博 士(理 学) 呉 子 良

学 位 論 文 題 名

Hydrogels with Multiscale Ordered Structures Based on Semi-Rigid Polyion Complex Formation

(半剛直高分子イオンコンプレックス形成による
マルチスケール構造規則ゲルの創製)

学位論文内容の要旨

Most bio-tissues are in a soft gel-like state and have multiscale well-ordered structures that give robust functions of living organisms. In these tissues, water-soluble rigid or semi-rigid macromolecules are ubiquitous and should play a crucial role in the structure formation. The biomacromolecules are usually with negative charges and rigid or semi-rigid structure, endowing them with great abilities to form advanced architectures by themselves or with multivalent cations, polycations, and cationic lipids via electrostatic interaction. However, the natural rigid-rod polyelectrolytes are formed by the secondary structure and are difficult to extracte without denaturation. Thus, it is of great meaning to study the self-assembly behaviors of synthetic semi-rigid polyanion in aqueous solutions and polymeric hydrogels. Through this research, we hope to find and control the hidden mechanisms that determine the well-ordered structures of semi-rigid macromolecules in living organisms.

Our laboratory has done a serial study on the synthetic semi-rigid polyanion, poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT), including the self-assembly behaviors of PBDT in aqueous solutions and the anisotropic PBDT-containing hydrogels. Its aqueous solutions show a significantly low critical concentration of nematic liquid crystal. With addition of simple salt, PBDT shows a variety of the self-assembled structures, ranging from semi-rigid single chain to isotropic cluster association in the aqueous solutions. Anisotropic, transparent polymeric hydrogels have been successfully developed by polymerization of cationic monomer N-[3-(*N,N*-dimethylamino)propyl]acrylamide methyl chloride quaternary (DMAPAA-Q) in the presence of a small amount of anionic PBDT as dopant.

In this work, we study further the PBDT and its polyion complex assemblies in aqueous solutions and hydrogels. The dissertation covers 6 chapters; chapter 1 is the general introduction, chapters 2~5 are the main text, and chapter 6 is the conclusions. The results are as follows:

In chapter 2, polymorphosim evolutions have been observed by diffusing poly(DMAPAA-Q) into a PBDT drop, where complexation, orientation, and phase separation compete with each other. We

found that the orientation process is predominated by the diffusion process. The smaller Mw of polycation, the faster diffusion velocity. Phase separation is depended on the electrostatic interaction between PBDT and polycation. If the PBDT concentration C_P is relatively low, phase separation has shallow quench depth, corresponding to a nucleation-growth phase separation process. On the other hand, high C_P induces deep quench and the occurrence of viscoelastic phase separation (VPS), where transient network-like structure and huge Maltese appear.

In chapter 3, hydrogels with dual networks, a micrometer-scale network of semi-rigid polyion complex nested in a nanometer-scale polycationic network, have been developed by polymerization of a cationic monomer with a relatively lower concentration C_Q in the presence of a small amount of semi-rigid PBDT as dopant. It shows that C_Q (ionic strength of reaction solution) and C_P determine the occurrence of phase separation and self-assembly, respectively. The precursor solution is optically isotropic. When polymerization is triggered, the polycations interact with anionic PBDT to form polyion complexes. The polyion complexes self-assemble to form small anisotropic aggregates with high viscosity. Meanwhile, phase separation occurs, because the polyion complexes are unstable in the solution with relatively low ionic strength. The phase separation rapidly develops into VPS, forming a typically network-like structure, which is permanently frozen by the following chemical cross-linking reaction.

In chapter 4, a hydrogel with cylindrically symmetric structure at macroscopic scale has been developed by polymerization of a cationic monomer DMAPAA-Q in the presence of a small amount of semi-rigid polyanion PBDT in a cylinder glass tube. The polyion complex radially aligns in the outer region of the synthesized cylinder gel. On the other hand, it orients in concentric and axial directions in the inner region. We elucidate that homeotropic alignment on the glass wall is energetically favorable for the semi-rigid polyion complex, resulting in the radial orientation in the outer region. In the inner region, the oriented structures result from the monomer difffusion (due to the heterogeneous polymerization) that induces PBDT orientation perpendicular to the diffusion direction. The structured gels showing sensitive response of birefringence to external force are expected to find applications in optical sensors.

In chapter 5, millimeter-scaled complex structure is found in the PBDT-containing plate hydrogel gelled from an isotropic precursor solution. PBDT or its polyion complex orients perpendicular to the gel surface in the outer regions, whereas PBDT forms arranged concentric LC cylinders in the middle region. Although the reaction mainly completes, monomer diffusion from the inner region to the outer exist, rendering the middle layer with a large swelling ratio and small mass ratio of polycation to PBDT. We speculate that the different PBDT alignments result from the heterogeneous polymerization by affecting the reaction velocity and monomer diffusion velocity. In the middle region, the reaction velocity and monomer diffusion velocity are relatively slow, thus, PBDT or its polyion complex has sufficient time to form a stable and ordered structure, concentric LC cylinders.

In this dissertation, several kinds of hydrogels with well-ordered structures of semi-rigid PBDT

are developed by self-assembly and phase separation. We believe that the research will open new avenues to design structured hydrogels and elucidate the hidden formation mechanisms of well-ordered structures in living organisms.

学位論文審査の要旨

主　査　教　授　龔　　剣　萍
副　査　教　授　佐々木　直　樹
副　査　教　授　玉　置　信　之
副　査　准教授　古　川　英　光（山形大学大学院
理工学研究科）

学位論文題名

Hydrogels with Multiscale Ordered Structures Based on Semi-Rigid Polyion Complex Formation

（半剛直高分子イオンコンプレックス形成による マルチスケール構造規則ゲルの創製）

様々な生体組織はソフトかつウェットなゲル状態で、マルチスケール規則構造によって豊富な機能を持っている。近年、生体組織の機能を模倣した構造規則ゲルを創製する研究が盛んに行われている。その多くはナノスケールな規則構造をゲルに導入することを目的としている。メゾスケールを含めたマルチスケールな規則構造を有するハイドロゲルの創製は未開拓の分野である。

本論文は、半剛直高分子イオンコンプレックス形成によるマルチスケール構造規則ハイドロゲルの創製に関する研究である。著者は、負電荷を持つ半剛直な合成高分子電解質である PBDT の水溶液中に、正電荷を持つビニルモノマーDMAPAA-Q を UV でラジカル重合し、イオンコンプレックスの自己組織化と相分離による構造規則性ゲルの創製を試みた。その結果、以下のことが明らかとなった。1）高分子イオンコンプレックスの粘弾性相分離によってマイクロスケールの網状構造がナノスケールのゲル中に形成されることを発見した。この粘弾性相分離は反応溶液のイオン強度に依存する。高分子イオンコンプレックスは高いイオン強度の溶液中では安定し、粘弾性相分離が抑制される。2）半剛直高分子イオンコンプレックスがモノマーの拡散と垂直する方向に配向することを発見した。この分子の拡散と高分子鎖の配向のカップリングを利用し、マクロスケールの円状または板状対称を持つ規則構造ゲルの創製に成功した。円柱状セル中で重合したゲルが円状対称規則構造を示し、半剛直高分子イオンコンプレックスは外側に放射状に真中に同心円と軸の方向に配向している。このマルチスケールの規則構造を持つゲルは光センサーなどマテリアルサイエンスへの応用が期待される。

これを要するに、著者は、マルチスケール構造規則ハイドロゲルについての創製と形成メカニズムの新知見を得た。本研究は生体組織メゾスケール規則構造の形成メカニズムに対し貢献するものである。

よって著者は、北海道大学博士（理学）の学位を授与される資格あるものと認める。