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論文題目：　生分解性高分子の固体構造と物性

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biodegradabl polymers.

Abstract

Recently aliphatic polyesters have been received much attention on their biodegradability particularly from an ecological view point, as studied extensively to replace some of synthetic polymers which make environmental problems due to their chemical stability. Furthermore, some synthetic polyesters are commercialized as biodegradable polymers, recent year. The mechanical properties and degradation rates of those polymers are associated with their morphology and crystallinity as well as their chemical structures. Therefore, the research results on the biodegradation of aliphatic polyesters obtained by individual researcher indicate a little difference, even though the starting specimens of similar chemical structure and molecular weights are examined. The relationship between structural features and crystallization conditions under an isothermal or nonisothermal processes will be required from a fundamental point of view.

In this study, we examine the crystallization characteristics of aliphatic polyesters under various thermal conditions with respect to their crystallinity and spherulitic morphology. We also investigate the morphological features of solution grown crystals, and examine its crystal data for some polyesters.

The purpose of this study is to clarify the relationship between chemical structures of aliphatic polyesters and their resultant fine textures, and also to elucidate the relationship between their fine structures and physical properties in the bulk state.

This thesis contains eight chapters. The first chapter correspond s to the general introduction, which describes the purpose of this study and an outline of the experimental plan.

In the second chapter, solution-grown crystals (SGC) of poly(L-lactide)-PLLA are prepared from its dilute acetonitrile solution by isothermal crystallization method. Their morphology and structural features are examined. Highly-ordered electron diffraction patterns of SGC provide the orthorhombic unit cell parameters : a = 1.078 nm, b = 0.604 nm, c (fiber axis) = 2.87 nm. This unit cell of the PLLA SGC contains 20 monomeric units in terms of density measurements. Crystallization characteristics of PLLA films of different molecular weights are studied. In nonisothermal crystallization modes from the isotropic melt, crystallinity of PLLA films increases remarkably with a decrease in the cooling rate. The PLLA polymer exhibits an Avrami exponent n = 4 in the isothermal crystallization experiments in the whole temperature range examined. Molecular parameters governing the isothermal crystallization behavior are estimated by the application of the secondary nucleation theory.

In the third chapter, changes of orientation and crystallinity in uniaxially stretched PLLA films are studied. Crystallinity, orientation of crystallites, refractive index, and storage moduli of drawn films increase monotonically with increasing draw ratio ; however, their physical properties are saturated at draw ratio (D.R.) = 2.5 ～ 3.0. Molecular chains of PLLA crystallize from random state with stretching. Most crystallites formed in the drawn sample would be oriented to the drawn direction at D.R. = 2.5 ～ 3.0.

The fourth chapter provides the bulk crystallization behaviors of poly(ε -caprolactone) - PCL. The crystallinity of PCL increases with a decrease in cooling rates during the cooling procedure from its melt. In isothermal crystallization, the linear growth rates of PCL spherulites are measured at various temperatures. Surface free energy of the PCL crystallite nucleus estimate from the secondary nucleation theory.

The fifth chapter shows the morphology and structural features of poly(ethylene succinate) - PES. Also we examine the bulk crystallization behaviors of PES. This unit cell of the PES SGC has the orthorhombic parameters : a = 0.755 nm, b = 0.541 nm, c (fiber axis) = 0.833 nm, containing 2 molecular chains. Crystallization characteristics of PES films of different molecular weights are studied.

In the chapter 6, the bulk crystallization behaviors of poly(tetramethylene succinate) - PTMS are studied in terms of cooling rate and supercooling. The crystallinity of PTMS increased with a decrease in cooling rate during the cooling procedure from its melt. The growth rate data of PTMS spherulites obtained at isothermal conditions are examinedin

terms of the secondary nucleation theory crystallization ; thus the nucleation parameters of PTMS are explained quantitatively.
In the chapter 7, we discuss the relationship between chemical structures of aliphatic polyesters and their physical properties, using results obtained in chapter 2 ～ 6, with paying attention to crystallization characteristics.

Finally, summarized comments and conclusive remarks are described in the chapter 8.