CHAPTER 1

INTRODUCTION AND OBJECTIVES
1.1 Introduction

Dendritic polymers have been recognized as the fourth class of the macromolecules. They have several attractive properties, such as high degree of branching units, high density of surface functional groups, nano-scaled size and low-dispersity. Generally, dendritic polymers consist of three main structural components: a multi-functional core, repeated branching units and surface functional groups. They are further classified into three subclasses: random hyperbranched polymers, dendrigraft polymers and dendrimers. Among these subclasses, dendrimers and hyperbranched polymers have been widely investigated\(^1\).

Dendrimers are perfect artificial macromolecules, which are synthesized by a step-wise method. Two strategies, namely the divergent strategy and the convergent strategy, were proposed to prepare dendrimers. The divergent method starts
from a central core and extends toward the surface, while the convergent one uses a top-bottom method that starts from the periphery of dendrimers. Tomalia et al. first reported the synthesis of polyamidoamine (PAMAM) dendrimers by using the divergent method in the early 1980s. Later in 1990, Hawker et al. proposed the convergent method for dendrimer construction. Up to now, most of the dendrimers, including the commercially available polyamidoamine (PAMAM) dendrimers and polypropylenenimine (PPI) dendrimers, are synthesized by the divergent method.

Unlike dendrimers, hyperbranched polymers with nonperfect structure are synthesized via one-step reactions. However, hyperbranched polymers and dendrimers built from $AB_2$ functional monomers have many common features because of their similarity in branching. Compared with dendrimers, hyperbranched polymers possess economical attraction due to the much cheaper one pot, one-step synthesis. They are promising products for industrial applications.

There are many potential applications for dendrimers and dendritic polymers such as hyperbranched polymers, which arise from their multifunctional surface and presence of internal cavities. These properties make dendrimers and hyperbranched polymers suitable for biomedical and industrial applications. Dendritic systems have been applied in *in vitro* diagnostics like cardiac testing. These are also used as contrast agents in magnetic resonance imaging, targeted drug delivery and other therapeutic applications. Dendritic polymers can also act as carriers in gene therapy.

Besides biomedical applications dendritic polymers can also be used to improve many industrial processes. They are useful in nanoscale catalysis. An alternative application of dendrimers that has gained some attention is based on nanostructures which can find use in environment friendly industrial processes. Dendrimers can encapsulate insoluble materials, such as metals, and transport them into a solvent within their interior. Hyperbranched polyglycerol is a hydroxyl functional dendritic macromolecule with an inert polyether backbone. It is a biocompatible polymer. Its densely populated hydroxyl groups makes it suitable for
a number of biomedical applications.

The present study utilises the ability of functionalisation of the peripheral hydroxyl groups of hyperbranched polyglycerol. This is to make them photoactive by introducing photochromic moieties by functional transformations. Moreover, the peripheral hydroxyl groups of hyperbranched polyglycerol forms polar voids by aggregation and this cavities are extremely suitable for encapsulating metal nanoparticles to make them stable.

A polymer is a macromolecule formed by the repetition of small, simple repeating units. They may possess different topological structures. They may be either be linear, branched or network. Polyvinyl alcohol (PVA), Polyethylene glycol (PEG), polyglycerol polyadipate etc. are examples of linear polymers.

Polyvinyl alcohols are polymers of vinyl alcohol. As vinyl alcohol cannot exist in the free form, poly vinyl alcohol (PVA) is manufactured by the polymerization of vinyl acetate. PVA contains a large number of hydroxyl groups. Polyvinyl alcohol is a water-soluble synthetic polymer with excellent film forming, emulsifying, and adhesive properties. These polymers offer outstanding resistance to oil, grease, and solvents, high tensile strength, flexibility and high oxygen barrier. Suitable applications for PVA are largely determined by these properties.

Polyethylene glycols are linear homopolymers of ethylene oxide. PEG are waxy materials and are soluble in water and many organic solvents. They find application in pharmaceutical preparations and cosmetics. PEG is used as a non-volatile solvent and substrate for paints, inks and adhesives. Polyvinyl alcohol, polyethylene glycol and polyglycerol polyadipate are linear analogues of hyperbranched polyglycerol due to the presence of hydroxy functional groups. The present work also utilises these core systems for designing photoresponsive polymeric coating materials.

The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, with at least one dimension in the nanometer range. Properties of materials of nanometric dimensions are significantly different from those of atoms as
well as those of bulk materials. It will offer better built, longer lasting, cleaner, safer, and smarter products for the home, for communications, for medicine, for transportation, for agriculture, and for industry in general. A key understanding of nanotechnology is that it offers not just better products, but a vastly improved manufacturing process. It covers fields from biology to material science, physics to chemistry, and can include development in a variety of specialties. Nanofilms explore in self-reactive thin films, nanocomposites and surfactants. Nanofilms are self-reactive thin films and are ultrathin and invisible on a surface. They chemically react with a substrate to bond with it, rather than being painted onto it. They impart new functionalities to the surface. Nanocomposites are another Nanofilm R&D area. Nanocomposites are the blend of nanomaterials into a matrix of another substance. This imparts characteristics of the nanomaterial to a larger body of matter.

Nanoparticles and metal clusters represent an important state of condensed matter. Such systems display many peculiarities and physical and chemical properties that were never observed earlier. Nanoparticles may be considered as intermediate formations, which are limited by individual atoms on the one hand, and the solid phase on the other. Such particles exhibit the size dependence and a wide spectrum of properties. Thus, nanoparticles can be defined as entities measuring from 1 to 100 nm and built of atoms of one or several elements. Presumably, they represent closely packed particles of random shapes with a sort of structural organization. One of the directions of nanoscience deals with various properties of individual nanoparticles. Another direction is devoted to studying the arrangement of atoms within a structure formed by nanoparticles. Moreover, the relative stability of individual parts in this nanostructure can be determined by variations in kinetic and thermodynamic factors.

Nanoparticles are larger than individual atoms and molecules but are smaller than bulk solid. Hence they obey neither absolute quantum chemistry nor laws of classical physics and have properties that differ markedly from those expected. There are two major phenomena that are responsible for these differences. First
is the high dispersity of nanocrystalline systems. As the size of a crystal is reduced, the number of atoms at the surface of the crystal compared to the number of atoms in the crystal itself, increases. Properties, which are usually determined by the molecular structure of the bulk lattice, now become increasingly dominated by the defect structure of the surface. The second phenomenon occurs noticeably only in metals and semiconductors. It is called size quantization and arises because the size of a nanoparticle is comparable to the de Broglie wavelength of its charge carriers (i.e. electrons and holes). Due to the spatial confinement of the charge carriers, the edge of the valance and conduction bands split into discrete, quantized, electronic levels. These electronic levels are similar to those in atoms and molecules.

Nanoscale functionalised entities and devices are in development for analytical and instrumental applications in biology and medicine, including tissue engineering and imaging. The application areas in which these advances in nanoscience are making their biggest impact include electronic, electro-optic and optical devices. The transition from semiconductor (conventional and organic) technology to nanoscale devices has anticipated improved properties and resolution, e.g. fluorescence labelling, scanning probe microscopy and confocal microscopy. Data storage devices based on nanostructures provide smaller, faster, and lower consumption systems. In medicine, greater understanding of the origin of diseases on the nanometre scale is being derived, and drug delivery through functionalised nanostructures may result in improved pharmacokinetic and targeting properties. A wide variety of functional nanoscale materials and functional nanoscale surfaces are in use in consumer products, including cosmetics and sunscreens, fibres and textiles, dyes, fillers, paints, emulsions and colloids.

Silver has been known to have extraordinary inhibitory and bactericidal properties since ancient times. While being relatively nontoxic to human cells, silver possesses antibacterial and antifungal properties for a broad spectrum of bacterial and fungal strains that are found in industrial processes as well as in the human body\(^1\). Because of these characteristics, silver in various forms is ide-
ally suited for a wide range of applications in consumer, industrial, and medical products.

Silver metal particles in nanometer range have attracted considerable interest in recent years, as they have tremendous applications in the area of biomedical, catalysis, optoelectronics, etc due to their unique size-dependent properties. Thus effort can be made to prepare stable nanoparticles of this metal with controlled size in the suitable matrices. Different matrices such as micelles, organic small molecules, linear polymers, mesoporous materials, dendritic polymers, etc are used for this purpose. Dendritic polymers are very effective protecting agents for silver nanoparticles. Especially dendritic polymers with polar terminal groups like amine, hydroxyl, amide etc are a very useful class of protective agents. The effective stabilization of nanoparticles by dendritic polymers may be due to the presence of large number of polar terminal groups located on their surface along with high solubility in different solvents and low solution viscosity. Among different subclasses of dendritic polymers, hyperbranched polymers are preferred over the others because of its easy one - pot, one step synthesis at a reasonable cost.

Polymer coated functionalized noble metal nanoparticles have recently emerged as an active field of research due to many novel properties of these materials. A growing interest has been developed in the antimicrobial modification of surfaces to prevent the growth of harmful organisms. Coatings based on a slow-release of toxic agents are very effective and have been employed successfully for a long time. However, due to environmental concerns many such systems are to be abolished. Therefore, systems which show antimicrobial effects toward germs on contact without releasing toxic biocides are of strong current interest. Silver nanoparticles possess antimicrobial property and are also non toxic and environment friendly. However due to the lack of binding properties to the surface, they are unsuited as an antimicrobial coating. Hyperbranched polyglycerol is an excellent coating material and it can effectively stabilize silver nanoparticles in its cavities.
Cyclodextrin make up a family of cyclic oligosaccharides, composed of 5 or more α-D-glucopyranoside units. Typical cyclodextrins contain a number of glucose monomers ranging from six to eight units in a ring, creating a cone shape. Cyclodextrins are able to form a host-guest complex with hydrophobic molecules given the unique nature imparted by their structure. As a result, these supramolecular host systems have found a number of applications in a wide range of fields.

The ability to form host guest complexes and the presence of large number of peripheral hydroxyl groups makes cyclodextrins as ideal stabilizing agents for nanoparticles. To ensure the specific biological applications of nanoparticles it is required that these silver nanoparticles to be present in aqueous media. But most of the method developed till date for the preparation of nanoparticles render nanoparticles in the organic solution. In recent years, large number of studies has been reported on the phase transfer of nanoparticles from organic to aqueous phase. Several works by Rotello and coworkers, Gittins and Caruso, Sastry and coworkers as well as Rao and coworkers have reported various methods for the phase transfer of metal nanoparticles from organic to aqueous phase. Diao and coworkers have reported the phase transfer of oleic acid stabilized silver nanoparticles from organic to aqueous phase using p- sulfonated calyx[4]arene. Yang and coworkers have reported the phase transfer of silver nanoparticles to aqueous phase using a β-cyclodextrin as capping agent13–19. The poor solubility of these systems in aqueous phase restricts their biological applications. The encapsulation of nanoparticles in β-cyclodextrin enables us to solubilize the metal nanoparticles in water and in polar solvents. Thus the synthesis of silver nanoparticle encapsulated β-cyclodextrins offers the development of a new class of water soluble antimicrobial agents which could be largely used in antibacterial and antifungal applications.
1.2 Objectives

The purpose of the current research work is to explore the synthesis of photochemically modified linear and hyperbranched polymers with photoresponsive properties. It also aimed to explore the synthesis of silver nanoparticle dispersed hyperbranched polyglycerols and assess their utility for biological and biomedical applications. In view of these challenges, the main objectives of the present work are:

1. To design novel dendritic macromolecules with specific structural architecture and to functionally modify them with photoresponsive groups.

2. To develop light harvesting antenna systems based on the photochemically modified dendritic macromolecules.

3. To develop photoresponsive analogues of linear polymeric systems such as poly [di (ethylene glycol)/glycerol-alt-adipic acid] polyol, polyvinyl alcohol and polyethylene glycol.

4. To generate silver nanoparticles protected by long aliphatic amines such as dodecyl amine.

5. To develop nanoparticle-dispersed linear and dendritic macromolecules modified with photoresponsive groups by substitution-type reactions.

6. To study the light induced trans-cis and reverse cis-trans isomerisation of the azo chromophoric system bound to linear and hyperbranched polymers.

7. To study the light absorption (UV visible radiant power), light stabilization and fluorescence emission properties of linear and dendritic polymers functionalized with photoactive groups.

8. To study the light fastening ability of the polymer bound chromophoric systems.
9. To study the electron modulation and molecular switching properties and photoresponsive behaviour of the photochemically modified and nanoparticle-dispersed linear and dendritic macromolecules.

10. To study the antibacterial and antifungal activities of the silver nanoparticle dispersed hyperbranched polyglycerols against various bacterial and fungal strains.

11. To develop silver nanoparticle encapsulated $\beta$-cyclodextrin as a unique system of host-guest nature for biomedical applications.

12. To study the antibacterial and antifungal activities of the silver nanoparticle dispersed $\beta$-cyclodextrin against various bacterial and fungal strains.

1.3 Outline of the Thesis

The thesis is divided into seven chapters. This chapter is the introductory chapter of the dissertation. The chapter gives a brief introduction to dendrimers, dendritic polymers such as hyperbranched polymers, nanomaterials, especially nanosilver stabilised in macromolecular matrices, and the photochemical, biological and biomedical applications of these systems. The important objectives of the study are listed at the end of this chapter.

Chapter 2 gives a detailed literature review on Dendritic Polymers, silver nanoparticles, its chemistry, material science, biology and biochemistry with special reference to the synthetic methods, properties and applications of dendrimers and hyperbranched polymers. This chapter also gives a detailed description on nanoparticles, including synthesis, characterization techniques, and applications. A detailed review on silver nanoparticles, its chemistry, material science, biology and biochemistry are included in this chapter. Special thrust is given to the chemistry and applications of hyperbranched polyglycerol and silver nanoparticles.

Chapter 3 gives a detailed description of the experimental methods. A general description of the materials and various experimental methods are included
here. It describes the synthetic methods, purification and characterization techniques of individual products used in this work. A summary of the protocols and the products obtained are given in tabular forms for ready reference (table 3.1 - 3.3).

Chapter 4 presents the experimental results obtained on functionally modified linear and hyperbranched polymers. The synthesis of various photoresponsive systems based on linear and hyperbranched polyglycerols are described in this chapter. Structural characterizations of the products are done by various spectroscopic techniques such as UV-visible, IR and NMR spectroscopic methods and by fluorescence measurements. The results of the spectroscopic analyses are discussed in detail in this chapter.

Chapter 5 deals with the studies on the photoresponsive properties such as light absorption, light stabilisation and fluorescence emission behaviour of the functionally modified polymers. The light induced trans - cis and reverse cis - trans isomerisation of azo chromophore functionalized polymers are also investigated. The light fastening ability of the photochemically modified polymeric systems was one of the main objectives. These studies are also included in this chapter. The effect of solvation on the UV visible and fluorescence emission spectra of the functionalized polymers is presented in this section. A detailed discussion on the results obtained is also included in this chapter.

Chapter 6 presents a detailed account of the experimental results of synthesis of silver nanoparticles by reduction technique and characterization by SEM, TEM and UV visible spectroscopic analysis. The structural characterization and investigation of the photophysical properties of chromophore functionalized and nanoparticle dispersed hyperbranched polymer are also presented here in detail. A detailed account of the antibacterial and antifungal property of the nanoparticle dispersed hyperbranched polymers is presented here. Silver nanoparticle encapsulated supramolecular host system such as β-cyclodextrins, their antibacterial and antifungal properties etc. are also discussed in chapter 6. The thermal stability of the nanoparticle dispersed hyperbranched polyglycerol was also
vestigated and presented in this chapter. This chapter also includes a detailed discussion of the results obtained. Chapter 7 presents the conclusions based on the above studies and suggestions for the future work.

1.4 References


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