学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on Synthesis and Properties of Thermo-Responsive Lamellar Hydrogels
熱応答性層状ハイドロゲルの合成と特性に関する研究

Nowadays, the drastic development of thermo-responsive polymers-based smart materials has been aroused due to their unique functionalities. The most well-known and extensively researched thermo-responsive polymers are poly(N-isopropylacrylamide) (PNIPAM) and its derivatives, which are lower critical solution temperature (LCST)-type. PNIPAM is generally characterized by the amide group and isopropyl moieties in the monomer structure, which possesses a LCST around 33 ℃ in aqueous media. PNIPAM-based smart materials, for example PNIPAM-based hydrogels, exhibit the distinct transparent/turbid transition and the extent of the swelling/shrinking behavior upon heating and cooling process, as it undergoes a reversibly alterable volume or phase separation behavior near LCST. Nowadays, extensive research interest in PNIPAM-based smart hydrogels has been aroused owing to their fascinating properties and functions. Importantly, the unprecedented properties of PNIPAM-based smart hydrogels permit various promising applications and functions, such as optical applications in smart windows, smart display, and biomedical applications in drug delivery.

Photonic hydrogels hold great promise as materials for smart display and optical sensors due to their fascinating structural colors and anisotropy, which possesses stimuli-responsibility that can be reversibly adjusted by periodic spacing through external stimuli such as variations in stress, temperature (*Temp*), pH, and solvent conditions or by varying the refractive index of the material. Therefore, photonic hydrogels can be promising materials for displays and sensors through utilizing stimuli-responsive structural colors rather than requiring colored filters or additional optical elements. Various attempts have been made to incorporate stimuli-responsive polymers or materials into such internal anisotropic or photonic hydrogels or be fabricated into periodic structures to bridge the gap between unique anisotropic hydrogels and conventional stimuli-responsive isotropic hydrogels, which have found numerous applications for the development of smart sensors. Therefore, in contrast with conventional PNIPAM-based hydrogels, the thermo-responsive PNIPAM-based hydrogels with ordered structure possess thermo-responsive properties but also anisotropy.

Recently, Gong's group has developed an anisotropic photonic hydrogel with lamellar structure by entrapping self-assembled bilayers inside a soft polyacrylamide (PAAm) layer. The rigid, water-impermeable bilayers, poly(dodecyl glyceryl itaconate) (PDGI), self-assembled into a periodic structure inside the PAAm layers by applying shear flow to diffract light and also serve as reversible sacrificial bonds to toughen the gel. The resulting PDGI/PAAm hydrogel with lamellar structure, not only possesses excellent structure color and color tunability by polymerization with another component to the gels, but also exhibits distinct one-dimensional swelling along the thickness direction owing to the presence of macroscopic bilayers.

As mentioned above, this research goal is to introduce thermo-responsive PNIPAM polymers into photonic PDGI/PAAm lamellar gels, so we can facilely not only tune the turbidity driven by phase separation behavior but also control the properties of PDGI/PAAm gels, such as tunable structural color and anisotropic swelling by temperature stimuli around LCST. Furthermore, to investigate the effect of incorporated PNIPAM concentration on the properties of the hydrogel, including anisotropic swelling, structural color tunability, and reversibility.

In **Chapter 1**, general introduction and outline of the dissertation are discussed.

In **Chapter 2**, the research background of this research topic (Reversible tuning of turbidity, structural color, and anisotropic swelling in thermo-responsive lamellar hydrogel) is summarized.

In **Chapter 3**, the strategy towards introducing thermo-responsive PNIPAM polymers into photonic PDGI/PAAm lamellar gels is introduced in detail and the synthetic procedure of PDIG/PAAm-PNIPAM hydrogel is included. The PDGI/PAAm-PNIPAM gels were synthesized by incorporating second networks (PNIPAM) into PAAm soft layers of PDGI/PAAm lamellar gels. The thermo-induced phase separation behavior of PDGI/PAAm-PNIPAM gel is introduced. Importantly, the PDGI/PAAm-PNIPAM hydrogel shows tunable turbidity and structural color by controlling incorporated PNIPAM concentration. The effect of

heating temperature and heating time on the transmittance of the PDGI/PAAm-PNIPAM$_{0.5M}$ gel is also been described in detail. The turbidity of the gel increases with increasing heating temperature above LCST. And the PDGI/PAAm-PNIPAM hydrogels undergo phase separation due to entropy-driven dehydration and collapse upon heating when heating temperature is above the LCST. The transmittance of the gel barely changed with increasing heating time at *Temp* > LCST, which is in associated with LCST-type gels where the turbidity is determined by the heating temperature after reaching equilibrium independent of the heating time.

In **Chapter 4**, the anisotropic lamellar structure of the thermo-responsive lamellar PDGI/PAAm-PNIPAM gel is investigated. After incorporation of thermo-responsive PNIPAM polymers, the photonic PDGI/PAAm hydrogel possesses the thermo-responsibility of PNIPAM around LCST. The deswelling/reswelling behaviors of PDGI/PAAm-PNIPAM gel during heating and cooling processes around LCST is also investigated. The thermo-responsive lamellar hydrogels show structural color/turbid transition during heating and cooling processes. The long-term thermo-responsive behaviors of the PDGI/PAAm-PNIPAM gels is introduced. The gels show long-term structural color tunability and anisotropic deswelling/reswelling behaviors. The turbidity and deswelling/reswelling ratios of the photonic PDGI/PAAm-PNIPAM gels can be tuned by temperature stimuli, leading the structure color/turbid transition of the gel around LCST.

In **Chapter 5**, the effect of PNIPAM concentration on PDGI/PAAm-PNIPAM gel during heating and cooling process around LCST is introduced in detail, including on turbidity, structural color, interplanar distance, anisotropic swelling, and reversibility. The structural color of PDGI/PAAm-PNIPAM gel can be tuned by controlling NIPAM concentration. Effect of the incorporated PNIPAM concentration on the ultrafast turbidity transition was investigated. High NIPAM concentration hydrogels show low turbidity. High NIPAM concentration gel shows larger shift in color during heating and cooling process. The concentration of incorporated PNIPAM networks significantly influences the extent of deswelling and reswelling. The higher the NIPAM concentration, the greater the extent of the decrease in peak wavelength, λ_{max} and interplanar distance, *d*. This indicates that the NIPAM concentration plays a rule in the variations of λ_{max} and *d* which is in accord with the color shift of the gel. The extent of deswelling/reswelling along diameter direction increases with the NIPAM concentration. On the other hand, swelling anisotropy became less obvious with increasing NIPAM concentration. The gels recovered to the original state upon cooling process, indicating fully reversible color shift independent of the NIPAM concentration.

In **Chapter 6**, the synthesis procedure of pattern PDGI/PAAm-PNIPAM in PDGI/PAAm hydrogel is described in detail. The preparation of PDGI/PAAm-PNIPAM star in PDGI/PAAm gel were introduced. We regioselectively introduced the PNIPAM networks into the PDGI/PAAm lamellar hydrogels by the photomasking during UV polymerization. The structure color/turbid transition of the PDGI/PAAm-PNIPAM gel pattern in PDGI/PAAm gel during heating and cooling process around LCST is investigated. The applications of the pattern gel are also introduced. The star region immediately turns turbid owing to the thermo-induced phase separation of PNIPAM. Like the normal PDGI/PAAm-PNIPAM hydrogels, the star region in the gel exhibited long-term shrinkage with blue-shift in gel color upon heating and recovery of the structural color upon cooling. This immediate structural color/turbid transition and long-term structural color shift of patterned gel can be used as smart stained glass or smart display.

In **Chapter 7**, conclusions of the whole dissertation are summarized.