One-step facile synthesis of monodisperse raspberry-like P(S–MPS–AA) colloidal particles

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This paper presents a one-step procedure for the facile synthesis of monodisperse raspberry-like polymer colloidal particles by soap-free emulsion polymerization of styrene (S), acrylic acid (AA), and 3-(trimethoxysilyl)propyl methacrylate (MPS). In this method, when S, AA, and MPS are mixed with water and stirred at a certain temperature, raspberry-like P(S–MPS–AA) colloidal particles with uniform shapes and sizes could be obtained in a reliable manner. Both the core particles and the smaller corona particles of core surfaces were formed in situ. A mechanism of formation based on the second nucleation induced by MPS-enriched segments on the core surfaces is proposed.

Introduction

Colloidal particles with hierarchical structures have drawn burgeoning interest in recent years, principally because such particles can surpass the inherent limitations of single-component colloidal particles, and they have shown potential in applications such as sensing, catalysis, self-assembly, and nanoelectronics.1–11

Raspberry-like colloidal particles are one of the main types of hierarchically structured colloidal particles. They consist of smaller corona particles placed over the larger core particles, which have attractive characteristics, such as unique morphology, surface roughness, large specific surface areas, and large amounts of scattering, which make them a promising class of materials for the construction of superhydrophobic and superhydrophilic surfaces.12–17 They can also be used to construct other materials with specific characteristics such as resistance to abrasion, UV-shielding, reactivity, and catalytic, optical, and electrical properties.18–20 Generally, raspberry-like colloidal particles are synthesized through the combination of the two kinds of particles by three different pathways: (i) both large core particles and small corona particles are formed or present in advance, then the smaller corona particles are anchored onto the larger core particles based on the interactions between the binary particles, including covalent bonding, hydrogen bonding, acid-base or electrostatic interactions.21–24 (ii) The larger core particles are formed or present in advance, then the smaller corona particles are formed in situ on the larger core particles by seed emulsion polymerization.25–28 (iii) Smaller corona particles are first formed, then larger core particles are synthesized in situ by Pickering emulsion polymerization.29–31 Clearly, all these strategies involve a multiple-step process, while synthesis of raspberry-like colloidal particles with both smaller corona particles and larger core particles formed in situ has rarely been reported to the best of our knowledge.7–34

Herein, we report a simple and versatile one-step synthesis of monodisperse raspberry-like polymer colloidal particles using soap-free emulsion polymerization of styrene (S), 3-(trimethoxysilyl)propyl methacrylate (MPS) and acrylic acid (AA). In this method, when S, MPS and AA were mixed with water and stirred at a certain temperature for a period of time, large amounts of raspberry-like P(S–MPS–AA) particles with uniform shapes and sizes were produced. Both the larger core particles and the smaller corona particles of the core surfaces were formed in situ without any sorting processes. The effects of the initial amounts of MPS and AA and the duration of MPS pre-hydrolysis on the morphology of the colloidal particles have been investigated. The formation mechanism of monodisperse raspberry-like P(S–MPS–AA) colloidal particles is believed to involve the second nucleation induced by the MPS-enriched segments on the surfaces.

Experimental section

Materials
Monomer styrene (S, 99%) and acrylic acid (AA, 98%) were purchased from Sinopharm Chemical Reagent Corp (China) and used as received. Acetic acid (HAc, 99.7%), 3-(trimethoxysilyl)propyl methacrylate (MPS, 97%) and initiator ammonium persulfate (APS, 98%) were purchased from Aladdin Chemical Reagent Corp. and used as received. Deionized water was used for all polymerization and treatment processes.

Synthesis of monodisperse raspberry-like polymer colloidal particles
The monodisperse raspberry-like colloidal particles were synthesized by a one-step emulsifier-free emulsion
polymerization. Typically, 2.0 g of S, 0.04 g of MPS, 0.30 g of AA, and 100 g of H_{2}O were first mixed in a 250 mL four-neck reaction flask equipped with a mechanical stirrer, a condenser, and a gas inlet and then stirred at 70 °C at 300 rpm for 5 h for the pre-hydrolysis and condensation of MPS. After that, the system was degassed by bubbling nitrogen for 30 min. Then the initiator APS solution (0.004 g mL^{-1}, 10 mL) was added and stirred at the same temperature for another 8 h to produce colloidal particles. The detailed experimental conditions and results are summarized in Table 1.

When acidic AA was replaced by non-polymeric acidic HAc and when the S monomer was homopolymerized for different times, the pre-hydrolyzed MPS was charged. Accordingly, colloidal particles with various structures were synthesized based on using the typical experimental recipe and conditions given above.

**Characterization**

TEM images were obtained on a Hitachi H-800 transmission electron microscope operating at 75 kV. SEM images were obtained using a Philips XL 30 field emission microscope at an accelerating voltage of 20 kV. Dynamic light scattering (DLS) measurements were carried out on the diluted reaction solutions to produce particles of average diameter and size distribution using a Nano-ZS90 (Malvern). The zeta-potential of the sample was obtained using a zeta potential analyzer (Zetaplus, Brookhaven Instruments Corp.). FTIR spectra were scanned on a Nicolet Nexus 470 FTIR spectrometer with powder-pressed KBr pellets. X-ray photoelectron spectroscopy (XPS) spectra were evaluated on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV) as the source of excitation at a wattage of 250 W and a voltage of 14 kV. The samples for FTIR and XPS were centrifuged and rinsed three times with deionized water and dried in an oven at 50 °C for 12 h before analysis. Scanning TEM (STEM) and element line scanning by X-ray energy dispersive spectroscopy (EDS) analyses were carried out with a JEOL-2100 F transmission electron microscope.

**Results and discussion**

**Synthesis and structure of P(S–MPS–AA) colloidal particles**

Typical SEM and TEM images and size distribution of the colloidal particles are shown in Fig. 1. All the as-obtained P(S–MPS–AA) colloidal particles clearly exhibit raspberry-like structures with a mean diameter of ca. 160 nm (by TEM). DLS measurement further indicated that the raspberry-like particles were monodisperse with a very narrow polydisperse index of 0.005 and an average diameter of 197 nm, which is a little larger than that indicated by TEM imaging (Table 1). This is reasonable because TEM measurements should be sensitive only to the electron-dense polymer particles, whereas DLS...
measurements are sensitive to the size of the whole composite nanoparticles containing the hydrated layer on the surfaces of the nanoparticles in aqueous medium. The raspberry-like polymer particles showed a zeta-potential of $-18.9$ mV, indicating that they have negative charges on the surfaces and good dispersion stability in aqueous medium (Table 1).

The typical FTIR spectra of the as-obtained $\text{P(S–AA–MPS)}$ and $\text{P(S–AA)}$ colloidal particles are indicated in Fig. 2. They showed absorption bands at $3025, 1601, 1493, 1452, 757$, and $699$ cm$^{-1}$, consistent with the characteristic peaks of the aromatic ring. The bands at $2923$ and $2849$ cm$^{-1}$ were attributed to the stretching absorption of methylene and methenyl groups, and the characteristic band at $1705$ cm$^{-1}$ was attributed to the stretching absorption of C=O bonds. The band at $1637$ cm$^{-1}$ assigned to the C=C bond had disappeared, indicating that the compounds with C=C bonds had already been copolymerized. In addition to absorptions similar to those of $\text{P(S–AA)}$ particles, the $\text{P(S–MPS–AA)}$ particles displayed another important absorption peak at $1109$ cm$^{-1}$, which was attributed to the stretching vibration of Si–O–Si bonds, further indicating that MPS had copolymerized with S and AA monomers by free radical polymerization and produced hydrolysis and condensation reactions. The typical sample was scanned using XPS (the scans are not present here), and showed $17.9$ atomic % of O and $1.50$ atomic % of Si on its surface, which was much higher than the theoretical values ($6.79$ atomic % of O and $0.42$ atomic % of Si) in $\text{P(S–MPS–AA)}$ assuming that the monomers have been completely polymerized. This suggested that the –COOH groups and the MPS segments are mainly distributed on the surfaces of the particles. The typical STEM and element line scanning by EDS analysis of the as-obtained $\text{P(S–AA–MPS)}$ colloidal particles, as indicated in Fig. 3, showed the Si elements at points A and B were relatively higher than those in other areas. Because the points A and B were corresponding to the highest points at the surface of the particles, namely the bugles on the surfaces of the raspberry-like particles, this result further indicated that the MPS segments were mainly distributed on the bugles of the raspberry-like particles.

**Effects of the initial amount of MPS**

Fig. 4 shows TEM and SEM images of the as-obtained $\text{P(S–MPS–AA)}$ colloidal particles as a function of the initial amount of MPS.
MPS. Without MPS monomer, the as-obtained particles had wrinkled surfaces with mean diameters of 130 nm (Fig. 4a). Such small roughness might be from the deposition of some oligomers to the surfaces of the seed particles, and no polymerization further occurred due to the depletion of the monomer. When 0.04 g of MPS was used, some lobes of about 20 nm in size were anchored on the surfaces of the core particles, forming a raspberry-like structure. The average size of the colloidal particles increased to 160 nm (Fig. 4b). When the amount of MPS was increased to 0.09 g, raspberry-like particles could also be obtained, and the mean diameter increased to 175 nm (Fig. 4c). However, when MPS was increased to 0.13 g, the latex became unstable, irregular, and partially aggregated latex particles with a mean size of around 265 nm were produced (Fig. 4d). These results indicate that MPS plays a vital role in the formation of raspberry-like colloidal particles. MPS was pre-hydrolyzed for 5 h with 0.30 g of AA (in this case, the pH value of the system was around 3), so the (CH₃O)₃–Si groups of MPS molecules hydrolyzed into metastable Si–OH groups, and some of them self-condensed further into low-molecular-weight linear and cyclic oligomers via the sol–gel process. These oligomers were more hydrophilic than MPS monomers and mainly distributed among the water phase and monomer droplets. Once the initiator APS solution was added into the system, these oligomers could undergo homopolymerization or copolymerization with AA and S monomers. The hydrophilic AA and oligomers were mainly distributed on the surfaces of the particles because the final morphology of the particles should minimize Gibb’s interfacial free energy of the system based on the thermodynamic criterion. And these MPS oligomers on the surfaces of the particles would further undergo hydrolysis and condensation reactions due to their contact with water to produce MPS-enriched segments on the surfaces of the particles. These MPS-enriched segments were unevenly distributed on the surfaces and also changed the distribution of –COOH groups on the surfaces. The more MPS used, the more MPS oligomers would distribute on the surfaces of the particles.

However, if too much MPS was used, too many free hydrophilic Si–OH groups would form at the surface of the particles, promoting interactions between adjacent latex particles, facilitating the formation of hydrogen bonds and chemical cross-linking reactions, producing unstable colloids.

**Effects of the initial amount of AA**

Fig. 5 shows the influence of the amount of AA on the morphology of the as-obtained colloidal particles. When no AA monomer was used, few lobes were observed on the surfaces of the colloidal particles (Fig. 5a). This is because the pre-hydrolysis and condensation reactions of MPS molecules are very slow without acidic catalysis. The MPS molecules were mainly involved in copolymerization with styrene inside the particles so that their contact with water was greatly hindered, and few hydrophilic species of the pre-hydrolyzed MPS would distribute on the surfaces of colloidal particles to come in contact with the water for further hydrolysis and condensation reactions. When AA was used in the pre-hydrolysis process of MPS, raspberry-like particles were produced easily. Larger amounts of AA were associated with bigger and randomly distributed bulges on the surfaces of the particles (Fig. 5b–d). Moreover, the average diameters of the colloidal particles were found to decrease slightly when larger amounts of AA were used. AA molecules have several functions. They act as catalysts and supply protons to attack the MPS for hydrolysis and condensation reactions, but hydrophilic molecules are usually enriched on the surfaces of the latex particles, and these act as emulsifiers, stabilizing the growing colloidal particles in conventional emulsion polymerization. In this way, the larger the AA amount, the smaller the mean diameters of the resulting colloidal particles.

**Effects of the duration of MPS pre-hydrolysis**

The morphologies of the as-obtained colloidal particles produced using various MPS pre-hydrolysis times are shown in Fig. 6. All the P(S–AA–MPS) colloidal particles unveil

![Fig. 4](image1.png) TEM and SEM images of the as-obtained colloidal particles with different amounts of MPS: (a) 0, (b) 0.04, (c) 0.09, and (d) 0.13 g.

![Fig. 5](image2.png) TEM and SEM images of the as-obtained colloidal particles with different amounts of AA: (a) 0, (b) 0.15, (c) 0.3, and (d) 0.6 g.
raspberry-like structures even for the MPS without pre-hydrolysis. However, as the duration of pre-hydrolysis was increased, the surface roughness of the colloidal particles also increased and the mean diameter of the particles decreased. MPS is only slightly soluble, but it becomes readily soluble in water when it is hydrolyzed and condensed into low-molecular-weight linear or cyclic species with Si–OH groups. These hydrophilic species are prone to distribute on the surfaces of the particles, and the longer the pre-hydrolysis, the more hydrophilic species of pre-hydrolyzed MPS are produced and migrate to the surfaces of the particles.

Formation of the raspberry-like colloidal particles
To understand the mechanism by which these raspberry-like colloidal particles form, the evolutorial morphologies vs. reaction time of the colloidal particles were observed online with TEM. As shown in Fig. 7, when the polymerization lasted 15 min, the particles were spherical with a mean diameter of 65 nm (Fig. 7a). They may have been composed of a hydrophobic PS-enriched core and a hydrophilic PAA-enriched shell. When polymerization lasted 30 and 45 min, the particles rapidly grew in size from 100 nm (Fig. 7b) to 130 nm (Fig. 7c). When the reaction lasted 60 min, some small bulges emerged on the particle surfaces, and mean diameter increased to 145 nm (Fig. 7d). As the polymerization reaction continued, more bulges were observed on the latex surfaces, showing a slight increase in size to 150 nm (Fig. 7e–g). After 8 h of polymerization, the mean size increased to the final value of 160 nm (Fig. 7h). These bulges (or nanoparticles) were only observed on the surfaces of colloidal particles, and no free nanoparticles were found in the aqueous phase. This suggests that the raspberry-like particles are formed by polymerization reaction rather than by coagulation among particles.

In a control experiment, the non-polymeric acid monomer HAc was used as the catalyst to replace the polymeric acid monomer AA at other equal parameters. Raspberry-like colloidal particles, despite irregularity, were still produced, as shown in Fig. 8. This suggests that MPS plays a vital role in the formation of raspberry-like colloidal particles, while polymeric AA can improve the monodispersity and the stability of the growing colloidal particles.

The morphologies of the colloidal particles synthesized by changing the feeding sequences of S, MPS, and AA are shown in Fig. 9. When PS colloids were used as the seed particles, the early charges of AA and MPS (e.g., after polymerization of styrene for 0.5 or 1 h, Fig. 9a and b) produced particles with much rougher surfaces than the late charge (e.g., after polymerization of styrene for 2 h, Fig. 9c). This was because more residual S monomers participated in the copolymerization reaction with AA and MPS in the early charge mode, producing hydrophobic PS segments with higher molecular weights. These segments pushed the production of more hydrophilic species derived from the pre-hydrolyzed MPS and caused them to move...
towards the surfaces of the particles. Obviously, the PS seeds with higher weight and density can also facilitate the separation of the hydrophilic species due to greater immiscibility between PS and the hydrophilic species from the pre-hydrolyzed MPS.\textsuperscript{61,62}

Based on these results, we could propose a possible mechanism of the formation of the raspberry-like P(S–AA–MPS) colloidal particles, as shown in Scheme 1. In acidic environments, MPS molecules underwent hydrolysis and condensation reactions, producing hydrophilic low-molecular-weight linear or even cyclical oligomers with many Si–OH groups.\textsuperscript{47} When the water-soluble initiator APS decomposed to produce free radicals, it initiated the polymerization of the free S, AA monomers, and the hydrophilic species derived from the pre-hydrolyzed MPS in the aqueous phase. These propagating chains then formed primary latex particles stabilized by hydrophilic AA and small amounts of hydrophilic species from the pre-hydrolyzed MPS molecules. As the polymerization reaction proceeded, more S molecules entered the latex particles and formed polymer chains. Because these hydrophilic species derived from the pre-hydrolyzed MPS were hydrophilic and immiscible with PS segments, more MPS-enriched segments were immigrating towards the surfaces of the polymer particles as more S molecules involved in polymerization inside the latex particles. These MPS-enriched segments, on the one hand, underwent further sol–gel reaction by themselves and/or through them with MPS molecules from the oil droplets due to their contact with water by acidic catalysis. On the other hand, these MPS-enriched segments contained C=C bonds and thus also captured some S molecules and MPS molecules from oil droplets by free radical polymerization. Both kinds of reactions caused the MPS-enriched segments to act as the second nucleating domains around the surfaces of colloidal particles.\textsuperscript{54,63} Because the transfer of MPS-enriched segments towards the surfaces of particles was driven by phase separation, these segments could not form uniform shells but rather corona around the particle surfaces after acting as the second nucleating domains and reacting by themselves or with other monomers.

**Conclusion**

In the present study, monodisperse raspberry-like polymer colloidal particles were successfully synthesized using a one-step soap-free emulsion polymerization of S, MPS, and AA. The sizes of the colloidal particles and the regularity of the bulges on the surfaces can be easily controlled by adjusting the amount of MPS, AA and the duration of MPS pre-hydrolysis. The mechanism by which the raspberry-like structures form could be elucidated by the further reactions of the hydrophilic species derived from the acid-catalyzed pre-hydrolyzed MPS molecules on the core surfaces. Any parameters that might affect the

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**Fig. 8** SEM image of the as-obtained colloidal particles with non-polymeric acid HAc.

**Fig. 9** TEM images of the as-obtained colloidal particles obtained by changing the feeding sequences of three monomers: PS seed particles: (a) 30, (b) 60, and (c) 120 min. The scale bar is 50 nm.

**Scheme 1** Schematic illustration of raspberry-like P(S–MPS–AA) colloidal particles.
hydrophilicity of the MPS-enriched species and further their enrichment on the surfaces of colloidal particles, such as higher levels of MPS and AA and longer pre-hydrolysis, would favor the formation of raspberry-like structures. These colloidal particles, which have controllable raspberry-like structures, are good candidates for the construction of functional colloidal films and complex colloidal architectures.

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