A Simple Route to Functionalize Siloxane Polymers for DMMP Sensing

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ABSTRACT: Hexafluoroisopropanol (HFIP) was the most widely used functional group for nerve agents detection. However, to incorporate HFIP group into a polymer backbone, highly toxic hexafluoroacetone gas was needed in a conventional synthetic route. In this article, a new route with low toxicity was proposed to synthesize a strong hydrogen-bond acidic (HBA) siloxane polymer by using 2-vinylhexfluoroisopropanol as the raw material in the hydrosilylation reaction. The synthesized fluoroalcoholic linear polysiloxane (LSFA) was characterized by FT-IR, confirming its molecular structure was much similar to SXFA, a well-established HBA polymer synthesized by the conventional route. TGA data verified the adduct's thermal stability. The dimethyl methylphosphonate (DMMP) sensing properties of LSFA and SXFA, along with PLF, were compared basing on the surface acoustic wave (SAW) platform. The results demonstrated that the conventional synthetic route was somewhat difficult to handle and control, while the new route was simpler, easier and was an effective and promising alternative. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4516–4520, 2013

INTRODUCTION

The threat of chemical warfare agents has always been motivating the research of highly sensitive and selective gas sensors in recent years.[1–4] Among them, the SAW sensors have been intensively studied, wherein much attention has been paid to the sorptive coatings of this sensor. Strong HBA polymers, such as SXFA, PLF, BSP3 shown in Figure 1, were demonstrated to selectively interact with the nerve agents by hydrogen bond.[5–8] These HBA polymers had siloxane or carbosilane backbones either in linear or branched architectures. Thus, their glass transition temperatures (T_g) were low, which facilitated the penetration of the analytes into the sorptive coatings. Meanwhile, strongly HBA functional groups were incorporated exclusively into the polymer backbones to promote the sorption. These HBA functional groups were fluorinated alcohols or phenols, among them, as shown in Figure 1, hexafluoroisopropanol (HFIP) was predominately used. HFIP was even grafted onto polythiophene[9] and carbon nanotubes[10–12] to enhance the sensitivity and selectivity of these materials to nerve agents. However, to introduce HFIP group into the polymeric backbones, hexafluoroacetone was inevitably used in the conventional method.[5,7,8,10,11,13–15] This chemical is a highly toxic gas at room temperature, so in a regular route, the reaction was took placed in a high-pressure steel Parr bomb reactor for safety.[15–19] However, transient releases of this toxic gas, along with the potential explosion of the high-pressure reactor, had imposed a very dangerous workplace to the relevant personnel. Therefore, a liquid based nontoxic reaction was undoubtedly desirable and worth pursuing.

In this article, hexafluoroacetone was replaced by 2-vinylhexfluoroisopropanol in the functional reaction, resulting a mild synthetic route with low toxicity. The resultant polymer, LSFA, had a similar molecular structure to SXFA and PLF. And its sensing responses to dimethyl methylphosphonate (DMMP), a stimulant of the nerve agents, were compared with that of the two counterparts.

EXPERIMENTAL

Material and Apparatus

The 2-vinyl hexafluoroisopropanol was bought from Matrix Scientific. Polymethylhydrosiloxane (PHMS) and DMMP were got from Acros Organics. Platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane [Pt(dvs)] was purchased from Fluorochem. Ethanol, acetone, 1,2-dichloroethane (DCE), 1,5-dichloropentane (DCP), hexane, and toluene were from J&K Scientific. All of the reagents above were of analytical grade and used as received without any further purification. Activated carbon was purchased from Chengdu Kelong chemical reagent factory, treated by 1 M nitric acid at 80°C for 2 h before being used. The synthesized polymer was characterized by Fourier transform infrared (FT-IR) spectrum, nuclear magnetic resonance spectrum (NMR) and thermogravimetric analysis (TGA). FT-IR spectrum
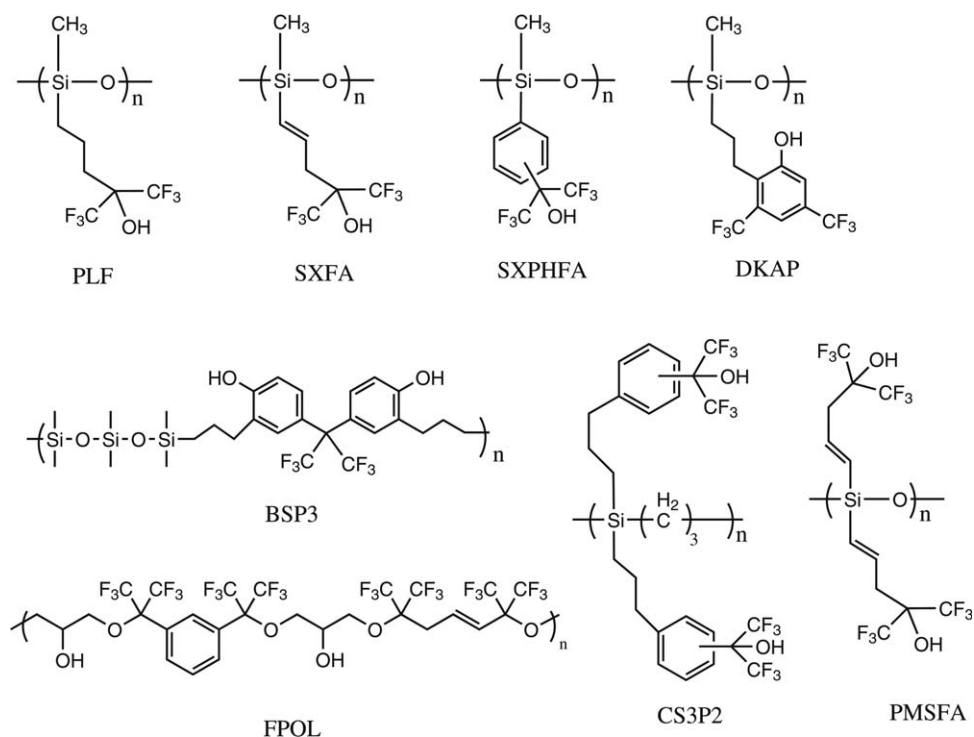
Figure 1. The hydrogen-bond acidic polymers.

was measured by a Shimadzu instrument system (8400S), potassium bromide tabletted. ^{1}H NMR spectra was recorded on a Bruker Avance-300 spectrometer in CDCl$_3$, tetramethylsilane as the internal reference. TGA was conducted on a Mettler-Toledo TGA/DSC 1 thermogravimetric analyzer at a heating rate of 10°C min^{-1} from 50 to 750°C under the air atmosphere.

The 433.92 MHz SAW two-port resonator devices were purchased from Luguang electronics, China. The device was fabricated onto a quartz substrate with Al electrode, having a loaded Q value of 7000 and an insert loss of −7 dB. The SAW device was uncovered, and the LSFA was dissolved in chloroform and spray-coated on the device by an airbrush apparatus. After film deposition, 740 kHz frequency shift was recorded, corresponding to a film thickness of about 20.5 nm. The coated SAW device had a Q value of 3000 and an insert loss of −15 dB, monitored by a network analyzer (E5070B, Agilent Technologies). The SAW sensor, as well as an uncoated SAW device, was mounted on a sensor printed circuit board. Each device was excited individually in an oscillator loop. Then, the frequency difference between the two devices was obtained by a mixer, and recorded by a SS7200A general counter (Suin Digital Instruments, China).

The DMMP and the interfering vapors were generated by a MF-3C dynamic vapor generator (China National Metrology Technology Development). The vapor generator had two digital mass flow controllers and one vaporizing chamber into which small amount of the analyte solvent (as less as 0.1 μL) was injected by a microsyringe. The vaporized solvent was fluxed by pure N$_2$ and stored in a sampling bag, and subsequently diluted by another pure N$_2$ stream to get a concentration as low as 0.1 mg m^{-3}. The diluted vapors were inlet into a small multicell

test chamber (0.2 mL for each cell) made up of aluminum and mounted gas tightly on the sensor printed circuit board.

Synthesis

LSFA is synthesized by one step hydrosilylation reaction as shown in Figure 2. 0.5 g PHMS and 1.6 g 2-vinylhexfluoroisopropanol was mixed in 30 mL toluene. Then a drop of Karstedt's catalyst, Pt(dvs) was added. The reaction mixture was stirred at room temperature for 24 h. When the solution turned yellow, activated carbon was added and stirred for another 2 h. Then solid was filtered, solvent and low boiling impurities was removed by rotary evaporation. After vacuum drying, 2.0 g yellow rubber-like product was obtained. ^{1}H NMR (CDCl$_3$): δ (ppm) 3.76 (1H, —OH), 1.26 (2H, Si—CH$_2$), 1.83 (2H, C—CH$_2$), 0.17 (3H, Si—CH$_3$). All the reagents were of analytical grade. The reaction took place in the presence of nitrogen (5N) atmosphere.

RESULTS AND DISCUSSION

FT-IR Characterization

LSFA, as well as the raw material PHMS was characterized by FT-IR. As shown in Figure 3, a strong and sharp Si—H vibration peak at 2146 cm^{-1} was present in PHMS spectrum. While in LSFA spectrum, this peak disappeared and new peaks at 3444

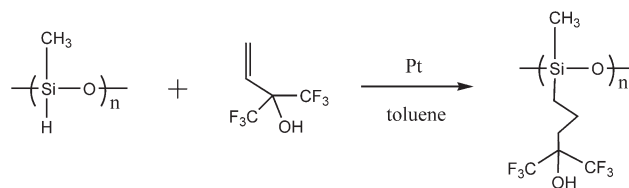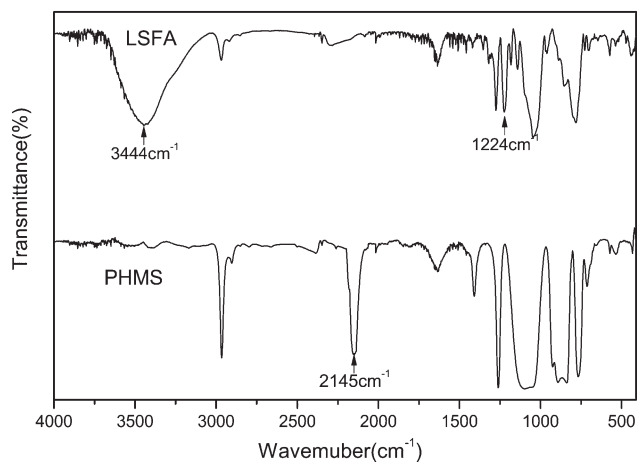**Figure 2.** The synthetic route of LSFA.

Figure 3. FTIR spectra of LSFA and PHMS.

Figure 5. Real-time response of the LSFA-coated SAW sensor to different concentrations of DMMP vapor. Insert is the frequency shifts of the sensor as a function of the DMMP concentrations.

and 1224 cm^{-1} which corresponding to stretching vibrations of —OH and C—F bond were observed, respectively. It is important to note that the absorption peak at 3444 cm^{-1} was strong and wide, which was consistent with the strong hydrogen bond. These data indicated that the hydrosilylation was completely reacted.

Thermal Property

Thermal stability of the sensing material was significant for the longevity of sensor's shelf life. TGA thermogram of LSFA at air atmosphere was illustrated in Figure 4. The thermal degradation behavior almost didn't occur under 120°C (weight loss <1%). The initial decomposition temperature (T_d),[20] defined by the 5% weight loss temperature($T_{5\%}$), was 183.5°C. Simonson et al.[21] had reported the TGA plot of FPOL (see Figure 1), a well-established sensing material in the early SAW studies, which showed a 5% weight loss in air at about 186°C. It indicated that the thermal stability of LSFA could fully satisfy the sensor application needs.

Response to DMMP

The real-time response of the LSFA-coated SAW sensor to DMMP vapor ranging from 1 to 50 mg m^{-3} was shown in
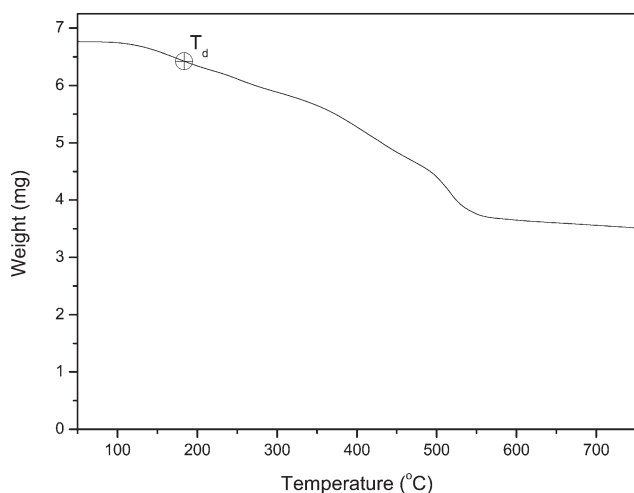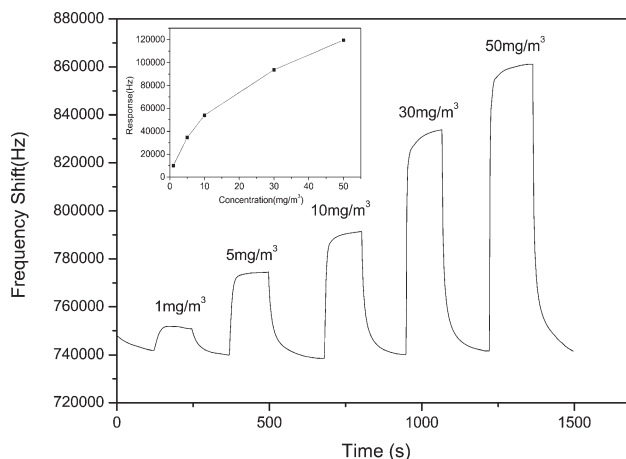

Figure 4. TGA thermogram of LSFA polymer.

Figure 5. It can be seen that the frequency changed immediately when the DMMP vapor was injected into the chamber, indicating that the adsorption occurred rapidly and subsequently achieved an equilibrium state. The frequency shifts reached to 80% maximum of the corresponding peak height (Δf) within 20 s at all of the tested concentrations. When the chamber was purged with pure N_2, desorption took place rapidly as well and the frequency could return to the original value. Thus, the whole adsorption–desorption process for each of the vapor exposure test showed a square wave curve. The sensor responses were plotted in terms of the DMMP vapor concentrations as shown in the insert of Figure 3. It was obvious that the sensor responses increased with the increasing of the analyte concentrations in a parabolic manner. At the lowest tested concentration of 1 mg m^{-3}, frequency shift of 10 kHz was recorded. Therefore, high sensitivity of the LSFA-coated SAW sensor was demonstrated.

Because the molecular structure of the sorbent polymer LSFA was much similar to that of SXFA and PLF (see Figure 1), its sensitivity to DMMP was compared with SXFA and PLF, based on polymer coated SAW sensors published previously in the literature.[22–26] To make the comparison feasible, several key factors should be taken into account and normalized. These factors included: (a) working frequency of the SAW sensor (there is a square relationship between Δf and f_0),[27] (b) coating thickness (Δf is roughly proportional to the coating thickness), (c) SAW device (Love wave sensor is more sensitive than the Rayleigh wave one), (d) test concentration (Δf rise in a parabolic manner with increasing concentration),[28–30] (e) temperature (adsorption decreases exponentially with rising temperature), and (f) humidity (HBA polymers are good sorbent for water vapor, at a damp atmosphere, the sensor response decreases remarkably).[5,28,31]

It can be seen from Table I, the SAW sensor used by Piqué et al.[22] at the Naval Research Laboratory (NRL) had the frequency and coating thickness most similar to our device. Frequency shift of 2.2 kHz at DMMP concentration of 0.1 mg m^{-3} was only reported in their paper. The 2.2 kHz response at 0.1 mg

Table I. Comparison between LSFA and SXFA, PLF-Coated Sensors to DMMP Vapor

Polymer	SAW device	Film thickness	Test condition	C (mg m^{-3})	Δf (kHz)	T_{80} (s)	Ref.
SXFA	Resonator, 417 MHz	15 nm/500 kHz	NA	0.1	2.2	<5	Auyeung [22]
SXFA	Delay line, 300 MHz	38 nm	14°C, 23RH%	1	1.3	<10[a]	Wang [23]
SXFA	Delay line, 100 MHz	NA	25°C, air	1	1.5[b]	–	Alizadeh [23]
PLF	Delay line, 98 MHz	30 nm	25°C, dry N$_2$	1.5	0.18	>1500[c]	Zimmermann [25,26]
LSFA	Resonator, 434 MHz	20.5 nm/740 kHz	15°C, dry N$_2$	1	10	20	This work
PLF	Resonator, 434 MHz	21 nm/765 kHz	15°C, dry N$_2$	1	3.2	55	This work

[a] Tested at 1000 mg m^{-3}, 24°C, 68RH%.
[b] The response should divided by an unknown preconcentration factor.
[c] Tested by a 108 MHz Love wave device at 10 mg m^{-3}.

m^{-3} was estimated to increase by a factor of 7, by referring to the nonlinear calibration curve of FPOL,[28] SXFA,[29] and BSP3[30] coated SAW sensors, and reached to about 15 kHz at 1 mg m^{-3}. Therefore, the sensitivity of LSFA synthesized by us was roughly equal to the sensitivity of the SXFA synthesized at NRL. SXFA was originally synthesized by Grate[5] at NRL in the middle of 1990s using the conventional hexafluoroacetone route, and then other groups synthesized SXFA polymer according to the same method in recent years. However, as can be seen in Table I, the SXFA polymers synthesized by Wang et al.[23] and Alizadeh et al.[24] were much less sensitive than the NRL polymer. After frequency, coating thickness and test concentration were normalized, their SXFA polymers were at least one magnitude less sensitive than the NRL counterpart. The huge difference between the same sorbent materials was quite astonishing. It indicated that the conventional hexafluoroacetone synthetic route was somewhat difficult to handle, resulting in some impurities in the target polymers. Thus, the simpler, easier and more effective new route present in this article was much highlighted.

In Table I, a strong HBA sorbent polymer dubbed PLF[25,26] is also listed. The PLF was spray-coated on a 98 MHz Rayleigh wave delay line device and several Love wave devices with frequencies ranging from 87 to 115 MHz. To facilitate the intercomparison, Δf of the Rayleigh wave sensor was only presented in Table I. After some preliminary normalization, it was clearly

that our LSFA had a fourfold higher sensitivity than the PLF. More importantly, the sorption of PLF coating towards DMMP or sarin was much slowly. It took more than 1500 s to saturate at a medium concentration of 10 mg m^{-3}, and at the initial 30 s, the response was <20% of the whole peak height. This much slow response behavior of a HBA polymer towards nerve agents was quite abnormal, suggesting that the PLF polymer was not pure and some nonhydrogen bond sorption mechanisms existed.

PLF was also synthesized by our team through the same hydrosilylation method, and the comparison between LSFA-coated and PLF-coated SAW sensor was investigated, shown in the bottom line of Table I. The LSFA-coated sensor exhibited three times the response value of the PLF-coated one, and the response time was just 1/3 to the counterpart.

Repeatability of the LSFA-coated sensor to 3 mg m^{-3} of DMMP was illustrated in Figure 6. It can be seen from the figure, the frequency shift value was almost invariable, four gas/on off cycles showed similar responses, indicating good repeatability of the sensor.

Selectivity

Figure 7 showed the responses of the LSFA coated sensor to DMMP as a comparison to some interfering vapors, among which ethanol and acetone were polar hydrocarbons, DCE and
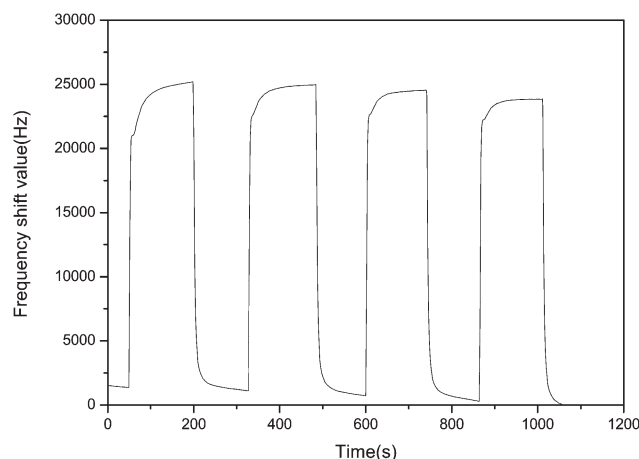

Figure 6. Repeatability of the LSFA-coated sensor to 3 mg m^{-3} of DMMP.
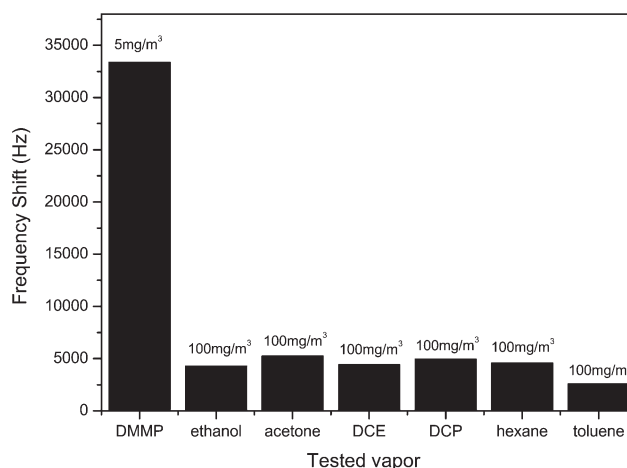

Figure 7. Responses to DMMP compared to interference gases.

DCP were halogenated hydrocarbons, hexane and toluene were nonpolar hydrocarbons. Although the concentrations of the interferences were 20 times higher, the LSFA sensor responded to the interferences were <15% of the response to DMMP. Thus, good selectivity of LSFA-coated SAW sensor to DMMP was demonstrated.

CONCLUSION

A new siloxane polymer (LSFA) for nerve agents sensing was synthesized by hydrosilylation reaction with 2-vinylhexfluoroisopropanol instead of highly toxic hexafluoroacetone. The gas sensitive properties of LSFA to DMMP as well as some common interferences were investigated using a 433.9 MHz SAW sensor platform. The exposure tests under 1–50 mg m^{-3} DMMP resulted a nonlinear calibration curve with a response of 10 kHz at 1 mg m^{-3} and response times <20 s for all the tested concentrations. Thus, high sensitivity, along with fast response, full recovery, and good selectivity of the LSFA sorbent coating was demonstrated. Comparing with SXFA and PLF, which had much similar molecular structure to LSFA, the excellent sensing properties of LSFA verified that the new synthetic route was feasible. The new route was much simpler, easier and low toxic, it can be a good alternative to the conventional ones.

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