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One-step template-free synthesis of monoporous polymer microspheres with uniform sizes *via* microwave-mediated dispersion polymerization†

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One-step facile synthesis of monoporous polymer microspheres *via* microwave-controlled dispersion polymerization is introduced. This template-free method employing the dispersion polymerization of styrene under microwave irradiation induces directly the formation of uniform monoporous polymer microspheres, with controllable morphologies and sizes, which can be tuned by simply adjusting parameters for the synthesis. A comparison to conventional heating indicates that microwave irradiation plays a vital role in the formation of this novel morphology.

1 Introduction

The chemical synthesis and assembly of polymer nanostructures, represented by hollow microspheres with well-defined shapes and sizes, have attracted considerable attention owing to their characteristics such as high surface area, low density, and low coefficient of thermal expansion and their promising prospects in guest molecule microencapsulation, controlled delivery and catalysis.[1] Hollow polymer microspheres are generally prepared *via* template-mediated methods, including inorganic hard templates[2] and organic soft templates such as micelles,[3] and liposomes.[4] There are also explorations on hollow nanostructures *via* emulsion polymerization,[5] phase separation,[6] suspension polymerization,[7] hydrothermal,[8] and self-assembly.[9] Recently, monoporous hollow microspheres have received much attention due to their higher effective diffusivity and straightforward connectivity between the interior and exterior of hollow spheres.[10] These monoporous microspheres offer enhanced rates of encapsulation as well as being suitable for other applications, *e.g.*, catalytic carriers, thermal insulation and drug targeting.[11] However, the design and preparation of monoporous microspheres present significant challenges because of the scarcity of facile processing methods. Most of current techniques use intricate physical methods and require highly specialized equipment, harsh processing environments and, often, template elimination. In most cases, unfortunately, complex processes are often involved.[12] Interestingly and exhilaratingly, our study shows a facile and effective one-pot route for synthesis of monoporous polymer microspheres *via* microwave irradiation.

Microwave-mediated synthesis of organic molecules and inorganic nanomaterials is of broad interest during the past decade.[13] Owing to the rapid and homogeneous heating as well as convenient control of the experimental condition, the microwave-mediated method often allows for ultrafast and high efficient preparation of organic molecules or nanomaterials with high yield. We have previously developed microwave-mediated quantum dots, PbS hexapods, silver nanocubes and nanowires in the organic phase.[14,15] These results have stimulated many interests in more extensive regions of microwave-mediated synthesis both in organic, polymer and inorganic nanomaterial chemistry. Herein, we demonstrate a facile, fast and environmentally friendly approach for fabrication of monoporous polymer spheres with anisotropic nanostructures. This template-free method employs directly the dispersion polymerization of vinyl monomer under microwave irradiation, giving rise to one-step synthesis of well-defined monoporous polymer microspheres. The microwave-mediated dispersion polymerization of styrene (St) was conducted at ~70 °C in alcoholic solution using azobisisobutyronitrile (AIBN) as radical initiator, and poly(vinylpyrrolidone) (PVP, $M_w = 30\,000$) as steric stabilizer. This polymer chemistry method only involves the mono-phase polymerization system and does not require an additional template removal step. The diameters of microspheres and the single pore sizes in microsphere surfaces could be tuned through changing the polymerization parameters such as the concentration of monomer, initiator and stabilizer as well as the polymerization time. So far as we know, it is the first report stating that polystyrene microspheres with this novel morphology are synthesized through a simple one-step dispersion polymerization method.

2 Experimental section

In a typical synthesis, AIBN (20 mg) and PVP (0.2 g) were added into ethanol (37.5 mL) with magnetic stirring at room temperature to dissolve. Then, styrene (2.5 mL) was added, after that the mixture was bubbled with nitrogen for 30 min. The reaction was allowed to proceed under 400 W microwave irradiation in a microwave reactor equipped with reflux condenser and internal temperature probe for

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10–60 min at ~70 °C. It was observed that the reaction mixture turned opalescent when polymerization was conducted for about 3 min, indicating the occurrence of PVP-stabilized polymer aggregates. Finally, the product was centrifuged at 6000 rpm for 10 min, washed three times with ethanol, and then dried in vacuum for 24 h. The polymer aggregates were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3 Results and discussion

The prepared polymer microspheres were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1a and b indicate the well-defined polymer microspheres with an average size of ~1.1 μm, with different sized pores in their surfaces, that is 200–300 nm (~250 nm in average) in Fig. 1a and ~110 nm in Fig. 1b, respectively. Fig. 1c presents the magnified SEM image of the microspheres in Fig. 1a, which exhibit the monoporous morphology evidently. Similar to that of microspheres in Fig. 1a, it is reasonable that the pores of some polymer microspheres cannot be observed in the same image, because many of them are hidden behind microspheres. Moreover, no polymer microspheres with two or more pores are observed, indicating the superiority of the microwave polymerization process towards monoporous polymer microspheres synthesis. To further demonstrate the monoporous feature of polymer microspheres, the sample shown in Fig. 1a and c was investigated by TEM. As shown in the typical TEM image (Fig. 1d), there is only one pore formed throughout each sphere. From Fig. 1d, it is estimated that the average pore size is about 250–300 nm in diameter and depth, which correlates with the observed results in Fig. 1a and c. The results indicate that monoporous polymer microspheres are successfully synthesized *via* microwave-mediated dispersion polymerization.

It is demonstrated that polymer microspheres with sizes ranging from nanometres to micrometres, with no pore or a sole pore in the surface of each sphere, can be fabricated. Both the diameter of the spheres and the pore in the surface of each sphere can be controlled simply by tuning the synthesis parameters. Firstly, the concentration of the initiator AIBN is found to have a significant influence on both the morphologies and sizes of the polymer spheres. When 0.125 mg mL^{-1} of initiator is utilized, nanospheres with an average diameter of ~350 nm are obtained. Just as shown in Fig. 2a, the nanospheres are not very uniform in size, and few spheres with single pores are observed. Increasing the AIBN concentration to 0.25 mg mL^{-1}, the resulting products are still spheres without pores in their surfaces, whose mean diameters are about 520 nm with narrow size distribution (Fig. 2b). From the above observation, it is found that the initiator at lower concentration leads to smaller spheres. For a small concentration of the initiator, the concentration of produced oligomeric radicals is also low, resulting in low coagulation efficiency of unstable nuclei to form primary particle nuclei.[16] As a result, the growth speed of polymer microspheres is slow, and accordingly a non-porous structure with a small diameter is formed. It is deduced that the nonporous spheres are formed because the cavity inside has been filled by polymers. And as polymerization goes on, no pore comes into being (Fig. S1, ESI†). When the concentration of AIBN reaches 0.375 mg mL^{-1}, a single pore in the surface of each sphere appears, just as shown in Fig. 2c. The average diameter of the spheres increases to about 800 nm, and that of the pores is about 200 nm. Uniform monoporous spheres are obtained when the concentration of AIBN is increased to 0.5 mg mL^{-1}. Fig. 2d presents the homogeneous microspheres with an average diameter of about 1.1 μm. The mean size of pores increases slightly to about 250 nm. The spheres continue growing larger when the concentration of AIBN is further increased. Fig. 2e depicts the spheres obtained when the concentration of AIBN is 0.625 mg mL^{-1}. As shown in the SEM image, the polymer spheres are about 1.3 μm in diameter, while the sizes of the

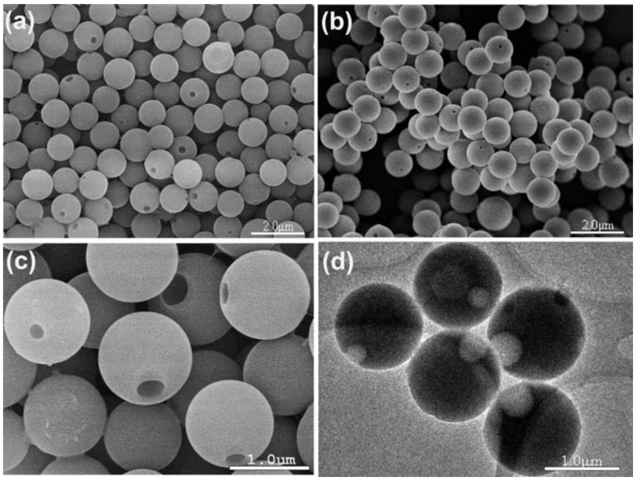

Fig. 1 Typical SEM and TEM images of the monoporous polymer microspheres. (a and b) SEM images of spheres with different sized pores in their surfaces; (c) magnified SEM image of monoporous microspheres in (a); and (d) TEM image of microspheres in (a). Most of the microspheres have single hole, but not each one can be discerned, since many holes are hidden in the back of the microspheres.

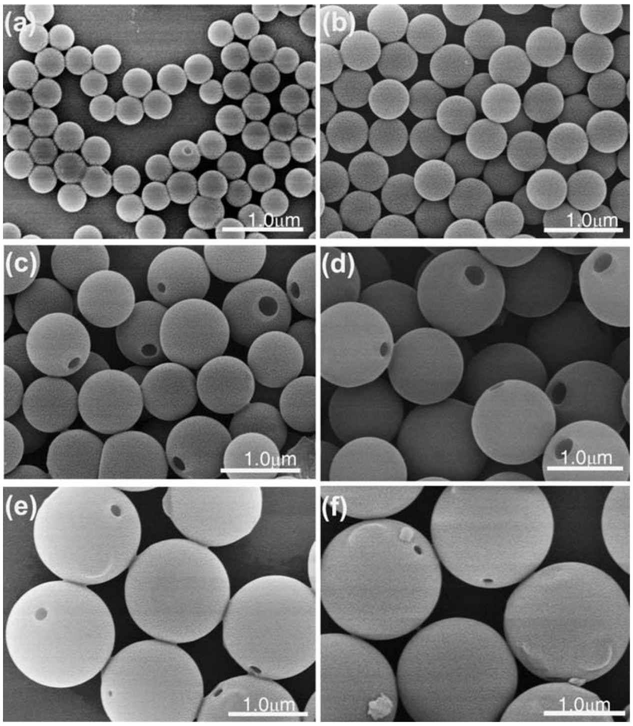

Fig. 2 Polystyrene spheres obtained at different concentrations of AIBN while other conditions are kept the same: (a) 0.125 mg mL^{-1}, (b) 0.25 mg mL^{-1}, (c) 0.375 mg mL^{-1}, (d) 0.5 mg mL^{-1}, (e) 0.625 mg mL^{-1}, and (f) 0.75 mg mL^{-1}.

pores shrink to about 130 nm. Interestingly, the SEM image reveals that the surfaces of the spheres are no longer smooth, instead, some bulges appear. One plausible explanation is that the microsphere surface captures secondary small particles, which are favorably formed when more initiator is added.[16] Larger spheres are synthesized when the initiator is added at the concentration of 0.75 mg mL^{-1}. The spheres are about 1.5 μm in diameter and the sizes of pores are about 90 nm (Fig. 2f). In addition, the bulges in the surfaces become more and more apparent and universal. It is evident that given enough initiator for the formation of pores in the surfaces, more initiator leads to smaller pores. Increasing the initiator concentration leads to oligomeric radicals of higher concentration in the continuous phase, and thus promotes nucleation and induces higher efficiency of oligomeric radical entry and polymerization inside. When the effect of promoting growth is predominant against expansion of cavity, larger spheres with smaller pores are obtained.

In order to investigate the growth process of polymer microspheres, time-resolved evolution of the polymer microstructures during microwave-controlled dispersion polymerization was monitored by SEM. Fig. 3 shows the time-dependent SEM images of polymer nanostructures in the one-step reaction. It is observed that during the first 3 min upon the microwave irradiation, the products are mainly nanoparticles with diameters of about 50 nm or less and some vesicles whose diameters are about 1 μm (Fig. 3a). It is shown (Fig. 3a, inset) that the vesicles are formed through aggregation of the small nanoparticles due to Brownian diffusion of colloidal nanoparticles and the shear stress of the fluid.[17] When the reaction time is prolonged to 5 min, microspheres or semispheres, as well as small nanoparticles are generated (Fig. 3b). It is observed that the larger spheres resulting from aggregating nanoparticles are hollow with the size ranging from 500 nm to about 1 μm, while the smaller nanoparticles grow to a size of about 200 nm. During this early stage of dispersion polymerization, microspheres formed from aggregation of nuclei nanoparticles are monomer-swollen, and the polymerization of St is not completed within spheres. After microwave irradiation for 7 min, spheres with a "pothole" in the surfaces are formed (Fig. 3c). At this stage, the small unstable particles are adsorbed by stable particles.[17] And, due to the ultrafast scavenge and kinetic trapping of St monomers in microwave-mediated polymerization, the polymer shell sinks or splits at a relatively thinner site of the shell around the monomer-swollen cavity, thus, monoporous polymer microspheres appear *via* anisotropic contraction of the monomer-swollen spheres.[17] As particle growth goes on, size focusing occurs and allows for narrower size distribution of polymer microspheres due to their aggregative mechanism of growth.[16] Uniform monoporous microspheres are obtained after irradiation for 10 min (Fig. 3d). It is revealed in Fig. 3d that the size distribution of the spheres at this stage is monodisperse, and pores shrink from the big open mouth (300–400 nm) to about 240 nm. Afterward, the polymer spheres grow larger with a decrease of mean pore size and broadening of the size distribution (Fig. 3e–h). As shown in Fig. 3h, when the reaction is prolonged to 1 h, spheres ranging from about 1.5 μm to 1.9 μm are fabricated. As shown by arrows, many of the pores shrink to less than 100 nm, even as small as 50 nm. Theoretically, the pores at the early stage of polymerization are formed under kinetic controlled reaction conditions, and they have high surface energy. With reaction time prolonging, the pores are gradually filled with freshly produced polymers, switching to a thermodynamically stable state. Besides, it is observed that some bulges are formed on their surfaces, too. Actually, some smaller spheres are also observed in the sample as shown in Fig. S2 (ESI†). It is deduced that part of the secondary stabilized particles are absorbed by those existing stable spheres, while some others become newly formed stable particles themselves.

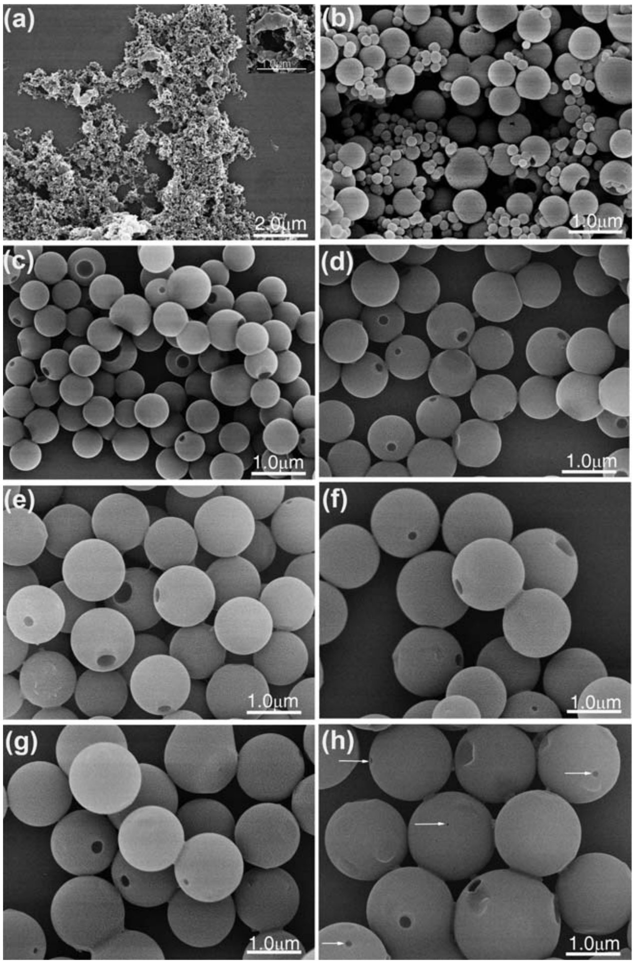

Fig. 3 Time-dependent morphological evolution of polymer microspheres. (a), (b), (c), (d), (e), (f), (g), and (h) refers to polymer spheres at 3 min, 5 min, 7 min, 10 min, 20 min, 30 min, 40 min, and 60 min, respectively.

The influence of monomer concentration is also considered. It was reported that an increase of monomer concentration resulted in larger particle nuclei swollen by the monomer to a larger extent, and led to an increase of the final particle size.[17,18] In our system, as revealed by Fig. S3 in ESI†, when monomer is insufficient, the size distribution of polymer microspheres becomes broad, due to hindering of the size distribution narrowing mechanism that takes effect only when the monomer concentration is high enough.[17] No obvious difference in sphere sizes is observed with further increase of monomer concentration, while the size of pores increases because highly swollen spheres caused by higher concentration of monomers endow stronger volume contraction along with the polymerization, resulting in a larger cavity. However, when monomer is excessive, coalescence of large particles occurs, which is consistent with the previous report.[17] Besides, steric stabilizer is believed to play an important role in synthesis of uniform polystyrene microspheres *via* dispersion polymerization. As shown in Fig. S4a in ESI†, without stabilizer, large

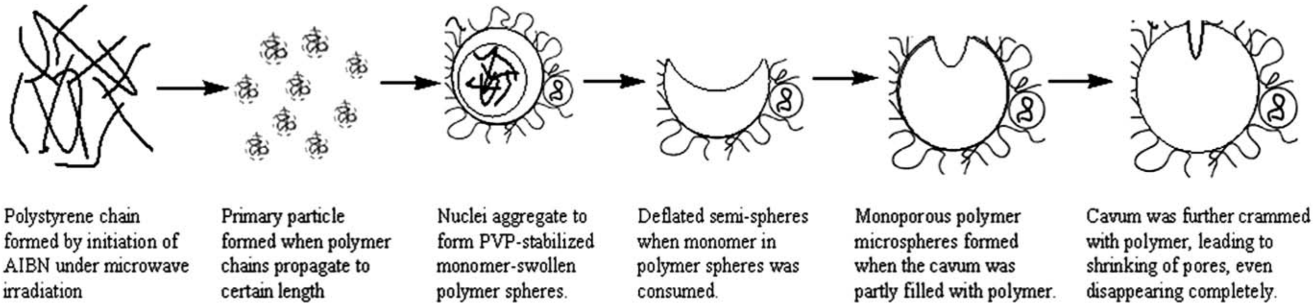

Fig. 4 Schematic illustration of one-step preparation of monoporous polymer microspheres *via* microwave-controlled dispersion polymerization.

multiporous or bowl-like spheres with diameters of ~2 μm are formed. Interestingly, Fig. S4a† clearly reveals the large cavity in the spheres. It is reported that nuclei particles coagulate with each other until all the surfaces are covered by stabilizer molecules.[17] So when no or little PVP is added, aggregation will take place during a longer stage, producing larger monomer-swollen particles and larger cavities after monomers are consumed. Then the greater difference in pressures between cavities and the continuous phase causes deswelling to a larger extent, and eventually results in collapse at more loci or of a larger region. At low PVP concentration, the size distribution of spheres is wide because particle aggregation is prone to occur without enough stabilizer on their surfaces (Fig. S4b, ESI†). Overall, from Fig. S4†, it is revealed that PVP plays a key part in tuning both morphologies and sizes of the microsphere.

Table S1† lists the monoporous polymer microspheres resulting from microwave-mediated dispersion polymerization of St under various reaction feed ratios and reaction times. From Table S1†, one can see that the sphere size increases with an increase in concentration of the AIBN initiator and prolongation of the reaction time, whereas the sphere size decreases with an increase in concentration of PVP stabilizers. On the other hand, it is found that longer reaction time causes a decrease of the pore size. An optimized feed ratio of AIBN/St/PVP plus optimal reaction time affords well-defined polymer microspheres with tunable sizes.

The schematic illustration of growth process of monoporous polymer microspheres is deduced in Fig. 4. In the dispersion polymerization system, monomer (St), initiator (AIBN) and stabilizer (PVP) are dissolved completely in ethanol to form a homogeneous solution. Under microwave irradiation, the solution is swiftly heated in seconds, up to the boiling point of ethanol, *i.e.* 70 °C. AIBN thermally decomposes and produces a radical to initiate polymerization of St. When polymer chains propagate to a certain length and become immiscible in ethanol, they start to aggregate and precipitate from ethanol, forming nanoparticles with PVP adsorbed on the surfaces. These polymerized nuclei extract monomers from the continuous phase, and aggregate with each other because of Brownian diffusion and the shear stress of the fluid, forming monomer-swollen polymer nanoparticles.[16] When all the particles are coated and stabilized by PVP molecules covering on their surfaces, no more aggregation occurs. However, because of the enormous number of stable particles, the remaining oligomeric radicals in continuous phase cannot reach a sufficient degree of polymerization to form new particles.[19] Alternatively, these oligomeric radicals are absorbed by the stabilized particles, leading to further growth of the particles. At the same time, as another motivator for particle growth, polymerization within these monomer-swollen particles is also predominant along with the continuous diffusion of monomer into particles. This process will be underway until all the monomer is consumed completely.[17,20] Microwave-accelerated polymerization causes fast consumption of St monomers inside the swollen microspheres and thus strong deswelling of the microspheres, giving rise to mechanical stress at the shells and collapse of the polymer shells at relatively thinner sites. This is unavoidable because these microspheres are formed by aggregation of small particles, and the difference in mechanical strength at different locations of the spheric shell must exist. Finally, polymer hemispheres with large cavity are formed. Some hemispheres can also be observed due to incomplete surrounding of the monomer by the polymer when samples are taken out from the reaction system in the early stage, just as shown in Fig. 3a inset. Styrene continues diffusing into the disperse phase of polymer nanoparticles because of the monomer partition between the polymer and ethanol phases. Fast polymerization of St in deflated microspheres, which has higher surface energy, promotes the epitaxial polymerization along with the open edge of microspheres, giving rise to an increase of the shell thickness and curvature of polymer hemispheres and decrease of the size of the opening mouth. Finally, the monoporous polymer microspheres are produced after St is depleted. In this process, microwave irradiation plays an indispensable role by accelerating the consumption of St, which results in formation of kinetic-controlled products, monoporous polymer microspheres. In comparison, conventional polymerization favors formation of thermodynamic-controlled products, solid polymer microspheres (Fig. S5, ESI†), which highlights the distinct difference between microwave and conventional polymerization.

4 Conclusions

In conclusion, we reported one-step fast synthesis of uniform and monoporous polymer microspheres *via* microwave-controlled dispersion polymerization. The size of hollow spheres and the pores in their surfaces can be tuned to some extent depending on the reaction conditions. The experimental results reveal that microwave irradiation allows us to design and prepare many kinetic-controlled nanoscale products, which are difficult to be obtained by the classic heating method. Considering the ingenuity of the microwave-mediated strategy, this scalable fast route will provide unprecedented opportunities to synthesize well-defined polymer nano/micro-structures.

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