Doctoral Dissertation Evaluation Review

Degree requested Doctor of Life Science Applicant's name Chengtao Yu

Examiner :

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Title of Doctoral Dissertation

Water Diffusion-Governed Thermal History of Self-Healing Hydrogels and Their Applications for Dynamic Materials
（水拡散によって支配される自己修復ハイドロゲルの熱履歴現象とその動的材料への応用）

Results of Evaluation of the Doctoral Dissertation (Report)

Smart materials are the materials that can respond to the change of external stimuli. Thermal responsive hydrogels are a type of smart materials exhibiting thermal sensitive phase transition, which have applications in many fields, such as *in vivo* drug release, intelligent display, and functional materials with switchable hydrophilic/hydrophobic surface. The existing thermal responsive hydrogels, no matter with upper critical solution temperature (UCST) or lower critical solution temperature (LCST), usually show obvious changes in transparency, volume and mechanical performance at the critical temperature, which is independent on the experienced thermal history. However, in both LCST and UCST gels, the phase transition only occurs at the critical temperature, limiting their applications to a specific temperature. Moreover, the dramatic changes in size and mechanical performance of the existing thermal responsive hydrogels around the critical temperature also hinder their applications.

This dissertation reported a new thermal responsive behavior of self-healing hydrogels containing abundant physical bonds (PB gels). The PB gels show marked transparency change upon cooling at arbitrary temperature, with negligible changes in size and mechanical performance, which is distinctly different from the temperature-induced polymer solubility change in conventional thermal responsive hydrogels. Moreover, this thermal responsive behavior is thermal history dependent, and it is fast and sensitive to temperature change.

Polyampholyte (PA) gels containing abundant ionic bonds are typical PB gels and they have good self-healing and toughness. The author chooses PA gels as a model system for studying thermal responsive behaviors of PB gels. At first, the author demonstrates that the transparency change in PA gels is thermal history dependent. The cooling rate, heating temperature, and cooling temperature all influence the transparency of the gels after cooling. The transparent-to-opaque transition of the gels is fast and does not have a specific critical temperature, unlike the UCST and LCST gels. The gel with turbid appearance, induced by the formation of frustrated structure, is unstable and in nonequilibrium state, and opaque-to-transparent transition spontaneously occurs from the surface to the center of the gel, controlled by water diffusion. Interestingly, even though the frustrated structure endows the opaque appearance to the gels, it makes no obvious influences on the mechanical performance. This is because the frustrated structure is formed by temporarily aggregating of free water that has no interactions with polymer networks, and the bicontinuous structure in PA gels has no obvious change.

Then, the author investigated the asymmetry of swelling kinetics during heating and shrinking kinetics

during recovery of PA gels at cooling. The cooperative diffusion coefficient for swelling is nearly 2 orders larger than that for shrinking. This strong asymmetric swelling/deswelling kinetics is attribute to the formation of large-scale frustrated structure, not due to the formation of skin layer or more bound water. When the heterogeneity of this frustrated structure decreases, the asymmetry of swelling/shrinking kinetics becomes weak. Moreover, this asymmetry decreases with decreasing ionic bond strength of PA gels, and *vice versa*.

At last, the author uses this new thermal responsive behavior of PA gels to achieve the memorizing-forgetting behavior based on the asymmetric swelling/shrinking kinetics and the thermal history dependent transparency change of these gels. Furtherly, other applications of this thermal responsive behavior of PA gels, such as controllable drug release, 2D thermal imagery, and security paper for recording temporary information, are also discussed.

In conclusion, the author reported a novel thermal responsive behavior of PB gels, demonstrated the mechanism behind this unique behavior, and discussed the applications of this behavior. This work can actively inspire further research on expanding the design of novel thermal responsive smart materials.

Therefore, we acknowledge that the author is qualified to be granted a Doctorate of Life Science from Hokkaido University.