1.1 Organic–inorganic nanocomposite materials

In material science, study of nanostructured material has become now an identifiable, very broad and multidisciplinary, field of research. It is one of the most visible and emergent research areas in materials science in its broadest sense. The fabrication of nanomaterials has become a highly active research area involving scientists in many different fields, e.g., physics, chemistry, biology, materials science, and engineering. Nanostructured materials include atomic clusters, layered or lamellar films, filamentary structures, and bulk nanostructured materials. Nanostructured materials are...
those materials whose structural elements, clusters, crystallites or molecules, have at least one dimension in the order of the nanometers, i.e., smaller than 100 nm. The physics of such nanoscale materials can be very different from the macroscale properties of the same substance. The properties of materials at nanoscale are often superior that grows the interest behind the research in these materials.

The field of nanostructured materials/nanocomposites involving organic and inorganic components is a rapidly growing area because of their unique properties, and numerous potential applications. In general, nanocomposites can be broadly defined as a mix of dissimilar components; organic and inorganic components are mixed or hybridized at nanometer scale with virtually any composition leading to the formation of hybrid/nanocomposite materials. These materials are nanostructured materials that combine the characteristics of organic and inorganic constituents at the nanoscale. By tailoring the structure of these materials at the nanometer length scale, it should be possible in principle to significantly change their properties at a larger scale. Applications are various and concern optics, electronics, catalysis, coatings, and biotechnologies [1–13].

The construction of organic–inorganic nanostructured materials is an important target of modern materials research to develop functional materials. In the emerging and popular field of nanostructured materials (organic–inorganic composite materials), structural manipulations at an atomic, molecular and/or supramolecular length scale are essential pathways permitting the design of different novel materials. Depending on the desired structures and the exploitation of unique properties that emerge at the nanometer scale, there are several approaches to achieve such a goal. In the nanostructure preparation process, the use of organic manipulators (polymers or surfactants) has been particularly attractive. The organic materials act primarily as templates, leaving an imprint of the organic presence even after their removal. Hybrid nanomaterial/nanocomposites with novel properties can results from the organization of organic templates and the interaction of the inorganic material with organic templates. The reason behind the choice of organic materials in order to prepare the inorganic nanostructure and the organic/inorganic hybrid structures is
probably due to the advantage of tunability of the different properties of organic matrix controlled by the responses of external parameters. Depending upon the prerequisite specific knowledge of the organic templates and the type of inorganic precursor, there are different routes for formation of nanostructured material. In recent literature a variety of significantly different preparation methods have been described [14–36].

Polymeric systems have always played an important role in many nanostructure preparation processes. Among the several million organic compounds (polymer/copolymer systems and different surfactants) with specific self-assembly properties are particularly interesting. With self-organizing materials, including block copolymers, H- and \( \pi \)-bonded complexes, liquid crystals, and biopolymers, hierarchical structures can be formed. The main reason for using polymeric systems as templates is that they can form ordered nanoscale structures in bulk or in solution. These ordered nanostructures are tunable over a broad variety of morphologies ranging from discrete micelles to highly symmetric continuous network structures. Metal nanoparticle preparation in the polymeric system are one of the important building blocks for fabrication of nanostructured materials for wide range of optical, electronic, magnetic, catalytic and biosensing applications [1–13]. The most popular route of nanoparticle synthesis is the chemical reduction process, where metal salts dissolved in an appropriate solvent yields small metal particles of varying size on reduction. In the solution phase the colloidal metal nanoparticles have a tendency to grow in size and agglomerate due to their high reactivity. It becomes necessary to protect them using some capping agents and it is a common practice to use some organic matrix for capping the nanoparticles. Organic molecules such as the alkylthiol are extensively used for preventing the nanoparticle agglomeration [34–36]. Polymers/copolymers with self-assembly properties are also often used as capping agents for this purpose.

Block copolymers (BC) are the focus of intense research efforts because of their intrinsic ability to self-assemble into different nanoscale structures. Block copolymers provide the opportunity to design nanostructured materials, self-assembly of which can be tuned by different parameters such as polymer concentration, solution tem-
perature etc. One class of water soluble block copolymers that has attracted great interest in the literature is the triblock copolymer of poly (ethylene oxide)(PEO) and poly (propylene oxide) (PPO), abbreviated as PEO – PPO – PEO. In aqueous solution different blocks can self-assemble to form micelles with the hydrophobic PPO part as core and the hydrophilic block PEO as corona [37–39] as a result of energetic repulsion between the blocks and/or interaction with water molecules. PEO – PPO – PEO are also known to have demonstrated excellent properties for the synthesis and stabilization of metal nanoparticles [40–53] and are very efficient in both functions. The colloidal stabilization of the metal nanoparticles by PEO – PPO – PEO is due to their amphiphilic character and their ability to form micelles in solution and/or absorption on the surface of the particles [44,45].

In addition to the nanostructure formation in the copolymer matrix, there are molecules short length in size and aphiphilic in nature that can form highly organized Langmuir–Blodgett (LB) films. The ultra thin LB films are known to be suitable precursor for the growth of semiconducting nanostructures within the nanometric inter layer spacing through post deposition treatments. Ultrathin metal–organic films formed by the LB technique can be extremely useful to explore physics and chemistry in confined geometries due to possibility of having well–defined molecular orientation and ordering in these films. LB multilayers are a suitable precursor for the growth of semiconducting nanostructures within the nanometric inter layer spacing through post deposition treatments [54–60]. In this approach the multilayer structures act as a template and better control over size and shape of nanoclusters are expected. It was shown that by exposing a cadmium arachidate (CdA) LB film in a $H_2S$ environment CdS nanostructures can be formed [54,56]. There are important issues such as the kinetics of CdS formation, growth and organization of nanoclusters within the LB matrix and the over–all structure of the resulting composite multilayers that need to be addressed. These issues have important technological implications for the practical use of these nanocomposite systems in novel nanostructured devices. There is a fairly large amount of literature where different aspects of CdS–fatty acid LB systems have been discussed regarding growth
and organization of nanoclusters within the LB matrix. Several early papers describe these nanoclusters as nanoparticles [56–58]. Whereas, more recent publications claims they are quasi two dimensional sheets [54,59,60]. It is observed that different investigations with apparently similar LB films demonstrate different degree of modification on sulfidation [54,59–61]. It is also observed that larger exposure of $H_2S$ is required for thicker LB films for saturation of reaction [61]. It therefore indicates that initial structures of the LB films have control over the nature of CdS formation and structural modifications in these films. The kinetics of structural and morphological evolution due to CdS formation, growth and organization of nanoclusters within the LB matrix are very important issues that need to be understood properly to improve the technological implications of these nanocomposite systems in novel device application.

In this thesis we have studied the formation of nanostructures within two different organic matrices; long chain triblock copolymers and the short length aphiphilic molecules (fatty acid metal salts) have been used to explore the specific property of a particular molecule that can be used to prepare nano structure materials. A detailed study was performed to understand the structural properties as well as chemical modification due to the formation of nano structure inside the organic matrix. In the following two sections detail general properties of the two chosen organic templates have been discussed.

1.2 Triblock Copolymer: Long Chain Molecular Matrix

1.2.1 Block copolymer and its properties

Block copolymers are special type of polymers in which each molecule consists of two or more segments of simple polymers (blocks) joined covalently in certain arrangements. In particular, polymers can be divided in homopolymers and copolymers. Homopolymer is composed of the same type of monomers, and in case of copoly-
1.2. Triblock Copolymer: Long Chain Molecular Matrix

Two blocks joined

Three blocks joined

Three blocks joined

More than three blocks joined

Figure 1.2.1: The schematic diagram shows the arrangement of blocks in an AB-diblock, an ABA-triblock, an ABC-triblock, and a multiblock (starblock).

mers, each molecule is composed of more than one type of monomers in different arrangements. Different monomers are organized into distinct segments, or blocks. The number of blocks and their arrangements further classify the block copolymer: block copolymers with two, three, and more blocks are called diblocks, triblocks, and multiblocks respectively. During the formation of block copolymer different arrangements are possible; some arrangements are linear, in which the blocks are connected end-to-end and some are in star arrangement, in which all the blocks are connected via one of their ends at a single junction although more complicated arrangements may also be possible. The number of monomer types in a block copolymer may be less than or equal to the number of blocks. Thus, an ABC linear triblock consists of three monomer types, whereas an ABA linear triblock consists of two monomer types. Figure 1.2.1 shows a simple schematic of different numbers and arrangements of block copolymers.

The importance of block copolymers can be seen in their wide array of properties. These properties are made possible due to the combination of different polymers in alternating sequence. When more than one different polymer blocks are joined to
form a block copolymer, it is very obvious that different kinds of polymers can be used and it is very promising, since they (individual blocks) offer a morphological and chemical diversity which is not found in a single block (homopolymers). Depending upon the specific requirements one can introduce a polymer block having specific property into the block copolymer (diblock, triblock, and/or multiblock) that can serve the specific need.

Most importantly, for a given block copolymer system, a solvent may be a neutral (a good solvent for all the blocks) or selective (a good solvent for one but a non-solvent for others and vise versa). Therefore, depending upon the selectivity of the solvent, the dissolution and the phase behaviour of block copolymers can be varied, as a result, copolymer self-assembles to different aggregations such as stable micelles and a variety of structures [37–39, 62–67]. Solvent selectivity and, hence, copolymer self-assembly, have been observed for a variety of block copolymers in water, polar, and non-polar organic solvents. For this generality and the possibility of tuning the aggregate properties by varying several parameters such as kind of monomer, the size and block length, these copolymer self-assembled aggregates are able to provide a much wider range of applications than that observed for normal surfactants.

Particularly, we are interested to the water soluble triblock copolymers. A block copolymer with hydrophilic and hydrophobic moieties belongs to the class of surfactants, and depending on molecular characteristics, it may be soluble or insoluble in water. In other words these are amphiphilic in nature; hydrophilic part dissolve in water keeping the hydrophobic part insoluble which leads to the self-assembly in water to form micelles or other aggregates [37, 38, 67, 68]. A large number of literatures are found where different block copolymers have been examined in details and the most extensively studied copolymers are the ethylene oxide–propylene oxide (EO – PO) based diblock/ triblock copolymers [37–39, 67, 69–71].

Out of large number block copolymers, an interesting class of block copolymeric amphiphiles is of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), $PEO – PPO – PEO$ triblock copolymer with structure shown in the schematic (figure 1.2.2). In general $PEO_x – PPO_y – PEO_z$ is well-known commercially available
non–ionic macromolecular counterpart of ordinary surfactants, having widespread applications where \( x, y, \) and \( z \) denote the number of ethylene–oxide and propylene–oxide units per block and are available in a range of \( x, y, \) and \( z \) values. These are low–cost, biocompatible copolymers that may display varied solution behavior, depending on their \( PEO – PPO \) ratio and polymer molecular weight. The end \( PEO \) block is hydrophilic due to a very favourable fitting of the ethylene–oxide monomer into the water structure and \( PPO \) middle block is partially soluble in water. In water \( PPO \) develops a hydration shell characterized by the enhanced structuring of the water molecules. Although \( PPO \) has the same backbone structure as \( PEO, \) a most favourable water structures can not be formed, since the presence of methyl group \( (CH_3) \) in the side chain of \( PPO \) monomer unit constitute a steric hindrances. As a result the water molecules form less hydrogen bonding with \( PPO \) as compared to \( PEO. \) This is the reason why \( PPO \) is partially soluble in water.

This triblock copolymers \( (PEO – PPO – PEO) \) consisting a hydrophobic \( PEO \) leads to self–assembly into micelle structures in aqueous solutions with the hydrophobic \( PPO \) part as core and the hydrophilic block \( PEO \) as corona. Depending upon the molecular weight, the block sizes, the solvent composition and solubility of triblock copolymer, it is possible to have different kinds of micelles and micellar aggregation in solution. In regard to the solubility of the copolymer in water, an important feature of its solution behaviour is that \( PEO \) hydration is strongly temperature and concentration dependent, producing an upper critical solution conditions. The important consequence is that copolymer self–assembly, micelle formation and different micellar structures can be tuned by temperature and copolymer concentration.
1.2. Triblock Copolymer: Long Chain Molecular Matrix

1.2.2 Temperature and concentration dependent aggregation: CMC and CMT

A significant property of PEO – PPO – PEO is the ability of individual block copolymer molecules, termed unimers, to self-assemble into micelles in aqueous solutions. This aggregation process may be directed by changes in both concentration and temperature. During the initial aggregation step, from unimers to micelles, the concentration at which micelles start to appear is called critical micelle concentration (CMC), a process called micellization. Similarly, the temperature at which, for a given polymer concentration, micelles are formed, is called critical micelle temperature (CMT). The unimers form molecular solutions in water at block copolymer concentrations below that of the CMC and at temperature below CMT. Beyond CMC, if we increase the copolymer concentration further, aggregations can be formed at higher concentration as shown in figure 1.2.3. At higher polymer concentrations, ordered packing of spherical micelles of the PEO – PPO – PEO copolymers can form the homogeneous, immobile gel-like structures (usually a cubic structures; body centered cubic or face-centered cubic, bcc or fcc, respectively) and a large number of various lyotropic liquid crystalline phases [72]. We are interested here in the detailed study of the thermo-responsive nature of PEO – PPO – PEO.

Several techniques have been employed to study the aqueous solution behaviour of PEO – PPO – PEO block copolymers micellization, phase behaviour, and determination of CMC and CMT values, similar to investigations with normal surfactants. These include static and dynamic light scattering [73–77], SANS [70, 76, 78, 79], static and time resolved fluorescence [80, 81], FTIR [82, 83], surface tension [84, 85], viscosity [73, 86], etc.

Among the large number of methods dynamic light scattering (DLS) measurements can be used to study unimer and micellar distribution of the copolymer solution. It is also possible to have an idea of the CMC value of copolymers by this measurements. To find the CMC of the polymer, hydrodynamic size measurements for the polymer solutions have been performed for a range of concentrations using Dynamic Light
Micelles form further aggregate at a high enough concentration:

![Diagram of micelle formation](image)

**Figure 1.2.3:** The schematic diagram shows the individual block copolymer molecules (unimers) to self-assemble into micelles and to some higher aggregates in aqueous solutions.

Scattering (DLS). Hydrodynamic size measurements for the polymer solutions have been performed for a range of concentrations as shown in figure 1.2.4. At lower concentration two distributions of intensity was observed. The peak at lower size was due to the unimer contribution and that at higher size corresponds to the micelles. In the increasing solution concentration unimer contribution gradually reduces and the micellar contribution increases. At certain concentration (0.7 mM for our case) the micellar contribution was found to dominate over the unimer contribution. This transition concentration was taken as CMC of the polymer following the work of Brown et al [87].

Similar to the concentration dependence the amphiphilic character of PEO–PPO–PEO copolymer changes as a function of temperature. These lead to the interesting phase behaviour and/or copolymer self-assembly when dissolved in water. The temperature dependence is driven by the solubility of copolymer that depends on temperature. Water is unique in terms of its property as solvent, which arises due to the formation of strong hydrogen bridging network among polar solvent. It is well
Figure 1.2.4: Hydrodynamic diameter distribution observed from DLS for the pure triblock copolymer in terms of intensity (%) (relative percentage light intensity scattered by particles of different sizes) at different concentration. The curves are shifted vertically for clarity.

known that PEO and PPO is well hydrated and PEO - PPO - PEO copolymer exists as unimers in aqueous solution at lower temperature. At higher temperatures PPO moieties become hydrophobic and at certain temperature it form micelles with hydrophobic PPO as core and hydrated PEO as corona as we discussed earlier and the temperature is known as CMT. If we increases temperature far beyond the CMT, PEO also shows slight dehydration with increasing temperature but keep the water contact. If we continuously increase the temperature, the slightly dehydrated PEO chain lead to the dehydrated corona and thus the size of micelles may be reduced.

In order to see the thermal responses of the copolymer aqueous solution, a detail temperature dependent DLS measurements has been performed as shown in figure 1.2.5. Hydrodynamic size measurements for the polymer solutions of concentration slightly greater than the CMC have been performed for a range of temperatures (from room temperature to 90°C). At 25°C two distributions of intensity was observed as expected. The peak at lower size was due to the unimer contribution and that at higher size corresponds to the micelles. At higher temperature (30°C) the only
the micellar contribution exist with slightly smaller size of the micelles. As we have discussed earlier, the $PEO$ chain will also be slightly dehydrated at higher temperature which lead to the dehydrated corona and thus the size of micelles may be reduced. Thus the CMT of this copolymer solution of concentration slightly greater than CMC must be laid between $25°C$ and $30°C$. It is interesting to note that if we increase the temperature beyond this temperature a single peak corresponding to micelle of constant size was observed in a temperature range of $35$ to $90°C$. So from the above discussion we can say the $PEO-PPPO-PEO$ triblock copolymer is thermo-responsive which lead to the formation of different self-assembled structures that can be tuned by changing the temperature.

Another important property of $PEO-PPPO-PEO$ is that it can synthesize metal nano particles from their metal complexes and the polymer self-assembly stabilizes the reduced metal nano particles in the solution. It possesses dual properties and is efficient in both the functions. It is known that in the $PEO$ part of the copolymer the repeating ether units ($-CH_2CH-\cdot O\cdot$-) can bind cations and/or metal complexes and can form crown ether-like structures. Metal complexes can be reduced to the...
respective metal nanoparticles by the oxidation of the oxyethylene groups in air-saturated aqueous solutions [40–53]. We have already seen that PEO–PPO–PEO copolymer forms micelles which is affected by concentration and temperatures. The corona of the micelles are composed of hydrated PEO that forms the surface cavity which are in direct contact with the aqueous phase. Any cations and/or metal complexes in the solution can easily interact with the ether unit of the PEO in the corona of the micelles and the metal cation are reduced to respective metal nanoparticles. It is interesting to note that copolymer self-assembly can be easily varied by the temperature and concentration. Thus, any change in the micelle environments brought about by the temperature causes significant changes in the arrangements as well as the number of surface cavities. So it is possible to use the copolymer micelles as the templates for the preparation and colloidal stabilization of nanoparticles and/or copolymer–metal nanocomposites in absence of any organic reducing agents unlike the other standard synthesis process where organic reducing agents and stabilization components are required. It is environmentally benign and economical since it involves only water and non-toxic commercially available biocompatible block copolymers.

1.3 Langmuir–Blodgett film: short length molecular matrix

1.3.1 Langmuir monolayer forming amphiphiles

The Langmuir–Blodgett technique is a way of making ultra thin organic films with a controlled layer structures. It can be formed by the successive deposition of a series of monolayers of one or more types of amphiphilic molecules initially spread at the air–water interface onto solid substrates. This technique was first introduced by Irving Langmuir [88] and extensively applied by Katharine Blodgett [89, 90] involving the vertical movement of a solid substrate through monolayer–air interface. Langmuir–Blodgett films possess interesting properties such as controllable thickness,
surface uniformity, and a high degree of orientation, which make them potential candidates for technological application such as electronic device and sensors.

The molecules which can form a Langmuir monolayer are called amphiphiles [91–93] with a hydrophilic part (soluble in water) and a hydrophobic part (insoluble in water). On water surface these molecules take a preferential orientation with the hydrophilic part immerse in water while the hydrophobic part stay away from water surface. The water loving part is called head and the suspended hydrophobic part that stay in air is called tail. The most common class of molecules which has this properties are fatty acid with varying chain length such as arachidic acid, stearic acid and its higher homologous with the general chemical formula \( (C_nH_{2n+1})COOH \). Arachidic acid \( (C_{18}H_{39})COOH; n = 19 \) is one of the stable monolayer forming fatty acid on water surface. The polar acid group \((COOH)\) confers the water solubility while hydrophobic chain prevent it. The amphiphilicity depends on the balance between these two opposing forces that results in the formation of an insoluble monolayer at the air–water interface depending upon the hydrophilicity of head group and the hydrophobicity of tail. So in order to have stable monolayer, the hydrocarbon chain of the substance used for monolayer studies has to be long enough. A rule of thumb is that there should be more than 12 hydrocarbon units or groups in the chain \(((CH_2)_n, n > 12)\) [94]. If the chain is shorter, though still insoluble in water, the amphiphile on the water surface tend to form micelles. These micelles are water soluble, which prevents to build–up of a monolayer at the interface. On the other hand if the length of the chain is too long the amphiphile tends to crystallize on the water surface and consequently does not form a monolayer. It is difficult to determine the optimal length for the hydrocarbon chain because its film forming ability also depends on the polar part of the amphiphile. Figure 1.3.1 schematically shows the preferential orientation of arachidic acid on water surface with the hydrophilic head immersed in water while the hydrophobic tail stays away from water.

The most important physical property of Langmuir monolayer is its surface tension. But the measurable quantity is the surface pressure [88], one can measure
1.3. Langmuir–Blodgett film: short length molecular matrix

1.3.1: Schematic illustration of (left) typical amphiphilic molecule (arachidic acid) and (right) the orientation of arachidic acid adopted at air–water interface.

the difference in surface tension between a clean or pure liquid (subphase) and that covered by the monolayer. Surface pressure is thus defined [94] as

\[ \pi = \gamma_0 - \gamma_f \]  

where \( \gamma_0 \) is the surface tension of the pure liquid and \( \gamma_f \) is the surface tension of the film covered surface. The detail surface tension measuring procedure will be discussed later.

The equipment used for the preparation of Langmuir monolayer is traditionally known as ‘Langmuir Trough’. Figure 1.3.2 shows the schematic diagram of the trough holding the required liquid subphase is usually made of Teflon to prevent any leakage of the subphase over the edges. Two barrier compresses the monolayer up to a required pressure. The surface pressure measuring arrangement (Wilhelmy plate) and other supporting accessories are indicated in figure 1.3.2. Figure 1.3.3 shows the instrument used for our experiments where the important components are indicated. The surface pressure and the mean molecular area are continuously monitored during the compression. The surface pressure is measured by the Wilhelmy plate method.
1.3. Langmuir–Blodgett film: short length molecular matrix

In this method a measurement is made by determining the force due to surface tension on a plate suspended so that it is partially immersed in the subphase as discussed later. The trough and the barriers arrangements must provide the means for constraining and compressing the monolayer.

To prepare Langmuir monolayer of any material on water surface, the amphiphiles are dissolved in appropriate solvent and the solution is spread on water surface. It is desirable that the solvent should be capable of dispersing the molecules of the film forming material at the air–water interface and evaporate completely. So the solvent should be extremely volatile so that it evaporate within a short time and only the molecules then left spread over the whole water surface. The solvent which have boiling point in the range 40 – 80°C are generally most suitable for experiments under ordinary condition.

There are several properties of the monolayer like surface pressure, surface potential [91,94,95], and surface viscosity [91,93,94]. But the commonly characterized properties of a Langmuir monolayer is the surface pressure and its variation with surface area [96], temperature [92,96], metal ions [97,98], subphase pH [99], compression rate [100], time [101] etc.
Surface Pressure Measurement

In the Wilhelmy method, an absolute measurement is made by determining the force due to surface tension on a plate or other object suspended so that it is partially immersed in the Langmuir monolayer, and this is compared with a similar absolute measurement on a reference surface, e.g., a clean water surface. In the common form of the Wilhelmy [102] balance, a thin plate, usually of platinum, is suspended in the liquid surface as shown in figure 1.3.4. The forces acting on the plate then consist of the gravitational and surface tension effects, downward, partially offset by the buoyant effect due to the weight of liquid displaced.

For a rectangular plate of dimensions \( t \times w \) with thickness \( t \) of material density \( \rho_p \) immersed to a depth \( h \) in a liquid of density \( \rho_l \), the net downward force is given by the following equation

\[
| \mathbf{F} | = \rho_p g t w t + 2\gamma (t + w) \cos \theta - \rho_l g t w h
\]  

(1.3.2)

where \( \gamma \) is the liquid surface tension, \( \theta \) is the contact angle of the liquid on the solid plate, and \( g \) is the gravitational constant. The surface pressure is then determined by measuring the change in \( \mathbf{F} \) for a stationary plate between a clean surface and the same surface with a monolayer present as defined by the equation 1.3.1. If the
plate is completely wetted by the liquid (i.e., \( \cos \theta = 1 \)) the surface pressure is then obtained from the following equation with the help of equation 1.3.1 and 1.3.2:

\[
\Pi = - \Delta \gamma = \frac{\Delta |F|}{2(t + w)}
\]  (1.3.3)

If the plate is very thin, then the plate thickness \( t \) can be negligible with respect to \( w \) and the above equation can be written as

\[
\Pi = - \frac{1}{2} \rho g t \Delta h
\]  (1.3.4)

It is apparent from the above equation that the sensitivity can be increased greatly by using a very thin plate.

The most important and basic information about a monolayer is the surface pressure (\( \pi \))-specific molecular area (\( A \)) isotherm. Figure 1.3.5 shows the schematic of a typical surface pressure (\( \pi \))-specific molecular area (\( A \)) isotherm for a Langmuir monolayer. Usually an isotherm is recorded by compressing the film (reducing the area with the barriers) at a constant rate while continuously monitoring the surface pressure.

Different distinct regions is observed on examining the isotherm which are called phases [92]. When the monolayer is compressed it can pass through several different phases which are identified as discontinuities in the isotherm as indicated in figure...
1.3. Langmuir-Blodgett film: short length molecular matrix

![Figure 1.3.5: Schematic of a typical surface pressure (\(\pi\)) versus area (A) isotherm. The different phases are indicated [92].](image)

1.3.5. The phase behaviour of the monolayer is mainly determined by the different physical and chemical properties of the amphiphile such as the subphase composition, pH, and subphase temperature [103]. For example, various monolayer states exist depending on the length of the hydrocarbon chain and the magnitude of other cohesive and repulsive forces existing between head groups [103].

1.3.2 Langmuir–Blodgett film Deposition

The prepared monolayer at air–water interface of desired amphiphile can subsequently be transferred onto a solid substrate. It can be done by passing a substrate alternatively upwards and downwards through the monolayer while simultaneously keeping the surface pressure constant with a computer controlled feedback system between the electrobalance measuring the surface pressure and the barrier moving mechanism. As a result, the floating monolayer is absorbed to the solid substrate during each pass producing a monolayer film on the substrate. However, the molecules deposited on the upward pass have their polar head group oriented towards the substrate while the molecules deposited on the downward pass are oriented with the hydrophobic tails towards the substrates surface. During multiple dipping the head group adhere to the
1.3. Langmuir-Blodgett film: short length molecular matrix

headgroup of the previous layer during the upstroke and the tail stick to the tails of previous layers during downstroke, in accord with what we expect from amphiphilic molecules. In this way highly oriented multilayer structure can be produced, which are commonly called Langmuir-Blodgett or simply LB films. The deposition process is schematically shown in figure 1.3.6.

The LB film deposition is mainly carried out in the solid phase (as shown in figure 1.3.5) of the monolayer at air–water interface. The surface pressure is very high (20 – 40 mN/m for arachidic acid) so that the high cohesion between the molecules in the monolayer maintains the stability during transfer. The energetic amphiphilic interaction basically determines the engineering of structural modifications of the LB film. It is possible to produce different arrangements in the multilayer LB films depending upon the different situations. The most common type of LB deposition leads to Y-type centrosymmetric multilayer films, which is produced when the monolayer deposits to the solid substrate in both up and down directions. A typical structure is shown in figure 1.3.6. It is possible to form film only in up stroke or in downstroke, the multilayer structure is called either Z-type (upstroke deposition only) and X-type (downstroke deposition only).

The quantity and the quality of the deposited LB films on solid substrate is measured by transfer ration (TR). During the deposition the surface area of the Langmuir monolayer on subphase decreases due to the loss of molecules to the substrate. The transfer ratio is defined as ratio of the decrease on monolayer area ($A_1$) and the area of the substrate ($A_s$). For an ideal transfer, a TR of unity is indicative of good deposition and, in fact values near unity are often observed under certain conditions although LB transfer is a complicated process. In general, amphiphiles attempt to reach a new equilibrium (thermodynamic minimum) as they experience interactions with the solid substrate. If there is any changes in packing density during transfer or loss of molecules due to high hydrlphilic interaction with subphase, then TR = 1 will not be the indicator of a defect–free film.

Langmuir monolayers are used as models for two-dimensional system, as they are easily achieved and are robust enough for studying structural change [92] and phase
1.3. Langmuir–Blodgett film: short length molecular matrix

Monolayer on water

Figure 1.3.6: Conventional schematic of the LB film deposition technique using a hydrophilic substrate. First, suitable amphiphilic molecule is dissolved in a volatile solvent that is then spread at the air–water interface to form a Langmuir monolayer. Then, to prepare LB film a substrate is passed through the interface a given number of times, with each pass adding another monolayer to the LB film with alternating molecular orientations. The successive steps are shown by arrow.
1.3. Langmuir–Blodgett film: short length molecular matrix

transitions in two-dimension \cite{104,105}. Other than this basic interest, Langmuir monolayers are used of course as precursors for LB films on solid substrates \cite{89,90} and also can be used as templates for bio-mimetic growth, i.e., to grow specially oriented crystals from super saturated aqueous salts \cite{106,107}. The greatest advantage to work with Langmuir monolayers is that their structures and properties can be tuned easily by changing different physical and chemical properties like surface pressure \cite{96}, temperature \cite{92,96}, pH \cite{99}, dissolved metal ion concentration \cite{99} etc. It has also been observed that over and above pure organic monolayers, Langmuir monolayers in presence of inorganic materials makes the system rich both in structural and physical aspects. As an example, organic monolayers of long chain fatty acids in presence of divalent metal ions in the aqueous subphase shows rich 2–dimensional structural patterns of the organic and inorganic parts at the air–water interface.

In addition to the simple fatty acids, it is possible to form stable monolayers of several other amphiphilic molecules and/or organic compounds like phospholipids, alcohols, esters, acetates as well as polymers \cite{94}. Here, in the present thesis, we will concentrate on the most widely studied class of LB films of metal salts of fatty acids instead of simply fatty acid. In this case, bivalent metal ions are mixed with the water subphase at a very low concentration (~ $10^{-4}M$). A monolayer of the fatty acid forms at the air–water interface and ion exchange between the protons of the fatty acid and the metal ions in solution occurs if the pH and the metal ion concentration are in the required range as a result the metal ions attach themselves electrostatically to the dissociated fatty acid head groups. In the deposited layer, the bivalent metal ion coordinates four oxygen atoms in two fatty acid molecules in adjacent monolayers \cite{108}. Although several other coordination (unidentate, bidentate bridging, bidentate chelate etc \cite{109}) may possible depending upon the different subphase conditions (subphase pH, different divalent metal ions). For an example, an arachidic acid monolayer spread on a $5 \times 10^{-4}M\ CdCl_2$, the divalent metal ion and fatty acid proton exchange occurs above approximately pH 5 \cite{110,111}
1.4. Our work and outline of the thesis

and the exchange reaction can be written as

\[ Cd^{2+}(Cl^{-})_2 + 2(CH_3(CH_2)_nCOOH \rightarrow Cd(CH_3(CH_2)_nCOO^-) + 2HCl \] (1.3.5)

By the same reaction mechanism, several other divalent ions such as \( Ba^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} \) etc can be used for the preparation of LB film of fatty acid salts. For our experiments we have prepared the cadmium arachidate LB film of mono and multilayers.

1.4 Our work and outline of the thesis

In this thesis we have studied the formation of nanostructures within two different organic matrices. In order to do that we have studied the long chain triblock copolymer and short length amphiphilic molecules (metal salts of fatty acid) to explore the specific properties of molecular self-assembly that can be used to prepare nanostructured materials. A detailed study was performed to understand the structural properties as well as chemical modification due to the formation of nanostructures inside the organic matrix.

In Chapter 1, we have made a brief review on the two different organic templates used for our works. In Chapter 2, we have outlined the experimental techniques and the instruments that were used to perform the investigations described in the present thesis are discussed. Chapter 3 describe an important nanocomposite system; silver nanoparticles in the long chain amphiphilic molecules such as \( PEO - PPO - PEO \) triblock copolymer. \( PEO - PPO - PEO \) provide the opportunity to design the nanostructured materials, self-assembly of which can be tuned by temperature (thermo-responsive). Water soluble triblock copolymers \( PEO - PPO - PEO \) are also known to have demonstrated excellent properties for the synthesis and stabilization of metal nanoparticles [40-53]. These amphiphilic block copolymers act as reductants as well as colloidal stabilizers and are very efficient in both functions. Motivated by the fascinating self-assembly behaviour of \( PEO - PPO - PEO \) and its ability to
synthesize metal nanoparticles, detailed investigation of silver–PEO–PPO–PEO nanocomposite formation and their self-assembly were performed. As the copolymer are *thermo-responsive* effect of temperature on formation and stabilization of silver nanoparticles has been investigated systematically [112, 113]. The reactions were carried out in the PEO–PPO–PEO micellar cavities at different temperatures by in-situ reduction of a silver–ammonia complex \([\text{Ag(NH}_3\text{)}_2]^+\) without any additional post reduction treatment. It is known that in the PEO part of the copolymer the repeating ether units \((-\text{CH}_2\text{CH}_2\text{O}-\) can bind cations and can form crown ether-like structures. It was found that the silver ammonia complex ions \([\text{Ag(NH}_3\text{)}_2]^+\) can be bound in the copolymer matrix and the silver can be reduced by the oxyethylene groups [40–43, 112] of the copolymer. We have observed that silver nanoparticle formation and their colloidal stability can be tuned by changing the synthesis temperature [112].

In a temperature dependent study we have found that there was an intermediate temperature at which one obtains small silver nanoparticles of narrow size distribution. We observed that samples prepared at different temperatures were associated with different modifications or degradations of the block copolymer. However, there is no specific information regarding the chemical nature of the polymer due to the nanoparticle formation in the literature. Motivated by the absence of adequate information the present study was directed towards the characterization of the nanocomposite in general and understanding of the modified/degraded polymer formed as a result of in-situ reduction of the silver salt to metallic nanoparticles in particular.

In the present work the main emphasis was given to the synthesis and self-assembly of silver–PEO–PPO–PEO composites at various temperatures [112]. Specifically, details are provided on (i) the preparation and stabilization of nanoparticle dispersions [112] and (ii) self-assembly of nanocomposite onto different solid surfaces [113]. Self-assembled thin films from the solver–copolymer composite have been prepared by dip coating on silicon substrates. Different morphologies of the films prepared at different conditions on hydrophilic and hydrophobic substrates have been studied using SEM [113]. From the detailed XPS, NEXAFS and FTIR analysis we have
qualitatively explained the silver–copolymer nanocomposite formation mechanism and the effect of temperature were studied in detail.

In chapter 4 we have studied another system, Langmuir–Blodgett film of metal salt of arachidic acid for the preparation of nanostructure inside LB matrix. Ultrathin metal–organic films formed by the Langmuir–Blodgett (LB) technique can be extremely useful to explore physics and chemistry in confined geometries due to possibility of having well-defined molecular orientation and ordering in these films. It was shown that by exposing a cadmium arachidate (CdA) LB film in a $H_2S$ environment CdS nanostructures can be formed [54,56]. There are important issues such as the kinetics of CdS formation, growth, and organization of nanoclusters within the LB matrix and the over-all structure of the resulting composite multilayers that need to be addressed. These issues have important technological implications for the practical use of these nanocomposite systems in novel nanostructured devices. To examine the issues like the shape of the CdS clusters, time, and thickness dependence of chemical conversion and to study the correlation between the pre- and post-sulfidation structure of the LB films on CdS formation, a set of multilayer cadmium arachidate LB films grown with different morphology and thickness have been studied using AFM, TEM, X-ray reflectivity, and XPS [114]. Microscopic evidence of formation of nearly uniform CdS nanoparticles of around 4.5 nm in the LB matrix was observed. One important point has been addressed in this study is the generated pressure by the formation of CdS in the films and its expected outcome. Therefore to understand the nature of pressure induced changes and their correlation with the initial structure, a set of LB films with different initial compactness has been studied. In relatively compact films, mount like structures were found to develop due to out-of-plane molecular motion, whereas, for non-compact films, expansion and molecular rearrangement appears to reduce the height non-uniformity and smooth out the surface as a result of sulfidation. From the detailed chemical analysis it was found that full conversion of cadmium arachidate to CdS was not achieved in the LB matrix even after a long exposure and the time required for conversion was found to be independent of film thickness, both contrary to the earlier observation [114]. A partial conversion of a maximum of around 60%
could be achieved in the films of various thickness and compactness indicating that partial survival of the layered structure after sulfidation may be possible in initially compact films. Therefore it is very difficult to have structural information of the modified LB layer due to the presence unmodified layered structure after sulfidation which may often misinterprets the data of conventional technique.

We have employed a novel technique for the study of structural aspects of multilayer LB films of cadmium arachidate deposited on silicon substrates with the help of XPS. For insulating samples, when a photon creates a photoelectron, a net positive charge is left behind. These positive charges accumulate over the surface as the electron current flow into the insulator is insufficient to compensate for the electron loss. This causes differential charging which is often regarded as a problem in X-ray photoelectron spectroscopy (XPS) studies, especially for insulating or partially conducting samples [123]. Neutralization techniques have been developed to circumvent this effect. Instead of neutralizing the positive charge, which is often the technique to obtain good quality data, it is possible to exploit this phenomenon to get useful information about the sample. An attempt is made here to use this differential charging to study the mono and multilayer Langmuir–Blodgett (LB) films of cadmium arachidate on silicon substrate [116, 117]. The surface potential was probed by measuring XPS line shift with respect to their neutral position and was found to have correlation with the thickness of the films. No differential charging was observed in the mono layer LB whereas significant differential charging was observed for multilayer films. The total charging as well as the differential charging in these films increase with increasing number of layers. Analyzing the differential charging for multilayer films with the help of angle-dependent XPS measurements structural information was extracted. This technique has been successfully applied to study the structures of the modified LB films after nanostructure formation.

A schematic representation of the formation of different nanostructure studied in the present thesis is shown in the block diagram (figure 1.4.1). Lastly, in chapter 5, we have made a short summary and some outlook on the total works.
1.4. Our work and outline of the thesis

Nano scale design

Soft material (organic material)

Hard material (metal, semiconductor nanostructures)

Figure 1.4.1: A schematic representation of the formation of different nanostructure studied in the present thesis.