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Viscoelastic Analysis in the Formation of Organic Thin Films

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The initial stage of film formation has been analyzed using the quartz crystal microbalance (QCM) method. The resonance frequency and resistance of the QCM covered with paraffin thin film indicate that the viscoelastic properties of films can be changed even before the film formation from the melt or the solution, i.e., pre-transition phenomena can be observed. The QCM analysis also reveals that liquid crystalline molecules can be adsorbed as a solid phase in the vicinity of the interface even in the nematic liquid crystal phase.

Keywords: alignment; humidity; liquid crystal; polar group; surface

1. INTRODUCTION

Formation of organic thin films includes a solidification process from the melt, the solution or the vapor. Unfortunately, the details are hard to analyze by the methods used for metal or inorganic thin films, because organic materials can easily be damaged by the high incident energy, which is essential in the measurement of the structure, such as X-ray diffraction, electron diffraction and the electron microscopes. Hence numbers of researchers have been trying to develop a novel method using weak coupling between a probe signal and the sample material.

The quartz crystal microbalance (QCM) technique has been used to monitor mass variations of thin films by employing the linear relation given by Sauerbrey equation [1]. Using the relation, as reported in our

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previous paper, the average lifetime and the adsorption energy of admolecules on the substrate surface can be estimated on the basis of a modified adsorption model [2]. The QCM technique can also be used to analyze the viscosity of fluids. It was verified experimentally that quartz resonators could also respond to properties of a contact liquid [3,4]. Kanazawa *et al*. reported that the frequency shifts of the QCM in contact with homogeneous viscous fluids are proportional to the square root of the viscosity coefficients [5]. Furthermore, Muramatsu *et al*. have represented a simple linear relation between the resonant resistance and the square root of the viscosity coefficient [6]. In more general situations, such as nonrigid or viscoelastic films, QCM impedance measurements around the resonant frequency of the quartz crystal have been successfully employed. For example, the viscoelastic behavior during the electrodeposition of conducting polymer films has been reported [7].

In this study, we investigate the initial stage of the formation processes of organic thin films by using the QCM method, which can also give us information about the viscoelastic properties as well as the amount of adsorbate. Our particular interests are the visco-elastic behavior during the thin film formation.

2. ANALYTICAL DETAILS

2.1. Elastic Solid and Viscous Fluid Adlayers

The resonant frequency shift Δf is simply proportional to the mass m of the elastic adlayer on the AT-cut quartz crystal [1]. In the present apparatus, the proportionality constant is $-1.15\,\mathrm{Hz/ng}$, i.e., $\Delta f = -1.15 \times m$. On the basis of the shear vibration of the quartz crystal in contact with liquid, the resonant frequency shift Δf due to the viscosity η of the fluid is proportional to the square root of η [5]. In the present system, the proportionality constant is $-1.20 \times 10^2\,\mathrm{Hz/Pa^{1/2}}$, i.e., $\Delta f = -1.20 \times \eta^{1/2}$. For the viscous liquid adlayer, the resonant resistance R is also proportional to the square root of the viscosity coefficient [6]. Hence, the resonant resistance is proportional to the frequency shift if the adlayer is a pure viscous medium like liquid that exhibits no elasticity.

2.2. Viscoelastic Adlayer

The frequency shift for viscoelastic medium is rather complicated to analyze because it depends both on the mass and on the viscosity, whereas the resonant resistance is simply proportional to the square

root of the viscosity coefficient. On the assumption that the frequency shift is the sum of two contributions from the mass and the viscosity, it can approximately be expressed as follows:

$$\begin{aligned}\Delta f &= \Delta f_{\mathrm{m}} + \Delta f_{\mathrm{v}} \\ &= am + b\sqrt{\eta}, \end{aligned} \tag{1}$$

where Δf is the total frequency shift, Δf_{m} is the ideal frequency shift by adsorbed mass associated with the elasticity, Δf_{v} is the ideal frequency shift by viscous fluid, m is the adsorbed mass and a, b are constants. The constant a should be zero for a viscous liquid adlayer, while the constant b should be zero for an elastic solid adlayer. Here we will introduce a parameter by which we can estimate the contribution of elasticity. The ratio $-\Delta f/\mathrm{R}$ (>0) is suitable for this purpose,

$$-\frac{\Delta f}{R} = a' \frac{m}{\sqrt{\eta}} + b' \tag{2}$$

where a', b' are constants. If the adlayer consists of viscous liquid, the constant a' should be zero and the ratio $-\Delta f/R$ is constant, i.e., independent of the viscosity coefficient. As increasing elasticity, the constant a' increases and thus the ratio $-\Delta f/R$ become larger. Therefore we can separate the two contributions to the frequency shift, i.e., the mass change and the viscosity change. For example, if the frequency decreases but the ratio is constant, this change is attributed to the viscosity change but the adsorption of the mass.

3. EXPERIMENTAL

3.1. Preparation of Thin Films

Paraffin ($C_{20}H_{42}$) was dissolved in ethanol and the solution was cast on the surface of quarts crystal (9 MHz) with gold electrodes. The quartz crystals were set in a Teflon housing with synthetic rubber o-rings as shown in Figure 1. After the solvent was evaporated, a paraffin thin film was formed on the surface.

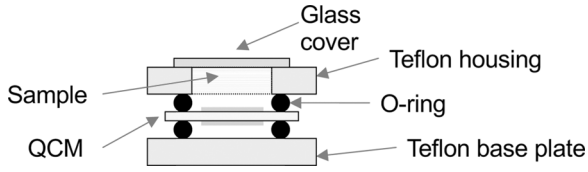

FIGURE 1 Schematic illustration of the QCM sensing head.

The liquid crystal used was *p*′-pentyl-*p*-cyanobiphenyl (5CB). A small amount of 5CB was dropped on the surface of quarts crystal (9 MHz) with gold electrodes to form thin adlayer of 5CB. Some of the substrates were coated with chitosan having polar functional groups on the surface. The chitosan films were prepared from chitosan dissolved in dilute hydrochloride by the dipping method.

3.2. Measurement

The resonance frequency shift Δf and the resistance R of the QCM were monitored with a quartz crystal analyzer QCA922 (Seiko EG&G). The sample was maintained at a constant temperature within the deviation of 1 K by a thermo-regulator. A cover glass was set on the top of the cell holder to avoid exposure to the humid air, as shown in Figure 1.

4. RESULTS AND DISCUSSION

4.1. Paraffin Films

Figure 2 shows time evolution of the frequency decrease $-\Delta f$ and R of the QCM covered with a paraffin solution. After 250 s from the drop of

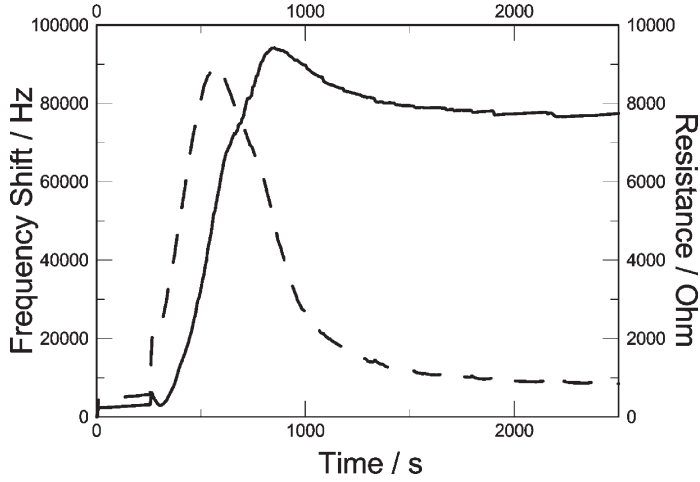

FIGURE 2 Time evolution of QCM results during the film formation by solution casting: resonant frequency shift $-\Delta f$ (solid line) and resonant resistance R (dashed line).

solution, $-\Delta f$ increases, i.e., the resonant frequency decreases, and R also increases. This indicates that the solvent evaporates and the viscosity of the solution increases. At 600 s, $-\Delta f$ increases but R decreases. This indicates that crystallization takes place and the contribution of viscosity decreases, i.e., elasticity becomes dominant. After 800 s, both $-\Delta f$ and R decrease indicating that the film become more elastic. The film was somewhat swollen, i.e., it may still contain the solvent in the space between crystals, and then solidified further as the solvent evaporates.

Figure 3(a) shows time evolution of $-\Delta f$ and R of the QCM covered with a paraffin thin film during cooling from the melt. First, both $-\Delta f$ and R increases in the same manner because each of them is proportional to the viscosity in the liquid phase. Next, the abrupt change can be seen at 320 s in both curves, indicating crystallization of paraffin from the melt. It should be noted that, before crystallization takes place, $-\Delta f$ exhibits remarkable change different from R, as clearly shown in Figures 3(a) and (b). This indicates that the nature of the film can be changed even before the crystallization from the melt, i.e., pre-transition phenomena can be observed. Crystallization may occur in the vicinity of the interface before the whole film is crystallized. Such crystallization would be associated with initial nuclei in the model of heterogeneous nucleation.

4.2. Liquid Crystal Films

Figure 4(a) shows time evolution of $-\Delta f$ and R of the QCM covered with a 5CB layer on a gold surface. After dropping 5CB onto the gold surface, both $-\Delta f$ and R asymptotically increase in the same manner with small fringes, indicating that the viscosity increases. Considering that the viscosity of liquid crystal strongly depends on the orientation of the director, the increase in the viscosity can be ascribed to the orientational change from planar to homeotropic because the molecules can more easily slip each other in the direction along the molecular axis than in the direction perpendicular to the molecular axis. Here it should be noted that the fringes are completely cancelled in the ratio $-\Delta f/R$ as shown in Figure 4(b). If the adlayer is liquid and thus the parameter a' in Eq. (7) associated with the degree of elasticity is negligible, the ratio $-\Delta f/R$ is independent of viscosity change. Therefore the fringes are due to the viscosity change associated with the temperature deviation ($\pm 1^{\circ}$C) of the thermo-regulator.

For a 5CB layer on a chitosan surface (Fig. 5), after dropping 5CB onto chitosan, R asymptotically increases with small fringes in the

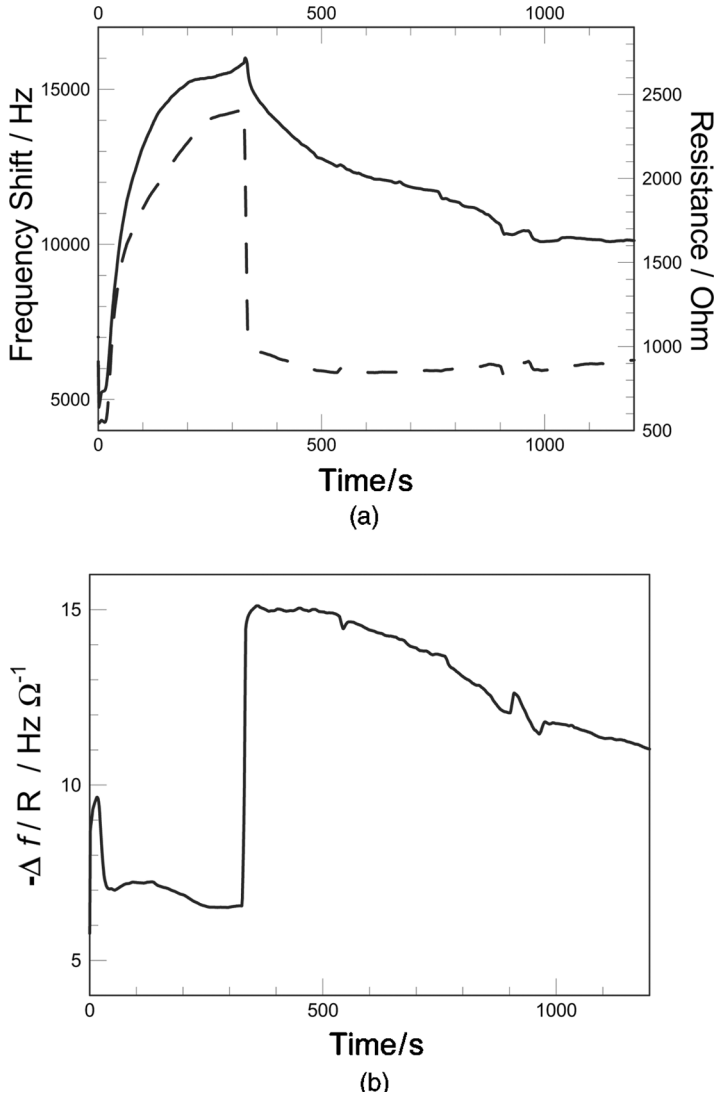

FIGURE 3 Time evolution of QCM results during the film formation from the melt: (a) resonant frequency shift $-\Delta f$ (solid line) and resonant resistance R (dashed line), and (b) the ratio $\Delta f/R$, which is associated with the contribution of viscosity.

same manner as in the case of the 5CB adlayer on gold, indicating an orientational change. In contrast, $-\Delta f$ increases at an almost constant rate, suggesting the viscoelasticity change of the adlayer.

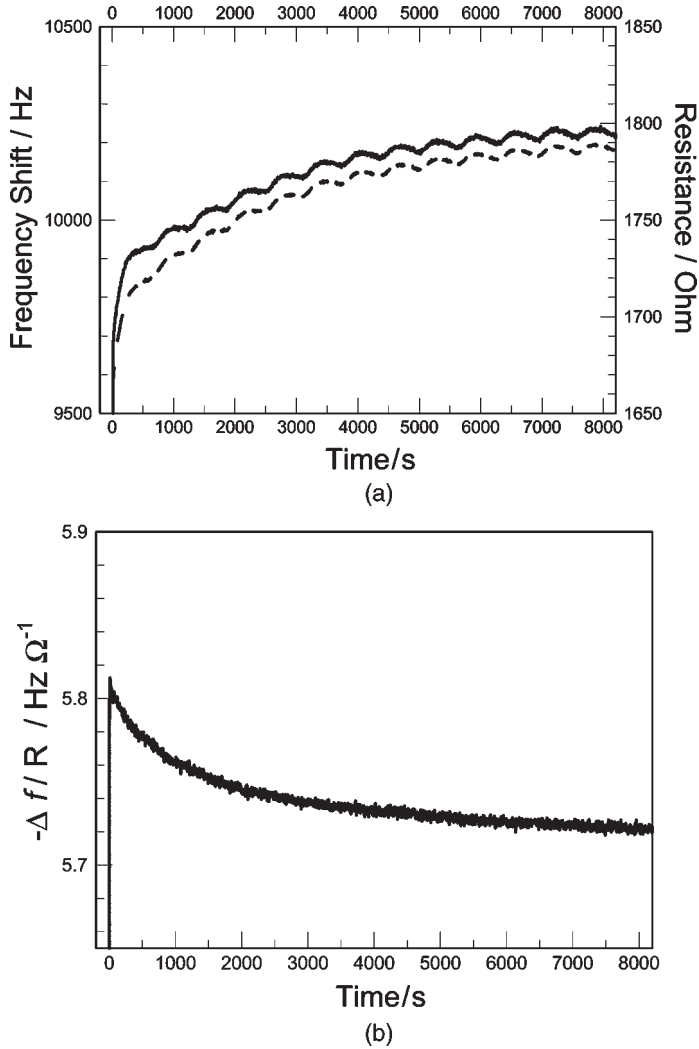

FIGURE 4 Time evolution of QCM results of liquid crystal adlayer on the gold electrode of the QCM: (a) resonant frequency shift $-\Delta f$ (solid line) and resonant resistance R (dashed line), and (b) the ratio $\Delta f/R$, which is associated with the contribution of viscosity.

Here it should be noted that the ratio $-\Delta f/R$ increases after 2500 s, as shown in Figure 5(b), whereas the ratio is almost constant for a 5CB adlayer on gold shown in Figure 4(b). Therefore the adlayer becomes more elastic, i.e., the liquid crystalline molecules can behave like a

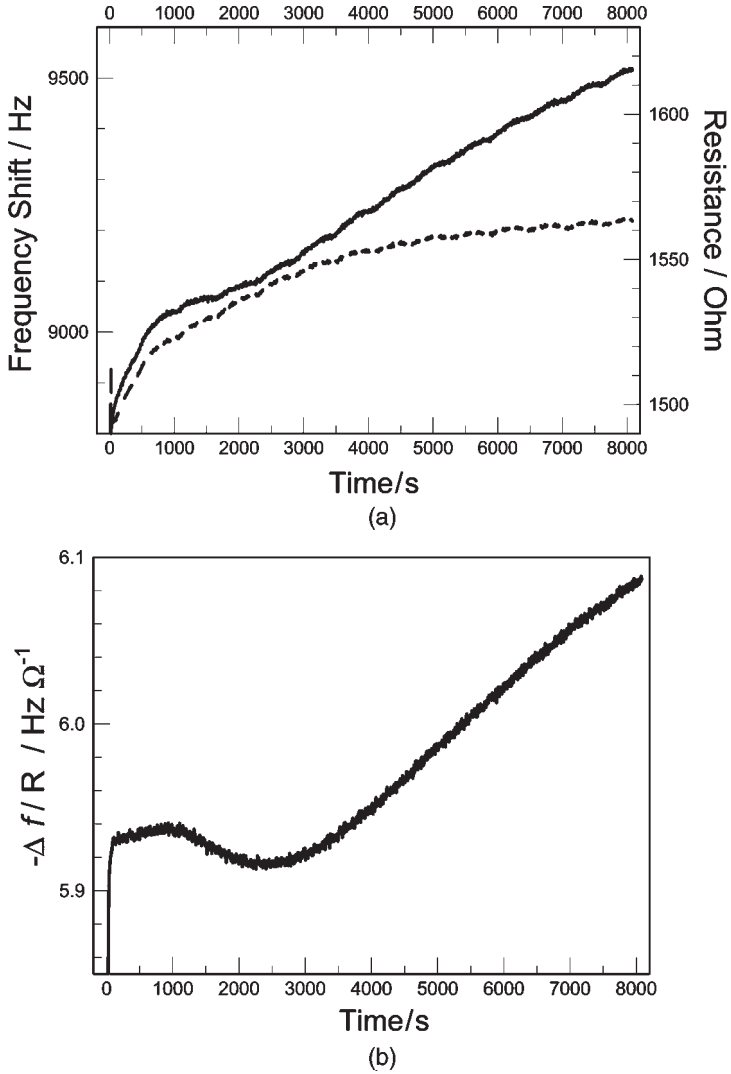

FIGURE 5 Time evolution of QCM results of liquid crystal adlayer on the chitosan film prepared in advance on the QCM surface: (a) resonant frequency shift $-\Delta f$ (solid line) and resonant resistance R (dashed line), and (b) the ratio $\Delta f/R$, which is associated with the contribution of viscosity.

solid. The strong interaction between functional groups of 5CB and chitosan may reduce molecular motion and could induce aggregation like crystallization in the interlayer even in the nematic temperature range.

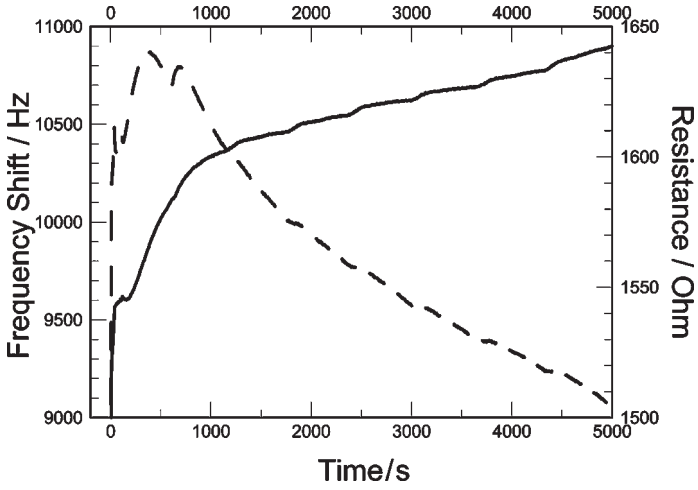

FIGURE 6 Time evolution of QCM results of liquid crystal adlayer on the chitosan film prepared in advance on the QCM surface with exposure to the humid air: resonant frequency shift $-\Delta f$ (solid line) and resonant resistance RR (dashed line).

4.3. Exposure to Humid Air

If water vapor in the atmospheric air is adsorbed on or dissolved in the adlayer, the viscoelastic properties should vary largely. We examined the humidity effects without using a cover glass shown in Figure 1, while in the previous experiment we used a cover glass to avoid exposure of the sample to the air. Figure 6 shows time evolution of $-\Delta f$ and R for a 5CB layer on a chitosan surface without a cover glass. After dropping 5CB onto chitosan, R asymptotically increases with small fringes in the same manner as in the case of the 5CB adlayer on gold or chitosan in the case of using a cover glass. However, $-\Delta f$ first increases but starts to decrease at 300 s. This shows that the viscosity significantly decreases after 300 s. This decrease is due to contamination of water. It is found that the QCM technique can be used to monitor extremely small quantity of contaminants coming from the atmosphere.

5. CONCLUSION

Analysis of visco-elasticity has been performed during thin film formation by using QCM. The solvent was evaporating even after solidification. It can evaporate from swollen crystal. The melt was partly

crystallized before apparent crystallization. Orientation of LC adsorbed on the substrate was changed from lateral to normal for several hours. LC molecules behave like a solid on chitosan substrate. If exposed in a humid air, LC shows a smaller apparent viscosity, because water molecules were diffusing through the LC layer to reach at the substrate surface. Visco-elastic measurement by QCM is one of the most promising tools for in-situ observation of thin film formation.

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