Supporting info for: A simple route to fabricate patchy nanoparticle via self-assembly of a multiblock copolymer chain in one step

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1 Definition of $C_{\infty v}$, $D_{\infty h}$, D_{3h} and T_d

Molecular symmetry in chemistry describes the symmetry present in molecules and the classification of molecules according to their symmetry. Molecular symmetry is a fundamental concept in chemistry, as it can predict or explain many of a molecule's chemical properties. The symmetry of a molecule can be described by a set of symmetry elements: [1]

E - the identity operation

$\mathbf{C}_n$ - rotation by $\frac{2\pi}{n}$ angle

$\mathbf{S}_n$ - improper rotation (rotation by $\frac{2\pi}{n}$ angle and reflection in the plane perpendicular to the axis)

σ_h - horizontal reflection plane (perpendicular to the principal axis)

σ_v - vertical reflection plane (contains the principal axis)

σ_d - diagonal reflection plane (contains the principal axis and bisect the angle between two C_2 axes perpendicular to the principal axis)

A point group is a set of symmetry operations forming a mathematical group, for which at least one point remains fixed under all operations of the group. We will introduce four of them ($C_{\infty v}$, $D_{\infty h}$, D_{3h} and T_d) used here to estimate the symmetry of the patchy particles, as shown in Table 1.

2 Definition of four parameters: R_g, S_c, A_p and S_p

Four important and experimentally relevant structural properties, i.e. the radius of gyration, the surface coverage, the symmetry parameter, and the asphericity parameter, are used to characterize the patchy particles. [2]

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2.1 Radius of gyration (R_g).

The radius of gyration is used to characterize the size of a polymer chain, with the definition:

$$R_g = \sqrt{\frac{1}{N}\sum(\mathbf{r}_i - \mathbf{r}_{cm})^2}, \tag{1}$$

$$\mathbf{r}_{cm} = \frac{1}{N}\sum \mathbf{r}_i, \tag{2}$$

where $\mathbf{r}_i$ is the position of bead i, $\mathbf{r}_{cm}$ is the center of mass of the polymer, and N is the total number of beads in the chain. [3]

2.2 Surface coverage (S_c).

We use a lattice point counting scheme to calculate S_c. First, we divide the simulation box into several cells with side length of σ, and locate the cells that contain B beads, C_B (B domain is the major domain). The total number of cells containing B beads is n_B. Then, we define two variables $C_{A,i}$ (A domains are the patchy domains) and $C_{border,i}$. If any neighboring cell of C_B contains A beads, $C_{A,i} = 1$, otherwise $C_{A,i} = 0$, i from 1 to n_B; if any neighboring cell of C_B is empty, $C_{border,i} = 1$, otherwise $C_{border,i} = 0$, i from 1 to n_B. In this way, we can calculate the interface area of A domains and B domain, and then divide it by the total surface area of the patchy particle to define the surface coverage, which can be expressed as

$$S_c = \frac{\sum C_{A,i}}{\sum C_{A,i} + \sum C_{border,i}}. \tag{3}$$

2.3 Asphericity parameter (A_p).

The asphericity denotes the shape of the aggregate and can be estimated by measuring the deformation of the micellar morphology away from a spherical geometry. [4] First, the radius of gyration tensor of the aggregate is constructed, [5]

$$\mathbf{A} = \begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{bmatrix} \tag{4}$$

Table 1 The definition of molecular symmetry: $C_{\infty v}$, $D_{\infty h}$, D_{3h} and T_d

Point group	Symmetry elements	Simple description	Example molecules
$C_{\infty v}$	E, $2C_\infty$, σ_v	linear	HCl
$D_{\infty h}$	E, $2C_\infty$, $\infty\sigma_i$, i, $2S_\infty$, ∞C_2,	linear with inversion center	CO_2
D_{3h}	E, $2C_3$, $3C_2$, σ_h, $2S_3$, 3σ	trigonal planar	BF_3
T_d	E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_v$	tetrahedral	CH_4

where

$$S_{xx} = \frac{1}{N}\sum(x_i - x_c)(x_i - x_c) \tag{5}$$

$$S_{xy} = \frac{1}{N}\sum(x_i - x_c)(y_i - y_c) \tag{6}$$

etc. Parameters λ_1, λ_2, λ_3 are the characteristic values of this matrix. After diagonalization process, we obtain

$$\mathbf{S} = \begin{bmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{bmatrix} \tag{7}$$

where $\lambda_1 < \lambda_2 < \lambda_3$. We can use these characteristic values to calculate the asphericity parameter

$$A_p = \frac{(\lambda_1^2 - \lambda_2^2)^2 + (\lambda_1^2 - \lambda_3^2)^2 + (\lambda_3^2 - \lambda_2^2)^2}{2(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^2}. \tag{8}$$

A_p varies from 0 to 1; 0 represents a perfect spherical globule, 0.25 for a circle, and 1 for a rod.[6]

2.4 Symmetry parameter (S_p).

S_p is defined through the root mean square deviation $(RMSD)$. We first find out the center of mass positions of each patch as well as the whole patchy particle. The root mean square deviation

$$RMSD = \sqrt{\frac{\sum\left(\mathbf{r}_{cm,i} - \mathbf{r}_{perfect}\right)^2}{n}} \tag{9}$$

can be calculated by using Visual molecular dynamics (VMD)[7] package, which can generate a perfect structure having the same point group as our patchy particle. The $RMSD$ shows the difference between the two structures. Then we define the symmetry parameter as

$$S_p = \frac{RMSD}{R_g}, \tag{10}$$

which is the ratio of symmetry difference to the particle size.

3 Snapshots of the dynamic pathway for the patchy particles with high symmetries

Fig. 1 shows the snapshots for the dynamic pathway for the formation of patchy nanoparticles with high symmetries.

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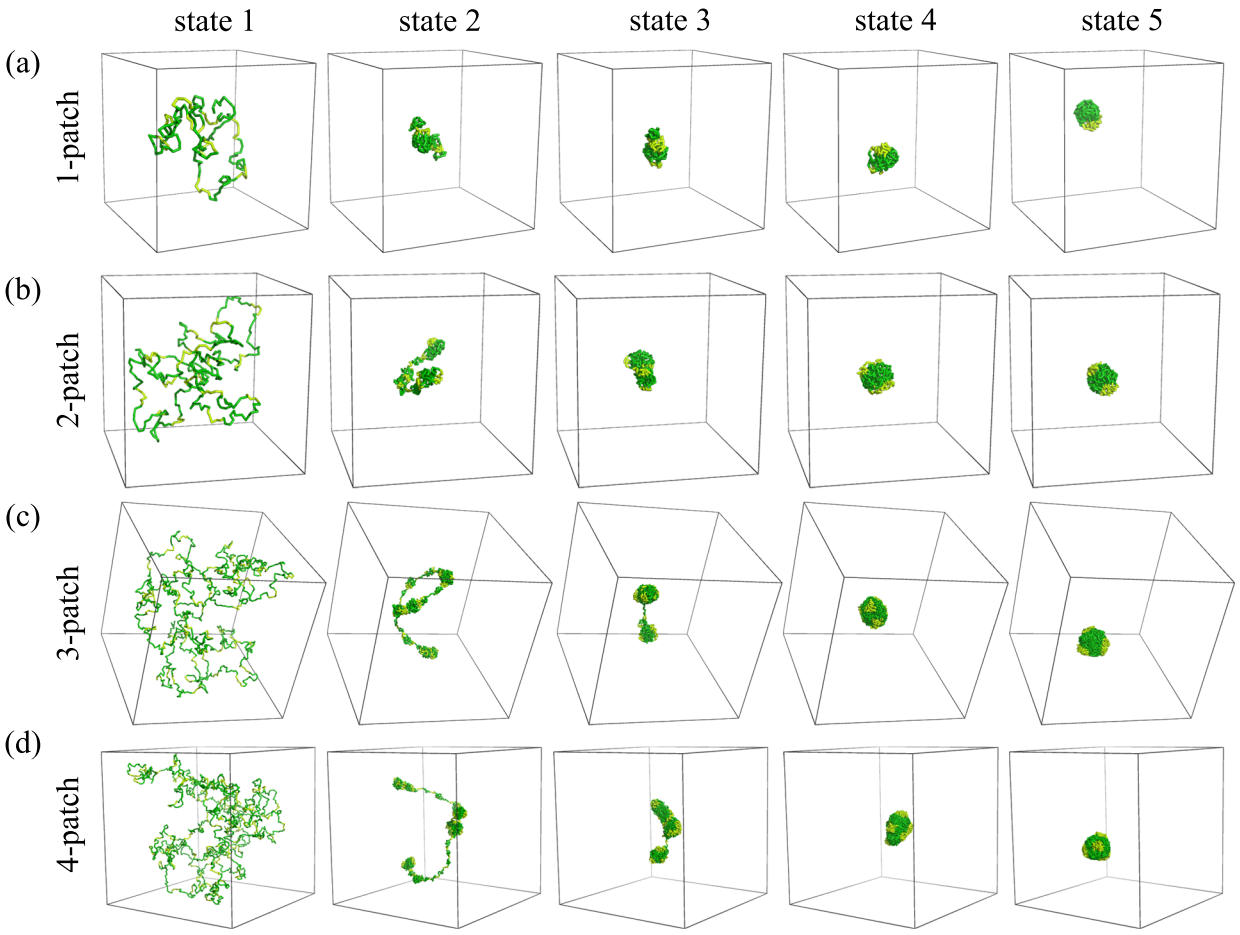

Fig. 1 Snapshots of the dynamic pathway for (a) one-patch, (b) two-patch, (c) three-patch and (d) four-patch structures, where state 1 represents for the initial single multiblock copolymer chain, state 2 to state 4 are the intermediate states, and state 5 corresponds to the structures with high symmetries in our simulations.