, 2 mg 2,6-di-*tert*-butylphenol in 4 cm^3 dry acetonitrile and 2 cm^3 dry chloroform was stirred at 55°C for 6 h in a nitrogen atmosphere. Evaporation of the solvent and precipitation from chloroform solution with diethyl ether gave 0.82 g HC-8. ^1H NMR ($CDCl_3$) for HC-8: δ 0.88 (t, 3H), 1.24–1.30 (m, 2H), 1.79 (m, 2H), 3.31 (s, 6H), 3.47–3.52 (2H), 5.07 (s, 2H), 5.32–6.35 (m, 1H), 5.79–5.84 (m, 1H), 6.68–6.74 (m, 1H), 7.38–7.63 (m, 4H) ppm. ^1H NMR ($CDCl_3$) for HC-10: δ 0.88 (t, 3H), 1.25–1.34 (m, 14H), 1.80 (m, 2H), 3.30 (s, 6H), 3.46–3.51 (m, 2H), 5.04 (s, 2H), 5.33–5.38 (m, 1H), 6.69–6.75 (m, 1H), 7.39–7.62 (m, 4H) ppm. ^1H NMR ($CDCl_3$) for HC-18: δ 0.88 (t, 3H), 1.24–1.30 (m, 30H), 1.79 (m, 2H), 3.32 (s, 6H), 7.38–7.63 (m, 4H) ppm. ^1H NMR ($CDCl_3$) for HC-Ole:

δ 0.88 (s, 3H), 1.26–1.33 (m, 22H), 1.79 (m, 2H), 1.96–2.01 (m, 4H), 3.31 (s, 6H), 3.47–3.53 (m, 2H), 5.07 (s, 2H), 5.31–5.38 (m, 3H), 5.78–5.84 (m, 1H), 6.67–6.73 (m, 1H), 7.31–7.66 (m, 4H) ppm.

Synthesis of TC-10

A mixture of 0.23 g magnesium, 5 mg iodine and 1.5 cm^3 dry tetrahydrofuran (THF) was stirred at 35°C for 1 h in an argon atmosphere. The THF solution (4.5 cm^3) containing 1.4 g *p*-chlorostyrene was added dropwise to the Mg-THF solution over 1 h and the resulting solution was stirred at 35°C for 18 h. The Grignard reagent was poured dropwise into a solution of 1.5 g 1,10-dibromodecane, 0.46 cm^3 Li_2CuCl_4 (0.1 mol dm^{-3} in THF) and 2 cm^3 dry THF at 4°C. The solution was stirred at a room temperature for 18 h and then quenched with 10 vol% HCl. Extraction with chloroform, drying over $MgSO_4$ and evaporation gave a paste product (1.24 g). The product was dissolved in acetone, the solution was filtered, and was then supplied for quaternization using trimethylamine, which was evolved by mixing trimethylamine hydrochloride with 2N KOH for 3 days at room temperature. After evaporation, the crude product was dissolved in chloroform and filtered to remove the diammonium salt. Precipitation with diethyl ether and drying under reduced pressure gave 0.21 g TC-10; yield 28.4%. ^{1}H NMR ($CDCl_3$): *δ* 1.26 (m, 12H), 1.73 (m, 2H), 2.58 (t, 2H), 3.45 (s, 9H), 3.56 (t, 2H), 5.17 (q, 1H), 5.68 (q, 1H), 6.69 (q, 1H), 7.15 (d, 2H), 7.33 (d, 2H) ppm.

Synthesis of TMC-10

1.2 g methacryloyl chloride in 20 cm^3 THF in a nitrogen atmosphere at 0°C was added dropwise to a mixture of 1.99 g 1-bromo-10-undecanol, 1.7 cm^3 triethylamine, 3 mg 2,4-di-tert-butylphenol in 35 cm^3 dry THF and the mixture was stirred at a room temperature overnight. Washing with aqueous Na_2CO_3 solution (5%) and extraction with chloroform, drying over $MgSO_4$, and evaporation of the solvent gave an oily product (2.5 g) of 11-bromoundecyl methacrylate. The reaction of the methacrylate with trimethylamine and successive purification were carried out in the same manner as described above. ^{1}H NMR ($CDCl_3$): *δ* 1.33 (m, 14H), 1.68 (m, 2H), 1,78 (m, 2H), 1.95 (s, 3H), 3.47 (s, 9H), 3.57 (t, 2H), 4.14 (t, 2H), 5.55 (d, 1H), 6.10 (d, 2H) ppm.

Synthesis of TA-10

75 mg *N*,*N*-dimethyl-4-aminopyridine and 1.0 g hydroxymethylstyrene, consisting of *para* and *meta* isomers, in chloroform (0.5 cm^3) were added to a 7 cm^3 dry *N*,*N*-dimethylformamide (DMF) solution of 1.8 g sebacic acid and the mixture was stirred at 0°C for 30 min in a nitrogen atmosphere. The chloroform solution (2.0 cm^3) of 1.84 g *N*,*N*'-dicyclohexylcarbodiimide was poured in the DMF solution, and the mixture was stirred at 0°C for 2 h and further at a room temperature for 1 day. Filtration and extraction with chloroform from aqueous solution three times gave the paste product. Dissolving the paste with hexane/chloroform (10/1 in vol) and successive filtration were repeated three times to remove the by-product urea. Evaporation and drying under reduced pressure gave 1.68 g TA-10; yield 73%. ^{1}H NMR ($CDCl_3$): *δ* 1.13–1.63 (m, 16H), 2.31 (m, 4H), 5.10, 5.41 (s, 2H), 5.08–5.12 (m, 1H), 5.75–5.79 (m, 1H), 6.69–6.73 (m, 1H), 7.31–7.64 (m, 4H) ppm.

Adsorption isotherm

The dry THF solution of each monomer was added to a colloidal silica-THF solution (3.0 cm^3) containing 0.345 g SiO_2 and the mixture was gently stirred at 28°C for 2 h in a nitrogen atmosphere; in all cases, adsorption of the monomer attained equilibrium in 20 min. The adsorption of the monomer on the silica was estimated from the concentration in the supernatant which was separated by centrifugation. The absorption coefficients of HC-8, HC-10, HC-18 and HC-Ole in THF at 284.5 nm were $\varepsilon = 648$, 984, 965 and 1080, respectively. Adsorption of TC-10, TMC-10, HC-8 and TA-10 on colloidal silica or *δ*-alumina in chloroform was measured in the same manner employing absorption coefficients, $\varepsilon = 1380$ at 294.5 nm for TC-10, $\varepsilon = 7130$ at 224.5 nm for TMC-10, $\varepsilon = 988$ at 284.0 nm for HC-8, and $\varepsilon = 13800$ at 249.0 nm for TA-10.

Polymerization

A typical run was as follows. After a 50 cm^3 three-necked flask was thoroughly purged with nitrogen, the suspension of colloidal silica in dry THF (12 cm^3), containing 1.4 g SiO_2, was added to the flask, followed by 24 cm^3 of HC-10-THF solution (2.0×10^{-2} mol dm^{-3}). The mixture was gently stirred at 60°C for 4 h in a nitrogen atmosphere. Centrifugal separation from the THF solution and drying under reduced pressure gave 1.4 g silica particles.

Determination of polymer bound to silica

The amount of polymer bound to silica after polymerization was determined from the weight decrease during temperature elevation from 100°C to 800°C, after keeping at 100°C for 1 h on thermal gravimetric analysis.

Results and discussion

Adsorption of cationic head-type monomers

Since colloidal silica generally has a negative charge under neutral condition, the ammonium monomer is expected to adsorb effectively on the silica and to give the Langmuir-type adsorption isotherm. As can be seen in Fig. 1, however, the adsorption of the head-type monomers, HC-8, HC-10, HC-18 and HC-Ole, on colloidal silica in THF gave unexpected isotherms having the individual maximum value in the monomer concentration range from 2×10^{-5} to 7×10^{-5} mol per unit gram of silica. In order to investigate the abnormal adsorption phenomena, we measured the changes of particle size distribution with monomer concentration in the suspension of the HC-10/silica system by a dynamic light-scattering method. Figure 2 shows particle size distributions in the suspension at monomer concentrations of 4.5×10^{-5}, 6.0×10^{-5} and 12.0×10^{-5} mol g^{-1}. At a monomer concentration lower than that giving the maximum adsorption, dynamic light-scattering analysis showed that the particles were distributed nearly in the same size range as those of the original colloidal silica. Around the monomer concentration giving the maximum adsorption, we observed not only the formation of small particles, possibly clusters, less than 30 nm in size, but also the appearance of large particles formed by coagulation of the colloidal silica in the range from 400 nm to 1200 nm. Above the monomer concentration giving the maximum adsorption, particles were observed in two fractions from 1 nm to 6 nm and from 300 nm to 3000 nm. These results suggest that monomer molecules adsorbed on silica particles at lower monomer concentration are in equilibrium with those in solution at low monomer concentration, simultaneously the ζ potential of the colloid surface possibly decreases with adsorption of the monomer. Therefore, above the monomer concentration giving the maximum adsorption, monomer molecules probably aggregate to form thermodynamically stable clusters with the removal of water molecules adsorbed on the silica surface. The removal of the adsorbed water possibly makes the colloidal particles instable and consequently coagulation of silica particles takes place to form large masses. Hence, the polymerization of the adsorbed monomer on silica was conducted at a monomer concentration lower than that resulting in maximum adsorption.

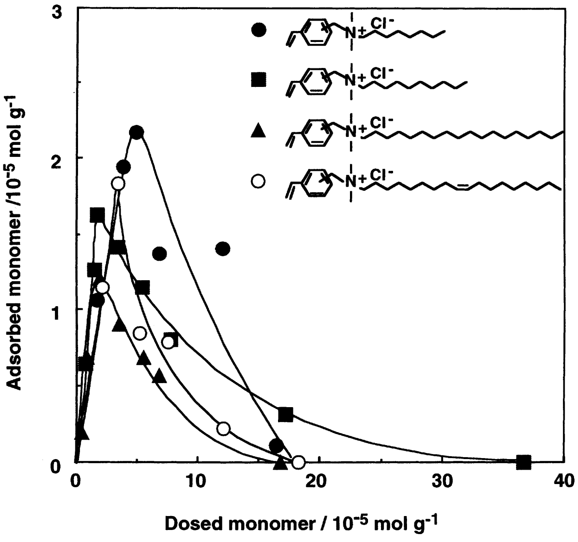


Fig. 1 Adsorption isotherms of head-type monomers on colloidal silica in THF at 28°C

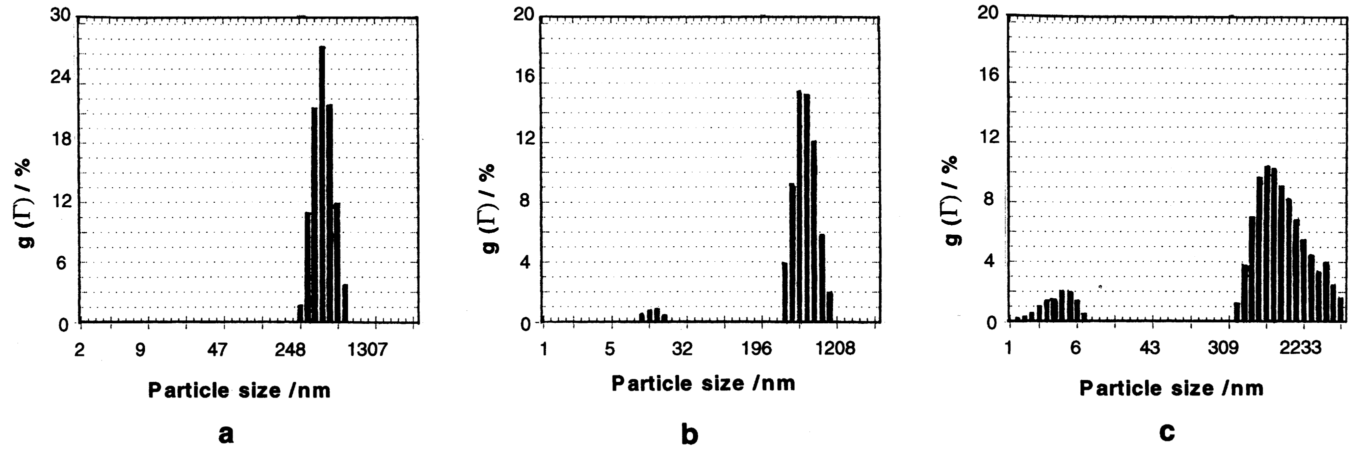


Fig. 2 Light-scattering intensity distribution, g(Γ), at HC-10 concentrations of **a** 4.5×10^{-5}, **b** 6.0×10^{-5}, and **c** 1.2×10^{-4} mol/g in the suspension of a HC-10/colloidal silica system

It was also observed that a monomer of HC-8 gave the highest adsorption in the head-type monomers. The head-type monomer adsorbed is considered to prefer a folding structure between the alkyl group and the vinyl phenylene group around the ammonium nitrogen atom. Thus, higher adsorption of HC-8 probably results from smaller steric repulsion for close packing than for long alkyl groups.

Adsorption of cationic tail-type monomers

The adsorption of tail-type monomers on silica was examined in chloroform, because a tail-type monomer of TC-10 is insoluble in THF, but soluble in chloroform. The adsorption isotherms of TMC-10, TC-10 and HC-8 on silica in chloroform are shown in Fig. 3. The isotherms have maximum values for each adsorption in the concentration range from 5×10^{-5} to 8×10^{-5} mol g^{-1} like those of head-type monomers in THF. TC-10 gave the highest adsorption on silica in chloroform. The high adsorption is probably due to aggregation through π-π interactions between vinyl phenylene groups of the adsorbed monomer.

Adsorption of anionic tail-type monomers

The anionic monomer, TA-10, is expected to adsorb effectively via electrostatic interaction on δ-alumina having a positive charge, or via hydrogen bonding with silanol on colloidal silica. In Fig. 4, adsorption isotherms of TA-10 on colloidal silica and on δ-alumina, which exhibited a ζ potential of +31 mV in water, at 28°C in chloroform are shown in a unit of the molecule per square nanometer, because δ-alumina having a high specific surface area adsorbed a considerably larger amount of monomer compared with colloidal silica. Adsorption of the monomer on δ-alumina reached a constant value, 0.46 molecules nm^{-2}, i.e. 7.6×10^{-5} mol g^{-1}, above a dosed monomer concentration of more than 1.5 molecules nm^{-2}, i.e. 2.5×10^{-4} mol g^{-1}, while the adsorption on colloidal silica showed the maximum value, 0.21 molecules nm^{-2}, i.e. 3.5×10^{-5} mol g^{-1}, at a dosed monomer concentration of 2.0 molecules nm^{-2}, i.e. 3.3×10^{-4} mol g^{-1}, which similarlis to the adsorption of the cationic monomer on colloidal silica. In this case, TA-10 probably adsorbs through hydrogen bonding between the carboxyl and the silanol groups on colloidal silica. Higher adsorption of TA-10 on δ-alumina, as compared to that on colloidal silica suggests that electrostatic interaction is more effective for adsorption than interaction due to hydrogen bonding between the monomer and the silica. As described above, the tail- or head-type monomer gave the maximum adsorption on colloidal silica at a dosed monomer concentration in the range from 2×10^{-5} to 6×10^{-5} mol g^{-1}. Therefore, these results indicate that adsorption of TA-10 on δ-alumina or colloidal silica is relatively weaker than adsorption of head- or tail-type ammonium monomers on colloidal silica. However, adsorption of TA-10 on δ-alumina in water-saturated chloroform also gave the maximum value, as shown in Fig. 4. Thus, this result suggests that the presence of adsorbed water molecules is significantly related to the formation of thermodynamically stable micelles or clusters from the monomer.

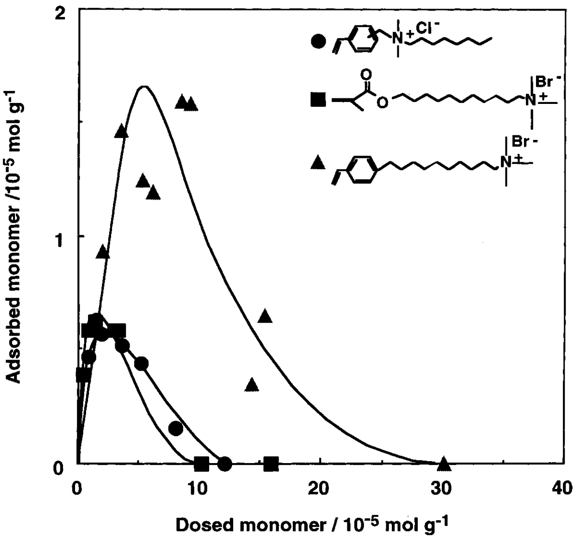


Fig. 3 Adsorption isotherms of HC-10, TC-10 and TMC-10 on colloidal silica in chloroform at 28°C

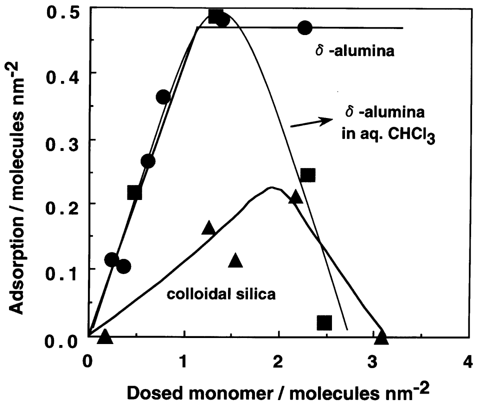


Fig. 4 Adsorption isotherms of TA-10 on δ-alumina and colloidal silica in chloroform at 28°C

Polymerization

According to the adsorption isotherms, we prepared a mixture of colloidal silica and the monomer in THF so as to give the maximum adsorption, and kept the suspension at 40°C or 60°C for 4 h in a nitrogen atmosphere. The resulting composite was washed with THF or chloroform to remove the monomer, and then the polymerized product was pealed out by washing with methanol. A typical ^{1}H NMR spectrum of the product from HC-18 is shown in Fig. 5 along with that of the monomer. From the spectrum, occurrence of the polymerization on the silica surface was confirmed by disappearance of proton signals at 5.32–5.37, 5.80–5.84 and 6.68–6.74 ppm, assignable to protons of vinyl groups, and broadening of the signals at 1.2–2.2 ppm, assignable to methylene and methine groups formed by polymerization. Therefore, the extent of polymerization was quantitatively estimated by the integration ratio of proton peaks due to methylene groups binding to phenylene groups, to those due to vinyl groups in the ^{1}H NMR spectrum (see Tables 1, 2). The results of the polymerization of head-type monomers are listed in Table 1. It was recognized that all head-type monomers were polymerized without an initiator at 60°C and the amount of polymer on the surface was mostly higher than that of the corresponding adsorption. Therefore, it is suggested that polymerization on the silica surface takes place by incorporation of the monomer or coagulation of the spontaneously polymerized product in the micelles or clusters formed in bulk solution. Although polymerization of HC-Ole took place at 40°C, the extent of polymerization of the other monomer was low. Therefore, high aggregation of the monomer on the silica surface probably leads to a high extent of polymerization. Tail-type monomers of TC-10 and TMC-10 as well as head-type monomers were observed to be polymerized in chloroform/THF (30/6 cm^3) at 60°C (Table 2). In these cases, the amount of the polymer layer on the silica was also slightly higher than that of adsorbed monomer. In both polymerizations, the composite particles produced exhibited narrow particle size distributions, as shown in the fourth columns (d_w/d_n) in Tables 1 and 2.

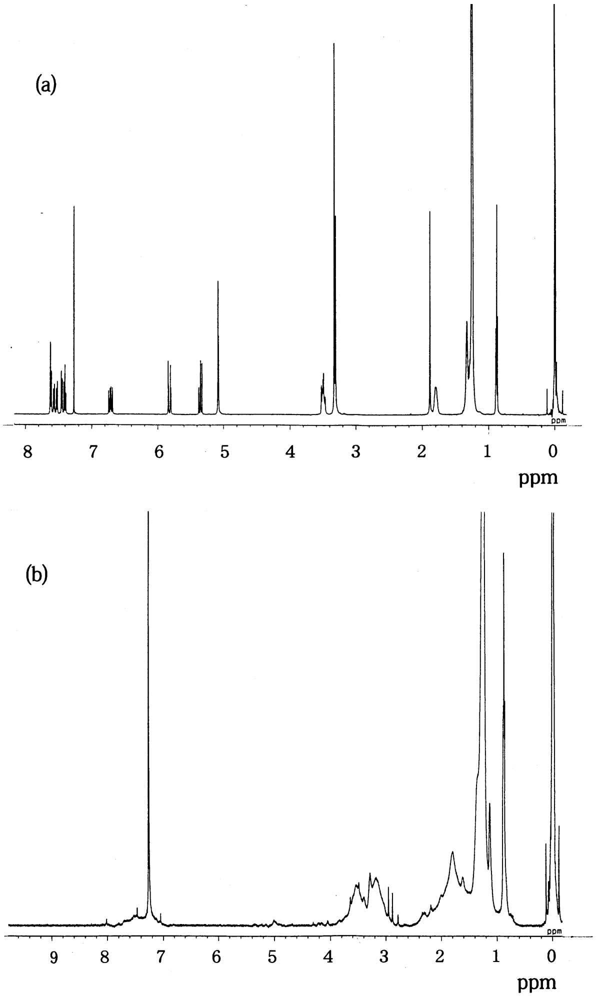


Fig. 5 ^{1}H NMR spectra of **a** HC-18 and **b** the polymerization product

On the other hand, the anionic monomer, TA-10, was scarcely polymerized in chloroform on δ-alumina, but gave a polymerization product on colloidal silica (Table 3). The extent of polymerization was again estimated by integration ratio of the methylene proton signals to vinyl proton ones in the ^{1}H NMR spectra (see Table 3). In both polymerizations, the resonance signals of the vinyl protons were not completely diminished, and hence the extent of polymerization was relatively low. These results suggested that polymerization was probably related to the adsorption force of the surface active monomer on the surface. The THF colloidal suspension contained 0.15 wt% adsorbed water molecules, which were unable to be removed by azeotropic evaporation of THF. Therefore, adsorbed water molecules probably play an important role in spontaneous polymerization, so addition of water to the mixture of δ-alumina and the monomer in chloroform is expected to promote polymerization. However, the use of chloroform saturated with water did not give the polymerization product.

SEM photographs of the original silica and the composite particles obtained from the polymerization of HC-10, TC-10 and TA-10 are shown in Fig. 6. In these cases, we can observe that there are many spots consisting of the polymer on the polymer-modified particles. Therefore, polymerization of the monomer possibly takes place as follows. The monomer adsorbed on the silica aggregates to form a water pool, in such a way that the micelle or the cluster forms, and subsequent concentration of the vinyl groups induces polymerization, as shown schematically in Scheme 2. This explanation is probably supported by the fact that polymerization did not take place on the surface of

Table 1 Polymerization of head-type surface active monomer on colloidal silica at 40°C and at 60°C in chloroform without an initiator[a]

Monomer	Concentration[b]	Weight decrease[c]	d_n[d]	d_w/d_n[e]	$I(CH_2)/I(vinyl)$[f]
	10^{-5} mol g^{-1}	mg g^{-1} (10^{-5} mol g^{-1})	nm		
HC-8	3.3	10.3 (3.3)[g]	510	1.01	h
		9.8 (3.2)	490	1.01	1.60
HC-10	1.7	10.3 (3.1)	520	1.17	h
		10.3 (3.1)	460	1.11	0.54
HC-18	1.7	10.5 (2.3)	480	1.01	h
		9.6 (2.1)	530	1.49	0.39
HC-Ole	3.3	9.2 (2.0)	500	1.06	h
		12.6 (2.8)	510	1.01	6.54

[a] The polymerization was carried out using 1.44 g SiO_2 and 24 cm^3 THF at 40°C (lower line) and at 60°C (upper line) for 4 h

[b] Initial concentration of the monomer in the polymerization

[c] Weight decrease of the composite, prepared by polymerization, during temperature elevation from 100°C to 800°C on thermal gravimetric analysis

[d] Avarage particle size in number base

[e] Distribution in particle size: the ratio of average particle size in weight base to that in number base

[f] Integration ratio of methylene proton signal benzyl position to that of vinyl proton in the ^1H NMR spectrum

[g] Values in parentheses are the weight decreases calculated by the monomer moles

[h] Signals of protons in vinyl goup were not observed in the ^1H NMR spectrum

Table 2 Polymerization of head- or tail-type surfce active monomer on colloidal silica at 60°C in chloroform without an initiator[a]

Monomer	Concentration	Weight Decrease	d_n nm	d_w/d_n	$I(CH_2)/(vinyl)$[b]
	10^{-5} mol g^{-1}	mg g^{-1} (10^{-5} mol g^{-1})			
HC-10	1.9	5.0 (1.5)[c]	510	1.01	d
TC-10	2.5	8.9 (2.3)	540	1.01	d
TMC-10	1.0	4.0 (1.0)	440	8.18	d

[a] The reaction was carried out for 4 h using 6 cm^3 colloidal silica/THF suspension, containing 1.44 g SiO_2 and 30 cm^3 chloroform

[b] Integration ratio of the methylene proton signal at the benzyl position for HC-10 and TC-10 or at the position of the ester group for TMC-10 to that of the vinyl proton in the ^1H NMR spectrum

[c] The weight decreases calculated by the monomer moles

[d] Signals of protons in vinyl groups were not observed in the ^1H NMR spectrum

Table 3 Polymerization of an anionic monomer, TA-10, on colloidal silica or δ-alumina at 60°C in chloroform without an initiator[a]

Particles	Concentration	Weight decrease		d_n	d_w/d_n	$I(CH_2)/(vinyl)$[b]
	10^{-24} mg nm^{-2}	10^{-19} mg nm^{-2}	(10^{-24} mol nm^{-2})	nm		
δ-Alumina	1.9	5.0	(1.6)[c]			9.6
	1.9[d]	4.6	(1.4)			8.4
Colloidal silica	1.1	0.6	(0.2)	530	1.01	50.0
	3.3	1.4	(0.4)	520	1.01	72.0
	5.5 (TC-10)[e]	19.5	(5.1)			f

[a] The polymerization was carried out using 6 cm^3 colloidal silica/THF suspension, containing 1.38 g SiO_2 and 30 cm^3 chloroform for 4 h

[b] Ingration ratio of $\gamma,\delta,\varepsilon,\zeta$-methylene proton signals in sebacinate to that of the α-proton in the vinyl group in the ^1H NMR spectrum

[c] The weight decrease calculated by the monomer moles

[d] The reaction was carried out for 17 h

[e] Values for polymerization of TC-10 on colloidal silica are shown for comparison

[f] Signals of protons in the vinyl group were not observed in the ^1H NMR spectrum

δ-alumina, having no adsorbed water, in anhydrous chloroform. Moreover, in the spontaneous polymerization of a polymerizable surfactant, the concentration of the vinyl group due to micelle or reversed micelle formation is generally essential for polymerization [11–14]. Also, the water pool mechanism is not in conflict with the fact that the micelle or the cluster was formed in bulk solution at high monomer concentration with removal of the adsorbed water molecules from the colloidal silica. In this regard, a relatively high affinity

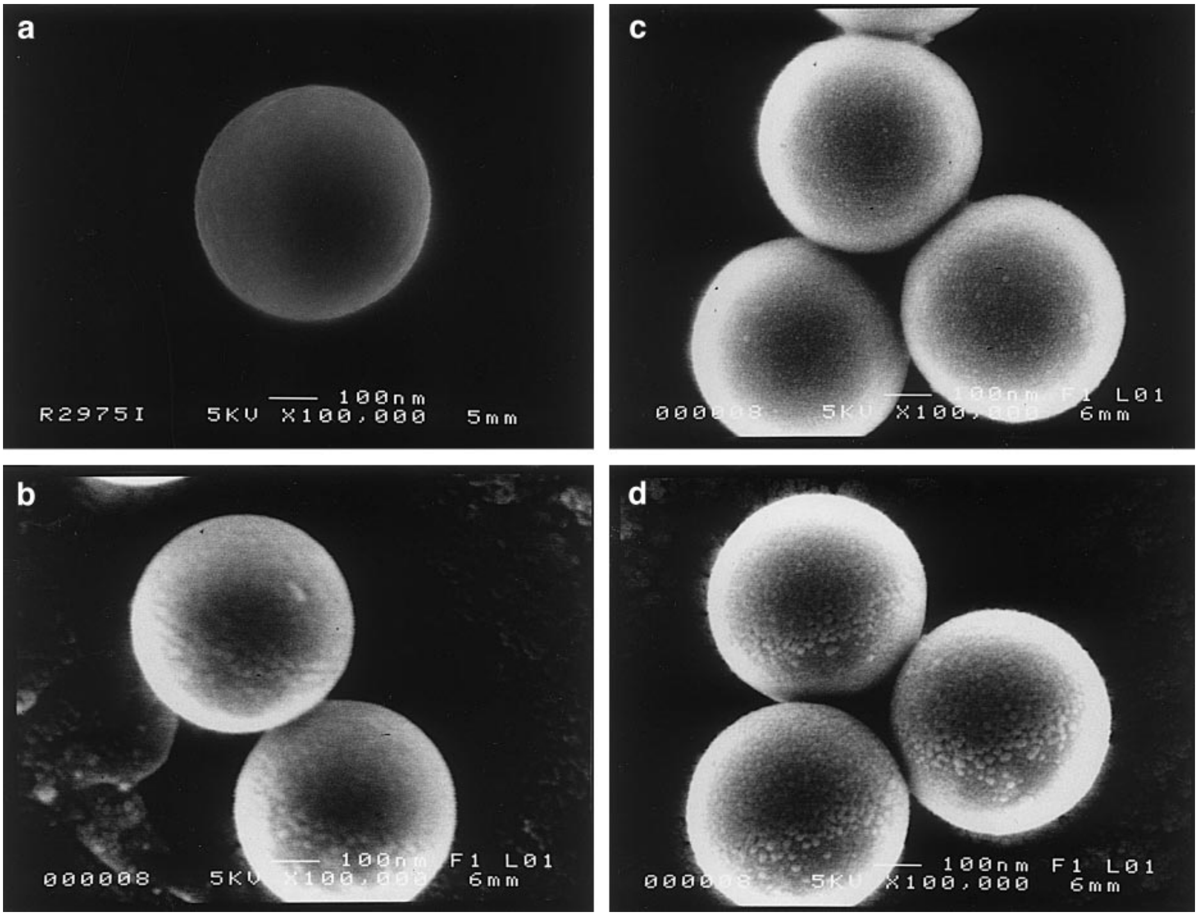
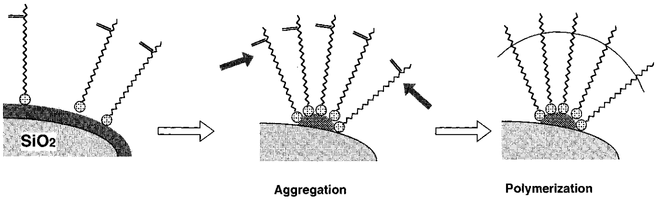


Fig. 6 Scanning electron micrographs of **a** the original colloidal silica and composite particles prepared by the polymerization of **b** HC-10, **c** TC-10, and **d** TA-10



Scheme 2 Schematic representation of the polymerization process of the surface active monomer on colloidal silica

between the water molecules and the particle surface seems to be needed to form the water pool due to the aggregation of the monomer. Therefore, the reason why polymerization of TA-10 on δ-alumina did not occur even in water-saturated chloroform is probably the low affinity between the water molecules and the alumina surface.

Conclusions

1. Adsorption of both head- and tail-type cationic vinyl monomers having long methylene chains on colloidal silica in THF or chloroform had maximum values at dosed monomer concentrations of 2×10^{-5}–8×10^{-5} mol g^{-1} silica. Since the adsorption was relatively weak, the monomer formed thermodynamically stable micelles or clusters above the concentration which gave the maximum adsorption, along with removal of adsorbed water molecules from the surface.

2. The adsorbed monomer was spontaneously polymerized on the silica surface in THF or chloroform without an initiator at 60°C and even at 40°C.

3. The adsorbed water molecules on the silica particle play an important role in spontaneous polymerization. It is suggested that polymerization proceeds via aggregation and concentration of adsorbed monomer on the water pool formed from the adsorbed water molecules on the silica surface.

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