

論文 / 著書情報  
Article / Book Information

題目(和文)	
Title(English)	The Role of Hydrogen Bonding Interactions in The Interfacial Phenomena Governing Functions and Behaviors of Biomaterials
著者(和文)	ASATYASSYIFA
Author(English)	Syifa Asatyas
出典(和文)	学位:博士(学術), 学位授与機関:東京工業大学, 報告番号:甲第11004号, 授与年月日:2018年9月20日, 学位の種別:課程博士, 審査員:林 智広,原 正彦,丸山 厚,北村 房男,柘植 丈治
Citation(English)	Degree:Doctor (Academic), Conferring organization: Tokyo Institute of Technology, Report number:甲第11004号, Conferred date:2018/9/20, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)  
Doctoral Program

## 論文要旨

THESIS SUMMARY

専攻 : Department of	Electronic Chemistry	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 Doctor of	(Philosophy)
学生氏名 : Student's Name	Syifa Asatyas		指導教員 (主) : Academic Supervisor(main)	Assoc. Prof. Tomohiro Hayashi	
			指導教員 (副) : Academic Supervisor(sub)	Prof. Masahiko Hara	

要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

The mechanisms governing compatibility of biomaterials with living systems have been intensively investigated for further development, design, and application of biomaterials. The structure of water, in particular its hydrogen bonding interactions, have been proposed as the key factor in the interactions between artificial materials and biological systems. Hydrogen bonding states of interfacial water as well as the hydrogen bonding interactions between functional group of biomaterials with water molecules in the solution have been reported playing important role in macroscopic behavior of biomaterials.

In this study, the role of hydrogen bonding interactions that govern properties and behaviors of biomaterials are studied. Self-assembled monolayers (SAMs) are model platforms that enable analysis of interactions between organic artificial surfaces and biomolecules or living cells because they provide high-ordered and well-defined structure, the physicochemical properties of their surface are easy to be controlled. SAMs were employed as the model system representing bioinert artificial surfaces. Behavior of interfacial water, especially the hydrogen bonding states between interfacial water, is proposed to give contribution to water-induced repulsion that govern bioinert behavior. Since most of biomaterials found nowadays are made from polymer, a polymer posing temperature-responsive behavior was employed as an example of biomaterials. Changes in hydrogen bonding interactions that involve functional groups of the polymer and water molecules in the solution are proposed to be involved in the phase transition mechanisms.

Employing vibrational spectroscopy methods, changes in hydrogen bonding interactions can be examined. Surface-enhanced infrared absorption (SEIRA) spectroscopy is suitable for investigation of changes in hydrogen bonding interactions of water molecules in the vicinity SAMs since it enables analysis of interfacial water and prevent spectra of bulk water. Temperature-dependent attenuated total reflection infrared (ATR-IR) spectroscopy is suitable to observed changes in hydrogen bonding interactions that involve functional groups of temperature-responsive polymer at the phase transition temperature.

Oligo (ethylene glycol)-terminated (OEG) SAMs formed on gold surface have been widely employed as a model of bioinert surfaces for the investigation of the mechanisms underlying bioinertness. Methoxy-terminated OEG SAMs formed on gold (EG3-OMe/Au) and silver (EG3-OMe/Ag) are suitable to study effects of the metal substrate on the protein- and cell-resistance

behavior. EG3-OMe/Au poses lower molecular packing density compared to that of EG3-OMe/Ag. Theoretical studies suggested that the molecular packing density affected the interactions between terminal group of SAMs and the interfacial water. Herein, EG3OMe SAMs were employed as the model system to clarify mechanisms underlying bioinert behavior of artificial surfaces at molecular level. Effects of molecular packing density of EG3OMe SAM on bioinertness employing gold-supported ( $3.5 \text{ molecules/nm}^2$ ) and silver-supported EG3OMe SAM ( $4.6 \text{ molecules/nm}^2$ ) have been systematically investigated. Protein adsorption and cell adhesion assays confirmed that gold-supported EG3OMe SAM exhibited bioinertness whereas silver-supported one allowed protein adsorption and cell adhesion. Surface force measurements on approach of two-identical gold-supported EG3OMe SAMs revealed repulsive forces that were not observed in the case of silver-supported ones. It has been proposed that the repulsive forces were originated from interfacial water in the vicinity of bioinert EG3OMe SAM. Results of surface-enhanced infrared absorption spectroscopy (SEIRA) measurements showed that hydrogen bonding networks of the interfacial water were modulated by interactions between water molecules and ethylene glycol moieties of EG3OMe SAMs that strongly depend on the molecular packing density. The hydrogen bonding states between interfacial water correlated with water-induced repulsion that govern bioinertness. The modulated hydrogen bonding interactions of water molecules in the vicinity of bioinert EG3OMe SAM plays important role as a physical barrier in the mechanisms underlying bioinertness.

This study also revealed the importance of hydrogen bonding interactions in the phase transition mechanisms of poly(allylamine)-co-poly(allylurea) PAU in aqueous solution. PAU is an example of temperature-responsive polymer that is compatible with biological system. Understanding the phase transition mechanisms of PAU in aqueous solution contributes to development, designs and applications of biomaterials posing temperature-sensitive behaviors. PAU is one of few polymers showing UCST (upper critical solution temperature) behavior in aqueous solution. UCST polymer solution is transparent at higher temperature and is opaque at lower temperature. In this study, phase transition mechanisms of PAU were investigated by temperature-dependent IR spectroscopy measurements and density functional theory (DFT) calculations. Temperature-dependent IR spectra of higher-molecular weight PAU showed shift in frequency of CO stretching modes from  $1604.5$  to  $1615 \text{ cm}^{-1}$  at the phase transition. DFT calculations for models of PAU showed that the model having hydrogen bonding interactions between ureido units exhibiting lower vibrational energy of CO stretching modes compared to that of without ureido-ureido hydrogen bonds. This study proposed that the breaking of hydrogen bonding interactions between ureido units was the key factor in the phase transition mechanisms PAU posing UCST behavior in aqueous solution.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

注意：論文要旨は、東工大リサーチリポジトリ(T2R2)にてインターネット公表されますので、公表可能な範囲の内容で作成してください。

Attention: Thesis Summary will be published on Tokyo Tech Research Repository Website (T2R2).

