One-step fabrication of multihollow polystyrene particles from miniemulsion system with nonionic surfactant

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ARTICLE INFO

ABSTRACT

This paper presented a new facile approach to fabricate polystyrene (PS) multihollow particles from miniemulsion polymerization. The surfactant used in this miniemulsion system was OP-10, a nonionic surfactant of nonyl phenyl polyoxyethylene with an average of 10 ethylene oxide units per molecule (hydrophilic–lipophilic balance, HLB = 13.9). Due to the partition characteristic of OP-10 in miniemulsion, W/O/W structured monomer droplets could be formed after ultrasonic dispersion. Under irradiation by γ-ray, styrene polymerized through a droplet nucleation mechanism, which was the feature of miniemulsion polymerization. The formation of multihollow structure was affected by the content of OP-10 (W_{OP}) and pre-added PS (W_{PS}). It was found that when W_{OP} was above 2 wt% and W_{PS} was in the region of 2–10 wt% based on the monomer, multihollow PS particles could be obtained. The molecular weight of the PS latex particles synthesized was determined to be 10^5 g/mol by GPC.

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1. Introduction

Miniemulsions are defined as aqueous dispersions of oil droplets within a size range of 50–500 nm and stabilized by surfactants and hydrophobic costabilizers [1,2]. Since the amount of the surfactants is typically below the critical micelle concentration (cmc) in miniemulsions, most surfactants are considered to be adsorbed onto the small oil droplets, unavailable for micelle formation. Hence, the monomer droplets become the primary nucleation loci instead of micelles in classical emulsion polymerization systems. As a result, latex particles from miniemulsion polymerization have the same size and number as the initial monomer droplets [3,4].

The one-to-one correlation of monomer droplets versus latex particles in miniemulsion polymerization can be utilized for particle design. Deng et al. [5] synthesized PS encapsulated nanosaponite composite suspension via miniemulsion polymerization successfully. Wu et al. [6] presented a controlled synthesis of SiO₂/ PS nanocomposite particles with "raspberry-like" and other interesting morphologies through miniemulsion polymerization. The successful preparation of functional or structured latex particles from miniemulsion is greatly dependent on the stability of the primary miniemulsion, which is controlled by the surfactants and costabilizers. Miniemulsion systems reported in open literatures

mainly focus on ionic surfactants since they can effectively prevent the coalescence of small monomer droplets owing to their static repulsion effect [7]. The number of reports on nonionic surfactant-stabilized miniemulsion systems is very limited. The short of attention on miniemulsion using nonionic surfactants may be related to their special properties. In conventional emulsion polymerization with nonionic surfactants, experimental results tend to show that the nonionic surfactants are readily partitioned into the inner side of the monomer phase because of their high oil solubility [8,9], while ionic surfactants prefer to stay at the interface of oil and aqueous phases. For example, Özdeger et al. [10–12] investigated emulsion polymerization using nonionic polyoxyethylene octyl phenyl ether with an average of 40 ethylene oxides (EO) per molecule (Triton X-405, HLB = 17.6). They pointed out that most of Triton X-405 (91%) existed in the styrene phase before the addition of initiator. Okubo et al. [13] observed that in an emulsion copolymerization of styrene and methacrylic acid (MAA), about 75% of polyoxyethylene nonyl phenyl ether (Emulgen 911, HLB = 13.7) was trapped inside the poly(styrene–MAA) particles. Thus, the incorporation of nonionic surfactants inside polymer particles during emulsion polymerization seems to be a general phenomenon owing to the high affinity between monomer and nonionic surfactant. This incorporation should be a disadvantage for stabilizing the emulsion system since it will decrease the stability of polymer colloids [14]. Moreover, it will bring a series of problems such as making the control of particle size distribution and polymerization kinetics more difficult [15]. However, the incorporation of nonionic surfactant can be useful for the preparation of hollow

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particles. Okubo et al. [16] successfully obtained multihollow particles by stepwise alkali/acid methods, in which the P(styrene–MAA) particles with incorporated Emulgen 911 was ionized to absorb water and form multihollow particles. To our knowledge, the unusual behavior of nonionic surfactant incorporating into the monomer droplets discovered in the conventional emulsion systems has not been applied to miniemulsion systems in literature. In miniemulsion systems, the diffusion of monomer is suppressed and the polymerization takes place in the individual droplets. Whether the advantages of miniemulsion polymerization can be transferred to the system with nonionic surfactants and be applied to prepare hollow structured particles is an interesting subject.

The widely used costabilizers in miniemulsion are HD and CA. Their solubility in water is much lower than that of the monomers, which can provide osmotic pressure to counteract the mass exchange of monomer droplets (Ostwald ripening) and keep the number of the oil droplets constant [3,4]. It has been found that the addition of a small amount of polymer (e.g. PS) into a miniemulsion polymerization system can help stabilize the miniemulsion and accelerate the polymerization. Miller et al. [17–19] carried out styrene miniemulsion polymerizations using PS accompanied with CA as costabilizer. Compared with that of miniemulsion system stabilized by CA alone, the final number of polymer particles was not affected by the concentration of the initiator and the monomer droplet nucleation rate was accelerated.

In this work, we attempted to study the partition of OP-10 in oil and aqueous phases in a miniemulsion system of styrene with pre-added PS and CA as the costabilizer. The polymerization of styrene was initiated by γ-ray irradiation at room temperature in order to improve the efficiency of droplet nucleation and maintain the stability of the miniemulsion. From this study, we developed a novel one-step method to fabricate PS multihollow particles via miniemulsion system.

2. Experimental

2.1. Materials

Styrene, OP-10 (the chemical structure is shown in Scheme 1) and CA were purchased from Shanghai Chemical Reagents Co., China. PS ($M_n = 10^5$ g/mol, solid spheres with a diameter of about 5 mm) was bought from Shandong Qilu Petrochemical Engineering Co. Ltd. Styrene was purified to remove the inhibitor by passing through a basic alumina column twice and stored in a refrigerator before use.

2.2. Miniemulsion polymerization of styrene

Emulsification. Distilled water was mixed with styrene solution containing pre-added PS, CA, and OP-10 under magnetic stirring for 30 min. *Homogenization.* The above emulsion was ultrasonicated for 5 min (AS3120, Tianjin Automatic Science Instrument Co., Ltd.) to achieve a stable miniemulsion. The recipes of the miniemulsions are presented in Table 1. *Polymerization of styrene.* The resultant miniemulsion was irradiated by ^{60}Co γ-ray (located in USTC, China) at a dose rate of 60 Gy/min after purging with nitrogen for 10 min to remove the dissolved oxygen in the system. The total absorbed dose was 30 kGy.
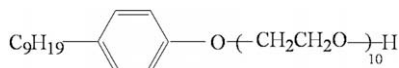
Scheme 1. The chemical structure of OP-10.

Table 1
The recipes and characteristics of the miniemulsions[a]

Sample ID	PS[b] (wt%)	OP-10 (g)		
		Total weight (g)	%[c] Partition into the styrened phase[d] (g/%)	%[c] Remained inside the PS[e] particles[e]
1	0	0.5	78	67
2	1	0.5	90	88
3	2	0.5	92	86
4	10	0.5	92	90
5	12	0.5	92	88
6	15	0.5	90	88
7	10	1.25	92	89
8	10	2.5	92	90

[a] The amount of styrene was 25 g and CA was 1 wt% based on the monomer in every recipe. The solid content was 10 wt%.
[b] Based on the monomer weight.
[c] Based on the total weight of OP-10.
[d] Measured by gravimetry before polymerization.
[e] Calculated from ^{1}H NMR after polymerization.

2.3. Measurement of droplet/particle size

The hydrodynamic radius of the monomer droplets and latex particles was measured by a dynamic light scattering (DLS) (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ($\lambda_0 = 632$ nm) as the light source. The samples were diluted with water, which was saturated with OP-10 and styrene, in order to avoid the diffusion of surfactant and monomer from the monomer droplets into water. The number of the initial monomer droplets $N_{m,i}$ and the final particles $N_{p,f}$ per gram miniemulsion can be calculated from the DLS measurements [1]:

$$N_{m,i} = \frac{W_m}{\frac{4}{3}\pi R_{m,i}^3 \rho_m W_w} \tag{1}$$

$$N_{p,f} = \frac{W_m}{\frac{4}{3}\pi R_{p,f}^3 \left(\rho_m(1-X) + \rho_p X \right) W_w} \tag{2}$$

where $R_{m,i}$ represents the hydrodynamic radius of initial monomer droplet and $R_{p,f}$ is the hydrodynamic radius of final particle. W_m, W_w, and X are initial monomer weight, total miniemulsion weight, and monomer conversion, respectively. ρ_m is the monomer density (0.90 g/cm^3) and ρ_p is the polymer density (1.05 g/cm^3). The nucleation efficiency is denoted by $N_{p,f}/N_{m,i}$.

2.4. Morphology of droplets and particles

The morphology of styrene miniemulsion droplets was studied by optical microscopy (OM, Shanghai Optical Instrument Co., Ltd.). Morphologies of PS particles were observed by transmission electron microscopy (TEM, Hitachi H-800, 200 kV) and field-emission scanning electron microscopy (SEM, JEOL JSM-6700). The samples were diluted and mounted on the copper grids for TEM and SEM studies. For microtomed samples, the sample powder was embedded into epoxy resin, which was then ultramicrotomed to a thickness of ca. 70 nm. The particle number average diameter ($\overline{D}_n$) could be calculated from TEM images following the Eq. (3):

$$\overline{D}_n = \sum N_i D_i / \sum N_i \tag{3}$$

where N_i is the number of polymer particles with diameter D_i.

The distribution of particles was calculated by Eq. (4):

$$\sigma = \sqrt{\frac{\sum N_i(D_i - \overline{D}_n)^2}{\sum N_i - 1}} \qquad (4)$$

2.5. Molecular weight of PS particles

The weight-average molecular weight (M_w) and number average molecular weight (M_n) of the PS synthesized from miniemulsion were measured on a Waters 515 gel permeation chromatography (GPC) equipped with a 104 Å Waters Ultrastyragel column, and using THF as eluent at a flow rate of 1.0 mL/min. Monodispersed polystyrene was used as calibration standards.

2.6. Quantitative analysis of OP-10 incorporated in the oil phase before and after polymerization

Styrene/OP-10/PS/water mixtures of the same composition as in the polymerization recipes of Table 1 were shaken vigorously, and then put aside until complete creaming occurred. The amount of OP-10 partitioned in the aqueous layer and styrene layer before polymerization was determined by gravimetry.

After polymerization, the PS latexes were centrifuged and washed with water for three times and then with ethanol for four times in order to completely remove the surfactants adsorbed on the particle surface. Subsequently, the particles were dried at room temperature under reduced pressure for 1 week before the ^{1}H NMR spectra of the particles were taken on a Bruker ACF (300 MHz) spectrometer using CDCl$_3$ as a solvent. The ^{1}H NMR spectrum of the purified PS latexes prepared in this study (Fig. 1A) reveals the presence of –OCH$_2$CH$_2$O– protons of polyoxyethylene block at δ 3.6 ppm. In contrast, this characteristic peak is clearly missing from the spectrum of PS polymerized through miniemulsion with ionic surfactant SDS (Fig. 1B). The relative ratio of the oxyethylene proton peak versus other proton signals was used to calculate the percentage of OP-10 in the polymerized latexes.

3. Results and discussion

3.1. Morphology of PS latex particles synthesized from mini-emulsion polymerizations using nonionic surfactant OP-10

All of the miniemulsions with formulations as shown in Table 1 were relatively stable. Creaming did not occur within 24 h before polymerization. Hence, nonionic surfactant OP-10 seems to be very effective at stabilizing the miniemulsions at a concentration level as low as 0.37 mmol/L based on water (2 wt% based on monomer weight) for all the samples. Latex particles formed from miniemulsion stabilized with OP-10 and CA (sample 1) exhibits a poly-dispersed particle size distribution ($\overline{D}_n = 123 \pm 41$ nm) as shown in

Fig. 2. Such a wide size distribution is often seen in the conventional emulsion polymerization of styrene using nonionic surfactants because of secondary nucleation [12]. On the other hand, CA is amphiphilic, which makes CA less effective at restricting Ostwald ripening compared to the strongly hydrophobic costabilizer such as HD. In the previously reported studies, CA is usually employed together with ionic surfactants such as sodium dodecyl sulfate (SDS) to form liquid-like and electrically charged interfacial barriers to maintain the stability of the droplets [20].

The latex particle size distribution became more uniform if a small amount of PS was added into the miniemulsion system. As shown in Fig. 3, monodispersed PS nanospheres ($\overline{D}_n = 115 \pm 5$ nm) were fabricated from sample 2 which contains 1% pre-added PS. The size of styrene droplets and the final PS latex particles formed from sample 2 was also measured by DLS. As seen clearly from Fig. 4, the size of the final PS latex ($R_{p,f} = 60$ nm, PDI = 0.04) is very close to that of styrene droplets ($R_{m,i} = 57$ nm, PDI = 0.14), which implies that the nucleation occurs within the droplets [21]. Moreover, the particle diameter remained unchanged during the whole reaction, suggesting that the initial styrene droplets are quite stable and the probability of secondary nucleation is eliminated [22]. According to Eqs. (1) and (2), the initial number of styrene droplets ($N_{m,i} = 1.23 \times 10^{17}$/g) is almost equivalent to the final number of PS particles ($N_{p,f} = 1.22 \times 10^{17}$/g). The nucleation efficiency is 99%, which agrees well to what was proposed by Blythe et al. [23,24].

In the radiation-induced polymerization, γ-ray radiation induces high rates of free radicals' formation and polymerization initiation, and the nucleation stage is quite short, which is beneficial to form monodispersed particles [25]. The radicals are easy to be captured by the small droplets because of their large surface areas. The as-proved constant number of the particles before and after polymerization makes the nucleated monomer droplets uniformed and results in the generation of monodispersed particles. The high monodispersity of the particle size and the lack of electrostatic repulsion on the surfaces of the particles facilitate the PS latex particles to assemble into a closely packed and highly ordered hexagonal structure. The molecular weight of the PS is relatively
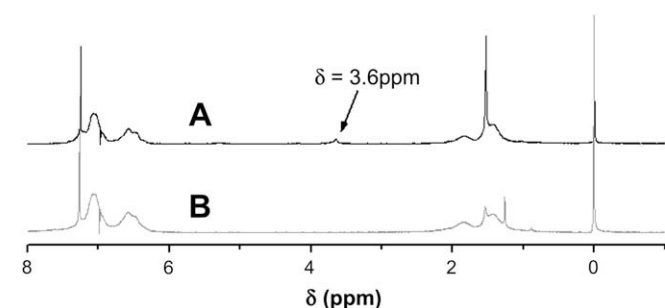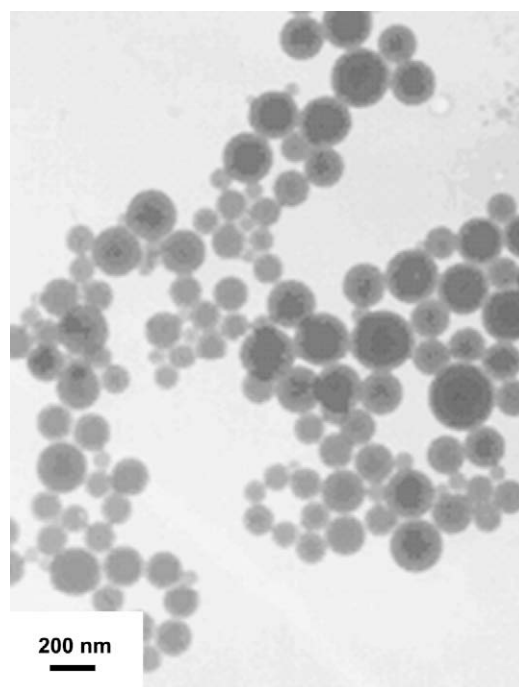

Fig. 1. ^{1}H NMR spectrum of (A) purified PS latex prepared from sample 4; (B) purified PS latex polymerized through miniemulsion using ionic surfactant SDS.

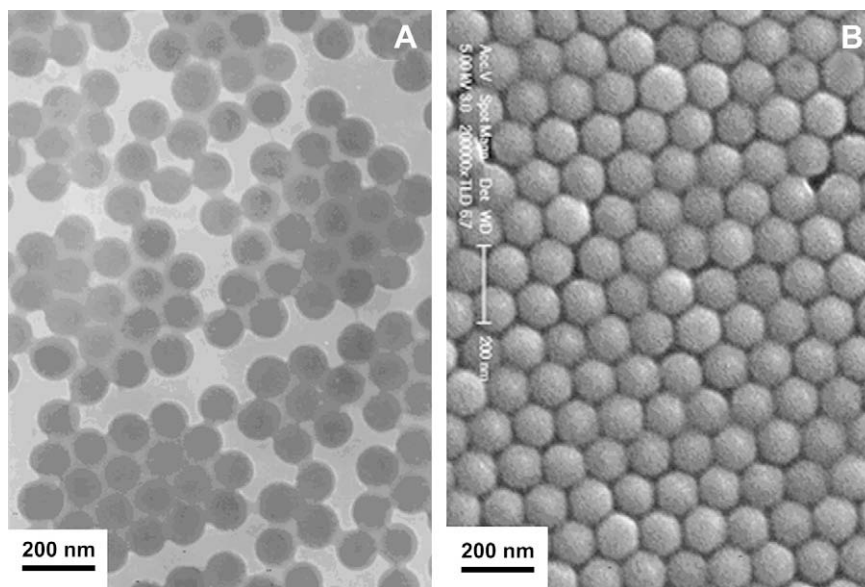**Fig. 2.** TEM image of PS particles prepared from miniemulsion without pre-added PS (sample 1).

Fig. 3. TEM (A) and SEM (B) images of PS particles prepared from sample 2.

high, with an M_n of 1.6×10^5 g/mol and M_w of 2.9×10^5 g/mol (polydispersity, PDI $= M_w/M_n = 1.77$) as determined by GPC. These results demonstrate that monodispersed particles with relatively high molecular weight could be easily manufactured using nonionic surfactant-stabilized miniemulsion system.

When the content of pre-added PS, W_{PS}, was increased to 2–10 wt% (samples 3 and 4), we observed some very interesting micro-scaled multihollow PS particles as shown in Fig. 5. The hollow cavities in the inner of particles are apparent. To our knowledge, this phenomenon has not been reported in the open literature. At the same time, all the PS particles prepared from different feeding conditions have similar molecular weight. For example, M_n of the multihollow particles prepared from sample 4 is 1.2×10^5 g/mol, and M_w is 2.3×10^5 g/mol (PDI $= 1.97$), very close to
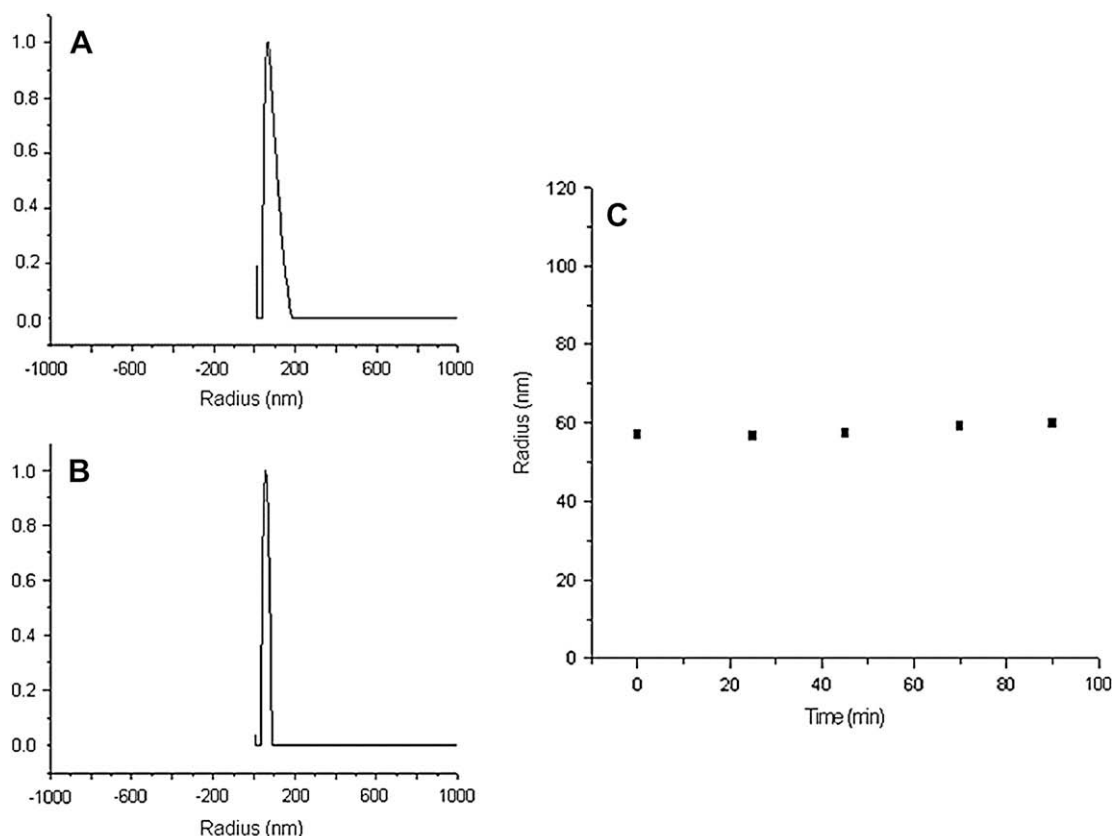

Fig. 4. Size distribution of sample 2 measured by DLS. (A) The initial styrene droplets ($R_{m,i} = 57$ nm, PDI $= 0.14$); (B) PS particles ($R_{p,f} = 60$ nm, PDI $= 0.04$); (C) the variation of the particle radius during the miniemulsion polymerization.
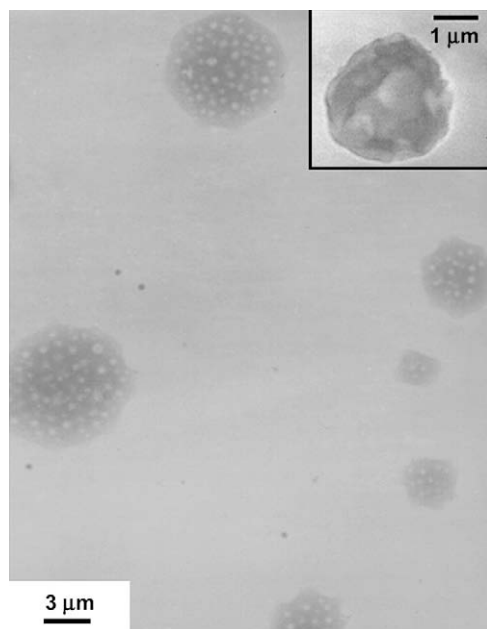
Fig. 5. TEM image of PS multihollow particles and microtomed slice (the image inserted) prepared from sample 3.

the solid PS particles prepared from sample 2. This fact suggests that the polymer particles prepared under the same mini-emulsification process have similar molecular weight whatever the final particle is solid or multihollow. In addition, the amount of pre-added PS has also no influence on the molecular weight of final particles. It also indicates that both solid and multihollow particles come from the droplet nucleation of initial miniemulsion droplets, and there is no monomer transfer during the formation of multihollow particles. With the continuing increase of W_{PS}, the multihollow particles disappeared. When W_{PS} was increased to 15 wt%, all the particles appeared as monodispersed solid spheres again.

3.2. Inclusion of nonionic surfactant OP-10 in monomer droplets

It is known that most nonionic surfactants which are dissolved in the monomer droplets in conventional emulsion [13,14] will diffuse into the inside of polymer particles swollen by monomer. Following this, the osmotic pressure produced by the trapped nonionic surfactants will push water into the latex particles to form small-sized water pools. Under the thermodynamic driving force, the small water pools can coalesce to minimize interfacial free energy during the subsequent emulsion polymerization until the particles solidify, leading to a clear hollow structure [8]. However, such a phenomenon has never been studied in mini-emulsion system. In order to clarify the formation of multihollow-structured particles in our system, gravimetrical and ^{1}H NMR measurements were conducted to detect the partition of OP-10. As summarized in Table 1, it is a general phenomenon that most of OP-10 stay inside the monomer droplets. For samples with pre-added PS, the ratio of surfactants inside the monomer droplets even exceeds 90%. The pre-added PS facilitates the partition of OP-10 into styrene droplets due to their similar chemical structure. The same phenyl chain in both OP-10 (see Scheme 1) and PS molecules increases their affinity to each other. We also noticed that in the samples with pre-added PS, the amount of OP-10 incorporated into the monomer droplets almost equals to that inside PS particles. This result strongly indicates that during the miniemulsion polymerization, most of the surfactants did not

diffuse into the aqueous phase. The surfactants remained in the styrene phase due to the strong affinity of nonionic surfactant to styrene and the pre-added PS. This conclusion coincides with the monomer droplet nucleation mechanism of miniemulsions. These results also reflect that almost all the OP-10 in the monomer phase is distributed in the inner side of styrene droplets instead of existing at the interface. We believe the inclusion of nonionic surfactant is the reason for multihollow morphology formation, as discussed in the following.

3.3. Illustration of the formation of multihollow particles

Based on the above discussions, an illustration of the formation of multihollow particles is proposed and depicted in Fig. 6. During the miniemulsion preparation, the nonionic surfactant OP-10 is included in the styrene phase after stirring the initial emulsion because of its strong affinity to styrene and pre-added PS. Afterwards, due to the osmotic pressure and the ultrasonic force, water was impressed into the styrene monomer droplets during the homogenization step. Under the thermodynamic driving force, water inside the monomer droplets either coalesces to form larger water pool leading to an appearance of W/O/W structured droplets or diffuses out into the aqueous phase. In the literatures, W/O/W droplets are usually unstable [26–29]. In our systems, however, the multiple droplets are relatively stable during the polymerization. We attribute this to the following two factors: First, CA is amphiphilic owing to its hydroxyl segment, and this property makes it easy for CA to diffuse to the surface of the particles. Therefore, CA is sometimes called "cosurfactant" in the miniemulsion systems [1]. In this experiment, the CA and OP-10 at the surface together stabilize the W/O/W droplets. Meanwhile, the hydrophobic groups of the inner OP-10 may surround and stabilize the water pools inside the droplets. Second, the pre-added PS increases the internal viscosity of the styrene droplets, which makes the water pools inside difficult to move out of the droplets. Correspondingly, stable W/O/W structured monomer droplets can be formed. Under γ-ray radiation, these monomer droplets nucleate and polymerize into particles with many voids after the polymer particles are dried in vacuum. On the other hand, when there is no PS in styrene phase, the monomer droplet has a low viscosity. The water pressed into the styrene droplets can easily move out of the monomer droplets. Ultimately, only solid particles can be formed.

This hypothesis is further verified by experimental studies on the variation of the morphology of particles with different monomer conversions. Many styrene monomer droplets after sonication at a micro-dimension could be seen by optical microscopy (Fig. 7A). This can be taken as evidence that the incorporation of water mainly caused the diameter increase of droplets from conventional nano-scale in miniemulsion system to micro-scale size, and the W/O/W structured droplets were formed after sonication. At a conversion of 20%, the particles might have many holes inside. However the hollow structure was difficult to observe under TEM (see Fig. 7B). It is possible that the amount of PS was too small to produce rigid particles at low conversion and the particles were too soft for TEM study. When 50% monomer became polymerized, PS particles having a small number of domains with less contrast were obtained. At a high conversion of 80%, multihollow particles emerged clearly.

It is noted that although the presence of PS facilitates the coagulation of small water pools, it does not suggest that further increase of W_{ps} will continuously facilitate the multihollow structure formation. Too much pre-added PS will limit the coagulation rate of water. As estimated from TEM photographs, the ratio of multihollow morphological particles to the total solid and multihollow particles reached a maximum value of 90% when W_{PS}
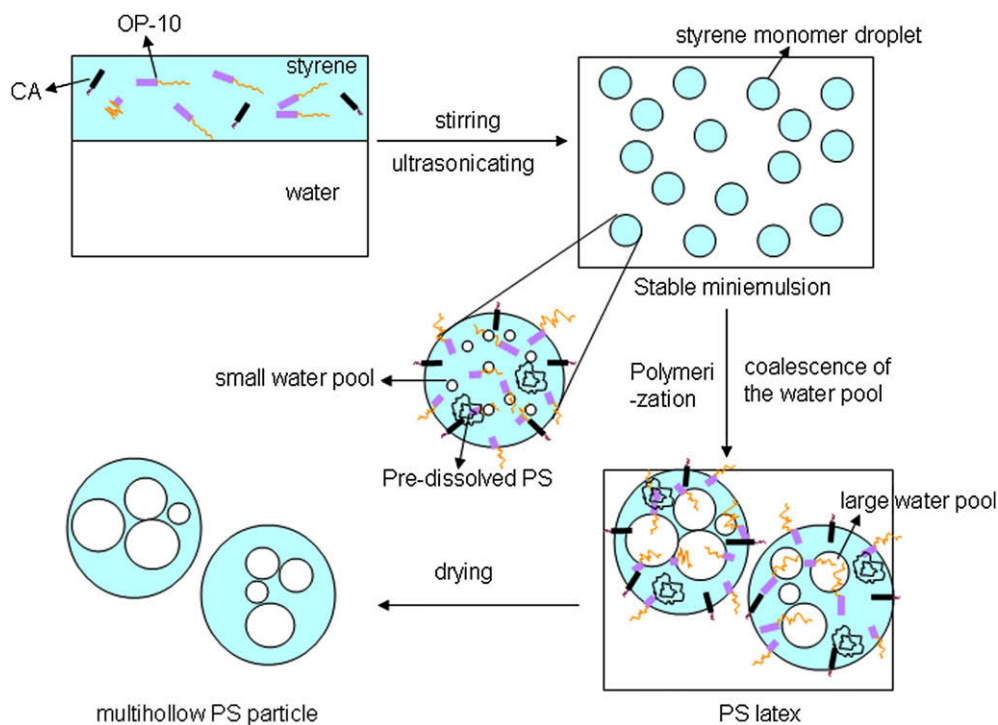
Fig. 6. Illustration of the formation mechanism of PS multihollow particles.

was increased to 10 wt% based on the monomer (sample 4). Once the weight ratio of pre-added PS further increased to 15 wt%, the multihollow particle morphology disappeared. It can be seen in Table 1 that most OP-10 were trapped inside the PS particles. This phenomenon could be explained as follows: the inner viscosity increases with increased amount of pre-added PS in the styrene droplets. When the internal viscosity reaches a critical value, it would be too difficult for the small water pools inside the droplet to coagulate to a visible scale.

3.4. Influence of surfactant content W_{OP} on the morphology of PS particles

In this series, miniemulsion systems at different OP-10 concentrations were investigated while keeping the W_{PS} at a constant level of 10 wt%. Clear multihollow particles were observed at W_{OP} of 2%, 5%, and 10% at a monomer conversion exceeding 50%, 40%, 25% for samples 4, 7, and 8, respectively. As mentioned previously, with the help of ultrasonication, water
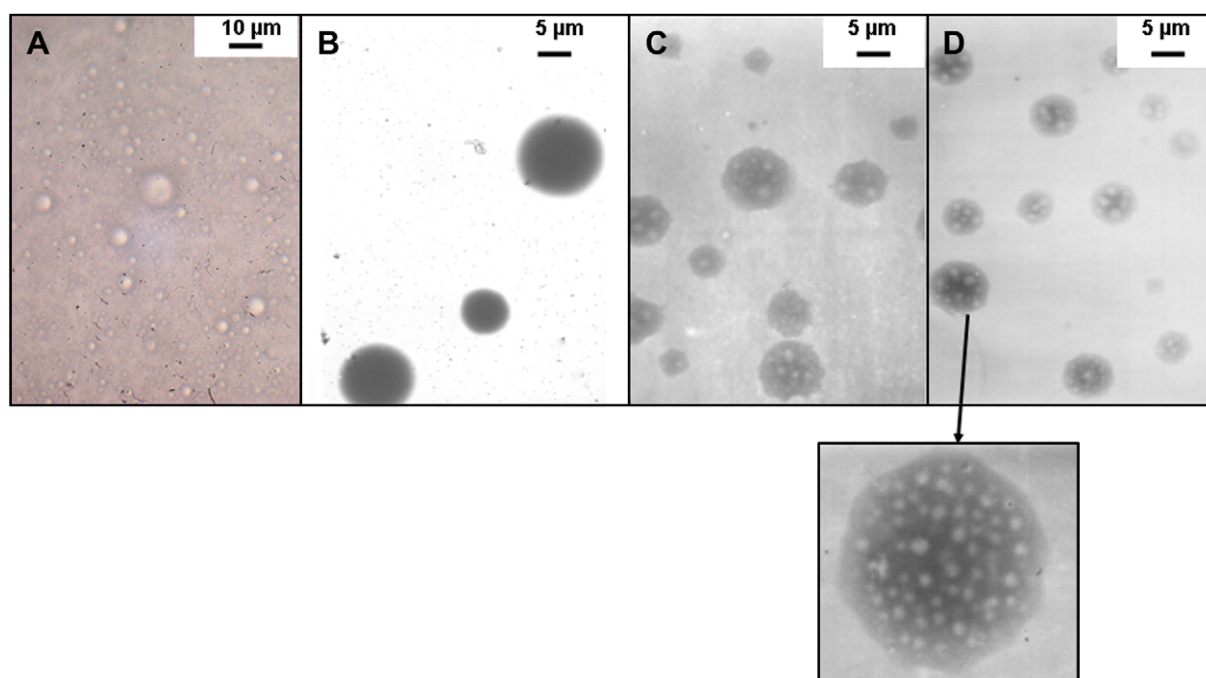

Fig. 7. OM (A) and TEM (B-D) images of PS particles for sample 4 at different monomer conversions: (A) 0; (B) 20%; (C) 50%; (D) 80%.

droplets are prone to penetrate into styrene droplets under the osmotic pressure π, which is generated from OP-10 inside the styrene phase. Here,

$$\pi = \frac{nRT}{V} \tag{5}$$

In which, n represents the molar number of the hydrophilic groups of OP-10 inside the monomer droplets. V, R, and T are the volume of the droplets, the universal gas constant, and the absolute temperature, respectively. When more surfactants are used for miniemulsion preparation, the amount of OP-10 included in the styrene droplets is increased, which leads to a higher osmotic pressure, according to Eq. (5). This will cause more water penetrate inside the droplets. Indeed, the observed experimental results correspond very well to this analysis.

4. Conclusion

In conclusion, nonionic surfactant OP-10 is shown to be effective for stabilizing miniemulsion systems. With the help of CA and pre-added PS, monodispersed solid nanospheres or multihollow particles could be fabricated in a one-step miniemulsion polymerization if the content of OP-10 and the pre-added PS are controlled at an appropriate value. The pre-added PS in this system plays two roles: first by acting as an efficient costabilizer to help CA prevent Ostwald ripening and preserve the particle number during the polymerization process; and second by increasing the internal viscosity to a certain degree to "fix" water pools already penetrated into the monomer droplets. When W_{PS} is 10 wt% based on the monomer, the yield of multihollow particles can reach as high as 90%.

According to the monomer droplet nucleation mechanism of miniemulsion polymerization, not only single-component but also multi-component copolymer multihollow particles can be manufactured easily through this simple and effective one-step miniemulsion polymerization route. We believe the synthetic methodology and multihollow particles as reported here will find broad applications in the micro-encapsulation and controlled release technology.

References

[1] Antonietti M, Landerfester K. Prog Polym Sci 2002;27:689–757.
[2] Landfester K. Macromol Rapid Commun 2001;22:896–936.
[3] Li M, Daniels E, Dimonie V, Sudol E, El-Aasser MS. Macromolecules 2005; 38:4183–92.
[4] Blythe PJ, Sodol ED, El-Aasser MS. J Polym Sci Part A Polym Chem 1997; 35:807–11.
[5] Tong ZH, Deng YL. Polymer 2007;48:4337–43.
[6] Zhang SW, Zhou SX, Weng YM, Wu LM. Langmuir 2005;21:2124–8.
[7] Tan CJ, Tong YW. Langmuir 2007;23(5):2722–30.
[8] Kobayashi H, Miyanaga E, Okubo M. Langmuir 2007;23:8703–8.
[9] Chaiyasat A, Kobayashi H, Okubo M. Colloid Polym Sci 2007;285:557–62.
[10] Özdeger E, Sudol ED, El-Aasser MS, Klein A. J Polym Sci Part A Polym Chem 1997;35:3813–25.
[11] Özdeger E, Sudol ED, El-Aasser MS, Klein A. J Polym Sci Part A Polym Chem 1997;35:3827–35.
[12] Özdeger E, Sudol ED, El-Aasser MS, Klein A. J Polym Sci Part A Polym Chem 1997;35:3837–46.
[13] Okubo M, Kobayashi H, Matoba K. Colloid Polym Sci 2003;281:182–6.
[14] Okubo M, Kobayashi H, Matoba T, Oshima Y. Langmuir 2006;22:8727–31.
[15] Piirma I, Chang M. J Polym Sci Polym Chem Ed 1982;20:489–98.
[16] Okubo M, Kanaida K, Fujimura M. Chem Express 1990;5:797–800.
[17] Miller CM, Sudol ED. Macromolecules 1995;28:2754–64.
[18] Miller CM, Sudol ED. Macromolecules 1995;28:2765–71.
[19] Miller CM, Sudol ED. Macromolecules 1995;28:2772–80.
[20] Asua JM. Prog Polym Sci 2002;27:1283–346.
[21] Landfester K, Bechthold N, Förster S, Antonietti M. Macromol Rapid Commun 1999;20:81–4.
[22] Wang H, Ge XW, Song LY, Liu HR, Zhang ZC. Colloid Polym Sci 2007;285: 1093–100.
[23] Blythe PJ, Morrison BR, Mathauer KA, Sudol ED, El-Aasser MS. Macromolecules 1999;32:6944–51.
[24] Blythe PJ, Morrison BR, Mathauer KA, Sudol ED, El-Aasser MS. Langmuir 2000;16:898–904.
[25] Wang XB, Zhang ZC. Radiat Phys Chem 2006;75:1001–5.
[26] Kim JW, Ko JY, Jum JB, Chang IS, Suh KD. Colloid Polym Sci 2003;281:157–63.
[27] Kim BS, Kim JW, Suh KD. J Appl Polym Sci 2000;76:38–44.
[28] Su JH, Flanagan J, Singh H. Food Hydrocolloids 2008;22:112–20.
[29] Hindmarsh JP, Su JH, Flanagan J, Harjinder S. Langmuir 2005;21:9076–84.