

Synthesis and Evaluation of Hexafluoroisopropanol-Functionalized Polysiloxane as a New Coating Material for Sensors

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ABSTRACT: A new polysiloxane polymer as a coating material for surface acoustic wave (SAW) sensors was synthesized. The polymer was a linear polysiloxane functionalized with hexafluoroisopropanol (HFIP) groups, poly{methyl [4-(hexafluoroisopropanol) phenylethyl] siloxane}. The polymer was spin-coated on a 200-MHz SAW sensor for the detection of a 2,4-dinitrotoluene vapor. A fast response time of 30 s and good reproducibility were

achieved. It was found that the frequency shift decreased as the polymer concentrations decreased. The new polysiloxane coatings showed excellent properties, such as a high sensitivity, high permeability, and low glass-transition temperature ($-40.5 \pm 1^\circ\text{C}$). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4136–4140, 2012

Key words: coatings; polysiloxanes; sensors

INTRODUCTION

Nowadays, more and more attention is paid to the security situation in the world. Antiterrorism has become the consensus of the international community. The development of chemical sensors to accurately detect toxic gases and explosives has become the focus of the study, particularly, in public places, such as airports, wharfs, and stations. There is a critical need for detectors and sensors that are able to provide warnings of imminent chemical warfare agents, hazardous gases, explosive vapors, and environmental pollutants. The objective of sensor technology is to supply reliable information to us by the realization of sensors that produce controllable signals for human interfacing.^{1,2} Compared to conventional and well-established analytical techniques, surface acoustic wave (SAW) devices used as chemical vapor sensors are very sensitive, have low detection limits, have a high dynamic range, and can be easily adapted to various gas or vapor detection.³

SAW chemical sensors are a kind of vapor sensor that can detect chemical toxic gases and explosives in real time. This sensor has attracted considerable attention because of its small size, good sensitivity, fast response, and low cost. The basic principle of

SAW gas sensors is the reversible sorption of chemical vapors by a sorbent coating that is sensitive to the vapor to be detected. The vapor is sorbed by the sensitive layer; this results in a mass increase of the coating, which alters the SAW in the device. The change of SAW velocity is measured with the device as the frequency-controlling element in an oscillator circuit, and the frequency shifts are measured by the vapor sorption.^{1,4}

The performances of SAW sensors, such as sensitivity, selectivity, response time, reversibility, and environmental stability, are predominated by the chemical natures and physical properties of the coating layers. Thin polymer films can be used as chemoselective coatings for SAW devices. The coating of SAW devices with different polymer films leads to sensors with different sensitivities toward a broad variety of possible analytes.^{5–7} A high sensitivity, fast vapor diffusion, reversible responses, and excellent ability to work at room temperature are necessary properties for polymers when sensing. Polymers can be flexibly modified or tailored toward different analytes.^{8,9} High-quality thin films of fragile chemoselective polymers with precise thicknesses, low densities, and chemical integrities are required for advanced chemical-sensor applications. Functionalized polysiloxanes can possess desirable physical properties for chemical-sensing applications,^{10–13} which show high permeability, good affinity, low glass-transition temperature (T_g), environmental stability, and good thermal stability. Polymers with hydrogen-bond acidity play an

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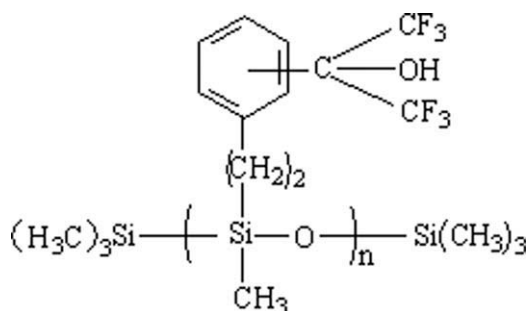


Figure 1 Structure of the HFIP-functionalized polysiloxane, that is, SXPHEFA.

important role during detection.^{14–17} It is effective to incorporate fluorinated alcohol groups to enhance the hydrogen-bond acidity of a polymer. Polysiloxanes functionalized with hexafluoroisopropanol (HFIP) groups are promising polymers for use in SAW sensors.

In this work, a new polysiloxane, poly{methyl [4-(hexafluoroisopropanol) phenylethyl] siloxane} (SXPHEFA), was synthesized. The polymer was coated on the piezocrystal by spin coating. In the gas supply system, 2,4-dinitrotoluene (2,4-DNT) was used as a simulation gas, and the responses of the SAW sensor were tested. The influence of hydroxyl content and analyte concentration on adsorbability is also discussed.

NEW POLYSILOXANE MATERIAL SXPHEFA

The structure of the sensitive coating polysiloxane polymer is given in Figure 1. The polysiloxane polymer was the linear polyphenethylmethylsiloxane (PMPES) functionalized with HFIP groups. The polysiloxane polymer was chosen because of its high permeability to gas and its low transition temperature, and the HFIP group imported acid function for action with 2,4-DNT vapor because 2,4-DNT is a vapor with strong hydrogen-bond basic properties. Silicon–oxygen bonds in the polymer backbone can lower the polymer T_g and improve the rate of vapor diffusion,¹⁵ so the polysiloxane polymer possesses good properties of low T_g and high permeability.

In this work, for organohalosilanes that have a very low reactivity of halogen, a metal oxide was employed to produce cyclic or linear oligomeric organosiloxanes; this was categorized as a nonhydrolytic reaction.¹⁸ This process provides a unique method of obtaining the siloxane trimer (P_3), which played an important role in the anionic ring-opening polymerization described later. Linear PMPES was obtained via an anionic ring-opening polymerization. Then, the objective product SXPHEFA was synthesized from PMPES functionalized with HFIP groups.

EXPERIMENTAL

Materials and devices

The chemosensitive coating material SXPHEFA was synthesized in our laboratory. Phenethylmethyl-dichlorosilane was purchased from ABCR GmbH & Co. KG (Karlsruhe, Germany) and *n*-Butyllithium (*n*-BuLi) was purchased from Alfa Aesar (Tianjin, China). Hydrate hexafluoroacetone and carbon disulfide were both analytical reagent grade and were obtained from San'aifu (China) and Kelong (China), respectively. Other materials, including ethyl acetate and zinc oxide, were all analytical reagent grade and were obtained from Kewei (China).

The 200-MHz SAW two-port resonator devices used in this study were obtained. The device was fabricated onto an stable temperature (ST)-quartz substrate with an Al electrode. Each interdigital transducer had 50 pairs of fingers with a spatial period of about 15.8 μm and an acoustic aperture of about 100 wavelengths. Two reflecting gratings, with 300 fingers at each side, were located externally to the interdigital transducer. The insert loss of the device was 7 dB, and the loaded Q (Quality factor, a parameter which determines the frequency stability of oscillator) value was over 9000. A conventional dual-channel configuration, which consisted of a reference channel and a sensing channel, was used to reduce secondary interactions, such as temperature. Each channel was excited individually by an oscillator circuit. Then, the frequency difference between the two channels was obtained by a mixer circuit, recorded by a frequency counter, and subsequently transferred to a microcomputer. The two SAW devices were placed closely on the same side of the printed circuit board.

Procedures

The synthetic procedures of the polysiloxane SXPHEFA are shown in Figure 2.

All glassware, needles, and syringes were dried in an oven at 130°C for more than 24 h. In a typical reaction, zinc oxide (4.46 g) was suspended into ethyl acetate (40 mL) in a 100-mL, three-necked, round-bottom flask reactor with vigorous stirring. In each reaction, a 10% excess of zinc oxide was used to ensure complete reaction with the dichlorosilane. Cupric chloride (0.57 g) was added as a catalyst. Phenethylmethyl-dichlorosilane (10 mL) was added slowly over 1 h with a dropping funnel. The reaction mixture was stirred for 24 h at room temperature. Upon completion of the reaction, P_3 was obtained after several separations.

P_3 (4.03 g) was added to the reactor, and a magnetic stirrer bar was placed inside. The reactor was sealed with a rubber septum and purged with N_2 gas by a needle. At the same time, another needle was inserted

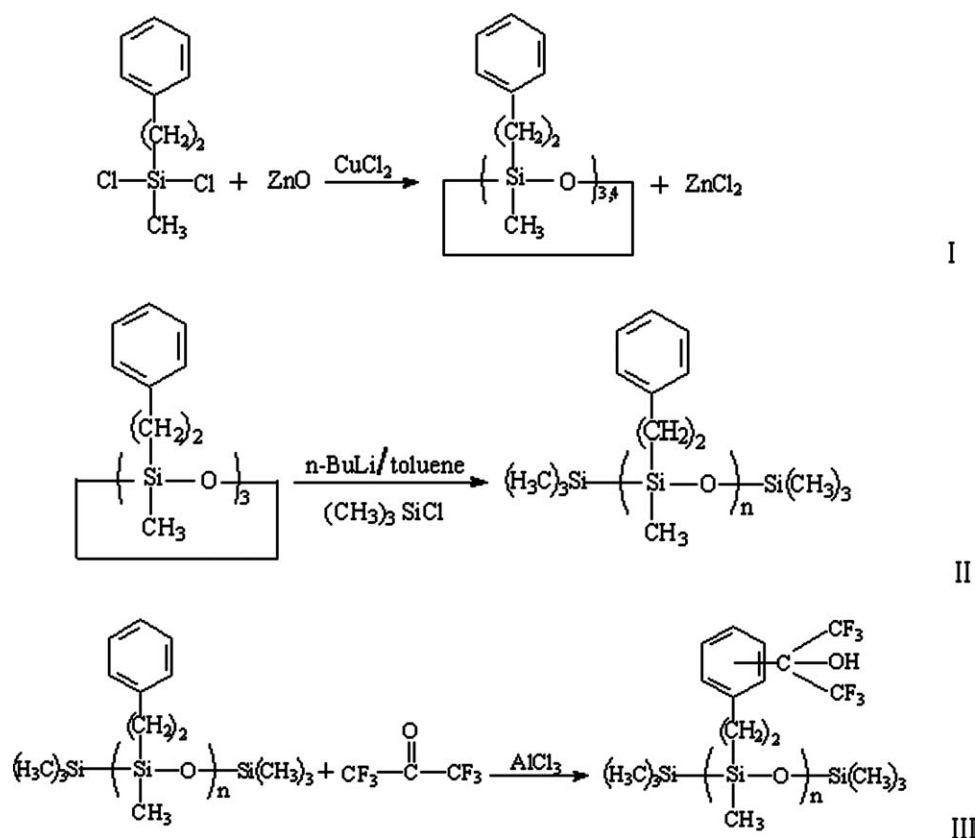


Figure 2 Process of the synthesis of SXPHEFA, a three-step reaction. (I) Cyclic siloxane oligomer (P3) was synthesized by a polycondensation reaction with phenethylmethylchlorosilane and zinc oxide, (II) PMPES was synthesized by an anionic ring-opening reaction, and (III) SXPHEFA was synthesized from PMPES and hexafluoroacetone.

through the septum so that moisture could escape from the reactor. Distilled solvent (10 mL of toluene) was transferred directly into the reactor by a transfer needle to avoid possible air contact. After that, the reactor was immersed in the oil bath or cold bath, depending on the desired temperature, which was already set. As an initiator, *n*-BuLi (0.08 g) was injected through the rubber septum at one time, and the distilled promoter, hexamethylphosphoramide (0.14 g), was also inserted through the rubber septum with a syringe after 10 min. Polymerization was left for the desired time period, up to 20 h. Then, the terminating agent, chlorotrimethylsilane (10 mL), was added to the reactor to terminate the polymerization and left another 1 h to ensure complete termination. PMPES was obtained after separation.

Distilled solvent (carbon disulfide, 10 mL), PMPES (1.82 g), and AlCl₃ (0.15 mg) were added successively to a 100-mL four-necked flask. A gas generator supplied hexafluoroacetone (HFA) gas via a dehydration reaction between hydrate hexafluoroacetone and concentrated sulfuric acid. The reaction between HFA and PMPES was a gas-liquid reaction. Upon completion of the reaction, the reaction system was purged with nitrogen to make the HFA gas absorbed completely by water. The solution was transferred to a separatory funnel and washed with deionized water

to remove the aluminum chloride. The solvent was distilled in a constant-temperature water bath at 60°C for 5 h and was subsequently put in a vacuum oven to remove the residual moisture.

RESULTS AND DISCUSSION

The PMPES and the sensitive coating material (SXPHEFA) were characterized by infrared spectroscopy (Figs. 3 and 4).

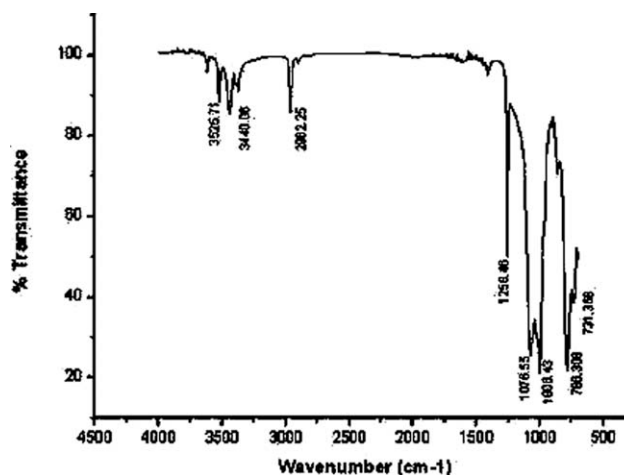


Figure 3 Infrared spectrum of PMPES.

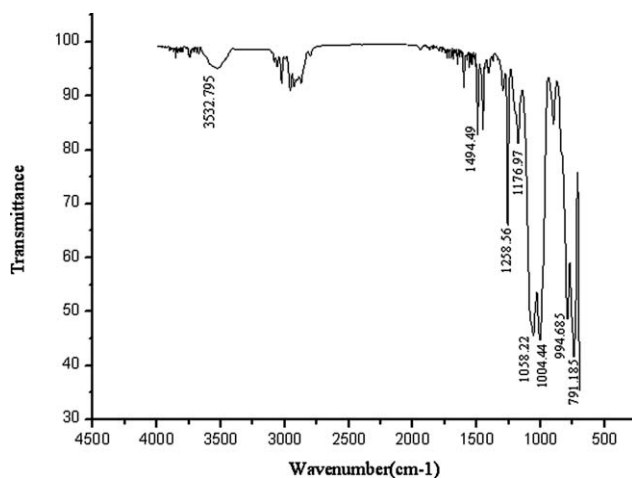


Figure 4 Infrared spectrum of SXPHEFA.

Both spectra exhibited the stretching vibrations of Si—O—Si at 1000–1083 cm^{-1} . The spectra in Figure 4 shows the characteristic stretching vibrations of —OH at 3532.795 cm^{-1} . The absorption of peaks at 1168–1270 cm^{-1} was attributed to the stretching vibrations of C—F bonds. These data indicate that the linear PMPES was functionalized with HFIP groups.

Figure 5 shows the gel permeation chromatograph of PMPES; through analysis, we obtain the following results: weight-average molecular weight (M_w) = 4223, number-average molecular weight (M_n) = 3681, and $M_w/M_n = 1.147$. The molecular weight distribution was narrow; this illustrated that the active centers in the anionic ring-opening polymerization reaction were uniformly distributed and that the chain length of polysiloxane that we obtained was relative to the average.

The sensitive polymer was analyzed by differential scanning calorimetry. The polymer displayed a clear T_g of $-40.5 \pm 1^\circ\text{C}$ (Fig. 6). (Taking into account the various error factors, we allowed 1°C of fluctuation). It is beneficial to operate SAW sensors at a low temperature.

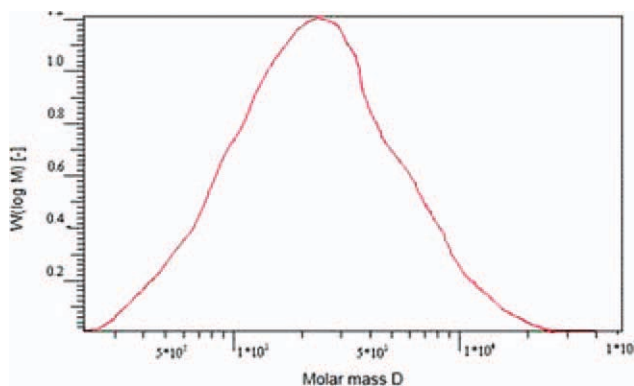


Figure 5 Gel permeation chromatography curve of PMPES: W = weight; M = molecular weight; D = distribution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

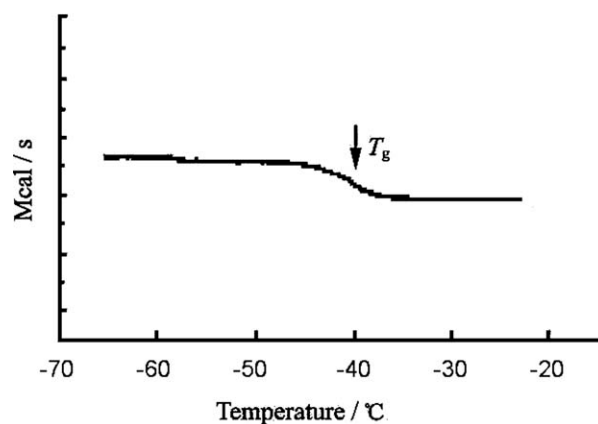


Figure 6 Differential scanning calorimetry curve of SXPHEFA, which displayed a T_g of -40.5°C . Vertical axis is the heat flow rate, $1 \text{ Mcal/s} = 10^6 \text{ cal/s}$.

Ion chromatography¹⁹ was used to analyze the content of elemental fluorine (A), and its principle was to combust the sample in an oxygen bottle. The hydrogen fluoride gas generated in combustion was absorbed by 25 mL of deionized water, and 5 mL was taken and diluted by corresponding multiples to be measured with ion chromatography. By comparing the ion chromatography of the sample with the ion chromatography of a standard sample of fluorine, we calculated A in the analyte. The formula is given as follows:

$$A = \frac{25 \times 0.025hn}{Hm} \times 100\%$$

where h is peak height of elemental fluorine, H is the standard peak height of elemental fluorine, n is the dilution multiple, and m is quality of the sample.

In this study, H was 2797. h in the sample was 1796. In the experiment, n was 5, and m was 15.68 mg. The calculated result was 12.8%; this proved that HFA and PMPES had a good reaction.

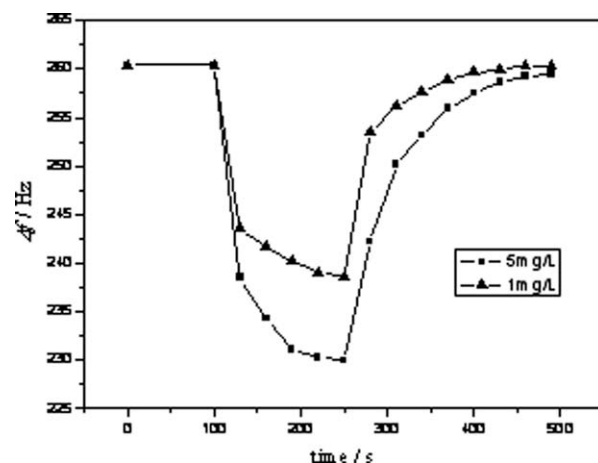


Figure 7 Response curve of the substrate with different concentrations.

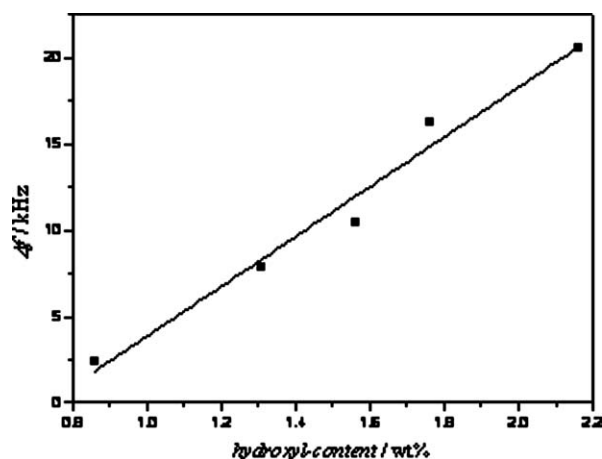


Figure 8 Influence of the hydroxyl content of the polysiloxane polymer on the adsorption performance of the coating material.

The sensitive polymer was coated onto the substrates 1 and 2 at concentrations of 5 and 1 mg/mL, respectively. We chose a standard blank substrate, which was treated with the following process: we (1) scrubbed the surface with acetone, (2) cleaned it with deionized water, (3) treated it with ultrasound in tetrahydrofuran for 15 min, and (4) kept it in a vacuum oven at 25° for 20 h. The response curve is shown in Figure 7. When the 2,4-DNT was injected into the chamber, the frequency changed immediately with the absorption of the vapor. From Figure 4, we can see that equilibrium was reached after about 30 s; this was a fast response, compared with that seen in other data (100 s).²⁰ The frequency shift (Δf) in substrate 1 reached 21.9 kHz, whereas the frequency shift in substrate 2 reached to 16.9 kHz; this indicated that the frequency shift decreased as the polymer concentration decreased.

After desorption, we did the same experiments and found that the polymer we synthesized still had a good adsorption capacity, which showed its good reversibility.

The functional group —OH was the critical group in the polysiloxane polymer, which could affect the adsorption performance of the coating material because it showed high hydrogen-bond acidity. To investigate the influence of the hydroxyl content on adsorption, five polymer coatings were tested. By plotting the frequency shifts against the hydroxyl contents, we observed a linear evolution. Figure 8 shows the influence of the hydroxyl content on adsorption and indicates that the frequency shift increased with increasing hydroxyl content.

The quality of the film directly determined the sensitivity. We knew that the process of coating with

a polymer of higher concentration led to a stronger adsorption. The more hydroxyls the polysiloxane polymer had, the more easily adsorption happened. In addition, the sensitivity of the coating also had a relationship with the concentration of the analyte. Future study on the mechanism and performance is needed.

CONCLUSIONS

The synthesis and evaluation of HFIP-functionalized polysiloxane as a new coating material for sensors have been described. SXPHEFA, a linear polymer functionalized with HFIP groups, showed sensitive characteristics when tested. A fast response, high sensitivity, good reversibility, and reproducibility were realized. Therefore, we succeeded in developing a new coating material for SAW sensors that promises excellent performance.

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