

Crystalline Precursor Formations under Steady-State Isothermal Planar Elongational Stretching of *n*-eicosane: A Comparison Between Simulation and Experiment

Introduction

The crystallization of polymer melts under flow has generated a tremendous amount of interest over the years. Understanding crystallization mechanisms, kinetics and crystallite morphologies are just a few of the problems that present an ongoing interest among research communities. The research interest dedicated to solving these problems has been almost exclusively experimental. With the rapid advancements in computation capabilities and the development of new simulation strategies, simulation techniques are playing an increasingly important role in elucidating these problems. Short and long chain *n*-alkanes have been extensively used to model the behavior of polyethylene in particular and polymers in general. Crystallization of long chain molecules through equilibrium molecular simulation techniques is particularly difficult, due to long simulation times needed to observe such phenomena [1, 2]. However, driving the system away from equilibrium has been shown to reduce such simulation times by a few orders of magnitude [3, 4]. Alternative techniques to induce the crystal formation have been developed, which include crystallization induced by the presence of a surface in the system [2], crystallization induced by uniaxial

stretching of the chains, followed by quenching [3, 4] etc. To the best of our knowledge, we are the first to report crystalline-like structure formation from purely steady-state elongational stretching under isothermal conditions. In the present work we investigate the structures of a series of *n*-eicosane at high elongation rates.

Approach

The system under investigation consisted of linear *n*-eicosane. Non Equilibrium Molecular Dynamics (NEMD) simulations have been performed, using an in-house developed algorithm. The oriented structures were generated via steady-state isothermal planar elongational stretching at constant volume. The interactions between atoms were modeled using the united atom approach of Siepmann et al [5].

Results

The simulated structures are compared to experiment using the structure factor ($s(k)$) approach. Structure factors are computed as the Fourier transforms of the total pair correlation functions. Excellent agreement has been found between the simulated liquid structure factors and the x-ray diffraction determined ones under the same conditions of pressure and temperature. The structure factor for the elongated melt can be decomposed into an intra-molecular and an inter-

molecular region. In the intra-molecular region we found evidence of molecules adopting the all-*trans* stretched conformation, which is in excellent quantitative agreement with the experimental x-ray diffraction investigation also performed for this work. In the inter-molecular region, we found a shift of the first inter-molecular peak towards higher k values, which is indicative of closer chain side packing. This shift is also in excellent agreement with experimental x-ray diffraction data for crystalline C₂₀.

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