博士（理学）　Md. Arifuzzaman

学位論文題名

Study on Superstructure Formation of a Semi-Rigid Macromolecule in a Polyelectrolyte Hydrogel by the Swelling Induced Mechanical Instability

（電解質ゲルの膨潤過程における力学不安定性による半剛直高分子の超構造形成に関する研究）

学位論文内容の要旨

Biological soft tissues possess sophisticated structure that enables them to exhibit outstanding performances over a wide range. Among all, intricate structural pattern found in the human brain, the intestine, and plant leaves, are believed to be formed via non-equilibrium, dynamic process during the growth, which are frozen by the physical/chemical interaction among the molecules. Elucidation of the mechanism of such structure formation induced by non-equilibrium chemistry in living bodies is an attractive research topic. Furthermore, introducing sophisticated structures into hydrogels, which are soft, wet materials similar to the biological tissues, by the non-equilibrium process is one of the ultimate challenges for the polymer scientists. Recently, it has been discovered for the first time that a piece of sheet-like polyelectrolyte gel containing an oppositely charged semi-rigid polymer exhibits a periodic birefringence pattern in millimetre range after full swelling in water. The hydrogel is synthesized from a cationic monomer, *N*-[3-(*N,N*-dimethylamino)propyl] acrylamide methyl chloride quaternary (DMAPAA-Q), in the presence of a small amount of the negatively charged poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) that has a semi-rigid nature. Although some plausible explanations for such a large and periodic structure formation could be derived, the exact structure formation mechanism remains a mystery. The purpose of this thesis is to reveal the detailed mechanism of this novel structure formation, and consequently to develop a novel strategy for introducing a long-range ordered structure in amorphous hydrogels through dynamic mechano-complexation coupling into a non-equilibrium process. This strategy can be applied to soft, wet systems in a variety of contexts, namely, for developing various ordered structures with macro-scale correlation by proper designing of the hydrogel-geometry.

This dissertation mainly consists of 5 chapters. **In Chapter 1**, the background and the purpose of this thesis are introduced. **In Chapter2,** a short review is presented about some specific properties of the semi-rigid polymer PBDT in aqueous solution and in hydrogels previously carried out in our laboratory.

In Chapter 3, the detailed mechanism of millimetre-scaled periodic structure formation in a sheet-like hydrogel is revealed. Such structure in the polyelectrolyte hydrogel is created by the fast-heterogeneous swelling process, and is frozen by the polyion complexation of the polyelectrolyte network with the oppositely charged, semi-rigid polymer. During swelling process, surface creasing occurs due to the large mismatching of swelling degree between the surface layer and the inner one of the poly DMAPAA-Q (PDMAPAA-Q) gel, which induces highly oriented semi-rigid PBDT molecules along the

tensile direction of the crease pattern. In accompany with the evolution of surface creasing, a lattice-like periodic birefringence pattern is formed, which is frozen permanently by the strong polyion complex formation, even after the surface instability pattern of the gel disappears completely throughout the dynamic coalescence. Rationally it is clarified that formation of such a long-range ordered non-equilibrium structure in the polyelectrolyte hydrogel requires the following three indispensable conditions: (i) swelling-induced surface creasing instability; (ii) polyion complex formation; and (iii) a semi-rigid or rigid dopant.

In Chapter 4, A simple and robust method is developed in order to to control the semi-rigid molecular orientation in the mesoscale structure formed in a polyelectrolyte hydrogel by the swelling induced strong mechanical instability. The molecular orientation of the semi-rigid polymer or, its fibrous bundles is successfully controlled by changing the shape and size of the synthesized gel prior to swelling. It has already been revealed that the stable regular/periodic birefringence pattern, representing the ordered orientation of semi-rigid molecules, is developed owing to the mismatching of internal stress from the surface layer to the immediate foundation layer of the gel built by the fast and heterogeneous swelling process. Based on the initial geometry and the dimensional aspect ratio of the gel, the induced internal stress field within the hydrogel built by swelling is tunable, leading to the various distribution of stress, from the edge to the inside. Therefore, different rod-like molecular orientation is obtained due to the various distributions of internal stress inside the gel.

In Chapter 5, A regular long-range molecular orientation of PBDT like folded structure is successfully created in a disk shape polyelectrolyte hydrogel by the formation of circumferential creasing instability during restricted-heterogeneous swelling process. Such regular mesoscale molecular orientation is induced by the simultaneously occurring circumferential compression as well as radial tension resulted from the creasing instability due to the mismatching of swelling degree among the hydrogel layers from the periphery to the inside. From the investigations throughout this work it might be anticipated that rod-like molecular orientation can be tuned successfully by changing the method/condition of swelling as well as the geometry of the hydrogel.

Eventually, this research indicates for the first time a successful and robust method for the development of highly periodic structure in hydrogel by the non-equilibrium chemistry which couples ion-complexation and non-linear instability mechanics. We believe this sort of non-equilibrium structure formation mechanism may help understand how biomacromolecules that are rigid polyelectrolytes, such as deoxyribonucleic acid (DNA), microtubules (MT), and actin filaments (F-actin), form rich architectures during the growth of biological organs. The presented results might motivate more versatile directions of research to elucidate more complex structural phenomena in hydrogels near future.

学位論文審査の要旨

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Intricate structural pattern found in the biological soft tissues such as human brain, intestine, and plant leaves, are believed to be formed via non-equilibrium, dynamic process during the growth, which are frozen by the physical/chemical interaction among the molecules. Elucidation of the mechanism of such structure formation induced by the non-equilibrium chemistry in living bodies is an attractive research topic. Furthermore, introducing sophisticated structures into hydrogels, which are similar to the biological tissues, by the non-equilibrium process is one of the ultimate challenges for the polymer scientists. Recently, it has been discovered for the first time that a piece of sheet-like polyelectrolyte gel containing an oppositely charged semi-rigid polymer exhibits a periodic birefringence pattern in millimeter range after full swelling in water.

In this dissertation, the detailed mechanism of such novel macroscopic structure formation was clearly revealed. That is, such long-range structure in the hydrogel is created by the fast-heterogeneous swelling process, and is frozen by the polyion complexation of the covalently cross-linked network with the oppositely charged, semi-rigid polymer. Based on this mechanism, a successful and robust method was consequently developed for introducing a long-range ordered structure in amorphous hydrogels by the non-equilibrium chemistry which couples ion-complexation and non-linear instability mechanics. This method can be applied to soft, wet systems in a variety of contexts, namely, for developing various ordered structures with macro-scale correlation by proper designing of the hydrogel-geometry. This sort of non-equilibrium structure formation mechanism may help understand how rigid biomacromolecules, such as deoxyribonucleic acid (DNA), microtubules (MT), and actin filaments (F-actin), form rich architectures during the growth of biological organs.

Therefore, we acknowledge that the author is qualified to be granted the degree Doctor of Science (D. Sc.) from Hokkaido University.