

Hybrid Organic/Inorganic Materials Based on Functionalized Dendritic Polymers: Methods of Preparation, Applications and Future Prospects

Michael Arkas*

Institute of Physical Chemistry, NCSR Demokritos, Greece

Dendritic polymers [1-6] is a special class of macromolecules consisting of monomeric units branching out from a common centre. The name dendritic is derived from the Greek word “Dendritic” meaning “tree-like”. They consist of four subcategories which correspond to different topologies:

- i) dendrimers: perfectly symmetric macromolecules with precisely fixed number of monomeric units
- ii) hyperbranched polymers: non-symmetrical, polydisperse, randomly polymerized macromolecules
- iii) dendrons: monodisperse wedge-shaped dendrimer sections
- iv) dendrigrafts: dendritic structures that are grown on reactive linear polymers or oligomers

The distinctive highly branched chemical structure of dendritic polymers has nanosized dimensions and consists of the central core, the repeating units and the terminal functional groups. Due to these structural features, they possess nanocavities that are able to encapsulate various molecules, while their external surfaces can be easily functionalized. In addition, their terminal groups can exhibit the so-called polyvalency effect [7,8], which enhances their binding with other substrates.

The diversity of dendritic polymers nanocavities as far as the size, polarity and interaction ability are concerned, provides the basis for the formation of devices bearing nanosized containers for effectively encapsulating metal ions. Thus, colloidal silver nanoparticles are obtained by the reduction Ag^+ ions encapsulated into Polyethylene Imine (PEI) Hyperbranched Polymer even in the absence of another reductant [9]. Dendritic polymers also stabilize colloidal suspensions of gold by in situ reduction of $HAuCl_4$ encapsulated into Polyamidoamine PAMAM Dendrimers by aqueous $NaBH_4$ solution [10]. These dendritic polymer/noble metal composites have unique potential for applications such as catalysis.

On the other hand the terminal functional groups can be involved in a variety of interactions/modifications. For example the amines of the poly (propyleneimine) and poly (amidoamine) dendrimers and hyperbranched polymers act as templates for biomimetic silica nanospheres formation [11]. The sol-gel reactions proceed at room temperature by the addition of metastable silicic acid into the dendrimer solution in phosphate buffer, pH 7.5. The dendritic polymers, although incorporated in the nanospheres, retain their property of encapsulating metal ions and therefore, can be applied for catalysis. In addition a variety of other compounds can be encapsulated depending on the microenvironment of the nanocavities, which is primarily affected by the structural characteristics of the repeating units. In this manner, encapsulation of impurities dissolved in water leads, using appropriate methods, to novel bulk water purification technologies [12] and the solubilisation of bioactive compounds in their interior could lead to the development of effective drug and gene delivery systems [13].

The reactivity of the functionalized terminal groups of the dendritic polymers can result in chemical bond formation with

different substrates. In this manner covalent attachment of a polymer with desired properties to a solid support can be achieved. For example by employing ethoxysilylated derivatives of diaminobutane poly (propylene imine) and polyglycerol by hydrolysis and subsequent cross-linking nanostructured networks can be produced which interact with ceramic filters, forming a covalently bound film that has the potential to encapsulate pollutants of water through continuous filtration.

In a combination of the two above mentioned methods cross-linking of hyperbranched macromolecules functionalized with silica precursors along with hydrolysis and poly-condensation reactions leads to the formation of novel silica network architecture. In this case the solid support is synthesized by the sol gel reactions of the terminal groups.

Another approach for the production of hybrid dendritic/inorganic materials is the direct propagation of dendrons on the surface of inorganic materials such as silica gel through solid-phase synthesis via a conventional divergent pathway. For example the propagation of PAMAM (polyamidoamine) dendrons on silica can be accomplished by a series of alternate Michael addition and amidation reactions [14]. PAMAM modified silica is further functionalized with long aliphatic chains to the periphery of the dendron for applications in pollutant encapsulation. PAMAM dendritic polymers are also phosphonated in order to provide an attractive coordination site for rhodium. The resulting complexes are used for the catalytic hydroformylation of olefins. Another modification of the periphery of PAMAM dendrons by salicylaldehyde affords a substrate that immobilizes Mn(II) onto PAMAM-SiO₂ dendrimers for the preparation of catalysts for olefin epoxidation.

In another aspect, by combining the chemical attachment of dendritic polymers to a solid support with biomimetic synthesis, a hydroxyapatite layer, with characteristics similar to those of biogenic apatite, firmly attached on the titanium surface is produced. This approach includes titanium surface activation by proper chemical pretreatment, chemical bonding with an appropriately functionalized siloxane polymer intermediate layer and subsequent chemical attachment of hyperbranched poly(ethylene imine) (PEI) that is able to promote the formation, of a firmly attached calcium phosphate layer [15]. These composites have potential applications in manufacturing dental implants and in orthopedics for bone-anchoring systems.

*Corresponding author: Michael Arkas, Institute of Physical Chemistry, NCSR Demokritos, Aghia Paraskevi 15310 Attiki, Greece, E-mail: markas@chem.demokritos.gr

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The manufacturing of hybrid dendritic-inorganic materials can thus be achieved by employing several convenient methods and techniques including, chemical reactions such as sol-gel and biomimetic synthesis, covalent attachment of a dendritic compound to an inorganic support direct propagation of a dendron from the inorganic matrix or encapsulation of metal ions into the dendritic polymers. These materials receive very high scientific interest since they have many other potential applications. For example dendritic polymers produce a vast variety of differently colored metal complexes, property which is preserved in the hybrid materials as well. Possible applications for the detection of explosives, chemical warfare agents, and other substances even in small concentrations can be investigated. The use of biogenic silica produced by a complex of DNA with a dendrimer could simplify DNA transfection process. Hybrid nanoceramics derived from silica, alumina, zirconia and titania and dendritic polymers can be tested as drug-delivery vehicles because of their inert nature and high compatibility with biological systems. It is evident that the formation of composite devices which will have extended applications for specific cases can be accomplished by careful selection of the suitable materials and processing parameters. It is thus hoped that the work performed and reviewed in this editorial will show the potential of the methodology and will trigger interest to other researchers to further contribute and exploit this promising area of research.

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