1.0 INTRODUCTION

1.1 Nanotechnology
1.2 Synthetic Strategies to synthesis NPs
1.3 Triblock Polymer
1.4 Biomineralization
1.5 Review of Literature
1.6 Objective and Justification
1.7 References
Chapter 1
INTRODUCTION

This work is related to the *in vitro* synthesis and the growth mechanism of the gold (Au) nanoparticles (NPs) by using different kinds of block polymers and water soluble proteins so as to explore the industrial potential of polymer or protein conjugated nanomaterials. This section is devoted to the introduction and objectives to accomplish this study.

1.1 Nanotechnology

“Nano” comes from the Greek word “Nanos” which means “Dwarf” is a prefix in science denoting one billionth of a unit. It means that 1 nm is one billionth of a meter \(10^{-9}\) m. It is the size of a small molecule which is 50,000 times smaller than a human hair and is 80,000 nm wide. The size of the atom is approximately one-tenth of a nanometer. Nanotechnology is basically the design, characterization, production and application of structures, devices and systems by controlled manipulation of size and shape at the nanometer scale. A number of important breakthroughs have already been achieved in nanotechnology. These developments are used throughout the world in devices for computers that read from and write to the hard disk, catalytic converters in automobiles that help to remove air pollutants, certain sunscreens and cosmetics that transparently block harmful radiation from the sun. Still many scientists believe that they have only scratched the surface of nanotechnology’s potential and it will have a major impact on medicine and health care, energy production and conservation, environmental cleanup and protection, electronics, computers, sensors, world security, and defense.

To grasp the size of the nanoscale, consider the diameter of an atom, the basic building block of the matter. The hydrogen atom, one of the smallest naturally occurring atoms, is only 0.1 nm in diameter. In fact, nearly all atoms are roughly 0.1 nm in size, too small to be seen by human eyes. We know that atoms bond together to form molecules, the smallest part of a chemical compound. Molecules that consist of about 30 atoms are only about 1 nm in diameter. Molecules, in turn, compose cells, the basic units of life. Human cells range from 5,000 to 200,000 nm in size, which means that they are larger than the nanoscale. However, the proteins that carry out the internal operations of the cell are just 3 to 20 nm in size and so have nanoscale
dimensions. Viruses that attack human cells are about 10 to 200 nm, and the molecules in drugs used to fight viruses are less than 5 nm in size. It means that nature is working at nanoscale. Nanoscale is unique because nothing solid can be made smaller than this and at this scale the physical properties of materials are different as compared to the bulk state for example copper wire which is malleable and ductile in bulk state and it can be bend up to 50 nm below which it is considered to be super hard materials that do not exhibit the same malleability and ductility as in bulk copper\(^1\). Ferroelectric materials smaller than 10 nm switch their magnetization direction using room temperature or thermal energy and becomes useless for memory storage\(^2\). At nanoscale particles, often show unexpected visual properties for example Au NPs appear deep red to black in solution depending upon the size of gold.

An important aspect of nanotechnology is the highly increased ratio of surface area to volume of nanoparticles which makes new quantum mechanical effects\(^3\), electronic property of materials are also altered with great reduction in particle size. Nanomaterials take advantage of their dramatically increased surface to volume ratio and the optical properties e.g. fluorescence\(^4\) becomes a function of the particle diameter. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometer size range is reached. NPs also strongly influence the mechanical properties of the materials like stiffness or elasticity. Traditional polymer can be reinforced by NPs resulting in novel materials which can be used as light weight reduction of metals. So the novel mechanical properties of NPs are a subject of nanomechanics research. NPs are also used as a chemical catalyst in various reactions due to their large increase in surface to volume ratio, so the nanocatalyst is an interesting area of research these days. High surface area to volume ratio of nanoparticles produces a tremendous driving force for diffusion especially at elevated temperature. Sintering is only possible at lower temperature and over shorter duration for larger particle. The surface effect of NPs also reduces the incipient melting temperature. Thus, the development of nanoscience and nanotechnology is in line with trend towards miniaturization and it makes a barrier between scientific and technological disciplines more permeable.

1.2 Synthetic Strategies to synthesis NPs

There are two different approaches to synthesize nanomaterials.

(a) Bottom up approach
Top-down approach

In the Bottom up (Figure 1) approach, there is miniaturization of materials components (up to atomic level) with further self assembly process leading to the formation of nanostructure. During the self assembly, the physical forces (hydrogen bonding, Π-Π interactions, electrostatic interactions and electromagnetic effect) operating at nanoscale are used to combine basic units into stable nanostructure. Typical examples are the quantum dot formation during epitaxial growth and formation of NPs from colloidal dispersion. The Top-Down approach uses larger macroscopic initial structures which can be externally controlled in the process of nanostructures. Typical examples are etching through mask, ball milling and application of severe plastic deformation.

Creating nanostructure materials based on bottom-up method is a fast-growing field of research. Particularly the two-dimensional arrays of nanocrystals (NCs) are of great interest, which have been shown to display unique optoelectronic, magnetic, or catalytic properties that can be tuned by varying their size and interparticle separation distance. Advanced functional
materials incorporating well-defined NCs architectures have potential for practical applications in many areas, including miniaturized nanoelectronics,\textsuperscript{6} ultrafast quantum computing,\textsuperscript{7} high-density memory/data storage media,\textsuperscript{8} ultrasensitive chemical sensing/biosensing,\textsuperscript{9} generation of high-efficiency catalytic substrates\textsuperscript{10} and high-throughput templating for the growth/attachment of other types of bio- or inorganic nanomaterials.\textsuperscript{11}

1.3 Block copolymer

Water soluble polymers have been frequently used in the synthesis of NPs and block polymers possess unique characteristic features which help in the growth and stabilization of NPs. They are one of the most versatile macromolecules with unique fundamental properties and wide industrial applicability. Recently, water soluble block polymers have fetched a great interest due to environmental concerns and their water based food and pharmaceutical formulations. Among these block copolymer triblock copolymers and tetronic block copolymers are of great interest.

Triblock copolymer (TBP) which are made up of different combinations of polyethylene oxides (PEO) and polypropylene oxides (PPO) units, have fetched considerable fundamental as well as industrial importance.\textsuperscript{12,13} Fundamentally, they have tremendous advantages than conventional neutral polymers due to the presence of both hydrophilic (i.e. PEO) and hydrophobic predominant (i.e. PPO) moieties in the same polymer macromolecule. The PEO-PPO-PEO triblock copolymers are commercially available in a range of molecular weights and PEO-PPO composition.\textsuperscript{14} The notation for PEO-PPO-PEO Pluronics starts with a letter giving their pristine appearance: L for liquid, P for paste, and F for flakes. The symbol R refers to reverse architecture Pluronics: PPO-PEO-PPO. The first one or two numbers are indicative of the molecular weight of the PPO block (in units of 0.01 g mol\textsuperscript{-1}), and the last number indicates the weight fraction of the PEO blocks (in units of 10\%). An appropriate variation in the number of PEO and PPO repeating units enables one to shift the overall nature from hydrophilically to hydrophobically predominant TBPs. Such a versatile flexibility of these polymers makes them widely useful in various industrial applications such as detergency, emulsification, dispersion, lubrication, stabilization, foaming etc.\textsuperscript{15} Not only this, these polymers also act as non-ionic surfactants since amphiphilic character of block copolymers leads to a self-assembled behavior resembling to that of classical non-ionic surfactants.\textsuperscript{16-19} Various techniques such as light
scattering, fluorescence spectroscopy, NMR, specific volume, and SANS have been frequently used to gain new insight into the aggregation behavior of these systems. The results of these investigations clearly show that at low polymer concentration and low temperature, TBPs dissolves in water as unimers. The process of self-association (Figure 2) can be induced by increasing the concentration of TBPs above the \( \text{cmc} \) and or adjusting the temperature to exceed the critical micellization temperature (cmt).

### Figure 2. Micellization of triblock polymers.

Micellization in triblock polymers (Fig. 2) occurs due to following reasons as the temperature of a block copolymer solution is raised, the PPO block progressively loses its hydration sphere, resulting in greater interactions between the PPO blocks. On the other hand, the PEO blocks retain their strong interaction with water; thus as is common for all amphiphilic molecules, the differing phase preferences of the blocks drive the copolymers to form micelles. Structural studies have shown that the micelles form a hydrophobic core consisting mainly of weakly hydrated PPO blocks, which are surrounded by an outer shell known as corona of almost fully hydrated PEO blocks. There is a broad temperature range above the critical micelle temperature (cmt) where micelles coexist in solution with unimers. Above the transition region most of the block copolymer molecules form micelles. At higher temperature well above the cmt, a cloud point is reached and the copolymer solutions become opaque because the phase
separation of the micellar solution into the two phases occurs at this temperature. The parameter of greatest fundamental value is the critical micelle concentration (cmc), the copolymer concentration at which micelles start forming.\textsuperscript{45} Triblock polymers are non-ionic surfactants, which limits the number of techniques available to measure their cmc in comparison to those of ionic surfactants. Also, in comparison with conventional low molecular weight surfactants, there is some inherent complexity in the micellization of block copolymers, which depends strongly on their composition\textsuperscript{46}. The blocks are not completely monodisperse even for a copolymer with a narrow distribution of molecular weight and accordingly no sharp cmc or cmt has been observed for block polymers. Generally, the cmc spans over a much larger concentration interval than observed with conventional surfactants. The cmc is also sensitive to temperature which is likely to extend the concentration range over which the cmc occurs.\textsuperscript{46} Micelle – solution interface of a TBP micelle acts as a site for the site-specific redox reaction due to the presence of ether oxygens in the surface cavities produced by the PEO units. Thus, a greater number of PEO units generate greater number of surface cavities and hence possess greater reduction potential. As one polymer molecule is mainly contributing towards the formation of one surface cavity in a micelle, it accepts one guest ion (oxidizing agent) per cavity but the host – guest fit is very much related to the size of the PEO block. A smaller cavity is formed with few PEO units (i.e. a smaller PEO block) and thus unable to properly accommodate a guest molecule. On the contrary, a larger number of PEO units (i.e. a larger PEO block) will form a large bucket quite big enough to accommodate a guest molecule. Hence, the reducing ability of a TBP micelle is also very much related to the size of the surface cavities and several surface cavities present on the surface of a micelle can simultaneously reduce almost equivalent number of oxidizing agents if all oxidizing agents can be accommodated in the cavities.

Another important category of block copolymers is star shaped tetronics block copolymer (Figure 3) which has unique physiochemical properties. Their self-assembled behavior is highly temperature sensitive.\textsuperscript{43,44} A slight increase in the temperature induces dehydration to poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) blocks resulting in micelle like assemblies. In addition, the presence of diamine core makes tetronics highly pH sensitive and hence their physiochemical properties closely depend on the pH variation.\textsuperscript{50-53} Low pH turns the amine moiety into ammonium groups and macromolecule acquires a net positive charge which restricts its aggregation. High pH allows it to attain a neutral form which under the effect of
concentration and temperature produces micelle like aggregation. The micelle formation in
tetronics is considered to be somewhat different from the conventional micelles of pluronics
which are long chain block polymers and devoid of amine functionality. It is much easier to
predict the morphology of long chain pluronic micelle in which predominantly hydrophobic PPO
blocks are accommodated in the core and hydrophilic PEO blocks are arranged in the shell.
However, it is not that simple to predict this type of arrangement for star shaped polymers like
tetronics in which both PPO and PEO blocks exist in the form of four arms connected to the
diamine moiety residing in the centre of the molecule to produce star shaped geometry. This
geometry is obviously not expected to generate a conventional micellar arrangement as observed
in pluronics due to steric constrains in four arms of PPO/PEO blocks which may lead to a highly
hydrated micelles.

Figure 3. Structural formula of star shaped T904 and its schematic representation.

Micelles of both pluronics as well as tetronics act as fine nanoreactors for the synthesis of
Au NPs where ether oxygens of PPO as well as PEO blocks act as mild reducing agents and the
redox reaction is mainly carried out in the micelle surface cavities which act as active reaction
sites due to the entrapment of gold ions. Similar redox reactions are also expected in the micelles
of tetronics due to the presence of PPO or PEO blocks. But the presence of diamine moiety is
considered to have additional influence on the overall redox process because ammonium groups
at low pH could act as favorable sites for the electrostatic interactions with negatively charged
AuCl$_4^-$ ions. Since we expect a dramatic change in the aggregation behavior of tetronics with temperature, therefore redox process resulting in the synthesis of Au NPs is also expected to be significantly affected.

1.4 Biomineralization

Synthesis of functional inorganic materials by organisms (Figure 4) is a unique natural process where biomolecules are directly involved in their synthesis and this process is known as biomineralization. Biomineralization$^{54-65}$ is a fast developing area to synthesize biofunctional nanomaterials by directly using biomolecules in their shape control synthesis$^{66-68}$ with several biological applications.$^{69-74}$ Biomolecules such as amino acids and phospholipids also act as fine capping/stabilizing agents$^{75-78}$ to achieve appropriate geometries. They occupy low energy crystal planes selectively$^{66-68}$ and hence reduce their participation in overall nucleation process that directs the overall crystal growth at uncapped or poorly capped high energy crystal planes to achieve desired morphologies.

![Figure 4. Magnetite crystals in magnetotactic bacteria. These are tiny compasses that guide these organisms to move vertically in river bed sludge. MV indicates empty vesicles.](image)

Low molecular weight water soluble globular proteins are less surface active than fibrous proteins due to their relatively less interfacial adsorption.$^{79,80}$ On the other hand, unfolded proteins are always more surface active than folded ones.$^{81,82}$ Unfolded protein with its large surface area can also provide soft-template effects$^{83-85}$ for growing nucleating centres. Use of simple and low molecular weight proteins such as bovine serum albumin (BSA) sometimes makes it easier to follow and understand their involvement in the bioconjugate materials. The conjugation of protein with metal NPs not only affords stabilization to the system but also
introduces biocompatibility functionalities into these nanoparticles for further biological interaction or coupling. Proteins (BSA, Cytochrome C) initiate\textsuperscript{86-89} the biomineralization of metal NPs simply by following the reduction of metal. Once atoms are produced, they undergo nucleation process which is simultaneously controlled by the capping/stabilizing behaviour of protein. Here, the physical state of protein that is folded or unfolded plays a governing role in configuring the overall shape and size of NPs.

BSA is composed of 580 amino acid residues with 17 inter-chain disulfide bonds.\textsuperscript{90-92} The overall shape of BSA is oblate and it consists of three domains I, II, and III, which are divided into nine loops. Each domain is made up of a sequence of large-small-large loops forming a triplet. BSA remains in native state up to 40 °C, between 40 - 50 °C, the reversible changes in its conformation occur whereas they become irreversible between 50 - 60 °C. Above 60 °C, unfolding of BSA with $\beta$-aggregation begins which ultimately leads to a gel formation around 70 °C\textsuperscript{44} (Figure 5). The unfolded gel form of BSA is expected to act as a soft template and is the most ideal candidate to study the protein film formation in its soft state. Thus, temperature is the main contributing factor to achieve the gel state, but it also speeds up the reduction and nucleation of NPs. Therefore, an appropriate balance between the temperature and
concentration parameters of a biomineralization process is required to achieve an appropriate protein film formation.

Likewise, DEAE-D (diethylaminoethyl dextran chloride), a bioactive polycationic derivative of dextran, is used for the green chemistry synthesis of bionanomaterials. DEAE-D has high affinity for negatively charged DNA while its cellulose counterpart is used in ion exchange chromatography, protein and nucleic acid purification as well as separation.\textsuperscript{93-95} It is also used as adjuvant in vaccine production,\textsuperscript{96-97} enhances protein and nucleic acid uptake,\textsuperscript{98-99} gene therapy,\textsuperscript{100} and protein stabilizer,\textsuperscript{101} and flocculating agent.\textsuperscript{102-103} Its non-toxic nature allows it to use in oral formulations especially designed to decrease serum cholesterol and triglycerides. These applications primarily related to its water soluble nature based on amphiphilic behavior that arises from neutral sugar backbone and charged quaternary amine side chains. Such amphiphiles are excellent shape directing agents of metal or semiconductor nanoparticles (NPs)\textsuperscript{104-106} due to their versatile colloidal stabilizing behavior. Polymer coating of NPs surface is related to the nature of polyelectrolyte and based on its conformational properties due to the polymer architecture and solvent affinity. Surface adsorption behavior of polyelectrolyte is also closely associated with the fundamental aspect of crystal growth of NPs. Generally, the shape and size of NPs are greatly influenced by the effective passivation of different crystal planes of particular crystal geometry due to the surface coating of a stabilizing agent. A complete passivation of all crystal planes yields a somewhat spherical shape while selective coating allows uncoated planes to preferentially participate in the crystal growth to generate a specific shape. For instance, selective adsorption of an amphiphilic molecule on \{100\} or \{110\} crystal planes of face centered cubic (fcc) geometry leads to the formation of rod shape structures and that is quite common in gold (Au) and silver (Ag) NPs, otherwise it generates plate like morphologies. DEAE-D also possesses the potential of producing shape control morphologies in a typical green chemistry aqueous phase process without using any reducing or stabilizing agent in a single step reaction. Thus, DEAE-D is considered to be an important candidate for a shape control green chemistry synthesis of bionanomaterials with potential applications in bionanotechnology.

1.5 Review of Literature

In this section, the work already done in this direction has been compiled. Hatton et al.\textsuperscript{107} studied the $cmt$ and $cmc$ values of 12 Pluronic poly(ethylene oxide)-poly(propylene
oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers, covering a wide range of molecular weights (2900-14600) and PPO/PEO ratios (0.19-1.79), were determined employing a dye solubilization method. A closed association model was found to describe adequately the copolymer micellization process for the majority of the Pluronics and used to obtain the standard free energies, enthalpies, and entropies of micellization. It was determined that the micellization process is entropy-driven and has an endothermic micellization enthalpy. The hydrophobic part of the pluronics, PPO was responsible for the micellization, apparently due to diminishing hydrogen bonding between water and PPO with increasing temperature. The cmc dependence on temperature and size of head group (PEO) of Pluronics follows a similar trend with lower molecular weight CjEj nonionic surfactants, the effect of temperature being more pronounced with the Pluronics. The PEO-PPO-PEO block copolymers were compared to PPO-PEO-PPO block and PEO-PPO random copolymers, in an attempt to probe the effect of molecular architecture in the formation of micelles. No micelles were observed in aqueous PPO-PPE-PE block copolymer solutions with increasing temperature up to the cloud point.

Thunemann et al.\textsuperscript{108} developed a dedicated combined small-angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) setup to monitor nanoparticles formation in solution. The capabilities of simultaneously deriving particle sizes and oxidation states of atoms/ions are illustrated for the formation of spherical Au NPs by the reduction of hydrogen tetrachloroaurate (HAuCl\textsubscript{4}). Particles with initial radii of 4.60nm and final radii 5.67nm were produced in a levitated droplet with a volume of 4 \(\mu\text{L}\). An ethylene oxide/propylene oxide Triblock copolymer PEO-PPO-PEO (Pluronic F-127) functions as reducing agent and colloidal stabilizer. XANES shows in situ how the gold was reduced in the droplet from Au (III) to Au (0), and simultaneously SAXS recorded the size distribution of the formed nanoparticles.

Liu et al.\textsuperscript{109} studied the effect of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer micelles and their hydrophobicity on the stabilization of gold nanoparticles. Au NPs were prepared by a method developed by Sakai et al. An absorption centered at 300-400 nm in time-dependent UV spectra provided evidence that the very first step of the synthesis was to form primary gold clusters. Then the gold clusters grew in size and were stabilized by block copolymer micelles. The stabilization capacities of the micelles were modulated by tuning the block copolymer concentration, composition and by adding salts. With good stabilization, gold particles were spherical and uniform in size with a diameter of 5-10 nm.
Otherwise they were aggregates with irregular shapes such as triangular, hexagonal, and rod like. The presence of a small amount of NaF significantly increased the stabilization capacity of the micelles and consequently modified the quality of the gold particles. Using FTIR and \textsuperscript{1}H NMR spectroscopy, micellization of the block copolymers and hydrophobicity of the micelles were proven very important for the stabilization. A higher hydrophobicity of the micelle core was expected to favor the entrapment of primary gold clusters and the stabilization of gold nanoparticles.

*Alexandridis et al*\textsuperscript{110} report here the effects of solution properties of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers on the reduction of H\textsubscript{4}AuCl\textsubscript{4} and the size of Au NPs produced. The amphiphilic block copolymer solution properties were modulated by varying the temperature and solvent quality (water, formamide, and their mixtures). They identified two main factors, (i) block copolymer conformation or structure (e.g., loops v/s entanglements, non associated polymers v/s micelles) and (ii) interactions between AuCl\textsubscript{4}\textsuperscript{-} ions and block copolymers (attractive ion-dipole interactions v/s repulsive interactions due to hydrophobicity)\textsuperscript{111} to be important for controlling the competition between the reactivities of AuCl\textsubscript{4}\textsuperscript{-} reduction in the bulk solution to form gold seeds on controlling the shape and size of gold particles. It was observed that the particle size increase with increased temperature in aqueous solutions and attributed to enhanced hydrophobicity of the block copolymer, which favors AuCl\textsubscript{4}\textsuperscript{-} reduction on the surface of seeds. The lower reactivity and higher particle sizes observed in formamide solutions are attributed to the shielding of ion-dipole interaction between AuCl\textsubscript{4}\textsuperscript{-} ions and block copolymers by formamide, which overcomes the beneficial effects of formamide on the block copolymer conformation (lower micelle concentration).

*Burt and colleague*\textsuperscript{112} were the first to explore the use of BSA in Au NPs synthesis. In this initial study, NaBH\textsubscript{4} was utilized to reduce gold ions in the presence of BSA and yielded well-dispersed nanoparticles less than 2 nm in size. Formations of Au NPs were studied by utilizing a variety of spectroscopic characterization techniques. They determined that BSA was conjugated, most likely through its cysteine residues to the surface of the gold nanoparticles. In a separate study, larger gold nanospheres (7.7 ± 0.9 nm in diameter under pH 7 reaction conditions) were obtained when gold ions were reduced in the presence of BSA with UV irradiation.
Singh and colleagues\textsuperscript{113} utilized the surfactant like properties of BSA to produce gold ion charged foams of BSA. These Au ion charged foams were reduced with hydrazine hydrate vapors, producing irregularly shaped gold nanoparticles <100 nm in size. NPs composed of gold-silver alloys were also reported to be produced with this BSA foam and reduction method.

Xie et al\textsuperscript{114} have recently utilized the intrinsic reducing and shape-directing capabilities of BSA to produce gold nanoprisms and nanopolygons in high yields (up to 80\%) under acidic conditions at 37 °C. These authors attributed the appearance of gold nanoplatelets to the slow reaction kinetics imposed by the mild reducing power of BSA and a “surface wrapping” model of nanoparticles formation, where shells of new material sweep across the faces of the growing nanostructures. Au NPs yield and size could be adjusted through the manipulation of reaction temperature, pH, and addition of silver ions.

Gao et al.\textsuperscript{115} examined the effects of plasticization of a kafrin (highly homologous with the maize storage protein zein) film by glycerol in the absence of water by a combination of spectroscopic (NMR and infrared), rheological, and calorimetric methods. The results suggested that at low glycerol levels the glycerol was absorbed onto and possibly into the protein. Increasing the level of glycerol increased the motion of the protein and changed the protein conformation. There were corresponding changes of the mechanical properties of protein films. At 40\% (w/w) of glycerol, two glass transition temperatures were observed, one of which corresponded to the glass transition temperature of pure glycerol. This result indicated that at this level of plasticizer there were sufficient glycerol/glycerol interactions occurring to allow a separate glass formation process for glycerol.

In view of all these studies, a systematic and comprehensive work has been carried out to synthesize and characterize Au NPs by using a series of block copolymers and biomolecules. In all the cases, the aim was to achieve the shape controlled synthesis by utilizing the surface active properties of these complex molecules. Various factors such as folding/defolding of proteins, hydrophilic/hydrophobic properties of block copolymers, and their interfacial adsorption to achieve shape control morphologies at nanoscale have been compared and discussed. Likewise, the materials properties related to the nucleation and subsequent growth of NPs under the capping and stabilizing effects of these molecules have been explored and discussed on the basis of crystal structures of various gold NPs. Finally, all reactions have been carried out and
standardized in aqueous phase so as to preserve the biofunctionalities of biomaterials in view of environmental concerns and green chemistry.

1.6 Objectives and justification

This study is based on the following objectives;

1. **Synthesis of gold nanoparticles by using various block copolymers under the effect of polymer polarity i.e. hydrophilicity or hydrophobicity, Temperature, and their shape controlling abilities of Au NPs.**

2. **Effect of block polymer micelle formation and micelle soft template effect on the self–assembled behavior of Au NPs.**

3. **Understanding the folding – unfolding behavior of various water soluble proteins during the in vitro synthesis of Au NPs and to produce environmental friendly biodegradable protein films for industrial applications.**
1.7 References

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