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SHORT COMMUNICATION

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# Production of micron-sized monodispersed composite polymer particles by seeded polymerization utilizing the dynamic swelling method

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**Abstract** In order to develop the seeded polymerization technique utilizing the dynamic swelling method (DSM) proposed by authors for the production of micron-sized monodispersed "composite" polymer particles consisting of two kinds of polymers, the seeded polymerization for the dispersion of ethyl methacrylate (EMA)-swollen PS particles prepared utilizing DSM was carried out. Monodispersed PS/poly(ethyl methacrylate) (PEMA) composite particles having 7 $\mu$m in diameter were produced by the addition of NaCl to lower the solubility of EMA in medium and by the addition of $CuCl_2$ as a water-soluble inhibitor to depress the by-production of submicron-sized PEMA particles.

**Key words** Dynamic swelling method – micron size – monodisperse – composite – seeded polymerization

## Introduction

Recently, micron-sized monodispersed polymer particles have been used in the biomedical field, microelectronics, etc. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodispersed polymer particles [1–4]. Corner [5] and Almog et al. [6] suggested that dispersion polymerization is a useful technique for the production of micron-sized monodispersed polymer particles. We have been producing micron-sized monodispersed composite polymer particles having functional groups such as chloromethyl [7] and vinyl groups [8, 9] by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2 $\mu$m-sized monodispersed polystyrene (PS) seed particles. Micron-sized monodispersed polymer particles having multihollow structures were also produced by extraction of PS with toluene under reflux from micron-sized monodispersed PS/poly(styrene-divinylbenzene) composite particles produced by seeded dispersion copolymerization [10].

Moreover, in order to produce monodispersed polymer particles having the diameter above 5 $\mu$m, we suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named "dynamic swelling method (DSM)" [11–13]. In fact, about 7 $\mu$m-sized monodispersed PS particles were produced by seeded polymerization utilizing DSM and a thermodynamic background of DSM was discussed [14].

In this article, in order to develop the technique for the production of micron-sized monodispersed "composite" polymer particles, seeded polymerization for the dispersion of ethyl methacrylate (EMA)-swollen PS particles prepared utilizing DSM was carried out.

## Experimental

### Materials

Styrene and EMA were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobisisobutyronitrile (AIBN) and 2,2′-azobis(4-methoxy-

2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Ltd., Japan) of reagent grade were purified by recrystallization. Deionized water with a specific conductivity of $5 \times 10^6$ Ωcm was distilled with a Pyrex distillator. Poly(vinyl alcohol) (PVA) was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: $P_n$, 1700; degree of saponification, 88%). Sodium chloride (NaCl), cupric chloride ($CuCl_2 \cdot 2H_2O$) of reagent grade, and the other materials were used as received.

### Measurement of the solubilities of EMA and styrene in ethanol/water medium

EMA (5.0 g) and styrene (5.0 g), respectively, was added to ethanol/water (0/20–11/9, w/w) media (20 g) in 30 ml glass cylindrical reactors (inner diameter: 27 mm) and these reactors were left at 20 °C for 4 h. The amounts of EMA and styrene dissolving in ethanol/water media were measured by gas chromatography (Yanaco, G-2800, Japan) with nitrogen as a carrier gas. Chromosorb W AW-DMCS (stationary phase, 25% polyethyleneglycol) was used as the column packing. Each temperature of the gas chromatographic measurement was: injector, 200 °C; column, 120 °C; detector, 200 °C.

### Swelling of PS seed particles with EMA utilizing DSM

Monodispersed PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous work [7]. Swelling of PS seed particles with a large amount of EMA was carried out under the conditions listed in Table 1 as follows. To the homogeneous solution of ethanol, water, EMA, V-70, and PVA, PS particles were dispersed. Finally, water (12 g) was added to the dispersion with a microfeeder at a rate of 2.88 ml/h under stirring with a magnetic stirrer at 20 °C.

### Seeded polymerization

The seeded polymerization for the dispersion of EMA-swollen PS particles was carried out in a sealed tube under a nitrogen atmosphere at 30 °C for 24 h. The sealed tube was shaken horizontally at 120 cycles/min (2 cm strokes). The conversion was measured by gas chromatography.

### Diameter measurements

The number-average diameter ($D_n$), weight-average diameter ($D_w$), and coefficient of variation ($C_v$) were determined by measuring 150–200 droplets and particles on optical micrographs and transmission electron microscopic (TEM) negative films with the Personal Image Analysis System (PIAS Co., Ltd., LA-525).

## Results and discussion

Figure 1 shows a TEM photograph of PS seed particles produced by dispersion polymerization in an ethanol/water medium according to the previous article [7]. The size distribution of PS seed particles was: $D_n$, 1.71 μm; $D_w/D_n$, 1.004; $C_v$, 2.2%.

Figure 2 shows solubility curves of EMA and styrene in ethanol/water media at 20 °C. The solubilities of EMA and styrene decreased with decrease in the ethanol content. This indicates that EMA is continuously separated

**Table 1** Recipes for the preparation of EMA-swollen PS particles utilizing the dynamic swelling method

| Ingredients | | No. 1 | No. 2 | No. 3 |
|---|---|---|---|---|
| PS particles[a)] | [mg] | 6 | 6 | 6 |
| EMA | [g] | 0.5 | 0.5 | 0.5 |
| V-70 | [mg] | 10 | 10 | 10 |
| PVA | [mg] | 15 | 15 | 15 |
| Ethanol | [g] | 4.0 | 4.0 | 4.0 |
| Water | [g] | 4.0 + 12.0[b)] | 4.0+12.0[b)]+11.5[c)] | 4.0+12.0[b)]+11.5[c)] |
| NaCl | [g] | — | 2.5[c)] | 2.5[c)] |
| $CuCl_2$ | [g] | — | — | Variable[d)] |

[a)] $D_n$, 1.71 μm; $C_v$, 2.2%.
[b)] 12.0 g of water was added using a microfeeder at the rate of 2.88 ml/h at 20 °C.
[c)] 11.5 g of water dissolving 2.5 g of NaCl was added using the microfeeder at the rate of 2.88 ml/h at 20 °C.
[d)] $CuCl_2$ aqueous solution (80 g/l) was added collectively at 20 °C.
Abbreviations: PS, polystyrene; EMA, ethyl methacrylate; PVA, poly(vinyl alcohol); V-70, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile).

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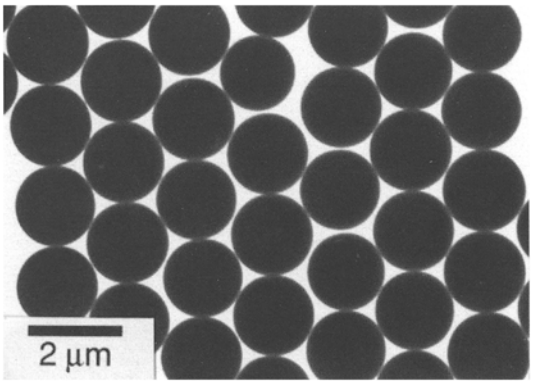


**Fig. 1** A TEM photograph of PS seed particles produced by dispersion polymerization according to the previous article [7]

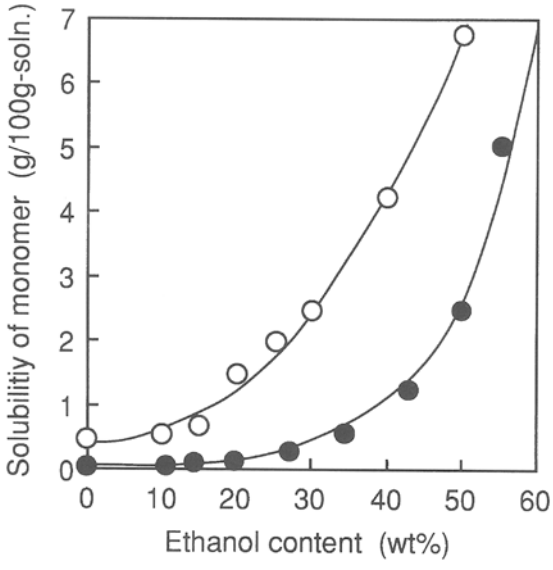


**Fig. 2** Solubility curves of monomers in the ethanol/water media at 20 °C: ○, EMA; ●, styrene

from the homogeneous solution of ethanol–water–EMA by slow dropwise water addition as well as styrene in the previous article [10].

In DSM, it is important to control the separation rate of monomer from medium for the preparation of monodispersed highly monomer-swollen polymer particles [10, 14]. Therefore, on the basis of the swelling conditions in the styrene system [10], swelling conditions of EMA utilizing DSM such as recipe and additional rate of water were decided as shown in Table 1.

Figure 3 shows variations of the amounts of EMA and styrene separated independently from each ethanol/water solution by water addition, which were calculated with corresponding solubility curves shown in Fig. 2. In the

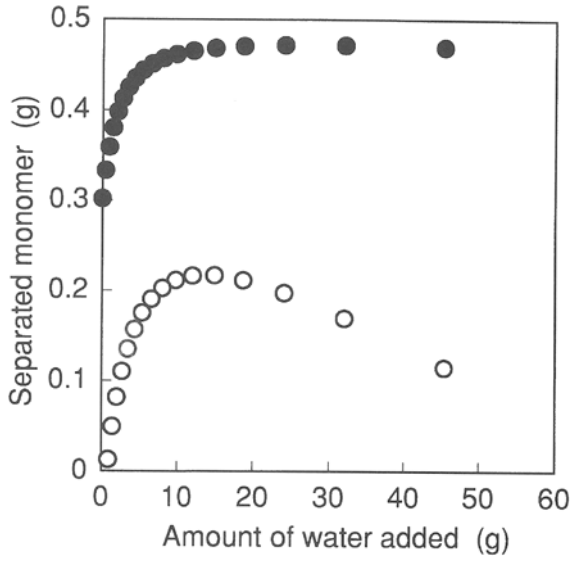


**Fig. 3** The amount of EMA (○) and styrene (●) separated from ethanol (4 g)/water (4 g) media of corresponding monomers (0.5 g) by water addition, which were calculated with corresponding solubility curves at 20 °C

case of styrene, as the amount of water addition was increased, the amount of styrene separated increased to a maximum value at 24 g of water addition, which corresponded to 94% of total amount in the solution, and above that the maximum value was almost kept. On the other hand, in the case of EMA, the amount of EMA separated attained a maximum value at 12 g of water addition, which corresponded to 48%, and above that it markedly decreased. In this way, because EMA is more hydrophilic than styrene, rather much monomer still dissolved in the medium even at the maximum amount separated.

Figure 4a shows an optical micrograph of the EMA-swollen PS particles prepared utilizing DSM at 20 °C under the conditions listed in No. 1 of Table 1, where the amount of EMA dissolving in the medium was minimum. The particle-size distribution was: $D_n$, 7.03 μm; $D_w/D_n$, 1.012; $C_v$, 5.8%. Monodispersed "highly" swollen particles in which the PS seed particles absorbed about 70 times weight of EMA monomer were prepared utilizing DSM.

Seeded polymerization for the dispersion of the EMA-swollen PS particles was carried out at 30 °C for 24 h with V-70 initiator of which half-life period at 30 °C is 10 h. The difference in the solubilities of EMA at 20 °C and 30 °C was very small. Throughout the seeded polymerization, macrocoagulum was formed, and no micron-sized particles and a lot of ca. 200 nm-sized by-produced polyethyl methacrylate (PEMA) particles were observed with TEM. When 75% of the medium consisting of the ethanol/water

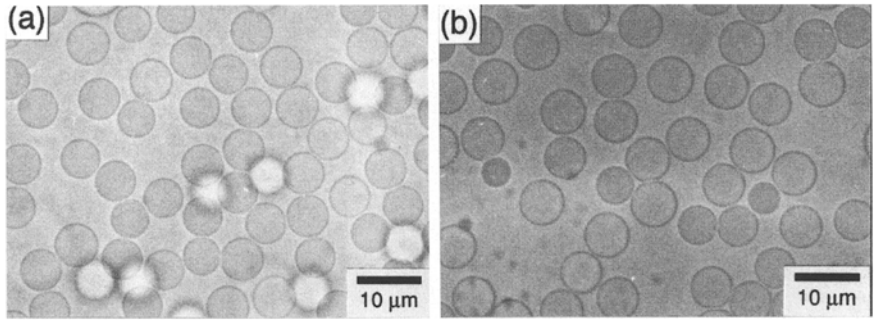


**Fig. 4** Optical micrographs of EMA-swollen PS particles prepared utilizing the dynamic swelling method before (a) and after (b) the addition of NaCl in the medium. Conditions are listed in Table 1

ratio of 4/16 (w/w) was removed to decrease the amount of EMA dissolving in the medium by centrifugation ($112 \times g$, 2 min) prior to the seeded polymerization, the formation of macrocoagulum was obviously depressed. After this, the removal of 75% of medium was always carried out prior to seeded polymerization to depress coagulation. However, in the system, the size of the produced PS/PEMA composite particles was 1.87 $\mu$m which was extremely small in comparison with the presumed size (6.33 $\mu$m) based on the recipe assuming that the polymerization of all EMA in the system is completely carried out within the PS seed particles, and a lot of ca. 200 nm-sized by-produced PEMA particles were still produced. The amount of by-produced PEMA particles per total PEMA was determined to be 99.6% by calculation from the $D_n$ values of PS seed and PS/PEMA composite particles. These suggest that the polymerization hardly proceeded in the swollen particles. This seems to be based on the high solubility of EMA (1.28 g/100 g-medium) in ethanol/water (4/16, w/w) medium at 30 °C.

On the other hand, in the seeded polymerization of divinylbenzene (DVB) in an ethanol/water (7/43, w/w) medium at 70 °C utilizing DSM carried out in the previous article [11], the polymerization proceeded smoothly in swollen particles and 4.29 $\mu$m-sized monodispersed PS/polydivinylbenzene particles were produced from highly DVB-swollen PS particles (4.30 $\mu$m in size). The solubility of DVB in the ethanol/water medium at 70 °C was 0.01 g/100 g-medium, which was much lower than the solubility of EMA at 30 °C in the above seeded polymerization system. Therefore, in order to decrease the solubility of EMA in the medium, 11.5 g of water dissolving 2.5 g of NaCl was added to the dispersion with a microfeeder at a rate of 2.88 ml/h, as listed in No. 2 of Table 1. The solubility of EMA in the ethanol/water (8/55, w/w) medium dissolving NaCl at 30 °C was lowered to be 0.26 g/100 g-medium which corresponded to about 1/5 of that before the addition of NaCl solution.

Figure 4b shows an optical micrograph of the EMA-swollen PS particles prepared utilizing DSM at 20 °C under the conditions listed in No. 2 of Table 1. The particle-size distribution was: $D_n$, 7.52 $\mu$m; $D_w/D_n$, 1.003; $C_v$, 5.2%. This indicates that the addition of NaCl did not reduce the monodispersity.

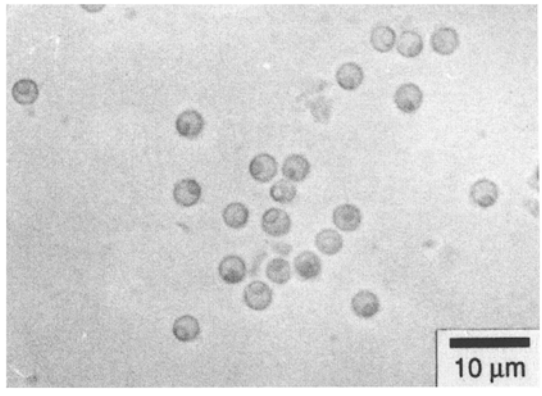


**Fig. 5** An optical micrograph of PS/PEMA composite particles produced by seeded polymerization under the conditions listed in No. 2 of Table 1

Figure 5 shows an optical micrograph of PS/PEMA composite particles produced by seeded polymerization for the dispersion of EMA-swollen PS particles shown in Fig. 4b. The size of the produced composite particles increased to about 3–4 $\mu$m, but they were polydisperse and a lot of ca. 200 nm-sized PEMA particles were still by-produced. The composite particles had uneven surface because of the adsorption of the by-produced PEMA particles on them, and their sizes were larger than that (1.87 $\mu$m) of particles (photograph was omitted) produced in the system without NaCl but still smaller than the presumed one (6.92 $\mu$m).

Incidentally, in the seeded polymerization of styrene in an ethanol/water (6/44, w/w) medium at 70 °C utilizing DSM carried out in the previous articles [10, 12], the polymerization proceeded smoothly in swollen particles, and about 6 $\mu$m-sized monodispersed PS particles and no by-produced PS particles were produced by adding $NaNO_2$ (0.1 g/l-medium) as a water-soluble inhibitor. The solubility of styrene in the ethanol/water medium at 70 °C was 0.12 g/100 g-medium, which was about half as that of EMA (0.26 g/100 g-medium) in the ethanol/water medium

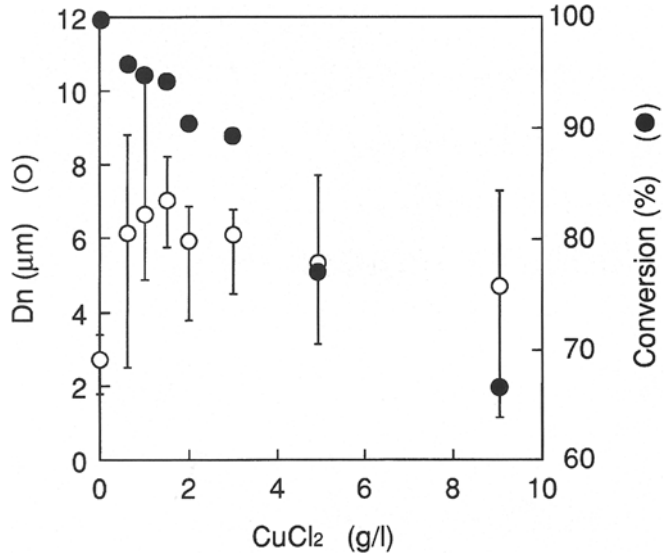


**Fig. 6** Effects of $CuCl_2$ concentration on the $D_n$ (○) value of PS/PEMA composite particles produced by seeded polymerization under the conditions listed in No. 3 of Table 1 and the conversion (●)

dissolving NaCl at 30 °C. On the basis of this result, in order to depress completely the by-production of PEMA particles in this study, water-soluble inhibitors such as $NaNO_2$, hydroquinone, and $CuCl_2$ were examined. As a result, $CuCl_2$ was the most useful for the purpose.

Figure 6 shows effects of $CuCl_2$ concentration on the $D_n$ value of the produced PS/PEMA composite particles and the conversion of EMA. Below 1.0 g/l, as the $CuCl_2$ concentration increased the $D_n$ value of PS/PEMA composite particles increased, and the conversion of EMA attained above 95%. However, the $D_n$ values were still smaller than the presumed one (6.92 $\mu$m), and submicron-sized by-produced PEMA particles were still observed. Above 2.0 g/l, by-produced PEMA particles were not observed. However, as the $CuCl_2$ concentration increased the $D_n$ value decreased and size distribution became broad, and the conversion was less than 90%. At

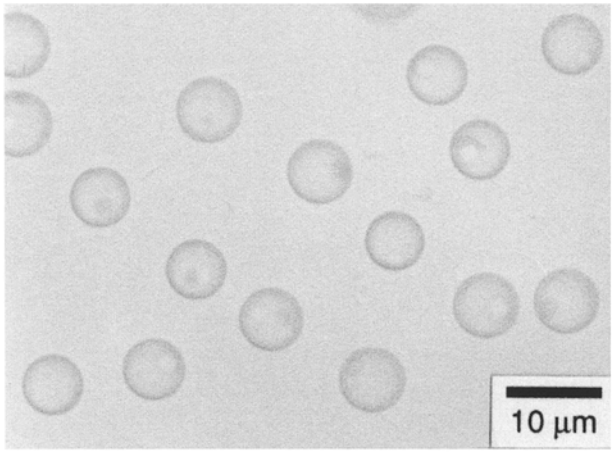


**Fig. 7** An optical micrograph of PS/PEMA composite particles produced by seeded polymerization at an optimum concentration of $CuCl_2$ (1.5 g/l) under the conditions listed in No. 3 of Table 1

1.5 g/l, no submicron-sized by-produced particles was observed and the conversion attained 95%. The size distribution of the composite particles was: $D_n$, 7.04 $\mu$m; $D_w/D_n$, 1.013; $C_v$, 6.4% (see Fig. 7). The $D_n$ value obtained agreed well with the presumed one (6.92 $\mu$m).

When only $CuCl_2$ (1.5 g/l) existed in the dispersion of monodispersed swollen particles without the addition of NaCl after the removal of 75% of the medium, a lot of submicron-sized by-produced PEMA particles and polydispersed PS/PEMA composite particles were observed after the seeded polymerization, and the size distribution of PS/PEMA composite particles was: $D_n$, 4.84 $\mu$m; $D_w/D_n$, 1.059; $C_v$, 13%.

From the above results, it is concluded that 7 $\mu$m-sized monodispersed PS/PEMA composite particles can be produced by seeded polymerization for the dispersion of monodispersed "highly" EMA-swollen PS particles prepared utilizing DSM, in which the polymerization in the medium must be depressed.

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