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Computer simulation on the self-assembly of associating polymers

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Abstract

We present the results of Monte Carlo simulations of self-assembly in melt of pseudo-block copolymer formed through the association of associating polymer chains with attractive end-groups (sticker sites). Complexities of the phase structures result from these pseudo-block copolymers strongly depend on parameters, such as attractive interaction strength between two stickers and chain length of associating polymers. The weak, intermediate and strong interactions between two stickers lead, respectively, to the macro-separated, disordered and ordered lamellar phase structures. The ordered lamellar phases formed by these pseudo-block copolymers are more stable than that formed by pure diblock copolymers. Pseudo-block copolymers with shorter associating polymer chain prefer to form ordered lamellar phase and that with longer associating chain tend to form disordered phase.

Keywords: Associating end-groups; Self-assembly; Pseudo-block copolymers

1. Introduction

The sophisticated use of self-organizing materials, such as, liquid crystals, block copolymers, hydrogen- and π bonded complexes, and many natural polymers is the key to obtain some fine functional materials. The spontaneous assembly of block polymers was long well known, with which many complex phase morphologies [1–8] were obtained in melts or solutions. Lamella phase structure is the most common morphology for block copolymer. The covalent bonds connecting two incompatible segments play the essential role in the formation of lamellar morphology and other ordered phase structures [9]. Chains can change from one configuration to another only in certain ways and exhibit ordered structures through spontaneous assembly under the confinement of covalent bond. However, as well known, syntheses of block copolymers are so complicated that only a few kinds of monomers were successfully synthesized into the desired architectures. By comparison, productions of associating polymers through introducing a number of sites that strongly attract each other, i.e. stickers, are relatively simple. These associating polymers are able to be stuck each other to form pseudo-block copolymers and are expected to have spontaneous assembly behaviors similar to that of block copolymers.

Theoretical calculations [10–17] and experiments [18–22] have verified that the mixture of the pseudo-block copolymers lead to the fine ordered structures. Some ordered morphologies, such as string, tube and disc, were presented by theoretical calculation of Bredas et al. [10] in zwitterionic associating polymers. Broze et al. [18] observed the lamellar phase structure by small angle X-ray scattering in halato-telechelic polymers which can be associated by interactions between carboxyl at ends of chains and metal ions dispersed. Micelle-like structures were found by Jiang et al. [19–22] in solutions of incompatible polymers with specific interactions. Therefore, specific interactions of unlike polymers provide us a new way to prepare materials with controllable phase structures. In this simulation, our focus is on the relationship of morphologies of pseudo-block copolymer mixture with the attractive force strength between the end stickers.

2. Simulation

Lattice model and 'single-site bond fluctuation' method [23–25] were used to investigate the polymer configuration

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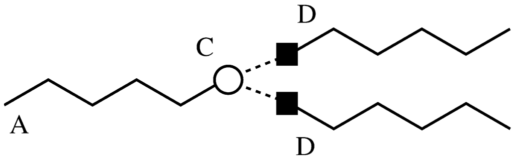

Fig. 1. Sketch of chain model of associating polymer A and B with sticker at the end of chain, sticker C is on the end of chain A, sticker D is on the end of chain B.

and evolution of phase morphologies of diblock and associating polymer chains in 2D simulations. Cifra et al. [26,27] showed that there is no essential difference in the phase behavior between a two- and three-dimensional simulation. Multiple-chain configurations were generated on a planar square 60 × 60 lattice. Diblock copolymers or associating polymers with varied chain length are put in the square lattice. A standard periodic boundary condition was imposed on the lattice to mimic an infinite-size system [28]. The volume concentration of polymer was as high as 0.95. As a result, the simulations correspond to a bulk. In addition, the volume of segment A is the same as that of B. The left 0.05 vacancy is handled as free volume. The 'vacancy diffusion' algorithm suggested by Lu et al. [29] was employed to improve the Monte Carlo simulation efficiency. The evolution of the chain configuration in simulation was achieved by randomly displacing of a single vacancy site to its eight nearest-neighboring sites on the lattice. The distance between the single unit and the eight nearest-neighboring sites are restricted to lengths of 1 and $\sqrt{2}$. Each attempted move may change the bond length, but the chain connectivity restricts the bond length to 1 and $\sqrt{2}$. The excluded volume interaction ensures no more than one bead per lattice site. The excluded bond cross guarantees no crossed-bond in system. If one attempted move violates either the excluded volume, the bond length restriction or excluded bond-crossing criterion, it is rejected. The acceptance or rejection of one attempted move, which satisfies the excluded volume, excluded bond crossing and bond length restriction, is further governed by the Metropolis transition probability [30] ω,

$$\omega = \min[1, \exp(-\Delta E/k_{\mathrm{B}}T)]$$

where

$$\begin{aligned}\Delta E = (&\Delta N_{\mathrm{AA}}\varepsilon_{\mathrm{AA}} + \Delta N_{\mathrm{BB}}\varepsilon_{\mathrm{BB}} + \Delta N_{\mathrm{CC}}\varepsilon_{\mathrm{CC}} + \Delta N_{\mathrm{DD}}\varepsilon_{\mathrm{DD}} + \\ &\Delta N_{\mathrm{AB}}\varepsilon_{\mathrm{AB}} + \Delta N_{\mathrm{AC}}\varepsilon_{\mathrm{AC}} + \Delta N_{\mathrm{AD}}\varepsilon_{\mathrm{AD}} + \Delta N_{\mathrm{BC}}\varepsilon_{\mathrm{BC}} + \\ &\Delta N_{\mathrm{BD}}\varepsilon_{\mathrm{BD}} + \Delta N_{\mathrm{CD}}\varepsilon_{\mathrm{CD}})\end{aligned}$$

is the energy change associated with one movement, ΔN, the difference of the number of the nearest-neighboring pairs of the sites occupied by monomers after and before the movement, and ε is the reduced interaction energy gained when the two neighboring sites are occupied by monomers; the subscripts A, B denote monomers A, B; the subscripts C, D denote sticker C and D, respectively.

In our simulations, $1/k_{\mathrm{B}}T = 0.5$ is invariable to simulate the constant temperature process in experiments.$\varepsilon_{\mathrm{AA}} = \varepsilon_{\mathrm{BB}} = \varepsilon_{\mathrm{CC}} = \varepsilon_{\mathrm{DD}} = 0$, $\varepsilon_{\mathrm{AB}} = \varepsilon_{\mathrm{AC}} = \varepsilon_{\mathrm{AD}} = \varepsilon_{\mathrm{BC}} = \varepsilon_{\mathrm{BD}} = 1$ which mean the existence of repulsion forces between the A and B, A and C, A and D, B and C, B and D segments, respectively. $\varepsilon_{\mathrm{CD}}$, interaction energy between segments C and D, is a variable to control the attractive interaction strength between stickers C and D. In this simulation, the values of $\varepsilon_{\mathrm{CD}}$ are set to be -1, -2, -3, -4, and -5, respectively. With the increase of absolute

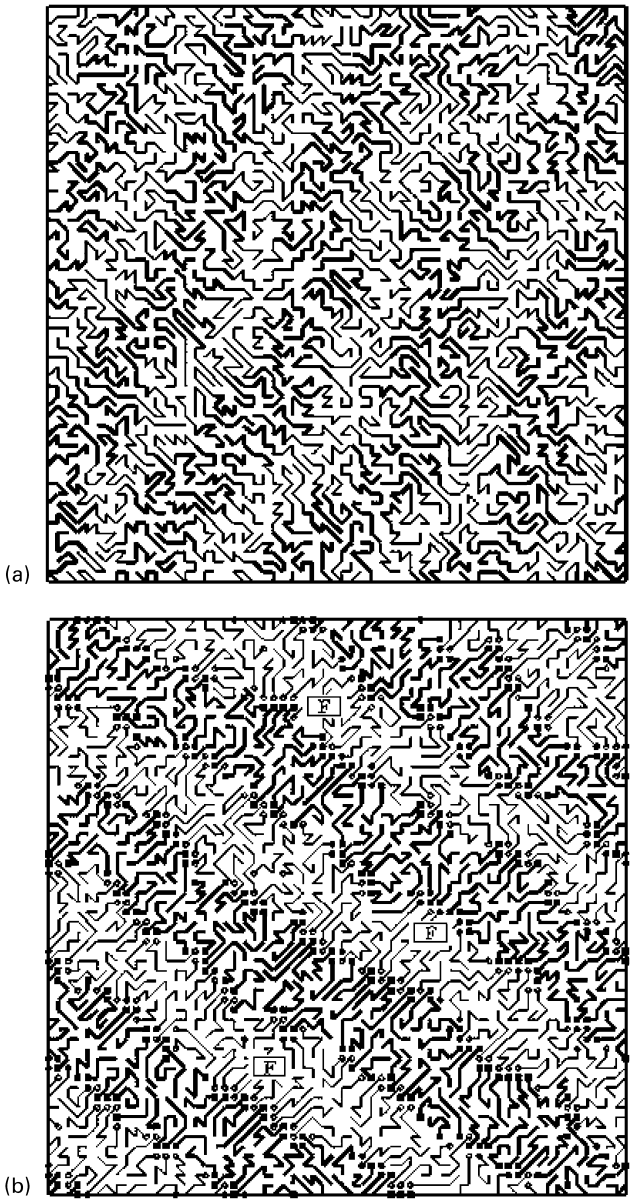

Fig. 2. Typical lamellar phase structures of diblock polymer and pseudo-block polymer (a) symmetrical diblock coppolymer with block length $L = 6$ segments; (b) associating polymer with chain length $L = 6$ segments and interaction parameter $\varepsilon_{\mathrm{CD}} = -5$.

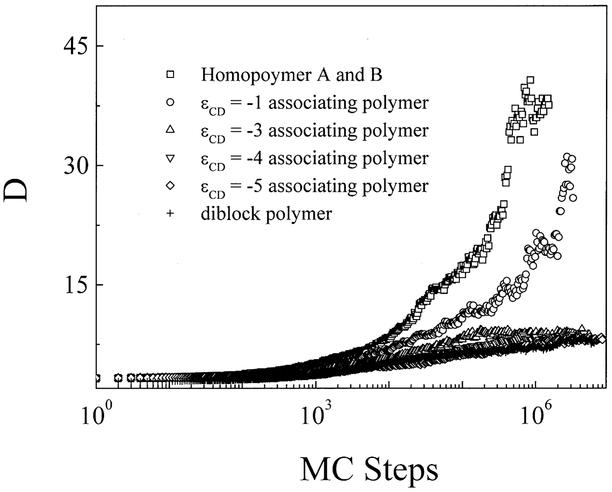

Fig. 3. Monte Carlo (MC) steps dependence of domain size (*D*) of dispersed phase of different kinds of blend, The chain length of homopolymer and associating polymer is 6 segments, respectively, and that of symmetrical diblock copolymer is 12 segments.

value of ε_{CD}, the attractive interaction between stickers C and D becomes stronger.

3. Results and discussion

As shown in Fig. 1, the polymer with an associating site, or sticker, on the end of the chain will be described in term of associating polymer. The associating sites or stickers, C and D in Fig. 1, are able to associate with one or more unlike stickers due to the attractive interaction to formed pseudo-block copolymers. The behavior of sticker here is similar to the interaction between ions with contrary charge. In general, the typical association process of stickers is characterized with lifetime, which strongly depends on chemical nature of sticker, e.g. interaction strength between stickers. Because of the similarity of the architecture between the pseudo-block copolymer and diblock copolymer, phase structures formed by the pseudo-block copolymers are hoped to be analogous to that of corresponding diblock copolymers. As expected, these pseudo-block copolymers can spontaneously assemble into the ordered lamellar phase as diblock copolymers do, shown in Fig. 2. However, to our surprise, the detailed analysis of Fig. 2a and b reveals that the lamellar phase of pure A–B diblock copolymer are laden with defects, i.e. the stripes formed by block A or B are zigzag. In contrast with diblock copolymer, the stripes formed by pseudo-block copolymers are relatively straighter; namely, the interfaces of phase A and B are parallel to each other. The associating polymer chains A and B are confined in the space of these parallel interfaces

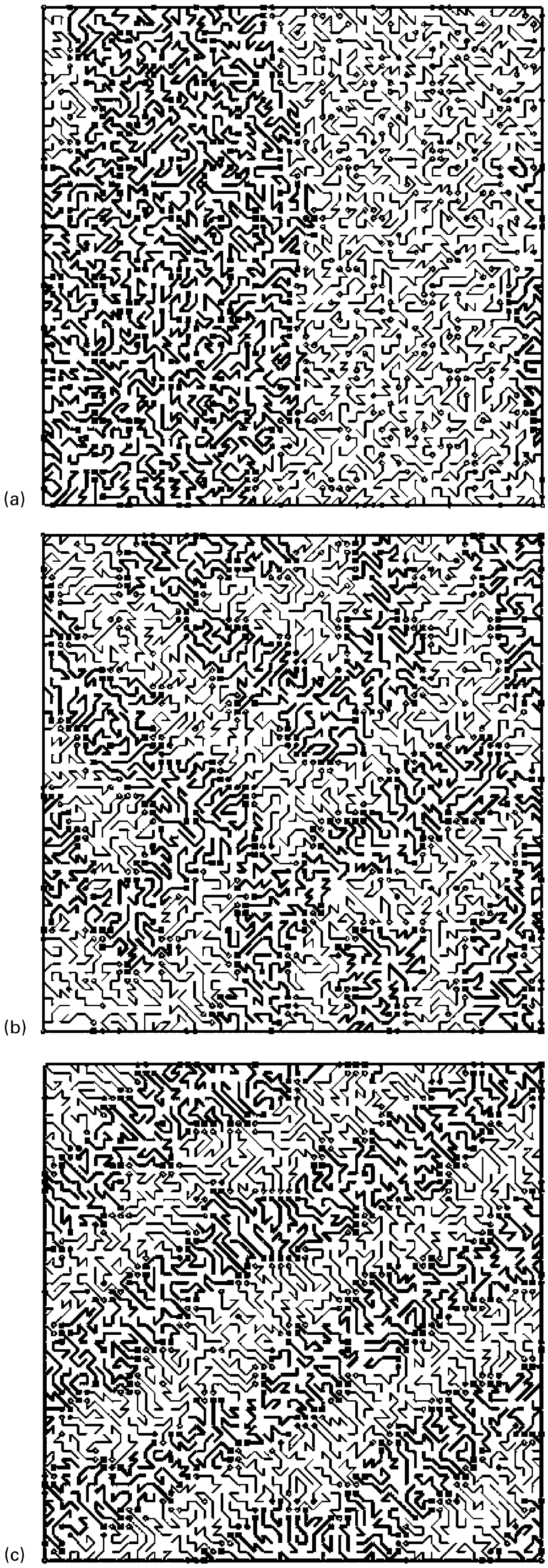

Fig. 4. Typical snapshots of phase morphologies of blend of associating block copolymer with various interaction ε_{CD} (a) $\varepsilon_{CD} = -1$; (b) $\varepsilon_{CD} = -3$; (c) $\varepsilon_{CD} = -4$.

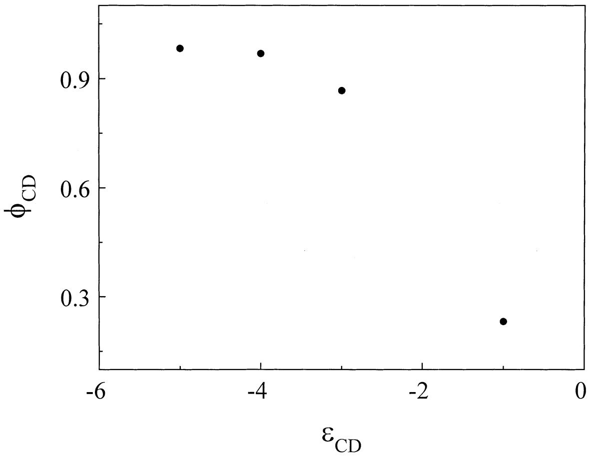

Fig. 5. Interaction parameterε_{CD} dependence of the fraction of associated polymers Φ_{CD}, number of associated stickers is divided by the total number of stickers.

and lead to the formation of defect-free lamellar phases. This implies that the lamellar phases of pseudo-block copolymers are more stable. Next, the domain size of phase formed by pseudo-block A (shown in Fig. 3) was investigated dynamically and compared with that of corresponding homo- and diblock copolymers. The domain size (D) is defined as N/N_d, where N and N_d are the lattice numbers and the number of segment A on the lines drawn parallel to the borderline [31]. In the case of $\varepsilon_{CD} = -1$, the change of domain size of pseudo-block copolymers with Monte Carlo steps is in the behavior closed to that of homopolymer A/B blends, indicating the occurrence of macrophase separation. Direct evidences for the macrophase separation are shown in Fig. 4a. On the contrary, in the case of $\varepsilon_{CD} = -3$, -4, and -5, evolution of the phase structures with Monte Carlo steps are more like that of A–B diblock copolymer, implying the occurrence of microphase separation. As matter of fact, only a part of associating polymers is able to be jointed into the pseudo-block copolymers, so in the system it is the mixture of the associating polymer A, B, and pseudo-block copolymer. When attractive interaction between two stickers is weak, such as $\varepsilon_{CD} = -1$, as shown in Fig. 5, the fraction of associated polymers, ϕ_{CD} (the number of associated stickers is divided by the total number of stickers), are about 0.2, indicating that only about 20% associating polymers are jointed together. These small parts of associated polymers are not able to stop the occurrence of macrophase separation. With the increase of the attractive interaction strength between stickers, such as $\varepsilon_{CD} = -3$, 86% associating polymers are stuck to each other (Fig. 5), namely, 14% associating polymers leave free. In such a system, the microphase separation happens. The typical disordered microphases resulting from the blend of associating polymers and associated polymers are shown in Fig. 4b. By further increase of attractive interaction strength of stickers, as in the cases of $\varepsilon_{CD} = -4$ and -5, the quantity of free associating polymers is reduced to less than 4%, the

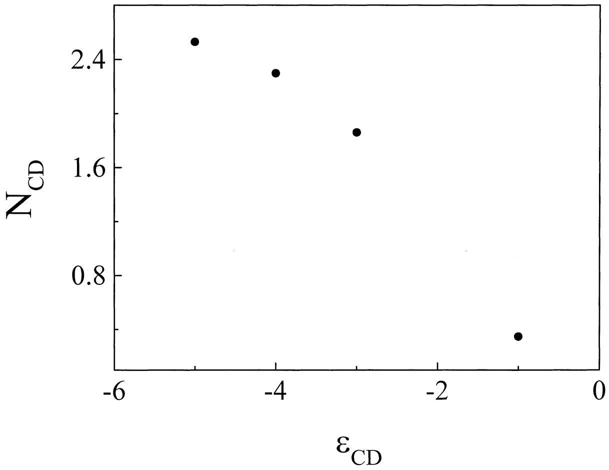

Fig. 6. Interaction parameter ε_{CD} dependence of N_{CD}, the average number of associated stickers on one unlike sticker.

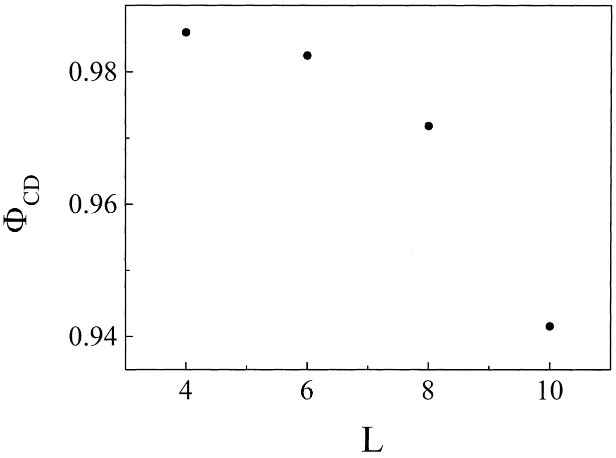

Fig. 7. Chain length L dependence of the fraction of associated polymers Φ_{CD}, number of associated stickers is divided by the total number of stickers, and with the same interaction parameter$\varepsilon_{CD} = -5$.

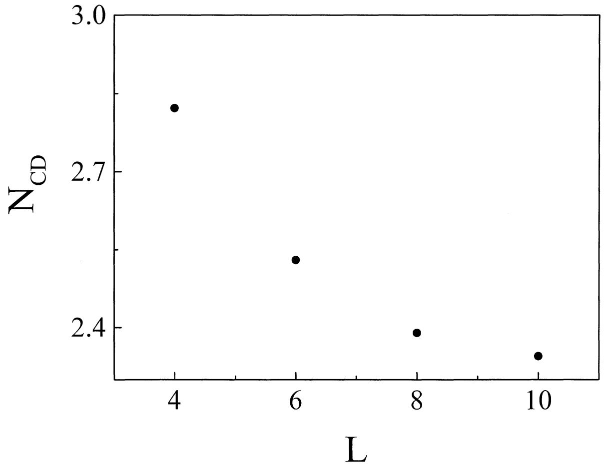

Fig. 8. Chain length L dependence N_{CD}, the average number of associated stickers on one unlike sticker, with fixed interaction parameter $\varepsilon_{CD} = -5$.

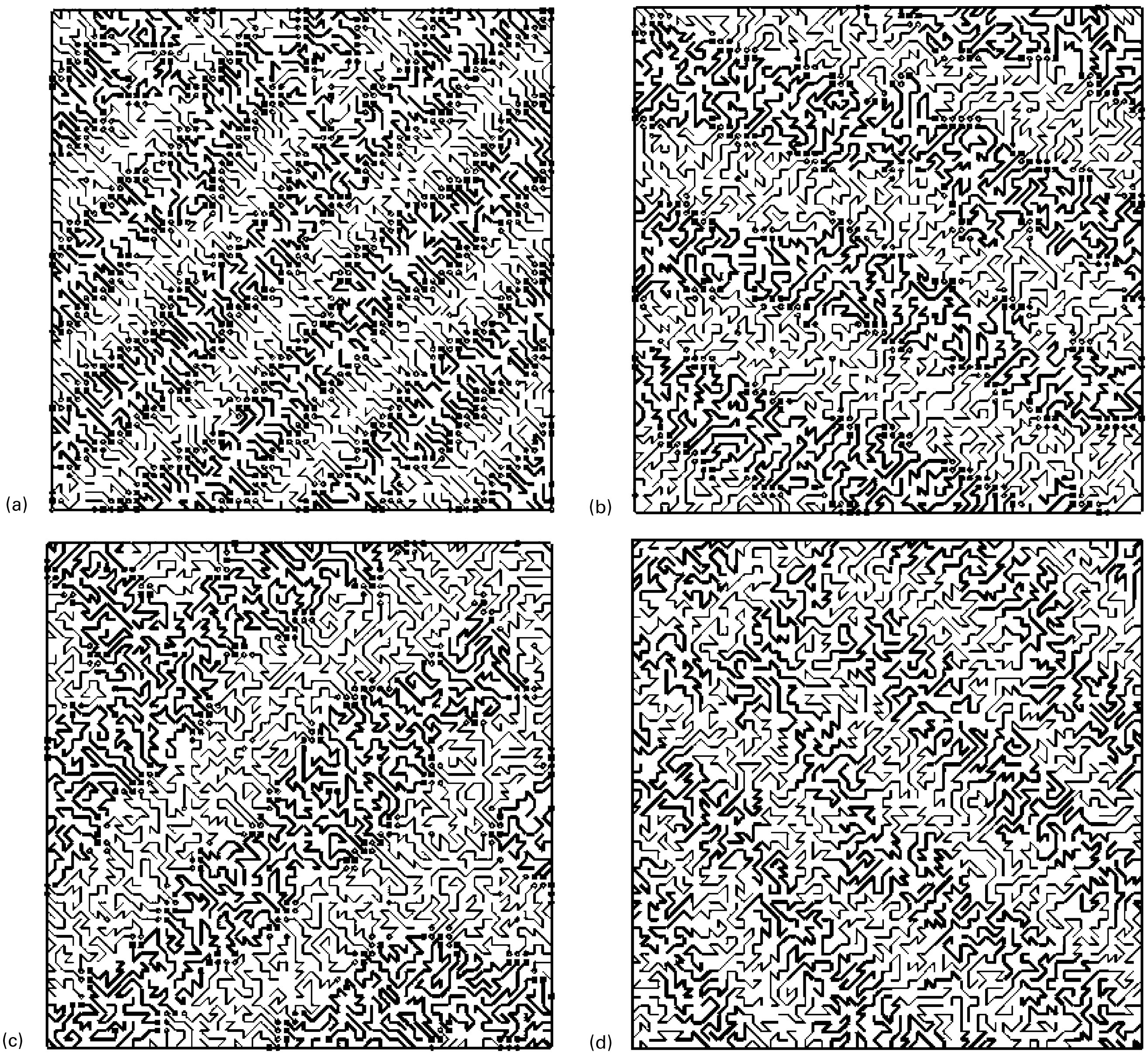

Fig. 9. Typical snapshots of phase structure of pseudo-block polymers with various chain length L and constant interaction parameter $\varepsilon_{\mathrm{CD}} = -5$. (a) $L = 4$ segments, ordered; (b) $L = 8$ segments, ordered; (c) $L = 10$ segments, defects start to appear; (d) diblock copolymer A-*b*-B with block length 8 segments, microphase separation, but disordered.

ordered lamellar phase forms through the assembly of these pseudo-block polymer chains (or associated polymers). What is more, the stripes of lamellar phase became somewhat thicker than that assembled from the diblock copolymers due to the existence of the few percent free associating polymers in the system. On the other hand, in the case of weak interaction of stickers ($\varepsilon_{\mathrm{CD}} = -1$), the number of associated stickers on one unlike sticker, N_{CD} (one sticker is enabled to stick with N_{CD} other unlike stickers) is below 0.5 (shown in Fig. 6), indicating seldom associating polymer chains are stuck to each other, which is in coincidence with the conclusion from Fig. 5. For the case of $\varepsilon_{\mathrm{CD}} = -3$, $N_{\mathrm{CD}} = 1.9$ which means one sticker are able to associate with about two other stickers. When ordered lamellar phase are formed, as in the case of $\varepsilon_{\mathrm{CD}} = -4$ and -5, the value of N_{CD} approaches to 3 (Fig. 6), implying the stickers tend to aggregate into the pattern as that indicated by letter F in Fig. 2b, namely, the aggregated stickers tend to stand in straight lines. These aggregated stickers cooperate with each other and have positive contribution to the stability of the ordered lamellar phase. What is more, as indicted in Section 2, that the lamellar phase of pure A–B diblock copolymer are zigzag, but that of pseudo-block copolymer are relatively straight. This is also origin from the value of variable N_{CD}. As matter of fact, with the increase of N_{CD} values, the stronger repulsions should exist between phases A and B. As a result, this system should have relatively lower energy and, correspondingly, have a straighter interface. As in the case of pseudo-block copolymers with $\varepsilon_{CD} = -5$, N_{CD} is near to 3, which induces the straighter interface. However, as in pure diblock copolymer system, the value of N_{CD} is reasonably regarded as 1, it is understandable that the interfaces are zigzag due to the lower N_{CD}.

The chain length of associating polymers should be another parameter to be responsible for the stability of the ordered microphase of associating polymers. As imaginable, the associating probability of unlike sticker on longer associating polymers should become lower, because the stickers on the end of associating polymers tend to be buried into the coils formed by long polymer chains due to their flexibility. As shown in Figs. 7 and 8, both the fraction of associated stickers ($\varepsilon_{CD} = -5$), ϕ_{CD}, and the number of associated stickers on one unlike sticker, N_{CD}, decrease with the chain length of associating polymer chain. These lead to the evaluation of the ordered lamellar phase (Figs. 2b, and 9a and 9b) toward to mixed ordered lamellar and disordered phase (Fig. 9c). By further increase of the chain length, the completely disorder phase should appear, which we did not do it here. It is worth noting that, when the associating polymers are made of 4 segments, almost all the polymer chain (98.5%) are associated each other (shown in Fig. 7) and every sticker is associated with about three other stickers (Fig. 8), which are benefit to form the perfectly ordered lamellar phase as discussed in Section 2. In Fig. 9a, almost all the chains are perpendicular to the interface, which is the behavior of the rigid polymer. On comparison of Fig. 9b with d, we found when the pseudo-block copolymer length are 16 segments, i.e. each associating polymer has 8 segments, the ordered lamellar phase still appear, but for the diblock copolymer chain with some length as pseudo-block copolymer (16 segments), the defects, or disordered phases, start to appear. This demonstrated that the ordered lamellar phase through the association of associating polymer are more stable in comparison with that formed by the corresponding pure diblock copolymer.

4. Conclusions

The self-assembly of associating polymer with a sticker at the end of chain was studied by the Monte Carlo simulation technique. These associating polymers form pseudo-block copolymers through the association of stickers. Macro- and microphase separation in the system happen depending on the attractive interactions between stickers. Ordered and disordered lamellar phases exist in the system depending both on the attractive interaction of stickers and length of associating polymer chain. The ordered lamellar phases formed by the pseudo-block copolymers are more stable in comparison with that of corresponding diblock copolymers. The interfaces of ordered microphase of diblock copolymer are laden by defects, but the interfaces of ordered microphase of pseudo-block copolymer are relatively smooth.

Acknowledgements

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