

Innovative one-step synthesis of hollow polymer particles by microsuspension polymerization of styrene and methyl acrylate with $\text{Mg}(\text{OH})_2$ as dispersant

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Abstract Several methods consisting of two or multi-step processes have been so far proposed for the preparation of sub- and micrometer-sized hollow polymer particles. In this study, we proposed an innovative one-step synthesis of the hollow polymer particles by applying microsuspension copolymerization of styrene and methyl acrylate with $\text{Mg}(\text{OH})_2$ as dispersant. In this method, $\text{Mg}(\text{OH})_2$ acted not only as dispersant, which covered densely at the surface of the monomer droplets, but also caused hydrolysis reaction of MA unit within styrene-methyl acrylate copolymer particles during the polymerization due to giving alkaline pH in the aqueous medium. It is also important that methyl acrylates are predominantly polymerized over styrene at the initial stage of the microsuspension copolymerization.

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Introduction

In recent years, one of the considerable interests in the field of colloid science have centered on the design and synthesis of hollow polymer particles driven by their widespread application including functional coatings, fillers, catalyst loading, and controlled release of drugs due to the excellent properties of their unique cavity structures [1–10]. Therefore, various approaches have been developed to prepare such hollow polymer particles, which can be divided into the post-treatment type and the direct type according to the formation stage of internal hollow structures. For the first type, the hollow structures are formed by post-treatment after the polymerization, including osmotic swelling method [11], stepwise alkali/acid [12, 13], selective removal of core method [14, 15], alkali/cooling method [16, 17], and phase inversion method [18]. Methods such as the dynamic swelling method (DSM) [19, 20], self-assembling of phase-separated polymer method (SaPSeP) [21, 22], seed polymerization [10, 23], and interfacial polymerization [24], in which the hollow structures are generated during the polymerization stage, belong to the direct type. However, most of the methods demand complex processes, the first type needs special procedures after polymerization while the second type often needs to prepare seed polymer before the synthesis of the hollow particles, so they seem to be relatively complicated for mass production. Besides, the use of organic solvent in the latter type is also bound to do harm to the environment, hence a simple and environmentally

friendly one-step strategy to fabricate hollow particles is desired.

In order to simplify complex processes of fabricating hollow polymer particles, we propose an innovative one-step method of preparing micrometer-sized hollow polymer particles by microsuspension copolymerization accompanying a hydrolysis process. The microsuspension copolymerization of styrene (S) and methyl acrylate (MA) was performed with $\text{Mg}(\text{OH})_2$ as dispersant, where $\text{Mg}(\text{OH})_2$ particles also acted as a hydrolysis agent of MA unit in the copolymer particles indirectly due to giving alkaline pH in the aqueous medium. Besides, MA were predominantly polymerized over S at the initial stage of the copolymerization because of the difference in the reactive activity of S and MA, this is also very important for us to prepare hollow polymer particles. The validity and utility of the proposed one-step synthesis of micrometer-sized hollow polymer particles were demonstrated.

Experimental

Materials

Analytical-grade S and MA (Sinopharm Chemical Reagent Company, China) were purified by distillation under reduced pressure and kept at 0 °C before use. All other materials were also purchased from the Sinopharm Chemical Reagent company and used as received, including *p*-phenylenediamine (PPDA; 97%), benzoyl peroxide (BPO; 98%), *tert*-dodecylthiol (TDM; 98%), magnesium chloride hexahydrate, and guaranteed reagent grade of sodium hydroxide (NaOH; 97%). Deionized water was used throughout the experiments.

Preparation of $\text{Mg}(\text{OH})_2$ as dispersant

NaOH (8.40 g) was dissolved into deionized water (76.3 g) and added dropwise to an aqueous solution (194 g) of magnesium chloride hexahydrate (15.0 g) under stirring. When the addition was completed, a formed $\text{Mg}(\text{OH})_2$ suspension was stirred additionally for 30 min at room temperature before being used as a dispersant.

Synthesis of hollow S-MA copolymer (P(S-MA)) particles by microsuspension polymerization with $\text{Mg}(\text{OH})_2$

A typical synthesis was carried out as follows. TDM (0.75 g) and BPO (5.0 g) were dissolved in a mixture of S (90 g) and MA (10 g) to form a monomer phase. PPDA (0.1 g), which was added as one of the water-soluble inhibitors to depress the complication of emulsion polymerization in an aqueous medium, was dissolved in deionized water (40 g) as a water phase. The mixture of the monomer phase, the water phase, and the dispersant was first pre-dispersed by stirring slightly

for 0.5 h and then vigorously with a high shear dispersing machine (ERS 2000/04) at 12,000 rpm for 30 min to obtain a stable dispersion. The dispersion was transferred to a 500-mL four-neck round flask equipped with a reflux condenser, a temperature controller, and an agitator. The microsuspension copolymerization was performed at various temperatures (60–90 °C) for 2 h and followed at 90 °C for 4 h under a nitrogen atmosphere. The reaction was terminated by cooling to room temperature. Formed particles were filtrated with a filter paper (pore size, 10–15 μm) and washed with deionized water three times and then dried at room temperature.

Simulation for copolymerization of S and MA

Simulation for copolymerization of S and MA was performed using PREDICI software from CiT GmbH (Rasfede, Germany). The simulation model consists of individual reaction steps (initiation, propagation, termination, and chain transfer reactions) described as Eqs. (I)–(X) in Table s1. Variation of polymer composition at the initial stage of bulk copolymerization of S and MA at different temperatures (60–90 °C) was simulated as a function of polymerization time under the same recipe as the monomer phase of No. 1 shown in Table 1 except for TDM. The rate coefficients at 60 °C and frequencies and activated energies of Arrhenius equation used for the simulation are listed in Table s2.

Characterizations

Weight- and number-average molecular weights were measured with a gel permeation chromatograph (GPC; PL-GPC220, UK). Composition of P(S-MA) synthesized by the microsuspension polymerization was estimated using Fourier transform infrared spectroscopy (FT-IR), $^1\text{H-NMR}$, and a differential scanning calorimetry (DSC). FT-IR spectra were recorded on a NEXUS-670 spectrometer (Thermo Nicolet Co., Ltd., Beijing, China) in the range from 4000 to 400 cm^{-1} by the KBr pellet method. $^1\text{H-NMR}$ was performed on a 300-MHz Bruker AV-300 NMR using CD_2Cl_2 as a solvent. DSC was carried out with a NETZSCH DSC Polyma at 20 °C/min from –20 to 120 °C.

External surface of obtained particles was observed with a scanning electron microscope (SEM; JSM6360L, JEOL, Japan). All the samples were treated with a gold coating before observation. Internal structure of the particles was estimated by the observation of ultrathin cross sections of the particles with a transmission electron microscope (TEM; JEM-1400, JEOL, Japan). The ultrathin cross sections were prepared by the procedures that dried particles were cured with epoxy matrix at room temperature for 24 h and microtomed (LKB-V, LEICA, Co., Ltd., Switzerland).

Table 1 Recipes for microsuspension copolymerization of styrene with methyl acrylate or acrylic acid in the presence of $Mg(OH)_2$ or PVA as dispersant

Ingredients	Amounts (g)		
	No. 1	No. 2	No. 3
S	90 (0.86 mol)	90	90
MA	10 (0.12 mol)	0	10
AA	0	10 (0.14 mol)	0
BPO	5.00 (188 mmol/L monomer)	5.00	5.00
TDM	0.75 (34 mmol/L monomer)	0.75	0.75
PPDA	0.10 (2.91 mmol/L water)	0.10	0.10 (3.28 mmol/L water)
$Mg(OH)_2$ aq. soln. (1.47 wt%)	293 (13.53 g/L water)	293	0
PVA aq. soln. (0.42 wt%)	0	0	241 (2.50 g/L water)
Water	42	42	42

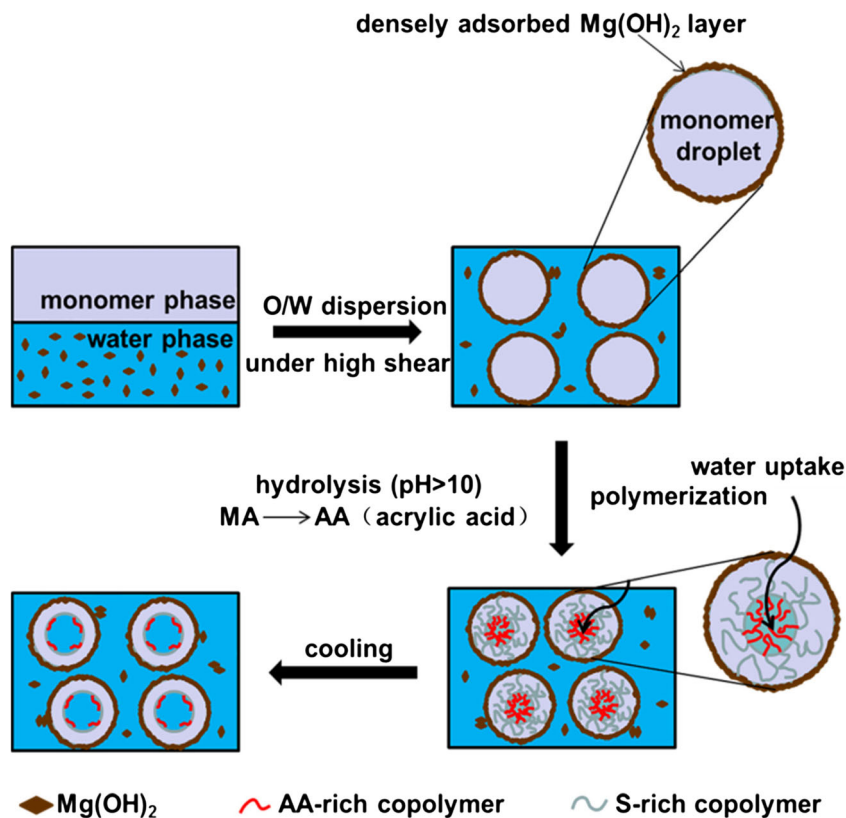
Abbreviations: *S* styrene, *MA* methyl acrylate, *AA* acrylic acid, *BPO* benzoyl peroxide, *TDM* *tert*-dodecylthiol, *PPDA* *p*-phenylenediamine, $Mg(OH)_2$ magnesium hydroxide, *PVA* polyvinyl alcohol

Results and discussion

Figure 1 shows a schematic illustration for an innovative one-step synthesis of micrometer-sized hollow polymer particles by applying microsuspension polymerization of *S* and *MA* with $Mg(OH)_2$. Where most of $Mg(OH)_2$ particles had less than 100 nm in diameter as described later. $Mg(OH)_2$ particles act as not only dispersant by adsorption densely on the P(*S*-*MA*) particle but also hydrolysis agent of *MA* unit in the

copolymer within particles indirectly due to giving a high pH value in the aqueous medium. In actual, pH value of poly(*MA*) emulsion (10 wt%), where the initial pH value was adjusted at 12.6 (by NaOH), which was the same as that of the monomer dispersion stabilized with the $Mg(OH)_2$ particles, obviously decreased faster with stirring time at 90 °C, but the rate at 60 °C was not so high (see Fig. s1). In the schematic illustration, if *MA* monomers dissolving in an aqueous medium rapidly hydrolyzed and finally most of *MA*

Fig. 1 Schematic illustration showing the formation mechanism of micrometer-sized hollow polymer particles by the microsuspension copolymerization of styrene (*S*) and methyl acrylate (*MA*) in the presence of $Mg(OH)_2$ as dispersant



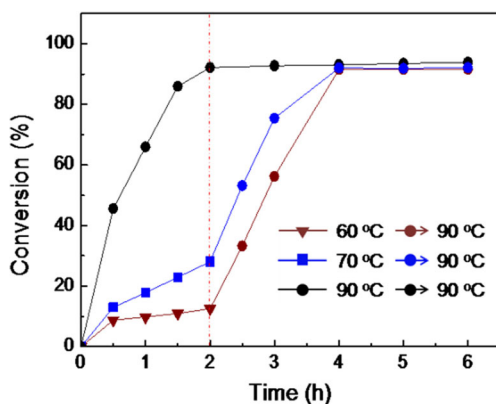


Fig. 2 Conversion-time plots of microsuspension copolymerization of S and MA with Mg(OH)₂ as dispersant at 60 °C, 70 °C, and 90 °C for initial 2 h, following at 90 °C for 4 h, under the recipe of No. 1 listed in Table 1

partitioned firstly in S droplets also are transformed to acrylic acid (AA) in an aqueous medium before the copolymerization, practically the copolymerization of styrene becomes with not MA but AA. As described in the literature, it is important to distribute carboxyl groups predominantly in the core for the formation of hollow polymer particles [15]. Therefore, in carboxylated polymer particles prepared by emulsion copolymerization with AA, rather amount of carboxyl groups tend to localized at particle surface layer [25], it is difficult to prepare hollow polymer particles from them by the alkali treatment. In actual, P(S-AA) (14.0 mol% AA) particles prepared by the microsuspension polymerization of S and AA with Mg(OH)₂ particles under the conditions of No. 2 shown in Table 1 had no hollow structure (see Fig. 9d). So, in order to avoid the hydrolysis reaction of MA monomer in the aqueous medium, the microsuspension copolymerization was first carried out at different temperatures (60–90 °C) and then followed at 90 °C.

Figure 2 shows conversion-time plots of the microsuspension polymerization. In comparison with it, those of microsuspension copolymerization at 70, 80, and 90 °C are shown in Fig. s2. In all polymerizations, the polymerization was fast at 90 °C and completed for 2 h. Here, as shown in Table 1, the amount of BPO used as initiator was set at 5 wt% relative to the monomers, which is more than tenfold compared with a conventional radical polymerization system. The objective is to proceed

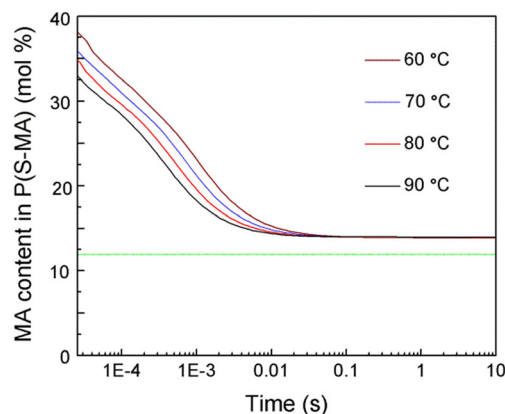


Fig. 4 Simulated MA content in P(S-MA) prepared at the initial stage of bulk copolymerization of S (M_1) and MA (M_2) under the recipe of the monomer phase (except for TDM) of No. 1 listed in Table 1 at different temperatures using the reactivity ratios ($r_1 = 0.75$, $r_2 = 0.18$) [26]. A flat straight line indicates the MA content in the monomer mixture

predominantly the copolymerization of S with MA in the droplets before MA monomer is hydrolyzed. As shown in SEM photographs in Fig. 3, the P(S-MA) (11.8 mol% MA) particles prepared at the different temperatures for the initial 2 h had similar nonspherical shapes and polydisperse micrometer-sized in diameter.

Figure 4 shows simulation results on polymer composition prepared at the initial stage of bulk copolymerization of S (M_1) and MA (M_2), conducted under the recipe of the monomer phase of No. 1 except for TDM as listed in Table 1 at 90 °C using reactivity ratios that r_1 and r_2 are, respectively, 0.75 and 0.18 [26]. Although it is limited only in the initial stage, the simulation result clearly indicates that higher MA content copolymer than 11.8 mol% is formed in the monomer droplets even at 90 °C, although the tendency become more obvious with an decrease in the temperature. This is desirable for our objective of this research based on the knowledge for the preparation of hollow polymer parties from carboxylated polymer particles obtained in the previous article [15].

Figure 5 shows DSC curves of the P(S-MA) particles after washing with HCl aqueous solution to remove Mg(OH)₂, which were obtained at 0.5 and 6 h of the microsuspension copolymerization at 90 °C. The conversions were, respectively, 43 and

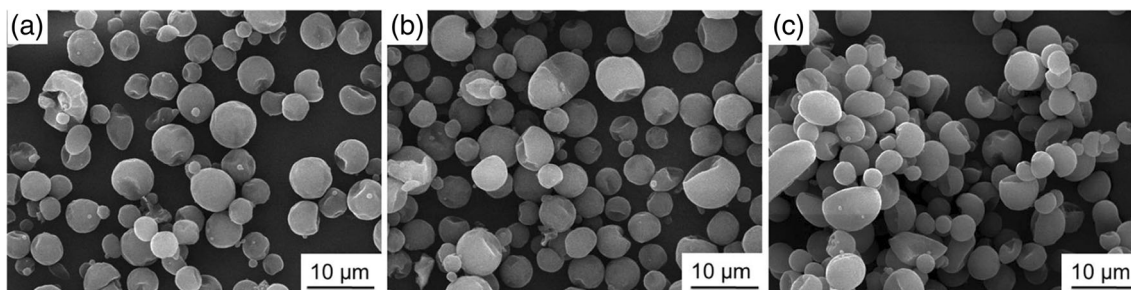


Fig. 3 SEM photographs of P(S-MA) (11.8 mol% MA) particles prepared by the microsuspension copolymerization at 60 °C (a), 70 °C (b), and 90 °C (c) for initial 2 h, following at 90 °C for 4 h, under the recipe of No.1 listed in Table 1

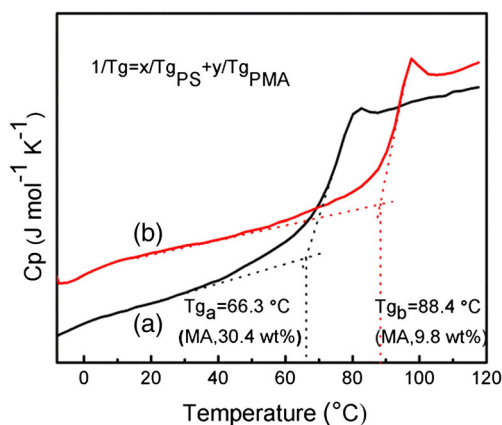


Fig. 5 DSC curves of the P(S-MA) (after washing with HCl and extracted with CH_2Cl_2), which were obtained at 0.5 h (a) and 6 h (b) of the microsuspension copolymerization at 90 °C under the recipe of No. 1 listed in Table 1

92% (Fig. 2, black closed circles). Glass transition temperature (T_g) values of the copolymers obtained from the DSC curves were, respectively, 66.3 and 88.4 °C, which indicates that MA contents were, respectively, 34.5 and 11.6 mol%. These results were well in accord with the above simulation results.

Figure 6 shows $^1\text{H-NMR}$ spectra of the poly(MA) (a), which was prepared by emulsion polymerization with ammonium persulfate as initiator and polyoxyethylene alkyl ether sodium sulfate as emulsifier, and P(S-MA) (b, c) obtained at the conversions of 43% (b) and 92% (c) of the microsuspension polymerization at 90 °C, respectively, for 0.5 and 1 h. In the spectrum (a), a strong signal at 3.6 ppm due to $-\text{COCH}_3$ was observed. However, in the spectra (b, c), the signal was not observed. These results indicate that hydrolysis reaction of the MA unit in the particles completely proceeded in the process of the microsuspension copolymerization, and all $-\text{COOCH}_3$ groups in the copolymer were changed to $-\text{COO}^- \text{Mg}^{2+}$. Unexpectedly,

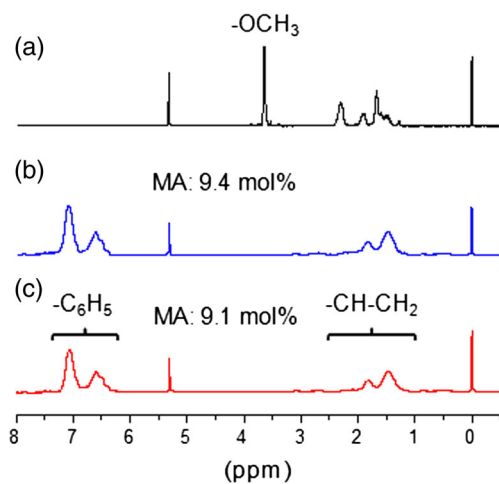


Fig. 6 $^1\text{H-NMR}$ spectra (in CD_2Cl_2) of PMA (a) prepared by emulsion polymerization and P(S-MA) (b, c) (after extracted with CH_2Cl_2), which were obtained at 45 min (b) and 60 min (c) of the microsuspension copolymerization under the recipe of No. 1 listed in Table 1

the MA contents, which were calculated from integrated values of the signals of $-\text{C}_6\text{H}_5$ at 6.2–7.4 ppm and $-\text{CH}_2-\text{CH}-$ at 1.0–2.5 ppm, were, respectively, 9.1 and 9.4 mol%, which were less than 11.8 mol% of the MA content in the monomer mixture, but this result can be reasonably understood as follows. The P(S-MA) samples used for the $^1\text{H-NMR}$ measurement were obtained from the lower CH_2Cl_2 layer separated after the P(S-MA) dispersions and CH_2Cl_2 were mixed and then kept in vials. As shown in a schematic view shown in Fig. s3, the upper water layer was transparent and the lower CH_2Cl_2 layer was slightly turbid and an intermediate layer was turbid. Hydrolyzed P(S-MA) (i.e., P(S-AA)) does not dissolve in CH_2Cl_2 if the AA content is high. Accordingly, a part of the copolymer that had comparatively low MA (i.e., AA) content was extracted by CH_2Cl_2 and analyzed by the NMR. In other words, the latter $^1\text{H-NMR}$ data also suggest that in the former stage of the microsuspension copolymerization, P(S-MA) having higher MA content than that (11.8 mol%) of the monomer mixture were predominantly formed, and the MA unit in the copolymer were hydrolyzed during the microsuspension copolymerization.

Figure 7 shows the FT-IR spectra of P(S-MA) obtained by the microsuspension polymerization with PVA (a) or $\text{Mg}(\text{OH})_2$ (b) as dispersant and the latter one (c) after washing with HCl aqueous solution. The peak strength due to $\text{C}=\text{O}$ of MA unit at around 1730 cm^{-1} was stronger in the PVA system (a), where MA unit is not hydrolyzed because of no pH adjustment at alkali condition, than in the $\text{Mg}(\text{OH})_2$ system (b), where MA unit is hydrolyzed because of initial pH of 12.6. In the $\text{Mg}(\text{OH})_2$ system, COO^- peak at 1550 cm^{-1} was observed. When it was treated with HCl aqueous solution to remove $\text{Mg}(\text{OH})_2$, the peak at 1550 cm^{-1} due to the COO^- group disappeared and the peak due to $\text{C}=\text{O}$ became stronger because it changed to COOH . When the P(S-MA) prepared with the PVA system was treated with NaOH aqueous solution, a peak at 1550 cm^{-1} due to $\text{COO}^- \text{Na}^+$ appeared (see Fig. s4). Moreover, these points were obviously supported in FT-IR

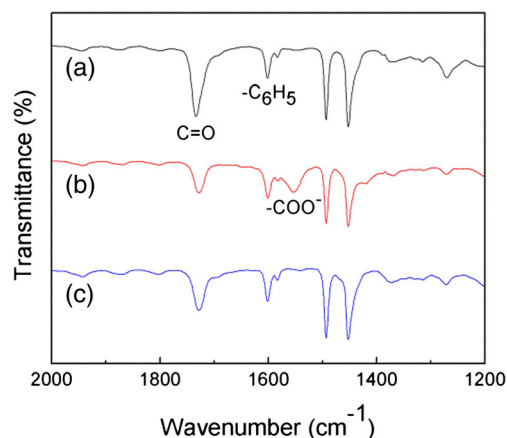
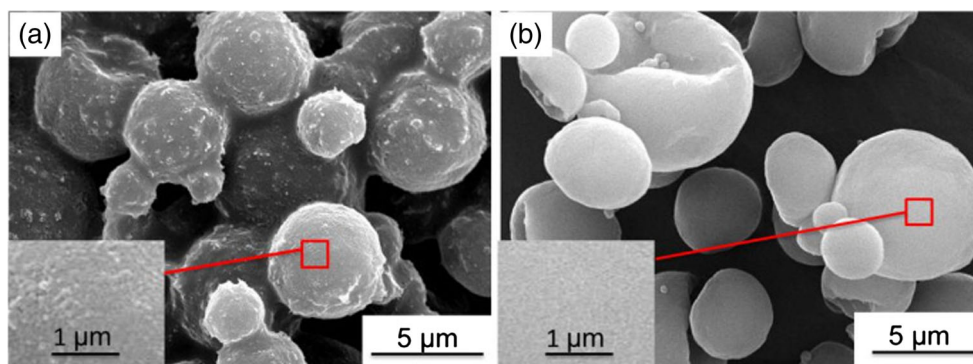


Fig. 7 FT-IR spectra of P(S-MA) prepared by the microsuspension polymerization with PVA (a) or $\text{Mg}(\text{OH})_2$ (b) as dispersant and the latter one after washing by HCl aqueous solution (c)

Fig. 8 SEM photographs of P(S-MA) particles prepared by the microsuspension copolymerizations of S and MA with $\text{Mg}(\text{OH})_2$ at 90 °C for 6 h before (a) and after (b) washing with HCl aqueous solution to remove $\text{Mg}(\text{OH})_2$



data of P(S-AA) prepared by the microsuspension copolymerization of S and AA with PVA or $\text{Mg}(\text{OH})_2$ as dispersant and latter one after washing with HCl aqueous solution as shown in Fig. 5. In the PVA system, no peak due to COO^- was observed, whereas in the $\text{Mg}(\text{OH})_2$ system, it was obviously observed and disappeared after washing with HCl.

From the above results, it is concluded that MA units in the copolymer within particles were hydrolyzed during the microsuspension polymerization with $\text{Mg}(\text{OH})_2$.

Figure 8 shows SEM photographs of P(S-MA) particles prepared by the microsuspension polymerization at 90 °C for 6 h before (a) and after (b) washing with HCl aqueous solution. The $\text{Mg}(\text{OH})_2$ particles could be removed completely by the washing. In comparison with the surfaces of both particles, the particle surfaces before washing had uneven, on the other hand, after washing they were smooth. Even in the enlarged SEM photograph of the former particles, it was difficult to identify clearly the interface among the $\text{Mg}(\text{OH})_2$ particles adsorbed on the P(S-MA) particle except for the

coagulated $\text{Mg}(\text{OH})_2$ particles thereon. It seems that the size of the most of $\text{Mg}(\text{OH})_2$ particles was less than 100 nm. In Fig. 8b, submicrometer-sized ($d_n \sim 0.64 \mu\text{m}$) particles were observed a little, but the percentage was less than 1 wt%. Weight- and number-average molecular weight measured by GPC were, respectively, 52,300 and 29,700, which are within the scope of the assumption because TDM as chain transfer agent and high concentration of BPO initiator dissolved in the monomer droplets as mentioned before, and these values indicates that the submicrometer-sized particles were not formed by the compliment of emulsion polymerization. In the preparation of monomer dispersion, small amount of such submicrometer-sized droplets may be prepared, because the monomer dispersion was prepared with a high shear dispersing machine (ERS 2000/04) at 12,000 rpm for 30 min. We assume that all of particles were formed from corresponding monomer droplets, in other words, the complication of emulsion polymerization was depressed because of the water-soluble PPDA inhibitor. When the microsuspension

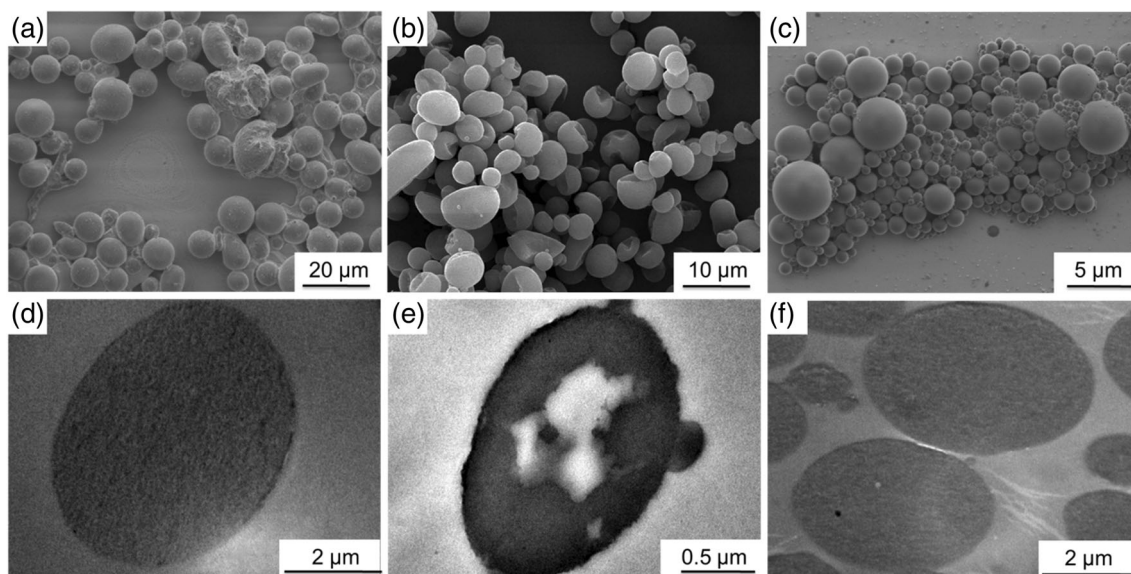


Fig. 9 SEM photographs of P(S-AA) (a) and P(S-MA) (b) particles (after washing with HCl to remove $\text{Mg}(\text{OH})_2$) prepared by the microsuspension copolymerizations of S with AA or MA with

$\text{Mg}(\text{OH})_2$ as dispersant at 90 °C for 6 h, and P(S-MA) particles (c) prepared with PVA as dispersant and TEM photographs (d–f) of ultrathin cross sections of corresponding particles

polymerization was carried out with PVA as dispersant, rather amount of submicrometer-sized particles were observed on SEM photographs (Fig. 9c), which may be based on the complication of emulsion polymerization in the aqueous medium. In this way, $Mg(OH)_2$ is suitable dispersant for the objective of this study. Although there is no experimental proof, densely adsorbed $Mg(OH)_2$ surface layer on the monomer droplets may depress exit of the monomers into the aqueous medium, which causes emulsion polymerization.

Figure 9 shows SEM photographs of P(S-AA) (a) and P(S-MA) (b) particles after washing with HCl aqueous solution, which were, respectively, prepared by the microsuspension copolymerizations of S with AA and MA with $Mg(OH)_2$ particles at 90 °C for 6 h, and TEM photographs (d, e) of ultrathin cross sections of both particles. In the case of P(S-AA) (a), a fiber-like polymer was observed at the surfaces of particles and coagulated ones. It seems that such a fiber-like polymer was formed by self-assembling of water-soluble polymer, that is, AA-rich copolymer. On the other hand, in the case of P(S-MA) (b), no fiber-like polymer was observed. In the case of P(S-AA), most of particles formed had a spherical shape independent of the size although a small amount of nonspherical big particles were observed, which may be produced by partial coagulation of spherical particles during the microsuspension polymerization. TEM photograph of the ultrathin cross-sectioned specimens of P(S-MA) particles (e) shows obviously that the particles had a hollow structure, of which internal surface was irregular. On the other hand, in those of P(S-MA) particles (c, f) prepared with PVA and P(S-AA) particles (a, d) prepared by the microsuspension copolymerization with $Mg(OH)_2$, such a hollow structure was not observed.

Conclusion

We have successfully demonstrated one-step synthesis of micrometer-sized hollow polymer particles by applying the microsuspension polymerization of S and MA with $Mg(OH)_2$ particles as mentioned in the schematic illustration shown in Fig. 1, where the $Mg(OH)_2$ particles acted not only as dispersant but also as hydrolysis reagent of MA unit within P(S-MA) particles during the polymerization due to giving alkaline pH in the aqueous medium. The validity and utility of the proposed one-step synthesis of micrometer-sized hollow polymer particles were confirmed by SEM and TEM. In addition, it is shown that the difference in the reactive activity of S and MA can be used to prepare hollow polymer particles in the appropriate pH and polymerization temperature.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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