Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information:

The influence of side-chain conformations on the phase behavior of bottlebrush block polymers

Yuguo Chen[1], Xinghua Zhang[2],* and Ying Jiang[1,3]*

[1]*School of Chemistry & Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education & Center of Soft Matter Physics and Its Applications, Beihang University, Beijing 100191, China*

[2]*School of Science, Beijing Jiaotong University, Beijing 100044, China,*

[3]*Beijing Advanced Innovation Center for Biomedical Engineering, Beihang University, Beijing 100191, China*

E-mail: zhangxh@bjtu.edu.cn; yjiang@buaa.edu.cn

*To whom correspondence should be addressed

Theoretical formalism of SCFT

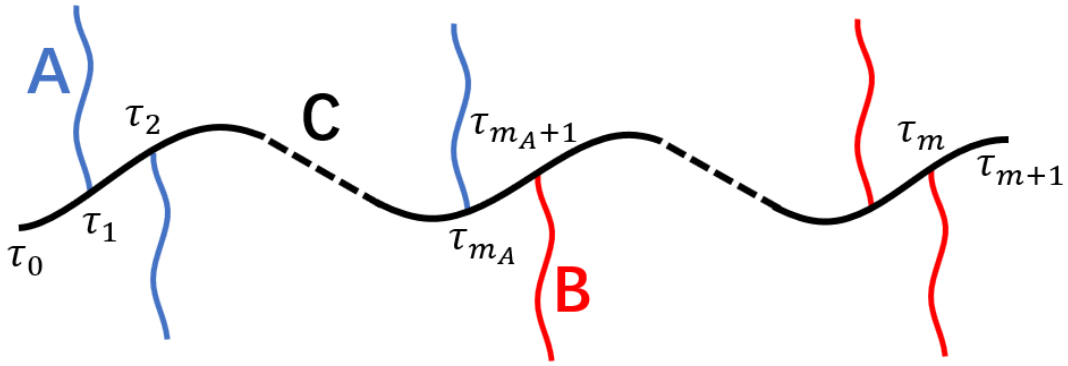

Figure S1: Schematic of the bottlebrush diblock polymer chain composed of side chains A (blue), B (red) and the backbone C (black). The grafting points along the backbone are labelled as τ_i, $i = 1, 2, 3, \cdots, m$ and the free ends are labelled as τ_0 and τ_{m+1}, respectively.

We consider a system of volume V, which is comprised of n monodisperse and indistinguishable bottlebrush polymer chains. Each of chain has m side chains including m_A A-chains and $m_\mathrm{B} = m - m_\mathrm{A}$ B-chains, which uniformly divide the C backbone into $m+1$ equal segment, as illustrated in Fig.S1. We assume that each monomer on all blocks shares the same statistical length b and then occupies the same volume ρ_0^{-1}. The degree of polymerization of side chains A and B is N_A and N_B, while the degree of polymerization of backbone is N_C. Thus, the summed total segment number of a single bottlebrush polymer is $N = m_\mathrm{A}N_\mathrm{A} + m_\mathrm{B}N_\mathrm{B} + N_\mathrm{C}$. The persistence length for the individual block is λ_α, $\alpha = \mathrm{A}, \mathrm{B}, \mathrm{C}$. The volume fraction for each component is calculated by $f_\mathrm{A} = m_\mathrm{A}N_\mathrm{A}/N$, $f_\mathrm{B} = m_\mathrm{B}N_\mathrm{B}/N$, and $f_\mathrm{C} = N_\mathrm{C}/N$. The i^{th} grafting point on the backbone is located at $\tau_i = i \times f_\mathrm{C}/(m+1)$, where the grafting point index i ranges from 1 to m. Then, two remaining free ends of backbone are designated as τ_0 and τ_{m+1}, respectively.

The Helmholtz free energy per chain for multicomponent block copolymers in the mean field approximation[1] can be written as

$$\frac{F}{nk_\mathrm{B}T} = -\ln Q + \frac{1}{V}\int d\mathbf{r}\left\{\sum_{\alpha\neq\beta} N\chi_{\alpha\beta}\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r}) - \sum_\alpha \omega_\alpha(\mathbf{r})\phi_\alpha(\mathbf{r}) - \xi(\mathbf{r})\Big[1 - \sum_\alpha \phi_\alpha(\mathbf{r})\Big]\right\} \quad (1)$$

The Flory-Huggins parameter $\chi_{\alpha\beta}$ describes the interaction energy between dissimilar species. The average density for species $\phi_\alpha(\mathbf{r})$ which is conjugated to the mean field $\omega_\alpha(\mathbf{r})$ is enforced by the Lagrangian multiplier $\xi(\mathbf{r})$ due to the incompressibility constraint to $\sum_\alpha \phi_\alpha(\mathbf{r}) = 1$. k_B is the Boltzmann constant and T is the temperature of the system. For the wormlike chain model used here, the single chain partition function for bottlebrush copolymers can be computed by

$$Q = \frac{1}{4\pi V}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{u} q_\mathrm{C}(\mathbf{r},\mathbf{u},f_\mathrm{C}) \tag{2}$$

The backbone propagator $q_\mathrm{C}(\mathbf{r},\mathbf{u},t)$ represents the probability of finding the t terminal, starting from the free end τ_0, which is located at a spatial position specified by $\mathbf{r}$ and points to a direction specified by the unit vector $\mathbf{u}$.

In our model, the backbone is divided into $m+1$ blocks. The propagator within the i^{th} block is designated as

$$q_\mathrm{C}(\mathbf{r},\mathbf{u},t) = q_\mathrm{C}^{(i)}(\mathbf{r},\mathbf{u},t) \qquad \text{here,} \quad \tau_i \le t < \tau_{i+1} \quad i = 0,1,2,\cdots,m \tag{3}$$

which satisfies the modified diffusion equation[2]

$$\frac{\partial}{\partial t} q_\mathrm{C}^{(i)}(\mathbf{r},\mathbf{u},t) = \left[\frac{Nb}{2\lambda_\mathrm{C}}\nabla_\mathbf{u}^2 - Nb\mathbf{u}\cdot\nabla_\mathbf{r} - \omega_\mathrm{C}(\mathbf{r})\right] q_\mathrm{C}^{(i)}(\mathbf{r},\mathbf{u},t) \tag{4}$$

This equation is subject to the following initial conditions

$$q_\mathrm{C}^{(0)}(\mathbf{r},\mathbf{u},0) = 1 \tag{5}$$

and

$$q_\mathrm{C}^{(i)}(\mathbf{r},\mathbf{u},\tau_i) = q_\mathrm{C}^{(i-1)}(\mathbf{r},\mathbf{u},\tau_i)\times\frac{1}{4\pi}\int \mathrm{d}\mathbf{u} q_\alpha(\mathbf{r},\mathbf{u},t = f_\alpha/m_\alpha) \quad i = 1,2,\cdots,m \tag{6}$$

Herein, we assume that the side chain is grafted on the backbone in an orientation-independent manner. It means that side chains are grafted to the backbone with the equal probability for all

directions. The species index $\alpha = \mathrm{A}, \mathrm{B}$ is determined by the component of the side chain grafted at the specific point along the backbone. The propagator for the side chain satisfies

$$\frac{\partial}{\partial t} q_\alpha(\mathbf{r}, \mathbf{u}, t) = \left[\frac{Nb}{2\lambda_\alpha} \nabla_{\mathbf{u}}^2 - Nb\mathbf{u} \cdot \nabla_{\mathbf{r}} - \omega_\alpha(\mathbf{r}) \right] q_\alpha(\mathbf{r}, \mathbf{u}, t) \tag{7}$$

which is subject to the initial condition $q_\alpha(\mathbf{r}, \mathbf{u}, 0) = 1$ for the free end.

Because the side chains grafted at two sides of the backbone are distinct, a complementary segment distribution function for the backbone $\tilde{q}_{\mathrm{C}}^{(i)}(\mathbf{r}, \mathbf{u}, t)$ is also required. It represents the probability of finding the t terminal belonging to the i^{th} block along the backbone, starting from the other free end τ_{m+1}, which is at the spatial position $\mathbf{r}$ and points in a direction specified by the unit vector $-\mathbf{u}$. The propagator within the $(j-1)^{\mathrm{th}}$ block is designated as

$$\tilde{q}_{\mathrm{C}}(\mathbf{r}, \mathbf{u}, t) = \tilde{q}_{\mathrm{C}}^{(j-1)}(\mathbf{r}, \mathbf{u}, t) \qquad \text{here,} \quad \tau_{j-1} < t \leq \tau_j \quad j = m+1, m, m-1, \cdots, 1 \tag{8}$$

which satisfies the modified diffusion equation

$$\frac{\partial}{\partial t} \tilde{q}_{\mathrm{C}}^{(j-1)}(\mathbf{r}, \mathbf{u}, t) = \left[-\frac{Nb}{2\lambda_{\mathrm{C}}} \nabla_{\mathbf{u}}^2 - Nb\mathbf{u} \cdot \nabla_{\mathbf{r}} + \omega_{\mathrm{C}}(\mathbf{r}) \right] \tilde{q}_{\mathrm{C}}^{(j-1)}(\mathbf{r}, \mathbf{u}, t) \tag{9}$$

This equation is subject to the following initial conditions

$$\tilde{q}_{\mathrm{C}}^{(m)}(\mathbf{r}, \mathbf{u}, t = f_{\mathrm{C}}) = 1 \tag{10}$$

and

$$\tilde{q}_{\mathrm{C}}^{(j-1)}(\mathbf{r}, \mathbf{u}, \tau_j) = \tilde{q}_{\mathrm{C}}^{(j)}(\mathbf{r}, \mathbf{u}, \tau_j) \times \frac{1}{4\pi} \int \mathrm{d}\mathbf{u} q_\alpha(\mathbf{r}, \mathbf{u}, t = f_\alpha / m_\alpha) \quad j = m, m-1, m-2, \cdots, 1 \tag{11}$$

where the species index $\alpha = \mathrm{A}, \mathrm{B}$ is determined by the component of the side chain grafted at the junction point. Similarly, the other segment distribution function for the side chain propagating

from the i^{th} junction point satisfies

$$\frac{\partial}{\partial t}\tilde{q}_{\alpha}^{(i)}(\mathbf{r},\mathbf{u},t)=\left[-\frac{Nb}{2\lambda_{\alpha}}\nabla_{\mathbf{u}}^{2}-Nb\mathbf{u}\cdot\nabla_{\mathbf{r}}+\omega_{\alpha}(\mathbf{r})\right]\tilde{q}_{\alpha}^{(i)}(\mathbf{r},\mathbf{u},t) \tag{12}$$

which is subject to the initial condition

$$\tilde{q}_{\alpha}^{(i)}(\mathbf{r},\mathbf{u},t=f_{\alpha}/m_{\alpha})=\frac{\frac{1}{4\pi}\int \mathrm{d}\mathbf{u}q_{\mathrm{C}}^{(i-1)}(\mathbf{r},\mathbf{u},t=\tau_{i})\tilde{q}_{\mathrm{C}}^{(i)}(\mathbf{r},\mathbf{u},t=\tau_{i})}{\left[\frac{1}{4\pi}\int \mathrm{d}\mathbf{u}q_{\alpha}(\mathbf{r},\mathbf{u},t=f_{\alpha}/m_{\alpha})\right]^{2}} \tag{13}$$

Minimization of free energy functional Eq. (1) with respective of functions $\phi_{\alpha}(\mathbf{r})$, $\omega_{\alpha}(\mathbf{r})$, $\xi(\mathbf{r})$, we directly arrive at a set of saddle-point approximation equations

$$\omega_{\mathrm{A}}(\mathbf{r})=N\chi_{\mathrm{AB}}\phi_{\mathrm{B}}(\mathbf{r})+N\chi_{\mathrm{AC}}\phi_{\mathrm{C}}(\mathbf{r})+\xi(\mathbf{r}) \tag{14}$$

$$\omega_{\mathrm{B}}(\mathbf{r})=N\chi_{\mathrm{AB}}\phi_{\mathrm{A}}(\mathbf{r})+N\chi_{\mathrm{BC}}\phi_{\mathrm{C}}(\mathbf{r})+\xi(\mathbf{r}) \tag{15}$$

$$\omega_{\mathrm{C}}(\mathbf{r})=N\chi_{\mathrm{AC}}\phi_{\mathrm{A}}(\mathbf{r})+N\chi_{\mathrm{BC}}\phi_{\mathrm{B}}(\mathbf{r})+\xi(\mathbf{r}) \tag{16}$$

$$\phi_{\mathrm{A}}(\mathbf{r})+\phi_{\mathrm{B}}(\mathbf{r})+\phi_{\mathrm{C}}(\mathbf{r})=1 \tag{17}$$

$$\phi_{\mathrm{A}}(\mathbf{r})=\frac{1}{4\pi Q}\sum_{i=1}^{m_{\mathrm{A}}}\int \mathrm{d}\mathbf{u}\int_{0}^{f_{\mathrm{A}}/m_{\mathrm{A}}}\mathrm{d}tq_{\mathrm{A}}(\mathbf{r},\mathbf{u},t)\tilde{q}_{\mathrm{A}}^{(i)}(\mathbf{r},\mathbf{u},t) \tag{18}$$

$$\phi_{\mathrm{B}}(\mathbf{r})=\frac{1}{4\pi Q}\sum_{i=m_{\mathrm{A}}+1}^{m}\int \mathrm{d}\mathbf{u}\int_{0}^{f_{\mathrm{B}}/m_{\mathrm{B}}}\mathrm{d}tq_{\mathrm{B}}(\mathbf{r},\mathbf{u},t)\tilde{q}_{\mathrm{B}}^{(i)}(\mathbf{r},\mathbf{u},t) \tag{19}$$

$$\phi_{\mathrm{C}}(\mathbf{r})=\frac{1}{4\pi Q}\sum_{i=0}^{m}\int \mathrm{d}\mathbf{u}\int_{\tau_{i}}^{\tau_{i+1}}\mathrm{d}tq_{\mathrm{C}}^{(i)}(\mathbf{r},\mathbf{u},t)\tilde{q}_{\mathrm{C}}^{(i)}(\mathbf{r},\mathbf{u},t) \tag{20}$$

In the present work, we are mainly interested on the lamellar phase self-assembled by the symmetric bottlebrush copolymers. The system can be simplified further that only one spatial variable z and one orientational variable θ are concerned. Then, Eqs.(4), (7), (9) and (12) can be numerically solved by the pseudo-spectral methods.[1,3] Once the propagators are calculated, we are ready to revise the external fields ω_{α} according to the newly obtained component density. In order

to accelerate the convergence, we use the Anderson mixing scheme,[4,5] which updates the original field by incorporating the results from several preceding iterations. The free energy in Eq. (1) is used to analyze the thermodynamical stability of a specific morphology.

The degree of microphase segregation for bottlebrush copolymers strongly depends on the number of side chains m. For a fixed Flory-Huggins parameter χ, a larger m commonly results in a stronger phase segregation. In order to estimate the degree of segregation varying with the increase of m, we set $N\chi_{AB} = (m/2)(N_A + N_B)\tilde{\chi}_{AB}$, where $(N_A + N_B)\tilde{\chi}_{AB} = 15$ corresponding to the intermediate degree of segregation is fixed. On account of the radial stretching of side chains, we assume that the backbone is neutral to side chains, i.e. $\chi_{AC} = \chi_{BC} = 0$. Then, the distribution of the backbone is affected by the steric congestion of side chains and the incompressibility constraint, as a consequence of A-B segregation. The present model facilitates us to understand the impact of polymer conformations of the backbone and side chains on the self-assembly behaviors for bottlebrush block polymers.

References

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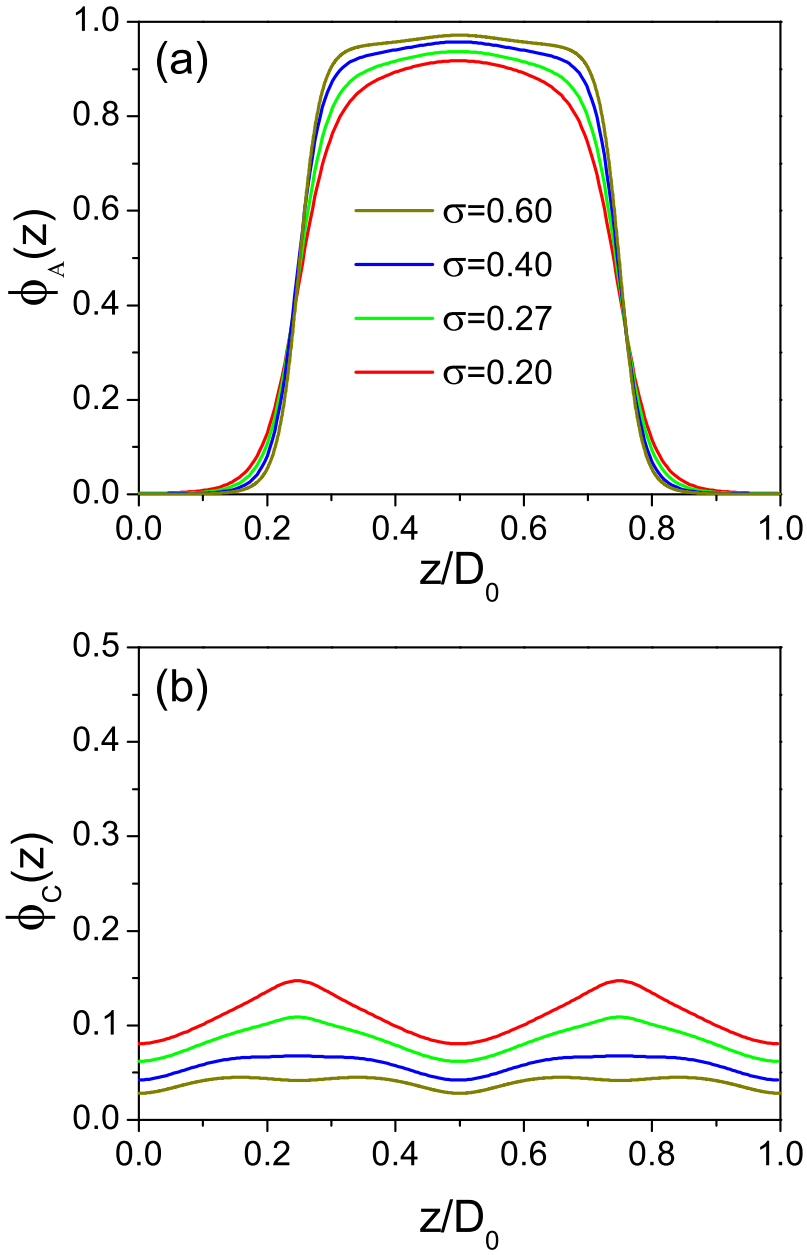

Figure S2: The density profiles for (a) the side chain A and (b) the backbone C in the relative length unit over one domain spacing of lamellar phase with the various grafting density σ. The chain flexibility parameters $L_A/2\lambda_A = 40$ and $L_C/2\lambda_C = 7.5$ are used for the block A and the block C, respectively.

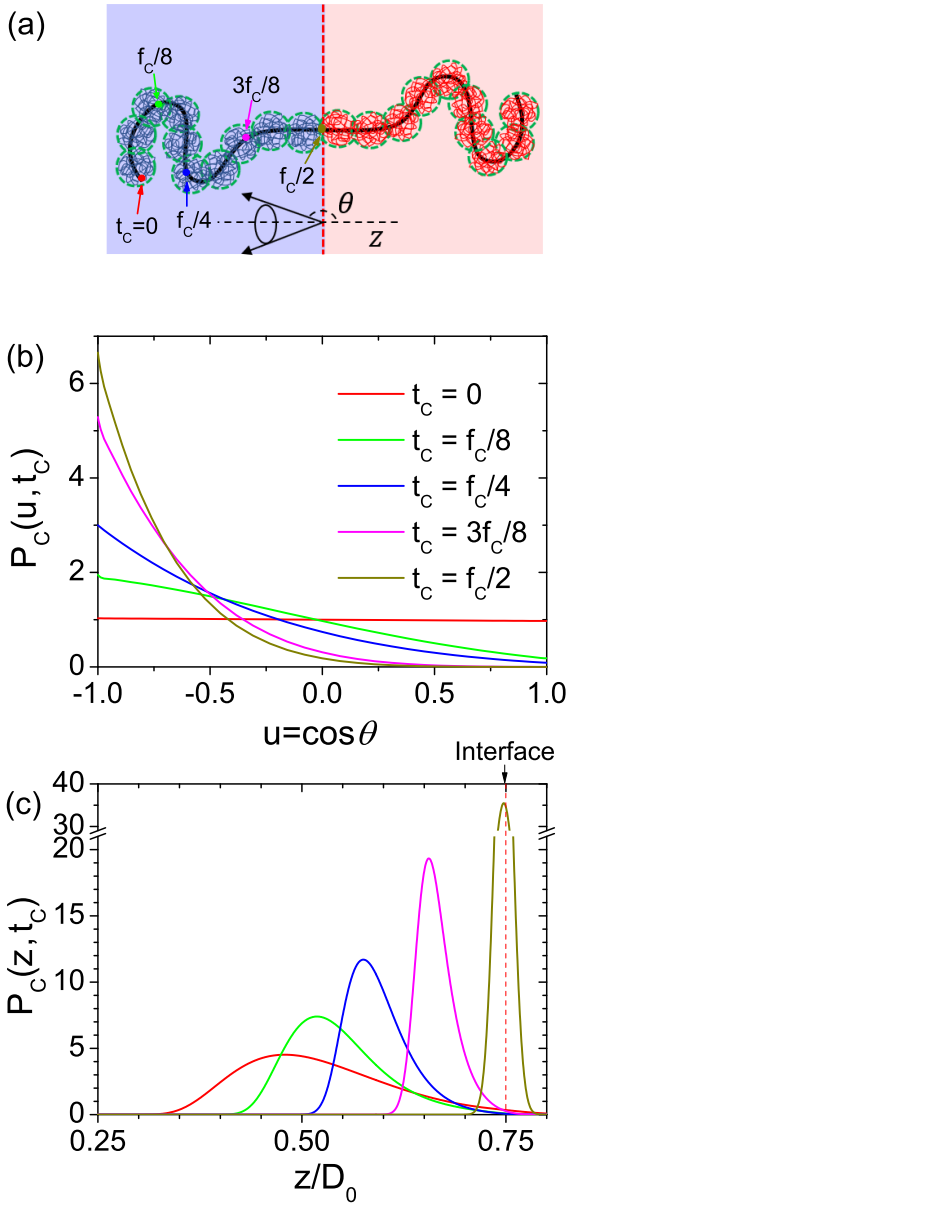

Figure S3: The probability distribution of the backbone segments in lamellae at the given grafting density $\sigma = 0.53$. (a) The schematic chain conformation of bottlebrush polymers which are specifically investigated in plots (b) and (c). (b) The orientational probability distribution $P_{\mathrm{C}}(u, t_{\mathrm{C}})$ of the backbone monomer labelled by the contour variable t_{C}. (c) The positional probability distribution $P_{\mathrm{C}}(z, t_{\mathrm{C}})$ of backbone monomers labelled by the contour variable t_{C}. The chain flexibility parameters $L_{\mathrm{A}}/2\lambda_{\mathrm{A}} = 40$ and $L_{\mathrm{C}}/2\lambda_{\mathrm{C}} = 7.5$ are used for the block A and the block C, respectively. Note, we calculate the probability distribution for the bottlebrush molecule whose junction point is located at one specifically selected interface by imposing a restriction of a the interface-location dependence. Thus, herein, the orientation perpendicular to the interface is identified by $u = -1$, which is distinguishable from $u = 1$.

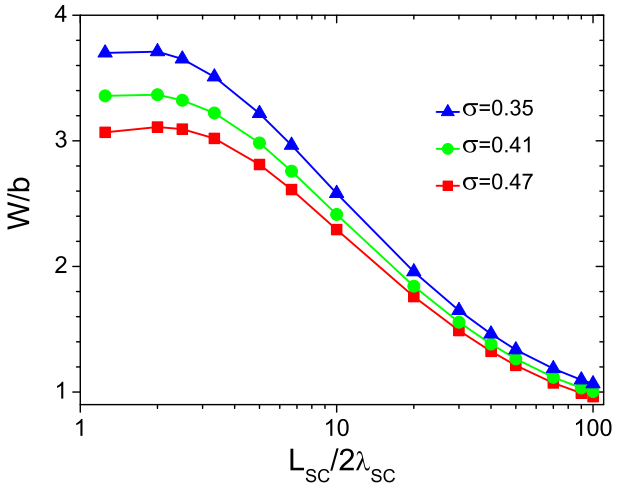

Figure S4: The interfacial width W in the relative length unit over b as the function of the chain flexibility parameter $L_{SC}/2\lambda_{SC}$ of side chains for the given grafting density as labelled in the plot.

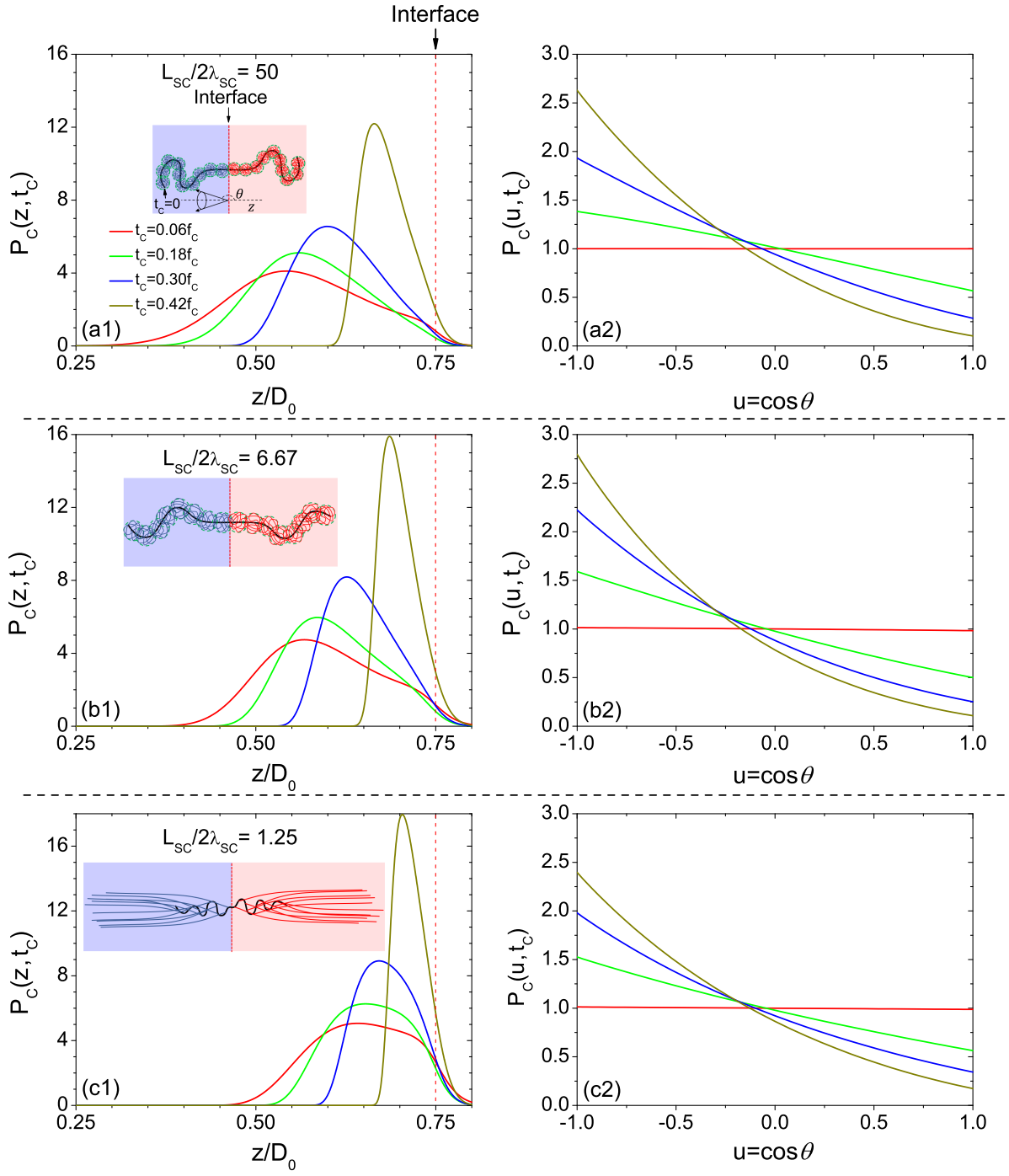

Figure S5: Positional and orientational probability distributions of the backbone segments specifically for three different side-chain conformations parameterized by the flexibility parameter (a) $L_{SC}/2\lambda_{SC} = 50$, (b) $L_{SC}/2\lambda_{SC} = 6.67$, and (c) $L_{SC}/2\lambda_{SC} = 1.25$ at the grafting density $\sigma = 0.47$. The probability functions follows the same definitions in Fig. S3. The chain flexibility parameter $L_C/2\lambda_C = 17$ for the backbone is used here.

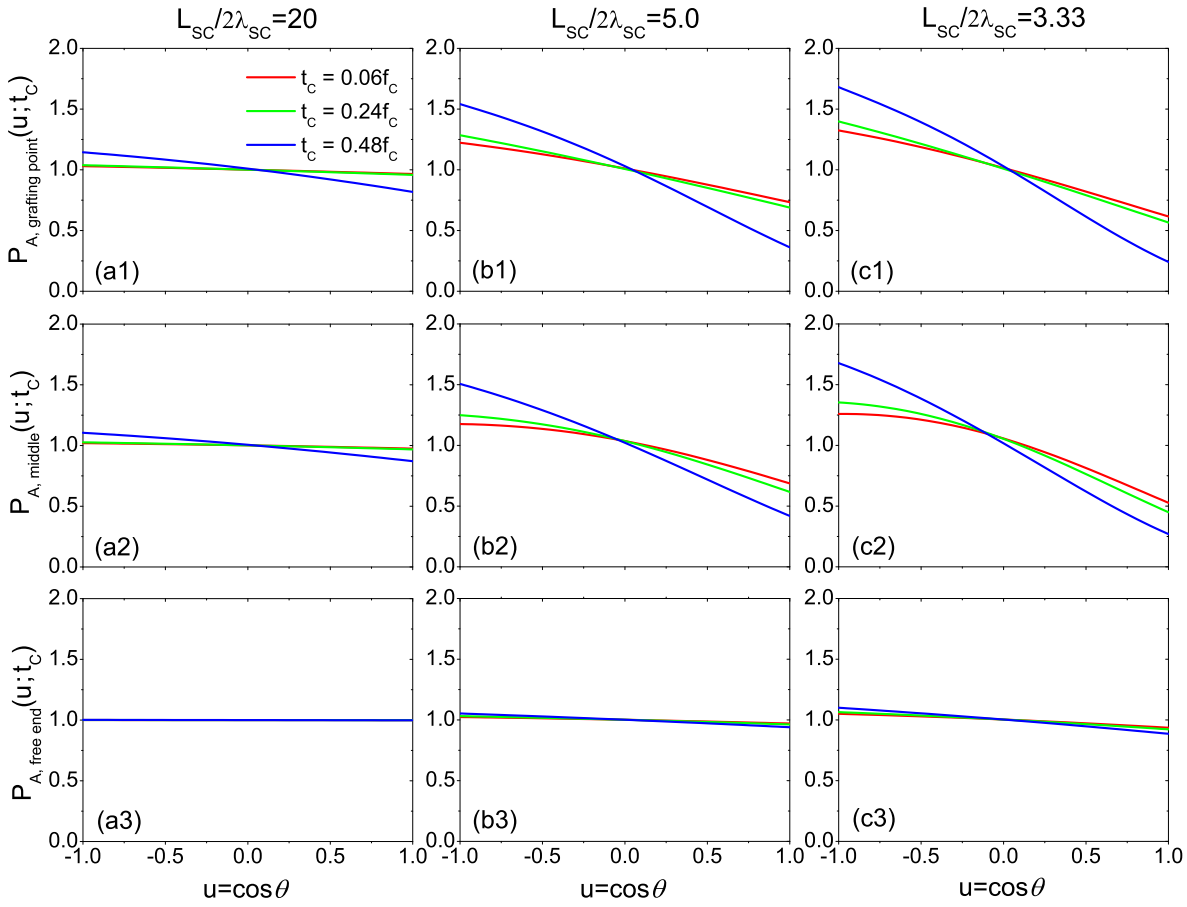

Figure S6: The orientational probability distributions for different segments along the side-chain A with the various side-chain flexibility (a) $L_{SC}/2\lambda_{SC} = 20$, (b) $L_{SC}/2\lambda_{SC} = 5.0$, and (c) $L_{SC}/2\lambda_{SC} = 3.33$ at a given grafting density $\sigma = 0.47$. The probability function $P_{A,\gamma}(u;t_C)$ represents the orientational probability of finding the specific segment γ along the side-chain A attached to the backbone segment labelled by the contour variable t_C. The definition on t_C is same as the one in Fig. S3a. The side-chain segment index γ denotes the grafting point (1), middle segment (2), and free end (3) of the specified side chain. The orientational variable is defined as $u = \cos\theta$, where the angle θ is graphically defined in Fig. S3a. Note, herein, the orientation perpendicular to the interface is identified by $u = -1$, which is distinguishable from $u = 1$, because the restriction of one specifically selected interface is imposed on the computation of $P_{A,\gamma}(u;t_C)$.

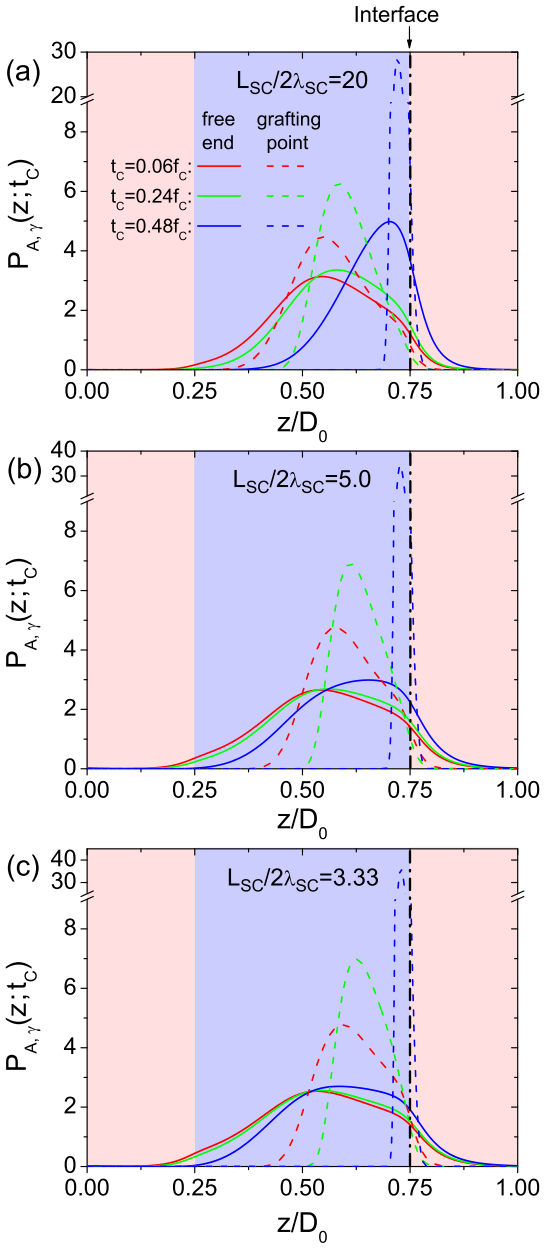

Figure S7: The positional probability distributions for two different ends of one side-chain A with the various side-chain flexibility (a) $L_{SC}/2\lambda_{SC} = 20$, (b) $L_{SC}/2\lambda_{SC} = 5.0$, and (c) $L_{SC}/2\lambda_{SC} = 3.33$ at a given grafting density $\sigma = 0.47$. The probability function $P_{A,\gamma}(z;t_C)$ represents the positional probability of finding the specific segment γ along the side-chain A attached to the backbone segment labelled by the contour variable t_C. The definition on t_C is same as the one in Fig. S3a. The side-chain segment index γ denotes the free end (solid lines) and the grafting point (dotted lines) of the specified side chain. Note, we calculate $P_{A,\gamma}(z;t_C)$ for the bottlebrush molecule whose junction point is located at one specifically selected interface as indicated, by imposing a restriction of the interface-location dependence.