論文題目：Development of Novel Bioabsorbable Sol-gel Systems Based on Enantiomeric Block Copolymers of Polylactide and Poly(oxyethylene)

氏名：YU-I HSU

要約：

This dissertation deals with the temperature-dependent sol-gel transition of the mixed micelle solutions consisting of enantiomeric block copolymers of poly(ethylene glycol) (PEG) and polylactide (PLA: denoting either poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA) depending on the enantiomeric block chain). On mixing the micelle solutions of the enantiomeric block copolymers, stereocomplex formation takes place between the enantiomeric block chains to cause sol-gel transition around the body temperature. The sol-gel transition can be tuned not only by changing the PEG/PLA composition and molecular weight but also by using enantiomeric diblock/triblock copolymer mixtures such as F-PEG-PLA/PLA-PEG-PLA for which the PEG terminals of the diblock copolymers are modified with furanyl group. Furthermore, the gel strength can be highly increased when the mixed micelle solution of the enantiomeric diblock/triblock copolymer mixtures is allowed to undergo chain-extending Diels-Alder reaction with 1,8-bis(maleimido) diethylene glycol (BMG). The content of each chapter is summarized as follows:

Chapter 1 deals with the sol-gel transition systems consisting of enantiomeric tri-block copolymers of PLLA-PEG-PLLA and PDLA-PEG-PDLA. It was found out that the composition window of the copolymers for allowing the spontaneous sol-gel transition around the body temperature is considerably narrow, being affected by how easily the PLLA and PDLA blocks of the copolymers can form the stereocomplex in the mixed micelle solutions.

Chapter 2 describes the synthesis and properties of the diblock/triblock copolymer mixtures of F-PEG-PLA/PLA-PEG-PLA for which the PEG terminals of the diblock copolymers were modified with furanyl (F) group. The sol-gel transition behavior was found to depend on the diblock/triblock copolymer ratio. The strength of the resulting gel was highly improved by the increased stereocomplexation of the enantiomeric block chains.

Chapter 3 describes the mixed micelle solution of diblock copolymers MePEG-PLLA-F and MePEG-PDLA-F for which the PLA terminals were modified with furanyl (F) groups. When BMG was added to the mixed micelle solution, the gel strength was highly enhanced by the terminal of the copolymers driven by the Diels-Alder reaction with BMG. The chain coupling was effective not only for

increasing the number of crosslinks between the micelles but also for enhancing the ability of stereocomplex formation of the enantiomeric block chains.

Chapter 4 deals with the mixed micelle solutions of the copolymer mixtures of F-PEG-PLA/PLA-PEG-PLA identical to those of Chapter 2, and to which BMG was added for inducing the chain-extending Diels-Alder reaction. On addition of BMG, Diels-Alder coupling was induced at hydrophilic terminals in the mixed micelle solutions to increase the crosslinks between the micelle particles with the gel strength enhanced to a level of 11 kPa in storage modulus.