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ARTICLE

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

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The branched copolymer self-assembled micelles, based on amphiphilic branched poly(styrene-*alt*-maleic anhydride) (BPSMA) synthesized by one-pot method, are prepared and employed as particulate emulsifiers to stabilize the white oil-*in*-water Pickering emulsions. The influences of micelle concentration, branching degree, salinity, and oil type on the emulsifying performance of self-assembled micelles are comprehensively investigated, and the distinction between BPSMA micelles and linear poly(styrene-*alt*-maleic anhydride) (LPSMA) self-assembled micelles on micellar structure and emulsifying performance is also studied. The results show that the branched structure of copolymer plays an important role in emulsification. The emulsifying performance of BPSMA micelles is superior to that of LPSMA micelles, reflected in emulsifying efficiency and the long-term stability of emulsions. It is attributed to the much better structural stability of BPSMA micelles compared to LPSMA micelles, which is probably due to the postponing of hydrolyzing of maleic anhydride and ionization of carboxyl to some extent caused by the introduction of branched structure in copolymers. It is also worth noting that, salinity plays a great effect on the emulsifying performance of LPSMA micelles, but little impact on that of BPSMA micelles. Additionally, BPSMA micelles can also well stabilize the oil-*in*-water emulsions with some other types of natural oils. Thus the findings are not only of theoretical interest but also of great practical application in cosmetics area.

Introduction

Pickering emulsions stabilized by colloidal particles exhibit super stability, lower toxicity, reduced cost, and higher discontinuous phase volume fractions over the traditional emulsions stabilized by surfactants.[1-3] Thus they have been widely applied in food,[4] cosmetic,[5] medicine,[6] oil exploitation,[7] and wastewater treatment.[8] Recently, with the fast development of nanotechnology and nanomaterials, Pickering emulsions have aroused particular attention in fabricating functional materials, such as Janus particles,[9,10] colloidosomes,[11,12] porous/hollow materials,[13,14] and nanocomposites,[15,16] which are of potential significance in the fields of drug controlled release, bioimaging, diagnostics, adsorbents, sensors, and biphasic catalysis.

Up to now, various types of colloidal particles have been used as particulate emulsifiers to stabilize Pickering emulsions, including inorganic particles,[17,18] surface-modified inorganic nanoparticles,[19,20] organic latexes,[21,22] natural macromolecular particles,[23] polymer microgels,[24-26] and self-assembled

micelles.[27-31] Thereinto, the self-assembled micelles based on amphiphilic macromolecules appear to be a good model to elucidate the relationship between the structure and emulsifying performance of particulate emulsifiers, on account of the excellent controllability and tailor-ability of their structure. Since the pioneering work of Armes and co-workers employing linear triblock copolymer micelles as pH-responsive particulate emulsifiers to stabilize 1-undecanol-*in*-water emulsions,[27] it has greatly aroused our interests to investigate the surfactivity and emulsifiability of the self-assembled micelles from amphiphilic copolymers. In our previous studies, a series of self-assembled micelles based on linear amphiphilic random or alternating copolymers were successfully prepared and used as particulate emulsifiers, and the relationship between the structure of micelles and their emulsifying performance was deeply explored.[28-31] It is found that the micellar structure largely affects the emulsifying performance of micelles.

Branched and hyper-branched copolymers have received much attention because of their attractive features such as multiple end groups, improved solubility, lower viscosity, and

three-dimensional globular structure.[32] Yan et al. prepared a series of self-assembled micelles based on hyper-branched copolymers, and applied them as platform in drug delivery.[33-35] Considering the unique structure and properties of branched copolymers, it is promising that the self-assembled micelles of branched copolymers will exhibit different structure and interfacial performance from that of linear copolymers at oil/water interface. Therefore, studying the emulsifiability of branched copolymer micelles, and elucidating the difference between linear and branched copolymer micelles on structure and emulsifying performance, are valuable and beneficial to understand the relationship between the structure and emulsifying performance of micellar emulsifiers. However, there is a shortage of related research at present.

Thus in this study, the branched copolymer self-assembled micelles, based on amphiphilic branched poly(styrene-*alt*-maleic anhydride) (BPSMA) synthesized by one-pot method contributed in our previous work,[36] were prepared in selective solvent and employed as particulate emulsifiers to stabilize Pickering emulsions (Scheme 1). The influences of micelle concentration, branching degree, salinity, and oil type on the emulsifying performance of self-assembled micelles were comprehensively investigated, and the distinction between BPSMA micelles and linear poly(styrene-*alt*-maleic anhydride) (LPSMA) self-assembled micelles on micellar structure and emulsifying performance was also studied.
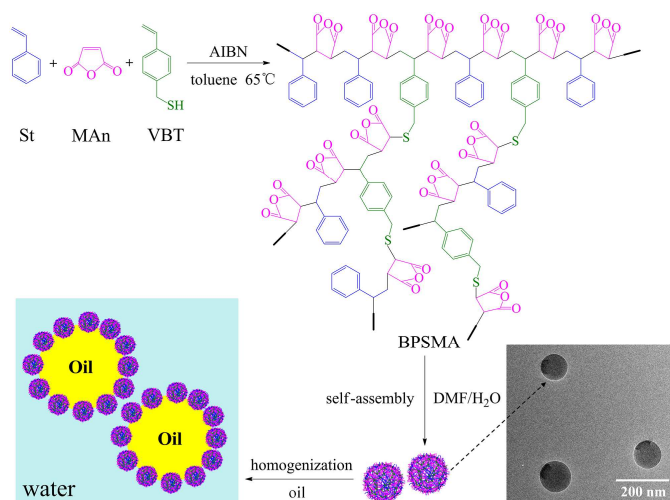
Scheme 1 Schematic illustration of the preparation and self-assembly of BPSMA, and the use of the self-assembled micelles as particulate emulsifiers to stabilize o/w Pickering emulsions.

Experimental

Materials

Styrene (St, 99% purity), purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China), was distilled under reduced pressure and then stored at -5 °C before use. 2,2'-Azobis(isobutyronitrile) (AIBN, AnalaR grade) and maleic anhydride (MAn, AnalaR grade) were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China) and recrystallized twice

from methanol prior to use. 4-vinyl benzyl thiol (VBT) was synthesized according to our previous work.[36] *N,N*-dimethylformamide (DMF, AnalaR grade), toluene (AnalaR grade), and NaCl (AnalaR grade) were received from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China) and used without further purification. White oil (No. 26), dicaprylyl carbonate, propylheptyl caprylate, silicone oil, and isooctyl palmitate were supplied by Wenhua Chem. Co., Ltd. (Shanghai, China). Deionized water was first deionised by reverse osmosis and then purified to a resistivity of 18.2 MΩ cm using a Millipore water purification system. Rhodamine B (RhB, AnalaR grade) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China).

Preparation of BPSMA and LPSMA copolymers

BPSMA copolymers were synthesized through the free-radical copolymerization of electron-donating monomer St, electron-accepting monomer MAn, and chain transfer monomer VBT, using AIBN as a initiator according to our previous study.[36] The synthesized copolymers with different molar fractions of VBT (VBT mol% in the feed: 3, 6, 9, and 12 mol%) were named as BPSMA-3, BPSMA-6, BPSMA-9, and BPSMA-12, respectively. Take BPSMA-9 for example, in a 100 mL one-necked round-bottom flask, 1.04 g of St, 1.18 g of MAn, 0.3 g of VBT, and 0.39 g of AIBN were added and dissolved in 30 mL of toluene. After the mixture was degassed by nitrogen gas flow for 30 min, the flask was sealed and immersed in a preheated oil-bath at 65 °C for 24 h under stirring. The resultant copolymer was purified by precipitation from toluene for three times, and then dried under vacuum at room temperature for 24 h. LPSMA copolymer was prepared in the absence of VBT, and the average molecular weight of which was controlled at the same level with that of the branched copolymers. Table S1† shows the characteristic parameters of BPSMA and LPSMA copolymers.

Self-assembly of BPSMA and LPSMA

For both BPSMA and LPSMA, the typical self-assembly process is as follows: The copolymer was first dissolved in DMF to form a solution with the concentration of 20 mg mL⁻¹. The solution was then stirred for more than 24 h. To induce self-assembly, ultrapure water was added dropwise into the solution at a rate of 7–8 μL per minute until blue opalescence appeared. The solution was continued to stir for 3 h and then quenched into an excess amount of water, followed by dialysis (molar mass cutoff: 14,000) against water to remove DMF. The water was changed every 8 h. After one week, the aqueous dispersion of self-assembled micelles was obtained. To trace the self-assembly of copolymer, the absorbance of the copolymer solution in DMF at 621 nm was recorded by UV-Vis spectrophotometer (TU-1901, Purkinje General Instrument Co., Ltd., Beijing, China) as water is added into the solution.

Preparation of the emulsions with BPSMA and LPSMA micelles as emulsifiers

The oil (white oil, dicaprylyl carbonate, propylheptyl caprylate, silicone oil, and isooctyl palmitate) with different volumes and the aqueous dispersion of micelles (with a micelle concentration of 0.25-1.00 mg mL^{-1}) were placed in glass vessels at room temperature. Then the mixtures were homogenized at 8000 rpm for 2 min by a XHF-D H-speed dispersator homogenizer (Scientz Biotechnology Co., Ltd., Ningbo, China) equipped with 1 cm head at room temperature. After homogenization, the emulsion was measured to calculate the emulsion ratio (defined as the volume of creamy layer over the whole volumes of oil and water phase). The type of emulsions was determined by drop test.

Characterization of BPSMA and LPSMA self-assembled micelles and emulsions

DYNAMIC LIGHT SCATTERING (DLS)

DLS was carried out using an ALV-5000 laser light scattering spectrometer (Langen, Germany). All the particle dispersion samples were filtered by 0.45 μm Milli-pore filters to remove dust before light scattering measurements. DLS measurements were performed at a fixed scattering angle of 90°. The hydrodynamic radius R_h was obtained by the CONTIN program.

TRANSMISSION ELECTRON MICROSCOPY (TEM)

The TEM images of micelles were obtained on a JEM-2100 (HR) LaB6 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. The samples were prepared by dropping micelle solutions onto copper grids coated with a thin polymer film.

CONFOCAL LASER SCANNING MICROSCOPY (CLSM)

The micelle aqueous phase was labeled by RhB (abs/em 555/580) fluorophore at 0.11 mg mL^{-1} by stirring for 24 h at room temperature. Then the labeled self-assembled micelles were used as emulsifiers to stabilize white oil. The images of the emulsions were acquired using a TCS SP8 confocal microscope (Leica, Germany).

OPTICAL MICROSCOPY

Emulsion droplets were imaged with a DM-BA450 optical microscope (Motic China Group Co., Ltd.) fitted with a digital camera after a 1:6 dilution in the continuous-phase liquid for better optical clarity, to estimate the mean droplet diameter with Image-Pro Plus version 5.1 software. The emulsion type was inferred by observing whether a drop of the emulsion dispersed or not when added into a small volume of water or oil by optical microscopy.

Results and discussion

Self-assembly of BPSMA and LPSMA

The self-assembly of BPSMA and LPSMA into micelles through the selective solvent method is similar to that reported by Eisenberg.[37] The self-assembly process was monitored by the change in absorbance of the polymer solutions with the addition of water. Fig. 1a shows that, for all the cases, the absorbance is initially low and approximately invariable. When the water content reaches a certain value, the absorbance

increases dramatically, implying that the polymers start to aggregate and form colloidal particles. This point is defined as the critical water content (CWC).[38] At CWC, the solvent DMF/H$_2$O becomes worse enough for the hydrophobic moieties of the polymers, leading to the aggregation of polymers by the hydrophobic interaction.[39] As Fig. 1b shows, the CWC increases with increasing the VBT mol% of BPSMA. This is probably due to that the increase of the branching degree of BPSMA enhances the solubility of polymer in DMF. Thus more water content is needed to generate a stronger hydrophobic interaction to balance the increased solubility and impel copolymer chains curled up to form micelles.
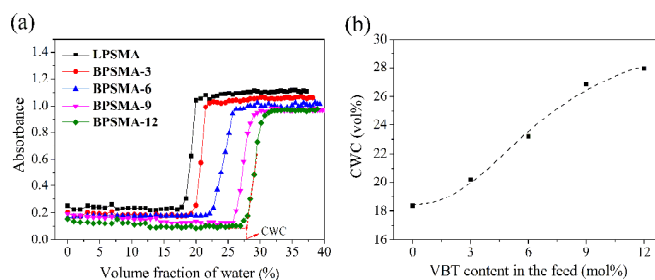

Fig. 1 (a) Changes of the absorbance of polymer solutions at λ = 621 nm in response to water content increase. (b) Influence of VBT mol% on the CWC of polymer solutions. The initial concentration of copolymer solutions in DMF is 20 mg mL^{-1}.

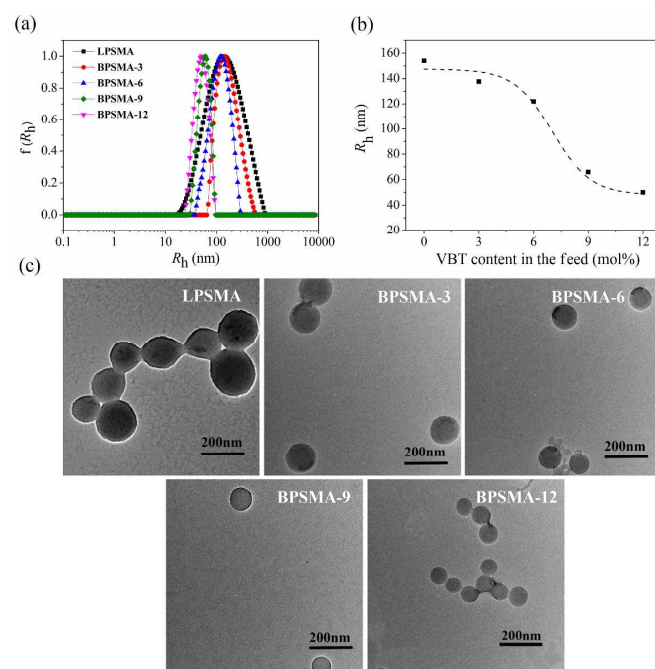### Characterization of BPSMA and LPSMA micelles

Fig. 2 (a) Size and distribution of LPSMA and BPSMA micelles. (b) Influence of the VBT mol% on the hydrodynamic radius (R_h) of micelles. The micelle concentration is 0.25 mg mL^{-1}. (c) TEM images of LPSMA and BPSMA micelles. The micelle concentration is 0.1 mg mL^{-1}.

The self-assembled micelles were characterized by DLS as shown in Fig. 2a and b. All the BPSMA micelles show a

narrower size distribution than the LPSMA micelles. And the hydrodynamic radius (R_h) of the polymer micelles decreases from 154.5 nm to 50 nm as the VBT mol% of polymers increases from 0 to 12 mol%. This variation is probably due to the decrease of the aggregation number of polymers in the formed micelles. Polymer with higher branching degree has larger CWC, to a certain extent, the polymer is more hydrophilic, resulting in the decrease of aggregation number. The results are also confirmed by TEM in Fig. 2c, and all the formed micelles are spherical.

Emulsification performance

INFLUENCE OF MICELLE CONCENTRATION ON THE STABILITY OF EMULSIONS

The BPSMA micelles were used as particulate emulsifiers to stabilize the white oil/water interface. To emphasize the role of polymer structures on the emulsifying performance of their self-assembled micelles, appropriate micelle concentration and volume ratio of oil to water phase should be taken into consideration firstly.

Generally, the larger the particulate emulsifier concentration is, the more stable the Pickering emulsion is. However, excessive concentration may increase the complexity in the stabilizing mechanism of the particulate emulsifiers at the oil/water interface, such as double layer mechanism, aggregation of emulsifiers.[40,41] Meanwhile, a low concentration means less emulsifier consumption, namely, higher efficiency the particulate emulsifier exhibits. As Fig. S1† shows, increment in the micelle concentration plays little role in the emulsifying performance of BPSMA micelles, as the concentration elevated over 0.75 mg mL⁻¹. As a comparison, the emulsifying performance of LPSMA micelles is apparently different at this concentration. Hence, the micelle aqueous solution with a concentration of 0.75 mg mL⁻¹ was used to homogenize with oil phase in following experiments.

INFLUENCE OF VBT CONTENT ON THE STABILITY OF EMULSIONS

A batch of white oil-in-water emulsions were prepared with the volume ratio of white oil to water phase as 5:1 at the micelle concentration of 0.75 mg mL⁻¹. By comparing the appearance of the emulsions stabilized by LPSMA and BPSMA micelles at 1 h and 14 days, as Fig. 3a and b show, about 27 vol% of white oil and 6 vol% of water separate out from the emulsion stabilized by LPSMA micelles after 14-day incubation, while no oil separates out from the emulsions stabilized by BPSMA micelles, only about 7.5 vol% and 4.5 vol% of water separate from the emulsions stabilized by BPSMA-3 and BPSMA-6 micelles, respectively. It is demonstrated that, the white oil/water emulsions stabilized by BPSMA micelles can succeed in trapping the added white oil (V_{oil} = 83.3%), forming high internal phase emulsions (HIPE), while the emulsion stabilized by LPSMA micelles fails in trapping 83 vol% oil (actually only 67 vol%, as displayed in Fig. S2†).

The stability of emulsions was further assessed in terms of the change of emulsion ratio over time. As shown in Fig. 3c, the emulsion ratio of the emulsion stabilized by LPSMA

micelles decreases significantly after homogenization, which decreases to only 57% after 14 days. To the contrary, the emulsion ratio of the emulsions stabilized by BPSMA micelles is more stable. For the emulsions stabilized by BPSMA-3 and BPSMA-6 micelles, the emulsion ratio just decrease to 92.5% and 95.5% after 14 days, respectively. Even more, the emulsions stabilized with BPSMA-9 and BPSMA-12 micelles are almost unchanged, the emulsion ratio of which is still nearly 100%. Therefore, the emulsions stabilized by BPSMA micelles exhibit much better long-term stability than that stabilized by LPSMA micelles.
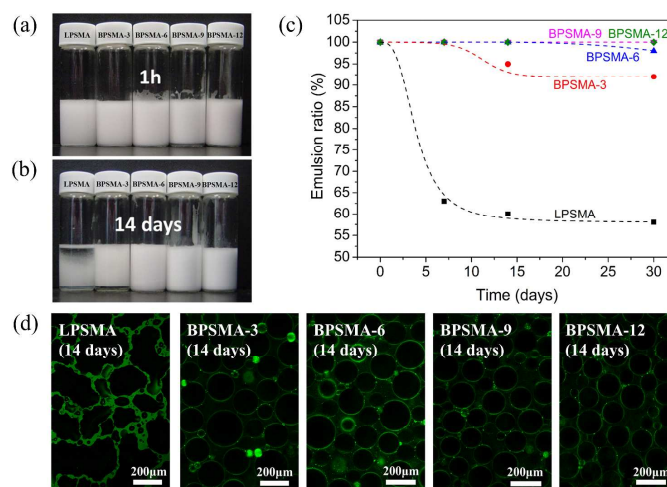

Fig. 3 (a and b) Appearance of the white oil/water emulsions stabilized by LPSMA and BPSMA micelles with different incubation time after homogenization, 1 h (a) and 14 days (b). (c) Emulsion ratio of the white oil/water emulsions stabilized by LPSMA and BPSMA micelles over time. (d) CLSM images of the white oil/water emulsions stabilized by the LPSMA and BPSMA micelles labeled by RhB (green) at 14 days after homogenization. All the emulsions were prepared with the volume ratio of oil to water phase as 5:1, and the micelle concentration was 0.75 mg mL⁻¹.

To investigate the stabilizing behavior of micelles at white oil/water interface, the LPSMA and BPSMA micelles labeled by RhB were used to stabilize the emulsions with 83 vol% white oil. As shown in the CLSM images from Fig. 3d, BPSMA micelles (green) can be observed on the surfaces of emulsion droplets and display a fluorescent ring, indicating that BPSMA micelles indeed closely wrapped the surface of emulsion droplets serving as particulate emulsifiers even after 14 days. The configuration of BPSMA micelles at oil/water interface was confirmed by SEM, as shown in Fig. S3†. It is also obvious in Fig. 3d that, for the emulsions stabilized by BPSMA micelles, all of the oil droplets are spherical, no change of shape and no coalescence of oil droplets happen. Comparatively, the emulsion stabilized by LPSMA micelles demulsifies and the oil droplets coalesce with each other forming irregular coalescence, which is in accordance with the results of Fig. 3b.

Emulsifying performance mainly depends on the structure of the micelles at oil/water interface, which is influenced by the structure of the micelles in aqueous phase before immigrating to the interface.[30] It has already been known from Fig. 3b that,

BPSAM-9 micelles possess outstanding emulsifying performance and the further increase in VBT mol% of BPSMA has little influence on the stability of emulsion. Herein, BPSAM-9 micelles were chosen to compare with LPSMA micelles to elucidate the discrepancy in the stability of emulsions.

The structural stability of micelles in aqueous solution with various incubation time was investigated. Fig. 4 gives the correlation functions and the corresponding size distributions of LPSMA micelles (a) and BPSMA-9 micelles (b) in aqueous solution at different incubation time obtained from DLS measurements. The micelle size distributions were determined by the CONTIN analysis of correlation functions. As shown in Fig. 4a, the mean diameter of LPSMA micelles changes from 309 nm to 2300 nm (14 days) because of the hydrolyzing of maleic anhydride and the ionization of carboxyl (the pH of LPSMA micelle solution was 2.7), making LPSMA micelles gradually swell and scatter in aqueous phase. Extremely, LPSMA micelles may dissolve, and cannot be detected in experiments. Compared with LPSMA micelles, BPSMA micelles present much better stability. Little change happens in the diameter of BPSMA micelles during 30 days (see Fig. 4b). The significant difference of the Tyndall phenomenon of BPSMA-9 micelle solution with that of LPSMA micelle solution is well coincident with the results of micelle size analysis, as shown in the insert of Fig. 4. For LPSMA micelles, the intensity of scattering light significantly weakens over time, even no Tyndall phenomenon is found after 30-day incubation, while only a little changes occur in the BPSMA-9 micelle solution. The branched structure of BPSMA is probably available for postponing the hydrolyzing of maleic anhydride and the ionization of carboxyl to some extent. That may explain the difference between linear and branched polymer micelles in stabilizing white oil/water emulsion.
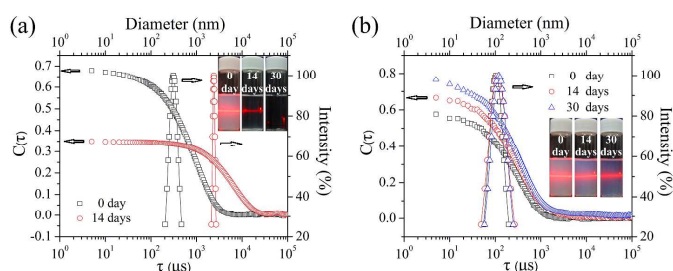

Fig. 4 Correlation functions $C(\tau)$ and corresponding size distributions of LPSMA micelles (a) and BPSMA-9 micelles (b) in aqueous solution at different incubation time (0 day, 14 days, and 30 days) measured by DLS. The concentration of micelles is 0.75 mg mL^{-1}. Insert: Tyndall phenomenon recorded by digital photographs.

INFLUENCE OF NaCl SALINITY ON THE STABILITY OF EMULSIONS

It has been proved in our previous work that, the shielding effect of NaCl can reduce the electrostatic repulsion of the charged particles.[28] Herein, a batch of LPSMA and BPSMA-9 micelle aqueous solutions with different NaCl concentrations were prepared to stabilize the white oil/water emulsions, in order to further explore the relationship of micellar structure with emulsifying performance. The optical microscopy images are shown in Fig. 5a and b. Obviously, the size of the emulsion droplets stabilized by LPSMA micelles decreases with increasing NaCl concentration. For the emulsion droplets stabilized by BPSMA-9 micelles, however, the size changes little in the given range of salinity.

Fig. 4a has showed that LPSMA micelles swell and scatter in aqueous phase easily because of the hydrolyzing of maleic anhydride and the ionization of carboxyl. It is further found that the shielding effect of NaCl can effectively restrain above progress. As shown in Fig. 5c, the size of LPSMA micelles decreases and the Zeta potential increases significantly, with increasing NaCl concentration. Correspondingly, the size and Zeta potential of BPSMA-9 micelles do not show an obvious response to salinity changes compared with that of LPSMA micelles. It is indicated that the inherent branch structure of BPSMA-9 micelles can postpone the hydrolyzing of maleic anhydride and ionization of carboxyl to some extent. Therefore, salinity plays a great effect on the emulsifying performance of linear polymer micelles, but little impact on that of branched polymer micelles. The result is in accordance with that in Fig. 4.
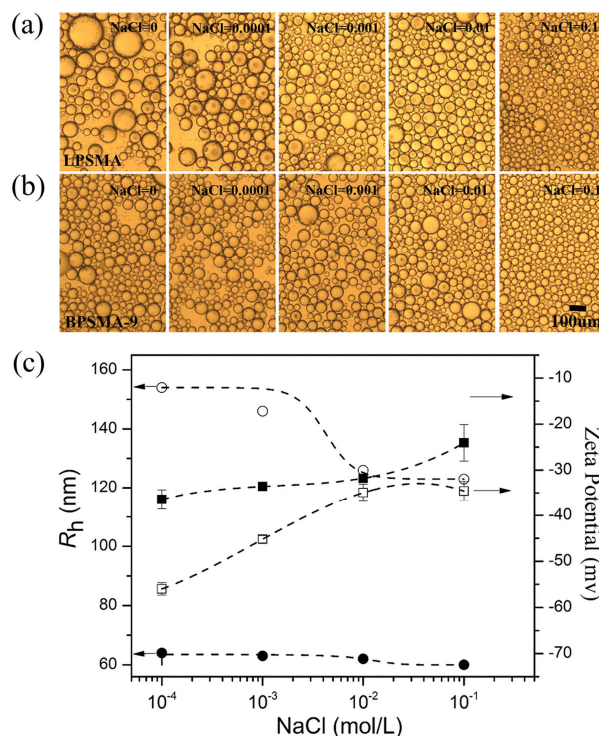

Fig. 5 (a and b) Optical microscopy images of the white oil-*in*-water emulsions stabilized by LPSMA (a) and BPSMA-9 (b) micelles at different NaCl concentrations (0, 0.0001, 0.001, 0.01, and 0.1 mol L^{-1}). The concentration of micelles is 0.75 mg mL^{-1}. All the images were taken under quiescent conditions with the placement duration of 24 h after homogenization. (c) Effects of NaCl concentration on the R_h (○-LPSMA, ●-BPSMA-9) and Zeta potential (□-LPSMA, ■-BPSMA-9) of self-assembly micelles.

INFLUENCE OF OIL PHASE ON THE STABILITY OF EMULSIONS

As a kind of long-termly effective emulsifier, BPSMA-9 self-assembled micelles can stabilize not only the white oil-*in*-water emulsions but also the oil-*in*-water emulsions with other types of natural oils, like dicaprylyl carbonate, propylheptyl caprylate, silicone oil, and isooctyl palmitate. The volume percentage of above oil phases are all above 83%, as the digital photos show in Fig. 6.
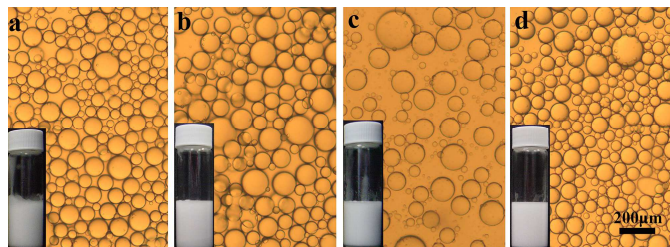

Fig. 6 Emulsions with different types of oils (dicaprylyl carbonate (a), propylheptyl caprylate (b), silicone oil (c), and isooctyl palmitate (d)) stabilized by BPSMA-9 micelles. The micelle concentration is 0.75 mg mL^{-1}. The digital and optical microscope images were taken at 24h after homogenization.

As is well-known, demulsification of the extremely stable Pickering emulsions is a challenge. In this study, the BPSMA micelles exhibited pH-responsive property due to the introduction of maleic anhydride units in the polymer structure, and thus the Pickering emulsions stabilized by the BPSMA micelles can be easily broken by pH adjustment, as shown in Fig. S4†.

Conclusions

The polymeric particulate emulsifiers based on the self-assembled micelles of amphiphilic branched copolymers BPSMA have been successfully prepared to elucidate the correlation between the structure and emulsifying performance of polymeric soft particles. By comparing the structure and emulsifying performance of the branched copolymer micelles with that of the corresponding linear ones, it is found that the branched structure of copolymer plays an important role in the structural stability and emulsifying performance of the self-assembled micelles. The BPSMA micelles exhibit much better structural stability than the corresponding linear micelles due to the possible postponing of the hydrolyzing of maleic anhydride and the ionization of carboxyl to some extent caused by the introduction of branched structure in copolymers, resulting in their superior emulsifying performance reflected in the extremely high emulsifying efficiency and the excellent long-term stability of emulsions. Even at 0.75 mg mL^{-1}, a quite low concentration of self-assembled micelles in aqueous phase, the maximum volume fraction of the white oil that can be trapped in the emulsions stabilized by BPSMA micelles is as high as 83%, surpassing the emulsifying efficiency of linear copolymer micelles and the reported other particulate emulsifiers including inorganic particles,[18] organic latexes,[21] and microgels.[24] It is also worth noting that salinity plays a great effect on the emulsifying performance of linear polymer micelles, while little impact on that of branched polymer micelles. Additionally,

BPSMA micelles can emulsify not only white oil but also other types of natural oils, such as dicaprylyl carbonate, propylheptyl caprylate, silicone oil, and isooctyl palmitate. Therefore, this study may contribute to understand the relationship between the structure and emulsifying performance of micellar emulsifiers, and fabricate the high-efficiency particulate emulsifiers with potential application in cosmetics area.

Notes and references

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† Electronic Supplementary Information (ESI) available: Table S1, Fig. S1-S4. See DOI: 10.1039/b000000x/

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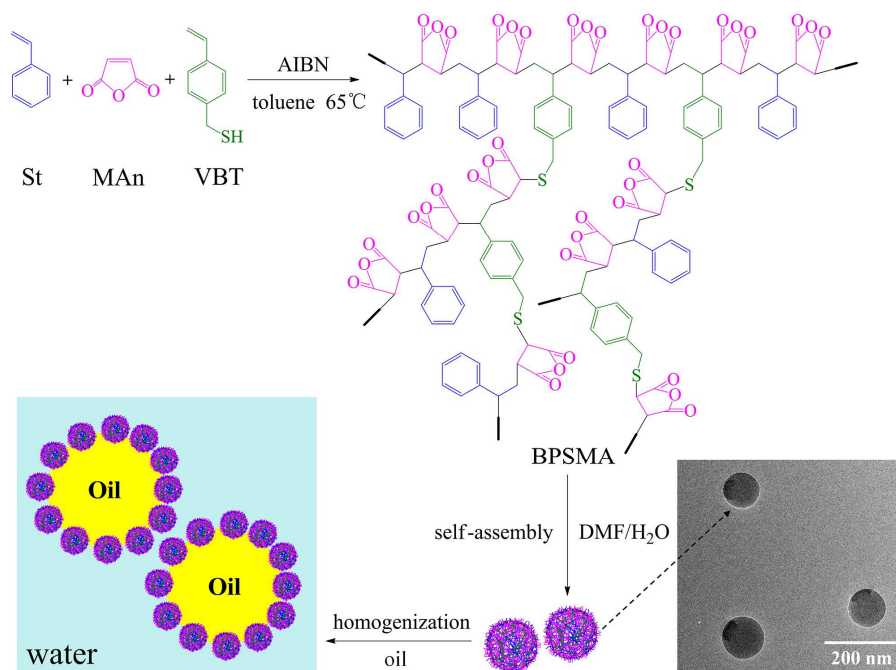
The self-assembled micelles of amphiphilic branched poly(styrene-*alt*-maleic anhydride) (BPSMA) are prepared and employed as particulate emulsifiers to stabilize Pickering emulsions, which exhibit much superior emulsifying performance over the corresponding linear copolymer micelles.