

The Investigation of Swelling Behaviors of Copolymer Thin Films Exposed to Various Organic Vapors by Quartz Crystal Microbalance Technique

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Abstract

In this work, the swelling behaviours of the poly(CINOEMA-co-DEAEMA) Langmuir-Blodgett (LB) films were investigated with respect to volatile organic compounds (VOCs) at room temperature by using Quartz Crystal Microbalance (QCM) method. The changes in resonance frequency associated with mass changes can be attributed to the swelling behaviour of copolymer thin films during vapor absorption. The diffusion coefficients are found to be 31.07×10^{-16} , 15.61×10^{-16} and $1.22 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for dichloromethane, chloroform, and benzene, respectively. The response of copolymer LB films to the chosen VOCs has been investigated in conditions of physical properties of the solvents, and the films were obtain to be largely sensitive to dichloromethane vapor compared to other studied vapors.

Keywords – Swelling, Diffusion, LB thin film, QCM technique, Copolymer

1 Introduction

In recent years, polymeric materials are used as environmentally responsive coatings in volatile organic compounds (VOCs) detection due to their ability to absorb a variety of different molecules. VOCs such as chloroform, dichloromethane, acetone, benzene, toluene, ethyl alcohol, xylene and hexane are a large group of air pollutants. The majority of VOCs found in the indoor environments originate from building materials, indoor furnishings, cleaning supplies, consumer products and processes, such as printing, cooking, cleaning and pesticide applications [1,2]. The effects of VOCs exposure depends on several parameters including the type of VOCs, the amount of VOCs and the length of time a person is exposed. High concentration exposure to some VOCs over a short or long term may cause diseases

or serious irreversible effect [3,4]. The detection of VOCs is one of the most important issues for the protection of human health and environment. Therefore, a significant interest in chemical sensing applications of organic materials such as carbon nanotubes [5], porphyrins [6], phthalocyanines [7], perylenes (PDIs) [8], indane [9], calix[n]arene [10] and polymers [11] are studied in order to fabricate a highly sensitive, easy to use, cheap, selective and a long life sensor.

There are few research studies about the swelling behaviors of the polymer and its derivatives using QCM technique in literature [12]. Therefore, the purpose of the present work is to use a poly(CINOEMA-co-DEAEMA) as an active material for producing LB thin films. These LB films were subjected to various saturated VOCs to study the swelling mechanism in sensor

applications. Using the QCM measurement system, variations on frequency shift were monitored in real time during swelling in which organic vapor was introduced into a gas cell. Early-time Fick's law of diffusion was adopted to fit the QCM results.

2. Experimental details

All poly(CINOEMA-co-DEAEMA) molecules were dissolved in dimethylformamide (DMF) with a ratio of concentration of 3.2 mg ml⁻¹. A computer controlled NIMA 622 LB film trough was employed to investigate the behavior of poly(CINOEMA-co-DEAEMA) molecules at the air-water interface. 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. Solutions were spread onto the water surface using a microliter syringe and approximately 15 min were allowed for the DMF to evaporate before the area enclosed by the barriers was reduced. The isotherm (Π -A) graph of poly(CINOEMA-co-DEAEMA) was recorded as a function of surface area at pH 6.0 using the compression speed of barriers at a value of 200 cm² min⁻¹. Monolayer of poly(CINOEMA-co-DEAEMA) at the water surface was found to be stable and surface pressure of 18 mN m⁻¹ was selected for LB film deposition onto quartz crystal substrates for QCM measurements.

QCM measurement system was also employed to study the kinetic response of the LB sample against different organic vapors. A gas cell was constructed to study the LB film response on exposure to organic vapors by measuring the frequency change and these measurements were performed with a syringe. The sample was periodically exposed to organic vapors at least for 2 min, and was then allowed to recover after injection of dry air. The changes in resonance frequency were recorded in real time during exposure to organic vapors. The exposure to VOC vapor for 2 min was followed by flushing of the cell with dry air for another 2 min. This procedure was carried out over several cycles to observe the reproducibility of the LB film sensing element.

3. Results and Discussion

3.1. Isotherm Properties and Transfer Ratio

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 using this following relation:

$$a_m = AM_w / cN_A V \quad (3.1)$$

where, A is the area of the water surface enclosed by the trough barriers, M_w is the molecular weight, c is the concentration of the spreading solution, N_A is the Avogadro's number, and V is the volume of solution spread over the water surface. The Π -A isotherm graph for poly(CINOEMA-co-DEAEMA) monolayer at pH 6 is shown in Figure 1. Using Π -A graph and Equation 1 the limiting area per molecule can be obtained by extrapolating the slope of low compressibility to zero pressure and indicates 1.98 nm² for $V=700 \mu\text{l}$. The surface pressure value of 18 mN m⁻¹ is a common value for the solid phases for all copolymer isotherms and it was selected as the fabrication pressure value in this study. POT-CdA monolayer is also transferred onto substrate at the same surface pressure value of 18 mN/m [13]. The isotherms are reproducible within an error of $\pm 0.04 \%$ and each isotherm is obtained by averaging at least three runs. Our results for poly(CINOEMA-co-DEAEMA) material indicate good stability and reproducibility of the monolayers at the water surface. Therefore, this surface pressure value was selected for copolymer LB film deposition. Copolymer monolayer was sequentially transferred, by vertical dipping, onto quartz crystal at room temperature for QCM measurement.

The transfer ratio given in Equation (3.2) is an important parameter used to characterize LB deposition. This parameter is defined as the ratio of the area of the LB film removed from the water surface to the area of the substrate moved through the air-monolayer-water interface.

$$\tau = A_L / A_S \quad (3.2)$$

Where, A_L is the decrease in the area occupied by the monolayer on the water surface, and A_S is the coated area of the substrate. The poly(CINOEMA-co-DEAEMA) monolayers during the deposition onto quartz glass substrate for 2 bilayers is given in the inset of Figure 1. It is found that the average reduction of the area for each bilayer is almost the same during the deposition process of monolayers onto quartz glass substrate. Using Equation 2, transfer ratio values is found to be ≥ 0.92 for quartz crystal substrate. With these results it can be concluded that uniform Y-type poly(CINOEMA-co-DEAEMA) LB films are deposited onto quartz crystal substrates.

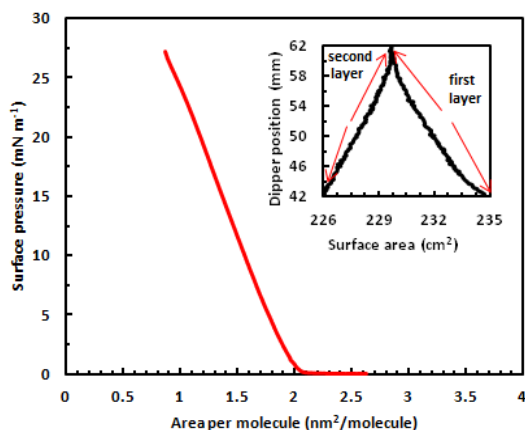


Figure 1: Isotherm graphs of poly(CINOEMA-co-DEAEMA) monolayer. Inset: The deposition graphs of poly(CINOEMA-co-DEAEMA) LB film on the quartz substrate.

3.2. Sensing properties of the copolymer LB film

In order to study the potential application of poly(CINOEMA-co-DEAEMA) LB film in the field of vapor sensing, the kinetic response of the LB sample to several organic vapors is recorded by measuring the frequency changes as a function of time. The poly(CINOEMA-co-DEAEMA) LB film is periodically exposed to the organic vapors for 2 min, followed by the injection of dry air for a further 2 min period. Figure 2 shows the kinetic

response of sensor molecule to chloroform vapors. In the initial step, sensor molecule expose to dry air for 120 seconds and the response was a stable value in this period of time. The initial response of sensor molecule in the QCM system for all vapors increased sharply between 120 and 125s due to surface adsorption effect. When the vapor molecules moved into the sensor molecule, the response decreased exponentially resulted from bulk diffusion effect. In the 240s, after flushing dry air, a rapid decrease of response was observed and then recovery process occurred between 240 and 244s for all vapors due to desorption of vapor. After 245s, the response of sensor molecule reached a stable value and the sensor obtained initial baseline. As a result, response of the sensor molecule to chloroform vapor is fast, reproducible and reversible. As a result, it can be considered that kinetic response mechanism occurs by a 3-stage (adsorption, diffusion, and desorption processes, respectively).

Figure 3 shows the kinetic response of the poly(CINOEMA-co-DEAEMA) LB film to the vapors. This LB film shows a response to all vapors with a fast, reproducible and reversible response after flushing the gas cell with fresh air. The response of the LB film in the form of QCM responses to saturated dichloromethane exposure is much higher than the other vapors with recovery and response times in the order of a few seconds when the gas cell is flushed with dry air.

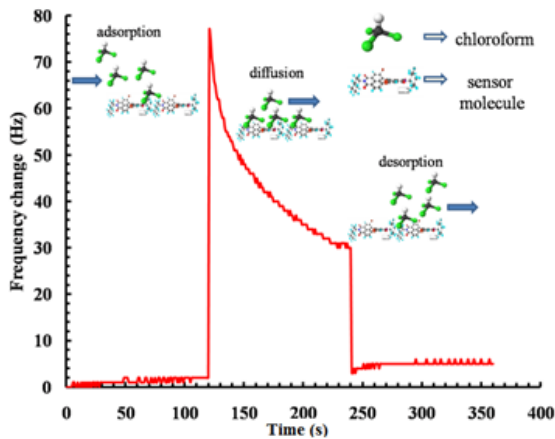


Figure 2. The mechanism of gas permeation into the sensing material.

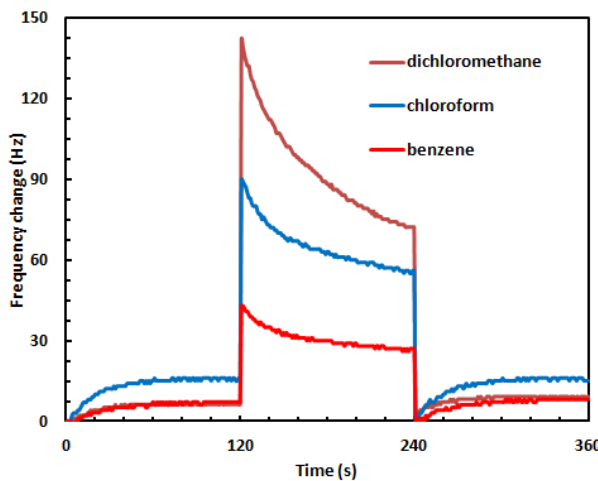


Figure 3. The frequency change of poly(CINOEMA-co-DEAEMA) LB film against organic vapors.

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 time [14]:

$$\frac{C}{C_0} = \frac{x}{d} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n} \sin \frac{n\pi x}{d} \exp\left(-\frac{Dn^2\pi^2}{d^2}t\right) \quad (3.3)$$

where d is the thickness of the slab, D is the diffusion coefficient, and C_0 and C are the concentration of the diffusant at time zero 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:

$$M = \int_V C dV \quad (3.4)$$

Where M is the mass uptake and V is the volume element. When Equation (3.3) is considered for a plane volume element and substituted in Equation (3.4), the following solution is obtained [15].

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D\pi^2}{d^2}t\right) \quad (3.5)$$

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:

$$\frac{M_t}{M_{\infty}} = 4\sqrt{\frac{D}{\pi d^2}}t^{1/2} \quad (3.6)$$

which is called early-time equation and this square root relation can be used to interpret the swelling data [16,17].

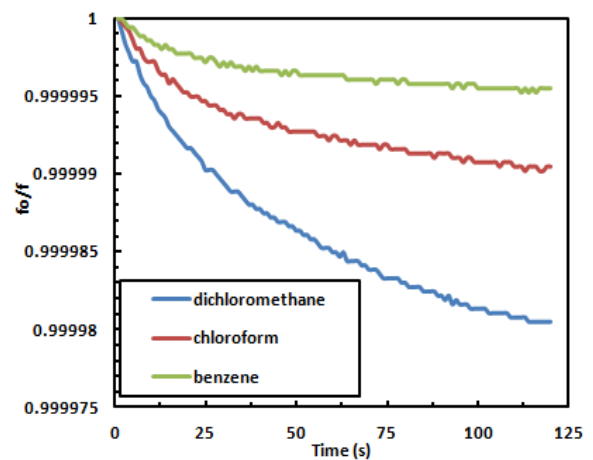


Figure 4. Normalized frequency changes during gas exposure versus time.

In order to quantify the kinetic data (given in the Figure 3), it is necessary to extract the copolymer LB film parameters due to swelling for three different organic vapors. Figure 4 displays the normalized frequency change against swelling time, t_s . The period of swelling time started at $t=0$ for each swelling event. This process was obtained for all organic vapors at saturated concentrations. The decrease in the normalized frequency (given in Figure 4) can be explained with the chain inter diffusion between copolymer chains during vapor exposure. These results can be related to the amounts of organic vapor molecules entering the copolymeric film M_t ; that is, Δ_{ft} should be directly proportional to M_t [18]. Equation (3.6) now can be written as:

$$\left(\frac{M_t}{M_\infty}\right) \cong \left(\frac{\Delta_{ft}}{\Delta_{f\infty}}\right) = 4\sqrt{\frac{D}{\pi d^2}}t^{1/2} \quad (3.7)$$

where Δ_{ft} and $\Delta_{f\infty}$ are the normalized frequency shift at any time, t and saturation point in Δ_f , respectively. The normalized Δ_f values [$\Delta_{ft}/\Delta_{f\infty}$] are plotted in Fig. 5 for the square root of swelling time according to Equation (3.7). The slopes of the linear relations in Figure 5 found the diffusion coefficients, D_s for the swelling of copolymeric film and those values are given in Table 1 vs. saturated organic vapors content.

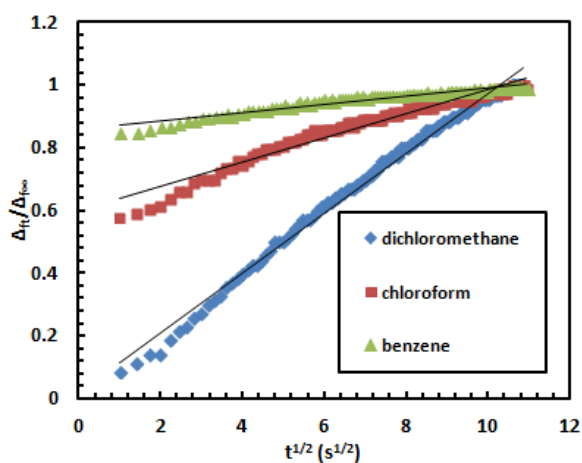


Figure 5. Plot of the normalized frequency against square root of swelling time, t_s . The solid line represents the fit of the data to Equation (3.7).

These results can be explained in terms of molar volume and viscosity of organic vapors. The physical properties given in Table 1 of the VOCs used in this work. VOCs molecules enter into the copolymer chains and expand the volume of chain causing swelling. The interaction of produced poly(CINOEMA-co-DEAEMA) thin films with VOCs molecules depended on physical properties of organic vapors such as molar volume and viscosity. Dichloromethane has the lowest molar volume ($64.10 \text{ cm}^3 \text{ mol}^{-1}$) among organic vapors used in this work. Benzene vapor has the highest molar volume ($86.36 \text{ cm}^3 \text{ mol}^{-1}$), and the viscosity value of benzene vapor (0.744 cSt) is higher than dichloromethane (0.324 cSt). While dichloromethane molecule can easily penetrate into copolymer LB films, the diffusion of benzene molecules into the same LB films is slower.

Table 1: The physical properties of the VOCs.

Organic vapors	Molar volume ($\text{cm}^3 \text{ s}^{-1}$)	Viscosity (cSt)	Ds ($\text{cm}^2 \text{ s}^{-1}$) $\times 10^{-16}$
Dichloromethane	64.10	0.324	31.07
Chloroform	80.70	0.380	15.61
Benzene	86.36	0.744	1.22

4. Conclusions

In this study, poly(CINOEMA-co-DEAEMA) LB film was exposed to dichloromethane, chloroform and benzene vapors. It is shown that the penetration of organic vapors into poly(CINOEMA-co-DEAEMA) LB film is quick enough and diffusion coefficients are connected on the VOCs used. This result can be related in terms of molar volume and viscosity parameter of swelling items. Diffusion coefficients found to be between 31.07×10^{-16} , 15.61×10^{-16} and $1.22 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for

dichloromethane, chloroform and benzene vapors, respectively. Diffusion coefficients for dichloromethane are higher than other organic vapors because dichloromethane has lowest molar volume and viscosity parameter which indicates that dichloromethane molecules are more mobile than the other organic molecules and diffuse easily into the poly(CINOEMA-co-DEAEMA) LB film. Otherwise, benzene has a larger viscosity parameter and also a larger molar volume which means these molecules are slow to diffuse into the poly(CINOEMA-co-DEAEMA) LB film, indicating lower diffusion coefficients than other organic vapors used in this work. As a result, this poly(CINOEMA-co-DEAEMA) material can be used as a sensing material and may find potential applications in the development of room temperature organic vapor sensing devices.

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