Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information for:

The Intriguing Ordering and Compatibilizing Performance of Janus Nanoparticles with Various Shapes and Different Dividing Surface Designs in Immiscible Polymer Blends

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[Content]

1. Idendification of phases and phase boundaries

To identify different phases and determine the transitions between them, besides a direct view of various structures, several structural properties are analyzed. Among these, the compositional (collective) structure factor $S(\mathbf{k})$ is defined as[1,2],

$$S(\mathbf{k}) = \left\langle [\sum_j \exp(i\mathbf{k}\cdot\mathbf{r}_j) f(\varphi_j)]^2 \right\rangle / m^3 \quad \text{(s1)}$$

where $f(\varphi_j)$ is the concentration fluctuation, $f\left(\varphi_j(r,t)\right) = \varphi_B^j - \varphi_A^j - \left\langle \varphi_B^j - \varphi_A^j \right\rangle$, m is the number of divided cells in each direction and is set as m=20, and $\langle\ \rangle$ denotes thermal statistical average. The position-correlation structure factor is defined as[3]

$$S_J(\mathbf{k}) = \frac{1}{N_J} \sum_{i=1}^{N_J} \exp[i\mathbf{k}\cdot\mathbf{r}_i^{cm}(t)] \quad \text{(s2)}$$

where N_J represents the number of Janus nanoparticles in system, and $\mathbf{r}_i^{cm}(t)$ is the position of the center of mass of Janus nanoparticle i at time t.

As mentioned in the main text, symmetric binary polymer blends with the addition of Janus nanoparticles may form a bicontinuous microemulsion-like ($B\mu E$) phase under appropriate conditions. To identify $B\mu E$ phase, the spherically averaged compositional structure factor $S(k)$ is fitted by the T-S equation, which is derived by Teubner and Strey on the basis of phenomenal Landau theory and defined as follow[4],

$$S(k) \sim \frac{1}{a_2 + c_1 k^2 + c_2 k^4}. \quad \text{(s3)}$$

For bicontinuous microemulsions, the fitting parameters a_2, c_1 and c_2 in the T-S equation meet with criteria of "a_2>0, c_1<0, c_2>0, and $4a_2c_2$-c_1^2>0, -1< $c_1/(4a_2c_2)^{1/2}$<0".

Figures S1 show the snapshots and the corresponding **s**tructure factors for characteristic phases selected from the ternary systems in our simulations. In the phase-separated 2P state, as shown in Figure S1 (a), the Janus nanoparticles form two discrete monolayers at the interfaces between two immiscible homopolymer-rich phases due to the periodic boundary conditions. The corresponding spherically

averaged compositional structure factor is given in Figure S1 (d). The peak position (denoted as k^*) in $S(k)$ maintains at its minimum value $2\pi/L$, where $L = \sqrt{L_x^2 + L_y^2 + L_z^2}$, L_x, L_y, and L_z are the box lengths along *x*, *y*, and *z* axes, respectively. Generally the macrophase separation takes place at $k^* = 0$. Finite value

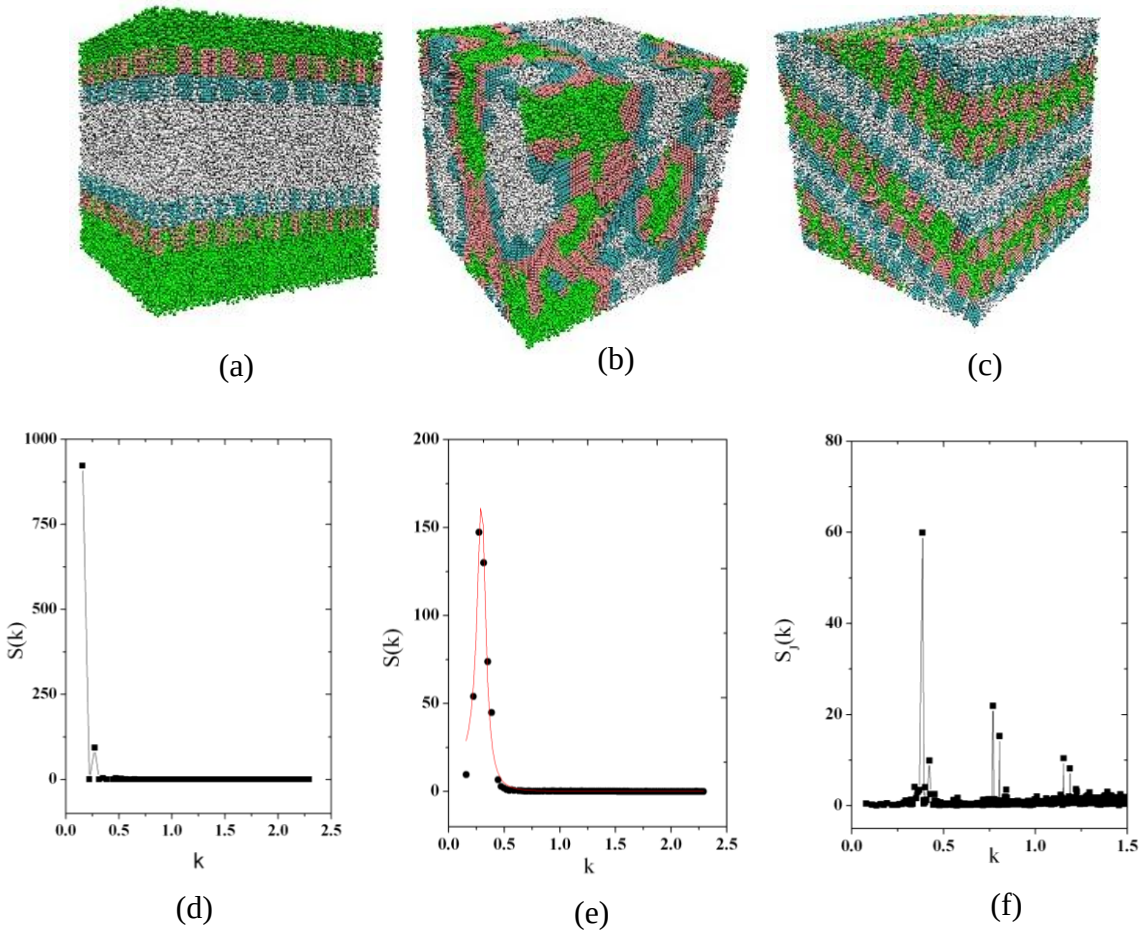


Figure S1. Snapshots for (a) the 2p phase in c1-10-15 system, (b) the $B\mu E$ phase in d1-25-25 system, (c) the LAM phase in c1-30-10 system and the corresponding structure factors. The green, gray, pink, and cyan colors correspond to homopolymers A, homopolymers B, p and q parts of Janus nanoparticles, respectively. Note that the compositional structure factors in (d) and (e) are derived from the phase structures in (a) and (b), respectively, and the position-correlation structure factor in (f) is calculated from the center of mass of Janus particles in (c). Lines are guided for eyes except (e), in which the compositional structure factor data are fitted according to the T-S equation, $S(k) \sim 1/(a_2 + c_1 k^2 + c_2 k^4)$, where fitting parameters are $a_2 = 0.02942$,

$c_1 = -0.61297$, $c_2 = 3.5391$ and thus $4a_2c_2 - c_1^2 = 0.04075$, $c_1/(4a_2c_2)^{1/2} = -0.95$" in (e).

of k^* as shown in Figure S1 (d) is due to the finite system size. For the *BμE* phase, homopolymers A and B form co-continuous interwoven networks and are divided by undulating monolayers formed by Janus nanoparticles. The snapshot in Figure S1 (b) indicates that these monolayers are disorderedly oriented without any long-range order. The compositional structure factor, $S(k)$ in the *BμE* phase exhibits a single peak at $k^* > 2\pi/L$. When it is fitted by the T-S equation, the fitting coefficients fully satisfy the criteria of "a_2>0, c_1<0, c_2>0, and $4a_2c_2$-c_1^2>0, -1< $c_1/(4a_2c_2)^{1/2}$<0", as illustrated in Figure S1(e). In the lamellar phase (LAM), Janus nanoparticles form periodic layers with a long-range order and homopolymers are distributed in the corresponding lamellar layers, as typically shown in Figure S1 (c). Furthermore, the scattering peaks with a position ratio of 1:2:3 on the $S_J(k) \sim k$ curve provide definite evidence that periodic lamellar layers are formed by Janus nanoparticles, as manifested in Figure S1 (f).

The phase boundaries are determined according to structure factors. For example, the transitions between 2P and LAM or between 2P and *BμE* could be mainly fixed by the peak position of spherically averaged compositional structure factor $S(k)$. When the blend is in a macrophase-separated 2P state, k^* stays at its minimum value $2\pi/L$, while in the LAM or *BμE* phase $k^* > 2\pi/L$. Furthermore, the boundary between LAM and *BμE* can be drawn at the point where the spherically averaged compositional structure factor displays a single broad peak and can be fitted by T-S model or the position-correlation structure factor loses the higher-order peaks. Herein, we take a typical ternary system containing "lying" nanorods with different particle volume fractions as an example. As shown in Figure S2, we clearly see that at low particle volume fractions from $\phi_{c2} = 5\%$ to $\phi_{c2} = 12\%$, the peak position k^* is kept

at its minimum value of $2\pi/L$. Upon further increasing the particle volume fraction to $\phi_{c2} = 20\%$ a broad peak suddenly appears at $k^* > 2\pi/L$ and the structure factor is fitted by T-S model well, indicating the transition of 2P to $B\mu E$ in c2-filled systems is located within $\phi_{c2} = 12\%$ ~15% at fixed $a_{Ap} = a_{Bq} = 15$.

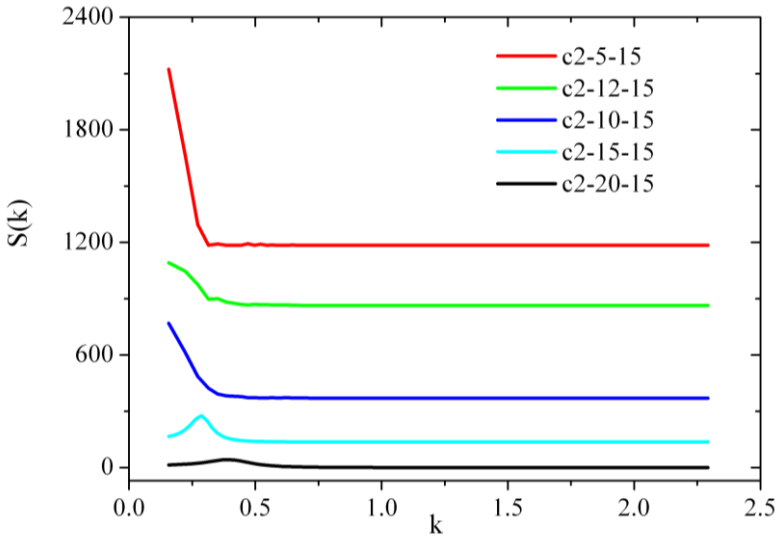
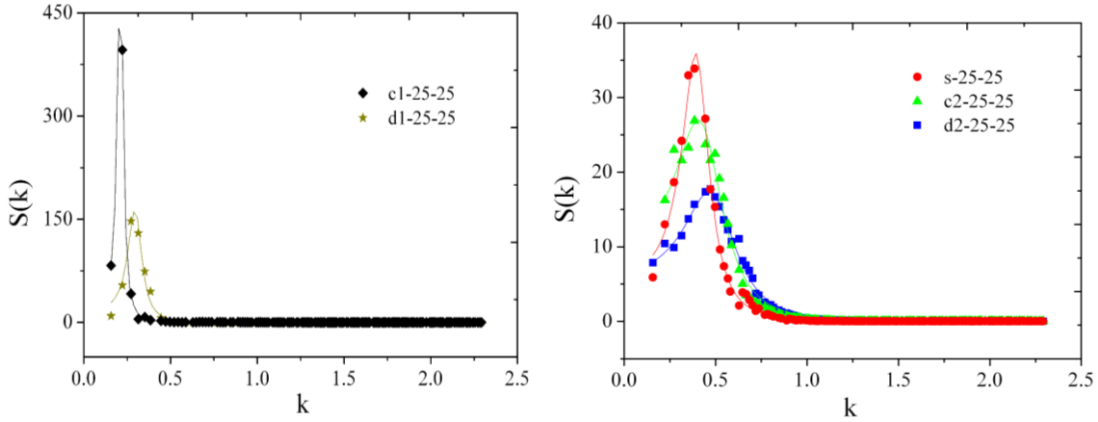


Figure S2. The compositional structure factors $S(k)$ for c2-filled systems with various particle volume fractions at fixed $a_{Ap} = a_{Bq} = 15$. The $S(k) \sim k$ curves are shifted vertically for clarity.

2. The structure factor for the ternary systems containing JNs with various shapes and different dividing surface designs at $\phi_J = 25\%$ and $a_{Ap} = a_{Bq} = 25$

We use the T-S equation in equation (s3) to identify whether the bicontinuous microemulsion structure is formed in the ternary systems containing different types of Janus nanoparticles at $\phi_J = 25\%$ and $a_{Ap} = a_{Bq} = 25$. The compositional structure factors at $t = 4000\tau$ for ternary systems with "standing" particles such as c1-25-25 and d1-25-25, and for systems with "lying" particles or Janus nanospheres such as s-25-25, c2-25-25 and d2-25-25 systems are shown in Figure S3 (a) and (b), respectively. Remarkably, the T-S equation fits all curves very well and the fitting coefficients fully satisfy the criteria of "a_2>0，c_1<0，c_2>0，and $4a_2c_2$-c_1^2>0，-1< $c_1/(4a_2c_2)^{1/2}$<0", confirming that these systems form bicontinuous microemulsion-like

structures.



(a) (b)

Figure S3. The compositional structure factors for (a) ternary systems with "standing" particles, such as c1-25-25 and d1-25-25 systems; (b) ternary systems with "lying" particles or Janus nanospheres, such as c2-25-25, d2-25-25 and s-25-25 systems. The solid lines correspond to the predictions of the T-S equation.

4. Reference

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