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SHORT COMMUNICATION

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Formation of colloid crystals from polymer-modified monodisperse colloidal silica in organic solvents

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Abstract The formation of colloid crystals from monodisperse and polymer-modified silica particles in organic solvents was investigated. Maleic anhydride–styrene copolymer-modified silica formed crystals in polar organic solvents, which dissolve the copolymer, while the original colloidal silica formed crystals in organic solvents which were miscible with water. The critical volume fraction in the crystal formation of the polymer-modified silica was lower than that from the unmodified silica in the same solvent. Polystyrene- and poly(methyl methacrylate)-modified silica particles also crystallized in organic solvents, but the features of the formation were different from those of poly(maleic anhydride-styrene)-modified particles.

Key words Colloid crystal – Polymer-modified colloidal silica – Organic media – Maleic anhydride-styrene copolymer – Polystyrene – Poly(methyl methacrylate)

Introduction

Lately, the fabrication of chemical or physical properties on ultrafine particles has received great attention for developing new materials [1–5]. We have developed a convenient polymer modification of monodisperse colloidal silica particles using a polymeric coupling agent of trimethoxysilyl-terminated maleic anhydride-styrene (MA-ST) copolymer [6, 7]. The modification led to the preparation of monodisperse and stable composite particles in acidic or alkaline aqueous solution by using the reaction of the MA moiety with diisocyanate, and to the introduction of amino and carboxyl groups on the surface [8]. Further, binding of the secondary polymer to the poly (MA-ST)-modified silica successfully brought about control of the surface polarity [9].

For an aqueous or alcoholic colloidal suspension, it was observed that spherical colloidal particles periodically arrayed in extremely deionized solution [10–18]. The ordering of the colloidal particles, i.e. "colloid crystal", was based on a strong electrostatic repulsive and/or attractive interaction among the particles, arising from spreading of the electric double layer [19–21]. If it is possible to prepare monodisperse hybrid particles which are compatible with organic media the particles are in principle able to form crystals like "colloid crystals" in organic solvents. Moreover, if the crystallization of the colloidal particles took place in a polymerizable compound, successive polymerization could result in particle-arrayed matrices having the intrinsic properties of the inorganic particles.

Incorporation of arrayed-monodisperse composite particles into a polymer matrix leads to new functional materials. For example, nanoscale periodic materials are useful for manufacturing optical devices which efficiently diffract light in the visible or near-infrared spectral region.

This paper describes the formation of colloid crystals from monodisperse polymer-modified silica particles in organic solvents and the effects of the polymer on crystallization.

Experimental

Materials

Ethanolic monodisperse colloidal silica, containing 23 wt% SiO_2 of 120 nm diameter, was obtained from Catalysts & Chemicals Co., Japan. Trimethoxysilyl-terminated poly(MA-ST) [P(MA-ST)-Si(OMe)$_3$] of number-average molecular weight (M_n) 5700, -polystyrene [PST-Si(OMe)$_3$] of M_n 5,600, 16,000 and 24,000, and -poly(methyl methacrylate) [PMMA-Si(OMe)$_3$] of M_n 11,500 were synthesized according to the method described previously [6, 7]. All solvents for the colloid crystal formation were purified by drying and distillation before use.

Preparation of P(MA-ST)-modified silica

Colloidal silica (20 cm^3) was added to a mixture of 3.5 g P(MA-ST)-Si(OMe)$_3$ in 300 cm^3 1,2-dimethoxyethane and 20 cm^3 tetrahydrofuran. The suspension was stirred at 90 °C and 300 cm^3 solvent was removed by azeotropic distillation. Centrifugal separation from the suspension and drying under reduced pressure gave the composite P(MA-ST)/SiO_2. IR (KBr): 2950 (ν_{C-H}), 1857 and 1789 ($\nu_{C=O}$) cm^{-1}.

Preparation of PST- and PMMA-modified colloidal silica

The reaction of colloidal silica with the polymeric silane coupling agents PST-Si(OMe)$_3$ and PMMA-Si(OMe)$_3$ was carried out in the same manner as described above. IR (KBr) for PST/SiO_2: 3025 (ν_{C-H}, phenyl), 2921 (ν_{C-H}), 1581 ($\nu_{C=C}$, phenyl) cm^{-1}. IR (KBr) for PMMA/SiO_2: 2923 (ν_{C-H}), 1753 ($\nu_{C=O}$), 1456 (δ_{C-H}) cm^{-1}.

Observation of colloid crystals and determination of critical volume

Polymer-modified or unmodified colloidal particles (120 nm) were dispersed in 1.0 cm^3 organic solvent under ultrasonic-wave irradiation and the test tube was left at room temperature for 5 min in order to observe the formation of colloid crystals by the naked eye or using a digital camera connected to a personal computer. The critical volume fraction (ϕ_0) of the particles to form the colloid crystal was determined by the lowest fraction at the brilliance due to the Bragg light reflection that was observed by successive addition of 0.05 cm^3 solvent to the suspension.

Results and discussion

When the composite particles of P(MA-ST)/SiO_2 were dispersed in organic solvents, the formation of colloid crystals was observed by the appearance of the Bragg light reflection. We also observed the crystal formation from unmodified colloidal silica in polar organic solvents which were miscible with water, as reported by Okubo [16]. In the case of P(MA-ST)-modified silica the formation of crystals was observed in polar solvents, which dissolved the MA-ST copolymer, such as acetonitrile or acetone. Therefore, it is suggested that the copolymer chains grafted onto the silica particles contribute to the induction of crystallization. Typical photographs of colloid crystals in suspensions of P(MA-ST)/SiO_2 are shown in Fig. 1. Values of ϕ_0 for polymer-modified and unmodified colloidal silica particles are listed in Table 1. Interestingly, the modified silica particles formed crystals in nitrobenzene, whereas unmodified particles did not form crystals. In the present case, it is noteworthy that the values of ϕ_0 for the

$\phi < \phi_0$ $\phi > \phi_0$

Fig. 1 Photographs of poly(maleic anhydride-styrene) [*P*(*MA-ST*)]/SiO_2 suspensions in acetonitrile

Table 1 The critical volume fraction in the formation of colloid crystals from poly (maleic anhydride-styrene) [*P*(*MA-ST*)]

Solvent	Dielectric constant	ϕ_0		ζ potential of P(MA-ST)/SiO_2 (mV)
		Unmodified	P(MA-ST)/SiO_2	
Methanol	32.6	0.045 ± 0.002	–[a]	
Ethanol	24.6	0.073 ± 0.003	–	
Isopropyl alcohol	19.9	0.084 ± 0.003	–	
Acetone	20.7	0.034 ± 0.001	0.026 ± 0.001	−148.8
Acetonitrile	37.5	0.021 ± 0.001	0.013 ± 0.001	−119.3
Acrylonitrile		0.045 ± 0.002	0.042 ± 0.002	
N,*N*-Dimethyl formamide	36.7	0.070 ± 0.003	0.050 ± 0.002	−130.9
Nitrobenzene	34.7	–	0.050 ± 0.002	−61.5
Tetrahydrofuran	7.58	–	–	
Ethyl acetate	6.02	–	–	

[a] – signifies nonformation of the crystal

unmodified particles are lower than those for the modified particles in the same solvent systems. In general, it is well known that there are two conflicting theories for the formation of colloid crystals based on the electrostatic repulsion and/or attraction between the particles in aqueous solution [19–21]. Therefore, the polymer chains probably contribute to the enhancement of electrostatic interactions between the particles, and consequently the critical volume fraction of P(MA-ST)/SiO_2 is lower than that of unmodified silica; however, we cannot find a simple correlation between the zeta potential of P(MA-ST)/SiO_2 and values of ϕ_0 for crystal formation. Moreover, we have observed that ϕ_0 has the maximum value, 0.0212, at 28.4 mg g^{-1} grafted P(MA-ST) and then decreases with increasing amount of grafted polymer to reach 0.0136 at the upper grafting limit of 90.2 mg g^{-1}. In the case of P(MA-ST)/SiO_2, therefore, it is suggested that the interparticle interaction through the electric double layer in the colloid crystal is controlled by the properties of the original silica at lower polymer grafting amounts giving the maximum ϕ_0 value, and then by the grafted polymer at higher amounts of grafted polymer.

In order to clarify the origin of the crystal formation, we investigated the effects of an electrolyte additive, NH_4PF_6, on ϕ_0 in the crystallization of P(MA-ST)/SiO_2 in acetonitrile. The dependence of ϕ_0 on NH_4PF_6 concentration is shown in Fig. 2. In the case of P(MA-ST)-modified particles, ϕ_0 gradually increased with concentration for salt concentrations below 3.81×10^{-6} mol l^{-1}, and markedly increased around a concentration of 4.76×10^{-5} mol l^{-1}; however, above a salt concentration of 9.52×10^{-5} mol l^{-1}, crystal formation was not observed. As can also be seen in Fig. 2, ϕ_0 for unmodified silica increased with the increasing salt concentration, and the crystallization did not take place above a concentration of 2.04×10^{-5} mol l^{-1}. Thus, these results suggest that electrostatic interaction between the particles contributes to the formation of colloid crystals from P(MA-ST)-modified silica. Also, the fact that the critical concentration of the salt for crystallization of polymer-modified silica is higher than that for unmodified silica suggested that steric interaction and/or electrostatic interaction stemming from polymer chains on the modified silica possibly contribute to crystal formation.

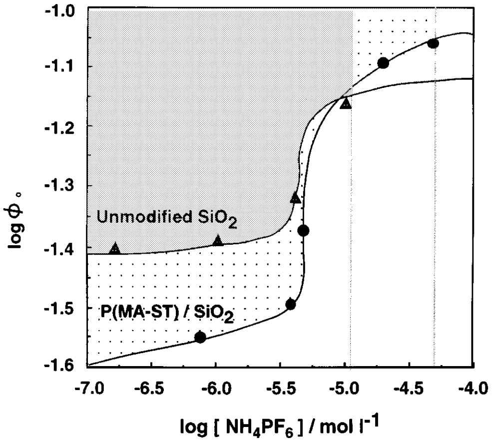

Fig. 2 Dependence of the critical volume fraction on the additive NH_4PF_6. *Gray* and *dotted* areas represent the ranges of colloid crystal formation from unmodified and P(MA-ST)-modified silica, respectively

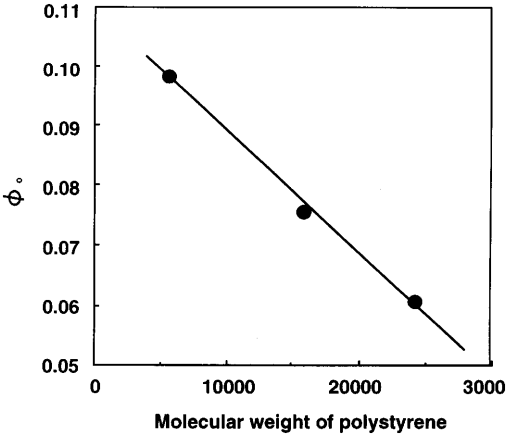

Fig. 3 Relation between critical volume fraction and the molecular weight of polystyrene bound to silica

Table 2 The critical volume fraction in the crystallization of P(MA-ST)/SiO_2, polystyrene (*PST*)/SiO_2 and poly(methyl methacrylate) (*PMMA*)/SiO_2

Particles	$10^{-3} \times M_n$[a]	A.P.[b] (mg/g)	ϕ_0			
			Acetonitrile	Acetone	Nitrobenzene	Acrylonitrile
P(MA-ST)/SiO_2	5.7	90.2	0.013 ± 0.001	0.021 ± 0.001	0.050 ± 0.002	0.042 ± 0.002
PST/SiO_2	24.4	24.8	–	–	0.060 ± 0.002	–
PMMA/SiO_2	11.5	31.0	0.075 ± 0.003	0.089 ± 0.003	–	0.105 ± 0.003

[a] Number-average molecular weight of polymer

[b] Amount of grafted polymer on silica

The contribution of grafted polymer chains is also supported by the fact that PST- and PMMA-modified silica showed characteristic features for crystal formation in organic solvents, as shown in Table 2. The amounts of grafted polymer in Table 2 are the maximum ones. PST-modified silica only crystallized in nitrobenzene, while PMMA-modified silica crystallized in acetonitrile, acetone, and acrylonitrile, but not in nitrobenzene. These polymer-modified particles formed crystals at higher ϕ_0 than P(MA-ST)-modified particles in organic solvents. The reason for the high critical volume in the crystal formation from PST- or PMMA-modified particles might be due to the greater flexibility of polymer chains than of P(MA-ST) chains.

In the present study, the radical copolymerization in the presence of a charge-transfer reagent of 3-thiopropyl-trimethoxysilane was unable to produce molecular-weight-controlled MA-ST copolymer. Thus, we investigated the effects of the molecular weight of the polymer on the critical volume fraction in the crystallization employing PST. Figure 3 shows that the critical volume decreases linearly with the molecular weight of the PST grafted onto the silica, in spite of the decreasing ratio of the grafted polymer. The grafted amounts of PS of M_n 5,600, 16,000 and 24,000 in Fig. 3 were 46.5, 36.1 and 24.8 mg g^{-1}, respectively, which were the upper grafting limits. This result strongly emphasizes the fact that the length of the grafted polymer chains plays a significant role in the interparticle interactions in crystal formation.

In conclusion, the formation of colloid crystals from polymer-modified silica is through interparticle interactions based on the electrostatic interaction and/or repulsion by polymer chains bound to the silica. The investigation into the factors involved in the crystal formation from polymer-modified silica is now in progress.

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