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Abstract

Title	Homo- and Stereocomplex Crystallization Behavior of Linear 1, 2-Arm and Branched 4-Arm Poly(L-lactide) and Poly(L-lactide)/Poly(D-lactide) Blends : Effects of Chain Directional Change and Branching

(800 words)

Crystallization behavior of linear 1-arm and 2-arm and branched multi-arm poly(L-lactide) (PLLA) is a matter of concern because its crystallinity affects in vivo degradation behavior and drug release profile. Differential scanning calorimetry (DSC), thermogarvimetry, wide-angle X-ray diffractometry (WAXD), viscometry, rheological measurements, tensile and impact testing, and swelling measurements were applied for multi-arm PLLA and L-lactide copolymers to investigate the effects of branching on the physical properties and highly ordered structures. In previous studies, the effects of an additional arm attached to linear PLLA on the physical properties, crystallization, and spherulite growth behavior were studied using 1-arm and 3-arm PLLA prepared with 1-dodecanol and glycerol as monofunctional and trifunctional coinitiators by employing DSC and polarized optical microscopy (POM). 3-arm PLLA showed slower non-isothermal crystallization during heating and isothermal spheruilte growth compared to those of linear 1-arm PLLA prepared with 1-dodecanol. However, the effects of only one extra arm or branching point, which is attached to linear 1-arm PLLA, seem too high to disturb the crystallization of linear 1-arm PLLA. Another probable reason for the disturbed crystallization of 3-arm PLLA is the chain directional change and the incorporation of the coinitiator moiety as an impurity in the middle of the molecule compared to that of 1-arm PLLA, in which the chain direction is unvaried and the coinitiator moiety is incorporated in the chain terminal. However, to the best of knowledge, detailed study on the pure effects of the chain directional change and branching on the crystallization behavior (spherulite growth rate and crystalline growth mechanism), crystalline form, and physical properties of PLLA and PLLA/poly(D-lactide) (PDLA) blends with a wide range of molecular weight has not been reported so far. Therefore, in this study the pure effects of the chain directional change and branching on the crystallization behavior and physical properties of PLLA and PLLA/PDLA blends using linear 1- and 2-arm and branched 4-arm PLAs were investigated. The thermal properties were evaluated by the use of DSC. The crystallinity (X_c), crystalline species, and crystalline form were estimated by WAXD. The spherulite growth and crystalline growth mechanism were studied by the use of POM.

General introduction based on characteristics, synthesis, crystallization, spherulite growth, regime analysis, and stereocomplex of poly(lactic acid), and characteristics of linear 2-arm and branched multi-arm poly(lactide)s were carried out (**Chapter 1**).

To study on the pure effect of chain directional change on the crystallization behavior and physical properties of PLLA using linear 1- and 2-arm PLLA synthesized by bulk ring-opening polymerization of L-lactide initiated with tin(II) 2-ethylhexanoate in the presence of the monofunctional coinitiator of L-lactic acid, 1-dodecanol, and the bifunctional coinitiator, ethylene glycol was carried out (**Chapter 2**). DSC and POM measurements indicated that the chain directional change, the incorporation of the coinitiator moiety as an impurity in the middle of the molecule (chain directional effect), and their mixed effect disturbed the crystallization of linear 2-arm PLLA compared to that of linear 1-arm PLLAs, in which the chain direction is unvaried and the coinitiator moiety is incorporated in the chain terminal.

The pure effect of branching on the crystallization behavior and physical properties of PLLA using linear 2-arm and branched 4-arm PLLA synthesized by bulk ring-opening polymerization of L-lactide initiated with tin(II) 2-ethylhexanoate in the presence of the bifunctional coinitiator, 1,3-propanediol, and tetrafunctional coinitiator, pentaerythritol was studied (**Chapter 3**). DSC and POM measurements indicated that branching architecture of 4L delayed or disturbed the non-isothermal and isothermal crystallization, compared to linear architecture of 2L, but had no significant effect on the segmental mobility and crystalline thickness when compared in terms of M_n and M_n(arm), respectively. WAXD measurement showed that the T_c values at which the transition from the δ-form to the α-form took place [$T_c(\alpha)$] were not affected by the presence of branching and $T_c(\alpha)$ of 4L depended on M_n(arm) not M_n, and were similar to those of 2L, when plotted as a function of M_n(arm).

The effects chain directional change and branching on crystallization behavior and physical properties of PLLA/PDLA blends were investigated (**Chapter 4**). The linear 1- and 2-arm and branched 4-arm PLA synthesized by bulk ring-opening polymerization of L- and D-lactide initiated with tin(II) 2-ethylhexanoate in the presence of the monofunctional coinitiator, 1-propanol, the bifunctional coinitiator, 1,3-propanediol, and tetrafunctional coinitiator, pentaerythritol, respectively. DSC and POM measurements exhibited that the segmental mobility was insignificantly altered and significantly increased by the chain directional effects and branching effects, respectively, and non-isothermal and isothermal stereocomplex crystallization was disturbed by chain directional effect and branching effect, but stereocomplex crystalline thickness was determined by M_n(arm) and was not affected by the chain directional effects or branching effects. WAXD measurement indicated that the final fraction of the chains which can be incorporated in crystalline regions was decreased by the chain directional effect and branching effect.

Chapter 5 summarizes the results obtained from this thesis.