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ORIGINAL CONTRIBUTION

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Influences of the locations of monomer and initiator in the seeded polymerization systems on the morphologies of micron-sized monodispersed composite polymer particles

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Abstract Three kinds of micron-sized monodispersed polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) composite particles (PS/BMA = 2/1, wt. ratio) were produced by two kinds of seeded polymerizations of *n*-butyl methacrylate (BMA) in the presence of about 2 μm-sized monodispersed PS particles, and their morphologies were examined. One was produced by a seeded dispersion polymerization where almost monomers and initiators exist in an ethanol/water (1/1, w/w) medium. The others two were produced by seeded polymerizations utilizing the dynamic swelling method, where almost monomers exist in the PS seed particles, with 2,2′-azobisisobutyronitrile initiator in the monomer-swollen particles and with 2,2′-azobis [2-(2-imidazolin-2-yl)propane] initiator in an ethanol/water (1/5, w/w) medium. In the former polymerization, the produced composite particles had a core-shell structure consisting of a PS-core and a PBMA-shell, whereas in the latter two polymerizations, they had a POO (Polymeric Oil-in-Oil) structure consisting of a PS-matrix and many PBMA-domains, regardless of the location of initiator in the systems. From these results, it is concluded that the location of BMA monomer in the seeded polymerization systems with micron-sized monodispersed PS seed particles greatly affects the morphologies of produced PS/PBMA composite particles.

Key words Composite polymer particles – seeded polymerization – dispersion polymerization – morphology – dynamic swelling method

Introduction

Micron-sized monodispersed polymer particles can be used as carriers for chromatography, spacers for the gap between two phases of a liquid crystal display, and toners for xerography. Almog et al. [1] showed that the dispersion polymerization technique is useful for the production of such particles though they did not use the term "dispersion polymerization" in their paper. In this method, the system is entirely homogeneous before the polymerization, and the particles are formed by aggregation of polymers produced by the polymerization.

We also produced about 2 μm-sized monodispersed polystyrene (PS) particles by the dispersion polymerization of styrene (S) using poly(acrylic acid) as a colloidal stabilizer and 2,2′-azobisisobutyronitrile (AIBN) as an initiator in ethanol/water mixture medium [2]. The seeded dispersion copolymerization of S and chloromethylstyrene, and that of S and divinylbenzene (DVB) in the presence of the PS particles resulted in about 2 μm-sized monodispersed polymer particles having chloromethyl groups and vinyl groups at the surfaces, respectively [2, 3]. The latter particles had a cross-linking structure. During the seeded dispersion polymerizations, almost monomers do not exist in the seed particles, but in the medium.

Moreover, in order to produce monodispersed polymer particles having more than 5 μm in diameter, we suggested seeded polymerization utilizing a new type of swelling method which was named "the dynamic swelling method (DSM)" [4, 5]. DSM enables the PS particles to swell with a large amount of monomer. By seeded polymerization of DVB [6] and by seeded copolymerization of S and DVB [7] with DSM, about 5 μm-sized monodispersed highly cross-linked polymer particles were produced.

The cross-linking structure and the distribution of vinyl groups due to DVB unit in PS/S-DVB copolymer composite particles produced by the seeded copolymerization utilizing DSM were different from those by the seeded dispersion copolymerization [7]. This seems to be based on the difference in partition states of the S and DVB monomers between particle and medium in both seeded copolymerization systems. In the former system, almost monomers exist in the seed particles, whereas in the latter system almost monomers exist in the medium. This suggests the possibility to control morphology in micron-sized monodispersed composite polymer particles though they were a special system because DVB is a cross-linking monomer.

In this article, in order to clarify the influences of the locations of monomer and initiator in the seeded polymerization systems on the particle morphologies, seeded polymerizations utilizing DSM and seeded dispersion polymerization with *n*-butyl methacrylate (BMA) as one of general methacrylic monomer were carried out with 1.76 μm-sized monodispersed PS seed particles.

Table 1 Recipe for the production of PS/PBMA composite particles by seeded dispersion polymerization[a]

Ingredients				
PS particles[b]	(g)	0.4		
BMA	(g)	0.2		
AIBN	(mg)			2.3[c]
Ethanol	(g)	15	+	3[c]
Water	(g)	18		

[a] 70 °C, 24 h, N_2; Prior to the polymerization, the dispersion was kept at 0 °C for 24 h under gentle stirring.
[b] *Dn*, 1.76 μm; *Cv*, 2.2%.
[c] 3 g of ethanol dissolving 2.3 mg of AIBN was added just before the polymerization.
Abbreviations: PS, polystyrene; BMA, *n*-butyl methacrylate; AIBN, 2,2'-azobisisobutyronitrile.

Table 2 Recipe for the production of PS/PBMA composite particles by seeded polymerizations[a] with VA-061 (A) and AIBN (B) initiator for dispersion of BMA-swollen PS particles prepared utilizing DSM

Ingredients		(A)	(B)
PS particles[b]	(g)	1.2	1.2
BMA	(g)	0.6	0.6
VA-061	(mg)	10.6[c]	
AIBN	(mg)		6.9
Ethanol	(g)	18	18
Water	(g)	9 + 72[d] + 9[c]	9 + 81[d]

[a] 70 °C, 24 h, N_2.
[b] *Dn*, 1.76 μm; *Cv*, 2.2%.
[c] 9 g of water dissolving 10.6 mg of VA-061 was added just before the polymerization.
[d] 72 or 81 g of water was post-added at the rate of 8.64 ml/h at room temperature.
Abbreviations: PS, polystyrene; BMA, *n*-butyl methacrylate; VA-061, 2,2'-azobis[2-(2-imidazolin-2-yl)propane]; AIBN, 2,2'-azobisisobutyronitrile.

Experimental

Materials

S and BMA were purified by distillation under reduced pressure in a nitrogen atmosphere. AIBN and 2,2'-azobis [2-(2-imidazolin-2-yl)propane] (VA-061, Wako Pure Chemical Industries, Ltd., Japan) of reagent grade were purified by recrystallization. Deionized water with a specific conductivity of $5 \times 10^6\ \Omega \cdot$cm was distilled. Reagent-grade ethanol and acetic acid were used as received.

Preparation of seed particles

Monodispersed PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous work [2]. The PS seed particles were observed with a JEOL JEM-200CX transmission electron microscope (TEM). The number-average diameter (*Dn*) and the coefficient of variation (*Cv*) measured with the Personal Image Analysis System (PIAS Co., Ltd., LA-525, Japan) were, respectively, 1.76 μm and 2.2%.

Seeded dispersion polymerization of BMA

Seeded dispersion polymerization of BMA was carried out in the presence of PS seed particles in a sealed glass tube under a nitrogen atmosphere at 70 °C for 24 h under the conditions listed in Table 1. The tube was horizontally shaken at 120 cycles/min (2-cm strokes). The mixture was kept at 0 °C for 24 h under shaking prior to the polymerization. The produced PS/poly(*n*-butyl methacrylate) (PBMA) composite particles were observed with TEM and with a Hitachi S-2500 scanning electron microscope (SEM).

Seeded polymerization of BMA utilizing DSM

Two types of DSMs were carried out under the conditions listed in Table 2. PS seed particles were dispersed in a homogeneous solution of ethanol, water, and BMA. In the first type of DSM (A), water was added dropwise to the mixture at a rate of 8.64 ml/h with a micro feeder under stirring at room temperature and finally VA-061 initiator solution was added. In the second type of DSM (B), AIBN initiator was dissolved in the medium, then water was added dropwise to the mixture at the rate of 8.64 ml/h.

The seeded polymerizations for the dispersions of BMA-swollen PS particles produced utilizing the two types of DSMs were carried out at 70 °C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask. The reaction mixtures were stirred at 60 rpm.

Determination of the amount of BMA monomer in the medium

The dispersion media of BMA-swollen PS particles in the seeded dispersion polymerization system and in the seeded polymerization system utilizing DSM were separated by centrifugation, and then the amount of BMA dissolved in each medium was determined by gas chromatography.

Extraction of PBMA from PS/PBMA composite particles

The medium of each PS/PBMA emulsion was changed from ethanol/water to acetic acid by repeated centrifugation. Acetic acid dissolves PBMA but not PS. Acetic acid dispersion of each PS/PBMA composite particles was maintained under stirring at 40 °C for 72 h.

Observation of ultrathin cross-sections of PS/PBMA composite particles

Dried PS/PBMA composite particles before and after the extraction treatment of PBMA with acetic acid were exposed to RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution, and then dispersed in epoxy matrix, cured at room temperature for 24 h, and microtomed. The ultrathin cross-sections were observed with TEM.

Results and discussion

Figure 1 shows TEM photographs of PS/PBMA composite particles produced by seeded dispersion polymerization under the conditions listed in Table 1, before (a) and after (b) centrifugal washing. A small amount of 200 nm-sized by-produced PBMA particles were observed, but they were easily removed by the washing. The produced composite particles had an anomalous shape.

Figure 2a shows a TEM photograph of PS/PBMA composite particles produced by seeded polymerization with VA-061 initiator dissolved in medium for dispersion of BMA-swollen PS particles prepared utilizing DSM under the conditions listed in Table 2A. Figures 2b, c show those by seeded polymerization for dispersion of BMA-swollen PS particles containing AIBN initiator prepared utilizing DSM under the conditions listed in Table 2B, before (b) and after (c) centrifugal washing. In all photographs in Fig. 2, spherical particles were observed regardless of the location of each initiator in the polymerization systems. In the former polymerization (Fig. 2a), no by-produced PBMA particle was observed. In the latter one (Fig. 2b) a small amount of 90 nm-sized by-produced PBMA particles were observed, but they were easily removed by the washing.

Table 3 shows the partition states of BMA between the medium and the particles in the seeded dispersion polymerization and in the seeded polymerization with DSM.

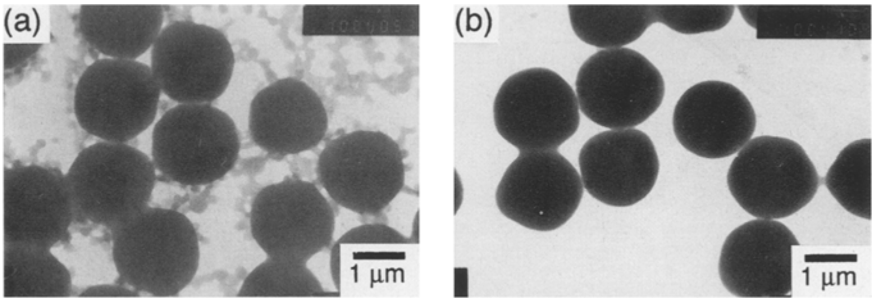


Fig. 1 TEM photographs of PS/PBMA composite particles produced by seeded dispersion polymerization under the conditions listed in Table 1, before (a) and after (b) centrifugal washing to remove by-produced PBMA particles

Fig. 2 TEM photographs of PS/PBMA composite particles produced by seeded polymerizations with VA-061 (a) and AIBN (b, c) initiators for dispersions of BMA-swollen PS particles prepared utilizing DSM under the conditions listed in Table 2, before (a, b) and after (c) centrifugal washing to remove by-produced PBMA particles

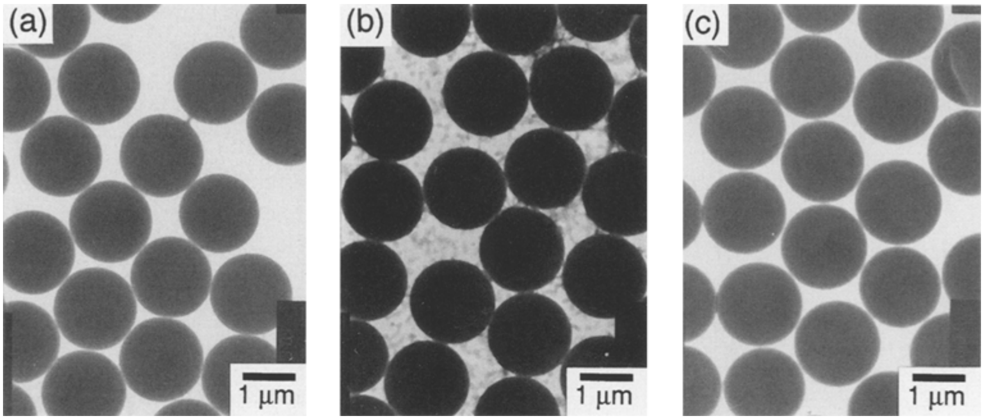


Table 3 Distributions of BMA monomer in the particles and in the medium after the swelling process in the seeded dispersion polymerization system and in the seeded polymerization system utilizing DSM

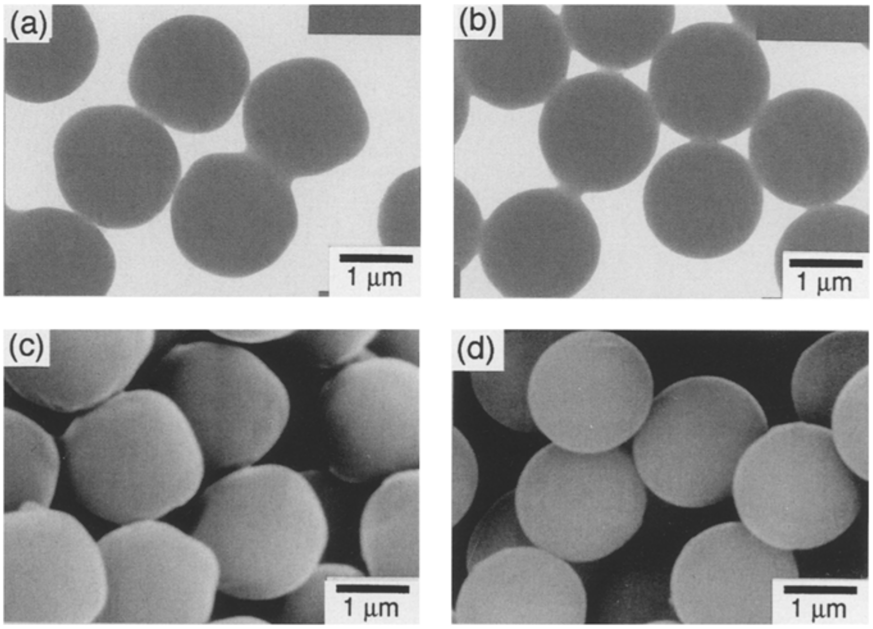
	BMA monomer in particles	BMA monomer in medium
Seeded dispersion polymerization system	8.6%	91.4%
Seeded polymerization system utilizing DSM	93.8%	6.2%

In the seeded dispersion polymerization, almost all BMA monomers dissolved in the medium, whereas in the seeded polymerization almost all the monomers existed in the seed particles.

These results suggest that the partition state of monomer affects the shape of the composite particles.

Figure 3 shows TEM (a, b) and SEM (c, d) photographs of PS/PBMA composite particles produced by the seeded dispersion polymerization in which almost all BMA monomers and AIBN initiators existed in the medium, before (a, c) and after (b, d) extraction with acetic acid. The anomalous particles were changed to spherical particles by the extraction. TEM photographs of their ultrathin cross-sections are shown in Fig. 4. These photographs indicate that the composite particles have a core-shell structure consisting of a PS-core and a PBMA-shell. The PBMA-shell layer gave the anomalous shape and the removal of the shell layer by acetic acid resulted in the spherical particles, though they looked like ellipsoidal

Fig. 3 TEM (a, b) and SEM (c, d) photographs of PS/PBMA composite particles produced by seeded dispersion polymerization under the conditions listed in Table 1, before (a, c) and after (b, d) extraction with acetic acid



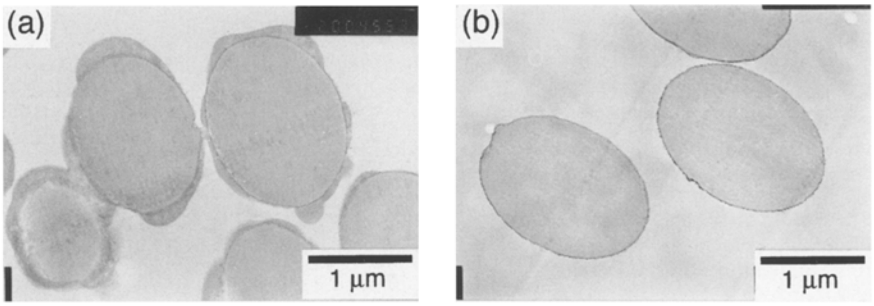


Fig. 4 TEM photographs of ultrathin cross-sections of PS/PBMA composite particles produced by seeded dispersion polymerization under the conditions listed in Table 1, before (a) and after (b) extraction with acetic acid

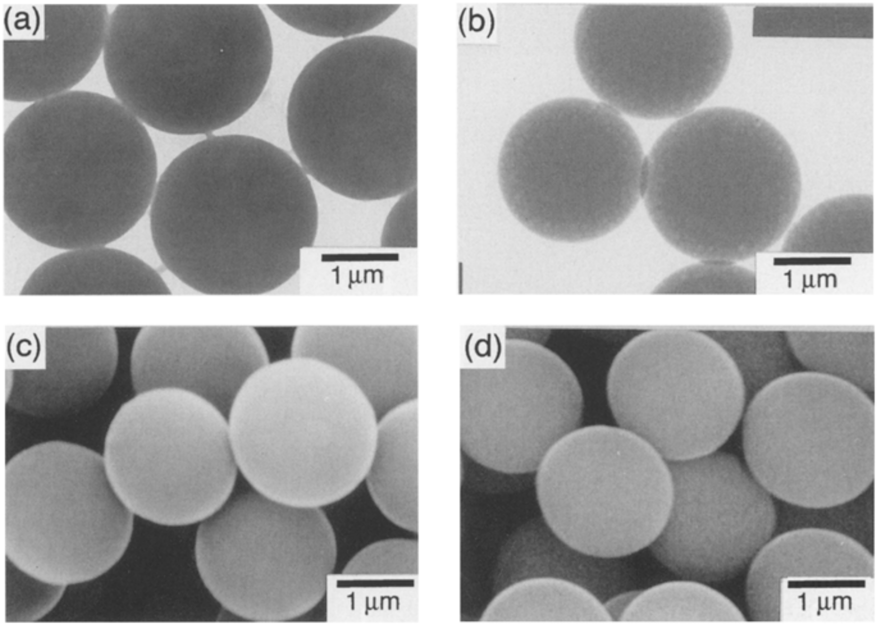


Fig. 5 TEM (a, b) and SEM (c, d) photographs of PS/PBMA composite particles produced by seeded polymerization with VA-061 initiator dissolved in medium for dispersion of BMA-swollen PS particles prepared utilizing DSM under the conditions listed in Table 2, before (a, c) and after (b, d) extraction with acetic acid

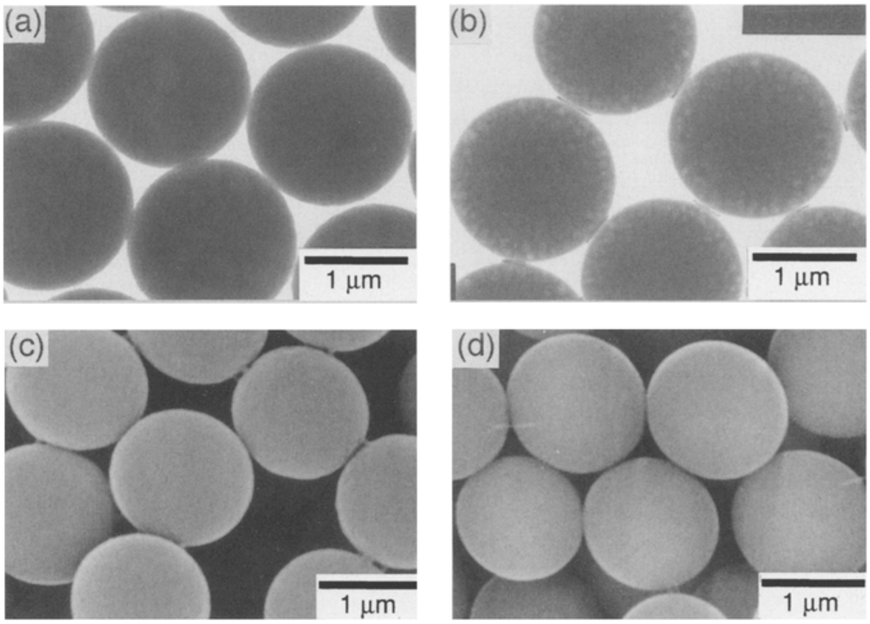


Fig. 6 TEM (a, b) and SEM (c, d) photographs of PS/PBMA composite particles produced by seeded polymerization for dispersion of BMA-swollen PS particles containing AIBN initiator prepared utilizing DSM under the conditions listed in Table 2, before (a, c) and after (b, d) extraction with acetic acid

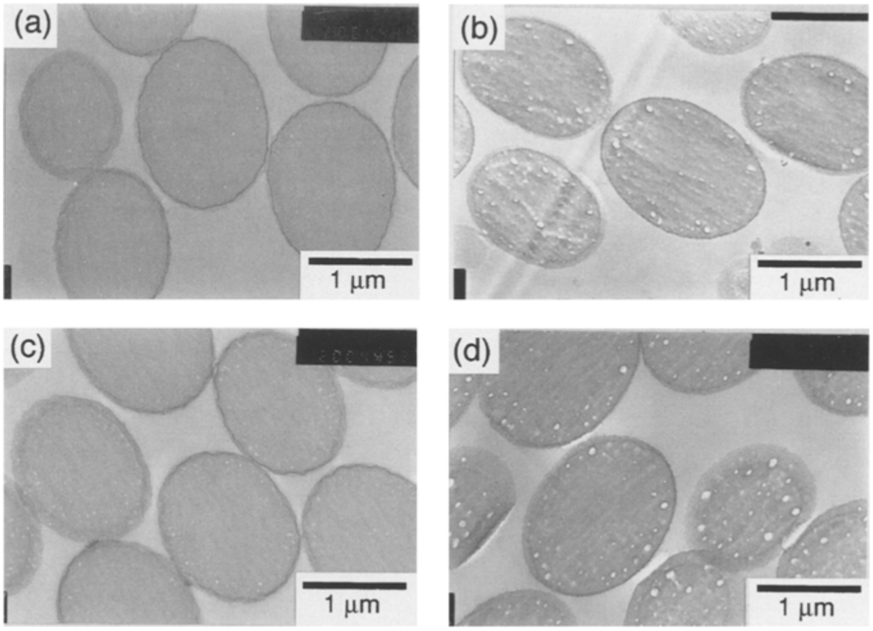


Fig. 7 TEM photographs of ultrathin cross-section of PS/PBMA composite particles produced by seeded polymerizations with VA-061 (a, b) and AIBN (c, d) initiators for dispersions of BMA-swollen PS particles prepared utilizing DSM under the conditions listed in Table 2, before (a, c) and after (b, d) extraction with acetic acid

shape in Fig. 4 because of compressive stress deformation by microtome.

Figures 5 and 6 show TEM (a, b) and SEM (c, d) photographs of PS/PBMA composite particles produced by seeded polymerizations, respectively, with VA-061 (Fig. 5) and with AIBN (Fig. 6) initiators utilizing DSM, before (a, c) and after (b, d) extraction with acetic acid. In the TEM photographs shown in Figs. 5b and 6b, it was observed that both acetic acid-treated particles had many low-contrast regions. In the SEM photographs shown in Figs. 5d and 6d it was observed that the both acetic acid-treated particles had a spherical shape without unevenness.

Figure 7 shows TEM photographs of ultrathin cross-sections of their particles exposed with RuO_4 which stains not PBMA, but PS [8]. In Figs. 7a, c, many small PBMA domains were observed at the surface layer of the composite particles and in Figs. 7b, d many hollows which were formed by the removal of PBMA domains with acetic acid treatment were observed. These photographs indicate that the PS/PBMA composite particles produced by seeded polymerization utilizing DSM, in which almost BMA monomers existed in the PS seed particles, had a POO (Polymeric Oil-in-Oil) structure consisting of a PS matrix and PBMA domains, regardless of the location of the initiators.

From these results, it is concluded that the location of BMA monomer in the seeded polymerization systems with micron-sized monodispersed PS particles greatly affects the morphology of the produced PS/PBMA composite particles.

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