Pickering emulsions stabilized by self-assembled colloidal particles of copolymers of P(St-alt-MAn)-co-P(VM-alt-MAn)

Xiaoya Liu, Chenglin Yi, Ye Zhu, Yiqun Yang, Jinqiang Jiang, Zhenggang Cui, Ming Jiang

Abstract

A new type of copolymer containing two alternating segments, poly( -alt-maleic anhydride)-co-poly( -maleic anhydride) P(St-alt-MAn)-co-P(VM-alt-MAn) (PSVM), was prepared. The copolymer self-assembled into nanoparticles with internal microphase structures in water because the hydrophilicity of segment P(VM-alt-MAn) is higher than that of P(St-alt-MAn). The particle size, morphology, and potential and surface properties and their dependence on the pH and salt concentrations were studied with a combination of techniques. The nanoparticles of PSVM showed surface activity and pH sensitivity for producing Pickering oil-in-water emulsions. The emulsion volume increased and the size of oil/water droplet decreased with increasing salt concentration. Furthermore, cross-linked nanoparticles (CLPs) were obtained by photo-dimerization of the pendant coumarin groups in PSVM under UV irradiation. The emulsions produced by using the CLPs as emulsifiers showed even better stability upon standing. Solid oil-phase droplets were obtained by preparation of CLPs-stabilized Pickering emulsions with an oil phase of styrene containing the initiator AIBN followed by the polymerization of styrene. Thus, the enrichment and aggregation of the CLPs on the emulsion droplets was visible because the solid droplets remained unchanged during the SEM sample preparation.

1. Introduction

Using colloid particles to prepare and stabilize emulsions, so-called "Pickering" emulsions, has drawn increasing interest in recent years [1–4]. In contrast to conventional emulsions, which are usually thermodynamically unstable and stabilized by surfactants or amphiphilic linear copolymers, Pickering emulsions are often super-stable due to the nearly irreversible adsorption of the colloid particles at the oil/water interface because of the their high energy of attachment, which makes the final emulsions extremely stable with shelf life stabilities of months or even years [3,4]. In Pickering emulsions, the colloid particles are wetted partially by oil and partially by water so they become surface-active, and then they are preferentially located or adsorbed at the oil/water interface. These surface-active particles, i.e., solid emulsifiers, can be prepared in different ways [5,6]. The most common way is surface modification of natural or commercial inorganic nanoparticles [2], such as silica [4], calcium carbonate [7,8], and Smectites [9]. These surface-active nanoparticles are functional materials with a wide range of potential applications including biomedical materials, pharmaceuticals, electronics, photonics, cosmetics, functional food and coatings [10].

Binks and co-workers have systematically studied the formation, stability and structure of Pickering emulsions stabilized by entirely solid particles, including inorganic particles, organic/inorganic composite particles and pure polymeric particles [8]. For example, Binks and Lumsdon reported that commercial hydrophobic silica sols acted as emulsifiers in the preparation of water-in-toluene emulsions [11]. Armes and Binks et al. studied lightly cross-linked poly(4-vinylpyridine)-silica particles [12]. Armes and co-worker also prepared surface-active polystyrene latex particles as individual emulsifiers; the polystyrene latex particles were prepared by dispersion polymerization using amphiphilic diblock copolymers as steric stabilizers [13]. Ngai et al. synthesized PNIPAM microgels using the surfactant-free precipitation copolymerization of N-isopropylacrylamide, methacrylic acid (MAA) and the cross-linker N,N-methylene bisacrylamide. The microgel stabilized octanol-in-water emulsions well at room temperature at pH > 6 [14]. Overall, most of the polymeric emulsifiers used are cross-linked particles, which obviously make the solid emulsifier more stable.

It is worth noting that surface-active, cross-linked polymeric nanoparticles can be obtained via self-assembly of well-designed...
block copolymers. As a pioneering work in this approach, Fuji and Arms et al. prepared cross-linked (SCL) micelles of PEO-PSACMA-PDEA triblock copolymer with a PEO outer corona, PSAGMA inner shell and pH-responsive PDEA core. This cross-linked (SCL) micelle showed a good ability in emulsification [15]. Compared with other methods to prepare nanoparticles of polymers, the self-assembly of amphiphilic copolymers is most popular and fascinating. It is easy to control the structure and properties of nanoparticles, not only by changing the copolymer structures but also by varying the processes of self-assembly. Therefore, the self-assembly of polymers has been a hot topic over the past 10 years, and most studies on self-assembly have focused on block or graft copolymers [16,17]. However, the applications of these regular copolymers are still limited due to their relatively high price and strict conditions of synthesis. Compared to regular copolymers, random copolymers are much easier to synthesize and can self-assemble various nanostructures. Thus, using low-cost materials, such as ionomers or random copolymers, to replace block copolymers in preparing solid emulsifiers is of great significance in practice. Li and Jiang first reported that ionomers with a few ionic groups on the hydrophilic chain backbone can self-assemble into narrowly distributed nanoparticles in water because the ionic groups richen on the particle surface [18]. The formation and the various properties of such surfactant-free particles were reviewed by Zhang and Wu et al. [19]. Furthermore, Giant, Li et al. reported that some amphiphilic random copolymers were able to self-assemble into nanoparticles as well [20,21]. Our previous works also investigated the self-assembled and cross-linked nanoparticles of random or alternating copolymers [22–25]. However, although these fascinating and inexpensive polymer nanoparticles offer a more practical possibility for Pickering emulsions, to the best of our knowledge, no attempt has been reported so far.

Here, we desire to demonstrate a straightforward procedure to fabricate stable particulate emulsifiers from the self-assembly of a random copolymer. First, we present a simple route to prepare a photosensitive copolymer, P(St-alt-MAn)-co-P(VM-alt-MAn) (PSVMVM) (see Fig. 1a), which can form novel cross-linked particles (CLPs, typically 40–100 nm diameter) from self-assembly and subsequent cross-linking in water. The CLPs were shown to be an excellent nanoparticle emulsifier for oil-in-water emulsions (Fig. 1b). In addition, the surface structure of the droplets in emulsions is difficult to observe unless a combination of freeze-fracture techniques and field emission scanning electron microscopy is used [26–28]. Herein, we used monomer styrene with the initiator AIBN to control the structure and properties of nanoparticles, not only by free radical polymerization of styrene. Therefore, the surface morphologies of the droplets could be visualized simply by SEM.

2. Materials and methods

2.1. Materials

Styrene (St, Sinopharm Chemical Reagent Co., Ltd. SCRC) (St) was dried by CaH2 for 24 h, distilled under reduced pressure and then stored at −5 °C before use. The photosensitive monomer 7-((4-vinylbenzoyl)oxy)-4-methylcoumarin (VM) was synthesized from 4-vinylbenzyl chloride (Acros Organics) and 7-hydroxy-4-methylcoumarin (Acros Organics) according to reference [29]. The alternating-like copolymer PSMVM was dissolved in DMF as a mobile phase at a flow rate of 1.0 mL min⁻¹ during the rest times. After 3 days, self-assembled PSMVM nanoparticles in water because the ionic groups richen on the particle surface [18]. The formation and the various properties of such surfactant-free particles were reviewed by Zhang and Wu et al. [19]. Furthermore, Giant, Li et al. reported that some amphiphilic random copolymers were able to self-assemble into nanoparticles as well [20,21]. Our previous works also investigated the self-assembled and cross-linked nanoparticles of random or alternating copolymers [22–25]. However, although these fascinating and inexpensive polymer nanoparticles offer a more practical possibility for Pickering emulsions, to the best of our knowledge, no attempt has been reported so far.

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2.2. Synthesis and characterizations of P(St-alt-MAn)-co-P(VM-alt-MAn)

Photosensitive alternating-like copolymers PSMVM were synthesized through the free-radical copolymerization of electron-donating monomers of styrene (St), styrene derivative containing photosensitive coumarin moieties (VM) and electron-accepting monomer maleic anhydride (MAAn) using AIBN as a initiator according to the reference [29] (Fig. 1a). St, VM and MAAn were dissolved in dioxane at molar ratios of 8:2:10 and 6:4:10, respectively, and AIBN, 2.0% of the total molar weight of monomers, was added into a 100 mL one-necked round-bottom flask. The mixture was degassed three times using the freeze–pump–thaw procedure and sealed under vacuum. After 30 min of stirring at room temperature, the ampoule was placed in a preheated oil bath (65 °C) for 12 h under stirring. The resultant copolymers were purified by recrystallization three times into toluene and then were dried under vacuum at room temperature for 24 h (yield: 70%). 1H NMR spectra were recorded on a Bruker DMAX500 MHz spectrometer with tetramethylsilane as an internal standard. The molecular weight and molecular weight distribution index of the copolymers were determined using gel permeation chromatography (GPC, HP1100) with DMF as a mobile phase at a flow rate of 1.0 mL min⁻¹ at 35 °C. Polystyrene standards were used for the calibration of the molecular weight.

2.3. Preparation and cross-linking of PSMVM nanoparticles

The alternating-like copolymer PSMVM was dissolved in N,N-dimethylformamide (DMF), forming a solution with a concentration of 20 mg mL⁻¹. The solution was stirred overnight. To induce self-assembly, super-purified water was added dropwise into the solution at a rate of 0.2 vol.% per minute until the water content reached 25 vol.%. The solution was stirred for 3 h and then quenched into an excess amount of water, followed by dialysis (molar mass cutoff: 14,000) against water to remove the dioxane. The water was changed every 4 h in the first 12 h and then every 8 h during the rest times. After 3 days, self-assembled PSMVM nanoparticles were obtained. The turbidity of the PSMVM copolymer in DMF solution during the self-assembly process was detected by TU-1901 UV–vis spectrophotometry. The PSMVM nanoparticles contained pendant coumarins, which could be dimerized under UV irradiation [32]. To prepare cross-linked particles (CLPs), UV irradiation was carried out with a UV-vis spot curing system. The irradiation efficiency was controlled by adjusting the light intensity and the distance between the lamp and particle solution. The surrounding temperature of the samples was controlled at about 30 °C by a cold plate. The samples were monitored by a UV–vis spectrophotometer over different irradiation time intervals.

2.4. Emulsification

Equal volumes (3.0 mL) of oil (toluene or styrene) and aqueous dispersion of nanoparticles (with a copolymer concentration of 1.5 × 10⁻¹ g mL⁻¹) at different pH values or salt concentrations were placed in glass vessels (inner volume 10 mL) at room temperature. The mixtures were kept in a thermostated bath at 25 °C for 10 min and then homogenized at 8000 rpm for 2 min by a XHF-D H-speed dispersator homogenizer (1 cm head) at 25 °C. The type of emulsions was determined by drop test.
2.5. Solidifying emulsion droplets

Styrene with 2.0 mol% AIBN (rather than toluene) was used as the oil phase to prepare emulsions using CLPs as emulsifier with 0.1 M NaCl at pH 2. After emulsification, the emulsion was diluted by water first, and then the oil phase in the emulsion droplet was solidified by the polymerization of styrene at 65 °C. The solidified emulsion droplets with CLPs 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 °C overnight. The processes of self-assembly, photo-cross-linking, emulsification and solidifying of the emulsion droplet is illustrated in Fig. 1b.

2.6. Characterization of colloidal particles and emulsifiers

TEM images of the nanoparticles were taking by a Philip Tecnai F20 microscope with a 120-kV accelerating voltage. A drop of the diluted particle suspensions was deposited on copper grids pre-coated with a thin film of poly (vinylformaldehyde) and with carbon and then dried at room temperature. The ζ potentials of the emulsion were measured by a Malvern Mastersizer 2000 instrument at room temperature. It was calculated from the electrophoretic mobility (u) using the Smoluchowski relationship, \( \zeta = \eta u / \varepsilon \), where it is assumed that \( \kappa \alpha \ll 1 \) (where \( \eta \) is the solution viscosity, \( \varepsilon \) the dielectric constant of the medium, \( \kappa \) and \( \alpha \) are the Debye-Hückel parameter and the particle radius, respectively). The Z-average diameter of aqueous dispersion was measured using a Malvern Zetasizer ZS90. Contact angles of the PSMVM copolymers, the nanoparticles and CLPs were measured with a water droplet on sample disks that were prepared by pressing the sample powder on KBr plates with the same conditions and dipping into toluene, by using a DropMeter A-100 instrument. A drop of the diluted emulsion was placed on a microscope slide and viewed using an optical microscope (DM-BA450, Motic China Group Co., LTD) fitted with a digital camera 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 (DM-BA450, Motic China Group Co., LTD). DLS was carried out using an ALV-5000 laser light scattering spectrometer. All the particle solution samples were filtered through 0.45 µm Millipore 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. Scanning electron microscopy (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.

3. Results and discussion

3.1. PSMVM copolymer and nanoparticles

It is well known that a pair of electro-donating and electron-accepting monomers may form a 1:1 charge-transfer complex, which leads to an alternating copolymer by free radical polymerization [30,31]. In the present case we used two pairs, composed of a common electron acceptor maleic anhydride (MAN) and electron donors of styrene (St) and a styrene derivative containing photosensitive coumarin moieties (VM) [29]. Free-radical copolymerization of the two pairs of MAN/St and MAN/VM was expected to form two different segments, which were randomly connected. In this copolymer P(St-alt-MAN)-co-P(VM-alt-MAN) (PSMVM), as discussed below, the segment MAN/VM is more hydrophilic than that of MAN/styrene. Two PSMVM samples with similar molecular
weights but different St/VM ratios were used in this study, and the characteristic data of the samples are listed in Table 1.

The number average molecular weight \( (M_n) \), weight-average molecular weight \( (M_w) \), and molecular weight distribution index \( (M_w/M_n) \) of the copolymers were characterized by GPC; the data are shown in Table 1.

In preparing PSMVM nanoparticles, water was gradually added into the copolymer solutions in DMF. The formation of the nanoparticles was monitored by turbidity measurements.

Fig. 2 shows typical results of the turbidity changes when the water was added into the solutions of PSMVM1 and PSMVM2 in DMF. For both cases, the turbidity was initially almost zero and remained unchanged when the water content was low. When the water content reached a certain value, the turbidity dramatically increased, indicating that the VM/MAn segments started to aggregate in solution and form particles. The water content at this point is defined as critical water content (CWC). Then, the turbidity reached a plateau, which means that the aggregate structure became stable.

The CWC values for PSMVM1 and PSMVM2 were found to be 17.3 vol.% and 41.2 vol.%, respectively. The significant difference in CWC between the two copolymers can be attributed to the composition difference; the PSMVM1 and PSMVM2 have the same MAN contents, but the VM unit in PSMVM2 is four times longer than that in PSMVM1. In other words, the VM/MA segment is more hydrophilic than St/MA is because the VM unit contains more polar carbon–oxygen bonds.

### 3.2. Morphology of the PSMVM Particles

The morphology of the resultant particles formed by PSMVM1 in water was observed by TEM (Fig. 3). The TEM image shows clearly that all the particles are spherical and in the size range of 40–100 nm. An outstanding feature of the particles is that, within the particles, black and white microdomains tightly interpenetrate each other. Obviously, this morphology is different from the typical core–shell structure for the amphiphilic block copolymer micelles. The formation of this interesting particle morphology is due to the chain structure of PSMVM. As mentioned above, the St/MAn segment is less hydrophilic than VM/MAn, and thus the St/MAn segment aggregates first when the medium with water is gradually added into the DMF solution of PSMVM1. Finally, in the resultant nanoparticles the St/MAn segment may form much denser microdomains, showing dark regions in the TEM images. Because the segments of St/MAn and VM/MAn were chemically connected, only very fine microdomain structures were observed.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>( n(\text{St}):n(\text{VM}):n(\text{MAn}) )</th>
<th>( M_n^b \times 10^{-4} ) (mol g(^{-1}))</th>
<th>( M_w^b/\text{PDI}_b )</th>
<th>CWC(^c) (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSMVM1</td>
<td>11.7: 1.0: 11.7</td>
<td>5.1</td>
<td>1.80</td>
<td>17.3</td>
</tr>
<tr>
<td>PSMVM2</td>
<td>8.0: 4.0: 11.6</td>
<td>5.2</td>
<td>1.84</td>
<td>41.2</td>
</tr>
</tbody>
</table>

\( ^a \) The molar ratio of copolymers composition obtain from the \(^1\)H NMR.

\( ^b \) The number average molecular weight and PDI of copolymers obtained from the GPC.

\( ^c \) The initial concentration of PSMVM was \( 2 \times 10^{-2} \) g mL\(^{-1}\).

### 3.3. Effect of salt concentration and pH on \( \zeta \) potential and particle size

Fig. 4a shows the \( \zeta \) potential of PSMVM1 nanoparticles as a function of the concentration of NaCl. The \( \zeta \) potential is negative in the whole range of salt concentrations because of the partial hydrolyzing of the maleic anhydride units during the process of self-assembly. When the salt concentration continuously increases to above 0.1 M, the \( \zeta \) potential rapidly decreases to \( -12 \) mV, which shows that the shielding effect of NaCl reduced the electrostatic repulsion of the charged particles.

The size distributions of PSMVM 1 nanoparticles with different NaCl concentrations are shown in Fig. 4b. Initially, the electrolyte concentration had little effect on the particle size and distribution when the NaCl concentration was in the range of 0–0.1 M. However, when the salt concentration was further increased to above 0.1 M, electrostatic repulsion among the nanoparticles decreased, and the particles partially flocculated, leading to an increase in the particle size. A similar salt effect on the aggregation number of the micelles prepared from polyelectrolyte copolymer was reported by Armes et al. [33] and Forster et al. [34].

The pH of diluted nanoparticle solutions containing 0.1 M NaCl was adjusted as required. Fig. 5 shows variations of both the \( \zeta \) potential and Z-average diameter of nanoparticle solutions against pH. Clearly, the \( \zeta \) potential becomes more negative with increasing pH. Meanwhile, starting from pH 3.8 (the initial pH of the aqueous dispersion), the Z-average diameter dramatically increases with increasing pH. However, the change of both the \( \zeta \) potential and diameter with pH are understandable. That nanoparticles may...
formed the flocs in the high salt concentration (0.1 M NaCl) which is a better stabilizers indicated by Binks BP group and many other reports. This experiment can prove that the flocs with larger size and more negative \( \zeta \) potential can be formed at higher salt concentration and can increase the emulsification of solid emulsifier.

### 3.4. Surface properties of PSMVM and its particles

Fig. 6 shows that at the toluene/water interface the contact angle of the raw copolymer is 128°, and it apparently decreases to 98° for the assembled nanoparticles. It implies that during the process of self-assembly, the hydrophilic groups of \(-\text{COOH}\) tend to adsorb on the surface of the nanoparticles. Moreover, after photo-cross-linking, the CLPs show the smallest contact angle of 72°. In fact, the photo-cross-linking caused the particles to shrink and therefore increased the surface charge density, leading to a further contact angle decrease. Hence, the contact angle of the nanoparticles could be adjusted with UV irradiation.

### 3.5. Effect of pH on emulsification

Stable toluene-in-water (i.e. o/w) emulsions were obtained using the PSMVM nanoparticles as a “Pickering”-type emulsifier at pH 4.5 (Fig. 7b), and the type of these emulsions was confirmed by the drop test. The PSMVM 1 nanoparticles, which were strongly absorbed at the oil–water interface, showed excellent surface activity due to the amphiphilicity and the characteristic micro-structures of the PSMVM nanoparticles revealed by the TEM images; more discussion will be presented later. The adsorption of stabilized nanoparticles at the oil–water interface was expected to be pH dependent because of the pH sensitive properties of the PSMVM 1 nanoparticles. As shown in Fig. 7c, with the dropwise addition of 2.0 M aqueous NaOH into the emulsion, demulsification occurred, and macroscopic phase separation was completed within 48 h. A possible explanation is that as the pH increased the \(-\text{COOH}\) groups in the nanoparticles, causing a more negative surface charge, and the nanoparticles became more hydrophilic. Thus, the nanoparticles tended to move from the surface of droplet into the water phase [15]. This observation of demulsification is generally consistent with the earlier report of Binks and Clint, which showed that the particles with very hydrophilic surfaces were poor emulsion stabilizers [4]. We believe that such pH-responsive nanoparticles have a great potential for applications in the field of cosmetic or pharmaceutical formulations.

### 3.6. Effect of salt concentration on emulsification

Digital photographs of the emulsions of toluene and water stabilized by PSMVM 1 nanoparticles with different salt concentration.

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**Fig. 4.** The effect of NaCl on the \( \zeta \) potential (a) and Z-average diameter (b) of the nanoparticles of PSMVM 1. The mass concentration of the nanoparticles was \( 1 \times 10^{-4} \) g mL\(^{-1} \), 0.1 M NaCl aq.

**Fig. 6.** Contact angle of raw copolymer PSMVM 1: (a) PSMVM nanoparticle and (b) the CLPs.

**Fig. 7.** Digital photographs of a 50:50 mixture of toluene and water with the nanoparticles of PSMVM 1: (a) before and (b) after homogenization at pH 4.5 for 24 h, and (c) macroscopic demulsification caused by the addition of several drops of 2.0 M aqueous NaOH solution to the emulsion shown in (b) for 48 h.
concentrations are shown in Fig. 8a. It can be seen that the volume of the creamy emulsion phase increased with increasing of salt concentration, except in the case of 1.0 mol L$^{-1}$. Furthermore, the aqueous phases became more transparent with increasing salt concentration, especially when the salt concentration was above 0.1 mol L$^{-1}$. This trend indicates that most of the nanoparticles were incorporated into the emulsion phase. This variation can be visualized by microscopy observations. As shown in Fig. 8b, the oil drops became smaller because of more nanoparticles adsorbed into the oil/water interface with increasing NaCl concentration.

However, it is observed that the nanoparticles were more inclined to flocculate when the salt concentration was above 0.1 mol L$^{-1}$ because the high ionic strength decreased the Debye screening length and hence reduced the repulsive electrostatic forces between the charged groups on the nanoparticles, as shown in Fig. 4. The size of the emulsion droplet decreases as the salt increases. The reason is likely due to the formation of flocs in the highly concentration salt solution and which is a better stabilizers, as indicated by many reports, for example from Binks BP group.

The long-term stability of the PSMVM nanoparticles stabilized emulsions is more than 6 months under room temperature.

3.7. Cross-linking of colloidal nanoparticles

The self-assembled PSMVM 1 nanoparticles used as a Pickering emulsifier generally showed good surface activity due to the nearly irreversible adsorption of particles at the o/w interface. Obviously, to fix the particle structure by cross-linking is a simple way to improve the particle stability [14,15] because it can prevent the dis-assembly of the particle when the emulsions undergo execrable conditions. In the present case, the presence of photo-sensitive groups of coumarin in PSMVM makes the cross-linking of the nanoparticles occur easily under mild conditions. Thus, in the cross-linked nanoparticles (CLPs) the fine micro-separated phase structure was locked, which maintains surface-actives.

UV–vis spectroscopy was used to trace the UV-cross-linking process of the nanoparticles. As shown in Fig. 9a, when the nanoparticle solution was exposed to UV light at $\lambda > 310$ nm, the
absorption of coumarin moieties at around 320 nm decreased continuously with increasing irradiation time, indicating the occurrence of dimerization of coumarin groups of the polymeric chains, resulting in inter-chain cross-linking in the nanoparticles (Fig. 9a).

Fig. 9b compares the hydrodynamic radius distributions of the photosensitive nanoparticles measured by DLS with different UV irradiation times. With the irradiation, the particle size decreases from 100 nm to 50 nm, which means that under the UV irradiation, the inter-chain photo-cross-linking induces the shrinkage of the whole nanoparticles. A similar phenomenon has also been observed in other UV cross-linked micelle systems [22].

3.8. Interface action of CLPs

Although it is widely accepted that in Pickering emulsions the surface-active nanoparticles are preferentially located at the oil–water interface with few exceptions, this argument has not been confirmed by experimental observations because the emulsion droplets were inevitably destroyed in the ordinary sample preparation processes for TEM or SEM. In order to solve this problem, we prepared a Pickering emulsion of styrene containing the initiator AIBN in water using CLPs as the emulsifier. Then, the styrene/water droplets were solidified by the polymerization of styrene, which made SEM observation possible.

Optical microscopy studies revealed that the emulsion droplets of CLPs were spherical and polydisperse with diameters in a range from 5 to 15 µm (Fig. 10a). After the solidification of the emulsion droplets by the polymerization of styrene at 65 °C and purification with ethanol several times, the robust solidified polystyrene-in-water droplets, which can keep their shape and morphology during the sample preparation, were obtained. The SEM image (Fig. 10b) shows that because of the shrinkage of styrene during polymerization, the solid droplets are around 5–10 µm in diameter, which is smaller than before solidification. The image shows the aggregation of the CLPs on the oil/water interface, and a few free nanoparticles in the visual field were observed (Fig. 10b). Fig. 10c shows one emulsion droplet at a higher magnification. Thus, these observations provide convincing evidence that the emulsion droplets were stabilized by the CLPs layers. In addition, we also noticed that the size of the CLPs (around 1 µm) adsorbed on the surface of the solidified droplets was larger than that of the original CLPs (100 nm, Fig. 3). This result may be due to the particle coalescence on the interface during the solidification of styrene/water droplets of the diluted emulsion at a high temperature.

4. Conclusion

In conclusion, we present a novel and effective approach to design and prepare Pickering emulsifiers based on a new type of copolymer, P[St-alt-MAn]-co-[P(VM-alt-MAn)] (PSVM). The copolymer self-assembled into nanoparticles with enriched VM-alt-MAn segments on the surfaces because it was more hydrophilic than the St-alt-MAn segments. This approach can readily be applied to other random copolymers with segments of different hydrophilicities. The performance of PSVM nanoparticles and their UV cross-linked products (CLPs) as Pickering emulsifiers compared to nanoparticles made of some specially prepared amphiphilic block copolymers was excellent. The strawberry-like morphology of the emulsion droplets was clearly observed by SEM, demonstrating the enrichment and aggregation of CLPs on the droplet surfaces. The successful observations of the morphology of the emulsion droplets by SEM can be attributed to the solidification of emulsion droplets by the polymerization of styrene used as the oil phase in emulsions.

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