



Crystallization of double crystalline symmetric diblock copolymers



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ABSTRACT

We report dynamic Monte Carlo simulation results on the crystallization of double crystalline symmetric A-B diblock copolymer, wherein the melting temperature of A-block is higher than B-block. Crystallization of A-block precedes the crystallization of B-block upon cooling from a homogeneous melt. The morphological development is controlled by the interplay between crystallization and microphase separation. With increasing segregation strength, we observe a gradual decrease in crystallinity accompanying with smaller and thinner crystals. During crystallization, A-block crystallizes first and creates confinement for the crystallization of B-block. Thus, crystallization of B-block slows down influencing the overall crystal morphology. At higher segregation strength, due to the repulsive interaction between blocks, block junction is stretched out, which is reflected in the increased value of mean square radius of gyration. As a result, a large number of smaller size crystals form with less crystallinity. The onset of microphase separation shifts towards higher temperature with increasing segregation strength. Isothermal crystallization reveals that the transition pathways strongly depend on segregation strength. The value of Avrami index shows the formation of two dimensional lamellar crystals of both the blocks. Two-step (sequential), compared to one-step (coincident) isothermal crystallization, produces higher crystallinity in A-block, however, the crystallinity of B-block is almost identical in both the cases.

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1. Introduction

Spatially ordered structure formation through self-assembly in diblock copolymer has emerged as a potential field of research due to its numerous applications in nano materials and medical applications [1]. Diblock copolymers comprise of two chemically distinct units, covalently bonded together. In majority of the cases, the blocks are incompatible (viz. immiscible) with each other. The thermodynamic incompatibility between the blocks drives the self-organization (viz. self-assembly) via microphase separation, in which the contacts between similar units are maximized and dissimilar units are minimized [1]. The Flory–Huggins interaction parameter (χ), block composition and chain length, N (viz. degree of polymerization) dictate the extent of separation and final morphology of diblock copolymer. The value of (χN) determines the strength of segregation. For a weakly segregated system the value of (χN) is around 10.5 whereas for a strongly segregated system the value is more than 10.5 [2,3]. Diblock copolymer produces a large variety of morphologies including lamellar structure, hexagonally packed cylinder or body centred cubic phases that are stable over a wide range of copolymer composition [3,4].

A decade of research has been focused on the crystallization of diblock copolymer with one crystallizable block [5–10], whereas the crystallization of double crystalline diblock copolymer has been recently emerged as an exciting field of research. Recent advancement of synthetic chemistry enables to synthesize polymers with complex molecular architectures. Diblock copolymers with crystalline blocks are usually synthesized either via anionic polymerization [3,11,12] or ring opening metathesis polymerization [13] with a polydispersity index close to 1.0. In the presence of two crystalline blocks, phase behaviour is determined by the interplay between crystallization and microphase separation along with the competition for crystallization between two crystalline blocks. Usually, the block with higher melting point crystallizes first followed by the second block with lower melting point [13–17]. During crystallization, first crystallizing block creates confinement for the crystallization of second block. As a result, the crystallization of second block slows down with the formation of less crystalline materials [12,16–22]. Diblock copolymer of PE and PEO with 1:1 composition, exhibits two sharp exothermic peak at 95.4 °C and 12.9 °C during DSC experiments, which is attributed to the sequential crystallization of PE and PEO blocks respectively [16]. In the diblock copolymer of linear polyethylene (LPE) and hydrogenated polynorbornene (hPN), although the melting points of hPN (156 °C) and LPE (145.8 °C) are marginally different, the final morphology of symmetric diblock copolymer is dictated by the hPN

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block while LPE block is forced to crystallize in between existing hPN lamellar morphology [13].

Polymer crystallization is not a truly thermodynamically equilibrium process. Therefore, the crystallization temperature (T_c) and cooling pathways (viz., isothermal and non-isothermal) play a crucial role to establish final semi-crystalline morphology. The crystalline–crystalline diblock copolymer, PCL-*b*-PE quenched from a microphase separated melt produces PE lamellar morphology. This lamellar morphology is preserved after crystallization of PCL block when $T_c < 30$ °C. But when the polymer is crystallized at $T_c > 30$ °C and < 45 °C, PCL block completely destroys the previous morphology of PE, producing PCL lamellar morphology in which PE crystals are fragmentally dispersed [23]. Symmetric diblock copolymer PPL-*b*-PE, cooled from a microphase separated melt at a constant cooling rate (viz., non-isothermal crystallization), exhibit coincident crystallization; however, during isothermal crystallization both block crystallized separately (viz., sequential crystallization) [18].

Apart from the difference in melting points and cooling effects, the magnitude of mutual immiscibility, governed by the χ parameter influences the phase behaviour. The magnitude of χ changes with changing the type of the blocks present in the diblock copolymer. Consequently, the extent of microphase separation and the resultant morphology changes which would enable to tune the properties of the final materials. For example, PEO in PLLA-*b*-PEO diblock copolymer lowers the glass transition temperature (T_g) of PLLA and makes it more flexible. However, the crystallization of PEO blocks is restricted by PLLA blocks [24]. On the other hand, the presence of PCL block in the PLLA-*b*-PCL diblock copolymer increases the stability of the resulting block copolymer while keeping the biodegradability of PLLA intact [25]. Crystallization of PCL is slowed down by PLLA block while the crystallization of PCL preserves the morphology set by PLLA block [26]. PEG in PLLA-*b*-PEG diblock copolymer makes its use as a suitable compatibilizer for the blend of bio degradable PLLA and PEO [27]. The presence of PEG block slows down the crystallization of PLLA block and the degradation of PLLA-*b*-PEG diblock copolymer happen faster than pure PLLA [27].

In most of the cases, first crystallizing block suppresses the crystallization of second block. However, it has also been observed that during crystallization, both the block may crystallize together (viz., coincident crystallization) even if their melting points are widely different, or one block accelerates the crystallization of the other. For example, the crystallization behaviour of PPDx-*b*-PCL diblock copolymer with a significant difference in the melting point of PPDx (100 °C) and PCL block (57 °C) exhibits coincident crystallization. This is attributed to the extremely slow crystallization rate of PPDx block [28,29] compared to homopolymer. Recently, Monte Carlo simulation on lattice polymer reveals that the crystallization of one block accelerates the crystallization of other [30].

In this work, we report dynamic Monte Carlo simulation results on the crystallization of symmetric diblock copolymer with two different crystallizable blocks to explore how the crystallization of one block influences the crystallization of other. Our results show a monotonically decreasing trend in crystallinity with thinner crystallites with increasing magnitude of segregation strength. Isothermal experiments reveal that the transition pathway is strongly influenced by segregation strength.

We organize our paper as follows: we describe model and simulation technique in Section 2. We discuss our key results in Section 3 followed by conclusion in Section 4.

2. Modelling and simulation technique

To simulate crystallization of diblock copolymer, we employ dynamic Monte Carlo (DMC) method, which has been successfully

applied to investigate phase transition of bulk polymers [31–34]. A polymer chain is represented by joining the successive sites in a lattice with size $32 \times 32 \times 32$. A total 480 polymer chains each having 64 repeat units are placed successively one by one ensuring that the connectivity of the chain is maintained. Thus, the lattice occupation is as high as 0.9375, representing a bulk polymer system. The degree of polymerization of polymer is N (viz., 64) which includes N_A and N_B number of A-type and B-type repeat units respectively. A homogeneous and monodisperse melt is generated by applying a set of microrelaxation algorithms. The microrelaxation algorithm consists of a set of Monte Carlo move such as bond fluctuation, end bond rotation and slithering diffusion [33–37]. The coordination number of our lattice model is 26 (6 along the lattice axis, 12 along the face diagonals and 8 along the body diagonal). Thus, bond length can be 1 (along the axis), $\sqrt{2}$ (along the face diagonal) or $\sqrt{3}$ lattice units (along the body diagonal). We start our simulation by selecting a vacant site randomly from the available vacant sites and then search for a nearest neighbour site occupied either by A-type or B-type monomer. Appropriate microrelaxation moves are selected in accordance with the position of monomers along the chain. To give further details, if the selected monomer is terminal one, then end bond rotation and slithering diffusion is implemented with equal probability. On the other hand, if the unit is non-terminal, then single site bond fluctuation move is implemented [34].

The interaction between A-type and B-type is modelled as the repulsive interaction to represent their mutual immiscibility. The energy penalty to create A–B contact is modelled by U_{AB} . The crystallization driving force is modelled as an attractive interaction between neighbouring parallel bonds and collinear bonds within A- or B-type units and given by U_p and U_c respectively. The change in energy per Monte Carlo move is then:

$$\Delta E = -(\Delta N_p U_p + \Delta N_c U_c)_A - (\Delta N_p U_p + \Delta N_c U_c)_B + \Delta N_{AB} U_{AB} \quad (1)$$

where, ΔN_A and ΔN_B represents the net change in the number of parallel and collinear bond respectively for the A and B block, and ΔN_{AB} represents the change in the number of contacts between A and B units.

As the block copolymer consists of two different crystallizable blocks, the melting temperatures of the blocks are different. We model B-block as the low melting one and less facile to crystallize upon cooling from a high temperature melt. Therefore, the crystallization driving force of B-block is smaller than that of A-block. To implement this, we use $U_{pB} = \lambda_m U_{pA}$ and $U_{cB} = \lambda_m U_{cA}$ for the parallel and collinear bond respectively. We set $\lambda_m = 0.75$ (< 1) to represent that B-block has less driving force for crystallization compared to A-block. Further, we assume that $U_p = U_c$, for the coarse grained interactions used in our simulation. U_{AB} is calculated as λU_p , where λ represents the segregation strength (viz., A–B demixing energy) relative to the parallel bond interaction energy, and equivalent to Flory's χ parameter. In our work $\lambda \geq 0$ and higher λ implies stronger segregation strength between the blocks. In terms of Flory's χ parameter, segregation strength is calculated as χN , which may be correlated to $(q-2) \times U_{AB} \times N$ in our system [38], where q is coordination number and N is the degree of polymerization. All the energies are normalized by $k_B T$, where, k_B is the Boltzmann constant and T is temperature in Kelvin; thus, $U_p \sim 1/T$. Now the change in energy per MC move is modified as follows:

$$\Delta E = [-(\Delta N_p + \Delta N_c)_A - \lambda_m (\Delta N_p + \Delta N_c)_B + \lambda \Delta N_{AB}] U_p \quad (2)$$

We use the Metropolis sampling scheme with periodic boundary conditions to sample the conformations. We strictly implement excluded volume criteria and avoid bond crossing throughout the

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