学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on functional soft materials
based on ultra-high molecular weight polymers
（超高分子量ポリマーからなる機能性ソフトマテリアルに関する研究）

Ion gels are soft materials composed of polymer networks and ionic liquids (ILs), which are room temperature molten salts. Ion gels possess unique properties, such as high ionic conductivity, non-volatility, non-flammability, and thermal stability derived from ILs, while being soft, wet, and solid consistency of general polymer gels. In recent years, it has been reported that ion gels exhibiting robust mechanical property and/or self-healing property can be prepared by precisely fabricated network structure, overcoming the mechanical fragility which is a problem of polymer gels for practical application. Numerous efforts have been devoted to apply ion gels with excellent mechanical properties to wearable and flexible devices that contribute to the IoT society. However, the problem was that ion gels with excellent mechanical properties could not be easily prepared because they required sophisticated technique of organic chemistry and of polymer synthesis.

Herein, I developed a new class of ion gels that are formed solely by physical entanglement of ultra-high molecular weight (UHMW) polymers in ILs, that is, UHMW ion gels. A simple operation of one-pot synthesis without further purification provides UHMW ion gel which exhibit high stretchability, self-healing capability, and recyclable property, in addition to general characteristics of ion gels such as high ion conductivity. Furthermore, the mechanical properties of UHMW ion gels can be controlled by taking advantage of the infinite number of structural possibilities of ILs (i.e., structural designability).

Firstly, I investigated the formation process of UHMW polymer (poly(methyl methacrylate): PMMA) network in an IL (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide: [C_2mim][TFSI]). It was found that the molecular weight (M_w) was increased significantly by radical polymerization conducted in [C_2mim][TFSI]. The monomer conversion was found to reach almost 100% even when extremely low initiator concentrations were selected. With the increase of M_w, the resulting ion gels exhibited excellent shape stability and kept mechanical robustness over a wide temperature and a frequency range. The UHMW ion gels also exhibited self-healing properties at room temperature, implying the reformation of the polymer entanglements across the damaged interfaces. Furthermore, I found that the nonequilibrium state of UHMW polymers at the interfaces immediately after cutting plays important roles in the healing process.

Then, I achieved precise control of the mechanical properties of the UHMW ion gels by selecting not only the chemical structures of polymer networks but also that of the ILs. The toughness of UHMW ion gels depended on the glass transition temperatures (T_gs) which was strongly influenced by the chemical structure of polymers and ILs. On the other hand, self-healing properties depended not only on T_gs but also on microscopic interactions between polymers and ILs. Molecular dynamics

simulations revealed that the solvation structures of the polymers in ILs were reflected in the entanglement structures, resulting in different self-healing properties.

In conclusion, I established in this thesis a method for synthesizing functional ion gels that exhibit excellent physical and mechanical properties by utilizing the entanglement of UHMW polymers. The self-healing behavior of UHMW ion gels and its mechanism were also discussed in terms of chemical structure of polymer and IL solvent.