3988 *J. Am. Chem. Soc.* **1996,** *118,* 3988−3989

Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 10. Preparation and Properties of Chemically Sensitive Dendrimer Surfaces

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Received January 12, 1996

This report is the first account of covalent surface confinement of dendrimers[1,2] and the characterization of the resulting monolayer films as chemically sensitive interfaces for chemical-sensing applications. Dendrimer monolayer films[3−5] represent a new type of interfacial architecture: voids within the dendrimer superstructure serve as endoreceptors,[6−8] and the terminal functional groups of dendrimers serve as exoreceptors.[9,10] The vapor-phase dosing experiments discussed here illustrate that this dendrimer architecture responds to vapor-phase probe molecules in a chemically logical way that depends on both the chemical nature of the dendrimer-probe interaction and the dendrimer size.

Scheme 1 illustrates our procedure for linking poly(amidoamine) (PAMAM) dendrimers[11] to a mercaptoundecanoic acid (MUA) self-assembled monolayer (SAM) *via* amide bond formation. To confirm covalent attachment, we obtained FTIR-ERS spectra of surfaces modified with five different generations (sizes) of PAMAM dendrimers (G0, G2, G4, G6, and G8). Figure 1 shows the amide and carbonyl region of these spectra. There are two important points. First, we do not observe residual infrared absorbance from the MUA carbonyl groups, which would be present in the region between 1720 and 1740 cm^{-1} (indicated by the arrow in Figure 1), after linking. This indicates complete or nearly complete reaction between all five dendrimers and the MUA surface. Second, the principal infrared-active functionality of PAMAM dendrimers are amides, and the total area of the amide I and II bands increases with increasing dendrimer generation. Further, the inset of Figure 1 shows that both the dendrimer diameters[11] and the measured ellipsometric thicknesses[12] of the dendrimer monolayers scale linearly with the amide I and II peak area. Since the two-dimensional projection of the dendrimer monolayer onto the surface is the same for all five generations, these results demonstrate how the anticipated three-dimensional film structure scales with dendrimer size.

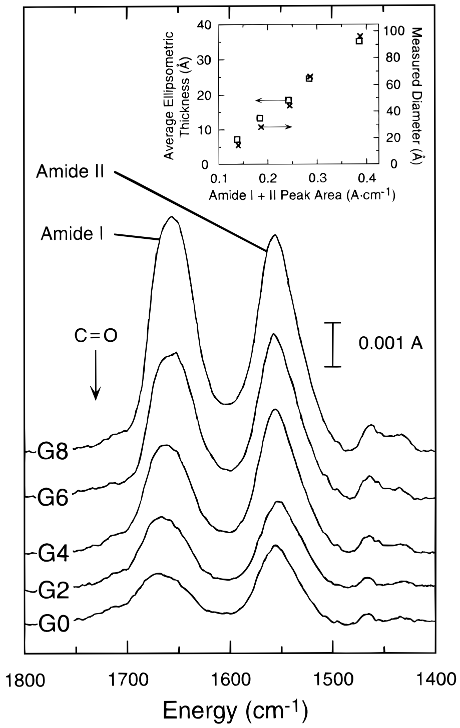
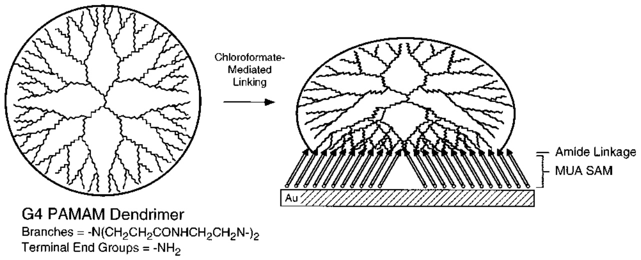


Figure 1. FTIR-ERS and ellipsometric results from analysis of five generations of dendrimer films. The inset illustrates how both the average ellipsometric film thickness and dendrimer diameter scale linearly with the total amide peak area. Data in the inset represent a mean of five or more separate experiments.

Scheme 1



Because dendrimers of different size and chemical composition may prove suitable for integration into array-based chemical sensors,[13] it is essential that we be able to prepare surfaces ofvarying chemical composition. To provide an illustrative example that such transformations are straightforward, we prepared methyl ester-terminated dendrimers using the Michael addition of methyl acrylate to the primary amine terminal groups of surface-confined dendrimers.[14] Following conversion, we observe the characteristic signature of the methyl ester 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 this carbonyl band, and the square of the dendrimer radius (r_d^2). The graph illustrates two important points. First, below the threshold at which PAMAM dendrimers adopt a globular geometry (G0 and G2),[1,8] the dendrimer films show no reactivity because all or most of the outer functional groups react with the surface during attachment. Second, above the threshold at which PAMAM dendrimers adopt a globular geometry (G4−G8),[1,8] the number of dendrimer film reactive

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[1] Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138 and references therein.

[2] Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

[3] Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. *Chem. Mater.* **1995**, *7*, 1440.

[4] Saville, P. M.; Reynolds, P. A.; White, J. W.; Hawker, C. J.; Fréchet, J. M. J.; Wooley, K. L.; Penfold, J.; Webster, J. R. P. *J. Phys. Chem.* **1995**, *99*, 8283.

[5] Watanabe, S.; Regen, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8855.

[6] Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226.

[7] Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. *J. Am. Chem. Soc.* **1995**, *117*, 4417.

[8] Ottaviani, M. F.; Bossmann, S.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 661.

[9] Caminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 8515.

[10] Turro, C.; Niu, S.; Bossmann, S. H.; Tomalia, D. A.; Turro, N. J. *J. Phys. Chem.* **1995**, *99*, 5512.

[11] Dendrimers and related information supplied by Dendritech, Inc., Midland, MI. See ref 1.

[12] The dendrimer overlayer has a corrugated profile. Thus the average ellipsometric thicknesses of the dendrimer monolayers are smaller than the corresponding bulk-phase dendrimer diameters. Also, we anticipate some flattening of the dendrimer structure after linking.

[13] Ricco, A. J. *Electrochem. Soc. Interface* **1994**, *3*, 38.

[14] Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466.

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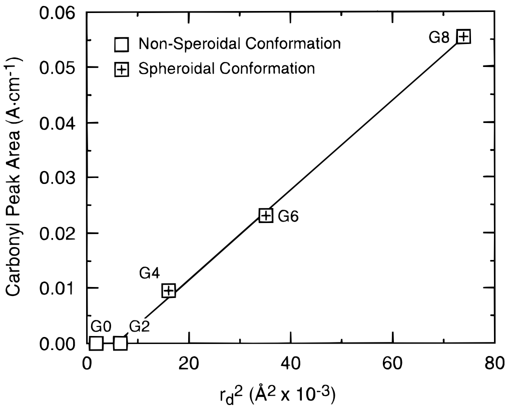

Figure 2. Plot of the reactivity (indicated by carbonyl peak area) of dendrimer film exoreceptors with vapor-phase methyl acrylate versus the square of the dendrimer radius (r_d^2).

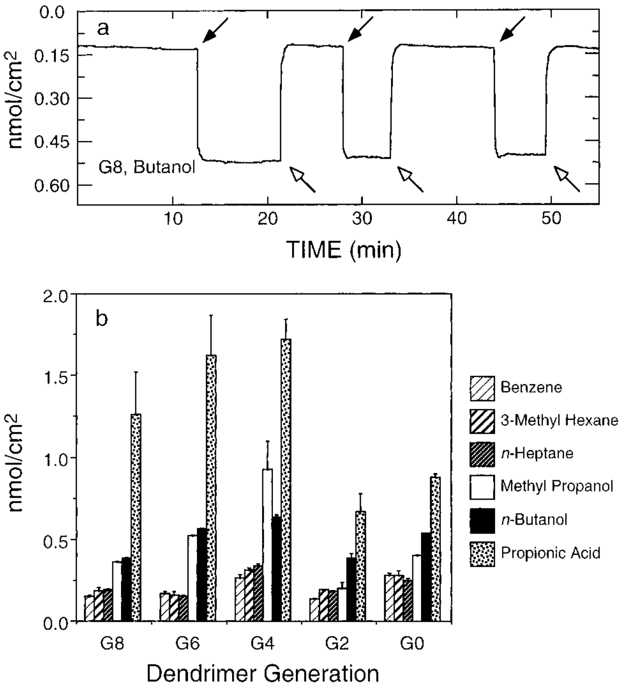

Figure 3. (a) Unprocessed response from a G8-modified SAW device dosed with vapor-phase butanol. Solid arrows mark the beginning of butanol dosing and hollow arrows mark the end. (b) Results from dosing dendrimer-modified SAW devices with six VOCs. Error bars represent the standard deviation of the average results from 3 SAW devices, each cycled three times per dosant. All dosing experiments were performed using 25% of saturation VOC mixed down in N_2.

sites increases linearly with r_d^2, indicating that methyl ester conversion is proportional to the surface area of the surface-confined dendrimer spheroids. This is consistent with the three-dimensional evolution of film structure.

To determine the suitability of dendrimer surfaces as chemically sensitive interfaces, we sequentially dosed dendrimer-modified surface acoustic wave (SAW) mass balances with volatile organic compounds (VOCs) having different functional groups (Figure 3).[13,15] Figure 3a is an example of unprocessed data from a typical SAW experiment. It illustrates how the dendrimer-modified device response possesses three of the essential attributes for an ideal chemical sensor: (1) the response to dosants is very rapid, and there is no detectable permeation transient, (2) the signal-to-noise ratio of the data is excellent, and (3) the response is typically completely reversible.[16] Figure 3b summarizes the results from vapor-phase dosing of dendrimer-modified surfaces. The response to VOCs 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. The G4-modified surface is the most responsive material probably because, although it is the smallest of the spheroidal dendrimers, its interior endoreceptors are most accessible. 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.

In summary, there are two principal results of this study. First, we have provided the first example of a covalently bound dendrimer monolayer. Second, we have shown that dendrimer monolayers are suitable interfaces for chemical sensing applications and that films incorporating higher generation dendrimers, that is dendrimers possessing characteristic exo- and endo-structure, are more reactive and selective toward vapor-phase dosants than films incorporating nonspheroidal (G0 and G2) dendrimers.

Acknowledgment. We are grateful to the National Science Foundation for support of this research (CHE-9313441). M.W. gratefully acknowledges an EPA graduate fellowship. We thank Dr. Laurel McEllistrem for her assistance with organic synthesis and Mr. Dan Dermody and Dr. Antonio J. Ricco (Sandia National Laboratories) for their suggestions and assistance with SAW experiments. We also thank Dr. Greg Wall of Sigma Chemical Co. for technical advice.

JA960097I

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(15) Yang, H. C.; Dermody, D. L.; Xu, C.; Ricco, A. J.; Crooks, R. M. *Langmuir* **1996**, *12*, 726.

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