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A b s t r a c t

Title	Synthesis, Crystallization, and Hydrolytic Degradation of Stereo Multiblock Poly(lactic acid)s
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(800 words)

Poly(lactic acid) (PLA), a plant-derived polyester, have a leading success stories in bioplastics, moving from the laboratory into the plastics marketplace within the last decade, in addition to the biomedical and pharmaceutical applications. Wider physical properties and various hydrolytic degradation rates are required to widen the applications of PLA-based materials. Stereocomplex crystallization of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) is known to enhance the mechanical performance and thermal/hydrolytic degradation resistance of PLA-based materials. Stereocomplex crystallization can readily occur in stereoblock copolymers of PLLA and PDLA compared with that of PLLA/PDLA blends. The physical properties and hydrolytic degradation properties of the stereoblock copolymers can be manipulated by varying stereoblock length (v_{av}). In this study, stereo multiblock PLAs were synthesized to have different v_{av} values by melt-polycondensation of low molecular weight poly(L-lactide) (PLLA)/poly(D-lactide) (PDLA) blends with a wide variety of weight-average molecular weights (M_w s) in the range of $1.1-5.2 \times 10^3$ g mol⁻¹ and their crystallization and hydrolytic degradation behavior were investigated. General discussion based on classification and applications of biodegradable polymers and synthesis, crystallization, spherulite growth behavior, and hydrolytic degradation properties of PLA were carried out (**Chapter 1**).

Stereo multiblock PLAs were synthesized to have different stereoblock lengths and their molecular weight, v_{av} , and crystallizability of the resultant stereo multiblock PLAs were studied by gel permeation chromatography, ¹³C NMR, differential scanning calorimetry, and wide-angle X-ray scattering (**Chapter 2**). The v_{av} values of synthesized stereo multiblock PLAs strongly affected by blend molecular weight, reaction temperature and time. The v_{av} of the stereo multiblock PLAs increased with increasing the M_w of blend and reaction temperature, whereas the M_w and M_w /number-average molecular weight of stereo multiblock PLAs increased with increasing the M_w of blend, reaction time and temperature. The stereo multiblock PLAs with v_{av} higher than 7 were crystallizable to form stereocomplex crystallites and the crystallinity and melting temperature of crystallizable stereo multiblock PLAs increased with increasing M_w of the blend and reaction temperature (or v_{av} and M_w of stereo multiblock PLAs).

The effects of block length on crystallization and spherulite growth behavior of stereo multiblock PLAs and stereo diblock PLA (DB) with a wide variety of block length of 15.4-61.9 lactyl units were investigated at different crystallization temperatures (T_c), in comparison with neat PLLA, PDLA, and PLLA/PDLA blend (**Chapter 3**). Only stereocomplex crystallites as crystalline species were formed in the stereo multiblock PLAs and DB, irrespective of block length and crystallization temperature. The maximum crystallinities (X_c s) (33-61%), maximum radial growth rate of spherulites (G_{max}) (0.7-56.7 $\mu\text{m min}^{-1}$) and equilibrium melting temperatures (182.0-216.5°C) increased with increasing block length but were less than those of PLLA/PDLA blend (67 %, 122.5 $\mu\text{m min}^{-1}$, and 246.0°C). The spherulite growth rates and overall crystallization rates of the stereo multiblock PLAs and DB increased with increasing block length and were lower than that of PLLA/PDLA blend.

Hydrolytic degradation behavior of stereo multiblock PLA and DB, poly(DL-lactide) (PDLA), and poly(DL-lactic acid), with a wide variety of block length values of 3.8-61.9 lactyl units were investigated at 37°C and pH 7.4 using amorphous-made samples of these polymers, in comparison with amorphous-made neat PLLA, PDLA, and PLLA/PDLA blend to elucidate the effects of block length sequence (**Chapter 4**). ¹³C NMR spectra revealed that the chain cleavage during hydrolytic degradation occurred rapidly on the atactic segments connecting relatively long isotactic L-lactyl unit and D-lactyl unit segments. The rates of weight loss and hydrolytic degradation of stereo block PLAs, PDLA, and poly(DL-lactic acid) decreased with increasing average stereo block length. Surprisingly, the hydrolytic degradation of the stereoblock PLAs with v_{av} exceeding 27 lactyl units was disturbed compared to that of the PLLA/PDLA blend, whereas the hydrolytic degradation of stereoblock PLAs with v_{av} exceeding 15 lactyl units was disturbed compared to that of the neat PLLA and PDLA. The stereocomplex crystallization occurred during hydrolytic degradation of stereo block PLAs and PDLA with v_{av} more than 7 lactyl units, in agreement with the results reported for stereocomplex crystallization from the melt. The crystallization rate of stereo block PLAs during hydrolytic degradation became higher with increasing v_{av} , but even the rate of the diblock PLA having the highest v_{av} was lower than that of the PLLA/PDLA blend.

Chapter 5 summarizes the results obtained from this thesis.