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Review Article

"Dendrimers: A Comprehensive Review of Synthesis, Properties, and Applications"

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ABSTRACT:

Dendrimers are nanoscale, radially symmetrical macromolecules characterized by a highly defined, uniform, and monodisperse architecture. Structurally, they consist of a central symmetric core, surrounded by successive inner and outer layers, forming a branched, tree-like framework. In contrast to the three conventional classes of macromolecular architectures—which typically yield polydisperse products with a range of molecular weights—dendrimers offer precise molecular control. A wide array of dendrimer types has been developed, each exhibiting valuable biological properties, including polyvalency, self-assembly, electrostatic interactions, chemical stability, low cytotoxicity, and excellent solubility. These attributes collectively position dendrimers as promising candidates for numerous biomedical applications, which are thoroughly discussed in this review. The field of dendrimer chemistry represents a rapidly evolving frontier in modern chemical research. Dendrimers are distinguished by their three-dimensional, highly branched structures, multifunctionality, and unique chemical and physical behavior. These characteristics make them especially suitable for a range of advanced applications in nanotechnology, pharmaceuticals, and medicinal chemistry. Increasing interest from both academic and industrial sectors has fueled significant research into dendrimers and related hyperbranched polymers, largely due to their structural precision and functional versatility. This review article aims to provide a comprehensive overview of dendrimer structures and the synthetic methodologies employed to construct them at both the laboratory and industrial scales. The synthesis strategies explored include the convergent and divergent methods, alongside more recent accelerated techniques designed to enhance efficiency and scalability.

INTRODUCTION

Dendritic polymers encompass both dendrimers and hyperbranched polymers. The term dendrimer is derived from the Greek words "dendron," meaning "tree-like," and "meros" meaning "part" or "unit." True to their name, dendrimers exhibit a tree-like architecture and possess a highly symmetrical three-dimensional structure. During their synthesis, the extensive branching results in the formation of large macromolecules featuring numerous terminal functional groups.(1) Dendrimers are synthetic macromolecules with a tree-like, hyperbranched architecture. These monodisperse, three-dimensional structures are known for their well-defined molecular weights and the ability to encapsulate guest molecules within their internal cavities—a property referred to as host–guest entrapment Synthesized through a controlled, stepwise process using branched monomer units, dendrimers allow precise manipulation of their shape, size, flexibility, density, and solubility. These characteristics can be tailored by selecting specific surface functional groups and branching units (2) To date, dendrimers have been employed in various fields, including electrochemistry (Credi et al., 2004), photochemistry (Momotake and Arai, 2004), supramolecular and host–guest chemistry (Al-Jamal et al., 2005), nanoparticle synthesis (Wu et al., 2006), dye decolorization (Cheng et al., 2005), environmental pollution management (Xu and Zhao, 2005), epoxy resin curing (Cheng et al., 2007), catalysis (Lee et al., 1994), and monomolecular membrane fabrication (Sayed-Sweet et al., 1997).(3) Furthermore, dendrimers can incorporate both polymeric and organic components within their framework, granting them unique chemical and physical

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properties. Owing to these versatile features, dendrimers have fo++und applications across a wide range of scientific disciplines.[4] In biomedical applications, dendrimers have shown significant promise in drug delivery (Aulenta et al., 2003; D'Emanuele and Attwood, 2005; Svenson and Tomalia, 2012) and gene transfection (Dufès et al., 2005). In recent years, their role in drug delivery systems has attracted considerable attention, often surpassing interest in other application areas (Esfand and Tomalia, 2001; Gillies and Frechet, 2005). Dendrimers are hyperbranched polymeric structures characterized by a controlled architecture. The terminal groups located on the periphery can be functionalized, enabling the tuning of their physicochemical and biological behaviors.[5] Dendritic macromolecules are gaining significant attention in anticancer therapy and diagnostic imaging. Their unique and well-defined structures position them as a promising new class of nanoscale delivery systems. As dendrimer generation increases, their size expands linearly, and their shape becomes more globular. This makes them excellent candidates for studying how polymer characteristics such as size, charge, and composition influence biological processes, including interactions with lipid membranes, toxicity, cell uptake, circulation time, distribution in the body, and elimination. The efficiency of dendrimers in enhancing solubility is primarily determined by variables such as generation number, concentration, solution pH, structural core, temperature, and surface functionalities. Strategic control of these parameters can yield substantial improvements in solubilization performance.[6]

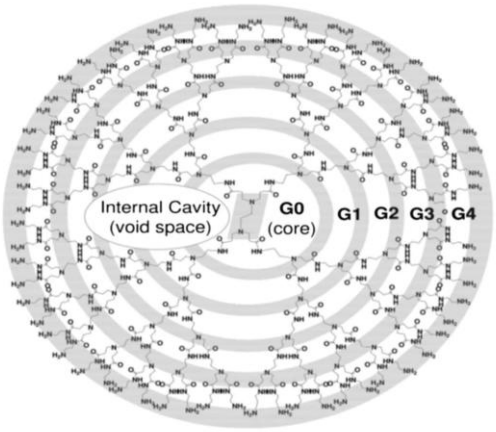

Figure 1:- Generation G4 dendrimer with 64 amino groups at the periphery

Synthesis:-

Dendrimers are produced through a series of repetitive chemical reactions that gradually build the molecule in successive layers, known as generations. Their synthesis generally follows one of two main approaches. Starting from a multifunctional core molecule, the dendrimer grows outward toward the periphery. The core first reacts with monomer units that have one reactive site and two inactive sites, forming the first-generation dendrimer. The outer surface of this new structure is then activated to react with additional monomers, and by repeating this process, higher-generation dendrimers are formed.The divergent approach is effective to produce large quantities of dendrimers. However, problems can occur due to side reactions and incomplete reactions of peripheral groups, leading to structural defects. To solve these problems, a large excess of reagents is needed, inducing unfortunately major difficulties for the purification of the final product.[7]

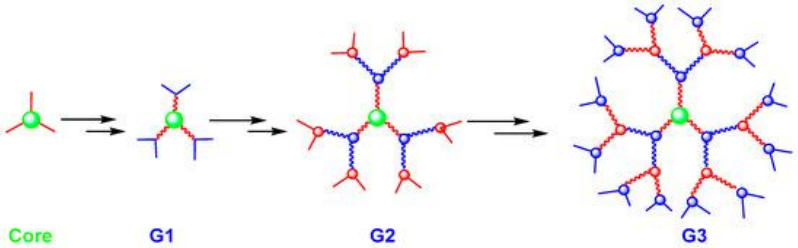

Figure 2:-Dendrimer synthesis using the divergent approach.

Convergent methods were developed with the aim of limiting the purification problems encountered in divergent methods. In this approach, the dendrimer is constructed in several steps, starting from the peripheral clusters, and progressing inwards to the core, unlike the divergent method. When the desired branching polymeric arms, i.e., dendrons. are formed, they are attached to a central multifunctional molecule.The concept of using a convergent approach for the synthesis of dendritic macromolecules has several advantages, including the following: the small number of coupling reactions for each growth step allows for a better control of the synthesis; the appearance of defects in the final structure is minimized and large excesses of reagents are avoided, which simplifies the purification. However, this approach does not allow the formation of high generations because steric problems arise in the reactions between the dendrons and the central molecule[8]

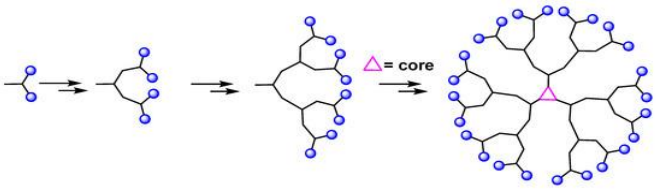

Figure 3:-Synthesis of dendrimer via the convergent approach.

Classification of Dendrimers:-

1.Simple dendrimers:

Simple dendrimers are constructed from basic monomer units. Their synthesis often follows a convergent method using symmetrically substituted benzene tricarboxylic acid esters.

Structure: Composed of 4, 10, 22, or 46 benzene rings linked symmetrically.

Size: Approximately 45 Å in molecular diameter.

Applications: Used in fundamental molecular scaffolding and early-stage dendrimer research.[9]

2. Liquid Crystalline Dendrimers:

These dendrimers are designed with mesogenic monomers, such as mesogen functionalized carbosilane dendrimers.

Key Feature: 36 mesogenic units attached via a C-5 spacer.

Behaviour: Exhibits a broad smectic liquid crystalline phase in the temperature range of 17°C to 130°C.

Applications: Advanced materials, liquid crystal displays, and optoelectronic devices.[10]

3. Chiral Dendrimers:

Built by assembling constitutionally assorted but chemically similar branches on an chiral core.

Example: Pentaerythritol-derived dendrimers.

Importance: Useful in asymmetric catalysis and enantioselective drug delivery due to precise control of molecular chirality.[11]

4. Micellar Dendrimers:

These dendrimers mimic unimolecular micelles.

Characteristics: Fully aromatic and water-soluble, capable of forming a microenvironment for small organic molecules.

Applications: Drug solubilization, molecular encapsulation, and targeted delivery systems. [12]

5. Hybrid Dendrimers:

Formed by combining dendritic and linear polymer chains into block or graft copolymers.

Advantages: Provides surface-active properties, improved interfacial adhesion, and material compatibility.

Applications: Used as compatibilizers, adhesives, and surface-active agents in polymer blends.[13]

6. Amphiphilic Dendrimers:

Globular in shape with an asymmetric but controlled distribution of hydrophilic and hydrophobic chain ends.

Function: Orients at interfaces to form interfacial liquid membranes.

Applications: Stabilization of aqueous-organic emulsions in pharmaceutical formulations and material sciences. [14]

7. Metallo Dendrimers:

Dendrimers functionalized with metal ions, either in the core or at the periphery.

Example: Ruthenium bipyridine-based dendrimers.

Properties: Exhibit unique electrochemical and luminescence characteristics.[15]

Properties of dendrimers:-

In comparison to other nanoscale synthetic structures, such as conventional polymers, buckyballs, or carbon nanotubes, dendrimers stand out due to their well-defined architecture and greater structural diversity. While traditional polymers often exhibit structural heterogeneity and carbon-based nanostructures have fixed geometries, dendrimers offer precise control over size, shape, and surface functionality, making them highly versatile for various applications. [16]

1.Pharmacokinetic Properties of Dendrimers:-

Pharmacokinetic properties play a crucial role in the successful biomedical application of dendrimers, including drug delivery, imaging, photodynamic therapy, and neutron capture therapy. The wide range of potential medical applications has driven significant interest in studying dendrimer pharmacokinetics. One key advantage of dendrimers is the ability to modify their peripheral functional groups, allowing the development of various conjugates such as antibody-dendrimer and peptide-dendrimer systems. Additionally, dendrimers can serve as molecular containers—known as dendritic boxes—that encapsulate guest molecules, further enhancing their versatility in targeted delivery and therapeutic applications.[17]

2.Covalent Conjugation Strategies:-

Covalent conjugation of small molecules to polymeric scaffolds has been explored for over three decades as a method to improve pharmacological properties. In dendrimer-based systems, this approach often results in a

pro-drug design, where the dendrimer–drug conjugate remains inactive until internalized by the target cell. Once inside, the conjugate undergoes cleavage, releasing the active drug moiety (see Figure 6). This strategy enhances targeted delivery and reduces systemic toxicity. [18]

3.Polyvalency:

One of the key advantages of dendrimers is their polyvalent nature, which allows for multiple functional groups to be displayed on the surface. This feature enables the simultaneous interaction with several biological receptor sites, significantly enhancing binding affinity and selectivity. Polyvalency is particularly useful in the development of antiviral therapeutics, where multivalent binding improves therapeutic efficacy by engaging multiple receptor targets on viruses or infected cells. [19]

4.Self-Assembling Dendrimers:

Self-assembly refers to the spontaneous and precise organization of molecular components through specific intermolecular forces such as hydrogen bonding, π–π stacking, or metal coordination. Dendrimers are ideal candidates for self-assembly due to their well-defined structural architecture, comprising three key parts: the core, Three main strategies are employed in dendrimer self-assembly:

a. Core recognition – Designing dendrons with core units that recognize each other, leading to the spontaneous formation of dendrimers.

b. Ditopic or polytopic cores – Structures that promote the assembly of multiple dendrons into a complete dendrimer architecture.

c. Pseudorotaxane formation – A well-studied method where molecular recognition drives the organization, as demonstrated by Gibson and colleagues. This area is rapidly expanding, offering new possibilities in supramolecular chemistry nanotechnology.[20]

5. Electrostatic Interactions:

The dendrimer surface is often densely populated with identical terminal groups, which can be charged, giving the dendrimer polyelectrolyte properties. Such charged surfaces enable strong electrostatic attraction of oppositely charged molecules. Typical examples of these interactions include:

a. Aggregation of methylene blue dye molecules onto the dendrimer surface.

b. Binding of EPR probes, such as copper complexes or nitroxide cation radicals.

These interactions are exploited for drug delivery, molecular recognition, and diagnostic applications. [21]

APPLICATIONS OF DENDRIMERS:-

Dendrimers have distinctive structural features such as nanometer size, spherical shape, extensive branching, and internal cavities. These structural traits contribute to their unique properties, including low viscosity, high solubility, and strong reactivity. Dendrimers can be applied in many areas, such as medicine, disease diagnosis, gene therapy, sensors, drug delivery, adhesives, coatings, solar energy harvesting, catalysts electronics, and separation techniques, along with several other.

1.Dendrimers in biomedical field:

Dendrimers hold immense promise in nanomedicine, especially for targeted and controlled drug delivery in cancer treatment. One of the major challenges in oncology today is enhancing the pharmacokinetic profiles of therapeutic agents.

In the biomedical field, dendritic polymers offer significant advantages. Their highly branched structure resembles that of proteins, enzymes, and viruses, and they can be easily functionalized. Molecules can be attached to their outer surface or encapsulated within their internal cavities. Because of these unique properties, dendrimers are increasingly being used as advanced materials in modern medicine.[22]

2.Dendrimers as Carriers for Anticancer Drugs:

Early research on dendrimers as drug delivery systems focused on their use as unimolecular micelles or "dendritic boxes" for noncovalent encapsulation of therapeutic agents. For instance, DNA was complexed with PAMAM dendrimers for gene delivery applications, while hydrophobic drugs and dye molecules were incorporated into dendrimer cores. One key advantage of dendritic unimolecular micelles over conventional polymeric micelles is their structural stability at any concentration, since the hydrophobic segments are covalently linked. However, controlling drug release from the dendrimer core remains challenging—some systems require harsh conditions for release, while others release drugs too quickly. [24]

An alternative strategy involves covalently attaching drug molecules to the dendrimer periphery, exploiting their well-defined multivalency. Drug loading capacity can be adjusted by modifying the dendrimer generation, while drug release can be precisely controlled by incorporating degradable linkers. For example, encapsulating cisplatin in PAMAM dendrimers resulted in conjugates that released the drug more slowly, accumulated in tumors more effectively, and exhibited lower systemic toxicity compared to free cisplatin. [25]

Malik et al. developed anticancer prodrugs by complexing carboxylate-terminated PAMAM dendrimers with cisplatin. These prodrugs showed controlled hydrolysis-based release (<1% over 80 hours), enhanced maximum tolerated dose, improved bioavailability of cisplatin, and prolonged survival in tumor-bearing mice. Similarly, Malik and Duncan demonstrated that dendritic polymer platinates could be administered via multiple routes—intravenous, oral, parenteral, subcutaneous, or topical—to achieve significant tumor inhibition. These dendritic

conjugates offered high drug efficiency, excellent carrying capacity, water solubility, storage stability, reduced toxicity, and enhanced in vivo antitumor performance.

Moreover, Balogh et al. reported that PAMAM dendrimers encapsulating silver salts provided conjugates with slow silver release and demonstrated antimicrobial activity against *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Escherichia coli*. [26]

3. Dendrimers as Tissue Regenerators:

Tissue engineering has advanced significantly in recent decades, aiming to regenerate native tissues by supporting the body's natural healing processes or creating entire organs for transplantation. A critical first step in tissue engineering is selecting an appropriate scaffold material. Scaffolds can range from simple two-dimensional surfaces that support cell growth to complex three-dimensional structures that encapsulate multiple cell types. Typically, scaffolds are designed as porous matrices, facilitating nutrient diffusion to cells and the removal of waste products.

The ultimate goal is for encapsulated cells to synthesize a new extracellular matrix (ECM), gradually replacing the scaffold as it biodegrades. Therefore, scaffold degradation must be carefully tuned to match ECM biosynthesis.

Scaffold materials are broadly classified into natural and synthetic polymers. Natural scaffolds are often based on proteins, carbohydrates, or glycoproteins. Collagen remains the most widely used protein scaffold due to its biocompatibility. Fibrin is also employed, valued for its ability to form mesh-like networks. Structural components such as hyaluronic acid and chondroitin sulfate have been extensively applied for their biological relevance in tissue scaffolding. Additionally, carbohydrates like alginate, dextran, and chitosan are favored for their hydrated network-forming properties.

Synthetic linear polymers also play a major role in scaffold development. Common examples include poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(caprolactone) (PCL), and poly(ethylene glycol) (PEG). These materials are chosen for their tunable mechanical properties, biodegradability, and ease of processing.

Dendrimers, with their well-defined branched architecture and modifiable surfaces, offer exciting potential as next-generation scaffold materials, providing enhanced control over cell interactions and degradation behavior.

This version enhances clarity, streamlines technical detail, and improves coherence while keeping the core scientific information intact. [27]

4. Transdermal Drug Delivery:

The clinical use of nonsteroidal anti-inflammatory drugs (NSAIDs) is often limited by adverse effects such as gastrointestinal irritation and renal toxicity when administered orally. Transdermal drug delivery systems (TDDS) offer a solution by bypassing the gastrointestinal tract and providing sustained therapeutic drug levels over an extended period. However, the main challenge remains the poor permeability of many drugs across the skin due to its strong barrier function. Dendrimers have emerged as promising carriers in TDDS, particularly for hydrophobic drugs with low water solubility, improving their solubilization and permeation through the skin.

5. Gene Delivery:

Despite advances in understanding disease pathways and sequencing the human genome, gene therapy has not yet fully realized its potential in clinical practice. A major hurdle is the safe and efficient delivery of genetic material to target cells. Dendrimers offer a solution by forming stable complexes with DNA, protecting it from degradation, and enabling its delivery without loss of function. To preserve DNA activity during dehydration, dendrimer/DNA complexes are encapsulated in fast-degrading, water-soluble polymer films. This method enhances localized gene transfection. Studies using PAMAM dendrimers demonstrated their effectiveness in substrate-mediated gene delivery, showing strong potential for localized and efficient transfection. [28]

6. Dendrimers as MRI Contrast Agents:

Dendrimers functionalized with metal chelates are used as contrast agents in magnetic resonance imaging (MRI). Their well-defined branched architecture allows multiple metal ions to be incorporated, improving imaging efficiency. Due to their monodispersity, high solubility, and multiple functional surface groups, dendrimers serve as effective MRI contrast media.[29]

CONCLUSION:-

Dendrimers possess distinct characteristics that make them promising for numerous applications. These are precisely structured synthetic macromolecules, notable for their large number of functional groups and compact architecture. Since their initial development, the field of dendrimer chemistry has grown rapidly, with extensive research focused on synthesis techniques and the study of their unique properties as a new class of macro- and micromolecules. However, even after more than twenty years since their discovery, the multi-step synthesis of dendrimers continues to be a complex and demanding process. [30]

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