Functional dendrimers, hyperbranched and star polymers

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Abstract

Over the past decade, a number of excellent reviews on hyperbranched polymers and dendrimers have been published covering the topics from details to highlights and perspectives. The purpose of the present article is to review the synthesis, properties, and functionality of dendrimers, hyperbranched polymer, and star polymers with emphasis on functional aspects. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer architectures; Branched polymers; Polymer structures

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1. Introduction

Since the pioneering work of well-defined, three-dimensional structural ordered macromolecules by Vögtle [1], Tomalia [2,3], and Newkome [4], interest in dendrimers and hyperbranched polymers has been increasing at an amazing rate. The study of these polymers, expands to all areas including theory, synthesis, characterization of structures, and properties, and investigations of potential applications.

In the beginning the research on dendrimers focused on the synthesis, characterization, and properties of perfect dendrimers of higher generations. For the synthesis of dendrimers constructed by step-by-step sequences, two fundamentally different strategies, the divergent approach (from the inside out) [2–4] and convergent approach (from the outside in) [5], were employed. In either way, dendrimers can be prepared with high regularity and controlled molecular weights, and the macromolecules consist of a polyfunctional central core covalently linked to layers of repeating units (generations) and a number of terminal groups. These units are interdependent and create a unique molecular shape, leading to intrinsic properties such as high solubilities and low viscosity. Concomitant with the development of dendrimers, hyperbranched polymers that can be prepared by a faster and easier way have become more important materials. In this one-pot polymerization of $AB_x$ monomers (where $x$ is 2 or greater), however, the competitive reaction leading to the formation of linear chains and branching occurs, and consequently the structure is imperfect and the control over layers or generations vanishes. Methods to prepare dendrimers efficiently or hyperbranched polymers with more regular structures have been explored by many researchers.

A broad range of dendrimers and hyperbranched polymers is now available, some dendrimers even commercially. Emphasis is shifting to an exploration the investigation of potential uses and applications. These involve:

1. Micelles and encapsulation.
2. Self-assemblies and liquid crystals.
3. Layers.
4. Electroactive dendrimers and electroluminescent devices.
5. Sensors.
6. Conductive and ionic conductive polymers.
7. Photochemical molecular devices (energy transfer and electron transfer, nonlinear optics).
10. Dendrimers in analytical chemistry.

Over the past decade, a number of excellent reviews on hyperbranched polymers and dendrimers have
Fig. 1. Typical dendrimers that are frequently studied as functional macromolecules.
been published covering the topics from details to highlights and perspectives [6±16]. The purpose of the present article is to review the synthesis, properties, and functionality of dendrimers, hyperbranched polymer, and star polymers with emphasis on functional aspects. The study of these polymers, however, inextricably expands into many fields and a comprehensive discussion of all these fields is near-impossible to present in this article.

2. Synthesis and properties

2.1. Synthesis of dendrimers

The synthesis of dendrimers is more closely related to “organic chemistry” rather than “traditional polymer synthesis” regarding with the requirement for a number of synthetic processes and procedures including repeating purification and exact characterization. Two different synthetic strategies, a divergent [2±4] and a convergent growth approach [5] are generally employed to construct dendritic frameworks. In both step-by-step synthetic approaches quantitative coupling reactions are required to construct high generation dendrimers. A host of dendrimers have been presented in the literatures: polyamidoamine (PAMAM), poly(propyl imine)(DAB-dendr-NH2), polyethers, polyesters, poly(ester amides), poly(ether amides), polyalkanes, polyphenylenes, poly(phenylacetylenes), polysilanes,
phosphorus dendrimers and others [6–10]. In addition to these covalently linked dendrimers, various types of coordinated dendrimers have also been reported [6,12–14,16]. In Fig. 1 typical examples used are shown.

For the sake of the rapid growth of exploration of dendrimers, the development of more efficient synthetic processes circumventing the laborious and time-consuming steps of activation or protection of monomers, condensation reactions, and purification by chromatographic separations, is highly desirable. Several methods to reduce the number of synthetic steps and to obtain the desired dendrimer in high yields have been demonstrated; a double-stage convergent growth approach [17] a hypercore or branched monomer approach [18], [19] double-exponential dendrimer growth [20], and orthogonal coupling strategies [21].

In a double-stage convergent growth approach reported by Hult and Fréchet [17], the focal points of dendrons are coupled in a divergent manner to the periphery of a monodendron or a dendrimer prepared by convergent or divergent growth (Fig. 2(a)). Both core (hypercore) and wedges are of lower generations (e.g. AB₂ and AB₄ monomers). In this way, for example, the fourth generation dendritic aliphatic polyester starting with 2,2-bis(hydroxymethyl)propionic acid (1) could be synthesized in six steps only involving two purifications by column chromatographic separations. If the macromolecule having the same generation is prepared by a conventional divergent approach, the number of purification steps corresponding to the generation is required. Thus, the newer method can reduce the number of growth step and facilitate the purification of the final dendrimer product.

Fréchet et al. [18,19] also demonstrated alternate methods utilizing hypercores and hypermonomers which are pre-branched analogs of the cores and monomers. The pre-branched oligomers can then be linked together to give dendrimers in fewer steps and higher yields.

In the double exponential growth approach developed by Moore et al. [20], first both functional groups of AB₂ monomer are masked so as to be deprotected selectively, and then the two growth monomers, one with protected B functional group is prepared by the deprotection of A functional group (divergent-type monomer) and other B functional group with protected A functional group (convergent-type monomer) in separate reactions (Fig. 2(b)). The divergent-type monomer was condensed with convergent-type monomer to give a protected dendritic molecule. The dendrimers of higher generations were synthesized by the repetition of selective deprotection and coupling processes. Thus, the degree of polymerization (DP) depends on the generation number raised to double exponential functions in terms of generation (n), i.e. DP = 2ⁿ⁻¹ - 1.

Contrast to these methodologies, following two methods can be eliminated laborious (de)protection or activation processes. In two monomer approach, two different monomers are used in which one of two different functional groups of AB₂ is designed to react selectively with one of two different functional group of CD₂, i.e. functional groups, A and C react with the reactive sites D and B, respectively. A typical example was reported in the synthesis of poly(ether urethane) dendrimers from 3,5-diisocyanatobenzyl chloride (2) and 3,5-dihydroxybenzylalcohol (3) [22]. The generations can be grown in one pot without intermediate purification steps.

Recently, Zeng and Zimmerman [21] demonstrated less-time consuming synthesis of dendrimer based an orthogonal coupling strategy [23]. Utilizing the Mitunobu esterification reaction [24] or the Sonogashira reaction [25], the sixth generation dendrimer consisted of polyphenylacetylene linked with polyesters was synthesized in three steps and two chromatographic separations. The poly(phenylene vinylene) dendrimers were also prepared by this strategy [26], using the Horned–Wadsworth–Immense reaction and the Heck coupling reaction [27]. The dendrimer synthesis via an orthogonal coupling reactions
eliminates (de)protection or activation steps and reduces the number of synthetic and purification steps required.

A different approach to avoid time consuming purification process of dendrimers has been reported by Bradley et al. [28]. They used polystyrene–polyethylene glycol resins for the synthesis of PAMAM dendrimers. Authors comment that this approach is simple and effective for the preparation of dendrimers up to third generation.

More recently, one pot synthesis of pure dendrimer has been reported. In this study, poly(amino carbonate) dendrimer from 2,6-dimethyl-4-heptanol and 1-bis(2-hydroxyethyl) amino-2-propanol was prepared by utilizing highly selective reaction of carbonyldiimidazole [29].

The incorporation of metal component utilizing non-covalent interaction at the exterior surface of or embedded within dendrimer framework is attractive strategy for the design of applicable dendrimers. Based on a number of established coordination chemistry, a variety of organometallic units as a core, junction units, modification motif on the periphery, and repeat unit throughout the dendrimer are incorporated into the structures. Among them the dendrimers with metals as repeat units are constructed by a strategy called “complexes as metal/complexes as ligand”, utilizing rigid organic molecules with two or three metal-binding sites, which are subsequently bridged with the complementary metal component. Balzani and colleagues [12] studied in details the construction of dendrimers based on polypyrididine-transition metal complexes(4). For such dendrimer syntheses, key components are 2,2'-bipyridine (bpy, 5) as terminal ligand, 2,3-bis(2-pyridyl)pyrazine (2,3-dpp, 6) as bridging ligand and its methylated form. A typical example was shown in Fig. 3 (M_c, M_b, and M_p were metal ions located at central core,
interior, and periphery). Terpyridine and tetra(2-pyridyl)pyridine derivatives are also useful scaffold for the construction of metallodendrimers [16]. The most striking characteristic of these metallodendrimers is that each building block has intrinsic properties and that different ligands—metal component or organic units can be placed into the specific sites in dendrimers. So far, metals such as Fe, Cu, Zn, Ni, Au, Co, Pd/Pt, Os/Ru, Rh, and Ge have been incorporated as branching units or periphery of dendrimers. Some of these metallodendrimers are widely studied as mimics of biological redox potential, sensors, catalysts, new materials for energy conversion, and organic semiconductors. Details will be illustrated in the later sections.

From the applicable point of view, the chiral dendrimer is especially of interest, because the combination of well-defined structure with chiral groups leads to the possibility of controlling sizes and shapes of internal voids of dendrimers which may ensure the development of the various fields derived from the chirality, e.g. catalysts, molecular recognition, sensors, and enantioselective separation and others. Most importantly, controlled three-dimensional structure in such macromolecules resembles natural macromolecular systems and therefore opens new possibilities for biological and medical applications. The chiral dendritic molecules can be classified to four categories [30]: (a) dendrimer with chiral core; (b) dendrimer with chiral terminal units; (c) dendrimer with chiral building blocks; and (d) dendrimer with different branches attached to a non-planar core. The excellent reviews [31,32] of synthesis and properties of chiral dendrimers have been recently reported in detail elsewhere, only the brief framework will be described here.

Fig. 4. A chiral dendrimer prepared by Sharpless and co-workers.
Following the synthesis of dendritic poly(α,ε-L-lysine) by Denkewalter [33], Tam [34] synthesized branched peptide dendrimers, known as multiple antigen peptides (MAP), which were prepared by the coupling of dendritic lysine core with selected peptide antigen. A variety of MAPs have been used as immunogenes, vaccines, serodiagnostics, peptide inhibitor and intracellular delivery vehicles. Recently, synthesis of nucleic acid based dendrimers has been published by Damaha et al. [35,36].

The example of chirality at the surface of dendrimer was demonstrated by Newkome et al. [37], which was prepared by modifying terminal group of arborols containing tris[carboxyethoxymethyl]amino-metane with tryptophan residues. The molecular ellipticity of macromolecules was found to be proportional to the number of chiral group. The same results were reported for dendrimers containing amino acids and glycodendrimers on the periphery of poly(propylene imine) and poly(amidoamine) dendrimers. The functionality and optical activity properties of these dendrimers will be described later.

Sharpless et al. [38] succeeded in the synthesis of chiral polyether dendrimers up to fourth generations by double exponential dendrimer growth strategy, with the goal to create the chiral cavity in dendrimers (7, Fig. 4). They used achiral 1,3,5-benzenetricarbonyl moiety as a core and chiral 1,2-diol of chloromethylphenyl derivatives prepared by the osmium-catalyzed asymmetric dihydroxylation as a building block. The 1,2-diol units were protected as their acetonide derivatives to avoid undesired reactions during dendrimer synthesis. They observed that the molar specific rotation is approximately proportional to the number of chiral repeat units.

A similar approach has been reported by McGrath and coworkers [39–43]. They synthesized dendrimers up to the third generation, using achiral core and protected chiral hydrobenzoin building blocks (8, Fig. 5) prepared from stilbene derivatives. The liberation of the protected 1,2-diols in dendrimers can be achieved by the treatment with HCl in CH3CN. The hydroxy group formed should have ability to interact selectively with encapsulated guest molecules. In a next series of experiments, dendrimers that are designed to have different distance between a generation shell consisted of chiral (R,R)-hydrobenzoin
Fig. 6. Fully chiral dendrimers: diastereoselective coupling of benzylic bromide (15) and (16) with triol (14).
derivatives and the focal point of dendron have been synthesized in order to study of chiroptical properties. The observed values of molar optical rotation per chiral unit of second, third, and fourth shell dendrons (11)–(13) are significantly higher than that of the first shell dendron. From the comparison of these values with that of chiral model compound, they proposed that the enhancement of optical activity was not due to the conformational order but constitutional changes in the dendritic structure.

Chiroptical properties of layer block chiral dendrimers with combinations of opposite chirality sense have been studied by Chow and Mak [44,45]. R,R- and S,S-tartaric acid derivatives were employed, which serve as the chiral linker between peripheral groups and the branching juncture, or between branching junctures. The molar rotation of the dendrimer was related with the number of chiral units in excess and the individual R,R- or S,S-tartaric acid unit did not influence each other.

Seebach research group [30,32,46–49] synthesized a variety of chiral dendrimers employing chiral core units (14), and branching units prepared from (R)-3-hydroxybutanoic acid which is available from the biopolymer PHB. For higher generation dendrimers composed of achiral branches and chiral core the dilution of the molar optical rotation was observed. They found the diastereoselective formation of chiral dendrimers or the occurrence of chiral recognition during the synthesis of dendrimer. The coupling reaction of the chiral triol core (14) with dendritic wedge (15) gave fully substituted dendrimer (17), whereas for the diastereomeric wedge (16) only two hydroxy groups in the core were substituted to give dendritic alcohol (18). When the enantiomeric core was used, 15 and 16 were attached to give fully substituted dendrimers. The specific rotation and molecular ellipticity of 17 with (S)-configuration wedges were found to be different from optical properties of all other dendrimers which have specific rotations comparable to the values of sum of contributions of the peripheral, interiors, and core units. It is suggested that in the dendrimer 17 conformational substructures are formed (Fig. 6).

Recently, the importance of spatial position of wedges surrounding chiral center has been demonstrated (Fig. 7) [50]. The CD spectra of backfolding dendrimer (S)-19 exhibited a weak signal at 280 at 15°C, indicative of an induced chiral effect, although the peak vanished at more elevated temperatures. In contrast to this, dendrimer (S)-20 did not exhibit an optical activity. The results show that the wedges...
Fig. 8. Phosphorus-containing dendrimers prepared by Majoral and co-workers.
designed so as to grow inwards make it possible to produce rigid structure even low generation dendrimers and to create specific environment around the chiral center.

Rapid growth of applications based on dendrimers requests appearance of new types of dendrimers. The functionalization of specific positions in internal framework of the dendrimers as well as the controlled functionalization of the dendrimer surface with different groups is attractive for the development of applicable dendrimers. However, only few examples have been presented.

Newkome and Moorefield [51,52] have shown the preparation of metallo- and metallonido dendritic macromolecules by the postmodification of the internal functional group of cascade molecules. For example, tetra- and dodecaacetylene units in the interior of first and second generation dendritic macromolecules were converted into carborane (B_{10}H_{14}) derivative superclusters.

The selective modification of surface with different functional groups is highly difficult. Majoral research group [53–56] however, succeeded in the chemoselective substitution of surface groups in a series of phosphorus-containing dendrimers (21). The reaction of dendrimers bearing P(X)Cl_{2} (X = O, S) units on the periphery with allylamine gave monosubstituted dendrimers with P(X)(NHCHCH=CH_{2})Cl terminal moiety, which underwent the subsequent substitution with sodium salt of p-hydroxybenzaldehyde to give P(X)(NHCHCH=CH_{2})(OC_{6}H_{4}CHO-p). The aldehyde end groups allow further development of modification, for example, through the Schiff and Wittig reactions. Thus, the terminal functional units P(X)Cl_{2} can be monosubstituted and then disubstituted with not only amines and aldehydes but phosphorus ylids, hydrazine, and chiral compounds. The internal layer of dendrimer possessing 18 P=N±(S) units can also be post-modified with allyl and propargyl triflates to give chemoselectively allylated (22) and propargylated dendrimers (23), indicating that the accumulation of a defined number of functional groups is possible within well-defined, globular macromolecules. These dendrimers with rich surface- and interior-functionalization might possess potential applicability in various fields, especially in catalysts.

An example reported by Vögtle [57] is the functionalization of the interior layer of the first, second and third poly(propylene imine) dendrimers. The bifunctionalized dendrimers was obtained by the reaction of the terminal amino group of dendrimers with sulfonyl chloride followed by the displacement of the resulting sulfoamides with halides such as benzyl bromide, 10-bromodecanethiol, and Fréchet’s dendron possessing benzyl bromide at the focal point, although the yields were low. Such an incorporation of different functional groups at the exterior surface of or precisely placed functional groups in the internal layers paves the way for the further development of functional-oriented dendrimers.

As another intriguing concept in construction of dendritic polymers with high molecular weights, syntheses of linear-dendrimer block copolymers by the coupling reaction of traditional linear polymer with dendron or divergent approach employing terminal functional group as core or reactive sites have been reported by several research groups. As an example, Fréchet et al. [58,59] synthesized polystyrene-dendrimer block copolymers. The living character of anionic polymerization was utilized for the preparation of the block polymer. As usual manner, the living polystyryl anions were endcapped with 1,1-diphenylethylene to avoid side reactions and then the living polymers were coupled with the fourth generation poly(benzyl ether) dendrimer with bromomethyl group at the focal point (Fig. 1, R = -CH_{2}Br) to give linear-dendrimer block copolymers. These polymers can maintain fundamental properties and functionality of dendrimer units as will be described in later sections.
2.2. Synthesis of hyperbranched polymers

Although various methods to reduce synthetic steps of dendrimers have been reported as described above, the stepwise synthetic schemes required for the preparation of dendrimers limit their broad range of applications. From a technological point of view, syntheses of polymers possessing a high degree of branching in a single step from AB$_x$ monomers are highly attractive [60–62]. A number of hyperbranched polymers involving polyesters [63,64], poly(ether ketones) [65,66], polyuretanes [67,68], polyamides [69–71], poly-carbosilanes [72–75] and others [76,77]. However, the structure of such hyperbranched polymers is not as controlled as that of dendrimers, and functional groups are not located at an ordered position. This is due to the statistical nature of the coupling steps, steric hindrance of growing chains, and reactivity of functional groups, i.e. the propagation occurs at only two sites among branching units, which gives irregular and linear segments. Thus, the degree of branching for dendrimers and hyperbranched polymer is very different, although the overall composition is similar each other. So, hyperbranched polymers might have intermediate properties between those found for linear and dendritic polymers.

The simplest branched materials are called star polymers in which several linear polymer chains are attached to only one branching point (core). These polymers contain chemically same or different arms (miktoarm star polymer) linked to the core. Star-block copolymers that all the arms consist block or triblock copolymers have also been presented. Several methods have been utilized for the synthesis of star polymers. Recently, an excellent review of star polymers derived from addition polymerization has been published by Hadjichristidis [78].

Fig. 9. One pot synthesis of hyperbranched analogue of Tomalia’s poly(amidoamine) dendrimer.
In general, the degree of branching ($f_{br}$) has been calculated by the following equation defined by Fréchet et al. [79].

$$f_{br} = \left( \sum \text{dendritic units} + \sum \text{linear units} \right) \left( \sum \text{linear units} + \sum \text{dendritic units} + \sum \text{terminal units} \right)$$

A hyperbranched polymer takes $f_{br}$ values between 0 and 1, where $f_n = 0$ and 1 imply the formation of a linear polymer and a dendrimer structure, respectively. The degree of branching can be determined by spectroscopic method or degradation method of the hyperbranched backbone. The former is convenient, e.g. $f_{br}$ can be easily determined from the peak area in NMR spectra. As described above, the control of degree of branching is difficult, and an irregular, polydisperse macromolecules with $f_{br} \approx 0.4\text{–}0.7$, in general, are obtained. This results in the formation of a large number of geometrical isomers which increase with increasing molecular weights and reactive sites of monomers [80]. It appears that such geometrical isomers also affect on the properties of hyperbranched polymers.

One of the most intriguing aspects in the hyperbranched polymers is how to get hyperbranched polymers with narrow molecular weight distribution and $f_n$ close to 1 in a one-pot polymerization of $AB_2$ monomers. Examples based on the statistical theory shown by Flory [80] have been reported. In these studies additional B$_3$ or B$_4$ molecule was used in order to increase the degree of branching. Here, small pieces of these examples are described.

The synthesis of hyperbranched polyesters was reported from 2,2-bis(hydroxylmethyl)propionic acid (bis-MPA, 2) as $AB_2$ monomer and a core molecule, 2-(hydroxymethyl)-1,3-propanediol [81]. In this preparation, bis-MPA was added in successive portions corresponding to the stoichiometric amount for generation to keep the concentration of free bis-MPA as low as possible. The resulting polyesters have high degree of branching (96–83\%) and fairly narrow polydispersities ($M_w/M_n = 1.36\text{–}1.92$). For the synthesis of polyesters by the copolymerization of dimethyl-5-(2-hydroxyethoxy)isophthalate as $AB_2$ monomer and trimethyl-1,3,5-benzenetricarboxylate as a terminator core, Feast and Stainton [82] showed that the number-average molecular weights of hyperbranched polyesters obtained at high core: monomer ratios are close to the calculated values of perfectly regular dendrimers with the same composition, and that their polydispersities become narrow as increasing with the
terminator core in the polymerization mixture. From the theoretical study and computer simulation, Frey et al. [83] suggested that the enhancement of degree of branching by a stepwise addition of AB\textsubscript{2} monomer to a core could not be expected. Instead, they proposed that the slow addition of monomer AB\textsubscript{x} to terminator core B\textsubscript{t} in solution (core-dilution/slow addition technique) is effective to prepare hyperbranched polymers with controlled molecular weight and high extent of branching. The terminator core contributes, thus, not only the molecular weights but also the polydispersity of the hyperbranched polymers.

More successful direct polymerization of AB\textsubscript{x} was reported by Bharathi and Moore [84], who used a solid support linked B\textsubscript{2} core, 3,5-diiodophenyl unit. The polymerization of 3,5-diiodophenylacetylene as AB\textsubscript{2} monomer on the solid support gave very hyperbranched polymers with very narrow molecular distribution ($M_w/M_n \approx 1.3$).

In principle, in addition to condensation polymerization, various polymerization methods such as addition polymerization and ring-opening polymerization can be utilized for the synthesis of hyperbranched polymers. Some of polymers have relatively long chain lengths and high molecular weights which may contribute to improve the defects of the dendrimers and hyperbranched polymers, i.e. lack of entanglement of polymer chains which is necessary to enhance mechanical properties. Several synthetic approaches have been presented.

The synthetic route used by Tomalia et al. [85] was repeated reactions of poly(2-ethyl-2-oxazoline) onto poly(ethylene imines), in which the reactive amine groups in the polymer chains were regenerated by hydrolysis. The grafting yield of comb-burst branching poly(ethylene imines) formed was achieved in more than 80%. Similarly, in the arborescent polymer synthesis reported by Gauthier et al. [86,87], chloromethyl functional groups were introduced on the linear polystyrene chains and then coupled with polystyryl anion to give comb-shaped polymers (core). The hyperbranched polymers with relatively narrow molecular weight distribution can be obtained by the repetition of functionalization and coupling reaction. The arborescent graft copolymers consisted of hydrophobic polystyrene core and hydrophilic shell were also synthesized from the coupling reaction of poly(ethylene oxide) with chloromethylated, comb-branched polystyrene. These synthetic approaches gave a structurally similar to dendrimers.

Vinyl monomers containing a pendant group that is transformed to an initiating species are potential to give hyperbranched polymers. Fréchet et al. [88,89] reported a convenient method to prepare hyperbranched polymers, named it self-condensing vinyl polymerization, from $p$-chloromethylstylene under cationic conditions. In a similar way, dendritic vinyl ethers from 1-[(2-vinyloxy)ethoxy]ethyl acetate in the presence of Lewis acid [90] or 4-acetylstryrene-based hyperbranched polymers by a Markovnikov and an anti-Markovnikov addition [91] have been synthesized. Fig. 9 showed another example, in which poly(amideamines) were obtained in one-pot polymerization of $N$-acyryloyl-1,2-diaminoalkane hydrochlorides, $\text{CH}_2\text{=CHCONH(CH}_2\text{)}\text{nNH}_3\text{Cl}^-$ ($n = 2–7$; $n = 2$, 24) via a Michael addition [92]. The degree of branching was achieved to $f_{br} > 0.9$ for the melt polymerization of 24. In this polymerization the length of alkyl chains affects on the degree of branching and $f_{br}$ value decreases with increasing alkyl units. The intrinsic viscosity has a tendency to decrease with increasing molecular weight, reflecting high degree of branching. Recently, a theoretical treatment of hyperbranched polymer via the self-condensing vinyl polymerization has been reported by Müller et al. [93,94].

The hyperbranched poly($\varepsilon$-caprolactone) was synthesized by transesterification of AB\textsubscript{2} macromonomers, which were prepared by ring-opening polymerization of $\varepsilon$-caprolactone employing aluminum benzyl oxide as initiator followed by functionalized with $\alpha$-carboxylic acid-o-dihydroxy groups at the polymer ends [95,96]. In the Pd-catalyzed ring-opening polymerization of cyclic carbamate (25) in the
presence of benzylamine as initiator (core), the propagating ends of hyperbranched polyamines formed (26) multiply with the progress of polymerization [97]. A similar enhancement of the degree of branching was reported for the synthesis of poly(triallyl)silane [98].

Since the pioneering work of living radical polymerization utilizing a stable radical, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), by Georges et al. [99], various living radical systems have been reported by the groups of Matyjaszewski [100], Sawamoto [101], and Percec [102]. These developments in free radical living polymerization allowed more facile synthesis of hyperbranched polymers. The synthetic routes used by Frechet [103,104] and Matyjaszewski [104] were the two-step reactions of TEMPO derivative mediated living radical copolymerization of styrene and p-halomethyl-substituted styrenes. The halomethyl groups in the linear copolymers obtained were used as subsequent graft-initiating sites of vinyl polymerization of styrene and methyl methacrylate. Details of synthesis of hyperbranched polymers by addition and ring-opening polymerizations with polyfunctional initiators will be described in the section “catalysts” (Fig. 10).

2.3. Properties and shape

In general, the dendrimers are more soluble in common solvents compared to analogous linear
polymers. For higher generation dendrimers, solubility characteristics depend predominantly on the properties of their surface groups. As an example, dendrimers with very hydrophobic interiors such as polyethers and polycarbosilanes can be made water soluble by introducing hydrophilic groups into their surface groups. Oppositely, water soluble dendrimers can be made hydrophobic by converting their surface groups into hydrophobic units [105]. The modification of surface clearly offers alternative opportunities as useful materials in various fields from parent dendrimers.

Another important feature of dendritic macromolecules is that the viscosity in solution and in melt is lower than their linear analogs. The plots of intrinsic viscosity vs. molecular weight of dendrimers showed unusual bell-shaped curves, indicating the decrease in the intrinsic viscosity of the dendrimers of higher generations [106] and that the chain entanglement is hardly operative. That is, the intrinsic viscosity of dendrimer does not obey well known the Mark–Houwink–Sakurada equation, \([\eta] = K[M]^a\). The behavior is ascribed to the transition from an extended structure for lower generation to globular shapes at increased generations [107,108], which has been well recognized through studies of spectroscopic measurements and computer molecular modeling. For example, Fréchet et al. [109] reported that the dramatic change of UV spectra of solvatochromic chromophore, 4-(N-benzyl-N-methylamino)-1-nitrobenzene attached to the focal point was observed on going from third to fourth generation dendrimers in low polar solvents and that this behavior can be related with the transformation from extended to a globular structure. Thus, in general, the transition is considered to occur between the third and fourth generation, although which is dependent on the chemical structure of repeating units. The
viscosity of hyperbranched polymers depends on the degree of branching. The polymers with high degrees of branching display behavior similar to dendrimer, while chain entanglement becomes significant for the polymers with low degrees of branching.

Polymers have a variable hydrodynamic radii depending on the property of solvents. Hydrodynamic radii of hyperbranched polymers are smaller than those of their linear analogs with the same molar mass. This indicates that the molecular weights of dendrimers and hyperbranched polymers determined by SEC using polystyrene standards must be regarded with some skepticism. The hydrodynamic radii were also susceptible to the polarity of functional groups on the periphery. For example, Newkome et al. [110,111], showed that hydrodynamic radii of dendrimers functionalized with carboxylic acid on the periphery were found to be largest at neutral pH and to shrink at acidic pH. For the dendrimers possessing identical internal skeleton but with amino terminal group, dendrimers expand at acidic pH and contracted at basic pH. These dendrimers undergo a maximum 35% change in hydrodynamic radius when the number of functional groups on the periphery is 108. The dendrimer size in solution was determined by this research group, employing diffusion NMR technique. Recent experimental and molecular dynamic simulation studies on the solvent-dependent swelling of the dendrimers suggest that the size (Rg) increases as $R_g \propto N^{\frac{1}{3}}$ ($N$; number of monomers per dendrimer) [112,113].

For the potentiometric titration of DAB-dendr-(NH$_2$)$_n$ dendrimers, peripheral primary amine ($pK_a$) and inner tertiary amine ($pK_t$) of lower generation dendrimers ($n = 4, 8, 16$) are, respectively, titrated in the two separate pH regions but for higher generation dendrimers ($n = 32, 64$) the curves have no clear inflection point [114]. This indicates that polyelectrolyte effects, electrostatic interactions of protonated amine groups, become an important factor for the ionization of higher generation dendrimers.

Thermal properties of dendrimers and hyperbranched polymers are also significantly different from those of analogous linear polymers. It is indicated that the glass transition temperature ($T_g$) was a function of backbone depending on the structure, the number of end-groups, and the number of cross-links or branching points. For the dendrimers, the increase in the number of end-groups lowers the glass
transition temperature, while it is increased by an increasing number of branch point and the polarity of end group [108,115]. Stutz [116] showed that the transition temperature based on these parameters comes closer a final value after approximately the fourth or the fifth generation and that significant changes do not occur for further increased generation dendrimers. The influence of the terminal groups of hyperbranched polymers on the thermal properties was studied in details by Hawker and Chu [117], who prepared poly(ether ketones) with the same building block, but with different degree of branching and terminal units such as fluoro, hydroxy, and benzophenone groups. They demonstrated that thermal properties of hyperbranched polymers with different degrees of branching are independent of macromolecular architectures, but depend on strongly on the properties of the terminal groups. Kim and Webster [118] proposed that the glass transition of hyperbranched polymers is due to translational motion of molecule rather than segmental chain motion. They also pointed out that the properties depend more on the chain length between the branching points rather than the molecular weight, in other words, the hyperbranched polymers with shorter chain length behave just like oligomers even though total molecular weights are high.

Recently, Hawker et al. [119] have unequivocally demonstrated that dendrimers have indeed different properties from linear analogs by making comparison between the properties of dendrimer (27) and exact linear analog (28), which has the same molecular weight and repeating units as the dendrimer but not hyperbranching structure. A hydrodynamic volume of 28 with 31 repeat units is larger than that of the fifth generation dendrimer, reflecting the difference of structures, i.e. the random coil and globular structures. The linear polymer 28 is highly crystalline and melt at 150°C, while 27 is completely

Fig. 14. Schematic representation of properties of dendrimers and their potentials as functional macromolecules.
amorphous and has a glass transition temperature of 42°C. The solubility is significant different; 25 is highly soluble in THF, acetone, or chloroform, while 28 can crystallized from these solvents (Fig. 11).

Although dendrimers possess a precise composition and constitution, there are no direct informations such as X-ray crystallography, providing detailed data concerning their structures. However, as described above various indirect experiments and molecular simulations indicate that the shape of dendrimers change from extended, open, structure to a spherical, densely packed structure, depending on the generation. Recently dendritic macromolecules with shape-persistent properties and rod shaped, cylindrical structures have been synthesized with several aims in mind. Here, small pieces of works related with molecular shape are described.

Percec et al. [120,121] demonstrated that for the polymers with tapered or conical monomeric units
the shape can be controlled from spheroids to cylindrical structures by the degree of polymerization of backbone, indicating that the pendant dendritic units affect on the polymer backbone conformation. For example, the polymerization of tapered monomers with dendritic side groups, 3,4,5-tris(4'-dodecyloxybenzyl)xybenzoic acid ethylene glycol methacrylate (29), gave polymers which self-assemble to form a tubular supramolecular architecture. Recently, Tomalia et al. [122] reported on the transformation from random coil to rod shaped, cylindrical conformation of linear poly(ethylene imine) bearing poly(amido amine) dendrimers (30). This transformation depends on the generation of dendrimers, which occurs at the fourth generation dendrimer. Related work has been shown by Schlüter et al. [123,124], who succeeded in the synthesis of poly(p-phenylene) bearing third generation Fréchet type dendron (DP₉ = 110 (31)). A molecular model obtained by molecular dynamics simulation showed the formation of cylindrical dendrimers and scanning force microscopy (SFM) of the polymer adsorbed on the graphite indicates the formation of multilayer films with densely packed nanorods.

Various shape-persistent dendrimers are also prepared by using rigid components [125–127], which are especially important for designing the rigid nanostructures with controlled functional-group arrangement or in areas required for vectorial functionality such as energy transfer and electron transfer. These involve phenylacetylene-based dendrimers which are useful as photosensitizing materials [125,126], nanosized polyphenylene dendrimers, e.g. (33), prepared from [2 + 4] cycloaddition-deprotection sequence using tetraphenylcyclopentadienone and tetraethynylphenyl [127], and bowl-shaped dendrimers based on cyclotriphosphazene core [128] (Fig. 13).

Detailed characterizations of dendrimers are often far easier than those of linear polymers. It becomes increasingly difficult with higher generation dendrimers even employing modern instrumental analysis. Molar masses of linear polymers are commonly determined by size exclusion chromatography (SEC). Since SEC technique is a relative method based on hydrodynamic volume of polymer, where polymer standards of known molar mass and dispersity are needed for calibration, the interpretation results in difficulty, i.e. the observed values are often lower than expected values. Another problem is that dendrimers with polar groups such as hydroxy groups interact with the gel in the column. Regardless, the SEC measurements are still useful to verify the monodisperse character of dendrimers. The most effective characterization is matrix-assisted laser desorption ionization mass spectroscopy, and molecular ions of synthetic polymers up to the 200 000 Da range can be obtained. It is important to have analytical tools capable reliably and accurately assessing the purity of dendrimers and also identifying the structural features of impurities and defects in dendrimers. Recently, Newkome et al. [129] showed the qualitative analysis procedures to detect residual terminal carboxylic acid moiety in dendrimers prepared by divergent process, using 9-anthryldiazomethane.

3. Functionality

3.1. General aspects

A manifold linear polymers were employed as functional materials, and attempts to develop and improve functionalities have been examined by the selection and modifications of main chain or side chains containing functional units. These traditional functional polymers, however, are always heterogeneous, and their components and the location of functional groups are not well defined. Further, the construction of sharply controlled microenvironment around functional sites in linear polymers is near-impossible, due to the
entanglement property of polymer chains. Some of these drawbacks might be ameliorated by use of dendrimers with homogeneous, three-dimensional structures with a defined size. In other words, dendrimers may provide a new controlled “place of chemical and physical events” and opportunities required for achievement of high selectivity, high efficiency, high recognition, and other functionalities.

The characteristic features of application-oriented dendrimers are shown in Fig. 14.

The chemical and physical properties of dendrimers are determined by the shape and multiplicity of the core and building block, and by the size and shape of end groups, in addition to their chemical composition. It is implicit that dendrimers prepared by divergent and/or convergent step-growth schemes contain reactive groups at the surface according to the synthetic route used. Hence, a number of functional groups on the periphery can be used as scaffold for the construction of desired dendrimers. Controllable surface-functionalization of dendrimers provides segregated properties between surface and interior or core. Numerous modifications of reactive groups like amines, alcohols, or halides on dendritic surface by nucleophilic, electropilic, and radical reactions have been reported. In general, the modification reaction is efficient if the reactive site is not highly densed and packed. Such modifications of the numbers and types of chain-end functionalities have led to dendrimers with potential applicable materials. Binding groups on the interior and periphery are called *endo*-receptor and *exo*-receptor, respectively.

Dendrimers adopt a roughly spherical and globular shape in solution and their cores are relatively loosely linked and have enough space to encapsulate guest molecules. One of the most characteristic features of higher generation dendrimers is that controlled cavities become developed, depending on
chemical composition, flexibility, and number of branching arms at junction points. Another intriguing aspect is that the functional units involving ligands can be placed in intended sites in dendrimers, interior and/or surface, which is profitable to construct functional materials required for vectorial interaction. The properties of shape-persistency with controlled size are useful in the area of nanotechnology. The functionality of dendrimers that have been described in the literatures might be amplified by more judicious choice of the core, building block, and terminal units according to the research needs.

Due to the imperfect structure, polydispersity of molecular weight, lack of ordered-location of functional groups and of controlled shape for hyperbranched polymers, their role as functional materials are
different from that of dendrimers. The advantages of hyperbranched polymers, easier synthesis, highly solubility, and lower viscosity may be useful in the fields such as coating and modifiers.

### 3.2. Micelles and encapsulation

Numerous reports of amphiphilic dendrimers with a variety of different interior have been presented, including poly(amidoamines), poly(amides), poly(ethers), and poly(esters). Like micelles, the amphiphilic dendrimers possess the capability to solubilize insoluble organic substrate in aqueous media and hence are considered to be model systems of classical micelle. But unlike micelles that are affected remarkably by physical environment such as pH, concentration, ionic strength, and temperature, the dendrimer micelle structure is stable under general conditions. Hence amphiphilic dendrimers offer new isolated or compatibilizing place for polar and apolar compounds at nanoscopic levels.

As early as 1986, the application of dendrimers as unimolecular micelles was proposed by Newkome [130]. Turro et al. have unequivocally demonstrated characteristics of unimolecular micelles of PAMAM (polyamidoamine) derivatives by EPR and fluorescence techniques, employing Cu(II) [131,132], Ru(phen)$_3$ [133], and nitroxide-labeled Ru(II) phenanthroline [134]. Recent study of solubilizing ability of PAMAM dendrimers using pyrene indicated that even low generation dendrimers play as host molecule [135]. It is suggested that the polarity in the cavity of second generation PAMAM dendrimer is approximately to that of ether, from the $I_1/I_3$ ratio of the fluorescence intensity of the first to the third vibration peak of pyrene.

Hydrocarbon cascade polymer (34) with 36 tetramethylammonium carboxylate groups radiating out from neopentyl core does not aggregate and can therefore exist as monomeric micelle [136,137] (Fig. 15(a)). In contrast to this, the dendrimer (35) with ammonium salts aggregates by intermolecular hydrogen bonding, showing that the terminal groups affect on the dendrimer–dendrimer interaction in solution. The dendrimer 34 has ability to trap guest molecules such as chlorotetracycline and naphthalene within hydrophobic framework. Micellar dendrimers with a compact lipophilic interior and carboxyl groups on the periphery, using adamantanetetra-carboxylic acid as building core, were also prepared [138].

Recently, a similar enhancement of solubility of alkyl-substituted benzene derivatives was shown for the completely hydrophobic second generation carbosilane dendrimers bearing 16 sulfonate units on the surface (36, Fig. 15(b)) [139]. The dendrimer was synthesized by attachment of amphiphilic groups through thioether linkage of terminal chloromethyl group on the dendrimer prepared from tetravinylsilane (core), methyldichlorosilane, and vinylmagnesium bromide. Solubilization behaviors of toluene, ethylbenzene, and propylbenzene were evaluated from $^1$HNMR spectra. The inherent solubilities of guest molecules determined were in qualitatively agreement with the reported values for aqueous solubility, and roughly 2 or 3 guest molecules per dendrimer molecule were trapped. However, no appreciable solubilization of naphthalene or anthracene was observed.

Meijer and coworkers [140] reported that the modification of terminal group of hydrophilic dendrimers with hydrophobic alkyl chains leads to the formation of inverted unimolecular dendritic micelles(37, Fig. 15(c)). They modified poly(propylene imine) dendrimers (DAB-conjugate-$\text{NH}_2$)$_{4,64}$ into their amido analogs with alkyl chains ($-\text{CO(CH}_2)_n\text{CH}_3$, $n = 5, 9–15$). Hydrophilic dye, rose bengal (RB), was trapped into the inverted micelles by dissolving dendrimer and dye in ethanol followed by pouring the solution into acetonitrile. The number of RB trapped is strongly dependent on both generation and alkyl chain length on the surface. The RB trapped in the micelles in hexane could not be
released from the solution by washing with water, but the guest molecule could be removed from the
micelle by the addition of toluene. In a next investigation [141], the liquid±liquid extraction behavior of
DAB-dendr-(NH₂)ₙ modified with palmitoyl chloride in the pH range 4–14 was reported. The extraction
yield of anionic dyes such as RB, fluorescence, and erythorsine was highly sensitive to pH. From the
comparison of effects of generation on extraction, the extraction is directly related to the number of
tertiary amines in the interior of dendrimers. The dendritic extractant is less sensitive toward change in
organic solvents, due to the segregation of interior derived from structural character of dendritic micelle.
RB was selectively extracted into organic phase from the mixture of even in the ratio, 10 000:1
fluorescence—RB at pH range 8–10. It is concluded that a high selectivity in the extraction of
compounds with different PKₐ and hydrophobicity is attributable to the high concentration of tertiary
amine interior in dendrimers. These dendritic extractants might be useful in the selective purification of
anionic compounds.

Likewise, PAMAM dendrimers modified with epoxyalkane was shown to behave as unimolecular
inverse micelles and the interior has enough space to encapsulate guest molecules (38, Fig. 15(d)) [142].
Cupper sulfate in an aqueous solution was transported into toluene or chloroform phase by modified
fourth generation PAMAM dendrimer, indicating that the dendrimer act as a phase transfer agent with
sufficient interaction at the interface between organic and water phases.

The application of the properties of encapsulation ability of dendritic micelles to the area of extraction
chemistry is also demonstrated by Cooper and his coworkers [143]. They have found that dendritic
Fig. 19. Dendritic molecules that are capable to bind guest molecule via hydrogen bonding interactions.
micelle with a fluorinated shell can transfer organic dyes such as methyl orange and RB from an aqueous solution to liquid carbon oxide. The dendritic micelle was synthesized from the reaction of DAB-dendr-(NH$_2$)$_{32}$ with CO$_2$-philic shell, prepared from a heptamer acid fluoride of hexafluoropropylene oxide (39, Fig. 15(e)). A 90% of the peripheral amine groups was displaced with perfluoropolyether chains. The dendrimer is insoluble in water and common organic solvents, but soluble in liquid CO$_2$ at pressure above 76 atm. When the ratio of dye to micelle is low, for example, dye/micelle ~1, a complete extraction of dye from aqueous phase to CO$_2$ is possible, since the micelle can trap around 12 dye molecules per dendritic core. Although the mechanism of this interesting behavior remains unclear, it is suggested that the occurrence of conformational distortion at the water–CO$_2$ interface brings about the diffusion of significant amounts of water into the highly hydrophilic interior which accompanies the phase transfer of dyes.

Example of an amphiphilic poly(benzyl ether) dendrimer (40) consisted of different properties connected to biphenyl core was reported by Hawker et al. [144]. In this dendrimer, one monodendron was modified with carboxylate salt on the external surface and the other had relatively nonpolar benzyl ether groups on the periphery (Fig. 16). The dendron with carboxylate end groups used was soluble in water and could behave as static unimolecular micelle, i.e. the dendrimer was able to solubilize pyrene in water. The stable emulsion was formed in a mixture of water and dichloromethane in the presence of 40, indicating the occurrence of the orientation of 40 at the interphase. The dendrimer that all terminal groups were modified with carboxylate group (41) functions as unimolecular micelle, which has high solubilizing power toward pyrene and other aromatic compounds, probably due to the π–π interactions between phenyl rings in the framework and guest molecules. The use of dendrimers as solubilizing agent was also demonstrated. The potential use in the recyclable solubilization and extraction system by changing the surface charge was demonstrated.

Meijer research groups [145–148] have prepared poly(propylene imine) dendrimers with a tight, congested shell and a flexible interior that can serve as internal cavities for guest molecule, dendritic box (42, Fig. 17). The optical activity of dendritic box bearing t-BOC-L-Phe residues decreased with increasing generation of dendrimers. The racemization was not responsible for this unusual behavior of optical activity. It is believed that the highly dense packing of chiral moieties being enhanced by hydrogen bonding at higher generations interferes to take a preferred conformation and consequently the optical activity decreased. This interpretation is consistent with the observation that the introduce of the spacer between the box and t-BOC-L-Phe residues leads to the roughly constant optical rotation, independent of the generation.

For low generation dendrimers the shell is not dense enough to capture the guest molecules and they can be removed by extraction. Various guest molecules such as 3-carboxy-proxyl, tetracyanoquinoid-dimethane(TCNQ), and RB were encapsulated into poly(propyleneimine) dendrimer with 64 end groups modified by N-t-BOC-L-Phe. When 3-carboxy-proxyl was used as guest molecule, 0.3–6 molecules can be entrapped in the box. The ESR spectrum of two or more radicals encapsulated in the box exhibited the occurrence of intermolecular ferromagnetic alignment of radicals into a triplet state radical pairs. Such a formation of triplet radical pairs is considered to occur in a statistical fashion, although details remain unclear. It is well known that TCNQ forms a charge transfer complex with tertiary amine. Dendrimers used have a number of tertiary amine as branching units, so the formation of charge transfer complex of polyamine core with TCNQ is likely to occur. ESR spectra showed well-resolved hyperfine coupling associated with TCNQ$^-$, indicating the occurrence of electron transfer from branching amines to TCNQ. The absorption bands assignable to TCNQ$^-$ were lost after dialysis, but the absorptions at
615 and 663 corresponding to a dimer of the TCNQ radical anions were observed. This result indicates that the dendritic core can trap and stabilize TCNQ radical anion as $\pi-\pi$ dimers. Interestingly, the dendritic box has ability to recognize the molecular size. They encapsulated 8–10 molecules of 4-nitrobenzoic acid and 4 molecules of RB. By deprotection of terminal N-$t$-BOC-$t$-Phe moiety, the small guest molecule, 4-nitrobenzoic acid, dissociated from the dendrimer, but the large guest, RB, still remained in the box. Further removal of amino acid groups by acid hydrolysis led to the complete dissociation of RB from the dendrimer. Thus, the controlled release of molecules depending on the bulkiness of peripheral groups may contribute to the field of drug delivery system. For this purpose, however, the development of selective and controlled removal of “cap” under more mild conditions, e.g. enzymatic way, might be required.

Host–guest interactions and clathration in a dendritic architecture are intriguing properties of dendrimers, especially, if they have an ability to recognize chirality. Interestingly, the chiral dendritic box with one molecule of RB exhibited an induced circular dichroism (ICD) spectrum, whereas for the dendrimer box containing four RB molecules an exciton-coupling spectrum was observed [148]. The ICD effects suggest that a certain chiral site is present in the cavities and RB molecules are close proximity with a certain fixed orientation in the dendritic box, although the conformationally ordered place is only limited. Recently, the molecular dynamics theoretical studies of encapsulation of RB in the dendritic box have been reported [149].

The functionality of hyperbranched polymer with carboxylate groups as unimolecular micelle was
already reported in 1990 by Kim and Webster [150]. They prepared hyperbranched polyphenylene by homocoupling of 3,5-dibromophenylboronic acid under modified Suzuki conditions. Then, the polymer was treated with $n$-BuLi followed by quenching with carbon dioxide. $^1$H NMR spectra of carboxylate polymer gave only a broad peak, due to the ordered structure of water in the interior restricting the rotation of phenyl rings. The incorporation of guest molecule, $p$-toluidine, into hyperbranched carboxylated polyphenylene was confirmed by the observation of the upfield shift and broadness of all proton peaks corresponding to guest molecule in $^1$HNMR spectra.

Contrast to the nonspecific physical encapsulation of guest molecules within the dendritic branches, the location of the guest molecules can be controlled by the incorporation of specific binding sites utilizing hydrophobic interaction, hydrogen-bonding, and a metal ion coordination site within dendrimers. The binding of organic molecules to the surface of dendrimers has been well documented. For the interaction of polyanionic PAMAM dendrimers with dodecyl tetramethylammonium bromide, the generation affects significantly on the binding, probably due to the intrinsic change in dendrimer morphology from a dispersed terminal groups on the surface to highly densed one [151]. Such a behavior has also been observed in the interaction between polyanionic PAMAM-based dendrimers with poly(dimethylallylammonium chloride) and with a cationic organic dye, methylene blue (MB). In the latter example, it is suggested that MB molecules stack perpendicular to the surface of the dendrimer [152].
Diederich et al. [153–155] reported on the synthesis and binding properties of a new class of watersoluble dendrophanes (dendritic cyclophanes) which consist of cyclophane with a cavity as core (43) and first, second, and third generation poly(ether amide) dendrons modified with carboxylate groups on the periphery (Fig. 18). The first generation dendrophane (45) was synthesized from the reaction of 43 with monomer 44 in the presence of DCC and 1-hydroxy-1H-benztriazole. The second (46) and third (47) generation dendrophanes were synthesized from similar coupling reactions of lower generation dendrophanes with 44. 1H NMR and fluorescence binding titrations showed that 45–47 act as host for benzene and naphthalene derivatives. When a relatively large cyclophane core prepared from naphthyl(phenyl)methane derivative was used, steroid testosterone was bound with dendrophane bearing the same dendritic wedges to form 1:1 complex. The core 43 without dendritic wedge forms complexes with stoichiometry of 2:1 cyclophane—guest molecule. Apparently, bulkiness diverged from the core prevents the complex formation by on-top-stacking fashion for monomeric cyclophane. The complex stabilities of dendrophane with aromatic compound guests were similar to those of the parent cyclophanes. From the changes in 1H NMR chemical shifts observed for both the cyclophane core and the guest molecules upon complexation, guest molecules are located at the binding site of the central cyclophane rather than non-specific incorporation within poly(ether amide) frameworks. In other words the recognition site of dendrophane cores remains open and accessible even though high generation dendrons were attached. It is suggested that the accessibility is due to the relatively large cyclophane core and electrostatic repulsion of carboxylates on the surface, both of which can produce space around cyclophane cores, allowing the guest molecules to enter the dendrimer cavity. Further, the spectra of fluorescence probe, 6-(toluidino)naphthalene-2-sulfonate(TNS), suggested that the micropolarity at the binding site of the dendrophanes 45–47 is reduced significantly with increasing generation, and that the polarity around core of third generation dendrophane is similar to that of ethanol.

Hydrogen bonding sites within dendrimer frameworks are powerful tool as predetermined place for binding of guest molecules. Newcome and coworkers [156] reported on the molecular recognition of guest molecules such as glutarimide and barbituric acids with flexible dendritic hosts containing 2,6-diamindopyridine moiety as hydrogen-bonding group. 1H NMR titration experiments showed the formation of complex between diamindopyridine units and the guest molecules by complementary hydrogen bonding in lower generation dendrimers. For higher generation dendrimers, the host–guest interaction

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{dendritic_metalloporphyrins.png}
\caption{Dendritic metalloporphyrins (52 and 53) and dendritic imidazoles (54).}
\end{figure}
became complicated by the self association between host molecules and the occurrence of complexation on additional binding sites within the host.

Effects of connecting units in the dendritic molecules on the complexation behavior based on hydrogen bonding between the core and guest molecules (Fig. 19, e.g. 48) have been studied by Zimmerman et al. [157]. They synthesized two different types of dendrimers up to third generation, i.e. the core and branching units are the same but the connecting units are different, one is used polar oxymethylene OCH₂ units and another apolar phenylacetylene units (49). For all host molecules, the guest molecule was trapped at naphthyridine core by hydrogen bonding, and the stoichiometry was determined to be 1:1. The binding constants between dendritic host and guest were almost the same to those of non-dendritic naphthyridine core, indicating that the binding site is open. These results suggest that the guest molecule can enter without any specific chemical- and physical- interactions of framework.

Synthetic polyamino acids have shown promise as useful polymers in the broad area, especially in chiral recognition. Inoue et al. [158,159] reported that the membrane of star-shaped 3α-helix bundle poly-L-glutamates carrying triethylene glycol monomethyl ether (50) as side chain on the cyclophosphazene core has an excellent ability to resolve amino acids such as tryptophan (Trp), tyrosine (Tyr), and phenylalanine (Phe). The polymers were prepared by the ring-opening polymerization of N-carboxyanhydride of γ-benzyl-L-glutamate with hexakis(4-benzylamino-1-oxy)cyclotriphosphazene, followed by the displacement of benzyl group with triethylene glycol monomethyl ethers (TEG) (Fig. 20). The spectroscopic analysis and the molecular weight determined by GPC-light scattering measurement showed that the polyglutamates have narrow molecular weight polydispersity and the chains take a right-handed α-helix form. For the permeation of D,L-Trp using the membrane 50 with Mₙ = 36000
(number of residue per chain, DP/6 = 28), only d-Trp permeated and a complete optical resolution was achieved for over 200 h. For the permeation of Phe, the permselectivity of D isomer was 80% ee for the membrane 50. These enantioselective permeation was not observed for the membrane prepared from conventional linear polyglutamate with TEG units. Inoue suggests that the short oxyethylene chains around hexaarmed polyglutamate could assemble side to side to form relatively narrow channel along the α-helical structure, which makes possible molecular recognition of racemates in the vicinity of α-helical polyglutamate backbone.

A number of metal binding of dendrimers with a variety of ligands on the surface have been documented [160–164], for example, carboxylate-terminated PAMAM dendrimers complexed with alkali metal ions and Mn$^{2+}$, Fe$^{3+}$, Gd$^{3+}$, Pr$^{3+}$, and Y$^{3+}$ [160], dithiocarbamate-functionalized PAMAM dendrimers complexed with Ru$^{3+}$ ion [161], and metal complexes based phosphorus-containing dendrimers [162,163]. Some of these dendrimer–metal complexes have been shown to be useful as catalysts, sensors, and luminescent, and to display redox properties. These will be illustrated in Sections 3.5–3.8. There are few examples of dendrimer with predetermined metal binding sites in the framework. These dendrimers have potential to use as bifunctional materials by introducing different functional groups on the surface.

Shinkai [165] reported on the complexation ability of diaza-18-crown-6 units incorporated in the framework (51), using two-phase solvent extraction of alkali metal picrates (Fig. 21). The azacrown ether units in the dendrimers act independently and form a 1:1 metal ion-azacrown ether complex. A 1:2 metal ion-azacrown ether sandwiched complex, which was observed for parent host molecule, was not formed even high generation dendrimers. This indicates that the formation of the latter complex is energetically unfavorable for azacrown dendrimers. Interestingly, the addition of first generation dendrimer brought about the enhancement of solubility of myoglobin in DMF, which has a number of NH$_3^+$ and CO$_2^-$ M$^+$ groups, while such a solubilizing ability was lost for second and third generation dendrimers. It is assumed that myoglobin is not solubilized by the complexation with dendrimers but the cover on the protein surface with the dendrimers. The diminishing of solubilizing ability of second and third generation dendrimers might be due to either steric crowding of crown ether or bulkiness of dendrimers with higher generations.

Recently, dendrimers containing piperazine moiety as the metal binding site in the interior have been synthesized from $N,N'$-bis(3-aminopropyl)piperazine, tris(tert-butyl ester), and glutaric acid chloride [166]. Stable, orange microcrystalline Pd(II)-dendrimer complexes were formed. NMR spectra suggested that the piperazine ring takes the boat conformation for the metal chelation. Similarly, Cu complexes were formed. The dendrimer capable to bind metal ions in the interior might be useful as metallo-unimolecular micelles and supercluster.
Fig. 25. A stimuli-responsive star-copolymer with dendritic group.
The functionality based on dendrimers with well defined ordered structure seems to be a nice model to mimic biological function. Dendrimers with porphyrin units are of particular interest because the study of their binding and redox properties could help clarify the role of porphyrin in the biological systems.

Aida et al. [167] reported on the interpenetrating interaction between aryl ether dendrimers with Zn porphyrin 52, LnPZn, n = 1–5 and dendritic imidazoles 53, LnIm, n = 1, 2, 4 (Fig. 22). The change of the Solet band absorption of LnPZn in CH2Cl2 upon titration with LnIm indicates that the zinc porphyrin dendrimer form a 1:1 complex with LnIm irrespective of the number of generation of both dendrimers. The zinc porphyrin core with relatively large dendritic wedge can interpenetrate to coordinate with dendritic imidazole, although the binding constant decreases significantly as the generations of LnPZn and LnIm increase. It is suggested that the complex is formed by the cooperative interaction of a van der Waals attractive force, overcoming size repulsion of dendron wedges. In a next experiment, Jiang and Aida [168,169] demonstrated the reversible dioxygen binding activity of iron porphyrin surrounded with the same dendron wedges 54. The dioxygen-binding activity of (LnP) FeII and 1-methylimidazole complexes, covalently encapsulated in the interior of dendrimers, was studied in anhydrous or in water-saturated toluene. The absorbance at 538.5 of (Im)2L3PFeII shifted to 548.5 characteristic of the dioxygen adduct (Im)2L3PFeII(O2) when oxygen gas was bubbled. This adduct is revived to deoxygenated form by introducing of nitrogen gas. The oxygen adducts were stable more than...
2 months, even in wet condition, when the iron porphyrin dendrimer of fifth generation was used. The results apparently showed that the hydrophobic dendrimer effects are operative, that is, controlled bulky wedges protect the active center to avoid unfavorable $\mu$-oxo dimer formation or/and $\text{H}^+$ driven auto-oxidation. During this study, they found a significant difference of gas permeability between $\text{O}_2$ and $\text{CO}$
through dendrimer framework. The rate of transformation of dioxygen adduct \((\text{Im})_2\text{L}_2\text{PFe}^{\text{II}}(\text{O}_2)\) to carbonyl adduct in a CO atmosphere was much faster for third generation than that of fifth generation dendrimer, showing the dependence of gas-permeation on the generation of dendrimers. From such a behavior, the application as gas separator was highlighted.

Likewise, Diederich et al. [170] reported on \(\text{O}_2\) and \(\text{CO}\) gas equilibrium binding ability of first (55) and second generation (56) dendritic \(\text{Fe}^{\text{II}}\) porphyrins (Fig. 23). Instead of 1-methylimidazole, 1,2-dimethylimidazole, which is known to form a 1:1 high spin iron (II) adduct, was used. Both dendritic porphyrins have unexpectedly reversible \(\text{O}_2\) binding ability. Their \(\text{O}_2\) gas equilibrium binding constants are 1500 times greater than those of T-state haemoglobin and slightly low compared to \textit{Ascaris} with high oxygen affinity. The \(\text{CO}\) affinities are low and comparable to T-state haemoglobin. From high \(\text{O}_2\) and low \(\text{CO}\) affinities, \(M\) value \((K_{\text{CO}}/K_{\text{O}_2})\), the ratio of the two equilibrium binding constants, is very low. Molecular models suggested that high oxygen affinities of dendritic porphyrin might be due to the formation of additional hydrogen bonding between terminal oxygen atom of bound oxygen and amide NH groups, and the lower \(\text{CO}\) affinity may be caused by steric hindrance of \(\text{CO}\) binding site by congested framework, although the conclusion must wait further information.

3.3. Self assemblies and liquid crystals

Molecular self assemblies by non-covalent interactions, hydrogen bonding, van der Waals force, hydrophobic and Coulombic interactions, bring about stable aggregates with well-defined composition and structure. Self-assembling dendrimers are considered to be model compounds for biological systems like vesicles or micelle systems.

Bis-arborols (60) that are bi-directional molecules consisted of lipophilic central chains and terminal polyalcohol groups form thermally reversible gels or rod-shaped aggregates in water, depending on the

Fig. 29. A hyperbranched lyotropic liquid crystalline.
length and rigidity of chains [171] (Fig. 24). The arborol gels formed in the pH range of 2–12 in solutions containing inorganic ions are stable for more than two months. The formation of gels can be ascribed to both hydrophobic interaction of alkyl chains and hydrogen bonding of head groups between bolaamphiphiles. Further, Newkome and coworkers [172] reported on the formation of high order aggregates of poly(amido alcohol) with two spherical head groups which were connected to a central triple bond through alkyl chains. In contrast to the saturated analogs, for these dumbbell-shaped arborols the formation of rodlike structure by a helical stacking was detected by TEM. The construction of superstructure was considered to be due to the stacking of rigid alkyne units.

The behavior in solution of dendritic AB and ABA block copolymers has been studied, which consisted of two blocks having different shapes, flexibility, and solubility, i.e. polyethylene glycol as B block and poly(benzyl ether) dendron as A block [173–175]. $^1$H NMR spectra of the ABA block copolymer (61) showed that the ratio of peak area of the PEG to fourth generation dendrimer moiety in THF-d$_8$ lower than the theoretical value, which can be obtained in CDCl$_3$, whereas in methanol-d$_4$, proton signals assignable to the dendritic wedge of fourth generation dendrimer were very broad and weak. The results are closely related with the behavior of aggregation of block copolymers, in CHCl$_3$ the copolymer exists in an extended conformation while in THF, the PEG block was tightly packed, and conversely the dendrimer block is wrapped by an extended PEG chains in methanol. SEC measurements in methanol-water showed that regardless of the PEG length block copolymers with first generation dendrimer unit form species that have small hydrodynamic volumes compared to those of linear precursor, due to the formation of monomolecular micelles. For the block copolymers with second
and third generations, they aggregate to form supramolecules or multimolecular micelles as observed in higher molecular weight region in SEC profiles, which correspond to a supramolecular entity formed by assembling of 12 copolymer molecules. The increase in the opportunity of hydrophobic effect and $\pi-\pi$ interactions between dendritic blocks might contribute to conformational change depending on the properties surrounding medium. These copolymers consisted of dendrimer block with higher generations and high molecular weight PEG block are able to crystallize in spherulites, axialites, or inherent structure based on dendritic structure, depending on the overall composition of the copolymers and the solvent used. In a series of block copolymers, Gitsov and Fréchet [176] synthesized a new type of stimuli-responsive macromolecule composed of flexible PEG linked with hydrophobic poly(benzyl ether) dendrimer at the chain ends and a pentaerythritol core (Fig. 25). Such amphiphilic star copolymers are also able to change their conformation depending on the environment (62 and 63). Again, $^1$H NMR spectra exhibited that in polar solvents such as methanol, hydrophobic dendron moiety is wrapped by oxyethylene chains while in THF oxyethylene chains are packed in interior surrounded by dendrimer units. Thus, the results indicate that the star copolymers can form monomolecular micelles with different core-shell structure as a function of the environment. It is suggested that these stimuli-responsive macromolecules might be useful as delivery vehicles of encapsulation and release of hydrophobic or hydrophilic species.

In contrast to these dendrimers with flexible framework, Moore et al. [177] reported on the synthesis and characteristics of water-soluble rigid dendritic polyphenylacetylenes functionalized with polycarboxylic acids (64) or triethylene glycol monomethyl ethers (65) on the periphery via thermal transformation of tert-butyl esters or hydrolysis of ester of triethylene glycol monomethyl ether. During transformation, unfortunately, an undesirable cross-linking occurred, especially for higher generation dendrimers with tert-butyl ester groups. The dendrimers obtained displayed lower critical solution temperature (LCST), although details have not been reported. The interior of the dendrimers is believed to be more hydrophobic and stiff compared to poly(benzyl ether) and PAMAM dendrimers, and hence
the dendrimers might offer a specific compartment for guest molecules or as thermal responsive materials.

Linear polymers with dendritic chain ends were prepared by Chapman et al. [178]. Methoxy-terminated poly(ethylene oxides), which served as the platform for the synthesis of linear-dendrimer block polymers, were esterified with Boc-glycine. The dendritic poly(L-lysine) at the end of the PEO chain was prepared by the repetition of cycle of the deprotection and the coupling reaction of pentafluorophenyl-N-\(\alpha\)-N-\(\varepsilon\)-di-Boc-L-lysinate. From the surface tension measurements, the cmc of these hydraamphiphiles was estimated to be about \(8 \times 10^{-5}\) M and the fourth generation hydraamphiphile solubilizes the dye, orange-OT, in water.

Meijer research group [179–181] reported on the aggregation of novel amphiphilic copolymers (Fig. 27), in which hydrophobic polystyrene (molecular weight of polystyrene, \(M_n = 3200\), \(M_w/M_n = 1.04\)) was linked with poly(propylene imine) dendrimers with polar and hydrophilic groups such as amine (e.g. 66) and carboxyl groups (e.g. 67). The polystyrene core has been prepared by 4 step processes; end-capping of living polystyryl anion with \(\text{CO}_2\), reduction of terminal \(\text{COOH}\) group to the corresponding alcohol, cyanoethylation, and then hydrogenation of the nitrile group to a primary amine. The dendrimer moiety of various generations was synthesized starting with terminal amino group by the divergent approach. The amphiphilic behaviors have been studied by dynamic light scattering, conductivity measurement, and transmission electron microscopy (TEM). TEM exhibited that PS-\(\text{dendr}\)-(NH\(_2\)\(_{32}\)), PS-\(\text{dendr}\)-(NH\(_2\)\(_{16}\)), and PS-\(\text{dendr}\)-(NH\(_2\)\(_{8}\)) in aqueous solutions form spherical micelles, micellar rods, and vesicular micelle structures, respectively. The macromolecule with the lowest generation dendrimer, PS-\(\text{dendr}\)-(NH\(_2\)\(_{4}\)), in toluene formed inverted micelles. The critical association concentration of PS-\(\text{dendr}\)-(NH\(_2\)\(_{8}\)) determined by the fluorescence technique using pyrene probe was as low as \(4 \times 10^{-7}\) M. Thus, as decreasing in the number of amino group and hence the size of terminal head groups, the aggregation varies from spherical to inverted micelles. This behavior is in qualitative agreement with the theoretical prediction of Israelachvili [182], the geometry of amphiphile is determined by apolar chain.

![Fig. 32. Ferrocene-containing liquid crystalline dendrimer.](image-url)
volume, head-group area, and chain length. However, the quantitative comparison between the determined and calculated packing parameters, which were obtained on the basis of both the head group area determined with monolayer techniques and the volume of chains estimated from van der Waals of styrene unit, showed a discrepancy. For amphiphilic copolymers with carboxyl groups on the terminal dendrimer units, PS-\textit{dendr}-(COOH)\textsubscript{n} \((M_n = 3200, n = 4, 8, \text{ and } 16)\), also formed inverted micelles in CHCl\textsubscript{3}, while in D\textsubscript{2}O at high pHs polystyrene blocks in dendrimers with \(n = 8, 16, \text{ and } 32\) were confined inside the aggregates. The strong electrostatic interaction between dendrimer head groups brings about

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**Fig. 33.** Chiral liquid crystalline: (a) key components for hyperbranched polymers; and (b) dendritic macromolecule.

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**Fig. 34.** Poly(propyleneimine) dendromesogen giving rise to hexagonal columnar mesophase.
the formation of large network structures, except for the dendrimer with $n = 8$, which showed the formation of worm-like micelle.

Zimmerman et al. [183] reported on self assembly of dendrons, which possess Fréchet polyaryl ether wedge carrying polycyclic two isophthalic acid moieties at the focal points. Size exclusion chromatography, vapor pressure osmometry, laser light scattering, and $^1$H NMR spectra showed that dendrons (e.g. 68) with first through fourth generations self-assemble to form cyclic hexamer(69), in which one above other piles in a double-decker fashion, or a linear aggregate in apolar solvent such as chloroform and dichloromethane. In polar solvents such as DMSO and THF dendrons exist in monomeric form. The tetraacids with small peripheral groups formed unstable aggregates with concentration-dependent molecular weights, whereas stable cyclic hexamers were formed for higher generation dendrons. The large peripheral rigid groups are required for the formation of cyclic hexamer. The aggregate formed from fourth generation dendron has a central cavity a 14 Å across, enough size to trap molecules such as porphyrins in the cavity. However, such molecules can not be bound into the cavity, although solvents are encapsulated. Authors pointed out that the stability may originated in the subtle interplay between

Fig. 35. Dendrons giving rise to supramolecular dendrimers reported by Peacec and co-workers.
the favorable hydrogen bonding and van der Waals contacts located aromatic rings on adjacent
dendrimers and unfavorable steric repulsion (Fig. 28).

Liquid crystal (LC) polymers with rod-shaped mesogens in the linear main chains or in the side chain
have been studied intensively for their scientific interests and technological applications during the past
decades. Several research groups focused on the self-organization of dendrimers and hyperbranched
polymers in liquid crystalline phases.

Kim [184] first reported liotropic behavior of hyperbranched poly(aromatic amide) \((70)\) prepared from
3-aminoisophthaloyl chloride hydrogen chloride (Fig. 29). Solutions containing more than 40 wt% of
hyperbranched polymers exhibit nematic phase, and the birefringence holds up to 150°C.

Percec and co-workers [185–187] reported a series of thermotropic liquid crystal hyperbranched
polymers and dendrimers, which were prepared by the polycondensation of \(\text{AB}_2\) monomers \(71–74\)
that are flexible rodlike structure taking either \textit{anti} \(m\) or \textit{gauche} conformations. Differential scanning
calorimetry (DSC) and polarizing optical microscopy (POM) studies showed that among hyperbranched
polymers derived from the monomers \(71–73, 73\)-based hyperbranched polymer displays the most stable
enatiotropic nematic-mesophase. The formation of nematic phases results from the folding ability of the
molecules into anisotropic shapes, originated from the change of their monomer units from \textit{gauche} to
\textit{anti} conformation. These hyperbranched polymers are considered to minimize their free energy by
lowering free volume via a nematic mesophase above glass transition temperature. The polymers,
however, have not pure hyperbranched structure since some of functional groups in growing chains
react intramolecularly to give cyclic structures or to eliminate. In a next experiment, their research group
synthesized regular dendrons and dendrimers \((\text{Gn})_3\) consisted of \(74\) repeat units and 10-undecyl

\[
R = \text{-OC}_{12}\text{H}_{25}
\]

Fig. 36. A all \textit{trans}-stilbenoid dendrimer that aggregates to form descotic oblique phase.
terminal group by convergent strategy. Dendrons Gn(OH) (cf. 74, n = 2–4), Gn(Br) (n = 2,3), and all dendrimers that were prepared from coupling reaction of Gn(OH) and 1,3,5-benzenetricarbonyl chloride as a core, exhibited enantiotropic mesophases; nematic mesophase for G2(OH) and G2(Br), and nematic and smectic mesophases for G3(OH) G3(Br), G4(OH), and all dendrimers. G1(OH) displayed only monotropic nematic mesophase with narrow transition temperature range and G1(Br) was crystalline. The stable liquid crystalline phase tends to be formed as the generation increases, and all the repeat units take anti conformation so that the overall shape of the dendrimers is rod-like with a compact structure (75). Interestingly, the formation of the nematic phase of (G4)3 having the highest molecular weight in the molecular liquid crystals is much faster than that of hyperbranched polymers or linear polymers with similar molecular weights, reflecting lower viscosities of dendrimers compared to those of monodendrons or linear counterparts (Fig. 30).

The thermotropic liquid crystalline of hyperbranched polyesters have been prepared from direct polycondensation of two monomers, 2-[(10-(4-hydroxyphenoxy)decyl)oxy]- and 2-[(10-(4′)-hydroxy-1,1-biphenyl)phenoxy)decyl)oxy]terephthalic acids [188]. These polymers with terminal polycarboxylic acids display nematic mesophase whereas the esterification of the terminal groups results in non-liquid crystalline materials. It is suggested that the directional interaction of hydrogen bonding between carboxyl groups is a major driving force for the formation of nematic phases. The influences of star-shaped polyesters on the nematic phase were reported by Kricheldorf [189].

Liquid crystalline dendrimers based on flexible carbosilane have been reported. Shibaev et al. [190] prepared the first generation carbosilane dendrimers (76) with eight mesogenic moieties such as cyanobiphenyl, methoxyphenyl benzoate, and cholesteryl groups, which are dispositioned on the surface of dendrimer (Fig. 31(a)). All dendrimers described above exhibit thermotropic liquid crystal phases. The mesophases depend on the terminal mesogenic groups; smectic A phase for cyanobiphenyl group,
smectic A-smectic tilted Sc phases for cholesteryl group, and tilted Sc mesophase for methoxyphenyl benzoate group. Independently, Frey et al. [191–193] also reported on liquid crystalline of a second generation carbosilane dendrimer with 36 cyanobiphenyl groups (77) or dendrimers with 12, 36, and 108 cholesteryl groups on the periphery. A broad smectic A phase is formed in the temperature range of 17–130°C for 77. Both first and second generation dendrimers bearing cholesteryl groups formed smectic mesophases with transition temperatures between 80 and 90°C, and isotropization occurred at 130°C, but the third generation dendrimer did not show the formation of mesophase, probably due to high congestion of mesogen groups in the limited surface area. It is considered that the flexibility of the dendritic interior in these systems allows the peripheral mesogens to acquire smectic organization. The same research group introduced perfluorohexyl(C₆F₁₃–) group via radical grafting procedure on the surface of carbosilane dendrimers (78, Fig. 32(c)). The dendrimers showed generation-dependent thermal characteristics, the first generation displayed smectic mesophase, but the second and third generations did not form smectic mesophases. Instead a wide-angle X-ray scattering (WAXS) pattern of the third generation indicated the formation of a hexagonally packed array of cylindrical domains. The stiffness and immiscibility of perfluoroalkyl group with the core of carboxsilane dendrimers are considered to lead to the formation of superstructure.

Recently, mesophase behavior of organometallic dendrimers has been reported by Deschebax et al. [194] They synthesized ferrocene-containing thermotropic dendrimer (79) in which a cholesterol framework was used as mesomorphic promoter and attached to the periphery of a first generation dendrimer. POM and X ray data revealed that 79 displayed an enantiotropic smectic A phase. Such a dendrimer with ferrocene groups is attractive with potential for elaborating dendrimer-based switchable molecular device.

The hyperbranched liquid crystalline polymer decorated with chiral terminal groups has been published [195]. The polymers prepared by melt-polycondensation of AB₂ monomer 80 were functionalized with chiral units 81. The chirality of polymer was verified by the observation of optical activity. DSC exhibited two transition temperatures at approximately 95°C and 151°C and POM showed the formation of a uniform Grandjean texture characteristic of a cholesteric mesophase. Analysis of the XRD pattern led to a similar conclusion.

More recently, a ferroelectric dendritic liquid crystalline polymer has been published by Hult et al. [196]. The third generation dendritic aliphatic polyester (82) with 24 hydroxy groups on the periphery based on 2,2-bis(hydroxymethyl)propionic acid(bis-MPA, 1) was modified with 4‴-(R)-1-methylheptyloxy)phenyl-4-(4‴-10-(hydroxycarbonyldecyloxy)phenylbenzoyl chloride. DSC and POM indicate that the dendrimer exhibits chiral SmA⁺ (132–148°C) and SmC⁺ (80–105°C) phases, in addition to two well-ordered intermediate phases. The electrooptical measurement indicates that induced tilt angle is a linear function of the applied voltage. The ferroelectric state of the SmC⁺ phase formed by applying a DC electric field at 101°C stays locked even when the filed is turned off. The formation of anisotropic mesophase from radial symmetric dendrimers with chiral mesogen opens new avenue for liquid crystalline polymers (Fig. 33).

Thus the results described here indicate that in the liquid crystalline dendrimers the mesomorphism of entire compounds is determined by mesogenic units introduced. In general, the phase transition temperature is low, and the transition rate is fast compared to linear polymer analogs. These properties are apparently ascribed to the intrinsic topology of dendrimers.

A different type of liquid crystallines has been reported by Lattermann et al. [197,198], who prepared dendrimers by the displacement of terminal amino groups of poly(propylene imine)
DAB-dendr-((NH)2)n am(n = 2, 8, 16, 32, 64) with bis(decyloxy) benzoyl groups. In a previous paper [197], they demonstrated that simple primary amides possessing alkoxy-substituted benzoyl group displayed ionic liquid crystals when these compounds were protonated or reacted with transition metal compounds. The first generation dendrimer exhibits a monotropic mesophase, while second, third, and fourth (83) generation dendrimers displayed enantiotropic phases, and X-ray investigation exhibited the formation of a hexagonal columnar phase. The lattice constants indicate that a spheroid structure, which is widely accepted in solution, can not be applied to these dendrimers. Authors proposed that the columnar structure in the mesophase is constructed by piling up three-dimensional cylindrical segments, consisting of polar core, open space at the cylindrical cross-section, and an hydrophobic alkyl chain shell. Likewise, the formation of hexagonal columnar mesophases has been reported for the first generation polyethylene imine dendrimer bearing N-[3,4-bis(decyloxy)benzoyl]ethylene amine units [199] (Fig. 34).

Such supramolecular dendrimers have been widely studied by Percec and his colleagues. [200–205] They employed flat tapered monodendron, 3,4,5-tris[4-alkyl-1-oxy)benzyl]oxybenzoate (84) and conical shaped monodendron, 3,4,5-tris[3',4',5'-tris(4-alkyl-1-oxy)benzyl]oxybenzoate (86) as key compounds for supramolecular dendrimers. For the latter, alkyl chains are introduced so as to enable only a restricted-cooperative rotation of external benzyl ether moieties. These monodendrons were functionalized by introducing endo-receptors such as crown ethers and polymerizable vinyl groups at the focal points. The cylindrical self-assembly is formed from the tapered first generation dendron, and conical and semispherical monodendrons self-assemble into spherical supramolecular dendrimers. These self-assemblies construct hexagonal columnar and cubic thermotropic liquid crystal phases by self-organization. As an example, the complexation of the tapered monodendrons with benzo-15-crown-6-ether (85) as end-receptors with NaCF3SO3 induces a cylindrical self-assembly which displays thermotropic hexagonal columnar mesophase, where the stratum of the column is formed by ca.5.8 molecules of 85. The mechanism of self-assembly via complexation with metal ion resembles that of the tobacco mosaic virus.

Liquid crystalline of shape-persistent phenyleneacetylene tridendrons has been reported by Pesak and Moore [206] in which the surface was functionalized with isophthalic acid bis-(2-[2,2-methoxyethoxy-ethoxy]ethyl) ester (65) (Fig. 26). For the tetramer and decamer (number of phenyl groups) completely planar conformation can be adopted but not for 22mer (65). DSC profile showed that tetramer and decamer display enantiotropic phases but 22mer exhibits only one reversible transition. These dendrimers showed a formation of hexagonal columnar discotic liquid crystalline phase.

Meier and Lehmann [207] synthesized all trans stilbenoid dendrimers utilizing the Wittig-Honor reaction, which contain tris(dodecyloxy)phenyl group in the periphery in order to enhance the solubility (e.g. 91, Fig. 36). The formation of trans-configured double bond was confirmed by 1H and 13C NMR spectroscopies. The second generation dendrimer aggregates to form discotic oblique phase via discotic hexagonal disordered phase. The DSC profiles of third and fourth generation dendrimers exhibited no thermal transition in the temperature range from room temperature to 500°C, showing both are glassy materials. This might be due to steric congestion at the periphery. In solution, the dendrimers have a tendency to aggregate in nonpolar solvents as the generation increases, and the aggregates in cyclohexane decomposed rapidly upon irradiation. Related poly(phenylenevinylene) dendrimers with benzaldehyde at the focal point have been prepared by orthogonal synthesis approach [26]. These dendrimers are expected to have unique photophysical and photochemical properties.
Recently, Lehn, Zimmerman and their coworkers [208] have demonstrated that 2,3-dihydrophthalazine-1,4-dione derivatives bearing Fréchet type dendron at 6 and 7 positions (92) can self-assemble to form a tautomeric lactim-lactam cyclic trimer through hydrogen bonding. As expected, the addition of a solvent such as DMSO decreases the thermodynamic and kinetic stability of the aggregates. They also showed that phthalhydrazides introduced alkylxoy units at 4 and 5 positions form disks and self-organize into a thermotropic, columnar, discotic liquid crystal.

The self-association properties of dendrimers consisting of phthalocyanines core, which has shown promise as electro-optical materials, and four Fréchet dendron wedges have been reported [209]. In spite of bulkiness of dendrons, phthalocyanine units associate in dilute solution. DSC profiles of phthalocyanines bearing four first generation dendrons (93) and dendrimers consisted of one poly(aryl ether) units and three diethylene glycol monomethyl ether groups (94–96) showed the formation of hexagonal columnar mesophase on cooling from isotropic melt, although several annealing hours at 105°C are required to obtain a texture for the dendrimer with the highest generation wedge. Interestingly, anisotropic glassy state of 95 and 96 was hold below glass transition temperature, i.e. a columnar structure is frozen. Such properties might be potentially useful as optical or electronic materials (Fig. 37).

In a series of self-assembling dendritic molecules, Percec et al. [210,211] have demonstrated that polymeric shape can be controlled from spherical to cylindrical supramolecules by a degree of polymerization of backbones bearing quasi-equivalent dendritic side groups. They prepared two dendritic monomers, conical dendrons functionalized with styrene (12G2AG-S, (88)) and methyl acrylate (12G2AG-MA, (89)) (Fig. 35). The radical polymerization of monomers initiated with AIBN underwent rapidly and gave a spherical or a cylindrical polymers, depending on the degree of polymerization. That is, for the polymer of 12G2AG-S and 12G2AG-MA with DP = 20 and 15, respectively, a spherical polymer is formed, while the polymers with above these values form cylindrical supramolecules. Kinetic evidences of the polymerization confirm that the polymerization occurs at the room (reactor) constructed by self assembling of monomers, in which the local concentration of vinyl group becomes high, leading to fast polymerization. The formation of these supramolecules via self assembly followed by the polymerization was confirmed by DSC profiles, X-ray diffraction, and transmission electron microscopy (TEM). Percec et al. refer to this novel polymerization as being self-encapsulated, self-accelerated and self-controlled. They highlighted that the procedures will provide new approaches for the design of organized supramolecular materials in various fields such as molecular devices, nanotechnology, and membranes.

In relation with these works, Tomalia et al. [122] reported on the transformation of random coil to rod shaped, cylindrical dendrimers, depending on the generation of poly(amido amine) dendrimers appending on linear, random coil poly(ethylene imine) core (Fig. 12, 30). Dendronization of linear poly(ethylene imine), prepared by the living cationic polymerization of 2-ethyl-2oxazoline followed by hydrolysis, was carried out by using divergent, in situ branch cell synthesis strategy. TEM exhibited that second and third generation poly(amido amine) dendrimers the nondescript or elongated nonspherical clusters are formed, but the fourth generation polymer self-assembles to form a rod-shaped cylindrical dendrimer with diameter of 25–32 Å. The dependence of generation on the molecular morphogenes is similar to that of PAMAM dendrimers with NH₃ core, in which molecular shape changes between third and fourth generations. Likewise, Schlüter et al. [123,124] have attempted to prepare a cylindrical dendrimer based on rigid-rod polymer backbone such as poly[1.1.1]propellane or poly(p-phenylene), aiming at the development of dendritic copolymers with two different polarity and/or peripheral
functional group on a cylindrical structure. For the poly(p-phenylene) bearing dendron units, unequivocal characterization was difficult due to strong aggregation of polymers. Recently, they succeeded in the determination of molecular weight of poly(p-phenylene) with appendant third generation Fréchet type dendron. The degree of polymerization of this polymer was extraordinary high, DP = 110 (Fig. 12, 31). A molecular model obtained by molecular dynamics simulation showed the formation of cylindrical dendrimer, and SFM on the polymer adsorbed on the graphite indicates that the dendrimers are packed parallel to each other in a multilayer film.

Fig. 38. A photofunctional dendrimer that is capable to form monolayer.

Fig. 39. Fullerrens possessing gylcodendrons.

3.4. Layers

Due to their properties such as uniform shapes, controllable surface functionality, and chemical stability, dendrimers are useful tools for the construction of Langmuir–Blodgett (LB) monolayers, self-assembled monolayers (SAMs), cast films, colloids, and nanoclusters [212]. Dendrimer monolayers have several advantages compared to corresponding linear polymers; strong interaction of a number of terminal groups with surface, much higher density for higher generation dendrimers on the surface, a facile modification of surface without loss of dendrimers from surfaces, leading to the constructions of multilayers with controlled thickness. The preservation of original shape of dendrimers depends on the flexibility of framework, property of terminal groups and the extent of interaction between the dendrimer and surface. That is, dendrimers with flexible framework and polar terminal groups tend to flattering and spreading due to the strong interaction between the terminal groups and functionalized surface, while the weak interactions or rigid dendrimers preserve original shapes of dendrimers on the surface. Organic thin film, especially metal island film, are of interest, because of their prospective applications in the fields of adhesives, chemical sensor, photonics, electronics, and membrane chemistry.

White et al. [213] reported on the formation of Langmuir mono- and bilayers of Fréchet type polyether dendrimers with (see Fig. 1, R = OH) hydroxy group at the focal point at the air–water interface, which were prepared from 3,5-dihydroxybenzylalcohol(3). A change from surfactant to non-surfactant surface behavior occurs, depending on the generation of monodendrons. For the fifth and sixth generation monodendrons, a stable monolayer is formed. Neutron reflectivity studies of the fourth generation monodendron indicates the formation of a stable bilayer, where the top layer at the air interface contains no or little water and the bottom layer at the water interface contains 25% water. In this layer, benzyl groups and hydroxy group behaves to avoid the water interface and to associate with the water surface, respectively. The molecular shape of the monodendron was initially spherical, but the compressed monodendron in the lower layer laterally becomes an ellipsoid shape with axial ratio of 2:1. The result indicates that the dendrimers are flexible enough to take a prolate conformation in response to the surface pressure. In the related work [214], the behavior of second generation poly(aryl ether) dendrimer bearing eight alkyl chains at the air–water interface has been examined. The II/A curves of the dendrimer with carboxyl group at the focal point showed a somewhat higher collapse surface pressure compared to that with hydroxymethyl group. Both polymers form stable Langmuir films reflecting the introduce of alkyl chains on the dendrimer surface.

A different behavior was observed for hydrophobic PAMAM dendrimers which were synthesized using ammonia and various alkylenediamine (Fig. 1, R = >N(CH₂)ₙN <, n = 2, 4, 8, and 12) as core and then modified at the terminal amino groups with several epoxyalkanes (Z = –NH–CH₂CH(OH)R, R = C₆H₅, C₈H₁₇, and C₁₂) [142]. No significant shape change of the surface pressure vs. area curves of these dendrimers were observed, and the chain length of PAMAM surface did not affect on the limiting area of the dendrimer at the collapse points. Authors comment that the isotherms are either insensitive to the dendrimer size, terminal hydrophobe length, and the length of the core or that all dendrimers are interacted with the subphase in a similar manner. The dendrimers used behaved as unimolecular micelle and can transport copper sulfate from an aqueous solution into organic solvents. The isotherm shape of copper-loaded dendrimer was similar to those without copper, indicating that metal-loaded dendrimers can still form monolayer at the air–water interface.

Irie et al. [215] reported on the monomolecular layer of Fréchet-type dendrimer with chromophore core, a diarylethene derivative, which undergoes thermally irreversible and fatigue resistant photochromic
reaction. AFM showed that at the air–water interface, the third generation dendrimer (97) forms stable, homogenous, transferable Langmuir monolayer films with defined thickness, whereas the second generation dendrimer could not form monolayer but rather aggregate (Fig. 38).

Buckminsterfullerene (C_{60}) possessing unique physical properties is attractive building block for the construction of advanced materials and the modification provides novel materials for the investigation of the physical properties of thin film consisted of individual isolated carbon clusters. The lipophilic fullerene has a tendency to aggregate at the air–water interface, and hence the introduce of hydrophilic head groups on the fullerene is one of useful methods to overcome unfavorable aggregation at the interface. Diederich and Stoddart et al. [216] reported on the Langmuir monolayer of amphiphilic buckminsterfullerenes possessing bulky glycodendrons (Fig. 39). The fullerene dendrimer conjugates were synthesized from dicarboxylic acid of fullerene prepared via cyclopropanation and O-acetylated trisglycoside wedge. The $A_0$ value obtained from $II/A$ isotherm of the fullerene with one dendron (98) is in agreement with the expected value for the formation of two-dimensional close-packed monolayer, in which the hydrophilic head group oriented toward water phase. In the case of bisadduct (99) bearing the bulky dendrons the fullerene spheres are kept at a distance, which is larger than that of close contact.

Fig. 40. Schematic representation of dendrimer-only monolayer and lateral compression of the dendrimer by alkyl thiol.
between the fullerene spheres. The compression/expansion cycles showed the almost the same $P/A$ curves, indicating that no irreversible fullerene aggregation occurred upon compression. The monolayer could be transferred as X-type Langmuir–Blodgett onto quartz surface. Thus, the glycodendron head groups play a role to form stable, ordered Langmuir monolayers. Such films are potentially useful in optical technology and as biosensors for glyco proteins. Recently, the size and monolayer morphology of amino acid-based dendrimers in Langmuir films, which were prepared by the convergent way using 3,5-bis(t-Boc-aminoethoxy)benzoic acid methyl ester, have been investigated by means of Brewster Angle microscopy [217].

Wells and Crooks [218] reported modified-mercaptoundecanoic acid (MUA) self-assembled monolayer (SAM) on Au by PAMAM dendrimers with generation number of 0, 2, 4, 6, and 8 via amide bond formation. They studied the surface reactivity of these dendrimer-modified monolayers using the Michael addition to methyl acrylate to the terminal amine group of the dendrimers. FTIR-external reflection spectroscopy (FTIR-ERS) showed that the reactivity increased linearly as a function of dendrimer radius for the dendrimers adopted a globular geometry (G4-G8). In contrast, no surface reactivity was observed in lower generation monolayers (G0 and G2). These results suggest that for lower generation dendrimers most of amine groups linked to SAM to form a extended structure but for higher generation dendrimers only a fraction of amine groups attached to the surface, and that a more spherical dendrimer monolayer is formed as the generation increases. Interestingly, the modified SAMs by dendrimers with the generation number of 4, 6, and 8 response selectively, rapidly, and reversibly to several volatile chemicals such as benzene and methyl propanol. The chemical sensitivity was significantly influenced by the properties and density of functional group on the surface of dendrimers [219].

Two methods in the preparation of monolayer were examined; (1) attachment of PAMAM with 64 terminal amines groups on the mixed mercaptoundecanoic acid/mercaptopentane self-assembled

![Fig. 41. A arborescent graft polystyrene reported by Möller and co-workers.](image-url)
monolayer followed by modification of unattached terminal amine with functional units and (2) attachment of prefunctionalized-dendrimers, in which some terminal groups remain unfunctionalized, on the monolayer. The surface concentration and density of surface functionalities of resulting monolayers are significant different depending on the preparation procedure. The method (2) leads to a high density of functionalities on each dendrimer but a low surface density of dendrimers, while the method (1) gives dendrimer-confined monolayer with relatively high surface density but a modest degree of functionality. For the detection of volatile compounds such as benzene and trichloroethylene, the best result was obtained for the benzamido-terminated dendrimer prepared by method (2). The sensitivity and selectivity were rationalized with the $\pi-\pi$ interactions between aromatic group on the dendrimers and volatile compounds. These results showed that dendrimer-modified surfaces can potentially be applied for the chemical sensing field.

Permselective membranes responding to external stimulus, a change of pH, were constructed by self-assembled monolayer of PAMAM with fourth generation and poly(maleic anhydride-co-methyl vinyl ether) by the repetitive sequential deposition method on Au wafers [220,221] The redox probes $[\text{Ru(NH}_3)_6\text{]}^{3+}$ and $[\text{Fe(CN)}_6\text{]}^{3-}$ were used to examine the permeability of the membranes. The membranes function as supramolecular gates as a function of pH: at low pH anions easily penetrate but cations are excluded from the film while at high pH the opposite results were obtained. The layers could be also formed on the silicon or glass-wafers modified by aminosilylation. Further, Crooks and co-workers [222] showed that amine- or hydroxy-terminated PAMAM dendrimers can form monolayer on the Au surface by a simple immersion as evidenced by FTIR-ERS. For the fourth–eighth generation dendrimers stable and nearly closed-packed monolayers are constructed. The dendrimer thickness calculated from the ellipsometric measurement by using Bruggemann effective medium approximation model was significantly smaller than the bulk-phase diameter. The exposure of dendrimer-modified Au substrate in a solution of mercaptoundecanoic acid results in the formation of dendrimer monolayers sandwiched by C$_{16}$SH without significant desorption of PAMAM, which causes them to reorient from an ablate to prolate in shape (or configuration). When redox probe molecules such as $[\text{Ru(NH}_3)_6\text{]}^{3+}$ and $[\text{Fe(CN)}_6\text{]}^{3-}$ were used, the cyclic voltammogram showed that the $[\text{Fe(CN)}_6\text{]}^{3-}$ at pH $\approx$ 6.3 and both probes at pH = 11.0 penetrate into the layer and undergo the electron exchange with the electrode. The authors conclude that the both probes penetrate the dendrimer portions but not at the interface between PAMAM and C$_{16}$SH, from the results of careful control experiments (Fig. 40).

Another example to construct adlayers on Au surface has been demonstrated by Gorman et al. [223], using dendrons with reactive thiophenol moiety at the focal point. The ellipsometry showed that for the first and second generation dendrons the thickness was close to the expected value. However, the layer of third generation dendron had approximately half thickness of the expected value for fully packed and extended molecules, due to hyperbranched structure. The second generation was found to be more densely packed than the first or third generation. After exposure of the dendron self-assemblies to a solution of n-hexadecanethiol, the permeability of modified adlayer was explored by using ferricyanide redox probe. It was shown that the dendron with the second generation blocks the penetration of the redox probe effectively to the Au surface compared to that of first or third generation. The behavior observed for third generation dendron-modified assembly suggests that the layer is in a more open and porous structure regardless its hyperbranch structure. Interestingly, $trans$-1,2-cyclohexanediol was encapsulated into the first generation adlayers and tenaciously held but for third generation some of diol trapped were removed by soaking adlayer in water. However, $cis$-isomer was not held into these adlayers.
The molecular organization of arborescent graft polystyrene cast film on mica has been reported by Möller et al. [224]. Such hyperbranched polystyrenes were prepared by the repetition of coupling reaction of polystyryl anions and chloromethylated polystyrenes (101, Fig. 41, where the number implies generation). Scanning force microscopy (SFM) exhibited that polystyrenes with high branching points can restore globular conformation after annealing above the glass transition temperature, which leads to the formation of monolayers with uniform thickness. Contrary to this, the pancake structure remained for the polystyrenes with lower branching density due to strong adsorption forces. The most regular packing was achieved for the rigid polystyrene corresponding third generation which has a high branching functionality. The molecular packing, however, was significantly affected by the contaminant of linear polystyrene.

The solvent cast ultrathin films of carbosilane dendrimers bearing mesogenic 12, 36, 108 cholesteryl groups on the periphery have been investigated by Frey et al. (Fig. 31(b)) [225]. As described in the section of Liquid Crystals, both first and second generation dendrimers form smectic mesophases with transition temperatures between 80 and 90°C, and isotropization occurs at 130°C, whereas third generation dendrimer does not show the formation of mesophase. The AFM indicates that the flat, homogeneous films of 2–4 dendrimer layers are formed from high concentration of dendrimers in solution, while for lower dendrimer concentrations, the monolayer with an irregular cellular pattern of holes is formed. Annealing of first and second generation dendrimer films at 105°C induced reorientation on the surface but not for the dendrimer with 108 cholesteryl groups, probably due to their dense stacking on the periphery.

Tsukruk et al. [226] reported on the fabrication of self-assembled monolayer from PAMAM dendrimers with amine groups for generations 4, 6 and 10 and with carboxyl groups for 3.5, 5.5 and 9.5 generations by an electrostatic layer-by-layer deposition technique. Homogeneous, stable monolayers with light grainy surface morphology were formed for all even generation dendrimers on a silica surface. The thickness determined by SPM images and X-ray reflectivity increases from \( d = 1.8 \) nm for fourth generation dendrimer to \( d = 5.6 \) nm for tenth generation dendrimer. In agreement with previous reports, these values are smaller than those in solution, indicating the collapse and flattening of dendrimers along the surface normal. In the fabrication of films of (AB), type up to 20 layers by electrostatic layer-by-layer deposition of oppositely charged PAMAM dendrimers, the thickness was proportional to the number of deposition and the increment of the film thickness per molecular layer was again smaller than the expected values for ideal spherical dendrimers. This indicates that the dendrimers do not preserve their shapes and are compressed within multilayer films, due to strong interaction between oppositely charged groups of dendrimers from adjacent molecular layers. AFM exhibited that absorbed PAMAM monolayers are stable under mechanical stress but partially swollen in water.

Watanabe and Regen [227] prepared self-assembled films on a Pt\(^{2+}\)-coated silicone wafer which was prefunctionalized with (3-aminopropyl)triethoxysilane, using fourth and sixth generation PAMAM dendrimers. The alternating deposition of the wafer into dendrimer solutions followed by reactivation of K\(_2\)PtCl\(_4\) results in the linear growth of the film thickness. For the fourth generation dendrimers the thickness of individual layer was about 50 Å, which corresponds to the size of the globular shape dendrimer (40 Å), indicating the persistence of the shape in the multilayer film.

As another approach to prepare monolayer of hyperbranched polymers, the graft polymerization procedure on the Au surface has been reported [228]. In this method, the mercaptoundecanoic acid self-assembled monolayer was used, and the carboxylic groups were activated via a mixed anhydride followed by the reaction with an \( \alpha,\omega \)-diamino-terminated poly(tert-butyl acrylate). The grafted polymer
was hydrolyzed with \( p \)-TsOH to form poly(acrylic acid) layer. The layered, hyperbranched polymer film was constructed by the repetition of these steps. The ellipsometric thickness of the polymer film did not vary linearly with the number of grafting steps and increased rapidly at first few layers. These polymers contain a high density of functional carboxylic acid groups that provide new applicable platforms, e.g. chemical sensing fields.

Bar et al. [229] used PAMAM dendrimers as platforms for the deposition of gold and silver colloid monolayers on the silicon oxide, glass, and ITO. The monolayers were prepared by simple method, modification with PAMAM dendrimer on the surface followed by the metal colloid deposition onto the dendrimer layer. XPS measurement exhibited the spontaneous attachment of the dendrimer on the silicone oxide surface, due to hydrophilic interaction between the large number of amino groups and silicone oxide. The SEM micrographs of Ag colloids deposited on the adhesive layer of dendrimer exhibited that most of Ag particles are well isolated from each other. A similar conclusion was obtained from AFM images. The particle size, the extent of next-neighbor interplace spacing, and surface coverage can be controlled by the colloid concentration and the immersion time of modified substrate into the colloid solution. Such metal colloid films are stable over a periods of weeks.

The usefulness of PAMAM dendrimers as stabilizer of the gold particles has been also reported by Esumi et al. [230]. The electron micrographs of gold colloids obtained by reduction of metal salt with UV irradiation at amine group of dendrimer and HAuCl\(_4\) molar ratio of 4:1 exhibited the formation of gold particles with a diameter less than 1 for third, fourth and fifth generation dendrimers. The amine groups in higher generation dendrimers function as effective protective colloids compared to other colloids using conventional poly(N-vinyl-2-pyrrolidone).

In a related work, Majoral et al. [162] reported on the Au metal ion complex utilizing the binding ability of phosphorus-containing dendrimers with 12, 24, 48, 96, 192, and 3072 phosphino end-groups (cf. Fig. 8). The binding of the last three dendrimers with AuCl gave complexes as stable white powders. The gold complexes were directly visualized by high-resolution electron microscopy as isolated spheres with diameters depending on the generation of dendrimers. The chemical reactivity of functional group of the tenth generation dendrimer is, interestingly, almost the same with that of first generation dendrimer.

Nanoscale, zerometal clusters are considered to be useful materials especially in optoelectronics and catalysts. Recently, Tomalia [231] and Crooks [232] research groups independently report on novel approach of copper nanocluster formation based on PAMAM dendrimer. Tomalia’s group used fourth and fifth dendrimers modified with terminal hydroxy, amino, and pivalate groups. The nanocomposite was simply prepared by the addition of Cu(II) acetate solution to a dendrimer solution. Depending on the polarity of surface substituents, Cu\(^{2+}\) ions are bound near surface or deeper into inside. The resultant copper(0)\(_n\)-PAMAM nanocomposites are stable in oxygen-free solution for a long period at room temperature. Similar results have been described by Crooks et al. [232], who also used the fourth generation PAMAM dendrimer with terminal hydroxy group. Spectrophotometric titration and TEM showed that 16 Cu\(^{2+}\) ions bind to the dendrimers and that the diameter of Cu clusters obtained after reduction is less than 1.8 nm, which is much smaller than that of parent dendrimer (4.5 nm). The change of surface functional group from hydroxy to amino groups results in the binding of maximum of 36 Cu\(^{2+}\) ions and Cu clusters are >5 nm in diameter, indicating the occurrence of agglomeration of Cu particles adsorbed to the unprotected surface of dendrimers. These results indicate that modified dendrimers...
are an excellent nanoreactor for the preparation of nanocomposites which are suited for catalysis and various nano-devices.

3.5. Electroactive dendrimers and electroluminescent devices

Dendrimers with electroactive groups at the center or on the periphery are of great importance in understanding biological electron transfer and are excellent candidates for use in practical applications such as catalysts, electron transfer mediators, energy conversion, ion sensors and in electronic devices. The dendrimer can influence the microenvironment around the electroactive center and hence studies are focused on both the dendritic wedge effect on the electroactive center (core) and the redox behavior of multiple electroactive sites on the higher generation dendrimer surfaces. The

Fig. 42. A Zn-porphyrin core with Fréchet dendron.
cyclic voltammetry and related techniques provide information on electron transfer between electroactive moiety and electrode surface, where a decrease in the peak current, an increase in the potential difference, and a broadening of the voltammetric wave are realized as degree of the inhibition of electron transfer increases.

The redox properties of metalloporphyrins are well-documented, which are characterized by two, reversible one-electron transfer involving both the metal and the ligand. The dendritic metalloporphyrins are designed in attempts to mimic the properties of heme proteins and chlorophylls. The first dendritic porphyrins were reported by Inoue et al. [233], who synthesized poly(aryl ether) dendrimer with tetra-kis(3',5'-dihydroxyphenyl)porphyrin as a core, although the electrochemical behavior was not described. Electrochemical properties of dendritic porphyrins were reported by Diederich et al. [234]. They synthesized Zn-porphyrin dendrimers with polyether amide branches 57–59 (Fig. 23). From X-ray
Fig. 44. Ferrocenyl-containing dendrimers.
crystal of model compound without dendritic branches, it is suggested that the four arms used as linker between porphyrin core and dendritic branches are located above and below the zinc porphyrin plane. The cyclic voltammograms exhibited that the first reduction potential decreases and the oxidation potentials are up to 300 mV less positive value for parent (model) zinc porphyrin with increasing the generation of dendrimers. For the third generation irreversible cathodic and anodic cycles were observed. The authors rationalized these behaviors to the change of the microenvironment of Zn-porphyrin due to the interaction between increasingly electron-rich dendritic shell and Zn-porphyrin core. In a next experiment, Diederich et al. [235] prepared iron-porphyrin dendrimers (56) bearing oxyethylene chains on the periphery. The dendrimers are soluble in the broad polarity range from water to \( p \)-xylene. The redox potential was strongly affected by the environmental polarity. The potential difference of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) couple in an aqueous solution between the more open and the more densely packed iron-porphyrin dendrimers was found to be ca. 300 mV, suggesting the occurrence of the solvation of the core for lower generation dendrimers but not for higher generation. These behavior indicates that dendritic porphyrins could regard as models for electron-transfer protein like cytochrome \( c \), for which the oxidation potential of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) couple in an aqueous solution is 300–400 mV more positive than that of similar ligated heme model systems that lack the hydrophobic peptide shell.

Different results were reported by Fréchet et al. [236], for benzyl ether dendrimers with Zn-porphyrin core (102, Fig. 42). The intensity of redox processes decreased as the dendrimer generation increased, and anodic and cathodic cycles showed irreversibility for the third and second generations, respectively. Finally for the fourth generation dendrimer no oxidative process was observed. The inhibitory effect of dendron wedges on the electron transfer is due to the rigidity of benzyl ether units surrounding porphyrin core, which hinders the access of the core to electrode surface. The values of \( E^{0}_{\text{ox}}(I) = +0.81 \) and \( E^{0}_{\text{ox}}(II) = +1.08 \) V of second generation dendrimer were consistent with those of small metalloporphyrins. This result indicates no significant effect of shell attached to the core on the oxidation potentials and that dendron wedges do not interact strongly with porphyrin core in contrast to the results of dendrimers reported by Diederich et al. [234]. The dissimilar redox behavior between dendrimers might be attributed to the structural difference of porphyrin-bound phenyl groups.

Gorman [237,238] synthesized dendrimer (103) with electroactive iron–sulfur core prepared by ligand exchange reaction of thiol functionalized dendron at the focal point and \((n\text{-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{S}-\text{t}-\text{Bu})_4]\), in hope with that dendron units function as an effective insulator (Fig. 43). The dendron ligands up to fourth generation were symmetrically arranged around the pseudotetrahedral core which is capable of existing in two stable redox states. As increasing the generation, the first reduction potential of the core have a tendency to shift to negative values. The kinetics of electron transfer, as indicated by the voltage difference between the current maximum of the reduction and reoxidation waves, slowed considerably, and the fourth generation dendrimer did not display a clear reoxidation wave. Further, the measurement of the longitudinal relaxation time constants \( (T_1) \) indicates that \( T_1 \) values of all protons of paramagnetic (iron–sulfur) core dendrimer are smaller than those of a similar dendrimer with the diamagnetic core. This suggests that the repeating units within dendrimers exist in close proximity to the core. In these types of molecules, dendrons act as an insulating coating around an electroactive center and may ultimately be useful in molecular switch and information storage.

Ferrocenyl-based polymers are established as useful materials for the modifications of electrodes, as electrochemical biosensors, and as nonlinear optical systems. Various types of ferrocenyl dendrimers have been prepared and studied their electrochemical behaviors.

Astruc et al. [239] prepared heptametallic hexaferrocenes from 4-ferrocenylbutyl iodide and
[FeIIICp(C8Me6)]PF6. The voltammogram of 104 (Fig. 44(a)) showed that six ferrocene moieties are electrochemically equivalent. The potentials of the dendrimers with the same periphery but different core were almost the same each other, indicating that the core did not affect on the oxidation process.

Similar results and conclusion have been reported for organosilicon [240] and poly(propylene imine) [241] dendrimers bearing ferrocene groups on the periphery. Even for highly congested dendrimers with 64 peripheral ferrocene units, the ferrocenyl moieties behaves independently and the oxidation occurred at the same potentials.

Kaifer et al. [242] reported on the electrochemical behavior of asymmetric dendrimers with ferrocene units at the focal point (e.g. 104), which were prepared from the reaction of chlorocarbonylferrocene with Behera’s amine (Fig. 44(b)). The results obtained from these dendrimers might provide important insights to the understanding of the mechanism of interfacial reaction between an electrode and branched redox active species. The heterogeneous electron transfer rate constant decreased for the second and third generation dendrimers, and the half-wave potentials for ferrocene oxidation decreased with increasing the generation. For such dendrimers the rate of electron transfer might be changed by the control of the direction of dendrimers approaching to electrode surface, i.e. the approach of dendritic side to the electrode results in slow kinetics, while the approach of ferrocene side should occur fast electron transfer. The controlled electrochemical event might be achieved by judicious choice of dendrimer component and electrode surface. The asymmetric electroactive dendrimers could find applications in the sensing fields.

The inclusion complex of ferrocenyl units on the periphery with β-cyclodextrin (CD) has been published [243]. The aqueous solubility of dendrimers up to third generation was enhanced by the addition of CD, indicating the formation of inclusion CD/ferrocene complex. This was supported by the observation that the addition of 2-naphthalene sulfonate, which forms easily inclusion complex with CD, to a solution of CD/ferrocene complex results in immediate precipitation of dendrimers. A solution of the dendrimer with 8 ferrocene units in the presence of CD exhibited one voltammetric wave, but two redox waves corresponding to complexed and uncomplexed ferrocene units with CD for higher generation dendrimer were observed, indicating that some of functional groups remained uncomplexed due to the steric congestion on the surface.

Higher generation dendrimers have been observed in several instances to physisorb onto the electrode. Recently, Alonso et al. [244] reported on the synthesis and the formation of electrodeposited film of dendrimers possessing interacting silicon-bridged biferrocenyl units on the Pt disk electrode surface. The biferrocene was prepared by the reaction of ferrocenyllithium with vinylmethyl dichlorosilane. Two ferrocenyl groups introduced into the periphery are oriented at ca. 90 relative to one another (Fig. 44(c)). The dendrimer 106, for example, showed two well separated and reversible oxidation waves in CH2Cl2 (NBu4PF6). The electrochemical behavior suggests that two ferrocenyl units linked together at the same silicon atoms interact significantly. The first oxidation occurs at nonadjacent ferrocene sites, and the subsequent removal of electrons from the remaining ferrocene units neighboring those already oxidized are difficult. Upon continuous scan in the potential range of 0–1 V(vs. SCE), the formation of electroactive film on the electrode was confirmed by the observation of the successive increase in the peak current. The voltammetric response of the electrodeposited film of 106 exhibited reversible oxidation–reduction wave, indicating the formation of surface-confined electroactive dendrimer film. In a further study, Takada et al. [245] showed that the electrodeposited multilayer equivalents of DAB-dendr-(NHCOFc)n (n = 8, 32, and 64) bearing ferrocenyl units on the Pt electrode surface desorbed upon rereduction, and only monolayer equivalent remained. For the multilayer coverages the adsorbed
dendrimers are flexible, and solvents and/or salts exist within the layers, but the monolayer coverage exhibits rigid film behavior. The tapping mode atomic force microscopy suggests that the apparent size on the surface is significantly large compared to the calculated values, indicating the flattering of the dendrimers upon adsorption.

Fig. 45. A tetrathiafulvalene-containing arborol.

Fig. 46. Dendrimers with peripheral tetrathiafulvalenes.
Tetrathiafulvalene (TTF) derivatives are a typical \( \pi \)-electron donor and have unique properties, reversible oxidation to thermodynamically stable mono- and dication radicals, and aggregates of oxidized TTF.

Bis-arborol (107) containing TTF connector has been synthesized with an aim of construction of a self-assembling molecular wire [246]. The aggregates were formed when a hot solution of 107 in ethanol–water or DMF-water was cooled. The cyclic voltammetry established that the redox potentials of the TTF units were not altered by arborol substituents. The phase contrast optical microscopy and AFM showed the formation of stringlike aggregates with the lengths on the order of microns and diameters of 30–100 nm range. The UV–Vis-NIR spectra of the aggregate oxidized with iodine exhibited a characteristic absorption corresponding to TTF dimers or oligomers. This observation indicates that the TTF units are stacked in the aggregates, in a manner similar to that of alkane-bisarborols reported by Newkome et al. [172] (Fig. 45).

Bryce et al. [247–251] have synthesized a series of poly(aryl ester) dendrimers appending up to 12 tetrathiafulvalene units on the periphery by a convergent strategy and reported their electrochemical and charge-transfer properties. Dendrimers such as (108), (109), and (110) exhibited two redox couples corresponding to the TTF cation radical and the TTF dication (Fig. 46). The higher generation dendrimer linked to benzene triester core is stable only at \( 0^\circ \text{C} \), whereas the dendrimers containing diphenyl ether core 110 have good stability and are soluble in organic solvents. As the number of TTF unit increases, the first and second redox waves tend to broaden and sharpen, respectively, probably due to the adsorption or precipitation on the Pt electrode. TTF is well-known to form charge transfer complexes with electron acceptors. Indeed, the dendrimers with TTF units form charge transfer complexes with \( I_2 \). UV spectra of these complexes exhibited the absorption in the 516–590 nm and 810–836 nm region assignable to TTF cation radical and cation radical dimers, respectively. The formation of cation radicals depends on the dendrimer structure. All dendrimers decorated with 4-(hydroxymethyl)TTF units on the
periphery showed both the lower and higher energy bands, while the higher energy band was not observed for dendrimers derived from 4,5-(2-hydroxymethylpropane-1,3-diyl)dithio)TTF, i.e. dimerization is favored for these dendrimers. The absorption in the lower energy band decreased with increasing dilution, indicating that the dimers form intermolecularly and the oxidized dendrimers self-associate in solution. The subtle conformational factors at the surface are believed to affect on the formation of the dimers.

Recently, this research group synthesized dendrimers composed of 21 TTF units linked with ethylene glycol units and 1,3,5-trimethylbenzene core, in which TTF units are emplaced at all layers of the structural hierarchy, and star-shaped TTF macromolecule attached to phthalocyanine core (Fig. 47, e.g. 111, Pc-(TTF)$_8$) [248,250]. The TTF-glycol dendrimer was synthesized by a convergent strategy, using the caesium salt of TTF thiolate anions. The thin layer cyclic voltammetric techniques showed that all TTF units undergo oxidations to yield the 42$^+$ redox state. The spectroelectrochemistry upon oxidation at 1.0 V showed the absorption attributed to $\pi-\pi$ intramolecular interactions between partially oxidized TTF units even very low concentration, reflecting the flexibility of oxyethylene chains. The dendrimer, Pc-(TTF)$_8$, in which both phthalocyanines and TTFs used as scaffold are liable to self-assemble by face-to-face $\pi-\pi$ stacking, aggregates depending on the solvent properties. The spectroscopic data showed that the rapid intramolecular electron transfer between the excited singlet state of the core and peripheral TTF units is operative.

More recently, redox-switchable polyester dendrimers consisting of TTF as $\pi$-donor and anthraquinone groups as $\pi$-acceptor have been synthesized [251]. The first generation dendrimer with two anthraquinone and four (TTF)$_4$ groups at the periphery exhibited clean amphoteric redox behavior with reversible between the +8, +4, 0, −2 and −4 charged states. For the second generation dendrimer with four anthraquinone and eight (TTF)$_4$ groups intramolecular charge transfer interaction is operative. Such electrochemical, optical and coordinating properties of dendrimers consisted of Pc or anthraquinone units and TTF units are expected to provide new optoelectronic materials.
A novel series of dendritic macromolecules incorporating covalently linked diaminoanthraquinones (112, Fig. 48) were investigated by Newkome et al. [252]. The reduction potentials shifted in more positive values from parent anthraquinone of $E_{1/2} = -1.577$ V as going to higher generations and the congestion of around electroactive center brought about slow electron transfer kinetics and hence irreversible electrochemistry. Such dendrimers might be potentially useful as cation transporting switches. Recently, Roncali et al. [253] reported on the electrochemical behavior of dendritic π-conjugated tetraethiénylenevinylene bearing Fréchet dendron of first, second (113, Fig. 49) and third generations. The attachment of dendrons does not affect on the planarity and rigidity of the π-conjugated backbone and brings about the prevention of the formation of π-dimer. The redox potentials were independent of the generation of dendrons, owing to the relatively large π-conjugated core.

One of the most important properties of C$_{60}$ is its ability to accept sequentially up to six electrons. Recently, buckminsterfullerene-containing dendrimers have been synthesized by several research groups [254–256]. The fullerene bearing dendron synthesized from the reaction of dendritic benzyl azide with C$_{60}$ is soluble in organic solvents (unlike C$_{60}$) [254]. The cyclic voltammogram of the fullerene dendrimer exhibited three reduction waves at $E_{1/2} = -0.65$, $-1.05$, and $-1.50$ V (vs. Ag/AgCl). These values are significantly low, probably due to the insulating influence of the globular dendritic macromolecule. Diederich [257] et al. showed that the redox potential of bis-malonate fullerene core in dendrimers is not affected by differences in size and density of the surrounding poly(ether amide) dendrons (e.g. 100), suggesting that there exists no significant intramolecular electronic communication between the fullerene and aromatic ring. However, upon changing from bis-adduct to the all-cis-2 tris- and tetrakis-adducts, the first reduction potentials shifted to more negative values. The results indicate that multiple all-cis-2 addition causes a larger perturbation of the initial fullerene π chromophore and raise in LUMO energy.

Pyridine derivatives are useful scaffold for the construction of electroactive dendrimers. Newkome [258] and Chow [259] research groups, independently, synthesized homodimeric and heterodimeric dendrimers utilizing bis-(2,2':6'2''-terpyridine)ruthenium units as connector. Newkome et al. [256]...
Fig. 50. Assemblies of metallodendrimers reported by Newkome and co-workers.
prepared supramolecular assemblies using first and second generation dendritic Ru-terpyridine complexes which could connect with first through fourth generation dendritic terpyridines. The electrochemical behavior of bisdendrimers is affected by the generation of ligands and irreversible redox processes were observed when the fourth generation dendritic terpyridine was used. This behavior indicated that electroactive center is encapsulated in the assembly and that the congested dendritic shell affects on electron transfer process even though flexible chains exists between redox center and dendritic moiety. Similar results and conclusion were reported for the homodimeric dendrimers with Ru-terpyridine redox active center by Chow [259]. Recently, Newcome’s research group [260] prepared dendrimers 114 and 115 which have an identical molecular formula and are constitutional isomers. The solubility and decomposition temperature of these isomers are similar each other but their internal density and void regions are different. Interestingly, the voltammograms of 114 and 115 are similar but the $E_{1/2}$ values of two quasi-reversible waves corresponding to redox processes on the two terpyridine units of 115 were slightly more negative than those of 114. This can be explained again by steric hindrance due to relatively large wedge surrounding redox active center. In addition, $\Delta E_{1/2}$ values observed indicate that the rate of electron transfer for one of the ligands in 114 is slower than that of others (Fig. 50).

A number of metalloendrimers based on the complexes-as-metals and complexes-as-ligands synthetic strategy have been reported [12–14,16,261–263]. Banzani and co-workers [258–261] have prepared various metalloendrimers using 2,3-bis(2-pyridyl)pyrazine (2,3-dpp) and its monomethylated salt, and 2,2'-bipyridine (bpy) as a bridging and terminal ligands, respectively, and studied their electrochemical and photophysical properties. The authors emphasize that these metalloendrimers are different from dendrimers constructed with organic framework in following points: each metal-containing units could exhibit intrinsic properties, and different metals and/or ligands can be placed in intended sites in dendrimers. The ligands used have significantly different electrochemical properties, bpy acts as high electron-donor compared to 2,3-dpp, and monochelated 2,3-dpp is easier to reduce than coordinated bpy. As an example, for the dendrimer composed of Ru coordinated with 2,3-dpp and bpy, CV and differential pulse voltammetry in acetonitrile exhibited oxidation potential at 1.53 V and reduction potentials at $-0.73$ and $-1.22$ V, which correspond to six, six, and three electron processes. The six-electron oxidation is attributed to one- electron oxidation of the six peripheral Ru ions, and the oxidation potential of inner Ru ions is outside the range of solvent window. The six- and three-electron reductions are attributed to the peripheral and inner Ru ions, respectively. Recently, Balzani et al. [263] have prepared zero, first, and second generation metalloendrimers consisted of osmium-based core and ruthenium-based branching units (cf. Fig. 2). A reversible one-electron oxidation process occurred first at the Os-based core and was then followed by ruthenium complexes located in interior or at peripheral surface. The reduction showed very complex pattern because of the presence of number of polypyridine ligands, which suffered reductions via several processes. In addition to redox active properties, these dendrimers display an interesting range of properties including strong absorption and luminescence in UV/visible spectral region.

3.6. Sensors

Dendrimers with electroactive groups or molecular recognition groups on the surface could find applications as components in sensors and electrooptical devices.

Alonso and co-workers [264] documented the physisorption of the carbosilane dendrimers modified with ferrocenyl units on the surface onto electrodes. Dendrimers-glucose oxidase-carbon paste electrodes were
prepared, which composited four or eight ferrocenyl moiety connected with repeating –CH₂CH₂Si units linking to the central >Si < core. The electrode response to glucose concentrations was significantly affected by the number of ferrocenyl units and length of spacer connected between the ferrocenyl units and dendritic framework. The system based on the dendrimers possessing 8 ferrocenyl groups linked with the longer spacer is the most efficient electron transfer mediator. The polyredox sites on the surface as well as the flexibility of the backbone are important to function as mediator in amperometric biosensors.

Astruc et al. [265] have reported that ferrocene-modified PAMAM dendrimers with 1, 9, and 18 terminal functional units act as redox sensors for the relatively small inorganic salts. The dendrimers were synthesized from nonaallylation of mesitylene, hydroboration, followed by oxidation to the nonol, Michael addition of acrylonitrile, reduction of nitrile to amine, and finally reaction of ferrocenyl acid chloride with the resultant amine. The CV of these dendrimers showed a single anodic reversible wave at \( E^0 = 0.69 \text{ V(SCE)} \), indicating the redox centers on the periphery are independent each other and

Fig. 51. Dendrimers with boronic acid (116) and platinum complex (117) as molecule recognition site.
equivalent. A progressive shift of the wave was observed for the titration of the dendrimers by the addition of inorganic salts. The $E^0$ values increased with increasing the number of dendrimer generation, showing dendritic effect. This effect is maximum for the dendrimer with 18 terminal ferrocene groups. The apparent association constants were significantly affected by the inorganic salts and increased in the order of $\text{H}_2\text{PO}_4 > \text{HSO}_4 > \text{Cl}^ > \text{NO}_3$. The usefulness of the dendrimers as redox sensors was highlighted.

Dendrimers carrying terminal boronic acid groups function to complex with a variety of the saccharides. Sinkai et al. [266] prepared second generation PAMAM dendrimer bearing boronic acid group (116) as recognition site toward sugar and anthracene units as sensor units on the surface (Fig. 51(a)). The binding behavior can be monitored by changes in the fluorescence intensity of the host. For the monosaccharide such as $\text{d}$-galactose and $\text{d}$-fructose, a more stable 1:2 monosaccharide–boronic unit complex was formed compared to monoboronic acid or flexible diboronic acid, i.e. a high local concentration of binding site on the dendrimer surface enhances the stability. In these systems, $10^{-6}$ M monosaccharide concentrations can be detected.

Recently, Koten et al. [267] have reported on SO$_2$ gas sensor using polyester dendrimers with platinum complexes at the periphery. The dendrimer 117 reacts instantaneously with SO$_2$ gas to form bright orange colored 117-SO$_2$ adduct (Fig. 51(b)). The dendrimer was positive to concentration of 10 mg/dm$^3$ of SO$_2$ when platinum/SO$_2 = 0.2$ was used. The desorption could be achieved simply by heating at 40°C or reducing pressure. No significant loss of activity was observed for repetitive adsorption/desorption cycles, although the influence of the presence of other gases on the absorption of SO$_2$ was not stated. The sensitivity and/or efficiency may be improved by adjustment of the ligand array around the Pt metal center or using higher generation dendrimers. In addition to these examples, the self-assembled monolayer prepared from PAMAM dendrimers, which can response selectively and rapidly to several volatile chemicals has been reported [218,219]. The sensing behavior of these dendrimers has been described in Section 3.3. Various types of dendrimers that are potentially useful as sensors have been synthesized, but the utility of dendrimers is still in infancy.

Fig. 52. p-Electron dendrimers as electroluminescent devices.
Fig. 53. A hyperbranched polycarbazole (120) and a linear polycarbazole (121) prepared by Tao and co-workers.
3.7. Electroluminescent devices

Organic electroluminescent (EL) devices based on polymer layers have attracted much attention because of low operating voltages, the ability to tune the color of the emitting light, and ease of fabrication. Despite of extensive studies in this field, the quantum efficiency and brightness of polymeric LEDs remain still modest. In addition, one of problems associated with such devices is that the lifetime of the cell is too short to use for all practical purposes, due to the degradation of the cell caused by the gradual crystallization. Electroluminescence in such systems is generated by recombination of holes and electrons in the emitting layer and hence the enhancement of hole injection and transport from an anode to electron transporting layers and electron confinement in the layers are known to be essential to realize efficient hole–electron recombination.

Shirota and coworkers [268, 269] have synthesized π electron dendrimers, 118 and 119 (Fig. 52). The \( T_g \) values of these dendrimers are higher than that of parent 1,3,5-tris(4-methylphenylphenylamino)benzene. 119 functions as the hole-transporting material in the multilayer LED. The device fabricated on the ITO glass, using 119, rubrene-doped TPD (\( N,N' \)-diphenyl-\( N,N' \)-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine), and tris(8-quinolinato) aluminum, emitted yellow light. The luminance at 10 mA/cm² was 516 cd/m² and luminous efficiency was 2.6 lm/W. The amorphous glassy state of these dendrimers is very stable and no crystallization was observed for a long period. As an additional functionality, these triarylamines might be useful building blocks for high-spin polyelectrolytes. The cyclic voltammogram exhibited multiredox processes, involving as many as six- and nine- electron reversible oxidations for 118 and 119, respectively. Recently, high molecular weight of TPD analog was synthesized from the reaction of bis(4-bromophenyl)benzenemethan amine and diphenyllithium amide in the presence of Pd[P(o-tolyl)₃]₂ [270].

Tao et al. [271] synthesized hyperbranched polycarbazole (HBPC, 120) as an electron transfer layer (ETL) and a linear of poly(tetradecanyl-3,6-dibutadanyl)carbazole (PTDBC, 121) as a hole-transfer layer (HTL) for double layer LEDs, in hope with the improvement of stability and efficiency over those of linear polymer systems. HBPC was prepared by the esterification of 3,6-diformyl-9-(11-hydroxyundeceyl)carbazole with cyanoacetic acid followed by condensation in the presence of \( N,N' \)-dimethylaminopyridine. PTDBC was synthesized by the \( \text{CuCl} \)-catalyzed polymerization of 9-tetradecanyl-3,6-diethynylcarbazole. The electroluminescence spectrum of the device exhibited two peaks with maximum around at 480 nm and at 540 nm. The peak in the shorter wavelength resembles the photoluminescence spectrum of HBPC. This suggests that the emission comes from the radiative decay of singlet state of carbazole moiety in the hyperbranched polymer excited by the recombination of electrons and holes. The observed spectrum in the longer wavelength is due to disordered structure of HBPC. The external quantum efficiency (photons/electron) of the device was calculated to be 0.08%. The authors believe that this value can be improved by using low work function metals as cathode. For the single layer devices which HBPC was sandwiched between two electrodes with ITO as anode and Al as cathode, no visible emission was observed. The results showed that hyperbranched polymers are new candidates as emitting materials in LEDs.

The EL device of cumarin-based hyperbranched polymers starting with 3-carboxycumarin have been reported [272]. The polymers are blue light emitter and the increase of cumarin concentration in the polymer has a tendency to lower operation voltage (Fig. 53).

Strohriegl et al. [273] reported on the synthesis and functionality of star shaped dendritic oxadiazoles and phenylquinoxalines, which are promised as electron transporting materials that enhance the
efficiency of light emitting diodes. All dendrimers, of which 122 is a typical one, have an excellent film-forming property and high thermal stability. The measurement with poly(1,4-phenylene vinylene) (PPV) as the active emitting layer in heterolayer LEDs exhibited that all oxadiazoles function as efficient electron transport and injection layers, especially for dendrimer 123 0.4% of the external quantum efficiency was achieved, which was two order of magnitudes higher than that of PPV single-layer device or linear polymer containing oxadiazole units. The results are consistent with the theoretical prediction [274] that dendrimers possess enhanced carrier mobility compared to linear counterparts. Similarly, a significant improvement of external quantum efficiency and brightness was observed for two-layer LED devices with the configuration of ITO/PPV/phenylquinoxaline 122/Ag. Authors commented that the observed values can be further enhanced by preparing higher quality of

![Diagrams of molecules 122, 123, 124, 125](image_url)

Fig. 54. A star-shaped phenylquinoxaline (122) and a dendritic oxazole (123) as light-emitting devices.

Fig. 55. Luminescent phenylacetylene dendrimers.
film. Likewise, polyamide dendrimers containing electron-deficient 5-membered oxadiazole units have been reported [275], although electroluminescent behavior was not examined. For this dendrimer, the tendency toward self-association can be enhanced by increasing of amide groups in the molecule (Fig. 54).

The cell structure having an interface between the two organic layers, where only the weak interaction exists between the layers and the interface, may be not so strong; therefore, one-layer-type device may achieve an improvement of structural stability. Moore et al. [276] reported that novel electroluminescent diodes with single organic layer configuration based on polyphenylacetylene dendrimers. They designed dendrimers consisting of a fluorescent core, 9,10-bis(phenylethynyl)anthracene, a phenylacetylene monodendron for electron capture, and triphenylamine periphery to promote efficient hole transport and recombination. As will be described later, polyphenylacetylene framework can transfer convergently and directly excitation energy to the focal point luminophor. They utilized this feature to the filed of light-emitting system, i.e. if the recombination of electrons and holes occurs in the dendritic segment, energy transfer to the luminescent appended at the central core is expected. A high quality amorphous thin film of dendrimer (Fig. 55, 124 or 125) on the ITO surface was obtained by spin coating. As an electron injection electrode, Mg/Ag alloy or Al was used. The current-voltage characteristics of device obtained from 125 exhibited an onset voltages of 3V with Mg/Ag and its current density was found to be one order of magnitude larger than that of 124. These results indicate that triphenylamine group in the periphery of the dendrimers contributes to improve the hole injection and trapping. The photoluminescences of films of 124 and 125 exhibited the structureless peaks in the longer-wavelength, indicating the solid state aggregation of dendrimers, which caused low electroluminescent intensity (Fig. 55).

As described above, PPV has attracted much attention as an electroactive material. In general compounds with shorter conjugation lengths have a higher photoluminescence quantum yield. The dendrimers consisting of PPV units have been synthesized, but their functionality as electroluminescence materials have not reported. A structurally well defined dendrimer might be useful for the active organic layers in LEDs, but the new development and construction of dendrimers as electroluminescent materials are required to achieve a much higher efficiency.

3.8. Photochemical molecular devices

A number of photoharvesting linear (co)polymers with donor and acceptor groups or polymers with antenna effect have been documented by Fox [277] and Guillet [278]. Due to the random coil conformation of these polyemrs, however, the excimer formation by inter- or intramolecular interaction, leading to low efficiency of energy transfer, is unavoidable. Various design and fabrication to diminish the excimer formation have been proposed.

Dendritic structures seem to be suitable to achieve a high efficient energy transfer, since the spatial position of a number of absorbing units and the acceptor groups as a reaction center and fluorescent trap and rigidity of architectural skeleton can be controlled. Most importantly, the construction of polymeric systems with an energy gradient so that there can be a directional, vectorial transport of excitation energy is possible. Dendritic molecules with functional groups capable of absorbing and emitting light and reversibly exchanging electrons as a building block including a solvatochromic probe have been reported by several research groups.

Fox [279,280] synthesized first, second, and third generation Fréchet dendrons with chromophores
such as pyrenyl and naphthyl groups on the periphery and $N,N$-dimethylaminophenoxy group at the focal point and investigated the fluorescence behavior of these polymers. The fluorescence measurement indicates no peak corresponding to naphthalene excimer but predominant formation of excimer for pyrene-capped dendrons. The fluorescence yields of dendron with two naphthalene group on the same peripheral phenyl moieties were significantly low compared to that of dendron with one chromophore group in acetonitrile, due to the involvement of self-quenching process. For the pyrenyl-capped second generation dendron possessing 3-(dimethylamino)phenoxy group as the focal point, an efficient quenching (almost 90%) can be achieved. The quenching efficiency of the third generation dendron,
However, decreased relative to the second analog. This is ascribed to the decrease of the concentration ratio of donor group to chromophore groups and additional distance between donor and acceptor. The occurrence of substantial electronic coupling between chromophores and quenchers across dendrimer framework was also supported by the observation of increase in the quenching efficiency in polar solvents. In a next experiment, attempts have been done to prepare rigid linear-dendron hybrid polymers by utilizing a ring opening polymerization of norbornenyl monomer carrying a second generation naphthyl-capped dendrons, in hope that chromophore acts as dendritic antenna [279,280]. However, the excimer emission was observed even very low concentrations of the polymers, indicating that pendant dendrimer units attached to rigid main chain are flexible more than expected. Such polymers are hardly difficult to use as a medium for vectorial electron or energy transport but could find applications in the fields based on light-harvesting properties.

A successful directional-energy transfer system has been reported by Moore et al. [281–285], who prepared phenylacetylene-based dendrimers with perylene luminophor at the focal point (Fig. 56). For these dendrimers, the important event is constructed by linking at meta position of each branching benzene node, i.e. this connecting mode could inhibit any conjugate delocalization of electrons across the dendrimer framework. This is realized by the observation that compact dendrimers (126) bearing branches with identical length exhibit no spectral shift with change in molecular size. The excitation of phenylacetylene moiety at 310 nm leads to emission from the perylene chromophore, indicating that the intramolecular energy transfer occurs in the dendrimers. For the higher generation, the fluorescence quantum yields decreased and the extent of residual fluorescence from phenylacetylene moiety increased. The excitation spectra monitored at 515 nm, and then normalized spectra of dendrons bearing perylene group indicate that more photons are collected and transmitted to perylene appended to the larger generation dendrimers. Even the highest generation the level-off of the intensity was not observed, indicating that the increase in phenylacetylene moieties brings about the development of photon-harvesting ability. The extended dendrimers (e.g. 127) consisted of the linear segments of phenylacetylene and single phenylacetylene moieties exhibited a more complex behavior.

For higher generation dendrimers the spectra exhibited the peaks corresponding to the length of linear phenylacetylene units, i.e. they can function as individual absorbing units with different energy levels. Comparison of absorption spectra with excitation spectra of dendrimer 127 exhibited that nonradiative intramolecular energy transfer with 96% efficiency occurs from the dendrimer antenna to the perylenic acceptor. The intermolecular energy transfer can be ruled out. Thus, extended dendrimers behave as an efficient energy funnel, and the decrease in efficiency and slow trapping rates were not observed even larger dendrimers. The theoretical evidences [286,287] as well as the experimental results indicate that the molecules can contain enough energy gradient to overcome the geometric bias toward periphery. Moore highlighted that the dendrimers will be used as supertips for optical nanoprobes and nonsensors, microscopy, and organic light-emitting diodes.

Recently, Jiang and Aida [288] demonstrated that the morphology is important for singlet energy transduction for porphyrin dendrimers bearing Fréchet’s poly(aryl ether) wedges. Fully substituted porphyrin bearing four fourth generation dendron units (L5)4P, which is highly constrained in conformation, exhibited an efficient energy transfer quantum yield (Φ = 80.3%). Contrast to this, partially substituted dendrimers or fully substituted but lower generation dendrimers result in lower quantum yields, indicating that the energy transfer is highly sensitive to the morphology of the dendrimers. They assumed that the excitation energy first migrates among the continuos array of chromophore
(dialkoxybenzyl units) and is then transferred to the porphyrin core. This result might open a new avenue for the molecular design of light-harvesting materials.

Transition metal dendrimers also appear attractive potential light-harvesting materials. Balzani and coworkers [12,263,289–292] have prepared a number of metallodendrimers employing ruthenium and/or osmium as central, intermediate, and peripheral metal ions and 2,3-bis(2-pyridyl)pyrazine (2,3-dpp) as bridging ligand. One of characteristic features of these dendrimers, different metals and/or ligands can be placed in desired sites of supramolecular array by choice of building block. By employing known order of the energy of the lowest MLCT (metal to ligand charge transfer) excited state of each block, the direction of energy flow within dendrimers might be possible. For the heterometallodendrimer, 128 (Fig. 3, M_0 = Os, M_1 = M_p = Ru), The emission spectra indicate that the lowest excitation energy state is localized on the osmium core, and the energy of peripheral Ru complexes is lower than that of interior Ru complexes. That is, the energy transfer from peripheral units to Os core is at least in part prevented. In the homonuclear Ru-based dendrimers, the lowest excitation energy is located on the peripheral ruthenium units coordinated with bipyridyl and 2,3-bis(dipyridylpyrazine), and hence the energy transfer occurs from the interior to the periphery. Their ability to absorb light increased with increasing the dendrimer in size but the emission lifetime and the quantum yield were hardly affected. This suggests
that large dendrimers can function as antennae for light harvesting. Similar systems have been described by Gourdon et al. [293].

The lifetime of the excited state of ruthenium ions surrounded with dendron carrying bipyridine units at the focal point is significantly prolonged compared to the corresponding complex without dendron wedge [294]. Such a dendritic shell effect on the lifetime of Ru complexes has been reported for starburst dendrimers with positively or negatively charged surfaces [295,296]. The increase in lifetime of complexes bound to dendron ligands is attributed to the partial prevention of quenching processes by dissolved oxygen or solvents.

Chelates with lanthanide ions such as Eu$^{3+}$, Tb$^{3+}$, and Sm$^{3+}$ are examined as potential probes, sensors, and labels for a variety of chemical and biological applications. To obtain strong luminescence, metal ions are bound to chromophoric ligands, which are able to absorb energy and transfer it efficiently to metal ions, and to protect the metal ion from the unfavorable quenching of luminescence. A number of macro(bi)cyclic and podand ligands containing chromophores are used for this purpose. Kawa and Fréchet [297] reported fluorescence properties of the self-assembly complexes of the polyether dendron with carboxyl group at the focal point (c.f. Fig. 1, R = COOH, 129) with lanthanoid ions such as Er$^{3+}$, Tb$^{3+}$ and Eu$^{3+}$. The formation of Ln-cored dendrimer complexes, in which an ion is entrapped with three 129 molecules, was evidenced by FT-IR, elemental analysis and luminescence measurements, and solubility in common organic solvents. In solution, the intensity of fluorescence of lanthanoid ions increased with increasing the generation of dendritic subunits. It was shown that the enhancement of fluorescence intensity is attributed to the antenna effect of aromatic framework and shell effect that encapsulates lanthanoid ion within a dendritic sphere leading to suppression of self-quenching process. The number of coordinated water molecules that are known to quench the luminescence, which can be determined by the Horrocks and Sudnick equation, increased with the generation of dendritic subunits. This result is explained in terms of steric hindrance around the Ln$^{3+}$ core for higher generation dendrimers, leading to weak assembly. The bulk state luminescence properties of dendrimer-Ln$^{3+}$ complexes have also investigated, with a goal to application in optical fiber communications in mind. For the third and fourth generation dendrimer Ln$^{3+}$ complexes, the luminescence was enhanced compared to the first generation dendrimer complex, indicating that the shell effect is operative effectively. Authors comment that the approach employing dendritic shell may be useful to develop improved laser-related devices.

Another example is reported by Latva et al. [298], who prepared four binuclear building blocks, bis(4-pyridine-2,6-dicarboxylic acid) derivatives (BCA, 130). Eu$^{3+}$ and Y$^{3+}$ ions are linked together by BCA to form hyperbranched polymers. Due to the large number of BCA ligand acted as energy donors and energy transfer from Y$^{3+}$-BCA complexes to Eu$^{3+}$ ions via triplet–triplet migration, the luminescence intensity of Eu$^{3+}$ was strongly enhanced. Among BCAs, ligand linked with acetylene moiety showed the highest relative luminescence intensity, which has the shortest distance between different Ln$^{3+}$ ions and the lowest triplet energy level. Authors suggest that the energy transfer for such a polymer does not proceed by the Forster dipole–dipole mechanism but occurs along the polymer framework (Fig. 57).

Azobenzene derivatives have been used to create photosensitive and photoswitchable devices for many years. McGrath et al. [299] reported that the second generation poly(benzyl aryl ether) dendrimer with azobenzene central core isomerizes from trans- to cis-form upon UV irradiation and from cis- to trans-form either thermally or visible light irradiation. These processes were not affected by bulkiness of dendrimers. It has been suggested that the dendrimers containing azo unit could be used to grab small molecules upon irradiation.

Jiang and Aida [300] found an interesting behavior, on exposure to the infrared radiation, cis-form of
poly(benzyl aryl ether) dendrimers with fourth (131) and fifth generations isomerize rapidly to \textit{trans}-forms. The rate of isomerization was 23 times larger than that of visible light irradiation. The monochromatized infrared radiation at 1597 cm\(^{-1}\), which corresponds to a stretching vibrational band for aromatic rings, leads to \textit{trans}-form, but on radiation at 1155 cm\(^{-1}\) (stretching vibrational band for CH\(_2\)–O–) or 2500 cm\(^{-1}\) (transparent of dendrimers) the isomerization was not observed. The photoisomerization process depends remarkably on the dendrimer framework: neither the dendrimers of lower generations nor non-spherical-dendritic azobenzene isomerized on the infrared radiation. These results indicate the importance of morphology of dendrimers for isomerization. The isomerization of \textit{cis} dendrimer with fifth generation occurred under excitation at 280 nm being absorption band of dendrimer framework. They conclude that the dendrimers with higher generations play two important roles, protection against collisional de-excitation and efficient photon-harvesting antenna (Fig. 58).

Vögtle [301,302] prepared poly(propylene imine) dendrimers with up to 32 para and meta azobenzene units in the periphery (132). All \textit{trans}-azobenzene dendrimers isomerized to \textit{cis} form in a manner similar to the carboxamide-substituted azobenzene model compounds. The quantum yield related to a single chromophoric unit is the same regardless of the dendrimer generation. The results indicate that even high generation the chromophore units are not constrained towards photoisomerization. Thin films of good optical quality could be prepared from some of dendrimers. The functionality of these dendrimers as holography material was tested. It is shown that the holographic gratings with diffraction efficiencies of 20% can be recorded for the second generation dendrimer with meta azobenzene units, although the value is still less effective than commonly used polymers.

In contrast, for the dendrimers consisting of 1,3 alternate calix[4]arene derivative as a core and azobenzene-based diaminocarboxylic acid as a branched building block, complete isomerization was
not achieved [303]. The ratio of trans- to cis-form at the equilibrium was affected by the generation, due
to the increased steric repulsions in the higher generations.

Photoinduced electron-transfers have been an active field of research because of its importance of
photosynthesis as well as technical applications. Turro et al. [295] reported on the intermolecular
electron transfer between methyl viologen (MV$^{2+}$) and tris(2,2$^\prime$-bipyridine)ruthenium in the presence
of dendrimers bearing carboxyl group on the periphery. In this system, dendrimers did not directly
participate in electron transfer process but act as platform of the donor and acceptor. Positively charged
dendrimers were also used as platform for the luminescence decay of the triplet metal-to-ligand charge
transfer excited state of Ru(4,7-SO$_3$C$_6$H$_5$)-phen)$_3$ with MV$^{2+}$, K$_4$Fe(CN)$_6$, and K$_3$Fe(CN)$_6$ [294].

As described earlier section, Inoue et al. [233] have prepared poly(benzyl ether) dendrimer with
porphyrin core and determined the rate of fluorescence quenching with vitamin K which acts as an
electron acceptor. They found that the rate of quenching for the fourth generation dendrimer was higher than
that for the first generation dendrimer. Similar results were reported by Fréchet et al. [236], who showed that
the quenching of fourth generation poly(benzyl ether) dendrimer by MV$^{2+}$ is 33% more efficient
compared to that of lower generation analogs. It is suggested that the increase in quenching efficiency
of higher generation dendrimers is due to both $\pi-\pi$ interaction and the globular conformation, and that
small molecules can access to the porphyrin core, although conclusion must wait further information.

The photoinduced electron transfer through dendritic framework has been reported by Aida et al.
[304], in which the zinc porphyrin core was linked with second and fourth generation poly(benzyl ether)
dendron modified with carboxylates on the surface. The dendrimer, [KO$_2$C$_3$L$_4$PZn (133), exhibited a
hypochromicity depending on the ionic strength or the pH of the solution. This behavior was attributed to
the shrinkage of the hydrophobic dendrimer framework accompanied by change of surface ionicity. The
addition of MV$^{2+}$ to a solution of the second generation dendrimer leads to dramatic change of UV
spectra but not for the fourth generation. The profiles of fluorescence quenching of the fourth generation
dendrimer by MV$^{2+}$, in which the Stern Volmer plots was saturated, are different from that of the second
generation. From these results, authors conclude that the photoinduced electron transfer occurs between
the core and the electron acceptor noncovalently assembled on the periphery through dendritic framework.

![Fig. 59. A metalloporphyrin dendrimer with folding arms.](image-url)
A similar conclusion have been reported by Kimura et al. [305], who showed that occurrence of electron transfer through dendrimer framework from the Zn phthalocyanine core to MV$^{2+}$ accumulated on the carboxylate surface.

Recently, Sanders et al. [306] synthesized new dendrimers consisting of zinc porphyrins as the main building block, which mimic light-harvesting photosynthetic systems. Unsymmetrical and symmetrical porphyrins as building blocks, and 3,5-diiodobenzylalcohol and 5-iodoisophthalic acid as the branching units were used for the construction of dendrimer(134). The MALDI-TOF mass spectrum of 134 showed a maximum at $m/z = 10087$, in agreement with the expected structure. UV/Vis spectra of 134 in the presence of 1,4-diazabicyclo[2,2,2]octane (DABCO) exhibited a Solet maximum at 420, which can be assigned to the formation of 2:1 Zn-porphyrin units–DABCO complex. The observed blue shift of 6 nm from characteristic absorption at 426 nm of 1:1 porphyrin-DABCO complex is due to exciton coupling between parallel porphyrin units. This is also supported by $^1$HNMR spectra. The result indicates that each of the arms of the porphyrin at the periphery can be brought together with the other to bind DABCO cooperatively. Authors comment that the introduce of electron donor or electron acceptor core and the conformational sensitivity of dendrimer to ligands have profound effects on its photophysics (Fig. 59).

Meijer et al. [307] showed that the fullerene anions (C60$^{-}$) is formed from the mixture of DAB-dendr-(NH-$t$-Boc-$t$-Phe)$_n$ and C60 by the filtered light illumination of a mercury lamp. As described in earlier section, the dendrimers serve as a electron donor towards strong electron acceptor such as TCNQ. Although the charge-transfer interaction between the dendrimers and C60 in the ground state was not observed for the generation number of $n = 4, 8, 16, 32$, and 64, ESR spectra of the mixtures upon irradiation exhibited the peaks corresponding to fullerene anion except for the lowest generation dendrimer–fullerene system. It was shown that the dendrimers with higher generations function as an efficient electron donor by at least two order of magnitudes compared to small model compounds, tripropylamine or $N$-( tert-butoxycarbonyl)-l-phenylalanine. The spectrum of the fullerene anions could be observed over several days at room temperature. This persistent photoinduced electron transfer is rationalized with the fast intramolecular fragmentation and/or disproportionation of initially formed aminium radicals, which leads to the irreversible electron-transfer and provides for diamagnetic counter ion. Thus, DAB-dendr-(NH-$t$-Boc-$t$-Phe)$_n$ functions as efficient electron donors in quenching photoexcited states.

Moore et al. [308] found that the fluorescence maximum of a CT state in higher generation poly (phenylacetylene) dendrimers shows an anomalous spectral shift. In this experiment, $p$-dimethoxybenzene moiety was attached as an electron donor at the focal point, and tolan segment of dendrimers functions as an electron acceptor (135)(cf. Fig. 56). By changing from cyclohexane to pentane the fluorescence maximum of the fifth generation dendrimer shifted largely from 380 nm to 421 nm but not for the lower generation dendrimers. In addition, such a shift was not observed for the dendrimer with benzene moiety instead of $p$-dimethoxybenzene moiety. The generation-dependency of the shift may result from the change in size and shape of the dendrimers. They suggest that the behavior affords important informations on the design of dendrimers capable of undergoing long-range intramolecular electron transfer. The fluorescence of poly(phenylacetylene) dendrimers are quenched by both electron acceptors ($p$-dicyanobenzene and $m$-dicyanobenzene) and donors(1,4-diazabicyclo[2,2,2]octane and $p$-dimethoxybenzene) [309]. Among quenchers, donors with lower oxidation potentials and acceptors with higher reduction potentials quench more efficiently the fluorescence. The higher generation dendrimers tend to form exciplexes whereas lower generation dendrimers form ion pair. Exceptionally, 1,4-diazabicyclo[2,2,2]octane forms ground state complex with higher generation dendrimers. The results showed
that polyphenylacetylene-based dendrimers act as either electron acceptors or donors. Authors comment that these dendrimers are suitable bridging medium for model compounds to mimic photosynthesis.

Polysilanes are known to exhibit unusual properties, dependency of absorption spectra and photoluminescence on chain length and thermochromism, resulting from their $\sigma$-delocalization. As an example, Sakurai et al. [310] synthesized polysilane dendrimer (136) containing 30 Si–Si bonds from 2-lithio-1,3-diphenylpentamethyltrisilane as a key compound. The wavelength absorption maximum of 136 was observed in the similar range to that of linear analog, despite the absence of all-trans chain configurations required for efficient $\sigma$-delocalization. Excitation coefficients observed are somewhat higher than those of linear polysilanes, probably due to the multiplicity of pathways suitable for electron delocalization within the dendritic framework. Contrast to this, the fluorescence spectrum exhibited different behaviors from linear counterpart. Polysilane dendrimer reported by Suzuki et al. showed two feeble peaks in the region of 300–450 nm [311]. Similarly, in the hyperbranched polysilane (137), (Si)$_m$(Me$_2$Si)$_n$ and [(SiMe$_2$)$_n$Si]$_n$ prepared by Matyjaszewski et al. [312], the excitation at 250 nm and 295 nm exhibited a visible emission at 456 nm that was not observed for linear analog, in addition to the Stokes shifted emission. [(SiMe$_2$)$_n$Si]$_n$ exhibited much weaker emission than (Si)$_m$(Me$_2$Si)$_n$. Authors concluded that the delocalized $\sigma$-$\sigma^*$ transition is more effective in the latter compared to the former, due to occurrence of effective energy transfer from Me$_2$Si arms to silicon cluster.

Nanjo and Sekiguchi [313] synthesized dendritic molecules with alternating Si and Ge atoms backbone (138), using chloromethylphenylgermane and bis(dimethylphenylgermyl)(methyl)silyllithium. The molecular structure of the first generation dendrimer was confirmed by X-ray diffraction. Although details of optical properties were not reported, the UV spectrum of 132 exhibited the $\sigma$–$\sigma^*$ band of Si–Ge bonds at 271 nm at 300 K. By lowering temperature, the absorption band shifted to the shorter wavelength, together with the appearance of new absorption at 243 nm, probably due to the break of the $\sigma$-conjugation of Si–Ge bonds (Fig. 60).

Organic nonlinear optical materials have been studied extensively for applications in electrooptic devices, which have advantages such as a large susceptibility, fast response, and high optical damage
threshold compared to inorganic materials. Polymeric materials offer additional advantages in device fabrication such as film preparation. One of critical problems of second order non-linear optical polymers, however, is to stabilize the dipole alignments induced by an electric fields at elevated temperatures. Crosslinking reactions have been utilized to hold the dipole orientation.

Dendritic polymers with NLO-functional units were also prepared with the hope that these polymers have controlled dipole orientation.

Wada et al. [314–316] synthesized hyperbranched polymers containing 4-(2-cyano-2-methoxy-carbonylvinyl)aniline (139) as a second-order nonlinear chromophore and branching units from 4-formyl-N,N-di(2-hydroxyethyl)aniline by Knoevenagel polycondensation. The hyperbranched polymer was stable up to 330°C. The second harmonic generation signal was observed from poled hyperbranched polymer film but its coefficient (\(d_{33}\)) was small. The NLO chromophores are crosslinked so that the alignment is difficult in such a hyperbranched polymer. In following experiments, carbazole-based hyperbranched polymers (120) that can form amorphous solid films with good optical quality and starburst dendrimers (140) were tested as NLO materials. The second-order nonlinear optical coefficient values of carbazole-based starburst dendrimers depend on the acceptor groups (−CHO, −NO₂, and −CH=C(CN)₂) and the highest value
(d$_{33}$ = 49.6(pm/V) was obtained for ─CH=C(CN)$_2$ [316]. Recently, polyester dendrimers bearing carbazole units on the periphery have also been synthesized but their optical properties have not been described [317] (Fig. 61).

Nonlinear optical properties of LB films of azobenzene dendrons and dendrimers have been reported [318]. For these polymers the second harmonic generation signal is based on π–π transition of azobenzene units. SHG values of dendrimers of up to third generation were negligibly small, indicating that the dendrimers are a centrosymmetric molecule.

McKeown et al. [319] synthesized silicon phthalocyanines with axial Fréchet dendron of first, second, and third generations in order to inhibit cofacial intermolecular excitonic interaction of phthalocyanine molecules in the film, which may be useful as nonlinear optics. The dendrimers were prepared by the substitution of chloro ligands of dichloro(phthalocyaninato)silicon by poly(aryl ether) dendron with benzyl alcohol group at the focal point. Fortunately, single crystal suitable for X-ray analysis could be obtained phthalocyanine bearing second generation dendron (141). The ORTEP showed that the distance between cofacial phthalocyanine cores is 14 Å, which is too large for exciton coupling, although there are short edge-to-edge contacts between adjacent phthalocyanine cores. Polarized optical microscopy (POM) suggests that the spin coated films of second and third generation dendrimers are uniform and isotropic. These readily processable, nonscattering phthalocyanine films may be useful for optical applications (Fig. 62).
3.9. Conductive dendrimers and hyperbranched polymers

The dendrimers-based films are quite different structurally and morphologically from typical conducting polymers which have long conjugated chains. Wang et al. [320] reported on the conductivity of star-shaped polymers consisted of regioregular poly(3-hexylthiophene) arm attached to polyphenylene core.

![Diagram of an electrically conducting star-shaped polymer]

Fig. 63. An electrically conducting star-shaped polymer.

![Chemical structures of PAMAN dendrimers with cationically substituted naphthalene diimides]

Fig. 64. Electrically conductive PAMAN dendrimers with cationically substituted naphthalene diimides.
They first synthesized dendritic polyphenylene capped with bromothiophene to serve as a linking point and then the star polymer 142 stepwisely by the addition reaction of 2-bromo-(5-bromomagnesio)-3-hexylthiophene to the brominated linking point. From the comparison of UV–VIS spectra of film of 142 with that of linear counterpart, it is suggested that domains with more extensive π-overlap is likely to form in the star polythiophene. The atomic force microscopy (AMF) showed that the film surface is a much smoother compared to conventional linear polythiophene, indicating that the dendrimers are densely packed. The conductivity of iodine-doped dendrimer film was 65 S/cm, which was 1.5 times higher than that of polythiophene (Fig. 63).

The conductivity of the PAMAM dendrimers modified with cationically substituted naphthalene diimides (143–145) have been reported by Miller and Tomalia [321]. The reduction of dendrimers with sodium dithionate gave a dark brown colored film. The conductivity of the fully reduced and half-reduced dendrimer films were $10^{-3}$ and $10^{-2}$ S/cm, respectively. The conductivity was electronic, not ionic. The PAMAM dendrimers bearing 143 units except for the first generation dendrimer showed similar conductivities. The conductivity was little influenced by the structural difference of diimides located on the surface. Near-IR spectra showed the formation of intra- and intermolecular π stacking correlated with conductivity. Apparently, the flexibility of framework of PAMAM dendrimer enables efficient π interactions. The conductivity increased with increased humidity above the films reaching as high as 18 S/cm at 90% relative humidity. The value observed was only slightly lower than that reported for traditional conducting polymers. The structural characteristic of such conducting polymers is their conjugated π-system extending over a large number of recurrent monomer units. This characteristic results in low-dimensional materials with a high anisotropy of conductivity which is higher along the chain direction. Contrast to this, the dendrimers have the potential to form three dimensional π-stack and the isotropic nature of the films. The dendrimers could find new practical applications in the fields based on isotropic properties, although the improvement of poor film-forming properties due to the lack of interpenetration of polymer chains is required (Fig. 64).

The conductivity of dendrimers peripherally decorated with thiophenes (146 and 147) has been studied by Miller et al. [322]. The conductivity of films oxidized with I$_2$ was $10^{-3}$ S/cm. When the I$_2$-oxidized film of 146 was exposed in the vapors of acetone and ethanol, the conductivities increased 800 and 380 times higher than those of the original values, respectively, but water has little effect on the
conductivity. The enhancement of conductivity is also affected by the number of conjugated thiophene on the periphery. Such large changes in conductivity was not observed for conducting main chain polymers. It was proposed that the plasticization due to adsorbed molecules allows faster electron transport between the stacks of oxidized thiophene units on dendrimers. The results showed that the utilization of dendritic structure is useful to improve the sensitivity and selectivity, compared to other corresponding linear polymer sensors (Fig. 65).

The conductivity based on tetrathiafulvalene dendrimers was reported by Bryce and Devonport [323]. The charge transfer complex formed between 14 and TCNQ was isolated as an insoluble black powder. The stoichiometry of the complex was established to be TTF units: TCNQ units \( \hat{=} \) 8:3 by elemental analysis. The conductivity of this material was \( \sigma = 2.2 \times 10^{-3} \) S/cm.

Recently, molecular asterisks have been synthesized by employing the MacNicol reaction of hexachlorobenzene or dodecachlorororonene and \( p \)-phenylene sulfides (148, \( \text{C}_6\text{H}_4\text{S}^– \), \( n = 2, 3, 4 \)), although the conductivity has not been reported [324]. The synthesis of branched poly (triphenylamine) via coupling reaction of \( N,N\)-bis(bromophenyl)-\( N\)-(4-bromo-magnesiophenyl) amine in the presence of Ni(acac)\(_2\) has been reported [325]. In the branched polymer with an average molecular weight of 4000, a \( \pi-\pi^* \) transition band attributed to the conjugation between biphenylene units and nitrogen atoms was observed. The VIS-nearIR spectra of electrochemical BF\(_4^–\) doping of the polymer exhibited that three bands around 500, 750, and 1500 nm at applied voltage of 1.0 V, indicating that electrochemically created charge carriers are polaron species. These polymers potentially act as a conductive material.

Attempts to create an insulated molecular wires have been described by Schenning et al. [326], who synthesized poly(triacetylene) oligomers bearing Fréchet type dendron of up to third generation (e.g. 149, Fig. 66). UV–Vis spectra and electrochemical experiments exhibited that the insulating layers created by the dendritic wedges protect and stabilize the conjugated polyacetylene backbones without alternating their electrochemical properties (Fig. 66).

Studies of solid polymer electrolytes have been also actively pursued as a major contribution to the development of high energy density batteries, particularly lithium secondary batteries. Solid solutions of salt such as LiClO\(_4\) in polyethylene oxide have been studied extensively as ionically conducting...
Fig. 67. Ionically conductive polymers.
In these systems, the polymer electrolytes are required to solubilize high carrier ion concentrations and to have high segmental mobility.

Inoue et al. [327] reported on ionic conductivity of Li$^+$ salt complexes with star-shaped and dendritic polyelectrolytes based on cyclophosphazene core. The conductivities depend on the number and length of oxyethylene units ($\text{(CH}_2\text{CH}_2\text{O)}_n\text{CH}_3$ (150 ($n = 7.2$) and 151 ($n = 11.8$)). For DSC measurement, the peak corresponding to the melting of crystallinity was not observed for the Li$^+$ salt complexes, indicating the polymer system of amorphous phase which is prerequisite to achieve a high ionic conductivity. The extent of $T_g$ elevation polymer–Li$^+$ complexes was significantly small compared to that of linear counterparts. The maximum conductivity of $4 \times 10^{-5} \text{ S/cm}$ at 30°C was observed for the star-shaped polymer with $n = 11.8$-Li$^+$ salt complexes. The observed values are somewhat higher than those of the polystyrenes carrying pendant oligo(oxyethylene)cyclophosphazene–Li$^+$ salt system. This improvement is ascribed to the high segmental mobility of oxyethylene chains, as judged from the behavior of $T_g$ elevation (Fig. 67).

The ionic conductivity of complexes of hyperbranched polyelectrolytes with Li$^+$ ions have been published [328]. The hyperbranched poly(ether ester) was synthesized by the polycondensation of AB$_2$ monomers prepared from the reaction of 3,5-dihydroxymethylbenzoate with di- (152), tri- (153), or hexaethylene glycol (154) derivatives. In the polycondensation, hyperbranched polymers obtained from 152 were more fine structure compared to 154-based polymers. As expected, DSC traces showed that the polymers were amorphous and that the glass transition temperatures decreased with increasing of oxyethylene units. The conductivity of hyperbranched polymer linked with $-(\text{CH}_2\text{CH}_2\text{O})_n\text{Li}^+$ salt complexes was $7 \times 10^{-5} \text{ S/cm}$ at 60°C with a concentration of [Li$^+$] of 0.62 mol per repeat unit.

Fig. 68. A dendritic molecule (155) brings about an increase in conductivity of the MEEP-LiSO$_3$CF$_3$ system.
Hyperbranched poly(oxyethylene) attached to cyclotriphosphazene core was used as ion transport assistance in the poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP)–Li$^+$ systems [329], which is a typical ion conductive system. Hyperbranched poly(oxyethylene)cyclotriphosphazenes (e.g. 155) were synthesized by the coupling reaction of hexachlorocyclotriphosphazene and dendron with hydroxy group at the focal point, which was prepared by the reaction of 3-(benzyloxy)-1,2-propanediol and 2,3-bis(2-methoxyethoxy)propyl toluene-$p$-sulfonate, followed by hydrolysis. The addition of hyperbranched polymers to the MEEP-LiSO$_3$CF$_3$ system improved the conductivity, and of cyclophosphazenes studied 155 gave the highest conductivity. It is suggested that the hyperbranched cyclophosphazenes contribute to decrease the degree of ionic crosslinking between metal ion and oxyethylene chains in MEEP (Fig. 68).

3.10. Catalysts

Dendrimer-based catalysts is one of the most promising areas of applied dendrimer researches. In the last few decades a number of polymeric catalysts possessing active sites in the main or side chains and the surface or interior of polymeric gels were prepared, which have the potential to be easily separated from the reaction mixture by simple filtration and recycled. However, the catalytic activities of most of
polymers prepared for this purpose were low compared to those of parent catalysts. This is due to the entanglement of randomly introduced catalytic sites in coiled chains, which causes the change of circumstances around the catalytic center, the decrease in net active sites and in diffusion rate of substrate to the active sites and of product from the sites. Further, catalysts bound on linear or cross-linked polymers tended to suffer from leaching of the metal from the particles. It is well-recognized that homogeneous catalysts are the most selective and effective owing to their well-defined structures and their small sizes (typically 10–15 Å). The dendrimers which can be controlled molecular size and shape and disposition of functional groups are highly attractive as scaffold of polymer catalysts. As pointed out by van Koten [330], dendrimers are considered to be at the interface between homogenous and heterogeneous catalysis. The leaching of metal from the particle might be solved or improved through multi-point binding sites on the dendrimer surface.

The catalytic sites can be introduced on the periphery and at the central core and at both locations within the dendritic structure. Van Koten and co-workers [330] synthesized catalysts possessing tetra- and dodecanikel complexes on the surface of silane dendrimers and employed as homogenous catalysts for the Kharashc addition reaction of polyhalogenoalkanes to an olefinic carbon–carbon double bond. The dendrimers prepared by the divergent growth step from Si(CH₂CH₂CH₂)₄ and Si((CH₂CH₂CH₂)₃)₄, were converted with HSiCl(CH₃)₂ to Si–Cl terminal functional groups and then replaced them with aryl bromide moiety. The dendrimer (156) obtained from the reaction of peripheral aryl bromide units with Ni(PPh₃)₄ catalyzed the reaction of methyl methacrylate and carbon tetrachloride to give 1:1 addition product regioselectively without polymerization of MMA or production of C₂Cl₆ from CCl₃ radical. The catalytic activity, however, was somewhat low compared to the corresponding monomeric nickel catalyst. The result suggests that catalytic sites are separated form one another but not completely “free” like monomeric catalyst. As another approach to prepare modification of surface with transition metal, this research group [331] synthesized σ-bonded palladated carbosilane dendrimers by insertion reaction of palladium(0) into carbon–iodine bond at the periphery (Fig. 69).
An example reported by Moore and co-workers [332] was the regioselective oxidation of olefins with sterically hindered dendrimer–metalloporphyrin, in which first and second generation poly(phenyl ester) dendrons was appended to *meta*-positions of magnesium porphyrins (e.g. 157). For the oxidation of nonconjugated diene such as 1,4-octadiene and 4-isopropenyl-1-methylcyclohexene in the presence of dendrimers and iodosylbenzene as an oxygen donor, the external double bond undergoes epoxidation more readily than internal double bond. The selectivity increased for both first and second generation dendrimers compared to the parent Mn(TPP)Cl catalyst. For the epoxidation of mixture of 1-alkene and *cis*-cyclooctene with unhindered catalysts, predominant oxidation of electron rich *cis*-cyclooctene is expected. However, the oxidation with dendrimer-metalloporphyrin catalysts again exhibits preferential epoxidation of a less hindered 1-alkene. The selectivity of epoxidation of 1-alkene toward *cis*-cyclooctene increased for the second generation dendrimers and was two- or three-fold higher than that of MnTPP(Cl) catalyst. The observed selectivity, however, is not as high as that of complex of bis-pocket porphyrin. It is suggested that the low selectivity of dendrimer-metal porphyrins is due to the difference of steric crowding around the metal porphyrin (Fig. 70).

Recently, Reetz et al. [333,334] reported the catalytic activity of dendritic diphosphane metal complexes. The 16 amine end groups of 1,4-diaminobutane-based polyamino dendrimer (DAB-dendr-(NH₂)₁₆) were functionalized by double phosphinomethylation, using Ph₂PCH₂OH prepared in situ from formaldehyde and HPPh₂. The complete or partial loading giving rise to dendrimers with metals such as Pd, Ir, and Rh on the periphery was accomplished by the reaction of dendrimer with phosphine group with [PdCl₂(PhCN)₂], [Pd(CH₃)₂(tmeda)] and Rh(cod)₂BF₄. The catalytic activities of 158 and 159 were tested by using the Heck reaction and the hydroformylation of 1-octene. For the reaction of bromobenzene with styrene at 130°C in the presence of 159 (Heck reaction), stilbene (89%) and 1,1-diphenylethylene (11%) were formed at a conversion of 85–90%. No significant lowness of catalytic activity for the re-used catalyst was observed. As described above, one of serious problems of polymeric catalysts is that metals bound on the polymers often leave from the sites, depending on the solvent, temperature, and circumstance around binding sites. However, the leaching of Pd from
dendrimer was not observed, whereas the parent Pd-complex underwent partial decomposition to give Pd precipitates under the same conditions. The stability of catalysts lead to, as expected, the increase in the turnover number of dendritic catalyst (TON = 50) which is significant higher than the corresponding model catalysts with low molecular weight (TON = 16). These results indicate that a dendritic structure can offer soluble, structurally defined catalytically active sites as separable and re-usable macromolecular catalyst. The reason why the catalyst with dendritic structure is stable remains unclear but authors suggest that the ridity and suitable shielding of catalytic sites enhance the thermal stability. For the hydroformylation of 1-octene, the quantitative formation of aldehyde was observed when Rh-containing dendrimer 160 and a small excess of free parent dendrimer-ligand were used. They also performed a Pd-catalyzed allylic substitution reaction involving allylic compound (161) and morpholine (162) in the presence of dendritic catalysts. For such a reaction using conventional catalysts, the recovery of catalysts is known to be difficult. With catalytic amount of 158 the 100% conversion and 95% regioselectivity giving rise to 163 were achieved. Interestingly, the catalyst with more excellent properties was obtained by treating of 158 with excess CH3I, i.e. which has a higher catalytic activity relative to 158 and can be recovered easily without loss of its catalytic activity (Fig. 71).

Dendrimer-encapsulated Pd and Pt nanoparticles have an excellent catalytic activity for the hydrogenation of simple alkenes and an electron-deficient alkenes [335]. Such catalysts were simply prepared by the incorporation of metal ions into hydroxy-terminated PAMAM dendrimers and then reduced with BH4. High resolution transmission electron microscopy showed that the intradendrimer metal nanoparticles are quite monodisperse, and stable before, during, and after hydrogenation reactions. The fourth generation dendrimer-encapsulated Pd40 nanoparticles exhibited a high catalytic activity for the hydrogenation of N-isopropyl acrylamide and allyl alcohol. Interestingly, the hydrogenation rates were affected by the generation: the rates of higher generation dendrimers were significantly slow, probably due to their less porous surface. Authors comment that the selective catalysis is possible by adjusting the “mesh” of the dendrimer nanofilter.

The effect of bis(oxazoline) copper (II) complex (165) as catalytic core on the rate of Dies- Alder reactions was studied, employing the reaction of cyclopentadiene with crotonyl imide [336]. The polyether dendrimers were used as sector. The binding constants and rates of reaction decreased for higher generation dendrimers. It is suggested that the steric crowness around catalytic site might be responsible for the low activity of the complexes of higher generation dendrimers.

Ford et al. [337] showed that the rates of unimolecular decarboxylation of 6-nitrobenzoisoxazole-3-carboxylate and the bimolecular hydrolysis of p-nitrodiphenylphosphate catalyzed by o-iodosobenzoate are accelerated by dendrimers with 12 and 36 quaternary ammonium ions on the periphery. The enhancement of rate is interpreted by the increase in the reactant concentration bound to the polymers and/or reactivity of bound reactants. Although the higher generation dendrimers are effective for the decarboxylation compared to the lower generation catalysts, the rate of decarboxylation is not as high as that of lipophilic polystyrene latex which contains 60 mol% of (styrylmethyl)trimethylammonium ion. The low activity might be due to the high density of quaternary ammonium ions on the dendrimer surface that limits binding of high concentrations of lipophilic organic compounds. The introduce of lipophilic quaternary ammonium ions on the surface or in the interior would be expect to show the improvement of catalytic activity.

The base catalyzed selective-acylation of alcohols with diphenylketene by concave pyridines on the periphery of poly(arylalkyl ether) dendrimers was reported [338]. In the intermolecular competitive reaction of primary, secondary, and tertiary alcohols with diphenylketene, the selectivity in the presence
of dendrimer with concave pyridine units increased compared to that of linear analog or use of concave pyridine on the Merrifield polymer resin. The hydrolysis of nitrophenyl esters with polyethylenimine dendrimers possessing β-cyclodextrin as cavity of the esters was also reported [339]. Dendritic phosphonium or ammonium salt supported on poly(methyl methacrylate-chloromethylstyrene)-montmorillonite was examined as phase-transfer catalysts [340].

In the electrochemical reduction of carbon dioxide to carbon monoxide using phosphine containing dendritic palladium complex, the catalytic activity was comparable to those of monomeric catalysts [341]. The separation of catalytic palladium sites on the dendritic periphery was suggested to provide higher turnover numbers. The cathodic reduction of nitrates and nitrites to ammonia on Hg cathode by the star-shaped redox complex (166) has been reported [342]. The precursor complex attached on the periphery was prepared by the reaction of FeII(C5H4CO2H)(C6-Me6)PF6 with thionyl chloride, then with propylamine, and finally with BH3 in THF. As expected, the six redox sites behave independently. The observed rate constant of reduction of the substrate was almost the same to that of mononuclear catalyst. The complex might be useful as electron reservoirs in redox catalysts (Fig. 72).

Dendrimers with chiral terminal groups, interiors, and core possess a potential for enantioselective clathration of small, chiral molecules, and are expected to have an ability as an excellent asymmetric catalyst.

The dendrimer based on diphenyl phosphine ligand which is known to function as enantioselective transition-metal catalyst has been prepared by Brunner [343,344] and the activity of catalyst (dendrizyme) was investigated for: (i) the hydrogenation of (α)-N-acetoamidocinnamic acid; (ii) the hydroxylation of acetophenone with diphenylsilane; and (iii) the cyclopropanation of styrene with ethyl diazaacetate. However, the enantioselectivities in these reactions were low, probably due to the high flexibility of the dendritic units or the presence of conformationally different sites in the dendrimers.

An example reported by Peerlings and Meijer [31] was the enantioselective addition of diethyl zinc to benzaldehyde using chiral aminoalcohol attached to the peripheral NH2 groups of poly(propylene imine) dendrimers of different generations. In this reaction, the both yield and enantiomeric excess decreased...
with increasing generation of dendrimers. The results might be related with the observation that the fifth generation poly(propyl imine) dendrimer carrying 64 chiral units on the periphery showed almost no optical rotation. That is, the loss of catalytic activity and selectivity for higher generation dendrimers was ascribed to multiple interactions by different conformations of the chiral groups caused by denser packing on the surface.

A similar result has been reported on the enantioselective addition of diethyl zinc to $N$-diphenylphosphinylimines in the presence of (1R,2S)-ephedrine derivatives attached to peripheral 4 or 8 amino groups of PAMAM (167) [345]. Both yield and enantiomeric excess were considerably low compared to those of monomeric catalyst and decreased with increasing generations. According to authors, the intramolecular interaction of dendrimer catalysts was responsible for the decrease in the activity.

The hyperbranched catalyst having achiral dendritic wedge attached to a chiral pyridyl alcohol moiety (168) has been prepared by Bolm et al. [346]. The aforementioned enantioselective addition reaction was
used to examine the catalytic activity. The enantioselectivity were slightly low compared to that of the parent pyridyl alcohol system. The values of enantiomeric excess observed were not influenced by the generation of dendritic wedge (Fig. 73).

Optically active dendritic binaphthols (169) were synthesized from 6,6'-dihydroxy-2,2'-binaphthol and dendritic benzyl bromide [347]. The functionality of the Ti-binaphthol dendrimer was examined for the allylation reaction of the aldehyde and allyl stanane. The chiroptical properties in THF showed that the [α]D value decreased with increasing generation from first to fourth but the molecular optical rotation was almost identical and independent of the generation. The selectivity observed using chiral dendritic catalysts was almost identical with that of the parent binaphthol. These results showed that the dendritic catalyst exists as almost the same
chiral environment without significant influence of the bulky dendritic substituents. It seems likely that the relative large chiral core makes easy to access the substrate to active site (Fig. 74).

Seebach et al. [32,348] prepared a series of dendrimers with tetraaryl-1,3-dioxolane-4,5-dimethanols (TADDOL) as chiral unit at the core or on the periphery. The catalytic activity of Ti(OCHCH₃)₄ complex of the six TADDOL moieties attached to the first generation dendrimer was tested using the reaction of Et₂Zn addition to benzaldehyde. The enantioselectivity is almost the same to that of monomeric TADDOL catalyst. They also prepared styryl-substituted TADDOL-dendrimer that acts as chiral active site and crosslinker (170). The Ti-loaded chiral polystyrene beads (size, 100–600 μm), prepared by suspension copolymerization of styryl TADDOLs and styrene followed by treatment with Ti(OCHMe₂)₄, were again used for the aforementioned enantioselective addition reaction. The enantioselectivity of dendrically cross-linked gel exhibited similar enantioselectivity to that of conventional linear polystyrene analogue, but the rate of addition reaction of Et₂Zn to the aldehyde with dendritic catalyst is much faster than that with the linear polystyrene catalyst. The authors suggest that dendritic cross-linking ligands make it possible to access more easily to polymer-incorporated active sites. Another example utilizing (S,S)-1,4-bis(dimethylamino)-2,3-dimethoxybutane (172) as a core unit was reported by the same research group for a dendritic amine catalyst. The dendritically expanded diamines (e.g. 171) were tested in the enantioselective addition of methanol to methylphenyl ketene. In this system, (R)-methyl-2-propionate was selectively formed and the value of enantiomeric excess observed was three times higher than that of monomeric 172. The same enantioselectivity was observed for the catalysts with achiral branching units or non-dendritic dibenzyl ether. It was proposed that the sizes of the whole dendritic branch or parts thereof influence the selectivity in this reaction (Fig. 75).

Recently, Togni et al. [349] prepared dendrimers bearing chiral ferrocenyl diphosphine ligands (e.g.
for the asymmetric hydrogenation reaction, employing (R)-(S)-Josiphos derivative and benzene-1,3,5-tricarboxylic acid trichloride or adamantane-1,3,5,7-tetracarboxylic acid tetrachloride. $^{31}$P NMR spectra of dendrimers showed only one pair of doublets peak with $^4J_{pp}$ coupling constant of ca. 34–37 Hz, indicating equivalence of the ferrocenyl units. The catalyst was prepared in situ by the mixing dendrimer ligand and $[\text{Rh(COD)}_2]\text{BF}_4$, and dimethyl itaconate was chosen as model compound for asymmetric hydrogenation reaction. The enantioselectivities obtained in the presence of dendritic catalysts are more than 98%ee, which is slightly lower than that of parent mononuclear Josiphos catalyst (99%ee). The enantioselectivity has a tendency to decrease with increasing size of dendrimers. As expected, these dendrimers are completely recovered by a nanofiltration membrane (Fig. 76).

Although some reports showed that the functionalities of dendrimer catalysts are comparable to or superior to catalysis of non-dendritic materials, several examples based on dendritic framework result in decrease in the rate and the selectivity. It appears that the densely packed, crowded situation of dendrimers prevents catalytic activity. Although the combination of a highly
accessible molecular surface with defined molecular shape offers a peculiar place for the catalytic reaction, more efforts need to control the microenvironment around reactive sites.

As a different application of dendrimers, several research groups reported on the dendrimers capable to initiate vinyl and ring-opening polymerizations. The polymer−dendrimer block copolymers possess many interesting properties based on dendrimers and have become an increasingly scientific and technical significance.

Such macromolecules could be obtained, in principle, either by the polymerization of monomers with an appropriately functionalized dendron or by appending dendrimer segments to existing polymers. For the vinyl polymerization, either benzylic 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) units or benzylic halides are incorporated into dendrimers, both of which can serve as an initiating site for living radical polymerization [350].

Dendrimer initiators (e.g. 174) have been prepared by the reaction of the TEMPO derivative carrying hydroxy group and poly(aryl ether) dendron with a bromobenzyl group at the focal point [103,104,350,351]. The molecular weights of dendrimer−styrene block copolymers were in agreement with the calculated values and their polydispersities were narrow, indicating that the polymerization proceeds via living radical polymerization mechanism. Dendron with chlorobenzyl (176) or bromobenzyl group (177) at the focal point can also act as an initiating site of atom transfer radical polymerization (ATRP). For example, the polymerization of styrene in the presence of the third generation of Fréchet type dendron with bromobenzyl group and CuCl/4,4′-(di-n-heptyl)-2,2′-dipyridyl complex gave hybrid polymers with $M_w/M_n = 1.1−1.2$, although the polydispersity increases for the block copolymers with molecular weights higher than ca. 30 000, probably due to the involvement of side reactions such as chain transfer and thermal initiation. In such a polymerization, it is suggested that styrene can diffuse inside the cavity of dendrimer and polystyrene is partially compatible with the dendrimer [103]. Likewise, the functional linear-dendrimer block copolymers with carboxylic acid, amide, benzyl alcohol, and benzyl halide moieties on the periphery of dendron units were prepared from ATRP polymerization of isophthalate ester-functionalized dendrons carrying benzyl halide group at the focal point [351]. For the block copolymer carrying carboxyl group on the dendrimer surface, the aggregation occurs in CHCl₃, in agreement with the observation for the block copolymers reported by Meijer [145]. In a similar fashion, dendritic graft copolymers have been prepared by TEMPO-assisted polymerization and/or ATRP [352]. In the first step, the copolymer was prepared from styrene and chloromethylstyrene or $p$-(4′-chloromethylbenzylxoxymethyl)styrene. Then, the chloromethyl group in the copolymers was displaced with TEMPO group. The repetition of the copolymerization of styrene and $p$-chloromethylstyrene provided a graft polymer (178) which has now numerous initiating sites for ATRP polymerization or TEMPO assisted polymerization. For an example, the polymerization of butyl methacrylate with 178 under ATRP conditions gave highly branched block copolymers. These materials could be useful in the area surface science, adhesion, and coating technologies (Fig. 77).

Further application of dendrimer as an initiator has been reported for the ring opening polymerization of ε-caprolactone [353]. The potassium salt of the fourth generation poly(benzyl ether) dendrimer acts as an effective initiator to give dendrimer-polyester block copolymers with high molecular weights and narrow molecular weight distributions. However, the increase of reaction time reduces the yield and causes the increase in molecular weight distribution. In addition, the polymerization with the first generation dendrimer resulted in low conversion and the formation of oligomers. These results can be interpreted in term of polarity within polybenzyl ether dendrimer, which was shown to be significantly high from the solvatochromic study, leading to the partial immobilization of the active centers within
dendritic globule. The bulky dendritic blocks, thus, play to prevent the intramolecular transesterification and consequently the high molecular weight block copolymer was obtained with narrow molecular weight distribution when higher generation dendrimers were used.

Hedrick et al. [354,355] reported on the synthesis of dendrimer-like polyester using a hexahydroxy-functionalized dendritic core as the initiator, which was prepared from 2,2'-bis(hydroxymethyl)propionic acid (bis-MPA) and 1,1,1-tris(hydroxyphenyl)ethane, for the stannous-2-ethylhexanoate-catalyzed ring-opening polymerization of ε-caprolactone. The terminal groups of the polyester were modified with benzylidene-protected bis-MPA, then deprotected and used again as macroinitiator for the polymerization of ε-caprolactone under the same conditions. In this way, the third generation poly(ε-caprolactone) dendrimer with a narrow molecular weight distribution ($M_w/M_n = 1.14$) was synthesized. This research group have also shown that the polymerization of methyl methacrylate with bromo-functionalized dendritic initiators (core), prepared from bis-MPA derivatives and 1,1,1-tris(hydroxyphenyl)ethane, gave 6 and 12 armed star-like poly(methyl methacrylate)s with well controlled molecular weights.
and narrow molecular weight distributions. [356] Authors comment that these star-shaped polymers are useful for the preparation of materials of organic–inorganic hybrids with precise microphase or nano-phase morphologies.

A similar approach was used in the synthesis of multiarmed star polymers [357]. The polylithium carbosilane dendritic initiator (179), where carboanionic sites generated by the addition of n-BuLi are screened each other, gave star-shaped polymers such as hexamethylcyclotrisiloxane, ethylene oxide, and styrene with narrow molecular weight distributions. Hyperbranched polyester-polyMMA block copolymers were also prepared by employing hyperbranched polyesters containing polyazo initiator groups on the surface (Fig. 78).

3.11. Biochemicals and pharmchemicals

Dendrimers, a number of reactive sites or ligands on the surface of three-dimensional dendritic macromolecules with controllable molecular size are considered to be the most suitable platform for the enhancement of binding of biological substrates.

Carbohydrate–protein interactions are ubiquitous in many biological recognition processes such as immune defense response, viral replication, parasite infection, cell–cell adhesion, and inflammation. The interaction of carbohydrate binding-protein, the so-called lectins, is weak. Lee and co-workers [358] have pointed out the importance of multivalency or glycoside clustering of the saccharide for the enhancement of binding affinity in carbohydrate–protein interactions.

PAMAM-, DAB-dendr-(NH₂)n-, and L-lysine-based dendrimers were used as platform for glycodendrimers. Lindhorst and Kieburg [359] have been prepared PAMAM based dendrimers...
bearing α- and β-d-mannose, β-d-glucose, β-d-galactose, β-cellobiose, and β-lactose units by employing their isothiocyanate derivatives. In works of Roy and coworkers [360–365], various divergent glycodendrimers based on l-lysine were used, which were conjugated to α-thiosialosides, β-d-lactosides, N-acetylglucosaminides, N-acetyllactosaminides, α-d-mannosides, and 3'-sulfo-LewisX-(Glc) analogs. The binding properties of 3,3'-iminobis(propylamine) based sialodendrimers of valencies between 2–16 were evaluated using horseradish peroxidase labeled wheat germ agglutinin in an enzyme-linked lectin assay (ELLA) (e.g. 180, Fig. 79). The binding affinity increased with increasing valency and of fourth generation (16 valencies) glycodendrimer was comparable to that of glycopolymer with $M_w$ around 100 kDa. Likewise, the glycodendrimer with 16 valencies was the most effective inhibitor of hemagglutination of human erythrocytes by influenza A viruses, representing a 158-fold increase over that of analogous monosialic acid. Recently, the same research group compared the inhibition ability of different types of glycodendrimers, tethered dendrimers and divergent dendrimers, which are structurally similar but carbohydrate density, conformations, and interglycosidic spacings are different [362]. The tethered dendrimer cores with valencies of 4, 6, 8, and 12 were prepared by tethering of carbobenzyloxy(Cbz)-protected dimer and tetramer with hexamethylenediamine and tris(2-aminoethyl)amine (e.g. 181). The surface of dendrimers was functionalized with thiolated carbohydrates. The results for the inhibition of the binding of horseradish peroxidase labeled LFA to

Fig. 80. Dendrimers with α-d-Mannopyranoside residues prepared by Stoddart and co-workers.
human α₁-acid glycoprotein exhibited that all dendrimers have effective binding affinities compared to standard compound, 2-Ac-ethylamido-5-deoxy-d-glycero-α-d-galacto-2-nonulo-pyranosonyl azide (NeuAcaN₃). Interestingly, in the series of divergent dendrimers, the most pronounced inhibitory effect was observed for the tetravalent α-thiosialodendrimer (180), and the dendrimers with 12 or more sialic acid moieties showed a poor inhibition behavior. Contrast to this, in the tethered dendrimers the increase in multivalency results in the increase in inhibitory potential. From the comparison of IC₅₀ values of these dendrimers, authors indicated that the tethered dendrimers are more effective than the divergent dendrimers and that only increase in multivalency is not responsible for the enhancement of inhibition.

In a series of experiments, the binding ability of 181 was found to be higher than the second generation PAMAM-based α-sialodendrimer (182). However, the inhibitory potential increased with increasing the generation of the PAMAM dendrimers and the inhibition ability of a per sialoside residue of fifth generation dendrimer was ca. 4 times higher than that of 181. It is considered that the increase in the concentration of the multivalent carbohydrate ligands on the dendrimers is responsible for the higher avidity of molecules (Fig. 79).

The synthesis and biological activity of glycodendrimers by the modification of DAB-dendr-(NH₂)ₙ, with 4, 8, 16, 32, and 64 amine end groups have been reported by Stoddart and co-workers [366–370]. The attachment of d-galactose and lactose to the terminal amine groups has been achieved by N-hydroxysuccinimide coupling strategy. In these dendrimers, dendritic core and carbohydrate residues were connected with relatively long spacer, which may have a beneficial effect on the binding with
protein. They also synthesized trisgalactoside-modified DAB dendrimers by convergent approach and \( \alpha\)-d-mannopyranoside-containing dendrimers from tris-branched saccharide dendritic wedge and 1,3,5-benzenetricarbonyl chloride as a core unit. The results of biological potencies of \( \alpha\)-d-mannopyranoside-containing dendrimers by an enzyme-linked lectin assay, employing the inhibition of binding of concanavalin A lectin to a purified yeast mannan fraction Sc500, exhibited that the highest activity was attained for the dendrimer with 9 valencies (183), the inhibition potential of which was 4 times higher than that of corresponding monomer. Different from the case of PAMAM-based \( \alpha\)-sialo-dendrimers, the dendrimers bearing 18 (184) and 36 \( \alpha\)-d-mannopyranoside residues (185) have similar activity each other and their activities are not much greater than 183. This implies that the clustering effect is most pronounced between dendrimers of 9 and 18 valencies. This result was in agreement with the observations that the valency required for maximum binding capacity is not necessarily correlated with the number of ligands. It appears that for higher generation dendritic cores the steric crowding of saccharides on the surface causes weaker protein–carbohydrate interactions (Fig. 80).

Aoi and Okada [371–374] have synthesized second, third, and fourth generation PAMAM dendrimers conjugated with \( \alpha\)-glucose and \( \alpha\)-galactose, named them Sugar Balls. Spectroscopic data suggested that all amine groups on the surface are modified with saccharides. The recognition ability of these dendrimers was evaluated by the quantitative precipitation method in a solution containing \( \alpha\)-glucose bearing third generation dendrimer and lectin, Con A. As expected, the dendrimers recognized Con A molecules to form a precipitate. This binding began to disrupt when 24-fold molar amount of \( \alpha\)-glucose was added to the system. Likewise, for the interaction of \( \alpha\)-galactose bearing dendrimer with peanut agglutinin, the formation of aggregation was observed. In a series of sugar balls, they prepared surface-block dendrimers such as 186 and glycopeptide dendrimers. In the synthesis of A–B surface-block dendrimers, two building blocks, the second generation PAMAM dendrons modified with \( \alpha\)-glucose moiety and phthalo-loyl units were first prepared using half-protected initiator core, \( N\)-benzoyloxycarbonyl(Z)-protected ethylene diamine, and then coupled after removal of protected groups (186). The surface-block dendrimer has recognition ability toward the protein receptor. The authors commented that block dendrimers obtained from half-protected initiator core are useful for adhesives and drug delivery systems (Fig. 81).

Magnusson et al. [375] showed that oligomeric saccharides can inhibit agglutinations of human erythrocytes by the Gram-positive bacterium Streptococcus suis. The dendritic galabiosides (e.g. 187) were synthesized by the reaction of the galabiosides, which were functionalized with 2-\( \alpha\)-trichlorooracetimidine, 2-bromoethyl and 2-aminoethyl groups, with 1,3- and 1,4-benzenedimethanethiol and their
acid derivatives or tetra(4-carboxy-2-thiabutyl)methane. The inhibitory efficacy of dendritic galabiosides can be related with the number of glycolipid and a large increase in inhibitory power, several hundred times more efficient than monomeric analog, was obtained for di- and tetravalent galabiosides. These contain relatively long and flexible linkers between galabioside units and core, allowing effective adhesion to the surface proteins of bacteria (Fig. 82).

As early as in 1988, Tam and coworkers [376–378] developed a method of multimerization, the peptide dendrimers with branched structure, which are known as multiple antigen peptide (MAP). MAPs are used as immunogens, vaccines, serodiagnostics, inhibitors, diagnostic products, and artificial enzymes. Recently, Tam [34] published an excellent review of advances in the development of MAPs. The Merrifield technique was used to synthesis peptide dendrimers, employing phenylacetamidomethyl modified poly(styrene-co-divinylbenzene) beads [376]. Recently, Shao and Tam [377] succeeded in the synthesis of peptide dendrimers by direct ligation of L-lysine core with unprotected peptide segment as building blocks. In this synthesis, primary amines of dendritic L-lysine core were modified to aldehyde groups, and then reacted with a cystein terminated polypeptide to form thiazolidine ring. The thiazolidine ligation is superior compared to the ligation via oxime or hydrazone group introduced at peptide end. Cyclic peptides [378] have also been prepared by this research group which have several advantages, metabolic stability and receptor selectivity, over their open-chain counterparts. Details of bioactivity of these peptide dendrimers with non-native bonds have not reported.

PAMAM dendrimers with primary amines on the surface have been shown to interact with plasmid DNA encoding for luciferase or bacterial β-galactosidase by Szoka and Haensler [379]. The transfection efficiency of firefly luciferase in host cells depended on the generation of dendrimers and ratio of surface ammonium groups to DNA phosphate. The highest value was obtained for the sixth generation dendrimer and at a 6:1 ammonium-phosphate ratio. Recently they showed that the perfect sixth generation dendrimer-DNA complexes are not effectively transfected and that transfection activity is due to the existence of high molecular weight dendritic macromolecules formed from a heat treatment step, which have high flexibility compared to parent dendrimers [380]. Baker et al. [381]. have shown that DNA complexes formed with PAMAM dendrimers of higher than third generation are stable under physiological conditions and that the disruption is effected only with strong ionic surfactants. The gene transfection is the most efficient for the sixth–eighth generation PAMAM dendrimers in most cell lines.

Magnetic resonance imaging (MRI) was one of the most useful tools in medical diagnostics. The contrast agents may be used to image target organs, or to detect changes in blood flow and blood pool of
an organ. Contrast agents should remain in the blood vessel for an extended period of time. High relaxivities are required to reduce the dose of contrast agent employed but produce high quality image.

Wiener and co-workers [382] reported on the functionality of second and sixth generation PAMAM dendrimers bearing gadolinium-chelated 2-(4-isothiocyanotobenzyl)-6-methyl-1-diethylenetriaminopentaacetic acid on the surface as MRI agent. The results of a biological evaluation of PAMAM dendrimers have been showed that their toxicity in vivo is quite low except for the seventh generation dendrimer [383]. The great enhancement of proton relaxation was observed for these dendrimer based gadolinium chelators compared to those of gadolinium-chelated diethylenetriaminetetraacetic acids attached to albumin, dextran, and polylysine. For the sixth generation dendrimer, a long half-life (200 min) was achieved which was ca. 10 times longer than that of monovalent gadolinium agent. This enhancement of half-life is extremely useful for 3D TOFMR angiography and as blood pool contrast agents. Usefulness of dendrimer-based gadolinium chelates as MRI contrast agent have been also reported [384–386]. In the experiments described by by Margerum et al. [384,385], polyamidoamine dendrimers coupled with macrocycle 1-(4-isothicyanatobenzyl)amido-4,7,10-triacetic acid-tetraazacyclododecane and their polyethylene glycol (PEG) derivatives were used. The blood elimination half-life of gadolinium-chelated azacrown dendrimers bearing PEG units was found to be longer than that of parent contrast agent and the seven-day liver uptake dropped to 1–8% of the injected dose. It is suggested that the pharmacokinetics and biodistribution of the contrast agent can be controlled by the molecular weight and properties of terminal groups on polychelates (Fig. 83 and 84).

Dendrimers are suggested to be suitable as platform to prepare boron rich compounds for boron neutron capture therapy, electron loss spectroscopy, and electron spectroscopic imaging. As an example, the boronated dendrimer was prepared by the reaction of 48 amine groups on the surface of fifth generation PAMAM dendrimer with Na(CH₃)₃NB₁₀H₈NCO [387]. By this way, the heterogeneity for the conventional linear polymer-based boron compounds was significantly improved and the dendrimer can contain 1840–2200 boron atoms. This level seems to be sufficient to deliver 10⁹ atoms of ¹⁰⁷B required to each tumor cell and to sustain lethal reaction with thermal neutrons. However, most of them is filtered out by the liver and the concentration of boron was not so high. Recently, homogeneous and defined poly-(α,ε-l-lysine) dendrimer bearing 8 dodecaborane cage as protein probes in electron spectroscopic imaging has been synthesized [388]. The boron neutron capture therapy has been reviewed [389].
Based on their unique physical properties, dendrimers have been used in the area of analytical chemistry, including micellar electrokinetic chromatography (MEKC) and ion-exchange displacement chromatography. Micellar electrochemical chromatography is a modification of capillary electrophoresis which separates charged or neutral compounds utilizing properties of micelles. The ionic surfactants such as sodium dodecyl sulfate and cetyltrimethylammonium bromide are often employed as pseudo-stationary phases. These are dynamic systems and their heterogeneity may result in peak broadening. Tanaka and coworkers [390–392] first reported on the utility of homogenous and static system, dendrimer micelle, as carriers in electrokinetic chromatography. A variety of modified dendrimers have been studied [390–396]. Dendrimers have different selectivity for neutral compounds such as substituted benzenes and naphthalenes relative to micelles of SDS. The differences in selectivity for hydroquinone and resorcinol are explained by the greater hydrogen bond accepting capabilities of tertiary amine group in the interior, which interacts with hydrogen-bond donating compounds. The separation and selectivity of amino acids such as phenylalanine, tyrosine, DOPA, and methyl-DOPA were reported by Gao et al.
[393], who showed that good separation and selectivity are obtained with low generation poly(amidoamine) dendrimers bearing terminal carboxylate at low pHs. The dendrimers may function as pseudo-stationary phase with a wide range of chemical separation in MEKC. This separation technique based on unimolecular micelles may be developed by plentiful supply of dendrimers with cheaper cost and modification of molecular structures of both the exterior and interior of the dendritic micelles. From different point of view, Kuzdazal et al. [397] reported that the distribution coefficient and thermodynamic parameters of dendrimer-solute interactions can be determined by electrokinetic chromatographic procedure.

Besides the examples discussed above, polycationic pentaerythritol-based dendrimers were used as displacers for an ion-exchange displacement chromatography, which is suitable for the large-scale purification of proteins [398].

As future organic magnetic materials, attempts to increase the spin multiplicity of macromolecules utilizing dendritic architectures have been carried out. Recently, Rajca [399] and Rovia et al. [400] have published excellent reviews concerning on star-branched and dendritic polyradicals. In these molecules, dendritic branching is used to ensure a more robust intramolecular spin alignment that can not be obtained in linear or branched structures. As an example, Rajca and Utamapanya [401] reported on the synthesis and magnetic properties of a series of robust super high-spin dendrimers consisting of arylmetane derivatives substituted with tert-butyl and dimethyl groups. The complex conformational equilibrium exist in these dendrimers and consequently ESR spectra showed a broad single peak. For the dendrimers with nominally $S = \frac{31}{2}$ the effective $S$ value for ferromagnetically coupled electrons resulted in lowering to $S < \frac{4}{2} - \frac{5}{2}$. Rovira et al. [402] synthesized a series of dendrimers consisting of the chlorinated 1,3-connected polyalkylaromatic radicals (e.g. 188). In these dendrimers the chlorine atoms are incorporated in order to increase life expectancies and thermal and chemical stabilities. The polyradicals were obtained by the treatment of the dendrimer consisting of substituted triphenylmetane units with an aqueous solution of $n$-Bu$_4$OH$^-$ followed by oxidation of the resulting anions with $p$-chloranil. ESR spectra exhibited complex signals, showing only the presence of complex mixtures of polyradicals. The tetraradical species from 188 was elusive even though the excess of base was used. From these results, the large overcrowding in the dendritic architectures used to produce super high-spin system is considered to have some practical disadvantages, involving the limit of the sizes and effective $S$ values. In order to overcome the problems, Rajca et al. [403] synthesized macrocyclic dendrimer 189, a precursor of polyradicals with high spin(190), from the coupling reaction of 191 and 192. From the fitting curve to a modified Brillouin function, $S = 10$, which is the highest value in organic molecules, was obtained at 5 K, although it is significantly lower than the theoretical value of $S = 12$ expected for 24 ferromagnetically coupled unpair electron. They suggests that the low value is due to the presence of impurity or imperfect generation of unpaired electrons (Fig. 85).

Triarylamines are also building blocks for high-spin species by chemical oxidation which have ferromagnetic coupling. Hartwig et al. [270]. have synthesized the second generation triarylamine dendrimer by convergent strategy. In this synthesis, bis(4-bromophenyl)benzenemethanamine and lithium ditolylamine were used. The oxidation potential was substantially lower than that of $p$-tritolyamine. The delocalized radical cation was formed by the addition of bis(trifluoroacetoxy)iodobenzene, which was relatively stable at room temperature. Further development of ultra-high yield methods for generation of polyradicals and understanding important aspects of magnetism are necessary to put them practical use.

Dendritic poly(benzyl ether) bearing phenol group at the periphery and calix[4]resorcinarene core was
used as alkaline developable positive-working photoresist [404]. Spin casting film containing the dendrimer and 30 wt% 2,3,4-tris(1-oxo-2-diazonaphthoquinone-4-sulfonyloxy) benzophenone as dissolution inhibitor was exposed to i-line (100 mJ cm⁻²) though mask in contact mode and postexposure baked at 120°C. The resist was found to be capable of resolving a 10 μm feature.

As described earlier, polymers with polyacetylene units have interesting electronic, nonlinear optical and monomorphoric properties. In addition to these functionalities, polyacetylene derivatives are used in the area of selective gas permeation. Recently, Oikawa et al. reported that the rhodium-catalyzed selective polymerization of terminal acetylene group in the monodendrons, which were prepared by repetition of the coupling reaction of 3,5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene with phenylacetylene derivatives, gave polyacetylenes carrying dendritic phenylacetylene groups [405]. The oxygen gas permeability coefficient (PO₂) and oxygen separation factor (α = PO₂/PN₂) of the polymer film were 72 barrers and 3.78, respectively. The α value was found to be higher than that of parent polyacetylene. The result indicates that the incorporation of dendritic structure in the membrane is one of effective methods to improve the selectivity of gas permeation.

Fluorinated polymers are known to have low cohesive and adhesive forces, low surface energy, high chemical and thermal resistances. Wooley et al. [406]. have reported on the synthesis of hyperbranched polyfluorinated benzyl ether polymer (193) from 3,5-bis[(pentafluorobenzyl)oxy]benzyl alcohol as AB₂ monomer (194). The molecular weight and molecular weight distribution were affected by the surface area of sodium particles used as base, monomer concentration, and temperature. The resulting polymers contain an overall average composition of one pentafluorophenyl group per repeating monomer unit and one additional pentafluorophenyl end group. The resultant polymers were modified by incorporation of perfluoroalkyl chains, utilizing nucleophilic aromatic substitution of p-fluorines. All the hyperbranched polymers were characterized by standard techniques. Thermogravimetric analysis exhibited no mass loss up to 300°C. The contact angles of water and hexadecane on the films were determined by the sessile drop method. The substitution of 36% of the chain ends of 193 with 1H,1H,2H,2H-perfluorodecanoxy group (195) leads to increase in contact angles from Θ_water = 96° to Θ_water = 120°, which is higher than that of poly(tetrafluoroethylene, PTFE, Θ_water = 115°). Further substitution did not affect on the hydrophobicity. The lipophilicity of hyperbranched fluorinated polymer was higher than that of PTFE. Lateral force AFM indicates that the coefficient of friction and the adhesive force of perfluorodecanyloxy group substituted hyperbranched polymers are significantly lower than those of PTFE, regardless of higher fluorine content of the latter. They proposed that very short fluoroalkyl chains with high mobility are highly effective to modify the surface properties (Fig. 86).
The UV curing behavior of hyperbranched acrylate was tested by Jahansson et al. [407]. Polyhydroxy groups in hyperbranched aliphatic polyesters prepared from 2,2-bis(hydroxymethyl)propionic acid bis(MPA) and 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) was functionalized by introducing photosensitive acrylate and propionate units or acrylate and benzoate units. As expected, the viscosity varied depending on the terminal groups, and the lowest value was obtained for the hyperbranched polymer with acrylate and propionate units. The acrylate units are cured on UV irradiation to give films with pendulum hardness of 115–127 (s), corresponding to that of a conventional crosslinked acrylate resin.

In general, hyperbranched polymers have a characteristic of amorphous morphology, and their globular, branched structures bring about the lack of interchain entanglement. Therefore, the polymers exhibit poor mechanical strength and toughness, and brittle film-forming properties. Instead they have high solubility in common organic solvents and low viscosity compared to linear analogs, which can probably be useful in the area of resins, coating, and rheology modifiers.

Hyperbranched polymers analogous to linear polymers used as high performance polymers have been prepared. For examples, Miller et al. [408] prepared hyperbranched polyaryl ether from AB₂ monomers containing one phenolic hydroxy group and two aryl fluorides linked with carbonyl, sulphonyl or tetrafluorophenyl groups. The concentration of AB₂ monomers and activation units affected on molecular weights ($M_w = 11,300 – 134,000$). Thermogravimetric analyses showed that more than 95% of initial mass retain up to 500°C, and thus have thermal stability comparable to linear poly(ether ketones) and poly(ether sulfones). The hyperbranched polymers have unexpectedly high glass transition temperatures (135–231°C) and noncrystalline nature. Recently, Bolton and Wooley [409] reported on the synthesis of hyperbranched polycarbonates with fairly high molecular weights by the polymerization
of an AB₂ monomer derived from 1,1,1-tris(4′-hydroxyphenyl)ethane (196), in which one of hydroxy group was protected with a tert-butyldimethylsilyl group and remaining two phenolic groups were functionalized with 1,1′-carbonyldiimidazole. The polymerization was carried out in the presence of AgF in acetonitrile-THF at 70° C. The hyperbranched polycarbonates with molecular weights of 23 000–83 000 were obtained. The thermal behavior of the hyperbranched polycarbonates was similar to that of linear counterparts.

Kakimoto et al. [71] synthesized the hyperbranched polyaramide from thermal self-polycondensation of 3,5-bis(4-aminophenoxy)benzoic acid (197). The polymers obtained have high molecular weights ($M_w = 74 600$) and a better solubility compared to linear polyaramide prepared from 3-(4-aminophenoxy)benzoic acid. Hyperbranched phenol-formaldehyde resins that are enriched in o-p position were prepared by repetition of addition and condensation reaction [410]. The thermal behaviors of these polymers were significant different from conventional novolak resin.

Polymer blends of hyperbranched polymers and linear polymers have not been studied in details. Kim and Webeter [118] showed that for the blend brominated poly(phenylene) branched polymers and polystyrene the mixture is clear up to 2 wt% of branched polymer and turbid blends was observed with larger amount of the branched polymer. The reological property and thermal stability were significantly affected. The addition of the branched polymer reduces the melt viscosity. Regardless of the poor miscibility, the improvement of modulus was observed for 2 wt% branched polymer blended polystyrene, probably due to the weak interaction between aryl–ary interactions.

Mechanical properties of blends of hyperbranched and linear polymer have been studied, although such toughness and strength based on the entanglement of linear polymer chains would not be expected. Massa et al. [411] reported on the blend of 3,5-dihydroxyphenyl(198) and 3,5-diacetoxyphenyl-terminated (199) hyperbranched polymers and various linear polymers such as polyamides and polyesters. Hydroxy terminated hyperbranched polymers were miscible with these linear polymers in a manner similar to poly(vinylphenol). This indicates that the hydrogen bonding is a governing factor to determine phase behavior rather than polymer architecture. Mechanical properties of 22.5 wt% 198 and 199 blended polycarbonates were also examined, although these blends are both phase separated. For both blends the tensile modulus increased by 32% for 198 blend and 15% for 199 blend, and tensile elongation decreased from 82% to 3%. The compression moduli increased by 15 and 7.5% for 198 and 199, respectively. These results suggest that hyperbranched polyesters act as reinforcing agent of polycarbonates (Fig. 87).

Blends of PAMAM dendrimers and poly(vinyl chloride) or poly(vinyl acetate) have been reported [412]. Dynamic mechanical analysis, xenon nuclear magnetic resonance, and tensile property showed that the interaction of poly(vinyl acetate) with dendrimers is much higher than that of poly(vinyl chloroform.)
chloride). However, this interaction was restricted to the surface region of dendrimers and not so strong enough to improve the modulus of blend polymers.

It is well-known that block copolymer additives can effectively compatibilize immiscible polymer blend. The compatibilizers act as surfactants and localize at interfaces, and lower interfacial tension. Inoue et al. [413] reported that heteroarm star-shaped copolymers comprised of polystyrene and nylon-6 arms emanating from cyclophosphazene core (200) act as a useful compatibilizer for polyphenylene oxide and nylon-6 blend. For the ternary blend 45:45:10 PPO/Nylon 6/200, a single glass transition temperature was observed corresponding to the PPO/polystyrene phase. SEM exhibited that PPO

![Dendritic organic-inorganic hybrid gel](image)

Fig. 89. A dendritic organic-inorganic hybrid gel.

![Hyperbranched polymers](image)

Fig. 90. Hyperbranched polymers used for the preparation of organic–inorganic hybrid materials.
disperses regularly and finely with 0.3 μm size in the nylon domain. This indicates that the adhesion at
the PPO/Nylon 6 interface is improved by using heteroarm star-shaped polymers. Reflecting this, the
blends have high modulus, strength and elongation (Fig. 88).

Organic-inorganic hybrid materials can exhibit both properties associated with the organic and
inorganic framework. Corriu et al. [414] reported on the sol-gel reaction of carbosilane dendri-
mers bearing 12 and 36 methoxysilane groups on the surface and arborols of the first and second
generation with octadecyl or phenyl group at the focal point (201). The polycondensation by the
sol-gel reaction of second generation dendrimer gave a porous material. The second generation arborol
with octadecyl group formed nonporous materials, while the different gels depending on the solvents
used were formed for the arborol with phenyl group. Both first generation dendrimer and arborol,
however, did not form gels. The oxidative thermal treatment of hybrid materials resulted in the forma-
tion of porous silica with similar porosity and pore size, independent of the size of dendrimers or
arborols (Fig. 89).

Chujo et al. [415] reported that nanoscale structure can be obtained when strong interactions
between components are operative. Hedrick et al. [416] synthesized thermally stable hyper-
branched polymers from 3, 5-dihydroxybenzoic acid and poly(aryl ether phenylquinoxaline)
which has a $T_g$ of 190°C and an intrinsic viscosity of 0.48 dl/g. Hybrid materials were prepared
from poly(silsesquioxane) and hyperbranched polymers with hydroxyphenyl group (202) or
triethoxysilane group (203) as terminal units. The samples were initially cured at 180°C and then at
410°C. The thermal stabilities of the composites were comparable to those of poly(silsesquioxane). TEM
showed that terminal groups of hyperbranched polymer affect on the phase separation and morphology.
Optically transparent film with nanometer scale phase separation is formed from poly(silsesquioxane)
and triethoxysilane modified hyperbranched polymer whereas for the phenol terminated hyperbranched
polymer translucent materials with micron-sized phase separation are formed. Thus, the size in compo-
nites depends on the properties of terminal groups. The hyperbranched polymer with triethoxysilyl group
leads to tough composite materials, which has superior properties compared to the parent sol–gel
materials (Fig. 90).

Attempts to prepare ultrasmall cell in the polymer resin by utilizing degradable dendrimer were
reported by Möller et al. [417]. The polyalkyloxsilane dendrimer as degradable polymers was

Fig. 91. A biodegradative dendrimer.
embedded in methacrylate resin. The aggregation of dendrimers, however, occurs and the creation of fine holes in the resin could not be achieved.

Seyferth and Son [418] synthesized carbosilane dendrimers with a high Si/C ratio in order to study their potential usefulness as SiC ceramic precursors. Higher generation dendrimers gave reasonable ceramic yields, whereas lower generation analogs resulted in poor yields due to their high volatilities during calcination. Authors comment that the drawback of small molecules might be overcome by a crosslinking reaction preceding calcination.

Biodegradative dendrimers were synthesized from (R)-3-hydroxybutanoic acid (HB) and trimesic acid [419]. The biodegradability of dendrimers (e.g. 204, Fig 91) was tested, using a PHB-depolymerase. The linear HB dimer was not degraded by this enzyme. Contrast to this, the dimeric HB elongated dendrimers with end carboxylic acids were moderately good substrates for the enzyme, but the dendrimers protected with benzyl ester group were not degraded. The observed rate of degradation of dendrimers with tetrameric HB units is about 100 times faster than that of dendrimers with dimeric HB units. The dendrimers were also degraded by an esterase, a lipase, and a protease. The biological degradative properties of dendrimers may have applications in nanocavities and drug carriers.

4. Conclusion

Dendrimers, hyperbranched polymer, and star-polymers described in this review are rich area for findings of new and unusual properties. Clearly the development of these polymers is still infancy and many discoveries still lie ahead. The synthetic methodology is significantly improved, but from the point of view of material science, further development of new synthetic methods of dendrimers and hyperbranched polymers with low polydispersity is needed before these materials can be used in practical materials. Apparently this will also allow systematic and fundamental study of relationship between polymer structure and functionality.

Although tremendous progress has been made in the potential applications of dendrimers and hyperbranched polymers during past decade, we have only vague answer concerning what type of structures meets the target applications and many areas remain to be explored. One of the most useful applications of dendritic structures is in the area that multifunctional groups in ordered array are required, e.g. as we have seen in photohervesting dendrimers for energy or electron transfer. Three-dimensional chiral dendrimers containing chiral units in the interior and/or on the surface have many features, which can offer the opportunity to meet functionalities such as high molecular recognition, chemical separation, and asymmetric catalysts. Considering future advanced materials, the combination of functional dendrimers and well-controlled linear polymers might be useful tools for creating new functional materials made up for the defects of each component.

References

[34] Tam JP. Proc Natl Acad Sci USA 1998;85:5409.