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Rheology of self-assembled monolayers on solid-liquid interface oscillating at MHz frequency

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ABSTRACT

The rheology properties (viscosity and elasticity) of chemisorbed soft matters on a solid-liquid interface oscillating at MHz were investigated using a quartz crystal microbalance (QCM). As a chemisorbed soft matter, we employed the self-assembled monolayers (SAMs) of mercapto oligo(ethylene oxide) methyl ethers, $HS(CH_2CH_2O)_nCH_3$ ($n = 5$, 11, 12, 19, 27, 35 and 43), where those molecular weights had unity. The systematical analyses on the basis of the Voight model revealed the relationships of $\eta \propto M_n^{0.180}$ and $\mu \propto M_n^{0.344}$, where η and μ are the viscosity and elasticity of the SAM, and M_n is the molecular weight of $HS(CH_2CH_2O)_nCH_3$. As a result, we found that the SAM consisting of the oligomer followed the formula of polymer.

1. Introduction

The rheology properties of soft matters (proteins, DNA, lipid, polymers and so on) on a solid-liquid interface are surly hot topics for several decades [1–6]. This interest is due to importance of thin coating of soft matters in many applications including the field of a biosensor. A biosensor is an analytical device composed of a biological sensing element integrated within a signal transducer. A quartz crystal microbalance (QCM) is well taken advantage of as one of transducers in a biosensor [7–10].

The technique of QCM measurement derives from the property of a quartz crystal operating in thickness-shearing mode at MHz. A small amount of mass deposited on the surface of the QCM leads to its resonant-frequency shift. Thus, the mass changes for order of subnanogram can be detected by measurement of a resonant-frequency shift. Therefore, the QCM has traditionally been used as a mass sensor for adsorption of, for example, proteins, polymers and synthetic polyelectrolytes from solutions [7–10]. Moreover, the simultaneous measurement of the resonant-frequency shift and energy dissipation shift has enabled the QCM to supply its utilization as a high-frequency interfacial rheometer [11]. This finding gives drastic impacts for the field of a biosensor with soft elements.

In many cases of biosensors, the self-assembled monolayers (SAMs) composed of oligo ethylene oxide have been employed to prevent nonspecific adsorption of soft matters onto a solid-liquid interface [12–15]. Alkane thiols are known to form the SAMs through chemisorption on a gold surface with bond formation. Thus, the SAMs composed of oligo ethylene

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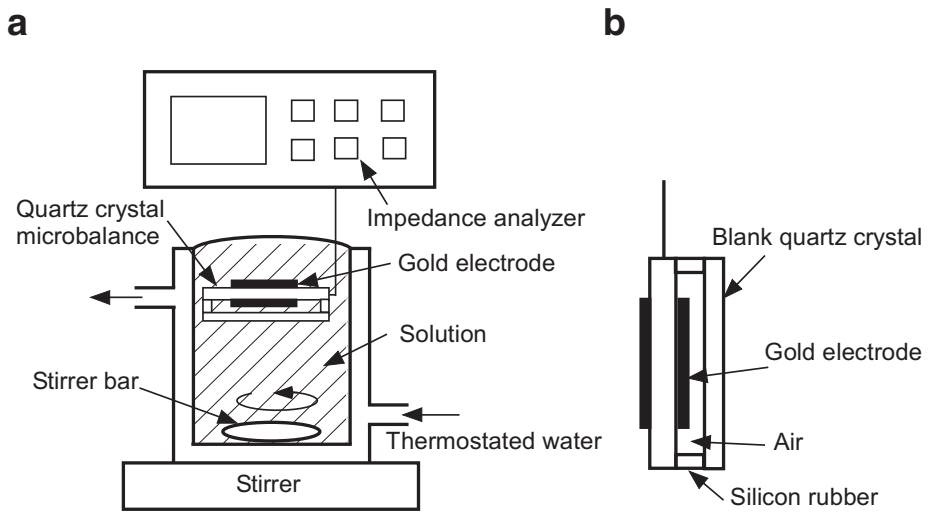

Fig. 1. (a) Schematic illustration of an experimental apparatus. (b) Schematic illustration of a one-face sealed QCM.

oxide could be useful as a model of chemisorbed soft matters on a solid-liquid interface oscillating. Therefore, in the present paper, we examined systematically the rheology properties (viscosity and elasticity) for chemisorbed molecules of oligo ethylene oxide on the solid-liquid interface oscillating at MHz. In other words, with the help of the QCM, we focused on the relationship between rheology and molecular weight on a solid-liquid interface oscillating at MHz.

In this paper, we used the SAMs constructed from mercapto oligo(ethylene oxide) methyl ethers, $HS(CH_2CH_2O)_nCH_3$ ($n = 5$, 11, 12, 19, 27, 35 and 43). The compounds, $HS(CH_2CH_2O)_nCH_3$, where $n = 5$, 11, 12, 19, 27, 35 and 43, hereafter are referred to as $(EO)_5$, $(EO)_{11}$, $(EO)_{12}$, $(EO)_{19}$, $(EO)_{27}$, $(EO)_{35}$ and $(EO)_{43}$, respectively.

2. Experimental

2.1. Synthesis of $(EO)_n$

The compounds of $(EO)_5$, $(EO)_{11}$, $(EO)_{12}$, $(EO)_{19}$, $(EO)_{27}$, $(EO)_{35}$ and $(EO)_{43}$ were synthesized, where those molecular weights had unity [16]. In other words, the variance values of molecular weights were 0.

2.2. Sample preparation

A 9 MHz AT-cut QCM with a pair of gold electrodes was used for all the experiments. The QCM was purchased from Nihon Dempa Kogyo (Tokyo, Japan). One side of the QCM was sealed with a blank quartz crystal casing, maintaining it in an air environment (Fig. 1b).

The 1 mM aqueous solutions of $(EO)_n$ were employed in all the experiments. The SAMs were prepared by immersing the QCMs in $(EO)_n$ solutions at 25 ± 0.1 °C. The QCMs with SAMs were rinsed by pure water after construction of the SAMs and were used for the impedance measurements.

2.3. QCM measurement

The cell was 8 mL and had a water jacket to maintain constant temperature. The QCM with SAM was immersed into the cell with pure water, where the QCM was mounted in level with the water surface and the immersion depth of the QCM was set at 0.5 cm. The temperature of cell was kept at 25 ± 0.1 °C. Under this condition, we carried out the impedance measurement of the QCM.

An impedance analyzer (Agilent Technologies 4395A) was used for the measurement of impedance properties of the QCM (Fig. 1a). The impedance data and phase data associated with 801 frequency data points centered at the frequency of minimum impedance were recorded on a personal computer. The values of the resonant-frequency shift, ΔF, and the energy dissipation shift, ΔD, at the 1st, 3rd, 5th, 7th and 9th overtones of a fundamental resonant frequency were calculated using admittance analysis [7,9].

3. Results and discussion

In all the experiments, we used the SAMs of $(EO)_n$ with closed-packed mass on gold electrode of the QCM. The closed-packed condition was verified by the QCM or CV. These results of experiments indicated that the immersion time more than