

Assembling Hyperbranched Polymerics

Sergiy Peleshanko, Vladimir V. Tsukruk

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Correspondence to: V. V. Tsukruk (E-mail: vladimir@mse.gatech.edu)

Received 26 July 2011; accepted 26 July 2011; published online 26 September 2011

DOI: 10.1002/polb.22361

ABSTRACT: A condensed overview discusses the existing grafting approaches and the surface behavior of various hyperbranched polymers. We focus on the recent strategies and corresponding characterization of the resulting surface morphologies and structures with a number of relevant recent results from the authors' own research and existing literature. Some results discussed here are important for prospective

applications of hyperbranched polymers in biomedical fields, for resistive coatings, tough blends, and reinforced nanocomposites are briefly summarized as well. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 50: 83–100, 2012

KEYWORDS: adsorption; hyperbranched; LB films; structural characterization; surfaces

INTRODUCTION This publication presents a condensed overview of the existing grafting approaches as applied to hyperbranched polymers and discusses the surface morphologies of these polymers and corresponding composites and coatings. We mostly focus on the recent strategies and corresponding characterization of the resulting surface morphologies and structures developed in the authors' group with some relevant examples from current literature. A number of relevant results are also included here especially in relation to recent developments related to novel synthetic approaches of hyperbranched molecules as well as emerging applications of hyperbranched polymers and coatings for biomedical purposes, as resistive coatings, tough blends, and reinforced nanocomposites. Some comprehensive recent reviews on highly branched polymers, which are focused mainly on synthetic aspects can be found in literature.^{1–6}

One of the most popular classes of polymers extensively studied in last couple decades are highly branched polymers. Some of new classes such as dendrimers and hyperbranched macromolecules with their fractal structure and multitude of branches have been widely exploited in recent years.^{7–11} Highly branched polymers with cores, joints and branches, tree-like architecture, and a low level of entanglements possess different physical properties when compared with linear polymers.^{12,13} Other macromolecular architectures, such as star-shaped block copolymers, have been found to exhibit interesting aggregation behavior,^{14–21} which can be used for a guided formation of fluorescent nanofibers and microfibers.^{22,23} The multiple terminal groups are used to control the assembly of the molecules in solution, and at surfaces and interfaces^{24–32} as well as their stimuli-responsive behavior.^{33,34} Unique morphologies were found in branched and

star block copolymers that are not observed for linear block copolymers.^{35–39} At the air–water interface, the hydrophobic chains collapse into globules while the hydrophilic chains spreads out to form a brush-like or a flat (pancake-like) structures.^{40–47}

Hyperbranched molecules possess a tree-like structure similar to that of dendrimers with the same enhancement in chemical and physical properties but at a great reduction in cost and time of synthesis when compared with dendrimers. Often, these molecules are created in one-pot synthesis without the lengthy stages of stepwise reaction and purification necessary with traditional dendrimers. Although significant polydispersity and inherit defects of their chemical structure caused by internal cyclization and side reactions, hyperbranched polymers possess, to a great extent, similar characteristics of compact structures with a significant fraction of terminal groups located on the exterior of the molecules.¹

Despite their irregular chemical structures, multiple weak intermolecular interactions can facilitate a hyperbranched polymer assembly into well-ordered one-dimensional microscopic or even macroscopic fibrils.⁴⁸ Amphiphilic branched copolymers with hydrophilic and hydrophobic segments have been the subject of numerous studies.^{49,50} The amphiphilic nature of these copolymers containing dissimilar segments gives rise to special properties in selective solvents, at surfaces, as well as in the bulk.⁵¹

From synthetic prospective, modified hyperbranched poly(phenylenes) can be utilized as macroinitiators for the synthesis of star polymers by anionic polymerization.⁵² Promising results were obtained by free radical polymerization based on hyperbranched polymeric azo initiators and living

Sergiy Peleshanko graduated with honors from National Technical University of Ukraine in 1997 with a M.S. degree in Chemical Engineering. He also received M.S. and Ph.D in Materials Science and Engineering from Iowa State University, and was a postdoc at Georgia Institute of Technology. He is a recipient of the MSE Graduate Research Excellence Award (2006) and Zaffarano Prize for Graduate Research (2006). Currently, he is a chemist at Hewlett-Packard, San Diego, USA.



Vladimir V. Tsukruk received his M.S. degree in Physics from the National University of Ukraine, Ph.D and DSc in Chemistry from the National Academy of Sciences of Ukraine, and was a postdoc at U. Marburg and U. Akron. Currently, he is a Professor at the School of Materials Science and Engineering, Georgia Institute of Technology. He has coauthored around 300 refereed articles, 20 invited reviews, and four books in the field of surfaces/interfaces and nanoinspired and bioinspired materials. He is a recipient of the Humboldt Award (2009) and NSF Special Creativity Award (2006) among others and is a Fellow of APS and MRS. He serves on the editorial advisory boards of five professional journals and has trained about 40 graduate students and post-docs.



radical polymerization.^{53–55} In addition, Gauthier et al. described the successful preparation of amphiphilic arborescent graft copolymers with a poly(ethylene oxide) (PEO) shell via the “grafting from” method.⁵⁶ Voit et al. presented a multifunctional hyperbranched macroinitiator prepared by a one-step modification of terminal reactive groups into initiating moieties.⁵⁷ Allyl-ether hyperbranched polyester of three generations was synthesized based on Boltorn-based cores.⁵⁸ Frey et al. reported a strategy for controlled preparation of the hyperbranched polyglycerol (PG) with narrow polydispersity via ring-opening multibranching polymerization.⁵⁹ Novel macroinitiators based on hyperbranched PG were used in the synthesis of multiarm poly(methyl acrylate) star block copolymers.⁶⁰ In another work, the same group demonstrated that the solubility and flexibility of these polyether polyols can be tailored by the attachment of oligo(propylene oxide) (PPO) segments.⁶¹ These PPO-modified hyperbranched PGs were used as initiator-cores in the synthesis of hydroxyl-terminated PEO⁶² and poly (ϵ -caprolactone) star block polymers⁶³ with a low polydispersity ($M_w/M_n < 1.5$).

The placement of hyperbranched polymers on solid substrates is required for a variety of prospective applications of these materials for sensing, catalysis, fouling, selective binding, and lubrication. To form stable surface layers, coatings and films can be connected by using either strong physical interactions or direct covalent grafting to a properly chosen and prefunctionalize surfaces as summarized in Figures 1 and 2 based on comprehensive review of current literature.⁶⁴

A variety of chemical reactions between surface groups and functionalized groups of highly branched molecules are presented in Figure 2. One of the most widely used reactions is the reaction between surface epoxy groups, carboxyl or hydroxyl terminal groups. The robust coatings are frequently prepared on glass substrates functionalized with the popular 3-aminopropyltriethoxysilane or 3-glycidyloxypropyltriethoxysilane self-assembled monolayers. Ultraviolet (UV) technolo-

gies offer the use of photoreactive molecules for a unique modification of the polymer substrate through immobilization of other polymers.^{65,66}

Surface composition and, hence, the surface energy, adhesion, friction, and wettability can be “tuned” to a desired physical state by designing proper chemical architecture.^{67–69} Ultimately, this provides a means for the fabrication of on-demand switchable properties such as self-cleaning abilities and switching from ultrahydrophobic to ultrahydrophilic behavior and back.^{70,71} Stimuli-responsive surfaces can be designed by using a variety of approaches including reversible photoisomerization reactions of grafted photochromic segments, reversible swelling/collapse of water-soluble grafted polymers and phase separation in mixed polymer brushes or di-block copolymers.^{24,72–74} Recent sophisticated designs have resulted in the preparation of polymer coatings with unique adaptive properties such as reversible switching of surface properties under solvent or temperature treatments which can be applied to a range of emerging applications.^{75–77} For these systems, different conformational changes of dissimilar polymer chains tethered to a solid surface resulted in dramatic structural reorganization on exposure to different environments.^{78–82}

Relevant surface layers from dendrimers, which are popular, regular, highly branched polymers, have been fabricated and studied since mid-1990s.^{23,83–87} For instance, Xiao and coworkers have created thin films from SiCl₃-terminated dendrons on mica.⁸⁸ Van Duijvenbode and coworkers fabricated surface layers from five generations of 1,4-diaminobutane poly(propylene imine).⁸⁹ Muller et al. have described the use of atomic force microscopy (AFM) in liquid to study the adsorption kinetics of poly (amido amine) (PAMAM) dendrimers on different substrates.⁹⁰ Sui et al. have exploited an environmental scanning electron microscopy to confirm the edge-on orientation of the amphiphilic dendrimers at the air/water interface.⁹¹

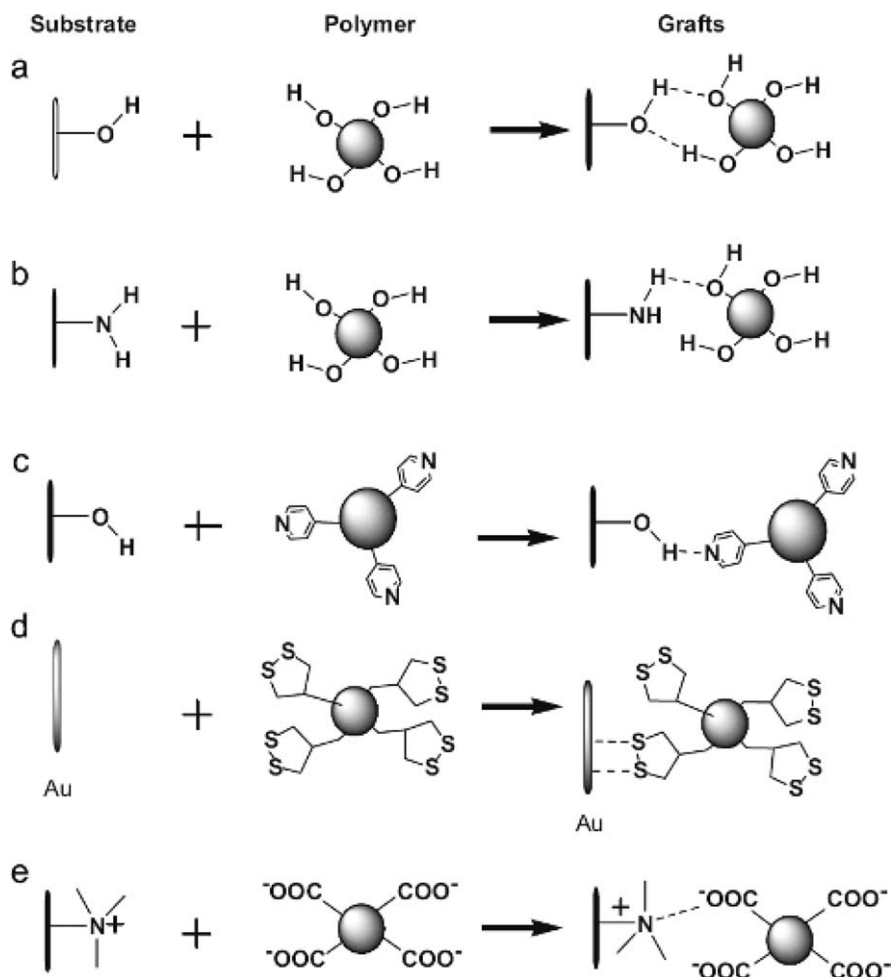


FIGURE 1 Summary of synthetic routes of noncovalent formation of surface layers of highly branched molecules onto different substrates: (a–c) hydrogen bonding; (d) thiol coordination; (e) coulombic interaction. From Peleshanko and Tsukruk, *Prog. Polym. Sci.*, 2008, 33, 523–580, © Elsevier Ltd., reproduced by permission.⁵⁸

Unlike intense studies conducted on dendrimers and star molecules, which will be not considered further here, relatively few studies are focused on placing, growing, assembling, and grafting of hyperbranched molecules with different core and peripheral groups in order to passivate, control, tune, enhance, and modify the physical properties of the solid substrates all of those to be discussed here.

GROWTH AND GRAFTING OF HYPERBRANCHED POLYMERS

Surface modification with hyperbranched polymers can be done either by “grafting from” (Routes 1 and 2) or “grafting to” (Route 3) approaches (Fig. 3). These approaches involve either covalent or noncovalent tethering of the hyperbranched macromolecules via appropriate linkages (Fig. 3). All grafting routes start by introducing proper functional groups (X) onto the surface by using a variety of chemical reactions such as oxidation or self-assembled monolayer (SAM) surface modification. The grafted hyperbranched polymers can be anchored to a surface by one branch, by multiple branches, or by the core.

Route 1 starts with the reaction of AB_2 monomers with the functional groups and repeating the reaction between AB_2 and CD (Fig. 3). By this method, a large amount and high concentration of the functional groups can be introduced onto the surface. The “grafting from” approach can be used in Route 2, which involves the surface initiating polymerization. The most popular techniques include step polycondensation, radical polymerization, and ring-opening polymerization (ROP). Route 3, which represents a “grafting to,” approach is used for covalent or noncovalent tethering of the preformed hyperbranched polymers to a proper functionalized surface (Fig. 3). Usually, it involves the chemical reaction of the hydroxyl or amino-terminated groups with carboxyl or epoxy groups.

Relevant earlier studies include functionalization of the natural polymers such as chitosan.⁹² It was found that hyperbranched PAMAM structure was propagated from the chitosan surface (Fig. 4). Because of the heterogeneous conditions and steric hindrances, this technique resulted in PAMAM hyperbranched modification of the chitosan. Further post-grafting of the hydrophilic poly(2-methyl-2-oxazoline) and

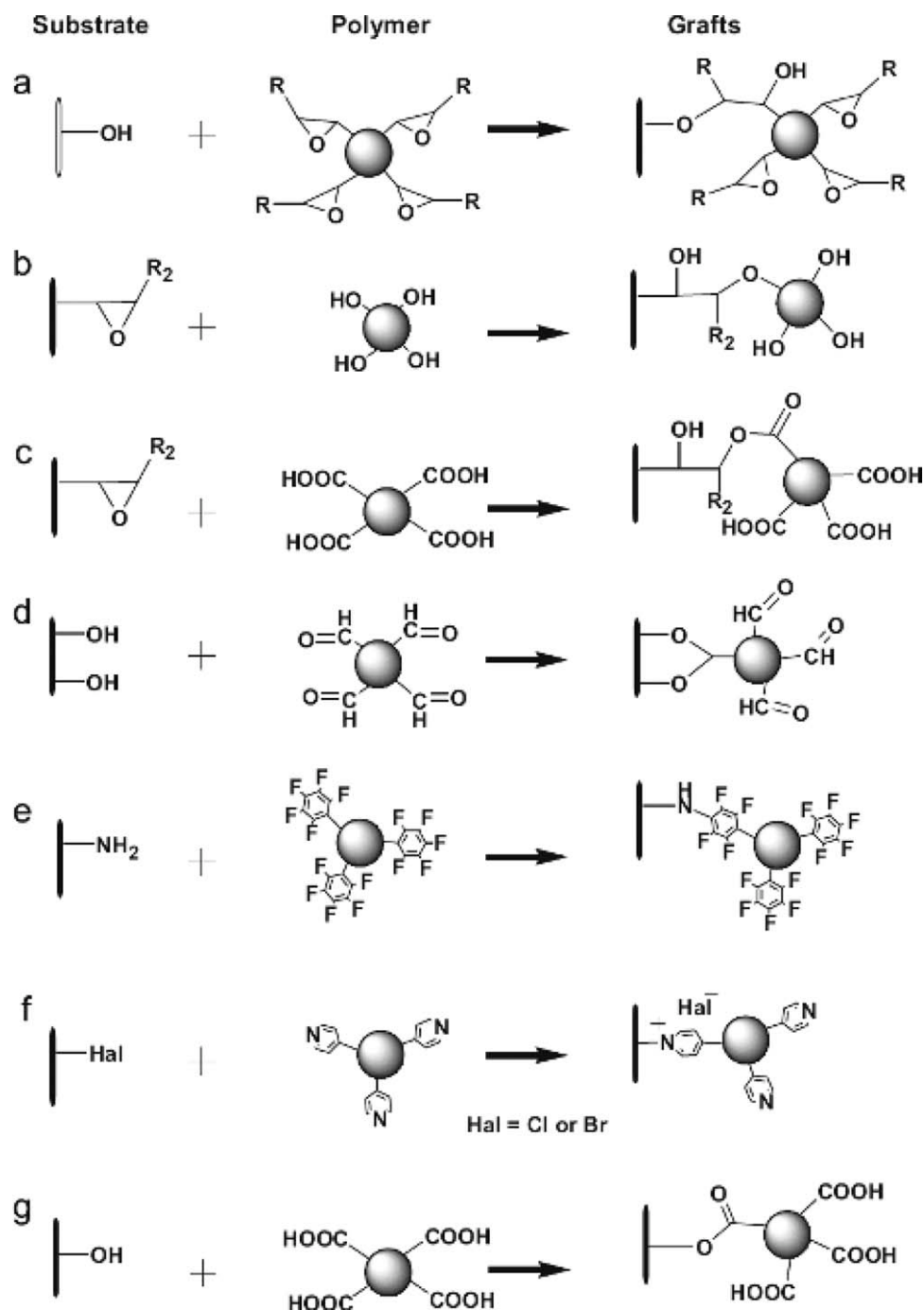


FIGURE 2 Summary of synthetic routes explored for covalent grafting of highly branched polymers: (a) and (b) ether; (c) and (g) ester; (d) acetal; (e) amine and (f) tertiary amine bonding. From Peleshanko and Tsukruk, *Prog. Polym. Sci.*, 2008, 33, 523–580, © Elsevier Ltd., reproduced by permission.⁵⁸

hydrophobic poly(isobutyl vinyl ether) to the hyperbranched grafted layer allowed to control the surface wettability.

In another fundamental study, Crooks and coworkers⁹³ have developed a new technique by using a single macromolecule as a monomeric unit for growing a hyperbranched film. The synthetic procedure uses an activation of a gold substrate with a monolayer of mercaptoundecanoic acid (MUA) as an

intermediate adhesive layer. The carboxylic acid groups were activated via a mixed anhydride followed by the reaction with an diamino-terminated poly(*tert*-butyl acrylate) ($\text{H}_2\text{N-PtBA-NH}_2$) (Fig. 5).^{94,95} This reaction resulted in the grafted polymer layer, whose *t*-Bu ester groups were further hydrolyzed to create the grafted poly(acrylic acid) (PAA) surface layer. The repetition of these steps resulted in additional grafting and the formation of a multilayered film.

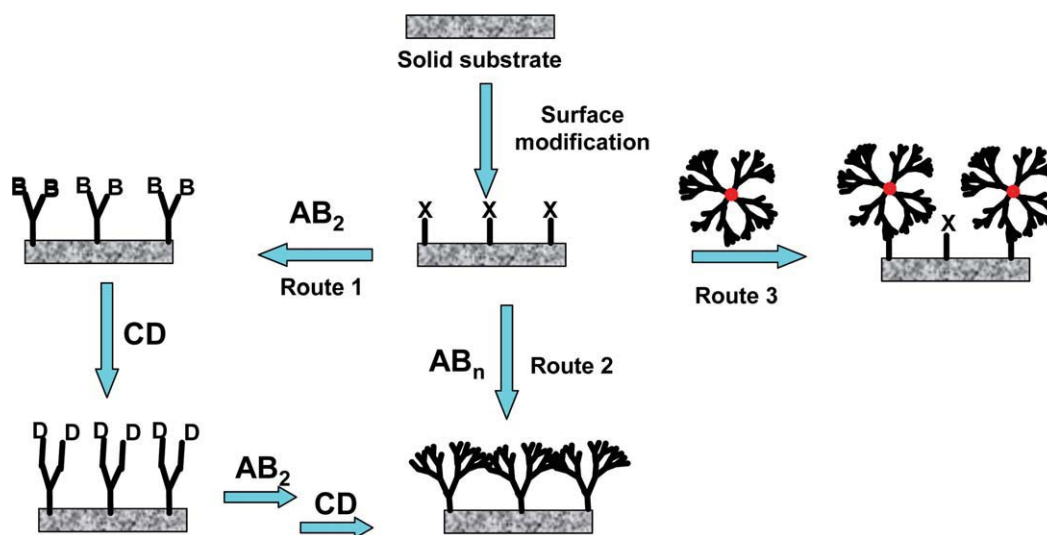


FIGURE 3 General routes of grafting of hyperbranched polymers.

In another system, Bruening and coworkers⁹⁶ applied graft-on-graft deposition techniques described above to produce hyperbranched PAA membranes on porous alumina supports. They observed that ultrathin hyperbranched PAA films could efficiently cover underlying microscopic pores without filling them.

Bergbreiter et al.⁹⁷ utilized the graft-on-graft method to build robust hyperbranched PAA films on polyethylene (PE) surfaces. Similarly to the work described above, diaminopoly(*tert*-butyl acrylate) was attached to the oxidized PE surface with carboxylic acid functional surface groups.⁹⁸ Another approach utilized the polyvalent hyperbranched PAA grafts on the gold surface or the PE surface. A soluble hydrogen-bond acceptor polyacrylamide, such as poly(*N*-isopropylacrylamide) was used for a mild hydrogen-bond-based grafting method.⁹⁹ Hyperbranched polyurethanes (PUs) have been synthesized by Deka et al.¹⁰⁰ Hyperbranched PU materials showed the high thermal stability and improved mechanical properties.

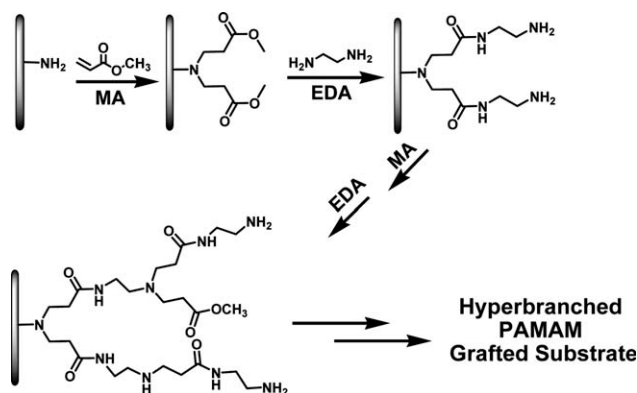


FIGURE 4 General route for the step-by-step grafting methodology for PAMAM surface layer. From Peleshanko et al., Prog. Polym. Sci., 2008, 33, 523–580, © Elsevier Ltd, reproduced by permission.⁵⁸

In another example, the chemical modification of polypropylene surfaces by the chemical grafting with the hyperbranched PAA surface layer was carried out by using grafting techniques described above for gold, aluminum, silicon, and PE surfaces.¹⁰¹ Selective treatment of the activated surfaces by pentadecylfluorooctylamine allowed the alternation of the surface properties from initially hydrophilic to completely hydrophobic. Bergbreiter and Tao¹⁰² have introduced new synthetic methods for modifying the carboxylic acid groups of hyperbranched surface films. Various procedures such as amidation, esterification, and alkylation reactions of carboxylic acid groups were used to generate functional surfaces.^{103,104} The method is faster than the graft-on-graft

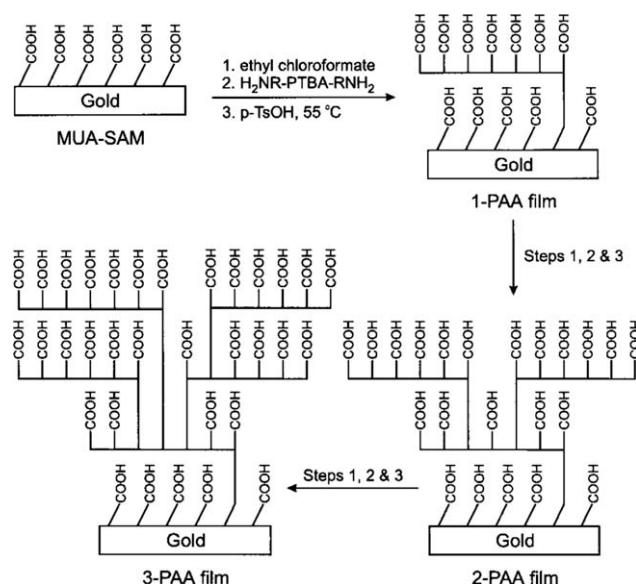


FIGURE 5 The preparation of the hyperbranched PAA surface layer on a gold substrate. From Peez et al., Langmuir 1998, 14, 4232–4237, © American Chemical Society, Inc, reproduced by permission.⁸⁸

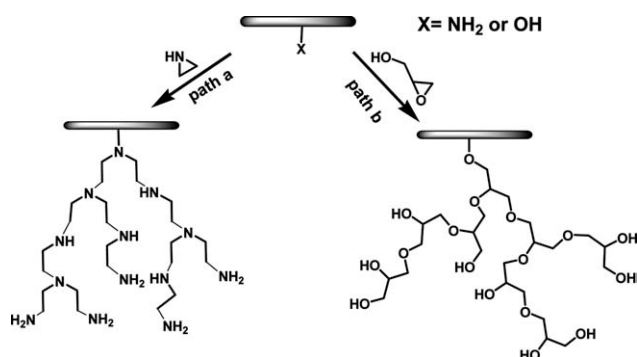


FIGURE 6 Formation of the grafted hyperbranched polymer by ROP. From Peleshanko et al., *Prog. Polym. Sci.*, 2008, 33, 523–580, © Elsevier Ltd., reproduced by permission.⁵⁸

technique and allows the production of graft copolymers with a suitable combination of monomers. Another method of introducing mixed functionalities is microcontact printing (μ -CP) followed by polymer grafting.¹⁰⁵ Another approach is based on the μ -CP of a passivating monolayer and deposition of the MUA, followed by the hyperbranched polymer grafting.¹⁰⁶

The preparation of hyperbranched polymers from premodified silicon wafer using self-condensing vinyl polymerization (SCVP) was suggested by Mori et al.¹⁰⁷ Nakayama et al.¹⁰⁸ have demonstrated a novel strategy to grow multigeneration hyperbranched graft architecture. Kim et al.¹⁰⁹ treated amino-functionalized silicon substrates with aziridines in

order to prepare grafted hyperbranched polymers via ROP (Fig. 6). AFM indicated that the polymerization is rather regular and that the morphology of surface does not change significantly after polymerization.¹¹⁰ Kim et al.¹¹¹ have found that hydroxyl groups are able to initiate the ROP of aziridine, resulting in highly branched poly(ethyleneimine) (PEI) surface layer. Khan and Huck¹¹² have demonstrated a new procedure to synthesize covalently linked hyperbranched polyglycidol on silicon oxide surfaces via anionic ring-opening (Fig. 6). This way, the surface layers with the controlled thickness and tailored surface properties were formed.

A variety of ultrathin surface layers from functionalized hyperbranched polymers have been fabricated by using the “grafting to” approach which, in many cases, is simpler and more robust than other approaches discussed above. Preference was given to grafting from melt to assure relatively high grafting density. For instance, Sidorenko et al.¹¹³ have reported the melt grafting of epoxy-functionalized hyperbranched polyesters (EHBP) to a bare silicon surface by the reaction of secondary epoxy groups with the hydroxyl groups at elevated temperature (Fig. 7). They demonstrated that robust and uniform nanometer-thick surface layers can be firmly grafted to the silicon dioxide surface (Fig. 7).¹¹⁴ Mikhaylova et al.¹¹⁵ produced ultrathin hyperbranched films by spin coating of hydroxyl terminated aromatic hyperbranched polyesters on epoxy-functionalized silicon wafers. Sangermano et al.¹¹⁶ exploited ethoxysilyl-hyperbranched aromatic polyesters as a efficient coupling agent for thin coatings.

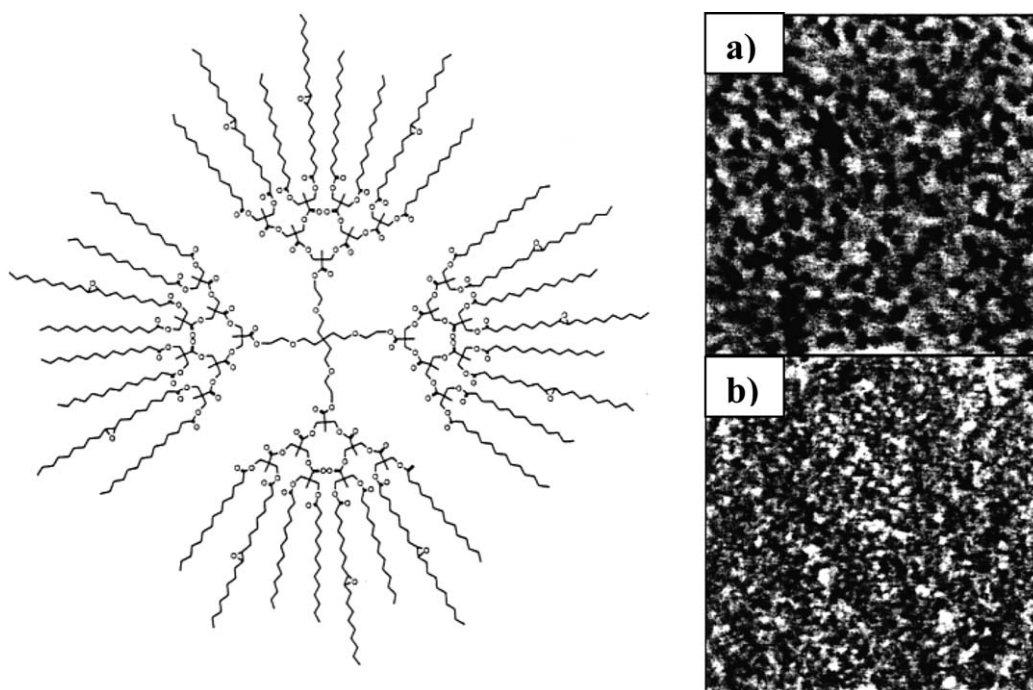


FIGURE 7 Chemical formula and AFM images of grafted monolayers of EHBP with commonly occurring dewetting pattern (a) and uniform monolayer (b) obtained under optimal grafting conditions: scan size $1 \times 1 \mu\text{m}^2$. From Sidorenko et al., *Langmuir* 2002, 18, 3408–3412, © American Chemical Society, reproduced by permission.¹⁰⁷

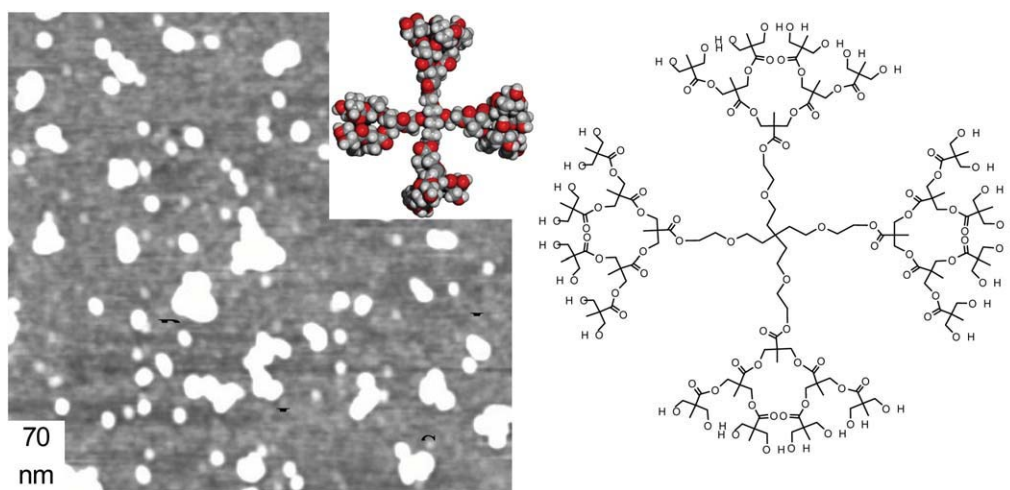


FIGURE 8 Chemical formula of third generation hyperbranched molecules and AFM image of adsorbed molecules. From Tsukruk, et al., *Appl. Phys. Lett.* 2003, 82, 907, © American Chemical Society, reproduced by permission.¹²

SURFACE MORPHOLOGIES OF HYPERBRANCHED POLYMERS

A variety of ordered monolayers have been fabricated from amphiphilic hyperbranched molecules, which are capable of forming stable Langmuir monolayers. Sheiko et al.¹¹⁷ investigated the surface behavior of hyperbranched polymers containing trimethylsilyl or hydroxyethyl end groups in comparison with carbosilane dendrimers. Analysis of the spreading behavior revealed that the hyperbranched polymer exhibited a spreading mechanism similar to that of isotropic liquids. In other study, Zakharova et al.¹¹⁸ studied the surface behavior of the poly(4-vinylpyridine) and the hyperbranched perfluorinated poly(phenylenegermane). They found that change in the pH of the subphase has no effect on the surface pressure isotherms of these compounds.

The surface properties of hyperbranched molecules have been probed with the micromapping of the surface stiffness with nanoscale resolution (Fig. 8).¹² It has been observed that adsorbed molecules form individual and multimolecular clusters on functionalized substrates (Fig. 8). To anchor dendritic molecules with hydroxyl terminal groups and reduce tip-molecule interactions, a modification of the silicon surface with an amine-terminated SAM is utilized. The nanomechanical response was analyzed in the terms of sequential deformation of dendritic molecules and alkyl-silane monolayers. The higher elastic modulus of individual dendritic molecules of the fourth generation in comparison with the corresponding third generation was observed.

The surface behavior of amphiphilic hyperbranched polyesters with a variable composition of alkyl-terminated groups have been reported by Zhai et al (Fig. 9).¹³ A comprehensive study of the surface properties of the Langmuir monolayers with X-ray reflectivity revealed that organized monolayers could be formed at the air-water interface if the number of alkyl tails is higher than two per a single hyperbranched core. Similarly to regular dendrimers, the alkyl tails of hyper-

branched molecules at modest surface pressure formed the quasi-hexagonal lattice. Finally, at high surface pressure, the alkyl tails became arranged in an up-right orientation with squashed hyperbranched cores (Fig. 9).

In another study, Peleshanko et al. reported on the synthesis of novel hyperbranched amphiphilic (PEO-PS)_n copolymers obtained by controlled radical polymerization (Fig. 10).¹¹⁹ The macroinimers used to synthesize copolymers have the general structure AB*, where A stands for PEO with a terminal double bond and B* stands for a PS block with a terminal initiating group. Langmuir monolayers from these hyperbranches displayed reversible surface behavior. The random, mixed character of short hydrophilic and hydrophobic fragments results in peculiar surface behavior: unlike regular linear and star block-copolymers the amphiphilic hyperbranched macromolecules with higher PEO content are spread at the air-water interface and short PEO fragments are not submerged into the water subphase even at high compression. By minimizing the total energy of the macromolecules, the molecular conformations of the polymers were optimized in order to maximize PEO fragments contact with water subphase and promoting formation of uniform LB monolayers (Fig. 11).

For the hyperbranched copolymers with small content of the hydrophilic block and longer hydrophobic segments, PS or PEO chains are separated on different sides of the interface and serve as a “limiting” factor for the monolayer compression under different pressures similar to conventional star and linear block copolymers (Fig. 12).^{38,120,121} Other important factors, such as high PDI, a low degree of polymerization and the presence of a considerable amount (10–15%) of unreacted macroinimers, also played a role in the formation of smooth monolayers of the hyperbranched polymers at the interfaces. The hyperbranched copolymers with a comparable length of PS and PEO segments and considerably high degree of branching exhibit different surface behavior.

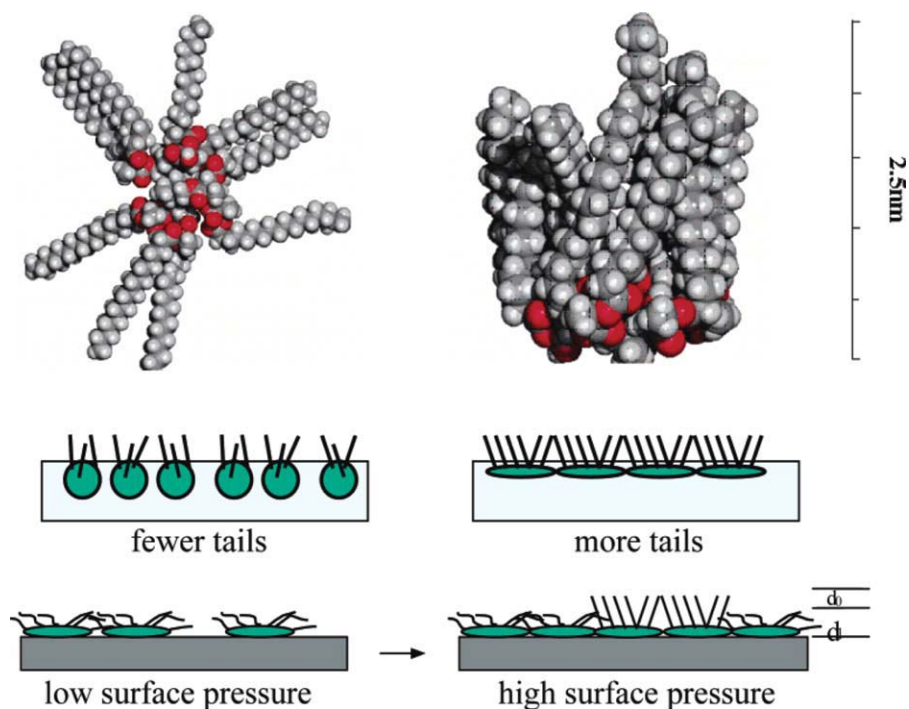


FIGURE 9 Amphiphilic hyperbranched polymers with different number of alkyl tails at the air–water interface at low (left) and high (right) surface pressures. From Zhai et al., *Macromolecules*, 2003, 36, 3101–3110, © American Chemical Society, reproduced by permission.¹³

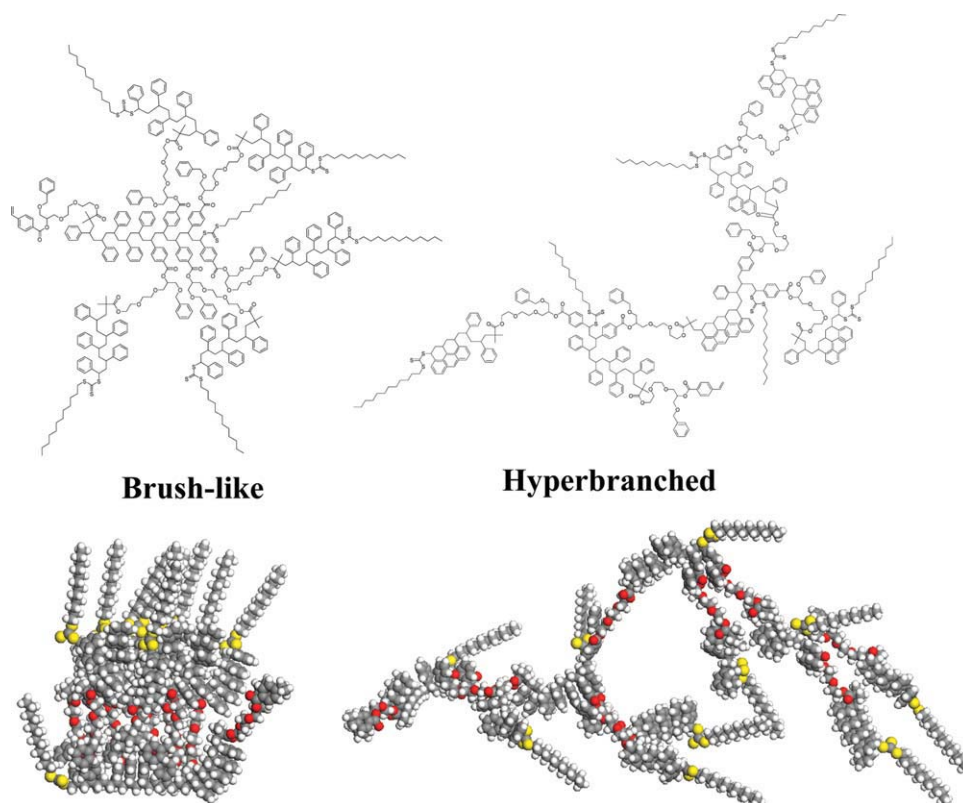


FIGURE 10 Chemical structure and corresponded molecular models of two possible architectures of the PEO-PS hyperbranched polymers. From Peleshanko et al., *Macromolecules*, 2006, 39, 4756–4766, © American Chemical Society, reproduced by permission.¹¹³

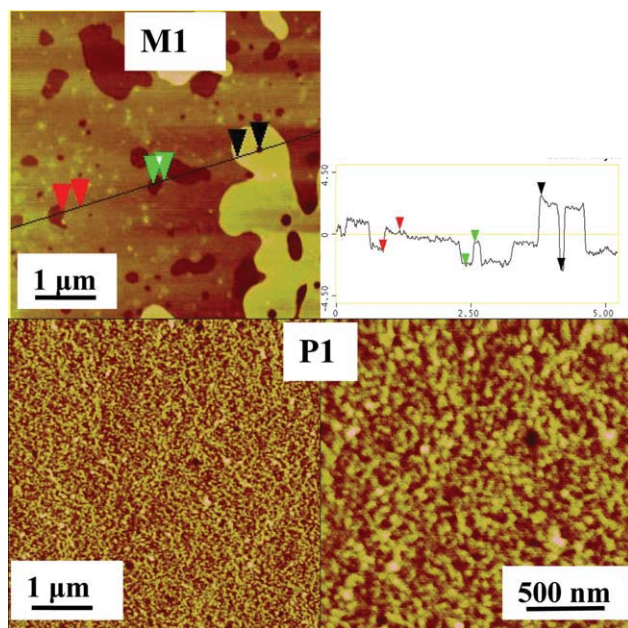


FIGURE 11 AFM topography of amphiphilic polymers: **M1** initiator (top, left) and its cross-sectional analysis) and LB monolayers from hyperbranched PEO-PS polymer (**P1**). From Peleshanko et al., *Macromolecules*, 2006, 39, 4756–4766, © American Chemical Society, reproduced by permission.¹¹³

In a different study, Ornatska et al. investigated the surface properties of the amphiphilic hyperbranched polymers with different substitutions of the terminal palmitoyl and amino-hexanoic groups.¹⁵ The authors have observed that the amplification of weak multiple interactions between numerous peripheral branches of irregular, flexible, polydisperse, and highly branched molecules can facilitate their self-assembly into well-organized nanofibrillar micellar structures at the hydrophilic solid surfaces with continuous nanofibers showing monomolecular diameter (Fig. 13).

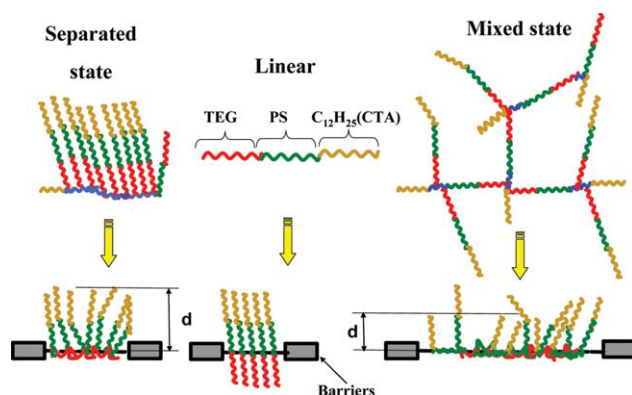


FIGURE 12 The PEO-PS macromolecules at the air–water interface: left—separated hydrophobic and hydrophilic segments and right—mixed hydrophobic and hydrophilic segments confined to the water surface. From Peleshanko et al., *Macromolecules*, 2006, 39, 4756–4766, © American Chemical Society, reproduced by permission.¹¹³

In further studies, a series of amphiphilic hyperbranched polymers with a polyester-polyol core and 64 terminal hydroxyl groups was modified by substituting various terminal groups: alkyl tails, amino, and carboxyl groups to test the variability of nanofibrillar morphologies at different compositions.¹²² The effect of the pendant groups' chemical composition on the resulting surface morphology within LB monolayers in respect to their ability to form nanofibrillar surface structures was investigated. It has been demonstrated that the amphiphilicity of the polyester core with 64 hydroxyl groups can be achieved if a fraction of alkyl tails (C15) is higher than $1/4$.

Nanofibrillar morphology was consistently formed as the highly polar functional groups were added to the polyester cores in combination with a significant ($>30\%$) fraction of alkyl terminal groups (Fig. 14). Addition of amino end groups was observed to be much more effective in the promotion of nanofibril assembly than the addition of carboxyl end groups. In fact, AFM shows a dramatic change of the surface morphology in both amino-containing compounds when compared with initial alkyl-modified cores (Fig. 14). Amphiphilic hyperbranched molecules with combined alkyl and amino terminal groups are capable of forming nanofibers with molecular dimensions. At low pressure, unique structures of closely spaced parallel stacks of these nanofilaments and isolated fibrillar structures were formed.

The hyperbranched molecules with 11 amino groups formed very few nanofibers scarcely placed over the surface (Fig. 14). Driving forces for this assembly come from two major factors: hydrogen bonding among the carbonyl groups of the core structure and the amino groups of aminohexanoic acid, as well as crystallization of alkyl tails under compression. The inclusion of COOH terminal groups showed the most dramatic effect on the modified hyperbranched compounds' surface behavior. These terminal COOH groups shifts the balance between the hydrophilic cores and hydrophobic alkyl tails, making the cores much more compact. The alkyl tails then take on more upright orientations at higher surface pressures.

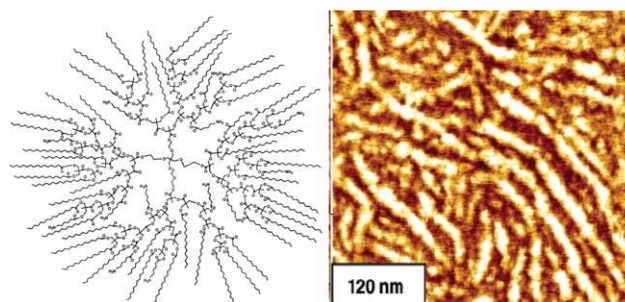


FIGURE 13 Chemical structures of the modified hyperbranched polymer and AFM phase images of its nanofibrillar assemblies within LB monolayers. From Ornatska et al., *J. Am. Chem. Soc.* 2004, 126, 9675–9684, © American Chemical Society, reproduced by permission.¹⁵

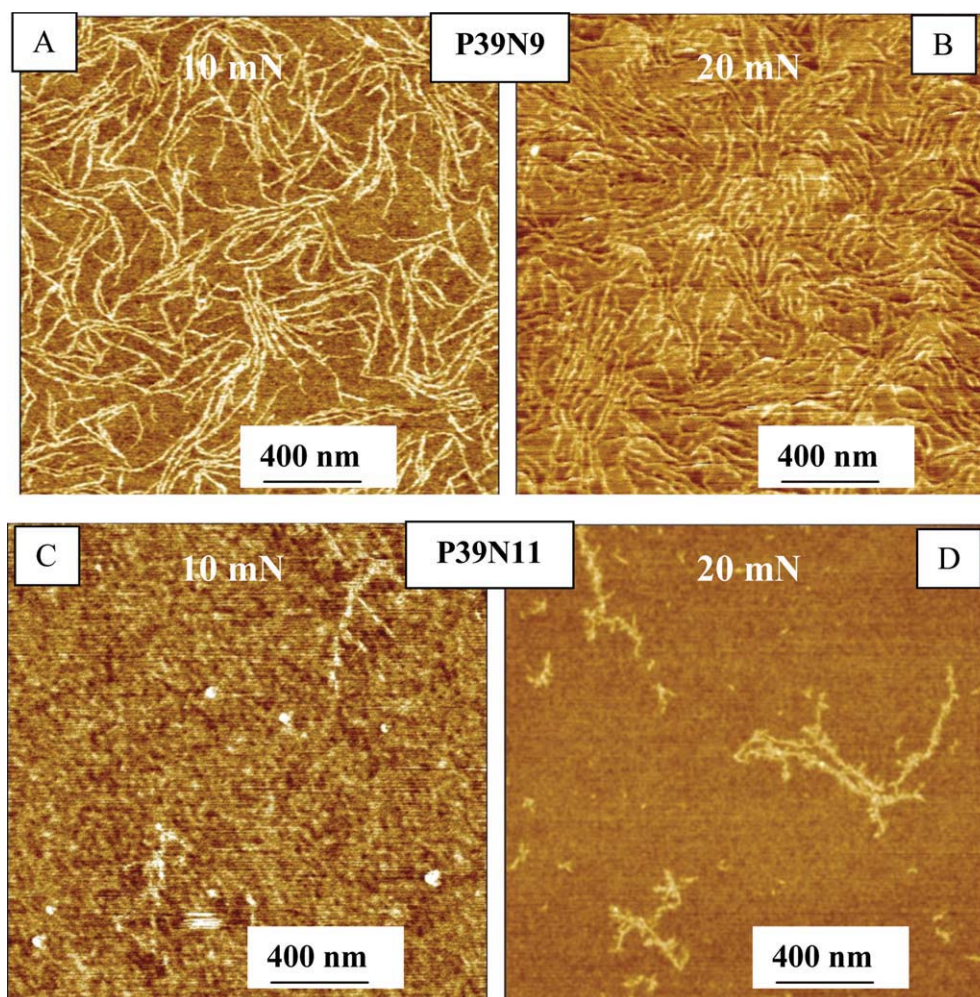


FIGURE 14 AFM images of LB monolayers from functionalized hyperbranches at different pressures. From Ornatska et al., *Polymer*, 2006, 47, 813–8146, © Elsevier Ltd., reproduced by permission.¹¹⁶

HYPERBRANCHED POLYMERS AND NANO-MICROPARTICLES FOR COMPOSITES

Hyperbranched polymers are a popular media for chemical modifications of a wide variety of nanoparticles and microparticles to modify their colloidal behavior and their interfacial behavior for improving processing and properties of composite materials. Particles utilized include soft rubbery particles, silica, metal, carbon, and polymer structures of different sizes and compositions or as important components of polyelectrolyte and microporous membranes.^{123,124}

The synthesis of branched microspheres composed of poly (divinylbenzene) (PDVB) cores with grafted linear and branched glycopolymer chains were reported by Pfaf and Muller.¹²⁵ PDVB particles of 1.5 μm across exhibit a layer of lightly crosslinked PDVB in the periphery of the particle and therefore enable a “grafting through” approach due to the residual vinyl groups on the surface and the core-shell morphology and high degree of branching in outer shells

Hyperbranched aromatic polyamides were grafted to nanosilica particles via “one-pot” melt polycondensation with par-

ticles first treated with a silane coupling agent to introduce amine groups.¹²⁶ The high surface grafting density was achieved by controlling reaction conditions in order to avoid steric hindrances at nanoparticles surfaces during polymerization. The mixing of hyperbranched polymers with suspensions of silica and glass particles significantly affects their physical properties.¹²⁷ Changes in chain dynamics observed and the progressive suppression of aging were attributed to immobilization effects of the hyperbranches at the surface of the particles. The thickness of the immobilized hyperbranched shell was 1–2 nm, depending on chemical composition.

Hyperbranched coatings with enhanced parameters such as increased surface hardness, scratch resistance, chemical resistance, and flexibility were obtained by using clay nanoplatelets.¹²⁸ In this study, unmodified nanoclay, montmorillonite (MMT), was added to a polymer matrix from the hyperbranched polyester Boltorn. Smooth and transparent films were prepared and X-ray diffraction and TEM revealed a mainly exfoliated structure in these films. Increases in glass transition, thermal stability, and elastic modulus all were observed for these coatings.

Covalent grafting of the hyperbranched polymers was conducted to glass beads using functionalized SAMs chemistry by Xu et al.¹²⁹ After selective introduction of carboxyl acid groups into hyperbranched polyols the residual hydroxyl groups were modified with silane. A different approach has been used by Shi et al. to graft hyperbranched polyesters onto silica nanoparticles.¹³⁰ Modified hyperbranched polymers, which possess 50% end carboxylic groups and 50% end hydroxyl groups and end-capped with octadecyl isocyanate (C₁₈), have been grafted onto 3-glycidioxy-propyltrimethoxysilane premodified silica nanoparticles.

Fujiki et al. have described the chemical grafting of hyperbranched PAMAM polymers onto different particles.^{131,132} These researchers also applied this methodology for the grafting of hyperbranched polymers onto silica nanoparticles preliminary treated with 3-glycidioxypropyl trimethoxysilane.^{133,134} Scale-up synthesis of hyperbranched PAMAM grafted onto ultrafine silica nanoparticles was successfully achieved by Murota et al.¹³⁵ Furthermore, the postgrafting polymerization of different monomers onto PAMAM-modified silica nanoparticles resulted in polymer-inorganic nanoparticles with high surface grafting density.^{136,137}

Tsubokawa et al. have broadened applications for the grafting of hyperbranched PAMAM by exploring carbon black and PS surfaces.^{138,139} Nakada et al. applied similar approach to the modification of the ultra-high molecular weight PE powder.¹⁴⁰ After repeating the grafting cycle several times, they produced an ultrathin surface film, which possesses an anion exchange capacity. Similarly, Gao et al. has applied an *in situ* polycondensation approach to functionalize multiwall carbon nanotubes (MWNTs).¹⁴¹ The polyurea-coated MWNTs showed interesting self-assembling behavior with flower-like morphologies in the solid state. The growing of hyperbranched polymer by SCVP has been expended on highly curved inorganic surface such as silica nanoparticles and MWNTs.^{142,143} Hydrolysis of the ester functional groups of branched PtBA chains created novel core-shell materials. Tsubokawa et al.^{144,145} exploited the grafting of polymers having pendant peroxy carbonate or azo groups onto silica nanoparticles to control the wettability properties. Recently, the hyperbranched PAMAM nanoparticles with biodegradability and autofluorescence have been prepared by Wen et al.¹⁴⁶ The resultant nanoparticles displayed strong photoluminescence, high photostability, broad absorption, and emission in visible range due to the tertiary amine chromophore. The incubation of these nanoparticles with the liver cancer cells showed their nontoxicity important for bioimaging and drug delivery.

The study of Gunawidjaja et al.¹⁴⁷ reported the behavior of organic-functionalized core-shell polyhedral oligomeric silsesquioxane (POSS-M) derivatives with various hydrophobic-hydrophilic terminal group compositions in the bulk state and within monolayered and multilayered films at the air-water interface and on solid surface. POSS-M refers to mixed silsesquioxanes cores, in contrast to the geometrically specific POSS compounds (Fig. 15). It is composed of polyhedra, incompletely condensed polyhedra, ladder type structures,

open structures, linear structures, and all the possible combinations thereof and attracts great interest due to their facile preparation, low polydispersity, high yield, and low cost.

The level of reorganization of POSS-M molecules under compression is controlled by the content of alkyl peripheral chains (Fig. 15). The absence of hydrophobic groups in POSS-M cores resulted in their unstable behavior at the air-water interface. On the other hand, the presence of hydrophobic alkyl chains in the fully hydrophobic POSS-M molecule prevents their dissolution into the water subphase. The presence of some polar ester and urethane groups in the molecule provides the necessary amphiphilic character for the molecules to form a stable monolayer at the air-water interface when subjected to surface compression with area per molecule increasing linearly as the amount of alkyl tails increases. The surface morphologies of hyperbranched POSS-M at low, intermediate, and high surface pressures are very different (Fig. 16).

Overall, the molecules formed three distinct geometries: one-dimensional, circular, and planar aggregates. The lengths of these one-dimensional and the diameters of the circular aggregates are in the micron range. From one-dimensional to planar aggregates, the geometrical curvature increases as the amount of the hydrophobic content is gradually increased. Such a phenomenon is consistently observed and governed especially by the hydrophobic-hydrophilic balance, but the stability is affected by other external variables, for example, temperature, architecture, and terminal groups.^{35,38,41,148–152} Except for one compound, all amphiphilic POSS-M compounds eventually formed a uniform LB monolayer at a high surface pressure. At the highest surface pressure, the overall morphology is eventually dominated by the crowding of the POSS-M cores and alkyl branches.

In another study, POSS-M compounds were reported as a new type of nanomodifiers for PUs to produce organic-inorganic hybrids.¹⁵³ Two different series of PU-POSS copolymers (branched and crosslinked) were based on PU mixtures with POSS-M. Microphase segregation and the formation of domains enriched with the inorganic POSS phase was observed for blends containing 66 vol % of silica nanoparticles with dimension of 2–3 nm. In contrast, crosslinked PU-POSS-M composites are characterized with a diffusion-limited segregation with dimensions about 10 nm.

Functionalized amphiphilic hyperbranched molecules in the form of nanofibers were utilized to fabricate silver nanoparticles at the air-water interface.¹⁷ The amine-hydroxyl hyperbranched cores organized into nanofibrillar micellar structures served as a matrix for the nanoparticle formation from the ion-containing water subphase. The silver nanoparticles formed within the monolayer were typically 2–4 nm in diameter as controlled by the core and interfibrillar surface areas (Fig. 17). Furthermore, at higher ion concentration, the Langmuir monolayer was observed to template the chain-organized nanoparticles along the nanofibrillar structures. The nanoparticle formation was suggested to occur via the oxidation of primary amino groups by silver catalysis facilitated

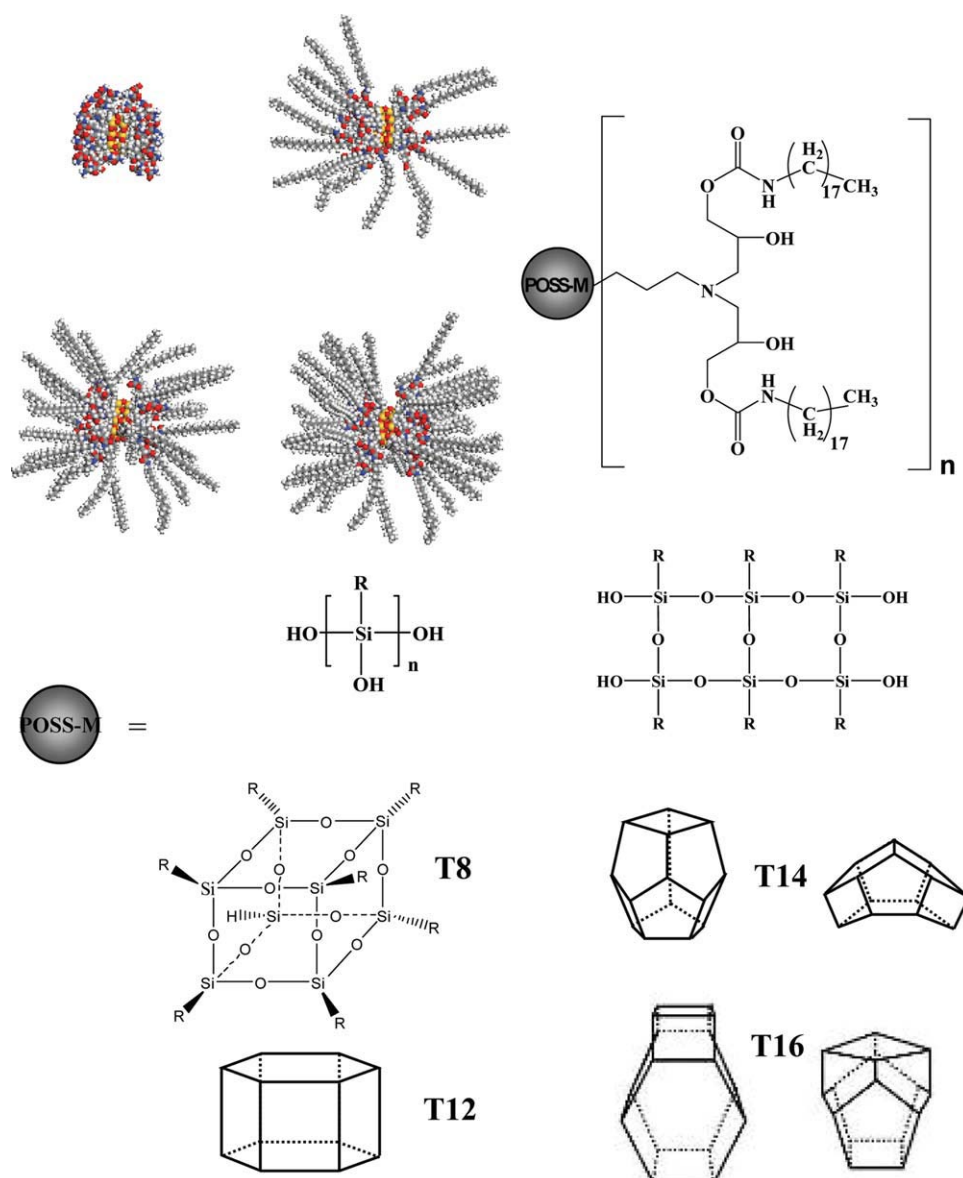


FIGURE 15 POSS-M composition, where T_n refers to the number of silicon corners for the three-dimensional POSS cages and molecular models for POSS with different number of branches. From Gunawidjaja, R. et al., *Langmuir*, 2009, 25, 1196–1209, © American Chemical Society, reproduced by permission.¹⁴¹

by “caging” of silver ions within surface areas dominated by the multibranching cores. This result indicates that as was suggested from comparison of X-ray data at the air–water interface and AFM data at solid supports the AgNO₃ crystals were formed directly in the water subphase.

The silver nanoparticles at modest subphase concentration were randomly located within the LB monolayer with clearly visible nanofibrillar morphology (Fig. 17). The ability of the functionalized hyperbranched polymer organized into nanofibrillar bundles of semicylindrical micelles to template one-dimensional nanoparticle aggregation was studied with various subphases concentrations and compositions. When the subphase was 5 mM AgNO₃, the largest numbers of linear aggregates were observed to be tem-

plated by the polymeric monolayer. The smaller nanoparticles may have formed in the hyperbranched cores surrounded by the alkyl shell, thus constraining their growth and limiting their size (Fig. 17). Formation of small nanoparticles in these “trapped” regions would have caused minimal increase in the limiting cross-sectional area in the π -A isotherm. The larger particles, on the other hand, could have attained their increased size due to a less-constrained growth surface area at the air–liquid interface between the neighboring nanofibrils and their bundles. It was observed that the larger nanoparticles actually punctuate the nanofibrils in several places; however, the fibrils continued uninterrupted on the opposite side of the particle. This behavior suggested that the nanoparticles may be embedded into

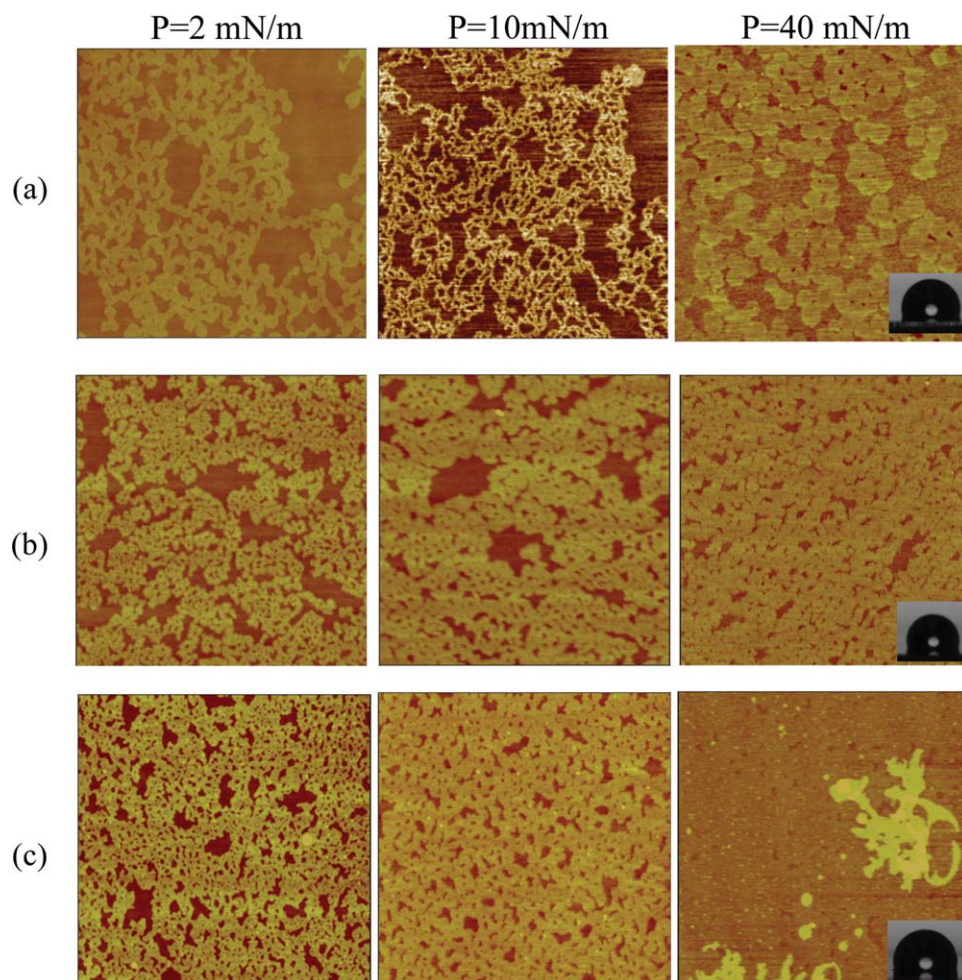


FIGURE 16 AFM images of LB monolayers at different surface pressures for POSS-M with (a) 75%, (b) 50%, and (c) 25% modifications. $5 \times 5 \mu\text{m}^2$, z-scale is 10 nm. Insets are photographs of water droplets on coatings. From Gunawidjaja, R. et al., *Langmuir*, 2009, 25, 1196–1209, © American Chemical Society, reproduced by permission.¹⁴¹

nanofibrils by a complexation between the silver atoms and the terminal NH_2 groups.

HYPERBRANCHED POLYMERS FOR BIOMEDICAL APPLICATIONS

A number of recent studies considered hyperbranched polymers for various biomedical-related applications such as designing bioresistive surfaces, gene therapy, drug delivery containers, bioadhesives, biospecific binders, cell encapsulation, and others,^{154–159} with some of them to be summarized below. For instance, Haag et al. prepared protein-resistant, highly branched PG SAMs on gold substrates by a simple chemical modification of these readily available polymers with a surface-active disulfide (thioctic acid) linker group.¹⁶⁰ Because of the higher thermal and oxidative stability of the bulk PG as compared to the PEG and the easy accessibility of these materials, branched PGs can be considered promising candidates for biomedical applications.

Controlled interactions and cell surface modifications have shown tremendous utility in various biomedical applications. Hyperbranched molecules frequently show different binding

behavior. For instance, peptides that bind to linear and branched poly(phenylene vinylene) (PPV) were identified by the phage display method.¹⁶¹ Aromatic amino acids were enriched in these peptide sequences, suggesting that a π – π interaction is critical for binding the peptides and PPV. The surface affinity to hyperbranched PPV was 15-fold greater than its affinity for linear PPV due to favorable location of two Trp residues in a helical conformation. In another study, dramatically enhanced cell surface modifications by up to 10-fold were observed for proper “additive” polymers.¹⁶² The cell compatibility was demonstrated for red blood cells, leukocytes, platelets, and Jurkat cells.

Amphiphilic hyperbranched core-shell PEG polymers with folate moieties based upon hyperbranched polyester Boltorn were synthesized by Si et al.¹⁶³ The inner part and the outer shell of the amphiphilic polymers were composed of hydrophobic PC segments. To achieve tumor cell targeting property, folic acid was incorporated to the branches of the amphiphilic polymers, and two antineoplastic drugs, 5-fluorouracil and paclitaxel, were encapsulated into the collapsed molecules. The drug release results showed that the drug-

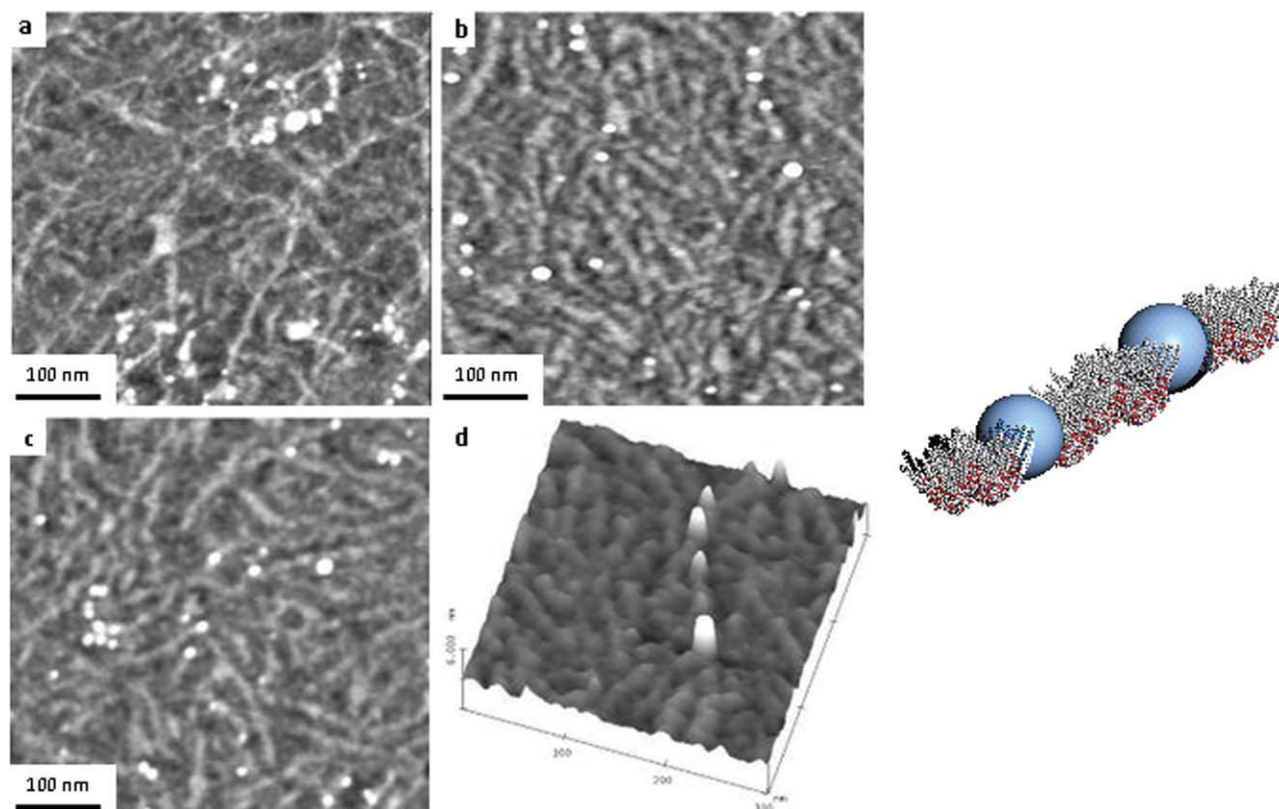


FIGURE 17 AFM images for LB monolayers obtained on: (a) A subphase of 5 mM AgNO_3 7 h (z-scale is 10 nm). (b) A subphase of 0.1 mM AgNO_3 for 24 h (z-scale is 8 nm). (c) A subphase of 0.1 mM AgNO_3 and 22 KNO_3 for 7-h experiment (z-scale is 8 nm); (d) Three-dimensional AFM image showing how particles follow nanofibrils. Schematic represents nanoparticle arrangement along the individual nanofibril. From Rybak et al., *Langmuir*, 2006, 22, 1027–1037, © American Chemical Society, reproduced by permission.¹⁷

loaded nanoparticles exhibited enhanced cell inhibition because folate targeting increased their cytotoxicity. Hyperbranched PGs were synthesized with ROP by Yeh et al.¹⁶⁴ The adsorption and formation of uniform thin films of these compounds on gold was studied and compared with that of linear PEG thiols. It was observed that hyperbranched thiols formed lower grafting density compared to PEG thiols. Incubation of both polymer-coated surfaces with bovine serum albumin and Ig showed that the high hyperbranched PG was more resistant to protein adsorption than linear PEG thus suggesting that hyperbranched coatings could be a good alternative to regular PEGs as nonfouling functional surfaces.

Dendritic core-shell architectures based on hyperbranched PGs for the solubilization of hydrophobic drugs have been recently synthesized.¹⁶⁵ The core has been modified with hydrophobic biphenyl groups or perfluorinated chains to increase its hydrophobicity and domain morphology was confirmed with AFM. These hydrophobic core-shell architectures were then used to solubilize analytes such as pyrene, Nile red, and a perfluoro tagged diazo dye, as well as the drug nimodipine. It has been demonstrated that the transport capacity increased dramatically even for very low polymer concentration.

THIN COATINGS FROM HYPERBRANCHED POLYMERS

A number of robust coatings have been demonstrated from hyperbranched polymers, which are deposited, grafted, or crosslinked on solid substrates as has been already mentioned above. In one of the earlier studies, it has been demonstrated that chemical modification of the hyperbranched PAA films with amide or ester linkages makes them polymerizable under UV light.¹⁶⁶ UV photocrosslinking was applied to produce robust coatings as well as fluorinated coatings. Such films were exploited to block the electrochemical reactions on gold electrodes, which made them attractive for corrosion-inhibiting coatings. In another study, it has been demonstrated that selective functionalization of the carboxylic groups can produce the hyperbranched polymer films, which are able to reversible sorption of the polyvalent cationic polyelectrolytes.⁸⁸ It has been suggested that such ionic nanocomposite polyelectrolyte surface films can be used as a host matrix in biosensors.¹⁶⁷ Finally, the glass transition of PS with systematically varied topologies (linear, star-like, and hyperbranched) confined in nanoscale films showed only a marginal depression in glass transition temperature for the thinnest films analyzed.¹⁶⁸

Lemieux et al.¹⁶⁹ have fabricated a stratified nanoscale polymer surface film with tunable thickness through UV-initiated polymerization of temperature-sensitive pNIPAAm layer confined beneath hydrophobic coating. The strong characteristic volume-transition behavior was observed in water, with a 100% change in thickness above and below this transition. The AFM nanomechanical testing reveals vertical gradients of the elastic response tunable to a desired state by the external temperature. Hyperbranched polyesters with different chemical compositions and core designs were reported by Kishore et al.¹⁷⁰ FTIR spectroscopy showed the formation of hydrogen bonding network with parameters controlled by chemical composition. Triethoxysilyl-functionalized hyperbranched polysiloxysilanes of different types were adsorbed onto a silicon dioxide surface. The AFM images indicated the formation size of dot-like structures with few hundred nanometers across and different hydrophobicity as controlled by the difference in adsorption terminal or core segments of hyperbranched compounds.

Among recent application-driven research, examples of corrosion protective coatings were composed from a covalently crosslinked silica network with hyperbranched poly(ethylene imines) used as a crosslinking agent were reported by Roussi et al.¹⁷¹ The coatings with corrosion inhibitors included into hyperbranched component fabricated by means of sol-gel technique showed much enhanced corrosion resistance than regular coatings. As reported by Sangermano et al.,¹⁷² UV curing of epoxy based blends with hyperbranched polymers facilitated increased flexibility and toughness. In addition, adding the functionalized alkoxysilanes as a precursor of silica phase resulted in a higher surface hardness and scratch resistance without affecting the toughness of crosslinked composites.

Fine crosslinked blends of a tetrafunctional epoxy resin and a hydroxyl-functionalized hyperbranched polyester Boltorn H40 were prepared by Jin et al.¹⁷³ These blends show dispersive morphologies with dispersed phase of different modalities containing hyperbranched component. The presence of hyperbranched components causes significant increase in the fracture toughness due to the formation of hydrogen bonding between the epoxy network and the hyperbranched polyester modifier.

In conclusion, we suggest, that the multifunctional coatings from surface-grafted and crosslinked hyperbranched polymers represent a novel example of the engineering surfaces with their surface properties such as adhesion, shear properties, wear resistance, corrosion resistance, biofouling properties, loading functions, and elastic resistance which can be also responsive to fluidic, chemical, light, and temperature variations can be of interest for a range of prospective applications in biomedical, sensing, tribological, advanced nanocomposites, and drug delivery fields.

ACKNOWLEDGMENTS

Funding from the National Science Foundation, DMR-00308982 and DMR-1002810, is gratefully acknowledged. V. V. Tsukruk thanks the Humboldt Foundation for support during preparation of this review.

Note: The chapter from which this Review was adapted and upgraded appeared in the book "Hyperbranched Polymers: Synthesis, Properties, and Applications," edited by Deyue Yan, Chao Gao, and Holger Frey and published by John Wiley and Sons (ISBN: 978-0-471-78014-4). Print and online versions are available, respectively, at http://amzn.to/hyperbranched_polymers and http://bit.ly/hyperbranched_online.

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