学 位 論 文 審 査 の 要 旨
Doctoral Dissertation Evaluation Review

博士の専攻分野の名称　博士（生命科学）　　氏　名

Degree requested: Doctor of （Life Science）　　Name: Huijie Zhang

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学 位 論 文 題 名
Title of Doctoral Dissertation

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）

博士学位論文審査等の結果について（報告）
Results of Evaluation of the Doctoral Dissertation (Report)

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. Recently, a lot of work has been done to develop tough hydrogels. Among them, the double network hydrogels (DN gel) stand out for the 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. 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, according to the toughening mechanism of sacrificial bonds, the author performed research on the synthesis of tough hydrogels based on hydrophobic association and hydrogen bonds, aiming at the development of tough, recoverable hydrogels that are stable in saline solution. In detail, 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 acting 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 final 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 elastic modulus (~1MPa) and high toughness (~3000J/m^2), which is comparable with different kinds of tough hydrogels and rubbers, as well as natural skin and cartilage. The tough hydrogels in this study also show recovery, self-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.

In conclusion, the author has made remarkable contribution to the hydrogels research by development of a novel class of tough hydrogels that are even sustainable in saline solutions. The novel materials have great potentials as supporting tissues in physiological condition and structure materials in sea environment.

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