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Polymers for Chemical Sensors Using Hydrosilylation Chemistry

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Summary

Sorbent and functionalized polymers play a key role in a diverse set of fields, including chemical sensors, separation membranes, solid-phase extraction techniques, and chromatography. Sorbent polymers are critical to a number of sensor array or "electronic nose" systems. The responses of the sensors in the array give rise to patterns that can be used to distinguish one compound from another, provided that a sufficiently diverse set of sensing materials is present in the array. Figure S1 illustrates the concept of several sensors, each with a different sensor coating, giving rise to variable responses to an analyte that appear as a pattern in bar-graph format. Using hydrosilylation as the bond-forming reaction, we have developed a versatile and efficient approach to developing sorbent polymers with diverse interactive properties for sensor applications. Both the chemical and physical properties of these polymers are predictable and tunable by design.
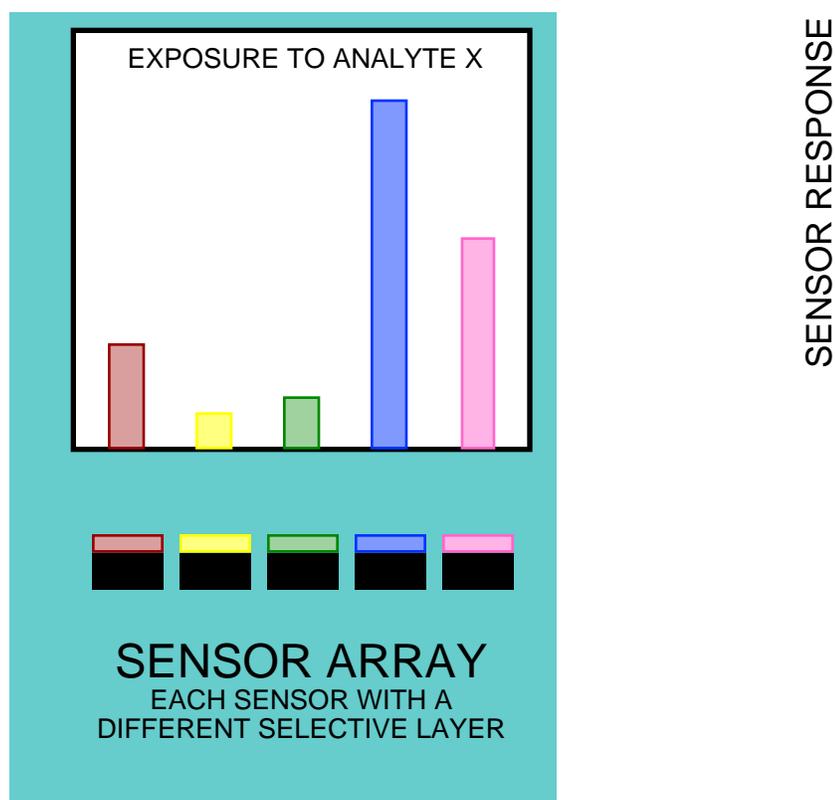
Figure S.1. Schematic Diagram of the Sensor Array Concept, Showing an Array of Sensors Coated with Different Materials and Their Respective Responses to an Analyte, Giving Rise to a Pattern Shown in Bar-Graph Format

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Introduction

Many types of sensor devices can and have been used in sensor arrays for gas-phase vapor detection. These arrays involve diverse interactive coatings on multiple sensors with the resulting multivariate data analyzed by pattern-recognition techniques. Array detectors are sometimes referred to as electronic noses because the nose uses multiple receptors whose signals are processed by neuronal pattern-recognition processes. Some of the most well known examples of gas-phase sensor arrays employ polymers as the interactive coatings.

Arrays based on acoustic-wave sensors use quartz crystal microbalance (QCM), surface acoustic wave device (SAW), or the flexural plate wave (FPW) devices as the sensing transducers.[1] Signals are generated that are proportional to the mass of the vapor sorbed by each of the polymer coatings on the device surfaces. The observed signals may also include a polymer modulus change contribution.

Vapor sorption by sorbent polymers can also be transduced using chemiresistor configurations where the insulating polymer is loaded with (typically) 20% of carbon-black particles. Vapor sorption swells the insulating polymer and increases the resistance through the polymer/carbon-black composite. These types of chemiresistor sensors have served as the basis for sensor arrays.[2–5]

Alternatively, sorbent polymers may serve as the matrix for fluorescent dyes such as Nile Red. Vapor sorption alters the fluorescence signal from the incorporated dye molecules. Arrays have been prepared with various dyes in various polymers on the ends of fiber optic bundles.[6–8]

Thus, sorbent polymers are important as sensing materials on a number of types of array-based electronic noses, either as neat polymers, as composites containing conducting particles within the polymer film, or as composites incorporating fluorescent dyes. All of these approaches can benefit from rational polymer design and synthesis.

Polymers for Chemical Vapor Sensing

Polymers are useful materials for chemical vapor sensing for several reasons, including their capability to collect and concentrate vapor molecules on sensor surfaces by reversible sorption; their suitability for application on devices as thin adherent films; and the fact that their chemical selectivity is determined by chemical structure, which can be easily varied through synthesis. Polymers can yield sensors with rapid, reversible, and reproducible responses. In addition, diverse sets of polymers can be assembled for use in sensor arrays, providing the variable selectivity across the array that is required for obtaining useful chemical information for pattern-recognition analysis.

The chemically interactive properties of polymers for chemical vapor sensing have been systematically examined using linear solvation energy relationships (LSERs).[9,10] These linear free-energy relationships model the sorption of vapors by polymers in terms of fundamental interactions, such as dispersion interactions, interactions involving dipoles and induced dipoles, and hydrogen-bonding interactions. Models derived by this approach can be used for prediction and understanding, the latter usually being the most important. The role of fundamental vapor/polymer interactions and LSERs for designing sensor arrays was first set out in detail in 1991.[10] Subsequent treatments have demonstrated applicability to many related aspects of chemical sensor development.[1,11,12] Sensor-array design for detecting organic vapors entails the selection of a set of polymers where each emphasizes a different interaction, leading to requirements for polymers that are nonpolar, polarizable, diplolar, hydrogen-bond basic, and hydrogen-bond acidic.

However, having the required chemically interactive properties alone is not sufficient for a polymer to be useful in chemical sensing. A sensing polymer must also have a number of desirable physical properties. Polymers promote rapid chemical sensor responses, which are usually desirable, with glass-to-rubber transition temperatures below the operating temperature of the sensor. Vapor diffusion in and out of polymers is rapid under these conditions. Response times of sensors with glassy polymers are typically much slower than those based on rubbery polymers. The method by which the material will be applied to a chemical sensor as a thin film may also impose requirements on the polymer or pre-polymer formulation. For example, solubility in organic solvents may be necessary, or a certain viscosity for a prepolymer may be necessary as part of a coating process. Particular sensor platforms may impose their own requirements, such as refractive index requirements, for an optical sensor. Therefore, the synthesis of a polymer for a sensor or sensor-array application must consider not only the chemical interactions, which have been studied in detail, but also the desired physical properties for film application and sensor performance.

Hydrosilylation Polymerization

Given the multiplicity of performance criteria for optimized sensing polymers, it would be useful to have a single synthetic approach that would be versatile enough to yield individual polymers that combine desirable chemical and physical properties and also able to create diverse sets of such materials for various applications and arrays. In this way, each new sensing material would not present a new and unique synthesis problem. In addition, it would be desirable to be able to tune and formulate these polymers for various types of sensor devices, each of which may impose different requirements on physical properties and thin film deposition methods.

With these considerations in mind, we have explored the use of hydrosilylation polymerization for design and synthesis of polymers for sensors and sensor arrays. In its most typical form, the hydrosilylation reaction involves the formation of a silicon-carbon (Si-C) bond by adding a silicon hydride (Si-H) bond across a carbon-carbon double bond in the presence of a noble metal catalyst such as Pt.[13,14]

Equation 1
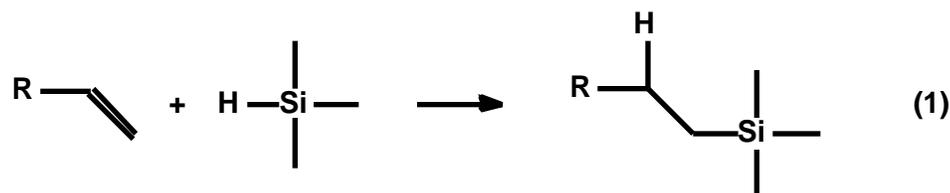
Linear polymers with alternating monomers can be formed when one monomer has two carbon-carbon double bonds and the second monomer has two silicon hydride groups. Three such polymerization reactions are shown in Figure 1. Typically, the monomer with two silicon hydride groups is an α,ω-dihydridooligosiloxane, although it could also be a silane monomer, such as diphenylsilane. The monomer with two carbon-carbon double bonds may also be an oligosiloxane, silane monomer, or organic diene. Polymers combining siloxy linkages and carbon-carbon bonds in the polymer backbone are called carbosiloxane polymers. When the monomer with two carbon-carbon double bonds is an organic compound and the second monomer is an α,ω-dihydridooligosiloxane, hybrid organic-inorganic polymers result.
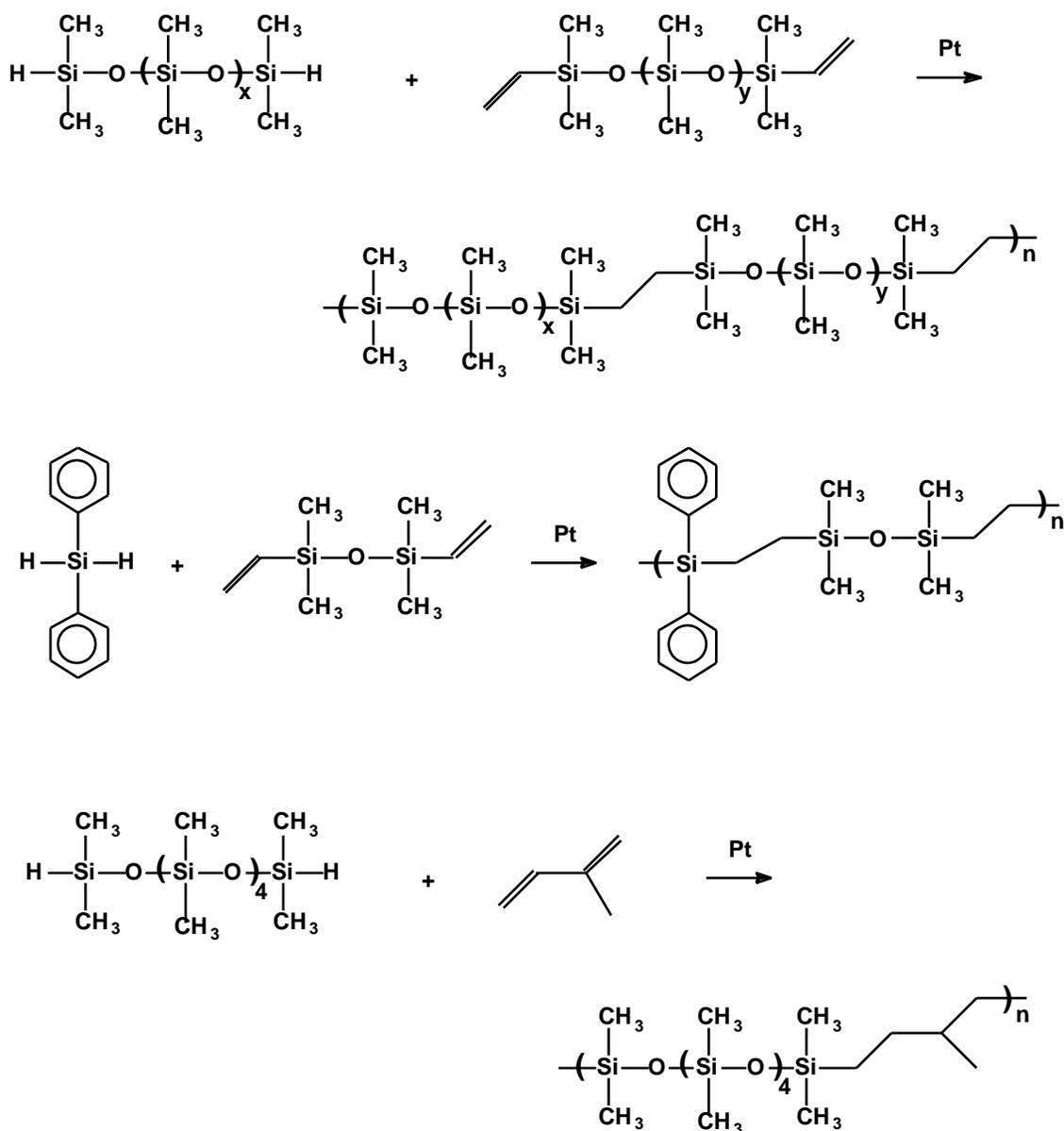
Figure 1. Three Hydrosilylation Polymerization Reactions

In most of the original examples of hydrosilylation polymerization, the substituents on silicon were typically methyl, ethyl, or phenyl, and hexachloroplatinic acid was used as the catalyst.[15–17] The reaction of isoprene with ,-dihydridododecamethylhexasiloxane was an early example of an organic/inorganic material prepared by hydrosilylation polymerization (see Figure 1).[18] Despite the fact that the use of the hydrosilylation reaction for polymerization was demonstrated over 35 years ago, it was noted by Itsuno et al. as recently as 1993 that "the direct use of the hydrosilylation reaction in preparation of organosilicic polymers has been limited so far."[19] Furthermore, Dvornic noted in 1994 that early studies on the use of hydrosilylation polymerization "resulted only in low molecular weight oligomeric products" and indicated that the "versatile reaction has not yet been successfully developed for the synthesis of truly high molecular weight linear polymers."[20,21]

Dvornic went on to demonstrate that "truly high molecular weight polymers" methyl-substituted polymers could be obtained by this reaction using Pt divinyltetramethyldisiloxane catalyst (Karstedt's catalyst) rather than hexachloroplatinic acid.[20,21]

Several examples of functionalized polymers and novel architectures were recently described in a brief review of hydrosilylation polymerization.[22] The hydrosilylation reaction has been used to make liquid-crystal polymers, chiral polymers, hyperbranched and dendritic structures, and macromolecules with redox active centers. The remainder of this article will focus on development of functionalized polymers and polymer thin films for chemical sensors and arrays using hydrosilylation chemistry. It may be of interest to note that hydrosilylation chemistry is also being used to functionalize silicon surfaces.[23]

Sensing Polymers should be synthesized to

- put rational design principles to work in sensor material development

- prepare materials that combine the desired chemically interactive properties with necessary physical properties for performance as thin films on sensors

- prepare materials with selectivities that are not available in commercial polymers

- overcome shortcomings in the performance of commercial polymers as layers on sensors

- obtain rigorous control over composition and properties

- prepare polymers and prepolymers that can be crosslinked and/or grafted to surfaces

- prepare and adapt polymer and prepolymer formulations for application as sensing thin films on various sensing platforms

- formulate polymers for photopatterning.

Rational Polymer Design and Synthesis

The hydrosilylation polymerization method is capable of incorporating a variety of organic structures and functional groups into a polymeric structure. 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.[14,24] In addition, it is well known that oligosiloxane segments in polymers often lead to low glass-to-rubber transition temperatures. Therefore, this polymerization approach meets two primary criteria for the synthesis of chemical sensing polymers: diverse polymers with various functional groups can be prepared, and the resulting polymers should exhibit low glass-to-rubber transition temperatures. Functional groups can be selected to obtain the vapor/polymer interactions discussed above. The length of the oligodimethylsiloxane segment can be varied to influence the glass-transition temperature and other physical properties.

The approach also has a number of other desirable features. The bond-forming reaction produces silicon-carbon bonds and does not introduce any polar functionalities into the final material. Thus, the bond-forming reaction itself does not "bias" the selectivity of the resulting polymers, as would be the case if all polymers were formed by amide or ester linkages, for example. The method allows control of end-group functionality. Polymers or oligomers may be terminated with primarily carbon-carbon double bonds or silicon hydride bonds, which may be useful for subsequent crosslinking of a polymer film (see below). Alternatively, the reactivity of the chain ends could be used for endcapping with specific molecules or functionalities. In addition, the method can be adapted to

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deliberately produce oligomers rather than polymers when the ratio of monomers is not 1:1. Thus, this polymerization approach provides the opportunity to tune molecular-weight distribution for polymer or prepolymer formulations.

Diverse Sorbent Polymers

Figure 2 illustrates four of the sorbent and functionalized polymers that we have prepared by this method. Some of the monomers used in the preparation of these and other polymers are shown in Figure 3. Each polymer in Figure 2 is designed to emphasize different properties and interactions. The methyl-substituted carbosiloxane polymer, dubbed CSME in the figure, is a nonpolar material that is good for sorbing aliphatic hydrocarbons. It is the same or similar to other carbosiloxane polymers prepared previously (see Figure 1),[20,21] and has sorbent properties similar to poly(dimethylsiloxane) and poly(isobutylene).

The phenyl-substituted polymer, CSPH, was prepared because phenyl groups provide greater polarizability than simple aliphatic groups. On sensors, these polymers offer sensitivity to aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as to chlorinated hydrocarbons. Both these classes of compounds are environmental contaminants of concern. Although other phenyl-substituted polymers with low glass-to-rubber transition temperatures are available, such as the gas-chromatographic stationary phase OV-25, we were motivated to prepare our own carbosiloxane polymer in order to have control over composition, properties, and formulation for sensing films. OV-25 is a polysiloxane with 75% phenyl substituents and 25% methyl substituents. Similarly, CSPH was designed to have a high ratio of phenyl-to-methyl groups (67%). Commercial OV-25, however, has been shown to have slight hydrogen-bond acidity that is probably attributable to residual Si-OH groups.[25] This compromises the desired chemical selectivity. In our experience, commercial polymers often contain functionalities or contaminants that are not indicated by the nominal polymer structure, and sometimes these can be seen in the infrared spectrum. In addition, we observed erratic behavior of OV-25-coated SAW devices under humid conditions that was empirically resolved by using our carbosiloxane polymer instead.

The polymer containing the urea group, UR3, was prepared in order to obtain a basic polymer for chemical sensor arrays. Urea groups are known to be very basic and dipolar. The hydrosilylation polymerization proceeded smoothly, and this material has yielded well-behaved chemical sensors when applied to SAW devices. Other basic polymers, such as polyvinylpyrrolidone and polyethyleneimine, have basic properties and have been applied to SAW devices as sensor coatings.[26,27] However, polyvinylpyrrolidone does not have the low glass-to-rubber transition temperature that is desirable, and poly(ethyleneimine) has yielded sensors with poor reproducibility. Again, shortcomings of commercial materials for our application prompted us to synthesize our own low glass-to-rubber transition-temperature basic polymer.

The bisphenol-containing polymer, BSP3, is one of our most interesting and useful polymers.[28,29] This polymer was rationally designed to have strongly hydrogen-bond acidic properties that are desirable for sorbing basic vapors. A great many basic organic solvents exist that are used industrially that one might want to detect. In addition, some of the vapors of national security concern, such as nerve agents, are strong hydrogen-bond bases. Recent work has shown that polymers in this class are also useful for detecting nitroaromatic explosives.[30] Thus, the desirability of strongly hydrogen-bond acidic polymers for basic vapor detection is evident. In addition, these polymers are desirable in sensor arrays to enhance chemical diversity within the array.
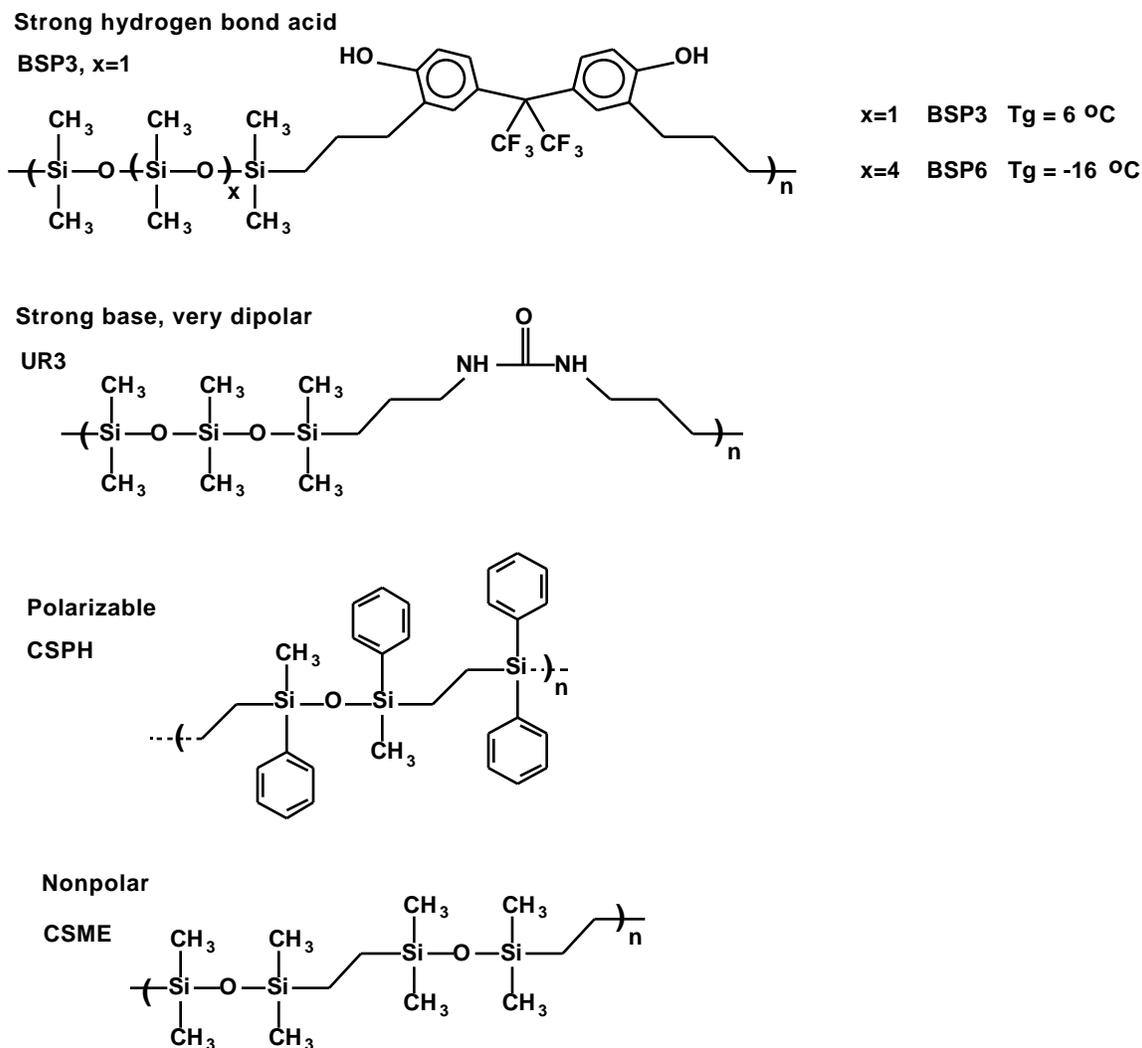
Figure 2. Four Examples of Sorbent Polymers Prepared by Hydrosilylation Polymerization, Illustrating the Diversity of Polymers that can be Prepared

A consideration of the chemical structures that lead to hydrogen-bond acidity leads to a choice of fluorinated alcohols and phenols as the functionality that should be incorporated into a polymer.[10] However, commercial polymers with these functionalities and low glass-to-rubber transition temperatures have not been available. Accordingly, a number of synthetic materials have been prepared and investigated as sensor phases, most of which incorporate hexafluoroisopropanol moieties as the hydrogen-bond acidic group.[28–39]

A study several years ago compared the hydrogen-bond acidities of several propyl- or allyl-substituted bisphenol structures using inverse gas chromatography and LSERs.[40] It was shown that fluorinated bisphenol-A structures were substantially more hydrogen-bond acidic than non-fluorinated analogs; fluorination improved sorption of basic compounds by factors of 100 or more. These considerations provided the rational-design criteria for synthesis of polymers containing the fluorinated bisphenol structure in the polymer chain. The BSP3 polymer shown in Figure 2 has three silicon atoms in the repeat unit. Variants have also been synthesized with longer oligosiloxane units. The interaction of a BSP polymer with a basic vapor is shown in Figure 4.
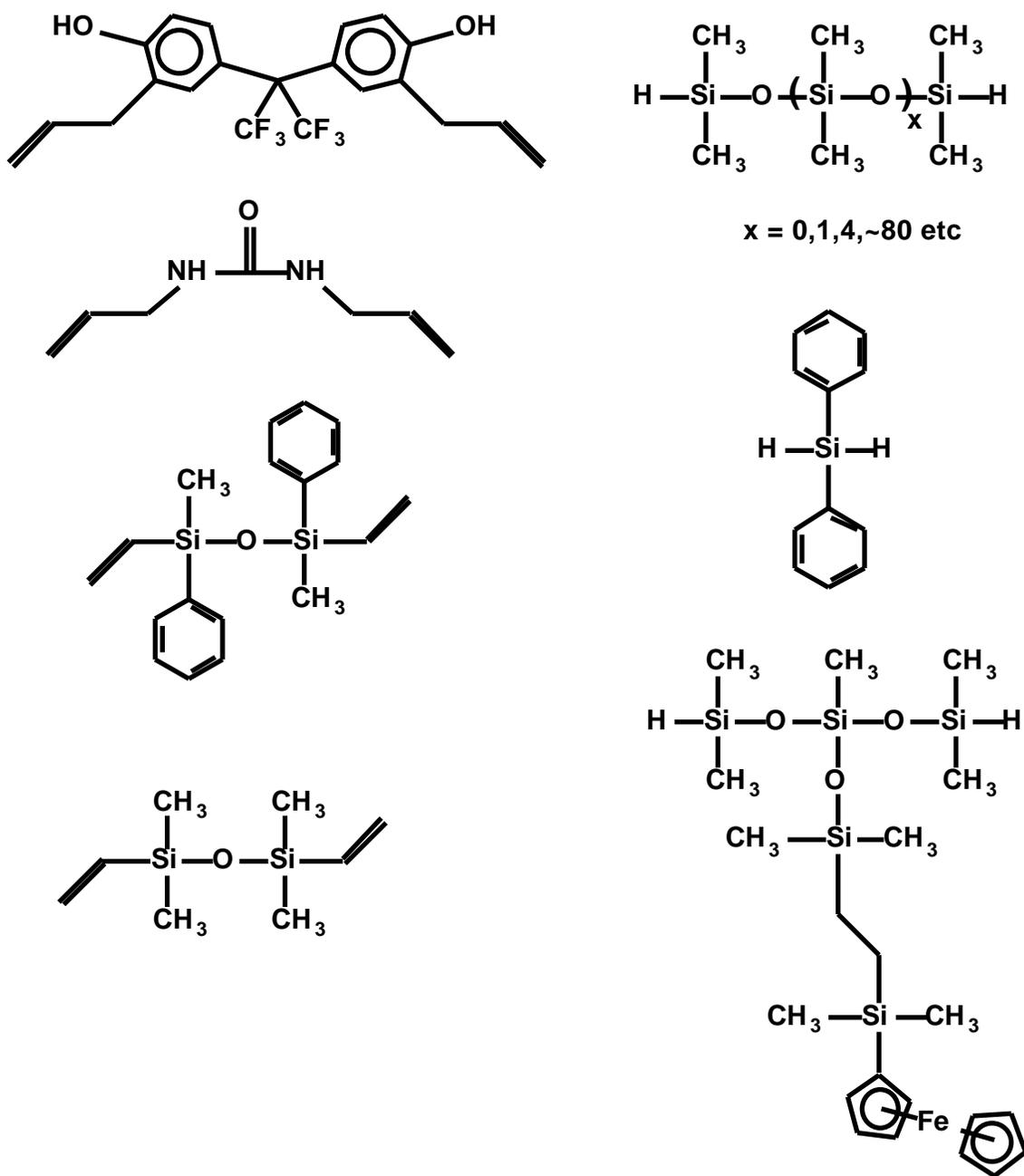
Figure 3. Examples of Monomers Used in Hydrosilylation Polymerization

Experiments on SAW sensors have shown that these phenolic polymers are useful in sensing basic vapors and nerve-agent simulants and have properties that are equal to or superior to previous materials in this category.[28,29,41] Figure 5 shows the calibration curves for SAW sensors coated with BSP3, fluoropolyol (FPOL), and polydimethylsiloxane (PDMS) when tested against dimethyl methylphosphonate, a nerve-agent simulant. FPOL is a sensor coating for nerve agents described in the past,[26,27,33,42] and PDMS serves as an example of a sorbent polymer lacking functionalities designed for sorption of basic vapors. Signals of greater than 20,000 Hz are observed at a

concentration of only 8 mg/m^3 using BSP3. This corresponds to a concentration of 1 to 2 ppm, indicating that detection limits for a minimum detectable signal of 10 Hz would be at about 1 ppb.[28]
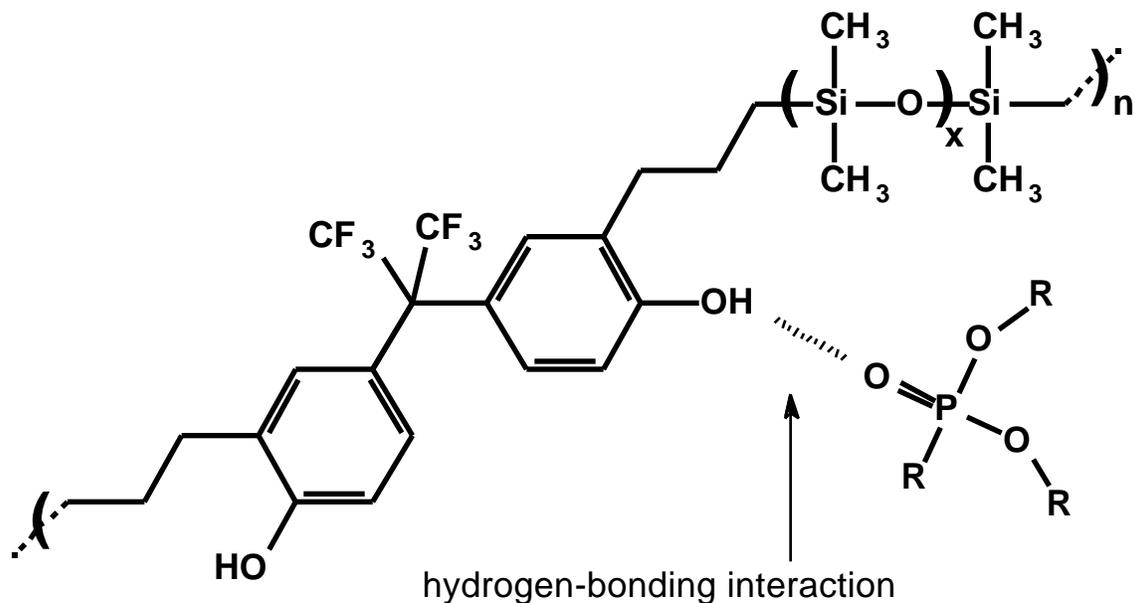
Figure 4. Hydrogen-Bonding Between an Organophosphonate Compound and a Sorbent Polymer Containing Phenolic Hydroxyl Groups
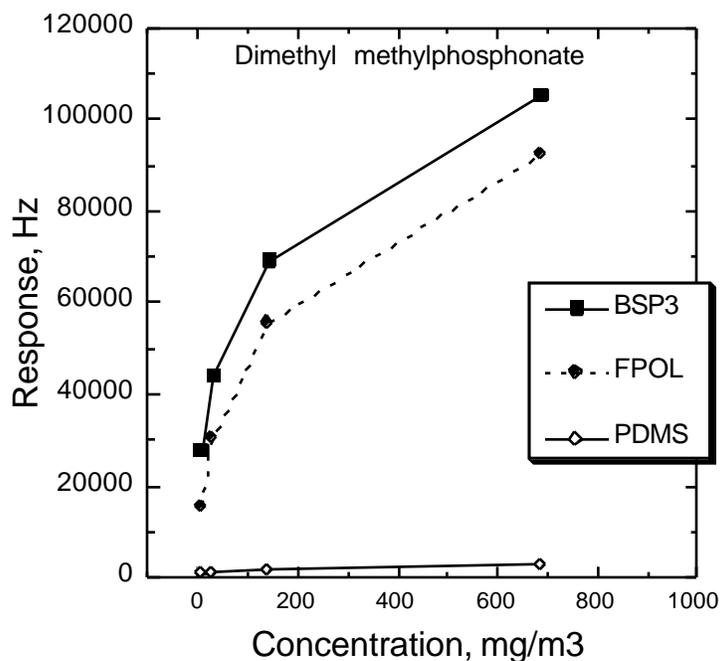
Figure 5. Calibration Curves Comparing the Sensitivities of SAW Vapor Sensors Coated with BSP3, FPOL, and PDMS in Response to Dimethyl Methylphosphonate

Together, the polymers in Figure 2 can provide the chemical diversity that is desirable in small sensor arrays.[1,10] It is also worth noting the variety of monomers that can be applied in this synthetic approach, some of which are shown in Figure 3. There exist many organic dienes that could be combined with , -dihydridooligosiloxanes to yield carbosiloxane polymers. Any monomer on the left side of Figure 3 could, in principle, be combined with any monomer on the right side. While this is not combinatorial chemistry per se, and so far we have prepared polymers in individual batches rather than in parallel, it does illustrate the principle that a variety of materials can be efficiently prepared by various combinations of a limited number of starting monomers.

Electrofunctional Polymers

We have prepared a ferrocene-derivatized monomer shown in Figure 3 in which ferrocene is appended to an oligosiloxane chain that is terminated in Si-H groups. We successfully combined this monomer with the bisphenol monomer also shown in Figure 3, producing a polymer whose repeat unit is shown in Figure 6. Cyclic voltammetry on both solutions and thin films of this resulting material confirmed the presence of redox-active ferrocene groups. The usefulness of electrofunctional polymers in the analytical sciences and especially in sensor development has been noted.[43] In principle, one could prepare a whole series of functionalized redox-active polymers by combining the ferrocene-containing monomer with various monomers on the left side of Figure 3 or with other organic dienes.

REDOX ACTIVE FUNCTIONALIZED POLYMER
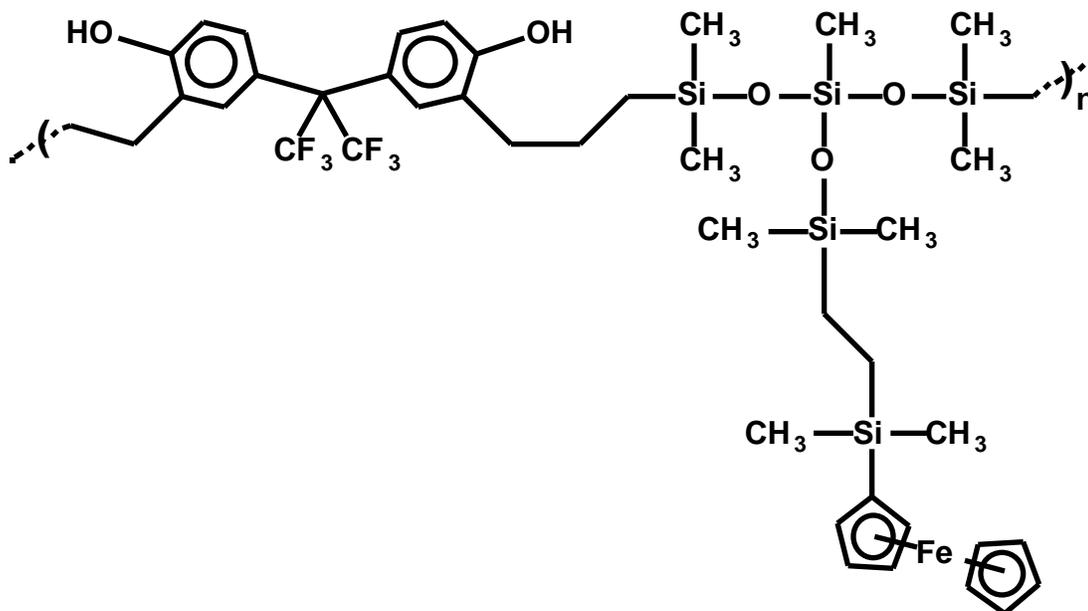
Figure 6. Repeat Unit for an Electrofunctional Polymer Prepared by Hdyrosilylation Polymerization

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Fiber Optic Cladding

It is also possible to vary the properties of these materials in order to meet other sensor requirements. We were interested in coating a hydrogen-bond acidic polymer as the cladding on silica optical fibers. This platform imposed the requirement that the refractive index of the polymer be lower than that of silica (approximately 1.46) in order to efficiently guide light. In addition, the material had to be formulated as a prepolymer that could be coated on a fiber pulled freshly from the melt using an automated optical-fiber drawing tower. The prepolymer is then cured in a tube furnace before the clad fiber is wound onto the drum of the fiber drawing system. A viscosity in the range of 1000 to 3000 centipoise was desired to permit delivery of prepolymer to a cladding cup through 1/4-in. or 3/8-in. tubing. BSP3 is unsuitable for direct use in this application because its refractive index is 1.48, and it is a gum phase.

We prepared a liquid prepolymer with a viscosity in the range of 1500 cSt. and a refractive index of 1.42 using a much longer α, ω-dihydridooligosiloxane as a macromonomer (ca. 80 dimethylsiloxane repeat units) under conditions leading to a lower molecular weight product. Two equivalents of the fluorinated bisphenol in Figure 3 were reacted with one equivalent of this macromonomer, yielding an allyl-terminated bisphenol-containing prepolymer. This material was combined with a platinum catalyst and miscible crosslinker (phenyltris(dimethylsiloxy)silane) (see Figure 7) containing three Si-H groups and applied to fibers as described above. Sections of fiber clad by this approach were as effective at guiding light as commercially available plastic fibers or silica fibers clad in our own laboratory with commercial polydimethylsilicone cladding formulations. This example illustrates the versatility of the approach for synthesizing polymers and oligomers containing a desired functionality while tuning the physical properties for a particular sensing platform.

Crosslinking and Grafting

The carbosiloxane polymers prepared by hydrosilylation polymerization are intrinsically terminated with groups that can be used for crosslinking. By design, these can be essentially all terminal silicon-hydride or all terminal vinyl or allyl groups. Adding a platinum catalyst and a multifunctional crosslinker, such as those shown in Figure 7, yields a formulation that will crosslink on curing. The use of hydrosilylation is one of a number of reactions that are conventionally used for crosslinking vinylmodified polysiloxanes.[44,45] Crosslinking is required for some sensor formats, such as the optical fibers described above, and may be desirable for other sensor formats. A crosslinked film will have mechanical stability and is less likely to fail by dewetting the surface.[46] In addition, crosslinked films may offer enhanced sensor stability and lifetime. Rapp and coworkers investigated the UV-initiated free-radical crosslinking of polysiloxane films on SAW devices.[47] It was found that crosslinking offered sensors with superior stability compared to uncrosslinked polysiloxanes. Hydrosilylation chemistry provides a clean reaction for crosslinking that can often be conveniently carried out in air.

H
|
SiMe$_2$
|
O
|
Me —Si —O·SiMe$_2$·H
|
O
|
SiMe$_2$
|
H

H
|
SiMe$_2$
|
O
|
Si —O·SiMe$_2$·H
|
O
|
SiMe$_2$
|
H

H   H
| |
SiMe$_2$ SiMe$_2$
| |
O   O
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Si —O —Si
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O   O
| |
SiMe$_2$ SiMe$_2$
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H   H
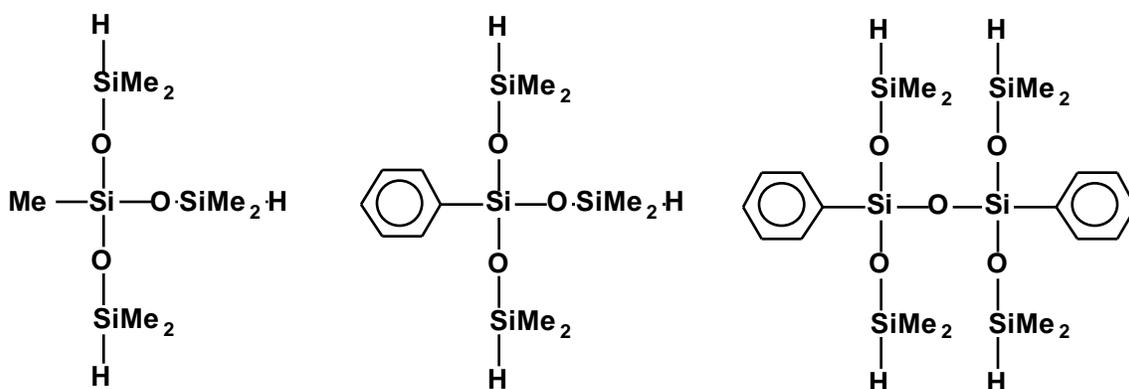
Figure 7. Examples of Multifunctional Compounds for Crosslinking Using the Hydrosilylation Reaction

Furthermore, polymer films can be grafted to surfaces at the same time by the same reaction chemistry. Modification of surfaces with silanes to give Si-H or vinyl terminated surfaces is well known. These surface groups can participate in the crosslinking reactions to covalently attach some of the polymer chains to the surface. Evidence that such grafting actually occurs is apparent when solvents are used in an effort to remove uncrosslinked films, crosslinked films, and crosslinked-grafted films. We have found cases where lightly crosslinked films are dissolved or detached from unmodified surfaces by suitable solvents, but the corresponding crosslinked *and* grafted films on modified surfaces remain adherent. Another approach for grafting sensing films using hydrosilylation has been described by Yang and coworkers.[48]

Our overall scheme for polymer synthesis, crosslinking, and grafting is shown in Figure 8. Hydrosilylation polymerization generates polymers or oligomers incorporating interactive groups (indicated in the figure by squares with the letter I inside) for chemical selectivity. These may also have a redox-active center or reporter group incorporated in the structure, as indicated by "R" in the figure. By design, this approach yields chains with terminal vinyl (shown) or silicon hydride groups for crosslinking. Formulation with multifunctional crosslinkers (vinyl or Si-H substituted) and catalyst offer curable films. The same procedure on modified surfaces (vinyl or Si-H modified) can yield crosslinked and grafted films. Thus, hydrosilylation is used in polymer synthesis, polymer crosslinking, and polymer grafting.

Patterned Polymer Films

The fact that solubility varies depending on crosslinking and grafting suggests that hydrosilylation could also be used for photopatterning polymer films. This would simply require a catalyst that was inactive until exposed to light. Platinum(II) bis(-diketonates), such as platinum(II) bis(acetylacetonate) or Pt(acac)$_2$, offer these properties. These compounds have been used as photoactivated hydrosilylation catalysts for solution reactions, polymerization of vinyldimethylsilane in solution, and for curing and patterning preceramic polymer films.[49–54]

11

Synthesis

HSi ⌇⌇⌇⌇⌇ SiH $\xrightarrow{\text{Pt}}$

$\left(\text{—} \boxed{I} \text{—Si} ⌇⌇⌇⌇ \text{Si} \right)_n$

HSi ⌇⌇⌇⌇ SiH $\xrightarrow{\text{Pt}}$
R

$\left(\text{—} \boxed{I} \text{—Si} ⌇⌇⌇ \text{Si} \right)_n$
R

Crosslinking

POLYMER

SiH
HSi ⌇⌇⌇⌇ SiH   CROSSLINKER
X

Grafting

SiH   SiH   SiH   SiH

SURFACE TO GRAFT TO
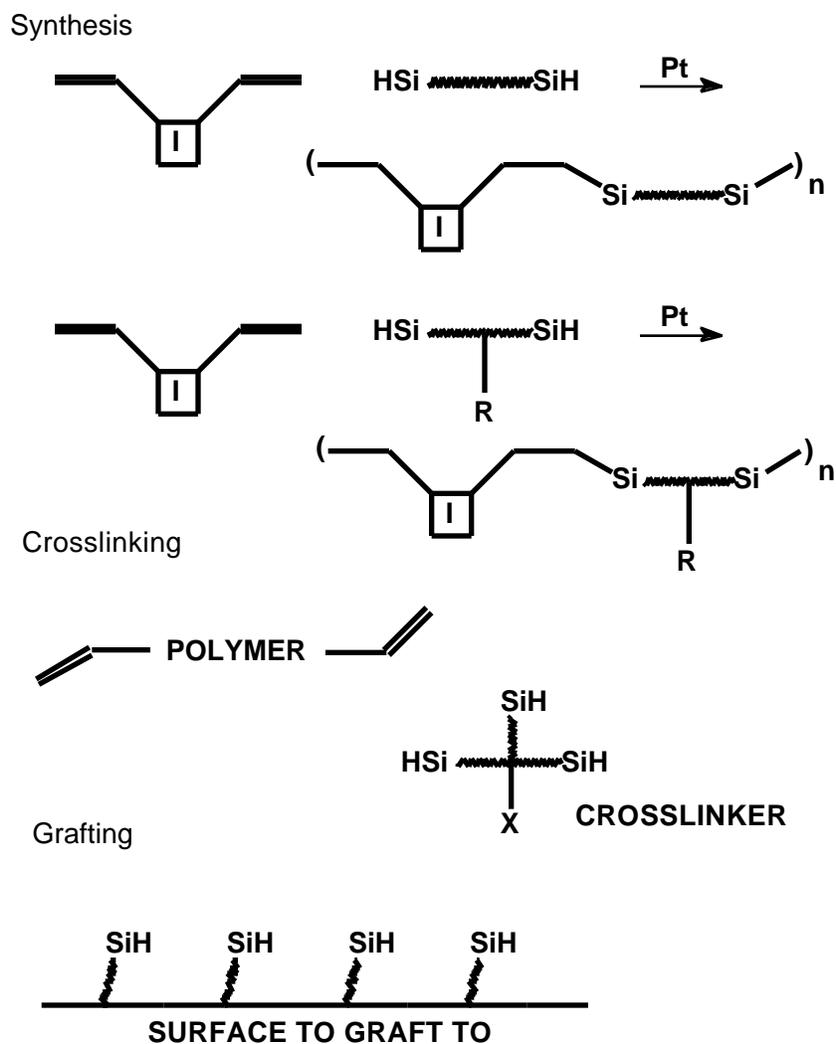
Figure 8. Scheme for Synthesis of Diverse Interactive Polymers, Crosslinking of Films, and Grafting to Surfaces, all Using Hydrosilylation Chemistry

We have found this chemistry to be useful for patterning sorbent and functionalized siloxane and carbosiloxane polymers. Figure 9, for example, shows the results of patterning a polydimethylsiloxane formulation using Pt(acac)2 as the photoactivated catalyst in the reaction of vinyl-terminated polydimethylsiloxane with a methylhydrodimethylsiloxane copolymer.   Only those regions of a spin-cast film of these components that were exposed to light to activate the catalyst underwent hydrosilylation crosslinking. After exposure, the pattern was developed by dissolving and removing unexposed material. We have photopatterned films from 50 nm to 5 µm in thickness by this method. The 5 x 5 array of squares in Figure 10 has individual squares that are 100 µm by 100 µm in area. A human hair is included in the picture for reference.
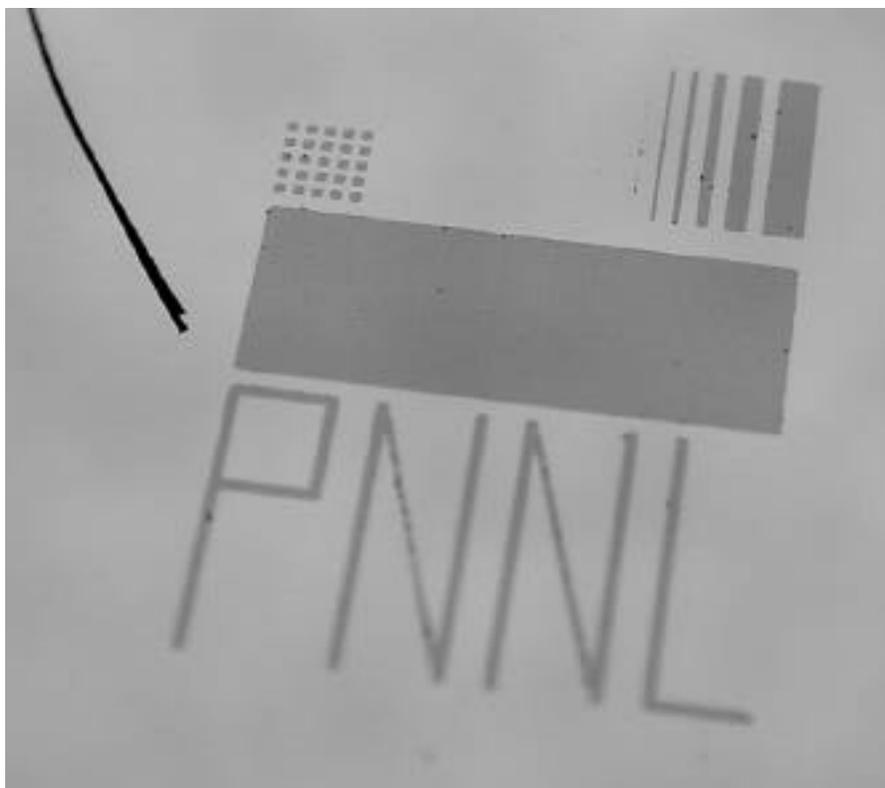
Figure 9. Photopatterned Polydimethylsiloxane Formulation Using a Photoactivated Hydrosilylation Catalyst

Similarly, a variety of other functionalized sorbent materials can be photopatterned by these methods. Care must be taken to use crosslinkers that are miscible with the vinyl-functionalized polymer and to allow an adequate dark reaction time before developing the pattern by dissolving away uncrosslinked materials. Simultaneous grafting to the surface is often necessary to retain the pattern. We have patterned phenyl- and cyano-substituted siloxane formulations in this way.

While the reactions above are based primarily on photoactivated hydrosilylation crosslinking, it is also possible to photoactivate polymerization as part of the patterning process. For example, we have formulated a prepolymer film containing Pt(acac)2, the bisphenol monomer shown in Figure 3, and a silicon hydride terminated oligomer that was prepared and isolated from the reaction of the same monomer with excess of an ,-dihydrodimethylsiloxane. A small amount of crosslinker was also included in the prepolymer. Photoactivated polymerization and pattern development on a vinyl-modified silicon surface gave the lines shown in Figure 10.

Alternatively, patterns of highly crosslinked network polymers can be obtained by formulating functionalized monomers or oligomers with multifunctional crosslinkers. However, excessive crosslinking can significantly raise the glass-to-rubber transition temperatures. Obtaining sufficient crosslinking to retain polymer patterns on the substrate after rinsing with the pattern-development solvent, while maintaining a low glass-to-rubber transition temperature requires a delicate balance of polymer formulation, crosslinker, surface modification for grafting, dark reaction time, and solvent selection.

Figure 10. Photopatterned Lines of a Carbosiloxane Polymer Containing Fluorinated Bisphenol Groups Prepared Using a Photoactivated Hydrosilylation Catalyst to Photopolymerize, Crosslink, and Graft the Film to the Surface

We have found that a variety of functionalities, including all those in Figure 2 as well as cyano groups, can be incorporated in photopatterned siloxane or carbosiloxane polymer films. Thus, the patterning approach has great potential for use in sensors and sensor arrays.

Acoustic Wave Sensor Array-on-a-Chip

Acoustic wave sensors such as the QCM and SAW device are often the basis for polymer-coated sensor arrays.[1] FPW devices can also be coated with polymers for chemical sensing.[55] In this case, the active surface of the device is at the bottom of an etch pit in a silicon chip. It is possible to fabricate several of these devices on a single chip, leading to an array-on-a-chip. Different polymers can then be applied to the active devices in their individual etch pits.

A picture of a packaged FPW array-on-a-chip is shown in Figure 11. Sensor responses to the vapors from two industrial solvents, toluene and methylisobutylketone, are shown in Figure 12. The array was coated with three of the carbosiloxane polymers shown in Figure 2 (BSP3, UR3, and CSPH) and three other commercial polymers (poly(isobutylene
, OV-275, and Eypel-F). These two bar graphs illustrate the generation of distinguishable patterns for different vapors, as first suggested by Figure S1. Pattern recognition analysis of data from FPW array sensors has been described in detail by Zellers et al.[56] The patterns in Figure 12 support some of the chemical-selectivity principles that are the basis for our rational design approach. The most sensitive of these diverse polymers for toluene is the polarizable CSPH polymer. The most sensitive polymer for basic methylisobutylketone is BSP3. (The BSP3 polymer has also been used on an acoustic wave sensor-array-on-a-chip.[41])
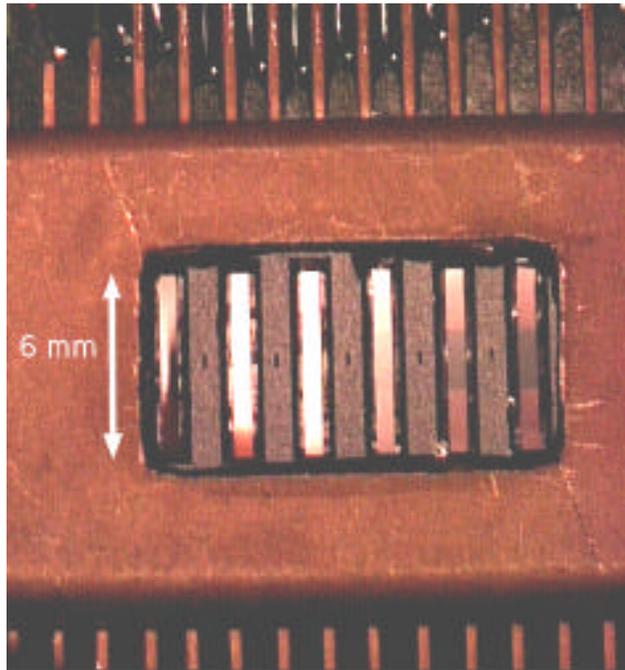
Figure 11. A Packaged FPW Array-on-a-Chip
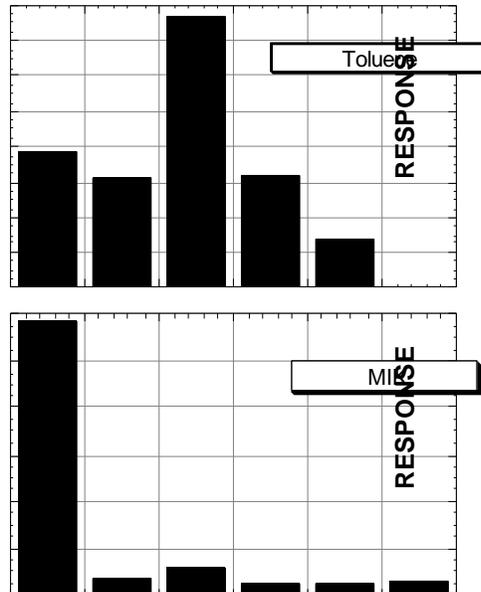
Polymer-coated FPW sensors

Figure 12. Patterns Generated by the Responses of the Polymer-Coated FPW Array-on-a-Chip in Response to Two Vapors, Toluene and Methylisobutylketone (MIK)

Conclusion

Hydrosilylation chemistry offers tremendous versatility in the development of sorbent and functionalized polymers and thin films. Diverse sets of polymers can be prepared with control over chemical and physical properties of the resulting materials. The chemistry can be further used in the crosslinking, grafting, and patterning of thin films. The materials can be adapted to a variety of sensor types. These types of materials and films are useful or potentially useful for chemical sensors, sensor arrays, membranes, solid-phase extraction, chromatography, and lab-on-a-chip[41] applications.

References

(1)	Grate, J. W. *Chemical Reviews* **2000**, *in the press.*,
(2)	Doleman, B. J.; Lonergan, M. c.; Severin, E. J.; Vaid, T. P.; Lewis, N. S. *Anal. Chem.* **1998**, *70*, 4177-4190.
(3)	Lonergan, M. c.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298-2312.
(4)	Severin, E. J.; Lewis, N. S. *Anal. Chem.* **2000**, *72*, 2008-2015.
(5)	Severin, E. J.; Doleman, B. J.; Lewis, N. S. *Anal. Chem.* **2000**, *72*, 658-668.
(6)	Michael, K. L.; Taylor, L. C.; Schultz, S. L.; Walt, D. R. *Anal. Chem.* **1998**, *70*, 1242-1248.
(7)	Walt, D. R. *Acc. Chem. Res.* **1998**, *31*, 267-278.
(8)	Walt, D. R.; Dickinson, T.; White, J.; Kauer, J.; Johnson, S.; Engelhardt, H.; Sutter, J.; Jurs, P. *Biosens. Bioelectron.* **1998**, *13*, 695-699.
(9)	Abraham, M. H. *Chemical Society Reviews* **1993**, *22*, 73-83.
(10)	Grate, J. W.; Abraham, M. H. *Sens. Actuators B* **1991**, *3*, 85-111.
(11)	Grate, J. W.; Abraham, M. H.; McGill, R. A. In *Handbook of Biosensors: Medicine, Food, and the Environment*; E. Kress-Rogers and S. Nicklin, Ed.; CRC Press: Boca Raton, FL, USA, 1996; Vol. ; pp 593-612.
(12)	McGill, R. A.; Abraham, M. H.; Grate, J. W. *CHEMTECH* **1994**, *24(9)*, 27-37.
(13)	Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.
(14)	*Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon Press: Oxford, 1992.
(15)	Greber, V. G.; Metzinger, L. *Makromol. CHem.* **1960**, *39*, 189-217.
(16)	Andrianov, K. A.; Kochetkova, A. S.; Khananashvili, L. M. *Zhurnal Obshchei Khimii.* **1968**, *38*, 175-178.	(Journal of General Chemistry of the USSR, English translation pages 174-176.)
(17)	Andrianov, K. A.; Gavrikova, L. A.; Rodionova, Y. F. *Vysokomol. Soyed.* **1971**, *A13*, 937-940.	(Polymer Science, USSR, English translation pages 1057-1061.
(18)	Andrianov, K. A.; Rodionova, Y. F.; Luky'yanova, G. M. *Vysokomol. Soyed.* **1967**, *A9*, 2647-1650.	(Polymer Science, USSR, English translation pages 2994-2998.
(19)	Itsuno, S.; Chao, D.; Ito, K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 287-291.
(20)	Dvornic, P. R.; Gerov, V. V.; Govedarica, M. N. *Macromolecules* **1994**, *27*, 7575-7580.
(21)	Dvornic, P. R.; Gerov, V. V. *Macromolecules* **1994**, *27*, 1068-1070.
(22)	Grate, J. W.; Kaganove, S. N. *Polymer News* **1999**, *24*, 149-155.
(23)	Buriak, J. M. *Chem. Commun.* **1999**, 1051-1060.
(24)	Ojima, I. In *The Chemistry of Organic Silicon Compounds*; S. Patai and Z. Rappoport, Ed.; John Wiley and Sons Ltd: New York, 1989; Vol. ; pp 1479-1526.
(25)	Abraham, M. H.; Whiting, G. S.; Andonian-Haftvan, J.; Steed, J. W.; Grate, J. W. *J. Chromatography* **1991**, *588*, 361-364.
(26)	Ballantine, D. S.; Rose, S. L.; Grate, J. W.; Wohltjen, H. *Anal. Chem.* **1986**, *58*, 3058-3066.
(27)	Rose-Pehrsson, S. L.; Grate, J. W.; Ballantine, D. S.; Jurs, P. C. *Anal. Chem.* **1988**, *60*, 2801-2811.
(28)	Grate, J. W.; Kaganove, S. N.; Patrash, S. J.; Craig, R.; Bliss, M. *Chem. Mater.* **1997**, *9*, 1201-1207.
(29)	Grate, J. W.; Kaganove, S. N.; Patrash, S. J. *Anal. Chem.* **1999**, *71*, 1033-1040.
(30)	McGill, R. A.; Mlsna, T. E.; Chung, R.; Nguyen, V. K.; Stepnowski, J.; Abraham, M. H.; Kobrin, P. *Proc. SPIE-Int. Soc. Opt. Eng.* **1998**, *3392*, 384-389.
(31)	Chang, Y.; Noriyan, J.; Lloyd, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1987**, *27*, 693.
(32)	Barlow, J. W.; Cassidy, P. E.; Lloyd, D. R.; You, C. J.; Chang, Y.; Wong, P. C.; Noriyan, J. *Polym. Eng. Sci.* **1987**, *27*, 703-715.
(33)	Grate, J. W.; Snow, A.; Ballantine, D. S.; Wohltjen, H.; Abraham, M. H.; McGill, R. A.; Sasson, P. *Anal. Chem.* **1988**, *60*, 869-875.

(34)   Snow, A. W.; Sprague, L. G.; Soulen, R. L.; Grate, J. W.; Wohltjen, H. *J. Appl. Poly. Sci.* **1991**, *43*, 1659-1671.

(35)   Grate, J. W.; Klusty, M.; Barger, W. R.; Snow, A. W. *Anal. Chem.* **1990**, *62*, 1927-1924.

(36)   Abraham, M. H.; Andonian-Haftvan, J.; Du, C. M.; Diart, V.; Whiting, G.; Grate, J. W.; McGill, R. A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 369-378.

(37)   Martin, S. D.; Poole, C. F.; Abraham, M. H. *J. Chromatography, A* **1998**, *805*, 217-235.

(38)   McGill, R. A.; Chung, R.; Chrisey, D. B.; Dorsey, P. C.; Matthews, P.; Pique, A.; Mlsna, T. E.; Stepnowski, J. L. *IEEE Trans. Ultrason., Ferroelec., Freq. Contr.* **1998**, *45*, 1370-1379.

(39)   Demathieu, C.; Chehimi, M. M.; Lipskier, J. F. *Sens. Actuators* **2000**, *B62*, 1-7.

(40)   Abraham, M. H.; Hamerton, I.; J. B. Rose; Grate, J. W. *J. Chem. Soc. Perkin Trans. 2* **1991**, 1417-1423.

(41)   Heller, E. J.; Hietala, V. M.; Kottenstette, R. J.; Manginell, R. P.; Matzke, C. M.; Lewis, P. R.; Casalnuovo, S. A.; Frye-Mason, G. C. *Proc. - Electrochem. Soc. - Chemical Sensors IV* **1999**, *99-23*, 138-142.

(42)   Grate, J. W.; Rose-Pehrsson, S. L.; Venezky, D. L.; Klusty, M.; Wohltjen, H. *Anal. Chem.* **1993**, *65*, 1868-1881.

(43)   Lewis, T. W.; Wallace, G. G.; Smyth, M. R. *Analyst* **1999**, *124*, 213-219.

(44)   Thomas, D. R. In *Siloxane Polymers*; S. J. Clarson and J. A. Semlyen, Ed.; PTR Prentice Hall: Englewood Cliffs, New Jersey, 1993; Vol. ; pp 567-615.

(45)   Filas, R. W.; Johnson, B. H.; Wong, C. P. *IEEE Trans. Components, Hybrids, and Manufacturing Techn.* **1990**, *13*, 133-136.

(46)   Grate, J. W.; McGill, R. A. *Anal. Chem.* **1995**, *67*, 4015-4019.

(47)   Barie, N.; Rapp, M.; Ache, H. J. *Sens. Actuators, B* **1998**, *B46*, 97-103.

(48)   Yang, X.; Shi, J.; Johnson, S.; Swanson, B. *Langmuir* **1998**, *14*, 1505-1507.

(49)   Salvi, G. D. Thesis, 1993.

(50)   Lewis, F. D.; Salvi, G. D. *Inorg. Chem.* **1995**, *34*, 3182-9.

(51)   Fry, B. E.; Neckers, D. C.. *Macromolecules* **1996**, *29*, 5306-5312.

(52)   Fry, B. E.; Guo, A.; Neckers, D. C. *J. Organomet. Chem.* **1997**, *538*, 151-162.

(53)   Fry, B. E. Thesis, 1996.

(54)   Guo, A.; Fry, B. E.; Neckers, D. C. *Chem. Mater.* **1998**, *10*, 531-536.

(55)   Grate, J. W.; Wenzel, S. W.; White, R. M. *Anal. Chem.* **1991**, *63*, 1552-1561.

(56)   Cai, Q.-Y.; Park, J.; Heldsinger, D.; Hsieh, M.-D.; Zellers, E. T. *Sens. Actuators* **2000**, *B62*, 121-130.

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