Hyperbranched Surface Graft Polymerizations

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Abstract This review summarizes the synthesis of irregular hyperbranched polymer grafts on various inorganic and organic substrates. The synthesis of these hyperbranched grafts are generally based on "graft on a graft" polymerizations and include diverse sorts of graft polymers. The "graft-on-a-graft" strategies discussed here include chemistry leading to the synthesis of hyperbranched poly(acrylic acid) grafts, polysiloxane grafts, dendrimer/polyanhydride graft nanocomposites, ring-opening polymerization grafts, and polyamidoamine grafts. Other relevant chemistry of these grafts including chemistry leading to derivatives of hyperbranched poly(acrylic acid) grafts, further modification by polyionic interactions, polyvalent hydrogen bonding, and functional group manipulation is discussed. Examples of reactions of monomers with polyvalent surfaces that lead to hyperbranched grafts are also briefly discussed.

Abbreviations

PAA   poly(acrylic acid)
PTBA   poly(*tert*-buyl acrylate)
MUA   mercaptoundecanoic acid
FTIR-ERS   Fourier Transform Infrared external reflection spectroscopy
XPS   X-ray photoelectron spectroscopy
PE   polyethylene
PP   polypropylene
ATR-IR   attenuated total reflectance infrared
PNIPAM   poly(*N*-isopropylacrylamide)
TEA   2-thipheneethyleneamine
ROP   ring opening polymerization
APES   3-aminopropyltriethoxysilane

1
Introduction

There is great interest in designing functional interfaces. Hyperbranched
grafts are alternatives to existing "linear" grafts for formation of such inter-
faces. They are of interest because they can provide interfaces with different
sorts of properties. Hyperbranched grafting is also conceptually more attrac-
tive than other approaches because the multiple grafting of oligomeric graft-
ing reagents can compensate for inefficiencies in reactions at surfaces (Fig. 1).
If, for example, an initial surface graft has coverage defects or if defects are
introduced during the graft-on-a-graft synthesis due to incomplete reactions,
subsequent hyperbranched grafting stages can "heal" these defects more ef-
ficiently than the traditional monomer grafting strategies that produce linear
graft chains (Fig. 1b versus 1a). This same effect was noted previously by Fer-
guson in layer-by-layer grafting of mica particles and polycationic polymers
on hydrophobic surfaces like octadecyltrichlorosilane treated Si/SiO_2 wafers
and hexadecanethiol-modified silver films and is a general feature common
to other layer-by-layer grafting chemistry [1, 2]. As shown in Fig. 1, the ad-
vantages of hyperbranching are considerable. In the particular schematic
drawing of three graft stages shown in Fig. 1b, hyperbranched grafting is far
more effective than linear grafting through three stages in Fig. 1a even when
there is a relatively low (50%) efficiency in the first step of grafting.

The synthetic strategies that lead to irregularly hyperbranched grafts
based on surface confined "graft-on-a-graft" polymerization reactions are
the focus of this review. Limited examples of monomers reacting with poly-
valent surface-bound reagents leading to hyperbranched polymers are also
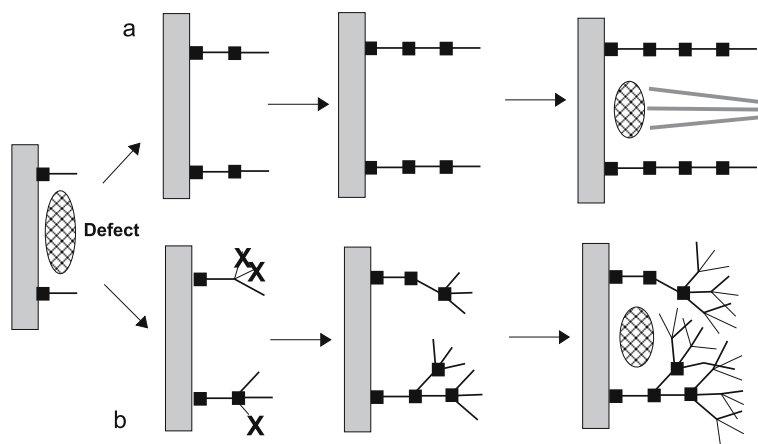discussed. In general, the chemistry described here is confined to reactions

Fig. 1 A schematic drawing comparing linear grafting **a** with hyperbranched grafting **b** in coverage or "healing" of surface defects. An efficiency of 100% is assumed in all three steps in linear grafting (**a**). In the hyperbranched graft example (**b**), a 50% efficiency is assumed in the first step but 100% efficiency and three branches per graft stage are assumes in steps two and three

that involve condensation polymerization reactions or reactions that involve the reaction of an electrophile with a nucleophile. This review begins with hyperbranched grafting of poly(acrylic acid) on hard inorganic or metal surfaces and soft polymer surfaces. Methods for derivatizing these films either by covalent modification or with polyvalent noncovalent interactions are discussed. Limited examples of applications of these materials are described. For example, Crooks' group has used some of these synthetic methods to prepare patterned surfaces. In cases like this where this subject has been reviewed, it is only briefly discussed here. Other hyperbranched grafting strategies including multilayer grafting of polyvalent nucleophiles and electrophiles, grafting via ring opening polymerizations, and the synthesis of dendritic grafts using polyvalent surface-bound reagents and monomers are discussed subsequently. There are other very successful synthetic strategies for preparing hyperbranched films based on free radical polymerizations that will not be a topic of discussion in this review. For example, Müller has developed a novel method of hyperbranched graft polymerization of inimers (initiator-monomers) by self-condensed vinyl polymerization (SCVP) via atom transfer polymerization (ATRP) [3, 4]. Another example would be Matsuda's preparation of hyperbranched grafts by iniferter (initiator-transfer agent-terminator) polymerization [5, 6]. A detailed description of these iniferter polymerizations can be found in Matsuda's contribution in this volume. A similar approach by Tsubokawa is described as a post-graft polymerization of vinyl monomers and is useful as a route to hyperbranched grafts [7–9]. Surfaces with hyperbranched grafts can also be prepared by

grafting commercially available hyperbranched polymers to surfaces. For example, Tsukruk has studied grafted hyperbranched polyesters with terminal epoxides that are attached to Si – OH surfaces [10, 11]. There are many examples where dendrimers are attached to surfaces by covalent or non-covalent interactions [12–17]. This chemistry too is not discussed here unless the dendrimers are used as reagents with linear polymers or oligomers to prepare hyperbranched grafts.

2
Hyperbranched Poly(acrylic Acid) Grafts

The synthesis of hyperbranched grafts of poly(acrylic acid) (PAA) using a "graft-on-a-graft" strategy is a general method for modifying a variety of surfaces. It requires as a starting material a surface that contains some functional groups though the amplification of functionality inherent in the chemistry means that a surface with only a modest level of functional groups can produce an interface with a macroscopically detectable concentration of functional groups. Examples of surfaces that have been modified include silicon (using the hydroxyl groups of the $Si(OH)_x$ layer), gold with functional self-assembled monolayers, glass, and surface-oxidized polyolefin films and powders. In each case, robust ultrathin supported-films are the products. This covalent multistep strategy is based on functional group protection/deprotection and affords modest control over the product film thickness. In PAA grafting, this control is based on the number grafting stages that are used. The product hyperbranched grafts range in thickness from ca. 30 Å to greater than 1000 Å. The film thickness initially increases rapidly in a non-linear fashion since each additional layer is added in a branching fashion multiplying the number of grafting sites (Fig. 2). After several grafting stages the thickness increases in a linear fashion. This variable extent of progress of this grafting chemistry as measured by either ellipsometry on reflective metal surfaces or as measured by titration of the $-CO_2H$ groups being introduced on higher surface area materials is very similar substrate to substrate (Fig. 2) [18, 19].

The graft-on-a-graft strategy was conceived of as a synthetically "forgiving" alternative to an attempted but ineffective borane-based radical graft polymerization onto vinyl terminated self-assembled monolayers [20] on gold and was based on earlier observations that a poly(acrylic acid) graft modified with new graft sites could be used to prepare a more dense and presumably thicker graft with subsequent polymerization or grafting steps [21]. It was also conceptually more attractive than other approaches that used monomers as grafting agents because the multiple grafting of oligomeric grafting reagents could compensate for inefficiencies in reactions at surfaces as discussed above (Fig. 1).
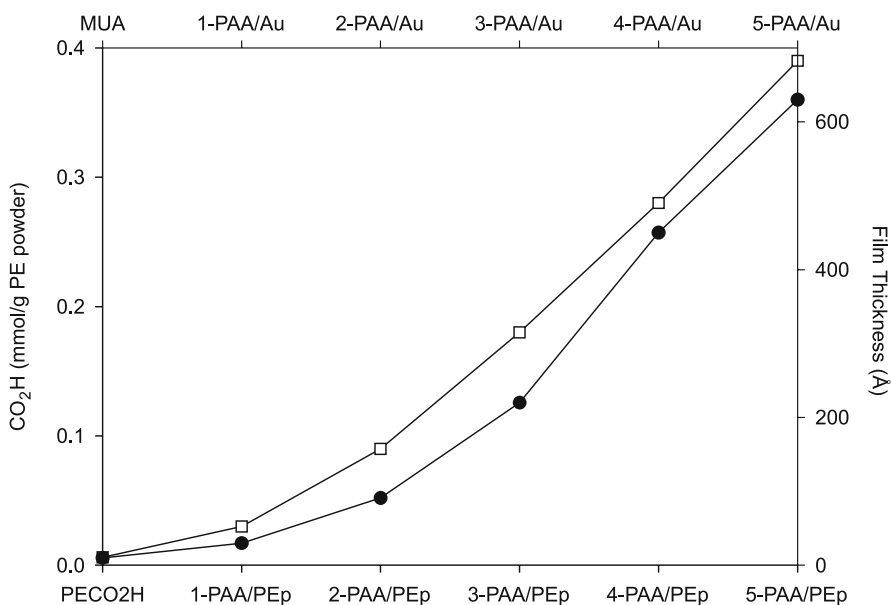
Fig. 2 Progress of hyperbranched poly(acrylic acid) graft formation on smooth gold films as measured by ellipsometry (●) or on polyethylene powders as measured by titration (□) of the supported − CO_2H groups

2.1
Hyperbranched Poly(acrylic Acid) Graft Synthesis on Gold Surfaces

The synthesis of surface grafted hyperbranched films of poly(acrylic acid) was first described on gold substrates [18]. This synthesis of hyperbranched grafts of poly(acrylic acid) (PAA) on gold, shown in Scheme 1, began with a self-assembled monolayer of mercaptoundecanoic acid (MUA). Activation of the carboxylic acid groups of this monolayer was accomplished by formation of mixed anhydrides with ethyl chloroformate. While other activating agents (e.g. carbonyl diimidazole or DCC worked), the best yields were obtained with alkyl chloroformates. Subsequent amidation of this electrophilic surface by an oligomeric reagent, α,ω-diamino-poly(*tert*-butyl acrylate) (PTBA), yielded a 1-PTBA graft on MUA functionalized gold (1-PTBA/Au). This 1-PTBA/Au graft was initially converted to a 1-PAA/Au graft by acidolysis with *p*-toluene sulfonic acid/H_2O. Subsequent work showed that this acidolysis proceeded equally well using methane-sulfonic acid (15 min, room temperature). Activation of the carboxylic acid groups of this first 1-PAA/Au graft with more ethyl chloroformate followed by treatment of the new polyanhydride surface with more α,ω-diamino-poly(*tert*-butyl acrylate) oligomer produced a 2-PTBA/Au graft. Acidolysis of this second graft layer of PTBA produces a 2-PAA/Au graft. Repeating
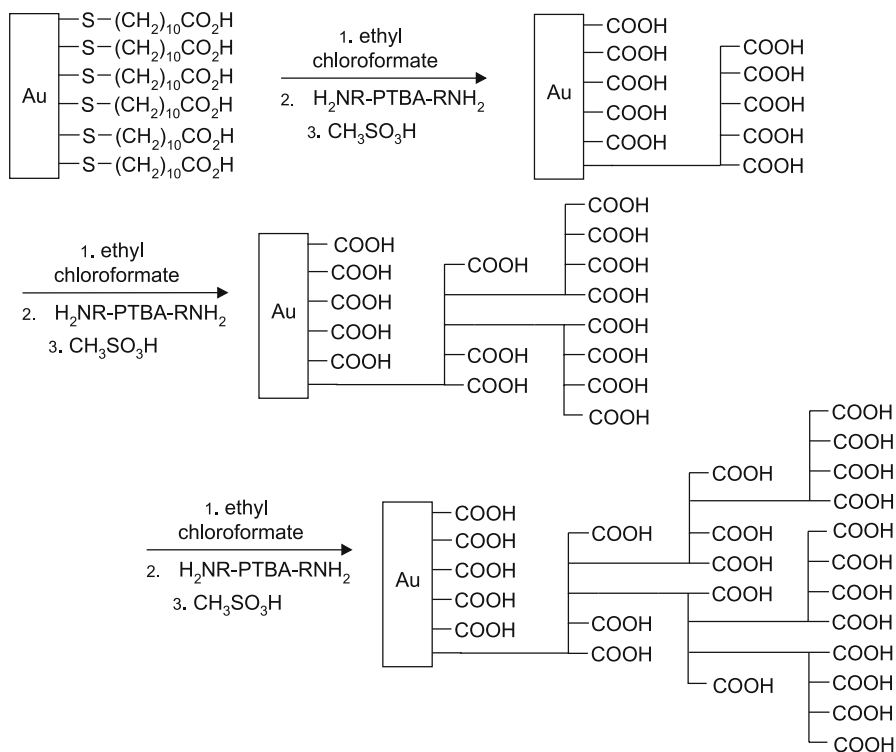
Scheme 1 Repetitive step-by-step synthetic scheme leading to formation of a hyper-branched graft of poly(acrylic acid) on a mercaptoundecanoic acid self-assembled monolayer on a supported gold film

this process for several generations produces a dense, highly functionalized surface. Films containing as many as seven graft layers were successfully prepared.

The use of appropriate functionalized oligomers is a key to the success of this synthesis. The necessary functionalized oligomers were prepared by polymerization of *tert*-butyl acrylate ($n = $ ca. 120) with a functional AIBN initiator (Eq. 1). Since
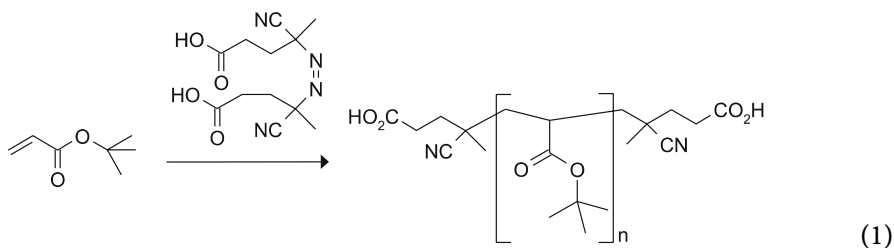
$$(1)$$

tert-butyl acrylate polymerizations terminate mainly by coupling [22], the product is principally a difunctional poly(*tert*-butyl acrylate). The carboxylic acid terminated oligomers so-formed were subsequently converted into primary amines (Eq. 2). The product polymer was characterized by end group analysis at both the $-CO_2H$ stage and at the $-NH_2$ stage and had a M_n of 12 000–18 000 Daltons in various preparations.

$$(2)$$
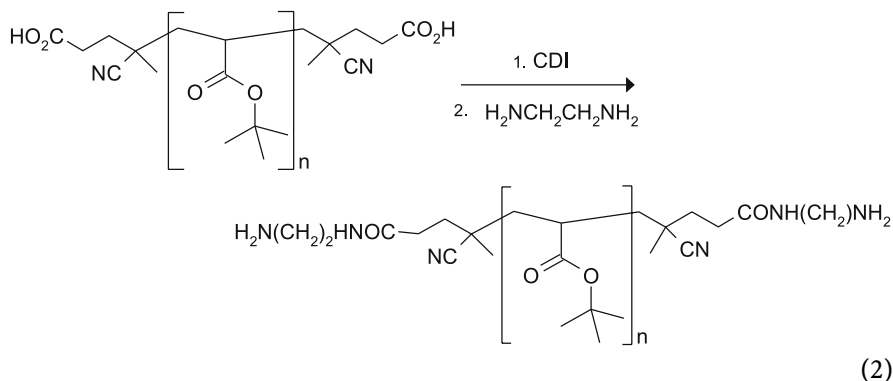
The progress of this surface graft chemistry was followed by Fourier transform infrared external reflection spectroscopy (FTIR-ERS), water contact angle goniometry, X-ray photoelectron spectroscopy (XPS), and ellipsometric analysis. The thickness of these films increased in a nonlinear fashion (Fig. 1). Ellipsometric analysis showed the thickness changed from ca. 30 Å for a single PAA/Au graft to greater than 1000 Å for films that were prepared using more than 5 grafting stages [23]. Activation of the MUA/Au film by formation of the mixed anhydride was shown to be quantitative by FTIR-ERS spectroscopy. Upon treatment with the diamino-oligomer of PTBA ($M_n = 14\,600$), evidence for the formation of a 1-PTBA/Au graft was seen in the FTIR-ERS spectrum which showed a small amide peak and a large *tert*-butyl ester peak. After acidolysis, the absorption peaks for *tert*-butyl esters disappeared. Water contact angle goniometry showed that the $-CO_2H$-rich surface was more hydrophilic as expected. The carbonyl peak intensity in the infrared spectrum increased with each additional grafting stage. The amide peaks in the infrared spectrum from covalent grafting were also detectable in the IR spectrum. These grafts were found to be stable to extensive solvent treatment. No change in the carbonyl intensity in the FTIR-ERS spectrum was observed after Soxhlet extraction with methylene chloride or sonication with acetone or acid.

Tapping-mode atomic force microscopy studies showed that as these hyperbranched PAA films became somewhat less smooth as they increased in thickness through successive grafting stages [24]. For example, a very smooth initial single-crystal Au(111) surface with a root mean square (RMS) roughness of 0.2 nm (over a $2\,\mu m \times 2\,\mu m$ area) had its roughness increased to

Table 1 Root mean square roughness of PAA grafts on Au/Si measured over a $5 \times 5 \, \mu m$ area

| Graft	RMS (nm)
MUA/Au/Si	2.01
1-PAA/Au/Si	1.44
2-PAA/Au/Si	1.15
3-PAA/Au/Si	1.02
4-PAA/Au/Si	1.53

0.3 nm for a 1-PAA/Au graft and 0.8 nm for a 3-PAA/Au graft. However, grafting on a rough Au/Ti/Si surface that was prepared from Au deposition on Ti/Si resulted in some surface smoothing after several grafting layers (Table 1). In this case the 1-PAA/Au, 2-PAA/Au, 3-PAA/Au, and 4-PAA/Au grafts were all smoother than the initial Au/Ti/Si surface. The PTBA grafts were generally less smooth. The relative smoothness of these surfaces leveled off after 2 or 3 graft stages and the surface became increasingly rough with additional grafting layers following the trend noted earlier with grafting of PAA on single-crystal Au(111) surfaces.

2.1.1
Derivatives of Hyperbranched Poly(acrylic Acid) Grafts

Hyperbranched grafts of poly(acrylic acid) on gold can easily be derivatized. The most common approach has been to use derivatizing agents that contain reactive amines or alcohols to form carboxylic acid amides or esters. Examples of compounds covalently incorporated into these PAA/Au interfaces are shown in Fig. 3. Equation 3 illustrates this general method which involves first activating the poly(acrylic acid) grafts with ethyl chloroformate. Subsequent treatment (here with an amine) then produces a mixture of derivatized $-CO_2H$ groups and unmodified $-CO_2H$ groups in the interface. The covalent amidation strategy has been used to prepare low-energy fluorinated surfaces [25–27]. Amidation or esterification has been used to incorporate pyrene fluorescence probes, molecular recognition elements like crown ethers cyclodextrin [28], ferrocene, poly(ethylene glycol), and dye chromophores [23]. Other chemistry typical of $-CO_2H$ groups can also be carried out with the $-CO_2H$ groups in these interfaces. This includes acid-base chemistry, reductions, ion exchange, and non-covalent modifications through hydrogen-bonding. Finally, the polyvalent nature of these films can be used to advantage in molecular assembly procedures. Specifically, these films have been noncovalently functionalized using ionic entrapment of polycations [29] and enzymes [30] and through

polyvalent hydrogen bonding interactions with polyvalent hydrogen-bond acceptors [31].

(3)
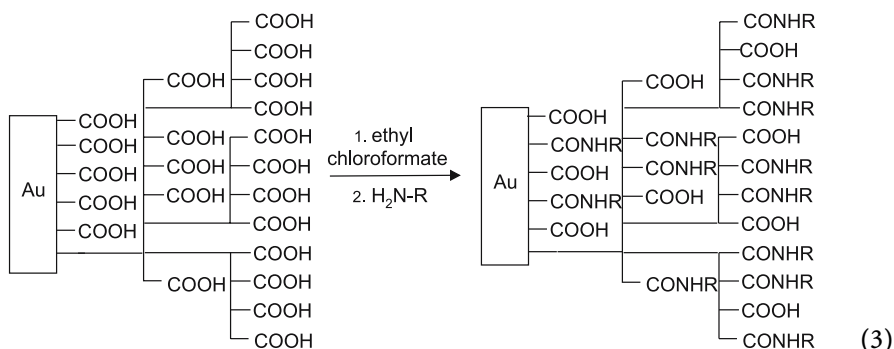
Hydrophobic, fluorinated hyperbranched grafts were synthesized from an ethyl chloroformate activated hyperbranched 3-PAA/Au graft using the fluorinated alkyl amine $H_2N(CH_2)(CF_2)_6CF_3$. Reaction of an activated 3-PAA/Au film with $H_2N(CH_2)(CF_2)_6CF_3$ produced a fluorinated film that almost doubled in thickness. XPS analysis showed 46 atom-% F in the product fluoramidated graft which is 86% of the theoretical atomic concentration for a homogenous
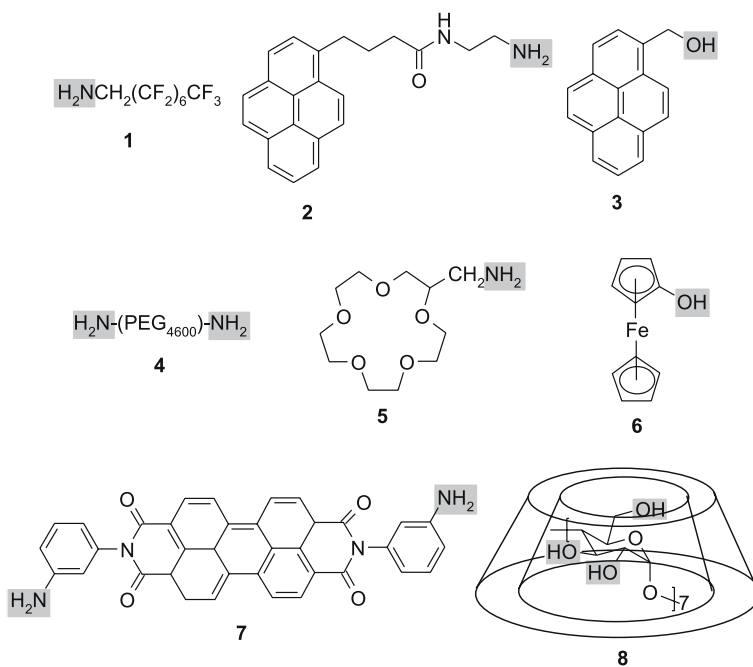

Fig. 3 Functionality that has been incorporated into PAA/Au interfaces through amidation or esterification chemistry

fluorinated graft. A second activation and $H_2N(CH_2)(CF_2)_6CF_3$ treatment increased the films' F content to 50 atom-%, 93% of the theoretical concentration for a homogenous graft [25]. No Au peak was observed from the underlying gold support indicating good coverage. Films were also synthesized where the internal grafts layers were fluorinated and the external grafts layers were either hydrophilic PAA grafts or fluorinated [26]. The control of the fluorine content of the core and shell of these grafts demonstrates the flexibility of this "graft-on-a-graft" strategy and the ability of later graft stages to cover defects in earlier grafts. This is illustrated by steps where the small amount of residual $-CO_2H$ groups remaining after formation of a fluorinated graft like that described above were used as the base for formation of a hydrophilic graft with a fluorinated hydrophobic interior. In this example, a film with a hydrophobic interior was first prepared by adding $H_2N(CH_2)(CF_2)_6CF_3$ to a grafting solution of diamino-PTBA in the early grafting stages. In the final fluorine-grafting step, a grafting mixture containing a 500 : 1 mol : mol ratio of $H_2N(CH_2)(CF_2)_6CF_3$ to diamino-PTBA of 500 : 1 was used. At this point, the supported hyperbranched graft film had a water contact angle of $100°$. Then two additional grafting stages were carried out using only the diamino-PTBA polymer. These steps only produced hydrophilic $-CO_2H$ on the exterior or shell of this original fluorinated graft. Formation of this hydrophilic exterior or shell was confirmed by absence of F peaks in the XPS spectrum in the final product and by the change in contact angle from $100°$ to $14°$.

These hydrophobic, fluorinated hyperbranched films on gold passivate the underlying gold metal toward electrochemical reactions. For example, under basic conditions a fluorinated 3-PAA/Au interface had a measured charge-transfer resistance that was 40 times more than the resistance of an unfluorinated 3-PAA film under the same conditions. These fluorinated hyperbranched grafts were significantly more passivating than a simple monolayer. For example fluorinated 3-PAA/Au grafts were shown to passivate the underlying gold to a 10^4 times greater extent than a MUA coated electrode and about 10 times more than a hexadecanethiol monolayer [25]. The fluorinated 3-PAA/Au grafts' passivation was greater under basic conditions in contrast to the unfluorinated 3-PAA/Au grafts that were more passivating under acidic conditions. For example, the fluorinated grafts' had charge-transfer resistance that increased 10-fold as pH was changed from 3 to 10 while the unfluorinated 3-PAA/Au grafts' charge transfer resistance decreased 19-fold as the pH changed from 3 to 10. Presumably that reflects the fact that PAA grafts have pH-dependent swelling (vide infra) that is lacking in the fluorinated 3-PAA/Au grafts [27].

Modification of PAA/Au grafts with the amine and alcohol functionalized pyrenes **2** and **3** produced highly fluorescent films [23]. These derivatized films exhibited both monomer and excimer fluorescence. The relative amounts of monomer and excimer emission depended on the pyrene concentration used in the derivatization process. When modest concentrations

(ca. 0.05 M) of pyrene derivative **2** were used in amidation, films with only excimer fluorescence emission were produced. Mixed anhydride interfaces that were treated with very dilute concentrations (ca. 10^{-6} M) of **2** in contrast produced films that exhibited monomer fluorescence. It was also possible to incorporate pyrene during grafting. For example, films prepared by treatment of 2-PAA interfaces with a (1 : 50) (mol : mol) mixture of **2** and diamino-PTBA (in step 2 of Scheme 1) followed by hydrolysis also exhibited only monomer fluorescence. This suggests that intra-interface interactions of substituents on these hyperbranched grafts are facile even though the interfaces have some crosslinking due to the difunctionality present in the grafting oligomer $NH_2 - PTBA - NH_2$.

In a typical amidation reaction, ca. 55% of carboxylic acids were converted to carboxamides. The extent of conversion varied depending on the amine nucleophile. To quantitatively convert the $- CO_2H$ groups in the hyperbranched graft into $- CONHR$ groups, the alkyl chloroformate activation followed by amine treatment process was simply repeated. In some cases, up to six repetitions of this process were required to achieve very high conversions of acid to amide. This need for repetitive amidations reduced the synthetic utility of this process. This amidation reaction is presumably limited in effectiveness because the nucleophilic amine can attack either of the anhydride carbonyl derived from the $- CO_2H$ or the chloroformate. The former reaction leads to the desired amide product. The latter reaction produces a soluble amide and a salt of the PAA $- CO_2H$ group and the amine nucleophile. Other activation reagents (e.g. carbonyl diimidazole or DCC) were also studied. However, ethyl chloroformate was the most effective activating agent.

Esterification of the PAA grafts could be carried out either by ethyl chloroformate activation and alcohol treatment or by simple Fischer esterification. The latter reaction proved to be very effective in spite of the harsh conditions employed. Indeed, the stability in thickness of a 3-PAA/Au surface in the presence of toluene and a sulfuric acid catalyst was notable. A direct comparison of the effectiveness of various esterification procedures showed that the use of sulfuric acid as a catalyst in excess alcohol or the use of *p*-toluenesulfonic acid (*p*-TsOH) as a catalyst in toluene were both effective in esterification (Eqs. 4–6). Either acid-catalyzed procedure (Eq. 5 or 6) produced > 90% ester formation in contrast to the 40–60% ester yield using the EtOCOCl activation shown in Eq. 4. For example, a poly(ethyl acrylate) film was formed from a 3-PAA/Au using a toluene solution containing EtOH with 0.1 M *p*-TsOH as a catalyst after an overnight reflux. These conditions produced a product film with < 10% remaining $- CO_2H$ groups after 12 h of reflux. Ellipsometric thickness of the hyperbranched ester film showed that the original 3-PAA film thickness of 344 Å had changed to 424 Å. A concomitant change in advancing water contact angle from 24° to 93° was consistent with esterification. This result contrasted with results for a similar esterification of a MUA monolayer on gold where there was no detectable remaining

monolayer after an overnight reflux in a toluene-EtOH mixture in the presence of *p*-toluenesulfonic acid. The greater stability of the hyperbranched graft vis-à-vis the monolayer was ascribed to the light crosslinking of the hyperbranched graft by the mostly telechelic oligomeric grafting agent.

$$
\begin{array}{c}
\text{—CO}_2\text{H} \\
\text{—CO}_2\text{H} \\
\text{—CO}_2\text{H} \\
\text{—CO}_2\text{H}
\end{array}
\quad
\xrightarrow[\substack{2.\ \text{CH}_3\text{CH}_2\text{OH} \\ 3.\ \text{NaOH (-CO}_2\text{Na formation)}}]{\substack{1.\ \text{ClCOOCH}_2\text{CH}_3 \\ N\text{-methylmorpholine}}}
\quad
\begin{array}{c}
\text{—CO}_2\text{Na} \\
\text{—CO}_2\text{CH}_2\text{CH}_3 \\
\text{—CO}_2\text{Na} \\
\text{—CO}_2\text{CH}_2\text{CH}_3
\end{array}
\tag{4}
$$

$$
\begin{array}{c}
\text{—CO}_2\text{H} \\
\text{—CO}_2\text{H} \\
\text{—CO}_2\text{H}
\end{array}
\quad
\xrightarrow[\substack{2.\ \text{NaOH (-CO}_2\text{Na formation)}}]{\substack{1.\ \text{CH}_3\text{OH, H}_2\text{SO}_4 \\ 6\ \text{h reflux}}}
\quad
\begin{array}{c}
\text{—CO}_2\text{CH}_3 \\
\text{—CO}_2\text{CH}_3 \\
\text{—CO}_2\text{CH}_3
\end{array}
\tag{5}
$$

$$
\begin{array}{c}
\text{—CO}_2\text{H} \\
\text{—CO}_2\text{H} \\
\text{—CO}_2\text{H}
\end{array}
\quad
\xrightarrow[\substack{2.\ \text{NaOH (-CO}_2\text{Na formation)}}]{\substack{1.\ \text{H}_2\text{C=CHCH}_2\text{OH} \\ 0.1\ \text{M } p\text{-TsOH, toluene} \\ 12\ \text{h reflux}}}
\quad
\begin{array}{c}
\text{—CO}_2\text{CH}_2\text{CH=CH}_2 \\
\text{—CO}_2\text{CH}_2\text{CH=CH}_2 \\
\text{—CO}_2\text{CH}_2\text{CH=CH}_2
\end{array}
\tag{6}
$$

Reduction of the $-CO_2H$ groups in a PAA hyperbranched graft was of interest as a route to poly(allyl alcohol) hyperbranched grafts. Surprisingly, reducing agents known to be effective in solution-state organic chemistry for reduction of $-CO_2H$ groups to $-CH_2OH$ groups were not effective in derivatizing these PAA grafts. Reactions using BH_3-SMe_2 or $LiAlH_4$ both produced interfaces that contained unreacted $-CO_2H$ groups based on IR analysis of films after attempted reduction followed by acidification. Complete reductions (Eq. 7) were only possible if the PAA hyperbranched graft was first activated with ethyl chloroformate and then treated with BH_3-SMe_2. These poly(allyl alcohol) grafts on polyethylene substrates were subsequently used as substrates for further radical grafting using Ce(IV) [32].

$$\tag{7}$$

Hydroxyl-functionalized hyperbranched grafts were also accessible from ester grafts by organometallic chemistry. IR analysis of the reaction of an esterified 3-PAA/Au hyperbranched graft with methylmagnesium bromide showed that the absorbance due to the ester carbonyl group completely disappeared. The thickness change (370 Å to 285 Å) and the change in the IR spectrum for this film were interpreted in terms of the simple Grignard chemistry shown in Eq. 8.

$$\text{(8)}$$
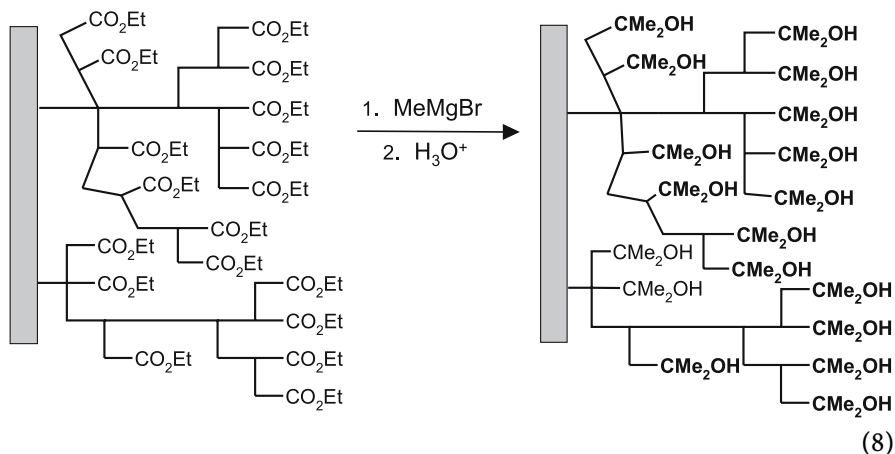
The simplest derivatization chemistry is deprotonation of the $-CO_2H$ groups of a PAA hyperbranched graft. Experiments showed that deprotonation/protonation chemistry was fast with aqueous acids and bases. The extent of protonation and deprotonation could be followed by assaying the change in absorbance of the $-CO_2H$ carbonyl (as the $-CO_2H$ group became a $-CO_2Na$ group the $\nu_{C=O}$ peak shifted to 1560 cm^{-1}) (Fig. 4). The p$K_{1/2}$ for the point where the integrated intensity of the ν_{CO_2H}/ν_{CO_2Na} absorbances was 1 : 1 was 4.3, a value very similar to the pK_a of poly(acrylic acid) in solution. This similarity in acid-base chemistry for these interfaces versus solution state chemistry of a similar weak acid contrasts with the very dissimilar pK_a of $-CO_2H$ groups at the surface of oxidized polyethylene versus the solution pK_a of acetic acid [33].

As noted below, such deprotonation/protonation chemistry occurs repeatedly without any loss of the hyperbranched graft as measured by ellipsometry (vide infra). This stability to acid and base mirrors the stability noted above for these hyperbranched grafts in continuous extractions and acid-catalyzed esterification chemistry and is thought to be a consequence of the light cross-linking that occurs during the grafting process.

The ready formation of polyanions from poly(acrylic acid) grafts or of polycations from a polyaminated surface leads to a polyvalent anionic or cationic interface. Such interfaces can be modified ionically (as in ionic
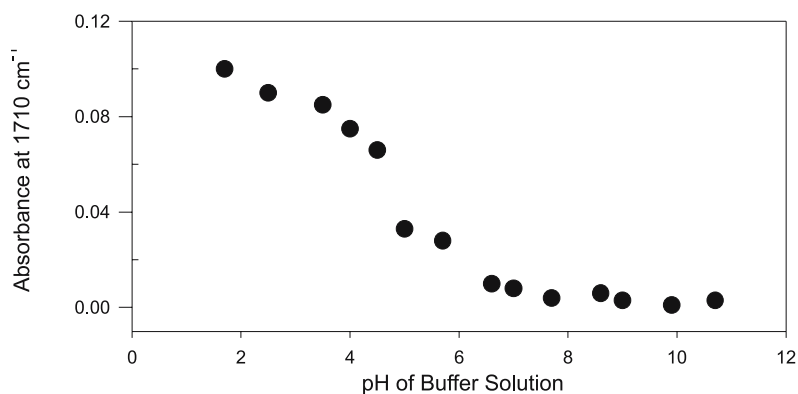
Fig. 4 The change in the absorbance at $1710\,\mathrm{cm}^{-1}$ as a 3-PAA/Au film is immersed in buffers of varying pH. An increase in intensity of a peak assigned to $-CO_2Na$ was seen concomitant with the decrease in intensity of the $-CO_2H$ peak at $1735\,\mathrm{cm}^{-1}$

layer-by-layer assembly) [2]. This ionic modification offers an alternative to covalent modification procedures. Electrostatic interactions between polycationic polymers or enzymes with cationic surface groups with poly(sodium acrylate) grafts were effectively used as examples of this method for post-graft functionalization of a hyperbranched interface. Linear cationic poly(allyl amine), poly-*D*-lysine, and dendritic PAMAM all chemisorbed into a 3-poly(sodium acrylate)/Au film. The ionically assembled composites so formed were stable to washing with polar solvents. Thickness measurements of the ionically modified hyperbranched grafts showed a significant increase due to the exchange of sodium cations with larger polymeric cations. In general, these ionic assemblies fully disassemble after acid treatment [29].

The poly(sodium acrylate) hyperbranched graft formed in a simple deprotonation was used to ionically immobilize enzymes. Studies showed that immobilized glucose oxidase in a 3-poly(sodium acrylate)/Au film retained significant activity on immobilization and that the enzyme in this ionic assembly remained active for more than 60 days of storage [30].

Derivatives of hyperbranched 3-PAA/Au grafts were also used as polymeric filters for chemical sensors [28]. This chemistry took advantage of the fact that these hyperbranched grafts are ultrathin. Earlier work that used chemically selective supported polymer membranes generally used thicker coatings which slowed mass and electron transfer. As a proof of concept, a 3-PAA hyperbranched graft was selectively modified first with β-cyclodextrin (after $ClCO_2Et$ activation of the PAA$-CO_2H$ groups). Then this graft that contained a homogeneous dispersion of covalent immobilized β-cyclodextrin was allowed to react with *N*-hydroxysuccinimide in the presence of a water soluble carbodiimide (EDC). The NHS ester-containing film so formed was next allowed to react for 18 h with an aqueous solution of poly-*D*-

lysine in a pH 8 buffer. This produced films with a PAA-(β-cyclodextrin) bulk and a poly-*D*-lysine modified surface presumably because the poly-*D*-lysine diffusion into the bulk of the ca. 250-nm thick film was slow relative to the rate of reaction of the lysine ε-amino groups with the NHS esters.

Films formed in this way exhibited pH dependent permeability to redox probe molecules. For example, benzyl viologen did not permeate the film at low pH where the poly-*D*-lysine cap was protonated. However at high pH where the cap is neutral and the underlying $-CO_2H$ groups are in their carboxylate form, benzyl viologen was electrochemically reduced. Opposite pH dependence was seen with a negatively charged redox molecule, anthraquinone-2-sulfonate.

2.1.2
Aqueous Solvation of Hyperbranched Poly(acrylic Acid) Films

Hyperbranched thin films of poly(acrylic acid) can be highly solvated and their solvation is pH dependent (Eq. 9). The solvation properties of hyperbranched grafts of poly(acrylic acid) prepared on a gold substrates were studied after acid and base treatment both as "dry" films (films that had been removed from a buffer, EtOH washed and dried under N_2) and in situ in the presence of an aqueous buffer [29]. Ellipsometric analysis showed that a dry 3-PAA/Au film had a thickness of 230 Å. This thickness changed in a fully reversible manner to ca. 450 Å after deprotonation (Fig. 5). The thickness of these films was even greater in a buffer solution as measured by in situ ellipsometry. After immersion in a pH 1.7 buffer solution, the solvated acid form of the 3 PAA/gold graft swelled to a thickness of 430 Å. A buffer with pH 7.2 increased the swelling of the graft layer to 560 Å. A thickness titration curve between pH 2.6 to 7.2 for hyperbranched poly(acrylic acid) films on gold was made by in situ ellipsometric analysis. As noted above, the $pK_{1/2}$ (buffer pH at thickness midpoint) is pH 4.3 which is similar to the pK_a of poly(acrylic acid).

$$(9)$$
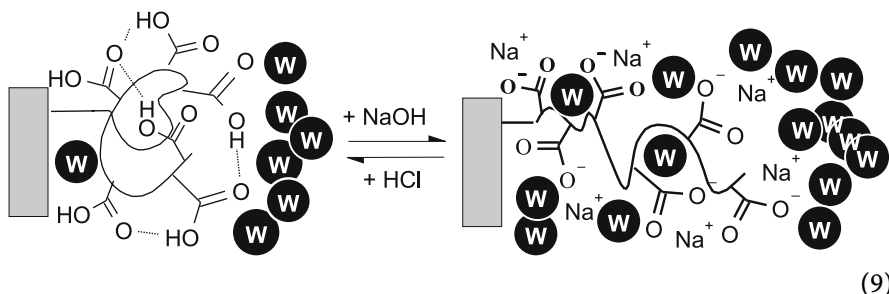
The pH responsiveness of a 3-PAA/Au graft that was amidated with *N,N*-dimethylaminoethylenediamine was also studied by in situ ellipsometry [32]. This amine-containing graft had pH dependent swelling characteristics that were opposite to those of the $-CO_2H$-rich graft because the amine-rich film
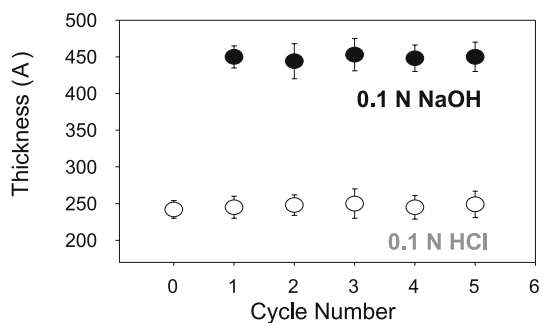
Fig. 5 Reversibility of protonation/deprotonation of a 3-PAA/Au film with 0.1 N NaOH and 0.1 N HCl respectively as measured by ellipsometry of the acidic or basic form of a 3 PAA/Au graft after removal form the acid or base solution, an ethanol rinse and drying under N_2
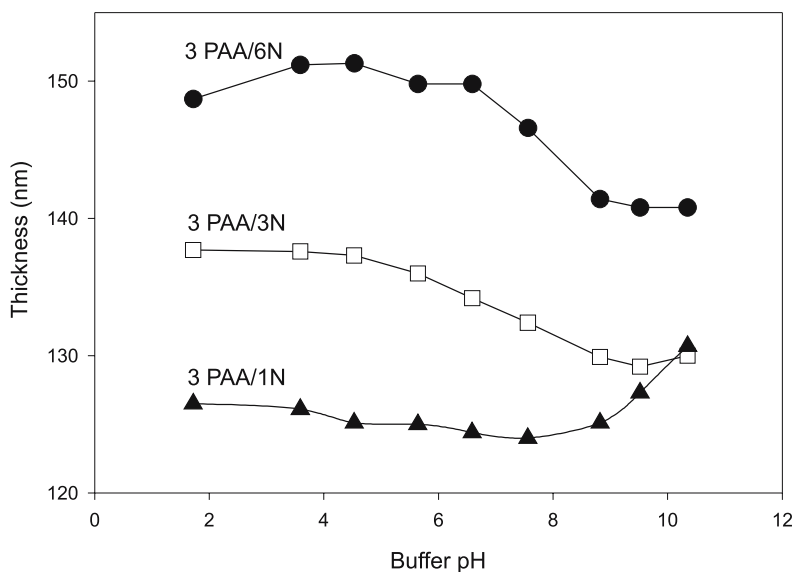

Fig. 6 Ellipsometric analysis of films containing various mixtures of amines and carboxylic acids: 3-PAA/1N (ca. 55% – CO_2H); 3-PAA/3N (ca. 17% – CO_2H); and 3-PAA/6N (no – CO_2H groups could be distinguished from carboxamide carbonyl peak in the FTIR-ERS spectrum). The 1N, 3N and 6N refers to the number of times the amidation in Eq. 3 was repeated using $NH_2CH_2CH_2N(CH_3)$ as the amidating reagent

is cationic at low pH and neutral at high pH (Fig. 6). Thickness changes measured ellipsometrically as a function of pH were also very sensitive to the extent of conversion of carboxylic acid to amide. Only after six repetitions of activation followed by amidation was the expected ellipsometric thickness change as a function of pH observed. In this case, the thickness of the basic graft decreased as the pH increased. The inflection point for this titration

of thickness change was at ca. pH 7.9. Studies of pH-dependent thickness changes for films with lower conversions of acid to amide were more complicated. Such amphoteric interfaces contained variable mixtures of amine and acid groups and did not show a clear inflection point.

2.1.3
Patterning of Hyperbranched Poly(acrylic Acid)-Derived Grafts

Crooks' group has used photolithographic and μ-contact printing technology to form patterned hyperbranched grafts. This topic is the subject of a review [34] but a few examples will be mentioned here. Using photolithography, features as small as 5 μm have been prepared as shown in Scheme 2 [35]. Beginning with a 3-PTBA/Au graft, a coating of the photoacid triphenylsulfonium hexafluoroantimonate was applied to the film. Irradiating the coated 3-PTBA/Au film through a photomask with UV light caused the exposed regions of poly(*tert*-butyl acrylate) to undergo acidolysis to form poly(acrylic acid). The hyperbranched poly(acrylic acid) regions were activated with ethyl chloroformate and treated with an amine-terminated dansyl fluorophore. The patterned region was then visualized by fluorescence microscopy with an
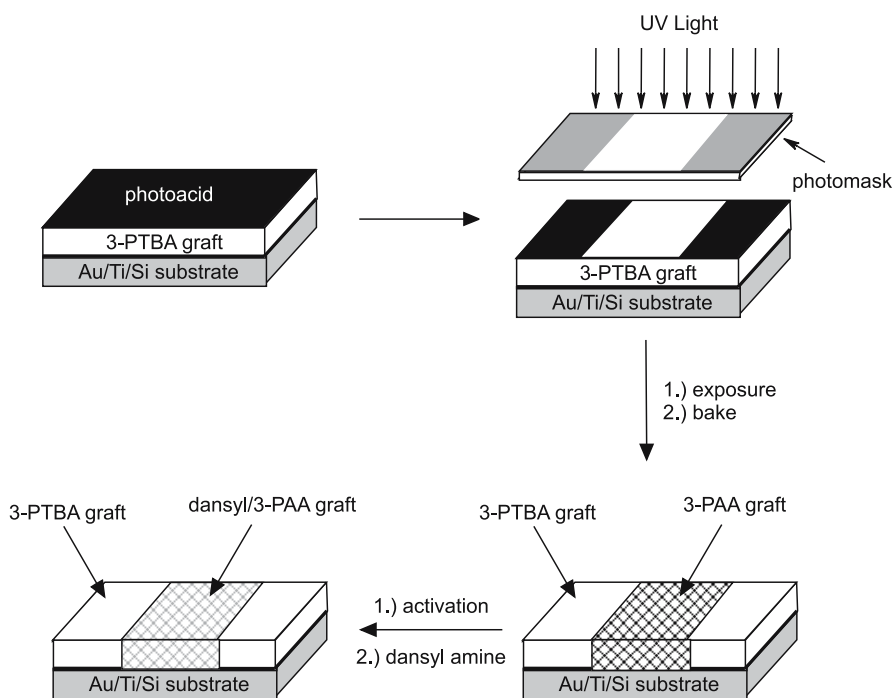
Scheme 2 Photolithographic process for preparing patterned hyperbranched grafts of poly(acrylic acid)
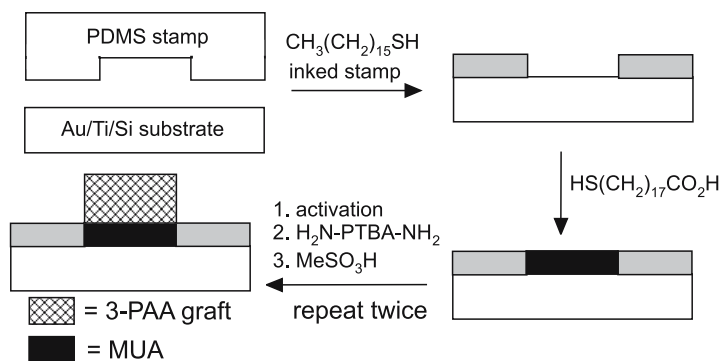
Scheme 3 Procedure used for preparing patterned hyperbranched poly(acrylic acid) films by μ-contact printing

excitation wavelength of 330–380 nm and emmision wavelength at 420 nm. A second coating of photoacid followed by UV light exposure converted the remaining regions of 3-PTBA/Au grafts to 3-PAA/Au grafts. Activation followed by treatment with the amine-terminated eosin fluorophore with an excitation wavelength of 540–580 nm and an emmision wavelength of 600–660 nm produced a patterned film with two dyes. Fluorescence microscopy showed that the dyes were segregated from each other.

Several approaches and applications of patterned hyperbranched grafts of poly(acrylic acid) by μ-contact printing have been described. An example of patterning hyperbrached grafts of poly(acrylic acid) by μ-contact printing is shown in Scheme 3 [36]. A pattern of $CH_3(CH_2)_{15}SH$ was first applied to an gold surface using a poly(dimethylsiloxane) (PDMS) stamp. The remaining naked gold regions were then functionalized with MUA and a 3-PAA/Au graft was prepared on the MUA modified gold as previously described in Scheme 1. This patterning chemistry has been extended to include polyethylene substrates [37], biopatterning [38–40], and dendrimer/poly(maleic anhydride)-c-poly(methyl vinyl ether) (Gantrez) composites [41].

2.2
Hyperbranched Grafts on Polymer Surfaces

The modification of polymeric surfaces is of great interest as it affords a way to enhance the surface properties of a polymer without affecting the bulk properties of a polymer. Thus, it is not surprising that the synthesis of hyperbranched PAA grafts has been extended to include both soft two dimensional (films, wafers, blocks) and three dimensional (powder) polymer surfaces. These approaches used the same general synthetic grafting scheme previously described for graft-on-a-graft hyperbranched grafting on hard metal surfaces.

2.2.1
Synthesis of Hyperbranched Poly(acrylic Acid) Grafts on Polyethylene Films

The surface modification of polyethylene (PE) films, PE powders, and polypropylene (PP) wafers with hyperbranched poly(acrylic acid) grafts was carried out as shown in Scheme 4 [19, 42, 43]. First, the polyolefin substrates were functionalized by oxidation with $CrO_3 - H_2SO_4$. Subsequent activation with ethyl chloroformate followed by grafting with α,ω-diamino-poly(*tert*-butyl acrylate) oligomer then produced a 1-PTBA/PE graft. Acidolysis of the *tert*-butyl esters of the 1-PTBA/PE film produced the poly(acrylic acid) or 1-PAA/PE graft. A $(1 + x)$-PAA/PE graft was prepared by repeating the ac-
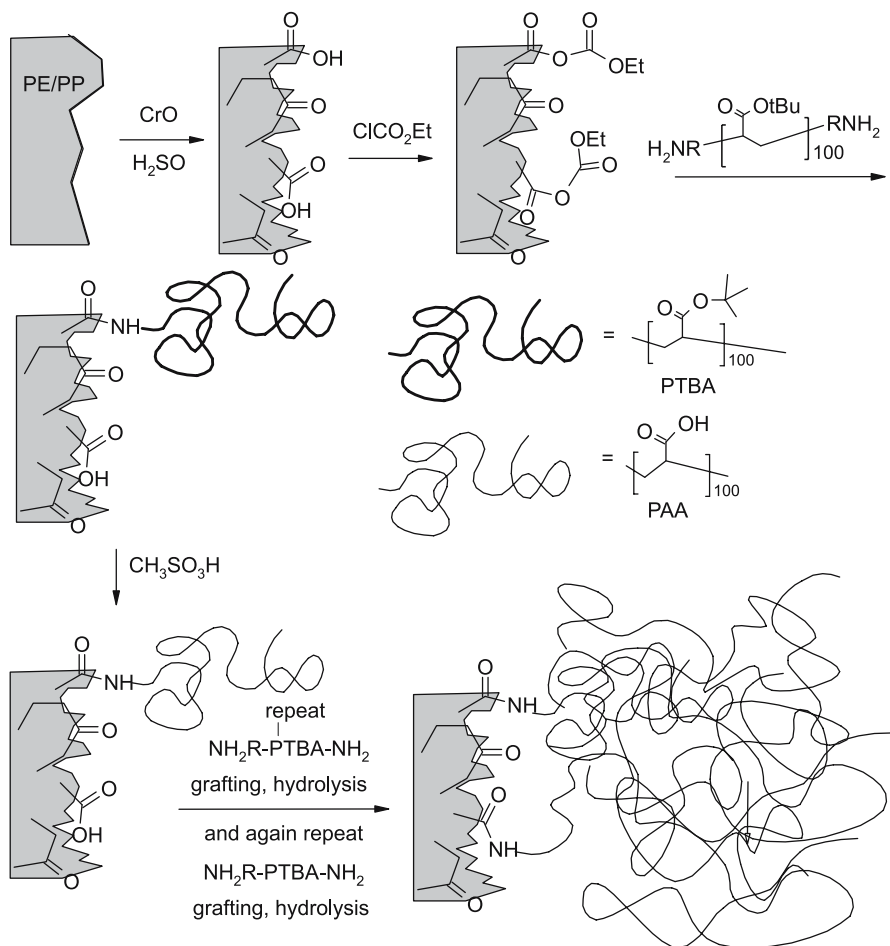
Scheme 4 Chemistry used to prepare hyperbranched poly(acrylic acid) grafts on polyethylene film, polyethylene powder or polypropylene wafers

tivation step, the α,ω-diamino-poly(*tert*-butyl acrylate) grafting, and then acidolysis x times.

The initial oxidation product of a polyethylene film or powder is a surface that includes some $-CO_2H$ groups. These groups' presence can be detected by attenuated total reflectance infrared (ATR-IR) spectroscopy as a peak at $1710\,cm^{-1}$. These $-CO_2H$ groups served the same purpose as the $-CO_2H$ groups of MUA/Au, serving as starting points for the hyperbranched grafting scheme. The hyperbranched grafts that were formed were characterized by water contact angle goniometry, ATR-IR spectroscopy, and XPS analysis. With each additional grafting stage the intensity of the acid carbonyl at $1710\,cm^{-1}$ increased relative to the intensity for the C-H absorption in the ATR-IR spectrum. The poly(acrylic acid) peak at $1710\,cm^{-1}$ was the dominant peak in the ATR-IR spectrum after 3–4 grafting stages on PE film. The carboxamide peak from the grafting was also visible at $1650\,cm^{-1}$.

The stability of these hyperbranched films was tested with repeated acid/base treatments and by Soxhlet extraction of grafted films with CH_2Cl_2. The reversibility of the deprotonation/protonations effected by base/acid treatment was confirmed both by water contact angle analysis and ATR-IR spectroscopy. The ATR-IR spectra showed that on base treatment that the carbonyl peak due to the acid carbonyl disappeared concomitant with the appearance of a new carbonyl peak due to formation of a carboxylate group. These spectral changes were reversible on dilute acid treatment with the carboxylic acid carbonyl peak reappearing. The relative peak intensities of IR peaks for the graft functionality in the ATR-IR spectrum of the 3-PAA/PE film after this deprotonation/protonation cycle were unchanged after repeated deprotonation/protonation cycles. Water contact angle analysis confirmed this reversibility – a protonated films' water contact angle Θ_a was 48° and the deprotonated film's water contact angle was 15°. This reversibility was consistent with that seen for similar hyperbranched grafts on gold (Fig. 5).

The uniformity of these hyperbranched PAA grafts on PE films was studied by forming derivatives with visible and fluorescent dyes. These hyperbranched films were modified by treating an activated 3-PAA/PE film with an amine terminated *p*-methyl red dye (MR) **9** or with a dansyl amine **10** to form MR/3-PAA/PE or dansyl/3-PAA/PE films, respectively. Visual inspection under a light or fluorescence microscope showed that the methyl red-labeled and fluorescently labeled films were uniform in color and fluorescence. The methyl red/3-PAA/PE film derivative showed a responsive color change with change in pH. The MR labeled 3-PAA/PE film was red after immersion in an acidic ethanol solution and yellow after treatment with a basic ethanol solution.

Since these films only contained common elements (i.e. C, O, and N), derivatives of the hyperbranched films were prepared that were more useful in XPS analysis. For example, a 3-PAA/PE film was analyzed and shown to have 67.2 atom-% C, 31.3 atom-% O, and 1.5 atom-% N by XPS analysis.
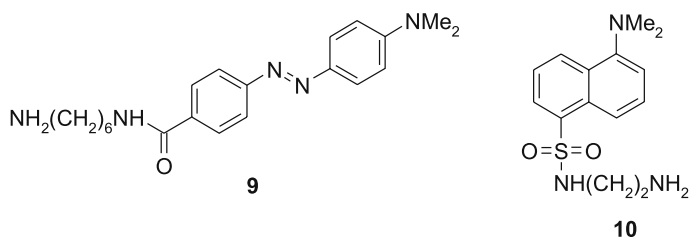
After treating the activated film with pentadecafluorooctylamine, the film contained 42.9 atom-% C, 8.9 atom-% O, 2.1 atom-% N, and 45.9 atom-% F. The fluorinated film had an advancing water contact angle of 135°, a stark contrast to the 48° water contact angle for the starting 3-PAA/PE film. Carboxylate salts formed by base treatment were also used as probes in XPS analysis [44]. For example, a 3-PAA-PE film was treated with an ethanolic CsOH solution that produced a film that contained 6.3 atom-% Cs.

2.2.1.1
Polyvalent Functionalization of Supported Hyperbranched Films

The hyperbranched poly(acrylic acid) graft films' $-CO_2H$-rich interface on polyethylene can be modified by noncovalent methods just like CO_2H-rich interfaces of PAA/Au grafts. This was shown by treating deprotonated 3-PAA/PE films with cationic polyelectrolytes like poly-D-lysine, and amine terminated PAMAM dendrimers at pH 7 [31]. Equation 10 illustrates the entrapment of PAMAM dendrimers in a 3-poly(sodium acrylate)/PE film. In these cases, polyvalent entrapment of the cationic electrolyte was evidenced in the ATR-IR spectrum by the appearance of amide $C = O$ and $N - H$ peaks of the guest dendrimer that were not present in the host 3-poly(sodium acrylate)/PE film.
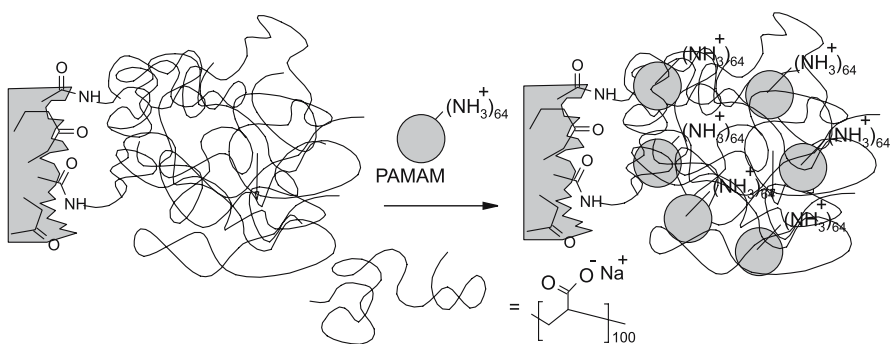
(10)

Analysis by XPS after incorporation of the linear or dendritic cationic polymers showed an increase in the atom % N consistent with incorporation of an *N*-rich polycation. The polyvalent interactions between the cationic polyelectrolytes and the poly(sodium acrylate)graftson PE were stable to Soxhlet extraction with 95% ethanol, repeated acid/base treatment, and soaking or sonication in isopropanol and THF. However, in these cases, simple acid treatment did not release the cationic polymer as was the case with PAA/Au grafts even though grafting in both cases was reportedly ionic and not covalent.

Both poly(acrylic acid)/PE and poly(acrylamide)/PE hyperbranched grafts (derived from poly(acrylic acid)/PE using ethyl chloroformate and H_2NR) can react with soluble polyacrylamide or poly(acrylic acid) reagents by hydrogen bonding. This was also shown to be a viable noncovalent method for modification of these hyperbranched grafts and constitutes a mild method for further grafting (Scheme 5) [31, 42]. In this chemistry, polymers made of hydrogen bond donors (poly(acrylic acid)) or acceptors (polyacrylamide) self assemble into the complimentary donor or acceptor hyperbranched graft interface. While a hydrogen bond is normally considered a weak bond, polyvalency magnifies the importance of each individual intermolecular hydrogen bond to produce in the aggregate strong bonding that forms a tenacious composite of the original hyperbranched graft and the added polymer [45]. This chemistry provided a readily reversible method for further grafting at a surface. For example, immersing a hydrogen-bond donating 3-PAA/PE
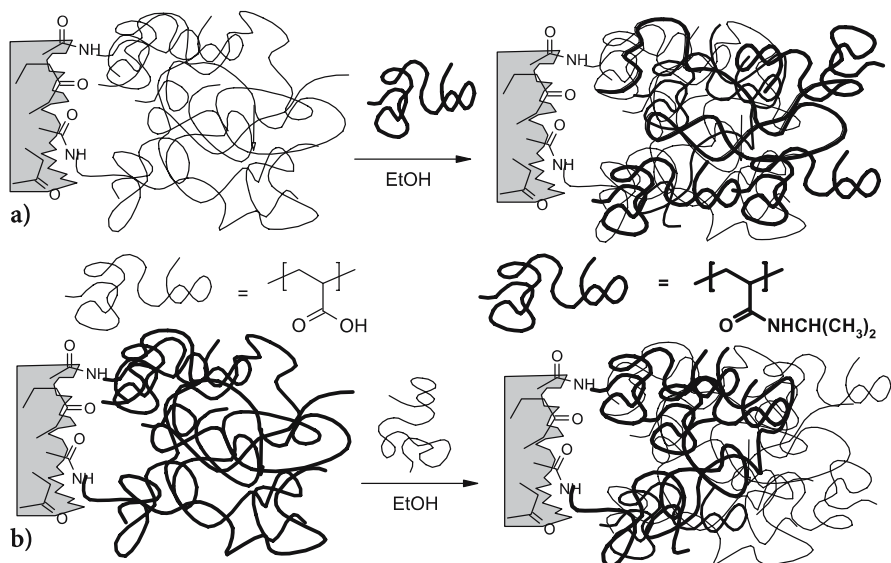
Scheme 5 Polyvalent hydrogen bonding of **a** a soluble poly(*N*-isopropylacrylamide) to a 3-PAA/PE hyperbranched graft or **b** a soluble poly(acrylic acid) to a hyperbranched poly(*N*-isopropylacrylamide) graft on PE

film into a hydrogen bond accepting poly(*N*-isopropylacrylamide) (PNIPAM) polymer solution formed a new hydrogen bond graft. This grafting was characterized by ATR-IR spectroscopy and XPS analysis. The amide peaks from the hydrogen-bond grafted PNIPAM increased in the ATR-IR spectrum of the film, and the atom concentration of N increased from ca. 1.5 atom-% N for a 3-PAA/PE film to ca. 5.8 atom-% N for the hydrogen-bond grafted 3-PAA/PE film. In these experiments, the initial 3-PAA/PE film contained a small amount of nitrogen because the film was assembled from amine-terminated poly(*tert*-butyl acrylate) oligomers and a surface-bound mixed anhydride (cf. Schemes 1 and 4).

The hyperbranched hydrogen-bond grafts formed in these self assembly processes are stable to solvent extraction. This was shown by preparing fluorescently labeled poly(*N*-isopropyl acrylamide) **11** and poly(acrylic acid) **12**.
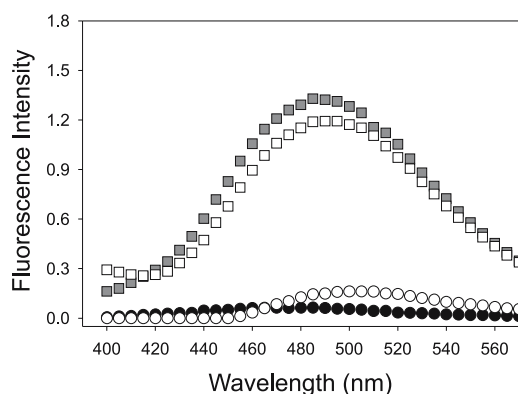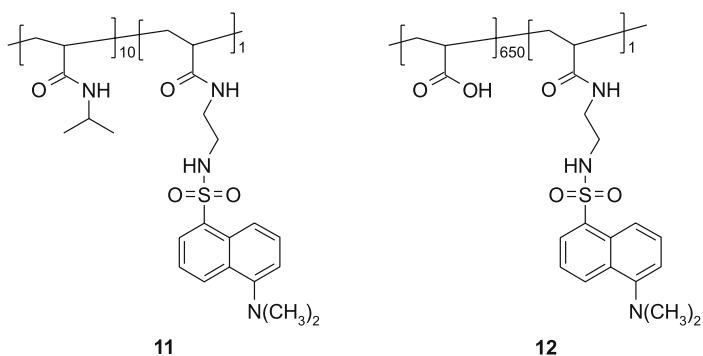

Fig. 7 Fluorescence spectra of a 5-PAA/PE graft (a) after treatment with **10** (*filled squares*); (b) after washing with THF in a Soxhlet apparatus for 24 h (*open squares*); (c) after treatment with NaOH (*open circles*). For comparison purposes, a fluorescence spectrum for an oxidized polyethylene film without any hyperbranched graft (but with $-CO_2H$ groups) that was also treated with **10** is also shown (*filled circles*)

Either fluorescently labeled polymer could self assemble into a 3-PAA/PE graft. Only the hydrogen-bond donor polymer **12** assembled into a poly(*N*-isopropylacrylamide) hyperbranched graft (prepared from 3-PAA/PE using the chemistry in Eq. 3). The fluorescent films so formed had fluorescence that was much greater in than that seen in treatment of a simple oxidized PE film with **11** or **12** (Fig. 7). Moreover, the fluorescence intensity of a hydrogen-bond grafted 3-PAA/PE film showed essentially no change after 45 h of Soxhlet extraction with THF. Reaction of the hydrogen-bond grafted 3-PAA/PE film with basic ethanol followed by THF washing led to disassembly of the hydrogen bonded graft.

2.2.1.2
Grafting onto Hyperbranched Grafts

Hyperbranched grafts have also been used as substrates for further covalent grafting chemistry. One method involved the reduction of the PAA film to poly(allyl alcohol)s which were then converted to trichloroacetate esters for $Mn_2(CO)_{10}$-promoted free radical grafting [46]. For example, a trichloroacetate-containing ester interface was used successfully in grafting of more PTBA onto the interface using $Mn_2(CO)_{10}$ and light initiation. In this case, the trichloroacetate-containing ester reacts with $Mn(CO)_5$ generated by photolysis of $Mn_2(CO)_{10}$ to form radicals that can react in surface-initiated grafting monomers in solution. Monomers that were successfully used include styrene (2 M in benzene), acrylonitrile (3 M in benzene) and *tert*-butyl acrylate (1 M in benzene) [32]. These hyperbranched poly(allyl alcohol) films were also used as scaffolds for Ce(IV) redox initiated free radical polymerization of acrylates and acrylamides [32]. This second example of free radical grafting used the known Ce(IV) redox-initiated grafting procedure [47] and was successfully used for free radical grafting of the water soluble monomers methacrylic acid, acrylic acid, acrylamide and *N*,*N*-dimethylacrylamide onto polyethylene.

Hyperbranched grafts are interfaces and functional groups within interfaces like these can interact with one another as was noted in fluorescence studies of pyrene-labeled PAA/Au grafts. Such interactions are presumably entropically disfavored as they produce a more crosslinked species. The extent to which covalent bonds can form within these functional interfaces has been studied using thiophene oligomerization [48]. Beginning with hyperbranched grafted PAA on PE films, thiophene monomers were introduced by amidation and esterification chemistry. The thiophene-derivatized grafts were then polymerized by oxidation with $FeCl_3$ (Eq. 11). The extent of oligomerization (and, indirectly, the extent to which functional groups within the interface can react with one another) was then probed spectroscopically by monitoring the characteristic emission of thiophene oligomers.

$$(11)$$
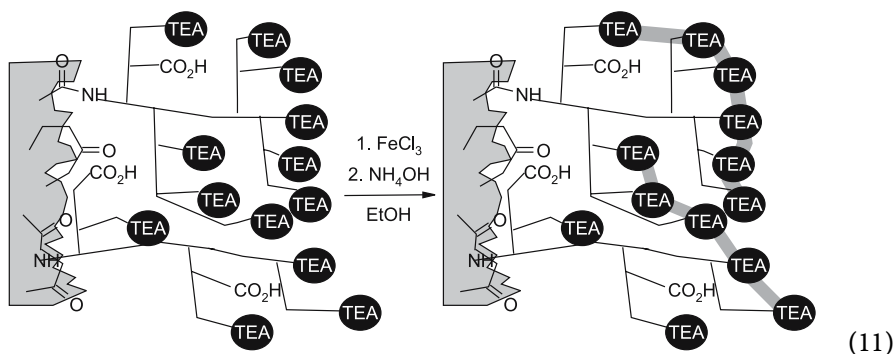
The necessary thiophene-monomer containing surface was prepared using amidation with aminothiophene derivatives or by esterification using a thiophene containing a pendant hydroxyethyl group. The amide thiophene derivative was prepared by ethyl chloroformate activation of a 3-PAA/PE interface. Subsequent reaction with 2-thiopheneethyleneamine (TEA) produced a surface that had about 50% amide based on the equal intensities of the ν_{CO_2H} and ν_{CONHAr} carbonyl peaks in the ATR-IR spectrum. The extent of amidation of the interface was increased to 65% after a second treatment. Alternatively, the 3-PAA/PE hyperbranched graft was esterified with 2-(3-thienyl)ethanol using H_2SO_4 as a catalyst. In addition to the expected appearance of amide and ester peaks in the ATR-IR spectrum of these products, an absorption at 777 cm^{-1} due to the thiophene rings was also observed confirming thiophene incorporation into the graft. The coupling yield for the esterification reaction was greater than 90%. While the yield for the esterification method is superior to the amidation chemistry, esterification involved very long reaction times (65 h) compared to 2–3 h reaction times for coupling by amidation chemistry.
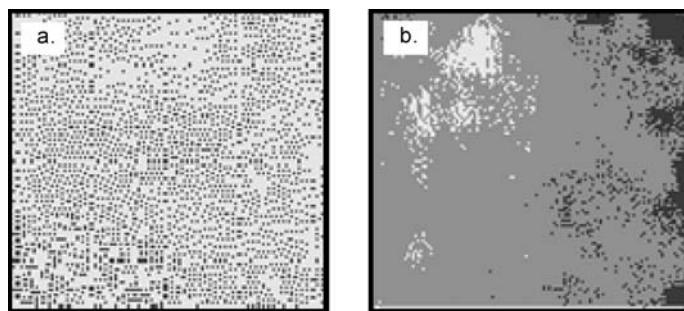

Fig. 8 Fluorescence micrograph of 0.025 mm^2 area of PE film **a** before oligothiophene formation showing no fluorescence and **b** after oligomerization show even fluorescence due to the presence of oligothiophene throughout the interface. The *figures* here are false colored *white* to show no fluorescence in (**a**) and *gray* to show fluorescence in (**b**)

Oligomerization of the immobilized thiophene monomers within the interface was accomplished using FeCl₃. The oligomerized film fluoresced under a UV lamp. The uniformity of the film was assayed by fluorescence microscopy (Fig. 8). While there are slight variations as shown in the fluorescence as shown in Fig. 8, analysis of a $50\,\mu m \times 50\,\mu m$ region of the oligothiophene-PAA/PE composite film showed less than 8% variation in fluorescence intensity. This uniformity in a 2-dimensional sense is consistent with the uniformity in coverage of the grafting seen in earlier fluorescence and UV-visible assays and with the relative smoothness of these hyperbranched grafts. Based on the known correlation between chain length and excitation and emission wavelengths, [49] the oligomerization reaction was estimated to couple 6 to 9 thiophene rings.

2.2.2
Hyperbranched Grafts on Polypropylene Wafers

Hyperbranched grafts of poly(acrylic acid) were prepared on polypropylene (PP) wafers using the same method as described for PE films [43]. Unlike the PE grafting chemistry, a carbonyl peak was not noticeable in the ATR-IR spectrum until the 2-PAA/PP grafting stage. This peak became a dominant feature in IR spectrum of the 5-PAA/PP graft. These hyperbranched grafts could be synthetically modified just like the PAA/PE films and were amenable to the same polyionic interactions as described for PE. For example, 5-PAA/PP had an advancing water contact angle of 61° that changed to 27° after formation of a sodium carboxylate salt. Likewise, formation of a fluoramide using ethyl chloroformate and $H_2NCH_2(CF_2)_6CF_3$ had 40 atom % F by XPS analysis and an advancing water contact angle of 124°.

Conversion of a 5-PAA/PP hyperbranched graft into a basic graft was accomplished by amidation using $H_2NCH_2CH_2N(CH_3)_2$ after ethyl chloroformate activation. Three cycles of this activation followed by amidation were required to achieve > 90% conversion of the $-CO_2H$ groups into aminoamide groups. The resulting basic surface that formed in this chemistry also proved amenable to modification with an acidic polymer like **13** (Eq. 12). Indeed, when this $-N(CH_3)_2$ rich surface was allowed to react with the pyrene-labeled poly(acrylic acid) **13** in a pH 7 buffer solution, a fluorescently labeled PP film formed. Subsequent treatment of this surface with 0.1 N aqueous NaOH for 2 h disassembled this ionic assembly (Fig. 9).

Given that significant amounts of poly(acrylic acid) were introduced onto a polypropylene wafer's surface and given that polar polymers can penetrate into this interface it is not surprising that hyperbranched grafting affects polypropylene's mechanical adhesion strength [43]. Adhesion tests comparing the adhesive strengths of hyperbranched grafted PP and unmodified PP using a double cantilever beam test with a commercially available epoxy adhesive showed that the adhesion strength as measured by the critical strain
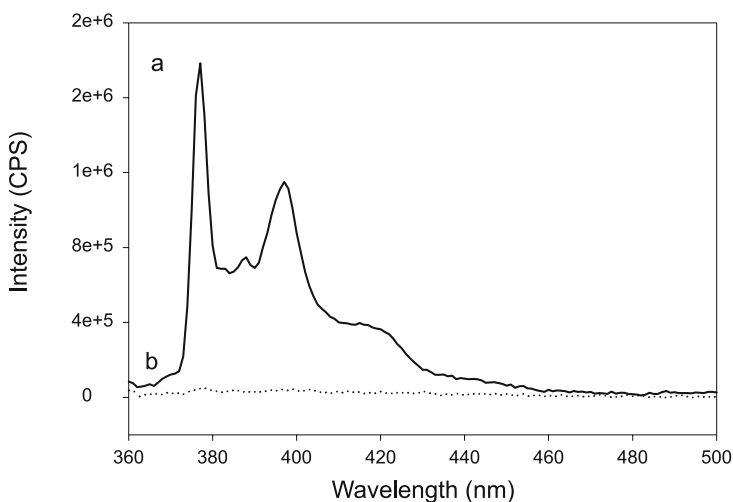
Fig. 9 Fluorescence spectra of a 5-PAA/PP wafer that was first aminoamidated with $NH_2CH_2CH_2N(CH_3)_2$ and then treated with **11** in a pH 7 buffer. The first spectrum (a) is the ionic assembly that forms at pH 7 from ion pairing of $-N(CH_3)_2H^+$ groups of the graft with $-CO_2^-$ groups of the poly(acrylic acid). The second spectrum (b) shows complete removal of **11** after treatment of the interface with 0.1 N NaOH (which converts the $-N(CH_3)_2H^+$ groups to $-N(CH_3)_2$ groups)

energy release rate of unmodified but physically roughened PP was $2\,J/m^2$ while this same value for grafted PP averaged ranged from $20-30\,J/m^2$.

$$(12)$$
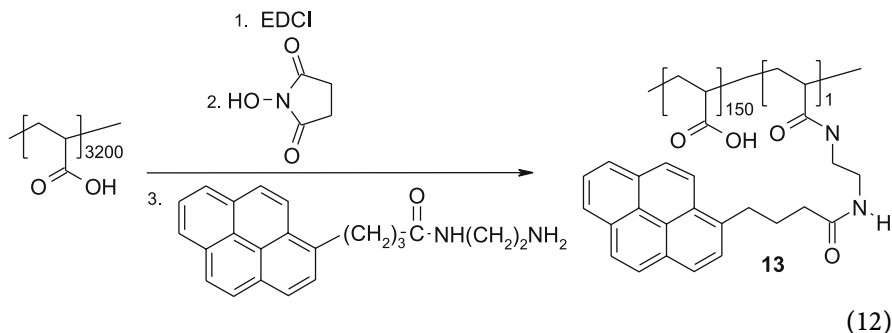
2.2.3
Hyperbranched Grafts on Polyethylene Powders

The hyperbranched grafting chemistry used with polyolefin films and wafers was also extended to modification of 200 µm diameter high density PE powder substrates [19]. However, because of the relatively high surface area of the 200 µm-diameter polyethylene powder (the measured BET surface area was

$0.7 \, m^2/g$), hyperbranched grafting produced a titratable amount of CO_2H groups PAA after only a few stages of grafting. For example, while a 1-PAA/PE powder had a virtually undetectable ca. $0.02 \, mmol$ of $-CO_2H/g$ of powder, a 4-PAA/PE powder sample had $0.4 \, mmol$ of $-CO_2H/g$ of powder. Analysis by titrimetry of the increase in $[CO_2H]/graft$ stage directly paralleled the results seen in thickness changes based on ellipsometric analysis for PAA hyperbranched grafts on gold (Fig. 1).

The chemistry and procedures for modification of the $-CO_2H$ groups of PAA hyperbranched grafts on PE powder were analogous to those used for PAA grafts on PE or PP films and wafers. For example, a 90% yield in ester formation was possible using acid-catalyzed Fisher esterification. Likewise, quantitative reduction (ethyl chloroformate activation, borane-dimethyl sulfide reduction) to hyperbranched poly(allyl alcohol)s and amidation all could be carried out using procedures like those used for PAA/Au surfaces.

2.2.3.1
Hyperbranched Grafts as Catalyst Supports

Polyethylene powders that have been modified with hyperbranched grafts were shown to be useful as supports for both heterogeneous and homogeneous Pd(0) catalysts. In the first example of this chemistry, a route to dispersions of Pd(0) crystallites that are active hydrogenation catalysts was described. The catalysts were synthesized by first exchanging the poly(sodium acrylate) grafts with $Pd(OAc)_2$. The Pd(II)-containing hyperbranched graft that resulted was then exposed to H_2, forming Pd(0) (Eq. 13).


$$= Pd(0)$$
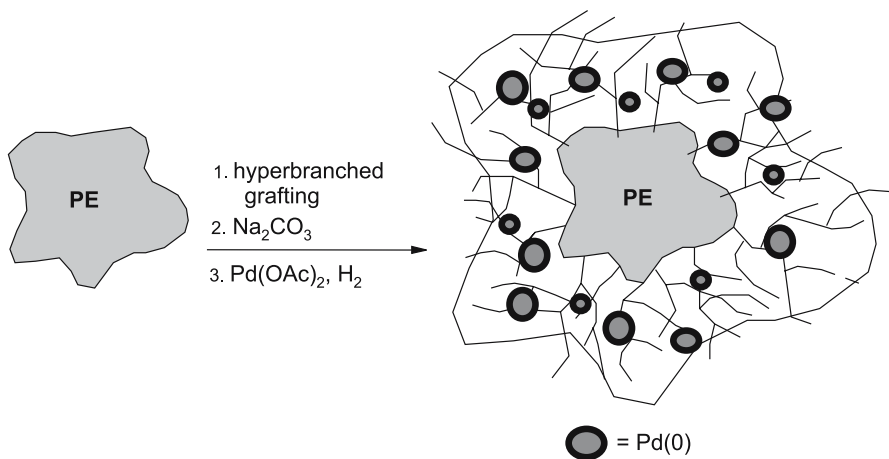
(13)

These Pd colloids dispersed in a poly(acrylic acid) interface were essentially a supported Pd/poly(acrylic acid) nanocomposite and these nanocom-

posite catalysts were shown to have excellent reactivity in simple hydrogenations. Limited studies showed that these catalysts were also active in other Pd(0) chemistry (e.g. in Suzuki couplings) [50]. An attractive feature of these hyperbranched graft Pd nanocomposites supported on PE powder was the physical stability of the support. For example, these PE-supported catalysts had the physical robustness associated with the bulk PE support. They did not require special procedures such as a "tea bag" to prevent the physical degradation seen with more commonly used polystyrene-supported catalysts [51, 52].

Hyperbranched grafts on PE powder were also suitable as supports for analogs of homogeneous phosphines-ligated Pd(0) catalysts (Eq. 14) [53]. In this case, a phosphine ligand was first introduced into the poly(acrylic acid) hyperbranched graft by reaction of a ethyl chloroformate activated 4-PAA/PE graft with 3-diphenylphosphinopropyl amine. The resulting 3-diphenylphosphinopropyl amide-containing polymer was then treated with Pd(dba)$_2$ to form a yellow polyethylene powder-supported phosphine-ligated Pd(0) catalyst. This catalyst was active in allylic amination chemistry and was shown to be recyclable for up to 5 cycles. As is true for homogeneous phosphines-ligated Pd(0) catalysts, exposure of the catalyst to adventitious oxygen oxidized the phosphines ligands leading to a darkening of the support due to formation of Pd colloids.

$$\tag{14}$$
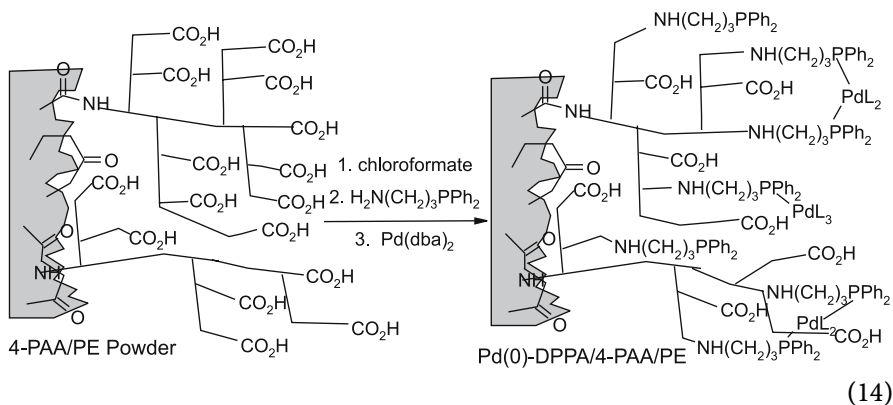
Because of the relatively high loading of functional groups on these hyperbranched PE powders, it was feasible to characterize the products and intermediates in this catalysts synthesis by ^{31}P CP-MAS NMR spectroscopy, ATR-IR spectroscopy, and XPS analysis. ^{31}P CP-MAS NMR spectroscopy was especially useful for in distinguishing the phosphinated powder, phosphine-palladium complex, and any adventitiously formed phosphine oxide. Similar NMR analyses were not successfully carried out on hyperbranched grafts on PE films. However, when this same phosphine ligand synthesis and introduction of Pd was carried out on a PE film sample, it was possible to analyze

the products by XPS spectroscopy. In that case, multipoint XPS analysis over a 1 mm^2 region of a Pd(0)-DPAA/3-PAA/PE film showed that the P/Pd ratio varied only 2% from the expected 3/1 value indicating both that the complex immobilized was similar to that seen in solution and that the functionalization was homogeneous in a two dimensional sense.

3
Hyperbranched Nanocomposites

Hyperbranched multilayer composites prepared by condensation reactions of amine-containing polymers and commercially available electrophilic polymers like poly(maleic anhydride)-*c*-poly(methyl vinyl ether) (Gantrez) copolymers are a second type of covalent hyperbranched polyfunctional graft. These hyperbranched nanocomposite grafts have been prepared using glass, silicon, gold, aluminum, alumina and polymers as substrates [54–57]. A typical synthesis scheme leading to these sorts of ultrathin-film nanocomposites composites starting with amine-functionalized silicon using a 4th generation – NH$_2$-functionalized PAMAM dendrimer is shown in Scheme 6. In this instance, the synthesis began with an amine-rich silicon surface that was prepared by modification of the native oxide layer of silicon with aminopropyltriethoxysilane. This resulting amine-rich surface was first treated with the polyanhydride polymer Gantrez. Since an excess of Gantrez was used, this produced a new surface that contained some amic acids from reaction of surface-bound amines and anhydrides of the Gantrez copolymer along with a large excess of unreacted anhydride groups. Even though all the amines at the surface probably did not react, the surface at this stage mostly contained unreacted anhydride groups. This new anhydride-rich, electrophilic surface was then allowed to react with a dendrimer that contained nucleophilic – OH or – NH$_2$ groups on its periphery. Both PAMAM dendrimers and cascade dendrimers were successfully used in this chemistry. This reaction also used an excess of the solution-phase reagent. The resulting surface contained covalently bound dendrimers that were attached to the anhydrides via acid-ester or acid-amide (amic acid) bonds. Since an excess of the dendrimer was used, the surface was at this point rich in dendrimer and thus rich in – OH or – NH$_2$ groups. At this stage, unreacted anhydride groups from the earlier stage presumably had reacted with the reaction solvent ethanol to form acid-ester groups and were not involved further in this covalent assembly chemistry. Repetition of this sequence of reactions served to build up a covalent composite of dendrimer and the polyanhydride polymer layer by layer with covalent amic acid or ester links between the reactive components.

The progress of these reactions was followed by various techniques (Table 2). Ellipsometric analysis showed that the increase in film thickness after treating a silicon/Gantrez film with a fourth-generation PAMAM den-
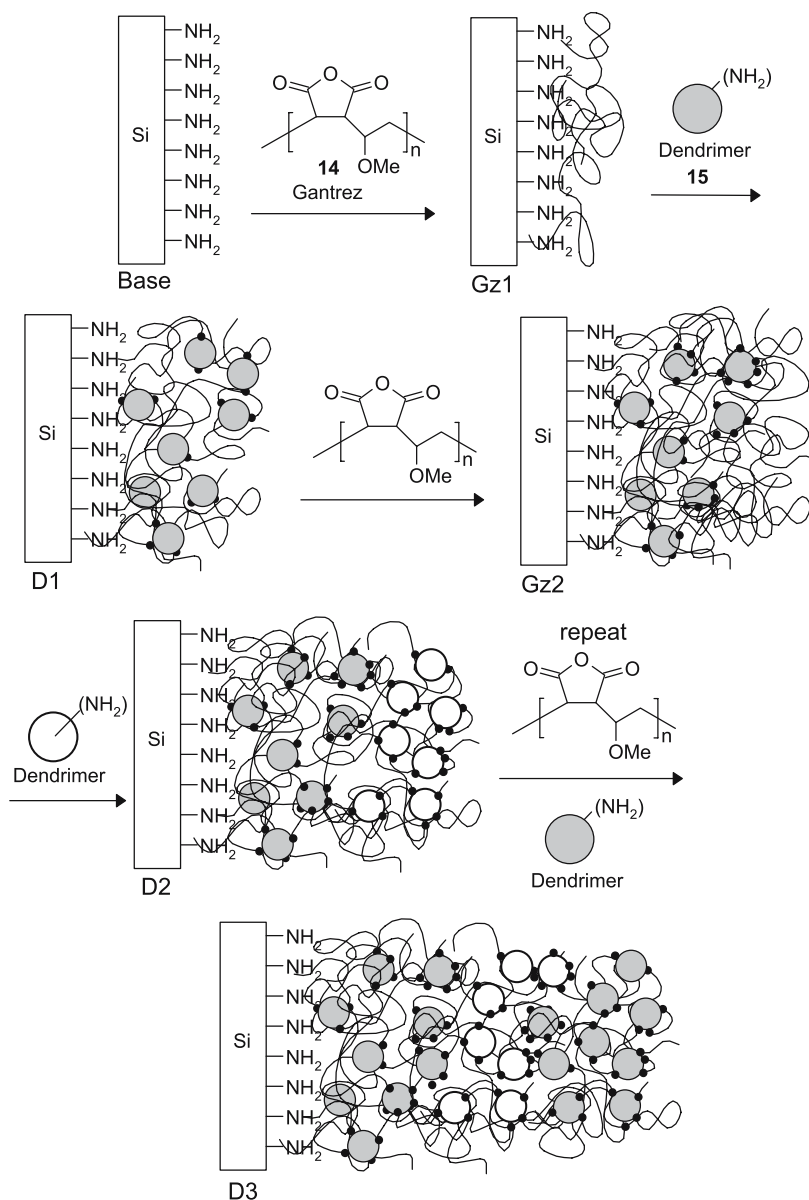
Scheme 6 Formation of hyperbranched thin film nanocomposites using an electrophilic polymeric reagent **14** and a nucleophilic amine-functionalized PAMAM dendrimer **15**

drimer was greater than the diameter of the dendrimer indicating that the dendrimer addition steps in the process incorporate more dendrimer than a single dendrimer monolayer. Similar ellipsometric analysis of the increased

Table 2 Contact angle measurements, XPS analysis, and ellipsometric thickness of Gantrez/4th Generation PAMAM dendrimer composites

	Θ_a (°)	% C	% O	% Si	% N	Thickness (nm)
Base	64	30	37	28	4.9	4.2
Gz1	70	64	31	3	0.8	6.7
D1	31	68	20	0	12.0	14.6
Gz2	56	69	30	0	1.8	19.3
D2	31	65	19	0	17.0	29.4
Gz3	55	—	—	—	—	34.9
D3	29	67	17	0	16.0	45.9
D3 (+ Δ)	97	69	16	0	14.0	39.1

thickness for the second and subsequent synthetic steps where polyanhydride polymer was added to the dendrimer-rich surface also showed that the increase in thickness for this step was greater than that seen in the addition of the first Gantrez layer to the aminated silicon surface.

The thickness of these PAMAM dendrimer/Gantrez composites is slightly dependent on the dendrimer size. For example, composites that are made with a smaller second-generation PAMAM dendrimer were shown to have an ellipsometric thickness of 33 nm at the D3 stage, compared to 46 nm for the larger fourth generation dendrimer. The molecular weight of the Gantrez used in this chemistry did not have an effect on the interface thickness.

Syntheses of similar nanocomposites on substrates such as gold, aluminum, and functionalized polymers have also been carried out with the main differences being in the first steps of the reaction. For example, in the case of gold, the initial step involved activating the $-CO_2H$ groups in a monolayer of MUA by ethyl chloroformate and treating this material with the dendrimer. Alternatively films that are composed of $-OH$ terminated dendrimers on Au substrates were used as substrates. In this case, a hyperbranched nanocomposite graft was prepared by allowing this monolayer of 11-mercaptoundecanol to react first with the polyanhydride polymer and then with the hydroxyl-terminated dendrimer. In the case of aluminum substrates, the native oxide layer at the surface was reactive enough to immobilize a thin film of Gantrez directly to the surface to produce the first layer.

The films formed in these covalent layer-by-layer assembly procedures are similar to the ionic assemblies prepared by other layer-by-layer self assembly procedures. Unlike the more defined Langmuir-Blodgett multilayer assemblies that have well defined layers, the layers of electrophilic polymer and nucleophilic polymer are intermixed to an extent. Similar effects are seen in ionic layer-by-layer assemblies.

Most applications of these nanocomposite films have focused on the effects of these films on the electrochemical reactivity of their metal supports. For

example, the hyperbranched nanocomposite graft formed in Scheme 6 was used as a pH-switchable permselective supported membrane. In this case, the nanocomposite formed in this chemistry consisted of $-CO_2R$, $-CONHR'$, $-CO_2H$ and NH_2 groups. When placed in an acidic solution, this amphoteric supported membrane contained $-CO_2H$ and $-NH_3^+$ groups and was net cationic. Under these conditions, it was impermeable to electroactive cations like $Ru(NH_3)_6^{3+}$ but permeable to electroactive anions like $Fe(CN)_6^3$ (Fig. 10). Under basic conditions, this same nanocomposite film contained $-CO_2^-$ and $-NH_2$ groups and had a net anionic charge. Under these conditions, the film was only permeable to cations. At neutral conditions, this supported amphoteric membrane was permeable to both cations and anions [54]. Similarly made dendrimer/Gantrez composites prepared on high-surface-area alumina have been described by Crooks' group. These latter films on alumina substrates limit or prevent the adsorption of vapor phase volatile organic hydrocarbons to the alumina substrate with the extent of this effect depending on the film thickness [57]. This effect of hyperbranched film structure on permeability was also seen with other hyperbranched grafts as noted earlier [25, 27].

Thermal treatment of the nanocomposite film formed in Scheme 6 converts the amic acid groups of the film to imides (Eq. 15). In addition to evidence by IR spectroscopy, ellipsometry showed that the film thickness decreased by ca. 15% and contact angle goniometry showed that the film became more hydrophobic (see Table 2). This thermally treated film also did not have the pH dependent permeability of redox-active ions previously described for dendrimer/Gantrez films on gold substrates [55].
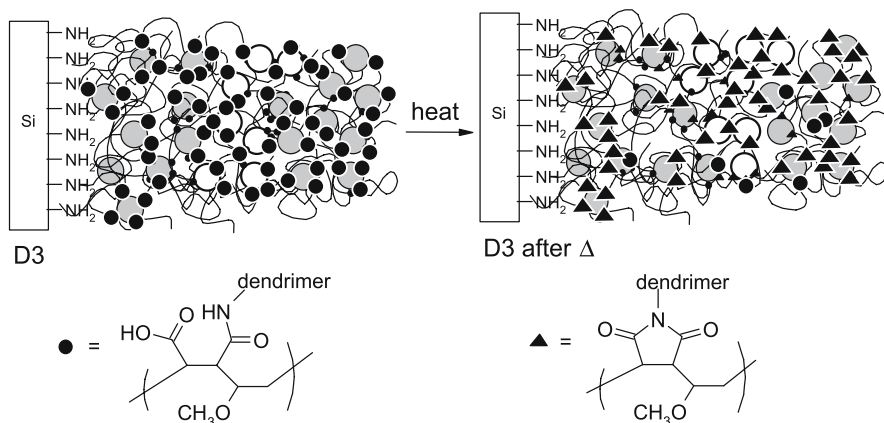
(15)

Indeed, the thermally treated film was completely impermeable to either anion. The very low permeability of these films was explained by the notion
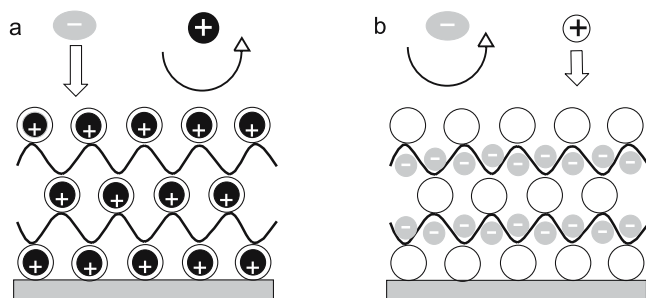
Fig. 10 pH-Dependent permeability of the anions $Fe(CN)_6^{3-}$ and the cation $Ru(NH_3)_6^{3+}$ in nanocomposite dendrimer-poly(maleic anhydride) grafts that contain $-CO_2H/-CO_2^-$ and $NH_2/-NH_3^+$ groups in the film with **a** anion permeability at low pH where the $-NH_2$ groups in the film are protonated; and **b** cation permeability at high pH where the $-NH_2$ groups in the film are neutral and the $-CO_2^-$ groups make the film anionic

that these interfaces are thin film thermosets. Along with imide formation, multilayer composites based on PAMAM/Gantrez films are expected to undergo retro-Michael addition reactions to form free amines and acrylamides (Fig. 11). Reversal of this retro-Michael reaction in both an intra- and inter-dendrimer sense is expected to produce a highly crosslinked film. Crosslinks are presumably also formed from amines (either unreacted amines or amines
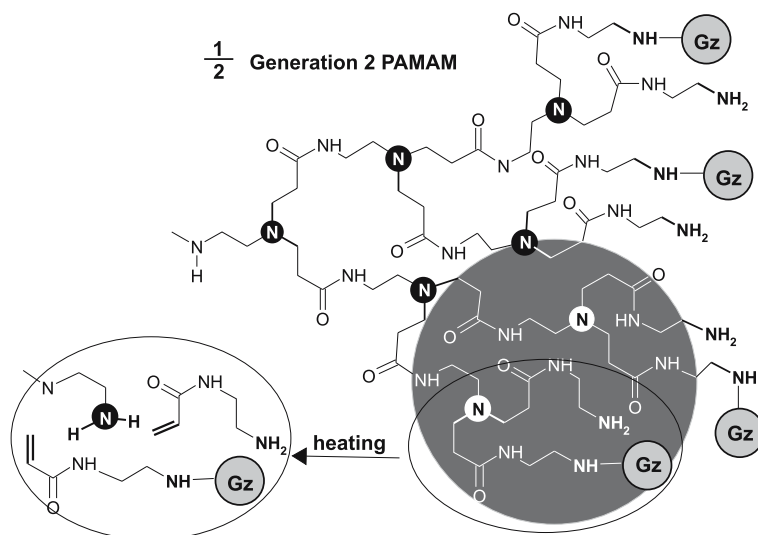

Fig. 11 In situ formation of amine nucleophiles and α,β-unsaturated carboxamides that react further in thermosetting of hyperbranched dendrimer-polyanhydride nanocomposite thin films

formed in situ) undergoing additional imide formation with half acid-half ester groups from anhydrides that did not form amic acids in earlier steps.

In work like that described in Scheme 6, Bruening reported the synthesis of multilayer composites by alternating deposition of Gantrez and the linear polyvalent nucleophile poly(allylamine) [58]. The impermeable films that were produced by this multistep hyperbranched graft chemistry were shown to passivate aluminum surfaces.

An approach that is related to these examples was used in the preparation of hyperbranced surfaces useful in conjugation of biological substrates like polynucleotides to surfaces [59]. In this chemistry (Eq. 16), an amine-functionalized glass slide was first activated by treatment with trifunctional cyanuric chloride (**16**). The selective reaction of the most reactive chloride [60] of the cyanuric chloride with the amine groups of the surface introduces a dichlorotriazene. One or both of the remaining chloride leaving groups of the triazene was then allowed to undergo a nucleophilic aromatic substitution reaction with hyperbranched polyethyleneimine (PEI). The resulting hyperbranched amine-rich surface that formed was then allowed to react with more cyanuric chloride. In chemistry that is conceptually like that in Scheme 6, this led to an electrophilic dichlorotriazene-rich surface with some crosslinked PEI. While this process could have been continued, at this point these surfaces were used to bind polynucleotides.

$$(16)$$
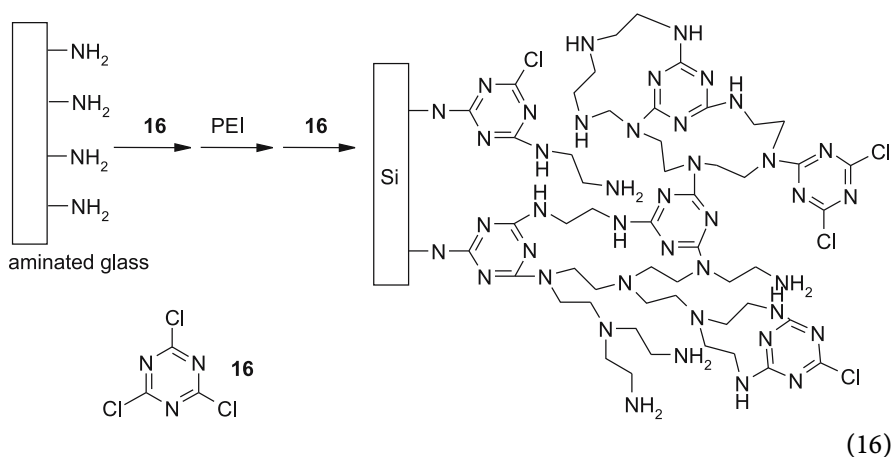
4
Hyperbranched Grafting by Surface Initiated Ring Opening Polymerization

Thus far this review has emphasized methods of producing hyperbranched grafts using graft-on-a-graft chemistry involving condensation of a carboxylic acid derivative with an amine or hydroxy nucleophile. This chemistry

typically requires activation of a surface bound carboxylic acid or the use of activated carboxylic acid derivatives. In most cases, it requires the preparation of suitable functionalized polymers for grafting too, though commercially available materials are used in some instances. Alternative strategies for grafting rely on ring opening polymerizations. These strategies include ring opening polymerizations using heteroatom nucleophiles [61–65] and ring-opening metathesis polymerization (ROMP) [66–71]. Both of these synthetic methods have been used to produce linear grafts on surfaces. Hyperbranched grafts can also be produced from ring opening polymerizations using multifunctional monomers or monomers that produce polyvalent nucleophiles. Recent work by both Huck's [72] and Park's [73, 74] groups show how hyperbranched grafts can be prepared by ring opening polymerization. This approach of hyperbranched grafting from a monomer is particularly attractive since it can eliminate the repetitive steps that are typically involved in producing hyperbranched thin films.

4.1
Grafting Hyperbranched Polyglycidol

Huck's group recently explored new hyperbranched grafting syntheses using Si – OH groups as initiators for the anionic ring opening polymerization of glycidol [72]. This grafting chemistry shown in Eq. 17 begins with deprotonation of the Si – OH surface with sodium methoxide. This deprotonated surface (initiator) is then dried and immersed in the neat glycidol monomer and heated at 110 °C. The polymerization reaction begins with the anionic surface attacking the less substituted epoxide carbon. This forms an ether bond and secondary alkoxide group that can react with another monomer or generate a primary alkoxide nucleophile by proton transfer of the neighboring primary alcohol. The mechanism of growth was studied by ellipsometry. For thicker films, mulitple cycles could be used. In subsequent cycles, the grafted polyglycidol is again deprotonated by treatment with sodium methoxide and the resulting anionic surface is immersed in more monomer. Ellipsometry showed that these films grew to 15 nm in a single reaction and that this thickness could be increased to ca. 70 nm after a third cycle. The increase in thickness from cycle to cycle increased after each grafting stage. This change in thickness in each cycle was explained by assuming that the initiator concentration (the hydroxyl groups of the grafted polyglycidol) was increasing from cycle to cycle and is similar in concept to what was seen in hyperbranched grafting via condensation polymerization (Fig. 1).

In this example of hyperbranched grafting, it was possible to study the grafted polyglycidol polymer by NMR spectroscopy. While the surface graft was not studied in situ, it was possible to characterize a graft after cleavage of the graft polymer from a surface. To accomplish this, a hyperbranched grafted material was prepared on a higher surface area support. The product

polymer was then cleaved from the support and analyzed by NMR spectroscopy. For this experiment, silica gel was used as the substrate for grafting

$$(17)$$
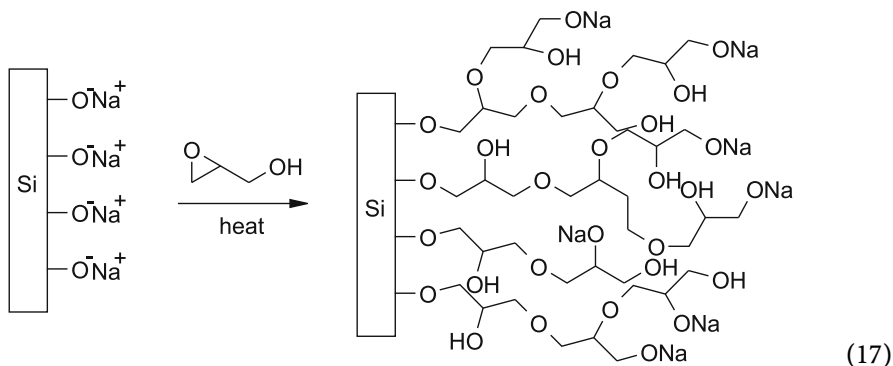
and the polymer was cleaved from this support using HF. The recovered polymer was studied by ^{13}C NMR spectroscopy. The degree of branching (DB) was determined to be 0.31 using the peak intensities of known peaks in the ^{13}C NMR spectrum. This contrasted with the degree of branching of 0.46 for polyglycidol prepared from bulk polymerization of glycidol using 1,1,1-(trishydroxymethyl)propane as an initiator. The differences between the solution polymer and the hyperbranched graft were rationalized by assuming that the lower degree of branching for the surface initiated hyperbranched polyglycidol was due to high monomer to initiator ratios. This change was presumed to lead to higher propagation rates. The higher steric demands of a surface-initiated polymerization were also assumed to be important. The cleaved polymer was also characterized by gel permeation chromatography which showed that the product had an M_n of 5800 and polydispersity (M_w/M_n) of 1.8.

4.2
Grafting of Hyperbranched Poly(ethyleneimine)

Park's group has explored hyperbranched graft chemistry of aziridine on amine functionalized silica surfaces (Eqs. 18 and 19) [74]. Using silicon and silica substrates that have been functionalized with (3-aminopropyl)diethoxymethylsilane as initiator substrates, hyperbranched polyethyleneimine grafts were synthesized using aziridine monomers.

The growth of these films was characterized by measuring the ellipsometric thickness and measuring the concentration of primary amine groups in the grafts using an indirect spectrophotometric assay for the amount of amine groups. The method used to determine the concentration of primary amines contained within the interface was to first form an imine of surface-bound amines with 4-nitrobenzaldehyde using a surface with known surface

area. The surface-bound imine was then separated from excess soluble ben-
zaldehyde and then hydrolyzed to generate a solution of the aldehyde amines
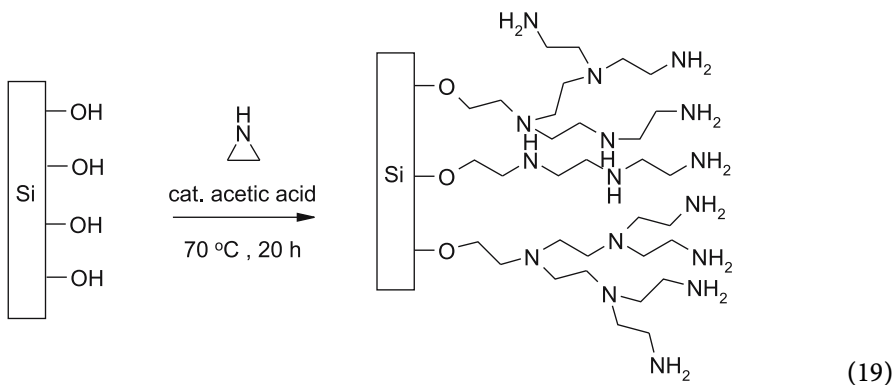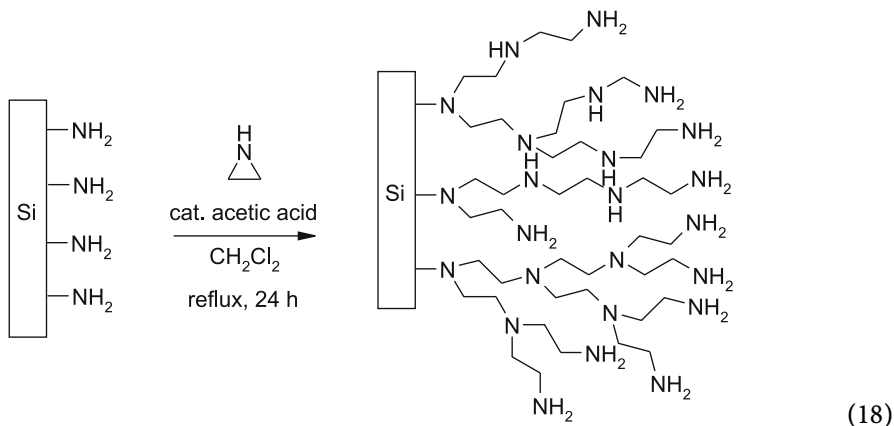
(18)

(19)

contained within the interface was to first form an imine of surface-bound
amines with 4-nitrobenzaldehyde using a surface with known surface area.
The surface-bound imine was then separated from excess soluble benzalde-
hyde and then hydrolyzed to generate a solution of the aldehyde that was
analyzed by UV-visible spectroscopy [75]. A starting surface that had been
functionalized with (3-aminopropyl)diethoxymethylsilane was shown to have
3.5 amines/nm^2 and a film thickness of 8 Å. After a typical reaction with
aziridine, the film thickness increased to 36 Å. By assaying the change in
surface density of primary amines with time, it was possible to show that
this grafting was producing a hyperbranched polymeric graft. The surface
density of primary amines was measured to be 66 amines/nm^2 after reac-
tion of the amine-functionalized surface with aziridine for 24 h. This cor-
responds to a very dense graft with a concentration of 18 amines/nm^3.
The maximum concentration of total amines for polyethyleneimine assum-
ing that polyethyleneimine has a density of 1 g/cm^3 would be ca. 14 amine

groups/nm^3. This increase in density of amine groups is in accord with formation of a hyperbranched graft and is presumed to be the result of re-action of the secondary amines of a linear graft with aziridine monomer. If the secondary amines were not reactive and if no hyperbranching had oc-curred, the original density of primary amine groups would have remained constant.

Park's group later reported the hyperbranched grafting of aziridine to fused silica, silicon wafers, and glass [73]. Grafting was achieved by heat-ing the aziridine monomer solution containing a catalytic amount of acetic acid to 70 °C in the presence of a cleaned silica substrate. The thickness and primary amine density increased rapidly during the first 10 h and reach a maximum after 40 h. After grafting for 20 h the thickness of the graft layer as determined to be 27 Å and the primary amine density was reported to be 23 amines/nm^2.

5
# Hyperbranched Grafts of Organic/Inorganic Hybrid Polymers

While polymers most commonly consist of carbon, nitrogen and oxygen, hy-brid materials containing metals or other elements represent an important class of materials [76–78]. Hybrid materials too have been used as hyper-branched grafts. Two examples of such materials are described here. The first is a polysiloxane graft. The second is a dendritic coordination polymer based on a thermally and oxygen stable Pd(II) pincer complex [79].

5.1
Polysiloxane Hyperbranched Grafts

The synthesis of branched polysiloxane grafts on silica surfaces has recently been described [80]. This chemistry involves grafting a living anionic silox-ane polymer onto a surface that contains reactive Si – Cl groups (Scheme 7). The living polymers were prepared by anionic ring opening polymerization of cyclotrisiloxane monomer(s) using butyllithium initiator. By taking advan-tage of reactivity ratios for the anionic copolymerization of monomers **17** and **18**, a copolymer grafting agent was prepared that had functional vinyl groups more concentrated at one end of the graft oligomer. Thus, the re-sulting grafted surface contained more vinyl groups on the periphery of the graft. The new vinyl groups of these grafted surfaces were then modified to include more Si – Cl groups by a second platinum catalyzed hydrosilyla-tion using HSiCl(CH$_3$)$_2$. Branched polysiloxane grafts on silica particles were prepared by treating this activated surface with yet another batch of living an-ionic siloxane copolymer grafting agent. This chemistry was been extended to the synthesis of branched polysiloxane grafts with phosphine ligands for im-
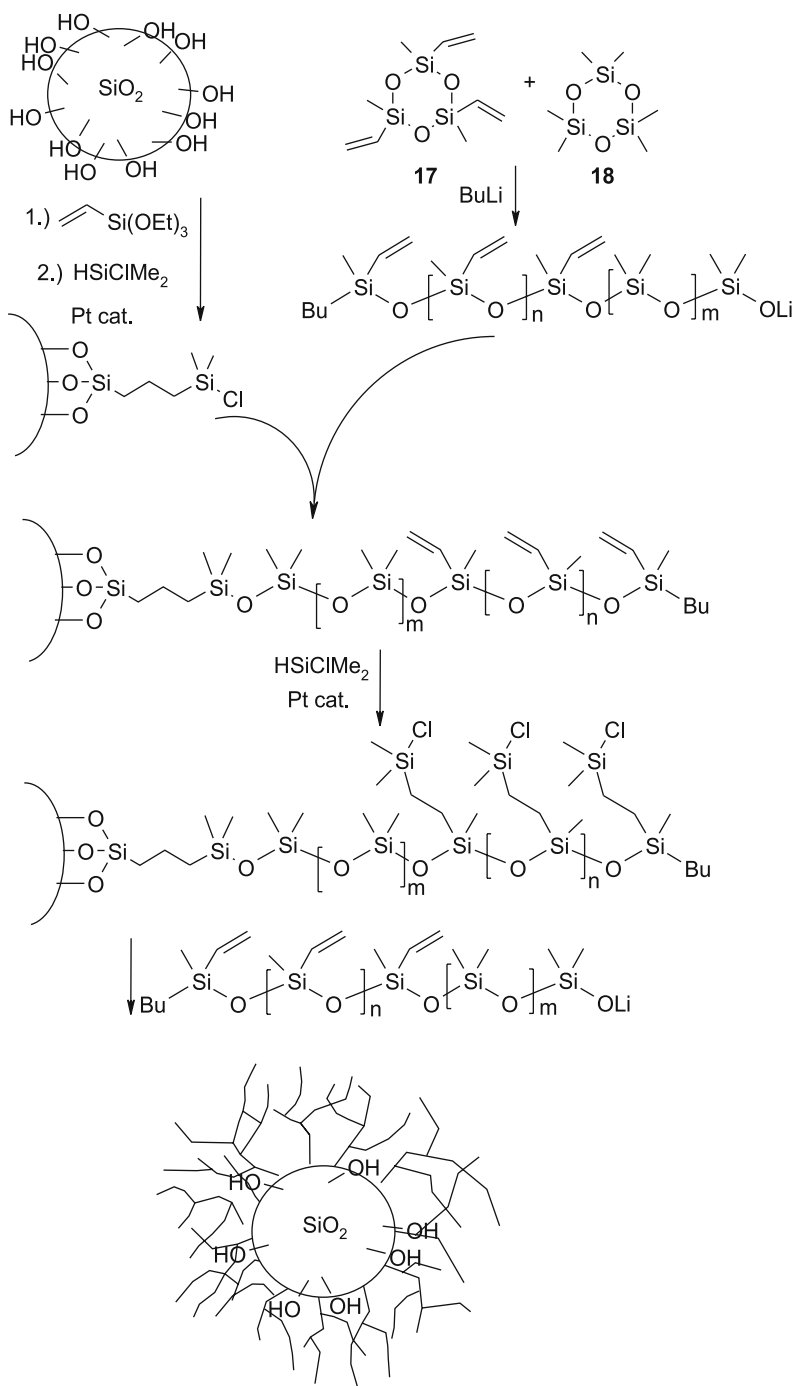
Scheme 7 Synthesis of hyperbranched polysiloxane grafts on silica

PPh₂
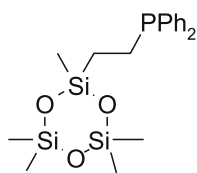
19

mobilization of transition metal catalysts [81, 82]. The living anionic siloxane polymer containing phosphine groups necessary for this latter chemistry was synthesized by ring opening polymerization of **19**.

5.2
### Dendritic Hyperbranched Grafts of Pd(II) Coordination Polymers

Pincer compounds with a general structure like **20** are common in organo-metallic chemistry [832]. They are useful as precursors to catalysts and as components of hybrid organometallic polymers [84–86]. In most cases, they have high stability to oxygen and water in addition to high thermal stability.

A recent report described the use of a pincer compound like the so-called SCS-Pd(II) complexe **20** in formation of dendritic grafts on gold surfaces [88]. In this chemistry, the organometallic dendrimer **21** was prepared in solution and then immobilized on gold as part of a self assembled monolayer. The di-alkyl sulfide group on the dendrimer binds to the surface at defects in the self assembled monolayer surface. Tapping-mode atomic force micrscopy was used to show that these organometallic dendrimers were incorporated onto the gold surface with their concentration on gold being dependent on the length time the self assembled monolayer was exposed to **21**.

Similar SCS-Pd(II) complexes have also been used to prepare isolated nanometer-sized objects within a decanethiol self assembled monolayer on gold [88]. In this chemistry, the thioether derivative of a pyridine complex of the SCS-Pd(II) complex **22** was first prepared and immobilized on gold as part of a self assembled monolayer. Then the much better phosphine ligand

Ligand .... Metal .... Ligand
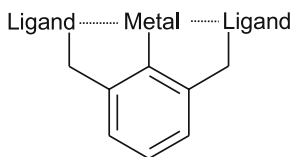
20
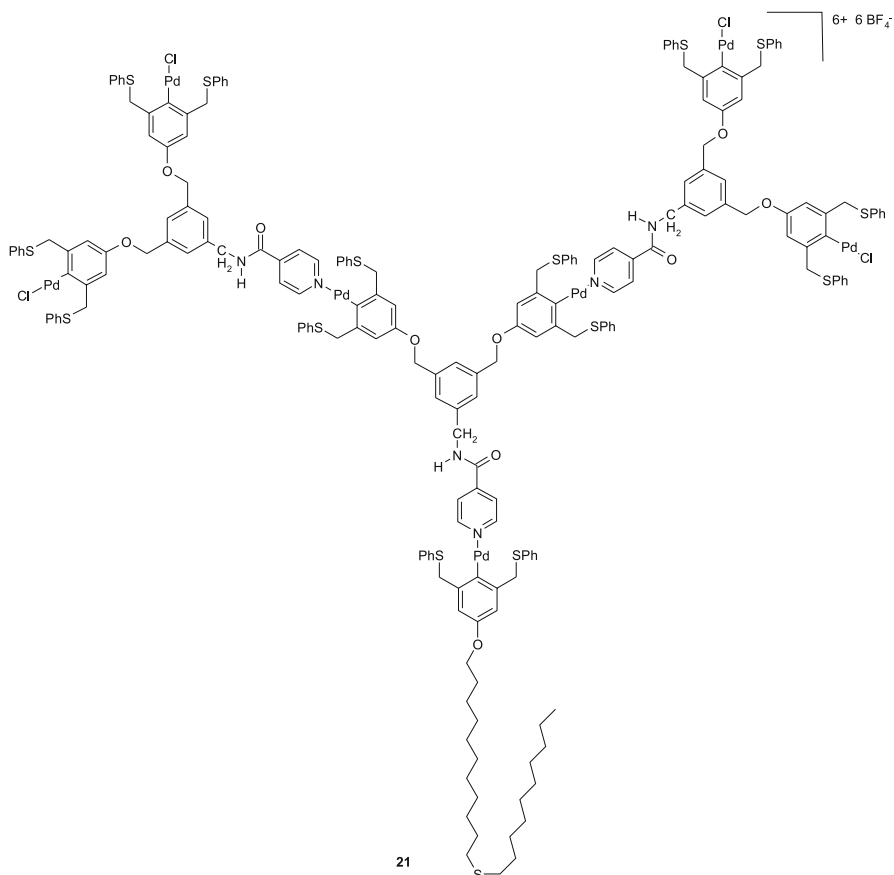
23 was added to form a dendritic graft (Eq. 20). This reaction was facilitated by the fact that the necessary ligand exchange chemistry is quantitative and rapid. Extensions of this chemistry would lead to Pd-based organometallic dendrimers on gold. In this initial report, the isolated complexes **24** were characterized by tapping-mode atomic force microscopy. The height of the dendritic graft that was exposed above the decanethiol monolayer was 4.3 nm, in rough agreement with computer modeling that predicted a height for the dendritic unit of 3.4 nm.

(20)
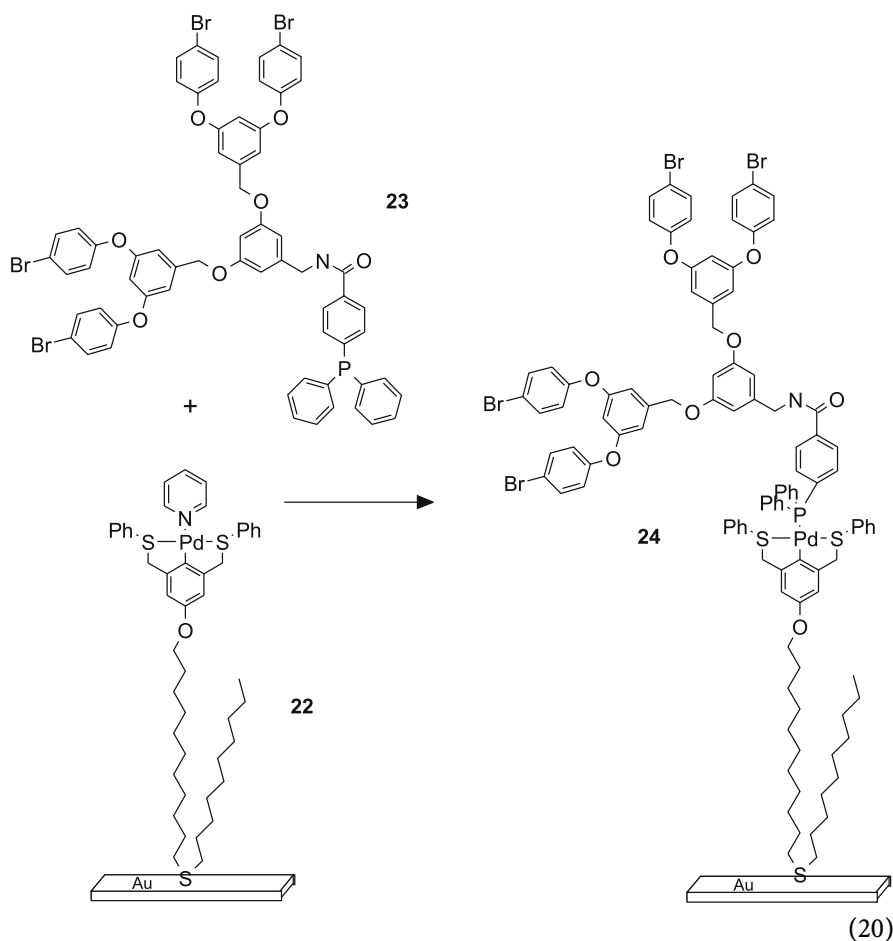
6
# Dendrimer Analogs as Hyperbranched Grafts

Hyperbranched poly(amidoamidoamine) (PAMAM) polymers have been grafted on carbon black [89], chitosan [90], glass fibers [91], silica [92–95] and polyethylene [96]. This grafting chemistry introduces highly branched surface immobilized polymers that are better described as hyperbranched polymers rather than dendrimers based on the evidence of incomplete reactions as shown in Scheme 8. The hyperbranched polyamidoamine grafts were synthesized by a two step process from an amine functionalized surface. The hyperbranched grafting in this case involved Michael addition of methyl acrylate to the amine-functionalized surface. Amidation of the resulting surface-bound esters with ethylenediamine then formed a new amine-rich surface. The results were surfaces with amine-rich grafts that could be ana-
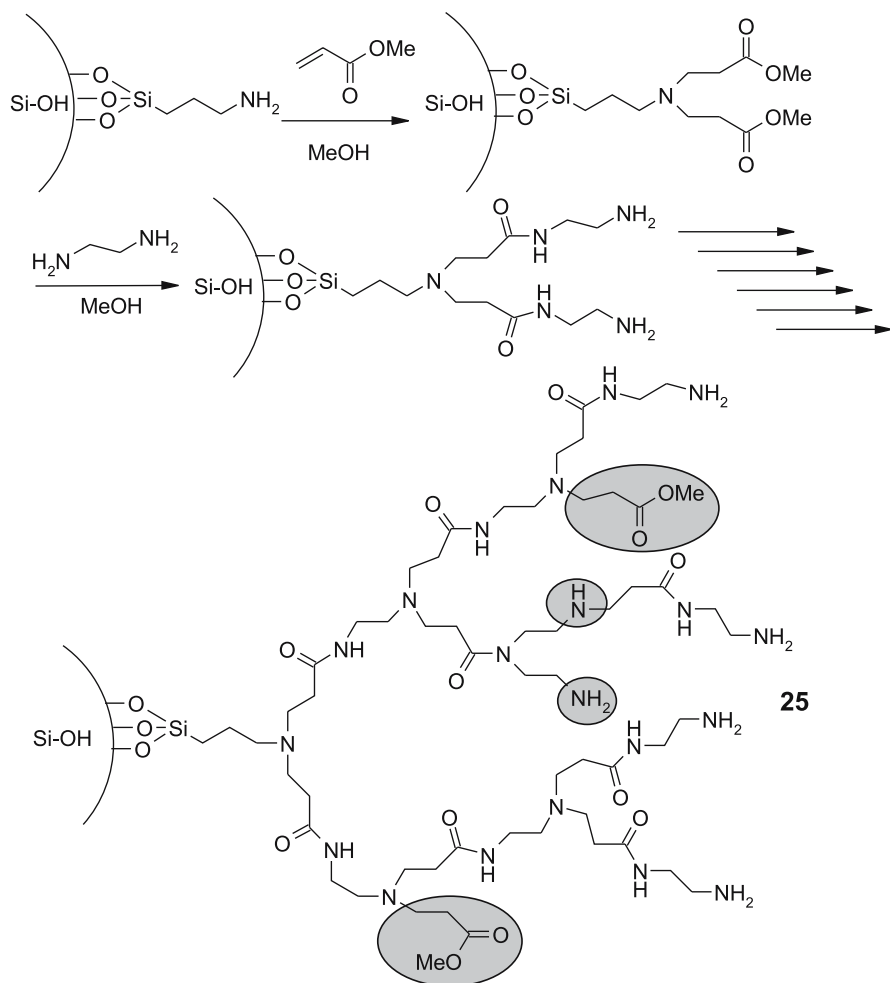
Scheme 8 PAMAM graft synthesis with incomplete branches highlighted in *gray*

lyzed by various methods. For example, beginning with amine-functionalized silica that was assayed by titration to have 0.4 mmol – NH_2/g, a tenth generation graft was prepared and analyzed by thermogravimetic analysis (TGA). At this stage, the measured graft loading was ca. 6% of the theoretical loading [92]. Higher loadings relative to the theoretical amount of grafting were seen with lower generation grafts. TGA was only useful for thermally robust silica and glass fiber substrates. Titrimetric analysis of the primary amines was more generally useful and was used to measure graft loadings on silica, glass fiber, carbon black. Titrimetry also was reportedly used for a polyethylene film. For the polysaccharide chitosan and polyethylene films, the graft loadings were also measured by gravimetric analysis.

These amine terminated hyperbranched PAMAM grafts on chitosan [90] and glass fiber [91] have been used to support further grafting chemistry. For example, a living poly(isobutyl vinyl ether) (PIBVE) was prepared using a HCl/ZnCl$_2$ initiator system. This living polymer was then added to a graft like **25** on glass fibers. Presumably the grafting occurs by reaction of the cationic centers in the living cationic polymer with the terminal amines of **25** to form aminals or imines. TGA analysis of the PIBVE grafted on an eighth
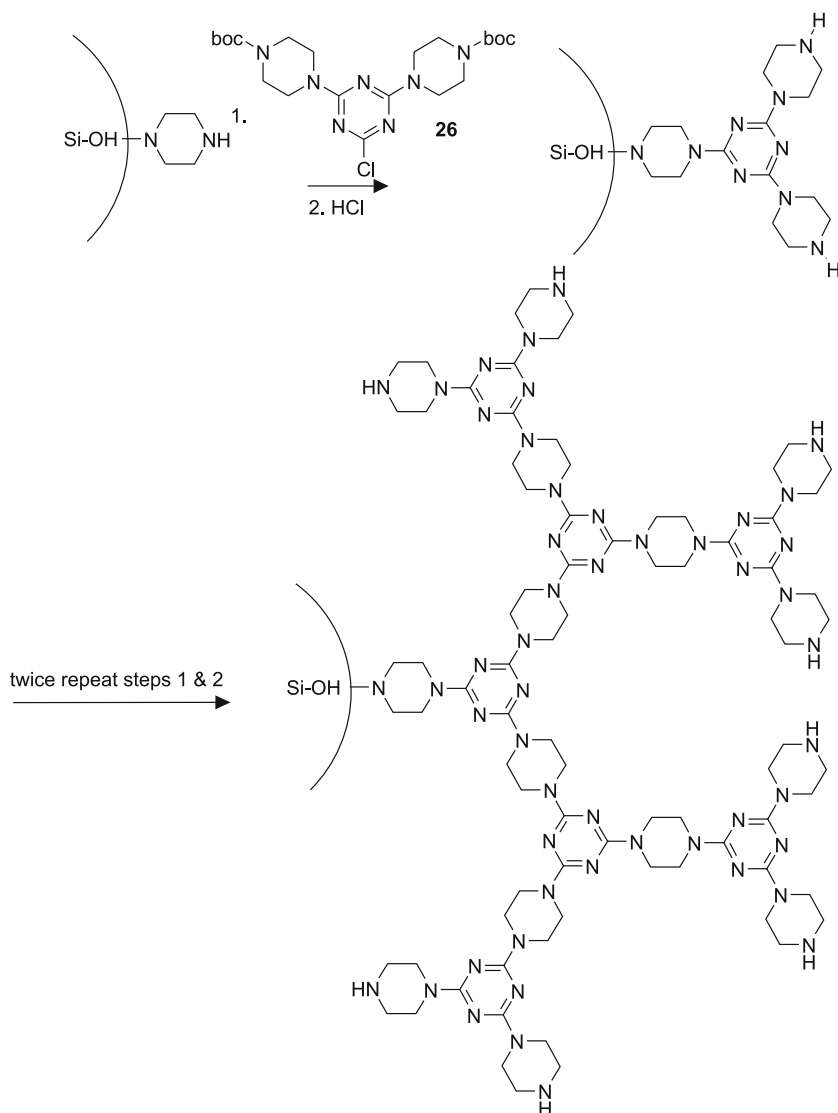
Scheme 9 Synthesis of three generation melamine dendrimer on silica surfaces

generation PAMAM graft **25** on glass fiber showed a 5.2% increase in weight (with an overall grafting of 16.2 weight percent).

Simanek's group has recently compared two methods of grafting melamine-based dendrimers to piperazine functionalized silica [97]. The first method involves the stepwise grafting of a three generation melamine-based dendrimer shown in Scheme 9. This chemistry begins by treating with piperazine functionalized silica with **26**. The *tert*-Boc protecting group was removed by HCl treatment. The grafting and hydrolysis steps were repeated two more times producing a grafted third generation dendrimer. The second grafting approach involved directly grafting a third generation melamine-based dendrimer that was prepared in solution to silica. The progress of either the monomer growth of melamine dendrimers on silica or grafting of a dendrimer to silica was followed by ATR-IR spectroscopy, XPS analysis, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), and TGA analysis. While ATR-IR spectroscopy, XPS analysis, and TGA analysis were all consistent with grafting, the MALDI-MS spectra after HF digestion of the silica supports proved to be the most useful characterization technique. For example, the MALDI-MS spectrum of a third generation melamine-based dendrimer that was synthesized in a stepwise fashion showed peaks that indicated incomplete branching. Peaks were observed that corresponded to the grafted dendrimer and that were consistent with a dendrimer missing one, two, and three branches were detected. In contrast, the MALDI-MS spectrum of grafts prepared using the soluble third generation dendrimer and silica only showed peaks for the third generation dendrimer.

7
Conclusions

Irregularly hyperbranched grafts provide a useful way to modify surfaces. A variety of chemistry can be used and a wide variety of grafts can be prepared. The hyperbranched grafts can serve as supported membranes, as catalyst supports or as substrates for further covalent graft chemistry. Functional groups within these interfaces can be readily modified by solution-state chemistry. The interfaces themselves can be used as media for further chemistry within the interface or as substrates in molecular recognition and self assembly of other macromolecules.

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