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Versatile Materials for use as Chemically Sensitive Interfaces in SAW-based Sensor Arrays

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ABSTRACT

The primary research objective of the work described here is to design, synthesize, and characterize new materials for use as chemical sensor interfaces, integrate these materials, using appropriate transducers, into sensor arrays, and then develop appropriate mathematical algorithms for interpreting the array response.

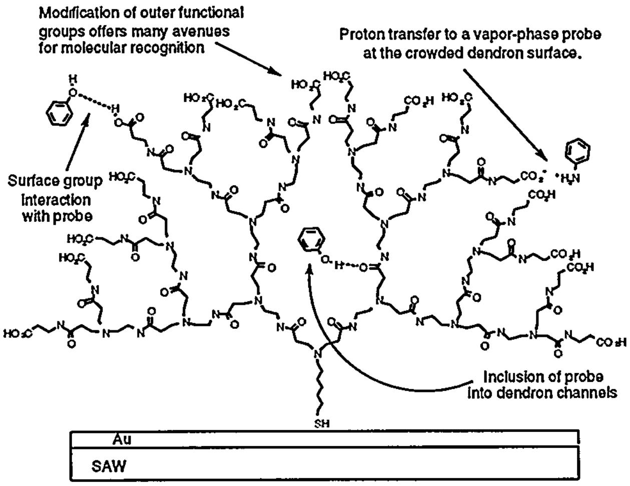
In this paper, we will discuss two new types of materials we have developed that are ideally suited for use as chemically sensitive interfaces for array-based chemical sensing applications, since they: (1) provide general specificity towards classes of functional groups rather than individual compounds; (2) are intermediate in structure between monolayers and polymers; (3) exhibit both endo- and exo-recognition. The first class of materials is surface-confined dendrimers and the second is hyperbranched polymers.

INTRODUCTION

Dendrimer thin films represent a new type of interfacial architecture that resides on the border between self-assembled monolayers (SAMs) and polymer films [1]. The response to vapor-phase dosing experiments we describe here demonstrates how this architecture is particularly well suited to chemical sensing because, like polymers, it displays the sensitivity of thicker films, but, like monolayers, it does not suffer from permeation transients. In addition, we show that the response of these surfaces to vapor-phase probe molecules is dependent in a chemically logical way on both the chemical nature of the dendrimer-probe interaction and the dendrimer size.

Dendrimers are a class of hyperbranched polymer that have regularly repeating branch sequences emanating from a central core that terminate in a large number of surface-end groups [2,3]. These supramolecular species offer a unique and unexplored venue for the creation of chemically-sensitive interfaces that act through dual-mode reception; voids within the dendrimer superstructure serve as endoreceptors and the terminal functional groups of dendrimers serve as exoreceptors (Scheme 1). Importantly, the chemical functionalities of dendrimer exoreceptors and endoreceptors are both subject to rational synthetic control. In spite of the exceptional promise of dendrimers as receptors in thin films, there are no prior published accounts describing the covalent surface-confinement of dendrimers or their integration into chemical sensors, and only three accounts that deal with the formation of organic dendrimer films [4-6].

In addition to dendrimer monolayers, we have also prepared thin films of new highly branched polymers, which we term 'hyperbranched polymers,' that are relevant to boundary layer phenomena such as adhesion, wetting, and chemical sensing [7]. Specifically, we synthesized surface-grafted, hyperbranched poly(acrylic acid) (PAA) films on self-assembled organomercaptan monolayers. These films grow in discrete steps, but unlike most layer-by-layer approaches, film thickness increases nonlinearly as a function of the number of layers because of the branched polymeric architecture. Moreover, these polymer films contain a high density of carboxylic acid groups, which can act as receptor sites themselves or serve as reactive sites for subsequent derivatization.

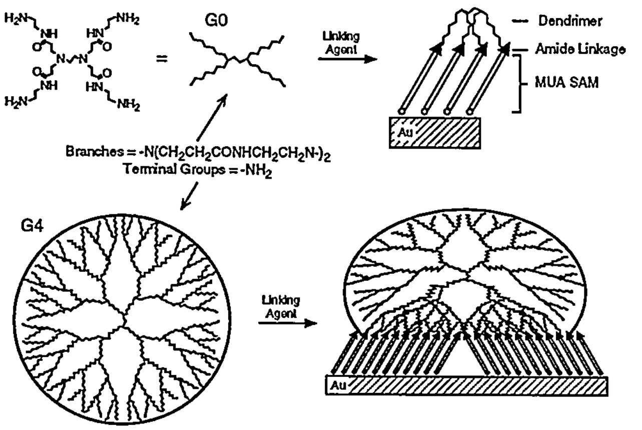


Scheme 1

RESULTS AND DISCUSSION

Scheme 2 illustrates our procedure for attaching poly(amidoamine) (PAMAM) dendrimers to a mercaptoundecanoic acid (MUA) SAM using an asymmetric anhydride intermediate. This intermediate, formed by reacting the MUA SAM with ethyl chloroformate, is highly active and rapidly condenses with the amine-terminated dendrimers to form amide linkages. We characterized the dendrimer surfaces, each of which incorporated one of five generations of PAMAM dendrimers (G0, MW=517; G2, MW=3256; G4, MW=14,215; G6, MW=58,048; G8, MW=233,383), by Fourier transform infrared-external reflectance spectroscopy (FTIR-ERS) and ellipsometry.

To confirm the attachment of dendrimers to MUA SAMs, we obtained FTIR-ERS spectra of G0-, G2-, G4-, G6-, and G8-modified surfaces. Figure 1 shows the amide and carbonyl region of these spectra. There are two important points. First, we do not observe residual IR absorbance from the MUA carbonyls (C=O), which would appear between 1720 and 1740 cm^{-1}, after linking dendrimers to the SAMs. This indicates complete or nearly complete reaction between all five dendrimers and the MUA surface (from control experiments we estimate that residual carboxyl group sites in excess of 10%



Scheme 2

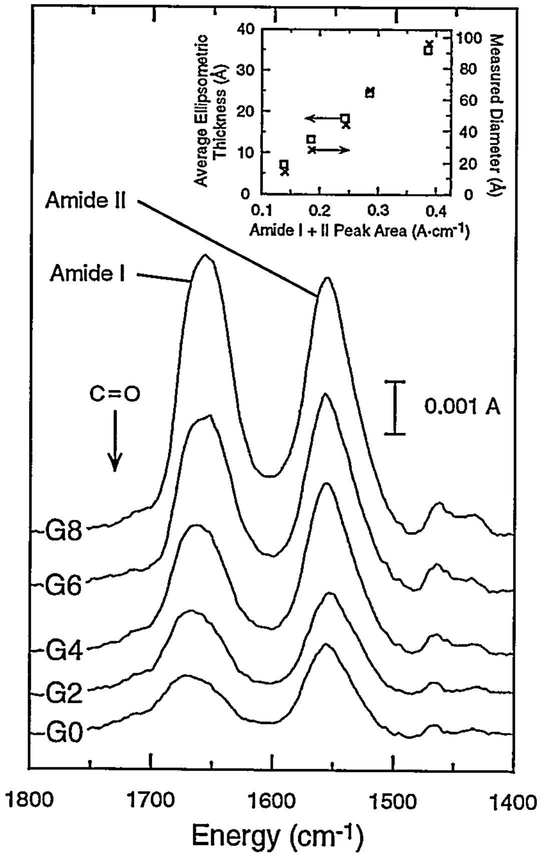


Figure 1. FTIR-ERS and ellipsometric results from analysis of five generations of dendrimer films. The infrared spectra show the quantitative attachment of dendrimers to SAM active sites, via an absence of residual carbonyls, and concomitant increase in dendrimer amide bands and generation. The inset illustrates how both the average ellipsometric film thickness and dendrimer diameter scale linearly with the total amide peak area. Taken together these data show that, for a constant two-dimensional dendrimer coverage, three-dimensional growth is dependent upon dendrimer generation. Data in the inset represents a mean of five or more separate experiments.

would be discernible). Second, amides are the principal infrared-active functionality of PAMAM dendrimers, and the total area of amide I and II bands increases with increasing dendrimer generation. Since the two-dimensional projection of the dendrimer overlayer onto the surface is the same for all five generations, this result demonstrates the anticipated three-dimensional film structure.

The inset of Figure 1 shows that there is a correlation between the diameters of the bulk-phase dendrimers and the thickness of the dendrimer monolayers since both the dendrimer diameter, measured by size-exclusion chromatography, and the measured ellipsometric thicknesses of the dendrimer monolayers scale linearly with the amide I and II peak area. The FTIR-ERS and ellipsometric results attest to the approximately monolayer-level dendrimer surface coverage and three-dimensional film growth that scales with dendrimer generation.

For the reasons discussed earlier, dendrimers of different size and chemical composition are ideally suited for integration into array-based chemical sensors [8], and therefore we monitored the response of these surfaces to vapor-phase probe molecules. In the first experiment of this type, we used methyl acrylate to probe the primary amine functionalities at the dendrimer terminal arms. Michael addition of methyl acrylate to primary amines is known to target only the primary amines of the PAMAM structure. The resulting product is a methyl ester whose signature is evident in the carbonyl region of the infrared spectrum (1720-1740 cm^{-1}). Figure 2 shows the relationship between surface reactivity, gauged by the area of the carbonyl band, and the square of the dendrimer radius (r_d^2).

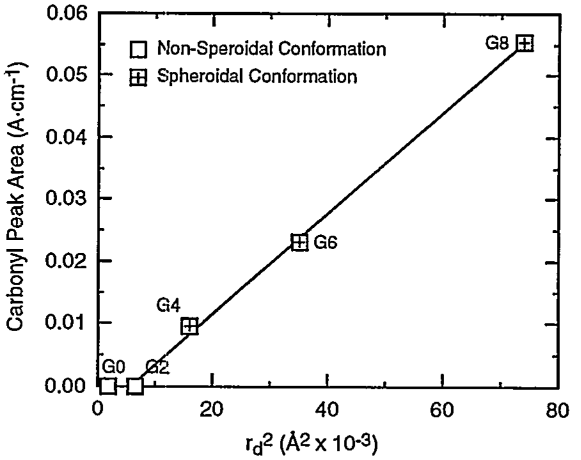


Figure 2. The relation between r_d^2 *and the reactivity (indicated by carbonyl peak area) of dendrimer film exoreceptors with vapor-phase methyl acrylate. Nonspherical dendrimers (G0 and G2) react completely with MUA SAMs at the time of attachment and produce dendrimer films that are unreactive to methyl acrylate. Spheroidal dendrimers (G4-G8) retain a globular structure subsequent to surface attachment and hence, for the constant two-dimensional dendrimer coverage observed in these experiments, have reactivity with methyl acrylate that is directly related to the amount of three-dimensional surface area of the dendrimer film.*

These data illustrate two important points. First, below the threshold at which PAMAM dendrimers are known to adopt a globular geometry (G0 and G2), the dendrimer films show no reactivity. Since G0 and G2 dendrimers are geometrically malleable, all or most of the outer functional groups react with the MUA surface during attachment, and therefore there are no amines left to react with methyl acrylate. A second notable feature of Figure 2 is that at or above the threshold at which PAMAM dendrimers adopt a globular geometry (G4-G8), the number of dendrimer-film reactive sites increases linearly with r_d^2 ($r_d^2 \propto$ exoreceptive surface area of a spheroid). This is a result of the spheroidal geometry of G4-G8 surface-confined dendrimers, which prevents all the terminal functional groups from reacting completely with the MUA surface (Scheme 2). Thus increased reactivity with vapor-phase methyl acrylate is a direct consequence of the enhanced number and accessibility of exoreceptors in dendrimer films with three-dimensional film structure.

We conducted a second experiment to investigate the response of dendrimer-modified surfaces to unreactive vapor-phase probes. In this experiment we sequentially dosed dendrimer-modified surface acoustic wave (SAW) devices with several molecular probes of varying chemical nature. To examine functional group specificity, we chose benzene, 3-methyl hexane and *n*-heptane as hydrophobic probes, methyl propanol and butanol as hydrogen-bonding probes, and propionic acid, which is a hydrogen bonding probe capable of proton transfer.

SAW devices are best known for their ability to function as highly sensitive mass balances capable of quantitatively detecting as little as 100 pg/cm^2, and as excellent platforms for chemical microsensor systems [8]. In this experiment, we first modify the Au-coated active area of a SAW device with a dendrimer film, and then load the device into a flow cell for vapor phase dosing [9]. Figure 3a is an example of unprocessed data from a typical SAW experiment. It illustrates how the dendrimer-modified device response in these experiments possesses three of the essential attributes of an ideal chemical sensor: 1) the response to dosants in these experiments is rapid with no detectable permeation transient, 2) the signal-to-noise ratio of the data is excellent, and 3) the response is typically completely reversible [10].

Figure 3b summarizes the results from vapor-phase dosing experiments of dendrimer-modified surfaces carried out as described for Figure 3a. We dosed a total of three independently prepared devices for each dendrimer generation, and each device was sequentially dosed three or more times with each dosant. All dendrimer-modified devices are most responsive to propionic acid, to which, as with methyl acrylate, the response of G4-, G6-, and G8-modified devices is much greater than that of G0- and G2-modified devices. The response of the G4-modified device to propionic acid is statistically differentiable from the responses of both the G0- and G2-modified devices. However, unlike methyl acrylate, the response to propionic acid does not increase with increasing dendrimer size. This is an interesting point inasmuch as the methyl acrylate probe targets the dendrimer outer functional groups (exoreceptors) *only*, whereas propionic acid may probe dendrimer endoreceptors as well. Partial or complete intercalation of probes into the dendrimer structure (endoreception) generates a mass loading that would not yield the linear response shown in Figure 2. Although the void volume, and hence endoreceptive capacity of dendrimers, increases greatly with increasing generation, the larger dendrimers have a very high density of outer surface groups that may sterically obstruct probe penetration into interior dendrimer voids. In this context, we note that the G4-modified surface is simultaneously the most responsive surface to all probes used in the SAW device study as well as the least constricted of the spheroidal dendrimers that we investigated. That is, while the surface area of G4 is the smallest of the spheroidal dendrimers, its interior is most accessible.

Another key point about the SAW device responses in Figure 3b is that the response to probes decreases in the order acid > alcohols > hydrophobic dosants. This response order is more pronounced for the G4-G8 modified surfaces and is dictated by the PAMAM structure which possesses hydrogen-bonding exoreceptors and endoreceptors. G0 and G2 dendrimer films are not as effective at discriminating between the three different classes of probes since these surfaces have few or no free amine terminal groups, and no coherent endoreceptive ability.

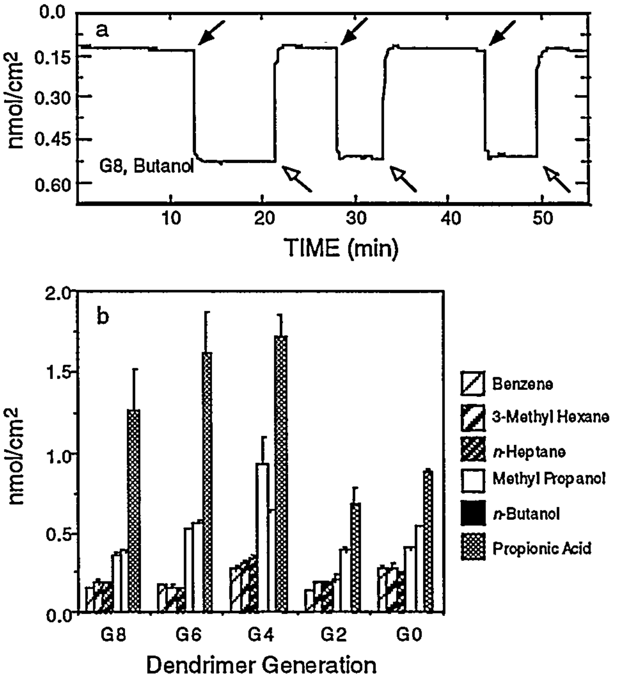


Figure 3. a) Unprocessed response from a G8-modified SAW device dosed with vapor-phase butanol (25 % of saturation in N_2*). This trace shows how a typical response of dendrimer modified devices is instantaneous, stable, and reversible. The solid arrows indicate butanol dosing and the closed arrows indicate purging with pure* N_2*. b) Results from dosing dendrimer-modified SAW devices with six VOCs. The response order acid > alcohols > hydrophobic dosants is a result of the high number of polar receptor sites associated with the PAMAM structure. Higher generation dendrimers (G4-G8) discriminate the chemical nature of the probe more effectively due to the three-dimensional structure of these films, however the magnitude of response is not directly related to dendrimer size since the dosants in this experiment probe the dendrimers' dual-mode receptive capacity.*

As with the dendrimer monolayers, synthesis of hyperbranched polymer films (Figure 4) begins with a mercaptoundecanoic acid (MUA) SAM. The acid groups react with an α,ω-diamino-terminated poly(*tert*-butyl acrylate) (H_2NR-PTBA-RNH_2) to yield a grafted polymer layer. Hydrolysis then forms a grafted PAA layer. Repetition of these steps produces additional grafting at multiple sites on each prior graft leading to a layered, hyperbranched polymer film.

This procedure has several desirable attributes. First, it compensates for inefficiencies in reactions at surfaces. Because there are many grafting sites on each polymer chain, this method produces a thick polymer layer even if reactions proceed in relatively poor yield. Second, the grafted polymer films contain a high density of reactive functional groups that are suitable for further elaboration. Finally, because branching infers that each subsequent layer contains more polymer chains, this method leads to increasingly thicker and more tightly packed polymer layers.

Because of the high density of functional groups, PAA films can serve as specific metal-ion binders . After exposure to an equimolar ethanolic solution of $Fe(ClO_4)_3$ and $Ni(ClO_4)_2$, the intensity of the acid carbonyl FTIR absorption (1731 cm^{-1}) decreased by >80% and new peaks corresponding to the symmetric and asymmetric stretches of carboxylate appeared (1582 cm^{-1} and 1440 cm^{-1}) (Figure 5). These changes demons-

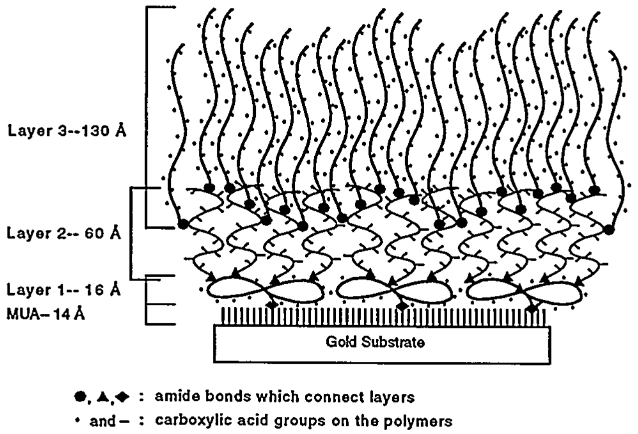


Figure 4. Illustration of a three-layer hyperbranched polymer attached to a mercaptoundecanoic acid (MUA) self-assembled monolayer. The layers are composed of poly(acrylic acid) polymer chains covalently linked to one another through terminal amide bonds. The asterisks denote carboxylic acid receptor groups.

strate metal complexation by the carboxylate receptors. In this competitive binding experiment, the films complex high levels of Fe^{3+} (XPS: O / Fe = 6, consistent with each Fe^{3+} coordinated to three carboxylates), but no detectable Ni^{2+}. This result is in accord with the formation constants of Fe^{3+}- and Ni^{2+}-carboxylate complexes.

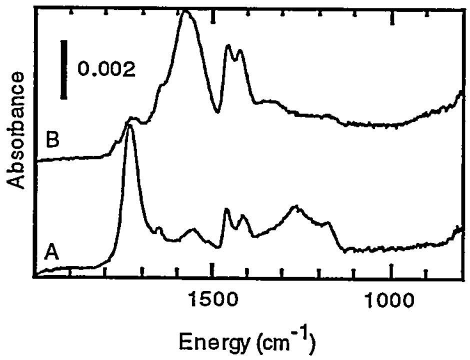


Figure 5. FTIR-ERS spectra of (A) 1 layer of PAA grafted on MUA and (B) the same sample after immersion in an equimolar ethanolic solution of $Fe(ClO_4)_3$ and $Ni(ClO_4)_2$ (0.006 M) followed by an ethanol rinse.

SUMMARY AND CONCLUSIONS

In summary, we have demonstrated for the first time that monolayers of dendrimers can be covalently linked to surfaces, and we have shown that films incorporating higher generation dendrimers, that is, those possessing characteristic exo- and endo-structure, show superior response (methyl acrylate, propionic acid) and selectivity (propionic acid > alcohols > hydrophobic dosants) to vapor-phase probes than films incorporating non-spheroidal molecules (G0 and G2 PAMAM dendrimers) lacking endo- and exo-structure.

Hyperbranched PAA films can also be easily synthesized on a MUA SAM via sequential grafting with polymeric building blocks. The film thickness increases rapidly as a function of the number of grafting steps. In addition, these films contain a high density of carboxylic acid groups that can selectively bind metal ions or be chemically modified. Hyperbranched polymer films thus provide new platforms for chemical sensing applications and for tailoring polymer surface properties for a wide variety of technological applications.

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10. In some cases, particularly for higher generation dendrimers, we observe that up to 30% of the total mass loading for propionic acid is bound irreversibly. This is likely due to proton transfer from propionic acid to the dendrimer primary amine terminal groups.