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Review Article

A Review Article on Dendrimers

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ABSTRACT

A dendrimer is typically described as a macromolecule, which is characterized by its highly branched 3D structure that provides a high degree of surface functionality and adaptability. Dendrimers are a new class of polymeric materials. They are highly branched, monodisperse macromolecules. The structure of those materials features a great impact on their physical and chemical properties. As a results of their unique behaviour dendrimers are suitable for a good range of biomedical and industrial applications. The paper gives a concise review of physio-chemical properties and their possible use in various areas of research, technology and treatment. The bioactive agents can be easily encapsulated into the interior of the dendrimers or chemically attached that is conjugated or physically adsorbed onto the dendrimer surface, serving the desired properties of the carrier to the precise needs of the active material and its therapeutic applications. The review aims to stress on construction, characterisation, drug delivery and possible application of dendrimers in various areas of research, technology and treatment.

INTRODUCTION

Dendrimers are repeatedly branched molecules. The huge number of papers on dendritic architectures such as dendrimers, dendronized, hyperbranched and brush- polymers has generated a vast variety of inconsistent terms and definitions making a clear and concise unfolding of this topic highly difficult. A dendrimer is generally described as a macromolecule, which is characterized by its highly branched three diamentional structure that provides a high degree of surface functionality and versatility. Dendrimers have often been referred to as the "Polymers of the 21st century". Dendrimer chemistry was first introduced in 1978 by Fritz Vogtle and co- workers. He synthesized the first "cascade molecules". In 1985, Donald A. Tomalia, synthesized the first family of dendrimers 121. The word "dendrimer" originated from two words, the Greek word dendron, meaning tree, and meros, meaning part. At the same time, Newkome et al 31 independently reported synthesis of similar

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macromolecules. They called them 'arborols' from the Latin word. 'arbor' also meaning a tree. The term cascade molecule is also used, but 'dendrimer' is the best established one. Due to their multivalent and monodisperse character, dendrimers have stimulated wide interest in the field of chemistry and biology, especially in applications like drug delivery, gene therapy and chemotherapy. Dendrimers then experienced an explosion of scientific interest because of architecture. Their unique molecular architectural. Dendrimers possess three distinguished architectural components (Figure 1), namely an initiator core, interior layers (generations) composed of repeating units, radically attached to the interior core and exterior (terminal functionality) attached to the outermost interior generations [4.5].

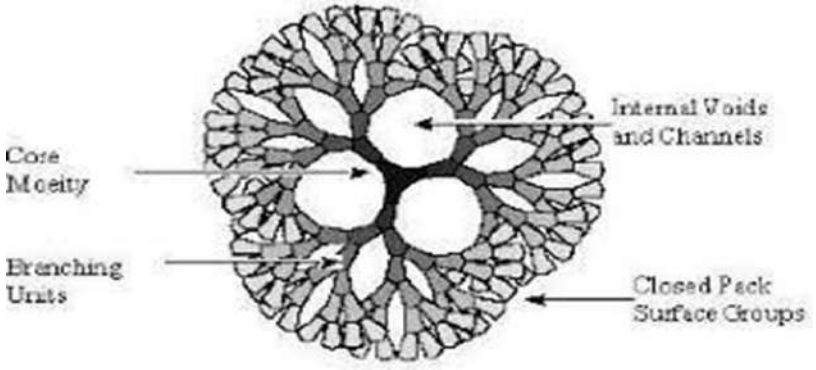

Figure 1. Architecture of a dendrimer.

History Of Dendrimer: -

In the design of plants and animals nature often ends up creating dendritic solutions to enhance particular properties as evidenced in the respiratory system of animals. Similarly, above the soil plants make use of their dendritic features to enhance the exposure of their leaves to sunlight also beneath the ground they have the maximum need to expose a large functional surface when collecting water from the soil. Therefore a dendrimer is both a covalently assembled molecule and a distinct nanoparticle [3]. The very first successful attempt to create and design dendritic structures by divergent synthesis was carried out by Fritz Vögtle and coworkers in 1978, followed by R.G. Denkewalter at Allied corporation in 1981, Donald Tomalia at Dow chemicals in1983 and George Newkome in 1985. In 1990 Jean Frechet introduced the covagent synthetic approach. Although a lot of researchers have concluded work in studying the different properties and applications of dendrimers but another school of thought believes the research on the properties and applications of dendrimers is still in its infancy.

Types Of Dendrimers:-

1] Radially llayere poly (amidoamineorganosilicon) dendrimers (PAMAMOS)

In 1990, Dr. Petar Dvornic and his colleagues at Michigan Molecular Institute discovered this unique first commercial silicon containing dendrimers. Consist of hydrophilic, nucleophilic polyamidoamine (PAMAM) interiors and hydrophobic organosilicon (OS) exteriors.

Excellent its networks regularity and ability to complex and encapsulate various guest species offer unprecedented potentials for new applications in nanolithography, lectronics, photonics, chemical catalysis etc. and useful precursors for the preparation of honeycomb like networks with nanoscopic PAMAM and OS domains.

2] Poly (amidoamine) dendrimers (PAMAM)

Synthesized by the divergent method, starting from initiator core reagents like ammonia or

ethylenediamine. When looking at the structure of the high generation in two-dimensions, star like pattern observed. They are commercially available as methanol solutions and ingeneration G 0-10 with 5 different core type and 10 functional surface groups.

3] Poly (Propylene Imine) dendrimers (PPI)

Poly (Propylene Imine) dendrimers (PPI) generally having poly-alkyl amines as end groups, and numerous tertiary trispropylene amines present in interior portion. It commercially available up to G5, and wide applications in material science as well as in biology. PPI dendrimers are available as Astramol TM.

4] Chiral dendrimers

The chirality in these dendrimers is based upon the construction of constitutionally different but chemically similar branches to chiral core. Their potential use as chiral hosts for enantiomeric resolutions and as chiral catalysts for asymmetric synthesis.

5] Liquid crystalline dendrimers

A highly-branched oligomer or polymer of dendritic structure containing mesogenic groups that can display mesophase behaviour. They consist of mesogenic (liq. Crystalline) monomers e.g. mesogen functionalized carbosilane dendrimers.

6] Tectodendrimer

Tecto Dendrimer are composed of a core dendrimer, perform varied functions ranging from diseased cell recognition, diagnosis of disease state drug delivery, reporting location to reporting outcomes of therapy.

7] Hybrid dendrimers

Hybrid dendrimers are hybrids (block or graft polymers) of dendritic and linear polymers. Obtained by complete monofunctionalization of the peripheral amines of a “zero-generation “polyethyleneimine dendrimer, provide structurally diverse lamellar, columnar, and cubic selforganized lattices that are less readily available from other modified dendritic structures.

8] Multilingual Dendrimers

Multilingual Dendrimers contains multiple copies of a particular functional group on the surface.

9] Micellar Dendrimers

Micellar dendrimers are unimolecular water soluble hyper branched polyphenylenes micelles.

Synthesis Of Dendrimer:-

The classical polymerization process which results in linear polymers is usually random in nature and produces molecules of different size, whereas size and molecular mass of dendrimers can be specifically controlled during synthesis.

1. Divergent Method
2. Convergent Method
3. Double Exponential and Mixed Method
4. Hypercores and Branched Monomers Growth

1] Divergent Method:-

Characteristic:- Dendrimer formation start from core.

Merit:- Lagre quantity of dendrimer produced by this method.

Demerit:- To prevent problem during synthesis large quantity of reagent required.

Product purification is very tedious task.

• Diagram:-

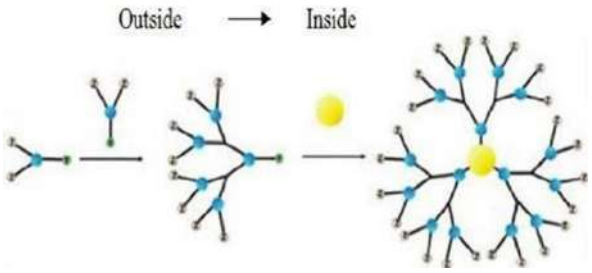

Figure 2 :- Divergent method of dendrimer synthesis.

2] Convergent Method:-

Charactristics :- Dendrimer formation from Surface.

Merit:- Defects in the final structure are less. Product easily purified.

Demerit:- Due to steric hindrance higher generation dendrimer cannot be formed.

•Diagram:-

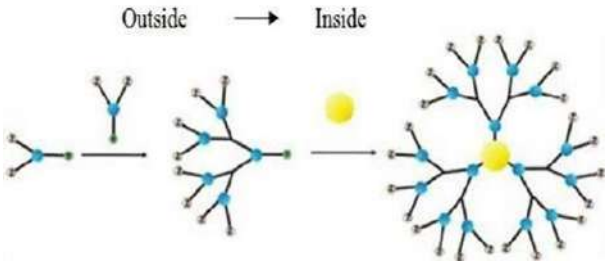

Figure 3 :- Convergent method of dendrimer synthesis.

3] Double exponential and mixed method:-

Charactristics:-This method both Divergent and Convergent method used.

Merit:- Rapid growth technique for linear polymers, fast method.

• Diagram :-

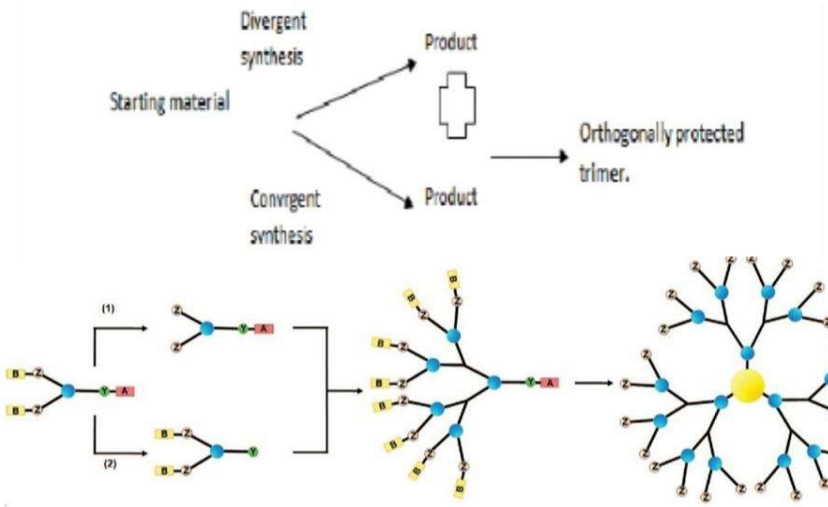

Figure 4 :- Double exponential method of Dendrimer synthesis.

4] Hypercores and Branched monomers growth:

Characteristics:-

This method involved the pre-assembly of oligomeric species which can be linked together to give dendrimers.

Merit :-Fewer steps, Higher yields.

Factor Affecting Dendrimer:-

There are various factors which affect dendrimer synthesis are following:

a)Incomplete addition reaction.

b)Intermolecular cyclization.

c)Fragmentation.

d)Solvolysis of terminal functionalities.

Properties Of Dendrimer:-

1] Nanoscale dimensions and shapes

Dendrimers possess nanoscale dimensions because of their wellorganized synthesis process and properties that allow for size control. As the PAMAM dendrimer family evolves from generation 1 to 10, the diameter of dendrimers with an ethylenediamine core increases from 1.1 to 12.4 nm. Dendrimer morphology is subject to change. High-generation PAMAM dendrimers (G4–G10) with well defined cavities have roughly spherical shapes, whereas lowgeneration PAMAM dendrimers (G0–G3) with an ethylenediamine core and no internal characteristics have ellipsoidal forms [22–24]. 2] Monodispersity

Compared to normal linear polymers, step-by-step-manufactured dendrimers exhibit well-organized structures and a very low polydispersity (Mw/Mn 1.01–1.05) [25]. It is a result of the precise synthesis and purification method used in the preparation procedure. The monodisperse feature of dendrimers has previously been characterized using high-performance liquid chromatography (HPLC), size exclusion chromatography (SEC), gel electrophoresis, mass spectrometry (MS),and transmission electron microscopy (TEM) [26]. 3] Polyvalency

Variable functionalization is made possible by polyvalency, which is particularly essential for the development of antiviral medicinal medicines since it permits a variety of interactions with biological receptor sites [26].

4] Solubility and reactivity

Dendrimer solubility is influenced by surface functional groups, dendrimer formation, repeating units, and even the core [27]. It has been discovered that dendrimers are fully soluble in a variety of solvents. They dissolve quickly and can be characterized in several ways due to their high solubility in organic solvents [28]. Moreover, they can be employed as solubility enhancers for hydrophobic guest molecules due to their high water solubility. Conversely, PAMAM dendrimers have a high density of surface functional groups (-NH2, COOH, -OH) that can form conjugations with a range of bioactive substances. These surface-modified dendrimers with diverse functions have allowed us to develop new approaches for designing nanodevices. Due to their high reactivity and solubility, dendrimers are a useful platform in the biological sciences [29].

5] Dynamic structures

Dendrimers' conformation is impacted by their origins as well as their surroundings. Welch and Muthukumar found that altering the pH or salt content in aqueous solutions might cause dendrimers to shift from dense core to dense shell shape using Monte Carlo simulations. Dendrimer formations in solutions are therefore thought to be quite dynamic. Conversely, it is believed that dendrimers of higher generation maintain their roughly spherical shapes in solutions [30]. 6] Low viscosity One of the most important characteristics of dendritic macromolecules is their low viscosity. Compared to linear polymers, dendrimers have a substantially reduced viscosity in liquids. While the number of monomers rises, viscosity in dendritic macromolecules decreases after a certain generation (usually generation 4).Because of this, dendrimers of a higher generation have a lower viscosity and more functional groups than those of a lower generation. The intrinsic viscosity of these structures increases in lockstep with the molecular mass, which distinguishes their behavior from that of linear polymers. Because it makes the dendrimer–drug complex formation easier and permits faster drug release, the low viscosity is advantageous [31, 32]

Application Of Dendrimer:-

Specific properties such as unparalled molecular Uniformity, multifunctional surface and presence of Internal c dendrimers suitable for a variety of high technology uses and are as follows:

(A) Pharmaceutical application:-

1] Dendrimer in ocular drug delivery

PAMAM dendrimers with carboxylic or hydroxyl surface Groups, improvingresidence time and enhance Bioavailability of pilocarpine in the eye.

2] Dendrimers in pulmonary drug delivery

Positively charged PAMAM dendrimers (G2 and G3 Generation) increased the relative bioavailability of Pulmonary drug delivery of Enoxaparin.

3] Dendrimer in transdermal drug delivery

Dendrimers are able to improve drug properties such as Solubility and plasma circulation time via transdermal Formulations and to deliver drugs efficiently due to its Highly water soluble and biocompatible nature. For Example improving the drug permeation through the skin When PAMAM dendrimer complex with NSAIDs like Ketoprofen, Diflunisal and Enhanced bioavailability of PAMAM dendrimers by using Indomethacin as the model drug in transdermal application.

4] Dendrimer in oral drug delivery

Oral drug delivery studies using the human colon Adenocarcinoma cell line, which have indicated that lowgeneration PAMAM dendrimers cross cell membrane Through a combination of two processes, i.e. paracellularr transport and adsorptive endocytosis. Increase in the

Cytotoxicity and permeation of dendrimers when increase In the concentration and generation.

5] Dendrimers in targeted drug delivery

Dendrimers have ideal properties which are useful in targeted drugdelivery system. For example PAMAM dendrimers conjugated with the folic acid and fluorescein isothiocyanate for targeting the tumor cells and imaging respectively.

6] Dendrimers for controlled release drug delivery

Encapsulation of 5-fluorouracil into PAMAM dendrimers(G=4) modified with carboxy methyl PEG5000 surface chains revealed reasonable drug loading, a reduced release rate and reduced haemolytic toxicity. Controlled release of the Flurbiprofen achieved by formation of complex with amine terminated generation4 (G4) PAMAM Dendrimers.

7] Dendrimers in gene delivery

Dendrimers are extensively used as non-viral vector for gene delivery. Various polyatomic compound such as PEI, polylysine, and cationic have been utilized as non-viral gene carrier.

8] Dendrimer as solubility enhancer

Dendrimers are unimolecular micellar nature, due to have hydrophilic exteriors and hydro-philic interiors and form covalent as well as non-covalent complexes with drug molecules and hydrophobes, and enhance its solubilisation behaviour. 9] Cellular delivery using dendrimer carrier

PAMAM dendrimers with lauryl chains to reduce toxicity And enhance cellular uptake, for example Dendrimer-Ibuprofen complexes entered the cells rapidly compared With pure drug (1 hr versus>3 hr), suggesting that Dendrimers can efficiently carry the complexes drug Inside cells.

10] Dendrimers as Nano-Drugs

Dendrimers as Nano-Drugs, useful as antiviral drugs, Against the herpes simplex virus can potentially prevent/reduce transmission of HIV and other sexually transmitted diseases (STDs) when Poly(lysine) dendrimers modified with sulfonated naphthyl groups. Show potent antibacterial biocides against Gram positive and Gram negative bacteria when PPI dendrimers with tertiary alkyl ammonium groups attached to the surface and Chitosan- dendrimer hybrids have been found to be useful as antibacterial agents, carriers in drug delivery systems, and in other biomedical applications.

11] Dendrimers as bio mimetic artificial proteins

The term “artificial proteins” is frequently used to describe dendrimers because of its limited size distribution, dimensional length scaling, and other biomimetic characteristics. As an illustration, the PAMAM family closely resembles the sizes and shapes of numerous significant proteins and bioassemblies, such as insulin (3 nm), cytochrome C (4 nm), and hemoglobin (5.5 nm), which are roughly the same size and shape as the corresponding ammoniacore PAMAM dendrimers, generations 3, 4, and 5. The diameter of a DNA duplex (which forms stable interactions with histone clusters to compress and store DNA within the nucleosome of cells) is matched by the generation 2 dendrimer (2.4 nm). And the widths of PAMAM dendrimers from generations 5 and 6 are roughly equal to the lipid bilayer membrane thickness (~5.5 nm) of living cells.

12] Dendrimers as nano-scaffolds

Decreasing the contact with body defense system macromolecules and imaging tags as a result of the good platform that dendrimer surface provides for the attachment of cell-specific ligands, solubility modifiers, and stealth molecules. For instance, boron isotopes have been successfully delivered using folate-PAMAM dendrimers in the context of boron neutron-capture therapy for cancerous tumors. (B) Therapeutic application:

1] Dendrimers in photodynamic therapy (PDT)

Cancer treatment involves the administration of a light-Activated photosensitizing drug that selectively concentrates in diseased tissue. For example The photosensitizer 5-aminolevulinic

acid has been attached to the surface of dendrimers and studied as an agent for PDT of tumorigenic keratinocytes.

2] Dendrimers for boron neutron capture therapy (BNCT)

The radiation energy generated from the capture reaction of low energy thermal neutrons by 108 atoms has been used successfully for the selective destruction of tissue. Due to their well defined structure and multivalency, Dendrimers are a very fascinating compound for use as boron carriers.

(C) Diagnostic application:

1] Dendrimers as molecular probes

Due to their distinct morphology and unique characteristics, use as molecular probes. For Example, the immobilization of sensor units on the surface of dendrimers is a very efficient way to generate an integrated molecular probe, because of their large surface area and high density of surface functionalities.

2] Dendrimers as X-ray contrast agents

Dendrimers are currently under investigation as potential polymeric X-ray contrast agents. Potential dendritic X-ray contrast agents using various oregano metallic complexes such as bismuth and tin are used to obtain a high-resolution X-ray image, several diseases or organs, such as arteriosclerotic vasculature, tumours, infarcts, kidneys or efferent urinary etc.

3] Dendrimers as MRI contrast agents

Introduction of target specific moieties to the dendritic MRI contrast agents, to improve the pharmacokinetic properties of dendrimer contrast agents, for example folate conjugated Gd (III)-DTPA PAMAM dendrimer, which increased the longitudinal relaxation rate of tumour cells expressing the high affinity folate receptor.

(D) Dendritic Catalysts / Enzymes:

Dendrimers useful as nanoscale catalysts due to its combination of high surface area and high solubility. Dendrimers have a multifunctional surface and all catalytic sites are always exposed towards the reaction mixture and by easy ultra filtration methods, can be recovered from the reaction mixture. Dendritic shells can be used to create a microenvironment which is favourable for catalysis or provide shielding for functional groups at the dendritic core.

(E) Industrial Processes:

Dendrimers can encapsulate insoluble materials, such as metals, and transport them into a solvent within their interior. For example, fluorinated dendrimers, which are soluble in supercritical CO2 and can be used to extract strongly hydrophilic compounds from, water into liquid CO2. This may help develop Technologies in which hazardous organic solvents are replaced by liquid CO2.

Advantages Of Dendrimer:-

1] Dendrimers reveal a structural homogeny and monodispersed:

Dendrimers have concerned much interest because of Their attractive structure and distinct properties. Dendrimers are globular, size monodisperse, Macromolecules in which all bonds appear radially from a middle focal point or core with a expected Branching pattern and with repeated units that each Contribute a branch point.

2] For enhanced targeting efficiency due to the of functional groups on the dendrimer:

Earlier research shows that water-soluble synthetic Polymers conjugate with antibodies or their Fragments offer a potential targetable drug carrier System facilitates exact delivery of anticancer drugs To model tumours or tumour cells immunize into Mice. A condition for the biological activity of the Conjugate is addition of the drug to the polymer Carrier via biodegradable spacer enable drug release and it's target.

3] Surface alteration may authorize dendrimer Mimicking biological exo- receptors, substrates, Inhibitors or cofactors:

The comparison of dendrimers structure with 1gM Antibodies (pentamers radially distributed) advise that They may be used to function as antibodies

e.g. Activation of macrophages, recognition, and high attraction to antigen. Dendrimers have the aptitude to Deliver drug within cell or they may recover Intracellular trafficking polymers which are Connection when the drug is released. Dendrimers Has constrained toxicity and immunogenicity but Superior biodegradability. They have better Colloidal, biological and shelf-stability. They may be Basically anticancer agents in nature due to interferon Tumour necrosis factor inducing properties of Acrylates, Baker and his colleagues use poly (amidoamine) dendrimers to transport anticancer drugs.

CONCLUSION:

Since the synthesis of the first dendrimer, there has been a noticeable surge in interest in the chemistry of dendrimers. The many kinds, characteristics, and popular synthetic approaches used in dendrimer preparation are outlined in this article. Dendrimer synthesis is still a multi-step process that takes a lot of work. Individual characteristics of dendrimers make them promising candidates for numerous applications. Dendrimers find use in a wide range of fields, particularly in the production of materials and pharmaceuticals. The review will facilitate the exchange of ideas among scientists and enable the development of new, better performing dendritic structures.

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