

# Role of Architecture and Molecular Weight in the Formation of Tailor-Made Ultrathin Multilayers Using Dendritic Macromolecules and Click Chemistry

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**ABSTRACT:** The high efficiency and mild reaction conditions associated with the Cu(I) catalyzed cycloaddition of azides and alkynes were exploited for the covalent layer-by-layer synthesis of dendritic thin films on silicon wafers. The preparation of azide and alkyne-terminated dendrimers based on bisMPA was accomplished by a divergent strategy; combinations of these monodisperse building blocks from the 2nd to the 5th generation were used for construction of the thin films. The layer-by-layer self assembly process proceeds under ambient conditions and was monitored by ellipsometry, XPS, and ATR-IR, which showed extremely regular growth of the dendritic thin films. Film thickness could be accurately controlled by both the size/generation number of the dendrimers as well as the number of layers. In comparison with linear analogues, the growth of the dendritic films was significantly more controlled and defect-free with each layer being thinner than the corresponding films prepared from the isomeric linear polymers, demonstrating the well-defined, three-dimensional nature of the dendritic architecture. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 2835–2846, 2007

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## INTRODUCTION

Two major, emerging themes in materials chemistry are the development of facile techniques for the preparation of layered nanostructures and the elucidation of structure/property rela-

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tionships for molecular architecture and physical properties of polymeric materials. In developing layered nanostructures, significant attention has recently been devoted to thin films of controlled thickness and composition, driven by the use of these films in a variety of applications,<sup>1</sup> including sensors,<sup>2,3</sup> gas separation,<sup>4</sup> and electronic applications such as displays.<sup>5,6</sup> An excellent method for obtaining these well-defined films is layer-by-layer (LbL) deposition of polymers and small molecules with the most common technique for films of nanoscale thicknesses involving the layered deposition of oppositely charged polyelectrolytes.<sup>7–11</sup> Other noncovalent interactions that have been used for deposition include hydrogen bonding<sup>12,13</sup> and hydrophobic/hydrophilic interaction.<sup>14,15</sup> A drawback with these techniques is the limited robustness of the films since they are not covalently linked and their stability depends on different factors such as solvent, pH, polyelectrolyte concentration, additives, and so forth. In addition, the poor specificity of these noncovalent interactions limits the versatility of the overall process. These issues can be partially addressed by incorporating reactive groups into the film that can be used as secondary crosslinking sites following the ionic LbL deposition.<sup>16,17</sup> However, this process necessitates additional steps, and the formation of the thin films still suffer from issues such as solvent polarity, salt concentration, and so forth. As a result, new strategies for fabricating well-defined, multilayer thin films that are both stable to various environmental conditions and are based on specific interactions would be valuable for the preparation of tailored surfaces and interfaces.

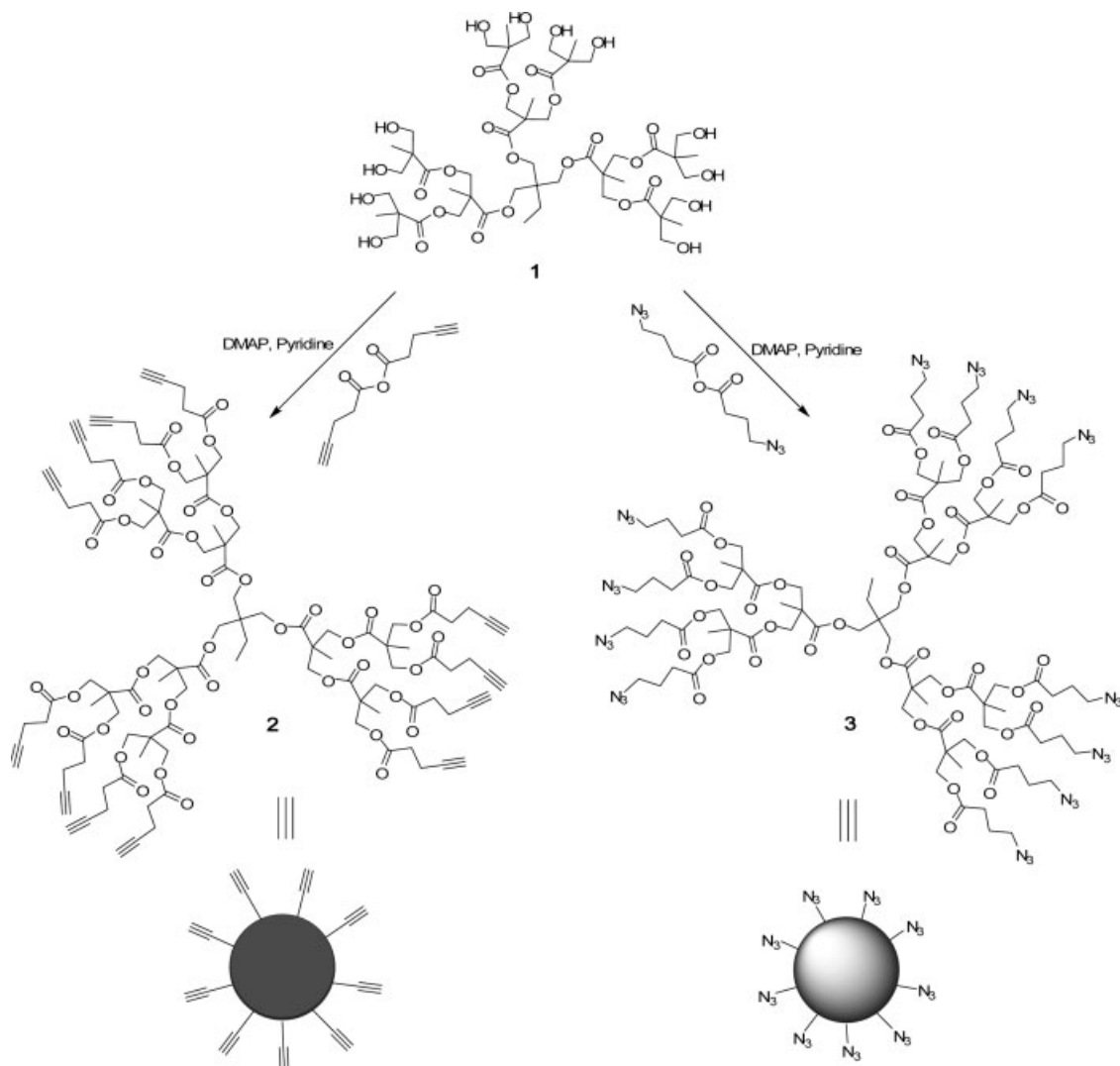
In analogy with ALD (atomic layer deposition), these problems can be overcome by the selective and sequential coupling of functionalized polymers to a solid support through covalent bonding.<sup>17–25</sup> For good control over film formation and structure the deposition reaction must be very efficient with high yields and few byproducts. In addition it is advantageous if the functional groups formed from the deposition/coupling reaction are thermally and chemically stable. The recent development of “Click” chemistry employing the copper(I)-catalyzed cycloaddition between terminal acetylenes and organic azides satisfies all of these criteria and has been demonstrated to be exceptionally broad in scope.<sup>26</sup> The reaction proceeds to very high conversion under mild reaction conditions with

virtually no side reactions or byproducts and the resulting aromatic triazole linkage is extremely stable<sup>27</sup> making the reaction of particular interest in the formation of covalently linked thin films. A secondary requirement for the formation of robust, covalently linked thin films by the LbL deposition of macromolecules is a high density of functional groups that are accessible for reaction. Dendrimers,<sup>28–32</sup> which contain a high number of end groups located primarily at their surfaces, are therefore well suited for the formation of these LbL assemblies.<sup>33–36</sup> In addition, dendrimers have a well-defined size and structure, which may further enhance the controllability of film composition and thickness, while also allowing functionality to be incorporated into the film through the interior of the dendrimer.

In prior work, “click” chemistry has been used to create a library of end-functional dendrimers, unsymmetric dendritic structures and as dendritic crosslinkers for nanoparticles.<sup>37,38</sup> This wide array of synthetically accessible dendritic structures demonstrates the potential of “click” chemistry in LbL fabrication of well-defined thin films and this work further explores the versatility of Click-capable materials by creating covalently bonded multilayer assemblies of dendrimers using a LbL approach. The influence of architecture was further examined by the synthesis of linear analogues of the dendritic macromolecules used in this study and comparison of their performance in the fabrication of multilayer LbL assemblies with their isomeric dendritic derivatives.

## RESULTS AND DISCUSSION

To demonstrate the efficiency of “click” chemistry for the construction of covalent LbL films, hydroxyl functional 2,2-bis(methylol)propionic acid (bisMPA) dendrimers with a trimethylolpropane (TMP) core were synthesized using literature procedures.<sup>39,40</sup> The hydroxyl chain ends of the bisMPA dendrimers were then converted to the desired azide and acetylene functional groups by reaction with 4-azidobutanoic anhydride and 4-pentynoic anhydride, respectively. Using this strategy, functional azide or acetylene dendrimers of Generation 2, 4, and 5 were synthesized with 12, 48, and 96 chain end functional groups (Scheme 1). These materials were

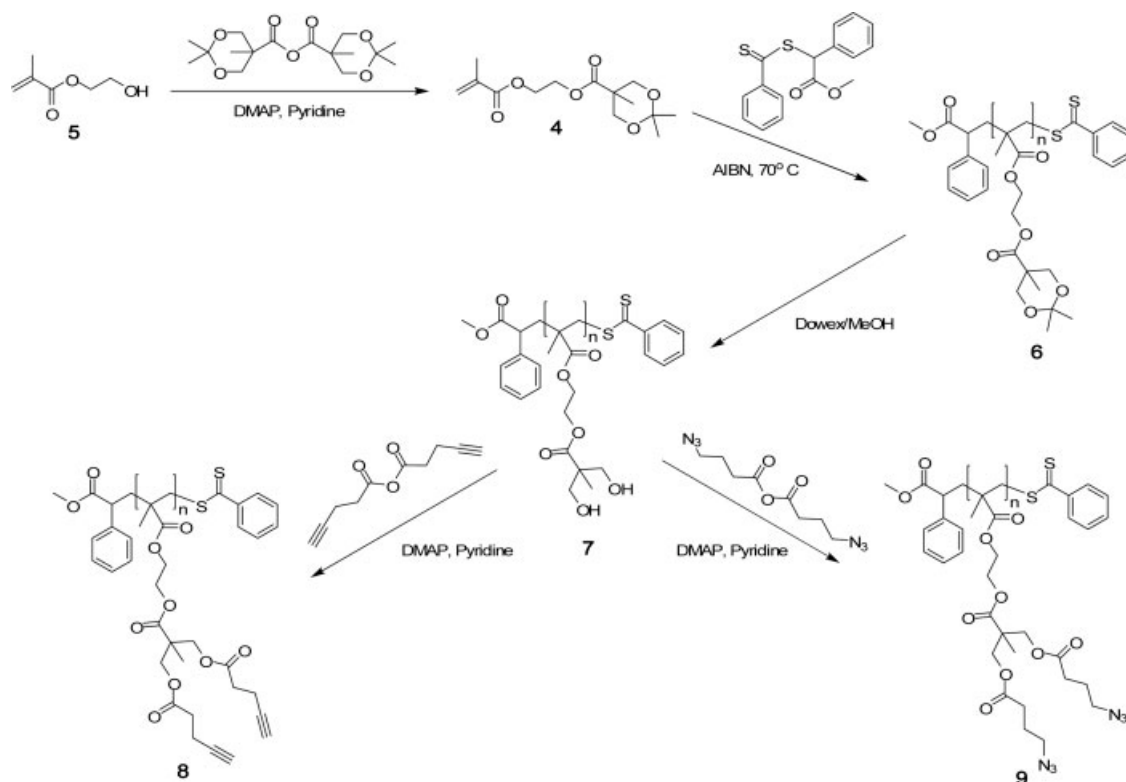


**Scheme 1.** Synthesis of  $[G = 2]$  acetylene, **2**, and azide, **3**, functional dendrimers containing 12 chain end functional groups from the starting bisMPA dendrimer, **1**.

fully characterized and shown to be essentially monodisperse with diameters of 1.9, 3.2, and 4.2 nm in  $\text{CHCl}_3$  solution.<sup>40</sup>

For comparative purposes, low polydispersity, controlled molecular weight linear polymers with acetylene and azide functional groups were synthesized according to Scheme 2. These polymers were designed to be the vinyl analogues of the dendrimers and are based on a methacrylate backbone and a bisMPA side chain. In the first step a bisMPA functional methacrylate monomer, **4**, was synthesized by reacting 2-hydroxyethyl methacrylate (HEMA), **5**, with the anhydride of acetonide protected bisMPA.<sup>39,41</sup> The monomer was then polymerized by reversible addition fragmentation chain transfer<sup>42</sup> proce-

dures to control the molecular weight and polydispersity of the polymer, **6**, using methyl 2-phenyl-2-(phenylcarbonothioylthio)acetate<sup>43</sup> as chain transfer agent and azobisisobutyronitrile (AIBN) as the initiator. The absolute molecular weight obtained was 6800 Da with a polydispersity index of 1.20, giving an average of 23–24 repeat units. The acetonide protecting groups were removed using acidic Dowex ion exchange resin yielding a hydroxy functional polymer, **7**,<sup>44</sup> which could then be transformed into acetylene, **8**, and azide, **9**, functionalized derivatives by reaction with 4-pentynoyl anhydride and 4-azidobutanoic anhydride, respectively, in the same fashion as for the hydroxyl functional dendrimers. The number of functional groups and



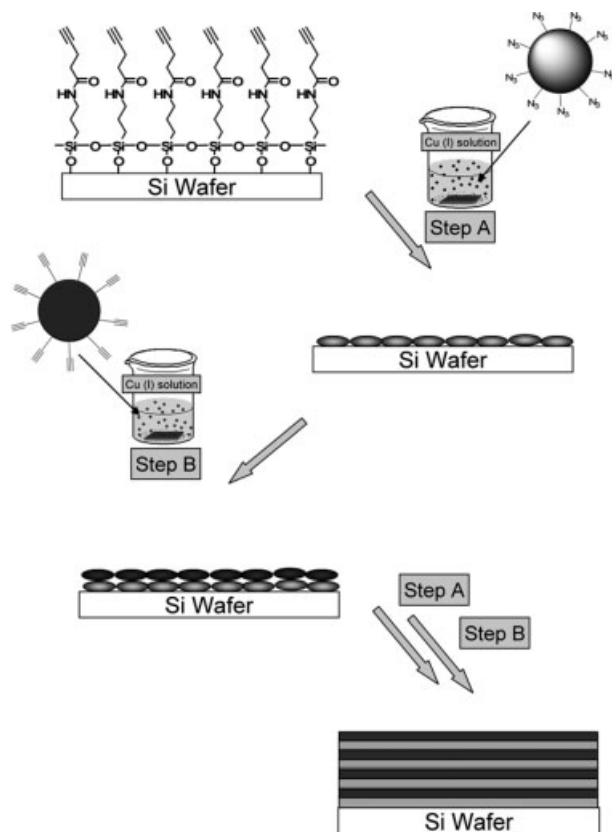
**Scheme 2.** Synthetic strategy for the preparation of acetylene, **8**, and azide, **9**, functionalized poly(methacrylate) derivatives, which are the linear vinyl analogues of bisMPA dendrimers such as **2** and **3**.

the molecular weight was calculated from the degree of polymerization (DP) obtained from the acetone-protected polymer. The average number of functional groups was  $\sim 46$ – $48$ , which makes these polymers vinyl analogues of a Generation 4 dendrimer, which has 48 functional groups and a comparable molecular weight.

Thin films were then fabricated by initially functionalizing the surface of silicon wafers with 3-aminopropyl trimethoxysilane to give an amino functionalized surface that could be transformed into an azide or acetylene surface by reacting with 4-azidobutanoic anhydride or 4-pentynoic anhydride, respectively. The functionalized silicon wafers were then dipped into solutions containing the alternative dendrimer (azide dendrimer for an acetylene surface and vice versa) and  $\text{CuBr}(\text{PPh}_3)_3$  and then subsequently washed with tetrahydrofuran (Scheme 3). In all cases, thirty repetitions of the growth step were performed to obtain consistent and reliable growth data with the thickness increase being measured by ellipsometry after each growth step.

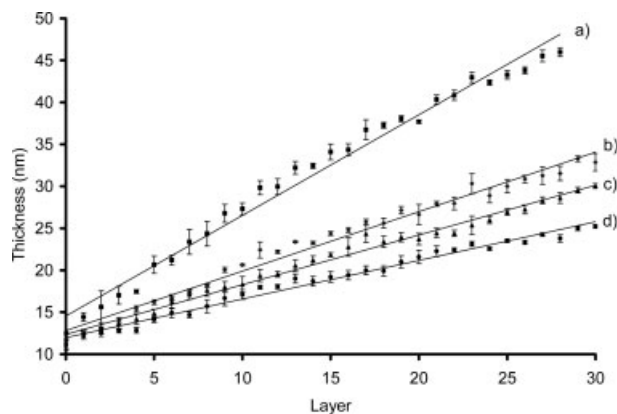
An example of typical thickness increase measured by ellipsometry for a  $G = 5$  system, (Acetylene) $_{96}$ -[G-5]-TMP and (Azide) $_{96}$ -[G-5]-TMP is shown in Figure 1(a). As can be seen in the graph the layers grow with a regular thickness increase averaging 1.22 nm per layer, demonstrating that dendrimers deposited with “click” chemistry allow excellent and reproducible control over film thickness.

Thin film growth and ellipsometer measurements were also performed for other dendrimer combinations, [G-4] + [G-4] Figure 1(b), [G-2] + [G-4] Figure 1(c), and [G-2] + [G-2] Figure 1(d). Of significant note is the controlled increase in film thickness that can be directly correlated with the generation number of the dendrimer, which allows the thickness of the dendritic LbL films to be accurately controlled by either the number of layers and/or the generation number of the dendrimers used in their construction. In contrast to solution behavior where the average diameter of bisMPA dendrimers in THF is  $\sim 1.9$  nm for [G-2], 3.2 nm for [G-4], and 4.2 nm



**Scheme 3.** Graphical representation of the strategy for covalent multilayer formation of dendritic thin films by covalent layer-by-layer deposition, using “click” chemistry. Step A – dipping the wafer into a tetrahydrofuran solution of copper(I) and azide functional dendrimer followed by washing; Step B – dipping the wafer into a tetrahydrofuran solution of copper(I) and acetylene functional dendrimer followed by washing. All reactions and washing steps were performed at room temperature under ambient atmospheric conditions.

for [G-5],<sup>40,45</sup> from Table 1 it can be seen that the average increase in thickness for the LbL films is significantly smaller than the average size of the dendrimers in solution. This indicates that the dendrimers can change shape on deposition and assume a more oblate, flattened structure on the surface. This ability to change shape at interfaces and surfaces has been previously reported for dendrimers deposited on surfaces, or at the air water interfaces as LB films, and represents an unique attribute for these three-dimensional systems.<sup>36,46</sup> It can also be seen that the increase in thickness is significantly larger for the Generation 5 dendrimers when compared with the other generations. This tran-



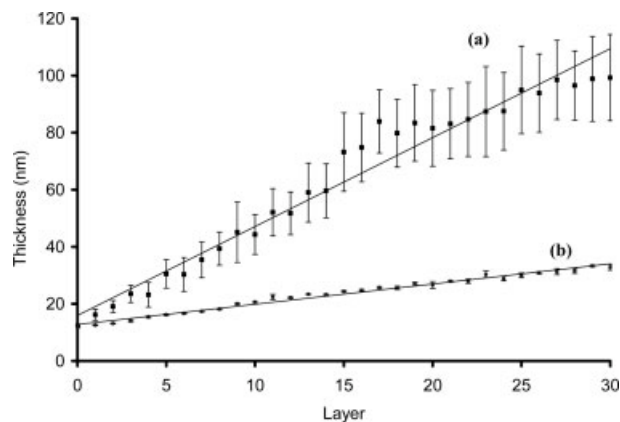
**Figure 1.** Relationship between film thickness as determined by ellipsometry and number of layers for the covalent LbL assembly of dendritic films, using Click chemistry. (a) (acetylene)<sub>96</sub>-[G-5]-TMP/(N<sub>3</sub>)<sub>96</sub>-[G-5]-TMP. (b) (acetylene)<sub>48</sub>-[G-4]-TMP/(N<sub>3</sub>)<sub>48</sub>-[G-4]-TMP. (c) (acetylene)<sub>24</sub>-[G-2]-TMP/(N<sub>3</sub>)<sub>48</sub>-[G-4]-TMP. (d) (acetylene)<sub>24</sub>-[G-2]-TMP/(N<sub>3</sub>)<sub>24</sub>-[G-2]-TMP.

sition and abrupt change in behavior on going from [G = 4] to [G = 5] correlates well with the onset of the “dendritic” effect<sup>47</sup> where an abrupt change in molecular structure occurs on going from [G = 4] to [G = 5]. This increased steric congestion of the fifth generation dendrimer prevents it from spreading out and assuming an oblate structure on the surface to the same extent as the lower generation dendrimers.

Significantly when the average thickness increase for the linear polymers with ~48 reactive groups (analogous to [G = 4] dendrimers with 48 functional groups) is compared with the results for the dendritic derivatives dramatically different results are obtained, which again demonstrates the unique nature of dendritic macromolecules. For the linear polymers, the thickness increase is much larger than for the equivalent dendrimers and the roughness of each

**Table 1.** Average Size Increase for Deposited Layers

Generation Acetylene	Generation N <sub>3</sub>	Thickness (nm)
G2	G2	0.46
G2	G4	0.60
G4	G2	0.63
G4	G4	0.71
G5	G5	1.22
Linear G4 analogue	Linear G4 analogue	3.12



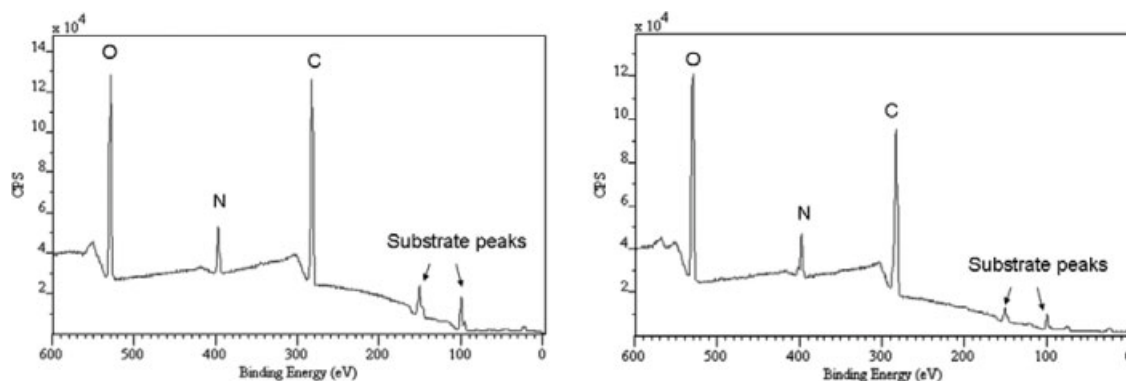
**Figure 2.** Relationship between film thickness as determined by ellipsometer and number of layers for the covalent LbL assembly of polymeric thin films, using Click chemistry. (a) linear [G-4]-(acetylene) and linear [G-4]-azide analogues; (b) (acetylene)<sub>48</sub>-[G-4]-TMP/(N<sub>3</sub>)<sub>48</sub>-[G-4]-TMP.

layer is much greater for the linear polymers with a RMS of >5 nm for the linear polymers compared with 0.75 nm for the dendrimers (Fig. 2). This comparison of macromolecular isomers demonstrates the critical influence of architecture and shows that the random coils of the linear polymers are not as compact as the dendrimers and that their irregularly arranged functional groups leads to a rougher, less controlled surface with increased defects.

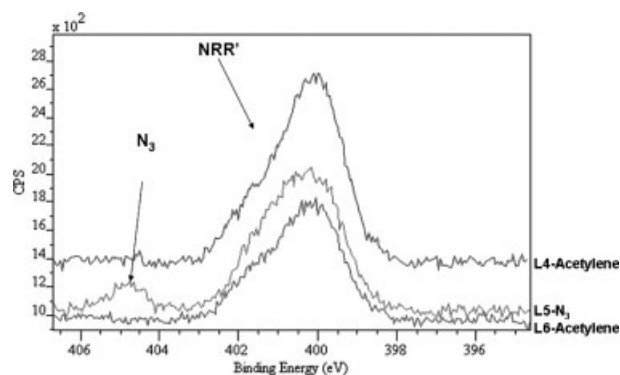
Structural characterization of the multilayer films was performed by X-ray photoelectron spectroscopy (XPS) to follow the chemical reactions occurring in these LbL films. Figure 3 shows the XPS spectra for the starting surface with only the acetylene layer (left) (zero den-

dimer layers) and a surface with five layers of [G-4] + [G-4] dendrimers deposited (right). Since XPS is a surface sensitive technique and penetrates only the first ~10 nm of the film, growth of the film is clearly demonstrated by the decrease in the substrate peaks (peaks around 100–150 eV) as layers are deposited. This sequential decrease in substrate peaks was found to correlate with the number of layers of dendrimers deposited with a much poorer correlation being observed for the linear analogs.

Closer examination of the peaks near 400 eV in the XPS spectrum, representing nitrogen-containing functional groups, allows monitoring of the disappearance of the azide groups during alternating growth of the LbL thin film by Click chemistry. This can be visually seen in Figure 4 where the 4th dendritic layer is formed from the acetylene-terminated dendrimer and essentially only contains nitrogen atoms corresponding to a triazole ring (peak at 400 eV). On generation of the next dendritic layer by reaction with the corresponding azide-terminated dendrimer, a new peak is observed at 405 eV, which is due to unreacted azide groups present at the “surface” of the thin film. Reaction of this film with the acetylene-terminated dendrimer to give the 6th layer leads to essentially complete loss of the azide peak, which clearly demonstrates the repetitive nature of the functional group interchange from azide to acetylene to azide, and so forth, as the LbL films are constructed as well as the quantitative nature of Click chemistry (Fig. 4). It should also be noted that XPS did not reveal any chelated or physisorbed Cu demonstrating that the Cu catalyst is effectively removed after the coupling reaction.



**Figure 3.** XPS measurements of LbL dendritic thin films composed of different number of [G-4] + [G-4] layers. Zero layers (acetylene functional) (left) and five layers (azide functional) of Generation 4 dendrimers.



**Figure 4.** XPS of dendritic LbL thin films showing the 395–406 eV region for nitrogen groups. The top curve is the fourth layer film prepared from an acetylene-terminated dendrimer (excess acetylene functionality), the middle curve is the fifth layer film prepared from an azide-terminated dendrimer (excess azide functionality), and the bottom curve is the sixth layer film prepared from an acetylene-terminated dendrimer (excess acetylene functionality).

This interchange and conversion of the Click functional groups could also be monitored by Fourier Transform infrared spectroscopy, which also allowed the thickness increase of the LbL assemblies relative to the substrate to be determined. With increasing layer number, the strength of the signal due to the dendritic esters ( $1735\text{ cm}^{-1}$ ) increased with respect to that of the amides from the 0th layer ( $1640\text{--}1655\text{ cm}^{-1}$ ), which indicates a steady and reproducible growth in the thickness of the LbL films with layer number. Additionally, the alternating appearance and disappearance of the azide peak and the decreased relative signal strength of this peak relative to the dendritic esters provides strong evidence for the stepwise growth of layers via Click chemistry.

## CONCLUSIONS

The Cu(I) catalyzed “Click” reaction of multifunctional terminal alkyne and azide derivatives has been shown to be a very efficient strategy for the formation of well-defined, covalent LbL films and allows the effect of molecular architecture on the structure of these films to be accurately defined. By exploiting the orthogonality and mild reactions conditions of Click chemistry, dendritic multilayer films have been prepared by the sequential reaction of acetylene and azide-terminated dendrimers under ambient

conditions. The use of these monodisperse building blocks revealed an extremely regular and defect-free growth of the dendritic thin films, the thickness of which can be accurately controlled by either the size/generation number of the dendrimers and/or the number of layers. Interestingly, a dramatic increase in the film thickness per growth step was observed on going from the 4th generation to the 5th generation dendrimers, which correlates with the increase in three-dimensionality or “dendritic” effect that has been observed previously. Comparison with linear analogues was instructive with the growth of the LbL films being more regular and significantly smaller with the dendrimers than for the corresponding linear polymers, demonstrating the well-defined modular nature of the compact, three-dimensional dendritic architecture.

## EXPERIMENTAL

### General Methods

Analytical TLC was performed on commercial Merck Plates coated with silica gel GF254 (0.24 mm thick). Silica Gel for flash chromatography was Merck Kieselgel 60 (230–400 mesh, ASTM).  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) measurements were performed on a Bruker AC 200 spectrometer at room temperature. Size exclusion chromatography was carried out at room temperature on a Waters chromatograph connected to a Waters 410 differential refractometer and six Waters Styragel<sup>®</sup> columns (five HR-5  $\mu\text{m}$  and one HMW-20  $\mu\text{m}$ ) using THF as eluent (flow rate: 1 mL/min). A Waters 410 differential refractometer and a 996 photodiode array detector were employed. The molecular weights of the polymers were calculated relative to linear polystyrene and poly(methyl methacrylate) standards. The layers were analyzed by Fourier transformed infrared spectroscopy, using an Nicolet Magna 850 IR-Raman instrument, fitted with a grazing angle attenuated total reflection single bounce accessory (Harrick Scientific, Ossining, NY). The spectra were acquired at a  $4\text{ cm}^{-1}$  resolution and 512 scans. The resulting spectra were processed using the smoothing binomial function in Igor Pro 5.02. XPS was performed on a Kratos Axis Ultra (Kratos Analytical, Manchester, UK). Survey spectra were taken at normal and 70 degrees off-normal take-off angles at a pass energy of

160 eV using a monochromated 225 W Alk-alpha X-ray. High resolution scans were taken at 20 eV pass energy and 270 W. Ellipsometry was performed with an AutoEl II (A9819) automatic ellipsometer from Rudolph Research at a wavelength of 632.8 nm and an angle of 70°. The refractive indexes of the films were set to 1.462 for all the films and at least five different measurements were performed for each layer.

### Materials

CuBr(PPh<sub>3</sub>)<sub>3</sub>,<sup>48</sup> bisMPA dendrimers,<sup>39,40</sup> chain transfer agent (methyl 2-phenyl-2-(phenylcarbonothioylthio)acetate)<sup>43</sup> and 4-azidobutanoic acid<sup>49</sup> were synthesized according to previous described procedures. 100 mm diameter single side polished, 100 Si wafers from Virginia Semiconductor were used as substrates. All other reagents were obtained from Aldrich and used as received.

*Note:* All azido compounds should be considered as potentially hazardous and an excellent review<sup>50</sup> on their preparation and precautions in handling should be consulted.

### 4-Azidobutanoic Anhydride

To a stirred solution of 4-azidobutanoic acid (14.35 g, 111.1 mmol) in dichloromethane (50 mL) was added 1,3-dicyclohexylcarbodiimide (11.46 g, 55.7 mmol). The reaction mixture was stirred at room temperature overnight, filtered and evaporated to dryness. The byproducts were removed through precipitation into ether (2 × 20 mL) and filtration. After evaporation the product was obtained as colorless oil (12.9 g, 96.6%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.94 (quin, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 4H), 2.54 (t, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 4H), 3.40 (t, *J* = 6.6 Hz, CH<sub>2</sub>COO, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 23.54 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 2C), 32.08 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 2C), 50.15 (s, CH<sub>2</sub>COO, 2C), 168.41 (s, CH<sub>2</sub>COO, 2C).

### General Procedure for Functionalizing Hydroxyl-Terminated Dendrimers and Polymers with Azides and Acetylenes. Exemplified with (N<sub>3</sub>)<sub>12</sub>-[G-2]-TMP, 3

To a stirred solution of (HO)<sub>12</sub>-[G-2]-TMP, **1** (1.00 g, 0.85 mmol), pyridine (4.03 g, 51.0 mmol, 5 eq/-OH), and 4-(dimethylamino)pyridine (DMAP) (0.25 g, 2.0 mmol, 0.2 eq/-OH) in

CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added 4-azidobutanoic anhydride (3.67 g, 15.3 mmol, 1.5 eq/-OH). The reaction mixture was stirred overnight, diluted with 150 mL CH<sub>2</sub>Cl<sub>2</sub>, and washed with 10% NaHSO<sub>4</sub> (3 × 50 mL), 10% Na<sub>2</sub>CO<sub>3</sub> (3 × 50 mL), and brine (50 mL). The organic phase was dried with MgSO<sub>4</sub>, filtered, concentrated, and purified by column chromatography eluting with hexane and gradually increasing the polarity to 40:60 ethyl acetate:hexanes to yield **3** as a colorless oil (2.00 g, 94%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.95 (t, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 3H), 1.24 (s, CCH<sub>3</sub>, 18H), 1.28 (s, CCH<sub>3</sub>, 9H), 1.58 (q, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 2H), 1.89 (quin, *J* = 7 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 24H), 2.43 (t, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 24H), 3.36 (t, *J* = 6.6 Hz, CH<sub>2</sub>COO, 4H), 4.10 (s, CCH<sub>2</sub>O, 6H), 4.15 (s, CCH<sub>2</sub>O, 12H, CCH<sub>2</sub>O, 24H), 4.27 (s, CCH<sub>2</sub>O, 24H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 17.41 (s, CCH<sub>3</sub>, 3C), 17.867 (s, CCH<sub>3</sub>, 6C), 24.41 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 48C), 30.75 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 48C), 46.28 (s, CCH<sub>3</sub>, 6C), 46.67 (s, CCH<sub>3</sub>, 3C), 50.38 (s, CH<sub>2</sub>COO, 48C), 65.02 (s, CCH<sub>2</sub>O, 6C, and CCH<sub>2</sub>O, 12C), 171.60 (s, COO, 3C), 171.87 (s, COO, 6C), 172.09 (s, CH<sub>2</sub>CH<sub>2</sub>COO, 12C).

### (Acetylene)<sub>12</sub>-[G-2]-TMP, 2

Starting from the hydroxyl-terminated (HO)<sub>12</sub>-[G-2]-TMP derivative, **1**, reaction with 4-pentynoic anhydride according to the procedure earlier afforded the desired (Acetylene)<sub>12</sub>-[G-2]-TMP, **2**, which was purified by column chromatography, using hexane as eluent, increasing the polarity to 40/60 EtOAc/hexane, to yield a colorless oil (93%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.92 (t, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 3H), 1.22 (s, CCH<sub>3</sub>, 18H), 1.25 (s, CCH<sub>3</sub>, 9H), 1.57 (q, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 2H), 1.98 (bs C≡CH, 12H), 2.3–2.7 (bm, CH<sub>2</sub>C≡CH, 24H, and CH<sub>2</sub>CH<sub>2</sub>C≡CH, 24H), 4.06 (s, CCH<sub>2</sub>O, 6H), 4.21 (s, CCH<sub>2</sub>O, 12H, CCH<sub>2</sub>O, 24H), 4.31 (s, CCH<sub>2</sub>O, 24H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.28 (s, CH<sub>2</sub>C≡CH, 12C), 17.57 (s, CCH<sub>3</sub>, 3C), 17.84 (s, CCH<sub>3</sub>, 6C), 33.12 (s, CH<sub>2</sub>CH<sub>2</sub>C≡CH, 12C), 46.36 (s, CCH<sub>3</sub>, 6C), 46.81 (s, CCH<sub>3</sub>, 3C), 65.23 (s, CCH<sub>2</sub>O, 6C, and CCH<sub>2</sub>O, 12C), 69.35 (s, C≡CH, 12C), 83.33 (s, C≡CH, 12C), 171.13 (s, COOCH<sub>2</sub>CH<sub>2</sub>C≡CH, 12C), 171.67 (s, COO, 3C), 171.91 (s, COO, 6C).

### (N<sub>3</sub>)<sub>48</sub>-[G-4]-TMP, 10

Starting from the hydroxyl-terminated (HO)<sub>48</sub>-[G-4]-TMP derivative, reaction with 4-azidobuta-



noic anhydride according to the procedure earlier afforded the desired (Azide)<sub>48</sub>-[G-4]-TMP, which was purified by column chromatography, using hexane as eluent, increasing the polarity to 50/50 EtOAc/hexane, to yield a colorless oil (93%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.92 (t, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 3H), 1.2–1.5 (bm, CCH<sub>3</sub>, 9H, CCH<sub>3</sub>, 18H, CCH<sub>3</sub>, 36H, and CCH<sub>3</sub>, 72H), 1.59 (q, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 2H), 1.86 (quin, *J* = 6.8 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 96H), 2.40 (t, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 96H), 3.33 (t, *J* = 6.6 Hz, CH<sub>2</sub>COO, 96H), 4.0–4.5 (bm, CCH<sub>2</sub>O, 6H, CCH<sub>2</sub>O, 12H, CCH<sub>2</sub>O, 24H, CCH<sub>2</sub>O, 48H, and CCH<sub>2</sub>O, 96H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 17.55 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, and CCH<sub>3</sub>, 12C), 17.75 (s, CCH<sub>3</sub>, 24C), 24.14 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 48C), 30.87 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 48C), 46.40 (s, CCH<sub>3</sub>, 24C), 46.61 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, and CCH<sub>3</sub>, 12C), 50.51 (s, CH<sub>2</sub>COO, 48C) 65.04 (s, CCH<sub>2</sub>O, 6C, CCH<sub>2</sub>O, 12C, CCH<sub>2</sub>O, 24C, and CCH<sub>2</sub>O, 48C), 171.55 (s, COO, 3C, COO, 6C, and COO, 12C), 171.96 (s, COO, 24C), 172.10 (s, CH<sub>2</sub>CH<sub>2</sub>COO, 48C).

#### (Acetylene)<sub>48</sub>-[G-4]-TMP, 11

Starting from the hydroxyl-terminated (HO)<sub>48</sub>-[G-4]-TMP derivative, reaction with 4-pentynoic anhydride according to the procedure earlier afforded the desired (Acetylene)<sub>48</sub>-[G-4]-TMP, which was purified by column chromatography, using hexane as eluent, increasing the polarity to 50/50 EtOAc/hexane, to yield a colorless oil (92%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.91 (t, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 3H), 1.2–1.5 (bm, CCH<sub>3</sub>, 9H, CCH<sub>3</sub>, 18H, CCH<sub>3</sub>, 36H, and CCH<sub>3</sub>, 72H), 1.57 (q, *J* = 7.0 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 2H), 2.02 (bs, C≡CH, 48H), 2.3–2.7 (bm, CH<sub>2</sub>C≡CH, 96H, and CH<sub>2</sub>CH<sub>2</sub>C≡CH, 96H), 4.1–4.4 (bm, CCH<sub>2</sub>O, 6H, CCH<sub>2</sub>O, 12H, CCH<sub>2</sub>O, 24H, CCH<sub>2</sub>O, 48H and CCH<sub>2</sub>O, 96H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.28 (s, CH<sub>2</sub>C≡CH, 48C), 17.60 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, and CCH<sub>3</sub>, 12C), 17.83 (s, CCH<sub>3</sub>, 24C), 33.11 (s, CH<sub>2</sub>CH<sub>2</sub>C≡CH, 48C), 46.35 (s, CCH<sub>3</sub>, 24C), 46.63 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, and CCH<sub>3</sub>, 12C), 65.23 (s, CCH<sub>2</sub>O, 6C, CCH<sub>2</sub>O, 12C, CCH<sub>2</sub>O, 24C, and CCH<sub>2</sub>O, 48C), 69.49 (s, C≡CH, 48C), 82.45 (s, C≡CH, 48C), 171.11 (s, COOCH<sub>2</sub>CH<sub>2</sub>C≡CH, 48C), 171.57 (s, COO, 3C, COO, 6C, and COO, 12C), 171.91 (s, COO, 24C).

#### (N<sub>3</sub>)<sub>96</sub>-[G-5]-TMP, 12

Starting from the hydroxyl-terminated (HO)<sub>96</sub>-[G-5]-TMP derivative, reaction with 4-azidobutanoic anhydride according to the procedure earlier afforded the desired (Azide)<sub>96</sub>-[G-5]-TMP, which was purified by column chromatography, using hexane as eluent, increasing the polarity to 20/80 EtOAc/hexane, to yield a colorless oil (89%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.2–1.5 (bm, CCH<sub>3</sub>, 9H, CCH<sub>3</sub>, 18H, CCH<sub>3</sub>, 36H, CCH<sub>3</sub>, 72H, and CCH<sub>3</sub>, 144H), 1.90 (quin, *J* = 6.8 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 192H), 2.42 (t, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 192H), 3.35 (t, *J* = 6.6 Hz, CH<sub>2</sub>COO, 192H), 4.0–4.5 (bm, CCH<sub>2</sub>O, 6H, CCH<sub>2</sub>O, 12H, CCH<sub>2</sub>O, 24H, CCH<sub>2</sub>O, 48H and CCH<sub>2</sub>O, 96H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 17.56 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, CCH<sub>3</sub>, 12C, and CCH<sub>3</sub>, 24C), 17.77 (s, CCH<sub>3</sub>, 48C), 24.15 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 96C), 30.84 (s, CH<sub>2</sub>CH<sub>2</sub>-N<sub>3</sub>, 96C), 46.40 (s, CCH<sub>3</sub>, 48C), 46.64 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, CCH<sub>3</sub>, 12C, and CCH<sub>3</sub>, 24C), 50.49 (s, CH<sub>2</sub>COO, 96C) 65.03 (s, CCH<sub>2</sub>O, 6C, CCH<sub>2</sub>O, 12C, CCH<sub>2</sub>O, 24C, CCH<sub>2</sub>O, 48C, and CCH<sub>2</sub>O, 96C) 171.59 (s, COO, 3C, COO, 6C, COO, 12C, and COO, 24C), 171.97 (s, COO, 48C), 172.10 (s, CH<sub>2</sub>CH<sub>2</sub>COO, 96C).

#### (Acetylene)<sub>96</sub>-[G-5]-TMP, 13

Starting from the hydroxyl-terminated (HO)<sub>96</sub>-[G-5]-TMP derivatives, reaction with 4-pentynoic anhydride according to the procedure earlier afforded the desired (Acetylene)<sub>96</sub>-[G-5]-TMP, which was purified by column chromatography, using hexane as eluent, increasing the polarity to 80/20 EtOAc/hexane, to yield a colorless oil (87%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.2–1.5 (bm, CCH<sub>3</sub>, 9H, CCH<sub>3</sub>, 18H, CCH<sub>3</sub>, 36H, CCH<sub>3</sub>, 72H, and CCH<sub>3</sub>, 144H), 2.04 (bs, C≡CH, 96H), 2.3–2.7 (bm, CH<sub>2</sub>C≡CH, 192H, and CH<sub>2</sub>CH<sub>2</sub>C≡CH, 192H), 4.1–4.4 (bm, CCH<sub>2</sub>O, 6H, CCH<sub>2</sub>O, 12H, CCH<sub>2</sub>O, 24H, CCH<sub>2</sub>O, 48H, CCH<sub>2</sub>O, 96H, and CCH<sub>2</sub>O, 192H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.29 (s, CH<sub>2</sub>C≡CH, 96C), 17.62 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, CCH<sub>3</sub>, 12C, and CCH<sub>3</sub>, 24C), 17.85 (s, CCH<sub>3</sub>, 48C), 33.07 (s, CH<sub>2</sub>CH<sub>2</sub>C≡CH, 96C), 46.33 (s, CCH<sub>3</sub>, 48C), 46.63 (s, CCH<sub>3</sub>, 3C, CCH<sub>3</sub>, 6C, CCH<sub>3</sub>, 12C, and CCH<sub>3</sub>, 24C), 65.26 (s, CCH<sub>2</sub>O, 6C, CCH<sub>2</sub>O, 12C, CCH<sub>2</sub>O, 24C, CCH<sub>2</sub>O, 48C, and CCH<sub>2</sub>O, 96C), 69.53 (s, C≡CH, 96C), 82.41 (s, C≡CH, 96C), 171.16 (s, COOCH<sub>2</sub>CH<sub>2</sub>C≡CH,

96C), 171.59 (s, COO, 3C, COO, 6C, COO, 12C, and COO, 24C), 171.91 (s, COO, 48C).

**2-(Acetonide-2',2'-bis(hydroxymethyl)propionatoethylmethacrylate, 4**

To a stirred solution of HEMA (10.0 g, 76.8 mmol), pyridine (18.2 g, 230 mmol), and 4-DMAP (0.939 g, 7.68 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (80 mL) was added the anhydride of acetonide-protected bisMPA (38.1 g, 115 mmol). The reaction mixture was stirred overnight, and the conversion of bisMPA anhydride was monitored by <sup>13</sup>C NMR. The reaction was quenched with water and extracted into 150 mL CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with 10% NaHSO<sub>4</sub> (3 × 50 mL), 10% Na<sub>2</sub>CO<sub>3</sub> (3 × 50 mL), and brine (50 mL). The organic phase was dried with MgSO<sub>4</sub>, filtered, concentrated, and purified with column chromatography eluting with a 90:10 mixture of hexanes:ethyl acetate, to give **4** as a clear liquid (17.96 g, 81%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.20 (s, COCCH<sub>3</sub>, 3H), 1.40 (d, *J* = 9.4 Hz, COCCH<sub>3</sub>, 6H), 1.94 (t, *J* = 1.6 Hz, CCH<sub>2</sub>CH<sub>3</sub>, 3H), 3.63 (d, *J* = 11.8 Hz, COCCH<sub>2</sub>, 2H), 4.18 (d, *J* = 11.8 Hz, COCCH<sub>2</sub>, 2H), 4.39 (m, COOCH<sub>2</sub>CH<sub>2</sub>COOC, 4H), 5.59 (t, *J* = 1.6 Hz, CH<sub>3</sub>CHCO, 1H), 6.12 (t, *J* = 1.6 Hz, CH<sub>3</sub>CHCO, 1H).

**Poly(2-(acetonide-2',2'-bis(hydroxymethyl)propionate)ethylmethacrylate), 6**

A mixture of 2-(methacryloyloxy)ethyl propionate, **4**, (5.00 g, 17.5 mmol), methyl 2-phenyl-2-(phenylcarbonothioylthio)acetate (0.220 g, 0.73 mmol), and AIBN (0.022 g, 0.13 mmol) was added to a glass ampule, which was degassed by performing freeze-pump-thaw cycles. The ampule was sealed under vacuum and then heated to 70 °C for 40 min (conversion of **4** was 43%). The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and precipitated into cold ether to give the polymer, **6**, as a pink gum (1.92 g, 38%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.8–1.1 (bm, CCH<sub>2</sub>C, 2H), 1.20 (s, COCCH<sub>3</sub>, 3H), 1.40 (d, *J* = 11.8 Hz, COCCH<sub>3</sub>, 6H), 1.6–2.0 (bm, CCH<sub>2</sub>C, 2H), 3.66 (d, *J* = 11.6 Hz, 2H), 4.18 (d, *J* = 11.6 Hz, COCCH<sub>2</sub>, 2H), 4.35 (d, *J* = 11.6 Hz, COCCH<sub>2</sub>, 2H), 4.2–4.5 (bm, COOCH<sub>2</sub>CH<sub>2</sub>COOC, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ, 172.29, 50.77, 50.47, 49.88, 46.52, 32.68, 31.11, 30.91, 26.20, 17.71.

**Poly(2-(2',2'-bis(hydroxymethyl)propionate)ethylmethacrylate), 7**

To 1.85 g of polymer **6** was added Dowex acidic resin (5.0 g) in 50 mL methanol. The suspension was stirred at 50 °C for 18 h. The resin was removed by filtration, and the organic phase was concentrated under vacuum to give the deprotected polymer, **7**, which was purified by precipitation into hexanes (0.90 g, 95%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.8–1.1 (bm, CCH<sub>2</sub>C, 2H), 1.20 (s, COCCH<sub>3</sub>, 3H), 1.6–2.0 (bm, CCH<sub>2</sub>C, 2H), 3.86 (d, *J* = 11.6 Hz, 2H), 4.38 (d, *J* = 11.6 Hz, COCCH<sub>2</sub>, 2H), 4.35 (d, *J* = 11.6 Hz, COCCH<sub>2</sub>, 2H), 4.2–4.6 (bm, COOCH<sub>2</sub>CH<sub>2</sub>COOC, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 172.29, 50.77, 50.47, 49.88, 46.52, 32.68, 31.11, 30.91, 26.20, 24.54.

**Poly(2-(2',2'-bis(4''-azidobutanoxymethyl)propionate)ethylmethacrylate, 8**

Starting from the hydroxyl-terminated linear polymer, **7**, reaction with 4-pentynoic anhydride according to the procedure earlier afforded the desired azido linear polymer, **8**, which was purified by precipitation into cold ether, yielding a peach colored gum (92%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.8–1.3 (bm, CCH<sub>2</sub>C, 2H), 1.25 (s, COCCH<sub>3</sub>, 3H), 2.03 (s, CH<sub>2</sub>CH<sub>2</sub>CCH, 1H), 2.3–2.7 (bm, CH<sub>2</sub>CH<sub>2</sub>CCH, CH<sub>2</sub>CH<sub>2</sub>CCH, 4H), 3.9–4.5 (bm, COOCH<sub>2</sub>CH<sub>2</sub>COOC, 4H; COCCH<sub>2</sub>, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 172.29, 172.06, 65.11, 62.32, 50.77, 50.47, 49.88, 46.52, 32.68, 31.11, 30.91, 26.20, 24.54, 24.14, 17.71.

**Poly(2-(2',2'-bis(4''-azidobutanoxymethyl)propionate)ethylmethacrylate, 9**

Starting from the hydroxyl-terminated linear polymer, **7**, reaction with 4-azidobutanoic anhydride according to the procedure earlier afforded the desired azido linear polymer, **9**, which was purified by precipitation into cold ether, yielding a peach-colored gum (87%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.8–1.3 (bm, CCH<sub>2</sub>C, 2H), 1.25 (s, COCCH<sub>3</sub>, 3H), 1.6–2.0 (bm, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>, 2H), 2.2–2.6 (bm, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>, 2H), 3.2–3.5 (bm, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>, 2H), 4.1–4.5 (bm, COOCH<sub>2</sub>CH<sub>2</sub>COOC, 4H; COCCH<sub>2</sub>, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 172.28, 171.6, 83.21, 69.56, 65.29, 62.34, 46.25, 44.81, 33.16, 26.19, 25.43, 24.69, 17.74, 14.73.

### Substrate Preparation

Silicon wafers were cleaned by soaking in Piranha solution (3/1 v/v sulfuric acid/hydrogen peroxide) for 30 min, washed with water, ethanol, and THF. Extreme caution should be taken when working with Piranha solution since it reacts violently with organic compounds. A solution of ethanol/water/3-aminopropyltrimetoxysilane (9/1/0.5 w/w) was stirred for 1 h, pooled on the surface of a freshly cleaned wafer, left to react for 1 min then spin coated (2500 rpm, 60 s) to remove the excess. The wafer was then cured at 110 °C for 1 h, cleaned with ethanol and dried at 110 °C for 5 min. The amino functionalized wafers were placed in a bath of THF (20 mL), triethylamine (100 mg), and 4-pentynoic anhydride or 4-azido butanoic anhydride added and the reaction mixture left to react overnight at room temperature followed by washing with THF.

### General Procedure for LbL Deposition

The deposition solutions were prepared from 100 mg of azide/acetylene functional dendrimer/polymer and 100 mg of diisopropylethylamine in 20 mL of DMF. The acetylene functional wafers were dipped into the solution containing acetylene-terminated dendrimers and 10 mg  $\text{Cu}(\text{PPh}_3)_3$  per mL of solution were added. The wafers were reacted overnight at room temperature and washed three times with THF. The next layer was deposited in the same way using the corresponding acetylene solution. This procedure was repeated alternating with the azide and the acetylene solutions until 30 layers were deposited.

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