# Hybrid Organic/Inorganic Copolymers with Strongly Hydrogen-Bond Acidic Properties for Acoustic Wave and Optical Sensors

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Hybrid organic/inorganic polymers have been prepared incorporating fluoroalkyl-substituted bisphenol groups linked using oligosiloxane spacers. These hydrogen-bond acidic materials have glass-to-rubber transition temperatures below room temperature and are excellent sorbents for basic vapors. The physical properties such as viscosity and refractive index can be tuned by varying the length of the oligosiloxane spacers and the molecular weight. In addition, the materials are easily cross-linked to yield solid elastomers. The potential use of these materials for chemical sensing has been demonstrated by applying them to surface acoustic wave devices as thin films and detecting the hydrogen-bond basic vapor dimethyl methylphosphonate with high sensitivity. It has also been demonstrated that one of these materials with suitable viscosity and refractive index can be used to clad silica optical fibers; the cladding was applied to freshly drawn fiber using a fiber drawing tower. These fibers have potential as evanescent wave optical fiber sensors.

## Introduction

The application of a sorbent thin film to a suitable electronic or optical device represents a general approach to the development of a chemical sensor. For the detection of organic vapors, polymers offer a number of advantages as the sorbent material. Diffusion of absorbed vapors within the material is quite rapid, provided that the glass-to-rubber transition temperature ($T_g$) is below the operating temperature of the sensor. Polymers are processable into thin films on sensor devices, although attention must be paid to adhesion and dewetting issues for very thin films.[1] The sorbent properties and hence the chemical selectivities of polymer materials vary with the chemical structure. Polymers also offer selectivities among volatile organic compounds comparable to various cavitands on acoustic wave vapor sensors, despite claims for molecular recognition using the latter types of films.[2] For efficient sensor development, it is necessary to be able to select or design polymers so that they will absorb organic vapors of interest in a predictable manner.

The influence of chemical structures and the resulting solubility properties of sorbent polymers on the sorption of organic vapors has been studied systematically using linear solvation energy relationships (LSERs).[3−7] In these and related sensor studies, we have screened and characterized a variety of polymers with particular solubility properties for participation in dispersion, dipole−dipole, and hydrogen-bonding interactions.[3−9] For the sorption and detection of basic vapors, it is advantageous to incorporate strongly hydrogen-bond acidic functional groups into the polymer.[3,10,11] Such polymers are not readily available. None of the conventional gas chromatographic stationary phases are strong hydrogen-bond acids, and those that are more modest hydrogen-bond acids (docosanol, sorbitol, and diglycerol) are not polymers.[12−14] Moreover, of the vast number of commercially available polymers, very few have strong hydrogen-bond acidic properties.

In past sensor studies, an oligomeric epoxy dubbed “fluoropolyol” emerged as a useful material for the detection of basic vapors such as organophoshorus compounds using surface acoustic wave (SAW) sensors

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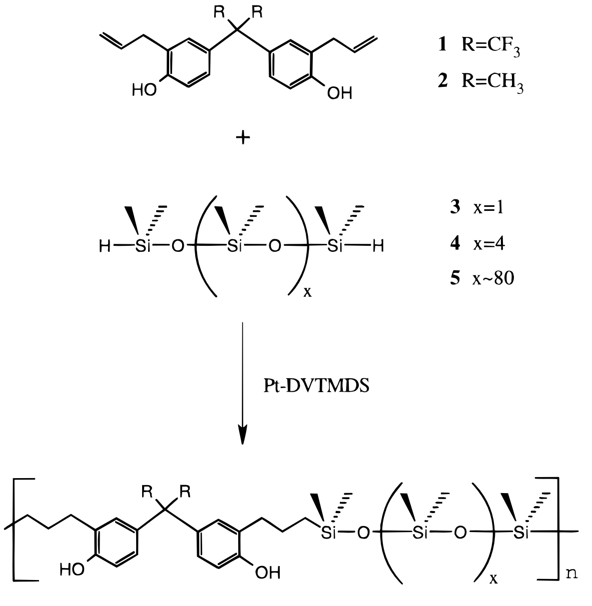
**Scheme 1**



**1** R=CF$_3$

**2** R=CH$_3$

**3** x=1

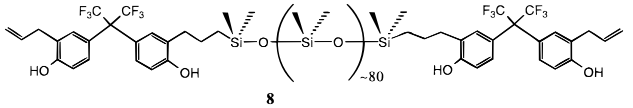
**4** x=4

**5** x~80

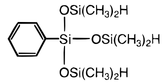
**6** x=1, R=CF$_3$

**7** x=4, R=CF$_3$

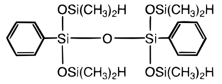
**Scheme 2**



**8**



**9**



**10**

and for use in sensor arrays.[8−11,15,16] This material has also been used as a component of a polymer/phthalocyanine composite Langmuir−Blodgett films on chemiresistor sensors.[17] This fluorinated polymer has hydroxyl groups along the polymer backbone that are responsible for its hydrogen-bond acidic properties.

On the basis of a survey of solubility interactions and hydroxylic organic functional groups, fluorinated alcohols, and fluorinated or fluoroalkyl-substituted phenols appear to be the best target structural units to use in designing new selective hydrogen-bond acidic materials.[3] Fluorination increases the hydrogen-bond acidity of the hydroxyl group and decreases the basicity at the same time. Minimizing basicity in such materials reduces the extent and strength of self-association, which would otherwise tend to lessen the driving force for interacting with basic vapors. Self-association is a problem with carboxylic acids, for example, which are good hydrogen-bond acids as monomers but are nearly always self-associated in condensed phases. The use of fluorinated alcohols in polymers to promote interactions with basic vapors was recognized in early studies by Barlow and co-workers, who modified polystyrene with hexafluoro-2-propanol (HFIP) groups.[18,19] Snow and co-workers synthesized and investigated a series of materials incorporating HFIP groups into polymers based on poly(styrene) and poly(isoprene).[10] These materials on SAW devices afforded vapor sensors with high sensitivities to organophosphorus compounds, but both the parent polymers and the HFIP-containing materials were glassy at room temperature. Recently, an HFIP-containing polymer based on a polysiloxane backbone has been described and demonstrated to be a good hydrogen-bond acid on the basis of inverse chromatography and LSER studies.[4] The polysiloxane backbone provides a material with a $T_g$ well below room temperature.

We now turn our attention to the development of hydrogen-bond acidic polymers using phenolic functionalities. The groundwork for this effort was laid by Abraham and co-workers when they investigated the hydrogen-bond acidic properties of a series of phenolic liquids using inverse GLC and LSERs.[20] In this study, the most strongly hydrogen-bond acidic materials were a fluoroalkyl-substituted bisphenol with pendant allyl groups, **1**, and a variant with pendent propyl groups. (See Schemes1 and 2 for structures of numbered materials.) These were significantly more acidic than similar compounds without the fluorination, such as **2**. The LSER *b* coefficient, which measures hydrogen-bond acidity, was 4.56 for fluorinated **1,** compared to only 2.41 for unfluorinated **2**.[20] Since these coefficients are used in an equation that predicts the *logarithm* of a partition coefficient, an increase in the *b* coefficient of 2 units corresponds to increasing the extent of sorption due to the hydrogen-bonding interaction by a factor of 100. Indeed the observed partition coefficients for ethylamine into **1** and **2** were 10 800 and 56, respectively,[20] demonstrating the profound advantage in using the fluorinated material to promote the sorption of basic vapors.

In the present study, we have created hybrid organic/inorganic polymers and oligomers, incorporating hexafluorobisphenol A as the organic portion and using oligomers or polymers of dimethylsiloxane as the inorganic portion. The organic portion has interactive sites providing the desired sorbent properties, whereas the inorganic portion is used to tune the physical properties. The resulting materials have $T_g$ values below room temperature, facilitating rapid vapor diffusion. The physical properties such as refractive index and viscosity can be systematically varied. In addition, these materials have been designed so that they can be cross-linked. We are interested in these materials for both acoustic wave and optical fiber sensors for the detection of basic organic vapors.

## Experimental Section

**Materials**. Solvents and reagents obtained from commercial sources were used as received. 2,2-Bis(3-allyl-4-hydroxyphenyl)hexafluoropropane was obtained from Organic Consultants, Inc., Eugene, OR, who characterized their product by IR and NMR and confirmed the purity by gas chromatography. They prepared it according to the method described

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by Abraham.[20] Platinum catalysts were obtained from United Chemical Technologies, including platinum divinyldisiloxane complex in xylene (PC072) and platinum cyclovinylmethylsiloxane complex (PC085). Both catalysts are reported to contain 2−3% platinum. Dodecamethylhexasiloxane was prepared using the method of Uchida.[21] All other siloxanes were obtained from United Chemical Technologies or Gelest.

**Characterization Methods**. Spectroscopic charaterization was obtained on a Nicolet 740 FT-IR spectrometer, a Varian VXR-300 NMR spectrometer and a Perkin-Elmer 552A UV/vis spectrophotometer. Thermal analysis was performed under nitrogen on a Seiko SSC/5200 equipped with DSC 220C and TA/DTA 320 modules. $T_g$ is reported as the inflection point in the DSC trace. $T_d$ is reported as the point of 10% weight loss. Viscosity was measured with a Bohlin VOR Rheometer. Refractive index was measured on a Leica Mark II Abbe Refractometer. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN. Gel permeation chromatography (GPC) results were obtained from Scientific Polymer Products, Inc., Ontario, NY. Samples were analyzed on a Pnenomenex linear 500 Å−$10^6$ Å column at 30 °C using THF as the mobile phase. Molecular weights are referenced relative to polystyrene standards.

**Copolymer 6:** 1,1,3,3,5,5-Hexamethyltrisiloxane (**3**, 0.566 g, 0.002 72 mol) was added to a magnetically stirred solution of 2,2-bis(3-allyl-4-hydroxyphenyl)hexafluoropropane (**1**, 1.192 g, 0.002 86 mol) in 20 mL of toluene, giving a molar ratio of reacting functional groups, $r = [SiH]/[CH_2{=}CH]$, equal to 0.95. One drop of the platinum-1,3-divinyltetramethyldisiloxane catalyst in xylene was added, and the solution was heated to 100−112 °C in an oil bath. The disappearance of Si−H (2127 $cm^{-1}$) was monitored by FTIR. After 20 min all Si−H functionality had been consumed. Additional quantities of **3** (to a total of 0.736 g, 0.003 53 mol, $r = 1.18$) were repeatedly added to the heated reaction mixture until excess Si−H functionality was detected. Finally, excess 1,3-divinyltetramethyldisiloxane (0.057 g, 0.000 31 mol) was added to ensure that all polymer chains would be terminated with allyl or vinyl functionality, and the mixture was heated for an additional 2 h. Catalyst was removed by treating the reaction mixture with activated charcoal and then filtering. After removal of solvent by rotary evaporation, residual volatiles were removed by heating under vacuum for 19 h at 60 °C and then for 40 min at 138−143 °C. Yield 1.717 g, 86%. The GPC data indicate a bimodal mass distribution; for peak 1 (79% peak area), $M_w = 116\,800$, $M_n = 10\,300$ ($M_w/M_n = 11.4$); for peak 2 (20% peak area), $M_w = 940$, $M_n = 890$ ($M_w/M_n = 1.1$). Anal. Calcd: C, 51.90; H, 6.13; F, 18.24. Found: C, 50.66; H, 6.05; F, 17.33. $n^{22} = 1.482$. FTIR (neat) 3607, 3430, 3075, 3043, 2958, 2928, 2873, 2797, 1612, 1508, 1428, 1343, 1253, 1214, 1191, 1133, 1050, 964, 922, 838, 798, 761, 741, 716 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 7.37 (d), 7.07−7.13 (m, 4H), 6.88 (br), 6.79 (d), 6.72 (d, 2H), 5.34 (br, 2H), 5.03 (br, 2H), 2.53−2.61 (m, 4H), 1.56−1.61 (m, 4H), 0.49−0.58 (m, 4H) −0.02−0.10 (m). $^{13}C$ NMR ($CDCl_3$) $\delta$ 153.8, 133.0, 123.4, 129.2, 129.1, 128.2, 128.1, 125.6, 124.5 q ($CF_3$), 114.8, 114.6, 63.7 hept ($C^{CF_3}$), 33.5, 33.3, 23.6, 23.1, 18.0, 17.8, 1.2, 1.0, 0.1, −0.3. $^{19}F$ NMR ($CDCl_3$) $\delta$ −77.23 (relative to $CFCl_3$ standard). UV (MeOH) $e_{max}$, 4,500; $\lambda_{max}$, 275 nm, $e_{max}$, 4,300; $\lambda_{max}$, 282 nm. $T_g$(DSC) 6 °C. $T_d$(TGA) 350 °C.

**Copolymer 7:** 1,1,3,3,5,5,7,7,9,9,11,11-Dodecamethylhexasiloxane **4** (1.961 g, 0.004 55 mol), **1** (1.995 g, 0.00479 mol), and one drop of platinum-1,3-divinyltetramethyldisiloxane catalyst were reacted in 40 mL of toluene at 100−110 °C ($r = [SiH]/[CH_2{=}CH] = 0.95$). Si−H functionality was greatly diminished but still visible after 30 min and was just visible at the baseline after another hour. The mixture was heated 16.5 more h, followed by addition of **4** (0.062 g, 0.000 14 mol) to increase $r$ to 0.98. After another 24 h of heating the Si−H peak had diminished to the point where it was barely distinguishable from the baseline. Further polymerization was not attempted. After treatment with activated charcoal, filtration, and rotary evaporation, the product was heated under vacuum at 60 °C for 72 h and 139−144 °C for 1.5 h. The product (3.546 g, 88%) is a thick, yellow oil. The GPC data indicate a bimodal mass distribution; for peak 1 (86% peak area), $M_w = 120\,100$, $M_n = 12\,200$ ($M_w/M_n = 9.8$); for peak 2 (8% peak area), $M_w = 1200$, $M_n = 1200$ ($M_w/M_n = 1.0$). Anal. Calcd: C, 46.78; H, 6.66; F, 13.45. Found: C, 46.67; H, 6.40; F, 13.00. $n^{20} = 1.471$. FTIR (neat) 3612, 3443, 3074, 3042, 2961, 2929, 2873, 2798, 1612, 1509, 1428, 1344, 1259, 1211, 1133, 1058, 965, 922, 860, 837, 803, 742, 715 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 7.04−7.17 (m, 4H), 6.70−6.76 (m, 2H), 5.22 (br, 2H), 2.60 (t, 4H), 1.61 (quint, 4H), 0.56 (t, 4H), 0.06 (s, 12H), 0.04 (s, 12H), 0.03 (s, 12H). $^{13}C$ NMR ($CDCl_3$) $\delta$ 153.9, 132.4, 129.2, 127.9, 125.5, 124.4 q ($CF_3$), 114.8, 63.6 hept ($C^{CF_3}$), 33.5, 23.6, 17.8, 1.1, 0.1. $^{19}F$ NMR ($CDCl_3$) $\delta$ −77.19 (relative to $CFCl_3$ standard). UV: $e_{max}$, 4400; $\lambda_{max}$, 276 nm, $e_{max}$, 4300; $\lambda_{max}$, 282 nm. $T_g$(DSC) −16 °C. $T_d$(TGA) 377 °C.

**Material 8:** Hydride terminated poly(dimethylsiloxane) (**5**, 8.671 g, $M_n = 6000$) and one drop of platinum-1,3-divinyltetramethyldisiloxane complex were added to **1** (1.208 g, 2.901 mol) in 40 mL of toluene, and the solution was heated to 110−120 °C. Si−H functionality was undetectable after 40 min. Treatment with activated charcoal, filtration, and rotary evaporation yielded the product (9.705 g, 98%) as a light yellow fluid of moderate viscosity (~1500 cSt measured by rheometer). GPC gave monomodal distribution with $M_w = 34\,300$ and $M_n = 15\,400$ ($M_w/M_n = 2.2$). Anal. Calcd: C, 35.51; H, 7.64; F, 3.34. Found: C, 35.49; H, 7.47; F, 3.11. $n^{20} = 1.422$. FTIR (neat) 3827, 3763, 3701, 3614, 3460, 3080, 3041, 2962, 2905, 2801, 1945, 1613, 1512, 1413, 1345, 1260, 1214, 1189, 1093, 1024, 864, 800, 744, 704, 662 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 7.07−7.14 (m, 4H), 6.70−6.79 (m, 4H), 5.90-6.16 (m), 5.08−5.35 (m), 3.37 (d), 2.59 (t, 4H), 1.58−1.64 (m, 4H), 0.55 (t, 4H), −0.12−0.27 (m). $T_d$(TGA) 400 °C.

**Cross-linking of 6−8:** Material **8** (1.239 g), phenyltris(dimethylsiloxy)silane (**9**, 0.040 g, 0.000 12 mol) and platinum cyclovinylmethylsiloxane complex (0.0008 g, 16 ppm) were mixed together in a glass vial and degassed by evacuating and purging with $N_2$ several times. The vial was heated to 100 °C for 1 h under an $N_2$ flow, converting the pourable liquid to a solid transparent elastomer. Polymers **6** and **7** were cross-linked with 1,3-diphenyl-1,1,3,3-tetrakis(dimethylsiloxy)disiloxane (**10**) and phenyltris(dimethylsiloxy)silane (**9**), respectively, in an analogous fashion. Due to the high viscosity of **6** and **7**, the polymer, cross-linker, and catalyst were first dissolved in a few drops of $CH_2Cl_2$ to promote mixing. The vials were then placed on a hot plate on low heat for 1 h to remove most of the solvent prior to degassing. Cross-linking at 100 °C under an $N_2$ converted these materials from sticky gums or oils to solid elastomers. SiH to vinyl ratios in these various cross-linking reactions generally varied from 1:1 to 1.5:1.

**SAW Resonators, Oscillators, and Frequency Data Collection.** The SAW devices used in this study were 200 MHz two-port resonators described and used in previous studies.[1,15,22] These devices are made of ST-cut quartz with aluminum metallization and a thin silicon dioxide overcoat. The SAW resonators and oscillator electronics to drive them were obtained from Femtometrics, Costa Mesa, CA. Frequency measurements were made using a Hewlett-Packard 53131A high-performance universal counter with a medium-stability timebase, transferring the data to a Macintosh computer using the IEEE-488 bus and collecting data with Labview software. Sensor temperatures were controlled using a single brass heat sink clamped against the lids of both the sampling sensor (array) package and the reference device package. Water from a refrigerated circulating water bath circulated through the brass heat sink. Temperatures were monitored with a type K thermocouple (0.005 in. diameter, Omega) in contact with the header. All experiments were conducted with the sensor temperature at 25 °C.

The resonators were always cleaned in a Harrick plasma cleaner prior to polymer film application.[1] Spray-coated polymer films were applied to the SAW resonators as described

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previously,[15,22,23] using an airbrush supplied with compressed dry nitrogen and a dilute solution (0.2% by weight) of the polymer in chloroform. The frequency was monitored during deposition, using the change in frequency as a measure of the amount of material applied. After application, the films were annealed at 50 °C overnight. Spray-coated films were always examined by optical microscopy with a Nikon microscope using reflected light Nomarski differential interference contrast.

**Vapor Generation.** Vapor streams were generated from bubbler sources that were maintained at 15 °C in machined aluminum blocks with inlets and outlets for water from a refrigerated circulating water bath. The carrier gas for bubbler vapors and dilution of saturated vapor streams was dry nitrogen. The saturated bubbler vapor streams were diluted using a pulse-width modulation method described in detail in ref 24. The vapor generation system used was a custom system at Pacific Northwest National Laboratory (PNNL): the hardware was assembled by Microsensor Systems, using components normally used in their VG7000 and VG400 systems. The sytem was constructed with stainless steel components, except the valves, which used Teflon-wetted surfaces. In our custom design, all gas flows were regulated with electronic mass flow controllers and eight selectable bubbler sources were included in the system. The vent system was modified and adjusted at PNNL (see ref 24), and all system programming was done at PNNL. The instrument output is either the diluted vapor stream or clean carrier gas, each at a flow rate of 100 mL/min.

Vapor exposure experiments were carried out by first generating and equilibrating a vapor stream for 20 min while delivering clean carrier gas to the sensor. Vapor was then delivered to the sensor for 10 min, followed by 15 min of clean carrier gas for sensor recovery, followed by one or two additional 10 min vapor exposures separated by 15 min of clean carrier gas. After each experiment, the system was flushed for 10 min (clean carrier gas output to sensor) to remove the previous vapor concentration. The frequency shift data reported in this paper represent the absolute value of the difference between the sensor baseline frequency under clean carrier gas and the steady-state signal during vapor exposure. All such frequency shifts were in the correct direction for a mass-loading response.

**Optical Fiber Drawing and Cladding.** Material **8** (38.7503 g, $M_n = 12\,300$) was combined with phenyltris(dimethylsiloxy)silane (**9**, 1.8468 g, 0.005 584 8 mol) and platinum cyclovinylmethylsiloxane complex (0.0239 g, corresponding to 0.0006 g of Pt). The viscous mixture was stirred until well blended and degassed under vacuum. The polymer was applied to a fused silica fiber as it was freshly drawn from a Heathway fiber drawing apparatus through a 205 $\mu$m Sandcliff cladding cup, and into a 45 cm long clamshell furnace for curing. The polymer was supplied to the cladding cup under a pressure of 0.8−1.5 psi. The optimal furnace temperature and fiber draw speed were 520 °C and 8−9 m/min, respectively. These conditions gave a fairly uniform coating that was light yellow in color and slightly tacky to the touch.

## Results and Discussion

**Design and Synthesis of AA/BB Copolymers.** The bisphenol **1** is easily prepared from hexafluorobisphenol A[20] and is thus a convenient starting material for the preparation of polymers with fluoroalkyl-substituted phenolic functionality. The pendant allyl groups provide potentially useful reactive sites for polymerization, provided that the chemistry used is selective for the double bonds and does not alter the hydroxyl groups, which must remain intact for the desired chemical interactions as a sensor material. In addition, the polymerization approach must yield a material with a low $T_g$. Oligosiloxane linkages were selected as a means to achieve this objective. The logical chemistry to link olefinic molecules to siloxane oligomers is hydrosilylation, in which Si−H bonds add across the allyl group in the presence of a suitable catalyst, typically Pt . However, we were initially concerned that the hydroxyl groups might undergo a competing dehydrocondensation reaction under hydrosilylation conditions. This reaction is well-known for alcohols and other protic species.[25−27] Nevertheless, Mathias[32] reported in a short communication in 1993 that a bisallyl derivative of bisphenol A (**2**) underwent rapid hydrosilylation with 1,1,3,3-tetramethyldisiloxane and 1,1,3,3,5,5-hexamethyltrisiloxane (**3**). Not only was the reaction selective for the allyl groups, but it proceeded surprisingly rapidly at ice bath temperatures to yield AA/BB block copolymers. Therefore we investigated this approach for the synthesis of our sensor materials.

AA/BB-type polymers **6** and **7** were synthesized from the reaction of the bis(allyl) bisphenol A derivative **1** with SiH-terminated trisiloxane **3** and SiH-terminated hexasiloxane **4**, respectively (see Scheme 1). The reaction of fluorinated **1** with **3** did not proceed noticeably at or below room temperature, in contrast to the reaction of unfluorinated **2** with **3** reported by Mathias. Upon heating to reflux in methylene chloride, the reaction proceeded mostly to completion in under an hour, as indicated by reduced intensity of the SiH peak at 2128 $cm^{-1}$ in the IR spectrum. At this point, the reaction slowed dramatically. After several days of reflux the SiH peak never completely disappeared, even when a slight excess of **1** was used. Under similar conditions, the reaction of **1** with dodecamethylhexasiloxane (**4**) was slower than the reaction with trisiloxane **3**. Significant rate enhancements were achieved at higher temperatures by conducting the reactions in toluene above 100 °C. With a slight excess of **1**, all SiH functionality was consumed in under an hour in the case of **3** and within several hours in the case of **4**.

With these conditions established, polymers **6** and **7** were prepared using the “one monomer deficient method”.[28−31] Thus, when **1** and **3** were mixed together in the synthesis of **6**, the molar ratio of reacting functional groups $r = [SiH]/[CH_2{=}CH]$ was initially set to 0.95. When IR analysis indicated complete consumption of SiH functionality, an additional amount of **3** was added to increase $r$ to 0.98. The process was continued until the SiH peak failed to disappear, which occurred when $r = 1.18$. The significant excess of **3** required to obtain a persistent SiH peak is probably due to evaporative loss of the slightly volatile trisiloxane. All remaining SiH functionality was consumed by the addition of excess 1,3-divinyltetramethyldisiloxane and heating for several hours. (Olefinic end groups were

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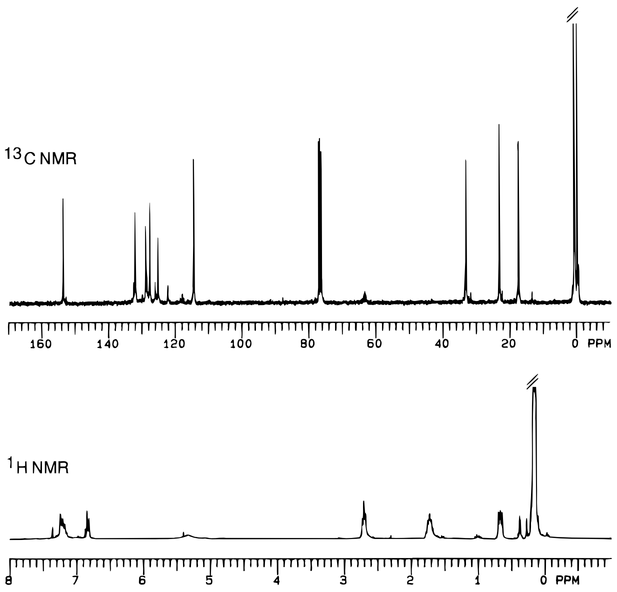

**Figure 1.** $^{1}$H and $^{13}$C NMR spectra of polymer **7**.

also desired so that the polymer could be cross-linked by hydrosilylation; see below.)

The “one monomer deficient method” was more difficult to use for the synthesis of polymer **7** from **1** and **4**, because the reaction rate was slower. When *r* reached 0.98, approximately 24 h of heating above 100 °C was required to consume all SiH functionality. Addition of **4** was discontinued at this point and product was recovered as described in the Experimental Section. Because bisphenol **1** was in excess and the SiH functionality disappeared, this material is terminated in allyl groups.

The preparation of polymers **6** and **7** from fluoroalkyl-substituted **1** required substantially higher temperatures and longer reaction times than Mathias’s hydrosilylation polymerization using unfluorinated **2**. Consequently, in our syntheses, it was not obvious that hydrosilylation polymerization was occurring rather than competing dehydrocondensation reactions. The desired hydrosilylation reaction consumes allyl groups and leaves phenolic hydroxyl groups free, whereas dehydrocondensation consumes hydroxyl groups and leaves allyl groups. Spectroscopic characterization of **6** and **7** (as well as **8**, described below) indicated reasonably clean formation of the desired polymers with no major impurities present other than cyclic oligomers. The IR spectra clearly showed hydroxyl groups in the products. $^{1}$H and $^{13}$C NMR spectra provided diagnostic data on the conversion of allyl groups to trimethylene linkers, and representative spectra of polymer **7** are shown in Figure 1. Peaks similar to the allyl methylene peak of **1** at 3.4 ppm in the $^{1}$H NMR spectra and 35.1 ppm in the $^{13}$C NMR spectra are not present in the polymer. Product methylene groups are clearly seen at 2.6, 1.6, and 0.6 ppm in the $^{1}$H NMR spectrum and at 33.5, 23.6, and 17.8 ppm in the $^{13}$C NMR spectrum.

GPC analysis of polymer **6** indicated a bimodal weight distribution with a broad peak of high molecular weight ($M_w$ = 116 800, $M_n$ = 10 300, $M_w/M_n$ = 11.4) and a relatively narrow peak of low molecular weight ($M_w$ = 940, $M_n$ = 890 $M_w/M_n$ = 1.1). The low molecular weight peak is indicative of cyclic oligomers which could not be removed by vacuum. The sample contained approximately 80% of the higher molecular weight linear polymer as determined from the peak areas. The GPC data of polymer **7** also shows a bimodal weight distribution with high ($M_w$ = 120 100, $M_n$ = 12 200, $M_w/M_n$ = 9.8) and low ($M_w$ = 1200, $M_n$ = 1200, $M_w/M_n$ = 1.0) molecular weight peaks. In this case the high molecular weight linear polymer was 85−90% of the samples tested. The weight-average molecular weights observed for polymers **6** and **7** are higher than the value reported by Mathias for his bisphenol-containing copolymers ($M_w$ = ca. 27 000 by GPC and polydispersity of 12)[32] and roughly comparable to the highest molecular weight polymers obtained by Dvornic ($M_v$ = 75 900) as determined by intrinsic viscosity measurements.[30] Dvornic described his materials as “truly high molecular weight linear polycarbosiloxanes”.

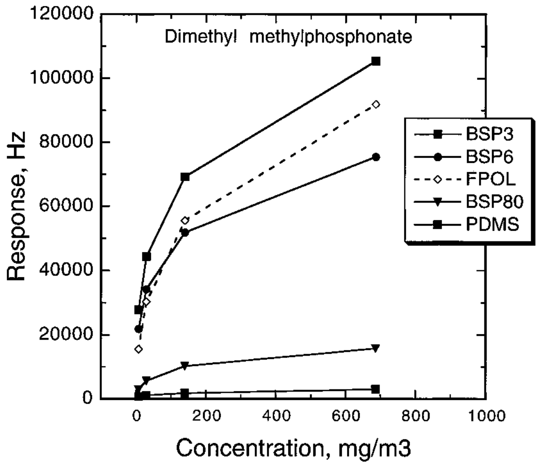

**Figure 2.** Calibration curves of 200 MHz SAW vapor sensors coated with bisphenol-containing materials (un-cross-linked). The test vapor is DMMP, and results for poly(dimethylsiloxane) are shown for comparison. All data are normalized to coating “thicknesses” of 250 kHz. Abbreviations: BSP3 = **6**; BSP6 = **7**; BSP80 = **8**; PDMS = poly(dimethylsiloxane); FPOL = fluropolyol.

**Adjusting the Physical Properties.** The syntheses of polymers **6** and **7** successfully incorporated the fluoroalkyl-substituted phenol functionality from **1** into polymers and the resulting materials had $T_g$ values below room temperature (6 and −16 °C, respectively). These polymers proved to be good sorbents for basic vapors and suitable as materials for SAW vapor sensors (see further results below). However, for application as chemically sensitive claddings on optical fibers, these polymers were too viscous for processing in the cladding apparatus, and their refractive indexes were too high. At indexes of 1.482 and 1.471 for **6** and **7**, respectively, these claddings would not guide light down a silica fiber with a refractive index of approximately 1.46. Materials for this application should be liquid polymers with refractive indexes less than 1.46 and viscosities (1000−3000 cP) that would permit delivery to a cladding cup through $^{1}/_{4}$ or $^{3}/_{8}$ in. tubing. In addition, it is mandatory that the material be curable.

We prepared a liquid material with a viscosity in the range of 1500 cSt and a refractive index of 1.422 using a much longer polysiloxane linker (ca. 80 dimethylsi-

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loxane links) under conditions leading to a lower molecular weight product. Allyl-terminated material **8** was obtained from the reaction of hydride-terminated poly(dimethylsiloxane) (**5**) with 2 equiv of **1**. Consumption of all SiH-containing starting materials was complete within 2 h due to the large excess of vinyl functionality. On the basis of the stoichiometry and assuming a material with a polydispersity of 1, the product would have the structure as shown for **8** in Scheme 1 (AA/BB/AA) and the molecular weight would be about 7000. The actual product in the small scale synthesis described in the Experimental Section had a polydispersity of 2.2 and number average molecular weight of 15 400; this corresponds roughly to a material consisting of two poly(dimethylsiloxane) spacers from **5** and three bisphenol groups, noting that there was no SiH detectable in the product. In a separate larger scale synthesis, we obtained a material with a number average molecular weight of 12 300 and polydispersity of 2.1.

**Cross-Linking Methods.** Commonly used chemistries for polysiloxane cross-linking include free radical reactions, condensation reactions, hydrosilylation addition reactions, and hydridosilane/silanol reactions.[33,34] We required a cross-linking method that would be effective under the conditions of an optical fiber drawing tower and not alter the hydroxyl groups included for interaction. The fiber drawing tower pulls a fiber from a melted fused silica preform to the desired diameter. A liquid polymer cladding material is applied and cured as the fiber is pulled through a cladding cup and an electric clamshell furnace. Finally, the clad fiber travels through a capstan, a dancer and is wound on a 1 m circumference drum. The fiber does not contact any surfaces until after it exits the curing furnace. This process can be automated once the drawing parameters are established, and the drawrate can be in the tens of meters per minute when using thermally cured claddings. (Commercial fiber draws, using UV curable coatings, move at several hundred meters per minute.) Even under the relatively slow drawrates used in this study, the cross-linking method must be rapid when compared to casting planar films. Cross-linking must also occur in air and be highly reliable. The use of hydrosilylation addition chemistry to cross-link poly(dimethylsiloxane) polymer claddings on optical fibers has been widely used in the past, and cladding formulations using this approach are commercially available.

All of the materials described above can be prepared with terminal olefin groups, either by having the allyl groups of **1** on the chain end, or by subsequent reaction with 1,3-divinyltetramethyldisiloxane. Cross-linking can then proceed by linking chain ends using a hydrosilylation catalyst and a cross-linker with multiple (three or more) SiH groups.[33,35] In our application, it is critical that the cross-linking reaction does not convert the liquid material to a glass. By cross-linking only at the chain ends, the liquid character of the material is maintained at a microscopic level, preserving rapid diffusion of vapors to and from sites for hydrogen-bonding interactions.

Choosing a suitable cross-linking agent was a potential concern since organosiloxane liquids with different types of organic funtionality are often not miscible. We found that phenyltris(dimethylsiloxy)silane (**9**) and 1,3-diphenyl-1,1,3,3-tetrakis(dimethylsiloxy)disiloxane (**10**) were both miscible with polymers **6**−**8**. By combining polymer, cross-linker, and hydrosilylation catalyst,[35] these materials were cross-linked in bulk samples, converting sticky gums or oils to solid elastomers as described in the Experimental Section.

**Optical Fiber Cladding.** A sample of material **8** was mixed with trifunctional cross-linker **9** and platinum cyclovinylmethylsiloxane complex and applied to freshly drawn silica optical fiber in an automated system as described above and in the Experimental Section. The cyclovinylmethylsiloxane complex of platinum was chosen as the catalyst, as opposed to platinum divinyldisiloxane complex, because it cures more slowly, giving a longer pot life. Adequate curing of the copolymers was acheived at slow drawrates of 8−9 m/min; this draw-rate necessitated manual control of the drawing conditions, resulting in variable core diameters and coating thicknesses. The copolymer viscosity increased during the fiber drawing and the delivery pressure was increased from 0.8 to 1.5 psi over the course of about 2 h. Half to one meter sections were hand selected for quality. The best fiber sections had a smooth 25 $\mu$m thick coating over a 180 $\mu$m diameter core. These fibers are as effective at guiding light as commercially available plastic fibers or silica fibers clad in our own laboratory with commercial polydimethylsilicone cladding formulations. They are under investigation at evanescent wave chemical sensors.

**Evaluation on SAW Devices.** The new hydrogen-bond acidic materials were applied to SAW devices (without cross-linking) and tested against organic vapors at various concentrations. Upon exposure to a vapor, polymer-coated acoustic wave devices undergo a shift in frequency that is proportional to the amount of vapor sorbed by the polymer.[3,7,15,36,37] Times to steady-state response, corresponding to equilibrium partitioning of the vapor into the film, were under 10 s using our vapor delivery system. From frequency shift data for a vapor at multiple concentrations, calibration curves were constructed. Figure 2 shows the calibration curves for materials **6**−**8** against dimethyl methylphosphonate (DMMP), a strongly hydrogen-bond basic organophosphorus compound. In addition, data are also provided for a poly(dimethylsiloxane)-coated SAW device and a fluoropolyol-coated device. These data are all normalized to a film "thickness" of 250 kHz for each material. AA/BB copolymer **6**, with the greatest density of hydrogen-bond acidic sites, shows the highest sensitivity to DMMP, followed by copolymer **7**. Signals of greater than 20 000 Hz were observed at a concentration of only 8 mg/m$^3$. This corresponds to a concentration of 1−2 ppm, indicating that detection limits for a minimum detectable signal of 10 Hz would be at about 1 ppb. Material **8**, with a lower density of hydrogen-bond acidic sites, is less sensitive than copolymers **6** and **7**. All the hybrid organic/inorganic materials are more sensitive to DMMP than poly(dimethylsiloxane), illustrating the significance of incorporating the hydrogen-bond acidic

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organic functionality in promoting sorption of basic vapors. The increase in sensitivity with increasing density of phenolic groups (as well as the very large signals) demonstrates that the responses are due to bulk absorption in the film. The calibration curves are nonlinear, which is consistent with hydrogen-bonding interactions at a finite number of sites in the polymer.[10] The calibration curves also show that at trace concentrations new materials **6** and **7** are superior to fluoropolyol, which has been the most useful hydrogenbond acidic polymer in previous SAW sensor studies.[8−11,15,16]

**Concluding Remarks.** The rational design of a sensing material requires that both the chemical and physical properties of the material can be controlled and tailored for the sensing application and the sensor platform (e.g., type of sensor device, such as acoustic wave, optical, chemiresistor, electrochemical, etc.) For use on planar acoustic wave devices, the material must incorporate organic functionalities providing the desired sorbent properties in a physical form that is nonvolatile and allows rapid vapor diffusion to and from sites of interaction. Polymers with static glass-to-rubber transition temperatures below room temperature fit these criteria. Cross-linking is not strictly necessary for a functional sensor. For cladding on freshly drawn optical fibers, the material must have a viscosity permitting application to the fiber using the cladding cup, and the refractive index must be lower than the glass so that waveguiding will occur. In addition, cross-linking is required so that the cladding will have adequate mechanical strength during processing and handling.

The approach we have described, using hydrosilylation chemistry to create hybrid organic/inorganic materials, represents a highly flexible approach to preparing materials to meet the above objectives. In this potentially generic approach for design of sorbent sensing materials, the organic portion provided the desired interactive properties, while the inorganic portion provided a means for tuning the physical properties. Use of oligosiloxane spacers lead naturally to materials with low glass-to-rubber transition temperatures, and the hydrosilylation reaction for polymerization also leads to materials with functionalities for cross-linking on the chain ends. It is a significant advantage that the addition of Si−H across a carbon−carbon double bond does not introduce any polar functionalities into the material: polymers can be synthesized and cross-linked without altering the selectivity imparted to the material by interactive groups independently designed into the material. In addition, the hydrosilylation reaction is selective and tolerates many functional groups including esters, nitriles, amines, amides, nitro, ketone, ether, phosphate, sulfide, and sulfones, to name just a few.[27,38] Thus, the approach appears to be ideally suited for the design and synthesis of sorbent sensor materials with a variety of chemical and physical properties. Such sorbent materials may be used neat on chemical sensors, or as the matrix material in composites containing additional components with a function in sensing and transduction (electronically conducting materials, for example).[17]

In previous studies, the systematic investigation of vapor sorption using LSERs has provided guidance for the selection of materials and functional groups to achieve particular objectives in sensing properties. The present paper has described a versatile synthetic approach that can be used to create materials incorporating these groups and to obtain desirable physical properties at the same time. Specifically, we have demonstrated that this approach can be used to prepare sensor materials with strong hydrogen-bond acidic sites for interaction, and that the physical properties of the materials can be varied to satisfy the requirements of two different sensing platforms, planar acoustic wave devices and optical fibers.

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