Dendrimers as Building Blocks for Multilayer Construction[1]

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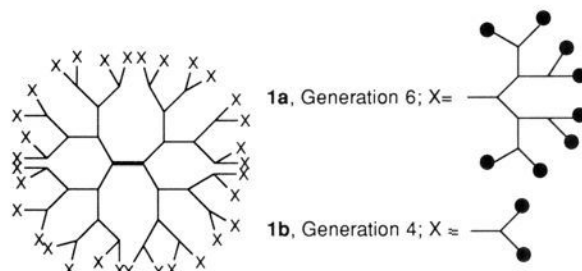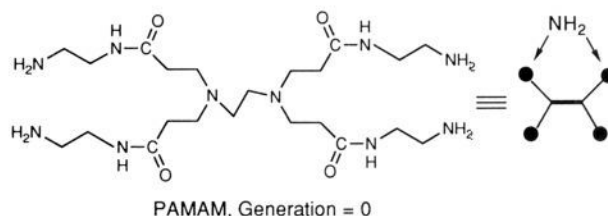
Received July 6, 1994

Early pioneering studies by Iler, reported almost 30 years ago, demonstrated the feasibility of growing multilayers of organic and inorganic polymer colloids on glass by sequential deposition.[2] Although such materials bear a resemblance to Langmuir–Blodgett films (both may be viewed as stacks of two-dimensional arrays), they differ, significantly, by being porous and nonuniform, i.e., their supramolecular structure reflects the fact that they are composed of spherical particles of varying diameter.[3,4] In this report, we describe the preparation of "Iler-like" arrays that have been constructed from dendrimer molecules.[5–12] The ability to synthesize dendrimers with *perfect* uniformity and the possibility of introducing chromophores, redox active species, catalytic sites, etc. at defined locations make them unique as building blocks for the construction of novel and exploitable materials.[13,14]

The procedure that we have developed for growing dendritic multilayers is reminiscent of Mallouk's approach to organometallic thin films.[15] In essence, it involves the deposition of amine-terminated dendrimers onto a Pt^{2+}-bearing surface, followed by reactivation with K_2PtCl_4 (Scheme 1). Solutions of a poly-(amidoamine) dendrimer (**1a**; PAMAM, Generation 6, MW 58 048; Aldrich Chem.) and K_2PtCl_4 were prepared in freshly distilled DMSO; final concentrations of primary amine and K_2-$PtCl_4$ were 2.0 mM. In a typical preparation, a silicon wafer (2 cm²) was first silylated with (3-aminopropyl)triethoxysilane, immersed in a solution of K_2PtCl_4 (30 min), and rinsed with water and methanol.[16] One complete growth cycle was then carried out by immersion of the wafer in a solution of **1a** (30 min), rinsing with water and methanol, reactivation with K_2-$PtCl_4$ (30 min), rinsing, and drying under a stream of nitrogen;

Scheme 1
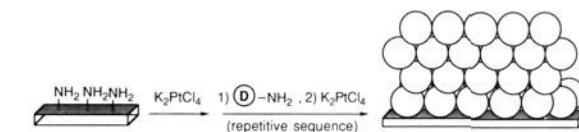
repetition of this protocol yielded corresponding multilayers. All stages of growth were carried out at 23 °C under an argon atmosphere.

PAMAM, Generation = 0

1a, Generation 6; X=

1b, Generation 4; X ≈

Ellipsometric film thicknesses that were measured as a function of cycle number are shown in Figure 1; similar multilayers that were prepared using growth periods of 10 and 60 min are also shown. From these results, we conclude that 30 min is the minimum time that is needed to produce a maximum growth of ca. 80 Å per cycle; the contribution from each Pt^{2+} half-cycle was ca. 10 Å (not shown).[17] Control experiments that were carried out in the absence of Pt^{2+} half-cycles showed negligible growth of dendritic film. The required presence of Pt^{2+} for multilayer growth implies that some fraction of the immobilized metal ion is bonded to a minimum of two amino groups, one per neighboring *dendrimer in adjoining monolayers.* An analogous assembly grown from **1b** (PAMAM, Generation 4, MW 14 215; Aldrich Chem.) showed a maximum thickness of ca. 50 Å per cycle (Figure 2). Previous size-exclusion chromatographic analyses of PAMAM dendrimers having an ammonia (as opposed to an ethylenediamine) core indicate apparent diameters of 40 and 67 Å for generations 4 and 6, respectively.[6a] In view of the conformational flexibility that is inherent in the dendrimer structure, we regard these experimental and estimated values as being in good agreement.[6a] We also regard this agreement as strong evidence for the existence of dense monolayer coverage by the dendrimer.

Examination of 4.5- and 5.0-cycle multilayered assemblies by X-ray photoelectron spectroscopy (XPS, Scienta ESCA-310)

(1) Supported by the U.S. Army Research Office (Grant DAAL03-91-G-0081), and by the Divison of Basic Energy Sciences and the Department of Energy (DE-FG02-85ER-13403).

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(16) The silylation reagent, which was freshly distilled under reduced pressure, was used as a 5 mM "wet" chloroform solution (100 mL of Burdick & Jackson, HPLC + 10 μL of water). Typically, a silicon wafer was first treated for 30 min at room temperature with this solution, followed by washing with $CHCl_3$ and drying under a stream of nitrogen. Prior to silylation, the silicon wafer was cleaned by immersion in concentrated $H_2SO_4/30\%$ H_2O_2 (7/3 v/v) for 30 min at 90 °C, washed with Milli-Q water and CH_3OH, and dried under a stream of nitrogen. Dendrimer samples that were used in this work are estimated by the manufacturer (Dendritech, Midland, MI) to consist of ca. 80–90% of a single molecular form (gel electrophoresis); 10–20% of each sample contains defects due to incomplete growth.

(17) Film thicknesses are based on a refractive index of 1.59, which has been estimated, ellipsometrically, from a film that was grown to 800 Å in thickness.

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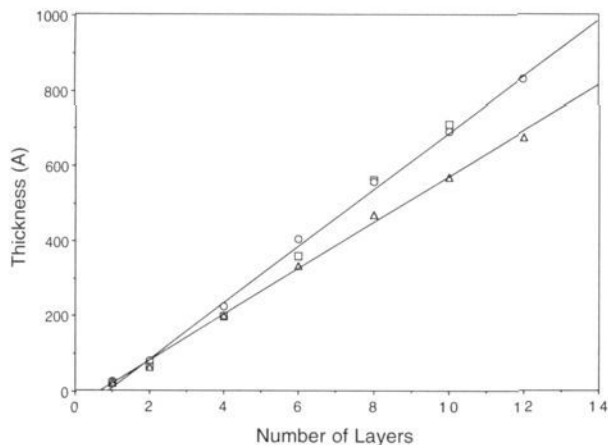
Figure 1. Ellipsometric film thickness (Å) for multilayers of **1a**. Incubation periods used were 10 (△), 30 (○), and 60 min (□). Values reported represent the average of four measurements.
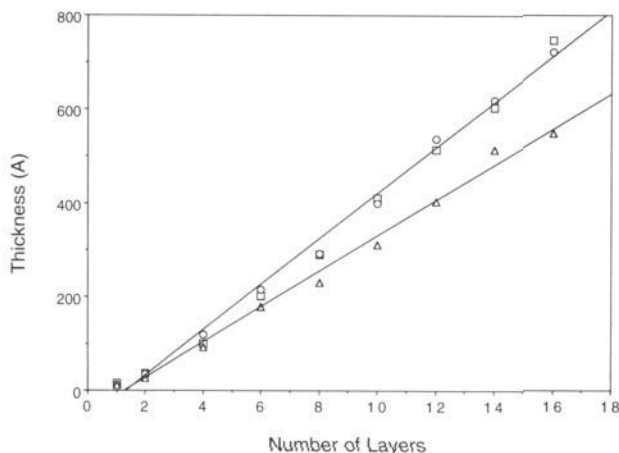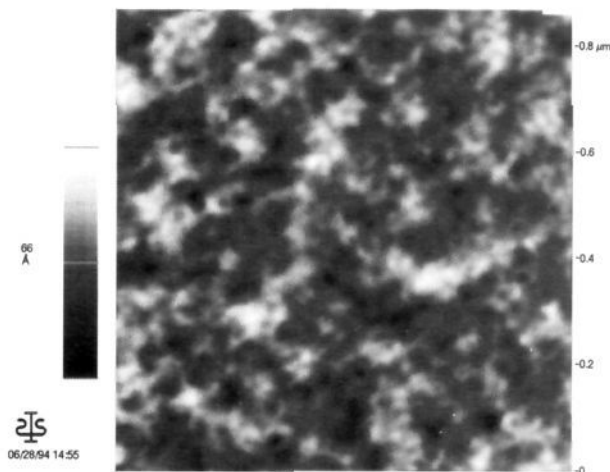

Figure 2. Ellipsometric film thickness (Å) for multilayers of **1b**. Incubation periods used were 10 (△), 30 (○), and 60 min (□). Values reported represent the average of four measurements.

Figure 3. Atomic force micrograph of a 5.0-cycle multilayered sample of **1a** in a 0.88 × 0.87 μm^2 area. A vertical 66 Å scale is also indicated.

Table 1. Atomic Composition of 4.5- and 5.0-Cycle Multilayered Assemblies from Angle-Dependent XPS

element (%) or ratio of elements	4.5-cycle take-off angle			5.0-cycle take-off angle		
	90°	30°	10°	90°	30°	10°
C	60.8	63.3	65.0	60.8	60.7	61.1
N	21.8	21.2	19.5	21.8	21.1	20.8
O	15.3	14.9	15.2	11.9	12.7	11.8
Pt	0.9	0.5	0.3	3.4	3.5	3.1
Cl	0.3	0.1	0.0	2.1	2.1	3.1
N/Pt	24	42	65	6	6	7
N/Cl	73	210		10	10	7

confirmed the presence of the dendrimer and Pt^{2+} on the silicon wafers and also revealed the expected alternation in surface composition during film growth. Analysis of each sample for C, N, O, Pt, and Cl at three different take-off angles (i.e., the angle that is defined by the macroscopic surface of the film and the photoelectrons that are accepted by the analyzer), gave the atomic compositions that are listed in Table 1. By using take-off angles of 10°, 30°, and 90°, one measures the atomic concentrations throughout relative depths of 0.17, 0.5, and 1.0, respectively. Although these percentages must be considered as approximate, due to the variable attenuation of subsurface atoms by the overlying material, the similarity between the observed C, N, and O values and those that would be expected for **1a** and **1b** (i.e., C, 62.5; N, 25.0; O, 12.5) provides strong support for the presence of a PAMAM structure. In addition, the $4f_{7/2}$ binding energy that was observed for Pt (72.8 eV) indicates that the Pt is

maintained in the 2+ oxidation state.[19] In the case of the 5.0-cycle film (last growth medium used was Pt^{2+}), the N/Pt atomic ratio was found to be essentially independent of take-off angle. In striking contrast, the N/Pt ratios for the 4.5-cycle sample (last growth medium was dendrimer) were found to be much larger in magnitude and decreased sharply with increasing sample depth. Similar trends were also evident from the N/Cl ratios (Table 1). These results clearly show that the outermost dendritic layer for the 4.5-cycle sample is relatively deficient in platinum and chlorine and that it effectively covers over the prior Pt^{2+}-bearing monolayer. They also indicate that migration of Pt^{2+} on the dendrimer surface is negligible during the 30 min growth period that was used plus the intermittent time that the assembly was allowed to spend in the dry state (ca. 15 h) prior to XPS analysis. Examination of a 5.0-cycle multilayered sample of **1a** by atomic force microscopy (AMF, Autoprobe CP, Park Scientific Instruments), using a scan rate of 1 Hz in a noncontact mode, revealed that the dendrimer coverage was extensive and that the surface is smooth at the *molecular level*, i.e., the average roughness, which was calculated over a typical 0.88 × 0.87 μm^2 area, was 7.1 Å (Figure 3).

In principle, the use of dendrimers as building blocks for the construction of multilayered assemblies should lead to fundamentally new classes of thin films with unique and exploitable properties. One can imagine, for example, that by using appropriately-sized dendrimers, novel gel electrophoretic media could be created that possess a relatively uniform pore structure (interstitial space) that is capable of exceptionally high resolution. One can also imagine the utility of such gels in the fabrication of heterogeneous catalysts that exhibit size selectivity or as a basis for optical filters and optical devices.[13,14,20,21] In our view, dendritic multilayers open up a rich new area that complements LB films and self-assembled analogs. Studies that are currently in progress are aimed at expanding the scope of dendritic multilayers by use of ionic, covalent, and hydrogen bonds for network formation.

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