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論文審査の要旨及び審査員

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論文審査の要旨（800 字程度）

This thesis entitled “Crystallization Mechanism and Chain Folding of Polyethylene Oxide as Investigated by Atomic Force Microscopy” is composed of eight chapters and written in English. This study investigated the chain-level structures and its transition under different conditions to study the crystallization mechanism at molecular level by atomic force microscopy (AFM) based single-molecule force spectroscopy (SMFS).

Chapter I “Introduction” introduces the information of PEO typical crystal structures, the classical chain folding models and crystallization mechanisms. However, recent experiment results challenged traditional theory, and other important models were proposed. We used advanced technique AFM-SMFS to investigate the transition of chain structure during crystallization and examine the crystallization conditions effect on crystal formation. This study provides a novel method for exploring chain-level structures during crystallization and crystallization mechanisms.

Chapter II “Background” describes the details of different crystallization mechanism and corresponding chain models. To discover the chain structure in nanoscale, it reports characterization techniques on the chain-folding structure, the data analysis and the technical limitations. The crystallization mechanism at molecular level is still in debate. So, AFM-SMFS in single chain is expected to be a new method to study the crystallization mechanism.

Chapter III “Basical Principal of AFM-SMFS” lists the fundamental knowledge of atomic force microscopy including the different experiment mode and its basic principle. It mainly exhibits the AFM-SMFS novel strategy to investigate the property and structure of single polymer chain in different materials. In this study, we used AFM-SMFS in crystalline polymers to investigate the chain-level structure and its transition.

Chapter IV “Experiments” describes the detail of samples used in this study and that of experimental instruments.

Chapter V “AFM-SMFS Study of the Crystallization Mechanism of PEO in Dilute Solution” reports AFM-SMFS study of the crystallization mechanism of PEO in dilute solutions and providing a new method to study the chain-level structure. The crystal structure at different length scales including morphology and single chain is systematically investigated as functions of kinetics and crystallization time. By analyzing the force-extension curve of single chain in crystal and combining the differential scanning calorimetry (DSC), we found that polymer chains will first fold to form clusters, then these clusters will continue attracting each other to form crystal by van der Waals force. In consequence, our result denies the one-step LH model and supports the two-step model that polymer chains fold initially to form clusters which aggregate subsequently to form crystals.

Chapter VI “Temperature Effect on the Solution-grown Crystal Structures Including Morphology, Chain-folding and Inter-chain structures” investigates the crystallization temperature effect on the solution-grown crystal structures including morphology, property, chain-folding and 3D inter-chain structures. The force-extension curves and morphology of crystals formed at different crystallization temperatures indicate that the chain folding structure in multiple layer crystal is different from its in single layer crystal. By examining the details of stretching force in force-extension curves and calculating the surface energy barrier, supercooling is found to have a main effect on the formation of final chain folding structure. The result indicates that polymer chains will firstly self-fold as many similar nanoclusters, which form the intermediate model at low crystallization temperature and form the adjacent re-entry model at high crystallization temperature.

Chapter VII “The Melting Behavior of Chain Folding Structure in PEO Solution-grown Crystal” focuses on the melting behavior of chain folding structures in PEO solution-grown crystal. The chain sliding in single crystal is simple and shows one peak in DSC melting curve. However, the melting behavior of multiple layer crystal is complex and shows two peaks in DSC melting curve. The corresponding morphology and force-extension as temperature increases show the melting behavior and its transition in molecular level. Polymer chains will slide to form thicker and more stable adjacent re-entry model in the early stage of melting representing the second peak in melting curve, which proves the recrystallization step during melting.

Chapter VIII “Summary” summarizes all results about chain folding behavior, 3D inter-chain structure and crystallization mechanism in polyethylene oxide (PEO) from this dissertation. The remaining questions about polymer crystallization in the future are also briefly introduced.

This study investigates the chain folding structure and crystallization mechanism under different conditions, which provides a new novel method for exploring chain-level structures, advancing the understanding of crystallization mechanisms in nanoscale and guiding the design of crystal-based materials over a broad range of properties. Therefore, this thesis is considered to be of sufficient value for the doctor’s degree of science.