Temperature Dependence of the Rheology of Soft Matter on a MHz-oscillating Solid-liquid Interface

Minoru Yoshimoto1, Shigeru Kurosawa2, and Mutsuo Tanaka3*

1 Department of Information Science and Biomedical Engineering, Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, JAPAN
2 Health Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 6, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8566, JAPAN
3 Department of Life Science & Green Chemistry, Saitama Institute of Technology, 1690, Fusaiji, Fukaya, Saitama, 369-0293, JAPAN

Abstract: The temperature dependence of the resonant length, molecular weight, and rheology (shear viscosity and shear modulus) of chemisorbed soft matter on a solid-liquid interface oscillating at a megahertz frequency was studied using a quartz crystal microbalance. As a form of chemisorbed soft matter, self-assembled monolayers (SAMs) formed from six types of mercapto oligo(ethylene oxide) methyl ethers were used. A systematic analysis using the Voigt model showed that the variation in effective hydrated thickness (sensed mass), which is related to the resonant length, was classified into three types based on the molecular weight. As a result, a 2.2-nm change in the resonant length occurred in the studied temperature range from 10 to 35°C. Moreover, the variation in the effective hydrated thickness was dependent on the shear viscosity and shear modulus of the SAMs. A further investigation revealed that the relationships \( \eta \propto M_n^{0.13} \) and \( \mu \propto M_n^{0.30} \) could be estimated regardless of the temperature, where \( \eta \) and \( \mu \) are the shear viscosity and shear modulus of the SAM, and \( M_n \) is the molecular weight of mercapto oligo(ethylene oxide) methyl ether. As a result, we revealed that the experimental results followed the polymer formula irrespective of temperature.

Key words: QCM, oligo ethylene oxide, solid-liquid interface, self-assembled monolayer, Voigt model

1 Introduction

The rheology of soft matter (polymer, lipid, DNA, protein, etc.) on a solid-liquid interface has been an important subject for several decades owing to its significance in applications such as medical devices, diagnostic tools, and biosensors1. Adsorption of soft matter on a solid-liquid interface forms a thin layer, causing adverse biological responses and thereby significantly affecting device performance2.

The quartz crystal microbalance (QCM) has widely been used as a sensor to measure mass changes of subnanogram order because of its simplicity, low cost, and real-time response3-8). Assuming a continuous body, a theory for the utilization of the QCM as a rheometer was recently proposed by Voinova et al.9). An analysis based on the QCM theory is also useful for revealing the rheology of soft matter.

In biosensors, oligo (ethylene oxide) (OEO) and poly (ethylene oxide) (PEO) are often used to prevent nonspecific adsorption because surfaces coated with OEO or PEO are resistant to irreversible protein adsorption10-19). That is, OEO and PEO are appropriate for modeling soft matter. We previously reported the relationship between resonant length and frequency in OEO and PEO and quantitatively discussed the frequency dependence of the resonant length; a characteristic that indicates that the molecular length moves with an oscillating solid-liquid interface20-22). However, the relationship between temperature, resonant length, molecular weight, and rheology has not yet been examined in detail.

Temperature variation induces changes in the rheological properties (viscoelasticity, shear viscosity, and shear modulus) of soft matter and, as such, varies the resonant length. Therefore, in this study, we systematically investigated the temperature dependence between the resonant length, molecular weight, and rheology of soft matter using self-assembled monolayers (SAMs) formed of OEO.
2 Experimental Methods

2.1 Synthesis of mercapto oligo(ethylene oxide) methyl ethers

We employed SAMs formed of the mercapto oligo(ethylene oxide) methyl ethers HS(CH<sub>2</sub>CH₂O)ₙCH₃ (n = 5, 12, 19, 27, 35, and 43). The compounds HS(CH₂CH₂O)ₙCH₃, where n = 5, 12, 19, 27, 35, and 43, hereafter are referred to as (OEO)<sub>5</sub>, (OEO)<sub>12</sub>, (OEO)<sub>19</sub>, (OEO)<sub>27</sub>, (OEO)<sub>35</sub>, and (OEO)<sub>43</sub>, respectively. The synthesis methods are explained in Ref. 20. In the present study, we used compounds with a single molecular weight; in other words, the variance values of the molecular weights were zero.

2.2 Sample preparation

Nine MHz AT-cut QCMs with a pair of gold electrodes were used (Nihon Dempa Kogyo, Tokyo, Japan), where one side of each QCM was sealed with a blank quartz crystal case to maintain an air environment (Fig. 1b).

We used (OEO)<sub>n</sub> SAMs with a closed-packed mass on the gold electrode of the QCM. The closed-packed condition aqueous compound solutions of 1 mM is sufficient to construct SAMs with the closed-packed condition on the gold electrode<sup>20</sup>; therefore, the QCMs were left in the compound solutions for 24 h at 25°C. Then, the QCMs with SAMs were rinsed with pure water and immersed in the cell with pure water at the desired temperatures; the QCMs were mounted level with the water surface, and the immersion depth was set at 0.5 cm. After preparation, the QCMs were left for 24 h in pure water at the desired temperatures prior to impedance measurement.

2.3 QCM measurement

The impedance properties of the QCMs were measured using an impedance analyzer (Keysight 4395A) (Fig. 1a). The impedance and phase data centered at the frequency of the minimum impedance were recorded on a personal computer. The values of the resonant frequency shift (ΔF) and energy dissipation shift (ΔD) at the first, third, fifth, seventh, and ninth overtones of the fundamental resonant frequency were estimated via admittance analysis<sup>4,20</sup>. Six different temperatures were employed, that is, 10, 15, 20, 25, 30 and 35°C.

3 Results and Discussion

The ΔF and ΔD results of six (OEO)<sub>n</sub> SAMs at each temperature are illustrated in Figs. S1-S6 (Supporting Information). In all cases, the ΔF values increased linearly with the resonant frequency, and the ΔD values decreased linearly. Based on the data, we discuss the temperature dependence of the resonant length, molecular weight, and rheology.

3.1 Voigt model

To investigate the temperature dependence of the rheology and resonant length, we used the equations derived from the Voigt model on the premise of continuum mechanics. The changes in the signal due to the dipping of the SAMs in a Newtonian liquid are given by the following equations<sup>5,20</sup>:

\[
\Delta F = \frac{h_s \rho_b \omega_s q}{2\pi \rho_s h_s} \left[ 1 - \eta \frac{\eta_s}{\rho_s (\mu_s^2 + \omega_s^2 \eta_s^2)} \right],
\]

\[
\Delta D = \frac{2h_s \eta \eta_s}{\rho_s h_s} \times \frac{\mu_s \omega_s}{\mu_s^2 + \omega_s^2 \eta_s^2},
\]

where \( \omega_s \) is the QCM angular frequency; \( \rho_s \) and \( h_s \) are the quartz crystal density and thickness, respectively; \( \rho_b \) and \( \eta_b \) are the bulk liquid density and viscosity, respectively; and \( \rho_s, h_s, \mu_s, \eta_s \) are the density, thickness, shear modulus, and shear viscosity of the SAM, respectively. In this case, we must obtain the values of the sensed mass \( m_{qcm} \), effective hydrated thickness \( h_{qcm} \), and effective hydrated density \( \rho_{qcm} \) of the SAMs. The \( m_{qcm} \), that is, mass per unit area, is expressed as

![Fig. 1](image-url) (a) Schematic illustration of an experimental apparatus. (b) Schematic illustration of a one-face sealed QCM.
\[ m_{\text{QCM}} = h_{\text{eff}} \rho_{\text{SAM}} \tag{3} \]

\[ m_{\text{QCM}} \] denotes the mass, including the mechanically trapped water per unit area. At this stage, to calculate the \( h_{\text{eff}} \) and \( \rho_{\text{eff}} \) values of the SAMs, we must obtain the dry mass values of the SAMs. Therefore, we employed the CV data reported in Ref. 20. The \( \rho_{\text{eff}} \) and \( h_{\text{eff}} \) values of the SAMs can be determined from the CV and impedance data using the following equations:

\[ h_{\text{eff}} = \frac{m_{\text{QCM}}}{\rho_{\text{eff}}}, \tag{4} \]

\[ \rho_{\text{eff}} = \rho_{W} \frac{m_{\text{QCM}} - m_{\text{CV}}}{m_{\text{QCM}}} + \rho_{S} \frac{m_{\text{CV}}}{m_{\text{QCM}}}, \tag{5} \]

where \( m_{\text{CV}} \) is the SAM dry mass per unit obtained from the CV measurement, and \( \rho_{W} \) and \( \rho_{S} \) are the water and SAM density, respectively\(^{20, 23, 24}\). In this study, the water densities were set to the values for each temperature. In addition, the SAM density was set to 1200 kg/m\(^3\) at the studied temperatures\(^{11, 13, 20, 23}\).

The \( h_{\text{eff}} \) values are related to the resonant lengths. In fact, as described below, the \( h_{\text{eff}} \) values can be discussed using \( m_{\text{QCM}} \) and the relative water content (\( \% \)).

### 3.2 Sensed mass

The parameter values of equations (1) and (2) were determined from the data of the five harmonic overtones in Figs. S1-S6 (Supporting Information) using a genetic algorithm. Figure 2a shows a three-dimensional view of the \( m_{\text{QCM}} \) results against temperature and molecular weight \( (M) \). The two-dimensional views of Fig. 2a mapped on the \( m_{\text{QCM}}-M \) and \( m_{\text{QCM}} \)-temperature planes are shown in Figs. 2b and 2c, respectively. The results shown in Fig. 2b were used to evaluate the relative water content. Here, we discuss the results presented in Fig. 2c, which shows that the data tendencies can be classified into three types.

- (1) In \( \text{OEO} \)\(_{3} \), \( \text{OEO} \)\(_{12} \), and \( \text{OEO} \)\(_{19} \), the \( m_{\text{QCM}} \) values increased with temperature.
- (2) In \( \text{OEO} \)\(_{27} \), the \( m_{\text{QCM}} \) values increased with temperature at 25°C or below and then decreased.
- (3) In \( \text{OEO} \)\(_{35} \) and \( \text{OEO} \)\(_{43} \), the \( m_{\text{QCM}} \) values decreased with increasing temperature.

In this paper, we first focus on the physical causes of the three types using the relationship between temperature and resonant length and then describe the temperature dependence of rheology. Therefore, we discuss the physical properties of SAMs in terms of the relative water content, effective hydrated thickness, shear viscosity, and

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**Fig. 2**  (a) Three-dimensional view of \( m_{\text{QCM}} \) against temperature and \( M \). (b) Two-dimensional view of Fig. 2a mapped on the plane of \( m_{\text{QCM}}-M \). The mcv values are shown as reference. The black solid line for \( m_{\text{CV}} \) is a guide to the eye. (c) Two-dimensional view of Fig. 1a mapped on the plane of \( m_{\text{QCM}} \)-temperature. The error bars represent standard deviation. Measurements were repeated 6 times.
3.3 Relative water content

Figure 2b illustrates $m_{\text{QCM}}$ against $M_n$ with the $m_{\text{CV}}$ values. The $m_{\text{QCM}}$ values are usually greater than the $m_{\text{CV}}$ values because $m_{\text{QCM}}$ includes mechanically trapped water. However, the $m_{\text{QCM}}$ values of (OEO)$_{35}$ from 20 to 35°C and (OEO)$_{43}$ were smaller than those of $m_{\text{CV}}$. In addition, the $m_{\text{QCM}}$ value for (OEO)$_{35}$ at 15°C was almost equal to that of $m_{\text{CV}}$. These results indicate that the QCM could not obtain the exact mass values of the SAMs. That is, the molecular lengths of (OEO)$_{35}$ and (OEO)$_{43}$ were greater than the resonant lengths at those points; therefore, we could not calculate the $h_{\text{eff}}$ values of the SAMs at these points.

In (OEO)$_{27}$, as shown in Fig. 2c, the $m_{\text{QCM}}$ values increased with temperature up to 25°C and then decreased. It is probable that the molecular length of (OEO)$_{27}$ was smaller than the resonant length at 25°C or below and increased past the resonant length above this temperature due to the change from the 7/2 helical conformation to the all-trans conformation. Therefore, we could not calculate the $h_{\text{eff}}$ values of SAMs formed of (OEO)$_{27}$ above 25°C.

For (OEO)$_{19}$, (OEO)$_{22}$, and (OEO)$_{43}$, we calculated all the $h_{\text{eff}}$ values using equations (4) and (5) at each temperature. However, we could not estimate the partial $h_{\text{eff}}$ values of (OEO)$_{27}$ and (OEO)$_{35}$, and all those of (OEO)$_{43}$. In (OEO)$_{27}$, the $h_{\text{eff}}$ values could be estimated at 25°C or below, but not above 25°C. For (OEO)$_{35}$ at temperatures above 10°C, we could not calculate the $h_{\text{eff}}$ values. Similarly, for (OEO)$_{43}$, the $h_{\text{eff}}$ values could not be estimated at the studied temperatures. This is because the molecular length was greater than the resonant length. As a result, the water content could not be estimated and hence, we needed to estimate the $h_{\text{eff}}$ values using another method. Specifically, we evaluated the $h_{\text{eff}}$ values for the SAMs of (OEO)$_{27}$, (OEO)$_{35}$, and (OEO)$_{43}$ from the relationship between the $w$% value and temperature. The $w$% values were evaluated using

$$w\% = 100 \times \frac{m_{\text{QCM}} - m_{\text{CV}}}{m_{\text{QCM}}},$$

where it was assumed that water was uniformly distributed in the SAMs$^{20,24}$. The $w$% values were calculated using equation (6), as illustrated in Fig. 3. In (OEO)$_{19}$ and (OEO)$_{22}$, the $w$% values increased with temperature. Additionally, the $w$% values for the SAM of (OEO)$_{19}$ were almost equal to those of (OEO)$_{27}$ at 25°C or below. That is, the results showed that the SAMs formed from the molecular weight of (OEO)$_{19}$ or greater had approximately the same $w$% values at the studied temperatures. The results also suggested that the maximum value of $w$% in the SAMs constructed from (OEO)$_{19}$ was approximately 20%. The (OEO)$_{43}$ SAMs adopted a helical conformation; however, the SAMs of (OEO)$_{22}$, (OEO)$_{19}$, (OEO)$_{27}$, (OEO)$_{35}$, and (OEO)$_{43}$ likely had an amorphous structure constructed from the 7/2 helical and all-trans conformations at approximately $w$%.

3.4 Effective hydrated thickness

Under the conditions that the $w$% values of the SAMs formed from the molecular weight of (OEO)$_{19}$ or greater were the same and the thicknesses of the SAMs were uniform, we determined the $h_{\text{eff}}$ values using equations (1) – (5). Figure 4 shows a three-dimensional view of $h_{\text{eff}}$ against temperature and $M_n$. To clarify the results, the two-dimensional view of Fig. 4a mapped on the plane of $M_{n}$-$M_s$ is shown in Fig. 4b. The theoretical values of the molecular lengths of the 7/2 helical and all-trans conformations against $M_s$ are illustrated in Fig. 4b$^1$. At the studied temperatures, for (OEO)$_{27}$ or below, the $h_{\text{eff}}$ values increased with $M_s$, and had values between the 7/2 helical and all-trans conformations. In contrast, the $h_{\text{eff}}$ values of (OEO)$_{35}$ and (OEO)$_{43}$ were smaller than the molecular lengths of the 7/2 helical conformation. The $h_{\text{eff}}$ values inevitably existed between the molecular lengths of the 7/2 helical and all-trans conformations; therefore, the values of (OEO)$_{35}$ and (OEO)$_{43}$ were related to the values of the resonant lengths. However, Fig. 4c shows that the $h_{\text{eff}}$ values of (OEO)$_{35}$ and (OEO)$_{43}$ were the same at 15°C or above but differed at 10°C. This indicates that the resonant length was longer than the molecular length of (OEO)$_{35}$ at 10°C. However, at 10°C, the $h_{\text{eff}}$ value of (OEO)$_{43}$ was greater than the resonant value. The result suggested that the $h_{\text{eff}}$ of (OEO)$_{43}$ corresponded to the resonant length in the studied temper
perature range. Therefore, we revealed that the resonant lengths varied from 10.2 (10°C) to 8.0 nm (35°C) based on the Voigt model. That is, the 2.2-nm change in the resonant length was determined using the systematic change in molecular weight.

In Fig. 4c, which depicts a two-dimensional view of Fig. 4a mapped on the plane of the $h_{\text{eff}}$-temperature, the results of $(\text{OEO})_{a}$ are equal to those of Fig. 2c and can be classified into three groups. These are discussed in detail in section 3.7; therefore, in this section, we do not discuss the relationship between $h_{\text{eff}}$ and temperature. Instead, we suggest that the increase in the $h_{\text{eff}}$ values of $(\text{OEO})_{a}$, $(\text{OEO})_{22}$, $(\text{OEO})_{25}$, and $(\text{OEO})_{27}$ with temperature in Fig. 4c originated from the increase in the ratio of the all-trans conformation.

3.5 Shear viscosity and shear modulus of SAMs

The $h_{\text{eff}}$ values of $(\text{OEO})_{a}$, that is, the resonant length, decreased with temperature. This may indicate that the SAMs become softer as the temperature increases. To clarify the cause of the temperature dependence, the shear viscosity and shear modulus of the SAMs were evaluated using equations (1) and (2) with $\rho_{\text{eff}}$ and $h_{\text{eff}}$. In this case, the frequency dependence of the shear viscosity and shear modulus was estimated with a constant density and thickness. Figures S7-S18 show the shear viscosity and shear modulus against the overtone number $(N)$ in $(\text{OEO})_{a}$. The relationship is expressed as the following equations:

\begin{align}
\eta_N = \eta_1 \times (1 + a(N - 1)), \\
\mu_N = \mu_1 \times (1 + b(N - 1)),
\end{align}

where $a$ and $b$ are parameters related to the slopes of the lines, and $N$ is the overtone number. The shear viscosity decreased with increasing QCM frequency (Figs. S7-S12), while the shear modulus increased (Figs. S13-S18). In this study, the shear viscosity ($\eta_1$) and shear modulus ($\mu_1$) of the fundamental frequency (9 MHz) were calculated from the data in Figs. S7-S18 using the least-squares method.

In Fig. 5a, the results of $\eta_1$ against temperature and $M_n$ are shown from a three-dimensional view. To clearly investigate the results, the two-dimensional view of Fig. 5a mapped on the plane of $\eta_1$-$M_n$ is shown in Fig. 5b. The $\eta_1$ values in the SAMs of $(\text{OEO})_{a}$ increased slightly with $M_n$.

Figure 5c shows a two-dimensional view of Fig. 5a mapped on the plane of $\eta_1$-temperature. The temperature change from 10 to 35°C induced a decrease in $\eta_1$. Figure 6a shows a three-dimensional view of $\mu_1$ against temperature and $M_n$, and Figs. 6b and 6c show two-dimensional views of Fig. 6a. Figure 6b indicates that the $\mu_1$ values increased with the molecular weight, while Fig. 6c indicates that the $\mu_1$ values decreased with increasing temperature. The results in
Fig. 5  (a) Three-dimensional view of $\eta_1$ against temperature and $M_n$. (b) Two-dimensional view of Fig. 5a mapped on the plane of $\eta_1$-$M_n$. (c) Two-dimensional view of Fig. 5a mapped on the plane of $\eta_1$-temperature. The error bars represent standard deviation. Measurements were repeated 6 times.

Fig. 6  (a) Three-dimensional view of $\mu_1$ against temperature and $M_n$. (b) Two-dimensional view of Fig. 6a mapped on the plane of $\mu_1$-$M_n$. (c) Two-dimensional view of Fig. 6a mapped on the plane of $\mu_1$-temperature. The error bars represent standard deviation. Measurements were repeated 6 times.
Figs. 5c and 6c reveal that the variation in the resonant length was due to the change in SAM stiffness caused by temperature. The results in Figs. 5b and 6b are discussed in detail in the next section.

3.6 Physical properties of SAMs

In this section, we discuss the relationship between temperature and rheology. In other words, we discuss the results in Figs. 5b and 6b. In a polymer, the relationship between viscosity ($\eta$) and $M_n$ is expressed as

$$\eta \propto M_n^\alpha,$$

where $\alpha$ is a constant. Using equation (9), log $\eta$ was plotted against log $M_n$. Figure 7a shows that the linear slopes slightly increased and were approximately 0.13 at the studied temperatures. This result indicates that equation (9) is applicable to the relationship between $\eta$ and $M_n$. In addition, the relationship between elasticity ($\mu$) and $M_n$ is expressed by

$$\mu \propto M_n^\beta,$$

where $\beta$ is a constant. Using equation (10), we investigated the relationship between log $\eta$ and log $M_n$. Figure 7b indicates that this relationship was linear and the slopes were approximately 0.30 over the studied temperature range. It is clear that equation (10) is valid for the relationship between $\mu$ and $M_n$.

It is well known that the rheology of a polymer can be described by the Rouse model, where it is assumed that the polymer takes a random coil in the bulk. The values of $\alpha$ and $\beta$ are 1 and -1, respectively. In this study, these values were approximately 0.13 and 0.30, respectively, which are almost zero and differ from those of the Rouse model. The rheology was measured on the solid-liquid interface oscillating at a megahertz frequency, and the SAM structure was the amorphous structure of the 7/2 helical and all-trans conformations. These factors may have caused the deviation from the Rouse model. However, regardless of the temperature, it is important to note that the properties of the SAMs follow equations (9) and (10).

3.7 Three types of sensed masses and effective hydrated thicknesses

Here, we discuss the physical causes of the three types of sensed masses observed in Figs. 2c and 4c. Because the physical meanings of the $m_{QCM}$ tendencies are equal to those of $h_{eff}$ we use "$h_{eff}$" in this section. First, in (OEO)$_{12}$, (OEO)$_{15}$, and (OEO)$_{19}$, the $h_{eff}$ values increased with temperature (Figs. 2c and 4c). The increase in the $h_{eff}$ values was derived from the increase in the ratio of the all-trans conformation to the increase in the water content of the SAMs. Second, in (OEO)$_{27}$, the $h_{eff}$ values increased with temperature at 25°C or below and then decreased (Figs. 2c and 4c). This was because, at 25°C or below, the increase in $h_{eff}$ values originated from the decrease in shear viscosity and shear modulus with an increase in temperature (Figs. 5c and 6c). Third, in (OEO)$_{35}$ and (OEO)$_{43}$, the $h_{eff}$ values decreased with increasing temperature. This phenomenon was caused by the decrease in shear viscosity and shear modulus with an increase in temperature (Figs. 5c and 6c).

4 Conclusions

We investigated the relationship between the temperature, resonant length, molecular weight, and rheology of chemisorbed soft matter on a solid-liquid interface oscillating at a megahertz frequency. This study revealed that the relationships between $h_{eff}$ and temperature were classified into three types based on molecular weight and the causes were explained by the relative water content, conformation change, shear viscosity, and shear modulus. Under the assumption that the relative water content of (OEO)$_{43}$ was
equal to that of \((\text{OEO})_{2}\), the 2.2-nm change in the resonant length was confirmed in the studied temperature range using the systematic molecular weight. We also found that the variation in the resonant length was due to the change in the SAM stiffness with temperature.

The shear viscosity and shear modulus increased with molecular weight and decreased with temperature. In addition, the physical properties of \(\eta \propto M_{n}^{0.13}\) and \(\mu \propto M_{n}^{0.30}\) were estimated independently of temperature. These results show that temperature significantly affects the dynamics of soft matter in the megahertz region, and these novel findings may be important for studying the new dynamics of soft matter in the megahertz region.

**Supporting Information**

\(\Delta \rho\) and \(\Delta \sigma\) against the QCM frequency at each temperature in \((\text{OEO})_{1}\) (Figs. S1-S6), \(\eta\), against the overtone number of the QCM at each temperature in \((\text{OEO})_{1}\) (Fig. S7-S12), \(\mu\), against the overtone number of the QCM at each temperature in \((\text{OEO})_{1}\) (Fig. S13-S18). Supporting Information is available. This material is available free of charge via the Internet at doi: 10.5650/jos.ess22049

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