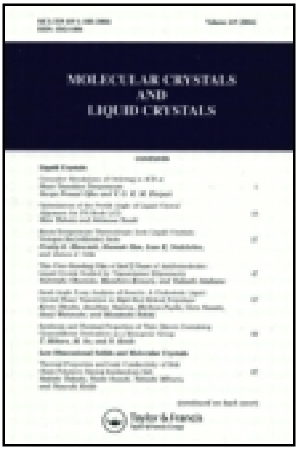

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Detection of Fluorinated Compounds Using Quartz Crystal Microbalance Coated with Plasma Polymerized Styrene Derivatives

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DETECTION OF FLUORINATED COMPOUNDS USING QUARTZ CRYSTAL MICROBALANCE COATED WITH PLASMA POLYMERIZED STYRENE DERIVATIVES

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Abstract We report preliminary results of the detection of fluorinated compounds using a quartz crystal microbalance coated with plasma-polymerized styrene (pp-St) and pentafluorostyrene (pp-PFSt). The sorption of fluorinated compounds on pp-PFSt is 1.2 - 4.8 times larger than that of these compounds on pp-St.

INTRODUCTION

Plasma polymerization has recently been used to form ultrathin films on a variety of substrates. A plasma-polymerized film adheres firmly to a substrate and is highly resistant to chemical and physical treatments.[1] For these properties, the film is expected to be useful as a molecular recognition film immobilized rigidly on a quartz crystal microbalance (QCM). We have found that a QCM coated with plasma-polymerized phthalocyanine film has good sensitivity and long lifetime for the detection of various organic gases.[2, 3] Styrene is a well-investigated monomer for reactivity of polymerization. Polystyrene is a widely used polymer for many application fields, but gas sorption for polystyrene is not well-known. Polystyrene has a phenyl group to affect a special interaction with aromatic compounds. We want to know the effect of fluorinated substitution of styrene derivatives for the detection of various organic gases. In this paper, plasma-polymerized films are prepared from two monomers, styrene and pentafluorostyrene. Gas sorption is performed using QCMs coated with plasma-polymerized styrene (pp-St) and pentafluorostyrene (pp-PFSt) films. We use fifteen kinds of gases, *e.g.*, n-hexane, benzene, monofluorobenzene and α,α,α-trifluorotoluene.

EXPERIMENTAL

The apparatus and procedure for plasma polymerization of styrene derivatives are the same as those described previously.[2] QCM is placed on the lower side electrode of the plasma polymerization equipment. The distance between two electrodes is 35 mm. Electric discharge produced by radio frequency power (RF) of 13.56 MHz is used for plasma polymerization. The conditions of plasma polymerization are 100 Watt RF, 80 Pa of vapour pressure for styrene and 40 Pa for pentafluorostyrene, respectively. The thickness of films on QCM are controlled due to the time of plasma polymerization. FT-IR and elemental analysis data show that these films contain phenyl- or pentafluorophenyl groups (data not shown). The characterization of plasma polymers will be described elsewhere.

The apparatus and procedure for gas sorption experiment are also carried out using the previous method.[2] Saturation vapour pressure is referred from ref. 4 or is measured using a vacuum line. The QCM used is AT-cut with a fundamental frequency of 9 MHz. The pp-St or pp-PFSt-coated QCM is fixed in a 100 ml round flask and connected to an oscillation circuit. The oscillating frequency of the QCM is measured using a universal counter and these time course are stored in a microcomputer. The transistor-transistor logic (TTL) electronic circuit used is shown in circuit II of ref. 5. The relationship between the amount of adsorbed material and the frequency decrease is expressed in units of 1 ng/Hz.[5] All the experiments are carried out at 25 ± 0.1 °C.

RESULTS AND DISCUSSION

When 12.687 kPa of benzene is applied, the oscillation frequency of the pp-PFSt-coated QCM decreases immediately and becomes constant after about 60 min (data not shown).

The tendency of time course of pp-St-coated QCM is similar to that for pp-PFSt-coated QCM. The amount of gas sorption is defined as the frequency change between initial and steady values (ΔF_g). The amount of plasma polymer coated is determined by the frequency difference between uncoated and coated values (ΔF_m). Figure 1 indicates the frequency responses in the pp-PFSt coated QCM under various organic compounds. These responses for 12.687 kPa of benzene are linear in these experiments. The regression line is $\Delta F_g = 0.035 + 0.663 \times \Delta F_m$, correlation coefficient = 0.993 for pp-PFSt. The frequency response is reproducible with a relative error of 6 %. All experimental results show a similar behaviour. The slopes of linear line indicate the amount of gas sorption of plasma polymer per weight under saturation vapour. We define individual gas sensitivity of plasma polymer using the slope of sorption per 1 Pa. The selectivity is used for comparing the sensitivity of pp-PFSt to that of pp-St

Table I shows the sensitivity and selectivity of pp-PFSt- and pp-PSt-coated QCM for various compounds. The sensitivity of n-hexane on pp-PFSt film is the same as that of n-hexane on pp-St film. The sensitivity of benzene on pp-PFSt is 42 times larger than that of n-hexane on pp-PFSt. The selectivity of benzene on pp-PFSt is 1.58 times larger than that of benzene on pp-St. The sensitivity of α,α,α-trifluorotoluene on PFSt is 361 times larger than that of n-hexane on pp-PFSt.

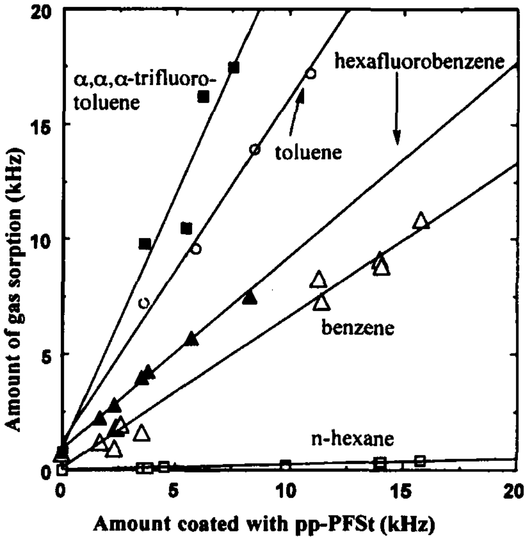

FIGURE 1 Linear relationship between the amount of gas sorption and amount coated with pp-PFSt measured by QCM. Organic vapours used are noted.

The selectivity of α,α,α-trifluorotoluene on pp-PFSt is 4.81 times larger than that of α,α,α-trifluorotoluene on pp-St. These results reveal that pp-PFSt and pp-St exhibit a very large sensitivity for aromatic compounds compared to non-aromatic compounds. The halogenated compounds also show a larger selectivity on pp-PFSt than that on pp-St. This may be due to the pentafluorophenyl structure which remains in the plasma polymer. The good selectivity for fluorinated compounds of pp-PFSt is useful to construct a gas sensor for these compounds. The frequency response of QCM increases with fundamental frequency of quartz. Surface acoustic wave (SAW) devices have the same characteristics. We are planning to use the SAW device at 433.9 MHz of fundamental frequency instead of QCM to improve frequency responses.

TABLE I Response of the present system to various compounds.

compound	sensitivity $\times 10^{3}$ $^{a)}$		selectivity$^{b)}$
	pp-St	pp-PFSt	pp-FPSt / pp-St
n-hexane	1.24	1.24	1.00
n-dodecane	3.21	4.41	1.37
cyclohexane	10.37	8.53	0.82
benzene	33.11	52.26	1.58
monofluorobenzene	91.74	108.70	1.18
toluene	345.68	397.78	1.15
α,α,α-trifluorotoluene	89.64	448.58	4.81
o-xylene	664.04	910.94	1.37
ethylbenzene	618.30	486.59	0.79
styrene	1433.21	1643.22	1.15
p-fluoroaniline	4185.31	6129.37	1.46
ethyl alcohol	43.78	41.41	0.95
diethyl ether	0.76	0.59	0.78
ethylacetate	91.12	90.47	0.98
chloroform	18.63	24.20	1.30

a)Sensitivity is defined by the slope of gas sorption for plasma polymer divided by the saturation gas pressure (Pa). b) Selectivity is calculated from sensitivity of pp-FPSt divided by that of pp-PSt.

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