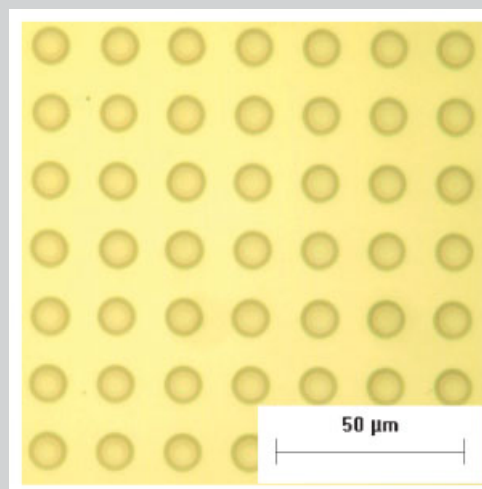


Summary: Microcontact printing was used to deposit stable, nanostructured, amphiphilic and crosslinkable patterns of poly(amidoamine organosilicon) (PAMAMOS)-dimethoxymethylsilyl (DMOMS) dendrimer multilayers onto silicon wafers, glass, and polyelectrolyte multilayers. The effects of dendrimer ink concentration, contact time, and inking method, on the thickness, uniformity, and stability of the resulting patterns were studied using optical microscopy, fluorescence microscopy, atomic force microscopy (AFM), and contact-angle analysis. Microarrayed dendrimer film thickness was found to be controllable by conditions used during spin self-assembly.

Optical micrograph of the circular patterns, obtained from a 0.5% PAMAMOS dendrimer solution, on a glass substrate.



Nanostructured Crosslinkable Micropatterns by Amphiphilic Dendrimer Stamping

Neeraj Kohli,¹ Petar R. Dvornic,² Steven N. Kaganove,² Robert M. Worden,¹ Ilsoon Lee*¹

¹Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI-48824, USA
Fax: (+1) 517 432-1105; E-mail: leeil@egr.msu.edu

²Michigan Molecular Institute, 1910 W. St. Andrews Rd., Midland, MI 48640, USA

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Introduction

Functional, three-dimensional (3-D) nanostructures and microstructures on surfaces can serve as excellent molecular templates for applications in optoelectronics^[1,2] and biotechnology.^[3–5] Coupling stable, amphiphilic films with hydrophobic biological molecules can yield biomimetic interfaces able to reproduce biological functions *in vitro*.^[6] Recently, thin films of amphiphilic molecules have been used to couple proteins to carbon nanotubes.^[7,8] 3-D patterns of amphiphilic molecules can also be used in photon harvesting, organic and polymeric electroluminescent devices (e.g., light-emitting diodes), organic solid-state lasers, and photonic band gap materials.^[9–12] Micro- and nano-scale partitioning of regions with different chemical composition, charge, or environmental conditions is a widely used biological motif, as evidenced by the many membrane-separated organelles and membrane-mediated signaling mechanisms found in cells.^[13,14]

Dendrimers make up a unique, highly diverse class of polymers that have well-defined macromolecular architectures and are almost perfectly monodisperse. Radially layered poly(amidoamine organosilicon) (PAMAMOS) dendrimers are especially versatile, amphiphilic, and crosslinkable globular-shaped macromolecules.^[15] PAMAMOS dendrimers having dimethoxymethylsilyl (DMOMS) end-groups can be denoted as PAMAMOS-DMOMS (p , q), where p and q are integers that define the generation of the polyamidoamine (PAMAM) interior and the number of exterior layers of organosilicon (OS) branch cells, respectively (see Figure 1). PAMAMOS are generally prepared from commercially available PAMAMs with different relative degrees of amino end-group conversion (i.e., OS substitution).^[16] In this study, PAMAMOS-DMOMS (2,1) dendrimers were used (see Experimental Part).

Microcontact printing (μ CP) is a soft lithographic technique used in physics, chemistry, materials science, and biology to transfer patterned thin organic films to surfaces

with sub-micron resolution.^[17,18] Unlike other fabrication methods that merely provide topographic contrast between the feature and the background, μ CP also allows chemical contrast to be achieved by selection of an appropriate ink. Microcontact printing offers advantages over conventional photolithographic techniques because it is simple to perform and is not diffraction limited. These techniques have been used to make patterns of various small and large molecules on metals and silicon substrates^[19–21] as well as to deposit proteins, biological cells,^[22–24] polymer thin films (POPS),^[25] controlled particle cluster arrays^[26] and

their selective metal plating,^[27] and polyelectrolyte aggregates.^[28] Microcontact printing of PAMAM dendrimers has recently been reported.^[29–34] In these studies, the effect of dendrimer concentration on the pattern thickness was evaluated, and new approaches for electroless metalization of these patterns were suggested. However, no attempt was made to study the effect of other process parameters controlling the patterns.

In this paper we report the first application of microcontact printing of the amphiphilic and crosslinkable PAMAMOS-DMOMS dendrimers on glass slides, silicon wafers, and polyelectrolyte multilayers (PEMs) in which the pattern average thickness was controlled by spin self-assembly (i.e., spin-inking). The resulting 3-D micro-patterned amphiphilic networks were characterized by optical microscopy and atomic force microscopy (AFM). In addition, the effects of dendrimer ink concentration, inking method, and contact time on the thickness, uniformity, and stability of the deposited patterns are presented. The results provide a framework for controlling the geometry of the deposited patterns. The lateral footprint of the pattern can be controlled by the shape of the elastomeric stamp, and the thickness of the patterns can be controlled by adjusting the spin coating method, the surface properties of the stamp, and the substrate used. The results also confirmed the well-known influences of spin speed, concentration, and solvent on the thickness of spin-coated films.^[35,36]

Experimental Part

Glass slides (Corning Glass Works, Corning, N.Y.) were cleaned with Alconox precision cleaner (Alconox Inc., New York, NY) in a Branson ultrasonic cleaner (Branson Ultrasonics Corporation, Danbury, CT) followed by sonication in pure water. They were then dried under nitrogen flow and subjected to oxygen plasma treatment in a Harrick plasma cleaner (Harrick Scientific Corporation, Broadway Ossining, NY) for 5 min at 20 Pa vacuum. Polyelectrolyte multilayers (10 bilayers) were deposited on the glass slides using a standard procedure described elsewhere^[26,37] with sulfonated polystyrene (SPS) as the polyanion and poly(dimethyldiallylammonium chloride) (PDAC) as the polycation.

Si (100) wafers (Silicon Sense Inc., Nashua, NH) were cleaned by immersion in Piranha solution (70% sulfuric acid and 30% hydrogen peroxide) at room temperature for 30 min, then rinsed with deionized water and dried under nitrogen.

Patterned poly(dimethylsiloxane) (PDMS) stamps were fabricated by pouring a 10:1 mixture of Sylgard 184 elastomer/curing agent (Dow Corning, Midland, MI) over a patterned silicon master. The mixture was cured for approximately 24 h at 60 °C and then carefully peeled off the master.

Second generation (G2) PAMAMOS-DMOMS (2, 1) dendrimers were obtained as a 20% wt./wt. methanolic solution from Dendritech, Inc. (Midland, MI). This solution was further diluted to the desired concentrations (from 0.01 to 1 wt.-%) with methanol.

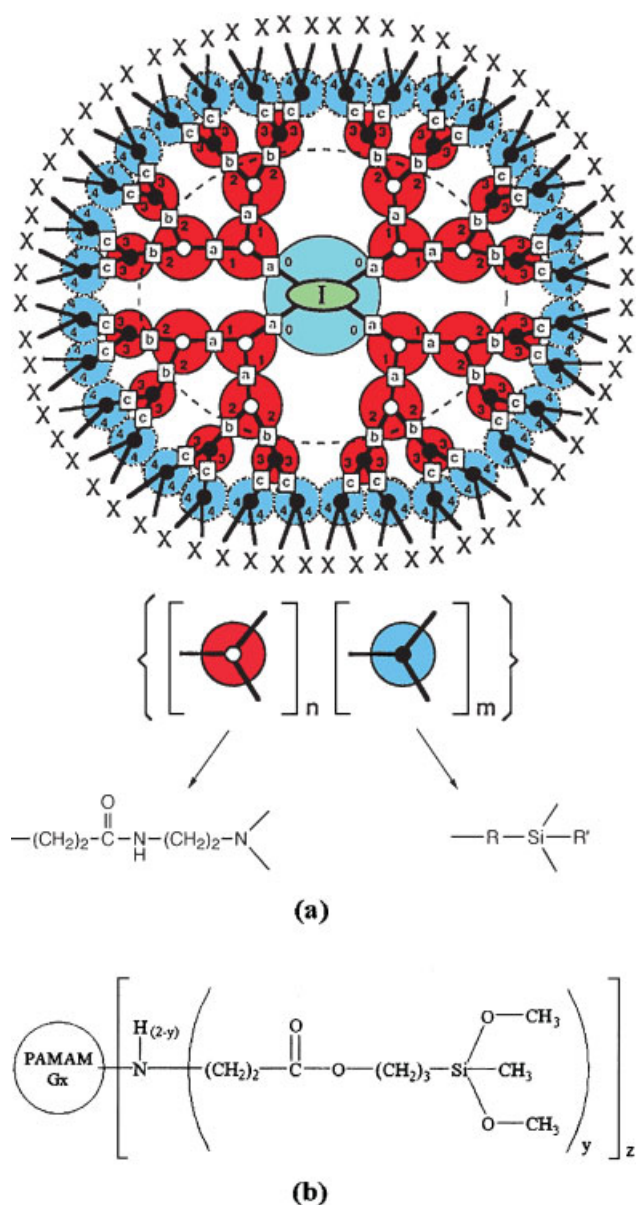


Figure 1. Schematic representation of (a) radially layered poly(amidoamine organosilicon) (PAMAMOS) dendrimer having three layers of red (i.e., PAMAM) branch cells and one layer of blue (i.e., OS) branch cells; (b) PAMAMOS-DMOMS dendrimer.

Two different methods were utilized to apply the ink: spin inking and dip inking. For spin inking, the stamps were cleaned and treated in the plasma cleaner for 30 s to make their surfaces hydrophilic. They were then coated with ink using a pipette, and subsequently spun at 3 000 rpm for 20 s. Monolayer coating of polymers by this spin self-assembly has been reported previously.^[38,39] In the dipping method, the stamps were immersed in ink for several minutes and then dried under nitrogen flow. The ink was then transferred to the silicon substrate by bringing the stamp into conformal contact with the substrate.

PAMAMOS dendrimers were labeled with fluorescein isothiocyanate (FITC) using the standard procedure.^[40] FITC was predissolved in acetone and added to methanol solutions of PAMAMOS. The resulting solutions were then allowed to stand overnight with occasional stirring. The total amount of dye was adjusted to label just one amino group per PAMAMOS molecule on average, assuming perfect reaction efficiency. The PAMAMOS solutions were then dialyzed against pure water using sterilized and rinsed membrane tubing. Water for rinsing and dilution was supplied by a Barnstead Nanopure Diamond-UV purification unit (Barnstead International, Dubuque, Iowa) equipped with a UV source and a final 0.2 μm filter.

Optical-microscope images were obtained using a Nikon Eclipse ME 600 microscope, and fluorescence images were obtained using the Nikon Eclipse E 400 microscope (Nikon, Melville, NY). Advancing contact-angle measurements were performed with a SEO Contact Angle Analyzer (Phoenix 450, Surface Electro Optics Corporation Ltd., Korea). Atomic force microscopy (AFM) images were obtained with a Nanoscope

IV multimode scope (Digital Instruments, Santa Barbara, CA). The microscope was equipped with tapping-mode etched silicon probes. The thickness of the micropatterned films was determined using cross-sectional analysis of the AFM images.

Results and Discussion

The thickness of nanostructured micropatterns was found to be controllable, and the optimum stamping conditions for the uniform nanostructured, micropatterned, amphiphilic films with high lateral resolution were determined (see Figure 2 and 3). For all substrates tested, the pattern average thickness increased with dendrimer concentration over the concentration range from 0.1 to 1 wt.-% when the stamp was spin-coated at 3 000 rpm for 20 s. In this way, the transferred pattern average thickness can be controlled in the range of 100 to 550 nm by controlling the spin-coating conditions. Thin and unstable patterns (e.g., see Figure 2a) were formed at concentrations less than 0.5 wt.-%, while higher concentrations (>0.5 wt.-%) resulted in thicker and stable patterns (e.g., see Figure 2(b–d) and 3). These results confirm the suitability of the spin-inking method as an alternative to dip-inking^[18] to control the height and uniformity of the nanostructured and micropatterned films, and is consistent with the previously reported dependence of spin-coated film thickness on concentration, spin speed, and solvent.^[35,36,41]

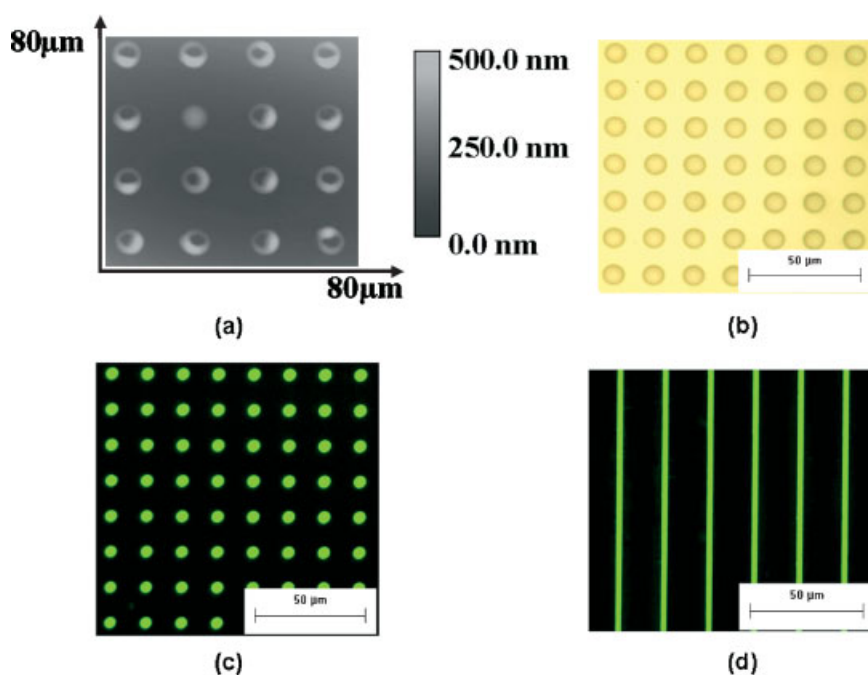


Figure 2. (a) An example of an AFM image showing unstable circular patterns on a glass slide obtained from a 0.5% PAMAMOS dendrimer solution; (b–d) Visualization of PAMAMOS dendrimer patterns on various substrates, (b) Optical micrograph of the circular patterns on a glass substrate, (c) Fluorescence image of the circular pattern on a glass substrate, (d) Fluorescence image of the line pattern on an SPS surface.

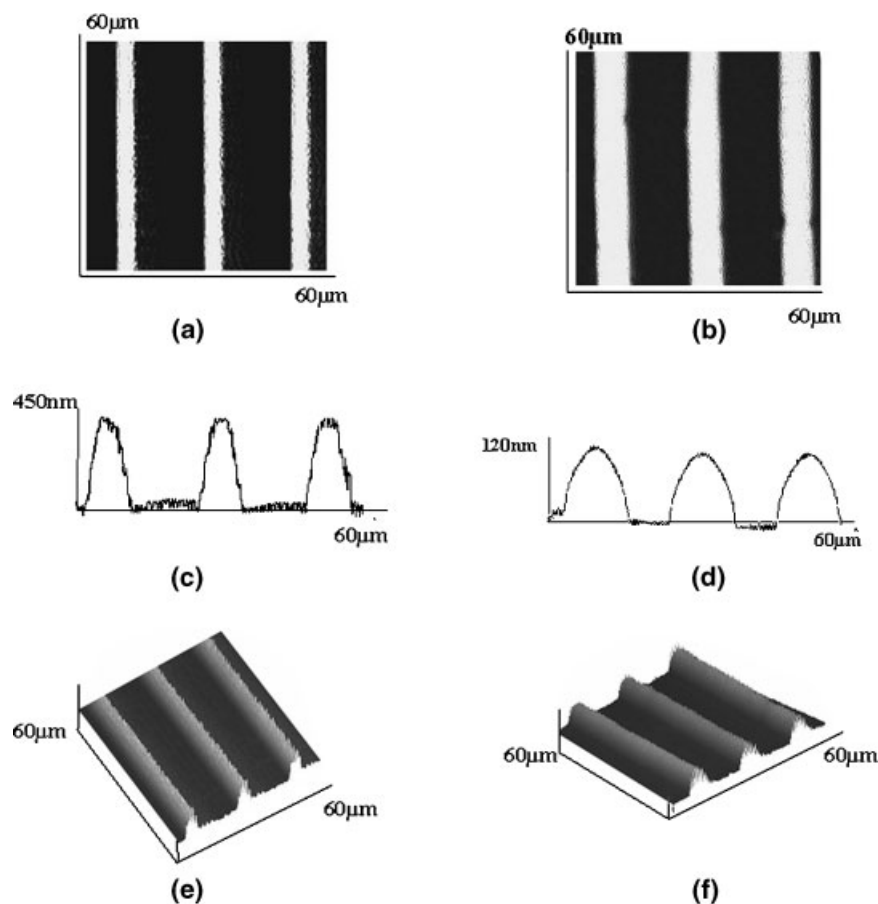


Figure 3. AFM images of crosslinked PAMAMOS dendrimer patterns: (a) Patterned glass substrate stamped by 1 wt.-% dendrimer solution in methanol for a contact time of 5 min; (b) Patterned silicon wafer stamped by a 1 wt.-% dendrimer solution in methanol for a contact time of 25 min; (c) Pattern height on glass substrate; (d) Pattern height on silicon wafer; (e) 3-D image of the patterned glass substrate; (f) 3-D image of the patterned silicon wafer.

Several parameters were systematically varied to obtain high-quality patterns having smooth, intact regions of deposited ink, whose shape faithfully reproduced the topography of the stamp. Under nonoptimal conditions, undesirable pattern features were observed, including ink diffusion at the boundaries, which resulted in ragged edges, and dendrimer aggregation within inked regions, which resulted in irregularly shaped ink microdomains, separated by fissures in the case of line patterns and doughnut-shaped structures in the case of circular patterns (e.g., Figure 2a). The effects of dendrimer concentration and contact time on pattern characteristics are presented qualitatively in Table 1 for glass slides, silicon wafers, and polyelectrolyte multilayer-coated substrates having SPS as the surface layer. As can be seen in Table 1, silicon wafers and polyelectrolyte coated glass slides with sulfonated polystyrene (SPS) as the top-most layer required longer contact times for pattern transfer than bare glass surfaces. For a glass substrate, a 1 wt.-% solution of PAMAMOS spin-coated at 3 000 rpm

for 20 s and a contact time of 5 min resulted in the formation of uniform, stable patterns. For silicon wafers, a 1 wt.-% solution of PAMAMOS dendrimers spin-coated twice at 3 000 rpm for 20 s and a contact time of 30 min resulted in uniform, stable patterns. For an SPS surface, a 1 wt.-% solution dip-coated for 30 min and with a contact time of 1 h resulted in the best patterns. At lower concentrations and contact times, thinner and unstable patterns were formed that showed ink aggregation. The reasons for dendrimer aggregation under these conditions are not clear from these data alone. However, mechanisms involved in polyelectrolyte aggregation under similar conditions have been explained elsewhere.^[28] While aggregation could be eliminated by increasing the dendrimer concentration and contact time, at very high concentrations and contact times, diffusion also became a problem.

The optical microscopy image presented in Figure 2b shows excellent contrast between the PAMAMOS pattern produced and the substrate, indicating successful

Table 1. Effects of concentration and contact time on the stability and uniformity of patterns on different substrates.

Surface	Contact time min	Dendrimer solution concentration ^{a)}		
		wt.-%		
		0.1	0.5	1.0
Glass slide	1	Poor coverage with aggregation	Fair coverage with some aggregation	Fair coverage with very little aggregation
	3	Fair coverage with some aggregation	Fair coverage with very little aggregation	Good coverage
	5	Good coverage with some aggregation	Good coverage	Good coverage
	10	Good coverage with diffusion and aggregation	Good coverage with diffusion	Good coverage with diffusion
Silicon wafers	30	Fair coverage with some aggregation	Good coverage	Good coverage
SPS surface	60	Fair coverage with some aggregation	Good coverage	Good coverage

^{a)} Concentration less than 0.1 wt.-% resulted in negligible and unstable pattern transfers.

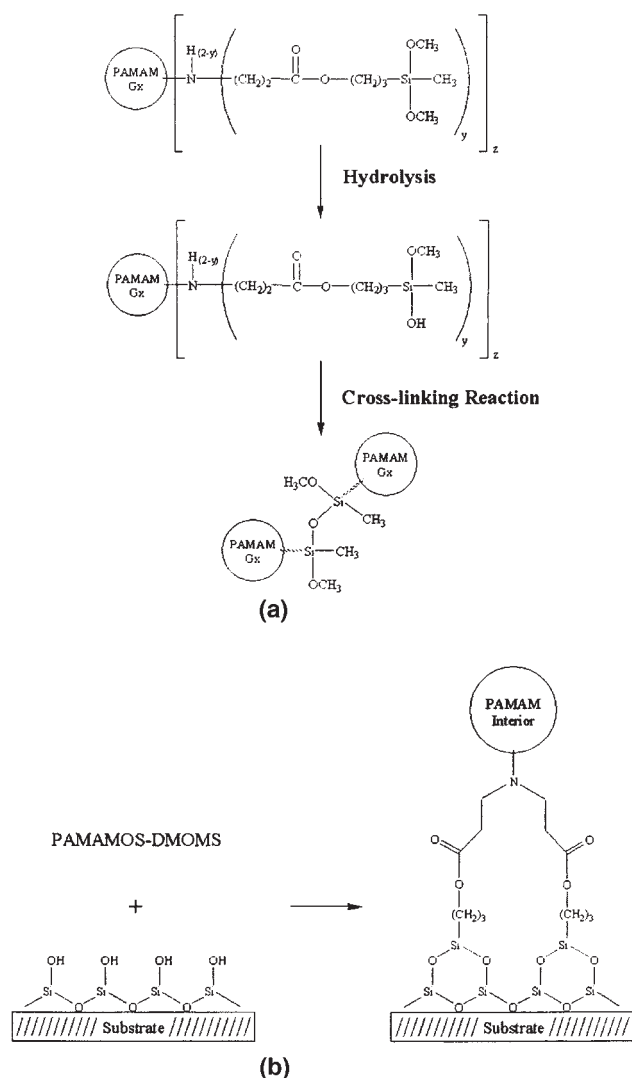
multilayered deposition of PAMAMOS. Fluorescent labeling of PAMAMOS-DMOMS was necessary for lower concentrations of dendrimer inks, because printed features were difficult to visualize by optical microscopy alone. Previous developmental work on PAMAMOS-DMOMS has shown that up to 80 or 90% of the amino end-groups of the PAMAM starting material typically react with (3-acryloxypropyl) dimethoxymethylsilane, leaving approximately 10–20% of the end-groups as primary or secondary amines that are available for reaction with suitable electrophiles.^[15] Hence, the dendrimers could be covalently bound to fluorescein isothiocyanate. Figure 2c and 2d show fluorescence images of circular patterns on a glass substrate and the line patterns on a polyelectrolyte-coated glass slide with SPS as the top surface.

Figure 3a shows an AFM image of a patterned glass substrate stamped with a 1 wt.-% dendrimer solution, for a contact time of 5 min, and Figure 3b shows an AFM image of patterned silicon wafer stamped with the same dendrimer solution for a contact time of 30 min. The light areas are deposited dendrimers, while the dark areas are the underlying substrate. The structure heights for these patterns are depicted in Figure 3c and 3d, respectively. The results indicate consistent coverage where the stamp met the substrate, and uniform average thickness across the pattern. The pattern shape, as seen in the cross-sectional views (Figure 3c and 3d), was found to be round for most of the patterns transferred. This surface curvature, we believe, arises from a complex interplay of forces that occur during deposition and drying of the dendrimer ink, as well as unavoidable edge effects arising from the size and shape of the AFM tip. The 3-D images shown in Figure 3e and Figure 3f indicate that the upper edges of the line patterns exhibited a slight height variance, which tended to decrease with the thickness of the patterns for all substrates examined. Although rinsing with water after deposition smeared the patterns, very stable patterns could be obtained if the substrates were air-dried for an hour or cured in an oven at

120 °C for an hour. This high stability is attributed to the crosslinking reaction depicted in Scheme 1. The reaction is reported^[42,43] to proceed through two steps: (i) water hydrolysis of methoxysilyl (Si–OCH₃) end-groups to yield the corresponding silanols, Si–OH, and (ii) subsequent condensation of these silanols to form siloxane (Si–O–Si) inter-dendrimer bridges. The second reaction is self catalyzed by the basic PAMAM interiors and is easily accomplished either by direct exposure of methoxysilyl-functionalized PAMAMOS-DMOMS dendrimer precursors to atmospheric moisture, or by controlled addition of water either in the form of vapor (e.g., in a humidity chamber), or blended as liquid into a dendrimer solution. Since the process is a chain reaction in which the water consumed in the hydrolysis step is regenerated in the condensation step, less than the stoichiometric amount of water is needed.

Dip-inking produced thinner and relatively non-uniform (i.e., poorly covered and aggregated) features, while spin-inking produced thicker and more uniform features. This effect is attributed to spin coating giving a thicker layer of dendrimer ink than dip coating. An untreated stamp had a water advancing contact angle of 102° before plasma treatment and 6° after plasma treatment, indicating that the plasma treatment rendered the stamp surface hydrophilic. Coating the plasma-treated stamps with hydrophobic PAMAMOS dendrimer ink increased the surface hydrophobicity, and hence the contact angle. Spin-coated stamps had a higher contact angle (60°) than those dip-coated (around 45°), suggesting that the roughness, thickness, and morphology of the thin films formed in both cases are different. Because the thickness of the dendrimer ink layer can be controlled by adjusting the spin rate, spin coating should allow the properties of the patterned surface to be more finely controlled than dip coating.

As a result of the very regular size and globular shape of the dendrimers and their controlled amphiphilicity and crosslinkable nature, the micropatterned arrays of PAMAMOS films offer advantages over other macromolecular



Scheme 1. (a) Crosslinking of PAMAMOS-DMOMS dendrimers into a covalently bonded network structure; (b) Covalent bonding of PAMAMOS-DMOMS dendrimers to glass surfaces having silanol surface groups.

materials in the fabrication of the 3-D bioconjugate surfaces and biomimetic interfaces for applications including producing biochips for proteomics, pharmaceutical screening processes, and addressing fundamental questions in cell adhesion.^[3,22–24,44,45] The cage-like structure and controllable porosity of dendrimers, coupled with the unique ability of PAMAMOS dendrimers to form highly crosslinked structures, makes the structures developed in this paper well suited to encapsulate molecular mediators and cofactors for redox enzymes used in bioelectronic applications.^[46] Moreover, these versatile dendrimer arrays could serve as templates for nanoparticle growth or electroless metalization in development of nano metal reactors on micro-patterned films.^[47,48] Further characterization of patterned surfaces and in situ chemical reactions of these films

is currently underway for electronic devices and sensor applications.

Conclusion

This paper reports the first micropatterned deposition of stable, nanostructured, amphiphilic and crosslinkable PAMAMOS-DMOMS dendrimer multilayers onto silicon wafers, glass surfaces, and polyelectrolyte multilayers. Using optical microscopy, fluorescence microscopy, AFM, and contact-angle analysis, the effects of dendrimer ink concentration, contact time, and inking method, on the thickness, uniformity, and stability of the resulting patterns were studied. In the spin self-assembly process, pattern average thickness increased with increasing dendrimer ink concentration at constant spin speed. Interdendrimer cross-linking by siloxane condensation allowed the 3-D amphiphilic and multilayered structures to remain stable for several days, even after washing if they were kept in air for an hour or heat treated at 120 °C in an oven. The resulting highly crosslinked networks have the ability to encapsulate nanoparticles and to serve as molecular templates for chemical and physical modifications in opto-electronic and biomimetic interface applications.

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