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SHORT COMMUNICATION

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Surface modification of fine colloidal silica with copolymer silane-coupling agents composed of maleic anhydride

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Abstract The reactivity of copolymer silane composed of maleic anhydride in the modification of fine colloidal silica was studied. The reaction of colloidal silica of 10 and 45-nm diameter with trimethoxysilyl-terminated poly(maleic anhydride-*co*-styrene) [P(MA-ST)] and poly(MA-*co*-methyl methacrylate) in tetrahydrofuran resulted in effective surface modification without particle aggregation. From the results that the reaction using the polystyrene silane of low molecular weight led to partial aggregation, itwas suggested that the steric interaction between relatively rigid copolymer chains having a maleic anhydride moiety adsorbed on the silica prevented the aggregation in the reaction. The ^{29}Si cross-polarization magic-angle-spinning NMR spectra of P(MA-ST)-modified silica showed that the polymer silane was bound to the silica surface by the direct reaction with silica hydroxyl groups and via the polymerization.

Keywords Colloidal silica · Surface modification · Polymeric silane · Maleic anhydride · ^{29}Si NMR

Introduction

Recently, the fabrication of chemical or physical properties on nanosized particles has been receiving great attention for developing new materials [1–6]. Hybrid materials derived from nanosized inorganic particles and organic compounds are also promising new functional materials exhibiting specific properties, such as quantum effects. In this respect, we have developed the surface modification method of colloidal fine particles using polymeric silane-coupling agents [7, 8]. Especially, the modification with trimethoxysilyl-terminated maleic anhydride–styrene copolymer [P(MA-ST)] successfully led to the preparation of monodisperse and stable composite particles in acidic or alkaline aqueous solution by employing the reaction of the MA moiety with diisocyanate, and to the introduction of amino or carboxyl groups on the surface. Further, attachment of the secondary polymer to the P(MA-ST)-modified silica effectively brought about control of the surface polarity [8].

This article describes the specific reactivity of trimethoxysilyl-terminated copolymer coupling agents composed of MA in the modification of colloidal silica particles, of 10 and 45-nm diameter, and surface structure analysis of fine composites on ^{29}Si NMR spectra.

Experimental

Materials

Monodisperse colloidal silicas (CS-10, CS-45 and CS-120), containing SiO_2 of 10, 45 and 120-nm diameter suspended in ethanol, were kindly offered by Catalysts & Chemicals, Japan; the suspensions of CS-10, CS-45 and CS-120 contained 30, 30 and 18 wt% SiO_2, respectively. Silica gel of 10–20 mesh was purchased from Wako Chemicals Co, Japan. Trimethoxysilyl-terminated polymers of P(MA-ST) [P(MA-ST)-Si(OMe)$_3$] and poly(MA-*co*-methyl methacrylate) [P(MA-MMA)-Si(OMe)$_3$] with a number-average molecular weight (M_n) of 6,400 (weight-average molecular weight, $M_w/M_n = 1.82$) and 4,400 ($M_w/M_n = 2.05$), respectively, were synthesized by the method reported previously [9, 10]. The polymers of P(MA-ST)-Si(OMe)$_3$ and P(MA-MMA)-Si(OMe)$_3$

were composed of equimolar MA and ST, and three parts of MA and five parts of MMA, respectively.

Measurements

The ^{29}Si cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded using a 7-mm rotor probe on a Bruker Avance 300. The particle size distribution was measured by a light scattering method using a Ohtsuka DLS7000. The molecular weight of the polymers was determined by gel permeation chromatography on TSK gel 3000H with a tetrahydrofuran eluant, based on calibration with polystyrene (PST) standard. Thermogravimetric analyses were carried out using a Shimadzu TGA-50.

Synthesis of PST-trimethoxysilane

A typical synthesis was carried out as follows. To 6.5 cm^3 freshly distilled ST was quickly added 2.5 cm^3 butyl lithium in hexane (1.6 M) at −50 °C in an argon atmosphere. The mixture was stirred for 5 min and then carbon dioxide was blown into the mixture until the solution turned clear. The resulting solution was poured into methanol to precipitate the PST after the neutralization with 6N HCl. The precipitation from the tetrahydrofuran solution with methanol and drying under reduced pressure gave 5.5 g carboxyl-terminated PST, of $M_n = 8{,}600$ and of $M_W/M_N = 1.24$. To a solution of 4.1 g PST in dry chloroform (20 cm^3) was added 1.7 cm^3 3-aminopropyltrimethoxysilane and 1.0 g *N*,*N′*-dicyclohexylcarbodiimide and the mixture was stirred at 0 °C for 2 h and then at room temperature for 24 h. The precipitation from the solution with methanol gave 4.0 g trimethoxysilane-terminated PST [PST-Si(OMe)$_3$]; the conversion of carboxyl-PST to the silane was above 95%.

Reaction of colloidal silica with polymer-trimethoxysilane

A typical reaction of colloidal silica with the polymer silane was as follows. To 20 cm^3 acetone solution containing 0.1 g P(MA-ST)-Si(OMe)$_3$ was added 2.9 cm^3 colloidal silica suspension and the mixture was gently stirred under refluxing for 5 h in a nitrogen atmosphere. In the case of the modification with PST-Si(OMe)$_3$, the reaction was carried out in tetrahydrofuran solution. After, 1 g granular silica (10–20 mesh) gel was added to the solution to remove unreacted polymer silane by the reaction with hydroxyl group, and then the heterogeneous solution was heated at 65 °C for 1 h without stirring. The suspension containing the composite was separated from the silica gel by decantation. Complete removal of the polymer silane by the reaction with the hydroxyl group on silica gel was confirmed by observation of no signals in the ^{1}H NMR spectrum of the solution.

Determination of grafted polymer

The evaporation of the solution gave a colorless solid. The grafted polymer was determined by the weight loss during a temperature elevation from 100 to 1000 °C, after keeping the solid obtained by evaporation of the suspension at 100 °C for 1 h, at a rate of 5 °C min^{-1} on the thermal analysis.

Results and discussion

Modification with MA-copolymer silane

The surface modifications of inorganic particles with copolymer silane composed of MA are significantly useful and convenient, because the MA group is available to graft the secondary polymer or functional groups. Plots of the amounts of grafted copolymer versus dosed copolymer silane in the modification using CS-45 in units of moles per square nanometer of silica are shown in Fig. 1. It is observed that the amounts of the grafted copolymer increased linearly with increasing dosed copolymer silane, and, therefore, these copolymer silanes efficiently bound to the surface of the silica particles. In both cases, it is especially noteworthy that below the polymer silane concentration of 0.5×10^{-23} mol nm^{-2}, above 80% of the dosed silane was able to react with the hydroxyl group on the colloidal silica with considerably high efficiency. Each highest value represents the maximum amount of the grafting. As shown in Fig. 1, the maximum grafting corresponds to 5.0 and 3.4 chains nm^{-2} for the modification with P(MA-MMA)-Si(OMe)$_3$ and P(MA-ST)-Si(OMe)$_3$, respectively. It has been reported that the numbers of hydroxyl groups on the surface of silica gel are generally 3–5 groups nm^{-2} [11, 12], so this result shows that a considerably high extent of the surface modification can be achieved in the present modification. Recently, Yamamoto et al. [13] reported that the graft density in the grafting of PMMA on a SiO$_2$ substrate by surface-initiated atom-transfer radical polymerization is changed in the range from 0.07 to 0.7 chains nm^{-2}. Thus, the graft density in this work, 3.5 or 5.0 chains nm^{-2}, was considerably higher than that obtained by Yamamoto et al. The high graft density is possibly due to attachment of polymerized silane to the fairly reactive hydroxyl group of CS-45 and to effective grafting of polymer chains on the curvature of silica fine spheres (discussed later).

The results of the surface modifications of colloidal silica of CS-10, CS-45 and CS-120 with P(MA-ST)-

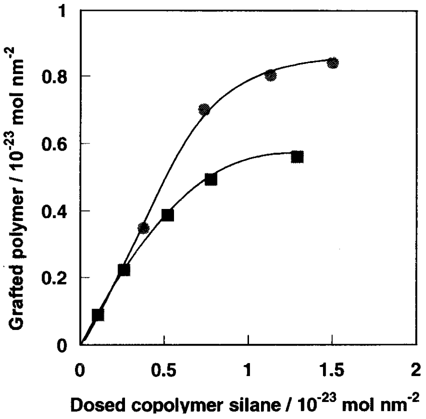

Fig. 1 Plots of grafted polymer versus dosed trimethoxysilyl-terminated poly(maleic anhydride-*co*-methyl methacrylate) [*P(MA-MMA)-Si(OMe)*$_3$] (*circles*) and trimethoxysilyl-terminated MA–styrene copolymer [*P(MA-ST)-Si(OMe)*$_3$] (*squares*) in the modification of CS-45

$Si(OMe)_3$ in acetone are shown in Fig. 2. The P(MA-ST) grafted onto CS-10 linearly increased with dosed P(MA-ST)-$Si(OMe)_3$. It is also interestingly observed that the polymer grafted onto CS-45 showed the same dependence on the dosed copolymer silane as that grafted onto CS-10. In the case of modification of CS-120, however, the amount grafted was lower than that grafted onto CS-10 and CS-45. Therefore, these results show that the surfaces of CS-10 and CS-45 have extremely high activity for the reaction of the surface hydroxyl groups with P(MA-ST)-$Si(OMe)_3$. In these cases, the highest amount of grafting shows maximum values corresponding to 3.4, 3.4 and 0.30 chains nm^{-2} for the modification of CS-10, CS-45 and CS-120, respectively. Hence, these results indicate that hydroxyl groups on CS-10 and CS-45 are fairly reactive for the reaction with P(MA-ST)-$Si(OMe)_3$ and much more so than those on CS-120. The high reactivity of the hydroxyl groups on CS-10 and CS-45 probably arises from the small radius of the curvature on the surface, compared with the reactivity of the hydroxyl groups on CS-120.

Modification with PST-$Si(OMe)_3$

In order to clarify the specific high reactivity of P(MA-MMA)-$Si(OMe)_3$ and P(MA-ST)-$Si(OMe)_3$ with the hydroxyl groups on CS-10 and CS-45, we investigated the reaction of CS-45 with PST-$Si(OMe)_3$ prepared via anionic polymerization of ST. In this case, the effects of the molecular weight of polymeric silane on the surface modification of colloidal silica were also studied, because it was impossible to vary the molecular weight in the copolymerization of MA. The reaction of colloidal silica with PST-$Si(OMe)_3$ was carried out using CS-45 in tetrahydrofuran, because of the solubility of the polymer silane.

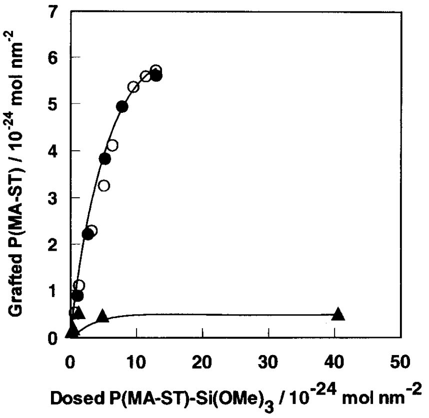

Fig. 2 Plots of grafted P(MA-ST) versus dosed P(MA-ST)-$Si(OMe)_3$ in the modification of CS-10 (*open circles*), CS-45 (*filled circles*)and CS-120 (*triangles*)

The relation between dosed PST-$Si(OMe)_3$ and grafted PST on CS-45 is shown in units of moles per square nanometer in Fig. 3. When the reaction was carried out using PST-$Si(OMe)_3$ prepared from carboxyl-PST of $M_n = 2{,}000$, the colloidal silica partially aggregated in the concentration range from 1×10^{-24} to 5×10^{-24} mol nm^{-2}; however, the reaction at a dosed polymer silane concentration of 6.76×10^{-24} mol nm^{-2} gave dispersible composite particles. In the case of the modification using PST-$Si(OMe)_3$ prepared from carboxyl-PST of $M_n = 4{,}300$, the reaction at polymer concentrations below 5.37×10^{-25} mol nm^{-2} and above 1.72×10^{-24} mol nm^{-2} afforded dispersible PST/silica. In these cases, the reason why no aggregation took place in low concentrations of the polymer silane is probably that the surface of colloidal silica still has a high enough intrinsic negative charge to maintain dispersion since the adsorption of the silane is extremely low. However, in the reaction using PST-$Si(OMe)_3$ prepared from carboxyl-PST of $M_n = 8{,}600$, it was observed that the reactions never led to particle aggregation even at a low concentration of 0.25×10^{-24} mol nm^{-2}. These results suggest that at an early stage of the reaction PST-silane of higher molecular weight or at high concentration effectively adsorbs on colloidal silica to prevent aggregation through steric interaction between the polymer chains, but the silane of low molecular weight or at low concentration cannot overcome the attractive interaction among the particles through the steric interaction between adsorbed PST chains. Therefore, the results of the reaction using PST-$Si(OMe)_3$ clearly show that both polymer silanes of P(MA-ST)-$Si(OMe)_3$ and P(MA-MMA)-$Si(OMe)_3$ exhibit a characteristic reactivity in the modification of CS-10 and CS-45, in spite of a comparable molecular weight with

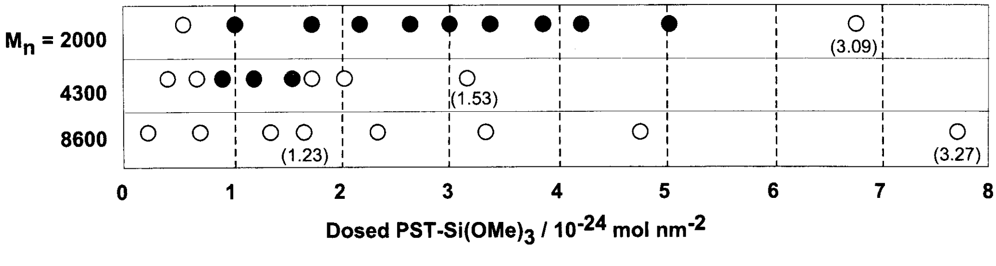

Fig. 3 Effects of molecular weight of polystyrene (*PST*)-$Si(OMe)_3$ in the modification of CS-45. *Open* and *filled circles* denote keeping dispersion and giving rise to aggregation in the reaction, respectively. The values in *parentheses* represent amounts of grafted PST

PST-Si(OMe)$_3$. Probably, the specific and characteristic reactivity of P(MA-ST)-Si(OMe)$_3$ and P(MA-MMA)-Si(OMe)$_3$ without particle aggregation comes from steric interaction, i.e. volume-excluding effects, between adsorbed P(MA-ST) chains on the colloidal silica owing to their structural rigidity. Hence, we can imagine the process in the reaction of colloidal silica with the copolymer silane composed of MA as follows:

1. Adsorption of the polymer silane on the surface along with assembling and orientating of the trimethoxysilyl group toward the silica surface in a good solvent for the copolymer.
2. Successive efficient reaction of the silane with the surface hydroxyl group.

Further, in the case of PST modification it is noteworthy that the rates of PST grafting to dosed PST-Si(OMe)$_3$ for the resulting dispersible composite particles are relatively high, in the range from 0.4 to 0.5, being comparable to those of P(MA-ST) and P(MA-MMA), as also shown in Fig. 3.

Binding between the polymer and silica

In the present modification, it is very important and interesting for practical application of the composite particles obtained by the reaction using MA-copolymer silane to unveil the bonds formed between the polymer and the surface of colloidal silica.

The ^{29}Si CP/MAS NMR spectra of P(MA-ST)-modified silica obtained from CS-10, CS-45 and CS-120 are shown in Fig. 4. The resonance peaks at −100 and −110 ppm were assignable to silicon of Q^3 and Q^4 sites in silica [14, 15], respectively, and the peaks in the range from −45 to −70 ppm were assignable to silicon originating in polymer silane. According to the literature values of ^{29}Si chemical shifts [16], the resonance peaks of a, b and c in Fig. 4 were assigned to silicons formed by direct reaction of the silane with one or two hydroxyl groups and to those formed by the reaction of polymerized silane. As can be seen in Fig. 4, unexpectedly, significant differences of ^{29}Si signal patterns in the spectra of P(MA-ST)-modified CS-10, CS-45 and CS-120 were not observed. These results suggest that the reactivity of colloidal silica in the reaction with the copolymer silane composed of MA is not reflected in covalent bonds formed between the polymer and the silica surface. Since it is also impossible to distinguish the silicons from the polymer silane bound to hydroxyl groups on the silica from those in polymerized silane, the relation between the reactivity of the hydroxyl group on colloidal silica and a mode of the covalent bonds formed is still unclear. In any case, the high reactivity of the hydroxyl groups on CS-10 and CS-45 probably accelerates the polymerization of the silane or the attachment of the polymerized silane on the surface to lead to a high graft density. A detailed investigation of the reaction mechanism of the colloidal silica with the polymer silane is now in progress.

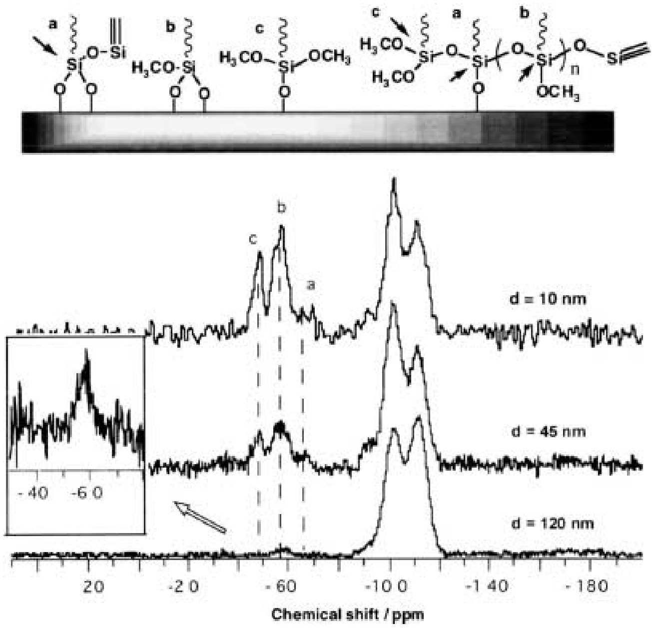

Fig. 4 ^{29}Si cross-polarization magic-angle-spinning NMR spectra of P(MA-ST)-modified silica

Conclusion

The copolymer silane coupling agents P(MA-ST)-Si(OMe)$_3$ and P(MA-MMA)-Si(OMe)$_3$ showed specific reactivity in the surface modification of colloidal silica of 10, 45 and 120-nm diameter. The maximum graft densities of 5.0 and 3.5 chains nm^{-2} were achieved in the reaction of the colloidal silica of 10 and 45-nm diameter with P(MA-MMA)-Si(OMe)$_3$ and P(MA-ST)-Si(OMe)$_3$, respectively. From the results that the modification using PST silane of low molecular weight led to particle aggregation, the prevention of the aggregation in the modification using the copolymer silane composed of MA is probably due to the steric interaction between relatively rigid structural polymer chains adsorbed on colloidal silica. The ^{29}Si CP/MAS NMR spectra of P(MA-ST)-modified silica showed the formation of covalent bonds through the direct reaction of the polymer silane with hydroxyl groups and through polymerization of the polymer silane on the colloidal silica.

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