

Hierarchical structures of dendritic polymers

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Abstract

Dendritic polymers' highly specific and three-dimensional architectures set them apart from linear and slightly branched polymers. Their unique properties also allow them to form hierarchical organizations, which can be classified as planar or non-planar. The preparation of a planar hierarchy consisting of dendritic polymers can be achieved by conventional techniques of adsorption or Langmuir monolayer and Langmuir–Blodgett accumulation, and the resultant hierarchy is well ordered. Non-planar hierarchies are built on non-planar scaffolds, for example by self-assembly. In this mini-review, the practical/potential applications of dendritic polymers such as for electrical or optical devices, sensing systems, or medical diagnosis are also reviewed in association with their structures.

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Keywords: hierarchical structure; dendritic polymer; adsorption; Langmuir monolayer; Langmuir–Blodgett accumulation; self-assembly

INTRODUCTION

Dendrimer is a generic name for molecules that have regularly repeating branch units from their cores.^{1–3} Since the concept of dendrimers was proposed,⁴ a great number of dendrimers have been synthesized and investigated. The characteristics of dendrimers depend on their highly symmetric and designed structures with strictly controlled molecular weights. Moreover, in a dendrimer molecule, functional groups can be introduced into the core, into branches at each generation and at terminals, depending on the intended purpose. Dendrons, which are the constitutional units of dendrimers, consist of a focal point and dendritic branching. Dendrons are not only utilized themselves as functional molecules but are also mounted on linear polymers as side groups. Thus dendrimers, dendrons and polymers with dendron side chains are named generically as dendritic polymers.

The application of dendritic polymers can cover medical diagnoses, gene therapies, electrical or optical devices, sensing systems, chemical reactors, catalysis reservoirs and pollution removal. For instance, to use functional dendritic polymers in electrical devices, dendrimer molecules can be immobilized on electrodes. For sensing systems, chips or microarrays are convenient for handling. When dendritic polymers work as chemical reactors, they can be held on substrates to minimize loss in subsequent processes. Furthermore, dendritic polymers are also highly effective scaffolds for other functional materials. Dendrimers and dendrons possess many terminal groups for binding other materials, and their functionalities can combine with those of the bound materials. Thus, the immobilization of dendritic polymers is a very important process for various applications, and a variety of hierarchical structures including layers of immobilized dendritic polymers have been reported.

In this mini-review, various hierarchical structures of dendritic polymers are introduced with their fabrication, characterization and possible applications. In the next section, planar hierarchies, which are fabricated by dendritic polymers in flat mode, are the focus. Such hierarchies are prepared by self-assembling or self-ordering of dendritic polymers by means of techniques such as adsorption or spreading at interfaces, Langmuir–Blodgett

(LB) accumulation and liquid crystalline formation. The planar hierarchies can also be constructed from composites of dendritic polymers and other functional materials, which can be linear (conventional) polymers and nanoparticles. The non-planar hierarchies of dendritic polymers are then discussed. Scaffolds of spherical and linear shapes are sometimes employed in these constructions, in addition to self-hierarchy of dendritic polymers. Thus this review provides researchers with clues for developing novel and valuable hierarchies of dendritic polymers, which can be designed and applied for various purposes.

PLANAR HIERARCHY OF DENDRITIC POLYMERS

Planar hierarchies consisting of multilayer films of dendritic polymers have been designed using conventional techniques of adsorption, LB and liquid crystal assembly, which are described below in detail. AFM^{5–7} and X-ray or neutron reflectometry^{8–10} have been used to evaluate the obtained planar hierarchies of dendritic polymers. The properties of these hierarchies, such as molecular recognition¹¹ and pH sensitivity¹² of the lamellar structures of dendritic polymers, have been used in sensing systems. Chemical reactors with outer functional groups¹³ or immobilized enzymes¹⁴ on dendrimers and photoelectric conversion devices (e.g. organic light-emitting¹⁵ and field-effect transistor devices¹⁶ and photocells^{17,18}) with dendrimers have also been reported.

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Fabrication of hierarchy by adsorption

Although conventional dendrimer molecules are highly symmetric and likely take a spherical structure in media,³ a single dendrimer molecule can be recognized as a dot or disc and distributed randomly on a substrate.¹⁹ Adsorption of dendrimer molecules onto substrates is stimulated and controlled by physical and chemical interactions, which include electrostatic interactions,^{20,21} hydrogen bonding²² and specific chemical reactions.²³ The interaction varies depending on the conditions such as the combination of dendrimer and substrate. Hexagonal lattice nanoarrays of dendrimers have been reported on graphite substrates.²⁴ Hence the ordered array of carbons in graphite can be a template for a dendrimer array. In general, to effectively immobilize a dendrimer molecule on a substrate, a covalent binding procedure is most effective. Self-assembled monolayers (SAMs) of thiol-substituted poly(amido amine) (PAMAM) dendrimers on gold substrates²⁵ and films of dendrimers bound through terminal siloxy groups on silicon substrates^{26,27} are examples of this. The former is a typical monolayer prepared on a substrate and adopted as the so-called first layer in a multilayer. In the case of siloxy-substituted dendrimers, a sol-gel reaction produces thicker polymer films.

The adlayer formation of dendrimers is affected by interactions between them. When PAMAM dendrimers form adlayers on substrates, the thickness and roughness of the adlayer depend on the terminal groups of the dendrimer and the pH of the solution (Fig. 1(a)).²² While amino-terminated dendrimers form a relatively smooth film surface, adlayers of carboxyl-terminated dendrimers display a roughness of several tens of nanometers in width and about a nanometer in height (Fig. 1(a)). The film thickens at pH = 6–7 and becomes thinner at lower/higher pH. The hierarchical construction of carboxyl-terminated dendrimers is explained in terms of hydrogen bonding and electrostatic attraction between dendrimer molecules. When both internal amino groups and terminal carboxyl groups are charged at medium pH, dendrimer molecules form a hierarchy via electrostatic interactions, and the carboxyl groups also contribute to the hierarchy formation via hydrogen bonding.

Dendrimers have advantages as regards the adsorption process, since their terminal groups can be designed for multiple-point adsorption, providing strong and specific interactions with substrates. Moreover, when the interactions between the

dendrimer and the other components (i.e. the substrate or the other dendrimers) are strong enough, the dendrimer changes its conformation to increase the adsorption point as much as it can. Commercially available PAMAM dendrimers vary their morphology from sphere to ellipsoid in adlayer films.²¹ In contrast, newly designed PAMAM dendrimers, which have longer spacers to make the molecules flexible, take an extended conformation to orient the terminals towards the substrate.²¹ Furthermore, the conformation of this dendrimer changes as the adlayer develops. Namely, the dendrimer adsorbs as a flat surface on the substrate initially, and the conformation changes to a vertical one at a later stage. Such a stepwise variation of the adsorption process has also been reported for Janus-type PAMAM dendrimers on *in situ* observation.⁵ Long alkyl terminals in the hemisphere of Janus-type PAMAM dendrimers are perpendicularly aligned to the substrate, and the dendrimer forms a bilayer with the hydrophobic moieties inside the bilayer. These phenomena could suggest ways to control the conformation of dendrimers in a spontaneously formed adsorption hierarchy.

The morphology of dendrimer molecules is affected by their chemical structures. Whereas conventional dendrimers of higher generation tend to take more spherical shapes, dendrons have an asymmetric structure that is often likened to a fan (planer taper) or cone. In solution, fan-like rigid dendrons aggregate to cylinders and hexagonal liquid crystals, and similarly cone-like rigid dendrons create spherical supramolecular aggregates and form a cubic liquid crystalline phase.^{28,29} To control the liquid crystalline orientation of functional groups in dendritic polymer films, the generation and flexibility of the dendrimer should be considered. When a poly(benzyl ether) dendron is attached onto a side chain of a linear polymer, the polymer tends to be rigid and rod-like.³⁰ Functional polymers that are encircled by dendrons possess efficient charge separation³¹ and show a characteristic luminescence phenomenon.³² These rigid and rod-like polymers easily align in the same direction in a cast film (Fig. 1(b)).

Fabrication of hierarchy in Langmuir monolayers and LB accumulation

The LB method is an adequate technique to accumulate monolayers of amphiphilic molecules.^{33,34} Molecules spreading at an air-water interface generally orient to minimize the surface

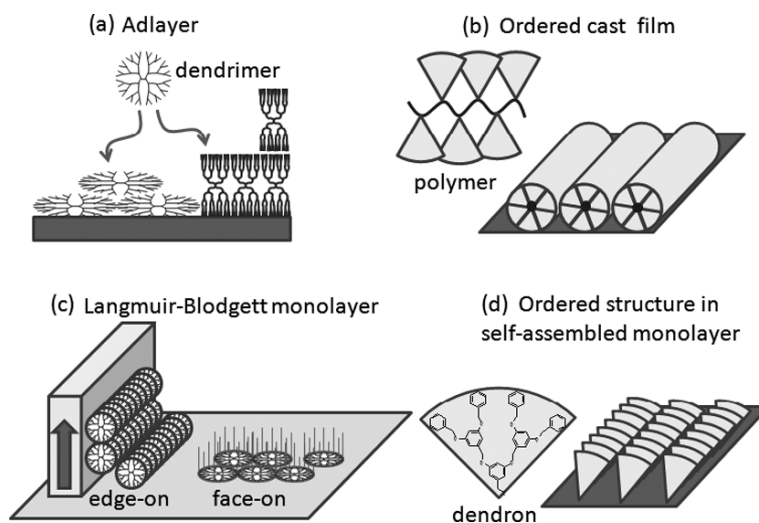


Figure 1. Schematic of planar hierarchies of dendritic polymers.

free energy, and the hydrophilic moiety in the molecule faces towards the water subphase. This orientation is promoted as the surface pressure rises by film compression. Since conventional dendrimer molecules have a symmetric nature and a chemically bound branch structure, the Langmuir monolayer arrangement as described above is not expected at the air–water interface. Thus dendritic polymers with asymmetric or flexible chemical structures should be synthesized. For instance, dendrons with dendritic and core moieties of different solvophilicity and amphiphilic polymers with blocks of dendritic side chains are prepared as asymmetric dendritic polymers.

An amphiphilic PAMAM dendrimer that possesses 10,12-pentacosadiynoyl terminals changes its conformation at the air–water interface and takes a ‘face-on’ conformation on the water subphase, as the monolayer is compressed (Fig. 1(c)).³⁵ At an early stage of monolayer compression, the surface dipole moment, which can be measured with a surface potential sensor, rapidly increases as the terminal chains are aligned perpendicular to the water subphase. Once the face-on conformation is achieved, the surface dipole moment levels off. The compressed monolayer can be irradiated with UV light to polymerize the diacetylene groups in the periphery of the dendrimer molecules. Since the terminal chains are closely packed on the air side of the Langmuir film, polymerization proceeds easily to form a crosslinked dendrimer monolayer at the air–water interface. This indicates that molecular ordering controlled by the surface pressure forms a hierarchy consisting of layers of PAMAM moieties and polydiacetylene moieties at the air–water interface.

On the other hand, from the surface potential *versus* molecular area behavior of PAMAM dendrimers with 12-hydroxydodecyl terminals, it is suggested that the dendrimers take an ‘edge-on’ conformation in the monolayer at the air–water interface, as the surface pressure increases (Fig. 1(c)).³⁶ These PAMAM dendrimer molecules lie sideways in the Langmuir film to make packed columnar structures. This one-dimensional orientation in the monolayer is observable as stripes of 20 nm (for first generation) or 30 nm (for second generation) in width in AFM images of the LB films. A comparison with a LB film of PAMAM dendrimers without hydroxyl groups in the periphery³⁵ shows that the terminal hydroxyl groups play important roles for determining the alignments of dendrimer molecules. This contribution of hydroxyl groups should be expected to the molecular orientation in the monolayer hierarchy.

Poly(benzyl ether) dendrons with thiol groups at the focal point adsorb on a gold substrate to form a SAM, and the SAM becomes a striped monolayer after annealing (Fig. 1(d)).³⁷ The striped architecture of the poly(benzyl ether) dendron can be prepared even at the air–water interface, when the dendron is spread on the water subphase.⁶ This phenomenon is assumed to be due to the fan-like shape of the dendron molecules. At high surface pressure, the monolayer takes a close-packed ordering and cylindrical morphology by stacking of dendron fans. Since the interaction between dendron molecules is not so strong, annealing of the SAM or compression of the Langmuir film is required to form definite monolayer stripes. Poly(phenylene sulfide) (PPS) dendrons have fan-shaped chemical structures similar to poly(benzyl ether) dendrons. However, while SAMs of PPS dendrons are monolayers without any texture and shrink to flat terraces after annealing, their LB films consist of a hierarchy of several hundred nanometers in width and tens of nanometers in height.³⁸ This difference in film structures could be because of the difference in cohesive force and the flexibility of molecules between poly(benzyl ether)

dendrons and PPS dendrons. Incidentally, PPS dendrimers with symmetric molecular structures form LB films with many holes, unlike PPS dendrons.³⁸ The shape and rigidity of molecules and molecular interactions should affect the molecular alignment of PPS dendrons and dendrimers.

PLANAR HIERARCHY OF DENDRITIC POLYMER HYBRIDS

For fabricating multilayer hierarchies with a defined structure, a layer-by-layer deposition technique is preferably applied. After the first adlayer is formed on a substrate by means of a technique as described in the previous section, the second layer is deposited by adsorption from a solution. As a result of successively repeating the adlayer formation, multilayered hierarchies are accumulated.⁷ Intercalation of small molecules between layers in layered materials like graphite and clay minerals is also a potential route for the preparation of hybrid hierarchies. Intercalation between layers in clays is generally carried out using small molecules but dendrimers also have a small enough size to be used instead of currently investigated molecules.

Hybrids with polymers

To construct hybrid hierarchies of dendrimers, other polymers are available as binders. Since amino-terminated PAMAM dendrimers have many amino groups at branches and terminals, anionic polymers can be used as the counter polymers.⁷ Since the amino groups are protonated and positively charged, dendrimers can adsorb onto the negatively charged layer by electrostatic interactions. A hybrid of cationic dendrimer molecules and anionic linear polymers develops well-defined two-dimensional structures, since dendrimers have uniform molecular size and enough thickness of a few nanometers, although the thickness depends on the pH (Fig. 2(a)).⁹ The utilization of dendrimers is advantageous for fabricating a thick film:³⁹ the layer-by-layer accumulation can reach more than 10 nm in height at seven adlayers. Such a thick adlayer can be useful for molecular devices involving energy transfer systems. Hydrogen bonding is also a motive force for layer-by-layer accumulation as exemplified in the hybrid of carbonic acid-terminated PAMAM dendrimer and poly(methacrylic acid).¹² The film obtained is stable only in a solution of pH = 3–5. At a pH above 5, electrostatic repulsion between $-\text{COO}^-$ groups results in the collapse of the film. At a pH below 3, the film also becomes unstable, since the electrostatic affinity between $-\text{COO}^-$ groups and protonated amine groups of the dendrimer decreases. This pH sensitivity is valuable for applications such as pH-sensing devices.

Since most biopolymers are negatively charged, due to carboxyl or phosphate groups, they easily bind on an adlayer of a cationic dendrimer as the counterpart polymer.⁴⁰ As a preliminary, the interactions of DNA,⁴¹ polypeptide^{42–45} and polysaccharide⁴⁶ with amino-terminated PAMAM dendrimers have been examined in their solutions. The PAMAM dendrimer was immobilized via amide linkages with resultant carboxyl groups on patterned SAMs, which were photolithographically prepared by irradiation of vacuum UV light on a masked octadecyltrimethylsilane SAM on a silicon substrate.⁴⁷ The patterned layer of PAMAM dendrimer can then be used for adlayer formation of biopolymers, and the selective adsorption of biopolymers on a PAMAM dendrimer pattern has been confirmed, suggesting the molecular recognition of biopolymers and the utilization of patterned dendrimer substrates as sensing systems.

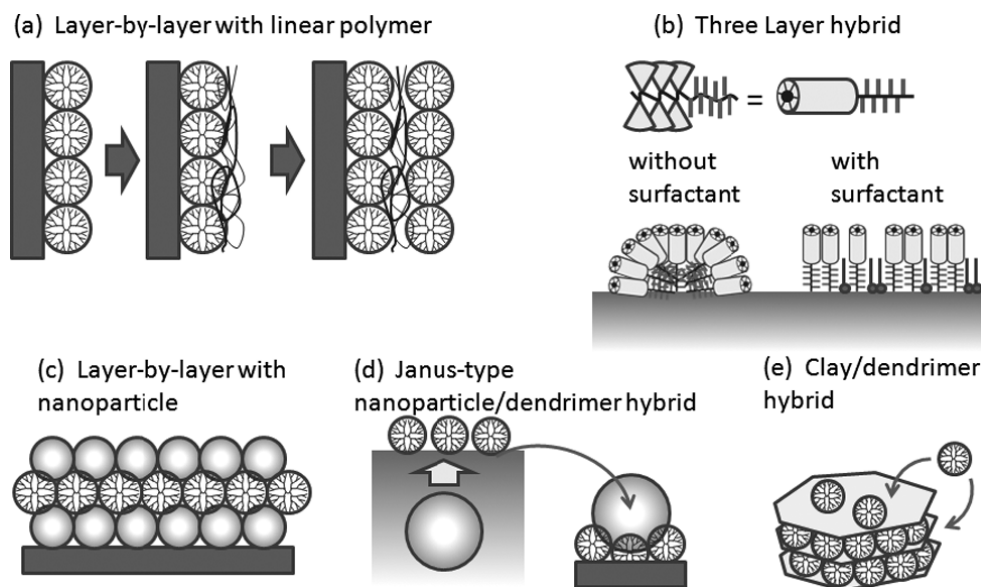


Figure 2. Schematic of planar hierarchies of dendritic polymer hybrids.

The interaction of adlayers with biopolymers is not limited to electrostatic attraction. Specific antigen–antibody interactions, e.g. avidin–biotin binding, also allow the preparation of a stable hybrid hierarchy.⁴⁸ Two approaches are proposed to provide biotin-functionalized dendrimer layers. In the first approach, biotin-labeled dendrimer is synthesized by reacting amino-terminated PAMAM dendrimer with commercially available sodium sulfosuccinimidyl-6-(biotinamido)hexanoate (NHS-biotin), and the obtained biotin-labeled PAMAM dendrimer is accumulated with avidin derivatives using the layer-by-layer method. Compared with linear or randomly branched polymers, the dendrimer provides a monomolecular deposition of avidin derivatives. In the second approach, the residual amino groups on the PAMAM dendrimer SAM are labeled using activated biotin reagent (NHS-biotin). Since the avidin–biotin system is widely used in biochemistry and the labeled materials (antibodies, enzymes, peptides and nucleotides) are commercially available, these techniques are practical for biochemical applications, e.g. molecular recognition.

Rod-shaped polymers usually take planar alignments in a film.⁴⁹ However, block copolymers consisting of rigid and rod-like (dendron and perfluoroalkyl) side-chain blocks take on a different morphology.⁵⁰ LB films of these block copolymers display a zonal pattern of several tens of nanometers in width and about 6 nm in height. Obviously, since this zone texture does not correspond to a single polymer chain, it appears that copolymers form hemi-micelle aggregates at the air–water interface.^{51,52} The thick and long dendron blocks form the shell of the hemi-micelle, and the thin and short perfluoroalkyl blocks face inward. Furthermore, addition of amphiphilic perfluorooctadecanoic acid changes the zone texture to a planar film (Fig. 2(b)).⁵² The additional perfluoroalkyl acid is inserted between the array of the perfluoroalkyl blocks in the copolymers, and the perfluoroalkyl moieties planarize the polymer array. This hybrid film then consists of three layers: a lipophilic dendron block; a lipophobic–hydrophobic perfluoroalkyl block or moiety; and a hydrophilic moiety of surfactant. Spontaneous formation of the three different hierarchies with totally different natures opens a new vista of techniques to fabricate novel materials.

Hybrids with nanoparticles

Nanoparticles can also be the counterpart materials of dendrimers in hybrid hierarchies. Since noble metal nanoparticles enhance light absorption^{53–55} and Raman scattering⁵⁶ via their surface plasmon, a nanoparticle–dendrimer hierarchy can be used as a sensing device.⁵⁷ Silver nanoparticles and polypropylenimine dendrimers can be accumulated using a layer-by-layer method on a glass substrate (Fig. 2(c)) and are provided for Raman scattering of 2-naphthalenethiol in the film. It has been found that the generation of the dendrimer affects the surface enhancement of Raman scattering. This result suggests the possibility of chemically specific sensing devices using the nanoparticle–dendrimer hybrid hierarchy. Multilayer films formed using the layer-by-layer method can also be prepared from metal nanoparticles protected with PAMAM dendrimers. The counter layer is a linear polymer⁵⁸ or other dendrimer–nanoparticle composite.⁵⁹ This is a promising technique for fabricating nanomaterials consisting of hypercomplex components.

While gold nanoparticles protected by alkyl thiols form a hexagonal close-packed film,⁶⁰ gold nanoparticles protected by poly(benzyl ether) dendron thiols assume a linear array.⁶¹ Since the spacing between lines of gold nanoparticles in the array is smaller than double the size of the dendrons, an interdigitation of dendrons between adjacent lines is suggested. The interparticle distance in a line is much shorter (almost touching) than the line spacing. This indicates that the distribution of dendron molecules on a nanoparticle is not homogeneous. However, when a dendron of third generation or higher is used in the synthesis of gold nanoparticles, the gold nanoparticles are not protected well, and the particle size is polydisperse. Although the mechanism of stripe build-up has not been explained in detail, it is supposed that the structure and electronic interaction ($\pi - \pi$) of the dendron molecules play a certain role in this stripe build-up along with the arrangement of corresponding dendrons to stripes in LB films⁶ and SAMs.³⁷

Unlike the fan-shaped dendron, PAMAM dendrimers are not likely to be arranged in stripes because of their symmetric and spherical shapes. However, PAMAM dendrimers can form

stripes in films, if they are hybridized with nanoparticles.⁶² CdS nanoparticles protected by generation four or eight PAMAM dendrimers adsorb onto polydimethylsiloxane (PDMS) substrates, and the morphology of the architecture is stripes of several hundred nanometers in width. Only fresh composites on PDMS substrates produce the stripes, while aged composites or silicon substrates are not suitable for preparing these ordered structures. Although the reason for the morphology variation is not clear, it is assumed that specific interactions between the composites and PDMS substrate affect this phenomenon.

Thus attempts to construct hybrid hierarchies from nanoparticles and dendritic polymers have not necessarily been successful for two-dimensional arrays of nanoparticles. However, there is a report of ordered monolayer formation of nanoparticles on the scaffold of a dendrimer Langmuir film (Fig. 2(d)).¹⁰ That is, when a monolayer of PAMAM-type dendrimer with aza-crown core is spread at an air–water interface, gold nanoparticles adsorb from the water subphase onto the hexagonal array of the dendrimer monolayer. A denser hexagonal monolayer array of nanoparticles is accomplished by compression of the dendrimer monolayer. The resulting film then has a Janus-type nanoparticle–dendrimer hierarchy, where one hemisphere of nanoparticles is covered with amphiphilic dendrimers but the other hemisphere is free from dendrimer layers. This Janus-type aspect of the nanoparticle–dendrimer hybrid hierarchy inspires us with the possibility of unique applications. The procedure for the construction of the nanoparticle–dendrimer hybrid hierarchy is comparable to aggregate formation of gold nanoparticles, where aggregates partially protected by the dendrimer form a characteristic horseshoe-shaped structure on a substrate.⁶³

Hybrids with layered materials

Clay minerals have a layer structure, which contains exchangeable counterions between layers. Using their ion exchange ability, many ionic compounds are intercalated into clays.^{64,65} While low-molecular-weight compounds easily penetrate into the clays, hierarchical structures of linear polymers with clays are prepared by intercalation of the corresponding monomers and subsequent polymerization.^{66,67} A nylon–clay hybrid which is obtained by the *in situ* polymerization of intercalated monomer can be applied as a gas-barrier film. In contrast, dendrimers can be intercalated directly between the clay layers. Hybridization of a PAMAM dendrimer (negatively charged by virtue of terminal carboxyl groups) and cationic hydroxalcite has been reported.⁶⁸ This hybridization results in an increase of the interlayer spacing and flattening of the intercalated dendrimer molecules. The flattening of the dendrimer is also found for LB films of this hybrid.^{69,70}

The one-pot preparation of nanocomposite hierarchies using the intercalation technique is preferable as a more convenient method than the LB or layer-by-layer technique, which requires a multistep process, although the number of layers depends on the size of the clay fragments and cannot be controlled. Thus, this technique could be applied for the purpose of hybrid hierarchy formation of inorganic clay and organic dendritic polymer (Fig. 2(e)). Furthermore, silver nanoparticle–dendrimer nanocomposites have been synthesized in a PAMAM dendrimer solution,⁷¹ and the resulting nanocomposites hybridized with hydroxalcite.⁷² Thus this technique is promising for the triple hybridization of clay–polymer–nanoparticle.

NON-PLANAR HIERARCHY OF DENDRITIC POLYMERS

The hierarchies of dendritic polymers are constructed not only with a planar aspect such as on substrates but also with a non-planar aspect. Self-assembled polymer micelles are a typical case; others are hierarchies on scaffolds with non-planar shapes. There are many reports of polymer micelles consisting of block copolymers, but dendritic polymer-based micelles or aggregates have not been well investigated. Correspondingly, little work has been carried out on the formation of hierarchies by dendritic polymers on spherical and linear scaffolds.

Self-assembled hierarchical aggregates of dendritic polymers

Conventional amphiphilic block copolymers can form spherical dendron micelles in polar solvents. Core and shell as concentric hierarchies are large enough in size but dense, because the micelles are filled by component linear polymers. One study has been carried out of micelle formation of block copolymers consisting of a hydrophilic linear chain block and a hydrophobic bulky block with dendron side chains (Fig. 3(a)).^{73,74} In water, spherical micelles of about 70 nm in diameter can selectively solubilize dozens of molecules of pyrene and related dyes within their hydrophobic core. Moreover the polymer micelles take in a few hundred hydrophobic radicals. These results suggest that the micelle core of a polymer with bulky dendritic pendants has a large void to encapsulate guest molecules.

Fullerodendrons consist of PAMAM dendrons diverging from the focal point of C₆₀ aggregates in micelles of *ca* 46 nm in diameter with a narrow dispersion in a chloroform solution.⁷⁵ When the solution is spread on a mica substrate and dried, circular islands of 100–220 nm in diameter and 3–5 nm in height are observed. This island texture is assumed to be formed by adsorption of micelles. Comparing the volume of an aggregate in solution with that on a substrate, the micelle in solution is rather swollen. Furthermore, the observation of dish- or ring-shaped aggregates on the substrate implies a hollow micelle or low-density core in the solution. A vesicle formed of penta-substituted C₆₀ potassium salt has been reported.⁷⁶ Fullerodendrons change their molecular orientation in Langmuir and LB films, depending on the generation.⁷⁷ At low generations (0.5 and 1.5), a Langmuir film forms a bilayer with the C₆₀ moiety inside. In contrast, fullerodendrons of high generations (2.5) form a monolayer. A strong interaction between C₆₀ moieties contributes to the bilayer formation at low generations. Thus hierarchical structures of fullerodendrons depend on the generation and the morphology of assembly. The bilayer structure of fullerodendrons has been utilized as one of the components in field-effect transistors, and it was found that the ordered C₆₀ layer improves the mobility of field-effect transistors in comparison with spin-coated films.¹⁶

Hierarchies on spherical scaffolds

Inorganic particles such as silica beads and latexes come to mind as spherical scaffolds. Polystyrene (sub-micrometer in diameter)⁷⁸ or melamine formaldehyde (MF; several micrometers in diameter)^{78–80} particles have been covered with anionic poly(sodium 4-styrenesulfonate) (PSS) and generation-four PAMAM dendrimers by layer-by-layer accumulation (Fig. 3(b)). Then Ca²⁺ (for bridging the sulfonate groups in PSS) and doxorubicin hydrochloride (to increase the hydrophobic interactions) must be added in order to reinforce the multilayer. These additives are efficient for improving the yields when removing the MF core at low

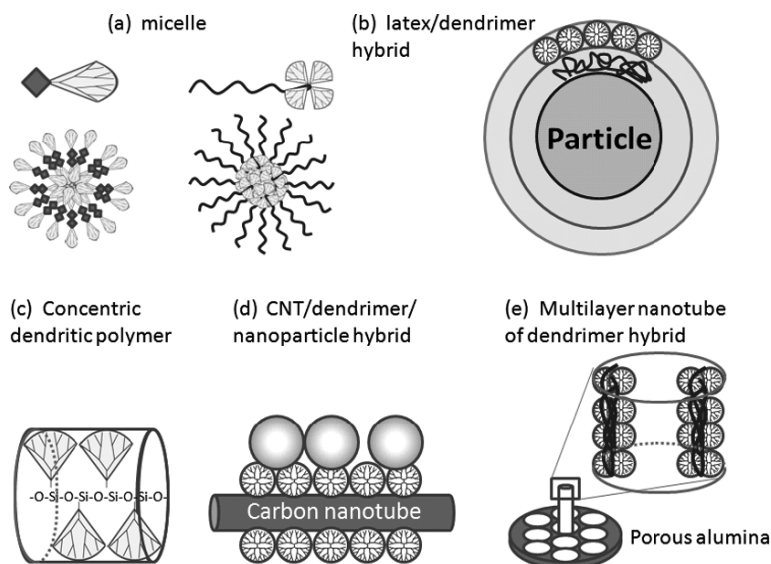


Figure 3. Schematic of non-planar hierarchies of dendritic polymers.

pH to obtain a hollow capsule. Another capsule has been prepared from the hierarchy of DNA and cationic phosphorus-containing dendrimers on MF particles.⁸⁰ These hollow spherical hierarchies are useful for drug delivery systems.

Hierarchies on spherical scaffolds are also useful for sensors and reactors in bulk. It has been reported that silica beads coated with PAMAM dendrons are able to absorb dyes and surfactant molecules efficiently from solution.⁸¹ In this system, PAMAM dendrons have long alkyl chains at their terminals to increase the affinity for hydrophobic moieties in the guest molecules. Such hierarchical dendron shells are valuable for molecular recognition and applied for the removal of pollutants in water. TiO₂ nanoparticles in hierarchies with amphiphilic PAMAM dendrimers or PAMAM dendrons are effective for decomposing pollutants in aqueous solution by photocatalytic reactions.^{82,83} The cationic dendritic polymers surrounding the TiO₂ nanoparticles act as a reservoir of guest molecules as well as a protector of particles, accelerating the photoreaction for guest molecules.

Iron oxide nanoparticle–dendrimer nanocomposites have been synthesized and applied in biomedical diagnosis.^{84–86} The dendrimers are modified with folic acid for targeting cancer cells and labeled with fluorescein isothiocyanate for observation with a fluorescent microscope. Using a layer-by-layer method⁸⁴ and crosslinking technique⁸⁵ to prepare protective layers, the labeled dendrimers are efficiently immobilized on the nanoparticles and detected by microscopic observation. Since the iron oxide nanoparticles are superparamagnetic, they can be detected using magnetic resonance imaging.^{85,86} Thus, these multifunctional nanocomposites are useful for *in vitro* and *in vivo* experiments in biomedical research.

Hierarchies on linear scaffolds

Strong interactions between dendrimer molecules spontaneously result in fibrous assemblies in solution. Hydrogen bonding^{87,88} and $\pi - \pi$ stacking^{88–90} have been proposed as such strong interactions in dendrimer assemblies. Solutions of these assemblies of dendritic polymers easily gelate due to their fibrous structures. Such fibrous structures can also be prepared by polymerization of PAMAM dendrons with a siloxane focal point that are synthesized

from aminopropyltrialkoxysilane.⁹¹ When these PAMAM dendrons are hydrolyzed and polymerized through sol–gel reaction of the alkoxy silane focal points, uniform nanofiber networks are formed in viscous solutions, if the concentration of the reaction solution is high enough. However, microgels are prepared in a fluid solution at low dendron concentration. It is found that microgels consist of dendritic branch structures of polysiloxane fibrils with PAMAM dendron side chains (Fig. 3(c)). In other words, the fibrils are nanowires of polysiloxane with a PAMAM dendron shell, i.e. a cylindrical linear hierarchy.

The spontaneous assembly to fibers can be used for gelation of solutions. Nanofibers are also applicable as a scaffold for the formation of a linear hierarchy. The construction of dendrimer-mediated nanoparticle hierarchies on carbon nanotubes (CNTs) has been reported.^{92,93} Multi-walled CNTs are oxidized for generating defects on the wall, and the resultant –COOH groups are activated for further reaction. Then amino-terminated PAMAM dendrimers are immobilized on the CNT via amide bonding. One of the merits of this modification is that the obtained dendrimer-modified CNTs are water-dispersible and useful for various kinds of chemical reactions through the functional terminal groups of the anchored dendrimers. For instance, various metal (copper, silver, platinum, gold) and metal oxide (TiO₂, SiO₂) nanoparticles can bind to the dendrimers on the CNTs by reduction or hydrolysis of corresponding metal ions (Fig. 3(d)).

Not only a fibrous core but also a porous template is useful for providing a linear organization of dendritic polymers. A multilayer of 20 bilayers has been formed using layer-by-layer accumulation of cationic and anionic dendrimers (Fig. 3(e)).⁹⁴ After removal of the template, the multilayer is recovered as a nanotube. The length (80 μm) and diameter (*ca* 400 nm) correspond to the dimensions of the template, and the thickness is 40 nm (2 nm per bilayer). The tubes consist of a concentric hierarchy of cationic and anionic dendrimers.

CONCLUSIONS

Hierarchical structures of dendritic polymers can be constructed in both planar and non-planar mode. Typical planar hierarchies

are formed by adsorption, self-assembly, Langmuir monolayer, LB accumulation, layer-by-layer deposition and intercalation, and non-planar hierarchies are built on non-planar scaffolds. The thickness, morphology and arrangement of the adsorption hierarchy are strongly affected by the ambient conditions, and the molecular conformation is optimized by interactions between dendritic polymers and with the substrate. For monolayers of amphiphilic dendritic polymers at air–water interfaces, the molecular conformation can be controlled by the surface pressure. Terminal groups and shapes of the dendritic polymers also play a significant role in determining the array of the monolayers. Fan-shaped dendrons and linear polymers with dendritic pendant chains are used to form one-dimensional structures on substrates. Layer-by-layer accumulation is a convenient technique to prepare a well-controlled multilayer. Applications in biochemistry using hybrids of biopolymer–dendrimer multilayers have been discussed. Hybridization with nanoparticles is also useful for applications such as in sensing devices, since functional metal and semiconductor nanoparticles can be arranged, by means of dendritic polymers, in a multilayer or one-dimensional structure. Layered fillers are beneficial for fabricating organic–inorganic hybrids. In contrast to linear polymers, dendrimers can easily penetrate into the interlayer of layered fillers. Recent research on preparing asymmetric nanoparticle–dendrimer nanocomposites has also been mentioned. Micelles of dendritic polymers, concentric multilayers on CNTs and hollow structures using templates (polymer particles and porous alumina) have been reported as novel components for nanotechnology. Hierarchies that take advantage of the structural aspects of dendritic polymers will be developed more in the future, and some of them will be expected to have practical applications.

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