

学 位 論 文 題 名

# Molecular Structure on the Organic Thin Film Interface Studied by Sum Frequency Generation(SFG)

(和周波発生 (SFG) 分光法による有機薄膜界面分子構造の研究)

## 学位論文内容の要旨

In the present thesis, molecular structures on the interfaces of the organic thin films such as polymers, polymer blends and self-assembled monolayers (SAMs) have been investigated by sum frequency generation (SFG) in combination with other techniques of infrared reflection absorption spectroscopy (IRRAS), quartz crystal microbalance (QCM) and X-ray photoelectron spectroscopy (XPS) measurements. The differences between the molecular structures on the surface and in the bulk are compared on a molecular level in order to understand the special property and functionality of organic thin films.

Chapter 1 gives a brief description of surfaces and interfaces. SFG is concisely introduced as a surface vibrational spectroscopy. Recent studies of SFG on various surfaces and interfaces are also reviewed. The objective and outline of the present thesis are given in the last section.

Chapter 2 gives a basic theoretical background of the SFG process and its analysis.

Chapter 3 summarizes the information about the chemicals, sample preparations and characterization techniques used in the work.

Chapter 4 reports the studies on SAMs of alkanethiol with different chain lengths ( $C_nH_{2n+1}SH$ ,  $n=4, 8, 12, 18$ ) constructed on the GaAs surface. By adding a certain amount of  $NH_4OH$  in the modification solution, well-defined SAMs with long alkyl chain ( $n \geq 12$ ) can be formed on the GaAs surface. Formation of the S-As bond between alkanethiol molecules and the GaAs surface is confirmed by XPS measurements. The film thickness, tilt angles and ordering of SAMs are also characterized by the angle-resolved XPS and SFG measurements. The modification of the GaAs surface by SAMs is expected to remove the surface states of GaAs surface in order to improve its efficiency in the application of high-frequency telecommunication.

Chapter 5 shows the behavior of bisphenol A absorption, which is a one of hydrogen-bond donor molecules, in poly(acrylate)s such as poly(2-methoxyethyl acrylate) (PMEA), poly(ethyl acrylate) (PEA), poly(*n*-butyl methacrylate) (PBMA) and poly(methyl methacrylate) (PMMA) polymer thin films. Hydrogen bonding between the carbonyl groups in poly(acrylate)s and the hydroxyl groups in bisphenol A is clearly observed by IRRAS measurements in the polymer bulks. Compared with PMMA, PBMA and PEA films, more bisphenol A molecules are adsorbed in the PMEA thin film. This behavior can be attributed to the lower  $T_g$  of PMEA than other poly(acrylate)s films. By using a QCM electrode modified by PMEA thin films, 1 ppb detection of bisphenol A has been realized in the present work. Furthermore, IRRAS results show that phase separation occurs in PMEA bulk after bisphenol A absorption.

Chapter 6 shows the molecular structures on the interface of PMEA investigated by SFG vibrational spectroscopy. By controlling the thickness of the intermediate polystyrene (PS) film between the PMEA and Au substrate, we are able to selectively explore the molecular structure at air/PMEA (free) and PMEA/PS (buried) interface due to interference effects between the SFG signals generated from different interfaces. The ether methyl (OCH<sub>3</sub>) group in the side chain of PMEA at both interfaces has the same vector orientation with respect to the Au substrate, i.e., pointing into air at the free interface and pointing into PMEA at the PMEA/PS buried interface. The OCH<sub>3</sub> groups at the PMEA interfaces are likely to stand up and the interfacial ordering on the PMEA is increased by the bisphenol A absorption. The structural changes in the PMEA bulk and on its interface induced by absorption and desorption of bisphenol A are reversible.

Chapter 7 gives a quantitative description about the interference effect of SFG signals in the organic thin films on the solid substrate surface. The interference effect has been quantitatively calculated in order to understand the origin of the SFG signals from the different interfaces in the thin films. The calculation demonstrates that it is possible to exactly probe the molecular structure at the different interfaces by controlling the thickness of thin films, especially on a substrate with a high reflectivity such as Au and Ag.

Chapter 8 exhibits experimental results about hydrogen bonding on the surface and in the bulk of poly(acrylate)s with water molecules investigated by SFG and IRRAS measurements, respectively. It was found that the majority of the carbonyl groups on the PMEA surface are hydrogen bonded with the hydroxyl group of water molecules while no hydrogen bonding is found in its bulk. This is a first direct evidence for the formation of hydrogen bonding on the

polymer surface with water molecules. However, the hydrogen bonding of water molecules with other poly(acrylate)s surface such as PBMA and PMMA seemed to be much weaker. This result is expected to correlate with PMEA's excellent blood compatibility as one of the hopeful biomaterials. SFG measurements can be used to distinguish the hydrogen bonding between different hydrogen-bond donor molecules and the poly(acrylate)s surfaces. SFG vibrational spectroscopy is also used to probe surfaces of PMMA/poly(4-vinylphenol) PVPh blends in combination with IRRAS. Preliminary results show that surface ordering on PMMA/PVPh blends largely increases after annealing at 170°C, which is higher than the  $T_g$  of the two polymers.

Chapter 9 gives a general conclusion and future prospect based on the experimental and theoretical results obtained in this thesis.

The present work confirmed that SFG vibrational spectroscopy is a very powerful method to investigate the molecular structures on the surfaces and interfaces of organic thin films, especially, of polymer materials. The surface structural information is extremely useful to understand and to control the surface chemical/physical properties of the functional materials.

# 学位論文審査の要旨

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触媒反応から生体の新陳代謝まで様々な化学や生化学反応が種々の物質の表面や界面で起こっている。それらの反応の機構を理解し、さらに人為的に制御または利用するためには、その界面における原子・分子構造の微視的な評価と制御が不可欠である。例えば、人工臓器や医療器具用の高分子材料開発において、材料表面の分子設計は非常に重要である。しかしながら、研究手法の欠如により、高分子表面における分子構造について分子レベルでの検討は殆ど行われていない。申請者は表面選択性と界面感度が極めて高い和周波発生(SFG)二次非線形振動分光法を用い、機能性有機薄膜の表面分子構造と性能との関係について研究した。

申請者は、血漿タンパク質への適合性が非常に高いポリ-2-メトキシエチルアクリレート(PMEA)の表面分子構造について調べた結果、高分子表面での分子構造が内部と大きく異なっていることを見出した。他のポリアクリレート高分子と比べると、PMEA 表面は水分子と特異的に水素結合することを初めて観測した。さらに PMEA とポリ-2-ヒドロキシエチルメタクリレート(PHMEA)の共重合体を用い、定量に高分子表面分子構造と血液適合性の関係について調べた結果、水分子と PMEA 表面と形成した水素結合が、ポリアクリレート系高分子材料の生体適合性に重要な役割を果たしていることを明らかにした。今後の医用高分子材料の開発に役にたつものと考えた。

申請者は、この他にも各界面で発生した SFG 光の干渉効果を利用し、金属基板表面に構築した異種高分子薄膜の界面における分子構造の測定に成功した。高分子薄膜の膜厚を制御することにより、高分子表面、高分子-高分子界面、または高分子-基板界面における分子構造の計測について、実験と理論の両面からその可能性について示した。また、ナノグラムレベルで質量変化を検出できる水晶振動子マイクロバランス(QCM)の電極を機能性高分子薄膜で修飾し、高選択性かつ高感度の内分泌攪乱化学物質(環境ホルモン)の計測や回収技術の開発にも従事した。測定条件を最適化することにより、環境ホルモンの一種と疑われているビスフェノール A の高感度検出に成功した。申請者はさらに SFG と赤外分光測定による、擬似生体膜におけるビスフェノール A の吸着状態につい

て分子レベルで調べ、環境ホルモンと擬似生体膜との相互作用を明らかにした。

こうした申請者の一連の研究は、これまでに研究が非常に困難とされてきた高分子薄膜表面における分子構造の解析に大きく貢献した。こうした成果は今後、高分子の基礎物性の研究だけではなく、新しい機能性高分子の開発にも寄与するものと考えられる。審査員一同は、これらの成果を高く評価し、また研究者として誠実かつ熱心であり、特に研究において粘り強く、化学反応中に起こる微小な変化を見逃さないという真剣さや大学院単位取得などを併せ、申請者が博士（地球環境科学）の学位を受けるに十分な資格を有するものと判定した。