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Higher-Order Structure Formation, Phase Transition, and Distribution of Polymorphic Crystals of Biodegradable Polymers Studied Using Time-Resolved Infrared Spectroscopy, X-ray Scattering, and High-Resolution Raman Imaging Techniques

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Semicrystalline biodegradable polymers, which have been widely used in our daily life, are very important kinds of polymer materials. The performance of the semicrystalline biodegradable polymers is highly related to their inner physical structures. This thesis mainly focused on investigating the phase transition and the distribution of polymorphic crystals of semicrystalline biodegradable polymers.

The crystal phase (structure) of polymer usually forms through a phase transition process from another phase. Phase transition is a multiple process, contains the evolution of complex hierarchical structures, which determines the final crystal structure. Therefore, investigating the phase transition process is one of the most important research topics of polymers. Moreover, to get more detailed and reliable results, suitable research methods should be used. In this thesis, crystallization process of poly(3-hydroxybutyrate) (PHB) during solvent (chloroform) evaporation (SEC) was systematically investigated by time-resolved attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy and grazing incidence wide angle X-ray diffraction (GI-WAXD) methods. Especially, the local molecular structure evolution of PHB during SEC was achieved by ATR-FTIR for the first time. The author also challenged to reveal the long-term controversial problem about the mechanism of the β-to-α phase transition of poly(butylene adipate) (PBA) through the techniques of the time-resolved FTIR measurement as well as the simultaneous time-resolved WAXD/small-angle X-ray scattering (SAXS) measurement in the quick and stable temperature jumping process, by which the time-dependent structural change had been traced quite clearly.

The crystal morphologies and the distribution of the different phases within the polymeric material system can also affect the performance of polymers. When PBA isothermal melt-recrystallization at 30–33 ℃, it exhibits ring-banded spherulites, and in each of such spherulite, two crystal forms of PBA coexist. To find out the relationship between ring-banded spherulites and polymorphic crystals behavior of PBA, Raman imaging technique was performed. The characteristic Raman bands for α, β-form crystals and the amorphous phase of PBA, have been identified. Through Raman imaging, the α- and β-form crystals of

PBA uniformly distributed rather than alternate distributed within the ring-banded region as suggested by previous study, and they grow together when the ring-banded PBA spherulites are formed.