A new polysiloxane coating on QCM sensor for DMMP vapor detection

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Abstract A new material-poly{methyl [3-(2-hydroxyl, 4,6-bistrifluoromethyl)phenyl]propylsiloxane} (PMTFMPS), which was sensitive to toxic organophosphate vapor, was synthesized via *O*-alkylation, claisen rearrange reaction and hydrosilylation reaction. The polymer was coated on quartz crystal microbalance (QCM) to investigate its gas sensitive properties to nerve agents' simulant dimethyl methylphosphonate (DMMP) vapor, as well as other interfering vapors. It was found that QCM sensor responded linearly to DMMP vapor with a slope of 27 Hz/ppm in the 10–50 ppm range. The material was much more sensitive to DMMP than to other interfering vapors, thus high selectivity to DMMP was demonstrated. The influence of humidity on the sensor response was also examined. The results showed that the frequency shifts were about 60% when tested in 77% RH wet air than in dry N_2. When compared with our previously studied unfluorinated phenol-modified siloxane PMPS, PMTFMPS exhibited sensitivity enhancement of 2.3 times and an increased resistance to humidity variations.

Introduction

Nerve agents are among the most potent of chemical warfare agents. The intentional use of chemical agents for war and terrorism has created an imperative for the development of an early warning system. Such a system should be portable, field-deployable, robust, and inexpensive. It should yield fast and sensitive identification of an unknown sample on location, and it should function autonomously. Up to now, a wide variety of chemical sensors which are suitable for field analysis are under investigation, including electrochemical sensors [1, 2], semiconductor sensors [3, 4], quartz crystal microbalances (QCM) [5, 6], surface acoustic wave (SAW) sensors [7, 8], optical-fiber sensors [9, 10], microelectromechanical systems [11–13], fluorescent sensor [14–16], microcapacitors [17, 18], and so on. Among them, SAW and QCM sensors have generated considerable interest due to their high sensitivity, simplicity, and ease of use.

A typical configuration for a chemical sensor includes a sorbent coating deposited on the active area of a transducer. The role of the sorbent coating is to interact with the target analyte, and the resultant physical change in the coating is transduced into an electrical signal for ease of recording or display. Thus, the sorbent coating is of critical importance to enhance the sensitivity and selectivity of a chemical sensor. A large number of sorbent materials [19], especially polymers, have been investigated as sensing coatings as well as preconcentration layers for nerve agents' detection. Among them, the hydrogen-bond acidic (HBA) polymers have been paid much attention. The HBA polymers can interact with the strongly hydrogen-bond (HB) basic organophosphorus compounds by hydrogen bonding. These interactions promote sorption of the vapors into the polymer film, which increase the sensor response. Therefore, it is mandatory for HBA polymer to have maximum HB acidity and minimum HB basicity, namely, the highest ratio (*a*/*b*) of HB acidity to HB basicity [20, 21]. To increase the HB acidity of the polymers, fluorinated alcohols or phenols have been incorporated into the linear or hyperbranched polymer backbones [22–28]. Recently, a

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polysiloxane functionalized with phenol, dubbed PMPS, was demonstrated by us [29] to be well sensitive to dimethyl methylphosphonate (DMMP). However, phenol is unfluorinated and its HB acidity and basicity are 0.60 and 0.30, respectively, resulting *a/b* ratio of only 2. As a comparison, the *a/b* ratio of hexafluoroisopropanol, the most widely applied HBA functional group, is 7.7, much larger than that of phenol.

In this study, a fluorinated phenol, 3,5-bistrifluoromethyl-phenol, was used as the functional group and incorporated into a polysiloxane for DMMP detection. The resultant polymer was poly{methyl [3-(2-hydroxyl, 4,6-bistrifluoromethyl) phenyl] propylsiloxane} (PMTFMPS). Although the HB acidity/basicity of 3,5-bistrifluoromethylphenol was not documented to our knowledge, it is expected, when comparing it with other halogen substituted phenols (see Table 1), to have excellent HBA properties. Thus, PMTFMPS should be a promising sensitive material for nerve agent detection. PMTFMPS was synthesized via *O*-alkylation, claisen

rearrange reaction, and hydrosilyation reaction using 3,5-bistrifluoromethylphenol, allyl bromide, and polymethylhydrosiloxane as raw materials. This polymer was then coated on a QCM sensor to investigate its gas sensitive properties to DMMP vapor as well as some common interfering vapors. The test result was compared with our previous PMPS-coated QCM sensor.

Experimental

Reagents and devices

3,5-Bistrifluoromethylphenol (97%) was obtained from Meryer Chemical (China); platinum-1,3-divinyltetramethyldisiloxane (99%); and DMMP (97%) were purchased from Alfa Asar and Aldrich, respectively; polymethylhydrosiloxane was purchased from Sihai Chemical (China); toluene, dichloroethane, chloroform, anhydrous potassium carbonate, and sodium hydroxide were of analytical reagent grade, obtained from Kelong (China). All of the chemicals and solvents were used directly without further purification. AT-cut 8 MHz quartz crystals with Ag electrodes of 4 mm diameter on both sides were purchased from Benyue Technology Ltd., China.

HBA polymer synthesis and characterization

The molecular structure and synthetic route of PMTFMPS is shown in Fig. 1.

Table 1 LSER coefficients for HBA molecules [20, 31, 32]

Molecule	Acidity	Basicity	*a/b*
Phenol	0.60	0.30	2
3-Fluorophenol	0.68	0.17	4
3-Chlorophenol	0.69	0.15	4.6
3-Trifluoromethylphenol	0.72	0.09	8
3,5-Dichlorophenol	0.83	0	NA

Fig. 1 The molecular structure and synthetic route of the HBA polymer
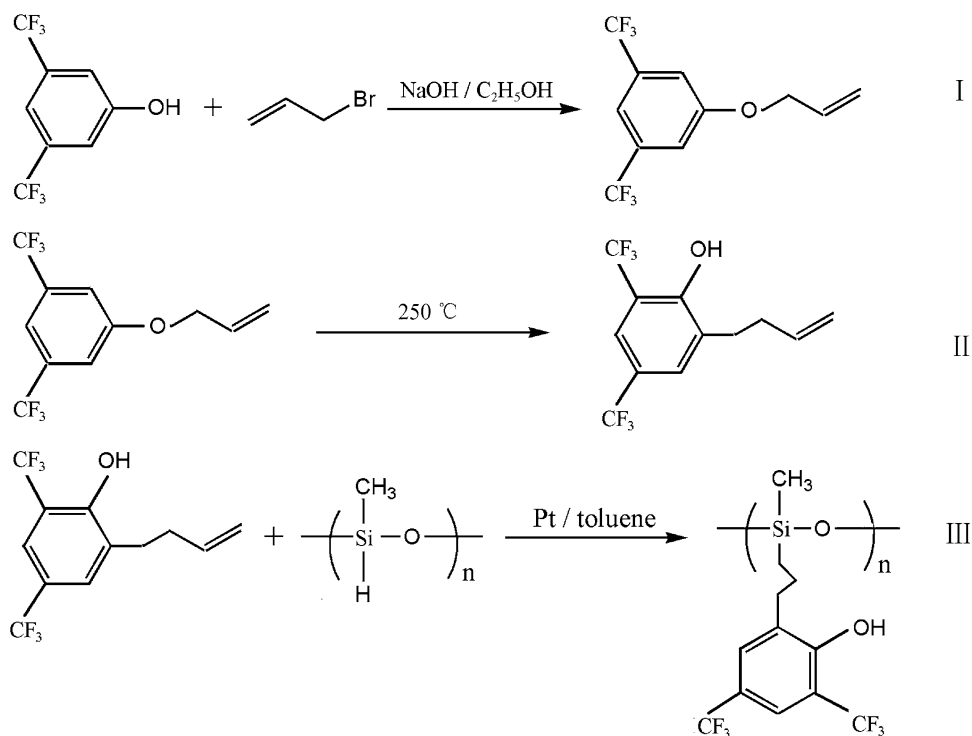
One equivalent of 3,5-bistrifluoromethylphenol was reacted with one equivalent of ally bromide in presence of alcohol and sodium hydroxide at about 65 °C, and the product (I) of this reaction was heated to 250 °C for 24 h, undergoing a Claisen rearrangement. Then intermediate product (II) was reacted with polymethylhydrosiloxane with toluene as solvent, platinum-1,3-divinyltetramethyldisiloxane as catalyst at 100 °C for 6 h to yield the target product (III).

The target polymer as well as the intermediate products was characterized by FT-IR (MX-1E, NICOLET) and ^{1}H-NMR (AVANCE 300, BRUKER). The ^{1}H-NMR of PMTFMPS (300 MHz, CDCl$_3$, TMS): δ (ppm) 7.53–7.45 (t, 4H, Ar–H), 7.32–7.28 (d, 5H, Ar–H), 5.22–5.13 (m, 5H, ArO–H), 2.15–1.62 (m, 5H, ArC–H), 1.35–1.21 (m, 4H, CH$_2$CH–H), 0.97–0.89 (m, 2H, SiCH–H). The FT-IR spectra of PMTFMPS (KBr): ν (cm^{-1}) 3617 (free OH), 3438 (HB OH), 2960, 2878 (CH$_2$), 1681, 1612, 1462, 1438 (aromatic C=C), 1681 (aromatic C–H), 1373, 1317 (phenolic C–O), 1275, 1229 (CF$_3$), 1128 (Si–O–Si), 1170, 1034, 1001, 978, 941 (benzene ring = C–H), as shown in Fig. 2. The stretching vibration of Si–H at 2280–2080 cm^{-1} is not observed, indicating complete conversion of poly(methylhydrosiloxane) into PMTFMPS is occurred. It is also confirmed by ^{1}H-NMR by observing the disappearance of signals characteristic to the Si–H proton of poly(methylhydrosiloxane) (δ: 4.7 ppm) and the allylic group of protons from the intermediate product (II).

DMMP vapor test

The synthesized polymers were dissolved in chloroform, and subsequently drop-coated on a QCM by a microsyringe. The thickness of the films was determined to be about 250 nm by the Sauerbrey equation. The vapor exposure tests were carried out in a homemade cell as shown previously [30], and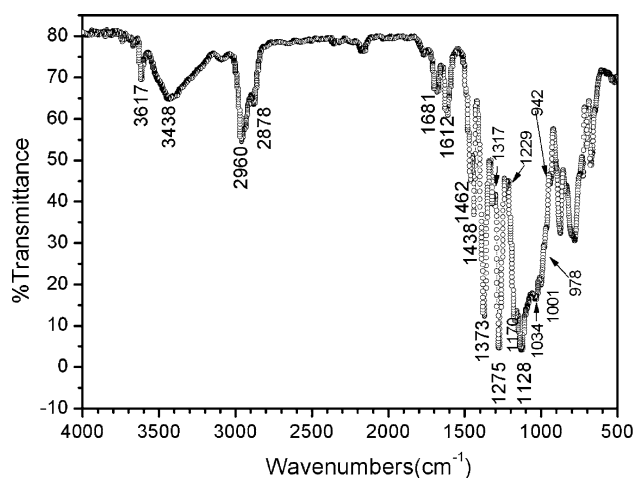 herein described briefly. The DMMP vapor was generated by a static dilution method, using a syringe to extract the saturated vapor from the headspace above the liquid solvent in a closed container and then injected into an airtight test chamber. After each vapor exposure, the test chamber was thoroughly flushed by N$_2$. All the vapor tests were performed at room temperature of about 20 °C.

Result and discussion

Sensitivity to DMMP vapor

After the deposition of PMTFMPS film on QCM, the resonant frequencies of the sensor were measured. The real-time response of the sensor to DMMP vapor ranging from 10 to 50 ppm is shown in Fig. 3. When the DMMP vapor was injected into the chamber, the frequency changed immediately with the absorption of the vapor. Equilibrium was reached after several tens of seconds. The response time, defining as the time interval between the gas on and the frequency shift Δf reaches to 80% maximum, was about 60–80 s. When the test chamber was purged with N$_2$, desorption process took place and the frequency of the PMTFMPS-coated QCM sensor can return to the original value after a longer time with desorption time around 170 s. Thus, the sensor exhibited fairly fast response and negligible baseline drift.

To investigate the sensitivity of the QCM sensor, the frequency shifts (Δf) are plotted against the vapor concentrations (C) as shown in Fig. 4. It can be seen that the frequency shifts of the sensor were linear to the DMMP vapor concentrations in the range of 10–50 ppm. The linear fitting curve can be expressed as $\Delta f = 47.1 + 27.01C$ with a correlation coefficient $R^2 = 0.992$. Thus, according to the slope of regression curve, the sensitivity of the sensor was nearly 27 Hz/ppm.
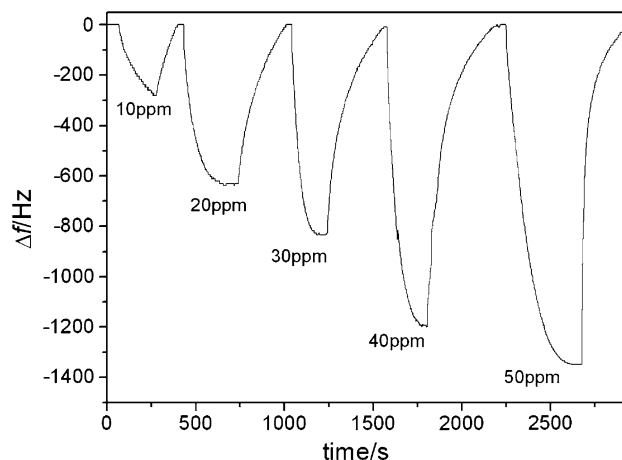
Fig. 2 The FT-IR spectra of PMTFMPS

Fig. 3 The response curve of PMTFMPS-coated QCM sensor to different concentrations of DMMP
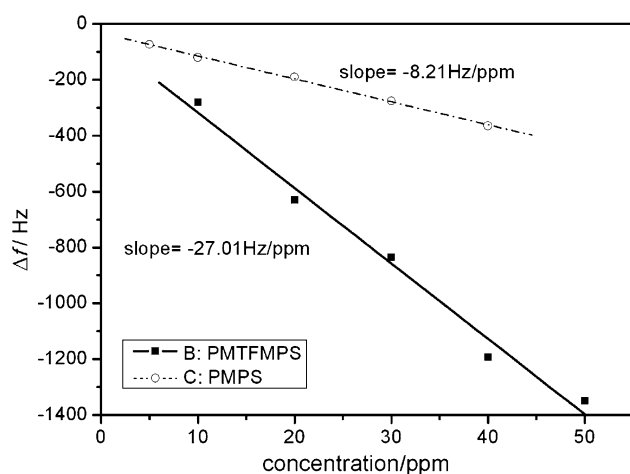
Fig. 4 The frequency shifts of polymer-coated QCM sensors against the concentrations of DMMP

The responses of polymer-coated QCM sensors to vapor sorption can arise from both gravimetric and viscoelastic changes in the polymer coating film, depending on the high-frequency polymer shear modulus and on the acoustic thickness of the polymer film prior to, and during, vapor exposure. For acoustic wave devices with acoustically thin polymer coatings, the calibration curve should yield a straight line in the low concentration range, where Henry's law holds. At higher concentrations, positive deviations from Henry's law are expected. The linear ranges differ among the vapor/sensor pairs [33]. The PMTFMPS-coated QCM sensor studied in this article showed linear behavior in the test range, indicating that the sensor response arise entirely from gravimetric effect.

The limit of detection (LOD) of the QCM sensor was calculated by the measured sensor sensitivity (Hz/ppm). The noise level of the PMTFMPS-coated QCM sensor was about 1 Hz, by taking into account the signal-to-noise ratio of 3:1, the theoretical LOD of the sensor was as low as 0.11 ppm.

Sensitivity comparison to PMPS

To compare the sensitivity of the PMTFMPS with that of the PMPS, PMPS was coated on the 8 MHz QCM with approximately the same thickness and then tested in the 5–40 ppm range of DMMP. The real-time curves (data not shown) exhibited fast response and good reversibility. But a small baseline drift was also observed. The calibration curve of PMPS is shown in Fig. 4 as well, presenting a straight line with a slope of −8.21 Hz/ppm. Hence, the sensitivity of PMTFMPS is about 2.29 times higher than that of PMPS. The result is in good agreement with what we expected. The enhanced sensitivity can be attributed to the increased HB acidity of the polymer, indicating that the

3,5-bistrifluoromethylphenol is much more HB acidic than the unfluorinated phenol.

Sensitivity to interfering vapor

The PMTFMPS-coated QCM sensor was also tested against several conventional volatile organic vapors (VOCs), including acetone, ethanol, dichloroethane, n-hexane, and toluene. Each organic vapor, which may act as potential interferences, was at 30% saturated concentration produced by the same injection method at room temperature. It can be seen from Fig. 5 that the QCM sensor responses much more slowly to the interferences than to DMMP. The response times of the sensor to ethanol, n-hexane, and toluene were about 200 s. While the resonant frequency of the QCM sensor exposed to acetone could not reach an equilibrium state at this time interval, indicating an even larger response time. The sensitivities of the sensor to VOCs than to DMMP, as shown in the inset of Fig. 5, are less than 0.1. Therefore, the sensitivity to DMMP was absolutely greater than to the interferences. Good selectivity of the sensor was achieved.

Influence of relative humidity

To investigate the influence of humidity on the sensor response, the DMMP vapor exposure test was also conducted at a moist environment. The relative humidity of 77% was produced in the test chamber by water vapor injection and monitored by a humidity sensor (Honeywell HIH 3610). As shown in Fig. 6, the sensitivities of the sensor damp about 40% in RH77% wet air than in dry N_2. It indicates that the humidity has a remarkable effect on the sensor stability. In our previous study, the PMPS-coated SAW sensor attenuated about half at 70% relative humidity [29]. Therefore, the newly synthesized polymer PMTFMPS had enhanced humidity resistance than PMPS.
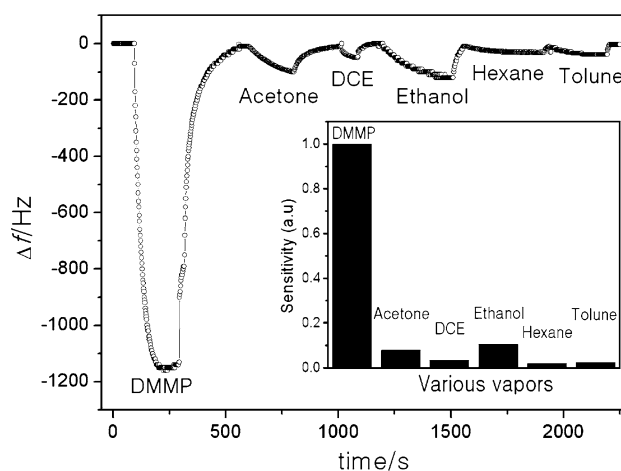

Fig. 5 Responses of the QCM sensor to interferences at 30% saturated vapor concentrations
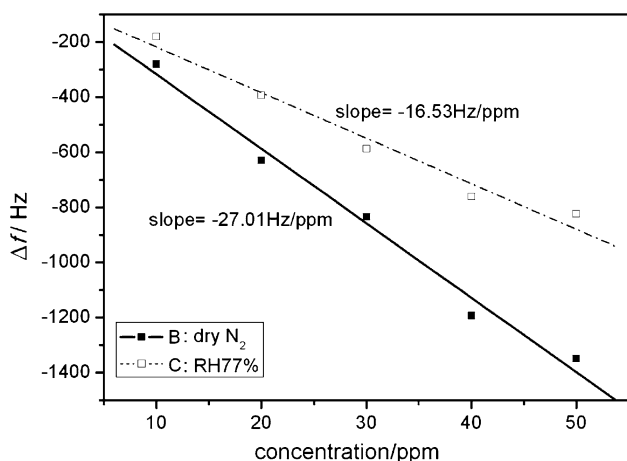
Fig. 6 Comparison of the sensor responses to DMMP at dry N_2 and RH77% atmosphere

Conclusions

PMTFMPS, a new HBA polymer for organophosphonate vapor detection, was synthesized. It was a linear polysiloxane polymer functionalized with 3,5-bistrifluoromethylphenol group. The sensitive characteristic of the polymer was tested under DMMP vapor in the 10–50 ppm range, as well as some conventional VOCs by a QCM sensor platform. High sensitivity, fast response, and good selectivity of the sensor were demonstrated. When compared with our previously studied polymer PMPS, also a linear polysiloxane but modified with unfluorinated phenol, the PMTFMPS-coated sensor responded 2.3 times higher than its PMPS counterpart. The PMTFMPS also showed a better resistance to humidity variations than to PMPS. Thus, PMTFMPS is a very promising polymer for nerve agents' detection.

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