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SHORT COMMUNICATION

Synthesis of large-sized monodisperse polystyrene microspheres by dispersion polymerization with dropwise monomer feeding procedure

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Abstract Highly monodisperse polystyrene (PS) microspheres in the size range of 3.75–7.09 μm were synthesized by dispersion polymerization with dropwise monomer feeding procedure. The morphology, size, and particle size distribution (PSD) of the PS microspheres obtained by different monomer feeding modes, including batch polymerization and various feeding rates, were investigated. The PSD of particles showed a close dependence on feeding rate. The PS microspheres with low coefficient of variation (CV) values all less than 4.8% obtained by the optimum feeding rates revealed better uniformity than those by batch polymerization (CV values all more than 8.2%). According to the time courses of monomer conversion and particle numbers, the effects of monomer feeding modes on the polymerization reaction of the large-sized PS microspheres were clarified. It is found that the dropwise monomer feeding procedure is promising for the synthesis of large-sized monodisperse PS particles in 3.75–7.09 μm.

Keywords Dispersion polymerization · Polystyrene microspheres · Monomer feeding procedure · Particle size distribution

Abbreviations

PS	polystyrene
PSD	particle size distribution
CV	coefficient of variation
ACF	anisotropic conductive films
St	styrene
AIBN	2, 2′-azobisiso-butyronitrile
PVP	poly-vinyl-pyrrolidone

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Introduction

In recent years, uniform polystyrene (PS) microspheres of large size, especially beyond 3 μm, have found ever-increasing applications in the fields of microelectronics [1], colloid sciences [2], biotechnology [3], etc. For example, 3–5-μm particles with a low coefficient of variation (CV) value less than 5%, which act as conductive particles in anisotropic conductive films, are in great demand [4]. Typical methods developed in the past for synthesizing large-sized PS particles are dispersion polymerization [5], seeded polymerization [6], two-step swelling [7], and dynamic swelling techniques [8]. However, the last three methods are rather tedious and often difficult to be carried out, characteristics which stand as obstacles to their application. In contrast, dispersion polymerization is relatively simple and effective to use in preparing large-sized PS microspheres, despite the fact that PS particles beyond 3 μm synthesized by dispersion polymerization are nonuniform in size. This procedure involves the polymerization of monomer dissolved in a solvent or solvent mixture and then the nuclei precipitate from the medium to give growing particles, which can grow to their final sizes gradually by absorbing monomers in the presence of a stabilizer [9].

The fabrication of large-sized PS microspheres with narrow distribution via dispersion polymerization has attracted considerable attention in recent years. For example, using vinyl-terminated polyurethane macromonomer as a stabilizer, Jung et al. prepared monodisperse PS microspheres by dispersion polymerization [10]. Nakashima et al. also

prepared monodisperse PS microspheres by dispersion polymerization, using sodium polyaspartate as a dispersion stabilizer in ethanol/water medium [11]. Moreover, Yoshida synthesized PS microspheres by dispersion polymerization in supercritical carbon dioxide using a poly(dimethylsiloxane)-based macroazoinitiator [12]. These methods were considered to be effective for the synthesis of monodisperse PS microspheres with diameters less than 4 μm. However, with further increases in particle size, the monodispersity will be difficult to realize via dispersion polymerization. In addition, those macromonomers are often unavailable and costly. As a consequence, the preparation of highly monodisperse PS particles of large size, especially to diameters beyond 4 μm, continues to be a great challenge.

There were few articles dealing with the preparation of large-sized monodisperse PS microspheres by dispersion polymerization with dropwise monomer feeding procedure. Moreover, most researchers considered that small-sized particles with diameters less than 3 μm obtained by dropwise monomer feeding procedure showed lower uniformity than those by batch polymerization because the former had a longer nucleation period than the latter group [13, 14]. In this work, we studied the dispersion polymerization of styrene with dropwise monomer feeding procedure. Highly monodisperse PS microspheres in the size range of 3.75–7.09 μm were prepared by dispersion polymerization at the optimum feeding rates. This paper described the effect of various monomer feeding modes on the particle size distribution (PSD) of those particles. The mechanism of synthesizing large-sized PS microspheres with dropwise monomer feeding procedure was also investigated.

Experimental

Materials

Styrene monomer (Guangzhou Xilong Chemical Factory, chemically pure grade) was washed with 2 M sodium hydroxide aqueous solution, distilled under reduced pressure to remove the inhibitor, and then stored in a refrigerator before use. 2,2′-Azobisiso-butyronitrile (AIBN, Shanghai Forth Chemical Plant, analytical grade), polyvinyl-pyrrolidone (PVP K-30, $M_w=4.0\times10^4$ g mol^{-1}, Beijing Yili Chemical, chemically pure grade), and ethanol (Beijing Chemical Factory, analytical grade) were used without further purification.

Table 1 Recipe for preparing PS microspheres in the size range of 3.75–7.09 μm

Ingredients	3.75 μm	4.32 μm	5.21 μm	6.23 μm	7.09 μm
Styrene (g)	25.00	26.00	28.00	30.00	32.00
AIBN[a] (g)	0.25	0.26	0.28	0.30	0.32
PVP K-30[b] (g)	0.75	0.78	0.84	0.90	0.96
Ethanol (g)	75.00	74.00	72.00	70.00	68.00

Seventy degrees Celsius; 24 h; total weight of monomer and dispersion medium was 100 g

[a] One weight percent of AIBN based on the weight of monomer was added

[b] Three weight percent of PVP K-30 ($M_w=4.0\times10^4$ g mol^{-1}) based on the weight of monomer was added

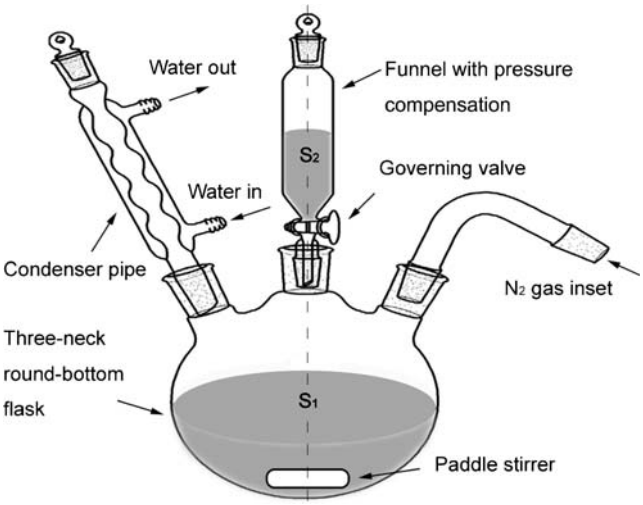

Fig. 1 Sketch of the reaction apparatus for dropwise monomer feeding procedure

Polymerization procedure

The standard recipe used in this paper is given in Table 1. A 250-mL, three-neck, round-bottom flask was employed, which was equipped with a reflux condenser, a nitrogen gas inlet, a Teflon stirrer paddle, and a funnel with pressure compensation involving a governing valve. The reaction apparatus is schematically presented in Fig. 1. A solution (S_1) containing PVP dissolved in ethanol was poured into the reaction flask under a nitrogen atmosphere at 70 °C and with magnetic stirring at 300 rpm. Subsequently, a solution (S_2) composed of styrene and AIBN in the constant-voltage funnel was introduced into the flask with a controllable rate by adjusting the valve. Feeding time was recorded accurately with a stopwatch and feeding rate was calculated according to the feeding time and the volume of solution S_2. The dispersion polymerization was carried out for 24 h and nitrogen gas was maintained throughout the period. The resulting PS microspheres were purified by means of centrifugation, decantation, and redispersion in sequence to remove the residual styrene and PVP. PS microspheres in the size range of 3.75–7.09 μm were prepared similarly by various feeding modes.

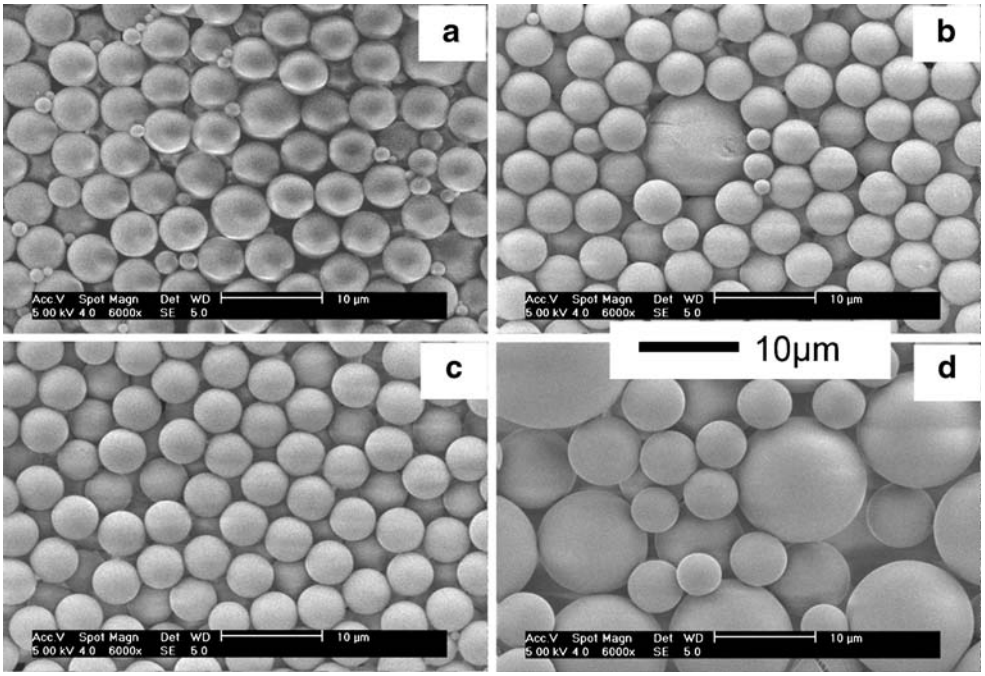

Fig. 2 SEM images of 5.21-μm PS microspheres prepared by different monomer feeding processes. **a** Batch polymerization, **b** a feeding rate of 164.85 μL/s, **c** a feeding rate of 99.53 μL/s, and **d** a feeding rate of 35.48 μL/s

Characterization

A FEI-SIRION scanning electron microscope (SEM) was used to observe the morphology of PS particles. The average particle diameter (D_n) and CV were calculated with the following formulas by counting more than 100 individual particles from SEM microphotographs:

$$D_n = \left(\sum n_i d_i / n_i\right) \tag{1}$$

$$\mathrm{CV} = \frac{\left(\sum (d_i - d_n)^2 / \sum n_i\right)^{1/2}}{D_n} \times 100 \tag{2}$$

where n_i denotes the number of particles with d_i. Monomer conversion was measured gravimetrically. Particle numbers were calculated from D_n and monomer conversion.

Results and discussion

Effect of different monomer feeding modes

Figure 2 shows the morphology of 5.21-μm PS microspheres synthesized by dispersion polymerization with different monomer feeding strategies. It can be seen that the feeding rate of the monomer significantly influences the size distribution of 5.21-μm PS microspheres. Figure 2a shows that the uniformity of PS particles prepared by batch polymerization is very poor and a lot of little particles are produced, which indicates that large-sized PS microspheres with well monodispersity cannot be prepared using batch polymerization. In contrast, 5.21-μm PS microspheres with very narrow size distribution without secondary particles can be obtained when the feeding rate is 99.53 μL/s (Fig. 2c), while size distribution of particles significantly broadens when the feeding rates are 164.85 and 35.48 μL/s, as shown in Fig. 2b and d, respectively. This result indicates that 5.21-μm PS microspheres with narrow size distribution can be obtained when the feeding rate is appropriate.

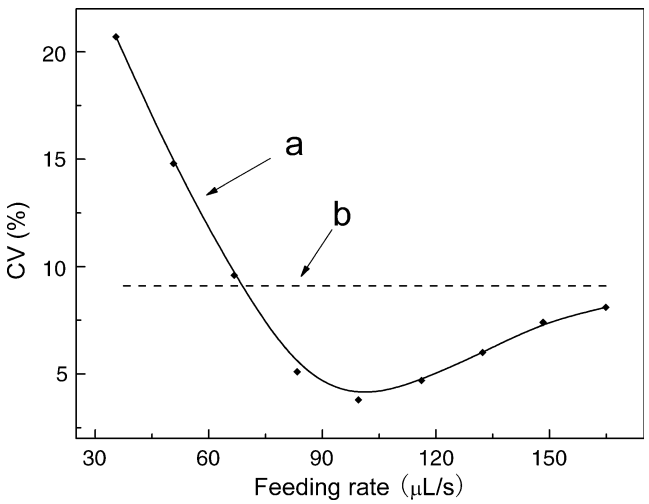

Fig. 3 Effect of monomer feeding rate on CV of PS particles in 5.21 μm. *a*, dropwise monomer feeding procedure and, *b*, batch polymerization method

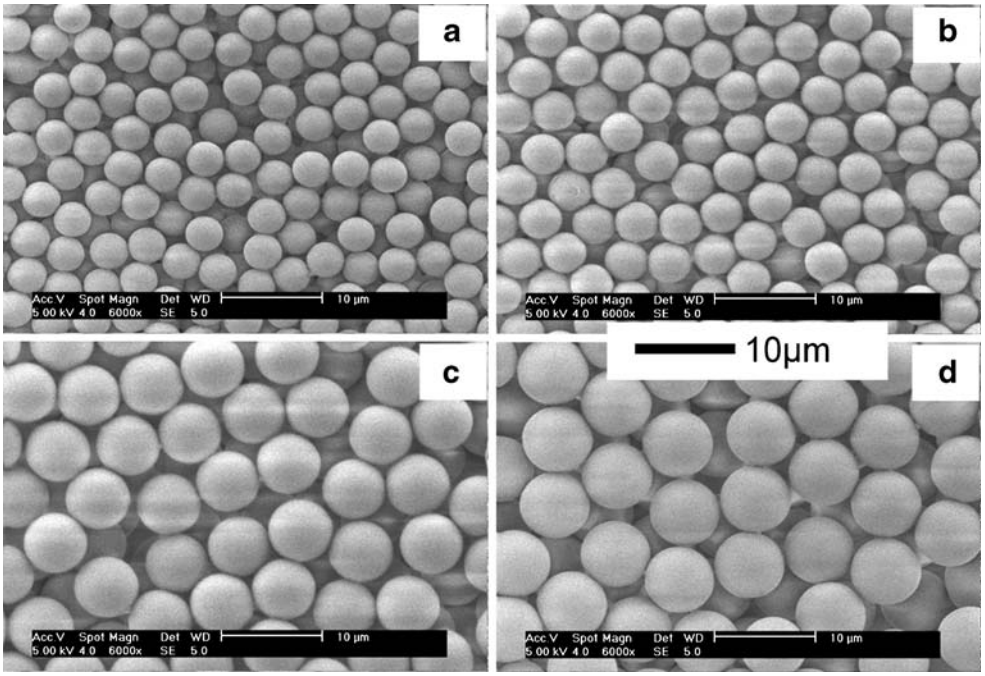

Fig. 4 SEM images of monodisperse PS particles in **a** 3.75, **b** 4.32, **c** 6.23, and **d** 7.09 μm are prepared by dropwise monomer feeding procedure at optimum feeding rates

The CV of 5.21-μm particles, as an indicator of PSD, changed with monomer feeding rate, as is represented in Fig. 3. The broken line in the figure represents the CV of particles by batch polymerization (CV value is 9.5%). Since the feeding processes are controlled accurately, the dependence of the CV of particles on feeding rate is well observed. As the monomer feeding rate decreases from 164.85 to 99.53 μL/s, the CV value of particles steadily decreases from 8.12% to 3.51%. Subsequently, the CV value of PS particles shows a dramatic increase from 3.51% to 20.67%, with the feeding rate further decreasing from 99.53 to 35.48 μL/s. The CV value of particles is the lowest, 3.51%, when the monomer feeding rate is 99.53 μL/s.

To see whether the effect of the monomer feeding rate on CV of particles can only be applied to 5.21-μm particles, we have synthesized PS particles with various diameters, including 3.75, 4.32, 6.23, and 7.09 μm. Figure 4 shows SEM images of those particles prepared by optimum feeding rates. It can be seen that the particles are highly spherical in shape and have good uniformity. Table 2 summarizes the CV of PS microspheres in the size range of 3.75–7.09 μm prepared by different monomer feeding modes. The CV values of the particles prepared by optimum feeding rates are all less than 4.8%, which are much lower than for those prepared by batch polymerization (CV values all more than 8.2%). Moreover, the tendency of CV values of these particles to vary with monomer feeding rates is similar to that of 5.21-μm particles. Therefore, it is confirmed that, in the synthesis of large-sized monodisperse PS microspheres, dropwise monomer feeding procedure is more effective than batch polymerization when feeding rates are appropriate.

Figure 5 shows the dependence of D_n on optimum feeding rate and CV. The optimum feeding rate decreases from 128.71 to 86.62 μL/s and CV values of PS particles show an approximately linear increase from 2.51% to 4.78%, with an increase of the average diameter from 3.75 to 7.09 μm.

Polymerization kinetics in different monomer feeding modes

Figure 6 shows the time courses of styrene conversion and particle numbers of 5.21-μm PS microspheres. It is clear

Table 2 CV of PS microspheres in the size range of 3.75–7.09 μm prepared by different monomer feeding processes

CV by different feeding modes	3.75 μm	4.32 μm	5.21 μm	6.23 μm	7.09 μm
Batch polymerization[a] (%)	8.23	8.95	9.50	10.51	19.40
Dropwise feeding procedure[b] (%)	2.51	2.79	3.51	4.38	4.78

[a] CV of particles by monomer's batch polymerization method
[b] CV of particles by optimum feeding rate of monomer

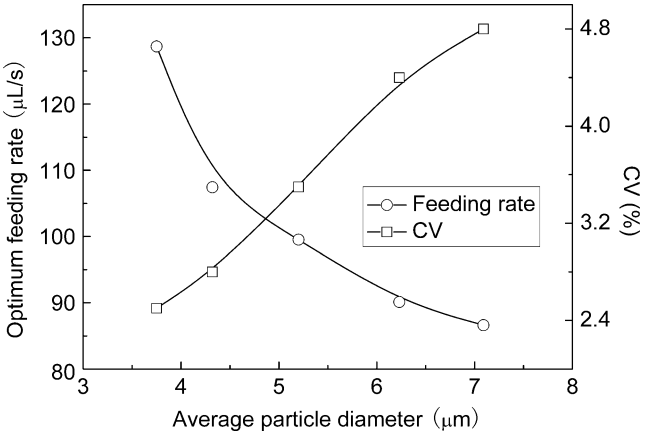

Fig. 5 Dependence of D_n on optimum feeding rate of monomer and CV of particles

that quite different polymerizations take place when monomer feeding modes are different. As shown in Fig. 6a, the polymerization rate with batch polymerization is much faster than other systems. In addition, a decrease in monomer feeding rate results in a significant decrease in polymerization rate and retardation in nucleation period. From Fig. 6b, it is seen that particle numbers decrease with time until the particles stabilize and then trend toward constant values. This implies that obvious coalescence of particles takes place in the polymerization reaction. Moreover, the coalescence reaction has a trend to reduce with the decrease of monomer feeding rate, which indicates that the decrease of monomer feeding rate is an effective route to prevent the coalescence reaction.

Mechanism for different monomer feeding modes

The PSD of resulting particles in ab initio heterophase polymerizations is the result of at least two essential factors: the nucleation and the stability of the particles. In order for the final particles to be uniform in size, the nucleation period should be short and the coalescence of growing particles should be prevented [15, 16]. Obviously, in this study, the final PSD is determined by the interplay between the duration of the nucleation period, the number of nucleation events in the course of the polymerization, and the extent of particle coalescence.

When the batch polymerization is used, a large amount of growing particles appear due to the drastic reactions between the initiator radicals and the solute monomer molecules. This leads to a significant coalescence of particles, and therefore the uniformity of final particles is very poor and a lot of little particles can be observed (Fig. 2a). On the contrary, when the dropwise addition method was used, with the feeding rate decreasing, the free monomer concentration increases due to the lower consumption of the monomer by polymerization. Styrene as the composition of the continuous phase is a solvent for PS chains, whereas ethanol is not (or only for low molecular weight oligomers), namely, the styrene/ethanol ratio that governs the solubility of the growing chains and also their precipitation out of the continuous phase. The greater the free monomer concentration, the stronger the solvency of the continuous phase is [17]. Therefore, it is thought that the growing particles under the condition of more spread own polymer chains due to their better stability at higher free monomer concentrations. This behavior leads to the situation of longer nucleation periods, decreased numbers of growing particles, and reducing coalescence reactions. Moreover, a decrease in the number of growing particles causes the enhancement of stabilizer absorbed on the particles. This also contributes to protect against coalescence processes in polymerization. In this case, although the nucleation period would be somewhat prolonged, the decreased coalescence reactions and reducing number of growing particles may be major influencing factors on the PSD of resulting particles. Therefore, the number of little particles decreases and the PSD of PS particles becomes narrow with the decrease of feeding rate (Fig. 2b).

However, at lower feeding rate, the growing particles can absorb enough monomers to grow to very large sizes due to the excessive solvency of the continuous phase. In addition, the very long nucleation period may result in newly formed oligomeric radicals and growing particles. In

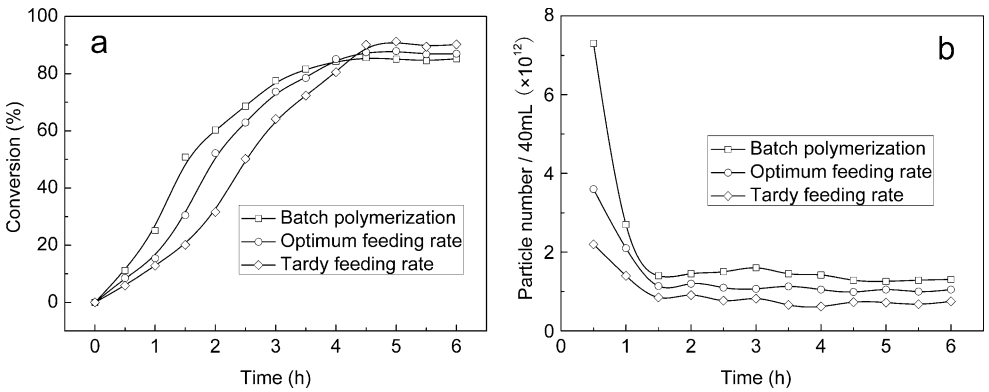

Fig. 6 Time courses of **a** monomer conversion and **b** particle numbers of 5.21-μm PS microspheres are prepared by different monomer feeding modes

this case, the prolonged nucleation period followed by nonuniform growth of the particles is a major influencing factor on the PSD of final particles, despite the fact that the inhibiting effect on the coalescence of particles is still effective. Therefore, lots of large particles appear and the PSD of particles becomes broad drastically with the feeding rate further decreasing (Fig. 2d). Only an appropriate feeding rate can ensure the formation of PS particles with narrow size distribution (Fig. 2c). In this case, the free monomer concentration is appropriate, which results in the uniform growth of the growing particles and the decrease of the coalescence reaction. A delicate equilibrium effect may be maintained between the reducing coalescence reactions, decreased number of nucleation events, and the elongation of nucleation period.

In addition, large-sized PS microspheres have longer reaction processes and need more monomers than those of small microspheres. As a result, the coalescence reactions during the prolonged polymerization process increase. Therefore, the optimum feeding rate decreases with the increasing particle diameters to meet the aforementioned equilibrium. The decrease of feeding rate results in a decrease of free monomer concentration followed by longer nucleation periods and decreased numbers of growing particles. Therefore, the CV value of PS particles shows an approximately linear increase with the increase of D_n.

Conclusions

Highly monodisperse PS microspheres in the size range of 3.75–7.09 μm have been synthesized by a dropwise monomer feeding procedure. The PS microspheres obtained by optimum feeding rate show higher monodispersity than those by batch polymerization. The uniformity of particles shows a strong dependence on feeding rate. With a decreasing feeding rate, the CV of particles decreases gradually and then increases quickly. This indicates that a delicate equilibrium between the reducing coalescence reactions, decreased number of nucleation events, and the elongation of the nucleation period can be reached by adjusting the monomer feeding rate. In addition, with increasing values of D_n, the optimum feeding rate tends to be lower, and the CV values of PS particles show an approximately linear increase. It is obvious that the dropwise monomer feeding procedure is a simple and effective route to prepare large-sized monodisperse PS microspheres 3.75–7.09 μm in size.

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