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One-Pot Synthesis of Highly Folded Microparticles by Suspension Polymerization

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Ⓢ *Supporting Information*

ABSTRACT: A facile method of preparing highly folded cross-linked polymeric microparticles has been developed via one-pot suspension polymerization under high-speed homogenization. The wrinkles result from the evaporation of solvent in the cross-linked microparticles. The effects of microparticle cross-linking density and solvent on the polymer have been studied in detail. It was found that a medium cross-linking density (DVB/St = 0.5 by weight) is optimal for producing the most folded surface and the higher the solvent content, the deeper the surface wrinkles. This method is very simple and in principle can be applied to produce wrinkled microparticles with other chemical compositions.
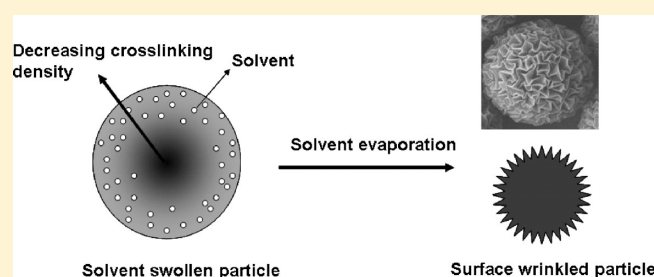
INTRODUCTION

Microparticles with various surface morphologies, such as popcorn-like,[1,2] raspberry-like,[3] wrinkled labyrinth patterned,[4] snowman-like,[5] and patched,[6] have attracted considerable attention recently. These surface-structured microparticles have potential applications in biomedical[7] and electrical materials,[8,9] controlled drug delivery,[10] catalysis,[11] and monolithically structured microparticle columns.[12] Microparticles with nonsmooth surfaces are especially interesting for their large specific surface area, multi-microdomains, and micro/nanoscale features. Jiang et al. have synthesized microparticles with nonsmooth surfaces such as urchin- or rambutan-like spheres showing superhydrophobicity.[13−16]

Microparticles with different surface morphologies can be synthesized by various methods such as seeded emulsion polymerization, dynamic swelling, and templating;[3,17−19] however, those methods normally involve multiple steps and thus are time-consuming or result in limited yields.[20−22] Through one-step suspension polymerization, cross-linked particles with slightly wrinkled surfaces or porous structures have been synthesized, with sizes on the order of millimeters.[23−25] An efficient approach to preparing microparticles with nonsmooth surfaces is still lacking. In this letter, we introduce a facile method to synthesize microspheres with highly folded surfaces where all reactants are mixed in one pot and converted in a single step.

EXPERIMENTAL SECTION

Materials. Styrene (St, Aladdin Chemistry Co. Ltd.) and divinylbenzene (DVB, J&K Scientific Ltd.) were purified via passage through a basic alumina column to remove the inhibitor before use. Reagent-grade 2,2′-azobisisobutyronitrile (AIBN, Sinopharm Chemical Reagent Co., Ltd.) was purified by recrystallization in ethanol. Maleic anhydride (MA, Aladdin

Chemistry Co. Ltd.) was copolymerized with St by precipitation polymerization according to ref 26. Copolymer SMA (St-alt-Ma) was then hydrolyzed in the proper amount of 3 wt % sodium hydroxide solution. The product was named HSMA and used as the stabilizer.[26]

Synthesis of Highly Folded Microparticles. The microparticles were produced by suspension polymerization, where a mixture of certain amounts of St, DVB, toluene (as a cosolvent for monomers), AIBN, and water were mixed with 10 wt % HSMA by stirring at 13 000 rpm for 2 min. The as-formed dispersion was then heated to 70 °C to finish the polymerization process. The microparticles were collected by centrifugation (8000 rpm, 5 min) and washed with water to remove HSMA on the surface and then with ethanol twice and then were vacuum dried at room temperature for 24 h (Supporting Information). A high HSMA concentration is essential to stabilize the resultant particles, probably because of the weak adsorption of HSMA because only such high HSMA solution concentrations can drive adsorption on particle surfaces. Indeed, there is still a substantial amount of HSMA in the bulk solution that can be easily isolated from the microparticles by centrifugation.

Characterization. The surface morphology of the resultant microparticles was investigated by scanning electron microscopy (SEM, JEOL JSM6700) and transmission electron microscopy (TEM, Hitachi H800, JEOL JEM-2200FS).

RESULTS AND DISCUSSION

First, polymerizations at two different St/DVB ratios in the absence of toluene were conducted. The morphology of the formed microparticles at different polymerization intervals is shown in Figure 1. It is clear that the cross-linking density plays a
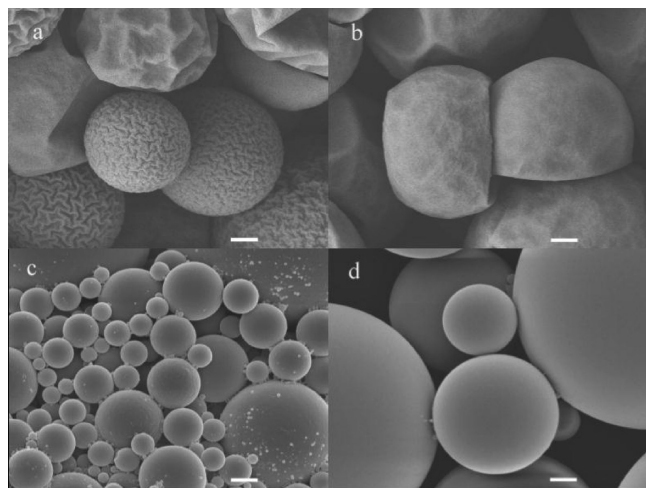
Figure 1. SEM images of polymer microparticles in the absence of toluene. (a) St/DVB = 2:1, 2 h; (b) St/DVB = 2:1, 8 h; (c) St/DVB = 3:0, 8 h; and (d) St/DVB = 0:3, 8 h. The scale bar is 1 μm.

Figure 2. SEM images of polymer microparticles produced at different polymerization intervals: (a) 2, (b) 4, (c) 6, and (d) 8 h. The recipe was 10 g of toluene, 2 g of St, 1 g of DVB, 0.06 g of AIBN, and 87 g of a 10 wt % HSMA water solution. The scale bar is 1 μm. (Inset) TEM images. The scale bar is 1 μm.

Scheme 1. Illustration of the Formation of Surface-Wrinkled Particles

vital role in determining the surface morphology of the formed polymeric microparticles. Both the un-cross-linked and highly cross-linked samples (Figure 1c,d, respectively) had smooth surfaces, and the one with an intermediate cross-linking density had slightly wrinkled surfaces (Figure 1b). Also, it is very interesting that the surface morphology of the formed microparticles changes with polymerization time. Taking the sample with St/DVB = 2:1 (by weight) as an example, when polymerized for 2 h, about half of the microparticles (Figure 1a) had highly folded surfaces and the other half had slightly wrinkled surfaces; when polymerized for 8 h (Figure 1b), only microparticles with slightly wrinkled surfaces were observed; and after 8 h, no further changes in surface morphology were observed. Within this range of conditions, the optimal cross-linking density is an St/DVB ratio of 2:1 by weight.

On the basis of the above observations, it is reasonable to infer that the formation of wrinkled surfaces is associated with both the cross-linking nature of the polymeric network and the presence of small organic molecules. A possible mechanism for the formation of wrinkled microparticles can be proposed. Because AIBN is oil-soluble, the initiation and propagation of polymerization should take place in the oil droplets. In the presence of DVB, a cross-linked polymer micronetwork in oil droplets will gradually form, which is swollen by monomer molecules at low monomer conversion (e.g., polymerized for 2 h). After the removal of monomer, the microparticles collapse to form a wrinkled surface (as seen in Figure 1a). At high monomer conversion (e.g., polymerized for 8 h), few monomer molecules are left and the cross-linked polymer micronetwork becomes less swollen, thus the wrinkles on the surface become much shallower (as seen in Figure 1b). In the case of a non-cross-linked system, no elastic contraction will happen, whereas in the case of a high cross-linking density, the microparticles become too rigid to be swollen; therefore, no wrinkled surfaces are observed in either of these extreme situations (as seen in Figure 1c,d, respectively).

The above systems do not produce microparticles with highly folded surfaces, especially at high monomer conversion. According to the proposed mechanism, we envisage that by incorporating a nonreacting cosolvent one would be able to produce microparticles with more folded surfaces even at high monomer
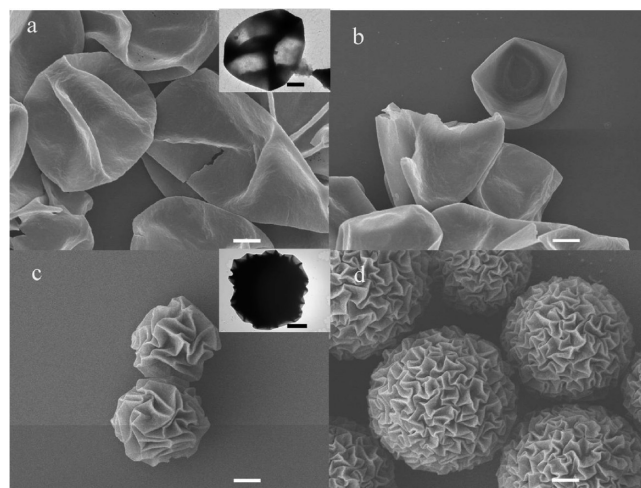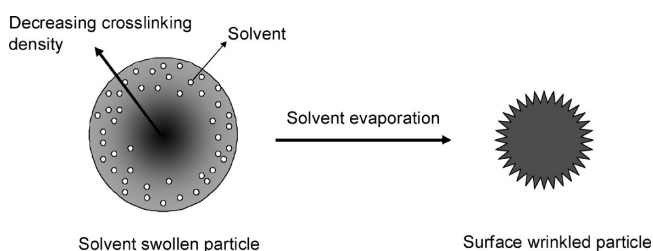
conversion. Toluene was thus added as a cosolvent to the monomer and formed polymer, with the optimized St/DVB ratio determined earlier, and they were then polymerized under otherwise identical conditions. The morphologies of the resultant microparticles at different polymerization intervals are shown in Figure 2. It is worth noting that the particles prepared by this approach are essentially polydisperse, reflecting the size distribution of the monomer droplets. After polymerization for 2 h, hollow, heavily collapsed microparticles were formed; after 4 h, the microparticles became less collapsed; after 6 h, microparticles with highly folded surfaces were observed; and after 8 h, these microparticles grew larger but still maintained highly folded surfaces. Similar to the case without toluene, after 8 h, no further morphological changes were observed. It is interesting to find that at low monomer conversion, microparticles were heavily collapsed (e.g., after being polymerized for 2 h, Figure 2a), which is very different from that in the absence of toluene (Figure 1a), confirming the key role of a swelling agent (solvent or monomers) in the evolution of particle morphology. It is now clear that the presence of a cosolvent plays an important role in the formation of wrinkled surfaces, presumably via maintaining a highly swollen cross-linked polymer micronetwork all the way through the polymerization process. Thus, with toluene involved, we are able to produce cross-linked microparticles with highly folded surfaces even at high monomer conversion.
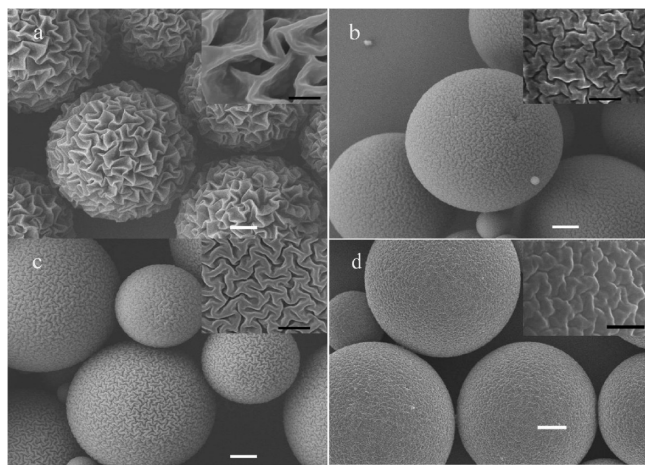
Figure 3. Scanning electron microscope (SEM) images of different solvent-to-monomer ratios of toluene/St/DVB (w/w/w) after polymerzation for 8 h: (a) 10:2:1, (b) 10:3:1.5, (c) 10:4:2, and (d) 10:6:3. The scale bar is 1 μm. (Inset) At higher magnification. The scale bar is 300 nm.
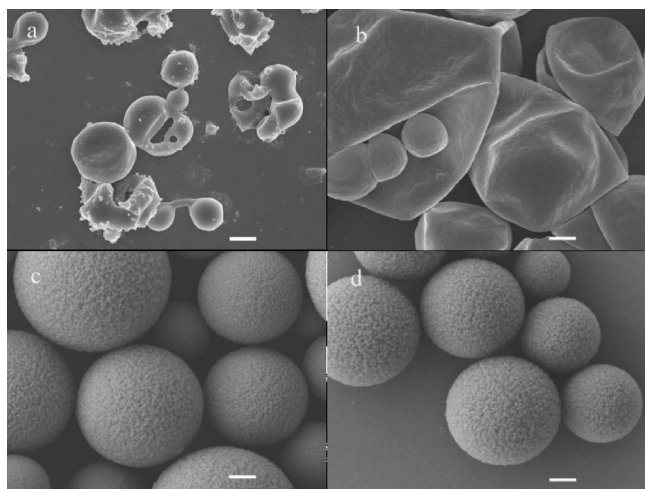

Figure 4. SEM images of microparticles obtained at different DVB/St ratios after polymerization for 8 h: (a) 0:3, (b) 0.3:2.7, (c) 0.9:2.1, and (d) 1.5:1.5. The scale bar is 1 μm.

Previously, millimeter-sized wrinkled particles were produced with suspension polymerization in the presence of toluene, where the resultant particles are only slightly wrinkled on the surface but exhibit a large porosity.[23−25] The formation mechanism for those nonsmooth/porous particles involved the aggregation of primary particles. It is worth noting that according to Figure 2c the microparticles are wrinkled only on the surface (i.e., the center is solid). In support of this conclusion, BET measurements showed a specific surface area of less than 5 $m^2 g^{-1}$, which is much smaller than what would be expected for porous particles. These observations help us to understand the formation of wrinkles on the particle surface (Scheme 1). The cross-linking density in the center of the microparticles is very likely to be higher than closer to the surface, thus the outer part of the particle is more swollen by solvent. Once the solvent has been removed, the outer particle shrinks, resulting in particles with solid centers and wrinkled surfaces. Although not directly

measured in our study, a similar distribution in cross-linking density has been observed in other cross-linked polymeric particles.[27,28]

Considering the important role of toluene in controlling the microparticle surface morphology, the solvent/monomer ratio was examined further (Figure 3). Generally, upon decreasing the solvent to monomer ratio, the wrinkles became shallower (Figure 3a−d), which is in good agreement with the proposed mechanism.

The influence of the cross-linking density was also investigated in the presence of toluene. Without DVB, linear polystyrene dissolved in toluene; consequently, only broken polymer pieces were observed (Figure 4a). With DVB/St = 0.3:2.7, heavily collapsed particles were observed (Figure 4b), presumably resulting from the removal of trapped solvent in the cross-linked polymer particles. When the DVB/St ratio increased to 0.9:2.1, intact spherical microparticles with wrinkled surfaces were formed (Figure 4c). A further increase in the DVB content resulted in more folded surfaces (Figure 3a, with DVB/St = 1:2). Interestingly, when the DVB/St ratio continued to increase to 1.5:1.5, the surface became less folded again (Figure 4d). The surface morphology evolution with cross-linking density in the presence of cosolvent toluene follows a similar trend as in the absence of toluene. This similarity again supports the argument that an appropriately cross-linked polymer network is a prerequisite for the formation of surface-wrinkled microparticles.

CONCLUSIONS

We have developed a one-pot dispersion polymerization method to prepare cross-linked spherical polymeric microparticles with folded surfaces. It was found that both the cross-linking nature of the polymeric network and swelling agents were essential to producing such a surface morphology. A medium cross-linking density gives the most folded surfaces; either too high or too low a cross-linking density will diminish the surface wrinkles. Swelling agents, such as residual monomer or a cosolvent for the polymer, will facilitate the formation of surface wrinkles. This methodology in principle can be applied to the preparation of wrinkled cross-linked microparticles with other chemical compositions.

ASSOCIATED CONTENT

S **Supporting Information.** FTIR spectra of resultant polymer microparticles before and after being washed with water. This material is available free of charge via the Internet at http://pubs.acs.org.

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