CHEMICAL REVIEWS

Hydrogen-Bond Acidic Polymers for Chemical Vapor Sensing

Jay W. Grate

Chem. Rev., **2008**, 108 (2), 726-745 • DOI: 10.1021/cr068109y

Chemical Reviews is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Hydrogen-Bond Acidic Polymers for Chemical Vapor Sensing

Jay W. Grate*

Pacific Northwest National Laboratory, P.O. Box 999, Richland Washington 99352

Received May 31, 2007

Contents

1. Introduction

Strongly hydrogen-bond acidic polymers for vapor sensors were introduced in the mid 1980s. Originally, these polymers were of interest for obtaining high sensitivity to organophosphorus nerve agents using acoustic wave sensors. The polymer served as the sorbent layer on the sensor and interacted with the strongly hydrogen-bond basic organophosphorus compounds by hydrogen bonding. These interactions promoted sorption of the vapors into the polymer film on the device surface, which increased the sensor response. The property of hydrogen-bond acidity was incorporated into the polymer by including fluorinated alcohol or fluorinated phenol functional groups in the polymer structure. These polymers have also been demonstrated in explosives sensing applications. From the time of the earliest sensor studies using hydrogen-bond acidic polymers, they were included in sensor arrays where they increase the chemical diversity and help to discriminate among vapors.

Jay W. Grate is a Laboratory Fellow at the Pacific Northwest National Laboratory (PNNL) and an Affiliated Professor with the Chemistry Department of the University of Washington. He received his B.A. degree in Chemistry at Rollins College and Ph.D. degree in Chemistry from the University of California, San Diego. After postdoctoral research at the University of California Irvine, he joined the Naval Research Laboratory in 1984, moving to PNNL in 1992. He spent a sabbatical at the Scripps Research Institute prior to joining PNNL. His research has focused on chemically interactive polymers and nanomaterials, chemical vapor sensors, radiochemical separations and sensing, and bioanalytical fluidics for biothreat detection. His work integrates aspects of the chemical sciences, material sciences, and measurement sciences into new microanalytical principles, methods, and systems. He is noted for developing a rational approach to understanding vapor sorption and polymer design as it relates to chemical detection with polymer-coated sensors. He has published over 100 papers in peer-reviewed journals and numerous book chapters and is author or coauthor on over a dozen patents, several of which have been licensed. He received an R&D 100 Award in 2004 for his work in developing a rationally designed polymer for chemical threat detection and an American Chemical Society Regional Industrial Innovation Award in 2007.

In addition to their use in important applications, this class of polymers has been significant because no hydrogen-bond acidic polymers with the desirable low glass to rubber transition temperatures (T_g) were commercially available. Furthermore, none of the conventional gas chromatographic stationary phases were strongly hydrogen-bond acidic. Those phases that were rather modest hydrogen-bond acids (e.g., docosanol, sorbitol, and diglycerol) were not polymers. Therefore, developing this class of polymers for chemical sensors required design and synthesis.

A great variety of hydrogen-bond acidic polymers and architectures have now been developed, from linear organic polymers containing fluoroalcohols to silicon-containing polymers with phenolic or fluoroalcohol functionalities in linear and branched architectures. While they remain useful on acoustic wave sensors for chemical agent detection, these polymers have also been demonstrated in chemiresistor

---

* To whom correspondence should be addressed. Phone: 509-376-4242. Fax: 509-376-5106. E-mail: jwgrate@pnl.gov.

10.1021/cr068109y CCC: $71.00

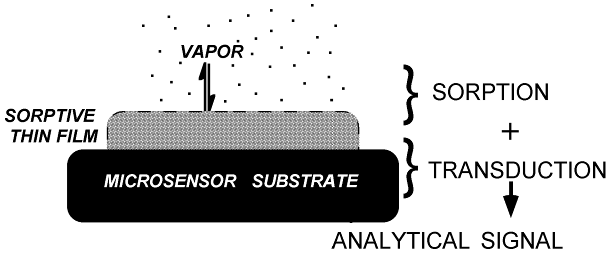


Figure 1. Sorption-based sensor.

sensors, chemicapacitor sensors, microcantilever sensors, and a variety of optical approaches.

This review aims to describe the original motivation and principles behind the use of hydrogen-bond acidic polymers on chemical sensors and review the types of polymers developed. Accordingly, this review covers the period from 1986 to early 2007. The polymer materials designed and synthesized to be hydrogen-bond acidic sorbents will be presented in detail, followed by selected illustrative examples of their use in sensing. These polymers have been most widely used on acoustic wave sensors; their use on other types of sensors are less well known, and this review will seek to bring such examples forward. This review will also describe some examples where they have been used in separation or preconcentration approaches for vapor analysis. Vapor concentrations will be reported in either mg/m^3 or parts by volume (ppm or ppb) according to the units used in the work being reviewed with conversions sometimes provided.[1]

Priority will be given to covering research published as original contributions in peer-reviewed journals, and dates noted will refer to journal publication rather than proceedings when possible. Proceedings papers will be cited in this review, at the author's discretion, in order to include relevant findings likely to be of interest to the sensor community. It is unfortunate that some polymers and application studies have been published only in proceedings papers or in articles from journal issues that are, in actuality, conference proceedings. For some polymers, syntheses and characterization have never been provided in a peer-reviewed journal. In some peer-reviewed journals, including *Sensors and Actuators*, *Talanta*, and even *Science*, sensor results have been published where the structures of the sensing polymers and/or their synthesis and characterization are not given, and the references do not lead to published synthesis and characterization in peer-reviewed journals. These practices can undermine the scientific credibility of the published sensor results.

2. Background

2.1. Sorption-Based Sensors

A sorption-based sensor in the context of this review comprises a sorbent material that collects and concentrates vapor molecules from the gas phase in combination with a means to transduce the reversible sorption process into an analytical signal. Typically, transduction arises from an acoustic wave, mechanical, optical, or electronic device to which the sorbent is applied as a thin film. This concept is shown in Figure 1.

Acoustic wave devices such as the quartz crystal microbalance (QCM) or surface acoustic wave (SAW) device represent the most fundamental sorption-based sensors; when acting as pure gravimetric devices, they detect the amount of vapor sorbed as a mass and the response is not dependent on any other analyte property other than those that influence sorption. Nevertheless, several other types of devices provide platforms for sorption-based sensors including microcantilevers responding to mass uptake and/or bending forces, chemiresistor devices responding to changes in the conductivity of a sorbent thin film, chemicapacitors responding to dielectric changes, and optical fibers, waveguides, or other configurations responding to the change in refractive index, absorbance, or fluorescence of a sorbent material.

While the sorbent material for these sensors could, in principle, be selected from a great variety of material types,[2] polymers or polymer-based composites are most often used. As polymers are the subject of this review, we will typically refer to the sorbent material interchangeably as a polymer or sorbent.

2.2. Partition Coefficients and Sensor Responses

The equilibrium distribution of a vapor between the gas phase and a sorbent polymer phase is characterized by the thermodynamic partition coefficient, K. Taking the concentration in the gas phase as C_v and the equilibrated concentration in the sorbent phase as C_s, the partition coefficient is the ratio defined according to eq 1. Higher values indicate a greater degree of collection and concentration of vapors in the polymer phase, where their presence can be transduced into an analytical signal. The relevance of the partition coefficient to vapor detection using coated acoustic wave sensors was noted in both quartz crystal microbalance (QCM) sensor studies[3-5] and SAW sensor studies.[6,7]

$$K = C_s/C_v \tag{1}$$

The partition coefficient is related to the Gibb's free energy of solution of a gaseous solute, $\Delta G_S{}^\circ$, according to eq 2. The R_{const} in this equation is the gas constant as usual, and T is the temperature. (The subscript was added to R_{const} here to clearly distinguish it from the R_2 vapor solvation parameter to be described later in this review.)

$$\Delta G_S{}^\circ = -R_{const} T \ln K \tag{2}$$

Since the response of a sorption-based chemical sensor is based on the amount of vapor sorbed into the film, which is related to the amount of vapor in the gas phase by the partition coefficient ($C_s = C_v K$), the response is a function of the partition coefficient and the vapor-phase concentration according to eq 3. Hence, promoting interactions that increase the sorption of vapors will increase sensor responses. The partition coefficient may be a constant in the case of linear absorption isotherms but will be a function of vapor concentration in the case of nonlinear sorption isotherms.

$$\text{response} = \mathrm{f}(C_s) = \mathrm{f}(C_v K) \tag{3}$$

This generalized response function can alternatively be written according to eqs 4 and 5, i.e., as a function of the amount of vapor in the film times a sensitivity factor, S. The sensitivity factor may, in turn, be a function of factors specific to the vapor molecule, i.e., analyte-specific factors, as well as specific factors related to the sensing device and its transduction mechanism.

$$\text{response} = SC_s = SC_v K \tag{4}$$

$$S = \text{f(analyte-specific factors, transduction-specific factors)} \tag{5}$$

For a purely gravimetric polymer-coated acoustic wave sensor the response, a frequency shift denoted by Δf_v, is related to the partition coefficient and vapor concentration according to eq 6.

$$\Delta f_v = \Delta f_s C_v K/\rho_s \tag{6}$$

The parameters Δf_s and ρ_s are transduction-specific factors, where Δf_s is a measure of the amount of polymer on the sensor surface (specifically the frequency shift due to deposition of the film material onto the bare sensor) and ρ_s is the density of the sorbent polymer phase. For a purely mass-sensitive device, the analytical signal is related to the amount of vapor absorbed as a mass without dependence on other analyte-specific factors.

The response of a sensor to the amount of vapor sorbed, where the transducer detects the volume rather than the mass of vapor, can be expressed as in eq 7.

$$R = v_v S' C_v K \tag{7}$$

The parameter S' is a sensitivity factor as in eq 4. Of particular note is that the volume sensitivity is related to the vapor-specific volume, v_v, which relates to the volume fraction of vapor in the polymer/vapor solution, $\phi_v = v_v C_v K$.[8] The vapor-specific volume represents an analyte-specific sensitivity factor as expressed in eq 5.

The quartz crystal microbalance (QCM) is a purely gravimetric sensor for sufficiently thin polymer films that move synchronously with the device surface.[9-15] The SAW device can be gravimetric but often contains sensitivity to changes in the modulus of the polymer upon vapor sorption. The modulus change is related to the volume of the sorbed molecules through their influence on polymer film free volume.[8-10,16-21] Accordingly, a SAW sensor acting as a mass-plus-volume-transducing device has a response that can be expressed as in eq 8. The first term has no analyte-specific sensitivity factors, while the second term has v_v, an analyte-specific sensitivity factor which will vary from vapor to vapor.

$$\Delta f_v = (\Delta f_s C_v K/\rho_s) + v_v S' C_v K \tag{8}$$

Since rapid sensor responses are typically required or at least desired, use of polymers with T_g values below the operating temperature of the sensor is preferable. Vapor diffusion is much more rapid above this transition temperature due to greater polymer free volume and polymer segmental chain motion, leading to more rapid equilibration of the film material with the gas-phase vapor concentration.

2.3. Fluorinated Alcohols and Phenols

The interactions that promote sorption of vapor molecules into a polymer film, where the vapor molecules act as solutes and the polymer acts as the solvent, are, by definition, solubility interactions.[22-25] These interactions include van der Waals interactions and the hydrogen-bonding interactions of interest in this review. Figure 2 shows the concept of hydrogen bonding between a fluorinated alcohol or a fluorinated phenol with a hydrogen-bond base, represented in this case by the nerve agent simulant dimethyl methylphosphonate (DMMP).

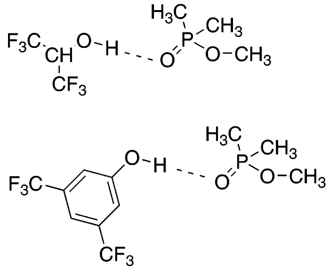


Figure 2. Hydrogen-bonding interactions between fluorinated hydrogen-bond acidic molecules hexafluoroisopropanol or 3,5-bis-(trifluoromethyl)phenol and DMMP, a hydrogen-bond basic organophosphorus compound.

Table 1. Hydrogen-Bonding Solvation Parameters[a] for Selected Hydrogen-Bond Acidic Molecules

molecule	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$
ethanol	0.37	0.48
2,2,2-trifluoroethanol	0.57	0.25
hexafluoroisopropanol	0.77	0.10
phenol	0.60	0.30
3-fluorophenol	0.68	0.17
3,5-bis(trifluoromethyl)phenol	0.82	
acetic acid	0.62	0.44

[a] Values are from refs 115 and 22.

The solvation parameters $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ have been developed to characterize the hydrogen-bond acidity and hydrogen-bond basicity, respectively, of solute molecules. It is important to distinguish hydrogen-bond acidity and hydrogen-bond basicity as they relate to hydrogen-bonding *interactions* from proton-transfer acidity and basicity as they relate to acid−base *reactions*. These are fundamentally different processes, and there is no general relationship between pK_a values and hydrogen-bond acidity, for example.[24-26] Resonance stabilization of a conjugate base can be quite significant in influencing proton dissociation but is not so relevant to hydrogen-bonding interactions. Though general correlations can sometimes be made within chemical families, no general relationship exists between proton-transfer acidities and basicities and hydrogen-bonding acidities and basicities. For example, phenol and acetic acid have similar hydrogen-bond acidities as indicated by their $\Sigma\alpha_2^H$ values of 0.60 and 0.62, respectively, but acetic acid is a stronger proton dissociation acid in water by 5 orders of magnitude. Similarly, although urea is a weaker proton-acceptor base than triethylamine, it is a stronger hydrogen-bond base ($\Sigma\beta_2^H = 0.90$ for urea and 0.79 for triethylamine).

Use of solvation parameters in linear solvation energy relationships (LSERs) will be described below. Solvation parameters can also be used to relate the structural features in molecules to the resulting solubility properties. This can provide insight into the structures that one might incorporate into a polymer to obtain particular properties and potential interactions.

The solvation parameters for the hydrogen-bond acidity and hydrogen-bond basicity of several hydrogen-bond acidic molecules are given in Table 1. These two parameters are scaled to free energies in the same way. The first three molecules illustrate increasing hydrogen-bond acidity of alcohols as the fluorination is increased, as indicated by the $\Sigma\alpha_2^H$ values. Simultaneously, the hydrogen-bond basicity goes down, which can decrease self-association. Hexafluoroisopropanol, the most hydrogen-bond acidic of these alcohols, is shown in Figure 2. It is also apparent that the unfluorinated alcohol, ethanol, is only a weak to moderate hydrogen-bond acid while being even a better base. The next three molecules illustrate increasing hydrogen-bond acidity of phenols as the fluorination is increased. A phenol is intrinsically a better hydrogen-bond acid than an aliphatic alcohol and becomes even better if fluorinated. 3,5-Bis(trifluoromethyl)phenol, the most hydrogen-bond acidic of these phenols, is included in Figure 2.

Accordingly, strong hydrogen-bond acidity can be obtained by incorporating fluorinated alcohol or fluorinated phenolic functional groups as substituents in a polymer structure.[7,22,27] These groups maximize the hydrogen-bond acidity of the hydroxyl groups by the electron-withdrawing effect of the fluorine atoms while simultaneously minimizing the hydrogen-bond basicity of the hydroxylic oxygen atoms, and they contain no other significantly basic heteroatoms.

Minimizing hydrogen-bond basicity within the structure is important to minimize self-association. The energetic gain of the interaction of a basic analyte vapor with a formerly free hydroxyl group hydrogen, where there is no cost to breaking a pre-existing hydrogen bond, will be substantially greater than the gain from the basic vapor interacting with a formerly hydrogen-bonded hydroxyl group hydrogen and hence will provide a greater driving force for sorption.

Finally, acetic acid is included in Table 1, since carboxylic acids are well known as acidic organic functional groups in the sense of proton dissociation acidity. Carboxylic acids are both hydrogen-bond acids and hydrogen-bond bases, and so can be expected to self-associate in condensed phases. In fact, even in the gas phase acetic acid exists primarily as a hydrogen-bonded dimer. The carbonyl oxygen provides a basic heteroatom that promotes self-association. For these reasons, carboxylic acids are not ideal functional groups for strongly hydrogen-bond acidic polymers.

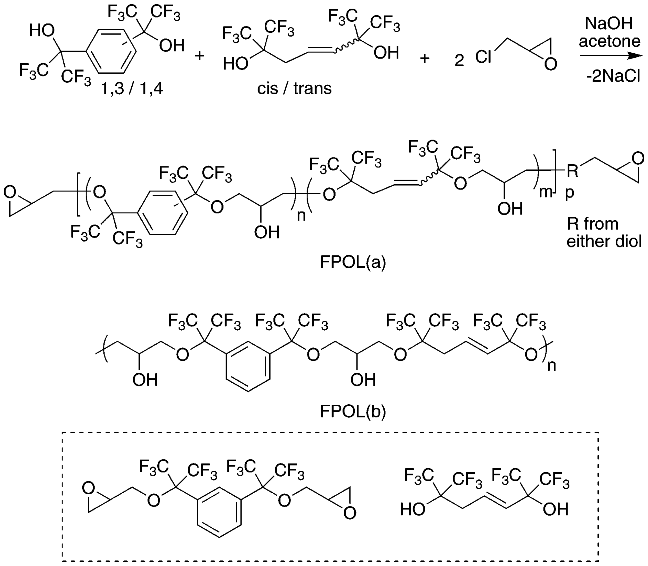
3. Fluoroalcohol-Containing Organic Polymers

This section on organic polymers (section 3) and the subsequent section on silicon-containing polymers (section 4) will focus on the structures and synthesis of the hydrogen-bond acidic polymers being described as well as sorptive or spectroscopic studies that establish their interactions with basic solutes via hydrogen bonding. Use of these polymers on sensors and devices for vapor detection will be highlighted in later sections (sections 6−10) of the review.

Use of hexafluoroisopropanol substituents in a polymer to promote the sorption of organophosphorus vapors was recognized in early studies published in 1987 by Barlow et al.[28,29] These authors used both analog calorimetry and measurements of vapor uptake on a QCM to demonstrate and investigate sorption of DMMP by a modified polystyrene copolymer material, which interacted by hydrogen bonding to the pendant hexafluoroisopropanol groups. These studies followed those of Pearce, who first modified polystyrene with pendent hexafluoroisopropanol groups as part of a study on promoting the miscibility of polymer blends through polymer−polymer hydrogen bonding.[30]

At around the same time as Barlow's initial report in 1984,[31] scientists at the Naval Research Laboratory (NRL) were testing a fluoroepoxy prepolymer, dubbed fluoropolyol (FPOL), as a sorbent on SAW devices for organophosphorus vapor detection.[7,27,32,33] This prepolymer was originally prepared as a random copolymer containing a mixture of isomers for the development of protective coatings for naval applications.[34] The synthesis is shown in Scheme 1, producing FPOL(a).[35] In most publications, the nominal repeat unit structures of these types of materials have been represented more simply by structures like that in FPOL(b), which illustrate the functional groups and dominant isomers.[7,33,34,36] (In subsequent work to be described below, specific isomeric FPOL polymers were prepared using diglycidyl ether and diol reagents as indicated in the dashed box.) Hydroxyl groups along the polymer backbone, with electron-withdrawing fluorine and oxygen atoms, are responsible for the hydrogen-bond acidic properties. The FPOL sample used in early SAW sensor studies had a reported T_g of 10 °C. Thus, it had desirable fluoroalcohol interactive groups in a polymer with a low T_g. Additional studies of FPOL synthesis are described below.[37−39]

Scheme 1

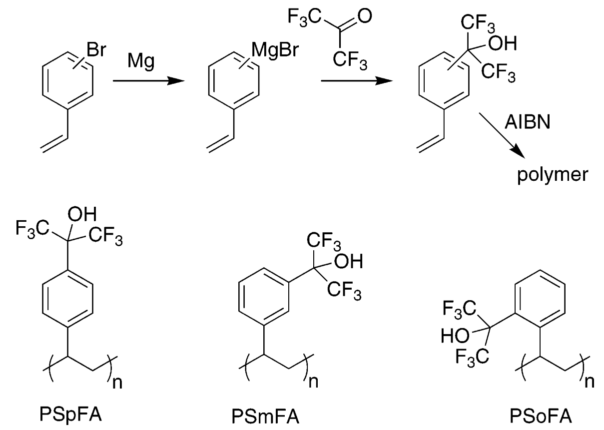


FPOL has been used in early SAW array studies, organophosphorus simulant and agent detection, comparisons of synthesized hydrogen-bond acidic polymers, studies of polymer solubility properties using LSERs, development of new chemometric approaches, sensor array systems, polymer film deposition methods, and development of other types of sensors including chemiresistors.[7,8,21,22,27,32,33,37−62] It represented the de facto standard for hydrogen-bond acidic sensor materials for many years.

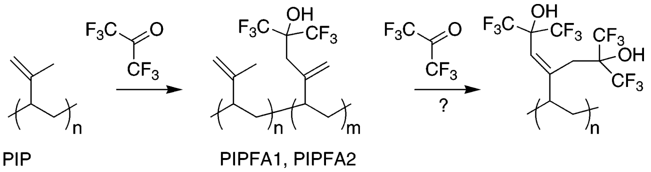
Subsequent to the studies of Barlow et al. and the initial demonstration of FPOL as a sensor coating, Snow et al. published a detailed study of a variety of fluoroalcohol-containing polymers in 1991.[27] Among these were a series of hexafluoroisopropanol-substituted polystyrenes as shown in Scheme 2. These were prepared by first making the corresponding hexafluoroisopropanol-substituted styrene monomers containing ortho-, meta-, or para-substituted phenyl groups and polymerizing them by a free-radical-initiated reaction to obtain the product homopolymers. The monomers were prepared from the reactions of bromostyrenes with magnesium to prepare Grignard reagents that were then reacted with hexafluoroacetone. The parent polymer in this group, polystyrene, has a T_g of 100 °C, while the para- and meta-substituted polymers had T_g values of 122 and 84 °C, respectively. No value was reported for the ortho-substituted polymer because the ortho-substituted monomer polymerized rather poorly, possibly due to a steric effect, and the yield was low.

In the same paper, Snow et al. described the modification of polyisoprene with hexafluoroacetone to produce hexa-

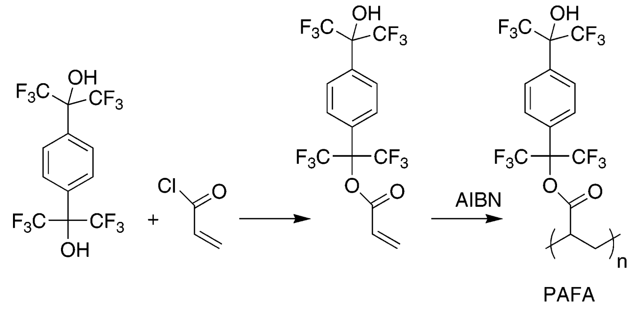
Scheme 2



Scheme 3



Scheme 4



fluoroisopropanol-substituted hydrocarbon polymers as shown in Scheme 3. This reaction of hexafluoroacetone with double bonds at elevated temperatures follows the chemistry described by Urry et al.[63] The reaction proceeds most readily on terminal double bonds. In principle, up to two hexafluoroacetone groups could be incorporated per isoprene repeat unit. However, there was no evidence to indicate that more than one hexafluoroacetone was added to any single isoprene repeat unit. Two samples were prepared with different hexafluoroacetone to monomer ratios, yielding samples with 80% (PIPFA1) and 46% (PIPFA2) of repeat units functionalized as determined by elemental analysis. The PIPFA2 was a dense glassy material with a T_g of 32 °C, while the more substituted PIPFA1 reported to be a fibrous glassy material with a T_g of 60 °C.

One additional fluoroalcohol polymer based on an acrylic ester backbone was prepared by Snow et al. Both the fluoroalcohol-substituted PAFA polymer shown in Scheme 4 and a control polymer without a free fluoroalcohol PA were prepared. The T_g values for PA and PAFA were 96 and 175 °C, respectively.

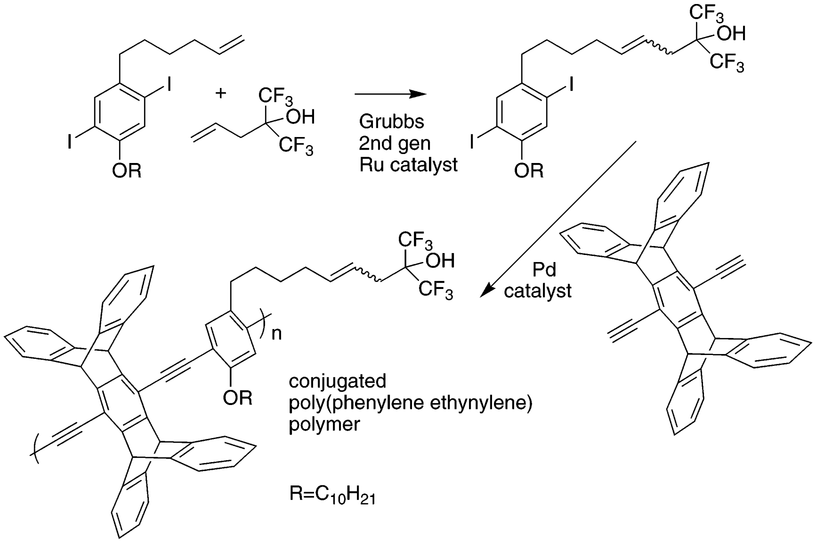
All these polymers were examined as films on SAW devices to measure DMMP vapor uptake and in infrared (IR) spectroscopy studies to demonstrate hydrogen bonding to DMMP. SAW sensor responses were plotted against the vapor concentration as P/P_{sat}, i.e., the test vapor partial pressure relative to the saturated vapor pressure. Since the SAW response is proportional to the amount of vapor sorbed, these are related to sorption isotherms. (If the response were purely gravimetric, the calibration curve would be the same as the sorption isotherm, but modulus effects may occur.) For each type of fluoroalcohol polymer, the curves of the test polymer or polymers were compared with one or more controls. For example, the response of FPOL-coated sensor was compared with that of a sensor coated with a FPOL derivative that had been acetylated to convert the free hydroxyls to non-hydrogen-bond acidic esters. The sensor response to DMMP at the lowest concentrations, using the FPOL with free hydroxyl groups, was about 5 times greater than that for the sensor coated with the acetylated derivative of FPOL. The polystyrene polymers with pendant hexafluoroisopropanol groups were compared with unmodified polystyrene and an acetylated derivative of the para-substituted polymer. The para- and meta-substituted polymers with free fluoroalcohols sorbed DMMP more than 5 times greater than the acetylated control and more than 10 times greater than the polystyrene control. Similarly, fluoroalcohol-containing polymers in the polyisoprene and polyacrylate cases were about 10 times more sorbent than the controls. These experiments clearly confirmed the importance of the fluoroalcohol hydroxyl groups for promoting DMMP sorption, consistent with the hydrogen-bonding rationale for polymer design.

IR spectroscopy studies were also carried out comparing the fluoroalcohol hydroxyl region before and after DMMP sorption. The absorption frequencies of the free hydroxyls were reported and compared with the shifted frequency in the presence of DMMP. Hydrogen-bond formation was clearly evident in these spectral comparisons. In carbon tetrachloride, hexafluoroisopropanol is known to hydrogen bond to DMMP with a spectral shift from 3600 to 3190 cm^{-1}.[28] The fluoroalcohol polymers showed similar shifts. It was noted that prior studies of hydrogen-bond formation between hexafluoroisopropanol and various Lewis bases had demonstrated that the size of the IR spectral shift of the hydroxyl region could be related to the enthalpy of hydrogen bonding.[64] This prior study noted that the fluorinated alcohol was a better hydrogen-bond acid than an unfluorinated phenol.

These studies by Snow et al., published in 1991, successfully demonstrated the approach of using fluoroalcohols incorporated into polymer structure to promote DMMP sorption by hydrogen-bonding interactions. However, all of the new polymers had T_g values above room temperature. Hence, they were not ideal in making a sensor coating yielding a very rapid response.

In work published in 1997 and 1998, researchers from France investigated FPOL in detail, working with samples of the original prepolymer as well as samples that they synthesized themselves.[37,38] These investigators noted that the original FPOL was a mixture of isomers and that the material contained low molecular weight oligomers. Both of these factors could have a plasticizing effect that lowers the T_g. They set out to synthesize FPOL polymer samples for each of the possible isomer combinations. Since there are meta- and para-isomers with regard to the phenyl group in the repeat structure and cis- and trans-isomers with regard to the double bond, there are four isomer combinations, each of which was prepared as the pure polymer. The original FPOL sample contained primarily the meta-aromatic/*trans*-ethylenic units. The dashed box in Scheme 1 shows the reactants used to prepare one of the isomeric fluoropolyol

Scheme 5

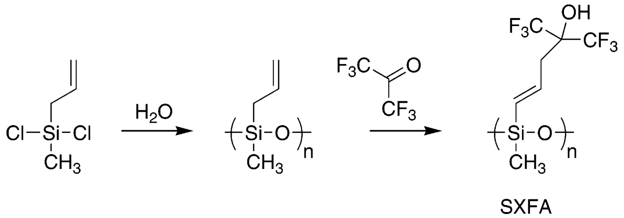


materials, shown as FPOL(b). These authors found a T_g value for the original FPOL sample of 16 °C, whereas they reported T_g values from 35 to 45 °C for the pure isomeric polymers. In terms of vapor sensitivity in tests with chemical agent GB, these authors reported that the polymer with meta-aromatic/*trans*-ethylenic units provided the best responses. Response times at temperatures below the T_g (30 °C) were extremely slow and much faster above the T_g (40 °C). These results are consistent with the expected slow diffusion of vapors in glassy polymers and the design rationale of selecting polymers with low T_g in order to obtain rapid sensor responses.

Additional preparations of fluoropolyol-type materials were reported in 2004.[39] These authors used reactions of epichlorohydrin and fluorinated diols to produce their epoxy polymers and tested them on 10 MHz QCM sensors. The resins obtained were pale yellow to light brown liquids at room temperature with molecular weights on the order of 1600−1800, confirming their oligomeric nature.

Swager et al. synthesized a hexafluoroisopropanol-substituted organic polymer with a conjugated backbone structure, which they reported in 2005.[65] Three poly(phenylene-ethynylene) polymers were prepared, one of which is shown in Scheme 5. The pendant hexafluoroalcohol groups did not appear to influence the polymerization process by the palladium-catalyzed Sonogashira−Hagihara cross-coupling reaction. The rigid iptycene groups on the polymer provide several benefits, including reduced solid-state aggregation, increased solubility, and increased free volume that facilitates vapor diffusion within the solid polymer material for binding and fluorescence response. These materials were investigated as fluorescent sensors (see below) in experiments with nitroaromatic and pyridine vapors.

Scheme 6



4. Silicon-Based Fluoroalcohol and Fluorinated-Phenol Polymers

4.1. Linear Silicon-Containing Polymers

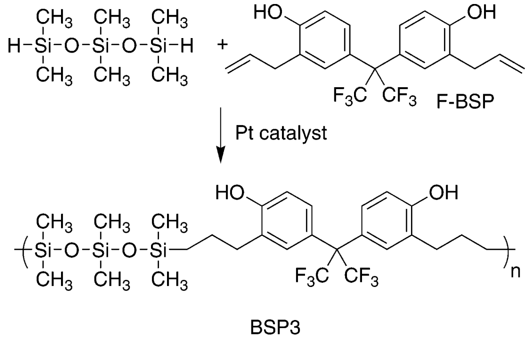
To address the issue of obtaining a fluoroalcohol-containing polymer with intrinsically low T_g, Grate turned to the use of a siloxane polymer backbone.[44,66,67] Polydimethylsiloxane has one of the lowest T_g values known among polymers. Unless the silicon atoms in a polysiloxane have large substituents, the siloxane (Si−O−Si) linkage can move and rotate with very little hindrance, resulting in low T_g values. Polysiloxanes are also the most popular sorbent stationary phases used in gas−liquid chromatography due to their chemical and thermal stability, favorable wetting characteristics for coating columns or supports, low T_g values, and fast vapor diffusion. Synthetically, their selectivity can be readily tailored by variation of the substituent organic groups, and there are a variety of cross-linking and immobilization approaches available.

Grate designed and synthesized a polysiloxane with a pendant hexafluoroisopropanol group on each repeat unit.[66,67] The synthesis of this polymer, dubbed SXFA for siloxane fluoroalcohol, was published in 1995 as part of a study of sorbent sensing polymers using LSERs.[44] Reaction of hexafluoroacetone with a terminal alkene was used to generate the pendant group, after first preparing a polysiloxane polymer containing pendant allyl groups, as shown in Scheme 6. Thus, this synthesis uses the reaction of hexafluoroacetone with terminal alkenes on a pre-existing polymer much like the reaction with polyisoprene introduced by Snow (see Scheme 3). The product was a viscous liquid.

SXFA has been used by several investigators on a variety of sensor platforms, including SAW devices, microcantilevers, flexural plate wave devices, and chemicapacitors for applications including chemical agent detection and explosives detection, and it has been used in studies of vapor sorption and coating deposition methods.[8,44,46,47,51,52,57,61,68−75]

In subsequent work reported in 1997, Grate and Kaganove created hybrid organic/inorganic polymers incorporating oligosiloxanes as the inorganic segment in the polymer backbone.[49] The functional organic segment was derived from a diallyl-substituted fluorinated bisphenol (2,2-bis(3-allyl-4-hydroxyphenyl)hexafluoropropane; F-BSP), as shown

Scheme 7



in Scheme 7. These polycarbosiloxane polymers, assembled using Pt-catalyzed hydrosilylation chemistry, incorporated both siloxane and carbosilane linkages. Careful characterization of the products confirmed that the reaction occurred by hydrosilylation to produce Si−C bonds rather than potentially competing dehydrocondensation reactions that could have produced O−Si bonds and consumed the desired phenolic hydroxyl groups.[49] Materials were made with three, six, or tens of silicon atoms in the inorganic segment. The first of these, now commonly known as BSP3, is shown in Scheme 7. Use of the silicon-containing inorganic segment succeeded in yielding polymers with low T_g values, reported to be 6 °C for BSP3. BSP3 was isolated as a very viscous gum phase.

Hydrosilylation polymerization to produce a carbosiloxane polymer containing a nonfluorinated bisphenol (2,2-bis(3-allyl-4-hydroxyphenyl)propane; H-BSP) had been previously demonstrated by Mathias in a brief communication.[76] Similar polymers with unfluorinated bisphenols have been investigated for surface modification applications by Boileau.[77,78]

Selection of fluorinated phenolic functional groups in BSP3 was motivated, in part, by prior work by Abraham and Rose, where a variety of low volatility liquid phenolic materials were compared using gas−liquid chromatographic measurements and LSERs.[79] The F-BSP monomer shown in Scheme 7 along with a propyl-substituted variant were the most strongly hydrogen-bond acidic phenols in the study. Moreover, they were much more acidic than nonfluorinated bisphenols (H-BSP and a propyl analog), confirming the role of electron-withdrawing fluorine atoms to yield more strongly hydrogen-bond acidic hydroxyl groups. For example, the observed partition coefficient for ethylamine at 25 °C was 10 800 in F-BSP, whereas it was only 56 in the nonfluorinated H-BSP.

In experiments with SAW devices, BSP3 polymer proved to be an excellent sorbent for DMMP, yielding sensors that were twice as sensitive at trace concentrations compared to FPOL-coated sensors.[49] BSP3 has been used in SAW sensor studies, SAW array systems with preconcentrators and gas chromatographic separation systems, comparison of polymer-coated SAWs with nanoparticle chemiresistor sensors, fluorescence chemical agent sensors, solid-phase microextraction, and studies on the use of nanoparticles to suppress polymer dewetting on surfaces.[49,51,55,57,59,80−90]

The synthesis of BSP3 introduced hydrosilylation chemistry to the development of hydrogen-bond acidic polymers for sensors and was the first to examine a polymer with a fluorinated phenol rather than a fluorinated alcohol. In addition, these authors set out hydrosilylation polymerization as a versatile method to produce low T_g polymers with a variety of chemical selectivities, including hydrogen-bond basic, dipolar, polarizable, and nonpolar,[55,59] as required to obtain chemical diversity in sorptive sensor arrays.[2,22,26]

Hydrosilylation chemistry was also shown to be a viable route to cross-link such hybrid polymers. In addition, using a photoactivated hydrosilylation catalyst, Pt(acac)$_2$, sorptive polymers could be photopatterned.[55,91] Illuminated regions of the film that are crosslinked by the photoactivated catalyst are retained, while regions that are not illuminated or crosslinked are removed in the wash step to develop the pattern. The ability to photopattern a sorptive polymer may be desirable for some sensor types in order to localize the polymer onto a specific region of the transducer. In principle, photopatterning could also be used to prepare large numbers of coated sensors in parallel at the wafer level. To obtain hydrogen-bond acidic photopatterned films, a method was developed that combined photoactivated Pt-catalyzed polymerization and cross-linking in a single step. The monomers and cross-linker used to prepare photopatterned film materials related to BSP3 are shown in Scheme 8. An image showing photopatterned domains of this polymer as curved lines on a silicon wafer is shown in Figure 3.

Poole and Abraham developed a new fluoroalcohol-substituted siloxane polymer dubbed PSF6, as shown in Scheme 9.[92] Platinum-catalyzed hydrosilylation chemistry was used to add a trimethylsilyl-protected hexafluoroisopropanol-functionalized alkene to a preexisting methylhydrosiloxane−dimethylsiloxane copolymer material. Residual unreacted silicon hydrides were then capped by addition of octene, and finally, the alcohol was deprotected. Approximately 26% of the repeat units were functionalized with the fluoroalcohol, and the molecular weight was estimated at 4700. This polymer was developed as a high-temperature gas chromatographic phase.

A control polymer with the corresponding unfluorinated alcohol was also prepared for comparison. Using the LSER

Scheme 8

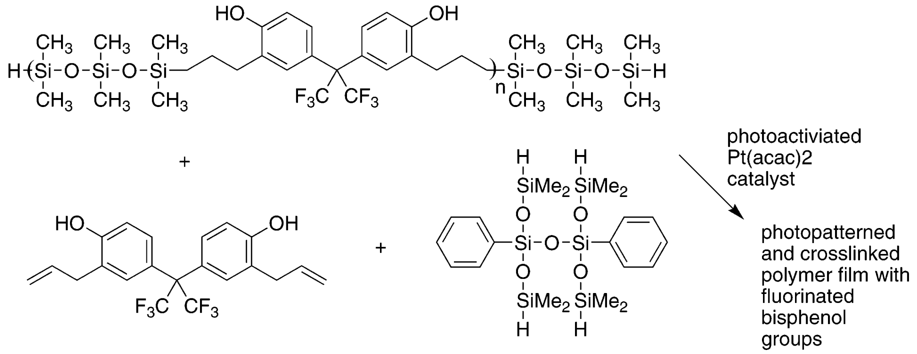
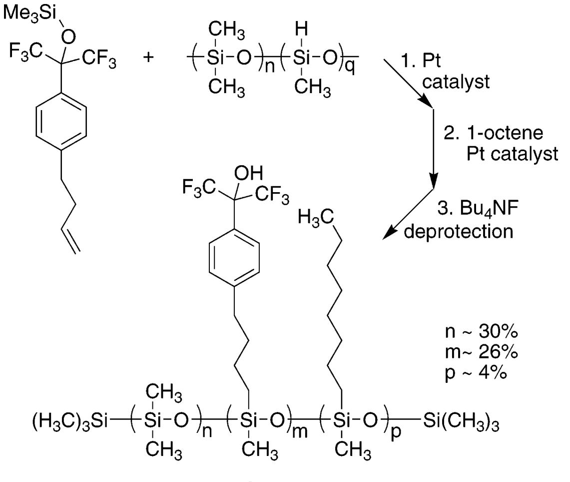


Figure 3. Image of a small silicon wafer on which a film of the materials in Scheme 8 was photopatterned to produce three lines of polymer material containing fluorinated bisphenol repeat units. Reprinted with permission from ref 55. Copyright 2000 American Chemical Society.

Scheme 9

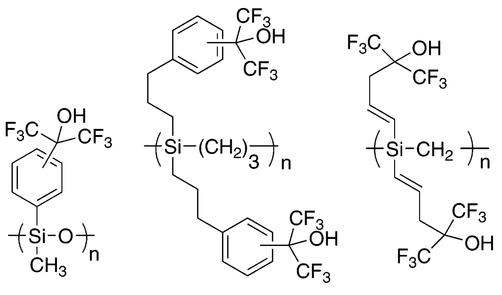


PSF6

method to evaluate the solubility properties of these polymers (see below), it was found that the fluorinated material was a strong hydrogen-bond acid with virtually no hydrogen-bond basicity. By contrast, the unfluorinated control was a significantly weaker hydrogen-bond acid and actually a better hydrogen-bond base than acid. These studies further confirmed the principles used to select fluoroalcohols as one of the best hydrogen-bond acidic groups for obtaining selective sorbent materials for hydrogen-bond bases. Fluorination increases hydrogen-bond acidity by two effects: by the inductive electron-withdrawing effect increasing the intrinsic hydrogen-bond acidity of the unassociated hydroxyl group and by reducing self-association as a result of the lower hydrogen-bond basicity of the alcohol, resulting in more free hydroxyls available for hydrogen-bonding interactions. This paper also reviewed a variety of hydrogen-bond acidic phases that had been prepared and evaluated by LSERs up to that date, including FPOL, PSpFA, SXFA, and some nonpolymeric bisphenol molecules.

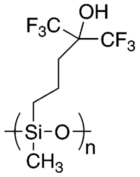
In a 2001 journal paper describing explosives detection with coated SAW devices,[61] McGill and Houser reported a polysiloxane and two linear carbosilane polymers, all with pendant hexafluoroisopropanol-substituted phenyl groups. Two of these, SXPHFA and CS3P2, are shown in Scheme 10. This paper introduced hydrogen-bond acidic polycarbosilanes; like polysiloxanes, many carbosilane polymers have low T_g values. However, neither this paper nor preceding proceedings articles[93−96] that described the use of SXPHFA provided the synthetic procedures or characterization. A series of subsequent proceedings papers, such as *Polymer Preprints* or *PMSE Preprints*, provided synthetic methods and characterization for various hydrogen-bond polymers prepared by this group[97−102] and described polycarbosilanes with hexafluoroalcohol groups derived from the reaction of hexafluoroacetone with alkenyl-substituted linear polycarbosilanes (isolated as yellow oils).[99,102] One of these, PMSFA, is also shown in Scheme 10. (The designation PMSFA is by this review author, not the inventors.)

Scheme 10



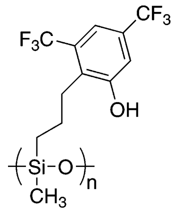
SXPHFA CS3P2 PMSFA

Scheme 11



PLF

Scheme 12



DKAP

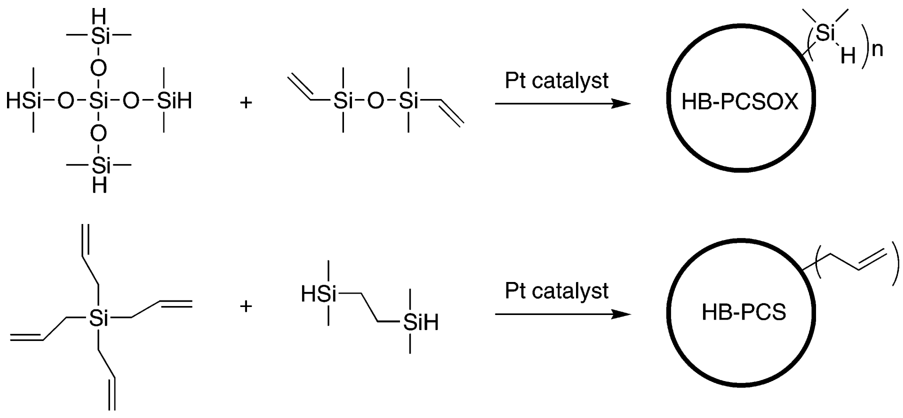
Another group reported the linear polysiloxane dubbed PLF (shown in Scheme 11), which was prepared with pendant hexafluoroisopropanol substituents added to an existing polymethylhydrosiloxane (PMHS) polymer by Pt-catalyzed hydrosilylation chemistry, in 2000 with additional papers appearing in 2001 and 2004.[103−105] Synthesis and characterization details were not given.

A linear polysiloxane with pendant fluorinated phenol groups has been prepared by Wheeler at Sandia using Pt-catalyzed hydrosilylation chemistry to add an allyl-substituted 3,5-bis(trifluoromethyl)phenol to an existing PMHS polymer.[84,106] This polymer, dubbed DKAP, has the repeat unit shown in Scheme 12. It has been used on SAW sensors as part of Sandia's microChemLab SAW array system[84] and mentioned in connection with studying the effects of nanoparticles for suppressing the dewetting of polymer films from substrate surfaces.[107] The synthesis and characterization remains unpublished.

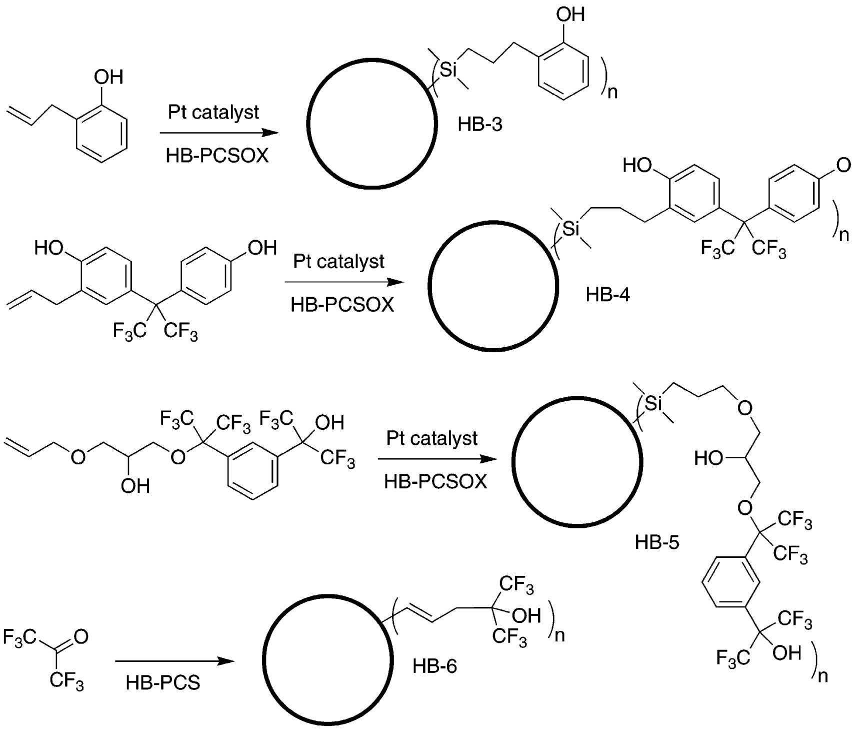
4.2. Hyperbranched and Polyhedral Architectures

Hyperbranched polysiloxane and polycarbosilane structures have also attracted interest. A hyperbranched material

Scheme 13



Scheme 14

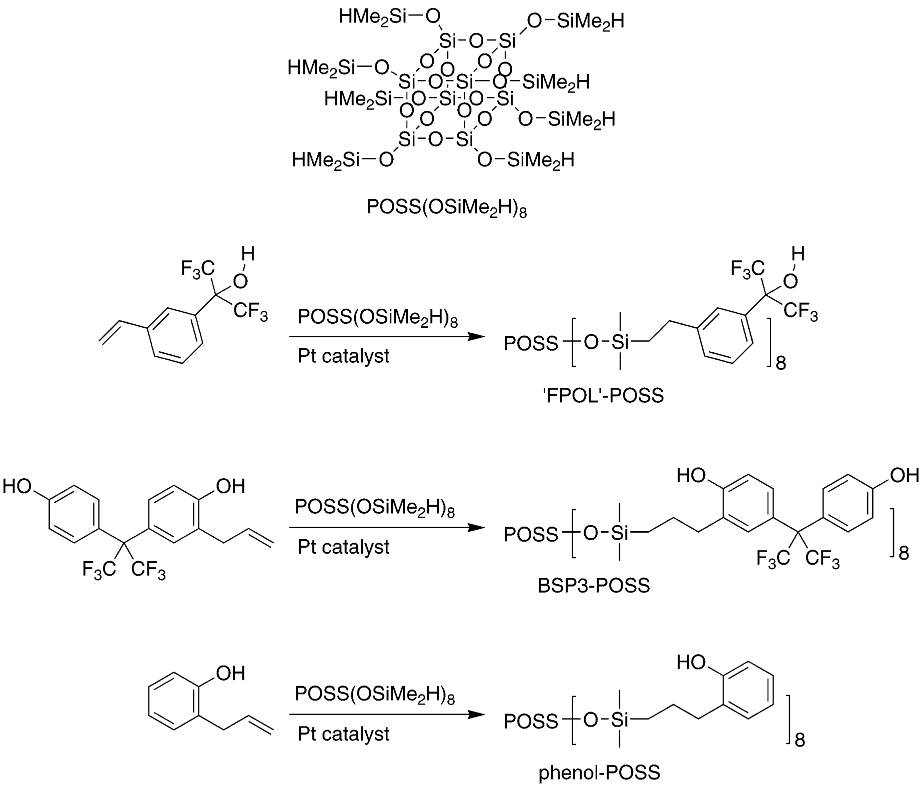


dubbed PBF, containing both siloxane and carbosilane linkages, was claimed in 2000.[103] A proposed structure corresponding to a branched version of PLF (Scheme 11) was depicted, but no synthesis or characterization data were reported.

A thorough full journal paper on hyperbranched polymers with strongly hydrogen-bonded acidic groups was published in 2004 by Dvornic and co-workers at the Michigan Molecular Institute.[108] These authors generated hyperbranched silicon-based polymers using hydrosilylation as shown in Scheme 13, which were subsequently functionalized as shown in Scheme 14. The functional groups include fluorinated alcohols and phenols similar to those in previous linear polymers, added using either hydrosilylation chemistry or the reaction of hexafluoroacetone with an allyl group (as in SXFA, Scheme 6). The resulting polymers were all yellow oils. The hyperbranched backbones had reported molecular weights of 2913 and 6322 for HB-PCSOX, a hyperbranched polycarbosiloxane, and HB-PCS, a hyperbranched polycarbosilane, respectively. The molecular weights were not degraded by functionalization. The molecular weight gains due to functionalization and the resulting polydispersity were quite variable. (The names in Scheme 14 were created here by combining “HB” for hyperbranched and the number corresponding to the number in these authors manuscript.) These polymers were coated onto 500 MHz SAW devices and tested against DMMP.

In a series of reports in *PMSE Preprints* and *Polymer Preprints* starting in 2003, Houser, Simonson, and McGill described hyperbranched polycarbosilanes with fluoroalcohol groups and indicated their synthetic approaches.[99−102] The fluoroalcohol-substituted polymers are viscous oils.[102] A hyperbranched structure dubbed HC, used in a number of subsequent sensor studies, was developed. The pendant functional groups on HC are shown in ref 74 and correspond to those in the linear PMSFA (Scheme 10).[109] Linear and hyperbranched polycarbosilanes have been used in SAW devices for explosives and chemical agent detection, on microcantilever beams, with chemicapacitive sensors, and as sorbents on microfabricated preconcentrators.[61,74,99,110−112]

Scheme 15

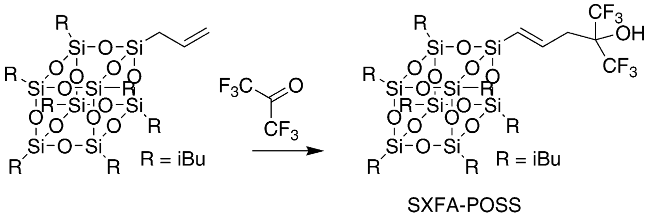


Full publication of the synthesis and characterization of the linear and hyperbranched polycarbosilane polymers in a peer-reviewed journal would be desirable and would help to support the published performance of HC-coated sensors and devices.

Polyhedral oligosilsesquioxane (POSS) compounds represent yet another silicon-containing architecture that has been functionalized with hydrogen-bond acidic groups, as shown in Schemes 15 and 16.[113] This report appeared in early 2007. The POSS starting materials used were of a precisely defined size of the general formula $R_8Si_8O_{12}$ with the R groups on the corners of the nanoscopic cubic structure. Hydrosilylation chemistry was used to create octafunctionalized POSS compounds starting with the octa(oxidimethylsilane)POSS shown in Scheme 15. Functionalization was designed to match prior linear polymers, leading to octasubstituted BSP3-POSS, for example, which has bisphenol groups similar to BSP3 (Scheme 7). The octasubstituted material designated ‘FPOL’-POSS (quotation marks added by this author), however, has functionalization more similar to PSmFA (Scheme 2), PSF6 (Scheme 9), or SXPHFA (Scheme 10) than to the original FPOL (Scheme 1). An unfluorinated phenol was also used to prepare an octasubstituted phenol-POSS. A monosubstituted SXFA-POSS was prepared to mimic the linear SXFA (Scheme 6) polymer, as shown in Scheme 16.

All the new POSS compounds were fully characterized. The BSP3-POSS and phenol-POSS were isolated as white solids. ‘FPOL’-POSS and SXFA-POSS were isolated as yellow gums. These compounds were investigated as functionalized “nanofillers” in nanofiller−polymer blends used as sorptive coatings on SAW sensors. The POSS compounds were blended with either the corresponding linear fluoropolymer or an unfunctionalized polycarbosilane. The vapors used to test the coatings were nitroaromatic compounds.

Scheme 16



5. Linear Solvation Energy Relationships

Linear solvation energy relationships, or LSERs, are semiempirical models for solubility-dependent phenomena, expressing a measure of the phenomenon as a linear combination of terms related to fundamental interactions. The partition coefficient, for example, is a measure of the sorption of a vapor from the gas phase into a sorbent phase serving as the solvent. The vapor is the solute, and the interactions are by definition solubility interactions. LSERs have been successful in correlating a vast amount of solubility-dependent phenomena, often to the precision of the available data.[23,25,114−116]

For a sensor whose response is directly proportional to the amount of vapor sorbed in a polymer layer, the sensor response represents a measure of the solubility-dependent phenomenon. Application of LSERs to the study of polymer-coated chemical sensors was introduced in 1988[7] and has been described in detail in a number of articles and reviews by Abraham, Grate, and McGill.[2,11,22,26,57,117] LSERs have been discussed independently by Hierlemann et al.[118]

The basic form of the LSER developed by Abraham for vapor sorption is given in eq 9, where K is the partition coefficient as defined in eq 1.[22,23,26,115]

$$\log K = c + rR_2 + s\pi_2^{\mathrm{H}} + a\Sigma\alpha_2^{\mathrm{H}} + b\Sigma\beta_2^{\mathrm{H}} + l\log L^{16} \quad (9)$$

A set of solvation parameters R_2, π_2^{H}, $\Sigma\alpha_2^{\mathrm{H}}$, $\Sigma\beta_2^{\mathrm{H}}$, and $\log L^{16}$

Table 2. LSER Coefficients[a] for Selected Polymers and Phenolic Liquids Determined at 298 K

material[b]		LSER coefficients				
abbreviation	type	polarizability, *r*	dipolarity/polarizability, *s*	basicity, *a*	acidity, *b*	dispersion/cavity, *l*
FPOL	HBApolymer[c]	−0.67	1.45	1.49	4.09	0.81
PSpFA	HBApolymer[c]	−1.54	2.49	1.51	5.88	0.90
SXFA	HBApolymer[c]	−0.42	0.60	0.70	4.25	0.72
PIB	LPpolymer[c]	−0.08	0.37	0.18	0.00	1.02
PECH	LPpolymer[c]	0.10	1.63	1.45	0.71	0.83
SXPH	LPpolymer[c]	0.18	1.29	0.56	0.44	0.89
F-BSP	HBAliquid[c]	−0.48	1.04	0.89	4.56	0.863
H-BSP	HBAliquid[c]	−0.92	2.24	2.79	2.41	0.975

[a] Data are from refs 44 and 79 for measurements at 298 K. [b] The polymers are fluoropolyol (FPOL, Scheme 1), poly(4-vinylhexafluorocumyl alcohol) (PspFA-Scheme 2), a hexafluoroisopropanol-substituted polysiloxane (SXFA, Scheme 6), poly(isobutylene) (PIB, Scheme 17), poly(epichlorohydrin) (PECH, Scheme 17), and a 75%-phenyl−25%-methylpolysiloxane (SXPH, Scheme 17). The phenols are 2,2-bis(3-allyl-4-hydroxyphenyl)hexafluoropropane (F-BSP in the table, shown in Schemes 7 and 8) and the unfluorinated 2,2-bis(3-allyl-4-hydroxyphenyl)propane (H-BSP in the table). [c] HBApolymer = hydrogen-bond acidic polymer, LPpolymer = low-polarity polymer, and HBA liquid = hydrogen-bond acidic bisphenolic liquid.

characterize the solubility properties of the monomeric vapor molecules.[23,115,119] Their corresponding coefficients, *r*, *s*, *a*, *b*, and the letter *l* represent the complementary properties of the sorbent phase acting as the solvent. These coefficients, and the constant *c*, are obtained by regressing the measured partition coefficients of a series of diverse solute compounds against the known solvation parameters of those compounds by the method of multiple linear regression. Typically, the required partition coefficients are determined from the retention times of injected solutes on a gas−liquid chromatographic column using the sorbent phase of interest as the stationary phase. The coefficients that characterize sorbent phase properties are of particular interest in the context of this review.

The solvation parameter R_2 is a calculated excess molar refraction parameter that provides a quantitative measure of polarizable nonbonding and π electrons. The parameter π_2^H measures a molecule's ability to stabilize a neighboring charge or dipole through dipole−dipole or dipole−induced dipole interactions, for example. The hydrogen-bonding parameters $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ measure effective hydrogen-bond acidity and basicity, respectively. The log L^{16} parameter is the liquid/gas partition coefficient of the solute on hexadecane at 298 K (determined by gas−liquid chromatography). The log L^{16} parameter is a combined measure of exoergic dispersion interactions that increase log L^{16} and the endoergic cost of creating a cavity in hexadecane leading to a decrease in log L^{16}. All of these parameters, except R_2, were derived from equilibrium measurements of complexation or partitioning,[23,120−124] and the LSER method is free-energy related. However, the parameters do not all scale with free energy equivalently. While the parameters for hydrogen-bond acidity and basicity are similarly scaled, for example, the log L^{16} parameter is quite different. Free energy contributions must be calculated for particular solvent/solute pairs for comparison as we shall illustrate below.

The complicated notation for the solvation parameters arose from the process of developing the scales and revising them, each revision requiring a modification of the notation. As the descriptor scales are now well established, the notation was recently revised,[23] such that solvation parameters R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and log L^{16} are now denoted by **E**, **S**, **A**, **B**, and **L**, respectively. The LSER eq 9 is then more easily written as eq 10. The coefficients remain the same except the *r* coefficient is now represented as an *e* coefficient. The development of the solute descriptors and the new notation were described in detail in a recent review.[23] In the current treatment we will retain the old notation in eq 9 for consistency with the papers being reviewed.

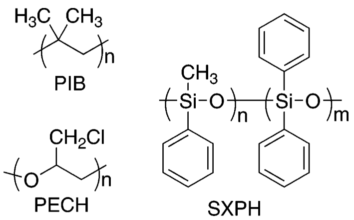
$$\log K = c + e\mathbf{E} + s\mathbf{S} + a\mathbf{A} + b\mathbf{B} + l\mathbf{L} \qquad (10)$$

In eq 9, the *l* coefficient to log L^{16} is related to dispersion interactions and the cost of cavity formation in the sorbent phase. The *s* coefficient is related to the sorbent phase dipolarity and polarizability. Similarly, the *r* coefficient is related to polarizability. The *a* and *b* coefficients, being complementary to the vapor hydrogen-bond acidity and basicity, represent the sorbent phase hydrogen-bond basicity and acidity, respectively. Thus, the *b* coefficient can be used to characterize hydrogen-bond acidic polymers.

A preliminary equation for FPOL was provided in 1991,[22] and LSER equations for four fluoroalcohol polymers were published in 1995 as part of a study of 14 sorbent phases at 25 °C.[44] This set included FPOL (Scheme 1), PSpFA (Scheme 2), SXFA (Scheme 6), and a hydroxy-terminated Fomblin Z-dol liquid. Also published in 1991 was a paper examining a large set of phenolic liquids, such as F-BSP, which is the fluorinated bisphenol monomer shown in Schemes 7 and 8. Results of these studies were also summarized in a 1998 paper that introduced the fluoroalcohol-substituted siloxane PSF6, shown in Scheme 9. LSER coefficients for PSF6 were determined at temperatures from 81 to 171 °C. In 2000, Chehimi et al. reported gas chromatographic characterization and LSER coefficient determination for PLF (Scheme 11) and PBF at 35 °C.

The LSER coefficients for selected polymers and bisphenols at 25 °C are summarized in Table 2. We are particularly interested in hydrogen-bonding properties, given by the *a* and *b* coefficients, which like their corresponding solvation parameters scale equivalently with free energy. (However, the *a* and *b* coefficients cannot be compared directly with the *l* coefficient, for example, which scales differently) Three low-polarity polymers, whose structures are shown in Scheme 17, are included for comparison. The fluoroalcohol polymers all have large *b* coefficients, indicating their hydrogen-bond acidity, while the *a* coefficients are low. By comparison, the low-polarity polymers without fluorinated alcohol or phenolic groups lack significant *b* coefficients. Like the fluorinated alcohol polymers, the fluorinated bisphenol F-BSP also has a large *b* coefficient and a low *a* coefficient. By contrast, the unfluorinated bisphenol H-BSP has a much smaller *b* coefficient than the fluorinated bisphenol and is actually a stronger hydrogen-bond base than

Scheme 17



acid, as noted previously. These studies confirm the importance of fluorination in achieving high hydrogen-bond acidity and simultaneously lowering hydrogen-bond basicity. The latter factor improves overall selectivity and simultaneously reduces self-association; reduced self-association then also contributes to stronger hydrogen-bond acidity.

For a given vapor/polymer combination, the LSER expresses the log of the partition coefficient as a linear combination of terms. Given the respective solvation parameters and coefficients for a specific vapor-polymer pair, the magnitude of each term can be calculated and compared to determine which interactions make the largest contributions. While dispersion interactions are nearly always important, the hydrogen-bonding interaction between a strongly hydrogen-bond acidic polymer and a moderately to strongly basic vapor can also be quite significant.[26]

Table 3 illustrates the determination of interactions using SXFA as a representative hydrogen-bond acidic polymer and four vapors. Polarizability and dipolarity interactions can be taken as the sum of ($rR_2 + s\pi_2^H$), where the rR^2 term is normally a small correction to the overall dipolarity/polarizability interaction indicated by $s\pi_2^H$. The hydrogen-bonding terms $a\Sigma\alpha_2^H$ and $b\Sigma\beta_2^H$ represent hydrogen-bonding interactions where the polymer is a base or an acid, respectively. It is difficult to separate the dispersion interactions favoring sorption from the cost of forming a cavity. Together, these can be best represented as the sum of the regression constant c and the $l \log L^{16}$ term.[92] It is clear in Table 3 that when the polymer is an acid (SXFA) and the vapor is a base (e.g., triethylamine, DMF, or ethanol), the hydrogen-bonding term is a significant contributor to the magnitude of log K. Dispersion interactions are significant contributors for most vapors from compounds that are condensed liquids at room temperature.

Sensor signals can also be used to develop LSER equations for sorbent polymers if the response is proportional to the amount sorbed as a mass, as shown above in eq 6, since responses are directly proportional to the partition coefficient without any analyte-specific sensitivity factors. Thus, the responses of a polymer-coated QCM or SAW could be used to develop an LSER equation for the polymer if the responses are purely gravimetric. For a SAW sensor with a modulus contribution to the response, this condition is not strictly true, and variations in vapor-specific volumes will cause the observed responses to vary in their proportionality to K values (see above, eq 8). In this regard, determining LSERs from SAW sensor responses is somewhat less rigorous than using true partition coefficients or responses of purely gravimetric sensors.

Nevertheless, it has been shown empirically that good correlations can be obtained between SAW sensor responses and vapor solvation parameters, providing LSER coefficients that characterize the polymer solubility properties in a sensible way. This approach was first shown by Zellers in 1993 for four polymers, none of them hydrogen-bond acids.[125] Hierlemann, Zellers, and Ricco further discussed the use of SAW sensor responses for determining LSER coefficients in 2001.[118] Also in 2001, Grate et al. reported LSER equations determined from SAW sensor responses for 14 polymers that were "well-behaved" as sensor coatings and 6 less well-behaved materials.[57] Among the well-behaved polymers were three hydrogen-bond acidic polymers, including SXFA (Scheme 6), BSP3 (Scheme 7), and a BSP3 analog with longer oligosiloxane segments. The b coefficients for these three polymers were significantly higher than any of the other well-behaved polymers, consistent with the hydrogen-bond acidity expected from the fluorinated functional groups.

The first use of QCM devices to obtain data for determination of LSER coefficients was reported in 2001 by Hierlemann et al. Results for six polysiloxanes were reported, none with fluorinated alcohol or phenol functionality.[118] One polysiloxane with 10% carboxylic acid groups was listed as an acidic polymer; however, the LSER analysis showed little hydrogen-bond acidity and much greater hydrogen-bond basicity. These results reaffirm the principle that fluorinated alcohols or phenols are preferred for obtaining hydrogen-bond acidity in a sorptive polymer for the purpose of sorbing hydrogen-bond basic vapors[22] and provides experimental evidence that pendant carboxylic acids do not result in effective hydrogen-bond acidic polymers for vapor sensing. The latter result is consistent with the notion that carboxylic acids will self-associate.

The conventional use of LSERs in sensor research has been to characterize sorptive polymers or develop LSER equations that can be used to predict partition coefficients and/or sensor responses based on the polymer parameters and vapor solvation parameters. Grate and Wise proposed instead that the responses of an array of sensors could be used to determine the solvation parameters of the sensed vapor.[52] Given an array with a suitably diverse set of known coatings and gravimetric sensor responses, the array pattern vector could be transformed into a vector containing the solvation parameters as descriptors of the vapor. In this way, an array detecting a vapor that had not been included in a prior training set might be able to characterize the vapor in terms of these descriptors and suggest what vapor it might be based on comparison of the found descriptors with those for known vapors. In order to be a diverse array, hydrogen-bond acidic polymers would be required.

A method similar to classical least-squares (CLS) calibration (often used in spectroscopy) was derived for simultaneously obtaining the full set of descriptor values from the array response vector. The approach requires that the interactive properties of the sorbent sensing layers be known and quantified as LSER coefficients (polymer parameters). In addition, inverse least-squares (ILS) methods could be used to process the array response vectors, in which case individual models are developed for each vapor descriptor. The ILS approach does not require advance knowledge of polymer parameters, but it does require that an adequate calibration data set be available to derive the ILS models. Once the CLS or ILS models are developed, an array might be used to characterize an unknown vapor in terms of its descriptor values, even if the specific unknown vapor had not been in the training set. This approach stands in contrast to most conventional pattern recognition approaches that are based on matching patterns from unknowns to patterns from known compounds in the training set.

Table 3. Calculated Interaction Terms[a] for Four Vapors Sorbed by SXFA, a Hydrogen-Bond Acidic Polymer

vapor	dipolarity/polarizability ($rR_2 + s\pi_2^H$)	hydrogen bonding, a, $\Sigma\alpha_2^H$	hydrogen bonding, b, $\Sigma\beta_2^H$	dispersion/cavity ($c + l \log L^{16}$)	partition coefficient,[b] log K
n-hexane				1.84	1.84 (1.74)
triethylamine	0.05		3.36	2.10	5.51
DMF[c]	0.64		3.15	2.20	5.99
ethanol	0.15	0.26	2.04	0.99	3.44 (3.54)

[a] No data indicate terms calculated to be zero. [b] These are calculated values, each derived from the sum of the interaction terms plus the constant. Values in parentheses are measured values. [c] *N*,*N*-Dimethylformamide.

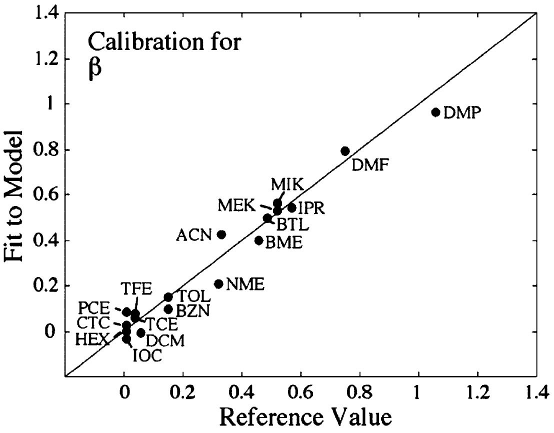


Figure 4. Calculated vs reference values for the $\Sigma\beta_2^H$ vapor solvation parameter for calibration from six-factor PCR models. Reprinted with permission from ref 57. Copyright 2001 American Chemical Society.

These approaches for converting array responses to chemical information were initially derived for mass-transducing sensors such as acoustic wave sensors,[52] extended to volume-transducing sensors[17] such as chemiresistors with carbon particle/polymer composite sensing layers,[126,127] and then extended to mass-plus-volume-transducing sensors.[8,16,57]A polymer-coated SAW device can be regarded as a mass-plus-volume transducing sensor if the response includes a modulus contribution as well as a gravimetric contribution.

Actual SAW array response vectors were used to derive ILS models that could correlate and predict vapor solvation parameters.[57] Successful correlations can be developed by multiple linear regression (MLR), principal components regression (PCR), and partial least-squares (PLS) regression. The best fits to the training data were obtained using MLR; however, cross-validation indicated that prediction of vapor descriptors for vapors not in the training set was significantly more successful using PCR or PLS. The array data included responses from sensors coated with strongly hydrogen-bond acidic polymers such as SXFA (Scheme 6) and BSP3 (Scheme 7). Having at least one of these types of polymers in the array is essential for obtaining good information about a vapor's hydrogen-bond basicity as represented by the $\Sigma\beta_2^H$ solvation parameter. Figure 4 shows the correlation between the $\Sigma\beta_2^H$ values found for vapors in the training set, using six-factor PCR models to process the array data, and the known reference $\Sigma\beta_2^H$ values for those vapors. The correlation is very good.

6. Acoustic Wave Sensors and Arrays

A significant portion of the development of acoustic wave sensor arrays has been focused on surface acoustic wave (SAW) devices. Wohltjen introduced these devices as the basis for chemical vapor sensors,[128,129] and they have since been investigated by several groups.[2,11,12,15,53,125,130−141] The SAW device is a member of a family of devices called acoustic wave devices that include the QCM (also referred to as a thickness shear mode or TSM device), surface transverse wave devices, Love wave devices, flexural plate wave devices, Leaky SAW devices, and shear horizontal acoustic plate mode devices. Acoustic wave devices have been reviewed in many prior treatments,[9−11,20,22,142−154] and acoustic wave devices in arrays for chemical vapor sensing were specifically reviewed in this journal.[2]

Polymer-coated acoustic wave devices are sorption-based sensors as shown in Figure 1. They detect the mass loading and sometimes the modulus changes that occur upon vapor sorption in the polymer film. The signal measured is typically a resonant frequency. Hydrogen-bond acidic polymers are relevant in two primary senses. First, they afford sensitivity to hydrogen-bond basic analytes of interest such as chemical agents and explosives (see below), and second, they help to ensure the diversity of chemical selectivities in a sensor array.[22] Diverse chemical selectivities help to ensure that the array collects as much chemical information as possible about the sample by probing all of the available interactions and solubility properties that can be used to distinguish one vapor from another. Hydrogen-bond acidic polymers ensure that the array responds to the hydrogen-bond basicity of sorbed vapors. Such arrays can be useful for a variety of volatile organic compound detection applications. While generally useful for this purpose, the importance of including a hydrogen-bond acidic polymer in an array depends on the analytical task the array is expected to perform.[2,51]

6.1. Chemical Agent Detection

Hydrogen-bond acidic polymers emerged as key coatings for acoustic wave sensors to promote the sorption and detection of organophosphorus chemical agents and their simulants. The principle of hydrogen bonding in this application was shown in Figure 2 above. Organophosphorus compounds are particularly strong hydrogen-bond bases; the $\Sigma\beta_2^H$ value for DMMP, for example, is 1.05. For comparison, the $\Sigma\beta_2^H$ values for other basic volatile organic compounds such as nitromethane, acetone, and ethyl amine are 0.27, 0.49, and 0.61, respectively. Much of the synthetic work described in the preceding sections was motivated by this application need. Typically, DMMP or diisopropyl methylphosphonate (DIMP) was used as a simulant, although in a few cases responses to actual chemical agents such as GD (soman) or GB (sarin) have been reported.[37,38,43,84,105]

The benefit of including a polar hydrogen-bond acidic functional group for improving sensitivity to organophosphorus compounds can be seen in Figure 5. This plot shows the calibration curves for SAW sensors coated with two hydrogen-bond acidic polymers, FPOL and BSP3 plotted with solid lines, compared with sensors coated with nonacidic

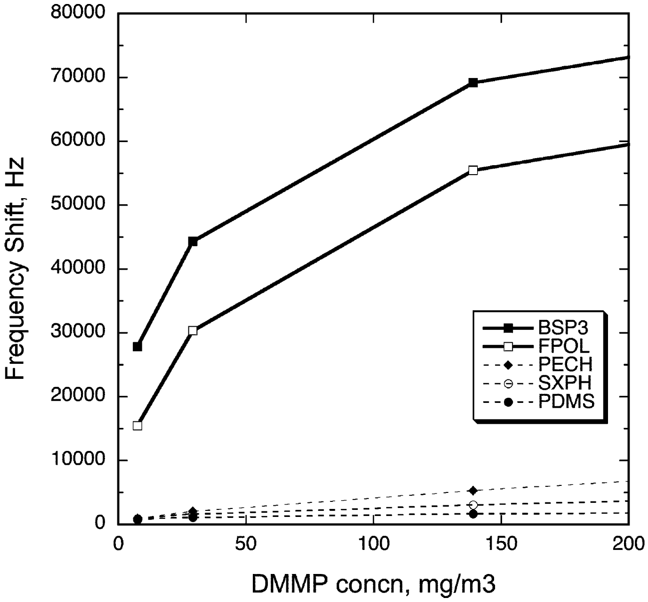


Figure 5. Calibration curves for organophosphorus compound DMMP as sensed by polymer-coated SAW sensors, comparing the hydrogen-bond acidic polymers BSP3 and FPOL with nonacidic polymers PDMS, SXPH, and PECH.

polymers PECH, SXPH, and polydimethylsiloxane (PDMS) shown with dashed lines. The PDMS polymer is a nonpolar polymer containing the same repeat units that are found in the oligosiloxane segments of BSP3 and hence illustrates DMMP sorption by a polymer if the polar organic groups are left out altogether. Promotion of sorption and response by including hydrogen-bond acidic functional groups is clearly evident and confirmed by including other nonacidic but somewhat more polar polymers, PECH and SXPH (see Scheme 17 for their structures).

Most acoustic wave sensors for agent detection have been based on SAW sensors; however; there are reports using other acoustic wave devices such as Love wave sensors.[104,105] A number of reports give an indication of the sensitivity of polymer-coated SAW sensors to organophosphorus compounds. Using FPOL (Scheme 1) on 158 MHz SAW devices, signals of over 1000 Hz were reported at 1 mg/m^3 DMMP.[43] Using BSP3 (Scheme 7) on 200 MHz SAW devices, signals of over 20 000 Hz were observed in response to 8 mg/m^3. Taking the noise to be about 3 Hz, for a minimum detectable signal of about 10 Hz at a signal-to-noise ratio of 3, the detection limit would be 0.004 mg/m^3 or about 1 ppb by volume.[49] Using SXFA (Scheme 6) on a 250 MHz SAW device, responses of 65 000 Hz to10 mg/m^3 DMMP were reported.[68] SAW sensors (500 MHz) freshly coated with HB-4 (Scheme 14), which has phenolic functionality similar to BSP3, were reported to give responses of 3629 Hz to 0.5 mg/m^3 DMMP.[108] Signals and detection limits depend on several factors, including the sensor temperature, SAW device frequency, noise, and polymer coating thickness, which vary among different studies. These data therefore provide indications of the high sensitivity without necessarily providing rigorous quantitative comparisons. Value as a SAW coating also depends on other factors such as the quality of the thin film that can be prepared on sensor. The variety of polymers shown in the previous sections provides a wealth of choices for developing effective sensors.

One group reported that SAW sensors coated with hydrogen-bond acidic polymers rapidly lose their sensitivity to basic compounds after the initial coating application and testing.[108,113] These authors spray-coated polymer films onto 500 MHz SAW devices and tested with DMMP or DNT. In one paper, it was reported that a BSP3-coated SAW device lost 90% of its sensitivity in just 10 days.[113] Indeed, all their hydrogen-bond acidic polymer-coated sensors showed significant declines in sensitivity with time. By contrast, Grate and Rapp examined BSP3 on Rapp's SAW sensor system.[155,156] Coatings were applied by electrospray[157] to 434 MHz SAW sensors. As shown in Figure 6, these sensors did not show a significant aging effect. Thus, it would appear to be unlikely that poor aging behavior represents an intrinsic property of the hydrogen-bond acidic polymers themselves, as opposed to an operational property of a polymer film on a surface.

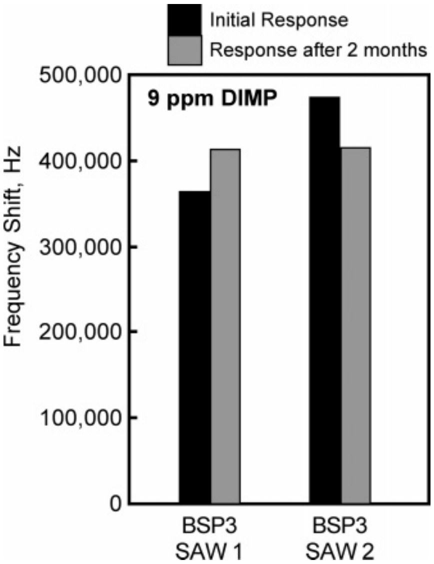


Figure 6. Responses of two electrospray BSP3-coated SAW sensors to DIMP, initially and over 2 months later.

6.2. Acoustic Wave Sensor Array Systems

In sensor systems with preconcentrators, even greater operational sensitivities and lower detection limits can be achieved relative to those for direct sensing as just described. Indeed, much of the development of SAW sensors for agent detection has focused on sensor arrays and sensor arrays preceded by preconcentrators. More recent systems have also placed gas chromatographic separation columns between the preconcentrator and the SAW array. In the first investigations of SAW sensor arrays with pattern recognition analysis,[33,40] FPOL was included in the polymer coatings and provided the highest sensitivity to simulant DMMP. On the basis of hierarchical cluster analysis, FPOL was one of the most distinctive polymers in the data set, and it was among the coatings selected for a subset of four polymers that could successfully discriminate between one class of vapors including chemical agent simulants and another class of vapors containing a diversity of potential interferences.[33] This work eventually lead to a complete prototype SAW array system with automated sample preconcentration using FPOL as the agent-sensitive coating.[43] This was the first example of an acoustic wave sensor array system with on-board preconcentration.

The Sandia microChemLab system has integrated a microfabricated preconcentrator, a microfabricated chromatographic column, and an array of polymer-coated SAW sensors. Use of BSP3 and DKAP (Scheme 12) polymers has been essential to the success of this platform in detecting DMMP and chemical agents.[84,136] Zellers developed portable gas chromatographic instruments for chemical vapor analysis using SAW array detectors and included BSP3-coated sensors in the array.[83,85] Similarly, he included BSP3 in a personal vapor monitor based on SAW sensors.[87] Flexural plate wave acoustic sensors and systems have also used hydrogen-bond acidic polymers.[54,55,72]

6.3 Explosives Detection

Detection of nitroaromatic compounds as simulants for nitroaromatic explosives such as trinitrotoluene (TNT), using a sensor coated with a hydrogen-bond acidic polymer, was first described by McGill et al. These authors used SXPHFA (Scheme 10) as the polymer to promote sorption of the nitroaromatic compounds through hydrogen bonding with basic nitro groups.[93,94] In tests using 250 MHz SAW sensors, the authors observed responses of 8500 Hz to 400 ppb of 2,4-dinitrotoluene (2,4-DNT), which was generated by passing nitrogen through a column of 2,4-DNT-coated sand. The authors extrapolated these results to a detection limit of 0.235 ppb at a signal-to-noise ratio of 3. Infrared spectroscopic studies of SXPHFA containing sorbed nitrobenzene (NB) were carried out to support hydrogen bonding between nitro groups and the polymer hydroxyl groups. Free hydroxyl groups declined (but did not disappear), and hydrogen-bonded hydroxyl groups increased, as shown in difference spectra between the neat polymer and polymer containing sorbed NB.

McGill's group provided more results on explosives detection on SAW devices in 2001, including IR spectroscopic studies of polymers with and without sorbed NB or DMMP.[61] Both of these basic sorbates reduced the free hydroxyl stretch. The OH stretch for the hydroxyl group hydrogen bonded to analyte appeared at lower wavenumbers, with DMMP shifting the stretch significantly farther as a result of its stronger hydrogen-bond basicity. Response behaviors of 250 MHz SAW devices coated with CS3P2 (Scheme 10) and CS6P2 (a similar polymer with a longer methylene chain between silicon atoms) were presented and discussed. These polymers had similar responses to DNT in tests at 31 ppb, and a detection limit of 0.095 ppb was extrapolated at a signal-to-noise ratio of 3.

The nitroaromatic compound DNT has also been used in the evaluation of the POSS compounds shown in Schemes 15 and 16, which were blended with linear polymers to prepare composite SAW sensors coatings.[113]

When explosives are compared to organophosphorus compounds with regard to sorption to hydrogen-bond acidic polymers, the relative roles of hydrogen-bonding and dispersion interactions may differ. The effective solvation parameter $\Sigma\beta_2^{\mathrm{H}}$ for NB, DNT, and TNT has been reported to be 0.28, 0.47, and 0.61, respectively.[93] For comparison, nitromethane has a value of 0.27, similar to NB. The nitro group is not intrinsically a very strong hydrogen-bond base, whereas the phosphoryl group of an organophosphorus compound is quite a strong hydrogen-bond base (e.g., DMMP has a $\Sigma\beta_2^{\mathrm{H}}$ value of 1.05). On the other hand, explosives have much higher log L^{16} values than DMMP. This parameter is related to promotion of sorption by dispersion interactions. For example, the log L^{16} values for TNT and 2,4-DNT are 7.85 and 6.26, respectively, whereas that for DMMP is only 3.75. In general, nitroaromatics are more prone to interact by dispersion interactions and less prone to interact by hydrogen bonding than typical organophosphorus compounds related to chemical agents. It is also the case that nitroaromatics have large R_2 and π_2^{H} parameters, indicating a very good ability to interact by dipole−dipole and dipole−induced dipole interactions.

7. Microcantilever Sensors

Micromachined cantilever structures represent a more recent transducer for chemical and biological sensors and arrays.[158−160] The cantilever structure is supported at one end by the bulk chip material and extends either over an etch pit or over the end of the chip like a diving board. These structures can be made in various sizes with 200 μm long by 50 μm wide by 1 μm thick being a representative size. Several such devices can be fabricated as part of a single chip for array-on-a-chip configurations. Two transduction mechanisms are typically used, either the resonant frequency shift or a bending mode observation. The resonant frequency is shifted by mass loading on the surface or in a surface-applied film. Bending arises not from the weight of collected analyte but rather from the effect of the sorbed analyte on surface stresses, leading to bending. Microcantilever movements can be monitored with optical methods or operated using capacitive, piezoresistive, or piezoelectric methods.

Thundat et al. reported detection of 2,4-DNT using a polymer-coated microcantilever in 2004.[70] A commercial "V"-shaped cantilever was coated by SXFA (Scheme 6) using matrix-assisted pulsed laser evaporation (MAPLE)[69,161] to deposit a uniform film of the polymer on one side of the cantilever. The other side of the cantilever was coated with gold, which facilitated reflection of a laser bean for optical detection of cantilever motions. The film thickness was reported to be roughly 600 nm. 2,4-DNT concentrations obtained by passing carrier gas over a temperature-controlled 2,4-DNT sample were determined by trapping a known volume on a Tenax trap and analyzing the amount of sorbate by gas chromatography with mass spectrometric detection.

Reversible and repeatable responses at 45 ppb 2,4-DNT were observed in 5 s exposures, leading to an observed sensitivity of 4.5 nm/ppb. These results were extrapolated to a detection limit of 0.300 ppb at a signal-to-noise ratio of 3. Several advantages of using the SXFA polymer were noted. Bending mode responses were found to be critically dependent on the film thickness, with coatings of 150 nm or less yielding very small responses compared to those with the 600 nm film. This paper also presented mass-loading responses from resonant frequency shifts. Frequency decreased with added mass as expected. The signal-to-noise for this mass-transduction mechanism was clearly less than that obtained in the bending mode response for the type of cantilevers being used. This group has also described detection of nitroaromatic compounds using cantilevers coated with a monolayer of 4-mercaptobenzoic acid.[162]

A cantilever beam sensor with a hydrogen-bond acidic coating for chemical agent detection has also been described.[111] A sophisticated device design for operating the cantilever in a resonant frequency mass detection mode was developed, incorporating an electrostatic actuation mechanism to drive the beam and a piezoresistive transduction method. The device also incorporated an on-beam heater. A functionalized polycarbosilane dubbed HCSA2[163] was deposited from dilute chloroform solution using a piezoelectric

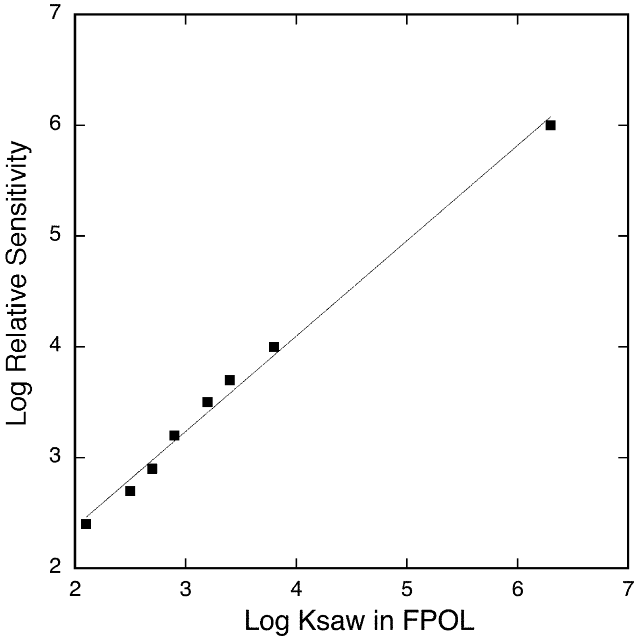


Figure 7. Correlation of the relative sensitivities of a NiPCCP/FPOL chemiresistor to a range of vapors with the tendency of those vapors to be sorbed by FPOL as indicated from measurements on SAW devices. Figure plotted from data in ref 41.

inkjet dispensing head. Response to dilute DMMP at 0.1 mg/m^3 or 20 ppb was reported to be 30 Hz at a 10 Hz noise level. Hence, this concentration represents the detection limit at a signal-to-noise ratio of 3.

8. Sensors Responding to Electrical Properties

In this section, we consider sensors that respond to conductivity changes or capacitance changes and include a hydrogen-bond acidic polymer as a component.

8.1. Chemiresistors

In 1990, Grate and co-workers at NRL described the use of FPOL−phthalocyanine composite films on interdigitated electrodes at room temperature as chemiresistor sensors for organic vapors.[41] At a constant test voltage, these sensors respond with a change in current as sorbed vapors alter the resistance of the sensing film. Chemiresistor sensors with phthalocyanine films were already well known. This paper sought to use the FPOL in the film to promote the sorption of organophosphorus vapors and hence influence the sensitivity. The phthalocyanines were tetrakis(cumylphenoxy)-phthalocyanines (PCCP) with various metal ions; Ni PCCP provided the most sensitive sensors in response to DMMP.

The films were applied by the Langmuir−Blodgett (LB) technique, resulting in contiguous nanometer-scale disc-shaped crystallites of the semiconducting phthalocyanine in a matrix of FPOL.[164] Thus, this sensor represents dispersed conducting particles as a first component in sorbent insulating polymer matrix as a second component. Indeed, it was found that response sensitivity was strongly correlated with the sorption of organic vapors in the FPOL matrix material. Figure 7 shows the log of the relative sensitivity of the Ni PCCP/FPOL chemiresistor for a range of vapors against a measure of the sorption of those vapors by FPOL as determined on a SAW device,[7] taking the data from a table in ref 41. While all the analyte-specific factors that may influence the response of a composite Ni−PCCP-containing film are not necessarily known, it is clear that the amount sorbed in the film (see eqs 3−5) is a dominant influence on the sensitivity and selectivity among the tested vapors.

The Ni PCCP sensor was very sensitive to DMMP, with responses at 17 mg/m^3 providing a signal-to-noise of 684, suggesting an extrapolated detection limit on the order of 0.1 mg/m^3 at a signal-to-noise of 3. The strategy of using the sorptive polymer to influence the sensitivity and selectivity of a conducting particle/insulating polymer composite on a chemiresistor sensor has also been used in the development of arrays of carbon black/polymer composite chemiresistors.[126,165]

FPOL and SXFA have been used as overcoats on conductive polymer fabric sensors in an effort to promote sensitivity and selectivity for organophosphorus compounds.[47] However, the fluoroalcohol-containing polymers did not increase the responses to DMMP.

8.2. Chemicapacitors

Chemicapacitors[166,167] represent a relatively new platform for the use of hydrogen-bond acidic polymers.[71,74,75] Patel and Mlsna described microfabricated devices in parallel plate and elevated interdigitated electrode configurations. The latter design provides excellent access of vapors to the polymer coated on the electrodes. The parallel plates are designed with openings in the “top” plate for polymer deposition into the capacitor gap and vapor access to the polymer. In chemical agent tests it was observed that the interdigitated design was faster to respond but slightly less sensitive than the parallel plate design. Chemicapacitors respond to changes in the permittivity within the sensed volume of the capacitor that contains the sorptive polymer. Changes in the polymer due to vapor sorption (e.g., swelling) and analyte-specific dielectric properties influence the observed response. Polymers are typically applied from solution using a piezoceramic inkjet head. Using a variety of polymers, including some hydrogen-bond acidic polymers, these investigators reported detection limits for many volatile organic compounds, warfare agent simulants, and nitroaromatic compounds.

In one study using parallel plate capacitors,[71] SXFA-coated devices were reported to respond to DMMP at 0.18 ppm (ca. 1 mg/m^3) with a signal-to-noise of 300, leading to an extrapolated detection limit of 2 ppb (ca. 0.01 mg/m^3) at a signal-to-noise of 3. A detection limit of 0.1 ppb was indicated for nitrotoluene. SXFA was also shown to give low ppm detection limits for many volatile industrial solvent vapors. In subsequent work, these authors reported an extrapolated limit of detection of 2 ppb for 2,6-DNT using SXFA.[74] In actual chemical agent tests, limits of detection of 0.047 mg/m^3 for GD using SXFA and 0.4 mg/m^3 for GB using HC were reported.

Although hydrogen-bond acidic polymers are useful for nitroaromatic compound detection on this platform, this class of polymers is not the only choice that provides high sensitivity to nitroaromatics, at least as far as chemicapacitive sensing is concerned. Polymers such as OV-225 and OV-275 have been shown to provide sensitive sensors.[75] OV-275 is a polysiloxane that contains dipolar nitrile groups, while OV-225 contains nitrile groups and phenyl substituents. These dipolar and polarizable groups apparently promote sensitivity through dipole−dipole and dipole−induced dipole as well as dispersive interactions.

Chemicapacitors have also been reported by Snow and Houser that are based on semiconducting single-walled carbon nanotubes prepared as an electrically continuous network acting as one plate of the capacitor. The other electrode was a heavily doped silicon substrate, and the two were separated by a thermal oxide layer.[112] Fringing electric fields radiate outward from the ca. 1 nm diameter nanotubes when a bias is applied. The fields are strongest at the nanotube surfaces where adsorbates can be detected as a change in the capacitance. The hydrogen-bond acidic polymer HC was applied to the sensor in a ca. 100 nm thick layer to promote responses to organophosphorus compounds. Compared to an uncoated sensor, the polymer-coated sensor gave responses to DMMP that were 500 times greater. The detection limit was estimated to be 0.5 ppb (0.0025 mg/m^3) with a response time of 370 s to reach 90% of response. A monolayer with a pendant hexafluoroisopropanol functionality was fabricated on nanotube surfaces to provide a thinner chemoselective coating; while the responses were faster, it was 100 times less sensitive.

These authors previously described chemiresistors and transistors using carbon nanotube networks for chemical vapor sensing.[168] While HC was mentioned in this work, it was used as a component of an upstream filter to remove response to DMMP rather than as a chemoselective sensor layer.

9. Optical and Luminescent Sensors

Polymers are important components to many optical sensors, either as a sorbent layer or as a matrix for other functional components. Polymers related to BSP3 were coated onto optical fibers for potential sensing applications.[49] A polymer formulation including cross-linker and hydrosilylation catalyst was delivered to a cladding cup. A glass fiber freshly pulled from the melt passed through the cladding cup, a furnace, and finally was collected onto a roller. The polymer formulation coated onto the fiber was cured in the furnace. The best sections of coated fiber had 25 μm thick polymer coatings on 180 μm diameter cores and guided light as well as similar fibers coated with PDMS, a standard cladding material.

A number of polymers, including FPOL, were examined as sorbent matrixes for Reichardt's betaine, a solvatochromic dye whose absorbance peak shifts significantly in response to polarity changes in the local solvent environment.[62] The spectra due to inclusion in the polymer environment were examined as well as spectral shifts arising from the sorption of vapor in the polymers. FPOL was a rather unique polymer among those tested because of its strong interaction with the dye, and as a result, the responses of the dye in FPOL were also distinctive. FPOL has also been investigated as a matrix for chemiluminescent reagents (luminol, KOH, and ferric ion catalyst) used in developing sensors for detection of oxygen or nitrogen dioxide.[45]

Use of hydrogen-bond acidic polymers as components of fluorescence sensors appears to be particularly promising. Nile Red, another solvatochromic dye well known for use in chemical vapor sensors,[169−173] was incorporated into films of BSP3 and PSmFA.[82] Additional experiments were carried out using poly(methyl methacrylate) (PMMA) as a control non-hydrogen-bond acidic matrix polymer. Several fluorescent dyes in each of these polymers were evaluated for responses to DMMP vapor. Of all the combinations, Nile Red in BSP3 gave the strongest responses with a large blue shift and strong fluorescence enhancement. Large (relative to the noise) fluorescence signals were observed at DMMP vapor diluted to 100−200 ppb (0.5−1 mg/m^3) concentrations. Extrapolated detection limits were not reported. The response behavior was interpreted in terms of a competition between Nile Red and DMMP for hydrogen-bonding sites on the polymer. The interaction of the Nile Red by hydrogen bonding with hydroxyl groups in BSP3 greatly reduced the dye fluorescence. Displacement of basic dye functional groups by DMMP, a stronger hydrogen-bond base, freed the dye from the quenching hydrogen bond and the fluorescence light output increased, providing the analytical signal. In a subsequent study, Nile Red and a second dye were incorporated into BSP3 to set up a fluorescence signal enhancement system.[81]

The phenylene−ethynylene polymer shown in Scheme 5 is a fluorescent polymer with hydrogen-bond acidic groups pendant to the conjugated polymer chain.[65] These polymers with and without hexafluoroisopropanol substituents were coated on the inside of a glass capillary, and their fluorescence was monitored in response to vapors. Response consists of a fluorescence quenching effect. For the nitroaromatic compound 2,4-DNT, similar responses were observed regardless of whether pendant hexafluoroalcohol groups were present or not. The strong electrostatic interaction between the nitroaromatic compound and the phenylene−ethynylene polymer apparently overwhelms any influence the hydrogen-bond acidic groups may have. On the other hand, pyridine induced strong poorly reversible decreases in fluorescence only in the polymers that contained the fluoroalcohol substituents. The authors suggested that the electron-deficient, strongly hydrogen-bonded pyridinium species in the film could undergo photoinduced charge-transfer reactions, a mechanism supported by additional experiments on more electron-rich substituted pyridines that did not lead to a large fluorescence response.

10. Separations and Preconcentration

As noted above, hydrogen-bond acidic polymers developed for chemical vapor sensors have been used as gas chromatographic stationary phases in the investigation of the polymer solubility properties and development of LSERs. However, in the case of PSF6 (Scheme 9), the phase was developed primarily for gas chromatography.[92] These authors noted the lack of hydrogen-bond acidic polymers for chromatographic purposes and set out to prepare a stationary phase with the desired solubility properties and high thermal stability. The material was routinely used at temperatures from 50 to 200 °C. It was an efficient material providing 1500−1800 theoretical plates per meter of packed column, which was noted to be similar to other conventional poly(siloxane) stationary phases on the same support material. The desired hydrogen-bond acidity was achieved, and although hydrogen-bond acidity decreases with increasing temperature, the phase still retained significant and useful hydrogen-bond acidity at 200 °C. It had essentially no hydrogen-bond basicity, as is also desirable.

The polymer BSP3, originally prepared as a sensing polymer, has been used as the sorbent phase in solid-phase microextraction (SPME) studies for chemical agent analysis.[80] This technique involves a polymer-coated fiber that is equilibrated with a sample to extract the analyte or analytes of interest. It is then retracted into a syringe needle and inserted into a gas chromatographic injection port, where the fiber is pushed out of the needle and analytes are released into the instrument by thermal desorption. The vast majority of the initial SPME studies used PDMS as the polymer. Packed column chromatographic studies demonstrated that BSP3 polymer had much greater affinity for GB than PDMS. To demonstrate SPME with this polymer, BSP3-coated fibers were used to sample GB in the headspace above a hexane solution and then desorbed into the gas chromatograph at 150 °C. These fibers could be used repeatedly, and they exhibited 10−20-fold higher affinity for sarin than PDMS fibers.

A hydrogen-bond acidic polymer, dubbed HCSA2, has been applied as a sorbent to a microfabricated thermally desorbed vapor preconcentrator.[110] The device was fabricated as a flow-through microhotplate array with the polymer applied to the hot plate using an inkjet device. The polymer was a hyperbranched polycarbosilane with pendant hexafluoroisopropanol groups.[163] Vapors collected by sorption in the polymer could be released by heating the preconcentrator to 180 °C in just 40 ms. The device was interfaced as a sampling front end to commercial ion mobility spectrometer instruments. In DMMP analyses with 60 s collection times, uncoated devices provided no measurable sample enrichment while the polymer-coated device increased the signal by six times. In explosives detection tests using TNT, a signal increase of three times was observed in preliminary tests. The sample enrichment factors appear to be based on detector peak heights rather than areas, so these numbers may underestimate the actual enrichment that was achieved.

11. Discussion

Fluorinated hydrogen-bond acidic polymers for chemical sensing began with organic polymers for acoustic wave sensors. The polymers were not commercially available, and scientists wishing to use them needed to make or borrow samples. With the introduction of silicon-containing polymers with hydrogen-bond acidic groups, there has been a significant expansion in the numbers of polymers and polymer architectures that have been developed. Macromolecules in this class now range from linear polymers to hyperbranched materials and even POSS nanoarchitectures. Many of these are easier to make than the early polymers such as FPOL, fluorinated reagents and monomers are now more readily available, and some of the polymers can be obtained commercially.

With increasing recognition and increasing availability, these polymers have been applied to many other sensing approaches. Sensitive sensors for explosives, chemical agents or simulants, and/or volatile organic compounds have been developed using these polymers on various acoustic wave devices, chemiresistors, chemicapacitors, and microcantilevers and in fluorescence sensing methods. These materials are also finding their way into separation and preconcentration applications.

Creation of functionalized nanomaterials, other than polymers, with hydrogen-bond acidic groups is also beginning. The POSS materials[113] have just been mentioned, and carbon nanotubes modified with hexafluoroisopropanol groups[112] have also been cited. Gold nanoparticles have been prepared with monolayers that have terminal phenolic groups or fluoroalcohol groups.[174,175] Undoubtedly, more such nanomaterials with fluorinated hydrogen-bond acidic groups will be developed in the future.

12. Acknowledgments

The author would especially like to acknowledge former co-workers and collaborators who played key roles in the development of polymer-coated acoustic wave sensors, hydrogen-bond acidic polymers, and LSERs, including Hank Wohltjen, Arthur Snow, Michael Abraham, and Steven Kaganove. The author thanks Arthur Snow for additional discussions on polymer structures during the preparation of this manuscript. Michael Rapp is acknowledged for providing independent sensor testing data for BSP3. The author gratefully acknowledges funding from the U.S. Department of Energy, National Nuclear Security Administration, Office of Nonproliferation Research and Development (NA-22), for past funding and Laboratory Directed Research and Development funds of the U.S. DOE, administered by the Pacific Northwest National Laboratory, for current funding. The William R. Wiley Environmental Molecular Sciences Laboratory, a U.S. DOE scientific user facility operated for the DOE by PNNL, is also acknowledged. The Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute.

13. References

(1) Chemical agents and simulant concentrations are typically reported in mg/m^3, the international standard units for gas-phase concentrations. These units will be used here, and conversions for concentrations originally reported in ppb will be provided. Explosives, however, have been typically reported in ppb, and these units will be retained for this class of analytes.

(2) Grate, J. W. *Chem. Rev.* **2000**, *100*, 2627.

(3) Janghorbani, M.; Freund, H. *Anal. Chem.* **1973**, *45*, 325.

(4) Edmunds, T. E.; West, T. S. *Anal. Chim. Acta* **1980**, *117*, 147.

(5) McCallum, J. J.; Fielden, P. R.; Volkan, M.; Alder, J. F. *Anal. Chim. Acta* **1984**, *162*, 75.

(6) Snow, A.; Wohltjen, H. *Anal. Chem.* **1984**, *56*, 1411.

(7) Grate, J. W.; Snow, A.; Ballantine, D. S.; Wohltjen, H.; Abraham, M. H.; McGill, R. A.; Sasson, P. *Anal. Chem.* **1988**, *60*, 869.

(8) Grate, J. W.; Wise, B. M.; Gallagher, N. B. *Anal. Chim. Acta* **2003**, *490*, 169.

(9) Grate, J. W.; Martin, S. J.; White, R. M. *Anal. Chem.* **1993**, *65*, 987A.

(10) Grate, J. W.; Martin, S. J.; White, R. M. *Anal. Chem.* **1993**, *65*, 940A.

(11) Grate, J. W.; Frye, G. C. In *Sensors Update*; Baltes, H., Goepel, W., Hesse, J., Eds.; VSH: Weinheim, 1996; Vol. 2, p 37.

(12) Martin, S. J.; Frye, G. C.; Senturia, S. D. *Anal. Chem.* **1994**, *66*, 2201.

(13) Martin, S. J.; Frye, G. C. *Technical Digest of the 1992 IEEE Solid State Sensor and Actuator Workshop*, IEEE, Hilton Head Island, South Carolina, June 22−25, 1992, pp. 27−31.

(14) Martin, S. J.; Frye, G. C. *Proc. IEEE Ultrason. Symp.* **1991**, 393.

(15) Bodenhofer, K.; Hierlemann, A.; Noetzel, G.; Weimar, U.; Goepel, W. *Anal. Chem.* **1996**, *68*, 2210.

(16) Wise, B. M.; Gallagher, N. B.; Grate, J. W. *J. Chemometrics* **2002**, *17*, 463.

(17) Grate, J. W.; Wise, B. M. *Anal. Chem.* **2001**, *73*, 2239.

(18) Grate, J. W.; Zellers, E. T. *Anal. Chem.* **2000**, *72*, 2861.

(19) Grate, J. W.; Kaganove, S. N.; Bhethanabotla, V. R. *Faraday Discuss.* **1997**, *107*, 259.

(20) Grate, J. W. In *Assignment of the Glass Transition*; Seylor, R. J., Ed.; ASTM STP 1249; ASTM: Philadelphia, PA, 1994; p 153.

(21) Grate, J. W.; Klusty, M.; McGill, R. A.; Abraham, M. H.; Whiting, G.; Andonian-Haftvan, J. *Anal. Chem.* **1992**, *64*, 610.

(22) Grate, J. W.; Abraham, M. H. *Sens. Actuators B* **1991**, *3*, 85.

(23) Abraham, M. H.; Ibrahim, A.; Zissimos, A. M. *J. Chromatogr. A* **2004**, *1037*, 29.

(24) Abraham, M. H.; Doherty, R. M.; Kamlet, M. J.; Taft, R. W. *Chem. Br.* **1986**, *22*, 551.

(25) Kamlet, M. J.; Doherty, R. M.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *CHEMTECH* **1986**, *16*, 566.

(26) Grate, J. W.; Abraham, M. H.; McGill, R. A. In *Handbook of Biosensors: Medicine, Food, and the Environment*; Kress-Rogers, E., Nicklin, S., Eds.; CRC Press: Boca Raton, FL, 1996; p 593.

(27) Snow, A. W.; Sprague, L. G.; Soulen, R. L.; Grate, J. W.; Wohltjen, H. *J. Appl. Polym. Sci.* **1991**, *43*, 1659.

(28) 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.

(29) Chang, Y.; Noriyan, J.; Lloyd, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1987**, *27*, 693.

(30) Ting, S. P.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci., Part C: Polym. Lett.* **1980**, *18*, 201.

(31) Barlow, J. W. 1984 Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, Nov 1984.

(32) Wohltjen, H.; Snow, A. W.; Barger, W. R.; Ballantine, D. S. *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.* **1987**, *UFFC-34*, 172.

(33) Ballantine, D. S.; Rose, S. L.; Grate, J. W.; Wohltjen, H. *Anal. Chem.* **1986**, *58*, 3058.

(34) Field, D. E. *J. Coatings Technol.* **1976**, *48*, 43.

(35) Field, D. E.; Griffith, J. R. Fluorinated Polyether Network Polymers, U.S. Patent 4132681, Jan 2, 1979.

(36) Field, D. E.; Griffith, J. R. *Ind. Eng. Chem. Prod. Res. Dev.* **1975**, *14*, 52.

(37) Rebiere, D.; Dejous, C.; Pistre, J.; Lipskier, J.-F.; Planade, R. *Sens. Actuators B* **1998**, *B49*, 139.

(38) Rebiere, D.; Dejous, C.; Pistre, J.; Planade, R.; Lipskier, J.-F.; Robin, P. *Sens. Actuators B* **1997**, *B43*, 34.

(39) Gupta, D. C.; Gutch, P. K.; Lal, G.; Vyas, K. D.; Jaiswal, D. K. *Def. Sci. J.* **2004**, *54*, 229.

(40) Rose-Pehrsson, S. L.; Grate, J. W.; Ballantine, D. S.; Jurs, P. C. *Anal. Chem.* **1988**, *60*, 2801.

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

(42) Fox, C. G.; Alder, J. F. *Anal. Chim. Acta* **1991**, *248*, 337.

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

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

(45) Collins, G. E.; Rose-Pehrsson, S. L. *Anal. Chem.* **1995**, *67*, 2224.

(46) Grate, J. W.; Patrash, S. J.; Abraham, M. H. *Anal. Chem.* **1995**, *67*, 2162.

(47) Collins, G. E.; Buckley, L. J. *Synth. Met.* **1996**, *78*, 93.

(48) Grate, J. W.; Kaganove, S. N. *Polym. Prepr.* **1997**, *38*, 955.

(49) Grate, J. W.; Kaganove, S. N.; Patrash, S. J.; Craig, R.; Bliss, M. *Chem. Mater.* **1997**, *9*, 1201.

(50) Zellers, E. T.; Park, J.; Tsu, T.; Groves, W. J. *Anal. Chem.* **1998**, *70*, 4191.

(51) Grate, J. W.; Kaganove, S. N.; Patrash, S. J. *Anal. Chem.* **1999**, *71*, 1033.

(52) Grate, J. W.; Wise, B. M.; Abraham, M. H. *Anal. Chem.* **1999**, *71*, 4544.

(53) Park, J.; Groves, W. A.; Zellers, E. T. *Anal. Chem.* **1999**, *71*, 3877.

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

(55) Grate, J. W.; Kaganove, S. N.; Nelson, D. A. *Chem. Innovations* **2000**, *30* (11), 29.

(56) Bubb, D. M.; Horwitz, J. S.; McGill, R. A.; Chrisey, D. B.; Papantonakis, M. R.; Haglund, R. F., Jr.; Toftmann, B. *Appl. Phys. Lett.* **2001**, *79*, 2847.

(57) Grate, J. W.; Patrash, S. J.; Kaganove, S. N.; Abraham, M. H.; Wise, B. M.; Gallagher, N. B. *Anal. Chem.* **2001**, *73*, 5247.

(58) Shen, C.-Y.; Shen, Y.-T.; Wu, L. *J. Mater. Sci.* **2002**, *37*, 295.

(59) Grate, J. W.; Nelson, D. A. *Proc. IEEE* **2003**, *91*, 881.

(60) Shen, Y.-T.; Shen, C.-Y.; Wu, L.; Huang, C.-L. *Jpn. J. Appl. Phys. Part 1* **2003**, *42*, 1358.

(61) Houser, E. J.; Mlsna, T. E.; Nguyen, V. K.; Chung, R.; Mowery, R. L.; McGill, A. R. *Talanta* **2001**, *54*, 469.

(62) Krech, J. H.; Rose-Pehrsson, S. L. *Anal. Chim. Acta* **1997**, *341*, 53.

(63) Urry, W. H.; Niu, J. H. Y.; Lundsted, L. G. *J. Org. Chem.* **1968**, *33*, 2302.

(64) Purcell, K. F.; Stikeleather, J. A.; Brunk, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 4019.

(65) Amara, J. P.; Swager, T. M. *Macromolecules* **2005**, *38*, 9091.

(66) Grate, J. W. Siloxanes with Strongly Hydrogen Bond Donating Functionalities, U.S. Patent 5,756,631, May 26, 1998.

(67) SXFA was originally invented and synthesized by Grate at the Naval Research Laboratory. He supplied a sample to Abraham and McGill in England for LSER characterization. SXFA has since been used by several investigators, including Grate, who moved to the Pacific Northwest National Laboratory, McGill, after he moved to the Naval Research Laboratory, and their various collaborators.

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

(69) Pique, A.; McGill, R. A.; Chrisey, D. B.; Leonhardt, D.; Mlsna, R. E.; Spargo, B. J.; Callahan, J. H.; Vachet, R. W.; Chung, R.; Bicaro, M. A. *Thin Solid Films* **1999**, *536*, 355−356.

(70) Pinnaduwage, L. A.; Thundat, T.; Hawk, J. E.; Hedden, D. L.; Britt, R.; Houser, E. J.; Stepnowski, S.; McGill, R. A.; Bubb, D. *Sens. Actuators B* **2004**, *99*, 223.

(71) Patel, S. V.; Mlsna, T. E.; Fruhberger, B.; Klaassen, E.; Cemalovic, S.; Baselt, D. R. *Sens. Actuators B* **2003**, *B96*, 541.

(72) Cunningham, B. T.; Kant, R.; Daly, C.; Weinberg, M. S.; Pepper, J. W.; Clapp, C.; Bousquet, R.; Hugh, B. *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, *4036*, 151.

(73) Chrisey, D. B.; Pique, A.; McGill, R. A.; Horwitz, J. S.; Ringeisen, B. R.; Bubb, D.; Wu, P. K. *Chem. Rev.* **2003**, *103*, 553.

(74) Mlsna, T. E.; Cemalovic, S.; Warburton, M.; Hobson, S. T.; Mlsna, D. A.; Patel, S. V. *Sens. Actuators B* **2006**, *116*, 192.

(75) Patel, S. V.; Hobson, S. T.; Cemalovic, S.; Mlsna, T. E. *Proc. SPIE-Int. Soc. Opt. Eng.* **2005**, *5986*, 59860M/1.

(76) Mathias, L. J.; Lewis, C. M. *Macromolecules* **1993**, *26*, 4070.

(77) Tronc, F.; Lestel, L.; Boileau, S. *Polymer* **2000**, *41*, 5039.

(78) Tronc, F.; Lestel, L.; Amiel, C.; Boileau, S. *Langmuir* **1999**, *15*, 7080.

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

(80) Harvey, S. D.; Nelson, D. A.; Wright, B. W.; Grate, J. W. *J. Chromatogr., A* **2002**, *954*, 217.

(81) Levitsky, I. A.; Krivoshlykov, S. G.; Grate, J. W. *J. Phys. Chem. B* **2001**, *105*, 8468.

(82) Levitsky, I.; Krivoshlykov, S. G.; Grate, J. W. *Anal. Chem.* **2001**, *73*, 3441.

(83) Lu, C. J.; Zellers, E. T. *Analyst* **2002**, *127*, 1061.

(84) Lewis, P. R.; Manginell, R. P.; Adkins, D. R.; Kottenstette, R. J.; Wheeler, D. R.; Sokolowski, S. S.; Trudell, D. E.; Byrnes, J. E.; Okandan, M.; Bauer, J. M.; Manley, R. G.; Frye-Mason, G. C. *IEEE Sens. J.* **2006**, *6*, 784.

(85) Lu, C. J.; Whiting, J.; Sacks, R. D.; Zellers, E. T. *Anal. Chem.* **2003**, *75*, 1400.

(86) Bhadury, P. S.; Dubey, V.; Singh, S.; Saxena, C. *J. Fluorine Chem.* **2005**, *126*, 1252.

(87) Hsieh, M. D.; Zellers, E. T. *J. Occup. Environ. Hyg.* **2004**, *1*, 149.

(88) Holmes, M. A.; Mackay, M. E.; Krishnan, R. S.; Giunta, R. K.; Hawker, C. J.; Malkoch, M. *PMSE Prepr.* **2004**, *90*, 692.

(89) Holmes, M. A.; Mackay, M. E.; Giunta, R. K. *PMSE Prepr.* **2004**, *91*, 1049.

(90) Cai, Q.-Y.; Zellers, E. T. *Anal. Chem.* **2002**, *74*, 3533.

(91) Grate, J. W.; McGill, R. A.; Abraham, M. H. *Proc. IEEE Ultrason. Symp.* **1992**, 275.

(92) Martin, S. D.; Poole, C. F.; Abraham, M. H. *J. Chromatogr. A* **1998**, *805*, 217.

(93) McGill, R. A.; Mlsna, T. E.; Chung, R.; Nguyen, V. K.; Stepnowski, J. *Sens. Actuators B* **2000**, *B65*, 5.

(94) Mlsna, T. E.; Mowery, R.; McGill, R. A. *Technical Digest of the 7th International Meeting on Chemical Sensors*, International Academic Publishers: Beijing, China, July 27−30, 1998; p 65.

(95) McGill, R. A.; Mlsna, T. E.; Mowery, R. *Proceedings of the IEEE 1998 International Frequency Control Symposium*, IEEE: 1998; p 630.

(96) 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.

(97) Simonson, D. L.; Houser, E. J.; Stepnowski, J. L.; Stepnowski, S. V.; McGill, R. A. *Polym. Prepr.* **2005**, *46*, 1186.

(98) Simonson, D. L.; Houser, E. J.; Stepnowski, J. L.; McGill, R. A. *Polym. Prepr.* **2004**, *45*, 558.

(99) Houser, E. J.; Simonson, D. L.; Stepnowski, J. L.; Ross, S. K.; Stepnowski, S. V., III.; McGill, R. A. *Polym. Prepr.* **2004**, *45*, 541.

(100) Simonson, D. L.; Houser, E. J.; Stepnowski, J. L.; Pu, L.; McGill, R. A. *PMSE Preprints* **2003**, *89*, 866.

(101) Simonson, D. L.; Houser, E. J.; Stepnowski, J. L.; McGill, R. A. *PMSE Prepr.* **2003**, *88*, 546.

(102) Houser, E. J.; Simonson, D. L.; Stepnowski, J. L.; McGill, R. A. *PMSE Prepr.* **2003**, *88*, 548.

(103) Demathieu, C.; Chehimi, M. M.; Lipskier, J. F. *Sens. Actuators B* **2000**, *B62*, 1.

(104) Zimmermann, C.; Rebiere, D.; Dejous, C.; Pistre, J.; Chastaing, E.; Planade, R. *Sens. Actuators B* **2001**, *B76*, 86.

(105) Zimmermann, C.; Mazein, P.; Rebiere, D.; Dejous, C.; Pistre, J.; Planade, R. *IEEE Sens. J.* **2004**, *4*, 479.

(106) Wheeler, D. (Sandia National Labs) Personal communication, May 2007.

(107) Holmes, M. A.; Mackay, M. E.; Giunta, R. K. *J. Nanoparticle Res.* **2006**, *DOI:10.1007/s11051*-006-9118-*1*.

(108) Hartmann-Thompson, C.; Hu, J.; Kaganove, S. N.; Keinath, S. E.; Keeley, D. L.; Dvornic, P. R. *Chem. Mater.* **2004**, *16*, 5357.

(109) A chemical structure diagram for HC has been given in a poster: http://www.nrl.navy.mil/nanoscience/files/nanochemistry_poster.pdf.

(110) Voiculescu, I.; McGill, R. A.; Zaghloul, M. E.; Mott, D.; Stepnowski, J.; Stepnowski, S.; Summers, H.; Nguyen, V.; Ross, S.; Walsh, K.; Martin, M. *IEEE Sens. J.* **2006**, *6*, 1094.

(111) Voiculescu, I.; Zaghloul, M. E.; McGill, R. A.; Houser, E. J.; Fedder, G. K. *IEEE Sens. J.* **2005**, *5*, 641.

(112) Snow, E. S.; Perkins, F. K.; Houser, E. J.; Badescu, S. C.; Reinecke, T. L. *Science* **2005**, *307*, 1942.

(113) Hartmann-Thompson, C.; Keeley, D. L.; Dvornic, P. R.; Keinath, S. E.; McCrea, K. R. *J. Appl. Polym. Sci.* **2007**, *104*, 3171.

(114) Kamlet, M. J.; Taft, R. W. *Acta Chem. Scand. B* **1985**, *39*, 611.

(115) Abraham, M. H. *Chem. Soc. Rev.* **1993**, *22*, 73.

(116) Abraham, M. H.; Poole, C. F.; Poole, S. K. *J. Chromatogr. A* **1999**, *842*, 79.

(117) McGill, R. A.; Abraham, M. H.; Grate, J. W. *CHEMTECH* **1994**, *24* (9), 27.

(118) Hierlemann, A.; Zellers, E. T.; Ricco, A. J. *Anal. Chem.* **2001**, *73*, 3458.

(119) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G.; Leo, A.; Taft, R. W. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 1777.

(120) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Duce, P. P.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. II* **1989**, 699.

(121) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans.* **1990**, *2*, 521.

(122) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. *J. Chromatogr.* **1991**, *587*, 213.

(123) Abraham, M. H.; Fuchs, R. *J. Chem. Soc., Perkin Trans. II* **1988**, 523.

(124) Abraham, M. H.; Grellier, P. L.; McGill, R. A. *J. Chem. Soc., Perkin Trans. II* **1987**, 797.

(125) Patrash, S. J.; Zellers, E. T. *Anal. Chem.* **1993**, *65*, 2055.

(126) Severin, E. J.; Lewis, N. S. *Anal. Chem.* **2000**, *72*, 2008.

(127) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298.

(128) Wohltjen, H.; Dessy, R. E. *Anal. Chem* **1979**, *51*, 1465.

(129) Wohltjen, H. *Sens. Actuators* **1984**, *5*, 307.

(130) Rapp, M.; Boss, B.; Voigt, A.; Bemmeke, H.; Ache, H. J. *Fresenius J. Anal. Chem.* **1995**, *352*, 699.

(131) Zellers, E. T.; Batterman, S. A.; Han, M.; Patrash, S. J. *Anal. Chem.* **1995**, *67*, 1092.

(132) Bodenhoefer, K.; Hierlemann, A.; Seemann, J.; Gauglitz, G.; Christian, B.; Koppenhoefer, B.; Goepel, W. *Anal. Chem.* **1997**, *69*, 3058.

(133) Hierlemann, A.; Ricco, A. J.; Bodenhoefer, K.; Goepel, W. *Anal. Chem.* **1999**, *71*, 3022.

(134) Ricco, A. J.; Crooks, R. M.; Osbourn, G. C. *Acc. Chem. Res.* **1998**, *31*, 289.

(135) Ricco, A. J.; Crooks, R. M.; Xu, C.; Allred, R. E. In *Interfacial Design and Chemical Sensing*; Mallouk, T. E.; Harrison, D. J., Ed.; ACS Symposium Series 561; American Chemical Society: Washington, DC, 1994; p 264.

(136) 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., Chem. Sens. IV* **1999**, *138*, 99−23.

(137) Groves, W. A.; Zellers, E. T.; Frye, G. C. *Anal. Chim. Acta* **1998**, *371*, 131.

(138) Frye, G. C.; Martin, S. J.; Ricco, A. J. *Sens. Mater.* **1989**, *1*, 335.

(139) Liron, Z.; Kaushansky, N.; Frishman, G.; Kaplan, D.; Greenblatt, J. *Anal. Chem.* **1997**, *69*, 2848.

(140) Liron, Z.; Greenblatt, J.; Frishman, G.; Gratziani, N. *Sens. Actuators B* **1993**, *12*, 115.

(141) Shaffer, R. E.; Rose-Pehrsson, S. L.; McGill, R. A. *Field Anal. Chem. Technol.* **1998**, *2*, 179.

(142) Alder, J. F.; McCallum, J. J. *Analyst* **1983**, *108*, 1169.

(143) Guilbault, G. G.; Jordan, J. M. *CRC Crit.l Rev. Anal. Chem.* **1988**, *19*, 1.

(144) Fox, C. G.; Alder, J. F. *Analyst* **1989**, *114*, 997.

(145) D'Amico, A.; Verona, E. *Sens. Actuators* **1989**, *17*, 55.

(146) Nieuwenhuizen, M. S.; Venema, A. *Sens. Mater.* **1989**, *5*, 261.

(147) Ballantine, D. S.; Wohltjen, H. *Anal. Chem.* **1989**, *61*, 704A.

(148) McCallum, J. J. *Analyst* **1989**, *114*, 1173.

(149) Frye, G. C.; Martin, S. J. *Appl. Spectrosc. Rev.* **1991**, *26*, 73.

(150) Thompson, M.; Kipling, A. L.; Duncan-Hewitt, W. C.; Rajakovic, L. V.; Cavic-Vlasak, B. A. *Analyst* **1991**, *116*, 881.

(151) Nieuwenhuizen, M. S.; Venema, A. In *Sensors A Comprehensive Survey*; Goepel, W., Jones, T. A., Kleitz, M., Lundstrom, J., Seiyama, T., Eds.; VCH: Weinheim, 1991; Vol. 2, p 647.

(152) Grate, J. W.; Baer, R. L. In *Current Topics in Biophysics: Biosensors*; Frangepol, P. T., Nilolelis, D. P., Eds.; Iasi University Press: Iasi, Romania, 1996; p 51.

(153) Ballantine, D. S.; White, R. M.; Martin, S. J.; Ricco, A. J.; Zellers, E. T.; Frye, G. C.; Wohltjen, H. *Acoustic Wave Sensors. Theory, Design, and Physico-Chemical Applications*; Academic Press: New York, 1997.

(154) Thompson, M. H.; Stone, D. C. *Surface-Launched Acoustic Wave Sensors: Chemical Sensing and Thin-Film Characterization*; John Wiley and Sons: New York, 1997.

(155) Unpublished results, with permission. Grate supplied BSP3 polymer to Michael Rapp, whose group independently coated and tested sensors in his laboratories.

(156) Bender, F.; Barie, N.; Romoudis, G.; Voigt, A.; Rapp, M. *Sens. Actuators B* **2003**, *B93*, 135.

(157) Bender, F.; Waechter, L.; Voigt, A.; Rapp, M. *Proceedings of IEEE Sensors 2003. IEEE International Conference on Sensors, 2nd, Toronto, ON, Canada, Oct 22−24, 2003;* IEEE: 2003; Vol. 1, p 115.

(158) Sepaniak, M. J.; Datskos, P. G.; Lavrik, N.; Tipple, C. *Anal. Chem.* **2002**, *74*, 569A.

(159) Thundat, T.; Chen, G. Y.; Warmack, R. J.; Allison, D. P.; Wachter, E. A. *Anal. Chem.* **1995**, *67*, 519.

(160) Pinnaduwage, L. A.; Ji, H.-F.; Thundat, T. *IEEE Sens. J.* **2005**, *5*, 774.

(161) Houser, E. J.; Chrisey, D. B.; Bercu, M.; Scarisoreanu, N. D.; Purice, A.; Colceag, D.; Constantinescu, C.; Moldovan, A.; Dinescu, M. *Appl. Surf. Sci.* **2006**, *252*, 4871.

(162) Pinnaduwage, L. A.; Hedden, D. L.; Gehl, A.; Boiadjiev, V. I.; Hawk, J. E.; Farahi, R. H.; Thundat, T.; Houser, E. J.; Stepnowski, S.; McGill, R. A.; Deel, L.; Lareau, R. T. *Rev. Sci. Instrum.* **2004**, *75*, 4554.

(163) The polymer designated by HCSA2 is apparently the hyperbranched HC, a polycarbosilane with hexafluoroalcohol substituents.

(164) Barger, W. R.; Dote, J.; Klusty, M.; Mowery, R.; Price, R.; Snow, A. *Thin Solid Films* **1988**, *159*, 369.

(165) Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* **2000**, *100*, 2595.

(166) Kummer, A. M.; Hierlemann, A.; Baltes, H. *Anal. Chem.* **2004**, *76*, 2470.

(167) Cornila, C.; Hierlemann, A.; Lenggenhager, R.; Malcovati, P.; Baltes, H.; Noetzel, G.; Weimar, U.; Gopel, W. *Sens. Actuators B* **1995**, *25*, 357.

(168) Novak, J. P.; Snow, E. S.; Houser, E. J.; Park, D.; Stepnowski, J. L.; McGill, R. A. *Appl. Phys. Lett.* **2003**, *83*, 4026.

(169) Johnson, S. R.; Sutter, J. M.; Engelhardt, H. L.; Jurs, P. C.; White, J.; Kauer, J. S.; Dickinson, T. A.; Walt, D. R. *Anal. Chem.* **1997**, *69*, 4641.

(170) Albert, K. J.; Gill, S. D.; Pearce, T. C.; Walt, D. R. *Anal. Bioanal. Chem.* **2002**, *373*, 792.

(171) Albert, K. J.; Myrick, M. L.; Brown, S. B.; James, D. L.; Milanovich, F. P.; Walt, D. R. *Environ. Sci. Technol.* **2001**, *35*, 3193.

(172) White, J.; Kauer, J. S.; Dickinson, T. A.; Walt, D. R. *Anal. Chem.* **1996**, *68*, 2191.

(173) Barnard, S. M.; Walt, D. R. *Environ. Sci. Technol.* **1991**, *25*, 1301.

(174) Grate, J. W.; Nelson, D. A.; Skaggs, R. *Anal. Chem.* **2003**, *75*, 1868.

(175) Snow, A. W.; Wohltjen, H.; Jarvis, N. L. 2002 NRL Review, pp 45−55, 2002. [Online]. Available: http://www.nrl.navy.mil/content.php?P=02REVIEW45.

CR068109Y