



# Modeling of vapor sorption in polymeric film studied by surface plasmon resonance spectroscopy

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## ARTICLE INFO

### Article history:

Received 28 January 2008

Accepted 21 April 2008

Available online 25 April 2008

### Keywords:

Vapor sorption

Chemical sensor

Poly(methyl methacrylate) film

Diffusion

## ABSTRACT

Sorption process by surface plasmon resonance (SPR) was studied by exposing polymeric film made from anthracene labeled poly(methyl methacrylate) (An-PMMA) chains to various concentrations of saturated chloroform vapor. It was observed that the reflectivity changes were fast and reversible. The changes in reflectivity implied the swelling behavior of polymeric film during adsorption and can be explained by capturing of chloroform molecules. When clean air is introduced into gas cell similar behavior is observed but this time in the opposite direction as a result of desorption. Fick's law for diffusion was used to quantify real time SPR data for the swelling and desorption processes. It was observed that diffusion coefficients ( $D_s$ ) for swelling obeyed the  $t^{1/2}$  law and found to be correlated with the amount of chloroform content in the cell. Diffusion coefficients ( $D_d$ ) during desorption were also measured and found to be increased as the saturated chloroform vapor content is increased in the cell.

Published by Elsevier Inc.

## 1. Introduction

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 usable in many sensor types based on different transduction principles for the detection of a variety of analytes. Polymer chains are flexible, and molecules can easily be absorbed into polymer networks. This absorption process results in a swelling and a mass increase of the polymer materials.

Moisture and organic vapor sorption in polymeric films and their concurrent swelling is important in many applications, such as coating, microelectronics manufacturing and chemical sensors. Conventional gravimetric methods are not always suitable for studying these phenomena in polymeric films [1]. Although there is extensive literature on polymer swelling, only in recent years extensive work has been performed to exploit this phenomenon for chemical sensing. The lifetime of most sensors based on polymer swelling is limited by delamination of the polymeric film [2].

The major difficulty in gas identification is the fabrication of stable sensors with high sensitivity and very good selectivity of the substance to be detected. Several measurement techniques such as Surface Plasmon Resonance (SPR) and Quartz Crystal Microbalance (QCM) are used to monitor and detect various chemical gases be-

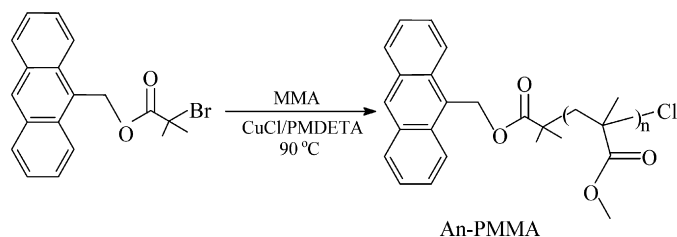
cause of their wide range of potential applications. An example is environmental monitoring, such as detecting the presence and concentration of toxic or otherwise dangerous gases that are released through spillage or leakage [3]. Another broad application area is quality control and industrial monitoring, particularly in such industries as food processing, perfume, beverage and other chemical products [4,5]. Monitoring and determining the constituents of a sample gas typically involves collecting samples and analyzing them in a gas chromatograph–mass spectrometer (GC–MS) of significant size and cost [6]. Although GC–MS systems work very well, many applications need sensor systems that are smaller, more portable, cheaper and even disposable [7].

SPR is a total internal reflection system with a thin metal film on top of the high-index dielectric surface. The resonance of surface polaritons at the metal–dielectric interface is extremely sensitive to the dielectric constant and thickness of the medium adjacent to the metal film [8–10]. Using flow-injection type electrochemical SPR sensing system, adsorption and desorption of water-soluble polymers on gold surfaces have been observed [11]. It has also been found that lightly crosslinked molecularly imprinted polymer particles can serve as the basis of a sensitive and selective membrane for the detection of organic contaminants such as pharmaceuticals in aquatic environments [12].

In the present work polymeric film formed from anthracene labeled linear poly(methyl methacrylate) (An-PMMA), chains were subjected to various concentrations of partially saturated chloroform vapors to study swelling and desorption mechanism. Using SPR measurement system, variations in the intensity of reflected

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Scheme 1. Synthesis of poly(methyl methacrylate).

light was monitored in real time during swelling in which organic vapor is introduced into a gas cell and desorption when clean air is injected into it. The organic vapor uptake causes an increase in the transparency of polymeric film that explains the changes in reflected light intensity during swelling and desorption. Fick's second law for diffusion [13] was employed to determine the diffusion coefficients for the swelling and desorption processes.

## 2. Materials and methods

### 2.1. Synthesis of poly(methyl methacrylate)

The general procedure for atom transfer radical polymerization (ATRP) was followed; to a Schlenk tube equipped with magnetic stirring bar, ligand, catalyst, degassed monomer, solvent and initiator were added in the mentioned order. Tube was degassed by freeze–pump–thaw cycles, left under vacuum and placed in thermostated oil bath at a constant temperature of 90 °C. After polymerization, the reaction mixture was diluted with tetrahydrofuran (THF) and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer were evaporated under reduced pressure. PMMA samples were dissolved in THF and precipitated in methanol, filtered and dried overnight in vacuum oven at 50 °C. This procedure was repeated at least twice for the sample in order to remove unbounded initiator species if there are any. The conversions were determined gravimetrically. PMMA was prepared in 50 vol% diphenylether (DPE) solution at 90 °C using CuCl/*N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDTA) as the catalyst and 9-anthryl methyl 2-bromo-2-methyl propanoate, as the initiator. This led to the formation of anthracene labeled poly(methyl methacrylate)s (An-PMMA)s. Syntheses of poly(methyl methacrylate) were prepared as illustrated in Scheme 1. Details and characterization of polymer chains are given in the literature [14].

### 2.2. Deposition of polymeric films

For the SPR measurements 50 nm thick gold layer was thermally evaporated onto the glass substrates with the rate of 2 nm s<sup>−1</sup> under vacuum of about 10<sup>−3</sup> Pa. Solution of An-PMMA molecules was prepared using chloroform as a solvent at a concentration of 2 mg ml<sup>−1</sup>. Spin coating of the An-PMMA polymer was performed by dispensing 100 μl of solution onto the gold coated substrate which was rotating with a rotation speed of 2000 rpm. For the spectroscopic ellipsometry measurements thin films were fabricated onto silicon substrates using the same film fabrication procedure. Woolam M-2000VTM model spectroscopic ellipsometry rotating analyzer in the spectral range of 370–1000 nm was used where the angle of incidence have been fixed at 70°.

### 2.3. Characterization of polymeric films

Spectroscopic ellipsometry which is based on measuring and analyzing the polarization change of the reflected light was em-

ployed for the characterization of the An-PMMA polymer films. In this technique, the measured ellipsometric parameters  $\psi(\lambda)$  and  $\Delta(\lambda)$  which are the angles related to the polarization change of the light caused by its interaction with a sample are used to obtain thickness, refractive index and extinction coefficients of the polymer films [15]. The relation of the ellipsometric parameters with the p and s components of the polarized incident wave can be expressed by  $R_p/R_s = \tan(\psi) \exp(i\Delta)$  where  $\tan(\psi)$  is the ratio of amplitudes and  $\Delta$  is the phase difference between p and s components of polarized light. The optical parameters were obtained using software based on Fresnel reflection equations.

### 2.4. SPR set-up and gas sensing measurements

The experimental SPR set-up was based on the Kretschmann configuration [16] and was identical to that reported elsewhere [17]. The thin film coated slides and semi-cylindrical prism (with a refractive index of 1.515) were brought into optical contact using ethyl salicylate (99% Aldrich) as an index matching fluid. P-polarized beam with a wavelength of 632.8 nm was obtained using a He–Ne laser source for the excitation of surface plasmons. The prism and sample combination were placed on a  $\theta$ – $2\theta$  rotation stage driven by a microprocessor controlled stepping motor (with resolution of 0.01°) to record SPR curves which shows the variation of the reflected light intensity against the angle of incidence. For the kinetic measurement, poly (tetrafluoro ethylene) (PTFE) gas cell with a rubber O-ring was sealed by the coated slides to allow measurements of the reflected light intensity as a function of time at a fixed angle  $\theta^*$  during vapor exposures. Different concentrations of saturated chloroform vapor were mixed with dry air in a sealed syringe and injected into the gas cell for 2 min followed by 2 min recovery by injecting dry air into the gas cell.

### 2.5. Theoretical consideration

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 [13]:

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

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 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

$$M = \int_V C dV. \quad (2)$$

When Eq. (2) is considered for a plane volume element and substituted in Eq. (1), the following solution is obtained [13].

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D\pi^2}{a_0^2}t\right), \quad (3)$$

where  $M_t$  and  $M_\infty$  represent the amount of diffusant entering the plane sheet at time  $t$  and infinity, respectively. This equation can be reduced to a simplified form still 99% accurate:

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

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