INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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This research work focuses on the understanding of interplay between crystallization and microphase separation, and their influence on the final crystal morphology of diblock copolymer. The aim is to relate the crystallization mechanism with segregation strength and block asymmetry. We investigate the crystallization of double crystalline symmetric A-B diblock copolymer, wherein the melting temperature of A-block is larger than B-block. As a result, crystallization of A-block is followed by the crystallization of B-block upon cooling from a homogeneous melt. The morphological evolution is dominated by the interplay between crystallization and microphase separation. With the increasing of segregation strength, we observe a gradual decrease in crystallinity accompanying with smaller and thinner crystals. During the process, A-block crystallizes first and offers confinement for the crystallization of B-block. Therefore, the crystallization of B-block is reduced significantly influencing the overall crystal morphology. At higher segregation strength, due to the repulsive interaction between two blocks, block junction is stretched out, which is exhibited by an increased value of mean square radius of gyration. As a result, large number of smaller size crystals generate with less crystallinity. The onset of microphase separation moves towards higher temperature with increasing segregation strength. Isothermal crystallization reveals that the transition kinetics is primarily governed by segregation strength. The value of Avrami index indicates the presence of two dimensional lamellar crystals. Two-step, compared to one-step isothermal crystallization, yields higher crystallinity in A-block whereas the crystallinity of B-block is almost similar in both cases. To unfold the inherent relationship between block asymmetry and crystallization behavior, we have investigated the crystallization of diblock copolymer by varying block compositions (viz., by varying the relative block length of A- and B-block) with weak and strong segregation strength between the blocks. In weak segregation limit, we observe that with increasing the composition of B-block, the crystallization temperature of B-block increases accompanying with higher crystallinity. In contrast, A-block crystallizes at a relatively low temperature along with the formation of thicker and larger crystallites with the increase in B-block composition. This non-intuitive crystallization trend relates with the dilution effect imposed by B-block. When the composition of the B-block is large enough, it behaves like a "solvent" during the crystallization of A-block. Therefore, A-block segments are more mobile and hence less facile to crystallize, ensuing depression in crystallization temperature with the formation of thicker crystals. At strong segregation limit, crystallization and morphological development are driven by the confinement effect, rather than block asymmetry.