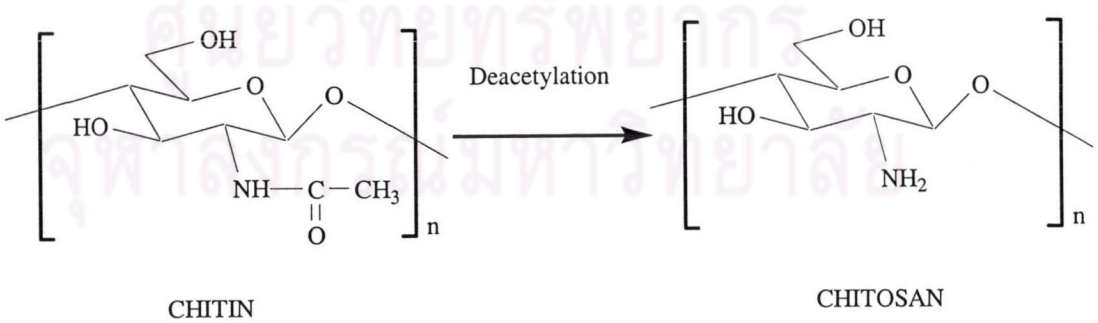
CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Chitosan

Chitosan, a linear cationic polyelectrolyte, has a structure similar to cellulose. Chitosan is produced by deacetylation of chitin. Conversion of chitosan generally is achieved by treatment with concentrated sodium or potassium hydroxide to remove some or all of acetyl groups from the polymer. 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. It has been observed that the degree of acetylation of chitosan influences physical and chemical properties as well as biological activities of chitosan, tensile strength of chitosan films, enzyme binding and immunological activity [1]. Various techniques can be used for determination of % DD such as IR [2], NMR [3], and metachromatic titration [4]. The structures of chitosan and chitin are shown in Figure 2.1.



CHITIN CHITOSAN

Figure 2.1 Structures of chitin and chitosan.

Chitosan is dissolved in inorganic acids such as HCl, HNO_3 and organic acids preferably acetic acid and formic acid. Pure chitosan precipitates from solutions if the pH rises above 6.

Chitin, the secound-most abundant natural polymer, is harvested mainly from the exoskeleton of crustaceans such as crabs, krill, lobsters and shrimp. Chitin and chitosan have recently been interesting choices for uses in various medical and pharmaceutical applications due to their attractive chemical, physical and mechanical properties. For instance, inter - and intramolecular hydrogen bonding, similar to cellulose, imparts excellent film and fiber-forming properties in chitosan for the development of hemodialysis membranes, artificial skin, wound dressings, physical barriers to prevent post-surgical adhesions and suture materials. The polycation structure of chitosan allows the formation of pH- sensitive drug delivery systems, polyelectrolyte complexs and microcapsules, bile and fatty acid binders and self-assembling. Chitosan does possess the necessary properties for preparation of ultrathin films. Chitosan is also shown to enhance osteogenesis and improve wound healing and is then used for some biomaterial applications such as artificial skin, wound dressing and sutures. However, it is indicated in the literature that chitosan has the capacity to activate both complement and blood coagulation systems.

In 2000 and 2002 Takeshi, et al. studied formation of polymer layer-by-layer assemblies having alternating bioactivity. Dextran sulfate and chitosan were selected as polymers with anti- and procoagulant activities, respectively. Heparin, which is another well-known anionic polymer showing anticoagulant activity, was also used in a layer-by-layer assembly with chitosan. Its bioactivity was analyzed [5], [6].

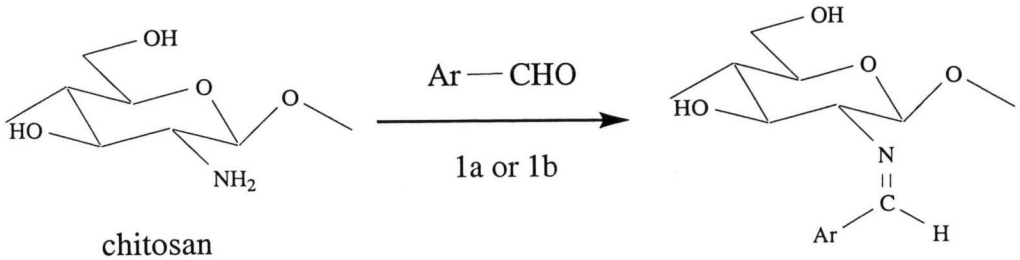
In 2002 Johan and Petti prepared thin chitosan films by glutaraldehyde crosslinking of chitosan onto APTES coated surfaces. Biocompatibility of the supported thin film was analyzed after incubating in serum or plasma. Polyclonal antibodies towards a few selected serum proteins were used to detect the binding and activation of complement factors and the intrinsic pathway of coagulation proteins. The adsorbed amounts of serum and antibodies were quantified by single wavelength null ellipsometry. However, acetylation turned the chitosan coating into a strong

alternative pathway activator. Large amounts of fibrinogen and other plasma proteins bound to chitosan but not to acetylated chitosan. The present results confirms that chitosan can activate the complement cascade and that the activation depends on degree of acetylation [7].

Recently, attempts have also been made to improve blood compatibility of chitosan with physical blends, surface modification and synthesis of blood compatible derivatives. Previous work reported the preparation of sulfonated derivative of chitosan to improve blood compatibility. The method involved the chemical modification of chitosan by grafting with negatively-charged modifiers containing sulfonic acid. Recent studies have shown that ionomers containing sulfonic acid have favorable blood-contacting responses including anticoagulant nonthrombogenic, reduced complement activity and anti-calcification properties.

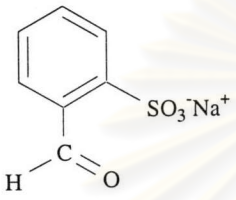
In 1997 Gregorio, et al. synthesized N-benzyl sulfonated derivatives of chitosan by reactions with 2-furmylbenzene sodium sulfonate and 4-formylbenzene sodium disulfonate in the presence of sodium cyanoborohydride. One-dimensional and two-dimensional NMR spectroscopy were used for the characterization of the products [8].

In 1998 Mansoor, synthesized an amphoteric derivative of chitosan by reacting the polymer with the sodium salt of 5-formyl-2-furansulfonic acid to obtain the sulfonated chitosan derivative. In vitro blood compatibility of the sulfonated chitosan was evaluated by measuring the number of adherent platelets and the extent of platelet activation. The sulfonated chitosan appeared to possess non-thrombogenic properties and may be suitable for some blood-contacting applications [9].

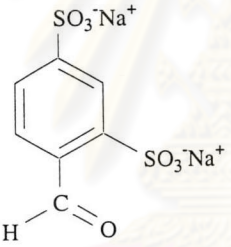


chitosan

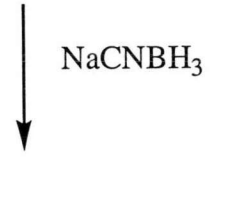
intermediate schiff base

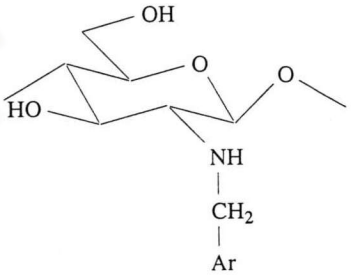


1a 2-formylbenzenesulfonic acid



1b 4-formyl-1,3-benzenedisulfonic acid





sulfonate derivative

Figure 2.2 Reaction scheme for the synthesis of sulfonate derivatives of chitosan [8].

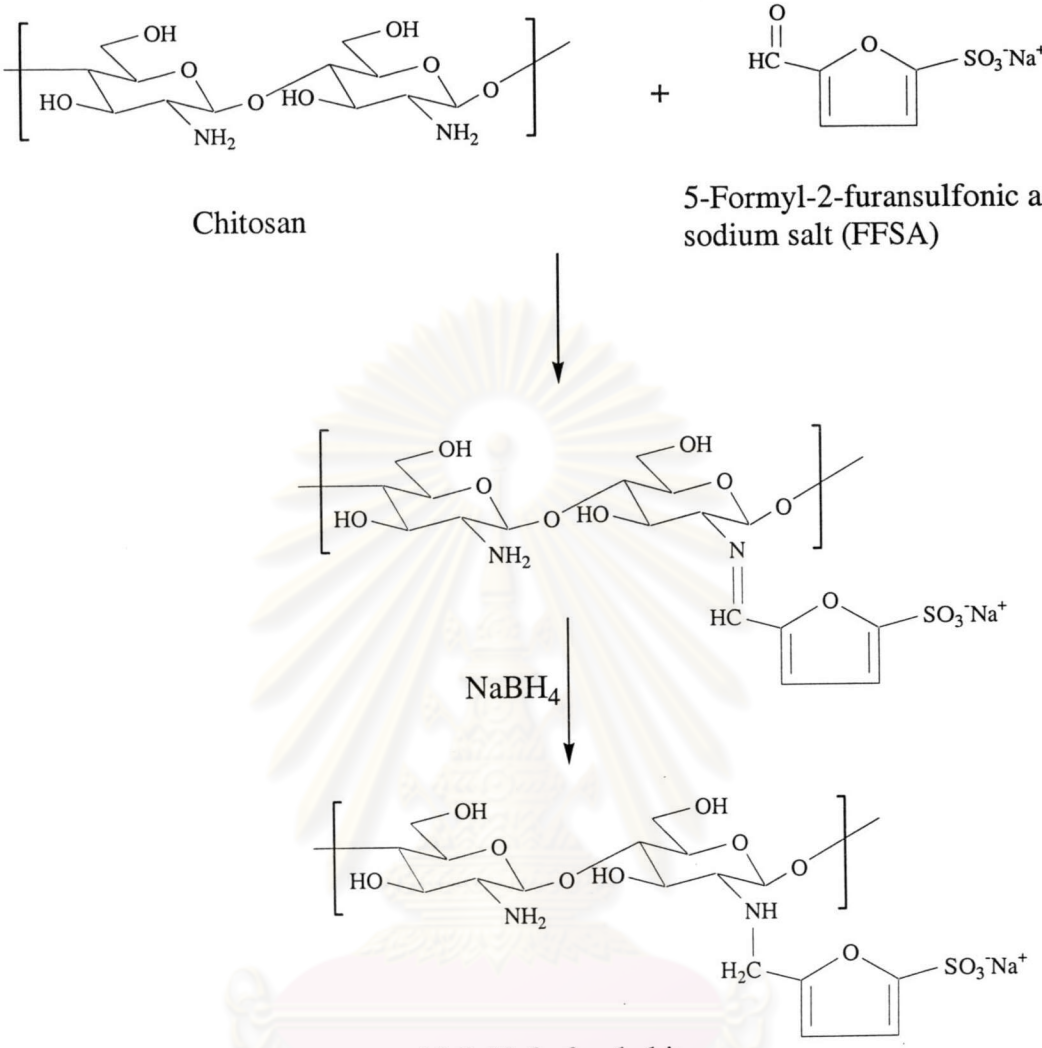


Figure 2.3 Reaction scheme for the synthesis of N-sulfofurfuryl chitosan [9].

In 2002 Preeyanat, et al. prepared chitin from the shells of rice-field crabs (*Somanniathelphusa dugasti*) which was converted into chitosan and then sulfated with chlorosulfonic acid in N,N-dimethylformamide to give water-soluble sulfated chitosan. The sulfated chitosan preparation showed strong anticoagulation [10].

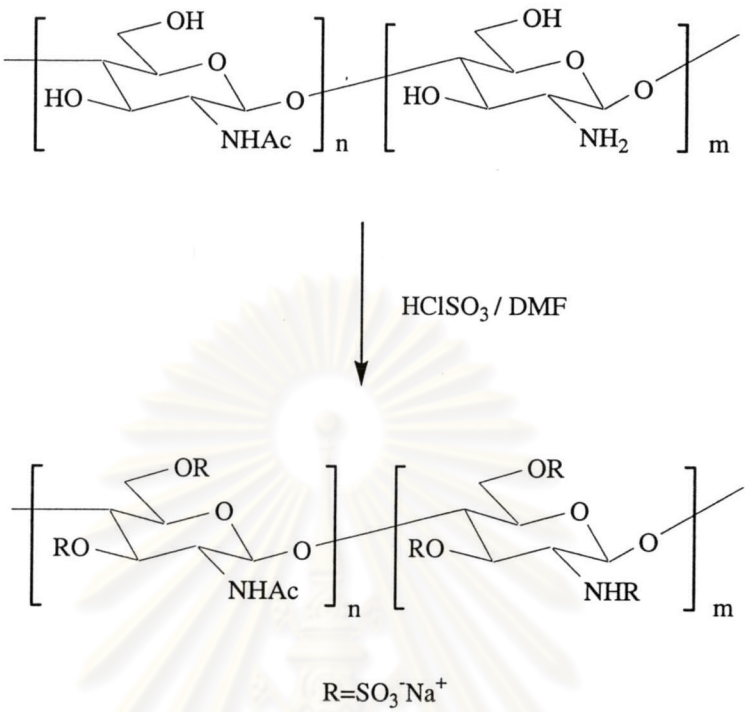


Figure 2.4 Reaction scheme for the synthesis of sulfated chitosan [10].

Other numerous materials have been used to coat artificial surfaces in an attempt to improve biocompatibility such as coating with naturally occurring bioactive or bioinert substance like polysaccharide. An additional advantage using the polysaccharide in human could be its non-mammalian source, which eliminates the risk of contamination with pathogenic agents.

2.2 Polyelctrolyte Adsorption

When charges are present in macromolecular solution near a surface, several features show up that do not play a role in uncharged systems. If the polymer is charged, the mutual repulsion between the segments opposes accumulation in the surface region. In addition, the surface carries a charge, there is an electrostatic contribution to the segment surface interaction that either promotes or counteracts the adsorption, depending on the types of charges. The structure aspects of

adsorption must imply changes in their shape. The usual description of conformations at an adsorbing interface, first proposed by Jenkel and Rumbach and depicted schematically in Figure 2.5 is in terms of three types of subchains: trains, which have all their segments in contact with the substrate, loops, which have no contacts with the surface and connect two trains, and tails which are non adsorbed chain ends [11].

In polyelectrolyte adsorption, electrostatic interactions play a very important role. Since this interaction is of variable range and strength, depending on charge densities (for both the surface and the polyelectrolyte chains) and salt concentrations, the adsorbed amount depends strongly on these two variables. The ionic strength of polyelectrolyte solutions can be adjusted by the addition of salts (e.g. KNO_3, NaCl, $MnCl_3$). The magnitude of changes in solvent properties and interactions between ionic species (inter-and intramolecular interactions of polyelectrolyte and the substrate) in the solution are varied with the amount of salt added. The conformation of an adsorbed polyelectrolyte layer is markedly dependent on the ionic strength of the solution from which the adsorption takes place. For strong polyelectrolyte systems, polymer chains adsorb in very flat conformations (trains with few loops and tails) especially to highly charged surfaces with low adsorbed amount at low salt concentration. At higher salt concentration, intra-and interchain repulsions of segments in loops or tails are suppressed and polyelectrolytes behave essentially like neutral polymer. Increasing ionic strength is related to decreasing the solvency, and promotes more adsorption. Polymer segments tend to form more loops, tails and eventually extended chains as the adsorbed amount and layer thickness increase. At very high ionic strength, however, where all charges on polymer segments are completely screened, a more random coil-like conformation with a smaller radius of gyration is more favorable than the extended chain.

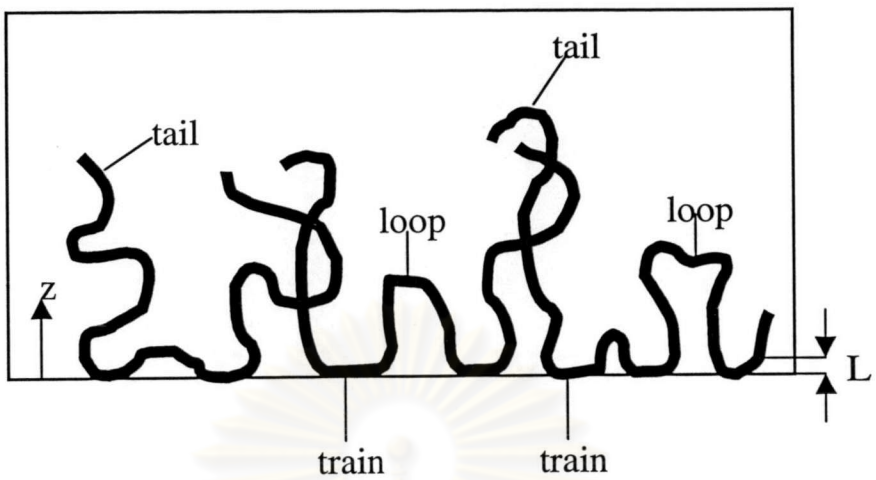


Figure 2.5 Pictorial representation of an adsorbed polymer layer, indicating loops, tails and trains (L : thickness of chain) [11].

2.3 Layer-by-layer Adsorption

The surface modification of materials by organic or inorganic layers is significant for biomedical applications, because the intact materials can be engineered for specific bioaffinities. Coating a substrate surface with polymeric ultrathin films can maintain the original mechanical properties and/or fine structures of the substrate. If the polymers used are insoluble in an aqueous biological phase, then the coating is easily performed by methods such as dip-or spin-coating. However, when the polymers are water-soluble, they should be immobilized by chemical bonds between the polymers and the substrate material. There are limitations in the latter case, and control of the chemical composition of the film surface is also necessary.

The fabrication of ultrathin polymer films on material surface is important for various scientific applications such as in biomedical fields [12], biosensor electronic parts [13], membrane [14] in order to modify or improve the intact characteristic of surfaces, which can be exposed to various environments. The effective coating of surface with polymers thus results in a potentially drastic change

in surface affinity. In most case, the material characteristics seem to be governed by the chemical composition of surface.

Layer-by-layer assembly, which can be achieved by the alternate immersion of certain substrate into oppositely charged polymers, is a promised methodology that uses electrostatic interaction, which was first introduced by Decher in 1991 [15] , as a versatile method for preparing supported multilayer films (Figure 2.6). One of the most important properties of such multilayers comes from the fact that they exhibit an excess of alternatively positive and negative charges [16]. The outmost layer usually showed any specific properties of adsorbed polymer. Many compounds were used for layer-by-layer adsorption such as linear polyelectrolytes and other macroions including protein, enzyme and colloidal nanoparticles [12,17,19,20, 22].

The process, in its simplest form, involves sequentially dipping a charged substrate into dilute aqueous solutions of oppositely charged polyelectrolytes and allowing the polymer to adsorb and reverse the charge of the substrate surface. The sequential adsorption of an anionic and a cationic polyelectrolyte allow the buildup of multilayer film structure. Thick films with a rather well-controlled thickness have been obtained with the introduction of the multilayer conditions and number of deposition. In exploring growth conditions, it is generally observed that salt has the strongest influence on the amount deposited (layer thickness) per cycle. Polymer concentration, molecular weight and deposition time are known to be less important variables [17].

Recently, many research publications reported the use of the layer-by-layer adsorption for preparing ultrathin polymer film. The method concerns electrostatic interactions between cationic and anionic polyelectrolytes to modify and to improve surface properties of materials for biomedical applications.

In 1994 Yuri, et al. prepared densely packed charged virus sandwiched in multilayer films of charged polyelectrolytes by successive adsorption of poly(styrene sufonate) (PSS) and poly(allyamine hydrochloride) (PAH). It was demonstrated that the surface created by particle deposition was smooth. Very precise data on the

thicknesses of sublayers were derived from suitable model fitting [18]. In the same year, they prepared multilayer films by means of alternate adsorption of positively charged globular protein (myoglobin or lysozyme) and anionic poly(styrene sulfonate). Regular growth alternate adsorption was analyzed by UV spectroscopy and quartz crystal microbalance (QCM) [19].

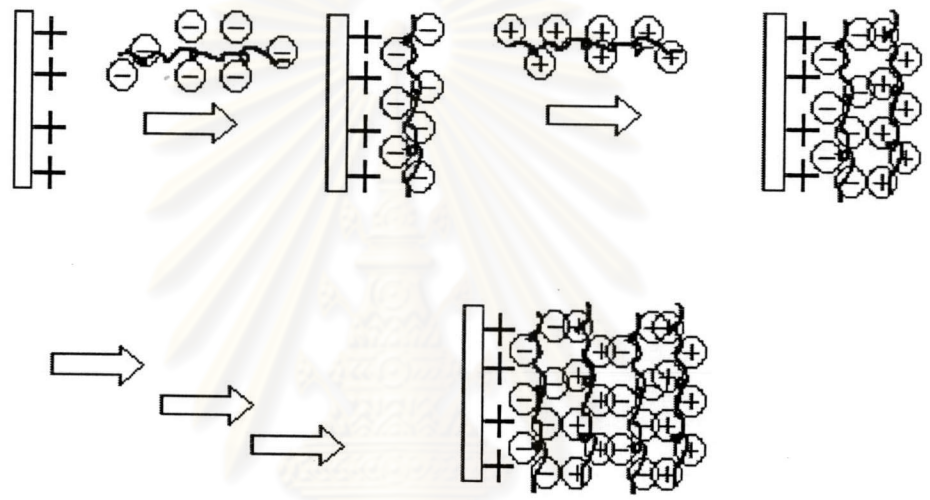


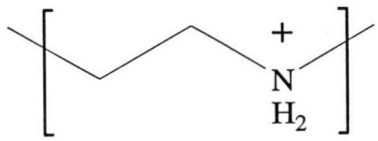
Figure 2.6 Schematic illustration of alternate layer-by-layer adsorption of polyanion and polycation onto a positively charged substrate.

In 1998 Frank, et al. prepared protein-containing polyelectrolyte multilayer films of PSS and PAH fabricated by the sequential adsorption of polyelectrolyte and anti-immunoglobulin G (anti-IgG) on solid substrate. The deposited films were characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM) and fourier transform infrared reflection-absorption spectroscopy. Both types of films fabricated are attractive for biosensing applications. Not only they can provide ordered, functional protein layers within a polyelectrolyte matrix for sensing investigations, they can also serve as useful functional films for applications where an increased binding capacity of the film is sought [20].

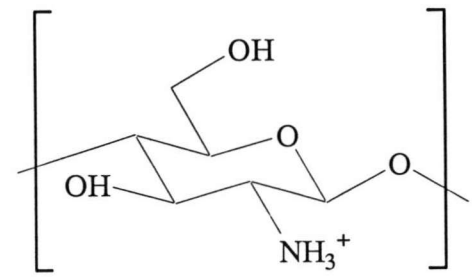
In 1999 Donald, et al. studied the formation of thin polymer films on models of tissue surfaces using polyelectrolyte multilayer techniques in order to evaluate the feasibility of using such technique to build barrier materials onto the surfaces of tissue to improve postsurgical healing, or on the surfaces of tissue-engineered implants. By incubated heterogeneous surface with a polycation (alginate), followed by a polyanion (polylysine), layers of polyelectrolyte were deposited onto surfaces, as confirmed by ellipsometry and water contact angle measurement. Surfaces that were treated with multilayer techniques included gelatin, fibroblast extracellular matrix, and fibrillar type I collagen [21]. In the same year, they also prepared assembled multilayer of bovine serum albumin (FITC-BSA) and immunoglubulin G (IgG) by assembling on 640 nm diameter polystyrene (PS) latex particles. The regular, controlled, stepwise assembly of the protein and polyelectrolyte multilayer films was studied by electrophoretic mobility (EPM), single particle light scattering (SPLS), and transmission electron microscopy (TEM) methods. The formation of these novel, biologically functional, core-shell particles is expected to impact the areas of biotechnology and biochemical engineering [22].

In 2000 Guy, et al. investigated the interaction between poly(styrene sulfonate) (PSS) and polyallylamine (PAH) multilayers with human serum albumin (HSA). The results showed that the underlying complexity of concentration and pH dependent adsorption/desorption equilibrium often simply termed "protein adsorption" was the result of antagonist competing interactions that were mainly of electrostatic origin [23].

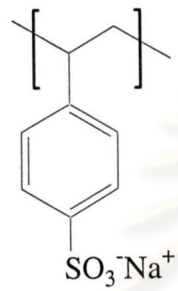
In 2000 Hyun, et al. prepared alternate layer-by-layer depositions of G4 poly(aminoamine) dendrimers and periodate-oxidized glucose oxidase (Gox). The cyclic voltammograms obtained from the Au electrodes modified with the Gox/dendrimer multilayers revealed that bioelectrocatalytic response was directly correlated to the number of deposited bilayers, that is, to the amount of active enzyme immobilized on the Au electrode surface. A new approach to construct a multilayered enzyme films on the Au surface for using as a biosensing interface was described [24].



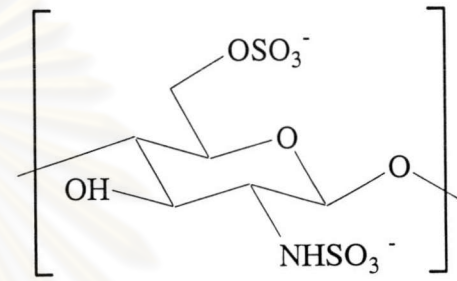
Poly(ethyleneamine) (PEI)



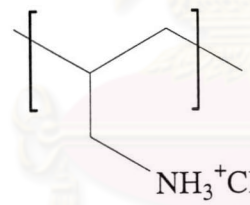
Chitosan



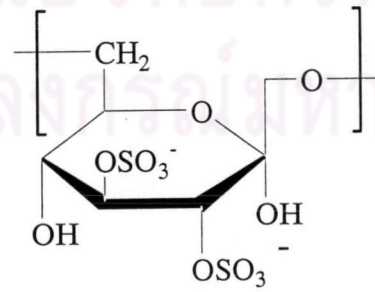
Poly(styrene sulfonate)
(PSS)



Heparin



Poly(allylamine hydrochloride) (PAH)



Dextran sulfate

Figure 2.7 Examples of polycations and polyanions used for multilayer assembly.

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

In 1998 Yuri. et al. 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 [1].

In 1999 Lutz. et al. prepared composite membranes by alternating electrostatic adsorption of chitosan and PSS on a porous PAN/PET supporting membrane (a polyethyleneterapthalate fleece coated with thin layer of polyacrylonitrile). The use of composite membranes with ultrathin self-assembled polyelectrolyte in gas, liquid and ion separation was described [25].

In 2000 Takeshi. et al. studied the alternating anti-vs procoagulation activity of ultrathin polymer films prepared by layer-by-layer assembly technique against human blood. Dextran sulfate (Dex) and chitosan were selected as polymers with anti-and procoagulation activities, respectively. The layer-by-layer assembly of these polymers was quantitatively analyzed by a quartz crystal microbalance (QCM). They also investigated the influence of salt concentration in the polymer aqueous solutions on the assembly process, which ultimately led to thicker films. This study demonstrated that biocompatibility of multilayers can be controlled. [5]. Later in 2002, Takeshi. et.al. continued their study on multilayer systems. 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 [6].

2. 4 Blood Compatibility

The term "biocompatibility" encompasses many different properties of the materials, however, two important aspects of biomaterial screening refer to their in vitro cytotoxicity and blood compatibility behavior. Artificial surfaces were in contact with blood trigger a number of biological systems through the adsorption of protein and cells. It is generally believed that the nature of adsorbed protein layer determined all adverse events that impair the use of artificial materials in medical devices: thrombus formation as a result of platelet adhesion, platelet activation, initiation of coagulation and activation of the complement system that in turn results in leukocyte adhesion and activation.

2.4.1 Human Plasma

Human blood is a highly complex substance. Its major components are red blood cells, which carry oxygen from the lungs to the body; white blood cells, which have major roles in disease prevention and immunity; and platelets, which are key elements in the blood clotting process. These blood elements are suspended in blood plasma, a yellowish liquid that comprises about 55 % of human blood. When the blood was spin in a centrifuge, the red cells went to the bottom of the container, and the white cells and platelets went to the middle, leaving the yellowish plasma at the top.

The plasma is the river in which the blood cells travel. It carries not only the blood cells but also nutrients (sugars, amino acids, fats, salts, minerals, etc.), waste products (CO_2, lattic acid, urea, etc.), antibodies, clotting proteins (called clotting factors), chemical messengers such as hormones, and proteins that help maintain the body's fluid balance.

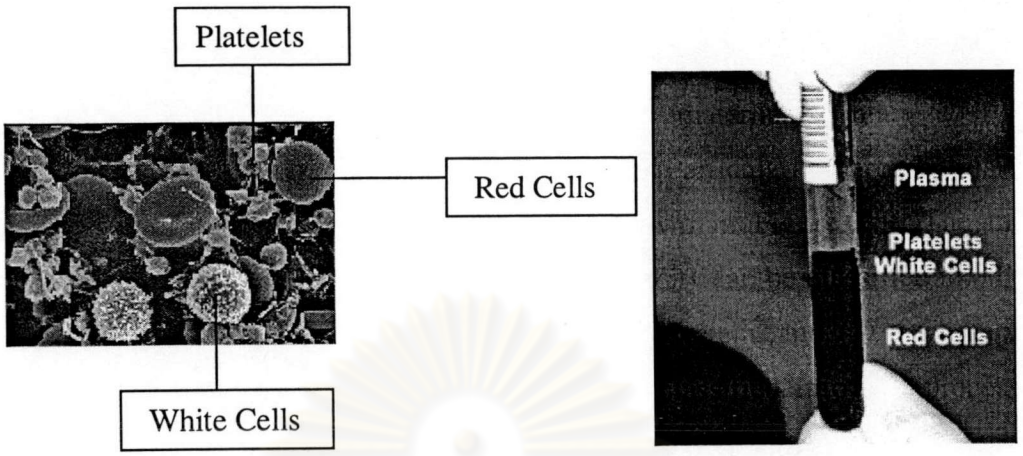


Figure 2.8 Pictorial representation of human blood.

Many specific functions of blood are carried out by proteins found in plasma. Human plasma contains a number of proteins such as albumin (Alb), immunoglubulins (Ig), complement factors, fibrinogen (Fg), Fibronectin (FN), coagulation factors (activators and down regulators) , and lipoprotein (LP). These proteins all have various biological roles: Alb is considered a biological passivator ; immunoglobulin G (IgG) activates the complement system and, for example, binds lymphocytes; the complement factors (including C3) are a part of immune defense ending in the lysis of cells with the membrane attack complex repturing the cell types and bacteria have receptors for FN, α_2-macroglobulin (α_2M) is a down regulator of the coagulation cascade that ends in the formation of blood clot in which factors like high molecular weight kininogen (HMWK), factor XII (F XII), factor VII (F VII) and prekallikrein (PK) are component, anti thrombin III (ATh III) is another potent down regulator of coagulation, as it binds thrombin, LP can act as transport protein of such agents as cholesterol [26].

2.4.2 Mechanism of Thrombus Formation on Polymer Surface

When artificial materials contact a living organism, severe biological responses are induced. Particularly, thrombus is formed when blood encounters a foreign surface as shown in Figure 2.9. The mechanism of coagulation is very complicated, but simplicity can be classified into three processes: (1) the coagulation system, (2) the platelet system, and (3) the complemental system. The coagulation system can be further classified into two processes. One is started by Factor VII when the tissue is damaged extrinsically (i.e. outside the body). The other is induced by Factor XII (Hageman Factor) which is activated via an inflammation originating within the body (i.e. intrinsic pathway).

It is well known that platelets also contribute to thrombus formation. A foreign substrate induces adhesion and activation of platelets with the adsorbed protein layer serving as a controlling factor of the platelet response. The adhesion of platelets to a biomaterial surface is followed by the platelet release reaction taking place in the adhering platelets and then platelet aggregation on the surface.

The complement system can also be classified into two processes: (1) the classical pathway and (2) the alternative pathway. The classical pathway is started from the interaction between the immunocomplex contained within immunoglobulin G (IgG) or immunoglobulin M (IgM) and C1q in the C1 complex. The alternative pathway is started with C3a work for adhesion of leukocyte and activation of C5.

These three mechanisms of coagulation are not independent. Normally, thrombus formation on a foreign surface results in an interaction between platelets and intrinsic pathway. Initiation of the intrinsic coagulation cascade may be induced by thromboplastins liberated from platelets or by Factor XII activation caused by platelets stimulated by released adenosine diphosphate (ADP). Thrombin formation caused by activation of the intrinsic pathway induces the production of a fibrin monolayer on a biomaterial surface and the promotion of platelet adhesion and aggregation.

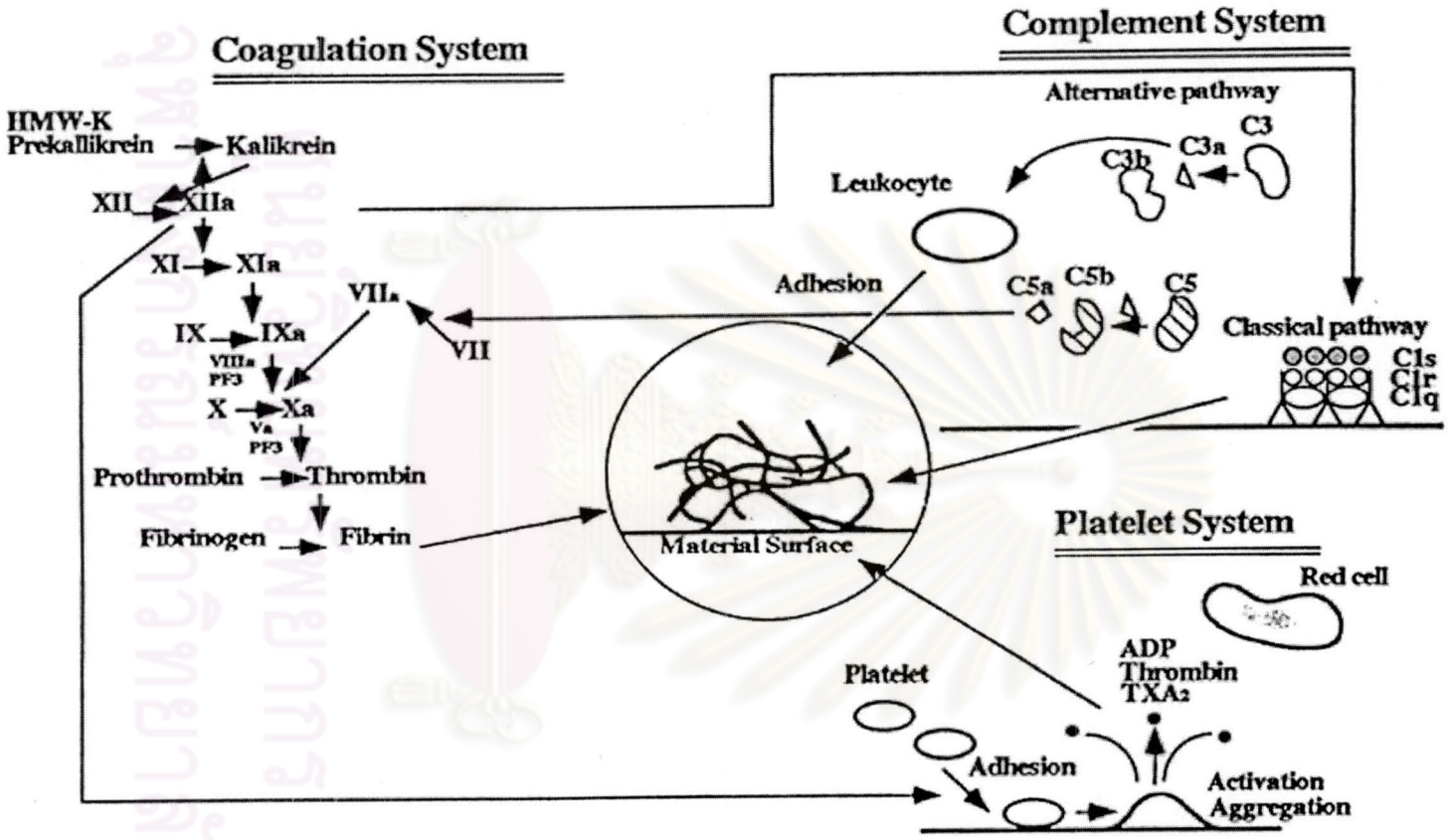


Figure 2.9 Schematic representation of blood coagulation system.

2.5 Surface Characterization Techniques

Surface characterization is a method used for analyzing chemical and physical properties of material surface. In this research, surfaces of deposited films were analyzed in order to confirm the layer formation and stratification of multilayer films. Various techniques were used.

2.5.1 Ellipsometry

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.

$$\mathrm{Tan}(\Psi)\, e^{i\Delta} = \frac{R_p}{R_s} \qquad \text{.....(1)}$$

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 will also change. Measuring these changes in the reflection properties allowed us to deduce the actual change in the film's thickness.

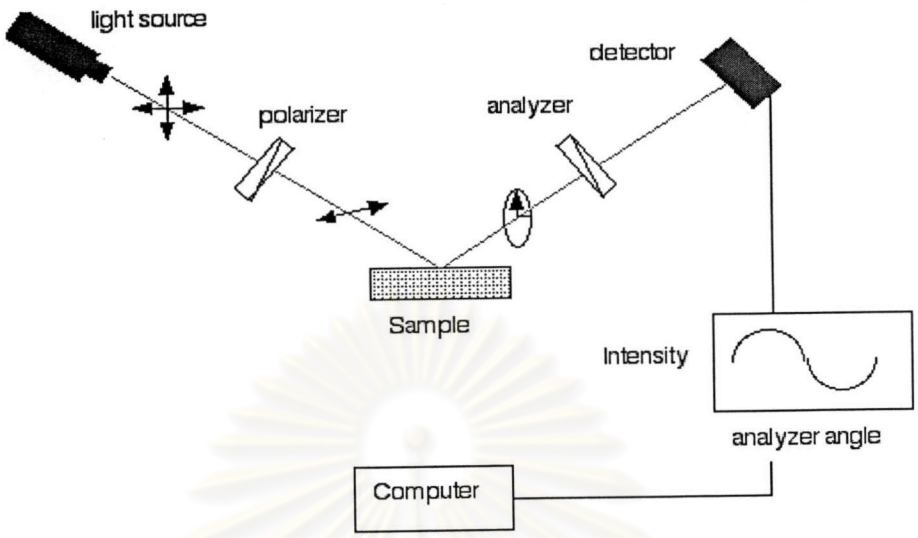


Figure 2.10 Schematic of the geometry of an ellipsometry experiment.

2.5.2 Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)

The infrared beam from the spectrometer is focused onto the beveled edge of an internal reflection element (IRE). The beam is then reflected, generally numerous times, through the IRE crystal, and directed to a detector (Figure 2.11).

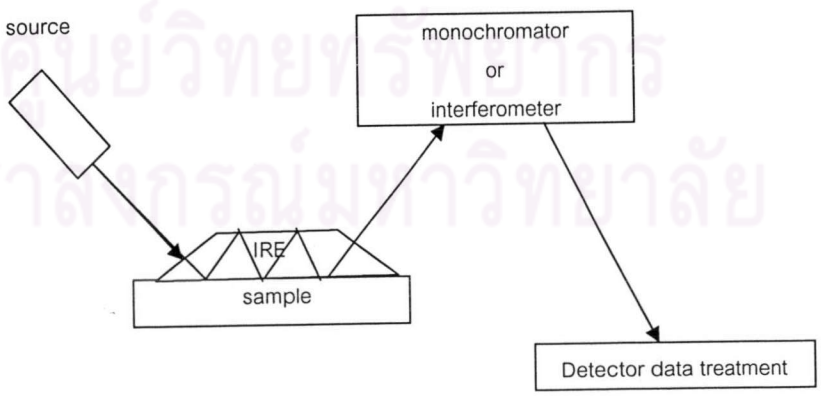


Figure 2.11 Diagram of ATR-IR.

The radiation can penetrate a short distance into the sample, thus interacts with any functionalities existing within that depth. The depth of penetration (d_p, defined as the distance from the IRE-sample interface where the intensity of the evanescent wave decays to 1/e of its original value) can be calculated using the formula in the following equation:

$$d_p = \frac{\lambda}{2\pi n_p(\sin^2\theta - n_{sp}^2)^{1/2}} \quad \text{.....(2)}$$

where λ = wavelength of the radiation in the IRE, θ = angle of incidence, n_{sp} = ratio of the refractive indices of the sample vs. IRE, and n_p = refractive index of the IRE. Practically, the sample is placed in close optical contact with one of the crystal. In this study, ATR-IR was used for identifying functional groups on the surface of multilayer films. Sampling depth of characterization is 1-1.5 μm.

2.5.3 X-ray Photoeiectron Spectroscopy (XPS)

XPS is a surface analysis method that provides information on atomic composition of the first 10 nm layer of material surface. In general, the sample is put inside a high-vacuum chamber (pressure 10^{-10} -10^{-8} Torr), and irradiated with soft x-rays, usually Mg Kα (1253.6 eV) or Al Kα (1486.6 eV). The primary event is photoemission of a core electron as shown in Figure 2.12. Electrons are also photo-emitted from molecular orbitals occupying the valence band, but with much lower intensity. Spectrum is obtained by passing the emitted electrons into an electrostatic energy analyzer. The binding energies, E_B, of the photoelectron are obtained via the Einstein relation:

$$E_B = h\nu - E_K - \phi \quad \text{.....(3)}$$

where hν is the x-ray photon energy, E_K is the electrostatic energy and ϕ is the sample work function. Peak intensities are proportional to the number of atoms sampled, and with the aid of appropriate sensitivity factors, atomic compositions can be calculated, with detection limits of ~0.2 atom%. In this research, the result was used to confirm the layer formation.

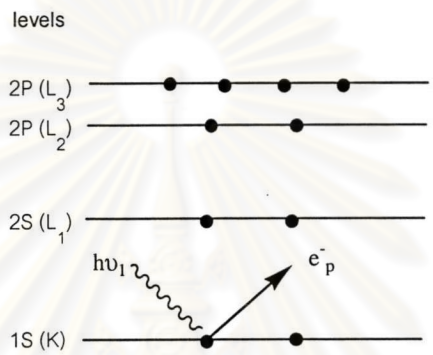


Figure 2.12 Photoemission of a core electron.

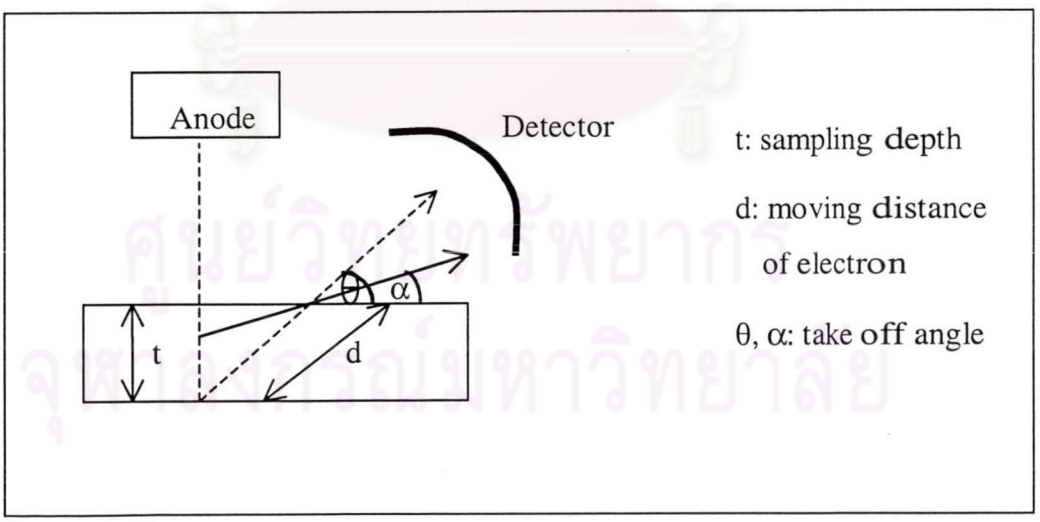


Figure 2.13 Effect of take-off angle to the depth profile.

In XPS, take-off angle can be adjusted in order to analyze atomic composition at each depth from the outmost surface. The higher the take-off angle is, the deeper film layer the analysis can be carried out.

2.5.4 Contact Angle Measurement

Contact angle measurement is probably the most common method of surface tension measurement of solids. Contact angle data, especially in the case of polymeric materials, can be obtained with low-cost instruments and with simple techniques. The basis of the measurement of solid surface tension by contact angle is the equilibrium of the three-phase boundary, shown in Figure 2.14 which can be described by Young's equation. As the surface becomes more hydrophobic, θ will be larger if water is used as a probe fluid.

In this research, air-water contact angle was used for determining the wettability and the stratification of multilayer films.

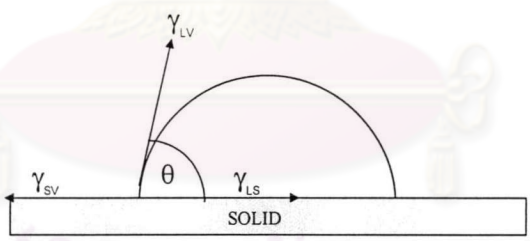


Figure 2.14 Equilibrium of the three-phase boundary on solid surface.

Young's Equation : $\gamma_{SV} - \gamma_{LS} = \gamma_{LV} \cos\theta$

γ_{LV}: interfacial tension between liquid and vapor phases

γ_{SV}: interfacial tension between solid and vapor phases

γ_{LS}: interfacial tension between liquid and solid phases

2.5.5 Atomic Force Microscopy (AFM)

AFM is a type of scanning probe microscopy (SPM), allowing three-dimensional topographical imaging of surface. In AFM contact mode, 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 2.15. The tip of the probe, which is commonly made of silicon nitride, is attached to a cantilever bearing a reflective surface upon which 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.

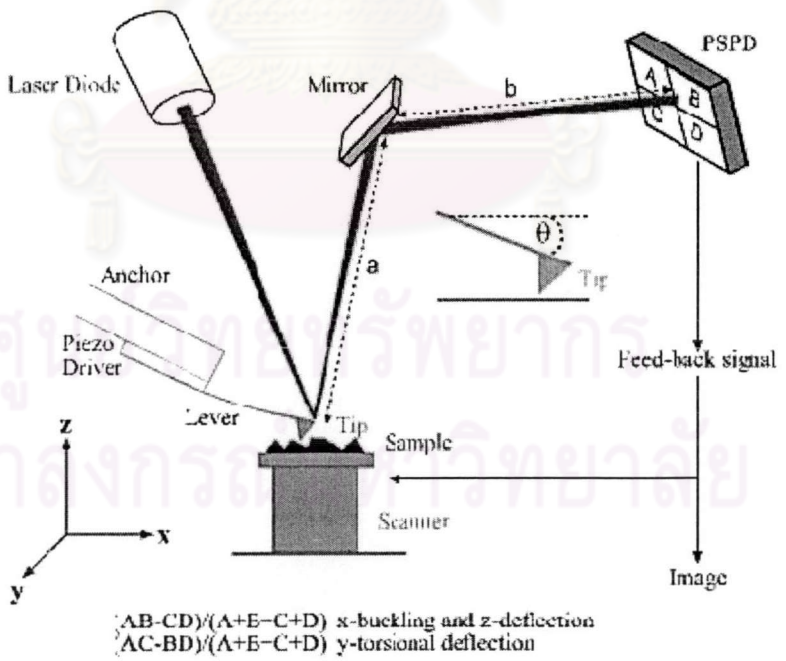


Figure 2.15 Schematic diagram of an atomic force microscope.