Abstract

The functions of biomolecules have been significantly elucidated by single-molecule imaging and measurement techniques. Recently, it has been recognized that the structure of individual polymer chains strongly influences their physical properties, even in synthetic polymers, making single-molecule imaging an area of great interest. Conventional spectroscopic methods and microscopy could only provide static information, but the development of fast-scanning atomic force microscopy (FS-AFM) has allowed the simultaneous observation of function and structure. This advance has rapidly revealed polymer structures and dynamics that were previously inaccessible, establishing FS-AFM as a highly effective tool in the analysis of synthetic polymers. However, the number of studies using FS-AFM remains limited.

If molecular motors driven by thermal fluctuations that perform mechanical work could be realized, they could find applications in artificial muscles and molecular transport systems. In addition, because these systems are driven by thermal fluctuations, they have great potential as a powerful means to address energy-related challenges. In biological systems, molecular motor systems driven by thermal fluctuations, such as actomyosin and microtubule-kinesin, have been realized. In synthetic molecules, molecular machines such as rotaxanes and light-driven molecular rotors have been developed, but none has demonstrated practical functionality comparable to that of biomolecular motors.

This study aims to elucidate the dynamics of single synthetic polymer chains using FS-AFM and to develop synthetic polymer motors. In addition, to further understand the functions of synthetic polymers, force measurements of interaction between synthetic polymer chains were performed using an optical trapping system. Overviews of each chapter are as follows:

Chapter 1: This chapter explains the general background of the study and provides an overview of the apparatus.

Chapter 2: A chiral helical poly(phenylacetylene) with amide groups and bulky cholesteryl groups as pendant was synthesized, and FS-AFM imaging was performed. Although the structure was expected to form a rigid structure, dynamic analysis revealed that the molecule exhibited flexible micro-Brownian motion.

Chapter 3: Structural analysis of poly(pseudo-rotaxane) composed of high molecular weight poly(ethylene glycol) (PEG) and α-cyclodextrin (α-CD), which has been difficult to analyze in solution using conventional methods, was performed at the solid-liquid interface. Dynamic analysis revealed structural changes involving the shuttling of α-CD. Furthermore, these structural changes were simulated by MD calculations.

Chapter 4: A chiral helical poly(phenylacetylene) with cholesteryl groups as pendants was synthesized and FS-AFM imaging was performed. Observations revealed molecular motor functionality, with long-range translational motion driven by thermal fluctuations in an organic solvent at room temperature. This discovery suggests the potential for creating synthetic polymer molecular motors comparable to biomolecular motors.

Chapter 5: Two types of porphyrin-based supramolecular polymers with cholesteryl groups as pendants and coordinated with either Cu or Zn were synthesized, and microscopic imaging was performed. Both supramolecular polymers exhibited multiple types of higher-order structures, leading to the proposal of a stepwise growth process based on their structural features. Furthermore, FS-AFM imaging revealed intermolecular interactions between polymer chains, which are thought to be the origin of the molecular motor functionality.

Chapter 6: Molecular motor functionality induced by electrostatic interactions between the cationic polymer and the anionic polymer was observed using FS-AFM. In addition, the unidirectional motion of composite molecular chains formed by the interaction of these polymers was confirmed. Furthermore, an optical trapping system was used to demonstrate that these phenomena involve mechanical work.

Chapter 7: This chapter provides a general discussion of the overall study and explains how the newly discovered phenomena relate to societal issues and challenges in polymer field.

Keywords: Single-Molecule Imaging, Polymer Molecular Motor, Polymer Dynamics, Chiral Polymer, Supramolecular Polymer