

## Shifting Paradigms in Polymer Crystallization

*M. Muthukumar*

Department of Polymer Science and Engineering  
University of Massachusetts  
Amherst, MA 01003 USA

muthu@polysci.umass.edu

### Introduction

The role of conformational entropy of polymer chains in polymer crystallization is investigated by molecular modeling and theory. The entropy of folded loops dominates at experimentally relevant temperatures to dictate short equilibrium lamellar thicknesses, which are much smaller than the extended chain thickness. Also the entropic barriers control the kinetics of polymer crystallization. These results based on chain entropy are different from the classical views of how polymer chains crystallize.

### Theory

The ordering process of topologically connected chains into a crystalline state is distinctly different from that of low molar mass substances. One of the key differences arises fundamentally from entropic barriers due to substantial reduction in configurational entropy of the system during the ordering process.

Due to chain connectivity, the crystalline phase assumes lamellar morphologies. The anisotropy of lamellae is due to different strengths of barriers in the lateral and normal directions of the lamellae. Simulations show generally that there are many barriers for growth in the normal direction, which make the lamellar thickness to be very long-lived. While these barriers are very high, the barrier for lateral growth is much weaker, and the lamellae grow laterally with measurable speeds.

### Results and discussion

We [1-8] have derived a new theoretical model with the following essential features:

(1) For a single lamella, all possible folded states (with the corresponding thicknesses) are allowed. The free energy landscape for this model exhibits a barrier, many metastable states (separated by free energy barriers), and a globally stable state. Among the metastable states, even the first viable state with its free energy just below that of the melt is long-lived, due to the barrier for thickening. The thickness of this long-lived metastable state increases with temperature, in a qualitatively similar manner to the Gibbs-Thompson law. However, if enough time is granted for this metastable state to evolve, then the equilibrium thickness would be reached for each temperature. The equilibrium thickness decreases with temperature, until the approach of the equilibrium melting temperature. In the present model, the equilibrium melting temperature does not correspond to that of extended chain dimensions.

(2) The lateral growth faces a free energy barrier, due to temporal crowding of entangled chains at the growth front. A general formula is derived for the growth kinetics of the growth front. The linear growth rate  $G$  assumes the form,

$$G \sim (D_i/D) \exp(-1/T \Delta T) [1 - \exp(\Delta H \Delta T/kT_m T)],$$

Where  $\Delta T$  is the quench depth,  $T_m$  is the melting temperature,  $\Delta H$  is the latent heat of fusion,  $T$  is the temperature,  $D_i$  is the diffusion coefficient inside the growth zone with the barrier, and  $D$  is the diffusion coefficient away from the zone. The first two terms on the right hand side become unimportant for small molecules and for dilute solutions of the polymer. The predictions are compared with some experimental data.

### References

1. C. Liu and M. Muthukumar, *J. Chem. Phys.* 109, 2536 (1998).
2. M. Muthukumar and P. Welch, *Polymer*, 41, 8833 (2000).
3. M. Muthukumar, *Eur. Phys. J. E3*, 199 (2000).
4. P. Welch and M. Muthukumar, *Phys. Rev. Lett.* 87, 218302 (2001).
5. I. Dukovski and M. Muthukumar, *J. Chem. Phys.* 118, 6648 (2003).
6. M. Muthukumar, *Phil. Trans. R. Soc. Lond.* A361, 539 (2003).
7. J. Zhang and M. Muthukumar, to be published.
8. A. Kundagrami and M. Muthukumar, to be published.