Self-assembly of non-linear polymers at the air/water interface: the effect of molecular architecture

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In comparison with conventional linear polymers, due to the presence of joints, branches, end groups, etc, non-linear polymers possess more variables that allow for the tailoring of steric constraints, stacking interactions, and hydrogen bonding of these polymers at the air/water interface to precisely control the self-assembly process to yield functional Langmuir–Blodgett (LB) films for various applications. This Review summarizes recent developments in the field of self-assembly of non-linear polymers at the air/water interface, focusing on the influence of molecular architecture. Four classes of non-linear systems (polymer brushes, star-like polymers, dendritic polymers, and linear–dendritic polymers) with representative examples are highlighted to elaborate their interfacial behaviors originating from different molecular architectures.

Introduction

Due to the surface effect, polymer thin films and micro- or nanostructured patterns usually adopt different configurations or self-assembled states from those in bulk, resulting in unique surface structures and chemical compositions, and thus, intriguing properties, including friction, shearing, lubrication, abrasion, wetting, adhesion, adsorption, and indentation.\textsuperscript{1–5} In addition, hierarchical structures composed of polymers that exhibit controlled ordering at different length scales are highly desirable for many applications in optical, electronic, optoelectronic, and magnetic materials and devices.\textsuperscript{6} Self-assembly has been widely recognized as a most promising route to organizing...
pre-programmed building blocks into hierarchically ordered structures. In this context, a fundamental understanding of the supramolecular structure and dynamic self-assembly process at the surface is of great importance in designing and engineering new generation polymer films and patterns with novel functional properties. Recent research has witnessed rapid advances in polymer synthesis techniques that yield a myriad of polymers with unique molecular architectures and properties, and their self-assembly in bulk form are fairly well understood. In stark contrast, their self-assembly in ultrathin films and the resulting supramolecular organization at surfaces and interfaces are far less researched.

One of the most commonly used methods to scrutinize the supramolecular structure and dynamic self-assembly of polymers in ultrathin films or at an interface is the Langmuir–Blodgett (LB) technique, which renders the self-assembly of polymers at an air/water interface under well controlled conditions. The Langmuir–Blodgett (LB) method, named after Irving Langmuir and Katharine Blodgett, is perhaps the earliest approach to realize what is now called 'supramolecular assembly', providing the opportunities to exercise molecular level control over the structure of organic thin films. Various characterization techniques, including high-resolution X-ray diffraction, scanning probe microscopy, electron microscopy, and Brewster angle optical microscopy can be integrated with the LB trough and have proven to be effective at addressing many fundamental questions regarding the LB film. Several comprehensive books describing the state-of-the-art LB method are available, offering many aspects of the background science, from LB film deposition and characterization to their applications.

To date, a great diversity of molecules and polymers, primarily linear, have been investigated with the LB technique, and the resulting films have been widely used in the areas of microolithography, thin film devices, and biomimetic films. Among them, linear amphiphilic block copolymers (BCP) are the most well studied systems. Ever since the seminal work by Eisenberg and Lennox, the polymers of different linear BCPs, e.g., polystyrene-b-poly(ethylene oxide) (PS-b-PEO) and polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA), have been intensively investigated, and different models, including “pancake” and “brush” models, have been proposed to successfully illustrate the self-assembly process. Upon deposition of these polymers on the water surface, the unfavorable interfacial interaction between the hydrophobic block and water induces the aggregation of hydrophobic blocks, forming different morphologies to reduce the overall free energy of the system. On the other hand, the hydrophilic block tends to adsorb on the water surface or dissolve in the water subphase depending on the surface pressure, forming so-called surface micelles. During this process, the hydrophobic block acts as a buoy, anchoring the polymer chain at the air/water interface and preventing the hydrophilic blocks from dispersing into the water subphase. Under the applied surface pressure, the hydrophilic blocks are desorbed from the water surface and pushed into the water subphase, yielding the so-called “brush” structure (i.e., transitions from the “pancake” to the “brush”). During this transition, the surface area decreases dramatically while the surface pressure is maintained constant, resulting in a plateau region in the isotherm. The length of the plateau region is determined by several parameters, including the ratio of hydrophilic block to hydrophobic block and the chemical composition of the BCP. Consequently, three characteristic regions (i.e., liquid, plateau, and condensed regions) are yielded for amphiphilic linear BCPs.

For amphiphilic linear BCPs, the resulting monolayer (supramolecular organization) depends heavily on the characteristics of the blocks (e.g., amphiphility, solubility, molecular weight, block ratio, etc.) and processing conditions (e.g., solvent used, concentration of spreading solution, temperature, compression speed, etc.). Among these variables, the shape of the surfactant micelles of linear BCPs is found to depend mainly on the relative size of the two blocks. Circular micelles are usually formed at high hydrophilic block composition and rod-shaped micelles are preferentially formed when the proportion of the hydrophilic block is reduced, while a uniform structure of surface micelles is no longer observed if the hydrophilic block content is too low. Therefore, the structure and chemical composition of LB films can be readily tuned by designing the polymer chains and modifying the relative block ratio. These LB films, however, are still limited for use in the areas of surface modification and patterning where self-assembled structures with higher complexity and larger variety are needed.

In order to obtain surface morphologies other than dots and rods (or ribbons), a rational molecular design that allows for the manipulation of steric constraints, stacking interactions due to crystallization and π–π stacking, and hydrogen bonding is postulated to be critical to precisely control the self-assembly process. The variation in the shape of molecules, architecture of the polymer backbone and specific intermolecular interactions have been proven to be very effective in tailoring the air/water interfacial behavior of polymeric materials. Thus, polymers with more complex structures have been exploited to modify their self-assembly process and ultimately well controlled morphology. This activity has in turn stimulated the proper design of a large number of polymers with new structures and chemical compositions. To date, self-assembly of many non-linear polymers, including polymer brushes, star copolymers, and dendritic polymers, at the air/water interface have been studied, in which a broad range of morphologies, such as dots, worms, ribbons, and islands, were observed. For non-linear BCPs, the presence of joints, branches, and a low degree of entanglement significantly alters the physical properties compared to their linear counterparts, resulting in a totally different but more controllable self-assembly process. In addition to structural influences (both chemical composition and chemical structure), the functional end groups in non-linear BCPs play a much more important role in determining their self-assembly behaviors. Simple modification of the end group can dramatically affect the physical properties of polymers. As noted above, changing the hydrophobic/hydrophilic ratio is the most viable means of controlling the morphology. In contrast to linear BCPs, in which alteration of the ratio can only be realized by changing the percentage of hydrophobic and hydrophilic blocks, the branched structures in non-linear BCPs offer more variables to modify the ratio, including the architecture (e.g., the number of...
of arms in the star-like polymers, grafting density in polymer brushes) and functional end groups because of increased ends at the periphery of the chain, which in turn enable the self-assembly of much more complex yet well controlled structures.

Over the past decade, the self-assembly of non-linear polymers has received much attention due to increased synthesis capabilities. The influence of the molecular architecture and the existence of end groups on the self-assembly and supramolecular organization of non-linear BCPs has not yet been systematically outlined in the literature regardless of some models proposed for specific polymers.\(^6\)\(^8\)\(^7\) This Review seeks to summarize the recent developments in the field of self-assembly of non-linear polymers at the air/water interface, focusing primarily on the influence of molecular architecture. Four categories of non-linear systems, i.e., polymer brushes, star-like polymers, dendritic polymers, and linear--dendritic polymers are highlighted. Within each category, we make no attempt to thoroughly cover the literature but rather select a number of representative examples to elaborate the interfacial behavior of these intriguing polymers originating from their different molecular architectures.

**Polymer brushes**

One the most studied non-linear polymers at the air/water interface are graft polymers,\(^7\)\(^6\) also known as molecular brush or comb-like polymers. They are typically synthesized by attaching polymer chains along a flexible backbone with different grafting densities.\(^7\)\(^7\)\(^8\)\(^8\)\(^9\) Significant advances in synthesis techniques make it feasible to prepare novel brush-like polymers, including comb-like (identical type of side chains),\(^8\)\(^1\) centipede (two different types of side chains),\(^8\)\(^2\) and barbed wire (multiple types of side chains)\(^8\)\(^3\)-\(^8\)\(^4\) that are named based on the presence of side chains, possessing different kinds of architectures (e.g., tadpole,\(^8\)\(^5\) tablet-like,\(^8\)\(^6\) and bottle-shaped brushes\(^8\)\(^7\)) which are defined based on the shape of polymer as whole). Depending on the distribution of side chains along the backbone, polymer brushes are also classified as regular,\(^8\)\(^6\) random,\(^7\)\(^8\)\(^8\)\(^9\) and gradient brushes.\(^8\)\(^7\)

Because of the steric repulsion of densely grafted side chains, polymer brushes usually adopt a wormlike conformation in solution.\(^8\)\(^7\)\(^8\)\(^9\)\(^1\) When adsorbed on the surface (water or solid substrate), the interaction between the side chain and the surface changes the orientation of the side chain relative to the backbone and breaks the symmetry and the dimensionality of the system,\(^9\)\(^2\)\(^9\)\(^1\) thus allowing for more conformations that depend on the fraction of adsorbed side chains, \(\phi_a\) (Fig. 1).\(^7\)\(^3\) Two distinct conformations are usually observed, resulting from a competition between the energetically favorable interaction of side chains with the substrate and entropically unfavorable extension of adsorbed side chains. A brush with a high \(\phi_a\) adopts a rod-like conformation (Fig. 1a). Conversely, a brush with a relatively small \(\phi_a\) prefers a globular conformation favored by the aggregation of desorbed side chains (Fig. 1b).\(^8\)\(^7\)

As the free energy of these two conformations varies with respect to the contact area and the interaction strength, the brush was shown to undergo a phase transition at a certain surface pressure or at a certain spreading coefficient.\(^9\)\(^3\) Such a conformational transition was reported for cylindrical brushes of poly (n-butyl acrylate) (PnBA) due to lateral compression at the air/water interface.\(^7\)\(^5\)-\(^7\)\(^3\)\(^9\)\(^3\) A series of three PnBA brushes with different lengths and grafting densities of the side chains were investigated and clear morphological changes induced by the lateral compression were observed (Fig. 2a–c). As the surface pressure was increased, the polymer underwent a transition from a rod-like to a globular conformation with a coexistence range clearly present at medium pressure (Fig. 2b). This transition was fully reversible. In addition, the side chain length and grafting density, which determine \(\phi_a\), are key parameters governing this transition. The transition became less distinct as the length of side chain decreased and eventually vanished below a certain critical value. The denser brushes exhibited a rod-globule transition, while the loose brushes (i.e., with a low grafting density) retained their extended conformation under surface pressure. To confirm the model, cylindrical molecular brushes with a gradient grafting density along the backbone at the air/water interface were investigated, revealing a transition from rod-like to the so-called “tadpole” conformation: upon compression, the rod-
globule transition took place at the end where the brush was densely grafted, leaving behind a molecule with a globular “head” and an extended “tail” (Fig. 2d).

In addition to the rod–globule transition observed within the molecule, certain modifications of molecular architecture can also lead to more complicated self-assembly processes, forming various novel surface morphologies. Recently, the interfacial behavior of a novel bottlebrush block copolymer (BBCP; i.e., polystyrene–polylactide (PS–PLA)) with ultrahigh molecular weight was reported. Both PS and PLA chains are hydrophobic and densely grafted along the polymethacrylate backbone through the ester group. Because of steric crowding of the PLA and PS arms, the BBCP adopted a relatively rigid cylindrical morphology in solution. When placed on the water surface, the PS part of the BBCP aggregated, forming dot-like domains to reduce its surface energy (Fig. 3a). The presence of certain hydrophilic moiety (i.e., ester group) led to an attractive interaction between PLA and the water subphase in comparison with PS. As a result, PLA formed cylindrical arms surrounding the PS domain (Fig. 3a). Rather than undergoing a “pancake” to “brush” transition as commonly seen in amphiphilic BCPs, the pancake-like morphology of BBCP formed at low pressure transformed into an interdigitated, and eventually an island-like morphology at high pressure (Fig. 3b).

Recently, self-assembly of a newly synthesized, amphiphilic comb block copolymer (CBCP) at the air/water interface was systematically explored using the LB technique. The CBCP had an ultra high molecular weight with PS arms grafted along one block of the long hydrophilic backbone (Fig. 4a). The block with PS arms assumed a rigid rod shape due to the steric crowding between the arms, resulting in elongation of the backbone polymer in that block. After being placed on the water surface, ribbon-like structures were observed at zero surface pressure, and an increase in self-assembly time led to an increase in the ribbon length (Fig. 4c). It was found that two CBCP molecules aggregated head to head to yield a pair (i.e., red B blocks on the top and the bottom with blue C blocks in the middle). Then this polymeric pair assembled side by side with adjacent pairs to form a long ribbon (for example, ribbon 1 in Fig. 4b). The long hydrophilic B chains were adsorbed on the water surface around the chemically linked PS arms (i.e., C blocks), keeping the neighboring ribbons apart. Since the tip of ribbon was not shielded by B blocks, free molecules could diffuse to the tip site and self-assemble along the axis, resulting in the increase in ribbon length over time. The morphological evolution under surface pressure was explored. Upon compression, the “pancake” to “brush” transition occurred: hydrophilic B blocks partially submerged into the water subphase to form a brush-like structure, and consequently, the ribbons associated side by side. At extremely high surface pressure, the hydrophilic chains were completely submerged into water, and the PS chains aggregated to form an island-like morphology. By using a less volatile solvent, a state relatively closer to the final equilibrium state was achieved by providing CBCP molecules with a longer time to self assemble, yielding a cellular pattern (i.e., interconnected network structures; Fig. 4d) composed of ribbons of the same width and height as those shown in Fig. 4c. This phenomenon can be attributed to the dewetting of the thin film. During the solvent evaporation, the concentration of CBCP was greatly increased, leading to the aggregation of PS chains (i.e., C blocks) and thus the formation of ribbon-like structures to reduce the overall free energy of the system. Because the formation of a cellular pattern could eliminate the existence of ribbon tips, a position possessing high free energy, the ribbons tended to be connected, forming a continuous cellular pattern.

In addition to carbon-based polymers, the monolayer assembly of comb polymers containing fluorocarbon side chains...
have also been extensively investigated by several groups. These fluorinated polymers possess unique tribological behavior due to the low energy surface and negative surface potential. They also have excellent thermal stability and chemical resistance for practical use as lubricants at low temperature. Recently, Langmuir monolayer of comb polymers containing perfluoroalkyl)ethyl and (partialfluoroalkyl) side chains with various chain lengths have been explored by AFM, friction force microscopy (FFM), and out-of-plane and in-plane X-ray diffraction. For all the comb polymers studied, the fluorocarbon side chains were found to pack into ordered two dimensional lattice structures in the condensed state. As shown in Fig. 5, hexagonal, orthorhombic, and triclinic packing of fluorocarbon side chains were revealed by in-plane X-ray diffraction measurements. The characteristic friction behavior of the multilayer films composed of comb polymers prepared by the LB technique depended strongly on the chemical constituents of the outermost layer on the film surface.

Notably, various other fluorocarbon comb copolymers (e.g., binary copolymers and ternary comb copolymers) were also studied. The fine structure in the solid state and phase transition behavior of methacrylate comb copolymers with fluorocarbon and hydrocarbon side chains obtained from immiscible monomers of octadecyl methacrylate and 2-(perfluorodecyl)ethyl methacrylate (FF10EMA) at different ratios were reported. The results showed that fluorinated and hydrogenated side chain crystals of these comb copolymers were independently packed and formed hexagonal subcells in a two dimensional lattice. The phase transition independently occurred at different temperature regions between the fluorocarbon and hydrocarbon side chain crystals during the heating process, as measured by differential scanning calorimetry (DSC). AFM measurements showed that the size of hydrogenated domains in these phase-separated, methacrylate monolayer structures were at the submicron scale (i.e., island-like structures as illustrated in Fig. 6b), whereas corresponding acrylate copolymer monolayers formed a surface morphology on the 10–30 nm scale (i.e., island-like structures in Fig. 6a). This was caused by the hindrance of packing of fluorinated side chains due to the arrangement of the low mobility main chains. Recently, self-assembly of ternary comb polymers containing N-vinylcarbazole (NVCz) in the main chain obtained by copolymerizing hydrogenated and fluorinated long-chain vinyl compounds was also reported (Fig. 7). It was found that monolayers of these ternary copolymers on the water surface were highly condensed, and side chains and side-chain crystals cannot form phase-separated structures in two-dimensional films due to the enhancement of π–π interactions between the arranged carbazole rings. The side chains of the copolymer in the film were in a miscible state, and monolayers formed a homogeneous amorphous surface because of the cancellation of the difference in van der Waals forces between the two types of side chains (i.e., octadecyl acrylate and 2-(perfluorodecyl)ethyl acrylate).

Due to a large electric field associated with aligned helix dipoles, polymer brushes of α-helical synthetic polypeptides are of particular interest for use in colloid stabilization, actuation and sensing, nanotechnology, and biotechnology. Recently, a series of studies have focused on the brush BCP consisting of a hydrophobic block of hairy-rod poly(γ-methyl-l-glutamate-ran-γ-stearyl-l-glutamate) with stearyl substituents (PMLGSGL) and a hydrophilic block of rigid-rod poly(α,γ-glutamic acid) (PLGA) (Fig. 8). The monolayers of these diblock copolypeptides exhibited a brush structure composed of densely packed parallel α-helices that were tilted at an angle with respect to the water surface normal (Fig. 8). The helix orientation of such diblock copolypeptides was strongly affected by the chain length. The average tilt angle between the helices and the surface normal decreased upon compression due to an increase in chain density. The hydrophobic block length was found to significantly affect the maximum surface chain density and thus the helix orientation of the diblock copolypeptides. The helix tilt in the monolayer can be attributed most likely to the off-axis interactions of the unscreened peptide...
dipoles between parallel α-helices. The correlation of the helix tilt angle and the PMLGSLG block length arose from the change in the tilting potential as a function of the number of dipoles. The influence of the dipping position relative to the previous transfer position on the azimuthal helix orientation was also investigated. The dipping position can be manipulated, yielding an azimuthal alignment of α-helices in the transferred films parallel to or tilted by an angle of 45° with respect to the dipping direction. In addition, the effects of annealing on the structure and helix orientation in the monolayer were also explored. Upon annealing at 100 °C for 24 h, α-helices became less tilted toward the surface normal, and the surface area reduced, forming more compact and uniform films. Moreover, the annealing process facilitated the removal of the bound water, leading to significant interchain interactions between the carboxyl group of the PLGA segments. The melting of the side chain mantle into a liquid-like state of the PMLGSLG block during annealing, and then favored the helices to be further oriented toward the surface normal.

**Star-like polymers**

Star-like polymers are also an important class of non-linear polymers, in which several linear polymer chains (i.e., arms) are attached to one compact core. These chains can be chemically similar or different, thus producing heteroarm or miktoarm star-like polymers. Star-like polymers with compact, low-generation dendrimers as a core are usually called dendritic stars. The self-assembly of star-like polymers at the air/water interface was only studied rather recently due mainly to the difficulty in their synthesis with high structural uniformity.

Star-like BCP can behave like either a linear BCP or a unimolecular micelle (i.e., composed of single copolymer molecule), or somewhere in between, depending heavily on the number of arms and physical properties of the arms. With an increased number of arms, the molecules become more compact, resulting in less entanglement and more defined supramolecular organization. When absorbing on the surface, the unfavorable interaction with the surface leads to the formation of globular structures, while the favorable interaction usually allows the arm to spread, adopting an extended conformation.

One of the earliest studies on star-like polymers was reported in 1991. An amphiphilic star-shaped copolymer composed of a hydrophobic styrene–divinylbenzene (St–DVB) microgel core and hydrophilic poly(methacrylic acid) arms was investigated for the purpose of improving the thermal and mechanical stabilities of LB films which were rather poor when produced from linear BCPs. These amphiphilic macromolecules were spread on the water surface in aggregates, which finally dissolved in the water subphase with the increase of the hydrophilic components of the polymer. Due to limited availability of characterization techniques at that time, the comprehensive understanding of the self-assembly process was not possible.

Recently, the self-assembly of a series of amphiphilic three-arm star BCP with different molecular structure and chemical composition at the air/water interface has been explored. The interfacial behavior of a three-arm star amphiphilic BCP, PEOr-β-PS3 (inner PEO block and outer PS block), was investigated by performing AFM measurements on the monolayer deposited on mica. Spontaneous aggregation was observed after spreading the polymer solution on the water surface. Hexagonally packed spherical domains were seen at low compression pressures. It was then transformed into a rod-rich morphology at intermediate pressures, and clusters and collapse of the film occurred at high pressures. Later on, the surface morphology of the three-arm star BCP, (PS-or-β-PEO)3 (inner PS block and outer PEO block) containing the same inner PS core but with different lengths of PEO block at the air/water interface was examined. They possessed circular domains at low pressure. Longer PEO chains were found to lead to greater intermolecular separation, resulting in smaller circular domains. While for shorter PEO chains, closely packed, larger domains were yielded. The number of domains increased as surface pressure increased. Eventually, the domains were pushed close enough to undergo chaining in which both the domain area and aggregation number increased dramatically. Such micelle chaining occurred more readily in stars than in linear systems of similar chemical composition. The surface micelle chaining process was carefully explored. The circular domains were composed of aggregated PS blocks separated by PEO coronas (Fig. 9a and b). Upon compression, the PS cores were brought closer together. The PEO chains between the PS cores were thus forced to shift to the side, forming a higher local density. Eventually, the PS cores moved close enough to chain with one another, and the PEO chains were pushed to either side of elongated PS aggregation. Thus further chaining was more
likely to occur in the area of low PEO density, and the most probable location for additional aggregation was the position as illustrated in Fig. 9c.120

Subsequently, the influence of the chemical composition and the molecular architecture on the self-assembly of both conventional and dendritic-like star BCPs containing either a PS core and PEO corona or vice versa were systematically explored (Fig. 10).121 Three distinct regions in the isotherm were seen when the stars contained 20% or more PEO, which absorbed at the air/water interface, forming pancake-like structures. The length and the pressure of the pseudoplateau region increased with PEO content, indicating that the molecular arrangement can be controlled by varying the relative ratio of the two blocks. Additionally, the architecture as reflected through the placement of PEO in either the core or corona and the number of branches also greatly influenced the self-assembly process (Fig. 10).121 The PEO-core star BCPs were more compact while the PS-core star BCPs spread more. A larger number of branches in the core led to greater spreading for PEO but higher compactness for PS; and PEO chain length determined the surface film behavior more than the number of PEO branching.121

Another interesting molecular structure explored at the air/water interface is the so-called “Janus” structure, which contains two types of polymer chain grafted on each side of a core. Recently, a “Janus micelle”, an asymmetric star BCP, was crafted by cross-linking the spherical domains of the polybutadiene (PB) middle block of polystyrene-block-polybutadiene-block-poly (methyl methacrylate) triblock copolymers (inset in Fig. 11).122 The “Janus micelle” can be divided into a “northern” hemisphere composed of PS and a “southern” hemisphere composed of PMMA.122 The “Janus micelle” formed arrays of circular domains (Fig. 11). By contrast, the monolayer of the precursor triblock copolymer was mainly composed of significantly smaller elongated domains due to their much lower molecular weight. In the “Janus micelle”, PMMA chains spread out on the water surface, while the hydrophobic PS and PB chains dewetted from the water surface. As the number of Janus micelles forming a domain in the monolayer was similar to the number of Janus micelles associating in solution, it was concluded that association already occurring in the spreading solvent influenced the domains finally formed in the monolayer.122

It is worth noting that in addition to chemical composition and molecular architecture, the functional end group also exerted a profound influence on the self-assembly of star-like BCPs at the air/water interface. For example, the role of combined functional terminal groups in (X-PEO)2-(PS-Y)2 heteroarm star copolymers was investigated with respect to their interfacial behavior and surface morphology.66 Various terminal functional groups (i.e., X and Y), including bromine, amine, tert-butyldiphenylsilane (TBDPS), hydroxyl, and carboxylic groups, were combined and explored.66 The results showed that the opposite nature of polymer chains and their end groups (e.g., hydrophobic chains–hydrophilic ends or hydrophilic chains–hydrophobic ends) were crucial in the formation of a stable circular morphology, rather than a cylindrical morphology expected for the given chemical
composition of star BCPs. The hydrophobic terminal groups linked to hydrophilic PEO chains anchored them on the water surface, preventing neighboring micelles from merging. Meanwhile, adding hydrophilic amine terminal groups to the PS chains changed the aggregation behavior and also prevented the lateral aggregation of PS domains. Additionally, it was found to be more effective in producing a stable and very fine circular nanodomain morphology when the functional end groups of hydrophobic chains were modified.

It is noteworthy that the number of arms in the amphiphilic star-like BCPs discussed above was usually very limited and did not exceed more than six, thereby making their self-assembly at the air/water interface similar to that of linear BCPs (i.e., hydrophilic chains form a partially submerged pancake-like structure as the hydrophobic chains collapse into segregated globules). To reveal the effect of the crowding of arms attached to a single core on the interfacial behavior and surface morphology, a series of PEO$_n$PS$_n$ star BCPs with a large number of arms and different chemical compositions were studied. The LB monolayer morphology was found to be determined by the fraction of hydrophilic PEO. With an increase of PEO content, the morphology changed from cylindrical domains to circular domains, and finally to a bicontinuous network. At low PEO content, the shorter PEO chains limited contact between PEO arms of neighboring molecules, thereby allowing the PS chains to form continuous one-dimensional structures via lateral aggregation. As the PEO content increased, the cylindrical structure collapsed into densely packed circular micelles due to increased repulsion originating from neighboring PEO arms. With the highest PEO content, the star polymer formed a virtually uniform morphology with an underlying PEO layer covered with a PS phase, leading to a bicontinuous morphology. Besides the PEO content, the number of arms also had a crucial influence on the morphology of monolayers. By reducing the crowding of PS and PEO chains, for polymers with the highest PEO content, a novel dendritic superstructure (branched textures) was observed upon compression, which was caused by microphase segregation at the air/water interface and PEO crystallization due to reduced constraints from the lowered number of arms in the molecules.

Recently, the self-assembly of an amphiphilic heteroarm star polymer containing 12 alternating hydrophobic/hydrophilic arms of PS and poly(acrylic acid) (PAA) connected to a well-defined rigid aromatic core air/water interface was studied (Fig. 12). Under compression, confined phase separation of dissimilar polymer arms occurred upon their segregation on the opposite sides of the rigid disk-like aromatic core, with PAA phase dissolved in water and PS aggregating laterally in air, forcing the rigid cores to adopt a face-on orientation with respect to the interface. As a result, pancake-like micellar aggregates formed in the gas state and gradually merged into a dense monolayer as the surface pressure increased.

**Dendritic polymers**

Due to the promising properties stemming from functionalized polymer chains and nanoparticle-like compact molecular architecture, dendritic polymers have received considerable attention over the past decades. Two major classes of dendritic polymers are hyperbranched polymers and dendrimers. Dendrimers have regular, tree-like architectures, divergent from a single, point-like core with very regular branches radially extending from a single center. Because of their well-defined globular architecture, the dendrimers at the air/water interface have been extensively investigated. The “edge on” and “face on” models have been widely used to explain the self-assembly of a variety of dendrimers at the air/water interface. We refer the reader to several comprehensive reviews on dendrimers and their assemblies. Here we only focus on the hyperbranched polymers with tree-like architectures, which are quite similar to dendrimers but have a lower degree of branching and less regular architecture. The morphology and overall shape of hyperbranched polymers as well as their interfacial behavior can also be altered by modifying the internal chemical architecture, the nature and distribution of terminal groups, and the strength of the polymer/surface interaction. Compared to dendrimers, despite the similarity in architecture, hyperbranched polymers show a very different self-assembly process, which is due to their much higher molecular weight and less defined architectures.

Recently, several second-generation hyperbranched polyesters with a variable composition of alkyl-terminated groups have been synthesized (Fig. 13). Chemical modification of the hyperbranched cores by substituting a controlled fraction of the terminal hydroxyl groups with hydrophobic alkyl chains was found to be an effective method to control amphiphilic balance of hyperbranched cores, and thus their self-assembly at the air/water interface. Microstructural analysis showed that the organized monolayers formed at the air/water interface only
when the number of alkyl tails was higher than two per core. In this case, the alkyl tails of hyperbranched molecules at high surface pressure formed intramonomer ordering of the quasi-hexagonal type, which was similar to regular dendrimers (Fig. 14). Due to irregular branching and random attachments of the terminal alkyl tails in the hyperbranched molecules, the alkyl tails became arranged in an up-right orientation at high pressure, instead of crystallizing with regular lateral ordering usually observed for modified dendrimers (Fig. 14).

Because of their compact structure (i.e., smaller hydrodynamic volume and radius of gyration) and high concentration of functional terminal groups, dendritic polymers usually have much less interchain entanglement as compared with linear polymer counterparts; this promotes the formation of “unimicelle” (i.e., surface micelles composed of only a single molecule). Recently, the interfacial behavior of dendritic PS–PEO copolymers was researched (Fig. 15). Such a dendritic copolymer formed a “unimicelle” that possessed a large hydrophobic PS core surrounded by a thin hydrophilic PEO corona. The dendritic PS–PEO unimolecular micelles displayed properties comparable to sterically stabilized colloids (Fig. 16a). Their self-assembly was governed by a competition between van der Waals attractive forces between adjacent PS cores and the repulsive steric interaction between the coronas due to the elastic deformation of PEO chains. The interaction of dendritic copolymers can also be modified by varying the branching functionality (i.e., generation) and composition, as well as by adjusting the length of the chains in the core, to control the structural rigidity of the molecule.

For low PS chain branching samples, the film topology was greatly influenced by composition for copolymers incorporating a relatively low number of long, flexible PS segments. With an increase of the PEO content from 15% (Fig. 16b) to 31% (Fig. 16c), the topology evolved from large circular island-like domains to ribbon-like superstructures. For low PEO content samples, van der Waals interactions between the PS cores were more significant, leading to the coalescence of molecules into large island-like clusters (Fig. 16b). With an increase of the PEO content, repulsive forces became dominant to prevent coalescence, the islands gradually collapsed into ribbons (Fig. 16c). The branching of PS core also governed the polymer association. Highly branched samples were more rigid and the deformability of the PEO chains in hyperbranched samples was lower than that in low branched samples, leading to a lower degree of association. Consequently, the hyperbranched molecules remained isolated or formed low-order aggregates with the decrease of the PEO content (Fig. 16d). When aggregated, individual molecules due to their very stiff structure are clearly visible and are mainly arranged into a regular, hexagonally packed array.

Later on, the influence of surface pressure and subphase temperature on the association of these copolymers was...
investigated. Under surface pressure, the isolated molecules can associate into short ribbon-like structures through the side-by-side assembly. As shown in Fig. 17, the molecules in the gas state formed a "unicelle" consisting of a PS-rich rigid core surrounded by adsorbed flexible PEO chains. During compression, the increased van der Waals attractive forces between the PS cores became larger than the elastic deformation forces of the flexible PEO chains, resulting in the association of molecules. In the meantime, sideways displacement of the PEO chains led to an increased lateral PEO chain density, rendering the exclusive formation of ribbons with a width and thickness comparable to the size of the individual molecules. When the subphase temperature increased from 12 °C to 27 °C, the same effect was also observed even in the absence of compression. The temperature-induced association was attributed to increased van der Waals attractive forces between the PS cores relative to the steric repulsive forces between PEO chains in the coronas, which was induced by decreased solvent quality of PEO segments at higher temperature.

It is well known that only dendrimers with peculiar symmetry architecture can form self-assembled, one-dimensional supramolecular structures, such as rods, fibers, ribbons, and helices. Recently, one-dimensional supramolecular structures were shown, for the first time, to be assembled from irregular, highly branched polymer. The molecule used was a hyperbranched polyester modified with terminal alky and amino groups (Fig. 18). The isolated individual nanofiber was achieved at low surface pressure (Fig. 19a). With an increase in surface pressure, individual nanofibers became more uniform and well-defined. In the condensed state, they formed densely packed bundles weaving across large surface areas with overall lengths exceeding several micrometres (Fig. 19c,d). The molecules possessed a hemispherical conformation in which the hydrophilic cores were compressed against the solid surface. The dense lateral stacking caused by directional crystallization of alkyl tails was proposed as a means of assembling these branched molecules in one-dimensional continuous rows resembling hemicylindrical micelles.

Recently, the surface morphology of novel hyperbranched amphiphilic (PEO–PS)$_n$ copolymers obtained by controlled radical polymerization was reported. The molecular structures of brush-like and hyperbranched polymers are shown in Fig. 20a. In stark contrast to conventional linear and star PEO–PS BCPs, dissimilar segments of these hyperbranched polymers were not clearly separated into/out of water/air but rather formed a mixed uniform phase at the surface (Fig. 20b). The random chemical architecture of relatively short hydrophilic and hydrophilic cores were compressed against the solid surface. The dense lateral stacking caused by directional crystallization of alkyl tails was proposed as a means of assembling these branched molecules in one-dimensional continuous rows resembling hemicylindrical micelles.

![Fig. 17](image1.png)  
**Fig. 17** Influence of pressure on the self-assembly of high PEO content, low branching functionality copolymers at (a) low pressure and (b) high pressure; Scanning size = 1.5 x 1.5 µm$^2$. (c) Top view of the reversible association model proposed for the reversible formation of ribbon-like superstructures. Reprinted with permission from ref. 68, (2008 American Chemical Society).

![Fig. 18](image2.png)  
**Fig. 18** Chemical structure of amphiphilic hyperbranched polyester. Reprinted with permission from ref. 63, (2004 Wiley).

![Fig. 19](image3.png)  
**Fig. 19** AFM phase images of nanofibrillar structures formed from low pressure to extremely high pressure, $\pi$. (a) $\pi = 0.2$ mN m$^{-1}$, (b) $\pi = 5$ mN m$^{-1}$, and (c, d) $\pi = 30$ mN m$^{-1}$. Reprinted with permission from ref. 63, (2004 Wiley).
fragments was believed to be responsible for such mixed interfacial structure.

**Linear–dendritic polymers**

As noted previously, dendritic polymers are monodisperse, tree-like macromolecules with a regular and highly branched architecture consisting of a dendritic core and peripheral sites. This peculiar structural feature opens many opportunities for their use in drug delivery (serving as host for foreign molecules), interfacial liquid membranes for stabilizing aqueous–organic emulsions, catalysis and reaction sites, etc. However, such compact structure often leads to little or no entanglements, thus limiting certain applications where highly robust and cohesive films are needed. One way to overcome this problem is to capitalize on a dendrimeric polymer containing a linear block or segment (Fig. 21). The linear block increases entanglements, thus enhancing the mechanical integrity, whereas the self-assembly nature of BCPs can be exploited to assist the assembly of organized films. Most importantly, the unique properties of dendritic polymers can be easily retained in linear–dendritic polymers. Because of such a novel hybrid structure, intriguing interfacial behavior may be expected when self-assembled at the air/water interface. Compared with the non-linear polymers discussed above, linear–dendritic polymers cover a wider range of materials, but have received far less attention to date.

Due to the compact structure, the dendritic components usually assume a rigid rod-like morphology, thereby forming a rod (semi-rod)–coil structure when a flexible linear chain is attached to the dendritic block. Recently, the self-assembly of PEO-dendronized polymethacrylate (PDMA) linear–dendritic polymer (PEO–PDMA) was studied (Fig. 22). PDMA assumed a coil–semi-rod molecular morphology. The interfacial behavior of this macromolecule was very unique although the isotherm was typical of an amphiphilic polymer with three distinct regions. Wormlike surface micelles were first observed after an increase in surface pressure (Fig. 23A). These micelles were rather flexible and can be extended to accommodate the reduced surface area under compression. As a result, when further compressed, the micelles were orderly packed, and their long axis was nearly perpendicular to the compression direction (Fig. 23B). During this process, the short PEO chains were immersed into the water subphase, and in the meantime the PDMA blocks became close enough to assemble into the core of the surface micelles. As the compression progressed, two typical morphologies were observed in the plateau region of the isotherm: the cylindrical micelles became bent and broken (Fig. 23C) and later twisted and even interwound into bundles (Fig. 23D) with further increase in surface pressure. The micelles can be twisted with both right- and left-handed sense (Fig. 23D*). It was proposed that micelles packed in a parallel fashion were forced to rotate along their long axis with the increased compression, and the friction between the neighboring micelles may cause such a micelle twisting. The surface morphology of the LB film after collapse was also investigated. Two types of characteristic 3D aggregates, springlike (Fig. 23E and E*) and disklike (Fig. 23F) were obtained. These morphologies were believed to originate from the rolled packing of the micelles, i.e., compression at the final stage can squash the “springs” to give away the space therein, and the micelles then collapsed and even joined together to form “disks”.

![Fig. 20](image1.png)

**Fig. 20** (a) Chemical structure of two kinds of hyperbranched polymers. (b) Two possible scenarios of state of the macromolecules at the air/water interface in comparison with linear block copolymer (center). Left: separated hydrophobic and hydrophilic segments. Right: mixed hydrophobic and hydrophilic segments confined to the water surface. Terminal chains added to reflect the presence of terminal alkyl ends. Reprinted with permission from ref.141, (2006 American Chemical Society).

![Fig. 21](image2.png)

**Fig. 21** Molecular structure of a linear–dendritic polymer.

![Fig. 22](image3.png)

**Fig. 22** Chemical structure of PEO–PDMA linear–dendritic block polymer. Reprinted with permission from ref. 73, (2006 American Chemical Society).
Recently, a new kind of dendron–coil molecule with various dendron structures and chemical functionalities was reported (Fig. 24a).144,145 The molecule has a linear hydrophilic PEO block and a dendritic hydrophobic polyamidoamine (PAMAM) block. The dendrimer generations can be modified from one to four, and the end group can be functionalized with a variety of groups. Among these end groups, stearate terminated linear–dendritic diblocks were found to be highly amphiphilic, and produced the most stable monolayer at the air/water interface. Additionally, dendrimer generation was found to be another key factor determining the self-assembly process. Surface micelle formation did not occur for generations 2 and higher, indicating a totally different self-assembly process from linear block copolymers.144,145

Using specular neutron reflectivity, the structure of the monolayers formed from linear–dendritic diblock copolymers with third or fourth generation dendrons was measured. For the third generation case (Fig. 24b), at low surface pressure, stearate groups existed primarily on the top of the monolayer, minimizing the interfacial energy at the air/water interface. They spread as much as possible across the water phase to lower interfacial tension, leading to a thinner monolayer with PEO being situated on the subphase.144,145 Under extremely high pressure, the monolayer was at its most compressed state (Fig. 24c). The stearate groups can form a well-ordered phase oriented perpendicular to the interface, yielding a thicker monolayer.144,145 Different from the third generation, where the stearate layer was composed of stearate groups and located above the PAMAM layer, the stearate layer, for the fourth generation case (Fig. 25), was a mixture of stearate and PAMAM (Fig. 24d), whose composition varied with the surface concentration. The intermixing of stearate groups and PAMAM occurred since the outer edge of the fourth generation dendrimer had significant curvature.144,145 Thus the ordering of the stearate groups on the dendrimer can be controlled by tuning the dendrimer generation and surface pressure.

In comparison to the dendron–coil structure, dendron–rod structure has been less researched. It is not surprising that more novel self-assembly behaviors may be observed due to the rigid structure of dendron–rod polymers. Recently, amphiphilic dendron–rod molecules with three hydrophilic PEO branches...
attached to a hydrophobic octa-p-phenylene rod stem at interfaces was investigated (Fig. 26a). Two kinds of amphiphilic molecules, one terminated with methyl (molecule A) and one with hydroxyl group (molecule B), were used in the study. The terminal groups determined the self-assembly process although both molecules had nearly identical architecture (i.e., a rod-like hydrophobic fragment with highly branched hydrophilic side chains). For molecule A, ring-shaped surface nanostructures were found to randomly pack within the topmost surface of the outer layer, and ribbon-like surface structure can be formed from these molecules under extremely high lateral compression. In the ring-shaped structure, the rod-like fragments were placed in the interior due to steric interactions, and the bulkier hydrophilic branches constituted the outer edge of the ring. Such structures can be stabilized by strong hydrophobic interactions between polyphenylene chains (right in Fig. 26b). Under further compression, the bulkier hydrophilic branches were displaced from the interface and submerged while rod-like fragments interdigitated to compensate for remaining cross-sectional mismatch, thereby yielding ribbon-like structures (left in Fig. 26b). The presence of hydrophobic terminal groups in hydrophilic PEO branches was considered to be a critical factor in the formation of these surface structures as it stabilized the formation of organized surface structures. Replacement of the hydrophobic terminal groups in molecule A with hydroxyl groups in molecule B led to the disappearance of these surface nanostructures, leaving behind a uniform surface topography without any characteristic surface micellar structures. In this case, the amphiphilic balance, by adding 12 hydroxyl terminal groups, was shifted toward highly hydrophilic branched PEO, resulting in a much less stable monolayer as the molecules tended to submerge into the water subphase at higher surface pressure without forming organized 2D structures.

Conclusions and outlook

In this Review, the interfacial behavior of four classes of non-linear polymers, i.e., polymer brushes, star-like polymers, dendritic polymers, and linear–dendritic polymers, have been highlighted. However, they only represent a small fraction of non-linear polymers, and many other nonlinear systems (e.g., crosslinked, arborescent, etc.) are not covered. Within the four systems reviewed, the self-assembly of some intriguing architectures at the air/water interface has not yet been explored (for example, random and barbed wire brushes, although the polymer brushes have been the most well studied non-linear system to date). On the other hand, little work was reported on novel linear–dendritic polymers. In sharp contrast to the intensive research on the bulk system, the progress in the field of LB monolayers of non-linear polymers is comparatively slow, which may be due primarily to the availability of powerful characterization techniques to explore the much reduced dimensions of LB films. Synchrotron-based techniques (scattering and reflectivity) are of key importance to probe the configuration and crystallization of LB film due to the limited amount of materials to be detected, and more interfacial assembly research will be performed using this technique. With more knowledge and fundamental understanding gained from the comprehensive study, we anticipate elucidation of the complex self-assembly process of non-linear polymers at the air/water interface, which in turn will provide the guidance to design new generation untra-thin films and polymer patterns with novel properties and enhanced performance.

We note that only a few surface micelles produced from the air/water interface can be arrayed into well ordered structures, which are of technological interest in the areas of microelectronics, information processing and storage, and nano/microfluidics. For example, ribbon-like surface micelles can be readily prepared from polymer brushes. However, such ribbons are usually randomly dispersed within the LB film. Several techniques have emerged to arrange surface micelles within the frame of LB methodology. First, the dewetting of a polymer solution on the LB trough during the solvent evaporation process can be harnessed to assemble surface micelles into cellular patterns or parallel wires. Moreover, the shear force induced by vertically withdrawing the solid substrate from the water subphase can also be utilized mainly through the control of the withdrawing speed and surface pressure to pattern surface micelles. A number of ordered patterns (e.g., dendritic structures and parallel stripes) have already been made possible. However, such successes are limited to several polymer systems, such as L-α-dipalmitoylphosphatidylcholine (DPPC), colloidal particles, and comb-block copolymer. Non-linear polymers, especially those having extremely compact structures (e.g., densely grafted brushes, star-like polymers with more arms, dendritic polymers with more generations), have much less intermolecular entanglements, which would facilitate the arrangement of the molecules. For example, some hyperbranched dendritic polymers, which behave like colloidal particles, are highly likely to be organized into parallel polymer stripes.

Fig. 26 (a) Chemical structures of molecule A, methyl-terminated branches and molecule B, hydroxyl-terminated branches. (b) Molecular model of the packing of molecule A, showing interdigitated layered (left) and a circular planar structure (right). Reprinted with permission from ref. 72, (2005 American Chemical Society).
(or microchannels) using the strategy developed for colloidal particles. Furthermore, ordered stripes with specific performance can be readily designed by integrating different kinds of polymer chain into the core of the dendritic polymers.

Another important area that may demand much research is the specific applications of the resulting LB films. Current work on non-linear systems is centered on conventional polymer chains, such as PS and PEO, for fundamental research. A wide range of non-linear polymers with advantageous optical, electrical, optoelectronic properties can be synthesized. Of particular interest is the non-linear polymer composed of luminescent conjugated polymer chain, such as poly(3-hexylthiophene) (P3HT) and poly[2-methoxy,5-(2-ethyl-hexoxy)-1,4-phenylenevinylene] (MEH-PPV). The application of the LB technique to conjugated polymers has produced a variety of electrical and optical ultra-thin film devices, such as light emitting diodes, thin film transistors, memory devices, ferroelectric thin films, nonlinear optical devices, sensors, and field-effect transistors. The ability to pattern the conjugated non-linear polymers may promise new opportunities to fabricate flexible integrated circuits. The other technologically important functional polymers are adaptive polymers. By integrating the adaptive chains, which respond to very subtle changes in the surrounding environment, such as pH, temperature, and light, into non-linear polymer systems, the resulting surface structures may hold the promise of numerous applications in colloid stabilization, drug delivery and biomimetic materials, chemical gates, and tuning lubrication, friction, adhesion, and wettability for tailored surfaces.

Notes and references
