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Supplementary Information

The self-assembly behavior of polymer brush induced by the orientational ordering of rod backbones: A dissipative particle dynamics study

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1. Dissipative particle dynamics

The Dissipative particle dynamics (DPD) method was first proposed by Hoogerbrugge and Koelman[1] in 1992 and subsequently modified by Espaol[2] and Warren[3] by introducing conservative forces, which promoted the development of it. The DPD method is a coarse-grained particle-based mesoscale simulation technique. In DPD, molecules are divided into a set of soft beads each representing a group of atoms that is large on the atomistic scale but still macroscopically small. All beads comply with Newton's equation[4, 5]

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \quad m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i \tag{1}$$

where r_i, v_i, m_i, and f_i denote the position vector, velocity, mass of the i particle and the acting force on the i particle, respectively. The force ($\mathbf{f}_i$)is composed of three different pairwise-additive forces[6, 7]:

$$\mathbf{f}_i = \sum_{i \neq j} \left(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \right) \tag{2}$$

Where F_{ij}^C is the conservative repulsive force representing excluded volume effect, F_{ij}^D is the dissipative force representing viscous drag between moving beads, and F_{ij}^R is the random force representing stochastic impulse. These forces conserve net momentum and all acts along the line joining two interacting particles. Specifically, the conservative, dissipative, and random forces are given as follows[8]:

$$\mathbf{F}_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij})\theta_{ij}\hat{\mathbf{r}}_{ij} & (r_{ij} < 1) \\ 0 & (r_{ij} \geq 1) \end{cases} \tag{3}$$

$$\mathbf{F}_{ij}^D = \begin{cases} -\gamma\omega^D(r_{ij})(\hat{\mathbf{r}} \cdot \mathbf{v}_{ij})\hat{\mathbf{r}}_{ij} & (r_{ij} < 1) \\ 0 & (r_{ij} \geq 1) \end{cases} \tag{4}$$

$$\mathbf{F}_{ij}^R = \begin{cases} \sigma w^R(r_{ij})\theta_{ij}\hat{\mathbf{r}}_{ij} & (r_{ij} < 1) \\ 0 & (r_{ij} \geq 1) \end{cases} \tag{5}$$

Where a_{ij} is interaction parameter between beads, r_{ij} is the distance between beads; σ is the standard deviation of random forces, γ is the viscosity coefficient, which denotes the intensity of dissipative force and random force, respectively. w^D and w^R

are two weight functions depending on the distance r_{ij}, which represent the case that the dissipative force and the random force show a gradual decay as the distance between the beads increases. In addition, θ_{ij} is a random number generated from 0 to 1 with Gaussian distribution and unit variance. And θ_{ij} satisfies the relationship of $\langle \theta_{ij}(t) \rangle = 0$ and $\langle \theta_{ij}(t)\theta_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t-t')$ to ensure the random forces generated between the pairs of beads are independent and do not affect each other and $\theta_{ij} = \theta_{ji}$.

2. Interaction parameters (a_{ij}) calculation

In DPD simulation, it is a very important step to calculate interaction parameters a_{ij} is the maximum repulsive parameter between beads i and j, depending on the underlying atomistic interaction, which is linearly related to the Flory-Huggins parameter χ_{ij} by the equation as follows[9]:

$$a_{ij} = a_{ii} + 3.27\chi_{ij} \tag{6}$$

where a_{ii} is equal to 25. The repulsive parameters a_{ij} can be obtained from Flory−Huggins parameters χ_{ij}[10].

$$\chi_{ij} = \frac{\Delta E^{mix} V_r}{RT\phi_i\phi_j V}. \tag{7}$$

where χ_{ij} is mapped from a long chain to a short DPD chain and bridges the gap between atomistic MD and mesoscale DPD methods. R is the gas constant and T is temperature, ϕ_i and ϕ_j are the volume fractions of beads i and j, respectively. V is the total volume, and V_r is a reference volume. ΔE_{mix} is the mixing energy of two different types of beads, which can be estimated by[10]:

$$\Delta E^{mix} = E_{ij} - (E_i + E_j) \tag{8}$$

where E_{ij}, E_i, and E_j are the total potential energy of a binary mixture and the potential energies of pure components i and j, respectively. ΔE_{mix} has been determined by MD simulations using the COMPASS force field.

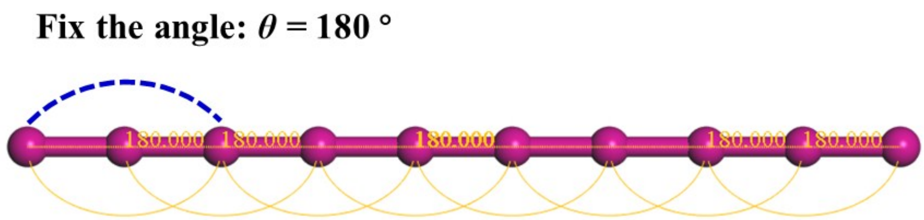

Fig. S1 Schematic diagram of setting rigidity of rod blocks

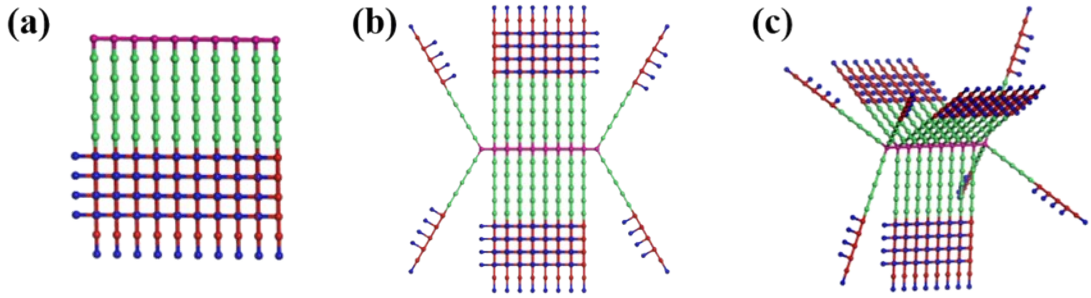

Fig. S2 Schematic structure of CNC-*g*-PCL-*b*-PDMAEMA (full rigid backbone) at different graft density of side chains ((a) 1/3, (b) 2/3 and (c) 1).

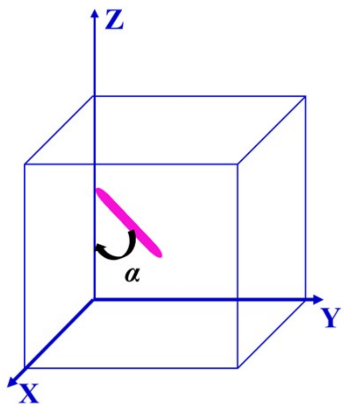

Fig. S3 Schematic diagram of the angle α between the rod chain and the Z axis.

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