The purpose of this study is clarification of crystallization behaviors of linear polymers in spin-coating film-forming processes on the molecular scale by time-resolved measurements of grazing-incidence small-angle and wide-angle X-ray scattering (GISAXS and GIWAXS: GISWAXS) measurements using synchrotron radiation. A sample used in this study was a commercially-available poly(3-hydroxybutyrate) (P3HB) (Sigma-Aldrich, Mw=437,000, Mw/Mn=1.67, Tg= 276 K) which was a biobased and biocompatible polyester. By spin-coating at rotational speeds of 1000 – 4000 rpm with using 0.49, 1.0, and 2.1wt% chloroform solutions of the P3HB, P3HB thin films with thicknesses of ca. 30 – 600 nm were formed on silicon substrates. In these spin-coating processes at 296K, GISAXS and GIWAXS patterns from the sample on the substrate were simultaneously detected at BL45XU of SPring-8 (Hyogo, Japan). At the beginning of spin-coating, an isotropic scattering pattern from the solution was observed. Next, anisotropic Bragg reflections from oriented orthorhombic crystals of P3HB appeared and increased in intensity for several tens seconds. This indicated that P3HB chains crystallized as chloroform evaporated from the sample. It was also found that P3HB orthorhombic crystal having edge-on orientation was preferentially formed in thinner films. When the rotational speed of the substrate increased, the apparent induction period of crystallization slightly increased and the crystal growth rate decreased. This implied that the chain mobility of P3HB for crystallization might reduce due to a reduction in quantity of the solvent molecules and an increase in magnitude of the centrifugal force. These results obtained in this research would be important knowledge to improve film processing technologies for biobased polymeric materials.

**Keywords:** Crystallization Kinetics of Polymers, Spin-coating Film-forming Process, Time-resolved GISWAXS Measurements using Synchrotron Radiation