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[Contents](#)
[Featured content](#)
[Current events](#)
[Random article](#)
[Donate to Wikipedia](#)
[Wikipedia store](#)

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[Help](#)
[About Wikipedia](#)
[Community portal](#)
[Recent changes](#)
[Contact page](#)

Tools

[What links here](#)
[Related changes](#)
[Upload file](#)
[Special pages](#)
[Permanent link](#)
[Page information](#)
[Wikidata item](#)
[Cite this page](#)

Print/export

[Create a book](#)
[Download as PDF](#)
[Printable version](#)

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[Wikimedia Commons](#)

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[Dansk](#)
[Deutsch](#)
[Eesti](#)
[Español](#)
[فارسی](#)
[Français](#)
[한국어](#)
[Italiano](#)
[עברית](#)
[Magyar](#)
[Nederlands](#)
[日本語](#)
[Piemontèis](#)
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Dendrimer

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Dendrimers are repetitively **branched molecules**.^{[1][2]} The name comes from the **Greek** word δένδρον (**dendron**) which translates to "tree". Synonymous terms for dendrimer include **arborols** and **cascade molecules**. However, dendrimer is currently the internationally accepted term. A dendrimer is typically symmetric around the core, and often adopts a spherical three-dimensional morphology. The word **dendron** is also encountered frequently. A dendron usually contains a single chemically addressable group called the focal point or core. The difference between dendrons and dendrimers is illustrated in the top figure, but the terms are typically encountered interchangeably.^[3]

The first dendrimers were made by divergent synthesis approaches by Fritz Vögtle in 1978,^[5] R.G. Denkewalter at **Allied Corporation** in 1981,^{[6][7]} **Donald Tomalia** at **Dow Chemical** in 1983^[8] and in 1985,^{[9][10]} and by **George R. Newkome** in 1985.^[11] In 1990 a convergent synthetic approach was introduced by **Craig Hawker** and **Jean Fréchet**.^[12] Dendrimer popularity then greatly increased, resulting in more than 5,000 scientific papers and patents by the year 2005.

Contents [hide]

- [Properties](#)
- [Synthesis](#)
 - [Divergent methods](#)
 - [Convergent methods](#)
 - [Click chemistry](#)
- [Applications](#)
 - [Drug delivery](#)
 - [Gene delivery](#)
 - [Sensors](#)
 - [Blood substitution](#)
 - [Nanoparticles](#)
 - [Crop protection and agrochemicals](#)
- [See also](#)
- [References](#)

Properties [edit]

Dendritic molecules are characterized by structural perfection. Dendrimers and dendrons are **monodisperse** and usually highly **symmetric**, spherical compounds. The field of dendritic molecules can be roughly divided into low-**molecular weight** and high-molecular weight species. The first category includes dendrimers and dendrons, and the latter includes **dendronized polymers**, hyperbranched polymers, and the **polymer brush**.

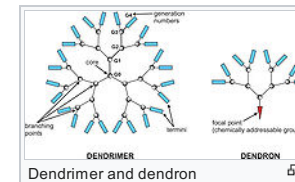
The properties of dendrimers are dominated by the **functional groups** on the **molecular surface**, however, there are examples of dendrimers with internal functionality.^{[13][14][15]} Dendritic **encapsulation** of functional molecules allows for the isolation of the active site, a structure that mimics that of active sites in biomaterials.^{[16][17][18]} Also, it is possible to make dendrimers water-soluble, unlike most **polymers**, by functionalizing their outer shell with charged species or other **hydrophilic** groups. Other controllable properties of dendrimers include **toxicity**, **crystallinity**, tecto-dendrimer formation, and **chirality**.^[3]

Dendrimers are also classified by generation, which refers to the number of repeated branching cycles that are performed during its synthesis. For example, if a dendrimer is made by convergent synthesis (see below), and the branching reactions are performed onto the core molecule three times, the resulting dendrimer is considered a third generation dendrimer. Each successive generation results in a dendrimer roughly twice the molecular weight of the previous generation. Higher generation dendrimers also have more exposed functional groups on the surface, which can later be used to customize the dendrimer for a given application.^[19]

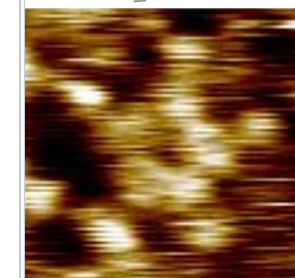
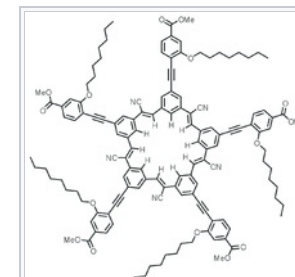
Synthesis [edit]

One of the very first dendrimers, the Newkome dendrimer, was synthesized in 1985. This **macromolecule** is also commonly known by the name arborol. The figure outlines the mechanism of the first two generations of arborol through a divergent route (discussed below). The synthesis is started by **nucleophilic substitution** of 1-bromopentane by *triethyl sodiomethanetricarboxylate* in **dimethylformamide** and **benzene**. The **ester** groups were then **reduced** by **lithium aluminium hydride** to a **triol** in a **deprotection** step. Activation of the chain ends was achieved by converting the alcohol groups to **tosylate** groups with **tosyl chloride** and **pyridine**. The tosyl group then served as **leaving groups** in another reaction with the tricarboxylate, forming generation two. Further repetition of the two steps leads to higher generations of arborol.^[11]

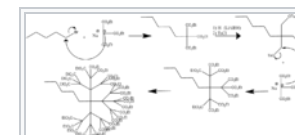
Poly(amidoamine), or PAMAM, is perhaps the most well known dendrimer. The core of PAMAM is a diamine (commonly **ethylenediamine**), which is reacted with **methyl acrylate**, and then another



Dendrimer and dendron



A first-generation "cyanostar" dendrimer and its STM image.^[4]



Synthesis to second generation

ethylenediamine to make the generation-0 (G-0) PAMAM. Successive reactions create higher generations, which tend to have different properties. Lower generations can be thought of as flexible molecules with no appreciable inner regions, while medium-sized (G-3 or G-4) do have internal space that is essentially separated from the outer shell of the dendrimer. Very large (G-7 and greater) dendrimers can be thought of more like solid particles with very dense surfaces due to the structure of their outer shell. The functional group on the surface of PAMAM dendrimers is ideal for [click chemistry](#), which gives rise to many potential applications.^[20]

Dendrimers can be considered to have three major portions: a core, an inner shell, and an outer shell. Ideally, a dendrimer can be synthesized to have different functionality in each of these portions to control properties such as solubility, thermal stability, and attachment of compounds for particular applications. Synthetic processes can also precisely control the size and number of branches on the dendrimer. There are two defined methods of dendrimer synthesis, [divergent synthesis](#) and [convergent synthesis](#). However, because the actual reactions consist of many steps needed to protect the [active site](#), it is difficult to synthesize dendrimers using either method. This makes dendrimers hard to make and very expensive to purchase. At this time, there are only a few companies that sell dendrimers; [Polymer Factory Sweden AB](#)^[21] commercializes biocompatible bis-MPA dendrimers and Dendritech^[22] is the only kilogram-scale producers of PAMAM dendrimers. NanoSynthons, LLC^[23] from Mount Pleasant, Michigan, USA produces PAMAM dendrimers and other proprietary dendrimers.

Divergent methods [\[edit\]](#)

The dendrimer is assembled from a multifunctional core, which is extended outward by a series of reactions, commonly a [Michael reaction](#). Each step of the reaction must be driven to full completion to prevent mistakes in the dendrimer, which can cause trailing generations (some branches are shorter than the others). Such impurities can impact the functionality and symmetry of the dendrimer, but are extremely difficult to purify out because the relative size difference between perfect and imperfect dendrimers is very small.^[19]

Convergent methods [\[edit\]](#)

Dendrimers are built from small molecules that end up at the surface of the sphere, and reactions proceed inward building inward and are eventually attached to a core. This method makes it much easier to remove impurities and shorter branches along the way, so that the final dendrimer is more monodisperse. However dendrimers made this way are not as large as those made by divergent methods because crowding due to [steric effects](#) along the core is limiting.^[19]

Click chemistry [\[edit\]](#)

Dendrimers have been prepared via [click chemistry](#), employing [Diels-Alder reactions](#),^[25] thiol-ene and [thiol-yne reactions](#)^[26] and [azide-alkyne reactions](#).^{[27][28][29]}

There are ample avenues that can be opened by exploring this chemistry in dendrimer synthesis.

Applications [\[edit\]](#)

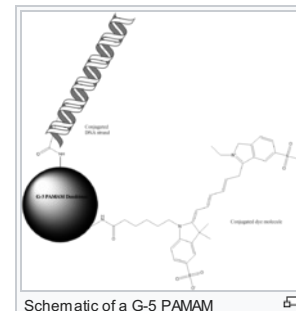
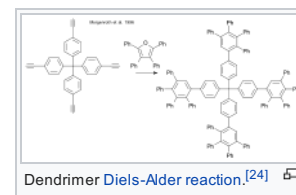
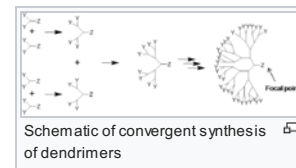
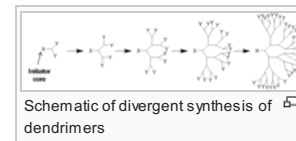
Applications of dendrimers typically involve conjugating other chemical species to the dendrimer surface that can function as detecting agents (such as a [dye](#) molecule), affinity [ligands](#), targeting components, [radioligands](#), [imaging agents](#), or [pharmaceutically active compounds](#). Dendrimers have very strong potential for these applications because their structure can lead to [multivalent](#) systems. In other words, one dendrimer molecule has hundreds of possible sites to couple to an active species. Researchers aimed to utilize the hydrophobic environments of the dendritic media to conduct photochemical reactions that generate the products that are synthetically challenged. Carboxylic acid and phenol-terminated water-soluble dendrimers were synthesized to establish their utility in drug delivery as well as conducting chemical reactions in their interiors.^[30] This might allow researchers to attach both targeting molecules and drug molecules to the same dendrimer, which could reduce negative side effects of medications on healthy cells.^[20]

Dendrimers can also be used as a solubilizing agent. Since their introduction in the mid-1980s, this novel class of dendrimer architecture has been a prime candidate for host-guest chemistry.^[31] Dendrimers with hydrophobic core and hydrophilic periphery have shown to exhibit micelle-like behavior and have container properties in solution.^[32] The use of dendrimers as unimolecular micelles was proposed by Newkome in 1985.^[33] This analogy highlighted the utility of dendrimers as solubilizing agents.^[34] The majority of drugs available in pharmaceutical industry are hydrophobic in nature and this property in particular creates major formulation problems. This drawback of drugs can be ameliorated by dendrimeric scaffolding, which can be used to encapsulate as well as to solubilize the drugs because of the capability of such scaffolds to participate in extensive hydrogen bonding with water.^{[35][36][37][38][39][40]} Dendrimer labs throughout the planet are persistently trying to manipulate dendrimer's solubilizing trait, in their way to explore dendrimer as drug delivery ^{[41][42]} and target specific carrier.^{[43][44][45]}

For dendrimers to be able to be used in pharmaceutical applications, they must surmount the required regulatory [hurdles](#) to reach market. One dendrimer scaffold designed to achieve this is the Poly Ethoxy Ethyl Glycinamide (PEE-G) dendrimer.^{[46][47]} This dendrimer scaffold has been designed and shown to have high [HPLC](#) purity, stability, aqueous solubility and low inherent toxicity.

Drug delivery [\[edit\]](#)

Approaches for delivering unaltered natural products using polymeric carriers is of widespread interest, dendrimers have been explored for the encapsulation of [hydrophobic](#) compounds and for the delivery of anticancer drugs. The physical characteristics of dendrimers, including their monodispersity, water solubility, encapsulation ability, and large number of functionalizable peripheral groups, make these [macromolecules](#) appropriate candidates for evaluation as drug delivery vehicles. There are three methods for using dendrimers in drug delivery: first, the drug is covalently attached to the periphery of the dendrimer to form dendrimer prodrugs, second the drug is coordinated to the outer functional groups via ionic interactions, or third the dendrimer acts as a unimolecular [micelle](#) by encapsulating a pharmaceutical through the formation of a dendrimer-drug supramolecular assembly.^{[48][49]} The use of dendrimers as drug carriers by encapsulating hydrophobic drugs is a potential method for delivering highly active pharmaceutical compounds that may not be in clinical use due to their limited water solubility and resulting suboptimal [pharmacokinetics](#). Dendrimers have been widely explored for controlled delivery of antiretroviral bioactives^[50] The inherent antiretroviral activity of dendrimers enhances their efficacy as carriers for antiretroviral drugs.^{[51][52]} The dendrimer enhances both the uptake and retention of compounds within cancer cells, a finding that was not anticipated at the onset of studies. The encapsulation increases with dendrimer generation and this method may be useful to entrap drugs with a relatively high therapeutic dose. Studies based on this dendritic polymer also open up new avenues of research into the further development of drug-dendrimer complexes specific for a cancer and/or targeted organ system.^[53] These encouraging results provide further impetus to design, synthesize, and evaluate dendritic polymers for use in basic drug delivery studies and eventually in the clinic.^{[48][54]}



Gene delivery [edit]

The ability to deliver pieces of **DNA** to the required parts of a cell includes many challenges. Current research is being performed to find ways to use dendrimers to traffic genes into cells without damaging or deactivating the DNA. To maintain the activity of DNA during dehydration, the dendrimer/DNA complexes were encapsulated in a water-soluble polymer, and then deposited on or sandwiched in functional polymer films with a fast degradation rate to mediate gene **transfection**. Based on this method, PAMAM dendrimer/DNA complexes were used to encapsulate functional biodegradable polymer films for substratemediated gene delivery. Research has shown that the fast-degrading functional polymer has great potential for localized transfection.^{[55][56][57]}

Sensors [edit]

Dendrimers have potential applications in **sensors**. Studied systems include **proton** or **pH** sensors using poly(propylene imine),^[58] cadmium-sulfide/polypropylenimine tetrahexacontaamine dendrimer composites to detect **fluorescence** signal **quenching**,^[59] and poly(propylenamine) first and second generation dendrimers for metal **cation photodetection**^[60] amongst others. Research in this field is vast and ongoing due to the potential for multiple detection and binding sites in dendritic structures.

Blood substitution [edit]

Dendrimers are also being investigated for use as **blood substitutes**. Their steric bulk surrounding a **heme**-mimetic centre significantly slows degradation compared to free heme,^{[61][62]} and prevents the **cytotoxicity** exhibited by free heme.

Nanoparticles [edit]

Dendrimers also are used in the synthesis of **monodisperse** metallic nanoparticles. Poly(amidoamide), or PAMAM, dendrimers are utilized for their tertiary amine groups at the branching points within the dendrimer. Metal ions are introduced to an aqueous dendrimer solution and the metal ions form a complex with the lone pair of electrons present at the tertiary amines. After complexation, the ions are reduced to their zerovalent states to form a nanoparticle that is encapsulated within the dendrimer. These nanoparticles range in width from 1.5 to 10 nanometers and are called **dendrimer-encapsulated nanoparticles**.^[63]

Crop protection and agrochemicals [edit]

Given the widespread use of pesticides, herbicides and insecticides in modern farming, dendrimers are also being used by companies to help improve the delivery of agrochemicals to enable healthier plant growth and to help fight plant diseases.^[64]

See also [edit]

- Dendronized polymer
- Metallo dendrimer
- Ferrocene-containing dendrimers












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