Swelling behaviour of perylendiimide langmuir-blodgett films and organic vapor sensing applications

Yaser AÇIKBAŞ [*]

Department of Material Science and Nanotechnology Engineering, Faculty of Engineering, University of Usak, TURKEY

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Abstract

In this study, the swelling behaviours of the N,N'-(glycine tert-butylester)-3,4,9,10-perylenediimide (FY1) Langmuir-Blodgett (LB) films were investigated with respect to volatile organic compounds (VOCs) at room temperature. The sensing responses of the films against to chloroform, benzene and toluene vapors were measured by Quartz Crystal Microbalance (QCM) method. The changes in resonance frequency associated with mass changes can be attributed to the swelling behaviour of FY1 thin films during organic vapor molecules absorption. The response of FY1 LB films to the choosed VOCs has been investigated in conditions of physical properties of the solvents, and the films were obtain to be largely sensitive to chloroform vapor compared to other studied vapors.

Keywords: *Perylenediimide; thin films; QCM; Langmuir-Blodgett films; sensors.*

Perilendimid langmuir-blodgett ince filmlerin şişme davranışı ve organik buhar duyarlılık uygulamaları

Özet

Bu çalışmada, N,N'-(glycine tert-butylester)-3,4,9,10-perylenediimide (FY1) Langmuir-Blodgett (LB) filmlerin oda sıcaklığında uçucu organik buharlara karşı şişme davranışları incelenmiştir. Bu ince filmlerin kloroform, benzen ve toluen buharlarına karşı tepkileri Kuartz Kristal Mikrobalans tekniği kullanılarak ölçülmüştür. Organik buhar moleküllerinin absorbsiyonu esnasında kütle değişimine bağlı rezonans

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[*] Yaser AÇIKBAŞ, yaser.acikbas@usak.edu.tr, Tel: 0 (276) 221 2136.

frekansındaki değişim, FY1 ince filmlerinin şişme davranışı ile açıklanabilir. FY1 LB filmlerin bu çalışma için seçilen organik buharlara karşı tepkisi bu organik buharların fiziksel özellikleri ele alınarak incelenmiş ve bu ince filmlerin kullanılan organik buharlar içerisinde en çok kloroform buharına karşı duyarlı olduğu gözlenmiştir.

Keywords: *Perilendimid; ince filmler, QCM; Langmuir-Blodgett filmler; sensörler.*

1. Introduction

In the recent years, perylene derivatives are promising and versatile candidates for use in organic gas sensor applications. These sensor materials can be investigated by using interferometry, ellipsometry, surface plasmon resonance (SPR) or quartz crystal microbalance (QCM) techniques [1-3]. Among them, QCM has recently attracted a large interest due to its potential applications such as thin film characterization [4] and gas sensor applications [5]. For the purpose of sensing gas molecules, the thin film must be functionalized with a gas sensitive layer. Perylene diimides and their derivatives are excellent materials to organize as a monolayer on the water surface, due to being aromatic molecules with an extensive π-system and considerable planarity. The Langmuir-Blodgett (LB) technique is a suitable method for the fabrication of thin films with perylenediimides and most organic compounds.

There are few research studies about the swelling behaviours of the perylene and its derivatives using QCM technique in literature [6,7]. Therefore, the purpose of the present work is to use N,N’-(glycine tert-butylester)-3,4,9,10-perylenediimide (FY1) as an active material for producing LB thin films. These LB films were subjected to various concentrations of partially 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

The synthesis process of FY1 materials are given in the literature [8]. The surface pressure versus surface area (Π–A graph) is an important graph to understand the characteristic surface behaviour of a floating monolayer on the water surface. The floating monolayers at the air-water interface was found to be stable at a surface pressure of 22.5 mN m^{-1}; therefore, this surface pressure value was selected for FY1 LB film deposition. FY1 monolayer was sequentially transferred, by vertical dipping, onto quartz crystal at room temperature for QCM measurement.

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 6 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. During this procedure the volume of VOC vapor introduced into the gas cell varied between 2-10 ml. The exposure to VOC vapor for 6 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

The Π-A graph of FY1 obtained from the floating monolayer on the water subphase is given in Figure 1. The insets (a) and (b) in Figure 1 show the chemical structure of FY1 molecule and the plot of the change in the resonant frequency against number of layers for FY1 LB film, respectively. It is clear that a systematic change in the frequency is observed with the increase in the number of monolayers. This linear change between the deposited mass and the number of layers confirms the uniform transfer process of the LB film and the process was shown to be highly reproducible.

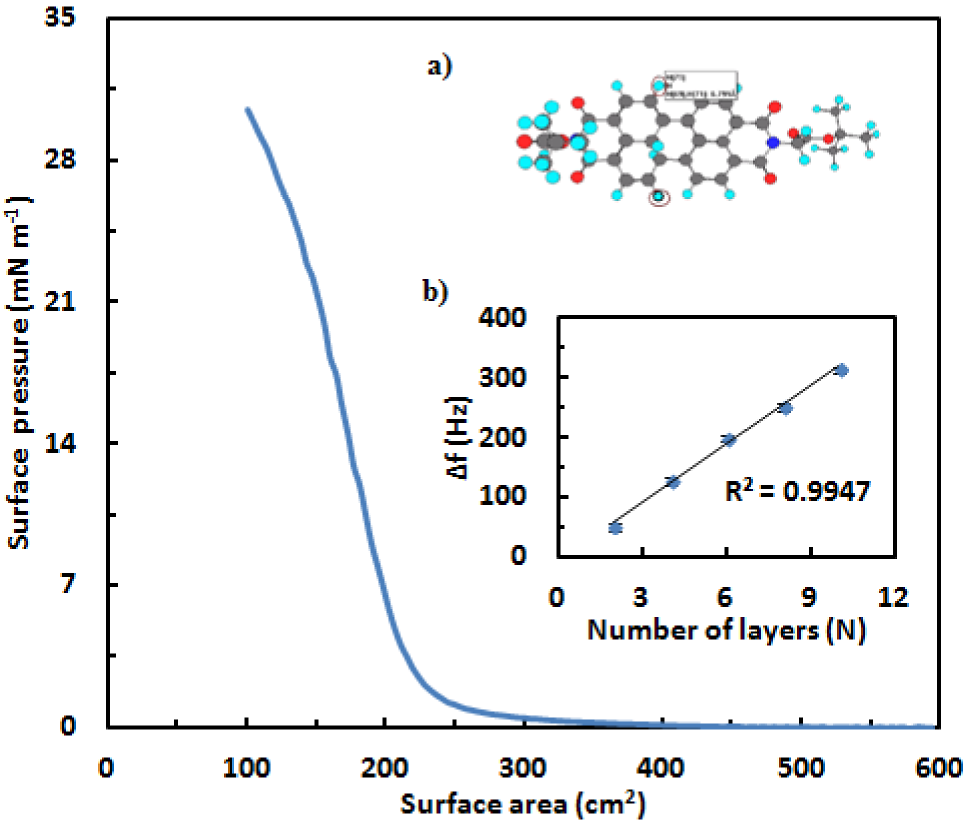

Figure 1. Isotherm graph of FY1 monolayer. Inset: a) The transfer graph of FY1 LB film on the quartz crystal, b) Chemical structure of FY1 molecule.

The reduced surface area change of FY1 monolayers during the deposition onto a glass substrate for three bilayers is given in Figure 2. It is found that the average reduction of the area for each bilayer was almost the same during the deposition process of monolayers onto the glass substrate. The labels in the Figure 2 was pointed from position (a) to position (b) right-to-left direction when the first LB film layer deposited onto the solid substrate. Similar labeling was made for the second and third layers. In this study, the Langmuir-Blodgett films were deposited onto glass substrates with both Z-type. In this study, alternate layer Langmuir through, which has two comparments with a fixed barrier in the centre to separate the two sections, was used for Z-type deposition. The central barrier includes a rotating clamp, which carries the substrate between the two sections. The substrate, thus, rotates through each water-monolayer (first section) and air-monolayer (second section) water interface. But the molecules were only spread on the first section to be fabricated Z-type Langmuir-Blodgett thin films.

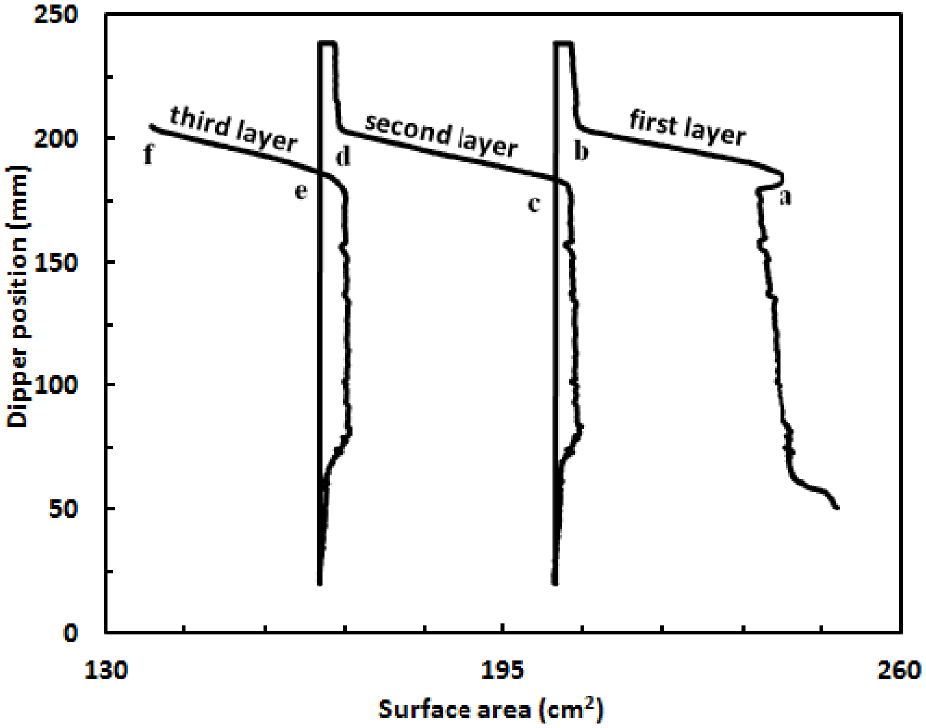

Figure 2. The number of LB deposition cycles of FY1 thin film onto glass substrate.

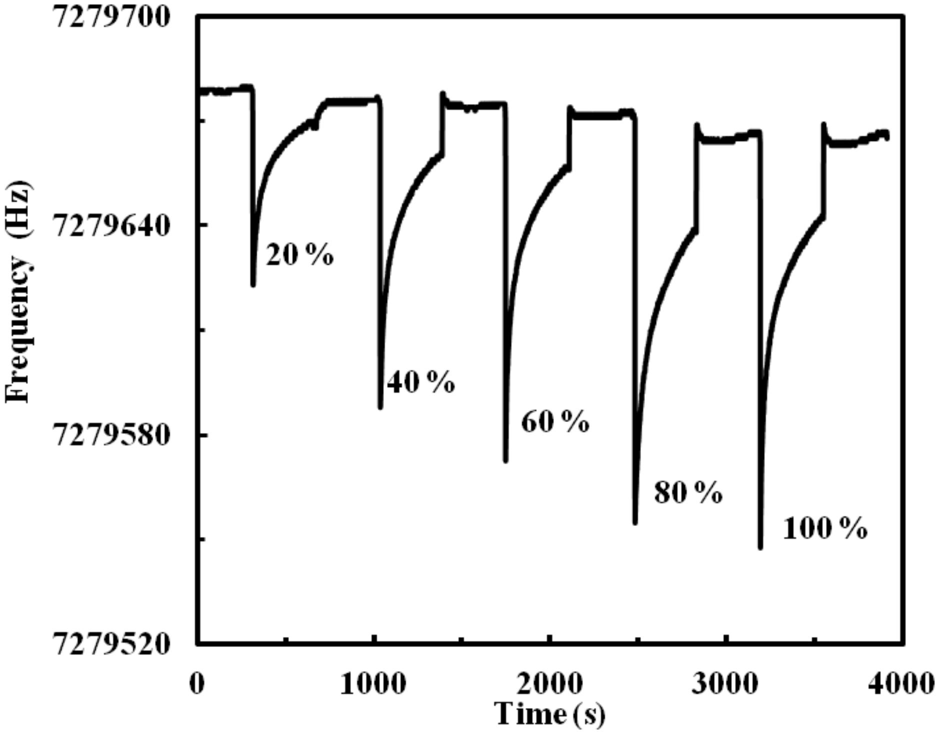

Figure 3. The response of FY1 LB sensor to different concentrations of chloroform vapor.

Figure 3 shows the kinetic response for 10 layers FY1 LB films against chloroform vapor at different concentrations at room temperature. It can be seen that as the concentration of the percentage increases, the frequency shifts increases proportionately. Furthermore, the FY1 LB film exhibits a rapid and fast reversible response with the injection of air or gas into the gas cell.

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 [5]:

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

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:

$$M=\int_V C\,dV \tag{2}$$

where M is the mass uptake and V is the volume element. When Equation 1 is considered for a plane volume element and substituted in Equation 2, the following solution is obtained [9].

$$\frac{M_t}{M_\infty}=1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2D\pi^2}{d^2}t\right) \tag{3}$$

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:

$$\frac{M_t}{M_\infty}=4\sqrt{\frac{D}{\pi d^2}}t^{1/2} \tag{4}$$

which is called early-time equation and this square root relation can be used to interpret the swelling data [10, 11].

To measure the kinetic data given in Figure 3, it is required to take the FY1 LB film parameters due to swelling. Figure 4 represents the normalized frequency change against swelling time where the consolidation process involves setting starting times to $t=0$ for each swelling cycles. As seen in Figure 4, the normalized frequency decreased as the time of vapor exposure increased. It is also seen that changes in the normalized frequency against the time of vapor exposure decreased very fast as the chloroform percentage concentration injected into the gas cell is increased. These behaviours can be declared with the chain inter diffusion between perylene chains during vapor exposure. As the saturated chloroform vapors penetrate into FY1 film, the perylene chains interdiffuse, which results in the decrease of the normalized frequency from the FY1 film. These results can be related to the amounts of diffusant entering the FY1 film M_t; that is, Δ_{ft} should be directly proportional to M_t [5,12]. Equation 4 now can be written as:

$$\left(\frac{M_t}{M_\infty}\right) \square \left(\frac{\Delta f_t}{\Delta f_\infty}\right) = 4\sqrt{\frac{D}{\pi d^2}}\, t^{1/2} \tag{5}$$

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 Figure 5 for the square root of swelling time according to Equation (5). The slopes of the linear relations in Figure 5 found the diffusion coefficients, D_s for the swelling of FY1 film and those values are given in Table 1.

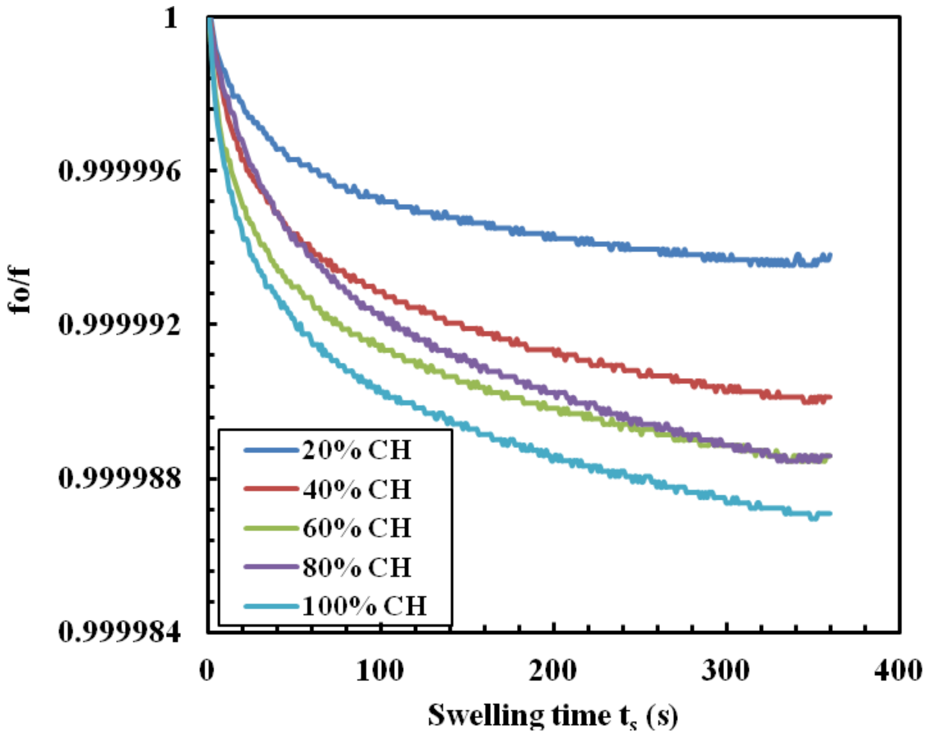

Figure 4. Normalized frequency changes during gas exposure versus swelling time.

Table 1. The physical properties of the VOCs.

LB thin film	Organic vapors	Ds(cm^2 s^{-1})×10^{-19}				
		20 %	40 %	60 %	80 %	100 %
FY1	Chloroform	2.27	6.81	8.69	14.56	18.81
	Benzene	1.97	4.08	6.50	12.40	15.30
	Toluene	0.90	1.21	3.22	5.32	11.30

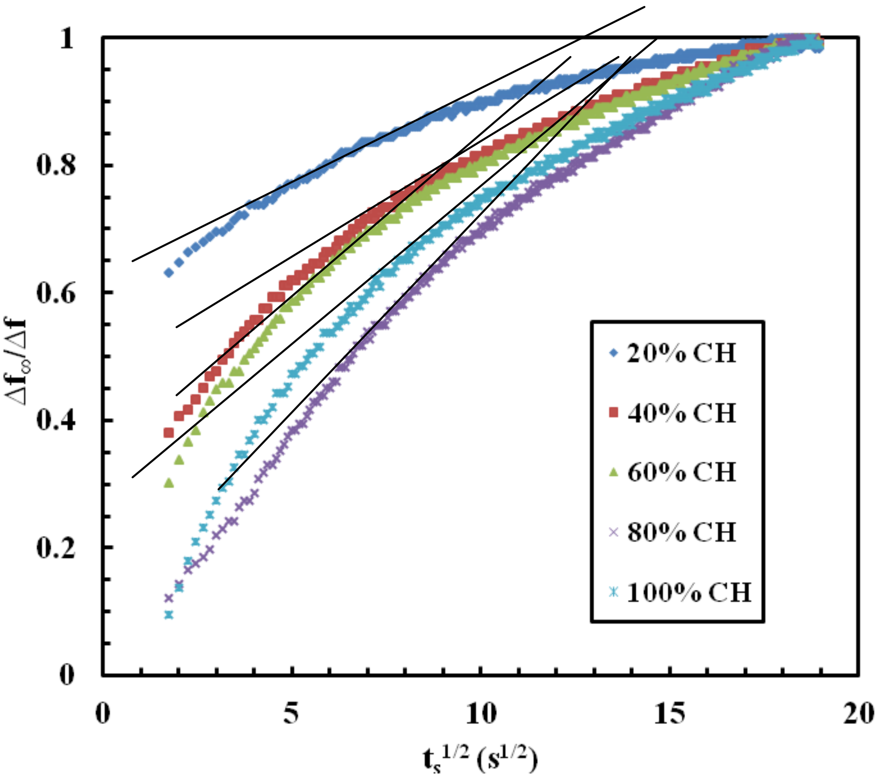

Figure 5. Plot of the normalized frequency against square root of swelling time, t_S . The solid line represents the fit of the data to Equation 5.

The interaction of the produced thin films with VOCs molecules can be explained by physical properties of organic vapors such as molecular weight and molar volume. The molecular weights of organic vapors is ordered as chloroform (119.38 g mol^{-1}) > toluene (92.14 g mol^{-1}) > benzene (78.11 g mol^{-1}). A larger molecular weight of vapor leads to higher sensitivity, which is in good agreement with the previous findings in the literature [13]. However, the sensitivity of FY1 LB film sensor against benzene vapor is larger than toluene vapor. This can be explained with the molar volumes of organic vapors. The molar volume of benzene (86.36 cm^3 mol^{-1}) is smaller than toluene (107.00 cm^3 mol^{-1}). While benzene molecule can easily penetrate into FY1 LB film, the diffusion of toluene molecules into the same LB films is slower.

In our previous study, using the QCM measurement system, vapor sensing properties were investigated and FY1 [8] novel material showed similar results. The response of FY1 LB film in the form of QCM response to same organic vapors is reproducible and reversible, which is ordered as chloroform > benzene > toluene.

3. Conclusions

QCM results show that the FY1 LB film transfer onto a glass substrate is found to be successful and monolayers are transferred uniformly onto gold-coated glass substrates with a linear relationship between number of layer and the frequency shift. This relationship suggests that equal mass per unit area is deposited onto the glass substrate during the transfer of FY1 LB film layers. The potential application of FY1 LB film as a vapor sensing material using chloroform, benzene and toluene vapors is investigated and the kinetic measurement of this LB film shows fast, reproducible and reversible response to all used vapors. A larger response to chloroform occurred compared to the other organic vapors. The FY1 material can be used as a sensing material and may find potential applications in the development of room temperature organic vapor sensing devices.

References

[1] Edmiston, P. L., Campbell, D. P., Gottfried, D. S., Baughman, J. and Timmers, M. M., Detection of vapor phase trinitrotoluene in the parts-per-trillion range using wabveguide interferometry. **Sensors and Actuators B: Chemical**, 143, 574-582, (2010).

[2] Hassan, A. K., Nabok, A. V., Ray, A. K. and Kiousis, G., The interaction of ozone with polyphenilsulfide thin films studied by ellipsometry and SPR. **Materials Science and Engineering: C**, 22, 197-200, (2002).

[3] Homola, J., Surface plasmon resonance sensors for detection of chemical andbiological species. **Chemical Reviews,** 108, 2,, 462-493, (2008).

[4] Venugopal, N. and Mitra, A., Influence of temperature dependent morphology onlocalized surface plasmon resonance in ultra-thin silver island films. **Applied Surface Science,** 285P, 357-372, (2013).

[5] Erdogan, M., Capan, R. and Davis, F., Swelling behaviour of calixarene film exposed to various organic vapours by surface plasmon resonance technique. **Sensors and Actuators B: Chemical,** 145, 66-70, (2010).

[6] Acikbas, Y., Erdogan, M., Capan, R. and Yukruk, F., Characterization and organic vapor sensing properties of Langmuir-Blodgett film using perylendiimide material. **Journal of Research on Engineering Structures and Materials**, 2, 99-108, (2015).

[7] Acikbas, Y., Erdogan, M., Capan, R. and Yukruk, F., Fabrication of Langmuir-Blodgett thin film for organic vapor detection using a novel N,N'-dicyclohexyl-3,4:9,10 perylenebis (dicarboximide). **Sensors and Actuators B: Chemical**, 200, 61-68, (2014).

[8] Acikbas, Y., Capan, R., Erdogan, M. and Yukruk, F., Thin film characterization andvapor sensing properties of a novel perylenediimide material. **Sensors and Actuators B: Chemical**, 160, 65-71, (2011).

[9] Crank, J., The Mathematics of Diffusion. **London: Oxford University Press**, (1970).

[10] Erdogan, M., Capan, I., Tarimci, C. and Hassan, A. K., Modeling of vapor sorption in polymeric film studied by surface plasmon resonance spectroscopy. **Journal of Colloid and Interface Science**, 323, 235-241, (2008).

[11] Erdogan, M., Ozbek, Z., ¸Capan, R. and Yagci, Y., Characterization of Polymeric LB Thin Films for Sensor Applications. **Journal of Applied Polymer Science**, 123, 2414-2422, (2012).

[12] Pekcan, O., Adiyaman, N. and Ugur, S., Energy-Transfer Method to Study Vapor-Induced Latex Film Formation. **Journal of Applied Polymer Science**, 84, 632–645, (2002).

[13] Xu, L. G., Hu, X., Lim, Y. T. and Subramanian, V. S., Organic vapor adsorption behaviour of poly(3-butoxythiophene) LB films on quartz crystal microbalance. **Thin Solid Films**, 417, 90-94, (2002).