

The architectures and surface behavior of highly branched molecules

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Abstract

This review presents recent developments in the field of the highly branched molecules (excluding dendrimers) with emphasis on their surface behavior, microstructure, surface morphology, and properties. In our consideration, we included popular types of highly branched molecules, such as star molecules with multiple arms, brush macromolecules of different kinds, and hyperbranched molecules, many of them available in relatively large quantities, which is crucial for future applications.

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1. Introduction

Steady and growing interest is quite noticeable for research directed toward molecules and macromolecules with highly branched structures. This growing interest is primarily related to the presence of multiple branches. And thus high concentration of functional terminal groups, along with architectural constraints, lead to significant changes of chemical and physical properties of highly branched molecules as compared with their linear analogs [1]. For example, highly branched polymers generally exhibit much lower solution and melt viscosities compared to linear polymers of the same molar mass, a characteristic that may help facilitate coating, extrusion, or other manufacturing processes [2]. On the other hand, the encapsulation of metal nanoparticles or organic molecules has been suggested and successfully demonstrated for a number of different dendrimer structures.

The most popular class of highly branched molecules, dendrimers, has been intensively studied for two decades. A lot of exciting results related to chemical architectures, synthetic routines, encapsulating properties, aggregation behavior, assembly in solution and surfaces in conjunction with prospective applications in drug delivery, nanocomposite materials, and catalytic systems have been reported [3–5]. However, several factors limit the prospective use of conventional dendrimers for large-scale applications. Most important factors include the enormous cost in synthesis and purification causing unavailability of this material in significant quantities. Indeed, each generation of branching increases the time of reaction and decreases the product yield, thus increasing the overall cost of synthesis in a highly progressive manner [6]. Many prospective applications, although suggested for

highly branched materials upon the birth of the field, have been implemented only in several very special cases. This is due not only to the extremely high cost of complex materials, but also to scarce understanding of their actual, and not “cartoonish” behavior, while interacting with a complex environment. Considering these issues, related highly branched structures, other than dendrimers, with potentially interesting properties and microstructures, have been introduced and intensively studied over the past decade.

Thus, this review is devoted to the discussion of recent developments in the field of the most interesting and promising (from the authors’ prospective) highly branched molecules and, more specifically, their behavior, structure, and properties on various surfaces and interfaces in relationship with their chemical architecture. To keep this focus, we included only a brief introduction of their chemical architectures with proper referencing and excluded extensive discussion of synthetic efforts in this field, which was a subject of recent reviews. Moreover, we focused on highly branched molecules primary introduced within the past decade, staying away from conventional dendrimers which have already been discussed in a number of excellent reviews and books [3,4,7–11].

In our final section, we included popular types of highly branched molecules, such as star molecules with multiple arms, brush macromolecules of different kinds, and hyperbranched molecules. This section addressed the role of the overall chemical architecture and molecular symmetry, number and length of various branches, and the nature of terminal groups in their microstructure and properties at surfaces and interfaces. Moreover, due to relatively simple and accessible synthetic routines, many of these materials became available in

relatively large quantities (grams–kilograms instead of traditional milligrams for dendrimers) at a very reasonable cost. Therefore, the practical use of these materials for many prospective applications is not out of reach and several successful examples are already available (e.g., hyperbranched polyesters introduced by Polyols [12,13]).

Another focus of this review brings us to the behavior of the highly branched molecules onto various solid surfaces either as isolated molecules, or in the form of dense monomolecular layers, ultrathin surface films, and as chemically grafted coatings. In several selected instances, we discuss combinations of these molecules and nanoparticles as well. We believe that the understanding of the surface and interfacial behavior of these molecules is critical for their prospective utilization in life science, engineering, nanotechnological, sensing, and catalytic applications suggested for this class of materials a long ago.

The level of research activities in this field is still modest if compared to the burst of research in the field of conventional dendrimers at surfaces (a number of annual publications reaching several hundred since the mid-1990s). The number of papers focused on highly branched molecules (excluding dendrimers) at surfaces constituted only a small fraction of related publications with virtually non-existent publication records in this field before 1995 (see publication records for the past two decades in Fig. 1). Very few papers have been

published annually in this field, even long after pioneering studies on synthesis of first hyperbranched [14–17]. However, the sharp upward trend in a number of publications is a recent characteristic of this field with a rapid, threefold increase in a number of publications in the past 5 years (2001–2006) as compared to the previous 5 years (1995–2000). Currently, the annual number of publications, dealing with the surface behavior of highly branched molecules, is approaching 50 and still growing (Fig. 1).

The rapid increase in publication reflects the shifting of the focus to multifunctional materials that are more “practical” (characterized, available, accessible, and affordable). The availability of such “poor man dendrimers” allowed the exploration of not only chemical composition and architecture in very dilute solutions, but also the exploration of studies of the variety of properties (surface, thermal, mechanical, optical) of highly branched molecules in the bulk state, in ultrathin films and coatings, at surfaces and interfaces, which are relevant to their prospective applications.

The review is composed of several sections each with its own focus. First, we briefly introduce a range of general synthetic routes and chemical compositions suggested for making highly branched molecules. We also describe the most commonly exploited architectures, ranging from comb-like brushes to star block copolymers. After this brief introduction, accompanied with proper referencing for further in-depth reading, we discuss some specific surface-placement approaches. The simplest of them places molecules on a surface in diluted or densely packed forms by simply employing casting or spin-casting routines. In this case, the final conformation and organization of molecules are controlled by weak physical interactions between different molecular segments and surface groups. On the other hand, the surface modification usually involves covalent bonding with two well-known general strategies, known as “grafting to” and “grafting from” routes. Although very different, both approaches rely on a balance of physical and chemical interactions which control surface organization of molecules. Frequently, they are used in a combination: e.g., “melt grafting” includes a first step of spin-casting thin films and a treatment at elevated temperature to allow chemical grafting. We treat these approaches as highly complementary and thus consider both of them here.

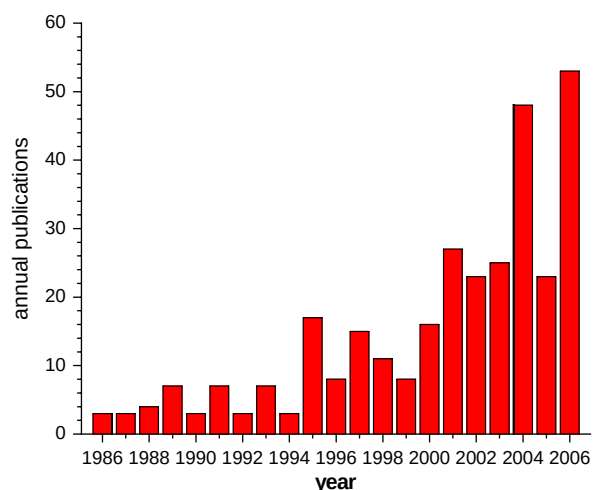


Fig. 1. Annual number of refereed publications in the general field of highly branched and hyperbranched molecules at surfaces. Data compiled with SciFinder, May 2007.

The most extensive section covers a wide range of surface structures and morphologies of various highly branched molecules along with various methods of their fabrications. We discuss surface structures and properties for highly branched molecules placed on various solid surfaces via casting and spin-casting, chemical grafting, Langmuir–Blodgett (LB) deposition, and electrostatic assembly. The most common well-characterized surfaces, widely exploited in current studies, include bare glass, mica, graphite, and silicon wafers as well as their modified analogs. Although direct comparison of surface behavior on different surfaces can be found very rarely, we discuss the substrate-dependent organization whenever available. We also present few examples of the placement of highly branched molecules onto non-planar, highly curved surfaces of inorganic nanoparticles.

Finally, it is worth to note that these days, the direct visualization of molecular and nanoscale surface structures at ambient conditions is a common practice. Thus, a number of high-resolution atomic force microscopy (AFM) images are included to illustrate different aspects of surface organization and assemblies of highly branched molecules. We used our judgement to select these images and filtrate, to some extent, numerous artifacts still appearing in the literature. However, we do not have the space for discussing these results in technical detail and thus refer a reader to the original sources when appropriate.

2. Architecture of highly branched polymers

2.1. Major types of macromolecule structures

In addition to regular dendrimers, the most common branched architectures include graft, arborescent, hyperbranched, and star-shaped types (Fig. 2). A common theme for all these branched architectures is a presence of a central reactive part of different dimensions (e.g., backbones, single groups, or nanoparticles) which serves as the attachment of different types of branches (Fig. 2). Rigid, flexible, or semi-rigid branches might have different architectures (radial, side, or tree-like). An important portion of these structures is terminal groups, which can be reactive, polar, hydrophobic, bulky, etc., and which, in many cases, constitute a loosely defined “shell”. A few examples of hybrid structures, combining several major designs, will also be discussed. Each of these major types of branched polymers include a wide variety of possible chain configurations and shapes which depend upon the synthetic path exploited and chemical composition of backbones, cores, branches, and terminal groups.

2.2. Chain architectures and nomenclature

One of the simpler highly branched architectures introduced and studied long ago are graft polymers (Fig. 2a), also called molecular brush or comb-like

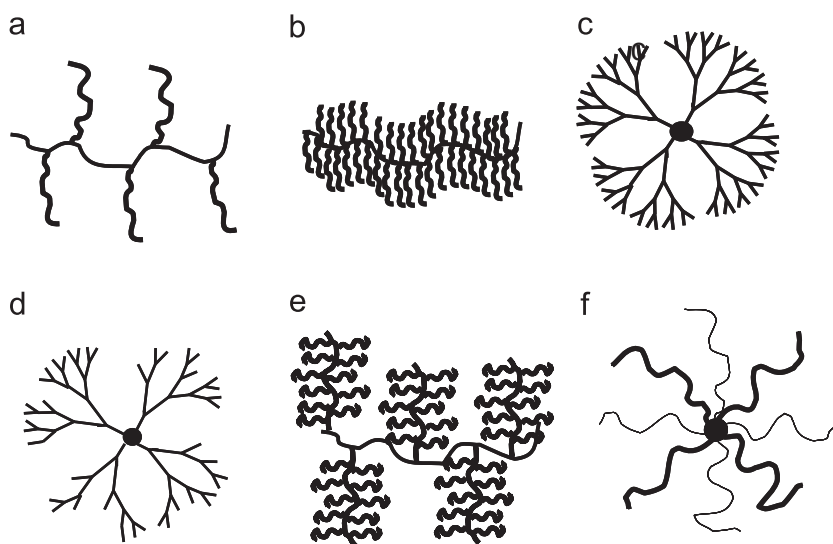


Fig. 2. Selected common types of chain architectures for highly branched molecules: (a) graft, (b) brush, (c) dendrimer, (d) hyperbranched, (e) arborescent, and (f) star architectures.

polymers (especially in the case of short side chains [18]) (Fig. 2b). These types of macromolecules, sometimes also termed cylindrical brushes, consist of a flexible polymeric backbone and grafted side chains with different grafting densities. Recent developments in synthetic approaches stimulated an appearance of novel macromolecules structures mainly discussed here. Depending upon the types of side chains attached, comb-like (identical type of side chains) [19], centipede (two types of side chains attached) [20], or barbwire (multiple types of side chains) [20,21]. In this review, we discuss only macromolecules with *polymeric/oligomeric* side chains. In most cases, the backbone and side chains differ in chemical composition. Within this class of molecules, some molecular architectures are called tadpole [22], tablet-like [23] or bottle-shaped [24] brushes, which correspond to the particular shape (expected or observed), of collapsed macromolecules. Depending upon the distribution of the side chains along the backbone, different types of cylindrical brushes such as regular [25], random [26], or gradient [27] are recognized as well. Recently, a new type of comb-like polymers, with asymmetric statistically distributed polymeric side chains, is synthesized by radical polymerization [28].

Usually, the name dendrimer implies highly regular, tree-like architectures, divergent from a single, point-like core with very regular branches radially extending from a single center (Fig. 2c). Dendrimers can be considered as an extreme case of comb brushes with tree-like branch structures grafted to a single core instead of a linear polymer backbone. Varieties of dendrimers with different architectures and chemical compositions have been synthesized and their properties have been reported to date but those will not be considered in this review because of several excellent recent publications [4,8,11,29,30].

Hyperbranched molecules compositionally are not very far from conventional dendrimers but show a lower degree of branching and a less regular architecture (Fig. 2d). These molecules, with their fractal structure and multitude of branches, have attracted the most attention in this field in recent years especially when prospective applications were considered [31–35]. Often, these molecules are created in one-pot synthesis without the lengthy stages of stepwise reaction and purification necessary with traditional dendrimers. Similar to dendrimers, hyperbranched polymers are usually composed of short monomeric units. However, the

new type of hyperbranched polymers recently developed consists of oligomeric or polymeric chains as a repeating unit and will be discussed further in this section [36–41]. Highly branched polymers with a small, but controllable number of branches, are also of interest because such materials may offer a practical compromise between superior physical properties and processing difficulties.

One particular class of highly branched polymers—arborescent polymers—is composed of randomly grafted polymeric chains with different levels of grafting density (Fig. 2e) [42,43]. Some authors have called them “graft-on-graft-on-graft” or simply dendrigraft polymers. Other researchers incorrectly called these polymers “hyperbranched” or “tree-like” polymers. Indeed, unlike dendrimers or hyperbranched polymers, arborescent polymers are not composed of repeatable monomeric units throughout the whole macromolecule, but only the side chains. Nevertheless, this new architecture provided a higher level of macromonomeric grafting ability along with the capability to build a densely grafted layered structure using different monomers at each step.

Star polymers containing several chains radiating from a relatively compact core represent a special case of branched polymers. They are usually composed of a few well-defined polymeric arms of one or two types (Fig. 2f). Asymmetric star polymers are star macromolecules having arms with different molecular weights and chemical natures. Until recently, very little was known about their properties due to difficulties in the preparation of these products with high structural uniformity. Lately, many researchers have reported the synthesis of the star-shaped polymers with multiple and different arms (also called hetero- or miktoarm star) by using different types of polymerizations [44–48]. Star block copolymers contain lengthy chains (blocks) as arms [49]. Star polymers with compact, low-generation dendrimers as a core are usually called dendritic stars [50–52].

Hyperbranched star polymers or simply hyperstars consist of hyperbranched molecules as a multifunctional core [53–55]. So-called dendrimer-like star molecules contain a macromolecular (oligomeric or polymeric) fragment as a monomer unit between branching points [56–59]. Some star polymers are also named after expected (sometimes even confirmed) molecular shapes. Thus, H-type [60–63], π -shaped [64,65], Y-shaped [44,62,66,67], palm-tree and other types can be found in the literature [68].

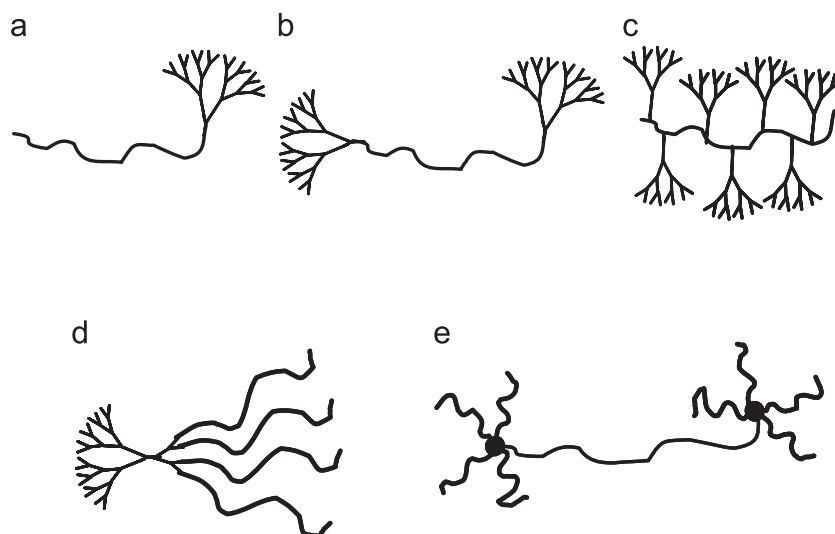


Fig. 3. The selected hybrid architectures of highly branched molecules: (a) dendron-linear, (b) barbell-like, (c) dendronized, (d) “bow-tie” and (e) dumbbell types.

A number of studies discussed hybrid types of highly branched molecules that are composed of one or several highly branched fragments connected to one or both ends of linear or rod-like polymers. In the case of one end substitution, these dendron-linear diblock copolymers are sometimes called fan-shaped polymers (Fig. 3a) [69–71]. Similar polymers with two dendritic ends are named barbell-like polymers (Fig. 3b) [72–74]. Several linear polymer chains attached to selected terminal groups of the dendritic molecules form polymer with “bow-tie” hybrid architecture (Fig. 3d) [75]. Dendronized rod structures are formed by attaching branched oligomeric units to short, rod-like rigid backbones (Fig. 3c) [76]. Polymers with dendritic branches connected to the backbone are called dendronized [77,78] or jacked polymers (Fig. 3e) [79]. Several polymeric arms connected to both ends of the linear backbone form dumbbell macromolecular structures [80] (sometimes called pom–pom structures [81,82]).

2.3. Synthetic strategies

Three synthetic routes have been successfully applied for the synthesis of highly branched molecules and macromolecules: “grafting from” a linear macroinitiator, “grafting onto” multifunctional linear chains, and the “grafting through” of macromonomers [83]. The “grafting to” approach exploits preformed, terminally functionalized polymer chains reacting with a multifunctional quencher

molecule that forms the core of the macromolecules [84–86]. However, the reaction of several polymer chains with a single core molecule is often difficult because of steric hindrance, which leads to defective stars with missing arms.

The alternative “grafting from” approach involves growing polymer chains from a multifunctional initiator or precursor polymer [87–89]. Here, the core reacts only with monomers, which is a less sterically demanding process. However, for some type of polymerizations, such as ionic polymerization, the application of the “grafting from” approach requires the use of multiple charged initiators, which usually result in poor solubility and cause wide molecular weight distribution. The third method is a slight variation of the macro-monomer technique discussed in detail elsewhere [90–92].

A wide selection of synthetic preparation methods is employed for the synthesis of highly branched polymers with diverse chemical compositions [93]. Synthesis of hyperbranched [94,95], dendronized [96], dendrigraft [43], and star polymers [9] has been discussed extensively in recent publications. These specialty polymers are synthesized by living anionic [46,97], cationic [98], living radical polymerizations such as nitroxide mediated living radical (NMP) [99], atom transfer radical polymerization (ATRP) [100], reversible addition–fragmentation chain transfer (RAFT) polymerization [101], living radical photo polymerization [102], and their combinations [103,104]. Recently, Sharpless and co-workers

proposed a new approach in organic synthesis called a ‘click’ reaction [105]. This method has numerous advantages, including a high yield, along with a high tolerance to the nature of functional groups and solvents.

3. Surface grafting

The nature of surface grafting along with chemical composition play significant roles in the controlling of surface morphologies of the surface layers, which can be formed either by “grafting from” or “grafting to” methods [106,107]. Both grafting approaches may involve either covalent or non-covalent tethering of the branched macromolecules onto the surface via appropriate functionalized linkages, which promote selective adsorption, binding, growth, or spreading of branched molecules. In this section, we discuss a variety of specific “surface placements” designed for different surfaces and substrates, which can be applicable for different surface chemistries.

Generally speaking, all known grafting routes start by introducing or using a proper reactive group (X) onto the surface by using a variety of chemical reactions. The grafted branched polymers are typically anchored to a surface via a single branch or by the core, such that the whole molecule or some branches extend away from the surface (Fig. 4). The most popular route includes surface oxidation or surface modification with functionalized self-assembled monolayers (SAMs) (Fig. 4) [108].

The “grafting from” approach, presented as Route 1, involves the surface initiating polymerization by using surface functionalized groups (e.g., functionalized SAMs) and a solution of a proper monomer (Fig. 4). Depending upon the nature of the surface functionalized groups, several different polymerization routines are exploited. The most popular polymerization techniques include a step-

by-step method, radical polymerization, ring-opening polymerization (ROP), and polycondensation.

Route 2, which represents the alternative, “grafting to” approach is employed for covalent or non-covalent bonding of the pre-formed highly branched polymers with appropriate chemical functionality to a proper functionalized surface (Fig. 4). Usually, it involves the reaction of the hydroxyl or amino-terminated groups of terminal branches or cores with surface carboxyl or epoxy groups with the formation of covalent bonding. On the other hand, specific and non-specific non-covalent interactions such as van der Waals, hydrogen bonding, or Columbic interactions are exploited for relatively weak physical grafting of highly branched molecules.

3.1. “Grafting from” approach

3.1.1. Step-by-step methodology

The step-by-step methodology is widely used to synthesize a range of highly branched polymers on various surfaces. Despite the complexity of the multi-step grafting procedure, the step-by-step methodology can be employed to introduce a high concentration of surface functional groups within ultrathin layers. Moreover, further surface modification may be used for the alteration of surface properties on modified substrates.

To this end, Tsubokawa and Takayama [109] have exploited this approach to functionalize natural polymers such as chitosan. It was found that the hyperbranched PAMAM structure is propagated from the chitosan-coated surface by repeating two primary steps: (1) Michael addition of methyl acrylate (MA) to amino groups at the functionalized surface and (2) amidation of the resulting esters with ethylenediamine (EDA) (Fig. 5). It has been suggested that due to heterogeneous conditions and steric hindrances in the course of growth, this technique resulted in hyperbranched architecture. Further post-grafting of the

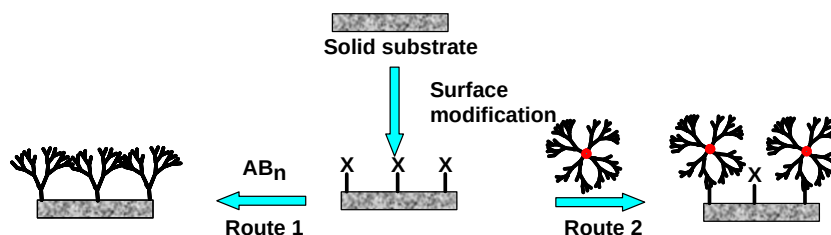


Fig. 4. General grafting routes for tethering highly branched polymers onto a functionalized surface.

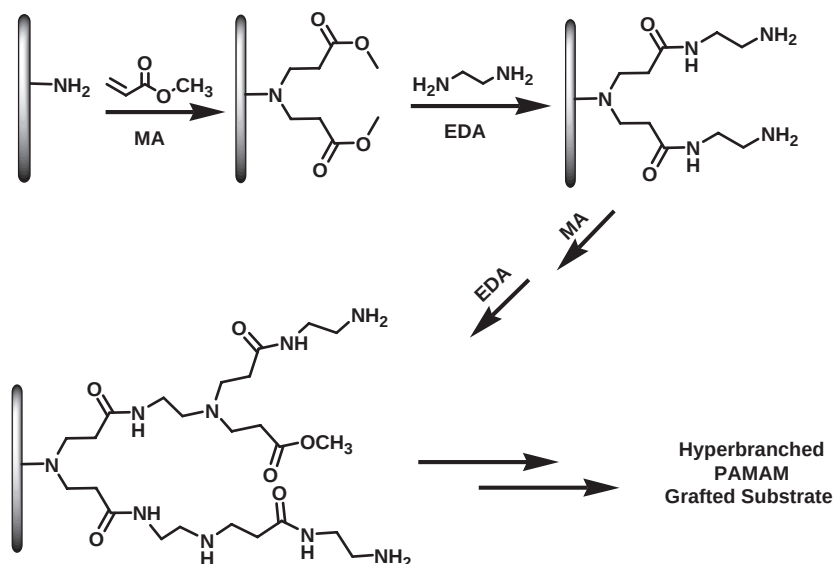


Fig. 5. General route for the step-by-step grafting methodology for synthesis of hyperbranched PAMAM surface layer.

hydrophilic poly(2-methyl-2-oxazoline) and hydrophobic poly(isobutyl vinyl ether) branches to the hyperbranched grafted layer allowed to control the wettability of the modified chitosan surface. On the other hand, the scale-up synthesis of hyperbranched PAMAM structures chemically grafted onto ultra-fine silica nanoparticles has been successfully achieved by Murota et al. [110] in a solvent-free dry-system. Furthermore, the post-grafting polymerization of different monomers onto PAMAM-modified silica nanoparticles resulted in hybrid polymer-inorganic nanoparticles with high surface grafting density, which can be suitable for solar cell technologies [111,112].

In the related development, the step-by-step methodology has been expanded for the functionalization of various inorganic and organic surfaces. For example, Fujiki et al. [113] have described the chemical grafting of hyperbranched PAMAM polymers onto glass, alumina, and carbon fibers. Significant alternation of the wettability of these polymer-grafted inorganic fiber surfaces after the grafting procedure was observed in all cases that indicated effective surface coverage. These researchers also applied this methodology for the grafting of hyperbranched polymer onto silica nanoparticles preliminary treated with 3-glycidoxypopyl trimethoxysilane SAM [114]. Finally, Tsubokawa et al. broadened the applications for the grafting of hyperbranched PAMAM by exploring carbon

black [115] and PS [116] surfaces, although in these cases grafting routines are not well defined.

Nakada et al. [117] have applied a similar approach to the modification of the ultra-high molecular weight polyethylene (PE), an extremely non-trivial task for its highly inert and hydrophobic surface. After repeating the grafting cycle several times, they produced ultrathin surface films, which possess anion exchange capacity and absorb acid dye. However the integrity and microstructure of the PE surface after this procedure was not considered. In addition, a one-pot method for the fabrication of hyperbranched poly(amine ester)-grafted silica nanoparticles was developed by Liu and coworkers [118]. A dense surface grafting was achieved which led to a good solubility of hybrid silica-polymer nanoparticles. These nanoparticles with dense surface layers were suggested as nanofillers for composite materials such as reinforced polyesters and nylons.

3.1.2. Graft-on-graft technique

The step-by-step technique described in the previous section has significant disadvantages for practical use including the severe limiting of surface layers' overall achievable thickness. This is due to the small increment of the growing thickness on each grafted layer per a single growing step. To overcome this problem, Crooks et al. have developed a novel technique by using a single

macromolecule as a monomeric unit for growing a hyperbranched film. The synthetic procedure suggested by these researchers started with the activation of a gold substrate with a monolayer of mercaptoundecanoic acid (MUA) as an intermediate adhesive SAM layer [119]. The carboxylic acid groups of this SAM were activated via a mixed anhydride followed by the reaction with a diamino-terminated poly(*tert*-butyl acrylate) ($\text{H}_2\text{N-PtBA-NH}_2$). This reaction resulted in a densified 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 yielded additional grafting at multiple sites on each previous graft, leading to multilayered, hyperbranched polymer architectures formed with the thickness increment significantly increased. The thickness and the surface roughness of surface films from hyperbranched PAA synthesized in this manner increased very rapidly with the number of grafting steps and the following surface modifications [120]. Further modification of obtained hyperbranched PAA films through amide or ester linkages produced novel films containing a high density of various internal and external functional groups. The substitution of the MUA intermediate layer with a diacetylene containing molecule $\text{HS}(\text{CH}_2)_{10}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_{10}\text{COOH}$, which polymerizes under UV light, led to the robust crosslinked polymer films to be stable even under aggressive external conditions, a very important feature for some demanding applications [121].

Upon further development, Crooks et al. reported the synthesis and the surface passivation properties of hydrophobic surface layers formed from highly fluorinated, hyperbranched PAA material [122]. These films blocked the electrochemical reactions on gold electrodes, which made them attractive as prospective corrosion-inhibiting coatings [123]. Selective functionalization of the carboxylic groups within branches could also produce surface films with inner hyperbranched architecture, which are capable of reversible adsorption of polyvalent cationic polyelectrolytes [124]. This approach allowed the formation of ionic nanocomposite polyelectrolyte surface films, which might be used as a host matrix in biosensors [125].

In another twist, Bruening et al. applied the graft-on-graft deposition technique described above to produce hyperbranched PAA membranes deposited on a porous alumina support [126]. They observed

that even ultrathin hyperbranched PAA films (40 nm thick) could efficiently and uniformly cover underlying microscopic pores without filling them, thus essentially forming freely suspended membranes on a microscopic scale which could be utilized for membrane-based sensing applications [127,128].

In another study, these authors utilized the graft-on-graft method to build robust and ultrathin hyperbranched PAA films on PE surfaces [129]. Similar to the work described above, diaminopoly(*tert*-butyl acrylate) was attached to pre-oxidized PE surfaces. The oxidation with $\text{CrO}_3\text{--H}_2\text{SO}_4$ generated a high concentration of carboxylic functional surface groups. The resulting grafted surface film exhibited potential for further modification. Furthermore, it has been demonstrated that by using hyperbranched grafting chemistry, not only planar surfaces but also PE particles can be functionalized with densely grafted carboxylic surface groups [130]. Another approach utilized the polyvalent hyperbranched PAA grafts for the surface modification of gold or PE surfaces. A soluble hydrogen-bond acceptor polyacrylamides, such as poly(*N*-isopropylacrylamide) was used in this mild hydrogen-bond-based grafting method [131]. This hydrogen-bonded polymeric ensemble was robust and stable when subjected to extensive washing and the addition of external acid.

In another example, the chemical modification of polypropylene (PP) surfaces by chemical grafting with a hyperbranched PAA was carried out by using grafting techniques applied earlier for gold, aluminum, silicon, and PE surfaces [132]. Bergbreiter and co-workers demonstrated that selective treatment of the activated surfaces by pentadecylfluorooctylamine allowed the alternation of the surface properties making them either hydrophilic or hydrophobic on demand. As a next step, this research group has introduced a new synthetic method for modifying the carboxylic acid groups of initially formed hyperbranched surface [133]. The utilization of various procedures such as amidation, esterification, reduction, and alkylation reactions of terminal carboxylic acid groups generated functional surfaces not accessible by conventional graft polymerization. Moreover, the oligomerization of covalently attached thiophene monomers with FeCl_3 resulted in the formation of fluorescent oligothiophenes within hyperbranched PE grafts with potentially interesting electrooptical properties [134].

An alternative approach, suggested by the Bergbreiter and co-workers, is based on employing acrylic acid and Ce(IV) to assist graft-on-graft chemistry [135]. After the functionalization of the oxidized PE surface with the polyhydroxylated oligomer, the hydroxyl surface groups were successively grafted with Ce(IV). Then, the carboxylic acid surface groups were reduced into hydroxyl groups. This method, suggested by the authors, appears to be more appropriate for the fabrication of more dense, robust, and relatively thick surface films with a high concentration and uniform composition of terminal surface groups. In addition, the method itself is faster than the conventional graft-on-graft technique and allows producing dense graft copolymers with a wide range of combination of monomers. In addition, these studies demonstrate the versatility of the step-by-step approach and expose new ways for the functionalization of a variety of technologically important surfaces.

In a complementary development, a variety of novel methods were introduced to produce versatile patterned surface films for the preparation of new functional nanocomposites. One of the novel methods relied on the passivation of the reactive surface on plastic substrates by conventional microcontact printing (μ -CP) followed by polymer grafting to selected surface areas [136]. Another approach particularly useful for the modification of gold-coated substrates is based on the microcontact printing on passivated monolayers (*n*-hexadecanethiol), deposition of the MUA on unprotected surface areas, followed by grafting the hyperbranched molecules and subsequent functionalization of their terminal groups [137].

3.1.3. Radical polymerization

Recent advances in controlled radical polymerization have allowed sophisticated synthesis of well-defined functionalized polymers with different macromolecular architectures grafted onto solid substrates [138]. New developments in the synthesis and characterization of hyperbranched methacrylates at surfaces have been summarized by Mori and Mueller [139]. They described a novel synthetic concept for the preparation of hyperbranched polymers on a functionalized planar surface (Fig. 6). A silicon wafer pre-modified with an initiator layer was used for self-condensing vinyl polymerization (SCVP) via ATRP [140]. The analysis of surface morphology with AFM revealed a large number of nanoscale protrusions with size, density,

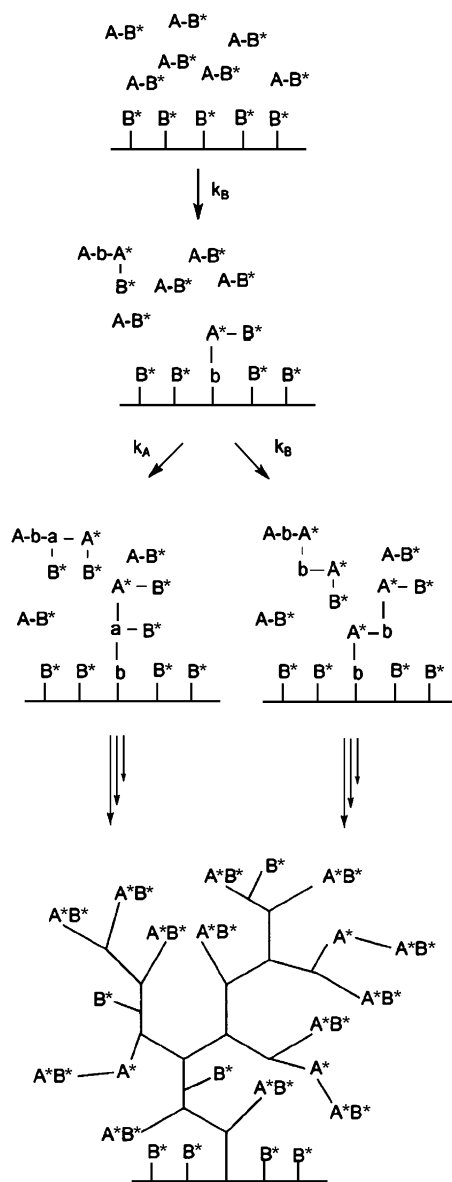


Fig. 6. Surface-initiated SCVP of grafted polymers obtained by copolymerization of BPEA and tBuA [140]. Reprinted from Mori et al. by permission of the American Chemical Society.

and heights dependent upon the conditions of the polymerization, which were assigned to the grafted macromolecules in individual and aggregated states. Using a similar approach, the researches synthesized grafted hyperbranched glycopolymers, which can be further used for surface modification due the presence of available functionalized groups [141].

Recently, the build-up of hyperbranched polymer by SCVP has been expanded by Muller and

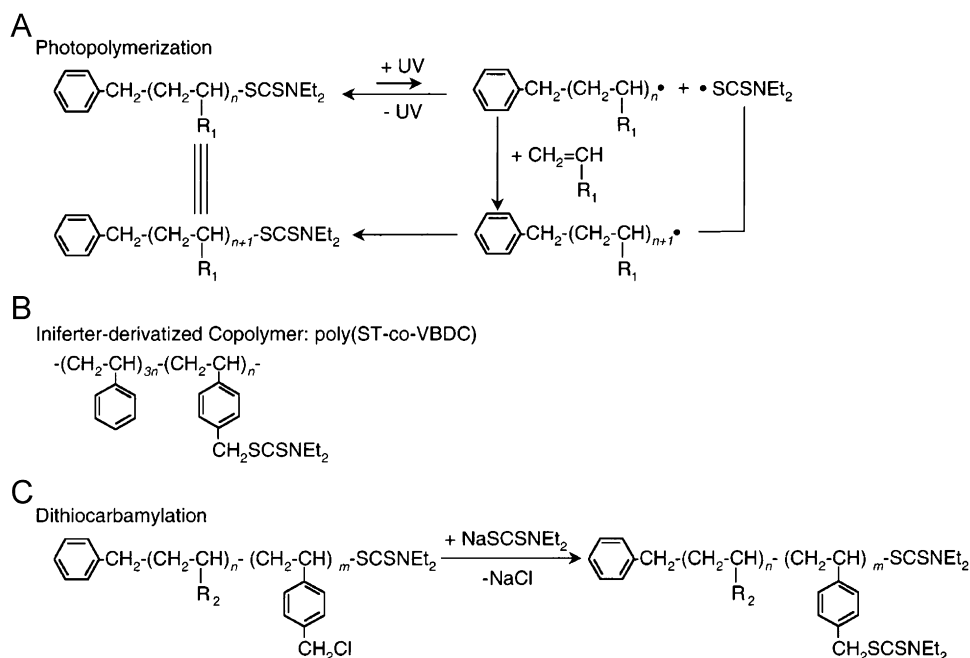


Fig. 7. (A) Reaction mechanism of the iniferter-based quasi-living radical polymerization. (B) Chemical structure of dithiocarbamate group derivatized polyST (poly(ST-co-VBDC)). (C) Reaction mechanism of dithiocarbamylation reacting with chloromethylstyrene groups of a derivatized polymer [147]. Reprinted from Nakayama et al. by permission of the American Chemical Society.

coworkers to include highly curved inorganic surfaces such as silica nanoparticles [142,143]. They presented innovative methods of fabricating these hybrid nanoparticles composed of silica cores and firmly grafted hyperbranched PtBA shells. Hydrolysis of the *tert*-butyl ester functional groups of the branched chains created novel nanostructured materials with core-shell, silica-PAA morphology. This approach was applied for the modification of silsesquioxane nanoparticles by glycomethacrylates [144]. Alternatively, deprotection of the isopropylidene groups resulted in water-soluble stars whose original structures were retained during hydrolysis. AFM data confirmed the presence of uniform and well-defined glycostars as spherical isolated particles.

Tsubokawa et al. have investigated the grafting of polymers having pendant peroxycarbonate [145] or azo [146] groups onto ultrafine silica nanoparticle surfaces. They found that the chemical grafting of mixed or uniform hydrophilic (HEMA and PVP) or hydrophobic (PMMA) chains can be used to control the surface wettability properties of these nanoparticles. In another development, Nakayama et al. [147] have demonstrated a novel strategy for growth of multigeneration hyperbranched graft architecture presented in Fig. 7. The iniferter

(initiator-transfer agent-terminator)-based quasi-living radical copolymerization of chloromethylstyrene (CMS) with a variety of vinyl monomers was readily initiated by benzyl *N,N*-diethyldithiocarbamate (DC)-functionalized surfaces using ultraviolet irradiation. Subsequent dithiocarbamylation of the CMS units in the graft copolymers led to the introduction of a new grafting center onto the parent chain thus resulting in hyperbranched architecture.

The preparation of *n*th generations (G_n) of graft architectures was successively achieved by repeating the cycles of photopolymerization and dithiocarbamylation according to the routine described above [147]. This approach allowed not only the control of overall chain length on each step by a photoirradiation time, but also fine tuning these chains' degree of branching by the variation of the composition of the CMS units (Fig. 8). The authors suggested that the increased density of grafted chains, the configuration of the chains, and general topology of these hyperbranched architectures can all be easily tuned by their approach. The resulting morphology controls the surface mechanical properties, which are expected to be different from those known for conventional brush surface layers from grafted linear chains.

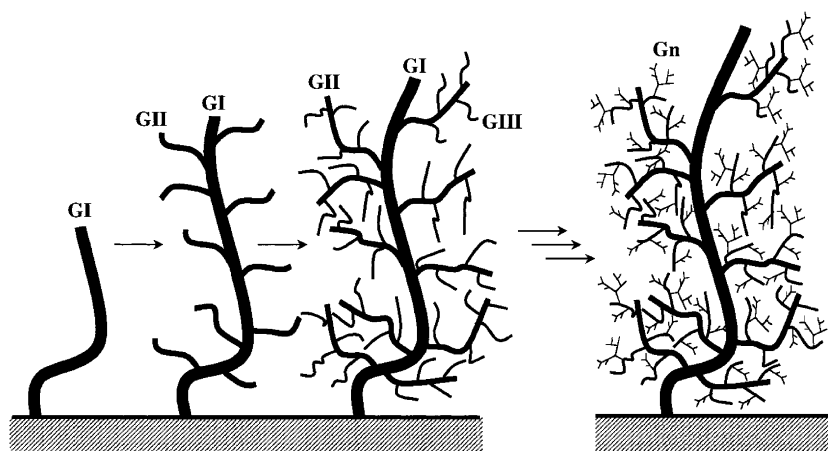


Fig. 8. Schematics of the highly branched surface grafts: first generation (GI) to n th generation (G_n) graft architecture [147]. Reprinted from Nakayama et al. by permission of the American Chemical Society.

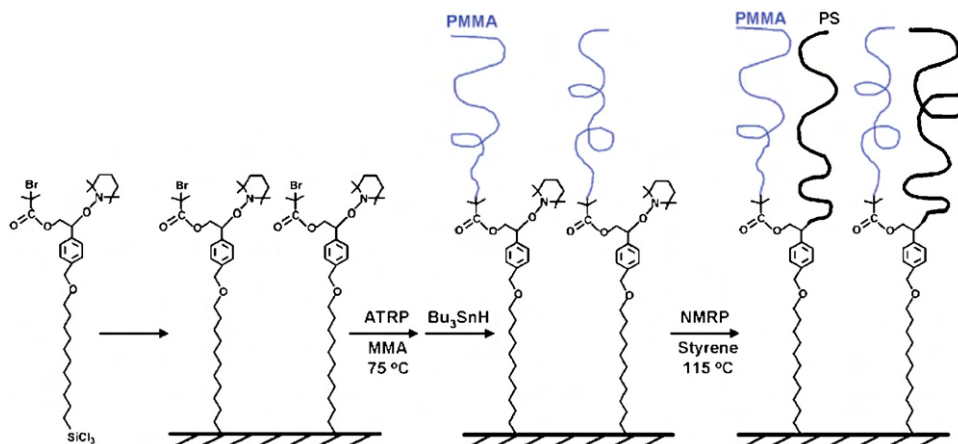


Fig. 9. Schematics of synthesis of mixed PMMA–PS brushes from an asymmetric difunctional initiator-terminated SAM (Y-SAM) by combining ATRP and NMRP techniques [149]. Reprinted from Zhao et al. by permission of the American Chemical Society.

In an alternative development, Zhao and co-workers successfully used a combination of different types of radical polymerization approaches to synthesize simple branched Y-shaped polymeric structures by grafting from a silicon surface (Fig. 9) [148,149]. In this approach, Y-shaped SAMs (Y-SAM) were prepared by immersing a cleaned silicon wafer into a toluene solution of asymmetric difunctional Y-silane with a subsequent ATRP of methyl methacrylate and NMRP of styrene. This modification produced a binary mixed PMMA–PS brush surface layer with morphology controlled by the chemical composition and the post-treatment with various selective solvents. Recently, this approach has been effectively applied for the

grafting of well-defined mixed PtBA–PS brush layers with nanoscale thickness onto silica nanoparticles to generate hybrid core–shell structures with potentially switchable surface properties [150]. This methodology was further modified to produce mixed brush on solid substrates in one-pot reaction [151]. Despite relatively small thickness, this grafted layer of PS–poly(2-phenyl-2-oxazoline) brush exhibited reversible behavior in response to changes in environment. However, even though the contact angle and XPS data were discussed, there are no direct microscopy data confirming the reorganization of surface morphologies of the mixed brush due to different solvent treatments.

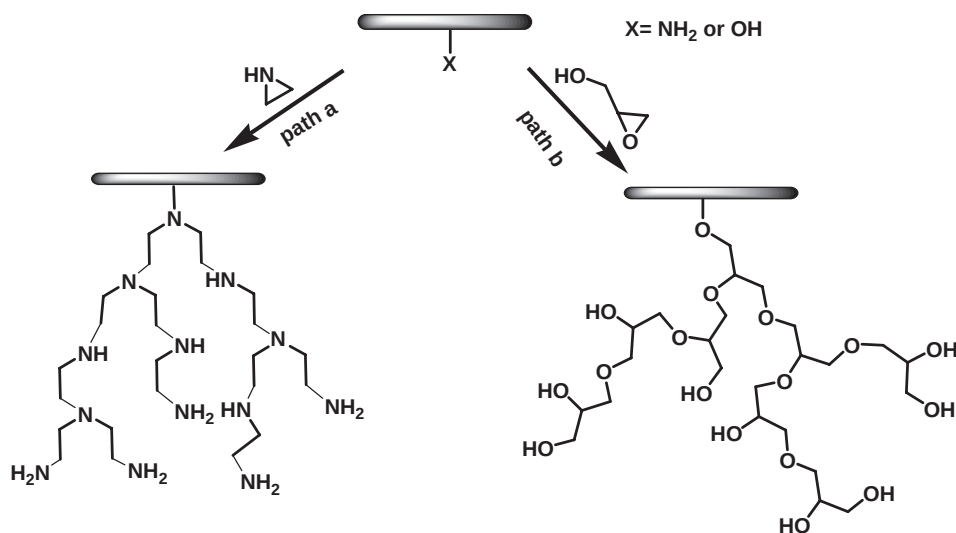


Fig. 10. Formation of the grafted hyperbranched polymer by ROP by two different paths.

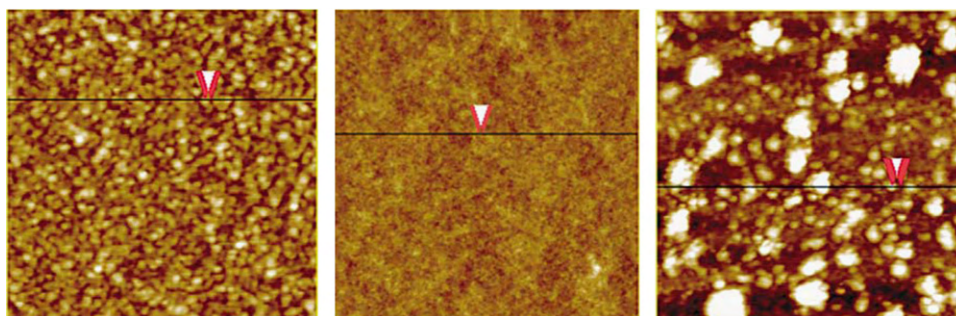


Fig. 11. AFM images ($1 \times 1 \mu\text{m}^2$) of aziridine-polymerized surface layer grown on SiO_2 in dichloromethane (left), toluene (center), and DMF (right) [156]. Reprinted from Kim et al. by permission of Elsevier Science (USA).

3.1.4. Ring-opening polymerization

An alternative approach for the surface grafting involves ROP which can provide a simple method of growing selected hyperbranched polymers in the absence of a catalyst. To implement this approach, Kim et al. [152] have treated amino functionalized silicon substrates with aziridines as a first step in preparation for grafted hyperbranched poly(ethylethimine) (PEI) surfaces (Fig. 10, path a). AFM imaging indicated that the surface-initiated polymerization conducted was rather regular and the resulting morphology of surface layers did not change significantly after the polymerization was completed [153].

In another recent study, Khan and Huck [154] have demonstrated a new procedure to synthesize covalently linked hyperbranched polyglycidols on a silicon oxide surfaces via anionic ring-opening (Fig. 10, path b). This reaction path resulted in the

formation of a multibranched glycidol surface layer with the thickness controlled by the reaction temperature. This way, the surface layers from hyperbranched polyglycidol with precisely controlled thicknesses can be formed. In addition, the esterification of the hydroxyl end groups in the post-polymerization reaction was used to tailor their surface properties in a wide range. Roller et al. [155] presented a further development of this approach by showing efficient grafting from hyperbranched polyglycidol layer on PS resin. This approach can be instrumental in the fabrication of a high-loading hybrid template for organic synthesis.

Recently, Kim et al. have demonstrated that hydroxyl groups on the silica substrates, such as fused silica or silicon wafers with a natural oxide layer, can efficiently be exploited to initiate the ROP reaction of aziridine in the presence of catalytic amount of acetic acid. This reaction can be utilized

for the formation of a dense surface layer composed of highly branched PEI chains [156]. The authors have shown that the rate of polymerization and the surface morphology of the resulting grafted layers depend heavily upon the choice of solvent. For instance, polymerization in toluene resulted in uniform ultrathin polymer films with smooth surface morphology while the polymerization in dichloromethane led to a non-uniform surface with nanoscale phase-separated texture (Fig. 11).

Bergbreiter et al. have reported another example of the surface-initiated ROP resulting in graft polymerization of 5-vinyl-2-oxazolidinone and the controlled growth of hyperbranched poly(1-amino-butadiene) (PVOX) grafts from an amine functionalized silicon wafer as a precursor [157]. The authors observed that the surface roughness of the graft polymer films increased with increasing thickness of the polyamine surface layer similar to that observed for the hyperbranched PAA film produced by the graft-on-graft technique.

3.1.5. Polycondensation

Polycondensation is a simpler and more useful method for the functionalization of the substrate surface and the growth of the highly branched surface structures in a facile one-pot procedure. This way, silica nanoparticles with grafted hyperbranched aliphatic polyester chains (HAPE-SNs) have been prepared via the polycondensation of an AB₂ monomer, 2, 2-bis(hydroxymethyl)propionic acid (bis-MPA) [158]. The polymerization reaction was conducted from the surface of the amino-terminated silica nanoparticles catalyzed with *p*-toluenesulfonic acid (*p*-TSA).

3.2. “Grafting to” approach

The grafting to approach relies on the strong interaction of pre-formed branched molecules possessing multiple reactive sites with a proper functionalized surface. It is a popular approach because of its relative simplicity and ease of control, especially in a situation when modest grafting densities are sufficient and small thicknesses (nanometer scale) of surface layers are required. We present the discussion of this approach sorted according to the resulting type of bonding.

3.2.1. Non-covalent bonding

One of the simplest approaches to graft highly branched polymers onto a surface is adsorption

from a dilute solution usually below critical micellar concentration (cmc) to avoid complications related to pre-formed micellar structures in solution. The deposition is followed by multiple rinsings and dryings to assure the presence of only an adsorbed monolayer of molecules. The formation of stable surface structures, ranging from anchored single molecules in different conformations to dense uniform surface layers, is usually achieved through hydrogen bonding and ionic interactions between various segments of molecules and appropriate functionalized surface groups. In Fig. 12, a series of combinations of anchoring surface groups and usual highly branched molecules' functional groups is presented. These combinations are accompanied with suggested types of interfacial bonding to be exploited for highly branched molecule surface anchoring. Below, we summarize several recent results illustrating some of these combinations, which are the most popular.

Bare silicon wafers with a native silicon oxide layer possessing dense hydroxyl groups (freshly prepared), as well as SAM modified silicon wafers, were used as atomically flat (microroughness below 0.1 nm) substrates with well-defined surface composition for a number of highly branched molecules. For instance, hydroxyl terminated hyperbranched polyesters of different generations were adsorbed onto bare silicon surfaces [159] (Fig. 12a) as well as at amino-functionalized silicon surfaces [160] (Fig. 12b), forming a variety of single molecular surface structures, their aggregates, and uniform films as well will be discussed below.

Mészáros et al. [161] investigated the adsorption of a high molecular weight highly branched PEI on silicon wafers. As observed, the structure of the adsorbed macromolecules as well as the desorption properties of weak branched polyelectrolytes was strongly affected by pH [162]. Minko and co-workers deposited the PS/poly(2-vinylpyridine) (PS₇-P2VP₇) heteroarm star copolymer onto mica or silicon wafers and thoroughly studied it with the AFM (Fig. 12c) [163]. High-resolution imaging showed that switching the solvents might cause significant changes in single molecular conformations of the adsorbed macromolecules. In acidic conditions, PS₇-P2VP₇ formed either unimolecular or multimolecular surface micelles depending upon concentration and pH. Upon treatment of the trapped micelles with toluene, the PS core became swollen and PS arms gradually adapted an extended conformation whereas P2VP trapped arms retained

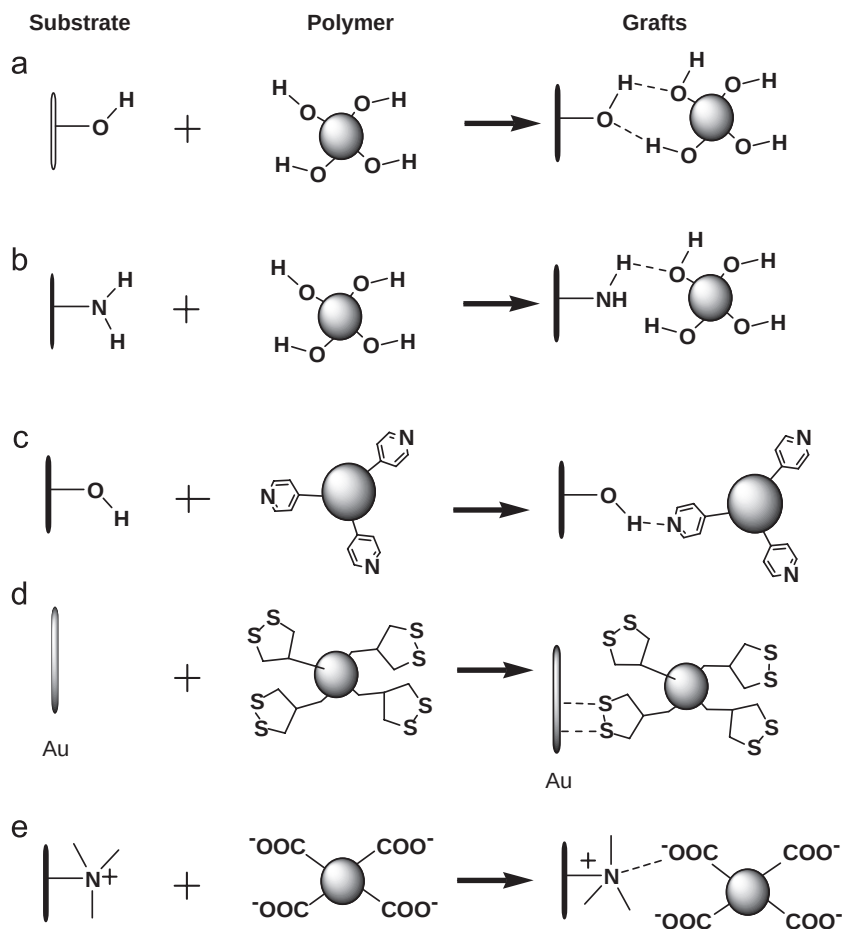


Fig. 12. Summary of synthetic routes of non-covalent grafting of highly branched molecules onto different substrates explored for highly branched molecules: (a)–(c) hydrogen bonding; (d) thiol coordination; (e) coulombic interaction. Spheres represent highly branched macromolecules.

their extended conformation due to the strong interaction with the mica substrate (see for more discussion below).

In a recent study, Haag et al. have prepared protein-resistant SAMs of dendritic polyglycerols (PGs) on gold by simple chemical modification of these readily available polymers with surface-active disulfide (α -lipoic acid) linker groups which form strong bonds with the gold substrate (Fig. 12d) [164]. Ishizu et al. [165] obtained poly(methacrylic acid) star-hyperbranched PS nanospheres and studied adsorbed poly(4-vinylpyridine) (P4VP) or partially quaternized P4VP driven by electrostatic interactions (Fig. 12e). The AFM revealed that the increasing degree of quaternization of the P4VP yielded high density and a uniform distribution of nanospheres on P4VP substrate.

An assembly routine for the formation of ordered surface films, beyond monomolecular layers discussed above, is layer-by-layer (LbL) assembly. As is well known, the LbL assembly may generate nanoscale multilayered films with controlled vertical distribution of components by exploiting Coulombic interactions between oppositely charged polyelectrolytes (Fig. 12e) [166]. This versatile assembly has been successfully applied to low molar weight molecules, linear polyelectrolytes, biological molecules, as well as inorganic particles [167–169].

LbL assembly has been also applied to PAMAM dendrimers of different generations long ago [170] and this approach has recently been extended towards functionalized hyperbranched molecules. Qiu et al. [171] have synthesized the carboxyl-terminated aryl-alkyl hyperbranched polyester

poly(5-hydroxyethoxyisophthalic acid) (PHEIA) and used it in electrostatic LbL assembly with poly(diallyldimethylammonium chloride) (PDAC). The AFM revealed sphere-like particles with sizes of several hundred nanometers, which were attributed to the aggregation of PHEIA molecules [172]. Further studies of anionic hyperbranched polymers with the same backbone, but different terminal groups, showed the critical role of the nature of the terminal groups on the resulting surface morphology of LbL films [173]. Several other examples of weakly attached surface layers from hyperbranched polymer have been reported as well. e.g., Bai et al. investigated the influence of hyperbranched polymer chemical composition (different cores, connecting groups, branches, and terminal chromophores) on the ultrathin films' optical properties. These films have been fabricated by spin coating, self-assembly, and LB deposition [174]. Comprehensive discussion of surface structures generated by employing these fabrication techniques will be discussed in the next section.

3.2.2. Covalent bonding

Ultrathin (several nanometers) surface layers have been fabricated from functionalized hyperbranched polymers by using the 'grafting to' approach with firm chemical binding of the molecules to the supporting surface which, in many cases, is simpler and more robust than other approaches discussed above. Generally, in many investigations a preference was given to the grafting from a melt approach vs grafting from dilute solution to assure relatively high grafting density and uniformity of the grafted layers onto bare and pre-functionalized surfaces. A variety of chemical reactions between surface groups and properly functionalized groups of highly branched molecules have been exploited for this purpose (Fig. 13). One of the most widely used approaches utilized for the highly branched polymers was the reaction between surface epoxy groups and carboxyl or hydroxyl terminal groups (Fig. 13a–c).

For instance, Sidorenko et al. have reported the melt grafting to approach for covalent bonding of partially epoxy-functionalized hyperbranched polyesters (EHBP) to a bare silicon surface by the thermally mediated reaction of secondary epoxy groups with the hydroxyl groups of silicon wafers at elevated temperatures (see an example in Fig. 13a) [175]. Robust and uniform surface layers with thicknesses of 4 nm have been formed this way

despite the presence of a significant fraction of non-reactive and hydrophobic alkyl-terminated branches (see below for detail).

In another study, Mikhaylova et al. [176] have produced ultrathin hyperbranched films by spin-coating hydroxyl-terminated aromatic hyperbranched polyesters on epoxy functionalized silicon wafers and subsequently annealing the surface layers above their glass transition temperature, thus initiating covalent bonding (Fig. 13b). A similar approach has been used by Shi et al. to graft hyperbranched polyesters onto silica nanoparticles [177]. Modified hyperbranched polymers, which possess 50% of terminal carboxylic groups and 50% of terminal hydroxyl groups while being end-capped with octadecyl isocyanate (C_{18}) have been grafted onto 3-glycidyloxy-propyltrimethoxysilane (GPTS) pre-modified SiO_2 nanoparticles. Another approach was used for covalent grafting of the hyperbranched polymers to glass beads using functionalized SAM chemistry [178]. After selective introduction of carboxyl acid groups into hyperbranched polyol backbones, the residual hydroxyl groups were additionally modified with isocyanate-containing silanes.

By applying a different reaction scheme, Park et al. [179] have immobilized the hyperbranched polymers on polyurethane films using photoreactive azidophenyl groups. The use of photoreactive molecules allowed for a unique modification of the polymer substrate through immobilization of other polymers without pre-forming functional surface groups. In a different development, Zhai et al. [180] fabricated novel grafted self-assembled films of hyperbranched conjugated poly(phenylene vinylene) (SPPV). The covalent grafting of these functionalized hyperbranched molecules was facilitated through the chemical reaction with a highly hydrophilic substrate such as mica. Wooley et al. [181,182] have conducted a comprehensive investigation into the influence of chemical composition on the surface morphology of the complex polymer coatings prepared by the in-situ phase separation and cross-linking of mixtures of hyperbranched fluoropolymer (HBFP) and diamino-terminated poly(ethylene glycol) (PEG) (Fig. 13e). The thin coatings composed of HBFP-PEG networks were prepared on glass substrates functionalized with the 3-aminopropyltriethoxysilane (APTS) SAM. In another study, a heteroarm star block copolymer PS_7-P2VP_7 was grafted onto a solid substrate to fabricate a responsive polymer surface consisting of a robust

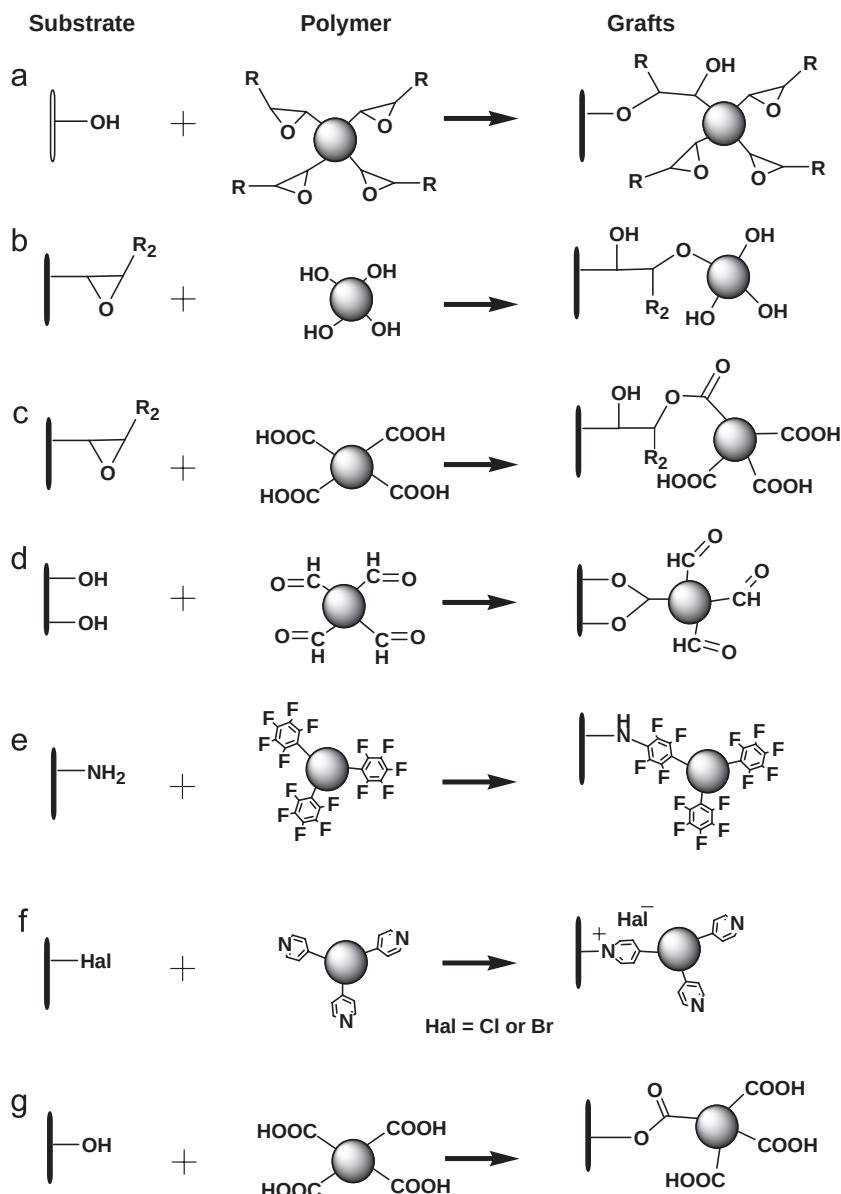


Fig. 13. Summary of synthetic routes explored for covalent grafting of highly branched polymers: (a) and (b) ether; (c) and (g) ester; (d) acetal; (e) amine and (f) tertiary amine bonding. Spheres represent highly branched macromolecules.

and densely packed monolayer of copolymer molecules (Fig. 13f) [183].

Considering that carbon nanotubes only have a remote relationship to most of the results discussed here, we will not review numerous publications on their functionalization with dendritic molecules, but rather include only few selected examples and refer an interested reader to corresponding publications. For instance, Gao et al. [184] and Xie and co-workers [185] applied the polycondensation approach to functionalize carbon

nanotubes by hyperbranched polyurea and poly(urea–urethane), respectively, by a one-pot reaction. On the other hand, lipophilic and hydrophilic dendrons were used to functionalize single-wall and multiple-wall carbon nanotubes via amidation and esterification reactions (Fig. 14) [186,187]. Wang et al. [188] have described functionalization with a hyperbranched aliphatic polyester by exploiting the reactions of carbonyl chloride surface groups and hydroxyl groups of branched polymers.

3.3. Combination of different approaches

A combination of different grafting approaches, which include mixing different types of polymerization and grafting could lead to a novel kind of highly branched polymer structures on solid surfaces. In one study, which exploits this strategy, comb-like polystyrene has been grafted to silica nanoparticles by exploiting a multistep procedure [189]. First, silica nanoparticles were modified with methacryloxypropyl silanes, serving as the initiator for free radical copolymerization and 4-vinyl benzyl chloride (VBC) with a solution polymerization method. Then, the VBC grafted silica nanoparticles (PVBC-SN) were used as a macroinitiator for the surface-initiated atom transfer radical polymerization (SI-ATRP) of styrene in toluene. The structurally well-defined polymer chains were then grown from the silica nanoparticle surfaces, resulting in

hybrid particles composed of a silica core and a well defined, densely grafted outer shell composed of the comb-like PS layer with high grafting density.

In another development, Byun et al. [190] used a combination of the “grafting to” and “grafting from” approaches for the preparation of surface-grafted PS beads with comb-like PEG chains (Fig. 15). In this study, hydroperoxide groups were first introduced onto the surface of gel-type PS beads by chemical treatment with ozone gas. Then, PMMA chains were grown via the following “grafting from” technique. The reduction of the ester groups of the grafted PMMA to hydroxyl groups followed by anionic polymerization of ethylene oxide (EO) allowed the PS-*sg*-PEG beads with highly branched shells. This approach permits easy control of the grafted PMMA and PEG chain lengths in the final hybrid core-shell beads.

Another combination of grafting techniques was employed to develop an effective and inventive method to synthesize comb-coil polymer brushes on the silica surface. Along this line, Zhao et al. fabricated PLA-PBA comb-coil polymer brushes combined with the terminal PHEMA chains on silica particles. They employed the combination of ATRP, AGET, ATRP, and ROP techniques as presented in Fig. 16 [191]. The comb-coil polymer brushes obtained in this study formed wormlike structures on the silica surface. The authors suggested that this approach could be extended to other materials, such as metal nanoparticles.

Very recently, non-traditional stratified polymer surface films, with a tunable thicknesses and unaltered surface properties, have been formed by using the multistep grafting approach [192]. Facile, room temperature UV-initiated polymerization were employed for grafted-to functionalized polymer surfaces, resulting in the formation of a

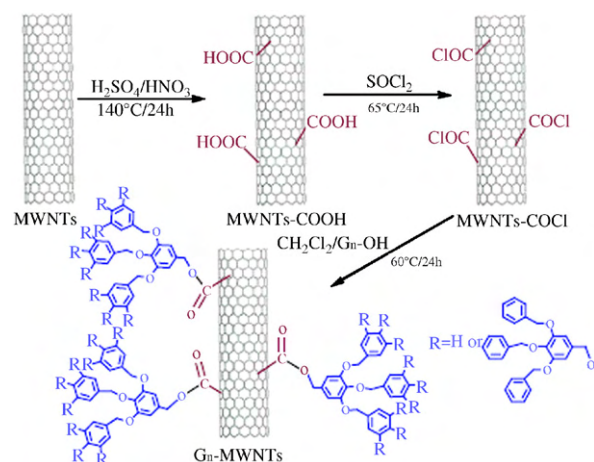


Fig. 14. Graphite surface modification of carbon nanotube with highly branched molecules [187]. Reprinted from Jiang et al. by permission of Elsevier B.V.

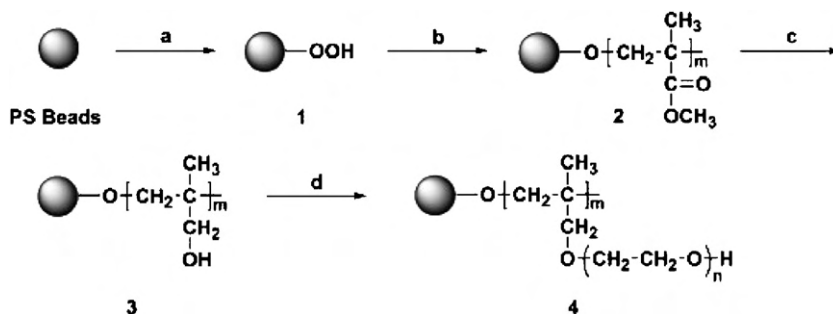


Fig. 15. Synthetic route for the formation of PS-*sg*-PEG beads [190]. Reprinted from Byun et al. by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

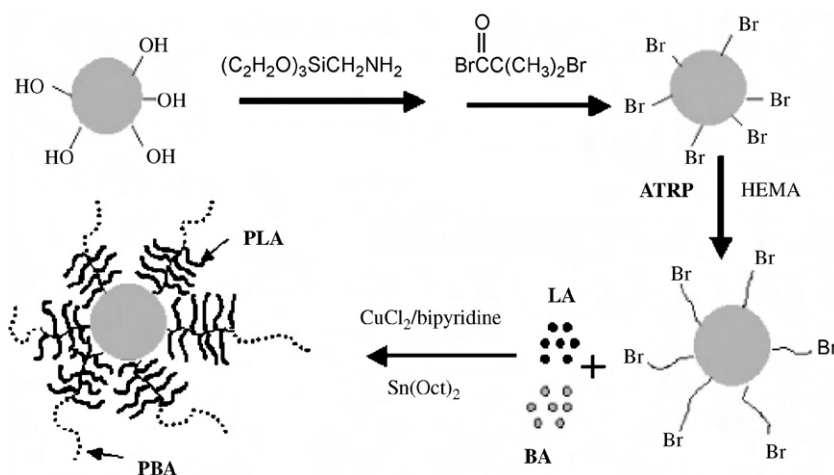


Fig. 16. The routine for the preparation of comb-coil polymer brushes on the surface of silica nanoparticles [191]. Reprinted from Zhao H. et al. by permission of the American Chemical Society.

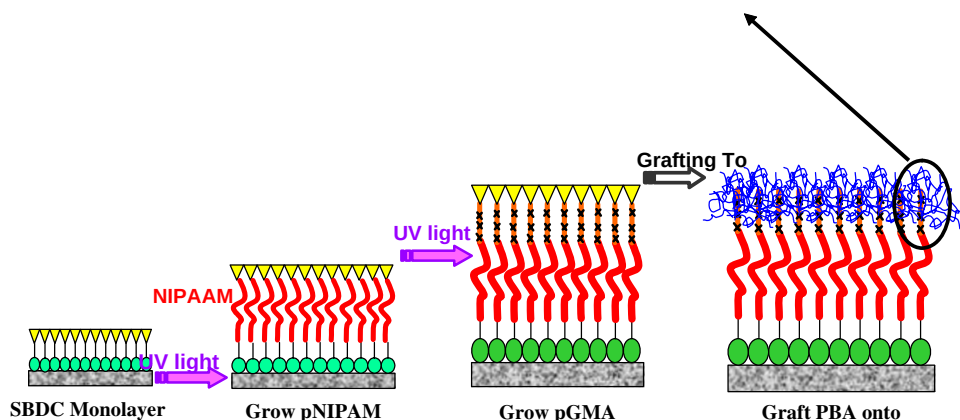


Fig. 17. Stratified layer construction starting with the SBDC SAM, UV-initiated polymerization of pNIPAM, UV-initiated polymerization of pGMA, and finally, grafting of COOH-PBA topmost layer [192]. Reprinted from LeMieux et al. by permission of the American Chemical Society.

temperature-sensitive pNIPAM layer confined beneath a hydrophobic, comb-like PBA brush layer (Fig. 17). Reversible temperature-controlled changes in the overall layer thickness (within 17–34 nm) has been demonstrated along with preservation, largely, of global surface properties controlled by the densely grafted dendritic topmost layer as will be discussed below.

4. Interfacial properties and organization

As we have already discussed in a previous section, highly branched molecules can be either physically or chemically grafted to various surfaces

by using a wide range of synthetic and grafting approaches well developed for linear and traditional block-copolymers. Among the most popular approaches for the placing/growth of branched molecules onto solid substrates traditional solution adsorption, drop casting, spin casting, grafting from solution, and grafting from melt can be singled out. These approaches are widely exploited to deposit individual molecules in collapsed and extended states, to form uniform monomolecular and ultra-thin surface films, and to design surfaces with stimuli responsive properties. The complex architecture of highly branched molecules, which usually includes different chemical compositions of the

core, shells, arms, and terminal groups combined with different ways of their tethering, is responsible for their peculiar surface behavior as will be discussed in this section. Obviously, depending upon the initial state of the surface and the deposition routine employed, the resulting surface structures and properties of highly branched molecules may vary. The initial molecular organization in solution frequently plays a critical role in the surface assembly although in many instances, this issue is not addressed properly. As a rule, very dilute solutions below cmc are used to avoid surface adsorption of “pre-fabricated” micellar structures.

A special case includes the use of Coulombic interactions for electrostatic LbL assembly of ultrathin films with inherently multilayered architecture. In addition, alternative approaches were exploited such as LB deposition, which allows for gentle deposition of amphiphilic molecules with controlled surface area per molecule and a build-up of multilayered films. Finally, some very recent reports have discussed grafting of highly branched polymers on extremely curved surfaces of nanoparticles to produce hybrid nanoobjects capable of forming complex surface nanostructures.

On the other hand, the substrates used for studying surface structures assembled by highly branched molecules are usually limited to model substrates, rather than actual practical surface. These substrates include relatively smooth (several nanometer surface microroughness) hydrophilic glass and quartz surfaces, highly charged and atomically flat (surface microroughness of a fraction of a nanometer) mica, hydrophobic highly oriented pyrolytic graphite (HOPG), atomically flat (microroughness below 0.1 nm) silicon single crystals with hydrophilic native silicon oxide or chemically modified surfaces, and relatively flat (surface microroughness of several nanometers with grainy surface morphology) gold films. A water surface is a stand alone example critical for the formation of Langmuir monolayers as a first step in their transfer to solid substrates. Each of these substrates is characterized by its own set of surface interactions and topologies, which affect molecular conformations and the ordering of highly branched molecules as will be discussed in many instances below.

4.1. Individual macromolecules on a surface

Amphiphilic cylindrical brush-coil block copolymers consisting of a hydrophobic PS coil and a

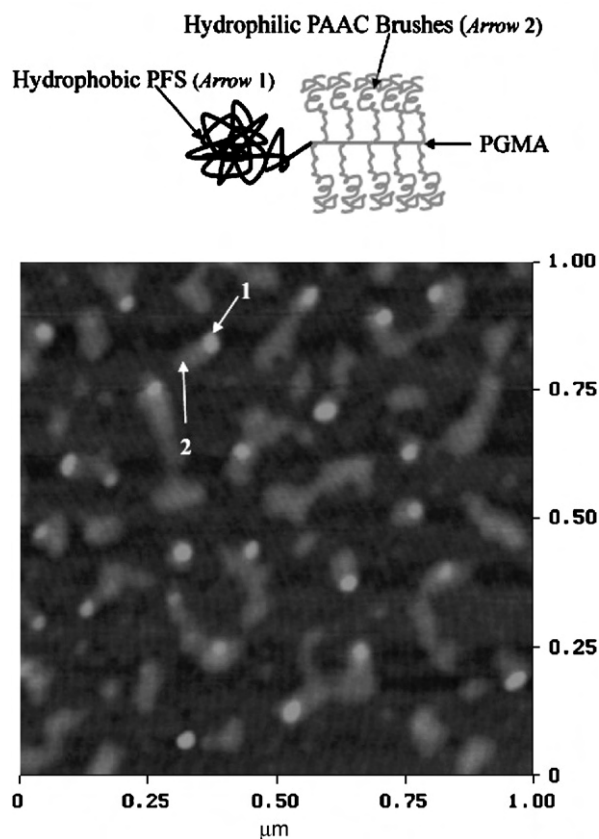


Fig. 18. The head-tail structure of the the rod-coil PFS-*b*-(PGMA-*g*-PAAC) macromolecules [22]. Reprinted from Fu et al. by permission of the American Chemical Society.

cylindrical brush block with hydrophilic PAA side chains synthesized by ATRP have been studied with AFM [83]. The formation of micelles in aqueous solution upon hydrolysis of the PtBA was confirmed by AFM imaging of the deposited macromolecules onto a bare silicon oxide surface. Tadpole-shaped (or rod-coil) block-graft copolymers, consisting of a pentafluorostyrene polymer (PFS) block and a glycidyl methacrylate polymer (PGMA) block with grafted PtBA side chains, or PFS-*b*-(PGMA-*g*-PtBA) copolymers, were reported (Fig. 18) [22]. Hydrolysis of the PtBA side chains in the block-graft copolymer gave rise to a strong amphiphilicity of PFS-*b*-(PGMA-*g*-PAAC) macromolecules and their domain texture with phase-separated appearance upon adsorption. A peculiar shape of the adsorbed macromolecules with a brush-shaped hydrophilic head (rod) and a collapsed hydrophobic tail (coil) was suggested to be controlled by the block composition. Another investigation of macromolecular brushes with a gradient of side-chain

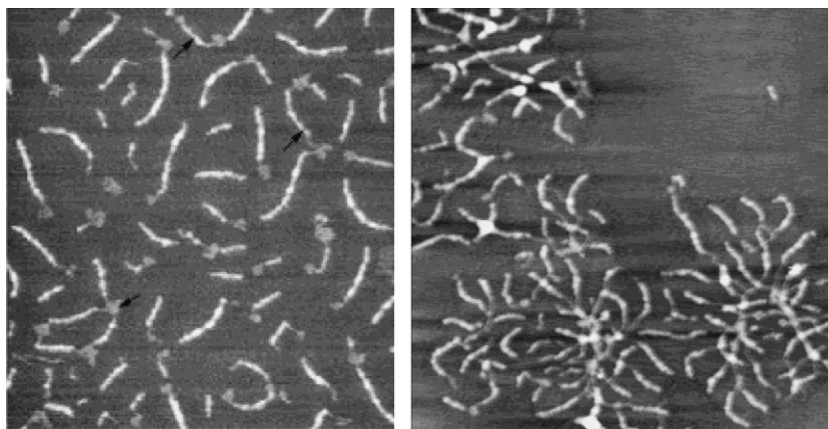


Fig. 19. PODMA-*b*-P(BPEM-*g*-*n*BuA)-*b*-PODMA brushes cast on mica: left: from chloroform; right: from acetone [193]. Reprinted from Qin et al. by permission of the American Chemical Society.

spacing along the backbone demonstrated the characteristic anisotropy of the molecular structures adsorbed on mica with a similar bulky head and a thin tail [26].

Adsorption of densely grafted molecular brushes with both AB and ABA “block-graft” architectures, PODMA [poly(octadecyl methacrylate)]-*b*-P(BPEM-*g*-*n*BuA) [poly(ethylene glycol 2-bromopropionate methacrylate-*g*-Bu acrylate)] and PODMA-*b*-P(BPEM-*g*-*n*BuA)-*b*-PODMA, have been recently reported [193]. AFM studies demonstrated that the backbones of the brushes composed of the pBPEM segments were almost completely stretched on the mica surface due to steric constraints introduced by the bulky and densely grafted side chains (Fig. 19). In contrast, PODMA segments tended to form aggregated structures, due to the crystallization of the relatively long C₁₈ alkyl side chains. The authors claimed that AB block brushes formed “dimers”. Finally, they observed that in contrast, ABA block brushes assembled into aggregates with different shapes, so-called “multimers” or “circles”, which demonstrated the critical role of the overall block symmetry in surface assembly.

In another example, cylindrical brush-like molecules with poly(L-lysine) and poly(L-glutamate) side chains displayed a uniform worm-like chain conformation when deposited on a mica [25]. New dendritic macromolecules of polypyrrole-graft-poly(ϵ -caprolactone) (Ppy-*g*-PCL) copolymers exhibited microphase separation between the polypyrrole and the polycaprolactone segments after deposition onto mica leading to the formation of an ultrathin film with nanodomain morphology [194]. In addition, the statistical, asymmetric

P2VP-PMMA cylindrical brush macromolecules after their spin casting onto the mica surface from different solvents displayed a variety of shapes; from worm-like to horseshoe or meander-like structures [28].

Switching our attention to hyperbranched molecules, we should note recent studies by Nishide et al. [195] who investigated surface morphology of the hyperbranched poly[(4-(3',5'-di-*tert*-butyl-4'-yloxyphenyl)-1,2,(6)-phenylenevinylene)] from a dilute solution onto mica and graphite surfaces. Although the authors observed that these molecules collapsed on a graphite surface due to unfavorable surface interactions, regular globular structures were detected on a mica surface. In another study, the surface microstructure of highly branched sulfonated polydiphenylamine, H-PSDA, was found to be sensitive to pH [196]. In the dedoped state (pH > 7), AFM imaging identified nanoscale particles of uniform size with diameters of about 40 nm, although larger and irregular particles (> 200 nm) were formed also at the same pH. Furthermore, when the pH was decreased below 5, the surface aggregates became dispersed as smaller nanoparticles because of the external-doping interaction caused by the HCl molecules.

Single molecular conformations and the associated surface morphologies for heteroarm star copolymers, which are deposited onto hydrophilic mica or silicon oxide surface of silicon wafers and exposed to a controlled environment, have been studied through the AFM (Fig. 20) [163]. The PS₇-P2VP₇ molecules were observed to form unimolecular or multimolecular micelles at acid conditions with type of aggregation depending on

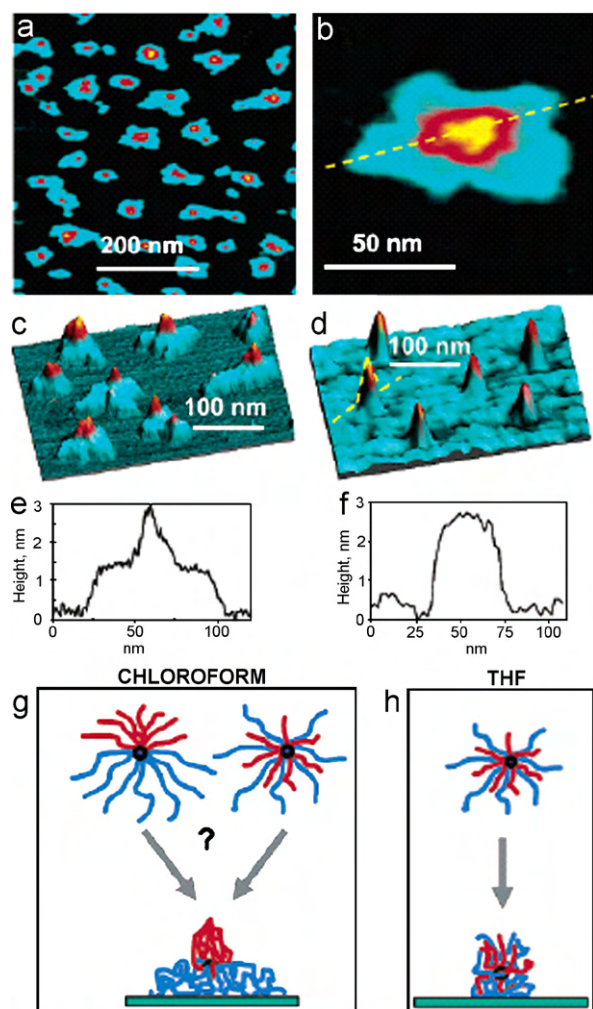


Fig. 20. AFM topographic images (a–c) and cross sections (e, f) of the PS₇–P2VP₇ molecules adsorbed from chloroform on mica. 3D-AFM image (d) and cross section (f) of unimers adsorbed on mica from THF. Suggested conformations for the PS₇–P2VP₇ adsorbed from chloroform (g) and THF (h), (red color indicates PS arms) [163]. Reprinted from Kiriya et al. by permission of the American Chemical Society.

concentration and pH of the solution. The micelles deposited onto mica from acidic water were trapped with P2VP extended arms caused by strong interaction with the mica surface. In contrast, the hydrophobic PS arms collapsed and formed elevated cores of star-like micellar aggregates (Fig. 20).

Upon post-treatment of these surface structures with toluene, the PS cores become highly swollen with the PS arms gradually adapting an extended conformation. Eventually, their spreading results in the very thin (down to a single chain) “squashed” structures that do not exist in any initial solvent

employed and could not be obtained from a simple, single-step adsorption procedure. In this way, the authors demonstrated that the star block copolymers, weakly anchored onto the solid substrate, could form environmentally responsive nanoscale structures with symmetry controlled by the chemical architecture [183]. Moreover, they observed that the cooperative reorganization of the multiple arms and cores of molecular aggregates upon solvent treatment resulted in switchable “dimple” and “ripple” surface structures within dense molecular layers. This example illustrates how dramatic response of the molecular shape upon alternating external stimuli (solvent nature and quality) is facilitated by core–shell transitions of a single star molecule weakly pinned to the surface, an unprecedented behavior of star-like molecules, which cannot be observed for regular linear or block copolymers.

At the next very interesting step, the authors fabricated unimolecular hybrid nanostructures by decorating the star molecules deposited on the surface in various conformational states with hexacyanoferrate anions or negatively charged clusters of cyanide-bridged complexes [197]. The decoration process, guided by selective interactions between ions and molecular backbones, initially allowed for an increasing contrast of AFM imaging. Hence, the fine molecular morphology with multiple arms became easily observable. However, the authors further advanced this approach towards a molecular template guided metallization on surface-pinned PS₇–P2VP₇ molecules. To accomplish this, they exploited highly selective Pd clusters deposition along the extended P2VP chains and reduced metal ions. Metallization of ion-containing P2VP arms of these star-shaped molecules led to the peculiar organic–inorganic hybrid single-molecule structures with nanoscale palladium clusters predominantly localized along the extended polymer arms (Fig. 21) [198]. By the variation of the metallization conditions, molecules with different numbers of metallized extended arms have been obtained and readily visualized with AFM.

Excellent AFM images with single molecule resolution of four-arm star-like, comb-like single molecules deposited on different surfaces have been recently conducted [199]. Different initial configurations were observed as controlled by initiation and propagation reactions with predominant four-arm shape easily visible on AFM images (Fig. 22). These molecules adopted various shapes with either widely extended arms or closely packed arms

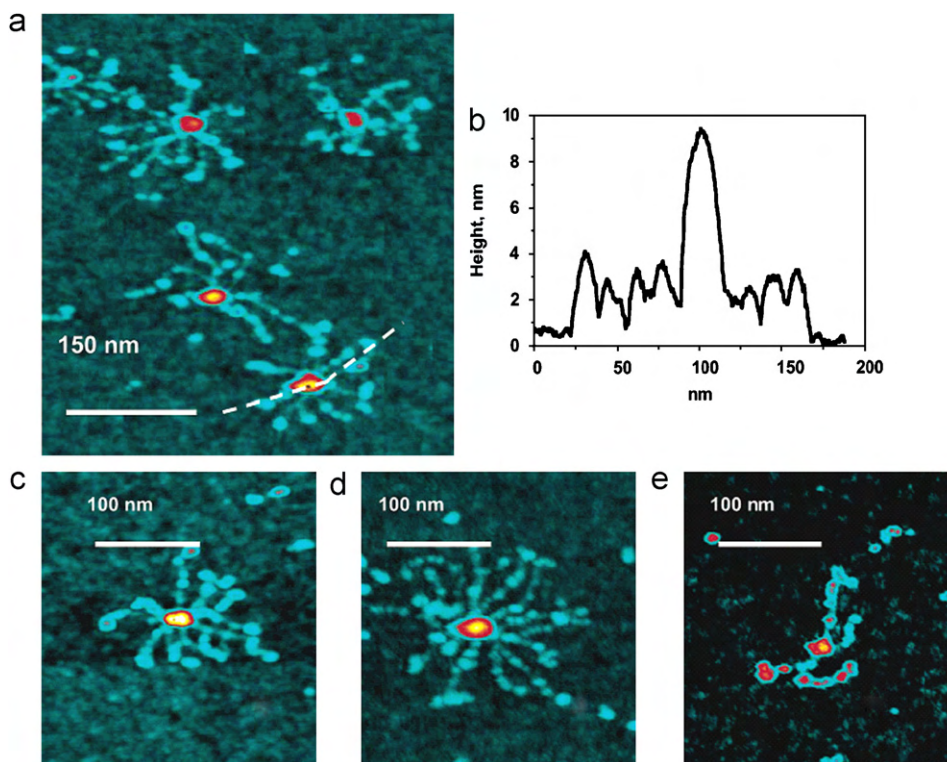


Fig. 21. Pd PS₇-P2VP₇ molecules on silicon (a); cross-section taken along two arms of the star (b); molecules with different number of metallized P2VP arms: 7 (c); more than 10 (d); and 4 (e) [198]. Reprinted from Gorodyska et al. by permission of the American Chemical Society.

depending upon deposition conditions demonstrating conformational flexibility on weakly interacting surfaces.

4.2. Dense ordered monomolecular layers and fibrillar structures from solution

In order to fabricate ultrathin nanoscale films with denser molecular packing rather than scarce individual molecules, a range of approaches such as slow solvent evaporation, higher solution concentration, effective wetting, multiple deposition, and spin casting are employed. Such ultrathin surface films can be monomolecular, multilayered, uniform, phase-separated, patterned, porous, and gradient depending upon the type of macromolecules, method of film formation, and the nature of the supporting surface, as we will illustrate on several occasions below.

In recent study, six-armed star molecules with PS and PMMA arms and a triphenylene core have been observed to show different self-assembling behavior on a surface than those discussed above [200]. For these star polymers, isolated PS cylinders on mica

have been observed in dense states (Fig. 23). In contrast, highly ordered cylindrical pores appeared within the films on a silicon oxide surface after drying at an ambient temperature (Fig. 23). The size and height of PS cylinders were reduced with the decrease in polymer concentration in THF. However, the dimensions of PMMA cylindrical pores increased under similar conditions. Finally, slow evaporation of the solvent and the lower molecular weight of arms both favored the formation of regular surface patterns not observed previously.

In another study, it has been demonstrated that highly branched molecules with a comb-like architecture, poly(chloroethyl vinyl ether)-*g*-PS (PCEVE-*g*-PS), form an ordered, layered organization within very thin film deposits [201]. Within these surface films, the molecules adopt an extended conformation with parameters controlled by the chemical composition favorable for lamellar organization [202]. The authors demonstrated that the surface organization of the PCEVE-*g*-PS molecules is controlled by the orientation of the side branches with respect to the surface. In contrast, water soluble dendrigrafts with a PS core and PS-*b*-poly(Me vinyl

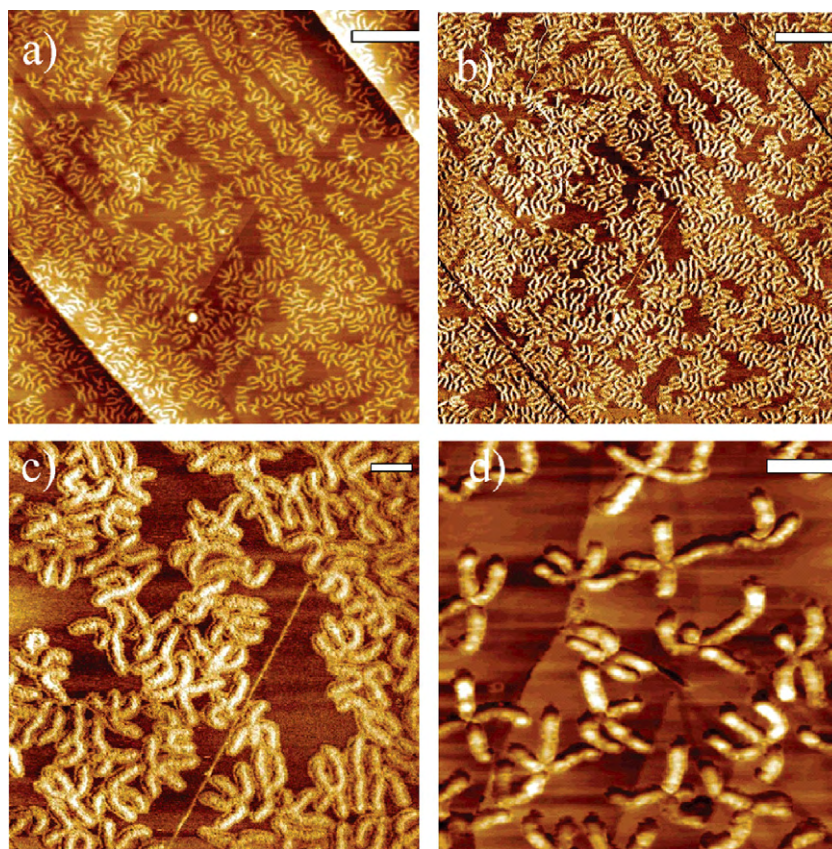


Fig. 22. Tetra-arm comb-stars (PS1-*b*-PCEVE-*g*-PS2)₄ molecules deposited on HOPG surface. (a, b) Higher-resolution phase and topographical images, scale bar is 300 nm and (c, d) zoomed images, scale bar is 100 nm [199]. Reprinted from Schappacher et al. by permission of the American Chemical Society.

ether) branches (PS-*b*-PMVE) were observed to form egg-like or long, cylindrical surface structures after deposition onto a solid substrate [203]. These structures can self-assemble into segregated domains, forming flower-like morphologies under certain conditions, such as adsorption from specific solvents (methanol, water, dichloromethane). In yet another example, dendronized polymers based on PS functionalized dendritic L-lysine macromonomers showed that all rod, short rod, or globular surface structures can be formed onto mica depending upon the backbones' degree of the polymerization [204].

Water soluble and amphiphilic dendrigrafts composed of a hydrophobic PS core and a hydrophilic PEO shell were prepared via the "grafting to" procedure from dendrigraft precursors [42]. It was observed that the deposition on a mica surface from a dilute solution generates a uniform film with smooth morphology. This film is composed of a single molecular layer of densely packed molecules,

which assembled in a regular hexagonal lattice (Fig. 24). On the contrary, casting these dendrigrafts on hydrophobic substrate (HOPG) leads to the formation of heterogeneous multilayered films due to the PEO dewetting from highly hydrophobic surface.

AFM studies of surface films fabricated from novel arborescent block copolymers comprised of rubbery polyisobutylene (PIB) and PS blocks polymers onto a silicon wafer by drop casting showed mixed spherical/cylindrical/lamellar PS domains irregularly distributed within the continuous PIB phase [205]. In a related example, hydrogen bonding for polyurea-malonamide dendron molecules controlled a wide range of surface structures with soft domains reinforced by the rigid dendritic side chains via strong hydrogen bonding interactions [206]. For these surface films, AFM imaging showed microphase separated surface structures with random morphology on a scale of 100 nm.

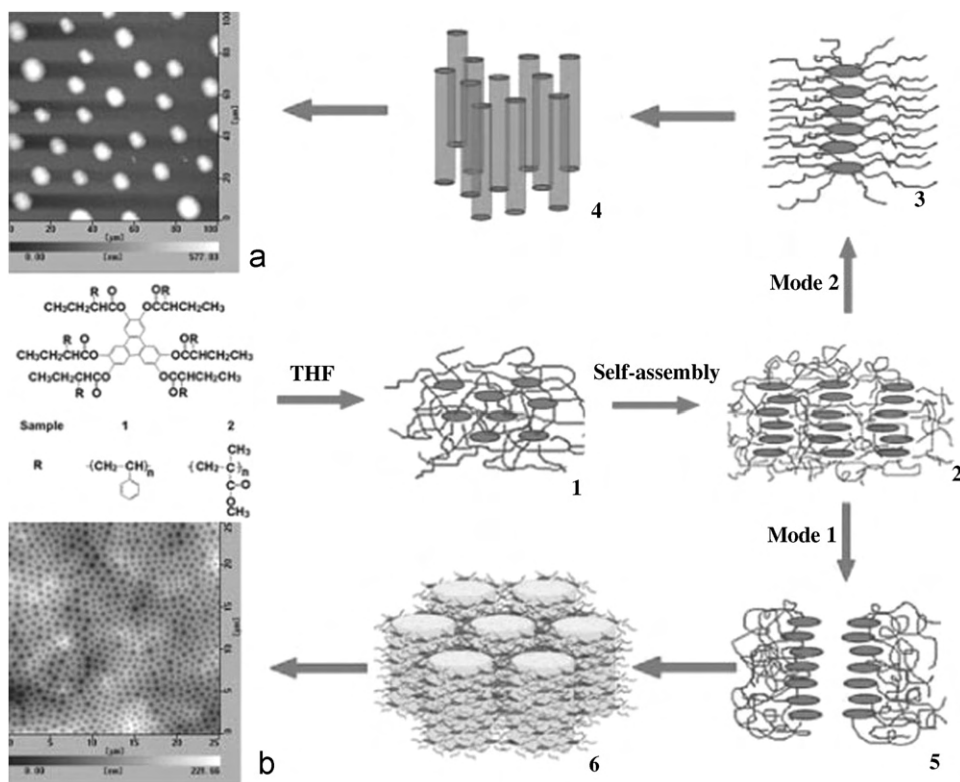


Fig. 23. Models and AFM images of PMMA star polymer on silicon oxide and for PS star polymer on mica [200]. Reprinted from Yu et al. by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

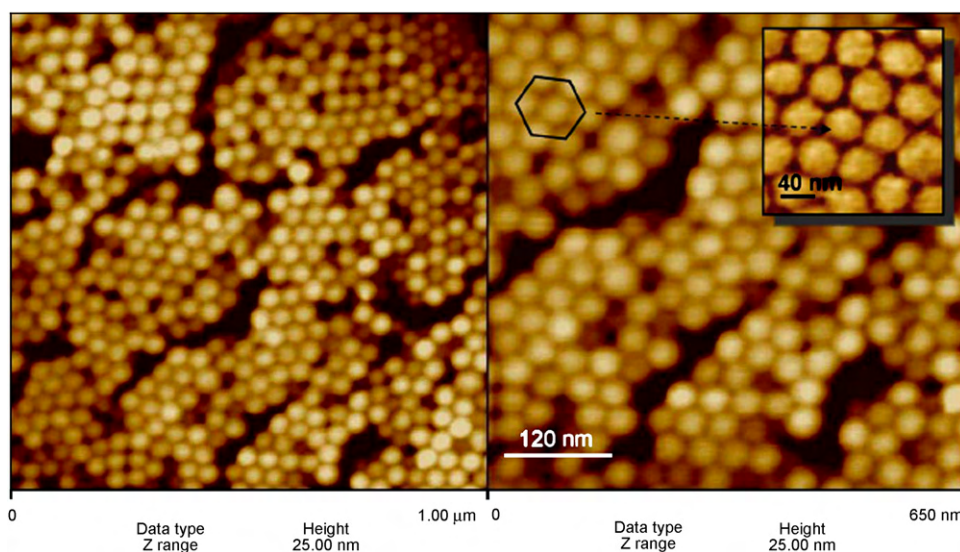


Fig. 24. AFM height images of a monolayer of the PS-PEO dendrigraft obtained from methanol solution deposited on a mica. The right inset is a phase image of the molecules that shows the absence of internal phase separation within the molecules [42]. Reprinted from Schappacher et al. by permission of Elsevier Science.

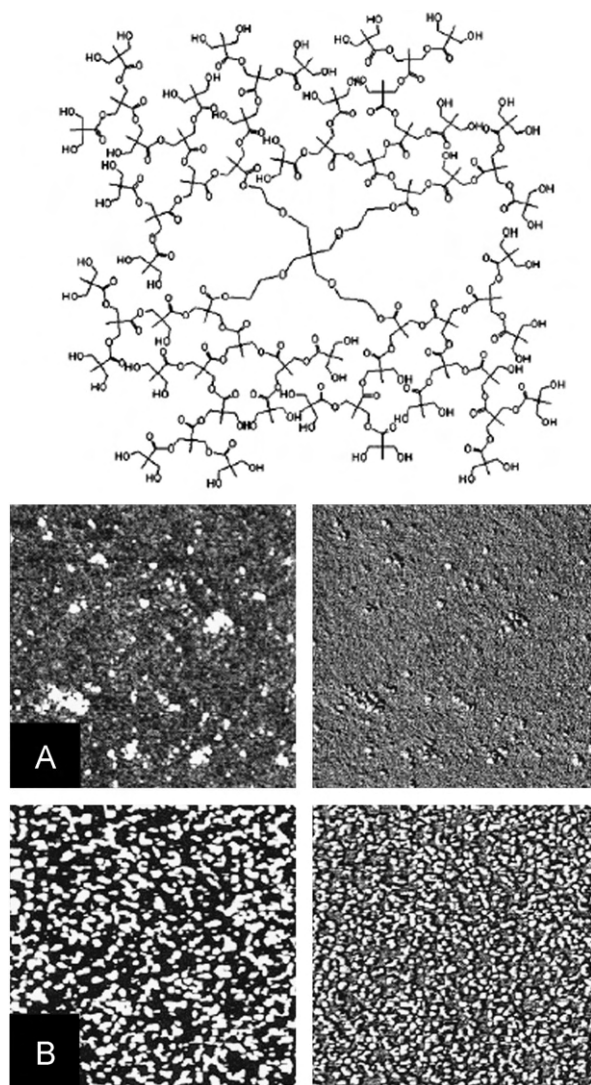


Fig. 25. Idealized chemical structure of hyperbranched polyester and AFM topographical images of adsorbed molecules from acetone solutions with different concentrations: 0.5 g/L (A), 1.5 g/L (B) [159]. Reprinted from Sidorenko et al. by permission of the American Chemical Society.

For a series of modified hyperbranched polyesters, it has been demonstrated that these molecules with proper chemical composition formed ordered and dense surface layers because of strong adsorption onto properly functionalized surfaces [159]. The surface behavior of third and fourth pseudo-generations of hyperbranched polyesters (Boltorn[®]) with average 32 and 64 hydroxyl-terminal groups was studied on a surface of freshly prepared, thermally grown silicon oxide with high concentration of hydroxyl groups (Fig. 25). The spontaneous adsorption of individual hyperbranched polyester

molecules and their coalescence into uniform monomolecular surface layers has been observed under different conditions. It has been shown that the molecular adsorption on a bare silicon oxide surface followed a typical Langmuir adsorption isotherm. However, the resulting surface structures were very different for low and high generations of hyperbranched molecules. The higher generation molecules kept their close-to-spherical shape in a highly dispersed state (Fig. 25). Globular molecular shape of individual molecules and their aggregates were also preserved within the densely packed adsorbed molecular layers. The average thickness of the molecular layer was close to the molecules' diameters in the compacted state.

On the other hand, lower generation hyperbranched polyester molecules with more compliant architecture and lower density of the terminal groups went through significant conformation changes after adsorption onto a silicon surface. This restructuring resulted in the highly flattened shape of the molecules at a low surface coverage, which is replaced with patch-like structures at intermediate coverage. At higher surface coverage, these hyperbranched molecules formed a densely packed monolayer with a uniform surface morphology in contrast to the packed globular aggregates observed for compounds with 64 hydroxyl groups. Instead, wormlike nanoscale structures were observed indicating coalescence of the individual molecules into uniform matter which can be related to the lower charged density of the terminal groups and higher compliance. In contrast, low-molar weight hyperbranched molecules with high concentration of carboxylated terminal groups and low polydispersity, showed not only single molecules but also well-developed surface aggregates after spin casting onto a mica surface [207]. Moreover, for very low molar weight compounds the authors observed extended and terrace-like surface structures with both mono- and bilayered microstructure.

An amphiphilic, hyperbranched poly(amidoamine) modified with palmitoyl chloride was demonstrated capable of forming the fascinating organized porous films caused by specific surface dewetting (Fig. 26) [208]. These films were prepared by drop casting onto a cleaned substrate such as silicon wafer, quartz, or mica. Moreover, highly fluorescent honeycomb-patterned films were successfully prepared in a wide range of humidities by loading solution with different dyes. The thickness of the

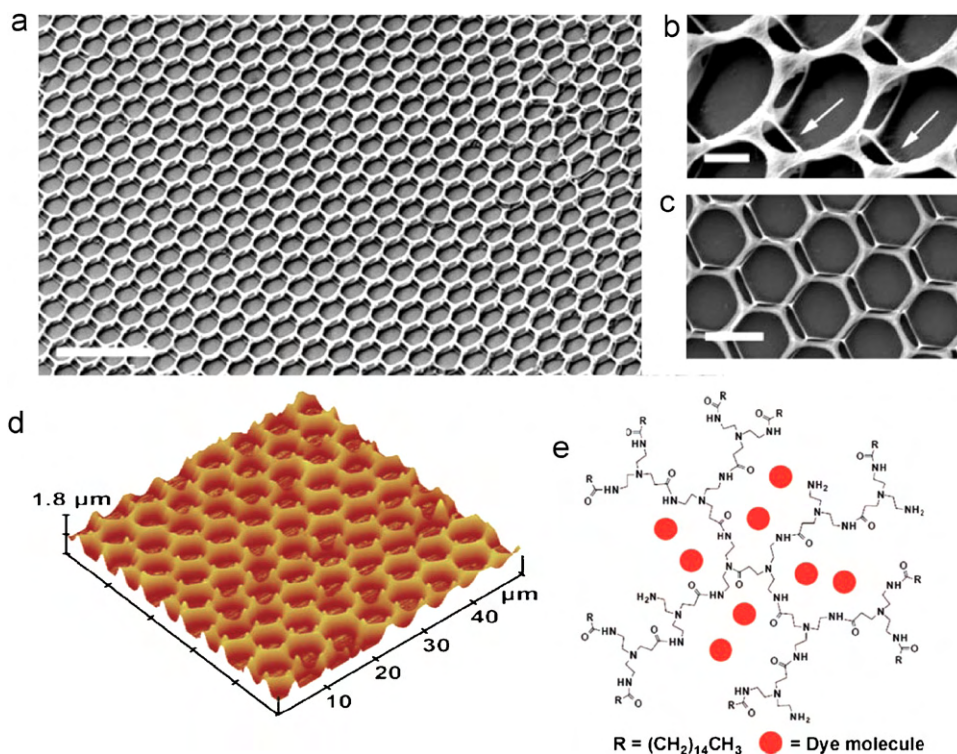


Fig. 26. SEM (a, b), TEM (c), and AFM images (d) of the honeycomb patterned films from amphiphilic hyperbranched polymer on a silicon wafer. Schematic illustration of dye-loaded hyperbranched polymer [208]. Reprinted from Liu et al. by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

patterned films varied from the nanometers to the micrometers due to different solution concentrations as was measured from AFM topographies (Fig. 26). The authors suggested that the organized patterns are fabricated during solvent evaporation forms small droplets on the surface of the solution with slow dewetting inducing a phase inversion and aggregation of the hydrophobic shell of the core-shell amphiphilic unimolecular micelles. The gradual condensation of the polymer solution forces aggregate formation that eventually leads to separated walls and pores. However, it is not clear what mechanism controls the formation of very regular lattices of different symmetries.

The nanoscale and elastic properties of these hyperbranched polyester molecules were probed using surface force spectroscopy, which allows for the micromapping of the surface stiffness with nanoscale resolution [160,209]. Unlike previous studies of surface morphology, the hyperbranched molecules were anchored to amine-terminated SAMs on a silicon substrate to prevent their lateral motion under the normal compression stress inserted by the AFM tip (Fig. 27). Moreover, the

AFM tip was chemically modified with methyl-terminated SAMs to control tip-surface interactions and reduce capillary forces.

A double-layer elastic deformational model has been applied to calculate nanomechanical properties of the monomolecular aggregates from hyperbranched polyesters tethered by the application of the modified Hertzian approach (the total thickness of molecular layers was below 3 nm) [210,211]. Complex shapes of both loading curves and elastic modulus depth profiles obtained from experimental AFM data were successfully fitted by the graded model with different stages of deformation and separated elastic responses of the monomolecular aggregates and supporting surface (Fig. 27). Analysis of individual molecules and molecular aggregates revealed a higher elastic resistance of fourth generation individual hyperbranched molecules in their tethered state in comparison with the corresponding third generation (the elastic modulus increased from 190 to 350 MPa). Higher nanoscale stiffness was also detected for molecules closely packed within long-chain aggregates as compared to individual molecules dispersed

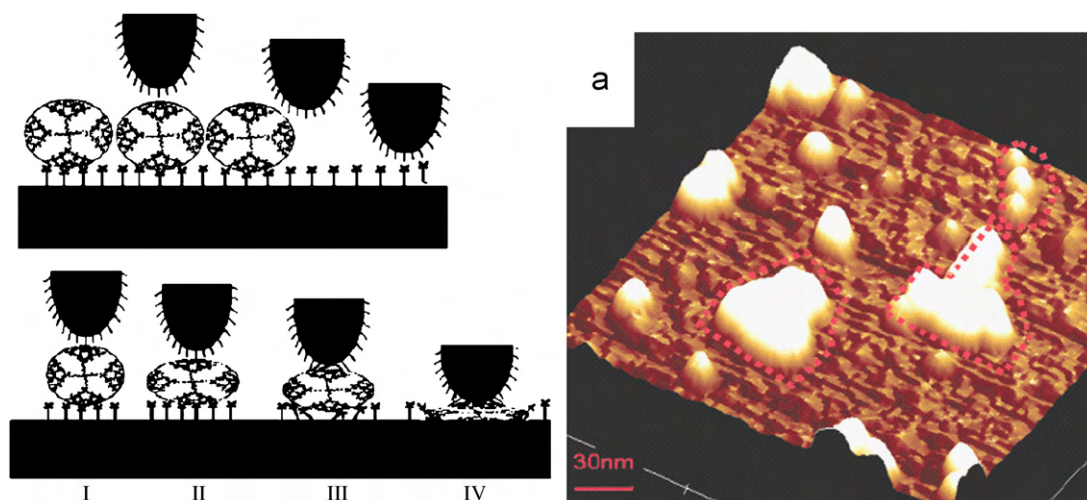


Fig. 27. Sketch of dendritic molecules tethered to a silicon surface through anchoring amine-terminated SAM and modified AFM tip during nanomechanical probing (top) and different stages of deformation of the molecules (bottom) (left). Surface aggregates of hyperbranched polyester molecules 3rd generation (right) [160]. Reprinted from Shulha et al. by permission of the American Chemical Society.

individually or packed within small molecular aggregates.

In another study of similar hyperbranched polyesters, Mackay et al. investigated their melt surface tension. A series of commercially available Boltorn[®] hyperbranched polymers was studied by using the micro-Wilhelm wetting technique and water contact angle measurements [212]. The surface tension was found to be extremely high for the hydroxyl-terminated hyperbranched polymers and approached that of water, indicating preferential surface segregation of hydroxyl terminal groups. Substituting hydroxyl terminal groups with alkane chains dramatically reduced the surface tension to the point where a large degree of substitution produced the surface tension equivalent to that of pure alkanes.

In a recent report, Voit et al. investigated the surface properties of ultrathin surface films of hyperbranched polyesters with different end groups by zeta-potential and contact angle measurements [213]. They observed that the differences in the molecular structure and the surface properties for different hyperbranched molecules with carboxylic, hydroxyl and acetoxyl end groups caused significant differences in their swelling behavior in humid atmosphere. Similar studies have been recently conducted testing different types of hyperbranched molecules with various chemical compositions. The hyperbranched poly(urea urethane)s with different terminal group substitutions have been analyzed in

this study [214]. It has been shown that the surface properties were mainly controlled by the strong interactions of the urea and urethane terminal groups within the internal branches. On the other hand, the authors concluded that the influence of the end groups and the degree of branching was minor in contrast with other hyperbranched polymer systems described above.

On the other hand, Moore et al. reported the strong effect of molecular architecture on the surface properties of polyether imides [215]. It has been shown that the surface properties of these spin-cast films obtained from these hyperbranched polymers strongly depend not only upon the functionality of end-groups, but also on the molecular architecture's fine details. They observed that the increasing number of branches in the molecules limited the mobility of polymeric segments, which inhibited the migration of interior end-groups to the film surfaces. As a result, the surface energy of randomly branched polymers scaled closely with the terminal segment composition. The variation of the functionality of end-groups of these molecules extensively altered the surface properties of the resulting films.

In a different approach, Hult and coworkers implemented the light-controlled switchable ability of molecular surface layers by using photosensitive hyperbranched polymers with azobenzene end groups [216]. Similar results have been obtained for the grafted azo-containing photosensitive

monodendrons [217,218]. AFM imaging demonstrated surface relief on the order of 1 nm in films undergoing a photoisomerization process, which is caused by intralayer disordering [219]. We established that the spacer, which links the chromophore to the dendritic core, has a much more profound influence on the photochromic optical properties than the composition of the dendritic core.

Mészáros et al. [161] investigated the adsorption of hyperbranched PEI molecules on a silicon oxide surface by using reflectometry. Authors demonstrated that PEI adsorption strongly depends on the pH and ionic strength of the initial solution as expected for these compounds. Authors also indicated that the observed interfacial behavior of PEI might have some important consequences for the stability of weak polyelectrolyte multilayers. Their recent studies as well confirmed the critical role of the charge density of PEI molecular backbone on kinetics of adsorption and desorption on and from silica. [162]. Nevertheless, this claim has not been confirmed independently.

The kinetics of adsorption of hyperbranched polyesteramides on a silicon oxide surfaces, as a function of pH and salt concentration, has been studied by Ondaral et al. [220]. The authors observed that these hyperbranched polymers formed thicker and more rigid adsorbed layer as compared to similar linear polymers with very minor dissipation of the mechanical energy after adsorption, thus indicating reduced viscous response. The difference in properties observed in this study was related to the absence of mobile loops and tails in adsorbed hyperbranched molecules. On the other hand, a high density of charged terminal groups stabilized the intralayer organization of the molecules and reduced their lateral mobility.

Recently, Haag et al. presented new nanostructured hyperbranched PMMA gradient surfaces obtained via self-assembly of semifluorinated hyperbranched polyglycerol amphiphiles (FPG) at the PMMA surface during free-radical MMA bulk polymerization [221]. The surfaces of the PMMA/FPG gradient materials obtained in this way were water and oil repellent. This very intriguing dual-face material exhibited unusual nanolayered superstructures composed of alternating fluorine-containing hydrophobic and fluorine-free hydrophilic nanometer-scaled regions.

In a recent series of publications, Wooley et al. have investigated the temporal evolution in the process of degradation of the cast hyperbranched

poly(silyl ester) films in liquid environment by monitoring the changes in the surface topography of the surface films [222]. The authors concluded that the unique two-stage surface degradation process observed in their studies was controlled by the composition and the architecture of the tethered branched molecules. In a related study, this group also studied the surface properties of hyperbranched polyfluorinated benzyl ether polymers [223]. Analysis of the AFM data suggested that partial 1*H*,1*H*,2*H*,2*H*-perfluorodecanoxy substitution led to a phase separation within surface films, which caused a significant decrease in friction and adhesive forces. In a later report, these HBFPs with a large number of pentafluorophenyl ends were crosslinked with diamino-terminated PEG or diamino-terminated poly(dimethylsiloxane) (PDMS) to form much more stable hyperbranched networks of different compositions with variable surface wettability on glass substrates, pre-functionalized by APTS SAM [224]. The AFM data revealed well-developed phase segregation of HBFP contained in PEG or PDMS matrices with the domain dimensions depending upon the stoichiometry and the thickness of these films (Fig. 28) [181]. As result, the increase of PEG content leads to an increasing hydrophilicity of the multicomponent coatings and their increasing resistance towards the adsorption of biomolecules such as bovine serum albumin (a lectin) and lipopolysaccharides. This interesting property can be further exploited for anti-biofouling applications [182].

Intriguing fibrillar structures with helical morphology have been recently observed for hyperbranched polymers crystallized from slow evaporating solution [225]. Yan et al. presented the macroscopic molecular self-assembly of an amphiphilic hyperbranched copolymer, poly(3-ethyl-3-oxetanemethanol) core and hydrophilic arms (HBPO-PEO) cast from acetone (Fig. 29). Optical images, observed with TEM, revealed the presence of very long, straight microtubes with their walls possessing lamellar organization. These tubular aggregates have a wall thickness of 400 nm, several millimeters in diameter, and a few centimeters in length (Fig. 29). It has been reported that this hyperbranched copolymer can also self-assemble from water to form giant polymer vesicles [226].

The introduction of rigid rod-like segments into dendritic molecules proved instrumental in obtaining unusual one-dimensional surface assemblies well known for regular dendrimers. Dendritic

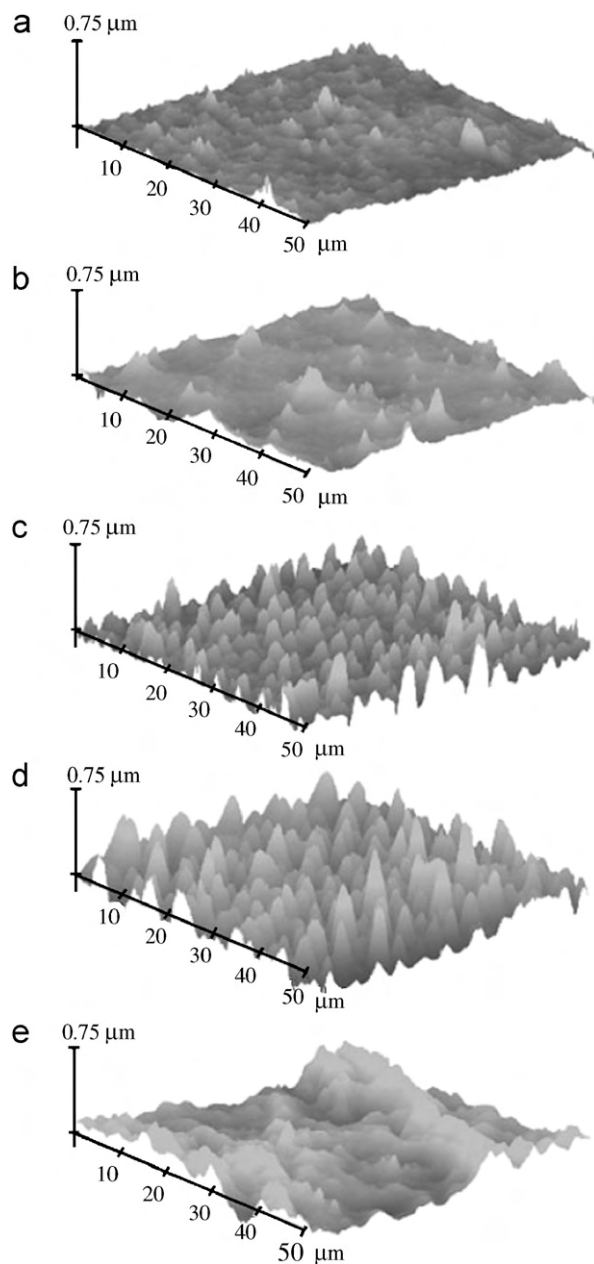


Fig. 28. AFM images of crosslinked surface films fabricated from HBFP-PEG networks as the PEG weight increases from 0% (top image) to 14% to 29% to 45% to 55% (bottom image) [181]. Reprinted from Gudipati et al. by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

amphiphilic rods formed peculiar one-dimensional structures such as microfibrils, ribbons, tubules, and twisted tubules depending upon chemical composition. A very interesting approach for the fabrication of solution-processable organic electronic has been suggested in a recent publication [227]. The authors

designed four-armed, star-shaped molecules with rigid thiophene segments linked to a carbosilane core. They observed that these molecules form smooth and uniform monolayers, which are more stable than those formed from linear molecules of similar composition. Moreover, the variable surface morphologies of these molecules which include e.g., nanowires, were found to improve charge-transfer parameters of thin-field transistors with noticeable increase in charge mobility and a threshold voltage, making them promising materials for organic electronic devices.

Peculiar web structures have been formed by rod-dendritic molecules after slow evaporation of solvent (1-octanol) on graphite and glass surfaces as was demonstrated in a recent study by Genson et al. (Fig. 30) [228]. The authors reported a novel mechanism of assembly of dendronized rod molecules into a dense supramolecular fluorescent web featuring self-propelled inward motion of star-shaped aggregates within a solution droplet in the course of one-dimensional growth of the pinned arms. An intriguing assembling mechanism discovered in this work involves microscopic (hundred micrometers) directional motion of the microscopic aggregates driven by one-dimensional molecular assembly, resulting in a dense mesoscopic supramolecular fluorescent web composed of micro and nanofibrils radiating from central regions (Fig. 30b).

Similarly, the formation of very long and straight microfibers in the course of crystallization from solution was observed for modified hyperbranched polyester molecules with bulky and planar anthracene end groups (Fig. 31) [229]. In this case, straight nanoribbons with a sheet-like lamellar surface morphology have been observed for these fibrillar aggregates with AFM at a higher magnification (Fig. 31). The authors speculated that the multiple intermolecular hydrogen bonding, polar interactions between flexible cores and strong π – π interactions between anthracene terminal groups stabilize these nanofibers and make them well-defined, shape-persistent, and near-perfect structures spanning over a range of spatial scales from nano- to macroscale. The surface aggregation of these molecules, which can be called “multi-branched amphiphiles,” resemble the surface behavior of conventional amphiphiles with clearly defined, single-group/chain polar and hydrophobic fragments but with much wider versatility. The authors suggested that the directional crystallization of multiple peripheral fragments attached

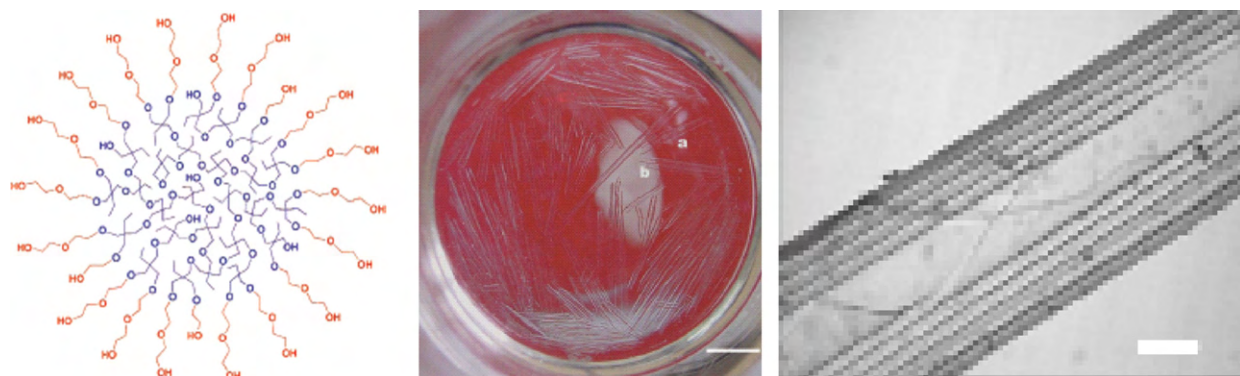


Fig. 29. Left—sketch of the HBPO-star-PEO multi-arm copolymer. Center—Macroscopic tubes from the HBPO-star-PEO multi-arm copolymer. Scale bar, 1 cm. Right—optical microscopy images pentawalled tube [225]. Scale bar, 300 μm . Reprinted from Yan et al. by permission of Science (UK).

to irregular cores could be responsible for assembling near-perfect, straight, uniform, multilength-scale supramolecular one-dimensional structures.

An alternative routine for the formation of 3D structured films with a nanoscale thickness is electrostatically driven LbL assembly which has been applied earlier to dendrimers [170,230] and has been recently expanded towards charged hyperbranched molecules (polyelectrolytes) [167]. Qiu et al. synthesized carboxyl-terminated aryl-alkyl hyperbranched polyester poly(5-hydroxyethoxyisophthalic acid) (PHEIA). They used these polyelectrolyte molecules for LbL assembly in combination with poly(diallyldimethylammonium chloride) (PDAC) [171]. AFM studies revealed sphere-like particles with sizes in the range of 100–225 nm, which were attributed to the aggregation of hyperbranched PHEIA within LbL films [172]. Further study of anionic hyperbranched polymers with the same backbone but different end-groups in the presence of PDAC confirmed the critical role of the terminal groups in the surface organization of resulting LbL films [173].

4.3. Dynamics of surface spreading

The vast majority of studies on the surface behavior and structures of highly branched molecules completed to date consider highly branched polymers at “post-deposited” conditions, frequently after multiple rinsing, washing, drying, and annealing. The general assumption is that the overall structure of the deposited molecules is not affected by post-treatment and the surface organization in air represents a “frozen” equilibrium state. This assumption is probably valid in most cases,

especially if the molecular weight of the macromolecular chains is high enough to exclude lateral mobility on a solid surface and a significant fraction of segments is frozen by being in a glassy state, which prevents vertical segregation in a bad solvent (air). However, the question of real-time dynamics of surface spreading, wetting behavior, dewetting phenomena, and surface restructuring remains a crucial issue for the branched molecules. To date, very few studies even addressed this issue. Selected important results are briefly discussed below.

Sheiko et al. have demonstrated a real time spreading behavior of a grafted polymer drop on a solid substrate, with molecular resolution, by using a high-resolution in-situ AFM monitoring (Fig. 32) [231]. Individual and collective motions of brush molecular chains confined within molecular layer have been tracked with excellent quality on a flat graphite surface, and pinning and molecular reorientation around the surface defects were visualized in real time. From the analysis of the independently measured microscopic spreading rate, the flow-induced diffusion rate of molecules, and the thermal diffusion coefficient of single molecules the authors concluded that the plug flow of polymer chains was the main mass-transport mechanism of molecular spreading. A very insignificant contribution from the actual molecular diffusion in the spreading process was suggested as well.

As a next step, Sheiko et al. studied in detail the real-time conformational transition of brush macromolecules in the process of their adsorption on a mica surface [232,233]. They visualized the spreading behavior of individual branched molecules and interpreted the observed variations in terms of interplay between enthalpic and entropic terms of

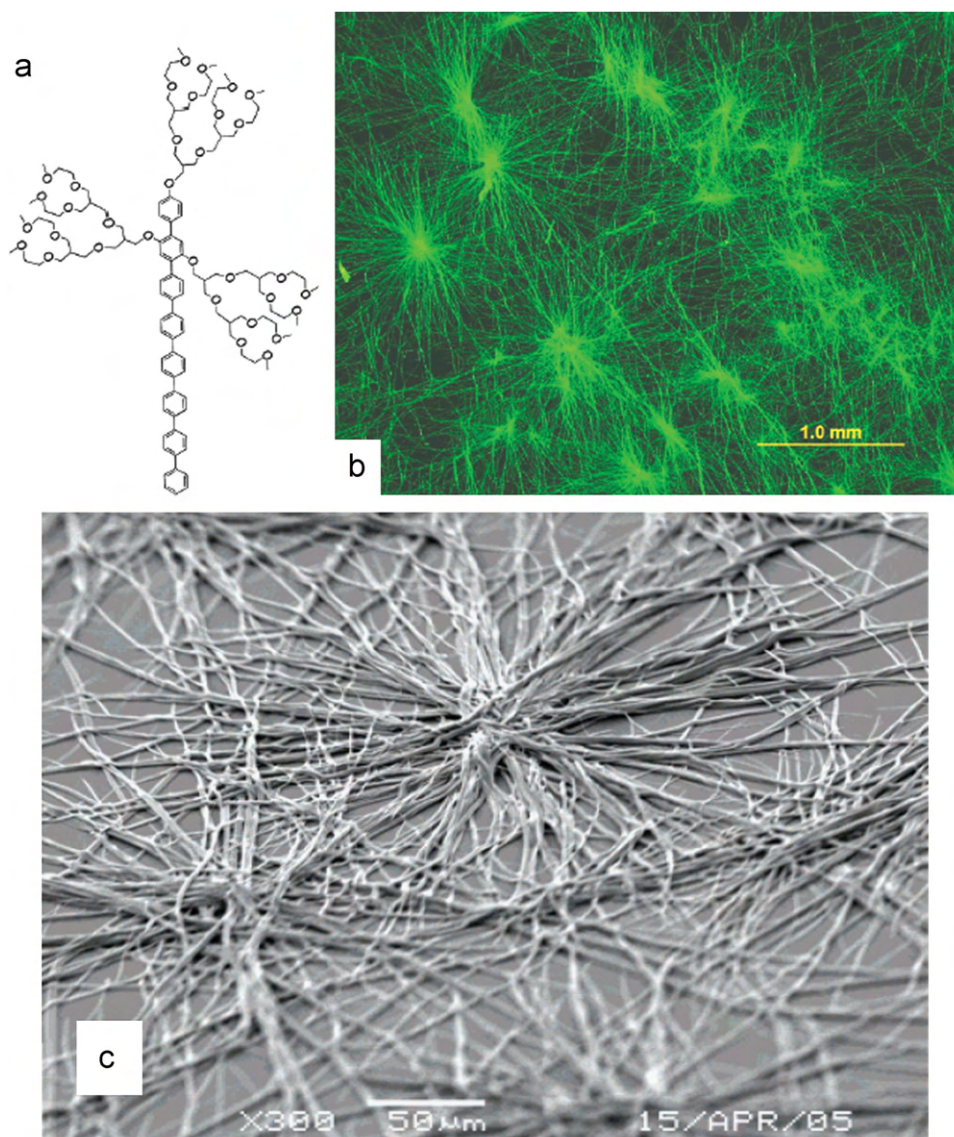


Fig. 30. Chemical formula of tree-like rod-dendrons (a) and fluorescent micrograph of a dense network of one-dimensional structures they formed (b). (c) SEM image of dense network of star-shaped aggregates at graphite surface (SEM image at an angle) [228]. Reprinted from Genson et al. by permission of the American Chemical Society.

individual molecules and accompanying variations of surface energies. The authors suggested that the co-adsorption of the small organic molecules from solution controls the adherence and spreading of the macromolecules, tuning the surface expansion and the collapse of the molecules in a predictable manner (Fig. 33).

In the most recent study the same group demonstrated that a physical adsorption of brush-like macromolecules with very long side chains can induce not only conformational reorganization and deformations, but also spontaneous rupture of

covalent bonds in the macromolecule backbone (Fig. 34) [234]. This unexpected surface behavior observed for dendritic polymers with very high molecular mass was attributed to the fact that the attractive interactions between the side chains and the substrate is maximized by the spreading of the side chains, which in turn induces significant tensile tension along the polymer backbone. Such a 2D spreading confined to the monomolecular surface layer conflicts with inherited 3D architecture of highly branched molecules, thus bringing significant intramolecular stresses into the overcrowded

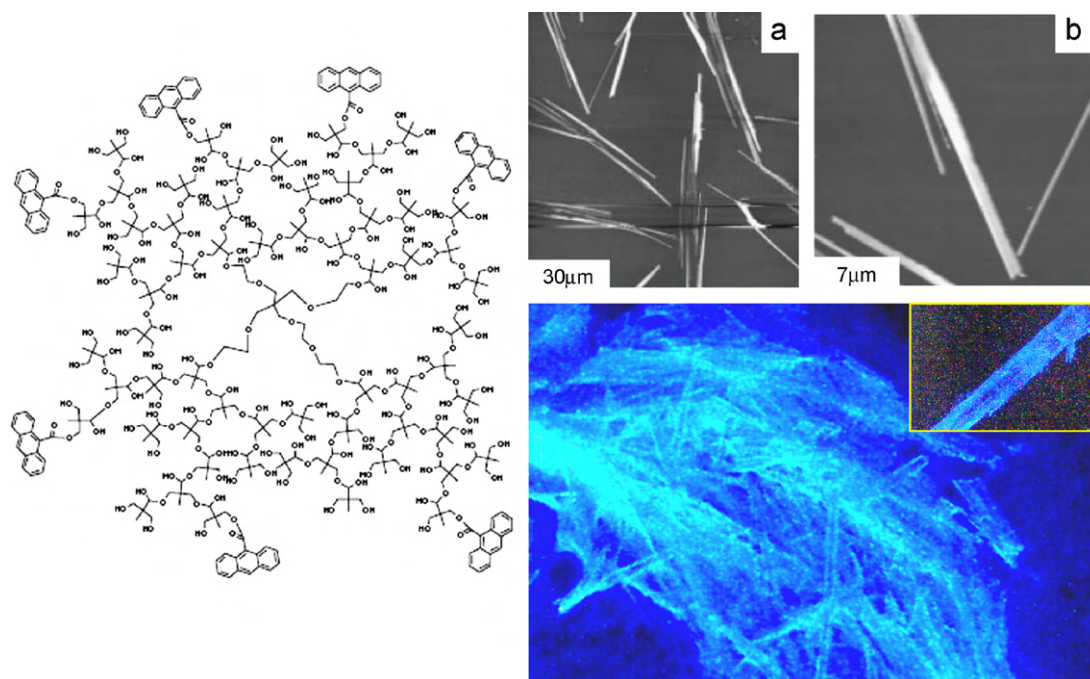


Fig. 31. Chemical structure of anthracene-functionalized hyperbranched polyester and optical images of straight polymer nanofibers and nanoribbons under normal (a and b) and UV (c) light. Insert shows an individual microfiber at higher magnification [229]. Reprinted from Ornatska et al. by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

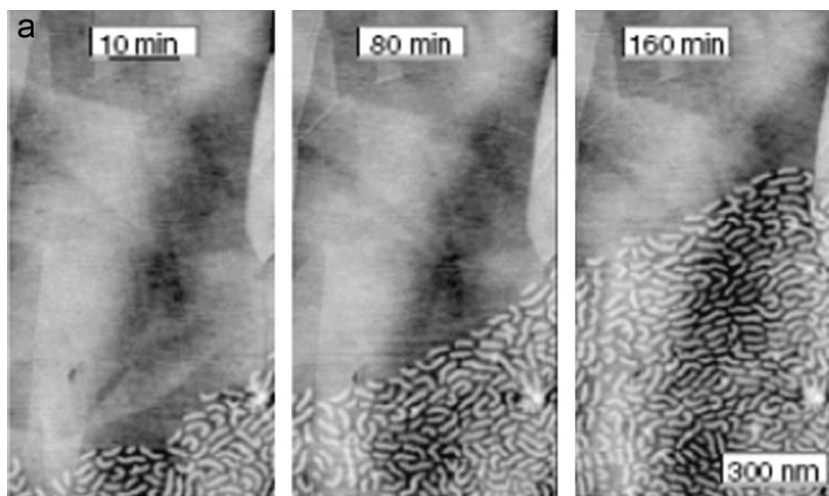


Fig. 32. The wetting behavior of the monolayer of PBA brushes on the HOPG surface. The images were captured at different spreading times: 10, 80, and 160 min after deposition [231]. Reprinted from Xu et al. by permission of the American Physical Society.

molecular interior after deposition on the flat surface. The authors suggested that similar adsorption-induced backbone scission might occur for all sufficiently long macromolecules with highly branched architectures. This scenario should be considered in studies of highly branched molecules'

surface behavior, especially in the case of "tree-like" architectures with a single covalent bond bearing multiple branches in the molecular core, in the case of strong interactions of terminal branches with the supporting solid surface, and for very high molecular weight species (a million Daltons and above).



Fig. 33. Schematic of the competition in spreading between the adsorbed polymer brush molecule and co-adsorbed small molecules. (a) A co-adsorbed layer of amphiphilic molecules efficiently lowers the surface energy and causes the collapse of the macromolecules. (b) A co-adsorbed layer of polar molecules does not decrease the surface energy of the substrate and causes spreading of the macromolecules [233]. Reprinted from Gallyamov et al. by permission of the Wiley-Blackwell.

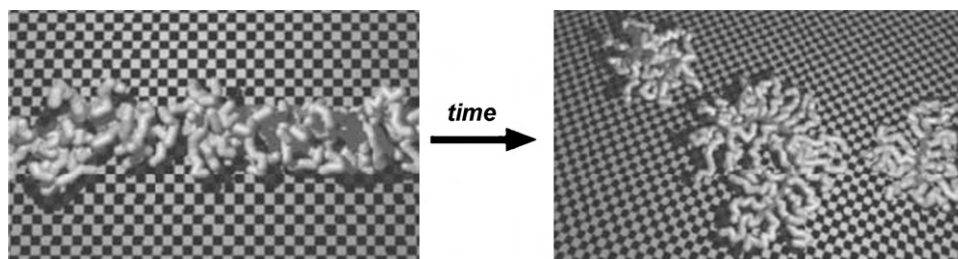


Fig. 34. Schematics of an adsorbed brush macromolecule (left) which undergoes spontaneous scission of the covalent backbone (right) [234]. Reprinted from Sheiko et al. by permission of Nature Publishing Group.

Direct comparison of the formation of Langmuir and Gibbs monolayers of hyperbranched polyols showed that the adsorption kinetics can be described as a two-stage process with a rapid diffusion stage flowing by slow reorganization at the air–water interface as was discussed in a recent publication [235]. The surface reorganization controlled by slow molecular diffusion and led to 2D first-order transition as concluded from corresponding isotherms. However, no direct microscopic data were provided to support and clarify the nature of transition observed in this study.

4.4. Grafted layers from highly branched molecules

Chemical grafting from solution or melt is considered as an effective way for the formation of tethered surface layers with modest and high grafting densities [236]. In fact, dense and firmly tethered monomolecular layers from highly branched molecules have been formed by direct chemical grafting from melt with several examples of robust and uniform nanoscale layers were recently reported (see previous section for chemical routines).

In recent report, the authors discussed star thiopene molecules with a single thiol group capable of forming self-assembled mono- and multilayers on gold [237]. The authors claimed that star-shaped

molecules form more robust and electrically conductive surface films but provided very limited data on their surface morphology and microstructure. In another example, the functionalized hyperbranched polyester with partially functionalized terminal branches, which include alkyl chains mixed with epoxy-functionalized chains, was exploited for chemical grafting to the silicon oxide surface (Fig. 35) [175]. A branched chemical architecture with multiple epoxy groups provided the firm grafting capability, inducing surface functionality along with hydrophobization of the surface due to alkyl tails.

In fact, the authors observed that these hyperbranched monolayers could be firmly tethered to the silicon oxide surface with layers (4–6 nm thickness), which are thicker than conventional SAMs and with elastic properties typical for cross-linked polymer layers. Grafted layers formed from these molecules were homogeneous on a nanoscale without any signs of the microphase separation usually observed for mixed layers. The authors suggested that architectural constraints caused by the attachment of the dissimilar branches with epoxy and alkyl terminal groups to a single core effectively suppress their phase separation on a large scale. Finally, they demonstrated that the efficient grafting of these surface layers leaves a fraction of epoxy groups localized at the film surface

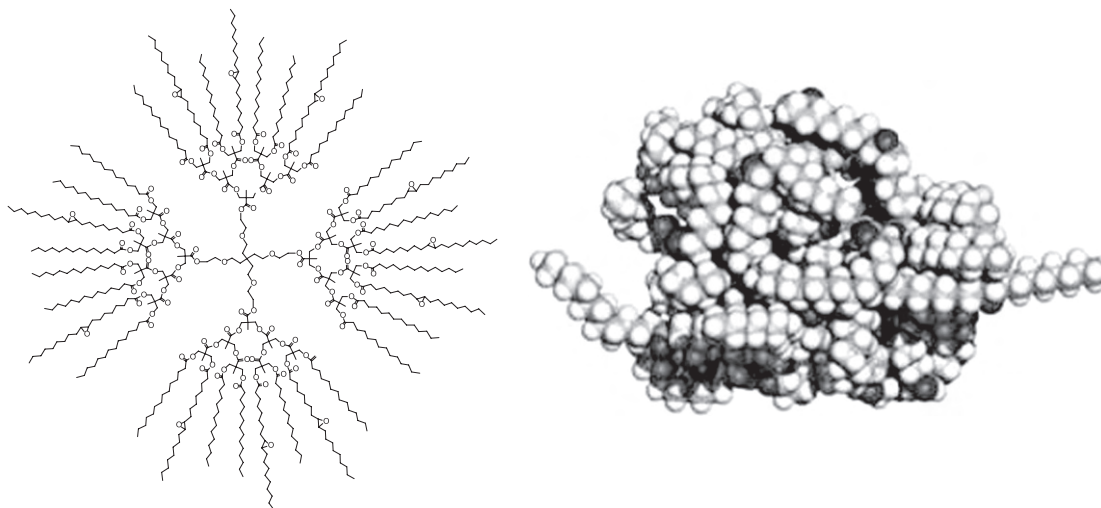


Fig. 35. Idealized chemical structures of the hyperbranched polyester with epoxy groups and the molecular model of a condensed randomized conformation after surface grafting [175]. Reprinted from Sidorenko et al. by permission of the American Chemical Society.

readily available for further hydrolyzation and grafting.

In contrast with these molecules, some other branched molecules with composite terminal groups formed highly heterogeneous surface morphologies after grafting to the solid substrate. E.g., novel nanoscale surface structures of segregated pinned micelles and craterlike micelles were observed from binary-branched molecules chemically grafted to a silicon surface [238,239]. These dense monomolecular layers with well-defined nanophase surface structures have been formed by grafted Y-shaped binary brush molecules having two incompatible polymer chains with modest lengths (PS and PtBA (further hydrolyzed to PAA)) attached to a functional stem like segment, capable of covalent grafting to a epoxy-functionalized silicon surface (Fig. 36).

Postgrafting hydrolysis of PtBA arms conducted after chemical grafting imparts the amphiphilicity to the brush layer and induces strong nanophase segregation of the dissimilar arms within the monomolecular surface layer (Fig. 37). The PS and PAA arms grafted to a single point are capable of local, reversible rearrangements leading to reversible surface structural reorganization in different solvents with very different structures and surface properties ranging from hydrophilic to highly hydrophobic, depending upon which arms are segregated at the layer surface (Fig. 37). Moreover, the authors suggest that characteristic asymmetric composition of the molecules is respon-

sible for the formation of nanoscale crater-like surface structures in a dry state when the polymer layer was immersed in a bad solvent (air). These nanoscale surface structures with unique switchable behavior can be considered as a promising step toward the patterning of solid substrates with adaptive nanowells, which could be used for trapping of adsorbing nanoscale objects.

The surface morphology and the nanomechanical properties of surface-grafted amphiphilic PS–PAA Y-shaped brushes were further examined directly in fluids (in-situ visualization) (Fig. 38) [240,241]. Direct, in-water observation of the surface morphology and nanomechanical properties of the mixed brushes composed of these Y-shaped binary molecules revealed nanoscale, network-like surface topography formed by coexisting, stretched, soluble PAA arms and collapsed insoluble PS chains. In water, a bimodal distribution of the elastic modulus of the grafted layer was detected. As suggested, this behavior is caused by the mixed and asymmetric chemical composition of the binary molecules (Fig. 38). In contrast, in toluene the topmost surface layer was completely dominated by longer PS chains giving rise to uniform elastic response. These binary layers with the overall nanoscale thickness of 3–4 nm in dry air and up to 10 nm in a swollen state can serve as adaptive nanocoatings with stimuli-responsive properties.

Indeed, the microtribological and nanomechanical characteristics of Y-shaped grafted layers were measured as a function of chemical composition and

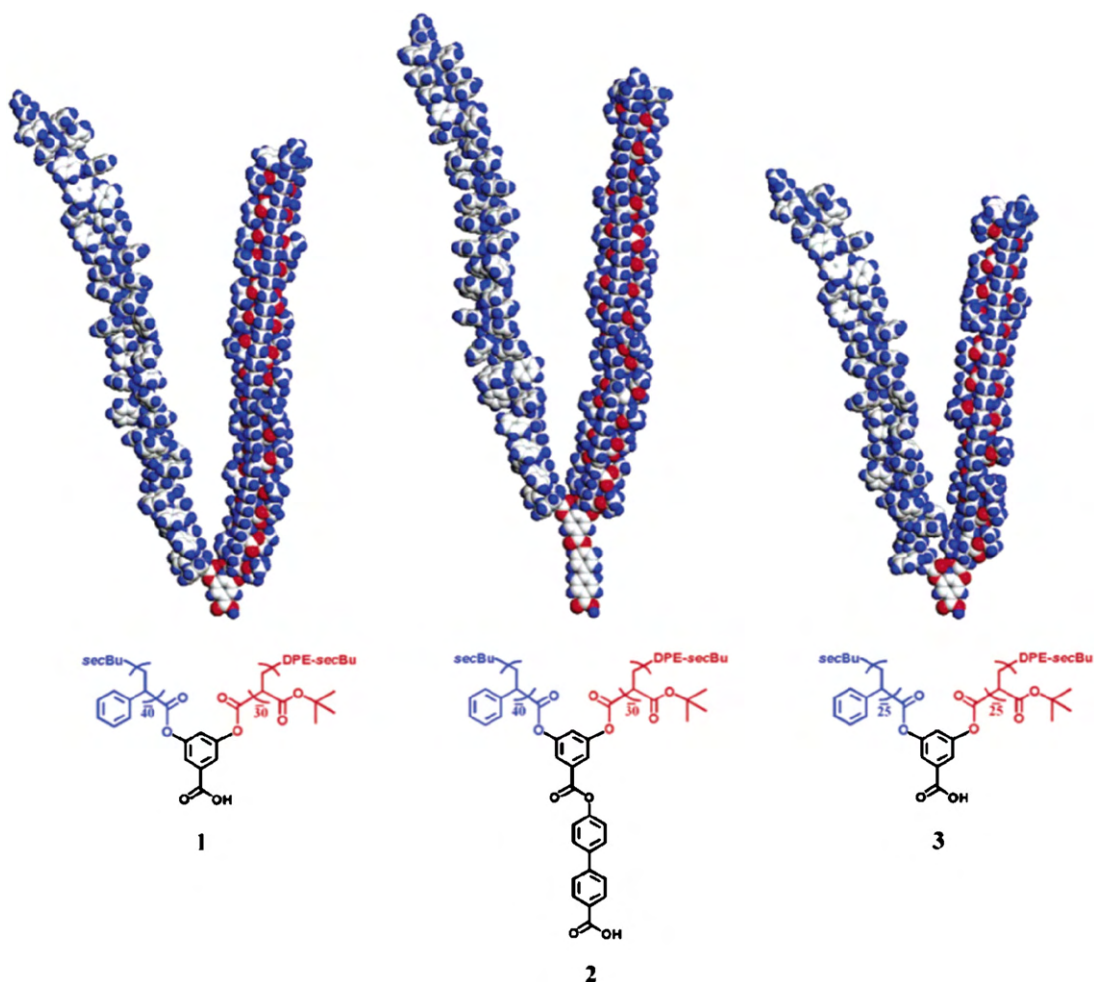


Fig. 36. Chemical structure and molecular models of Y-shaped block copolymers with a short (1, 3) and a long (2) aromatic functional stem. Molecules 1 and 2 contain 40 and 30 monomeric units in PS and PtBA arms [238]. Reprinted from Julthongpipit et al. by permission of the American Chemical Society.

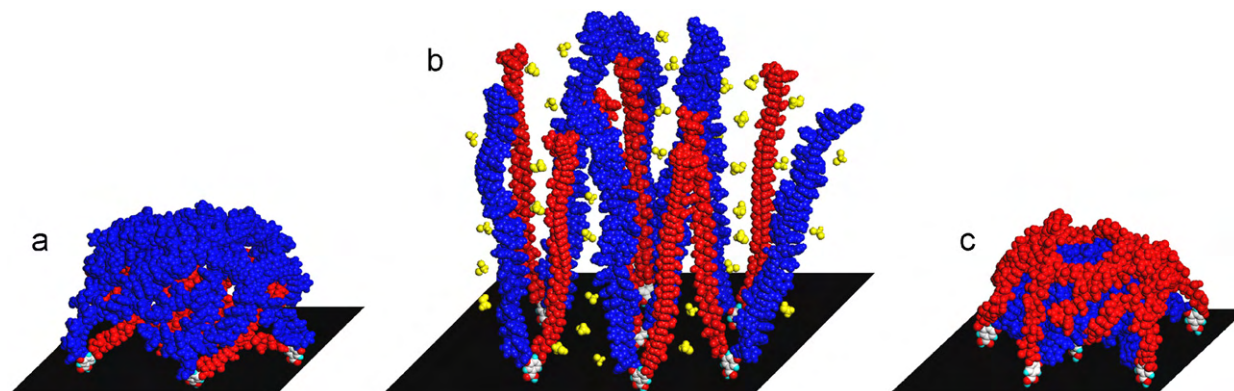


Fig. 37. Molecular models of the structural rearrangement in pinned micelle composed of seven grafted PS-PAA molecules under solvent treatment. (a) Upon treatment with toluene and the drying, the PS arms (blue) form corona covering the micelle's core consisting of seven PAA arms (red). (b) Molecules swelled in a nonselective solvent (yellow). (c) Crater-like structure containing seven collapsed PS arms partially covered by PAA chains [238]. Reprinted from Julthongpipit et al. by permission of the American Chemical Society.

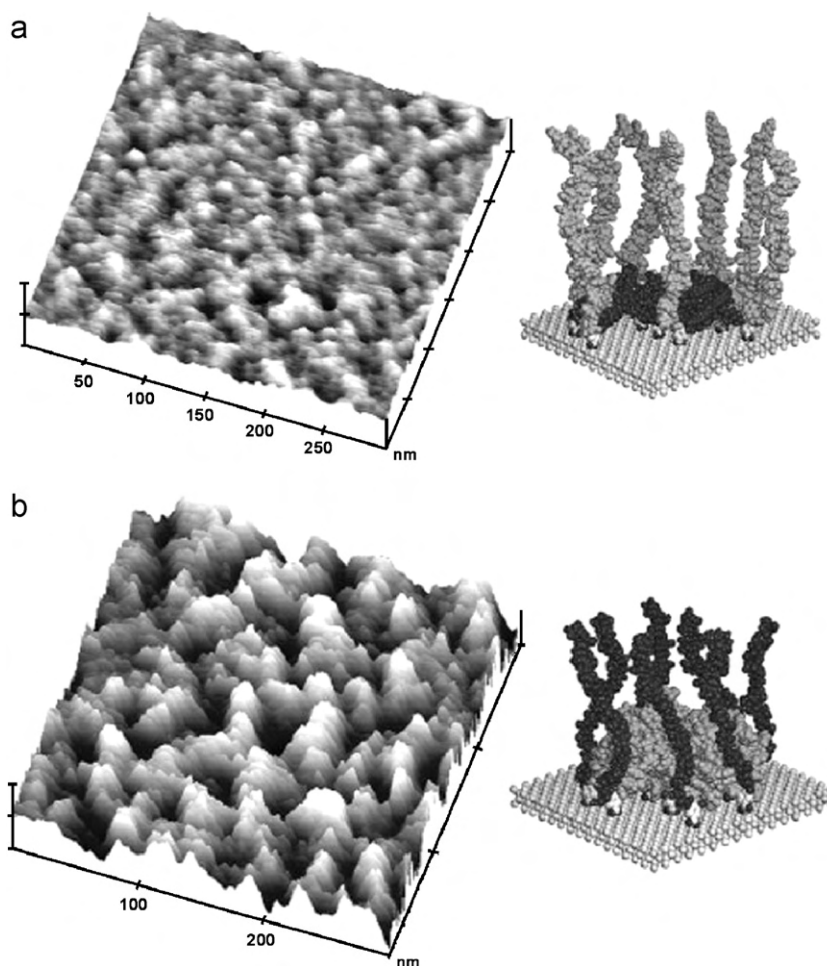


Fig. 38. AFM images of grafted Y-shaped molecules obtained directly in (a) water and (b) toluene with the corresponding molecular models [240]. Reprinted from LeMieux et al. by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

in conjunction with the treatment by selective solvents. The placement of Y-shaped brushes in different fluids resulted in the dramatic reorganization of their surface properties, ranging from a soft repellent layer covered by swollen PS arms after toluene treatment to an adhesive, mixed layer composed of coexisting swollen PAA and collapsed PS arms in water with surprisingly lower friction coefficient.

A stratified polymer surface film with a tunable thickness (within 17–34 nm) has been prepared through room temperature UV-initiated polymerization with a temperature-sensitive pNIPAAm layer confined beneath a dendritic hydrophobic layer (see preceding section) [192]. The characteristic behavior around low critical solution temperature (LCST) of pNIPAAm confined under the dendritic topmost layer was observed in water with a 100% change in thickness above and below this transition.

The AFM imaging revealed changes in surface morphology and thickness and the nanomechanical probing confirmed vertical gradient of the elastic response tunable to a desired state by the external temperature (Fig. 39). These temperature-sensitive, adaptive polymer structures with a pNIPAAm layer “hidden” beneath the rubbery, hydrophobic branched PBA topmost layer represent an interesting example of nanoengineering surfaces with multi-level structural reorganization responsive to fluidic and temperature variations. .

4.5. Langmuir–Blodgett films

Langmuir and LB techniques are informative methods of studying surface properties of single molecules in monolayers. In addition, LB deposition provides well-controlled placement of amphiphilic

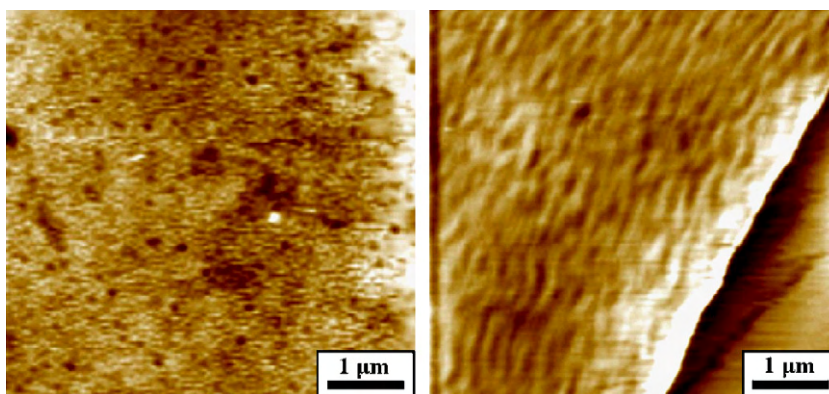


Fig. 39. AFM images of the brush layer with vertically segregated structure in water at different temperatures: 10 °C (left) and 50 °C (right) [192]. Reprinted from LeMieux et al. by permission of the American Chemical Society.

molecules onto a solid support with a precisely pre-defined surface area per molecule. The hydrophobic–hydrophilic balance in branched molecules is controlled by either a difference in chemical composition of different arms (e.g., heteroarm star polymers, arborescent polymers) or cores and branches (e.g., partially chemically modified hyperbranched cores, dendrimacs). Langmuir and LB monolayers have been fabricated from amphiphilic, highly branched molecules and have been studied in detail.

The surface properties of graft copolymers and the corresponding ungrafted “parent” homopolymer composed of a poly(ethyl acrylate) (PEA) main chain and pendant PS grafts at the air–water interface were reported long ago [242]. The PEA component in these graft copolymers provided sufficient hydrophilicity to form stable Langmuir monolayers transferable onto a hydrophilic silica substrate. The authors observed that at low surface concentration, the surface pressure of these copolymers is influenced mainly by the PEA backbone. However, the surface behavior at high surface pressure is mainly controlled by the number of PS grafts.

In recent reports, Zakharova et al. studied the surface behavior of the poly(vinyl pyridine) (PVP), the hyperbranched perfluorinated poly(phenylene-germane), and their polymerized product using Langmuir isotherms [243,244]. They found that the perfluorinated hyperbranched macromolecules with the effective radius of 1.75 nm are not affected by changes in the pH of a subphase. However, in the case of the polymerized material, a rise in the acidity of the substrate promoted an increase in the surface stability. However, the lack of AFM data did not allow discussing morphological changes in detail. In

other study, Sheiko et al. [245] investigated the surface behavior of hyperbranched polymers containing trimethylsilyl or hydroxyethyl end groups at the air–water interface. Comparison of the spreading behavior of the OH-terminated molecules with that of the polydisperse hyperbranched polymer with identical chemical composition revealed that the hyperbranched polymer did not show any well-defined intramonolayer transitions in the course of the monolayer compression and instead exhibited more smeared surface behavior similar to that of isotropic amphiphilic compounds.

A very intriguing example of the cylindrical molecular brushes $p[(\text{MMA-grad-BPEA})\text{-graft-}n\text{BA}]$ with a gradient of their grafting density along the backbone have been recently reported [27]. It has been observed that these peculiar molecules displayed a transition from rodlike to tadpole conformation upon compression (Fig. 40). AFM revealed the shapes of individual molecules and two distinct microphases composed of different blocks coexisting within individual molecules adsorbed on mica [246]. Furthermore, upon compression the rod-globule transition occurs, leaving a molecule with a globular “head” and an extended “tail” of the backbone with lower grafting density, a characteristic of tadpole conformation. Even more complex 3D morphologies have been observed within LB films of dendronized block copolymers, and were attributed to the coil-semirod architecture [247].

Recently, our group reported significant influence of amount of alkyl-terminated groups on the surface behavior of a series of pseudo-second-generation modified hyperbranched polyesters with a variable chemical composition [248]. Detailed investigation

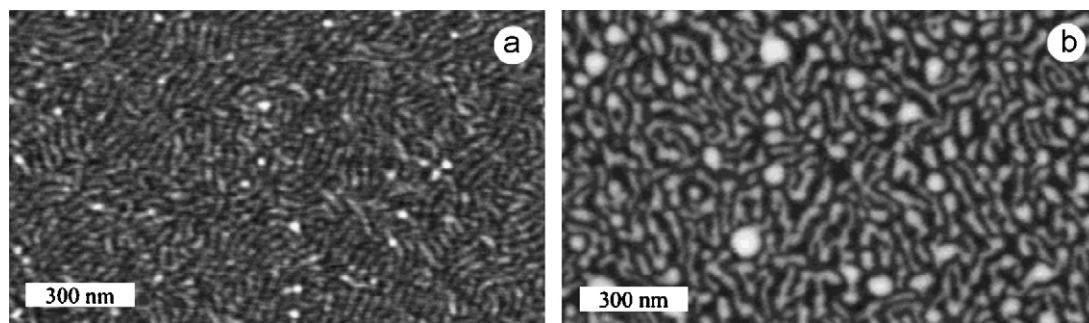


Fig. 40. AFM images of LB monolayers of p[(MMA-*grad*-BPEA)-*graft*-nBA] tad-pole gradient brushes. The monolayer were transferred onto mica surface at surface pressures $\pi = 5$ mN/m (a) 22 mN/m (b) [27]. Reprinted from Lord et al. by permission of the American Chemical Society.

of the surface behavior at the air–water interface and microstructural analysis with in-situ X-ray diffraction and reflectivity revealed that organized Langmuir monolayers are formed if the number of alkyl tails is higher than a certain threshold limit. For these molecules, the critical number was determined to be two alkyl chains per a hydrophilic core. From hyperbranched polymers with 2–9 attached alkyl tails the formation of well-developed domain surface morphology with round and dendritic shapes of domains was observed (Fig. 41). X-ray diffraction revealed that the alkyl tails of hyperbranched molecules at the higher surface pressure formed an intramonolayer quasi-hexagonal lattice and a straight, up-right orientation of tails (Fig. 41). As for hyperbranched molecules with fewer alkyl chains at high surface pressure, water-swollen hydrophilic cores of prolate shape and the partially submerged and standing-off alkyl tails have been observed. However, increasing of total number of alkyl tails to nine led the transformation of the core into an oblate, flattened shape with the preservation of standing-off orientation of the alkyl tails for hyperbranched molecules with crowded outer shells.

It has been suggested that the amplification of multiple weak interactions between numerous peripheral branches of irregular, flexible, polydisperse, and highly branched molecules can facilitate their self-assembly into nanofibrillar, micellar structures at solid surfaces. To this end, Ornatska et al. [249,250] investigated the surface structures of the modified hyperbranched polyester cores with different compositions of the terminal groups. A highly branched polyester core with hydroxyl terminal groups, synthesized by a “one-pot” approach with the presence of active core monomers

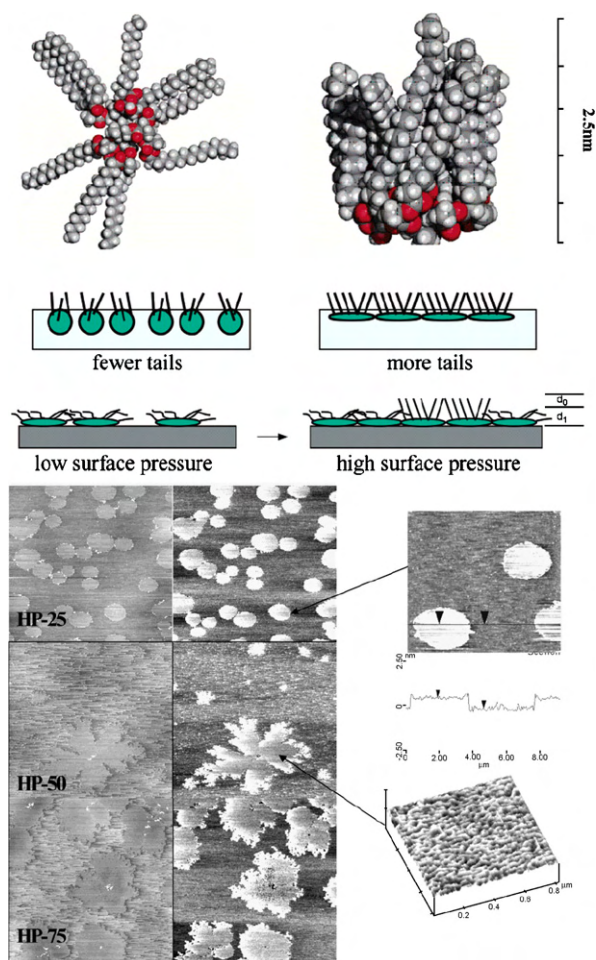


Fig. 41. Molecular models of a modified hyperbranched molecule and schemes of their ordering at the air–water interface (left) and AFM images of LB monolayers from molecules with different number of alkyl tails (HP-X corresponds to percentage of modified branches, 25%, 50%, and 75%) deposited at the high surface pressure [248]. Reprinted from Zhai et al. by permission of the American Chemical Society.

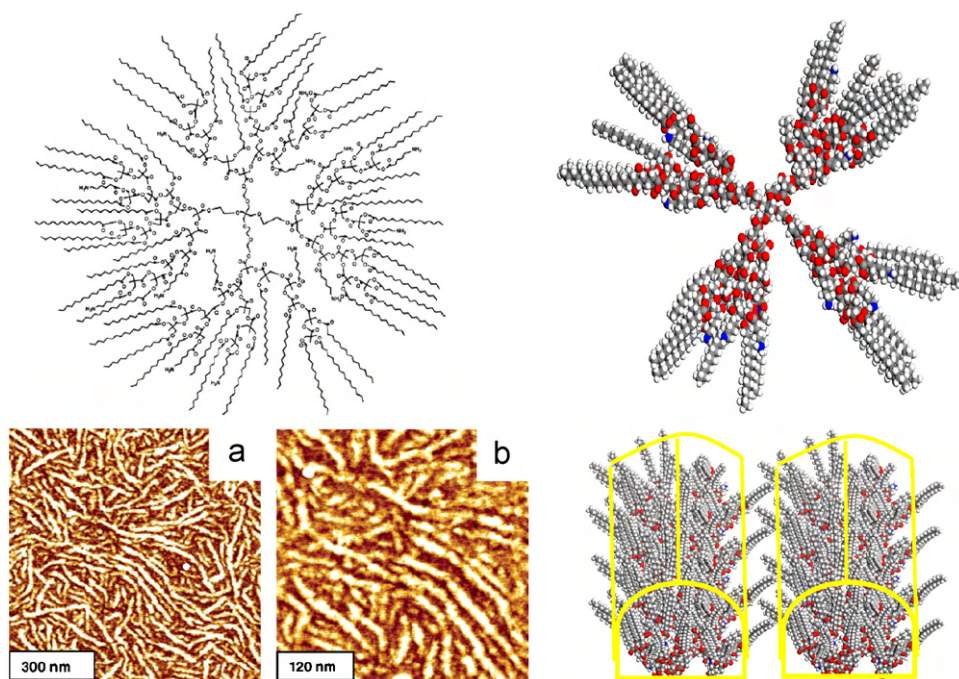


Fig. 42. Chemical formula of the amphiphilic hyperbranched polyester with modified terminal branches (left), corresponded high-resolution AFM phase images of nanofibrillar structures assembled at 20 mN/m (a, b) and suggested conformational reorganization, which leads to the formation of semi-cylindrical micelles upon compression [249]. Reprinted from Ornatska et al. Wiley-VCH Verlag GmbH & Co. KGaA.

(pseudo-fourth-generation) went via the purification and fractionation procedures before further chemical modification [251,252]. The esterification of hyperbranched cores generated modified branched molecules with 50 hydrophobic palmitic (C_{16}) alkyl tails, 14 amine- and 1–2 hydroxyl terminal groups, capable of forming nanofibrillar structures. The amine groups were introduced to enhance polar interactions with the silicon oxide surface in order to stabilize surface nanostructures, and were proven to be critical for the formation of robust nanofibrillar structures (Fig. 42). The core-shell architecture of the amphiphilic dendritic molecules provided exceptional stability for these one-dimensional nanofibrillar structures after complete drying.

The authors suggested that in order to form nanofibrillar structures of this type, the amphiphilic, hyperbranched molecules adapt a highly asymmetric conformation, which is very different from the symmetrical extended conformation observed for unmodified molecules. The proposed model suggests semi-cylindrical conformation in which the hydrophilic cores are squashed against the solid surface, and the hydrophobic terminal branches are concentrated in the topmost layer (Fig. 42). This

shape is appropriate for the face-on packing at the hydrophilic surface. The critical condition for the formation of the nanofibrillar structures is the presence of both alkyl tails in the outer shell and amine groups in the core-inner shell. The multiple intermolecular hydrogen bonding and polar interactions between flexible cores stabilize and make robust these nanofibers. The very peculiar internal organization of these stable nanofibers with a hydrophilic inner core and hydrophobic shell makes them an intriguing candidate for the templating of inorganic wired nanostructures that are distinguishably different from those already demonstrated for dendritic molecules with rigid segments.

Another type of amphiphilic, dendron-rod molecule with three hydrophilic PEO branches attached to a hydrophobic octa-*p*-phenylene rod stem was investigated for its ability to form two-dimensional, micellar structures on a solid surface during LB deposition (Fig. 43) [76]. A tree-like shape of the molecules was reported to be a major factor in the formation of non-planar micellar structures in solution and in the bulk state (cylindrical and spherical) but within LB monolayers, these amphiphilic dendritic molecules assembled themselves into

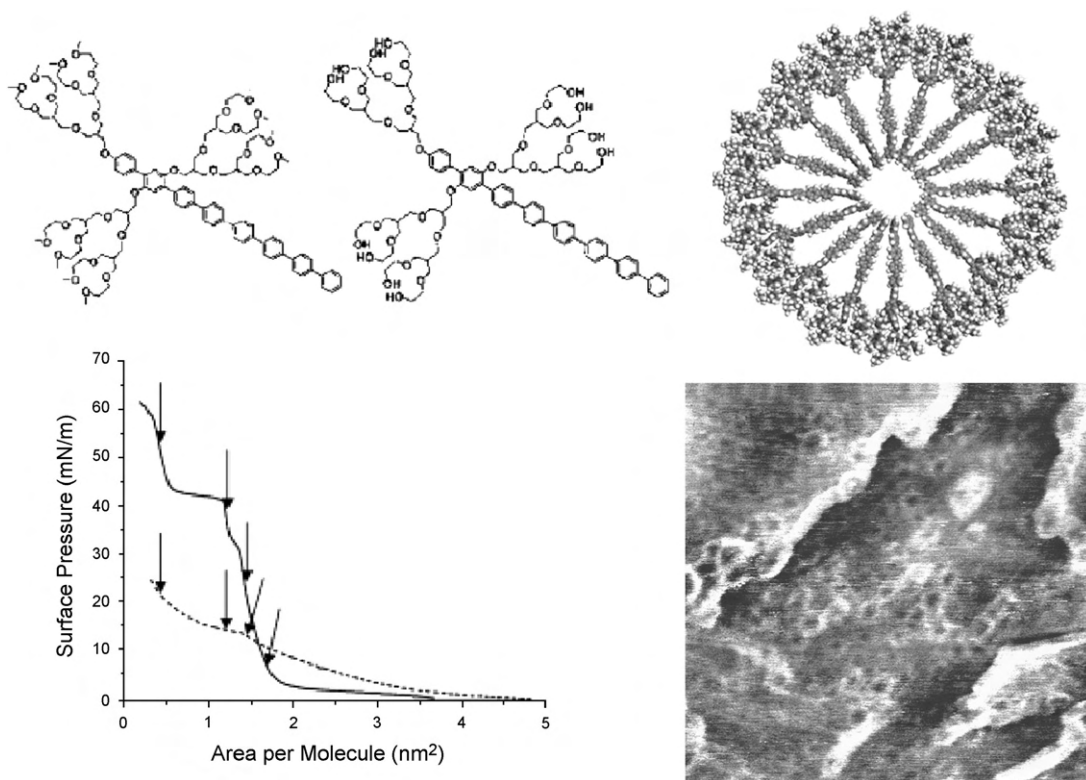


Fig. 43. Left top: Chemical structures of dendritic-rod molecules with methyl-terminated (A) and hydroxyl-terminated (B) branches. Left-bottom—Langmuir isotherms for molecule A (solid line) and molecule B (dashed line) with deposition points indicated by arrows. Right top—Molecular model of molecule A packing showing a circular planar structure (right). Right bottom: AFM phase image ($300 \times 300 \text{ nm}^2$) of LB monolayer from molecule (A) at molecular area 1.2 nm^2 [76]. Reprinted from Holzmüller et al. by permission of the American Chemical Society.

layered or circular micellar structures depending upon the surface pressure (Fig. 43). The authors suggested that the formation of the planar ribbon-like structures within the loosely packed monolayers is caused by interdigitated molecular packing. However, reduced compression stress and weaker interfacial interactions could result in the formation of circular, ring-like structures (2D circular aggregates) within the second layer, formed on top of the monolayer in the pre-collapsed state.

LB films from fluorinated branched polymers containing different kinds of fluorocarbon side chains with various chain lengths were investigated as potential molecular lubricants [253]. The surface morphology changed considerably with deposition conditions as well as with minor chemical modification of the fluorinated comb polymers. The microscopic friction behavior was found to depend strongly on, controlled by solvent treatment, the chemical constituents of the outermost layer [254]. These variations related to the reorganization of the

intralayer hydrogen bonding of the carbonyl groups of the long-chain esters. Shi et al. [255] have studied the microtribological properties of a different type of highly branched molecule, C₆₀-polystyrene hyperbranched polymer. Monolayers and multilayered LB films from these molecules were prepared on mica and AFM imaging revealed that the films were compact and highly ordered, providing a reduced friction coefficient.

A wide variety of LB monolayers have been fabricated from a series of amphiphilic PS-PEO star molecules of different compositions, the most popular choice of blocks. In recent reports from the Duran group, three-arm star PS-PEO block copolymers of various architectures have been synthesized and studied [256,257]. Within LB monolayers, circular domains representing 2D micelle-like aggregated molecules were observed at low surface pressures. Upon further compression, these domains underwent additional aggregation in a systematic manner, exhibiting micellar chaining

into long aggregates. It has been found that longer PEO arms led to greater intermolecular separation and enhanced the trend to reduced domain aggregation.

The surface properties of LB monolayers of a new set of $(\text{PB-}b\text{-PEO})_4$ and $(\text{PS-}b\text{-PEO})_4$ amphiphilic four-arm star block copolymers have been recently presented [258]. Surface pressure isotherms at the air–water interface possessed three characteristic regions, which correspond to a compact brush region, a pseudoplateau, and a pancake region

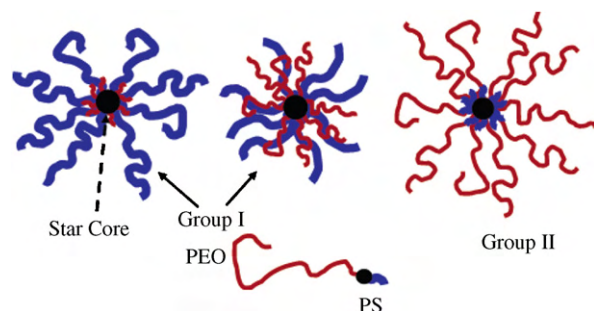


Fig. 44. Schematics of $\text{PEO}_n\text{-PS}_n$ heteroarm star polymers with a larger number of two types of arms and low (left), moderate (center), and high (right) PEO contents in comparison with a linear block copolymer molecule [260]. Reprinted from Gunawidjaja et al. by permission of the American Chemical Society.

where the observed surface area is mainly controlled by the PEO content. The elasticity properties of the monolayer were examined by repetitive compression–expansion cycling, which demonstrated a reproducible modest hysteresis at different pressures. Functionalized amphiphilic $\text{PS}_n\text{-}b\text{-PEO}_n$ star-block copolymers with chain ends chemically modified to generate hydroxyl groups can form stable Langmuir films [259].

Star polymers composed of an equal number of PEO and PS arms, with variable lengths, and a large (up to 38 arms total) number of arms, PEO_nPS_n (Fig. 44), have been examined for their ability to form domain nanostructures at the air–water and air–solid interfaces [260]. All amphiphilic star polymers presented in this study formed stable Langmuir monolayers, readily transferable to a solid substrate. A variety of nanoscale surface morphologies have been observed for various molecules, ranging from cylindrical or circular 2D domains to well-developed bicontinuous structures as the fraction of the PEO block varied from 19% to 88%, and the number of arms increased from 8 to 19. Furthermore, for the PS-rich stars at elevated surface pressure, a two-dimensional, supramolecular, net-like nanostructure has been observed.

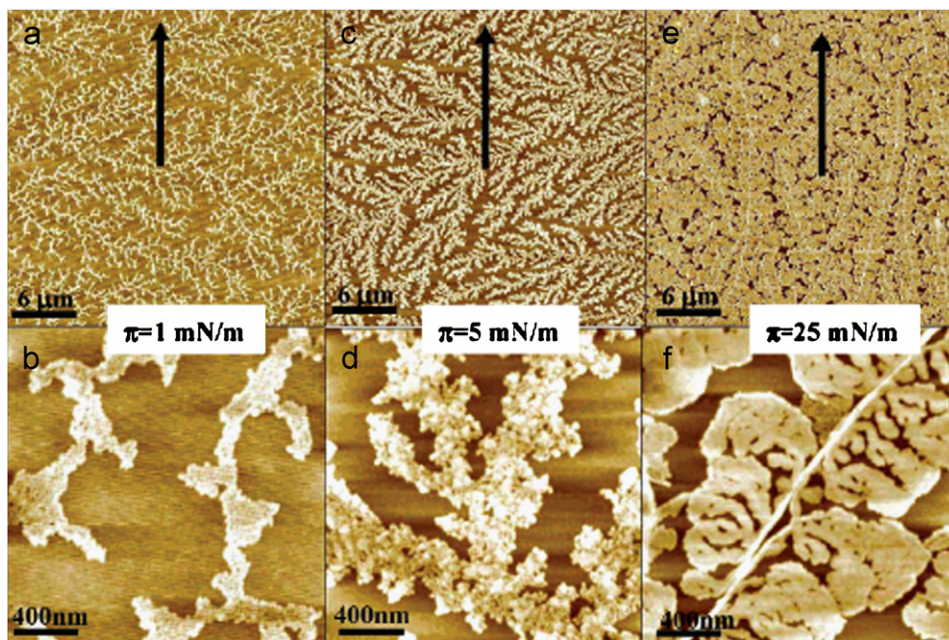


Fig. 45. AFM images of surface dendritic nanostructures in LB monolayers from multiarmed $\text{PEO}_{10}\text{-PS}_{10}$ molecules at 1 (a, b), 5 (c, d), and 25 mN/m (e, f). Arrows (images a, c, e) indicate the dipping direction [260]. Reprinted from Gunawidjaja et al. by permission of the American Chemical Society.

In contrast, for PEO-rich star polymer with the highest PEO content, peculiar dendritic superstructures were observed (Fig. 45). It has been suggested that these structures are caused by intramolecular segregation of non-spherical core-shell micellar structures. Based on Langmuir isotherms and observed monolayer morphologies, three different models of star polymer surface structures at the interfaces have been suggested for different compositions. These models suggest the critical role of the topological constraints at the interfaces in the surface localization of the various blocks.

Different types of star diblock copolymers containing PS and PEO segments were investigated at the air–water interface by the Duran and co-workers [261]. Both conventional and dendritic-like architectures of star molecules were studied. Each of these materials contained either a PS core or a PEO corona. These polymers displayed reproducible surface pressure–area isotherms with little hysteresis. For star molecules containing 20% or more PEO segments, three distinct regions appeared on the surface–pressure isotherms with the PEO blocks absorbing into pancake-like structures and PS globules forming at low surface pressure. Upon monolayer compression, a pseudoplateau transition region showed constant pressure until large compressions. At high surface pressure, the Langmuir monolayer became less compressible due to the dominating glassy PS phase at the surface. Comparison with surface behavior for conventional linear molecules showed that the star molecules with the PS-core are spread much more on the water surface. On the contrary, the star molecules with PEO cores were much more compact. In general, the authors stipulated that the effect of the star architecture was secondary to the role of either PEO chain length or the overall PEO content.

Several novel asymmetric heteroarm $\text{PEO}_n\text{--PS}_m$ star polymers have been recently studied on the air–water interface and on a solid substrate [262]. These amphiphilic star polymers with different numbers of hydrophobic arms differed not only by their architecture (four and three arm molecules, PEO-b-PS_3 and PEO-b-PS_2) but also by the molecular weight of PS chains (10,000 up to 24,000). AFM revealed well-developed circular domain morphology composed of PS arms for LB monolayers at low surface pressure (Fig. 46). At higher surface pressure, the packing of circular domains became denser, but no clear transition to cylindrical structures was observed in condensed

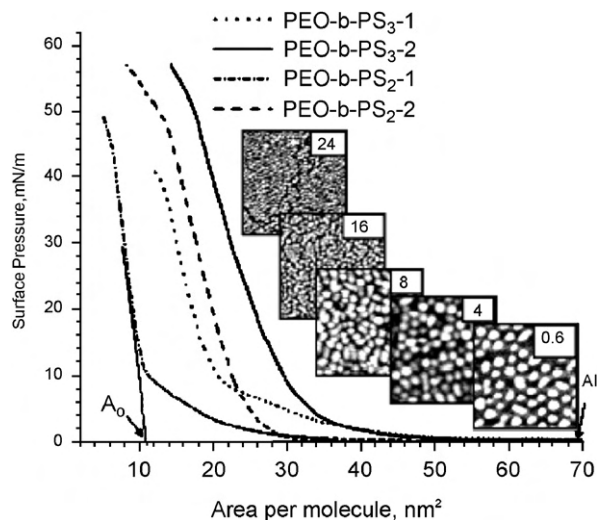


Fig. 46. Langmuir isotherms for monolayers of amphiphilic heteroarm PEO–PS star-block copolymers and corresponding AFM images of surface morphologies at different surface pressures [263]. Reprinted from Peleshanko et al. by permission of the American Chemical Society.

monolayers as usually happens for linear block copolymers of similar composition [263]. The authors suggested that star architecture favors the formation of highly curved interfaces and circular domains.

The role of functional terminal groups for $(\text{X-PS})_2\text{-(PEO-Y)}_2$ heteroarm star copolymers with respect to their interfacial behavior and surface morphology has been recently addressed [264]. A series of star copolymers with different combinations of bromine, amine, TBDPS, hydroxyl, and carboxylic terminal groups was considered in this investigation (Fig. 47). A surface isotherm showed significant changes in the shape for different terminal groups, indicating reorganization of the surface behavior after terminal group substitution (Fig. 47). The study concluded that hydrophilic functional groups attached to hydrophobic chains and hydrophobic functional groups attached to hydrophilic chains result in the stabilization of the spherical domain morphology, rather than the cylindrical morphology predicted for the given chemical composition of star copolymers.

The replacement of functional groups of hydrophobic polymer chains was found to be even more effective in promoting stable and very fine circular domain morphology. In addition, the author demonstrated that for $(\text{NH}_2\text{-PS})_2\text{-(PEO-COOH)}_2$ star copolymer, the ionization of carboxylic terminal groups at higher pH led to greater solubility of

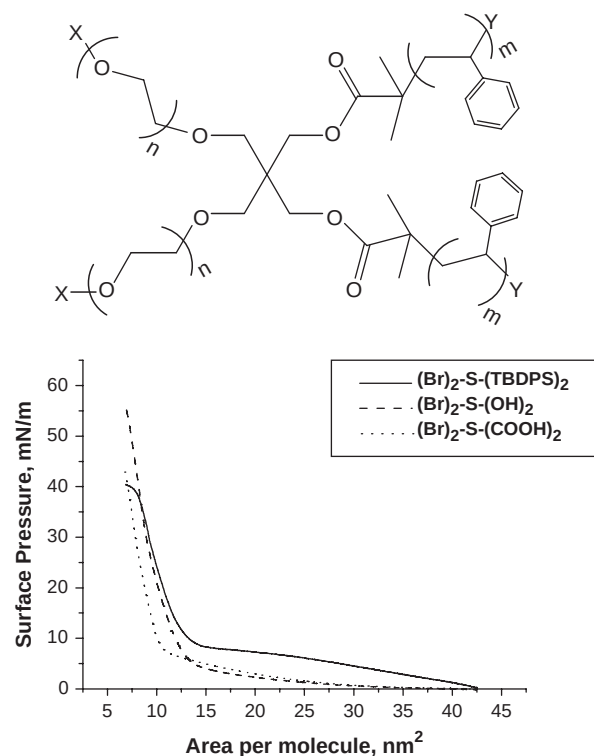


Fig. 47. Chemical structure of 4-arm $(X-PEO)_2-(PS-Y)_2$ heteroarm star copolymers (left) and Langmuir isotherms of $(Br)_2$ -Star- $(Y)_2$ Y is TBDPS, OH or COOH [264]. Reprinted from Gunawidjaja et al. by permission of the American Chemical Society.

PEO chains in the water subphase. This phenomenon along with the deionization of amine terminal group prevents the lateral aggregation of PS domains, further promoting the formation of nanoscale circular morphology.

A combination of hydrophobic and hydrophilic PS-PAA blocks is another popular choice in many recent studies. The synthesis of well-defined branched PS_nPtBA_{2n} copolymers (a PS core with 2, 4, 6, or 8 arms and a corona of PtBA with 4, 8, 12, or 16 arms) has been presented recently [265]. PS_nPAA_{2n} amphiphilic molecules subsequently generated from these molecules by the hydrolysis of the *tert*-Bu ester groups showed stable Langmuir films with surface morphology significantly changing with increasing surface pressure. In another study, it has been demonstrated that high resolution AFM can be exploited as an independent and powerful tool for the characterization of molecular parameters, a non-trivial task for branched molecules [266]. These studies enabled quantitative analysis of the molecular length distribution, molecular lengths, and side chain distribution for some multi-armed brushes with high molecular weight.

A new amphiphilic heteroarm star polymer containing 12 alternating hydrophobic and 12 hydrophilic arms of PS and PAA connected to a well-defined rigid aromatic core was investigated at the air–water and the air–solid interfaces in a recent

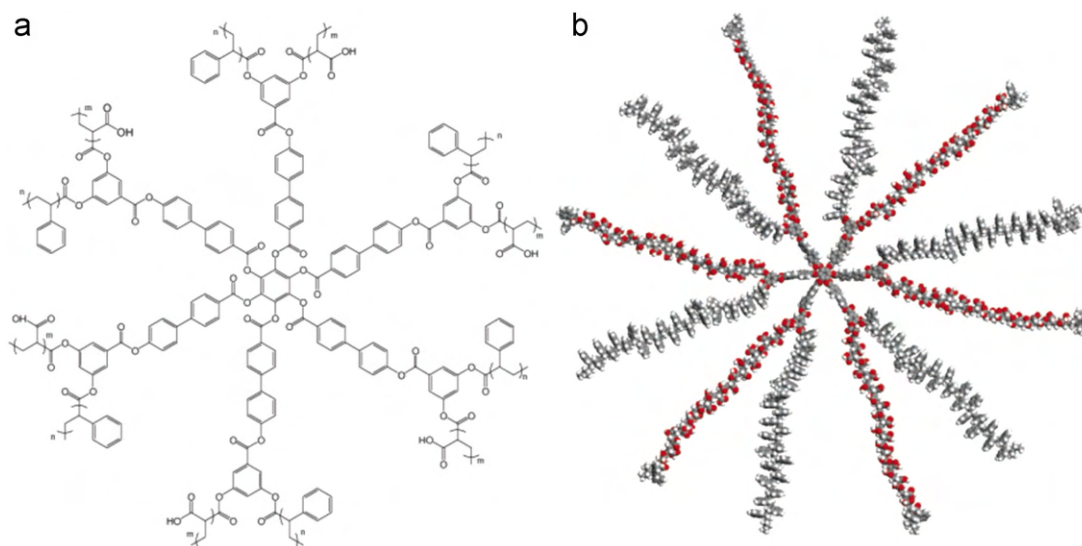


Fig. 48. (a) Chemical formula of $(PAA_m)_6-s-(PS_n)_6$ and (b) molecular model of $(PAA_{25})_6-s-(PS_{25})_6$ [267]. Reprinted from Genson et al. by permission of the American Chemical Society.

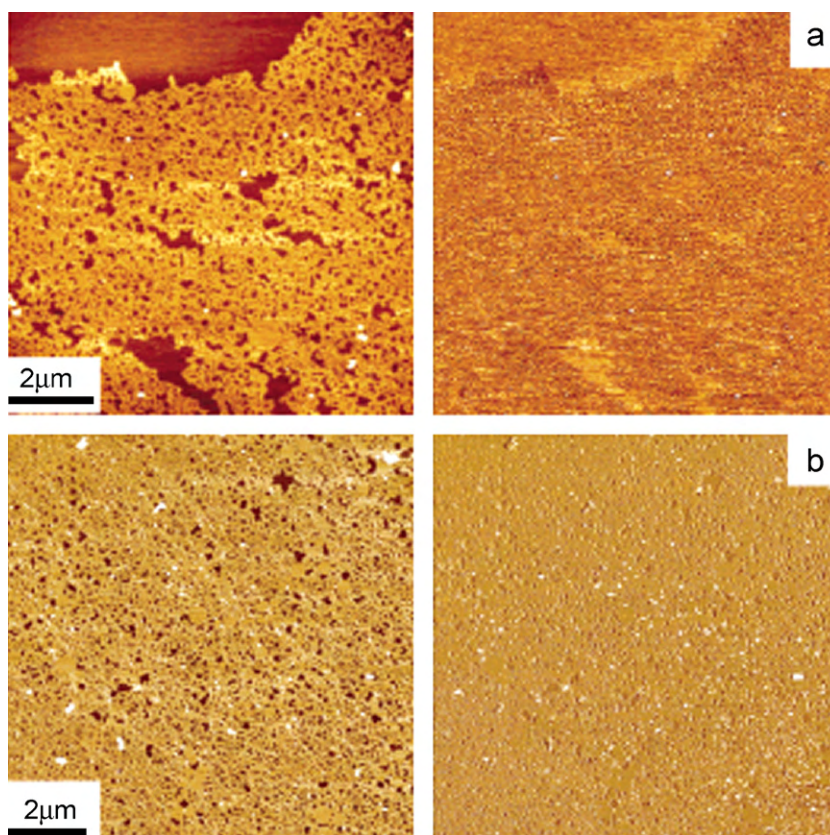


Fig. 49. AFM images (topography, left and phase, right) of two-dimensional micellar domains of $(\text{PAA}_{30})_6\text{-}s\text{-(PS}_{40})_6$ formed at (a) moderate surface pressure (10 mN/m) and (b) high surface pressure (30 mN/m) [267]. Reprinted from Genson et al. by permission of the American Chemical Society.

study (Fig. 48) [267]. The authors reported that at the air–water interface, the molecules spontaneously formed pancake-like micellar aggregates, which measure up to several microns in diameter and 5 nm in thickness. Upon the reduction of the surface area per molecule to 7 nm^2 , the two-dimensional micelles merged into a dense and uniform monolayer (Fig. 49). The authors suggested that the confined phase separation of dissimilar polymer arms occurred upon their segregation on the opposite sides of the rigid disk-like aromatic core, forcing the rigid cores to adopt a face-on orientation onto the interface with dissimilar arms placed on opposite sides.

Upon transfer of these molecules onto the solid support (hydrophilic silicon oxide), the PS chains localized at the air–film interface make it completely hydrophobic. In contrast, the PAA chains collapsed beneath the PS-dominated topmost layer and formed a thin flattened underlayer at the film–silicon oxide interface. This study points toward new

strategies to create large 2D microstructures with “two-face” amphiphilicity and suggests a profound influence of branched, star architecture on the assembly of these complex amphiphiles.

Hammond et al. presented a very different type of branched block copolymers, namely a series of PEO-PAMAM linear-dendritic diblock copolymers with various terminal functionalities [268]. These hybrid, amphiphilic, stearate-terminated diblocks were found to give stable Langmuir monolayers with the surface molecular area in the condensed state controlled by the architecture of molecules and their chemical composition. LB films of these diblocks transferred onto hydrophobically functionalized surfaces at the high surface pressure displayed continuous topography with few holes and a relatively smooth surface. Another recent example of highly branched hybrid molecules with a hydrophobic, helical polypeptide comb block and a hydrophilic polyester dendron block modified with PEG was presented by the same group as

prospective candidates for high-load drug vehicles [269]. The authors demonstrated that a cone-shaped structure of the tree-like molecules was responsible for the formation of spherical micelles at a very low solution concentration. These micelles were robust enough to preserve virtually spherical morphology after adsorption onto a solid substrate and complete drying.

An amphiphilic polymer composed of a hydrophobic divinylbenzene–styrene microgel core, PMMA branches, and some pendent vinyl groups attached to the core has been presented in recent study [270]. The surface morphology of LB monolayers and multilayers studied by SEM showed that these polymers spread on the water surface, forming surface aggregates, which become finer with the increase in the hydrophilic content. The authors demonstrated that LB multilayers can be polymerized further to form a robust, crosslinked structure. Janus micelles from asymmetric star block copolymers with the crosslinked PB block of PS-*b*-PB-*b*-PMMA triblock copolymers were demonstrated to form stable monolayers on a water surface [271]. It is worth noting another study of Langmuir monolayers fabricated from oxazoline-functionalized PMMA microgels and hyperbranched PVE and PS that showed nanoscale polymer hyperbranched particulates with long-range ordered packing [272].

4.6. Hybrid nanostructures with highly branched shell

Despite the fact that the vast majority of nanoparticles have been modified or stabilized by low molar weight organic molecules, linear homopolymer, or diblock copolymers, highly branched polymers found their way to nanoparticles modification due to their ability to form spherical or

cylindrical “containers”. These structures can be used for the reduction processes to form spherical or more complex metal or semiconducting nanoparticles and, especially, quantum dots. Novel methods of preparation of inorganic nanoparticles embedded/grown into dendritic cores and shelled by highly branched molecules have been described in several comprehensive recent reviews [273–276]. Here we will present only several very recent and most significant examples, which were not included in aforementioned reviews.

Highly branched molecules have been used as templates in the synthesis of various inorganic nanoparticles. For example, branched polyglycerols were found useful in the synthesis of gold [277] and palladium nanoparticles [278,279]. PAMAM hyperbranched polymers have been exploited for gold nanoparticle synthesis [280]. Similarly, amphiphilic hyperbranched PEI amide [281] and acrylate [282] copolymers have been used for silver nanoparticle growth. Other types of hyperbranched polymers have also been found to be very efficient in the stabilization of nanoparticles in solution. E.g., the PPV-based hyperbranched conjugated polymer [283] has been applied to gold nanoparticle growth. Hyperbranched poly(amine-ester)s [284] helped to reduce the gold and silver nanoparticles, and hyperbranched aramids [285] have been used for the formation of palladium nanoclusters.

In an interesting approach, the focus was on combining gold nanoparticle growth within a core region of star copolymer with grafting of thiol-functionalized arms [286]. This synthetic routine led to hairy nanoparticles with mixed hydrophilic and hydrophobic arms such as one presented in Fig. 50. Uniform gold nanoparticles with the average diameter of 3.7 nm have been grown by using this approach. Such hybrid nanoparticles might be

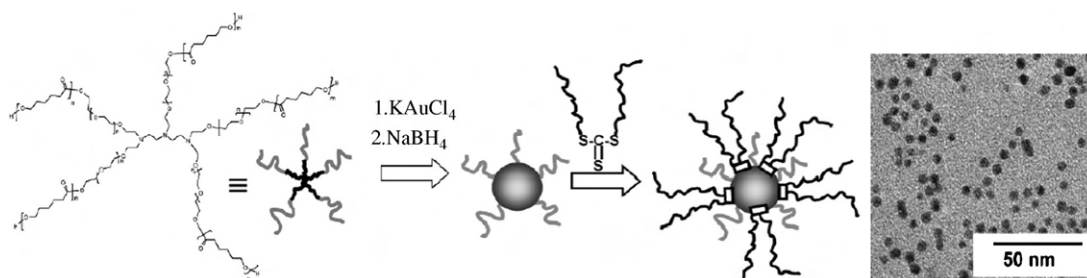


Fig. 50. Chemisorption of PAA-*s*-CS-*s*-PAA chains onto Au nanoparticle to form five-arm PEG-*b*-PCL star (left) followed by the formation of uniform hybrid nanoparticles with mixed shells (right) [286]. Reprinted from Fustin et al. by permission of the American Chemical Society.

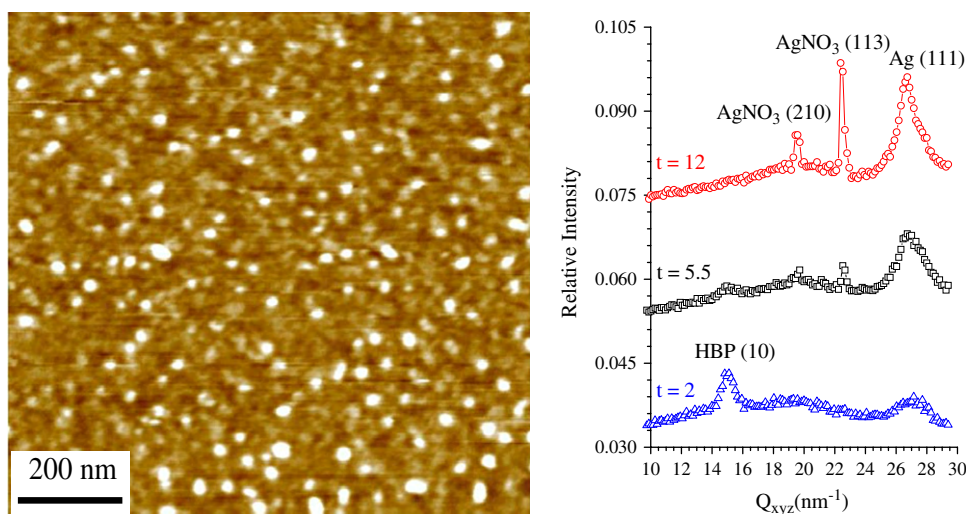


Fig. 51. Surface morphology of LB monolayer from hyperbranched molecules with silver nanoparticles (left). X-ray scattering of Langmuir monolayer on a 5 mM AgNO_3 subphase in the course of silver reduction (different times after the monolayer compression, hrs) [287]. Reprinted from Rybak et al. by permission of the American Chemical Society.

promising as stimuli responsive nanomaterials with their aggregation behavior tuned by environmental conditions.

In a recent study, nanofibrillar micellar structures formed by amphiphilic hyperbranched molecules within a Langmuir monolayer were utilized as a template for silver nanoparticle formation from the ion-containing water subphase [287]. The authors observed that uniform silver nanoparticles were formed from the subphase within the nanofibrillar surface structures of the multifunctional amphiphilic hyperbranched molecules at the water surface. The diameter of these nanoparticles varied from 2 to 4 nm (with standard deviation within 20–30%), and was controlled by the core dimensions and the interfibrillar free surface area as revealed by AFM and TEM imaging (Fig. 51). Furthermore, upon addition of potassium nitrate to the subphase, the nanoparticle formation was observed along the nanofibrillar structures rather than in a random manner.

The real-time silver formation process beneath the Langmuir monolayer has been monitored with in-situ synchrotron X-ray reflectivity, revealing gradual formation of silver crystal lattice with very limited dimensions (Fig. 51). The suggested mechanism of nanoparticle formation involves the oxidation of primary amino groups by silver catalysis facilitated by “caging” of silver ions within surface areas dominated by multibranched cores. This system provides an example of a one-step

process in which hyperbranched molecules with outer alkyl tails and compressed amine-hydroxyl cores mediated the formation of stable nanoparticles placed along/among/beneath the nanofibrillar micelles.

An interesting example of the formation of helical one-dimensional assemblies from inorganic nanoparticles by using assembled dendritic molecules has been demonstrated by Stupp et al. [288,289]. In this report dendron-rodcoil (DRC) macromolecules, which formed supramolecular ribbons, were successfully applied as ordered organic templates for the formation of single and double helices of cadmium sulfide (Fig. 52). These peculiar inorganic structures are considered for prospective applications as optical and electronic materials.

Even though the star polymers' utilization is more complicated and less straightforward than compared to hyperbranched polymers due to complexity of their microstructures, they have been successfully employed in the synthesis of gold [290,291], silver [292] and platinum [293] nanoparticles. The most recent results showed that by using star polymers, the surface properties of the hybrid gold nanoparticles could be altered from hydrophobic to hydrophilic by varying hydrophilic branched ligands [291]. Direct grafting of branched molecules onto nanoparticles resulted in interesting hairy structures with stimuli responsive properties (Fig. 53) [294]. Due to the segregation within binary shell, hybrid gold nanoparticles functionalized with amphiphilic

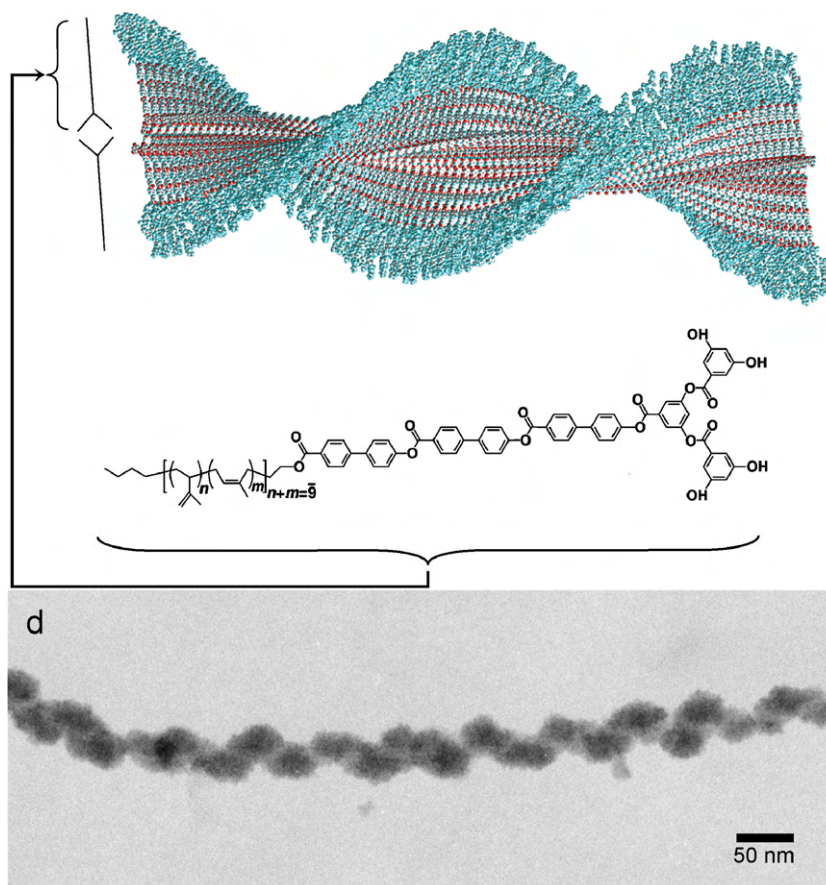


Fig. 52. Top: Chemical structure of the DRC molecules and a molecular model of an assembled twisted ribbon. Bottom: CdS single helix formed on the organic template [289]. Reprinted from Sone et al. by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

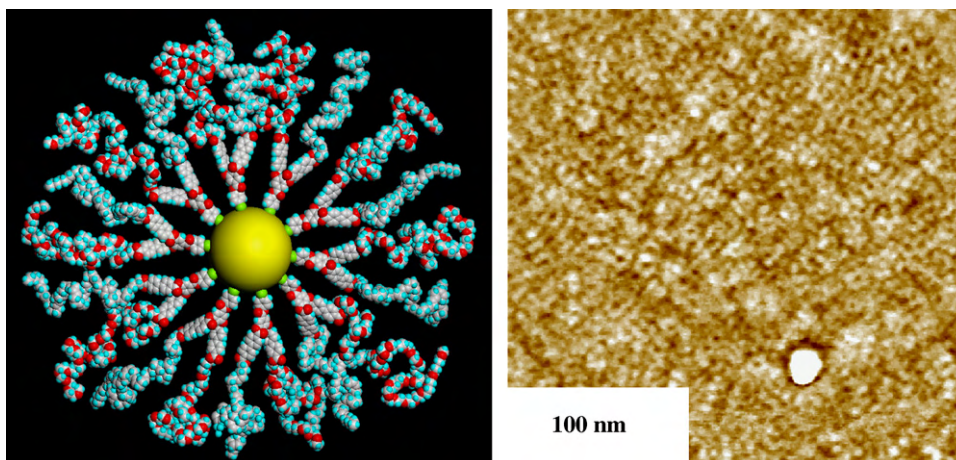


Fig. 53. Molecular model of gold nanoparticle with amphiphilic binary shell from V-shaped polymeric arms (left) and AFM phase image for the LB monolayer with ring-like structures (right) [294]. Reprinted from Genson et al. by permission of the American Chemical Society.

PB–PEG V-shaped arms formed stable monolayers at the air–water and the air–solid interfaces.

Similarly, the binary arms can be segregated into a dense polymer corona which surrounded the gold nanoparticles, preventing their large-scale agglomeration and keeping individual nanoparticles well-separated from each other and forming pancake micelles at the surface. AFM and TEM revealed the presence of 2 nm gold cores surrounded by the polymer shell with the diameter 11 nm (Fig. 53). The authors suggested that the amphiphilic, mixed shell drives the spontaneous organization of these hybrid nanoparticles into discrete 2D pancake-like structures with a high density of gold-polymer clusters.

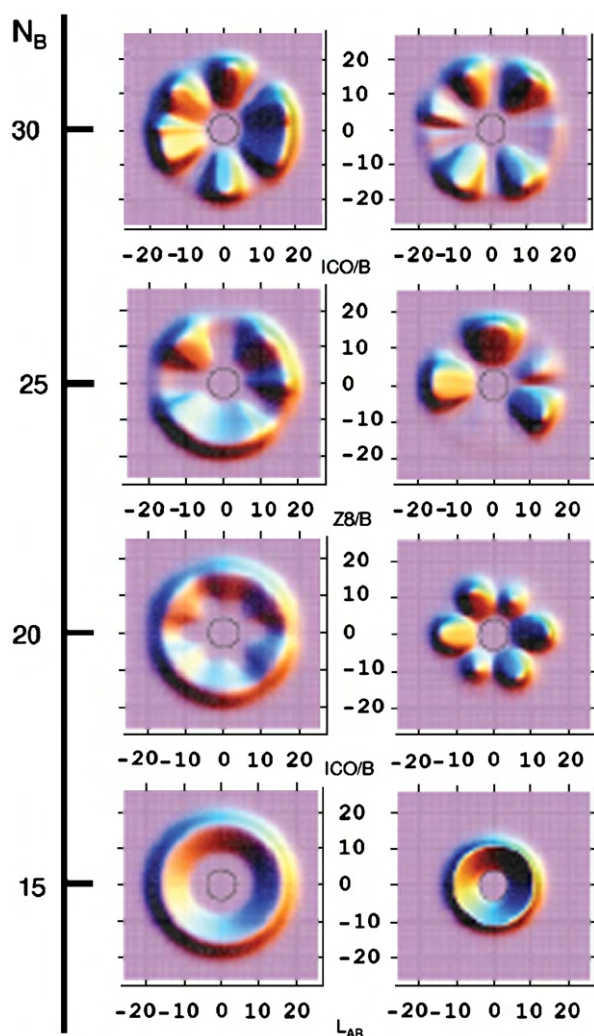


Fig. 54. Simulated patterns of nanophase separation in mixed brush shell of a single nanoparticle as controlled by chain length differences [295]. Reprinted from Roan et al. by permission of the American Physical Society.

An intriguing possibility for the formation of multifunctional complex nanoparticles templated via nanophase separation on mixed brushes has been recently suggested [295]. This approach could be applied for branched molecules such as Y-shaped brushes, as has been already discussed for planar surfaces [296]. Computer simulations of end-grafted, immiscible molecules showed that soft nanopolyhedra with localized structures similar to those found in small clusters of colloidal microspheres can be formed under appropriate grafting conditions such as composition, chain lengths, and grafting density (Fig. 54). This approach opens the way to nanoscale patterning of brush surfaces.

5. Conclusions

Summarizing the results presented in this review, we can conclude that, as was expected in the course of initial synthetic efforts, highly branched molecules show more complex surface behavior as compared with conventional linear and block copolymers due to their “multidimensional” architecture with complex core–shell composition, the different nature of multiple arms, and different terminal groups. Due to the dendritic nature of their backbones and general core–shell type of architecture, they demonstrate some interesting nuances in surface behavior that can be, in some cases, tracked to the contributions from their peculiar architecture.

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