I&EC research
Industrial & Engineering Chemistry Research

Article

Cite This: Ind. Eng. Chem. Res. 2019, 58, 20961−20968

pubs.acs.org/IECR

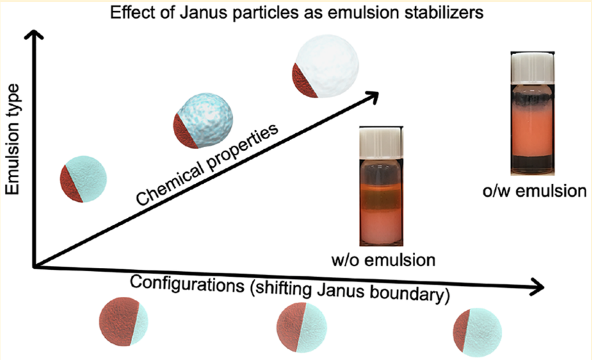
Janus Particles with Varying Configurations for Emulsion Stabilization

Yang Lan, Je Choi, Haoyang Li, Yankai Jia, Renjing Huang, Kathleen J. Stebe,* and Daeyeon Lee*

Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia 19104, United States

Supporting Information

ABSTRACT: Analogous to molecular surfactants, amphiphilic Janus particles can function as surface active agents to stabilize emulsions. For molecular surfactants, the shape and amphiphilicity, described by packing parameters and hydrophilic−lipophilic balance (HLB), respectively, determine the type of emulsions that are produced. However, it remains unclear which features of Janus particles determine the type of emulsion that can be stabilized by these particles. In this study, a homologous series of amphiphilic Janus particles with shifting Janus boundaries and tunable chemical properties are synthesized via seeded emulsion polymerization. We systematically study the effect of the relative size of the hydrophilic domain to the total particle (configuration) and chemical nature of Janus particles on their emulsification properties. The concept of the Janus structure parameter (JSP) is introduced to describe the configuration of Janus particles. The emulsification results show that the configuration of Janus particles has a limited effect on the emulsion type when the contrast in the water affinity of the two domains is weak. In contrast, the configurations of Janus particles determines the emulsion type when there is a significant difference in water affinity between the two regions of Janus particles. In this case, the threshold of JSP value for emulsion inversion is found to be 0.48, which indicates that Janus particles with larger hydrophobic domains prefer to stabilize water-in-oil (w/o) emulsion and those with larger hydrophilic domains stabilize oil-in-water o/w emulsion. Our findings on the correlations between the configurations of Janus particles and the type of emulsion that are stabilized are crucial for the design of Janus particles for the stabilization of multiphasic fluid mixtures and their applications.



■ INTRODUCTION

Janus particles are anisotropic colloids that have two regions with distinct physical properties.[1−3] Structurally analogous to molecular surfactants, amphiphilic Janus particles have been explored as solid amphiphiles to stabilize emulsion droplets.[1−14] There are, however, important differences between surfactants and Janus particles. In general, emulsions stabilized with molecular surfactants are kinetically stable except for a few special cases.[15] Recent studies based on free energy calculations have shown that Janus particles can generate thermodynamically stable emulsions due to substantially large energy associated with interfacial attachment of Janus particles from the bulk fluid phases.[16,17] In addition, the compartmentalized structure of Janus particles can imbue emulsions with additional functionalities such as stimuli-responsiveness[18−21] and catalytic activity.[22] It is thus of great scientific and industrial interest to develop scalable synthesis of amphiphilic Janus particles with precise control over morphology, amphiphilicity and functionality.

One of the most important functions of an emulsion stabilizer is the determination of the emulsion type, which in turn dictates the properties and applications of the emulsion. For molecular surfactants, it has been established that the shape and the amphiphilicity of a surfactant determine the type of emulsion that is formed.[23,24] The packing parameter of a surfactant, which accounts for its shape factor, is a powerful parameter that reliably predicts the type of emulsion that would be generated. Moreover, the hydrophilic−lipophilic balance (HLB), semiquantitatively determined values based on the composition and chemical nature of hydrophilic and hydrophobic groups in surfactants, accounts for their amphiphilicity and in turn influences the type of emulsions.

Analogously, the type of emulsions that would be formed when Janus particles are used as emulsifiers likely depends on their properties such as shape and amphiphilicity. However, the concepts of packing parameter and HLB are not directly applicable to Janus particles due to their structural complexity. For example, the comparison of two Janus particles with different configurations is not trivial. Even seemingly simple changes, like shifting boundaries between hydrophilic and hydrophobic domains, alter many other important factors. In addition to shifting the hydrophilic/hydrophobic balance, the

Special Issue: Mohamed El-Aasser Festschrift

Received: May 17, 2019
Revised: July 5, 2019
Accepted: July 20, 2019
Published: July 21, 2019

DOI: 10.1021/acs.iecr.9b02697
Ind. Eng. Chem. Res. 2019, 58, 20961−20968

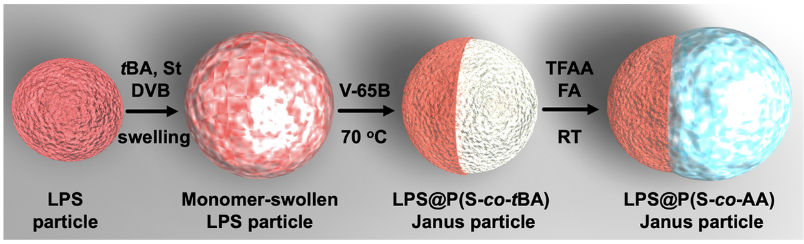


Figure 1. Synthesis of amphiphilic Janus particles. Schematic diagram of the synthetic procedure of seeded emulsion polymerization for amphiphilic LPS/P(S-*co*-*t*BA) and LPS/P(S-*co*-AA) Janus particles. The synthetic procedure includes three steps: monomer swelling, polymerization and hydrolysis.

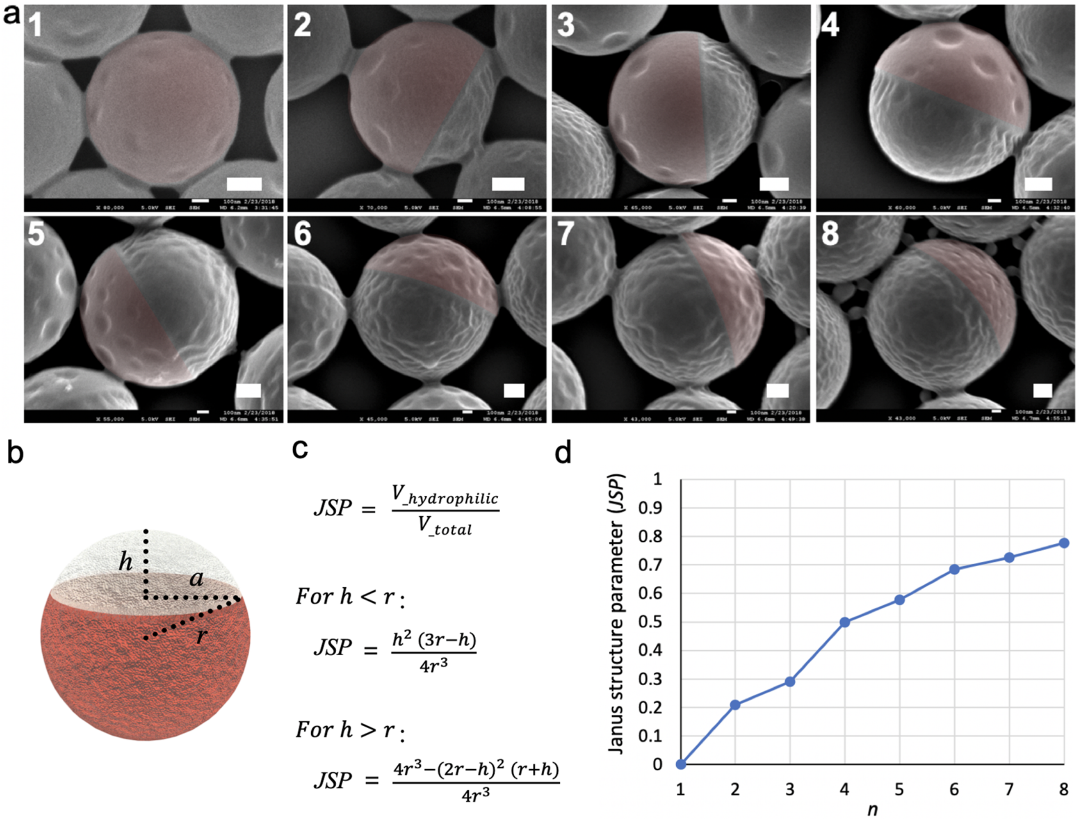


Figure 2. Homologous series of Janus particles with different Janus structure parameter. (a) SEM images of LPS/P(S-*co*-*t*BA)-*n* Janus particles prepared via seeded emulsion polymerization. Scale bars: 200 nm. The number in each SEM image indicates *n*. The LPS regions are highlighted by false red. (b) Schematic image of the structure of Janus particles. *r* is the radius of Janus particle, *a* is the radius of the base, and *h* is the height of the P(S-*co*-*t*BA) region. (c) Definition and equations of Janus structure parameter, assuming Janus particles are spherical. (d) Plot diagram of Janus structure parameter of LPS/P(S-*co*-*t*BA)-*n* Janus particles.

volume and shape of each domain also change. There are additional complexities, for example, for stimuli responsive Janus particles that undergo triggered reconfiguration, with concomitant change of Janus boundary location, domain shape, volume, and chemistry. Therefore, it is currently unclear which property of Janus particles determines the type of emulsions that are stabilized. To gain insight, systematic studies of homologous series of Janus particles are needed.

In this report, we experimentally study the effect of relative size of hydrophilic and hydrophobic regions (configuration) and the chemical nature of Janus particles on their emulsification property. A homologous series of pH-responsive Janus particles is synthesized using seeded emulsion polymerization, enabling large scale production of uniform Janus particles with tunable configurations and chemical properties. The volume ratio between the hydrophilic and hydrophobic parts of the Janus particles can be varied by changing the relative ratio of monomers to the seed particles during synthesis and/or the solution pH post synthesis. To characterize these Janus particles, we define the volume fraction of the hydrophilic regions to the entire Janus particles using the Janus structure parameter (JSP). Moreover, the chemical nature of the hydrophilic region of the Janus particles is adjusted by varying the solution pH. These particles, thus, allow us to systematically study and reveal correlations between the configuration and chemical properties of Janus particles and the types of emulsions that are stabilized by these particles.

RESULTS AND DISCUSSION

Synthesis of Homologous Janus Particles. Seeded emulsion polymerization is a powerful and scalable technique to prepare uniform polymeric colloids with advanced

DOI: 10.1021/acs.iecr.9b02697
Ind. Eng. Chem. Res. 2019, 58, 20961−20968

structures such as core–shell particles,[25] hollow colloids,[26] yolk–shell microspheres,[27] lens-shaped particles,[28] and anisotropic Janus particles.[20,29–33] Recently, we adopted this method to synthesize Janus particles with shape-changing and amphiphilicity-reversing properties.[20] In this report, we extend the seeded emulsion polymerization method to prepare a series of homologous Janus particles with high uniformity. Figure 1 illustrates the seeded emulsion polymerization method in which linear polystyrene (LPS) microspheres are used as seeds to accommodate a monomer mixture of *tert*-butyl acrylate (*t*BA), styrene (St), and divinylbenzene (DVB) in an aqueous environment. Subsequent polymerization of the monomer mixture within the seed particles, initiated by 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65B) at 70 °C, induces phase separation between the seed LPS polymers and newly formed P(S-*co*-*t*BA) polymers, and in turn produces anisotropic LPS/P(S-*co*-*t*BA) Janus particles that have a well-defined boundary.[34,35] The *t*BA repeat units in LPS/P(S-*co*-*t*BA) Janus particles can be subsequently hydrolyzed using a mixture of trifluoroacetic acid (TFAA) and formic acid (FA), resulting in amphiphilic and pH-respnsive LPS/P(S-*co*-AA) Janus particles.

A homologous series of Janus particles with different volume ratios of the hydrophilic and hydrophobic parts can be prepared by changing the amount of monomers at the swelling step of the seeded emulsion polymerization. By changing the volume ratio of the monomer mixture of *t*BA, St, and DVB to the LPS seed particles from 1 to 9 (defined as the swelling ratio), a series of LPS/P(S-*co*-*t*BA) Janus particles are prepared. For clarity, the Janus particles will be termed with *n* at the end of each chemical name to denote the swelling ratio. Figure 2a(2–8) shows the scanning electron microscopy (SEM) images of the LPS/P(S-*co*-*t*BA)-*n* Janus particles prepared with swelling ratio ranging from 2 to 8. Regardless of the swelling ratio, Janus particles are more or less spherical and have uniform shapes (also see in the Supporting Information, Figure S1). Well-defined Janus boundaries between the LPS-rich and the P(S-*co*-*t*BA)-rich parts can be observed on each Janus particle. The LPS-rich region is highlighted with false red color in the SEM images to guide the eye. The small dimples in the LPS-rich region are small domains of P(S-*co*-*t*BA).[20] It is clear that the Janus boundaries progressively shift toward the LPS-rich region as the swelling ratio is increased. In particular, the Janus boundary of the LPS/P(S-*co*-*t*BA)-4 Janus particles is located at the equator, dividing the Janus particle into two equal halves. These results show that seeded emulsion polymerization is a powerful method to prepare Janus particles with tunable Janus boundaries. In addition, no Janus particles are observed when the swelling ratio is outside the range of 2–8. Either “homogeneous” spherical particles with small dimples (swelling ratio 1, Figure 2a1) or big aggregates (swelling ratio 9) are obtained.

The shifting in the Janus boundary changes the configurations of Janus particles; it alters both the shape and the amphiphilicity of the homologous series of Janus particles (Figure 2a). On the basis of the structure of the Janus particles (Figure 2b), we introduce the concept of Janus structure parameter (JSP) to quantify the configuration of Janus particles prepared with varying swelling ratios. The JSP is defined as the volume fraction of the hydrophilic region with respect to the entire volume of the Janus particles, as illustrated in Figure 2c, regardless of the overall shape and composition of the Janus particles. In other words, JSP describes the configuration of the Janus particles, which accounts for their shape as well as composition-induced amphiphilicity. For LPS/P(S-*co*-*t*BA) Janus particles, the JSP value is the volume fraction of the P(S-*co*-*t*BA)-rich region. Figure 2d summarizes the JSP values of the homologous series of LPS/P(S-*co*-*t*BA) Janus particles. A large range of JSP values from 0.21 to 0.78 can be obtained. That is to say, the JSP values can be adjusted by a factor of 3 via altering the swelling ratio during synthesis. The quasilinear relationship between JSP value and swelling ratio shows that the structure of Janus particles can be precisely controlled via seeded emulsion polymerization.

The *t*BA repeat units in the network of LPS/P(S-*co*-*t*BA) Janus particles are subsequently hydrolyzed using a mixture of TFAA and FA to convert *t*BA to hydrophilic acrylic acid (AA). The hydrolysis treatment of LPS/P(S-*co*-*t*BA) Janus particles thus leads to the formation of a homologous series of pH-responsive LPS/P(S-*co*-AA) Janus particles (see Supporting Information, Figure S2 and S3). Under acidic conditions (pH < 7), the LPS/P(S-*co*-AA) Janus particles more or less maintain a spherical shape, likely due to minimal swelling of the AA-rich domains (see Supporting Information, Figure S3). These results imply that the overall morphology of LPS/P(S-*co*-AA) Janus particles under acidic conditions does not change significantly from that of their dry state. In other words, the JSP values of LPS/P(S-*co*-AA)-*n* Janus particles in acidic water are essentially the same as that of LPS/P(S-*co*-*t*BA) Janus particles shown in Figure 2d.

Basic pH above 7 can trigger a phase transition of the AA-rich region from the “solid” to “gel” due to ionization of AA (Figure 3b). Such a transition from protonated to deprotonated AA increases the hydrophilicity of the hydrophilic region by almost 10 times.[24] Figure 3b shows that the phase transition depends on the configuration of the Janus particles. LPS/P(S-*co*-AA)-4, LPS/P(S-*co*-AA)-5, LPS/P(S-*co*-AA)-6, and LPS/P(S-*co*-AA)-7 Janus particles start to show the transition at pH 9 and become fully deprotonated at pH 10 (apparent pK_a, highlighted by orange squares in Figure 3b). Similar transition of LPS/P(S-*co*-AA)-3 and LPS/P(S-*co*-AA)-8 Janus particles occurs between pH 12–13 and pH 8–9, respectively (Figure 3). No obvious transition for LPS/P(S-*co*-AA)-2 Janus particles can be observed at any given pH (Figure 3). This complex dependence of the swelling transition of the AA-rich region on the solution pH can be attributed to the fact that the apparent pK_a of AA is known to depend on the molecular weight of the polymer, the ratio of AA moieties in the polymer network, and the local polarity.[36]

Emulsions Stabilized by Homologous LPS/P(S-*co*-AA) Janus Particles. Recent studies have shown that amphiphilic Janus particles are effective stabilizers for emulsions.[16,17] The homologous series of Janus particles synthesized in this study allows significant changes in their JSP values and chemical nature. This platform thus presents a unique opportunity to establish the correlation between these parameters of Janus particles and the emulsion types that can be stabilized by those Janus particles.

Emulsions are produced with toluene as the oil phase with 0.5 wt % aqueous suspension of the Janus particles. The pH of the aqueous phase is adjusted using buffer solutions. The volume of oil and aqueous phases is kept at a ratio of 50:50 to avoid the influence of dominant fluid phase on regulating the type of emulsions.[37,38] A trace amount of Nile Red is added in toluene to facilitate the characterization of emulsions under a fluorescence microscope. The emulsions are prepared by

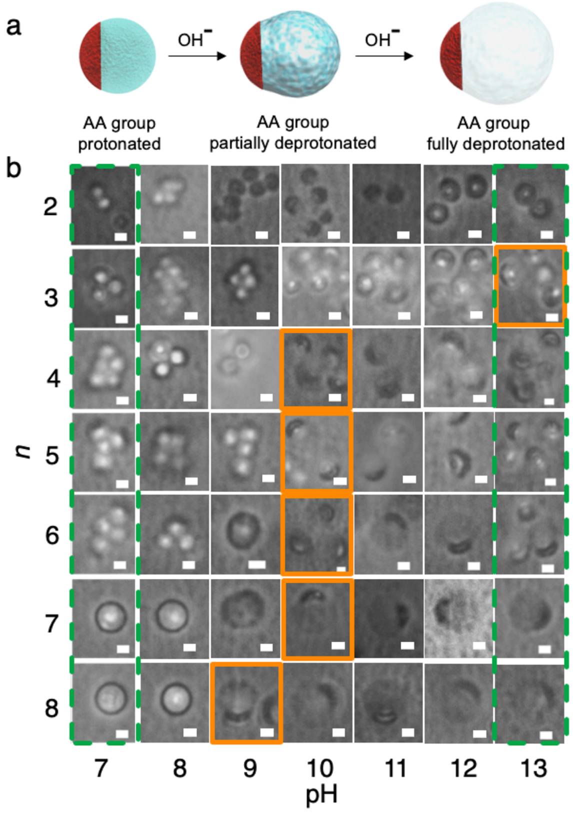


Figure 3. Homologous series of Janus particles LPS/P(S-*co*-AA)-*n* in water with different pH. (a) Schematics of LPS/P(S-*co*-AA)-6 Janus particles which show the hydrophilic region with different chemical strength. (b) Optical microscopy images of the LPS/P(S-*co*-AA)-*n* Janus particles at different pH. Scale bars: 2 μm.

vortexing a mixture of the oil and aqueous phases at 3000 rpm for 10 s. The resulting library of emulsions is shown in Figure 4a. These emulsions last for durations at least as long as several months; a detailed study on lifetimes is an important issue for future research. In general, emulsions made under acidic conditions (pH < 7) sediment to the bottom of the vials with excess oil phase on the top (Figure 4a). Based on the difference in the density of toluene and water, this observation indicates that these are water-in-oil (w/o) emulsions. Under basic conditions, most, but not all, of the emulsions stabilized by Janus particles are oil-in-water (o/w) emulsions, as can be distinguished from the creaming of the emulsion phase (Figure 4a).

To facilitate our understanding of how the configuration of Janus particles affects emulsion types, we summarize the types of emulsions stabilized by the homologous series of Janus particles versus pH in a phase diagram, where blue dots and red dots represent w/o and o/w emulsions, respectively (Figure 4b).

We first investigate the effect of JSP values, which solely describe the structural factor of the Janus particles, on the emulsion types that can be stabilized by LPS/P(S-*co*-AA) Janus particles under acidic conditions. Under the same conditions, the JSP values of LPS/P(S-*co*-AA)-*n* Janus particles vary from 0.21 to 0.78 (Figure 2d). This change indicates that the series of Janus particles undergoes structural transitions from a hydrophobic domain-dominated-“cone”-like structure to a hydrophilic domain-dominated-“inverse cone”-like structure. For a molecular surfactant, such a structural transition typically triggers the change of emulsion stabilized by the surfactant from the w/o to the o/w type.[39] Surprisingly, no similar transition of emulsions is observed when the homologous series of LPS/P(S-*co*-AA)-*n* Janus particles are used as stabilizers under acidic conditions: The LPS/P(S-*co*-AA)-*n* Janus particles stabilize only w/o emulsions, regardless of JSP values (Figure 4a). For example, at pH 7, LPS/P(S-*co*-AA)-*n* Janus particles exclusively produce w/o emulsions, even if the

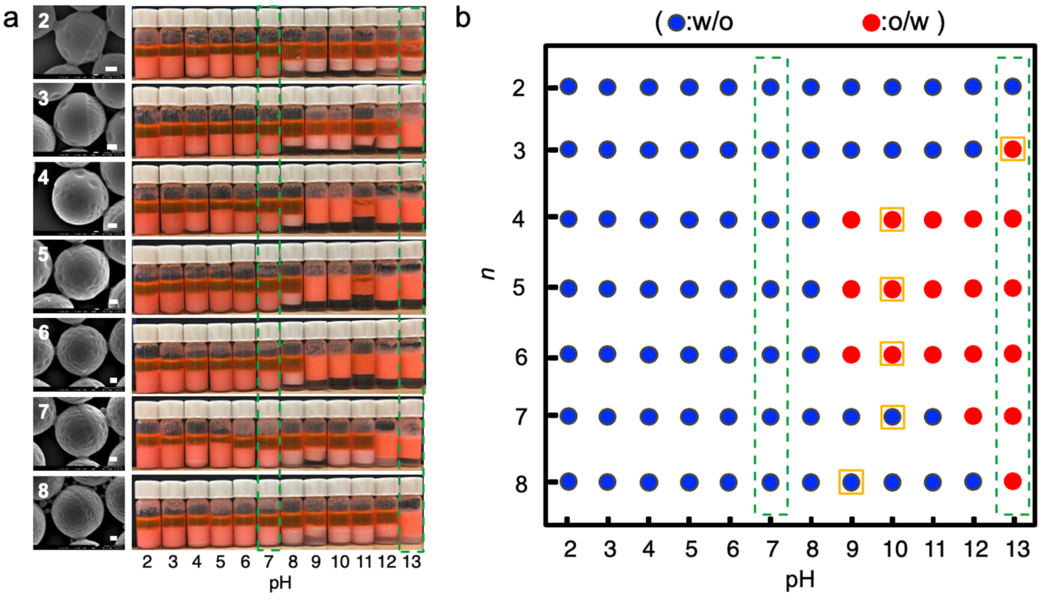


Figure 4. Emulsions stabilized by LPS/P(S-*co*-AA)-*n* Janus particles. (a) Emulsions stabilized by homologous LPS/P(S-*co*-AA)-*n* Janus particles under different pH conditions. Left column shows the SEM images of the corresponding LPS/P(S-*co*-*t*BA)-*n* Janus particles (the inset number indicates *n*). Oil phase: toluene with Nile Red, aqueous phase contains 0.5 wt % LPS/P(S-*co*-AA) Janus particles. The volume ratio of oil and aqueous phases is 50:50. Scale bars: 200 nm. (b) Phase diagram of emulsions stabilized by the homologous series of LPS/P(S-*co*-AA)-*n* Janus particles under different pH conditions.

JSP value of the Janus particles varies by a factor of 3 from 0.21 to 0.78 (Figure 4a, highlighted by left green rectangle; also see the Supporting Information Figure S6b). In these cases, the Janus particles behave as hydrophobic particles and stabilize only w/o emulsions.[40] The fluorescence microscopy images confirm that these emulsions are w/o type (Figure 5 top, dark dispersed phase) with an average diameter of 350 μm and a broad size distribution. This emulsification study shows that the JSP has minimal impact on the type of emulsions that can be stabilized by LPS/P(S-*co*-AA)-*n* Janus particles, when AA stays protonated and uncharged, likely due to small difference in the water affinity of the two regions.

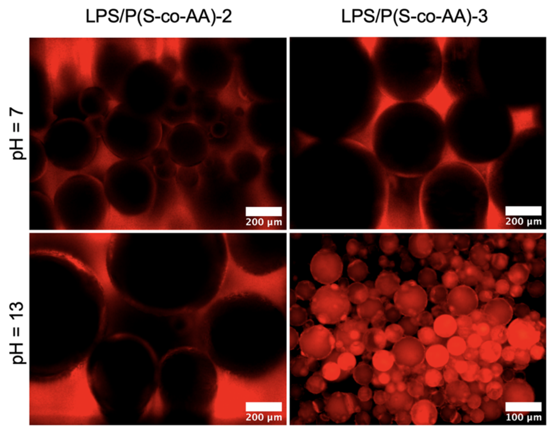


Figure 5. Effect of JSP on the types of Janus particle-stabilized emulsions. Fluorescence microscopy image of w/o emulsions stabilized by LPS/P(S-*co*-AA)-2 and LPS/P(S-*co*-AA)-3 Janus particles at pH 7 (top). Fluorescence microscopy image of w/o emulsions stabilized by LPS/P(S-*co*-AA)-2 Janus particles at pH 13 and o/w emulsions stabilized by LPS/P(S-*co*-AA)-3 Janus particles at pH13 (bottom).

Under basic conditions (especially when pH > 9.0), the effect of JSP of Janus particles on the emulsion types is more complicated than under acidic conditions. For instance, at pH 13, LPS/P(S-*co*-AA)-2 Janus particles stabilize w/o emulsions, whereas, LPS/P(S-*co*-AA)-*n* ($n \geq 3$) Janus particles stabilize o/w emulsions (Figure 4, highlighted by right green rectangle, Figures 4 and 5 bottom) with an average diameter of 130 μm, which is smaller than the droplets in the w/o emulsions. We attribute this change to interparticle repulsion between highly charged AA groups under basic conditions, which leads to a decrease in the size of emulsion droplet upon an increase of system pH.[41] Interestingly, this emulsion inversion coincides with the phase transition of the hydrophilic region of Janus particles from "solid" (for LPS/P(S-*co*-AA)-2 Janus particles) to "gel" (for LPS/P(S-*co*-AA)-3 Janus particles) (Figure 3). Similar coincidences are observed under other pH conditions (between LPS/P(S-*co*-AA)-3 and LPS/P(S-*co*-AA)-4 Janus particles at pH 9−12, Figure 4). These results show that the emulsion inversion requires both the change of particle configuration and a strong chemical difference between the two domains of the Janus particle; the enhanced hydrophilicity of the hydrophilic part of the Janus particles plays a key role in this process. In other words, the JSP of Janus particles can affect the type of emulsion only when the hydrophilicity difference between the two regions of the Janus particle is strong. Table 1 shows that, at pH 13, the JSP value changes from 0.21 for LPS/P(S-*co*-AA)-2 Janus particles to 0.48 for LPS/P(S-*co*-AA)-3 Janus particles. And at pH 9−12, the JSP value varies from 0.29 for LPS/P(S-*co*-AA)-3 Janus particles to over 0.70 for LPS/P(S-*co*-AA)-4 Janus particles. The critical JSP value to induce an emulsion inversion is deduced to be 0.48. This indicates that, with a sufficiently strong difference in hydrophilicity between the Janus domains, those Janus particles with the volume of hydrophobic region larger than hydrophilic part (JSP < 0.48) prefer to stabilize w/o emulsions. In contrast, an o/w emulsion forms when more than half of the Janus particles are hydrophilic (JSP > 0.48). Here we have focused only on the volume fraction of Janus domains and their hydrophilic contrast. It is worth noting that the size of Janus particles may affect the critical JSP value. In addition, even though JSP describes both the shape and amphiphilicity of a Janus particle, the shape transition of Janus particles from "cone" to "snowman" likely plays an important role in the emulsion inversion, which needs to be systematically explored in the future.

Table 1. JSP Values of LPS/P(S-*co*-AA)-*n* Janus Particles at pH > 8

	n						
pH	2	3	4	5	6	7	8
9	0.21	0.29	0.5	0.58	0.68	0.73	0.83
10	0.21	0.29	0.72	0.85	0.84	0.82	0.85
11	0.21	0.29	0.75	0.83	0.82	0.85	0.89
12	0.21	0.29	0.73	0.74	0.84	0.78	0.86
13	0.21	0.48	0.68	0.78	0.85	0.83	0.91

Interestingly, LPS/P(S-*co*-AA)-7 Janus particles at pH 9−11 and LPS/P(S-*co*-AA)-8 Janus particles at pH 9−12 stabilize w/o emulsions. These observations are inconsistent with the general trend; that is, despite having large swollen hydrophilic-regions of ionized AA rich domains, these particles stabilize w/o emulsions. We do not fully understand this trend in the lower right corner of the phase diagram in Figure 4. One potential possibility is that, since these particles are too hydrophilic and highly charged, their tendency to attach to the interface may not be very high and thus the emulsion type is not entirely determined by the configuration of the Janus particles. In addition, a small number of nanosized P(S-*co*-AA) particles are present in both the LPS/P(S-*co*-AA)-7 and the LPS/P(S-*co*-AA)-8 Janus particles (Figure 2a), which may affect the type of emulsion stabilized by those Janus particles. However, we believe the effect of these small particles is minimal, as they are likely far less surface active than the Janus particles due to their highly hydrophilic nature and small size.

To further investigate the importance of amphiphilicity of Janus particles on their emulsification properties, we focus on the emulsification of a specific Janus particle under different pH conditions. Figure 6 highlights the optical microscopy images and emulsification of LPS/P(S-*co*-AA)-6 Janus particles in three states where the AA groups on the P(S-*co*-AA) region are protonated, partially deprotonated, and fully deprotonated, respectively. When the AA groups are protonated (at pH < 8), a w/o type emulsion is obtained even if the JSP value of LPS/P(S-*co*-AA)-6 Janus particle is as high as 0.68 (which is much larger than the critical JSP 0.48). As the ionization of the Janus particle's hydrophilic domain is increased, the emulsion type switches from w/o to o/w. Similar emulsion inversion can be observed when LPS/P(S-*co*-AA)-4 and LPS/P(S-*co*-AA)-5 Janus particles are used as stabilizers at different pH (Figure 4). These results demonstrate again the ability of Janus

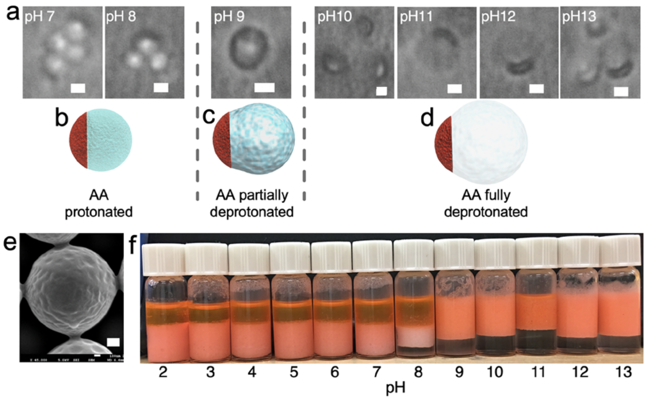


Figure 6. Effect of chemical factor on the types of Janus particle-stabilized emulsions. (a) Optical microscopy images of LPS/P(S-*co*-AA)-6 Janus particles at pH 7 to pH 13. Scale bars: 2 μm. (b)−(d) Schematics of LPS/P(S-*co*-AA)-6 Janus particles with the P(S-*co*-AA) region at different chemical state. (e) SEM image of Janus particles LPS/P(S-*co*-*t*BA)-6. Scale bars: 200 nm. (f) Photo of emulsions stabilized by LPS/P(S-*co*-AA)-6 Janus particles at different pH values.

particles to dictate emulsion type depends strongly on sufficient contrast in hydrophilicity of the Janus particle domains.

In this work, we only focus on the correlations between the configurations of Janus particles and the type of emulsions that can stabilized by theses Janus particles. It is likely that the adhesion energy of the Janus particles at the interfaces and thus the thermodynamic stability of emulsion formation depends on the configurations of Janus particles as well, which is an important topic to be studied in the future.

CONCLUSIONS

In summary, a homologous series of Janus particles with tunable configurations and chemical properties has been prepared via seeded emulsion polymerization, which allows us to systematically investigate their emulsification properties. We introduce the concept of Janus structure parameter (JSP) to describe the ratio of hydrophilic domain to total particle volume and study the effect of JSP on the type of emulsion that can be stabilized by those Janus particles. We find that the JSP of Janus particles has a limited effect on the determination of emulsion types when the difference in the water affinity of the two regions of a Janus particles is weak. In contrast, the JSP of Janus particles plays an important role in regulating the emulsion types when the water affinity of the hydrophilic region of a Janus particle is strong. When there is a significant difference in the water affinity of the two regions, a critical JSP value of 0.48 is determined as the threshold for emulsion inversion. Such findings on the correlations between the configuration of Janus particles and the types of emulsions that are stabilized by these particles are crucial for design and development of Janus particles as the next generation of amphiphiles for emulsion-based technologies.

EXPERIMENTAL SECTION

Materials and General Methods. Poly(vinylpyrrolidone) ($M_w \approx 55\,000$), styrene (99%), isopropyl alcohol (99.9%), ammonium persulfate (98%), *tert*-butyl acrylate (98%), divinylbenzene (55%), 2,2′-azobis(2,4-dimethylvaleronitrile) (from Wako), poly(vinyl alcohol) ($M_w = 13\,000−23\,000$, 87−89% hydrolyzed), trifluoroacetic acid (99%), formic acid (≥95), buffer solutions (Fluka), tuluene (anhydrous, 99.8%), and Nile red (98%) are purchased from Sigma-Aldrich and used as received unless stated otherwise. Dynamic light scattering (DLS) and ζ potential (ZP) measurements were performed on Malvern Zeta-sizer NS90 instrument. Fluorescence images were recorded using an Zeiss Axio Imager M1m.

Synthesis of Amphiphilic Janus Particles. The amphiphilic Janus particles are synthesized via a modified method of seeded emulsion polymerization:[20]

LPS Seed Particles. First, poly(vinylpyrrolidone) (PVP, 0.18 g) and styrene (St, 39.6 mL) are dissolved in isopropyl alcohol (IPA, 450 mL) in a 1 L round bottle flask (RBF). Then a mixture of deionized (DI) water (54 mL) and ammonium persulfate (APS, 0.12 g) is added to the flask. The flask is sealed with a rubber stopper and Teflon tape. Then, the mixture is mixed by shaking the flask for 60 s. Subsequently the mixture is purged with nitrogen for 30 min. Finally, the mixture is immersed into an oil bath at 70 °C and stirred (300 rpm) for 24 h. After polymerization, the LPS particles are washed five times with DI water using centrifugation. The purified LPS particles are dispersed in DI water (5 vol %).

LPS/P(S-co-tBA) Janus Particles. A monomer mixture of St, *tert*-butyl acrylate (*t*BA), divinylbenzene (DVB), and 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65B) is first prepared at a volume ratio of 90:90:1.8:1. The monomer mixture (2 × *n* mL, *n* indicates the swelling ratio) is well mixed with PVA aqueous solution (40 mL, 1 wt %) to make a monomer emulsion. Then, a dispersion of LPS particles (40 mL, 5 vol %) is mixed with the monomer emulsions in a 250 mL round-bottom flask. The overall mixture is vortexed for 1 min and then mounted on a rotator (Glas-Col) to rotate for 12 h at 60 rpm at room temperature. Subsequently, the mixture is immersed in an oil bath at 70 °C while tumbling (IKA RW 16 basic) at 100 rpm for 12 h. After the reaction, the particles are washed with DI water five times by centrifugation.

LPS/P(S-co-AA) Janus Particles. LPS/P(S-*co*-*t*BA) Janus particles are redispered in a mixture of trifluoroacetic acid (TFAA, 80 mL) and formic acid (FA, 20 mL), and the resulting mixture was stirred for 24 h. Then, the product is washed with DI water 10 times by centrifugation. The LPS/P(S-*co*-AA) Janus particles are dispersed in DI water (10 wt %)

Emulsification and Emulsion Characterization. Toluene (600 μL, containing 0.0001 wt % Nile red) is added to an aqueous dispersion of LPS/P(S-*co*-AA) Janus particles at different pHs (600 μL, 0.5 wt %). The mixture is vortexed at 3000 rpm for 30 s and kept still for 2 h before characterization. To image the emulsions, the Janus particle stabilized emulsions are loaded into a square glass capillary (1 × 1 mm). For w/o emulsions, the glass capillary tube is treated with octadecyltrichlorosilane (1 vol % in toluene) on a hot plate at 150 °C for 30 min.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b02697.

Further details of characterization of the Janus particles and the emulsions stabilized by those Janus particles, including SEM images, optical and fluorescence microscopy images, particle sizes, JSP values, emulsion photos (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: kstebe@seas.upenn.edu.

*E-mail: daeyeon@seas.upenn.edu.

ORCID

Kathleen J. Stebe: 0000-0003-0510-0513

Daeyeon Lee: 0000-0001-6679-290X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partly supported by NSF CBET-1705891 and Penn MRSEC (DMR 1720530).

■ REFERENCES

(1) Jiang, S.; Granick, S. Janus balance of amphiphilic colloidal particles. *J. Chem. Phys.* **2007**, *127*, 161102–5.

(2) Walther, A.; Müller, A. H. E. Janus Particles: Synthesis, Self-Assembly, Physical Properties, and Applications. *Chem. Rev.* **2013**, *113*, 5194–5261.

(3) Hu, J.; Zhou, S.; Sun, Y.; Fang, X.; Wu, L. Fabrication, properties and applications of Janus particles. *Chem. Soc. Rev.* **2012**, *41*, 4356–4378.

(4) Wurm, F.; Kilbinger, A. F. M. Polymeric Janus Particles. *Angew. Chem., Int. Ed.* **2009**, *48*, 8412–8421.

(5) Walther, A.; Müller, A. H. E. Janus particles. *Soft Matter* **2008**, *4*, 663–6.

(6) Binks, B. P.; Fletcher, P. D. I. Particles Adsorbed at the Oil–Water Interface: A Theoretical Comparison between Spheres of Uniform Wettability and "Janus" Particles. *Langmuir* **2001**, *17*, 4708–4710.

(7) Kumar, A.; Park, B. J.; Tu, F.; Lee, D. Amphiphilic Janus particles at fluid interfaces. *Soft Matter* **2013**, *9*, 6604–15.

(8) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100*, 503–546.

(9) Bradley, L. C.; Chen, W.-H.; Stebe, K. J.; Lee, D. Current Opinion in Colloid & Interface Science. *Curr. Opin. Colloid Interface Sci.* **2017**, *30*, 25–33.

(10) Park, B. J.; Lee, D. Particles at fluid–fluid interfaces: From single-particle behavior to hierarchical assembly of materials. *MRS Bull.* **2014**, *39*, 1089–1098.

(11) Ruhland, T. M.; Gröschel, A. H.; Ballard, N.; Skelhon, T. S.; Walther, A.; Müller, A. H. E.; Bon, S. A. F. Influence of Janus Particle Shape on Their Interfacial Behavior at Liquid–Liquid Interfaces. *Langmuir* **2013**, *29*, 1388–1394.

(12) Glaser, N.; Adams, D. J.; Böker, A.; Krausch, G. Janus Particles at Liquid–Liquid Interfaces. *Langmuir* **2006**, *22*, 5227–5229.

(13) Wu, D.; Chew, J. W.; Honciuc, A. Polarity Reversal in Homologous Series of Surfactant-Free Janus Nanoparticles: Toward the Next Generation of Amphiphiles. *Langmuir* **2016**, *32*, 6376–6386.

(14) Ku, K. H.; Lee, Y. J.; Yi, G. R.; Jang, S. G.; Schmidt, B. V. K. J.; Liao, K.; Klinger, D.; Hawker, C. J.; Kim, B. J. Shape-Tunable Biphasic Janus Particles as pH-Responsive Switchable Surfactants. *Macromolecules* **2017**, *50*, 9276–9285.

(15) McClements, D. J. Nanoemulsions versus microemulsions: terminology, differences, and similarities. *Soft Matter* **2012**, *8*, 1719–1729.

(16) Aveyard, R. Can Janus particles give thermodynamically stable Pickering emulsions? *Soft Matter* **2012**, *8*, 5233–5240.

(17) Tu, F.; Park, B. J.; Lee, D. Thermodynamically Stable Emulsions Using Janus Dumbbells as Colloid Surfactants. *Langmuir* **2013**, *29*, 12679–12687.

(18) Yamagami, T.; Kitayama, Y.; Okubo, M. Preparation of Stimuli-Responsive "Mushroom-Like" Janus Polymer Particles as Particulate Surfactant by Site-Selective Surface-Initiated AGET ATRP in Aqueous Dispersed Systems. *Langmuir* **2014**, *30*, 7823–7832.

(19) Tanaka, T.; Okayama, M.; Minami, H.; Okubo, M. Dual Stimuli-Responsive "Mushroom-like" Janus Polymer Particles as Particulate Surfactants. *Langmuir* **2010**, *26*, 11732–11736.

(20) Tu, F.; Lee, D. Shape-Changing and Amphiphilicity-Reversing Janus Particles with pH-Responsive Surfactant Properties. *J. Am. Chem. Soc.* **2014**, *136*, 9999–10006.

(21) Lu, C.; Urban, M. W. Tri-Phasic Size- and Janus Balance-Tunable Colloidal Nanoparticles (JNPs). *ACS Macro Lett.* **2014**, *3*, 346–352.

(22) Faria, J.; Ruiz, M. P.; Resasco, D. E. Phase-Selective Catalysis in Emulsions Stabilized by Janus Silica-Nanoparticles. *Adv. Synth. Catal.* **2010**, *352*, 2359–2364.

(23) Israelachvili, J. N. *Intermolecular and surface forces*; Academic Press, 2011.

(24) Davies, J. A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent. Gas/Liquid and Liquid/Liquid Interface. *Proceedings of the International Congress of Surface Activity*; Butterworths, 1957; pp 426–438.

(25) Lan, Y.; Yang, L.; Zhang, M.; Zhang, W.; Wang, S. Microreactor of Pd Nanoparticles Immobilized Hollow Microspheres for Catalytic Hydrodechlorination of Chlorophenols in Water. *ACS Appl. Mater. Interfaces* **2010**, *2*, 127–133.

(26) Lan, Y.; Zhang, M.; Zhang, W.; Yang, L. Enhanced Pd-Catalyzed Hydrogenation of Olefins within Polymeric Microreactors under Organic/Aqueous Biphasic Conditions. *Chem. - Eur. J.* **2009**, *15*, 3670–3673.

(27) Zhang, M.; Lan, Y.; Wang, D.; Yan, R.; Wang, S.; Yang, L.; Zhang, W. Synthesis of Polymeric Yolk–Shell Microspheres by Seed Emulsion Polymerization. *Macromolecules* **2011**, *44*, 842–847.

(28) Chen, W.-H.; Tu, F.; Bradley, L. C.; Lee, D. Shape-Tunable Synthesis of Sub-Micrometer Lens-Shaped Particles via Seeded Emulsion Polymerization. *Chem. Mater.* **2017**, *29*, 2685–2688.

(29) Kim, J. W.; Larsen, R. J.; Weitz, D. A. Synthesis of Nonspherical Colloidal Particles with Anisotropic Properties. *J. Am. Chem. Soc.* **2006**, *128*, 14374–14377.

(30) Mock, E. B.; De Bruyn, H.; Hawkett, B. S.; Gilbert, R. G.; Zukoski, C. F. Synthesis of anisotropic nanoparticles by seeded emulsion polymerization. *Langmuir* **2006**, *22*, 4037–4043.

(31) Sheu, H. R.; El Aasser, M. S.; Vanderhoff, J. W. Phase separation in polystyrene latex interpenetrating polymer networks. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 629–651.

(32) Park, J.-G.; Forster, J. D.; Dufresne, E. R. High-Yield Synthesis of Monodisperse Dumbbell-Shaped Polymer Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132*, 5960–5961.

(33) Bradley, L. C.; Stebe, K. J.; Lee, D. Clickable Janus Particles. *J. Am. Chem. Soc.* **2016**, *138*, 11437–11440.

(34) Escalé, P.; Save, M.; Lapp, A.; Rubatat, L.; Billon, L. Hierarchical structures based on self-assembled diblock copolymers within honeycomb micro-structured porous films. *Soft Matter* **2010**, *6*, 3202–3210.

(35) Cho, I.; Lee, K. W. Morphology of latex particles formed by poly(methyl methacrylate)-seeded emulsion polymerization of styrene. *J. Appl. Polym. Sci.* **1985**, *30*, 1903–1926.

(36) Swift, T.; Swanson, L.; Geoghegan, M.; Rimmer, S. The pH-responsive behaviour of poly(acrylic acid) in aqueous solution is dependent on molar mass. *Soft Matter* **2016**, *12*, 2542–2549.

(37) Binks, B. P.; Lumsdon, S. O. Catastrophic Phase Inversion of Water-in-Oil Emulsions Stabilized by Hydrophobic Silica. *Langmuir* **2000**, *16*, 2539–2547.

(38) Kralchevsky, P. A.; Ivanov, I. B.; Ananthapadmanabhan, K. P.; Lips, A. On the Thermodynamics of Particle-Stabilized Emulsions: Curvature Effects and Catastrophic Phase Inversion. *Langmuir* **2005**, *21*, 50–63.

(39) Nagarajan, R. Molecular Packing Parameter and Surfactant Self-Assembly: The Neglected Role of the Surfactant Tail. *Langmuir* **2002**, *18*, 31–38.

(40) Finkle, P.; Draper, H. D.; Hildebrand, J. H. The theory of emulsification. *J. Am. Chem. Soc.* **1923**, *45*, 2780–2788.

(41) Gautier, F.; Destribats, M.; Perrier-Cornet, R.; Dechézelles, J.-F.; Giermanska, J.; Héroguez, V.; Ravaine, S.; Leal-Calderon, F.; Schmitt, V. Pickering emulsions with stimulable particles: from highly- to weakly-covered interfaces. *Phys. Chem. Chem. Phys.* **2007**, *9*, 6455−6462.