

## Molecular dynamics simulation of polymer crystallization in confined nano-domains

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ナノ空間に閉じ込められた高分子系の結晶化にともなう秩序形成ダイナミクスを分子動力学法によって調べた。高分子は粗視化モデルを用い、また実験的な観点から非晶性媒体中での閉じ込めとしてモデル化した。秩序パラメータ及び結晶化度の時間発展を、平面界面、球状界面の2つの形状下で追跡し、これらをバルク中での高分子の秩序化過程と比較することにより、ナノ界面の秩序化に及ぼす効果について検討した。これにより、一般的な結晶界面のような下地となる境界層が存在しない場合においても、界面近傍における高分子運動の主鎖方向の制限により、結晶秩序化が誘起されやすくなることを見出された。

Control of the higher order structure in the microscopic level is important for the improvement of polymeric soft materials. Recently, polymer crystallization in the micro domains has been studied experimentally, mainly using crystallin-noncrystalline block copolymers. It was found that the structure and the properties of the polymer crystals in nano domains are different from those of bulk samples. However, it is not always easy to clarify the detailed ordering dynamics and the role of external conditions experimentally. This is partly due to the facts that the polymer crystallization in micro domains is affected by many factors such as the boundary condition, the geometrical constraint, and the crystallization temperature, and partly due to the effect impurities that is included inside the domains. Molecular simulation is useful to study these ordering dynamics during crystallization processes since it can trace the behavior of the individual molecules. Thus, we carried out the computer simulation of polymer melts confined in nano domains under supercooling conditions and considers the effect of boundary on the melt crystallization processes.

In the simulation, the coarse-grained molecular dynamics method was used. The polymer chain was expressed in two factors of connectivity and rigidity. The polymer model used in this study was generally similar to our previous studies on polymer crystallization except for the bending potential of main chains, which is the square of cosine of bending angle in this study. For the domain boundaries, we have to consider that the interface layer consists of different kind of segment molecules and takes amorphous state. This situation can be modeled by various ways including the atomistic approach that the boundary layer is represented by randomly arranged non-crystalline atoms, since the polymer chain trapped to each of boundary atoms. Although this arbitrariness can be avoided

by averaging over many different interface samples, heavy calculation time would be necessary. Thus, we used the flat purely repulsive interface potential in which no lateral dependency exists. We prepared two types of confined boundary conditions, which are cubic shape and spherical shape, for comparison. The number of segments per one polymer chain is 40 for short chain systems and 160 for long chain systems, and there are 25600 segments in the system. Initial states were prepared by thermally equilibrating the polymer melts well above the melting points. Then the samples were suddenly cooled by velocity scaling. The ordering processes after temperature quench were observed under isothermal isobaric conditions.

In the case of flexible polymer chains, the polymer melts in the bulk often lead to amorphous disordered states without formation of crystal structure. However, under some appropriate confined conditions, crystal growth was observed. In the case of polymer systems with moderate chain length, the order formation processes show large development at the initial stage, while in the case of longer polymer systems, the time evolution processes slow down significantly. Typical crystallization behaviors are shown in Figure 1. Ordering dynamics during the crystallization largely depends on the chain rigidity. In the case of rigid chain systems, the difference in order formation dynamics between bulk systems and confined systems become smaller, which can be explained by the frequency of nucleation. Even though there is no crystalline surface layer that attracts polymer chain in the melts, the restriction of the molecular motion of chain direction around boundary region induces the nucleation.

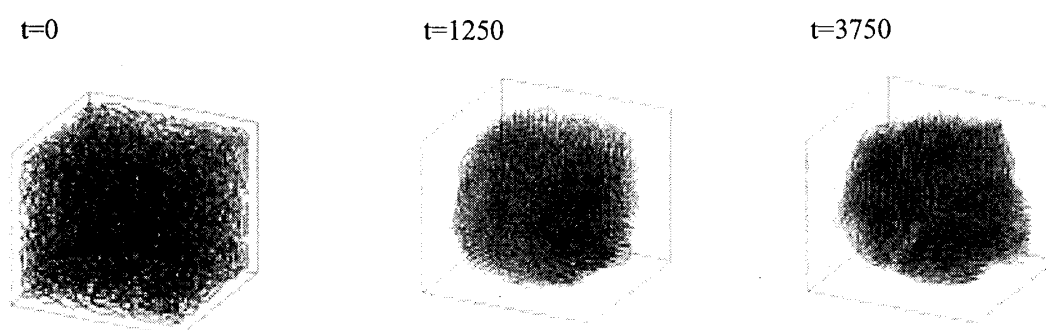


Figure 1. Crystallization processes under confinement.

## References

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