学 位 論 文 内 容 の 要 旨
Abstract of Doctoral Dissertation

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Development of Tough Hydrogels Based on Amphiphilic Tri-block Copolymers
（両親媒性トリブロックコポリマーを用いた強靭ハイドロゲルの開発）

Hydrogels consisting of polymer networks and water resemble biological tissues. Thus, hydrogels have drawn great attention in application as synthetic equivalents for use in biological systems. However, the applications of conventional hydrogels are limited by their mechanical weakness. The recently developed double network hydrogels (DN gel) show high toughness and the ability to generate polymer gels with a high Young's modulus (10^5-10^6 Pa) while being capable of large deformations. As the high toughness of DN gels comes from the fracture of covalent bonds, DN gels show permanent internal damage that should lead to poor fatigue resistance. Applying the toughening mechanism of DN gels, partly or completely recoverable tough hydrogels were successfully synthesized by using ionic bonds as recoverable sacrificial bonds. However, ionic bond was found unstable in saline condition, which limited some of its application in both physiological and engineering conditions. Applying physical bonds of hydrophobic association and hydrogen bonds is one possible way to remedy the limitation of ionic cross-linked tough gel. In most of the previous studies, without ionic bonds, the fracture tensile stresses of tough recoverable hydrogels applying hydrophobic association or hydrogen bonds barely exceeded MPa. Comparing with DN gel or tough soft tissues such as cartilage, these gels have inferior mechanical strength.

In this study, the amphiphilic tri-block copolymers, consisting of the hydrophobic end blocks of poly(butyl methacrylate) (PBMA) and hydrophilic mid-block of poly(methacrylic acid) (PMAA), PBMA-b-PMAA-b-PBMA, were firstly made into physical hydrogel with the hydrophobic domains act as crosslinks. Subsequently, linear polyacrylamide (PAAm) was used as the second network. The amide groups on PAAm are able to form hydrogen bonds with the carboxylic acid groups on the hydrophilic mid-block (PMAA). The hydrogen bonds between the first and second network act as sacrificial bonds for energy dissipation. The obtained hydrogels, containing physical bonds of hydrophobic domains and sacrificial hydrogel bonds, were named as B-DN gels. The B-DN gels exhibit outstanding properties with both high stiffness and toughness, which is comparable with different kinds of tough hydrogels and rubbers, as well as natural skin and cartilage. As the hydrophobic domains of the first network in the B-DN gel substantially enhance the formation of hydrogen bonds, the B-DN gel is much stronger and tougher than the c-DN gel with a chemically cross-linked first network consisting of PMAA, at the same AAm concentration and same elastic modulus of the first network. The mechanical property of B-DN gels is tunable by the block copolymer concentration of the first network, the chain length of the mid-block of the block copolymer and the AAm concentration. The tough hydrogels in this study also show recovery, healing property as well as stability in concentrated saline solution. The extraordinary property of the B-DN gel makes it a good candidate as a load bearing material.

Furthermore, the mid-chain of the tri-block copolymers was found being pre-stretched in the block copolymer gel. The pre-stretched mid-chain of the first network combining with the effect of hydrogen bonds caused that the strain hardening of B-DN gels start from very small strain during tensile test. Meanwhile, the fracture of bonds during stretching consequently caused strain softening of the B-DN gels. The combination of strain hardening and the strain softening during stretching made some viscoelastic B-DN gels show linear tensile behavior until the large fracture stress of ~10MPa and fracture strain of ~600%. The linear tensile behavior of some B-DN gels provides the gel with the advantages of preventing further damage from moderate strain to large strain, and the potential of being used as sensor material. Following the structure of B-DN gels, other viscoelastic material with linear tensile behavior can be obtained.

Tissues of living organisms usually have well-ordered structures. In order to expand the application

potential of B-DN gel, the hydrogels with ordered structures of spheres in cubic lattice, hexagonally packed cylinders, and lamellae were obtained using the PBMA-b-PMAA-b-PBMA by the drying and swelling process. The drying-swelling block copolymer hydrogels with continues hydrophobic laminar structure are quite stretchable and show high stiffness. The gels with the hydrophobic parts as disperse phase (sphere and cylinder) were toughened by adding PAAm as second network.