

Polymer-Coated Piezoelectric Quartz Crystal Sensor for Sensing the Nerve Agent Simulant Dimethyl Methylphosphonate Vapor

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ABSTRACT: A chemical vapor sensor based on a quartz crystal microbalance was fabricated with a 10-MHz quartz crystal oscillator. The quartz crystals were coated with four newly synthesized polymers and were studied for the detection of the nerve agent simulant dimethyl methylphosphonate vapor. The sensor was tested for immediate and extended periods of time. Various sensing parameters (e.g., the sensitivity, response time, and recovery time) were evaluated with respect to

different coating materials. All the polymers showed fairly good baseline stability even after several cycles. The highest frequency drift of 23.8 Hz/kHz was observed for one of the polymers, whereas another polymer showed the best sensing stability over an extended period of 250 days. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3708–3717, 2010

Key words: coatings; sensors; synthesis

INTRODUCTION

Organophosphorous compounds are intensively employed as pesticides and chemical warfare agents.^{1,2} The routine analysis of nerve agents in environmental and biological samples is carried out with analytical techniques such as gas chromatography,^{3,4} atomic emission detection,⁵ liquid chromatography,⁶ ion chromatography,⁷ gas chromatography coupled with mass spectrometry,⁸ capillary electrophoresis,⁹ capillary electrophoresis with conductivity detection,¹⁰ and capillary electrophoresis coupled with flame photometry.⁶ These methods have very high sensitivity, reliability, and precision. However, these techniques require expensive instrumentation and are unsuitable for field analysis. Because of this global scenario, there are urgent demands for the development of highly sensitive, selective, and portable field detection equipment for sensing organophosphorous compounds.

The concept of a piezoelectric sorption detector was first introduced in 1964 by King,¹¹ who used bulk acoustic wave quartz crystals. Detectors based on such crystals are frequently called quartz crystal microbalances (QCMs).¹² QCM sensors use a quartz

crystal oscillator in which a quartz crystal works as a sensing element. QCMs have been widely exploited for various types of chemical sensors, such as those used for organic vapor detection,^{13,14} bio-sensing applications,¹⁵ and environmental monitoring.¹⁶ Accordingly, a mass deposited onto quartz crystal electrodes produces a reduction in the resonance frequency of the oscillator, and this can be measured with a suitable electronic circuitry or frequency counter. The variation in the resonance frequency can be calculated with Sauerbrey's equation.¹⁷ To make a gas sensor using a QCM, a selective and sensitive coating of an adsorbent material is deposited onto the surface of the quartz crystal electrode. This coating makes a static shift in the resonance frequency of the oscillator. For efficient sensor development, it is necessary to be able to select or design polymers so that they will absorb organic vapors of interest in a predictable manner. Also, the adsorption phenomenon must be reversible at room temperature so that adsorbed vapors can be desorbed either by an increase in the temperature or via purging with air/nitrogen. This makes the sensor work reversibly.

Mass-sensitive QCM devices have been extensively used as selective sensors for the detection of organophosphorous compounds. Enhanced detection specificity of these crystals can be achieved by suitable modifications of the crystal surface with organic compounds or enzymes. The performance of QCMs as chemical sensors depends on the selectivity and

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TABLE I
Test Polymers, DP Values, and Physical Characteristics

Sample	DP ^a	M_w (Da)	PDI	T_g (°C)	Characteristics
P1	8	9,780	3.11	18	Highly viscous liquid
P2	42	48,300	4.22	22	Rubbery
P3	—	12,400	4.42	15	Highly viscous liquid
P4	3	8,298	1.98	11	Highly viscous liquid

M_w = weight-average molecular weight; PDI = polydispersity index.

^a Calculated from the feed.

sensitivity of the polymer coating material applied to the surface of the piezoelectric crystal. To collect the most chemical information for QCM gravimetric chemical vapor sensors, a variety of chemically diverse polymers are required. The polymers used as coating materials must cover the full range of solubility interactions (dispersion, dipole–dipole, and hydrogen-bonding interactions) and need to include nonpolar, polarizable, dipolar, hydrogen-bonded basic, and hydrogen-bonded acidic polymers.^{18–22} Grate²³ patented several hydrogen-bonded acidic fluorosiloxane polymers with glass-transition temperatures (T_g 's) below room temperature. These polymeric materials are excellent sorbents for basic vapors. Fluorinated and nonfluorinated carbosiloxane polymers,^{24–26} reported by several researchers, have been found to have good sensing characteristics for different organophosphorous compounds.

In this investigation, four new polymers were synthesized. These polymer materials were coated onto quartz crystal surfaces with a 10-MHz resonance frequency. A sensing instrument was fabricated, and the sensing capability of the instrument for the nerve agent simulant dimethyl methylphosphonate (DMMP) was investigated.

EXPERIMENTAL

Reagents and apparatus

Bisphenol A dianhydride (BPADA; 97%; Aldrich, St. Louis, MO) was heated at 120°C overnight before use. Aminopropyl-terminated polydimethylsiloxane (APPS; block length = 8.3), hydride-terminated polydimethylsiloxane (DMS-H11; average molecular weight = 1050, viscosity = 7–10 cSt), and platinum-1,3-divinyltetramethyldisiloxane (Pt-DVTMDS) were purchased from Gelest, Inc. (United States). 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (HFBPA; Fluoro Chem, Glossop, Derbyshire, UK) was used as received. 1,2-Dichlorobenzene (ODCB), allyl bromide (C₃H₅Br), toluene, and dichloromethane (DCM; E. Merck, India) were used as received. Methanol and *n*-butanol were purchased from Ranbaxy Fine Chemical, Ltd. (Mumbai, India). Bisphenol A (BPA) was

purchased from Loba Chemie (Mumbai, India) and was recrystallized from toluene. The physical properties of the polymers are listed in Table I.

The differential oscillator circuitry of the QCM sensor was used for recording the signals. The differential output of this circuit was buffered and fed to the microcontroller to actuate the alarm, light-emitting diodes, and recording of the sensing cycle on a personal computer dedicated to this purpose. A schematic diagram of the experimental setup is shown in Figure 1. The outlet of the vapor generator was connected at the sampling input of the crystal cell, and the nitrogen gas was connected at the purge input. The exhaust of the crystal cell was connected to an active charcoal canister to trap the eluted chemical vapor. A flow of XL-grade N₂ within the cell was maintained at 300 mL/min.

Methods of analysis

¹H-NMR and ¹³C-NMR for the monomer and polymers were recorded on 400- and 100-MHz instruments (Bruker, Switzerland), respectively, with CDCl₃ as the solvent. The T_g values of polymer samples (10 ± 2 mg) were analyzed by differential scanning calorimetry with a Netzsch DSC 200PC differential scanning calorimeter at a heating rate of 20°C/min. T_g values were taken as the midpoint of the change in the slope of the second heat cycle. Gel permeation chromatography was performed with a Waters Instrument model 2487 apparatus. Tetrahydrofuran (high-performance liquid chromatography grade) was used as the eluant. The flow rate was 0.5 mL/min, polystyrene was used as the standard, and a UV detector (dual λ absorbance detector) was used for this purpose. Empower 2 software was used for GPC data acquisition and processing. The synthesized monomer and polymers were characterized with Fourier transform infrared (FTIR) to analyze the functional groups present. Analyses were performed in a humidity-free atmosphere at room temperature with a Nexus 870 FTIR spectrophotometer (Thermo Nicolet, USA). Samples were prepared through the dissolution of the materials in DCM, and a drop of each solution was placed with a

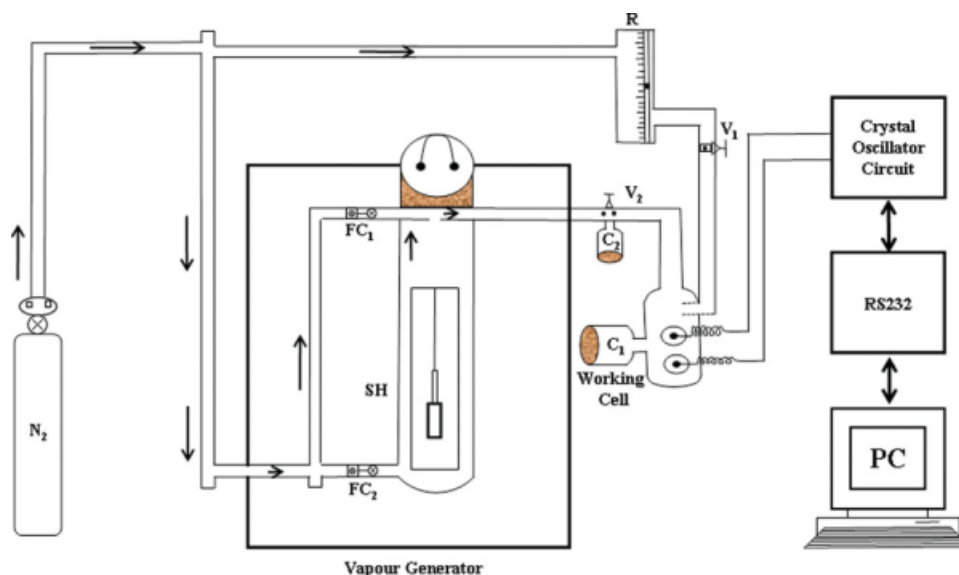


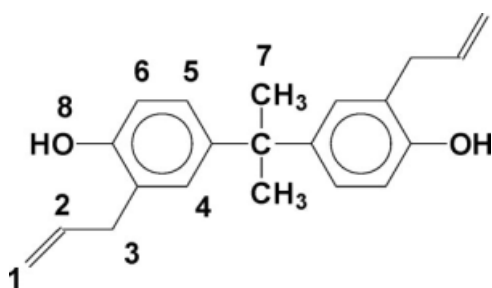
Figure 1 Schematic diagram of the sensing instrument (C_1 = canister 1; C_2 = canister 2; FC_1 = flow control 1; FC_2 = flow control 2; N_2 = nitrogen cylinder; PC = personal computer; R = rotometer; SH = sample vial; V_1 = one-way valve; V_2 = two-way valve). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

micropipette on a KBr disc. At least 32 scans at a resolution of 4 cm^{-1} were used.

Synthesis of the monomer diallyl bisphenol A (DABPA)

The DABPA monomer was synthesized in two steps. In the first step, BPA (25.01 g, 109.50 mmol), C_3H_5Br (29.15 g, 241.01 mmol), sodium hydroxide (NaOH; 13.14 g, 328.64 mmol), *n*-BuOH (85 mL), and CH_3OH (20 mL) were placed into a 250-mL, three-necked, round-bottom flask equipped with a reflux condenser. The mixture was heated with stirring for 5 h at 75°C . The reaction mixture was cooled to room temperature and filtered with a Buckner funnel, and the filtrate was concentrated. The residue was washed thoroughly with distilled water to remove the excess NaOH and NaBr that formed during the reaction. The off-white, viscous liquid was collected and dried over anhydrous $MgSO_4$. Finally, the product was dried *in vacuo* at 50°C for 8 h.

In the second step, the diallyl ether of BPA was heated in a vacuum oven at $175\text{--}180^\circ\text{C}$ for 14 h to obtain DABPA:



$^1\text{H-NMR}$ ($CDCl_3$, 400 MHz, δ , ppm): 7.0–6.97 (dd, 2H, $J^1 = 9.586$, $J^2 = 2.396$, H^5), 5.73–6.71 (d, 4H, H^4 , H^6), 6.03–5.98 (dd, 2H, H^2), 5.24 (s, 2H, H^8), 5.24–5.12 (dd, $J_{cis} = 6.57\text{ Hz}$, $J_{gem} = 1.68\text{ Hz}$, 1.46 Hz , $J_{trans} = 14.4\text{ Hz}$, 4H, H^1), 3.39 (s, 4H, H^3), 1.65 (s, 6H, H^7). FTIR (KBr, cm^{-1}): 3440 (aromatic $-\text{OH}$ stretching band), 3070 (aromatic C-H stretching band), 2969 and 2929 (aliphatic C-H stretching band), 1637 (allylic $>\text{C}=\text{C}<$ stretching band), 1605 (aromatic $>\text{C}=\text{C}<$ stretching band), 1258 (C-O stretching band).

Polymerization

Synthesis of the anhydride-terminated polyimides

The synthesis scheme for the anhydride-terminated polyimides P1 [degree of polymerization (DP) ~ 8] and P2 (DP ~ 42) is shown in Figure 2(a). A 250-mL, three-necked, round-bottom flask equipped with a nitrogen inlet, a Dean–Stark trap, and a reflux condenser was charged with BPADA (3.00 g, 5.76 mmol), APPS (3.89 g, 4.50 mmol), and ODCB (25 mL) as the solvent. The mixture was heated slowly to 185°C with stirring under a nitrogen flow, and the reaction was continued for 4 h. The reaction mixture was cooled to room temperature and was precipitated into a large excess of methanol ($\sim 600\text{ mL}$). The viscous liquid portion was isolated by the removal of methanol and was dried *in vacuo* at 40°C for 8 h:

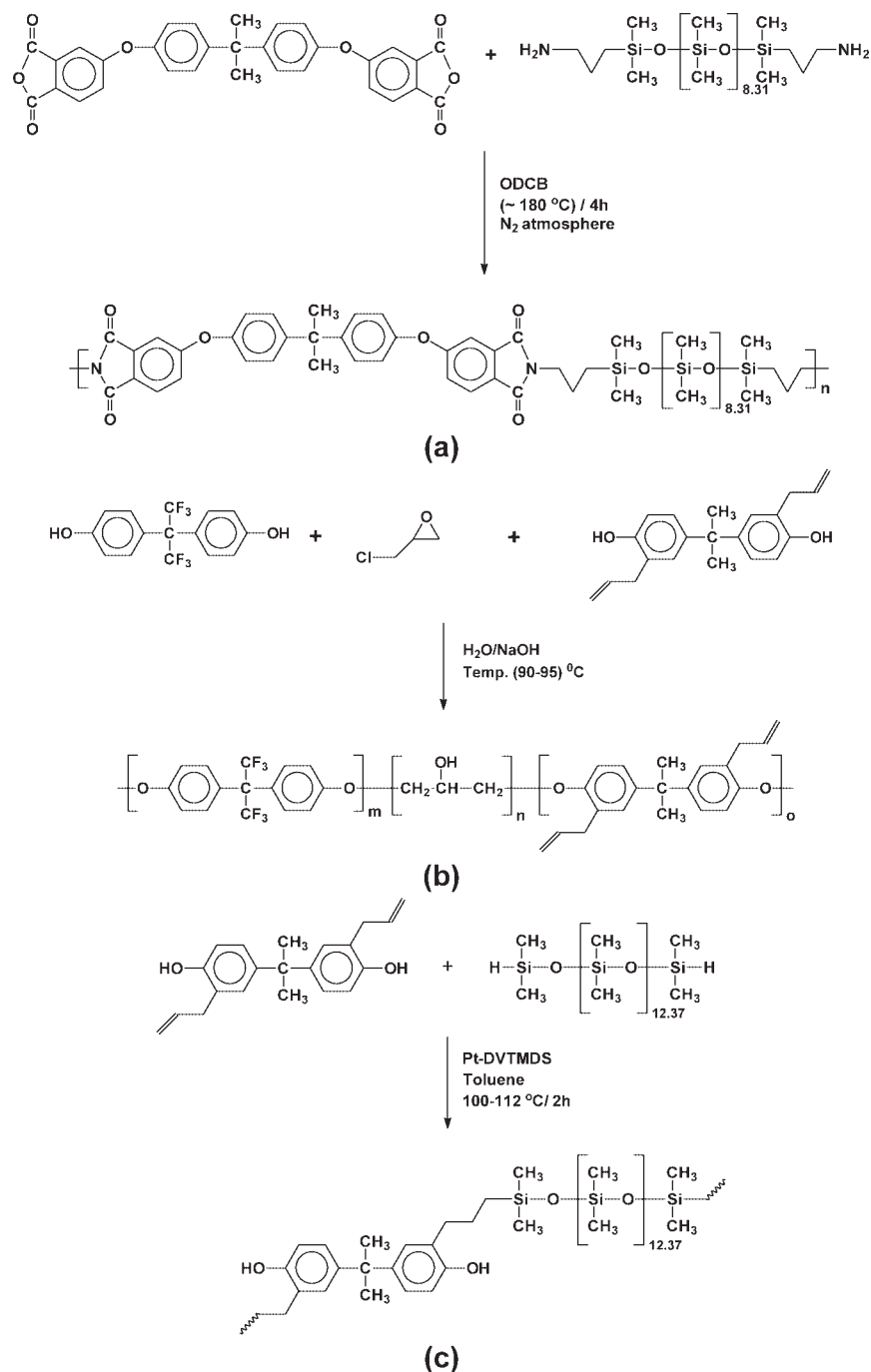
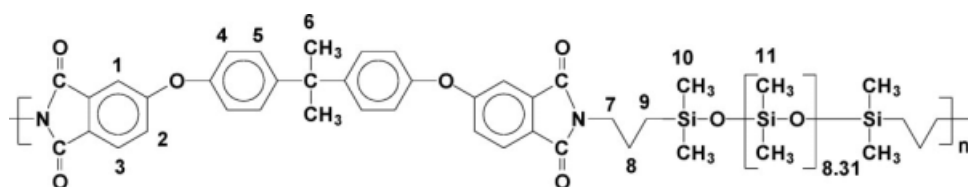


Figure 2 Reaction schemes for polymers (a) P1 ($n = 8$) and P2 ($n = 42$), (b) P3, and (c) P4.

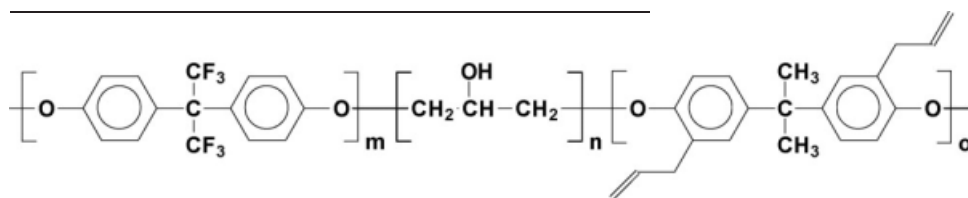


$^1\text{H-NMR}$ for P1 (CDCl_3 , 400 MHz, δ , ppm): 7.24 (d, 2H, H^3), 7.22 (s, 8H, H^1 , H^2 , H^5), 6.94–6.92 (d, 4H, $J = 8.28$ Hz, H^4), 3.55 (s, 4H, H^7), 1.66 (s, 10H, H^8 , H^6), 0.46 (s, 4H, H^9), 0.07 (s, 62H, H^{11} ,

H^{10}). FTIR (KBr, cm^{-1}): 3446, 3067, 2961, 2926, 2858, 1769, 1713, 1623, 1545, 1504, 1446, 1394, 1361, 1263, 1172, 1086, 1024, 801, 750, 703. T_g : 18°C. Density: 1.04 g/cm^3 .

Synthesis of the epoxy resin

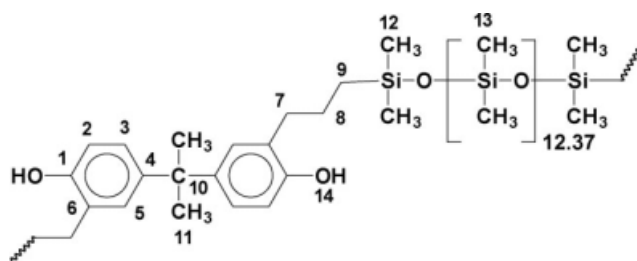
The synthesis scheme for epoxy resin P3 is shown in Figure 2(b). P3 was synthesized through the reaction of HFBPA (1.64 g, 4.88 mmol), DABPA (1.50 g, 4.88 mmol), epichlorohydrin (ECH; 18.02 g, 194.96 mmol), and 0.5 mL of water. The mixture was stirred in a 250-mL, three-necked, round-bottom flask equipped with a magnetic needle and a reflux condenser. The mixture was stirred until a clear solution



FTIR for P3 (KBr, cm^{-1}): 3458, 3077, 3046, 3024, 2962, 1630, 1609, 1505, 1437, 1362, 1328, 1260, 1189, 1172, 1086, 1021, 864, 796, 704. T_g : 15°C. Density: 1.38 g/cm^3 .

Synthesis of the hybrid organic/inorganic polymer

The synthesis of polymer P4 (DP \sim 3) is shown in Figure 2(c). DMS-H11 (average molecular weight = 1050; 2.52 g, 2.40 mmol), DABPA (1.48 g, 4.80 mmol), and 20 mL of toluene were charged into a 100-mL, round-bottom flask equipped with a condenser and a nitrogen inlet. One drop of the Pt-DVTMDS catalyst in xylene was added, and the solution was heated to 100–112°C for 2 h. The solution was treated with activated charcoal to remove the catalyst. Finally, the charcoal was removed by filtration, and the solvent was removed by distillation. The product was further dried at 60°C for 4 h:



$^1\text{H-NMR}$ for P4 (CDCl_3 , 400 MHz, δ , ppm): 6.99 (s, 2H, H^5), 6.91–6.81 (d, 2H, H^3), 6.66–6.64 (d, 2H, H^2), 4.90 (s, 2H, H^{14}), 2.61–2.59 (s, 4H, H^7), 1.63 (s, 10H, H^8 , H^{11}), 0.63–0.61 (s, 4H, H^9), 0.08 (s, 86H, H^{13} , H^{12}). $^{13}\text{C-NMR}$ for P4 (CDCl_3 , 100 MHz, δ ,

was obtained, and 0.234 g of NaOH was added to the clear solution. The temperature of the solution was raised to 95–98°C and kept there for 1 h. After 1 h, the temperature of the mixture was reduced to 90°C, and 1.36 g of NaOH was added in five batches; the stirring was continued for another 4 h. The excess ECH was distilled off *in vacuo*. The residue was extracted with DCM, and the product was dried *in vacuo*. A viscous liquid was obtained (yield = 90%):

ppm): 151.22 (C^1), 143.11 (C^4), 128.55 (C^5), 127.39 (C^6), 125.41 (C^3), 114.56 (C^2), 41.57 (C^{10}), 33.87 (C^{11}), 31.14 (C^7), 23.80 (C^8), 18.06 (C^9), 1.12 (C^{13}), 0.15 (C^{12}).

For FTIR (KBr), the peaks at 3753, 3702, 3615, and 3458 cm^{-1} corresponded to the aromatic hydroxyl group. The disappearance of the Si–H peak at 2127 cm^{-1} indicated no free DMS-H11 in the polymer. The other FTIR spectral bands were found at 3023, 2962, 2871, 2798, 1945, 1701, 1649, 1608, 1503, 1414, 1333, 1260, 1092, 1023, 799, and 702 cm^{-1} . T_g was 11°C, and the density was 1.40 g/cm^3 .

Coating of the sensitive layer

The synthesized polymers were used as coating materials and were deposited onto the surface of the QCM with a drop-coating method. The method was chosen because of its simplicity and the possibility of obtaining uniform films of good quality. A solution of the polymer material with a strength of 1 $\mu\text{g}/\mu\text{L}$ was prepared in DCM. A known amount of the solution was poured with a microsyringe into the center of the electrode while the crystal was kept connected to the oscillator circuit; its output was fed to the counter for frequency measurements. Then, the coated QCM crystals were baked around 70°C for 4 h to obtain a stable film. While the polymer material was loaded onto the crystal surfaces, the static frequency shift was monitored until the desired thickness was reached. Details of the various coated crystals and their static frequency shifts were observed in the range of 4.2–8.4 kHz and are presented in Table II.

TABLE II
Various Coated Crystals and Their Frequency Shifts

Sample number	Crystal (XTL) code	Frequency shift due to the material coating (kHz)	Estimated amount of the coating material (μg)
1	P1	8.425	7.455
2	P2	6.313	5.586
3	P3	4.192	3.708
4	P4	6.868	6.077

Calibration of the coated crystal

The sensor was calibrated with DMMP vapor (molecular weight = 124.08) of a known concentration. A known quantity of DMMP was injected into a clean and dried 1.25-L glass vessel. The bottle was kept at 50°C for thermal equilibrium and then was brought down to the desired temperature (29°C) for experiments. Details for the generated concentrations are listed in Table III. The available vapor concentration inside the vessel (mg/m^3 and ppm) was calculated with knowledge of the volume of the vessel and the mass of DMMP injected with the following relation.

$$\text{ppm} = \text{mg}/\text{m}^3 \times 24.4/\text{Molecular weight}$$

The coated piezoelectric crystal was housed in a test cell (volume = 15 cc) made of Pyrex glass. The crystal along with the cell was used for sensing the chemical vapor. To determine the sensitivity, the crystal along with the cell was placed in the bottle, and the lid of the bottle was closed. The output of the sensor circuit was connected to an online computer with the necessary software. The sensitivity of the sensor (Hz/ppm) was calibrated. Details are given in Table IV for polymers P1 and P2, and the graphical sensing patterns of the polymers are shown in Figure 3(a,b), respectively.

Calibration of the vapor generator

These measurements were carried out to check the performance of the chemical vapor sensor for

TABLE III
Details of the Vapor Concentration Generated in a Closed Vessel

Vessel volume	1250 mL
Amount of DMMP injected	1.0 μL or 1.1 mg (1 μL = 1.1 mg for DMMP)
Vessel temperature	29°C
Amount of vapor generated	0.88 mg/L or 173.5 ppm

TABLE IV
Calibration of the Coated Crystal and Evaluation of Its Normalized Sensitivity with a Closed Vessel

Sample number	Crystal (XTL) code	Static shift (kHz)	Vapor concentration (ppm)	Response (Hz)	Normalized sensitivity (Hz/ppm) ^a
1	P1	8.425	173.5	1984	11.40
2	P2	6.313	173.5	803	4.63

^a Vapor concentration/response.

dynamic sensing. This was carried out through the exposure of the crystal cell to the vapor coming from a dynamic vapor generator, as shown in Figure 1. The piezo response observed on the calibrated crystal was noted from the graphs shown in Figure 4(a,b), and the same was used to calculate the concentration of DMMP vapor coming from the vapor generator. Details of the vapor generator calibration are given in Table V. The study was conducted with two different crystals (coated with different materials), and the average concentration was calculated with the following relation:

$$\text{Vapor concentration (ppm)} = \frac{\text{Response observed/}}{\text{Normalized sensitivity of the crystal}}$$

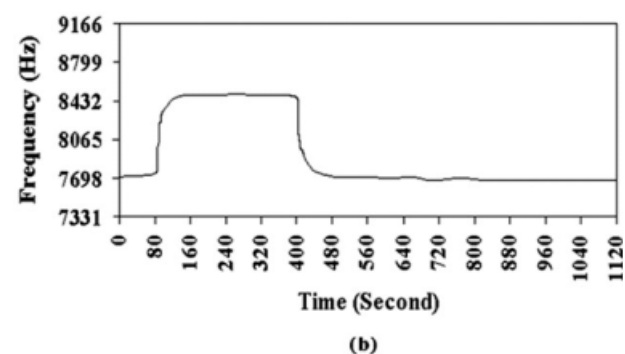
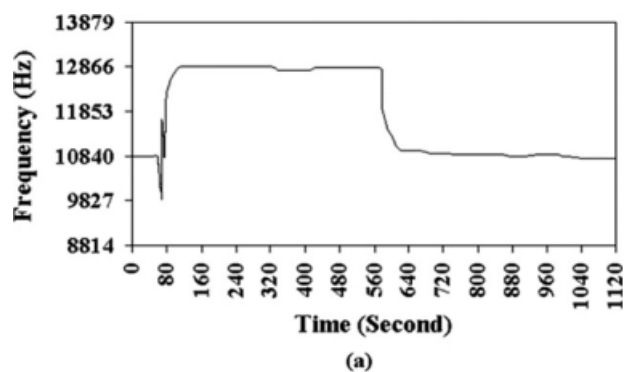


Figure 3 Piezo response of (a) the QCM coated with polymer P1 (8.43 kHz thick) and (b) the QCM coated with polymer P2 (6.31 kHz thick).

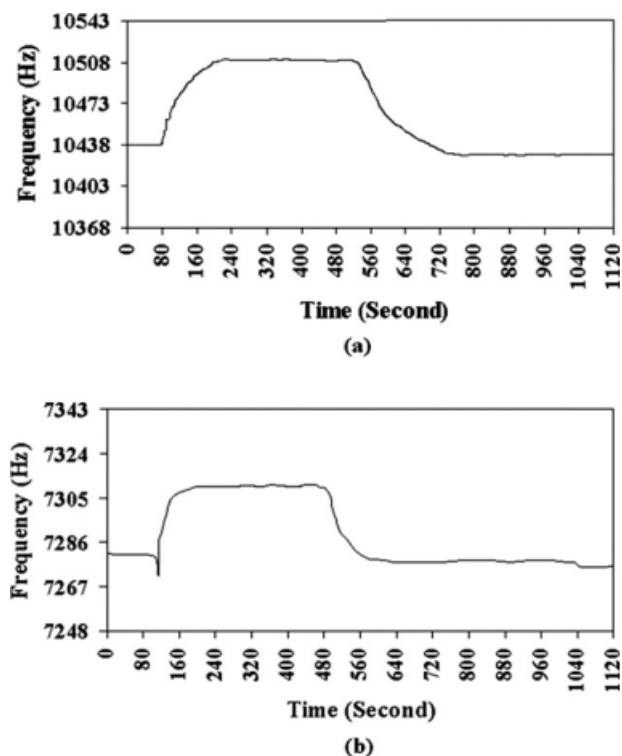


Figure 4 Piezo response observed on the calibrated crystal coated with (a) polymer P1 and (b) polymer P2.

RESULTS AND DISCUSSION

Synthesis of the monomer and polymers

All the monomer and polymers were synthesized with the procedure reported in the Experimental section. FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ data for the monomer and polymers support the chemical structures of the monomer and polymers. The formation of polymer P4 was confirmed by the observation of the disappearance of signals characteristic of the Si—H proton of DMS-H11 ($\delta = 4.72$ ppm). The FTIR spectral data support the different functional groups present in the monomer and also in polymers P1–P4. The absorption bands at 3458 and 1172 cm^{-1} were due to the O—H stretching frequency generated in the polymer-forming reaction and C—F stretching of the trifluoromethyl group, respectively. The polymers were soluble in several organic solvents such as dimethylformamide and dimethyl acetamide, ethyl acetate, tetrahydrofuran, DCM, and chloroform. The high solubility ($>10\%$ w/v) of these polymers in a low-boiling-point solvent allowed efficient coating of the crystal surfaces by these polymers. The physical characteristics of the polymers are given in Table I.

Recording of the sensing cycle for different sensing piezo crystals

The reproducibility of the sensors was checked through the exposure of DMMP (6.3 ppm) to poly-

mer (P1, P2, P3, or P4)-coated QCM sensors several times. The time-dependent frequency shifts were recorded (Fig. 5). For recording the measurement cycle, first the sampling knob of the test cell (Fig. 1) was opened, through which the test chemical vapors came into the cell and were absorbed by the polymer-coated crystals. This resulted in differences in the frequency shifts toward higher values. During all the measurements, the sensors were exposed to DMMP vapor for 1 min, and the resulting frequency shifting was plotted. After each exposure, XL-grade N_2 was purged through the chamber until full desorption was achieved; this generally occurred within 2 min. All the polymers showed high sensitivity toward DMMP with fairly good baseline stability even after several consecutive cycles (Fig. 5). This indicated that the interaction process between the polymer and the adsorbed vapor was a dynamic process. When the polymer-coated QCM crystals were exposed to DMMP vapor, the absorption and desorption processes occurred simultaneously. After dynamic equilibrium was reached, the number of adsorbed gas molecules was equal to the number of desorbed gas molecules, and the frequency attained a stable value. Initially, the frequency increased sharply with time, and this may have been due to the surface adsorption effect of DMMP by the polymer coatings. The later slow increases in frequency were due to the bulk diffusion effect.²⁷ The revival also showed the same trend, a rapid decrease followed by a slower decrease in the frequency, and this can be explained by the dissimilar surface and bulk desorption phenomena.²⁸ The reproducibility was checked, and the results showed a variation of ± 2 Hz for all the QCM sensors. The frequency shift values of QCM sensors coated with different polymers for DMMP vapor at a concentration of 6.3 ppm are tabulated in Table VI.

Sensing study

Acoustic wave devices (viz., QCM or surface acoustic wave devices) represent the most fundamental sorption-based sensors when they act as pure

TABLE V
Calibration of the Vapor from a Dynamic Vapor Generator Using a Calibrated Sensor (Coated Crystal)

Crystal (XTL) code	Normalized response Crystal (XTL) (Hz/ppm)	Response of the crystal with the vapor generator (Hz)	Vapor-generator concentration (ppm) ^a
P1	11.40	70	6.14
P2	4.63	30	6.47

^a Normalized response of Crystal (XTL)/response of the crystal with the vapor generator.

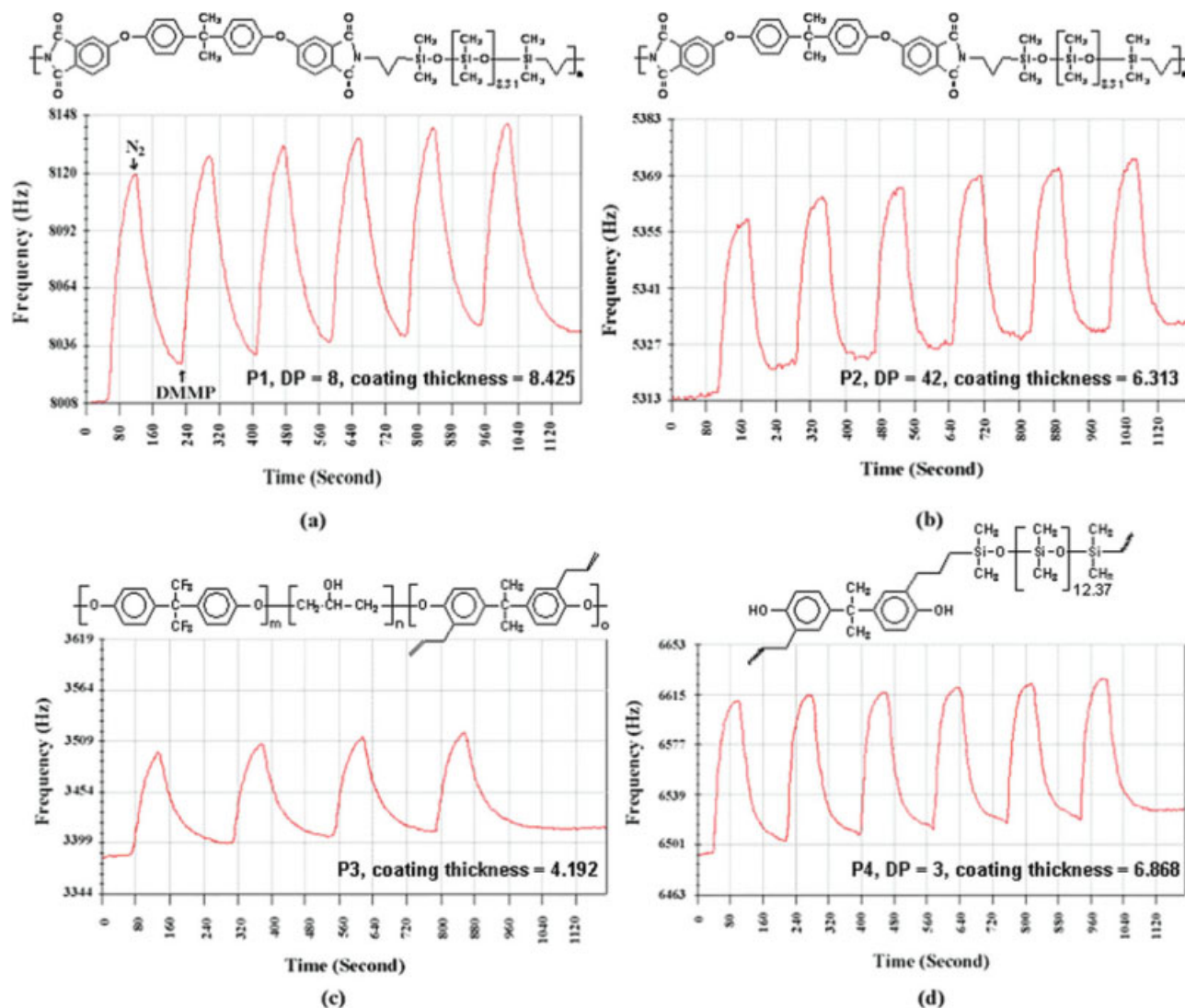


Figure 5 Piezo response of the sensor coated with different polymers: (a) P1 (8.42 kHz), (b) P2 (6.31 kHz), (c) P3 (4.19 kHz), and (d) P4 (6.87 kHz). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

gravimetric devices. These types of sensors detect the amount of vapor sorbed as a function of mass, and the response is not dependent on any analyte property other than those that influence sorption.²⁹ The sensitivity and selectivity of QCM sensors can be manipulated with suitable coatings on the crystal surfaces. Typically for a polymer coating, the sensor performance depends on the viscoelasticity, hydro-

phobicity, and polarity of the polymers employed.^{29–31} A QCM device coated with different polymers (P1–P4) was tested for DMMP vapor with nitrogen as the carrier gas. The amounts of the polymer coatings and the resultant frequency drifts of the QCM crystals are given in Table II. In general, all the polymers (P1–P4) showed high sensitivity to DMMP vapor. This was attributed to the donor–

TABLE VI
Initial Measurement of the Sensor Response Using Crystals Coated with Different Coating Materials

Material code	Frequency of coated Crystal (XTL) (kHz)	Estimated vapor-generator concentration (ppm)	Response from graphs (Hz)	Normalized response (Hz/kHz)	Response time (s)	Recovery time (s)
P1	8.425	6.30	95	11.3	60	120
P2	6.313	6.30	43	6.80	60	120
P3	4.192	6.30	100	23.80	60	120
P4	6.868	6.30	82	11.93	60	120

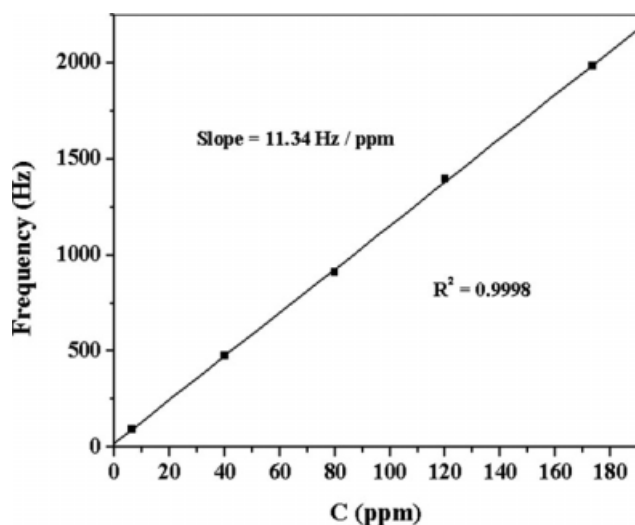


Figure 6 Response of the P1-coated QCM sensor to DMMP vapor at different concentrations.

acceptor interaction of the hydrogen-bonded donor polymers (P1–P4) with hydrogen-bond acceptor DMMP vapor.³² Polymers P1 and P2 were also tested for different DMMP concentrations. The responses were plotted against the concentration to check the linearity of the sensor against the vapor concentration. A representative plot with P1 as the coating polymer is shown in Figure 6. With an increase in the DMMP concentration, the shifting of the frequency increased. The regression coefficient (R^2) was greater than 0.9998, and this indicated that the frequency shifts of the sensors were linear to the vapor concentrations. The sensitivity of the sensors was as high as 11.34 Hz/ppm, in contrast to the previously reported sensitivity of poly(vinylidene fluoride) (3.19 Hz/ppm).³⁰ P1 showed higher sensitivity to DMMP than P2. P1 was a low-molecular-weight product (Table I) in comparison with P2. As a result, P1 was expected to have a higher number of terminal $-\text{COOH}$ groups (hydrogen-bond donors), and that resulted in more interactions with hydrogen-bond acceptor DMMP. The lower T_g value of P1 in contrast to P2 also facilitated the diffusion of DMMP vapor. P3, having trifluoromethyl groups, hydroxyl groups, and allylic double bonds, showed the highest frequency shift in the series (23.8 Hz/kHz) at a DMMP vapor concentration of 6.3 ppm. The very high sensitivity of this polymer was attributed to the presence of different types of electron-withdrawing groups and a relatively low T_g value (15°C). The electron-withdrawing trifluoromethyl groups possibly made this polymer more acidic in nature, and the polymer acted as a strong hydrogen-bond donor to DMMP through the hydroxyl groups.³² This type of observation was also made for a previously reported flu-

oro-epoxy prepolymer.³¹ P4 (DP \sim 3) showed a normalized DMMP sensitivity of approximately 12 Hz. The sensing mechanism was the same; the hydrogen-bond acceptor DMMP was absorbed by the acidic hydrogen-bond donor polymer (Ar–OH).³¹ The absence of any strong electron-withdrawing groups in this polymer could not influence the donor ability of the aromatic hydroxyl group, and hence the resulting drift in frequency was not prominent like that for P3. To check the hydrogen-bonding capability of Ar–OH groups, it was made with a higher DP (DP \sim 8) by a reduction of the stoichiometric imbalance between DABPA and DMS-H11 in the feed. The resulting polymer showed that the drift in frequency was 10 Hz/kHz in contrast to 12 Hz/kHz. This lowering of the drift in frequency of P4 with DP \sim 8 was attributed to the presence of fewer unreacted Ar–OH groups per unit of polymer mass in contrast to P4 with DP \sim 3. This observation was similar to the observation reported by Grate et al.²⁵ The polymers were superior in sensitivity to DMMP vapor in comparison with many reported polymers, such as poly(ethylene maleate), polyvinylpyrrolidone, acrylonitrile butadiene copolymer, polyamidoxime, polyepichlorohydrin, abietic acid, OV210, polyisoprene, and polyphosphazines.³²

The sensing elements, as indicated previously, were periodically tested at a fixed concentration of 6.3 ppm for an extended period of time (250 days). The response cycles were recorded as mentioned earlier, and the results are tabulated in Table VII. P1, P2, and P4 showed fairly good sensing stability (Fig. 7) for an extended time period of 250 days. P3 initially showed very high sensitivity toward DMMP, with a catastrophic fall within 50 days, and then showed a fairly stabilized sensor response. This could be due to the permanent interaction of DMMP with this strongly hydrogen-bond donor material, which reduced the efficiency of the coating material.

TABLE VII
Measurement of the Sensor Response for an Extended Period Using Crystals Coated with Different Materials

Material response (Hz)					Normal response (Hz)			
P1	P2	P3	P4	Test date	P1	P2	P3	P4
95	43	100	82	09/25/07	11.28	6.81	23.80	11.95
94	37	84	72	10/08/07	11.16	5.86	20.21	10.49
80	34	61	64	11/02/07	9.50	5.54	14.50	9.32
77	33	56	62	11/28/07	9.14	5.38	13.57	9.10
75	32	47	62	12/07/07	8.98	5.12	11.42	9.05
62	30	42	60	02/07/08	7.36	4.91	10.11	8.75
60	27	39	57	03/17/08	7.24	4.46	9.27	8.30
59	27	35	55	04/17/08	7.12	4.38	8.15	8.01
58	26	30	53	05/07/08	6.96	4.27	7.14	7.72
57	26	20	51	06/03/08	6.80	4.25	4.76	7.42

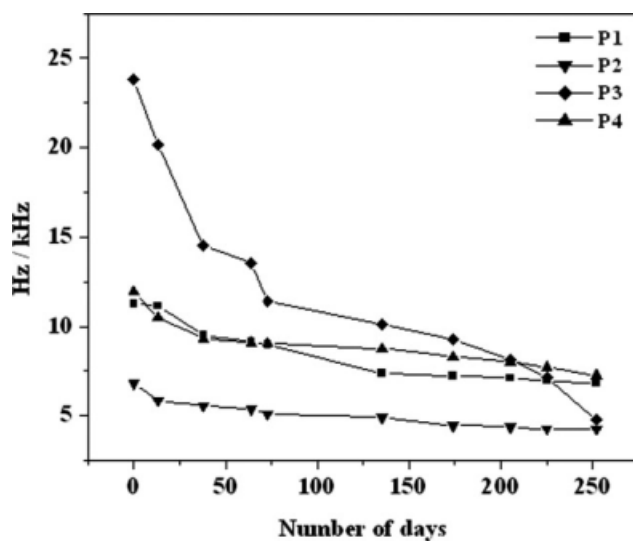


Figure 7 Sensing results for an extended period of time (250 days).

However, this needs further investigation. In this series, P4 showed the best performance with respect to sensing stability for 250 days.

CONCLUSIONS

Four new polymers (P1–P4), coated onto QCM sensors for the detection of the vapor of a nerve agent simulant (DMMP), were investigated. The sensors were thoroughly examined for their sensitivity toward DMMP vapor. A fast response, good sensitivity, and reproducibility were realized. Among the four polymers, P4 showed the best sensing stability for an extended time period of 250 days. Polymer P3, however, showed higher initial sensitivity, but gradually reduced sensitivity was found with time. This preliminary investigation indicates that these polymers are better candidate as coating materials in QCM-based sensors for sensing DMMP than many other previously reported polymers in the field.

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