SENSOR LETTERS
Vol. 6, 1–5, 2008

A09

Benzene Vapor Detection Using Spun Poly(methyl methacrylate) Thin Films

R. Capan[1,*], T. Tanrisever[1], A. K. Ray[2], and A. K. Hassan[3]

[1] *Science Faculty, Balikesir University, 10145 Çağış, Balikesir Turkey*
[2] *Department of Materials, Queen Mary College, Mile End Road, London E1 4NS, UK*
[3] *Materials and Engineering Research Institute, Sheffield Hallam University, City Campus, Sheaf Building, Pond Street, Sheffield S1 1WB, UK*

(Received: 29 December 2007. Accepted: 23 April 2008.)

A series of poly(methyl methacrylate) (PMMA) polymers of different molecular weights were synthesized using the Emulsifier-Free Emulsion polymerisation method. Using Atomic Force Microscopy (AFM) measurements the film surfaces are found to be a heterogeneous surface with a RMS surface roughness value of approximately 2.5 nm. The refractive index of the PMMA films was estimated between 1.527 and 1.565 using surface plasmon resonance (SPR) method. Furthermore, film thickness is found to depend on the PMMA molecular weight. Thin films of PMMA are found to exhibit a fast and reversible response on exposure to benzene vapor; this would probably suggest that PMMA in thin film form could have a significant role in the development of room temperature vapor sensing devices.

Keywords: PMMA, Spin Coating, Benzene, Sensors, Surface Plasmon Resonance, Atomic Force Microscopy.

RESEARCH ARTICLE

1. INTRODUCTION

Prevalent domestic and international regulations have stimulated intensive research activities of monitoring vapors of the BTEX compounds (benzene, toluene, ethylbenzene and xylene). Among the BTEX family, benzene is a carcinogen with a maximum permitted exposure limit in the atmosphere of 5 ppb. Direct exposure to benzene causes skin tissue and lung injuries, as well as irritation to eyes. Prolonged exposures to benzene vapor may damage the bone marrow, limiting the production of enough red blood cells, and in the long run causes anaemia and leukaemia.[1,2] Off-site chromatographic and spectroscopic analyses of BTEX are costly and time consuming. The development of portable and user-friendly sensors becomes a very important issue for *in situ*, real-time monitoring of benzene which can be based on the fabrication of suitable sensing membranes. Poly(methyl methacrylate) (PMMA) is well known material which has been employed extensively in recent years to design resonator type sensors for the detection of volatile organic compound (VOC) vapors.[3–5] Using a specially designed piezoelectric cantilever coated with PMMA films, the resonant frequency was found to be linearly dependent on the concentration of ethanol and methanol vapors.[6] The nanobalance sensor showed a full recovery when examined for the detection of ethanol vapor with an operating sensitivity of about 0.5 Hz/ppm.[7] A relatively lower sensitivity of 1.67 Hz/ppm was obtained for ethanol vapor using the piezoelectrically driven microbridge coated with the PMMA polymer as the sensing layer.[8] Molecularly imprinted polymers were prepared from methyl methacrylate as a monomer and divinylbenzene as a cross-linking agent, in the presence of toluene or *p*-xylene as solvents. When thin films of this polymer were used as sensing membranes employing quartz crystal monitor system, a selective and reversible response was observed for exposures of toluene and *p*-xylene vapors, however recovery was slow.[9]

A series of PMMA polymers were synthesized using the Emulsifier-Free Emulsion polymerisation method[10] and the polymerisation was carried out using potassium persulfate as the initiator, resulting in the incorporation of charged sulphate and uncharged hydroxyl groups onto the latex surface.[11] The chemical structure of PMMA with an end group of $SO_4^- K^+$ is given in Figure 1. Our previous work showed that spun films of PMMA derivatives having

*Corresponding author; E-mail: rcapan@balikesir.edu.tr

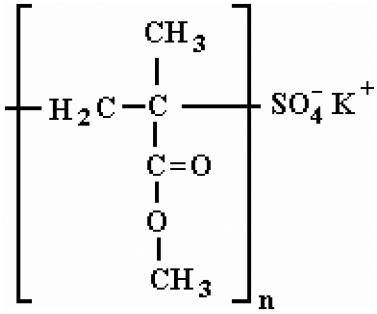

Fig. 1. Chemical structure of poly(methyl methacrylate) derivatives with two different molecular weights: (a) $n = 23658$ for PMMA (M_w = 970 kgmol^{-1}) and (b) $n = 26829$ for PMMA ($M_w = 1100$ kgmol^{-1}).

different refractive index (n) values were successfully deposited onto gold-coated glass substrates for use in surface plasmon resonance measurements.[12, 13] Spun films of PMMA derivatives with the molecular weight of 580 kgmol^{-1} showed a fast, large and reversible response to exposures of BTEX (benzene, toluene, ethylbenzene and *m*-xylene) vapors. The detection sensitivity was found to be significantly greater for benzene vapor than other BTEX compounds.[12] Similarly, fast and reversible response was observed for thin films of PMMA molecules of the same series but with different molecular weights in the range 540–760 kgmol^{-1}. The highest sensitivity was associated with the largest molecular weight.[13] Two new PMMA molecules have now been synthesized for further investigation of benzene vapor detection. The present article reports the results of Atomic Force Microscopy (AFM) and Surface Plasmon Resonance (SPR) measurements using PMMA molecules prepared as thin films by spin coating. This work also provides a comparative study of film's sensitivity to benzene vapor in relation to their molecular weights.

2. EXPERIMENT DETAILS

Two new PMMA polymers have been synthesized with molecular weights of 970 kgmol^{-1} and 1100 kgmol^{-1}. Using a photoresist spinner (model 4000 from electronic Microsystem), thin films of the two polymers were spun at 3000 rpm on gold-coated glass substrates, with gold film thickness of 40 nm, from a spreading solution of PMMA molecules in chloroform with the concentration of 1 mg ml^{-1}. Details of the substrate preparation have been given in earlier publications.[12, 13] PMMA film morphology was studied at room temperature in air using a Nanoscope III (Digital instruments) Atomic Force Microscope (AFM) in the standard tapping mode. The spring constant of the cantilever was 40 nm^{-1} and the resonant frequency was 300 kHz. The AFM picture was taken in an area of 0.5 μm $\times$ 0.5 μm. For the SPR measurements, a *p*-polarised monochromatic He-Ne laser light source (with wavelength $\lambda = 632.8$ nm) was employed to excite the surface plasmons using a semi-cylindrical prism (with refractive index $n_p = 1.515$) in a Kretschmann's type optical set-up system.[14] SPR measurements were carried out on PMMA films in contact with air and with water media for the unique determination of films' optical parameters.

For the study of PMMA films' kinetic response to exposures of benzene vapor, the substrates were placed in contact with the semicylendrical prism using index matching fluid. The sensing membranes are facing up and are sealed by a specially designed poly(tetrafluoroethylene) (PTFE) gas cell in a leak-proof environment using a rubber O-ring. For this measurement, SPR data were recorded as a function of time at a fixed angle of incidence of 46°. SPR signal was measured in response to exposures of benzene vapor, and film recovery was monitored during the injection of fresh air into the gas cell.

3. RESULTS AND DISCUSSIONS

An AFM image of PMMA ($M_w = 970$ kgmol^{-1}) thin film given in Figure 2 shows a heterogeneous surface with pores scattered randomly over the film surface. The sizes of these pores are approximately in the range of 20 nm to 50 nm with the depths of about 11 nm. The rms value of surface roughness was found to be 2.5 nm. Such pore dimensions were found in our previous work on spin coated PMMA films with lower molecular weights using AFM measurements.[13] Similar pores, pits or pinholes were observed in AFM images of other PMMA thin films prepared using spin coating method.[15–17] Surface morphology of PMMA films spun onto silicon substrates have also been studied by Semaltianos and co-workers using AFM measurements.[18] Initial images revealed no pits, pinholes or any other kind of defects, and the PMMA film surface appeared featureless. However, further AFM measurements revealed surface defects on PMMA films subjected

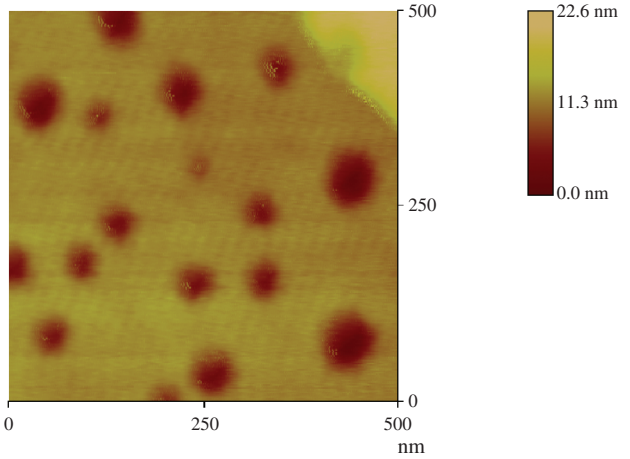

Fig. 2. Two dimensional AFM picture of PMMA ($M_w = 970$ kgmol^{-1}) film spun on silicon substrates.

RESEARCH ARTICLE

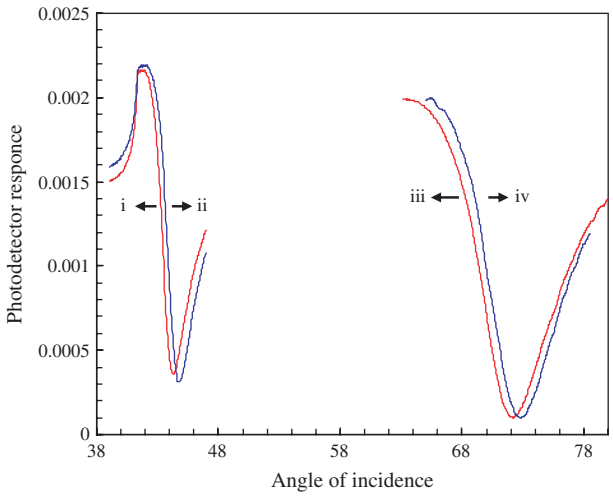

Fig. 3. SPR curves showing variation of reflected intensity as a function of the angle of incidence for (i) gold in contact with air, (ii) PMMA thin film over layer in contact with air, (iii) gold in contact with water and (iv) PMMA thin film over layer in contact with water. The molecular weight of PMMA is $M_w = 970$ kgmol^{-1} and the spin speed is 3000 rpm.

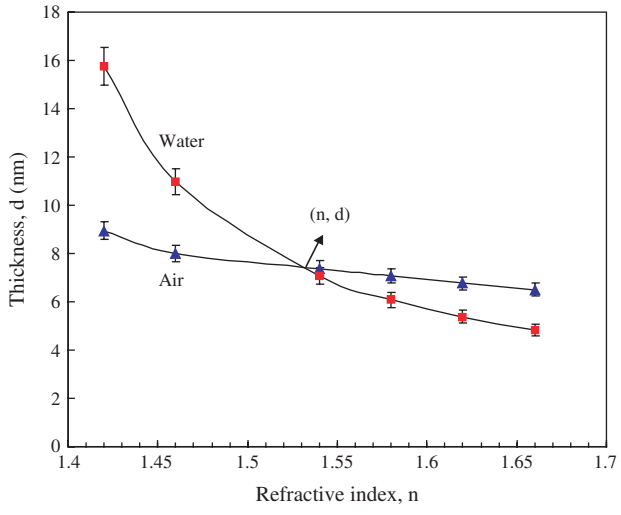

Fig. 4. A plot of thickness of a PMMA ($M_w = 970$ kgmol^{-1}) film as a function of refractive index using the theoretical fitting data for the SPR curves in air and water media.

to post deposition treatment, such as annealing at 170 °C in an oven, or kept under low vacuum for a few days.[18] The formation of pinholes on the PMMA film surface was thought to be caused by the additional evaporation of the solvent from the film matrix.

Figure 3 shows that the resonance shift in SPR curves measured in water ($\Delta\theta_w$) was larger than the resonance shift measured in air ($\Delta\theta_a$) for PMMA ($M_w =$ 970 kgmol^{-1}) layer deposited onto the 40 nm thick gold film. Figure 4 shows values of film thickness d plotted as a function of film refractive index n of PMMA film; both were obtained from the numerical solution of $\Delta\theta_a$ and $\Delta\theta_w$ using the Fresnel's equation in the form:[12, 14, 19]

$$\Delta\theta_{a,w} = 6.5 \times 10^{-12} \frac{(|\varepsilon_m|\varepsilon_{a,w})^{3/2} d}{\cos\theta(|\varepsilon_m| - \varepsilon_{a,w})^2 \varepsilon}(\varepsilon - \varepsilon_{a,w}) \quad (1)$$

where $|\varepsilon_m|$ is the modulus of the complex dielectric constant of gold, and ε is the complex dielectric constant of the PMMA film. The subscripts a and w refer to air and water respectively. The coordinates of the intersection point of the two curves give the values of 1.543 and 8.34 nm for the refractive index at 633 nm and thickness of the PMMA film, respectively. Similar calculations were performed for the other PMMA film ($M_w = 1100$ kgmol^{-1}) and the results are summarized in Table I. Figure 5 depicts the relationship between film thickness and refractive index as a function of PMMA molecular weight, which also includes, for the sake of comparison, values of previously studied PMMA molecules with lower molecular weights in this series. The thickness of PMMA films is found to increase with the molecular weight in a non-monotonous pattern, where it first increases sharply up to $M_w = 640$ kgmol^{-1} and then at slower rate up to the highest studied molecular weight. The refractive index, on the other hand, is shown to increase almost linearly with increasing molecular weight, reaching a maximum value of about 1.565.

SPR curves presented in Figure 6, curves (a) and (b), show the variation of the reflected light intensity as a function of angle of incidence (θ) for a bare gold film and for the same gold film coated with a PMMA film respectively. The minimum is shifted to the right by $\Delta\theta = 2.5°$ for the PMMA film compared to that of the bare gold film. Curve (c) in Figure 6 presents the SPR curve for the same PMMA film after exposure to benzene vapor with a view to investigating its benzene vapor sensing properties. The shift of the SPR minimum is usually explained in terms of an increase in the refractive index of the sensing layer and/or a change in the film thickness due to film

RESEARCH ARTICLE

Table I. Properties of PMMA molecules.

Molecular weight of PMMA (kg/mol)	Diameter of PMMA beads (μm)	Shift in resonance angle due to PMMA overlayer on gold substrate (°)	Shift in resonance angle when PMMA overlayer exposed to to benzene vapor (°)	Refractive index μ		Film thickness (nm)		Sensitivity (%)
				Before exposure	After exposure	Before exposure	After exposure	
970	0.24	2.246	0.145	1.543	1.573	8.34	8.55	93
1100	0.28	2.588	0.176	1.565	1.580	8.85	8.95	90

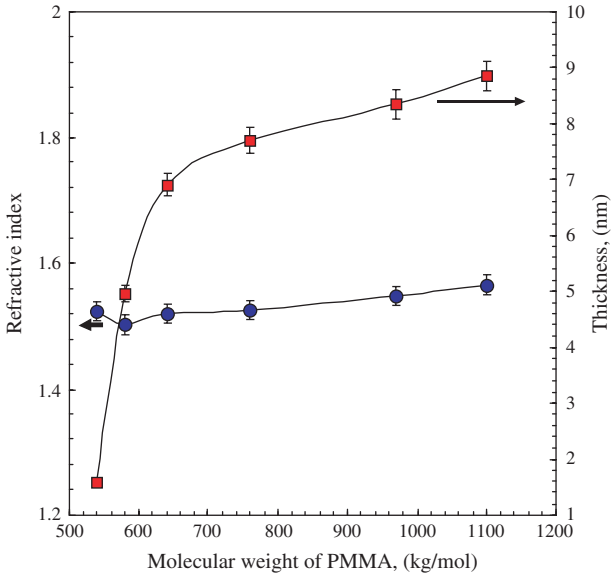

Fig. 5. Refractive index and thickness of PMMA film as a function of molecular weight. Spin speed is 3000 rpm.

swelling.[20] The dissolution of benzene in the bulk of the polymer film is believed to form a heterogeneous layer, primarily giving rise to the swelling of the film.[21] Benzene is a planar molecule and has zero dipole moment, with a refractive index of 1.5011 Ref. [22] which is close to the refractive index of the PMMA film, and the effect of benzene adsorption on the film's refractive index is not expected to be significant. It is therefore believed that the resonance shift is primarily caused by the change in the film thickness due to the swelling of the polymer film. Values of the thickness and refractive index for the benzene-treated PMMA films were obtained from the least square fitting of the experimental data to Fresnel equation, and the results are given in Table I.

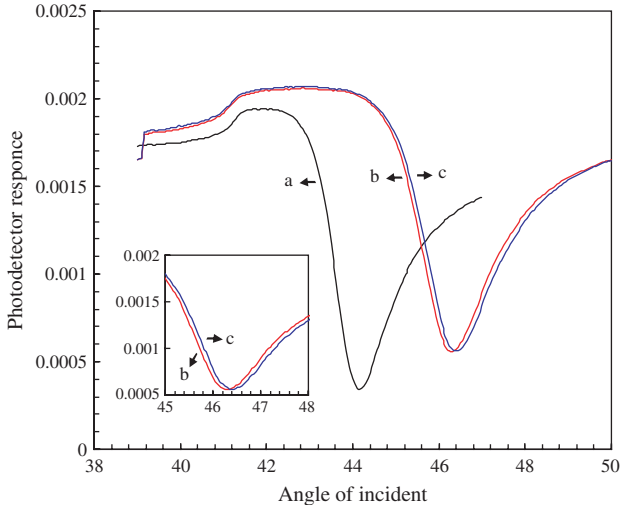

Fig. 6. SPR curves measured for (a) a bare gold substrate, (b) PMMA ($M_w = 970$ kgmol^{-1}) thin films, and (c) PMMA film after exposure to saturated benzene vapor.

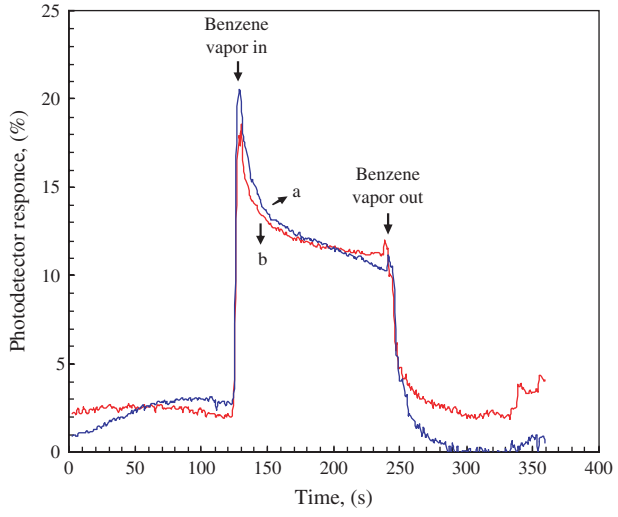

Fig. 7. Kinetic response of PMMA thin films to the exposure of benzene vapor (a) PMMA ($M_w = 970$ kgmol^{-1}) and (b) PMMA ($M_w = 1100$ kgmol^{-1}).

Kinetic response of PMMA films with different molecular weights to exposures of benzene vapor was recorded by measuring the reflectivity at a fixed angle $\theta^* = 46°$ which chosen very close to the resonance angle, to the left of the curve minimum, and the results are shown in Figure 7. PMMA films were exposed to benzene vapor for 2 min followed by the injection of dry air for a further 2 min period. PMMA films with different molecular weights show a fast response to benzene vapor. As soon as air was injected into the gas cell, PMMA films were found to recover almost fully. The sensitivity of the PMMA spun film to benzene is defined as the ratio $\Delta I/I_0$ where ΔI is the deviation of the photo-detector signal during vapor exposure and I_0 is the base line signal obtained in dry air. The calculated sensitivity values are given in Table I and molecular weight appears to have no effect.

4. SUMMARY

Two new PMMA molecules with different molecular weights were prepared as thin films by spin coating at 3000 rpm and were then used for the investigation of sensitivity for the benzene vapor using the SPR technique. The surface was found from the AFM images to be heterogeneous containing randomly scattered pores with sizes in the range of 20 nm to 50 nm. This implies that the film were not completely dry but possibly contained a considerable amount of solvent. The surface roughness of PMMA film was found to be 2.5 nm. Deposition of PMMA films onto gold-coated glass substrates has resulted in SPR curve shift for measurements taken both in air and water. The refractive index of PMMA films were estimated to be in the range of 1.527 and 1.565 using SPR measurements. Film thickness was found to increase with increased PMMA molecular weight. The response of PMMA film

to the exposure of benzene was observed to be fast, large, reproducible and reversible to a satisfactory degree leading to potential applications in the development of room temperature organic vapor sensing membranes.

Acknowledgments: One of the authors (R. Capan) acknowledge with gratitude for the award of a Leverhulme visiting fellowship of ten months to the UK.

References and Notes

1. M. G. Bird, H. Greim, R. Snyder, and J. M. Rice, *Chem. Biol. Interact.* 153, 1 **(2005)**.
2. E. Ahaghotu, R. J. Babu, A. Chatterjee, and M. Singh, *Toxicol. Lett.* 159, 261 **(2005)**.
3. E. Sarantopoulou, Z. Kollia, A. C. Cefalas, K. Manoli, M. Sanopoulou, D. Goustouridis, S. Chatzandroulis, and I. Raptis, *Appl. Surf. Sci.* 254, 1710 **(2008)**.
4. I. Çapan, Ç. Tarimci, and T. Tanrisever, *Sensor Lett.* 5, 533 **(2007)**.
5. Y. Li, H. C. Wang, and M. J. Yang, *Sens. Actuators B* 121, 496 **(2007)**.
6. S. Shin, J. K. Paik, N. E. Lee, H. D. Park, J. S. Park, and J. Lee, *Ferroelectrics* 328, 59 **(2005)**.
7. S. Shin, J. K. Paik, N. E. Lee, H. D. Park, J. S. Park, and J. Lee, *Integrated Ferroelectrics* 69, 333 **(2005)**.
8. S. Shin, N. E. Lee, H. D. Park, J. S. Park, and J. Lee, *Ferroelectrics* 338, 41 **(2006)**.
9. M. Matsuguchi and T. Uno, *Sens. Actuators B* 113, 94 **(2006)**.
10. T. Tanrisever, I. C. Okay, and J. Sonmezoglu, *Appl. Poly. Sci.* 61, 485 **(1996)**.
11. A. R. Goodall, J. Hearn, and M. C. Wilkinson, *J. Poly. Sci.* 17, 1019 **(1979)**.
12. R. Capan, A. K. Ray, A. K. Hassan, and T. Tanrisever, *J. of Phys. D: Appl. Phys.* 36, 1115 **(2003)**.
13. R. Capan, A. K. Ray, T. Tanrisever, and A. K. Hassan, *Smart Mater. Structures* 14, N11 **(2005)**.
14. A. K. Hassan, A. K. Ray, A. V. Nabok, and S. Panigrahi, *IEE Proc.-Sci. Measurement and Techn.* 147, 137 **(2000)**.
15. A. Alves, P. N. Johnston, P. Reichart, D. N. Jamieson, and R. Siegele, *Nucl. Instrum. Methods Phys. Res. B* 260, 431 **(2007)**.
16. J. Raczkowska, R. Montenegro, A. Budkowski, K. Landfester, A. Bernasik, J. Rysz, and P. Czuba, *Langmuir* 23, 7235 **(2007)**.
17. Y. Liao, J. You, T. Shi, L. An, and P. K. Dutta, *Langmuir* 23, 11107 **(2007)**.
18. N. G. Semaltianos, *Microelectron. J.* 38, 754 **(2007)**.
19. K. Welford, *Optical and Quantum Electronics* 23, 1 **(1991)**.
20. R. Casalini, J. N. Wilde, H. Nagel, U. Oertel, and M. C. Petty, *Sens. Actuators B* 57, 28 **(1997)**.
21. A. V. Nabok, A. K. Hassan, and A. K. Ray, *J. Mater. Chem.* 10, 189 **(2000)**.
22. R. E. Bolz and G. L. Tune, Handbook of Tables for Applied Engineering Science, The Chemical Rubber Co., Ohio **(1970)**, p. 68.