Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Synthesis of Nonspherical Polystyrene Particles Using "Giant" Surfactant and Its Superhydrophobic Property

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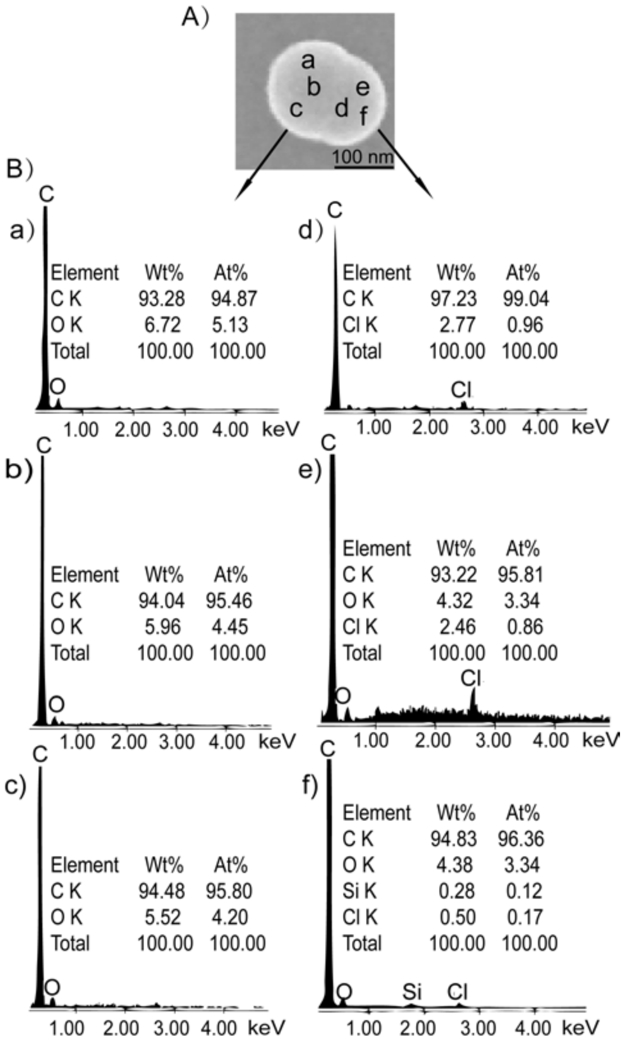
1. Synthesis of CPS-P4VBC particles

The dumbbell-shaped colloidal particles were prepared according to a modified method reported by Weitz et al. [1]. The spherical cross-linked seed particles (CPS) were first prepared via emulsion polymerization. Polymerization was performed in a 100 mL one-necked round-bottomed flask. Initially, 0.2 g of sodium dodecyl sulfonate was dissolved in 50 mL of distilled water, and then 2.5 g of St and 0.05 g of divinylbenze (DVB) were added under stirring. The mixture was dispersed under ultrasonic irradiation, and purged with Argon gas for 20 min to get rid of the oxygen. After it was heated to 70 °C, an aqueous solution of the initiator (APS, 0.05 g dissolved in 2 mL of distilled water) was added to the mixture to initiate the polymerization. The polymerization was stopped after 24 h to ensure complete conversion, and the reaction mixture was slowly cooled to room temperature. Finally, the latex particles diluted in water by 1:100 (v/v) for the measurements of Z-average size, scanning electron microscopy and transmission electron microscopy.

To prepare dumbbell nanoparticles (CPS-P4VBC) containing chloride groups, the seeded emulsion polymerization was carried out with the CPS particles. 0.5 g of CPS seed particles were swollen with a monomer emulsion. The monomer solution consisted of 4-vinylbenzyl chloride (4VBC, 1.5 g), DVB (0.04 g), sodium dodecyl sulfonate (0.16 g) and H_2O (40 g). The mixture was dispersed under ultrasonic irradiation, Then the mixture was stirred at speed of 60 rpm for 24 h at room temperature to allow the seed particles to swell. After swelling, the mixture was purged with Argon gas for 20 min to get rid of the oxygen. Then it was heated to 70 °C, an aqueous solution of the initiator (APS, 0.04 g dissolved in 1mL of distilled water) was added to the mixture to start the polymerization. After the polymerization, the latex dispersion was washed through three centrifugation cycles at a centrifuge speed of 12000 rpm, replacing the supernatant each time with methanol. The centrifugation process also helped remove small latex particles resulting from secondary nucleation events during the seeded growth polymerization.



a)

Element	Wt%	At%
C K	93.28	94.87
O K	6.72	5.13
Total	100.00	100.00

b)

Element	Wt%	At%
C K	94.04	95.46
O K	5.96	4.45
Total	100.00	100.00

c)

Element	Wt%	At%
C K	94.48	95.80
O K	5.52	4.20
Total	100.00	100.00

d)

Element	Wt%	At%
C K	97.23	99.04
Cl K	2.77	0.96
Total	100.00	100.00

e)

Element	Wt%	At%
C K	93.22	95.81
O K	4.32	3.34
Cl K	2.46	0.86
Total	100.00	100.00

f)

Element	Wt%	At%
C K	94.83	96.36
O K	4.38	3.34
Si K	0.28	0.12
Cl K	0.50	0.17
Total	100.00	100.00

Figure S1. (A) SEM images of CPS-P4VBC particle; (B) EDX map of (a~c) PS bulb and (d~f) P4VBC bulb.

2. Synthesis of spherical “giant” surfactants

The spherical cross-linked particles (CPS/P4VBC) were prepared via emulsion polymerization. Polymerization was performed in a 100 mL one-necked round-bottomed flask. Initially, 0.24 g of sodium dodecyl sulfonate was dissolved in 60 mL of distilled water, and then 2.5g of St, 0.5 g of 4VBC and 0.06 g of DVB were added under stirring. The mixture was dispersed under ultrasonic irradiation, and purged with Argon gas for 20 min to get rid of the oxygen. After the temperature was increased to 70 °C, an aqueous solution of the initiator (APS, 0.06 g dissolved in 2 mL of distilled water) was added to the mixture to initiate the polymerization. The polymerization was stopped after 24 h to ensure complete conversion, and the reaction mixture was slowly cooled to room temperature. The latex dispersion was washed through three centrifugation cycles at a centrifuge speed of 12000 rpm, replacing the supernatant each time with methanol.

Chemical treatment was carried out to incorporate hydrophilic MPEG-Na to spherical cross-linked particles (CPS/P4VBC). Spherical cross-linked particles (0.46 g) were mixed with 1.18 g of MPEG-Na in dried THF (30 mL). After stirring for 12 h at 50 °C, MPEG-Na and NaCl were removed by repeated centrifugation 3 times and replacement of the solvent with THF and water, respectively. The recovered spherical "giant" surfactants were dried in a vacuum oven at 40 °C and were stored in desiccator before use. The structures of the spherical "giant" surfactants were confirmed by EDX spectra and FT-IR spectra (Figure S1). The graft content (G%) was calculated as follows: G%= (W_g- W_0) / W_0 × 100%, where W_g and W_0 stand for the weights of CPS-P4VBC-MPEG and CPS-P4VBC, respectively.

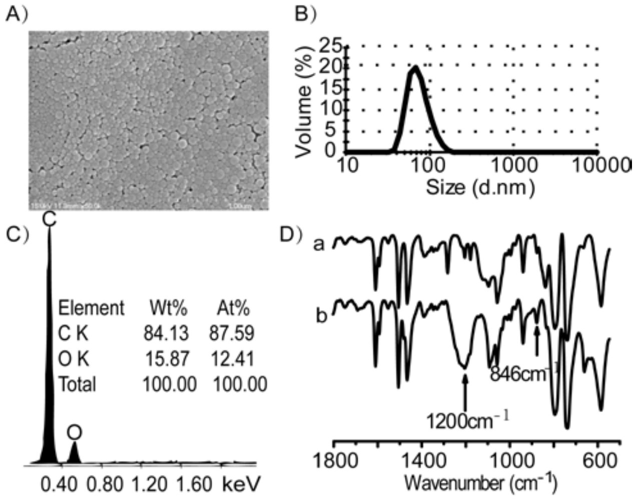


Figure S2. (A) SEM images and (B) particle size distribution (Z-average size = 83 nm, polydispersity index = 0.058) of CPS/P4VBC microspheres; (C) EDX spectrum of spherical "giant" surfactants and (D) FT-IR spectra of (a) CPS/P4VBC microspheres (b) spherical "giant" surfactants. Scale bar: 1000 nm (A).

3. Synthesis of polystyrene colloid particles with spherical "giant" surfactants

The polystyrene colloid particles were prepared via emulsion polymerization with styrene as the monomer, the spherical colloidal particles (CPS/P4VBC-MPEG) as "giant" surfactants and divinylbenzene (DVB) as cross-linker. Ammonium persulfate (APS) was used as initiator for the polymerization. A typical procedure for the emulsion polymerization can be described as follows: Polymerization was performed in a 100 mL one-necked round-bottomed flask. Initially, 0.05 g of spherical "giant" surfactants was dissolved in 50 mL of distilled water, and then 2.5 g of St and 0.05 g of DVB were added under stirring. The mixture was dispersed under ultrasonic irradiation, and purged with Argon gas for 20 min to get rid of the oxygen. After the temperature was increased to 70 °C, an aqueous solution of the initiator (APS, 0.05 g dissolved in 2mL of distilled water) was added to the mixture to initiate the polymerization. The polymerization was stopped after 24 h to ensure complete conversion, and the reaction mixture was slowly cooled to room temperature. Then the latex particles diluted in water by 1:100 (v/v) for the measurements of Z-average size and scanning electron microscopy (Figure S2).

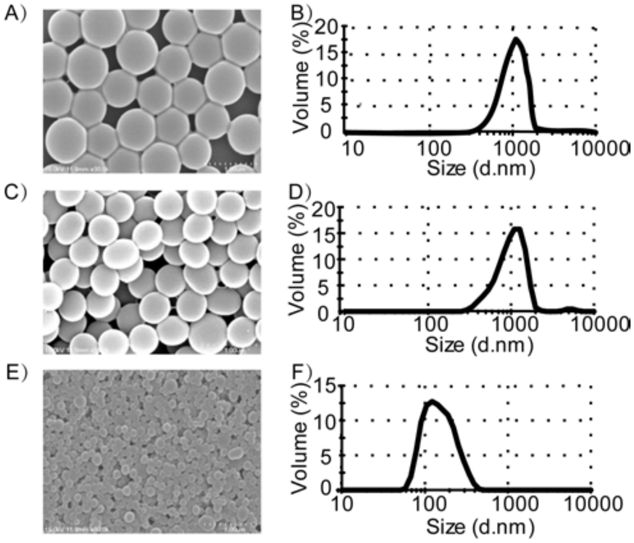


Figure S3. The SEM images and particle size distributions of polystyrene particles obtained from emulsion polymerization using spherical “giant” surfactants with the concentration of (A, B) 0.2 mg/mL (Z-average size = 772 nm, PDI = 0.110), (C, D) 1 mg/mL (Z-average size = 708 nm, PDI = 0.190), (E, F) 5 mg/mL (Z-average size = 155 nm, PDI = 0.137). Scale bar: 1000 nm (A, C, E).

4. Removing MPEG from the surface of spherical polystyrene colloid particles.

To remove MPEG from the surface of polystyrene colloid particles, 0.5 g of spherical polystyrene colloid particles were dispersed in 10 mL of concentrated hydriodic acid. After the mixture was stirred for 3 h at reflux temperature, it was poured into 100 mL of distilled water. The precipitate was collected on a filter and washed completely by distilled water, and then dried to give a light yellow powder (69 % yield).

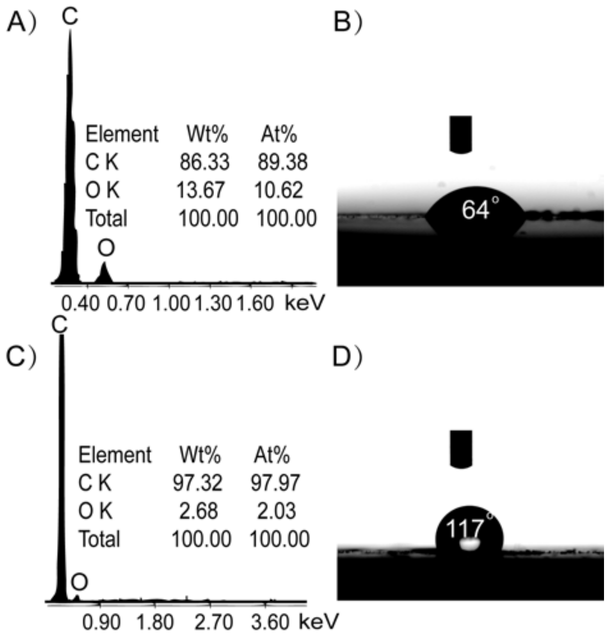


Figure S4. The EDX spectra and water contact angle photographs of the films from PS particles with smooth surfaces: (A, B) with MPEG, and (C, D) without MPEG on their surfaces.

References

1. J.-W. Kim, R. J. Larsen and D. A. Weitz, *J. Am. Chem. Soc.*, 2006, **128**, 14374-14377.