

Cationic Graft-Polymerization of 2-Methyl-2-oxazoline on Monodispersed Polymer-Coated Ultrafine Silica Particles

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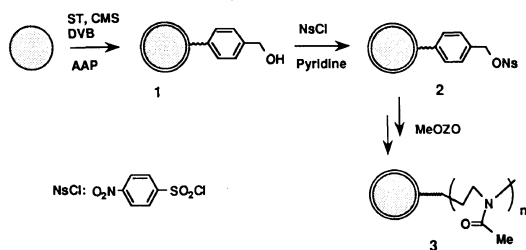
ABSTRACT: Cationic graft-polymerizations of 2-methyl-2-oxazoline on *p*-nitrobenzenesulfonate group-introduced silica composite particles, prepared by polymer coating of monodispersed colloidal silica of 470 nm in diameter, were studied. Ring-opening polymerization of the oxazoline was observed to take place on poly(styrene)-coated silica particles, derived from radical copolymerization of styrene, hydroxymethylstyrene and divinylbenzene, but most grafted polymer chains were dragged out for lack of cross-linking in the copolymer layer. The polymerization of the oxazoline on the composite surface, made from poly(maleic anhydride-styrene)-modified silica particles, led to the grafting of oligomer chains of octamer or nanomer, which were terminated by reaction with water molecules inside the particles.

KEY WORDS Graft Polymerization / Ultrafine Particles / Monodispersed Colloidal Silica / Cationic Polymerization / Polymer Modification / Polyoxazoline /

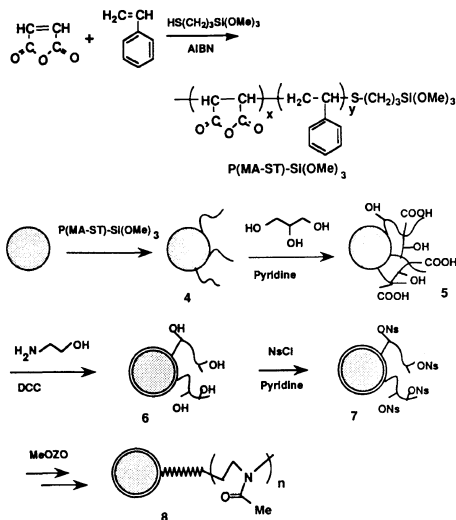
Monodispersed inorganic colloidal ultrafine particles are lately of interest for application to new functional materials, because of controllable size and spherical shape.^{1,2} We have been developing composite materials exhibiting specific functionality from polymer-modified colloidal silica particles. One goal is control of ordered structure in a polymer matrix or construction of reversible sol-gel systems, composed of unimodal colloidal particles, through surface hydrophobic or electrostatic interactions. Hence, surface polymer-coating of colloidal particles and introduction of hydrophobicity or electric charges are markedly significant processes. In our previous work, we reported effective polymer-coating on colloidal silica particles by use of polymer silane coupling agents^{3,4} and radical polymerizations^{5,6} without particles aggregation. Functional groups of amino, carboxyl,^{7,8} and hydroxyl⁹ were efficiently introduced on the composite surface.

To design elaborate materials from ultrafine composite, control of polymer chains grafted on the silica particles is sometimes required. In this regard, there are some reports on ionic polymerizations on inorganic surface.¹⁰⁻¹² Most of them were conducted by the introduction of active functional groups, which can form the cationic or anionic species, to propagate polymer chains. Colloidal particles, however, have generally adsorbed water molecules on the surface, participating in the stabilization of colloidal systems, so that the active electrophilic or nucleophilic group, being able to initiate the anionic or cationic polymerization, is impossible to introduce directly. Therefore, our strategy for graft-polymerization on colloidal silica particles is first the polymer-coating of the particles surface to prevent aggregation, and successive functionalization of the polymer layer to start the ionic polymerization.

This paper describes the introduction of



Scheme 1.



Scheme 2.

p-nitrobenzenesulfonate (NsO) group on the polymer-modified colloidal silica particles, prepared by radical copolymerization of styrene (ST), hydroxymethylstyrene (HMS), and divinylbenzene (DVB) (Scheme 1) and by coupling reactions with trimethoxysilane-terminated poly(maleic anhydride-styrene) (P(MA-ST)-Si(OMe)₃) (Scheme 2), followed by cationic ring-opening polymerization of 2-methyl-2-oxazoline (MeOZO).

EXPERIMENTAL

Materials

Monodispersed colloidal silica (SiO₂, 23 wt%) suspended in ethanol (EtOH), of mean diameter of 470 nm, was offered by Catalysts & Chemicals Co., Ltd. MeOZO was purchased

from Aldrich Chemical Co., Inc. and distilled on KOH before use. HMS was synthesized from chloromethylstyrene, composed of *m*- and *p*-isomers, by the literature method.¹³ ST and DVB were purified by distillation. Nitromethane, acetonitrile and chloroform were distilled over CaH₂. 3-Mercaptopropyl-trimethoxysilane was purchased from Chisso Co., Ltd.

Measurements

Spectrophotometric absorbance was measured by a JASCO-V520S. Infrared spectra were recorded with a diffuse reflectance method on a JEOL-JIR5500. Scanning electron micrographs (SEM) were taken by a JEOL-JCX733, and particle size distributions were measured by a Ohtsuka DLS700. Thermal gravimetric analyses were carried out by a gel permeation chromatography on TSK gel 3000H with a tetrahydrofuran (THF) eluent, based on calibration with poly(styrene) standards.

Preparation of Composite 1

To an ethanolic colloidal silica solution (40 ml), containing 1.15 g of SiO₂, were added 4 ml ST, 1 ml HMS and 0.11 ml DVB. After the addition of 40 mg 2,2'-azobis(2-amidino-propane) dihydrochloride (AAP), the mixture was stirred at 60°C for 5 h. Centrifugation of suspension, diluted with a mixture of ethylene glycol (8 ml) and EtOH (2 ml), separated the composite from copolymer particles. Washing with EtOH and drying of the paste under reduced pressure gave 1.61 g of composite 1. IR (KBr) 3500–3200 (O–H), 1606, 1493 and 1452 (phenyl), and 1130 cm⁻¹ (Si–O).

Reaction of Composite 1 with *p*-Nitrobenzenesulfonyl Chloride (NsCl)

A suspension containing 1.6 g composite 1 in dry pyridine (40 ml) was gently stirred with 0.64 g NsCl at a room temperature for 3 days. Centrifugation in chloroform, washing with diethyl ether and following drying under reduced pressure gave 1.37 g of colorless

composite **2**. IR (KBr) 3000—2850 (C—H), 1603, 1493 and 1452 (phenyl), 1525 and 1350 (NO₂), and 1130 cm⁻¹ (Si—O).

Preparation of Trimethoxysilane-Terminated Poly(maleic Anhydride-styrene) (P(MA-ST)-Si(OMe)₃)

A mixture of 6.0 g MA, 7.5 g ST, 0.4 g 3-mercaptopropyltrimethoxysilane, and 22 mg 2,2'-azobis(isobutyronitrile) (AIBN) in 10 ml THF was stirred under refluxing in nitrogen atmosphere for 2.5 h. The resulting solution was poured into diethyl ether to precipitate the crude polymer. Precipitation from acetone solution with diethyl ether and drying under reduced pressure gave 12.8 g P(MA-ST)-Si(OMe)₃, *M_n* of which was 6000. IR (KBr) 1857 and 1780 (maleic anhydride C=O), 1602, 1494 and 1454 (phenyl), 1222 and 924 cm⁻¹ (methoxy C—O); ¹H NMR ((CD₃)₃SO) δ 2.41 (s, CH₂), 2.82 (s, CH), 3.50 (s, Si(OCH₃)₃), 3.68 (s, COCHCHCO), and 7.84—7.26 (broad, phenyl).

Reaction of Colloidal Silica with P(MA-ST)-Si(OMe)₃

To 100 ml 1,2-dimethoxyethane (DME) containing 0.6 g P(MA-ST)-Si(OMe)₃ were added 10 ml ethanolic silica colloid. The suspension was refluxed in a 200 ml flask with a distilling trap to remove water and EtOH azeotropically, until eluent temperature attained the boiling temperature of DME. Separation from unreacted polymer by a centrifugation with acetone four times and drying under reduced pressure gave 0.55 g composite **4**, binding the polymer of 46.9 mg g⁻¹. IR (KBr) 1859 and 1780 (maleic anhydride C=O), 1494 and 1454 (phenyl), and 1132 cm⁻¹ (Si—O).

Reaction of Composite 4 with Glycerol

A suspension of 0.3 g composite **4**, attached polymer of 46.9 mg g⁻¹, in 30 ml chloroform solution containing 0.02 g glycerol and 0.3 ml dry pyridine was stirred under refluxing for

24 h. Centrifugation with 50 ml acetone three times and with 10 ml methanol (MeOH), and drying under reduced pressure gave 0.92 g composite **5** attaching a polymer component of 58.6 mg g⁻¹. IR (KBr) 1733 and 1722 (ester and carboxyl C=O), 1494 and 1454 (phenyl), and 1132 cm⁻¹ (Si—O).

Reaction of Composite 5 with 2-Aminoethanol

The suspension of 0.48 g composite **5** in 10 ml chloroform was stirred with 0.1 ml 2-aminoethanol and 50 mg *N,N'*-dicyclohexylcarbodiimide at a room temperature overnight. Washing with 20 ml chloroform three times and 10 ml MeOH by a centrifugation and drying under reduced pressure gave 0.47 g composite **6** containing a polymer component of 59.8 mg g⁻¹. IR (KBr) 1724—1714 (C=O), 1653—1640 (NC=O), 1495 and 1454 (phenyl), and 1132 cm⁻¹ (Si—O).

Reaction of Composite 6 with NsCl

The reaction was carried out in the same manner as for preparing composite **2**. Anal. of composite **7**; IR (KBr) 1736—1728 (C=O), 1648—1640 (NC=O), 1537 (NO₂), 1495 and 1454 (phenyl), and 1132 cm⁻¹ (Si—O).

Polymerization of MeOZO on Composite 2 or 7

A typical run was as follows. To a suspension of 50 mg composite **2** in 2 ml CH₃NO₂ were added 2 ml MeOZO, and the mixture was stirred under nitrogen atmosphere at 80°C for 48 h. After adding 0.5 ml water to terminate the polymerization, the suspension was agitated for 2 h. Centrifugation and washing with 5 ml EtOH three times and drying under reduced pressure gave 42.3 mg of composite **3**. IR (KBr) 3300—3200 (O—H), 1648—1639 (NC=O), 1603, 1495 and 1454 (phenyl), and 1130 cm⁻¹ (Si—O).

Determination of Polymer Attached to Silica Particles

The amount of polymer bound on silica particles, as weight of polymer per unit gram

of SiO₂, was determined by weight loss (mg) during temperature elevation from 100 to 1000°C, after keeping the sample at 100°C for 30 min, as follows:

$$\text{Attached polymer (mg g}^{-1}\text{)} \\ = \frac{RW_1 - RW_2}{SW_1 - (RW_1 - RW_2)}$$

Where RW_1 and RW_2 are weight reduction of the polymer-modified and unmodified silica on thermal gravimetry, respectively, and SW_1 is the amount of sample.

Determination of Surface Concentration of *p*-Nitrobenzenesulfonate (NsO) Group

A suspension of composite **2** or **7** (10 mg) dispersed in 5 ml 0.1 N KOH was stirred at 70°C for 3 h. The solution was separated from the particles by centrifugation and diluted with distilled water to 10.0 ml. The concentration of NsO species in the solution was spectrophotometrically determined by the absorption at 264 nm, based on the extinction coefficient (ϵ) 10,170 of NsO⁻ anion.

Preparation of Sample for SEM Measurement

A drop of the suspension of 0.5 mg composite in 3 ml EtOH was put on a coverglass (18 × 18 mm) and the plate was dried at 110°C under vacuum for 24 h.

RESULTS AND DISCUSSION

Preparation of Poly(styrene)-Coated Particles Possessing Surface NsO Group

Preparation of composite **2** was carried out via the copolymerization of ST, HMS, and DVB initiated by AAP in ethanolic silica colloid and esterification with NsCl. To prepare homogeneous polymer-coated silica particles of composite **1**, optimization in the copolymerization was required, because in many cases polymerization was accompanied by the formation of various size of polymer particles.⁹ Amounts of bound polymer on the silica particles increased with DVB mole fraction

(Table I), but polymerization in the presence of over 9.8 vol% DVB led to precipitation of the copolymer and silica. Particle size distributions of the composite **1** in Run 1 and 2 in Table I showed mean size to shift from 470 nm of the original size to 760 nm.

Therefore, it is suggested that the polymer coating by copolymerization of ST, HMS, and SVB gives rise to partial aggregation among particles. Increment of the HMS fraction in the polymerization system resulted in increase of surface hydroxyl group (Run 2 in Table I). However, considerable reduction of attached polymer was observed to take place during the reaction of composite **2** with NsCl in the presence of pyridine. Probably, noncross-linked polymer chains fell into the reaction mixture. A SEM image and particles size distribution of the composite **2** shows that the copolymerization gave relatively homogeneous coating of the silica particles, but also that aggregation occurred (Figure 1). Reaction of alcohol with NsCl in pyridine sometimes produces pyridinium compound along with the sulfonate.¹⁴ In the present case, composite **2** was colorless, so that surface concentration of NsO⁻ group, a counter anion of pyridinium compound, seems very low.

Graft-Polymerization of MeOZO on Composite **2**

The NsO or *p*-toluenesulfonate (TsO) group reacts with oxazolines to form oxazolinium ions, which initiate the ring-opening polymerization of 2-alkyl-2-oxazoline in polar solvent,^{15,16} as shown in eq 1. In this case, the group turned into a counter anion of NsO⁻ or TsO⁻ in polymerization.

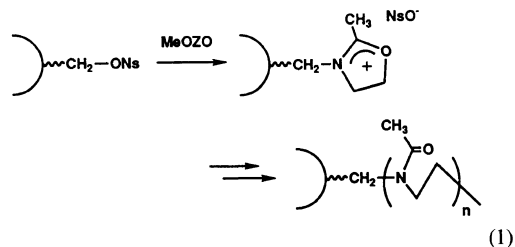


Table I. Preparation of P(ST-HMS)-coated silica particles and introduction of surface NsO group^a

Run	ST	HMS ml	DVB	Yield ^b g	A.P. ^c /mg g ⁻¹		Surface NsO group × 10 ⁴ /mol g ⁻¹
					1	2	
1	4.5	0.5	1.0	1.53	237.6	187.6	1.88
2	4.0	1.0	1.0	1.52	404.5	333.3	2.36
3	4.0	1.0	5.0	1.92	446.6	408.5	—
4	4.0	1.0	10.0	1.61	579.8	531.4	—

^a Polymerizations were carried out in ethanolic silica colloid solution containing 1.15 g of SiO₂.

^b Yield of composite 1, polymer and silica.

^c Amount of attached polymer.

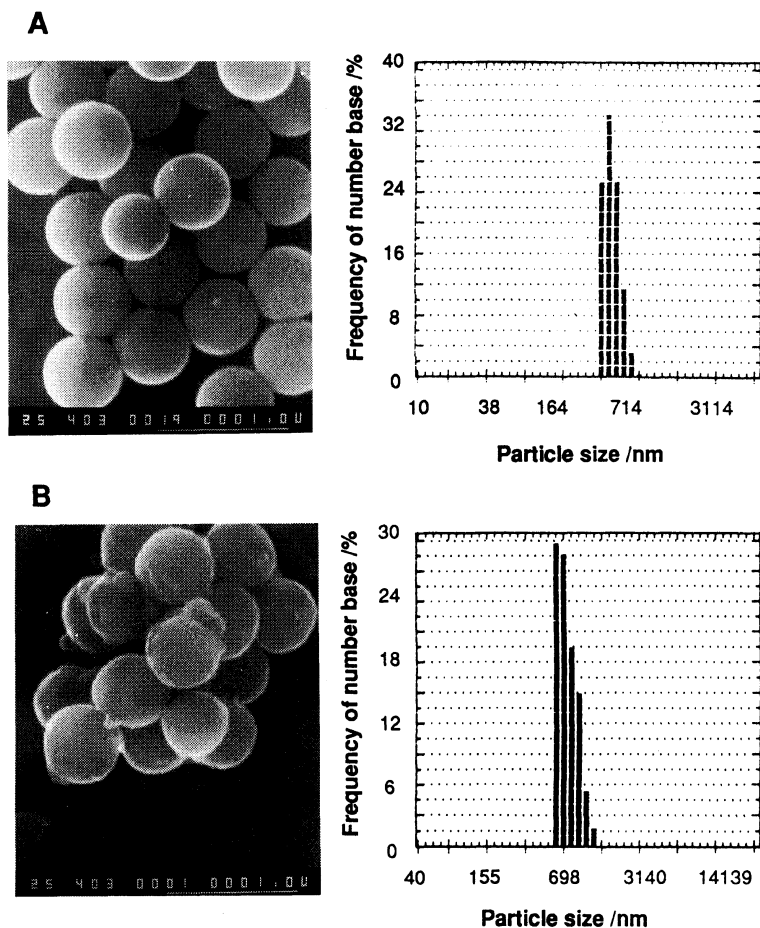


Figure 1. SEM images and particles size distributions of colloidal silica (A) and composite 2 (B). Scale bars on the bottom of photographs represent 1000 nm.

When MeOZO was added to composite 2 in a polar solvent, such as CH₃NO₂, at 60–80°C, the solution turned pale yellow, showing the formation of NsO⁻ and initiation of the

polymerization of MeOZO on composite 2. As can be seen in Figure 2, absorption bands at 1525 and 1349 cm⁻¹ on an IR spectrum of composite 2, assignable to respective asym-

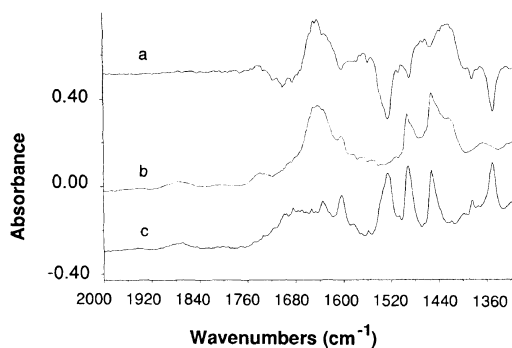


Figure 2. A difference FT-IR spectrum (a) between a spectrum (b) of composite 3 and that (c) of composite 2. The subtraction was done to offset absorption bands, assignable to combination vibrations of the SiO₂ lattice, at 1900–1840 cm⁻¹ on the spectrum of composite 3 by the bands on that of composite 2.

Table II. Ring-opening polymerization of MeOZO on composite 2^a

Solvent	Temp	Time	A.P.	Δ A.P. ^b
	°C	h	mg g ⁻¹	mg g ⁻¹
CH ₃ NO ₂	63	168	333.3	0.0
	80	5	340.5	+4.0
	80	168	331.6	-1.0
CH ₃ CN	Reflux	48	314.1	-8.1
CH ₂ ClCH ₂ Cl	Reflux	48	303.8	-17.3
THF	Reflux	48	293.7	-23.5

^a Polymerizations were carried out using 2 ml MeOZO and 2 ml solvent with 50 mg composite 2, surface NsO group of which was 2.36×10^{-4} mol g⁻¹.

^b Increment of attached polymer after the polymerization.

metric and symmetric stretching vibrations of NO₂ group, disappeared on the spectrum of composite 3. In most cases, the amounts of polymer bound on composite 2 unexpectedly and distinctly decreased during polymerization (Table II). Poly(2-methyl-2-oxazoline) (P(MeOZO)) chains on the surface of composite 3 were confirmed by observation of characteristic IR absorption bands at 1680–1640 cm⁻¹, assignable to amido C=O bond stretching vibration, and bands at around 1400 cm⁻¹, assignable to C–H bond bendings

of methyl and methylene, in the subtraction spectrum of composite 3 from that of composite 2 (Figure 2).

Evaporation of the solution separated from the polymerization mixture gave the copolymer of MeOZO, ST, and HMS, identified by observation of the characteristic absorption bands of P(MeOZO) at 1660–1625 cm⁻¹, assigned to the stretching vibration of amido C=O bond, and bands of poly(styrene-hydroxymethylstyrene) (P(ST-HMS)) at 1602, 1504 and 1450 cm⁻¹, assigned to stretching vibrations of phenyl C=C bonds. These results suggest that grafting of P(MeOZO) chains to P(ST-HMS) network proceeds on a composite surface, and that graft-copolymer chains noncross-linked are dragged out into the reaction solution during polymerization. This probably stems from the low extent of cross-linking in the polymer layer on the composite 2. As shown above, however, increasing DVB fraction in the preparation of composite 2 led to the formation of polymer particles, and it consequently seems difficult to make homogeneous grafting of P(MeOZO) to P(ST-HMA)-coated silica particles.

Preparation of Poly(MA-ST)-Modified Silica Particles with Surface NsO Group

To overcome shortcomings in the preparation of P(ST-HMS)-coated silica particles by radical polymerization, we developed a polymer modification of colloidal silica with P(MA-ST)-Si(OMe)₃, and introduction of carboxyl and hydroxyl groups and simultaneous cross-linking of the polymer layer by reactions with diols or triols.⁸

The reaction of colloidal silica with P(MA-ST)-Si(OMe)₃ at 60–80°C in THF or DME gave low polymer attachment less than 1.0 wt% on the silica surface. Probably, the low extent of surface modification arises from low affinity between hydrophilic silica surface and the hydrophobic polymer coupler. Since surface hydrophobicity is possibly due to high polarity of adsorbed EtOH and water, contributing to

stability of the colloidal system through hydrogen-bonding, removal of the bound molecules hindering silanol groups is expected to enhance the coupling reaction. Hence, ethanol and water from the reaction mixture were azeotropically removed with DME or dioxane during the reaction to lower the polarity around silica particle surface. This resulted in increase bound polymer to give an amount in the range of 50–60 mg g⁻¹, or about five times much than those in the reaction in THF or DME. The polymer-modified silica particles, dried solvent up, were redispersible in EtOH by ultrasonic irradiation. SEM micrographs and particle size distributions of redispersed composite also showed to be the same size as that of the original particles.

Cross-linkings in polymer layer on the composite **4** were carried out by esterification of surface MA moiety with glycerol. Bridging among bound P(MA-ST) chains was supported by distinct increase of attached polymer, *e.g.* from 50.9 mg g⁻¹ of composite **4** to 55.7 mg g⁻¹ of composite **5**, and disappearance of IR absorption bands at 1867 and 1780 cm⁻¹, assigned to asymmetric and symmetric stretching vibrations of anhydride carbonyl group, respectively. Although immersion of the non-cross-linked composite in pH 4 aqueous acetone solution brought about weight loss of over 60 wt% of the bound polymer, acid treatment of composite **5** led to 20–25 wt% decrease of attached polymer. It is therefore suggested that the polymer layer is partially cross-linked. In this case, incomplete bridging among bound P(MA-ST) chains is accompanied by the formation of hydroxyl groups. As shown in Scheme 2, the reaction of composite **4** with glycerol also gives cross-linking and simultaneous formation of carboxyl group. Thus, to make the surface concentration of NsO group on composite **7** high, conversion of carboxyl group on composite **6** to hydroxyl group was conducted by condensation of the group with 2-aminoethanol using *N,N'*-dicyclohexylcarbodiimide. For instance, the

reaction afforded increase of hydroxyl groups from 3.05 × 10⁻⁵ mol g⁻¹ on the composite **5** to 3.42 × 10⁻⁵ mol g⁻¹ on the composite **6**.

The reaction of composite **6** with NsCl in the presence of pyridine gave colorless composite **7** having a surface NsO concentration in the range of 2.4 × 10⁻⁵ to 3.4 × 10⁻⁵ mol g⁻¹, which corresponds to 2.7–3.8 groups/nm², or one tenth that on composite **2**. Composite **7** showed monodispersion, retained particles size and distribution of the original silica during coupling, cross-linking and esterification reactions, and redispersibility in organic solvents, such as EtOH.

Graft-polymerization of MeOZO on Composite **7**

The ring-opening polymerization of MeOZO on composite **7** in CH₃CN, CH₃NO₂ or CHCl₃ at 80–85°C resulted in obvious weight increase of attached polymer in the range of 6.6–9.5 mg g⁻¹ (Table III), the polymer chain of which corresponds to tetramer or pentamer of MeOZO, estimated by increment of attached polymer. Grafting of P(MeOZO) was observed by the appearance of characteristic absorption bands at 1650–1638 cm⁻¹ on a subtraction IR spectrum of composite **2** from that of composite **3** in Figure 3. However, the polymer grafted on composite **8** did not increase with prolonged reaction time. From the fact that

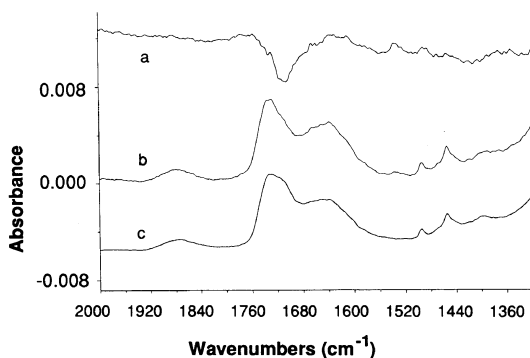


Figure 3. A difference FT-IR spectrum (a) between a spectrum (b) of composite **8** and that (c) of composite **7**. The offset was carried out by the same manner as in Figure 2.

Table III. Ring-opening polymerization of MeOZO on composite 7

7	MeOZO	Solvent	Temp	Time	8	
mg	ml	ml	°C	h	A.P./mg g ⁻¹	ΔA.P./mg g ⁻¹
130 (53.9, 3.2 × 10 ⁻⁵) ^a	4	CH ₃ NO ₂ (4)	85	13	62.4	+8.5
			85	24	62.6	+8.7
			85	38	63.9	+10.0
			85	61	63.4	+9.5
130 (53.9, 3.2 × 10 ⁻⁵) ^a	4	CH ₃ CN(4)	85	24	62.5	+8.6
			200 (56.5, 2.4 × 10 ⁻⁵) ^a	3	CHCl ₃ (3)	80
20 ^b (41.0, 3.0 × 10 ⁻⁵) ^a	1	CH ₃ NO ₂ (1)	80	48	50.1	+9.1
	1	CH ₃ CN(1)	80	48	47.6	+6.6

^a Values in parentheses are amounts of attached polymer (mg g⁻¹) and surface NsO group (mol g⁻¹), respectively.

^b Treated with trimethylchlorosilane.

Table IV. Effects of evacuation temperature on the ring-opening polymerization of MeOZO on composite 7^a

7				8	
Drying temp	A.P.	Concentration of NsO	λ _{max} ^b	A.P.	ΔA.P.
°C	mg g ⁻¹	× 10 ⁵ /mol g ⁻¹	nm	mg g ⁻¹	mg g ⁻¹
110	71.8	2.28	264	77.7	+5.9
130	57.3	2.46	264	75.9	+18.6
150	52.4	2.50	264	70.6	+18.2
190	37.7	2.99	264	58.4	+20.7
210	35.6	2.89	259	55.1	+19.5

^a Polymerizations were carried out employing 50 mg composite 7, 2 ml MeOZO in 2 ml CH₃CN at 80°C for 24 h.

^b λ_{max} of spectrophotometric absorption band of the aqueous solution (10 ml) obtained by alkali hydrolysis of composite 7.

the reaction mixture turned pale yellow on mixing the composite 7 with MeOZO, it was confirmed that NsO⁻ ion was produced to initiate cationic polymerization on the surface. Thus, the polymerization seems to be terminated at an initial stage. One of the causes for the termination is considered the reaction of oxazolinium cation shown in eq 1, with surface hydroxyl groups, which do not participate in nosylation. However, surface silylation of residual hydroxyl group on composite 7 with trimethylchlorosilane in triethylamine-chloroform solution did not give obvious increase of grafting polymer in the polymerization in

CH₃CN or CH₃NO₂ (lines 7 and 8 in Table III). Therefore, the influence of hydroxyl groups on terminating the polymerization seems to be negligible. A shoulder absorption band at 1740—1710 cm⁻¹ in an IR spectrum of composite 7, assignable to associated carboxyl groups, was observed to disappear on the spectrum of composite 8. These results also suggest that one plausible cause for the termination is nucleophilic attack of the free carboxyl group on the oxazolinium species.

Another cause is nucleophilic attack of adsorbed water molecules, being unable to remove by drying at 110°C under reduced

pressure, on the growing cationic species. We therefore examined the effects of evacuation temperature of composite 7 under the reduced pressure less than 1 mmHg on grafting P(MeOZO) on composite 8.

Regarding the thermal stability of composite 7, elevation of the evacuation temperature brought about decrease of attached polymer (Table IV). The weight loss possibly involves release of adsorbed and/or absorbed water and dehydration from polymer layer on the composite 7. As seen in Figure 4, elevation of

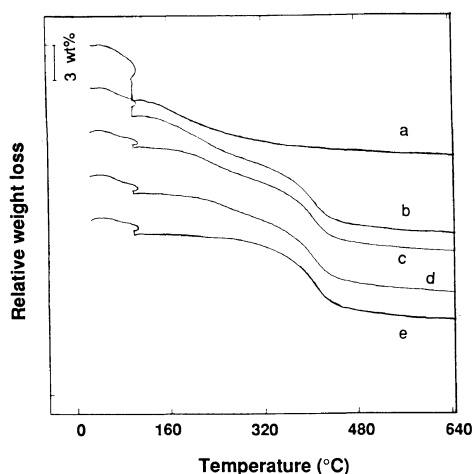


Figure 4. Thermal gravimetric analysis of silica gel (a), obtained by evaporation of silica colloid, and composite 7 evacuated at 110°C (b), 130°C (c), 150°C (d), and 210°C (e) under 1 mmHg for 24 h.

drying temperature gave rise to considerable removal of volatile compounds on composite 7 during elevation of temperature from 100 to 300°C with the thermal gravimetry. The IR spectrum of composite 7 dried over 150°C definitely showed the reformation of the acid anhydride moiety by appearance of absorption bands at 1860 and 1780 cm^{-1} due to C=O stretching vibrations (Figure 5). The surface NsO concentration apparently increased with evacuation temperature, but the solutions obtained by alkali hydrolysis of the composite 7 evacuated below 190°C showed maximum absorption bands at 264 nm, based on $\pi \rightarrow \pi^*$ transition of NsO^- . The solution derived from composite 7 dried at 210°C gave a maximum

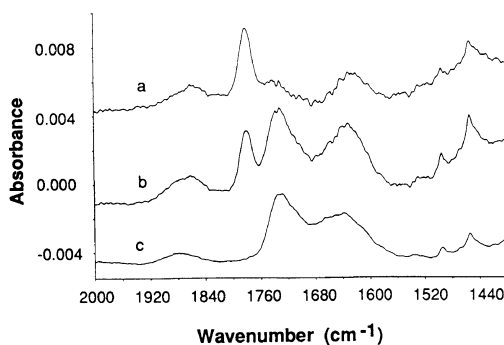


Figure 5. A difference FT-IR spectrum (a) between a spectrum (b) of composite 8, prepared by polymerization on composite 7 evacuated at 150°C, and that (c) of composite 7.

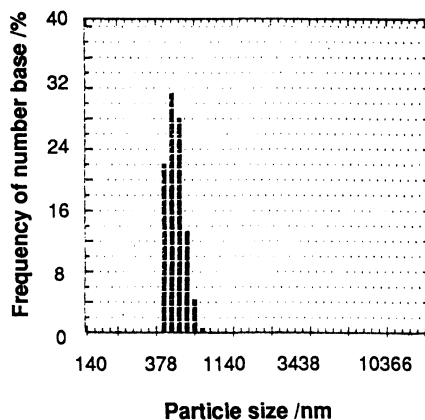
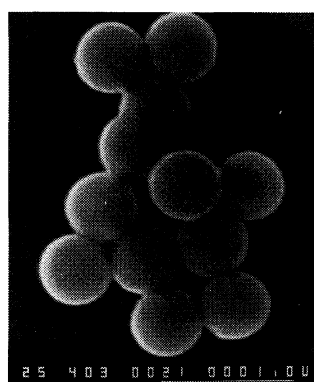


Figure 6. A SEM image and particle size distribution of composite 8. Scale bar, the same as in Figure 1.

peak at 259 nm (Table IV). This result shows that heating at 210°C partially decomposes the polymer layer.

Elevating the evacuation temperature afforded increased bound polymer in the range of 18.2 mg g⁻¹ to 20.7 mg g⁻¹, corresponding to the oligomer of the octamer or nanomer of MeOZO. The amounts of the grafted-polymer are two or three fold higher than those in the polymerization on composite 7 dried at 110°C (Table IV). In these cases, polymerizations were terminated at relatively early stages. One reason for the termination is probably water molecules, inside the silica particles. Thermal gravimetric analysis of unmodified silica gel in Figure 4, obtained by evaporation of the ethanolic silica colloid solution, showed components to be volatile even over 200°C. Adsorbed water molecules remain on silica gel dried under vacuum even over 200°C.¹⁷ Hence, water molecules inside the particles probably exude into the reaction system and affect the ring-opening polymerization of MeOZO on composite 7.

A SEM photograph and particle size distribution showed that composite 8, derived from composite 7 evacuated at 150°C, had the same particle size and distribution as those of the original colloidal silica (Figure 6).

CONCLUSIONS

1. The *p*-nitrobenzenesulfonate group on cross-linked poly(styrene)-coated silica particles, prepared by radical polymerization, initiated the ring-opening polymerization of 2-methyl-2-oxazoline, but the grafted polymer chains were dragged out into the reaction mixture, because of lack of cross-linking in coating poly(styrene) layer.

2. Graft-polymerization on monodispersed

polymer-modified silica particles, made by reaction of surface silanol with trimethoxysilyl-terminated poly(maleic anhydride-styrene) coupling agent, caused attachment of poly(2-methyl-2-oxazoline) oligomer chains of octamer or nanomer. The polymerization did not proceed in the propagation, because of termination with water molecules inside the particles.

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