

Interplay between the Relaxation of the Glass of Random L/D Lactide Copolymers and Homogeneous Crystal Nucleation: Evidence for Segregation of Chain Defects

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Random L isomer rich copolymers of poly(lactic acid) containing up to 4% D isomer co units have been cooled from the molten state to obtain glasses free of crystals and free of homogeneous crystal nuclei. The kinetics of enthalpy relaxation and the formation of homogeneous crystal nuclei have then been analyzed using fast scanning chip calorimetry. It has been found that the relaxation of the glass toward the structure/enthalpy of the supercooled liquid state is independent of the presence of D isomer co units in the chain. Formation of homogeneous crystal nuclei in the glassy state requires the completion of the relaxation of the glass. However, nucleation is increasingly delayed in the random copolymers with increasing D isomer chain defect concentration. The data show that the slower formation of homogeneous crystal nuclei in random L/D lactide copolymers, compared to the homopolymer, is not caused by different chain segment mobility in the glassy state but by the segregation of chain defects in this early stage of the crystallization process.