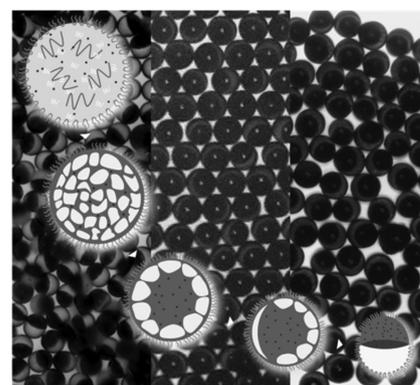


# Bicolored Janus Microparticles Created by Phase Separation in Emulsion Drops

Nam Gi Min, Tae Min Choi, Shin-Hyun Kim\*

In this work, a simple but versatile method to create bicolored Janus microparticles using phase separation of two immiscible polymers confined in emulsion drops is reported. With a capillary microfluidic device, monodisperse oil drops containing two immiscible polymers and dye molecules are generated in the continuous water phase. As the organic solvent is depleted by evaporation, the drops evolve to Janus microparticles with two compartments. One of the compartments is selectively stained by spontaneous migration of the dye molecules, thereby providing optical anisotropy. In addition, the Janus microparticles can be further rendered to be magneto-responsive by embedding aligned magnetic nanoparticles in the polymer matrix. Moreover, the configuration of Janus microparticles is exclusively selected from the core-incomplete shell, dumbbell, and acorn, according to the surfactant in the continuous phase. This phase separation approach will provide a new opportunity for designing Janus microparticles with advanced functionality.



## 1. Introduction

Janus particles are composed of two or more compartments that possess distinct properties originated from different composition or morphology.<sup>[1–4]</sup> Anisotropic characteristics of Janus particles make them useful in a wide range of applications. For example, Janus microparticles or nanoparticles that have both hydrophobic and hydrophilic compartments spontaneously adsorb at the oil–water interface to reduce interfacial energy, serving as interface stabilizers.<sup>[5–8]</sup> Janus microparticles whose compartments are made of biodegradable or environment-sensitive materials have been used as carriers for programmed release of multiple drugs.<sup>[9–11]</sup> Microparticles composed of different colored compartments have been designed to possess electric or magnetic anisotropy to use them as active display pigments.<sup>[12–15]</sup> By rotating the bicolored Janus particles

using the external field, two color states can be switched; this rotating ball type display is referred to as Gyricon display.

Microfluidic technology has been used to create Janus microparticles due to their high controllability over the size and composition. Typically, two parallel streams of distinct photocurable resins are formed in Y-shape channel, which are coemulsified into single drops in a microfluidic junction.<sup>[14,16–19]</sup> The biphasic emulsion drops are then rapidly solidified by photopolymerization of monomers to capture the distinct compartments before internal mixing. However, delicate controls over biphasic flows and optics are prerequisites for achieving high uniformity of Janus particles and high stability of a long-term production. Furthermore, materials are limited to photocurable resins responsible for fast solidification. Phase separation between two immiscible polymers is an alternative way to make Janus microparticles.<sup>[20–25]</sup> Two polymers confined in emulsion drops show phase separation as they are concentrated by solvent evaporation and finally form solid microparticles with two distinct compartments. For the production of Janus microparticles, only one homogeneous solution containing two

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immiscible polymers is needed to be emulsified. Moreover, any pairs of two immiscible polymers dissolvable in organic solvents are allowed to use. Therefore, the phase separation method potentially overcomes the limitations of the microfluidics that employ two parallel streams. Nevertheless, it remains a challenge to precisely control the compositions of two distinct compartments because two compartments are originated from one homogeneous phase.

In this work, we use phase separation of two immiscible polymers, polystyrene (PS) and poly(vinyl acetate) (PVAc), in oil-in-water (O/W) emulsion drops to create bicolored Janus microparticles with a magnetic response. It is, in common, difficult to render two compartments to have different colors from phase separation due to poor controllability over the compositions of the compartments. We dissolve a chemical additive of Sudan black B in the emulsion drops which has higher affinity to PVAc than PS. Therefore, the dye selectively stains the PVAc-rich compartment to be black during phase separation and consolidation. To render the Janus particles magneto-responsive, magnetic nanoparticles are additionally dispersed in the drop, which are aligned by the external magnetic field during the consolidation. The nanoparticles are embedded in the polymer matrix, while maintaining their alignment, thereby making a net magnetic moment in the Janus particles. Therefore, the orientation of the bicolored Janus particles can be controlled by external magnetic field. The relative area of one compartment to the other and shape of Janus microparticles are controlled by adjusting spreading parameter through the selection of surfactants in the continuous phase. For all experiments, emulsion templates are prepared by capillary microfluidic devices to make them highly monodisperse, which results in uniform Janus microparticles.

## 2. Experimental Section

### 2.1. Materials

Two different polymers, PS ( $M_w$  35000, Sigma-Aldrich) and PVAc ( $M_w$  500000, Sigma-Aldrich), were dissolved in toluene (Sigma-Aldrich) to have a concentration of 1% (w/w) for each polymer. The black pigment of Sudan black B (Sigma-Aldrich) was also dissolved in the toluene solution at the concentration of 0.01% (w/w), which was 0.5% (w/w) in toluene-free polymer basis. To render the PS-rich compartments of microparticles red or blue, either Sudan III (Sigma-Aldrich) or Sudan Blue II (Sigma-Aldrich) were additionally dissolved in the solution, respectively. Iron oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles with a diameter smaller than 50 nm (Sigma-Aldrich) were dispersed in the solution at the concentration of 0.03% (w/w) to make magneto-responsive microparticles. The toluene solutions were used as dispersed phases of emulsions. As a continuous phase, one of the three aqueous solutions

was used: the solution of 10% (w/w) poly(vinyl alcohol) (PVA,  $M_w$  13000–23000, Sigma-Aldrich), the solution of 0.3% (w/w) sodium dodecylbenzene sulfonate (SDBS, Sigma-Aldrich), and the solution of 1.5% (w/w) poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock-copolymer (F108,  $M_n$  14600, Sigma-Aldrich) and 8.5% (w/w) poly(ethylene glycol) (PEG,  $M_n$  6000, Sigma-Aldrich); PEG was dissolved to increase viscosity of the solution.

### 2.2. Preparation of Emulsion Drops Using Capillary Microfluidic Devices

Two cylindrical capillaries (1B100F-6, World Precision Instruments, Inc.) with an outer diameter of 1 mm were tapered by a micropipette puller (P97, Sutter Instrument) and sanded to have desired orifice diameters: one was 80  $\mu\text{m}$ , and the other was 160  $\mu\text{m}$ . These two cylindrical capillaries were assembled to have tip-to-tip coaxial alignment within a square capillary with an inner dimension of 1.05 mm (AIT glass) without surface modification. The dispersed phase of the polymer solution was injected through the capillary with an orifice diameter of 80  $\mu\text{m}$ , and the continuous phase of the surfactant solution was injected through the interstices between the cylindrical capillary and square capillary. Volumetric flow rates of the dispersed and continuous phases were typically set to 2 and 10  $\text{mL h}^{-1}$  using two syringe pumps (Legato 100, KD Scientific), respectively. The formation of monodisperse emulsion drops was observed with an optical microscope (Eclipse TS100, Nikon) equipped with a high-speed camera (Phantom Miro eX2, Vision Research).

### 2.3. Consolidation of Emulsion Drops and Characterization of Janus Microparticles

The emulsion drops were collected in a glass dish and incubated at room temperature for 3 h to evaporate toluene; a movable armhood was used to accelerate the evaporation. To clearly observe phase separation in a single drop, large drops with a diameter of 194  $\mu\text{m}$  were produced, which were continuously monitored with an optical microscope (Eclipse Ti-U, Nikon). When the drops contain the magnetic nanoparticles, the dish was sandwiched by a pair of magnetic disks during the incubation. The resulting microparticles were observed with scanning electron microscope (SEM, S-4800, Hitachi) and optical microscope (Eclipse L150, Nikon); the samples were coated with osmium tetroxide to render them conductive before SEM observation.

## 3. Results and Discussion

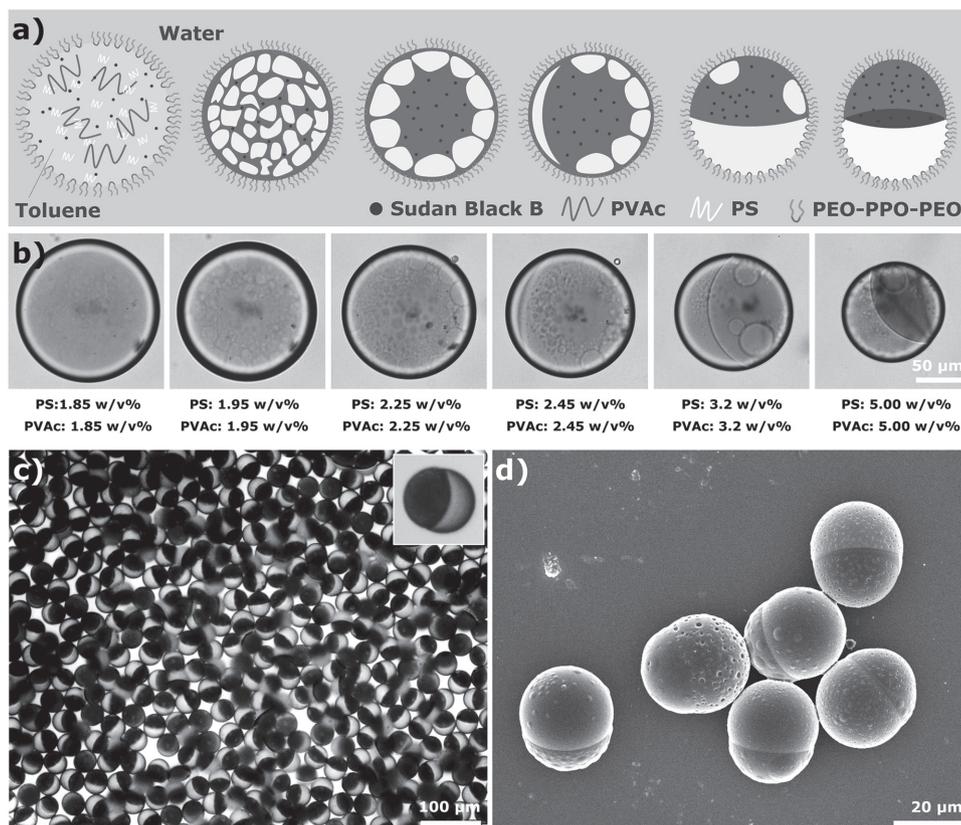
### 3.1. Phase Separation of Two Polymers in Emulsion Drops

To prepare Janus microparticles with uniform size and shape, monodisperse O/W emulsion drops are prepared as templates using glass capillary microfluidic devices, as shown in Figure S1 of the Supporting Information. The dispersed phase of polymer solutions is emulsified in the continuous phase at the tip of the cylindrical capillary in

a dripping mode.<sup>[26–28]</sup> The drops flow through the inner channel of the other cylindrical capillary, which are collected in a glass dish. The drops are highly monodisperse as shown in Figure S1b (Supporting Information), and their size is controlled in the range of 80–200  $\mu\text{m}$ . The volumetric flow rates of the dispersed and continuous phases are typically set to 2 and 10  $\text{mL h}^{-1}$ , respectively. The frequency of drop generation is estimated to be  $\approx 150$  per second from the flow rate of the dispersed phase and average diameter of drops, which is consistent with observation using a high-speed camera.

The drops float underneath the air–water interface due to the density lower than the aqueous solution of surfactants. Therefore, a thin water layer only separates the drops and air, which facilitates the evaporation of toluene to air. The drops lose their volume over the incubation time, which concentrates two polymers in the drops. The drops as prepared are homogeneous and maintain a single phase for a while, as shown in the first column of Figure 1a,b; a large drop with a diameter of 194  $\mu\text{m}$  is prepared for a clear observation of phase separation. At the low concentration, polymer molecules are randomly distributed in the volume of the drop as entropic

energy gain dominates over the disfavored interaction between two polymers. However, the drops become heterogeneous as the polymers are further concentrated, as shown in the second column of Figure 1a,b; the concentration of each polymer at the onset of phase separation is  $\approx 1.85\%$  (w/v), which is estimated from the diameter of the shrunken drop. At the high concentration, molecular motion is restricted by neighboring molecules, leading to a reduction of the entropic gain. Therefore, the disfavored interaction overwhelms the entropic gain above a certain concentration, initiating the phase separation. At this early stage of phase separation, very small domains are formed by diffusion-limited amplification of small fluctuation in composition; this is referred to as spinodal decomposition.<sup>[29,30]</sup> The small domains are then fused through Ostwald ripening to reduce interfacial energy.<sup>[31]</sup> The fusion lasts until two large compartments—one is PS-rich and the other is PVAc-rich—are retained, as shown in the remaining parts of Figure 1a,b. The concentration of each polymer is  $\approx 5.00\%$  (w/v) when two large compartments are formed. The phase separation process is clearly shown in Movie S1 of the Supporting Information.



**Figure 1.** a,b) Series of the cartoons and optical microscope (OM) images showing the phase separation of PS and PVAc in toluene emulsion drop containing Sudan black B. The concentrations of the polymers in the drop are denoted in each panel in (b). c) OM image of monodisperse Janus microparticles taken in the reflection mode. d) Scanning electron microscope (SEM) image of Janus microparticles. Pseudo color indicates the PVAc-rich compartment.

### 3.2. Compartment-Selective Staining and Formation of Janus Microparticles

In a course of the concentration, PVAc-rich phase becomes opaque, while PS-rich phase remains transparent, as shown in Figure 1b. The compartment with the convex inner interface is PVAc-rich and the other is PS-rich, which is confirmed by selective dissolution of PVAc with ethanol after the consolidation is completed, as shown in Figure S2 of the Supporting Information. Sudan black B molecules are uniformly distributed in the drop as-prepared. However, they spontaneously migrate to PVAc-rich compartment during the phase separation, thereby selectively staining the PVAc-rich compartment to be black. The selective staining is attributed to the higher affinity of Sudan black B to PVAc than PS. Sudan black B has secondary amine groups which are highly polar. This makes relatively small interaction parameter with polar PVAc in comparison with nonpolar PS, leading to the preferential migration of Sudan black B into the PVAc-rich domain. Janus microparticles formed by the complete consolidation possess two optically distinct compartments, as shown in Figure 1c; the PVAc-rich compartment with the convex inner interface is opaque, and the PS-rich compartment with the concave inner interface is transparent.

As the polymers are concentrated, the density of the emulsion drops increases. When the toluene is almost depleted by evaporation, the density of the drops becomes larger than that of the surrounding water; densities of PS and PVAc are 1.09 and 1.19 g cm<sup>-3</sup>, respectively. Therefore, the drops are submerged on the bottom of glass dish at the final stage of consolidation. The shape of Janus microparticles is dictated by minimum interfacial energy. When we use the aqueous solution of PEO-PPO-PEO triblock-copolymer, each Janus microparticle is composed of Sudan black B-stained PVAc-rich compartment with the convex inner interface and pigment-free PS-rich compartment with the concave inner interface, as shown in the inset of Figure 1c. Volumes of two compartments are comparable because two compartments are formed from the polymers with similar density at the same concentrations. The microparticles are highly uniform in size and shape, as shown in Figure 1c as they are templated by monodisperse emulsion drops with the same composition. The average size of the microparticles along the longitudinal direction is 36.3 μm, and its coefficient of variation (CV) is as small as 3%. The shape of the microparticles is further inspected by observing them with SEM, as shown in Figure 1d. A boundary between two compartments is clearly observed as the compartments have different curvatures of outer surfaces; the average radius of curvature for the PVAc-rich compartments is ≈1.06 times smaller than that of the PS-rich compartments.

### 3.3. Surfactants-Assisted Control over Microparticle Shape

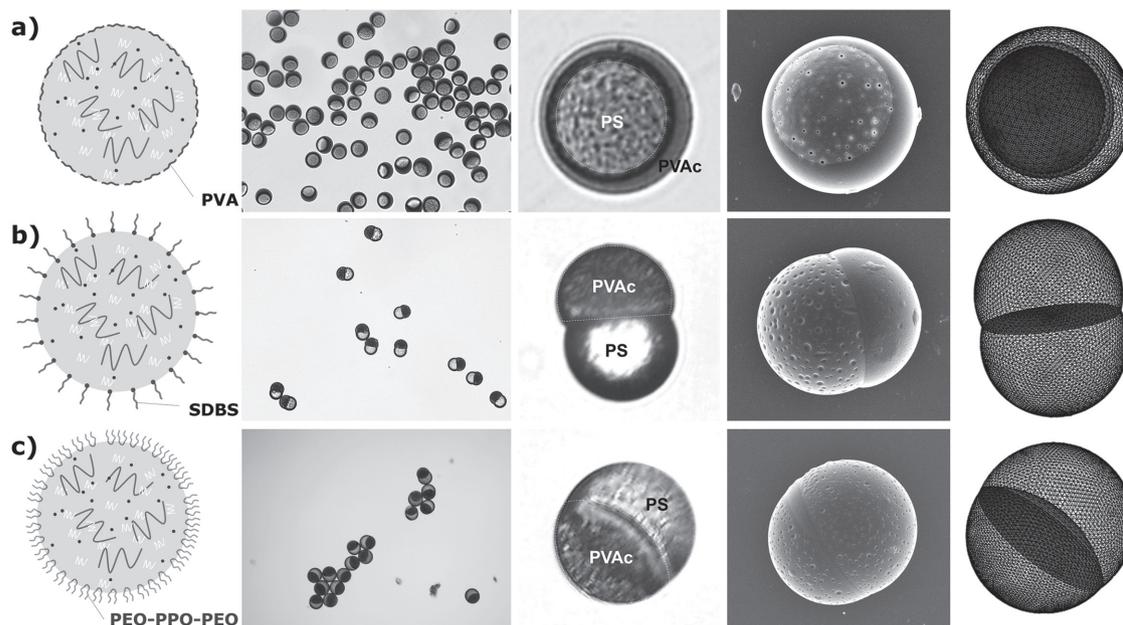
The shape of microparticles is dictated by minimum interfacial energy which is contributed from three interfaces:<sup>[32–35]</sup> PS-rich compartment/continuous phase (PS/C), PVAc-rich compartment/continuous phase (PVAc/C), and PS-rich compartment/PVAc-rich compartment (PS/PVAc). Surfactants in the continuous phase alter the interfacial tensions of the two outer surfaces,  $\gamma_{PS/C}$  and  $\gamma_{PVAc/C}$ , while no influence on the tension of inner interface,  $\gamma_{PS/PVAc}$ . Therefore, the shape of microparticles can be adjusted according to the selection of surfactants.<sup>[21]</sup> To study the influence, we use three different surfactants that are PVA, SDBS, and PEO-PPO-PEO triblock-copolymer.

When PVA is dissolved in the continuous phase, emulsion drops evolve to the microparticles that have PS-rich core partially covered by PVAc-rich shell, as shown in optical microscope and SEM images of Figure 2a. The core has two convex surfaces with different curvatures. The outer surface has a curvature comparable to that of the outer surface of the PVAc-rich compartment, and the inner interface has a larger curvature. This shape of microparticles is modeled with a Surface Evolver as shown in the last panel of Figure 2a.<sup>[36]</sup> The volumes of two compartments are set to be same and values of  $\gamma_{PS/C}$  and  $\gamma_{PVAc/C}$  relative to  $\gamma_{PS/PVAc}$  are set to 2.76 and 1.78, respectively; these values are set to satisfy Neumann's vector relation along triple line, at which three angles between interfaces are measured from optical microscope images. Relatively high interfacial tension at the surface of the hydrophobic PS-rich compartment in the aqueous surrounding causes the partial embedding of the PS-rich core into the PVAc-rich compartment with relatively low tension to minimize total interfacial energy. Spreading parameter for the PVAc-rich compartment,  $S_{PVAc}$ , can be expressed as<sup>[35]</sup>

$$S_{PVAc} = \gamma_{PS/C} - (\gamma_{PVAc/C} + \gamma_{PS/PVAc}) \quad (1)$$

The value of  $S_{PVAc}/\gamma_{PS/PVAc}$  is -0.02, which is weakly negative, yielding incomplete shell on the core. The microparticles composed of a core and incomplete shell are incongruent to be utilized as color pigments due to the large difference in surface areas of distinct compartments. To achieve a clear optical contrast between two states of microparticle orientation, two compartments should have comparable surface areas.

The use of surfactants that reduce the interfacial tension between the PS-rich compartment and the continuous phase can lead to the dewetting of the PVAc-rich compartment by decreasing the spreading parameter. Therefore, the surface areas of two compartments can be comparable. When SDBS is used as a surfactant instead of PVA, emulsion drops evolve to dumbbell-shaped Janus



**Figure 2.** a) A set of the cartoon, OM images, SEM image, and Surface Evolver model for a microparticle composed of core and incomplete shell templated by toluene drops containing PS and PVAc in the continuous phase of aqueous PVA solution. b,c) The same sets of data for dumbbell-shaped microparticles prepared with the aqueous solution of SDBS (b) and acorn-shaped microparticles prepared with the aqueous solution of PEO-PPO-PEO triblock-copolymer (c).

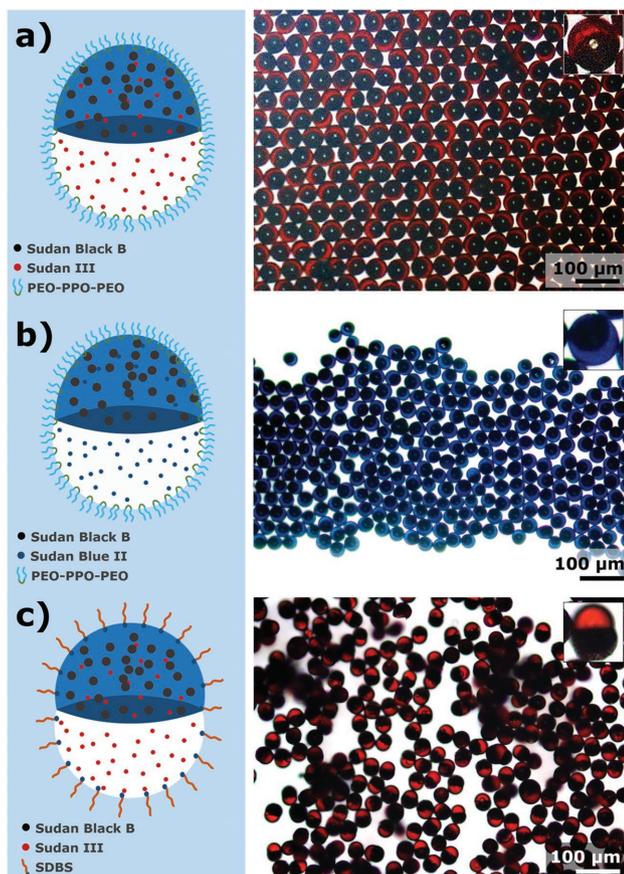
microparticles composed of two bulbs with similar size, as shown in Figure 2b. Shape modeling with a Surface Evolver yields values of  $\gamma_{PS/C}/\gamma_{PS/PVAc}$  and  $\gamma_{PVAc/C}/\gamma_{PS/PVAc}$  as 1.81 and 1.76, respectively. The value of  $\gamma_{PS/C}$  significantly decreases from that of the PVA-stabilized surface, whereas the value of  $\gamma_{PVAc/C}$  slightly decreases. This reduction is attributed to stronger adsorption of SDBS at the interface between the PS-rich compartment and continuous phase than PVA. Amphiphilic SDBS composed of a hydrophobic dodecylbenzene group and hydrophilic sulfonate group usually shows higher interfacial activity than PVA composed of a single component with intermediate affinity. The value of  $S_{PVAc}/\gamma_{PS/PVAc}$  is  $-0.95$ , which is close to  $-1$ , resulting in the significant dewetting of PVAc-rich compartments. The small difference in values of  $\gamma_{PS/C}$  and  $\gamma_{PVAc/C}$  results in the two compartments with comparable surface areas.

The dumbbell-shaped Janus microparticles can exhibit two distinct states of orientation. Nevertheless, the dumbbells are aspherical, which experiences high resistance for rotation. To further engineer Janus microparticles to be spherical, we use PEO-PPO-PEO triblock-copolymer as a surfactant in the continuous phase. The emulsion drops in the aqueous solution of the surfactant evolve to Janus microparticles with high sphericity, as shown in Figure 2c. The PVAc-rich compartment has a convex inner interface, whereas the PS-rich compartment has a concave inner interface; the microparticles are acorn-like. Two compartments have similar sizes of the outer surfaces. The modeling

with a Surface Evolver yields values of  $\gamma_{PS/C}/\gamma_{PS/PVAc}$  and  $\gamma_{PVAc/C}/\gamma_{PS/PVAc}$  as 1.07 and 1.73, respectively. The value of  $\gamma_{PS/C}$  is even smaller than that of  $\gamma_{PVAc/C}$ , thereby resulting in the partial engulfing of the PVAc-rich compartment in the PS-rich compartment, despite a low level. The value of  $S_{PVAc}/\gamma_{PS/PVAc}$  is  $-1.66$ , which is smaller than  $-1$ . The polymer surfactant that has two hydrophilic PEO blocks and one hydrophobic PPO block provides a higher reduction of the interfacial tension between the PS-rich compartment and continuous phase than SDBS.

### 3.4. Bicolored Janus Microparticles

The microparticles prepared by phase separation between PS and PVAc in the presence of Sudan black B possess two compartments of the black PVAc-rich compartment and transparent PS-rich compartment. The transparent compartments get colored by additionally dissolving dyes in the emulsion drops. For example, Janus microparticles prepared from the polymer solution containing both Sudan black B and Sudan III possess black and red compartments respectively, as shown in Figure 3a, where PEO-PPO-PEO triblock-copolymer is used as the surfactant. Sudan III has an intermediate affinity to PS and PVAc, thereby staining both compartments. Nevertheless, the PVAc-rich compartments get black because Sudan black B stains them. In the same manner, the PS-rich compartments can be blue-colored by dissolving Sudan Blue II in the polymer solution before preparation of emulsion



**Figure 3.** a) Cartoon and OM image of acorn-shaped Janus microparticles composed of black and red compartments. Sudan black B and Sudan III are used as staining dyes, and PEO-PPO-PEO triblock-copolymer is used as a surfactant. b) Cartoon and OM image of acorn-shaped Janus microparticles composed of black and blue compartments, where Sudan Blue II is used, instead of Sudan III. c) Cartoon and OM image of dumbbell-shaped Janus microparticles composed of black and red compartments, where SDBS is used, instead of PEO-PPO-PEO triblock-copolymer.

drops as shown in Figure 3b. When SDBS is used as a surfactant, dumbbell-shaped microparticles composed of two different colored compartments are produced, as shown in Figure 3c.

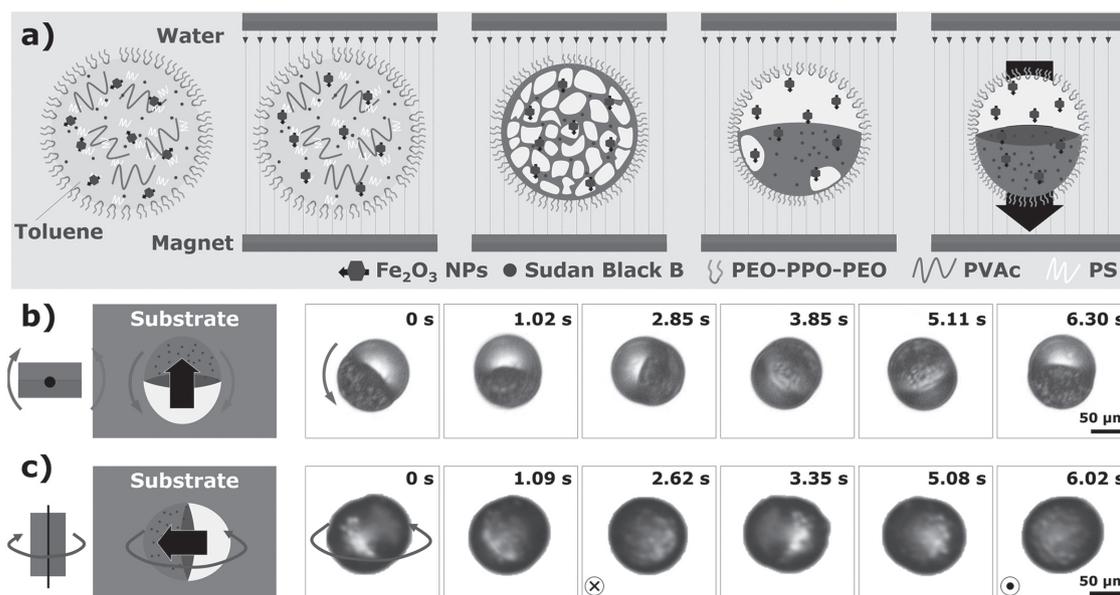
### 3.5. Janus Microparticles with Magnetic Anisotropy

The Janus microparticles with optical anisotropy can be further rendered to have magnetic anisotropy. The orientation of such microparticles can be controlled by external magnetic field, thereby enabling the color switching. To make the Janus particles to have a magnetic moment, weakly ferromagnetic iron oxide nanoparticles are dispersed in the polymer solution before preparation of emulsion drops. To align the magnetic nanoparticles within the microparticles, a pair of magnetic disks is used to

sandwich the drops during the consolidation, as shown in Figure 4a. The pair of magnets forms unidirectional magnetic fields in between them, thereby aligning the magnetic nanoparticles in the drops along the field direction. The magnetic nanoparticles aligned along the external field are captured in the consolidated matrix of both the PS-rich and PVAc-rich compartments, providing a net magnetic moment.<sup>[37,38]</sup> Therefore, the Janus microparticles align along the direction of the external magnetic field, and their rotational motion can be controlled by manipulating the direction of the field. When a magnet is rotated along the axis perpendicular to the substrate, the microparticles rotate along the vertical axis at fixed position, while maintaining the direction of net magnetic moment parallel to the substrate, as shown in Figure 4b and the first part of Movie S2 of the Supporting Information. When the axis of magnet rotation is set to be parallel to the substrate, the microparticles rotate along the horizontal axis, as shown in Figure 4c and the second part of Movie S2 of the Supporting Information. This rotational motion entails translational motion due to coupling between the rotating microparticles and the stationary substrate. The water film between the microparticles and substrate leads to low coupling efficiency and small displacement.<sup>[38]</sup> This control of microparticle motion is difficult to achieve if the Janus microparticles only have an uneven spatial distribution of magnetic nanoparticles without alignment. The Janus microparticles with optical and magnetic anisotropy are potentially useful for Gyration display operated by a magnetic field.

## 4. Conclusions

In this work, we produce monodisperse Janus microparticles with optical and magnetic anisotropy through phase separation of PS and PVAc confined in emulsion drops. A dye molecule of Sudan black which has higher affinity to PVAc than PS spontaneously migrates into the PVAc-rich domains during the phase separation, thereby rendering the resulting Janus microparticles to be optically anisotropic. In addition, magnetic nanoparticles dispersed in the emulsion drops are aligned by the external magnetic field during the consolidation of drops, which are finally embedded in the polymer matrix, providing a net magnetic moment on the microparticles. Therefore, the orientation of the Janus microparticles with optical anisotropy can be controlled by manipulating the direction of the external magnetic field. The shape of the microparticle can be exclusively selected from three different structures of the core-incomplete shell, dumbbell, and acorn, according to surfactants. The color of the PS-rich compartments can be changed by dissolving dye molecules in the polymer



**Figure 4.** a) Series of cartoons showing the formation of magneto-responsive bicolored Janus microparticle. Magnetic nanoparticles are aligned by the external magnetic field during the phase separation and consolidation, which yields a net magnetic moment on the resulting microparticles. (b) Cartoon and series of OM images showing the rotational motion of Janus microparticles along the vertical axis at fixed position, where a magnet is rotated along the axis perpendicular to the substrate. (c) Cartoons and series of OM images showing the rotational motion of Janus microparticles along the horizontal axis, where a magnet is rotated along the axis parallel to the substrate. The microparticles migrate during the rotation along the horizontal axis.

solution, while maintaining the black PVAc-rich compartments stained by Sudan black B. This simple approach to produce Janus microparticles through phase separation can be easily scaled up as a homogenous phase is required to be emulsified without the formation of biphasic parallel flow. Moreover, there is no limitation on the selection of polymer pairs responsible for phase separation. We believe that our simple but versatile approach is beneficial for the production of various Janus microparticles, including bicolored particles for Gyricon display, microcarriers for controlled release of drugs, and many others.

## Supporting Information

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

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