Dendrimers at surfaces and interfaces: chemistry and applications

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The highly compact and globular shape, as well as the uniform size and plurifunctionality of dendrimers make them ideal molecular building blocks for a wide range of interfacial materials involving self-assembled monolayers, Langmuir films, multilayers, and other surface-confined assemblies. Moreover, the study of the behavior of dendrimers at surfaces and interfaces provides unique insight into their chemical and physical properties. Dendritic macromolecules play an increasingly important role in the materials and surface sciences, where applications utilizing polymer thin films can benefit from their distinctive chemical and physical properties. Recent investigations have highlighted the use of dendrimers as functional surfaces and as interfacial materials for applications in membranes, adhesion, microelectronics or in chemical and biological sensing.

Introduction

Dendrimers constitute a unique class of polymers that are distinguished from all other synthetic macromolecules by their globular shape resulting from their perfectly branched architecture and their monodisperse nature.[1–3] The size, molecular weight, and chemical functionality of dendrimers can be easily controlled through the synthetic methods used for their preparation both by divergent[4] and by convergent[5] methods. With both of these approaches, a branch point is inserted in the dendritic structure at each monomer unit leading to a well-defined macromolecule with a 'degree of branching'[6] (DB) of

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Jean M. J. Fréchet obtained his first degree at the Institut de Chimie et Physique Industrielles (now CPE) in Lyon, France, and PhD degrees from the College of Environmental Sciences and Forestry and Syracuse University. Following academic appointments at the University of Ottawa (1973–1986) and Cornell University (1987–1996), he joined the Department of Chemistry at the University of California in Berkeley where he also heads the polymer program at the Lawrence Berkeley National Laboratory. J. Fréchet received both the American Chemical Society awards in Polymer Chemistry and in Applied Polymer Science; in 2000 he was elected a Fellow of the American Academy of Arts and Sciences, a member of the National Academy of Engineering, and a member of the National Academy of Science.

100%. This highly branched dendritic architecture causes the molecules to adopt three-dimensional globular conformations to minimize their free energy, with an immediate effect on macromolecular properties. In addition, the chemical composition of the chain-ends of the dendrimers has a determining effect on many of their physical properties such as solubility, glass transition temperature, or intrinsic viscosity. Finally, free energy considerations[2] dictate that the compositional contrast— match or mismatch—between the chain ends and the building blocks of a dendrimer will largely determine whether the chain-ends are mostly peripheral or distributed through their volume.

Over the past 16 years a wide range of 'designer' dendrimers[3] have been developed and synthesized, and their chemical and physical properties as well as their solution behaviors have been studied and well characterized.[3,7] In contrast, it is only recently that interest in the study and use of novel dendrimers for applications at surfaces and interfaces has grown.[7–9] As a result of their compact globular shape and easily controlled size and functionality, dendrimers constitute ideal molecular building blocks for a wide range of surface-related applications. Langmuir monolayers formed from amphiphilic dendrimers have recently been utilized by several research groups in order to probe behaviors such as shape, compressibility, and the localization of end-groups. Moreover, by studying their behavior at the air–water interface, one can gain further understanding of the relationship between physical properties and dendrimer generation. Similarly, the study of self-assembled monolayers of dendrimers on solid substrates has enhanced our understanding of the novel properties that are only accessible through surface confinement. Examples of applications of monolayers and other ultra-thin films assembled from tailor-made dendritic macromolecules have recently begun to appear in mission-oriented research such as functional materials for sensors or for microelectronics. Finally, the globular shape and multifunctional periphery of dendrimers makes them well suited for the construction of multilayer nanocomposite materials. These novel materials have recently been utilized to fabricate chemical and biological sensor devices as well as membranes responsive to external stimuli. The main goal of this article is to highlight the recent activity in both the study and the applications of dendrimers at surfaces and interfaces.

Dendrimers at the air–water interface

Initial studies of dendrimers at the air–water interface were carried out by Saville *et al.*[8] using convergent Fréchet-type poly(benzyl ether)† dendrons with a hydrophilic alcohol moiety at the focal point and hydrophobic benzyl groups at their periphery. Langmuir films were prepared from a homologous series of dendrons ranging from Generation 2 ([G-2]-OH) through Generation 6 ([G-6]-OH). As expected, surface pres-

† The IUPAC name for poly(benzyl ether) is poly(oxymethylphenylene).

sure *versus* molecular area (*Π–A*) isotherms for this series showed that the higher molecular weight dendrons better resist collapse as the pressure is increased. Within the same series, only the lower molecular weight dendrons, [G-2]-OH through to [G-4]-OH, exhibit surfactant-like behavior while the much larger [G-5]-OH and [G-6]-OH dendrons no longer behave as surfactants. This suggests that the focal point of the larger dendrons is sterically shielded within the interior of the molecule, and, as a result, is inaccessible for association with the water surface, in agreement with the results of solvatochromic studies on comparable dendrons with a dye at their focal point.[10]

Neutron reflectivity studies carried out on Langmuir films prepared from analogous [G-4]-OH dendrons with chain-ends deuterated for additional contrast, support a monolayer structure as shown in Fig. 1. The peripheral benzyl groups are located on the outside of the molecule and away from the water interface, while the alcohol at the focal point is associated with the surface of the water. Further evidence from these neutron reflectivity experiments indicates that the [G-4]-OH Langmuir monolayer collapses easily into a stable bilayer. The bottom layer of dendrons, which afforded full surface coverage at all compressions, contained approximately 25% water. Meanwhile, the top layer, which varied in the extent of coverage from 50 to 100%, contained little or no water. This suggests that the bottom dendrimer layer acts as a hydrophobic barrier and prevents water from penetrating this layer. Furthermore, at low compressions, the [G-4]-OH dendrons within the Langmuir film assumed a spherical shape. However, at higher compressions, the dendrons in the lower layer adopted an elliptical shape with a 2:1 aspect ratio as depicted in Fig. 2. This phenomenon will be discussed in further detail below.

Hawker, White, and co-workers also explored the effect of peripheral group chemistry on the surface activity of dendrimers at the air–water interface.[11] For this study, poly(benzyl ether) dendrons were again synthesized with a single alcohol at the focal point but also included either nitrile or methyl ester functional groups at their periphery. The Langmuir film structure of these dendrimers was also analyzed by neutron specular reflectivity and *Π–A* isotherm measurements. It was found that functionalization of the periphery of the dendrons with polar nitrile and ester functionalities leads to monolayers
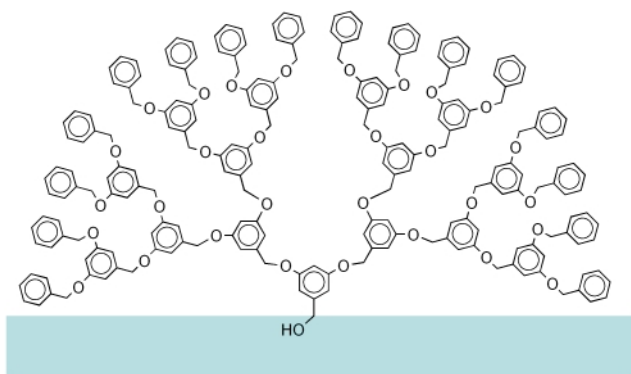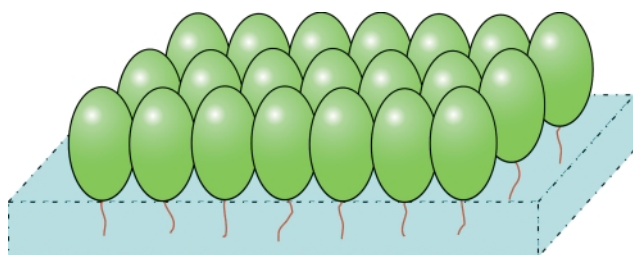
with a structure very different from that of the unfunctionalized, hydrophobic dendrons used in the previous study. In this case the dendrons formed thinner films in which the presence of polar, more hydrophilic nitrile and methyl ester groups increased the affinity of the molecule for the water surface leading to more spreading as the molecules flattened across the interface. In addition, the formation of a bilayer film was not observed as the more polar dendrons tended to move into the water sub-phase under high compression, rather than form bilayers.

A more systematic study was recently carried out by Hawker, Frank and co-workers, in which the researchers examined the Langmuir monolayer structure of a series of dendrimers by changing chemistry at the focal point.[12] Again, Fréchet-type poly(benzyl ether) monodendrons functionalized with benzyl ether groups at the periphery were used for this study. However, this time the chemistry at the focal point of the molecules was adjusted by incorporating oligo(ethylene glycol) chains of varying length. In particular, [G-3] and [G-4] dendrons with mono- through to hexakis-(ethylene glycol) chains at the focal point were used for this study (Fig. 3). Studies of the *Π–A* isotherms for the series of [G-3] dendrons led to the conclusion that the hydrophilic oligo(ethylene glycol) chains extended into the water sub-phase thereby increasing the stability of the monolayer. It was also found that the stability of the monolayers increased with the length of the oligo(ethylene glycol) chain. A similar relationship between monolayer stability and the chain length of the hydrophilic oligo(ethylene glycol) focal point was also observed for the series of [G-4] monodendrons. However, the study concluded that the stability trends for the dendrimer monolayers depended on the relative sizes between the hydrophobic dendron and the hydrophilic focal point chain, as opposed to the absolute size of the oligo(ethylene glycol) unit. The larger [G-4] dendrons produced more stable films, presumably due to the amplified dispersive interactions amongst larger neighboring hydrophobic moieties, which apparently result in a stronger attraction of the hydrophilic focal point for the water sub-phase in the larger dendrons. Previous studies on monolayers consisting of linear fatty acids have also found that monolayer stability was increased by increasing the length of the alkyl chains as a result of the increased attraction between chains.[13]

The comprehensive study by Hawker and co-workers[12] also provided additional insight into the molecular shape of monodendrons assembled into a Langmuir monolayer. The molecular area was measured as a function of molecular weight for the [G-3] through to [G-5] poly(benzyl ether) dendrons, each possessing a hexakis(ethylene glycol) chain at the focal point. A linear relationship was observed for the molecular area as a function of molecular weight [Fig. 4(A)]. However, this measured trend is much smaller than the analogous relationship
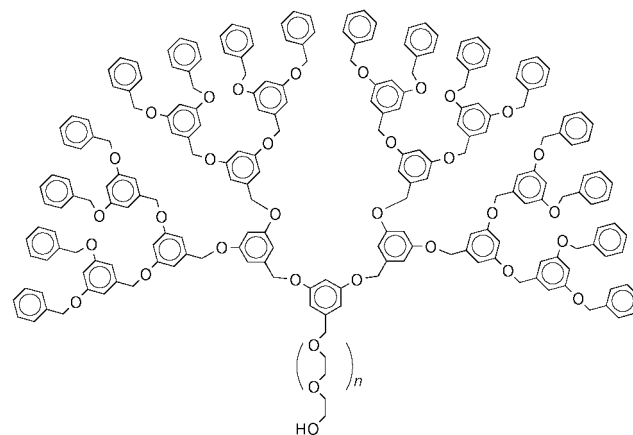

Fig. 1 Idealized structure of [G-4]-OH at the air–water interface.

Fig. 2 Poly(benzyl ether) dendrons assume a prolate shape at the air–water interface.

Fig. 3 Hydrophobic poly(benzyl ether) dendron functionalized with a hydrophilic oligo(ethylene glycol) focal point.

Poly(benzyl ether) Dendrons
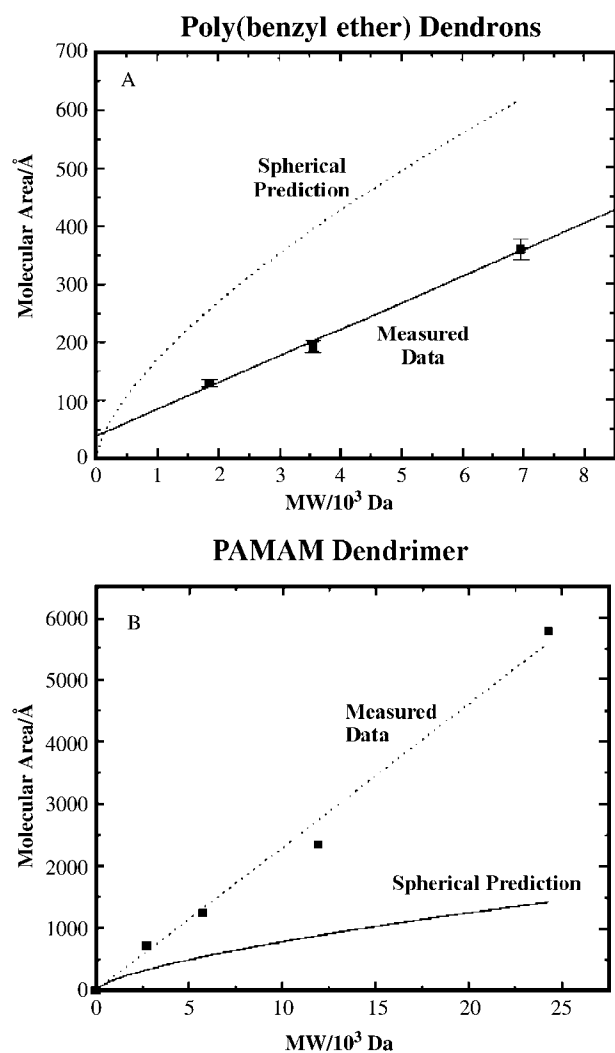

PAMAM Dendrimer

Fig. 4 A. Molecular area (in Å²) of poly(benzyl ether) dendrons as a function of molecular weight. B. Molecular area (in Å²) of PAMAM dendrimers as a function of molecular weight.

predicted for dendrons assuming a spherical shape. Hence, Hawker and co-workers concluded that the monodendrons assumed an ellipsoidal shape at the air–water interface (Fig. 2), in agreement with the conclusions drawn in the earlier studies by Saville *et al.*[8] that involved the same dendrons but with only a single hydroxy group at the focal point. Overall, these studies confirm that once a certain size is reached, poly(benzyl ether) dendrons possess and maintain an overall globular shape than can range from spherical to ovoid depending on the circumstances of their environment. As expected from simple structural considerations, it is only the largest structures or those with considerable steric requirements that can be expected to possess significant rigidity.

Percec and co-workers have used X-ray reflectivity and Π–A isotherm measurements to gain additional insight into the molecular structure of a series of functionalized poly(benzyl ether) monodendrons at the air–water interface.[14] In this study, the dendrons' periphery were functionalized with hydrophobic dodecyl chains, while the focal points were substituted with crown ether moieties or oligo(ethylene glycol) units. Their data provide additional evidence that the dendrimer Langmuir monolayers possess a structure consisting of a hydrophilic focal point at or beneath the water surface, and a high density region above the surface consisting of the dendritic block and the peripheral alkyl chains extending upwards from the surface.

The interfacial properties of PEG–poly(benzyl ether) linear-dendritic hybrid block copolymers were also recently examined.[15] Narrow polydispersity poly(ethylene glycol) chains with varying molecular weights were attached to the focal point of [G-2] poly(benzyl ether) dendrons to afford water-soluble hybrid block copolymers. These dendritic-PEG hybrids were then used to modify the surface properties of various polymeric substrates, which were then characterized by water contact angles on polymeric substrates submerged in oil. Treatment of hydrophobic poly(ethylene terephthalate) (PET) surfaces with a dilute aqueous solution of dendritic-PEG copolymer resulted in a marked decrease in the hydrophobicity of the PET surface. This is most likely due to the physisorption of the hydrophobic dendritic block to the lipophilic PET surface, while the hydrophilic PEG chain is extended into the aqueous phase. In contrast, modification of more polar regenerated cellulose resulted in a competitive adsorption between the dendritic head block and the PEG tail also leading to an overall increase in the hydrophilicity of the cellulose surface. These studies have significant implications in the context of stain-proofing fabrics and surface modification in general. They also demonstrate the promising utility of dendrons as modifiers for linear polymer chains as the relatively small dendritic block can impart significant functionality onto the end group of the linear polymer.

Tomalia and co-workers initially examined the behavior at the air–water interface of a series of poly(amido amine) (PAMAM) dendrimers that had been functionalized at the periphery with hydrophobic alkyl chains of varying length.[16] As part of this study, the researchers conducted a series of surface pressure *versus* molecular area isotherm measurements. It was found that the length of the hydrophobic end-group, when varied from hexyl to dodecyl, did not significantly influence the molecular area of the dendrimer at the collapse point in the isotherm. Tomalia and co-workers speculated that the lower generation dendrimers might adopt a conformation in which the hydrophilic dendrimer interior associates with the water surface, while the hydrophobic endgroups either extend upwards and away from the water surface or interdigitate with neighboring molecules. They also proposed a second model in which the dendrimers behaved like hydrophobic spheroids floating on the water surface, in order to account for the observation that the length of the alkyl chains at the periphery did not significantly affect the molecular areas even for the higher generation [G-4] and [G-5] dendrimers.

Shortly after Tomalia's initial account[16] Meijer and co-workers reported on a comprehensive study involving a series of poly(propyleneimine) dendrimers, [G-1] through to [G-5], that were functionalized with a wide variety of different hydrophobic end groups *via* acylation of the peripheral primary amines (Fig. 6).[17] Similar to PAMAM dendrimers, poly-(propyleneimine) dendrimers possess a relatively hydrophilic interior due to the presence of a large number of aliphatic tertiary amines. When functionalized at the periphery with either palmitoyl chains (**A**) or long *n*-alkyl chains (**C**) containing an azobenzene chromophore, the amphiphilic dendrimers form stable monolayers, as was shown in a series of Π–A isotherms. In addition, the molecular areas of the macromolecules increased linearly with molecular weight, and matched the values that could be calculated for monolayers comprised of palmitoyl chains or alkyloxy–azobenzene chain surfactants alone. Meijer and co-workers concluded that the behavior of these amphiphilic dendrimers could be explained by one model only: namely that the flexible dendrimers assume a flattened conformation in which the hydrophilic dendrimer interior maximizes its association with the water surface, while the hydrophobic end groups are forced upwards and away from the water surface (Fig. 5). Further proof was obtained upon examination of a monolayer that was formed with dendrimer **C** and then transferred to a glass substrate. UV-Vis absorption spectroscopy revealed that the absorption maximum was blue shifted, suggesting the formation of H-type aggregates.[18] This evidence further supports the conclusion by Meijer and co-

workers that the hydrophobic chains adopt a conformation involving a parallel-packed array oriented perpendicular to the water surface.

Although the molecular areas of the series of *n*-alkane-functionalized PAMAM dendrimers at the air–water interface was previously measured and reported by Tomalia and co-workers,[16] the authors did not specifically explore the fundamental relationship between area and molecular weight. Following Meijer's instructive study on poly(propyleneimine) dendrimers,[17] Hawker and co-workers re-examined Tomalia's data concerning the series of epoxy-alkane functionalized dendrimers.[12] They also showed that the molecular area increased linearly with molecular weight (Fig. 4B) in agreement with the data collected earlier for poly(benzyl ether) dendrons.[8,12] However, in contrast to the behavior of the more hydrophobic Fréchet-type dendrons, the measured molecular area for the PAMAM dendrimers was found to be much larger than expected for a spherical model. It appears that the PAMAM dendrimers also assume a flattened, or oblate, conformation when assembled into a Langmuir monolayer (Fig. 5), in a manner similar to the poly(propyleneimine) dendrimers, discovered by Meijer and co-workers.[17] Upon consideration of the chemistry of the three types of dendrimers, these models describing the molecular shapes of dendrimers at the air–water interface can easily be reconciled. Both the PAMAM and poly(propyleneimine) dendrimers possess a polar, hydrophilic interior, resulting from the presence of a large number of amides and tertiary amines. As a result, they minimize their free-energy by association of their polar interior with the water surface, leading to somewhat flattened macromolecules that occupy a larger area than a sphere of comparable volume. Similarly, the hydrophobic chain-ends of the alkyl-modified PAMAM and poly(propyleneimine) dendrimers minimize their free-energy by extending upwards, away from the water surface. Such reasoning, based on simple energy minimization concepts, also explains the initial observation of Tomalia and co-workers that the molecular area of the PAMAM dendrimers does not change upon varying the length of the hydrophobic chain ends from hexyl to dodecyl groups.

In contrast, when poly(propyleneimine) dendrimers were functionalized with bulky adamantyl groups (dendrimer **B**), a different behavior was observed altogether.[17] These dendrimers did not behave like amphiphilic molecules at the air–water interface, but rather formed multi-layers. In addition, the molecular area of these molecules demonstrated a non-linear dependence on molecular weight. As a result, Meijer and co-workers concluded that dendrimer **B** adopts a shape persistent spherical conformation due to the significant steric constraints resulting from the incorporation of bulky peripheral adamantyl groups.

A fifth generation poly(propyleneimine) dendrimer was then randomly substituted with equimolar ratios of palmitoyl chains and azobenzene groups (dendrimer **[G-5]D**).[19] Not surprisingly, this dendrimer also formed stable monolayers with a cylindrical molecular structure similar to that of monolayers formed from the dendrimer series **A** and **C** (Fig. 6). However, while the dendrimers functionalized with 100% azobenzene units (**C**)
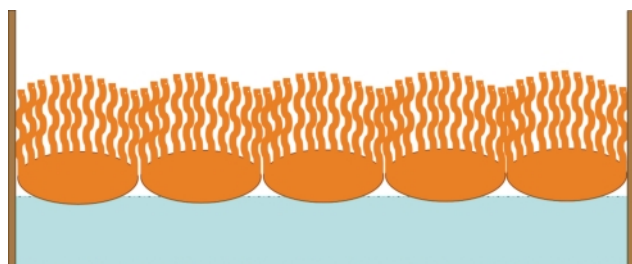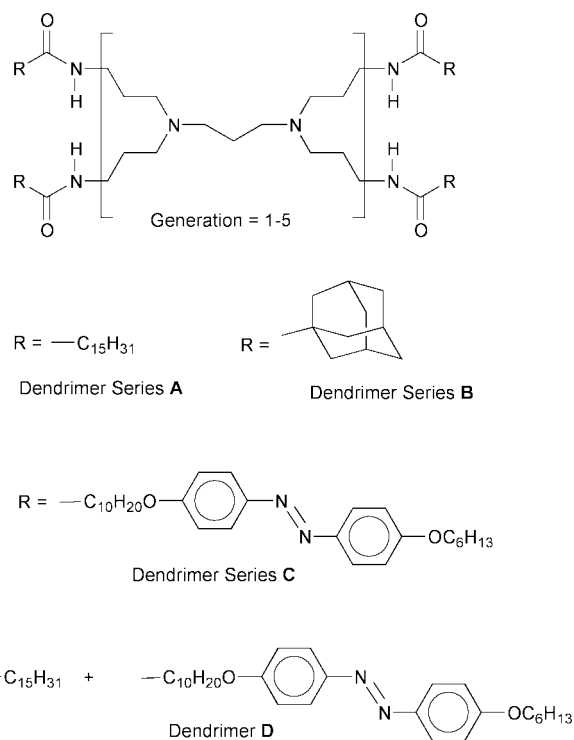

Fig. 6 Functionalized poly(propyleneimine) dendrimers.

exhibited a blue-shifted absorption maximum, indicating favorable π–π stacking among neighboring azobenzene moieties, dendrimer **[G-5]D** did not exhibit this behavior. Presumably the π-stacking of azobenzene groups is prevented by their dilution and solvation by the palmitoyl chains within the monolayer. As a result, reversible photo-switching is enabled for dendrimer **D** with the observation of changes in surface area at constant pressure when the monolayer was alternately irradiated with UV and IR.[19]

McGrath and co-workers have also developed photoresponsive Langmuir monolayers made from functionalized Fréchet-type poly(benzyl ether) dendrons.[20] In this case, the [G-1] through to [G-3] monodendrons were functionalized at their peripheries using *n*-decyl chains while their focal point consisted of an azobenzene unit. Each of the dendrons exhibited amphiphilic behavior and assembled into stable monolayers at the air–water interface. Upon UV irradiation of the [G-1] and [G-2] monolayers, a 10–20% increase in the cross-sectional molecular area A_0, was observed, which was attributed to the photo-switching of the azobenzene moiety from the *trans* to the *cis* isomer. With the monolayers prepared from the larger [G-3] dendrimer, illumination only afforded a minor change in A_0, suggesting that any change occurring within the azobenzene moiety is too small to have a significant effect on the large [G-3] dendron that surrounds it.

Dendrimers have also recently been employed as amphiphilic frameworks for the fabrication of derivatized C_{60} fullerene Langmuir monolayers. Hydrophobic C_{60} does not normally form stable monolayers at the air–water interface, and previous attempts have only led to the formation of ill-defined aggregates. However, in a collaborative effort involving the research groups of Stoddart, Diederich, Echegoyen, and Leblanc, an example of a stable Langmuir monolayer of a fullerene derivative was demonstrated.[21] This was accomplished by attaching C_{60} to hydrophilic glycodendrimer derivatives to afford fullerene–glycodendron conjugates **1** and **2** (Fig. 7). The stable Langmuir monolayers formed by C_{60}-glycodendrons **1** and **2** demonstrated reversible monolayer formation upon successive compression and expansion cycles. The researchers also succeeded in transferring the ordered monolayers onto a quartz substrate and concluded that the bulky
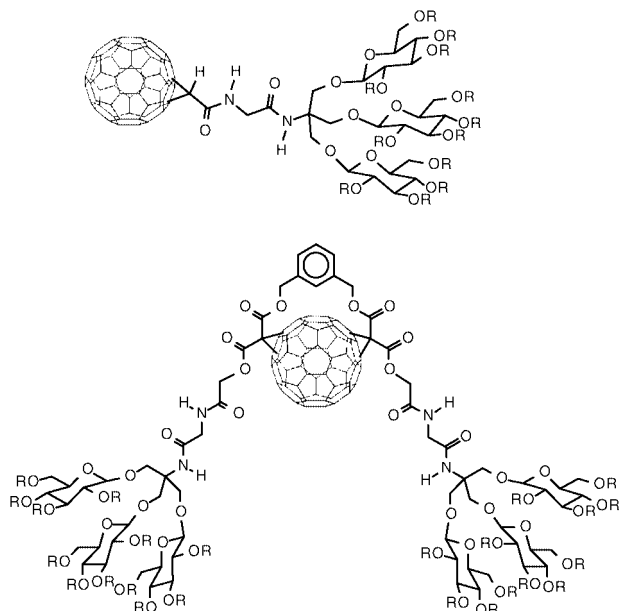

Fig. 5 Peripherally functionalized poly(propyleneimine) and PAMAM dendrimers assume an oblate shape at the air–water interface.

Fig. 7 Fullerene–glycodendron conjugates **1** (upper) and **2** (lower).

dendritic units were responsible for preventing aggregation of the fullerenes, thereby enabling the formation of stable monolayers.

Using an alternative approach, Nierengarten and co-workers functionalized the periphery of polyester dendrons with C_{60} units in order to promote stable monolayer formation at the air–water interface.[22] Upon successive compression and decompression cycles, reversible formation of Langmuir monolayers was observed. The researchers also succeeded in forming stable Langmuir–Blodgett films by transferring the fullerene functionalized dendrimer monolayers onto hydrophobic substrates.

Dendrimer self-assembled monolayers

Self-assembled monolayers (SAMs) of small organic molecules on metal and semiconductor surfaces constitute an area of widespread research.[23] Two systems that have undergone extensive study are alkanethiols on gold and alkylsiloxanes on hydroxylated silicon surfaces. A wide range of different surface chemistries has been employed in applications ranging from lithographic imaging[24–28] and chemical sensing[29] to corrosion passivation[30] and adhesion promotion or inhibition.[31]

The first example of covalent attachment of PAMAM dendrimers to a solid surface was reported by Crooks and co-workers nearly 5 years ago.[32] This was accomplished by forming amide bonds between the peripheral amino-groups of the PAMAM dendrimer and the carboxylic acid groups of a self-assembled monolayer (SAM) of mercaptoundecanoic acid on gold. This, and subsequent research by Crooks and co-workers[33,34] focusing on the development of dendrimer based films as surface-confined chemical sensor arrays has been the subject of a recent review,[29] and will therefore not be covered in detail in this article.

The chemical and physical properties of amine-terminated PAMAM dendrimers adsorbed to gold(111) surfaces have been thoroughly examined by Crooks and co-workers using a variety of analytical techniques.[35–37] When the gold substrate is immersed in a solution of PAMAM dendrimer in ethanol, a stable monolayer is formed presumably due to chemisorption of the terminal amines to the gold surface. PAMAM dendrimer monolayers prepared in this manner were found to be much more stable than monolayers of primary *n*-alkylamine on gold. The polydentate binding interactions between the amine groups of the dendrimer and the gold surface is thought to be responsible for the better stabilization of the dendritic mono-

layer. The surface-bound conformations of the dendrimers monolayers were also characterized by AFM.[36,37] Monolayer heights for the [G-8] dendrimers were measured to be only approximately 60% of their hydrodynamic diameter, again presumably due to the favorable interactions of the many peripheral amine groups with the gold surface. When the surface is subsequently treated with hexadecanethiol the heights of adsorbed dendrimer monolayers increase although their density on the surface decreases (Fig. 8). The change in height is presumably due to a distortion in the dendrimer shape from a flattened conformation to an upright, prolate shape, or possibly even an agglomeration of dendrimers as the surface amine interactions are replaced by those from a competing hexadecanethiolate monolayer.

Crooks and co-workers also functionalized the periphery of PAMAM dendrimers with varying amounts of thiol groups, and, as expected, these dendrimers formed stable monolayers on gold.[38] X-Ray photoelectron spectroscopy (XPS) suggests that fully thiolated dendrimers are bound to the gold surface utilizing only *ca.* 30% of their terminal thiol groups. Other dendrimers prepared by random functionalization of approximately 20% of their peripheral functionalities with thiol groups form monolayers in which nearly all the peripheral thiol functionalities are bound to the gold surface. This finding attests to the flexibility of the poly(amido amine) dendrimer framework, since randomly distributed peripheral thiols are able to become localized on the same side of the molecule in order to minimize their free energy through interaction with the gold surface.

Self-assembled monolayers of dendrimers on gold were also investigated by Gorman and co-workers,[39] who functionalized the focal point of poly(ether) dendrons with a thiol group. The dendrons, based on the 4,4-bis(4′-hydroxyphenyl)pentanol monomer unit previously developed by our group,[40] were protected at the periphery with hydrophobic benzyl ether groups and then functionalized at the focal point with a benzenethiol moiety (Fig. 9).[41] Self-assembled monolayers were prepared by
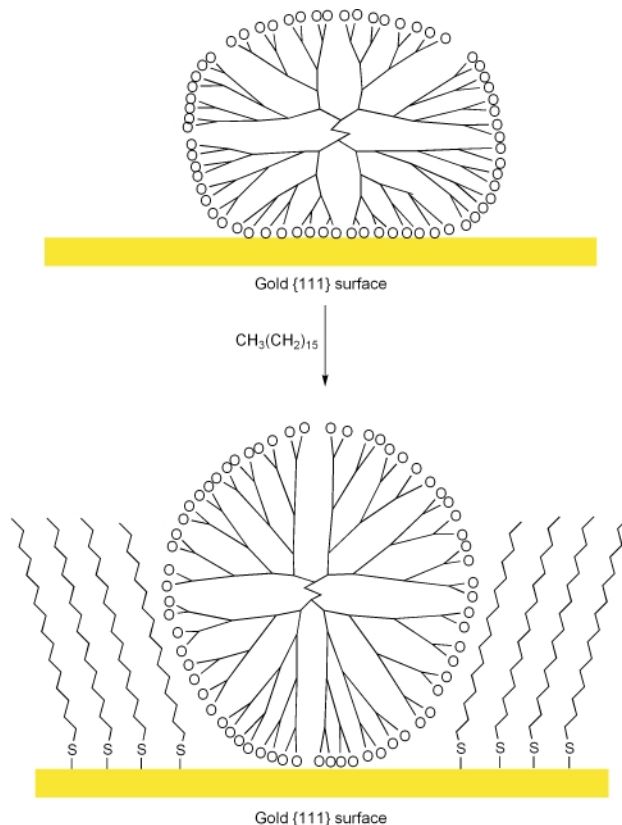

Fig. 8 PAMAM dendrimers adsorbed to gold change shape from oblate to prolate upon co-adsorption of hexadecanethiol.
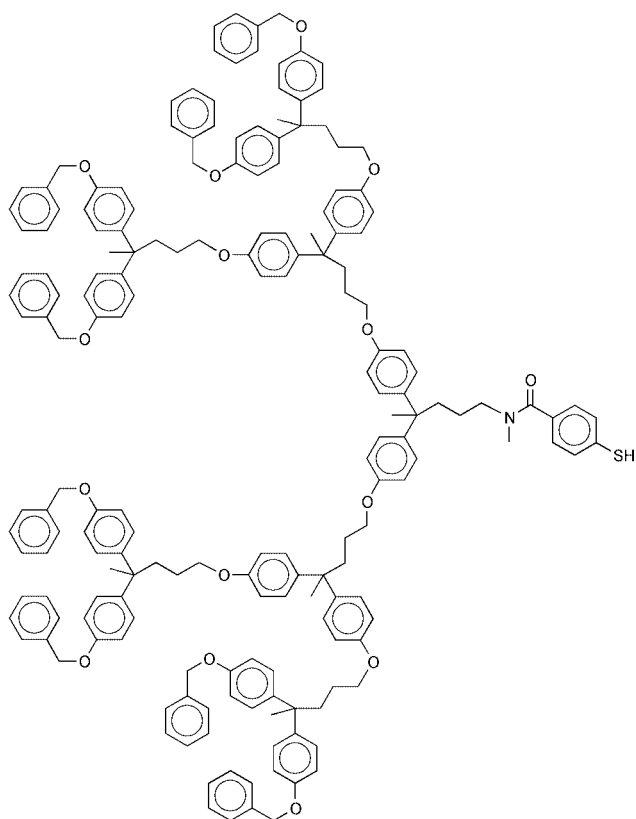
Fig. 9 Poly(ether) dendron with thiol-functionalized focal point.

immersing the polycrystalline gold substrate into a solution of the dendritic thiol. Analysis of the SAM structure by XPS verified that the dendrons were covalently bound to the gold substrate as the aryl thiolate, which is not unexpected considering the relatively flexible nature of the specific dendritic scaffold used. The extent of surface coverage for [G-1] and [G-2] dendrons analyzed by optical ellipsometry was close to 100%. Ellipsometric data for the SAMs formed from [G-3] dendrons showed thinner than expected film thicknesses, indicating either incomplete surface coverage or flattening of the macromolecules. In addition, the relative permeabilities of the dendrimer SAMs were determined using capacitance and redox probe measurements. The capacitance measurements showed that the dendrimer monolayers were more permeable to F^- and Cl^- anions than *n*-alkanethiolate SAMs of comparable thicknesses. This result is not unexpected given the disordered structure of a dendritic SAM in comparison to the ordered quasi-crystalline packing of *n*-alkanethiolate SAMs.

In our own laboratories, we have investigated the preparation of ultra-thin dendrimer films and self-assembled monolayers on silicon surfaces for their possible use as resist materials for scanning probe nanolithography.[42,43] In earlier studies, the scanning probe microscope (SPM) had been used as a direct-write-and-read tool for the lithographic patterning of passivated surfaces with several different chemistries, including self-assembled monolayers on gold[44–46] or silicon,[47–49] and thin polymer films.[50–52]

We first designed modified poly(benzyl ether) dendrimers covalently tethered to a silicon substrate that could serve as passivation resists in scanning probe lithography.[42] The concept of using dendrimers as lithographic resist materials stems from the consideration of their uniform size (several nm in diameter) and globular shape, which might serve as the ideal macromolecular template for a pixel-based approach to lithographic imaging. Specifically, an arrayed monolayer of dendrimers on a surface could act as a resist material for scanning probe lithography by protecting or passivating the surface against a wet etching process. Therefore, we prepared a series of

sterically congested, hydrophobic dendrons that could protect the surface of a silicon wafer from an aqueous fluoride etchant. Fréchet-type poly(benzyl ether) dendrons, protected at the periphery with either benzyl ether or *tert*-butyldiphenylsilyl ether groups, were functionalized at the focal point with a covalent tether, consisting of a long alkyl chain derivatized with a terminal chlorosilane coupling agent (Fig. 10). Covalently bound self-assembled monolayers were prepared under anhydrous conditions using these reactive dendrons, and the dendrimer films were characterized by standard analytical techniques.

In addition to covalently bound dendrimer SAMs we have also investigated the synthesis and preparation of ionically bound dendrimer films by an acid/base self-assembly process.[43] In this instance, the poly(benzyl ether) dendrons we designed had a tethered carboxylic acid moiety at their focal point (Fig. 10). A monolayer of dendrons could then be assembled onto an aminated silicon wafer surface prepared by pre-treatment of the clean silicon surface with (3-aminopropyl)triethoxysilane.

We then examined the ability of both types of dendrimer SAMs to serve as etch resists for scanning probe lithography. In the process of scanning probe lithography, the conductive tip of the scanning probe microscope acts as the exposure source (Fig. 11). After the tip is brought into contact with the monolayer surface, a voltage is applied between the tip and the substrate, normally a doped Si(100) wafer. When the process is performed in air, any organic monolayer within the proximity of the intense electric field created between the tip and the substrate undergoes oxidative decomposition. At even higher field strengths, the underlying silicon wafer may also be oxidized, resulting in the formation of raised oxide relief features on the substrate. This occurs as a result of the volume expansion of the silicon wafer due to the incorporation of oxygen into the silicon crystalline lattice. Finally, the latent image in the monolayer can be transferred into the underlying substrate using a selective etch process.
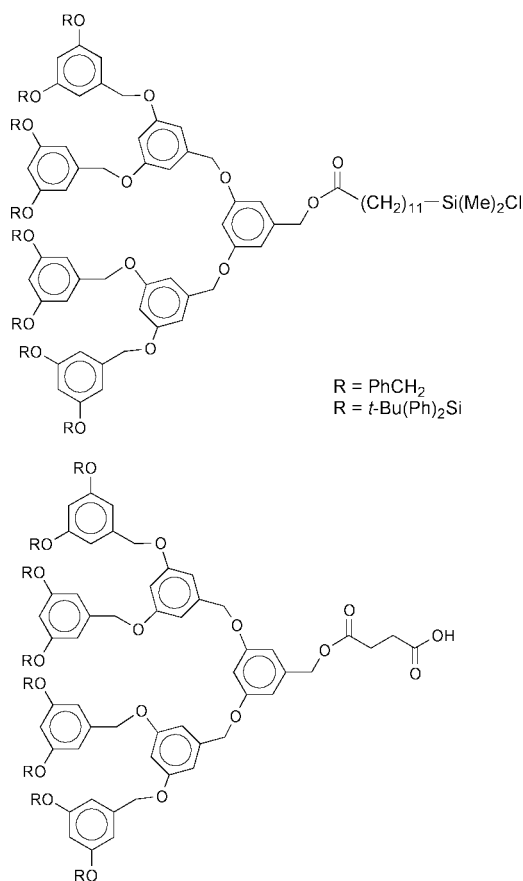

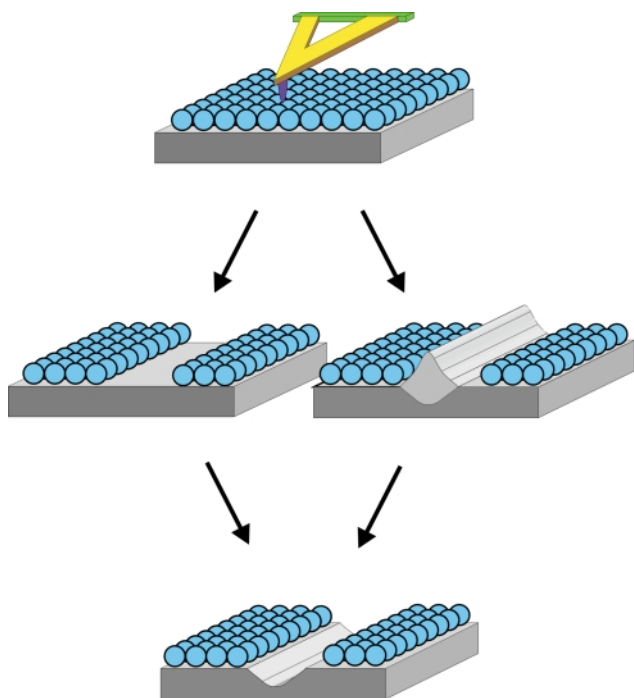**Fig. 10** Poly(benzyl ether) dendrons for covalent and ionic assembly.

Fig. 11 Schematic representation of field enhanced oxidation: dendrimer self-assembled monolayer (top); oxidative degradation of dendrimer monolayer at low field intensity (center left); oxidation of silicon substrate at high field intensity (center right); aqueous HF transfers pattern into positive tone image in silicon wafer (bottom).

Our experiments have demonstrated that dendrimer monolayers can indeed serve as effective passivation resists for scanning probe lithography. Although these experiments were performed without optimization of either the instrumental or the processing parameters, we were able to successfully create latent patterns on the surface that had feature sizes of *ca.* 35 nm. Furthermore, the dendrimer monolayers efficiently resisted the aqueous fluoride etching process, as evidenced from the lack of any line broadening or pitting in the unexposed regions of the film during the wet etching process. While the dimensions of imaged features far exceed the size of individual dendrimer molecules, it is clear that with optimization of the tip and of the processing conditions could lead to images with sizes in the range of 5–15 nm. Practical implementation would of course also require multiplexing of a very large number of tips.

Other interesting examples of applications involving dendritic SAMs include the use of biomolecule functionalized dendrimer monolayers for the development of affinity biosensors. Kim and co-workers have developed an electrochemical biosensor device that is capable of detecting the avidin–biotin interaction by monitoring the redox properties of free glucose oxidase in a glucose containing electrolyte solution using cyclic voltammetry. Self-assembled monolayers of amine-terminated PAMAM dendrimers were prepared on gold electrodes and the periphery was randomly functionalized with both ferrocenyl groups and biotin analogues.[53,54] In the absence of avidin, an electrochemical signal is generated by the enzymatic activity of glucose oxidase. As the concentration of avidin in the electrolyte solution is increased, the electrochemical signal is decreased due to steric blockage by the avidin adlayer formed on the modified electrode. Finally, the biosensor device can be regenerated by treating it with a solution of excess biotin, which results in desorption of avidin from the biotinylated dendrimer surface.

Multilayer dendrimer films

The earliest known study involving the assembly of dendrimers onto solid surfaces was based on the formation of dendrimer-

composite multilayers. Regen and Watanabe[55] first demonstrated this concept by using PAMAM dendrimers to construct multilayers using a method involving coordination chemistry to prepare the thin films. An oxidized silicon surface was treated with (3-aminopropyl)triethoxysilane, followed by adsorption of K_2PtCl_4 from solution to the aminated surface. Next, PAMAM dendrimers, terminated on the periphery with primary amines, were adsorbed to the Pt^{2+} activated surface. This process could be repeated many times over to build up a multilayer of dendrimers with thicknesses of *ca.* 100 nm.

Other examples of PAMAM dendrimer multilayer formation include the formation of dendrimer-polyanhydride composite films on a variety of substrates. Bergbreiter and co-workers developed a multistep process that involves the sequential deposition of orthogonally reactive functional polymers to prepare the composite films that constitute the basis for a variety of ultrathin membrane materials.[56] An amino-functionalized surface is first prepared by treating glass or oxidized silicon with (3-aminopropyl)triethoxysilane. The aminated surface is then treated with a solution of poly[maleic anhydride-*co*-(methyl vinyl ether)] (Gantrez™) that reacts with the surface amines through amide bond formation with the maleic anhydride monomer units. Next, treatment of this modified surface with a solution of amine terminated PAMAM dendrimer results in the grafting of dendrimer molecules onto the surface *via* reaction of the amines with any previously unreacted anhydrides remaining in the first layer of Gantrez. Further sequential deposition of Gantrez and PAMAM dendrimer results in an alternating layer-by-layer build-up of the two polymers. Deposition of the grafted polymers was verified by optical ellipsometry, which demonstrated a linear increase of thickness with each stage of deposition.

These Gantrez–PAMAM composite thin films were shown to function as pH-responsive permeable membranes, as confirmed by a variety of electrochemical experiments.[57,58] The internal chemical composition of the composite films is thought to be homogeneous, and the incorporation of poly(amine) segments and poly(carboxylic acid) segments results in an amphoteric copolymer film. Composite films were coated onto a gold electrode, and cyclic voltammetry was used to monitor the permeability of the films towards cations and anions at different pH. In acidic solution (pH = 3.0), the dendrimer–Gantrez composite films were permeable to anions, such as $Fe(CN)_6^{3-}$, and impermeable to cations, such as $Ru(NH_3)_6^{3+}$. Conversely, in an alkaline solution (pH = 11.0) the films are impermeable to anions and permeable to cations. Furthermore, at neutral pH, the composite films allowed both cations and anions to diffuse through to the electrode. Finally, thermally annealing the dendrimer–Gantrez composite films at 120 °C, for 2 h led to further crosslinking, and resulted in the formation of a new film that was highly impermeable to ionic species over the entire pH range studied.[58] This simple approach to highly-crosslinked, polyfunctional films is quite versatile, and one could easily conceive of variations on this theme that could easily be adapted to other applications. Furthermore, the chemically robust nature and impermeability of the annealed films demonstrates their potential for use as coating materials for the prevention of corrosion.

A recent report from Crooks and co-workers details the use of this sequential deposition technique in conjunction with microcontact printing[24,25] to fabricate patterned PAMAM–Gantrez composite multilayer films.[59] This was accomplished by initial formation of a patterned monolayer of *n*-hexadecanethiol on a gold-coated silicon wafer using a prefabricated poly(dimethylsiloxane) (PDMS) stamp. Next, the substrate was treated with a solution of amine-terminated [G-4] PAMAM dendrimer. A monolayer of this poly(amine) dendrimer was preferentially adsorbed only onto the regions of the gold surface that are not passivated with the *n*-hexadecanethiolate monolayer. Finally, the substrate is treated with a solution

of Gantrez, resulting in the selective deposition of the anhydride containing copolymer only onto the patterned dendrimer regions. This sequential layer-by-layer deposition is repeated in a fashion analogous to the method previously described[56] to build up patterned PAMAM–Gantrez composite films. This method provides a convenient approach to patterned ultrathin organic films for applications in which durable, polyfunctional films are required, such as the patterning of biological molecules or cells.

An alternative method for dendrimer multilayer formation was later developed by Tsukruk and coworkers,[60,61] which hinges on the technique of electrostatic self-assembly developed by Decher.[62] The motivation for this work was said to be related to the development of modified tribological surfaces for boundary lubrication, however no specific applications were reported. Although electrostatic self-assembly is a simple and versatile method for the deposition of polymer multilayers, the resulting films are not as chemically robust as those developed by Bergbreiter and co-workers due to the absence of any covalent bonds among the adjoining layers. Once again, PAMAM dendrimers functionalized with either primary amines or carboxylic acids at their periphery were used for this study. Deposition of an initial layer of amine-terminated dendrimers was performed at pH < 3 to promote adsorption of the positively charged ammonium salts to the anionic silicon surface. A layer of carboxylic acid terminated PAMAM dendrimer was then deposited at pH > 6, a value that favors assembly of the anionic carboxylate salts onto the positively charged ammonium salt layer. Alternating sequential deposition of oppositely charged dendrimers led to a multilayer dendrimer–salt composite film. Thickness measurements of the initial dendrimer layer and subsequent multilayers were performed using atomic force microscopy (AFM). The data showed that the thicknesses of the initial dendrimer monolayers were much smaller than the previously measured hydrodynamic diameters of the PAMAM dendrimers.[2] Furthermore, the thickness of the composite multilayers was also much less than expected for superposed layers of spherical macromolecules. This indicates again that the charged PAMAM dendrimers assume a highly compressed or flattened conformation when arranged on the surface. However, it is also likely that incomplete surface coverage contributes to the lower than expected thickness measurements that were obtained.

Tomalia and co-workers have also used the electrostatic deposition technique to form gold-dendrimer nanocomposite films.[63,64] A layer of cationic poly[dimethyl(diallyl)ammonium chloride] was first deposited onto a negatively charged substrate, followed by the deposition of anionic poly(sodium styrene-4-sulfonate). The bilayer modified substrate was then treated with a solution of positively charged PAMAM dendrimer–gold nanoparticle nanocomposite, which uniformly assembles onto the surface. The authors contend that such materials may be useful for catalysis or optoelectronic applications in which ultrathin nanocomposite films are required, however this concept has yet to be realized.

Dendrimers have also recently been employed as polyfunctional templates for the surface immobilization of biological macromolecules. Anzai and co-workers have recently demonstrated that alternating sequential deposition could be utilized to prepare dendrimer–protein composite multilayer films.[65] This was accomplished by first depositing a layer of fluorescein isothiocyanate-labeled avidin (FITC-avidin) onto a hydrophobic gold or quartz surface. Next, the substrate was treated with a solution of biotin-labeled PAMAM dendrimer, which then assembled onto the surface via the well-known avidin–biotin complexation. The sequential deposition process could be repeated to build up dendrimer–avidin composite multilayer films. Although these materials have no distinctive utility by themselves, their preparation constitutes a convenient generalized approach toward functional polymer–biomolecule thin

film materials that could potentially incorporate other useful functionalities.

Another example of dendrimer–protein composite multilayers was recently reported by Kim and Yoon.[66] This involves the deposition of an initial layer of periodate treated glucose oxidase (GOx) onto an aminated gold surface via the formation of Schiff bases between the aldehyde groups of oxidized GOx with the primary amines on the surface. In the next step, the substrate was treated with a solution of amine-terminated PAMAM dendrimer, which then reacts with any remaining GOx aldehydes also via imine formation to covalently bind the dendrimer molecules to the surface. Reductive amination of the Schiff bases was then employed to ensure against dendrimer desorption. Cyclic voltammetry was then used to probe the extent of active enzyme immobilized within the dendrimer–GOx multilayers. It was found that the electrocatalytic response of the electrode was significantly enhanced with respect to multilayer growth, suggesting that sensitivity is tunable by controlling the thickness of the multilayer films. Finally, the film stability with time was investigated, and it was found that over 80% of the initial electrode response was maintained after 20 days.

Solvent cast dendrimer films

There has been considerable interest in the properties and potential applications of dendrimer films prepared by drop- and spin-casting from solution onto solid substrates. A number of groups have focused on investigating the physical properties of dendrimers on solid surfaces using AFM. Sheiko and co-workers first examined the properties of hydrophobic carbosilane dendrimers deposited onto mica and pyrolytic graphite surfaces.[67] The wetting behavior was investigated by spin-casting dilute solutions of the dendrimer onto chemically different surfaces. AFM was then used to analyze the microscopic contact angles of the sub-micron sized droplets of dendrimers formed on the surface. It was found that the hydrophobic dendrimers did not interact specifically with the substrate and the molecules were observed to aggregate into large clusters that behaved like fluid droplets. When the periphery of the carbosilane dendrimers was functionalized with hydroxy groups, the resulting dendrimer possessed an amphiphilic structure with a hydrophobic interior and a hydrophilic periphery, hence leading to a reorganization of the films due to a preferential adsorption of the peripheral hydroxy groups onto the polar mica surface.[68]

Mülhaupt and co-workers used AFM to investigate the film formation of carbosilane dendrimers functionalized at the periphery with mesogenic cholesteryl groups.[69] Films of the mesogen-substituted dendrimers were prepared by drop-casting solutions of varying concentrations onto mica surfaces, followed by evaporation of the solvent. Analysis using AFM showed the formation of both monolayers and multilayers, depending on the initial concentration of the casting solution. Annealing of the lower generation dendrimers led to a reorientation of the molecules on the surface, presumably as a result of the reorganization of the mesogenic peripheral units.

De Schryver and co-workers have also used AFM to probe the physical properties of poly(phenylene) dendrimers.[70] By spin-casting from very dilute solution, poly(phenylene) dendrimers were deposited onto mica surfaces as well separated, individually resolved molecules. Using non-contact mode AFM, the researchers were able to obtain measurements of the dendrimer heights, which were in agreement with the sizes calculated using molecular dynamics simulations. In addition, the adhesion and stiffness properties of individual dendrimer molecules were measured using a pulsed force mode AFM. In comparison with the mica substrate, poly(phenylene) dendrimers and their aggregates exhibited low adhesion and high stiffness, which is not unexpected given the chemical composi-

tion of the hydrophobic, rigid molecular architecture of the poly(phenylene) dendrimer.

Klein and co-workers have used a surface force balance to measure surface interactions and friction in dendrimers adsorbed between mica surfaces. Their first report concerned low surface energy hydrophobic poly(propyleneimine) dendrimers that were functionalized at the periphery with *N*-Boc-phenyl-alanine.[71] Both shear and frictional forces were measured between two sliding surfaces treated with an adsorbed ultra-thin film of dendrimers. The compressibility of the dendrimer spheres was found to decrease as the molecules were progressively compressed. Furthermore, the researchers concluded that the behavior of these hydrophobic dendrimers was intermediate between that of a solid and a flexible polymer, as they did not exhibit stick–slip sliding. In the following study, Klein and co-workers examined the behavior of a high surface energy, or polar dendrimers under the same conditions.[71] For this comparative study, carbosilane dendrimers terminated with peripheral alcohol groups were used for the surface force balance measurements. In this case, the hydrophilic carbosilane dendrimer behaved more like a rigid sphere. Upon shearing, the molecules underwent relaxation of stored stress. In addition, these dendrimers exhibit stick–slip behavior similar to frozen monolayers of confined liquids.

We have recently investigated the interfacial properties of alkyl chain-modified dendrimers as surface primers for bonding polyolefin substrates. In this study, the end groups of poly-(propyleneimine) dendrimers were functionalized with long-alkyl chain aldehydes *via* imine formation followed by reductive amination.[72] A thin film of the alkyl-modified dendrimer was then used as a primer layer for the adhesive joining of a variety of different polyolefin surfaces. Initial studies made use of cyanoacrylate adhesives that are normally incapable of bonding polyolefin surfaces. Block-shear testing of the adhesive strength revealed that in most cases failure could be attributed to substrate rather than adhesive failure, thereby demonstrating that the dendrimer films functioned as highly effective primers for ethyl cyanoacrylate bonding of poly(ethyl-ene) and poly(propylene) substrates.

Recently, there have been a growing number of reports concerning the use of dendrimer-based thin films in a variety of microelectronics-related applications. Dendrimers in the condensed phase display many physical properties that differ significantly from their linear counterparts. We have been interested in exploring some of the unique properties of dendrimers for the development of new materials for applications in microelectronics. While our group has long been active in the areas of photolithography[73] and resist materials,[74] we have recently initiated a study of the various parameters that control resist material performance as a function of polymer architecture. The current state of the art resist materials incorporating chemical amplification[74] are all based on linear polymers as the matrix resin. The use of dendrimers as resist materials for 'next-generation lithography' may prove advantageous when the desired feature sizes approach macromolecular dimensions. In contrast to linear polymers, dendritic polymers are relatively free of chain entanglement. This may have important implications in designing resist materials for ultra-high resolution imaging, where parameters such as line-edge roughness, acid diffusion, and dissolution rates begin to have a serious impact on resist performance.

We have recently reported the first dendrimer-based chemically amplified resist.[75,76] Fréchet-type poly(benzyl ether) dendrimers with Boc (Fig. 12) or *tert*-butyl ester groups at their periphery were synthesized *via* a modification of the convergent route. Resist films were prepared by spin-casting a dendrimer-solution containing a catalytic amount of photo-acid generator (typically a triaryl sulfonium salt) onto a silicon wafer. These dendrimer films, normally several hundred nm thick, exhibited high sensitivity to both deep ultra-violet (DUV) and electron
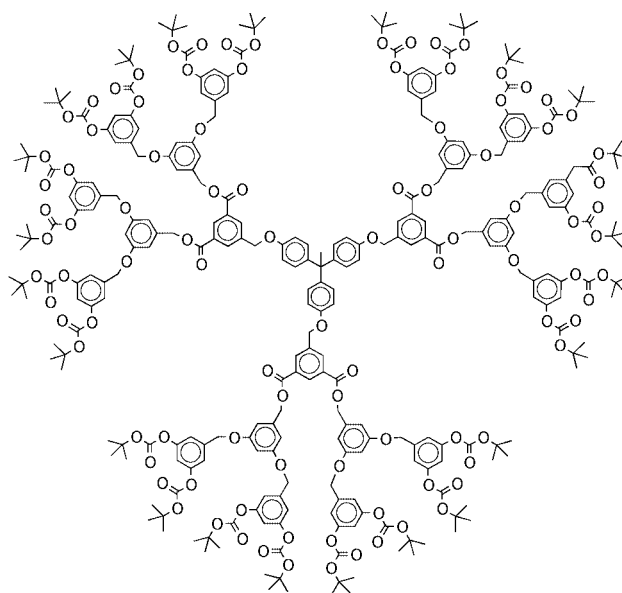
Fig. 12 Boc terminated [G-3] dendrimer.

beam radiation (E-beam). Since we are primarily interested in the performance of dendritic polymers for imaging feature sizes below 100 nm and there is a serious lack of imaging tools capable of such performance, we focused on electron-beam lithography and explored the performance of our dendrimer films as E-beam resists. As expected, these chemically amplified dendrimer resists displayed a high sensitivity to E-beam radiation while allowing image development in either the positive or the negative tone (Fig. 13). The scanning electron micrograph of Fig. 14 shows an example of a line pattern fabricated in a film cast from Boc terminated poly(benzyl ether) dendrimer. Even without optimization of the lithographic
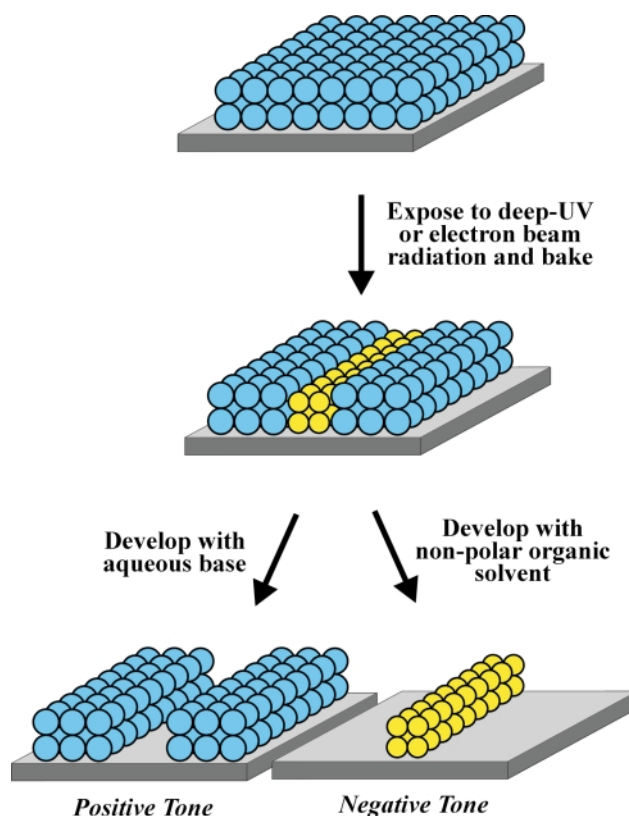
Fig. 13 UV or E-Beam exposure, followed by a bake step removes Boc protecting groups creating a latent, or chemical, image in the film. The dual tone resist can be developed with either aqueous base to afford positive tone images, or with anisole, to produce negative tone images.
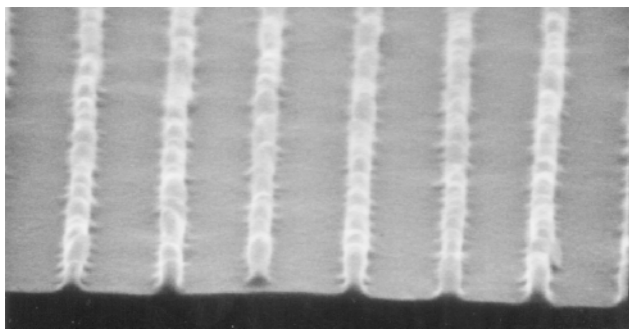
Fig. 14 SEM of negative tone images generated in Boc dendrimer resist. Linewidths: 50 nm; line heights: 100 nm; dose: 15 μC cm^{-2}.

processing parameters, feature sizes below 50 nm could consistently be printed. We are currently involved in the development of several new designs for dendritic polymers that may contribute to vastly enhanced lithographic resist performance. However there are undoubtedly serious limitations in the actual utility of dendrimers as commercial resist materials due to the obvious synthetic difficulty and expense of a multistep convergent dendrimer synthesis. As a result, the performance of a variety of related dendritic structures including hyperbranched polymers as chemically amplified resist materials is also under investigation.[77]

Functional dendritic polymers have also recently been used as templating agents to prepare nanoporous thin films for use as dielectric insulators. Therefore, Hedrick and co-workers have prepared highly branched copolymers by the ring opening polymerization of ε-caprolactone from dendritic initiators.[78,79] Composite films were made by spin-casting a solution of the dendritic polymer and a poly(silsesquioxane) precursor onto a silicon wafer. When the film is thermally annealed at 250 °C, a crosslinked organic–inorganic nanocomposite material is formed. Upon further heating to over 400 °C, the dendritic organic component of the film thermally decomposes into volatile byproducts, leaving behind a closed-cell nanoporous silicate foam. Since a significant proportion of the volume of this new material is occupied by air with a relative permittivity $k \cong 1.0$, an overall bulk relative permittivity below 2.0 is observed, making these materials promising candidates for high-end microelectronic applications where low-k dielectric materials are urgently needed. The commercial exploitation of this approach is now well under way.

Other recent applications that make use of dendrimer-based thin film materials include sensor devices that detect volatile organic compounds (VOCs). One such sensor device, developed by Miller and co-workers, detects VOCs on the basis of electrical conductivity changes in a dendrimer-based thin film.[80,81] The periphery of poly(amide) dendrimers was functionalized with oligothiophene derivatives, which function as the charge carriers. Thin films were prepared by first casting the neutral dendrimers from solution, followed by an oxidative doping with iodine vapor. The doped films were stable in air and exhibited true electronic conductivity ($\sigma = 10^{-3}$ S cm^{-1}). Upon exposure to organic vapors, the conductivity of the films was increased by as much as three orders of magnitude. Importantly, the conductivity response was fully reversible, and the magnitude of the response varied uniquely with the identity of the vapor.

The surface chemistry and interfacial properties of related classes of dendritic macromolecules,[2] such as hyperbranched polymers,[82–84] dendritic-linear hybrid block copolymers,[85] and dendronized or dendron-jacketed linear polymers,[86,87] have also recently become an area of growing interest, although they are beyond the scope of this brief review focusing specifically on dendrimers. Finally, the design and application of dendrimers and dendrimer-based films for opto-electronic applications such as light harvesting and light emitting diodes have been the focus

of a recent review,[88] and therefore will not be discussed in this article.

Conclusions and outlook

The past several years have seen a considerable growth in the use of dendrimers at surfaces and interfaces. This results from the realization that the unique dendritic architecture of dendrimers can translate into unusual chemical and physical properties. While the demanding methods used for the preparation of dendrimers currently negate their use as commodity materials, it is clear that they are well suited for practical application at surfaces and interfaces where small amounts of materials only are needed. Early work with self-assembled dendrimer monolayers in applications such as resists for scanning probe lithography, affinity biosensors, and chemosensor devices have already demonstrated some of the capabilities of dendrimers. Such findings, coupled to others related to the rheological properties of dendrimers,[89] their ability to encapsulate[90] or harvest and concentrate energy[88] will no doubt continue to fuel interest in numerous 'designer' dendrimers for applications in nanotechnology. Another area of growth for dendrimers will involve their use at biological interfaces as their shape and surface functionality make them ideally suited for accessing, recognizing, coating or penetrating cell membranes. The outlook for continued activity in this field is strong, and many new discoveries and developments in chemistry, materials science, and biology involving dendrimers at surfaces and interfaces can be anticipated.

Acknowledgements

Notes and references

1 D. A. Tomalia, A. M. Naylor and W. A. Goddard III, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 138.
2 J. M. J. Fréchet, *Science*, 1994, **263**, 1710.
3 G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH, Weinheim, Germany, 1996.
4 D. A. Tomalia, H. Baker, J. Dewald, J. M. Hall, G. Kallos, R. Martin and J. Ryder, *Polym. J.*, 1985, **17**, 117; G. R. Newkome, Z. Yao, G. R. Baker and V. K. Gupta, *J. Org. Chem.*, 1985, **50**, 2003.
5 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; S. Grayson and J. M. J. Fréchet, *Chem. Rev.*, 2001, in the press.
6 C. J. Hawker, R. Lee and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4583.
7 A. W. Bosman, H. M. Janssen and E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.
8 P. M. Saville, J. W. White, C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Phys. Chem.*, 1993, **97**, 293; P. M. Saville, P. A. Reynolds, J. W. White, C. J. Hawker, J. M. J. Fréchet, K. L. Wooley, J. Penfold and J. R. P. Webster, *J. Phys. Chem.*, 1995, **99**, 8283.
9 V. V. Tsukruk, *Adv. Mater.*, 1998, **10**, 253.
10 C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1993, **115**, 4375.
11 G. F. Kirton, A. S. Brown, C. J. Hawker, P. A. Reynolds and J. W. White, *Physica B*, 1998, **248**, 184.
12 J. P. Kampf, C. W. Frank, E. E. Malmström and C. J. Hawker, *Langmuir*, 1999, **15**, 227.
13 M. C. Petty, *Langmuir-Blodgett Films: An Introduction*, Cambridge University Press, Cambridge, 1996.
14 W. J. Pao, M. R. Stetzer, P. A. Heiney, W. D. Cho and V. J. Percec, *Phys. Chem. B*, 2001, **105**, 2170.
15 J. M. J. Fréchet, I. Gitsov, T. Monteil, S. Rochat, J. F. Sassi, C. Vergelati and D. Yu, *Chem. Mater.*, 1999, **11**, 1267.
16 Y. Sayed-Sweet, D. M. Hedstrand, R. Spinder and D. A. Tomalia, *J. Mater. Chem.*, 1997, **7**, 1199.

17 A. P. H. J. Schenning, C. Elissen-Roman, J. W. Weener, M. W. P. L. Baars, S. J. van der Gaast and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 8199.

18 M. Shimorura and T. Kunitake, *Chem. Lett.*, 1981, 1001.

19 J. W. Weener and E. W. Meijer, *Adv. Mater.*, 2000, **12**, 741.

20 A. Sidorenko, C. Houphouet-Boigny, O. Villavicencio, M. Hashemzadeh, D. V. McGrath and V. V. Tsukruk, *Langmuir*, 2000, **16**, 10 569.

21 F. Cardullo, F. Diederich, L. Echegoyen, T. Habicher, N. Jayaraman, R. M. Leblanc, J. F. Stoddart and S. Wang, *Langmuir*, 1998, **14**, 1955.

22 D. Felder, J. L. Gallani, D. Guillon, B. Heinrich, J. F. Nicoud and J. F. Nierengarten, *Angew. Chem., Int. Ed.*, 2000, **39**, 201.

23 A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.

24 Y. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, *Chem. Rev.*, 1999, **99**, 1823.

25 Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 1998, **37**, 550.

26 J. K. Schoer and R. M. Crooks, *Langmuir*, 1997, **13**, 2323.

27 M. Husemann, M. Morrison, D. Benoit, K. J. Frommer, C. M. Mate, W. D. Hinsberg, J. L. Hedrick and C. J. Hawker, *J. Am. Chem. Soc.*, 2000, **122**, 1844.

28 R. Maoz, S. R. Cohen and J. Sagiv, *Adv. Mater.*, 1999, **11**, 55.

29 R. M. Crooks and A. J. Ricco, *Acc. Chem. Res.*, 1998, **31**, 219.

30 R. M. Crooks and F. P. Zamborini, *Langmuir*, 1997, **13**, 122.

31 R. G. Chapman, E. Ostuni, S. Takayama, R. E. Holmlin, L. Yan and G. M. Whitesides, *J. Am. Chem. Soc.*, 2000, **122**, 8303.

32 M. Wells and R. M. Crooks, *J. Am. Chem. Soc.*, 1996, **118**, 3988.

33 M. Q. Zhao, H. Tokuhisa and R. M. Crooks, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2596.

34 H. Tokuhisa and R. M. Crooks, *Langmuir*, 1997, **13**, 5608.

35 H. Tokuhisa, M. Zhao, L. A. Baker, V. T. Phan, D. L. Dermody, M. E. Garcia, R. F. Peez, R. M. Crooks and T. M. Mayer, *J. Am. Chem. Soc.*, 1998, **120**, 4492.

36 A. Hierlemann, J. K. Campbell, L. A. Baker, R. M. Crooks and A. J. Ricco, *J. Am. Chem. Soc.*, 1998, **120**, 5323.

37 W. M. Lackowski, J. K. Campbell, G. Edwards, V. Chechik and R. M Crooks, *Langmuir*, 1999, **15**, 7632.

38 V. Chechik and R. M. Crooks, *Langmuir*, 1999, **15**, 6364.

39 C. B. Gorman, R. L. Miller, K. Y. Chen, A. R. Bishop, R. T. Haasch and R. G. Nuzzo, *Langmuir*, 1998, **14**, 3312.

40 K. L. Wooley, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4252.

41 K. Y. Chen and C. B. Gorman, *J. Org. Chem.*, 1996, **61**, 9229.

42 D. C. Tully, K. Wilder, J. M. J. Fréchet, A. R. Trimble and C. F. Quate, *Adv. Mater.*, 1999, **11**, 314.

43 D. C. Tully, A. R. Trimble, J. M. J. Fréchet, K. Wilder and C. F. Quate, *Chem. Mater.*, 1999, **11**, 2892.

44 L. Stockman, G. Neuttiens, C. Van Haesendonck and Y. Bruynseraede, *Appl. Phys. Lett.*, 1993, **62**, 2935.

45 M. J. Lercel, G. F. Redinbo, H. G. Craighead, C. W. Sheen and D. L. Allara, *Appl. Phys. Lett.*, 1994, **65**, 974.

46 J. K. Schoer and R. M. Crooks, *Langmuir*, 1997, **13**, 2323.

47 H. C. Day, D. R. Allee, R. George and V. A. Burrows, *Appl. Phys. Lett.*, 1993, **62**, 1629.

48 C. R. K. Marrian, F. K. Perkins, S. L. Brandow, T. S. Koloski, E. A. Dobisz and J. M. Calvert, *Appl. Phys. Lett.*, 1994, **64**, 390.

49 H. Sugimura and N. Nakagiri, *J. Am. Chem. Soc.*, 1997, **119**, 9226.

50 T. R. Albrecht, M. M. Dovek, C. A. Lang, P. Grütter, C. F. Quate, S. W. J. Kuan, C. W. Frank and R. F. W. Pease, *J. Appl. Phys.*, 1988, **64**, 1178.

51 K. Wilder, H. T. Soh, A. Atalar and C. F. Quate, *J. Vac. Sci. Technol., B*, 1997, **15**, 1811.

52 K. Wilder, C. F. Quate, B. Singh and D. F. Kyser, *J. Vac. Sci. Technol., B*, 1998, **16**, 3864.

53 H. C. Yoon, M. Y. Hong and H. S. Kim, *Anal. Biochem.*, 2000, **282**, 121.

54 H. C. Yoon, M. Y. Hong and H. S. Kim, *Langmuir*, 2001, **17**, 1234.

55 S. L. Regen and S. Watanabe, *J. Am. Chem. Soc.*, 1994, **116**, 8855.

56 Y. Liu, M. L. Bruening, D. E. Bergbreiter and R. M. Crooks, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2114.

57 Y. Liu, M. Zhao, D. E. Bergbreiter and R. M. Crooks, *J. Am. Chem. Soc.*, 1997, **119**, 8720.

58 M. Zhao, Y. Liu, R. M. Crooks and D. E. Bergbreiter, *J. Am. Chem. Soc.*, 1999, **121**, 923.

59 P. Ghosh, W. M. Lackowski and R. M. Crooks, *Macromolecules*, 2001, **34**, 2131.

60 V. V. Tsukruk, F. Rinderspacher and V. N. Bliznyuk, *Langmuir*, 1997, **13**, 2171.

61 V. N. Blitznyuk, F. Rinderspacher and V. V. Tsukruk, *Polymer*, 1998, **39**, 5249.

62 G. Decher, *Science*, 1997, **277**, 1232.

63 J. A. He, R. Valluzzi, K. Yang, T. Dolukhanyan, C. Sung, J. Kumar, S. K. Tripathy, L. Samuelson, L. Balogh and D. A. Tomalia, *Chem. Mater.*, 1999, **11**, 3268.

64 The subject of dendrimer-encapsulated nanoparticles has been recently reviewed: R. M. Crooks, B. I. Lemon, L. Sun, L. K. Yeung and M. Zhao, *Top. Curr. Chem.*, 2001, **212**, 81; R. M. Crooks, M. Zhao, L. Sun, V. Chechik and L. K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181.

65 J. Anzai, Y. Kobayashi, N. Nakamura, M. Nishimura and T. Hoshi, *Langmuir*, 1999, **15**, 221.

66 H. C. Yoon and H. S. Kim, *Anal. Chem.*, 2000, **72**, 922.

67 S. S. Sheiko, G. Eckert, G. Ignateva, A. M. Muzafarov, J. Pickermann, H. J. Rader and M. Moller, *Macromol. Rapid Commun.*, 1996, **17**, 283.

68 S. S. Sheiko, A. M. Muzafarov, R. G. Winkler, E. V. Getmanova, G. Eckert and P. Reineker, *Langmuir*, 1997, **13**, 4172.

69 M. C. Coen, K. Lorenz, J. Kressler, H. Frey and R. Mülhaupt, *Macromolecules*, 1996, **29**, 8069.

70 H. Zhang, P. C. M. Grim, P. Foubert, T. Vosch, P. Vanoppen, U. M. Wiesler, A. J. Berresheim, K. Müllen and F. C. De Schryver, *Langmuir*, 2000, **16**, 9009; H. Zhang, P. C. M. Grim, T. Vosch, U. M. Wiesler, A. J. Berresheim, K. Müllen and F. C. De Schryver, *Langmuir*, 2000, **16**, 9294.

71 X. Zhang, M. Wilhelm, J. Klein, M. Pfaadt and E. W. Meijer, *Langmuir*, 2000, **16**, 3884; X. Zhang, J. Klein, S. S. Sheiko and A. M. Musafarov, *Langmuir*, 2000, **16**, 3893.

72 M. Liu and J. M. J. Fréchet, *Polym. Bull.*, 1999, **43**, 379; US Patent Pending WO 99.15580 PCT/US98/19783.

73 For recent reviews on lithography and photoresists, see for example: G. M. Wallraff and W. D. Hinsberg, *Chem. Rev.*, 1999, **99**, 1801; E. Reichmanis, O. Nalamasu and F. M. Houlihan, *Acc. Chem. Res.*, 1999, **23**, 659.

74 S. A. MacDonald, C. G. Willson and J. M. J. Fréchet, *Acc. Chem. Res.*, 1994, **27**, 151.

75 D. C. Tully, A. R. Trimble and J. M. J. Fréchet, *Adv. Mater.*, 2000, **12**, 1118.

76 D. C. Tully, A. R. Trimble and J. M. J. Fréchet, *Poly. Prep.*, 2000, **41**, 142.

77 A. R. Trimble, D. C. Tully, J. M. J. Fréchet, D. R. Medeiros and M. Angelopolous, *Poly. Prep.*, 2000, **41**, 325.

78 J. L. Hedrick, R. D. Miller, C. J. Hawker, K. R. Carter, W. Volksen, D. Y. Yoon and M. Trollsås, *Adv. Mater.*, 1998, **10**, 1049.

79 C. V. Nguyen, K. R. Carter, C. J. Hawker, J. L. Hedrick, R. L. Jaffe, R. D. Miller, J. F. Remenar, H. W. Rhee, P. M. Rice, M. F. Toney, M. Trollsås and D. Y. Yoon, *Chem. Mater.*, 1999, **11**, 3080.

80 L. L. Miller, Y. Kunugi, A. Canavesi, S. Rigaut, C. N. Moorefield and G. R. Newkome, *Chem. Mater.*, 1998, **10**, 1751.

81 L. L. Miller, J. S. Bankers, A. J. Schmidt and D. C. Boyd, *J. Phys. Org. Chem.*, 2000, **13**, 808.

82 B. Voit, *J. Polym. Sci. Part A: Polym. Chem.*, 2000, **38**, 2505.

83 M. E. Mackay, G. Carmenzini, B. B. Sauer and W. Kampert, *Langmuir*, 2001, **17**, 1708.

84 D. E. Bergbreiter and G. Tao, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 3944.

85 V. Percec, C. H. Ahn, W. D. Cho, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. D. Cheng, A. Zhang, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 1998, **120**, 8619.

86 W. Stocker, B. Karakaya, B. L. Schürman, J. P. Rabe and A. D. Schlüter, *J. Am. Chem. Soc.*, 1998, **120**, 7691.

87 S. A. Prokhorova, S. S. Sheiko, C. H. Ahn, V. Percec and M. Möller, *Macromolecules*, 1999, **32**, 2653.

88 A. Adronov and J. M. J. Fréchet, *Chem. Commun.*, 2000, 1701.

89 P. J. Farrington, C. J. Hawker, J. M. J. Fréchet and M. E. Mackay, *Macromolecules*, 1998, **31**, 5043; C. J. Hawker, P. J. Farrington, M. E. Mackay, K. L. Wooley and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1995, **117**, 4409; T. H. Mourey, S. R. Turner, M. Rubinstein, J. M. J. Fréchet, C. J. Hawker and K. L. Wooley, *Macromolecules*, 1992, **25**, 2401.

90 S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed*, 2001, **40**, 74.