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Accounts

Functionalization of Inorganic Colloidal Particles by Polymer Modification

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The polymer modifications of inorganic colloidal particles, mainly silica, and the stabilization and functionalization were described. The polymer grafting procedures on colloidal silica via covalent bond bindings in order to stabilize and functionalize were presented along with the modification of inorganic particle powder. In the modifications, the reaction of the surface hydroxy groups with polymeric trialkoxysilane was effective for grafting the polymer in terms of controlling the attachment and of successive introduction of functional groups. Especially, the grafting of poly(maleic anhydride-co-styrene) (P(MA-ST)) onto colloidal silica by the reaction with P(MA-ST)-trimethoxysilane gave stable and dispersible composite particles (P(MA-ST)/SiO_2) in organic solvent. The introduction of secondary polymer to P(MA-ST)/SiO_2 successfully controlled the dispersion in organic solvent and ζ-potential in aqueous or highly polar solvents. The modification of colloidal titania with Ru(II)-(2,2′-bipyridyl) complex-tethered polymer gave a photo-active catalyst that exhibited photoinduced electron transfer to a donor by visible light irradiation. Moreover, colloidal crystallization was observed in the suspension of monodisperse, polymer-modified silica in organic solvent, which was a good polar solvent for grafted polymer. The colloidal crystallization of the modified silica took place through close-packing under the electrostatic repulsion among the particles, as well as the crystallization of unmodified silica in aqueous solution.

Recent developments of colloid and surface chemistry have made possible the preparation of various highly size-controlled inorganic oxide colloidal particles.[1] Fabrications of chemical or physical properties on the colloidal particles give great hope for new development of new functional materials. Controlling surface properties of colloidal materials is a major technological research subject in the wide area of pharmaceutical, cosmetic, semiconductor, catalysis, printing, painting, food, biological, and medical fields. Polymer modification, including adsorption, coating, or grafting, of colloidal particles is one of the set of convenient and practical procedures to modify surface characteristics of the particles. In many cases, however, surfactant compounds have been practically employed as stabilizer or emulsifier in heterophase suspension. In this respect, the polymer modification for the stabilization or the dispersion of colloidal particles has the advantage of keeping high efficiency in high dilution or in extremely low concentration, as compared to low molecular surfactants, because a release of the chemical compounds to environment is made more difficult. The modifications of colloidal particles with adsorbed or grafted polymer, so far, have been widely studied for improving stabilization and dispersion in organic or aqueous media.[2] Also, adsorption of polymer electrolytes on colloidal nanoparticles has been also extensively studied in maltilayer assemblies into ordered structures.[3] Furthermore, a recent noteworthy application of polymer electrolyte-adsorbed colloidal particles is chemical combinatorial libraries.[4] The libraries have been constructed on the surfaces of polymer electrolyte-adsorbed and stabilized colloidal silica. In many cases, however, the presence of the disperse agent leads to serious problems in functionalization and precise devising or processing, so that polymer modification via covalent bond bindings on the particles is required for functionalization to achieve the stability in dispersion media.

In this paper, surface modification methods of colloidal particles with polymer via covalent bond bindings to attain colloidal stability are first described along with those of inorganic particle powders to make features of colloidal particle modification clear. Then, specific functionalities and characteristic properties resulting from the polymer modification are also presented.

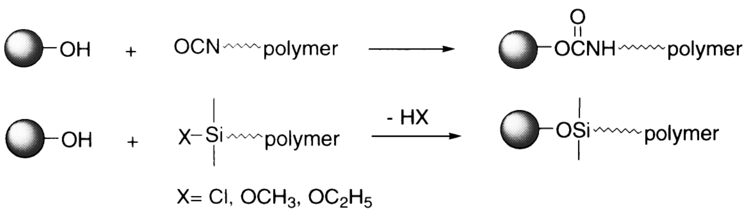
Polymer Modification

The reaction of a surface-active group on the inorganic particles with a chemically active polymer is effective for the polymer modification. In this case, it is common that the functional group on the particles must be activated enough to react with the end group of polymer. The procedure has the advantage of allowing bindings of well-defined polymers, which can be separately synthesized by a living polymerization, in spite of the difficulty of bindings of high molecular weight polymers. The reaction of hydroxy group on inorganic particles with polymers having isocyanate,[5] alkoxysilane,[6] and chlorosilane[6a] groups efficiently gave the polymer-grafted particles, as shown in Scheme 1.

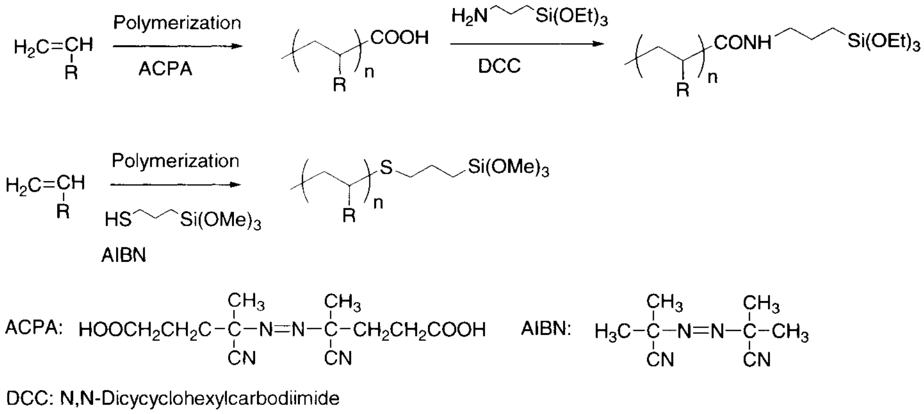
On the contrary, the reactive groups isocyanate, amino, and acid anhydride, introduced on inorganic particles via the reaction with respective coupling agents, can also give stable covalent-bond bindings to chemically active macromolecules capped with hydroxy,[7] carboxyl,[8] and amino[9] groups, respectively. For alumina, heating of the suspension with hydroxy-ended polyoxyethylene gave the polymer-grafted particles.[10]

The reactions for the polymer modification are sometimes inapplicable to those of colloidal particles, because of inducing flocculation or coagulation. For instance, the reaction of colloidal silica with polymeric chlorosilane immediately gives rise to flocculation to sediment due to making the suspension acidify and the surface charge lower. In this respect, the reactions of alkoxysilyl-terminated macromolecules with the surface hydroxy group of colloidal particles are useful and convenient surface modification procedures. A trialkoxysilane compound in the alkoxysilanes is commonly more active than mono- or dialkoxysilanes for the coupling reaction. The reaction using the alkoxysilane gives stable covalent bondings via siloxane bond on silica, titanium(IV) oxide, aluminium oxide, zirconium(IV) oxide, tin(IV) oxide, and nickel(II) oxide, but unstable bonding on boron oxide and iron(III) oxide. Thus, if it is possible to optimize the reaction conditions in the coupling in order to prevent the particle aggregation, the coupling reaction using polymer silane is available for the modification of inorganic colloidal particles. The polymer silanes can be easily synthesized by the condensation of carboxyl-terminated polymer with 3-(triethoxysilyl)propylamine and by the radical polymerization in the presence of 3-(trimethoxysilyl)propylthiol as a chain transfer reagent, as shown in Scheme 2.[11,12]

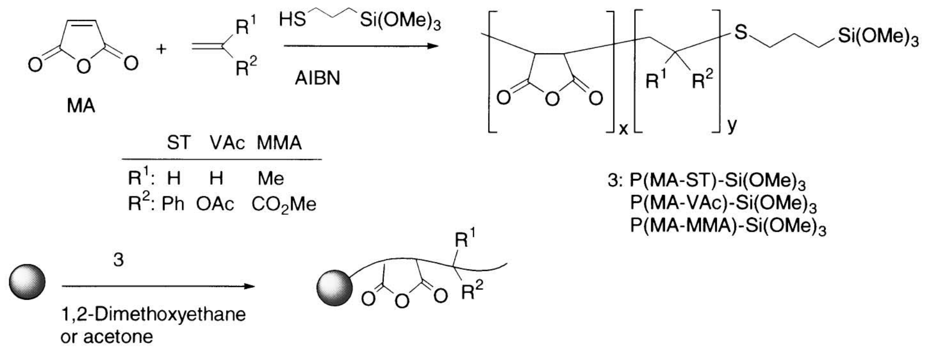
The reaction of the surface hydroxy group on the colloidal particles with the polymer silane can be carried out under relatively mild conditions. For example, the reaction of colloidal silica (0.5 g), of 550 nm in diameter, with 0.1 g polystyrene (PST)-trimethoxysilane of number average molecular weight, M_n, 26,000 in 50 cm^3 1,2-dimethoxyethane at 70 °C for 3 h gave monodisperse PST/SiO_2 with 115 mg/g of PST attached.[11] In this modification, particle aggregation was not observed during the coupling reaction. One factor preventing aggregation may be the use of a polar solvent, which is miscible with water and a good solvent for polymer silane. This modification procedure (Scheme 3) is applicable to the attachment of many polymers, such as poly(methyl methacrylate) (PMMA), polyoxyethylene (PEO), poly(maleic anhydride-co-styrene) (P(MA-ST)), poly(maleic anhydride-co-methyl methacrylate) (P(MA-MMA), and poly(maleic anhydride-co-vinyl acetate) (P(MA-VAc). Especially, the grafting of the polymer composed of maleic anhydride (MA) has a merit of allowing one to introduce successive functional centers. In Table 1, typical results of the reaction of the polymer silanes composed of MA with colloidal silica of 550 nm in diameter are shown.[12] In these modifications, azeotropical removal of ethanol and methanol produced during the reaction gave effective attachment of the respective polymer. Moreover, the polymer silane containing MA component showed characteristic reactivity in the attachment to colloidal silica. In Fig. 1, plots of attached P(MA-



Scheme 1. Polymer modification of inorganic particles with end-capped polymer.



Scheme 2. Typical examples of polymer silane preparation.



Scheme 3. Synthesis of polymer silanes composed of maleic anhydride and modification of colloidal silica with the silanes.

Table 1. Modification of Colloidal Silica with Polymer Silane Composed of Maleic Anhydride[a)][12]

Polymer silane	Solvent[b)]	Attached polymer
	$\mathrm{cm^3}$	wt%
P(MA-ST)-Si(OMe)$_3$	DME (15)	0.74
(M_n = 6100)	THF (15)	0.32
	THF/EtOH (10/5)	0.13
	DME (100)[b)]	3.96
	Dioxane (100)[b)]	2.27
P(MA-MMA)-Si(OMe)$_3$	DME (15)	0.80
(M_n = 7500)	THF (15)	1.04
	THF/EtOH (10/5)	0.15
	DME/EtOH (10/5)	0.56
	DME (100)[b)]	2.22
P(MA-VAc)-Si(OMe)$_3$	DME (15)	0.91
(M_n = 1500)	DME (100)[b)]	2.77
	Dioxane (100)[b)]	1.26

a) Ethanolic colloidal silica suspension, contained 23 wt% SiO_2; 2.3 $\mathrm{cm^3}$.
b) DME: 1,2-dimethoxyethane, THF: tetrahydrofuran.
c) Removed ethanol and methanol azeotropically.

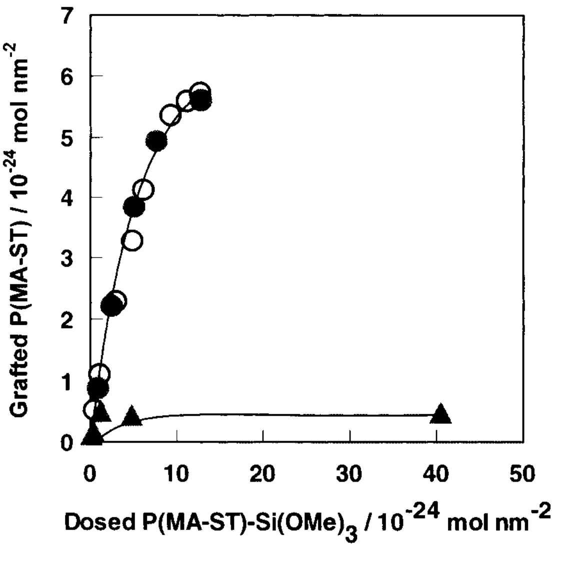
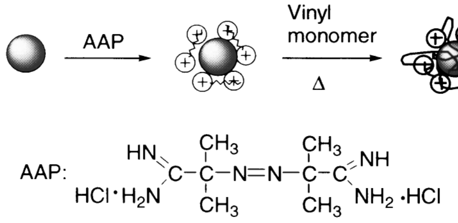


Fig. 1. Plots of grafted P(MA-ST) versus dosed P(MA-ST)-Si(OMe)$_3$ in the modification of colloidal silicas of 10 nm (○), 45 nm (●), and 120 nm (▲).[13]

ST) against dosed P(MA-ST)-trimethoxysilane (P(MA-ST)-Si(OMe)$_3$) in the reaction with colloidal silica of 10, 45, and 120 nm in diameter are also shown.[13] The copolymer silane could effectively react with the colloidal silica of 10 and 45 nm at the concentration of dosed silane less than 0.5×10^{-23} mol per square nanometer of silica to give maximum attachment of 3.4 chains $\mathrm{nm^{-2}}$ more than that (0.30 chains $\mathrm{nm^{-2}}$) on the silica of 120 nm. The specific and characteristic reactivity of P(MA-ST)-Si(OMe)$_3$ and P(MA-MMA)-Si(OMe)$_3$ without particle aggregation probably comes from steric interaction, i.e. volume-excluding effects, among adsorbed polymer silane chains on the colloidal silica owing to their structural rigidity. Hence, the process in the reaction of colloidal silica with the copolymer silane composed of MA may proceed as follows; (i) Adsorption of the polymer silane on the surface along with assembling and orientation of the trimethoxysilyl group toward the silica surface in a good solvent for the copolymer, and (ii) successive efficient reaction of the silane with surface hydroxy group. However, Fukuda et al.[14] have reported that the graft density of PMMA, synthesized by an atom transfer radical polymerization from the surface, is less than 0.7 chains $\mathrm{nm^{-2}}$, because of steric hindrance. Therefore, the modification of colloidal silica with the polymer silane composed of MA may include with the attachment of the silane oligomer formed by the condensation of the polymer silane. The grafting of the oligomer on the silica was suggested by ^{29}Si CP/MAS NMR spectra of P(MA-ST)/SiO_2 shown in Fig. 2.[13] The resonance peaks in the range from -45 to -70 ppm are assignable to silicon originating in polymer silane. According to the literature values of ^{29}Si chemical shifts,[15] the peaks of a, b, and c in Fig. 2 are assignable to silicons formed by direct reaction of the silane with one or two hydroxy groups and to those formed by the reaction of oligomerized silane.

Radical polymerization is also a convenient method for polymer grafting onto inorganic particles. In the radical polymerization, a functional group like azo or peroxy group,[16] able to give radical species, is usually introduced into the particle surface, and then heating of or ultraviolet light irradiation to the suspension of the azo- or peroxy-introduced particles and vinyl monomer initiates the radical polymerization to give polymer grafting. The introduction of the functional group of azo or peroxy has been sometimes carried out two- or three-step reactions using very reactive reagents, such as butyllithium or thionyl chloride. Therefore, some procedures in the functional group introduction are inapplicable to the modification of colloidal particles, because the reaction of colloidal particles with reactive basic or acidic reagents mostly leads to quick coagulation of the particles.

Inorganic colloidal particles generally have negative charge on the surface, and consequent electrostatic repulsion between the particles makes stable dispersion in solution. Hence, if it was possible to make radical initiator having cationic group adsorb on the colloidal particles under mild conditions without particle aggregation, subsequent heating or photoirradiation of the suspension containing colloidal particles and vinyl monomer would form the radical species to initiate radical polymerization, as shown in Scheme 4.



Scheme 4. Polymer modification of colloidal silica by radical polymerization using 2,2′-azobis(2-amidinopropane) dihydrochloride.

Polymerization of styrene in the suspension containing 5 wt% colloidal silica of 550 nm in ethanol with 2,2′-azobis(2-amidinopropane) dihydrochloride (AAP) as an initiator at 85 °C gave PST-coated silica composite.[17] The procedure was also applicable to the coating of colloidal silica by PMMA and poly(2-hydroxyethyl methacrylate). In these polymerizations, it was proposed that radical species was formed on the surface to initiate the propagation in the initial stage, and then polymer chains formed in the bulk solution by polymerization congregated on the surface. Thus, the procedure is appropriate for the preparation of polymer-coated silica containing attached polymer less than 100 mg g^{-1}. However, increasing of monomer concentration or elevating polymerization temperature gave arise to coagulation among particles owing to attractive low polar-low polar interaction between grafted polymer in ethanol. Radical polymerization of vinyl monomer in the suspension of colloidal silica with a macromonomer having a polymerizable vinyl group also resulted in giving polymer-coated silica particles, as shown in Scheme 5.[18] Heating a mixture of styrene and 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator in tetrahydrofuran suspension containing monodisperse colloidal silica in the presence of poly(*N*-vinylpyrrolidone) having a vinyl phenylene end group afforded the composite particles attached with the copolymer of 50–100 mg g^{-1} without aggregation. However, it is generally quite difficult for the polymer modification by the radical polymerization to control the amount of polymer grafting and to introduce functional groups for functionalization.[19]

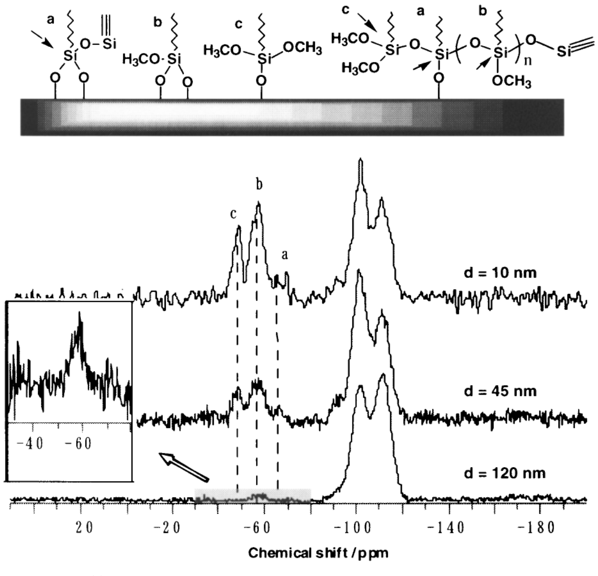
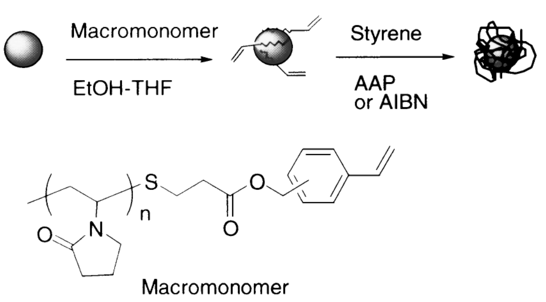
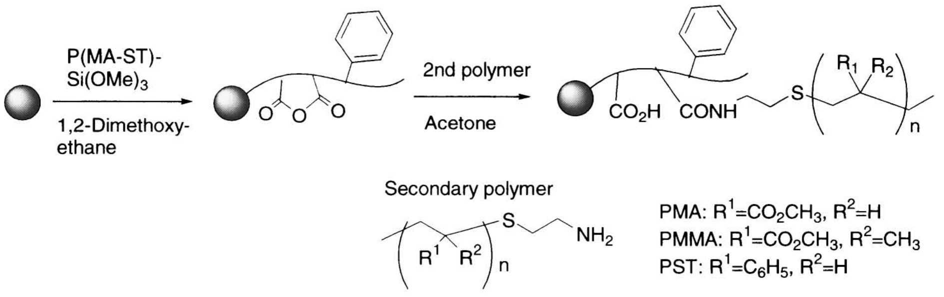


Fig. 2. ^{29}Si CP/MAS NMR spectra of P(MA-ST)-modified silicas.[13]

On the other hand, radical dispersion polymerization has recently been utilized in the encapsulation of colloidal silica modified with trialkoxysilane with vinyl group.[20] Especially, the modification employing atom transfer radical polymerization is a promising procedure for the preparation of well-defined polymer-grafted inorganic particles.[21]



Scheme 5. Polymer modification of colloidal silica by radical polymerization on macromonomer-adsorbed colloidal silica.



Scheme 6. Polymer modification of colloidal silica with P(MA-ST)-Si(OMe)$_3$ and grafting of secondary polymer.

Properties or Functionalities of Polymer-Modified Colloidal Particles

Dispersibility. When we design a functional material by use of polymer modified colloidal particles, we need to clarify such factors governing the stabilities in disperse media. In this respect, to unveil the factors, the composite particles were prepared by secondary polymer grafting to P(MA-ST)/SiO$_2$ via covalent bond bindings, as shown in Scheme 6.[22,23] Grafting of amino-terminated polymer onto P(MA-ST)/SiO$_2$ strongly effected on the dispersibility of the composite particles in solution. In Fig. 3, the dispersion-aggregation phenomena of poly(methyl acrylate) (PMA) or PMMA-grafted P(MA-ST)/SiO$_2$ in methanol–ethyl acetate cosolvent after 24 h are shown. In Fig. 3, the phenomena, i.e. turbidity of the suspension, were evaluated by spectroscopic absorption of the suspension containing 0.1 wt% composite particles at 500 nm as a function of methanol content in the cosolvent.[22,23] In the suspension, precipitation owing to aggregation of the particles makes the absorption zero. Attachment of relatively high molecular weight PMA and PMMA to P(MA-ST)/SiO$_2$ resulted in the aggregation in the solution over 50 vol% methanol content. This aggregation probably comes from low polar–low polar interaction between the secondary grafted polymer chains on the particles in methanol rich solution. On the other hand, interestingly the composite particles grafted by PMA showed aggregation in the solution around 60 vol% methanol solution, but increasing of methanol over 70 vol% content led to make dispersion of the particles.[23] Moreover, the dispersion of the composite particles in the cosolvent was independent of the ester group of polymethacrylate but dependent on the molecular weight and on the amount of attachment.[22] Therefore, the composite particles of PMA- and PMMA-P(MA-ST)/SiO$_2$ in ethyl acetate-rich solution were dispersible due to steric repulsion of solvated secondary polymer chains. Dispersibility of those particles in methanol-rich solution was controlled by the balance between the particle repulsion coming from electrostatic inter-particle interaction and the particle attraction coming from the low polar-low polar interaction. Moreover, attachment of secondary PST to P(MA-ST)/SiO$_2$ led to dispersion in methanol–ethyl acetate cosolvent.[23] The dispersibility of the particles was independent of the molecular weight and the amount of attached PST. From the fact that the particles show highly negative charges in the cosolvent, the dispersibility of the particles is probably due to electrostatic interaction between the particles.

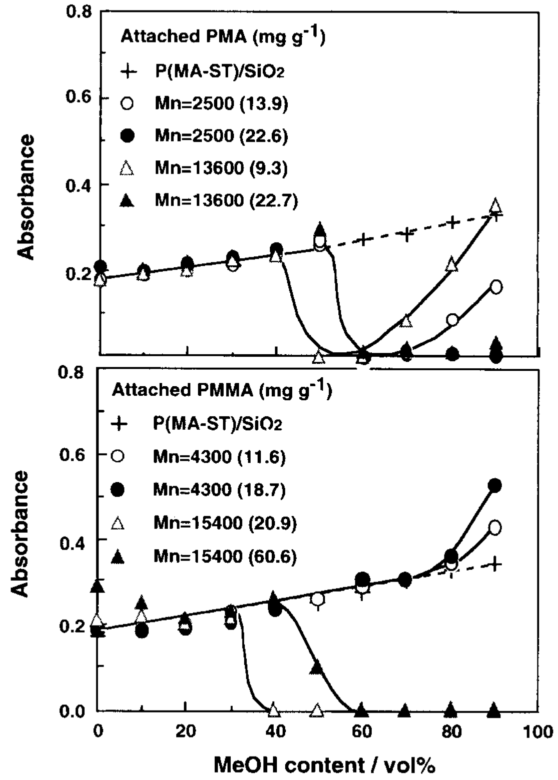
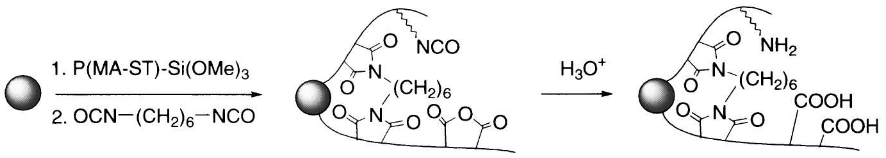


Fig. 3. Changes of absorbance of the suspension containing poly(methyl methacrylate)(PMMA)- and poly(methyl acrylate)(PMA)-grafted P(MA-ST)/SiO$_2$ with methanol content in methanol/ethyl acetate solution at 500 nm.[23]

When the particles were applied to a precise device, dispersion of the particles in media should be preserved by preventing particle coagulation for long time. Polymer-grafted colloidal particles prepared by the reaction with polymer silane usually release the grafted polymer chains in acidic or alkaline aqueous solution by occurring hydrolysis of Si–O–M bonds. For example, immersing of P(MA-ST)/SiO$_2$ prepared from 550 nm colloidal silica and P(MA-ST)-Si(OMe)$_3$ in cosolvent of acetone–pH 4 aqueous solution at room temperature for 24 h resulted in peeing out of 33% grafted polymer. In this respect, in order to make the composite particles stable in aqueous solution, colloidal silica modified with cross-linked polymer were prepared by the reaction of (P(MA-ST)/SiO$_2$ with diols and diamines,[24] or diisocyanate.[25] Especially, the crosss-linking of the surface polymer layer of P(MA-ST) by the reaction with diisocyanate via imide bonds, as shown in Scheme 7,



Scheme 7. Cross-linking of the polymer layer on P(MA-ST)/SiO$_2$ with diisocyanate.

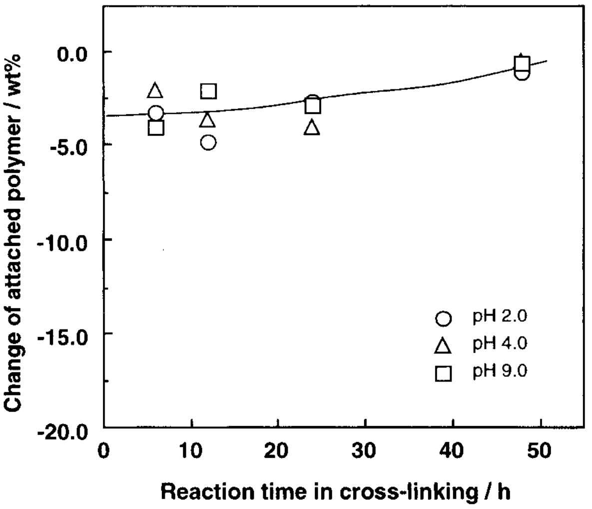
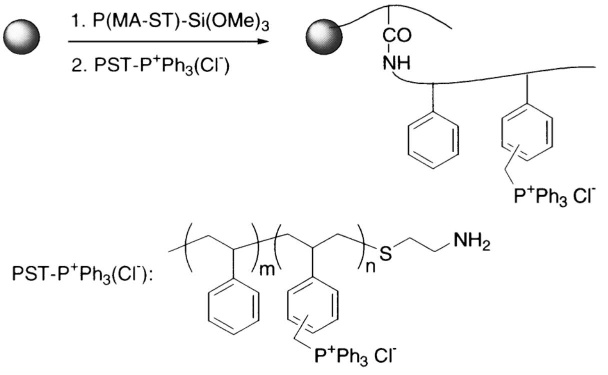


Fig. 4. Changes of attached polymer on P(MA-ST)/SiO$_2$ treated with 1,6-hexanediisocyanate by the acid or base treatment with the reaction time in the cross-linking.[25]

also led to the preparation of stable polymer-modified silica in pH 2 or pH 9 aqueous solutions.[25] As shown in Fig. 4, peeing out of grafted polymer was reduced to 2 wt% by the cross-linking using 1,6-diisocyanatohexamethylene. In this case, successive acidic hydrolysis of unreacted isocyanate group in cross-linked polymer layer promoted the formation of amino and carboxyl groups.

Control of ζ-Potential. The value of ζ-potential is an important and characteristic index of colloidal particle, as a measure of stability in the suspension. It is, therefore, sometimes necessary to control the potential for application of organic-inorganic hybrid particles to materials. Since colloidal particles are stably suspended in the solution due to electrostatic repulsion through electric double layer, controlling the potential based on the adsorption of an electrolyte usually induces aggregation or coagulation. Thus, it seems to be effective for controlling the potential to graft polyelectrolyte onto colloidal particles via covalent bond bindings.

In this respect, the two-step modification of colloidal silica, first with P(MA-ST) and subsequently with polyelectrolyte, successfully made the control of ζ-potential possible.[26,27] Attachment of viologen oligomer to P(MA-ST)/SiO$_2$ caused the particles to exhibit ζ-potential in the range from −15 mV to −7 mV in pH 7 buffer and ethanol, respectively; The particles of P(MA-ST)/SiO$_2$ exhibited ζ-potential of −37, −110, and −150 mV in pH 7 buffer, ethanol, and acetonitrile, respectively.[26] Also, grafting of triphenylphosphoniopolystyrene (PST-PPh$_3{}^+$Cl$^-$) to P(MA-ST)/SiO$_2$, shown in Scheme 8, afforded the particles, which exhibited the maximum potential of +23 mV in ethanol.[27] The potential of PST-polyelectrolyte-grafted P(MA-ST)/SiO$_2$ was also dependent on the molecular weight of the polyelectrolyte; PST-electrolyte of molecular weight 5000–6000 gave the particles, which showed the maximum potential. Interestingly, addition of a salt, NH$_4$Cl, to the ethanol suspension resulted in elevation of the potential, as shown in Fig. 5, and gave the maximum values at the salt concentration of 1×10^{-4} mol dm^{-3}. The characteristic phenomenon were explained by the following compensative effects of salt addition on the potential; (i) increasing of surface charge by shrinking polymer chains and (ii) making the electric double layer thin. Thus, grafting of dissociative polyelectrolyte to



Scheme 8. Grafting of polymer eletrolyte to P(MA-ST)/SiO$_2$.

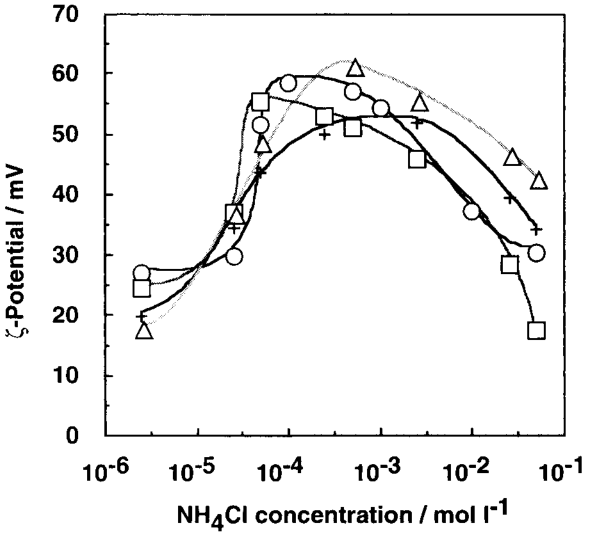


Fig. 5. Effects of NH$_4$Cl addition on ζ-potential of PST-PPh$_3{}^+$Cl$^-$-grafted P(MA-ST)/SiO$_2$ in ethanol. Molecular weight (M_n) and amount of attached polymer electrolyte, PST-PPh$_3{}^+$Cl$^-$: 3700, 213.1 mg/g (+); 6400, 261.3 mg/g (○); 11400, 228.7 mg (□); 18000, 261.1 mg/g (△).[27]

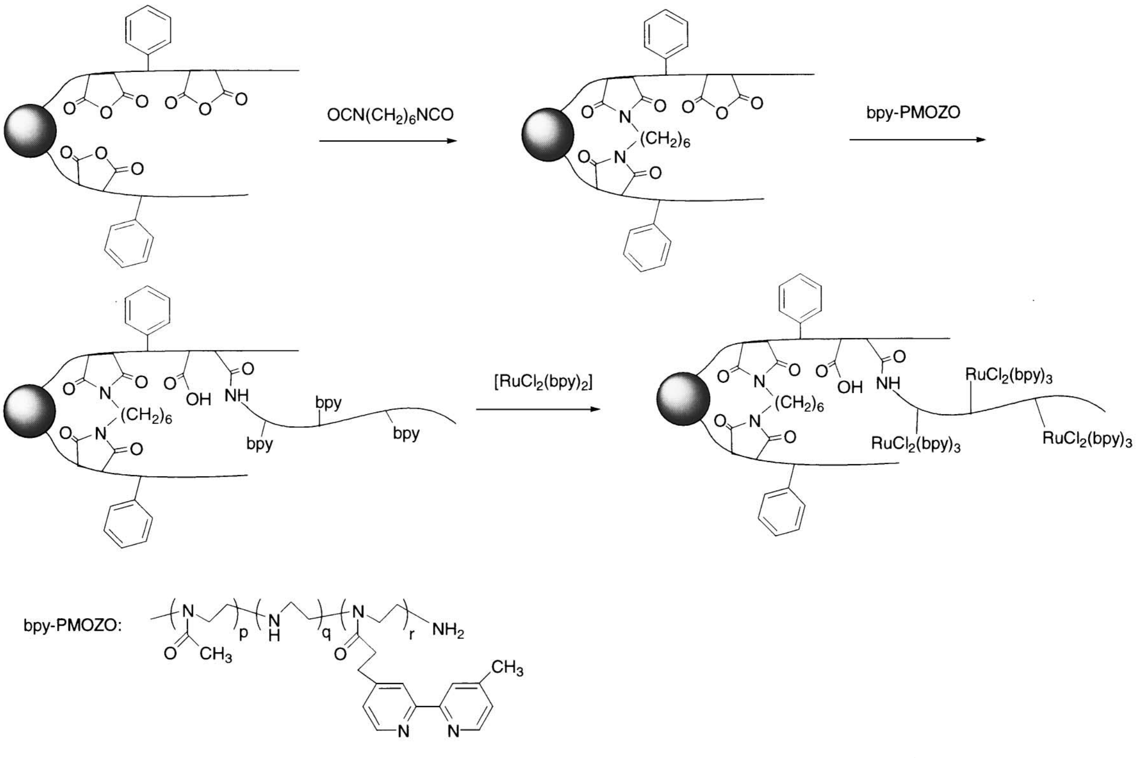
P(MA-ST)/SiO_2 led to elevation of ζ-potentials to give positive values in polar organic solvents.

Catalysis. Colloidal inorganic particles are widely used as starting materials or precursors in the catalyst preparation. Especially, metal or cluster colloidal nanoparticles incorporated into polymer are recently receiving great attention for their unique and characteristic catalytic properties, which are obviously different from those of bulk crystalline. In most cases, the nanoparticles are synthesized in the presence of a polymer, which plays a significant role in controlling the particle size and stabilization of resulting metal colloids.[28] Such hybridization of the colloidal nanoparticles with organic compounds is expected to contribute to new kinds of catalysis.

Incorporation of colloidal titania with polymer grafted [$RuCl_2$(2,2′-bipyridyl)$_3$] successfully led to the preparation of photocatalyst, which showed catalysis in the electron transfer to a donor by visible light irradiation.[29] Since the hybrid catalyst is stable and dispersible in aqueous solution, the catalyst is expected to be applicable to visible light-promoted photocatalysis, such as catalytic decomposition of toxic or harmful compounds, in the solution under mild conditions. The preparation was carried out first by modification of colloidal titania with P(MA-ST)-Si(OMe)$_3$ and then by grafting of 2,2′-bipyridyl-branched polymer, as shown in Scheme 9. Visible light irradiation of the Ru(2,2′-bipyridyl)$_3^{2+}$-tethered titania in the presence of ethylenediaminetetraacetic acid as a sacrifier in pH 7.0 buffer solution gave electron transfer to methyl viologen (MV^{2+}) to form the cation radical involved with electron migration from the Ru(II) complex to the titania surface. The photocatalytic efficiency in conversion of irradiated photon to the cation radical increased with amounts of grafted Ru(II) complex, but does not monotonously depend on the molecular weight of tethered polymer (Table 2). The maximum conversion efficiency was 1.52%.[30] Kinetic analyses of the photocatalysis showed that the electron transfer took place through two routes of a direct pass from anchored Ru(II) complex to MV^{2+} and an indirect pass via titania surface. In these cases, it was observed that titania played an important role not only as a carrier of the Ru(II) complex, but also as a medium in the electron transfer.

Colloidal Crystallization in Organic Solvents. For an aqueous or alcoholic colloidal suspension, it is well known that spherical colloidal particles periodically array in a limited range of volume fractions.[31] Such ordering of colloidal particles, the so-called "colloidal crystal," was based on a strong electrostatic repulsive interaction among the particles, arising from spreading of the electric double layer.[32] If it were possible to prepare monodisperse hybrid particles, which were compatible with organic media, the particles were in principle able to form such colloidal crystals in organic solvents. Moreover, if the colloidal crystallization took place in a polymerizable compound, successive polymerization could result in particle-arrayed matrices having the intrinsic properties of the inorganic particles. In this respect, incorporation of arrayed-monodisperse inorganic spheres, having high dielectric constant, into a polymer matrix would lead to new functional materials. For example, particle-arrayed materials from photonic crystals are promising in applications to optical devices, such as dielectric millers, photo-filters or optical wave guides.[33]

When the particles of P(MA-ST)/SiO_2, prepared from colloidal silica of 136 nm in diameter, was suspended in a organic solvent, such as acetonitrile or acetone, it was observed the



Scheme 9. Preparation of colloidal titania composite modified with Ru(2,2′-bipyridyl)$_3^{2+}$-grafted polymer.

Table 2. Photocatalytic Conversion Efficiency in Electron Transfer from Methyl Viologen (MV^{2+}) to the Radical by Poly(2-methyl-2-oxazoline)(PMOZO)-grafted $[RuCl_2(bpy)_3]$/titania or Silica under Visible Light Irradiation[a)30]

Colloid particle	M_n of PMOZO	Coordinated $[RuCl_2(bpy)_3]$		Conv. efficiency
	10^3	10^{-4} mol g^{-1}	Ru-atom nm^{-2}	%
Titania	1.5	0.36	1.44	0.84
	5.0	0.87	3.49	0.32
	5.0	1.17	4.71	0.53
	5.0	2.33	9.38	1.53
	14.0	2.43	9.80	0.69
	34.0	2.18	8.79	0.94
Silica	14.0	1.34	3.64	0.10

a) Reaction cnditions: composite, 0.3 mg; [MV^{2+}], 10 mM; EDTA, 20 mM; NaCl; 10 mM; pH 7 buffer; irradiation time (xenon lamp 500 W), 6 min.

Table 3. The Critical Volume Fraction (ϕ_o) in Colloidal Crystallization of P(MA-ST)/SiO_2, PST/SiO_2, and PMMA/SiO_2 in Organic Solvent[a) 34b]

Solvent	Dielectric constant	ϕ_o			
		Unmodified	P(MA-ST)/SiO_2	PST/SiO_2	PMMA/SiO_2
Acetonitirile	37.5	0.021 ± 0.001	0.013 ± 0.001	—[b)]	0.023 ± 0.001
N,*N*-Dimethylformamide	36.7	0.070 ± 0.003	0.050 ± 0.002	—	—
Nitrobenzene	34.7	—	0.050 ± 0.002	0.060 ± 0.002	—
Methanol	32.6	0.045 ± 0.002	—	—	—
Ethanol	24.6	0.074 ± 0.003	—	—	—
Acetone	20.7	0.035 ± 0.001	0.026 ± 0.001	—	0.053 ± 0.002
Isopropyl alcohol	19.9	0.084 ± 0.003	—	—	—
Tetrahydrofuran	7.5	—	—	—	—
Ethyl acetate	6.0	—	—	—	—
Chlororform	4.8	—	—	—	—
Dioxane	2.2				
Acrylonitrile		0.021 ± 0.001	0.042 ± 0.002	—	0.055 ± 0.002

a) Amounts of grafted polymer of P(MA-ST)(M_n = 5700)/SiO_2, PST/SiO_2(M_n = 24000)/SiO_2, and PMMA(M_n = 24000)/SiO_2 are 90.2, 24.8, and 49.8 mg/g, respectively.

b) A symbol of — signifies noncrystallization.

particles began to create the iridescent colors due to the Bragg light reflection in a few minute.[34] Values of the critical volume fraction, ϕ_o, for the colloidal crystallization of polymer-modified and -unmodified colloidal silica are listed in Table 3. A typical photograph of the colloidal crystal is shown in Fig. 6. The values of ϕ_o for the crystallization of polymer-modified silica were lower than those of unmodified silica. The colloidal crystallization of polymer-modified particles was observed to take place in a polar solvent that was a good solvent for the grafted polymer. As can be seen in Table 3, however, it was observed that there was matching between the grafted polymer and solvent for the colloidal crystallization. The reason why there is the matching for the crystallization is still unclear. From the fact that the addition of a salt, NH_4PF_6, to the suspension of P(MA-ST)/SiO_2 in acetonitrile resulted in elevation of ϕ_o, the colloidal crystallization of polymer-modified silica in organic solvent took place through the electrostatic inter-sphere interaction. In Fig. 7, the plots of inter-sphere space as a function of the volume fraction (ϕ) of polymer-modified silica are shown.[35] As can be seen from Fig. 7, the plots well agreed with calculated values, in spite of not taking the polymer layer into calculation. These results clearly show that the colloidal polymer-modified silica crystallizes through close packing under the electrostatic repulsion among the particles

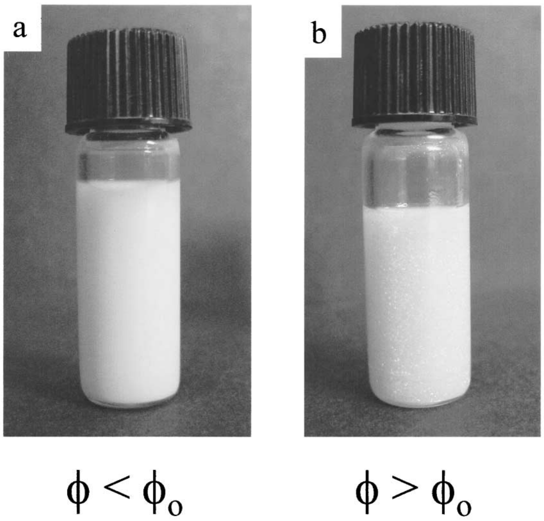


Fig. 6. Photographs of noncrystallized suspension (a) and colloidal crystal (b) of P(MA-ST)/SiO_2 in acetonitrile.[34b]

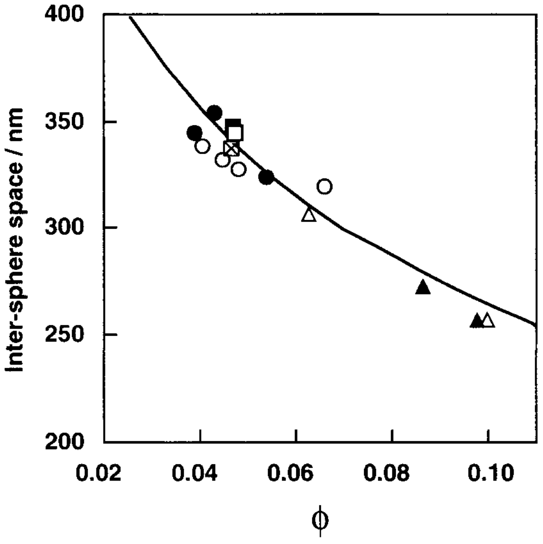


Fig. 7. Plots of inter-sphere space versus volume fraction (ϕ) of polymer-modified silica. A solid line shows calculated values based on closed packing from ϕ. P(MA-ST)/SiO$_2$; M_n = 6700 (80.0 mg/g) (○), M_n-6700 (18.0 mg/g) (●). PST/SiO$_2$; M_n = 11000 (34.4 mg/g) (▲), M_n = 28000 (29.3 mg/g) (△). PMMA/SiO$_2$; M_n = 11000 (34.4 mg/g) (□), M_n = 15000 (32.9 mg/g) (□), M_n = 21300 (52.6 mg/g) (■).[34b]

in organic solvent, as does unmodified silica in aqueous solution. The values of ϕ_0 were dependent on the molecular weight and amount of modified polymer. Thus, it is suggested that the polymer-modified silica were crystallized by additive interaction of grafted polymer chain and electrostatic repulsion in organic solvent. The rigidity of colloidal crystals of the polymer-modified silica in organic solvents was lower than that of unmodified silica in aqueous solution, in spite of higher crystallization rates.[35,36] Immobilization of the colloidal crystals in organic solvent incorporated into organic polymer gels is now in progress.

Summary

In this work, polymer modification methods of colloidal particles via covalent bond bindings to give stabilization in organic media were investigated. The modification of colloidal silica by the reaction with polymeric trimethoxysilane composed of maleic anhydride effectively gave stable and dispersible composite particles in organic solvent. The grafting of secondary polymer chains to poly(maleic anhydride-co-styrene)-modified silica resulted in controlling dispersibility and ζ-potential in organic solvent. The modification was applicable to preparation of titania photocatalyst systems which exhibited photo-induced electron transfer catalysis by visible light. Moreover, polymer-modified silica prepared with polymeric silane formed colloidal crystals in organic solvents.

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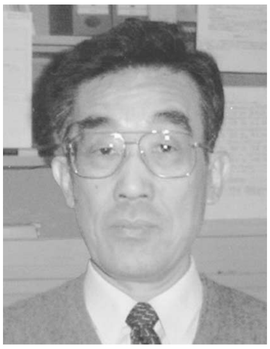

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