

Significantly Improved Stereocomplexation Ability in Cyclic Block Copolymers

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Abstract Stereocomplex crystallization in cyclic polymer blend and cyclic block copolymers was investigated by means of dynamic Monte Carlo simulations. Five polymer systems (linear polymer blend, linear diblock copolymer, cyclic polymer blend, cyclic diblock copolymer and tetrablock copolymer) were established. It was interestingly found that the cyclic polymer blend exhibited the weakest stereocomplexation ability, while the two cyclic block copolymers showed stronger stereocomplexation ability than the linear diblock copolymer. This abnormal improved stereocomplexation ability of the cyclic block copolymers can be attributed to the synergy between the ring chain topology and the block copolymer structure. Compared with the linear block copolymers, the ring chain topology confined segmental motions of cyclic polymer chains to smaller regions, and then the segments belonging to the different blocks in the cyclic block copolymers have more chance to contact with each other. In this way, the cyclic block copolymers had better miscibility between segments belonging to different types of blocks, leading to the stronger stereocomplexation ability.

Keywords Monte Carlo simulation; Stereocomplex crystallization; Ring chain topology; Cyclic block copolymers

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INTRODUCTION

Nowadays, the world-wide plastic ban is becoming more and more strict, and then it is urgent for human beings to find other alternative polymer materials, which should have wide sources for raw materials and do not generate pollutants. Luckily, poly(lactic acid) (PLA), which is produced from starch and can be recycled after natural degradation, is an ideal green material.^[1–3] In poly(L-lactic acid) (PLLA) or poly(D-lactic acid) (PDLA), homocrystallites (HCs) can be formed. However, the melting point of the HCs is only around 180 °C.^[4–10] Thus, among polymer materials that need to be used at high temperatures, PLA is not a good choice. Apart from the neat PLLA and PDLA, the PLLA/PDLA blends or the PLLA-PDLA block copolymers can lead to the formation of stereocomplex crystallites (SCs).^[11–13] PLA containing SCs (SC-PLA) exhibits a higher melting temperature, higher mechanical performances, better hydrolysis resistances and better gas barrier properties compared with those composed of HCs, so that the applications of PLA can be effectively broadened.^[14–17] For instance, SC-PLA is a good candidate as drug delivery carrier due to its high encapsulation efficiency.^[16] Another report illuminated that a kind of membrane made from SC-PLA materials display fabulous antifouling property.^[18] However, it is hard to achieve

complete SCs on account of the competition between the formation of HCs and SCs.^[7,19–22] It is inevitable that intramolecular chain folding of PLLA or PDLA occurs during crystallization, resulting in the formation of HCs.^[23,24] It is generally believed that the intermolecular ordering could induce the formation of stereocomplex crystals while homocrystals prefer to form due to the intramolecular chain folding.^[21–23,25,26] With the aid of Fourier transform infrared spectroscopy (FTIR) technique, several researchers found the presence of intermolecular hydrogen bond interactions between methyl and carbonyl groups in PLLA and PDLA chains, thus resulting in the formation of SCs.^[26,27]

Therefore, the key to broadening the engineering application of PLA is to make the SC formation overcome the HC formation, resulting in the formation of more SCs in PLA. In recent years, different methods have been attempted to improve the content of SCs.^[28,29] Liu *et al.* designed an efficient novel nucleator, which can remarkably increase the fraction of SC in both isothermal and nonisothermal crystallizations through forming considerable hydrogen bonds with PLA chains.^[20] In addition, some researchers focused on the effect of crystallization temperature on SC formation.^[5,30] Henmi *et al.* carried out a number of experiments about isothermal crystallization process of SC-PLA, and found that the crystallinity of SCs increases with increasing crystallization temperature.^[5] Previously, our group studied the SC formation in linear multiblock copolymers using Monte Carlo (MC) simulations and drew a conclusion that the SC content increases with the increase of block number, due to the better miscibi-

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lity among different types of blocks in the multiblock copolymers with more blocks.^[24] Namely, better miscibility provides two enantiomers with higher probability to interact with each other and form crystallites by intermolecular parallel arrangements.^[24,31–33] In addition to the miscibility, it was demonstrated that crystallization mode and chain mobility also contribute to the stereocomplexation ability.^[21,28,34–36]

Changing chain topology also affects the stereocomplexation ability.^[37,38] Some experimental work displayed that cyclic PLLA/PDLA blends have weaker stereocomplexation ability compared with the linear PLLA/PDLA blends.^[39,40] However, some research groups further showed that cyclic PLLA-block-PDLA copolymers exhibit strong ability to form SCs.^[41,42] In our present simulation work, we focused on the microscopic mechanisms dominating the SC formation in cyclic block copolymers. Based on dynamic MC simulations, we found that the cyclic block copolymers exhibit significantly improved stereocomplexation ability due to the synergistic effect between the ring chain topology and the block copolymer structure.

SIMULATION DETAILS

The simulation environment was a cubic lattice box, the side length of which was 64 lattice sites. 1920 Coarse-grained polymer chains were put into the box. The length of each coarse-grained chain was 128 beads. To investigate the effect of chain topology on the SC formation, five different systems was set up: cyclic polymer blend, cyclic diblock copolymer, cyclic tetrablock copolymer, linear polymer blend and linear diblock copolymer. In the system of the cyclic polymer blend, there are 960 cyclic A chains and 960 cyclic B chains. In the system of the cyclic diblock copolymer, all cyclic chains were composed of 64 uninterrupted A beads and 64 uninterrupted B beads. In the system of the cyclic tetrablock copolymer, two blocks with 32 A beads and two blocks with 32 B beads were alternately arranged in every cyclic chain. In the system of the linear polymer blend, there are 960 linear A chains and 960 linear B

chains. In the system of the linear diblock copolymer, all linear chains consisted of 64 consecutive A beads followed by 64 consecutive B beads. These chain structures could be understood more clearly through the structure diagram shown in Fig. 1. In our simulations, the two blocks are marked with different symbols, *i.e.*, the beads belonging to the A blocks were marked with 0, while the beads belonging to the B blocks were marked with 1. In this way, the two blocks can be distinguished in the simulations.

One bead could occupy one lattice site, and in this way the occupation density was 0.9375, mimicking a bulk polymer system. In our simulation method, the specific chemical structure of PLA chains was ignored, and one bead represents one Kuhn's statistical segment, which was made up of two C6.^[43] Previously, based on this simulation method, our group has successfully studied the mechanisms of the SC formation in different systems.^[21,24,32,33,44] One bond existed for every two consecutive beads, and the orientation of the bond was either along lattice axes or diagonals. The segments could move by jumping to the adjacent vacant lattice sites or sliding of local segments. In the motion processes of chains, the bond was not allowed to be broken. The coordination number of every bead was 26. Based on the Cartesian coordinate system, there were 6 lattice axes, 12 face diagonals and 8 body diagonals in the simulation box.

How chain segments moved in one MC cycle was controlled by the Metropolis sampling algorithm. There was an opportunity for each bead to move in one MC cycle. In this condition, whether chain segments could move or not was decided by the energy difference (ΔE) of the system before and after movements. The ΔE was given as follows:

$$\frac{\Delta E}{kT} = \frac{\Delta c E_c + \Delta p_1 E_{p_1} + \Delta p_2 E_{p_2}}{kT} = \left(\Delta c + \Delta p_1 \frac{E_{p_1}}{E_c} + \Delta p_2 \frac{E_{p_2}}{E_c} \right) \frac{E_c}{kT} \quad (1)$$

where E_c represents the potential energy change due to the presence of non-collinear conformation, related to the chain flexibility, E_{p_1} represents the potential energy change due to a

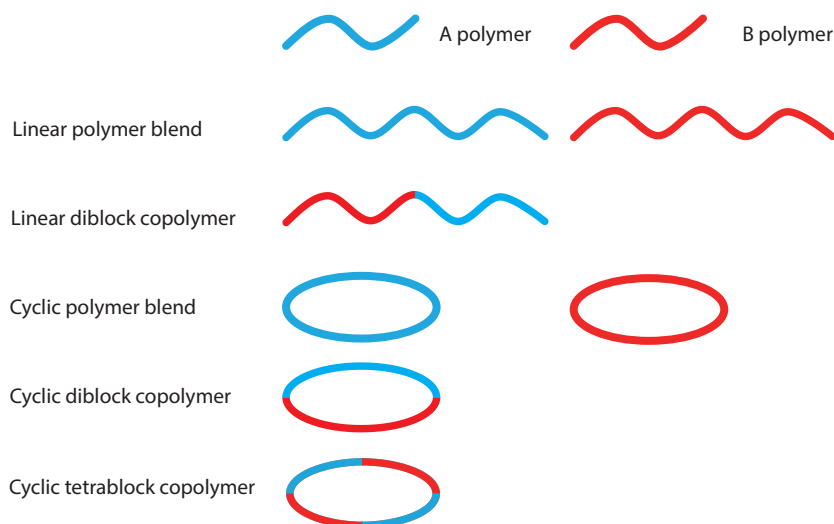


Fig. 1 The structure diagram of chains with different topologies, *i.e.*, linear polymer blend, linear diblock copolymer, cyclic polymer blend, cyclic diblock copolymer and cyclic tetrablock copolymer, respectively. A polymer chains are denoted by blue lines, and B polymer chains are denoted by red lines.

pair of nonparallel packed bonds of A beads or that of B beads, related to the thermodynamic driving force of HC formation, E_{p_2} represents the potential energy change due to a pair of nonparallel packed bonds containing one bond of A polymer and one bond of B polymer, related to the thermodynamic driving force of SC formation, Δc denotes the net increase of non-collinear conformation, Δp_1 denotes the net increase of pairs of nonparallel packed bonds of A beads or B beads, Δp_2 denotes the net increase of pairs of nonparallel packed bonds containing one A polymer bond and one B polymer bond, and k is the Boltzmann's constant. As mentioned above, intermolecular hydrogen bonds can form in SCs,^[26,27] resulting in higher energy reduction during SC formation, compared with HC formation. Therefore, two different parameters (E_{p_1} and E_{p_2}) were introduced in our simulations. According to the work of Hu's group,^[23] the value of E_{p_1}/E_c was assigned to 1.0, while that of E_{p_2}/E_c was assigned to 1.2, as illuminated in Fig. 2.

The detailed process of the simulation was as follows: firstly, the systems were relaxed for 10^6 MC cycles under an athermal condition to prepare a fully amorphous state; secondly, the amorphous state was quenched to different reduced simulation temperatures ($kT/E_c = 2.5, 3.0, 3.5$ and 4.0 , respectively) for further isothermal crystallization. In the following sections, we used T to denote the reduced temperature for brevity.

RESULTS AND DISCUSSION

The changes in crystallinity for the five different systems crystallized at different crystallization temperatures are shown in Fig. 3. Crystalline bonds were defined as the bonds that had more than five parallel bonds in their adjacent areas, regardless of whether the bonds were formed by A or B beads. Otherwise, we treated the bonds as amorphous bonds. Furthermore, we defined crystallinity as the proportion of the number of crystalline bonds to the total number of bonds. It can be clearly

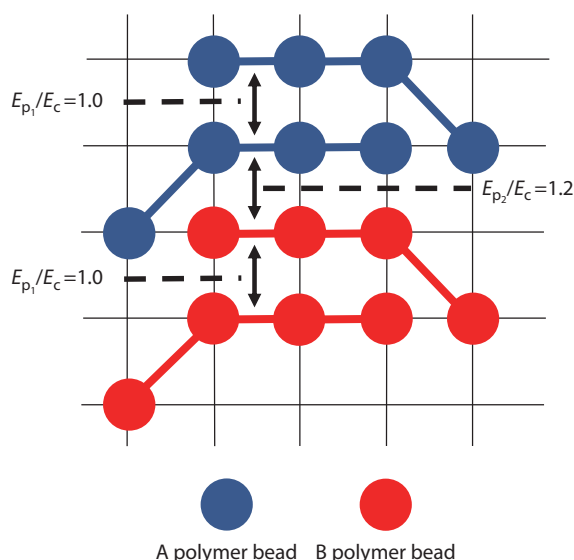


Fig. 2 Schematic illustration of $E_{p_1}/E_c = 1.0$ for a pair of A polymer bonds or a pair of B polymer bonds, and $E_{p_2}/E_c = 1.2$ for one A polymer bond and one B polymer bond.

seen that the crystallinity in all the five systems ascends with simulation time at different temperatures ($T=2.5, 3.0, 3.5$ and 4.0 , respectively), proving the occurrence of polymer crystallization. Besides, as the crystallization temperature rises, the crystallinity rate of these five systems decreases, which can be attributed to the decrease of the degree of supercooling caused by the temperature increase.^[45] In experiments, Yasuniwa *et al.*^[46] and Tsuji *et al.*^[47] observed that the spherulite density of PLA decreased with the increasing temperature, demonstrating that the temperature increment inhibited the nucleation process of PLA, and thus slowed down the overall crystallization rate.

It is worthwhile to pay attention to the content of SCs (the ratio of the number of SC bonds to the total number of crystalline bonds) for the five systems. An acceptable definition of SCs should be provided before calculating SC content. Inspired by the experimental work of Tashiro *et al.*,^[48] the definitions of SC bond and HC bond in our simulation model follow the following principles: if one bond is a crystalline bond and in its nearest neighbor space the ratio of the number of crystalline bonds of A beads to the number of crystalline bonds of B beads is greater than 0.5 and less than 2, the bond will be regarded as a SC bond. Conversely, if this ratio is less than 0.5 or greater than 2, the bond will be regarded as a HC bond. Fig. 4 depicts the relevant crystalline morphologies of HCs and SCs in the cyclic polymer blend system at $T=2.5$. A polymer bonds and B polymer bonds were printed by two distinct colors. As seen in Fig. 4, different arrangements of chain segments in HCs and SCs can be seen. The left snapshot shows the HCs, in which the A or B crystalline bonds are surrounded by the crystalline bonds belonging to the same polymers, and the right snapshot displays the SCs, in which the A and B crystalline bonds prefer to interweave together with each other. The crystalline morphologies of the HCs and SCs in the above two snapshots are in line with the experimental phenomena and theoretical analysis,^[49,50] confirming the validity of the current simulation model.

Subsequently, according to the definitions of SCs and HCs, the SC contents of the final status files (at crystallization time of 2×10^5 MC cycles) of the five systems at different crystallization temperatures were calculated, as illuminated in Fig. 5. The final SC contents of all the five systems increase with the increase of crystallization temperature. This dependence of the final SC contents on crystallization temperatures was also observed in some experimental work.^[5,51] Matsuba's group detected that the crystallinity of SCs gradually increased as crystallization temperature increased from 100°C to 180°C .^[5] In our previous simulations, it was also found that the increase of crystallization temperature can lead to the increase of the final SC contents in the filled polymer blends and the linear multiblock copolymers.^[24,44] At relatively low crystallization temperatures, the formations of HCs and SCs both have enough degrees of supercooling, and then the competition between HCs and SCs is fierce during crystallization, leading to the formation of SCs with relatively low content. As mentioned above, however, the melting temperature of HCs is lower than that of SC.^[6,52,53] Although the degrees of supercooling decrease in the formations of both SCs and HCs with the increase of crystallization temperature, the formation of SCs still remains the enough degree of supercooling at rela-

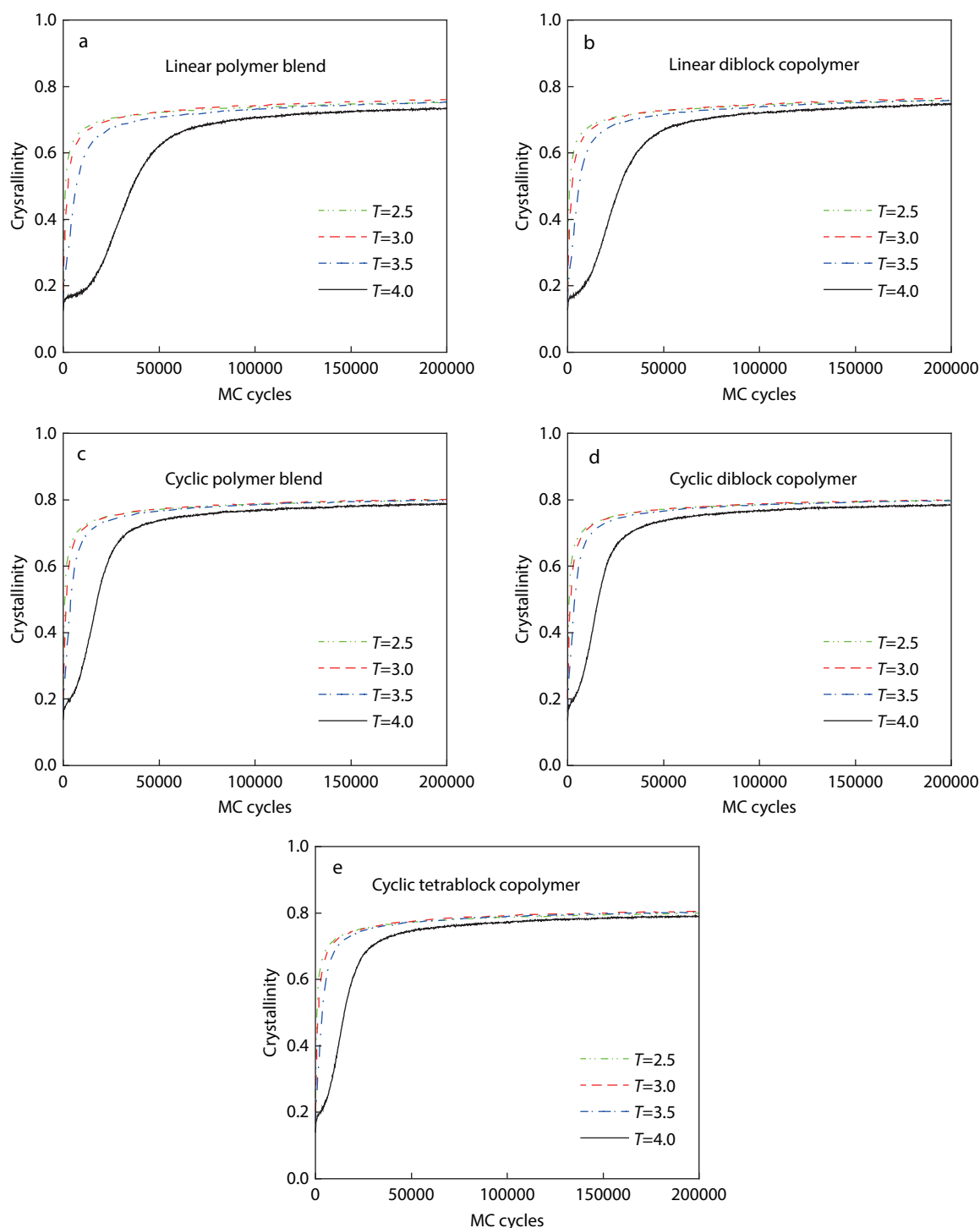


Fig. 3 Crystallinity curves of five different systems: (a) linear polymer blend, (b) linear diblock copolymer, (c) cyclic polymer blend, (d) cyclic diblock copolymer and (e) cyclic tetrablock copolymer, at different temperatures from $T=2.5$ to 4.0.

tively high temperatures while that of HCs does not, leading to the weakening of the competitiveness of HC formation and then the increase of SC content.^[33]

Fig. 5 also shows that the final contents of SCs at all crystallization temperatures are arranged in the following order from highest to lowest: the cyclic tetrablock copolymer, the cyclic diblock copolymer, the linear diblock copolymer, the

linear polymer blend and the cyclic polymer blend. Firstly, the final content of SCs in the cyclic polymer blend is lower than that in the linear polymer blend, indicating that the cyclic polymer blend has a weaker ability to form SCs than the linear polymer blend. This means that the special ring chain topology negatively impacts the SC formation. Previously, Sugai *et al.*^[39] and Meyer *et al.*^[40] found that the cyclic

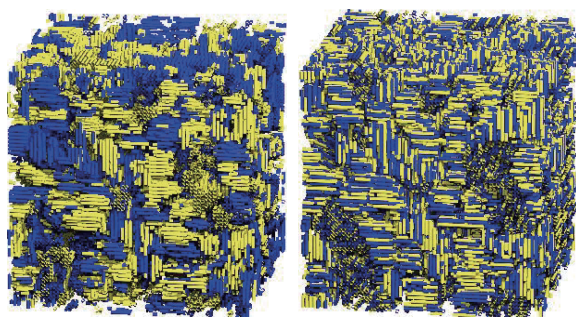


Fig. 4 Snapshots of HCs and SCs in cyclic polymer blend system at $T=2.5$; crystalline bonds in A polymer are represented by the yellow cylinders, and crystalline bonds in B polymer are represented by the blue cylinders.

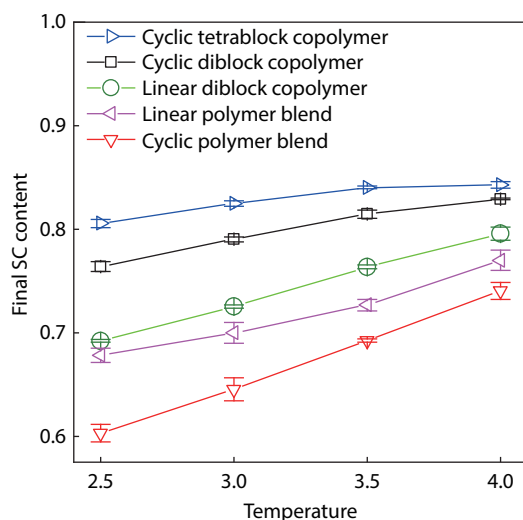


Fig. 5 Dependence of the final SC content of five different systems on the crystallization temperature.

PLLA/PDLA blends exhibited a weaker stereocomplexation ability compared with the corresponding linear PLLA/PDLA blends. Secondly, the final content of SCs in the cyclic diblock copolymer is higher than that in the cyclic polymer blend and the linear diblock copolymer, suggesting that the cyclic diblock copolymer exhibit a stronger stereocomplexation ability than the cyclic polymer blend and the linear diblock copolymer. In other words, the preparation of cyclic block copolymers not only can overcome the negative impacts of the ring topology structure, but also can effectively improve the stereocomplexation capacity. In experiments, Sugai *et al.* and Iwashima *et al.* successfully synthesized the cyclic diblock copolymers, and detected that the cyclic diblock copolymers had a strong stereocomplexation ability.^[41,42] Thirdly, the final content of SCs in the cyclic tetrablock copolymer is higher than that in the cyclic diblock copolymer, implying that the increase of the block number is beneficial for the improvement of the stereocomplexation ability. Previously, also using dynamic MC simulations, we demonstrated that the linear multiblock copolymer systems with larger block numbers exhibit a stronger ability for the SC formation.^[24] It should be noted that the effective enhancement in the ability of the SC formation of the cyclic multiblock copolymers should be attributed to the synergy between the ring topology structure

and the block copolymer structure.

In the following sections, we try to reveal the underlying mechanisms of this synergistic effect. Based on the previous experiment and simulation work,^[21–24,26,28–30,32,33,44,54,55] there are four factors affecting the formation of SCs: melting temperature, segmental mobility, crystallization mode and chain miscibility. Differing from linear polymer chains, cyclic polymer chains do not contain end segments, resulting in the appearance of compact conformations and thus low conformational entropy of cyclic chains.^[56,57] This change of chain conformations of cyclic polymer chains may cause the difference in the melting temperature between linear and cyclic polymer chains. In order to achieve the melting temperature of the different systems, the behaviors of crystallization during cooling followed by a heating process, in which the temperature homogeneously changed 0.01 units per 500 cycles, were simulated. This cooling-heating process is similar to the related operations in the experiments based on differential scanning calorimetry (DSC).^[58] The curve of crystallinity versus temperature during the heating process is shown in Fig. 6. During heating, the crystallinities of all the systems are constant at first, then drop to some minimum values and finally become almost unchanged. Furthermore, the melting temperature was defined as the value of the abscissa of the intersection of the two lines, as depicted with the orange dashed lines in Fig. 6. Herein, one line was used to fit the stage when the crystallinity decreases with the temperature increase, and the other line was used to fit the stage when the crystallinity is almost unchanged at high temperatures. The melting temperatures of all the systems obtained in this way are presented in Fig. 7. It can be seen that the melting temperatures of the cyclic polymer systems (the cyclic polymer blend, the cyclic diblock copolymer and the cyclic tetrablock copolymer) are apparently higher than those of the linear polymer systems (the linear polymer blend and the linear diblock copolymer). In experiments, Müller's group found that the melting temperatures of the cyclic PLAs are higher than those of the linear PLAs.^[59] In theory, the cyclic polymers lack end segments, and in this condition the conformational entropy of the cyclic polymers is lower than that of the linear polymers, resulting in the lower entropy change during crystallization. Thus, the melting temperature of the cyclic polymers is higher than that of the linear polymers. Using molecular dynamics simulation, Sommer and coworkers also detected that the cyclic polymer melts exhibited higher melting temperatures compared to their linear counterparts.^[60] In other words, though the difference in the melting temperatures between the cyclic and the linear polymer systems is small, the current simulation results are consistent with the corresponding experimental results, the theoretical analysis results and the simulation results. Namely, the conclusion that the cyclic polymer systems exhibit higher melting temperatures than the linear polymers based on the current simulation is reasonable.

For the cyclic polymer systems, owing to their higher melting temperatures, the degree of supercooling for the HC formation will be higher compared with the linear polymer systems. In this condition, the ability of the HC formation in the cyclic polymer systems should be stronger than that in

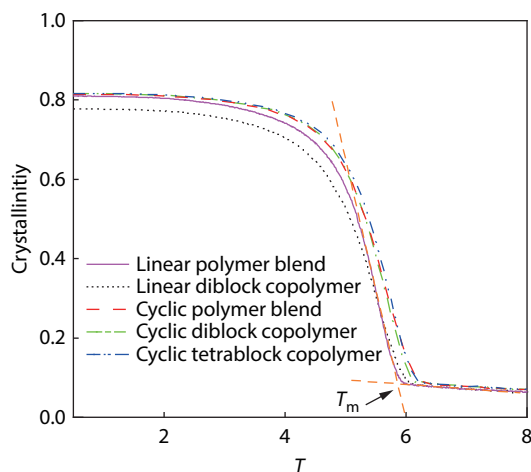


Fig. 6 Changes of crystallinities of five different systems during subsequent heating process after cooling.

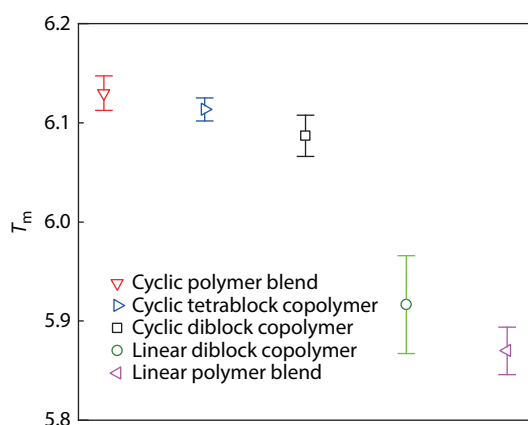


Fig. 7 The melting temperature of five different systems.

the linear polymer systems, leading to the weaker stereocomplexation ability in the cyclic polymer systems. However, the two different kinds of cyclic polymer systems (the cyclic polymer blend and the cyclic block polymers) exhibit the different stereocomplexation ability: the SC content of the cyclic polymer blend is lower than that of the linear polymer blend, but the cyclic diblock polymer has the higher SC content compared with the linear diblock polymer. In other words, the difference in the melting temperature between the linear and the cyclic polymer systems is not the key factor dominating the SC formation in the cyclic block polymer systems.

Chain mobility is another factor affecting the SC formation.^[28,35] In order to explore the influence of chain mobility on the SC formation in these five polymer systems, a parameter called the probability of segment movement (PSM) was used to characterize the ability of segmental motion. This parameter is described as the probability of one bead moving into the vacant lattices or slipping along local chain segments in one MC cycle, which can be calculated according to the following equation:^[61]

$$\text{PSM} = \min \left[1, \sum_{j=1}^n \exp \left(\frac{\Delta E_{ij}}{kT} \right) \right] \quad (2)$$

where n represents the number of vacant lattice sites around the bead occupying the lattice site i , and ΔE_{ij} represents the

energy change caused by one bead moving from the lattice site i to the lattice site j . Furthermore, the mean value of PSM, $\langle \text{PSM} \rangle$, can be used to reflect the segmental mobility of the system. Fig. 8 shows the values of $\langle \text{PSM} \rangle$ of the five polymer systems at $T=4.0$ and crystallization time of 10000 MC cycles. As can be seen in Fig. 8, the values of $\langle \text{PSM} \rangle$ of the linear polymer systems (the linear polymer blend and the linear diblock copolymer) are obviously higher than those of the cyclic polymer systems (the cyclic polymer blend, the cyclic diblock copolymer and the cyclic tetrablock copolymer), demonstrating that the segmental mobility in the linear polymer systems is significantly stronger than that in the cyclic polymer systems. In experiments, it was also detected that the chain movement capability of cyclic polymers is weaker compared with linear polymers.^[62] This difference in the chain mobility between the cyclic and linear polymer systems should be due to the special chain topology of cyclic polymers that do not have end segments. In more detail, as shown Fig. 8, the value of $\langle \text{PSM} \rangle$ of the cyclic copolymer blend is lower than those of the linear polymer blend and the linear diblock copolymer, but higher than those of the cyclic diblock polymer and tetrablock copolymer. As demonstrated in some experimental work and our former simulation work, segmental mobility plays an important role in the SC formation.^[28,35] However, this contribution of segmental mobility on the SC formation cannot explain that the two kinds of the cyclic block copolymers (the cyclic diblock copolymer and the cyclic tetrablock copolymer) with the lowest $\langle \text{PSM} \rangle$ exhibit the highest final SC content. In short, some other mechanisms dominating the SC formation in the cyclic block copolymers exist.

Nucleation mode or crystallization mode can also affect the stereocomplexation ability.^[21–23,26] Apparently, chain folding allows segments belonging to the same chain to approach each other and align in parallel to form crystals, which is beneficial for the HC formation. Then, the parameter (adjacent chain-folding probability), which was defined as the ratio of the number of crystalline stems connected by short loops composed of less than five beads to the number of total crystalline stems was used to quantify the probability of chain folding during crystallization.^[33,63–65] Fig. 9 displays the changes of the values of the adjacent chain-folding probabi-

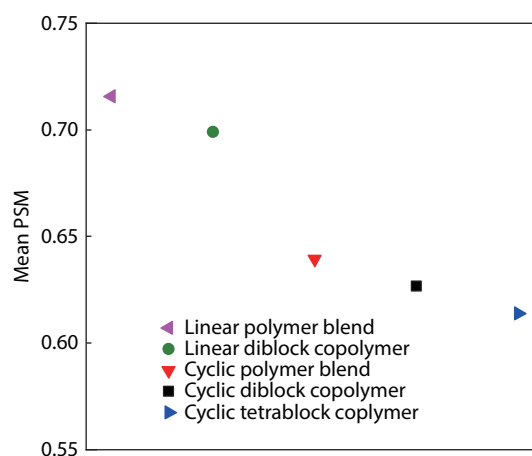


Fig. 8 The mean PSM values of the five different systems at $T=4.0$ and crystallization time of 10000 MC cycles.

lity of the five different systems during crystallization at $T=4.0$. It can be found that the values of the adjacent chain-folding probability of the three cyclic polymer systems (the cyclic polymer blend, the cyclic diblock copolymer and the cyclic tetrablock copolymer) are similar and significantly greater than those of the linear polymer systems (the linear polymer blend and the linear diblock copolymer). In other words, the cyclic polymer systems have a stronger chain folding ability than the linear polymer systems due to the absence of end segments. In the corresponding experiment and simulation work, it was demonstrated that the methods that can promote the polymer crystallization based on the mode of the intermolecular parallel alignments will effectively improve the stereocomplexation ability.^[21,22,34,44] For instance, Hu's group observed that the stretching of polymers can cause the deformation of polymer chains, leading to the preference of intermolecular parallel alignment mode during crystallization and thus the improved stereocomplexation ability of stretched polymer systems.^[34] Then, if the crystallization mode dominates the stereocomplexation ability, the cyclic diblock polymer should have lower SC contents compared with the linear diblock copolymer, which is inconsistent with our simulation results. This means the crystallization mode is not key mechanism controlling the SC formation in cyclic block polymers.

According to some pioneer experimental work, the miscibility of two enantiomers belongs to one of the important factors affecting the SC formation, because the better segmental miscibility can provide more chance for segments of two enantiomers to meet each other and then result in the formation of more SCs.^[49,54,66] Pan's group improved the miscibility by adding a third component, namely, poly(vinyl phenol), which can form intermolecular hydrogen bonds with PLLA and PDLA chains simultaneously. In this way, the two enantiomers (PLLA and PDLA) were indirectly tied together, and the miscibility between them was effectively improved, leading to the enhancement in the stereocomplexation ability.^[49] Then, we need to check whether the special synergy between the ring chain topology and the block copolymer structure results from the improvement in the miscibility

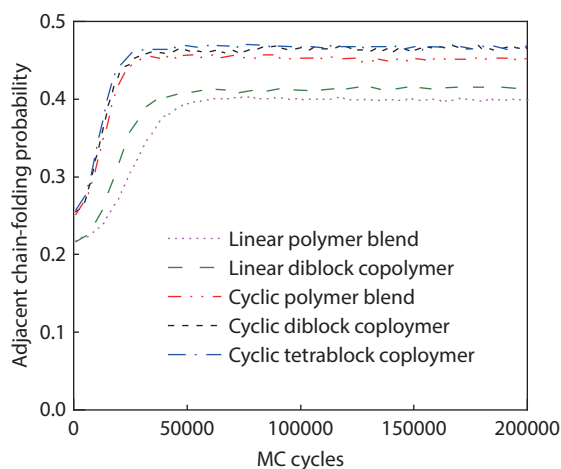


Fig. 9 Changes of adjacent chain-folding probability in crystals during crystallization at $T=4.0$ for the five different systems.

between segments of different types. Herein, the mixing parameter is used to quantitatively reflect the segmental miscibility in the five different systems,^[24,33,44,67] which is defined as the ratio of the average number of B polymer beads in the nearest neighbors of all the A polymer beads to the total number of the lattice sites in the nearest neighbors of one A polymer bead (26 lattice sites). The higher value of the mixing parameter indicates the better segmental miscibility. The mixing parameters in the five different systems at the completely relaxed state were calculated, and the corresponding results are shown in Fig. 10. Interestingly, it can be seen that the order of the mixing parameters from the largest to the smallest is as follows: the mixing parameter in the cyclic tetrablock copolymer, the mixing parameter in the cyclic diblock copolymer, the mixing parameter in the linear polymer blend and the mixing parameter in the cyclic polymer blend, which is completely consistent with the order of the final SC content in these five different systems. In other words, the polymer systems with the higher mixing parameter can have the more final SC contents, that is, the stronger stereocomplexation ability, suggesting that the stereocomplexation ability is closely correlated with the segmental miscibility.

It should be noted that the segmental miscibility is controlled by both of the chain topology and the chain structure. First, the cyclic polymer chains have no chain ends, and this special chain topology makes it difficult for them to interpenetrate each other, resulting in the lower mixing parameter for the cyclic polymer blends compared with the linear polymer blends. However, the segmental miscibility in the cyclic diblock copolymer is better than that in the linear diblock copolymer, but worse than that in the cyclic tetrablock copolymer. This significant improvement in the segmental miscibility of the cyclic block copolymers should be attributed to the synergy between the ring chain topology and the chain structure of block copolymers. As a matter of fact, the presence of the ring chain topology will confine the segmental motions of polymer chains to smaller regions. As demonstrated in Fig. 11, the mean square radius of gyration ($\langle R_g^2 \rangle$) of the two linear polymer systems is apparently higher than that of the three cyclic polymer systems. In the condition the segments belonging to the different blocks in the cyclic block copolymers

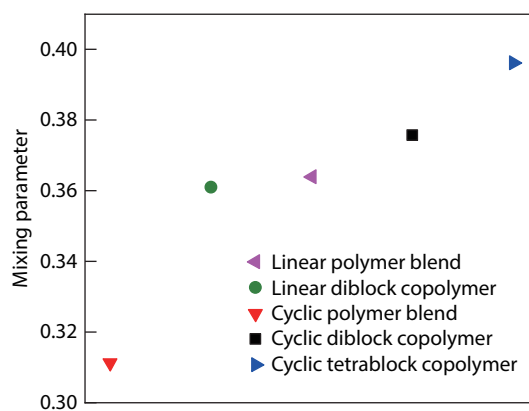


Fig. 10 Mixing parameter values of the five different systems at the completely relaxed state.

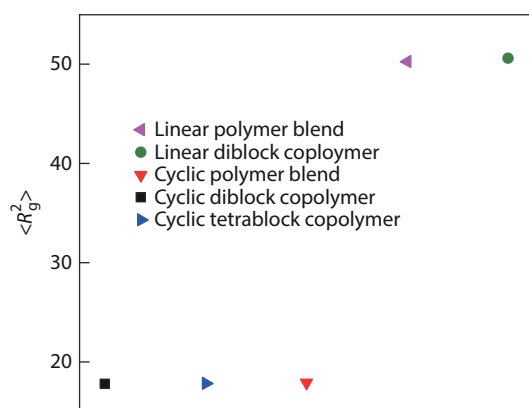


Fig. 11 Mean square radius of gyration of the five different systems at the completely relaxed state.

can have more chance to contact with each other, leading to the better segmental miscibility in the cyclic block copolymers. In addition, compared with the cyclic diblock copolymer, more blocks existing in the cyclic tetrablock copolymer will result in a higher chance of contact between segments belonging to different blocks and thus a better segmental miscibility. Namely, the excellent segmental miscibility in the cyclic block copolymers due to the synergistic effect between the ring topology and the chain structure of block copolymers trumps the other factors, such as the high melting temperatures, the low segmental mobility and the more chain folding, leading to the strong stereocomplexation ability.

It should be noted that the final SC content in the cyclic tetrablock copolymer with higher mixing parameter is higher than that in the cyclic diblock copolymer, indicating that the increase of the number of blocks can further cause the improvement in the stereocomplexation ability. Previously, we investigated the SC formation in the linear block copolymers, and also found that the stereocomplexation ability can be effectively enhanced by the increase of the block number.^[24] To our knowledge, there are few experimental or simulation work focusing on the SC formation in the cyclic multiblock copolymers. We hope that our current findings of the improved stereocomplexation ability in cyclic block copolymers will lead to more studies of SC formation in cyclic block copolymers.

In brief, the presence of the ring chain topology weakens the stereocomplexation ability in cyclic polymer blends. However, in the cyclic block copolymers, the synergistic effect between the ring chain topology and the chain structure of block copolymers exists, resulting in the significant improvement in the stereocomplexation ability.

CONCLUSIONS

With the help of dynamic MC simulations, the SC formation in the cyclic polymer blend and the cyclic block copolymers was studied in detail. Compared with the linear polymer blend, the cyclic polymer blend has higher melting temperature, lower segmental mobility, higher chain folding and lower miscibility between segments belonging to different types, thus resulting in the weaker stereocomplexation ability. However, the cyclic diblock copolymer has the stronger stereocomplexation ability

compared with the linear diblock copolymer. This special phenomenon can be owing to the presence of the synergistic effect between the ring chain topology and the block copolymer structure. Compared with the linear diblock copolymer, the ring chain topology in the cyclic diblock copolymers confines the segmental motions of polymer chains to smaller regions, and then the segments belonging to the different blocks have more chance to interact with each other, leading to the better segmental miscibility in the cyclic block copolymers. This improvement in the miscibility dominates the enhanced stereocomplexation ability in the cyclic diblock copolymer. In addition, the increase of the block number can further cause the improvement in the miscibility of segments of different types, resulting in the enhancement in the stereocomplexation ability of the cyclic block copolymers with more blocks.

NOTES

The authors declare no competing financial interest.

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