CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Surface-coating Techniques

For a large number of chemical and physical process, the bulk properties of a material as well as the structure and composition of its surfaces determine the performance of the entire system. In order to control the interaction of a material with its environment, coatings consisting of thin organic films are frequently applied to the surfaces of these solids. Depending on the type of interaction between the molecules which are constituents of the coating and the substrate which is to be modified, two classes of strategies for the deposition of thin organic coatings can be distinguished. In one of these, the molecules interact with the substrate by physical forces [1,2], whilst the other class consists of molecules which are attached to the surfaces through chemical bonds. In the latter case, a monomolecular layer or a surface-attached network is very strongly (irreversibly) attached to the surface.

A number of technologically important coating techniques rely on physical interactions between the deposited molecules and the substrate such as spray coating, spin coating and dip coating. Several of these processes allow the deposition of extremely thin film coatings (starting from just a few nanometers thickness), but essentially no upper limit to film thickness exists, if appropriate conditions are applied. In contrast, more sophisticated coating techniques have been developed, including the Langmuir-Blodgett technique [3], the adsorption of monomolecular layers of homo- and block copolymer [1] from solution, and the Layer-by-Layer (LBL) technique [4] in which multilayer stacks of oppositely charged polyelectrolytes are deposited onto a charged substrate. These techniques allow for much better control of the internal structure of the deposited layers, and also for extremely high precision with regard to the thickness of the coatings. The molecules are attached to their substrates by physical interactions, and consequently the forces holding them at

the surface are rather weak. Under unfavorable conditions, the films can be subject to destruction by the "Big Four Ds":

- desorption during solvent exposure
- displacement by molecules which have stronger interaction with the surface
- dewetting (for films above the glass transition temperature, T_g)
- delamination (for films below T_g)

An alternative to the above-mentioned which allows improvement in the long-term stability of coatings even in very adverse environment, is to attach the molecules of the coating to the surface of the substrate through chemical bonds. In this way, surface coatings can be obtained which are very stable and may even have a strong degree of positional and orientational order. One solution is the use of polymers carrying the functional groups along the chain, thus generating higher cross-sectional densities of these groups and simultaneously guaranteeing good accessibility.

2.2 Layer-by-Layer Adsorption

The fabrication of ultrathin polymer films on modified surfaces of material is important for various scientific and biological fields in order to modify the intact characteristics of these surfaces exposed to biological system. In most cases, the material characteristics seem to be governed by the chemical composition of the surface. Coating a substrate surface with polymeric ultrathin films can maintain the original mechanical properties and/or fine structure of the substrate.

The sequential adsorption of oppositely charged polyelectrolytes (PEL) by layer-by-layer (LBL) deposition technique is an efficient method for obtaining multilayer thin films with well-defined thickness, composition and functionalities. Due to the simplicity and the versatility of the buildup process, this technique opens enormously new opportunities to achieve the ideal model surface for use in applications such as biosensing [5], separation membrane [6] and optical devices [7]. LBL process was first introduced by Decher *et al.* in 1991. They have demonstrated

the basic principle of buildup of multilayer materials using alternating adsorption of PEL [8].

The crucial feature of the sequential adsorption is the excessive adsorption at every stage of the polycation/polyanion assembly, which led to the recharging of the outermost surface at every step of film formation (Figure 2.1). Hence, the electrostatic interaction between the surface and polyions in solution is usually considered as the driving force for multilayer formation. The adsorption behavior of polyelectrolytes is influenced by a number of factors such as the charge density [9], the ionic strength or the pH of the solutions and the solvent quality [10].

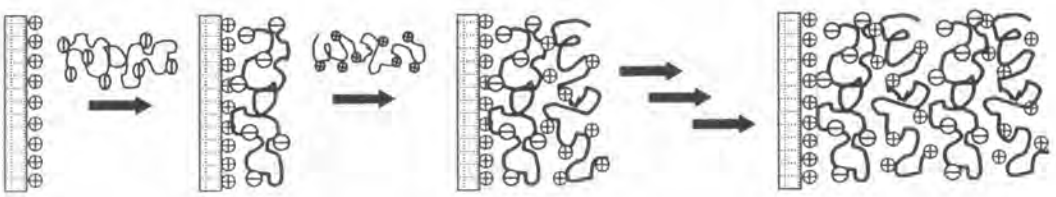


Figure 2.1 Alternate layer-by-layer adsorption of polyanion and polycation onto a positively charged substrate

In view of alternate layer-by-layer assembly of cationic chitosan and anionic PAA with oppositely charged polyelectrolytes, the following related publications have been reported.

In 1998, Lvov, *et al.* [11] prepared biocompatible molecular surfaces by an alternate assembly of cationic chitosan and anionic PSS at pH 4. Film growth and its dependence on ionic strength were analyzed by the QCM method. In addition, surface structure of the ultrathin films was examined by non-contact atomic force microscopy.

In 2002, Serizawa, *et al.* [12] generated multilayer systems based on chitosan. They varied concentration of NaCl as 0.2, 0.5 and 1 M. They found that the apparent film thickness increased upon increasing NaCl concentration. There was a critical concentration for the alternating activity; above a concentration of 0.5 M NaCl, both anti-and procoagulation could be observed on the dextran sulfate and chitosan surfaces, respectively. They also studied the formation of assembled film from a combination of chitosan and heparin, but the activity was different from that of the

former system. They suggested that the polymer species and/or the assembly conditions are key factors for realizing the alternating bioactivities of films prepared by the layer-by-layer assembly.

Although LBL assembly normally includes noncovalent interactions between polymers, the technique can be used for the formation of covalent bonds between polymers using sequential chemical reactions. For the assembly with covalent bonds, the formation of covalent bonds by heat treatment after polymer assembly [13], the assembly of polymers with activated functional groups [14] and assembly based on metal coordination [15] have been demonstrated. These assemblies should become more stable under certain atmospheres as compared to conventional assembly, and their applications will expand even more.

In 2002, Serizawa, *et al.* [16] prepared thermoresponsive ultrathin hydrogels by the sequential chemical reaction of poly(vinylamine-*co*-*N*-vinylisobutyramide) [poly(VAm-*co*-NVIBA)] and poly(acrylic acid) (polyAAc) on a gold surface. The carboxyl group of polyAAc was activated by 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide hydrochloride (EDC) for the reaction with the amino group of poly(VAm-*co*-NVIBA) to yield the amide linkage. Layer-by-layer assembly using chemical reactions will open a new field of research on the suitable selection of functional polymers.

In 2004, Yang, *et al.* [17] prepared bioinert polyelectrolyte multilayers comprised of poly(acrylic acid) and polyacrylamide, deposited on colloidal particles at low pH conditions by layer-by-layer assembly using hydrogen bonding interactions. The multilayer films were coated uniformly on the colloidal particles without causing any flocculation of the colloids, and the deposited films were subsequently cross-linked by a single treatment of a carbodiimide aqueous solution. The lightly cross-linked multilayer films show excellent stability at physiological conditions (pH 7.4, phosphate-buffered saline), whereas untreated multilayer films dissolved. The multilayer-coated surfaces, both on flat substrates and on colloidal particles, exhibit excellent resistance toward mammalian cell adhesion. With this new

solution-based cross-linking method, bioinert H-bonded multilayer coatings offer potential for biomedical applications.

2.3 The Formation of Polyelectrolyte Multilayer Assemblies on Polyelectrolyte Brushes

Polyelectrolyte built up by layer-be-layer adsorption represent a simple pathway to fabricate a film with well-controlled thickness. However, the stability of the multilayered system in different environment is generally of concern. Especially the adhesion of the first layer to the surface poses a problem which should not be neglected. Because the attachment of the first layer depends solely on the interaction of the polymers with surface charges, the whole multilayer assembly can be desorbed by either changing the sign of the surface charge of the substrate or by addition of competing low molecular weight electrolytes, which can displace the polymer molecules in the first monolayer [18,19]. Another general problem of the LBL method is the low thickness of each single deposited layer, which is on the order of 0.5 nm [20]. Such a small increase in film thickness per deposited layer is rather inconvenient if a thicker PEL multilayer assembly is desired, as in this case many layers must be deposited.

Recently, the use of the surface-attached polyelectrolyte brushes for layer-by-layer build-up of polyelectrolyte multilayers has been introduced as a way to overcome the above-mentioned problems. Because the PEL monolayers generated are directly in contact with the surface and are attached to it through chemical bonds, the PEL complexes and the PEL multilayers could, potentially, be very stable. In principle, the grafting density of the surface-attached polyelectrolyte brushes should be high enough to induce stretching of the polymer chains away from the surface. The thickness of the adsorbed polyelectrolyte should thus be as high as the polyelectrolyte brushes. For the formation of polyelectrolyte multilayers assemblies, the brushes are alternatively dipped into PEL solutions, one of which consists of a positively charged PEL, and the other of a negatively charged PEL.

In 2003, Zhang and Rühe [21] reported the deposition of poly(4-vinyl-N-methylpyridinum)iodide/poly(styrene sulfonate) sodium (MePVP/PSSNa) multilayer on positively charged MePVP brushes which were covalently attached on the silicon surface. It was found that when PSSNa was added to the MePVP brushes, which was swollen in salt-free water, the MePVP brushes collapsed rapidly. Once the MePVP collapses, the diffusion of PSS into MePVP layer essentially stops and a strongly nonstoichiometric, insoluble polyelectrolyte-polyelectrolyte complex is formed. From Figure 2.2(a), it can be seen that the increase in thickness due to the absorption of the second layer (PSSNa) is larger than that of the following layers deposited onto it. However, from the third layer onwards the thickness increases by only about 0.5 nm per deposition cycle (i.e., deposition of two monolayers), and a linear relationship between layer thickness and the number of deposited layers is observed. In this system, after deposition of a total of three or four PEL-layers the brush no longer affects the properties of the outer layers.

Later in 2005, Zhang and Rühe [22] reported the formation of poly(methacrylic acid)/ poly(4-vinyl-*N*-methylpyridinum)iodide (PMAA/MePVP) on nagatively charged PMAA brushes which were covalently attached on the silicon surface. It should be noted that PMAA brushes are weak polyelectrolyte. The film thickness of the PMAA/MePVP multilayer (Figure 2.2(b)) increases linearly with the number of dipping cycles. It is also clear that the thickness of each layer in the multilayer assembly depends heavily on the thickness of the initial brush layer. The increase in layer thickness per monolayer, and even when a very thick brush is used. The outermost layer resembles closely the intermost (the brush layer), and a very strong template effect is observed.

Even though the overall architecture of the two systems is very similar (surface-attached PEL brush with electrostatically attached monolayers of alternating charge sign), the film formation behavior of the two systems is very different, as shown schematically in Figure 2.3. Although this difference is not yet fully understood, it is evident that the basic difference between the systems is the water solubility of the PEL-PEL complex formed. This difference is directly evident if

solutions of the two PELs are mixed. While in the first (weak/weak) case the complex remains soluble if solutions containing equimolar amounts of polyanion and polycation are mixed, in the latter (strong/strong) case immediate precipitation occurs due to the hydrophobicity of the neutral complex formed.

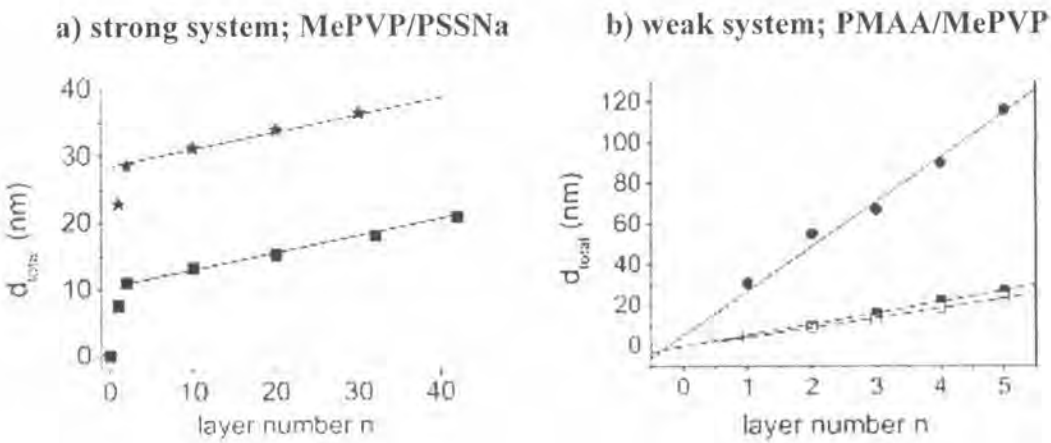


Figure 2.2 Film thickness as a function of the layer numbers for (a) MePVP/PSSNa multilayers using 7.6 nm(■) and 22.9 nm (★) MePVP covalently attached monolayer as the first layer and (b) PMAA/MePVP multilayers using 6 nm (□) and 30 nm (•) MePVP covalently attached monolayer as the first layer. The solid lines show a linear fit of the dependence of the film thickness on the number of deposited layers [21-22]

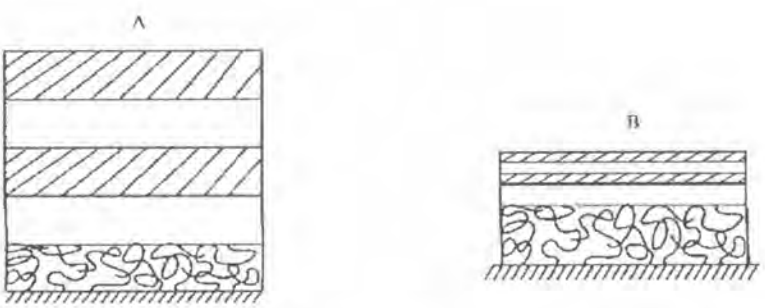


Figure 2.3 Schematic depiction of the formation of PEL multilayers through PEL brushes. (A) strong/weak system; (B) strong/strong system [22]

The formatiom of weak PEL-PEL complexes and multilayers at solid surfaces via polymer brushes is quite different from the case where two strong PEIs are used. Interestingly, in the strong/weak PEL system, each adsorbed layer has the same

thickness, which closely resembles that of the innermost brush layer. By contrast, in the strong/strong system the formation of PEL multilayers resembles more the traditional LBL technique in so far as the increase in layer thickness per deposition cycle is well below 1 nm. In the strong/weak case, however, more than 100 nm of polyelectrolyte can easily be deposited per dipping cycle, and this allows the simple generation of very thick PEL multilayers assemblies. However, the exact mechanism and the internal structures of the weak PEL complexes and multilayer assemblies are still not clear. Since many biopolymer (proteins, nucleic acids and DNA) are polyelectrolytes, the systems described here are interesting models for biomaterials.

2.4 Polymer Brushes

Polymer brushes refer to an assembly of polymer chains which are tethered by one end to a surface or an interface. Tethering is sufficiently dense that the polymer chains are crowded and forced to stretch away from the surface or interface to avoid overlapping, sometimes much further than the typical unstretched size of a chain. These stretched configurations are found under equilibrium conditions; neither a confining geometry nor an external field is required. This situation, in which polymer chains stretch along the direction normal to the grafting surface, is quite different from the typical behavior of flexible polymer chains in solution where chains adopt a random-walk configuration. A series of discoveries show that the deformation of densely tethered chains affects many aspects of their behavior and results in many novel properties of polymer brushes [23].

Polymer brushes are a central model for many practical polymer systems such as polymer micelles, block copolymers at fluid–fluid interfaces (e.g. microemulsions and vesicles), grafted polymers on a solid surface, adsorbed diblock copolymers and graft copolymers at fluid–fluid interfaces. All of these systems, illustrated in Figure 2.4, have a common feature: the polymer chains exhibit deformed configurations. Solvent can be either present or absent in polymer brushes. In the presence of a good solvent, the polymer chains try to avoid contact with each other to maximize contact

with solvent molecules. With solvent absent (melt conditions), polymer chains must stretch away from the interface to avoid overfilling incompressible space.

The interface to which polymer chains are tethered in the polymer brushes may be a solid substrate surface or an interface between two liquids, between a liquid and air, or between melts or solutions of homopolymers. Tethering of polymer chains on the surface or interface can be reversible or irreversible. For solid surfaces, the polymer chains can be chemically bonded to the substrate or may be just adsorbed onto the surface. Physisorption on a solid surface is usually achieved by block copolymers with one block interacting strongly with the substrate and another block interacting weakly. For interfaces between fluids, the attachment may be achieved by similar adsorption mechanisms in which one part of the chain prefers one medium and the rest of the chain prefers the other.

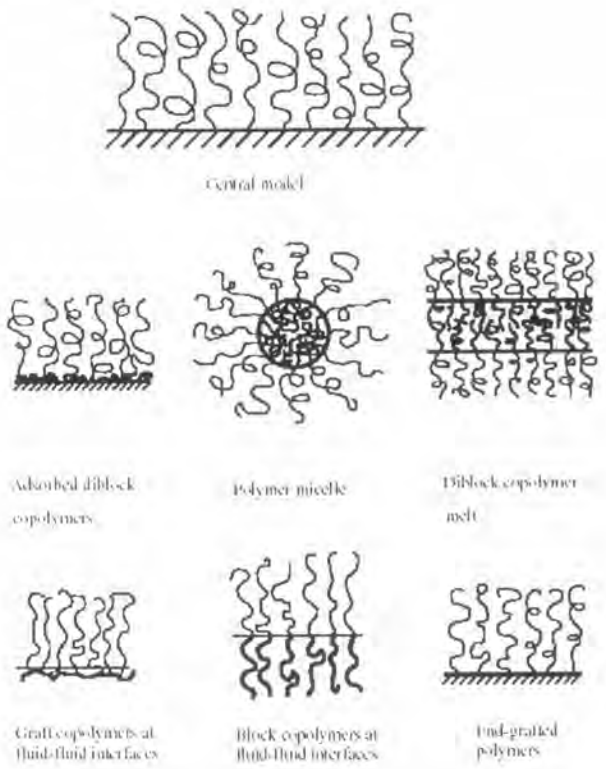


Figure 2.4 Examples of polymer systems comprising polymer brushes [23]

Polymer brushes (or tethered polymers) attracted attention in 1950s when it was found that grafting polymer molecules to colloidal particles was a very effective

way to prevent flocculation [23]. In other words, one can attach polymer chains which prefer the suspension solvent to the colloidal particle surface; the brushes of two approaching particles resist overlapping and colloidal stabilization is achieved. The repulsive force between brushes arises ultimately from the high osmotic pressure inside the brushes. Subsequently, it was found that polymer brushes can be useful in other applications such as new adhesive materials [24-25], protein-resistant biosurfaces [26], chromotographic devices [27], lubricants [28], polymer surfactants [23], and polymer compatibilizers [23]. Tethered polymers which possess low critical solution temperature (LCST) properties exhibit different wetting properties above and below LCST temperature [29]. A very promising field that has been extensively investigated is using polymer brushes as chemical gates. Ito and coworkers [30-32] have reported pH sensitive, photosensitive, oxidoreduction sensitive polymer brushes covalently tethered on porous membranes, which are used to regulate the liquid flowing rate through porous membranes. Suter and coworkers [33-34] have prepared polystyrene brushes on high surface area mica for the fabrication of organic–inorganic hybrids. Cation-bearing peroxide free-radical initiators were attached to mica surfaces via ion exchange and used to polymerize styrene. This process is important in the field of nanocomposites. Patterned thin organic films could be useful in microelectrics [35], cell growth control [36-37], biomimetic material fabrication [38], microreaction vessel and drug delivery [39].

In terms of polymer chemical compositions, polymer brushes tethered on a solid substrate surface can be divided into homopolymer brushes, mixed homopolymer brushes, random copolymer brushes and block copolymer brushes. Homopolymer brushes refer to an assembly of tethered polymer chains consisting of one type of repeat unit. Mixed homopolymer brushes are composed of two or more types of homopolymer chains [40]. Random copolymer brushes refer to an assembly of tethered polymer chains consisting of two different repeat units which are randomly distributed along the polymer chain [41]. Block copolymer brushes refer to an assembly of tethered polymer chains consisting of two or more homopolymer chains covalently connected to each other at one end [42]. Homopolymer brushes can be further divided into neutral polymer brushes and charged polymer brushes. They

may also be classified in terms of rigidity of the polymer chain and would include flexible polymer brushes, semiflexible polymer brushes and liquid crystalline polymer brushes. These different polymer brushes are illustrated in Figure 2.5.

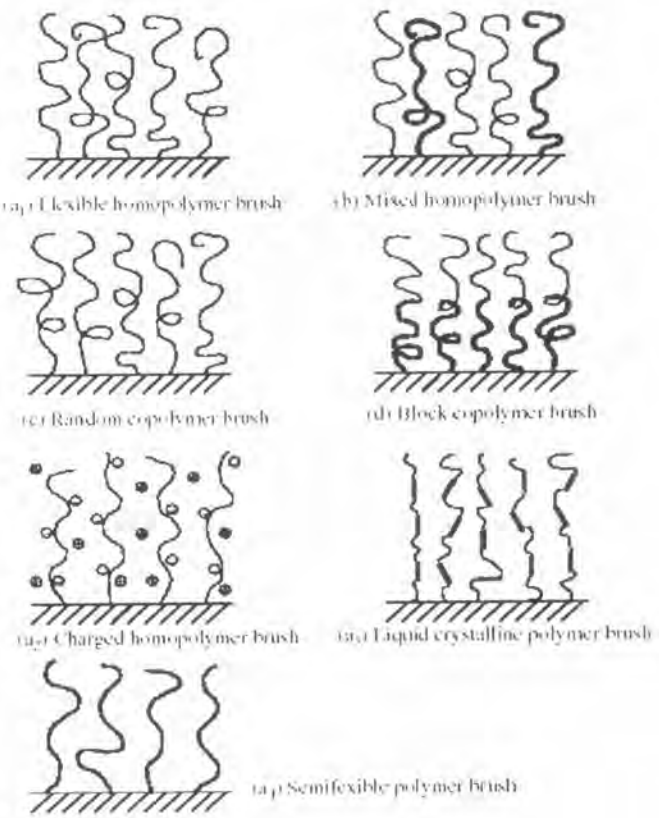


Figure 2.5 Classification of linear polymer brushes, (a_1–a_4) homopolymer brushes; (b) mixed homopolymer brush; (c) random copolymer brush; (d) block copolymer brush [23]

Generally, there are two ways to fabricate polymer brushes: physisorption and covalent attachment (Figure 2.6). For polymer physisorption, block copolymers adsorb onto a suitable substrate with one block interacting strongly with the surface and the other block interacting weakly with the substrate. The disadvantages of physisorption include thermal and solvolytic instabilities due to the non-covalent nature of the grafting, poor control over polymer chain density and complications in synthesis of suitable block copolymers. Tethering of the polymer chains to the surface is one way to surmount some of these disadvantages. Covalent attachment of polymer brushes can be accomplished by either "grafting to" or "grafting from" approaches. In

a "grafting to" approach, preformed end-functionalized polymer molecules react with an appropriate substrate to form polymer brushes. This technique often leads to low grafting density and low film thickness, as the polymer molecules must diffuse through the existing polymer film to reach the reactive sites on the surface. The steric hindrance for surface attachment increases as the tethered polymer film thickness increases. The "grafting from" approach is a more promising method in the synthesis of polymer brushes with a high grafting density. "Grafting from" can be accomplished by treating a substrate with plasma or glow-discharge to generate immobilized initiators onto the substrate followed by in situ surface-initiated polymerization. However "grafting from" well-defined self-assembled monolayers (SAMs) is more attractive due to a high density of initiators on the surface and a well-defined initiation mechanism. Also progress in polymer synthesis techniques makes it possible to produce polymer chains with controllable lengths. Polymerization methods that have been used to synthesize polymer brushes include cationic, anionic, TEMPO-mediated radical, atom transfer radical polymerization (ATRP) and ring opening polymerization.

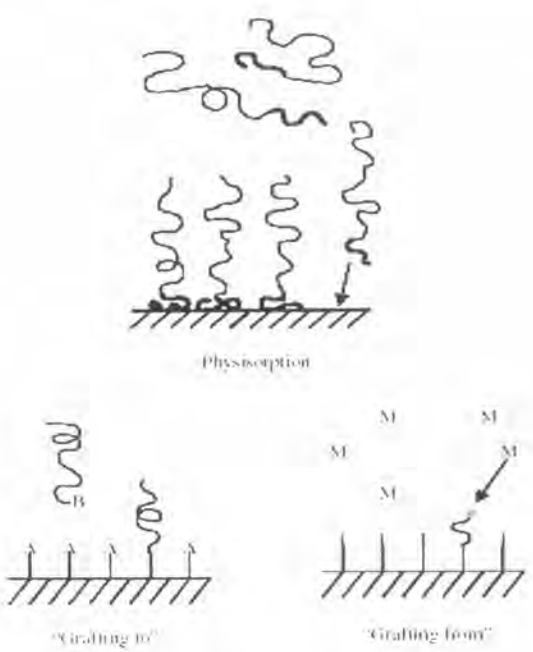


Figure 2.6 Preparation of polymer brushes by "physisorption", "grafting to" and "grafting from" [23]

In order to achieve a better control of molecular weight and molecular weight distribution and to obtain novel polymer brushes like block copolymer brushes, controlled radical polymerizations including ATRP, reverse ATRP, TEMPO-mediated and iniferter radical polymerizations have been used to synthesize tethered polymer brushes on solid substrate surfaces [43-48].

In recent years, ATRP has been the most widely empolyed technique for the formation of polymer brushes *via* surface initiated polymerization. ATRP is compatible with a variety of functionalised monomers. The living/controlled character of the ATRP process yields polymers with a low polydispersity (M_w/M_n) that are end-functionalized and so can be used as macroinitiators for the formation of di- and triblock copolymers. Equally important, surface-initiated ATRP is experimentally more accessible than for example, the living anionic and cationic polymerizations, which require rigorously dry conditions. The synthesis of thiol and silane derivatised surface-bound initiators is easier than AIBN-silane derivative or the nitroxide silane derivative for free radical and NMP polymerizations. In 1998, Fukuda and coworkers prepared poly(methyl methacrylate) brushes on silicon surface *via* surface-initiated atom transfer radical polymerization. The addition of free initiator to the polymerization solution yields free polymer which can be characterised by conventional methods. The relatively narrow polydispersities of these polymers in conjunction with the molecular weights were proportional to monomer conversion points towards the surface polymerization being controlled. The thickness of the polymer brushes was related to the concentration of the free initiator added, the lower concentration of free initiator the thicker the films being achieved [49].

Husseman and coworkers [45] applied ATRP in the synthesis of tethered polymer brushes on silicon wafers and achieved great success. They prepared SAMs of 5-trichlorosilylpentyl-2-bromo-2-methylpropionate on silicate substrates. The α-bromoester is a good initiator for ATRP. They have successfully synthesized PMMA brushes by the polymerization of MMA initiated from the SAMs. It has also been reported that tethered polyacrylamide has been obtained from surface initiated ATRP of acrylamide on a porous silica gel surface [46].

Matyjaszewski and coworkers [50] reported a detailed study of polymer brush synthesis using ATRP in controlled growth of homopolymer and block copolymers from silicon surfaces. They described that the persistent radical effect must be considered in controlled radical polymerizations. In other words, a sufficient concentration of deactivation must be available to provide control over chain lengths and distributions. The Cu (II) can be supplied by termination of initiator molecules in the early stages of the polymerization or by addition of the transition metal complex prior to commencement of the reaction. Moreover, the only factor affected is the kinetics of the reaction; in the former case, first-order consumption of monomer is dictated by the chains generated from the free initiator while in the latter, due to the extremely low concentration of alkyl halide bound to the surface and low monomer conversion, growth of polymer chains scales linearly with reaction time. Their conclusion suggested that the design of such complex structures whether in solution or at an interface, understanding of the relative rates of chain propagation, equilibrium constants, and the influences of the end group, metal, and ligand in crossover reaction are important. Factors such as initiator functionality and blocking efficiency can have a profound influence on the physical properties of the resulting material.

In 2001, Werne and Patten [51] reported the preparation of structurally well-defined polymer-nanoparticle hybrids by modifying the surface of silica nanoparticles with initiators for ATRP and by using these initiator-modified nanoparticles as macroinitiators. They found that polymerizations of styrene and methyl methacrylate (MMA) using the nanoparticle initiators displayed the diagnostic criteria for a controlled / "living" radical polymerization: an increase in the molecular weight of the pendant polymer chains with monomer conversion and a narrow molecular weight distribution for the grafted chains. Polymerization of styrene from smaller silica nanoparticles (75-nm-diameter) exhibited good molecular weight control, while polymerization of MMA from the same nanoparticles exhibited good molecular weight control only when a small amount of free initiator was added to the polymerization solution. For the polymerizaiton of both styrene and MMA from larger silica nanoparticles (300-nm-diameter) did not exhibit molecular weight control. Molecular weight control was induced by the addition of a small amount of

free initiator to the polymerization but was not induced when 5-15 mol% of deactivator (Cu(II) complex) was added. These findings provide guidance for efforts in using ATRP for the controlled grafting of polymers from high and low surface area substrates.

2.5 Living Polymerization

Synthetic polymers are long-chain molecules possessing uniform repeat units (mers). The chains are not all the same length. These giant molecules are of interest because of their physical properties, in contrast to low molecular weight molecules, which are of interest due to their chemical properties. Possibly the most useful physical property of polymers is their low density versus strength.

When synthetic polymers were first introduced, they were made by free radical initiation of single vinyl monomers or by chemical condensation of small difunctional molecules. The range of their properties was understandably merger. Random copolymers are greatly expanding in the range of useful physical properties such as toughness, hardness, elasticity, compressibility, and strength, however, polymer chemists realized that their materials could not compare with the properties of natural polymers, such as wool, silk, cotton, rubber, tendons, and spider webbing. The natural polymers are generally condensation polymers made by addition of monomer units one at a time to the ends of growing polymer chains. Polymerization of all chains stops at identical molecular weights. For some time polymer chemists have realized that to approach nature's degree of sophistication, new synthetic techniques would be needed.

Conventional chain-growth polymerizations, for example, free radical synthesis, consist of four elementary steps: initiation, propagation, chain transfer, and termination. As early as 1936, Ziegler proposed that anionic polymerization of styrene and butadiene, consecutive addition of monomer to an alkyl lithium initiator occured without chain transfer or termination. During transferless polymerization, the number of polymer molecules remains contant. Since there is no termination, active anionic

chain ends remain after all of the monomer has been polymerized. When fresh monomer is added, polymerization resumes. The name "living polymerization" was coined for the method by Szwarc [52]. because the chain ends remain active until killed. The term has nothing to do with living in the biological sense. Before Szwarc's classic work, Flory [53] had described the properties associated with living polymerization of ethylene oxide initiated with alkoxides. Flory noted that since all of the chain ends grow at the same rate, the molecular weight is determined by the amount of initiator used versus monomer (Eq. 2.1)

$$\text{Degree of polymerization} = [\text{monomer}]/[\text{initiator}] \qquad (2.1)$$

Another property of polymers produced by living polymerization is the very narrow molecular weight distribution. The polydispersity (D) has a Poisson distribution, $D = \overline{M}_w / \overline{M}_n = 1 + (1/dp)$; $\overline{M}_w$ is the average molecular weight determined by light scattering, $\overline{M}_n$ is the average molecular weight determined by osmometry, and dp is the degree of polymerization (the number of monomer units per chain). The values of $\overline{M}_w$ and $\overline{M}_n$ can also be determined by gel permeation chromatography (GPC). A living polymerization can be distinguished from free radical polymerization or from a condensation polymerization by plotting the molecular weight of the polymer versus conversion. In a living polymerization, the molecular weight is directly proportional to conversion (Figure 2.7, line A). In a free radical or other nonliving polymerization, high molecular weight polymer is formed in the initial stages (line B), and in a condensation polymerization, high molecular weight polymer is formed only as the conversion approaches 100% (line C).

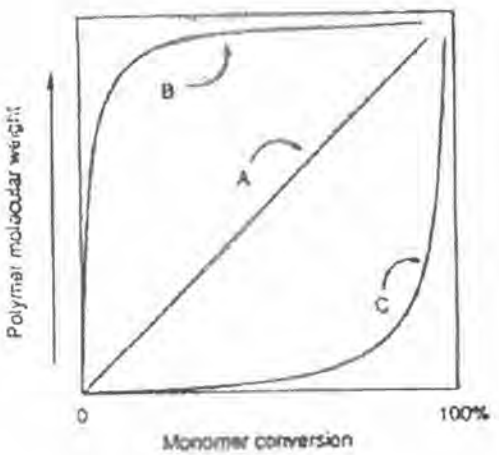


Figure 2.7 Molecular weight conversion curves for various kinds of polymerization methods: (A) living polymerization; (B) free radical polymerization; and (C) condensation polymerization [53]

Living polymerization techniques give the synthetic chemist two particularly powerful tools for polymer chain design: the synthesis of block copolymers by sequential addition of monomers and the synthesis of functional-ended polymers by selective termination of living ends with appropriate reagents. The main architectural features available starting with these two basic themes are listed in Figure 2.8 along with applications for the various polymer types. Although living polymerization of only a few monomers is nearly perfect, a large number of other systems fit theory close enough to be useful for synthesis of the wide variety of different polymer chain structures. In general, the well-behaved living systems need only an initiator and monomer, as occurs in the anionic polymerization of styrene, dienes, and ethylene oxide. For an increasing number of monomers, more complex processes are needed to retard chain transfer and termination. These systems use initiators, catalysts, and sometimes chain-end stabilizers. The initiator begins chain growth and in all systems is attached (or part of it, at least) to the nongrowing chain end. The catalyst is necessary for initiation and propagation but is not consumed. The chain-end stabilizer usually decreases the polymerization rate. When the catalyst is a Lewis acid (electron-pair acceptor), the stabilizer will likely be a Lewis base (electron-pair donor), and vice versa. In all systems, the initiation step must be faster than or the same rate as chain propagation to obtain molecular weight control. If the initiation rate is slower than the

propagation rate, the first chains formed will be longer than the last chains formed. If an initiator with a structure similar to that of the growing chain is chosen, the initiation rate is assured of being comparable to the propagation rate. A number of living systems operate better if excess monomer is present. A possible explanation is that the living end is stabilized by complexation with monomer [54]. Large counterions tend to be more effective than small counterions in living polymerization systems even when the ionic center is only indirectly involved.

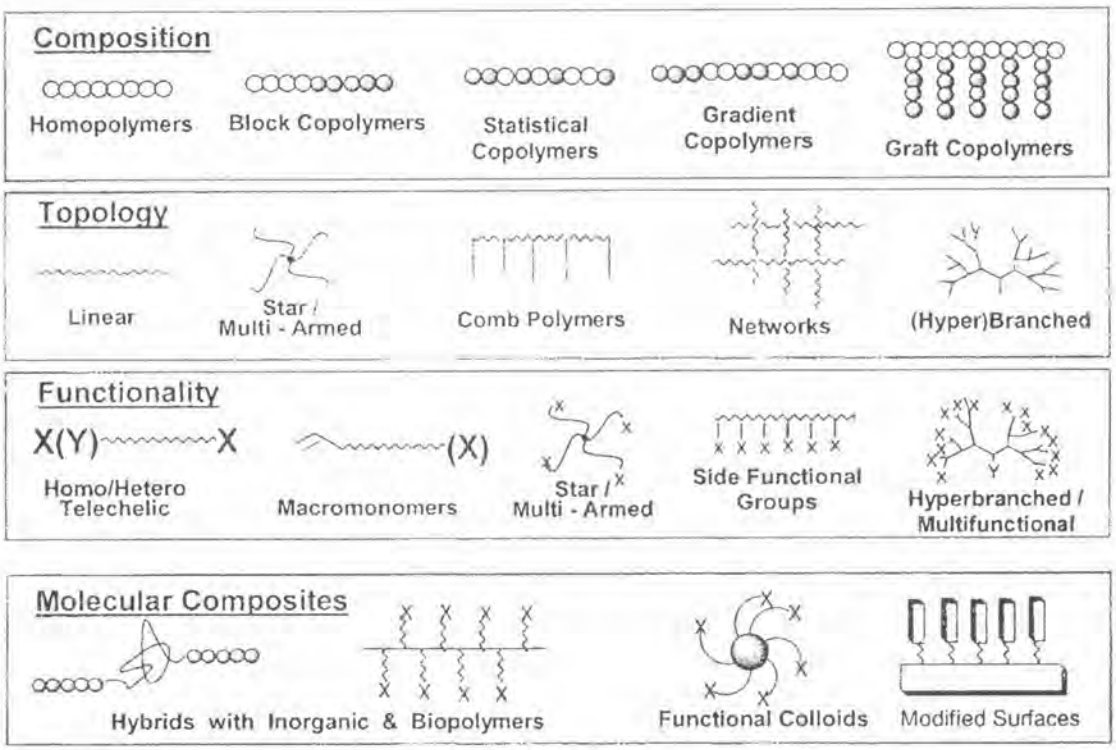


Figure 2.8 Architectural forms of polymers available by living polymerization techniques [65]

In this research, free radical process for living polymerization is selected and described. The concept of using stable free radicals, such as nitroxides, to reversibly react with the growing polymer radical chain end can be traced back to the pioneering work of Rizzardo and Mozd [55]. After further refinement by Georges [56], the basic blueprint for all subsequent work in the area of "living" free radical polymerization was developed. Subsequently, the groups of Sawamoto [57], Matyjaszewski [58], Percec [59], and others [60-61] have replaced the stable nitroxide free radical with

transition metal species to obtain a variety of copper-, nickel-, or ruthenium-mediated "living" free radical systems. These systems were called atom transfer radical polymerization (ATRP). This mechanism is an efficient method for carbon-carbon bond formation in organic synthesis. In some of these reactions, a transition-metal catalyst acts as a carrier of the halogen atom in a reversible redox process (Figure 2.9). Initially, the transition-metal species, M_t^n, abstracts halogen atom X from the organic halide, RX, to form the oxidized species, $M_t^{n+1}X$, and the carbon-centered radical $R^\bullet$. In the subsequent step, the radical $R^\bullet$ participates in an inter- or intramolecular radical addition to alkene, Y, with the formation of the intermediate radical species, $RY^\bullet$. The reaction between $M_t^{n+1}X$ and $RY^\bullet$ results in a target product, RYX, and regenerates the reduced transition-metal species, M_t^n, which further promotes a new redox process. The fast reaction between $RY^\bullet$ and $M_t^{n+1}X$ apparently suppresses biomolecular termination between alkyl radicals and efficiently introduces a halogen functional group X into the final product in good to excellent yields.

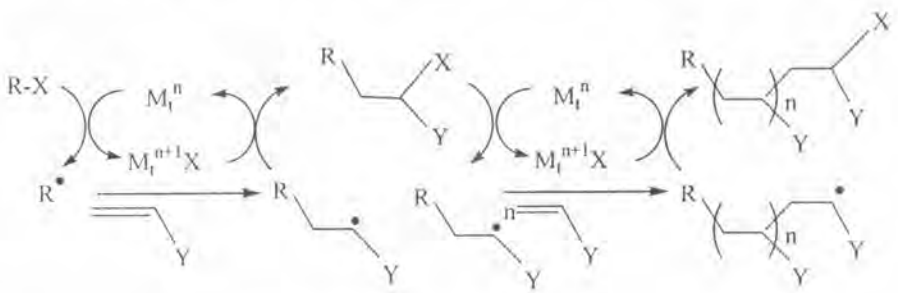


Figure 2.9 The mechanism of ATRP [64]

The ATRP system relies on one equilibrium reaction in addition to the classical free-radical polymerization scheme (Figure 2.10). In this equilibrium, a dormant species, RX, reacts with the activator, M_t^n, to form a radical $R^\bullet$ and deactivating species, $M_t^{n+1}X$. The activation and deactivation rate parameters are k_{act} and k_{deact}, respectively. Since deactivation of growing radicals is reversible, control over the molecular weight distribution and, in the case of copolymers, over chemical composition can be obtained if the equilibrium meets several requirements [62-63].

1. The equilibrium constant, k_{act}/k_{deact}, must be low in order to maintain a low stationary concentration of radicals. A high value would result in a high stationary

radical concentration, and as a result, termination would prevail over reversible deactivation.

2. The dynamics of the equilibrium must be fast; i.e. deactivation must be fast compared to propagation in order to ensure fast interchange of radicals in order to maintain a narrow molecular weight distribution.

$$R\text{-}X + M_t^n \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} R^{\bullet} + M_t^{n+1}X$$

Figure 2.10 Equilibrium reaction in ATRP [64]

Transition metal complexes (catalyst) are perhaps the most important components of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth, the ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. A variety of transition-metal complexes have been studied as ATRP catalysts.

Copper catalysts are superior in ATRP in terms of versatility and cost. Styrenes, (meth)acrylate esters and amides, and acrylonitrile have been successfully polymerized using copper-mediated ATRP. Examples of copper complexes used in ATRP are shown in Figure 2.11.

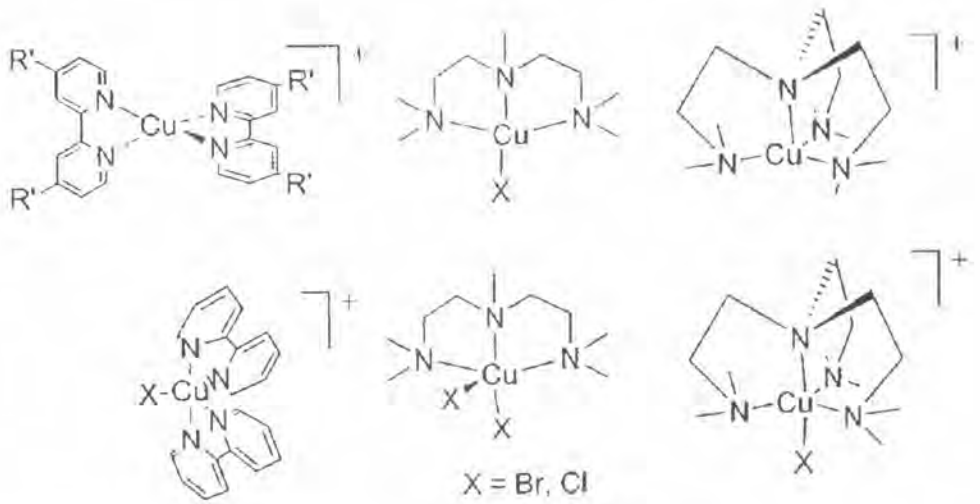


Figure 2.11 Copper complexes used as ATRP catalysts [65]

Nitrogen ligands have been used in copper-mediated ATRP. The monodentate (e.g., $N(nBu)_3$), bidentate(e.g., dNbpy), and multidentate nitrogen ligands have been applied to copper-based ATRP. The electronic and steric effects of the ligands are important. Reduced catalytic activity or efficiency is observed when there is excessive steric hindrance around the metal center or the ligand has strongly electron-withdrawing substituents. A recent survey summarized different ligands employed in copper-mediated ATRP. The effect of the ligands and guidelines for ligand design were reviewed. Activity of N-based ligands in ATRP decreases with the number of coordinating sites N4 > N3 >N2, N1 and with the number of linking C-atoms C2 > C3, C4. It also decreases in the order R_2N- ≈ PyrEnDash-> R-N= > Ph-N=> Ph-NR-. Activity is usually higher for bridged and cyclic systems than for linear analogues. Examples of some N-based ligands used successfully in Cu-based ATRP are shown in Figure 2.12.

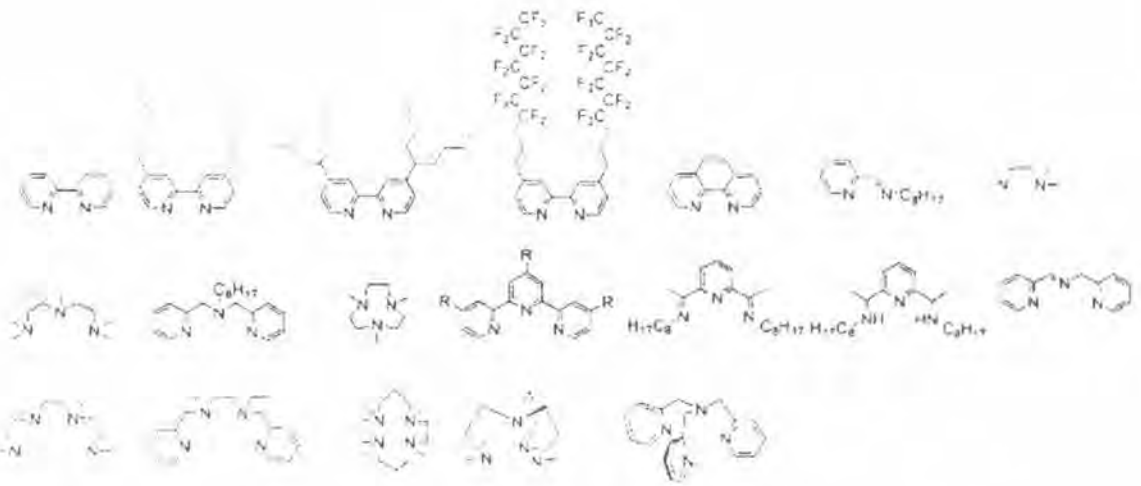


Figure 2.12 Example of ligands used in copper-mediated ATRP [65]

In 1995, Matyjaszewski has described the use of $Cu^{I}X$ (X = Br, Cl) with 2,2'-bipyridine (bpy) as a "solubilizing" ligand. The active species has been described as "CuBr·bpy". This system is active toward styrene, acrylates, and methacrylates under the appropriate condition [58]. Percec has also described the role of bpy as partially solubilizing the Cu(I)/Cu(II) catalyst [48]. The role of the bpy is to co-ordinate to Cu(I) to give a *pseudo*-tetrahedral Cu(I) center in solution (Figure 2.13).

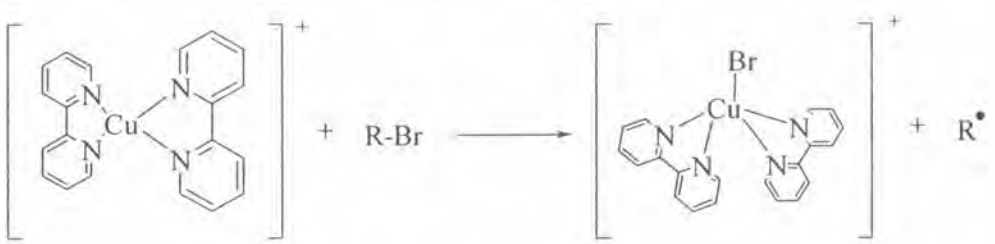


Figure 2.13 The rotation of the bpy ligands from the tetrahedral and co-ordination of halide at the Cu center [58]

Futhermore, in 1997 Matyjaszewski and coworkers [66] has described the use of simple amines as ligands for the copper mediated atom transfer radical polymerization (ATRP) of styrene, methyl acrylate and methyl methacrylate. The simple amines are of interest in ATRP for three general reasons. First, most of the

simple amines are less expensive, more accessible and more tunable than 2,2'-bipyridine (bpy) ligands. Second, due to the absence of the extensive π-bonding in the simple amines, the subsequent copper complexes are less colored. Third, since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bipy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates. The example of simple amine ligand is *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA). When this ligand was empolyed in ATRP, all the polymerizations were well controlled with a linear increase of molecular weights with conversion and relatively low polydispersities throughout the reactions. The rate of polymerization showed a significant increase, as compared to the corresponding bipy system. The higher polymerization rate of PMDETA as the ligand is partially attributed to the lower redox potential of the copper(I)-PMDETA complex than the copper(I)-bipy complex, which shifts the equilibrium from the dormant species toward the active species resulting in the generation of more radicals in the system. The structure of copper complex using PMDETA as the ligand was shown in Figure 2.14.

Figure 2.14 Proposed Cu(I) and Cu(II) species using PMDETA as a ligand [65]

2.6 Poly(acrylic acid)

Poly(acrylic acid) (PAA) are weak polyelectrolytes, in which the degree of ionization is governed by the pH and ionic strength of aqueous solution. PAA has been extensively investigated, owing to many scientific and industrial applications, such as intelligent environment-responsive surface [67] optical chemical sensing [68], and biomaterial carriers [69-70]. PAA can be covalently modified with a broad range of functional groups, such as fluorophores, electroactive groups, dyes, and other

biomolecules. Recent advances of the controlled/living polymerization techniques made it possible to produce well-defined polymer structures, such as graft copolymers, star polymers, polymer brushes, etc. The interest in synthesis and characterization of such complex polymer systems containing acrylic acid segments has increased enormously.

For the synthesis of well-defined polymers, controlled/living polymerization techniques have been traditionally employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination. Controlled/living polymerization of acrylic acid by ATRP presents a challenging problem because the acid monomer can poison the catalysts in system of ATRP by coordinating to the transition metal. In addition, nitrogen containing ligands can be protonated, which interferes with the metal complexation ability. Thus, typically, protected monomers have been employed, followed by a polymer-analogous deprotection, e.g. hydrolysis of protecting ester groups. Protected monomers with masked acid groups involve *tert*-butyl acrylate (*t*BuA), *tert*-butyl methacrylate (*t*BuMA), trimethylsilyl methacrylate (TMSMA), benzyl methacrylate (BzMA), 2-tetrahydropyranyl methacrylate (THPMA), and *p*-nitrophenyl methacrylate (PNPMA) (Figure 2.15). After acid hydrolysis, thermolysis, or catalytic hydrogenolysis, these protective groups liberate their original acid functionality. Essential prerequisites for the protected monomer are good 'livingness' under each polymerization condition and selective deprotection under mild conditions.

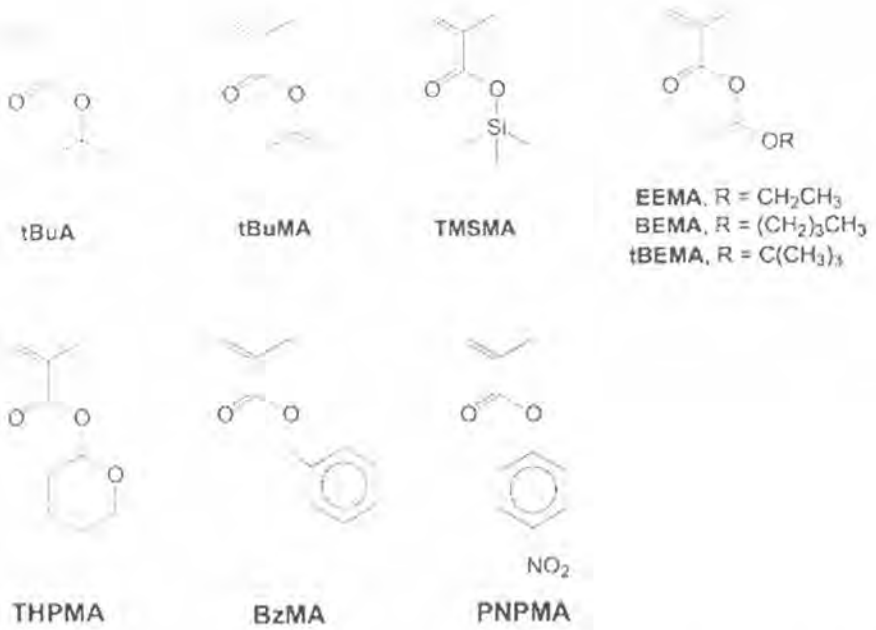


Figure 2.15 Representative examples of protected (meth)acrylic acid monomers with masked acid group [71-72]

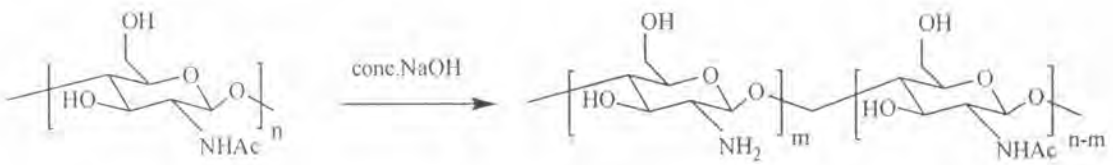
For the ATRP system, Matyjaszewski, *et al.* [71-72] reported controlled polymerization of *t*BuA using methyl 2-bromopropionate, as the initiator and the CuBr/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) catalyst system. In most ATRP based syntheses for block and further complex polymer systems, *t*BuA has been employed as a protected monomer, which may be due to the feasibility to control the polymerization and easy hydrolysis.

In 2003, Boyes, *et al.* [73] synthesize diblock copolymer polyelectrolyte brushes of either polystyrene (PS) or poly(methyl acrylate) (PMA) and poly(acrylic acid) (PAA) by ATRP. The polyelectrolyte diblock copolymer brushes were used for the synthesis of metal nanoparticles by treatment the PAA with aqueous metal salt subsequent reduction of the treated PAA.

2.7 Chitosan

Chitin, structurally similar to cellulose, is the natural polysaccharide which forms part of exoskeleton of crustaceans such as crabs and shrimps. Chitosan, a linear

polycationic biopolymer, is prepared by alkaline *N*-deacetylation of chitin. Chemical structures of chitin and chitosan are shown in Figure 2.16. Chitosan mainly consists of 2-amino-2-deoxy-D-glucose (GlcN) repeating unit with a small amount of 2-acetyl-2-deoxy-D-glucose residues. The amount of GlcN unit in chitosan is generally referred to the percent degree of deacetylation or %DD, influencing its physical, chemical properties as well as biological activities. Various techniques can be used for determination of % DD such as IR [74], NMR [75], and metachromatic titration [76].



Chitin Chitosan

Figure 2.16 Structures of chitin and chitosan

As a natural renewable resource, chitosan has a number of unique properties such as the physical, chemical, mechanical and biological properties including antimicrobial activity, nontoxicity, and biodegradability, which attract scientific interest in such fields as biotechnology, pharmaceutics, cosmetics, agriculture, food science, and textiles. Due to its reactive amino and hydroxyl groups, chemical modification of chitosan to achieve its derivatives is used to expand its application.

2.8 Poly 10,12-pentacosadiynoic acid (PPCDA)

Poly 10,12-pentacosadiynoic acid (PPCDA) vesicle chemical structure is shown in Figure 2.17. PPCDA is one of polydiacetylenes which are an interesting classes of ene–yne conjugated polymers that exhibit dramatic color change from blue to red upon exposure to various stimuli including light (photochromism), heat (thermochromism), mechanical stress (mechanochromism), solvents (solvatochromism), and binding of specific biological agents (biochromism). Polydiacetylenes can be prepared by topochemical polymerization of monomeric diacetylenes in numerous forms such as bulk solids, self-assembled films, and

vesicles suspended in liquids. Aqueous suspended polydiacetylene vesicles are generally produced from photopolymerization of vesicles formed from monomeric diacetylene lipids. The resulting nanospherical vesicles or liposomes of polydiacetylenes homogeneously dispersed in aqueous media have been successfully used as colorimetric sensors. Immobilization of polydiacetylene vesicles into thin films would enhance their storage stability and user-friendliness. Despite long and extensive research on polydiacetylene vesicles, reports on the fabrication of films containing these materials have just come to light in recent years. Monomeric diacetylenevesicles have been covalently fixed onto functionalized glass substrates followed by photopolymerization to form blue-phase polydiacetylene monolayer films. This approach is useful when monolayer deposition is desired, but the fabrication of multilayer films with sufficient visible color by this techniqueis not generally practical. The transfer of self-assembled polydiacetylene Langmuir–Blodgett films to flat substrates is somewhat less complicated, but is not suitable for the assembly of vesicles that have spherical hydrophilic surfaces. A little more than a decade ago, the polyelectrolyte multilayers (PEM) technique developed by Decher and co-workers emerged as an alternative method for the preparation of multilayer thin films. Although based on a very simple adsorption process, PEM assembly has proven to be a very powerful method for immobilizing charged species onto a substrate. It is important to emphasize here that in order for polydiacetylene vesicles to be usable in sensing applications, the characteristic blue color of the vesicles must be maintained during the film preparation process [77].

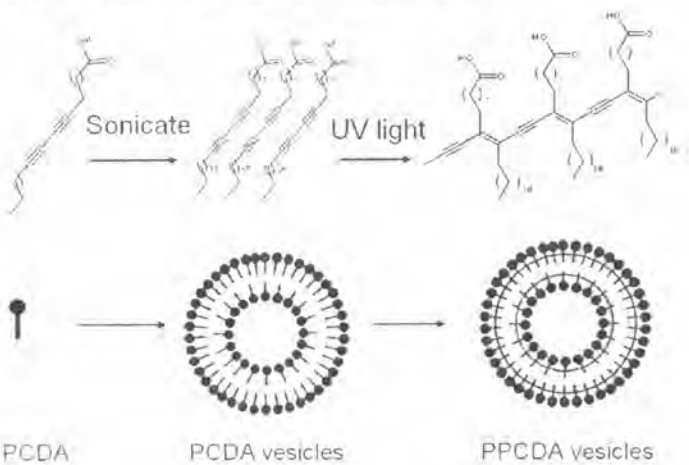


Figure 2.17 Chemical structure of PPCDA vesicle [77]

2.9 Characterization Techniques

2.9.1 Gel Permeation Chromatography (GPC) [78]

Gel permeation chromatography, more correctly termed *size exclusion chromatography*, is a separation method for high polymers, similar to but advanced in practice over *gel filtration* as carried out by biochemists, that has become a prominent and widely used method for estimating molecular-weight distributions since its discovery just over two decades ago in 1961. The separation takes place in a chromatographic column filled with beads of a rigid porous "gel"; highly cross-linked porous polystyrene and porous glass are preferred column-packing materials. The pores in these gels are of the same size as the dimensions of polymer molecules.

A sample of a dilute polymer solution is introduced into a solvent stream flowing through the column. As the dissolved polymer molecules flow past the porous beads, they can diffuse into the internal pore structure of the gel to an extent depending on their size and the pore-size distribution of the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded; smaller polymer molecules penetrate a larger fraction of the interior of the gel. The larger the molecule, therefore, the less time it spends inside the gel, and the sooner it flows through the column. The different molecular species are eluted from the column in order of their molecular size as distinguished from their molecular weight, the largest emerging first.

A complete theory predicting retention times or volumes as a function of molecular size has not been formulated for gel permeation chromatography. A specific column or set of columns (with gels of different pore sizes) is calibrated empirically to give such a relationship, by means of which a plot of amount of solute versus retention volume can be converted into a molecular-size-distribution curve.

As in all chromatographic processes, the band of solute emerging from the column is broadened by a number of processes, including contributions from the apparatus, flow of the solution through the packed bed of gel particles, and the

permeation process itself. Corrections for this zone broadening can be made empirically; it usually becomes unimportant when the sample has $\overline{M}_w/\overline{M}_n > 2$.

Gel permeation chromatography is extremely valuable for both analytic and preparative work with a wide variety of systems ranging from low to very high molecular weights. The method can be applied to a wide variety of solvents and polymers, depending on the type of gel used. With polystyrene gels, relatively nonpolar polymers can be measured in solvents such as tetrahydrofuran, toluene, or (at high temperatures) *o*-dichlorobenzene; with porous glass gels, more polar systems, including aqueous solvents, can be used. A few milligrams of sample suffices for analytic work, and the determination is complete in as short a time as a few minutes using modern high-pressure, high-speed equipment.

The results of careful gel permeation chromatography experiments for molecular-weight distribution agree so well with results from other techniques that there is serious doubt as to which is correct when residual discrepancies occur.

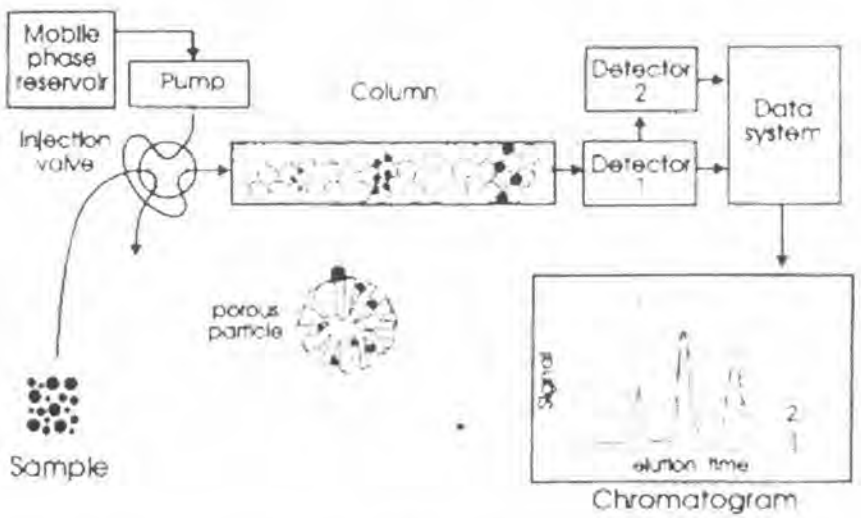


Figure 2.18 Schematic representation of the gel permeation chromatography [78]

2.9.2 Ellipsometry [79]

Ellipsometry is a sensitive optical technique for determining properties of surfaces and thin films. If linearly polarized light of a known orientation is reflected at oblique incidence from a surface then the reflected light is elliptically polarized. The shape and orientation of the ellipse depend on the angle of incidence, the direction of the polarization of the incident light, and the reflection properties of the surface. Ellipsometry measures the polarization of the reflected light with a quarter-wave plate followed by an analyzer; the orientations of the quarter-wave plate and the analyzer are varied until no light passes though the analyzer. From these orientations and the direction of polarization of incident light are expressed as the relative phase change, Δ, and the relative amplitude change, Ψ, introduced by reflection from the surface. These values are related to the ratio of Fresnel reflection coefficients, R_p and R_s for p and s- polarized light, respectively.

$$\mathrm{Tan}(\Psi)\, e^{i\Delta} = \frac{R_p}{R_s} \qquad (2.2)$$

An ellipsomer measures the changes in the polarization state of light when it is reflected from a sample. If the sample undergoes a change, for example, a thin film on the surface changes its thickness, then its reflection properties is also changed. Measuring these changes in the reflection properties allow us to deduce the actual change in the film's thickness.

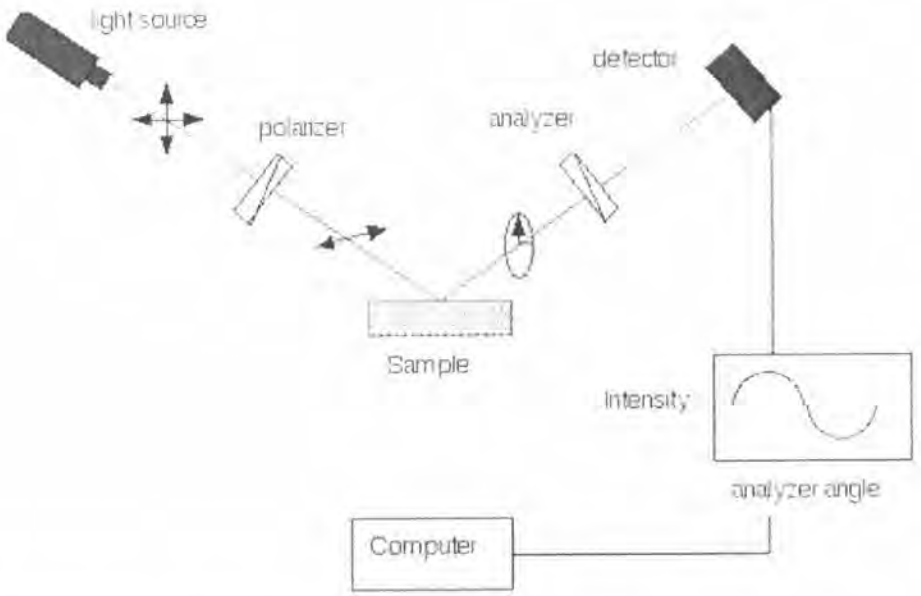


Figure 2.19 Schematic of the geometry of an ellipsometry experiment [79]

2.9.3 Contact Angle Measurement [80]

Contact angle measurements is often used to assess changes in the wetting characteristics of a surface and hence indicate a change in surface energy. The technique is based on the three-phase boundary equilibrium described by Young's equation.

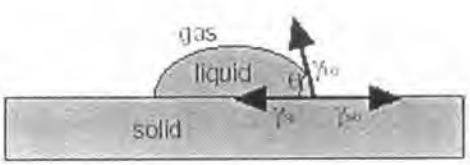


Figure 2.20 Schematic representation of the Young's equation [80]

$$\gamma_{LG}\cos\theta = \gamma_{SG} - \gamma_{SL} \qquad (2.3)$$

where γ_{LG}, γ_{SG} and γ_{SL} are the interfacial tension between the phases with subscripts L, G, S corresponding to liquid, gas, and solid phase respectively and θ refers to the equilibrium contact angle. The Young's equation applies for a perfectly homogeneous atomically flat and rigid surface and therefore supposes many simplifications. In the case of real surfaces, the contact angle value is affected by surface roughness,

heterogeneity, vapor spreading pressure, and chemical contamination of the wetting liquid. Although the technique to measure contact angles is easy, data interpretation is not straightforward and the nature of different contributions to the surface is a matter of discussion. Generally, we can define the complete wetting, wetting, partial wetting, and nonwetting according to Figure 2.21.

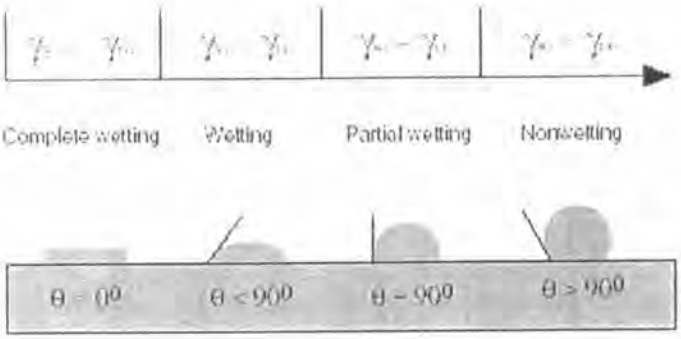


Figure 2.21 Schematic representation of wettability [80]

2.9.4 Atomic Force Microscopy (AFM) [81]

AFM is a type of scanning probe microscopy, allowing three-dimensional topographical imaging of surface. The AFM probe is in physical contact with the surface as it moves over the sample. Because it may be used on any surface, AFM is much more suited to polymer surface analysis. The essential features of AFM are shown in Figure 2.22. The tip of the probe, which is commonly made of silicon nitride, is attached to a cantilever bearing a reflective surface upon which is a laser beam is directed. The sample is mounted on a piezoelectric support, which moves in response to surface variations sensed by the probe. As the tip is scanned (or "rastered") over the surface, topological variations cause deflections in the cantilever that are monitored by recording the path of the reflected laser beam. A computer interprets the deflections as a three-dimensional profile of the polymer surface with resolution in the angstrom range, which is several orders of magnitude better than that obtained by SEM.

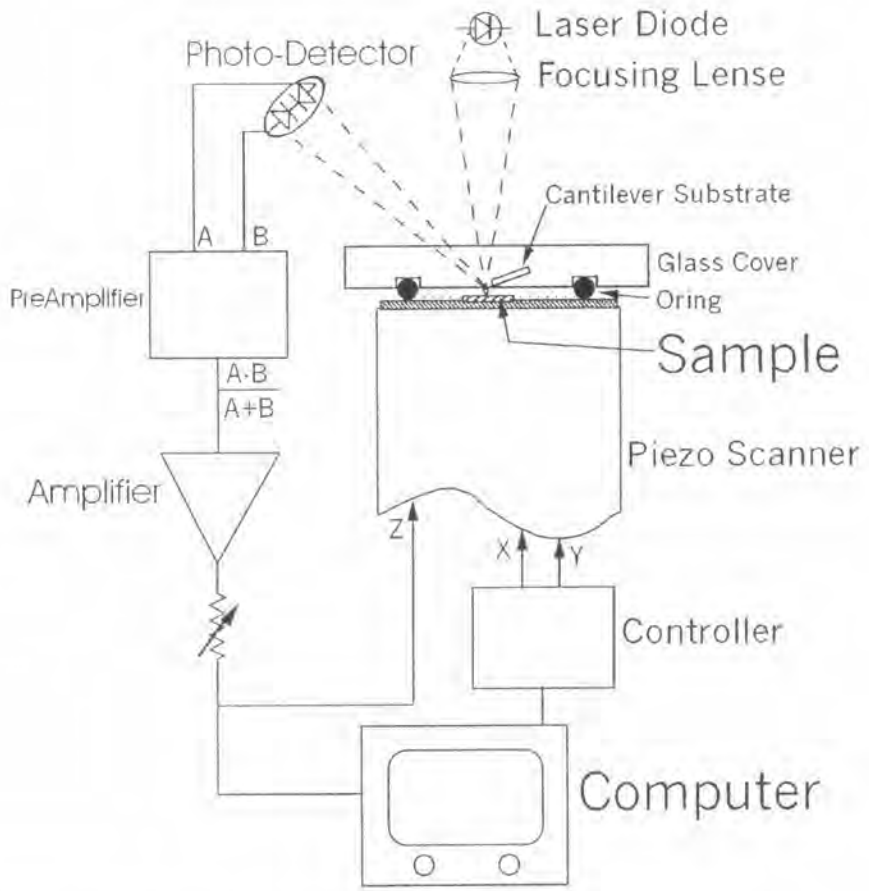


Figure 2.22 Schematic diagram of an atomic force microscope [81]

The Atomic Force Microscope (AFM) is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries. The materials being investigated include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. By using AFM, one cannot only image the surface in atomic resolution but also measure the force at nano-newton scale. The publications related to the AFM are growing speedily since its birth.

The first AFM was made by meticulously gluing a tiny shard of diamond onto one end of a tiny strip of gold foil. In 1985 Binnig and Gerber used the cantilever to

examine insulating surfaces. A small hook at the end of the cantilever was pressed against the surface while the sample was scanned beneath the tip. The force between tip and sample was measured by tracking the deflection of the cantilever. This was done by monitoring the tunneling current to a second tip positioned above the cantilever. They could delineate lateral features as small as 300 Å. The force microscope emerged in this way. In fact, without the breakthrough in tip manufacture, the AFM probably would have remained a curiosity in many research groups. It was Albrecht, a fresh graduate student, who fabricated the first silicon microcantilever and measured the atomic structure of boron nitride. Today the tip-cantilever assembly typically is microfabricated from Si or Si_3N_4. The era of AFM came finally when the Zurich group released the image of a silicon (111) 7X7 pattern. The world of surface science knew that a new tool for surface microscope was at hand. After several years the microcantilevers have been perfected, and the instrument has been embraced by scientists and technologists.

The force between the tip and the sample surface is very small, usually less than 10^{-9} N. How to monitor such small forces is another story. The detection system does not measure force directly. It senses the deflection of the microcantilever. The detecting systems for monitoring the deflection fall into several categories. The first device introduced by Binnig was a tunneling tip placed above the metallized surface of the cantilever. This is a sensitive system where a change in spacing of 1 Å between tip and cantilever changes the tunneling current by an order of magnitude. It is straightforward to measure deflections smaller than 0.01 Å. Subsequent systems were based on the optical techniques. The interferometer is the most sensitive of the optical methods, but it is somewhat more complicated than the beam-bounce method which was introduced by Meyer and Amer. The beam-bounce method is now widely used as a result of the excellent work by Alexander and colleagues. In this system an optical beam is reflected from the mirrored surface on the back side of the cantilever onto a position-sensitive photodetector. In this arrangement, a small deflection of the cantilever will tilt the reflected beam and change the position of beam on the photodetector. A third optical system introduced by Sarid uses the cantilever as one of

the mirrors in the cavity of a diode laser. Motion of the cantilever has a strong effect on the laser output, and this is exploited as a motion detector

The principles on how the AFM works are very simple. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si_3N_4 or Si, and extended down from the end of a cantilever. The nanoscope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode. The photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts to voltage. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode, the piezo-electric transducer monitors real time height deviation. In the constant height mode, the deflection force on the sample is recorded. The latter mode of operation requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope.

Some AFM's can accept full 200 mm wafers. The primary purpose of these instruments is to quantitatively measure surface roughness with a nominal 5 nm lateral and 0.01nm vertical resolution on all types of samples. Depending on the AFM design, scanners are used to translate either the sample under the cantilever or the cantilever over the sample. By scanning in either way, the local height of the sample is measured. Three dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position.

The concept of resolution in AFM is different from radiation based microscopies because AFM imaging is a three dimensional imaging technique. The ability to distinguish two separate points on an image is the standard by which lateral

resolution is usually defined. There is clearly an important distinction between images resolved by wave optics and scanning probe techniques. The former is limited by diffraction, and later primarily by apical probe geometry and sample geometry. Indeed, many authors have seen that it is the radius of curvature that significantly influences the resolving ability of the AFM. Even greater improvements in resolution have been attained with Tapping mode but contact imaging still is capable of high resolution imaging. The brief discussion on resolution was published by Keller

In order to obtain good AFM results, the vibration isolation platform is needed. The vibration isolation consists of a large mass attached to bungy cords firmly anchored to the building. Damping of the oscillation is believed to result from rubbing of the rubber fibres inside of the bungy cord against the outside lining material. Between the low resonance frequency of the bungy cord system and the high resonance frequency of the microscope hardware itself (>10 kHz), the AFM effectively comprises a band pass filter. This allows the microscopists to safely image their samples in the intermediate range of about 1-100 Hz and obtain atomic resolution.