Crystal Growth Theory for Random Copolymers of Crystallizable and Non-crystallizable Units HERVE MARAND, HADI MOHAMMADI, Virginia Tech, Department of Chemistry — While the presence of randomly distributed non-crystallizable units (e.g. short branches in metallocene linear low density polyethylene) has been carefully considered in the thermodynamics of copolymers crystallization, it has been mostly ignored in the analysis of crystal growth rate data. In this work, we present an extension of the Lauritzen-Hoffman (LH) secondary nucleation theory that considers crystal growth processes for random copolymers of crystallizable and non-crystallizable units. Concentrating on the distribution of crystallizable unit sequence lengths rather than the whole polymer chain, rate equations in the LH theory are modified to account for the population of crystallizable sequences able to form a specific number of folds. We then calculate the flux over the nucleation barrier for each lamellar thickness, the secondary nucleation rate, i, the substrate completion rate, g, and derive the crystal growth rate, G, as a function of crystallization temperature. The model also allows prediction of the lamellar thickness distribution as a function of crystallization temperature. In qualitative agreement with literature data, our model predicts lower crystal growth rates and higher average lamellar thicknesses for m-LLDPE than for linear polyethylene at the same undercooling.

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