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Detection of deposition rate of plasma-polymerized acrylate and methacrylate derivatives using quartz crystal microbalance

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Abstract

The deposition rates of plasma-polymerized (pp-)films of 12 acrylate derivatives ($CH_2{=}CHCOOR$: substitution R is –H, $–CH_3$, $–CH{=}CH_2$, $–CH_2CH_3$, $–CH_2CH_2CH_3$, $–(CH_2)_3CH_3$, $–C(CH_3)_3$, $–CH_2CH(CH_3)_2$, $–CH_2(CH_2)_4CH_3$, $–CH_2CF_3$, $–CH_2CF_2CF_3$, $–CH_2(CF_2)_2CF_3$), and 12 methacrylate derivatives ($CH_2{=}CCH_3COOR'$: substitution R′ is –H, $–CH_3$, $–CH{=}CH_2$, $–CH_2CH_3$, $–CH_2CH_2CH_3$, $–(CH_2)_3CH_3$, $–C(CH_3)_3$, $–CH_2CH(CH_3)_2$, $–CH_2(CH_2)_4CH_3$, $–CH_2CF_3$, $–CH_2CF_2CF_3$, $–CH_2(CF_2)_2CF_3$) are determined by the quartz crystal microbalance technique. Using the same polymerization conditions (100 W RF and 100 Pa vapor pressure) for the various monomers, it is found that the deposition rates were proportional to the polymerization time. The average deposition rate of pp-acrylate derivatives is larger than that of pp-methacrylate derivatives without pp-hexylacrylate. The average deposition rate of pp-fluoroalkylacrylates was higher than 7–25 times that of pp-alkylacrylate, and the average deposition rate of pp-fluoroalkylmethacrylates was higher than 10–31 times that of pp-alkylmethacrylates, respectively. The average deposition rate of pp-film depends on the chemical structure of the monomer suggesting different mechanisms under plasma-polymerization.
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Keywords: Plasma processing and deposition; Quartz crystal microbalance; Acrylate derivatives; Plasma polymers; Deposition rate

1. Introduction

Plasma-polymerization has been widely used to fabricate thin films of a variety of volatile compounds without chemical solvents in coating process. 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 facilitate the surface modification of materials [1,2]. Such films are expected to be useful as surface protection films rigidly fixed on the substrates [3,4]. Acrylate derivatives and methacrylate derivatives are one of the candidates of transparency coating materials. For the automobile industry and builder industry, the control of deposition rate of thin film on the body is one of the important problems [5]. The deposition rates in plasma-polymerization have been determined with a balance or by in situ measurement of the film thickness with a multi-interference thickness meter [6–10]. These methods cannot, however, detect the deposition rates of ultra-thin films. Piezoelectric quartz crystal is widely recognized as a useful 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 a fundamental oscillation frequency of 9 MHz is used, adsorption of approximately 1 ng of material decreases the oscillation frequency by 1 Hz [11,12]. Many attempts have been made to use these highly sensitive, convenient and portable devices as chemical sensors and biosensors [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 few of liquid monomers have been reported. It is well known that liquid monomer having high boiling point is easily liquefied in the reaction

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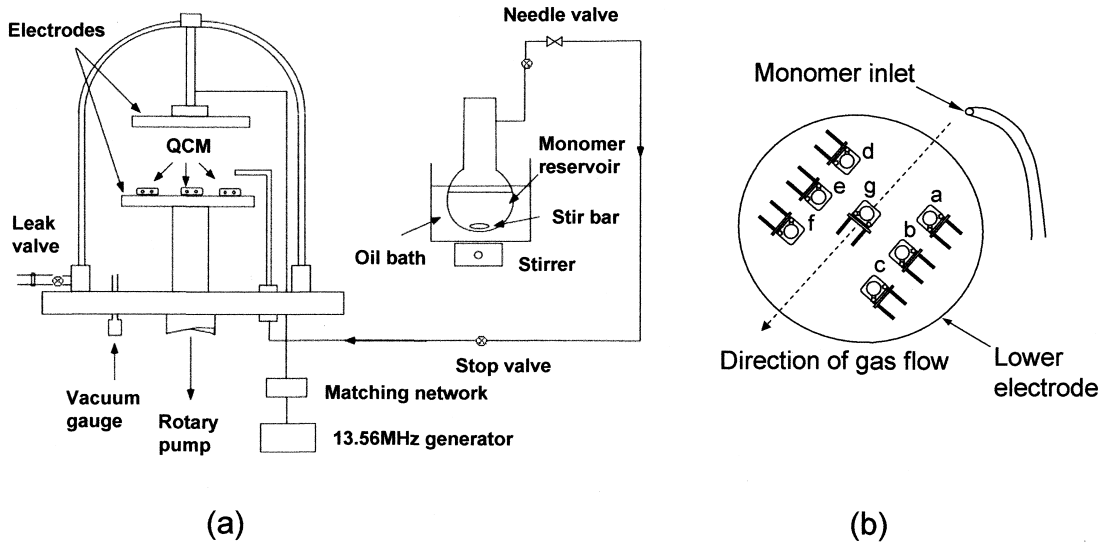

Fig. 1. (a) Schematic diagram of plasma-polymerization equipment. (b) Position settings (a–g) of seven QCMs on the lower electrode.

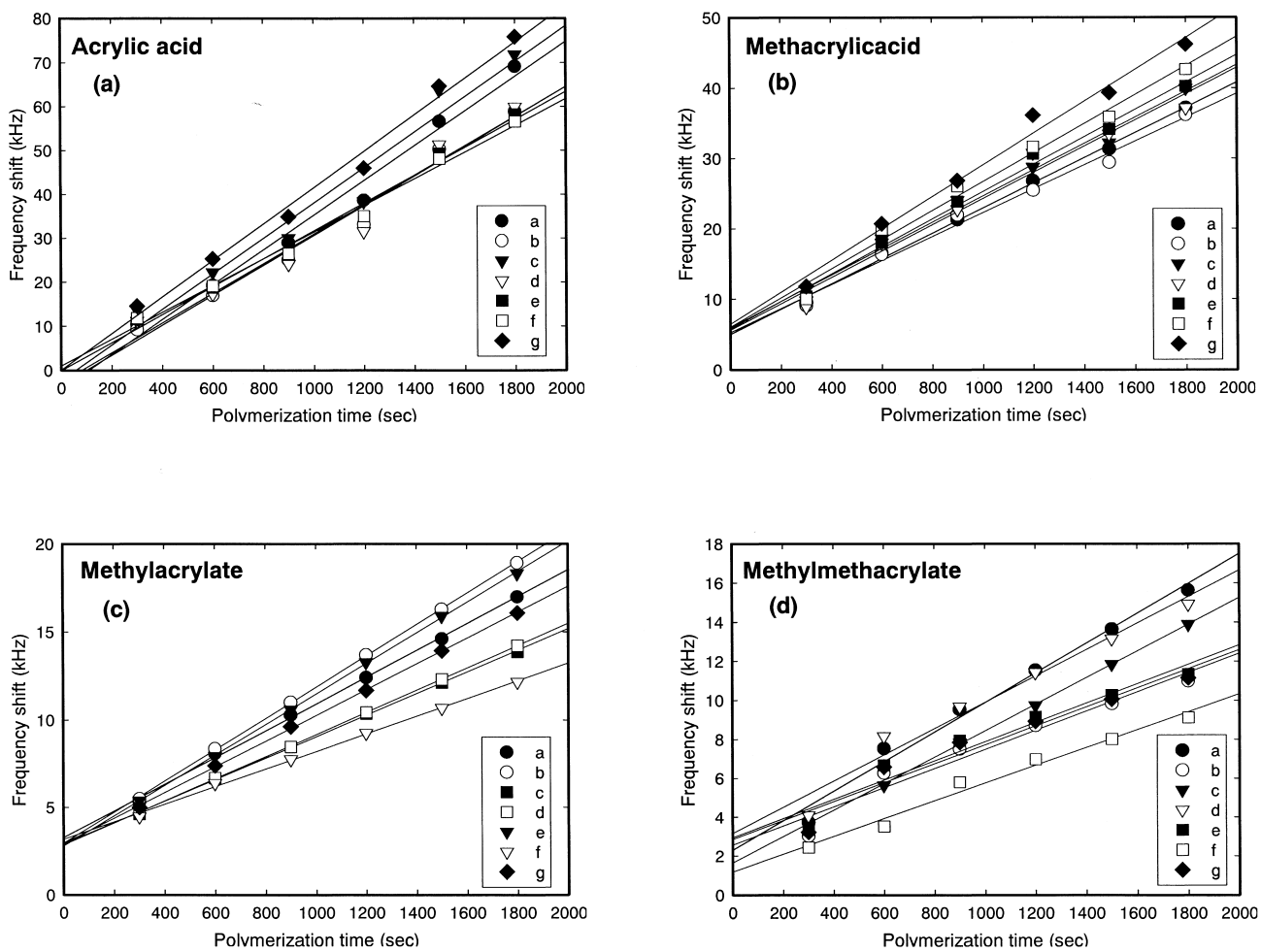

Fig. 2. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) Acrylic acid, (b) methacrylic acid, (c) methylacrylate and (d) methylmethacrylate.

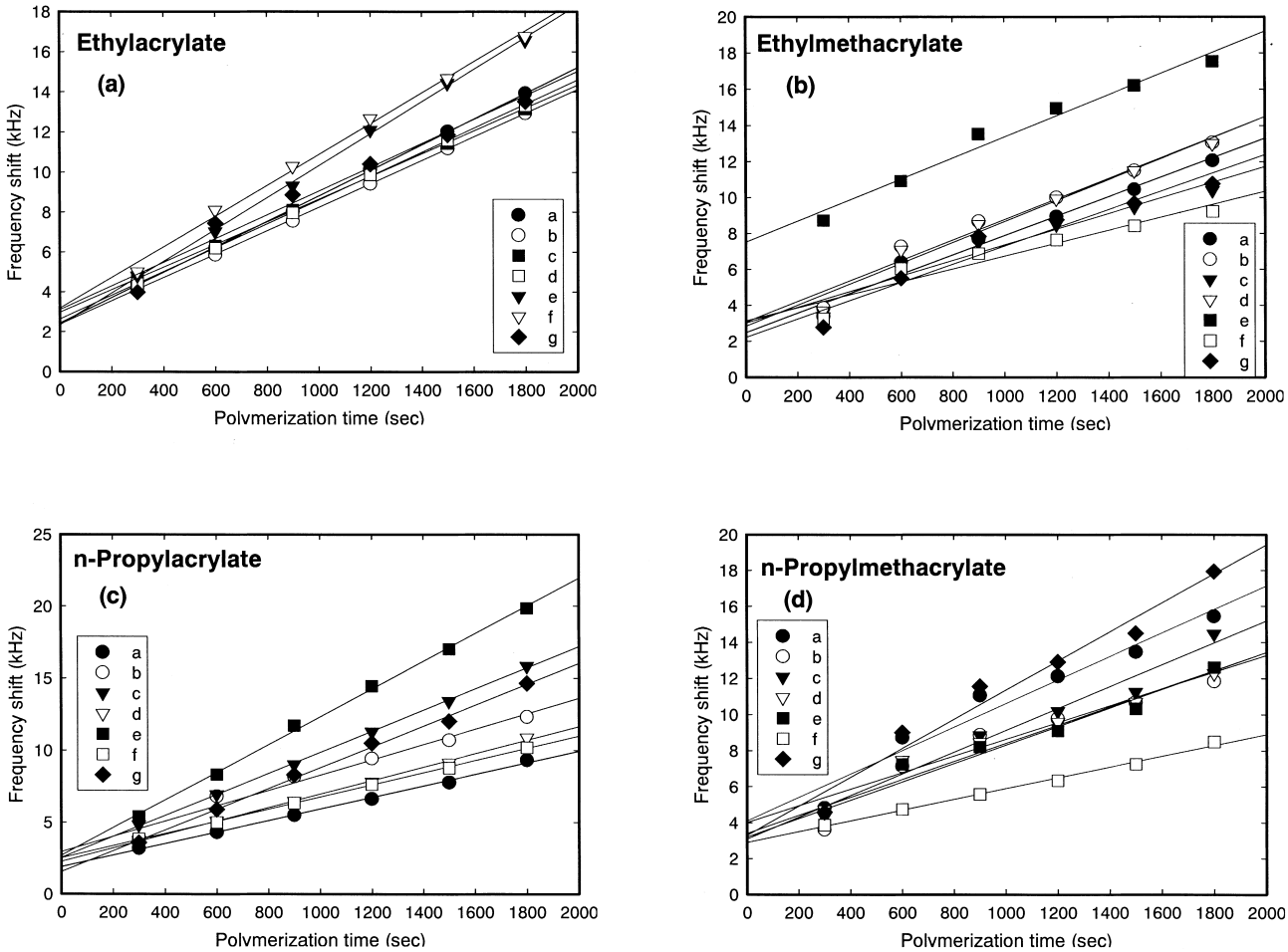

Fig. 3. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) Ethylacrylate, (b) ethylmethacrylate, (c) *n*-propylacrylate and (d) *n*-propylmethacrylate.

chamber. Therefore, the plasma-polymerization of liquid monomers has not been reported. We aim to construct polymer coating database for surface protection using plasma-polymers and to understand reaction mechanisms of plasma-polymerization.

In this paper, plasma-polymerized (pp-)films are prepared from 12 acrylate derivatives (acrylic acid, methylacrylate, vinylacrylate, ethylacrylate, *n*-propylacrylate, *n*-butylacrylate, *tert*-butylacrylate, *iso*-butylacrylate, *n*-hexylacrylate, 2,2,2-triflouroethylacrylate, 2,2,3,3,3-pentafluoropropylacrylate and 2,2,3,3,4,4,4-heptafluorobutylacrylate) and 12 methacrylate derivatives (methacrylic acid, methylmethacrylate, vinylmethacrylate, ethylmethacrylate, *n*-propylmethacrylate, *n*-butylmethacrylate, *tert*-butylmethacrylate, *iso*-butylmethacrylate, *n*-hexylmethacrylate, 2,2,2-triflouroethylmethacrylate, 2,2,3,3,3-pentafluoropropylmethacrylate and 2,2,3,3,4,4,4-heptafluorobutylmethacrylate). Each of these monomers is polymerized under the same polymerization condition at 100 Pa of monomer vapor pressure, 100 W of RF with 13.56 MHz of continuous wave (CW).

The present work is a preliminary study in using the QCM sensor array to detect the deposition rates of pp-films in order to investigate the deposition mechanism of acrylate and methacrylate monomers under plasma-polymerization.

2. Experimental section

The monomers used in this experiment were all of analytical or guaranteed grade and were purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan) or Kanto Chemical Co., Inc. (Tokyo, Japan) and used without further purification. For plasma-polymerization, the plasma-polymerization equipment Model BP-1 of Samco International Co. (Kyoto, Japan) was used [17,18]. Fig. 1a shows a schematic diagram of the plasma-polymerization equipment. The deposition rates of the pp-films were measured with the QCM during the polymerization process. The QCM had gold electrodes on both of its surfaces (AT-cut of 9 MHz; $8\times8\times0.15$ mm^3) and was purchased from Nihon Dem-

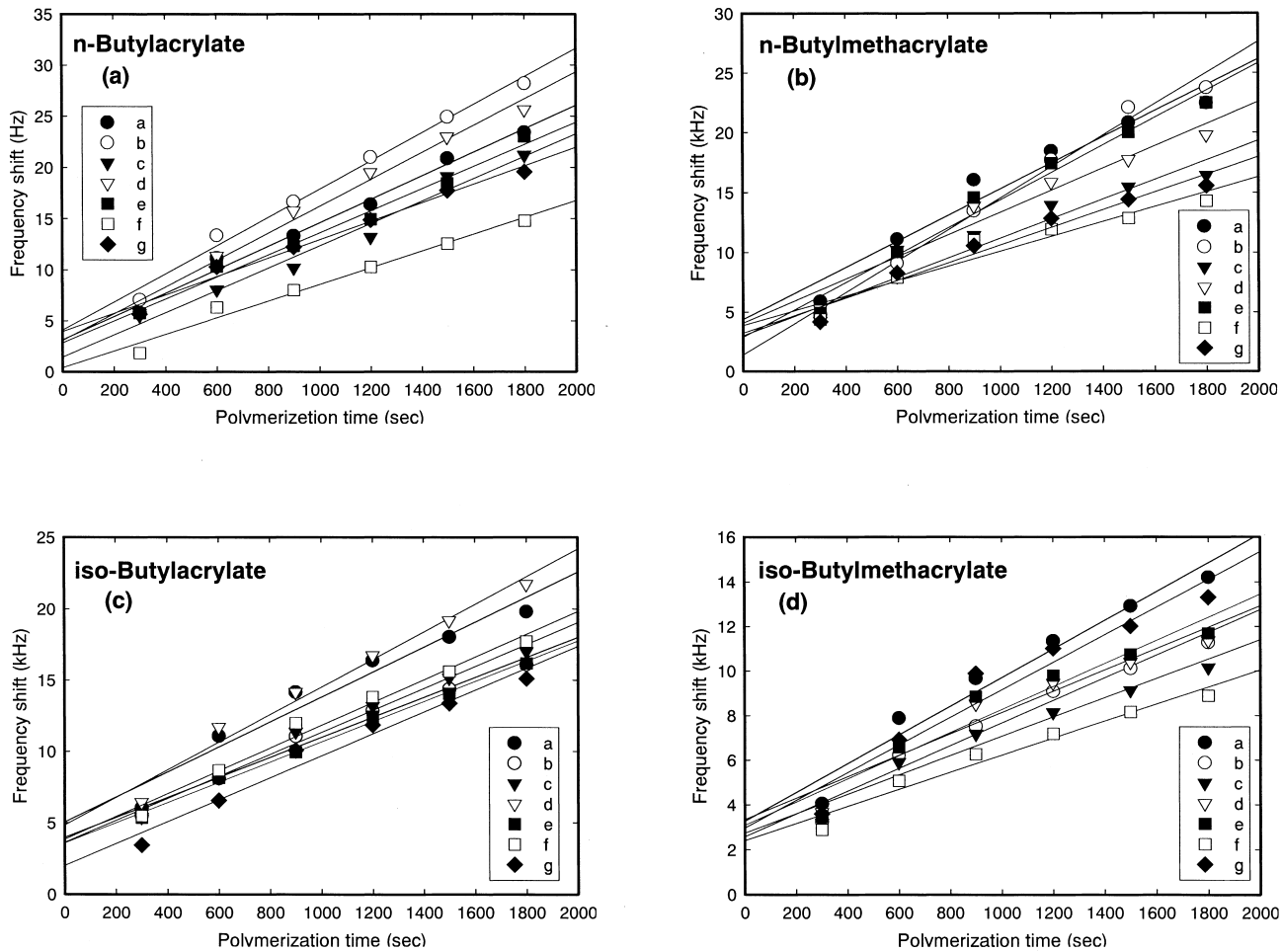

Fig. 4. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) *n*-Butylacrylate, (b) *n*-butylmethacrylate, (c) *iso*-butylacrylate and (d) *iso*-butylmethacrylate.

pa Kogyo Co. Ltd (Tokyo, Japan). The pp-films were deposited on one side of the QCM. The deposition rates of the pp-films depend on the positioning of the substrates. Therefore, the 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 in Fig. 1b. Prior to plasma-polymerization, the seven QCMs were treated by plasma sputtering for 5 s under 100 W RF power and 100 Pa of He pressure.

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 12 acrylate monomers and 12 methacrylate monomers: a vapor pressure of 100 Pa and RF power of 100 W with 13.56 MHz of CW. The monomers were vaporized at a constant liquid temperature, which was maintained by an oil bath, and a controlled vacuum. The distance between the electrodes was 6.0 cm and the power of the glow discharge was set at 100 W. The plasma-polymerization was performed for 300–1800 s by 300-s intervals. We obtained an optimum film-state of the polymers under these conditions.

The apparatus and procedure for determining the deposition rate have been described previously [17,18]. The oscillating frequency of the QCM was measured with a universal counter (Iwatsu SC7201, Tokyo, Japan) using data stored in a microcomputer (NEC PC9821, Tokyo, Japan). The laboratory made transistor–transistor logic electronic circuit used is described in Ref. [19] (circuit II). The relationship between the weight of the pp-films and the frequency shift is expressed in units of ng/Hz [12]. All of the experiments were carried out at 25 ± 2 °C. The chemical structure of pp-films was characterized by FT-IR, XPS and contact angle. These results will be published elsewhere [20].

3. Results and discussion

The deposition rates of the pp-films onto the QCM were measured directly by the shift in the oscillation

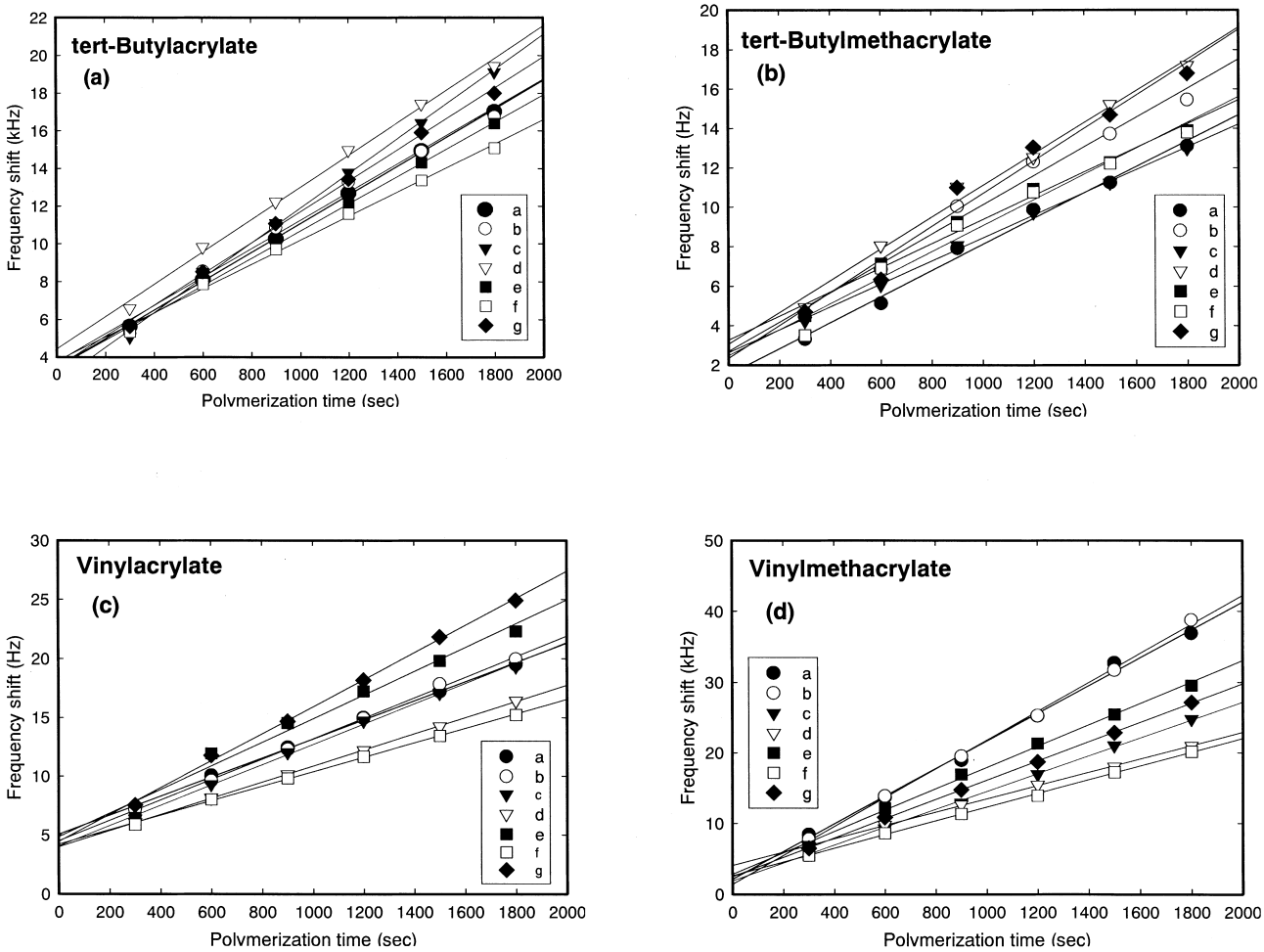

Fig. 5. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with pp-films. (a) *tert*-Butylacrylate, (b) *tert*-butylmethacrylate, (c) vinylacrylate and (d) vinylmethacrylate.

frequency. Fig. 2a shows the relationship between the deposition rates of pp-acrylic acid for the seven positions (a–g) of the lower electrode and the polymerization time. A linear relationship was observed up to a polymerization time of 1800 s. The correlation coefficient of each line (the polymerization time response for the positions a–g) is almost 1.0. We define the individual deposition rates of the pp-films using the slope of lines a–g for each sample. The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. The average of deposition rate for the pp-acrylic acid film is 2.15 μg/min. The value of the standard deviation (σ) and the coefficient of variation (CV) of pp-acrylic acid is 0.269 μg/min and 12.5%, respectively. The reproducibility of the deposition rate is high, in three independent experiments the CV within 15% (data not shown). Therefore, we confirm the accuracy of this technique.

Fig. 2b and Figs. 3–6d show the typical data between the frequency shift and polymerization time for pp-acrylic acid, pp-methylacrylate, pp-vinylacrylate, pp-ethylacrylate, pp-propylacrylate, pp-butylacrylate, pp-*tert*-butylacrylate, pp-*iso*-butylacrylate, pp-2,2,2-triflouroethylacrylate, pp-2,2,3,3,3-pentafluoropropylacrylate, pp-methacrylic acid, pp-methylmethacrylate, pp-vinylmethacrylate, pp-ethylmethacrylate, pp-propylmethacrylate, pp-butylmethacrylate, pp-*tert*-butylmethacrylate, pp-*iso*-butylmethacrylate, pp-2,2,2-triflouroethylmethacrylate and pp-2,2,3,3,3-pentafluoropropylmethacrylate, respectively. The range of linearity between frequency shift and the polymerization time is also included for the seven positions (a–g) of the lower electrode. Outside this range, or above the formed thickness, the QCM does not work as a microbalance.

Table 1 summarizes the averaged deposition rates for the 12-acrylate monomers of polymerization. The values are in the order of 2,2,3,3,4,4,4-heptafluorobutylacrylate > 2,2,3,3,3-pentafluoropropylacrylate > 2,2,2-triflouroethylacrylate > acrylic acid > *n*-hexylacrylate > vinylacrylate > *n*-butylacrylate > *iso*-butylacrylate > *tert*-butylacrylate > methylacrylate > ethylacrylate > *n*-propylacrylate. Table 2 summarizes the averaged deposition rates

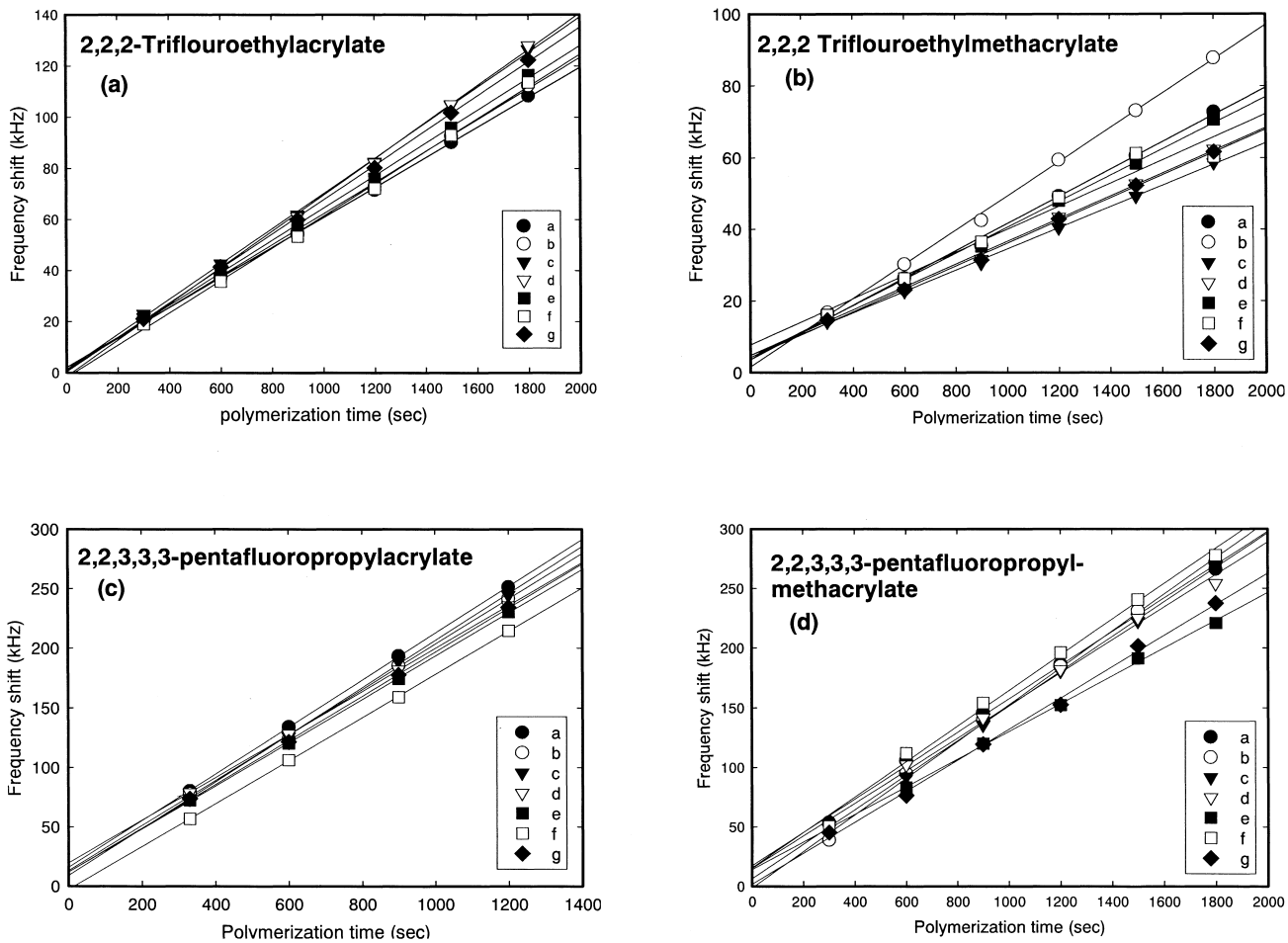

Fig. 6. Linear relationship between polymerization time and oscillation frequency shift of QCM coated with (a) 2,2,2-trifluoroethylacrylate, (b) 2,2,2-trifluoroethylmethacrylate, (c) 2,2,3,3,3-pentafluoropropylacrylate and (d) 2,2,3,3,3-pentafluoropropylmethacrylate.

for the 12-methacrylate monomers of polymerization. The averaged deposition rates for the 12-methacrylate monomers are in the order of 2,2,3,3,4,4,4-heptafluorobutylmethacrylate > 2,2,3,3,3-pentafluoropropylmethacrylate, 2,2,2-triflouroethylmethacrylate > *n*-hexylmethacrylate > methacrylic acid > vinylmethacrylate > *n*-butylmethacrylate > *tert*-butylmethacrylate > methylmethacrylate > *n*-propylmethacrylate > ethylmethacrylate = *iso*-butylmethacrylate.

The average deposition rate of pp-acrylate derivatives is larger than that of pp-methacrylate derivatives without pp-hexylacrylate. The average deposition rate of pp-fluoroalkylacrylates was higher than 7–25 times that of pp-alkylacrylate, and the average deposition rate of pp-fluoroalkylmethacrylates was higher than 10–31 times that of pp-alkylmethacrylates, respectively. The differences of the order of deposition rate were occurred under the small deposition values. Accordingly, the deposition rate of the pp-films is affected by the chemical structure of the monomer and, hence, the reaction mechanism.

All of the polymerizations were conducted under identical settings of the equipment, which caused higher gas phase concentration of the monomers with lower boiling points. The reaction pathway of the different monomers, however, often canceled this concentration effect. Polymerization is assumed to proceed via a free radical mechanism initiated through the collision of an electron with a monomer molecule (Eq. (1)). Dissociation of this molecule results in the formation of free radicals, which may add to intact monomers (Eq. (2)) denoted as the initiation:

$$\mathrm{M} + \mathrm{e}^- \rightarrow \mathrm{R}^\bullet \tag{1}$$

$$\mathrm{R}^\bullet + \mathrm{M} \underset{k_\mathrm{i}}{\rightarrow} \mathrm{RM}^\bullet \tag{2}$$

Polymerization (Eq. (3)) then proceeds in the gas phase and on the surface.

$$\mathrm{RM}^\bullet + n\mathrm{M} \underset{k_\mathrm{p}}{\rightarrow} \mathrm{RM}^\bullet_{n+1} \tag{3}$$

Table 1
Average of deposition rates of pp-films coated with 300 s of time intervals for the plasma-polymerization

Acrylates	Molecular formula	Adr	σ	CV
Acrylic acid	$CH_2{=}CHCOOH$	2.15	0.269	12.5
Methylacrylate	$CH_2{=}CHCOOCH_3$	0.43	0.085	19.7
Vinylacrylate	$CH_2{=}CHCOOCH{=}CH_2$	1.26	0.155	12.3
Ethylacrylate	$CH_2{=}CHCOOC_2H_5$	0.39	0.056	14.4
n-Propylacrylate	$CH_2{=}CHCOOCH_2CH_2CH_3$	0.36	0.124	34.1
n-Butylacrylate	$CH_2{=}CHCOO(CH_2)_3CH_3$	0.66	0.121	18.3
tert-Butylacrylate	$CH_2{=}CHCOOC(CH_3)_3$	0.47	0.055	11.9
iso-Butylacrylate	$CH_2{=}CHCOOCH_2CH(CH_3)_2$	0.48	0.057	11.9
n-Hexylacrylate	$CH_2{=}CHCOOCH_2(CH_2)_4CH_3$	1.31	0.147	11.2
2,2,2-Triflouroethylacrylate	$CH_2{=}CHCOOCH_2CF_3$	3.89	0.267	6.86
2,2,3,3,3-Pentafluoropropylacrylate	$CH_2{=}CHCOOCH_2CF_2CF_3$	11.2	0.446	3.97
2,2,3,3,4,4,4-Heptafluorobutylacrylate	$CH_2{=}CHCOOCH_2(CF_2)_2CF_3$	13.0	1.110	8.5

The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. σ and CV represent the standard deviation and the coefficient of variation, respectively. Adr, average deposition rate [μg/min]; σ, standarad deviation [μg/min]; CV, coefficient of variation [%].

Finally, collision between two radicals leads to termination of the reaction (Eq. (4)) by radical–radical coupling or disproportionation, as in the case of standard free radical polymerization.

$$R^{\bullet} + R' \underset{k_t}{\rightarrow} R - R' \tag{4}$$

If the monomers are polymerizable by conventional free radical polymerization, plasma-polymerization may proceed simultaneously with plasma-induced polymerization, resulting in high deposition rates. 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 k_i, and not by the rate of propagation [21]. The termination of growing chains is suppressed by the immobility of the pp-layer, making the termination rate k_t low. In this study all monomers are prone to free radical polymerization and the rate of deposition is governed by the availability of surface radicals to propagate adsorbed monomers. For the alkylacrylates the differences are not significant. In general, a small difference is seen between the acrylates and the corresponding methacrylates, which can be attributed to differences in vapor pressure. A slight increase in deposition rate is observed with larger alkyl groups going from methyl to *n*-butyl and to hexyl. The reason for this is not clear but could be due to higher rate of formation of initiating radicals with larger alkyl groups or increased rate of monomer adsorption onto the surface. Vinylacrylate and vinylmethacrylate both give higher deposition rate than corresponding saturated monomers due to increase possibilities of reactions with surface radicals. By substitution of the alkyl to fluoroalkyl, a substantial increase in rate was observed. As earlier stated [22,23] halogen-containing monomers are more prone to form radicals in the plasma leading to higher concentration of propagating surface radicals and hence higher rate of deposition. We are well aware that although the proposed reaction pathway and rate-deter-

Table 2
Average of deposition rates of pp-films coated with 300 s of time intervals for the plasma-polymerization

Methacrylates	Molecular formula	Adr	σ	CV
Methacrylic acid	$CH_2{=}CCH_3COOH$	1.16	0.111	9.61
Methylmethacrylate	$CH_2{=}CCH_3COOCH_3$	0.35	0.073	21.1
Vinylmethacrylate	$CH_2{=}CCH_3COOCH{=}CH_2$	0.91	0.249	27.3
Ethylmethacrylate	$CH_2{=}CCH_3COOC_2H_5$	0.31	0.051	16.6
n-Propylmethacrylate	$CH_2{=}CCH_3COOCH_2CH_2CH_3$	0.33	0.095	29.1
n-Butylmethacrylate	$CH_2{=}CCH_3COO(CH_2)_3CH_3$	0.57	0.147	25.8
tert-Butylmethacrylate	$CH_2{=}CCH_3COOC(CH_3)_3$	0.42	0.058	13.9
iso-Butylmethacrylate	$CH_2{=}CCH_3COOCH_2CH(CH_3)_2$	0.31	0.056	18.3
n-Hexylmethacrylate	$CH_2{=}CCH_3COOCH_2(CH_2)_4CH_3$	1.32	0.123	9.3
2,2,2-Triflouroethylmethacrylate	$CH_2{=}CCH_3COOCH_2CF_3$	2.12	0.370	17.4
2,2,3,3,3-Pentafluoropropylmethacrylate	$CH_2{=}CCH_3COOCH_2CF_2CF_3$	8.33	0.760	9.12
2,2,3,3,4,4,4-Heptafluorobutylmethacrylate	$CH_2{=}CCH_3COOCH_2(CF_2)_2CF_3$	11.6	0.630	5.4

The averages of deposition rates of the pp-films are calculated from the slope of the seven lines (a–g) in the figures. σ and CV represent the standard deviation and the coefficient of variation, respectively. Adr, average deposition rate [μg/min]; σ, standard deviation [μg/min]; CV, coefficient of variation [%].

mining steps support the experimental findings, they are not direct proofs of these mechanisms. The contribution of the step-growth mechanism proposed by Yasuda [24] is certainly also important although not dominant for the conditions used here. Furthermore, ablation, which is especially important for fluorine-containing monomers, will certainly occur in parallel. 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 cross-linked film.

Acknowledgments

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