Hydrogen-Bond Acidic Polyhedral Oligosilsesquioxane Filled Polymer Coatings for Surface Acoustic Wave Sensors

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ABSTRACT: A series of novel polyhedral oligosilsesquioxane nanofiller compounds functionalized with hydrogen-bond acidic sensor groups was prepared, characterized by IR, ^{1}H-, ^{13}C- and ^{29}Si-NMR, and MALDI-TOF MS, and formulated into polymer coatings for 500 MHz surface acoustic wave sensor platforms. Sensor responses to the explosives simulant dinitrotoluene and to the nerve agent simulant dimethyl methylphosphonate were studied, and the performances of the polyhedral oligosilsesquioxane formulations were compared with those of conventional hydrogen-bond acidic linear surface acoustic wave sensor polymers carrying the same sensor groups. The polyhedral oligosilsesquioxane formulations gave good initial responses to the simulants, maintained 40–65% of their original response over a period of 6 months and maintained their sensitivity down to a simulant vapor concentration of 1 ppb v. The surface compositions of the surface acoustic wave sensor coatings were characterized by sum frequency generation spectroscopy. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3171–3182, 2007

Key words: sensors; fillers; coatings

INTRODUCTION

In order for array-based gravimetric chemical vapor sensors such as surface acoustic wave (SAW) sensors to collect the most chemical information, each element in the array needs to be coated with a different polymer.[1,2] The collection of polymers must cover the full range of solubility interactions (dispersion, dipole–dipole, and hydrogen-bonding), and needs to include nonpolar, polarizable, dipolar, hydrogen-bond basic, and hydrogen-bond acidic polymers.[3–7] Most polymers exhibiting these types of interactions are commercially available, except for the key class of hydrogen-bond acidic polymers, which are essential for the detection of hydrogen-bond basic entities, such as nerve agents[8–15] (Fig. 1) and nitroaromatic explosives in security and defense applications.[15–20] Hydrogen-bond acidity may be introduced into a polymer by functionalizing it with phenol or fluorinated alcohol groups[4,7,13–15,19,21–25] (Fig. 2). Because these groups have high polarity, they increase the glass transition temperature (T_g) and lower the rate of vapor diffusion to an undesirable level. Hence silicon-oxygen bonds or silicon-carbon bonds are introduced into the polymer backbone to lower T_g.[4,15,16,18,19,22,23]

The use of linear polymers, such as BSP3,[2] SXFA,[4] PSpFA,[13,14] NRL5,[15] and FPOL[10,26] (Fig. 2) as coatings for SAW sensors is well established, and dendritic hydrogen-bond acidic SAW polymers with good initial sensitivity to the nerve agent simulant dimethyl methylphosphonate (DMMP, Fig. 1) have also been reported.[27–29] In addition to carrying the desired hydrogen-bond acidic sensor groups and having good initial sensitivity to species such as DMMP and nitroaromatics, hydrogen-bond acidic SAW sensor polymers must be robust enough to withstand multiple vapor challenges and maintain their sensitivity over time.[29–31] Since the linear and hyperbranched hydrogen-bond acidic polymers discussed earlier have low T_gs and tend to be fluids at room temperature, it is difficult to attain a combination of good sensor properties and robust coating properties in a single polymeric material, although some attempt has been made to address this issue by crosslinking polysiloxane SAW coatings.[31] In this study, robust nanocomposite SAW coatings that maintain a good response over time[32] when airbrushed onto 500 MHz SAW platforms were prepared by dispersing polyhedral oligosilsesquioxanes (POSS) carrying hydrogen-bond acidic sensor groups within a nonsensing polycarbosilane carrier, and also within linear hydrogen-bond acidic polymer

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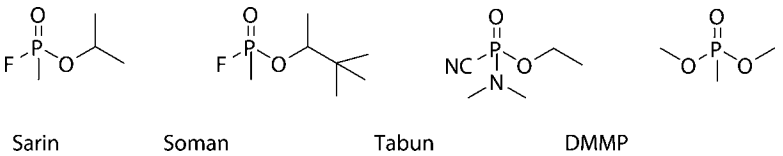


Figure 1 Examples of nerve agents and nerve agent simulant dimethyl methylphosphonate (DMMP).

carriers (Fig. 2), and the responses of these SAW coatings to the explosives simulant dinitrotoluene (DNT) and to the nerve agent simulant dimethyl methylphosphonate (DMMP) were measured.

POSS are stoichiometrically well-defined cage compounds that are prepared by the hydrolysis and condensation of trifunctional silanes of the form $RSiX_3$.[33,34] The condensation reactions can generate products ranging from small molecules, oligomers, and clusters to resins of highly complex structure, and the products obtained are highly dependent upon silane and water concentration, pH, temperature, solubility, and catalyst.[35] The nanoscopic polyhedral oligosilsesquioxanes used in this study are fully condensed compounds of the form $R_8Si_8O_{12}$ with a distance of 1.5 nm between R groups on adjacent corners of the POSS cage. They were selected because they are of a precisely defined size, they are commercially available with a variety of functional groups, and they have been used in an extremely wide range of syntheses and applications in the last few years including the modification and enhancement of the physical properties of polymeric materials.[36,37]

Here we describe the preparation and characterization of five new POSS compounds functionalized with hydrogen-bond acidic sensor groups, their formulation into polymeric SAW sensor coatings, their SAW sensor responses to the explosives simulant DNT, and to the nerve agent simulant DMMP, and the surface characterization of the coatings by sum frequency generation (SFG) spectroscopy.

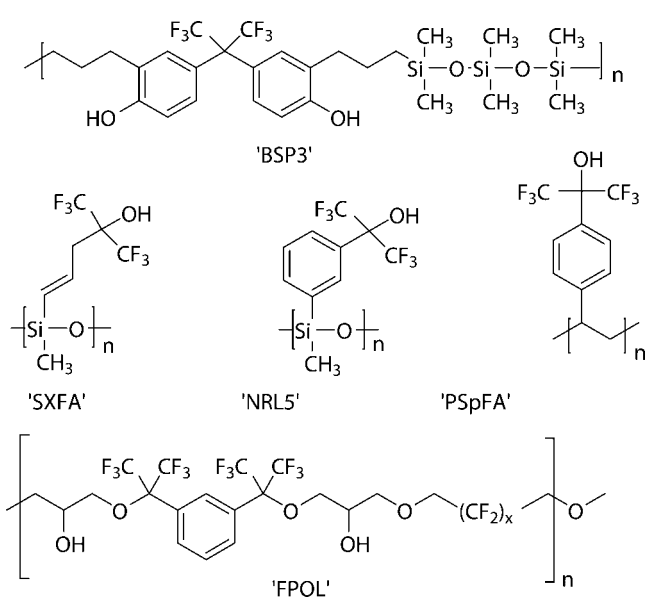


Figure 2 Examples of hydrogen-bond acidic linear polymers used in SAW sensors.

EXPERIMENTAL

Materials and apparatus

Reagents and solvents were purchased from Sigma-Aldrich, (Milwaukee, WI), Gelest, (Tullytown, PA), and Synquest (Alachua, FL), and they are used without further purification. POSS reagents were obtained from Hybrid Plastics (Fountain Valley, CA). High pressure experiments were carried out in a 300-mL stainless steel glass-lined Parr® bomb reactor fitted with a 600 psi Fike Metal Products relief valve, Ashcroft Duralife pressure gauge, Parr 4835 temperature controller, and appropriate safety shields. The reactor was connected to a 100-g hexafluoroacetone lecture bottle (Aldrich) using stainless steel Swagelok fittings and valves, and excess hexafluoroacetone was destroyed by bubbling through a solution of sodium borohydride in trimethylene glycol dimethylether (triglyme). Flash column chromatography was carried out using a column packed with silica gel (Davisil, grade 633, 200–425 mesh, 60Å, 99+%), and various fractions were monitored by thin layer chromatography using ME Science aluminum-backed silica gel 60 F-254 TLC plates. Vapor tubes were purchased from VICI Metronics (Poulsbo, WA).

SAW sensors

Surface acoustic wave (SAW, 500 MHz) sensor units were obtained from Sawtech (TriQuint Semiconductor, Hillsboro, OR) and epoxy-mounted onto 15 mm × 10 mm six-pin headers attached to gold leads. SAW responses were measured using a Femtometrics Individual Vapor Detector (IVD) containing a beat frequency reference SAW, an uncoated thermal reference SAW, and ports for six additional SAWs. The IVD was used in conjunction with an Agilent ADM2000 flowmeter, a VICI Dynacalibrator Model 340 vapor generator with a six-port automated valve attached to an HP 6024A DC power supply, and a laptop computer with a RS232 port connection. A more detailed account of the procedures for the solvent and plasma cleaning of SAW surfaces, the

airbrush application of coating solutions to SAW surfaces, the generation of vapors, and the measurement of SAW responses to vapors appears in an earlier publication.[29] SAW responses are quoted as positive difference frequencies relative to the reference SAW.

Characterization procedures

^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded on a Varian Unity 300 MHz NMR spectrometer equipped with a 5-mm four nuclei probe. Solvent signals were used as internal standards, and chemical shifts are reported relative to tetramethylsilane (TMS). IR spectra were recorded on a Nicolet 20DXB FTIR spectrometer, and the samples were prepared for analysis by solution casting onto potassium bromide discs. MALDI-TOF mass spectra were recorded using a Vision 2000 mass spectrometer from Thermobioanalysis. Samples were prepared by dissolving materials of interest in THF at 10 mg/mL and then mixing the solutions in a ratio of 1 : 10 with a 10 mg/mL solution of 2,4,6-trihydroxyacetophenone monohydrate (TAM) or dihydroxybenzoic acid (DHB) matrix material. The mixtures were spotted on the MALDI-TOF MS source target and allowed to air dry prior to analysis. Differential scanning calorimetry (DSC) measurements were performed using a DuPont Instruments Model 912 unit. Size exclusion chromatography (SEC) was carried out using a Waters 510 pump, a Waters 717 auto-injector, a Waters CHM column heater, two Polymer Laboratory PLgel columns, and a Polymer Laboratory PL-ELS 1000 evaporative light scattering detector (ELSD). Detector conditions appropriate to the eluting solvent were used, and the column was calibrated with Dow 1683 polystyrene standards. Sum frequency generation (SFG) studies were carried out by the Polymer Technology Group, Berkeley, CA. Different laser polarization modes were used (ssp, ppp, sps) to differentiate symmetric and asymmetric vibrational modes. Materials were spin-coated onto quartz substrates (three drops of material, 6000 rpm, 1 min) and scanned from 2800 to 3800 cm^{-1} to study methyl and hydroxyl bands.

Poly(methylphenylsilylhexane-1,6-diyl)(1)

A 25-mL one-necked round-bottomed flask was equipped with a Teflon coated magnetic stirrer bar and a condenser with a nitrogen inlet at its top. The flask was charged with 1.647 g methylphenylsilane (13.4 mmol), 1.107 g 1,6-hexadiene (13.4 mmol), 10-mL toluene, and one drop of platinum divinyltetramethyldisiloxane complex in xylene. The mixture was stirred at room temperature for 5 days and then stirred with activated charcoal at room temperature for an additional 24 h. The charcoal residue was removed by gravity filtration and the toluene was evaporated to give the polymeric product as an oil in quantitative yield. ^{1}H-NMR ($CDCl_3$) : δ (ppm) 0.23 (s, SiCH_3), 0.73 (m, SiCH_2), 1.27–1.35 (2m, SiCH_2CH_2, Si$(CH_2)_2CH_2$), 7.34 (m, Ar*H*), 7.48 (m, Ar*H*). ^{13}C-NMR ($CDCl_3$): δ (ppm) −5.1 (SiCH_3), 14.1 (SiCH_2), 23.7 (SiCH_2CH_2), 33.2 (Si$(CH_2)_2CH_2$), 127.6 (Ar*C*), 128.6 (Ar*C*), 133.8 (Ar*C*), 138.9 (Ar*C*Si). GPC (THF as elutant) : M_w = 15,875, M_n = 10,205, polydispersity = 1.56. DSC : $T_g = -49^{\circ}C$.

Octa(2-{3-[1,1,1,3,3,3-hexafluoro-2-hydroxyprop-2-yl]-phenyl}ethyl)POSS designated FPOL POSS(2)

A 10-mL one-necked round-bottomed flask was equipped with a Teflon coated magnetic stirrer bar and a condenser with a nitrogen inlet at its top. The flask was charged with 0.236 g octasilane-POSS (0.232 mmol), 0.500 g 1,1,1,3,3,3-hexafluoro-2-(vinylphenyl)propan-2-ol (8 equivalents, 1.85 mmol), 5-mL toluene and one drop of platinum divinyltetramethyldisiloxane platinum complex in xylene. Thin Layer Chromatography (TLC) showed that a product with aromatic content and a retention factor of R_f = 0.10 in dichloromethane formed, and that the aromatic starting material (R_f = 0.80 in dichloromethane) had disappeared after 8 days at 60°C. The mixture was stirred with activated charcoal at room temperature for an additional 24 h. The charcoal residue was removed by gravity filtration and the toluene was evaporated to give the product as a pale yellow gum in quantitative yield. IR (thin film): ν (cm^{-1}) 3601 (free OH), 3534 (hydrogen-bonded OH), 3045 (aryl CH), 2962, 2932, 2879 (CH_2), 1612, 1512, 1457, 1416 (aryl), 1360 (CF_3), 1164, 1213, 1264, 1098 (SiOSi, SiCH_2, SiCH_3), 839 (SiCH_3). No vinyl bands at 3080, 3010, 2985, 1640, 1415, 990, and 910 cm^{-1}. No SiH band at 2100–2250 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.02–0.14 (m, SiCH_3), 0.84–0.98 (m, SiCH_2), 2.59–2.71 (m, ArCH_2), 7.06–7.15 (m, Ar*H*), 7.15–7.22 (m, Ar*H*), 7.49–7.57 (m, 2Ar*H*). ^{13}C-NMR ($CDCl_3$): δ (ppm) −0.53 (SiCH_3), 19.3 (SiCH_2), 28.6 (ArCH_2), 118.4, 121.2, 124.1, 125.6, 126.2, 126.4, 126.6, 127.3, 128.0, 146.8, 147.0 (*C*$(CF_3)_2$OH septet and Ar*C*). MALDI-TOF MS (DHB): *m/z* 3200 (Calc. 3178, major peak associated with desired octa-substituted product **2**), 2871 (Calc. 2908, minor peak associated with hepta-substituted product).

Octa(3-{2-hydroxy-5-[2,2,2-trifluoro-1-(4-hydroxyphenyl)-1-(trifluoromethyl)ethyl]phenyl}propyl)-POSS designated BSP3-POSS(3)

A 10-mL one-necked round-bottomed flask was equipped with a Teflon coated magnetic stirrer bar and a condenser with a nitrogen inlet at its top. The

flask was charged with 0.070 g octa(oxydimethylsilane)POSS (0.069 mmol), 0.208 g 1,1,1,3,3,3-hexafluoro-2-(3-propenyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl) propane[29] (8 equivalents, 0.552 mmol), 4-mL toluene, and one drop of platinum divinyltetramethyldisiloxane complex in xylene. The mixture was heated at 80°C for 24 h and then stirred with activated charcoal at room temperature for an additional 24 h. The charcoal residue was removed by gravity filtration and the toluene was evaporated to give the product as a white solid in quantitative yield. IR (thin film): ν (cm^{-1}) 3406 (OH), 2959, 2926, 2869 (CH_2), 1611 (Ar), 1513 (Ar), 1436 (Ar), 1380 (CF_3), 1253 ($SiCH_3$), 1204 ($SiCH_2$), 1168, 1090 (SiOSi). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.10 (s, Si*CH*$_3$), 0.88–0.94 (t, Si*CH*$_2$), 1.83–1.88 (m, $SiCH_2$*CH*$_2$), 2.54–2.56 (t, Ar*CH*$_2$) 6.79–6.82 (m, Ar*H*), 6.97–7.00 (m, Ar*H*), 7.06 (s, ArH). ^{13}C-NMR ($CDCl_3$): δ (ppm) 1.0 ($SiCH_3$), 18.1 ($SiCH_2$), 29.7 ($SiCH_2CH_2$), 33.3 ($ArCH_2$), 114.9, 122.3, 125.3, 128.2, 129.1, 131.7, 137.9 (Ar*C*, *C*F$_3$, *C*(CF$_3$)$_2$). MALDI-TOF MS (DHB): *m/z* 4087 (Calc. 4026), 3711 (Calc. 3650).

Hepta(isobutyl)mono[5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)pent-1-en-1-yl]POSS designated SXFA-POSS(4)

A 300-mL steel Parr bomb reactor with a glass liner was charged with 0.28 g monoallyl isobutyl POSS (0.327 mmol). The reactor was purged and then charged with 17.73-g hexafluoroacetone (0.106 mol, ~ 300-fold excess). After 24 h at 90°C excess hexafluoroacetone was pumped out of the reactor and destroyed by bubbling through an appropriate quantity of sodium borohydride solution in triglyme. The product was isolated as a yellow gum. IR (thin film): ν (cm^{-1}) 3600 (free OH), 3489 (hydrogen-bonded OH), 2956, 2911, 2867 (CH_2), 1379 (CF_3), 1279, 1209, 1146, 1054 ($SiCH_2$). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.58–0.63 (m, Si*CH*$_2$), 0.92–0.95 (d, CH*CH*$_3$), 1.78–1.90 (m, *CH*(CH$_3$)$_2$), 2.75–2.95 (2 days; SiCH=CH*CH*$_2$C(CF$_3$)$_2$OH *cis* and *trans*), 5.69-6.12 (2m; Si*CH* = CHCH$_2$C(CF$_3$)$_2$OH), 6.29–6.48 (2m; SiCH = *CH*CH$_2$C(CF$_3$)$_2$OH). ^{13}C-NMR ($CDCl_3$): δ (ppm) 22.2, 23.8, 25.6 (iBu*C*), 33.4 (CH$_2$C(CF$_3$)$_2$OH *cis*), 37.0 (CH$_2$C(CF$_3$)$_2$OH *trans*), 117.1–140.9 (septet, *C*(CF$_3$)$_2$), 129.9 (SiCH=CHCH$_2$C(CF$_3$)$_2$OH *cis*), 131.2 (SiCH=CHCH$_2$C(CF$_3$)$_2$OH *trans*), 139.9 (SiCH=*C*HCH$_2$C(CF$_3$)$_2$OH *trans*), 141.2 (SiCH=*C*HCH$_2$C(CF$_3$)$_2$OH cis). ^{29}Si-NMR ($CDCl_3$): δ (ppm) −64.1, −64.6 (O$_3$*Si*CH). MALDI-TOF MS (TAM): *m/z* 1059 (Calc. 1024).

Octa[3-(2-hydroxyphenyl)propyl]POSS designated phenol-POSS(5)

A 10-mL one-necked round-bottomed flask was equipped with a Teflon coated magnetic stirrer bar and a condenser with a nitrogen inlet at its top. The flask was charged with 0.200-g octa(oxydimethylsilane)POSS (0.196 mmol), 0.210 g 2-allylphenol (8 equivalents, 1.57 mmol), 3-mL toluene, and one drop of platinum divinyltetramethyldisiloxane complex in xylene. The mixture was heated at 80°C for 24 h and then stirred with activated charcoal at room temperature for an additional 24 h. The charcoal residue was removed by gravity filtration and the toluene was evaporated to give the product as a white solid in quantitative yield. IR (thin film): ν (cm^{-1}) 3444 (OH), 2954, 2924, 2861 (CH_2), 1590, 1505, 1486, 1449 (Ar), 1250 ($SiCH_3$), 1172, 1087 (SiOSi). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.12 (s, Si*CH*$_3$), 0.64–0.70 (t, Si*CH*$_2$), 1.62–1.76 (m, $SiCH_2$*CH*$_2$), 2.59–2.64 (t, Ar*CH*$_2$) 6.73–7.33 (4m, Ar*H*). ^{13}C-NMR ($CDCl_3$): δ (ppm) 1.2 ($SiCH_3$), 17.6 ($SiCH_2$), 23.5 ($SiCH_2CH_2$), 33.6 ($ArCH_2$), 115.5 (ArCH), 121.0 (ArCH), 127.2 (ArCH), 128.6 (ArCH), 130.5 ($ArCCH_2$), 138.1 (ArCOH). ^{29}Si-NMR ($CDCl_3$): δ (ppm) 15.6 (O*Si*Me$_2$CH$_2$). MALDI-TOF MS (TAM): *m/z* 2117 (Calc. 2090).

Hepta(isobutyl)mono(3-{2-hydroxy-5-[1-(4-hydroxyphenyl)-1-ethyl]phenyl}propyl)POSS designated bisphenol-POSS(6)

A 100-mL one-necked round-bottomed flask was equipped with a Teflon coated magnetic stirrer bar and a condenser with a nitrogen inlet at its top. The flask was charged with 2.54 g heptaisobutylmonosilane POSS (3.11 mmol, 2 equivalents), 0.480 g 2,2′-diallyl bisphenol-A (1.56 mmol, 1 equivalent), 30-mL toluene, and one drop of platinum divinyltetramethyldisiloxane complex in xylene. The mixture was heated at 80°C for 6 days and then stirred with activated charcoal at room temperature for an additional 24 h. The charcoal residue was removed by gravity filtration and the toluene was evaporated to give a mixture of three products. The product with the highest OH content was isolated by flash column chromatography (1 : 2 v/v dichloromethane-hexane, gradient to 100% dichloromethane); hepta(isobutyl)mono(3-{2-hydroxy-5-[1-(4-hydroxyphenyl)-1-ethyl]phenyl}propyl)POSS **6**, 0.24-g yellow gum. R_f = 0.45 (CH_2Cl_2). IR (thin film): ν (cm^{-1}) 3615 (free OH), 3541 (hydrogen-bonded OH), 2956, 2926, 2904, 2874 (CH_2 and CH_3), 2630, 1804, 1605, 1497, 1457, 1398, 1379, 1364, 1327, 1261 ($SiCH_2$), 1228 (SiCH), 1109 (SiOSi), 1036, 836 (SiOSi). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.61–0.66 (m, Si*CH*$_2$ and iBu), 0.88–1.00 (m, *CH*$_3$), 1.64 (s, Ar$_2$C(*CH*$_3$)$_2$), 1.80–1.93 (C*H*(CH$_3$)$_2$), 2.51–2.57 (t, Ar*CH*$_2$), 6.09–6.22 (m, Ar*H*), 6.82–7.00 (m, Ar*H*), 7.30 (d, Ar*H*). ^{29}Si-NMR ($CDCl_3$): δ (ppm) −63.0, −61.0 (O$_3$*Si*CH). MALDI-TOF MS (TAM): *m/z* 1129 (Calc. 1085). Two other side-products were also isolated by flash column chromatography. Oxygen-monosubstituted compound **7**; R_f = 0.60 (CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ (ppm) as above with integrals showing a biphenyl to POSS

ratio of 1 : 1. ^{29}Si-NMR ($CDCl_3$): δ (ppm) −64.0, −62.0 (O_3SiCH), −104 (O_4Si). MALDI-TOF MS (TAM): *m/z* 1142 (Calc. 1126). Trisubstituted compound **8**; R_f = 0.90 (CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ (ppm) as above with integrals showing an aromatic to POSS ratio of 1 : 3. ^{29}Si-NMR ($CDCl_3$): δ (ppm) −65, −63 (O_3SiCH), −104 (O_4Si). MALDI-TOF MS (TAM): *m/z* 2751 (Calc. 2761).

Polydimethylsiloxane-*co*-methyl[3-(2-hydroxyphenyl)propyl]siloxane(9)

A 50-mL one-necked round-bottomed flask was equipped with a Teflon coated magnetic stirrer bar and a condenser with a nitrogen inlet at its top. The flask was charged with 0.582 g polydimethylsiloxane-*co*-methylhydrosiloxane (96 wt % hydro units, 9.32 mmol SiH), 1.25 g 2-allylphenol (9.32 mmol), 15-mL toluene, and one drop of platinum divinyltetramethyldisiloxane complex in xylene. The mixture was stirred at room temperature for 5 days and then stirred with activated charcoal at room temperature for an additional 24 h. The charcoal residue was removed by gravity filtration and the toluene was evaporated. The product was vacuum dried at 50°C and a viscous oil was obtained in quantitative yield. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.00–0.15 (m, SiCH_3), 0.58 (br m, SiCH_2), 1.64–1.74 (m, $SiCH_2CH_2$), 2.59–2.66 (m, CH_2Ar), 6.71 (m, Ar*H*), 6.86 (m, Ar*H*), 7.06 (m, Ar*H*). ^{13}C-NMR ($CDCl_3$): δ (ppm) −0.15 ($SiCH_3$), 17.6 ($SiCH_2$), 23.6 ($SiCH_2CH_2$), 33.8 (CH_2Ar), 115.5 (ArCH, ortho to OH), 121.0 (ArCH, para to OH), 127.2 (ArCH, meta to OH), 128.8 ($ArCCH_2$), 130.6 (ArCH, meta to OH), 153.6 (ArCOH). ^{29}Si-NMR ($CDCl_3$): δ (ppm) 20.3 ($O_2MeSiCH_2$). DSC: T_g = −21°C.

Variable concentration study for dinitrotoluene

A basic requirement of any calibration system is to maintain the vapor device at a constant temperature in a known carrier flow. When the permeation rate at that temperature and the dilution flow rate are known, the concentration of the calibration stream can be calculated. Thus the rate can be altered by changing the temperature, the flow rate or both in combination. The following three equations were used.

The permeation rate at various temperatures was calculated using eq. (1), where P_0 was the rate at temp T_0 (°C), P_1 was the new rate at temp T_1 (°C), and α was the temperature coefficient, which for this test was 0.030 (the literature constant for a high emission tube).

$$\text{Log } P_1 = \log P_0 + \alpha(T_1 - T_0) \quad (1)$$

The concentration of the calibration gas was calculated using eq. (2), where *C* was the concentration in ppm by volume, *P* was the permeation rate in ng/min, M_w was the molecular mass of the pollutant gas, and F_c was the total flow rate of the calibration mixture in cc/min corrected to the reference conditions. The constant 24.46 was the molar volume at the reference conditions.

$$C = \frac{P \times (24.46/M_w)}{F_c} \quad (2)$$

The flow rate for the type of measuring device used was calculated using eq. (3), where F_c was the flow rate at the reference conditions, F_m was the measured flow rate and 0.626 was the constant for a floating ball rotameter.

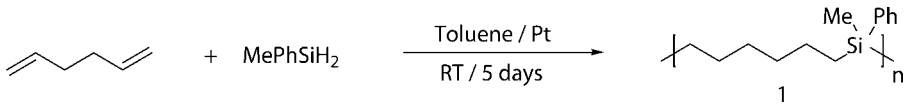
$$F_c = 0.626\, F_m \quad (3)$$

The concentration was lowered from 0.050 to 0.0013 ppm by first altering the flow rate, then both the flow rate and the temperature of the chamber in the vapor generator housing the vapor permeation tube. The flow rate for the dilution stream was varied while the flow rate into the vapor permeation tube chamber was kept constant at 250 mL/min. Between each change in the flow rate the unit was allowed to equilibrate for 30 min before the test was conducted. When the chamber temperature was varied, the unit was allowed to equilibrate overnight. For the range of 0.050–0.020 ppm the temperature of the vapor generator was set at 90°C, and only the dilution flow rate was changed to achieve varying concentration levels. For levels below 0.020 ppm the flow rate and the chamber temperature were varied.

RESULTS AND DISCUSSION

Polycarbosilane carrier polymer

A suitable carrier polymer for a hydrogen-bond acidic nanofiller should meet the following criteria. It should not contain any functional groups that will interfere or compete with the sensor groups on the nanofiller, it should be compatible with the nanofiller to enable high filler loadings and good filler dispersion, it should have good solubility in the coating solvent, and it should have suitable vapor diffusion properties. It should also be mechanically, thermally, and hydrolytically stable. A number of polymers could meet these criteria, but for the purposes of this study a polymethylphenylcarbosilane **1** was selected and synthesized in the hydrosilylation reaction shown in Reaction Scheme 1. The obtained product, poly(methylphenylsilylhexane-1,6-diyl) **1**, had an M_n of 10,205 measured by GPC, and a T_g of −49°C measured by DSC.



Scheme 1

Polyhedral oligosilsesquioxane sensor compounds

Five polyhedral oligosilsesquioxanes (POSS) functionalized with hydrogen-bond acidic sensor groups (Fig. 3) were prepared (Reaction Schemes 2–6).

FPOL POSS **2** was prepared by reacting octasilane-POSS with 1,1,1,3,3,3-hexafluoro-2-(vinylphenyl)-propan-2-ol in the presence of Karstedt's catalyst (1,3-divinyltetramethyldisiloxane platinum catalyst in xylenes) and toluene (Scheme 2). The observed MALDI-TOF MS mass (3200) was a good match to the calculated mass (3178) for the octa-substituted product. IR and NMR showed that the starting reagents had been consumed: no SiH band was observed at 2100–2200 cm^{-1} in the IR spectrum, no SiH peak was observed at 4.7 ppm in the ^{1}H-NMR spectrum, and no vinyl peaks were observed in the 5–6 ppm region of the ^{1}H-NMR spectrum. In addition, there was no evidence of an undesirable side reaction product in which the $C(CF_3)_2OH$ group in the aromatic compound had reacted with the POSS $SiMe_2H$ groups instead of the vinyl group.[38]

An octa-substituted POSS compound **3** with BSP3-type (Fig. 2) functional groups was prepared in a hydrosilylation reaction between octa(oxydimethylsilane)POSS and 1,1,1,3,3,3-hexafluoro-2-(3-propenyl-4-hydroxyphenyl)propane[29] as shown in Reaction Scheme 3, and characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and MALDI-TOF MS. The two-step synthesis of 1,1,1,3,3,3-hexafluoro-2-(3-propenyl-4-hydroxyphenyl)propane from 4,4′-hexafluoroisopropylidenediphenol has been described elsewhere.[29,39] A peak with a mass corresponding to the desired octa-substituted product was observed in the MALDI-TOF mass spectrum at 4087, and no allyl (5–6 ppm) or SiH (4.7 ppm) signals were observed in the ^{1}H-NMR spectrum. An absence of the SiH band at 2130 cm^{-1} in the IR spectrum also suggested that the reaction had gone to completion.

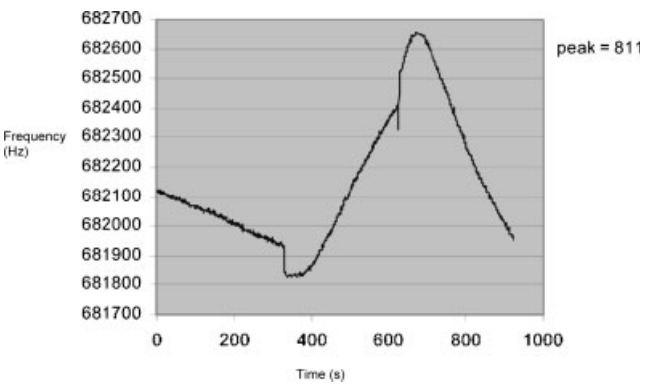


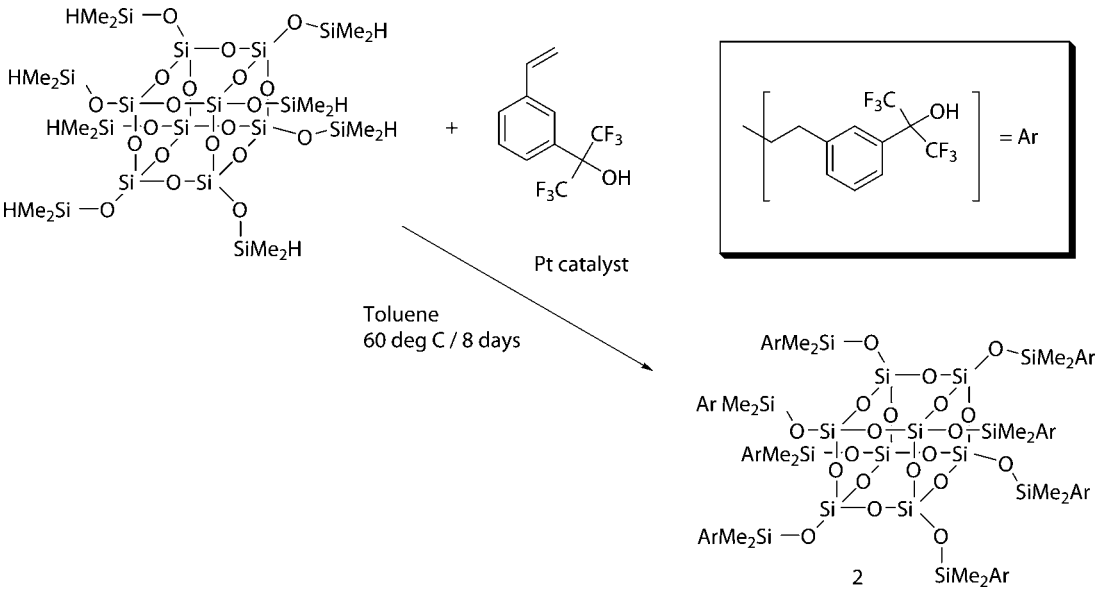
Figure 3 SAW plot showing DNT vapor response at 0.045 ppm for 20 wt % BSP3 POSS **3**, 80 wt % PCS **1** formulation. Vapor was switched on at 300 s and switched off at 600 s.

A mono-substituted POSS compound **4** with an SXFA-type (Fig. 2) functional group was prepared by reacting monoallyl-POSS with hexafluoroacetone in a high-pressure steel Parr bomb reactor at 90°C (Reaction Scheme 4) and characterized by IR, ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, and MALDI-TOF MS. Once again, a MALDI-TOF MS peak corresponding to the mass of the desired product was observed at 1059, and IR and NMR showed that the allyl groups had been consumed. Peaks at −64.1 and −64.6 ppm in the ^{29}Si-NMR spectrum showed that the polyhedral silsesquioxane (POSS) cage structure had survived the Parr bomb reaction conditions.

To expand the range of hydrogen-bond acidic POSS compounds beyond FPOL POSS **2**, BSP3-POSS **3**, and SXFA-POSS **4** described earlier, two additional phenol-functionalized POSS compounds were also prepared (Reaction Schemes 5 and 6).

A phenol-POSS compound **5** was prepared from 2-allylphenol and an octasilane POSS compound (also used in the preparation of Compounds **2** and **3**) in the hydrosilylation reaction shown in Reaction Scheme 5, and the product was characterized by IR, ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, and MALDI-TOF MS. In the MALDI-TOF mass spectrum, a peak corresponding to the octa-substituted product was observed at 2117, showing that all eight SiH groups in the POSS starting material had reacted.

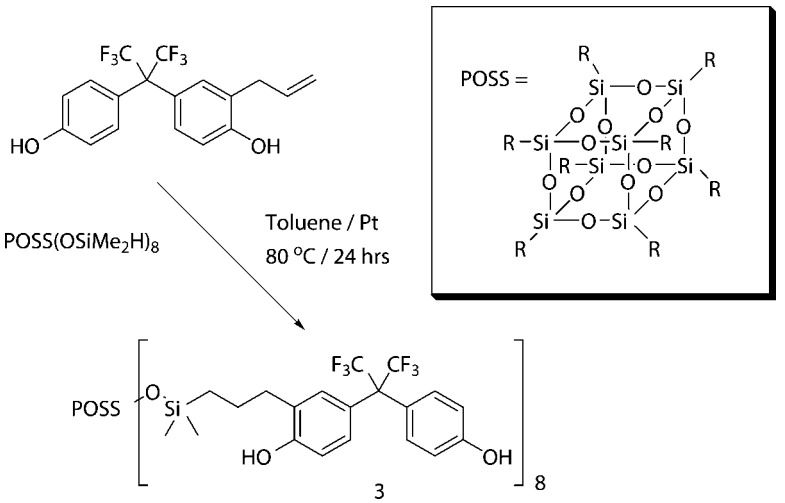
A bisphenol-POSS **6** was prepared by reacting a monosilane POSS with 2,2′-diallylbisphenol-A (Reaction Scheme 6). In contrast to the previous reactions of silane-functionalized POSS containing $OSiMe_2H$ groups (Reaction Schemes 2, 3, and 5), in this reaction the silane was of the form O_3SiH where the hydrido group was attached directly to the POSS cage. Reaction took place at both the allyl and hydroxyl positions in 2,2′-diallylbisphenol-A (Reaction Scheme 6). In platinum-catalyzed hydrosilylations, O_3SiH would be expected to be more reactive than OMe_2SiH for electronic reasons, but studies have shown that in reality O_3SiH is less reactive than Me_2OSiH for steric reasons.[38] Normally hydrosilylations are very much faster than the competing reaction between hydroxyl and SiH, but in this case the hydrosilylation of the allyl group was clearly slowed down, enabling significant numbers of



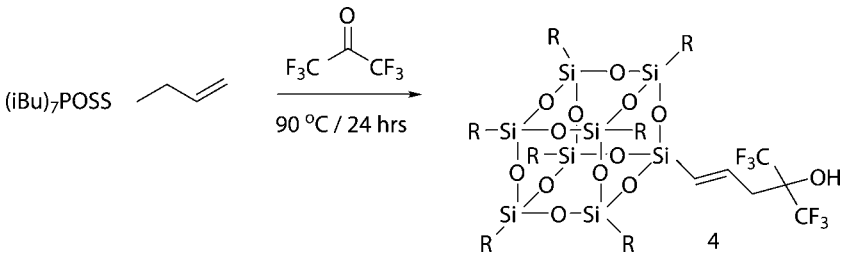
Scheme 2

hydroxyl groups to react.[38] This resulted in a mixture of products **6**, **7**, and **8** which were separated by flash column chromatography in a dichloromethane-hexane solvent system and then characterized by IR, ^{1}H-NMR, ^{29}Si-NMR, and MALDI-TOF MS. The ratios of POSS to bisphenol content for compounds **6–8** were determined from their ^{1}H-NMR integrals, and these were matched to mass values obtained in MALDI-TOF MS experiments. The substitution positions (allyl versus hydroxyl) were determined by ^{29}Si-NMR, since reaction at a bisphenol-A hydroxyl position results in an SiO_4 group with a distinctive ^{29}Si-NMR peak in the −100 ppm region, while reaction at a bisphenol-A allyl position results in the retention of the SiO_3R group with a ^{29}Si-NMR peak in the −60 ppm region. The retention factors (R_f) of compounds **6** to **8** increased with decreasing OH content and with increasing POSS content. Compound **6** was selected for further study as a SAW sensor material because it had the highest mass percent hydroxyl content.

Two octa-substituted POSS Compounds **3** and **5** were white solids, and their IR spectra contained broad hydroxyl bands in the 3400 cm^{-1} region corresponding to hydroxyl groups in the hydrogen-bonded state.[40] Octa-substituted FPOL POSS **2** and the two mono-substituted POSS Compounds **4** and **6** were yellow gums, and their IR spectra contained similar hydrogen-bonded hydroxyl bands in the 3400 cm^{-1} region but also sharp bands in the 3600 cm^{-1} region corresponding to free (non-hydrogen-bonded) hydroxyl groups.



Scheme 3



Scheme 4

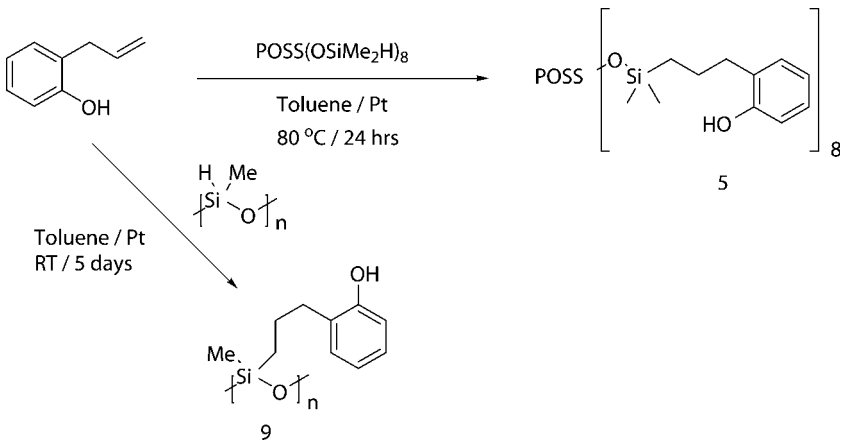
Linear hydrogen-bond acidic carrier polymers

For the purposes of comparison of the SAW sensor performances of conventional linear SAW polymers with the new POSS materials described in this study, linear polymer analogs of three of the five POSS compounds described earlier were also synthesized. Samples of these same linear sensor polymers were also used in formulating and studying coatings in which hydrogen-bond acidic POSS materials were dispersed in hydrogen-bond acidic linear carrier polymers containing similar functional groups. BSP3[23,39] and SXFA[4] (Fig. 2) were prepared following literature procedures, and a linear polysiloxane **9** carrying pendant phenol groups was synthesized in the hydrosilylation reaction shown in Reaction Scheme 5, and was obtained as a viscous oil with a T_g of -21°C measured by DSC.

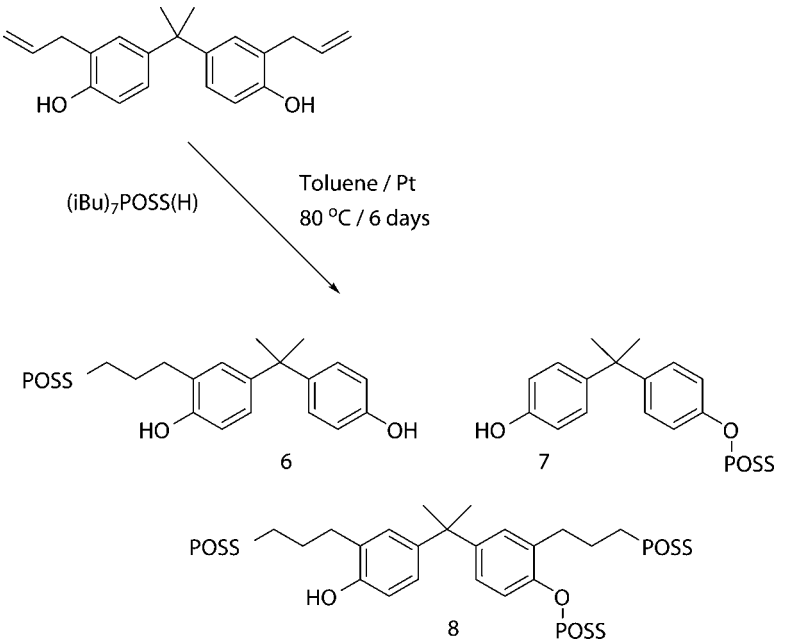
Initial SAW responses

SAW sensors were cleaned and airbrush-coated to a thickness corresponding to a frequency increase of 500 kHz. The coated SAW sensors were then tested against DNT vapor (0.045 ppm v, chamber temperature 90 °C), DMMP vapor, (0.050 ppm v, chamber temperature 50°C) and acetone vapor (0.060 ppm v, chamber temperature 80°C). The frequency response results are summarized in Table I. In DNT experiments, time lags of 30–90 s were observed for the initial SAW response and its return to baseline (Fig. 3), whereas time delays of 10 s were observed in the DMMP and acetone vapor experiments. This pattern was rationalized in terms of two effects. A ''wall'' effect contributes to the time delay when the vapor is switched on. In systems where vapors are flowing, it takes a finite time to achieve equilibrium such that the vapor concentration at a point downstream (i.e., at the SAW surface) matches the vapor concentration at the point of generation. This time delay is longer for low vapor pressure compounds such as nitroaromatics because of their increased tendency to come out of vapor phase and condense onto the walls. A kinetic diffusion effect contributes to the time delays when the vapor is switched on and also when it is switched off. Upon arrival at the SAW surface, vapors are slow to diffuse into the coating, and a slow build up to maximum response is observed. The vapor is also slow to diffuse out of the coating at the end of the experiment, and a signal with a long trail off is observed. Hence the magnitude of this effect is a function of both vapor and SAW coating composition.

Control experiments in which a SAW sensor was coated with pure polycarbosilane **1** gave responses in the noise region below 400 Hz for all three vapors. This demonstrated that polycarbosilane made no significant chemical contribution to the sensing function of the SAW coating. A second set



Scheme 5



Scheme 6

of control experiments in which SAWs were tested against acetone, a non-hydrogen-bond basic vapor, also gave responses below 400 Hz. This demonstrated that hydrogen-bond acidic SAW coatings could successfully differentiate hydrogen-bond basic vapors (DNT and DMMP) from non-hydrogen-bond basic vapors (acetone). It is also worth noting that the materials in this study gave zero responses when run against air for 18 h. Other interferent vapors (particularly water) have yet to be studied, but LSERs (linear solvation energy relationships)[7] give reliable insights into how phenolic and fluorinated aliphatic alcohol SAW sensor groups may be expected to respond to a range of common vapors of interest.

POSS Compounds **2** to **6** were formulated into polycarbosilane **1** at 10% by weight and at 20% by weight. Since 10 wt % formulations gave higher responses to DNT vapor than 20 wt % formulations (Table I), 10% formulations were selected for later experiments with DMMP vapor. Although the 20 wt % formulations had a slightly higher concentration of sensing hydroxyl groups, higher POSS filler content appears to lower the quality and homogeneity of the coating, and affects factors such as the rate of vapor diffusion into the coating, the vapor solubility in the coating , and coverage of vital components of the piezoelectric quartz SAW sensor surface. In contrast, in a second set of experiments, where the DMMP responses of 10 wt % POSS, 90 wt % PCS

TABLE I
SAW Sensor Responses of Various Coatings to Dinitrotoluene (DNT) and to Dimethyl Methylphosphonate (DMMP) Vapors

SAW Coating	DNT response (Hz)	DMMP response (Hz)
10% wt FPOL POSS **2** in PCS **1**	1026	710
20% wt FPOL POSS **2** in PCS **1**	660	–
10% wt BSP3 POSS **3** in PCS **1**	1067	638
20% wt BSP3 POSS **3** in PCS **1**	811	–
Linear BSP3	–	5148
50% wt BSP3 POSS **3** in linear BSP3	–	3834
10% wt SXFA POSS **4** in PCS **1**	906	475
20% wt SXFA POSS **4** in PCS **1**	913	–
Linear SXFA	–	3137
50% wt SXFA POSS **4** in linear SXFA	–	1737
10% wt Phenol POSS **5** in PCS **1**	750	1294
20% wt Phenol POSS **5** in PCS **1**	690	–
Linear phenol polymer **9**	–	3623
10% wt Bisphenol POSS **6** in PCS **1**	970	1163
20% wt Bisphenol POSS **6** in PCS **1**	706	–

TABLE II
Percent Weight Hydroxyl Contents for Various SAW Sensor Formulations

	BSP3	SXFA	Phenol
100% linear polymer	5.4%	6.0%	8.7%
10% wt POSS analog 90% wt polycarbosilane **1**	0.7%	0.2%	0.7%
50% wt POSS analog 50% wt linear polymer	6.1%	3.9%	–
100% wt POSS analog	6.8%	1.7%	6.5%

Percentages for pure POSS compounds appear in the bottom row for comparison, although no coatings of this composition were prepared.

formulations were compared with the DMMP responses of conventional linear SAW sensor polymers (BSP3, SXFA, and phenol polymer **9**) having an order of magnitude higher hydroxyl content than the corresponding POSS formulations (Table II), hydroxyl content became the dominating factor, and the linear polymers gave much higher responses than the POSS formulations (Table I). In a third set of experiments, the DMMP responses of 50 wt % POSS 50 wt % linear SAW polymer formulations were compared with the DMMP responses of the pure linear polymers for the BSP3 and SXFA systems (Table I). These four systems had comparable hydroxyl contents (Table II) and gave comparable frequency responses (Table I).

SAW responses as a function of vapor concentration

The effect of a gradual lowering of the concentration of DNT vapor (Fig. 4) was studied to determine the minimum vapor concentration at which responses could still be discerned before sinking into the noise region. This was to give an indication of the sensitivity of POSS-based SAW coatings to explosives vapors in real-life applications, particularly in the light of the fact that explosives have very low vapor pressures at ambient temperatures and pressures. An open container of DNT gives a concentration of 184 ppb v in air at 25°C, and an open container of TNT (trinitrotoluene) gives a concentration of 4 ppb v.[41] At the other extreme, concentrations of TNT in the air above buried landmines[42] are in the region of 5×10^{-7} ppb v, i.e., 3 million times lower than open container. Figure 4 shows that response is lost around 1 ppb v (i.e., 0.0013 ppm v). It was also observed that the responses returned to baseline after approximately 1200 s (i.e., 20 min after $t = 0$, and 10 min after DNT vapor was turned off). Hence it can be concluded that POSS-based SAW sensors are suitable for some, but by no means all, explosives detection applications.

Long term SAW responses

The stability of SAW response with time for the various coatings discussed earlier was also evaluated. SAW sensors were tested periodically over a period of 4–6 months, and these results are summarized in Figure 5. For ease of comparison of different SAW coatings, the responses (y-axes) are given as a percent of the initial response rather than as an absolute frequency response. These results show that all POSS-based systems (BSP3, SXFA, and phenol POSS materials in either PCS **1** or in their linear polymer analogs) maintained a good performance over time when air-brushed onto 500 MHz SAWs, and retained 40–65% of their initial response after several months. The single exception to this pattern was the long-term performance of SXFA POSS in linear SXFA, which behaved in a manner similar to pure linear SXFA. Linear SXFA is problematic among hydrogen-bond acidic SAW polymers because its pendant fluorinated alcohol groups (Fig. 2) are able to function as Bronsted acids[43] that catalyze the cleavage of the Si-O backbone bonds in the polysiloxane to which they are attached. Other linear hydrogen-bond acidic polymers (Fig. 2) also carry acidic hydroxyl groups capable of protonating siloxane oxygens, but appear to be more stable, possibly for steric reasons.

Sum frequency generation spectroscopy

The surfaces of several coatings were characterized by sum frequency generation (SFG). SFG is a comparatively novel technique for obtaining surface-specific vibrational spectra, and can be used to study the chemical groups at interfaces to a depth of 10 nm or less. SFG spectra are generated by a non-linear optical phenomenon that occurs when two pulsed laser beams (one of fixed visible wavelength and one of variable IR wavelength) hit a point on an interface at the same time.[44] SFG has several advantages over other surface characterization techniques. Conventional

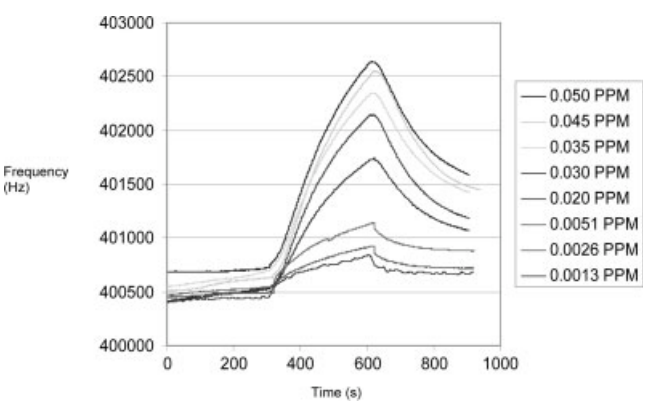


Figure 4 Responses for a SAW sensor coated with 20 wt % FPOL POSS **2**, 80 wt % PCS **1** at various DNT vapor concentrations.

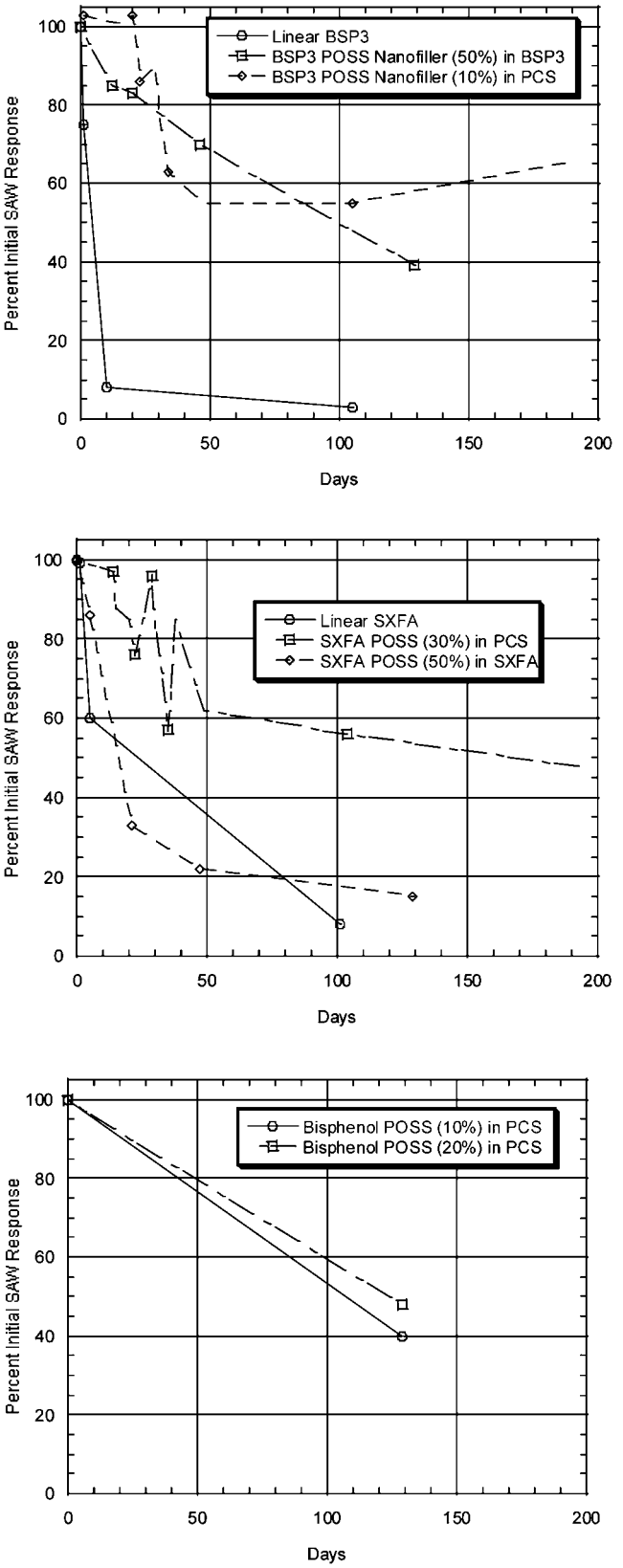


Figure 5 Changes in SAW responses with time for systems containing BSP3-type sensor groups, SXFA-type sensor groups and bisphenol-type sensor groups.

IR spectroscopy generates spectra with similar vibrational bands, but penetrates up to a depth of 1000 nm (1 μm) into the bulk of the material, and gives no surface-specific data. X-ray photoelectron spectroscopy (XPS) has comparable surface-specificity to SFG, but XPS must be carried out in a high vacuum, whereas SFG is carried out in air at room temperature. Hence SFG can be used to study many samples (e.g., volatile coatings, biological systems), which would be unstable under XPS conditions.

To study the general surface composition of the coating, and the hydrogen-bonding state of the hydroxyl sensor groups, several formulations were spin-coated onto quartz substrates and their coating-air interfaces were characterized by SFG (Table III). Highly ordered silicon-methyl surfaces dominated in the two linear nerve polymers with siloxane content (SXFA and BSP3, Fig. 1). Some hydrogen-bonded hydroxyl was also observed for linear SXFA. Highly ordered isobutyl surfaces dominated in SXFA POSS **4** (Scheme 4), the monosubstituted POSS-polycarbosilane system in which the remaining seven POSS positions were blocked with isobutyl groups. As the SXFA POSS **4** content decreased from 20 to 10%, silicon-methyl and silicon-phenyl groups from PCS also began to contribute to the surface composition. Some hydrogen-bonded hydroxyl was also observed at the two SXFA POSS **4** formulation surfaces. In contrast, highly ordered polycarbosilane surfaces (with contributions from silicon-methyl and silicon-phenyl groups) dominated in the FPOL POSS **2** system (Scheme 2) in which all eight POSS positions carried hydrogen-bond acidic groups, and none were blocked with isobutyl groups.

An SFG experiment at the interface between linear SXFA (liquid) and the quartz substrate was also carried out. In this experiment, the laser path went through the quartz substrate to the interface. Since the SFG technique requires a well-defined solid (quartz)-liquid (sample) interface, it was not possible to obtain solid-liquid interface SFG spectra for SAW formulations other than linear SXFA because the samples were not liquids. A hydrogen-bonded OH band was observed at 3470 cm^{-1} (ssp mode) and no methyl bands were observed. Quartz is a hydrophilic surface, and ordering and hydrogen-bonding of OH groups is consistent with this. An artifact signal was also observed at 3150 cm^{-1} resulting from a third order non-linear process in the bulk quartz.

CONCLUSIONS

The combination of good initial sensitivity and good response over time makes hydrogen-bond acidic POSS compounds promising materials for SAW

TABLE III
Sum Frequency Generation (SFG) Bands and Polarization Modes for Five Coating Formulations

Coating	SFG bands (cm^{-1}) and assignments	Mode
Linear SXFA	2905 (sym $SiCH_3$), 3400 (H-bonded OH)	ssp
	2955 (asym $SiCH_3$)	ppp
Linear BSP3	2910 (sym $SiCH_3$)	ssp
	2965 (asym $SiCH_3$)	sps
20% SXFA POSS **4** 80% PCS **1**	2870 (sym CCH_3), 2940 (sym CCH_3 Fermi resonance), 3455 (H-bonded OH)	ssp
	2960 (asym CCH_3)	ppp
10% SXFA POSS **4** 90% PCS **1**	2870 (sym CCH_3), 2940 (sym CCH_3 Fermi resonance), 2915 (sym $SiCH_3$), 3050 cm^{-1} (sym ArH), 3400 (H-bonded OH)	ssp
	2960 (asym CCH_3)	sps
10% FPOL POSS **2** 90% PCS **1**	2835 (weak), 2885 (sym CH_2), 2905 (sym $SiCH_3$), 2965 (weak), 3045 (sym ArH)	ssp

sensor devices for the detection of nerve agents and explosives.

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