

Characterization of Polymeric LB Thin Films for Sensor Applications

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ABSTRACT: The Quartz Crystal Microbalance (QCM) system is utilized to investigate the relationship between mass uptake and associated swelling for Langmuir-Blodgett (LB) organic thin films obtained from pyrene end-capped polystyrene (PS). The study was carried out using three different molecular weights of polymeric chains. The changes in resonance frequency associated with mass changes can be attributed to the swelling behavior of polymeric thin films during vapor absorption. This swelling is due to the capturing of organic vapor molecules in the sensor environment. To quantify real-time QCM data for swelling, early-time Fick's law of diffusion was adopted to fit the results, and a good linear relationship was observed

between the mass uptake and square root of the swelling time. The diffusion coefficients for swelling were thus obtained from the slopes of the fitting curves and was found to be correlation with the amount of organic vapor content in the cell. It was also observed that diffusion of the organic vapor into higher molecular weight polystyrene thin films are much faster than low molecular weight ones in sensor applications. Diffusion coefficients were found to be $0.2\text{--}3.0 \times 10^{-16}$, $5.0\text{--}13 \times 10^{-16}$, and $1.0\text{--}1.6 \times 10^{-15}$ cm²/s for PS1, PS2, and PS3 LB thin films, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2414–2422, 2012

Key words: LB film; swelling; gas sensor; QCM technique

INTRODUCTION

Polymers are fascinating materials that are different in many respects from ordinary solids. Although they possess all the normal characteristics of solids such as shape-retention and resistance to shear but they can also absorb solvent and swell to dimensions much larger than their dry size, depending on the chemical structure. Sensing low concentrations of chemical vapors and volatile organic compounds (VOCs) is an area of great interest for many applications. Polymer thin films have gained much interest because of their potential use in applications that require the presence of homogeneous films. Numerous technologies depend on thin and ultrathin polymer films include the following: optical coatings, next-generation data storage, high-resolution photoresists, and dielectric insulators.^{1,2}

Polymeric materials are often used as environmentally responsive coatings in sensors due to their ability to absorb a variety of different molecules. The versatility of polymers makes them appropriate for many sensor types based on different transduction principles in the detection of a variety of analytes.

Their chains are flexible and molecules can easily be absorbed into polymer networks. This absorption process results in swelling and mass increase of the polymer materials. The response of polymer materials to the absorbed molecules can be transduced into an electrical signal that can be measured based on different principles, e.g. electrical conductivity change,³ mass change using a quartz crystal microbalance (QCM),⁴ optical properties using spectroscopic ellipsometry,⁵ or surface plasmon resonance spectroscopy (SPR).⁶ Much better selectivity and rapid measurements have been derived by replacing classical sensor materials with polymers involving nanotechnology and exploiting either the intrinsic or extrinsic functions of polymers. The improving role of polymers as gas sensors are reviewed and discussed in this article.⁷ In recent years, a number of numerical models have been developed for predicting the movement of organic vapors in soils. All of these models are based on the assumption that Fick's law is an adequate representation of gas-phase diffusion.⁸

Langmuir-Blodgett (LB) thin film deposition technique has an important place in physics and chemistry to investigate floating monolayers on the water surface and to transfer the floating monolayer onto a solid substrate. This technique is a convenient method to produce a uniform and high-quality organic thin film. The film thickness and molecular architecture can easily be controlled using the LB

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film process.⁹ Polymer films with well-controlled thickness have been attracting considerable attention due to their broad range of potential applications in microlithography,¹⁰ organic-based electronic devices (polymer thin film transistors, optoelectronic devices, include light emitting diodes, sensor elements, photovoltaic cells, and nanoelectronic devices),¹¹ and biomimetic (biosensors) thin films.¹² The overall property of polymer LB films is closely related to their surface morphology, which is dictated by a number of parameters, including the solution concentration, surface pressure and temperature.^{13–15}

The diffusion coefficient is one of the most important transport parameters for many physicochemical and physiological processes, where it can be used on the direct estimation of molecular weight. It is strongly affected by the chemical composition of the solvent, temperature, and solute concentrations. PS-coated quartz crystal was studied as a sensor for volatile organic compounds (VOCs).^{8,16,17} The monitoring of (VOCs) such as chloroform, benzene, toluene, xylene, etc. . . has become a serious task due to regulations in many countries in the world. Although current monitoring methods (i.e., gas chromatography and infrared spectroscopy) have high sensitivity, they are expensive and are not used for real-time measurements. Recently, Surface Plasmon Technique was used for studying sorption of poly (methyl methacrylate) film at various concentrations of chloroform vapor, it was observed that diffusion coefficients for swelling obeyed the $t^{1/2}$ law and found to be correlated with the amount of vapor content in the cell.¹⁸

In this study, pyrene-end capped polystyrene (PS) polymer chains, having different molecular weights, were synthesized by atom radical transfer methods and were subsequently used to produce LB thin films. Although several other polymerization methods and coupling reactions such as "Click chemistry" can also be used,^{19,20} ATRP was deliberately selected so as to obtain well-defined pyrene-labeled polymers with exact functionality and low polydispersity. These LB films were subjected to various concentrations of partially saturated chloroform vapors to study the swelling mechanism in sensor applications. Using QCM measurement system, variations on frequency shift were monitored in real time during swelling in which organic vapor is introduced into a gas cell. Early-time Fick's law of diffusion was adopted to fit the QCM results. It was found that the diffusion coefficients for high molecular weight PS thin films are larger (roughly in the order of 10) than the diffusion coefficients for low molecular weight PS thin films.

THEORETICAL CONSIDERATION

The surface pressure versus surface area (Π -A graph) is an important graph to understand the

characteristic surface behavior of a floating monolayer on the water surface. The area per molecule for a floating monolayer can be calculated by using the following relation²¹:

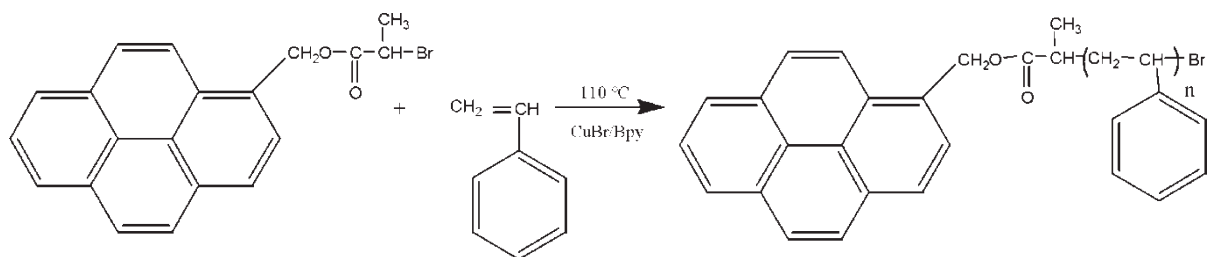
$$a = \frac{AM_w}{cN_A V} \quad (1)$$

where A is the enclosed area, M_w is the molecular weight of the material, c is the concentration of the solution, V is the volume of the solution spread onto the water surface, and N_A is the Avogadro number.

Among various types of gas sensors there has been an increasing interest in coating the surface of QCM sensors with functionalized polymers. QCM monitors the mass change induced by the analyte adsorbed into the polymer films which first introduced in 1964.²² QCM system consists of a thin, AT-cut quartz sandwiched between two electrodes and this quartz crystal resonates at a well-defined frequency. This frequency called resonance frequency depends on the area of the electrodes and thickness of the quartz. The linear relationship between mass change, Δm , and change of frequency, Δf , was first described by Sauerbrey.²³

$$\Delta f = \frac{-2f_0^2}{\rho_q^{1/2}\mu_q^{1/2}A} \Delta m, \quad (2)$$

where f_0 is the initial resonance frequency of quartz crystal, ρ_q is the density of quartz (2.648 g/cm), μ_q is the shear modulus of quartz (2.947×10^{11} g/cm/s), and A is the piezoelectrically active area (cm²). The values pertinent in the study presented in this article are $f_0 = 7,286,050$ Hz and $A = 1.13$ cm². The performance characteristics of the QCM sensor namely, selectivity, response time, and reversibility will depend on the chemical nature and physical properties of the polymeric coating. A number of polymeric coatings have been successfully used in gas sensor applications as they exhibit changes in mass when they interact with certain chemicals.⁷ Diluted in good solvents polymer chains tend to swell. In a poor solvent, they tend to coil, contract, and/or entangle. The interactions that contribute to the entangling of polymer chains play a role comparable to that of physical cross-links in the sense that the behavior of two entangled chains is interdependent. Unlike cross-linked chains, entangled chains do not form an infinite single macromolecule but can slip one with respect to others and flow. That affects, in turn, the physical behavior of polymer melts. Polymer melt chain dynamics and rheological properties have found a common physical frame work in the reptation model.^{24,25} This model is based on the assumption that large-scale transverse chain motions are hindered by topological constraints caused by



Scheme 1 Synthesis of pyrene-labeled polystyrene by atom transfer radical polymerization.

the neighboring chains. Chain dynamics is then restricted to a snake-like motion (reptation) along an imaginary tube formed by these neighboring molecules. The concept of the entanglement coupling of macromolecules in polymer condensed systems is commonly accepted to interpret viscoelastic properties of high-molecular weight polymers. An important parameter for entangled macromolecules is average molecular weight spacing between entanglement junctions, i.e., the entanglement molecular weight M_e or critical molecular weight M_c , where some polymer properties of viscoelastic nature are changed.²⁶ The transition from one regime to the other occurs precisely at M_c , the critical molar mass above which entanglements occur. The entanglement molecular weight, M_e is calculated from the plateau modulus (G_N^0) according to following equation^{25,27}:

$$M_e = K \frac{\rho RT}{G_N^0}, \quad (3)$$

where R is the universal gas constant, ρ is the density, T is the absolute temperature, and K is a constant with a value of $4/5^{25,27,28}$ depending upon convention.

When Fick's second law of diffusion is applied to a plane sheet and solved by assuming a constant diffusion coefficient, the following equation is obtained for concentration changes in time²⁹:

$$\frac{C}{C_0} = \frac{x}{a_0} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n} \sin \frac{n\pi}{a_0} \exp\left(-\frac{D_n^2 \pi^2}{a_0^2} t\right), \quad (4)$$

where a_0 is the thickness of the slab, D is the diffusion coefficient, and C_0 and C are the concentration of the diffusant at time 0 and t , respectively. x corresponds to the distance at which C is measured. We can replace the concentration terms directly with the amount of diffusant by using:

$$M = \int_V C dV, \quad (5)$$

where M is the mass uptake and V is the volume element. When eq. (4) is considered for a plane

volume element and substituted in eq. (5), the following solution is obtained.³⁰

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D \pi^2}{a_0^2} t\right), \quad (6)$$

where M_t penetrant mass sorbed into the deposited film, assuming a one-dimensional geometry. The quantity, M_∞ , represents the amount sorbed at equilibrium, t is the time. This equation can be reduced to a simplified form:

$$\frac{M_t}{M_\infty} = 4 \sqrt{\frac{D}{\pi a_0^2}} t^{1/2}, \quad (7)$$

which is called early-time equation and this square root relation can be used to interpret the swelling data.^{18,29}

EXPERIMENTAL DETAILS

Materials

PS with different molecular weights were synthesized by using a pyrene functional atom transfer radical polymerization (ATRP) initiator in the polymerization of styrene which was polymerized in bulk at 110°C using 1-Pyrenylmethyl-2-bromopropanoate (PMBP) and CuBr/Bpy as the catalyst (Scheme 1). Reactant ratio and molecular weights of PS molecules are summarized in Table I, and the preparation detail is found in the literature.³¹

Preparation of polystyrene LB thin films

The surface pressure of PS as a function of reduced area at the air-water interface was investigated using a NIMA 622 alternate layer LB trough. PS materials were dissolved in chloroform with a concentration of ~ 0.2 mg/mL which was spread onto ultra pure water subphase at pH 6. A time period of 15 minutes was allowed for the solvent to evaporate before taking the isotherm (Π -A) graph which

TABLE I
Synthetic Conditions and Molecular Weight Characteristics of Pyrene-labeled Polystyrenes

Material ^a	Reactant ratio ^b	Mn (PDI) ^c
PS1	130 : 1 : 1 : 3	4980 (1.18)
PS2	100 : 1 : 1 : 3	7540 (1.19)
PS3	200 : 1 : 1 : 3	9654 (1.15)

^a Temperature 110°C; reaction time 4 h; bulk.

^b [PS]₀/[PMBP]₀/[CuBr]₀/[Bpy]₀.

^c Determined by gel permeation chromatography relative to polystyrene standards.

records the surface pressure as a function of surface area using the compression speed of barriers at a value of 1000 mm/min. The temperature of the water subphase was controlled using Lauda Ecoline RE 204 model temperature control unit, and all experimental data were taken at room temperature. Isotherm graphs were taken for several volume values using the same experimental conditions. Y-type LB deposition mode and a vertical dipping procedure was performed at the selected surface pressure with a speed of 25 mm/min for both the down and up strokes. These materials were deposited onto a thinly cut wafer of raw quartz sandwiched between two gold electrodes in an overlapping keyhole design for the QCM measurements. After every monolayer deposition, LB film sample was dried and the change of surface area was monitored during the deposition process. The deposition of LB film layers was also monitored to check the reproducibility of the LB film with a home-made QCM system that can detect small changes in mass. This ability helps to check the reproducibility of multilayer LB film.

QCM measurement

QCM system measures mass per unit area by measuring the change in frequency of a quartz crystal

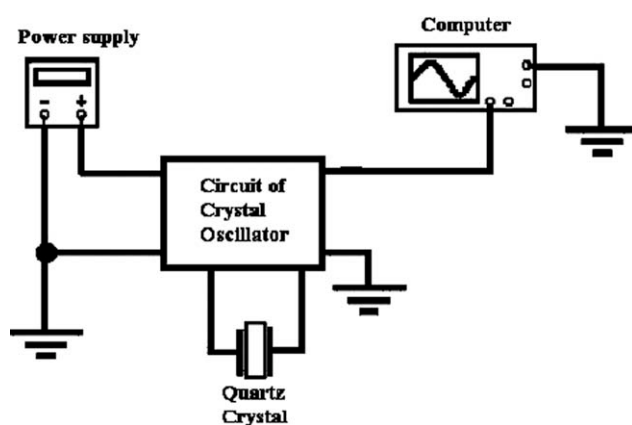


Figure 1 A home-made QCM measurement system.

resonator and has a piezoelectric sensor with nanogram sensitivity to mass changes on its surface. This technique is widely utilized in sensing applications for monitoring adsorption/desorption processes. A home-made QCM measurement system shown in Figure 1 was used to measure chloroform vapor response of these LB films. A custom software allows on-line recording of changes in quartz resonance frequency as the penetrating vapor is absorbed by the polymer sensing layer. All measurements were taken at room temperature using a standard quartz crystal with a nominal resonance frequency of 7 MHz. The quartz crystal was inserted into the electronic control unit, and the frequency of oscillation was monitored as a function of time. To monitor the response to the chloroform vapor, a special gas cell was constructed for this QCM system. After the introduction of organic vapor into the cell, the changes in frequency, which indicate the degree of response, were measured with an accuracy of 1%. The frequency change was monitored as a function of time when the sample was periodically exposed to the organic vapor for at least 10 min and was then allowed to recover after injection of dry air. These measurements were also taken for several vapor concentrations.

RESULTS AND DISCUSSION

The surface pressure change as a function of surface area (Π -A) isotherm of PS monolayer at the air-water interface at room temperature is shown in Figure 2. They were found to be reproducible and stable with phase transitions at the air-water interface. When the barrier is open, the PS molecules were packed randomly with large void spaces. As the barriers are closed, the LB molecules gather closer to

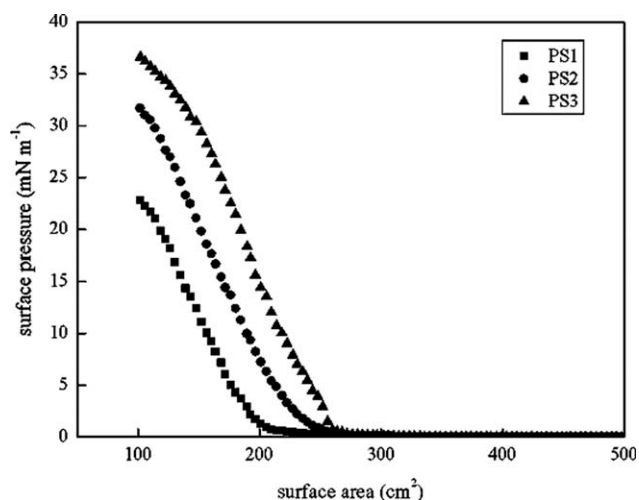


Figure 2 The surface pressure change as a function of surface area (Π -A) isotherm of PS monolayer.

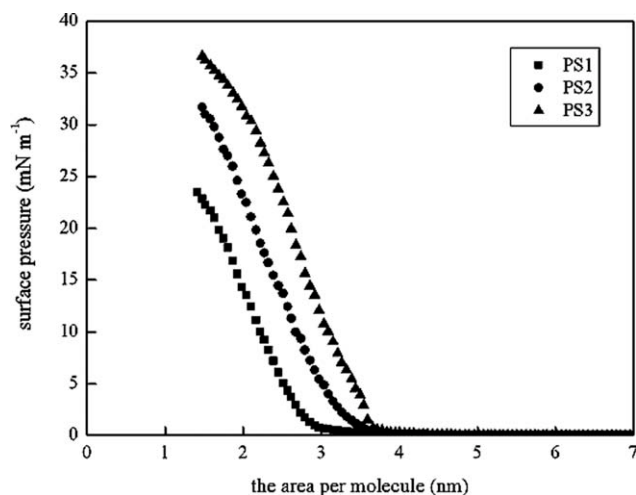


Figure 3 The area per molecule, a , versus surface pressure.

each other. The surface pressure increases dramatically as these molecules align to form the LB monolayer at the air–water interface. Isotherm graphs were taken for several volume values using the same experimental conditions. Using these graphs, surface pressures of 15, 20, and 22.5 mN/m were chosen as PS1, PS2, and PS3 respectively for LB film deposition onto quartz substrates. PS1 has the smallest area per molecule than others. The collapse of pressure at the air–water interface increases when the molecule weight increases. The effect of surface pressure on the formation of the LB monolayer of polystyrene,³² polystyrene-block-poly(2-vinylpyridine) (PS-*b*-P2VP) diblock copolymers,^{33,34} and polystyrene/poly-4-vinylpyridine AB diblock ionomer³⁵ materials are extensively studied in the literature. Similar phase transitions are observed with our results. It can be concluded that all three materials (PS1-3) organized as an LB film monolayer at the air–water interface and are suitable to be transferred as an LB film onto a solid substrate. Using the isotherm graph given in Figure 2, the area per molecule of PS thin films can be calculated from eq. (1). Figure 3 shows the area per molecule versus surface pressure. It is seen that as molecular weights of PS chains increase, the area per molecule, a also increases. In other words, the longer the PS chains, the more the area per molecule is on a PS thin film.

In general, it is considered that gas influence occurs by three “solution-diffusion” steps (absorption, diffusion, and desorption processes).³⁶ The frequency decreases suddenly at the time when initial contact takes place between PS film and vapors, which results from surface adsorption effect. Then, the frequency increases slowly, essentially resulting from bulk diffusion effect. The interaction process between sensitive film and the adsorbed vapors is a dynamic process. When the sensor is exposed to

vapors, both adsorption and desorption processes occur concurrently. After reaching dynamic equilibrium, the number of adsorbed vapor molecules will be equal to the number of desorbed vapor molecules. At that time, the frequency stabilizes. The changes in frequency for PS molecules are plotted versus the corresponding analyte concentrations as given in Figure 4. The frequency shift (Δf) of QCM results increases linearly with the vapor concentration as shown in Figure 4. This is expected since the more analyte molecules are provided in the test atmosphere, the more analyte molecules would be adsorbed by the PS molecules coated on the QCM substrate. It is also known that in cases where adsorption is the phenomenon responsible for the interaction between the coating and the analyte, the frequency shifts, observed after contact with the coated film with a known quantity of analyte, increase with the amount of coating just until saturation of the surface of the film. Therefore, the functions that can describe the responses of each coated film to a known amount of analyte, versus coating amount, needs to be known. The sensitivities of films, coated with different compounds, are often represented as a function of the amount of coating, which for most coating application methods is unknown. The amount of coating is then calculated by the Sauerbrey equation, given in eq. (2). It should be noted that the magnitude of the frequency shifts also depends on the flow rate of the gas into cell.³⁷ The crossover observed in Figure 4 should be caused by the flow rate of the gas. In other words, since the flow rate of the gas into cell is likely to affect the equilibrium between adsorption and dissociation of PS films and the response time, the fast flow rate for the PS1 film showed fast sorption kinetics for the gas presented in 20%. The slopes of these graphs

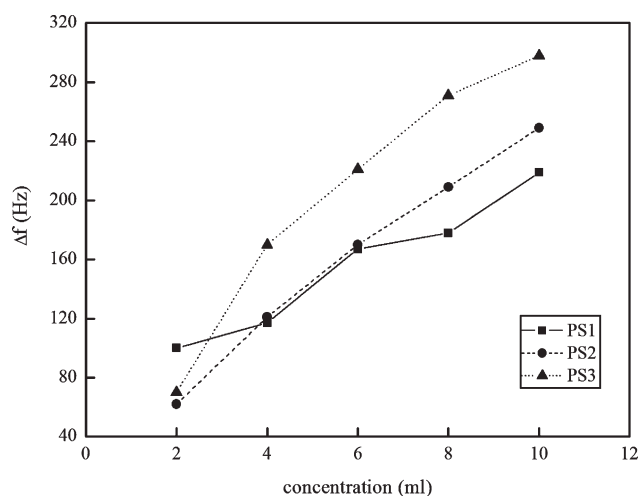


Figure 4 The frequency changes, Δf , for PS molecules versus concentration. The solid and dashed lines are for eye guide.

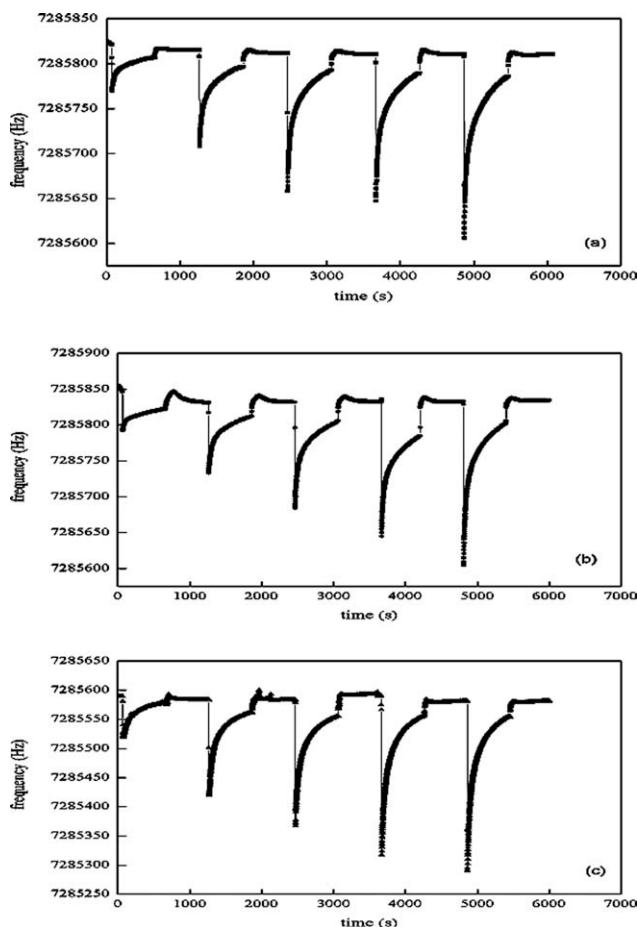


Figure 5 The kinetic response of PS LB films for chloroform vapor at different concentration.

increase with the increasing molecular weight or the increasing unit number of PS molecules. It seems that the physico-chemical properties of gas molecules such as polarity have an influence on the adsorption behavior when the gas molecules are attached to the sensing films. The PS molecules' polarity increases because chloroform (CHCl_3) has a larger dipole moment value (~ 1.01 D) than PS (~ 0.29 D).³⁸ Thus, PS3 has a strong polarizability due to the number of the functional group than others since the polarizability of the aromatic ring arises from p-electrons.³⁹ For the polar molecules, such as chloroform, the interaction among polar molecules could be caused by a polarizable coating. This might be to form stronger interaction with the sensing material; consequently more molecules were adsorbed.^{40,41} The response of QCM sensors based on films of PS in the thin film form, in the presence of chloroform vapor, have been analyzed and compared to the features of similar QCM sensors based on PS.^{42–46}

Figure 5 shows the kinetic response for four layer PS LB films against chloroform vapor at different concentrations. The response and recovery times are

in the order of a few minutes and the responses are almost reversible with the injection of air into the gas cell. These LB films were stable and have been used many times without significant losses in sensitivity and selectivity. A similar response to chloroform has been reported for the sensors based on different polymer materials. An exposure of the LB film to chloroform vapor yields a large change of the optical parameters of these thin films, and the film thickness increased as a result of film swelling.^{42–46} Use of PS in thin form as sensing element for a QCM sensor has been thoroughly discussed for detection of chloroform in vapor/liquid phase.^{42,47}

To quantify the data given in Figure 5, one has to extract the polymer film parameters due to swelling. Figure 6 shows normalized frequency against swelling time where the consolidation process involves setting starting times to $t = 0$ for each swelling cycles. As seen in Figure 6, the frequency decreased as the time of vapor exposure increased. It is also seen that normalized frequency decrease is faster as the chloroform vapor concentration is increased. These behaviors can be explained with the chain interdiffusion between polymer chains during vapor exposure. Entanglement molecular weight, M_e of PS chains were calculated by using eq. (3) and found to be around 12,000 g/mol. Here, the parameters such as, ρ (0.969 g/cm³) density of polymer, G_N^0 (0.2 MPa) plateau modulus, T (110°C) temperature, and K ($4/5$) constant were used for the polystyrene polymer.^{25,27,28} Since the molecular weights of the PS chains under consideration are much lower than the entanglement molecular weight, M_e value, one may then conclude that the reptation motion should be ruled out for the diffusion model. In addition, the molecular weights of PS chains are much lower than the entanglement molecular weight of PS, which also predicts that PS chains obey Fickian diffusion and behaves like a small molecule. That means all chains move independently from each other and there are no entanglements in the film.

The frequency changes in Figure 6 can be converted into mass changes by using eq. (2). The normalized mass changes against swelling time are given in Figure 7. The normalized mass uptake, M_t , is plotted in Figure 8 for the square root of swelling time according to eq. (7). The slopes of the linear relations in Figure 8 produce the diffusion coefficients, D_s , for the swelling of polymeric film. The obtained values of diffusion coefficients vary among $0.2\text{--}3.0 \times 10^{-16}$, $5.0\text{--}13 \times 10^{-16}$, and $1.0\text{--}1.6 \times 10^{-15}$ cm²/s for PS1, PS2, and PS3 LB thin films, respectively and are plotted in Figure 9 versus saturated chloroform vapor content. It is seen that D_s increased as the vapor content increased in the cell. In other words, a decrease in the vapor content prevents the film from swelling and the diffusion of

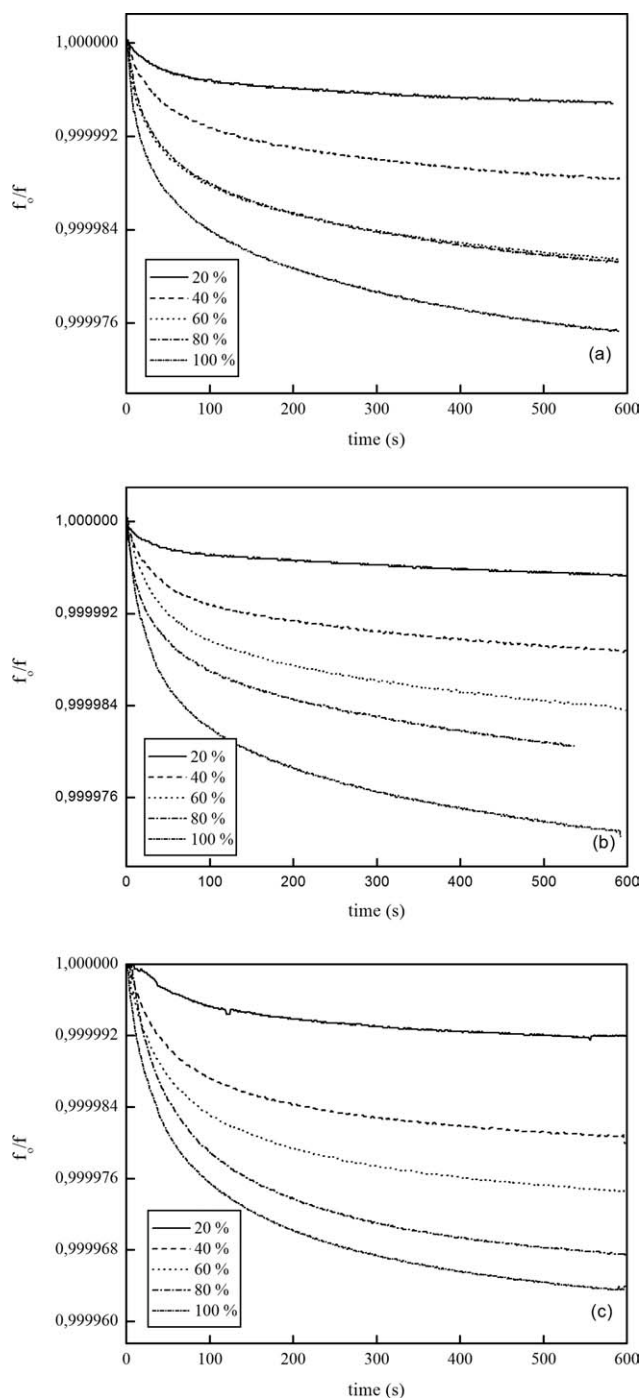


Figure 6 Normalized frequency changes during gas exposure versus time.

chloroform molecules into PS films slows down. Giordano et al.⁴⁴ used a film of syndiotactic polystyrene (sPS) in the nanoporous crystalline δ form has been used for the detection of chloroform and toluene in the liquid phase at very low concentration. In their study, reflectance measurements were carried out to detect very small amounts of chemicals (chloroform and toluene) in water down to concentrations of 5 ppm, and moreover, results achieved in

the case of chloroform by the optoelectronic sensor, were compared with that of a classical resonant quartz-crystal microbalance coated with the same sPS as sensing element, working, as well in an aqueous solution. Giordano et al. found that diffusion coefficients for sPS in chloroform and toluene were in the order of 10^{-12} and 10^{-13} cm^2/s for chloroform

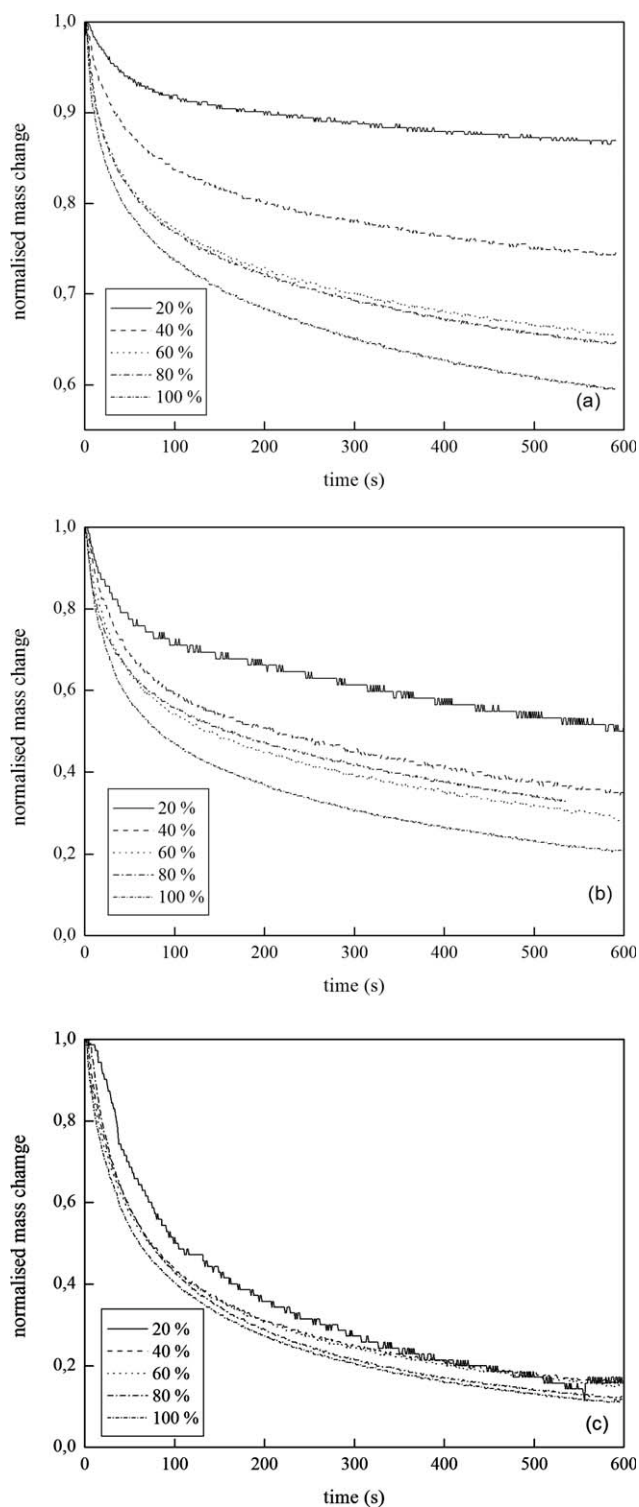


Figure 7 Normalized mass change versus time.

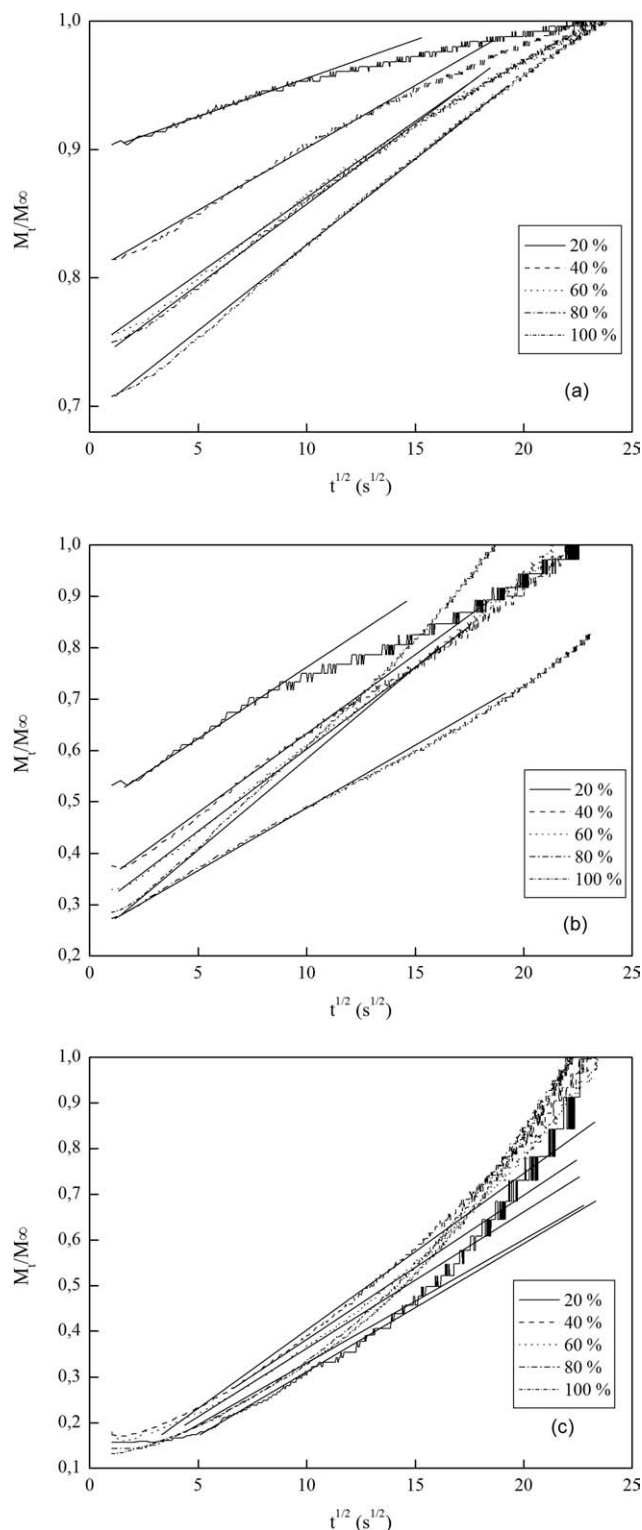


Figure 8 Linear regression of the data in Fig. 7 according to eq. (7). (a), (b), and (c) stand for PS1, PS2 and PS, respectively.

and toluene at 35°C, respectively which are rather high compared with our measurements. In fact, it is known that diffusion is always faster in an organic solvent than under organic vapor since organic

molecules penetrate much slower into PS film from the vapor phase than from a liquid solvent.

CONCLUSIONS

PS chains have been successfully transferred as PS monolayers from water surface onto quartz crystal substrates using LB thin film technique. Sensor response is highly affected by the properties of polymers as well as the successful production of PS thin films. The responses of PS LB films to chloroform vapor are fast, strong, reproducible and reversible after injecting the gas cell with fresh air. This time-dependent response for the investigation of the repeatability of the chloroform vapor sensor at room temperature shows relatively stable repeatability and almost uniform changes in frequency. These PS LB films showed not only good reproducibility but also high organic vapor sensitivity with almost the same frequency shifts, rapid response and fast recovery time. We introduced a model to employ the swelling behavior of PS polymeric films under exposure to different saturated chloroform vapor content in dry air. It is known that adsorption is the phenomenon responsible for the interaction between the coating and the analyte. It is understood that the penetration of organic vapor molecules into the polymeric film is faster for higher molecular weight PS thin films than lower molecular weight PS thin films and that the interdiffusion of polymer chains increases as the organic vapor content in the cell increases. In other words, diffusion coefficients for high molecular weight PS thin films are about 10 times larger than the diffusion coefficients for low molecular weight PS thin films. An explanation for this is, a higher molecular weight chain of PS has more space for organic vapor to adsorb to the surface, resulting in larger diffusion coefficients. As a result, these PS materials could be an alternative for other traditional

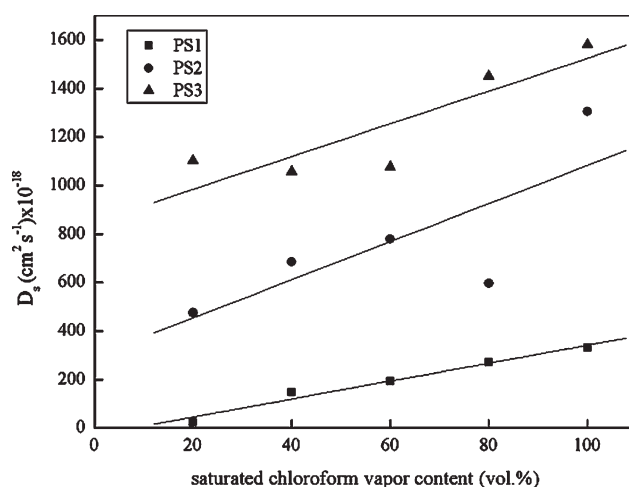


Figure 9 Diffusion coefficients, D_s versus saturated chloroform vapor content. The solid lines are for eye guide.

LB film materials and may find potential applications in the development of room temperature organic vapor sensing devices.

References

- Naito, K.; Hieda, H.; Sakurai, M.; Kamata, Y.; Asakawa, K. *IEEE Trans Magn* 2002, 38, 1949.
- Ross, C. *Annu Rev Mater Res* 2001, 31, 203.
- Lesho, M. J.; Sheppard, N.F. *Polym Gels Netw* 1997, 5, 503.
- Chen, W. L.; Shull, K. R.; Papatheodorou, T.; Styckas, D. A.; Keddie, J. L. *Macromolecules* 1999, 32, 136.
- Papanu, J. S.; Hess, D. W.; Bell, A. T.; Soane, D. S. *J Electrochem Soc* 1989, 136, 1195.
- Drake, P. A.; Bohn, P. W. *Anal Chem* 1996, 67, 1766.
- Adhikari, B.; Majumdar, S. *Prog Polym Sci* 2004, 29, 699.
- Sleep, B. E. *Adv Water Resour* 1998, 22, 247.
- Petty, M. C. *Langmuir-Blodgett Films*; Cambridge University Press: New York, 1996.
- Cheyne, R. B.; Moffitt, M. G. *Langmuir* 2006, 22, 8387.
- Fasolka, M. J.; Harris, D. J.; Mayes, A. M.; Yoon, M.; Mochrie, S. G. *J Phys Rev Lett* 1997, 79, 3018.
- Aksay, I. A.; Trau, M.; Manne, S.; Honma, I.; Yao, N.; Zhou, L.; Fenter, P.; Eisenberger, P. M.; Gruner, S. M. *Science* 1996, 273, 892.
- Zhu, J.; Eisenberg, A.; Lennox, R. B. *Macromolecules* 1992, 25, 6547.
- DaSilva, A. M. G.; Filipe, E. J. M.; dOliveira, J. M. R.; Martinho, J. M. G. *Langmuir* 1996, 12, 6547.
- Cheyne, R. B.; Moffitt, M. G. *Langmuir* 2005, 21, 5453.
- Fu, Y.; Finklea, H. O. *Anal Chem* 2003, 75, 5387.
- Mirmohseni, A.; Oladegaragoze, A. *Sens Actuators B: Chem* 2004, 102, 261.
- Erdogan, M.; Capan, I.; Tarimci, C.; Hassan, A. K. *J Colloid Interf Sci* 2008, 323, 235.
- Gacal, B. N.; Koz, B.; Gacal, B.; Kiskan, B.; Erdogan, M.; Yagci, Y. *J Polym Sci Pol Chem* 2009, 47, 5, 1317.
- Toiserkani, H.; Yilmaz, G.; Yagci, Y.; Torun, L. *Macromol Chem Phys* 2010, 211, 2389.
- Capan, I.; Capan, R.; Tanrisever, T.; Can, S. *Mater Lett* 2005, 59, 2468.
- King, W. H. *Anal Chem* 1964, 36, 1735.
- Sauerbrey, G. *Z. Physics* 1959, 155, 206.
- de Gennes, P. G. *Scaling Concept in Polymer Physics*; Ithaca, New York: Cornell University Press, 1979.
- Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, 1986.
- Dobkowski, Z. *Rheol Acta* 1995, 34, 578.
- Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; New York: Wiley, 1980.
- Larson, R. G.; Sridar, T.; Leal, L. G.; McKinley, G. H.; Likhtman, A. E.; McLeish, T. C. B. *J Rheol* 2003, 47, 809.
- Erdogan, M.; Capan, R.; Davis, F. *Sens Actuators B-Chem* 2010, 145, 66.
- Crank, J. *The Mathematics of Diffusion*; London: Oxford University Press, 1970.
- Erdogan, M.; Pekcan, O.; Yagci, Y. *Macromol Chem Phys* 2004, 205, 456.
- Ruan, W.; Lü, Z.; Ji, N.; Wang, C.; Zhao, B.; Zhang, J. *Chem Res Chinese U* 2007, 23, 712.
- Wen, G.; Chung, B.; Chang, T. *Polymer* 2006, 47, 8575.
- Chung, B.; Choi, M.; Ree, M.; Jung, J. C.; Zin, W. C.; Chang, T. *Macromolecules* 2006, 39, 684.
- Zhu, J.; Eisenberg, A.; Lennox, R. B. *J Am Chem Soc* 1991, 113, 5583.
- Wong, K.; Tang, Z.; Sin, J.; Chan, P. *ICSE'96 Proc IEEE* 1996, 217.
- Gomes, M.T.S. R.; Duarte, A. C.; Joao, A. B. P. *Oliveira Talanta* 1999, 48, 81.
- Serra, F.; Terentjev, E. M. *Macromolecules* 2008, 41, 981.
- Zhang, S.; Chen, Z. K.; Bao, G. W.; Li, S. F. *Talanta* 1998, 45, 727.
- Xu, L.; Hu, X.; Lim, Y. T.; Subramanian, V. S. *Thin Solid Films* 2002, 417, 90.
- Pilla, P.; Cusano, A.; Cutolo, A.; Giordano, M.; Mensitieri, G.; Rizzo, P.; Sanguigno, L.; Venditto, V.; Guerra, G. *Sensors* 2009, 9, 12, 9816.
- Mensitieri, G.; Venditto, V.; Guerra, G. *Sens Actuators B Chem* 2003, 92, 255.
- Feller, J. F.; Grohens, Y. *Sens Actuators B Chem* 2004, 97, 231.
- Giordano, M.; Russo, M.; Cusano, A.; Mensitieri, G.; Guerra, G. *Sens Actuators B Chem* 2005, 109, 177.
- Guerra, G.; Mensitieri, G.; Venditto, V. *U.S. Pat Appl Publ* 2002, 7.
- Musto, P.; Mensitieri, G.; Cotugno, S.; Guerra, G.; Venditto, V. *Macromolecules* 2002, 35, 2296.
- Arpaia, P.; Guerra, G.; Mensitieri, G.; Schiano Lo Moriello, R. *IEEE Trans Instrum Meas* 2005, 54, 31.