Electronic Supplementary Information

A Novel Approach toward Snowman-Like Polymer/SiO₂ Hybrid Nanoparticles via Gas-Driving

Qianqian Lin^a, Juan Wang^a, Jinfeng Yuan^{a, b}, Yuan Jiang^a, Lei Zhu^c, Mingwang Pan^{a,b,*}

^aInstitute of Polymer Science and Engineering, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, PR China

^bHebei Key Laboratory of Functional Polymers, Hebei University of Technology, Tianjin 300130, PR China

^cDepartment of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202, United States

*Corresponding author: mwpan@126.com

1. Experimental Section

1.1 Materials

Styrene (St, 98%, Tianjin Chemical Reagent Co., Ltd.), glycidylmethacrylate (GMA, 99.5%, Beijing Bai Yuan Chemical Co., Ltd.), divinylbenzene (DVB, 99%, Tianjin Guangfu Fine Chemical Research Institute) and vinylidene chloride (VDC, 98%, Tianjin Kangshun Chemical Co., Ltd.) were purified by distillation under reduced pressure to remove inhibitors and stored in a refrigerator prior to use. Potassium persulfate (KPS, 99.5%, China Medicine Group Chemical Reagent Co., Ltd.), methyltriethoxysilane (MTES, 98%, Macklin), ammonia solution (NH₃·H₂O, 25%, Tianjin Fengchuan Chemical Reagent Co., Ltd.), cyclohexane (CYH, 98%, Tianjin Kermel Chemical Reagent Co., Ltd.), dichloroethane (EDC, 99%, Aladdin) and hydrofluoric acid (HF, 99%, Tianjin Hengshan Chemical Technology Co., Ltd.) were used without further purification.

1.2 Synthesis

1.2.1 Synthesis of P(St-co-GMA) composite microparticles

The reaction was implemented in a 100 mL four-necked round-bottom flask equipped with a condenser, a Teflon blade mechanical stirrer, a nitrogen gas inlet and a thermometer. In a typical preparation, 1.50 g of St and 0.45 g of GMA monomers after purified were added into the flask containing 30.00 g of deionizer water and mixed at room temperature. Nitrogen was purged into the dispersion for 15 min to remove O_2 before polymerization, and it maintained purging during the entire polymerization process. Next, after the mixture was agitated for 20 min, the system was heated to 75 °C, and then a 5 mL aqueous solution containing 11.70 mg of KPS (i.e., 0.60 wt% of the monomers) was added. While the polymerization run at 75 °C for 1 h, the crosslinking agent of DVB was charged into the reaction system to crosslink the forming copolymer seed. The polymerization was completed after reaction for another 4 h.

The polymer particles were separated from the reaction mixture by centrifugation and purified by three water-ethanol washing/centrifuging cycles to afford the final product for further characterization. The resultant product was dried in vacuum for three days until a constant weight was reached, and then the solid content of the dispersion was calculated.

1.2.2 Preparation of P(St-co-GMA)/SiO₂ hybrid particles

P(St-*co*-GMA)/SiO₂ hybrid particles with diverse morphologies were synthesized by soap-free seeded emulsion polymerization using the P(St-*co*-GMA) particles as seeds. A typical procedure was described as follows. First, 9.00 g of P(St-*co*-GMA) dispersion with a solid content of 6.07 wt% was added into a beaker containing 20.00 g of deionized water at room temperature, and the mixture dispersion was further ultrasonicated for 40 min to avoid any colloidal particle agglomeration. The ultrasonicated P(St-*co*-GMA) latex dispersion, containing 0.55 g of P(St-*co*-GMA) solid particles, was introduced into a three-necked flask. Then, 0.85 g of purified VDC monomer and 0.70 g of MTES were added into the flask containing the P(St-*co*-GMA) dispersion. The mixture was mildly agitated for 20 min for the monomers to swell the P(St-*co*-GMA) colloidal particles. In addition, the boiling point of VDC was very low (31.2-31.7°C), in order to prevent its volatilization, the experiment needed to perform under an ice bath condition. Subsequently, a 0.5 mL of ammonia solution (28 wt.%) was added dropwise and then the mixture was held in ice bath for 2 h. The reaction was allowed to proceed for another 10 h at room temperature under mild stirring of 220 rpm. The detailed experimental recipes in this work are listed in Table S1.

Table S1. Recipes for synthesis of P(St-co-GMA)/SiO₂ composite colloidal particles

run	P(St-co-GMA)	VDC	MTES	NH ₃ ·H ₂ O	СҮН	EDC
	(g)	(g)	(g)	(mL)	(g)	(g)
1	0.55	0.85	0.70	0.50	0	0
2	0.55	0	0.70	0.50	0	0
3	0.55	0	0.70	0.50	0.85	0
4 ^a	0.55	0.85	0.70	0.50	0	0
5	0.55	1.70	0.70	0.50	0	0
6	0.55	2.54	0.70	0.50	0	0
7	0.55	3.40	0.70	0.50	0	0
8	0.55	0.85	0.20	0.50	0	0
9	0.55	0.85	1.40	0.50	0	0
10	0.55	0.85	0.70	1.40	0	0
11	0.55	0.85	0.70	2.30	0	0
12	0.55	0	0.70	0.50	0	0.85

in 20.00 g H_2O medium

Note: ^aThis experimental condition: first ice-bathing for 2 h, then heating to 60 °C and reacting for 10 h. Other experiments: first ice bath for 2 h, then reaction at room temperature for 10 h.

1.3 Characterization

1.3.1 Morphology observation of composite particles

A transmission electron microscopy (TEM, Talos F200S, FEI, U.S.A., operated at 80 kV) was used to investigate the structure of P(St-*co*-GMA)/SiO₂ hybrid particles. For TEM sample preparation, a small drop of the synthesized microspheres latex was diluted with deionized water to obtain a translucent suspension. After ultrasonication for 40 min, a drop of the suspension was cast on a 400-mesh copper grid coated with carbon layer, and dried under vacuum at room temperature for 48 h.

Morphologies of P(St-*co*-GMA) and P(St-*co*-GMA)/SiO₂ particles were characterized by field-emission scanning electron microscopy (FE-SEM, Nano 450, FEI, U.S.A., operated at 10 kV) with a scanning-transmission mode (STEM). For SEM sample preparation, a translucent suspension was prepared according to the same procedure as the TEM sample, except replacing the coated copper grid with a conductive silicon wafer.

1.3.2 Particle size measurement of composite particles

The average sizes and size distributions of P(St-*co*-GMA) seeds and P(St-*co*-GMA)/SiO₂ composite particles were measured at room temperature by a Zeta-Size 90 type of dynamic light scattering particle size analyzer (DLS, Malvern, U.K.). The wavelength of the incident light was 532 nm, and the scattering angle was 90°. For DLS sample preparation, the original dispersion needed to be diluted with deionized water to obtain a translucent suspension before analysis.

Fourier transform infrared spectrum (FTIR) measurement was performed on a Bruker Tensor-27 IR spectrometer. Before analysis, the dried particles were mixed with dry KBr power and pressed into translucent flake.

1.3.4 EDX-TEM analysis of elements of composite particles

Energy-Dispersive X-ray Spectroscopy–Transmission Electron Microscopy (EDX-TEM) mapping was carried out on Talos F200S transmission electron microscopy and operated at 80 kV. For sample preparation, a translucent suspension was prepared according to the same procedure as the TEM sample.

2. Results and discussion

2.1 FT-IR analysis of particles

The chemical compositions of the product were further tracked by FT-IR spectroscopy. Figure S1 demonstrates the FT-IR spectra of SiO₂, P(St-co-GMA), and snowman-like P(St-co-GMA)/SiO₂ particles. It can be observed from the SiO₂ spectrum (Fig. S1 A) that the characteristic absorption at 2973 and 2920 cm⁻¹ was indicative of the stretch vibration of C-H in Si-CH₃ group. Besides, a very pronounced band appeared at 1274 cm⁻¹, together with the absorption band at 777 cm⁻¹, which corresponded to the wagging and stretching vibrations of (Si–O–) Si–CH₃ group. The peaks at 1130 and 1034 cm⁻¹ were attributed to the stretch vibration of Si–O–Si and Si– OH. Furthermore, the absorption band at 442 cm⁻¹ was assigned to the bending vibration of Si–O–Si. For the P(St-co-GMA) spectrum (Fig. S1 B), the absorption peaks at 2924 and 2853 cm⁻¹ were ascribed to the asymmetric/symmetric stretch vibration of saturated C-H bonds. The characteristic absorptions at 1597, 1491, 1450 cm⁻¹ belonged to the C=C skeletal stretching vibrations of benzene ring. The peaks at 758 and 699 cm⁻¹ were attributed to the =C-H folding vibration of single substituted benzene ring. The stretching vibration triggered by =C-H bond in benzene ring was observed at 3026 cm⁻¹. In addition, the characteristic vibration absorption of epoxy groups appeared at 844 and 907 cm⁻¹. The strong absorption peak at 1729 cm⁻¹ was attributed to the stretching vibration of the carbonyl group (C=O) in PGMA. The very weak peak at around 3443 cm⁻¹ can be assigned to the vibration absorption of -OH groups, which could come from a trace amount of water absorbed during the sample preparation. As

a result, the characteristic peaks in **Figure S1 B** demonstrate that the monomers of St and GMA were successfully copolymerized. From the spectrum of snowman-like P(St*co*-GMA)/SiO₂ particles in **Figure S1 C**, it was noticed that the absorption peak from – OH groups of SiO₂ domains emerged at 3428 cm⁻¹ instead of at 3443 cm⁻¹, and strengthened. This could be attributed to that the association hydrogen bond between hydroxyl, epoxy and carbonyl groups makes the density of electron cloud average to result in the absorption peak shift towards a lower wavenumber. Just as we can observe, the FTIR spectrum of the snowman-like P(St-*co*-GMA)/SiO₂ particles appeared to be a superposition of both spectra of P(St-*co*-GMA) and SiO₂, indicating the conversion of MTES to silica and the successful polymerization of St, GMA and DVB.



Figure S1 FTIR spectra of (A) SiO₂, (B) P(St-*co*-GMA) and (C) snowman-like P(St-*co*-GMA)/SiO₂ particles (run 1 in Table S1).

2.2 Dual role of VDC in the system



Figure S2 (A) SEM and (B) TEM micrographs of $P(St-co-GMA)/SiO_2$ particles obtained without adding VDC (run 2 in Table S1); SEM micrographs of $P(St-co-GMA)/SiO_2$ particles obtained by respectively adding (C) CHY (run 3 in Table S1), (D) EDC instead of VDC (run 12 in Table S1), and (E) SEM micrograph of $P(St-co-GMA)/SiO_2$ particles obtained by raising the reaction temperature to 60 °C after the ice bath (run 4 in Table S1).

2.3 Effect of the ice bath time on the morphology

It is known that the time of the ice bath indicated the time that VDC presented in the system, which could affect the profile of silica bulges of the hybrid particles. Figure S3 shows the morphology development of P(St-*co*-GMA)/SiO₂ particles at different ice bath times, when the amount of ammonia solution was 0.5 mL, the MTES/VDC/P(St*co*-GMA) feed ratio was 0.70 g/1.70 g/0.55 g. As the ice bath time was 0.5 h (Figure S3 A), snowman-like P(St-*co*-GMA)/SiO₂ particles with partially wrinkled surface of silica were obtained, which shows the high softness. With the extension of ice bath time, the concave of silica gradually disappeared. The most probable reason is that VDC started to volatilize after a short ice bath time, at this time, MTES had a low degree of polycondensation, consequently silica layer was soft and prone to deformation. However, as the ice bath time became longer, the degree of polycondensation became larger and the depression gradually disappeared.



Figure S3. SEM micrographs of the snowman-like $P(St-co-GMA)/SiO_2$ particles synthesized at different ice bath times: (A) 0.5 h, (B) 1 h, (C) 2 h, and (D) 5 h (run 5 in Table S1).

2.4 Effect of addition amount of MTES on the morphology



Figure S4. SEM micrographs of $P(St-co-GMA)/SiO_2$ latex particles synthesized at different addition amounts of MTES: (A) 0.20 g, (B) 0.70 g, (C) 1.40 g with 0.55 g of

P(St-co-GMA) solid particles (runs 8, 1, 9 in Table 1).

2.5 Effect of addition amount of NH_3 · H_2O on the morphology



Figure S5. SEM micrographs of morphologies of the P(St-*co*-GMA)/SiO₂ particles synthesized at different addition amounts of ammonia solution: (A) 0.5 mL, (B) 1.4 mL, and (C) 2.3 mL (runs 1, 10, and 11 in Table S1).

2.6 Pickering Emulsion Stabilized by P(St-co-GMA) and P(St-co-GMA)/SiO₂ particles.

To investigate the capability of P(St-*co*-GMA) and P(St-*co*-GMA)/SiO₂ particles stabilizing oil/water emulsion, CYH was used as a model oil, and the volume ratio of oil versus water was kept at 1:2. Then, the effects of P (St-*co*-GMA) and P (St-*co*-GMA)/SiO₂ on emulsification of the mixture were investigated at a concentration of 0.8 wt%. The mixture emulsions in Fig. S6 A (a) and Fig. S6 B (d) were observed to be phase separation. When we placed the mixture emulsion in Fig. S6 A(a) in a 90 Hz ultrasonic bath and ultrasonicated for 40 min to obtain the emulsion as shown in Fig. S6 A (b). The emulsion stabilized by P(St-*co*-GMA) was unstable and the phase separation occurred immediately after stop the sonication. As we can observe, the CYH-in-water emulsion emulsified by P(St-*co*-GMA)/SiO₂ was more stable, as shown in Fig. S6 B (e). The formed emulsion height could reach the top of the dispersed phase, which originated from the immiscibility and density difference between oil and water.

Furthermore, the emulsion remained stable even after placement for 30 days, showing a good coalescence resistance (Fig. S6 B (f)). This clearly showed the enhancement in the emulsion stability when the P(St-*co*-GMA)/SiO₂ Janus particles were used as the Pickering emulsifier instead of P(St-*co*-GMA) particles.



Figure S6. Photographs of A: (a) P(St-*co*-GMA)-CYH-H₂O mixture, (b) the P(St-*co*-GMA)-CYH-H₂O mixture after emulsification, (c) after standing of the emulsified P(St-*co*-GMA)-CYH-H₂O mixture for 30 days; B: (d) P(St-*co*-GMA)/SiO₂ (run 1 in Table S1)-CYH-H₂O mixture, (e) the P(St-*co*-GMA)/SiO₂-CYH-H₂O mixture after emulsification, and (f) after standing of the emulsified P(St-*co*-GMA)/SiO₂-CYH-H₂O mixture for 30 days (CYH/H₂O volume ratio=1:2, 0.8 wt% addition weight of the particles relative to CYH). The inserted images were the SEM micrographs of the corresponding used particles.