Supporting Information (SI)

One-Step Template-Free Synthesis of Monoporous Polymer Microspheres with Uniform Sizes via Microwave-Mediated Dispersion Polymerization

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Experimental section

Materials and instrument

Styrene (chemical grade) was purchased from Tianjin Bodi Chemical Co., Ltd., China and redistilled before used. Azobisisbutyronitrile (AIBN) (Sigma-aldrich Co.) was recrystallized in ethanol, Ltd., China. Polyvinylpyrrolidone (PVP, M_W = 30,000) (analytical grade) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were used as received. Microwave reactor (XH-200A) equipped with reflux condenser was purchased from Beijing Xianghu Science and Technology Development Co., Ltd, China, and internal temperature probe was used to monitor the temperature of the reaction mixture.

Characterization

Scanning electron microscopy (SEM) was carried out on an S4800 scanning electron microscope (Hitachi, Japan). And the samples were prepared by dropping 10 μL of polymer sample dispersed in ethanol onto a silicon chip. Transmission electron microscopy (TEM) was carried out using a T20 transmission electron microscope (FEI, America) with an accelerating voltage of 200 kV. The sample was prepared by dropping 10 μL solution onto a carbon-coated Formvar copper grid (300 meshes) followed by solvent evaporation at room temperature.

Synthesis of monoporous polymer microspheres

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, and subsequently the mixture was bubbled with nitrogen for 30 min. The reaction was allowed to proceed under 400 W microwave irradiation in the microwave oven equipped with reflux condenser for 10-60 min at ~70 °C. It was observed that the reaction mixture turned opalescent when polymerization was conducted for about 3 min, indicating occurrence of PVP-stabilized polymer aggregates. Finally, the product was centrifuged at 6,000 rpm for 10 min, washed three times with ethanol, and then dried in a vacuum at 40 °C for 24 h. The polymer aggregates were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Control experiments using conventional heating

Control experiment was carried out by employing heating under reflux in oil bath instead of microwave irradiation while other conditions the same as that for preparing monoporous microspheres, namely with 0.5 mg/mL of AIBN, 55 mg/mL of St, and 5.0 mg/mL of PVP, at ~70°C. The reaction was allowed to proceed for 30~180 minutes.

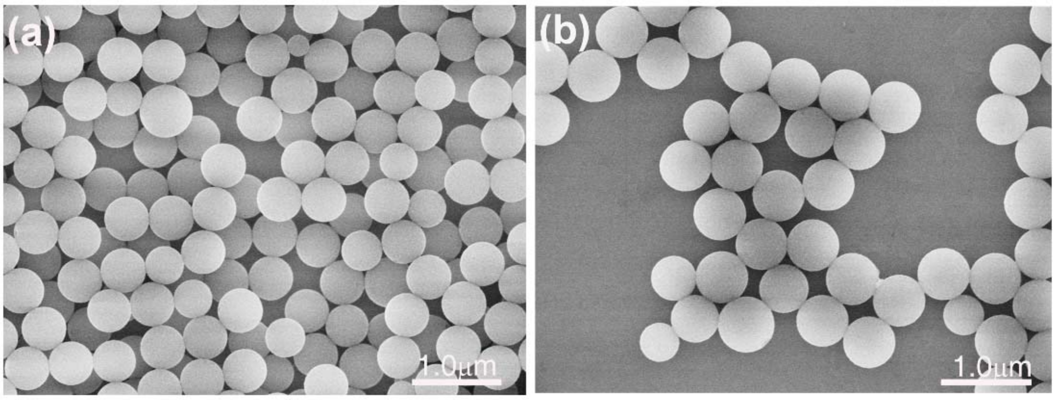

Fig. S1. SEM images of polystyrene microspheres obtained after irradiation of microwave for (a) 40 min and (b) 60 min at AIBN concentration of 0.125 mg/mL. As polymerization goes on, the spheres grow larger ((a): ~480 nm, (b): ~570 nm)), but no pore comes into being.

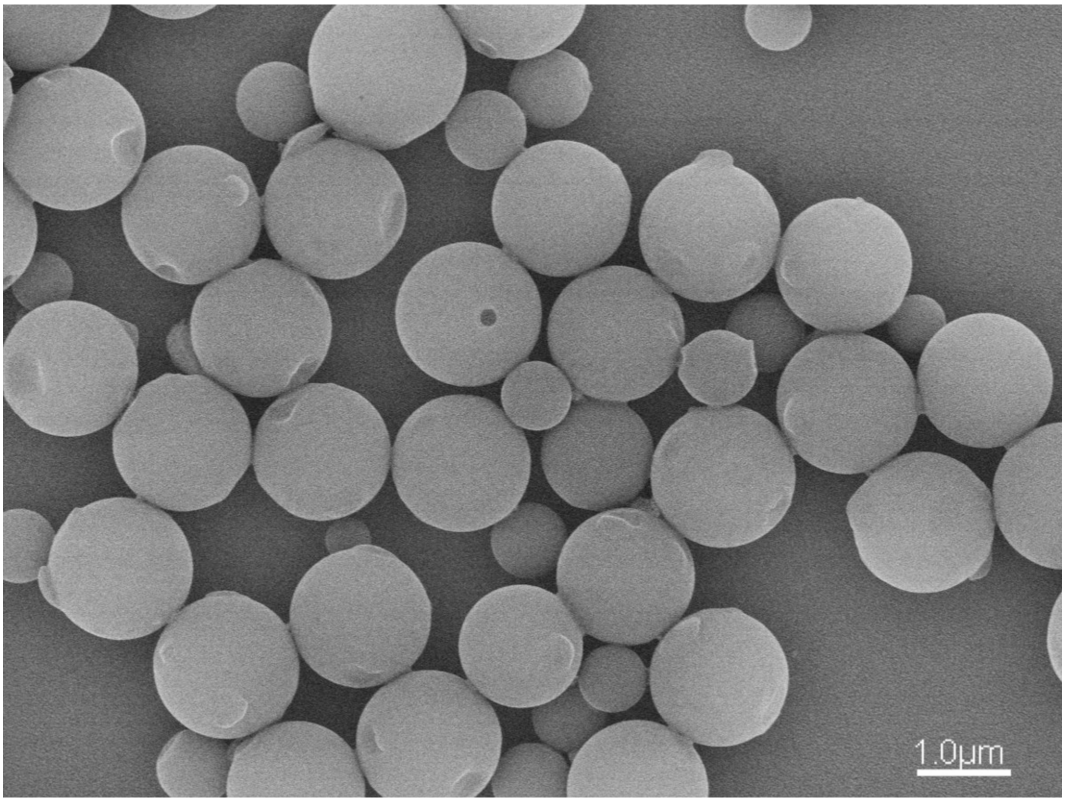

Fig. S2. SEM image of polystyrene microspheres obtained when the microwave-assisted polymerization is conducted for 60 min. From the SEM image, it is found that the surfaces of the spheres are not smooth, and at the same time some small spheres are also observed.

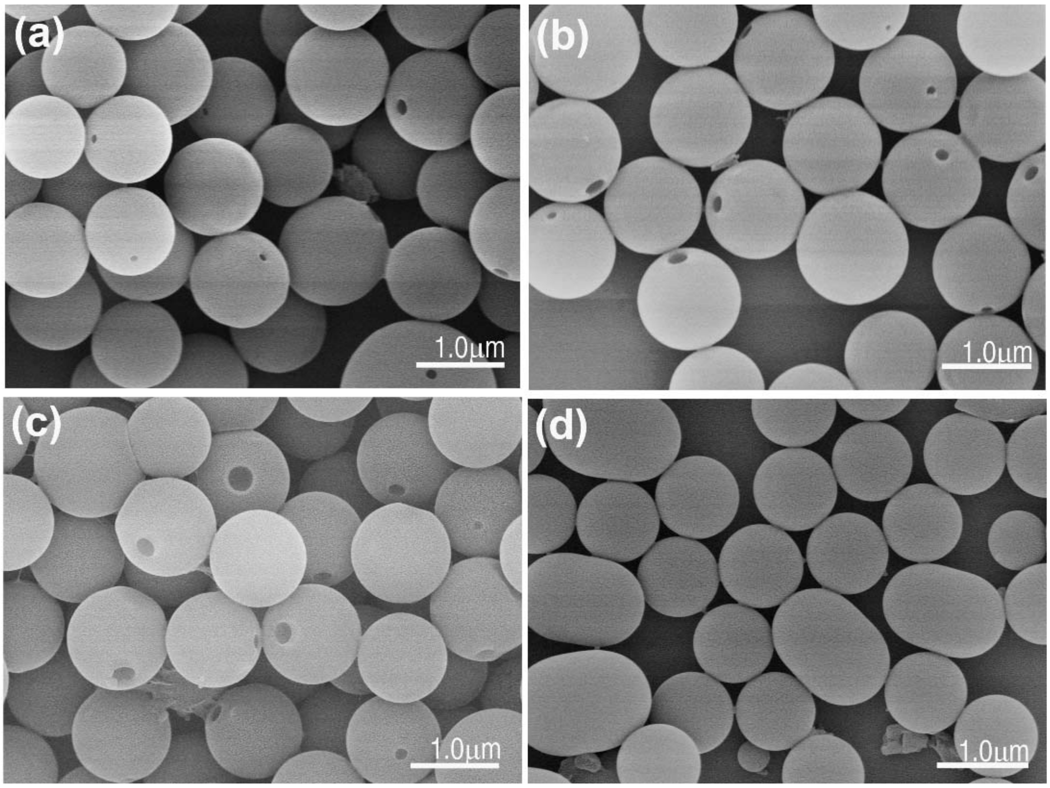

Fig. S3. SEM images of the obtained polystyrene microspheres when different amounts of monomer (styrene) are added: (a) 1.5 mL, (b) 2.0 mL, (c) 2.5 mL, (d) 4.0 mL. Insufficiency of monomer leads to broad size distribution, while an excessive monomer results in coalescence.

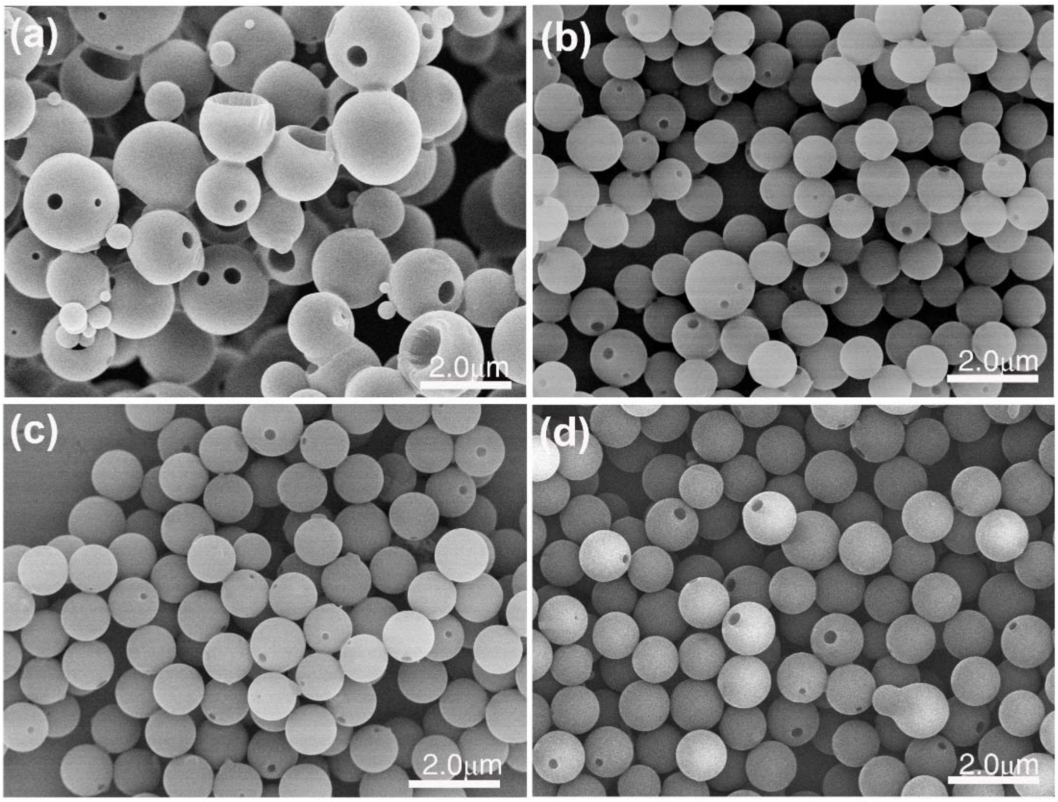

Fig. S4. SEM images of the obtained polystyrene microspheres when different amounts of PVP stabilizers are used: (a) 0.0 mg/mL, (b) 1.25 mg/mL, (c) 2.5 mg/mL, and (d) 5.0 mg/mL. It indicates that the polymer microspheres are polydispersed when PVP concentration is low (a, b), while in the range of 2.5-5.0 mg/mL, both the sizes of the spheres and pores do not show magnificent differences. The bowl-like spheres in Fig. S4a are formed due to sinking of polymer shells, which clearly reveals the hollow structures inside polymer spheres. The above results indicate that PVP stabilizers play an important role in formation of uniform microspheres.

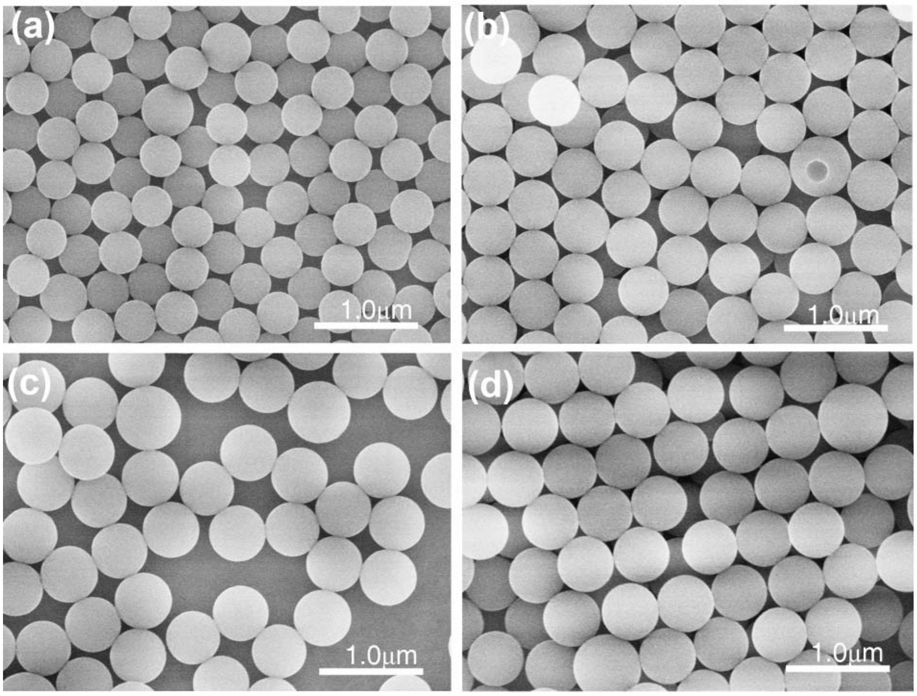

Fig. S5. SEM images of polystyrene microspheres prepared by conventional polymerization with reaction conditions of 0.5 mg/mL of AIBN, 55 mg/mL of St, and 5.0 mg/mL of PVP, at different heating time: (a) 30 min, (b) 60 min, (c) 120 min, and (d) 180 min. As revealed by the SEM images, through the conventional method, polymer spheres grow slower (~400 nm at 30 min, and ~530 nm at 180 min), and almost all the products are solid spheres without pores.

Table S1. Microwave-mediated dispersion polymerization of St.[a]

Run	[AIBN] (mg/mL)	[St] (mg/mL)	[PVP] (mg/mL)	Time (min)	Sphere size[b] (nm)	Pore size[b] (nm)
1	0.125	55	5.0	20	350	-
2	0.25	55	5.0	20	520	-
3	0.375	55	5.0	20	800	200
4	**0.5**	**55**	**5.0**	**20**	**1100**	**250**
5	0.625	55	5.0	20	1300	130
6	0.75	55	5.0	20	1500	90
7	0.5	30	5.0	20	1000	130
8	0.5	45	5.0	20	1100	170
9	**0.5**	**55**	**5.0**	**20**	**1100**	**240**
10	0.5	90	5.0	20	Coalescence	
11	0.5	55	0.0	20	2000	-
12	0.5	55	1.25.	20	1050	200
13	0.5	55	2.5	20	1100	210
14	**0.5**	**55**	**5.0**	**20**	**1100**	**240**
15	0.5	55	5.0	3	-	-
16	0.5	55	5.0	5	-	-
17	0.5	55	5.0	7	-	-
18	0.5	55	5.0	10	900	240
19	**0.5**	**55**	**5.0**	**20**	**1080**	**250**
20	0.5	55	5.0	30	1270	230
21	0.5	55	5.0	40	1270	180
22	0.5	55	5.0	60	1600	80-200

[a] Reaction condition: microwave power 400 W, T = 70 ^{o}C. Run 4, 9, 14, and 19 are samples obtained from different batches under the same reaction condition. [b] Estimated values from SEM images using the software of Image-Pro Plus. The sizes of both the sphere and pore are listed in the form of average values of diameters. “-” in the table means that there is no pores or spheres to be formed or the average values are not suitable to represent the overall results.