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SHORT COMMUNICATION

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Production of micron-sized, monodisperse composite polymer particles having epoxy groups by seeded dispersion polymerization

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Abstract Micron-sized, monodisperse polystyrene (PS)/glycidyl methacrylate–divinylbenzene copolymer core/shell composite particles having epoxy groups in the shells were produced by seeded dispersion copolymerization of glycidyl methacrylate and divinylbenzene in an ethanol/water medium with 1.65-μm-sized, monodisperse PS seed particles. By chemical modifications of epoxy groups with sodium hydrogensulfite and dimethylamine, composite polymer particles having sulfonate and dimethylamino groups, respectively, in the shells were prepared.

Key words Micron-size · Monodisperse · Composite particle · Core/shell · Seeded dispersion polymerization

Introduction

Recently, micron-sized, monodisperse polymer particles have been applied in the biomedical field, microelectronics, and other areas. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized, monodisperse polymer particles; Almog et al. [1] have suggested that the dispersion polymerization technique is useful for their production. Other groups have also recognized the usefulness of the technique [2–4].

Nevertheless, this technique seems to be restricted to a variety of monomers for producing particles having functional groups thereon, which would be required for use in the previously mentioned applications. Therefore, we have been producing about 2-μm-sized, monodisperse composite polymer particles having chloromethyl groups [4, 5] and vinyl groups [6, 7] at the surfaces by seeded dispersion copolymerizations of styrene (S) and chloromethylstyrene and of S and divinylbenzene (DVB), respectively, in an ethanol/water medium with 1.8-μm-sized, monodisperse polystyrene (PS) seed particles produced by dispersion polymerization. In their composite particles, the functional groups are preferentially distributed in the surface layers. These results show the advantage of seeded dispersion polymerization for the production of core/shell composite polymer particles. Poly(methyl methacrylate) (PMMA)/PS composite particles consisting of a PMMA core and a PS shell, which is a thermodynamically unstable morphology in a polar medium, were produced by seeded dispersion polymerization of S with 1.91-μm-sized, monodisperse PMMA seed particles in a methanol/water (4/1, w/w) medium [8, 9].

In the last 5 years, there have been some reports of the production of polymer particles having epoxy groups by copolymerization of acrylic monomers with glycidyl methacrylate (GMA) [10–12]. Micron-sized, monodisperse poly(GMA) (PGMA) particles have been produced by dispersion polymerization [13]. In most of the applications, epoxy groups are utilized not inside the particles, but at the surfaces.

In this work, seeded dispersion copolymerization of GMA and DVB with 1.65-μm-sized, monodisperse PS seed particles was carried out to produce micron-sized, monodisperse PS/GMA–DVB copolymer [P(GMA–DVB)] core/shell composite particles having epoxy groups in the shells. In addition, chemical modifications of the epoxy groups with sodium hydrogensulfite and dimethylamine was carried out to prepare composite polymer particles having sulfonate and dimethylamino groups in the shells, respectively.

Experimental

Materials

S, GMA, and acrylic acid (AA) were purified by distillation under reduced pressure in a nitrogen atmosphere. DVB of purity 96% was supplied by Nippon Steel Chemical, Co., Tokyo, Japan and was washed with 1 N sodium hydroxide and deionized water to remove the polymerization inhibitor before use. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Osaka, Japan) were purified by recrystallization. Guaranteed grade KBr, HCl, KOH, *N*,*N*-dimethylformamide, and 1,4-dioxane, and extra reagent grade ethanol and toluene, and reagent grade $(CH_3)_2NH$ were used as received from Nacalai Tesque Co., Kyoto, Japan. Guaranteed grade $NaHSO_3$ was used as received from Wako Pure Chemical Industries. Deionized water with a specific conductivity of 5×10^6 Ωcm was distilled. Poly(AA) used as a stabilizer was synthesized by solution polymerization of AA in 1,4-dioxane, according to the method described previously [4].

Preparation of PS seed particles

Micron-sized, monodisperse PS seed particles were produced by dispersion polymerization in a 2000-ml four-necked round-bottomed flask under the optimum conditions listed in Table 1, as reported in previously [4].

Production of composite polymer particles having epoxy groups in the shells

Seeded dispersion copolymerization of GMA and DVB was carried out with the PS seed particles in a sealed glass tube under the conditions listed in Table 2. By-product particles were removed by centrifugal washing. The composition of the composite polymer particles produced was measured with a Fourier transform (FT) IR spectrometer (FT/IR-615, Jasco, Tokyo, Japan) using the pressed-KBr-pellet technique and with an elemental analyzer (Sumigraph model NCH-21, Shimadzu, Kyoto, Japan).

Table 1 A recipe for the production of polystyrene (*PS*) seed particles by dispersion polymerization. N_2; 70 °C; 24 h; stirring rate, 60 rpm. 2,2′-Azobis(isobutyronitrile): *AIBN*; poly(acrylic acid): *PAA*

Ingredients	
Styrene (g)	100
AIBN (g)	1.68
PAA (g)	12
Ethanol (g)	685
Water (g)	200

Observation of ultrathin cross sections of the composite particles

Dried PS seed particles and the composite particles were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution and were then dispersed in an epoxy matrix, cured at room temperature for 24 h, and at 40 °C for 1 h, and microtomed. The ultrathin cross sections were observed with a Jeol JEM-2010 transmission electron microscope (TEM).

Introduction of functional groups in the shells of the composite particles

Chemical modifications of the epoxy groups in the shells of the composite particles were performed with $NaHSO_3$ and $(CH_3)_2NH$ in an aqueous medium. The sulfur atom in the sulfonate group and the nitrogen atom in the dimethylamino group introduced were confirmed using an energy dispersive X-ray (EDX) spectrometer (Voyager, Noran Instruments, Wis., USA) and an elemental analyzer, respectively. The ζ-potentials of the composite particles before and after the reactions with $NaHSO_3$ and $(CH_3)_2NH$ were measured with a laser electrophoresis ζ-potential analyzer (Leza-600, Otsuka Electronic Co., Osaka, Japan) at various pH values adjusted with 0.1 N KOH and 0.1 N HCl.

Particle size distribution

All the particles produced were observed with a TEM. The number-average diameter (D_n) and the coefficient of variation (C_v) of each particle were measured from the TEM photographs with image analysis software for Macintosh (Mac Scope, Mitani Co., Fukui, Japan).

Results and discussion

A TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1 is shown in Fig. 1. D_n and C_v were 1.65 μm and 2.4%, respectively.

Seeded dispersion copolymerization of GMA and DVB with the PS seed particles was carried out to produce micron-sized, monodisperse composite polymer particles having epoxy groups in the shells. When dispersion polymerization of GMA was performed in

Table 2 A recipe for the production of PS/glycidyl methacrylate–divinylbenzene copolymer [*P(GMA–DVB)*] (1/1, w/w) composite particles by seeded dispersion copolymerization. N_2; 36 °C; 24 h; shaking rate, 60 cycles/min (3-cm strokes). 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile): *V-70*

Ingredients	
PS seed particles[a] (g)	0.72
GMA (g)	0.65
DVB[b] (g)	0.07
V-70 (mg)	16.6
Ethanol (g)	6.20
Water (g)	2.66

[a] D_n, 1.65 μm; C_v, 2.4%
[b] Purity, 96% (by catalog)

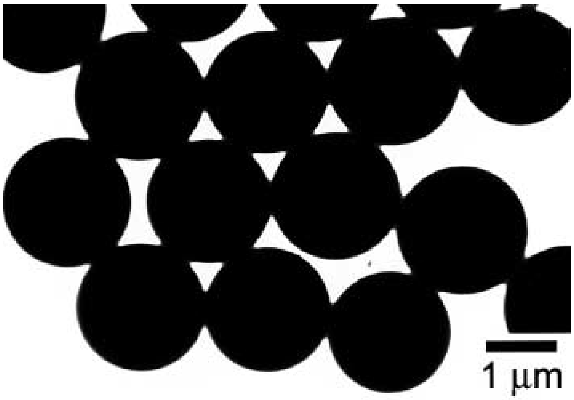
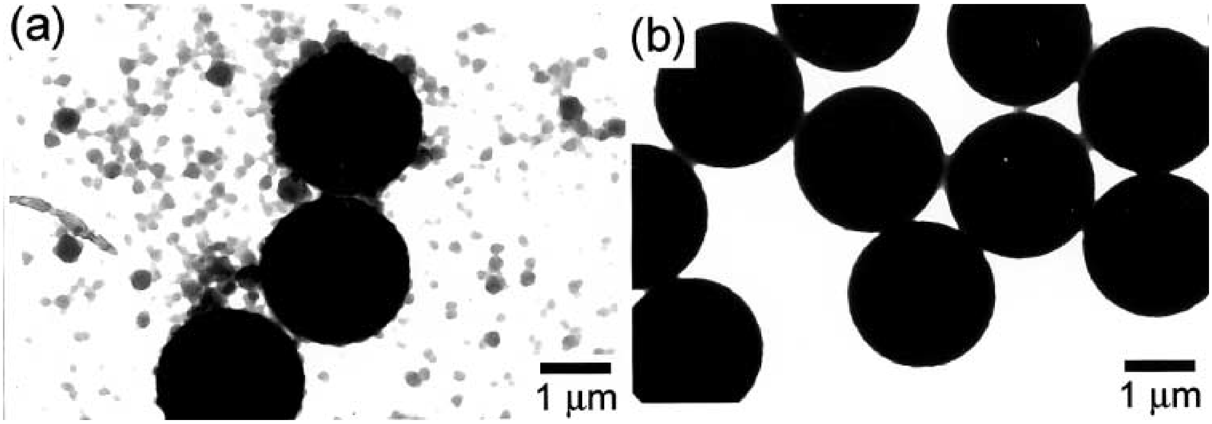


Fig. 1 A transmission electron microscope (*TEM*) photograph of polystyrene (*PS*) seed particles produced by dispersion polymerization under the conditions listed in Table 1

an ethanol/water medium at 70 °C using AIBN initiator, a white gel was obtained. The wet gel and the dried one at room temperature did not dissolve in a large amount of *N*,*N*-dimethylformamide, which is a good solvent for PGMA. This result suggests that the ring-opening reaction of the epoxy groups occurred in the polar medium at the high polymerization temperature. In a previous article [14], it was clarified that the ring-opening reaction of epoxy groups during emulsion copolymerization of ethyl acrylate and GMA could be depressed at neutral pH and low temperature conditions. Accordingly, to depress the ring-opening reaction, the seeded dispersion copolymerization was performed at 36 °C using V-70 initiator, which does not change the pH during polymerization, under the conditions listed in Table 2. In the copolymerization for 24 h, the conversions of GMA and DVB were 97 and 100%, respectively, measured by gas chromatography.

Fig. 2 TEM photographs of PS/glycidyl methacrylate–divinylbenzene copolymer [*P(GMA–DVB)*] composite particles before (a) and after (b) the centrifugal washing, produced by seeded dispersion polymerization under the conditions listed in Table 2



A TEM photograph of the particles produced is shown in Fig. 2a. P(GMA–DVB) particles were by-products, but were easily removed by centrifugal washing as shown in Fig. 2b. D_n and C_v of the PS/P(GMA–DVB) composite particles produced were 1.92 μm and 2.3%, respectively. The amount of P(GMA–DVB) in the composite particles, which was calculated from the total weight of the by-product particles, was about 85% of the total P(GMA–DVB). The GMA/DVB weight ratio in the composite particles, which was calculated from the carbon/hydrogen weight ratio measured by elemental analysis and the amount of P(GMA–DVB) in the composite particles, was almost equal to that of the monomers before the copolymerization. In following experiments, the composite particles after centrifugal washing were used.

FT-IR spectra of the PS seed particles, PGMA, and the PS/P(GMA-DVB) composite particles are shown in Fig. 3. The spectrum of the PS had absorption peaks at 3300–3000 cm^{-1} (aromatic C–H stretching vibration), 770–740 cm^{-1} and 710–680 cm^{-1} (aromatic C–H out-of-plane bending vibration). The spectrum of PGMA had absorption peaks due to oxirane ring symmetrical expansion and contraction vibrations at 1250 cm^{-1} and due to oxirane ring unsymmetrical expansion and contraction vibrations at 950–810 cm^{-1}. The vibration bands observed for the composite particles were reasonably assigned to those of the PS seed particles and PGMA. These results indicate that P(GMA–DVB) was successfully introduced into the PS seed particles.

TEM photographs of ultrathin cross sections of the PS seed particles and the PS/P(GMA–DVB) composite particles which were stained with RuO_4 vapor for 30 min and that of the latter section from which PS was selectively extracted by dropping toluene droplets thereon are shown in Fig. 4. It is known that RuO_4 predominantly stains PS [15]. The PS seed particle was homogeneous, whereas the composite particle had a shell which was brighter than the inside (core). The core was removed by toluene, but the shell remained. These results indicate that the composite particles had a core/

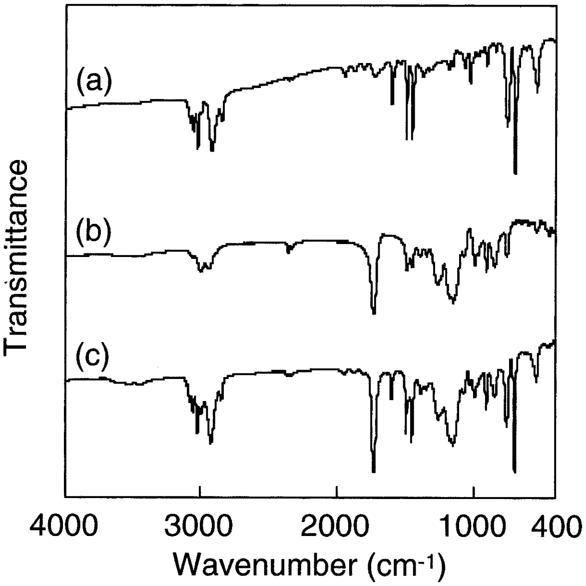


Fig. 3 Fourier transform IR spectra of PS seed particles (*a*), PGMA (*b*) and PS/P(GMA–DVB) composite particles (*c*) using a pressed-KBr-pellet technique

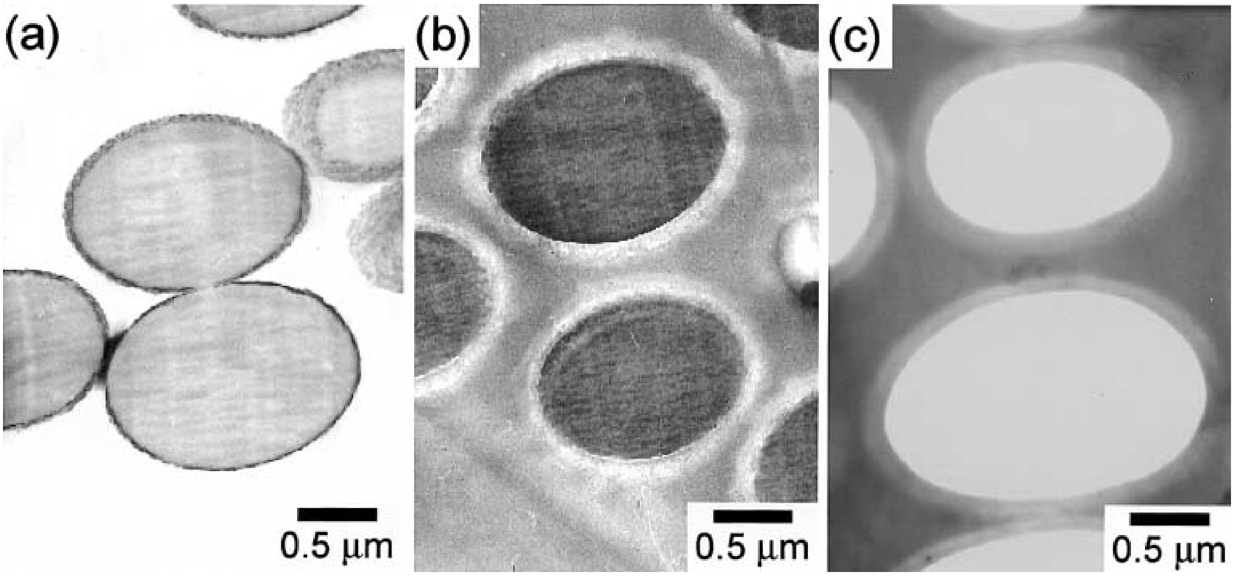
shell morphology having a PS core and a cross-linked P(GMA–DVB) shell.

Next, chemical modification of the epoxy groups in the shells of the PS/P(GMA–DVB) composite particles was carried out with $NaHSO_3$. The composite particles (42.6 g/l) were allowed to react with $NaHSO_3$ (443 g/l) in an aqueous medium at 80 °C for 9 h. These reaction conditions were based on those described in a previous article [16]. Throughout the reaction, no coagulation was observed and after the reaction the composite particles were sequentially washed four times with distilled water, 0.1 N HCl, and again with distilled water to remove the unreacted $NaHSO_3$. Before and after the reaction, there were no changes in the shape and the diameters of the particles from the TEM observation.

EDX spectra and the ζ-potentials of the composite particles before and after the reaction are shown in Figs. 5 and 6, respectively. In Fig. 5, after the reaction, the peak due to sulfur atoms was observed at about 2.3 keV. In Fig. 6, the ζ-potentials after the reaction always had values more negative than those before the reaction. This indicates that sulfonate groups were introduced in the shells by the reaction.

Moreover, in order to introduce amino groups in the shells of the PS/P(GMA–DVB) composite particles, the composite particles (42.6 g/l) were allowed to react with $(CH_3)_2NH$ (395 g/l) in an aqueous medium at 70 °C for 6 h. The composite particles after the reaction were washed ten times with distilled water to remove the unreacted $(CH_3)_2NH$. A TEM photograph of the reacted composite particles is shown in Fig. 7. In the reacted composite particles, a gap was observed between the core and the shell. This seems to be because the P(GMA–DVB) shell reacted with $(CH_3)_2NH$ swelled with water because of the high hydrophilicity. In other words, this result indicates that there is no significant mutual interpenetration of PS and P(GMA–DVB) molecules at the interface between the core and the shell. That is, P(GMA–DVB) molecules formed by seeded dispersion polymerization accumulated onto the PS seed particle. This strongly supports our opinion that

Fig. 4 TEM photographs of ultrathin cross sections of PS seed particles (a) and PS/P(GMA–DVB) composite particles before (b) and after (c) the extraction of PS with toluene on the TEM grid, after exposure to RuO_4 vapor for 30 min



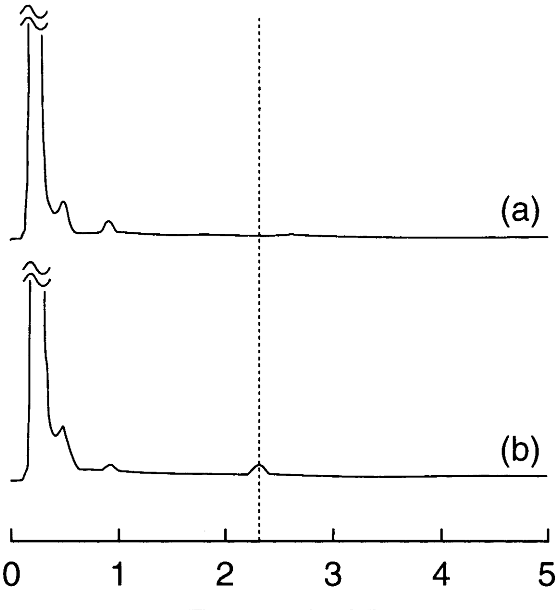


Fig. 5 Energy dispersive X-ray spectra of PS/P(GMA–DVB) composite particles before (*a*) and after (*b*) the reaction with $NaHSO_3$ (443 g/l) in an aqueous medium at 80 °C for 9 h at a particle concentration of 42.6 g/l

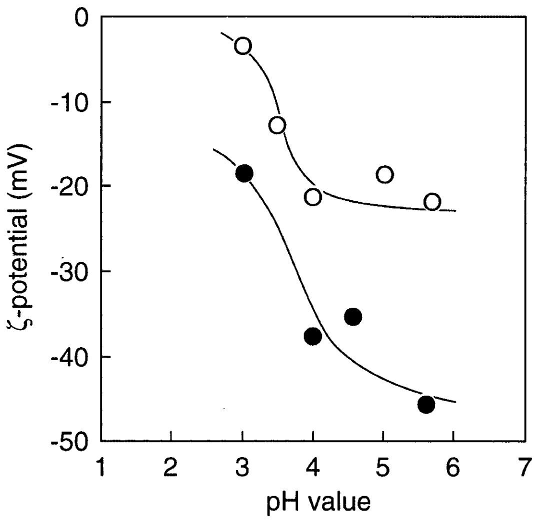


Fig. 6 Relationships between the pH values and the ζ-potentials of PS/P(GMA–DVB) composite particles before (○) and after (●) the reaction with $NaHSO_3$ (443 g/l) in an aqueous medium at 80 °C for 9 h at a particle concentration of 42.6 g/l

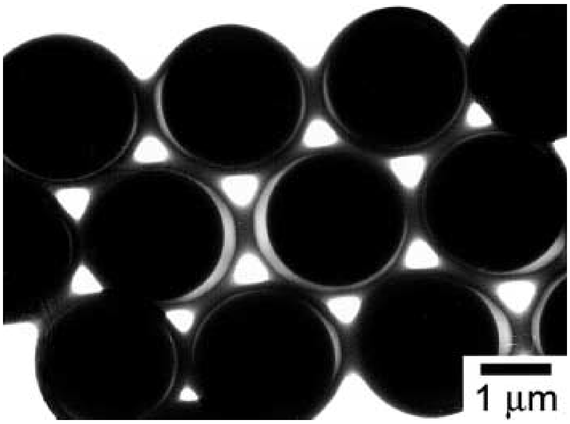


Fig. 7 A TEM photograph of PS/P(GMA–DVB) composite particles after the reaction with $(CH_3)_2NH$ (395 g/l) in an aqueous medium at 70 °C for 6 h at a particle concentration of 42.6 g/l

Table 3 Element analyses of PS/P(GMA–DVB) composite particles before and after the reaction with $(CH_3)_2NH$ at 70 °C for 6 h. $(CH_3)_2NH$ concentration, 395 g/l; particle concentration, 42.6 g/l

	Compostion (wt%)		
	C	H	N
Before the reaction	78.2	7.38	0.129
After the reaction	74.7	7.80	2.40

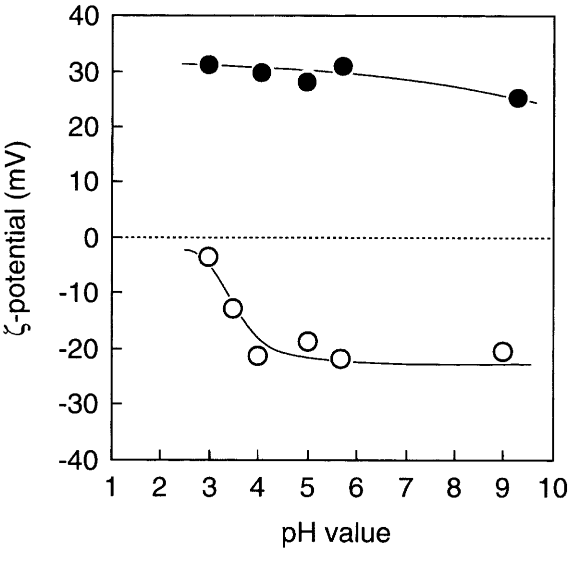


Fig. 8 Relationships between the pH values and the ζ-potentials of PS/P(GMA–DVB) composite particles before (○) and after (●) the reaction with $(CH_3)_2NH$ (395 g/l) in an aqueous medium at 70 °C for 6 h at a particle concentration of 42.6 g/l

seeded dispersion polymerization has the advantage to produce core/shell composite particles in which polymers accumulate in the order of formation regardless of the thermodynamic stability [4, 5, 8, 9, 17].

The results of elemental analyses of the composite particles before and after the reaction are shown in Table 3. The composite particles before the reaction had a very small number of nitrogen atoms, which were due to end groups derived from the V-70 initiator. The composite particles after the reaction had many nitrogen atoms due to the dimethylamino groups, the number of which corresponded to 80% of the GMA copolymerized. This indicates that almost all of the epoxy groups due to the GMA unit did not cleave during the seeded dispersion copolymerization, but remained in the shells of the composite particles.

The relationships between the pH values and the ζ-potentials of the composite particles before and after the reaction are shown in Fig. 8. The ζ-potentials of the composite particles after the reaction were always positive at any pH value.

From the results, it is concluded that micron-sized, monodisperse PS/P(GMA–DVB) core/shell composite particles having epoxy groups in the shells were produced by the seeded dispersion copolymerization of GMA and DVB and that the chemical modifications of the epoxy groups with $NaHSO_3$ and $(CH_3)_2NH$ gave composite polymer particles having sulfonate and dimethylamino groups in the shells, respectively.

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