HOKKAIDO UNIVERSITY

Title	Study on on-demand functionalization of hydrogel surfaces by force-induced rapid microstructure growth [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(ソフトマター科学)
Dissertation Number	甲第15228号
Issue Date	2022-12-26
Doc URL	https://hdl.handle.net/2115/88178
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	doctoral thesis
File Information	Qifeng_Mu_review.pdf, 審査の要旨

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Doctoral Dissertation Evaluation Review

Degree requested Doctor of Soft Matter Science Applicant's name MU QIFENG

Examiner:

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Title of Doctoral Dissertation

Study on on-demand functionalization of hydrogel surfaces by force-induced rapid microstructure growth
（力誘起急速微細構造成長による ハイドロゲル表面のオンデマンド機能化に関する研究）

Results of Evaluation of the Doctoral Dissertation (Report)

Living organisms share the ability to grow various microstructures on their surface to achieve functions. These microstructures on creature surfaces provide the author elegant paradigms for designing new biomimetic materials with specific functions and promising applications.

In an extension of mechanoresponsive self-growing hydrogels that respond to repetitive mechanical force through effective mechanochemical transduction, the author performed research on the mechanoradicals generated on the double-network (DN) hydrogel surfaces after selective indentation, aiming at improving the mechanoradical concentration and thereby developing new surface functions through force-induced radical polymerization. Thus, the author developed a surface-bulk transition technique in the synthesis of second network and precisely regulated the network structure of hydrogel surfaces. With the systematic mechanical investigations and theoretical calculation, the author confirmed that the double-network surfaces were successfully prepared, the mechanical hysteresis and re-swelling phenomena confirm the fracture of first network and mechanoradical generation on hydrogel surface layer. On the special DN hydrogel surface, the concentration of mechanoradicals can reach a level of ~10^{-5} M, which is high enough for the force-triggered radical polymerization.

The author observed the force-triggered fast radical polymerization in hydrogel bulk with the naked eye. In order to provide molecular evidence for the force-triggered rapid polymerization in bulk hydrogel, the author used the in-situ transmission Fourier-transform near-infrared (FT-NIR) spectroscopy to detect the monomer concentration change before and after mechanical stretching of monomer-fed DN hydrogel. Time-resolved near-infrared spectroscopy also reveals that the force-triggered radical polymerization of *N*-isopropylacrylamide (NIPAm) was almost completed within seconds (~10 s).

To realize surface microstructure growth, the author immersed DN hydrogels in different monomer aqueous solutions. Hydrogel surface after being indented in monomer solutions were immersed in pure water, they found that the rapid microstructure growth includes three main processes: bond breaking, chain growth, and swelling. Since the bond-breaking finishes in the loading process, and the radical polymerization almost finishes in several seconds, the swelling process in minutes is the rate-limiting process for the microstructure height change. The author established a quantitative relation between the topological feature of microstructure grown on the hydrogel surface and indentation parameters. They also demonstrated that the force-triggered microstructure growth is generic for different functional monomers.

The level of control and quality of force-triggered microstructure growth is sufficient to drive biomedical applications. In this research work, the author found that the PNIPAm-patterned DN hydrogel surfaces can induce adhesion, orientation growth and enhanced myogenesis of mouse myoblast cell line (C2C12). The

author also demonstrated that the anisotropic DN hydrogel surfaces with parallel PNIPAm patterns can also be used for regulating surface wettability and water droplet directional transportation.

In conclusion, the author has new findings of the way to engineering the DN hydrogel surfaces induced by selective mechanical indentation, and the author used real-time observations and molecular evidence to suggest the force-triggered rapid radical polymerization for the first time. This research work would lead the material's concept of productive use of mechanical force to physically and chemically remodel hydrogel surfaces for on-demand functions.

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