

**EARLY STAGE CRYSTALLIZATION OF A FLEXIBLE LINEAR  
POLYMER**

by

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## ABSTRACT

Polymer crystallization is an industrially and scientifically important phenomenon that has eluded detailed molecular description. For semicrystalline polymers, the morphology and properties of the materials are strongly influenced by the processing conditions under which crystallization occurs. Understanding how the crystals form is crucial for controlling the properties of polymers. However, the fundamental mechanisms of polymer crystallization, especially during early stages, are still poorly understood. To achieve the molecular level understanding of polymer crystallization, clear structural information during early stage crystallization is essential.

In this study, we investigate the early stage crystallization behavior of polyethylenes using small angle scattering (light and X-rays). Clear structural information during early stages of crystallization of polyethylenes is obtained. The results show that the early stage crystallization is characterized by large scale ( $> 1\mu\text{m}$ ) orientation fluctuations that precede the formation of local crystalline order manifest in X-ray scattering, and the initial collapse of these large scale anisotropic/ordered domains. During the early stages of crystallization, the scattering intensity increases exponentially with time initially, and the wave vector dependence of the growth rate of fluctuations is consistent with predictions for initial stages of a phase transformation process.

Furthermore, the scattering profiles obtained during early stage crystallization of a lightly branched polyethylene are analyzed using unified model by Beaucage. It is shown that the unified model gives good fits to the scattering data. Results show that the early stage crystallization can be divided into two distinct processes. Process I is the formation and subsequent 'global collapse' of the large scale disordered anisotropic domains. Process II is the local ordering of these domains leading to the stable crystals. There is an equilibrium process of the forming and dissolving of the 'baby nuclei' within these domains. Stable crystal nuclei that can grow further are formed as a result. These domains formed grow in a cooperative manner during early stage crystallization.