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\textsubscript{oo}v, D\textsubscript{ohh}, D\textsubscript{3h} and T\textsubscript{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:

- \textit{E} - the identity operation
- \textit{C\textsubscript{s}} - rotation by \(\frac{2\pi}{n}\) angle
- \textit{S\textsubscript{h}} - horizontal reflection plane (perpendicular to the principal axis)
- \textit{S\textsubscript{v}} - vertical reflection plane (contains the principal axis)
- \textit{S\textsubscript{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 (\(C\textsubscript{oo}v\), \(D\textsubscript{ohh}\), \(D\textsubscript{3h}\) and \(T\textsubscript{d}\)) 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.\(^2\)

2.1 Radius of gyration \((R_g)\)

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

\[
R_g = \sqrt{\frac{1}{N} \sum (r_i - r_{cm})^2},
\]

where \(r_i\) is the position of bead \(i\), \(r_{cm}\) 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 \(\sigma\), 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:

\[
S_c = \frac{\sum C_{A,i}}{\sum C_{A,i} + \sum C_{border,i}}.
\]

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:

\[
A = \begin{bmatrix}
S_{xx} & S_{xy} & S_{xz} \\
S_{yx} & S_{yy} & S_{yz} \\
S_{zx} & S_{zy} & S_{zz}
\end{bmatrix}
\]

\(S_{xx}\) is the principal axis, \(S_{xy}\) is the angle between the principal axis and the \(x\) axis, and \(S_{xyz}\) is the deformation parameter.
Table 1 The definition of molecular symmetry: $C_{\infty v}$, $D_{\infty h}$, $D_3h$ and $T_d$

<table>
<thead>
<tr>
<th>Point group</th>
<th>Symmetry elements</th>
<th>Simple description</th>
<th>Example molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\infty v}$</td>
<td>$E, 2C_{\infty}, \sigma_v$</td>
<td>linear</td>
<td>HCl</td>
</tr>
<tr>
<td>$D_{\infty h}$</td>
<td>$E, 2C_{\infty}, \infty \sigma_v, i, 2S_{\infty}, \infty C_2$</td>
<td>linear with inversion center</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>$D_3h$</td>
<td>$E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v$</td>
<td>trigonal planar</td>
<td>BF$_3$</td>
</tr>
<tr>
<td>$T_d$</td>
<td>$E, 8C_3, 3C_2, 6S_4, 6\sigma_v$</td>
<td>tetrahedral</td>
<td>CH$_4$</td>
</tr>
</tbody>
</table>

where

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

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

etc. Parameters $\lambda_1$, $\lambda_2$, $\lambda_3$ are the characteristic values of this matrix. After diagonalization process, we obtain

$$\mathbf{S} = \begin{bmatrix}
\lambda_1^2 & 0 & 0 \\
0 & \lambda_2^2 & 0 \\
0 & 0 & \lambda_3^2
\end{bmatrix}$$  \hspace{1cm} (7)

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

$$A_p = \frac{(\lambda_2^2 - \lambda_3^2)^2 + (\lambda_2^2 - \lambda_1^2)^2 + (\lambda_3^2 - \lambda_1^2)^2}{2(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^2}.$$  \hspace{1cm} (8)

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

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

$$RMSD = \sqrt{\frac{1}{n} \sum (r_{cm,i} - r_{perfect})^2}$$  \hspace{1cm} (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

$$S_p = \frac{RMSD}{R_g},$$  \hspace{1cm} (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.

References

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.