P.23 Crystallization mechanism in melts of short n-alkane chains

M Anwar, F Turci and T Schilling

Université du Luxembourg, Luxembourg

Despite the long-standing research interest in crystallization in polymer melts, many fundamental aspects of the crystal nucleation and growth mechanisms are still subject of discussion [1, 2].

Experiments in this field are usually restricted to a spatial and temporal resolution that is too coarse to capture atomistic details of individual nucleation events. Thus molecular dynamics provides an ideal instrument to complement experiment and offer insight into the mechanisms on the atomistic scale.

In the traditional picture of the early stages of the polymer crystallization, the Bragg peaks are observed after the induction period in wide angle X-ray scatter- ing(WAXS). No small angle X-ray scattering (SAXS) peak is expected before the Bragg peak. But in 1990's SAXS peaks were reported in many experiments during induction period before the appearance of the Bragg peaks [3, 4, 5]. These SAXS peaks were claimed to be due to the presence of ordered melt before occurrence of nucleation event. Theories have been proposed to explain these SAXS peak [6, 7].

Given the high degree of complexity that long polymer chains pose both, from the conceptual and the numerical point of view (due to folding and entanglement), a basic comprehension of how even relatively short chains crystallize is of fundamental importance in order to build a coherent theory.

Crystal nucleation in alkanes has been addressed in several computer simulation studies in the 90s [8, 9, 10, 11] and a scenario for the nucleation mechanism has been suggested. Due to the limited computer resources available at the time, however, these works were based on one simulation trajectory each (with the exception of ref. [8]).

Considering the limited amount of data available in the literature on the nucleation and growth mechanism in short chain alkanes, we have revisited the problem and present here a detailed analysis of the formation of crystal nuclei from the homogeneous melt and the subsequent growth process.

We study crystallization in a model system for eicosane (C20) by means of molecular dynamics simulation and we identify the microscopic mechanisms of homogeneous crystal nucleation and growth. For the nucleation process, we observe that chains first align and then straighten. Then the local density increases and finally the monomer units become ordered positionally. The subsequent crystal growth process is characterized by a *sliding-in* motion of the chains. Chains prefer- ably attach to the crystalline cluster with one end and then move along the stems of already crystallized chains towards their final position. This process is cooperative, i.e. neighboring chains tend to get attached in clusters rather than independently.

[1] Gnter Reiter Gert R. Strobl. *Progress in Understanding of Polymer Crystallization, Lect. Notes Phys. 714.* Springer-Verlag Berlin Heidelberg, 2007

[2] Gert Strobl. *Colloquium* : Laws controlling crystallization and melting in bulk poly- mers. *Rev. Mod. Phys.*, 81:1287–1300, Sep 2009

[3] M. Imai, K. Kaji, and T. Kanaya. Structural formation of poly(ethylene terephtha- late) during the induction period of crystallization. 3. evolution of density fluctuations to lamellar crystal. *Macromolecules*, 27(24):7103–7108, 1994

[4] Kanaya T Sakai Y Imai M, Kaji K. Ordering process in the induction period of crystallization of poly(ethylene terephthalate). *Phys. Rev. B*, 52:12696–12704, 1995

[5] T. A. Ezquerra, E. López-Cabarcos, B. S. Hsiao, and F. J. Baltà-Calleja. Precursors of crystallization via density fluctuations in stiff-chain polymers. *Phys. Rev. E*, 54:989–992, Jul 1996

[6] T. C. B. McLeish N. J.Terrill P. D. Olmsted, W. C. K. Poon and A. J. Ryan. Spinodal-assisted crystallization in polymer melts. *Physical Review Letters*, 81:373–376, 1998

[7] K. Kaji. *Handbook of Thermoplastic Polyesters: Homopolymers, Copolymers, Blends, and Composites*, chapter Structure Formation in PET during the Induction Period of Crystallization, pages 225–251. Wiley-VCH Verlag GmbH & Co. KGaA, 2005

[8] K. Esselink, P. A. J. Hilbers, and B. W. H. van Beest. Molecular dynamics study of nucleation and melting of n-alkanes. *The Journal of Chemical Physics*, 101(10):9033–9041, 1994

[9] Hisao Takeuchi. Structure formation during the crystallization induction period of a short chain-molecule system: A molecular dynamics study. *The Journal of Chemical Physics*, 109(13):5614–5621, 1998

[10] Susumu Fujiwara and Tetsuya Sato. Molecular dynamics simulation of structural formation of short polymer chains. *Phys. Rev. Lett.*, 80:991–994, Feb 1998

[11] Susumu Fujiwara and Tetsuya Sato. Molecular dynamics simulation of structure formation of short chain molecules. *The Journal of Chemical Physics*, 110(19):9757–9764, 1999