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# Bindings of a Secondary Polymer to Monodisperse Colloidal Silica Particles Modified with Poly(maleic anhydride–styrene) for Controlling the Surface Polarity

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A polymer modification of monodisperse colloidal silica (120 nm in diameter) and control of the surface polarity were studied. The binding of poly(maleic anhydride–styrene) to the silica particles and successive grafting of amino-terminated polymethacrylates with methyl, hexyl, and dodecyl ester groups afforded unimodal composite particles, which were dispersible in a low-polar solvent of ethyl acetate. The bindings of the secondary polymer were dependent on the molecular structure of the polymer as well as the reaction conditions. The surface polarity was estimated by aggregation of the particles in an ethyl acetate–methanol cosolvent, monitored by the absorbance of a suspension containing the composite particles at 500 nm. The polarity was significantly affected by the main chain length of the secondary polymer of the polymethacrylates rather than the bound polymer chain number or the branch alkyl ester group of the polymer. For highly modified composite particles, it was observed that the carboxyl group, simultaneously formed in the binding of the secondary polymer, contributed to the surface polarity.

Monodisperse ultrafine colloidal particles have recently received much attention concerning applications to composite materials.[1—3] We have been developing new kinds of functional materials using polymer-modified inorganic colloidal particles in a very narrow size distribution. For an aqueous or alcoholic colloidal suspension, it was observed that spherical colloidal particles periodically arrayed in extremely deionized solution.[4,5] The ordering of the colloidal particles, i.e. colloidal crystal, was based on a strong electrostatic repulsion among the particles, arising from a spreading of the electric-double layer. If it could control the surface hydrophobicity of colloidal particles by a polymer modification, it would be expected to make a two- or three-dimensional periodic array of the particles through a hydrophobic or nonpolar–nonpolar interaction among the particles in a polar organic solvent. A major interest is the formation and control of crystalline colloidal arrays in colloidal self-assembly processes.[7,8] Nanoscale periodic materials are useful for fablicating optical devices, which efficiently diffract light in the visible or near-infrared spectral region.

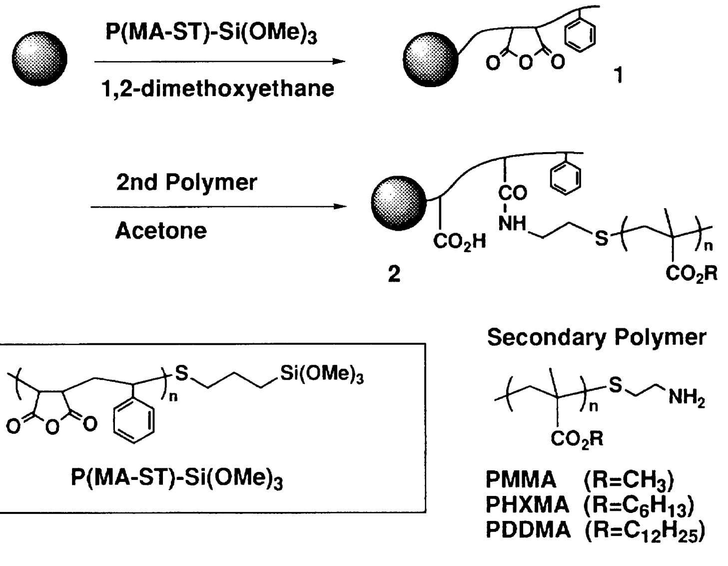
So far, we have reported on the effective polymer binding of monodisperse colloidal silica by the reaction of surface silanol with a polymeric silane coupling agent,[9,10] or by radical polymerization.[11] Especially, a modification of the colloidal silica with trimethoxysilyl-terminated poly(maleic anhydride–styrene) (P(MA–ST)–Si(OMe)$_3$) and a successive reaction of the composite with diols or diamines led to an efficient cross-linking of the surface polymer layer, and a simultaneous formation of a carboxyl or amino group on the surface, respectively.[12,13]

In this paper we describe the effects of polymethacrylate bindings on the surface polarity of poly(maleic anhydride–styrene)-modified silica particles (P(MA–ST)/SiO$_2$), shown in Scheme 1. The polarity was estimated based on the dispersibility in the cosolvent of ethyl acetate (AcOEt) and methanol (MeOH), spectrometrically monitored by the absorbance at 500 nm.

## Experimental

**Materials.** Monodisperse silica colloid, suspended SiO$_2$ (23 wt%) of 120 nm in mean diameter in ethanol, was kindly offered by Catalysts & Chemicals Ind. Co., Ltd. P(MA–ST)–Si(OMe)$_3$ of $M_n = 6000$ was prepared by a previously described method.[12] Amino-terminated poly(methyl methacrylate)s of $M_n = 4300$ and 15400 (PMMA(4.3 k) and PMMA(15.4 k), respectively), poly(hexyl methacrylate)s of $M_n = 7200$ and 14000 (PHXMA(7.2 k) and PHXMA(14.0 k), respectively) and poly(dodecyl methacrylate) of $M_n = 7600$ and 16300 (PDDMA(7.6 k) and PDDMA(16.3 k), respectively) were synthesized by polymerization of the respective monomer using 2,2′-azobis(isobutyronitrile) in the presence of 2-aminoethanethiol hydrochloride as a chain-transfer reagent in ethanol.[13]

**Measurements.** Spectroscopic measurements were carried out using a 10 mm quartz cell with a JASCO V-520 at 25 °C. Thermogravimetric analyses were performed with a Shimadzu TGA-50. IR spectra were recorded with a diffuse reflection method on a JEOL JIR-5500. Scanning electron micrographs (SEM) were taken on a JEOL JCX-733. Measurements of the particle size and distribution in ethanol were made by a dynamic light-scattering method on an Ohtsuka DLS-700. Gel-permeation chromatography (GPC) was carried out on a TSK gel 3000H column (30 cm) with a tetrahydrofuran eluent (0.5 ml min$^{-1}$) at 35 °C using a Shimadzu LC-



Scheme 1. Polymer modification of colloidal silica.

9A pump with a Shodex SE-51 RI detector. The calibration of the column was made with polystyrene standards (Poly Science).

**Preparation of Composite 1.** The composite particles were prepared by a previously reported method.[13] The amount of bound polymer was in the range of 43.9 to 65.9 $\mathrm{mg\,g^{-1}}$.

**Binding of Secondary Polymer to Composite 1.** A typical run was as follows. A suspension of composite **1** (0.2 g) containing amino-terminated PMMA(4.3 k) of 0.4 g in 3.5 ml dry acetone was stirred under refluxing in a nitrogen atmosphere for 16 h. The resulting particles were washed with 10 ml acetone three times in order to remove any unreacted polymer and 10 ml diethyl ether by a centrifugation. Drying under a vacuum gave 0.19 g of composite **2**, PMMA(4.3 k)–P(MA–ST)/$SiO_2$; the amount of bound polymer was 18.7 $\mathrm{mg\,g^{-1}}$. Anal. IR (KBr) 2958, 2937, and 2861 ($\nu_{C-H}$); 1868 and 1780 ($\nu_{C=O}$, maleic anhydride), 1733 ($\nu_{C=O}$, ester), 1132 $\mathrm{cm^{-1}}$ ($\nu_{Si-O}$, silica).

**Reaction of Composite 1 with 1H,1H,2H,2H-Perfluorodecanol (PFD).** A mixture of 0.2 g composite **1**, 0.5 g PFD, and 8 ml acetone containing 0.2 ml pyridine was stirred under refluxing in a nitrogen atmosphere for 24 h. Centrifugation with 10 ml acetone three times and 10 ml diethyl ether, and drying under a vacuum gave 0.2 g of PFD-modified particles. Anal. IR (KBr) 2960, 2937, and 2862 ($\nu_{C-H}$); 1863 and 1778 ($\nu_{C=O}$, maleic anhydride), 1727 ($\nu_{C=O}$, ester), 1240—1390 (shoulder, $\nu_{C-F}$), 1140 $\mathrm{cm^{-1}}$ ($\nu_{Si-O}$, silica).

**Determination of the Bound Polymer.** The amount of bound polymer on silica particles was determined by the weight decrease during temperature elevating from 100 to 1000 °C, after keeping at 100 °C for 30 min. The secondary polymer bound on the particles was estimated based on the difference between the amount of composite **1** and that of composite **2**.

**Spectroscopic Measurements.** After a suspension containing 10 mg of composite **1** or composite **2** in 10.0 ml cosolvent of ethyl acetate and methanol was irradiated with ultrasonic waves for 30 min, an aliquot of the solution was put into a 10 mm quartz cell at 25 °C. Changes in the absorbance at 500 nm with time were recorded on a microcomputer.

## Results and Discussion

**Binding of a Secondary Polymer to Composite 1.** In Table 1, the conditions in the bindings of the secondary polymers and their bound amounts are given. In these reactions, acetone of a good solvent for maleic anhydride–styrene copolymer was the most effective solvent. Binding of the secondary polymer showed a tendency in which amount of bound polymer decreased with the molecular weight and the side chain length in polymethacrylate. A bulky polymer of PDDMA(16.3 k) with a dodecyl ester group scarcely bound to the surface of P(MA–ST)/$SiO_2$. The bindings of the secondary polymers were confirmed by the appearance of IR absorption bands at 1730 $\mathrm{cm^{-1}}$, which were assigned to the stretching vibrations of the carboxyl and ester C=O bonds, and by the decreases of the bands at 1867 and 1784 $\mathrm{cm^{-1}}$, which were assigned to anti-symmetric and symmetric C=O stretching vibrations of the maleic anhydride moiety. In the binding of low-molecular-weight poly(methyl methacrylate) ($M_n = 1800$) to P(MA–ST)/$SiO_2$, the vibrational absorbance of the amide C=O bonds was clearly observed at 1640—1625 $\mathrm{cm^{-1}}$ on the IR spectrum.[12] Typical IR spectra of composite **1** and PMMA(14.5 k)–P(MA–ST)/$SiO_2$ are shown in Fig. 1. On the other hand, the reaction of composite **1** with PFD gave bindings of the perfluorodecyl group of 10.6—50.0 $\mathrm{mg\,g^{-1}}$, viz. 22.9—108.4 $\mathrm{\mu mol\,g^{-1}}$, corresponding to one or two orders of magnitude over the amount of bound polymethacrylates. All of these composites showed a narrow size distribution, which was estimated by the ratio ($d_w/d_n = 1.04$—$1.10$) of the average diameter in weight base ($d_w$) to that in number base ($d_n$). Therefore, aggregation and/or an agglutination of the particles did not take place during the reaction of composite **1** with the amino-terminated polymethacrylates. In Figs. 2 and 3, a typical SEM image and the particle size distribution of composite **2** (PMMA(15.4 k)–P(MA–ST)/$SiO_2$) are shown, respectively. All of composites **2** were dispersible in AcOEt of a low-polar solvent.

**Dispersibility in AcOEt–MeOH Cosolvent.** When the particles (10 mg) of composite **1** or composite **2** were suspended in an AcOEt–MeOH cosolvent (10 ml) under ul-

Table 1. Binding of Secondary Polymer on Composite **1**

| 2nd polymer | | | | Composite **1** | Acetone | Bound 2nd polymer |
|---|---|---|---|---|---|---|
| | $10^{-3}M_n$ | $n$[a] | $g$ | $g$ (mg g$^{-1}$)[b] | ml | mg g$^{-1}$ (μmol g$^{-1}$) |
| PMMA(4.3 k) | 4.3 | 43 | 0.2 | 0.20 (65.9) | 7.0 | 8.3 (1.83) |
| | | | 0.3 | 0.20 (65.9) | 3.5 | 12.6 (2.93) |
| | | | 0.4 | 0.20 (65.9) | 3.5 | 18.7 (4.35) |
| PMMA(15.4 k) | 15.4 | 154 | 0.2 | 0.15 (65.9) | 3.5 | 20.9 (1.36) |
| | | | 0.5 | 0.15 (65.9) | 3.5 | 28.1 (1.82) |
| | | | 0.6 | 0.15 (65.9) | 3.0 | 60.6 (3.94) |
| PHXMA(7.2 k) | 7.2 | 42 | 0.4 | 0.15 (43.9) | 6.0 | 14.4 (2.00) |
| | | | 0.6 | 0.15 (43.9) | 6.0 | 21.9 (3.04) |
| | | | 0.4 | 0.15 (43.9) | 6.0 | 49.4 (6.09) |
| PHXMA(14.0 k) | 14.0 | 82 | 0.5 | 0.15 (43.9) | 6.0 | 24.5 (1.67) |
| | | | 0.9 | 0.15 (43.9) | 6.0 | 39.0 (2.79) |
| | | | 1.1 | 0.15 (43.9) | 6.0 | 51.8 (3.70) |
| PDDMA(7.6 k) | 7.6 | 30 | 0.7 | 0.30 (43.9) | 12.0 | 9.6 (1.26) |
| | | | 1.0 | 0.26 (43.9) | 10.4 | 16.1 (2.12) |
| | | | 1.5 | 0.25 (43.9) | 10.0 | 13.3 (1.75) |
| PDDMA(16.3 k) | 16.3 | 64 | 1.5 | 0.30 (43.9) | 12.0 | 0.0 (0.00) |

a) Average polymerization degree. b) Values in parentheses are amounts of bound poly(maleic anhydride–styrene) to silica.

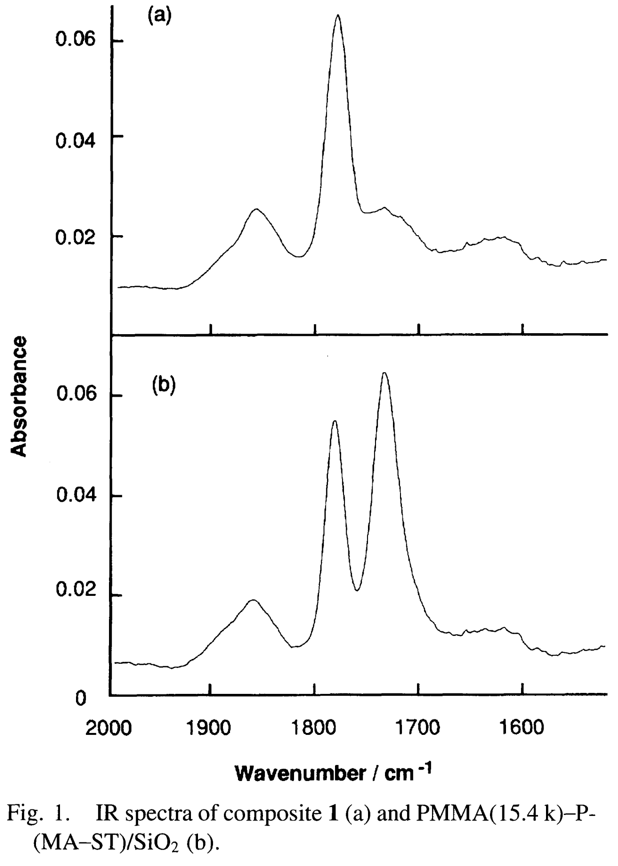


Fig. 1. IR spectra of composite **1** (a) and PMMA(15.4 k)–P-(MA–ST)/SiO$_2$ (b).

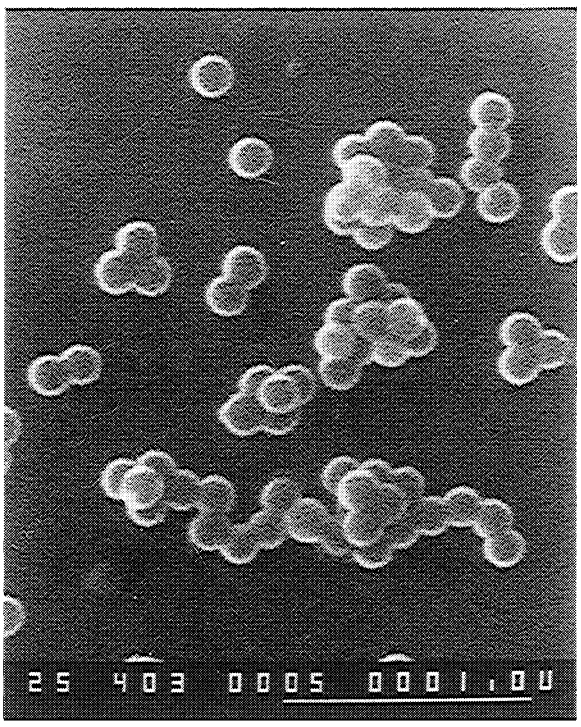


Fig. 2. A typical SEM image of PMMA(15.4 k)–P-(MA–ST)/SiO$_2$. A scale bar on the bottom represents 1 μm.

trasonic irradiation, the absorbance of the solution at 500 nm, i.e. the turbidity, decreased with time, and then attained a constant value. The time dependency of the absorbance varied with the composite. In most cases of composite **1** and **2** suspensions, it was observed that the absorbances reached constant values within 30 min, increasing with the MeOH content in the solvent, as shown in Fig. 4. In general, the assembling of fine particles in a diluted suspension make the absorbance increase, because of an increase of the light scattering. The particles of composite **1** are considered to be dispersed throughout the solvation of P(MA–ST) chains with AcOEt in a high AcOEt-content solution, and on the interaction between surface residual silanol and MeOH in a high-MeOH content solution. Therefore, the increase in the absorbance, along with the MeOH content, of an insoluble component for surface P(MA–ST) or polymethacrylates, showed the assembly of particles due to a nonpolar–non-

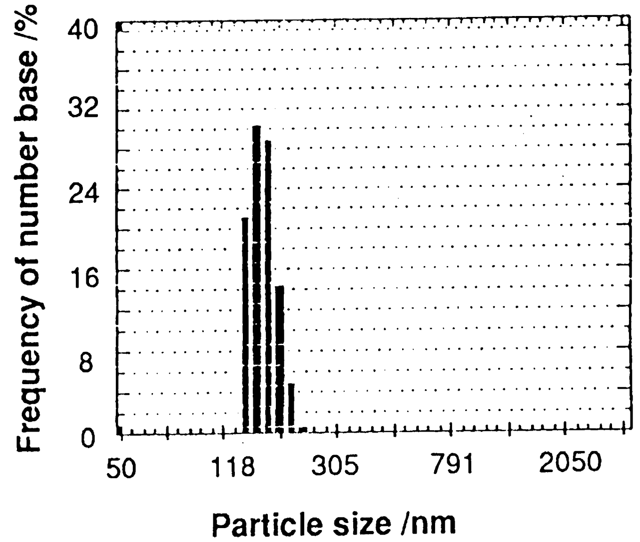


Fig. 3. A particle size distribution of PMMA(15.4 k)–P-(MA–ST)/SiO$_2$.

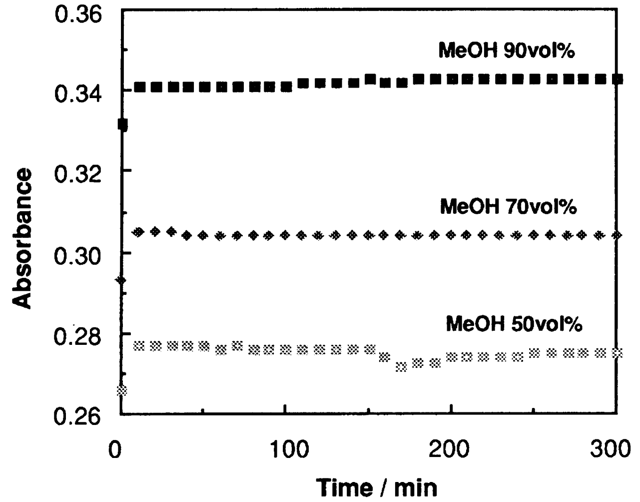


Fig. 4. Changes of the absorbance of P(MA–ST)/SiO$_2$ (**1**) suspension (1 mg ml$^{-1}$) at 500 nm with time in AcOEt/MeOH cosolvent.

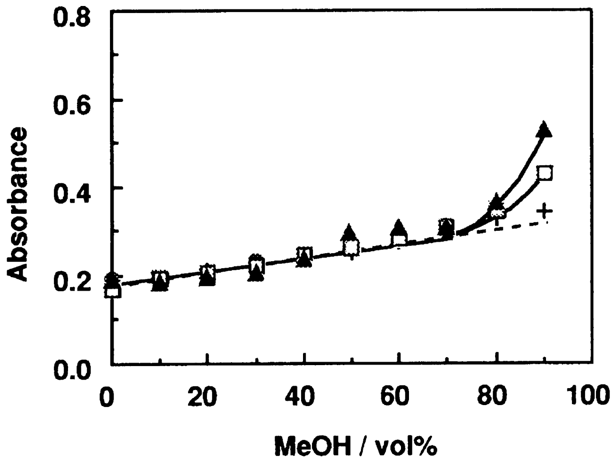


Fig. 5. The absorbance changes of composite **1** (+) and PMMA(4.3 k)–P(MA–ST)/SiO$_2$ suspensions with MeOH content in the cosolvent. Amounts of bound PMMA(4.3 k) are 11.6 (●), 12.5 (□), and 18.7 (▲) mg g$^{-1}$.

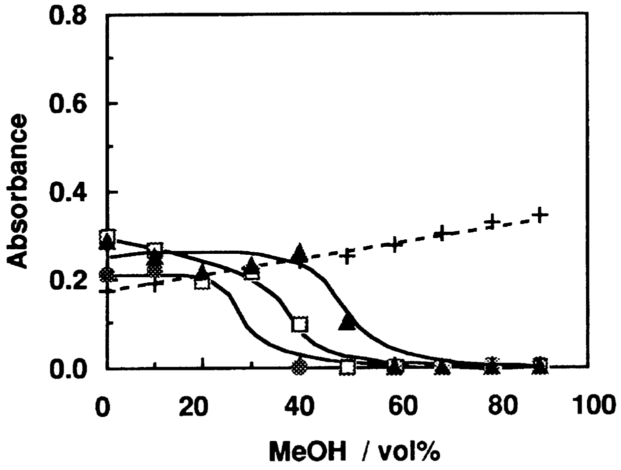


Fig. 6. The absorbance changes of PMMA(15.4 k)–P-(MA–ST)/SiO$_2$ suspensions with MeOH content in the cosolvent. The absorbance of composite **1** (+) is plotted for comparison. Amounts of bound PMMA(15.4 k) are 20.9 (●), 28.1 (□), and 60.6 (▲) mg g$^{-1}$.

polar interaction arising from desolvation of the polymer chains. In a PMMA(15.4 k)–P(MA–ST)/SiO$_2$ suspension, the absorbance quickly decreased with time, and dropped to mostly zero absorbance after 120 min in a high MeOH content solvent. In this case, the enhancement of the interaction among the particles at high MeOH content possibly induces aggregation, and makes large masses to precipitate. Hence, the surface polarity of the composite particles was evaluated based on the spectroscopic absorbance of a suspension containing 1.0 mg ml$^{-1}$ of the particles at 500 nm after 12 h. Figures of Figs. 5, 6, 7, 8, and 9 show changes in the absorbances of polymethacrylates–P(MA–ST)/SiO$_2$ suspensions with the MeOH content in the cosolvent.

In the case of the PMMA(4.3 k)–P(MA–ST)/SiO$_2$ suspension (Fig. 5), the absorbance gradually increased with the MeOH content due to particle assembly. The changes were independent of the amount of the bound polymer. A driving force in the dispersion is probably due to the solvation of poly(methyl methacrylate) chains with AcOEt in an AcOEt-rich solution, and the solvation of the residual silanol and carboxyl groups with MeOH in a MeOH-rich solution. In the present two-step modification, bindings of the secondary polymer to the maleic anhydride moiety on the particles were involved with a simultaneous formation of the carboxyl group. The suspension of PMMA(15.4 k)–P(MA–ST)/SiO$_2$ showed a marked decrease of their absorbances in the range from 30 to 60 vol% MeOH content to give zero absorbance (Fig. 6). These results suggested that the nonpolar interaction among the long polymer chains on the particles due to desolvation were stronger than the solvation of the silanol and carboxyl groups with MeOH, so that assembling of the particles remarkably accelerated to make a sufficient number of large particles to precipitate in a solvent containing

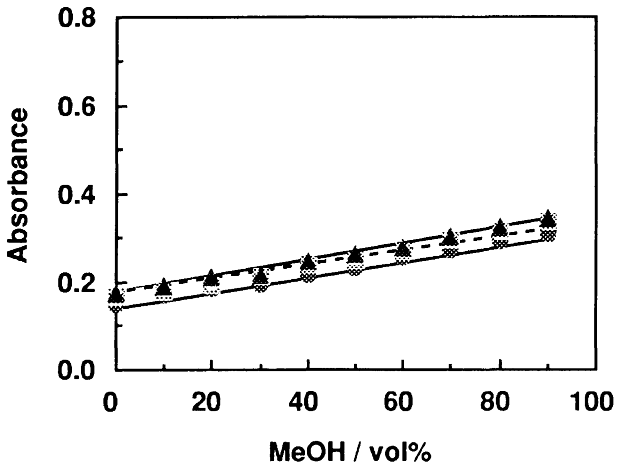


Fig. 7. The absorbance changes of PHXMA(7.2 k)–P-(MA–ST)/SiO$_2$ suspensions with MeOH content in the co-solvent. The absorbance of composite **1** (+) is plotted for comparison. Amounts of bound PHXMA(7.2 k) are 14.4 (●), 21.9 (□), and 49.4 (▲) mg g$^{-1}$.

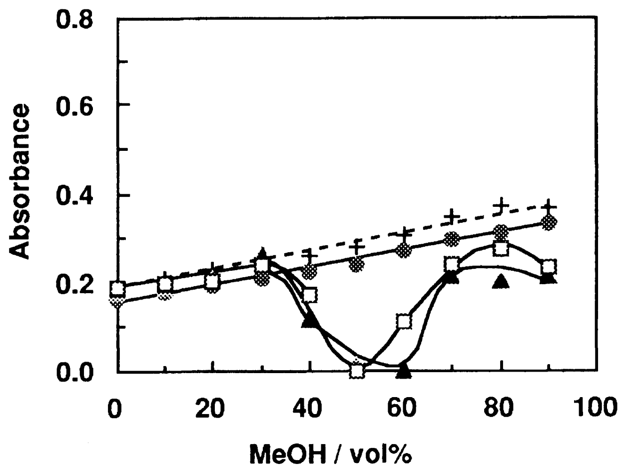


Fig. 9. The absorbance changes of PDDMA(7.6 k)–P-(MA–ST)/SiO$_2$ suspensions with MeOH content in the co-solvent. The absorbance of composite **1** (+) is plotted for comparison. Amounts of bound PDDMA(7.6 k) are 9.6 (●), 13.3 (□), and 16.1 (▲) mg g$^{-1}$.

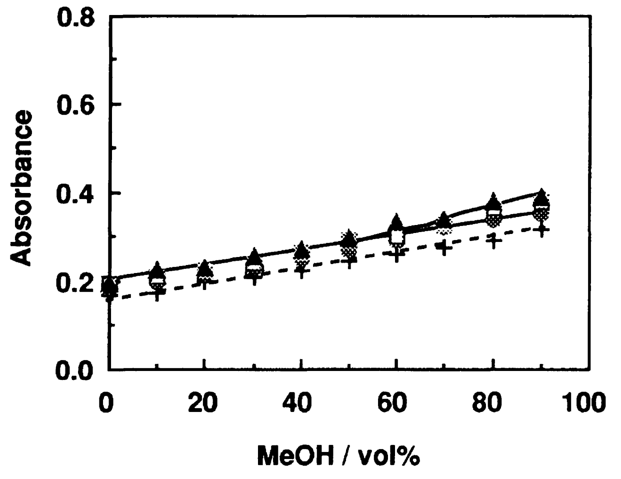


Fig. 8. The absorbance changes of PHXMA(14.0 k)–P-(MA–ST)/SiO$_2$ suspensions with MeOH content in the co-solvent. The absorbance of composite **1** (+) is plotted for comparison. Amounts of bound PHXMA(14.0 k) are 24.5 (●), 39.0 (□), and 51.8 (▲) mg g$^{-1}$.

more than 40 vol% MeOH. Interestingly, the higher was the amount of bound polymer, the lower did the MeOH content to take place the precipitation become. Probably, the formed carboxyl group compensated for a lowering of the surface polarity resulting from the hydrophobicity of the polymethacrylates. Thus, the precipitation of highly polymer-bound particle takes place under high-polar circumstances. These phenomena are similar to aggregation in the formation of polymer complexes due to desolvation of the polymer chain in a polar solvent, and a successive hydrophobic and/or nonpolar interaction.[14—16] Ohno et al.[17] have reported that the aggregation of a poly(acrylic acid)–poly(1-vinyl-2-pyrrolidone) system in aprotic and protic solvents is dependent on the polymer chain length and the polarity of the solvent.

As can be seen in Figs. 7 and 8, the suspension of PHXMA(7.2 k)– and PHXMA(14.0 k)–P(MA–ST)/SiO$_2$ exhibited gradual increases of the absorbance with the MeOH content, as well as suspensions of PMMA(4.3 k)–P(MA–ST)/SiO$_2$. Hence, the hexyl ester group in the secondary polymer, even having a molecular weight of 14000, did not significantly contribute to the nonpolar interaction in a high MeOH-content solution. Further, the suspension of PMMA(4.3 k)–P-(MA–ST)/SiO$_2$ exhibited an increase in the absorbance, i.e. proceeding of the particle assembly in a solution of more than 80 vol% MeOH content (Fig. 5), while such an absorbance increase at a high MeOH content was not observed in the suspension of PHXMA(7.2 k)– or PHXMA(14.0 k)–P-(MA–ST)/SiO$_2$. The peculiar behavior of the particles in the suspension presumably resulted from the flexibility of the secondary polymer, poly(methyl methacrylate), as compared with a polymethacrylate having a long hexyl ester group. The attachment of PDDMA(7.6 k) to P(MA–ST)/SiO$_2$ gave a similar absorbance change with the MeOH content to those of PHXMA(7.2 k)– and PHXMA(14.0 k)-modified particles, as shown in Fig. 9. However, increasing of bound PDDMA(7.6 k) on composite **2** led to an unexpected phenomenon concerning the MeOH-content dependence of the absorbances. In this case, the particles of PDDMA(7.6 k)–P-(MA–ST)/SiO$_2$ precipitated in a cosolvent in the range from 50 to 60 vol% MeOH content, and then dispersed in a solvent containing over 60 vol% MeOH. The dispersibility in a higher MeOH-content solution is probably due to a solvation of the carboxyl group formed on the P(MA–ST) chains, despite the bindings of the nonpolar long alkyl ester group. Presumably, the polymethacrylate skeletal chains are relatively short, and the decyl ester group is flexible, so that the rearrangement or separation between the primary and secondary polymer chains on the particle occurs easily in a MeOH-rich solution.

On the other hand, the bindings of the 1H,1H,2H,2H-perfluorodecyl group to composite **1** resulted in the formation

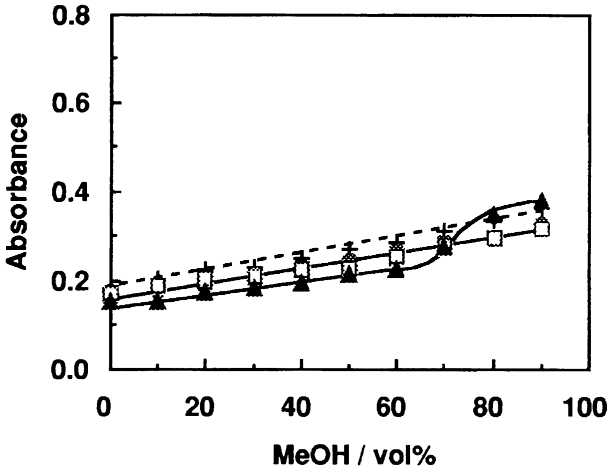


Fig. 10. The absorbance changes of PFD-modified silica suspensions with MeOH content in the cosolvent. The absorbance of composite **1** (+) is plotted for comparison. Amounts of bound PDF are 10.6 (●), 27.4 (□), and 50.2 (▲) $\mathrm{mg\,g^{-1}}$.

of the composite particles, which never precipitated in the cosolvent, as shown in Fig. 10, in spite of the binding of a strong hydrophobic 1H,1H,2H,2H-perfluorodecyl group of maximal 108.4 $\mu\mathrm{mol\,g^{-1}}$, viz. 62 molecules/nm$^2$. This result suggests that the hydrophobicity of the perfluorodecyl group is not sufficient to prevent an interaction between the surface silanol or the carboxyl groups and MeOH.

As listed in Table 1, the order of the average polymerization degree is PMMA(15.4 k) > PHXMA(14.0 k) > PHXMA(7.2 k)≅PMMA(4.3 k) > PDDMA(7.6 k). Also, the average molecule number of the bound secondary polymer, making a comparison at 20—30 $\mathrm{mg\,g^{-1}}$ of the bound polymer, increased in the following order: PMMA(4.3 k) > PHXMA(7.2 k) > PDDMA(7.6 k) > PHXMA(14.0 k)≅PMMA(15.4 k). Therefore, these results indicate that the surface polarity on the polymer-modified P(MA–ST)/$\mathrm{SiO_2}$ mainly depends on the skeletal chain length of the polymethacrylate. The long polymer chains possibly block the interaction between the carboxyl or the residual silanol groups and MeOH, and consequently bring about a low polarity. In the present case, however, the polarity is also competitively complicated by a branched alkyl ester group and the molecule number of the bound polymer, as can be seen in Figs. 5, 6, 7, 8, and 9

The relation of the dispersibility of polymer-modified colloidal silica in a nonpolar organic solvent with the surface potential or energy is now being investigated.

**Conclusions.** The main chain length of grafted polymethacrylate to poly(maleic anhydride–styrene)-modified silica particles predominantly contributed to the surface polarity, rather than the side alkyl chain length. For high polymer-bound particles, the carboxyl group formed in the binding of the secondary polymer compensated for a lowering of the surface polarity.

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