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Author(s)	Ihsan, Abu Bin
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Title of Doctoral Dissertation

A Novel Polyampholyte Hydrogel Based on Dynamic and Reversible Sacrificial Bonds: Toughness and Self-healing

(動的・可逆な犠牲結合を用いた新規両性イオン性ハイドロゲル：その高い靱性と自己修復特性)

Polyampholytes are polyelectrolytes carrying randomly distributed opposite charges. A neutral polyampholyte of equal amounts of opposite charges, due to intra-chain ionic bond formation, forms a globule structure and precipitates in dilute aqueous solution of low ionic strength. Chemically cross-linked polyampholyte hydrogels deswell near the equal charge composition. Recently, polyampholytes have been discovered to form tough physical hydrogels by employing the ionic bond as a reversible sacrificial bond that breaks and reforms dynamically. Owing to the random distribution, the opposite charges on the polyampholytes form multiple ionic bonds of wide distribution in strength. The strong bonds work as permanent cross-linkers, imparting the elasticity of the hydrogel. The weak bonds are fragile and they break under stress to dissipate energy, serving as reversible sacrificial bonds.

In this study, I attempt to design polymer hydrogels of multiple high mechanical performances, including a proper modulus, high strength and toughness, high fatigue resistance, and self-healing, based on dynamic reversible sacrificial bond. In chapter 2, a novel tough and self-healing supramolecular hydrogel based on strong bond/weak bond concept has been developed by random copolymerization of two oppositely charged monomers, sodium *p*-styrenesulfonate (NaSS) and acryloyloxethyltrimethylammonium chloride (DMAEA-Q). I systematically investigate the detail behavior of this polyampholyte system, viz., poly(NaSS-co-DMAEA-Q) without and with a slight chemical cross-linking. A phase diagram of formulation has been constructed in the space of monomer concentration C_m and cross-linker density C_{MBAA} . Three phases are observed for the as-synthesized samples: homogeneous solution at dilute C_m , phase separation at semi-dilute C_m , and homogenous gel at concentrated C_m . Above a critical $C_{m,c}$, the polyampholyte forms supramolecular hydrogel with high toughness by dialysis of the mobile counter-ions, which substantially stabilizes both the intra- and inter chain ionic bonds. Presence of chemical cross-linker ($C_{MBAA} > 0$) brings about a shift of the tough gel phase to lower $C_{m,c}$. The tough polyampholyte gel, containing ~ 50 wt% water, is highly stretchable and tough; exhibits fracture stress of $\sigma_b \sim 0.4$ MPa, fracture strain of $\varepsilon_b \sim 30$, and the work of extension at fracture ~ 4 MJ/m³. These values are in the level of toughest soft materials. It has been also revealed that owing to the reversible ionic bonds, the poly(NaSS-co-DMAEA-Q) gels exhibit complete self-recovery (100%) and high fatigue resistance upon repeated large deformation.

In chapter 3, I demonstrate that polyampholyte hydrogels of proper softness, along with the high toughness, possess excellent self-healing property. The self-healing is based on their forming of the ionic bonds at the fractured surfaces, in which the mobility and strength of the ionic bonds play important role. A simple power law was observed between the healing efficiency η_w and the elastic modulus E , $\eta_w \sim E^{-1.0}$, regardless the change in the healing temperature, chemical cross-linker density, and chemical structure of the polyampholyte hydrogels. These polyampholyte hydrogels exhibit excellent healing efficiency (~ 84% on average and maximum 99%) at room temperature without any external stimuli. This work may give insight to design supramolecular hydrogels with high toughness and healing efficiency.

In chapter 4, I revealed that polyampholyte gel shows strong velocity dependence on energy dissipation which is due to the internal fracture of fragile ionic bonds. At a high deformation speed, the reversible sacrificial ionic bonds in the molecular level cannot rearrange and thereby exhibits viscoelastic behavior. The hysteresis of the polyampholyte gels due to internal fracture of fragile ionic bonds was quantitatively analyzed. The polyampholyte gel also exhibits extraordinary crack blunting by suppressing the stress concentration at the crack tip. In addition, it was confirmed that the novel polyampholyte hydrogel shows excellent antifouling property and non-toxicity.

These results demonstrate that, the novel polyampholyte hydrogel have a great potential as a novel tough and self-healing material.