RSC Advances

ROYAL SOCIETY
OF CHEMISTRY

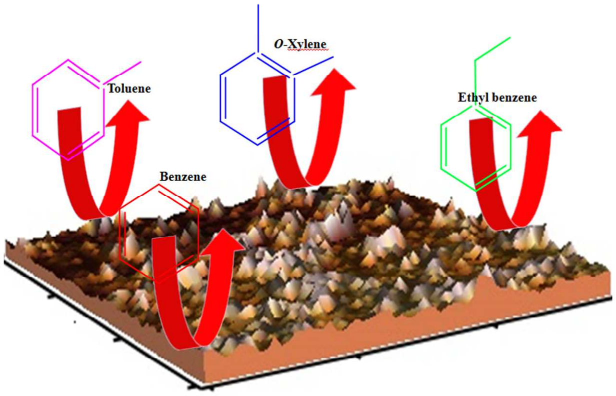
www.rsc.org/advances

Efficient Detection of Volatile Aromatic Hydrocarbon Using Linseed Oil-Styrene-Divinylbenzene Copolymer Coated Quartz Crystal Microbalance

Rashmita Das,[†] Rajib Bandyopadhyay,[†] Panchanan Pramanik*,[‡]

Abstract

The polymer film with high sensing ability in QCM for benzene, toluene, o-xylene and ethyl benzene vapors have been produced from the co-polymerization of styrene, divinyl benzene and linseed-oil with optimum ratio at 120^0C using benzoyl-peroxide as initiator in argon atmosphere. The cross linked polymers are used as sensing films on the surface of silver coated quartz crystal microbalance sensor. The films of sensors are developed by simple solution dip-dry method using precursor-solution followed by polymerization. The chemical composition of polymer is optimized for highest sensor response having 30µl Linseed oil-40µl Styrene-30µl Divinyl benzene (w/w) for all the analytes. Linear calibration curves are obtained for all the vapors for the concentration ranges from 5 ppm to 250 ppm and sensitivities are found to be approximately 1.1 to 1.7 Hz/ppm of organic vapors. The structure and surface morphology of the copolymer are analyzed by FTIR and FESEM. Surface morphologies and surface roughness of the sensing film before and after exposure to analytes are confirmed by AFM microscopy. The sensors are reactivated by desorption of analytes from the sensor surface by continuous flow of dry nitrogen gas into the sensor chamber. The sensing ability of the polymer film is a few times more than other reported materials. The film has no similar sensitivity with phenols and other polar aromatic derivatives.



Graphical abstract

1. Introduction

Volatile aromatic hydrocarbons, particularly benzene, toluene, ethyl benzene and xylene are used for the manufacturing of paints, synthetic rubbers, agricultural chemicals, chemical intermediates, petroleum products, such as fuel oil and gasoline. However, prolong inhalation of these compounds cause serious hazardous effects on the kidneys, heart, lungs and the nervous system[1, 2] for which monitoring of these hazardous aromatic hydrocarbon vapors in air is highly required by various industries. The analyses of VOCs are usually performed by using analytical method such as gas chromatograph–mass spectrometer (GC–MS) which provide accurate assessments of VOC concentrations, but the machines are very expensive for real time analyses[3]. Surface modified quartz crystal microbalance (QCM) sensors with polymeric materials have been widely used for the detection of organic gas[4-6], heavy metal ion [7-8], protein [9] and organic compounds[10-11]. QCM is a shear mode device consists of a thin quartz disk coated with silver electrode on both sides. The film on the surface of the quartz crystal after adsorption of analytes follows the increase of the mass of the film resulting in the decrease in resonance frequency. It has high sensitivity, fast response and can detect the trace amount of mass change in the order of nanogram. Most volatile and nonvolatile organic compounds having boiling point 40-200^{0}C can be detected by polymer-based QCM sensors[12]. The polymer-films like hexamethyldisiloxane, chitosan/polyaniline, thiophene and its derivatives poly(N-isopropylacrylamide) are attempted in various QCM based sensors[13-15]. However the sensitivities are not good. We have developed a co-polymer of linseed oil-styrene-divinyl benzene which shows a high response to the aromatic hydrocarbon vapors, but is not that sensitive to phenols or other polar aromatic derivatives. To the best of our knowledge this copolymer coated QCM sensors for gas sensing application have not been reported yet. In our previous reported work, we have polymerized linseed oil with benzoyl peroxide by free radical polymerization and the film is used for the detection of benzene, toluene, o-xylene and p-cresol[16].

Polydimethylsiloxane (PDMS) coated quartz crystal microbalance (QCM) is developed for the detection of organic vapors such as benzene, toluene, ethylbenzene, and xylenes[17]. But the frequency shift values (Hz/ppm) for the detection of aromatic hydrocarbon are not good as compared to our experimental values presented in this report. Table 1 represents the various polymers used as sensing films and their sensitivities in QCM systems. Quartz crystal microbalance coated with linseed oil-styrene-divinyl benzene co-polymer has higher frequency shift values than those of reported values. Our results show that 250 ppm of ethyl benzene, o-xylene, toluene and benzene has frequency shift values of 428 Hz, 396 Hz, 323 Hz and 257 Hz respectively which is better than other reported data.

Table 1. Comparisons of sensitivity of QCM sensors for VOCs detection

Polymer used	Ethyl Benzene (Hz/ppm)	Xylene (Hz/ppm)	Toluene (Hz/ppm)	Benzene (Hz/ppm)
Poly(3-ethylthiophene)[18]	-	0.3	-	-
Poly(3-odecylthiphene)[19]	-	-	0.08	-
CNT with PB[19]	-	0.6	-	0.09
Ni(SCN)2(4-Pic)$_4$[20]	-	-	1.99	1.89
Co(SCN)2(4-Pic)$_4$[20]	-	-	0.19	0.05
Ni(SCN)2(4-Pic)$_4$[20]	-	-	0.05	0.15
Co(SCN)2(4-Pic)$_4$[20]	-	-	0.09	0.08
Polybutadine(PBD)[21]	-	-	0.09	-
Polystyrene (PS)[21]	-	-	0.06	-
Polystyrene (PS)[22]	-	-	0.14	0.06
(11 w/w %) L-cyclodextrin embedded in polyurethane[23]	-	0.03	0.006	0.006
Tetra-tert-butyl copper phthalocyanine[24]	-	0.2	0.12	-
Polystyrene[25]	1.33	1.44	1.66	1.33
Linseed oil, Divinyl benzene, styrene (Our work)	**1.7**	**1.6**	**1.3**	**1.1**

Here, we have attempted for the synthesis of linseed oil-styrene-divinyl benzene copolymer having highest sensitivity for aromatic hydrocarbons such as ethyl benzene, o-xylene, toluene and benzene vapors. It seems that the polymer obtained from only styrene and divinylbenzene has the reasonable rigidity of the molecular-matrix with less free volume available for making molecular pores for accommodation of guest hydrocarbon vapors. To improve the availability of molecular-pores with reasonable flexibility we have attempted to modify polymerization of styrene and divinyl benzene with linseed oil. Polymer from only linseed oil has good hydrophobicity but it is not capable to retain molecular pores with time due to the softness of the matrix.

2. EXPERIMENTAL

2.1 Materials

Linseed oil and divinylbenzene were purchased from Sigma-Aldrich and benzene, toluene, o-xylene, ethylbenzene and benzoyl peroxide were procured from E. Merck, India. Styrene was purchased from Merck Chemical Co., Germany. All the chemicals were used in analytical grade. For this experiment, AT cut 10 MHz quartz crystals coated with silver on both sides were purchased from local markets.

2.2 Film preparation

A set of ten different solutions of linseed oil, styrene and divinyl benzene was prepared by taking different concentrations of precursor solvents in separate glass vial with choloform solvent and stirred vigorously. 0.05 gm benzoyl peroxide was added as an initiator to the solutions. QCM surfaces are cleaned with Piranha solution and then rinsed with deionized water before use for experimentation. The coating of the solution on the surface of the QCM was carried out by the simple solution dip-dry method and kept inside a chamber which was under the flow of pure argon. After complete removal of chloroform by flow of argon, temperature of the chamber was raised to 120^0C for 3 hours. A stable and cross linked polymer film was formed on the surface of the quartz crystal. The cross linked polymer film synthesis is optimized by repeated experiment.

2.3 Instrumentation

This experiment is based on static headspace sampling method. It is made of a Teflon chamber of 100 ml volume kept in a temperature controlled environment. The temperature inside the chamber is controlled by temperature controller. All the experiments are carried out at a standard atmospheric temperature of $25^0 \pm 2$. Sensor set up is placed inside a slab of Cu metal to maintain uniform temperature and a suction pump is attached to the chamber to exhaust the analyte gases to the outside of the chamber after each experiment. The prepared sensors are placed on a rigid base inside the sensor chamber which is connected to counter instrument. The oscillation frequencies of the crystals are generated by IC 8284 and are recorded into a computer through a National Instrument card. The analytes of different concentrations are injected in to the sensor chamber using a glass syringe through rubber septa. To avoid the interferences the analytes are dispersed with the help of a syringe pump so that the maximum impact in a short time period can be obtained. A reservoir of capacity 2 litres is attached to the vacuum pump as a buffer chamber so that any fluctuation of the pressure of the vacuum pump is arrested. The flow of the nitrogen gas is very slow (1-2ml/sec). Pressure drop between the buffer chamber and sensor chamber is approximately about 5-6 cm of Hg. Before injection of analytes to the sensor chamber, the vacuum pump is closed till the equilibrium is reached after sample injection and the frequency is recorded, then the vacuum pump is again switched on for purging of the sensor chamber. Hence there is no interference of vacuum pump pressure on the sensitivity of the sensor. QCM has not been typically used in high pressure environments because the pressure changes affect the frequency of oscillation, thus complicating interpretation of the measurements. Hence studies are performed near 1atm pressure. This experimental technique is simple and free from experimental variations.

The structural analysis of the polymer film was carried out by a Paragon-500 FTIR of Perkin Elmer spectrometer and the surface morphology of the polymer film is studied by JEOL JEM6700F field emission scanning electron microscope (FESEM). The surface topology and roughness of the films are analyzed by Tapping mode AFM (Pico plus 5500 ILM AFM, Agilent Technologies, USA) with a piezoscanner of maximum range of 100 µm and a Pico view software version 1.12 (Agilent Technologies, USA) is used for image processing.

3. RESULTS AND DISCUSSION

3.1 Structural characterization

The FTIR spectrum of the polymer film is shown in figure 1. The characteristic absorption peaks at 3475cm^{-1} indicates the presence of –OH stretching, 2931 cm^{-1} and 2850cm^{-1} is for –C-H stretching and the peak at 1743cm^{-1} confirms the presence of –C=O stretching respectively. The peaks at 1601cm^{-1}, 1450cm^{-1} and 1380cm^{-1} are observed for –C-C stretching (aromatic ring) and –C-H stretching (alkyl). The absorption bands at 1320cm^{-1} and 1158 cm^{-1} indicate the presence of –C-O stretching of esters and =C-H bending respectively. The FTIR spectrum reveal the presence of –C=CH$_2$ vinyl (strong) group through the peak at 906 cm^{-1} and =C-H bending (alkenes) group appeared at 766 cm^{-1}. Absorption peaks are slightly shifted which indicate, the formation of cross linking in the polymer.

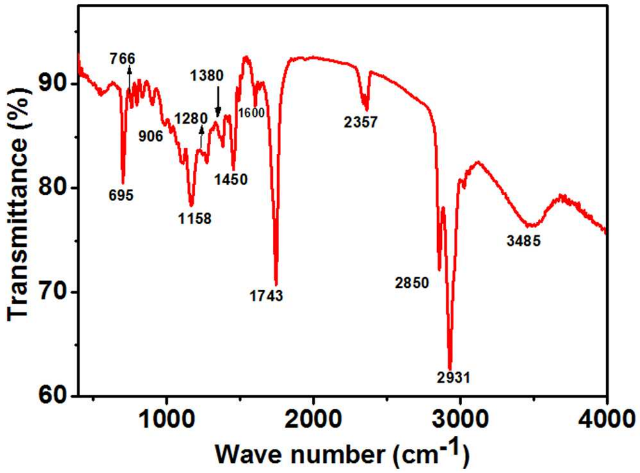


Figure 1. FTIR spectra of linseed oil-divinyl benzene-styrene co-polymer

Figure 2 represents the FESEM images of the copolymers of S1, S5 and S10 compositions of polymer and it is clearly observed that pores are uniformly distributed throughout the matrix. The diameters of the pores appeared in the nanometer range. The molecular pores are not formed in S1 polymer and S10 polymer the pores are not uniformly distributed throughout the matrix and less than S5 polymer which may affect the sensing mechanism.

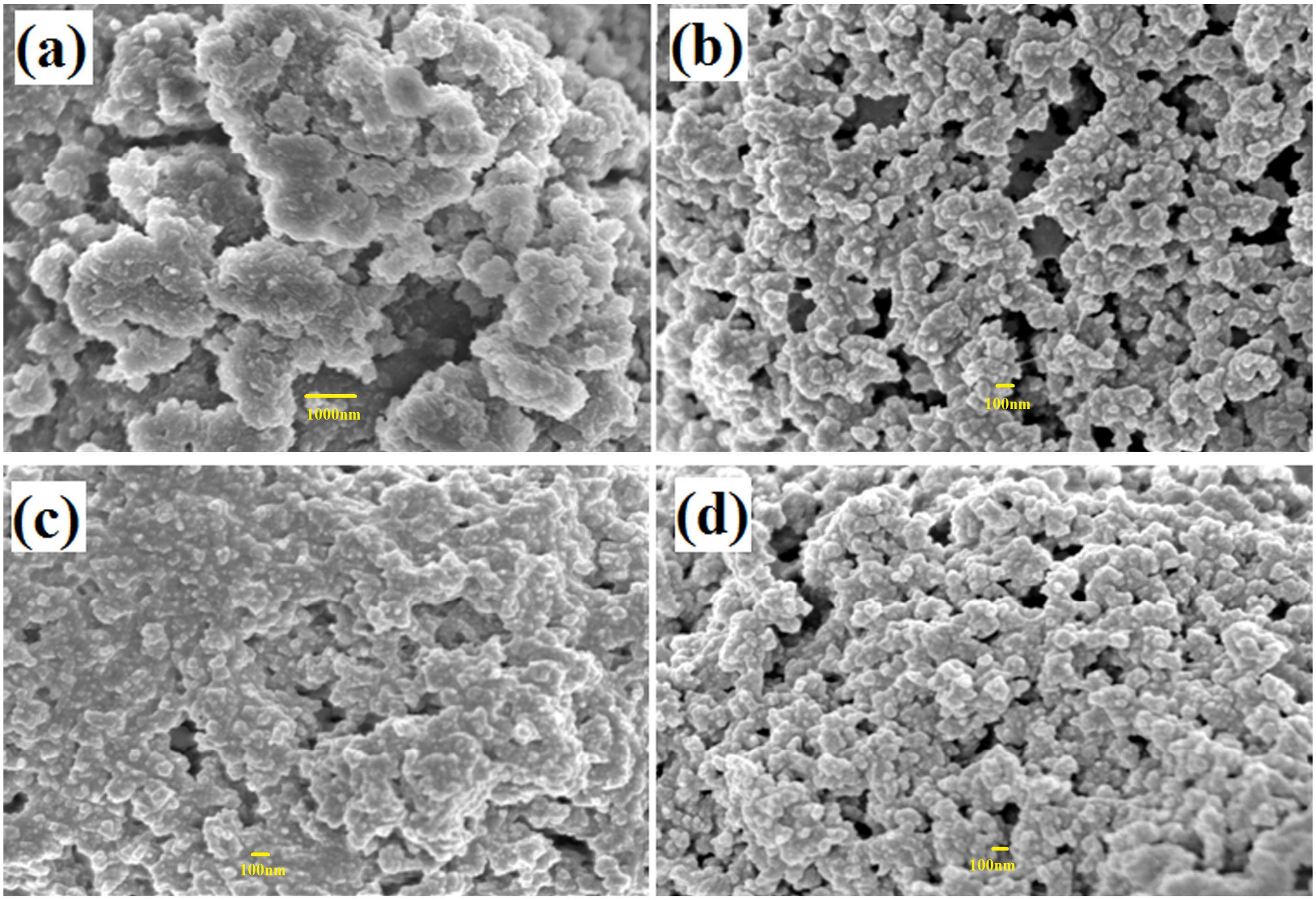


Figure 2. FESEM images of linseed oil-divinyl benzene-styrene co-polymer (a, b) S5 polymer (c) S1 polymer and (d) S10 polymer

3.2 Polymer optimization

The prepared ten sensors are labeled as S1, S2, S3, S4, S5, S6, S7, S8, S9, and S10 whose chemical compositions are presented in the table 2. The polymerization process is completed on the surface of QCM as mentioned above. It is observed that S5 sensor is most efficient among all prepared sensors for detection of aromatic hydrocarbon (figure 3). The frequency shift values of sensors before the adsorption of analytes are measured and considered as base frequency.

Different concentrations of gas molecules ranges from 5 ppm to 250 ppm are passed into the sensor chamber through a syringe pump of model no-LPM-50DN.

Table 2. Compositions of Linseed oil-Styrene-Divinyl benzene Copolymers

Sample ID	Linseed oil (µl)	Styrene (µl)	Divinyl benzene (µl)	Benzoyl peroxide (gm)	Chloroform (ml)
S1	10	40	50	0.05	9.85
S2	10	50	40	0.05	9.85
S3	20	30	40	0.05	9.86
S4	20	40	40	0.05	9.86
S5	30	40	30	0.05	9.85
S6	40	50	10	0.05	9.85
S7	50	30	20	0.05	9.85
S8	60	20	20	0.05	9.85
S9	70	10	20	0.05	9.85
S10	70	20	10	0.05	9.85

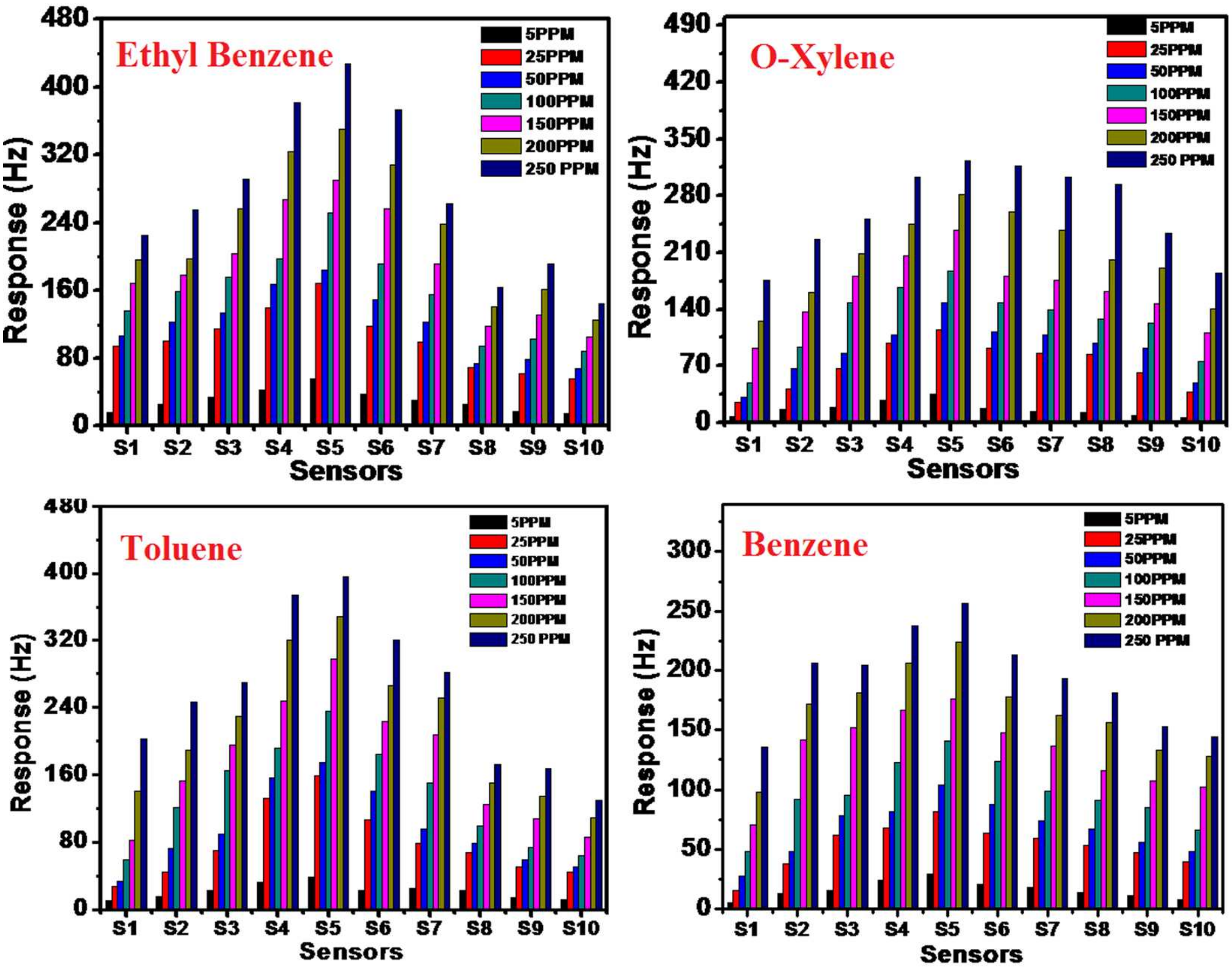


Figure 3. The optimization of polymerization of linseed oil-styrene-divinyl benzene copolymer

3.3 Sensor response

The concentrations of injected analytes in the sensor chamber are calculated in parts per million (ppm) by considering its density, purity, volume of the syringe and the volume of sensor chamber. Continuous flow of nitrogen gas is maintained for exhaustion of the analyte-gases from the sensor chamber. All the experiments are performed at a temperature of 25 ±2^0 C. Under the optimum condition, the responses of S5 sensor towards saturated concentration of common organic vapors, particularly aromatic are tested for six times for repeatability study and the average value is taken for analysis. Bubble method is used for the preparation of saturated concentrations of the vapors. In this method nitrogen gas is passed through organic liquids at low flux and blended vapors are transported to sensor chamber at room temperature[26]. It is clearly observed that S5 sensor has higher efficiency towards aromatic non- or weakly polar hydrocarbons such as benzene, toluene, o-xylene and ethyl benzene (table 3). Among these aromatic hydrocarbon compounds, the frequency shift is highest for ethyl benzene vapors in all concentration ranges. It is probably due to higher molar volume. For effective adsorption of aromatic hydrocarbon in polymer, there must have a molecularly rigid cavity of the order of greater than 3 Å. Only linseed oil cannot produce such class of cavity due to the formation of the soft matrix which has been tested in our earlier experiments. Hence styrene and divinyl benzene are added to make desired stereo regular harder polymer.

Table 3. Analytical characteristic parameters of S5 sensor to the volatile organic vapors

Volatile organic compounds	Standard deviation (S.D.)	Relative standard deviation (R.S.D)%
Ethylbenzene	5.11	0.84
O-xylene	5.09	1.07
Toluene	4.64	1.21
Benzene	3.81	1.25
Methanol	1.95	1.15
Ethanol	3.57	4.71
Propanol	3.44	1.87
Dicholomethane	3.41	2.21
Acetone	3.38	3.71
Ethyl methyl ketone	3.04	2.05
Chloroform	2.99	1.54
P-cresol	2.81	15.19
Formaldehyde	2.81	3.77
Aniline	2.75	2.66
m-cresol	2.36	14.30

The response is rapid and reversible, which confirms that there is no chemical interaction between the analyte and the polymer film.

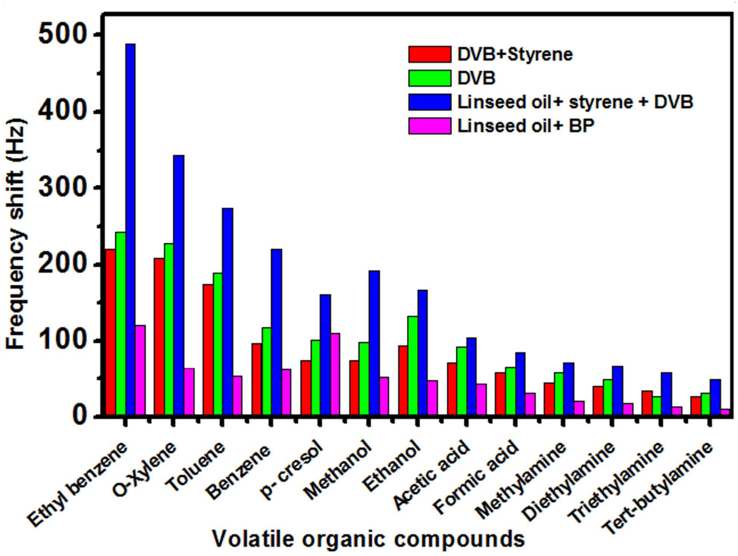


Figure 4. Comparison of four types of sensors to different volatile organic compounds

A comparison bar graph of four types of sensors prepared from polymerized linseed oil coated sensor, polydivinyl benzene sensor and the linseed oil-styrene-divinyl benzene copolymer (with optimized concentrations) coated sensor for different volatile organic compounds is presented in figure 4. It is noted that the highest sensitivity is obtained from optimized linseed oil-styrene-divinyl benzene copolymer than others polymer film. The aromatic monomers i.e., styrene and divinyl benzene enhances the cross linking of linseed oil and it is also observed that by increasing the concentrations of styrene and reducing the concentrations of DVB results in the formation of highly cross linked copolymers of linseed oil[27].

The response curve of the copolymer coated sensors is exposed to benzene, toluene, o-xylene and ethyl benzene vapors at the concentration range of 5-250 ppm are shown in figure 5. It is noted that the frequency shift values are increased linearly with respect to the concentration of analytes. The calibration curves are obtained by plotting of frequency shift (Δf) against various concentrations of vapors and the slopes of these curves are considered to be sensitivity and their values are expressed in (Hz/ppm).

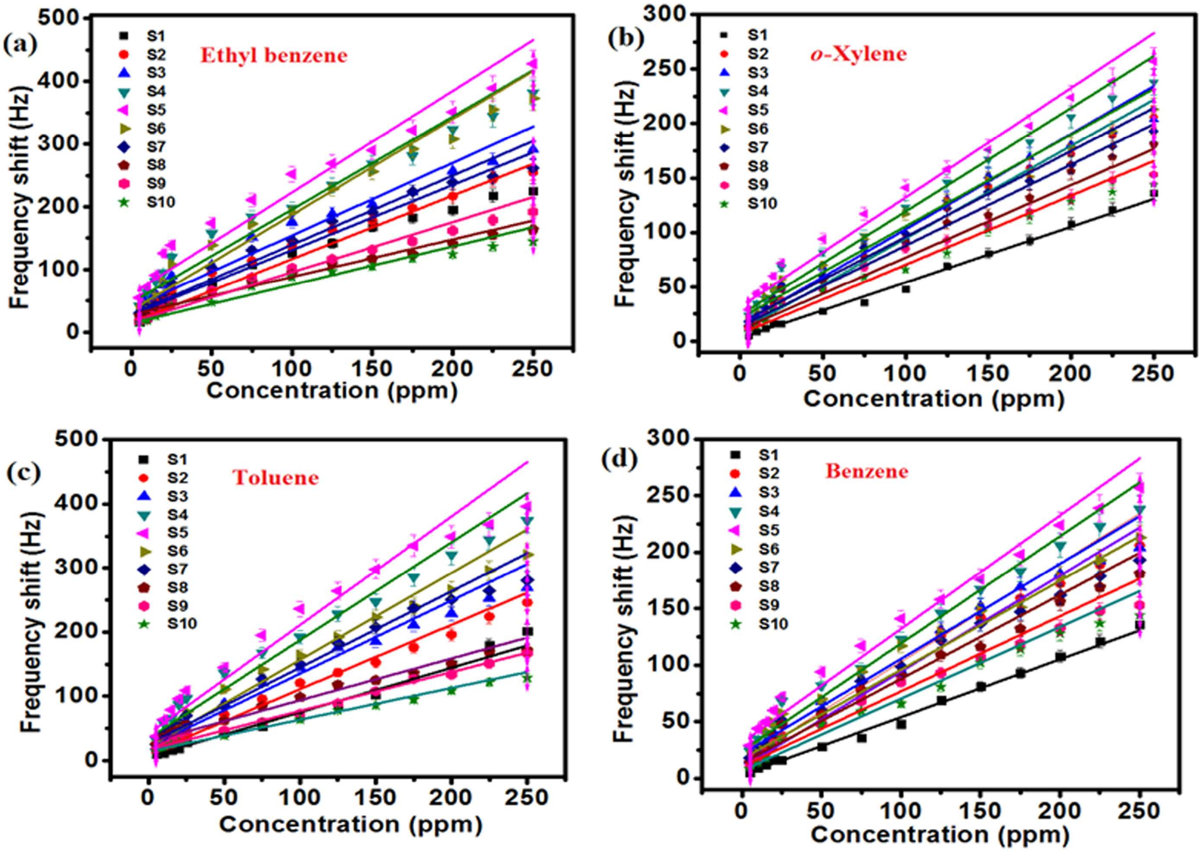


Figure 5. Response curves of benzene, toluene, ethyl benzene and o-xylene vapor in the range of 5-250 ppm

The sensitivity and the regression co-efficient values of S5 sensor to all four vapors are tabulated in table 4. The higher regression co-efficient values indicate that the frequency change values of the QCM sensor are linear to the vapor concentrations. The polymer has higher sensitivity towards ethyl benzene vapor and lowest for benzene vapors. The sensitivity of the sensor for the detection of ethylbenzene, o-xylene, toluene and benzene are calculated as 1.7, 1.6, 1.3 and 1.1 Hz/ppm respectively at 25^{0}C±2 and the values are reasonable for monitoring pollution due to aromatic hydrocarbons.

Table 4. Least square parameters of S5 sensor to analytes of 5-250 ppm concentration

Analytes	Sensitivity factor (Hz/ppm)	Correlation coefficient (R^2)
Ethyl benzene	1.7	0.99
O-xylene	1.6	0.98
Toluene	1.3	0.99
Benzene	1.1	0.99

It is expected that when volatile organic molecules are absorbed by the polymer films, there may be changes in its viscoelastic properties. A small change in baseline occurs during the repeated frequency measurement by the exposure of the analytes. The surface morphology of the polymer film before and after absorption of analytes is studied by AFM and the 2D and 3D images are presented in figure 6. The film is uniform over the whole area and the RMS (root mean square) surface roughness values before and after absorption of analytes are 493.9 nm and 846 nm respectively. It is noticed that, surface topography of the film is changed after adsorption of vapors and the surface roughness increases after adsorption of analytes. It can be concluded that the volatile aromatic compounds are diffused into pores of the polymer film causing swelling of the surface. Hence, the surface roughness increases after absorption of aromatic compounds. The cross linked polymer film is suitable for sensor applications, since the particles in the micrometer range lead to increase in the surface roughness which results the increased viscous interactions between the sensor layer and analytes.

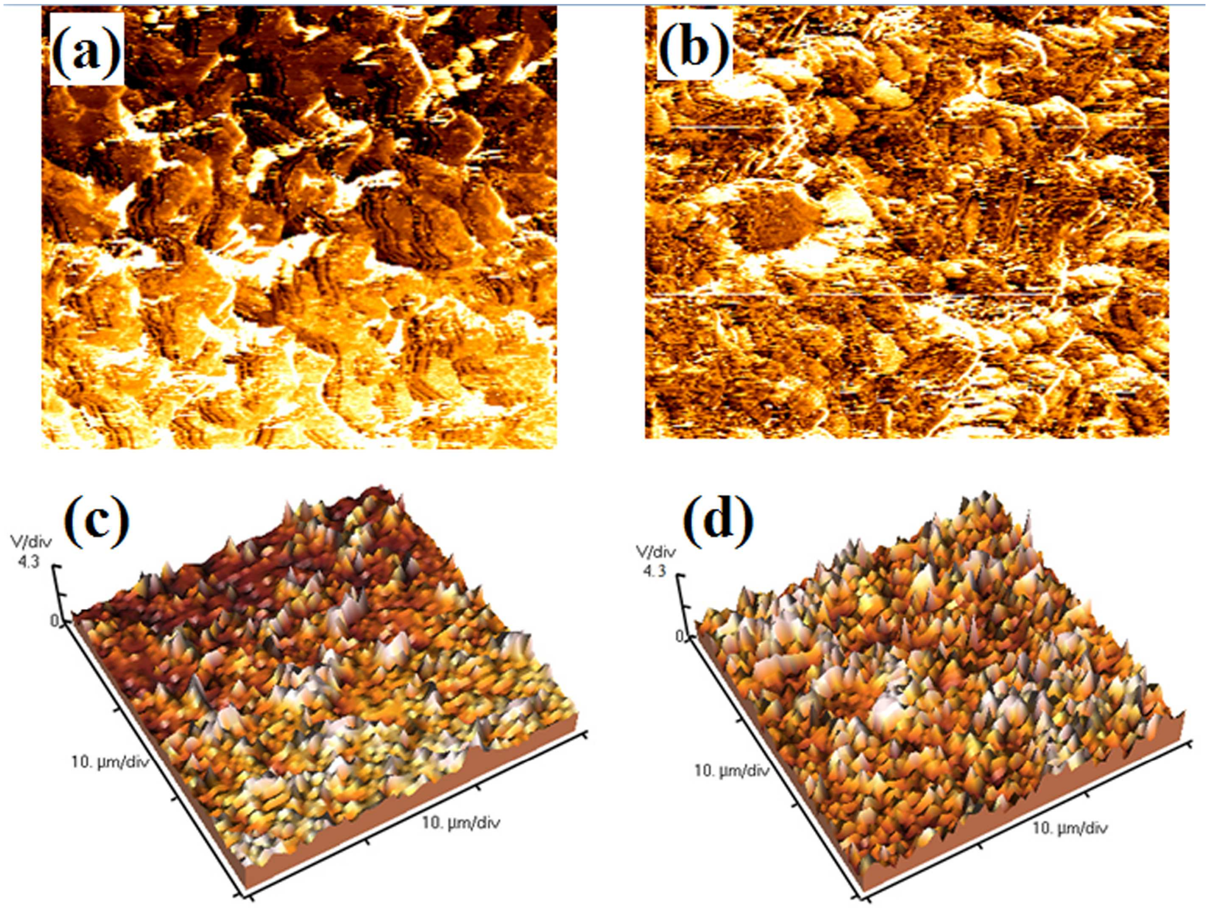


Figure 6. AFM images of QCM sensor surface (a) 2D, (c) 3D before and (b) 2D, (d) 3D after adsorption of analytes

3.4 Reproducibility

To investigate the reproducibility of the sensors, the copolymer coated sensors are exposed to a constant concentration of analyte for five times. Volatile organic compounds are passed to the sensor chamber and the frequency shift values are recorded after the equilibrium reached. The recovery of S5 sensor in response to 250 ppm of ethyl benzene vapor is plotted in figure 7. Similar response curves are obtained for toluene, o-xylene and benzene vapors.

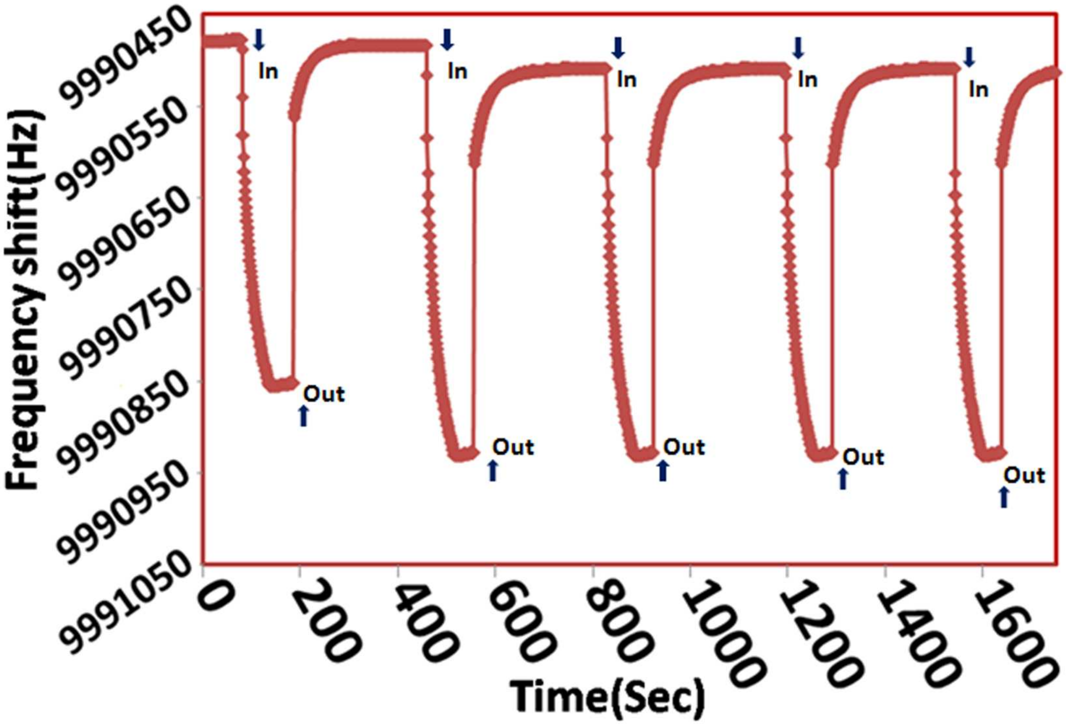


Figure 7. Reproducibility curves of S5 sensor exposed to 250 ppm of ethylbenzene vapor

It is clearly seen from the plot that the sensor responses and recovery time are fast. After each reading baseline is recovered as the continuous flow of dry nitrogen gas into the sensor chamber is maintained throughout the experiment. It confirms the physical sorption of polymer with the analytes take place on the QCM surface. The prepared QCM sensors are stored in vacuum desiccators to make it reusable. The real time sensor response of S5 sensor for 50 ppm of ethylbenzene, o-xylene, toluene and benzene is presented in figure 8.

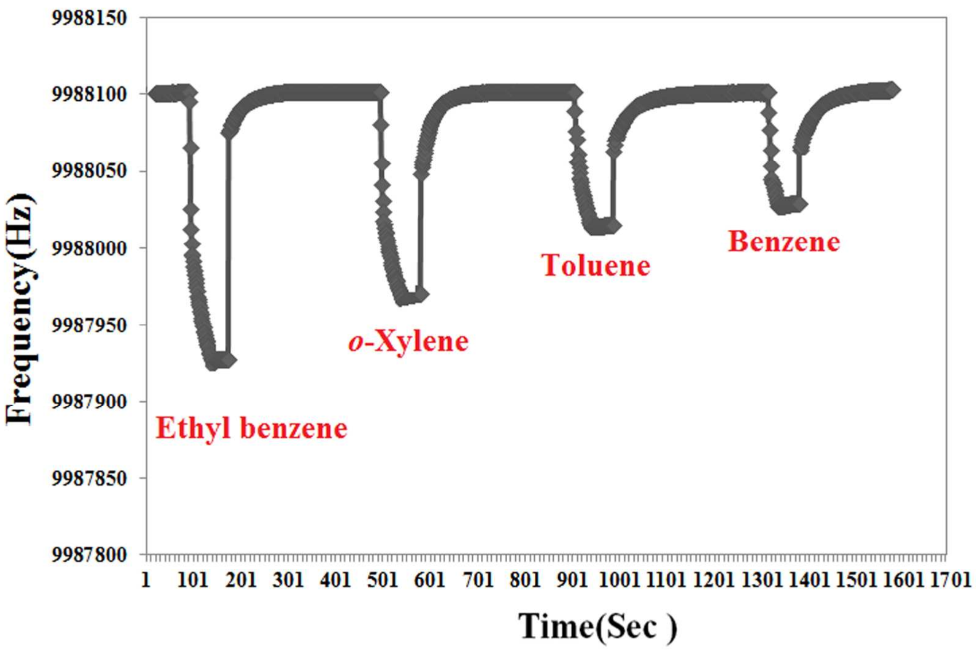


Figure 8. Real time sensor response of S5 sensor for 50 ppm of Ethylbenzene, O-xylene, Toluene and Benzene vapor.

4. CONCLUSIONS

The polymeric films synthesized from the mixture of linseed oil, styrene and divinyl benzene by using benzoyl peroxide as initiator at 120^0C for 3 hours in argon atmosphere show high sensitivity for detection of aromatic hydrocarbon in QCM based sensor. The maximum sensitivity is obtained for the polymer with the composition of 30µl styrene, 40µl divinyl benzene and 30µl linseed oil. Linear calibration curves are obtained between the frequency shift and the concentration of all the analytes in the range of 5-250 ppm. Sensors show sensitivity in the range of 1.1 – 1.7 Hz/ppm to the VOCs in the order of ethyl benzene, o-xylene, toluene and benzene respectively. These values are few times more than that of reported literatures. Fast response and recovery time of the sensor confirms the physical adsorption on the QCM surface. The sensors are reusable after complete removal of analyte by purging with dry nitrogen gas.

ACKNOWLEDGEMENTS

Analytical assistants from CRNN, University of Calcutta, Kolkata for FESEM and UGC-DAE consortium for scientific research, Kolkata centre for the FTIR analysis are gratefully acknowledged.

Notes and references

[†]Department of Instrumentation and Electronics Engineering, Jadavpur University, Salt Lake Campus, Kolkata 700 098, India

[‡] Deaprtment of Physical Science, MCKV Institute of Engineering, Liluah, West Bengal 711204

[*] Email: pramanik1946@gmail.com

1. M. Dekker, *Handbook of Water Analysis,* L. M. L. Nollet: New York, 2001.
2. R. M. Alberici, C. G. Zampronio, R. J. Poppi and M. N. Eberlin, *Analyst,* 2002, **127**, 230–234.
3. B. Tolnai, J. Hlavay, D. Möller, H.-J. Prümke, H. Becker and M. Dostler, *Microchem. J.,* 2000, **67,** 163–169.
4. Y. Fu and H.O. Finklea, *Anal. Chem.,* 2003, **75**, 5387–5393.
5. J. F. Ju, M. J. Syu, H.S. Teng, S.K. Chou and Y.S. Chang, *Sens. Actu. B: Chem*, 2008, **132**, 319–326.
6. P. Si, J. Mortensen, A. Kornolov, J. Denborg and P.J. Moller, *Anal. Chim. Acta,* 2007, **597**, 223–230.
7. S.C. Ng, X.C. Zhou, Z.K. Chen, P. Miao, H.S.O. Chan, S.F.Y. Li and P. Fu, *Langmuir,* 1998, **14**, 1748–1752.
8. S.J. Liu, H.G. Nie, J.H. Jiang, G.L. Shen and R.Q. Yu, *Anal. Chem.,* 2009, **81,** 5724–5730.
9. Y. Pei, H. Yu, Z. Pei, M. Theurer, C. Ammer, S. Andre, H.J. Gabius, M. Yan and O. Ramstrom, *Anal. Chem.,* 2007, **79,** 6897–6902.
10. K. Das, J. Penelle and V.M. Rotello, *Langmuir,* 2003, **19,** 3921–3925.
11. M. Cerruti, J. Jaworski, D. Raorane, C. Zueger, J. Varadarajan, C. Carraro, S.W. Lee, R. Maboudian and A. Majumdar, *Anal. Chem.*, 2009, **81**, 4192–4199.
12. S. Dissanayake, C. Vanlangenberg, S.V. Patel and T. Mlsna, *Sens. Actua. B: Chem*, 2015, **206,** 548–554.
13. M. Boutamine, A. Bellel, S. Sahli, Y. Segui and P. Raynaud, *Thin Solid Films*, 2014, **552**, 196–203.
14. M. Matsuguchi, N. Harada and S. Omori, *Sens. Actua. B: Chem*, 2014, **190**, 446– 450.
15. M. M. Ayad, N. A. Salahuddin, I.M. Minisy and A. Wael, *Sens. Actua. B: Chem,* 2014, **202**, 144–153.
16. R. Das, S. Biswas, R. Bandyopadhyay and P. Pramanik, *Sens. Actua. B: Chem*, 2013, **185**, 293–300.
17. A. Mirmohseni and V.Hassanzadeh, *J. Appl. Polym. Sci.,* 2001, **79**, 1062–1066.
18. P. Si, J. Mortensen, A. Komolov, J. Denborg and P. Møller, *Anal. Chim. Acta*, 2007, **597**, 223–230.

19. B. Pejcic, M. Myers, N. Ranwala, L. Boyd, M. Baker and A. Ross, *Talanta,* 2011, **85**, 1648-1657.

20. H. O. Finklea, M. A. Phillippi, E. Lompert and J. W. Grate, *Anal. Chem.* 1998, **70**, 1268-1276.

21. M. kimura, Y. liu, R. Sakai, S. sato, T. Hirai, T. Fukawa and T. Mihara, *Sens. and Mater.* 2011, **23**, 359-368.

22. B. Pejcic, C. Barton, E. Crooke, P. Eadington, E. Jee and A. Ross, *Sens. Actua. B: Chem,* 2009,**135**, 436–443.

23. F. L. Dickert and O. Hayden, *Trends Anal. Chem*, 1999, 18, 192-199.

24. A. Kumar, J. Brunet, C. Varenne, A. Ndiaye, A. Pauly, M. Penza and M. Alvisi, *Sens. Actua. B: Chem,* 2015, **210**, 398–407.

25. A. Mirmohseni and K. Rostamizadeh, *Sensors,* 2006, ***6,*** 324-334.

26. R. Das, S. Pradhan, S. Biswas, P. Sharma, A. Ghosh, R. Bandyopadhyay and P. Pramanik, *Sens. Actua. B: Chem*, 2014, **198**, 94–101.

27. V. Sharma, J. S. Banait, R. C. Larock and P. P. Kundu, *eXP. Polym. Lett.,* 2008, **2**, 265–276.