

Monte Carlo Simulation on Layered Polymeric Films^{*}

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Abstract Thin films of polymer blends composed of alternating copolymer, diblock copolymer and/or homopolymer are studied using Monte Carlo simulation. A multilayer morphology is observed in the film, that is, the blended polymers assemble into individual domains arranged from interior to the surfaces of the film. The coexisting components residing throughout the neighboring domains in the film make no distinguishable interface between any neighboring domains. By this means, it forms a vertical composition gradient in the polymeric film. Being different from layer-by-layer deposition of polyelectrolyte or hydrogen bonding approach *etc.*, the layered structure in this study is formed by polymer blending in one step. Alternating copolymers are found to be essential components to form vertical composition gradient (layered structure) in thin films.

Keywords: Monte Carlo simulation; Polymer blends; Alternating copolymer; Layered structure.

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INTRODUCTION

Polymer blends have been intensively studied. The properties of individual polymer component could be combined in the composite through blending^[1]. This is a convenient route for development of materials with less time-consuming and financial risk than those for novel polymers and prepared through new polymerization routes^[2]. However, the immiscible polymers tend to be segregated from each other, which usually makes polymer blends in bulk phase separate at macro scale, and thus affects the properties expected from polymer blending. In contrast, the block copolymers with segments connected by covalent bond have the ability to self-assemble into nanostructures^[3–8]. To control the phase separation of polymer blends at nano scale, previous studies showed that confining polymer blends into a thin film is an alternative to fabricate nano-device by polymers mixing^[9–12]. Here, the interaction between surface and polymers plays a dominant role in directing the assembly of polymer blends. Comparing with the symmetric geometries formed by self-assembly of block copolymer, which is periodically arranged, the polymer blends are more versatile to pattern nonuniform geometries^[13–16]. Furthermore, by adjusting the composition of the blend, nanostructures could be produced with

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lower density of defect than those from pure block copolymers^[17–19]. These studies indicate that the polymer blends have more potential on nano-manufacturing^[20–25].

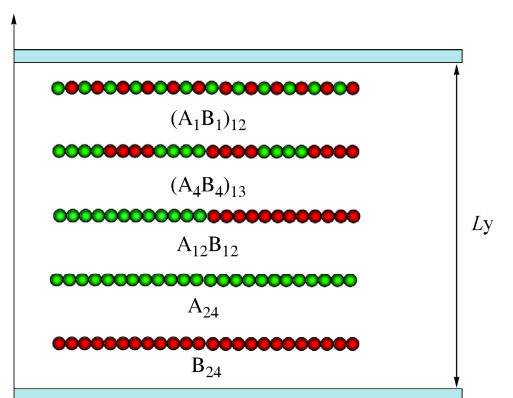
The multilayer nanostructures in a polymeric film has attracted much attention with the aim to fabricate stimuli-responsive device^[26], advanced coatings^[27], biological applications^[28] *etc.* Usually, the layered films are produced by layer-by-layer deposition of polyelectrolyte^[29], hydrogen bonding^[30] and spin^[31]/spray^[32] self-assembly *etc.* These technologies base on electrostatic adsorption or chemical bonding *etc.* to arrange neighboring layers, which require the polymers to have specific structures or functional groups. The fabrication processes aforementioned are multi steps and often rely on expensive devices^[33]. To our knowledge, there is no research on fabricating layered structure in thin film by polymer blending.

In this contribution, we carried out a simulation study on polymeric films formed by binary, ternary and quintuple components. Assembled structures and chains distribution are investigated in detail. The layered structures are formed by the blending of polymeric components in one step without direction of electrostatic adsorption or other potentials. Using Monte Carlo simulation, we predicted novel nanostructures by polymer blending and proposed a feasible experimental approach to fabricate layered structures.

MODEL AND PARAMETERS

Model

Thin films considered in this study are confined between two impenetrable and strictly neutral surfaces. As shown in Scheme 1, there are two physical boundaries with a distance L_y apart from each other. Five kinds of polymers with the same chain length of 24 beads are modeled. Only two kinds of segments A and B are considered in this study, as shown in Scheme 1, to mimic two immiscible segments. $(A_1B_1)_{12}$ and $(A_4B_4)_3$ are two alternating copolymers. $A_{12}B_{12}$ is a diblock copolymer. A_{24} and B_{24} are two homopolymers.



Scheme 1 Schematic illustration of the film geometry and components in the polymeric blends
 L_y is film thickness. A and B means two kinds of segments, the number of repeating units are shown as the subscript.

Monte Carlo Simulation and Parameters

An annealing Monte Carlo simulation in a canonical ensemble is employed in this study^[34]. Similar to previous move sets, the evolution of chain configuration is realized by the vacancy diffusion algorithm combined with the single-site bond fluctuation model. Metropolis rule governs each movement. The annealing strategy is used to gradually quench the system from its initial homogeneous state to the equilibrated state. We performed at least 10 million Monte Carlo steps (MCS) for each simulation. The lattice constant is used as dimension unit in this study. We have applied this simulation technology on the studies of copolymer self-assembly, the simulation detail can be found in our previous study^[34].

The volume fraction of segments was set at 70% to model a polymer melt. The film thickness is set at 56 in the unit of lattice constant, and limited film thickness shows no much influence on the phase separation (not shown in this contribution). We considered only repelling interaction between beads A and B to be 0.54 kT. The

interactions between beads and boundaries at Ly direction (Scheme 1) are set as zero to ensure two neutral surfaces. The periodic boundary conditions are imposed in the directions parallel to the surfaces to mimic a film condition.

RESULTS AND DISCUSSION

We calculated the distribution of individual components as a function of film thickness. For example, in the blend by $(A_1B_1)_{12}$ and $A_{12}B_{12}$ the distribution of $(A_1B_1)_{12}$ at film thickness Ly' is expressed with a general formula as follows:

$$\text{Density}(P, Ly') = \frac{N(P, Ly')}{N_0(Ly')}$$

Here, $N(P, Ly')$, $N_0(Ly')$ mean number of chains of polymer P (here is $(A_1B_1)_{12}$) at Ly' and number of all chains (here is the total number of $(A_1B_1)_{12}$ chains and $A_{12}B_{12}$ chains) at Ly' , respectively. We calculated the number of chains only once no matter that if the chain goes through the layer at Ly' for more than one time. The density value is ensemble-averaged for 10 times using the values at every 1000 MCS after the simulation has run for 10 million MCS.

Binary Blends of Alternating Copolymer and Diblock Copolymer

We first investigate thin film of binary blend by alternating copolymer $(A_1B_1)_{12}$ and diblock copolymer $A_{12}B_{12}$. The ratios of two segments (A and B) and chains lengths are exactly the same for these two kinds of copolymers. However, the difference in chain architectures endow them different self-assembly ability. Normally, the diblock copolymers $A_{12}B_{12}$ alone could self-assemble into a lamellar structure and $(A_1B_1)_{12}$ couldn't form regular structure. In bulk, the domains of $(A_1B_1)_{12}$ and $A_{12}B_{12}$ interpolate into each other in an arbitrary order (see Fig. S1 in supporting information). In contrast to it, for the film of this binary blend, the domains of $(A_1B_1)_{12}$ are segregated adjacent to the surfaces and the domain of $A_{12}B_{12}$ resides at the interior of the film. The components density distributions and equilibrated structures are shown in Fig. 1. At different $A_{12}B_{12}$ concentrations (0.33, 0.5, 0.67 shown in Fig. 1), the spaces adjacent to the surface are predominantly occupied by the polymer $(A_1B_1)_{12}$; the interior of film are mainly occupied by the polymer $A_{12}B_{12}$ with partial $(A_1B_1)_{12}$ chains being involved into the matrix of $A_{12}B_{12}$. In the interfacial layers between surface and interior domains, the concentration of $(A_1B_1)_{12}$ decreases gradually and the concentration of $A_{12}B_{12}$ increases accordingly. In Fig. 1, we find that the change of $A_{12}B_{12}$ concentration in the blend has no much influence on the maximum concentration of $A_{12}B_{12}$ in the interior of the film. For three kinds of $A_{12}B_{12}$ concentrations, the maximum concentrations of $A_{12}B_{12}$ in the interior of the film are always about 0.9. Correspondingly, The concentrations of $(A_1B_1)_{12}$ chains, those coexist with $A_{12}B_{12}$ in the interior of the film, are about 0.1. In the blend film, the domains sizes of each component are adjustable by changing the composition of the blend. As Fig. 1 shows, the domain of $A_{12}B_{12}$ shrinks with the decrease of concentration of $A_{12}B_{12}$.

Previous studies on assembly of polymer blends mostly consider lateral structures parallel to the film surface, and surface field is well designed and strictly applied to arrange the blended components into good orders^[15–20]. This is because without the covalent bonding between components in polymers blends, the macro phase separation will happen if there is no direction of surface field. In this study, the phase separation forms a thermodynamic equilibrium state with different polymers being segregated into individual domains, in which coexisting components in neighboring domains make materials in the film continuous. In short, it is an equilibrated film composed of continued domains by different polymers, which are arranged vertical to the surfaces.

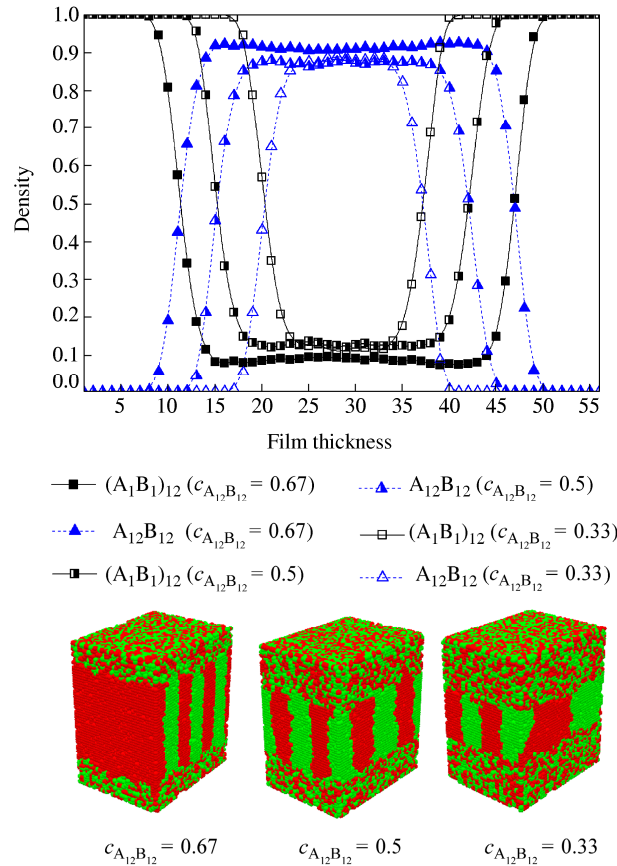


Fig. 1 The density distribution of binary blends ($(A_1B_1)_{12}$ and $A_{12}B_{12}$) as a function of film thickness (up), and equilibrated structures of the blends with different composition (down). The $A_{12}B_{12}$ concentrations in the blend change from 0.67 to 0.33 (the concentrations of $(A_1B_1)_{12}$ change from 0.33 to 0.67, correspondingly).

In fabricating layered structures of polymeric materials, the well-known layer-by-layer deposition requires the cyclic steps of consecutive adsorption with potentials such as electrostatic^[29], hydrogen bonding^[30] *etc.* It means the polymeric materials must be polyelectrolyte or with functional groups those can be used to layer-by-layer adsorption. In this study, the entropy alone drives the phase segregation of blended polymers into layered structures in one step. There is no requirement for the blended polymers to be polyelectrolyte or have specific groups.

In the film of blends, polymer in its individual domain remains self-assembly capability in bulk, which enable researchers introduce different self-assembly properties into a material. For the binary blend by alternating copolymers $(A_4B_4)_3$ and diblock copolymers $A_{12}B_{12}$, $(A_4B_4)_3$ shows an ability to self-assemble into a lamellar structures with smaller repeating periods (4 units of lattice constant) comparing with the periods by $A_{12}B_{12}$ (7 units of lattice constant). In bulk, the lamellar structures with different periods are randomly mixed (see Fig. S2 in supporting information). In the film, as Fig. 2 shows all chains of $A_{12}B_{12}$ are segregated inside of the film, while most chains of $(A_4B_4)_3$ are segregated adjacent to the surfaces with partial $(A_4B_4)_3$ chains coexisting with $A_{12}B_{12}$ in the interior of the film with concentration about 0.25. Therefore, the lamellar structures nearby the surfaces have repeating periods about 4 units and that inside the film have repeating periods about 7 units. In the cut views (a, b, c, d) of the film below the illustration of components density distribution, we find that the internal morphologies of individual domains (Figs. 2b and 2d) are well retained their lamellar structures with repeating periods 7 and 4 units, respectively; the interfacial layers between two domains (Figs. 2a and 2c)

show the evolution from one periods to the other periods. Usually, the equilibrated structures from self-assembly have only one repeating periods. Here, we predicted a hybrid lamellar structure with different periods in a material without direction of the surface field.

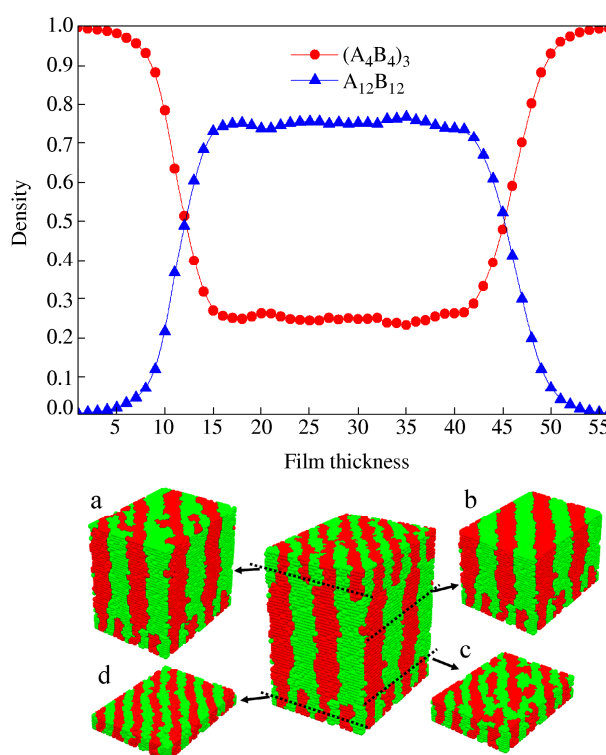


Fig. 2 The density distribution of binary blends ($(A_4B_4)_3$ and $A_{12}B_{12}$) as a function of film thickness (up) and equilibrated structure of the blends (down)
The cut views of equilibrated structure are shown: a and c show interfacial morphologies between neighboring domains; b and d show internal morphologies of individual domains.

For the polymeric nano-material, the researchers have fabricated the ordered structures using sparse pattern^[7, 35], nonuniform geometries by blends^[20], different structures on the surface and inside interlayer by confinement^[36], ultrasmall features by complex chain architectures^[37] *etc.* Together with these studies, we here demonstrate a new nanostructure that is the hybrid lamella with different repeating periods in a film.

Ternary Blend of Copolymers

It has been shown above the alternating copolymers tend to be segregated adjacent surfaces when being blended with diblock copolymers. The ternary mixture of two alternating copolymers $(A_1B_1)_{12}$ and $(A_4B_4)_3$ and block copolymer $A_{12}B_{12}$ is also studied and shows similar vertical phase separation as the binary blends. As shown in Fig. 3, chains of $(A_1B_1)_{12}$ occupy the surface domains of the film and chains of $A_{12}B_{12}$ are segregated into the interior of the film. The distribution of $(A_4B_4)_3$ chains is affected by the composition. When the concentration of $(A_4B_4)_3$ chains is low (0.17 in Fig. 3a), the $(A_4B_4)_3$ chains are involved into the domain of $A_{12}B_{12}$; for very large concentration (0.5 in Fig. 3c), the domain of $A_{12}B_{12}$ chains is reversely involved into the domain of $(A_4B_4)_3$ chains. At appropriate concentration (0.33 in Fig. 3b), three domains of two alternating copolymers and a diblock copolymer are evenly arranged in the film. It means the number of layers and thickness of the layer in thin films can be adjusted by the composition of the blend.

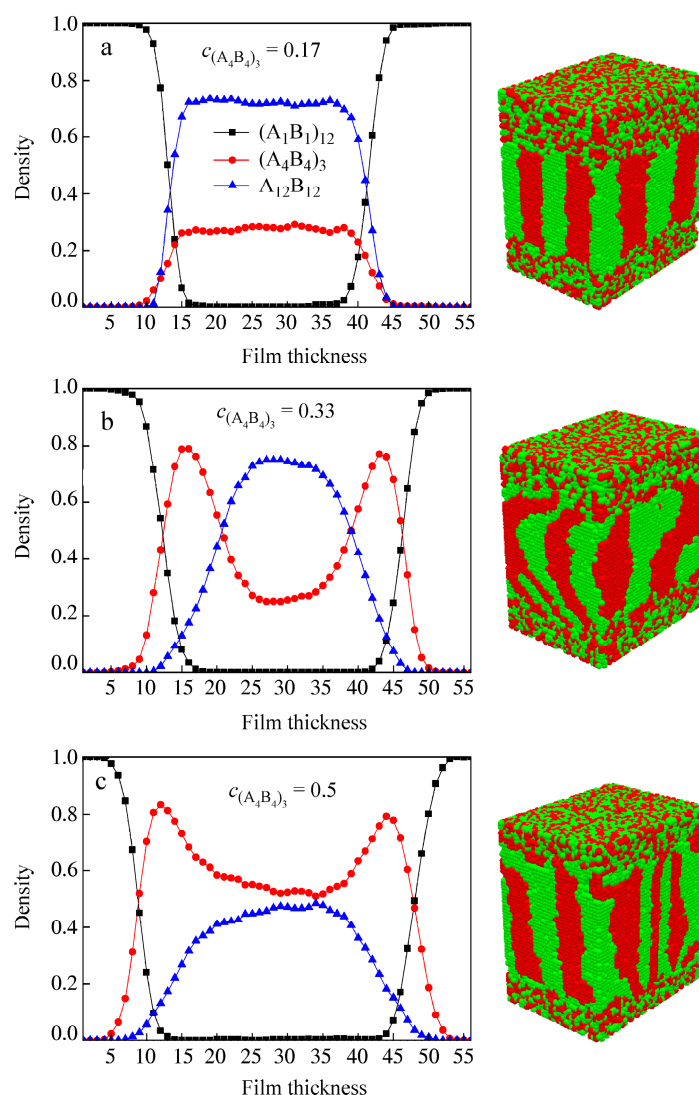


Fig. 3 The density distributions of ternary blends $((A_1B_1)_{12}, (A_4B_4)_3$ and $A_{12}B_{12})$ as a function of film thickness and the equilibrated structures, correspondingly. The concentration of $(A_4B_4)_3$ changes from 0.17 to 0.5, the concentrations of $(A_1B_1)_{12}$ and $A_{12}B_{12}$ are always the same.

Quintuple Blend of Copolymers and Homopolymers

Homopolymer has been largely applied in the fabrication of industrial polymeric materials. We studied the blends of copolymers and homopolymers to explore the possibility to modify the properties of homopolymer materials using varieties of copolymers. As shown in Fig. 4, five kinds of polymers are blended in a film, those are homopolymers A_{24} and B_{24} , diblock copolymer $A_{12}B_{12}$, alternating copolymers $(A_1B_1)_{12}$ and $(A_4B_4)_3$. The phase separation of this complex blend combines the phase separation behaviors in individual blends: two homopolymers (A_{24} and B_{24}) and diblock copolymer ($A_{12}B_{12}$) are segregated inside the film to form an internal domain which is enfolded by $(A_4B_4)_3$, and then $(A_1B_1)_{12}$ is located on the surface layers. As the illustration of components density distribution in Fig. 4 shows, in the interior of the film (film thickness = 15–42 units), chains of $(A_4B_4)_3$ coexist with chains of A_{24} , B_{24} and $A_{12}B_{12}$ in the internal domain with concentration being about 0.1. In the interfacial layers (film thickness = 7–15, and 42–50 units), five components coexist in the matrix by $(A_4B_4)_3$. From the outmost layers to the interfacial layers, chain density of $(A_1B_1)_{12}$ diminishes gradually and that

of $(A_4B_4)_3$ increases correspondingly. The simulation results indicate that the alternating copolymers can be used to modify the surface of the composites by homopolymer and/or diblock copolymers.

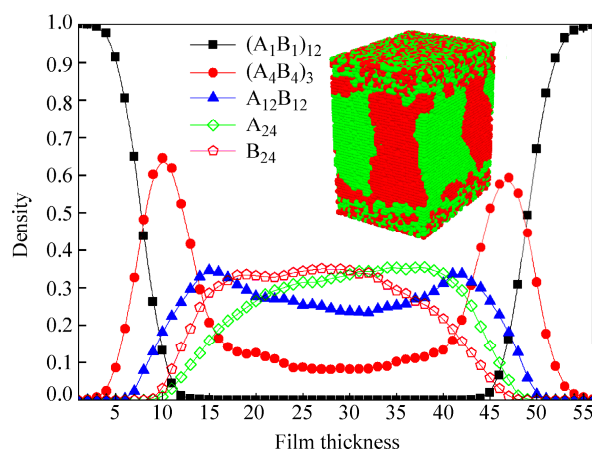


Fig. 4 The density distribution of quintuple polymeric blends as a function of film thickness and the equilibrated structure of the blend shown as an inset

It is clearly demonstrated, the alternating copolymers are essential components to fabricate vertical composition gradient in polymer films, the diblock copolymers or homopolymer has no capability to form layered structure in thin film without surface field. Herein we proposed a feasible experimental approach: blending alternating copolymers with diblock copolymers and/or homopolymer into a thin film, which will produce layered structure in one step. Considering the simplicity of our simulation parameters, there is no need to select specific polymers such as polyelectrolyte or those with functional groups.

CONCLUSIONS

In this contribution, we demonstrated the vertical phase separation of polymer blends in thin films using Monte Carlo simulation. The layered structure can be formed by polymers blending in one step. Alternating copolymers are essential components to induce vertical composition gradient in thin films without direction of surface field. The morphology and domain dimension of the film is adjustable according to the composition of the blend. We predicted a hybrid lamellar nanostructure with different periodic dimensions in a film. Our exploration should give valuable instructions on modification of polymeric materials and fabrication of nanostructures.

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Electronic Supplementary Material

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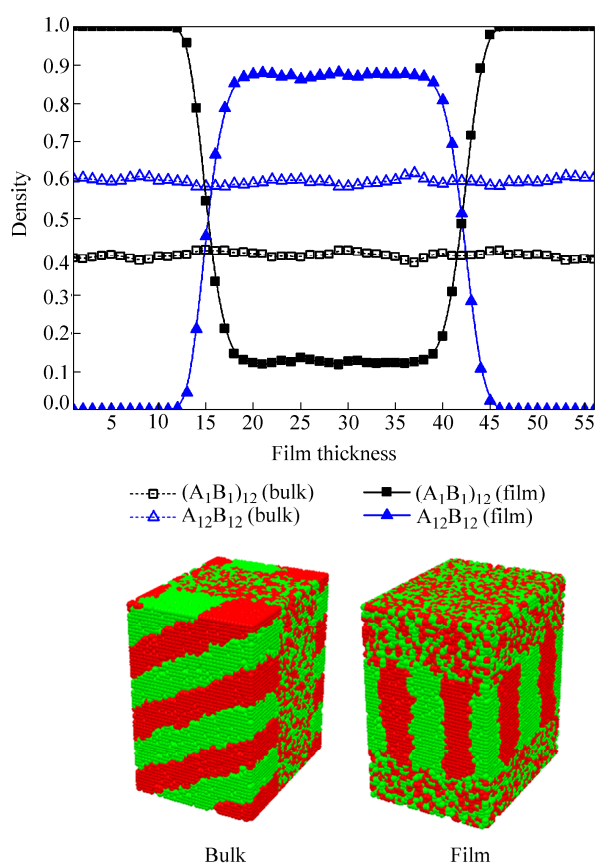


Fig. S1 The density distribution of binary blends ($(A_1B_1)_{12}$ and $A_{12}B_{12}$) in bulk and film (up), and equilibrated structures of the blends (down)

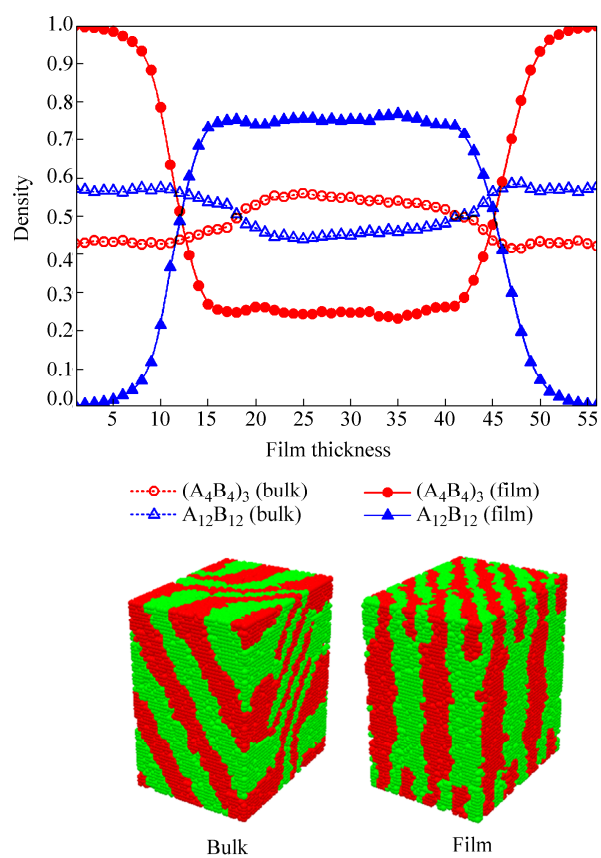


Fig. S2 The density distribution of binary blends $((A_4B_4)_3$ and $A_{12}B_{12}$) in bulk and film (up), and equilibrated structures of the blends (down)