

Early stage of polymer crystallization: Theoretical study based on chain statistics

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PhD Thesis

Early stage of polymer crystallization:
Theoretical study based on chain statistics

(高分子結晶化の初期過程：
高分子鎖の統計にもとづく理論研究)

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Introduction

Polymer crystal has a hierarchical structure over a wide range of length scales (from order of nm to μm). In the hierarchical structure, crystalline and amorphous regions coexist. Moreover the morphology of the structure depends on the crystallization process. Due to these properties of the polymer crystal, so far, there has been no theoretical framework to explain the mechanisms despite of the importance of controlling and understanding the hierarchical structure. To understand the emergence of the hierarchical structure, we focus on the crystallization process which is composed of some time regimes. To achieve this understanding, we will construct a multi-scale model of the polymer crystallization based on a strategy which is composed of 2 steps as follows. In the first step, we will try to model the phenomena in each time regime. In the next step, the multi-scale model is constructed by connecting these models.

The purpose of our research in this thesis is modeling the phenomena in two time regimes. The first time regime is before the critical nucleus is generated, which is called ‘induction period’. In the other time regime, the critical nucleus is generated. We call these time regions as ‘early stage of the crystallization’ in this thesis. Modeling the early stage of polymer crystallization is the first step toward the understanding of the polymer crystallization in a unified manner.

Model of induction period

We study the possibility of the spinodal decomposition (SD) in the induction period of the polymer crystallization from an initial uniform melt state, where SD is a phase separation mechanism due to a thermodynamical instability of the initial state. The SD during induction period was first found in an X-ray scattering experiment, and has still been controversial due to the existence of various experiments and theories that support or deny the phenomenon[1, 2]. In this thesis, we explain the condition for the SD to occur in polymer melts by deriving a Ginzburg-Landau model of the free energy as a functional of the density and the orientation of the segments, where we introduce the excluded volume and the nematic interactions through a combination of the random phase approximation and the transfer matrix for the polymer conformation. We show that, upon elimination of the degrees

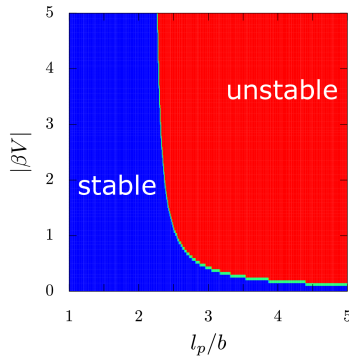


Figure 1: Stability diagram. The vertical and horizontal axes are the strength of the nematic interaction $|\beta V|$ and the persistence length l_p/b , respectively. The blue and red regions mean (meta)stable and unstable regions, respectively.

of freedom of the orientation, the nematic interaction reduces to an effective attraction whose strength increases with the stiffness of the polymer chain. Such an attraction induces spinodal decomposition especially for stiff polymer chain case. We show in Fig. 3.8 the stability diagram which gives us the criterion of the SD.

Model of nucleation

We construct two theoretical models of the nucleation of polymer crystallization based on classical nucleation theory (CNT)[3] which does not explicitly include conformation entropy. In the CNT, we can obtain the knowledge of a critical nucleus by calculating the free energy difference before and after the nucleation. We model the nucleation theory of single chain system (Model S) and that of multi-chain system (Model M). In these models, the nucleus is assumed to be composed of tails, loops and a cylindrical ordered region, where the conformation entropy is evaluated by using the transfer matrix. In Model S, we evaluate Helmholtz free energy difference before and after the nucleation, while in Model M, we evaluate grand potential difference instead of Helmholtz free energy. This is because as an independent variable, we choose the chemical potential conjugate to the number of chains in the nucleus which fluctuates in multi-chain systems. We found that the activation energy of Model M is smaller than that of Model S (see Fig. 2). This result means that the possibility of the nucleation in multi-chain systems is larger than that of the nucleation in single chain sys-

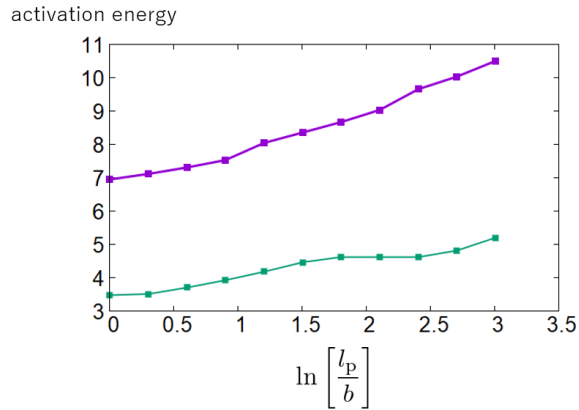


Figure 2: The activation energies versus $\ln [l_p/b]$ in Model S (purple) and Model M (green). l_p and b are the same as those in Fig. 3.8.

tems. This result is interpreted in terms of the effect of the conformation entropy, where the nucleus of Model S needs to create loops, while the nucleus of Model M does not necessarily do so.

Summary

In this thesis, we construct theoretical models of the early stage of the polymer crystallization, which is composed of the induction period and the time region of creation of the critical nucleus.

We propose a theoretical model explaining the possibility of the SD during induction period by discussing the stability of the initial uniform polymer melt. The occurrence probability depends on the strength of the effective attraction originated from the nematic interaction.

We construct nucleation theories of single chain systems and of multi-chain systems by extending the CNT, where the conformation entropy is explicitly evaluated. By using these theories, we found that the possibility of nucleation in multi-chain systems is larger than that in single chain systems, which is interpreted in the context of the conformation entropy.

These theoretical models of induction period and of nucleation will be the first step toward the understanding of the emergence of the hierarchical structure in a unified manner.

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