

Stereocomplex Crystallization in Asymmetric Diblock Copolymers Studied by Dynamic Monte Carlo Simulations

Ying Xu^a, Jun Yang^a, Zong-Fa Liu^a, Zhi-Ping Zhou^a, Zhao-Peng Liang^a, Tong-Fan Hao^b, and Yi-Jing Nie^{a*}

^a Research School of Polymeric Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

^b Institute of Green Chemistry and Chemical Technology, Jiangsu University, Zhenjiang 212013, China

Abstract Stereocomplex crystallization in asymmetric diblock copolymers was studied using dynamic Monte Carlo simulations, and the key factor dominating the formation of stereocomplex crystallites (SCs) was uncovered. The asymmetric diblock copolymers with higher degree of asymmetry exhibit larger difference between volume fractions of beads of different blocks, and local miscibility between different kinds of beads is lower, leading to lower SC content. To minimize the interference from volume fraction of beads, the SC formation in blends of asymmetric diblock copolymers was also studied. For the cases where the volume fractions of beads of different blocks are the same, similar local miscibility between beads of different blocks and similar SC content was observed. These findings indicate that the volume fraction of beads of different blocks is a key factor controlling the SC formation in the asymmetric diblock copolymers. The SC content can be regulated by adjusting the difference between the contents of beads of different blocks in asymmetric diblock copolymers.

Keywords Asymmetric diblock copolymers; Monte Carlo simulations; Stereocomplex crystallization

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INTRODUCTION

The development of degradable plastics based on renewable resources is a hot topic in the field of polymer materials and engineering.^[1–5] On the one hand, the application of these degradable polymeric products is conducive to environmental protection, since the “white pollution” caused by non-degradable plastics can be avoided. On the other hand, using polymeric materials generated from renewable resources can reduce the dependence of industry on petroleum, and this is especially important for countries lacking natural resources. Among these degradable plastics based on renewable resources, poly(lactic acid) (PLA) is one of the most concerned materials,^[3–7] and it has been used to manufacture a number of products, such as surgical sutures, membranes and fibers.

However, it should be noted that PLA still cannot totally replace the conventional plastics, owing to its relatively weak mechanical properties and low melting point.^[8–10] Ikada *et al.* first observed that stereocomplex crystallites (SCs) can form between poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) chains during crystallization.^[5] These SCs have much higher melting point compared with that of homocrystallites (HCs) formed in neat PLLA.^[11,12] In this case, the presence of the SCs in PLLA/PDLA blends can effectively improve thermal stability of PLA materials. However, in PLA blends with high

molecular weights, both SCs and HCs form together during crystallization,^[1,4,13,14] and the increase of molecular weights of PLA can lead to the decrease of SC content.^[15–17] Accordingly, nowadays, the key point of the research on the improvement of mechanical properties and thermal stability of PLA materials becomes the enhancement of the SC formation in PLA blends.^[3,18]

Some useful methods for promoting the SC formation have been proposed, such as stretching or shearing PLA chains,^[19–23] synthesizing PLLA-PDLA block copolymers or star-shaped polymers^[24–28] and adding some new components that can interact with both PLLA and PDLA chains.^[9,29,30] These excellent studies are mainly based on two mechanisms to control the SC formation: the change of nucleation/crystallization mode from intramolecular chain-folding to intermolecular packing and the improvement in local miscibility between PLLA and PDLA chain segments.^[22,29,31–36] For instance, Hu *et al.* used dynamic Monte Carlo (MC) simulations to explore the microscopic mechanisms of strain-enhanced stereocomplex formation in polymer blends, and detected that the improvement of the SC formation could be attributed to intermolecular packing of highly deformed chain segments during crystallization.^[22] Our former simulation work also showed that the increase of the grafting density of polymer chains grafted on substrate can cause the raise of chain extension and the dominance of crystallization mode of intermolecular packing during crystallization, thus promoting the appearance of more SCs.^[32] In addition, compared

* Corresponding author, E-mail: nieyijing@ujs.edu.cn

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with linear PLA chains, PLLA-block-PDLA copolymers have higher local miscibility and therefore stronger ability of SC formation.^[24–27,34,37]

For block copolymers, it can be speculated that the distribution of PLLA and PDLA blocks in chains should affect the SC formation. Pan *et al.* reported that symmetric PLLA-PDLA diblock copolymers exhibit stronger ability of stereocomplexation than the corresponding asymmetric diblock copolymers.^[24] Unfortunately, the corresponding research work focusing on the effect of the asymmetry of diblock copolymers on the SC formation is still lacking, and more work is urgently needed.

Previously, Hu's group and our group both demonstrated that dynamic MC simulations provide a very powerful research method for investigating the underlying mechanisms of polymer crystallization,^[38–53] including the SC formation.^[17,22,31,32,34,54] Thus, in the current simulation work, we further applied dynamic MC simulation to study the effect of asymmetry of diblock copolymers on the SC formation. It was detected that the SC content decreases with the increasing degree of the asymmetry of diblock copolymers, which can be mainly attributed to the reduction in the local miscibility between segments belonging to different blocks caused by the increase of the difference between the contents of segments of different blocks.

SIMULATION DETAILS

Our current simulations were carried out on a lattice, and the corresponding simulation box contained $32 \times 32 \times 32$ lattice sites in total. In the box, polymer beads could only exist on the lattice points. In this case, polymer chains used in the present simulations could be regarded as lattice chains (one kind of coarse-grained polymer chain model).^[46] Based on the current

lattice model, one bond formed by two consecutive beads had 26 possible orientations, that is, orientations along 6 axes, 8 body diagonals and 12 face diagonals. Then, the bond length of the lattice chains could be 1, $\sqrt{2}$ and $\sqrt{3}$. In order to reveal the effect of the asymmetry of diblock copolymers, 240 diblock copolymer chains with chain length of 128 beads but different degrees of asymmetry were introduced. Since the radius of gyration of random chain coils with chain length of 128 beads was around 12 lattice sites (smaller than the side length of the box (32 lattice sites)), no confinement effect existed in our current simulation systems. The diblock copolymers were marked as A-B diblock copolymers. The volume fraction of A beads in one diblock copolymer chain (f_a) was 0.5, 0.25, 0.125 and 0.0625, respectively, as illustrated in Fig. 1 (the corresponding volume fraction of A beads in these copolymer systems was also 0.5, 0.25, 0.125 and 0.0625, respectively). Then, the A-B diblock copolymer with $f_a=0.5$ was symmetric, while the other diblock copolymers with $f_a=0.25$, 0.125 and 0.0625 belonged to the asymmetric diblock copolymers. The bead density of these copolymers was 0.9375, thus these systems could be considered as the bulk ones. In addition, we also established the systems of the blends of two asymmetric diblock copolymers with the complementary volume fractions of A beads, that is, the volume fraction of A beads in the first copolymer chain (f_{a1})/that in the second copolymer chain (f_{a2})=0.25/0.75, 0.125/0.875 and 0.0625/0.9375, respectively. In the blends, the volume fractions of both the A and B beads were 0.5.

In order to achieve the formation of SCs, we should first understand the underlying mechanism inducing the appearance of SCs in PLA blends. Using infrared spectroscopy, Zhang *et al.* found that intermolecular hydrogen bonds can form between neighbouring PLLA and PDLA segments during crystallization in their blends,^[55] while no similar hydrogen bonds appear among neat PLLA or PDLA system. The

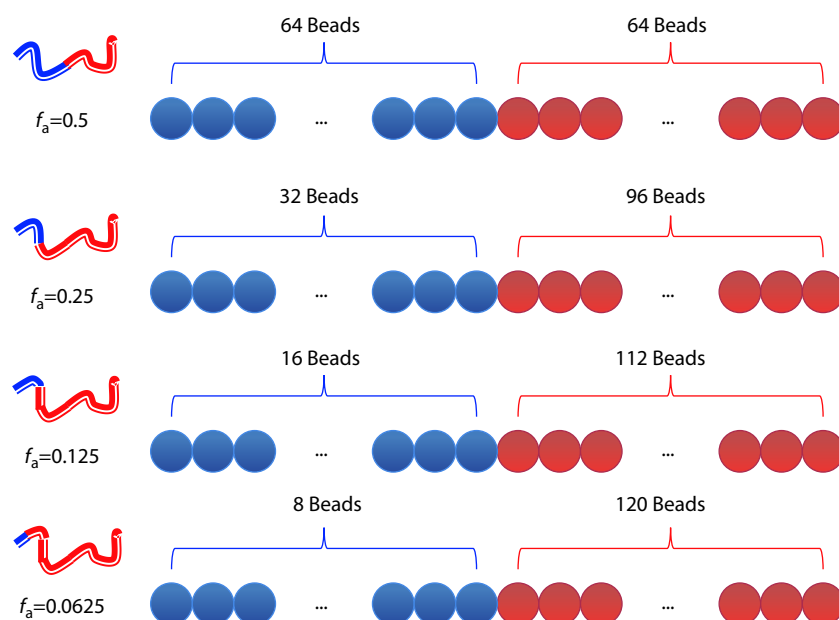


Fig. 1 Schematic drawing of typical chains of A-B diblock copolymer with different values of f_a : 0.5, 0.25, 0.125 and 0.0625. The blue lines and beads denote A blocks, and the red lines and beads denote B blocks.

formation of the hydrogen bonds in SCs can induce the appearance of higher energy reduction during crystallization and then higher thermal stability compared with HCs without the hydrogen bonds. Hu *et al.* firstly introduced a parameter for parallel interaction (E_p) to reflect the variation of compact packing energy of adjacent bonds.^[38,46] Apparently, the formation of the hydrogen bonds between adjacent PLLA and PDLA segments can result in the higher reduction of packing energy when the parallel packing of one PLLA bond and one PDLA bond occurs, compared to the energy change caused by the parallel packing of two PLLA bonds or two PDLA bonds. According to this phenomenon, in the simulations we should set a higher value of E_p for the packing of one A bond and one B bond. Hu *et al.* have found that the presence of a higher value of E_p for two parallel bonds of different types can promote the stereocomplex crystallization of polymer blends.^[22,31] Accordingly, on the basis of their pioneer simulation work,^[22,31] different values of E_p were set for the parallel bonds with different types.

For chain motions on the lattice, we adopted the micro-relaxation mode of chains. Then, chain segments could move based on the single-site jumping or chain segment sliding. We introduced periodic boundary conditions in the simulations. During simulation, whether the attempts of chain segment movements could be accepted or not was judged by the conventional Metropolis sampling algorithm. Each polymer bead had one opportunity to move at one MC cycle. In this condition, the simulation time could be reflected by the number of the MC cycles. The following equation was used to obtain the change of potential energy (ΔE) owing to chain segment motions:

$$\frac{\Delta E}{kT} = \left[\Delta c + \Delta p_1 \frac{E_{p1}}{E_c} + \Delta p_2 \frac{E_{p2}}{E_c} + \Delta p_3 \frac{E_{p3}}{E_c} + \Delta p_4 \frac{E_{p4}}{E_c} \right] \frac{E_c}{kT} \quad (1)$$

where E_c was the change in energy correlated with the non-collinear connection of two consecutive polymer bonds, E_{p1} was the change in energy correlated with two nonparallel packed bonds both belonging to A polymer (that is, A-A bonds) in neighboring regions, E_{p2} was the change in energy correlated with two nonparallel packed bonds both belonging to B polymer (that is, B-B bonds) in neighboring regions (E_{p1} and E_{p2} corresponded to driving force for HC formation), E_{p3} was the change in energy correlated with two nonparallel packed bonds of different types (A-A bond and B-B bond) in neighboring regions, which corresponded to driving force for SC formation, E_{p4} was the change in energy correlated with two nonparallel packed bonds, one of which was A-B bond (that is, the block junction bond), Δc was the change in number of pairs of bonds that were not collinear, Δp_1 was the change in number of pairs of A-A bonds that were not parallel packed, Δp_2 was the change

in number of pairs of B-B bonds that were not parallel packed, Δp_3 was the change in number of bond pairs containing one A-A bond and one B-B bond that were not parallel packed, and Δp_4 was the change in number of non-parallel packed bond pairs containing at least one A-B bond. As mentioned above, different values of the parameter for parallel interaction were set for the packing of two A-A bonds ($E_{p1}/E_c=1$) or two B-B bonds ($E_{p2}/E_c=1$), the packing of one A bond and one B bond ($E_{p3}/E_c=1.2$) and the packing of two bonds containing at least one A-B bond ($E_{p4}/E_c=0$), as shown in Fig. 2. Since the value of E_{p4}/E_c was set as 0, the block junction bonds of the block copolymers could not participate in crystallization. The similar parameter settings were also used in our former simulations on the SC formation in the mixed polymers grafted on a substrate, the multi-block copolymers and the polymer blends filled with two-dimensional nanofillers.^[32,34,54] In addition, we used lattice chain model in the simulations instead of the real PLLA and PDLA chains. It should be noted that the lattice chain model cannot be used to directly reflect the real PLA chains. Differently, for molecular dynamics simulations, the all-atom model, the united-atom model and some coarse-grained models can be used to directly reflect the real polymer chains. In this condition, the crystallization mechanisms of some special polymers can be successfully uncovered. In the current study, based on this lattice chain model, we focused on the universal mechanisms of stereocomplex crystallization.

Firstly, the copolymer systems were relaxed in an athermal condition for 10^6 MC cycles in order to gain an equilibrium random coil state, which was then used as the initial state for subsequent crystallization. The subsequent isothermal crystallization took place at the reduced temperature (kT/E_c) of 3.0. In the following sections, kT/E_c was marked as T^* for convenience.

RESULTS AND DISCUSSION

Asymmetric Block Copolymers

Fig. 3 shows the crystallinity evolutions for the different diblock copolymers including the symmetric and asymmetric diblock copolymers during isothermal crystallization at $T^*=3.0$. Here, crystallinity is treated as the ratio of the number of bonds having more than 5 parallel neighboring bonds to the total number of bonds in the systems.^[46] Besides, this bond will be regarded as a crystalline bond. It can be clearly seen that during crystallization the values of the crystallinity for all these diblock copolymer systems increase with increasing simulation time, indicating the occurrence of crystallization in these diblock copolymers. In addition, all these different diblock copolymers exhibit similar crystallization rates, attributed to the same crystallizability of the A and B blocks.

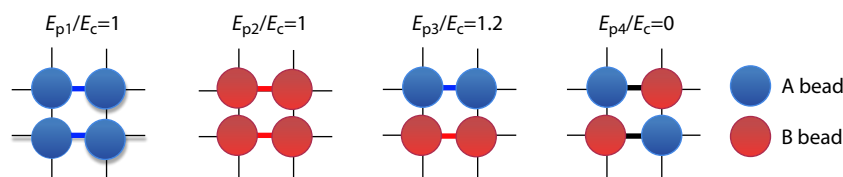


Fig. 2 Schematic diagram of sections of A and B coarse-grained chains and parallel interaction parameter between different bonds, i.e., $E_{p1}/E_c=1$ for two A-A bonds, $E_{p2}/E_c=1$ for two B-B bonds, $E_{p3}/E_c=1.2$ for one A-A bond and one B-B bond and $E_{p4}/E_c=0$ for two bonds containing at least one A-B bond.

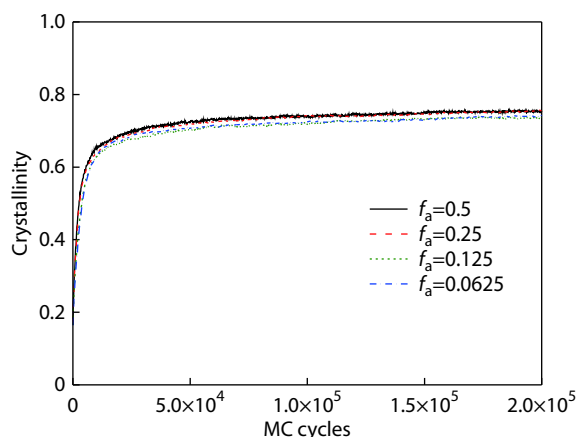


Fig. 3 Crystallinity evolutions in diblock copolymers with different values of f_a as a function of crystallization time during isothermal crystallization at $T^*=3.0$.

Furthermore, we try to reveal the effect of the asymmetry of the diblock copolymers on the formation of SCs. In the present work, we still use the same definitions of SC and HC bonds as those used in our former simulation work.^[32,34,54] When in the neighboring domain of one crystalline bond (A/B crystalline bond), the values of the ratio of the amount of A/B crystalline bonds to that of B/A crystalline bonds are between 0.5 and 2, this bond would be defined as one SC bond. Otherwise, when the values of this ratio are larger than 2 or smaller than 0.5, and this bond would be defined as one HC bond.^[32,34,54] Our definition of SC bond was inspired by the experimental results of Tashiro *et al.*, which revealed that in SCs the ratio of the amount of PLLA crystalline segments to that of PDLA crystalline segments is within a certain range.^[56] Then, to understand the difference between the two kinds of crystalline bonds (that is, HC and SC bonds) more intuitively,

the snapshots of the morphologies of the HCs and the SCs in the diblock copolymers with the different values of f_a are shown in Fig. 4. In the figure the crystalline bonds belonging to the different kinds of blocks are drawn with different colors. Obviously, for the HCs, the crystalline bonds belonging to the same kind of blocks (the cylinders with same color in Fig. 4) are parallel with each other in local domains. On the contrary, for the SCs, the crystalline bonds of the different kinds of blocks (the cylinders with different colors in Fig. 4) are aligned in parallel in local regions. In addition, it can also be seen in Fig. 4 that the number of the HC bonds increases with the decrease of the values of f_a , while that of the SC bonds decreases, indicating that the enhancement of the asymmetry of the diblock copolymers leads to the significant decline in the final SC content. In experiments, Pan *et al.* also observed that the formation ability of SCs in the asymmetric PLLA-PDLA diblock copolymers is weaker than that in the symmetric block copolymers.^[24] However, the detailed underlying mechanism of this phenomenon is still unclear.

To quantitatively reveal the dependence of the SC content on the asymmetry of the diblock copolymers, we further count the final SC fraction as a function of the values of f_a . Here, we define the final SC fraction as the value of the number of SC bonds divided by the total number of crystalline bonds at 2.0×10^5 MC cycles. As shown in Fig. 5, it can be seen that as the values of f_a decrease, the final SC fraction is also reduced, suggesting that the increase of the degree of the copolymer asymmetry can apparently weaken the formation ability of SCs. In addition, it can also be seen that the values of the final SC fraction linearly depend on the values of f_a , implying that the volume fraction of beads of different blocks or the degree of asymmetry is the key factor dominating the formation of SCs in the asymmetric diblock copolymers. Subsequently, we further focus on the mechanism controlling the formation of SCs in the asymmetric diblock copolymers.

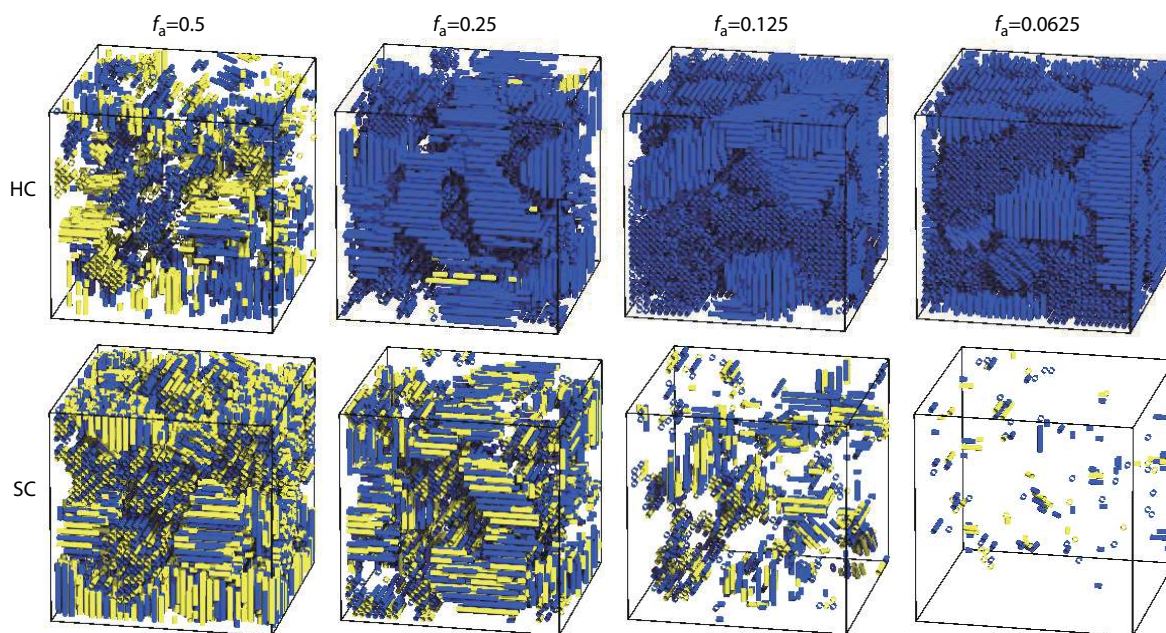


Fig. 4 Snapshots of HCs (upper panel) and SCs (bottom panel) in diblock copolymer systems with different values of f_a ; crystalline bonds in A polymer are denoted by yellow cylinders, and crystalline bonds in B polymer are denoted by blue cylinders.

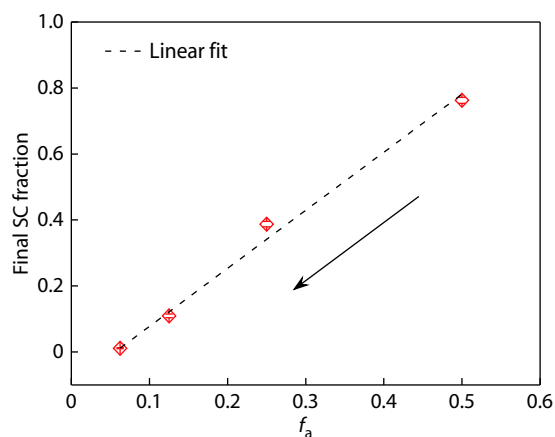


Fig. 5 Final SC fraction in diblock copolymers as a function of f_a ; the arrow is used to identify the direction in which f_a decreases (the degree of asymmetry of diblock copolymer increases).

As revealed in the previous corresponding experiment and simulation work, there are two main mechanisms controlling the formation of SCs, *i.e.*, the local miscibility of different polymer chain segments and the nucleation mode.^[22,29,31–35] Fig. 6(a) depicts the evolutions of mixing parameters of B beads during crystallization for these different diblock copolymer systems. The mixing parameter of B beads was defined as the fraction of A beads existing in the local neighboring regions of B beads.^[54] This mixing parameter of B beads can be used to reflect the local miscibility between A and B beads. As shown in Fig. 6(a), the diblock copolymers with the lower values of f_a exhibit the lower mixing parameters of B beads during crystallization process. For the diblock copolymer with a lower value of f_a (that is, the higher degree of asymmetry), the fraction of A beads is lower. In this condition, the possibility of B beads to meet A beads in the corresponding neighboring domains will be lower, thus resulting in the lower values of the mixing parameters of B beads. In short, the systems with the higher degree of asymmetry have weaker local miscibility, which is not conducive to the SC formation. Fig. 6(b) further displays the dependence of the mixing parameters of B beads in the initial state of the different block copolymers on the values of f_a . It can be seen that there is a linear relationship between the mixing parameters of B beads in the initial state and the values of f_a , demonstrating that the local miscibility is closely dependent on the fraction of different beads. It should be noted that, if the value of f_a is improved from 0.5, the diblock copolymer will also become asymmetric. Then, the systems with $f_a > 0.5$ (asymmetric diblock copolymers with higher volume fraction of A block) will also have lower mixing parameters and thus lower fraction of SCs compared with that with $f_a = 0.5$ (symmetric diblock copolymers).

Moreover, we go further to examine whether the change of asymmetry of block copolymers will affect the nucleation mode. Fig. 7 depicts the adjacent chain-folding probability in crystals during crystallization at $T^* = 3.0$ for these diblock copolymers with different values of f_a . The definition of the adjacent chain-folding probability is the same as that used in the former work.^[39,40] Namely, the adjacent chain-folding probab-

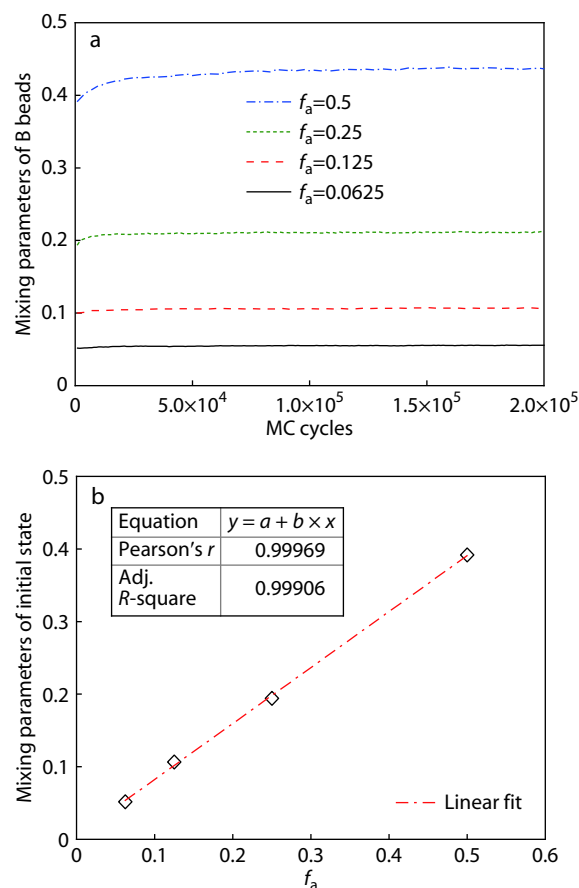


Fig. 6 (a) Mixing parameters of B beads during crystallization at $T^* = 3.0$ for block copolymers with different values of f_a ; (b) Mixing parameters of B beads in initial state of different block copolymers as a function of the values of f_a .

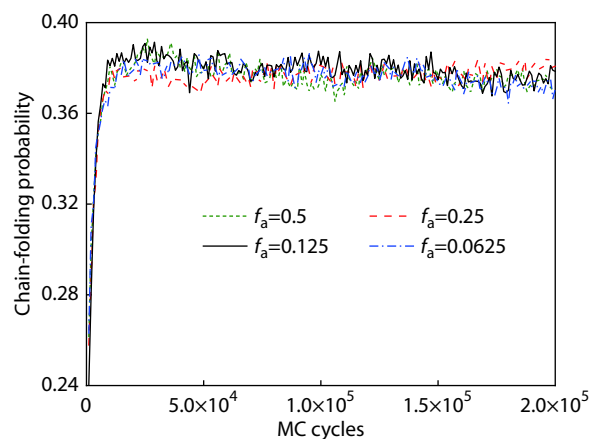


Fig. 7 Change of adjacent chain-folding probability in crystals during crystallization at $T^* = 3.0$ for diblock copolymers with different values of f_a .

ility in crystals is defined as the fraction of crystalline stems in crystals that are directly connected by short loops composed of less than five beads.^[32,38–40] Generally, the value of the adjacent chain-folding probability can be used to reveal the nucleation or crystallization mode of polymers.^[32,38–40] As depicted in Fig. 7, it can be found that all the block copolymers

exhibit the similar evolutions of the adjacent chain-folding probability due to the same chain length of these different diblock copolymers. In other words, the nucleation mode in the diblock copolymers with different asymmetry is not the mechanism affecting the formation of SCs. In the current systems, only the local miscibility between different blocks plays the important role in the SC formation.

Blends of Asymmetric Block Copolymers

In the above diblock copolymer systems, the diblock copolymers with higher degree of asymmetry (that is, smaller value of f_a) have lower volume fraction of A beads. In this condition, it is difficult to directly extract the influence of asymmetry on the SC formation without considering the influence of the fraction of beads. Thus, in order to reveal the effect of the asymmetry of diblock copolymers on the SC formation excluding interference from the volume fraction of beads, we further investigate the SC formation in the blends of the asymmetric diblock copolymers. In all the blends of the asymmetric diblock copolymers, the volume fractions of A and B beads are both fixed at 0.5, while the degree of asymmetry is different ($f_{a1}/f_{a2}=0.25/0.75$, $0.125/0.875$ and $0.0625/0.9375$, respectively). Then, the effect of the asymmetry of diblock copolymers can be revealed individually. As shown in Fig. 8, the crystallinity values of all the blends of the asymmetric diblock copolymers increase during crystallization, demonstrating that crystallization occurs in all the corresponding systems.

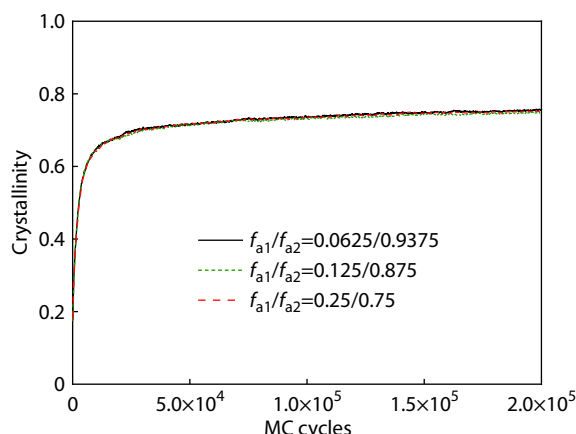


Fig. 8 Crystallinity evolutions in the different blends of asymmetric diblock copolymers as a function of crystallization time during isothermal crystallization at $T^*=3.0$.

Fig. 9 displays the dependence of the final SC fraction on the values of f_{a1} . It can be observed that the value of the final SC fraction is almost independent of f_{a1} , indicating that the degree of asymmetry of diblock copolymers is not the key factor affecting the SC formation. As shown in Fig. 10, the mixing parameters of B beads in the different blends of the asymmetric diblock copolymers are almost the same. In other words, these blends of the asymmetric diblock copolymers have the same volume fraction of beads, and then exhibit the similar local miscibility.

Based on these observations, it can be concluded that the volume fraction of beads belonging to different blocks is the key factor controlling the SC formation in the asymmetric

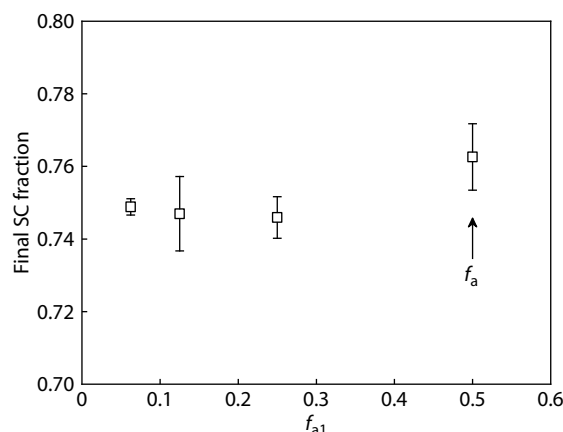


Fig. 9 Final SC fraction of the symmetric diblock copolymer ($f_a=0.5$) and the blends of asymmetric diblock copolymers with different values of f_{a1} . The error bars are also shown in the figure.

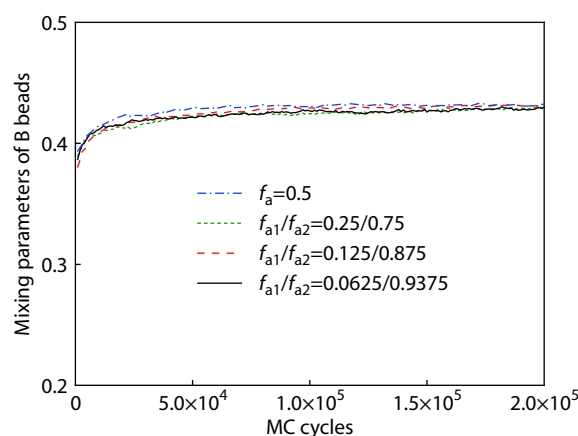


Fig. 10 Mixing parameters of B beads during crystallization at $T^*=3.0$ for the symmetric diblock copolymer ($f_a=0.5$) and the blends of asymmetric diblock copolymers with different values of f_{a1} .

block copolymers. In the asymmetric block copolymers with higher degree of asymmetry, the difference between the volume fractions of the two beads belonging to different blocks will be greater, resulting in the lower local miscibility and thus the smaller values of the final SC content. However, in the blends of the asymmetric block copolymers, although the degree of the asymmetry is still different, the volume fraction of the different beads is the same, leading to the similar local miscibility and also the similar values of the final SC content.

In addition, compared with the asymmetric blends, the asymmetric diblock copolymers should have higher local miscibility due to the presence of the block junction bonds. Then, the asymmetric diblock copolymers should have higher ability of the SC formation.

CONCLUSIONS

In the current simulations, we investigate the SC formation in the asymmetric diblock copolymers, and reveal that the key factor dominating the SC formation is the volume fraction of beads belonging to different blocks. In the asymmetric diblock

copolymers, the copolymers with the higher degree of asymmetry have larger difference between the volume fractions of beads belonging to different blocks, and then the local miscibility between the beads of different blocks would be lower, leading to the lower values of the final SC content.

In the blends of the asymmetric block copolymers, the volume fraction of beads belonging to different blocks is the same, then resulting in the similar local miscibility between beads of different blocks and also the similar values of the final SC content. The current new simulation results can supply some theoretical guidance for the regulation of the content of SCs in block copolymers.

DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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REFERENCES

- Lim, L. T.; Auras, R.; Rubino, M. Processing technologies for poly(lactic acid). *Prog. Polym. Sci.* **2008**, *33*, 820–852.
- Qi, H.; Zhou, H.; Tang, Q. Y.; Lee, J. Y.; Fan, Z. Y.; Kim, S.; Staub, M. C.; Zhou, T.; Mei, S.; Han, L.; Pochan, D. J.; Cheng, H.; Hu, W. B.; Li, C. Y. Block copolymer crystalsomes with an ultrathin shell to extend blood circulation time. *Nat. Commun.* **2018**, *9*, 3005.
- Tsuji, H. Poly(lactide) stereocomplexes: formation, structure, properties, degradation, and applications. *Macromol. Biosci.* **2015**, *5*, 569–597.
- Bai, H. W.; Deng, S. H.; Bai, D. Y.; Zhang, Q.; Fu, Q. Recent advances in processing of stereocomplex-type polylactide. *Macromol. Rapid Commun.* **2017**, *38*, 1700454.
- Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S. H. Stereocomplex formation between enantiomeric poly(lactides). *Macromolecules* **1987**, *20*, 904.
- Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. Poly(lactic acid) crystallization. *Prog. Polym. Sci.* **2012**, *37*, 1657–1677.
- Nampoothiri, K. M.; Nair, N. R.; John, R. P. An overview of the recent developments in polylactide (PLA) research. *Bioresour. Technol.* **2010**, *101*, 8493–8501.
- Cao, Z. Q.; Sun, X. R.; Bao, R. Y.; Yang, W.; Xie, B. H.; Yang, M. B. Role of carbon nanotube grafted poly(L-lactide)-block-poly(D-lactide) in the crystallization of poly(L-lactide)/poly(D-lactide) blends: suppressed homocrystallization and enhanced stereocomplex crystallization. *Eur. Polym. J.* **2016**, *83*, 42–52.
- He, S.; Bai, H.; Bai, D.; Ju, Y.; Zhang, Q.; Fu, Q. A promising strategy for fabricating high-performance stereocomplex-type polylactide products via carbon nanotubes-assisted low-temperature sintering. *Polymers* **2019**, *162*, 50–57.
- Deng, S.; Bai, H.; Liu, Z.; Zhang, Q.; Fu, Q. Toward supertough and heat-resistant stereocomplex-type polylactide/elastomer blends with impressive melt stability via *in situ* formation of graft copolymer during one-pot reactive melt blending. *Macromolecules* **2019**, *52*, 1718–1730.
- Zhang, J.; Duan, Y.; Sato, H.; Tsuji, H.; Noda, I.; Yan, S.; Ozaki, Y. Crystal modifications and thermal behavior of poly(L-lactic acid) revealed by infrared spectroscopy. *Macromolecules* **2005**, *38*, 8012–8021.
- Hirata, M.; Kimura, Y. Thermomechanical properties of stereoblock poly(lactic acid)s with different PLLA/PDLA block compositions. *Polymer* **2008**, *49*, 2656–2661.
- Xie, Q.; Chang, X.; Qian, Q.; Pan, P.; Li, C. Y. Structure and morphology of poly(lactic acid) stereocomplex nanofiber shish kebabs. *ACS Macro Lett.* **2020**, *9*, 103–107.
- Hu, J.; Wang, J.; Wang, M.; Ozaki, Y.; Sato, H.; Zhang, J. Investigation of crystallization behavior of asymmetric PLLA/PDLA blend using Raman imaging measurement. *Polymer* **2019**, *172*, 1–6.
- Pan, P.; Han, L.; Bao, J.; Xie, Q.; Shan, G.; Bao, Y. Competitive stereocomplexation, homocrystallization, and polymorphic crystalline transition in poly(L-lactic acid)/poly(D-lactic acid) racemic blends: molecular weight effects. *J. Phys. Chem. B* **2015**, *119*, 6462–6470.
- Tsuji, H.; Bouapao, L. Stereocomplex formation between poly(L-lactic acid) and poly(D-lactic acid) with disproportionately low and high molecular weights from the melt. *Polym. Int.* **2012**, *61*, 442–450.
- Xu, Y.; Wu, H.; Yang, J.; Liu, R.; Zhou, Z.; Hao, T.; Nie, Y. Molecular simulations of microscopic mechanism of the effects of chain length on stereocomplex formation in polymer blends. *Comput. Mater. Sci.* **2020**, *172*, 109297.
- Xie, Y.; Lan, X. R.; Bao, R. Y.; Lei, Y.; Cao, Z. Q.; Yang, M. B.; Yang, W.; Wang, Y. B. High-performance porous polylactide stereocomplex crystallite scaffolds prepared by solution blending and salt leaching. *Mater. Sci. Eng. C* **2018**, *90*, 602–609.
- Zhang, Z. C.; Sang, Z. H.; Huang, Y. F.; Ru, J. F.; Zhong, G. J.; Ji, X.; Wang, R. Y.; Li, Z. M. Enhanced heat deflection resistance via shear flow-induced stereocomplex crystallization of polylactide systems. *ACS Sustain. Chem. Eng.* **2017**, *5*, 1692–1703.
- Tsuji, H.; Nakano, M.; Hashimoto, M.; Takashima, K.; Katsura, S.; Mizuno, A. Electrospinning of poly(lactic acid) stereocomplex nanofibers. *Biomacromolecules* **2006**, *7*, 3316–3320.
- Hemmi, K.; Matsuba, G.; Tsuji, H.; Kawai, T.; Kanaya, T.; Toyohara, K.; Oda, A.; Endou, K. Precursors in stereo-complex crystals of poly(L-lactic acid)/poly(D-lactic acid) blends under shear flow. *J. Appl. Cryst.* **2014**, *47*, 14–21.
- Guan, X. C.; Wang, J. P.; Hu, W. B. Monte Carlo simulation of strain-enhanced stereocomplex polymer crystallization. *J. Phys. Chem. B* **2018**, *122*, 10928–10933.
- Wang, G.; Wang, K. Studies on the induction of poly(lactic acid) stereocomplex by thermal and tensile treating. *Acta Polymerica Sinica* (in Chinese) **2018**, 1221–1227.
- Han, L.; Xie, Q.; Bao, J.; Shan, G.; Bao, Y.; Pan, P. Click chemistry synthesis, stereocomplex formation, and enhanced thermal properties of well-defined poly(L-lactic acid)-*b*-poly(D-lactic acid) stereo diblock copolymers. *Polym. Chem.* **2017**, *8*, 1006–1016.
- Yui, N.; Dijkstra, P. J.; Feijen, J. Stereo block copolymers of L- and D-lactides. *Macromol. Chem. Phys.* **1990**, *191*, 481–488.
- Rahaman, M. H.; Tsuji, H. Isothermal crystallization and spherulite growth behavior of stereo multiblock poly(lactic acid)s: effects of block length. *J. Appl. Polym. Sci.* **2013**, *129*, 2502–2517.
- Shao, J.; Tang, Z.; Sun, J.; Li, G.; Chen, X. Linear and four-armed poly(L-lactide)-block-poly(D-lactide) copolymers and their stereocomplexation with poly(lactide)s. *J. Polym. Sci., Part B: Polym. Phys.* **2014**, *52*, 1560–1567.

- 28 Zhou, K. Y.; Li, J. B.; Wang, H. X.; Ren, J. Effect of star-shaped chain architectures on the polylactide stereocomplex crystallization behaviors. *Chinese J. Polym. Sci.* **2017**, *35*, 974–991.
- 29 Pan, P.; Bao, J.; Han, L.; Xie, Q.; Shan, G.; Bao, Y. Stereocomplexation of high-molecular-weight enantiomeric poly(lactic acid)s enhanced by miscible polymer blending with hydrogen bond interactions. *Polymer* **2016**, *98*, 80–87.
- 30 Li, Y.; Yu, Y. C.; Han, C. Y.; Wang, X. H.; Huang, D. X. Sustainable blends of poly(propylene carbonate) and stereocomplex polylactide with enhanced rheological properties and heat resistance. *Chinese J. Polym. Sci.* **2020**, *38*, 1267–1275.
- 31 Zhang, R.; Zha, L. Y.; Hu, W. B. Intramolecular crystal nucleation favored by polymer crystallization: a Monte Carlo simulation evidence. *J. Phys. Chem. B* **2016**, *120*, 6754–6760.
- 32 Nie, Y.; Liu, Y.; Liu, R.; Zhou, Z.; Hao, T. Dynamic Monte Carlo simulations of competition in crystallization of mixed polymers grafted on a substrate. *J. Polym. Sci., Part B: Polym. Phys.* **2019**, *57*, 89–97.
- 33 Bai, D. Y.; Liu, H. L.; Bai, H. W.; Zhang, Q.; Fu, Q. Powder metallurgy inspired low-temperature fabrication of high-performance stereocomplexed polylactide products with good optical transparency. *Sci. Rep.* **2016**, *6*, 20260.
- 34 Qiu, X.; Liu, R.; Nie, Y.; Liu, Y.; Liang, Z.; Yang, J.; Zhou, Z.; Hao, T. Monte Carlo simulations of stereocomplex formation in multiblock copolymers. *Phys. Chem. Chem. Phys.* **2019**, *21*, 13296–13303.
- 35 Naga, N.; Yoshida, Y.; Noguchi, K. Crystallization of poly(L-lactic acid)/poly(D-lactic acid) blend induced by organic solvents. *Polym. Bull.* **2019**, *79*, 3677–3691.
- 36 Xie, Q.; Guo, G.; Lu, W.; Sun, C.; Zhou, J.; Zheng, Y.; Shan, G.; Bao, Y.; Pan, P. Polymorphic homocrystallization and phase behavior of high-molecular-weight Poly(L-lactic acid)/poly(D-lactic acid) racemic mixture with intentionally enhanced stereocomplexation ability via miscible blending. *Polymer* **2020**, *201*, 122597.
- 37 Isono, T.; Kondo, Y.; Otsuka, I.; Nishiyama, R.; Borsali, T.; Kakuchi, T.; Satoh, T. Synthesis and stereocomplex formation of star-shaped stereoblock polylactides consisting of poly(L-lactide) and poly(D-lactide) arms. *Macromolecules* **2013**, *46*, 8509–8518.
- 38 Hu, W. The physics of polymer chain-folding. *Phys. Rep.* **2018**, *747*, 1–50.
- 39 Nie, Y.; Gao, H.; Yu, M.; Hu, Z.; Reiter, G.; Hu, W. Competition of crystal nucleation to fabricate the oriented semi-crystalline polymers. *Polymer* **2013**, *54*, 3402–3407.
- 40 Nie, Y.; Zhao, Y.; Matsuba, G.; Hu, W. Shish-kebab crystallites initiated by shear fracture in bulk polymers. *Macromolecules* **2018**, *51*, 480–487.
- 41 Nie, Y.; Hao, T.; Gu, Z.; Wang, Y.; Liu, Y.; Zhang, D.; Wei, Y.; Li, S.; Zhou, Z. Relaxation and crystallization of oriented polymer melts with anisotropic filler networks. *J. Phys. Chem. B* **2017**, *121*, 1426–1437.
- 42 Gu, Z.; Yang, R.; Yang, J.; Qiu, X.; Liu, R.; Liu, Y.; Zhou, Z.; Nie, Y. Dynamic Monte Carlo simulations of effects of nanoparticle on polymer crystallization in polymer solutions. *Comput. Mater. Sci.* **2018**, *147*, 217–226.
- 43 Nie, Y.; Gu, Z.; Zhou, Q.; Wei, Y.; Hao, T.; Liu, Y.; Liu, R.; Zhou, Z. Controllability of polymer crystal orientation using heterogeneous nucleation of deformed polymer loops grafted on two-dimensional nanofiller. *J. Phys. Chem. B* **2017**, *121*, 6685–6690.
- 44 Wu, H.; Qiu, X.; Zhang, Y.; Yang, R.; Yang, J.; Liu, R.; Liu, Y.; Zhou, Z.; Hao, T.; Gu, Z.; Nie, Y. Formation mechanism of reverse kebab structure inside hollow nanotubes studied by molecular simulations. *Comput. Mater. Sci.* **2018**, *153*, 348–355.
- 45 Qiu, X.; Zhang, Y.; Wu, H.; Yang, R.; Yang, J.; Liu, R.; Liu, Y.; Zhou, Z.; Hao, T.; Nie, Y. Blocked crystallization in capped ultrathin polymer films studied by molecular simulations. *Polym. Int.* **2019**, *68*, 218–224.
- 46 Hu, W.; Frenkel, D. Polymer crystallization driven by anisotropic interactions. *Adv. Polym. Sci.* **2005**, *191*, 1–35.
- 47 Nie, Y.; Gu, Z.; Wei, Y.; Hao, T.; Zhou, Z. Features of strain-induced crystallization of natural rubber revealed by experiments and simulations. *Polym. J.* **2017**, *49*, 309–317.
- 48 Hao, T.; Zhou, Z.; Nie, Y.; Wei, Y.; Gu, Z.; Li, S. Effect of the polymer-substrate interactions on crystal nucleation of polymers grafted on a flat solid substrate as studied by molecular simulations. *Polymer* **2017**, *123*, 169–178.
- 49 Liu, R.; Yang, L.; Qiu, X.; Wu, H.; Zhang, Y.; Liu, Y.; Zhou, Z.; Ming, Y.; Hao, T.; Nie, Y. One-dimensional nanofiller induced crystallization in random copolymers studied by dynamic Monte Carlo simulations. *Mol. Simul.* **2020**, *46*, 669–677.
- 50 Liu, R.; Zhou, Z.; Liu, Y.; Liang, Z.; Ming, Y.; Hao, T.; Nie, Y. Epitaxial orientation and localized microphase separation prior to formation of nanohybrid shish-kebabs induced by one-dimensional nanofiller in miscible diblock copolymers with selective interaction. *Polymer* **2019**, *166*, 72–80.
- 51 Liu, R.; Zhou, Z.; Liu, Y.; Liang, Z.; Ming, Y.; Hao, T.; Nie, Y. Competition between interfacial interaction and microphase separation in crystallization of filled block copolymers. *J. Polym. Sci., Part B: Polym. Phys.* **2019**, *57*, 1516–1526.
- 52 Liu, R.; Zhou, Z.; Liu, Y.; Liang, Z.; Ming, Y.; Hao, T.; Nie, Y. Differences in crystallization behaviors between cyclic and linear polymer nanocomposites. *Chinese J. Polym. Sci.* **2020**, *38*, 1034–1044.
- 53 Hao, T.; Xu, D.; Ming, Y.; Zhang, S.; Wei, Y.; Zhou, Z.; Nie, Y.; Yan, D. The study on correlation between molecular weight and confined crystallization behavior of polymers grafted on zero-dimensional filler. *CrystEngComm* **2020**, *22*, 1779–1788.
- 54 Gu, Z.; Xu, Y.; Lu, Q.; Han, C.; Liu, R.; Zhou, Z.; Hao, T.; Nie, Y. Stereocomplex formation in mixed polymers filled with two-dimensional nanofillers. *Phys. Chem. Chem. Phys.* **2019**, *21*, 6443–6452.
- 55 Zhang, J. M.; Sato, H.; Tsuji, H.; Noda, I.; Ozaki, Y. Infrared spectroscopic study of CH₃...O=C interaction during poly(L-lactide)/poly(D-lactide) stereocomplex formation. *Macromolecules* **2005**, *38*, 1822–1828.
- 56 Tashiro, K.; Kouno, N.; Wang, H.; Tsuji, H. Crystal structure of poly(lactic acid) stereocomplex: random packing model of PDLA and PLLA chains as studied by X-ray diffraction analysis. *Macromolecules* **2017**, *50*, 8048–8065.