Summary of Doctoral Thesis

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Title of Doctoral Thesis

**Synthesis of Novel Hydrogels from Linear Polyampholytes and Analysis of Their High Toughness and Viscoelasticity**

(線形両性電解質高分子による新規ハイドロゲルの合成とその高靭性と粘弾性機能の解析)

Hydrogel is a class of polymer network swollen with a large amount of water. Common hydrogels are weak, fragile and irreversible due to their highly swollen structure, which fairly limited their application. Recently, many researchers have reported the success in synthesizing hydrogels with good mechanical performance, such as a 'topological (TP) gel', a 'nanocomposite (NC) gel', and a 'double network (DN) gel'. These works have largely changed the traditional views on hydrogels and thus substantially broadened the potential applications of hydrogels in various kinds of fields. However, any given applications as load-bearing materials require a combination of mechanical properties including the stiffness, strength, fatigue resistance, damping, self-healing, high toughness, along with biocompatibility, which are rarely realized. In this study, a novel class of tough and viscoelastic hydrogels from linear polyampholytes that can be tuned to change multiple mechanical properties over wide ranges have been presented. These physical polyampholyte hydrogels are synthesized by random copolymerization of oppositely charged ionic monomers around the charge balance point at high concentration. The randomness of charges forms multiple ionic bonds with a wide distribution of strengths, via inter and intra chain complexation. The ionic bonds play two roles for the mechanical properties of the hydrogels: as strong bonds and weak bonds, different from other hydrogels in which they are used as weak bonds. The strong bonds serve as permanent crosslinks to maintain the shape of the gel, while the weak bonds perform several mechanical functions simultaneously: enhance the fracture resistance by bond rupture and therefore toughen the materials, enhance the shock absorb by generating high internal friction, enhance the fatigue resistance and self-healing by bond reformation. Accordingly, the physical polyampholyte hydrogels become tough in analogy to double-network hydrogels though they have different topological structure: the strong bonds form primary network and the weak bonds form sacrificial network. As all the ion groups form ion bonds, the polyampholyte gels have a supramolecular structure, and contain 50-70 wt% of water at an equilibrium state, which is much less than that of conventional hydrogels that usually have high water content (> 80 wt%). They are strongly viscoelastic and have a high toughness (fracture energy of 4000 $J/m^2$), 100% self-recovery, and high fatigue resistance. Some gels showed partial self-healing after cutting and solvent-induced shape memory effect. Young's modulus and damping ability can be tuned over a wide range by choosing the proper ion combination. In addition, they are non-toxic and anti-fouling to cell adhesion. Many studies on the properties of polyampholytes, both the solution and the chemically crosslinked hydrogels, have been reported. This is the first report on the possibility of polyampholytes as structural biomaterials. This polyampholyte approach has large advantages for practical applications of hydrogels: it is general and directly applicable to a variety of ionic monomer combinations with specific functions; it largely increases the choices of tough hydrogels with desirable combinations of mechanical properties; the one-step polymerization process is easy to scale-up for mass production. As the materials have the wide spectrum of excellent mechanical properties even in physiological solutions, they have high potential as structural biomaterials, for example, as artificial cartilages with high fatigue resistance, and shock-absorbing mouth guard for sports players. In addition, they are non-toxic and anti-fouling to cell adhesion, suggesting the potential use in hygiene and medical fields, for example, as contamination-free surgical gloves, blood bags, syringes, contraceptives, and implantable devices.