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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)

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 around the critical temperature also hinder their applications.

In this dissertation, we reported that self-healing hydrogels containing abundant physical bonds (PB gels), such as ionic bonds and hydrogen bonds, show 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, as thermal responsive behavior originates from the structure frustration upon cooling. The frustrated structure is formed by temporarily free water aggregating. As the free water gradually diffuses out of the gel, the frustrated structure spontaneously decays with the transparency change. Furtherly, we demonstrated that such new thermal responsive behavior has applications as dynamic materials in designing dynamic memory with forgetting ability, drug release, thermal imagery, and security paper.

In Chapter 1, the characteristics and applications of conventional thermal responsive hydrogels and polyampholyte (PA) hydrogels have been introduced.

In Chapter 2, the self-healing hydrogels, such as PA hydrogels and hydrogen bonding hydrogels, used in this dissertation are constructed, and PA hydrogels are employed as the model systems to study.

In Chapter 3, we demonstrated 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 spontaneously occurs opaque-to-transparent transition 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.

In Chapter 4, the asymmetry of swelling kinetics during heating and shrinking kinetics during recovery in PA gels was investigated. The cooperative diffusion coefficient for swelling is nearly 2 orders larger than that for shrinking. The formation of this obvious asymmetry is attribute to the formation of large-scale frustrated structure, not the formation of skin layer or more bound water. When the heterogeneity of this frustrated structure decreases, the asymmetry of swelling/shrinking kinetics turns to worse. Moreover, this asymmetry decreases with decreasing ionic bond strength in PA gels, and *vice versa*. These results indicate the asymmetry is controllable by tuning the component of the gels or the strength of dynamic bonds.

In Chapter 5, we use PA gels to achieve the memorizing-forgetting behavior based on the fast swelling kinetics and slow shrinking kinetics upon thermal stimulus, as well as the thermal history dependent

transparency change of these gels. More importantly, the recovery time of transparency and size is highly coupled. The PA gels can memorize two-dimensional (2D) information by thermal learning. Subsequently, the memorized information spontaneously decays, and the forgetting time is proportional to the thermal learning time, in analogy to the behavior of brain. The memory is stable against temperature fluctuation and large stretching; moreover, the forgetting process is programmable.

In Chapter 6, we further expand the applications of this thermal history dependent responsive behavior in PA gels, such as in controllable drug release, 2D thermal imagery, and security paper for recording temporary information. The applications of using the PB gels revealed here can inspire more research on this unusual thermal responsive behavior.

In Chapter 7, conclusion of the complete dissertation is summarized.