Supporting Information

An Efficient Approach for Production of Polystyrene/Poly(4-vinylpridine) Particles with Various Morphologies Based on Dynamic Control

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Experimental Part

Materials

Styrene (St), 4-vinylpyridine (4VP), divinylbenzene (DVB), sodium dodecyl sulfate (SDS) and ethylene glycol dimethacrylate (EGDMA) were supplied by Alfa Aesar. Potassium persulfate (KPS), 2,2′-azobisisobutyronitrile (AIBN), polyvinyl pyrrolidone (PVP, K30), NaOH, toluene and ethanol (C_2H_5OH) were purchased from Beijing Chemical Company. Benzoyl peroxide (BPO) was purchased from Tianjin Fuchen Chemical Agent Company and hydroquinol (HQ) was furnished by Shantou Xilong Chemical Company. St and DVB were washed with 5 wt % NaOH solution three times, and then deionized water until it becomes neutral. Other reagents were used as-received without further purification. Distilled and deionized (DDI) water was used in all experiments.

Synthesis of the PS microspheres

PS microspheres were prepared by dispersion polymerization. Ethanol (160g) and PVP (4g) were charged into a 500ml four-necked round-bottom flask equipped with a stirrer, a condenser and a nitrogen inlet. The system was bubbled through nitrogen gas for 60min under stirring (120 rpm). Then the initiator AIBN (1.2g) was dissolved in 40g St and added into the flask. After continuous bubbling through nitrogen for 15 min, the system was raised to 72ºC. The reaction was continued for 12 h, and was

stopped by cooling to room temperature. The microspheres were separated by centrifugation, washed with ethanol and deionized water, and subsequently dried by lyophilization.

Synthesis of the crosslinked PS microspheres

Crosslinked PS microspheres were synthesized by seeded swelling polymerization with the PS microspheres as seed. Table S1 summarizes the polymerization recipes. The deionized water was charged to a 500ml round-bottom flask equipped with a PTFE-coated stir bar and a nitrogen inlet. The PS microspheres, PVP, SDS, sodium bicarbonate and hydroquinone were added into the reactor. The St, DVB and AIBN mixture was added dropwise at a feeding rate of 3g/h. The mixture was stirred under 300rpm at room temperature for 24h. Then the mixture was moved to a single-necked flask equipped with a nitrogen inlet on a rotary evaporator, and the polymerization was carried out at 72ºC oil bath for 12 h. The crosslinked microspheres were separated by centrifugation, washed with ethanol and deionized water, and finally dried by lyophilization.

Table S1. Polymerization recipes for the crosslinked PS Microspheres

Ingredient	Grams
Polystyrene microspheres	6
Styrene monomer	18
Divinylbenzene	0.18
2,2′-azobisisobutyronitrile	0.54
Deionized water	120
Polyvinyl pyrrolidone（5% in water）	6
Sodium dodecyl sulfate（1% in water）	2

Sodium bicarbonate buffer	0.048
Hydroquinone inhibitor	0.04

Preparation of PS/P4VP composite particles

PS/P4VP composite particles were prepared by seeded swelling polymerization. Table S2 summarizes the polymerization recipes. The deionized water and the crosslinked PS microspheres were charged into a 250ml four-neck flask with an agitator, a condenser and a nitrogen inlet. The BPO and AIBN were dissolved in the 4VP, DVB and toulene mixture, and then the mixture was added into SDS aqueous solution and was emulsified by ultrasonication. The emulsified mixture was added into the flask. The mixture was stirred at 300rpm room temperature for 18h. Then the polymerizations were performed under nitrogen with stirring at 300 rpm at 70°C oil bath for 8 h. After reaction, the system temperature was cooled to 50°C to remove the toluene under bubbled with nitrogen gas for 12h.

Table S2. The recipes for PS/P4VP composite microspheres

Ingredient	**Grams**
Crosslinked PS microspheres	1
Deionized water	90
4-Vinylpyridine	3
Benzoyl peroxide	0.033
2,2′-azobisisobutyronitrile	0.033
Divinylbenzene	Variable
Toluene	Variable
Sodium dodecyl sulfate（1.5% in water）	33

Characterization

The morphologies of microspheres were observed by SEM (ZEISS SUPRA55) and SEM sample was prepared as follows: one drop of dilute dispersion was cast on silicon wafer; after drying, it was coated with a thin carbon film. The TEM (JEOL JEM-100CXII) sample was prepared by placing a drop of dilute dispersion on a copper grid. FTIR spectra were recorded on an infrared spectrophotometer (NEXUS670) using KBr pellet samples as a matrix.

Figure

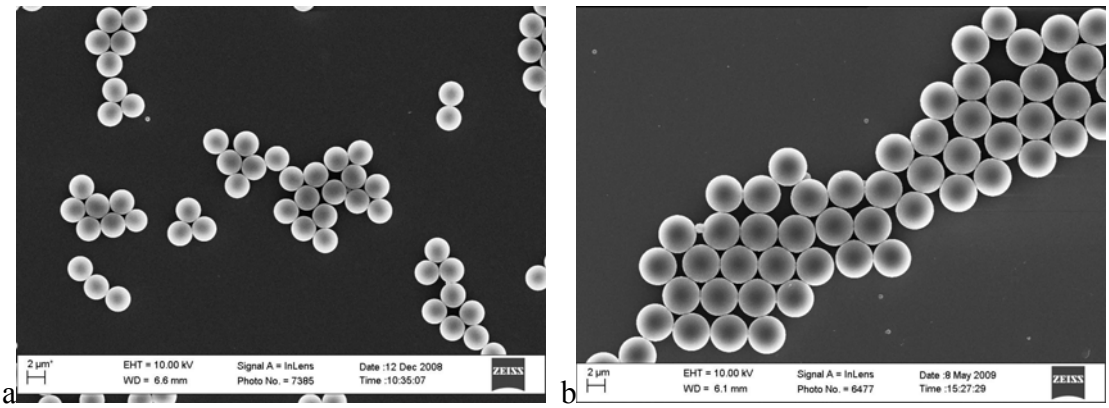

Figure S1. SEM images of a) PS microspheres and b) crosslinked PS microspheres.

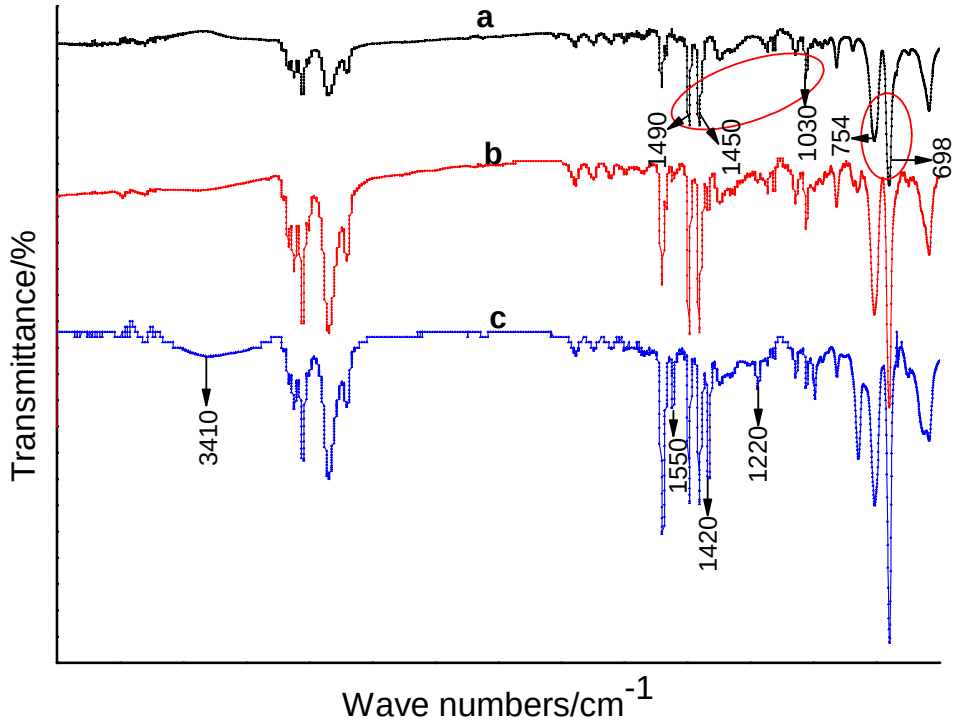

Figure S2. FTIR spectra of a) PS crosslinked microspheres and PS/P4VP composite particles prepared under various swelling ratios (Weight VP/PS): b) 3/1, c) 5/1.

Figure S2 shows the FTIR spectra of the PS crosslinked microspheres and the PS/P4VP composite particles prepared under different swelling ratios. In Figure S2a the benzene skeleton vibration at 1490cm^{-1}, 1450cm^{-1}and 1030cm^{-1} and the monosubstituted benzene vibration at 754 cm^{-1} and 698 cm^{-1} are both ascribed to PS. The C=N stretch vibration at 1550 cm^{-1} and 1420 cm^{-1}, the N-H stretch vibration at 3410cm^{-1} and N→O stretch vibration in pyridine ring at 1220 cm^{-1}are all assigned to P4VP. The presence of the characteristic peaks of P4VP and PS in Figure S2b and S2c evince the existence of P4VP and PS in the composite particles.

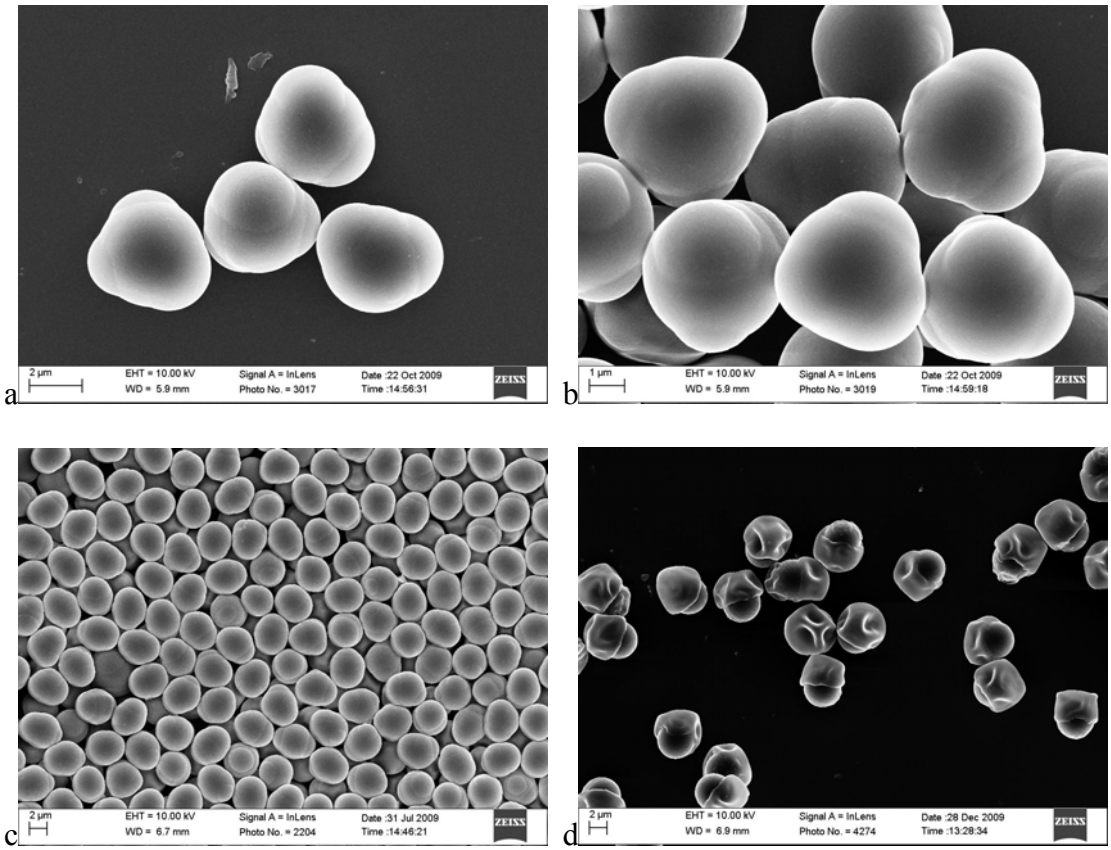

Figure S3. Low magnification SEM images of representative PS/P4VP composite particles (Figure2b, 3b, 3d): (a) (b) toluene/PS (w/w) =3/1, EGDMA/4VP (w/w) =1/20; (c) toluene/PS (w/w) =12:1, DVB/4VP (w/w) =1:20; (d) toluene/PS (w/w) =3:1, DVB/4VP (w/w) =3:4.

d  e  f 

Figure S4. Optical images of hexane/water system without and with PS/P4VP particles: a) methyl orange aqueous added into hexane, b) the system under ultrasonication, c) the system standing for 5 minutes; d) PS/P4VP composite particles added into the hexane/water system, e) the system under ultrasonication, f) the system standing for 30 minutes.

Figure S3 depicts the optical images of PS/P4VP non-spherical particles in hexane/water system. When aqueous methyl orange added into hexane, the system becomes divided in two phase state. Then the system is ultrasonically mixed. But phase separation takes place after 5min. The situation turns quite contrary with the addition of PS/P4VP composite particles into the system. The aqueous methyl orange droplets still remain distributed well in the hexane as the system is maintained for 30min after ultrasonication process. These results indicate that the amphiphilic PS/P4VP composite particles can stabilize the emulsion.