Exp. Theo. NANOTECHNOLOGY 1 (2017) 41–47 https://doi.org/10.56053/1.1.41

Copolysiloxane solvent detector using Langmuir-Blodgett surface potential method

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Received 28 Nov. 2016; *Accepted* 12 Dec. 2016; *Published* 15 Jan. 2017

A quick detection for volatile organic compounds (VOCs), especially in the indoor environment is a must as the build-up level of VOCs is multiple times greater than outdoor environment. By using a surface potential probe, we have analyzed the interaction between copolysiloxane Langmuir-Blodgett (LB) thin films with several commercially used VOCs solvent, specifically chloroform ($CHCl_3$), isopropyl alcohol (IPA) and dichloromethane (DCM). These copolysiloxane LB thin films, namely $P_{50:50}$ and $P_{25:75}$ had been deposited onto aluminium-coated substrates. Subsequently, the surface potential (ΔV) of copolysiloxane LB thin films were monitored during exposure to each solvent. Interaction of these thin films with each solvent produced non-identical changes in ΔV values. In addition, ΔV_{max} value and halftime response for half ΔV_{max} value (t_{50}) were determined. Later, a figure of merit, f was calculated to determine the optimum sensing material per solvent. The most promising candidates particularly as IPA solvent vapour sensors is $P_{50:50}$ copolysiloxanes LB thin film that presented ΔV_{max} (106 mV), smallest halftime response for half ΔV_{max} value achieved, t_{50} (65 s), and considerable f (1.631 mV/s), as compared to others.

Keywords: Langmuir-Blodgett; Surface potential; Organic compounds.

1. INTRODUCTION

Volatile organic compounds (VOCs) are briefly defined as any compounds that took part in atmospheric photochemical reactions [1]. They are widely used as the solvent in various consumer product and industry manufacturing activities. Excessive usage of these VOC solvents might result in severe health condition as most of these are harmful to human being particularly in vapor form. Polysiloxanes are distinctive hybrid inorganic and semi-inorganic polymers that exhibit high gas permeability, low volatile, good thermal and oxidative stability, high chemical and biocompatibility [2, 3]. These compounds have been used extensively in innumerable applications such as medical, aerospace and sensor [4]. Hence, for the first time, an investigation regarding the interaction of copolysiloxanes, $P_{50:50}$ and $P_{25:75}$ Langmuir-Blodgett (LB) thin films, with several extensively used solvents, namely chloroform ($CHCl_3$), isopropyl alcohol (IPA) and dichloromethane (DCM), have been carried out using a surface potential (NIMA S-POT) probe. This is to verify that these copolysiloxanes might hold the potential to be alternative candidates for VOCs vapor sensing in term of surface potential changes detection.

2. EXPERIMENTAL

2.1 Materials

Two types of copolysiloxanes were selected as the basic materials in this investigation, named $P_{50:50}$ and $P_{25:75}$ as illustrated in Figure 1 and 2. Chloroform from Sigma-Aldrich was used as the solvent to dissolve the copolysiloxanes and produced 0.2 mg/ml of copolysiloxane solutions. Metal evaporation technique prepared aluminium coated-cleaned glass slides acted as the substrates. Three types of common VOCs solvents in the laboratory were chosen, namely $CHCl_3$, IPA and DCM (Figure 3) as the target solvent for interaction with copolysiloxanes. No further purification process required for all the reagents and solvents.

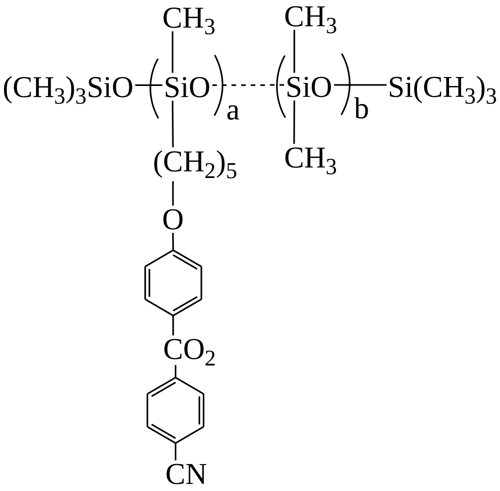
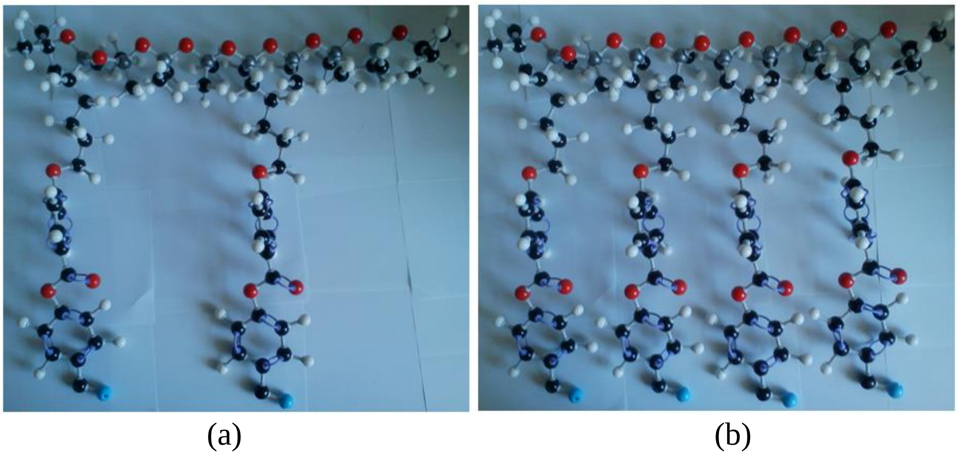


Figure. 1: General structure of copolysiloxanes, $P_{50:50}$ (a:b = 50:50) and $P_{25:75}$ (a:b = 25:75).



(a) (b)

Figure. 2: Ball and stick models of (a) $P_{50:50}$ and (b) $P_{25:75}$.

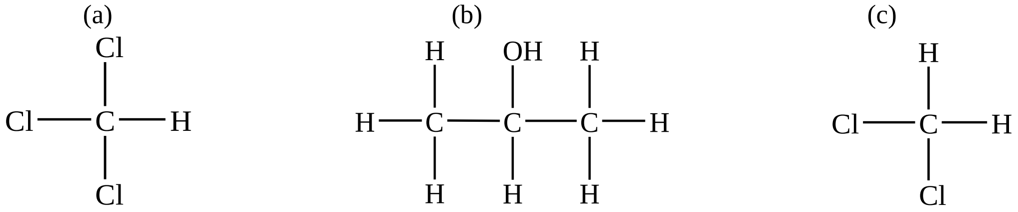


Figure. 3: Chemical structure of (a) $CHCl_3$, (b) IPA and (c) DCM.

2.2 Surface pressure-area isotherm and Langmuir-Blodgett thin films preparation

Surface pressure-area (Π-A) isotherms of copolysiloxanes, $P_{50:50}$ and $P_{25:75}$ were determined using a Langmuir trough (NIMA Model 611). Pure water (Elga Purelab water system, > 15 MΩcm) was utilized as the subphase. Chromatography paper acted as the surface pressure sensor. The solution was dispersed on subphase using a microsyringe. Then, 5 minutes were allowed for solvent evaporation before compression process. The similar procedure applied to the second copolysiloxane solution.

Later, 5 layers of Langmuir-Blodgett (LB) thin film were synthesized through LB deposition technique using the same trough for each copolysiloxanes. Surface pressure, 10 mN/m was selected as the deposition pressure since monolayer formed the compact solid state at this pressure as observed from the isotherm graph. Y-type deposition [4] was performed using 12 mm/min as the compression speed to develop the thin film on a substrate. Subsequently, the developed 5 layers LB thin films were utilized in the surface potential measurement against the VOCs vapor.

2.3 Surface potential measurement

The experiment was conducted in a sealed bag with a dimension of 0.125 m × 0.14 m × 0.095 m to prevent solvent leakage as illustrated in Figure 4.

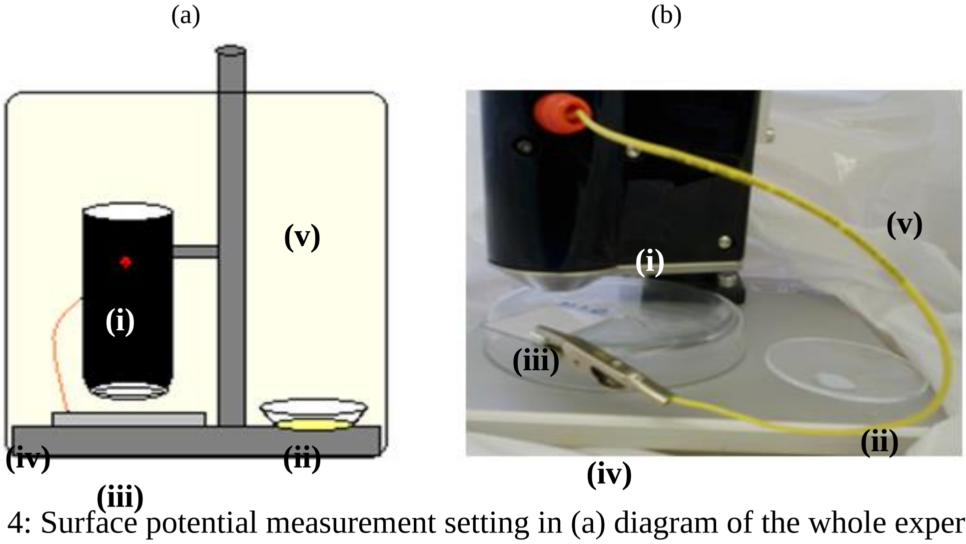


Figure. 4: Surface potential measurement setting in (a) diagram of the whole experimental setup and (b) actual experiment setup. Labels are (i) NIMA S-POT probe, (ii) solvents contained in a watch glass, (iii) LB thin film, (iv) Metal contact and (v) sealed bag.

Surface potential (ΔV) of LB thin films were measured using a S-POT probe (NIMA) with a precision of ± 2 mV attached directly to an Interface Unit software. A vibrating plate of the sensor was placed at a uniform distance (approximately 1 mm) to the LB thin film for ΔV measurement of interaction between copolysiloxane thin film and specific solvent. 1000µl of solvent was injected into the watch glass using a microsyringe from outside of the sealed bag. The duration of exposure time is about half an hour (0 – 2000 seconds) toward the solvents' vapor to determine the ΔV_{max} value and halftime response for half ΔV_{max} value achieved, t_{50} for each type of solvents. All experiments were performed under room temperature (21 ± 0.2 °C).

3. RESULTS AND DISCUSSION

3.1 Surface pressure (Π-A) isotherm

$P_{50:50}$ and $P_{25:75}$ monolayers were studied through Π-A isotherm graphs that displayed the surface pressure as a function of the molecular area at the air-water interface [5]. In Figure 5, both copolysiloxane formed stable monolayers until the collapse points start to occur at about 12.7 mN/m for $P_{50:50}$ and 19.4 mN/m for $P_{25:75}$. Direct phase transition from liquid expansion phase toward liquid condensed phase (~0 - 3 mN/m for $P_{50:50}$ and ~0 - 2 mN/m for $P_{25:75}$), followed directly by solid state formation (>3 mN/m for $P_{50:50}$ and > 2 mN/m for $P_{25:75}$) were observed. In the solid phase, stretched conformation follows by helical/loop structure conformation was demonstrated. A similar result in [6] proposed that in latter conformation, several functional groups are singled out from the subphase. Hence, 10 mN/m was chosen as the film deposition pressure because more uniform monolayer can be fabricated in stretched conformation than in helical/loop conformation.

The area per copolysiloxane chain was determined by extrapolating the steepest linear gradient of the curve to the x-axis in the solid phase before the area occupied per siloxane unit was calculated. Consequently, the diameter of siloxane unit was determined as an area of a circle was taken on the air-water interface by the siloxane unit. In Table 1, $P_{25:75}$ has a smaller value of area occupied per siloxane unit as compared to $P_{50:50}$ due to coiled and twisted structure of the copolysiloxane backbone, whereas $P_{50:50}$ retain a linear structure. Both copolysiloxane displayed general isotherm characteristics with their own specific signature.

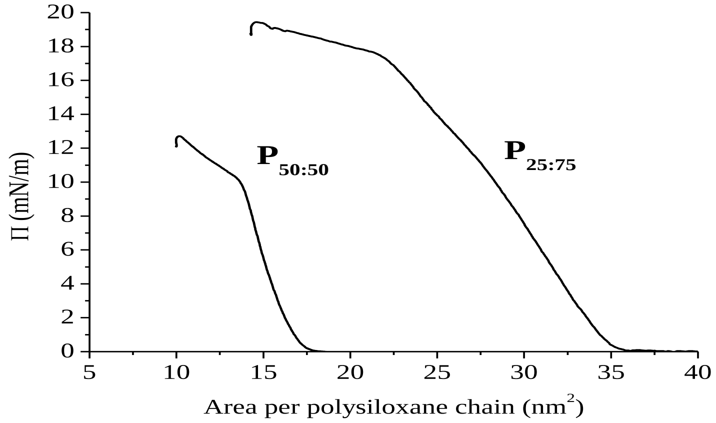


Figure. 5: Isotherm graphs of $P_{50:50}$ and $P_{25:75}$.

Table 1: Data from Π-A Isotherm of copolysiloxane, $P_{50:50}$ and $P_{25:75}$.

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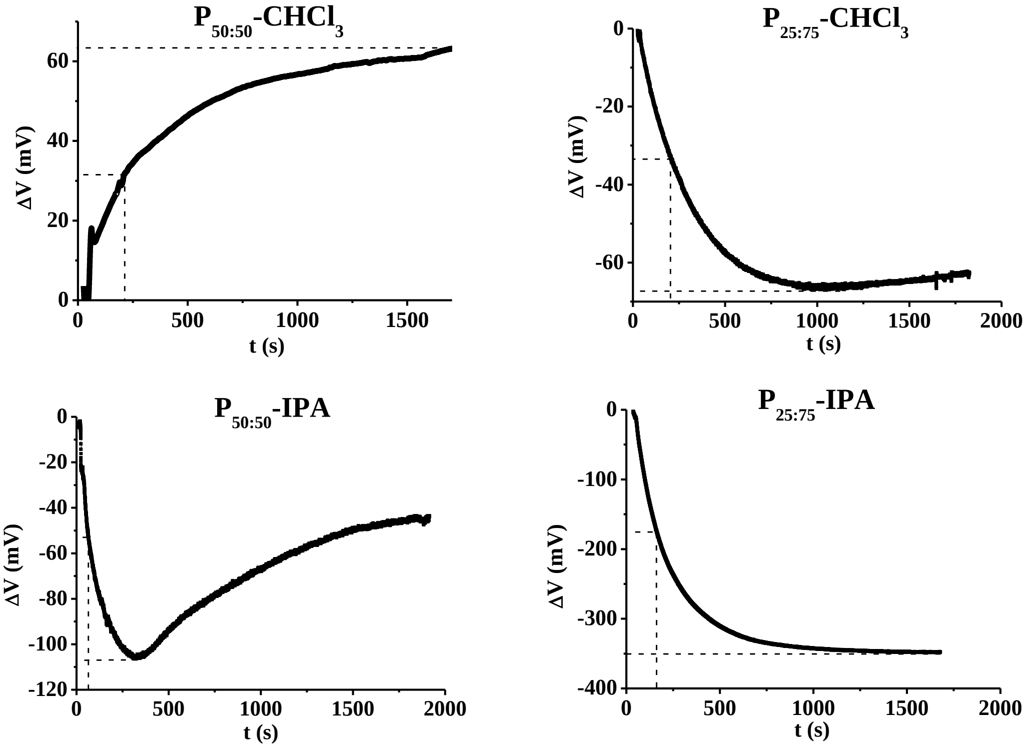
Copolysiloxane	$P_{50:50}$ (50:50)	$P_{25:75}$ (25:75)
Degree of polymerization / Number of repeating units	27	39
No. of unit siloxane	54	156
Limiting area per molecule (nm2)	17	35
Area occupied per siloxane unit (nm2)	0.31	0.22
Estimated siloxane unit size, d (nm)	0.63	0.53

3.2 Maximum surface potential (ΔV) and halftime response (t_{50})

By placing vibrating plate near to the copolysiloxane LB thin film, ΔV was recorded from the alternating current induction flowed in an external circuit due to capacitance changes in the air gap caused by vibration of air [7]. For this work, the ΔV is recorded from 0 s to 2000 s to determine the t_{50} and ΔV_{max} value. The results achieved were visualized in Fig. 6.

Large ΔV values and a quick t_{50} implies good sensor. Thus, a figure of merit, f (mV/s), has been formulated to indicate the optimum sensing material per solvent, which is expressed as:

$$f = \frac{\Delta V_{\max}}{t_{50}} \tag{1}$$



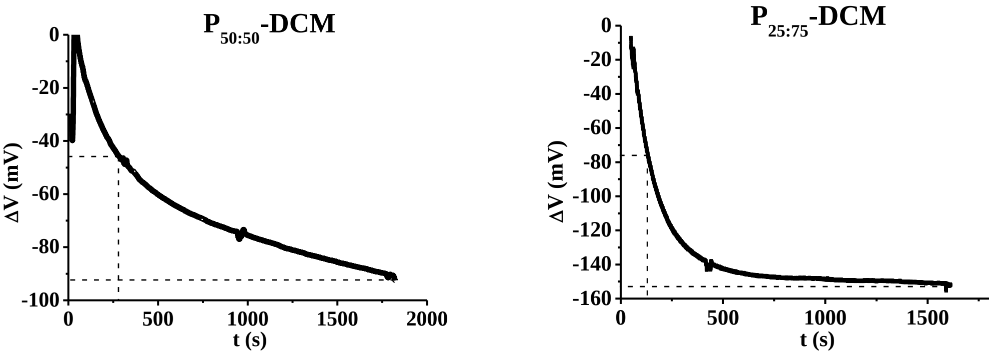


Figure. 6: ΔV and t_{50} for copolysiloxane LB thin films, $P_{50:50}$ and $P_{25:75}$ with $CHCl_3$, IPA and DCM

Table 2: ΔV_{max}, t_{50} and *f* for Copolysiloxanes LB Thin Films, $P_{50:50}$ and $P_{25:75}$ with each 1000µl Solvents.

Copolysiloxanes LB thin film	$P_{50:50}$			$P_{25:75}$		
	ΔV_{max} (mV)	t_{50} (s)	*f* (mV/s)	ΔV_{max} (mV)	t_{50} (s)	*f* (mV/s)
$CHCl_3$	63	210	0.300	67	208	0.322
IPA	106	65	1.631	348	162	2.148
DCM	92	288	0.319	152	134	1.134

Referring to Figure 6 and Table 2, the interaction of these thin films with each solvent produced unlike changes in ΔV values. Moreover, the t_{50} occurred between 65 – 288 s. None of both the copolysiloxanes LB thin films presented overall fast reaction with $CHCl_3$ as their t_{50} were more than 200 s. Both $P_{50:50}$ and $P_{25:75}$ thin films displayed almost similar ΔV_{max} and t_{50}. However, $P_{50:50}$ thin film gave positive changes in surface potential, whilst $P_{25:75}$ thin film displayed negative changes in surface potential as similar to the others in Figure 6.

$P_{50:50}$ thin film displayed the smallest t_{50} (65 s) toward IPA as compared to the others, demonstrated its potential as a sensor for this solvent. Meanwhile, $P_{25:75}$ thin film demonstrated the highest ΔV_{max} (348 mV) and *f* value (2.148 mV/s). This suggests that $P_{25:75}$ thin film still have good interaction with IPA but with a flaw from the aspect of detection time as t_{50} is large (162 s). On the other hands, $P_{25:75}$ thin film displayed better results in DCM as compared with $P_{50:50}$ thin film.

Through *f* values comparison, $P_{25:75}$-IPA showed highest values, followed by $P_{50:50}$-IPA, $P_{25:75}$-DCM, $P_{25:75}$-$CHCl_3$, $P_{50:50}$-DCM and the lowest $P_{50:50}$-$CHCl_3$. The structure of $P_{50:50}$ and $P_{25:75}$ differ only from the cavities in the chain, where $P_{25:75}$ has more cavities compared to $P_{50:50}$. Side chain structures of both copolysiloxanes are identical. Hence, after comparing the three characteristics that demonstrated by thin films with three types of solvents, the $P_{50:50}$ LB thin film was the most encouraging ones to be further studied as a sensor for IPA. However, the selectivity and sensitivity issue is still one of the major challenges in this kind of sensor as both copolysiloxanes can react with all three solvents but with the different results and certainly need to be improved.

4. CONCLUSIONS

The ΔV behavior of $P_{50:50}$ and $P_{25:75}$ copolysiloxane LB thin films interaction with several solvents, namely $CHCl_3$, IPA and DCM have been investigated. The results indicated that good interaction and fast time response between $P_{50:50}$ thin film and IPA, proposed a potential one-time use and throw-off type solvent vapor sensor candidate for that specific solvent. This has been strongly supported by the smaller t_{50} = 65 s and f = 1.631 mV/s which indicated the property of optimum sensing material per solvent.

Acknowledgements

F.L.S. acknowledges the University Research Grant from Sultan Idris University of Education (UPSI) and Government of Malaysia for the award of scholarship to conduct this work. The authors are thankful for copolysiloxanes, courtesy of Dr David Lacey's group, Department of Chemistry, the University of Hull for this investigation.

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