

Figure 3. Long-duration experiment on 2.6Pt-1.0V/H-ZSM-35 zeolite ( $n_{Si}/n_{Al} = 8$ );  $T_{cat} = 187^\circ\text{C}$ .

In an attempt to determine the reasons for the occurrence of the oscillations, the H-ZSM-35 samples loaded with Pt and/or V were investigated by means of temperature-programmed oxidation/reduction (Figure 4). On samples loaded with Pt or V only,

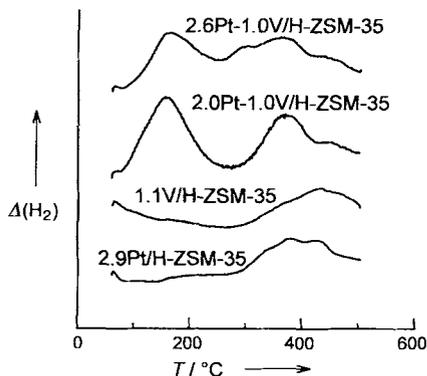


Figure 4. Results of the temperature-programmed reduction on different metal-containing H-ZSM-35 zeolites.  $\Delta(\text{H}_2) = \text{H}_2$  consumption.

no significant hydrogen consumption occurred at temperatures below  $300^\circ\text{C}$ . In contrast, on Pt-V/H-ZSM-35 large amounts of hydrogen were consumed already at  $150$  to  $200^\circ\text{C}$ , that is, exactly in the temperature range in which the oscillations occur. Furthermore, the total hydrogen consumption on these bimetallic zeolites was considerably larger. From this we conclude that the reducible portion of metals in the catalyst is enhanced through synergistic effects between platinum and vanadium. Hence, it is straightforward to assume that the observed oscillations have their origin in redox reactions; this hypothesis is further supported by the simultaneous presence of oxygen and propene in the feed.

### Experimental

The zeolites (ZSM-35, Beta, and ZK-5) were first transformed into their ammonium forms by ion exchange. The resulting samples were treated with aqueous solutions of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  and  $\text{VCl}_3$ ; the water was removed by heating after every step. Normally, the dry catalysts contained about 3 wt% Pt and 1 wt% V. The catalytic experiments were performed in a flow-type apparatus with a fixed-bed reactor at atmospheric pressure. The hydrated zeolite (200 mg) was activated in a flow of synthetic air for 1 h at  $500^\circ\text{C}$  and then overnight at  $450^\circ\text{C}$ . The gaseous components of the model exhaust gas were premixed in a pressure vessel, and then saturated with water vapor at  $45^\circ\text{C}$ . The feed typically contained  $\text{NO}_x$  (0.02 vol%),  $\text{C}_3\text{H}_6$  (0.06 vol%), CO (0.03 vol%),  $\text{CO}_2$  (4 vol%),  $\text{O}_2$  (9 vol%), and  $\text{H}_2\text{O}$  (10 vol%) in He at a flow rate of  $150\text{ cm}^3\text{ min}^{-1}$ . The product stream was analyzed for nitrogen oxides with a chemiluminescence detector; all other components were

analyzed by capillary gas chromatography. Prior to the temperature-programmed reduction with  $\text{H}_2$  (10 vol%) in Ar, the catalyst samples were oxidized in a gas stream containing  $\text{O}_2$  (10 vol%) in He.

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## Multilayer Dendrimer–Polyanhydride Composite Films on Glass, Silicon, and Gold Wafers\*\*

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Organic thin films are of current interest because of their use in adhesion, corrosion passivation, sensor chemistry, photonics, electronics, and membrane chemistry.<sup>[1]</sup> Here we describe a new way to prepare thin films using functional dendrimers and a reactive copolymer that is covalently attached to a surface as a solvent-swollen, brush-like polymer. The synthesis proceeds by an alternating deposition and reaction process leading to a covalent assembly of multilayers of dendrimers contained within layers of Gantrez (poly(maleic anhydride)-*c*-poly(methyl vinyl ether) lightly cross-linked with 1% ethylenediamine). The product films are densely functionalized, semi-organized, and easily modified. The chemistry used is general, and can be extended to include the synthesis of composite interfaces using other nano- or mesoscopic surface-functionalized objects or polyfunctional molecular assemblies.

Prior syntheses of organic thin films on inorganic solids include deposition of monolayers and multilayers by self-assembly or Langmuir–Blodgett techniques,<sup>[1]</sup> deposition of polymers by adsorptive binding,<sup>[2]</sup> sequential deposition of cationic and anionic polymers, organic polymers, and inorganic sheets or mutually reactive layers,<sup>[3–9]</sup> and graft polymeriza-

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tions.<sup>[8–10]</sup> The chemistry presented here combines features of these approaches for preparing thin-film composites containing highly functionalized nanomolecules in a polymeric network.

Silicon- or glass-wafer modification begins with aminosilylation.<sup>[11]</sup> The resulting aminated surface is then modified with a monolayer of Gantrez (Figure 1). Ellipsometry shows that this

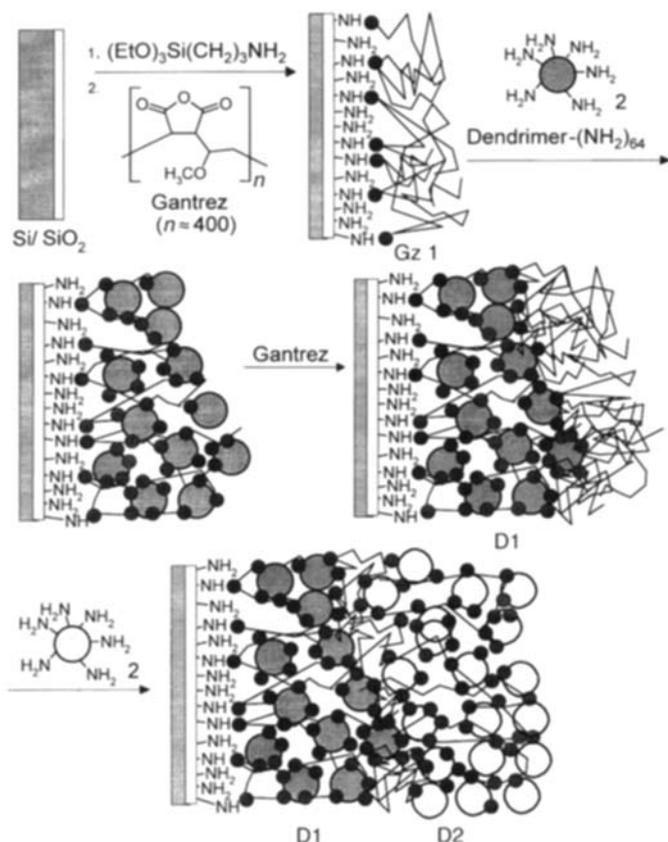
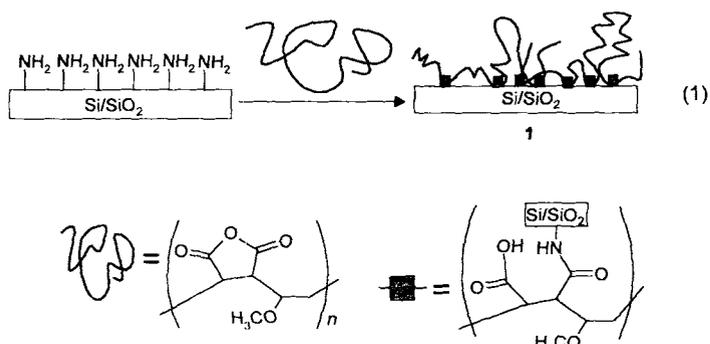


Figure 1. Schematic drawing showing the growth of multilayers of Gantrez and a PAMAM dendrimer beginning with an amino-functionalized silica/silicon-wafer surface (PAMAM = Starburst polyamidoamine). The amide acid binding sites of Gantrez are shown as small filled circles, and the fourth-generation PAMAM dendrimer as large filled circles (D1) or large open circles (D2).

layer (Gz1) is  $2.6 \pm 0.4$  nm thick. The silicon atoms of the underlying layer are detectable by X-ray photoelectron spectroscopy (XPS) at this stage, though the intensity of the  $\text{Si}_{2p}$  signal is attenuated from 28 to 3 atom% with silicon or from 19 to 2 atom% with glass as substrate. The Gz1 surface presumably consists of polymer chains covalently attached to the amino surface through amide acid groups at multiple sites distributed throughout the adsorbent. As Equation (1) and Figure 1 show,



this results in a polydisperse mixture (1) of random-sized loops containing unchanged anhydrides. This surface is presumably like those produced by chemisorptive binding of “sticky” polymers containing thiols or carboxylic acids to metal or metal oxide surfaces.<sup>[2, 7]</sup>

The key to this chemistry is the use of unchanged anhydride groups of these sticky surfaces for additional reactions.<sup>[17, 10]</sup> Since most of the anhydride groups of the film 1 have not reacted, the loopy brush-like polymer layer should react further, as suggested by the synthesis of cross-linked multilayer surfaces with another Gantrez derivative and 2-aminoethanol.<sup>[7]</sup> Exposure of this solvent-swollen reactive brush to a dendrimer that has terminal amino groups results in covalent attachment of multilayers of the dendrimer to the loopy brush surface through amide acids (Figure 1). Specifically, reaction of an amine-functionalized Starburst PAMAM dendrimer (2) with the initial Gz1 Gantrez layer yields a first-generation, dendrimer-modified surface (D1), whose ellipsometric thickness is  $14.6 \pm 0.4$  nm (an increase of 7.9 nm). Since the fourth-generation dendrimer 2 has a diameter of 4.5 nm<sup>[12]</sup> and previous depositions of a single layer of dendrimers yields a thickness of about 4 nm,<sup>[6]</sup> a change of 7.9 nm implies that more than a single layer of dendrimer is attached in each step.

Elaboration of these surfaces by sequential deposition of Gantrez and dendrimer leads to increasingly thick films (Figure 2). Subsequent Gantrez-deposition steps (Gz2, Gz3, and

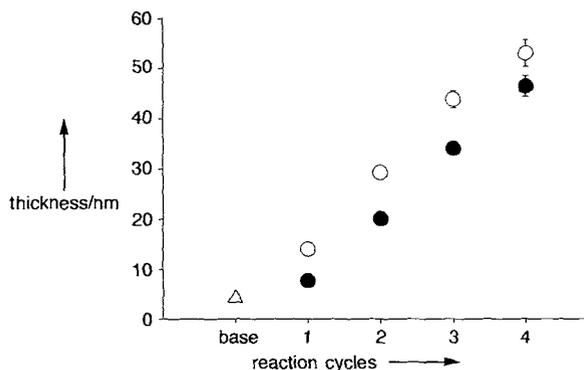


Figure 2. Ellipsometric thickness of Gantrez-dendrimer composite grafts on a silicon wafer. The thickness of the initial layer ( $\Delta$ ) includes the  $\text{SiO}_2$  and the grafted aminopropylsilyl layer. The other data are for films after deposition of Gantrez (Gz1–Gz4, ●) and after the addition of the multilayers of dendrimer (D1–D4, ○).

Gz4) lead to larger increases in film thickness (6 nm versus 2.6 nm for Gz1). Likewise, further dendrimer additions (D2, D3, and D4) lead to larger increases in thickness (10–11 nm versus the initial increase of 7.9 nm). These increases too are in accord with addition of more than a single layer of dendrimer at the D2, D3, and D4 stages. Control experiments in which a surface without amine groups was treated first with Gantrez and then with dendrimer 2 did not lead to film growth.

XPS and IR spectroscopy as well as contact-angle analysis provide further evidence for the structure of these composite dendrimer grafts. XPS data show the disappearance of the peak due to the underlying Si atoms at the D1 stage, and changes in atom percentage that are consistent with the alternating layered structure shown in Figure 1. The anhydride-rich Gz1 and Gz2 films contain an enhanced amount of oxygen (29 atom%) and a reduced amount of nitrogen (1 atom%), while the amine-rich D1, D2, and D3 films have 19 atom% oxygen and 15 atom% nitrogen. Contact-angle measurements also cycle as film growth

proceeds; the dendrimer-rich surface is more hydrophilic than the Gantrez-rich surface (Figure 3). The IR spectra also change with film growth. Bands for anhydride groups are observed at 1860 and 1790  $\text{cm}^{-1}$  (Figure 4) for sticky films (Gz1–Gz3).

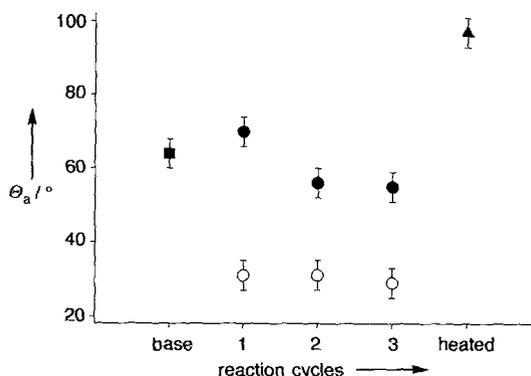


Figure 3. Contact-angle data ( $\theta_a$ , water) for silicon surfaces modified with Gantrez (base, ■; Gz1–Gz3, ●) and dendrimer multilayers (D1–D3, ○) showing the cyclic changes in hydrophilicity with layer deposition and the change in hydrophilicity of layer D3 on heating (▲).

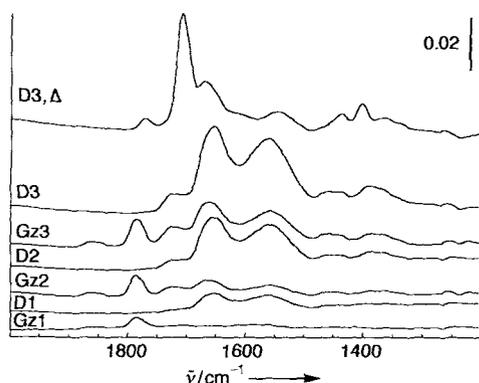


Figure 4. IR spectra (extinction) of films grafted onto silicon wafers that were polished on both sides. Spectra are shown for films after deposition of Gantrez (Gz1–Gz3) and after deposition of **2** (D1–D3) as well as for the final D3 layer after heating (D3, Δ); see text for details.

These bands disappear after addition of dendrimer **2**, and new bands for amides at 1660 and 1560  $\text{cm}^{-1}$  appear. Moreover, the latter gradually increase in intensity as the film thickness grows. We cannot distinguish between bands for amides within **2** and bands for amides of amic acids resulting from reaction of **2** with Gantrez.

Thermal treatment of a D3 film (2 h, 120 °C) leads to a decrease of 15% in thickness and the appearance of bands for imide carbonyl groups at 1772 and 1710  $\text{cm}^{-1}$  in the IR spectrum (Figure 4, top). We believe that imide groups form from the amic acid groups that are produced by reaction of Gantrez with the initial amine surface and with the amine-functionalized dendrimer. The IR spectrum shows that other changes occur in this film upon heating. Preliminary work with films on gold (see below) suggests that the “imidized” film is highly impermeable.

Use of a smaller second-generation Starburst PAMAM dendrimer (diameter 2.9 nm)<sup>[12]</sup> in place of the larger dendrimer **2** shows that dendrimer size may modestly affect the thickness of these multilayer films. Changes in ellipsometric thickness upon addition of the Gz1, D1, Gz2, D2, Gz3, D3, Gz4, and D4 layers were 2.3, 7.5, 4.5, 7.0, 4.6, 7.9, 5.5, and 8.5 nm, respectively.

Composite layers of **2** and Gantrez form on gold substrates upon use of an aminated base layer, which is formed by reaction of ethylenediamine with a self-assembled monolayer of 11-mercaptoundecanoic acid. In this case the D3 layer is 42.3 nm thick, as determined by ellipsometry. The D3 layer has modest blocking ability in electrochemistry experiments.<sup>[13]</sup> Heating this layer leads to an imidized film of 36.2 nm thickness that is electrochemically passivating.<sup>[13]</sup>

The chemistry described here is a new approach for the formation of thin-film composites. The coupling of a reactive surface to a polyfunctional polymer leads to a covalently attached reactive brush, that in turn allows us to incorporate multilayers of a large reactive structure (the dendrimer here) in a polyfunctional film of 40–50 nm thickness.

### Experimental Section

Typical procedure for preparing a film with alternating layers of Gantrez and a polyamine dendrimer: A base layer of Gantrez on an aminopropylated glass slide was prepared by dipping the slide in a clear, pre-formed solution of Gantrez (200 mg,  $M_n = 6.2 \times 10^4$ ,  $M_w/M_n = 3.4$ ) and 1,2-diaminoethane (0.8 mg) in THF (4 mL). The slides were then heated in an oven at 120 °C under vacuum for 5 min. Sonication in DMF (5 min) followed by washing in THF removed any physically adsorbed polymer. A dendrimer multilayer was then added to the base layer by immersing the slide in a solution of **2** in CH<sub>3</sub>OH (10% by weight). After maintaining the slides at 25 °C for 20 min they were placed in hot THF for 5 min, washed thoroughly with CH<sub>3</sub>OH, and dried under N<sub>2</sub>, before being characterized by ellipsometry, XPS, and/or FT-IR spectroscopy. The next Gantrez layer was attached to the dendrimer-modified surface by allowing the dendrimer-grafted slides to react with Gantrez in THF (50 mg mL<sup>-1</sup>) for 20 min with occasional heating of the reaction solution. The slides were then washed with THF and dried with N<sub>2</sub>.

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