STRUCTURE–PERFORMANCE RELATIONSHIPS IN SURFACTANTS

Second Edition, Revised and Expanded

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Association Behavior of Amphiphilic Dendritic Polymers

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I. INTRODUCTION

The main characteristics of amphiphilic molecules such as surface activity and association behavior originate in their unique chemical structure, which consists of hydrophilic and lipophilic moieties. Traditional low-molecular-weight surfactants are typical amphiphilic molecules and have a hydrophilic head and a hydrophobic alkyl chain tail. Such a structural character is dominant to associate into micelles, vesicles, microemulsions, liquid crystals, and other self-assemblies. These aggregates are utilized for huge industrial, cosmetic, and pharmaceutical purposes.

AB-type block copolymers are also a kind of amphiphiles, since every block in the copolymers has different affinities to solvents. Those are associated into micelles, but the micellar sizes are usually larger than the sizes of traditional surfactant micelles. Then polymer micelles create large hydrophilic and lipophilic domains, which are superior as a solubilization reservoir and a microreaction matrix. Amphiphilic $(AB)_n$-type block copolymers form unimolecular micelles, where blocks familiar to solvent are in the periphery of micelles. However, unimolecular polymer micelles are destroyed, like surfactant micelles, depending on conditions such as temperature, additives, and solvents.

Recently, novel polymers, dendrimers, are focused on as nanomolecules and expected as covalent-bonded "unimolecular micelles" or "dendritic boxes" for the encapsulation of small molecules and the chemical reaction [1–8]. Dendrimers are prepared from a functional core through the successive repeating synthesis of a spacer and a branching part (divergent method) or from a conjugation at the conic center of dendrons, units of a dendrimer (convergent method). When two steps are needed for the extension of a repeating unit, each step is called a half-generation. While structures of dendrimers at low generations are opened and asymmetric, the structures become concentrated and spherical during the increase of the generation.

In the process of the stepwise synthesis, it is possible to modify the central core, spacer, branch, and terminal group, and a variety of functional moieties are conjugated in dendrimers. Amphiphilic character could be introduced by designing the different generations or layers to be either hydrophilic or hydrophobic. On the other hand, hybrid copolymers with linear polymers and dendrimers (or dendrons) are synthesized. Such copolymers with a specific chemical structure may also possess unique characteristics such as amphiphilicity besides intrinsic dendritic and polymeric characters. Then, the amphiphilic concentric dendrimers and hybrid copolymers could be applied to many nanoscopic smart materials including drug deliveries, diagnostics, and segregations, as well as reaction catalysts, transport agents, and molecular recognitions.

In this section, the up-to-date investigations concerning the characteristic covalent-bonded structures of concentric dendrimers and hybrid copolymers are reviewed. Especially, their amphiphilic properties and association behavior are examined. Amphiphilic nanomolecules can make supramolecular architectures as self-assemblies in solutions and monolayers or thin films at interfaces between water and immiscible organic solvent, at air–water interfaces, and on solid substrates. The formation of architectures is discussed in relation to the structures of dendrimers and copolymers.

II. AMPHIPHILIC DENDRIMERS HAVING A CONCENTRIC STRUCTURE

When, during the stepwise synthesis of dendrimers, generations or terminal groups are modified by different chemical units, the dendrimers carry the amphiphilicity on the concentric layers. The terminal groups of poly(amido amine) dendrimers have been substituted by lactose and maltose derivatives [model (a) in Fig. 1] [9]. These globular dendrimers, called "sugar balls," are three-dimensional architectures of artificial glycoconjugates as mimics of natural multiantennary oligosaccarides. Sugar moieties with a well-controlled geometric arrangement in those sugar-substituted layer-block copolymers possess the function as molecular recognition sites.

Funayama et al. [10] have investigated the segment distribution and the water penetration in a sugar-terminated poly(amido amine) dendrimers and compared them with those in a hydroxyl-terminated poly(amido amine) dendrimer and a hydroxyl-terminated poly(trimethylene imine)/mono (amido amine) dendrimer. Bulky sugar terminals distribute in the periphery of dendrimers, while some hydroxyl terminals direct to the interior. In the case of a poly(trimethylene imine) dendrimer, the segment distribution increases from the interior to the periphery. The water penetration is not necessarily dependent on the segment distribution but relates to the affinity of the dendrimer-constituting units for the solvent. The encapsulation of small molecules, depending on the dendrimer species, implies the selective doping ability of dendrimers, which allows us the application of dendrimers as dendritic boxes.

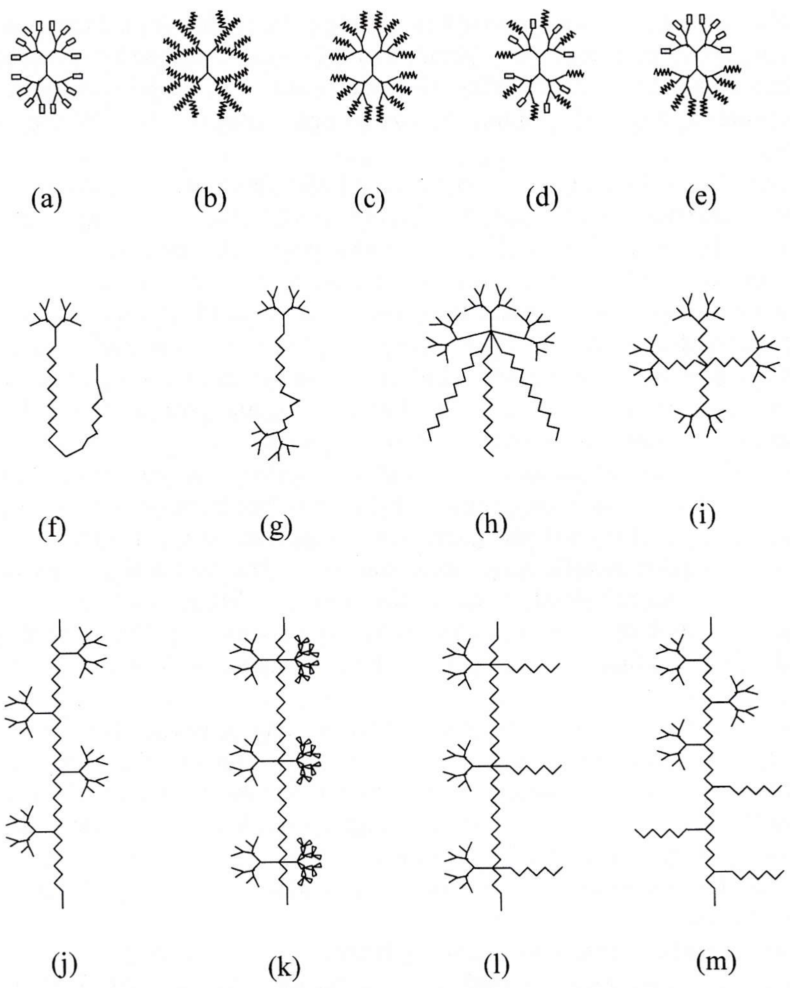


FIG. 1 Schematic models of amphiphilic dendritic polymers.

Poly(amido amine) dendrimers have been coupled with D-glucono-1,5-lactone, and the solubilization of pyrene and aromatic ketones in water has been investigated [11]. The solubility of hydrophobic molecules is increased, depending on the microcavities of dendrimers. This indicates the behavior of dendrimers like surfactant micelles. Glucose-substituted dendrimers aggregate through hydrogen bonding. The size of aggregates is 100–2000 nm in diameter.

Radially layered copolymers containing a hydrophilic poly(amido amine) dendrimer interior and a hydrophobic organosilicon exterior have been synthesized by Dvornic et al. [12]. Although the solubility and glass transition temperature of the copolymers are influenced by their chemical compositions and molecular architectures, their thermal and thermooxidative stability is mostly determined by the presence of the less stable poly(amido amine) component. Ponomarenko et al. [13] have synthesized a carbosilane liquid crystal dendrimer with cyanobiphenyl mesogenic groups. Molecular organization on films of the dendrimer was studied.

The modification of the terminal groups of hydrophilic poly(propylene imine) dendrimers with hydrophobic alkyl chains has been carried out by Stevelmans et al. [14], and the guest–host properties as an inverted unimolecular dendritic micelle have been examined. The terminal groups of poly(propylene imine) dendrimers of the first to fifth generations have been modified with long hydrophobic (palmitoyl) chains [15]. These amphiphilic dendritic surfactants aggregate at the air–water interface and in the solution.

Dendrimerlike star-block copolymers with a radial geometry [model (b) in Fig. 1] has been synthesized from a hexahydroxyl functional core by the living ring opening polymerization of ε-caprolactone producing a hydroxyl-terminated six-arm star polymer [16]. The copolymers have concentric structures with generations or layers of different components, which are comprised of high-molecular-weight linear polymers emanating from a functional core.

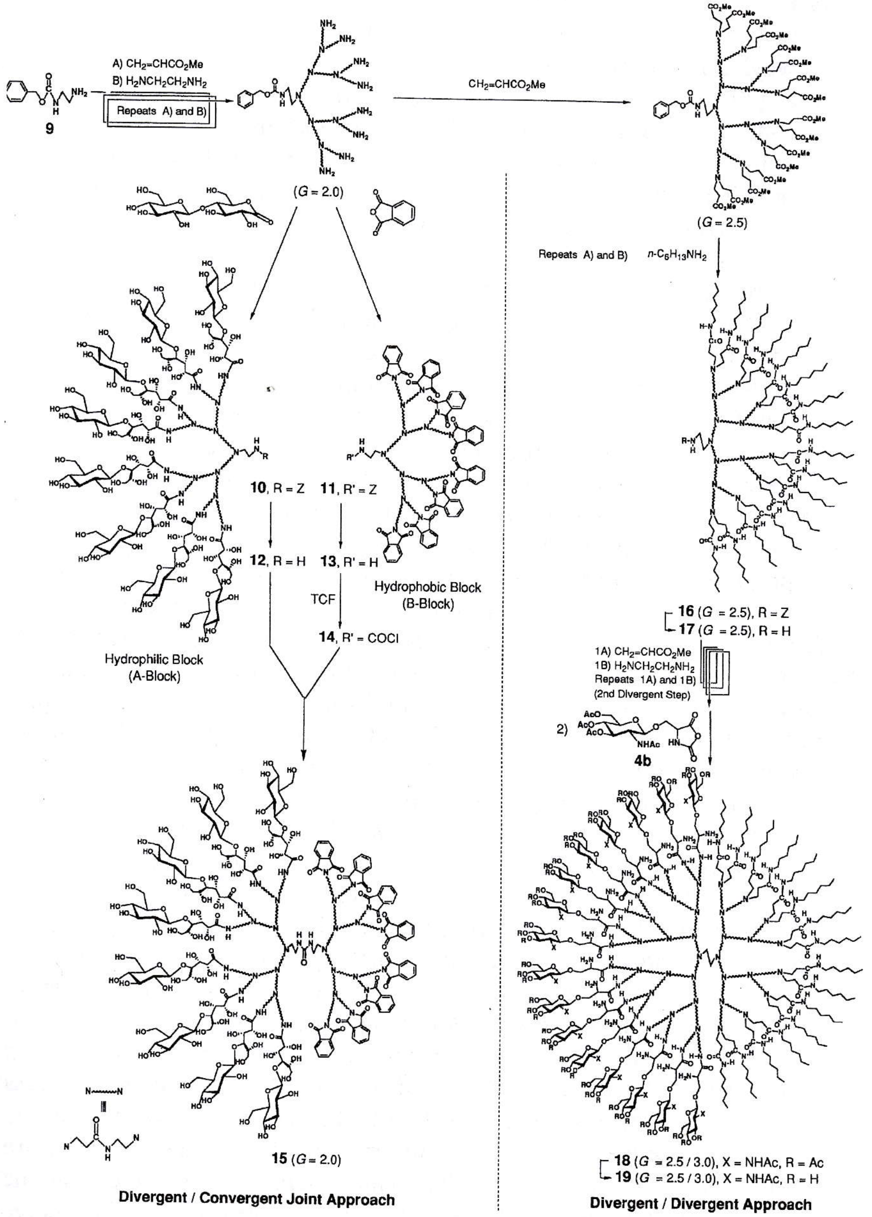
A star-shaped dendrimer has been synthesized by radial-growth polymerization of sarcosine *N*-carboxyanhydride initiated with poly(trimethylene imine) dendrimer [model (c) in Fig. 1] [17]. Polysarcosine chains linked with terminal groups of the dendrimer are shrunk in an aqueous solution. Core-shell copolymers, where the shell is formed from rigid, conductive ionic polyacetylene arms and an initiator interior is spheroidal aliphatic ply(amido amine) dendrimer, have been synthesized by Balogh et al. [18]. The thermal stability of the dendrimer improves dramatically as a result of copolymer formation. Kimura et al. [19] have synthesized the dendrimer-based multiarm copolymers as a temperature-sensitive nanoscopic capsule for catalysts. The catalytic activity of the poly(propylene imine) dendrimer with poly(*N*-isopropylacrylamide) arms is controlled in response to the change in polymer conformations.

As an approach for forming dendritic monolayers, dendritic amphiphiles of the first to third generations have been synthesized from a tripeptide with dioctadecylamino tails at the C-terminal and an acetyl head at the N-terminal [20]. The molecular area in the condensed phase on the surface-pressure-area isotherm is comparable to the total area of the alkyl chain cross sections, although the packing behavior somewhat depends on the generation. This approach provides a well-defined two-dimensional arrangement of the hydrophobic tails and polar heads with desirable sequences and combinations.

Poly(propylene imine) dendrimers with both hydrophilic triethylenoxy methyl ether chains and hydrophobic octyl chains at every terminal [model (d) in Fig. 1] have been synthesized by Pan and Ford [21]. The dendrimers converted to quaternary ammonium chlorides are soluble in both organic solvents and water and solubilize lipophilic compounds in aqueous solutions. The limiting solubility in quaternized cationic dendrimers is one pyrene per dendrimer molecule. The rates of the decarboxylation of 6-nitrobenzisoxazole-3-carboxylic acid in aqueous solutions of the cationic dendrimers are up to 500 times faster than in water alone.

Amphiphilic dendrimers having the concentric but asymmetric structure [model (e) in Fig. 1] have been constructed. Both hemispheres in these dendrimers, which are called surface-block dendrimers, have different chemical structures. Fréchet and his collaborators [22] have synthesized a carboxyl- and phenyl-terminated dendritic diblock copolymer and its analogs, where the interior is composed of benzyl ether pendant groups. The liquid membrane of amphiphilic dendrimers is aligned at the interface between water and an immiscible organic solvent.

AB-type surface-block dendrimers have also been synthesized by the divergent/convergent joint approach or divergent/divergent approach with a half-protected initiator core, as shown in Scheme 1 [23]. Amphiphilic AB-type surface-block dendrimers display characteristic surface activity. Surface tension versus dendrimer concentration curves for aqueous solutions of *N*-acetyl-*D*-glucosamine/*n*-hexyl and hydroxyl/*n*-hexyl terminated poly(amido amine) dendrimers show the remarkable decrease with increasing the dendrimer concentration and reach the constant value through a two-step decrease. The CMCs obtained are listed in Table 1. The two-step process of surface tension decrease, where the first CMC is one order lower than the second, implies the existence of a precursor like a dimeric aggregate before the formation of regular micelles. The cmcs increase with increasing the generation of the dendrimer, although those are not sensitive to the change of hydrophilic surface groups from *N*-acetyl-*D*-glucosamine to hydroxyl. This is attributed to the increase of the hydrophilicity/lipophilicity balance due to the fractional increase of amido amine moieties.



Scheme 1 Synthesis process of surface-block poly(amido amine) dendrimers. (From Ref. 23b.)

TABLE 1 Critical Micelle Concentration (CMC) of Amphiphilic Dendritic Polymers at 25°C

Generation		First CMC (10^{-4} M)	Second CMC (10^{-4} M)	Occupied area (A^2/terminal)
N-acetyl-D-glucosamine/*n*-hexyl terminated poly(amido amine) dendrimer	2.0		0.27	1.8
	3.0		0.82	5.2
	4.0		1.8	19
Hydroxyl/*n*-hexyl terminated poly(amido amine) dendrimer	3.0		0.87	6.3
Methyl ester-terminated poly-(amido amine) dendrimer-*block*-poly(2-methyl-2-oxazoline)	3.5		19	24
	4.5		—	36
	5.5		1.2	55

Source: Refs. 23 and 28.

Nierengarten et al. [24] have synthesized a globular diblock dendrimer, where a dendron conjugated C_{60} units in the branching shell and peripheral long alkyl chains is attached to a poly(benzyl ether) dendron with ethylene glycol terminal chains. The resulting dendrimer with hydrophobic chains on one hemisphere and hydrophilic ones on the other forms stable Langmuir firms with perfect reversibility in successive compression/decompression cycles and well-ordered multilayer Langmuir–Blodgett firms. This unique approach suggests that the nonamphiphilic molecules such as fullerenes attached in an amphiphilic structure can be efficiently incorporated in thin ordered films.

III. AMPHIPHILIC HYBRIDS OF DENDRIMERS WITH LINEAR CHAINS

One group of amphiphilic dendritic polymers is a head-tail block copolymer where a linear polymer is attached to a focal point of a dendron or a functional site of the core in a dendrimer. Polystyrene has been combined with poly(propylene imine) dendrimers [model (f) in Fig. 1], and the solution properties of the head-tail diblock copolymers as amphiphiles have been investigated [25]. The resulting amphiphilic macromolecules have the chemical structure composed of a hydrophilic head and a lipophilic tail as well as traditional surfactants.

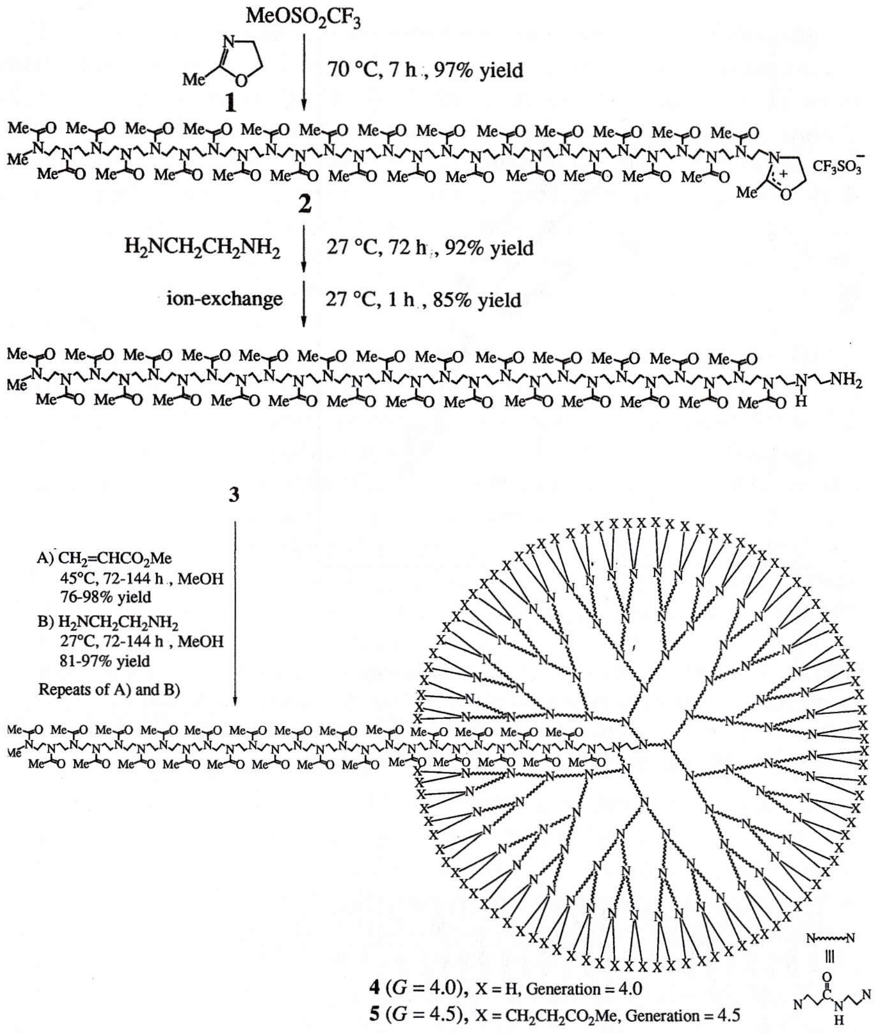
Fréchet and his collaborators [22b,26] have synthesized an amphiphilic dendritic-linear diblock copolymer with a hydrophobic poly(benzyl ether) dendron head and a hydrophilic poly(ethylene oxide) tail. It should be noticed that the solvent affinity of head and tail blocks in this copolymer is inverse to that in traditional surfactants. The stability and conformation of poly(benzyl ether) dendrons with linear oligo(ethylene glycol) tails have been studied by Kampf et al. [27].

Aoi et al. [28] have synthesized two dendritic-linear diblock copolymers. One is a surface-*N*-hexylamide-type poly(amido amine) dendrimer/polysarcosine [poly(*N*-methylglycine)] diblock copolymer, and another is a methyl ester-terminated poly(amido amine) dendrimer-*block*-poly(2-methyl-2-oxazoline) (Scheme 2). Both are a hydrophobic dendrimer-hydrophilic linear polymer hybrid identical to Fréchet's hybrid. These copolymers display surface activity as proved by the surface tensiometry: the surface tension of aqueous solutions of the latter diblock copolymer decreases with increasing copolymer concentration until the cmc, as seen in Fig. 2. The CMCs lower with increasing the generation of hydrophobic dendritic block (Table 1). This aspect is due to the increasing rigidity of the dendritic block occurring from the increase of generation, which is consistent with the increase in occupied area per terminal group, as seen in Table 1. The aggregation number of a diblock copolymer of generation 5.5 in an aqueous solution is about 103. Figure 3 illustrates an adsorption model of poly(amido amine) dendrimer/polysarcosine diblock copolymer at the air–water interface.

Solution properties of linear-dendritic diblock copolymers with a linear poly(ethylene oxide) block and a methyl ester-terminated dendritic poly (amido amine) block have been investigated by Iyer et al. [29]. Copolymers with a longer poly(ethylene oxide) chain length possess the unimolecular micellelike structure. Johnson et al. [30] have linked a linear poly(ethylene oxide) block to a dendritic poly(amido amine), where the amino terminal groups are functionalized with stearic acid to make the dendritic block hydrophobic. The structure of monolayers formed from the resulting macroamphiphile has been investigated at the air–water interface.

Amphiphilic AB-type diblock copolymers consisting of hydrophilic linear poly(ethylene oxide) and hydrophobic dendritic carbosilane have been synthesized by Chang et al. [31]. Their amphiphilic nature is highly dependent on the size of the hydrophobic dendron block: the first and second generations of dendritic carbosilane blocks form micelles in aqueous solutions. The average diameters of the micelles are 120 and 170 nm, respectively, which are one order larger than those of traditional surfactant micelles.

Both terminals of hydrophilic linear polymers, poly(ethylene glycol)s or poly(ethylene oxide)s, have been replaced by hydrophobic poly(benzyl ether) dendrons [model (g) in Fig. 1] [26,32]. These ABA-type hybrids change the conformation from the extended structure to the coiled one during an increase of hybrid concentration and form mono- and multimolecular micelles depending on the dendron generation, hybrid concentration, and solvent.



Scheme 2 Synthesis process of poly(amido amine) dendrimer-*block*-poly (2-methyl-2-oxazoline). (From Ref. 28a.)

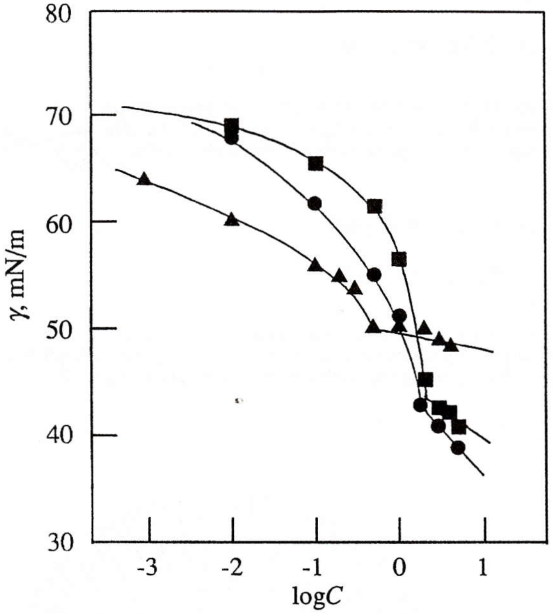


FIG. 2 Surface tension (γ) of aqueous solutions of dendritic-linear diblock copolymers, methyl ester-terminated poly(amido amine) dendrimer)-*block*-poly(2-methyl-2-oxazoline), as a function of logarithmic copolymer concentration (*C*) at 25°C. Generation: ■, 3.0; ●, 4.5; ▲, 5.5. (From Ref. 28b.)

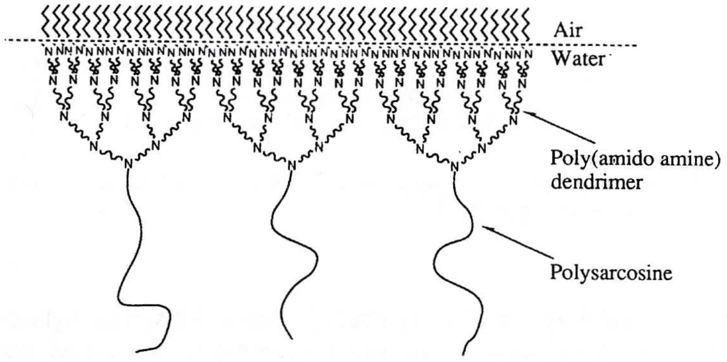


FIG. 3 An adsorption model of a surface-*N*-hexylamide-type poly(amido amine) dendrimer/polysarcosine [poly(*N*-methylglycine)] diblock copolymer of 2.5 generation at the air–water interface. (From Ref. 28b.)

Two poly(amido amine) dendrimers have been linked with aliphatic methylene chains from 2 to 12 [33]. A hybrid with a long aliphatic chain (C = 12) shows the ability to host the hydrophobic dye in an aqueous solution. This result implies a strong tendency of dye probe to associate with methylene chains. Moreover, the interactions of these hybrids with anionic surfactants generate supramolecular assemblies. The "dumbbell-shaped" triblock copolymers based on a linear oligothiophene and poly(benzyl ether) dendrons have been synthesized, and their aggregation behavior in solutions has been investigated [34]. Five to six molecules are assembled in aggregates.

Amphiphilic dendritic-linear block copolymers with a variety of AxBx-type topologies have been prepared [model (h) in Fig. 1] [35]. The A blocks are composed of the first- through third-generation dendrons from 2,2-bis(hydroxymethyl)-propionic acid, while the B blocks are poly(ε-caprolactone) chains. The macromolecules are amphiphilic polymer surfactants with polar hydrophilic heads and nonpolar hydrophobic tails.

Four-arm star poly(ethylene oxide) has been linked, at the periphery, with poly(benzyl ether) dendrons [model (i) in Fig. 1] [26,36]. Amphiphilic starlike hybrid copolymers with dendritic groups behave as the stimuli-responsible hybrid macromolecules for organic solvents.

IV. AMPHIPHILIC POLYDENDRIMERS

Side chains of linear polymers were modified by dendrons. Kaneko et al. [37] have synthesized polydendrimers by polymerizing dendritic phenylacetylene monomers [model (j) in Fig. 1], which are produced by the repetitive coupling reaction of 3,5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene with [4-(trimethylsilyl)phenyl]acetylene as a starting peripheral group. The polyacetylene-substituted polydendrimers with the well-defined dendritic and rodlike structure indicate the good membrane-forming ability and may possess additional properties such as electrical conductivity, nonlinear optics, and magnetism. The oxygen separation ability of the membrane of the first-generation polydendrimer is higher than that of the zeroth generation, affording potential application to a highly selective polydendrimer membrane.

Poly(phenylenevinylene)s substituted with dendritic side chains have been synthesized by using methyl-3,4,5-trihydroxybenzoate as a starting material [38]. These polymers self-order in the solid state and yield thermotropic nematic phases.

Polystyrenes with 3,4,5-tris[4-(*n*-tetradecan-1-yloxy)benzyloxy]benzoate or 3,4,5-tris[3′,4′,5′-(*n*-dodecan-1-yloxy)benzyloxy]benzyl ether side groups have been synthesized by Prokhorova et al. [39]. The monodendron-jacketed linear polystyrenes are visualized as wormlike cylinders. The conformational change and ordering of these polydendrimers depending on the branching density have been investigated. The positional and orientational order of the adsorbed wormlike cylinders is explained by the specific interaction of the alkyl substituents of the monodendrons with the highly oriented pyrolytic graphite surface used. However, if the substitution of the monodendrons by the alkoxy groups is too dense, regular adsorption of alkyl tails is embedded.

The conducting polythiophene, which is functionalized exclusively with aliphatic ether convergent dendrons as solubilizing groups, has been prepared from a dendrimer-oligothiophene hybrid monomer [40]. Both the dendrimer size and the dendrimer-to-thiophene unit ratio were varied in order to obtain an optimum solution-processable conducting polymer. Conductivities measured for iodine-doped thin films of the polythiophene with six thiophene repeating units for each third-generation dendron is as high as 200 S/cm.

Wormlike polydendrimers consisting of flexible and noninteracting segments have been synthesized by a stepwise chemical modification of a poly(methylhydrosiloxane) through alternating sequences of hydrosilylation and alkylation reactions on every monomer unit of the polymer [41]. The polysiloxane backbone is stretching out, upon carrying carbosilane dendrons, from the Gaussian random conformation for the zeroth generation to the almost fully extended rodlike conformation for the second generation, depending on the overcrowding of the branches at the periphery. However, even fully extended polymethylsiloxane polydendrimers prove incapable of the orientation and the liquid crystal formation because of their dynamic flexibility.

Dendrimers are also used for chemical modification of chitosan, which is a polysaccharide composed of mainly β-(1-4)-2-amino-2-deoxy-D-glucopyranose repeating units [42]. The sialic acid-bound chitosan-dendrimer hybrids have the potential for biological purposes because of nontoxic and biodegradable properties of chitosan and of biopharmaceutical advantages of dendrimers.

Grayson and Fréchet [43] have reported the divergent grafting of aliphatic polyester dendrons from a poly(p-hydroxystyrene) backbone. Wyatt et al. [44] have synthesized optically active polydendrimers by the polymerization of binaphthyl poly(benzyl ether) dendrimers. The energy migration from dendritic side chains to the conjugated polybinaphthyl main chain was observed. The increase in dendron generation influences the thermal transition of the polybinaphthyls.

Poly(*para*-phenylene)s with hydrophobic and hydrophilic pendant moieties have been synthesized as a prototype of an amphiphilic cylinder with the potential to segregate lengthwise [45]. Monomers equipped with unlike dendrons or combinations of hydrophilic dendron-hydrophobic linear chain and hydrophobic dendron-hydrophilic linear chain were polycondensed with diboronic acid [models (k) and (l) in Fig. 1]. The surface-pressure-area isotherms provide the evidence that these hybrid polymeric amphiphiles segregate lengthwise into hydrophobic and hydrophilic domains.

Diblock copolymers composed of polydendrimer and linear styrene polymer [model (m) in Fig. 1] have been synthesized by Sivaniah et al. [46]. In the polydendrimer, the semifluorinated alkane mesogens are attached as three-arm monodendrons to the isoprene backbone. The surface topology was reported.

Imae et al. [47] have synthesized methacrylate-acrylate diblock copolymers with unlike side chains, where the poly(methacrylate) block is modified by poly(benzyl ether) dendrons and the side chains of poly(acrylate) block are perfluorooctylethers. Copolymers form spherical aggregates with various sizes in solutions and thin films at the air–water interface. Further characterization is presently underway.

V. AGGREGATES OF AMPHIPHILIC DENDRITIC POLYMERS

Some dendrimers and hybrid copolymers are associated into various molecular assemblies due to their amphiphilic characters. The molecular arrangement of poly(benzyl ether) dendrimer at the air–water interface has been investigated by Saville et al. [48]. The dendrimer forms a bilayer structure. The molecules in the layer next to the water subphase are ellipsoidal in structure due to compression and contain water (about 25% in volume fraction), while the molecules in the layer next to air are spherical and contain no water.

Poly(propylene imine) dendrimers, where the terminal groups are modified with palmitoyl chains, form stable monolayers at the air–water interface [15]. Those adopt a cylindrical shape at the air–water interface: hydrophobic chains are aligned perpendicularly to the interface and the dendritic poly(propylene imine) interior faces the water subphase. In aqueous solutions at pH = 1, dendritic surfactants are self-assembled into small spherical aggregates with the bilayer structure. It was shown from the theoretical calculation of molecular volumes that the dendritic surfactants have the highly asymmetric conformation and the shape of the dendritic poly(propylene imine) interior is distorted within monolayer at the air–water interface and within the aggregates in the solution. These results indicate the high flexibility of the poly(propylene imine) dendrimers.

Spreading of a carbosilane dendrimer containing hydroxyethyl terminal groups has been investigated at the air–water interface [49]. The carbosilane dendrimer forms a monolayer, which shows a sharp transition presumably into the bilayer structure, while the hyperbranched polymer of an identical chemical composition does not show any transition.

The monolayer stability and molecular conformation at the air–water interface have been studied for Langmuir films formed from dendritic-linear diblock copolymers, poly(benzyl ether) dendrons with linear oligo(ethylene glycol) tails [27]. The copolymers with third- and fourth-generation dendrons form stable Langmuir films, but the fifth-generation dendron does not. Longer hydrophilic tails increase the stability of the Langmuir films. The molecular area of the dendrons at the air–water interface increases linearly with the molecular weight. It was certified that the dendritic blocks take a vertically elongated shape at the air–water interface and become flatter as the generation increases.

The monolayers of a linear poly(ethylene oxide) block linked to a poly(amido amine) dendron, where terminal groups are modified with stearic acid, have been investigated by Johnson et al. [30]. The hybrid diblock copolymer intermixes the linear blocks with the poly(amido amine) dendrons at low surface pressure, while it forms the stable, distinct monolayers with a linear block resting in the subphase and stearate groups extending into the air at high surface pressure. Stearate groups form a distinct ordered layer separating from the third-generation poly(amido amine) dendron, whereas those are intermixed with the fourth-generation poly(amido amine) dendron due to the surface curvature of the higher-generation dendron. Moreover, the poly(ethylene oxide) block is intermixed with the water subphase after being kept for at least 10 h.

Liebau et al. [50] have recently synthesized dendritic multisulfides of the first to fifth generations by the modification of poly(propylene imine) dendrons with dialkyl sulfide chains. At the air–water interface, the dendritic multisulfides form stable Langmuir monolayers with densely packed alkyl chains pointing to the air and dendron exposed to the water subphase. Langmuir–Blodgett films transferred onto a gold surface remain the original densely packed structure. Different surface architectures of the same compounds are prepared by solely varying the preparation procedure. Self-assembly of the dendritic multisulfides from a solution onto a gold surface leads to a flattened orientation of the dendrons on it. The formation of the surface-spread dendritic structure can be attributed to the adsorption onto the gold surface of not only the sulfide moieties in the alkyl chains but also the tertiary amines in the dendron.

The aggregation behaviors of dendrimers and dendritic-linear diblock copolymers as amphiphiles in solutions have been examined. Percec et al. [51] have reported the synthesis and characterization of hyperbranched dendrimeric polyethers with the spacers of alkyl chains and the alkylated phenol chain terminals. The copolymers present the thermotropic transformation between isotropic phase and enanthiotropic nematic liquid crystalline mesophase.

Generation-dependent aggregation of amphiphilic diblock copolymers of polystyrene with poly(propylene imine) dendrimers have been reported by van Hest et al. [25]. The morphological change of aggregates depends on the generation of hydrophilic dendrimer and the pH of solution: block copolymers composed of poly(propylene imine) dendrimers of 4.0, 3.0, and 2.0 generations form spherical micelles, micellar rods, and vesicles, respectively, which are similar in shape but different in size than those of traditional surfactant molecules. The block copolymer of the lowest generation shows the inverted micellar behavior.

Microphase separation of diblock copolymers consisting of linear polystyrene and carboxylic acid-functionalized poly(propylene imine) dendrimers has been reported by Román et al. [52]. The copolymers are spontaneously self-assembled into microdomains. By increasing the dendrimer generation, the microlattice morphology changes from hexagonally packed cylinders with styrene matrix to lamellar phase.

The dendritic structure is sometimes modified in order to control the morphological behavior. Donnio et al. [53] have functionalized the terminal groups of poly(amido amine) and poly(propylene imine) dendrimers by mesogenic units, which are derived from salicylaldimine bearing one, two, or three terminal aliphatic chains. The compounds exhibit liquid crystalline properties, correlating with the number of terminal chains grafted on the peripheral mesogenic units. The existence of one chain per mesogenic unit makes favorable the parallel arrangement of the molecules and induces smectic mesomorphism. On the other hand, molecules with two or three aliphatic chains take radial dispersion, leading to the formation of columnar structures.

Organized films of carbosilane liquid crystalline dendrimer with cyanobiphenyl mesogenic groups have been examined at different temperatures and film thicknesses [13]. Rectangular and hexagonal lattices are found in the single layer. With increasing film thickness, smectic layers are formed and, then, domains consist of aggregates of flat-on lying. Edge-on standing smectic layers are found in thick films. The domains exhibit the layered structure of different thicknesses and orientations. Height variation of domains caused by anisotropic changes of lattices of the smectic layers occurs with the change of temperature. The isotropization temperature increases with increasing the generation.

The surface topology has been investigated for diblock copolymers composed of linear polystyrene and polydendrimer that have semifluorinated alkane mesogens attached as three-arm monodendrons to the isoprene backbone [46]. The amphiphilic macromolecules in the smectic phase separate into diblock copolymer microstructures. There are periodic surface structures, so-called domes that arise from the arrangement of the semifluorinated mesogens at the polymer surface.

Imae et al. [54] have reported the formation of organized adsorption layers by amphiphilic surface-block poly(amido amine) dendrimers composed of two hemispheres with hydroxyl and *n*-hexyl terminals. On solid substrates, unlike which the adsorption film of a symmetric poly(amido amine) dendrimer is rather flat, the surface-block dendrimer displays the layer texture, indicating the formation of bilayers and their accumulation, as shown in Fig. 4. The bilayer is formed by pairing between hydrophobic terminals of two dendrimers (see Fig. 5). The surface of the adsorption film takes hydrophilic character, suggesting that the hydrophilic hydroxyl terminals face the solution. The adsorption is more abundant by the third-generation dendrimer than by the fourth-generation dendrimer, in agreement with the generation dependence of the cmc as seen in Table 1. Similar adsorption behavior is also observed by a surface-block poly(amido amine) dendrimer with amino and *n*-hexyl terminals but not by a dendrimer with *N*-acetyl-D-glucosamine and *n*-hexyl terminals (see Fig. 4).

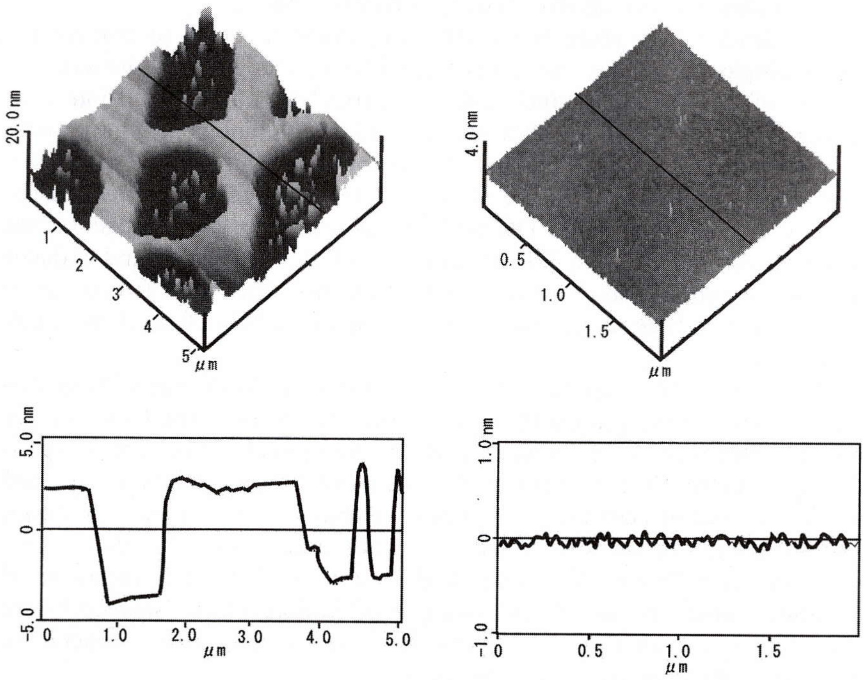


FIG. 4 Atomic force microscopic images and their section analyses of 15 min adsorption films on mica surface from aqueous 0.01 wt % solutions of the third-generation surface-block poly(amido amine) dendrimers. Left, hydroxyl/*n*-hexyl terminated dendrimer; right, *N*-acetyl-D-glucosamine/*n*-hexyl terminated dendrimer.

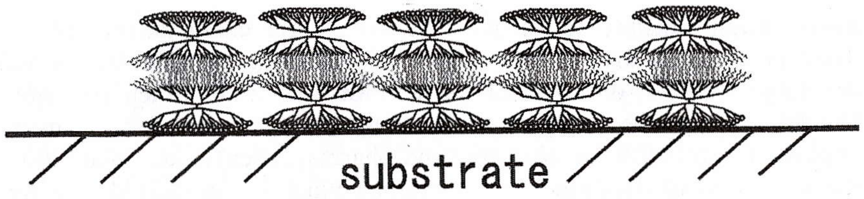


FIG. 5 A schematic model of coupled adsorption film of a surface-block hydroxyl/*n*-hexyl terminated poly(amido amine) dendrimer on substrate

Dendrons are focused as building blocks of supramolecular or self-assembled architectures. The role for controlling the architectural shape through the self-assemblies from tapered and conical nanodendrons has been reviewed [55]. Tapered nanodendrons are associated into cylinders and then hexagonal columns, that is, hexagonal liquid crystal, while conical dendrons form spheroidal assemblies in dilute solutions and cubic phase in concentrated solutions.

Poly(benzyl ether) dendrons with a carboxylate anionic focal point are self-assembled through central trivalent lantanide cations (Er^{3+}, Tb^{3+}, and Eu^{3+}) [56]. This self-assembly is applicable in the design of energy-harvesting devices and amplifiers for fiber optics. The complexes show the dependence of luminescence activity on the size of the dendritic shell. The observed luminescence enhancement is attributed to the large antenna effect and the site isolation effect of poly(benzyl ether) dendron framework for a lantanide cation within a dendritic sphere, preventing the mutual interaction of lantanide cations and decreasing their rate of self-quenching.

Characteristic and functional dendrimers can be also achieved by the molecular assemblies of simple dendrimers. A novel architecture of dendrimers, a core-shell tecto-(dendrimer), has been synthesized [57]. In the tecto-(dendrimer), a poly(amido amine) dendrimer molecule as a core is covalent-bonding with a shell of other poly(amido amine) dendrimers. The dimensions increase as a function of the sum of core-shell tecto-(dendrimer) generation.

VI. CONCLUSIONS

Dendrimers, named after their dendritic structure, are highly branched polymers, which have the strictly controlled chemical structure and geometric arrangement of layer moieties. The main characteristics of the dendritic structure are microcavity for encapsulating small molecules and the large number of terminal groups for acting as functional sites. Dendrimers may be conspicuous by these characteristics for the many applications in industrial, cosmetic, and pharmaceutical fields. In addition, the utilization of dendrimers as a building block for organized architectures is possible by the introduction of amphiphilicity in their chemical structure.

In this section, the structures and properties of amphiphilic dendritic polymers were reviewed. The amphiphilicity is accomplished by the derivation of unlike blocks in concentric dendrimers. Copolymers of dendritic blocks with linear polymers are also amphiphilic. Many investigations have reported the synthesis and characterization of amphiphilic dendritic polymers and the architectures by them in solutions, at the air–water interface, and on the solid surfaces. Some applications of amphiphilic dendritic polymers were also reported. The dendritic amphiphiles behave and are associated like traditional surfactants and linear block copolymers. However, we expect that future research will demonstrate more the predominance of dendritic amphiphiles over traditional surfactants and linear block copolymers. Especially, the water-soluble and nontoxic dendronized amphiphilic compounds are useful for biomedical applications, and studies must be carried out for determining their applicability.

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