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# Synthesis of porous poly(styrene-*co*-acrylic acid) microspheres through one-step soap-free emulsion polymerization: Whys and wherefores

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ABSTRACT

Synthesis of porous poly(styrene-*co*-acrylic acid) (PS-*co*-PAA) microspheres through one-step soap-free emulsion polymerization is reported. Various porous PS-*co*-PAA microspheres with the particle size ranging from 150 to 240 nm and with the pore size ranging from 4 to 25 nm are fabricated. The porous structure of the microspheres is confirmed by the transmission electron microscopy measurement and Brunauer–Emmett–Teller (BET) analysis. The reason for synthesis of the porous PS-*co*-PAA microspheres is discussed, and the phase separation between the encapsulated hydrophilic poly(acrylic acid) segment and the hydrophobic polystyrene domain within the PS-*co*-PAA microspheres is ascribed to the pore formation. The present synthesis of the porous PS-*co*-PAA microspheres is anticipated to be a new and convenient way to fabricate porous polymeric particles.

## 1. Introduction

In recent years, there has been great interest in the fabrication of porous or hollow polymeric particles for their potential applications including drug delivery, stationary phase for chromatography, supports for exchange of ionic compounds, carriers for catalysts, and so on [1–6]. The current approaches to the synthesis of porous microspheres are generally divided into two categories: (1) hard template synthesis [7–16] and (2) soft template synthesis [17–29], each of which involves several well-established procedures, although some other methods such as emulsion/solvent evaporation [30], spray drying [31], controlled phase separation [32,33], solvent swelling [34,35], incorporation of a blowing agent [36,37], and self-assembly [38] are also proposed. The hard template method, in which either the non-cross-linked polymeric microspheres or the linear polymers are employed as the pore-forming agent, has the advantage of the controllable tuning in pore size [10–13]. However, the synthesis of porous microspheres through the hard template method involves multiple and complex procedures. For example, the general method to fabricate hollow/porous microspheres by hard template polymerization includes synthesis of a suitable seed, polymerization of the shell-forming monomer on the seed to form coated microspheres, and then removal of the seed by solvent etching [9–14]. In the soft template synthesis of porous microspheres, diluents [17–20] or surfactant micelles [25–27] are usually employed as the pore-forming agent. With this method, template elimination is avoided, while the porous structure is not easy to control. When diluents are adopted as the pore-forming agent, the non-solvent is responsible for the formation of meso- and macro-pores in the internal structure of the resultant polymeric particles and the good solvent is responsible for the formation of microporous structure [17–20]. Porous microspheres are also prepared by the polymerization of the multiphase emulsion stabilized by unitary or binary surfactants [25–27]. For example, the typical methods for making W/O/W emulsions include a two-step process of the initial formation of an inverse water-in-oil emulsion and then emulsification in water by combination of binary surfactants, and the subsequent controlled polymerization of the W/O/W emulsion leads to the formation of porous particles [25].

This work presents and discusses the convenient synthesis of porous poly(styrene-*co*-acrylic acid) (PS-*co*-PAA) microspheres by one-stage soap-free emulsion polymerization. The present synthesis of the porous PS-*co*-PAA microspheres is much different from the general hard template synthesis and the soft template synthesis as introduced above. The reason for the synthesis of the porous microspheres is discussed and it is deemed that the phase separation between the encapsulated hydrophilic poly(acrylic acid) (PAA) segment and the hydrophobic polystyrene (PS) domain within the matrix of the PS-*co*-PAA microspheres is ascribed to the pore formation.

## 2. Experimental

### 2.1. Materials

The monomers of styrene (St, >98%, Tianjin Chemical Company), acrylic acid (AA, >99%, Tianjin Chemical Company), and methyl

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acrylic acid (MAA, >99%, Tianjin Chemical Company) were distilled under vacuum before being used. The initiator of $K_2S_2O_8$ (>99.5%, Tianjin Chemical Company) and other analytical reagents were used as received. Deionized water was used in the present study.

### *2.2. Synthesis of porous and solid PS-co-PAA microspheres*

To prepare the porous PS-*co*-PAA microspheres, neutral water (120.0 mL) and a given amount of AA were initially added into a glass flask. After the feeding AA being fully dissolved, a given amount of styrene was added. The total amount of the feeding monomers of AA and styrene was kept at 6.00 g. The flask content was vigorously stirred at about 300 rpm for about 30 min at room temperature, and then a given weight of the $K_2S_2O_8$ initiator (0.030–0.120 g) was added. The flask content was degassed under nitrogen purge, and the polymerization was performed with vigorously stirring at 80 °C for 24 h under nitrogen atmosphere. After the completion of the polymerization, the resultant colloid was washed with water (20 mL × 3), collected by centrifugation, and dried under vacuum at 40 °C to obtain the porous PS-*co*-PAA microspheres. The solid PS-*co*-PAA microspheres were prepared with the feeding monomers of styrene (4.80 g, 0.0461 mol) and AA (1.20 g, 0.0167 mol) as similar as the PS-*co*-PAA microspheres except NaOH (0.667 g, 0.0167 mol, which is equimolar amount relative to AA) being added into the solvent of water (120.0 mL) before addition of the monomers, and therefore the polymerization was performed in basic aqueous solution (pH = 13). Herein, it should be noted that solid PS-*co*-PAA microspheres are named, although the solid microspheres synthesized in basic aqueous solution should be poly(styrene-*co*-sodium acrylate) microspheres.

### *2.3. Synthesis of the reference solid polystyrene microspheres and the solid poly(styrene-co-methyl acrylic acid) microspheres*

The solid poly(styrene-*co*-methyl acrylic acid) (PS-*co*-PMAA) microspheres and the solid polystyrene (PS) microspheres were synthesized in neutral water with a similar way for the porous PS-*co*-PAA microspheres. For the synthesis of the solid PS-*co*-PMAA microspheres, neutral water (120.0 mL) and MAA (1.20 g, 0.0139 mol) were initially added into a flask and followed addition of styrene (4.80 g, 0.0461 mol). The flask content was vigorously stirred at room temperature for 30 min and then $K_2S_2O_8$ (0.060 g, 0.22 mmol) was added. The flask content was degassed under nitrogen purge, and polymerization was performed with vigorously stirring at 80 °C for 24 h under nitrogen atmosphere. The resultant PS-*co*-PMAA microspheres were collected by centrifugation, washed with water (20 mL × 3), and dried under vacuum at 40 °C to obtain the solid PS-*co*-PMAA microspheres. The solid PS microspheres were prepared and collected with the similar procedures except the polymerization that was performed in the absence of the hydrophilic monomer of MAA.

### *2.4. Characterization*

Transmission electron microscopy (TEM) measurement was conducted by using a Philips T20ST electron microscope at an acceleration voltage of 200 kV, whereby a small drop of the dispersion of the synthesized microspheres was deposited onto a piece of copper grid and then dried at room temperature under vacuum. The nitrogen adsorption–desorption analysis was carried out at 77 K on a Micromeritics Gemini V system. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the mesopore size distribution was calculated from the adsorption isotherms using the Barret–Joyner–Halenda method. The $^1$H NMR spectra were recorded on a UNITYPLUS-400 spectrometer using $CDCl_3$ as solvent. Dynamic laser scattering (DLS) measurements were taken on Nano-ZS90 (Malvern) laser light scattering spectrometer with He–Ne laser at a wavelength of 633 nm.

## 3. Results and discussion

### *3.1. Synthesis of the porous PS-co-PAA microspheres*

The present synthesis of the porous PS-*co*-PAA microspheres through one-step soap-free emulsion polymerization in neutral water is as similar as those of the core–shell microspheres discussed in the previous manuscript [39]. Fig. 1 shows the TEM images of the porous PS-*co*-PAA microspheres synthesized with different molar ratio of I/M, in which I represents the $K_2S_2O_8$ initiator and M represents the feeding monomers of St/AA (4/1 by weight). Generally, the PS-*co*-PAA microspheres have core–shell structure, which are somewhat as similar as the core–shell microspheres synthesized by one-stage soap-free emulsion polymerization as discussed elsewhere [39]. It is deemed that the core is mainly composed of the hydrophobic PS segment, and the shell is mainly composed of the hydrophilic PAA segment. However, different from the general core–shell microspheres [39], 4–10 nm pores can be discerned in all the PS-*co*-PAA microspheres as shown in Fig. 1. Typically as shown in Fig. 1A, dispersed microspheres with average size at about 165 nm are fabricated at I/M = 1. From the high-magnification TEM image shown in Fig. 1B, various pores, some of which are indicated by cycles, with size ranging from 4–10 nm have been discerned, confirming the synthesis of porous microspheres. DLS analysis shows that the hydrodynamic diameter $D_h$ of the porous microspheres centered at 180 nm is uniformly distributed (Fig. 2A). It is found that the feeding monomers are almost quantitatively converted into the porous PS-*co*-PAA microspheres. Based on the weight ratio of the feeding monomers of St/AA and the average size of the porous PS-*co*-PAA microspheres as shown in Fig. 1A, the shell thickness of the porous PS-*co*-PAA microspheres, 32 nm, is approximately estimated, assuming the core of the microspheres being composed of the sole PS segment and the shell being composed of the sole PAA segment. Clearly, the calculated value is as similar as those by the TEM image shown in Fig. 1B (32 nm vs. ~34 nm). The slight difference between the calculated and the measured values is discussed. It is believed that the shell should be composed of the copolymer of styrene and acrylic acid but not the sole PAA segment, which will make a thick shell and will be further discussed subsequently. Furthermore, it is found that porous PS-*co*-PAA microspheres with pore size at 4–10 nm can be fabricated within a wide I/M range, although the size of the porous PS-*co*-PAA microspheres is somewhat different. For example, 238 nm porous PS-*co*-PAA microspheres (Fig. 1C) are synthesized at I/M = 0.5, and 222 nm porous PS-*co*-PAA microspheres (Fig. 1D) are fabricated at I/M = 2. The DLS analysis shows that the hydrodynamic diameter $D_h$ of these both microspheres is uniformly dispersed (Fig. 2B and C).

The monomer of MAA is somewhat as similar as AA. For example, both MAA and AA are hydrophilic and contain the carboxyl group. It is expected that porous PS-*co*-PMAA microspheres should also be synthesized with the similar method as the porous PS-*co*-PAA microspheres. However, the speculation is not the fact. As shown in Fig. 3A, 180 nm solid PS-*co*-PMAA microspheres instead of porous microspheres are fabricated at I/M = 1.0% with the weight ratio of the feeding monomer of St/MAA = 4/1. The solid PS-*co*-PMAA microspheres are just as similar as the 330 nm solid PS microspheres synthesized at I/M = 1.0% (Fig. 3B). In comparison, both the solid PS-*co*-PMAA microspheres and the solid PS microspheres show no porous character, which are much different from the porous PS-*co*-PAA microspheres as shown in Fig. 1, although these three microspheres are synthesized under the same conditions.