Thesis Abstract

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Controlling Nano-ordered Structures by Stereocomplex Formation between Poly(L-lactide) and Poly(D-lactide) Macromolecular Chains

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Polylactides (PLAs) have been widely utilized as biomaterials for making bone implants, fixing screws, and absorbable sutures because of their excellent biocompatibility and bioabsorbability. However, their nano-order structure control is required for developing functional biomaterials that can be applied to tissue engineering and specific medical devices. Various nano-ordered morphologies have been found out thus far in various multi-component polymer blends and surface -immobilized macromolecules that are involved in phase separation and crystallization. However, little knowledge has been known on the nano-ordered morphologies that are created with enantiomeric poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), although they ought to be very important for designing PLA-based biomaterials. This study demonstrates two approaches for controlling the nano-ordered morphology by utilizing stereocomplex formation of PLLA and PDLA macromolecular chains. The first approach is based on surface immobilization of PDLA, and with which either enantiomeric PLLA homo polymer or PLLA-poly(ethylene glycol) (PEG) block copolymer is interacted to form specific morphology by stereocomplex crystallization (Chapters 1 and 2). The second is based on micelle formation of PEG-PLA block copolymers having different PLA blocks: PLLA, PDLA, and PDLA-PLLA block sequences. The crystalline structure of PLA in the core affects the nano structure of the core-shell micelles (Chapter 3). The content of each chapter is summarized as follows:

Chapter 1 describes the macromolecular organization of PLA immobilized on a flat surface. Namely, a silyl-terminated PDLA oligomer was first immobilized on a silicon wafer, and both PDLA and PLLA oligomers were deposited on it. It was found out that single crystallite arrays of homochiral and stereocomplex crystals can be formed on the

surface.

Chapter 2 deals with nano-ordered surface morphologies by the interaction between the surface-immobilized PDLA and PEG-PLLA block copolymers. Both AB diblock and ABA triblock copolymers of PLLA (A) and PEG (B) deposited on the PDLA pre-immobilized surface were found to form characteristic particle morphologies involving the hydrophilic PEG chains near their surfaces.

Chapter 3 describes stabilization of nano-structured micelles of PLA-PEG block copolymers along with the effect of sc formation of PLA blocks on the micelles. Here, a PEG-PDLA diblock copolymer, a mixture of enantiomeric diblock copolymers PEG-PDLA/PEG-PDLA, and PEG-PDLA-PLLA triblock copolymers having different block compositions were emulsified. It was found out that the triblock copolymers could form sc crystals in the core to highly stabilize the core-shell particles.