

Preparation of Highly Impermeable Hyperbranched Polymer Thin-Film Coatings Using Dendrimers First as Building Blocks and Then as in Situ Thermosetting Agents

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Received July 15, 1998

Abstract: This report describes the synthesis, characterization, and passivation properties of durable, polyfunctional, and highly cross-linked hyperbranched dendrimer/polyanhydride composite thin films. Such films are prepared from either amine- or hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers or amine-terminated poly(iminopropane-1,3-diyl) dendrimers (64-Cascade), and the copolymer poly(maleic anhydride)-*c*-poly(methyl vinyl ether), Gantrez. The dendrimers serve two roles in these composite films. First, they serve as building blocks, which permeate into and covalently cross-link a chemisorbed Gantrez copolymer. Then, in a separate thermal processing step, the dendrimers form highly impermeable monolithic films. In the case of amine-terminated dendrimers, the amic acid groups that attach the dendrimers to the original Gantrez network polymer form imides. Additionally, internal β -amino groups within both the amine- and hydroxyl-terminated PAMAM dendrimers undergo retro-Michael reactions. Subsequently, a combination of interdendrimer Michael reactions and interdendrimer imidization reactions leads to additional cross-links in the heated film. Before heating, the permeability of dendrimer/Gantrez composite films is pH-dependent. After heating, they become highly blocking over the pH range studied (3–11). These films have been prepared on Au, Si, and Al. When a hydrophobic octadecyl layer is attached as a final step on these composites on Al, Al is passivated against corrosion in alkaline solution or from pitting in neutral chloride-containing solution by these new materials.

Introduction

Thin organic films are of widespread interest because of their importance for applications in corrosion passivation,^{1,2} lithography,^{3,4} chemical sensing,⁵ and adhesion.^{6,7} A key technical objective in each of these areas is the assembly or synthesis of durable, polyfunctional films that thoroughly cover the substrate. In this paper, we describe chemistry that leads to highly cross-linked, hyperbranched thin-film grafts on Au, Si, and Al prepared from commercially available functional dendrimers⁸ and random coil poly(maleic anhydride)-*c*-poly(methyl vinyl ether) (Gantrez, Gz) copolymers (Chart 1). In this approach, the dendrimers play two important roles. First, they are structural building blocks that provide multiple covalent branching sites for Gantrez addition. Second, upon heating, the dendrimers act as thermosetting agents. This is a result of several key chemical reactions of the dendrimers within the hyperbranched composite

films that produce additional cross-links and increase the film's structural integrity. Specifically, the amic acid groups linking the dendrimers to the Gantrez network polymer form imides. Additionally, internal β -amino groups within the dendrimer undergo retro-Michael reactions. The resulting primary and secondary amines form additional cross-links by intra- and interdendrimer Michael reactions as well as by interdendrimer imidization. To the best of our knowledge, this is the first example of an organic thin film in which dendrimers are first used as building blocks to provide a hyperbranched structure and then as reagents within the structure to promote cross-linking. As described below, the cross-linked films so formed are promising candidates for corrosion passivation. More importantly, the approach of using the thermal decomposition chemistry of dendrimers can be generally applied in preparing technologically important new materials.⁹

The current interest in organic thin films is reflected by the many approaches available for preparing them. These include physical deposition methods, such as spin coating, spraying, and Langmuir–Blodgett techniques, and newer methods that rely on covalent and ionic chemical interactions.¹⁰ In general, chemical approaches lead to more structured, stable, and chemically versatile thin-film materials; relevant examples include the self-assembly of mono- and multilayers of organo-

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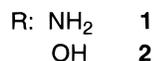
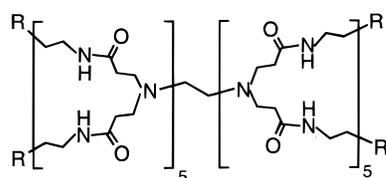
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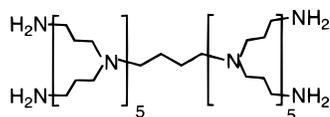
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Chart 1

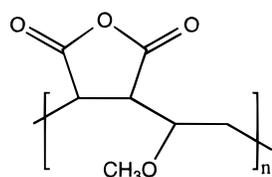


$$\text{Number of R} = 2 \times 2^5 = 64$$



3

$$\text{Number of NH}_2 = 2 \times 2^5 = 64$$

Gantrez, Gz ($n \approx 400$)

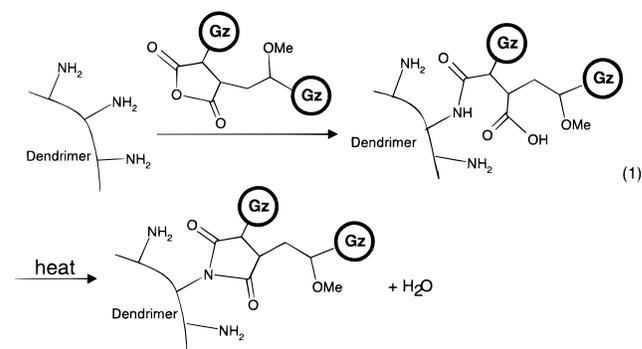
mercaptans and alkylsilanes on Au and hydroxylated Si-containing surfaces, respectively.^{10–12}

Deposition of polymers, rather than monomers, is a conceptually different strategy for preparing functional thin films. Several groups^{13–15} have shown that linear functional polymers incorporating “sticky” groups (e.g., thiols adsorbed to Au and phenyl acetates or carboxylic acids sorbed to metal oxides) react with surfaces to yield 2–10-nm-thick polymer layers. Even polymers that only weakly interact with a surface can be effective for this purpose because of the multidentate nature of the polymer/substrate interactions.^{16,17}

Repetitive, alternating deposition of polyanionic and polycationic polymers or related materials is a second chemical approach for thin-film preparation that efficiently yields ionically assembled multilayers on many different types of substrates.¹⁸ Films formed using this chemistry can be all organic or can be formed from mixtures of organic and inorganic polyelectrolytes.^{19,20}

We recently described a new strategy called hyperbranched grafting as a route for preparing chemically versatile, covalent assemblies of thin films.^{21–28} A key advantage of hyperbranched grafting and polyionic deposition is that both procedures are “forgiving” in that they rely on multistage processing in which subsequent reactions fill holes and compensate for surface irregularities arising from previous growth stages.

The layer-by-layer synthetic procedures described above usually (but not always)^{12,29} lead to non-cross-linked or lightly cross-linked thin organic films. Cross-linking is widely used to decrease permeability and increase stability of thicker organic films. Lacquer formation illustrates this principle.³⁰ Our new hybrid method for synthesizing thin films incorporates many of the attractive features of the thin- and thick-film approaches described above. The first step involves chemisorptive assembly of thiols, dendrimers, or polyanhydride polymers (Gantrez) onto metals or metal oxides. This layer ensures adhesion between the substrate and the rest of the film. Next, alternate deposition of dendrimers and the linear polyanhydride Gantrez (eq 1) atop



the organic adhesion layer yields a homogeneous hyperbranched polymer film 10–60 nm thick consisting of the dendrimers and random coil polymer. Thermal treatment of these films results in imidization (eq 1), and concomitant cross-linking and rigidification of the film. In addition, the dendrimer component undergoes retro-Michael eliminations followed by Michael additions to further cross-link the films. The studies described below examine the fundamental steps involved in these processes and demonstrate that the product thermoset films are highly impenetrable.

Experimental Section

Chemicals and Solvents. All solvents used were of reagent grade or better. Ru(NH₃)₆Cl₃ (Strem Chemicals) and K₄Fe(CN)₆ and K₃Fe(CN)₆ (Fisher Scientific) were used as received. Gantrez, poly(maleic anhydride)-*c*-poly(methyl vinyl ether) ($M_n = 6.2 \times 10^4$, $M_w/M_n = 3.4$), was a gift from GAF-ISP (Wayne, NJ) and was allowed to react with

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0.4 wt % ethylenediamine prior to use in film formation. Amine- and hydroxyl-terminated fourth generation (G4) starburst poly(amidoamine) (PAMAM) dendrimers (**1**, **2**) were generously provided by Dendritech, Inc. (Midland, MI). Amine-terminated G4 poly(iminopropane-1,3-diyl) dendrimer **3** [64-Cascade/1,4-diaminobutane[4]/(1-azabutylidene)/⁶⁰propylamine] (DAB-(NH₂)₆₄), was purchased from DSM Fine Chemicals. All dendrimer solutions were used as received. The dendrimer and Gantrez structures are shown in Chart 1.

Substrates. Au-coated substrates were prepared by electron beam deposition of 10 nm of Ti followed by 200 nm of Au onto Si(100) wafers. Al-coated substrates were prepared by electron beam deposition of 200 nm of Al onto Si(100) wafers. Before use, wafers were rinsed with ethanol, dried in a flowing stream of N₂ gas, and then cleaned in a low-energy Ar plasma (medium power, 1 min, Harrick Scientific Corp., New York, model PDC-32G).

Characterization. NMR spectra were recorded on a Varian XL-200E spectrometer. Chemical shifts are reported in ppm with TMS (δ 0.0) as an internal reference. Fourier transform infrared-external reflectance spectroscopy (FTIR-ERS) was performed using a Digilab FTS-40 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid N₂-cooled MCT detector. The FTIR-ERS spectra were obtained at 4-cm⁻¹ resolution using an average of 256 scans and were obtained using p-polarized light at an angle of incidence of 84° with respect to the substrate normal.³¹ Ellipsometric thicknesses were determined using a Gaertner model L2W26D ellipsometer (Chicago, IL), a wavelength of 633 nm and an incident angle of 70°, assuming a film refractive index (n_f) of 1.46. Errors in the thickness measurements were estimated by calculating the standard deviation of at least three ellipsometric measurements. Advancing water contact angles were measured using a FTÅ200 goniometer (First Ten Angstroms, Portsmouth, VA).

Buffer solutions for electrochemical experiments were as follows: 0.20 M CH₃COOH + 0.0026 M CH₃COONa (pH 3.0); 0.025 M KH₂PO₄ + 0.025 M Na₂HPO₄ (pH 6.3); 0.20 M NH₄OH + 0.036 M NH₄Cl (pH 10.0); and 2.0 M NH₄OH + 0.036 M NH₄Cl (pH 11.0). Supporting electrolyte (0.5 M Na₂SO₄) was also added to the cell, which resulted in a solution resistance of less than 100 Ω between the working and reference electrodes. Aqueous solutions were prepared with 18 M Ω ·cm deionized water (Millipore, Bedford, MA).

Cyclic voltammetric and ac-impedance measurements were performed in a five-necked, three-electrode cell using a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, West Lafayette, IN) and a Pt-gauze counter electrode, which was separated from the main compartment by a porous glass plug. The working electrode was cut from a Au- or Al-coated Si(100) wafer and contained within a Teflon holder that exposed a disk of area 0.09 cm². The cyclic voltammetry experiments were carried out using a BAS 100B electrochemical analyzer (Bioanalytical Systems) controlled by a microcomputer running BAS 100B software. Impedance measurements were performed using an EG&G PARC 273A potentiostat and a Solartron 1255 frequency response analyzer controlled by a microcomputer running ZPLOT software (Scribner Associates, Charlottesville, VA). Measurements were performed at 5 mV (root-mean-squared) around E° (275 mV) of the Fe(CN)₆⁴⁻³⁻ couple. Impedance values were determined at five discrete frequencies per decade over the range 10.0 mHz to 65 kHz. For all electrochemical experiments carried out at Au electrodes, solutions were deoxygenated with N₂. During ac impedance experiments, solutions were purged with N₂ at the rate of about two bubbles per second, and for cyclic voltammetry N₂ was gently blown over the solutions. The electrolyte solutions used to measure the extent of Al corrosion were air-saturated. All experiments were carried out at 20 \pm 2 °C.

The charge-transfer resistance R_{ct} , the total capacitance C_t , which is equal to the sum of the film capacitance (C_f) and the double-layer capacitance (C_{dl}),^{24,32} and some parameters, such as diffusion impedance and diffusion time of probe molecules through the films, relevant to the mass-transfer process were obtained by fitting the experimental

impedance data to Randles' equivalent circuit³³ using ZSIM/CNLS software (Scribner Associates). The Randles' equivalent circuit, while not the only possible representation, has frequently been employed to represent modified electrochemical interfaces,^{24,32,34,35} and in the present case provides an excellent fit of the data. The diffusion element in the Randles' equivalent circuit is represented by a generalized finite Warburg element.^{36,37}

Composite Thin Films Prepared from Gantrez and Amine-Terminated Dendrimers. The Gantrez/dendrimer composites were prepared on amine-functionalized Au or Si substrates. The Si substrates were modified by aminosilylation.²⁷ Au substrates were modified with amine-terminated PAMAM (**1**) or Cascade (**3**) dendrimers by either covalent linking to a chloroformate-activated mercaptoundecanoic acid (MUA) SAM via amide bond formation^{21,38} or by direct chemisorption to the Au surface via multidentate Au/amine bonds.^{16,17,39} The dendrimer or aminosilane layers were then allowed to react with Gantrez, to yield a first layer of Gantrez (Gz1) covalently linked to the amine-functionalized substrate via amic acid bonds. Repetitive, sequential deposition of dendrimer and Gantrez leads to addition of covalently linked dendrimer and Gantrez (D1, Gz2, D2, Gz3...Dn, Gzn). As discussed previously,^{27,28} the entire film, except for the outermost layer, is likely homogeneous rather than layered.

Imidization of the film and decomposition of PAMAM dendrimers in the film were accomplished by thermal treatment (120 °C, 2 h, 10⁻² mm Hg).

Composite Thin Films Prepared from Gantrez and Hydroxyl-Terminated Dendrimers. Composite films composed of Gantrez and hydroxyl-terminated dendrimers were prepared on Au substrates functionalized with 11-mercaptoundecanol. The hydroxyl-terminated SAM was immersed in a Gantrez solution (THF, 50 mg/mL) with occasional heating for 20 min. After reaction, the substrate was thoroughly rinsed with THF and blown dry with N₂. The substrate was then allowed to react with the hydroxyl-terminated (PAMAM) dendrimer in DMF with stirring for 20 min, washed thoroughly with DMF, and blown dry with N₂. Subsequent Gantrez and dendrimer layers were grafted onto the growing film by repeating this sequence of steps. Subsequent thermal treatment procedure of these films was the same as described in the previous section.

Hydrophobic Composite Grafts on Al Substrates. The chemistry required to prepare hydrophobic Gantrez/dendrimer grafts on Al substrates is similar to that used for the films on the other two substrates, except for significant variations at the initial and final stages of film preparation. Al substrates were first coated with Gantrez, which adheres well to the native oxide on the Al surface, by immersion in an anhydrous THF solution containing Gantrez (50 mg/mL). Subsequent layers of dendrimers and Gantrez were deposited sequentially by following the procedure used for the Au and Si substrates. Following preparation of the Gz2 film, the Al substrate was immersed in a stirred anhydrous DMF solution containing 1 M octadecylamine at 70 °C for 30 min. The substrate was removed, thoroughly rinsed with DMF and chloroform, and then blown dry with N₂. This modification resulted in an increase in the contact angle of the film from 61° (Al/Gz2) to 102° (Al/Gz2/NH₂-C₁₈). Subsequent thermal treatment of these films was the same as described in the previous sections.

Synthesis of N-(2-Acrylamidoethyl)succinimide (4). To a round-bottomed flask was added 15 mL of DMF and 300 mg of a 24.8 wt % methanol solution of an amine-terminated G2 PAMAM dendrimer (G2-NH₂). Next, 44 mg (1.2 equiv relative to the NH₂ group concentration of the dendrimer) of succinic anhydride, followed by 88 mg of triethylamine, was added to this solution. After the reaction mixture

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Table 1. Ellipsometric Data Obtained from Thin Films Prepared on Au Substrates from Dendrimers 1–3 and Gantrez at Different Grafting Stages

	thickness (nm)		
	1	2	3
base ^a	1.3 ± 0.1	1.6 ± 0.1	1.3 ± 0.1
D1	3.9 ± 0.1	<i>b</i>	3.7 ± 0.1
Gz1	8.3 ± 0.2	3.8 ± 0.1	7.0 ± 0.2
D2	14.8 ± 0.4	9.3 ± 0.4	13.5 ± 0.5
Gz2	20.4 ± 0.8	12.7 ± 0.5	18.9 ± 0.9
D3	28.7 ± 1.1	17.3 ± 0.9	26.4 ± 1.2
Gz3	33.9 ± 1.7	21.5 ± 1.1	33.1 ± 1.5
D4	42.6 ± 2.2	28.5 ± 1.7	40.9 ± 2.3
D4(heat) ^c	35.2 ± 1.9	25.6 ± 1.5	36.8 ± 1.9

^a The base layer is HSC₁₀COOH for **1** and **3** and HSC₁₀COH for **2**.

^b The first layer of Gantrez is directly linked to the base layer HSC₁₀COH via ester bonds, so there is no D1 stage for films prepared from **2**. ^c Films were heated to 120 °C for 2 h in N₂ at 10⁻² mmHg.

was stirred at ambient temperature for 5 h, diethyl ether (30 mL) was introduced and the resulting white precipitate was collected and washed with two 5-mL portions of diethyl ether. This white precipitate (100 mg) was placed in a 10-mL round-bottomed flask and heated at 120 °C for 1.5 h (10⁻² mmHg). A crystalline sublimate formed. The yield of the sublimate was not measured, but a portion of this sublimate was collected and characterized by NMR and MS (HR-FAB) as follows: ¹H NMR (200 MHz, D₂O) δ 6.02 (1H, dd, *J* = 17.1 Hz, 2.1 Hz), 5.96 (1H, dd, *J* = 9.8 Hz, 2.1 Hz), 5.59 (1H, dd, *J* = 17.1 Hz, 9.8 Hz), 4.68 (1H, s), 3.52 (2H, m), 3.33 (2H, m), 2.61 (4H, s); MS (HR-FAB) calcd for C₉H₁₂O₃N₂ 196.0848, found 196.0851.

Results and Discussion

The synthesis of dendrimer/polyanhydride composite thin films was discussed in the Experimental section.^{27,28} Table 1 lists changes in ellipsometric thickness measured through formation of the D4 grafting stage for composite films prepared from dendrimers **1**–**3** and Gantrez. The thickness data for the nanocomposite prepared from **1** are comparable to our previously reported values for identical films prepared on Si substrates.²⁷

The nanocomposite films prepared using dendrimers **1**–**3** and terminated at the D4 grafting stage (denoted as D4₁, D4₂, and D4₃, respectively) significantly reduce the rate of electrochemical processes compared to naked Au at certain pH values. Figure 1 shows cyclic voltammetry of naked Au and Au electrodes modified with D4₁, D4₂, and D4₃ in an aqueous solution containing 5 mM Fe(CN)₆³⁻ and buffered at pH 3.0, 6.3, and 11.0. The data indicate that composite films containing amine-terminated dendrimers **1** and **3** behave nearly identically at each pH (parts b and d of Figure 1), while the cyclic voltammetry of films prepared using hydroxyl-terminated dendrimer **2** is quite different (part c of Figure 1). Films prepared from **1** and **3** exhibit pH-dependent permeability as a consequence of their amphoteric character: these films contain both amine and carboxylic groups that derive from the unreacted primary and tertiary amine groups of **1** and **3** and the amic acid groups that result from Gantrez linking, respectively.²⁸ At each pH, the current resulting from Fe(CN)₆³⁻ reduction at the D4₂-coated electrode is substantially larger and less pH dependent than either the D4₁- or D4₃-coated electrodes. The lower pH sensitivity and higher permeability of D4₂ probably results, at least in part, from its relative thinness (Table 1),²⁸ but may also reflect significant differences in internal film morphology brought about by the different linking chemistry operative for the hydroxyl- and amine-terminated dendrimers (ester vs amide, respectively).

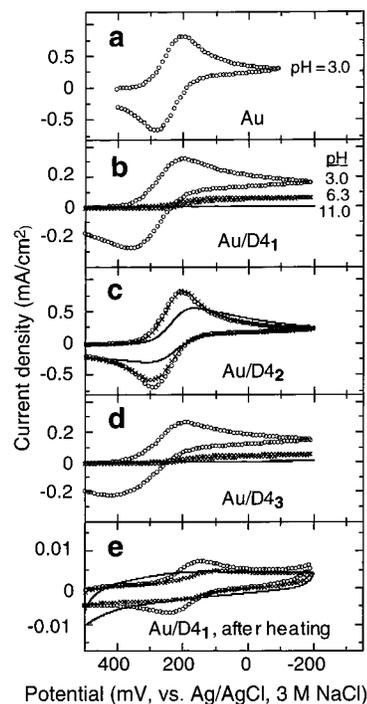


Figure 1. Cyclic voltammograms obtained using a (a) naked Au electrodes and Au electrodes modified with D4 films prepared from dendrimers (b) **1**, (c) **2**, and (d) **3** before heating and (e) dendrimer **1** after heating. Data were obtained in aqueous 0.5 M Na₂SO₄ containing 5 mM Fe(CN)₆³⁻ buffered at pH 3.0 (○), 6.3 (×), and 11.0 (—). The scan rate was 50 mV/s.

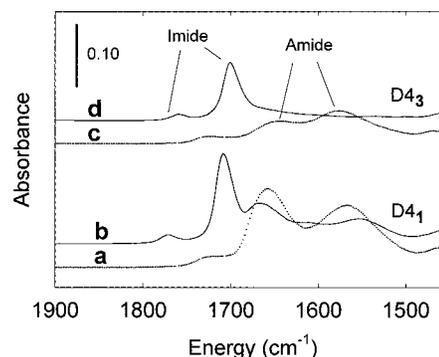
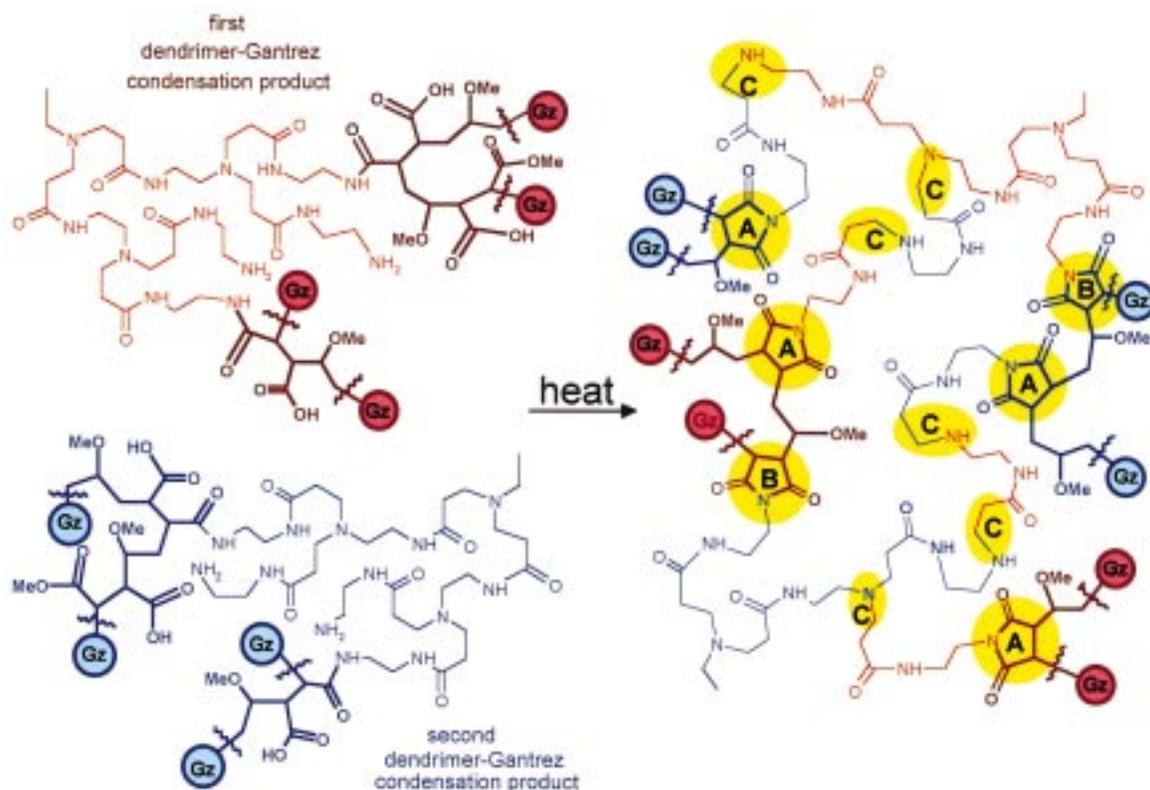


Figure 2. FTIR-ERS for D4 films grafted onto Au-coated Si wafers. Amine-terminated G4 PAMAM dendrimer/Gantrez (D4₁) composite film (a) before and (b) after heating to 120 °C for 2 h at 10⁻² mmHg. Amine-terminated G4 Cascade dendrimer (D4₃) film (c) before and (d) after heating.

The nanocomposite films formed from Gantrez and dendrimers **1** and **3** undergo notable changes upon heating. For example, infrared spectra of D4₁ and D4₃ films reveal significant changes in functional group composition upon thermal treatment (Figure 2). Prior to heating, the intense amide bands observed for D4₁ (1660 and 1560 cm⁻¹, part a of Figure 2) arise from amide groups within the PAMAM dendrimers and the amic acid groups responsible for linking the dendrimers to Gantrez. Heating this film leads to a decrease in the amide band intensity and the appearance of two new imide bands at 1772 and 1710 cm⁻¹ (part b of Figure 2).⁴⁰ In contrast to D4₁, the amide band intensity for D4₃ is only a consequence of the covalent dendrimer/Gantrez linkages (amic acid groups) since the Cascade dendrimers do not contain internal amides. Upon

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Scheme 1



thermal treatment of these films, we observed that the amide peaks due to the amic acid groups generated during D₄ film preparation essentially disappear and two new peaks typical of imides appear (parts c and d of Figure 2). Importantly, the changes in the D₄ film after heating are generally the same as for D₄: the amide bands decrease and new bands corresponding to imides appear. All of the spectral features shown in Figure 2 can be accounted for by the grafting and imidization chemistry illustrated in eq 1. Prior to heating we observe amide and carboxyl bands associated with the amic acid groups that result from dendrimer/Gantrez coupling (note that the interior amides of the PAMAM dendrimers are not shown in eq 1). After heating, both these amides and acids are lost due to formation of the five-membered imide.

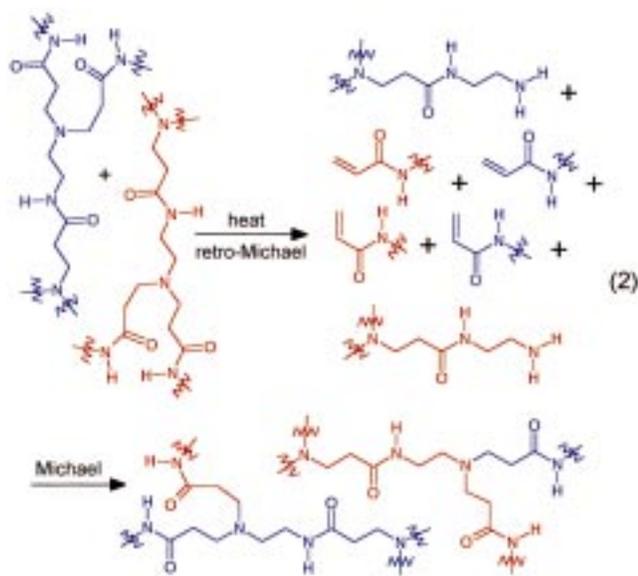
Ellipsometry and contact angle measurements provide confirming evidence for the chemistry shown in eq 1. For example, as a consequence of the condensation reaction, the D₄ film shrinks and the ellipsometric thickness decreases by ~15%. Additionally, the advancing contact angle increases from 30° to 97° after heating, indicating an increase in hydrophobicity consistent with conversion of the polar amic acid groups to the less polar imides.

Although the spectroscopic data shown in Figure 2 can be rationalized by the simple picture provided by eq 1, we believe that the actual heat-driven changes occurring in these composite dendrimer/Gantrez films are significantly more complex. Indeed, results described below indicate that all of the processes shown in Scheme 1 (and perhaps others) are relevant to this complex system. The left side of Scheme 1 is a representation of two dendrimer/Gantrez fragments prior to heating. The right side shows the heat-induced chemical changes and the cross-links formed. For example, while all of the imides in the D₄ films and most of the imides in the D₄ films derive from heat-induced intradendrimer condensation of amic acid groups present at the surface of the dendrimers (cross-links A in Scheme 1), we

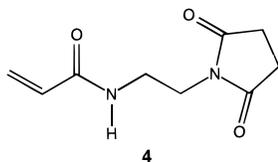
postulate that additional imides (cross-links B in Scheme 1) can also form between dendrimers, which we term interdendrimer imidization. Such interdendrimer imides could form by reaction of remaining unreacted primary amines at the surface of **1** or **3** with acid esters derived from reaction of Gantrez with the alcohol solvent used in dendrimer treatment. However, on the basis of studies with hydroxyl-terminated dendrimer **2** discussed below, we believe that at least some interdendrimer imidization in D₄ also results from the reaction of the original internal tertiary nitrogens of dendrimers in D₄ with acid esters derived from the original Gantrez. This chemistry is possible because the original tertiary amines can become primary amines through retro-Michael reactions and the primary amines thus formed can then react further.

Scheme 1 shows a third sort of cross-link (C). These cross-links are the result of an initial thermally induced retro-Michael reaction at β -aminocarboxamide group sites followed by a second Michael reaction. Equation 2 illustrates this reaction where four acrylamides and two primary amines form from two partial PAMAM dendrimer structures. The amines formed in this heating step can react with either of the acrylamides. Cross-over, illustrated by combination of the blue and red groups in eq 2, leads to cross-links such as those labeled C in Scheme 1. Reversible reactions of amines of one dendrimer with acrylamides from the same dendrimer also likely occur but are not detectable in the chemistry we have studied.

The key difference between the D₄, D₄, and D₄ films is that only the D₄ film can form imides A and cross-links B and C (Scheme 1). Heating film D₄ can only yield imides A and the imide cross-links B because **3** cannot undergo retro-Michael addition. Heating film D₄ (derived from the hydroxyl-terminated PAMAM dendrimer that has no "surface" amic acids such as those in eq 1) can only form cross-links such as imides B or the β -aminoamides C which arise from the decomposition of the PAMAM dendrimers via retro-Michael/Michael reactions.



We have performed several different sorts of experiments in an effort to confirm that reactions such as those shown in eq 1, eq 2, and Scheme 1 occur. For example, control experiments show that reaction of a second-generation PAMAM dendrimer (G2) with excess succinic anhydride results in quantitative conversion of the G2 exterior primary amine groups to amic acids. Heating this G2 derivative leads to at least two products: a solid residue that was analyzed by IR spectroscopy and shown to contain imide groups along with a condensate on the flask walls that was shown to be acrylamide **4**, the anticipated product



of a retro-Michael reaction of this G2 PAMAM derivative.

These bulk-phase reactions show that amic acid formation, subsequent imidization, and retro-Michael chemistry like that described in eq 1 and eq 2 can occur. However, these experiments do not establish that this chemistry occurs in the composite films. To obtain direct evidence for in situ retro-Michael chemistry and formation of primary amines from tertiary amines within **1** contained in films as shown in Scheme 1, we heated a D₄₂ film. The D₄₂ film should be similar to composite films derived from **1** with the exception that the dendrimers are attached to the reactive Gantrez brush via acid ester groups instead of via amic acid groups. Like film D₄₁, this film can undergo retro-Michael chemistry (eq 2) since it contains internal nitrogens β to carbonyl groups.

Figure 3 shows the infrared spectra of a D₄₂ film before and after thermal treatment. Prior to heating, amide I and II peaks from the intradendrimer amide bonds are apparent, in addition to a peak around 1730 cm⁻¹, which corresponds to the acid and ester carbonyl groups arising from the reaction between Gantrez and the hydroxyl-terminated dendrimer. The formation of imides is signaled by new bands at 1710 and 1772 cm⁻¹,⁴⁰ which increase in intensity as a function of heating time (time dependence not shown). Because the principal source of primary amines in this film is from retro-Michael reactions within the film, these data provide direct evidence for thermal decomposition of the PAMAM dendrimer within the film and subsequent

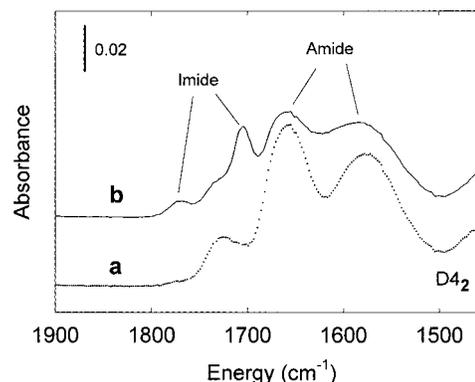


Figure 3. FTIR-ERS for a hydroxyl-terminated G4 PAMAM dendrimer/Gantrez composite film (D₄₂) (a) before and (b) after heating. The presence of the peaks corresponding to imidization in (b) demonstrates that the PAMAM dendrimer undergoes retro-Michael addition upon heating.

imidization of the resultant primary amines with acid esters. We also note that the dendrimer amide peaks decrease in intensity, perhaps partly due to the escape of some decomposition products from the film and to conformational changes within the heated film. It is plausible, although hard to prove, that at least some of the decomposed dendrimer species (acrylamides) may thermally polymerize/oligomerize among themselves upon heating. Polymerization of acrylamides generated by this retro-Michael chemistry would cross-link these films to an even greater extent than imidization and interdendrimer Michael reactions. In any case, a series of electrochemical measurements designed to compare the blocking abilities of the heated and unheated films strongly suggest that significant additional cross-linking does occur.

Part a of Figure 4 shows cyclic voltammetry obtained at a D₄₂-coated electrode in pH 3.0-buffered 5 mM Fe(CN)₆³⁻ or pH 11.0-buffered 5 mM Ru(NH₃)₆³⁺ aqueous solutions. As a consequence of the open structure of the polymer, the redox probe molecules easily penetrate the film and undergo electron transfer at the Au electrode prior to thermal treatment. Additionally, because the film has a net positive charge at low pH, as a result of protonation of the interior tertiary nitrogens of the dendrimers, the negatively charged Fe(CN)₆³⁻ probe may preferentially sorb into the film. Similarly, at high pH, the acid ester linkages between the dendrimers and Gantrez are negatively charged and likely sorb Ru(NH₃)₆³⁺. After heating, the D₄₂ film blocks mass transfer of both Fe(CN)₆³⁻ and Ru(NH₃)₆³⁺. This result is consistent with the decomposition of the dendrimer via retro-Michael addition reaction and subsequent cross-linking reactions that render the film more impermeable.

The permeability of D₄₁ films before heating is highly pH-dependent as shown in part b of Figure 1 and discussed in our previous work.^{28,40} In contrast, the permeability of these films after heating is much lower and nearly pH-independent; for example, essentially no current is observed for Fe(CN)₆³⁻ reduction at any pH (part e of Figure 1). This point is reinforced by part b of Figure 4, which compares the permeability of D₄₁ films before and after heating for Fe(CN)₆³⁻ at pH 3.0 and for Ru(NH₃)₆³⁺ at pH 11.0. These results suggest that the structure and properties of the D₄₁ film change dramatically upon heating, since electrostatic interactions between the film and redox probes cannot alone explain the experimental results for the heated films. For example, at pH 3.0, the heated film still contains positively charged primary and tertiary amine groups. Nevertheless, it cannot admit negatively charged Fe(CN)₆³⁻ because

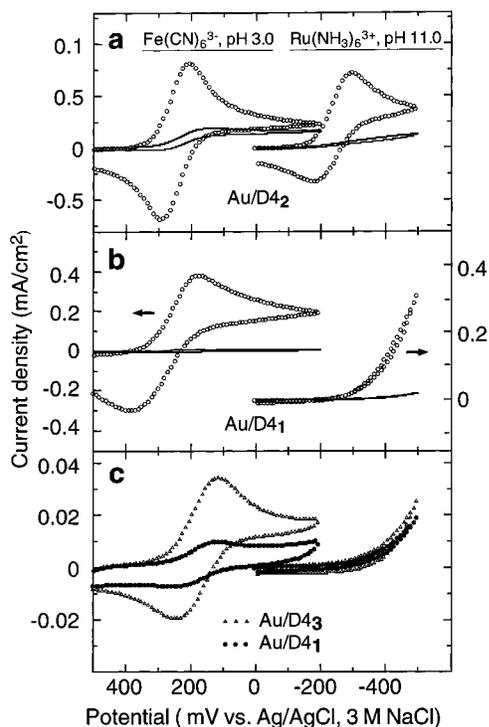


Figure 4. Cyclic voltammetry of electrodes coated with D4 films. (a) hydroxyl-terminated G4 PAMAM dendrimer/Gantrez composite (D4₂) before (O) and after (—) heating. (b) Amine-terminated G4 PAMAM dendrimer/Gantrez composite (D4₁) before (O) and after (—) heating. (c) Comparison of composites prepared with amine-terminated G4 PAMAM (1) and G4 Cascade dendrimers (3) after heating. In all cases, the electrolyte solution consisted of aqueous 0.5 M Na₂SO₄ containing either 5 mM Fe(CN)₆³⁻ buffered at pH 3.0 or 5 mM Ru(NH₃)₆³⁺ buffered at pH 11.0. The scan rate was 50 mV/s.

thermal imidization and the decomposition of dendrimers have extensively cross-linked the film structure and made the film more hydrophobic and compact, thereby closing channels and pinholes within the films that were originally available for probe penetration.

As discussed earlier, the Cascade dendrimer/Gantrez composite films (D4₃) also undergo imidization upon heating (parts c and d of Figure 2). Electrochemical results indicate that these films behave very much like those prepared from the amine-terminated PAMAM dendrimer **1** in that they become highly impermeable after thermal treatment. This suggests that the thermal imidization contributes most to the observed impermeability. However, the electrochemical data of the thermally treated D4 films prepared from the PAMAM or the Cascade dendrimers differ somewhat. Typical cyclic voltammograms obtained from electrodes modified with heated D4₁ and D4₃ films in a buffered pH 3.0 solution containing 5 mM Fe(CN)₆³⁻ and in a buffered pH 11.0 solution containing 5 mM Ru(NH₃)₆³⁺ are presented in part c of Figure 4 for comparison. Although both films are quite impermeable to both redox probes (note the sensitive current scale), the Cascade film is significantly more susceptible to Fe(CN)₆³⁻ penetration than the PAMAM film at pH 3.0, while both show more-or-less identical behavior to Ru(NH₃)₆³⁺ at pH 11.0. We believe this difference stems from differences in the internal structures of the two dendrimers and therefore their ability to undergo thermally induced chemical transformations. Specifically, retro-Michael reactions in the D4₁ film, which do not occur in the D4₃ material, reduce the number of tertiary amines and, thus, the total positive charge at pH 3. Consistent with our observations, however, the effect of retro-Michael addition on the electrochemistry of Ru(NH₃)₆³⁺ at high

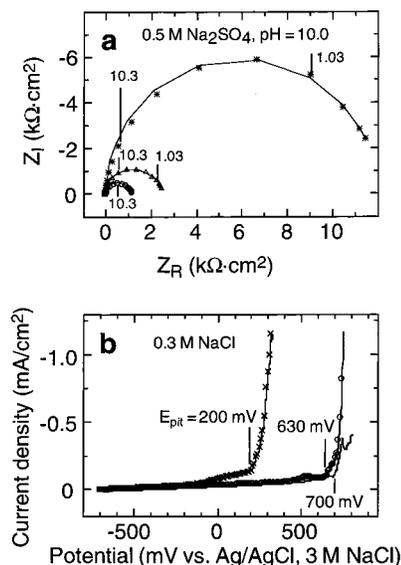


Figure 5. (a) Complex-plane impedance plots for naked Al (O, $R_{ct} = 950 \Omega \cdot \text{cm}^2$) and Al electrodes coated with Gz2/NH₂-C₁₈ films before (Δ , $R_{ct} = 2.1 \text{ k}\Omega \cdot \text{cm}^2$) and after ($*$, $R_{ct} = 11.8 \text{ k}\Omega \cdot \text{cm}^2$) heating for 2 h at 120 °C. Data were obtained in an aqueous pH 10.0-buffered solution containing 0.5 M Na₂SO₄. The range of frequencies was 260 mHz to 65 kHz. (b) Anodic polarization curves for naked Al (\times) and Al electrodes coated with Gz2/NH₂-C₁₈ films before (O) and after (—) heating. Data were obtained in an aqueous 0.3 M NaCl solution. E_{pit} is the pitting potentials as defined in the text. The scan rate was 2 mV/s, and the electrode area was 0.09 cm². The solution was saturated with air.

pH should be less important, because the presence or absence of unprotonated amines has no electrostatic influence on either redox probe.

A monolayer of dendrimers, instead of a mercaptoundecanoic SAM, can be used as an adhesion layer for preparing multilayer PAMAM or Cascade dendrimer/Gantrez composites (D3₁ and D3₃, respectively) on Au substrates. The spectroscopic characteristics of the D3 films built on a dendrimer base layer were virtually identical to the D4 films with the MUA SAM base. We also observed high impermeability when the D3 films were heated. These results suggest that this simpler approach to preparing dendrimer/Gantrez films is effective.

We also prepared dendrimer/Gantrez composite thin films on Al-coated Si wafers starting with an initial layer of Gantrez (Gz0), which adheres well to the native oxide on the Al surface using **1** as the dendrimer. The chemistry discussed previously yields Gz2 films (incorporating dendrimer **1**) having a thickness of 16.5 nm. The top Gantrez layer of these films was then modified with octadecylamine CH₃(CH₂)₁₇NH₂ (NH₂-C₁₈). The structure of this film was confirmed by FTIR-ERS. Contact angle measurements indicate that the resulting Gz2/NH₂-C₁₈ films are hydrophobic (advancing contact angle, 102°). Heating of these films results in their becoming more cross-linked and impermeable.

Part a of Figure 5 shows ac impedance plots for naked Al and the Al electrodes coated with Gz2/NH₂-C₁₈ films before and after heating. A simple Randles' equivalent circuit simulation of the experimental data (solid lines) results in a very good fit of the data for all the electrodes. It is known that, in the presence of sufficiently alkaline solutions, the native aluminum oxide passivation layer that forms on Al is not stable and that the Al beneath will react electrochemically with water and dissolve as AlO₂⁻.⁴¹ Accordingly, we observed a small R_{ct} (950

$\Omega \cdot \text{cm}^2$) for a naked Al electrode in an aqueous pH 10.0 solution. For the Al electrodes modified with Gz2/NH₂-C₁₈, a large-diameter semicircle ($R_{\text{ct}} = 2.1 \text{ k}\Omega \cdot \text{cm}^2$) is observed before heating, but much larger diameter semicircle ($R_{\text{ct}} = 11.8 \text{ k}\Omega \cdot \text{cm}^2$) is observed on the coated electrode after thermal treatment. This demonstrates the effective blocking properties of these films: OH⁻ penetration is retarded, especially after heating. This is a consequence of the film's hydrophobicity, thermally induced cross-linking, and net negative charge at high pH. Because the corrosion rate, manifested experimentally as the Faradaic current, is inversely proportional to R_{ct} , the corrosion rate of Al coated with thermally treated Gz2/C₁₈-NH₂ films is only 8% that of naked Al. Simulation results also show the diffusion resistance of the heated film to H₂O and/or OH⁻ is ~ 10 times larger than that of unheated film.

The Gz2/NH₂-C₁₈ films also protect Al from pitting. Pitting of metals such as Al, which form native passivation layers, can have serious consequences in practical applications.⁴¹ Because other methods, such as cathodic protection,⁴² are not useful for preventing Cl⁻-induced pitting of Al, thin organic films can be effective and practical. Part b of Figure 5 shows anodic polarization curves for naked Al and Al coated with Gz2/NH₂-C₁₈, before and after thermal treatment, in air-saturated, unbuffered aqueous 0.3 M NaCl. The almost zero anodic current over a wide range of potential indicates the oxide film on aluminum is complete and effective. For naked Al, when the applied polarization potential reaches 200 mV, the anodic current sharply increases due to dissolution of the oxide film. This potential is the pitting potential (E_{pit}). When the surface is covered with a barrier layer of Gz2/NH₂-C₁₈, E_{pit} shifts positive to 630 mV. An additional small positive shift occurs after heating the film ($E_{\text{pit}} = 700 \text{ mV}$). This suggests that both before and after thermal treatment Gz2/NH₂-C₁₈ films passivate the Al surface.

Summary and Conclusions

We have introduced a new and versatile method for synthesizing durable, polyfunctional, and highly cross-linked hyperbranched thin films containing dendrimers and the polyanhydride Gantrez. The dendrimers in such films are first used as building blocks and then as highly effective macromolecular, thermally

activated cross-linkers. We have demonstrated that, prior to thermal treatment, the permeability of these amphoteric films is quite pH-dependent: such films are open to cations at pH 11 and anions at pH 3. Heating dramatically alters the film properties, leading to a monolithic nanocomposite that is highly impermeable over the pH range studied. The nature of the thermally induced changes in these films depends on the incorporated dendrimer. Imidization is the only thermally induced change that occurs in the amine-terminated Cascade dendrimer/Gantrez films. For hydroxyl-terminated PAMAM dendrimer/Gantrez films, heating causes decomposition of the dendrimers via retro-Michael reactions. Subsequent interdendrimer imidization and Michael reaction of the primary amines formed by the retro-Michael chemistry enhance cross-linking of these films. All thermally induced changes that occur in the hydroxyl-terminated PAMAM dendrimer and amine-terminated Cascade dendrimer films also occur in the heated amine-terminated PAMAM dendrimer/Gantrez films. We believe that imidization contributes most to the extremely high impermeability of these materials. Importantly, the chemistry required to prepare these nanocomposite thin films is simple, general, and readily adaptable to other types of substrates. As an illustrative example, a Gz2/NH₂-C₁₈ film, when grafted onto an Al-coated Si wafer and after thermal treatment, can greatly reduce the rate of Al corrosion in alkaline solution or pitting in neutral chloride-containing solution.

Acknowledgment. Support of this work by the National Science Foundation (R.M.C., CHE-9313441; D.E.B., DMR-9634196), the Robert A. Welch Foundation, and the State of Texas (Texas Higher Education Coordinating Board Grant 010366-096) through the Advanced Technologies Program is gratefully acknowledged. We also thank Mr. Mark Kaiser of MMI/Dendritech (Midland, MI) for providing samples of the Starburst PAMAM dendrimers.

Supporting Information Available: Experimental and simulated complex-plane impedance plots for Au electrodes coated with G4₁ films. See any current masthead page for ordering and Internet access instructions. See any current masthead page for ordering information and Web access instructions.

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