Electronic Supplementary Information

Self-assembled micelles based on branched poly(styrene-*alt*-maleic anhydride) as particulate emulsifiers

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1. Synthetic formula and property parameters of BPSMA and LPSMA

Table S1 Synthetic formula and property parameters of BPSMA and LPSMA

Samples	n(St):n(MAn):n(VBT)		M_n[c]	M_w/M_n[d]	Degree of branch[b]
	Feed ratio	Actual ratio[a]	(g mol^{-1})	(PDI)	(%)
LPSMA	1:1.2:0	0.47:0.49:0	25108	1.87	0
BPSMA-3	1:1.2:0.07	0.45:0.49:0.02	26996	1.65	2.08
BPSMA-6	1:1.2:0.14	0.39:0.50:0.05	24468	1.53	5.32
BPSMA-9	1:1.2:0.20	0.39:0.50:0.06	20709	1.47	6.38
BPSMA-12	1:1.2:0.27	0.37:0.50:0.06	18523	1.80	6.45

[a,b] The actual ratio and degree of branch of copolymers were obtained from the elemental analysis.

[c,d] The number average molecular weight and PDI of copolymers were obtained from the gel permeation chromatography (GPC). The refractive index detector and BPSMA calibration standards were used for the GPC analysis of LPSMA with polystyrene as standard and THF as eluent (the elution rate was 1 mL min^{-1}), whereas a light scattering detector was employed for the GPC analysis of branched copolymer.

2. Influence of VBT mol% and micelle concentration on the stability of emulsions

The long-term stability was evaluated by tracing the changes of emulsion ratio with time. The emulsion ratio is defined as the creamy layer over the whole volumes of oil and water phases. Fig. S1 shows the changes of emulsion ratio of the white oil/water stabilized by LPSMA and BPSMA micelles at different micelle concentrations with time. As can be seen, all the BPSMA micelles exhibit marvelous long-term stability and keep stable for more than 3 months even in low concentrations of 0.25 mg mL^{-1}, compared with LPSMA micelles. For BPSMA micelles, the micelle concentration has little effect on the emulsifying performance and stability of emulsions when the concentration reaches 0.75 mg mL^{-1} and above. On the contrary, LPSMA micelles depend on the concentration greatly. The long-term stability of emulsion stabilized by LPSMA micelles improves as the increase of micelle concentration. For example, the emulsions stabilized by LPSMA in 0.25, 0.50, 0.75, and 1.00 mg mL^{-1} are broken after 3 days, 7 days, 14 days and 90 days, respectively.

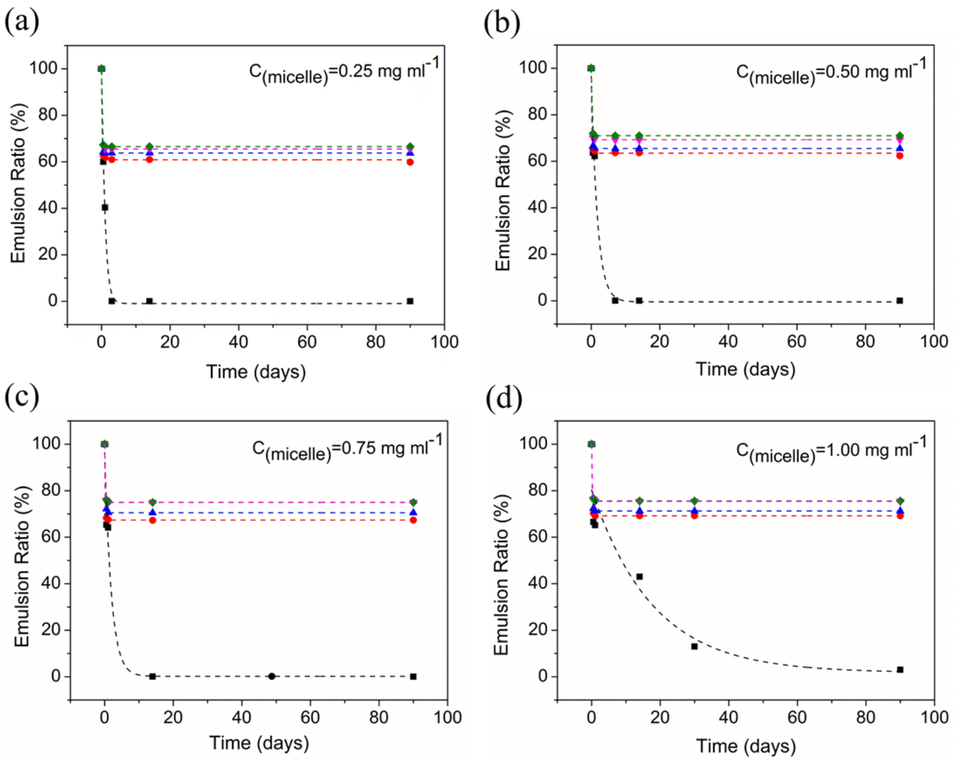

Fig. S1 Emulsion ratio of the white oil/water stabilized by LPSMA (■), BPSMA-3 (●), BPSMA-6 (▲), BPSMA-9 (▼), and BPSMA-12 (◆) self-assembled micelles at different micelle concentrations (0.25 mg mL^{-1} (a), 0.50 mg mL^{-1} (b), 0.75 mg mL^{-1} (c), and 1.00 mg mL^{-1} (d)) traced with time. The oil/aqueous phase ratio is 1:1.

It should be also noticed that at any fixed particulate emulsifier concentration, the emulsion ratio is successively increased while raising the VBT mol%. However when the VBT mol% reaches 9%, further increment in VBT mol% has little impact on the emulsifying property. That is because the degree of branching contributes to the compactness of polymer according to molecular geometry, and the branching degree of BPSMA-9 (6.47%) and BPSMA-12 (6.54%) are very close, as previously mentioned in Table S1.

3. Influence of VBT mol% on the maximum oil volume trapped in emulsions

To investigate the difference of emulsifying efficiency of LPSMA micelles and BPSMA micelles, they were employed as particulate emulsifiers to stabilize the white oil/water emulsions, among which the volume of oil phase ranges from 50% to 92%. As shown in Fig. S2, the maximum volume of oil phase trapped into the emulsions increases from 67% to 92%, as increasing the VBT mol% of copolymer from 0 to 12%.

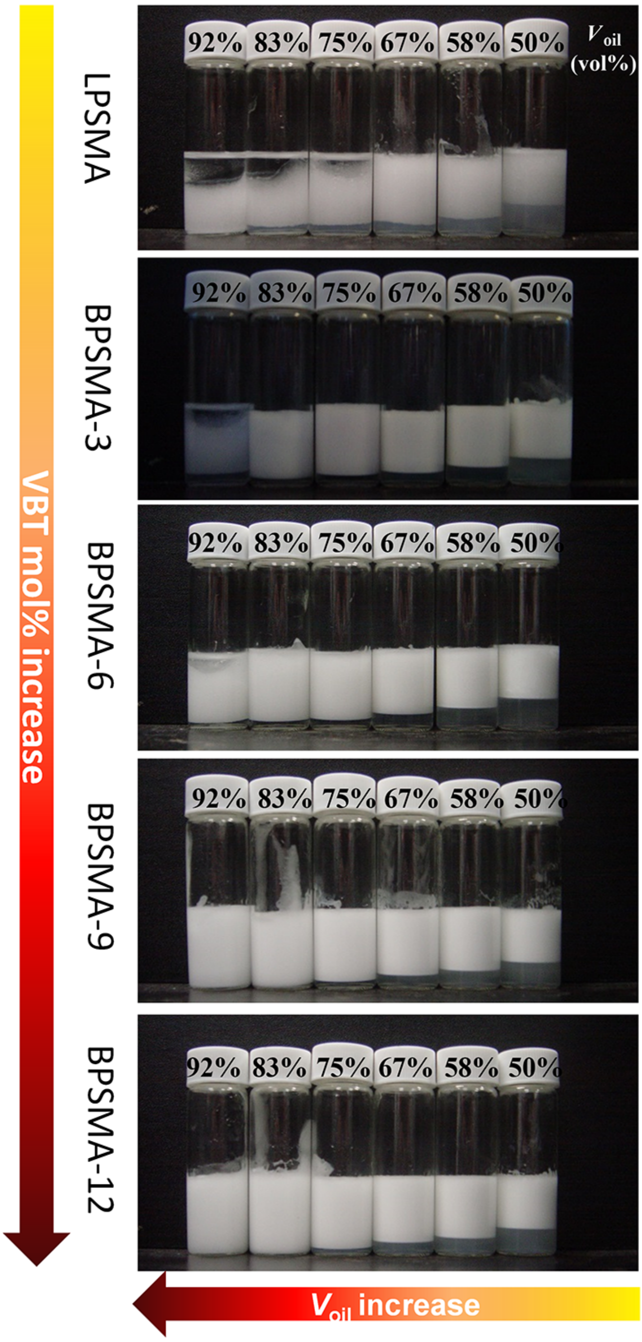

Fig. S2 Appearance of the white oil/water emulsions stabilized by LPSMA micelles and BPSMA micelles with the incubation time of 7 days after homogenization. The micelle concentration is 0.75 mg mL^{-1}. The emulsions was prepared with the volume ratio of oil to water phase as 5.5:0.5, 5:1, 4.5:1.5, 4:2, 3.5:2.5, and 3:3 (from left to right), correspondingly, the V_{oil} is 92, 83, 75, 67, 58, and 50 vol%.

4. Solidifying emulsion droplets and Scanning electron microscopy (SEM)

4.1 Solidifying emulsion droplets

The emulsion droplets were solidified to investigate the configuration of copolymer micelles in the oil/water interface. Styrene with 2.0 mol% AIBN was employed as oil phase to prepare emulsions using LPSMA and BPSMA micelles as emulsifiers. After emulsification, the oil phase in the emulsion droplet was solidified by the polymerization of styrene at 65 ^{o}C. The solidified emulsion droplets with copolymer micelles on the surface were purified by centrifuge and then redispersed into ethyl alcohol. The solidified droplets were collected by filtration and dried in a vacuum oven at 40 ^{o}C for 24 h.

4.2 Scanning electron microscopy (SEM)

SEM study was carried out using a Quanta-200 instrument operating at 20 kV. Solidified droplets were placed on a copper stub and sputter-coated with gold to minimize sample-charging problems.

4.3 Micelle structure at the oil/water interface

The configuration of copolymer micelles on the oil/water interface was investigated by employing styrene as oil phase and solidifying the emulsion droplets by the polymerization of styrene. Fig. S3 shows the morphology of the robust solidified polystyrene-in-water droplets stabilized by LPSMA and BPSMA micelles imaged by SEM. It is clearly seen that the particulate emulsifiers are adsorbed on the surface of the solidified droplets. And with the increase of VBT mol%, the larger surface coverage is displayed, that is, more numbers of particulate emulsifiers are absorbed on the surface of polystyrene. Therefore, branched polymer self-assembly micelles are more effective than linear emulsifiers at the same concentration.

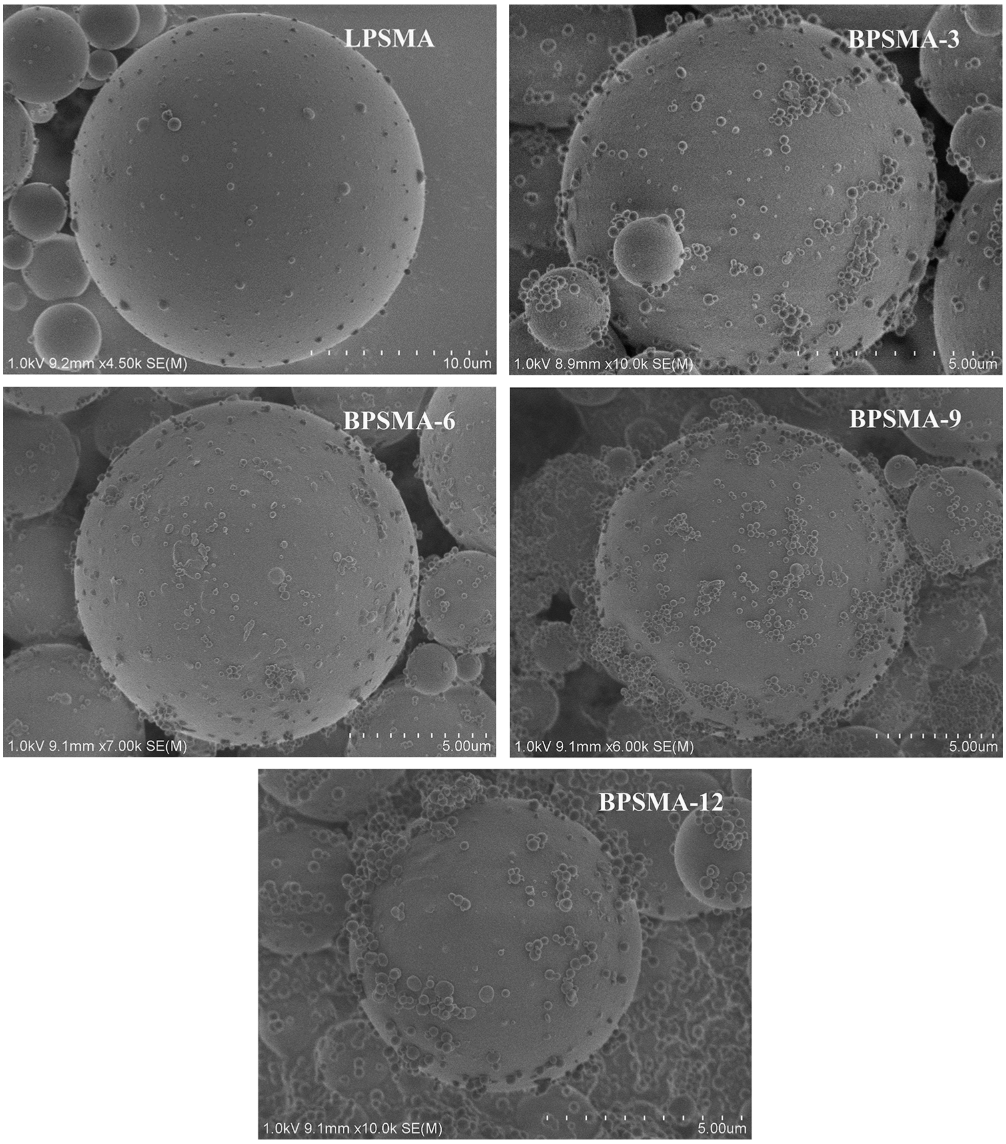

Fig. S3 SEM images of the solidified polystyrene-*in*-water droplets stabilized by LPSMA, BPSMA-3, BPSMA-6, BPSMA-9, and BPSMA-12 micelles with the micelle concentration of 0.75 mg mL^{-1}.

5. Influence of pH on the stability of emulsions

The demulsification of the extremely stable Pickering emulsions is a challenge, and has aroused great attentions due to its significant implication in petroleum industry. In this study, in order to achieve the demulsification by pH adjustment, maleic anhydride was adopted as one of the monomers to endow the synthetic copolymers and their self-assembly micelles with pH sensitivity. The influence of pH on the stability of the emulsions stabilized by the copolymer self-assembly micelles was investigated.

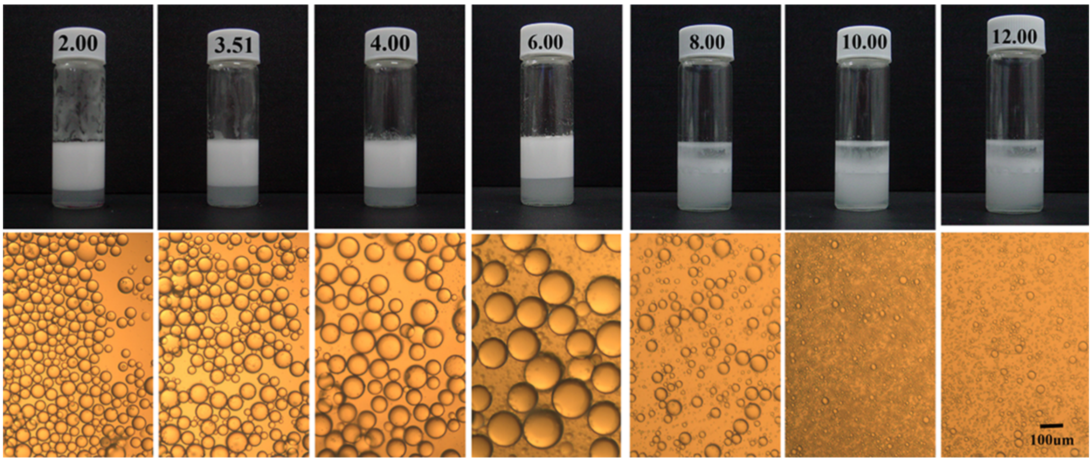

Fig. S4 White oil-*in*-water emulsions stabilized by BPSMA-9 self-assembled micelles at different pH. The micelle concentration is 0.75 mg mL^{-1}. The digital and optical microscope images were taken at 24 h after homogenization.

Fig. S4 shows the white oil-*in*-water emulsions stabilized by BPSMA-9 micelles at different pH values. The initial pH of BPSMA-9 micelle dispersions is 3.51. The pH is regulated by adding HCl solution (0.1 mol L^{-1}) and NaOH solution (0.1 mol L^{-1}). As the digital photos show, the Pickering emulsion stabilized by the branched copolymer self-assembled micelles exhibits pH-responsive property. It can exist steadily under acidic conditions (pH $\leq$ 6) while break under alkaline conditions (PH $\geq$

8). The optical microscope images in Fig. S4 show that the size of the emulsion droplets increases with adding OH^- and decreases with adding H^+. It is probably because that adding OH^- can promote the ionization of carboxyl generating lots of -COO^-, and the increasing -COO^- is much more hydrophilic, which results in the swelling of the BPSMA-9 micelles in water. On the contrary, adding H^+ can restrain the ionization of carboxyl, which leads to the shrink of BPSMA-9 micelles because of hydrophobic interaction.