

Detection of Deposition Rate of Plasma-Polymerized Films with a Quartz Crystal Microbalance

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The deposition rates of plasma-polymerized (pp-) films of vinyl acetate, vinyl trifluoroacetate, vinyl 2-chloroacetate, vinyl butanoate, vinyl pivalate, vinyl 2-butenate, vinyl hexanoate and styrene are determined by the quartz crystal microbalance. Using the same polymerization conditions (100 W RF and 100 Pa vapor pressure) for the various monomers, the deposition rates were determined to be constant within the interval measured. The deposition rates of pp-vinyl acetate, pp-vinyl trifluoroacetate, pp-vinyl 2-chloroacetate, pp-vinyl butanoate, pp-vinyl pivalate, pp-vinyl 2-butenate, vinyl hexanoate and pp-styrene were scattered on the different position of measure on the position of the lower electrode in the plasma polymerization equipment. The average deposition rate of pp-vinyl acetate was 0.28 $\mu\text{g}/\text{min}$. The average deposition rate of pp-vinyl trifluoroacetate was higher by 15 times, and that of pp-vinyl 2-chloroacetate was higher by 23 times than that of pp-vinyl acetate. The average deposition rate depended on the chemical structure of the monomer.

Keywords: plasma polymerization, deposition rate, quartz crystal microbalance, vinyl esters

1. Introduction

Plasma polymerization has been widely used to fabricate thin and ultrathin films from a variety of volatile compounds. These films adhere firmly to most substrates and are highly resistant to chemical and physical treatment. The plasma polymerization technique has also been conventionally employed to fabricate thin functional films that could facilitate the surface modification of materials [1-2]. Such films are expected to be useful as molecular recognition films rigidly fixed on the transducers of chemical sensors [3-5]. The deposition rates in plasma polymerization have been determined using a balance or by measurement of the film thickness

using a multi-interference thickness meter [6-10]. These methods cannot, however, detect the deposition rates of ultra-thin films. The piezoelectric quartz crystal is well known to be useful as a microbalance (quartz crystal microbalance: QCM). Adsorption of material on the surface of a crystal changes its oscillation frequency. When an AT-cut quartz crystal with its fundamental oscillation frequency of 9MHz is used, adsorption of about 1ng of material decreases the oscillation frequency by 1Hz [11-12]. Many attempts have been made to use these highly sensitive, convenient and portable units of equipment as chemical sensors and immunosensors [13-16]. The QCM has also been

used to monitor the thickness of films during vapor deposition and plasma processes. The deposition rates of gaseous monomers in plasma polymerization have been thoroughly investigated [6-10], whereas those of liquid monomers have not yet been reported.

In this paper, plasma-polymerized films are prepared from eight monomers; vinyl acetate, vinyl trifluoroacetate, vinyl 2-chloroacetate, vinyl butanoate, vinyl pivalate, vinyl 2-butenate, vinyl hexanoate and styrene. These monomers are polymerized under the polymerization conditions of 100 W RF and 100 Pa vapor pressure of each monomer. The present work constitutes a preliminary study aimed at detecting the deposition rates of plasma-polymerized films using the QCM in order to gain an understanding of the deposition mechanisms of vinyl esters.

2. Experimental

2.1. Materials

The monomers vinyl acetate, vinyl trifluoroacetate, vinyl 2-chloroacetate, vinyl butanoate, vinyl pivalate, vinyl 2-butenate, vinyl hexanoate and styrene used in this experiment were all of analytical or guaranteed grade and were purchased from Shin-Etsu Vinyl Acetate Co., Ltd. (Osaka, Japan), or Wako Chemical Co. Inc. (Tokyo, Japan) and used without further purification. Table 1 indicates the chemical structure of monomer for plasma polymerization and its boiling point. For plasma polymerization, plasma polymerization equipment, model BP-1 Mark II, from Samco International Co. (Kyoto, Japan) was used [17-19]. Figure 1(a) shows a schematic of the plasma polymerization equipment.

The deposition rates of the pp-films were measured with a QCM during the polymerization process. The QCM with gold electrodes on both its surfaces (AT-cut of 9 MHz: $8 \times 8 \times 0.15$ mm) was purchased from Yamagata Crystal Co. (Yamagata, Japan). The pp-films were deposited on one side of the QCM. The deposition rates of the plasma-polymerized films are dependent on the positioning of the substrates. Therefore, seven QCMs were placed on the lower electrode (diameter 100 mm) for the glow discharge. The position settings of the seven QCMs on the lower electrode are denoted as shown in Fig. 1(b). Prior to plasma polymerization, the seven QCMs were treated by plasma sputtering for 5 s under 100 W of RF power and 100 Pa of He pressure.

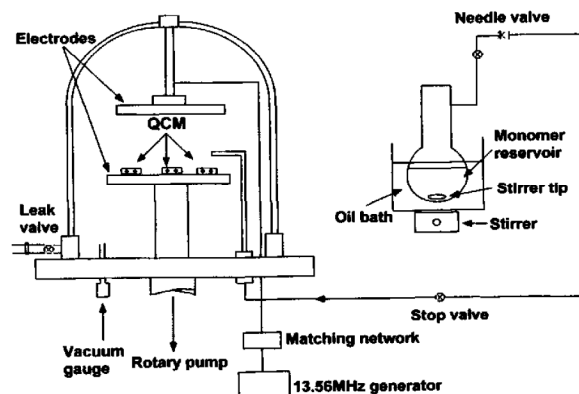


Fig. 1a. Schematic of the plasma polymerization equipment.

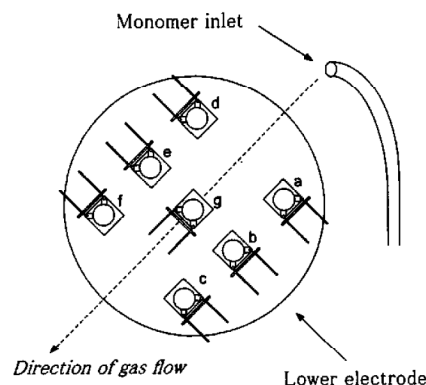


Fig. 1b. Position settings (a to g) of seven QCMs on the lower electrode.

The plasma polymerization conditions were controlled by two parameters: the vapor pressure of the monomer and the power of the glow discharge. We used the same polymerization conditions for all eight monomers: a vapor pressure of each monomer 100 Pa, and an RF power of 100 W. The monomers were vaporized at a constant temperature of liquid, maintained using an oil bath, and controlled vacuum. The distance between the electrodes was 6 cm and the power of the glow discharge was set at 100 W. The plasma polymerization was performed for 1,800 seconds with interruptions for measurements at 300, 600, 900, 1,200, 1500 s. We obtained an optimum film-state of the polymers under these conditions. The apparatus and procedure for determination of the deposition rate have been described previously [19]. The oscillating frequency of the QCM is measured using a universal counter with data stored in a microcomputer. The transistor-transistor logic

electronic circuit used is described in ref. 13 (circuit II). The relationship between the weight of the pp-films and the frequency shift is expressed in units of ng/Hz. All experiments for determination of the deposition rate of plasma polymer by QCM were carried out at $25 \pm 2^\circ\text{C}$.

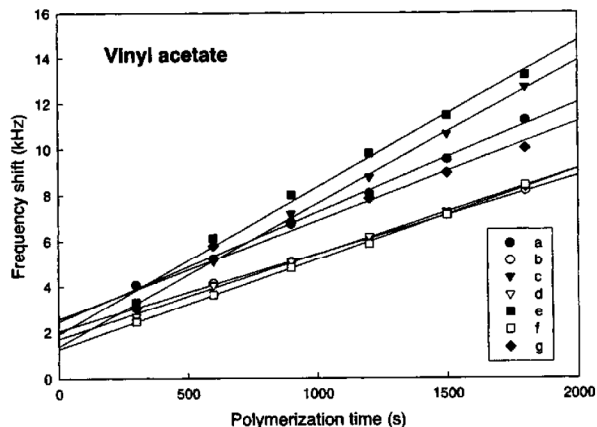


Fig. 2. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-vinyl acetate.

The deposition rates of the pp-films onto the QCM were measured directly by the shift in the oscillating frequency. Figure 2 shows the relationship between the deposition rate of pp-vinyl acetate for the seven positions (a to g) of the lower electrode and the polymerization time. A linear relationship was observed up to a polymerization time of 1,800 s. The regression of the polymerization time response for the positions a to g is summarized in Table 2. We define the individual deposition rates of the plasma-polymerized films using the slope of the line a to f for each sample. The averaged deposition rate for the pp-vinyl acetate film is 4.68 Hz/s ($0.28 \mu\text{g}/\text{min}$). Figures 3-9 show the same relationship for pp-vinyl trifluoroacetate, pp-vinyl 2-chloroacetate, pp-vinyl butanoate, pp-vinyl hexanoate, pp-vinyl pivalate, pp-vinyl 2-butenate, pp-vinyl hexanoate and pp-styrene, respectively. The range of linearity is also included. Outside this range, or above the formed thickness, the QCM does not work as a microbalance.

Table 3 summarizes the averaged deposition rates for the eight monomers. The values are in the order of vinyl 2-chloroacetate > vinyl trifluoroacetate > styrene > vinyl 2-butenate > vinyl hexanoate > vinyl pivalate > vinyl butanoate > vinyl acetate. Thus, the deposition rate of the pp-films is affected by the chemical structure of the monomer.

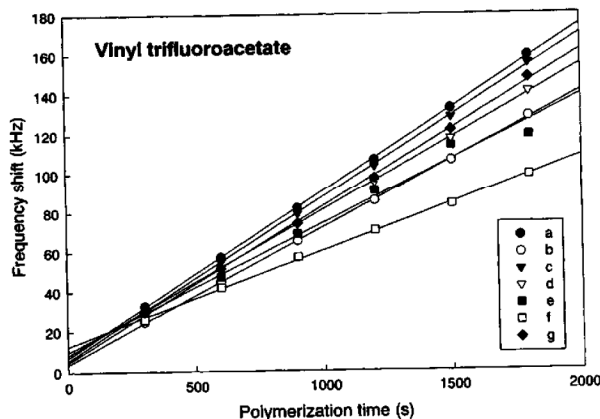


Fig. 3. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-vinyl trifluoroacetate.

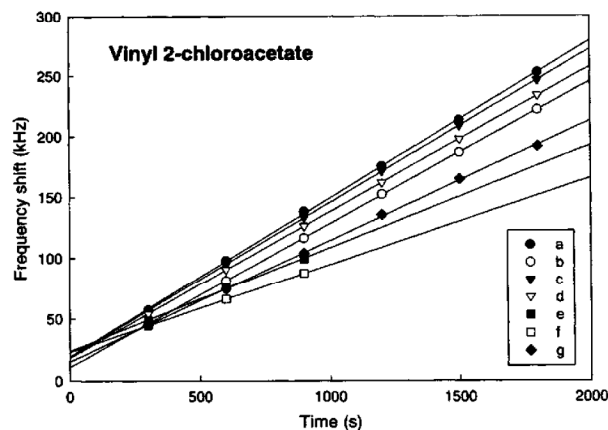


Fig. 4. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-vinyl 2-chloroacetate.

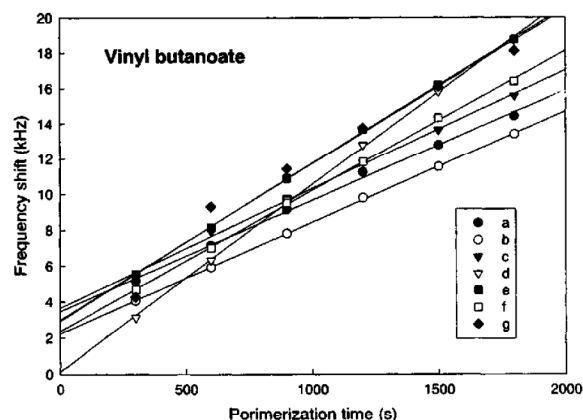


Fig. 5. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-vinyl butanoate.

Table 1. The chemical structure of vinyl esters for plasma polymerization

Monomer	chemical structure	b.p.(°C/mmHg)
Vinyl acetate	$\text{CH}_2=\text{CHOCOCH}_3$	72.7 / 760
Vinyl trifluoroacetate	$\text{CH}_2=\text{CHOCOCF}_3$	39.0 / 760
Vinyl 2-chloroacetate	$\text{CH}_2=\text{CHOCOCH}_2\text{Cl}$	136.0 / 760
Vinyl butanoate	$\text{CH}_2=\text{CHOCO}(\text{CH}_2)_2\text{CH}_3$	116.7 / 760
Vinyl hexanoate	$\text{CH}_2=\text{CHOCO}(\text{CH}_2)_4\text{CH}_3$	166.0 / 760
Vinyl pivalate	$\text{CH}_2=\text{CHOCOC}(\text{CH}_3)_3$	111.0 / 760
Vinyl 2-butenate	$\text{CH}_2=\text{CHOCOCH}=\text{CHCH}_3$	132.7 / 760
Styrene	$\text{CH}_2=\text{CHC}_6\text{H}_5$	145 / 760

Table 2. Deposition rates of pp-vinyl acetate films

Position	Slope $\times 10^3$	Intercept	Correlation coefficient
a	4.78	2.464	0.997
b	3.38	2.045	0.999
c	6.24	1.372	0.999
d	3.71	1.704	0.998
e	6.42	1.911	0.991
f	3.92	1.264	0.999
g	4.30	2.566	0.956

Table 3. Average of deposition rates of pp-films

Monomer	Deposition rate ($\mu\text{g}/\text{min}$)	σ $\times 10^2$	C.V. $\times 10^2$
Vinyl acetate	0.28	7.3	25.9
Vinyl trifluoroacetate	4.27	74.4	17.4
Vinyl 2-chloroacetate	6.40	134.2	21.0
Vinyl butanoate	0.47	9.5	20.1
Vinyl hexanoate	0.70	16.1	23.1
Vinyl pivalate	0.51	7.4	14.4
Vinyl 2-butenate	1.04	17.9	17.2
Styrene	2.08	39.0	18.7

The average of deposition rates of the pp-films are calculated from the slope of the seven lines (a to g) in the Figures. σ and C.V. represent the standard deviation and the coefficient of variation, respectively.

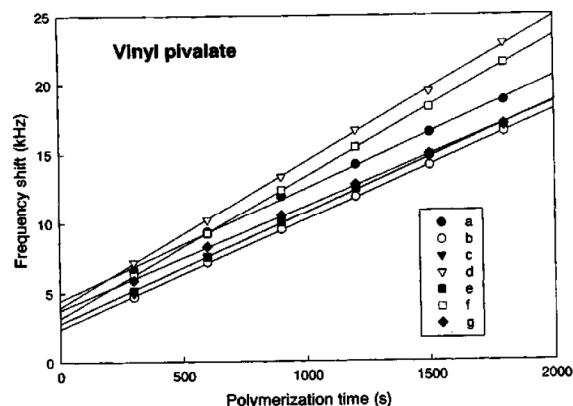


Fig. 6. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-vinyl pivalate.

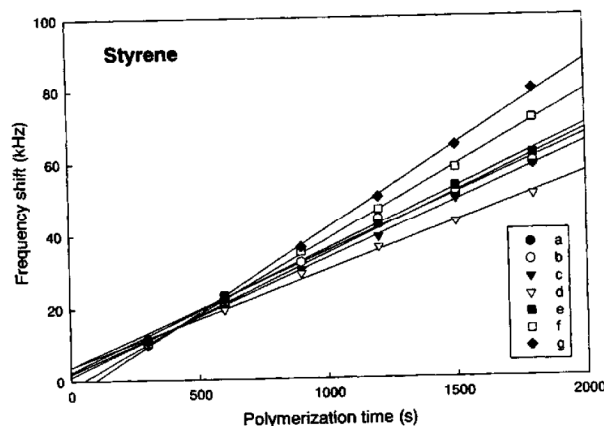


Fig. 9. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-styrene.

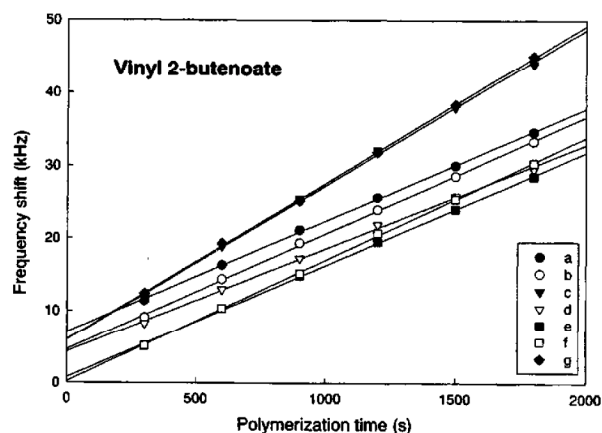


Fig. 7. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-vinyl 2-butenate.

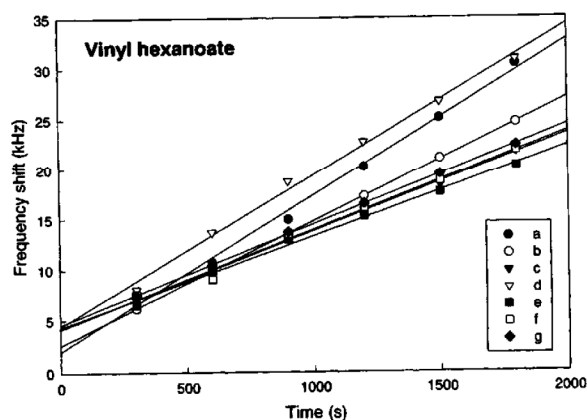


Fig. 8. Linear relationship between the polymerization time and oscillation frequency shift of QCM coated with pp-vinyl hexanoate.

All the polymerizations were conducted under the identical conditions in terms of the settings on the equipment, which give higher gas phase concentration of the monomers with lower boiling points. This concentration effect is, however, often cancelled by the reaction pathway of the different monomers. Polymerization is assumed to proceed via a free-radical mechanism initiated through the collision of an electron with a monomer molecule. Dissociation of this molecule results in the formation of free radicals which may add to intact monomers, denoted as the initiation. Polymerization then proceeds in the gas phase and on the surface. Finally, collision between two radicals leads to termination of the reaction by radical-radical coupling or disproportionation, as in the case of standard free radical polymerization.

If the monomers are polymerizable by conventional free radical polymerization, plasma polymerization may proceed simultaneously with plasma-induced polymerization, resulting in high deposition rates. In our study, styrene, vinyl trifluoroacetate and vinyl 2-chloroacetate were deposited at higher rates. Reaction may be considered as an "initiation" that is promptly followed by termination without any intermediate steps of propagation. A unique feature of plasma polymerization of "normal" monomers is that the system may become starved of monomers. We assume that the rate of polymerization is mainly determined by the rate of initiation and not by the rate of propagation [20]. The termination of growing chains is suppressed by the immobility of the plasma-polymerized layer, making the termination rate low. Actually, the typical values of the rates of propagation and rate of termination

are $4,600 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $220\times 10^{-6} \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, respectively, for vinyl acetate and 40 ± 20 and $80 \pm 40\times 10^{-6} \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, respectively, for styrene [21]. Our finding that styrene has an almost seven times higher deposition rate than vinyl acetate might at least in part be attributed to the effect of initiation-limited polymerization.

Our finding that styrene has an almost seven times higher deposition rate than vinyl acetate might at least in part be attributed to the effect of initiation-limited polymerization. Hence, a fascicle formation of the initiating radical increases its concentration and thereby the rate of polymerization. We hypothesizes that another way of increasing the initiating radical concentration is by higher yield of radicals produced in the plasma. It is generally known that halo-compounds are more prone to radical formation than hydrocarbons. Therefore will the halogen containing monomers, trifluoroacetate and 2-chloroacetate, more easy form radicals leading to high deposition rates upon plasma polymerization.

We are well aware that although the proposed reaction pathway and rate-determining steps support the experimental findings, they are not direct proofs of these mechanisms. Additional experimental support may be obtained by in-situ determination of the reactive species in the plasma, in the gas phase, and the volatile products formed, together with careful characterization of the crosslinked film.

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