

CHAPTER II

THEORY AND LITERATURE REVIEW



2.1 Definition and general description of polyelectrolyte [1]

The term “polyelectrolyte” is employed for polymer systems consisting of a “macroion,” i.e., a macromolecule carrying covalently bound anionic or cationic groups, and low-molecular “counterions” securing for electroneutrality. Examples of an anionic and a cationic polyelectrolyte (PEL) are presented in Figure 2.1

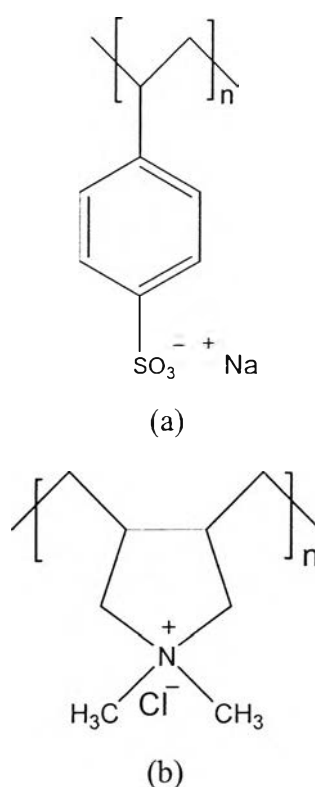


Figure 2.1 Chemical structure of (a) sodium poly(styrene sulfonate) and (b) poly(diallyldimethylammonium chloride).

Both Na-polystyrene sulfonate and poly(diallyldimethylammonium chloride) are dissociated into macroion and counterion in aqueous solution in the total pH range between 0 and 14. Also polymers like poly(acrylic acid) or poly(ethylene imine) are usually classified as polyelectrolytes, in spite of the fact that they form a polyion-counterion system only in a limited pH range, and remain as an undissociated

polyacid in the acid range or an undissociated polybase in the alkaline range as shown in Figure 2.2. This is a behavior typical for weak polyelectrolytes and quite analogous to weak low molecular electrolytes.

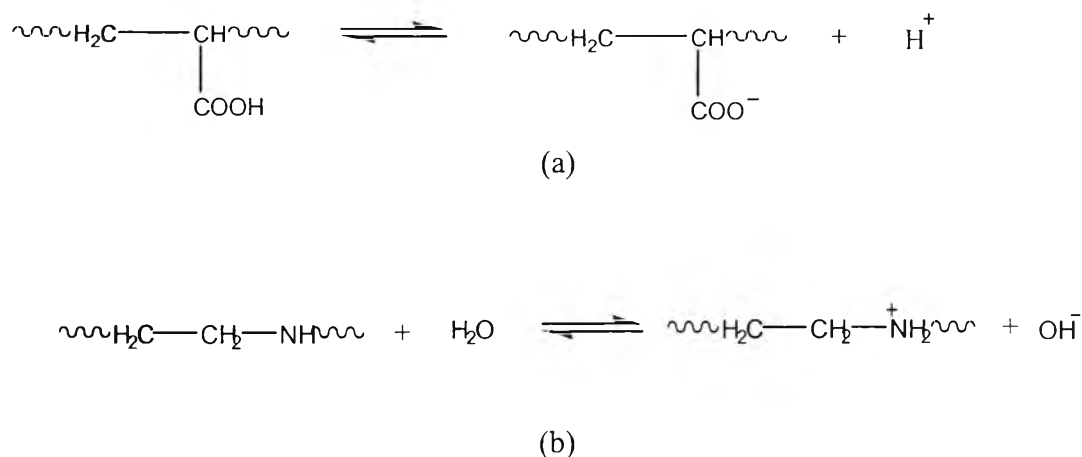


Figure 2.2 Dissociation equilibrium of the weak polyelectrolytes

(a) poly(acrylic acid) and (b) poly(ethylene imine).

On the other hand, a polymer like cellulose capable of dissociating partially into cellulosate anions and counterions at extremely alkaline conditions ($\text{pH} > 14$) cannot be classified as a polyelectrolyte, as in the conventional pH range of dilute aqueous systems the OH groups of polymer are not ionized.

A special case of polyelectrolytes, the “polyampholytes,” carrying both anionic and cationic groups covalently bound to the macromolecule, are represented in nature by an abundant number of proteins but can also be obtained by various synthetic routes. An example is presented in Figure 2.3 as a typical polyampholyte, this copolymer carries cationic charges in an acid and anionic charges in an alkaline medium, while at the so-called “isoelectric point,” in the example $\text{pH} 4$, no free net charge exists at the macromolecule.

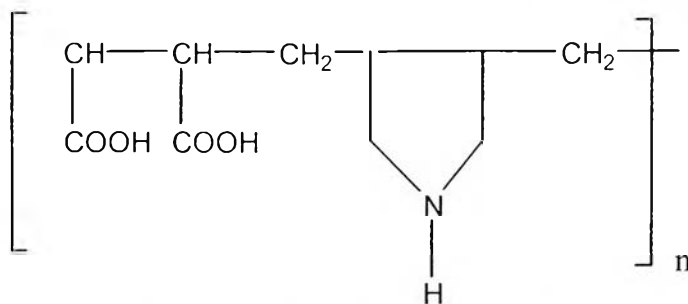


Figure 2.3 Chemical structure of a maleic acid-diallylamine copolymer.

In principle, any macromolecular chemical structure can be transformed into a polyelectrolyte structure by covalently attaching a reasonable number of ionic groups to the polymer backbone, with linear or branched macromolecules at a compound soluble in an aqueous medium of appropriate pH after introducing a sufficient number of ionic groups, while in the case of a crosslinked polymer its swell ability in aqueous media is enhanced by transferring into a PEL. Limiting our further considerations to linear and branched structures, a vast number of polyelectrolyte classes are known today, a section of which is listed in Table 2.1.

Table 2.1 Selected classes of polyelectrolytes

Anionic and cationic polysaccharides and polysaccharidic derivatives Nucleic acids Gelatin Lignosulfonic acids Polyacrylic and polymethacrylic acid and its copolymers Maleic acid anhydride copolymers Polystyrene sulfonic acid Polyethylene imine Polyamines and polyamidamines Ionenes Poly(diallyldimethylammonium chloride) Homo- and copolymers of cationic acrylic acid esters

Table 2.1 demonstrates the remarkable variability of polyelectrolyte chemical structure, resulting from the tremendous number of polymer backbone structures. Today's commercial polyelectrolytes are predominantly obtained by a polymerization, polycondensation, or polyaddition process. Also numerous important PEL also originate from nature, such as gelatin, as a representative of the widespread class of proteins or pectins belonging to the group of anionic polysaccharides. Furthermore, some PEL of practical importance result from a chemical modification of nonionic natural polymers such as cellulose or starch.

In contrast to the huge variability of the polymer backbone structure, the number of different chemical structures of anionic or cationic sites responsible for the peculiar behavior of PEL in solution is rather small as show in Table 2.2.

Table 2.2 Structures of ionic sites of PEL

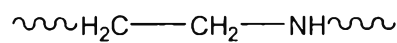
$-\text{COO}^-$	$-\text{NH}_3^+$
$-\text{CSS}^-$	$=\text{NH}_2^+$
$-\text{OSO}_3^-$	$\equiv\text{NH}^+$
$-\text{SO}_3^-$	$-\text{NR}_3^+$
$-\text{OPO}_3^{2-}$	

These ionic groups are usually classified as anionic and cationic; a further subdivision into weakly and strongly acid and basic groups is reasonable in analogy to “strong” and “weak” acids and bases of low molecular chemistry with the sulfonate, the sulfonate-half ester, and the tetraalkylammonium group being representative for the so-called “strong PEL.”

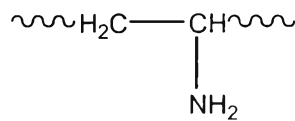
Besides the acid or base strength of the ionic site, the average distance between the adjacent anionic or cationic charges along the polymer chain is a decisive parameter determining PEL behavior, especially in the dissolved state. This charge carrier density or charge density is defined as the average distance between ionic sites, taking into account chain bond geometry, or as the average number of ionic sites per monomer unit in the case of copolymers, with the latter definition yielding comparable data only within the same class of copolymer with an ionic component. Besides this average charge density, the regularity of distribution of ionic sites along the chain can also influence PEL properties significantly, for example, with regard to

solubility. As a rule, typical PEL behavior can be expected if more than 1 ionic site per 10 monomeric units is present in a copolymer.

In addition to acid or base strength and charge density a third important point determining PEL properties is the location of the charged sites within the molecular geometry of the macroion. According to Figure 2.4, principally distinguish between an integral type of PEL with the ionic sites being part of the polymer backbone and the pendant type with the ionic sites being attached to the backbone as a side chain with a broad variability in spacer length. The geometric position of the charged sites is relevant especially in polyanion - polycation complex formation.



(a)



(b)

Figure 2.4 PEL of the integral of pendant type:

(a) linear poly(ethylene imine) as an example of the integral type and

(b) poly(vinylamine) as an example of the pendant type.

Besides these three parameters characterizing the macroion, the species of low molecular counterions has a strong influence on the properties of the whole system in solution, especially on solubility and structure formation. Two examples may illustrate this and demonstrate that the counterion is not just an anonymous particle securing electroneutrality: The chloride of the poly(diallyldimethylammonium) polycation is easily soluble in water, while the corresponding iodide is rather insoluble. The K^+ salt of some water-soluble high molecular cellulose sulfates forms a stiff, cuttable thermoreversible gel at a polymer concentration between 1 and 2 %, while the Na^+ salt of the same sample at the same concentration gives quite a normal polymer solution of the expected viscosity.

2.2 The Layer-by-Layer Deposition [2]

The so-called layer-by-layer (LbL) deposition technique (Figure 2.5) also falls into the category of template assisted assembly. Template assisted assembly is faster than self-assembly/chemical modification cycles whose outcome is often uncertain or difficult to predict. For the case of LbL-deposition, it can be tailored to even allow multimaterial assembly of several compounds without special chemical modifications, thus giving access to multilayer films whose complex functionality can fall into the two following categories:

1. Tailoring of surface interaction: Every object interacts with its environment via its surface. Thus all properties depending on this interaction are dictated by surface functionality which can be tailored for many needs (e.g. corrosion protection, antireflective coatings, antistatic coatings, stickiness or non-stickiness, surface induced nucleation, antifouling, hydrophilicity or hydrophobicity, biocompatibility, antibacterial properties, molecular recognition, chemical sensing or biosensor, microchannel flow control).

2. Fabrication of surface based devices: The sequence of deposition of different materials defines the multilayer architecture and thus the device properties. One may call this knowledge based (or programmed, or directed, or controlled, or template assisted) assembly, in contrast to self-assembly. It leads to property engineering by controlling the mostly one-dimensional spatial arrangement of functionality in multimaterial layered nanocomposites (membrane reactors, photonic devices such as light emitting diodes or complex waveguides, compartmentalized films with barrier layers or separation membranes).

The fabrication of multicomposite films by the LbL procedure means literally the nanoscopic assembly of hundreds of different materials in a single device using environmentally friendly, ultra-low-cost techniques. The materials can be small organic molecules or inorganic compounds, macromolecules, biomacromolecules such as proteins or DNA or even colloids (metallic or oxidic colloids or latex particles). The technique can be applied to solvent accessible surfaces of almost any kind and any shape, the more exotic ones being microcapsules, colloids or biological cells.

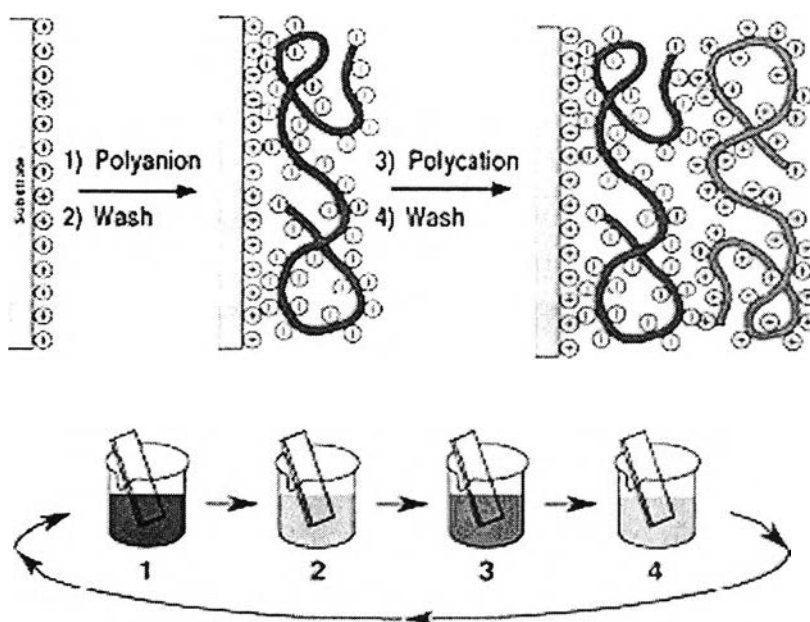


Figure 2.5 Schematic of the electrostatic self-assembly.

The theoretical understanding of the ESA technique is open yet (for a detailed discussion of proposed mechanisms, though theoretical approaches are upcoming. Kinetically controlled adsorption of polyelectrolytes must lead to overcompensation of the original surface charge, as shown experimentally by recording the ζ -potential. Although the ESA technique is based on electrostatic attraction between positively and negatively charged species, the primary driving force is presumably entropy, not enthalpy. Similar to polyelectrolyte complexes formed in solution, complexation of the polyions by a charged surface liberates undissociated low molar mass counterions, thus increasing the entropy of the system. An additional entropic gain may derive from the liberation of solvent molecules from the solvation shell of the polymer-bound ionic groups. In contrast, the number of electrostatic bonds in the overall system is not changed on polyion adsorption. Therefore in a first approximation, the change in enthalpy is naught. However, the number of ions per molecule/nanobject adsorbed may play a role for the binding, as well as the equivalence of this number for polycation and polyanion used. At a closer look, the case is more complicated. The interaction between most charged species is highly specific and goes much beyond the simple Coulomb law, though this is neglected in physico-chemical treatments frequently. Generations of chemistry freshmen have learnt e. g. the very different behavior of AgCl and AgNO_3 compared to KCl and

KNO_3 , though the ion radius and the hydration energy of Ag^+ and of K^+ are virtually the same. This review is not the right place to argue about the need of improving the theory of electrostatic interactions, but clearly, a deeper understanding of the specificity of ion-ion interactions remains a challenge for the future.

For most cases an LbL film has a unique layer sequence that depends strictly on the deposition sequence. This points to the fact that LbL deposition should be considered as an analogue to a chemical reaction sequence (Fig.2.6). While a chemical reaction takes place between different synthons and typically yields a unique molecule after each synthesis step, layer-by-layer deposition involves the adsorption of a single species in each adsorption step and yields a multilayer film with a defined layer sequence. While molecules are synthesized in several consecutive reaction steps, a multicomposite film is fabricated in several adsorption steps.

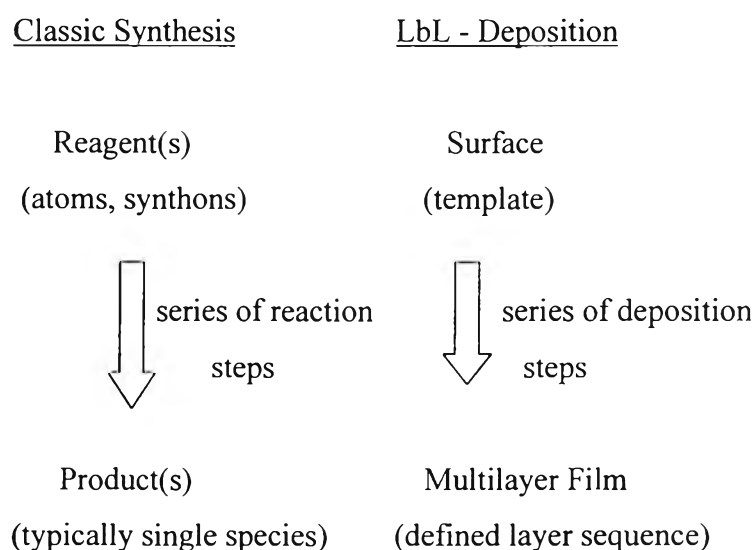


Figure 2.6 Schematic of chemical multistep synthesis and multilayer deposition.

The reagents in classic synthesis are typically molecules, in layer-by-layer deposition they can be chosen from a wide range of materials. This is represented schematically in Fig.2.7. While today most of the multilayer films have been fabricated using mainly electrostatic attraction as the driving force for multilayer buildup, this is by no means a prerequisite. There are many other interactions that have been used successfully for multilayer deposition including: donor/acceptor

interactions, hydrogen bonding, adsorption/drying cycles, covalent bonds, stereocomplex formation or specific recognition.

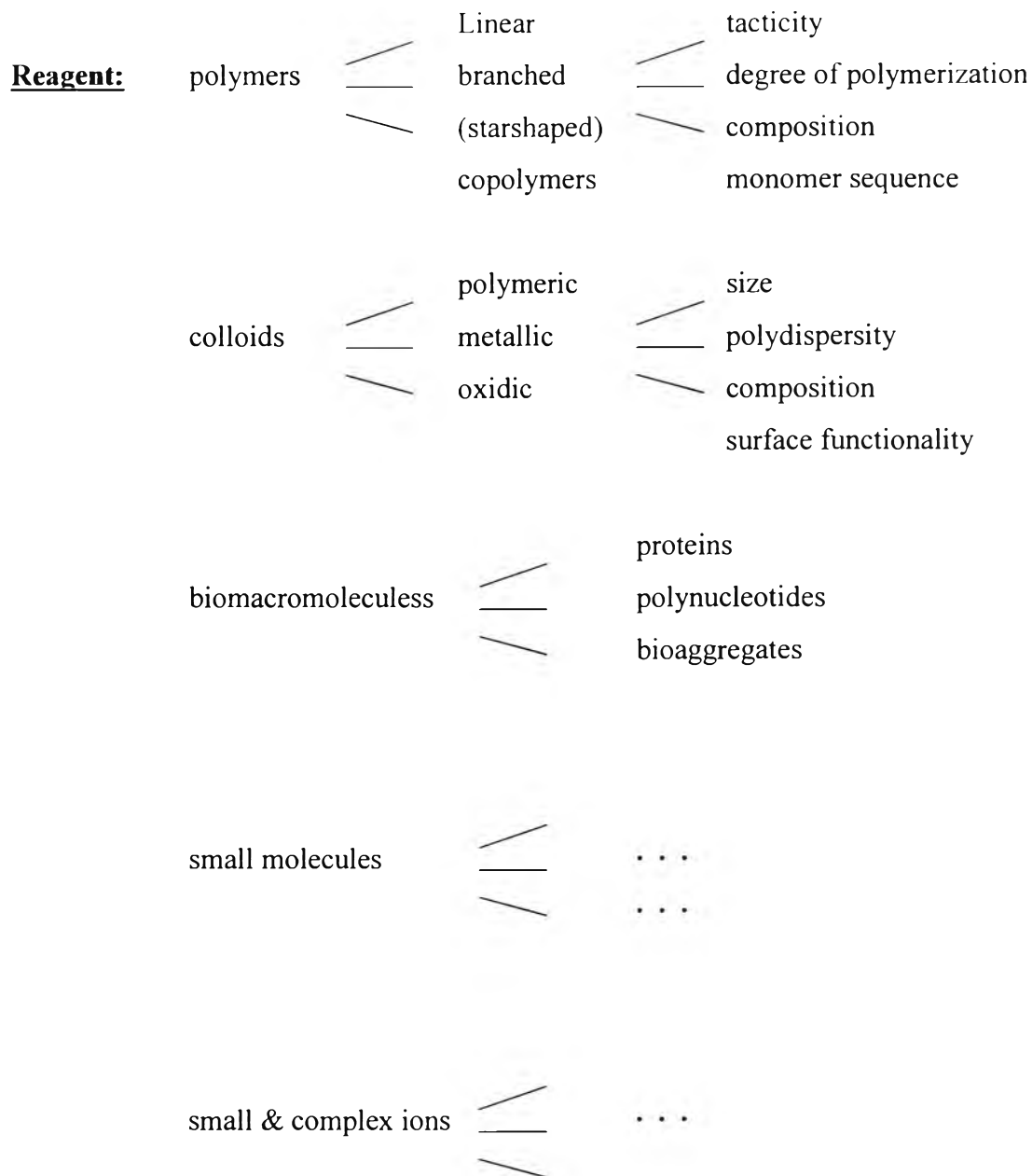


Figure 2.7 Schematic of reagents for layer-by-layer deposition.

In general one needs just any interaction (this may be one or several different interactions) between two species “reagents” in order to incorporate them into a multilayer film. The interaction can easily be tested in solution prior to carrying out the deposition if both film constituents are soluble in the same solvent. When both solutions are mixed and flocculation occurs it is a good sign that multilayer fabrication will be possible. This is only a very crude test: multilayer formation may also be possible in the absence of flocculation.

important compound. Silver chloride, bromide, and iodide are used in still photography because of their sensitivity to light. Solutions of certain protein complexes containing silver are used as antiseptics. A mirror can be made by coating glass with metallic silver derived from the reaction of a solution of a silver ammonia complex with an organic reducing agent such as formaldehyde. Although the metal is prepared in various ways depending upon the nature of its occurrence; the greatest quantity is obtained in connection with the refining of lead and copper. It is separated from lead by the Parkes process, which is based upon the fact that silver is soluble in molten zinc whereas lead is not. The cyanide process has largely replaced an amalgam process in which silver is dissolved in mercury. Some of the silver produced today is used, as in the past, in making coins. Large quantities are used for silver utensils and jewelry, and in plating tableware electrolytically from a solution of sodium silver cyanide

The preparation and study of metal nanoparticles is of a primary interest in both research and technology. The reason for this interest is the fact that metal nanoparticles possess specific properties not available in the cases of isolated molecules or bulk metals. These characteristic properties of the above-mentioned particles e.g. optical, magnetic, catalytic, electrochemical are dependent to a great extent on their dimensions, shape and chemical surroundings. These dependences can be advantageously utilized for the purposes of the development of novel biosensors, chemical sensors, electro optical devices, materials for high capacity data storage media or substrates for surface enhanced Raman spectroscopy. The metal of choice for many of the above mentioned as well as other applications is silver because of its facile preparation as well as good application properties of the silver colloidal particles.

2.3.1 The Formation of Colloidal Systems

Colloidal systems, being of transitional character between homogeneous and macroscopic heterogeneous systems can be in principle prepared by two ways – using condensation and dispersion methods. Condensation methods are based on connecting of individual atoms or molecules into larger aggregates, during the dispersion process a macroscopic phase is dispersed. A specific case of dispersion

method is the peptisation based on the transition of a precipitate, which is an aggregate of colloidal particles back into colloid solution.

The formation of small-sized particles via condensation mechanism is possible if sufficient amount of nuclei of a novel, thermodynamically more stable phase is formed and if the velocity of these nuclei's further growth has a suitable magnitude. The methods leading to the formation of such metastability of the systems can be (with certain restriction) divided into physicochemical and chemical. There is a vast amount of the chemical preparation methods – each reaction leading to the insoluble product formation can be employed for the purpose of a dispersion system preparation. Thus redox, hydrolytic, exchange, acidobasic and precipitation reaction can be used to obtain dispersion system.

Physicochemical methods leading to metastability of the initial system usually rely on temperature or less commonly pressure changes; a change in solvent composition is also frequently used.

Dispersing means increasing of a dispersion degree of solid or liquid materials in a dispersion environment, the result of which is the formation of a dispersion colloid having large specific interphase surface. Unlike dissolution the dispersion is usually not a spontaneous process but requires external work delivery to overcome the intermolecular forces necessary for material disintegration. Mechanical, ultrasound or laser disintegration, electric discharge sputtering belong to dispersion methods.

The importance of condensation methods for the preparation of dispersion systems is based on the fact that these methods can produce the finest dispersions usually impossible to be prepared by dispersion methods. Condensation methods have capability to control the dispersion degree as well as the degree of polydispersity of the resulting colloid. The most common methods used for the preparation of colloidal suspensions of metals (silver including) are the reduction of corresponding metal cation. In addition to inorganic or organic reduction agents an ultrasound, UV radiation and gamma radiation can be used to initiate the reduction.

2.3.2 Methods of Silver Particles Preparation

Laser ablation

Laser ablation of silver macroscopic material (e.g. silver foil) is a novel and promising physical method for the silver colloid particles preparation. The advantages of this method are namely an ease of the process, versatility with regard to metal identity or choice of solvent as well as the absence of additive chemical agents residues. Metal particles prepared by laser ablation are chemically pure and therefore suitable for the use in SERS as the presence of residual ions at the surface of colloidal particles significantly affects the absorption processes, particle stability and reproducibility of SERS measurement. For the purposes of SERS measurement not only the colloidal particles formed by laser ablation, but also the silver foil remaining after the process can be used. The size of the silver particles prepared by this method ranges from nanometer sizes up to 30-40 nm and depends on wavelength and intensity of the laser used, on irradiation time, presence of chlorides or surfactants and the solvent in which the irradiation is carried out.

The reduction by the action of ultrasound

Except for the above-mentioned usage of ultrasound in a dispersion method of colloid particle preparation it can be used also as a condensation method. The ultrasound is capable to decompose water into hydrogen and hydroxyl radicals. Subsequent reactions with suitable additives yield organic radicals which act as reducing agents. By sonification of aqueous silver salts solutions in the presence of surfactants (the frequency of ultrasound was 200 kHz) the silver particles of 13 ± 3 nm size were prepared.

The reduction by the action of gamma radiation

For the preparation of submicroscopic silver particles a direct radiolysis of silver salt aqueous solutions can be used. The advantage of this preparation method is that minimum interfering chemical substances are introduced into the reaction mixture, which could possibly absorb onto particles and thus change

their specific properties. During the irradiation of silver salt solution under hydrogen gas atmosphere hydrated electrons and hydrogen atoms are formed, which reduce the silver ions. Concomitantly OH radicals, which oxidise silver particles, are formed. In the presence of hydrogen gas a part of OH radicals reacts with hydrogen molecule yielding hydrogen atoms, which contribute to silver ion reduction. By the action of this simultaneous silver ions reduction/silver particles oxidation a gradual growth is achieved, the structural defects are therefore minimised and almost monodisperse particles with average size of 7.0 nm are prepared. The course of the reduction by gamma irradiation can be influenced by other chemical agents, e. g. 2-propanol. The binding of silver ions into complex with appropriate complex agent can be the other factor usable for the influence of the reduction by gamma irradiation.

The reduction by the action of UV radiation

Photochemical method of colloid particle preparation using UV radiation yields the particles with properties similar to the particles produced by the above mentioned radiolytic method, its advantage being the simpler and cost effective experimental equipment. Mercury discharge lamp is often used as the source of UV radiation. In addition to silver salt and eventual stabilisers the reaction mixture contains suitable organic substance whose interaction with UV radiation generates radicals which reduce silver ions.

The example of this method can be demonstrated by the system containing except for AgClO_4 an acetone, 2-propanol and polymeric stabilisers (polyethyleneimine, sodium polyphosphate, sodium polyacrylate and polyvinylpyrrolidone). Acetone is excited by the absorption of UV radiation; the excited state reacts with 2-propanol yielding strongly reducing ketyl radicals. With polyethyleneimine as stabiliser the particles with narrow size distribution and 7 nm mean size were prepared. Acetophenon, benzophenon or ascorbic acid can be used as photosensitive agent instead of acetone.

The reduction by inorganic agents

The most commonly used method for the preparation of silver sols is the reduction of silver salt by sodium borohydride, usually following the manuscript proposed by Creighton et al., frequently used especially in the area of SERS. The procedure after Creighton et al. is based on the addition of 25 ml of AgNO_3 (10^{-3} mol.dm⁻³) aqueous solution into 75 ml of the intensively stirred, ice cooled aqueous NaBH_4 (10^{-3} mol.dm⁻³) solution. Since the time of publication many modifications of Creighton procedure differing in the concentrations and molar ratios of the reactants appeared. Among other factors investigated which influence the reduction of silver salt by NaBH_4 are the temperature, the presence of surfactants, the presence of nonsaturated carboxylic acids, the presence of NaHCO_3 , the exchange of H_2O for D_2O or the method of stirring. By the standard methods of silver salt reduction by NaBH_4 the particles with units of nanometers sizes and narrow size distributions are prepared, however the preparations of larger particles is difficult. A modification for larger silver particles preparation was proposed by Schneider et al., in this modifications small particles are prepared by the reduction using NaBH_4 and are subsequently used as nuclei for further growth in which „weaker“ reducing agents is used (ascorbic acid). Colloid silver can be also prepared by the reduction by hydrazine or hydrogen, depending on the experimental procedure used the silver particles with sizes ranging from units of nanometers up to several tenths of nanometers are obtained. Basic solution of hydrogen peroxide can also be used. There are a useful method of preparation of silver colloid by the reduction of silver salt solution by the complex compounds of ferrous salt.

The reduction by organic reducing agents

Among reduction by organic substances the citrate reduction procedure according to Lee-Meisel is one of the most commonly used, especially for the purposes of SERS. Silver sol is prepared by the addition 10 ml of 1% trisodium citrate into 500 ml of aqueous solution containing 90 mg of AgNO_3 . The reaction

mixture is kept boiling for one hour. It was shown by spectroscopic techniques that the reduction of silver ions occurs during first two minutes after the addition of citrate, the primary particles are relatively large and polydisperse (60 – 80 nm). Subsequent heating of the reaction mixture leads to monodisperse particles with 27 nm average size. The reduction process can be carry out as two stage process, the particles created in the first step can serve as the nuclei for the further growth. The silver particles can be obtained also by the well known Tollens reagent - the silver ions in the form of ammonium complex being reduced by aldehydes or reducing sugars. Formaldehyde and sorbitol used as reducing agents give the particles with the sizes ranging from 20 to 50 nm. Colloid silver can be prepared also using ascorbic acid to reduce aqueous AgNO_3 solution. In the presence of the vinylalcohol and N-vinylpyrrolidone copolymer as additives the particles with resulting size from 3-7 nm were prepared depending on the amount of the added polymer.

In nonaqueous medium the solvent can serve as the reducing agent – e.g. N,N-dimethylformamide, dimethylsulfoxide or 2-propanol. The dimensions of the resulting silver particles range from several units of to twenty nanometers.

2.3.3 Silver Colloids Applications

Catalytic properties

The metal colloid dispersions are commonly used as the reduction catalysts, but are rarely used as the catalysts for oxidation. The colloid silver is the exception, it is often used as the oxidation catalyst e.g. in the process of the preparation of ethylene oxide from ethylene.

Redox properties of small metallic particles differ from these properties of the bulk metal. The experiments carried out with the commonly used metals (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au, Hg) proved that their catalytic properties are dependent on the particle size. The research in the area of the small metal particles' redox properties is focused mainly on the stable particles in the final stage of their growth, the reports of the growing particles' redox properties are scarce. During the growth of these small particles possessing renewing surface of extremely large area with excellent catalytic properties a smooth change of their redox potentials occurs.

The use of silver particles in sensorics

The optical response of noble metal nanoparticles is often characterised by the presence of a strong absorption band that is absent from the spectrum of the bulk metal. This is attributed to a resonance in the collective motion (oscillation) of the conduction electrons in response to an incident electromagnetic field and is called the surface plasmon resonance (SPR).

The localisation of peak absorption wavelength λ_{max} and shape of the band depends on the particle size and shape, on the degree of their mutual interactions, and local external dielectric environment. This dependence can be utilised for the development of a new class of high sensitive sensors. For example the λ_{max} peak of the surface plasmon resonance of the biotin-functionalised triangular silver nanoparticles is highly sensitive towards the chemical surroundings of the particle. Exposure of these nanoparticles to 100 nmol.dm^{-3} streptavidin caused a 27 nm red-shift in λ_{max} . The detection limit of this sensor lie in the range of 10^{-12} – $10^{-13} \text{ mol.dm}^{-3}$ and prospect new ways into an ultrasensitive analysis with low requirements on the laboratory equipment.

Antimicrobial activity of colloid silver

The antimicrobial activity of silver is known for a long time. Since the times of antient Greece and Rome the silver vessels were used for the conservation of water and other liquids to ensure their health safety. In middle age the powder silver was used as the food additive. However in this form the silver is not biologically well consumable and the symptoms of silver poisoning appeared after some time (argyria).

In the course of nineteenth and especially at the beginning of the twentieth centuries the silver colloid particles attracted the attention of microbiology and medicine. The study of antimicrobial properties of these particles however ceased because of the invention of antibiotics which took-over the leading position in the fight against bacteria. Recently the resistance of bacteria against antibiotics increases however most of microorganisms are unable to develop the self-defence against

the colloid silver. The mechanism of the silver antimicrobial activity is yet not known in detail. The optimum antimicrobial effect provide the silver colloid particles with 1 – 10 nm size.

2.4 Nylon Fibers [5]

Nylon fibres are made up of linear macromolecules whose structural units are linked by -NH-CO- group. Consequently the term polyamide is frequently used. However, in nylons the structural units are essentially aliphatic and, by definition, less than 85% of the amide linkages may be attached to two aromatic rings. In practice, in almost all examples of nylons none the amide links are attached to two aromatic rings. If 85% or more of the amide linkages are attached to two aromatic rings, then the fibres are the aramids and their production processes and properties differ markedly from those of the nylons. They will not be discussed further in this chapter.

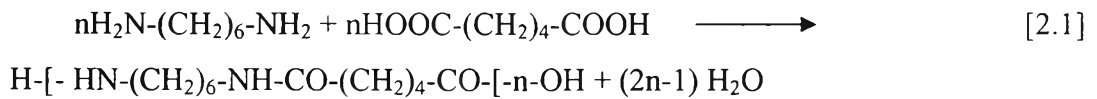
Nylon polymers can be formed in many ways. The four most important for industrial polymer are:

1. the condensation of diamines with diacids;
2. the self-condensation of amino acids;
3. the hydrolytic polymerisation of lactams, which involves partial hydrolysis of the lactam to an amino acid; and
4. the anhydrous addition polymerisation of lactams

Methods 1 and 3 are of major importance in the manufacture of fibres; method 2 is used for certain speciality nylons; and method 4 is used for reaction moulding, but not for fibre manufacture. The process developed by Carothers involved method 1, the condensation of two difunctional monomers, an amine and a carboxylic acid. Polyamides derived from diacids and diamines are generally referred to as the AABB type. They are identified as nylon x,y, where x and y are the numbers of carbon atoms in the diamine and the acid respectively. Although this route can from potentially many different polymers, the one that is of major commercial importance is nylon 6,6. The alternative process involves the condensation of an ω -amino acid with the amine and the carboxylic acid groups on opposite ends of the molecule. Nylons derived from amino acids are termed the AB type. They are identified as

Nylon x where x is the number of carbon atoms in the monomer. Nylon 6 is the member of this group which is of greatest commercial importance.

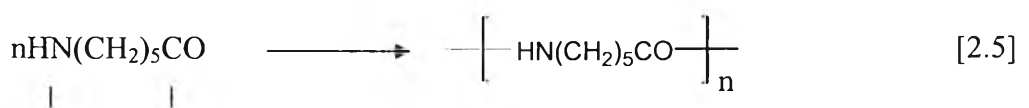
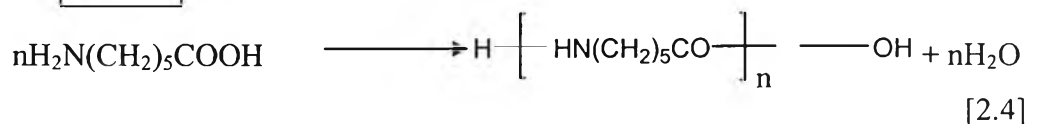
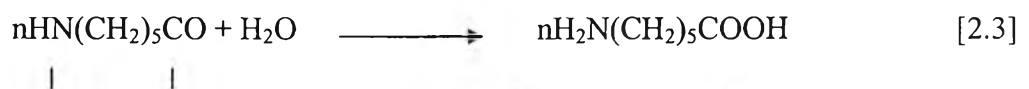
Nylon 6,6 is produced from the polycondensation of 1,6-diaminohexane, the traditional name of which is hexamethylenediamine, and hexandioic acid, which is often called adipic acid. The formation of nylon 6,6 may be represented by eq. 2.1



In the case of nylon 6, the normal monomer is caprolactam, which is formed when 6-aminohexanoic acid (ϵ -amino-caproic acid) loses water internally to form a lactam, as represented in eq. 2.2



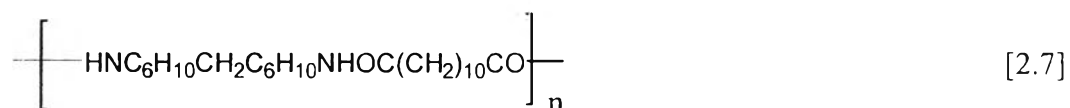
Caprolactam does not polymerise readily when it is dry. It may be converted to nylon 6 under anhydrous conditions by an anionic polymerisation using alkali or alkaline earth hydroxides, hydrides or alcoholates as catalysts. However, a hydrolytic polymerisation is normally used for fibres. A small quantity of water, aminocaproic acid or another monobasic carboxylic acid needs to be added to catalyse the reaction. An addition of 5-10% of water is often used in industry. The reaction involves a water-initiated ring opening of the caprolactam (eq. 2.3), which is a reversal of the reaction in eq. 2.2, followed by a condensation polymerisation (eq. 2.4) of the aminocaproic acid. Mechanistic studies indicate that a direct addition polymerisation of caprolactam also takes place in the reaction (eq. 2.5).



Some other nylons have been used commercially. Nylon 11 of the AB type is produced on a small scale as fibres under the trade name of *Rilsan*. It is still widely used as a plastic. The formula of the repeat unit is given in eq. 2.6:



A further nylon was introduced in 1968 by DuPont under the brand name of “Qiana[®]”. It was claimed to give a more silk-like handle and lustre in fabrics as well as imensional stability and wrinkle resistance similar to polyester. However, the complex diamine was more expensive, and a carrier was required for dyeing, making coloration more difficult than for nylon 6,6 and 6. It was later withdrawn from the market. The polymer, of the AABB type, was formed from the condensation of bis (4-aminocyclohexyl) methane and dodecandioic acid. The diamine exist as *cis* and *trans* isomers, and the monomer used in Qiana[®] was 20% *cis-trans* and 80% *trans-trans*. The repeat unit is shown in eq. [2.7], where C₆H₁₀ is a 1,4-disubstituted cyclohexylene ring:



Nylon 4,6 is produced as *Stanyl* by the DSM (Dutch State Mines) Group and is polymerised from 1,4-diaminobutane and adipic acid. It was first produced on a pilot plant scale in 1984 and marketed in 1989. The polymer has a higher melting temperature, 295 °C, than nylon 6,6 or 6. While this makes extrusion more difficult, the yarn has benefits, especially at elevated temperatures in terms of dimensional stability, heat capacity, creep and shrinkage behavior. It is used for V-and timing belts, tyre cord, hoses and abrasion-resistant fabrics. The formula of the repeat unit is given in eq. 2.8:



Two other nylons are used commercially to a small extent, nylons 6,10 and 6,12. The former is produced for press felts for paper-making (Rhodia, Fance) and is also used with nylon 6,6 in self-crimping bicomponent fibres. Nylon 6,12 is produced as a

monofilament under the brand name *Tynex* (DuPont, USA), for use in floor care, paint, tooth and cosmetic brushes. The reduced proportion of amide groups gives lower moisture absorption as well as enhanced chemical resistance.

2.4.1 Fibre production

The initial stage of fibre production is often referred to as 'spinning'. Inevitably there is some confusion with the process of assembling staple fibres into yarns. The term 'extrusion' will be used for the initial process. For most nylon fibres extrusion is followed by drawing, and frequently by texturing.

All of the aliphatic nylon fibres are produced by melt extrusion, as it is the most economical process of fibre formation. Melt extrusion requires a polymer that is stable in the molten condition, and no solvent are involved. The speeds at which the yarn is wound on to the package are comparatively high, normally above 1000 m min^{-1} . This means that the production rates from each spinneret are adequate for low linear density continuous filament yarn. Originally, almost all nylon was of this type, although as the overall production volume has increased, industrial yarns and fibre for carpets have become more important. These are normally medium to high linear density continuous filament yarn. A schematic diagram of an extrusion and drawing line is shown in Fig. 2.9.

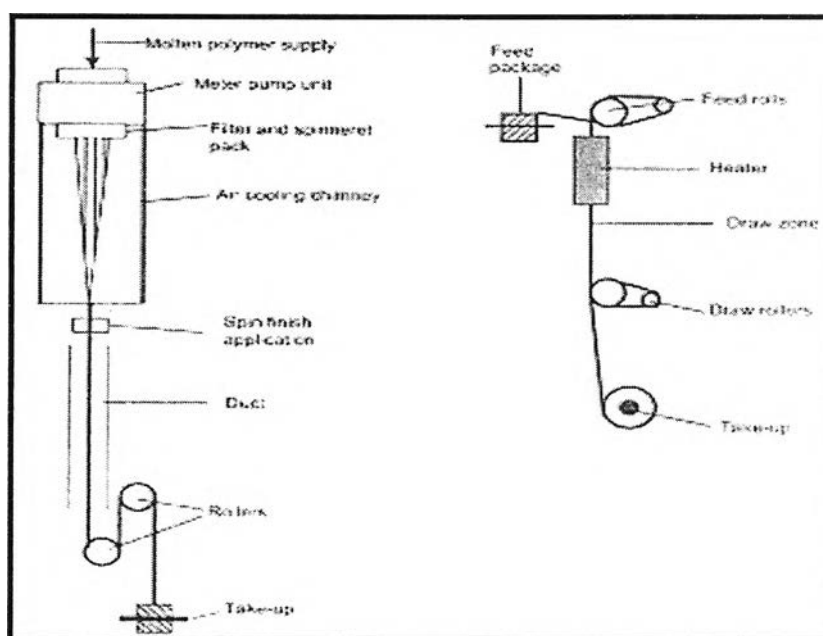


Figure 2.9 Schematic of nylon 6 fiber production.

2.4.2 Types of Nylon Yarn [6]

The diameter of the individual nylon filament is determined by the rate of delivery from the pump to the spinneret, by the number of holes in the spinneret, and by the rate at which the yarn is drawn away from the spinneret. The denier, or size, of the yarn before drawing is determined by the diameter and number of filaments in the yarn. The size of the yarn after drawing is determined by its original diameter and the amount of cold-drawing. If it is drawn three times its original length, the stretched yarn will be one-third of its original diameter. The individual filaments produced usually range from 1 to 15 denier (1-17 dtex).

Monofilament Yarns

Though single-filament, or monofilament, yarns of 7 denier (8 dtex) are produced, 12-denier (13 dtex), 15-denier (17 dtex), or heavier yarns are more often manufactured. The monofilament yarns are used for hosiery and for industrial filters. These yarns are very fine and have little or no twist. Consequently, they are relatively weak nylon yarns, Heavier and stronger monofilament yarns are also produced for various purposes.

Multifilament Yarns

Multifilament yarns are made in both standard and high-tenacity forms. The number of filaments in each yarn varies according to the purpose of yarn. The yarns generally range in denier from 20 to 210 (22-233 dtex). Multifilament yarns are stronger than monofilament yarns because of the numerous filaments. The strength can be further increased by the amount of twist given to the yarns.

Stretch Yarns

Nylon filaments can be processed to have a crimp or coiled characteristic. This gives yarns made of such nylon filaments the ability to be greatly stretched (like

a spring) and come back to shape when the tension is released. These yarns are produced under several trademarks, of which one of the better known is Helanca.

Textured yarns

Nylons filaments can also be processed to have a looped characteristic. Crimp-textured nylon is sometimes referred to as BCF nylon-that is, bulk continuous filament nylon. It is given a permanent crimp by the producer. Thrown yarns of these filament have a texture and hand similar to yarn made of a staple fibre, such as cotton , but retain all the other characteristics of filament yarns. One of the best known of these textured yarns is Taslan, which is used for sport shirts and similar apparel. Some textured filament yarns have a curly appearance that imparts a resilient, springy effect called loft.

Spun Yarns

Nylon filaments may be cut about 1 to 5 inches (25-125 mm) in staple length. The individual filaments range in denier from 1.5 to 15 (1.7-17 dtex). The staple is usually crimped and spun on a cotton system. These yarns are fuzzy and soft. They have lower tensile strength but greater abrasion resistance. They are not so elastic as the filament yarns and take longer to dry.

2.4.3 Molecular Structure

The chemicals from which nylon 6,6 is synthesized are adipic acid and hexamethylene diamine, as illustrated in Figure 2.10. Note that there are six carbon atoms in each molecule of adipic acid and six carbon atoms in each molecule of hexamethylene diamine. For this reason, this nylon was designated as nylon 6,6 (six carbons in each molecule of reacting chemical). In time, it came to be known as nylon 6,6.

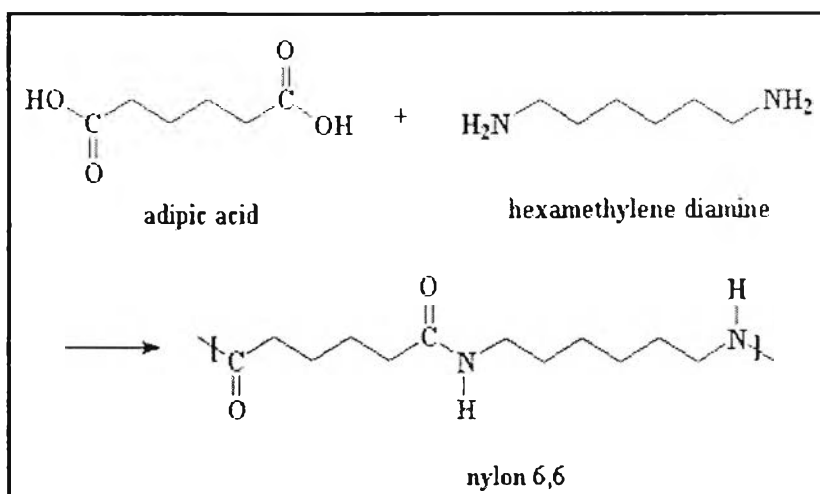


Figure 2.10 The synthesis of nylon 6,6 [20].

2.4.4 Microscopic Properties [7-9]

Nylon filaments are smooth and shiny. Normal nylon in microscopic appearance looks like a long smooth cylinder. When viewed in cross section, nylon is usually perfectly round. Longitudinal magnification shows relatively transparent fibers of uniform diameter with a slight speckled appearance.

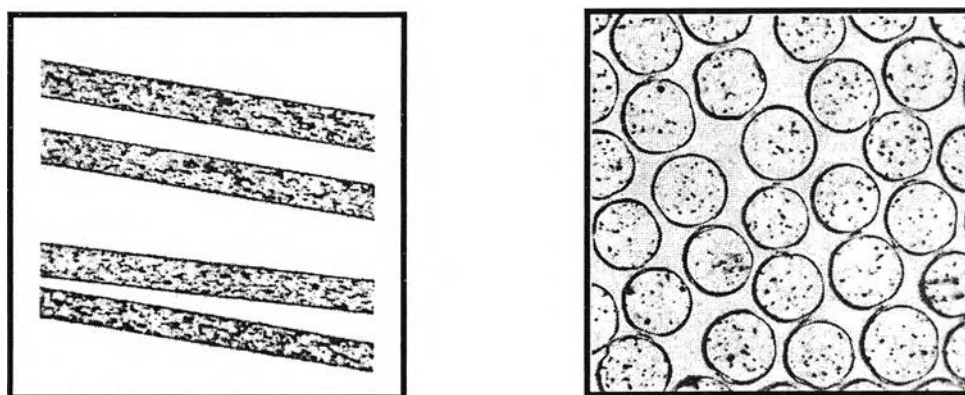


Figure 2.11 Photomicrographs of delustered, regular nylon in a cross section (right) and a longitudinal view (left) .

2.4.5 Physical Properties

Shape and Appearance Nylon is a man-made fiber; therefore the diameter and length of the filaments or staple fibers are determined by the manufacturer and by the ultimate end-use. It is transparent when produced and can be made bright or dull.

Strength One of the major advantages of nylon fibers is their strength. The tenacity or strength of nylon can be excellent. It is produced in a variety of tenacities. Regular tenacity nylon is rated at 3.0 to 6.0 g/d; high tenacity nylon is rated 6.0 to 9.5 g/d. Wet nylon retains much of its strength, but wet tenacity may drop to between 4.0 and 5.1 grams per denier and to 7.6 for high-tenacity fiber.

Elasticity and Resilience Contrary to most high-tenacity fibers, the elasticity of nylon is very high. Its resilience is good, although not quite as good as polyester. Nylon is a highly elastic fiber with relatively good elongation. The elastic recovery properties assure excellent shape retention of nylon fabrics. Nylon has good to very good recovery from creasing or wrinkling.

Density and Specific Gravity The specific gravity of nylon is 1.14, which is lower than most other fibers. Nylon can be made into very light, sheer fabrics, of good strength.

Absorbency and Moisture Regain Like many synthetics, nylon is low in absorbency. Which causes the fiber to resist some dyes. Other dyestuffs that are compatible with nylon have been developed. Nylon fabrics dry quickly after laundering. Compared with natural fibers, nylon has rather low moisture absorbency. Nylon 6,6 has a percentage moisture regain at standard conditions of 4.2 to 4.5; for nylon 6 the range is 3.5 to 5.0. At conditions of 95-percent relative humidity, nylon fibers will absorb approximately 8 percent moisture. Nylon 6 has a slightly higher absorbency than nylon 6,6 so it will accept dyes more easily. The low moisture regain of nylon results in fabrics that dry quickly after laundering. However, the low moisture absorption, plus poor electrical conductivity, causes and accumulation of static electric charges on nylon.

Dimensional Stability Nylon has good dimensional stability at low to moderate temperatures, neither shrinking nor stretching out of shape. At high temperatures, nylon fabrics may shrink. Washing and drying temperatures should be kept low.

2.4.6 Thermal Properties

Effect of Heat Nylon 6,6 melts at approximately 250°C (480 °F) and nylon 6 at 210°C (400°F). All nylon can withstand temperatures to 149°C (300 °F) for long periods of time without damage, but when temperatures exceed 300°F for a few hours, the fibers will discolor. If temperatures approach 177 to 205 (350-400°F), the fiber softens, and discoloration and loss of strength occur quickly.

Nylon melts away from a flame and forms a gummy gray or tan ash that hardens as it cools. The fiber will burn if held in an open flame, but it does not support combustion. The smoke is white or grayish in color, and the odor is likened to that of cooking celery or green beans.

2.4.7 Chemical Properties

Effect of Alkalines Nylon is substantially inert to alkalines.

Effect of Acids Mineral acids, such as hydrochloric, nitric, and sulfuric, will cause nylon to disintegrate or dissolve almost immediately. Even dilute solutions of hydrochloric acid will destroy the fiber. Organic acids, such as formic, will dissolve nylon in concentrations of 88 to 90 percent. Acid fumes in the air in industrial regions have been known to bring about fiber disintegration.

Effect of Organic Solvents Most organic solvents have little or no effect on nylon. Phenol, metacresol, and formic acid dissolve the fiber, but solvents used in stain removal and dry cleaning do not damage it.

Effect of Sunlight, Age, and Miscellaneous Factors Sunlight has destructive effect upon nylon, and there is marked loss of strength after extended exposure. If nylon is left in direct sun for several weeks, it may actually decompose. Bright nylon has better resistance to sunlight than the deluster one. These are important when the fiber must be subjected to the sun for long periods of time. Ages appears to have no effect on the fiber. If stored away from light and other deleterious influences, nylon will last for many years. Soaps, synthetic detergents, and bleaches do not damage nylon fibers.

Affinity for Dyes Nylon 6 has greater affinity for dyes than nylon 6,6 and can be more easily dyed with a wider range of dyes. Both types of nylon retain their color and have good resistance to fading.

2.4.8 Biological Properties

Resistance to Microorganisms and Insects Nylon is highly resistant to attack by most insects and microorganism. However, some insects normally found outdoors, including ants, crickets, and roaches, will eat nylon if they are trapped in folds or creases. Microorganism producing mildew may attack finishes used on nylon but do not damage the fiber itself. Bacteria have no effect on nylon.

2.5 Silk fibers

The exceptional mechanical properties of silk fibers and the efficiency of silk spinning in nature have produced an effort to understand the natural silk process as it proceeds from the biosynthesis of the silk protein (fibroin) through the spinning of the fiber. The aqueous silk phase existing as a liquid crystal at an intermediate stage of the silk spinning process. This liquid crystallinity aids in the molecular alignment necessary for high performance properties in the final fiber.

In addition to the silk spinning work, I have been investigating the effect of amino acid sequence on crystal structure and on chain conformation at interfaces in fibrous proteins and synthetic polypeptides. The general goal is to better understand how the physical environment and the protein sequence interact to direct crystal structure and properties.

The role of the surrounding environment in controlling protein structure and activity is profound. Globular proteins partition in water such that hydrophilic amino acid residues reside in or near aqueous contact while the hydrophobic residues become occluded within the structure and shielded from the water phase. Protein folding typically involves nonrepetitive amino acid sequences and complex three dimensional geometries, and not surprisingly is extremely difficult to understand.

Silk worm (*Bombyx mori*) silk contains about 60% of the crystallizable repeating sequence (GAGAGS)_n. This sequence occurs in crystallizable blocks which are separated by less repetitive sequences incorporating amino acids with bulkier side chains that do not crystallize. Prior investigators have reported two crystalline polymorphs for silk, designated silk I and silk II. Silk II is the common β -sheet crystal

found in the silk fibers spun by the silk worm, while silk I is a less well-characterized, metastable crystal structure which may be an important intermediate in the silk spinning process.^{2,3} In the past has recently reported the discovery of a third silk polymorph which forms specifically at the air-water interface and aqueous-organic liquid-liquid interfaces.^{4,5} The combination of the silk crystallizable sequence and the two-fold helical chain conformation of the silk-II structure places the side chains of both the alanine residues ($-\text{CH}_3$), and the serine residues ($-\text{CH}_2\text{OH}$) on the same side of the β -sheet. This arrangement poses no difficulty in bulk silk fibers but leads to an unfavorable situation if the structure is placed at an air-water or aqueous-organic interface because it fails to separate the hydrophilic serine side chains and the hydrophobic alanine side chains to opposite sides of the interface. Based on electron diffraction of silk crystallites, we have proposed a new crystal structure based on a threefold helical chain conformation which occurs specifically at interfaces. The combination of the six fold amino acid repeating sequence and the three-fold helix allows separation of the hydrophilic and hydrophobic side chains to opposite sides of the interface. This structure, which still resides in the allowable chain extended region of the Ramachandran conformational map, is similar to the three fold helical structure known as polyglycine II and also to the fold helix formed by collagen. Our molecular modeling calculations show that, while the three-fold helical silk structure has a somewhat higher steric energy than the stable bulk structure (silk II), the partitioning of alanine and serine residues more than compensates when the structure is placed at an interface.

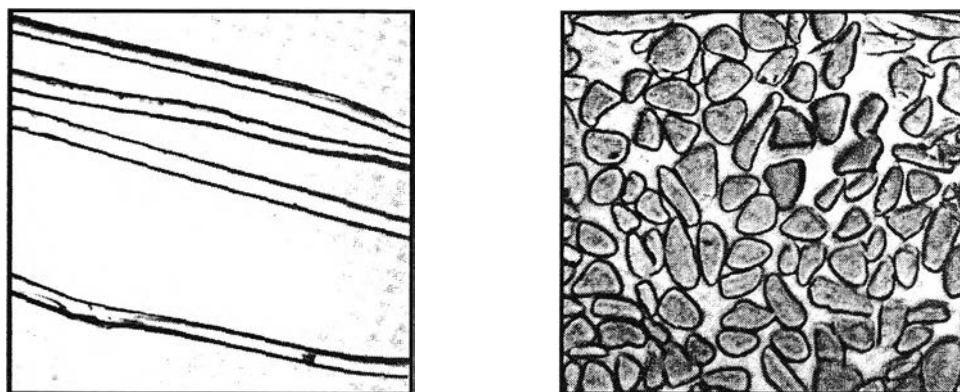


Figure 2.13 optical photographs of raw silk fiber
in a cross section (right) and a longitudinal view (left) .

Cross-sectional views of silk show triangular fibers with no markings. Two filaments usually lie with their flat sides together. This can be explained by the fact that two filaments are extruded simultaneously by each silkworm, and they come together as indicated in Figure 2.13.

2.5.3 Physical Properties

Color of Fiber The natural color of cultivated silk is off-white to cream color. Wild silk is brown

Shape In microscopic cross section silk is triangular in shape. The double silk filaments lie with the flat sides of the triangles together. The fiber has a smooth, transparent rodlike shape with occasional swelling or irregularities along its length. It is fine, having a diameter of nine to eleven microns, and filaments may be as short as 300 meters or as long as 1,000 meters. Individual filaments as long as 3,000 meters have been measured.

Luster Silk filaments have a high natural luster of sheen and are off-white to cream in color.

Strength Silk is one of the strongest of the natural fibers. It has a tenacity of 2.4 to 5.1 grams per denier when dry, and its wet strength is about 80 to 85 percent of the dry.

Elasticity and Resilience Silk has good elasticity and moderate elongation. When it is dry, the elongation varies from 10 to 25 percent; when wet, silk will

elongate as much as 33 to 35 percent. At 2% elongation the fiber has a 92% elastic recovery.

Silk has medium resiliency. Creases will hang out relatively well but not as quickly or completely as in wool.

Density and Specific Gravity The specific gravity of silk of 1.25 is less than that of cellulose fibers and is similar to that of wool. Lightweight fabrics can be made of silk because of the fine diameter of the fiber and its high tenacity.

Absorbency and Moisture Regain Silk has a relatively high standard moisture regain of 11.0%. At saturation the regain is 25 to 35%. The absorption property of silk is helpful in the application of dyes and finishes and making it a comfortable fiber to wear.

Dimensional Stability Silk fabrics have good resistance to stretch or shrinkage when laundered or dry cleaned.

2.5.4 Thermal Properties

Effect of Heat When placed in a direct flame, silk will burn, but when the flame is removed it will not continue to support combustion. Therefore, silk is not considered to be an especially combustible fabric. Like wool, silk is damaged by dry heat and should be ironed damp, at low temperatures and using a press cloth.

2.5.5 Chemical Properties

Effect of Alkalies Silk is damaged by strong alkalies and will dissolve in heated caustic soda (NaOH); however, silk reacts more slowly than wool, and frequently the identity of the two fibers can be determined by the speed of solubility in NaOH. Weak alkalies such as soap, borax and ammonia cause little or no damage to silk unless they remain in contact with the fabric for a long time.

Effect of Acids Silk protein can be decomposed by strong mineral acids. Medium concentrations of hydrochloric acid (HCl) will dissolve silk, and moderate concentrations of other mineral acids cause fiber contraction and shrinkage. The molecular arrangement in silk permits rapid absorption of acids but tends to hold the acid molecules so they are difficult to remove.

Effect of Organic Solvents Cleaning solvents and spot-removing agents do not damage silk.

Effect of Sunlight, Age, and Miscellaneous Factors Sunlight tends to accelerate the decomposition of silk. It increases oxidation and results in fiber degradation and destruction.

Silk requires careful handling and adequate protection in storage to withstand the ravages of age. Oxygen in the atmosphere cause a gradual decomposition of silk, and unless it is stored in carefully sealed containers, the fiber will lose strength and eventually be destroyed.

Silk is a poor conductor of electricity, which results in the buildup of static charges. Like other protein fibers, it has a lower thermal or heat conductivity than cellulosic fibers. This factor, coupled with certain methods of construction, creates fabrics that tend to be warmer than comparable fabrics of cellulosic fibers.

2.5.6 Biological Properties

Silk is resistant to attack by mildew and is relatively resistant to other bacteria and fungi. It is decomposed by rot-producing conditions.

2.6 Optical and Electron Microscopy [10]

Colloidal particles are often too small to permit direct microscopic observation. The resolving power of an optical microscope (i.e. the smallest distance by which two objects may be separated and yet remain distinguishable from each other) is limited mainly by the wavelength λ of the light used for illumination. The limit of resolution δ is given by the expression

$$\delta = \lambda/2n \sin \alpha \quad [2.11]$$

where α is the angular aperture (half the angle subtended at the object by the objective lens), n is the refractive index of medium between the object and the objective lens, and $n \sin \alpha$ is the numerical aperture of the objective lens for a given immersion medium.

The numerical aperture of an optical microscope is generally less than unity. With oil-immersion objectives numerical apertures up to about 1.5 are attainable, so

that, for light of wavelength 600 nm, this would permit a resolution limit of about 200 nm (0.2 μm). Since the human eye can readily distinguish objects some 0.2 mm (200 μm) apart, there is little advantage in using an optical microscope, however well constructed, which magnifies more than about 1000 times. Further magnification increases the size but not the definition of the image.

Owing to its large numerical aperture, the depth of focus of an optical microscope is relatively small. This is not always a disadvantage of the technique; for example, in microelectrophoresis it permits the observation of particles located at a narrowly defined level in the electrophoresis cell.

Particle sizes as measured by optical microscopy are likely to be in serious error for diameters less than c. 2 μm , although the limit of resolution is some ten times better than this.

Table 2.3 Determination of the diameter of spherical particles by optical Microscopy

True diameter (μm)	Visual estimate (μm)
1.0	1.13
0.5	0.68
< 0.2	0.5

In addition to the question of resolving power, the visibility of an object may be limited owing to lack of optical contrast between the object and its surrounding background.

Two techniques for overcoming the limitations of optical microscopy are of particular value in the study of colloidal systems. They are electron microscopy, in which the limit of resolution is greatly extended, and dark-field microscopy, in which the minimum observable contrast is greatly reduced.

2.6.1 The Transmission Electron Microscope

To increase the resolving power of a microscope so that matter of colloidal (and smaller) dimensions may be observed directly, the wavelength of radiation used must be reduced considerably below that of visible light. Electron beams can be produced with wavelengths of the order of 0.01 nm and focused by electric or magnetic fields, which act as equivalent of lenses. The resolution of an electron microscope is limited not so much by wavelength as by the technical difficulties of stabilizing high-tension supplies and correcting lens aberrations. Only lenses with a numerical aperture of less than 0.01 are usable at present. With computer application to smooth out 'noise' a resolution of 0.2 nm has been attained, which compares with atomic dimensions. Single atoms, however, will appear blurred irrespective of the resolution, owing to rapid fluctuation of their location.

The useful range of the transmission electron microscope for particle size measurement is c. 1 nm- 5 μm diameter. Owing to the complexity of calculating the degree of magnification directly, this is usually determined by calibration using characterized polystyrene latex particles or a diffraction grating.

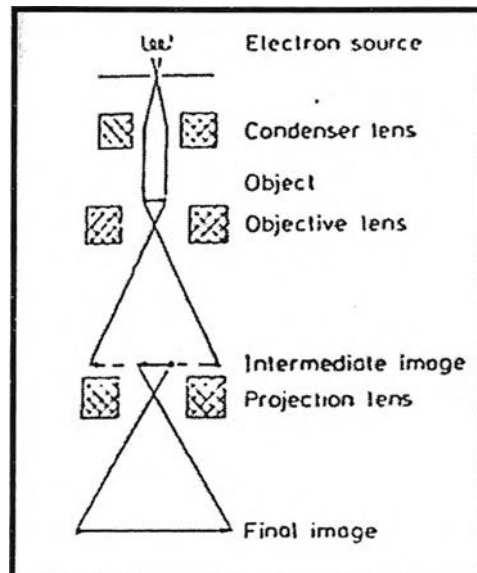


Figure 2.14 Schematic presentation of the transmission electron microscope.

The use of the electron microscope for studying colloidal system is limited by the fact that electrons can only travel unhindered in high vacuum, so that any system having a significant vapour pressure must be thoroughly dried before it can be observed. Such pretreatment may result in a misrepresentation of the sample under consideration. Instability of the sample to electron beams could also result in misrepresentation.

A small amount of the material under investigation is deposited on an electron-transparent plastics or carbon film (10-20 nm thick) supported on a fine copper mesh grid. The sample scatters electrons out of the field of view, and the final image can be made visible on a fluorescent screen. The amount of scattering depends on the thickness and on the atomic number of the atoms forming the specimen so that organic materials are relatively electron-transparent and show little contrast against the background support, whereas materials containing heavy metal atoms make ideal specimens.

To enhance contrast and obtain three-dimensional effects, the technique of shadow-casting is generally employed. A heavy metal, such as gold, is evaporated in vacuum and at a known angle on to the specimen, which gives a side illumination effect. From the angle of shadowing and the length of the shadows, a three-dimensional picture of the specimen can be built up. An even better picture can be obtained by lightly shadowing the sample in two directions at right angles.

A most useful technique for examining surface structure is that of replication. One method is to deposit the sample on a freshly cleaved mica surface on to which carbon (and, if desired, a heavy metal) is vacuum-evaporated. The resulting thin film, with the specimen particles still embedded, is floated off the mica on to a water surface. The particles are dissolved out with a suitable solvent and the resulting replica is mounted on a copper grid.

2.6.2 The Scanning Electron Microscope

In the scanning electron microscope a fine beam of medium-energy electrons scans across the sample in a series of parallel tracks. These interact with the sample to produce various signals, including secondary electron emission (SEE), back-scattered electrons (BSE), cathodoluminescence and X-

rays, each of which (with their varying characteristics) can be detected, displayed on a fluorescent screen and photographed. In the SEE mode the particles appear to be diffusely illuminated, particle size can be measured and aggregation behaviour can be studied, but there is little indication of height. In the BSE mode the particles appear to be illuminated from a point source and the resulting shadows lead to a good impression of height.

The magnification achieved in a scanning electron microscope (resolution limit of c. 5 nm) is, in general, less than that in a transmission electron microscope, but the major advantage of the technique (which is a consequence of the low numerical aperture) is the great depth of focus which can be achieved. At magnifications in the range of optical microscopy the scanning electron microscope can give a depth of focus several hundred times greater than that of the optical microscope. In colloid and surface science this large depth of focus is extremely valuable in the study of the contours of solid surfaces and in the study of particle shape and orientation.

2.7 Spectrophotometer [11]

Spectrophotometers are instruments that measure the reflectance from, or the transmittance through, materials as a function of wavelength. They have many uses besides color measurement. Spectrophotometry in the visible region (380 – 780 nm) as carried out on instruments especially designed for color measurement.

The main components of all spectrophotometers for color measurement are a source of optical radiation, an optical system for defining the geometric conditions of measurement, some means of dispersing light, and a detector and signal processing systems that converts light into signals suitable for analysis.

Physical properties of the specimens to be measured ultimately determine instrument design. In particular, many materials are fluorescent, using fluorescent colorants or fluorescent whitening agents: this affects the design of the illumination system. The absorption and scattering characteristics of colorants lead to slowly varying reflectances and transmittances as a function of wavelength thin the visible spectrum; this affects the design of the dispersing and detector and signal processing systems. Furthermore, because the visual system is such an excellent null detector,

signal processing requirements are stringent. That is, the instrument should be at least as sensitive in detecting small differences in color as an observer.

2.8 Kubelka - Munk Analysis .

For opaque systems, reflectance is transformed to the ratio of absorption, K , to scattering, S , $(K/S)_\lambda$, known as “K over S.” The scalability and additivity requirements apply to the individual absorption and scattering properties for each colorant.

$$R_{\lambda,i} = 1 + (K/S)_\lambda - [(K/S)_\lambda^2 + 2(K/S)_\lambda]^{1/2} \quad [2.9]$$

For opaque materials, Kubelka and Munk found that internal reflectance, $R_{\lambda,i}$, depended on absorption, K_λ , and scattering, S_λ . Reversing this equation gives the well-known relationship between (K/S) and $R_{\lambda,i}$

$$(K/S)_\lambda = (1 - R_{\lambda,i})^2 / 2 R_{\lambda,i} \quad [2.10]$$

When using these equations, be sure that reflectance is scaled between zero and unity, not as a percentage. Notice that K and S only appear as a ratio.

Literature reviews

These studies focused on the immobilization of silver nanoparticles on textile fibers and show antimicrobial properties. Hereafter is described some work already published.

Nicola E. Cant and co-workers [12] studied fabrication and characterization of self-assembled nanoparticle/polyelectrolyte multilayer films. They focused on the early stages of multilayer film formation of alternate gold-nanoparticle/polyelectrolyte layers. The formation of multilayer films was prepared through the layer-by-layer technique. The formation of multilayer film has been studied using a combination of x-ray photoelectron spectroscopy, spectroscopic ellipsometry, a Kelvin probe microscopy. The results suggested that the polyelectrolyte/nanoparticle film can be considered as a wide-band-gap semiconductor with a depletion width, at the substrate/film interface, extending several nanometers into the film. These results explain the poor conductivity found in these films.

Silver nanocomposite layer-by-layer films based on assembled polyelectrolyte/dendrimer were studied by Zelin Liu and co-workers [13]. Silver nanocomposite multilayer films were prepared through the *in situ* method. Multilayer thin films, prepared through the sequential electrostatic deposition of a positively charged third-generation poly(amidoamine) dendrimer (PAMAM) and negatively charged poly(styrenesulfonate) (PSS) and poly(acrylic acid) (PAA), were utilized as nanoreactors for the formation of silver nanoparticles. The silver ions were preorganized in layer-by-layer (LBL) films composed of PAMAM dendrimers and subsequently reduced with hydrogen to prepare the silver nanoparticles. The UV-vis spectrum and profilometer were used to characterize the regular growth of bilayers. UV-vis absorption from plasmon resonance at 435 nm and TEM images indicated the formation of the silver nanoparticles in the multilayer films. The silver nanocomposite LBL films were also constructed on the indium tin oxide-glass and investigated using cyclic voltammetry. The silver nanoparticles in the multilayer films have a stronger negative redox potential. The silver nanocomposite LBL films may have a potential application in the catalysis of reduction of 4-nitrophenol with sodium borohydride.

Tom C. Wang and co-workers [14] studied polyelectrolyte multilayer nanoreactors for preparing silver nanoparticle composites. The size of *in situ* prepared silver nanoparticles and the overall metal concentration within poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) multilayer films are systematically controlled through multilayer processing conditions. Carboxylic acid groups in the PAH/PAA-based multilayers bind silver cations by ion exchange with the acid protons. Subsequent reduction formed metallic nanoparticles. Because PAA has a pH-dependent degree of ionization, the multilayer film can be fabricated with different concentrations of free acid groups that are available to bind silver cations depending on the multilayer assembly pH. The nanoparticle size and silver concentration can be controllably increased by reducing the assembly pH of PAH/PAA-based multilayers.

Paul Podsiadlo and co-workers [15] studied the layer-by-layer assembly of nacre-like nanostructured composites with antimicrobial properties. They have presented the layer-by-layer (LbL) assembly of a biomimetic nanostructured composite from Na⁺montmorillonite clay nanosheets and poly(diallylmethylammonium chloride). The structure, deformation mechanism, and mechanical properties of the material are very similar to those of natural nacre and lamellar bones. This fact prompts further investigation of these composites as

potential bone implants. LBL assembly affords preparation of multifunctional composites, and here we demonstrate that not only mechanical strength, but also antibacterial activity, can be introduced in these implantable materials by alternating clay layers with starch-stabilized silver nanoparticles. The resulting composite showed excellent structural stability with no detectable levels of silver lost over a 1 month period. Evaluation of the antibacterial properties showed almost complete growth inhibition of *E. coli* over an 18 h period. The amount of silver eluted from the LBL composite over a 1 month period was determined to be only 0.5-3.0 $\mu\text{g/L}$. This concentration of silver did not prevent the growth of the mammalian tissue cultures. The LBL composite has shown biocompatibility with the human osteoblast cell line.

The preparation of nanostructured materials with defined composition and shape is of immense scientific and technological interest. Polyelectrolyte multilayers are promising nanoreactors which have been applied for a broad range of nanomaterials synthesis, because the multilayer films can be tuned with desired composition and thickness, can be deposited onto different substrates with predetermined morphologies, and can be easily removed after nanomaterials synthesis. Xiangyang Shia and co-workers [16] reported the recent advances on the synthesis and characterization of a variety of nanostructured materials generated by using polyelectrolyte multilayers assembled onto both planar and colloidal substrates as nanoreactors. By loading small molecular precursors (including metal ions, metal complexes, metal alkoxides, and polymer monomers) into such polyelectrolyte multilayers, followed by chemical or physical treatment, thin hybrid nanoparticulate films, core-shell colloids and hollow spheres can be prepared in a controlled manner. Polyelectrolyte multilayer-coated colloidal assemblies (colloid arrays or colloidal crystals) can also be used to prepare 2-dimensional surface arrays and 3-dimensional macroporous materials with tunable morphologies and compositions. The potential applications of these nanomaterials are briefly discussed.

From these relevant articles PEM from polyelectrolyte and silver nanoparticles were successfully constructed and then some published articles were studied about the parameters controlling the growth of PEM as follow.

Schlenoff et al.[17] studied the factors controlling the growth of polyelectrolyte multilayers and the dependence of polyelectrolyte multilayer thickness on salt concentration, salt type, solvent quality, deposition time, and polymer concentration is evaluated. Polymers are deposited on spinning silicon wafers. For the strong polycation/polyanion pair studied, film thickness is approximately proportional to the number of layers and the salt concentration. The irreversibility of overall molecule adsorption is indicated by the lack of exchange of surface (radiolabeled) for solution polymer. The hydrophobic nature of the driving force for polymer sorption is illustrated by the choice of salt counterion or solvent. Salt, competing with polymer segments for the surface, permits localized rearrangements. In the mechanism proposed, excess polymer is accommodated within several layers, rather than in one layer of loops and tails. Steric barriers coupled with slow conformational changes are responsible for long-term polymer adsorption. Considering the disorder and interpenetration, multilayer buildup has much in common with solution phase or coprecipitated polyelectrolyte complexes. Surface hydrophobicity can be enhanced using fluorinated surfactants as counterions.

Then Schlenoff et al. studied polyelectrolyte multilayers containing a weak polyacid [18] and found that the growth of multilayers made from a combination of a weak polyacid and a strongly dissociated polycation. Film thickness reaches a maximum at around 0.3 M salt and then decreases quickly. Preformed multilayers are shown to decompose rapidly and, for high molecular weights, completely when exposed to aqueous solutions of NaCl of concentration >0.6 M. The apparent dissociation of multilayer polyelectrolyte complexes is due to competition for polymer/polymer ion pairs by external salt ions. Similar experiments aimed at decomposing multilayers by protonating the weak acid, thus decreasing polymer/polymer interactions, lead to incomplete loss of polymer, probably due to additional hydrogen bonding from the protonated weak acid. A model based on ion exchange/swelling of multilayers is used to explain their stability and permeability as well as the dependence of film thickness on salt concentration and type.

Bjoern Schoeler et al.[19] investigated of the influence of polyelectrolyte charge density on the growth of multilayer thin films prepared by the layer-by-layer technique and found that the influence of the charge density along a polyelectrolyte chain on the buildup of multilayer films formed by the sequential adsorption of alternating layers of polyanions and polycations (the Layer-by-Layer technique).

Model random copolymers of diallyldimethylammonium chloride (DADMAC) and *N*-methyl-*N*-vinylacetamide (NMVA) having matched molecular weights and varying percentages (24-100%) of the cationic DADMAC component are alternated with polyanionic polystyrene sulfonate (PSS). When films are deposited from polyelectrolyte solutions containing added salt, a critical charge density limit (between 75% and 53%), below which no significant layer growth is possible, becomes apparent. Below the critical charge density, addition of the polyanion leads to almost complete removal of the previously deposited cationic copolymer and vice versa, and thus multilayers can not grow. Above the critical charge density, the rate of film growth and film morphology are strongly influenced by the solution structure of the adsorbing polyelectrolytes: thicker and rougher films are produced with increasing salt concentration in the adsorption solutions.