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PHYSICOCHEMICAL PROPERTIES OF DENDRIMERS AND DENDRIMER COMPLEX

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2.1. INTRODUCTION

Dendrimers are recognized as a kind of polymers, since they have high-molecular weights similar to conventional polymers [1–4]. However, the morphological structure of dendrimers synthesized via branching is rather sphere, different from that of linear polymers. The difference in morphology is reflected on their physicochemical properties. It should be made special mention that the viscosity of dendrimer solutions is very low like that of low-molecular weight molecules. Such unique morphological structure and physicochemical properties allow dendrimers the characteristic usages on industrial and biomedical demands.

One of typical dendrimers, poly(amido amine) (PAMAM) dendrimer, has an ethylenediamine core, tertiary amine branches, and alkyl amide spacers [5,6]. Similar type of dendrimer with tertiary amine branches is poly(propyleneimine) (PPI) dendrimer, which has alkyl chain spacers [7,8]. Namely, these dendrimers consist of simple biocompatible chemical units and are expected the characteristics of nontoxicity, nonimmunogenicity, and biodegradation. Moreover, their dendritic back bones are rather flexible and their interior should be cavitary. Accordingly, these dendrimers must be adequate for biomedical (pharmaceutical, therapeutical, and diagnostic) utilizations such as drug delivery systems (DDS), gene carriers, and diagnostic imaging.

In this chapter, biocompatible dendrimers and their physicochemical properties are reviewed and dendrimer complexes are subsequently introduced. In Section 2.2,

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PAMAM and PPI dendrimers as well as homologues relating are taken up as biocompatible dendrimers. Poly(amino acid) dendrimers and sugar-substituted dendrimers are also in the category of biocompatible dendrimers. Physicochemical properties of biocompatible dendrimers are explained in Section 2.3. Static and dynamic structures and doping, adhesion, aggregation, and luminescence properties of dendrimers are concerned there. Finally, in Section 2.4, the complexation of dendrimers with functional molecules (including drugs), polymers, and inorganic materials is described as biomedically applicable materials like DDS, medical imaging agents, gene vectors, and capsules of DDS.

2.2. DENDRIMERS

2.2.1. PAMAM Dendrimers

PAMAM dendrimers are the most distributed and investigated dendrimers, because their synthesis process is not so complicated and standard dendrimers are commercialized. The dendrimers can be typically synthesized by the divergent pathway through the two-step process of Michael addition of methylacrylate and of amidation of ethylenediamine [9]. When two-steps are complete, the “generation (G)” of the dendrimers comes up. In the case of PAMAM dendrimers, the defect of terminal groups occurs at more than fourth generation because of the crowded terminal groups. The dendrimers have methylester terminals after the Michael reaction but take carboxylic acid and amine terminals after hydrolysis and amidation reactions, respectively. These terminals of dendrimers are possible to modify into any expected functional groups such as alkyl chains, oligomers, polymers, enzymes, proteins, drugs, and so on. Thus, the physicochemical properties of PAMAM dendrimers including solvophilicity depend on the function of terminal groups. Then these core–shell block dendrimers are termed as “monomolecular polymer micelles” [10]. Meanwhile, star dendrimers with linear polymer terminals resemble “core–corona polymer micelles” [11,12].

When a monoamine compound is a core (focal point) material, a “dendron” is synthesized. Since the dendron has an additional functional species at a focal point besides branches/spacers and terminal groups, the functionality of the dendron increases. The focal point is sometimes used for anchoring dendrons on the target materials: A thiol focal point favorably anchors on gold substrates [12] and a siloxane group is adequate for metal oxide surfaces [13]. Conversely, if terminal groups of the dendron are bound on materials, the focal point can be a functional point. When two dendrons with different (hydrophilic and hydrophobic) terminal groups are combined at focal points by the divergent/convergent joint approach, surface block or Janus-type dendrimers are built [14–16]. These dendrimers accumulate into bilayers at the liquid–solid interface.

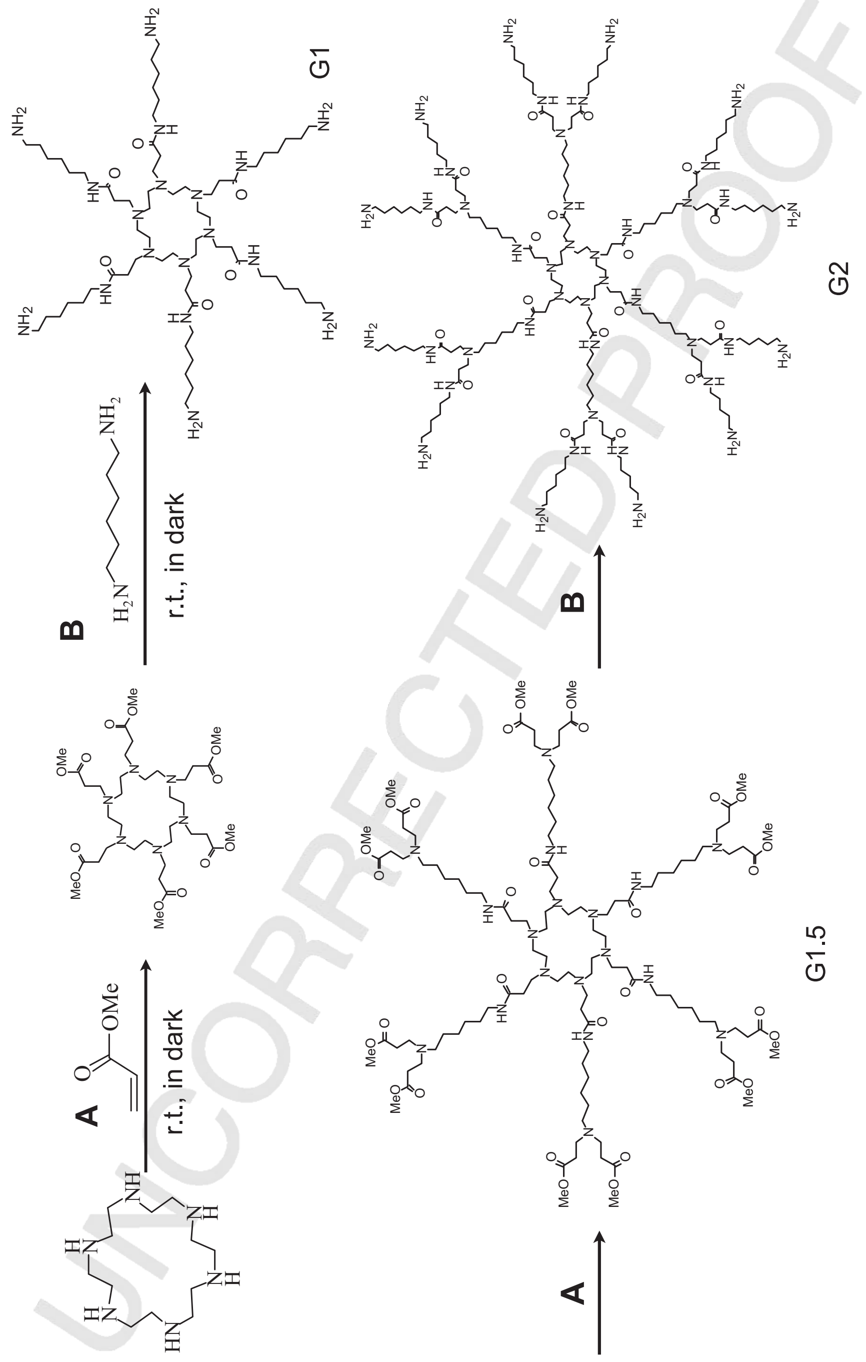
There are reports of the synthesis of dendrimers and dendrons with long alkyl (hexyl) chain spacers [17]. PAMAM-type derivatives are synthesized from an azacrown core and a siloxane or hydroxyl focal point through a Michael addition by methylacrylate and an amidation by hexamethylenediamine, as illustrated in Scheme 2.1 [13,18–20]. The derivatives are more flexible and have larger void volumes to encapsulate guest molecules than PAMAM dendrimers and dendrons.

Different types of dendritic polymers are synthesized using dendrons as components: Dendrons can be conjugated with linear polymers. When focal points of PAMAM dendrons are combined with a linear polymer, head-to-tail dendritic polymers are synthesized [21,22]. These polymers display behaviors of amphiphilic molecules, that is, the decrease of surface tension at critical micelle concentration (CMC), the aggregation to micelles or vesicles above cmc, and the formation of Gibbs monolayer at the air–water interface. Dendrons are combined on a linear polymer as side chains [23]. Then different types of amphiphilic dendritic polymers can be synthesized depending on the combination of a liner polymer and dendron side chains.

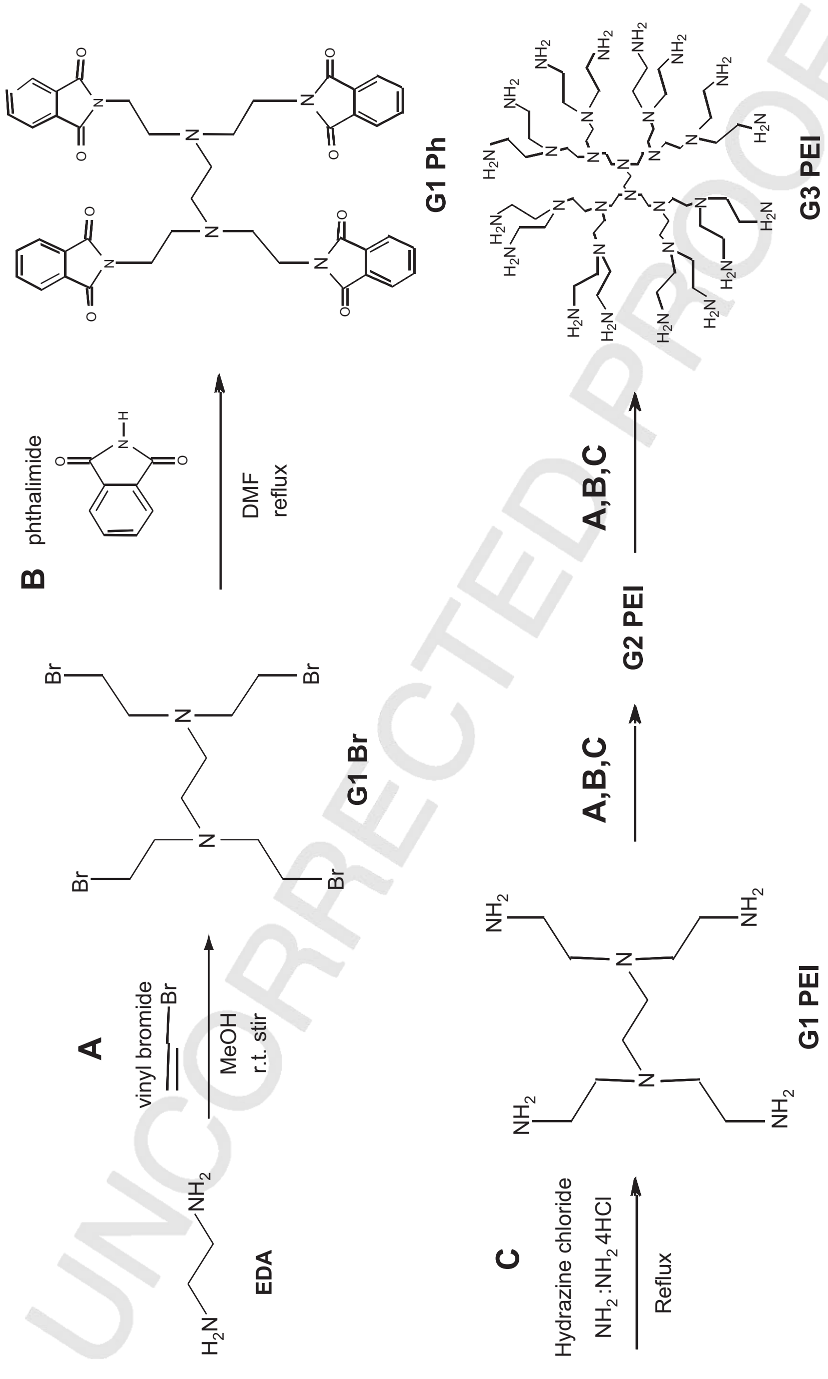
2.2.2. Other Dendrimers

Poly(propyleneimine) (PPI) dendrimer is another type of biocompatible dendrimer [7,8,24–27]. These dendrimers can be produced from a primary amine core by a repetitive reaction sequence of Michael addition of acrylonitrile followed by heterogeneous hydrogenation of the nitrile end groups to the primary amine end groups with a Raney cobalt catalyst. Head-to-tail dendritic polymers are also synthesized from PPI dendron and a linear polymer [28]. Poly(ethyleneimine) (PEI) dendrimers are a homolog of PPI dendrimers [29]. Different from the synthesis procedure of PPI dendrimers, PEI dendrimers are synthesized by the divergent process from an ethylenediamine core through Michael addition reaction for alkylation and Gabriel amine reaction for producing amine-terminal, as seen in Scheme 2.2. Since homologs of poly(alkyleneimine) dendrimers have spacers of alkyl chain $(CH_2)_n$ ($n = 2, 3$), they are more hydrophobic than PAMAM dendrimers.

Amino acids are also valuable biocompatible units, and dendritic and dendrigraft (hyperbranched) poly(amino acid)s are synthesized [30–42]. The synthesis of dendrigraft poly(L-lysine) is carried out by polymerization of *N*-carboxyanhydride in dimethylformamide or in water [31,32,38,39,41]. Meanwhile, dendritic poly(L-lysine) is prepared as follows [30,35,36]. *N*-*t*-butoxycarbonyl (Boc)-protected lysine is coupled with hexamethylenediamine by the 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyl-uronium hexafluorophosphate (HBTU)-1-hydroxybenzotriazol (HOBt) method, and then the deprotection (removing of Boc-groups) is performed by trifluoroacetic acid. For growing up to the upper generation, free amino terminal groups of lower generation dendrimers are utilized for the coupling reaction with *N*-Boc-protected lysine. Same procedure is applied to the synthesis of dendritic poly (L-ornithine) from an ethylenediamine core using *N*-Boc-protected ornithine [35]. These materials are useful for biomedical purposes [40]. Poly(ornitine) dendrimers/dendrons can be synthesized even by a different route [33]. The syntheses of dendrimers and dendrons are got started by reacting an ornitine derivative to a 1,4-diaminobutane dihydrochloride core and an alanine methylester hydrochloride focal point, respectively. Poly(glutamate) dendrimers are prepared via an iterative divergent/convergent binomial synthesis starting from a commercially available Boc-



SCHEME 2.1 Synthesis scheme of poly(amido amine)-type dendrimers with an azacrown core and long alkyl chain spacers.



SCHEME 2.2 Synthesis pathway of poly(ethyleneimine) dendrimers from an ethylenediamine core.

glutamic acid [42]. This procedure allows the production of the first-, second- and fourth-generation poly(L-glutamate) dendrimers and their stereochemical homologs, poly(D-alt-L-glutamate) dendrimers, and moreover enables versatile postfunctionalization of core and periphery in the dendrimers.

For the fabrication of dendrimers with biocompatibility, nontoxicity, and non-immunogenicity, the functionalization on the periphery of the dendrimers is also valuable. There are some reports of core–shell dendrimers, where terminal groups of core dendrimers are substituted by biocompatible molecules like amino acid or sugar. A simple one-step synthesis is adopted for end-capping the terminals of fourth-generation PAMAM dendrimers by amino acids (serine, cysteine, and aspartic acid) [43]. The resultant dendrimers bearing heterobifunctionality at the periphery can be chemoselectively conjugated by the multiple moieties such as drugs and imaging agents.

Sugar-substituted globular dendrimers (sugar balls) are synthesized: Amine terminals on PAMAM dendrimers synthesized by the divergent process are substituted by maltose or lactose derivatives [44]. When a sugar-substituted L-serine *N*-carboxyanhydride (NCA) is used, sugar-peptide type or star-type sugar balls are produced [45,46]. This polymerization reaction displays extremely high rate constants, due to the high condensation of NCA monomers on the highly polarized local surface area on the dendrimers. Sugar balls are synthesized even by the convergent method [47]. The surface block (Janus-type) dendrimers (half sugar balls), where one half surface of dendrimers is introduced sugar terminals but another half surface is occupied by alkyl chains, are synthesized by different synthesis routes [48]. These dendrimers easily aggregate through the cross-linkage with surfactants in aqueous solutions [49]. PAMAM dendrimers are also functionalized with mannose and glucose by sequentially adding isothiocyanato carbohydrate of mannose and glucose to dendrimers, and the relative affinities of the dendrimers with Concanavalin A are evaluated [50]. Sugar-containing poly(ornitine) dendrimers/dendrons are synthesized by terminating the periphery of dendrimers/dendrons with by maltose or lactose [33].

2.3. PHYSICOCHEMICAL PROPERTIES OF DENDRIMERS

2.3.1. Static and Dynamic Structures

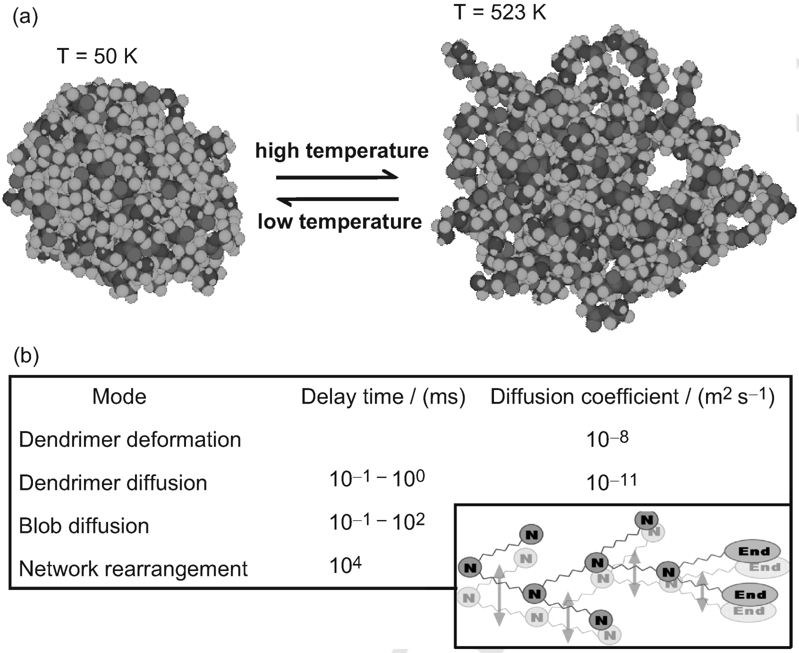
Since dendrimers are synthesized stepwise from a multifunctional core and raise the number of terminals via an *n*-functional branching unit, the functional terminals increase in number by *n*-times at each branching process, namely, so-called generation. With increasing the generation, the morphological structure of dendrimers becomes globule. In case of PAMAM dendrimers, fourth and above generations are required to be a globular structure, according to the simulation [27]. Since the periphery of high-generation dendrimers is dense due to large number of terminal groups, the lack of the branching growth occurs on the process of synthesis at generations such as more than fifth in the case of PAMAM dendrimers. Meanwhile the branching interior is expected to be rather less dense.

In an early stage where dendrimers have been discovered, some investigators theoretically estimate the conformational structures of dendrimers, from the viewpoint of segment distribution in dendrimers, on the basis of different theories and computer simulation. Especially, the distribution of the terminal groups is a main concern of physicists [51–54]. The computer simulation results in different conclusions. One investigation reports reported the gradual increase of the density from core to periphery [51] but another was opposite [52]. Otherwise, the intermediate region of the dendritic structure is densest [53,54]. The problem on such simulation is that the physicists do not care about the chemical structure of dendrimers. The radial sizes of dendrimers have also been estimated by means of the theoretical calculation [55–57]. The estimation coincides with the experimental hydrodynamic radius of PAMAM dendrimers [55]. The molecular structure of PPI dendrimers has been investigated on the basis of both theoretical and experimental viewpoints [27]. The calculation displays a maximum in radial distribution of density for generations higher than first.

The experimental evaluation of shapes, internal structures, and dynamics of small particles such as dendrimers is not necessarily easy but one of the techniques is small-angle scattering. The fine structures, for example, shapes, densities, and compositions of dendrimers are evaluated by a small-angle neutron and X-ray scattering (SANS and SAXS) [58]. It is clarified from SANS experiments that PAMAM dendrimers are positioned between a gauss chain and a sphere in their structure and behave like polyelectrolytes [59,60]. Moreover, the affect on their morphology is discussed as a function of pH, ion strength, solvent species, and temperature [61,62]. Figure 2.1a shows a structural variation of a PAMAM dendrimer depending on the temperature. On the other hand, PPI dendrimers with a short spacer distance behave rather like a hard sphere [27,63]. It should be noted that the protonation of tertiary amines in PPI dendrimers or the concentration increase of PPI dendrimers results in the characteristic correlation peaks in SANS [61,64,65]. When terminal groups of PPI dendrimers are substituted by polysarcosine chains, the chains behave like linear polymers in poor solvents, that is, they are contracted [11]. The analysis of molecular diameter is carried out for an aggregate of a 5.5th-generation poly(2-methyl-2-oxazoline)-block-PAMAM dendrimer [21,22]. Moreover, the interaction of Gaussian form between pairs of dendrimers is also derived from the shape [66].

The external contrast variation method on SANS, that is, the variation in mixing ratio of hydrogen and deuterium in solvent, allows us the calculation of molecular weight and radial scattering length density of dendrimers [67]. By using this procedure and labeled molecules, the distribution of terminal groups in dendrimers are analyzed [66–70]: The terminals of a PAMAM dendrimer are localized at the periphery of the dendrimer [68], but the urea terminals of a PPI dendrimer are interiorly embedded [69].

The segment density distribution and the solvent permeability depending on the molecular structure are evaluated by the computer simulation fitting for SANS intensity curves of fifth-generation dendrimers with different chemical species at interior and periphery, that is, hydroxyl-terminated PAMAM dendrimer, hydroxyl-terminated PPI/monoamido amine (AMAM) dendrimer, and glucopeptide-terminated PAMAM dendrimers (sugar balls) [71–74]. The analysis is carried out under



Mode	Delay time / (ms)	Diffusion coefficient / ($m^2\ s^{-1}$)
Dendrimer deformation		10^{-8}
Dendrimer diffusion	$10^{-1} - 10^{0}$	10^{-11}
Blob diffusion	$10^{-1} - 10^{2}$	
Network rearrangement	10^{4}	

FIGURE 2.1 (a) A static structural variation of an amine-terminated fourth-generation PAMAM dendrimer depending on the temperature. (b) A list of delay times and diffusion coefficients at various modes of PAMAM dendrimers with the estimated dynamic structure. (*See the color version of this figure in colour plate section.*)

the assumption of a "concentric five layers" model, where each generation has the different segment density distribution and solvent permeability. It is inferred that while the hydroxyl-terminated AMAM species on a PPI dendrimer exists at the periphery because of their hydrophilicity, hydroxyl-terminals on a PAMAM dendrimer have a tendency to turn into the interior due to the hydrogen bonding with tertiary amines/amides in the dendrimer. Sugar balls make a thick peripheral layer in the PAMAM dendrimer by the steric hindrance of bulky glucopeptide-terminals. In short, the segment density distribution profiles differ from dendrimer to dendrimer, although a PPI dendrimer is less dense than a PAMAM dendrimer as estimated from their chemical structures. By the way, the solvent, water, penetrates into dendrimers in proportion to the number of hydrophilic units like amine and amide groups. Of course, there is an exception of no or less water penetration in a dense segment density distribution layer such as the glucopeptide periphery.

Results of SANS analysis demonstrate that the segment density distribution in dendrimers strongly depends on their chemical structure, but the water penetration stands on the chemical species rather than the segment density distribution and the chemical structure of dendrimers. Moreover, enough water penetration occurs even in a dendrimer with dense periphery (shell). Incidentally, it is open to a question that how can water pass through such dense shell. Then the dynamics of dendrimers should be considered at the same time, since dynamic movements of segments can raise provisional water channels through even dense shell.

The proton and carbon-13 NMR relaxation investigations of PAMAM dendrimers indicate that the chain dynamics are insensitive to any steric crowding at the molecular surfaces [75,76]. Afterward, self-diffusion coefficients of dendrimers are evaluated by a pulsed magnetic field gradient NMR and the results indicate that they depend on the concentration of poly(allylcarbosilane) dendrimer [77]. This behavior is similar to that of globular proteins. From solid-state NMR investigations, fast and slow modes of dynamics are detected relating to the vibrations of phenyl terminals of poly(phenylene) dendrimers and substituted phenyl rings [78]. It can be claimed that the highly dense shells exist in these dendrimers.

The dynamic (quasi-elastic) neutron scattering and neutron spin echo (NSE) analyses are also valuable techniques on the evaluation of the fine structural dynamics of molecules in nanoscale. The segment dynamics of fluorocarbon-terminated poly (carbosilane) dendrimers are investigated by the dynamic neutron scattering [79]: the dynamic structure factors are contributed by the segment translational diffusion in a dendrimer interior and the rotational diffusion in fluorocarbon-terminals. The former is one order smaller than the latter. According to the dynamics of hydroxyl- and glucopeptide-terminated PAMAM dendrimers investigated by NSE, two (fast and slow) relaxation modes exist in a dilute aqueous solution but only one (slow) mode appears in the concentrated solution [73,80]. The fast mode is attributed to the deformation motion of dendrimers involving the harmonic motion of dendrimer segments. The slow mode is assignable to the translational diffusion and it is the same order as the diffusion coefficient from dynamic light scattering. The delay times and the diffusion coefficients at the various modes of PAMAM dendrimers are listed with the estimated dynamic structure in (Fig. 2.1b). After all, it can be noted that the water penetration should be promoted by not only the static structure of dendrimers but also by their dynamic structure. This result suggests the possible doping of small molecules like drugs in dendrimers. Dynamics of dendrimer are investigated even in the presence of linear polyelectrolytes [81–84].

2.3.2. Doping Property

From the analysis of the neutron scattering results of dendrimers, the additional valuable information besides the conformation of dendrimers is obtained in association with the solvent (water) penetration, as described above. Water penetrates abundantly in the interior of a hydrophilic PAMAM dendrimer rather than of a hydrophobic PPI dendrimer. Another unique result is that the water penetration in a PAMAM dendrimer is enough high even when it is shielded by a dense shell of oligosuger. The result of the dendrimer dynamics supports that the dynamic motion of dendrimer segments creates a provisional path (channel) for water (small molecules) to penetrate into a dendrimer through the dense shell.

Doping ability of dendrimers is examined by using some small molecules. The doping of a hydrophobic fluorescence-probe, pyrene, depends on the chemical structure and generation of dendrimers [85–94]. For instance, PAMAM dendrimers dope pyrene more preferably than PPI dendrimers, and fifth-generation dendrimers have a better ability of doping than the fourth-generation dendrimer, owing on the size of the void volume [90]. The doping ability of dendrimers with simple terminal groups like amine and hydroxyl is influenced by pH. Since PAMAM and PPI dendrimers are protonated below pK_a (6.65) of tertiary amines [95], and the repulsion force among tertiary amines increases with protonation of amine, the void volume in the interior of dendrimers increases and the amount of doped pyrene increases at acidic pH.

The chemical species of terminal groups also affects on the doping of small molecules. Since amine-terminated dendrimers are protonated below pK_a (9.20) of primary amine [95], such dendrimers assist the doping more than neutral terminal groups due to the open shell. In this connection, a hydroxyl-terminated fourth-generation PAMAM dendrimer encapsulates 2.5 pyrene molecules at pH 5.85, which is larger than the case of amine-terminated homolog [90]. However, the situation is different on the case of dendrimers with thick shells. When the terminal groups of PPI dendrimers are substituted by PAMAM dendrons, larger amount of pyrene are doped in the dendrimers at alkaline pH than acid pH [94], different from the amine-terminated PPI dendrimer [90]. The solubilization attains 2.7 pyrene molecules per PPI(third-generation)-PAMAM(third-generation) dendrimer at pH 11. The shrunk neutral PAMAM shell should inhibit the release of pyrene. Figure 2.2 makes a comparison of the pH-dependent doping of pyrene between two kinds of dendrimers.

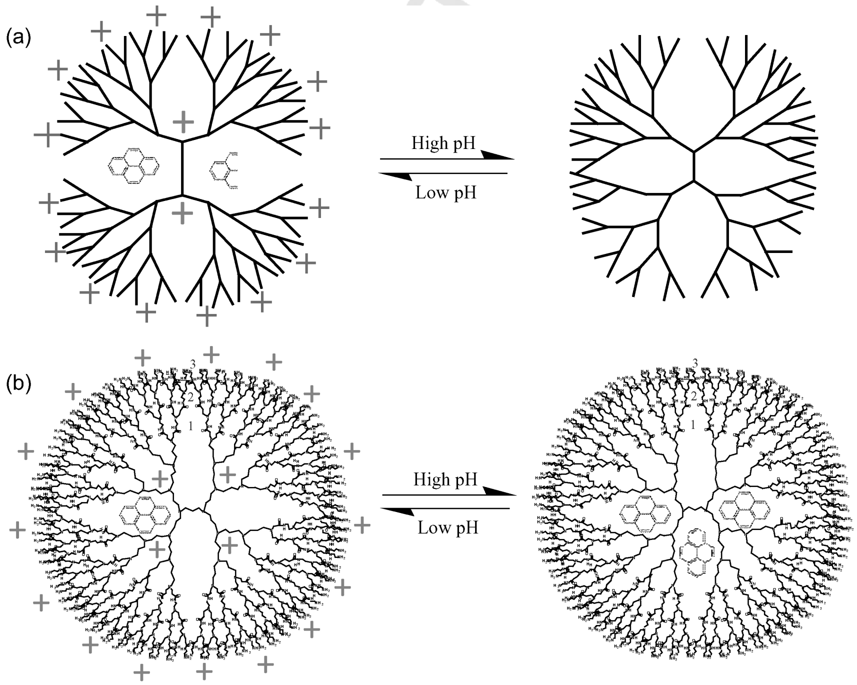


FIGURE 2.2 The pH-dependent doping of pyrene in dendrimers. (a) Amine-terminated fifth-generation PPI dendrimer. (b) PPI dendrimer-core:PAMAM-shell dendrimer.

Polymer micelles consisting of block copolymers with hydrophobic dendron-pendant side chains have many nanocavities owing to the steric hindrance of bulky dendrons (see Fig. 2.3a) [91]. Therefore, 23 pyrene molecules are doped in a dendron block core. Incidentally, same polymer micelles can encapsulate 36 molecules of oil yellow [91] and 200 to 300 molecules of water-insoluble organic 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical [92].

The doping ability is valuable for the removal of pollutants from water [96–101]. A hydrophilic compound is effectively extracted by means of fluorinated PPI dendrimers from water into supercritical CO_2 [96]. There are reports of the highly selective, efficient liquid–liquid extraction of various water-soluble organic dyes from water to organic solvents (dichloromethane and toluene) by propadecyl-terminated PPI dendrimers [97]. PPI dendrimers with octyl and octadecyl peripheries as “nanosponges” can be utilized for the removal of polycyclic aromatic hydrocarbons in water down to the ppb order [98–100]. Dendrimers utilized in these investigations are water insoluble amphiphilic molecules, that is, molecules bearing the hydrophilic interior and the lipophilic periphery in order to dope hydrophobic guests. The disadvantage of these dendrimers is a tedious procedure on the separation of dendrimers from doped molecules and extraction media. Creative trial is the development of solid phase adsorbents. The surface of porous silica particles is modified by amphiphilic dendrons, that is, PAMAM dendrons with alkyl chain terminals [101]. This kind of solid phase adsorbent can extract different types of

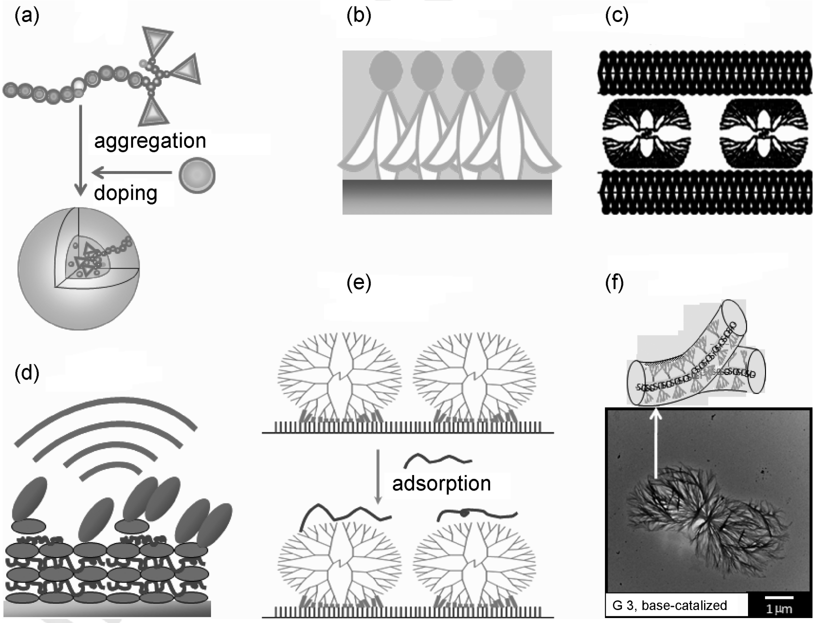


FIGURE 2.3 Various nanoarchitectures consisting of dendrimers/dendrons. (a) Polymer micelle. (b) Langmuir–Blodgett film. (c) Lamellar layer. (d) Layer-by-layer accumulation. (e) Dendrimer self-assembled monolayer. (f) Dendritic nanohydrogel. (*See the color version of this figure in colour plate section.*)

pollutants like dyes and detergents simultaneously. The adsorbent is easy to separate from the medium and to release guest molecules.

2.3.3. Adsorption and Aggregation Properties

One of unique characteristics, besides the void volume, on the chemical structure of dendrimers/dendrons is the multiple terminal groups. Such multifunctionality in a molecule presents unique adsorption/aggregation behaviors and architecture construction, different from conventional small molecules with mono- or oligo-functional groups [102]. Large number of terminal groups is effective for the adsorption of dendrimers on any interfaces [103,104]. While conventional dendrimers like PAMAM dendrimers cannot be adsorbed as Gibbs monolayers at air–water interfaces, nonspherical amphiphilic dendrimers can be adsorbed. It is common for amphiphilic molecules that the surface tension decreases with increasing their concentration and maintains almost plateau at the concentrations above a CMC. However, different from the surface activity behavior of conventional surfactants, some amphiphilic dendrimers (head-to-tail and Janus-type dendrimers) reveal the two-step process of surface tension decrease that CMCs are 10^{-4} and 10^{-5} M [21,22,48]. These results indicate the formation of preaggregates and the sequential normal micelles of dendrimers.

Head-to-tail dendrimers with hydrophobic head and hydrophilic tail fabricate Langmuir monolayers at air–water interfaces [105]. The stability of the monolayers depends on the hydrophobic and hydrophilic balance, and the molecular structure changes from vertically extended shape to horizontal one with increasing generation. Fullerodendron consisting of fullerene and anthracenyl PAMAM dendrons forms Langmuir and Langmuir–Blodgett films, since these dendrons are amphiphilic (see Fig. 2.3b) [106]. Molecular arrangement in the films depends on the generation of dendron and affects electrochemical properties of the films.

An adsorption of dendrimers occurs even at the interface of water and soft surface. PAMAM dendrimers are adsorbed on two bilayer surfaces of lamellar liquid crystal to form new lamellar layers consisting of the repeating structure of a surfactant bilayer and a dendrimer monolayer (see Fig. 2.3c) [107].

Many investigations are reported concerning to the adsorption of dendrimers on solid surfaces from solutions [108–114]. Adsorption layers constructed by a layer block carbosiloxane dendrimers with cholesterol terminals are the uniformly ordered monolayers or multilayers on mica surfaces, depending on the dendrimer concentration, and are rearranged to the loose layers by thermal annealing [111]. Surface-block (Janus-type) dendrimers with hydrophilic and hydrophobic half surfaces also form well-ordered stepwise adsorption layers on mica surfaces [15,16]. In this case, bilayers are built by coupling of two dendrimers by the hydrophobic interaction of half surfaces and accumulating bilayers to be multibilayers. Electrostatic layer-by-layer films of dendrimers on silicon substrates are also prepared by alternating adsorption of amine-terminated and carboxylic acid-terminated dendrimers [113]. Adlayer formation of carboxyl-terminated PAMAM dendrimers on mica and gold substrates depends on the dendrimer concentration and the solution pH [114]. However, monolayers are always preserved at whole pH region after desorption procedure to the solvent, indicating the formation of SAMS. Electrostatic layer-by-layer films are even possible to be created between dendrimers and linear polymers [115]. Such films can be utilized to control the spacer thickness, for instance, on the surface Plasmon fluorescence investigation of energy-transfer-controllable organic thin films (see Fig. 2.3d) [116]. In most cases described above, PAMAM dendrimers incorporated into adsorption layers are flattened to be oblate ellipsoid (axial ratio = 1/3 to 1/6), that is, the unit layer thickness is less than the diameter of the dendrimers in solutions, since the chemical structure of dendrimers is flexible.

Self-assembled monolayers (SAM) on substrates are fabricated using dendrons with functional focal points [117]. Dendrons with an organothiol focal point form homogeneously SAM on gold substrates with high packing efficiency. Structural difference of Langmuir films with adsorption films is investigated for poly(phenylene sulfide) dendrons with a carboxyl focal point as against for poly(phenylene sulfide) dendrimers [118]. The Langmuir firms are stably organized by facing a focal point of a dendron to the subphase but the rearrangement is demanded for dendrimers in Langmuir films. Identically, SAMs of dendrons are well ordered especially after annealing, although unidirectional domains exist in the adsorption films of dendrimers both before and after annealing. The behavior of poly(phenylene sulfide) dendrons is in contrast with a case of poly(benzylether) dendrons [119–121]. The difference originates in the crystalline ordering by the taper-type former dendron and the amorphous arrangement by the cone-type latter dendron.

There are trials to immobilize dendrimers on conventional SAMs [122,123]. PAMAM dendrimers are immobilized by covalent bonding on a mercaptoundecanoic acid (MUA) or MUA/mercaptopentane SAM. The dendrimer-immobilized substrate is applied for doping of gases as a receptor of the gas sensor. The response depends on the character and the size of dendrimers. Covalent-bonded SAMs of dendrimers is also fabricated onto a 3-mercaptopropionic acid (MPA) SAM on an Au substrate or onto a carboxylic acid-terminal pattern in photolithographic line patterns on a silicon substrate (see Fig. 2.3e) [124,125]. The SAMs can be turned to practical use for the selective adsorption of linear polymers such as poly(glutamic acid), sodium hyaluronate and DNA.

The adsorption layers of PAMAM and PPI dendrimers on conventional SAMs are also reported. Dendrimers are bound onto a MPA SAM on an Au substrate [126,127]. Adsorption occurs at the two-step process of monolayer and accumulation adsorption, and the adsorption structure is different between PAMAM and PPI dendrimers depending on the interaction of dendrimers with the MPA SAM, that is, the electrostatic interaction for both dendrimers and the hydrogen bonding for PAMAM dendrimers.

The surface modification by dendrimers/dendrons has an effect on the properties of solid surfaces. Especially the change of surface forces on the substrates remarkably affects on the utilization of the dendrimer-coating surfaces. The characteristics of the surface adsorption of hydroxyl-terminated PAMAM dendrimers is examined on glass substrates in water by the direct surface force measurement, and the forces between two surfaces are discussed in association with the adsorption mechanism and the adsorption state [71,128]. When the adsorption less than monolayer of dendrimers, the weak repulsion force at the "inward" process and the adhesion force at the "outward" process occur owing to the attractive force between the adsorbed dendrimers and the glass substrates. At the high adsorption state to be monolayer, the repulsion force increases at the "inward" process but the adhesion force at the "outward" process disappears due to the growing repulsion force between the adsorbed nonionic dendrimers, indicating that the steric repulsion force by the mixing (osmotic) effect becomes stronger than the van der Waals attractive force. That is, since the repulsion force works between the particles with the dendrimer-coating surface, the particles do not give rise to flocculation or aggregation in water. This result implies the advantage of surface modification by dendrimers rather than linear polymers for the dispersion of particles, since the latter sometimes plays a role of the cross-linkers between particles.

The attractive interaction between dendrimers/dendrons raises the self-aggregation in media. Amphiphilic dendrimers/dendrons, especially, head-to-tail dendrimers with hydrophilic head and hydrophobic tail fabricate assemblies, for example, spherical and rodlike micelles, wormlike micelles, reversed micelles, vesicles, networks etc., resembling conventional surfactants [129–134]. The structure and size of micelles depend on composition, concentration, solvents, temperature [135], and dendrimer generation [131,132] in accordance with the Israelachvili's prediction [136]. Diadic dendron-linear polymers produce variant aggregates from monomolecular to multimolecular micelles, depending on the size, component unit, and concentration of molecules [130]. Dendritic star polymers, where terminals of star polymers are substituted by dendrons, fabricate monomolecular core–shell micelles with different morphologies, standing on the medium [133]. The head-to-tail hybrids consisting of PPI dendrimers and polystyrene form micro domain, hexagonal, or lamellar structures, depending on the generation of dendrimers [137], and the core–corona hybrids with linear polymers replaced by terminal groups which promote the formation of liquid crystal yield the thermotropic liquid crystals [138].

The Israelachvili's prediction allows us to select another type of molecules, namely, dendrons, as building blocks of self-aggregates. It is easy for cone-type dendrons to form spherical micelles in dilute solutions and cubic mesophases in concentrated solutions, and taper-type dendrons aggregate into cylinders and construct hexagonal liquid crystals [139,140]. These architectures should be focused in relation to the construction of polyhedron virus, tobacco mosaic virus, or higher organisms. Linear polymers with side chains of pendant dendrons take a rigid rodlike morphology and display a thermotropic liquid crystal phase [141]. This kind of dendritic polymers must be worthy of being remarked as liquid crystal materials with novel structures and characters.

2.3.4. Luminescence Property

Fluorescent probes are extensively used as convenient and excellent markers in biological and medical sciences because of the easy detection and the highly sensitive power. A green fluorescent protein (GFP) is now popular as a biocompatible fluorescent dye, and fluorescent nanoparticles are also the targeted drugs on the diagnostic imaging. These fluorescent markers always fall on issues of the influence to biological organisms. Therefore, the development of adequate markers is still demanded. Then amine-branched dendrimers are one of expected biocompatible phosphors.

The strong blue luminescence from PAMAM dendrimers has been confirmed in 2004 and later [142–145], although the weak luminescence has been indicated before that [146–153]. Similar strong fluorescence is discovered even for PPI and PEI dendrimers [29,145,154], other amine-branched dendritic polymers like hyperbranched poly(amino ether)s, polysiloxanes with dendron side chain, poly(propyl ether imine) dendrimers, polyethyleneimines, or fullerodendrons [155–159], and even triethylamine [150]. The investigation is carried out at different conditions including generations, terminal groups (–OH, –COOH, $–NH_2$, etc.), pH, temperature, and aging time; and the origin of the luminescence has been discussed on the basis of the experimental evidences. A solvatochromic phenol blue, instead of oxygen, also can induce the luminescence of PAMAM dendrimers based on a host–guest complexation of phenol blue molecules with tertiary amino-branching sites [160]. An inherent photoluminescence is found even for oxygen-built-in poly(propyl ether imine) dendrimers, which emit fluorescence without any external oxygen owing to bear tertiary amines as branching sites and ether as linkers [158].

The important facts are as follows: (1) Fluorescent dendrimers have a tertiary amine branching in common; (2) Oxygen or oxydized molecules must be doped or oxygen atoms are built in the dendrimer; (3) Coexistent oxygen molecules enhance the fluorescence of dendrimers but do not quench it; (4) Number of oxygen molecules corresponding to number of tertiary amines exists in a fluorescent dendrimer [29]; (5) Doped oxygen molecules influence in particular on binding energies of tertiary amines, but they do not chemically react with dendrimers and can be released from dendrimers in vacuo [161]; and (6) Occupation by oxygen molecules in the void volume of the dendrimer is obvious from the fact that the successive complexation of the dendrimer with two dopants (oxygen and phenol blue) is a competitive process [160].

In association with the origin of fluorescence of amine-branched dendrimers, the formation of an ”exciplex” between two species, namely, a tertiary amine and an oxygen atom is first presumable as a driving force for the intrinsic fluorescence emission of the dendrimers, in consequence of the excitation of the lone-pair electrons of tertiary amine or oxygen through either incident light or electrochemical activation [160]. Another possibility is the formation of a peroxyl radical, which should be originated from tertiary amine and oxygen [162]. A short-lived radical species absorbs a near visible light, and then the fluorescence of the fast relaxation is blue. Incidentally, a particular peroxyl radical of triethylamine-$O_2\cdot$ and a strongly red-shifted transient absorption band at $\sim$380 nm are directly observed by a laser flash photolysis.

It should be noted that the visualization of fluorescent dendrimers is possible and indispensable for the utilization as an imaging agent. Dendritic nanohydrogels fabricated by the polymerization of PAMAM dendrons (see Figs. 2.3f and 2.4a) [156], cotton fibers dyed by PAMAM dendrimers (see Fig. 2.4b) [145], and porous silica particles (beads) surface-modified by PAMAM dendrons (see Fig. 2.4c) [160] are

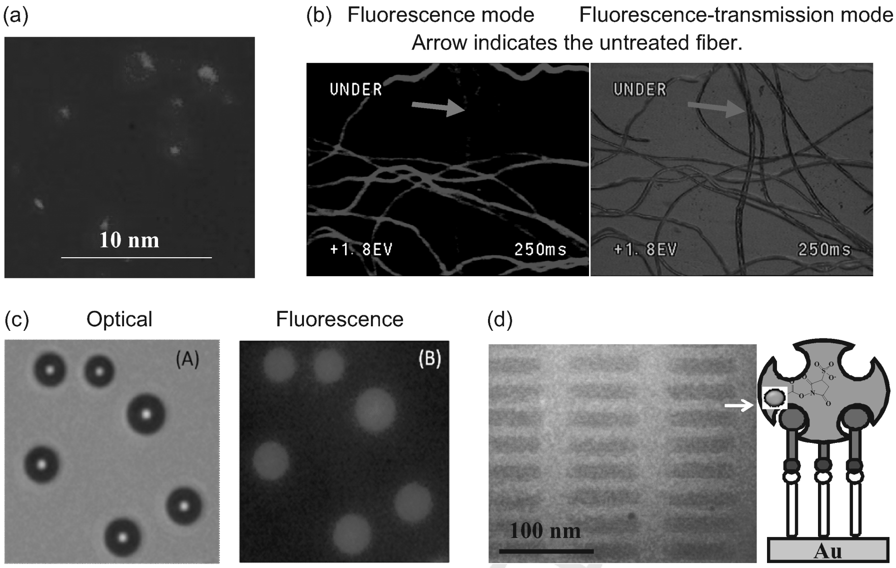


FIGURE 2.4 Visual observation of fluorescent dendrimers. (a) Fluorescent dendritic nanohydrogels. (b) Fluorescent cotton fibers. (c) Fluorescent beads. (d) Binding of Biotin with fluorescent avidin. (*See the color version of this figure in colour plate section.*)

visualized by a fluorescence microscope. The selective electrostatic adsorption of fluorescent dendrimers is visually observed on the substrates with counter ionic patterns and hydrophobic patterns [161]. An avidin molecule is labeled with $G_{4.5}$ PAMAM dendrimers through the amide chemical bond (see Fig. 2.4d) [163]. It is confirmed by the visual observation of fluorescent dendrimers that avidins bound fluorescent dendrimers interact selectively with biotins immobilized on the patterned substrates. These results suggest that the photoluminescent dendritic polymers are valuable as biocompatible and chemically stable fluorescent markers without quenching by oxygen.

2.4. DENDRIMER COMPLEXES

2.4.1. Complexes with Functional Molecules

The conjugation of functional molecules in dendrimers is valuable to encourage the functionality of dendrimers. The target of the functionalization is expanding from the simple ionic/nonionic and hydrophilic/hydrophobic characterization to the barrier function and the chemical and biomedical functions. Especially the incorporation of enzyme and immunologic/therapeutic/diagnostic drugs is considered in the field of the biomedical science.

There are three portions of core (or focal point), spacer/branching, and periphery in dendrimers for functional groups to be incorporated. The incorporation into core (or focal point) and spacer/branching portions in dendrimers must be carried out in the process of the synthesis of dendrimers. There are reports of syntheses of photofunctional dendrimers. One case is the dendrimer–porphyrin conjugations, where the porphyrin molecules are a core molecule [164–167]. Azobenzenes are also utilized as a core molecule and the building blocks as well as the substitutes on the periphery of the dendrimers [168–173]. These are visible light absorbers and photochromic materials. The mechanism of the molecular energy transfer in a dendrimer is similar to the principle of the energy transfer in the biological system and inductive for the development of the devices for the conversion of light energy into electrical energy.

Since PAMAM dendrimers with an azacrown core and long alkyl chain spacers acquire more flexibility of dendron branches than conventional PAMAM dendrimers, the dendrimers can take the “face-on” arrangement at the air–water interface and their Langmuir monolayer easily captures gold nanoparticles from the water phase [18–20]. Thus dendrimers and Au nanoparticles fabricate the Janus-type Langmuir monolayer. Spacer-modified PAMAM dendrimers with internal amide and isopropanol groups are synthesized [174]. This spacer is redox-active.

A focal point of dendrons can also be chemically functionalized. Focal points such as linear polymers, thiol, or siloxy species in dendrons can be effective in the formation of adsorption monolayers at the air–water interface or of self-assembled monolayers on the solid substrates, as described in Section 2.3.3. Fullerodendrons with a fullerene focal point behave as amphiphilic molecules and form Langmuir and LB films where fullerodendrons arrange regularly and such ordered structures can be possibly utilized on the controlled preparation of metal nanoparticles and as one of components in the field-effect transistor [106,159,175,176].

The functionalization of the periphery portion in dendrimers is most commonly achieved by postsynthesis. Lipase is covalent-bonded on poly(phenylene sulfide) (PPS) dendrimers. The hydrolysis activity of olive oil to fatty acid is effectuated with advantage on these enzyme-immobilized PPS dendrimers [177]. Marking of dendrimers by fluorescent molecules increases the potential versatility of dendrimers in biomedical utilization like imaging and targeting. The periphery in dendrimers is labeled by fluorophores (fluorescein derivative, rhgodamine, and carboxyfluorescence) [178,179].

2.4.2. Complexes with Polymers

One of the unique chemical characteristics of dendrimers is the large amount of terminal groups in their periphery, which are advantageous for complexation with other molecules. Especially the complexation with linear polymers is noticeable from the viewpoint of drug/gene carriers as well as the modification on the behavior of polymers in solutions like low solution viscosities. Charged dendrimers are conjugated electrostatically with oppositely charged linear polyelectrolytes, depending on the ionic strength and pH of the solution, namely, degrees of dissociation of dendrimers and polyelectrolytes, as well as their size and stiffness [81–83,180]. Possible complexations are (1) the penetration of linear chains in dendrimers, (2) the mutual penetration of dendrimers with linear chains, (3) the lapping of dendrimers by

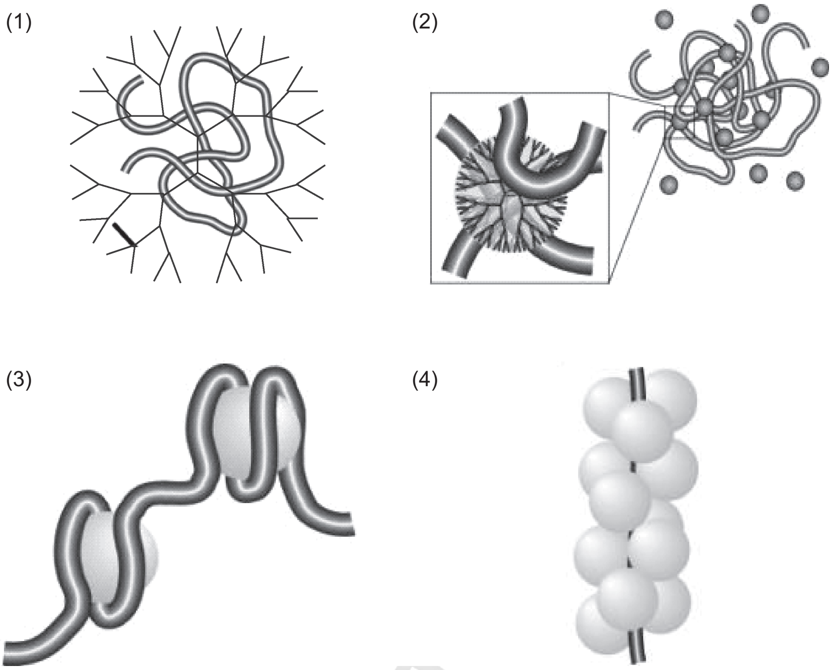


FIGURE 2.5 Possible complexations of dendrimers with polymers. (1) Penetration of linear chains in dendrimers. (2) Mutual penetration of dendrimers with linear chains. (3) Lapping of dendrimers by linear chains. (4) Surrounding of dendrimers on linear chains.

linear chains, and (4) the surrounding of dendrimers on linear chains (Fig. 2.5), depending on ionic strengths of the solutions and characters and sizes of dendrimers and linear chains [181].

The binding quantity of dendrimers is lower on glutamic acid than on hyauronic acid [84,95,182–184]. The former complexation is yielded by the electrostatic interaction and takes a configuration of mutual penetration. The binding of the latter should be reinforced by the hydrogen bonding besides the electrostatic attractive force to achieve the lapping of linear chains by dendrimers. Dendrimers are surrounded by linear DNAs and finally globules consisting of dendrimers and DNAs are created [185–187]. This structure is like a histone/DNA complex and considered to be its model. This is reasonable, since the size and shape of dendrimers are similar to water-soluble globular proteins [188]. This kind of complex is focused as artificial gene vectors for immunologic therapy.

There are many reports of the hybrids where dendrimers (or dendrons) are chemically bound with linear polymers. One group is intramolecular hybrids consisting of the combination of dendrimers/dendrons and linear polymers, which are known as head-to-tail, double-head, star, and core–corona type hybrids [103]. The hybrids occasionally behave as amphiphilic molecules, since the solvent affinity is different between dendrimers/dendrons and linear polymers. In some cases, amphiphilic hybrids distinctively display the surface activity and aggregation behaviors, as described in Section 2.3.3.

Another group of intramolecular hybrids is constructed by covalent-binding dendrons on linear (or branched) polymers [156,189–192]. The developed polydendrons take a worm-like cylindrical structure, and their adsorption films on substrates are well ordered because of the hydrophobic interaction between alkyl terminals and/or the interaction between terminals and substrates [190,191]. However, the flexibility of polydendrons decreases with the generation of dendrons [192]. Meanwhile, the polymerization of dendrons with a siloxy focal point produces dendritic polydendrons with polysiloxane backbone at low monomer concentrations and worm-like cylinders at high concentrations [156].

In some cases, dendrons are utilized as stabilizers of linear polymers. Polyphenylenevinylene, which is a constituent of photoelectronic devices, approves solubility in organic solvents through the modification of side chains by dendrons without the depression of the photoelectronic effect [141]. Side chains consisting of an aliphatic ether dendron play a role of the protection of a main chain, polythiophene, and the enhancement of solubility in media with conserving the conductivity of the main chain [193]. Chitosan, which substitutes primary amines by dendrons, is water soluble and has examined the validity as an inhibitor for virus pathogens [184–196].

Higher functionality can be obtained by bringing in different dendrons on side chains of a linear chain. Amphiphilic polydendrons with hydrophilic and hydrophobic dendron side chains form stable Langmuir monolayers, where rigid main chains are aligned parallel to the water surface and hydrophilic and hydrophobic dendrons are faced to water and air phases, respectively [197]. Such arrangement at the air–water surface is also possible even for hydrophobic linear chains with hydrophobic dendron side chains [198]. Amphiphilic copolymers consisting of a hydrophilic block and a block with hydrophobic dendron pendants fabricate polymer micelles which have enough void volumes to encapsulate guest molecules selectively [91,92]. Copolymers composed of a block with hydrophobic dendron pendants and a block with fluorocarbon side chains form spherical micelles in solutions and Langmuir monolayers at air–water interface [199–201]. The additional hybrid is the polyurethane network which incorporates dendrons as wedges by covalent binding in chains between knots in the network, and some properties of which are varied with the generation of the dendrons [202]. This hybrid is useful for evaluating effects of nanofillers in the polymer network on dynamics of the network.

2.4.3. Complexes with Inorganic Materials

The synthesis of nanoparticles consisting of metals and metal compounds is one of attracted subjects because of the expected availability on the energy field and the medical (therapeutic and diagnostic) practice. The investigation is focused on the minimization to be nanoparticles, clusters, and/or quantum dots with sizes of a few nanometers or less, the homogeneity of particle sizes, the stabilization of the particles, and the production of various nonspherical shapes. PAMAM dendrimers are used as stabilizers of various metal nanoparticles instead of surfactants and other polymers [159,203–211]. The reduction of metal ions to zero valence is proceeded by the chelation (by the coordinate bond) of metal ions with amine groups in a PAMAM dendrimer [212,213]. When the nucleation takes place in the dendrimers, clusters and/or quantum dots are produced in the interior of high-generation dendrimers with a spherical shape (see Fig. 2.6a).

As-prepared materials are stably distributed with keeping the distance in dendrimers without aggregation or association, since nanoparticles are distributed in the void volume in the dendrimers and protected from the mutual attraction by the branched backbone in the dendrimers [214,215]. The encapsulated nanoparticles are possible to be exchanged to other metal nanoparticles by using the ionization tendency, for example, from copper nanoparticles to silver nanoparticles [213]. When the generation of dendrimers is small like less than fifth, metal nanoparticles are difficult to be formed in dendrimers, because the structure of dendrimers are open rather than closed to encapsulate nanoparticles (or clusters/quantum dots) [85,86]. Then the particles are surrounded by dendrimers and occasionally nonspherical particles are produced (see Fig. 2.6a) [159,211,216–219]. Thus the particle size, the size distribution, and the stability in media strongly depend on the generation of dendrimers and the mixing ratio of metal ion and dendrimer.

The reduction of metal ions is carried out by adding a reducer such as $NaBH_4$, hydrazine, and sodium citrate. Then the process to remove the reducer is needed after

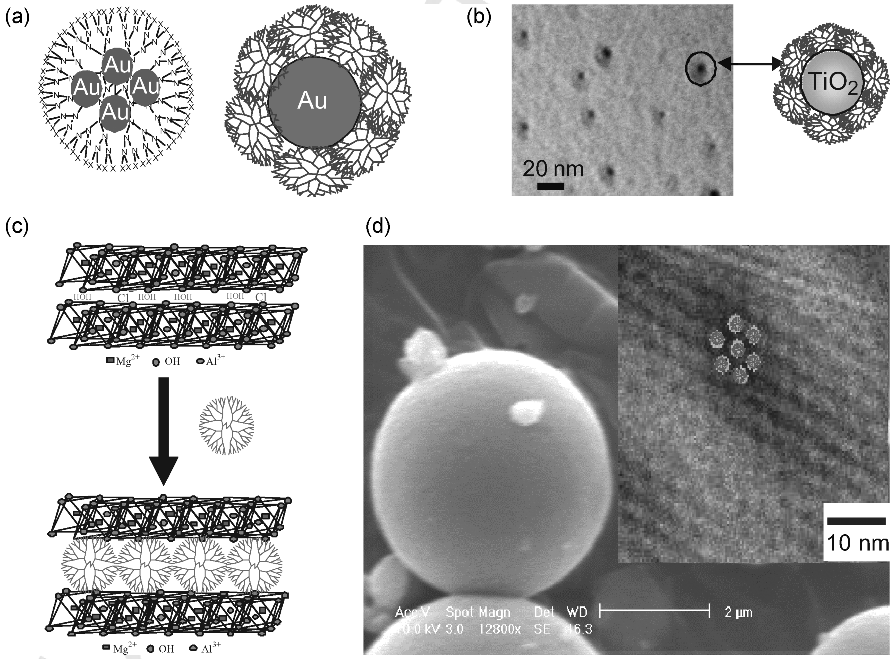


FIGURE 2.6 Complexes with inorganic materials. (a) With metal nanoparticles. (b) With metal oxide nanoparticles. (c) With clay. (d) With nanoporous material. (*See the color version of this figure in colour plate section.*)

the reaction. It is identified that metal ions are reduced to metals by the irradiation of electromagnetic waves (UV-light, X-ray, or laser) or the thermal treatment without the chemical reducer [205,210,220–222]. Although spherical particles are formed under the electromagnetic wave or the heating, the longer irradiation, the stronger light suppliance or the higher temperature results in the production of larger and heterogeneous particles. Such procedure occasionally produces various shapes of nanoparticles, for example, triangles, hexagonals, or polygonal plates and crown-shaped nanoparticles [216–219].

Metal compound nanoparticles are also possible to synthesize under protecting by dendrimers. Particles are stable in water, if dendrimers are added in the process of the synthesis, but they precipitate in the absence of dendrimers. In the synthesis of calcium carbonate nanoparticles, while the rhombohedron calcite is produced without dendrimers, the crystal structure is controlled to be spherical vaterite with $1{\sim}2\,\mu m$ size under the existence of dendrimers [223]. It should be noticed that the unstable vaterite does not transfer to the stable calcite because of the inhibition by dendrimers, carboxylate terminals of which combine on the particle surface through the Ca–O bond. Titanium dioxide nanoparticles can be fabricated by the oxidation of $TiCl_4$ or by the hydrolysis of $[(CH_3)_2CHO]_4Ti$ in the presence of PAMAM dendrimers/dendrons (see Fig. 2.6b) [13,224]. These water-dispersible nanoparticles work effectively on the photodegradation of water pollutants. Sulfide clusters or nanoparticles are synthesized by mixing sulfur ions with metal (Cd or Pb) ions [225–227].

Terminal groups of dendrimers sometimes influence on the formation and the stability of nanoparticles, and dendrimers not only contribute as a protector and a stabilizer but also are concerned with the reaction on the preparation of nanoparticles. The hydroxyl groups on sugar terminals in PAMAM dendrimers are oxidized to carbonyl groups, when gold ions are reduced to metals [228]. The complexation of β-dextrin on adamantyl terminals of PPI dendrimers strengthens the barrier ability of the dendrimer shell and inhibits the release of nanoparticles [229].

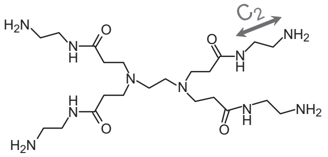
The stability of dendrimers which surround nanoparticles is occasionally broken down by the attack of compounds with the strong affinity to nanoparticles [230,231]. For instance, amine-terminated dendrimers on metal nanoparticles are easily exchanged by thiol compounds. This character is valuable for the extraction of nanoparticles from aqueous to nonaqueous media or for the modification of amphiphilicity of nanoparticles. The adherence of dendrimers is advantageous for the fabrication of films of nanoparticles [20,232–234]. On the other hand, dendrimers can be used as the “mortar” in self-assembled architectures of metal nanoparticles [211,235]. The selective adsorption ability of dendrimers also enables the domain formation, the patterned textures and the interlayer intercalation of nanoparticles [236–238].

One of characteristic physicochemical properties of metal nanoparticles is the plasmon phenomenon [239], although no plasmon absorption appears for smaller particles than 4 nm size due to the quantum dot effect [213]. Therefore, dendrimer-protected nanoparticles are useful as component materials of plasmonics. Metal/metal oxide nanoparticles are known as effective catalysts and some investigations report the efficiency of dendrimers on the catalytic activity by nanoparticles, although

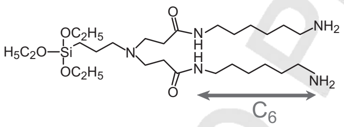
TABLE 2.1 The Guest Ability and Size of Dendrimer/Dendron and the Rate Constant based on the First-Order Reaction Mechanism of the Photodegradation

Sample	Number of guest per molecule	Size (nm)	Sample	Rate constant (min^{-1})
			TiO_2	3.2×10^{-3}
G4.5 dendrimer	5.3	~4	TiO_2 + G4.5 dendrimer	9.8×10^{-3}
G3 dendron	18.8	2.1	TiO_2 + G3 dendron	29×10^{-3}

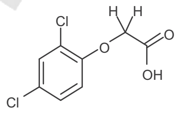
G1 PAMAM dendrimer:



G1 Silicate-focal PAMAM dendron with hexylspacer:



Guest molecule: 2,4-dichlorophenoxyacetic acid



the efficiency depends on the catalytic systems [13,221,224,240–242]. Generally, since the size of particles formed in dendrimers is small enough, the catalytic efficiency is high [240]. When the coverage or generation of dendrimers is high, the efficiency decreases because of the inhibition by the dendrimer shell for the approach of guest molecules to catalysts [221,241]. Moreover, it can be noticed that the dendrimers/dendrons have a role of a reservoir of guest molecules as well as a protector due to their large void volumes [13,224]. When the photodegradation is compared between TiO_2 nanoparticles protected by PAMAM dendrimer and silicate-focal PAMAM dendron with hexyl chain spacer, it should be noticed from Table 2.1 that the rate constant of the photodegradation is in proportion as the host ability of dendrimer/dendron against the guest molecule but not their size. It comes from the difference of the alkyl chain length in the spacer.

Clays are valuable fillers to encapsulate small molecules. The layer distance in clays depends on the packing molecules, but when dendrimers are intercalated between the charged layers of the clay, the repeating distance of clay layers is expanded slightly thinner than the size of dendrimers due to the deformation (flattening) of the dendrimer shape (see Fig. 2.6c) [243–245]. The intercalation is possible even by dendrimer-protected nanoparticles [238].

The porous materials are another kind of functional inorganic fillers which are useful as molecular sieves, adsorbers, catalysts, and drug delivery systems. Although surfactant micelles are used as porogens in the conventional procedure, there are reports the preparation of nanoporous materials using dendrimers and dendrimer-protected silver nanoparticles as porogens [246–249]. While tetraethyl orthosilicate and iron phosphate are used as a precursor in some cases, the ordering of pores by means of a silatrane precursor are excellent (see Fig. 2.6d) [249]. Different from the conventional procedure, where a porogen is removed by calcination and the postfunctionalization is carried out, the functionalization of the porogen is achieved at the one-step preparation by using the functionalized dendrimers as porogens.

2.5. CONCLUSIONS

The unique characters of dendrimers attract us, since their interior with enough void volume is utilizable for doping of small molecules like drugs and their multifunctional periphery is adequate for taking hold of molecules, anchoring on surfaces, and reacting with chemicals. The biocompatibility such as nontoxicity, nonimmunogenicity and biodegradation is required for molecules as biomaterials. Dendrimers can fulfill such conditions by choosing the components on the process of the synthesis. Thus biocompatible dendrimers as well as dendrons and dendritic polymers consisting of dendrons are produced using units of amine branching, amide and alkyl spacers or of amino acids and sugars.

The static structural characters like segment distribution and medium penetration depend on the constituents of dendritic structures (dendrimers, dendrons, and dendritic polymers). Meanwhile the doping ability of dendritic structures is contributed by not only their static structures but also their dynamic structures. Thus the possibility of utilization of the dendritic structures to DDS stands on their static and dynamic structures. Moreover, the characteristic behavior of adsorption and aggregation supports the anchoring of the dendritic structures as a DDS on the targets and the fabricating of the particularized DDS. Furthermore, the amine-branched dendritic structures with the characteristic photoluminescence can be used as a fluorescent probes (markers) on confocal laser scanning microscopic observation and magnetic resonance imaging.

The complexation of the dendritic structures with drugs is possible using chemical bonding or nonchemical bonding like electrostatic interaction, hydrogen bonding, and so on. The gene vector system is also possible to create using the interaction of the dendritic structures with DNA. The complexation with inorganic materials is responsible for the different types of DDS. The complexes with metal nanoparticles can be applied to the thermal therapy of cancers and the fluorescent marking on magnetic resonance imaging. Both dendrimer-intercalated clays and nanoporous materials with dendrimer porogens have a possibility to be fillers or capsules for drugs.

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