

Preparation of monodispersed polymer-modified silica particles by radical polymerization using silica colloid and introduction of functional groups on the composite surface

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Summary

Radical polymerizations of vinyl monomers using a initiator of 2,2'-azobis(2-amidinopropane) dihydrochloride on monodispersed silica colloid led to formation of spherical polymer/SiO₂ composites, retained particle size. Addition of hydroxypropyl cellulose to the reaction system resulted in yielding excellent dispersible composites into ethanol by short period ultrasonic irradiation. The polymerization of styrene in the presence of mercapto-amine or carboxylic acid derivatives could successfully introduce amino or carboxyl group on the Poly(styrene)/SiO₂ composite.

Introduction

Recently, monodispersed metal oxide colloids having various particle size in the range of nanometer to micrometer orders become to be commercially supplied. We have been developing a new kind of functional composite materials, derived from monodispersed colloid particles modified with polymer, for the purpose of utilizing the feature of perfect spherical shape or inherent physical properties of superfine particles.

So far, in order to give hydrophobicity, chemical modifications of inorganic fine particle surface have been widely studied (1,2,3,4) and some of them have been practically employed to improve dispersibility in organic phase and compatibility in polymer matrices. However, colloid particles generally exist as stable suspension in dispersion medium due to electrostatic repulsion through electrical double layer on the surface. In many cases, the colloids dispersed in solution contain water molecules on the surface, contributing to the stability. Therefore, some of the modification procedures for inorganic particles cannot be applied to the colloid particles, because of destruction of electrical double layer around particles. In this respect, we have lately prepared polymer-modified monodispersed silica particles, which are redispersible in nonpolar organic solvents such as chloroform, benzene and tetrahydrofuran (THF) after dryness, using poly(styrene) (PST), poly(methyl methacrylate) (PMMA) and poly(oxyethylene)-silane coupling agents (5).

In this paper, we wish to report effective polymer attachment on the particle surface of monodispersed silica colloid, which is used because of availability, by radical polymerization. Effects of cellulose derivative addition as steric stabilizer on dispersibility of the polymer/SiO₂ composites in organic solvent and introduction of functional groups on its surface using chain transfer reagents of thiols were also studied.

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Experimental

Materials and measurements

Monomers were purified by distillation. Monodispersed colloidal silica in EtOH, made by Catalysts & Chemical Co. Ltd., was employed; having mean particle size of 470 nm with standard deviation of 37 nm. The silica colloid constituted of SiO₂ (19.72 %), Al₂O₃ (0.88 %), Na (0.054 %) and H₂O (22.5 %); pH and ζ-potential in H₂O were 8.52 and -37.7 mV, respectively. Hydroxypropyl cellulose (HPC) (Mn 100,000) was purchased from Aldrich Chem. GPC analyses were conducted on TSKgel 3000H with THF eluent by poly(styrene) standards. IR spectra were recorded with diffuse reflectance method on JEOL-JIR 5500. Thermal gravimetric analyses were carried out by Shimadzu TG-50. SEM photographs were taken by JEOL JCX-733 and particle size distributions were measured in EtOH by light scattering method with Ohtsuka DLA-700.

Polymerization

A typical procedure was as follows. A mixture of silica colloid ethanolic solution (40 ml), containing 5 % SiO₂, and 2.5 ml of styrene (ST) and 20 mg of 2,2'-azobis(2-amidinopropane) dihydrochloride (AAP) was stirred at 85 °C for 5 h. An aliquot (5 ml) of the mixture was taken out and added to 10 ml of ethylene glycol, and then the pasty cake was separated from the mixture by centrifugation. The sediment containing PST/SiO₂ composite was centrifuged from ethanolic suspension of the cake three times, followed by drying under vacuum overnight.

Attached polymer on silica

Amount of attached polymer on silica surface was assigned to ignition loss during elevation from 100 °C to 1000 °C, after keeping the sample at 100 °C for 1 h, with thermal gravimetric analysis.

Determination of amino and carboxyl groups on composite

These groups were determined by titration with 0.01N HCl or 0.01N NaOH, respectively.

Preparation of samples for SEM measurement

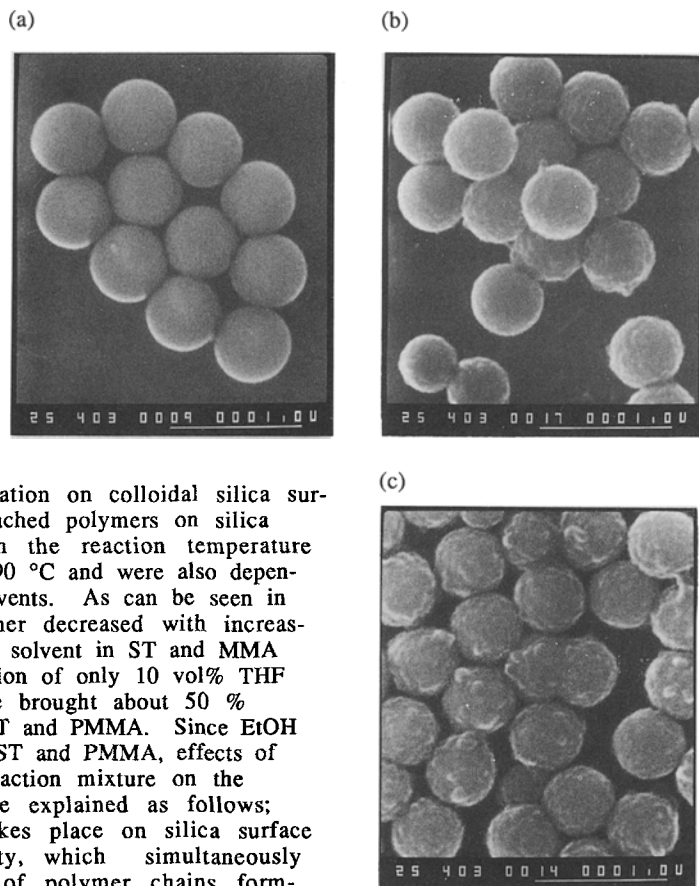
The polymer/SiO₂ composite (0.5 mg) was dispersed in EtOH (3 ml) under ultrasonic irradiation for 30 m. A droplet of the suspension were put on a coverglass (18 x 18 mm). The sample was dried at 80 °C under vacuum for 24 h.

Results and discussion

Since surface of silica colloid particles ordinarily has negative charges on electrical double layer, which contributes to preventing coagulation by electrostatic repulsion among particles, a radical polymerization initiator, AAP, is concentrated, and then radical species generated on the surface are expected to induce efficient polymerization of vinyl monomer.

Heating and stirring the monomer, such as ST, methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA), in ethanolic silica suspension containing AAP gave the formation of polymer/SiO₂ composites. SEM images in Fig. 1 show that each particle of these composites is wholly and homogeneously covered with PST or PMMA, having little rising on the surface, while colloidal silica particles exhibit more smooth surface than those of the composites. The use of azobis(isobutyronitrile) initiator for the ST polymerization brought about the formation of heterogeneous mixture of silica particles and PST masses, confirmed on SEM photographs. Therefore, this result means that AAP plays significant

Fig. 1. SEM images of colloidal silica (a), PST/SiO₂ (b) and PMMA/SiO₂ (c).



roles in the polymerization on colloidal silica surface. Amounts of attached polymers on silica surface increased with the reaction temperature in the range of 60 to 90 °C and were also dependent on polarity of solvents. As can be seen in Fig. 2, attached polymer decreased with increasing THF content in the solvent in ST and MMA polymerizations. Addition of only 10 vol% THF to the reaction mixture brought about 50 % decrease of attached PST and PMMA. Since EtOH is a poor solvent for PST and PMMA, effects of THF content in the reaction mixture on the polymer attachment are explained as follows; polymerization first takes place on silica surface to give hydrophobicity, which simultaneously promotes aggregation of polymer chains formed in ethanolic bulk solution.

On the contrary, attachment of poly(2-hydroxyethyl methacrylate) (HEMA) to silica increased with THF content in the reaction system. THF is a poor solvent for PHEMA, so that increment of THF content probably promotes the aggregation of the polymer chains on PHEMA-coated silica surface. Silica particles covered with these polymers were also confirmed by observation of characteristic vibrational absorption bands, 3025 ($\nu_{\text{Ph-H}}$), 1492 and 1452 (δ_{CH_2}), 758 and 698 ($\omega_{\text{Ph-H}}$) cm^{-1} for PST/SiO₂, 2998-2839 (ν_{CH_3} and ν_{CH_2}), 1730 ($\nu_{\text{C=O}}$), and 1483-1435 (δ_{CH_3} and

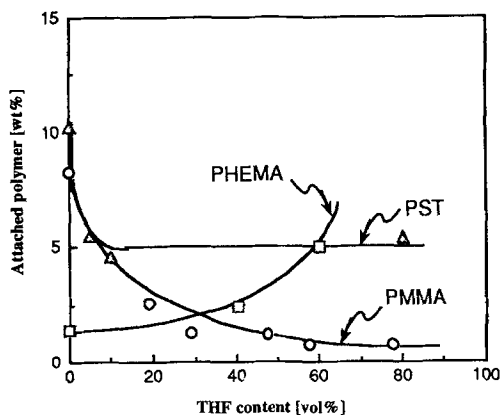


Fig. 2. THF content dependences of attached polymers in polymerizations of ST at 85 °C, MMA and HEMA in EtOH-THF at 60 °C.

δ_{CH_2}) cm^{-1} for PMMA/SiO₂, and 3400-3000 ($\nu_{\text{O-H}}$), 2996-2837 (ν_{CH_3} and ν_{CH_2}), 1730 ($\nu_{\text{C=O}}$), and 1483-1432 (δ_{CH_3} and δ_{CH_2}) cm^{-1} for PHEMA/SiO₂ after complete removal, realized by SEM analyses, of free polymers on respective IR spectrum. In regard to polymer chain growth, if radical chain transfer polymerization predominantly occurred on silica surface, both of molecular weight and amount of attached polymer would become increase with reaction time. In the present polymerizations, binding polymer to silica

surface is considered to be involved by electrostatic attraction, thus washing with acetone solution containing 5 % water possibly removes attached polymer from the silica surface. In Fig. 3, the time dependences of amount and Mn of peeled PST from the composite by acetone washing are shown. Complete removal of PST from the surface was confirmed by gravimetric analysis of the peeled silica. Attached PST proportionally increased with the reaction time, but its Mn attained constant values of 11,500 in 6 h after starting the polymerization. Thus, these results support the above explanation for THF content effects, that is, polymer chains grows at initial stage on the surface, and then PST-modified silica surface entraps polymer chains formed in the bulk solution because of low solubility in ethanol-rich solvent. Although composites of PST/SiO₂ and PMMA/SiO₂ were visually dispersible in chloroform, benzene and THF after ultrasonic irradiation, particle size distributions of these composites were wide-spread over the range of 500 nm to 1,400 nm, and sifted to small size side during ultrasonic vibration over one hour.

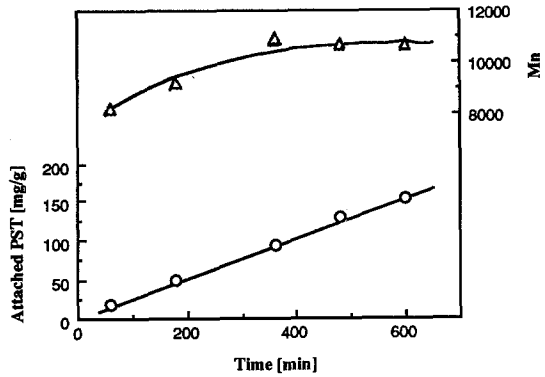


Fig. 3. Time dependences of attached PST and its Mn in the polymerization in EtOH at 85 °C.

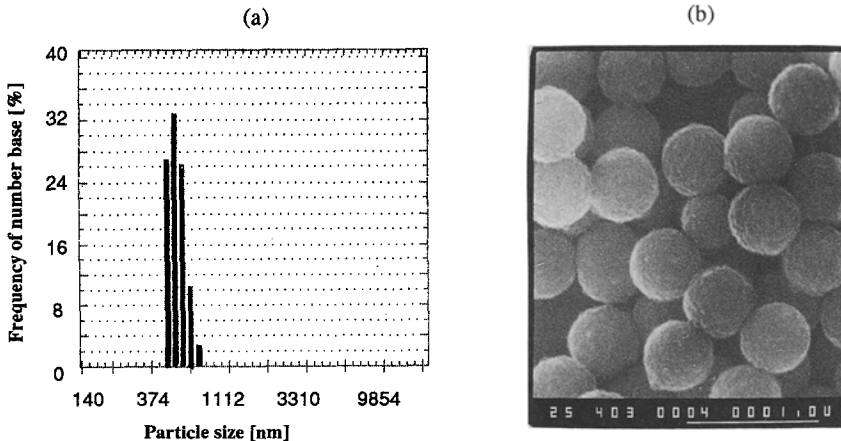


Fig. 4. Particle size distribution (a) and a SEM image (b) of PST/SiO₂ prepared in the presence of HPC (0.1 g).

Table 1. Introduction of amino and carboxyl groups on PST/SiO₂ composites in ST polymerization with 3-mercaptopropionic acid (1), thiomalic acid (2) and 3-mercaptopropylamine (3) at 80 °C^a

1	2	3	Attached PST	COOH	NH ₂	Mn
(mmol)			(wt%)	× 10 ² (mmol/g)		
			4.73			7000
0.11			8.65	0.40		5700
0.22			8.34	0.68		4700
0.57			6.17	0.73		<400
2.80			5.55	0.92		<400
	0.07		8.90	0.71		6400
	0.13		6.38	0.75		6200
	0.33		5.84	0.85		<400
	1.67		6.24	1.20		<400
		0.44	5.17		2.44	6700
		0.88	5.29		2.68	6800
		2.20	5.56		2.85	6500

^a The reactions were carried out in the suspension containing ST (22 mmol), AAP (1.1×10^{-1} mmol) and SiO₂ (2.3 g) in 40 ml of EtOH.

Probably, conglutination among polymer/SiO₂ composites occurs during drying up solvent.

Meanwhile, in the preparation of monodispersed PST microspheres, nonionic cellulose derivatives were employed to prevent growing spheres from aggregation as a steric stabilizer (6). In this regard, Paine et al. (7) have also proposed that HPC is grafted to PST chain ends to form the HPC-grafted PST, which protects the particles from conglutination, in the dispersion polymerization of ST in polar solvent, such as ethanol. In the present system, addition of HPC resulted in giving PST/SiO₂ composites showing rapid and smooth dispersibility and distinct monodispersion in ethanol after ultrasonic irradiation for only 5 m (Fig. 4). In this case, attached PST increased with HPC added. Presumably, formation and concentration of HPC-grafted PST, ends up on the surface, makes access and successive polymerization of the monomer on PST-coated silica surface promote, due to enhancement of surface hydrophobicity. However, molecular weight of attached PST was lowered by HPC additives; from Mn of 7,000 without HPC to 3,000 in the polymerization in the presence of HPC of 0.4 g pre unit gram of silica.

In order to introduce functional end groups in the radical polymerization, thiol derivatives as chain transfer reagent are usually used, so that we have also examined addition effects of 3-mercaptopropionic acid, thiomalic acid and 3-mercaptopropyl amine on ST polymerization. In cases of the polymerization with the acid, though carboxyl group was not clearly observed on IR spectra of the composites, alkali titration showed definite existence of carboxyl moieties (Table 1). The surface carboxyl group increased with thiol derivatives added, but molecular weight of attached PST on the surface decreased with amounts of the additives. Especially, additions of 3-mercaptopropionic acid and thiomalic acid more than 25 and 14.3 μmol per one gram of silica, respectively, drastically lowered molecular weight. Probably, mercaptocarboxylic acids are concentrated near the surface by electrostatic interaction between the amine salt initiator (AAP) and the carboxylic acid, so that PST chains with lower molecular weight are formed on the silica surface. In any rate, this procedure could successfully introduce carboxyl groups of around 7 μmol/g, corresponding to 0.2 COOH-

groups/nm². On the other hand, addition of 3-mercaptopropylamine also led to introduction of amino groups, 0.28 mmol/g corresponding to 0.86 NH₂-groups/nm², on the surface of the composite. On the contrary to the reaction with the mercapto acids, while addition of the amine did not bring about lowering molecular weight, concentration of surface amino group and molecular weight of attached PST were independent on amount of the additive.

Moreover, the dried PST/SiO₂ composites having amino or carboxyl groups also showed not only good dispersibility, also involved narrow particle size distributions. For the stabilizer-free PST/SiO₂ composites, surface amino or carboxyl groups probably ends up on the silica surface during growing polymer chains, contributing to protection of the particles from aggregation or conglutination due to electrostatic repulsion.

Further introductions of functional groups and functional polymers are now in investigation.

References

1. Kroger R, Schneider H, Hamann K (1972) *Prog Org Coatings* 1: 23
2. Laible R, Hamann K (1980) *Adv Colloid Interface Sci* 13: 65
3. Tsubokawa N, Kogure A, Sone Y, Shimomura M (1989) *Polymer J* 21: 475
4. Tsubokawa N, Kogure A, Sone Y (1990) *J Polym Sci, Polym Chem* 28: 1932
5. Yoshinaga K, Horie R, Saigoh F, Kito T, Enomoto N, Nishida H, Komatsu M, *Polym Adv Tech*, accepted for publication.
6. Ober CK, Lok KP (1987) *Macromol* 20: 268
7. Paine AJ (1990) *J Coll Int Sci* 138: 157