論文 / 著書情報
Article / Book Information

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Title(English)	Crystallization of Homopolymers and Block Chains Confined in Nanodomains
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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	有機・高分子物質　　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　　（工学）
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要旨（英文800語程度）
Thesis Summary（approx.800 English Words ）

Multi-component polymeric materials such as polymer solutions and blends have been an attractive research subject because the property of constituent polymer chains can be tuned or enhanced by the nanometer-scale morphology of the materials. On the other hand, polymer crystallization also affects various properties of the material. It is thus necessary to understand and control the crystallization of polymer chains confined in nanometer-scale spaces (nanodomains) in order to design multi-component polymeric materials containing crystallizable components. Block copolymers are extensively utilized to study polymer crystallization within nanodomains, owing to their ability to microphase-separate into well-ordered nanodomain structures. However, crystallization of block chains confined in nanodomains should be affected not only by the spatial restriction (space confinement) but also by chain-ends tethered at nanodomain interfaces (chain confinement). Recent studies have successfully demonstrated that the effects of chain confinement on crystallization can be evaluated using photocleavable crystalline-amorphous block copolymers. However, the interplay of chain confinement and space confinement is still unclear. In this study, the author investigates the crystallization behavior of crystallizable poly(ε-caprolactone) (PCL) homopolymers and block chains confined in identical nanodomains with various sizes and shapes to comprehensively understand the roles of chain confinement and space confinement in nucleation, growth, and thickening of polymer crystals.

This doctoral thesis comprises 7 chapters.

Chapter 1 describes the general background and aim of this study, which are already summarized above.

In Chapter 2, the crystallization behavior of PCL homopolymers and PCL block chains confined in nanocylinders with varying diameter D is investigated to clarify the effects of chain confinement and space confinement on the nucleation and growth mode of PCL crystals. The crystallization kinetics of PCL chains in nanocylinders is controlled by homogeneous nucleation. Chain confinement hinders the crystal nucleation at 13.0 nm $\leq D \leq$ 14.9 nm, whereas it decelerates the nucleation at D = 17.9 nm, clearly indicating that the effects of chain confinement on nucleation strongly depend on the extent of space confinement.

In Chapter 3, the author examines the crystal orientation of PCL homopolymers and PCL block chains confined in nanocylinders with different D to reveal the effects of space confinement and chain confinement on the crystal growth mode within nanocylinders. The crystal orientation depends significantly on D. In nanocylinders with small D (= 13.0 nm), the b axis of PCL crystals orients parallel to the long axis of nanocylinders for both PCL homopolymers and PCL

block chains, from which a one-dimensional crystal growth along the nanocylinder axis can be derived. However, at larger D (=17.9 nm), both the a and b axes of PCL crystals tilt against the nanocylinder axis, suggesting that the crystal growth along two directions is allowed in nanocylinders with D = 17.9 nm. Interestingly, chain confinement hardly affects the crystal orientation, indicating that the crystal growth mode in nanocylinders is controlled mainly by space confinement.

In Chapter 4, the crystallization behavior of PCL homopolymer/PCL block chain blends confined in nanocylinders is investigated as a function of D and the fraction of PCL homopolymers f_h to understand the coupled effects of space confinement and chain confinement on crystal nucleation. The f_h-dependence of the nucleation rate is discussed with the aid of classical theory of nucleation. In nanocylinders with D = 14.9 nm, the nucleation rate increases with increasing f_h, indicating that chain confinement hinders the molecular diffusion necessary for crystallizing PCL repeating units to cross the liquid-solid phase boundary. On the other hand, in nanocylinders with D = 17.2 nm, the increase of f_h decelerates the nucleation, suggesting that chain confinement reduces the energy barrier to form critical nuclei. It is concluded that the effects of chain confinement on nucleation in nanocylinders are strongly coupled with those of space confinement.

In Chapter 5, the author investigates the crystallization behavior of PCL homopolymers and PCL block chains confined in nanolamellae as a function of the nanolamella thickness d_{PCL} in which PCL chains are confined. The aim of this chapter is to reveal the roles of chain confinement on the nucleation and growth kinetics of polymer crystals. In nanolamellae with d_{PCL} = 8.7 nm, PCL homopolymers crystallize via the heterogeneous nucleation and growth mechanism, whereas the crystallization of PCL block chains is controlled by homogeneous nucleation. This result suggests that chain confinement significantly decelerates the crystal growth and eventually changes the nucleation mechanism. In larger nanolamellae with d_{PCL} = 15.8 nm, however, chain confinement merely decelerates the crystal growth without changing the nucleation mechanism, indicating that the effects of chain confinement are less significant in larger nanolamellae.

In Chapter 6, the crystallization behavior of PCL chains tethered at both ends, one end, and no end all confined in an identical nanolamella is investigated to comprehensively understand the effects of chain confinement on crystal growth kinetics. It is found that chain tethering at both ends or one end decelerates the crystal growth, and the effect of the former is much more significant than that of the latter.

Chapter 7 discusses the major findings of the preceding chapters on the viewpoint of the effects of space confinement and chain confinement on nucleation, growth, and thickening of polymer crystals.