

## Microphase Separation and Structural Evolution of Block Copolymers in Bulk and Thin Films

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Block copolymers consisting of chemically dissimilar blocks usually self-assemble on nanometer length scale. These materials have received widespread attention due to their potential applications in nanofabrication. The introduction of crystallizable blocks in block copolymers control the solid state structure and generate fascinating morphologies due to the complex interplay between microphase separation and crystallization. In the first part of the talk, the structural evolution of poly(L-lactide) (PLLA) during heating of the amorphous ABA triblock copolymers will be discussed. For that purpose, two triblock ABA copolymers poly(L-lactide-*b*-dimethylsiloxane-*b*-L-lactide) (PLLA-*b*-PDMS-*b*-PLLA) and poly(L-lactide-*b*-ethylene glycol-*b*-L-lactide) (PLLA-*b*-PEG-*b*-PLLA) containing poly(L-lactide) were synthesized. Upon heating of the glassy PLLA-*b*-PDMS-*b*-PLLA triblock copolymer, the amorphous PLLA transiently transformed to the mesophase just above the  $T_g$  of PLLA block (~ 45 °C) before crystallizing into the regular  $\alpha$  form. The  $T_g$  of the PLLA in the PLLA-*b*-PDMS-*b*-PLLA triblock copolymer is located at 45 °C, which is almost matching to that of the PLLA homopolymer demonstrating the immiscible nature of PLLA and PDMS. On the other hand, heating of the glassy PLLA-*b*-PEG-*b*-PLLA triblock copolymer, the mesophase of PLLA was found to appear at a lower temperature due to the reduction in the  $T_g$  of PLLA block in the miscible triblock copolymer system. These results suggested that the formation of the mesophase was clearly faster in miscible triblock copolymers due to the enhanced molecular mobility of the amorphous PLLA.

In the second part of the talk, the orientation changes of perpendicular cylindrical microdomains in polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP) thin films upon annealing in different solvent vapors were investigated. The selectivity of the solvent to constituting blocks together with the geometry of drying determines the orientation of the cylindrical microdomains with respect to the substrate plane. Preferential swelling of the PS matrix in the vapour of the selective solvent (1,4-dioxane) induces a morphological transition from cylindrical to ellipsoidal as a transient structure to spherical microdomains; subsequent solvent evaporation resulted in shrinkage of the matrix in the vertical direction, merging the ellipsoidal domains into the perpendicularly aligned cylinders. On the other hand, the swelling of the P4VP perpendicular cylinders ( $C\perp$ ) in chloroform, a non-selective solvent vapour leads to the reorientation to in-plane cylinders through a disordered state.

### References

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