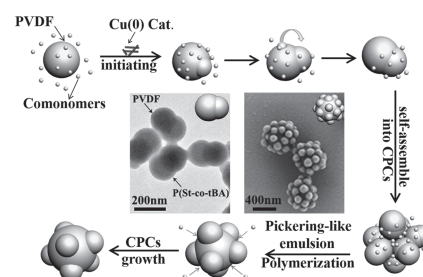


Self-Assembled Colloidal Particle Clusters from In Situ Pickering-Like Emulsion Polymerization via Single Electron Transfer Mechanism

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A simple route is reported to synthesize colloidal particle clusters (CPCs) from self-assembly of in situ poly(vinylidene fluoride)/poly(styrene-*co*-*tert*-butyl acrylate) [PVDF/P(St-*co*-*t*BA)] Janus particles through one-pot seeded emulsion single electron transfer radical polymerization. In the in situ Pickering-like emulsion polymerization, the *t*BA/St/PVDF feed ratio and polymerization temperature are important for the formation of well-defined CPCs. When the *t*BA/St/PVDF feed ratio is 0.75 g/2.5 g/0.5 g and the reaction temperature is 35 °C, relatively uniform raspberry-like CPCs are obtained. The hydrophobicity of the P(St-*co*-*t*BA) domains and the affinity of PVDF to the aqueous environment are considered to be the driving force for the self-assembly of the in situ formed PVDF/P(St-*co*-*t*BA) Janus particles. The resultant raspberry-like CPCs with PVDF particles protruding outward may be promising for superhydrophobic smart coatings.



1. Introduction

Anisotropic particles with various shapes or different chemical compositions have aroused great interest because of their promising applications in compatibilizers,^[1] building blocks for self-assembly,^[2,3] smart coatings,^[4] and colloid surfactants.^[5] Many methods have been developed to prepare anisotropic particles, including selective surface modification,^[6] surface nucleation,^[7]

seeded emulsion polymerization,^[8] controlled phase separation,^[9] and Pickering emulsion polymerization.^[10] Among these, seeded emulsion polymerization is efficient and potentially scalable for the preparation of anisotropic particles. A variety of nonspherical particles have been acquired using this method, such as snowman-like (or Janus),^[11] dumbbell-like,^[12] raspberry-like,^[13] and acorn-shaped particles.^[14]

One application for nonspherical particles, especially for Janus particles, is the solid surfactants for Pickering emulsion.^[5] As we know, stabilizing the emulsion system is important for emulsion polymerization. Traditional emulsion polymerization, which is stabilized by molecular surfactants, is inclined to suffer destabilization via latex coalescence and Ostwald ripening.^[15] In the past decade, Pickering emulsions stabilized by solid particles instead of molecular surfactants have shown superior emulsion stability. A wide range of inorganic and organic particles, such as clay, silica particles, and block copolymer micelles, no matter isotropic or Janus, are

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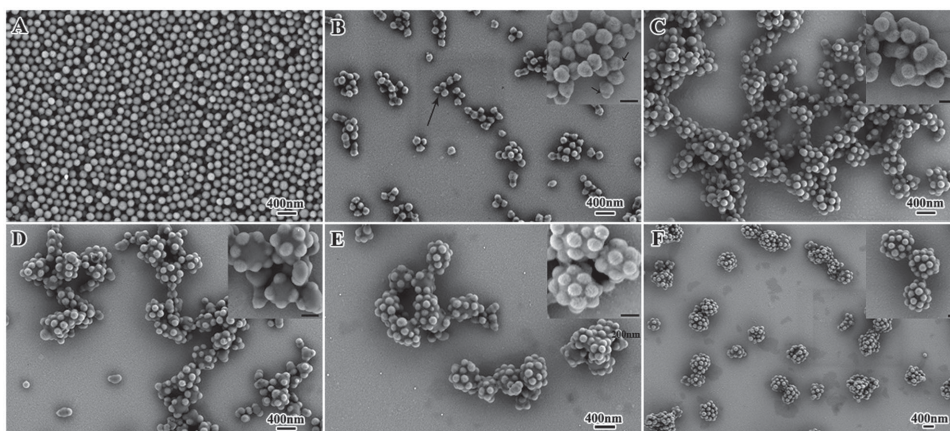


Figure 1. FE-SEM micrographs of PVDF/P(St-co-tBA) complex colloidal particles obtained at the polymerization time of A) 0, B) 1, C) 2, D) 3, E) 4, and F) 5 h when the tBA/St/PVDF feed ratio is 0.75 g/2.5 g/0.5 g. The polymerization temperature is 35 °C. The insets show SEM image at a higher magnification (scale bars are 200 nm).

capable of stabilizing Pickering emulsions.^[16,17] However, because of their intrinsic anisotropy, Janus particles offer more advantages in the stabilization of emulsions than isotropic particles, as proved by many theoretical, simulation, and experimental studies. Krausch and co-workers reported that Janus particles showed a significant reduction of the oil/water interfacial tension compared to similar isotropic particles.^[18] Aveyard found that thermodynamically stable emulsions can be generated using Janus particles as the solid surfactant based on free energy calculations.^[19] The pioneer work by Müller and co-workers demonstrated that Janus particles (≈ 20 nm in size) from block copolymers can be used as surfactants for Pickering emulsion polymerization.^[20]

As a simple building block, Janus particles have shown profound promise in constructing complex hierarchical structures. Nie and co-workers successfully prepared hollow and tube-like clusters via self-assembly of amphiphilic Janus particles in selective solvents.^[21] Kraft et al. found that patchy particles with surface roughness spontaneously organized into clusters at high depletant concentrations.^[22] Peng et al. acquired colloidal particle clusters (CPCs) using dumbbell-shaped particles, and a simple computer simulation correctly predicted the structures formed.^[23]

Recently, we reported facile and relatively large-scale syntheses of poly(vinylidene fluoride) (PVDF)/polystyrene (PS) Janus and nonspherical particles using seeded emulsion single electron transfer radical polymerization (SET-RP).^[24] Compared to other living radical polymerization methods, such as atom transfer radical polymerization, the SET-RP method presents advantages, e.g., mild reaction condition, colorless polymer product, and easy removal of copper catalyst after reaction.^[25–27] In this work, a comonomer, *tert*-butyl acrylate (tBA), is added in the seeded emulsion SET-RP of styrene (St) in the presence

of 180 nm PVDF latex particles. Intriguingly, under appropriate conditions, PVDF/P(St-co-tBA) Janus particles, which are formed in situ in the early stage polymerization, can self-assemble into the Pickering-like emulsion. Further polymerization eventually leads to raspberry-like CPCs with P(St-co-tBA) as the core and PVDF particles protruding outward. It is the first report that one-pot seeded emulsion polymerization enables the formation of Janus particles and their self-assembly into Pickering-like emulsion to form hierarchical CPCs.

2. Results and Discussion

To illustrate the formation process of PVDF/P(St-co-tBA) complex colloidal particles, morphology evolution of the colloidal particles during polymerization was first studied by field-emission scanning electron microscopy (FE-SEM) for sample aliquots at different time intervals. Here, we fixed the tBA/St/PVDF feed ratios as 0.75 g/2.5 g/0.5 g, and the total polymerization time was 5 h. The reaction temperature was 35 °C.

At the beginning of polymerization, regular spherical PVDF seed particles (average diameter ≈ 180 nm) were seen (Figure 1A). At 1 h (Figure 1B), complex colloidal particles were seen. First, individual PVDF particles with one or two tiny P(St-co-tBA) protrusions were observed, implying the initial formation of Janus particles. This could be attributed to the surface nucleation of the comonomer-swollen P(St-co-tBA) domains on PVDF.^[7] Second, several particle clusters with two and three PVDF seeds surrounding one P(St-co-tBA) domain were noticed; see the arrow in Figure 1B. Third, larger CPCs with many PVDF bulges were present. From these observations, it was inferred that the in situ PVDF/P(St-co-tBA) (monomer swollen) Janus particles, which behaved like particle

surfactants, self-assembled together in the aqueous media and formed raspberry-like CPCs for subsequent Pickering-like emulsion polymerization.

When the reaction time reached 2 h (Figure 1C), the average size of the CPCs became larger (≈ 426 nm for the average size along the particle long axes) as a result of continued polymerization within the inner monomer-swollen P(St-co-tBA) cores. Judging from the size and surface roughness (i.e., from lamellar PVDF crystals), the protruding bulbs should be PVDF seeds (see Figure S1 in the Supporting Information). After polymerization for 3–5 h (Figure 1D–F), the final average size of the PVDF/P(St-co-tBA) CPCs reached about 670 nm.

To confirm the microstructures in Figure 1, the morphology development of PVDF/P(St-co-tBA) complex colloidal particles was also studied by transmission electron microscopy (TEM), as shown in Figure 2. At 1 h (Figure 2B), newly formed PVDF/P(St-co-tBA) Janus particles were seen with the PVDF particles showing a darker contrast due to their higher density. At 2 h (Figure 2C), these Janus particles self-assembled into CPCs for the subsequent Pickering-like emulsion polymerization. As the polymerization continued, the raspberry-like CPCs became larger due to the gradual growth of the P(St-co-tBA) cores (Figure 2D–F).

The particle size and size distribution of the complex colloidal particles at 3 h were determined by dynamic light scattering, and the result is shown in the inset of Figure 2D. The number-average particle size was ≈ 577 nm and the polydispersity index (PDI) was 0.317. It is interesting to note that the histogram showed a narrow unimodal peak, but the PDI estimated seemed to be rela-

tively high. This could possibly be attributed to the irregular shape of the CPCs.

In our previous study,^[24] PVDF/PS composite latex particles with controllable morphologies were prepared using the same SET-RP method and similar reaction conditions. Snowman-like, raspberry-like, and popcorn-like particles were obtained as a result of St polymerization on the surface of PVDF seeds. However, CPCs from the self-assembly of the PVDF/PS Janus particles were never observed. We speculate that the tBA comonomer in the seeded emulsion polymerization provides opportunity for the self-assembly of the Janus particles into raspberry-like CPCs with PVDF seeds protruding outward. In the following work, we further studied the influence of tBA/St feed ratio on the self-assembled morphology.

In this experiment, we fixed the St/PVDF ratio (2.5 g/0.5 g), reaction time (5 h), and polymerization temperature (35 °C), but varied the tBA/St feed ratio at 0.25 g/2.5 g, 0.75 g/2.5 g, and 1.75 g/2.5 g, respectively. The corresponding FE-SEM and TEM images of the as-synthesized complex colloidal particles are shown in Figure 3. When the tBA/St feed ratio was 0.25 g/2.5 g, the resulting morphology showed a small size (average diameter ≈ 300 nm), and many complex colloidal particles had four PVDF seeds protruding outward with a tetrahedron shape (Figure 3A,D). It is likely that there is not enough tBA to induce the self-assembly with large aggregation numbers. When the tBA/St feed ratio increased to 0.75 g/2.5 g, relatively uniform complex colloidal particles with many PVDF seeds protruding outward were seen in Figure 3B,E. Further increasing the tBA/St feed ratio to 1.75 g/2.5 g (Figure 3C,F), two types

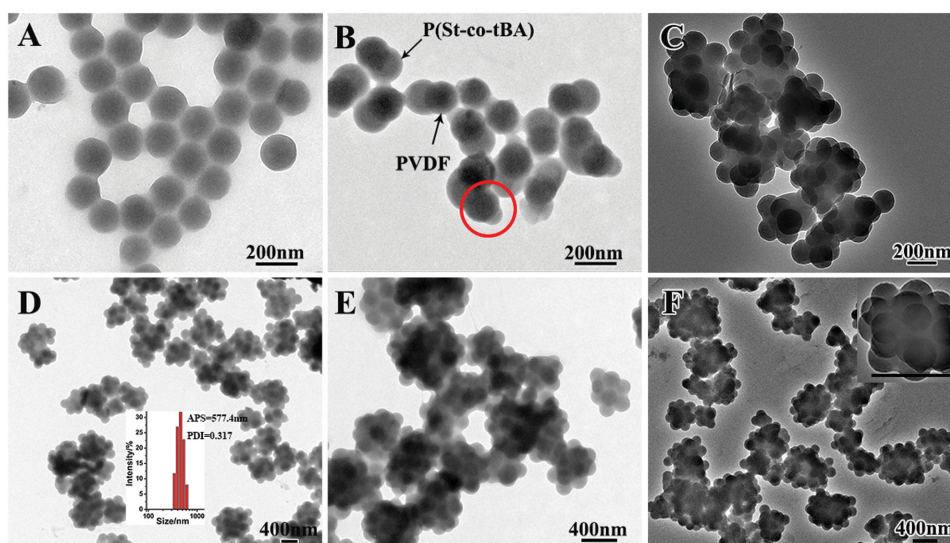


Figure 2. TEM micrographs of PVDF/P(St-co-tBA) complex colloidal particles obtained at the polymerization time of A) 0, B) 1, C) 2, D) 3, E) 4, and F) 5 h when the tBA/St/PVDF feed ratio is 0.75 g/2.5 g/0.5 g. The polymerization temperature is 35 °C. The inset in (D) shows particle size and size distribution of PVDF/P(St-co-tBA) complex colloidal particles obtained at 3 h. The inset in (F) is a TEM image at a higher magnification (scale bar is 400 nm).

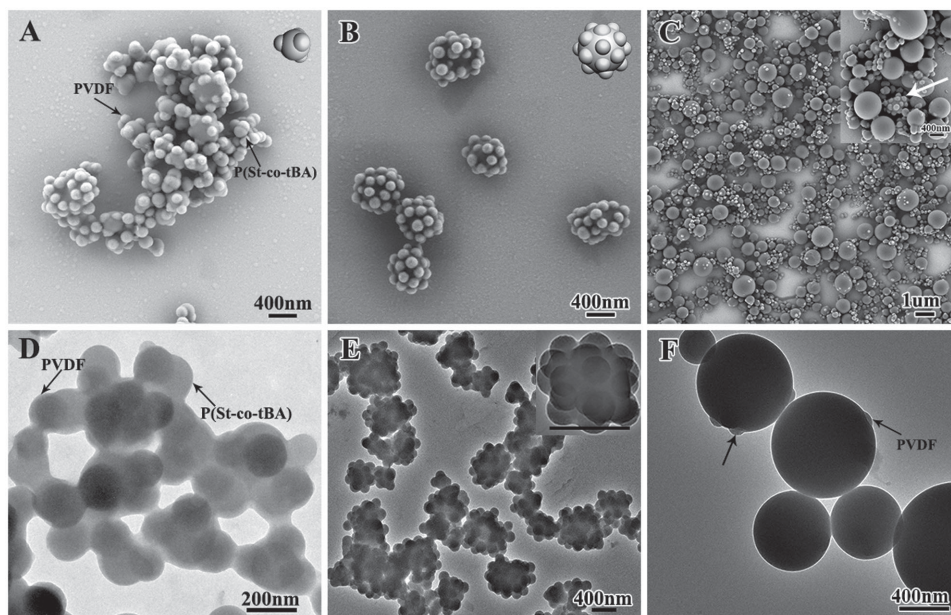


Figure 3. A,B,C) FE-SEM and D,E,F) TEM micrographs of the PVDF/P(St-co-tBA) complex colloidal particles synthesized at different tBA/St feed ratios: (A,D) 0.25 g/2.5 g, (B,E) 0.75 g/2.5 g, and (C,F) 1.75 g/2.5 g, when the St/PVDF feed ratio is fixed at 2.5 g/0.5 g. The polymerization temperature is 35 °C and the polymerization time is 5 h. The insets in (C,E) are the corresponding images at a higher magnification (scale bar is 400 nm).

of particles coexisted. One was the CPCs with smaller size (see the arrow in the inset of Figure 3C) and the other was larger spheres with a few PVDF protrusions. It is likely that excess tBA caused significant swelling and growth of the P(St-co-tBA) domains. Therefore, the optimum tBA/St feed ratio is determined to be around 0.75 g/2.5 g. Furthermore, the carbon, oxygen, and fluorine contents on the surface of the PVDF/P(St-co-tBA) complex colloidal particles at different tBA/St feed ratios were studied by X-ray photoelectron spectroscopy. The analysis results indicated that the higher the tBA/St feed ratio, the higher oxygen content on the sample surface (see Figure S2 in the Supporting Information). This is consistent with the above observations in Figure 3.

Although we found the optimum tBA/St feed ratio, it was still not clear why tBA was influential for the formation of the CPCs. Consequently, the seeded emulsion polymerization was carried out at different temperatures (25, 35, and 45 °C) by fixing the reaction time (5 h) and the tBA/St/PVDF feed ratios (0.75 g/2.5 g/0.5 g). When the temperature was 25 °C, grape-like colloidal aggregates with many PVDF seeds protruding outward were seen in the FE-SEM and TEM micrographs (Figure 4A,D). Raising the polymerization temperature to 35 °C, relatively uniform raspberry-like complex colloidal particles were obtained (Figure 4B,E). Further increasing the temperature to 45 °C, only snowman-like Janus particles were observed, and no complex colloidal particles or colloidal aggregates could be seen (Figure 4C,F).

On the basis of the above experimental results, we propose the formation mechanism of raspberry-like PVDF/monomer-swollen P(St-co-tBA) CPCs, as shown in Figure 5. During the initial comonomer swelling stage, the PVDF seed is stabilized by the anchored surfactants on its surface. The comonomers cannot swell the PVDF seed because St and tBA are highly immiscible with PVDF. When the Cu(0) wires are added into the system, the initiator [methyl 2-bromopropionate] in the swollen comonomer layer can receive the outer shell electron provided by the catalyst Cu(0) to produce primary free radicals, which then initiate the copolymerization of St and tBA. As a result of dewetting, the polymerized P(St-co-tBA) nucleates into a bulge on the surface of the PVDF seed. As the polymerization continues, snowman-like Janus PVDF/P(St-co-tBA) (monomer-swollen) particles form.^[7,24,28] The surface energies for water, PS, and PtBA are 70, 40.7, and 31.2 mN m⁻¹, respectively,^[29] indicating that PtBA is more hydrophobic than PS. Introduction of tBA units into PS makes the copolymer more hydrophobic. On the other hand, PVDF is a polar polymer and thus has a better affinity to the aqueous environment than the monomer-swollen P(St-co-tBA). As a result, the Janus PVDF/monomer-swollen P(St-co-tBA) particles (swollen with comonomers) tend to self-assemble into CPCs in the aqueous media with monomer-swollen P(St-co-tBA) as the core and PVDF seeds protruding outward, forming Pickering-like emulsion. Upon continued swelling with comonomers, the monomer-swollen P(St-

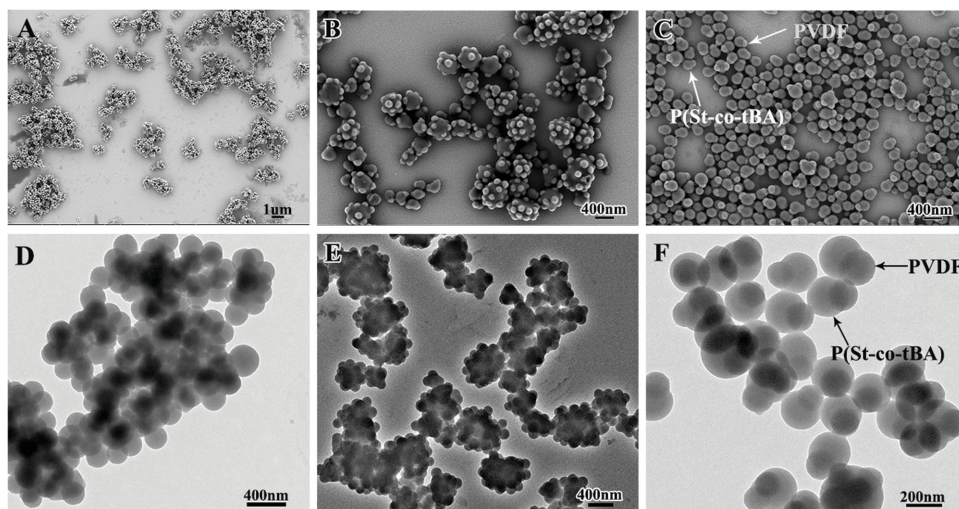


Figure 4. A,B,C) FE-SEM and D,E,F) TEM micrographs of the PVDF/P(St-co-tBA) complex colloidal particles obtained at different polymerization temperatures: (A,D) 25 °C, (B,E) 35 °C, and (C,F) 45 °C, when the tBA/St/PVDF feed ratios are 0.75 g/2.5 g/0.5 g. The polymerization time is 5 h.

co-tBA) cores gradually grow larger, and finally form raspberry-like CPCs.

Using this proposed mechanism, we can explain our experimental observations above. If there is no tBA in the monomer feed, the PS domains in the Janus particles are not hydrophobic enough to induce the self-assembly in the aqueous media. This is observed in our recent report.^[24] At a low tBA/St feed ratio (0.25 g/2.5 g), the aggregation strength of the monomer-swollen P(St-co-tBA) is so weak that only small clusters can form (see the tetrahedral particles in Figure 3A). When the tBA/St feed ratio is too high (1.75 g/2.5 g), the aggregation and monomer-swelling become so much that large spherical

particles with only a few PVDF seeds are observed (see Figure 3C). On the other hand, the self-assembly/clustering of the PVDF/monomer-swollen P(St-co-tBA) Janus particles must be assisted by the swelling of comonomers. At low temperatures (e.g., 25 °C), the polymerization rate should be low, and the monomer-swollen P(St-co-tBA) domains have enough time to assemble or aggregate together, forming grape-like aggregates. At high temperatures (e.g., 45 °C), the polymerization rate is so high that there may not be enough comonomer swelling in the P(St-co-tBA) bulge throughout the polymerization process. Consequently, the P(St-co-tBA) domains can never weld together, eventually leading to isolated

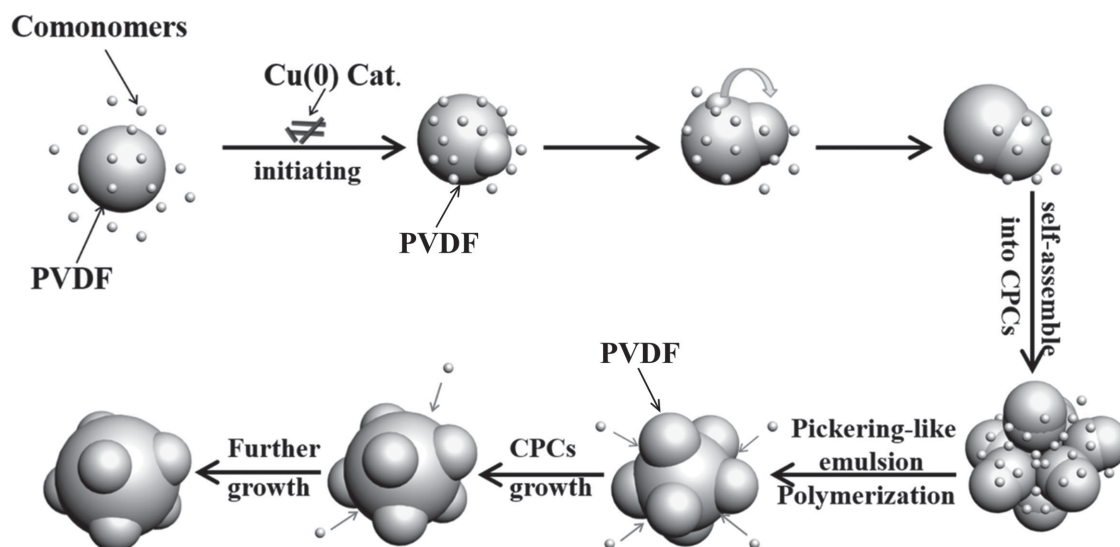


Figure 5. Schematic morphology evolution of as-prepared PVDF/P(St-co-tBA) complex colloidal particles triggered by SET-RP via surfactant-free seeded emulsion copolymerization. PVDF seeds are yellow, comonomers of tBA and St and monomer-swollen P(St-co-tBA) domains are gray.

Janus particles after polymerization. Therefore, there is a delicate balance between the polymerization rate and the swelling of comonomers in the P(St-co-tBA) domains for the self-assembly of Janus particles throughout the Pickering-like emulsion polymerization.

3. Conclusions

In conclusion, adding the tBA comonomer in the one-pot seeded emulsion SET-RP of St in the presence of 180 nm PVDF seeds enabled self-assembly or clustering of the in situ formed PVDF/P(St-co-tBA) Janus particles in the aqueous media. After Pickering-like emulsion polymerization, relatively uniform raspberry-like CPCs (≈ 600 nm) were obtained with PVDF seeds protruding outward. The tBA/St/PVDF feed ratios and polymerization temperature played an important role in achieving relatively well-defined CPCs. On the basis of the experimental results, a possible mechanism was proposed, where the hydrophobicity of the monomer-swollen P(St-co-tBA) domains, the swelling by the tBA/St comonomers, and the polymerization rate need to reach a delicate balance to ensure the self-assembly/clustering and the subsequent Pickering-like emulsion polymerization. These raspberry-like CPCs may find potential applications in superhydrophobic smart coatings.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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