Behavior of Polyethylene Glycol Molecules at an Oscillating Solid-Liquid Interface

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Abstract: The behavior of polyethylene glycol (PEG) molecules at an oscillating solid-liquid interface was examined using a quartz crystal microbalance (QCM). The number-average molecular weights (M_n) of PEG molecules were systematically varied. This study revealed that the shift in the energy dissipation factor, ΔD , of the QCM against square root of the density-viscosity product of the PEG solution is linear and has an intercept. Moreover, the systematical analysis revealed that the ΔD slope rapidly decreases with M_n , and the ΔD intercept becomes constant above 1.1×10^4 g/mol. Those results indicated that the resonant length of PEG molecules moving with the oscillating plate at 9 MHz is 97.6 Å. We also found that the difference between the resonant lengths calculated from ΔD and series resonance-frequency shift, ΔF , is related to the density of the thin PEG layer formed on the gold electrode.

Key words: QCM, solid-liquid interface, polyethylene glycol, energy dissipation, Debye process

1 INTRODUCTION

For a long time, a quartz crystal microbalance (QCM) has been used in vacuum and gaseous environments as a mass sensor¹⁻³. However, its oscillation in a liquid environment was later successful, and there have recently been many requirements for sensors, which can be used in a liquid⁴. They have several advantages such as ease of use, low detection limit and continuous operation that have attracted increased interest. The QCM was also applied to the Belousov-Zhabotinsky (BZ) reaction, which is known as a nonlinear chemical oscillation reaction⁵. This study revealed that the density and viscosity of the solution of the BZ reaction oscillated. This new finding produced novel concepts in the field of nonlinear science.

The properties of polymer solutions are of considerable interest to both theorists and experimentalists owing to their importance in many different fields⁶⁻¹⁵. Much effort has been devoted to obtaining a comprehensive understanding of polymer molecules in dilute, semidilute and concentrated bulk solutions. Recently, many studies have focused on the physical properties of polymer molecules at a solid-liquid interface¹⁶⁻³⁷. Most of those studies are supported by development of the measurement techniques of

the QCM¹⁶.

Polyethylene glycol (PEG) molecules are the most extensively studied linear polymers, whose chains are composed of oxyethylene units. Owing to the high water solubility and low toxicity of PEG molecules, they are employed in a wide range of applications in pharmaceutical, clinical and biomedical researches^{22, 23}. For example, PEG molecules have the ability to reduce nonspecific adsorption of proteins at a solid-liquid interface²⁴⁻³⁴. This is very useful for label-free biosensors such as the QCM, because nonspecific adsorption of biomolecules generates problems in quantitative estimation of target protein concentration and evaluation of the binding affinity between proteins. The degree to which the nonspecific adsorption of proteins is prevented is related to the PEG length. However, previous reports did not consider the dynamic properties of PEG molecules at the solid-liquid interface oscillating at MHz frequencies.

The QCM measurements rely on the frequency shift and energy dissipation shift of a quartz crystal oscillating in thickness-shearing mode at MHz frequencies¹⁶. This allows the QCM to be used for investigating nanoscale rheology. Therefore, understanding the dynamic properties of polymer molecules at an oscillating solid-liquid interface is

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Accepted August 6, 2013 (received for review August 2, 2013)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjocs>

very important from the viewpoint of both theory and experiment.

In a previous report³⁷⁾, we used the QCM to study the properties of PEG molecules oscillating at MHz frequencies at a solid-liquid interface. This study revealed that the slope of the series resonance-frequency shift against the number-average molecular weight decreases according to the Debye process. Using this method, we found that PEG of length of 54.2 Å moves with the oscillating plate at 9 MHz. However, this study only focused on the series resonance-frequency shift.

In the QCM measurements, the energy dissipation shift provides information about viscoelasticity of the polymers and characterizes those properties¹⁶⁾. In polymer studies, the investigation of energy dissipation shift is an important parameter, which is equivalent to series resonance-frequency shift. Therefore, in this paper, we examined the dynamic properties of PEG molecules at a solid-liquid interface oscillating at MHz frequencies in terms of the energy dissipation shift. With the help of the QCM, we investigate the transition behavior of PEG molecules by systematically varying the number-average molecular weight. Furthermore, by comparing series resonance-frequency shift and energy dissipation shift, we discussed the PEG resonant length moving with the oscillating solid-liquid interface in regions of the thin layer and the viscous penetration depth.

2 EXPERIMENTAL

2.1 Sample preparation

Water with specific resistance of 18.2 MΩ·cm was prepared with a Milli-Q apparatus (Millipore, Tokyo, Japan). PEG solutions were prepared using PEG-200 ($M_n = 246$ g/mol, $M_w/M_n = 1.05$), PEG-600 ($M_n = 576$ g/mol, $M_w/M_n = 1.04$), PEG-2K ($M_n = 1912$ g/mol, $M_w/M_n = 1.01$), PEG-6K ($M_n = 8798$ g/mol, $M_w/M_n = 1.00$), PEG-20K ($M_n = 21335$ g/mol, $M_w/M_n = 1.00$), PEG-500K ($M_n = 4 \times 10^5$ g/mol) and PEG-2M ($M_n = 1.75 \times 10^6$ g/mol) (Wako, Japan), where M_n and M_w are the number-average molecular weight and weight-average molecular weight, respectively^{6, 7)}. The values of M_n and M_w of PEG molecules were measured using MALDI-MS (Shimazu AXIMA-CFR plus). Unfortunately, we were unable to estimate the exact values of M_n and M_w of PEG-500K and PEG-2M because they exhibited a broad distribution of molecular weight. However, the values of M_n measured using MALDI-MS were approximately equal to the average molecular weight mentioned by Wako. Therefore, we used the average molecular weight depicted by Wako as the values of M_n .

The PEG molecules were dissolved in water by a magnetic stirring bar at room temperature, and after two days, the PEG solutions were used for viscosity, density and the

QCM analyses. For comparison, Newtonian liquids were prepared using sucrose (Wako, Japan).

2.2 Measurements of viscosity and density

The viscosities of the PEG solutions were measured using Cannon-Ubbelohde viscometers. The viscometers were placed in a constant temperature water bath, set at $25 \pm 0.1^\circ\text{C}$. 10 mL of the sample solutions was used for the measurements. The PEG solutions were allowed to equilibrate to the set temperature for 20 min prior to the viscosity measurements.

Density values of the PEG solutions were measured using a 10 mL pycnometer. The pycnometer was placed in a water bath kept at $25 \pm 0.1^\circ\text{C}$ for 20 min prior to the measurements. Weights were measured by an electronic balance (Shimazu, BW-420H).

2.3 QCM analysis

A 9 MHz AT-cut QCM with a pair of gold electrodes was used for all the experiments. This QCM had a mirrored surface, and the geometry of quartz crystal plate and gold electrodes was round. The quartz crystal plate and electrodes were 8 and 5 mm in diameter, respectively, and the geometry and size of gold electrodes were the same on both sides. The QCM was purchased from Nihon Dempa Kogyo (Tokyo, Japan).

We used an impedance analyzer (Agilent Technologies 4294A) for studying the resonant-frequency properties of the QCM. The 16047E test fixture (Agilent Technologies) was employed for direct impedance measurements (Fig. 1a). The source power was adjusted to 0.237 V. The frequency span was set at 10 kHz. The impedance and phase data associated with 801 frequency data points centered at the frequency of minimum impedance were recorded on a personal computer. The shift in the energy dissipation factor, ΔD , was calculated using admittance analysis^{38, 39)}.

The cell was 8 mL and had a water jacket to maintain constant temperature. One side of the QCM was sealed with a blank quartz crystal casing, maintaining it in an air environment (Fig. 1b). The QCM was mounted in level with the water surface, and the immersion depth of the QCM was set at 0.5 cm (Fig. 1a). The cell and QCM system were shielded by a grounded aluminum plate. The gold electrodes of the QCM were rinsed with piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 (30\%) = 3:1$) prior to impedance measurements. For measurements in PEG solutions, the cell temperature was set to $25 \pm 0.1^\circ\text{C}$. For physical adsorption equilibrium between the PEG molecules and the gold electrodes, the QCM was immersed in the PEG solutions for 3 h prior to the impedance measurements. For measurements in sucrose solutions, the cell temperature was set to $20 \pm 0.1^\circ\text{C}$, and the QCM was immersed in sucrose for 15 min prior to the measurements. PEG and sucrose solutions were stirred using a stirring bar. The stirring was stopped

Fig. 1 *a.* Schematic illustration of an experimental apparatus. *b.* Schematic illustration of the one-face sealed QCM. The cell and QCM system were shielded by a grounded aluminum plate.

during QCM measurements. The experiments were repeated to obtain statistically significant results.

3 RESULTS

3.1 Behavior of ΔD in a Newtonian liquid

Kanazawa and Gordon proposed the following equation to predict the linear relationship between series resonant-frequency shift and square root of the density-viscosity product in a Newtonian liquid⁴⁰⁾:

$$\Delta f_q = -\frac{f_q^{3/2}}{\sqrt{\pi} \rho_q \mu_q} \sqrt{\rho_1 \eta_1}, \quad (1)$$

where Δf_q is the series resonant-frequency shift, f_q is the resonant fundamental frequency of the quartz crystal, μ_q is the shear modulus of the quartz crystal, η_1 is the absolute viscosity of the Newtonian liquid, and ρ_q and ρ_1 are the densities of the quartz crystal and the Newtonian liquid, respectively. The subscripts q and 1 indicate the quartz crystal and Newtonian liquid, respectively. In addition, the shift in the energy dissipation factor, ΔD_q , is described by⁴¹⁾

$$\Delta D_q = \frac{2f_q^{1/2}}{\sqrt{\pi} \rho_q \mu_q} \sqrt{\rho_1 \eta_1}. \quad (2)$$

Figure 2 shows the experimental result for ΔD as a function of $\sqrt{\rho_1 \eta_1} - \sqrt{\rho_w \eta_w}$ for the Newtonian liquid, where the subscript w indicates pure water. Figure 2 shows that the experimental data of ΔD vary linearly with $\sqrt{\rho_1 \eta_1} - \sqrt{\rho_w \eta_w}$ and are approximately equal to the values calculated with equation (2).

Fig. 2 ΔD versus $\sqrt{\rho_1 \eta_1} - \sqrt{\rho_w \eta_w}$ in sucrose solutions. The solid line means the value calculated using equation (2). The error bar represents standard deviation. Measurements were repeated six times. We employed the solution concentrations of every 2wt% in 0 ~ 24wt%, and 30, 36, 40, 46, 50wt%.

3.2 Behavior of ΔD in PEG solutions

PEG solutions show properties of a non-Newtonian liquid^{6-21, 37)}. This means that the viscosities of PEG solu-

Fig. 3 ΔD versus $\sqrt{\rho_2\eta_2} - \sqrt{\rho_w\eta_w}$ in PEG solutions. ●: PEG-200, ■: PEG-600, ▲: PEG-2K, ▼: PEG-6K, ○: PEG-20K, △: PEG-500K, □: PEG-2M. The error bar represents standard deviation. Measurements were repeated six times. The solid line was calculated using equation (2). We employed the following solution concentrations (wt%). PEG-200: 0.5, 1, 2, 5, 10, 20, 50. PEG-600: 0.5, 1, 2, 5, 10, 20. PEG-2K: 0.5, 1, 2, 5, 10. PEG-6K: 0.5, 1, 2, 5, 10, 20. PEG-20K: 0.2, 0.8, 2, 5, 10, 20. PEG-500K: 0.1, 0.2, 0.5, 0.8, 2. PEG-2M: 0.1, 0.2, 0.5, 0.8.

tions are dependent on the oscillation frequency under oscillatory shear stress. In other words, the relaxation process of PEG solutions depends on the molecular weight. Therefore, we can employ the value of $\sqrt{\rho_2\eta_2} - \sqrt{\rho_w\eta_w}$ as an index of the difference between the Newtonian liquids and PEG solutions, where the subscript 2 indicates the PEG solution. Based on this difference, we can investigate the dynamic properties of PEG molecules of varying molecular weights at the solid-liquid interface oscillating at 9 MHz.

Figure 3 illustrates the results of ΔD as a function of $\sqrt{\rho_2\eta_2} - \sqrt{\rho_w\eta_w}$. For all the PEG solutions, the experimental data of ΔD vary linearly with $\sqrt{\rho_2\eta_2} - \sqrt{\rho_w\eta_w}$. The values of the ΔD slope of PEG-200, PEG-600 and PEG-2K are approximately equal to that of the Newtonian liquid. In contrast, the values of the ΔD slope of PEG-6K, PEG-20K, PEG-500K and PEG-2M are smaller than that of the Newtonian liquid.

To get further insight on the relationship between ΔD and $\sqrt{\rho_2\eta_2} - \sqrt{\rho_w\eta_w}$, we analyzed the ΔD data using a least-square method. A representative example is shown in Fig. 4, where the data of PEG-6K solution are presented. The

Fig. 4 ΔD versus $\sqrt{\rho_2\eta_2} - \sqrt{\rho_w\eta_w}$ in PEG-6K solutions. The error bar represents the standard deviation. Measurements were repeated six times. The solid line shows the value calculated using a least-square method.

ΔD intercept is caused by the formation of a thin PEG layer on the gold electrode^{16, 38}. The results of all the PEG solutions are summarized in Fig. 5. The values of the ΔF slope rapidly decrease in the region from PEG-600 to PEG-500K. In contrast, the ΔD intercept is observed in all PEG solutions and has a constant value of 1.75×10^{-5} above PEG-6K.

4 DISCUSSION

4.1 Behavior of ΔD slope in PEG solutions

Figure 5 shows that the values of the ΔD slope rapidly decrease in the region from PEG-600 to PEG-500K. This rapid variation arises from the dynamic properties of PEG molecules in the region of viscous penetration depth, generated at the solid-liquid interface oscillating at 9 MHz^{16, 38}. We discuss this rapid variation from the point of view of the Debye process, which explains a single-time relaxation process of a molecule⁷. In that process, the dynamical compliance, $J^*(\omega)$, is given by

$$J^*(\omega) = J' - iJ'' = \frac{\Delta J}{1 + \omega^2\tau^2} - i \frac{\Delta J\omega\tau}{1 + \omega^2\tau^2}, \quad (3)$$

where ΔJ is the relaxation strength of the molecule, τ is the relaxation time of the molecule and ω is the angular frequency of the oscillating plate. This equation shows that the imaginary part has the maximum value at $\omega = 1/\tau$. In other words, the molecule has the maximum energy loss at

Fig. 5 Slope and intercept of ΔD versus M_n in PEG solutions. ●: ΔD slope, ○: ΔD intercept. The mark (■) on y-axis means the slope value of equation (2). The solid line indicates the value calculated from real part of equation (3) using a nonlinear least-square method. The dashed line shows the value calculated from equations (4) and (12) with $\eta_1 = \eta_3 = 8.90 \times 10^{-4}$ Ns/m², $\rho_1 = \rho_3 = 997$ kg/m³, $\rho_q = 2648$ kg/m³, $h_q = 1.84 \times 10^{-4}$ m, $\omega_q = 5.65 \times 10^7$ rad/s and $\mu_3 = 5.0 \times 10^4$ N/m², where h_3 is kept constant above 1.1×10^4 g/mol.

this point and resonates with the oscillating plate. Furthermore, the value of the real part is $\frac{\Delta J}{2}$ at this point. This means that $\frac{\Delta J}{2}$ is related to the molecular length resonating with the oscillating plate, i.e., the resonant length. Therefore, we adapt this concept to the present experimental data.

In our experiments, the ΔD slope corresponds to J' of equation (3) and M_n is comparable to τ of equation (3). Therefore, we fitted the real part of equation (3) to the experimental values of the ΔD slope (Fig. 5). We found that the value of the ΔD slope corresponding to $\frac{\Delta J}{2}$ is 2.3×10^{-3} (gcm⁻²s^{-1/2})⁻¹.

Next, we investigated the relationship between $\frac{\Delta J}{2}$ and resonant length. From Fig. 5, the M_n value corresponding to 2.3×10^{-3} is ca. 1.1×10^4 g/mol. Furthermore, the following relationship is proposed between molecular weight, M and gyration radius, R_g ¹³⁾:

$$R_g = 0.215M^{0.583 \pm 0.031}. \quad (4)$$

When M_n is considered as M , the R_g value obtained is 48.8 Å ($= 0.215M^{0.583}$)^{6, 7, 13)}. That means that the PEG length of 97.6 Å ($= 2R_g$) moves with the oscillating QCM of 9 MHz.

4.2 Behavior of ΔD intercept in PEG solutions

The ΔD intercept arises from the thin layer of PEG formed by physical adsorption^{16, 38)}. From Fig. 3, we can see that the ΔD values vary linearly with $\sqrt{\rho_2 \eta_2} - \sqrt{\rho_w \eta_w}$. This means that the properties of the thin PEG layer are independent of the bulk concentration over the range of concentrations tested. In addition, we can see from Fig. 5 that the values of the ΔD intercept increase with M_n and become constant above PEG-6K. We can exactly determine the molecular weight above which the ΔD intercept becomes constant.

To obtain further insight into the ΔD intercept, we discuss properties of the thin layer on the basis of the following equations proposed by Voinova *et al.*¹⁶⁾:

$$\Delta f_V = \text{Im} \left(\frac{\beta}{2\pi\rho_q h_q} \right), \quad (5)$$

$$\Delta D_V = -\text{Re} \left(\frac{2\beta}{\omega_q \rho_q h_q} \right), \quad (6)$$

$$\beta = \kappa \xi \frac{1 - A \exp(2\xi h_3)}{1 + A \exp(2\xi h_3)}, \quad (7)$$

$$A = \frac{\kappa \xi + \lambda \zeta \tanh(\lambda h_1)}{\kappa \xi - \lambda \zeta \tanh(\lambda h_1)}, \quad (8)$$

$$\kappa = \eta_3 - i \frac{\mu_3}{\omega_q}, \quad \xi = \sqrt{-\frac{\rho_3 \omega_q^2}{\mu_3 + i \rho_q \eta_3}}, \quad (9)$$

$$\lambda = \eta_1, \quad \zeta = \sqrt{\frac{i \rho_1 \omega_q}{\eta_1}}, \quad (10)$$

where Δf_V is the series resonant-frequency shift, ΔD_V is the shift in the energy dissipation factor, h is the thickness and the subscript 3 indicates the thin layer. These equations describe properties of the one thin layer formed on the QCM in a Newtonian liquid, where the non-slip condition has been applied to the thin layer. Furthermore, the expansion of the β expression in $\text{Re}(\xi h_3) \ll 1$, $\text{Im}(\xi h_3) \ll 1$ leads to the following equations:

$$\Delta f_V = \frac{-1}{2\pi\rho_q h_q} \left\{ \frac{\eta_1}{\delta_1} + h_3 \rho_3 \omega_q - 2h_3 \left(\frac{\eta_1}{\delta_1} \right)^2 \frac{\eta_3 \omega_q^2}{\mu_3^2 + \omega_q^2 \eta_3^2} \right\}, \quad (11)$$

$$\Delta D_V = \frac{2}{\omega_q \rho_q h_q} \left\{ \frac{\eta_1}{\delta_1} + 2h_3 \left(\frac{\eta_1}{\delta_1} \right)^2 \frac{\mu_3 \omega_q}{\mu_3^2 + \omega_q^2 \eta_3^2} \right\}, \quad (12)$$

$$\delta_1 = \sqrt{\frac{2\eta_1}{\rho_1 \omega_q}}, \quad (13)$$

where δ_1 is the penetration depth.

Equations (11) and (12) show that the physical properties of the ΔD_V intercept are clearly different from those of Δf_V . The ΔD_V intercept depends on the thickness, viscosity and elasticity of the thin layer, but not the density of the layer. If elasticity of the thin layer is zero, the ΔD_V intercept does not appear. Thus, the appearance of the ΔD intercept means that the thin PEG layer has a non-zero value of elas-

ticity.

In our study, the values of the ΔD intercept are those at infinite dilution. In other words, the present experimental data of the ΔD intercept are of the thin layer immersed in pure water, which shows properties of a Newtonian liquid. In addition, the non-slip condition can be applied to the physical adsorption of PEG molecules onto the gold electrode at infinite dilution¹⁸⁾. As a result, the present experimental data of the ΔD intercept can be discussed on the basis of equation (12).

Equation (12) shows that the ΔD_V intercept arises from the second term in relation to the thin layer. This further supports the idea that the ΔD intercept is caused by the thin PEG layer. Figure 5 shows that the values of the ΔD intercept become constant beyond the thickness of a PEG-6K layer. This result suggests that the variation in the ΔD intercept with M_n is mainly caused by the thickness of thin PEG layer. Therefore, equation (12) leads us to the assumption that the ΔD_V intercept in a PEG thin layer is mainly dependent on h_3 , and the value of $\left(\frac{\eta_1}{\delta_1}\right)^2 \frac{\mu_3 \omega_q}{\mu_3^2 + \omega_q^2 \eta_3^2}$ is always independent of M_n . This means the variations in density, viscosity and elasticity of the thin layer due to M_n are negligible.

Based on the above assumption, in the case of infinite dilution at 25°C ($\eta_1 = \eta_3 = 8.90 \times 10^{-4}$ Ns/m² and $\rho_1 = \rho_3 = 997$ kg/m³), we can estimate the value of elasticity of the thin layer to be a constant at 5.0×10^4 N/m². The variation of the ΔD_V intercept with M_n (h_3 calculated from equation (4)) is shown in Fig. 5. The theoretical value is consistent with the experimental data, where h_3 is set at a constant value, when M_n is greater than 1.1×10^4 g/mol.

This result supports the assumption that the variation in the ΔD_V intercept in a thin PEG layer with M_n is mainly caused by h_3 . In addition, we can observe that the ΔD intercept becomes constant when the molecular weight is above 1.1×10^4 g/mol. The value of 1.1×10^4 g/mol is also equal to the resonant length of the ΔD slope. Thus, it can be derived that the thickness of the thin PEG layer above the resonant length does not affect the ΔD intercept.

In conclusion, we found that the main factor determining the variation in the ΔD intercept with M_n is the thickness of the thin layer and that the ΔD intercept becomes constant above the resonant length of the PEG molecule.

4.3 Comparison between the resonant lengths of ΔD and ΔF

In the previous report³⁷⁾, the series resonance-frequency shift, ΔF , was used to estimate the resonant length to be 54.2 Å in the regions of both the thin layer and the viscous penetration depth. On the other hand, in this work, the consideration of ΔD leads to a resonant length of 97.6 Å. The difference in the resonant length between ΔD and ΔF is 43.4 Å. In this section, we want to address this differ-

Fig. 6 Numerically calculated shift of Δf_v and ΔD_v versus thickness of the thin layer. The solid line and the dashed line show the values calculated from equations (5) and (6) with $\eta_1 = \eta_3 = 8.90 \times 10^{-4}$ Ns/m², $\rho_1 = \rho_3 = 997$ kg/m³, $\rho_q = 2648$ kg/m³, $h_q = 1.84 \times 10^{-4}$ m, $\omega_q = 5.65 \times 10^7$ rad/s and $\mu_3 = 5.0 \times 10^4$ N/m². The solid line and the dashed line show Δf_v and ΔD_v , respectively.

ence.

Using equations (5) and (6), we calculated the values of Δf_v and ΔD_v as a function of the thickness of the thin layer. The results are shown in Fig. 6. The thicknesses corresponding to the maximum values of Δf_v and ΔD_v are different and $h_f < h_D$, where h_f and h_D are the thickness corresponding to the maximum values of Δf_v and ΔD_v , respectively. The values of h_f and h_D correspond to the resonant lengths of PEG molecules. On comparing equations (11) and (12), it is obvious that this difference is based on the density of the thin layer.

In this work, we found that the density of the thin layer plays an important role in the dynamic properties of PEG at the solid-liquid interface, and that the resonant length is dependent on the measurement parameters.

5 CONCLUSIONS

We investigated the dynamic properties of PEG molecules on a QCM plate oscillating at 9 MHz in terms of ΔD . This study yielded the following results.

1. The values of the ΔD slope against M_n decrease according to the Debye process (equation (3)) and is caused by the effect of viscous penetration depth.
2. The values of the ΔD intercept increase according to equation (12) and become constant above the resonant length. This behavior is caused by the formation of a

thin layer of PEG on the QCM surface and is related to the length of the PEG molecule.

3. From the point of view of ΔD , PEG of length 97.6 Å moves with the oscillating plate at a frequency of 9MHz in the regions of the thin layer and viscous penetration depth.
4. The resonant length calculated using ΔD is larger than that calculated using ΔF . This difference between the resonant lengths of ΔD and ΔF results from the density of the viscoelastic thin layer.

In conclusion, the behavior of PEG solutions clearly differs from that of a Newtonian liquid. Identifying the length of the polymer molecule moving with the QCM plate is very important to understanding the dynamic properties of polymer molecules at a solid-liquid interface.

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