

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

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## Introduction

Polymer crystal has a hierarchical structure over a wide range of length scales (from order of nm to  $\mu\text{m}$ ). In the hierarchical structure, crystalline and amorphous regions coexist. For example, when the polymer melt is crystallized under the quiescent condition, the spherulite is observed. In 10 nm order, the folded chain crystal appears, where the polymer chain is folded. In larger scale, the folded chain crystal regions and amorphous regions alternately stack, whose structure is so called lamellar crystal. These lamellar crystals grow and branch to form a spherulite in  $\mu\text{m}$  order.

Moreover, the morphology of the structure depends on the crystallization process. For example, when the polymer melt is crystallized under the shear flow, we observe a shish kebab structure instead of the spherulite. In the shish-kebab structure which appears in  $\mu\text{m}$  scale, the polymer chain is oriented along the shear flow direction.

Concerning the above properties of the polymer crystal, it has been so far difficult to construct a 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 several time regimes. To achieve this understanding, we will construct a multi-scale model of the polymer crystallization in 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.

## Single chain statistics

In this thesis, we model a semi-flexible polymer chain by using the transfer matrix. The polymer chain is composed of the molecular units (for example  $\text{CH}_3$ ) connected by covalent bonds. In general, a polymer chain has many degrees of freedom of the conformation, which is originated from the rotation of the covalent bonds. However, the bond cannot rotate freely but it can take only trans or gauche conformations. The trans conformation is the stable state while the gauche conformation is a meta stable one. To describe such a polymer chain, we introduce a rod-like segment composed of consecutive two covalent bonds. We assume that the chain is composed of a sequence of rod-like segments (In the following, we call these rod-like segments simply 'segments'). Although we neglect the excluded volume interaction between segments, the orientations of the segments are influenced by the constraint condition on the trans and gauche conformations. This relationship is described by using a matrix which is defined in the space spanned by the orientations of two consecutive segments. The statistical weight of the trans and gauche conformations put in the components in the matrix. This matrix is called the "transfer matrix" which is well known as a tool to calculate the partition

function of a 1-dimensional Ising model system. In the transfer matrix for the polymer chain, the chain stiffness is described by using the energy difference between trans and gauche conformations. By using the transfer matrix, we obtain some physical quantities of a semi-flexible chain, for example, characteristic ratio, power spectra of segment density and of segment orientation, which are functions of the energy difference between trans and gauche conformations.

### Induction period

We study the possibility of the occurrence 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.

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 of freedom of the orientation, the nematic interaction reduces to an effective attraction between segments whose strength increases with the stiffness of the polymer chain. Such an attraction induces spinodal decomposition especially for stiff polymer chain case.

Based on our model, we obtain the stability diagram where the chain stiffness and the strength of the nematic interaction are chosen as control parameters. When both of these parameters are relatively large, the SD occurs. Such a picture is qualitatively consistent with some experimental results.

### Nucleation

We construct two theoretical models of the nucleation of polymer crystallization based on classical nucleation theory (CNT) 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 propose a 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. This result means that the possibility of the nucleation in multi-

chain systems is larger than that of the nucleation in single chain systems. 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.

## Perspectives

In this thesis, we constructed models of the phenomena during the early stage of the polymer crystallization. Especially, when we model these phenomena, we focus on the microscopic parameter, i.e., the chain stiffness which depends on the chemical species of the polymer. Based on these models, some observable quantities are calculated, for example, the power spectrum of the density and the induction time which is time before the critical nucleus appears. This means that extending our theory leads to the relationship between the microscopic parameters and the macroscopic observable quantities.

We discuss the future direction of our research. Now we achieved the first step for constructing the multi-scale model as discussed above. As the next step, we will consider the dynamics of the growth of the crystal. To describe the growth of the crystal by extending Model M, the 2 problems at least remain.

First problem is the boundary condition for the calculation of the conformation entropy in the amorphous region. As the ordering process in inhomogeneous crystallization starts from a surface of a crystal which has been created previously, the chains in the disordered region cannot enter the interior of the crystal region.

The second problem is how to introduce the contribution from the viscosity. The growth rate of the crystal depends on the actual temperature, where the contribution from the viscosity is dominant for the low temperature case.

If these problems are solved, the crystal growth will be described by extending Model M.

## 論文審査の結果の要旨

無秩序状態にある高分子鎖が秩序正しく整列していく高分子の結晶化は、ソフトマターの中でも最も重要な相転移現象の一つであるが、その複雑さから理論的な取り扱いが難しくソフトマター物理の最大の未解決問題の一つである。従来の研究により、高分子の結晶化には無秩序状態の高分子鎖が揃い始める誘導期間、揃った高分子鎖が結晶化を始める結晶核生成、結晶が成長して高次構造を形成する結晶成長の段階があることがわかっている。その中でも誘導期間・結晶核形成の段階は乱れた鎖が秩序化する最も重要な過程であり、特に誘導期間においては熱力学的な不安定性によって引き起こされるスピノーダル分解型のダイナミクスが見られるのかが相反する実験結果から大きな論争になっていた。

本博士論文の提出者である横田宏氏は誘導期間における秩序化過程に対して、自由エネルギーをセグメントの密度場と配向場で汎関数 Taylor 展開し、その二次の項の係数の正負を調べることによって、一様状態の熱力学的な安定性を議論した。この時、高分子鎖は、鎖の剛直性を表現する転送行列法によって表される。さらに、乱雑位相近似を用いて、セグメント間に働く排除体積効果とネマティック相互作用を導入した。このようなモデルにおいて、配向自由度の消去を行うことで、ネマティック相互作用がセグメント間の有効的な引力として働き、この引力がある閾値を超えたときにスピノーダル分解が起こることを明らかにした。スピノーダル分解型の秩序化が起こるかどうかは、その化学構造によってきまる高分子鎖の硬さとネマティック相互作用の強さに依存し、実験における相反する結果もこのモデルで説明することができることがわかった。

次に横田氏は粗視化された鎖の統計力学理論を用いて高分子結晶の核生成の理論を構築した。従来の高分子の古典核生成理論では、高分子鎖のコンフォメーションの情報が入っていない点、および結晶核形成に参加する複数の高分子鎖の影響が考慮されていない点が問題であった。本研究では結晶核に取り込まれた高分子鎖が tails, loops そして円柱状の ordered region によって構成されていると仮定し、このような結晶核が現れる前後でのコンフォメーションエントロピーを転送行列法を用いても計算した。また複数の鎖の影響は grand potential を計算することにより取り入れた。その結果、高分子融液の核生成において、高分子の種類に寄らずに、結晶核は複数の鎖で構成されていることを理論的に初めて示し、さらにその核生成の活性化エネルギーが高分子の剛直性に依存することを示した。

これらの研究は、今までは鎖のミクロスコピックな構造を取り入れてなかった高分子の結晶化の研究において、その分子構造の重要性を具体的に示した先駆的な研究である。さらに、この研究で今まで実験的に論争のあった高分子の結晶化誘導期間におけるキネティクスについても理論面から決着がつき、また、高分子鎖のコンフォメーションや複数の鎖の寄与を取り入れた現実に近い核生成の理論を提出したことは、今後この分野の発展を切り開く上で極めて重要な成果であり、高分子の結晶化過程を統一的に説明するための端緒を開くものと期待される。これは申請者が自立して研究活動を行うに必要な高度の研究能力と学識を有していることを示す。よって博士論文として合格であると認める。