Bull. Chem. Soc. Jpn., ***68**, 388—392(1995)*

Factors Affecting the Redispersibility of Organosilica Sols Prepared by a Modification of Silica Particles with a Polyol-Based Polymer[1]

Taketoshi Kito,* Makoto Yamaye,† Kohji Yoshinaga, Youichi Ishihara,
Michio Komatsu,†† and Hiroyasu Nishida††

Department of Chemistry, Kyushu Institute of Technology, Sensui-cho, Tobata-ku, Kitakyushu 804
†Faculty of Engineering, Kyushu Kyoritsu University, Orio, Yahatanishi-ku, Kitakyushu 807
††Catalysts & Chemicals Industry Co., Ltd., Kitaminato-machi, Wakamatsu-ku, Kitakyushu 808

(Received May 12, 1994)

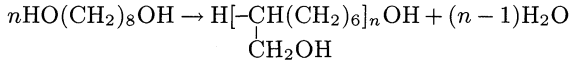
Organosilica sols which were redispersible in nonpolar or less polar organic solvents were prepared by a chemical modification of the silica surface with a polyol-based coupling polymer; the redispersibility was then examined in terms of the molecular weight of the coupling polymer, charged coupling polymer/silica (mmol g^{-1}) (P/S) ratio, and the size of modified silica particles. Fractionated coupling polymers with an $M_\mathrm{w}/M_\mathrm{n}$ of 2.0—2.8 were used. The charged P/S ratio was a leading factor for the redispersibility. The redispersibility was achieved when the charged P/S ratio exceeded approximately 0.3 mmol g^{-1}, using coupling polymers of various molecular weights. The particle size of the modified silica decreased along with an increase in the charged P/S ratio and the reaction time. The presence of a free polymer was not essential for the redispersibility when the saturation of the silica surface with the coupling polymer was nearly completed.

Inorganic–organic composite materials have recently attracted much attention because of their unique properties.[2—5] For their effective preparation, the surface of an inorganic compound may be modified with an organic coupling agent before compounding, in order to minimize any difference between the surface properties of the inorganic and organic components.[6—9] Such organic coupling agents can be divided into two types in terms of molecular weight: (a) low-molecular-weight agents and (b) high–molecular-weight agents derived from polymeric materials.[10,11] Similarly, there can be two types of coupling systems in which (c) a coupling agent is physically adsorbed on the surface of an inorganic compound and (d) a coupling agent forms covalent bonds to the functional groups on the inorganic surface.

As an example of combination (a)–(c), Favis reported the adsorption of coupling agents on a mica surface.[12] Chujo et al. synthesized trimethoxysilyl-terminated poly(*N*-acetylaziridine) as a novel silane coupling agent,[13] which belongs to combination (a)–(d). Examples of combination (b)–(c) were investigated mainly from a physicochemical point of view.[9,14,15] For combination (b)–(d), Tsubokawa has described various methods for the surface modification of inorganic particles via covalent-bond formation with a polymer.[11] Many of the surface modifications of carbon black also belong to combination (b)–(d).[16—18]

As for the modification of a silica surface with organic compounds, many reports have been published.[11,19,21] Auroy et al. reported that silica particles can be stabilized by grafting a long-chain polymer onto the particle surface. They used an OH group-terminated poly(dimethylsiloxane) to form covalent bonding on the silica surface.[21]

Our previous report[1] concerned combination (b)–(d). A hydrophilic silica surface can be modified with a novel coupling polymer containing silyl ether pendant groups (coupling polymer 2) prepared from polymeric polyol **1**, which was obtained by the condensation of a diol in the presence of potassium phenoxide[22] (see Eqs. 1 and 2). In this paper, the polymeric polyol **1** is



$$n\mathrm{HO(CH_2)_8OH} \rightarrow \mathrm{H[\underset{\displaystyle CH_2OH}{CH}(CH_2)_6]_{\mathit{n}}OH} + (n-1)\mathrm{H_2O} \qquad (1)$$

1 (PCH$_2$OH)

$$\mathrm{PCH_2OH + EtOSiMe_2(OEt)} \rightarrow \mathrm{PCH_2OSiMe_2(OEt) + EtOH} \qquad (2)$$

2

hereafter designated as **1** or P-CH$_2$OH.

There are three types of polymer adsorptions on an inorganic surface in the case of combination (b)–(c): tail, loop, and train types.[9,15] The same types of adsorption are also possible in the case of combination (b)–(d). Our method involves the conversion of **1** into coupling polymer **2**, followed by a surface modification of the silica particles with **2**, where the train- or loop-type modification occurs; a molecule of **2** forms several covalent bonds with a single silica particle through a siloxane linkage. The formation of a single covalent end-bonding between them, however, has been reported by Tsubokawa,[11,15,18] Favis,[12] Chujo,[13] Auroy,[21] and others.[20] After the evaporation of 1,2-dimethoxyethane (DME), the residual silica particles obtained by our treatment are redispersible, even in less-polar organic solvents, including chloroform.[1]

This paper describes several factors which affect the particle size of silica dispersed in DME as well as its redispersibility in other organic media.

Results and Discussion

In this work, coupling polymer **2** was prepared from the starting polymer **1**, which was fractionated into several portions in terms of the molecular weight, based on the degree of solubility in ether–$CHCl_3$.

In the study shown in Figs. 1, 2, and 3, five types of **2** (P_{2800}, P_{4100}, P_{5200}, P_{6500}, and P_{21200}, where the subscripts stand for molecular weight) were used. These samples demonstrated comparable M_w/M_n values (2.0—2.8). The coupling polymer **2** was soluble in DME, chloroform, THF, diethyl ether, toluene, benzene, hexane, and methyl methacrylate. The solubility of **2** in methanol and styrene is shown in Table 1.

A modification of the silica particles was perfomed by coupling polymer **2**. We selected DME as a dispersant for the following reason. Silica was well dispersed in dimethylformamide, diethylene glycol, dimethyl ether, and methanol, slightly dispersed in DME, and not dispersed in chloroform, benzene, and THF (these results were obtained by solvent exchange, as mentioned in Experimental Section). DME is inert and can be readily removed because of its low boiling point (82 °C), though it is not a good dispersing solvent for silica. The size of the silica particles increased from 3.71 to 98.2 nm along with a replacement of the original dispersant, methanol, by DME.

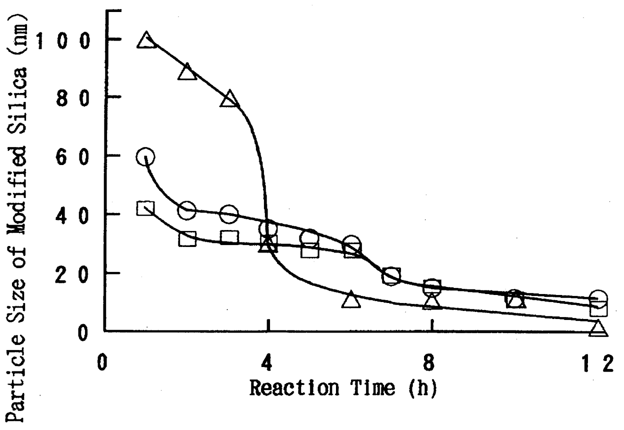


Fig. 1. Dependence of the particle size of modified silica dispersed in DME on reaction time. P/S ratio, 0.5 (mmol g^{-1}). ○ P_{4100}, □ P_{6500}, △ P_{21200} (All samples were redispersible).

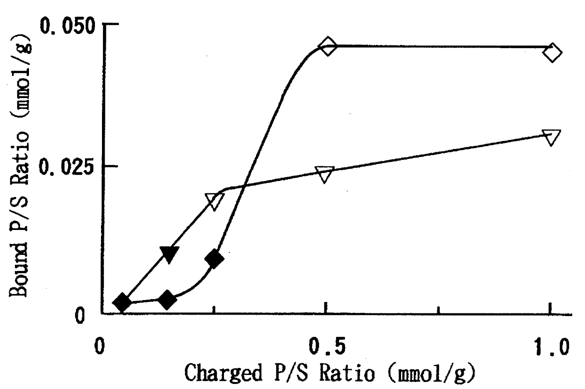


Fig. 2. Dependence of bound P/S ratio on the charged P/S ratio. Reaction time, 12 h. ◇ ◆ P_{2800}, ▽ ▼ P_{5200}, ◇ ▽ redispersible, ◆ ▼ not redispersible.

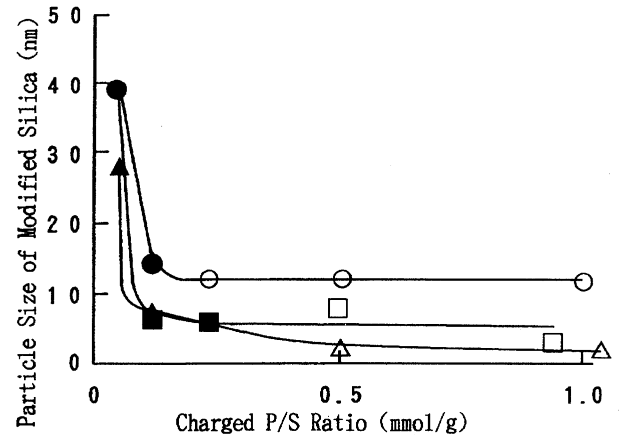


Fig. 3. Dependence of the particle size of modified silica dispersed in DME on the charged P/S ratio. Reaction time, 12 h. ○ ● P_{4100}, □■ P_{6500}, △ ▲ P_{21200}, ○ □△ redispersible, ● ■ ▲ not redispersible.

Table 1. Solubility of Coupling Polymer **2**

Polymer	Solubility[b] in	
Pn[a]	MeOH	Styrene
P_{2800}—P_{4100}	△	△
P_{5200}	△	○
P_{6500}—P_{21200}	×	○

a) "n" in Pn stands for M_n value. b) ○ soluble; × insoluble; △ partially soluble.

Silica particles when dispersed in methanol, a polar solvent, are effectively surrounded by methanol, to gain stabilization by a steric repulsion among the particles, a major stabilization factor for colloidal particles.[23] On the other hand, the particles, when dispersed in DME, might tend to form an aggregate because of their low polarity.

By fixing the ratio of charged coupling polymer **2**/silica (mmol g^{-1}) (P/S or Pn/S ratio, where n represents molecular weight) at 0.5, a mixture of the DME–silica sol and **2** was refluxed for 1—12 h, and the size of modified silica particles was determined by a quasi-elastic light scattering (QELS) method. The result is shown in Fig. 1. All of the sols examined were redispersible. The size of the silica particles modified with **2** was considerably large during the initial stage, compared with that of the starting silica particles, but decreased after refluxing for 6—8 h to reach nearly 10 nm, their original size. In this experiment, the particle size was not an important factor for redispersibility, as long as the particle size was controlled over a range of less than 100 nm.

The amount of **2** bound to the silica was determined by a thermogravimetric analysis; the bound P/S ratio is plotted against the charged P/S ratio in Fig. 2, where P_{2800} and P_{5200} are used. At a charged P/S ratio of 0.5, the bound P/S ratio was almost saturated, with 0.047 mmol g^{-1} when P_{2800} was used. A comparison between the amount of bound **2** for P_{2800} and that for P_{5200} at a charged P/S ratio of 0.5 showed that the former was about twice in mmol (0.024 mmol g^{-1} for P_{5200}) and nearly equal in weight. As for the behavior of P_{5200}, the amount of bound **2** gradually increased along with an increase in the charged P/S ratio, indicating that it takes a longer period for saturation. One of the major reasons for this lies in a possible crowing at the reaction site caused by coupling polymer **2** having a higher molecular weight. A similar tendency was observed in a previous experiment (in which the starting polymer **1** was not fractionated).[1)] In a reaction for less than 4 h (shown in Fig. 1) there were significant differences in the particle size, depending on the molecular weight of **2** used. This result can also be explained by the crowding effect described above; that is, P_{21200} may react with the silica surface more slowly than the other two (P_{4100} and P_{6500}).

The relationships between the charged and bound Pn/S ratios depending on the molecular weight of coupling polymer **2** were examined. From Fig. 2, the minimun values of the charged Pn/S ratios for obtaining a redispersible sol were estimated for $n=2800$ and 5200 to give 0.25—0.5 and 0.15—0.25 mmol of **2**/1 g of silica, respectively. The corresponding values of the bound Pn/S ratios were 0.0093—0.047 and 0.011—0.019 mmol of **2**/1 g of silica. This fact indicates that more than 90% of free **2** is required for the preparation of a redispersible sol when modification is carried out using **2** having a molecular weight of between 2800 and 5200.

In Fig. 3, the diameters of the modified silica particles are plotted against the charged P/S ratio for the case after the reaction was carried out at 130 °C for 12 h. Redispersibility was attained when the charged P/S ratio reached a range between 0.3 and 0.5 (0.24 for P_{4100}), and the particle size decreased to less than 10 nm, comparable to that of silica (3.71 nm) in the original methanol–silica sol. However, redispersibility could not be attained when the charged P/S ratio was less than 0.3 (less than 0.24 for P_{4100}), even if the particle size was reduced to about 10 nm. These results suggest that the redispersibility depends mainly on the charged P/S ratio as long as the ratio varies between 0.3 and 1.0.

As we previously reported,[1)] once free **2** and a dispersing solvent were both removed, the remaining silica could never be redispersible in organic solvents, including the original one. We explained this phenomenon based on the "depletion stabilization" proposed by Feigin and Napper.[24)] According to their theory, in the presence of unreacted **2** (free polymer), an attractive force operates between any two particles of the modified silica when they come close together within the diameter of a coil-shaped free polymer. In the present study, however, the remaining silica was able to be redispersible into organic solvents, even after both free **2** and the dispersing solvents had been completely removed.

These observations led us to the conclusion that the saturation of a silica surface with polymer **2** would suffice for redispersibility. When the whole surface of silica particles is almost completely covered with coupling polymer **2**, a steric repulsion would work among them to prevent coagulation.

The size of the silica particles increased due to a partial aggregation upon replacing the dispersant methanol by DME. We assumed that the particles loosely assemble each other, because the size can be reduced to the original one when the DME–sol is heated upon the addition of **2**.

Our modified silica particles, which were redispersible in DME, were also redispersible even in nonpolar or less-polar solvents, including hexane, benzene, and styrene, if necessary, with the application of ultrasonic waves.

If the charged P/S ratio was sufficiently large (for example, 0.5), redispersible sols could be obtained with in an hour in the present experiment, compared to the longer period of the reaction reported in a previous paper (for example, 24 h).[1)] A main reason for this observation lies in the ultrasonic-wave irradiation used in the present method (see Experimental Section). The use of fractionated **2** may be another reason, because, as shown in Fig. 2, coupling polymer **2** having a higher molecular weight can achieve redispersibility with a smaller number of **2** molecules than that having a lower molecular weight.

These results form the following conclusions:

(1) Basically, redispersibility can be achieved when the surface of silica particles has been effectively covered with coupling polymer **2**.

(2) The charged P/S ratio shows a substantial effect on the redispersibility. Low charged P/S ratios (less than 0.25 for P_{2800}) do not produce redispersible sol, even for a longer period of heating (for 12 h).

(3) The particle size of modified silica sols rapidly decreases along with an increase in the charged P/S ratio and reaction time, and finally reaches nearly the same size as that of the original silica particles.

(4) Although parts of the silica particles dispersed in DME assemble to form an aggregate due to an attractive force operating among them, the aggregate can be readily broken back to a sol of the original size upon treatment with **2**.

(5) The amount of **2** bound to the silica surface is nearly proportional to the molecular weight of **2** when the molecular weight is low.

(6) The presence of a free polymer is not always essential for redispersibility, when the silica surface is saturated with coupling polymer **2**.

Experimental

Ultrasonic waves were generated using a UO300FB (Kokusai Electric). The size of silica particles was measured by a dynamic light-scattering analyzer (Photal DLZA-700; Otsuka Electronics). A molecular-weight determination was carried out using a gel permeation chromatograph (Shimadzu LC-9A/CTO-6A (Column)) with Showa Denko Shodex (RI SE-51) as the detector. The amount of polymer **2** bound to silica was determined by a thermogravimetric analyzer (Shimadzu TG-50).

Preparation of Polymeric Polyol 1 (P-CH_2OH). A typical example is described.

Polymeric polyol **1** from 1,8-octanediol (14.6 g, 0.1 mol) was prepared according to a reported method.[22)] A crude reaction product, a mixture of polymers of various molecular weights, was fractionated into high- and low-molecular-weight portions (HMwP and LMwP) as follows.

A $CHCl_3$ solution (50 mL) of the product was neutralized with aq HCl and washed with water (250 mL). The addition of ether (200 mL) to the $CHCl_3$ solution caused the separation of a white mass. Collection of the mass, followed by removal of adsorbed water by azeotropic distillation with benzene (250 mL) in a stream of N_2, gave the HMwP of polymeric polyol **1**. From the remaining ether–$CHCl_3$ solution, LMwP was recovered.

The molecular weight of HMwP varied with the reaction time and the volume ratio of ether/$CHCl_3$. In this study, only HMwP with an M_w/M_n of 2.0—2.8 was used.

Determination of the Molecular Weight of Polymeric Polyol 1. The molecular weight and M_w/M_n ratio of **1** were determined by GPC using standard polystyrene samples as a reference M_n (M_w/M_n) of 3100 (1.05), 7600 (1.03), 13500 (1.03), and 43200 (1.16).

Preparation of the Organosilica Sol Dispersed in 1,2-Dimethoxyethane (DME–Sol). The DME-sol was prepared from methanol–silica sol (average diameter of silica particles, 3.7 nm) by solvent exchange, according to the reported method.[1)]

Preparation of Coupling Polymer 2. Polymeric polyol **1** (3.05 g) was successfully dispersed into THF (30 mL) by applying ultrasonic waves for 10 min. To this mixture, toluene (300 mL) containing diethoxydimethylsilane (18.9 g, 0.128 mol) was added. The toluene solution was gradually heated up to 112 °C; at that temperature it was allowed to reflux for 96 h. Evaporation of the solvents gave coupling polymer **2**. The reaction scheme is shown in Eq. 2.

The molecular weight of **2** was calculated based on the assumption that the hydroxyl hydrogen atoms on **1** were completely replaced by the ethoxydimethylsilyl groups [–$SiMe_2$(OEt)], as shown in Eq. 2.

Modification of Silica with Coupling Polymer 2. The reaction was carried out according to the reported procedure (see Eq. 3; HO–SiO_2 represents the silanol group on silica surface).[1)] The reaction scheme is shown in Eq. 3.

$$\text{P-CH}_2\text{OSiMe}_2\text{(OEt)} + \text{HO–SiO}_2 \rightarrow \text{P-CH}_2\text{OSiMe}_2\text{O–SiO}_2 + \text{EtOH} \quad (3)$$

Examination of Redispersibility. The redispersibility was examined according to the reported method.[1)] If necessary, ultrasonic wave irradiation was applied to the sample for 10 min.

Removal of Unreacted Coupling Polymer 2 (Free Polymer 2). Centrifugation (10000 rpm for 30 min) was applied to redispersible DME–silica sol (5 g) for 30 min and an upper layer was removed. To the residue, DME (5 g) was added and centrifugation was again applied to separate any settled product. This operation was effective for the complete removal of free polymer **2**. The thus-obtained residue was redispersible into the original dispersant, DME.

Determination of the Size of Modified Silica Particles. The particle size was determined by the QELS method on Dynamic Light Scattering Analyzer (Otsuka Electronics, Photal DLZA-700).

References

1) Redispersible Organosilica Sol. II. Preceding paper, Part I: T. Kito, M. Yamaye, K. Yoshinaga, M. Yoshimoto, M. Komatsu, and H. Nishida, *Ind. Eng. Chem. Res.*, **31**, 213 (1992).

2) T. Saegusa, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **34**, 804 (1993).

3) Y. Chujo, *Sinsozai*, **3**, 68 (1992).

4) B. M. Novak, *Adv. Mater.*, **5**, 422 (1993).

5) G. L. Wilkes, A. B. Brennan, H. -H. Huang, D. Rodrigues, and B. Wang, *Mater. Res. Soc. Symp. Proc.*, **171**, 15 (1990).

6) K. Mitsuishi, *Hyomen*, **28**, 49 (1990).

7) N. Tsubokawa, *Shikizai Kyokaishi*, **65**, 72 (1992); *Hyomen*, **28**, 286 (1990).

8) A. Krysztafkiewicz, *Surf. Coat. Technol.*, **35**, 151 (1988).

9) S. Kitahara, *Hyomen*, **30**, 664 (1992).

10) H. Yoshioka, *Shikizai Kyokaishi*, **59**, 176 (1986).

11) N. Tsubokawa, *Hyomen*, **30**, 303 (1992); *Shinsozai*, **3**, 34 (1992); *Polym. Digest*, **1990**, 2.

12) B. D. Favis, L. P. Blanchard, J. Leonard, and R. E. Prud'homme, *Polym. Composites*, **5**, 11 (1984).

13) Y. Chujo, E. Ihara, H. Ihara, and T. Saegusa, *Macromolecules*, **22**, 2040 (1989).

14) A. Takahashi, *Shikizai Kyokaishi*, **59**, 168 (1986); *Hyomen*, **23**, 158 (1985).

15) A. Takahashi, *Kobunshi Kako*, **32**, 448 (1985).

16) J. B. Donnett, G. Riess, and C. Majowski, *Eur. Polym. J*, **7**, 1065 (1971).

17) K. Ohkita, *Polym. Digest*, **1993**, 2.

18) N. Tsubokawa and S. Handa, *Shikizai Kyokaishi*, **66**, 468 (1993), and preceeding papers.

19) H. Utsugi, *Hyomen*, **16**, 525 (1978).

20) K. Yoshinaga, T. Yokoyama, and T. Kito, *Polym. Adv. Technol.*, **4**, 38 (1993); K. Yoshinaga, K. Nakanishi, K. Nagao, and T. Kito, *Kobunshi Ronbunshu*, **50**, 303 (1993).

21) P. Auroy, L. Auvray, and L. Leger, *J. Colloid Interface Sci.*, **150**, 187 (1992).

22) T. Kito, K. Yoshinaga, N. Hatanaka, E. Emoto, and M. Yamaye, *Macromolecules*, **18**, 846 (1985).

23) T. Sato, *Shikizai Kyokaishi*, **59**, 682 (1986); **61**, 346 (1988).

24) R. I. Feigin and D. H. Napper, *J. Colloid Interface Sci.*, **75**, 525 (1980).