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Characterisation and vapour sensing properties of spin coated thin films of anthracene labelled PMMA polymer

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ABSTRACT

In the present article thin films of poly (methyl methacrylate) (PMMA) polymer labelled with anthracene (Ant-PMMA) prepared by spin coating are characterised by UV–visible spectroscopy, surface plasmon resonance (SPR), spectroscopic ellipsometry (SE) and Atomic Force Microscopy (AFM) and their organic vapour sensing properties are investigated. Ant-PMMA films' thickness are determined by performing theoretical fitting to experimental data measured using SPR and SE. Results obtained show that the spin-cast films are of good uniformity with an average thickness of 6–8 nm. Organic vapour sensing properties are studied using SPR technique during exposures to different volatile organic compounds (VOCs). Ant-PMMA films' response to the selected VOCs has been examined in terms of solubility parameters and molar volumes of the solvents, and the films were found to be largely sensitive to benzene vapour compared to other studied analytes.

1. Introduction

Gas sensing studies have become widely popular over the last two decades due to strict environmental pollution control measures imposed by regulatory agencies. Much of these studies have been focused on exploring the most suitable gas sensing materials that can provide fast response and recovery, as well as demonstrating good selectivity.

Anthracene is a favourite organic material due to its low cost and depth of synthetic manipulation. Anthracene-based sensors have applications in many areas of molecular recognition such as, anion sensors and glucose sensors [1]. Due to its favorable photophysical properties, such as strong absorption and high quantum yield, several investigations have been carried out to fully explore their gas sensing properties. Fluorescence energy transfer is used in the determination of picric acid in real samples [2]. Anthracene labelled Pt electrode was found to be useful for the high-sensitive and selective detection of aromatic nitro compounds derived from landmines [3]. A fluorescence-based chemical sensor for fluorene was developed by molecularly imprinting a sol–gel comprising the bridged silsesquioxane, bis(trimethoxysilylethyl)benzene [4]. Using a specially designed fluorescence gas flow chamber, fluoroclathrand molecules were found to be sensitive to 1,4-dioxane and tetrahydrofuran [5]. Besides these fluorescence-based techniques, other gas sensing techniques such as quartz crystal microbalance have been used; for instance quartz crystal sensors coated with a monolayer of aminothiols with an ionically bound anthracene group was found to be preferentially sensitive to detect PAH anthracene in the liquid phase with a sensitivity of 2 ppb [6]. In terms of its gas sensing performance poly (methyl methacrylate) (PMMA) is also a promising chemical material. It has recently been found that PMMA thin films obtained by spin coating and self assembly are suitable candidates for the detection of several volatile organic compounds [7–9].

Considering the chemical sensing properties of both anthracene and PMMA molecules in this work, surface plasmon resonance (SPR) technique has been employed to investigate the vapour sensing performance of spin coated thin films of antracene labelled PMMA polymers (Ant-PMMA) with different molecular weights for the first time. AFM, UV–Visible spectroscopy and SE have been used to investigate the structural and optical properties of Ant-PMMA films while surface plasmon resonance technique has been employed to investigate their vapour sensing performance. Partition coefficients of the vapour molecules in the film structure were calculated using SPR curve measurements. Solubility parameter and molar volumes of the analyte molecules were found to be effective on films' sensing properties.

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2. Experimental details

2.1. Materials

Three different kinds of poly (methyl methacrylate) polymers labelled with anthracene have been used in this investigation. Polymerization process was performed under vacuum at a temperature of 90 °C. After polymerization the ligand, catalyst, degassed monomer, solvent and the initiator mixture at the above mentioned conditions THF was used for the dilution of the mixture and metal salt has been removed from the mixture [10]. Polymers have been labelled as Ant1-PMMA, Ant2-PMMA and Ant3-PMMA which have the molecular weights 12,800, 21,700 and 28,900 g mol^{-1} respectively.

2.2. Film preparation

Solutions of Ant-PMMA molecules were prepared using chloroform as a solvent at a concentration of 2 mg ml^{-1}. These solutions were used to obtain thin films via spin coating technique by dispensing 100 µl of solution onto ultrasonically cleaned substrates which was rotating with a speed of 2000 rpm for 30 s and then the films were allowed to dry for another 30 s. For film deposition, spin speed of 2000 rpm was empirically chosen as it allowed suitable condition to obtain thin films with appropriate thickness for gas sensing studies. Three kinds of substrates have been used for different measurements. For SPR measurements pre-cleaned glass substrates were coated with a thin layer of gold using vacuum thermal evaporation. This was performed under vacuum of 10^{-4} Pa at a deposition rate of 2 nm s^{-1}. For AFM and SE measurements similar Ant-PMMA film deposition conditions has been applied onto ultrasonically cleaned silicon substrates. For UV–Visible spectroscopy measurements quartz glass slides have been used as substrates.

2.3. Characterisation of thin films

SPR measurements have been performed using a home made SPR set-up in the Kretschmann configuration [11]. The film coated slides and the semi-cylindrical prism (with a refractive index of 1.515) were brought into optical contact using ethyl salicylate (99% purchased from Aldrich) as an index-matching fluid. For the excitation of surface plasmons p-polarised beam with the wavelength of 632.8 nm was obtained using a He–Ne laser source. The prism and sample combination have been placed onto a θ–2θ rotation stage which was driven by a stepping motor and controlled by a microprocessor.

UV–Visible measurements have been carried out using a Cary 5000 UV–visible spectrophotometer operating in the spectral range of 180–900 nm. For AFM measurements a nanoscope IIIa instrument has been employed for the surface morphology investigation of spin coated Ant-PMMA films.

Spectroscopic ellipsometry measurements were performed using a Woolam M-2000VTM rotating analyser spectroscopic ellipsometer in the spectral range of 370–1000 nm with the angle of incidence fixed at 70°. The dedicated software has been used to fit the experimentally measured ellipsometric data.

2.4. Gas sensing measurements

Chloroform, benzene and *n*-hexane vapours have been used as analyte vapours which were purchased from Acros Organics and Fisher Chemicals and used without further purification. For gas sensing measurements a poly(tetrafluoroethylene) (PTFE) gas cell with a rubber O-ring was sealed by the coated slides. The experimental SPR curves which shows the variation of reflected light intensity as a function of angle of incidence has been used to calculate the thin film thicknesses before, during and after exposure to saturated gas molecules. The least squares fitting of experimental data to the Fresnel equations of reflection have been used to calculate the film thickness using Eq. (1). The minimum value of the reflectance which corresponds to the resonance angle of incidence (θ_{SPR}) shows a shift ($\Delta\theta$) in the presence of a spun Ant-PMMA film on gold layer and during exposure of PMMA film to organic vapours. The resonance shift is expressed as [12];

$$\Delta\theta = \frac{(2\pi/\lambda)(|\varepsilon_{\mathrm{m}}|\varepsilon_{\mathrm{i}})^{3/2} d}{n_{\mathrm{p}}\cos\theta(|\varepsilon_{\mathrm{m}}| - \varepsilon_{\mathrm{i}})^{2}\varepsilon}(\varepsilon - \varepsilon_{\mathrm{i}}) \qquad (1)$$

where λ is the wavelength of the He–Ne laser light, n_{p} is the refractive index of the semi-cylindrical prism, $|\varepsilon_{\mathrm{m}}|$ is the modulus of the complex dielectric constant of the gold film and ε_{i} is the dielectric constant of the medium in contact with the Ant-PMMA layer. During the calculations the refractive index of the Ant-PMMA thin films were introduced as 1.4887 [13,14] to the SPR data fitting programme of PMMA films which allows narrowing the data fitting and also helps achieving good correspondence between SE and SPR data fitting.

The kinetic measurements were performed by fixing the incident angle of the laser beam at a constant value which corresponds to a point chosen on the linear region on the SPR curve close to the resonance angle. Different concentrations of analyte vapours have been injected into the gas cell for 2 min followed by 2 min recovery on the injection of dry air. The concentrations were calculated between 19,598 and 97,994, 32,127 and 160,635 and 43,897 and 219,486 ppm for benzene, *n*-hexane and chloroform vapours respectively.

3. Results and discussion

3.1. Characterisation of spin coated PMMA films

Fig. 1 shows the UV–Visible spectra of spin coated films of anthracene labelled PMMA polymers on quartz slides obtained at a deposition speed of 2000 rpm. Maximum absorbance appears at 256 nm which is in good agreement with the literature [15]. The inset in Fig. 1 shows the dependence of maximum absorbance value of Ant2-PMMA thin film at 256 nm versus spin coating deposition spin speed. The exponential correlation between the spin speed and the absorbance given in the inset of Fig. 1 shows that the variation of film thickness with increasing spin speed is in agreement with a model proposed in the literature [13,14].

The AFM image of Ant2-PMMA film spun onto silicon substrate at a deposition speed of 2000 rpm has been given in Fig. 2. It is clearly shown that the spin-cast film is characterised with a homogeneous structure with randomly scattered pores having an average diameter of 34 nm.

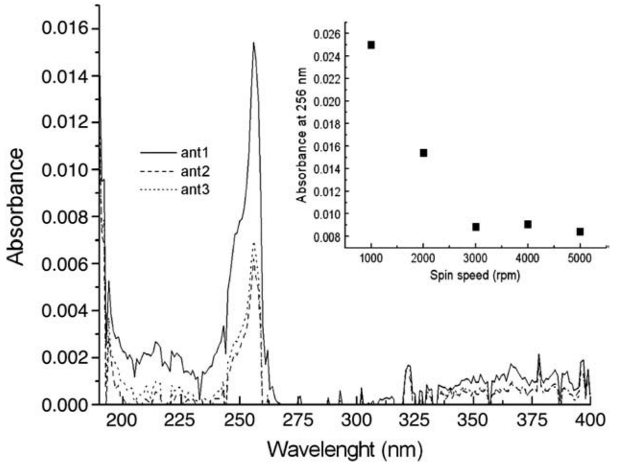

Fig. 1. UV–Visible spectra of polymers in the region 200–400 nm. The inset in the figure shows the variation of the maximum absorbance value of Ant2-PMMA thin film at 256 nm as a function of deposition spin speed.

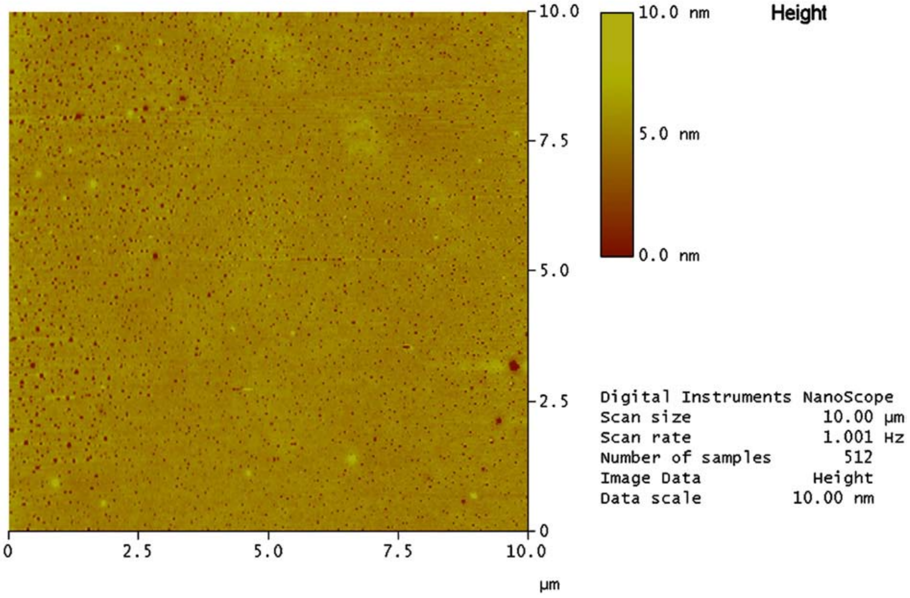

Fig. 2. The AFM image of the spin coated thin film of Ant2-PMMA polymer on silicon substrate at a deposition speed of 2000 rpm.

Similar morphology with randomly scattered pores on the surface has been observed for self assembled [8] as well as spin-cast [16] PMMA thin films. The rms value of film surface roughness was estimated between 0.819 and 0.642 nm for AFM images recorded at different scales.

Film thickness values were obtained using theoretical fitting of the spectroscopic ellipsometry as well as SPR data to Fresnel's Equations of reflection. Film thickness values of samples fabricated at a deposition speed of 2000 rpm are given in Table 1. The two sets of values agree well with each other, however the small differences between two measurements may be attributed to the different substrates used for the two types of measurements.

The results obtained using UV–Visible spectrophotometer, AFM, SE and SPR showed that uniform thin films can successfully be fabricated on the different substrates using the spin coating conditions described above.

3.2. Organic vapour sensing properties

Organic vapour sensing properties of Ant2-PMMA thin films have been investigated using SPR measurements. First full SPR curves have been recorded in the form of reflected light intensity as a function of angle of incidence during vapour exposure and then on recovery during injection of dry air. This was followed by performing kinetic measurements in the form of reflected light intensity as a function of time during repeated exposures of analyte molecules and dry air. In this work we have studied benzene, n-hexane and chloroform as the analyte molecules to investigate their interaction with the Ant-PMMA layers. Fig. 3 shows the measured SPR curves of Ant2-PMMA thin films spun at 2000 rpm. A shift of $\Delta\theta = 0.43°$ in the resonance position of the measured SPR curve has been observed during exposure to saturated chloroform vapour (219,486 ppm). Such shift in the resonance angle could be caused by swelling of the Ant-PMMA film (change in film thickness) due to vapour adsorption in the film matrix, or as a result of a change in its refractive index or probably both. In the present study we believe that the resonance shift is predominantly due to film swelling since both the Ant-PMMA film and chloroform vapour have closely similar index of refraction. The measured SPR curve is shown to revert to its initial position during the injection of dry air into the gas cell which indicates an almost full recovery of the sensing layer. Any deviation from full recovery after vapour treatments may be caused by vapour molecules trapped inside the film structure. Similar effects have been obtained for the other analytes, and also for measurements performed on the other anthracene-labelled PMMA films. The change in film thickness values (Δd) is calculated using the least square curve fitting and the results are given in Table 2. An increase in thickness up to 1.99 nm has been obtained. The partition coefficient (f_{pg}) which is defined as the ratio of the concentration of the individual gas molecules in polymer thin films to that in gas phase is given by the following relation [16]:

$$f_{pg} = \frac{\upsilon\rho RT}{cPM} \qquad (2)$$

where ρ, c, P and M are the density, concentration, saturated vapour pressure and molecular weight of the organic vapour, R is the universal gas constant and T is the temperature. Partition coefficient is

Table 1
The thickness values of the thin films obtained using the experimental SPR curve fitting and experimental ellipsometry measurements fitting.

Spectroscopic ellipsometry fitting	Thickness (nm)	SPR fitting
Ant1-PMMA	6.12	9.71 ± 1.59 (MSE = 13.05)
Ant2-PMMA	6.02	9.69 ± 2.56 (MSE = 24.74)
Ant3-PMMA	8.69	8.14 ± 1.89 (MSE = 16.67)

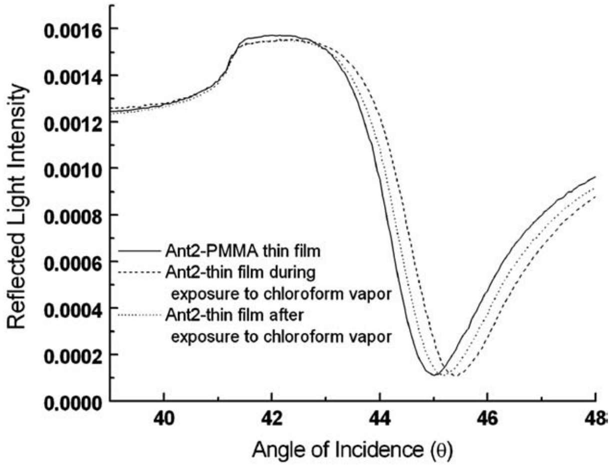

Fig. 3. Experimental SPR curves of Ant2-PMMA thin film spun at 2000 rpm. The SPR curves during and after exposure to saturated chloroform vapour have also been plotted.

Table 2
Changes in film thickness (Δd) due to exposure to analyte vapours, calculated partition coefficients and the sensitivities obtained using calibration curves.

Thin film	Analyte VOC	Change in thickness Δd (mm)	Partition coefficient	Sensitivity[a] %/ppm × 10^{-4}
Ant1-PMMA	Chloroform	0.64	122	2.39 (0.99)
	Benzene	1.06	531	3.62 (0.99)
	n-hexane	0.26	78	1.6 (0.95)
Ant2-PMMA	Chloroform	1.99	38	2.39 (0.98)
	Benzene	1.47	925	3.12 (0.98)
	n-hexane	0.36	109	1.26 (0.99)
Ant3-PMMA	Chloroform	1.36	183	4.95 (0.99)
	Benzene	1.56	596	8.64 (0.98)
	n-hexane	0.23	51	0.83 (0.99)

[a] Values in parenthesis shows the regression values of the fitting procedure of the calibration curves.

also dependent on the volume fraction (υ) which is described as the ratio of the change in film thickness due to interaction with the vapour molecules to its initial thickness. Partition coefficients have been calculated for all studied films on interaction with the analyte molecules and the results are listed in Table 2. The highest and lowest partition coefficient values have been obtained for benzene and *n*-hexane molecules respectively for all studied films.

The kinetic response of the thin films on exposure to saturated vapours of the three analytes has been given in Fig. 4. Response and recovery times are in the range of a few seconds and the recovery is shown to be almost complete. The drift in the baseline may be attributed to the temperature changes as a result of film surface cooling during vapour exposures. Kinetic measurements that were performed for the other ant-PMMA films on exposure to the different analyte molecules have not been given. Calibration curves are given in Fig. 5 which shows the normalised response plotted as a function of vapour concentration for Ant3-PMMA thin film on exposure to different concentrations of the three analytes. The straight lines are obtained by performing linear regression to the experimental. The gradient of these lines provides information on the sensitivity of the polymer films in terms of normalised response (%) per unit concentration (ppm). Calculated sensitivities for all studied films and analytes are given in Table 2.

It is clearly seen that both film's sensitivity and partition coefficients have maximum values for benzene vapour whereas the minimum values were observed for n-hexane vapour. Similar results were recently observed for PMMA thin films on exposure to BTEX vapours [7] with the highest sensitivity being for benzene vapour. The solubility parameters of benzene and chloroform molecules of 18.7 MPa$^{1/2}$ which are closely similar to that of PMMAs (18.6 MPa$^{1/2}$) may be largely responsible for such high sensitivity of PMMA-based sensing layer [17]. On the other hand *n*-hexane is characterised by a much higher solubility parameter (28.7 MPa$^{1/2}$). Furthermore, molar volumes of the penetrating vapour molecules may also have significant effect on films' sensing properties. The molar volumes of benzene and chloroform vapour are smaller than that of *n*-hexane's which is thought to enable the molecules to penetrate more easily into the film matrix [18].

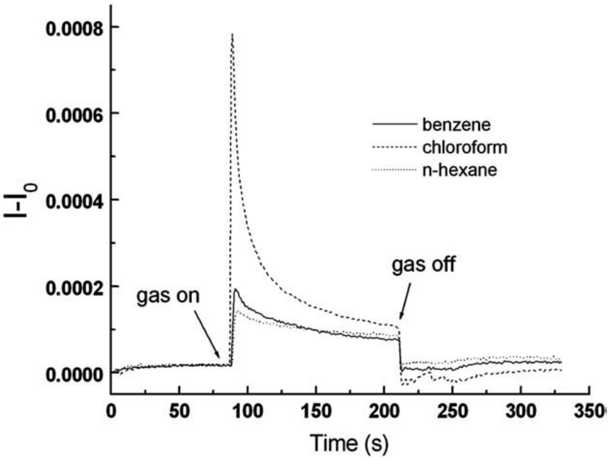

Fig. 4. Kinetic measurements performed using saturated vapours of benzene, chloroform and *n*-hexane.

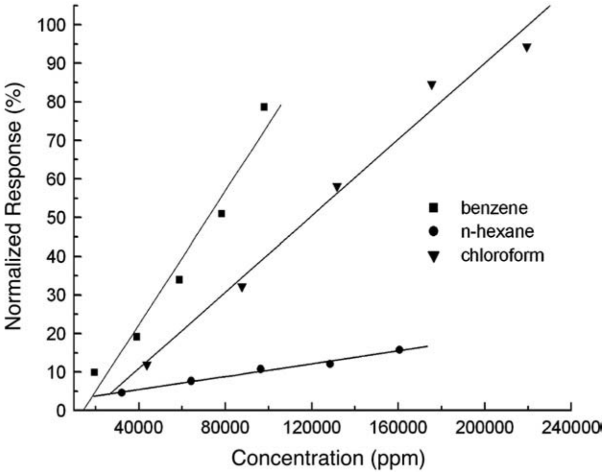

Fig. 5. The calibration curve for Ant3-PMMA thin film on exposure to different concentrations of the three studied analyte vapours.

4. Conclusion

Anthracene labelled poly (methyl methacrylate) polymer was found to be suitable for thin film fabrication via spin coating technique. Thin films characterisation shows that homogeneous films with thicknesses of approximately 6 to 8 nm have been fabricated. Organic vapour sensing studies on these films show that as low as a few ppm concentrations of investigated analyte molecules can be detected. Ant-PMMA films have demonstrated highest sensitivity to benzene vapour which has low molar volume and consistent solubility parameter value with that of Ant-PMMAs. Future work will concentrate on investigation of vapour sensing studies using different thickness Ant-PMMA thin films.

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