

Supplementary Information for

Dissipative Particle Dynamics Simulations on the Self-Assembly of Rod-Coil Asymmetric Diblock Molecular Brushes Bearing Responsive Side Chains

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1. Simulation Method

Dissipative particle dynamics (DPD) is a coarse-grained mesoscopic simulation approach, which was first introduced by Hoogerbrugge and Koelman and improved by Español and Warren.¹⁻³ In the DPD model, each bead represents a cluster of atoms or molecules. The movement of DPD beads obeys Newton's equation of motion,

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \quad m \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i \quad (\text{S1})$$

where \mathbf{r}_i , \mathbf{v}_i , \mathbf{f}_i , and m are the position, velocity, total force, and mass of the i th bead, respectively. The total force \mathbf{f}_i exerted on the i th bead is the sum of a conservative force \mathbf{F}_{ij}^C , a dissipative force \mathbf{F}_{ij}^D , a random force \mathbf{F}_{ij}^R , and a bonding force \mathbf{F}_{ij}^S , given by

$$\mathbf{f}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R + \mathbf{F}_{ij}^S) \quad (\text{S2})$$

The conservative force is a soft repulsion for nonbonded beads,

$$\mathbf{F}_{ij}^C = a_{ij} \sqrt{\omega^C(r_{ij})} \hat{\mathbf{r}}_{ij} \quad (\text{S3})$$

where a_{ij} is the maximum repulsive interaction between the i th and j th beads; $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$; $r_{ij} = |\mathbf{r}_{ij}|$;

$\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij} / r_{ij}$. The weight function $\omega^C(r_{ij})$ is given by

$$\omega^C(r_{ij}) = \begin{cases} (1 - r_{ij}/r_c)^2, & (r_{ij} < r_c) \\ 0, & (r_{ij} > r_c) \end{cases} \quad (\text{S4})$$

where $r_c = 1$ is the cutoff radius. The dissipative force, a friction force acting on the relative velocities of the beads, is

$$\mathbf{F}_{ij}^D = -\gamma \omega^D(r_{ij}) (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij} \quad (\text{S5})$$

where $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$; γ is the friction coefficient; $\omega^D(r_{ij})$ is weight functions describing the range of dissipative. The random force, which compensates for the loss of kinetic energy due to the dissipative

force, is given as

$$\mathbf{F}_{ij}^R = \mu \omega^R(r_{ij}) \Gamma_{ij} \Delta t^{-1/2} \hat{\mathbf{r}}_{ij} \quad (\text{S6})$$

where μ is the noise amplitude; $\omega^R(r_{ij})$ is random forces vanishing at $r = r_c$, respectively. Γ_{ij} is a randomly fluctuating variable with Gaussian statistics, that satisfies

$$\langle \Gamma_{ij}(t) \rangle = 0, \quad \langle \Gamma_{ij}(t) \Gamma_{kl}(t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t') \quad (\text{S7})$$

Only one of $\omega^D(r_{ij})$ or $\omega^R(r_{ij})$ can be chosen arbitrarily to satisfy the fluctuation-dissipation theorem and the equilibrium Gibbs-Boltzmann distribution. They are determined by the relation as follows.

$$\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2 = \omega^C(r_{ij}) \quad (\text{S8})$$

The values of parameters γ and μ are coupled by

$$\mu^2 = 2\gamma k_B T \Delta t \quad (\text{S9})$$

where T is the absolute temperature and k_B is the Boltzmann constant. Here, $k_B T$ and γ are chosen to be 1.0 and 4.5, respectively.

For the polymer system, the interaction force between bonded beads is described by a harmonic spring force,

$$\mathbf{F}_{ij}^S = k_S (1 - r_{ij} / r_{eq}) \hat{\mathbf{r}}_{ij} \quad (\text{S10})$$

where k_S is the spring constant, and r_{eq} is the bond equilibrium length. We chose $k_S = 100$ and $r_{eq} = 0.86$.

The angle force is added between every two consecutive bonds to guarantee the rigidity of rigid blocks.

The angle force \mathbf{F}^A is given by

$$\mathbf{F}^A = -\nabla \left[k_A (\pi - \theta)^2 \right] \quad (\text{S11})$$

where k_A is the angle constant and θ is the bond angle. The k_A was set to 80 to ensure the rigidity of the rod blocks. In the DPD method, reduced units are adopted for all physical quantities, including the

cutoff radius r_c , the bead mass m , and the temperature $k_B T$. The time unit τ can be formulated by

$$\tau = \sqrt{mr_c^2 / k_B T} \quad (\text{S12})$$

2. Formation Kinetics of Nanowires

To understand the polymerization process for the self-assembly of ADMBs, we propose a theoretical model to predict the growth of nanowires. The consumption of copolymer chains obeys the following rate equation

$$\frac{dC}{dt} = -kC^2 \quad (\text{S13})$$

where C is the concentration of copolymer chains. Unlike Flory's classic model, where the rate coefficient k is assumed to be constant during the overall polymerization process, our modified model assumes the fact that the mobility of building units depends upon their size. Namely, the variation of rate coefficient k can be estimated by the average number $\langle X \rangle_n$ of copolymer chains in the nanowires and the exponential factor α (*i.e.*, $k = k_0 / \langle X \rangle_n^\alpha$).⁴⁻⁶ Here, k_0 is the rate constant, and $\langle X \rangle_n = C_0 / C$, where C_0 is the initial concentration of copolymer chains. As a special case, the exponential factor $\alpha = 0$ refers to the classic Flory model. Substituting these variables into Eq. (S13) yields the analytic expressions of relevant variables as follows

$$\langle X(t) \rangle_n^{\alpha+1} = Kt + 1 \quad (\text{S14})$$

$$C_m(t) = \frac{C_0}{[Kt + 1]^{\frac{2}{\alpha+1}}} \quad (\text{S15})$$

$$C_p(t) = \frac{C_0 \left[(Kt + 1)^{\frac{2}{\alpha+1}} - 1 \right]}{[Kt + 1]^{\frac{2}{\alpha+1}}} \quad (\text{S16})$$

$$\text{PDI}(t) = 2 - \frac{1}{[Kt + 1]^{\frac{1}{\alpha+1}}} \quad (\text{S17})$$

where $K = (\alpha + 1)k_0C_0$ is the growth rate of nanowires; C_m is the concentration of free copolymer chains, and C_p is the concentration of nanowires; PDI is the polydispersity index of nanowires.

3. Self-Assembly Dynamics of Nanowires with Different Rigid C Chains

Fig. S1 shows the relationship between the number-average polymerization degree (X_n) of the aggregates and time (t) for different lengths of rod C chains. As shown, in a short period of time, the X_n of the assemblies changes little with increasing length of the C chains. However, as the length of the C chains increases, the exponential factor α gradually increases, causing the X_n of the assemblies to decrease as the C chain length increases over a long period of time. This process is similar to the growth of the A side chains, indicating that increasing the length of either the solvophilic or solvophobic side chains will hinder the movement of the aggregates.

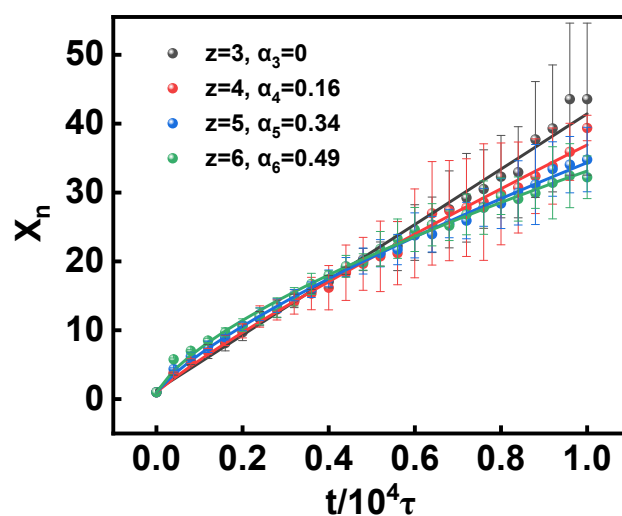


Fig. S1. Variation in the number-average polymerization degree (X_n) of the aggregates during the simulation of $(M_5-g-A_3/B_4)-b-(M_5-g-C_z)$ for different rod C branch lengths.

4. Orientational Arrangement of Rigid Side Chains

We used the order parameter S to evaluate the orientational arrangement of rod side chains in self-assembled aggregates. The order parameter S is defined as⁷

$$S_i = \frac{3(\mathbf{u}_i \cdot \mathbf{u}_d)^2 - 1}{2} \quad (\text{S18})$$

where \mathbf{u}_i and \mathbf{u}_d represent the normalized vector of the i th rod chains and the director, respectively.

The \mathbf{u}_d is calculated by iteration to find the maximum value of $\sum_{i=1}^N (\mathbf{u}_i \cdot \mathbf{u}_d)^2$. However, traditional order parameters cannot reveal the collection of rigid chains in the structures, such as a vesicular wall.

The local order parameter, the average over the order parameter of every rigid chain with neighboring rigid chains, can describe the arrangement of rigid chains in a vesicular wall. As illustrated in Fig. S2, the neighboring domain is defined by a cylindrical domain centered at a rigid chain. The cylindrical domain possesses radius R and length L , where R and L are chosen to be $2.0 r_c$ and $4.0 r_c$, respectively. The rigid chain with one or more beads located in this cylindrical domain is categorized as the neighboring rigid chain. This local order parameter derives from the short-ranged order parameter used in the study carried out by Sheng et al.⁸ In their study, the R and L were related to the length L_{rod} of the rigid chain ($L = L_{\text{rod}}$ and $R = \frac{L_{\text{rod}}}{2\sqrt{3}}$). Because of the relatively small cylindrical area for short L_{rod} , we found that this short-range order parameter would result in an irrational increment with short rigid chains. Consequently, we fixed the values of R and L to obtain the local order parameter.

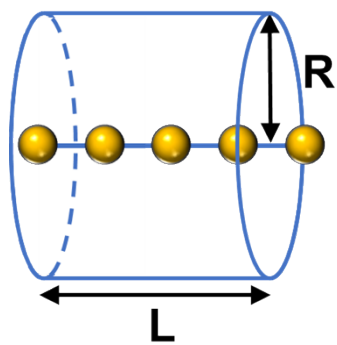


Fig. S2. Schematic of the neighboring cylindrical domain centered at a rigid chain.

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