Reaction of Methyl Thioglycolate with Chloromethylstyrene Microgel: Preparation of Core–Shell-Type Microgel by Chemical Modification

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Received 14 March 1997; accepted 22 January 1998

ABSTRACT: A uniform spherical polychloromethylstyrene (PCMS) microgel whose average diameter was 2.3 μm was prepared by dispersion copolymerization of chloromethylstyrene and divinylbenzene in ethanol–DMSO (25/3 v/v) in the presence of polyvinylpyrrolidinone. When the PCMS microgel was treated with an excess amount of methyl thioglycolate (MTG) in the presence of 1,8-diazabicylco[5.4.0]undec-7-ene (DBU) at room temperature in THF for 4 h, sulfenylated microgel was obtained. The introduction ratio of MTG corresponded well to the amount of DBU used. A transmission electron microscope (TEM) photograph and thermal analysis of the PCMS microgel partially modified by MTG showed that it had a core–shell structure, that is, an MTG-modified shell and an unchanged core. Since the reaction of the chloromethyl group and MTG was a diffusion-limited one, MTG was introduced into the PCMS microgel from the outer side layer by layer. The PCMS microgel in which 52% of the MTG was introduced was treated with an excess amount of pyridine in DMAc at 50°C for 48 h followed by acid-catalyzed hydrolysis in dioxane–water at 80°C for 48 h to give a zwitterionic microgel that formed a stable suspension. J Appl Polym Sci 69: 1863–1873, 1998

Key words: chloromethylstyrene; microgel; dispersion polymerization; polymer reaction; methyl thioglycolate; sulfenylation; pyridinium salt; hydrolysis; zwitterionic microgel

INTRODUCTION

Recently, various functional microspheres have been prepared and their applications have been extensively studied in various fields.[1–3] Especially, crosslinked polymeric microspheres, that is, microgels, have been paid much attention because they maintained an internal structure under various conditions. Functional groups can be introduced into a microgel by either the use of functional monomers or functionalization by a polymer reaction. Since the polymer reaction method can be accessible for various functional groups, a reactive microgel is important to obtain various functional microgels.

As the reactive polymers, polychloromethylstyrene (PCMS) is one of the most accessible and reactive ones.[4–6] Although many applications of PCMS have been reported, there have been only a few reports on the preparation and application of microgels consisting of PCMS.[7–15] One of the reasons may be hydrolysis of the chloromethyl group during the preparation of the PCMS microgel in water. However, since Margel et al. reported the dispersion polymerization of chloromethylstyrene in a methanol–DMSO mixture,[13] a pure PCMS microsphere can be used extensively.

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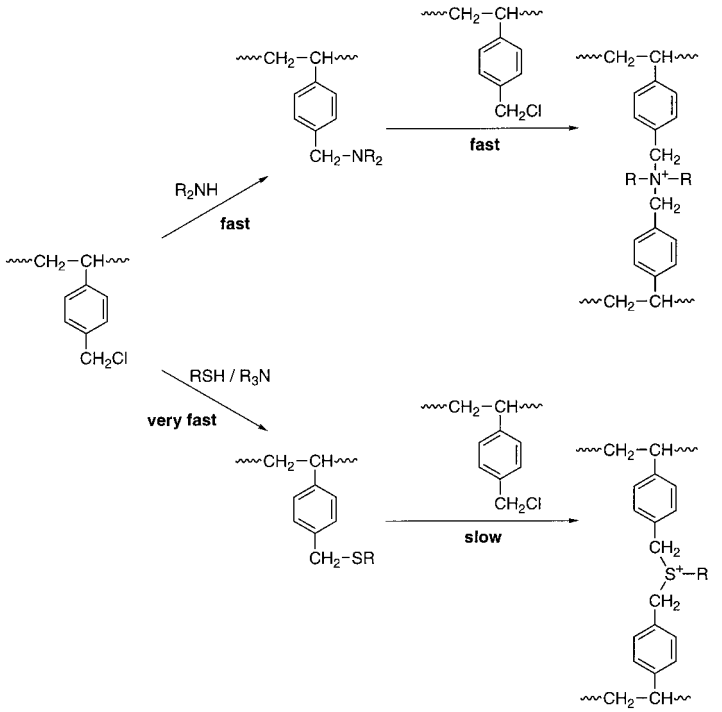
Journal of Applied Polymer Science, Vol. 69, 1863–1873 (1998)
 CCC 0021-8995/98/091863-11



Scheme 1

Conventionally, functional groups have been introduced into the PCMS microgel using the reaction with functional amines. Since alkylation of primary and secondary amines usually affords polyalkylated amines simultaneously, however, the structure and the functionality of PCMS microgels modified with amines are generally ambiguous. Although polyalkylation is negligible when a tertialy amine is used as a modifier, only the ionic microgels are obtained.

Based on these considerations, we have been prompted to use a thiol as a modifier of the PCMS microgel (Scheme 1). The alkylation of a thiol in the presence of a base proceeds quantitatively to afford a sulfide selectively under the very mild condition.[16] Thus, various functional microgels with a clear structure and functionality are expected to be obtained from the PCMS microgel by the reaction with functional thiols, although modification of the PCMS microgel by a sulfur nucleophile has been scarcely reported to our knowledge.[7]

Further, we have paid attention to the fact that the alkylation of the thiolate anion is very fast.[16] If the reaction of the thiolate anion with PCMS is a diffusion-limited one, it is expected that thiol would react from the outer side layer by layer, resulting in the formation of a core–shell-type microgel. To demonstrate the versatility of the thiol-modified PCMS microgel, the internal structure of the thus modified microgel should be examined because the internal structure of the microgel is the essential factor for its physical properties.[1–3] To construct the core–shell structure in the microgel, optimization of the reaction of PCMS with thiol is necessary. Although the reaction of alkyl halide with thiol is well established, the optimum condition that is suitable for a polymer reaction has not been established.

As a functional thiol, we selected methyl thioglycolate (MTG), which has a further functionalizable ester group. In this article, we report the optimum condition for the modification of PCMS with thiol and the structure of the MTG-modified PCMS microgel. Further, the derivation of an MTG-modified microgel to a zwitterionic microgel is also demonstrated as a one of the simplest applications.

In this article, the following abbreviations will be used: The ratio of the introduction of MTG will be denoted in the parentheses followed the code of the PCMS microgel (see Table I), that is, MG-1 in which 50% of chloromethyl group was modified by MTG will be denoted by MG-1 (50).

Table I Recipes of the Preparation of Microgels

CMS[a] (g)	DVB[b] (g)	PVP[c] (g)	AIBN (g)	Yield (%)	Diameter[d] (μm)	Code
15.0	0.15	3.45	0.30	51	2.3	MG-1
15.0	0.73	3.48	0.30	18	1.7	MG-2

Polymerizations were carried out in ethanol–DMSO (25/3 v/v) at 70°C for 20 h under a nitrogen atmosphere.

[a] Chloromethylstyrene.
[b] Divinylbenzene.
[c] Polyvinylpyrrolidinone.
[d] Estimated by SEM.

EXPERIMENTAL

Materials

Chloromethylstyrene, divinylbenzene, and MTG were used after distillation. 1,8-Diazabicyl-co[5.4.0]undec-7-ene (DBU) and dioxane were used after distillation from calcium hydride. Pyridine was used after distillation from sodium hydroxide. THF was distilled from lithium aluminum hydride before use. *N,N*-Dimethylacetamide (DMAc) was used after being dried on a 4 Å molecular sieve. Other chemicals were reagent grade and were used without further purification.

Polychloromethylstyrene (PCMS)

A solution of 3.0 g (20 mmol) of chloromethylstyrene and 164 mg (1.0 mmol) of AIBN in 20 mL of benzene was degassed and allowed to stand at 70°C for 24 h in a sealed tube. The reaction mixture was poured into a large amount of methanol. The white precipitate was isolated by filtration, washed thoroughly with methanol, and dried under reduced pressure to give 2.24 g (75%) of PCMS as a white powder.

PCMS Microgel (MG-1)[13]

A solution of 15.0 g (98 mmol) of chloromethylstyrene, 0.15 g (0.63 mmol) of divinylbenzene, and 3.45 g of polyvinylpyrrolidinone in 250 mL of ethanol and 30 mL of dimethyl sulfoxide was allowed to stand at 70°C for 30 min under a nitrogen atmosphere. After the addition of 0.30 g (1.8 mmol, 1.8 mol %) of AIBN, the reaction mixture was allowed to stand at 70°C for an additional 20 h under a nitrogen atmosphere with stirring. The reaction mixture was filtered via a membrane filter (Teflon, 0.22 μm), washed thoroughly with methanol and water, and dried under reduced pressure to give 7.65 g (51%) of the PCMS microgel as a white powder.

Reaction of Benzyl Chloride with MTG in the Presence of DBU

To a solution of 103 mg (0.81 mmol) of benzyl chloride and 87.5 mg (0.82 mmol) of MTG in 2.0 mL of THF, a solution of 122 mg (0.80 mmol) of DBU in 1.0 mL of THF was added under a nitrogen atmosphere. The white crystal was precipitated immediately, and the reaction mixture was allowed to stand for 4 h with stirring. The reaction mixture was purified by preparative TLC to obtain 153 mg (97%) of methyl(benzylthio)acetate as a colorless oil.

Reaction of PCMS with MTG in the Presence of DBU

To a solution of 106 mg (0.70 mmol unit) of PCMS and 76.1 mg (0.72 mmol) of MTG in 2.0 mL of THF, a solution of 109 mg (0.71 mmol) of DBU in 1.0 mL of THF was added under a nitrogen atmosphere. The reaction mixture was allowed to stand for 4 h with stirring. The reaction mixture was poured into a large amount of phosphate buffer (pH 6.86). The precipitate was isolated by filtration, washed thoroughly with methanol and water, and dried under reduced pressure to give 155 mg (100%) of the polymer (94% of the chloromethyl group was reacted with MTG) as a pale yellow elastic solid.

Reaction of MG-1 with MTG in the Presence of DBU

To a suspension of 103 mg (containing 0.67 mmol unit of the chloromethyl group) of MG-1 and 72.1 mg (0.68 mmol) of MTG in 2.0 mL of THF, a solu-

tion of 102 mg (0.67 mmol) of DBU in 1.0 mL of THF was added under a nitrogen atmosphere. The reaction mixture was allowed to stand for 4 h with stirring. The reaction mixture was poured into a large amount of phosphate buffer (pH 6.86). The precipitate was isolated by filtration, washed thoroughly with methanol and water, and dried under reduced pressure to give 159 mg (100%) of the microgel (95% of the chloromethyl group was reacted with MTG) as a pale yellow elastic solid.

Alkaline Hydrolysis of MTG-Modified PCMS Microgel [MG-1 (95)]

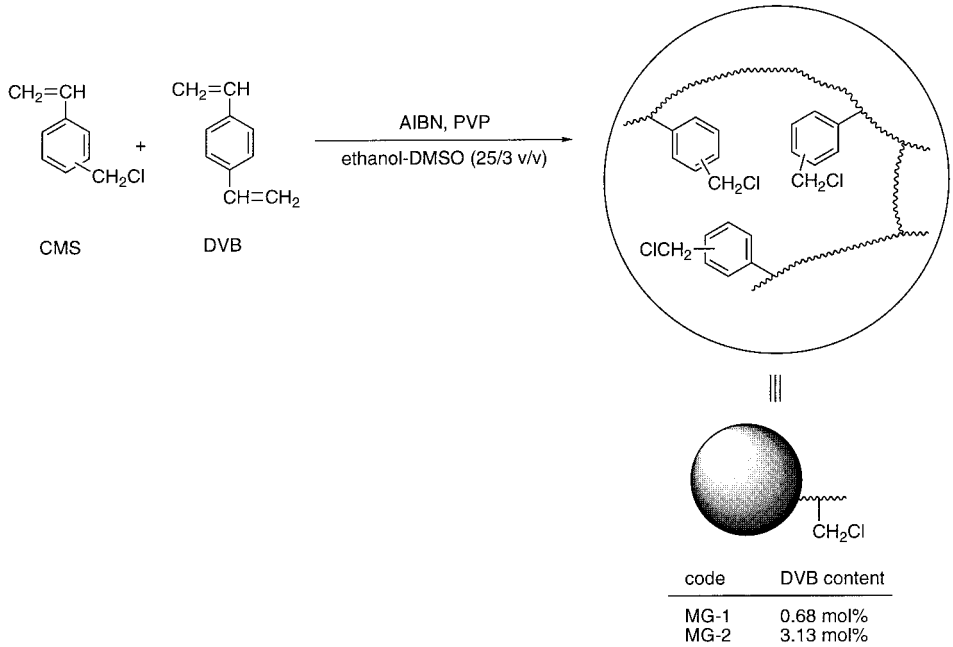
A suspension of 64.1 mg (containing 0.26 mmol unit of the ester group) of MG-1 (95) in 0.5 mL of DMAc was allowed to stand with stirring until the microgel swelled to become transparent. To the suspension was added 27.0 mg (0.70 mmol) of sodium hydroxide and 0.5 mL of water, and the reaction mixture was allowed to stand at 50°C for 24 h with stirring. The reaction mixture was poured into a large amount of diluted hydrochloric acid. The precipitate was filtered, washed thoroughly with water, and dried under reduced pressure to give 35.6 mg of the microgel (36% of the ester group was hydrolyzed) as a white powder.

Acid-Catalyzed Hydrolysis of MTG-Modified PCMS Microgel [MG-1 (95)]

A suspension of 40.0 mg (containing 0.17 mmol unit of the ester group) of MG-1 (95) in 1 mL of dioxane was allowed to stand with stirring until the microgel swelled to become transparent. To the suspension was added 4.3 mg (0.02 mmol) of *p*-toluenesulfonic acid monohydrate and 0.2 mL of water, and the reaction mixture was allowed to stand at 80°C for 24 h with stirring. The reaction mixture was poured into a large amount of water. The precipitate was filtered, washed thoroughly with water, and dried under reduced pressure to give 34.8 mg of the microgel (66% of the ester group was hydrolyzed) as a pale yellow powder.

Staining of Hydrolyzed MG-2 (52) by Cesium Ion

To a solution of 25.2 g (35 mmol) of cesium hydroxide in 35 mL of water, a 25.1 mg (containing 0.13 mmol unit of the carboxy group) of the microgel prepared by the alkaline hydrolysis of MG-2 (52) was added, and the suspension was allowed to stand at room temperature for 24 h with continuous stirring. The microgel was isolated by filtration, washed thoroughly with water, and dried under reduced pressure to give 23.2 mg (67%) of the microgel as a pale yellow powder.



Scheme 2

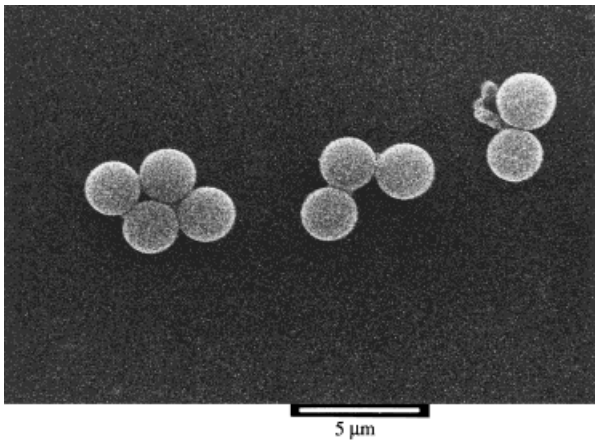


Figure 1 SEM photograph of MG-1.

Reaction of MG-1 with Pyridine

A suspension of 83.0 mg (containing 0.54 mmol unit of the chloromethyl group) of MG-1 in 0.25 mL of DMAc was allowed to stand with stirring until the microgel swelled to become transparent. To the suspension was added 0.25 mL (3.1 mmol) of pyridine, and the reaction mixture was allowed to stand for 24 h with stirring. The reaction mixture was poured into a large amount of acetone. The precipitate was isolated by filtration via a membrane filter (Teflon, 0.22 μm), washed thoroughly with acetone, and dried under reduced pressure to give 103 mg of the microgel (91% of the chloromethyl group was converted to the pyridinium group) as a white powder.

Zwitterionic Microgel (MG-ZI)

In 1 mL of dioxane, 47.4 mg (containing 0.11 mmol unit of the ester group) of the microgel prepared from MG-1 (52) by the reaction with pyridine was suspended. The suspension was allowed to stand with stirring until the microgel swelled to become transparent. To the suspension was added 4.9 mg (0.03 mmol) of *p*-toluenesulfonic acid monohydrate and 0.2 mL of water, and the reaction mixture was allowed to stand at 80°C for 48 h with stirring. The reaction mixture was poured into a large amount of water. The precipitate was filtered, washed thoroughly with water, and dried under reduced pressure to give 42.0 mg of the zwitterionic microgel (92% of the ester group was hydrolyzed) as a pale yellow powder.

Table II Reaction of Benzyl Chloride with MTG: $PhCH_2Cl + HSCH_2COOCH_3 \xrightarrow{base} PhCH_2SCH_2COOCH_3$

Base (equivalent)	Solvent	Time (h)	Yield (%)
tert-BuOK (0.96)	THF	4	75
tert-BuOK (0.99)	THF	8	36
tert-BuOK (1.01)	DMF	12	[a]
DBU (0.99)	THF	4	97

Reactions were carried out at room temperature in the presence of an excess amount of MTG.
[a] A complex mixture was obtained.

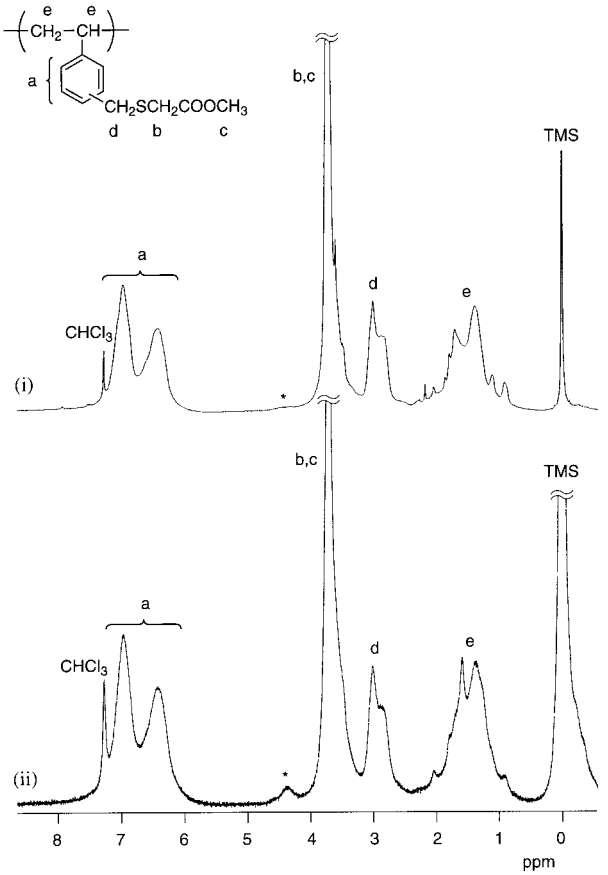


Figure 2 ^{1}H-NMR spectra of (i) MTG-modified (94%) PCMS ($CDCl_3$, 500 MHz) and (ii) MG-1 (95) ($CDCl_3$, 500 MHz). Remaining chloromethyl group is denoted by *.

RESULTS AND DISCUSSION

Reaction of PCMS Microgel with MTG

The PCMS microgel was prepared by dispersion copolymerization of chloromethylstyrene (CMS)

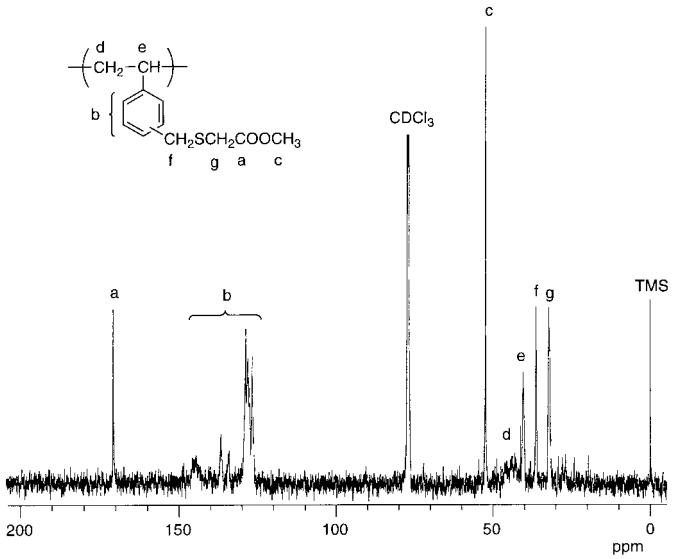


Figure 3 ^{13}C-NMR spectrum ($CDCl_3$, 125 MHz) of MTG-modified (94%) PCMS.

and divinylbenzene (DVB) in ethanol–DMSO (25/3 v/v) in the presence of poly(vinylpyrrolidinone) (PVP) (Scheme 2).[13] The recipes of the preparation of microgels and their average diameters are summarized in Table I. A scanning electron microscope (SEM) photograph of MG-1 is shown in Figure 1. A uniform spherical microgel whose average diameter was 2.3 μm was obtained. PCMS (M_n 5500, M_w/M_n 1.81) was also prepared by solution polymerization in benzene.

Before the polymer reaction of the PCMS microgels with MTG, the reaction of benzyl chloride with MTG was investigated to optimize the reaction conditions. The results are summarized in Table II. First, the reaction was carried out in THF using *tert*-BuOK as a base. Methyl(benzylthio)acetate was obtained in a 75% yield. When the reaction was carried out for a longer period, however, the yield, rather, decreased. When the reaction was carried out in DMF, the complex mixture including benzyl *tert*-butyl ether was obtained. On the other hand, when nonnucleophilic DBU was used as a base, the sulfide was obtained as a sole product in 97% yield.

The reaction of PCMS with MTG was carried out in THF using DBU as a base. Although the

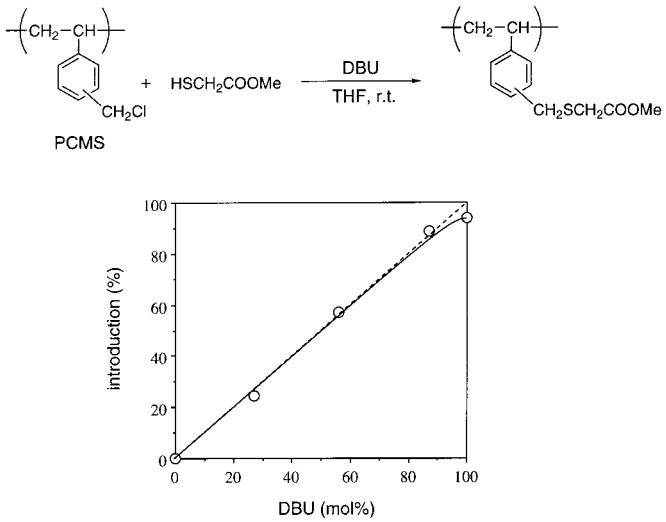
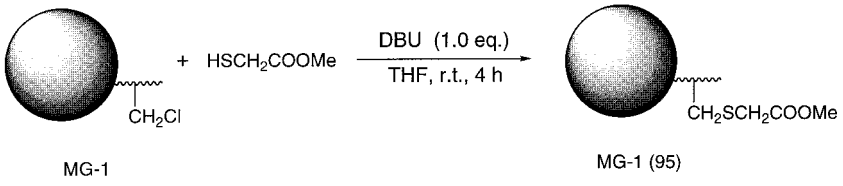


Figure 4 Relationship between the amount of DBU used (equivalent to the chloromethyl group) and introduction ratio of MTG into PCMS.



Scheme 3

polymer turned insoluble in THF, a quantitative reaction occurred. The ^{1}H- and ^{13}C-NMR spectra of the polymer are shown in Figures 2 and 3, respectively. In the ^{1}H-NMR spectrum, the peak corresponding to the chloromethyl group (4.5 ppm) disappeared while a peak of α-methylene of the ester group (3.0 ppm) and a coalescent peak of the methyl and benzyl groups (3.8 ppm) appeared. From the integration of each peak, the introduction ratio of MTG was estimated to be 94%. In the ^{13}C-NMR spectrum, the peak of the chloromethyl group (46 ppm) completely disappeared while peaks corresponding to MTG appeared, and no other peak was observed.

When the amount of DBU was controlled, the introduction ratio of MTG was easily controlled as shown in Figure 4. When the amount of DBU was higher than 85%, however, the introduction ratio was lower than the expected value because of a polymer effect. When the introduction ratio of MTG was 51%, the M_n of the polymer was 6500, which corresponds well to the calculated value (6800). Further, the M_w/M_n (1.88) did not increase. These results confirmed that the reaction of PCMS and MTG proceeded without any side reaction including a crosslinking reaction.[7]

Based on these results, the reactions of the PCMS microgel and MTG were investigated. When MG-1 was treated with a 1.0 equivalent of DBU in the presence of an excess amount of MTG at room temperature in THF for 4 h, a sulfenylated microgel was obtained (Scheme 3). The ^{1}H-NMR spectrum of the microgel is also shown in Figure 2. All the peaks are broad, but correspond well to those of the MTG-modified PCMS. From the integration of the corresponding peaks, the introduction ratio of MTG was estimated to be 95%. The polymer reaction in the microgel can be carried out as well as in a linear polymer. Thus, the control of the introduction ratio was investigated as well as PCMS. The results are shown in Figure 5. As expected, the introduction ratio corresponded well to the amount of DBU used. However, $>$ 97% of the sulfenylation could not be achieved even when an excess amount of DBU was used or when the reaction was carried out for the longer period.

Structure of MTG-Modified PCMS Microgel

Electron microscopic analyses showed that MG-1 (51) forms a coalesced aggregate because the MTG modification of PCMS decreases its T_g (see below). On the other hand, MG-2 (60) showed a spherical structure and its average diameter was closely related to that of MG-2 because of its higher crosslinking density. Thus, the internal structure of the MTG-modified PCMS microgel was studied using MG-2 (60).

To observe the internal structure of MG-2 (60), the selective staining of the sulfenylated region was investigated. We planned the hydrolysis of the ester group followed by conversion to cesium salt (Scheme 4).

First, the hydrolysis of MG-1 (95) was investigated to optimize the reaction conditions. The results are summarized in Table III. Treatment of the microgel with concentrated sulfuric acid resulted in carbonization. Alkaline hydrolysis of the

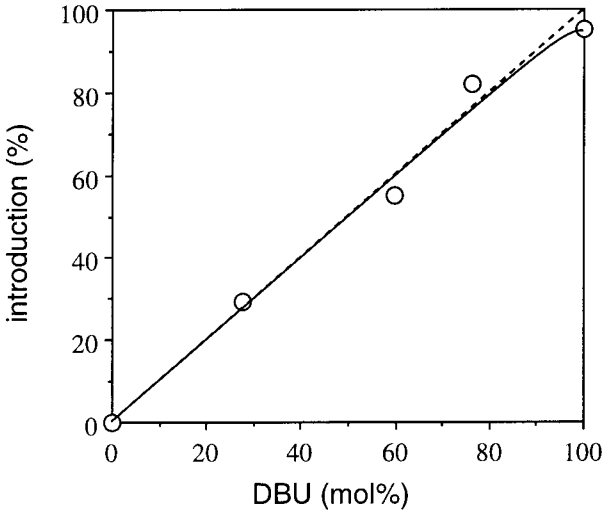
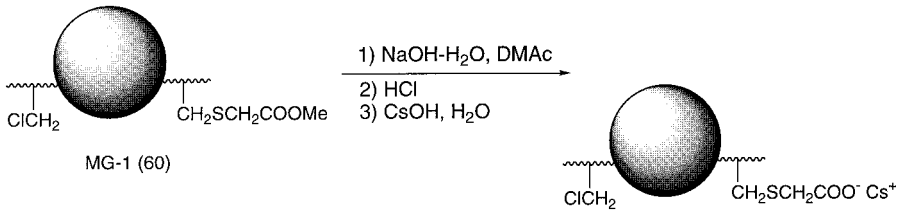


Figure 5 Relationship between the amount of DBU used (equivalent to the chloromethyl group) and introduction ratio of MTG into MG-1.



Scheme 4

microgel proceeded smoothly to obtain a microgel bearing a carboxy group even though alkaline hydrolysis was not effective for the hydrolysis of MMA.[17] The ^{1}H-NMR spectrum of the microgel is shown in Figure 6. The peak of the ester methyl group observed at 3.8 ppm decreased, and, instead, the characteristic peak of the carboxy group appeared at 12.5 ppm. The conversion of the ester group can be estimated from the decrease of the integration of the peak at 3.8 ppm. On the other hand, demethylation using lithium iodide was not effective in this case.[18] Acid-catalyzed hydrolysis in dioxane–water was as effective as base-catalyzed hydrolysis.

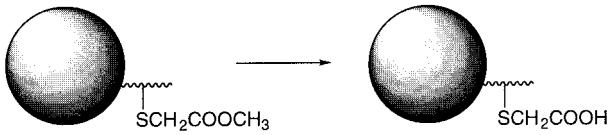
Based on these results, the alkaline hydrolysis of MG-2 (60) was carried out. Quantitative hydrolysis can be easily confirmed from the ^{1}H-NMR spectrum of the resulting microgel, that is, the appearance of the peak of the carboxy group at 12.5 ppm and decrease of the peak of the ester methyl group at 3.8 ppm. Further, the hydrolyzed microgel was treated by an aqueous cesium hydroxide solution. Thus, the region where MTG was introduced was selectively stained by the cesium ion.

Figure 7 shows a transmission electron microscope (TEM) photograph of the stained microgel sliced by 100 nm. Since the diameter of MG-2 was 1.7 μm, the photograph shows a sample where the center of the microgel was sliced. The opaque region surrounded the transparent region, and the border of both regions was very clear. These observations indicate that MTG was introduced into the PCMS microgel at the outer region of the microgel selectively, and the resulting microgel has a core–shell structure.

To exclude the possibility that the core–shell structure was formed during the hydrolysis, the thermal analyses of the microgels were carried out using DSC. MG-2 (60) showed two T_g's at 62.7 and −11.0°C, respectively. Since MG-2 showed a single T_g at 69.5°C and PCMS quantitatively modified by the MTG showed a single T_g at −14.5°C, the T_g at 62.7°C corresponds to the core PCMS region and the T_g at −11.0°C corresponds to the shell sulfenylated region. These analyses confirmed the core–shell structure of the MTG-modified PCMS microgel.

Consequently, it became evident that the core–shell-type microgel can be obtained by the chemi-

Table III Hydrolysis of MG-1 (95):



Reagent	Solvent	Temperature (°C)	Time (h)	Demethylation (%)
Concd H_2SO_4	None	RT	—	[a]
NaOH	DMAc–H_2O[b]	50	24	36
NaOH	DMAc–H_2O[b]	50	48	84
LiI	DMAc	80	24	27
LiI	DMAc	80	48	41
TsOH	Dioxane–H_2O[c]	80	24	66

[a] Carbonization.
[b] 1/1 v/v.
[c] 5/1 v/v.

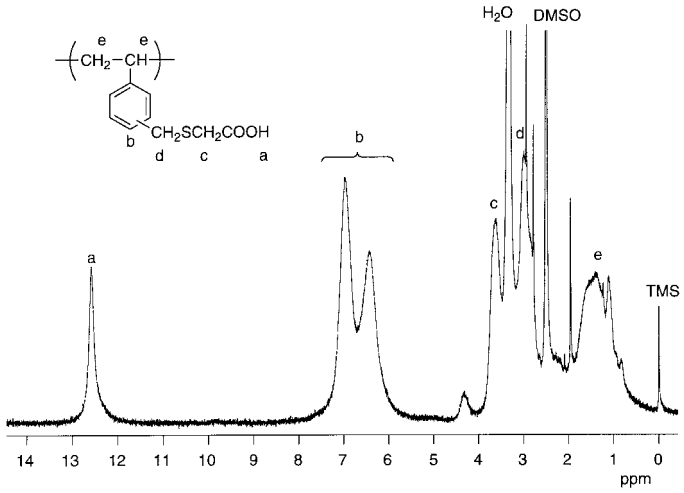


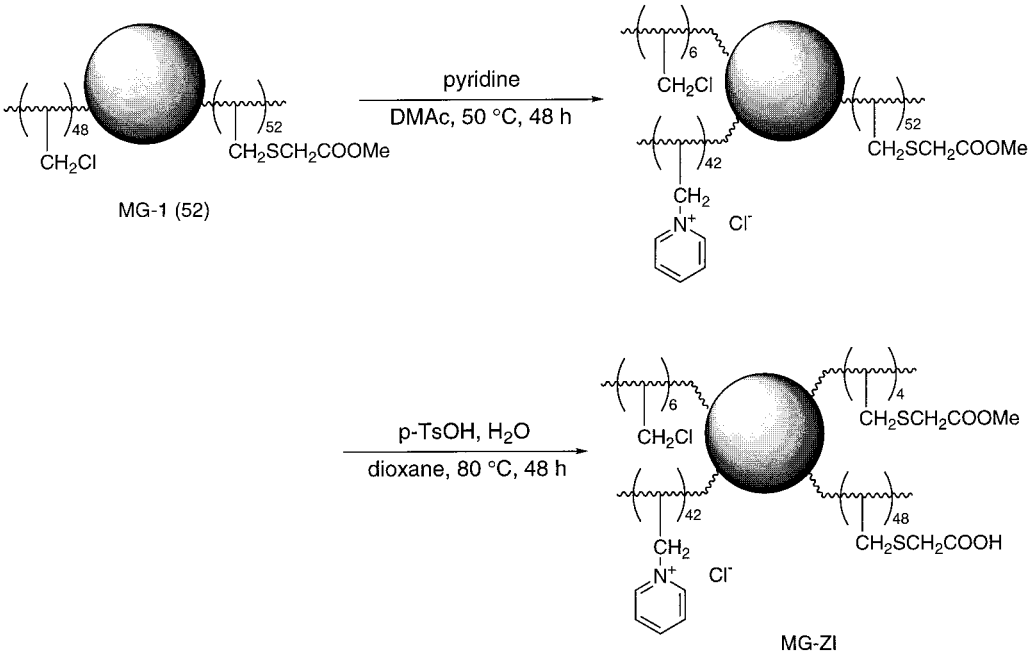
Figure 6 ^{1}H-NMR spectrum (DMSO-d_6, 500 MHz) of microgel obtained by alkaline hydrolysis of MG-1 (95). See Table III.

cal modification of the PCMS microgel with MTG. The core–shell structure with a clear border indicates that the reaction of the chloromethyl group and the MTG is a diffusion-limited one. Thus, MTG was introduced into the PCMS microgel from the outer side layer by layer.

Preparation of Zwitterionic Microgel Using MTG-Modified PCMS Microgel

As a simple application of the MTG-modified PCMS microgel, the preparation of the zwitterionic microgel was investigated. Since the MTG-modified PCMS microgel has a core–shell structure, a novel type of the zwitterionic microgel bearing cationic and anionic functions separately was expected to be obtained.[13]

A suspension of MG-1 in pyridine, in which MG-1 swelled, was stirred at room temperature for 6 h. The microgel shrunk during the reaction. An absorption of δ_{CH_2} corresponding to an unchanged chloromethyl group was observed in the IR spectra of the resulting microgel at 1265 cm^{-1}. Thus, DMAc was used as a cosolvent to maintain



Scheme 5

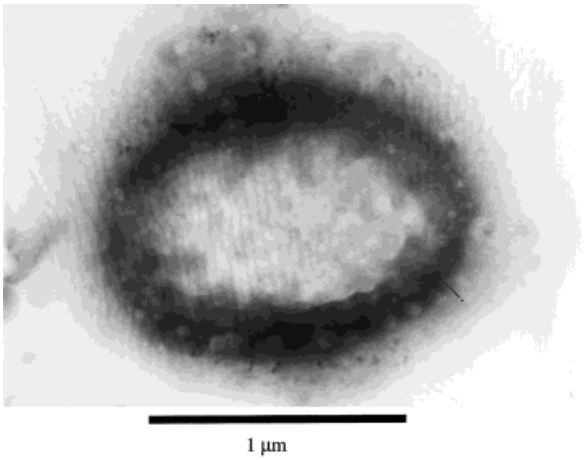


Figure 7 TEM photograph of microgel derived from MG-2 (60) by complete alkaline hydrolysis followed by the treatment with cesium hydroxide. The sample was sliced at the center (100 nm) of the microgel.

a swollen condition. When MG-1 was stirred in DMAc–pyridine (1/1 v/v) at room temperature for 24 h, the microgel swelled during the reaction, and 91% of the conversion of the chloromethyl group to the pyridinium group was estimated by its ^{1}H-NMR spectrum.

MG-1 (52) was treated with pyridine in the presence of DMAc at room temperature for 24 h, although the conversion of the chloromethyl group to the pyridinium group estimated from the ^{1}H-NMR spectrum was only 54%. It is assumed that the thioglycolate group in the shell layer reduced the reactivity of the remaining chloromethyl group in the core layer. Thus, the reaction was carried out under various conditions as summarized in Table IV. The conversion of the chloromethyl group to the pyridinium group increased as the reaction was carried out at a higher temperature for a longer period. When the reaction was carried out at 50°C for 48 h, 88% of the conversion was achieved.

Hydrolysis of the thus obtained microgel that consisted of 52% of the MTG group, 42% of the pyridinium group, and 6% of the remaining chloromethyl group was carried out (Scheme 5). When alkaline hydrolysis was carried out, the microgel immediately turned brown. Since the peak corresponding to the pyridinium group in the ^{1}H-NMR spectrum decreased, the pyridinium group decomposed under the alkaline hydrolysis condition. Thus, acid-catalyzed hydrolysis was carried out in dioxane–water at 80°C for 48 h as described above. The microgel swelled during the reaction. The ^{1}H-NMR spectrum of the resulting microgel is shown in Figure 8. Decrease of the peaks of pyridinium group was not observed, and the peak

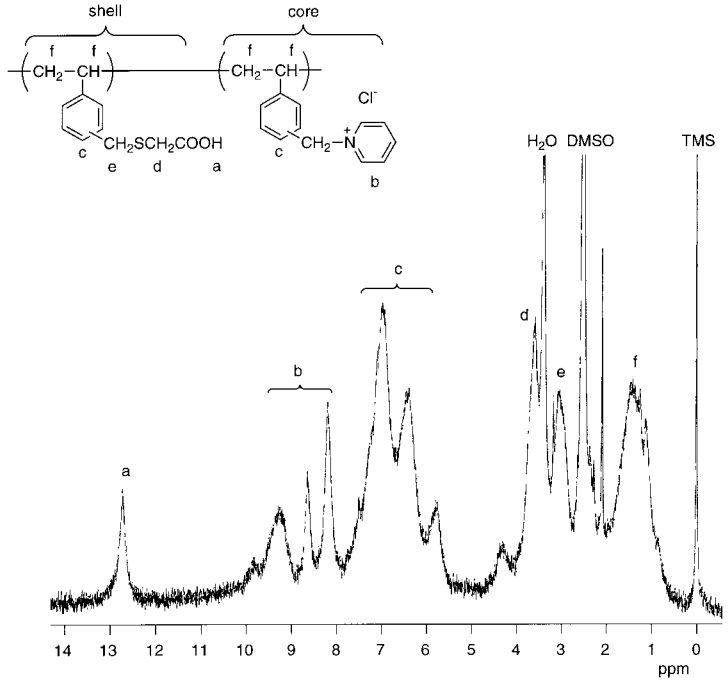
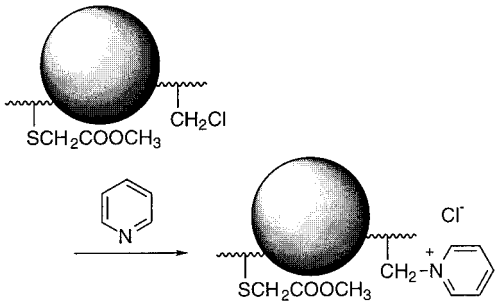


Figure 8 ^{1}H-NMR spectrum (DMSO-d_6, 500 MHz) of the zwitterionic microgel (MG-ZI).

Table IV Reaction of MG-1 (52) with Pyridine:



Temperature (°C)	Time (h)	Conversion of Chloromethyl Group (%)[a]
RT	24	54
50	24	83
50	48	88

Reactions were carried out in DMAc–pyridine (1/1 v/v).
[a] Estimated by ^{1}H-NMR spectra.

of the carboxy group was observed at 12.5 ppm, indicating that the expected zwitterionic microgel, which is denoted by MG-ZI, was obtained. The ratio of the hydrolysis was estimated by the ^{1}H-NMR spectra to be 92%.

MG-ZI was highly hygroscopic. Since MG-ZI formed a stable dispersion in water and various organic solvents, the isolation of MG-ZI from the suspension was difficult.

CONCLUSIONS

We demonstrated that the modification of the PCMS microgel by functional thiol can be one of the most effective methods to obtain functional microgels. We used MTG as a functional thiol in this study. We found that the desired amount of MTG can be introduced into the PCMS microgel and a corresponding core–shell type of microgel can be obtained extensively.[19,20]

In this study, we demonstrated the preparation of a zwitterionic microgel as a simple application of the MTG-modified PCMS microgel. Since this highly functionalized microgel has an interesting internal structure, further application including a functionalized catalyst, membrane, and reaction field may be expected. Moreover, it was proved that the chloromethyl group and the ester group can be functionalized independently. The preparation of various functional microgels using this novel promising system is in progress.

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