CHAPTER 2

NANOPARTICLE DISPERSED LINEAR AND DENDRITIC MACROMOLECULES CONTAINING PHOTORESPONSIVE GROUPS: AN OVERVIEW
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2.1 Introduction

Dendrimers and hyperbranched polymers belong to the same group of polymers with densely branched structures and a large number of reactive groups. They resemble each other in that they are both polymerized from \( A_2B \) or \( A_iB \) monomers. Both of them give branched structures with exponential growth with respect to end-group functionalities and molecular weights. However, there are
also differences. Dendrimers are defined as monodisperse hyperbranched polymers, while ordinary hyperbranched polymers are polydisperse. The fundamental synthetic approaches differ between the two. Dendrimers require absolute control of all synthesis steps, whereas manufacturing of ordinary hyperbranched polymers adopts a strategy of one-pot synthesis. This chapter describes the general characteristics of dendrimers and hyperbranched polymers, their physical and chemical properties, and applications.

Nanoparticles of noble metals continue to evince interest because of newer applications for which they are found suitable. Silver nanostructures are in focus for various reasons. They are found to have antimicrobial and antiviral property. They are found to have a variety of applications in dentistry such as formulation of dental resin composites and coating of medical devices. Besides, they are excellent candidates for Surface Enhanced Raman Spectra active substrates, optical filters, sensors etc.

2.2 Dendrimers and Dendritic Polymers

Dendrimers are novel macromolecules with regularly branched repeat units emanating from the core. This new class of topological macromolecules has been introduced in the mid-1980s by Tomalia et al. The term 'dendrimer' takes its origin from two Greek words 'dendra' tree and 'meros' part. The name itself describes graphically, the topology of this new class of macromolecules as a highly branched, three dimensional features that resemble the architecture of a tree. Dendrimers are synthesized by repeating the growth reaction and activation reaction in consecutive steps. A typical dendrimer can be divided into three distinct architectural regions, a multifunctional central core, the branching units and the surface groups. Figure 2.1 shows a schematic diagram of a typical dendrimer.

The branching units are organized in layers called "generations", and represent the repeating monomer unit of these macromolecules. It is the functional property of each of these regions modulated by the dendrimer as a whole that
makes these aesthetically pleasing macromolecules such an interesting system to study with a wide range of applications. The versatility of dendrimers is that functional groups can be placed at the core, internal building blocks or the periphery to prepare a library of functionalized dendrons. Moreover, the sizes of dendrimers matches with that of many proteins and hence can be extensively used to mimic biological systems.

### 2.3 Dendrimers Versus Linear Polymers

There are two basic types of polymers that consist entirely of branched repeat units: dendrimers and hyperbranched polymers⁴. Hyperbranched polymers are usually the product of a non iterative polymerization procedure⁵ and therefore exhibit an irregular architecture with incompletely reacted branch points throughout the structure⁶.

Dendrimers, unlike hyperbranched polymers, are usually, highly ordered, regularly branched, globular macromolecules prepared by stepwise iterative approach.
Their structure is divided into three distinct architectural regions: (1) the core or focal moiety, (2) layers of branched units starting from the core and (3) end groups at the surface of the dendrimers.

Differences between dendrimers and traditional linear polymers are:

1. Dendrimers can be isolated as an essentially monodisperse single compound, unlike most linear polymers whose synthesis affords a range of molecular species differing in molecular weight. Size monodispersity results from a well designed iterative synthesis that allows reactions to be driven to completion with minimum side reactions, and in most cases the intermediates in dendrimer synthesis can be easily purified.

2. As their molecular weight increases, the properties of dendrimers (e.g. solubility, chemical reactivity, glass transition temperature) are dominated by the nature of end groups. Unlike linear polymers that contain only two end groups, the number of dendrimer end groups increases exponentially with generation and therefore the end group frequently become the primary interface between the dendrimer and its microenvironment.

3. In contrast to linear polymer growth that theoretically can continue ad infinitum barring solubility issues, dendritic growth is mathematically limited. During the growth of a dendrimer, the number of monomer units increases exponentially with generation while the volume available to the dendrimer only grow exponentially to the cube of its radius. As a result of this the dendrimer develop a more globular conformation as generation increases.

As a result of the growth pattern of dendrimers where the volume of single molecule increases cubically with generation while its mass increases exponentially, the solution property of dendrimers are quite different from that of linear molecules. Hawker and coworkers (1997) have done a comparative study of the
dendrimer with that of their linear isomers having exactly the same number of repeat units and end group functionalities. They observed that the fifth and sixth generation dendrimers display different features when compared to their linear isomers. This difference in physical properties viz. a much smaller hydrodynamic volume of dendrimers compared to their linear analogues, has been attributed to the back folded globular structure of dendrimers. Hence dendrimers are amorphous and soluble in organic solvents while their linear analogues are crystalline and insoluble in organic solvents.

2.4 Synthesis of Dendrimers

The molecular structure of dendrimers is due to the controlled stepwise synthesis of these structures. The same chemistry and building blocks are used for synthesizing higher generations of dendrimers. Dendrimers are synthesized by an iterative chain of reaction steps. The synthesis of dendrimers primarily involves two different types of reactions- one is activation and the other is coupling. Dendrimers synthesis relies mostly on traditional organic reactions, such as Michael reaction and Williamson ether synthesis etc. Theoretically the process can be carried out infinitely, but in practice, there is a limit to the growth of the dendrimer, known as the "starburst" or "de Gennes dense packing". Growth of dendrimers beyond this limit leads to defect in the dendrimer structure. Synthetic methodologies for the construction of dendrimers are based on two distinctly different approaches, namely divergent and convergent. Recently a mixture of these two processes has been used to construct dendrimers.

2.4.1 Divergent synthesis

This is the oldest method of dendrimer synthesis. This strategy was independently introduced by Newkome and Tomalia for the synthesis of dendrimers with well defined architecture. Divergent synthesis involves the addition of branching units one after another successively till no further addition is possible because of starburst effect. In this type of synthesis, we start from the core of the molecule and all successive monomer units are added to it till the full size dendrimer is...
achieved. Figure 2.2 shows a schematic diagram of divergent synthesis.

![Schematic diagram of divergent synthesis](image)

**Figure 2.2:** Schematic representation of divergent synthesis

### 2.4.2 Convergent synthesis

Frechet and Hawker introduced the concept of convergent synthesis, in which we start from what eventually become the end of the dendrimer and build inwards by coupling end groups to each branch of the monomer. Figure 2.3 shows a schematic diagram of convergent synthesis.

The advantage of convergent synthesis over divergent one is the lesser number of reactions per steps, although the number of steps remains the same. Also this protocol makes the purification of the dendrimers simple, as the numbers of side products are less. Therefore the convergent synthesis can be referred to as the organic approach to dendrimers. Because of greater control over the reaction steps, in case of convergent synthesis, it is possible to introduce modification in the dendrimer structure for application of the dendrimer in different fields.

Therefore, the ability to precisely place functional groups throughout the struc-
Figure 2.3: Illustration of convergent synthesis

ture, to selectively modify the focal point or the side chains, and to prepare well-defined unsymmetrical dendrimers, the convergent synthesis is the widely used method.

2.4.3 Hypercores and branched monomers

After the development of convergent synthesis dendrimer research was directed towards acceleration of the dendrimer synthesis. This involved the assembly of the various components of the dendrimers and then linking them together. This method involved fewer steps and had better yield\textsuperscript{14}. Figure 2.4 gives a pictorial representation of this approach. The core and the branches are made separately and then joined together at the end.

2.4.4 Double exponential growth

Double exponential growth is the latest development in dendrimer synthesis. This method was reported by Moore and coworkers and is a very elegant strategy for the extremely rapid preparation of high molecular weight dendrimers in only
three or four steps\textsuperscript{15}. Double exponential growth involves an AB\textsubscript{2} monomer with orthogonal protecting groups for the A and B functionality. Using this methodology, monomers for both convergent and divergent growth can be made starting from a single starting material. These two products are reacted together to give an orthogonally protected trimer, which may be used to repeat the growth process again.

Figure 2.5 shows a schematic diagram of the AB\textsubscript{2} type synthesis of dendrimer. Orthogonal systems are defined as a set of independent class of protecting groups, such that each class can be removed in any order and in the presence of all other classes\textsuperscript{16}. Orthogonal protecting group strategy has been widely used in peptide chemistry. This strategy was employed for the acceleration of synthesis of oligosaccharides. Zeng and coworkers used the orthogonal protection strategy in the rapid synthesis of dendrimers\textsuperscript{17}. 

\begin{figure}
\centering
\resizebox{\textwidth}{!}{
\includegraphics[width=\textwidth]{dendrimer.png}
}
\caption{Accelerated growth of dendrimers}
\end{figure}
2.5 Purity of Dendrimers

The synthesis of dendrimers by divergent synthesis can often lead to impure and structurally imperfect dendrimers. The impurities increase with increase in dendrimer generations. For example, in the case of the synthesis of fifth generation poly (propylene imine) dendrimer (64 amine end groups and 248 reactions) with an average selectivity of 99.5% per reaction would result in 0.995248 = 28% defect free dendrimers. With convergent synthesis some of the disadvantages of the divergent synthesis have been circumvented, though the convergent synthesis also would result in imperfect structures. The \(^1\)H and \(^{13}\)C NMR spectra of dendrimers are simpler than what one might expect and can provide great deal of information about the defects and impurities in their structures. Matrix Assisted Laser Desorption and Ionisation- Time of Flight (MALDI-TOF) technique has been extensively used to judge the purity of dendrimers along with electrospray ionization (ESI) mass spectrometric methods.
2.6 Dendrimer Architecture

Dendrimers have a three dimensional architecture. The dendritic structure can be divided into three distinctly different architectural regions- the core, the branches and the surface. It is this precise architecture that differentiates dendrimer with other synthetic polymers and responsible for the various possible application in various fields. All the three topological distinct regions of dendrimers can be suitably modified according to the various needs.

2.6.1 Core of dendrimer

The core of the dendrimer is the primary template. Different cores can be used to produce dendrimers with different shapes, sizes, multiplicity, and functions. For example introduction of a specific function such as a chromophore or metal chelator in the initiator core represents stored information which will be buried by subsequent generations. Parameters such as size, shape, and multiplicity will be transcribed and displayed throughout the dendrimer development. These variables can have dramatic effect on the ultimate shape, the interior topology and the exterior surface properties of the developing dendrimer.

Another interesting aspect of dendrimer core is its site isolation property, implying that at least to some extent the core is shielded from the environment forming a typical microenvironment inside the dendrimer. This property of the core has been exploited to mimic certain biological systems as that of proteins. Dan-dliker and coworkers reported a water soluble second generation dendritic Fe(III) porphyrin as a Cytochrome C model[24].

2.6.2 Dendrimer branches

The branch shell topology of dendrimer can dramatically change not only the interior topology but also the exterior surface of a dendrimer. The branches have been used to trap guest molecules. Kuzdzal and coworkers showed that water soluble hydrophobic dendrimers act like micelles and can be used to trap hy-
drophobic guests, analogous to micelles. He used the term 'unicellular micelles' to describe these form of dendrimers25.

2.6.3 Dendrimer surface

Dendrimer surface can be suitably modified to perform various functions. Dendrimer surface chemistry has been used to introduce both reactive and passive chemical moieties for a wide variety of interior and exterior designs, for example, chelation, dendrimer stratification, optically active groups, molecular level templating (antigenic surfaces), modification of dendrimer stoichiometry and modification of dendrimer solubility26.

2.7 Different Types of Dendrimers

Towards the end of 1970's, a lot of interest was generated in the new areas of host guest and supramolecular chemistry27,28. Initial success in the field of supramolecular chemistry where macrocycles were successfully synthesised led Vogtle and others to explore the field. Vogtle and coworkers reported the first example of an iterative synthetic procedure towards well-defined branched structures29. A few years after Vogtle made his first attempt towards synthesis of cascade molecules, Denkewalter and coworkers (1981) patented the synthesis of L-lysine based dendrimers30. Around the same time Tomalia and coworkers (1986) reported the synthesis and characterization of the first family of dendrimers, the polyamidoamine dendrimers (PAMAM)31.

The PAMAM synthesis was initiated by Michael addition of a 'core' molecule of ammonia to three molecules of methyl acrylate, followed by exhaustive amidation of the trimester adduct using a large excess of ethylenediamine, a process that generates a molecule with three terminal amino groups. Iterative growth is then continued using alternating Michael addition and amidation steps with appropriate excess of reagents31.

Shortly after Tomalia’s synthesis, Newkome and coworkers (1985) reported the synthesis of another family of dendrimers, the trisbranched polyamido dendri-
Later Meijer and coworkers reported the synthesis of poly (propylene imine) dendrimers (PPI)\(^{32}\).

Frechet and coworkers developed yet another family of dendrimers, i.e. dendrimers having a poly (aryl) ether backbone\(^{12,13}\). Another family of dendrimers was developed by Moore, with phenylacetylene backbone\(^{33}\). These are the five classes of dendrimers most widely studied and reported up to high generations.

It is known that the dendrimer properties are affected by the branching of its monomer unit. Of the five classes of dendrimers mentioned above, the most widely studied systems are Tomalia's PAMAM (polyamidoamine) dendrimers\(^{31}\) and Newkome's "arborol"\(^{9}\) systems. Among them the Newkome type dendrimers have the maximum branching of monomer unit and as such is expected to provide a much better environment at the core of the dendrimers. These systems would be more important for mimicking biological system where the existence of microenvironment is of paramount importance.
Figure 2.7: Schematic representation for the synthesis of PPI dendrimer

Figure 2.8: Structure of a polyarylether dendrimer
2.8 Applications of Dendrimers

Dendrimers, since their inception has been thought of to be useful for a variety of applications. Dendrimers has found applications in the field of medicine, host-guest chemistry, catalysis, drug delivery etc. Dendrimers with multiple identical ligands are very attractive for pharmacochemists, since their structures can exhibit amplified substrate binding. Enhanced substrate binding originates from statistical effects or from cooperativity effects. Glycodendrimers, for example, shows enhanced substrate binding properties which are important in the field of medicine. Peptide dendrimers have potential applications as protein mimics, antiviral and anticancer agents, vaccines and drug and gene delivery systems.

Nanoparticle drug delivery systems are of interest because they might be able to increase the selectivity and stability of therapeutic agents. Dendrimer drug delivery systems of several different types have been proposed; encapsulation of guest molecules in the void spaces in the dendrimer interior is a common design. While studying drug delivery systems involving dendrimers, Pistolis and coworkers examined a model system based on diaminobutane poly(propyleneimine) dendrimers having 32 or 64 primary amine end groups, in the hydrophobic interior of which pyrene was solubilised. They found that the molecular composites resulting from the incorporation of pyrene in poly(propyleneimines) are pH sensitive, the release of pyrene is induced in acidic media and its incorporation is favoured in basic environments. These studies are very important for developing dendrimers as useful drug delivery systems. Preliminary results with low generation PAMAM dendrimers show that they can cross the Caco-2-cell monolayers without significant cytotoxicity.

Dendrimers, as their core is well shielded from the surroundings, presents a microenvironment inside them and this property has been used to mimic biological systems. Especially porphyrin based dendrimers have attracted a lot of
attention. Porphyrins are found in many natural systems, where they play an essential role as photoactive, redox, guest binding and catalytic entities. Newkome type dendrimers with a zinc porphyrin core has been extensively studied as mimics of biological systems\textsuperscript{43}.

One of the other interesting applications of the dendrimers is in the field of host-guest chemistry. The host-guest chemistry is also important for the use of these dendrimers as possible drug delivery systems. Unimolecular micelles are known to be used as host systems for guest molecules and Newkome type dendrimers have been found to be excellent systems to study such behaviour. Newkome and coworkers used an alkane dendrimer with 36 terminal carboxylates to bind several lipophilic probes such as phenol blue, 7-chlorotetracycline and diphenylhexatriene\textsuperscript{44}. Fluorescence and UV spectroscopy has been extensively used for studying the host guest interactions.

As dendrimers posses a hollow core and a dense shell, drugs can be encapsulated within a dendrimer by simple physical entrapment or by non bonding interactions with some specific structures within the dendrimer. Such systems may help in solubilizing poorly soluble drugs and may also enhance drug stability and bioavailability\textsuperscript{45}. Dendrimers whose surface has been modified with PEG is of particular interest for pharmaceutical applications because of its high water solubility, biocompatibility and ability to modify the biodistribution of carriers\textsuperscript{46}.

2.9 Hyperbranched Polymers

Hyperbranched polymers constitute a special class of branched macromolecules characterized by their randomly branched topology. Hyperbranched polymers are attractive because they resemble dendrimers, but they can be prepared on a large scale and at a reasonable cost in a single step synthesis as opposed to the controlled branching of dendrimers which requires a stringent sequential step
They possess irregularly branched non-perfect structures with one focal unit and at least two branching points.

### 2.10 Synthesis of Hyperbranched Polymers

Several methods can be used to synthesise hyperbranched polymers. The synthesis of hyperbranched polymers can be rationalized into three main strategies: (i) step-growth polycondensation of $AB_2$ and $A_2+B_3$ monomers, (ii) self-condensing vinyl polymerisation of $AB^*$ monomers and (iii) multi-branching ring-opening polymerisation of latent $AB_2$ monomers.

![Scheme 2.1](image)

**Scheme 2.1.** General scheme for the synthesis of a hyperbranched polymer

Utilising these polymerization strategies, a wide variety of hyperbranched architectures have been synthesised successfully, including polyesters, polyamides, polycarbonates and polyurethanes. The polymers generated in these methods exhibit an irregular architecture with incomplete branch points dispersed throughout the structure, in comparison to their perfect dendritic analogues (Scheme
The important strategies employed for the synthesis of hyperbranched polymers are step-growth polycondensation, self-condensing vinyl polymerisation of AB* monomers and multi-branching ring-opening polymerisation of latent AB* monomers.

2.10.1 Step-growth polycondensations

This strategy involves the polymerisation of AB_x (where x = 2) monomers via a one-step polycondensation. The primary advantage of this method is that normal step-growth polymerisation characteristics are obeyed. However, there are some drawbacks for this method. The main drawbacks are, (i) gelation may occur which makes the purification of the desired products more difficult, and (ii) undesirable side reactions such as cross-linking can occur in the polymerisation process. The step-growth polycondensation route had been utilised extensively in the synthesis of a diverse range of hyperbranched systems as many functionalities are tolerated. An example for this method is the synthesis of hyperbranched polyphenylene by Kim and Webster50–52.

2.10.2 Self-condensing vinyl polymerisation of AB* monomers

This process involves the use of monomers that feature one vinyl group and one initiating moiety (AB* monomers) to generate hyperbranched polymers. The activated species can be a radical, cation or even a carbanion. In this process, living/controlled polymerization systems are preferred in order to avoid crosslinking reactions and gelation caused by dimerisation or chain transfer reactions. An example is the synthesis of hyperbranched polystyrene reported by Frechet et al53. The synthesis involved the use of the styrenic monomer 3-(1-chloroethyl)-ethenylbenzene which features both the polymerisable vinyl moiety of styrene and the latent initiating moiety of 1-chloroethylbenzene (under cationic conditions).
2.10.3 Multi-branching ring-opening polymerisation of latent $AB^\ddagger$ monomers

This technique was first reported by Suzuki et al. in 1992 and involved the reaction of latent $AB_2$ monomers that did not feature branching units. The branch points are generated by propagation during the reaction. The use of multi-branching ring-opening polymerization has been utilised in the formation of hyperbranched polyethers. The first publication utilising this methodology was outlined in 1999 by Frey and coworkers, using glycidol as the latent $AB_2$ monomer. The hyperbranched polyglycerols thus produced were obtained via an anionic ring-opening polymerisation approach.

In addition to these three main synthetic routes, there are some other methods towards the synthesis of hyperbranched polymers. One of these methods is the polycondensation of $A_2$ and $B_3$ monomers. The success of this approach is dependent upon many factors, including the ratio of functionalities, solvent and reagent purity and the reaction time and temperature. This type of polymerisation is difficult to control and hyperbranched polymers are often obtained with high molecular masses. The first notable example was reported by Kakimoto and coworkers in 1999 and involved the synthesis of a hyperbranched polyamide from the reaction of a diamine ($A_2$) and trimesic acid ($B_3$).

Another concept in building hyperbranched polymers is the 'graft onto' and 'graft from' approaches. Both of these approaches led to polymers with topologies similar to that of comb or star shaped polymer architectures. In both approaches the issue of control of the polymerisation process has proved to be paramount, but in the case of the $i\Sigma_1$ graft onto$i\Sigma_1$ approach, polymers possessing a high degree of branching are produced, although steric and dilution effects limit the size of the polymer. In the case of the $i\Sigma_1$ graft from$i\Sigma_1$ approach, high degrees of control over the polymer architecture were obtained.
2.11 Physical Properties of Hyperbranched Polymers

The physical properties of hyperbranched polymers are of key importance with respect to their implementation in industrial applications. One of the most interesting properties of hyperbranched polymers is their low viscosity characteristics in comparison to linear analogues. The viscosity of hyperbranched polymers, both in solution and in the molten state have been found to be considerably lower than their linear analogues\textsuperscript{59,60}.

In addition, interesting chemical and physical properties of hyperbranched polymers include the globular conformations of these macromolecules and the degree of branching. The degree of branching indicates the flexibility of the branching components contained within the architecture as well as the intrinsic viscosity of the polymer. The higher the degree of branching the lower the viscosity of the hyperbranched polymer, which in turn also has an effect on the relative solubility of the polymers in various media. Hyperbranched polymers have high chemical reactivity and enhanced solubility when compared to linear analogues. They also exhibit enhanced compatibility with other polymers. Finally their mechanical properties such as initial modulus, tensile strength and compressive moduli reflect the compact highly branched structures of these relatively new polymer architectures\textsuperscript{59,61}.

2.12 Applications of Hyperbranched Polymers

The novel physical properties of hyperbranched macromolecules render these polymers ideal candidates for use in a wide range of applications. The low viscosity and the presence of large number of functional groups makes them suitable for many applications. Hyperbranched polymers have been utilised in applications in various fields ranging from additives to coatings\textsuperscript{62} and in more advanced technologies such as sensors, high loading supports in combinatorial chemistry studies and homogeneous catalysts\textsuperscript{63}. A schematic diagram of the most common
applications in which hyperbranched polymers have been used is shown in figure 2.9.

The applications of these polymers can be split into two categories: those that are based upon bulk properties such as their enhanced solubility characteristics and to more specialist technologies that include ion conducting materials.

Hyperbranched polymers blended with linear polymers results in new polymeric materials with improved thermal stability, melt viscosity and modulus. Kim and Webster blended hyperbranched polyphenylenes with polystyrene. The addition of the hyperbranched polyphenylene to the polystyrene improved the thermal stability and melt viscosity of the polystyrene as a consequence of thermal chain transfer. Another effect that was observed was the change in the mechanical properties of the polystyrene on blending. The initial modulus was greatly improved which was attributed to the weak cross-linking of the polystyrene through aryl-arylene interactions. In contrast, poly (aryl ester) dendrimers have been blended with poly (ethylene terephthalate) (PET). Both dielectric assessment and tensile testing of the blends was carried out and the results obtained revealed that the incorporation of the dendrimers had a noticeable effect on the material processing characteristics.

Simon and co-workers have studied the rheological behaviour of polymer blends that contain only hyperbranched polyesters of differing generation number. It was observed that the low generation hyperbranched polymers exhibited shear-thinning behaviour, whilst the higher generations exhibited Newtonian characteristics. This study revealed a new phenomenon, as Newtonian behaviour was found to be the dominant flow characteristic among the blends.

The application of hyperbranched polymers as coating components is widespread. The functionality in combination with the high solubility and low viscosity are excellent prerequisites for use in high solid coatings or powder coatings.
The use of hyperbranched polymers as surface coatings has been studied, especially in the area of polymer films\textsuperscript{66–67}. For example, Mie\v{s}\l\l er formed ultra-thin films from arborecent graft polystyrenes, formed from grafting poly(styryllithium) onto partially methylated polystyrene. Films were cast onto mica using hyperbranched polystyrene solutions in toluene, following annealing above the glass transition temperature of polystyrene. The films generated were of uniform thickness and the densely packed globular molecules did not reveal coalescence upon aggregation. Scanning force microscopy (SFM) was used to determine the morphology of the surface, which revealed that the hyperbranched polymers exhibited hard-sphere characteristics, reminiscent of the polymers topology in solution. The thickness of the film was found to be dependent upon the molecular weight and branching density of the hyperbranched polymer used in the casting\textsuperscript{66}.

Frey and co-workers has utilised recently hyperbranched polyglycerols as
molecular nanocapsules in the transportation of dye molecules. Studies revealed that the hyperbranched topology had a crucial role in the encapsulation process. Comparison with the linear analogue indicates that molecular encapsulation was related to the hyperbranched topology and the core-shell amphiphilicity of these polymers.

Hult and co-workers have reported the use of aliphatic hyperbranched polyesters based upon bis-MPA as the AB₂ monomer and ethoxylated pentaerytritol as the core molecule as scaffolds for different thermoset coating resin systems. The hyperbranched polyesters were studied for applications as: (i) liquid resins, (ii) solid resins, (iii) UV-cured thin films and (iv) resin additives. The results obtained revealed that these polyesters exhibited low melt viscosities as a consequence of the high molecular weights of the polymers and the highly functionalised core structures of the polymers. This report exemplified the advantageous use of hyperbranched resins as thermoset coating resins, as there is the reduced requirement for solvents and the low melt viscosities of the highly branched architectures.

Hawker and coworkers have studied the use of hyperbranched polymers as a new class of ion conducting materials. Globular, hyperbranched molecules, which are degradable, can act as pore forming material for a nanoporous system. For this, dispersion of the hyperbranched polymer in a stable matrix is required. Nanoporous material is of interest in chromatography and for the formation of aerogels and xerogels. Boury et al. described the use of dendrimers and arboroles with carboxilane cores for the preparation of hybrid xerogels. Muzaifarov et al. studied the degradation behavior of hyperbranched poly[bis(undecenyloxy) methylsilane]. The preparation of nanoporous polymers as low dielectric constant material for use as novel interlayer dielectric material (ILD) is also of high interest. Hyperbranched polymers have also been studied as nanoporosity templating agents in organosilicates. Hyperbranched poly(aryl
ether phenyl(quinoxaline)s\textsuperscript{74} were used for structure control in organic-inorganic hybrids for application in microelectronics. Also the use of hyperbranched polymers were reported in sensorics\textsuperscript{75−78}, as nonlinear optic\textsuperscript{79} and liquid crystal material\textsuperscript{80−82}, in molecular imprinting\textsuperscript{83}, in catalysis\textsuperscript{84}, and also as soluble functional supports\textsuperscript{85−86}. These examples demonstrate the very broad perspectives of hyperbranched polymers in all areas of modern polymer science.

2.13 Hyperbranched Polyglycerol

Hyperbranched polyglycerol represents the first hyperbranched polymer that can be prepared in a controlled manner. Hyperbranched polyglycerols possess an inert polyether scaffold. Each branch ends in a hydroxyl function and it is this densely populated peripheral hydroxyls that renders hyperbranched polyglycerols a highly functional material.

2.13.1 Synthesis and properties of hyperbranched polyglycerol

Glycidol, a commercially available and highly reactive hydroxy-epoxide, represents a latent AB\textsubscript{2} monomer that can be polymerized to hyperbranched polyethers with numerous hydroxyl end groups. Hyperbranched polyglycerols were synthesized by ring-opening multibranching polymerization of glycidol. The first attempt to polymerize glycidol was undertaken by Sandler and Berg\textsuperscript{87}. After that several groups tried to polymerize glycidol in presence of various catalysts\textsuperscript{88−91}. Uncontrolled ring opening polymerization and partial characterization of the branched polymers formed have been reported by Vandenberge et al. as well as by Penczek and Dworak. The elegant work by Penczek and Dworak polymerized glycidol cationically to branched polymers\textsuperscript{92−94}.

Frey et al established a synthesis for hyperbranched polyether polyols with controlled molecular weight and narrow polydispersities. The strategy is based on the ring-opening multibranching polymerization of glycidol using slow monomer-addition conditions\textsuperscript{95−97}. 

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Scheme 2.2. Synthesis of hyperbranched polyglycerol

The resulting polyglycerols possess molecular weights between 1000 and 30000 g/mol with polydispersities Mw/Mn typically below 1.5. In contrast to perfect dendrimers, these hyperbranched polyglycerols exhibit a lower degree of branching (DB) in the range 55-60% (Figure 2.10).

Hyperbranched polyglycerols is a clear viscous liquid. The glass transition temperature is considerably below room temperature, typically between -20°C and -26°C. At room temperature the polymer is highly viscous, and the viscosity increases with molecular weight. Hyperbranched polyglycerols is highly soluble in water and also in polar organic solvents, such as methanol. By comparison to linear non-branched polymers, solution viscosity is considerably lower. By simple heating to slightly elevated temperatures (80°C) it behaves like a free flowing liquid. Polyglycerols are essentially non-volatile at room temperature.

Hyperbranched polyglycerol possesses an inert polyether scaffold. Each branch ends in a hydroxy-function, which renders hyperbranched polyglycerol a
Figure 2.10: Schematic structures of (A) a perfect glycerol dendrimer \([G_1]\) possessing only dendritic and terminal groups and (B) a hyperbranched polyglycerol with about 40% linear groups incorporated. Circles represent generations (A) and pseudogenerations (B), respectively; the innermost circle encloses the focal unit (initiator).

A highly functional material, e.g., a molecule with a molecular weight of 5000 g/mol possesses 68 hydroxyl end groups. The high functionality in combination with the versatile and well-investigated reactivity of hydroxyl-functions is the basis for a variety of derivatives. Partial esterification with fatty acids yields amphiphilic materials, which behave as nanocapsules. Such nanocapsules can, for example, incorporate polar molecules as guests and solubilize them in an apolar environment. Selective modification can be achieved utilizing the reactivity of 1, 2-diol units, located preferentially at the periphery of the molecule. Complementary to functionalization by reactions of the large number of hydroxy-groups, a single functionality can also be introduced selectively as the ‘core’ of the molecule. A number of single core functionalities, such as a vinylic group, amines and thiols, have been incorporated.
Biocompatibility is one particularly advantageous feature of aliphatic polyether structures, such as polyglycerol. Thus, an essential prerequisite for applications as a delivery agent for biologically active compounds, cosmetics etc. are provided. In containing hydroxy-endgroups and a polyether-backbone, the hyperbranched polyglycerols resemble the well-known linear polyethylene glycols (PEG, PEO), which are approved for a large variety of medical, and biomedical applications.

2.13.2 Applications of hyperbranched polyglycerols

Hyperbranched polyglycerols, which possess low intrinsic viscosity and a very large number of derivatizable hydroxyl groups, find applications in nanotechnology and in nanobiotechnology. Because of the low viscosity and the high functionality, these polymers could find applications as cross-linkers and additives. The rheological properties of these polymers are also reported and analyzed. They could also find use as components in adhesives, advanced coatings, hydrogels and composites. Other applications can be envisaged in catalysis, drug delivery and nanotechnology.

Due to its excellent biocompatibility hyperbranched polyglycerols find numerous biological applications. Preliminary cell culture experiments have shown that hyperbranched polyglycerols are non-toxic. In addition, oligoglycerols, which possess 2-10 monomer units, have been studied in detail with respect to their biological properties and are approved as food and pharma additive by the FDA. Well defined biodegradable or biocompatible star polymers can be prepared, using polyglycerols or propoxylated polyglycerols as multifunctional initiator core. Such materials are promising with respect to slow or controlled drug release. Another application of hyperbranched polyglycerols is in hydrogels. Partial functionalisation of hyperbranched polyglycerols with methacrylate end groups and radical copolymerization with linear telechelics in aqueous media leads to struc-
tured hydrogels. These materials show excellent form stability and also possess a large number of hydroxyl groups that can be further modified. These hydrogels are excellent substrates for cell growth.

Simple esterification of hyperbranched polyglycerols with fatty acids offers potential for the preparation of amphiphilic core-shell structures. Unusual phase behaviour was observed for polyglycerols partially substituted with long fatty acids. The materials obtained are highly amphiphilic species with a hydrophobic shell and a hydrophilic interior due to remaining, unreacted hydroxyl groups\textsuperscript{103}. Such molecular nanocapsules do not exhibit aggregation in dilute solutions and can be considered as inverse unimolecular micelles. They possess the ability to irreversibly transfer a well defined number of water soluble guest molecules from an aqueous into apolar environment. The guests can be liberated by hydrolysis of the ester bond\textsuperscript{104}.

2.14 Photochemically Modified Dendritic Polymers

Large, well-defined multichromophoric arrays are receiving much attention due to the control they offer over the energy and electron transfer processes in restricted space. Formation of these arrays can be accomplished by either covalent coupling of chromophore building blocks into a single molecule or by the self assembly of interacting monochromophoric species where they are held together by relatively weak non-covalent interactions like hydrogen bonds, van der Waals interactions, electrostatic interactions, metal ion co-ordination and donor-acceptor interactions or $\pi$-stacking. Despite the progress that has been made in the synthesis of complex molecules, formation of multichromophoric arrays in single molecule of high symmetry is a challenge on its own. the photochemical processes in multichromophoric systems depend on several factors like interchromophoric distance, orientation, and nature of the bridge. dendritic polymers are excellent candidates for providing chromophore rich environments. In these mul-
tichromophoric systems the relative position and orientation of the chromophores can be fixed in space.

Dendrimer synthesis indeed allows changing the number, relative position and orientation of attached chromophores in a controlled way. Dendritic structures offer a unique opportunity to vary the physical and electronic properties independently. The ability to independently vary the physical and electronic properties arises from the fact that in higher dendrimer generations it is only the surface groups which are in contact with the environment. Many different forms of light-sensitive building blocks have been used in dendrimer construction, yielding macromolecules with interesting and diverse photophysical properties. In fact, traits of natural light harvesting antenna systems themselves have been identified and studied. A number of fascinating dendritic derivatives have been synthesized and studied by the groups of Mullen and De Schryver. Dendrimeric systems having many aromatic molecules, such as polyphenylbenzenes and perylene-3,4-dicarboximides, have been used to elucidate the details of energy transport within complex covalent structures as well as the photophysics of single molecules having multiple chromophores. The encapsulation of lanthanide ions (Ln³⁺) by dendritic ligands is a possible application for optical signal amplification. The impetus for this application originated from the self-quenching of fluorescence by lanthanide ions, such as erbium, when they are clustered together in the solid state. This self-quenching limits their effectiveness as signal amplifiers for optical fibre communications, since the poor solubility of Ln³⁺ ions in substrates such as silica leads to the formation of ion clusters.

Encapsulation of individual Er³⁺ and Tb³⁺ ions within a dendritic shell was expected to lead to their site isolation, thereby increasing interchromophoric distance and decreasing the self-quenching effect. Indeed, this site isolation was realized by self-assembly of suitably functionalized carboxylate-cored dendrons around the lanthanide ion, and the resulting assemblies possessed all the characteristics desired for use in signal amplification. During the course of photophysical studies on these ionically bound supramolecular assemblies, it was found
that irradiation at wavelengths where the dendrimer backbone absorbed (280 - 290 nm) resulted in strong luminescence from the lanthanide core. Apparently, energy absorbed by the peripheral dendrimer shell was efficiently transferred to the luminescent Ln\(^{3+}\) at the focal point by a mechanism postulated to be of the Förster type. At these wavelengths, energy transfer to Tb\(^{3+}\) was found to be more efficient than in the case of Er\(^{3+}\), likely due to the better overlap of dendrimer emission with Tb\(^{3+}\) absorption. This channeling of excitation energy from a dendrimer shell to a single core unit was termed the “antenna effect”. Interestingly, it was also found that this energy transfer phenomenon was critically dependent on the substitution pattern within the dendritic shell. The findings made with the dendrimer antennas can be extended to the design of single-layer multichromophoric light-emitting diodes. The dendritic framework provides for both the energy transfer interaction and the site-isolation of different chromophores, enabling them to fluoresce simultaneously.

2.15 Nanomaterials in Chemistry and Biology

Miniaturization is a general aim of the technology development that is taking place to produce smaller, faster, lighter and cheaper devices with greater functionality while using less raw materials and consuming less energy. Nanotechnology is a step toward the miniaturization of technology that will contribute significantly towards a sustainable usage of raw material and energy and creating novel materials that can be used for the construction of devices and systems.\(^\text{105}\)

The first introduction of the idea of nanomaterials took place in 1960, when Nobel Prize-winning physicist Richard Feynman pointed out in one of his articles entitled “There is Plenty of Room at the Bottom”. He pointed out that if a bit of information required only 100 atoms, then all the books ever written could be stored in a cube with sides 0.02 inch long.\(^\text{106}\) However the term nanoparticle came into frequent use only in the early 1990s by material science community to represent particles that are composed of up to tens of thousand of atoms but
confined to size less than 100nm.

The properties of nanomaterials are quite different and superior to those in the bulk state. Due to their smaller size and large surface to volume ratio, nanoparticles exhibit interesting novel properties including nonlinear optical behaviour, increased mechanical strength, enhanced diffusivity, high specific heat, magnetic behaviour and electric resistivity etc\textsuperscript{107}. Metal nanoparticles find a wide range of applications in the fields of biotechnology\textsuperscript{108}, sensors\textsuperscript{109}, medical diagnostics\textsuperscript{110}, catalysis\textsuperscript{111}, high performance engineering materials, magnetic recording media, optics and conducting adhesives\textsuperscript{112–114}.

Figure 2.11: Schematic representation of various applications of nanotechnology

### 2.16 Properties of Nanoparticles

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic and molecular structures. The principal parameters of nanoparticles are their size, shape and morphological substructures.
Bulk materials have constant physical properties but at the nanoscale the properties are largely size dependent. The important characteristics of nanoparticles are briefly discussed below.

### 2.16.1 Increased ratio of surface to volume

The first, very important, property of nanoparticles is the large surface-to-volume ratio which makes them distinct from larger particles. If, for example, one takes a 1 cm cube of metal and breaks it up into small cubes of 10 nm edge length, the overall surface area will increase $10^6$ times, although the amount of matter remains the same. In general, powders of nanoparticles have a specific surface area of $10^2 - 10^3 \, \text{m}^2/\text{g}$. From a purely geometrical consideration, in crystalline particles smaller than 10 nm size, the amount of atoms at the surface becomes relevant as it is comparable to that of atoms in the interior of the particle. This feature of nanoparticles is very useful for many applications. This is the case in catalysis, membranes, filters, electric capacitors, where the efficiency of a particular reaction is proportional to the area of the available surface. A large available surface of nanoparticles can be very useful in the field of gas storage. With more surface available, more amount of gas can be adsorbed and released without increase in the weight of the storing medium. In future, nanoparticles may have application in the hydrogen engine for those vehicles where weight saving is a necessity. Pt nanoparticles are now being investigated as promising candidates in hydrogen storage as they have a great permeability to hydrogen.

### 2.16.2 Electronic properties

In a crystalline solid, valence electrons occupy continuous energy bands and the width and separation of these bands determines most of the fundamental electrical, optical and magnetic properties of the solid. For individual atoms and molecules, the electronic density of state is discrete, resulting in intrinsically sharp spectral line widths. The electronic structure of a nanocluster or a nanocrystal
might fall somewhere between these two extremes. The electronic configurations in tiny particles (below 10 - 20 nm) are similar to those of the particle-in-a-box, exhibiting discrete electronic densities typical of single atoms. The increasing presence of the surface tends to perturb the periodicity of the infinite lattice of a regular crystal. In the case of metals, the electrical properties are determined by the electron mean free path, which typically ranges from 5 to 50 nm for most metals. If the crystal becomes comparable in size, the electrons are then also scattered at the surface, which apparently increases the resistivity of the nano-particles. One of the most important consequences of the size confinement is therefore the extremely small capacitance of isolated nanoclusters and crystals. This can give rise to an appreciable charging energy when a single electron is transferred to the cluster. The very small capacitance strongly affects its electronic structure, giving rise to single-electron charging effects. For these reasons metallic nanoparticles and nanowires are promising unit elements in building nanoscopic circuits with tunneling junctions involving jumps of single electrons.

2.16.3 Optical properties

Metal nanoparticles are optically active in the visible range of the spectrum. A colloidal solution of noble-metal nanoclusters has an intense color. When the crystal size becomes smaller than the wavelength of the visible light, nanoparticles partially transmit the light, which results in changes of the color of the dispersion. The reason for this modification is the presence of a strong optical absorption in the visible region, arising from the surface plasmon excitation in response to the external electromagnetic field. As nanocluster size decreases, there is a dramatic increase in the surface plasmon resonance bandwidth, accompanied by a shift in the resonance position (generally a red-shift). As an example, gold particles of 30-500 nm in size, appear blue to red in color from larger to smaller size. For the smaller Au nanoparticles, there is broad surface plasmon absorption between the green and yellow wavelengths, allowing only red light to be transmitted. This is one reason for the typical red color of stained glasses.
containing a dispersion of gold nanoparticles\textsuperscript{120}.

2.16.4 Magnetic properties

The magnetic properties of nanoparticles\textsuperscript{121} are different from those of bulk materials for sizes in the range of a few interatomic distances to about one micrometer. The magnetic properties of, e.g., 3d-metal clusters (like Fe and Co) differ significantly from the bulk\textsuperscript{122} and depend strongly on the particle size, the material they are embedded in, and their coverage. Early experiments at the beginning of the 1990s on small magnetic clusters in the gas phase\textsuperscript{123−126} have shown that the total magnetic moment depends on the size of the cluster, in particular it is a function of the number of atoms. Both orbital and spin moments on the surface of tiny magnetic nanoparticles are strongly enhanced. The spin moment then decreases to the bulk value as the size of the particle exceeds a few nanometer\textsuperscript{127}. This is a consequence of the fact that a high number of atoms with lower coordination number sit on the surface and therefore exhibit uncompensated distributions of magnetic moments (spins). This effect is very strong only for tiny clusters of less than 1000 atoms, but in some case it is still present for larger particles\textsuperscript{122}. Interesting applications of small magnetic particles are, e.g., in stable colloidal suspensions known as ferrofluids. The materials used are Fe\textsubscript{3}O\textsubscript{4}, BaFe\textsubscript{12}O\textsubscript{19}, Fe, Co and Ni, having a typical particle size of 10 nm. Ferrofluids are used as liquids in bearings and to monitor magnetic fields and domain configurations. Other systems, e.g., an array of Fe Pt particles on a substrate, are interesting candidates for high-density magnetic storage media\textsuperscript{128}.

2.16.5 Catalytic properties

Another property which is finding interesting applications for gaseous reactions in the chemical industry is catalysis. In a catalytic activity, a material is able to speed up a particular chemical reaction without changing itself and its properties. As the particle size is reduced, more atoms are on the surface and this makes small nanoparticles, specially metallic ones, highly reactive catalysts, as the surface atoms are the active centers for catalytic elementary processes\textsuperscript{116,129}.  

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Many of the industrial uses are aimed to reduce pollutants from domestic environment and car exhaust. As an example, gold nanoparticle catalysts have potential for this purpose because of their high performance in low-temperature combustion. It has been found that gold nanoparticles supported on a silicate catalyze the production of propylene oxide with a high selectivity of more than 90%. Since the only by-product of this reaction is water, application of gold nanoparticle catalysts is expected to be a clean process for partial oxidations. The selective oxidation processes that are used to make compounds contained in agrochemicals, pharmaceuticals and other chemical products can be accomplished more cleanly and more efficiently with nanoparticle catalysts.\textsuperscript{130}

### 2.17 Different Types of Nanoparticles

Nanoparticles can be separated into several different classes. The different classes of nanoparticles along with their basic properties and applications are discussed here.

#### 2.17.1 Fullerenes: Bucky balls and carbon tubes

Both members of the fullerene structural class, bucky balls and carbon tubes are carbon based lattice-like, potentially porous molecules. Bucky balls are spherical in shape while carbon tubes are cylindrical. Entrapment of metal atoms in the cavities of buckyballs changes its magnetic properties and they find applications in superconductivity.\textsuperscript{131–132} The functional modifications increase their biological and pharmacological activity and can be utilized in artificial photosynthesis and in photovoltaic devices.\textsuperscript{133–134} The buckyballs are powerful antioxidants and they react with free radicals that cause cell damage.\textsuperscript{135}

The diameter of a carbon tube can be several nm but the length can be much greater, up to several mm, depending on its intended use. Carbon tubes have many applications in materials science due to their strength and unique electrical properties. They have also found use in the field of biomedicine as carriers for vaccines, drugs and other molecules. A single wall carbon tube is a
one-atom-thick sheet of graphite, resembling chicken wire, rolled seamlessly into a tube. There are also multi-walled and other types of tubes depending on the shape, diameter, density (hollow versus solid) and other properties\textsuperscript{132}.

### 2.17.2 Liposomes

Liposomes are lipid-based nanoparticles used extensively in the pharmaceutical and cosmetic industries because of their capacity for breaking down inside cells, once their delivery function has been met. Liposomes were the first engineered nanoparticles used for drug delivery but problems such as their propensity to fuse together in aqueous environments and release their payload, have lead to replacement, or stabilization using newer alternative nanoparticles\textsuperscript{136}.

### 2.17.3 Quantum dots

Quantum dots are spherical nano-sized crystals. They can be made of nearly every semiconductor metal (e.g., CdS, CdSe, CdTe, ZnS, PbS), but alloys and other metals (e.g. Au) can also be used\textsuperscript{137}. The prototypical quantum dot is cad-

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*Figure 2.12: Schematic representation of a bucky ball*
mum selenide (CdSe). Quantum dots range between 2 and 10 nm in diameter (10 to 50 atoms). Generally, quantum dots consist of a semiconductor core, overcoated by a shell (e.g., ZnS) to improve optical properties, and a cap enabling improved solubility in aqueous buffers\(^\text{138}\).

Quantum dots take advantage of the quantum confinement effect, giving these nanoparticles unique optical and electronic properties. Fluorescence semiconductor quantum dots offer advantages in that they have a tunable absorption spectrum, which is very broad, extending from the ultraviolet to a cut-off wavelength in the visible spectrum. Emission is confined to a narrow band and can also be tuned. Absorption and emission characteristics are dictated by size for binary quantum dots or by composition/internal structure independently of size for alloyed semiconductor quantum dots, such as CdSeTe\(^\text{138}\). When illuminated, smaller binary quantum dots emit shorter wavelength, such as blue, whereas larger dots emit longer wavelength, such as red. Moreover, quantum dots have

\textbf{Figure 2.13}: Three dimensional view of a carbon nanotube
Quantum dots sorted by size, emitting different colours

brighter emission and good photostability.

Biomedical monitoring applications have taken considerable advantage of using quantum dots for sensitive optical imaging in fixed cells and tissues, living cells and animal models. Electronic applications of quantum dots are envisaged in future highspeed electronic and photonic devices. Quantum dots provide a promising way forward for a new generation of lasers\textsuperscript{139}, infrared photodetectors\textsuperscript{140}, photovoltaic devices\textsuperscript{141}, and optical data storage media\textsuperscript{142}.

2.17.4 Nanoshells

Also referred to as core-shells, nanoshells are spherical cores of a particular compound surrounded by a shell or outer coating of another, which is a few nanometers thick.

One application of nanoshells in biomedicine is to create nanoshells that absorb at biologically useful wavelengths, depending on the shell thickness. One common formula for the construction of nanoshells is to use silica for the core
and another sticky compound to adhere gold particles to the outside surface, creating the shell. Nanoshells such as these have been used to kill cancer cells in mice. Once injected into a tumor, radiation is applied and the nanoshells heat up enough to kill the tumor cells.$^{143-144}$

2.18 Applications of Nanoparticles

Metal nanoparticles have found more applications in many areas, including biomedical, materials science, and catalysis. This is because of their unique properties when compared with their bulk solid.

2.18.1 Biomedical applications

Gold and silver nanocages are used in the early detection of human cancer. For this nanocubes of 20-30nm size are prepared and are converted into hollow nanocages. these nanocages exhibit SPR bands in the near infrared region and this can be employed in optical coherence tomography (OCT). OCT is an efficient
technique to non invasively obtain image with biological features on the micrometer scale, which makes gold or silver promising candidates for the early detection of cancer. To detect cancer at an early and treatable stage using OCT, difference in optical properties between the tumor and surrounding healthy tissues must be enhanced. Gold nanocages can be employed as a contrast agent. Wiley et al. reported that they could functionalize gold nanocages with tumor-specific antibodies through thiol-based conjugation. Moreover, these antibodies enabled Au nanocages can specifically attach to tumor cells, making the contrast between tumor cells and the healthy tissue greater during OCT imaging. Notably, the relatively small size of the nanocages will enhance their biocompatibility and mobility within biological tissues.

2.18.2 Sensing applications

Gold and silver nanoparticles can be used in sensing applications. The sensitive response of surface plasmon resonance (SPR) peaks to environmental changes can be exploited to optically detect and monitor binding events on the gold or silver surface. The changes in the local environment of the nanoparticle usually leads to a shift in their SPR band positions. For example, if the refractive index of the surroundings is increased the SPR band will shift to shorter wavelengths. The applicability of this is to detect DNA and single-base mismatches in DNA hybridization, as well as to probe the protein occurrence for immunoassays.

2.18.3 Catalysis

Chemical catalysis benefits especially from nanoparticles, due to the extremely large surface to volume ratio. The application potential of nanoparticles in catalysis ranges from fuel cell to catalytic converters and photo catalytic devices. Catalysis is also important for the production of chemicals. Platinum nanoparticles are now being considered in the next generation of automotive catalytic converters because the very high surface area of nanoparticles could reduce the amount of platinum required. However, some concerns have raised due to experiments demonstrating that they will spontaneously combust if methane is mixed with the
ambient air\textsuperscript{129,130}.

### 2.19 Techniques for Characterizing Nanoparticles

The characterization of materials at the nanometer scale is central to nanoscience and technology. The observation of materials in the nanoscale can be done using electrons, photons, scanning probes, ions, atoms etc. A wide range of techniques is available in these areas and a systematic application of several tools leads to a complete understanding of the system. In electron microscopes, the wave nature of electron is used to obtain an image. There are two important forms of electron microscopy, namely scanning electron microscopy and transmission electron microscopy.

#### 2.19.1 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) is capable of producing high resolution images of sample surface. In SEM, electrons are thermo-ionically emitted from a tungsten or lanthanum hexa-boride (LaB$_6$) cathode filament towards an anode. LaB$_6$ has greater brightness and a longer life time as compared to tungsten. Field emission (FE) is another way of making electrons.

The electron beam which typically has an energy range from a few keV to 50 keV, is focused by two successive condenser lenses into a beam of very fine spot size. The beam then passes through the objective lens, where pairs of scanning coils deflect the beam either linearly or in raster fashion over a rectangular area of the sample surface. As the primary electrons strike the surface, they are inelastically scattered by the atoms in the sample. Through these scattering events, the primary beam effectively spreads and fills a tear-drop-shaped volume extending about 1 micrometer to 5 micrometer into the surface. Interactions in this region lead to the subsequent emission of electrons which are then detected to produce an image.

The spatial resolution of the SEM depends on the size of the electrons spot which in turn depends on the magnetic electron- optical system which pro-
duces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent of material which interacts with the electron beam. The spot size and interaction volume are both very large compared to the distances between atoms, so the resolution of the SEM is not high enough to image down to the atomic scale. The advantages of SEM include the ability to image materials and the variety of analytical modes available for measuring the composition and nature of the specimen.

2.19.2 Transmission electron microscopy (TEM)

A transmission electron microscope probes the internal structure of solids to give an access to the morphological fine structural details. In TEM, the transmitted electrons are used to create an image of the sample. Electron beam instruments are operated under high level of vacuum to avoid scattering of electrons from the air molecules and arcing due to high voltage. A TEM is operated under vacuum in the order of 10-7 torr, equipped with an electron gun capable of accelerating electrons through a potential difference in the range of 60 to 300kV. A thin sample fixed on the grid is illuminated by an electron beam to perform analysis in the TEM. Electron beam is partially transmitted through the sample, while part of it is scattered either elastically or inelastically. The elastically scattered electrons have undergone diffractions from the atomic planes of crystal whereas inelastic electrons arise from the phonon, plasmon or X-ray excitation. These electrons contribute towards formation of a diffuse halo around the transmitted beam, the diffracted beam and to the general background intensity between the diffraction spots. Most of the intensity at the exit surface of the crystal is in the transmitted and diffracted beam. In the bright field imaging mode, electrons transmitted through the sample are used to form image while intensity of scattered electron is filtered out.

2.19.3 X-ray diffraction

Radiations striking a material may scattered or absorbed. X-rays, high energy electrons and neutrons are used to extract structural information of the crystal...
lattice. Incident radiations of sufficiently smaller wavelength interact elastically with the regular arrays of atoms in a crystal lattice to yield a diffraction pattern. Both diffraction angles and the intensities in various diffracted beams are a sensitive function of the crystalline structure. The diffracted angles depends upon the Bravais point lattice and the unit cell dimensions, while the diffracted intensities depend on the atomic numbers of the constituent atoms and their geometrical relationship with respect to the lattice points.

The condition for a crystalline material to yield a discrete diffraction pattern is that the wavelength of the incident radiation should be comparable to or less than the interatomic spacing in the lattice. A convenient form of the geometrical relationship determining the angular distribution of the peak intensities in the diffraction pattern from a regular crystal lattice is the Bragg's equation

\[ n\lambda = 2dsin\theta \]

where "n" is an integer referring to the order of reflection, "\( \lambda \)" is the wavelength of the radiation, "\( d \)" is the spacing between the crystal lattice planes responsible for a particular diffracted beam, and "\( \theta \)" is the angle that incident beam makes with lattice planes. The path difference between the incident beam and the beams reflected from two consecutive crystal planes is shown in figure 2.16. Full width at half maximum of XRD pattern was used along with the Scherrer’s equation to estimate mean particle size. This equation is given by

\[ d = \frac{0.9\lambda}{\beta cos\theta} \]

where, "\( d \)" is the mean diameter of the nanoparticle, "\( \lambda \)" is wavelength of X-ray radiation source, "\( \beta \)" is the angular full width at half maximum of the X-ray diffraction peak at the diffraction angle "\( \theta \)".149
2.19.4 UV visible spectroscopy

When a beam of electromagnetic radiation strikes an object it can be absorbed, transmitted scattered, reflected or it can excite fluorescence. The processes concerned in the absorption spectroscopy are absorption and transmission. The conditions under which sample is examined for absorption are chosen to keep reflection, scatter and fluorescence to a minimum. An optical spectrometer records the wavelength at which absorption occurs together with the degree of absorption at each wavelength. UV-visible spectroscopy is used for quantitative analysis of the samples. The absorption of sample follows the Beer-Lambert law, which states that the concentration of a substance in a sample is directly proportional to the absorbance. UV-visible analysis could be performed on metal nanoparticles dispersed in a solvent or embedded in the insulator matrix. The absorption of the incident radiations takes place due to surface plasmon resonance of the metal nanoparticles. Surface plasmons are essentially the light waves that are trapped on the surface because of their interaction with the free electrons of
the metal. The surface plasmon resonance bands depend upon the nature of the metal, size of the particles and shape of the particles.

Of the several methods available, characterization techniques such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and UV visible spectroscopy are used in the experimental work reported here.

## 2.20 Silver Nanoparticles

Many nano forms of matter exist around us. A most prominent nanoproduct is nanosilver. Due to its unique optical and antimicrobial properties silver nanoparticles are emerging as one of the fastest growing product categories in the nanotechnology industry. The extraordinary optical properties of silver nanoparticles were used by glass founders as early as in the times of the Roman Empire. Gold and silver nanoparticles have been incorporated in glasses and vases to impart colour to them. The oldest of these is the so called Lycurgus cup made by the Romans in the fourth century AD. The main feature of this cup was its ability to change its colour from red in transmitted light to grayish green in reflected light. A detailed investigation of its composition revealed the presence of metal nanoparticles that consisted of silver (70%) and gold (30%) alloy\(^3\). Another example is the use of lemon-yellow glass in European cathedrals.

Silver nanoparticles exhibit a rare combination of valuable properties namely, unique optical properties associated with the surface plasmon resonance, well developed surfaces, catalytic activity, high electrical double layer capacitance etc. These properties make nanosilver an efficient material in the development of new generation electronic, optical and sensor devices\(^3\). Though silver nanoparticles have excellent optical properties and display a unique ability for amplifying signals in fluorescence and Raman spectroscopies, the fast oxidation and easy aggregation in solution complicates their use in sensors and optical instruments\(^4\).
2.21 Synthesis of Silver Nanoparticles

Several physical, chemical and biological methods have been developed for the synthesis of silver nanoparticles with better control over the particle size distribution and morphologies. The major conventional and novel syntheses of silver nanoparticles, their advantages and drawbacks briefly discussed below.

2.22 Conventional Syntheses of Silver Nanoparticles

2.22.1 Citrate synthesis (The Turkevich method)

The most popular method for the synthesis of silver nanoparticles is the citrate reduction method developed by Turkevich et al. Here a solution of the metal salt is boiled with a higher concentration of sodium citrate for a few minutes. This results in the formation of nanoparticles. The synthesized silver nanoparticles were spherical and had diameter in the range 60-200nm. A distinguishing feature of this method is that citrate ions simultaneously act as a reducing agent and a stabilizer.\(^\text{155}\).

2.22.2 Borohydride method

It is the most widely used method for the synthesis of silver nanoparticles in both homogeneous and heterogeneous systems.\(^\text{156}\). This involves the reduction of silver salts with excess sodium borohydride. Sodium borohydride is chosen as a reducing agent due to its high reactivity, easy handiness and low toxicity. The elegant work by Creighton et al. for the synthesis of silver nanoparticles involves the reduction of silver nitrate solution cooled to 0°C with a six fold excess of sodium borohydride solution on active stirring.\(^\text{157}\). The synthesis of polyvinylalcohol stabilized silver nanoparticles reported by Lee et al also involves the reduction of silver nitrate solution with 1.2 fold excess of sodium borohydride in the presence of PVA.\(^\text{158}\).
2.22.3 Organic reducing agents

Another method for the production of silver nanoparticles is the Tollens reaction. Here the silver ammonium salt is reduced using an aldehyde or a carbohydrate. Carbohydrates such as glucose, fructose, lactose, maltose and galactose can be used for the reduction. The diameter of the nanoparticles is found to depend on the temperature, ammonia concentration and pH of the medium during reduction. The particle size was found to be increased with the increase in temperature. At a temperature of 27°C the average diameter was ~ 20nm. At 30°C and 35°C, it was found that the average particle size is ~ 30nm and ~ 40nm respectively.

The diameter was also found to increase with increase in ammonia concentration. When the ammonia concentration was changed from 0.005 to 0.2mol litre$^{-1}$, the average nanoparticle diameter increased from 25 to 260 nm. The reaction occurs generally at sufficiently high solution pH. Strongly basic organic bases results in the formation of coarse particles. Weak bases lead to fine particles$^{159–161}$. It was reported that reduction of silver ammonium salts using Aloe vera leaves and Geranium leaves too leads to spherical particles$^{162,163}$.

2.23 Unconventional Syntheses of Silver Nanoparticles

Most of the conventional methods for the synthesis of silver nanoparticles have the drawback that they use large number of chemicals as surfactants and stabilizers in the course of the reaction which in turn leads to the contamination of the surface of the formed nanoparticles. The majority of applications of silver nanoparticles are in microelectronics, medicines, spectroscopy and catalysis. The presence of even trace amount of impurities is thus harmful and prevents their further usage. Some novel synthetic methods for the synthesis of chemically pure silver nanoparticles are described below.
2.23.1 Laser ablation method

In this method, the synthesis of silver nanoparticles is carried out by laser ablation of either bulk silver samples in liquid media or microparticles in aerosols. The number of nanoparticles formed was proportional to the radiation power and the average size of the nanoparticle is found to be increased with increase in laser power and decrease in the surfactant concentration\textsuperscript{164}.

2.23.2 Radiolytic method

Radiolytic method is a very promising method for the synthesis of silver nanoparticles. This method is based on the impact of electrons and high energy $\gamma$ - radiation on the sample. The advantage of this method is two fold. The most important benefit is that by regulating the radiation intensity, its rate and exposure time, we get absolute control over the size of the particles. Moreover, this method eliminates the use of conventional reducing agents and stabilizers and hence the contamination in the final product is prevented\textsuperscript{165}.

2.24 Optical Properties of Silver Nanoparticles

A characteristic feature of metal nanoparticles is their strong and specific interaction with electromagnetic radiation. Highly dispersed metal nanoparticles are intensely coloured and the colour depends on the metal and size of the nanoparticles. Gold nanoparticles are responsible for the brilliant red colour seen in stained glass windows and silver nanoparticles are usually yellow in colour.

A distinguishing feature of metal nanoparticles with particle size above 2nm is the presence of an intense absorption band in the visible range or in the adjacent near IR and UV ranges. This band is called the surface plasmon resonance (SPR) band. The SPR band arises from the interaction of incident radiation with the conduction electrons of the metal.

Of all metals, silver has the highest SPR band intensity. The SPR band is found to be red shifted with increase in particle size. The band broadening was also observed with increase in the diameter of the silver nanoparticles. The
absorption peak in the spectrum of silver nanoparticle also depends on the shape of the particles. The absorption peak was usually shifted to longer wavelengths for non-spherical particles. The wider the deviation in the particle shape from spherical the greater the absorption shift. They also contain several SPR bands. It is due to the non-equivalent particle orientation with respect to the incident light wave\textsuperscript{166}.

### 2.25 Antimicrobial Properties of Silver Nanoparticles

The study of bactericidal nanomaterials is particularly considering the recent increase of new resistant strains of bacteria to the most potent antibiotics. This has promoted research in the well-known activity of silver ions and silver-based compounds, including silver nanoparticles. The development of new resistant strains of bacteria to current antibiotics\textsuperscript{167} has become a serious problem in public health; therefore, there is a strong incentive to develop new bactericides\textsuperscript{168}. This makes current research in bactericidal nanomaterials particularly timely. Bacteria have different membrane structures which allow a general classification of them as Gram negative or Gram positive. The structural differences lie in the organisation of a key component of the membrane, peptidoglycan. Gram negative bacteria exhibit only a thin peptidoglycan layer (~2-3 nm) between the cytoplasmic mem-

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**Figure 2.17:** Plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.
brane and the outer membrane; in contrast, Gram-positive bacteria lack the outer membrane but have a peptidoglycan layer of about 30 nm thick.

Silver has long been known to exhibit a strong toxicity to a wide range of micro-organisms; for this reason silver-based compounds have been used extensively in many bactericidal applications. The bactericidal effect of silver ions on microorganisms is very well known; however, the bactericidal mechanism is only partially understood. It has been proposed that ionic silver strongly interacts with thiol groups of vital enzymes and inactivates them. Experimental evidence suggests that DNA loses its replication ability once the bacteria have been treated with silver ions. Other studies have shown evidence of structural changes in the cell membrane as well as the formation of small electron-dense granules formed by silver and sulfur. Silver ions have been demonstrated to be useful and effective in bactericidal applications, but due to the unique properties of nanoparticles nanotechnology presents a reasonable alternative for development of new bactericides. Metal particles in the nanometre size range exhibit physical properties that are different from both the ion and the bulk material. This makes them exhibit remarkable properties such as increased catalytic activity due to morphologies with highly active facets.

The antimicrobial activity of silver has been recognised by clinicians for over 100 years. In addition, reports suggest that hygienic benefits have been associated with the use of silver for considerably longer. Records show that Hippocrates recognised the role of silver in the prevention of disease and accounts exist that suggest that the Romans stored wine in silver vessels to prevent spoilage. However, it is only in the last few decades that the mode of action of silver as an antimicrobial agent has been studied with any rigour. Metallic silver is relatively unreactive however, when exposed to aqueous environments some ionic silver (Ag+) is released. Certain salts (eg silver nitrate) are readily soluble in water and have been exploited as antiseptic agents for many decades. The generation of silver ions can also be achieved through ion exchange using complexes of silver with other inorganic materials (eg silver - zeo-
Silver nano-particles have also been demonstrated to exhibit antimicrobial properties both against bacteria\textsuperscript{188} and viruses\textsuperscript{189} with close attachment of the nano-particles themselves with the microbial cells / virus particles being demonstrated with activity being size dependent\textsuperscript{190}.

Despite this, the principle activity of silver is as result of the production of silver ions within an aqueous matrix\textsuperscript{191}. This therefore implies that for silver to have an antimicrobial effect, free water must be present. Silver ions interact with a number of components of bacterial, protozoal and fungal cells. Toxicity to microbial cells is exhibited at very low concentrations with masses within the range of a few fg cell-1 being associated with bactericidal activity. The kinetics of kill vary depending on the source of silver ions with silver derived from ion exchange processes demonstrating delayed activity compared with that derived from soluble salts. Activity appears to increase with temperature and pH\textsuperscript{192}. Studies have demonstrated that silver ions interact with sulfydryl (-SH) groups of proteins as well as the bases of DNA leading either to the inhibition of respiratory processes\textsuperscript{193} or DNA unwinding\textsuperscript{194}. Inhibition of cell division and damage to bacterial cell envelopes is also recorded\textsuperscript{195} and interaction with hydrogen bonding processes has been demonstrated to occur\textsuperscript{196}. Interruption of cell wall synthesis resulting in loss of essential nutrients has been shown to occur in yeasts\textsuperscript{197} and may well occur in other fungi.

Antiviral activity of silver ions has been recorded and interaction with -SH groups has been implicated in the mode of action\textsuperscript{198}. The association of silver nano-particles with the envelope of certain viruses has been suggested to prevent them from being infective\textsuperscript{190}. Much of the research into the mechanism of action of silver ions has been associated with its use as a therapeutic agent especially as a topical dressing on burns. The concentration employed in and released from treated articles is significantly lower than in these applications\textsuperscript{192}. Under such conditions it has been suggested that in many cases the concentration of silver ions available following hydration of the surface of a treated article is too low to produce antimicrobial activity associated with many of the mechanisms de-
scribed above. However, silver ions have been demonstrated to interact with the proteins and possibly phospholipids associated with the proton pump of bacterial membranes. This results in a collapse of the membrane proton gradient causing a disruption of many of the mechanisms of cellular metabolism and hence cell death\textsuperscript{199}.

Silver ions clearly do not possess a single mode of action. They interact with a wide range of molecular processes within microorganisms resulting in a range of effects from inhibition of growth, loss of infectivity to cell death. The mechanism depends on both the concentration of silver ions present and the sensitivity of the microbial species to silver. Contact time, temperature, pH and the presence of free water all impact on both the rate and extent of antimicrobial activity. However, the spectrum of activity is very wide and the development of resistance relatively low, especially in clinical situations\textsuperscript{200}.

Resistance of bacteria to bactericides and antibiotics has increased in recent years due to the development of resistant strains. Some antimicrobial agents are extremely irritant and toxic and there is much interest in finding ways to formulate new types of safe and cost-effective biocidal materials. Previous studies have shown that antimicrobial formulations in the form of nanoparticles could be used as effective bactericidal materials\textsuperscript{201,202}. Recently, Klabunde and co-workers demonstrated that highly reactive metal oxide nanoparticles exhibit excellent biocidal action against Gram-positive and Gram-negative bacteria\textsuperscript{203}. Thus, the preparation, characterization, surface modification, and functionalization of nanosized inorganic particles opens the possibility of formulation of a new generation of bactericidal materials. It is well known that silver ions and silver-based compounds are highly toxic to microorganisms\textsuperscript{204,205} showing strong biocidal effects on as many as 16 species of bacteria including \emph{E. coli} \textsuperscript{206}. Recently, Tiller and co-workers showed that hybrids of silver nanoparticles with amphiphilic hyperbranched macromolecules exhibit effective antimicrobial surface coatings\textsuperscript{207}.

Silver and silver-based compounds are highly antimicrobial by virtue of
their antiseptic properties to several kinds of bacterium, including Escherichia coli and Staphylococcus aureus. Silver based antimicrobial agents receive much attention, because of the low toxicity of the active Ag ion to human cells, as well as it being a long-lasting biocide with high thermal stability and low volatility.

Silver is one of the strongest bactericides. It occurs under several oxidation states, including elemental silver (Ag⁰), which is the most common, monovalent silver ion (Ag⁺), and higher oxidation states (Ag²⁺ and Ag³⁺). The exact antimicrobial action of silver is not completely understood; several possible mechanisms have been proposed, which involve the interaction of silver with biological macromolecules, such as enzymes and DNA. Tetrasilver tetroxide (Ag₄O₄; a molecular crystal form) has been reported to be biocidal through an electron release mechanism. The effect of silver on microorganisms has been related to the inactivation of enzymes due to the formation of silver complexes with electron donors containing sulfur, oxygen, and nitrogen, such as thiols, carboxylates, amides, imidazols, indoles, and hydroxyls.

Silver has been considered as a potential disinfectant in many investigations due to its intense antimicrobial activity and low toxicity to mammalian cells and tissues. It is one of the most powerful natural disinfectants known. The possible mechanism of killing microorganisms by silver ions may be explained as follows: (1) silver ion inhibits ATP synthesis via binding to the ATP synthesis enzyme molecules in the cell wall, (2) silver ion enters the cell and binds with DNA, leading to the DNA denaturation, (3) silver ion blocks the respiratory chain of microorganisms in the cytochrome oxidase and NADH-succinate-dehydrogenase region. It has been reported that the mode of antibacterial action of silver nanoparticles is similar to that of silver ion. However, the effective biocidal concentration of silver nanoparticles is at a nanomolar level in contrast to a micromolar level of silver ions.

Silver-impregnated polymer matrix provides antimicrobial efficacy with a sustained release of silver. The silver/polymer fabric minimizes the trans-
mission of infective agents and enhances patient comfort as well as facile application for health care. Youngs et al. reported that the synthesized fiber encapsulating silver(I) N-heterocyclic carbene complexes facilitated the release of silver ions with maximum bactericidal activity over a longer period of time than that of aqueous silver\textsuperscript{226}. Kluech and coworkers demonstrated that silver-coated poly (ethylene terephthalate) fabric was prepared by the deposition of silver onto the polymeric substrate, and the resultant fabric effectively prevented the attachment of microorganisms on the silver active surface\textsuperscript{221}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure218.png}
\caption{Images of antibacterial activities to \textit{S. aureus} (a,b) and \textit{E. coli} of Ag colloids (c,d). (a,c) PVA-protected, (b,d) without PVA}
\end{figure}
2.26 Nanoparticle Dispersed Dendritic Macromolecules

Metal nanoparticles supported by polymeric materials are an active area of research due to their interesting applications in the areas of catalysis, conducting materials, non linear optical devices and colour materials\textsuperscript{227–230}. Dendrimer, like any other polymer, is a macromolecule, but unlike a usual polymer, is well defined at the molecular level. Dendrimers are symmetrical and spherical macromolecules with a relatively dense shell composed of a core, branching sites, and terminal groups that usually form a well defined surface\textsuperscript{231}. Their interior may be similar or different from the surface of the molecule. Dendrimers are considered as excellent candidates for preparing nanoparticles because of their unique properties. Dendrimers with an intrinsically well defined globular structure and highly modifiable surface groups are used as templates to control the size, stability and solubility of nanoparticles with diameter less than 20nm. Dendrimers are particularly well suited for hosting metal nanoparticles because of the following reasons.

- The dendrimer templates are of uniform composition and structure and so they yield well defined nanoparticle replicas\textsuperscript{232,233}.

- The nanoparticles are stabilized by encapsulation within the dendrimer, and therefore they do not agglomerate\textsuperscript{234,235}.

- The encapsulated nanoparticles are confined primarily by steric effects, and therefore a substantial fraction of their surface is unpassivated and available to participate in catalytic reactions\textsuperscript{236}.

- The dendrimer branches can be used as selective gates to control access of small molecules into the encapsulated nanoparticles\textsuperscript{237}.

- The terminal groups on the dendrimer periphery can be functionally modified to control the solubility of the polymer nanocomposites\textsuperscript{238–240}. 

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As a consequence of their three-dimensional structure and multiple internal and external functional groups, higher generation dendrimers are able to act as hosts for a range of ions and molecules. Dendrimers retain guest molecules selectively depending on the nature of the guest, the chemical composition of the dendrimer interior and periphery, and the cavity size. The driving force for guest encapsulation within dendrimers can be based on covalent bond formation, electrostatic interactions, complexation reactions, steric confinement, various types of weaker forces (van der Waals, hydrogen bonding, etc.), and combinations of any of these. Many examples of dendrimer-based host-guest chemistry have been reported\textsuperscript{241}.

There are several methods used for the synthesis of dendrimer encapsulated metal nanoparticles. The most widely used method is a two step process. First, the metal ions are incorporated into the dendrimer through complexation and then the ions are chemically reduced. As the synthesis relies on the dendrimer template, the resulting metal nanoparticles are monodisperse in size. Poly (amidoamine) (PAMAM) and poly (propylene imine) (PPI) are the two classes of dendrimers that are widely used as templates for the synthesis and stabilization of nanoparticles. The ability of these dendrimers to host Au, Pd, Pt, Ag and Cu nanoparticles is attributed to the spheroidal structure of the dendrimer, which contain void spaces and functional groups that are able to complex with the metal ions.

The preparation of dendrimer encapsulated metal nanoparticles by the method of complex formation followed by reduction is possible only if the corresponding metal ion is extracted into the dendrimer interior. This method is not suitable for metals whose precursor ions are not strongly complexed. An example for such a metal is silver. Silver nanoparticles are prepared inside the dendrimer through a metal displacement reaction. In this approach dendrimer encapsulated copper nanoparticles are initially prepared and upon exposure to Ag\textsuperscript{+}, the Cu particles oxidize to Cu\textsuperscript{2+}ions and Ag\textsuperscript{+} is reduced to yield a dendrimer encapsulated zerovalent silver nanoparticle. The silver nanoparticles synthesized by this
method are very stable. This method can also be applied to prepare other types of nanoparticles such as gold, platinum and palladium\textsuperscript{242}.

Transition metal nanoparticles are important in the field of catalysis. Catalytic nanoparticles are usually prepared by reduction of metal salts in the presence of stabilizers. These stabilizers, which are used to control particle size and shape and to prevent agglomeration, generally contaminate the surface of the nanoparticles and reduce its catalytic efficiency. However by using dendrimer as a stabilizer we could overcome these problems. Again, by using different generation dendrimers we could control the reaction rates and do selective catalysis. A few examples of reactions catalyzed by dendrimer encapsulated nanoparticles include hydrogenation of olefins\textsuperscript{243,244}, Heck reactions\textsuperscript{245}, oxidation reactions\textsuperscript{246}, reduction reactions\textsuperscript{247}, and Suzuki reactions\textsuperscript{248}.

Dendrimer silver complexes and nanocomposites can also be used as antimicrobial agents. Poly (amidoamine) dendrimer based silver complexes and nanocomposites proved to be effective antimicrobial agents \textit{in vitro}. As the dendrimer host is soluble, it is able to deliver the immobilized silver in the agar medium by its own diffusion. The silver clusters remain active because of their extremely high surface area. Reaction with chloride and sulfate ions neither blocks the diffusion of the silver nor the activity against \textit{S. aureus}, \textit{P. aeruginosa} and \textit{E. coli}. In the absence of dendrimers, silver ions quickly precipitated in the form of insoluble silver salts when contacted with chloride and sulfate ion containing solutions. The protected silver and silver compounds displayed high antimicrobial activity in several cases without the loss of solubility\textsuperscript{249}.

\subsection*{2.27 Cyclodextrin as a Supramolecular Host System}

Cyclodextrins are cyclic oligosaccharides consisting of multiple (\textalpha{}, D1-4) linked glucopyranose units that display amphoteric properties of a lipophilic central cavity and hydrophilic outer surface. Cyclodextrins are crystalline, homogenous and non-hygroscopic substance, which are torus-like macro ring shape. The hydrophilic exterior surface of the cyclodextrin molecules makes them water soluble,
but the hydrophobic cavity provides a microenvironment for appropriately sized non-polar molecules. Cyclodextrins are a general class of molecules composed of glucose units connected by α-1, 4 glycosidic linkages to form a series of oligosaccharide rings. In nature, cyclodextrin can be obtained with the help of cyclodextrin glycosyl transferases by enzymatic degradation of starch. The latter is a polysaccharide consisting of alpha- (1, 4) linked glucose units and is found as a left-handed helix with six units per turn. In the process, compounds with six to twelve glucopyranose units per ring are produced. Depending on the enzyme and how the reaction is controlled, the main product is α, β, or γ cyclodextrin (6,7,8-glucopyranose units, respectively). These are toxicologically harmless, crystalline compounds, which both in the solid state and in solution adopt a conical conformation where the height is about 800nm and the cavity’s inner diameter is between 500 and 800 pm wide. They have an endolipophilic cavity, which is made water-soluble by the many outward pointing off groups.

Commercially, cyclodextrins are still produced from starch, but more specific

Figure 2.19: Different types of cyclodextrins
enzymes are used to selectively produce consistently pure $\alpha$, $\beta$, or $\gamma$ cyclodextrin, as desired. All three cyclodextrins exhibit good flow properties and handling characteristics and are thermally stable, stable in alkaline and acidic solutions and is biocompatible. Besides molecular size, the other key difference in physical properties between the three cyclodextrin products is their water solubility. The differing number of glucose units leads to slight differences in conformational structure and flexibility of the ring. While all three products are water soluble, these differences result in higher exposure of hydrogen bonding hydroxyl groups to the aqueous environment and higher water solubility for $\alpha$ and $\gamma$ cyclodextrin$^{251}$.

Inclusion complexes between drugs and cyclodextrins are a topic of current interest to the pharmaceutical research and industry as they may improve the solubility, stability, and bioavailability of the guest molecules$^{252}$. Cyclodextrin inclusion is a molecular phenomenon in which usually one guest molecule interacts with the cavity of a cyclodextrin molecule to become entrapped and form a stable association. Molecules or functional groups of molecules those are less hydrophilic
than water, can be included in the cyclodextrin cavity in the presence of water.

![Diagram of cyclodextrin](image)

**Figure 2.21:** Structure of \( \beta \) cyclodextrin

In order to become complex, the ‘guest molecules’ should fit, at least partly, into the cyclodextrin cavity. The cavity sizes as well as possible chemical modifications determine the affinity of cyclodextrins to the various molecules. In the case of some low molecular weight molecules, more than one guest molecule may fit into the cavity. On the opposite, some high molecular weight molecules may bind more than one cyclodextrin molecule. Cyclodextrins are able to form inclusion complexes with broad range hydrophobic molecules as poorly soluble drugs, rapidly deteriorating flavors, volatile fragrances, toxic pesticides or dangerous explosives, even gases; entrapping these substances in their inner cavities.

### 2.28 References


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CHAPTER 2. NANOPARTICLE DISPERSED LINEAR AND DENDRITIC MACROMOLECULES CONTAINING PHOTORESPONSIVE GROUPS: AN OVERVIEW


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Chapter 2. Nanoparticle Dispersed Linear and Dendritic Macromolecules Containing Photoresponsive Groups: An Overview


