Chapter 1

Introduction

1.1 Supramolecular Assemblies

In conventional or molecular chemistry atoms unite to give more and more complex molecules, which in turn associate into aggregates and membranes. Chemistry is the science of matter and of its transformations, providing structures having specific properties. It also develops processes for the synthesis of structures.

Molecular chemistry has explained the covalent bond. Beyond molecular chemistry based on the covalent bond, lies supramolecular chemistry, which tries to understand and to gain control over the non-covalent intermolecular bond or forces. There is increasing complexity beyond the molecule towards the supramolecule and organized polymolecular systems, held together by non-covalent interactions. Non-covalent interactions define the intercomponent bond, the stability and fragility of multi-molecular assemblies, their tendency to associate or to isolate themselves and their selectivity i.e., their ability to recognize each other.

The design of molecular systems capable of displaying processes of high efficiency and selectivity requires the correct manipulation of the energy and stereochemical features of non-covalent, intermolecular forces (electrostatic interactions, hydrogen bonding, van der Waals forces, etc.) within a defined supramolecular structure.
1.2. Intermolecular Forces and Their Manipulation

Supramolecular species are characterized both by the spatial arrangement of their components and the nature of intermolecular bonds. Various types of interactions may be distinguished, with different degrees of strength, directionality, dependence on distance and angles: metal ion coordination, electrostatic forces, hydrogen bonding, van der Waals interactions, donor-acceptor interactions, etc. Their strengths range from weak or moderate as in hydrogen bonds, to strong or very strong for metal ion coordination. Intermolecular forces are in general weaker than covalent bonds, so supramolecular assemblies are thermodynamically less stable, more labile and more flexible than molecules.

Supramolecules are well-defined, discrete assemblies that result from intermolecular association of a few molecules whereas supramolecular assemblies are multimolecular entities that result from the spontaneous association of a large, undefined number of molecules into a specific phase having more or less well-defined microscopic organization and macroscopic characteristics depending on its nature, such as films, layers, membranes, vesicles, micelles, mesomorphic phases, solid state structures, etc. Thus supramolecular studies cover all types of molecular associations, from the smallest dimer to the largest, the organized phase, and to their designed manipulation [1].

The highly selective processes of molecular recognition are of stereochemical nature. Thus, a supramolecular stereochemistry may be defined that extends from supramolecules to polymolecular assemblies. Different spatial dispositions of the components of a supramolecule with respect to each other lead to supramolecular stereoisomers. Their eventual interconversion will depend on the properties of the interactions that hold them together, i.e., on the variation of the intermolecular interaction energy with distances and angles. There is thus an intermolecular conformational analysis like there is an intramolecular one [1].

1.2 Intermolecular Forces and Their Manipulation

Intermolecular forces can be broadly classified into three categories. In the first category are those of purely electrostatic origin arising from the Coulomb force, such as the interac-
1.2. Intermolecular Forces and Their Manipulation

Intermolecular forces are the forces that act between atoms, molecules, or ions that are not bonded to each other by chemical interactions. These forces arise from three main categories: (1) forces between charges, permanent dipoles, quadruples, etc.; (2) polarization forces that arise from the dipole moments induced in atoms and molecules by the electric fields of nearby charges and permanent dipoles, such as interactions in a solvent medium; and (3) forces that are quantum mechanical in nature. These three categories should be considered as neither rigid nor exhaustive: for certain types of forces, e.g., van der Waals forces, an unambiguous classification is not possible. Some intermolecular interactions (e.g., magnetic forces) are always very weak for the systems I shall consider.

Forces between unbonded discrete atoms or molecules are usually called 'physical forces' and they give rise to 'physical bonds', in contrast to 'chemical forces', which give rise to 'chemical' or 'covalent bond', that arise from complex quantum mechanical interactions within two or more atoms to form a molecule. Table 1.1 gives an overview of chemical and different physical bonds. Physical bonds usually lack the specificity, stoichiometry and strong directionality of covalent bonds. Strictly, physical ‘bonds’ should not be considered as bonds at all, for during covalent bonding the electron charge distributions of the uniting atoms change completely and merge, whereas during physical binding they are merely perturbed, the atoms remaining as distinct entities. Nevertheless, physical binding forces can be as strong as covalent bonds, and even the weakest is strong enough to hold all but the smallest atoms and molecules together in solids and liquids at room temperature, as well as in colloidal and biological assemblies. These properties, coupled with the long-range nature of physical forces, makes them the regulating forces in all phenomena that do not involve chemical reactions [2].

Table 1.1: Strength of chemical and different physical bonds at T=300K

<table>
<thead>
<tr>
<th>bond nature</th>
<th>molar cohesive energy (kJ mol⁻¹)</th>
<th>energy per bond (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>covalent bond</td>
<td>200-800</td>
<td>2-8</td>
</tr>
<tr>
<td>ionic bond</td>
<td>500-1000</td>
<td>5-10</td>
</tr>
<tr>
<td>ion-dipole</td>
<td>~ 100-400</td>
<td>~ 1-4</td>
</tr>
<tr>
<td>dipole-dipole</td>
<td>~ 1</td>
<td>~ 0.01</td>
</tr>
<tr>
<td>hydrogen bond</td>
<td>10-40</td>
<td>0.1-0.4</td>
</tr>
<tr>
<td>van der Waals ‘bond’</td>
<td>~ 1-10</td>
<td>~ 0.01-0.1</td>
</tr>
</tbody>
</table>

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The various types of physical forces that arise from straightforward electrostatic interactions involving charged or dipolar molecules, are fairly easy to understand and they can be coupled with external 'field's or parameters like, electric field, magnetic field or temperature and so they can be tuned easily. But the weak intermolecular forces of quantum mechanical origin act between all atoms and molecules, even totally neutral ones such as helium, carbon dioxide and hydrocarbons. These forces can be referred to collectively as dispersion forces. They make up the most important contribution to the total van der Waals force between atoms and molecules, and because they are always present they play a role in a host of important phenomena such as adhesion, surface tension, physical adsorption, wetting, the properties of gases, liquids and thin films, the strengths of solids, the flocculation of particles in liquids, and the structure of condensed macromolecules such as proteins and polymers. Their main features may be summarized as follows: (a) They are long-range forces and, depending on the situation, can be effective from large distances (greater than 10nm) down to interatomic spacings (about 0.2nm). (b) These forces may be repulsive or attractive, and in general the dispersion force between two molecules or large particles does not follow a simple power law. (c) Dispersion forces not only bring molecules together but also tend to mutually align or orient them, though this orienting effect is usually weak. (d) The dispersion interaction of two bodies is affected by the presence of other bodies nearby. This last feature is known as the the non-additivity of an interaction.

As already stated, dispersion forces are quantum mechanical in origin and amenable to a host of theoretical treatments of varying complexity, the most rigorous of which would take us into the world of quantum electrodynamics. Their origin may be understood intuitively as follows: for a non-polar atom such as helium, the time average of its dipole moment is zero, yet at any instant there exists a finite dipole moment given by the instantaneous positions of the electrons about the nuclear protons. This instantaneous dipole generates an electric field that polarizes any nearby neutral atom, inducing a dipole moment in it. The resulting interaction between the two dipoles gives rise to
an instantaneous attractive force between the two atoms, and the time average of this force is finite [2]. These non-directed physical forces cannot be tuned so easily because they have no coupling with the external fields like electric field, magnetic field etc. In my studies I have indicated the presence of a new external 'field' - confinement, through which this non-directed physical force can be tuned. This tuning, in turn, causes a number of phenomena, the most important of which is the tuning of cohesion in supramolecular assemblies and through it, a control of self-assembly of molecular aggregates. Change in cohesion can affect any directed (like, exciton transport along confinement directional [3]) and non-directional (like, surface transport and coalescence of material [4–7]) mechanism in the system.

Here I would like to add that the term ‘self-assembly’ is used with a variety of meaning in different scientific contexts. In the context of molecular materials, the term self-assembly is used to describe the reversible and co-operative assembly of predefined components into an ordered super structure [8]. Molecular self-assembly is very important for nanomaterials science and technology as it is a bottom-up approach to growth in the nanometer scale [9]. For reproducible results it is best to have this growth extend over very large length scales e.g., over wavelength of light for photonic and optoelectronic applications [10]. This requires avoiding uncorrelated nucleation centres of self-assembly in ordered structures and an overall decrease in the entropy of the system. The structural evolution in self-assembly can be controlled by tuning the interplay between the directed and non-directed non-bonded forces [11]. The directed forces, such as the J-aggregation interaction between transition dipole moments, can cause mixing of the local molecular electronic states and produce a coherent exciton delocalized over an aggregate of molecules [12]. A coherent supramolecular aggregate has a size in the mesoscopic range, and this size is decided by the competition between the intermolecular forces that tend to increase the coherent length of the delocalized exciton and the dephasing mechanism, e.g., static disorder (inhomogeneities and topological defects) and dynamic disorder (exciton-phonon scattering) that tend to reduce this length [13]. I have focused on the control of
supramolecular aggregation in polymers.

1.3 Polymers and Films: Cohesion and Surface Energy

In my dissertation I am solely concerned with polymers that are intrinsically amorphous in the solid state by virtue of their chemical structure. For polymers there are at least two controlling length scales characterizing the ranges of forces between molecules or between molecular segments, which may differ substantially in magnitude: the monomer segment length and the end-to-end length of the polymer chain. There are relatively strong interactions between segments of different polymer chains that are spatially adjacent. These interactions decay in strength rapidly as the distance between molecules increases but they are the source of the cohesion in the bulk state and in their essentials are identical to those between small molecules; they are mainly enthalpic in character and determine such properties as compressibility and surface tension [14].

On the other hand, many of the unusual and useful properties of polymers arise from the contiguity of segments joined together by covalent bonds to form a long chain. Thus polymer molecules are spatially extended objects, with a new length scale - the polymer chain dimension (generally expressed as a radius of gyration or end-to-end distance). For flexible polymers the connectivity of covalently bonded chains means that configurational entropy plays a leading role in determining the equilibrium, minimum free energy, state. A flexible polymer can adopt any one of a large number of configurations of equal energy; at thermodynamic equilibrium it is the configuration of maximum entropy that is chosen leading to the 'gyration sphere'. If the chain is somehow constrained to some other configuration the entropy is reduced from the maximum value associated with equilibrium and the free energy of the system is increased. The influence of entropy on interfacial properties is most clearly seen in mixed polymer systems, for example polymer solutions or blends. Here the short range cohesive forces impose an essentially constant density throughout
the system. However, within that overall constant density, gradients in composition are controlled by a length scale derived from overall chain dimensions. Thus we should expect that polymer/polymer interfaces and layers of adsorbed polymers at solid/liquid(air) and liquid/air interfaces will be much more spatially extended than their analogues in exclusively small-molecule systems. Dimensions of such regions will be of the order of the polymer molecule dimensions rather than a few Å. So, for the polymer/polymer interface, the important length scale is not the range of the force between segments but the overall size of the polymer chain. This is the competition between enthalpy and entropy [14].

In case of polystyrene, the common polymer used as a base sample in this thesis, a major source of structural disorder is tacticity. In polystyrene phenyl-groups are attached as side-group to the $C - C$ backbone chain, as shown in Figure 1.1. In polystyrene, as styrene (the monomer for polystyrene) is composed of two different groups, $CH_2$ and $C_7H_6$, in principle, either group can be attached to the growing chain and, in addition, the phenyl-group can be placed in either side of the $C - C$ backbone. Random attachments may result in steric disorder along the chain. Tacticity is the notion used to describe steric order. Polymers with a unique way of coupling of the monomeric units are called isotactic, and contrasted to those with an irregular steric structure which are addressed as atactic. If the coupling varies, but in a regular way, polymer chains are called syndiotactic. All three types are found for polystyrene, shown in Figure 1.2, depending on the process chosen for the synthesis. Polystyrene is usually atactic and does not readily crystallize at all [15].

Properties of organic materials, and in particular polymers, can be exploited to make
Figure 1.2: Top figures show tacticity in polystyrene (PS): isotactic (left), syndiotactic (middle), atactic (right). Bottom figure shows how it works: the regular lines are chemical bonds in the plane of the page. The dark heavy lines are chemical bonds pointing out of the page. The dashed lines are chemical bonds pointing into the plane of the page.

functional nanoscale devices, using them in the forms of ultrathin films and single-molecule layers (i.e., 1-dimensional confined systems). The exploitation of macromolecules at interfaces has historically been a central concern of colloid science, and already forms the basis of major industries. Some examples are: (i) submicron polymer coatings on plastic film to add functionality by controlling surface properties such as adhesion and printability; (ii) control of the wetting properties of surfaces by treatment with self-assembled monolayers, such as in the surface treatment of glass fibres for use in composite materials. (iii) control of interactions between submicron polymer particles to optimise the process
of film formation in water-based varnishes and paints; (iv) the use of interfacially grafted and adsorbed polymers to control colloid stability in industries such as food, pharmaceutical formulations and personal care products. As these technologies become refined and our understanding and control of them at the nanoscale becomes more precise, new areas exploiting the properties of regular arrangements of self-assembled macromolecules at interfaces are becoming important [16].

The presence of an interface between a material and the vacuum (i.e., its surface) represents a major perturbation, and the importance of this perturbation necessarily increases as the dimensions of a system approach the nanoscale. The size of the perturbation is measured by the surface energy. The surface energy— to be thermodynamically precise, a surface free energy, which is equivalent to a surface tension— tells us how much the system energy increases if new surface is created from bulk material. The origin of the surface energy lies in the cohesive force that binds together condensed matter of any kind, either solid or liquid. A crude but useful way of thinking about surface energy is to imagine the atoms or molecules in a solid or liquid to be held together by bonds of energy, say $\varepsilon$. If each molecule occupies a volume, say $V_0$, and each molecule has bonds to, on average, $z$ other molecules, then the total cohesive energy per unit volume of the solid or liquid is given by $L = ze/2V_0$. If to create some new surface, some bonds should be 'cut'— at a surface molecule will interact with fewer molecules than it does in bulk. If each molecule at the surface on average interacts with $z'$ other molecules, then the surface energy $\gamma = z'\varepsilon/2V_0^{2/3}$. From this it can be shown that the surface energy is directly proportional to the cohesive energy. Nanoscopically, the range of surface forces are the size of the materials themselves. Therefore, whatever the material, surfaces are very important in nanotechnology because it is via these surface forces that materials interact with each other [16].

The study of the properties of macromolecules at interfaces represents a fascinating interaction between fundamental surface physics and applied chemistry. In asking why surfaces and interfaces are so important for macromolecular systems, it is worth making
a fundamental comparison between the surface of a simple polymer, like polystyrene, and the surface of an elemental material such as silicon. Silicon has an open diamond structure with each atom separated by 0.54nm whereas polystyrene has a random coil structure, with a segment length of 0.67nm. However, as has already been pointed out, when considering the effect of a surface it is perhaps better to consider the size of the polymer chain, which scales as the square root of the number of monomer in the chain (or scales as the square root of molecular weight of the polymer). As an example, polystyrene of molecular weight 100000 g. mol$^{-1}$ has ~ 960 monomers and a chain size of ~ 8.5nm. To a first approximation, then, the effect of a surface can be considered relevant over a distance 15 times greater in polystyrene than in silicon. In macroscopic situations this may not always be significant but on length scales of several nanometers, it is particularly important because virtually every chain in a polystyrene nanoparticle will have some contact with the surface. This will not be true of silicon particles of similar size. From this point of view, polymers at surfaces are considerably more influential than small molecule system [16].

If for a given macromolecular sample (film) the cohesive energy can be tuned (or varied) by changing their molecular packing within the sample, i.e, varying $z$, or somehow varying their physical bond energy, $\varepsilon$, with any external parameter like confinement, then surface energy of the system can be expected to also show tuning effect with confinement. I have shown in Chapter 4 and 5 how confinement in case of polystyrene films exhibits tunability in its surface energy. The films, in effect, form a different kind of template for size tunable self assembly of monodispersed Au nanoparticles at the film surface. In this context I would like to add that an interface between two different solids, between two different liquids, or between a solid and a liquid also has an energy called interfacial energy associated with it, assuming the pairs of materials are not mutually soluble. It is clear that in any system consisting of a dispersion of nanosized droplets or particles, surface and interfacial energies provide a major driving force for change. The smaller the particle, the larger the proportional importance of the surface or interface energy. 

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1.4 Polymer Film: Nanoconfinement and Tunable Self-assembly

Before a discussion about the polymer film in confined geometry, prepared basically from spin-coating of polymer solution on a suitable substrate, I will discuss very briefly about the behaviour of polymer solutions in good solvents.

When a macromolecular chain is placed in a good solvent, each segment of the polymer tends to be surrounded by solvent molecules, so that, if the chain is not too rigid, it assumes a zigzag shape within the solvent (Figure 1.3). The spatial region within which all the units of a given macromolecule lie fluctuates in time, but on average the chain remains inside some sphere of radius $R_F$ [17], which is equivalent to unperturbed radius of gyration $R_g$, where $R_g = 0.272\sqrt{M_0}$ ($M_0 =$ molecular weight of the polymer) [2, 18]. This radius increases with the degree of polymerization (DP) of the polymer or with number of monomer ($N$), or with the molecular weight ($M_0$), and varies roughly as $DP^{0.6}$ ($R_F = N^{3/5}a$, where $a$ is the monomer length).

If the macromolecules are progressively added to the solvent, these are initially separated from one another (dilute solution, Fig.1.3 (a)) but when the concentration becomes large enough, the spheres occupied by the various macromolecules fill up all the available volume (Fig.1.3 (b)). Beyond this concentration, denoted $C^*$, the macromolecular chains begin to tangle up and the medium is referred to as semi-dilute (Figure 1.3(c)). At the beginning of the 1980s, P.G. de Gennes brought new light to bear on the way these chains organise themselves in semi-dilute polymer solutions, by applying the idea of scaling laws [19]. In a semi-dilute solution, each macromolecule can be described by a series of unperturbed sections, separated by regions tangled with other chains. This has been schematized in Figure 1.3(d), in which the chains mark out a 3-dimensional lattice; the nodes of the lattice represent points where the chains tangle. The lattice fluctuates in...
Figure 1.3: *Polymer solution in good solvent.* (a) General appearance of a flexible macromolecule in dilute solution. Macromolecules are separated from each other. (b) State of the solution at the critical concentration \( C^* \). Macromolecules are on the point of interpenetrating. (c) Semi-dilute solution. The chains interpenetrate. One of them has been distinguished (bold curve) and the points of steric constriction relative to the other chains have been marked with black dots. (d) Schematic representation of flexible-chain polymer in semi-dilute solution in a good solvent. The chains constitute a 3-dimensional lattice whose unit size corresponds to the mean separation \( \xi \) between two tangling points. Between such points (shown magnified), the section of chain behaves as if it were free in solution [17].

Space and time and the mean size \( \xi \) clearly depends on the polymer concentration \( C_P \). In fact, \( \xi/R_P = (C_P/C^*)^{-3/4} \) so that \( \xi \) decreases as the concentration goes up. Considering any given point of chain in semi-dilute solution, \( \xi \) is a measure of the mean distance to an obstacle (i.e., another chain) [17]. I have prepared my films from initially dilute solution of polystyrene in toluene but as the film is formed by evaporation of the toluene solvent from the film of solution on the substrate, it is progressively concentrated and the mean size is not expected to remain constant from these considerations of fluid dynamics. However, this predicted behaviour has to be weighed in the light of experimental findings on simple and complex fluids over the last decade. In this context I can mention some of the
studies showing existence of gyration sphere in bulk polymer as well as in thin polymer film, spin cast from solution. For example, small angle neutron scattering (SANS) studies on mixtures of normal and perdeuterated polystyrene allowed Benoit and co-workers [20] to prove that amorphous polymers in the bulk exhibit unperturbed Gaussian coil conformations. Also using by same technique T. P. Russell and co-workers [21] have shown that 170 nm thick as cast film of 50 percent mixture of 690K polystyrene and 760K deuterated polystyrene exhibits radius of gyration ($R_g$) of 47 nm, while theoretically expected value is $R_g \sim 23$ nm and this deviation from experimental result is explained as originating from either a demixing of the homopolymers or from the fact that the homopolymers are trapped in a nonequilibrium conformation during the spinning process. In a further work [22] they have shown that gaussian conformation of polymer chain is retained parallel to the surfaces, independent of film thickness in ultrathin (less than 100nm) polystyrene films. Another example is the work performed by Kraus and co-workers [23], where they could investigate, via diffuse neutron scattering in a reflection geometry, the chain conformation in thin polymer films with film thicknesses less than 20 nanometers. Using this technique they have shown that with decreasing film thickness $d$ below approximately 6 $R_g$ the in-plane dimension of the chains starts to increase which is caused by distortion of the chain conformations along the directions parallel and perpendicular to the surface of the film. This increase is quite significant below $d < R_g$ and these results were compared to theoretical predictions and simulations.

One-dimensional geometrical confinement of fluids causes the fluid to form layers normal to the confinement direction, even in systems without intrinsic order [24–28]. The exact point of commencement of such layer formation has not been determined, but the layer period has been shown to coincide roughly with an intrinsic length of the system - for 'nanoconfined' simple fluids the layer periodicity is equal to the molecular size while for polymers it is equal to $R_g$ [27]. Nanoconfined fluids exhibit radically new mechanical, thermal, dielectric and rheological properties [29,30]. In a recent study, a nanoconfined simple liquid has been observed to be in a 'laterally cooperative' state that behaves liquid-
like or solid-like depending on the kinematics of the measurement process [31]. These new properties suggest a basic reorganization at molecular levels and they are bound to have strong implications in any technology employing thin fluid films such as optoelectronic and magnetic coatings, adhesives, biological membranes and emerging nanotechnologies, in particular, photonics and nanofluidics.

I have shown that in PS, layering starts when the film thickness $\leq 4R_g$ and that this layering reduces the density between the molecular layers, thereby lowering the van der Waal's attraction or the cohesive force between these layers as expected from theoretical consideration [32] and borne out for liquid crystals [33]. This is how the van der Waal's forces can be controlled and it is expected to change the balance between the directional and nondirectional intermolecular forces. It is important to find out how this will affect the physical properties of molecular aggregates. An additional advantage of polymers is the tunability of the layer period by simply changing the polymer molecular weight as this decides its radius of gyration. Also, the extended chemical bonding network in polymers couples to these weaker forces, both directional and nondirectional, and leads to polymer configurations depending on whether such forces have a stronger intra- or intermolecular influence. In this context, my work has been to investigate what happens to the intramolecular configuration, exciton delocalization length and surface energy variation before and after layers are formed in a polymer due to confinement. This I have shown in Chapter 4 of this thesis. In this chapter I have shown that, polymer layers form only when film thickness is less than $4R_g$ and there is a reduction in cohesion between adjacent molecular gyration spheres [3], the detailed nature of this intermolecular reduction of cohesion with confinement and the intra-molecular mechanism behind this. I have also shown here that the exciton delocalized throughout the film thickness in spin-coated atactic polystyrene film via formation of molecular J-aggregate becomes localized after molecular layer formation. I have shown that pendant phenyl groups in spin-cast atactic polystyrene film form 'physical dimers' and that these 'dimers' change their configuration from 'oblique' (V-shaped) to 'head-to-tail' (slipped parallel) under nanoconfinement. This
confinement induced intramolecular rearrangement also leads to orientational anisotropy as manifested in the films responding to the polarization of incident ultraviolet radiation. Theoretical background for assignment of exciton in optical spectra, which indicates the formation of J-aggregates and physical dimers in polystyrene are discussed in detail in Chapter 3.

The organization of inorganic nanostructures within self-assembled organic or biological templates [34-37] is receiving the attention of scientists interested in developing functional hybrid materials. Previous efforts have concentrated on using such materials to spatially arrange nanoscopic elements as a strategy for tailoring the electrical, magnetic or photonic properties [38, 39] of the material. Recent theoretical arguments have suggested that synergistic interactions between self-organizing particles and a self assembling matrix material can lead to hierarchically ordered structures [37]. I have shown in my dissertation that gold nanoparticles, both 'bare' and 'thiol-capped, exhibit cooperative, coupled self assembly on self-assembled layered atactic polystyrene film with thickness < 4R\text{g} [4]. In particular, I have shown that the surface of such a polystyrene film consists of an assembly of gyration spheres separated from each other by narrow regions of low cohesion. When Au is sputter deposited on such surfaces, the regions cause a growth of highly monodisperse Au nanoparticles on the PS film surface at room temperature as segregation of the nanoparticles at room temperature between two gyration spheres at the surface of the films is influenced by the variation of interfacial interaction. Depending on the strength of these low cohesion regions, which in turn depends on PS film thickness, nanoparticle size is tuned. These intervening regions also serve as percolation pathways for a fluid containing Au nanoparticles, whose flow gives rise to a in-plane pattern. Organization of both the polymeric and particulate entities is thus achieved without the use of any external fields, opening a simple and general route for fabrication of highly monodispersed nanostructured materials with hierarchical order. This is discussed in Chapter 5.

The experimental techniques chosen for the above mentioned work are usually selected on the basis of their appropriateness for a particular task. These are discussed in detail in Chapter. Introduction
Chapter 2. Polymers like polystyrene that are soluble in volatile solvents and partially wet the substrate are particularly easy to form into films. I have prepared polystyrene films on fused quartz (SiO$_2$) substrates by spin-coating solutions of the polymer in toluene on the substrates. Au has been deposited on these films in two ways—by sputter-coating Au using a DC magnetron unit and by spin-coating a solution of chemically fabricated dodecanethiol-capped Au nanoparticles in toluene. It is convenient to study the changes in structure of polymers due to confinement and the localization of the exciton due to these changes, by independent experimental means. I have, in my studies, collected real-space data using Atomic Force Microscopy, reciprocal-space data using elastic scattering of x-rays and spectroscopic data over 0.05-9 eV energy range, i.e., from mid infrared (mid-IR) to vacuum ultraviolet (vuv) (140-25000 nm wavelength range), and have correlated these to get a more complete picture of these complex supramolecular assemblies. X-ray scattering at grazing incidence and in particular, specular x-ray reflectivity, has proved to be an excellent nondestructive tool to detect small oscillations in electron density along the depth of amorphous organic films, indicative of layer formation along film depth [40]. The amplitude of these oscillations with respect to the average electron density of the homogeneous film serves as an order parameter for the layering transition [11]. On the other hand, optical spectroscopy is a simple but reliable method, again nondestructive, to probe excitonic behavior, especially of molecular solids [41]. The surface morphology (from topography) and surface energy (from phase image) of pristine and Au designed polystyrene film are extracted from atomic force microscopy (AFM). It should be noted that, in this dissertation, I have referred to the optical wavelength ($\lambda$) in nm, corresponding wavenumber ($\tilde{\nu} = 1/\lambda$) in cm$^{-1}$, where $\tilde{\nu}$ (in cm$^{-1}$) $\equiv 10^4/\lambda$(in nm) and corresponding photon energy ($E$) in eV, where $E$(in eV) $\equiv 1245/\lambda$(in nm). I have expressed film thickness and roughness in terms of Å or nm, where 1nm = 10Å.

In Chapter 6, I have summarized my work and drawn conclusions pertaining to the whole dissertation. I have also drawn attention to the varying implications and extensions of this work. Some of these I have planned myself and some are left to the future!