

Liquid-crystal Assembly of Semiflexible-coil/Homopolymer Blends: a Dissipative Particle Dynamics Study

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Abstract The liquid-crystal assembly of semiflexible-coil diblock copolymers with coil or semiflexible homopolymers is studied by dissipative particle dynamics simulation. Phase diagrams of the blends and orientation ordering parameters among semiflexible blocks are constructed as a function of chain stiffness and homopolymer volume fraction. For semiflexible-coil/coil blends with varying stiffness of semiflexible blocks, we display the rich phase behaviors of the system transitioned from coil-coil/coil to rod-coil/coil blends. The disorder-lamellae or lamellae-liquid crystalline transition and “dry brush” phenomenon induced by coil homopolymers are observed. For semiflexible-coil/semiflexible blends, adding semiflexible homopolymers also leads to a disorder-order transition and even a transition between monolayer and bilayer smectic-A phase. The results demonstrate that blending homopolymers into semiflexible copolymers can induce liquid-crystal assembly and even improve the orientation ordering of semiflexible blocks effectively.

Keywords Liquid-crystal assembly; Semiflexible-coil; Homopolymers; Orientation

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INTRODUCTION

Block copolymers (BCPs) have attracted great attentions for potential applications in nanotechnology because of their novel ability of self-assembling into a variety of periodic nanostructures^[1–5]. Recently, more attention has been given to rod-coil (RC) block copolymer, which is composed of rigid rod and flexible coil blocks, due to their rich phase behaviors and potential applications, such as electronics, optoelectronics, and optical devices^[6–8]. In general, the rod-like block mainly originates from π -conjugated backbone, helical secondary structures, and aromatic groups; therefore, the additional geometrical asymmetry between rod and coil blocks and the orientation interaction between anisotropic rod blocks result in different phase behaviors of rod-coil BCPs, compared with that of coil-coil type^[9]. Previous experimental and theoretical studies have observed a number of intriguing phases in rod-coil BCPs melts, including smectic, zigzag, wavy, arrowhead, perforated lamellae, strips, and bicontinuous cubic; conventional phases, such as lamellae, spherical, and cylindrical micelles, are also recognized in this material^[10–15].

These experimental and theoretical studies restrict themselves to probing only “coil-like” or “rod-like” limit of block units. In fact, a semiflexible polymer chain is much closer to the real polymer system, which covers a

comprehensive conformation range between those of the extreme coil and rod limits. The structural properties in semiflexible BCPs can be significantly changed as the chain stiffness varies. Recently, some studies have focused on self-assembly of BCPs that consist of semiflexible segments^[16–23]. Shi *et al.* also concluded that PDMS-*b*-PBPCS BCPs exhibited a transition from coil-coil to rod-coil BCPs with increased temperature; this finding showed a thermoreversible order-order transition in BCPs through variation of PBPCS block rigidity^[17]. In addition, Tang *et al.* investigated the self-assembly of semiflexible-coil BCPs by using self-consistent field theory (SCFT), based on worm-like chain model^[18, 19] for semiflexible blocks and Gaussian chain model for coil block. The expected morphological transitions of semiflexible-coil BCPs, caused by tuning chain stiffness from near the flexible limit to the intermediate region^[20], were clarified. For instance, Yan *et al.* applied the dissipative-particle dynamics (DPD) to report the novel entropic effects that arise from the chain stiffness of semiflexible blocks in the semiflexible-coil BCPs, which can be harnessed to tailor the precise interfacial organization of Janus nanoparticles in the BCPs scaffold^[22].

Despite these advances, exploring and understanding the self-assembly behavior of BCPs system that contains semiflexible units remain an outstanding challenge, specifically of these polymers involving blending systems, such as semiflexible-coil BCPs mixed with semiflexible or coil homopolymers. Adding homopolymers into BCPs system is an effective method for controlling domain size, modifying morphology, and optimizing performance without

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additional synthesis^[23–25]. The phase behavior of blends has become more complicated than that of pure BCPs due to the interplay between microphase and macrophase separations. For the classic coil-coil/coil blending system, both experimental and theoretical studies demonstrate that blending with one of the component homopolymers can induce rich morphologies, sensitively affected by the molecular weight ratio of the added homopolymer to the corresponding block. This phenomenon is known as polymer brush theory^[26]. For rod-coil/coil or rod-coil/rod blends, both coil and rod homopolymers can not only enhance the stability of ordered phase but also control the domain size of ordered structure. Wu *et al.* investigated the rod-coil BCPs blended with rod or coil homopolymer by using DPD simulation and found that blending with rod or coil homopolymers into a rod-coil system is an effective method to induce bilayer liquid-crystal phase; moreover, just changing the length of homopolymer can control the domain spacing of the monolayer structure in liquid-crystalline^[27]. There are also some important studies about the hierarchical liquid crystalline structure^[28, 29]. Despite these successes, systematical investigation on the phase behaviors of semiflexible-coil BCPs blended with corresponding homopolymers remains a challenge, especially for semiflexible segment with tunable chain stiffness.

In this work, we utilize DPD simulation to systematically investigate the effects of chain stiffness on the phase behavior of semiflexible-coil BCPs blended with coil or semiflexible homopolymers. First, we focus on the self-assembly of semiflexible-coil BCPs melts, by constructing the phase diagram as a function of chain stiffness and phase segregation strength. Moreover, we explore the two blends of semiflexible-coil/coil and semiflexible-coil/semiflexible. We detect that the phase transition of blends and the orientation ordering between semiflexible components are sensitive to chain stiffness and homopolymer volume fraction.

SIMULATION METHOD AND MODELS

The dissipative-particle dynamics method^[30], which is introduced by Hoogerbrugge and Koelman in 1992, is a simulation technique that combines some of the detailed descriptions of classical molecular dynamics (MD) but allows the simulation of hydrodynamic behavior in a large length and time scale range. Within DPD, the technique uses the concept of coarse-grained particles of fluid, representing the mass center in a cluster of atoms or molecules. The position and momentum of the DPD particles obey Newton's equation of motion,

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i, m_i \frac{d\vec{v}_i}{dt} = \vec{f}_i \quad (1)$$

where $\vec{r}_i$, m_i , $\vec{v}_i$, and $\vec{f}_i$ are the position, mass, velocity, and force of the i^{th} particle, respectively. Particles i and j at positions $\vec{r}_i$ and $\vec{r}_j$ interact with each other *via* three forces: conservative ($\vec{F}_{ij}^C$), dissipative ($\vec{F}_{ij}^D$), and random forces ($\vec{F}_{ij}^R$), which are given by:

$$\vec{f}_i = \sum_{i \neq j} (\vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R) \quad (2)$$

$$\vec{F}_{ij}^C = a_{ij} \omega(r_{ij}) \hat{r}_{ij} \quad (3)$$

$$\vec{F}_{ij}^D = -\gamma \omega^2(r_{ij}) (\hat{r}_{ij} \cdot \vec{v}_{ij}) \hat{r}_{ij} \quad (4)$$

$$\vec{F}_{ij}^R = \sigma \omega(r_{ij}) \theta_{ij} \hat{r}_{ij} \quad (5)$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r_{ij} = |\vec{r}_{ij}|$, $\hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$, and $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$. The coefficients a_{ij} , γ , and σ determine the strength of conservative, dissipative, and random forces, respectively. The conservative force $\vec{F}_{ij}^C$ is the soft repulsion acting along the intermolecular vector. The weight function $\omega(r_{ij})$ is given by:

$$\omega(r_{ij}) = \begin{cases} 1 - r_{ij}/r_c & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \quad (6)$$

where, r_c is the cutoff radius, which gives the extent of the interaction range. The other two forces, $\vec{F}_{ij}^D$ and $\vec{F}_{ij}^R$, act as a heat sink and source, respectively, and together form a thermostat, which conserves momentum and provides the correct description of hydrodynamics to the system. Here, θ_{ij} is a randomly fluctuating variable with Gaussian statistics: $\langle \theta_{ij}(t) \rangle = 0$ and $\langle \theta_{ij}(t) \theta_{kl}(t') \rangle = (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk}) \delta(t - t')$. Additionally, Gibbs-Boltzmann distribution was used to generate a correct equilibrium in the relationship between the coefficients γ and σ :

$$\sigma^D(r_{ij}) = [\sigma^R(r_{ij})]^2, \sigma^2 = 2\gamma k_B T \quad (7)$$

where k_B is Boltzmann's constant, T is the temperature, γ is the friction coefficient, and σ is the noise amplitude. Here, we chose $\sigma = 3$ ($\gamma = 4.5$)^[31]. According to Groot *et al.*^[32], the conservative interaction strength a_{ij} in Eq. (2) is related to the Flory-Huggins χ -parameters by:

$$a_{ii} \rho = 75 k_B T \quad (8)$$

$$a_{ij} \approx a_{ii} + 3.27 \chi_{ij} \quad (\rho = 3) \quad (9)$$

where a_{ii} is the repulsion parameter between particles of the same type. In our study, a low bead number density ρ was set to 3. According to Eqs. (8) and (9), $a_{ii} = 25$. The variable a_{ij} corresponds linearly to the interaction parameter χ_{ij} .

In this study, the semiflexible-coil BCP was modeled as a coarse-grained linear bead-spring chain, $A_m C_n$ with m bead in a semiflexible (A) block and n bead in a coil (C) block. For coil blocks, a harmonic bond force was used between bonded coil beads $F_{ij}^{S1} = -C^{S1}(r_{ij} - r_{eq}^{S1})\hat{r}_{ij}$, where C^{S1} is the bond spring constant and r_{eq}^{S1} is the equilibrium bond length. A similar spring force for neighboring beads is also used in semiflexible blocks $F_{ij}^{S2} = -C^{S2}(r_{ij} - r_{eq}^{S2})\hat{r}_{ij}$. We set $C^{S1} = 10$, $C^{S2} = 100$ and $r_{eq}^{S1} = 0.86$, $r_{eq}^{S2} = 0.35$. Additionally, we attempted to control the chain stiffness by introducing bending potential between two consecutive bonds. The extra stiffness of semiflexible segment can be implemented by the following bending potential between three consecutive beads $U^\theta = k(1 + \cos \theta)$ and $F^\theta = -\nabla U^\theta$, where k is the bending constant and controls the chain stiffness^[33]. In DPD simulation, all the physical variables are scaled by the

particle mass (m), cutoff distance (r_c), and thermal energy ($k_B T$). Therefore, time, length, interaction parameters and bending constant are nondimensionalized by $t = t' / \sqrt{\frac{m r_c^2}{k_B T}}$, $r = r' / r_c$, $a_{ij} = a_{ij}' / \sqrt{\frac{k_B T}{r_c^2}}$, and $k = k' / k_B T$, where the superscript “'” denotes the dimensional variable. All the parameters listed in this work are dimensionless quantities, and their physical values can be straightforwardly obtained.

In this work, the constant NVT ensemble is used. The simulations are carried out by randomly placing the copolymers and homopolymers into a cubic box with periodic boundary conditions applied in three directions. We have investigated three simulated systems with different sizes ($15 \times 15 \times 15$, $20 \times 20 \times 20$, and $25 \times 25 \times 25$ DPD units) to check the finite size effects, which show the same results. In order to compare readily our results, we focus on the system with $25 \times 25 \times 25$ DPD units, containing about 46975 DPD beads (represented by N). The volume fractions of the coil homopolymers and semiflexible homopolymers are defined as $\phi_{hC} = N_{hC} / (N + N_{hC})$ and $\phi_{hA} = N_{hA} / (N + N_{hA})$, where N_{hC} and N_{hA} represent the bead number of added homopolymers. Our simulations are carried out based on a modified version of the DPD code named LAMMPS^[34]. The time integration of motion equations is calculated through a modified velocity-Verlet algorithm^[35], with λ at 0.50 and time step (Δt) at 0.01τ . A typical simulation requires 3.0×10^6 step (corresponding to about 3 μs of typical physical values of the parameters) and the first 1.8×10^6 step is used for equilibrium. The system has basically reached stability at 1.2×10^6 step. Our simulations run long enough, so that the results are independent of the starting states. To ensure the acquisition of every equilibrium structure, we check the thermodynamic consistency of simulated structures by monitoring the local temperature^[36].

RESULTS AND DISCUSSION

Semiflexible-coil BCPs Melts

In our work, we focus on a linear semiflexible-coil BCPs (A_8C_6). As shown in Fig. 1, we construct the phase diagram of A_8C_6 melts as a function of the chain stiffness of semiflexible blocks k and the repulsive interactions between semiflexible-coil blocks a_{AC} ($a_{AA} = a_{CC} = 25$). Three structures are observed as follow: disorder (D), lamellae (L), and lamellae with local liquid-crystal characteristic within semiflexible blocks domain (Lc). Here, the ordered lamellar structure distinguished from the disordered phase is identified easily by component density distribution. For example, as the peak value of A block corresponds to the valley value of C block, as a result, it is a well ordered lamellae, including the liquid crystalline lamellae. To further distinguish between the lamellar phase and the liquid crystalline lamellar phase, we also need to monitor the rod-like component orientation behaviors in detail. The symbols in Fig. 1 represent the calculated transition points, and the solid lines are used to divide different phases. As the chain stiffness k varies from 0 to 200, this diagram covers the cases from coil-coil to rod-coil BCPs. Interestingly, the critical

point of $(\chi N)_{ODT}$ for the disorder-order transition decreases with the increase of k , indicating that the increase in chain stiffness of semiflexible blocks can strengthen the incompatibility between semiflexible and coil blocks. This result agrees with the theoretical prediction by Matsen: the increase in the molecular stiffness of melts of semiflexible-coil BCPs shifted the ODT line to high temperatures^[37]. As chain stiffness k is further increased, A_8C_6 melts transform from disorder to lamellae with local liquid-crystal characteristic (Lc). This structure is driven by minimizing the coil-stretching entropy penalty while releasing packing frustration of semiflexible segments with strong stiffness. In the follow, we focus on the linear semiflexible-coil A_8C_6 with $\chi N = 50$, which always keeps the disordered structure regardless of chain stiffness k . Then we consider the two blends of semiflexible-coil/coil (A_8C_6/C_6) and semiflexible-coil/semiflexible (A_8C_6/A_8) by varying the stiffness of semiflexible components and volume fraction of homopolymers.

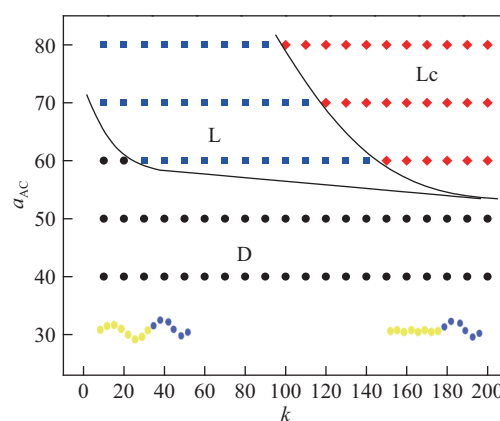


Fig. 1 Phase diagram of A_8C_6 melts plotted in the parameter space of chain stiffness of semiflexible blocks k and the repulsive interactions a_{AC} . The morphologies include disorder (D), lamellae (L), and lamellae with local liquid-crystal order within semiflexible blocks A domains (Lc). Blocks A and C are presented in yellow and blue, respectively.

Semiflexible-coil/Coil Blends

As shown in Fig. 2(a), we plot the phase diagram of A_8C_6/C_6 blends as functions of the stiffness of semiflexible blocks k and the volume fraction of coil homopolymers ϕ_{hC} . The phase diagram also displays three structures: disorder (D), lamellae (L), and monolayer liquid crystalline (MLc). For A blocks with low stiffness ($k = 0$ or 5), the results are similar with the expectation in the traditional of coil-coil/coil blends^[38–41]. The mechanism of homopolymer solubilization depends primarily on the ratio of homopolymer molecular weight and its corresponding blocks (α). In this study, the molecular weight of the added coil homopolymers is matched with the corresponding coil blocks. For A blocks with strong stiffness ($k = 100$ –200), we observe disorder-lamellae transition and even the monolayer liquid-crystalline phase with increasing ϕ_{hC} , which is similar to the results of rod-coil/coil blends studied by Song *et al.*^[24]. This result suggests that the stiffness of semiflexible blocks plays an

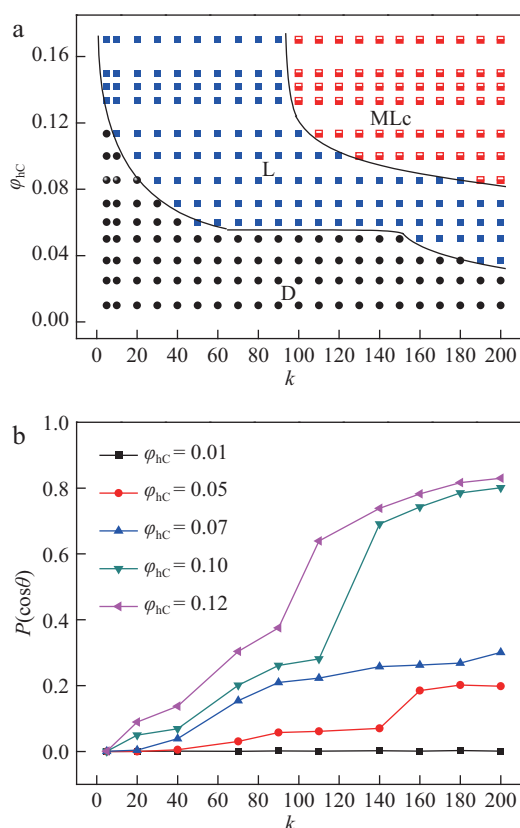


Fig. 2 (a) Phase diagram of A₈C₆/C₆ blends plotted in parameter space of k and the volume fractions of coil homopolymer ϕ_{hc} (The morphologies include disorder (D), lamellae (L), and monolayer liquid crystalline (MLC)); (b) Orientation order parameter $P(\cos\theta)$ of semiflexible blocks A

important role in the formation of monolayer liquid-crystalline structure.

To monitor the orientation ordering of semiflexible blocks in A₈C₆/C₆ blends varied with the chain stiffness k and homopolymer volume fraction ϕ_{hc} , the orientation order parameter $P(\cos\theta) = (3\cos^2\theta - 1)/2$ is used, where θ is the included angle between two vectors along the direction between the head and tail beads of semiflexible blocks. $P(\cos\theta)$ varies from 0 (representing random orientation) to 1.0 (representing completely liquid-crystalline alignment). Fig. 2(b) displays $P(\cos\theta)$ as a function of chain stiffness k with $\phi_{hc} = 0.01, 0.05, 0.07, 0.10$, and 0.12 , respectively. As ϕ_{hc} is equal to 0.01, 0.05 and 0.07, $P(\cos\theta)$ slightly increases, but is still lower than 0.5, corresponding to the disordered and lamellar structure in the phase diagram of Fig. 2(a). As $\phi_{hc} = 0.10$ and 0.12 , the value of $P(\cos\theta)$ obviously increases and reaches 0.8. This result further reveals that blending with coil homopolymers can induce the formation of monolayer liquid-crystalline phase. Further, the simulated morphologies of A₈C₆/C₆ blends with $\phi_{hc} = 0.01, 0.05, 0.06, 0.08, 0.10$ and $k = 150$, are shown in Fig. 3. With the addition of a small amount of coil homopolymers ($\phi_{hc} = 0.01$), the morphology of blends maintains disordered phase, and the coil homopolymers are solubilized. The lamellar structure occurs with $\phi_{hc} = 0.06$, where coil homopolymers are uniformly distributed in the overall coil blocks domains,

which is known as “wet brush”. When $\phi_{hc} = 0.08$, the excess coil homopolymers tend to aggregate into the center of coil blocks domains, forming the “dry” type within lamellae. Finally, a well-defined monolayer smectic-A liquid-crystalline phase appears at $\phi_{hc} = 0.10$, where semiflexible blocks assume an orientation roughly perpendicular to the normal of the lamellae. We find that the adding of coil homopolymers drives the semiflexible blocks to interdigitate with each other and finally enlarge the interfacial area for coil-stretching entropy.

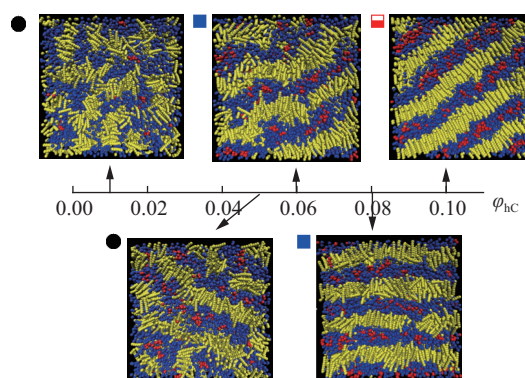


Fig. 3 Simulated morphologies of A₈C₆/C₆ blends with $\phi_{hc} = 0.01, 0.05, 0.06, 0.08, 0.10$, respectively (Here $k = 150$.)

Semiflexible-coil/Semiflexible Blends

In this part, we focus on the self-assembly of A₈C₆/A₈ blends. The system becomes more complex than the case of semiflexible-coil/coil blends, because the chain stiffness of semiflexible homopolymers can be the same as or different from that of corresponding semiflexible blocks. First, we consider the case of system that the stiffness of semiflexible homopolymers A₈ is matched with the corresponding blocks A₈. By changing the stiffness of the semiflexible blocks k and the volume fraction of semiflexible homopolymers ϕ_{hA} , the phase diagram of A₈C₆/A₈ blends is constructed as shown in Fig. 4(a). There are four structures: disorder (D), lamellar (L), monolayer liquid crystalline (MLC), and bilayer liquid crystalline (BLC). With a small amount of semiflexible homopolymers, the morphology of blends is transformed from disordered phase to lamellar structure. With increase of ϕ_{hA} , a monolayer liquid-crystalline phase also appears, which is similar to that of A₈C₆/C₆ blends. One interesting phenomenon is that the bilayer liquid crystalline is observed with further increasing ϕ_{hA} . In fact, blending semiflexible homopolymers has equivalently increased the composition of the semiflexible components, whereas adding coil homopolymers has an opposite effect. Comparing A₈C₆/A₈ with A₈C₆/C₆ blends, bilayer liquid-crystalline structures we present here only appear at the high composition of semiflexible component and the strong stiffness (greater than the critical value). With the incorporation of semiflexible homopolymers, semiflexible homopolymers interdigitate with semiflexible blocks to make coil blocks rearrange, to occupy more laterally interfacial area. By decreasing the interfacial energy, a transition from monolayer to bilayer liquid crystalline phase is induced^[42]. Meanwhile, the critical

point of φ_{hA} for the disorder-bilayer liquid crystalline transition decreases with increased k as shown in Fig. 4(a). When the stiffness is increased, the conformational entropy of the chain is decreased. Forming bilayer structure, the homopolymers have more free space and then the translational entropy is increased. This can compensate the loss of conformational entropy. This finding also agrees with the previous theoretical work of the phase behavior of semiflexible-coil BCPs melts, originating from different geometrical asymmetry between semiflexible and coil blocks^[20].

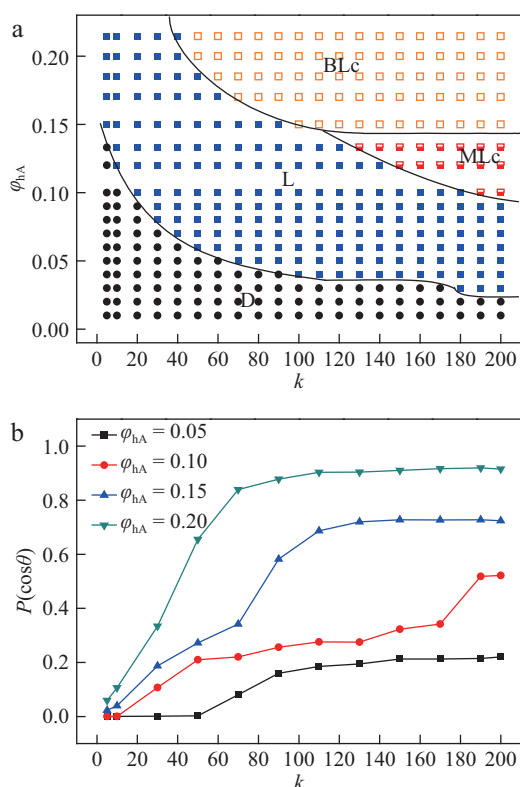


Fig. 4 (a) Phase diagram of A₈C₆/A₈ blends plotted in parameter space of k and the volume fractions of semiflexible homopolymer φ_{hA} (The morphologies include disorder (D), lamellae (L), monolayer liquid crystalline (MLC), and bilayer liquid crystalline (BLC)); (b) Orientation order parameter $P(\cos\theta)$ of semiflexible blocks A

To display the orientation ordering in A₈C₆/A₈ blends, we also calculate the orientation order parameter between semiflexible blocks $P(\cos\theta)$ as a function of k with different φ_{hA} . As shown in Fig. 4(b), when $\varphi_{hA} = 0.05$, $P(\cos\theta)$ increases slightly as k increases, corresponding to the transition of disordered phase to lamellar structure in the phase diagram shown in Fig. 4(a). As $\varphi_{hA} = 0.10$, $P(\cos\theta)$ has an obvious increase with the strong stiffness ($k = 190$ – 200), suggesting the appearance of monolayer liquid crystalline (MLC). Furthermore, with further increasing φ_{hA} to 0.15 or 0.20, $P(\cos\theta)$ increases quickly close to 1.0, indicating that the A₈C₆/A₈ blends underwent a disorder-bilayer liquid crystalline transition.

Correspondingly, Fig. 5 also displays the typical simulated

morphologies of A₈C₆/A₈ blends at various φ_{hA} with moderate ($k = 50$) and strong ($k = 150$) stiffness. For $k = 50$, A₈C₆/A₈ blend remains disordered morphology at $\varphi_{hA} = 0.05$, consistent with the result of A₈C₆ melts. The lamellar structure is observed at $\varphi_{hA} = 0.10$. With increase of φ_{hA} to 0.15, the liquid-crystalline phase with a good alignment between semiflexible segments appears. At $\varphi_{hA} = 0.20$, to balance the competition between coil-stretching entropy and interfacial energy, the semiflexible components tend to interdigitate with each other, including semiflexible homopolymers and semiflexible blocks, to form a well-defined bilayer smectic-A liquid-crystalline structure, where the semiflexible components are roughly perpendicular to the layer normal. In the case of strong stiffness ($k = 150$), A₈C₆/A₈ blend transforms from disorder into lamellar phase at $\varphi_{hA} = 0.05$, which is different from the case of $k = 50$, indicating that the increase in semiflexible component stiffness promotes the system to transform into ordered morphologies. As φ_{hA} increases from 0.10 to 0.13, significant difference in lamellar structure is the formation of monolayer liquid-crystalline phase at $\varphi_{hA} = 0.13$. As further increasing $\varphi_{hA} = 0.20$, the monolayer liquid-crystalline phase is transformed into bilayer liquid-crystalline phase. These findings suggest that the assembled structures of A₈C₆/A₈ blends can be switched between monolayer and bilayer liquid-crystalline phase by varying the volume fraction of semiflexible segments.

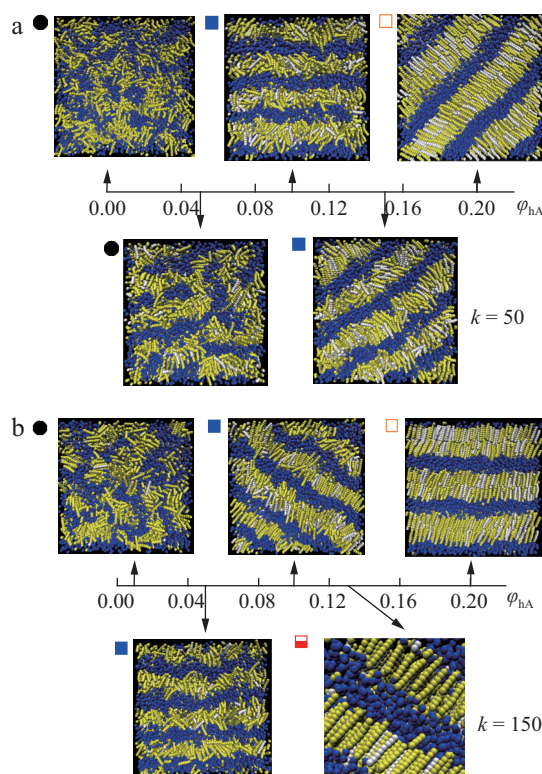


Fig. 5 Simulated morphologies of A₈C₆/A₈ blends at various k and φ_{hA} : (a) $k = 50$ with $\varphi_{hA} = 0, 0.05, 0.10, 0.15, 0.20$, respectively and (b) $k = 150$ with $\varphi_{hA} = 0.01, 0.05, 0.10, 0.13, 0.20$, respectively. Semiflexible homopolymers A₈ is presented in white, and a magnified MLC is displayed for clearing.

Finally, we consider the case of the stiffness of semiflexible homopolymers A's mismatched with that of corresponding blocks A₈, where the chain stiffness is characterized by k' and k , respectively. To compare with the case of A₈C₆/A₈ blends, we fix the volume fraction of semiflexible homopolymers to $\phi_{hA'} = 0.20$. Fig. 6(a) displays the orientation order parameter of semiflexible homopolymers $P(\cos\theta)$ as a function of semiflexible blocks stiffness k , at the low stiffness for $k' = 20$ and 40. As can be seen from simulated morphology in Fig. 6(a), a perfect bilayer liquid-crystalline structure is induced by increasing semiflexible blocks stiffness k . Surprisingly, the orientation arrangement of homopolymers with $k' = 20$ and 40 is improved obviously, which can be seen from the insets in Fig. 6(a). The semiflexible homopolymers shown in white are straightened and interdigitated with A₈ blocks formed bilayer liquid-crystalline phase together.

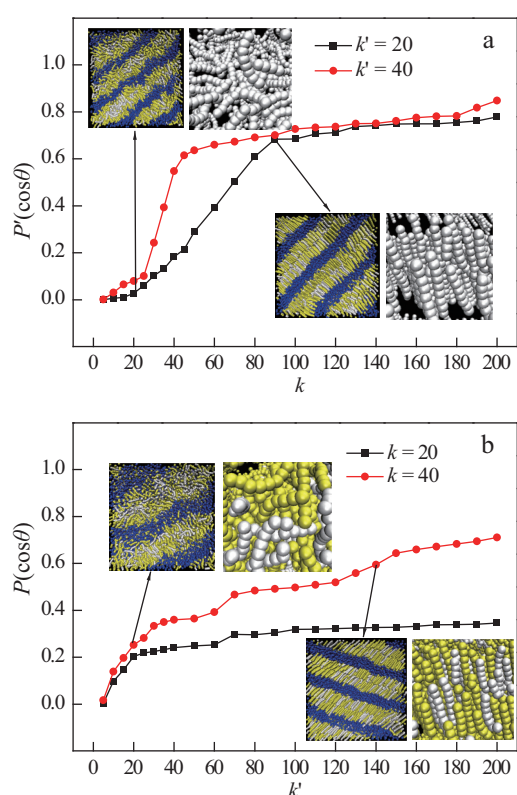


Fig. 6 The binary blends of A₈C₆/A's: (a) Orientation order parameter $P(\cos\theta)$ of homopolymers versus the stiffness of blocks, k ; (b) Orientation order parameter $P(\cos\theta)$ of blocks versus the stiffness of homopolymers k' . The insert shows the typical morphologies of A₈C₆/A's blends, where the coils are removed for easy viewing.

For comparison, we also calculate the orientation order parameter of semiflexible blocks $P(\cos\theta)$ as a function of semiflexible homopolymers stiffness k' , at the low stiffness for semiflexible blocks, $k = 20$ and 40. As shown in Fig. 6(b), the semiflexible blocks shown in yellow are also straightened and arranged in parallel, (*i.e.*, end-to-end in the semiflexible-layer). The blends transform from lamellar structure into a bilayer smectic-C liquid-crystalline phase,

where the semiflexible components are tilted with respect to the interfacial normal^[41]. This can be attributed to the fact that the orientation interactions between anisotropic rod-like homopolymers increase with increasing k' , leading to the ordering alignment of homopolymers along a common direction. Meanwhile, the ordered arrangement of A's homopolymers can further restrict and orient the alignment of A₈ blocks, thus finally promote the formation of liquid crystal phase.

CONCLUSIONS

We perform a DPD simulation on the liquid-crystal self-assembly of semiflexible-coil diblock copolymers blended with coil or semiflexible homopolymers systems. We investigate the phase behavior of blends and the orientation ordering of semiflexible components varied by the chain stiffness and the homopolymer volume fraction.

In semiflexible-coil/coil blends, with the addition of coil homopolymers and the increase of chain stiffness, not only the disorder-lamellae or disorder-monolayer liquid crystalline transition is observed clearly, but also the “dry brush” is induced by coil homopolymers. In semiflexible-coil/semiflexible blends, the chain stiffness of semiflexible homopolymers, which is matched with corresponding blocks, leads to the disorder-lamellae and disorder-monolayer liquid crystalline transition and even induces the transition between disorder and bilayer liquid-crystalline phase. The formation of bilayer liquid-crystalline phase mainly depends on the ratio of semiflexible blocks and the chain stiffness. Additionally, we investigate the case of mismatched stiffness between semiflexible homopolymers and corresponding blocks. The results demonstrate that homopolymers stiffness can indirectly improve the orientation ordering of blocks with low stiffness and even induce the bilayer liquid crystalline. In general, the final liquid-crystal assembly structure of copolymer/homopolymer blends containing semiflexible segments mainly depends on the chain stiffness and the composition of semiflexible components. This investigation can provide valuable guidance in manipulating the liquid-crystal assembly of polymer with low stiffness.

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