# Gas Adsorption Gates Based on Ultrathin Composite Polymer Films

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High surface area alumina coatings were prepared on surface acoustic wave (SAW) mass balances. These coatings were fabricated by anodic etching of evaporated aluminum films. The coatings consisted of roughly collinear pores penetrating through the monolithic alumina film. The nanoporous (NP) coatings were characterized by scanning electron microscopy, and the pore number density and diameter were found to be (3.8  $\pm$  0.5)  $\times$  10  $^3$ pores/ $\mu$ m<sup>2</sup> and 6.8 ± 4.8 nm, respectively. The mass of volatile organic compounds that adsorbed onto naked and chemically modified NP alumina coatings was measured using SAW mass balances and compared to the mass absorbed onto SAW devices having planar aluminum coatings. Thirty-four times more heptane adsorbed to the naked NP coating than to the planar coating. The mass loading response was also measured after modification with organic thin films (3-12 nm thick) that spanned the pores of the NP coating. These organic thin films were composed of sixth-generation, amine-terminated poly-(amido amine) dendrimers and poly(maleic anhydride)c-poly(methyl vinyl ether) (Gantrez). The key result of this study is that these organic thin films modulate adsorption of VOCs onto the pore walls of the NP alumina. Specifically, a single 3-nm-thick monolayer of the dendrimer reduces permeability of the VOCs by  $\sim$ 17%, whereas a 12-nm-thick G6-NH<sub>2</sub>/Gantrez composite reduces permeability by 100%. Thus, the polymer composite acts as a nonselective gate that controls access of VOCs to the underlying surface area of the pores.

In this report, we describe an approach for controlling the adsorption of vapor-phase volatile organic compounds (VOCs) onto high-surface-area alumina supports using an ultrathin polymer layer as a gate. Specifically, frame a of Scheme 1 shows that VOCs enter nanometer-scale pores anodically etched into aluminum thin films. However, in the presence of composite polymer coatings having thicknesses on the order of 3-12 nm (frames b–d of Scheme 1), adsorption of VOCs to the underlying alumina surface is attenuated and, for the thickest coatings, eliminated



altogether. Here we report fabrication of the nanoporous (NP) alumina substrate, synthesis of the polymer coatings, and preliminary VOC gating results. Soon we hope to design selectivity into nonselective polymer gates such as these in an effort to construct chemical sensors based on this general concept, but that is not the objective of the present report.

We have chosen to use gating layers consisting of composite films incorporating dendrimers, because we have previously shown that dendrimers can be used as chemically selective nanofilters.<sup>1</sup> For example, individual amine-terminated dendrimers coadsorbed onto a Au surface with an *n*-alkylthiol act as chargeselective gates that recognize and pass positively charged molecules at high pH but deny access when the dendrimers are protonated at low pH.<sup>2,3</sup> We have also shown that individual

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<sup>10.1021/</sup>ac0264473 CCC:  $25.00\ @$  2003 American Chemical Society Published on Web 05/24/2003

<sup>(1)</sup> Perez, G. P.; Crooks, R. M. *The Electrochemical Society Interface* **2001**, *10*, 34–38.

dendrimers can act as size-selective nanofilters in homogeneous solution.<sup>4</sup> A number of other groups have also reported on sensing strategies that incorporate dendrimers.<sup>5–12</sup> These studies have correlated interactions between dendrimers and VOCs to changes in color,<sup>5,6</sup> mass,<sup>7,10</sup> and electrical properties.<sup>8,9,11,12</sup> Thus, in the future, we anticipate that it will be possible to take advantage of the rich chemistry of dendrimers to build chemical selectivity into the types of films described here.

Surface-modified, porous-alumina filters have been investigated as selective gas permeation membranes for hydrocarbons, He, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and SF<sub>6</sub>.<sup>13–16</sup> In one such study closely related to that reported here, Bruening and co-workers investigated the gasseparation properties of alumina Anopore filters having 0.02- and 0.2- $\mu$ m pore diameters and coated with hyperbranched poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH). Upon fluorination of a 20-nm-thick PAA film, they observed increased gas permeation selectivity due to enhanced solubility of some gases within the polymer.<sup>13</sup> They also reported ultrathin (~14 nm) PAA/PAH polymer composite films that spanned 20-nm pores.<sup>14</sup> This group also described the synthesis of pore-bridging dendrimer/PAA bilayer coatings ranging in thickness from 1 to 400 nm.<sup>15</sup>

Here, we describe the VOC gating properties of ultrathin composite polymer films synthesized atop NP, alumina-coated SAW devices. The following three types of coatings were examined: a monolayer of generation-six, amine-terminated PAMAM dendrimers (G6-NH<sub>2</sub>), G6-NH<sub>2</sub> after reaction with Gantrez (an active anhydride copolymer), and the G6-NH<sub>2</sub>/Gantrez composite after reaction with additional G6-NH<sub>2</sub> (Scheme 1). The data indicate that VOC permeability is a strong function of the film composition: the thinnest films are fully permeable, and the thickest films (12 nm) are almost completely impermeable. The intermediate thickness range provides an opportunity for designing fast, sensitive, and potentially selective chemical sensors.

## **EXPERIMENTAL SECTION**

**Chemicals.** The following chemicals were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and were used as received: benzene (99.5%), *n*-heptane (99+%), dichloromethane

- (2) Oh, S.-K.; Baker, L. A.; Crooks, R. M. Langmuir 2002, 18, 6981-6987.
- (3) Zhao, M.; Tokuhisa, H.; Crooks, R. M. Angew. Chem., Int. Ed. Engl. 1997, 36, 2596–2598.
- (4) Niu, Y.; Yeung, L. K.; Crooks, R. M. J. Am. Chem. Soc. 2001, 123, 6840– 6846.
- (5) Albrecht, M.; Gossage, R. A.; Spek, A. L.; van Koten, G. Chem. Commun. 1998, 1003–1004.
- (6) Albrecht, M.; van Koten, G. Adv. Mater. 1999, 11, 171-174.
- (7) Heil, C.; Windscheif, G. R.; Braschohs, S.; Flörke, J.; Gläser, J.; Lopez, M.; Müller-Albrecht, J.; Schramm, U.; Bargon, J.; Vögtle, F. Sens. Actuators, B 1999, 61, 51–58.
- (8) Krasteva, N.; Besnard, I.; Guse, B.; Bauer, R. E.; Müllen, K.; Yasuda, A.; Vossmeyer, T. *Nano Lett.* **2002**, *2*, 551–555.
- (9) Miller, L. L.; Kunugi, Y.; Canavesi, A.; Rigaut, S.; Moorefield, C. N.; Newkome, G. R. Chem. Mater. 1998, 10, 1751–1754.
- (10) Schlupp, M.; Weil, T.; Berresheim, A. J.; Wiesler, U. M.; Bargon, J.; Müllen, K. Angew. Chem., Int. Ed. 2001, 40, 4011–4015.
- (11) Vossmeyer, T.; Guse, B.; Besnard, I.; Bauer, R. E.; Müllen, K.; Yasuda, A. Adv. Mater. 2002, 14, 238–242.
- (12) Koo, B. W.; Song, C. K.; Kim, C. Sens. Actuators, B 2001, 77, 432-436.
- (13) Nagale, M.; Kim, B. Y.; Bruening, M. L. J. Am. Chem. Soc. 2000, 122, 11670–11678.
- (14) Xiao, K. P.; Harris, J. J.; Park, A.; Martin, C. M.; Bruening, M. L. Langmuir 2001, 17, 8236–8241.
- (15) Kim, B. Y.; Bruening, M. L. Langmuir 2003, 19, 94-99.

(99.8%), and acetone (99.5%). Concentrated sulfuric acid (EM Science, Gibbstown, NJ) was used as received. All ethanolic solutions were prepared using 100% ethanol (Quantum Chemical Co., Tuscola, IL), which was used as received. Water was purified to a resistivity  $\geq$  18 M $\Omega$ -cm using a Milli-Q reagent water system (Millipore, Bedford, MA). Generation-six, amine-terminated poly-(amidoamine) dendrimers (G6-NH<sub>2</sub>, Dendritech, Inc., Midland, MI) were used as received. N<sub>2</sub> gas used for mass measurements and Fourier transform infrared external reflectance spectroscopy (FT-IR-ERS) was obtained from liquid N<sub>2</sub> boil-off and passed through a Drierite gas drying unit (Hammond 26800, Fisher Scientific Co., Pittsburgh, PA) before use.

**Substrates.** Nanoporous (NP) alumina coatings were prepared on quartz SAW devices using the following procedure.<sup>17</sup> First, 500 nm of Al metal was evaporated onto a quartz SAW device, which was maintained at a temperature of 250 °C to promote formation of columnar grain structures. Second, the Al coatings were anodized in a two-electrode cell to yield NP alumina. Following anodization, the substrate was removed from the electrolyte solution, rinsed thoroughly with purified water, dried under a N<sub>2</sub> gas stream, and then stored until needed in a N<sub>2</sub>-purged desiccant box. Additional details about the fabrication of the NP substrates are given in the Supporting Information.

Some experiments were carried out on planar Al substrates. These were prepared by evaporating Al onto Si(100) under conditions identical to those described in the previous paragraph. These were diced into  $2.6 \times 1.3$  cm pieces and used for ellipsometric measurements and FT-IR-ERS spectroscopy. Some control experiments were carried out using SAW devices coated with Al that was deposited as described earlier but not anodized. These are referred to as planar substrates and planar SAW devices, respectively, in the text.

**Chemical Modification of Substrates.** All SAW devices (planar and NP) and Al-coated Si wafers were initially cleaned in a low-energy ozone cleaner for 15 min (model 135500, Boekel Industries, Inc.). The substrates were then sonicated for 2 min in ethanol, rinsed with ethanol for 1-2 min, dried under a stream of N<sub>2</sub> gas, and then further dried in a clean oven for 2 h at 95 °C. In some cases, these substrates were then characterized prior to chemical modification. Subsequently, the SAW devices and the Si wafers were soaked for >16 h in 0.025 mM ethanolic solutions of G6-NH<sub>2</sub>. Upon removal from the soaking solution, they were rinsed in ethanol, sonicated for 2 min in ethanol, rinsed with ethanol again, dried with a stream of N<sub>2</sub> gas, and then dried under vacuum for 1 h at room temperature. These dendrimer-modified substrates were then analyzed using methods described later.

Composite polymer thin films consisting of G6-NH<sub>2</sub> and Gantrez were prepared on Al-coated Si wafers and SAW devices using previously reported procedures.<sup>18–20</sup> Briefly, reaction between dendrimeric monolayers and the Gantrez copolymer was carried out in THF (50 mg/mL) for 20 min with occasional

- (17) Yelton, W. G.; Pfeifer, K. B.; Staton, A. W. J. Electrochem. Soc. 2002, 149, H1–H5.
- (18) Liu, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. Angew. Chem., Int. Ed. Engl. 1997, 36, 2114–2116.
- (19) Liu, Y.; Zhao, M.; Bergbreiter, D. E.; Crooks, R. M. J. Am. Chem. Soc. 1997, 119, 8720–8721.
- (20) Zhao, M.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. J. Am. Chem. Soc. 1999, 121, 923–930.

<sup>(16)</sup> Javaid, A.; Ford, D. M. J. Membr. Sci. 2003, 215, 157-168.

warming of the solution.<sup>18</sup> This results in covalent linking of the dendrimers to Gantrez via amic acid bonds. The substrates were then sonicated for 5 min in THF, rinsed for 1-2 min with THF, dried under a stream of N<sub>2</sub> gas, and further dried in a vacuum for 1 h at room temperature. These modified substrates were then analyzed. An additional reaction between the surface-confined composite polymer and G6-NH<sub>2</sub> was carried out by soaking the substrate for 20 min in an ethanolic 0.025 mM G6-NH<sub>2</sub> solution, followed by immersion for 5 min in warm THF, sonication for 2 min in ethanol, and drying under streaming N<sub>2</sub> and vacuum.

**Mass Measurements.** Mass measurements were made in parallel at 21 ± 1 °C using two ST-cut quartz oscillators housed in a custom-built flow system as previously described.<sup>21,22</sup> SAW devices were dosed with vapor-phase probe molecules nominally present at 25% of saturation ( $p_o/p_{sat}$ ) in a flowing N<sub>2</sub> stream (flow rate, 0.5 L/min). Additional experimental details are provided in the Supporting Information. The relative volatility of the VOCs increases in the order heptane, ethanol, benzene, and dichloromethane.<sup>23</sup>

**Ellipsometric Thickness Measurements.** Ellipsometric thickness measurements were taken after each film deposition step using a Gaertner Scientific (Chicago, IL) model L2W26D ellipsometer.<sup>24</sup> Additional experimental details are provided in the Supporting Information.

**Fourier Transform Infrared-External Reflection Spectroscopy (FT-IR-ERS).** FT-IR-ERS measurements were obtained from modified Al-coated Si wafers using a Bio-Rad FTS-6000 spectrometer (Bio-Rad, Cambridge, MA).<sup>24</sup> Low surface reflectivity precluded direct measurement of IR spectra on the NP alumina substrates, and thus we infer the vibrational spectra of those samples from the planar Al substrates. Additional experimental details are provided in the Supporting Information.

**Field-Emission Scanning Electron Microscopy (FE-SEM).** FE-SEM imaging was performed using a Hitachi S4500 fieldemission scanning electron microscope (Tokyo, Japan). To minimize charging, a low acceleration voltage was utilized (5 KV; emission current, 20  $\mu$ A). Digital images were acquired with Princeton Gamma Tech hardware in conjunction with Imix software (PGT, Rocky Hill, NJ). The samples were coated with 1.9 nm of Cr using a Gatan, model 681 high-resolution ion beam coater (Pleasanton, CA). To produce the cross-sectional images, the samples were cleaved using a diamond tip scribe.

#### **RESULTS AND DISCUSSION**

SAW devices were coated with Al and then anodically etched in dilute, aqueous sulfuric acid to yield NP alumina substrates exhibiting a higher surface area, as compared to SAW devices that were not etched but otherwise prepared identically. Complete details of the etching procedure are given in the Experimental Section. Figure 1 shows representative field-emission scanning electron micrographs of the NP alumina substrates that result from this treatment. Figure 1a is a top view of such a NP coating. It shows a distribution of pores having an average diameter of

- (21) Dermody, D. L.; Crooks, R. M.; Kim, T. J. Am. Chem. Soc. 1996, 118, 11912-11917.
- (22) Yang, H. C.; Dermody, D. L.; Xu, C.; Ricco, A. J.; Crooks, R. M. Langmuir 1996, 12, 726–735.
- (23) Dean, J. A., Ed. Lange's Handbook of Chemistry, 13th ed.; McGraw-Hill: New York, 1985.
- (24) Sabapathy, R. C.; Crooks, R. M. Langmuir 2000, 16, 7783-7788.



**Figure 1.** FE-SEM images of the naked nanoporous alumina SAW substrates: (a) top view and (b) cross-sectional view showing the fully anodized alumina atop the underlying quartz. To eliminate charging of the surface, the substrate was coated with 1.9 nm of Cr prior to imaging.

6.8 ± 4.8 nm. This pore diameter is comparable to that of the G6-NH<sub>2</sub> dendrimers (6.7 nm)<sup>25</sup> discussed later. The pore number density, averaged over 5 different 0.1 × 0.1  $\mu$ m regions, is (3.8 ± 0.5) × 10<sup>3</sup> pores/ $\mu$ m<sup>2</sup>. Figure 1b is a cross-sectional view of the NP coating shown in Figure 1a. This micrograph shows that the pores traverse the full thickness of the alumina film and terminate at the interface with the underlying quartz substrate. It is possible to estimate the true surface area of these coatings on the basis of the pore number density, the average pore diameter, and the thickness of the NP alumina coating. This calculation results in a roughness factor (true area/projected area) of 42, assuming discrete, cylindrical pores. This value can be compared to experimentally determined roughness factors of 38, calculated by measuring the mass of adsorbed ethanol,<sup>17</sup> and 34, determined in this study by measuring the mass of adsorbed *n*-heptane.

Figure 2 shows the gravimetric response of naked and chemically modified planar Al and NP alumina SAW devices in the presence of four VOCs. Pairs of SAW devices (one planar Al

<sup>(25)</sup> Technical data supplied by Dendritech, Inc., Midland, MI.



**Figure 2.** Mass-loading profiles measured using surface acoustic wave (SAW) devices modified with (a) either nonporous, planar aluminum or nanoporous (NP) alumina. The planar aluminum and NP alumina coatings were further modified with (b) G6-NH<sub>2</sub>, (c) G6-NH<sub>2</sub>/Gantrez, or (d) G6-NH<sub>2</sub>/Gantrez/G6-NH<sub>2</sub>. The SAW devices were dosed with 25% of saturation heptane (C7), benzene (Benz), dichloromethane (DCM), and ethanol (EtOH).

and one NP alumina) having identical surface modifications were simultaneously dosed with VOCs present at 25% of saturation ( $p_0$ /  $p_{sat}$ ) in a N<sub>2</sub> carrier gas. The data are displayed as the normalized frequency change  $(\Delta f/f_0)$  vs time. Each analysis begins with a 5-min N<sub>2</sub> purge to establish a baseline corresponding to zero adsorbed mass. Next, each pair of SAW devices is dosed with heptane (C7), benzene (Benz), dichloromethane (DCM), ethanol (EtOH), and then heptane again. Each analyte was dosed twice in series for 60 s, and after each exposure to a VOC the system was purged with pure N<sub>2</sub> for 180 s. We have found that heptane provides especially reproducible mass changes on a wide variety of SAW coatings, including those used in this work, so it is used as a reference point to gauge the accessible surface area at the beginning and end of each experiment. All dosing experiments were performed on two independently prepared pairs of SAW devices, where differences in the initial heptane dosing responses varied by <5%.

Figure 2a compares mass-loading data for the naked planar Al and NP alumina substrates. The results demonstrate that the anodization procedure increases the surface area of the SAW device. Specifically, the NP alumina SAW device reversibly adsorbs 34 times more heptane than the reference planar aluminum device and 31, 48, and 14 times more mass for benzene, dichloromethane, and ethanol, respectively. Both the planar and NP coatings respond equally rapidly (>95% of maximum response within the 2-s sampling time) and reversibly to the dosing



**Figure 3.** Sequential FT-IR-ERS spectra of (a) a  $G6-NH_2$  monolayer, (b) after reaction with Gantrez copolymer, and (c) following modification with additional  $G6-NH_2$  (Scheme 1).

conditions. These data demonstrate that the high surface area of the NP coatings significantly increases the sensitivity of mass measurement without incurring the penalties sometimes encountered with thick polymer film coatings (slow response and ill-defined viscoelastic effects).<sup>26</sup>

It was not possible to spectroscopically characterize polymer films on NP alumina because it is insufficiently reflective. Accordingly, we performed these experiments using aluminum substrates prepared identically to those used for the mass loading experiments, except they were not etched electrochemically. The presence of a thin native oxide on the planar Al substrates simulates the NP alumina surfaces. Figure 3 shows FT-IR-ERS spectra of a planar Al substrate after sequential modification with a G6-NH<sub>2</sub> dendrimer monolayer, reaction with Gantrez copolymer, and after reaction with additional G6-NH<sub>2</sub>. Spectrum a reveals characteristic amide I and II peaks at 1659 and 1556 cm<sup>-1</sup>, confirming surface immobilization of G6-NH<sub>2</sub> as previously observed on Au.<sup>27,28</sup> Subsequent reaction with Gantrez (spectrum b) leads to covalent coupling with the dendrimer monolayer and the corresponding appearance of anhydride peaks at 1862 and 1789 cm<sup>-1</sup> arising from unreacted anhydride groups on the Gantrez.<sup>18</sup> The anhydride bands disappear after further reaction with additional G6-NH<sub>2</sub> (spectrum c), and greatly enhanced peaks for the amides appear, indicating addition of more than singlemonolayer quantities of dendrimer within the composite film (compare to spectrum a). Additionally, an acid carbonyl band at 1730 cm<sup>-1</sup> arises from the amic acid groups formed during the coupling reaction.<sup>19</sup> The ellipsometric thicknesses corresponding to the three FT-IR-ERS spectra shown in spectra a, b, and c of Figure 3 are 3, 6, and 12 nm, respectively.<sup>18,20</sup> These values are consistent with previously reported trends for dendrimer/Gantrez composite films, and they provide confidence that such films form on the nanoporous alumina surfaces discussed next.

<sup>(26)</sup> 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: San Diego, 1997.

<sup>(27)</sup> Tokuhisa, H.; Zhao, M.; Baker, L. A.; Phan, V. T.; Dermody, D. L.; Garcia, M. E.; Peez, R. F.; Crooks, R. M.; Mayer, T. M. J. Am. Chem. Soc. 1998, 120, 4492–4501.

<sup>(28)</sup> Wells, M.; Crooks, R. M. J. Am. Chem. Soc. 1996, 118, 3988-3989.



**Figure 4.** FE-SEM images of a SAW device modified with an NP alumina coating and subsequently with a G6-NH<sub>2</sub>/Gantrez/G6-NH<sub>2</sub> thin film (frame d, Scheme 1): (a) top view and (b) cross-sectional view showing the conformal G6-NH<sub>2</sub>/Gantrez/G6-NH<sub>2</sub> thin film atop the NP surface. The arrow and bars highlight the coated surface region.

Our model for the permeability characteristics of chemically modified NP alumina films (frames b-d of Scheme 1) suggests that the dendrimers and dendrimer/Gantrez composites act as pore-bridging nanofilters that nonselectively mediate access of VOCs to the underlying pore volume. The FE-SEM micrographs shown in Figure 4, which were obtained from an NP alumina SAW device coated with the composite dendrimer/Gantrez film shown in frame d of Scheme 1, confirm this model. For example, Figure 4a shows that the coating is conformal and continuous and that the pores in the NP alumina substrate are still visible through the ultrathin polymer film. The cross-sectional image shown in Figure 4b demonstrates that the pore apertures are bridged by the composite thin film but that the underlying porous structure has not been filled. Although the film is very thin, it is possible to roughly estimate the thickness from the micrograph to be 14  $\pm$ 2 nm, which is in close agreement with the ellipsometry data discussed earlier (12 nm).

The mass-loading data in Figure 2b show the result of dosing G6-NH<sub>2</sub>-modified planar aluminum and NP alumina-coated SAW

devices with the four VOCs. The addition of the dendrimer monolayer on the NP alumina-coated SAW devices results in a 17% attenuation in the response of C7 compared to the initially naked device, whereas only a 4% attenuation is observed for the planar Al SAW device (comparable results were obtained from a replicate pair of SAW devices). However, despite the presence of the dendrimer monolayer, the heptane response from the NP alumina device is still 31 times greater than that from the planar Al device. This indicates that a single monolayer of dendrimers does not prevent access of heptane to most of the pore area underlying the alumina surface (recall that in the absence of dendrimer, the NP alumina-coated SAW device adsorbed 34 times more heptane than the planar device). This is most likely a consequence of imperfect dendrimer bridging of the pores, which results in a high degree of analyte leakage (recall that the pores and the dendrimers are about the same diameter). This, in turn, is likely a consequence of the polydispersity of the pore diameters. Nevertheless, the relative attenuation in mass loading between the planar and NP substrates does suggest that the presence of the dendrimers may prevent heptane from accessing a small percentage of the pores. Benzene and dichloromethane respond similarly, but the mass loading of ethanol actually increases on the dendrimer-modified surface. These results are consistent with the strongly hydrogen-bonding nature of the dendrimer interior and results we have previously reported.28

Figure 2c shows the VOC response profiles for the planar and NP alumina SAW devices following ex-situ reaction with the Gantrez copolymer. The addition of the Gantrez polymer results in an approximate doubling of the film thickness while decreasing the heptane permeability on the NP alumina device by a factor of 4 compared to the presence of the dendrimer-only monolayer. In comparison to the similarly modified planar Al device, the NP alumina device now adsorbs only 7 times the mass of heptane. A reduction in polymer permeability, ranging from 2.1 to 4.3 times, is observed for all analytes in the set. Notice, however, that adsorption is not complete (has not attained a steady-state value) for the G6-NH<sub>2</sub>/Gz film during the 60-s VOC dosing interval. The same result was found during VOC desorption. These results suggest that the polymer composite slows VOC permeation, but probably does not eliminate it altogether.

Figure 2d shows the mass response of the planar Al and NP alumina SAW devices to the VOC set after reaction of the G4-NH<sub>2</sub>/Gantrez film with additional G4-NH<sub>2</sub> (frame d of Scheme 1). Here, permeation of VOCs through the film is essentially shut off, even though the film is only 12 nm thick. Specifically, there is only 20% more heptane adsorbed on the NP alumina surface than on the identically modified planar surface.

#### SUMMARY AND CONCLUSIONS

In this article, we showed that nanoporous coatings have enhanced sensitivity for VOCs, as compared to planar surfaces, as a result of the increase in accessible surface area. More importantly, however, access of VOCs to the high surface area underlying the polymer film could be fully modulated with films having thicknesses ranging from 3 to 12 nm. This provides a simple demonstration of an unusual and potentially useful sensing concept: using a polymer thin film as a nanoporous gate to modulate VOC adsorption onto underlying receptors (an alumina surface in this case). This situation contrasts with the usual approach of using the polymer coating as a sorbent for the VOC.<sup>29</sup> The advantage of the approach described here is that there should not be a significant sensitivity penalty for using very thin polymer layers as the sensing medium.

Having discovered a viable approach for modulating surface adsorption on the underlying thin films, our next goal is to design thin polymer layers that introduce selectivity (an issue not addressed in this paper) to the device. Our approach is to refine the electrochemical anodization of the aluminum films to a point where the pores are smaller and more monodisperse than those described in this report. It is possible that this will permit us to use even thinner films, perhaps even single monolayers of dendrimers, to introduce a high level of selectivity based on size, shape, and chemical recognition of analytes.<sup>1–12,19,20</sup>

## ACKNOWLEDGMENT

This work was supported via a subcontract from Sandia National laboratories, which is supported by the U.S. Department

of Energy (Contract DE-AC04-94AL8500). Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed-Martin company, for the U.S. Department of Energy. This work was also funded in part by the National Science Foundation (0211068). We gratefully acknowledge Bonnie B. McKenzie (Material Characterization Department, Sandia National Laboratories) for providing the micrographs.

### SUPPORTING INFORMATION AVAILABLE

Detailed experimental information regarding synthesis of the NP alumina-coated SAW devices, as well as details about how the mass measurements, ellipsometric measurements, and infrared spectra were obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

Received for review December 19, 2002. Accepted April 24, 2003.

AC0264473

<sup>(29)</sup> Grate, J. W.; Patrash, S. J.; Abraham, M. H. Anal. Chem. 1995, 67, 2162– 2169.