We report a simple and practical method for creating colloidal patchy particles with a variety of three-dimensional shapes via the evaporation-induced assembly of polystyrene- \textit{b}-poly(4-vinylpyridine) (PS-\textit{b}-P4VP) block copolymer (BCP) in an oil-in-water emulsion. Depending on the particle volume, a series of patchy particles in the shapes of snowmen, dumbbells, triangles, tetrahedra, and raspberry can be prepared, which are then precisely tuned by modulating the interfacial interaction at the particle/water interface using a mixture of two different surfactants. Moreover, for a given interfacial interaction, the stretching penalty of the BCPs in the patchy particles can be systematically controlled by adding P4VP homopolymers, which decreases the number of patches of soft particles from multiple patches to a single patch but increases the size of the patch. Calculations based on the strong segregation theory supported the experimental observation of various soft patchy particles and identified the underlying principles of their formation with tunable 3D structures.
both directional and reversible interactions of the particles with binding specificity and high levels of homogeneity are required. Therefore, it is urgent and important to develop a facile and scalable route to achieve patchy particles with tunable but predictable morphologies.

Due to their ability to self-assemble into various periodic structures, block copolymers (BCPs) have been extensively used as powerful building blocks for designing novel nanostructures.31–38 Interestingly, confining BCPs within emulsion particles can generate unconventionally structured particles with various internal structures and allow the size of the particles to be tuned, ranging from less than 100 nm to larger than 5 μm in size.39–44 Their morphological behaviors depend strongly on (1) the interfacial interaction between the BCP particle and the surrounding medium45 and (2) the stretching/bending penalty of BCP chains driven by the spatial confinement effect.46–49 In particular, the contributions of the interfacial interaction and bending energy of BCP chains to the phase behavior of BCPs and the shape variations of the particles will be amplified significantly if the confined volume becomes sufficiently small (i.e., the diameter of the particle becomes comparable to the periodicity of the BCPs). Indeed, small patchy particles of relatively short BCPs confined within emulsion droplets were very recently reported.50 Also, dual surfactants that spatially segregate at the interface may be used to precisely and systematically control interactions at the desired positions of the BCP particles. This ability to control interactions makes the approach of confining BCPs within small droplets particularly useful for producing the particles with precisely tuned three-dimensional geometries.

Herein, we report a simple and robust method for fabricating a series of patchy particles by confining polystyrene-β-poly(4-vinylpyridine) (PS-b-P4VP) in a very small volume through the oil-in-water emulsion technique. Patchy particles with different geometric structures, such as snowman, dumbbell, triangular, tetrahedron, and raspberry-shaped structures, can be controllably generated, depending on the volume of the particles. To elucidate the thermodynamic mechanism for the formation of the diverse patchy structures, we calculated the total free energy of the patchy particles as a function of particle volume and geometric structure based on strong segregation theory. Our calculations indicated that the geometric structures of the patchy particles were strong functions of particle volume, and that the particle’s structure could be determined by the balance between the interfacial interactions and the stretching penalty of the BCP chains in the particles. We performed a series of experiments to confirm the critical roles of these two factors in determining the structure and shape of the patchy particles. First, we explored the effect of the interfacial interaction at the particle surface/water by using a mixture of two different surfactants that had different affinities for each block. In the second set of experiments, we investigated the effect of the stretching penalty of the BCP chains by adding different amounts of P4VP or PS homopolymers, which tuned the stretching penalty of BCP chains at a given particle volume. These results demonstrated the versatility of our method in controlling the three-dimensional geometries of patchy particles.

RESULTS AND DISCUSSION

Figure 1 schematically describes the creation of various forms of patchy particles of PS-b-P4VP using oil-in-water emulsion through (i) encapsulation, (ii) evaporation, and (iii) reorganization. A 1 wt % chloroform solution of symmetric PS-b-P4VP BCPs (the molecular weight \(M_n\) = 399 kg/mol, P4VP volume fraction \(f_{P4VP}\) = 0.5, polydispersity index (PDI) = 1.09) was emulsified into the aqueous surfactant solutions (cetyltrimethylammonium bromide (CTAB), 0.5 wt %) using a homogenizer. Subsequent slow evaporation of the chloroform led to the formation of BCP particles in water. The size of the particles was limited to less than 300 nm, which was controlled by adjusting the rotation speed in the homogenizer and the centrifugation conditions.
The size distribution and morphology of the PS_{195k}-b-P4VP_{204k} particles were investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images, as shown in Figures 1 and 2a. The P4VP domains appear as dark regions due to the selective staining of the P4VP chains by iodine vapor. The particles had a relatively broad range of sizes from 100 to 300 nm, and the average size was about 200 nm, which was comparable to the domain spacing (~130 nm) of the PS_{195k}-b-P4VP_{204k} polymers in bulk. Interestingly, various types of patchy particles were observed with different numbers of P4VP hemispheres (n), ranging from 1 to more than 6. Snowman-like geometry (n = 1), which consisted of one PS hemisphere and one P4VP hemisphere, was obtained for the smallest particles. When the particle size was increased, a dumbbell-like structure (n = 2) was produced with two P4VP hemispherical patches on the opposite sides. For the larger particles, the number of P4VP domains increased, and the bonding angles between the P4VP domains decreased. For example, the triangular particles (n = 3) contained three P4VP patches arranged with an angle of 120°, and four patches were formed on the tetrahedron-like particles (n = 4) with a bonding angle of 109.5°. The particles with n greater than 4 were also produced, which we categorized them as raspberry-like particles (Supporting Information (SI) Figure S1).

The formation of these unique patchy structures of BCP particles can be ascribed to the structural reorganization of PS-b-P4VP micelles and their sequential assembly during solvent evaporation inside the BCP emulsion droplet.\(^54,55\) First, micelles of P4VP cores/PS shell (SI Figure S2) form within the chloroform droplet because chloroform is a more selective solvent for PS, based on the consideration that the solubility parameter of PS (18.6 MPa\(^{1/2}\)) is closer to the solubility parameter of chloroform (19.0 MPa\(^{1/2}\)) than to that of P4VP (22.5 MPa\(^{1/2}\)).\(^55\) Therefore, at this stage, the PS chains were more extended than the P4VP chains in the droplet. Next, the chloroform slowly evaporated through water, reducing the volume of the droplet, and the three-dimensional confined assembly of PS-b-P4VP occurred. As the chloroform evaporated, the P4VP chains swelled preferentially toward the particle/water interface because the hydrophilic P4VP chains have a stronger affinity for water than the nonpolar PS chains. This interfacial interaction between the BCP chains and the surrounding medium (water) in our small-sized particles became very important due to the extremely large surface-to-volume ratio of the particles. Therefore, the strong interaction between the P4VP chains and water facilitated the formation of P4VP hemispheres near the surface of the BCP particles, similar to the previously reported raspberry-like particles.\(^54–56\)

To gain a deeper insight into the formation of the patchy particles, we obtained the statistics for the volume of the BCP particles (Figure 2b). The volume of more than 500 particles (such as the ones shown in Figure 2a) was calculated based on the integral equations for cut spheres using the lengths and angles obtained from the TEM images (see eqs 1–4 in the SI for details). To calculate the volume of each particle, we assumed that the shape of the patchy particles was the sum of cut spheres composed of one PS sphere and n (n = 1, 2, 3, 4) P4VP spheres with the same diameter. The statistical distributions for the particle volume are denoted by different colors, depending on the shape of the particles: red (n = 1), green (n = 2), blue (n = 3), and purple (n = 4). It should be noted that the distribution of each structure was strongly dependent on the volume of each particle. The average volumes of the particles were calculated to be 6.9 × 10^5, 1.2 × 10^6, 1.6 × 10^6, and 2.6 × 10^6 nm\(^3\) for n = 1, 2, 3, and 4, respectively, showing a clear increasing trend in the particle volume for larger n value.
Figure 3. (a) Interfacial energy (dots) and stretching energy (lines) of each BCP particle with different geometric structure as a function of the volume of particles. (b) Total free energy (interfacial energy + stretching energy) of each BCP chain in the BCP particle was calculated in terms of the particle volume and the $n$: stable regions of the different particle structures were determined based on $n$ being the minimum free energy. Different colors represent different structures: core–shell (black), $n = 1$, (red), $n = 2$ (green), $n = 3$ (blue), $n = 4$ (purple).

This volume-dependent distribution of the particle shapes can be understood by the calculation of the total free energy of BCP particles, including interfacial energy and stretching energy on the basis of strong segregation theory (SST). SST enables separate calculation of stretching energy and interfacial energy of BCPs with large $\chi N$ (exceeding 100 in this case) from continuous field-based calculations as described in the following equation:

$$\frac{F}{kT} = \frac{3n_{BCP}N^2}{8f_{PS}N^2V_0} \int_0^{V_{PS}} z^2dz + \frac{3n_{BCP}N^2}{8f_{P4VP}N^2V_0} \int_0^{V_{P4VP}} z^2dz$$

$$+ A_{PS/P4VP}\gamma_{PS/P4VP} + A_{PS/water}\gamma_{PS/water}$$

$$+ A_{P4VP/water}\gamma_{P4VP/water}$$

where $f_{PS}$ and $f_{P4VP}$ are the relative volume fractions of the PS and P4VP blocks, respectively, $V = V_{PS} + V_{P4VP}$ is the total volume of particle, $A_{PS/P4VP}$ is the interfacial area between the two blocks, $A_{PS/water}$ is the total interfacial area between the PS domain and water, $A_{P4VP/water}$ is total interfacial area between the P4VP domain and water, $\gamma_{PS/P4VP}$ is the interfacial tension between two blocks, $\gamma_{PS/water}$ and $\gamma_{P4VP/water}$ are interfacial tensions between water and each block, respectively, $n_{BCP}$ is the number of BCP chains per particle, $N$ is the degree of polymerization, $a$ is monomer length, and $z$ is the distance from the interface between two blocks (see the SI for calculation details).

In this system, each block has a different value of interfacial tension with aqueous media, and these values are critical for determining the overall morphology of the BCP particles. Since the particle has phase boundaries between three different phases (PS, P4VP, and water), the difference in the interfacial energy between each block and water ($\gamma_{PS/water} - \gamma_{P4VP/water}$) cannot exceed the value of $\gamma_{PS/P4VP}$. Also, for the case of $\gamma_{PS/water} > 1.5\gamma_{PS/P4VP}$ or $\gamma_{P4VP/water} > 1.5\gamma_{PS/P4VP}$, a thermodynamically stable assembled structure could not be found for the particles with $n = 3$ and $n = 4$. In this manner, we modeled two different interfacial tensions of $\gamma_{PS/water}$ and $\gamma_{P4VP/water}$ to be comparable to that between PS and P4VP ($0.7\gamma_{PS/P4VP} < \gamma_{PS/water} < 1.5\gamma_{PS/P4VP}$ and $0.7\gamma_{PS/P4VP} < \gamma_{P4VP/water} < 1.5\gamma_{PS/P4VP}$).

Figure 3a indicates the interfacial energy (dot) and the stretching energy (line) of different $n$ values of BCP particles as a function of the volume of the particles. First, the interfacial energy generally increased for particles with a larger volume due to the increase of the surface area of the particle. However, the particles with higher $n$ (from $n = 1$ to $n = 4$) had higher interfacial energy at a given particle volume due to the increased number of P4VP patches and, thus, the larger total interfacial area with the water (Figure 3a). In addition, we calculated the free energies of core/shell structured particles, in which P4VP entirely covers the PS region. However, the core/shell particle was more unstable than any of the other structures for the entire range of the particle volumes due to the maximized interfacial energy between the PS and P4VP domains, which explains why we did not observe any PS/P4VP core/shell particle. On the other hand, the stretching energy also increased as the volume of the particle increased, but the extent of the increases was quite different depending on the particle’s $n$ values (i.e., the stretching energy for the particles with $n = 1$ increased much more rapidly than that for the particles with other $n$ values when the volume of the particles increased). Based on these two contributions to the free energy, the total free energy (interfacial energy + stretching energy) of the BCP particle was calculated in terms of the particle volume and $n$, and then it was normalized by the number of the BCP chains in each particle ($n_{BCP}$), as shown in Figure 3b. The curve had the lowest value of free energy at a certain volume of particles, corresponding to the most stable structure. The regions of the most stable structure were divided in the order of $n = 1, 2, 3,$ and $4$ as the volume of the particles increased, which was in excellent agreement with the statistics of the experimental results in Figure 2b.
To elucidate the effects of interfacial and stretching energies on particle structure, we attempted to tune these two factors individually. First, we tuned the interfacial energy between the surface of the BCP particle and the surrounding water by using a mixture of two different CTAB and PVA surfactants with specific preference for each block of the BCP. It is known that CTAB preferentially interacts with PS over P4VP due to its hydrophobic alkyl chains. In contrast, poly(vinyl alcohol) (PVA) has a hydroxyl group, which has a strong affinity with the nitrogen atoms in the P4VP chains. Therefore, by mixing PVA and CTAB surfactants with different weight ratios (1:0, 1:1, and 1:4), we were able to systematically control the interfacial interactions between the BCP particles and the aqueous media. Figure 4d and Figure S3b show the patchy particles stabilized by CTAB and PVA in a ratio of 1:1. The average volume for each structure was less than the volume of the particles stabilized by only CTAB (CTAB/PVA = 1:0, shown in Figure 4b). This trend...
was clearly observed as the ratio of PVA was increased in the CTAB/PVA mixture (i.e., CTAB/PVA = 1:4 as shown in Figure 4f). While the average volume of tetrahedron-shaped particles \( n = 4 \) in Figure 4b \((V_{n=4|1.0}, \text{CTAB/PVA} = 1:0)\) was 2.6 \( \times 10^6 \) nm\(^3\), the volume of particles in Figure 4d \((V_{n=4|1.1}, \text{CTAB/PVA} = 1:1)\) decreased to 2.2 \( \times 10^6 \) nm\(^3\). This value decreased further to 1.5 \( \times 10^6 \) nm\(^3\), in the case of Figure 4f \((V_{n=1.4}, \text{CTAB/PVA} = 1:4)\). For the snowman-like particles \((n = 1)\), the average volume also decreased as the ratio of PVA increased \((0.69 \times 10^6, 0.54 \times 10^6, \text{and} 0.48 \times 10^6 \) nm\(^3\) for the CTAB/PVA ratios of 1:0, 1:1, and 1:4, respectively). Interestingly, the amount of the decrease in the particle volume relative to the CTAB/PVA ratio was different for each structure. The difference in the average volumes of \( n = 4 \) particles \((\Delta V = V_{n=4|1.0} - V_{n=4|1.4})\) at two different CTAB/PVA ratios of 1:0 and 1:4 was significantly larger for that of \( n = 1 \) particles \((\Delta V = V_{n=1|1.0} - V_{n=1|1.4})\), producing a much narrower region for the intermediate \( n \) values (i.e., \( n = 2 \) and 3) (Figure 4b,4d). In addition, we observed a larger fraction of the patchy particles for higher \( n \) in the case of CTAB/PVA = 1:4. This trend was observed consistently for other samples such as 1:2 and 2:1 (Figure S3).

This variation of the particle morphology driven by a mixture of surfactants can be clearly explained by the results of the SST calculations. We calculated the free energy of the patchy particles stabilized by CTAB and PVA with different weight ratios of 1:0, 1:1, and 1:4 (Figure 4c,e,g). To simulate this condition, we applied different values of \( \gamma_{PS/water} \) and \( \gamma_{P4VP/water} \) for different CTAB/PVA ratios: 1.1 \( \gamma_{PS/P4VP} \) and 0.9 \( \gamma_{PS/P4VP} \) for CTAB/PVA = 1:1, and 1.2 \( \gamma_{PS/P4VP} \) and 0.8 \( \gamma_{PS/P4VP} \) for CTAB/PVA = 1:4. The calculated transition points of particle volume with \( n = 1 \) to 2 \((V_{12})\) were 0.78 \( \times 10^6, 0.75 \times 10^6, \text{and} 0.61 \times 10^6 \) nm\(^3\) for the CTAB/PVA ratios of 1:0, 1:1, and 1:4, respectively. Thus, the boundaries between the stable regions for each different \( n \) shifted to the left (toward the smaller particle volume). For example, for the transition point between \( n = 1 \) and 2, the difference between \( V_{12}(1:0) \) and \( V_{12}(1:4) \) was calculated to be 0.17 \( \times 10^6 \) nm\(^3\). In contrast, the transition points of \( n = 3 \) to 4 \((V_{34})\) found to be 1.65 \( \times 10^6, 1.42 \times 10^6, \text{and} 0.99 \times 10^6 \) nm\(^3\) for the CTAB/PVA ratio of 1:0, 1:1, and 1:4, respectively, producing a much larger difference of 0.66 \( \times 10^6 \) nm\(^3\) between \( V_{34}(1:0) \) and \( V_{34}(1:4) \). Thus, the regions in terms of the particle volume for \( n = 2 \) and 3 became significantly more narrow as the ratio of PVA was increased. The simulation results were in excellent agreement with the experimental observations in Figure 4b,4d. This is because particles with a higher \( n \) value have a larger surface area at a given volume, and thus, they had a much substantial decrease in interfacial energy than the particles with lower \( n \) value when the CTAB/PVA ratio is increased. Our results suggested that the tuning of interfacial energy affected the volume distribution of the particle in a batch as well as the geometric structure of the patchy particles at a given particle volume, providing an effective means of controlling the structure of patchy particles.

Next, we explored the effect of the stretching penalty of the BCP chains on the morphology of the patchy particles. The stretching penalty of BCP chains at a given particle volume can be reduced by adding P4VP homopolymers (hP4VP), which selectively swell the P4VP domains of the BCPs. Therefore, the contribution from interfacial interaction at the particle surface and water will be more dominant. To verify our hypothesis, we added different amounts of hP4VP chains to the symmetric PS-b-P4VP BCPs and fabricated a series of patchy particles using the same procedure. Figure 5b–e shows PS-b-P4VP/hP4VP patchy particles with various P4VP volume fractions \( (f_{P4VP}) \) ranging from 0.53 to 0.85. When hP4VP homopolymers were added and the \( f_{P4VP} \) was increased, the size of the P4VP domain was increased significantly. While the increase in the P4VP domain size certainly was expected for larger \( f_{P4VP} \) values, it was remarkable that only two types of particles (snowman-like and dumbbell-like particles) were observed, as presented in Figure 5d \( (f_{P4VP} = 0.73) \), which shows stark contrast to the case \( (f_{P4VP} = 0.50) \) in which there was no addition of hP4VP chains showing various structures of patchy particles. For even larger \( f_{P4VP} = 0.85 \), all of the particles in Figure 5e had the snowman structure \((n = 1)\), and no particle with a higher \( n \) value was found. Therefore, the average volume of the snowman-like particles was increased dramatically, from 7.5 \( \times 10^5 \) to 2.3 \( \times 10^6 \) nm\(^3\), as the \( f_{P4VP} \) value increased from 0.53 to 0.85 (Figure 5f). When hP4VP chains were added to the BCP domains, the hP4VP swelled the P4VP domains of BCPs, but they located preferentially outside of the P4VP blocks (far from the PS/P4VP interface) to relieve the stretching penalty of the microphase-separated BCPs. Also, SST calculations predicted that the reduction in the stretching penalty by the addition of hP4VP chains was more significant for the particles with lower \( n \) values. Therefore, our calculations explain that the stable region of particles with \( n = 1 \) for higher \( f_{P4VP} \) values should be widened in terms of the particle volume fraction. In contrast to the case of adding P4VP homopolymers, the addition of PS homopolymers generated the opposite results, favoring the production of patchy particles with higher \( n \) values (SI Figure S4). When the PS homopolymers were added, they located preferentially in the PS domain at the center of the particles, which was distant from the PS/P4VP interface. In this case, the stretching penalty of the BCP chains can be reduced more effectively by adopting a geometric structure with higher \( n \) values. Therefore, both the size and the number of P4VP hemispheres could be tuned precisely by controlling the amount of homopolymers, which modified the...
stretching penalty of the BCPs. Interestingly, these patchy particles of BCPs with tunable structures would be very practical in various fields because the P4VP parts of the particles can load various biological and chemical reagents, making the particles useful for drug delivery, nanoreactors, and molecule carriers. As an example, metal-loaded hybrid BCP particles were demonstrated by selectively loading Au nanoparticles in the P4VP domains (SI Figure S5).

CONCLUSIONS

In summary, we developed a convenient and effective method for producing soft PS-b-P4VP patchy particles with controlled geometries using oil-in-water emulsions. The geometric variations on the patchy-type nanostructures (such as snowman, dumbbell, triangle, tetrahedron, and raspberry-shaped particles) were observed as a function of the particle volume, which was clearly explained by SST calculations. We confirmed that the particles’ structural geometries can be precisely controlled by tuning their interfacial energy and stretching energy, which were achieved by varying the surfactant ratio or adding different amounts of homopolymer chains, respectively. In addition, the domains of patchy particles can be selectively hybridized by metal nanoparticles to enhance the anisotropic functionality of the particles. We believe that this study elucidates the formation mechanism of BCP-based patchy particles and opens new opportunities for various applications based on highly functional and structurally tunable colloidal particles.

EXPERIMENTAL SECTION

Fabrication of PS-b-P4VP Particles. The PS-b-P4VP copolymers ($M_n = 399$ kg/mol, $f_{P4VP} = 0.5$, PDI = 1.09 from Polymer Sources Inc.) were dissolved in chloroform to produce a 1 wt % polymer solution. The polymer solution (0.15 mL) was emulsified in deionized (DI) water (2 mL) containing 0.5 wt % of CTAB using a homogenizer for 2 min at 25 000 rpm. The organic solvent was slowly evaporated at room temperature for 2 days. Then, the sample was washed with DI water to remove the large excess of remaining surfactants by repeated centrifugation. To filter large particles whose diameter is larger than 500 nm, the centrifugation was performed at 3000 rpm first, and then, the supernatant were centrifuged at 12 000 rpm for 10 min. To control the interfacial property, 0.5 wt % of PVA aqueous solution was mixed with CTAB solution at various weight ratios (i.e., 4:1, 2:1, 1:1, 1:2, and 1:4) and used to emulsify the polymer solution.

Fabrication of PS-b-P4VP Particles with Addition of Homopolymer. Homopolymer P4VP ($M_n = 36$ kg/mol) was independently dissolved in chloroform to produce a 1 wt % polymer solution. Various amounts of homopolymer solution were mixed with the
Fabrication of Hybrid PS-b-P4VP Particles with Au NPs. An precursor (HAuCl4, 3H2O, Aldrich) solution was added to the dispersion of PS-b-P4VP particles in a 1:1 molar ratio with the P4VP units. The mixture was stirred for 24 h. The mixture was then purified by washing with DI water and repeated centrifugations at 12,000 rpm for 10 min.

Characterization. Field-emission SEM (Hitachi S-4800) and TEM (JEOL 2000 FX) were used to observe the surface and internal structures of the BCP particles. The samples were prepared by drop-casting BCP particle suspensions onto silicon wafers and TEM grids coated with a 20 nm thick carbon film. The prepared samples were exposed to iodine vapor to selectively stain the P4VP domains of PS-b-P4VP particles.

Calculation Method. We calculated total interfacial energy, stretching energy of the particle, and free energy of single chain as a function of particle volume based on the SST method. Calculation details are described in the Supporting Information.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.5b05058.

Details of the calculation, volume equations for the soft patchy particles with various structures, and additional supporting TEM images (PDF)

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REFERENCES AND NOTES
