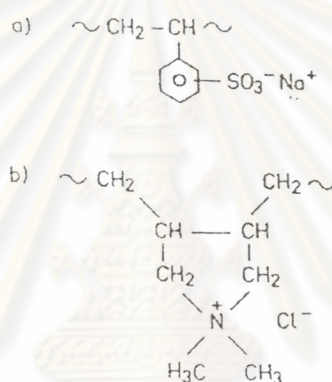


## CHAPTER II

### THEORY AND LITERATURE REVIEW

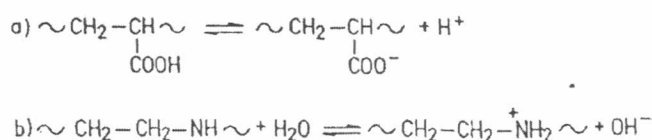
#### 2.1 Definition and general description of polyelectrolyte [1]

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. Example 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).

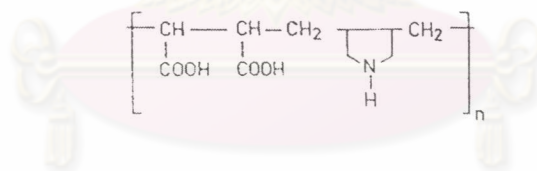
Both Na-polystyrene sulfonate and poly(diallyldimethylammonium chloride) are dissociated into macroion and counterion in aqueous solution in the total pH range between 0 and 14. Also polymers like poly(acrylic acid) and poly(ethylene imine) are usually classified as polyelectrolytes, in spite of the 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 undissociated polybase in the alkaline range, respectively (Figure 2.2), 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 presented 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.



**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. In the case of a crosslinked polymer its swell ability in aqueous media is enhanced by transferring into a PEL. A vast number of polyelectrolyte classes known today are listed in Table 2.1.

**Table 2.1** Selected classes of polyelectrolytes

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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
Ionenex
Poly(diallyldimethylammonium chloride)
Homo- and copolymers of cationic acrylic acid esters

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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 (Table 2.2)

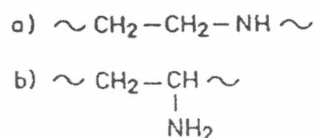
**Table 2.2** Structures of ionic sites of PEL

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

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.



**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.

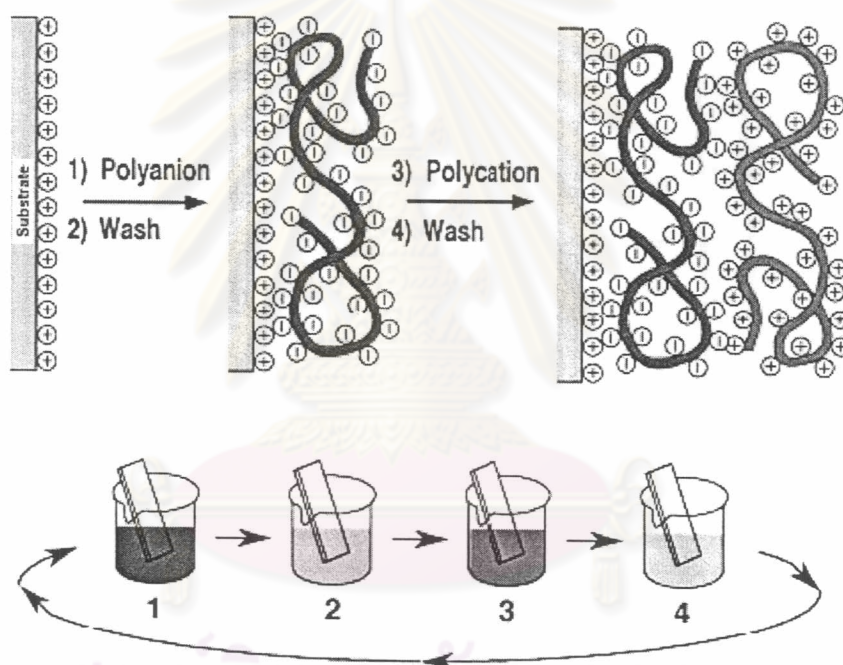
Besides these three parameters characterizing the macroion, the species of low molecular counterions has a strong influence on the properties of the whole system in solution, especially on solubility and structure formation. Two examples may illustrate this and demonstrate that the counterion is not 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  $\text{K}^+$  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  $\text{Na}^+$  salt of the same sample at the same concentration gives quite a normal polymer solution of the expected viscosity.

## 2.2 Formation of polyelectrolyte multilayer thin films [5]

Polyelectrolyte multilayer films created via Layer-by-Layer (LbL) deposition are currently used to modify the surface properties of materials. These polyelectrolyte based films are capable of self-organization. The self-organization process of polyelectrolyte films, also referred to as electrostatic self-assembly (ESA), has been well documented over the past ten years.

Starting in the early 1990s, Decher's group began work on the realistic method for the ESA of nanolayers over charged substrate. The process developed by Decher has increased in popularity since its introduction. This is a result of the method's simplicity and the fact that polyelectrolytes as well as charged nano objects can be deposited in a controlled manner. Biological compounds, conducting and light emitting polymers, and dyes have also been deposited onto suitable substrates via ESA.

The LbL process is based on the alternating adsorption of charged cationic and anionic species. The process begins by properly charging a substrate. The charged substrate is then primed by adsorbing a layer of a polyelectrolyte with an opposite charge sign to that imparted to the substrate. Once the substrate is primed, it is then dipped into a solution of a counterion polyelectrolyte. A rinse step is included between the two adsorption processes to remove excess as well as to prevent cross-contamination of the polyelectrolyte solutions. These simple steps complete the LbL deposition of the nanolayers. Multiple layers can be created by simply dipping the substrate in alternating anionic and cationic baths [5].



**Figure 2.5** Schematic of the electrostatic self-assembly (ESA) [4].

From Figure 2.5 top: Simplified molecular concept of the first two adsorption steps depicting film deposition starting with a positively charged substrate. The polyion conformation and layer interpenetration are an idealization of the surface charge reversal with each adsorption step which is the basis of the electrostatically driven multilayer build up depicted here. Counterions are omitted for clarity. Figure 2.5 Bottom: Schematic of the film deposition process using glass slides and beakers. Steps 1 and 3 represent the adsorption of a polyanion and polycation respectively, and

steps 2 and 4 are washing steps. The four steps are the basic buildup sequence for the simplest film architecture  $(A/B)_n$  where  $n$  is the number of deposition cycles. The construction of more complex film architectures requires additional beakers and an extended deposition sequence.

### 2.3 Parameters controlling the growth of PEM [2]

The parameters controlling the growth of PEM were studied because there are important for the multilayer formation.

#### 2.3.1 Type of polyelectrolyte

The type of polyelectrolyte affects the total thickness. For instance, the multilayer thickness increases in the order: poly (acrylamide sulfonate)/poly (diallyldimethylammonium chloride) (PAMS/PDADMAC) < poly (styrene sulfonate) /poly (allylamine hydrochloride) (PSS/PAH) < PSS/PDADMAC. All these polyelectrolytes are flexible. The intrinsic persistence length for PSS, PAMS and PAH is similar (approx. 1 nm) while the intrinsic persistence length of PDADMAC is slightly higher.

Therefore the chain stiffness cannot be the only reason for the differences in multilayer thickness. It is assumed that the balance between hydrophobicity and hydrophilicity of the polyelectrolytes plays an important role for the thickness. While PSS has a hydrophobic backbone and is not water soluble below a degree of charge of 0.33 even the neutral PAMS is water soluble.

The type of multilayer growth depends also on the type of polyelectrolytes. The thickness of PSS/PAH multilayers increases linearly with the number of deposition cycles, while the thickness of PSS/PDADMAC multilayers increases linearly or exponentially depending on the charge density of PDADMAC. The exponential growth is related to a higher surface roughness and internal roughness than in the case of linear growth.

#### 2.3.2 Effect of polymer charge density

A minimum charge density is required for the formation of multilayers. Below this charge threshold the charge reversal is not sufficient. In the case of strong

polyelectrolytes the charge density is varied by changing the chemical structure. For instance, a PSS/PDADMAC multilayer can be built up at polycation charges  $\geq 70\%$ . Above this threshold the charge density does not affect the polymer density (electron density between  $0.374$  and  $0.393 \text{ \AA}^{-3}$ ).

Not only the average charge density, but also the distribution of the charges along the chains plays an important role for building up multilayers. The adsorption of block-copolymers showed that a short strongly charged block (10–20% of the total number of monomer units per chain) is sufficient for the formation of multilayers, even if the average charge density is below the charge threshold that is required for multilayer formation.

### 2.3.3 Influence of ionic strength

The total multilayer thickness can be controlled with angstrom precision by adding salt to the aqueous polyion solutions. Due to the screening of the charges along the polyelectrolyte chains the polymer molecules are more entangled with increasing salt concentration. This results in a larger thickness and a stronger internal and external roughness of the adsorbed layers. The increase in thickness  $d$  is proportional to  $IB$  ( $I$ : ionic strength). Most of the studies in the literature report an exponent  $B$  of the salt dependence between 0.5 and 1 for different polyelectrolytes. Lo¨sche et al., showed by neutron reflectivity that the thickness of a layer pair (PSS/PAH) varies linearly with the ionic strength of the dipping solutions in the concentration range 0.5–3 mol/l NaCl additive. At low ionic strength, i.e. below 0.5 mol/l NaCl, a deviation from this linear behavior towards an  $I^{0.5}$  dependence is stated. The latter behavior is also reported by other groups against air or water. Above a salt concentration of 1 mol/l the thickness increase is less pronounced, but nevertheless,  $d$  increases up to a concentration of 3 mol/l.

PSS/PDADMAC multilayers increase proportional to  $I$  or  $I^{0.5}$  depending on the PDADMAC charge density.

Beside the segment–segment repulsion also the attraction between the polyelectrolyte and the oppositely charged interface is screened. Therefore, one would expect a decrease of adsorbed amount at high ionic strength. For some systems, as, e.g. PAMS/PDADMAC or PSS/PDADMAC, this decrease has been observed, but the thickness of PSS/PAH multilayers increases even above an ionic strength of 1 mol/l.



There seems to be a paradox: On one hand a minimum polymer charge density is required to form multilayers, on the other hand multilayers can be built up at high ionic strength where the electrostatic interactions are screened. These results indicate that macroscopic mean field theories like the Gouy Chapman theory do not describe the multilayer formation at high ionic strength. Two other explanations for the adsorption of polyelectrolytes are possible: Firstly, beside enthalpy contributions also the gain in entropy plays an important role due to the release of counterions during multilayer formation. Furthermore, charge (or ion) fluctuations near the surface should be taken into account. They make the surface 'visible' for the oppositely charged polyelectrolyte despite of (mean field) screening.

#### 2.3.4 Effect of type of salt

Beside the type of polyelectrolyte the type of salt also plays an important role for multilayer formation. Small ions have a relatively small polarizability, high electric fields at short distances and prefer to keep their water of hydration. They have a well-ordered large hydration shell (cosmotropic ions, water structure makers). Chaotropic ions are large with a significant polarizability, a weak electric field and their hydration water can be easily removed.

The thickness of multilayers which are prepared in the presence of different types of salt increases in the order:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  and  $\text{Cl}^- < \text{Br}^-$ . Both the results for cation and anion variation indicate an increasing interaction between the ions and the polyelectrolytes with decreasing hydration shell related to stronger polarizability of the small ions. This is associated with stronger coiling of the polyelectrolyte chain, which in turn increases thickness and roughness of the multilayers. The effect of anions is much larger than the effect of cations, since anions have a much larger difference in polarizability than typical cations due to their larger variety of their diameter.

The increasing interaction of  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  and  $\text{Cl}^- < \text{Br}^-$  with polyelectrolytes has also been observed in solution detected by decreasing viscosity and conductivity. Also, theoretical calculations predict an effect of the ion type on their distribution around a polyelectrolyte. Short-range dispersion forces have to be added to DLVO forces to describe this effect.

### 2.3.5 Type of solvent

The solvent of polyelectrolyte solution affects the interactions between the counter ions or salt ions and the respective polyelectrolyte. For instance, methanol and ethanol have a poorer solvating effect on the ions than water has, which leads to a stronger ion-polyelectrolyte association, i.e. a stronger coiling of the polyelectrolyte chains. This is the reason for increasing multilayer thickness with increasing ethanol concentration and a decreasing conductivity of polyelectrolyte solutions (the conductivity is dominated by the small free ions).

### 2.4 Useful substrates [3]

In a first approach, suitable support materials must carry a minimal surface charge which, if not inherent, can be created by surface treatment. If the charged substrate is brought into contact with the solution of a polyion of opposite charge, the first polymer layer is adsorbed and adheres by the same mechanism as the subsequent film growth by ESA.

The choice of substrates has so far been dominated by their convenience for particular analytical methods. Glass, quartz, silicon wafers, mica, and gold coated supports are materials used most frequently. Due to their transparency, glass and quartz are most suitable for the use of Vis- and UV-spectroscopy, as well as optical microscopy. Silicon wafers are well suited for ellipsometric studies and may serve for IR-spectroscopic investigations as they are transparent in a wide IR-range. Also, their smooth surface renders them well suited for X-ray reflectivity studies and for near-field microscopy. For these purposes, mica and float glass present alternatives. Gold coated surfaces enable electrochemical studies, investigations by quartz crystal microbalance (QCM) and studies by surface plasmon resonance (SPR) as well as by IR-RAS

All the above mentioned materials are additionally characterized by the simplicity with which charged groups can be created on the surface. The surface of cleaved mica sheets are inherently negatively charged in water, due to the dissociation of the potassium cations of this aluminosilicate in water. The silanol groups at the surface of glass and quartz, as well as of silicon wafers due to the thin surface layer of oxide, can be easily deprotonated by base. Treatment with various functionalized

silanes, such as trialkoxy-3-aminopropylsilane, provides an additional, “easy” access to positively charged surfaces. In a similar way, treatment of gold with functionalized thiols or disulfides, respectively, enables the tailoring of both positively (e.g. when applying cysteamine) or negatively (e.g. when applying mercaptoundecanoic acid) charged surfaces.

In this regime, the thickness per layer pair is characteristic for polyelectrolytes employed and conditions applied (polyion concentration, ionic strength, rinsing and drying steps etc., see below). Most studies found that this thickness increment is independent of the chemical nature of the support. However in a few cases, the thickness per layer pair was reported to depend on the detailed nature of the support even during stable multilayer growth.

Although the hitherto most widely employed supports such as quartz, silicon wafers, or gold surfaces may satisfy the requirements for thorough characterization, for practical applications other substrate materials will be desirable, notably organic polymers. These however are usually rather hydrophobic materials and were thought not to be suitable as substrates. Therefore, various methods of surface modification often oxidation reactions or plasma treatment were used to introduce a certain number of charged groups, before using polymers as supports for ESA. Nevertheless, a number of untreated polymers were found to be useful even without previous treatment, such as poly(ethylene terephthalate). Whether the successful adsorption is due to some carboxylic acid end groups, or whether it is due to dipolar interactions via the ester moieties, is yet an open question. The possibility to deposit ESA-films to a limited extent on untreated PMMA, poly(phenylene oxide), or poly(etherimide)s, too, or on form var points to the second explanation. As expected, supports made of untreated unpolar polymers however, such as polyolefins or poly(tetrafluoroethylene), give poor results only.

Only few studies exist investigating the effect of the geometry of the substrates. Planar solid supports have been mostly used, for convenience. Other geometries, such as fibers, seem to pose no particular problems.

## 2.5 Textile fiber substrates

### 2.5.1 Nylon fiber [6, 7]

Nylon fibers are, made up of linear macromolecules whose structural units are linked by the -NH-CO- group. Consequently the term polyamide is frequently used. However, 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 of the amide links are attached to two aromatic rings. If 85% or more of the amide linkages are attached the two aromatic rings, then the fibers are still polyamide but fall into a different generic group.

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

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

Nylon 6, the normal monomer is caprolactam, which is formed when 6-aminohexanoic acid loses water internally to form a lactam, as represented in reaction 2.1



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, hydride and alcoholates as catalysts. However the hydrolytic polymerisation is normally used for fibers. 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 (2.2), which is a reversal of the reaction in 2.1, followed by a condensation polymerisation (2.3) of the

aminocaproic acid. Mechanistic studies indicate that a direct addition polymerisation of caprolactam also take place in the reaction 2.4.

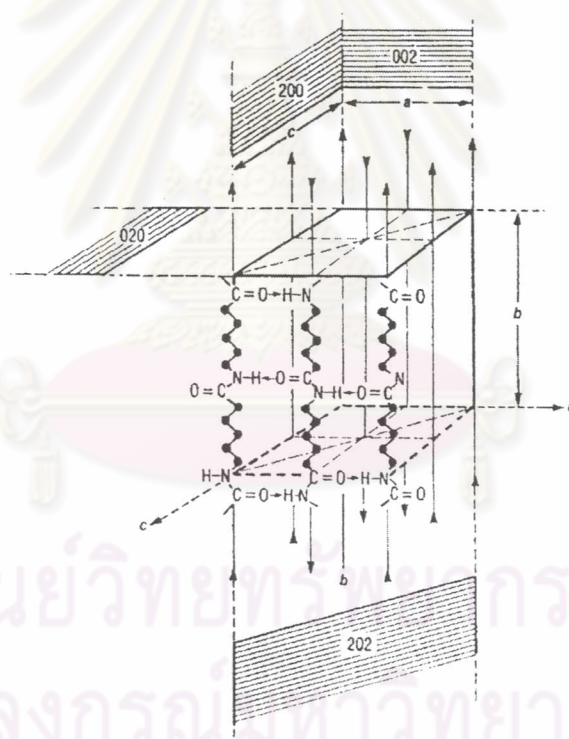
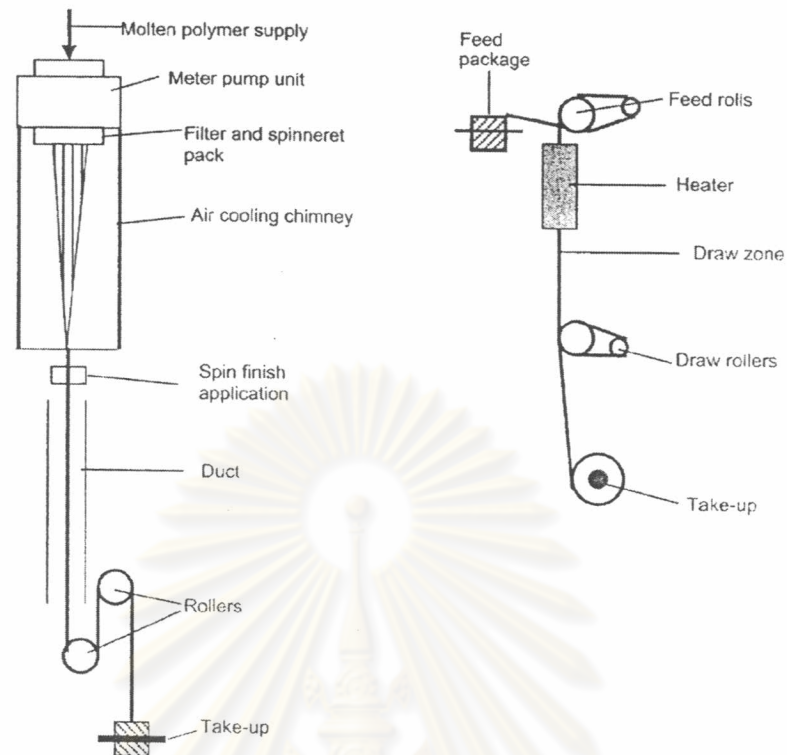


Figure 2.6 Unit cell of  $\alpha$ -form of nylon 6



**Figure 2.7** Schematic of nylon 6 fiber production

The properties of nylon fabrics depend on the type of nylon, the cross section of fiber, whether the fabric is made of multifilament or spun yarn, and how the fabric is constructed.

*Strength.* Nylon is produced in both regular and high tenacity strengths. Although one of the lightest textile fibers it is also one of the strongest. It is surpassed in strength only by aramid and glass. Its strength competes with high-tenacity viscose rayon as well as with polyester fibers.

*Elasticity.* Nylon is one of the most elastic fibers that exists today, though it does not have the exceptional elastic quality of spandex fibers. After being stretched, nylon has a strong natural tendency to return to its original shape. Like any other textile, nylon has its own limit of elasticity. If stretched too much, it will not completely recover its shape.

*Effect of heat.* Like acetate, nylon will melt if the iron is too hot; therefore, the iron should be set at the proper heat level. Special care must be taken with fabrics made of nylon 6 because it has a lower melting point at 216 °C than nylon 6,6 at 250 °C.

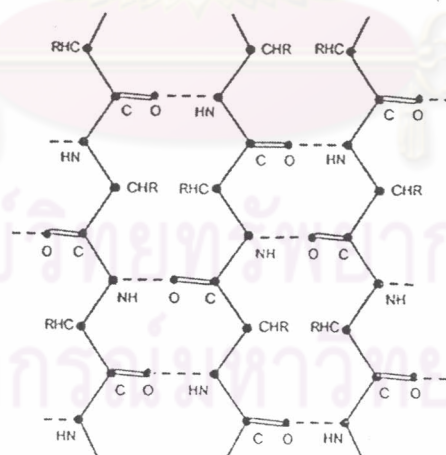
*Reaction in acids.* Nylon is decomposed by cold concentration solutions of such mineral acids as hydrochloric, sulfuric, and nitric acids. A boiling dilute 5 % solution of hydrochloric acid will be decompose the nylon.

*Reaction in alkalies.* Nylon is substantially inert to alkalies.

*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. Dye which can be used for dyeing nylon include: acid, basic, vat, direct, and disperse dyes.

### 2.5.2 Silk fiber [8]

Silk are mostly composed of protein. The fiber has only peptide linkages and present no cystine linkages. Silk has many advantages. Silk fabrics are luxurious in appearance and feel. Silk is a very strong fibers in relation to its filament fineness. It is very elastic and very wrinkle resistant. It dries quickly and gives up soil readily. Silk dyes and prints readily to beautiful, brilliant shades, it is adaptable to a variety of fabric construction, from very sheer drapable fabrics to heavy, stiff, bouffant fabrics. Silk fiber construction and the composition is shown in Figure 2.8 and Table 2.3



**Figure 2.8** Chemical structure of silk fiber [9].

Table 2.3 The side groups of silk fiber [9].

Type	Side group	Amino acid	Proportion (g amino acid per 100 g protein) in:		
			Silk fibroin	Wool keratin	Casein
Inert	—H	Glycine	43.8	6.5	1.9
	—CH <sub>3</sub>	Alanine	26.4	4.1	3.5
	—CH(CH <sub>3</sub> ) <sub>2</sub>	Valine	3.2	5.5	6.02
	—CH <sub>2</sub> -CH(CH <sub>3</sub> ) <sub>2</sub>	Leucine	0.8	9.7	10.55
	—CH(CH <sub>3</sub> )-CH <sub>2</sub> -CH <sub>3</sub>	Isoleucine	1.37	—	5.27
	—CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	Phenylalanine	1.5	1.6	6.46
Acidict	—CH <sub>2</sub> -COOH	Aspartic acid	3.0	7.27	6.70
	—CH <sub>2</sub> -CH <sub>2</sub> -COOH	Glutamic acid	2.03	16.0	22.03
Basic†	—CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	Lysine	0.88	2.5	8.25
	—(CH <sub>2</sub> ) <sub>3</sub> -NH-C(NH)NH <sub>2</sub>	Arginine	1.05	8.6	3.94
	$\begin{array}{c} \text{N:CH} \\   \\ \text{—CH}_2\text{—C:CH—NH} \end{array}$	Histidine	0.47	0.7	3.24
Hydroxyl	—CH <sub>2</sub> OH	Serine	12.6	9.5	5.87
	—CH(OH)-CH <sub>3</sub>	Threonine	1.5	6.6	4.53
	—CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> OH	Tyrosine	10.6	6.1	6.28
Ring‡	$\begin{array}{c} \text{—CH}_2\text{—} \\ \diagdown \quad \diagup \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{—CH}_2\text{—} \end{array}$	Proline	1.5	7.2	10.54
Double § Miscellaneous	—CH <sub>2</sub> -S-S-CH <sub>2</sub> —	Cystine	—	11.8	0.40
	$\begin{array}{c} \text{—CH}_2\text{—CH}_2\text{—S—CH}_2\text{—} \\   \\ \text{CH}_2\text{—C—} \\    \\ \text{CH} \\   \\ \text{NH} \end{array}$	Methionine Tryptophane	— —	0.35 0.7	3.50 1.37

\* After Harris [37]  
† May be present in ionized forms, e.g., —CH<sub>2</sub>-COO<sup>-</sup> and —(CH<sub>2</sub>)<sub>4</sub>-NH<sub>3</sub><sup>+</sup>. The acids may also be present as acid amides, e.g., —CH<sub>2</sub>-CONH<sub>2</sub>.  
‡ Fits into the chain molecule as:  

$$\begin{array}{c} \text{—N—CH—C—} \\ | \quad | \quad || \\ \text{CH}_2 \quad \text{CH}_2 \quad \text{O} \\ | \\ \text{CH}_2 \end{array}$$
  
This results in some distortion and loss of flexibility in the chain.  
§ Joins on between two protein chain molecules or between two positions in the chain. There may also be small amounts of the related cysteine and cysteinic acid groups, which are single amino acids.

The physical and chemical properties of silk fibers are given as follow,

### Physical properties

**Strength.** Strongest of the animal fibers. Loses 15 – 25 % of its strength when wet.

**Elasticity.** Very elastic. Will stretch 20% of original length.

**Resiliency.** Silk ranks next to wool in resiliency. Wrinkles hang out fairly readily but not as quickly as wool.

**Moisture absorption.** High, absorb 16% at 65% relative humidity and 70 °F. Water does not affect silk. Silk is more resistant to water than wool.

**Heat.** Can with stand finishing temperature up to 340 °F for short periods of time.



### ***Chemical properties***

*Acid.* Similar to wool. It is not damaged by most acid solutions. Concentrated strong acids will destroy silk; nitric acid causes silk to become yellow.

*Alkalies.* More resistant to alkalies than wool. Alkalies may affect some dyes used on silk. Silk can be dissolved by hot 5 % sodium hydroxide.

*Dyeing.* Much like wool, but takes a deeper shade. Silk will absorb dyestuff at lower temperature than wool. Acid, direct, basic, and vat dyes can be used.

## **2.6 Spectrophotometer [10]**

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.

## **2.7 Kubelka - Munk equation [10].**

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.

$$R_{\lambda,i} = 1 + (K/S)_{\lambda} - [(K/S)_{\lambda}^2 + 2(K/S)_{\lambda}]^{1/2} \quad (2.5)$$

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

$$(K/S)_{\lambda} = (1 - R_{\lambda,i})^2 / 2 R_{\lambda,i} \quad (2.6)$$

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.

## 2.8 Dyes for protein fibers [11]

Protein fibers are natural fibers derived from animal source, the most important of these being wool and silk. The principal component of the wool fiber is the protein keratin. The protein molecules consist of a long polypeptide chain constructed from the eighteen commonly encountered amino acids that are found in most naturally-occurring proteins. As a result of the diverse chemical nature of these amino acid, the protein side-chains are of widely character, containing functionality which includes, for example, amino and imino, hydroxy, carboxylic acid, thiols and alkyl groups and heterocyclic functionality. At intervals, the polypeptide chains are linked together by disulfide (-S-S-) bridges derived from the amino acid cystine. There are also ionic links between the protonated amino ( $-\text{NH}_3^+$ ) and carboxylate ( $-\text{COO}^-$ ) groups, which are located on the amino acid side-groups and at the end of polypeptide chains. Many of the functional groups on the wool fiber play some part in the forces of attraction involved when dyes are applied to the fibers. Protein fibers may be dyed using a number of application classes of dyes, the most important of which are acid, mordant and premetallised dyes.

Acid dyes derive their name historically from the fact that they are applied to protein fibers such as wool under acidic conditions. They are also used to a certain extent to dye polyamide fibers such as nylon. Acid dyes may be conveniently classified as either acid-levelling and acid-milling types. Acid-levelling dyes are group of dyes that show only moderate affinity for the wool fibers. Because the

intermolecular forces between the dye and the fiber molecules are not strong, these dyes are capable of migrating through the fiber and thus produce a level dyeing. Acid-milling dyes are a group of dyes, which show much stronger affinity for the wool fibers. Because of the strength of the intermolecular forces between the dyes and the fiber molecules, the dyes are less capable of migration and this can present difficulties in producing level dyeing. However, they give superior fastness to washing.

A characteristic feature of acid dyes for protein and polyamide fibers is the presence of one or more sulfonate ( $-\text{SO}_3^-$ ) groups, usually as sodium ( $\text{Na}^+$ ) salts. These groups have a dual role. Firstly, They provide solubility in water, the medium from which the dyes are applied to the fiber. Secondly, they ensure that the dyes carry a negative charge. When acid conditions are used in the dyeing process, the protein molecules acquire a positive charge. This is due mainly to protonation of the amino ( $-\text{NH}_2$ ) and imino ( $=\text{NH}$ ) groups on the amino acid side chains, to give  $-\text{NH}_3^+$  and  $=\text{NH}_2^+$  groups respectively, and to the suppression of the ionization of the carboxylic acid groups. The positive charge on the polymer attracts the acid dye anions by ionic forces, and these displace the counter-ions within the fiber by an ion exchange process. As well as these ionic forces of attraction, Van der Waals' forces, dipolar forces and hydrogen bonding between appropriate functionality of the dye and fiber molecules may also play a part in the acid-dyeing of the protein fibers. In term of size and shape, often an important consideration in the design of dye molecules, acid leveling may be described as small to medium-sized planar molecules. This allows the dyes to penetrate easily into the fiber and also permits a degree of movement or migration within the fiber as the ionic bonds between the dye and the fiber are capable of breaking and reforming, thus producing a level or uniform colour. However, as the dye is not very strongly bonded to the fiber, it may show only moderate fastness towards wet-treatments such as washing. Acid-milling dyes are significantly larger molecules than acid-leveling dyes and they show enhanced affinity for the fiber, and hence improved fastness to washing, as a result of more extensive Van der Waals' forces, dipolar forces and hydrogen bonding.

## 2.9 Color fastness to washing ISO 105-C01 [12]

### Scope

This part of ISO 105 specifies Test No. 1 of a series of five washing tests that have been established to investigate the color fastness to washing of coloured textiles and which cover the range of washing procedures from mild to severe.

### Principle

A specimen of the textile in contact with one or two specified adjacent fabrics is mechanically agitated under specified conditions of time and temperature in a soap solution, then rinsed and dried. The change in colour of the specimen and the staining of the adjacent fabric(s) are assessed with the grey scales.

### Apparatus and reagent

- Soap solution, containing 5 g of soap per litre of water.
- Adjacent fabrics
- A multifiber adjacent fabric complying with ISO 105-F01

### Test specimen

If the textile to be tested is fabric, either

- a) attach a specimen measuring 40mm x 100mm to a piece of the multifiber adjacent fabric, also measuring 40mm x 100mm. by sewing along one of the shorter sides, with the multifiber fabric next to the face of the specimen; or
- b) attach a specimen measuring 40mm x 100mm between the two single fiber adjacent fabrics, also measuring 40mm x 100mm, by sewing along one of the shorter sides.

Where yarn or loose fiber is to be tested, take a mass of the yarn or loose fiber approximately equal to one-half of the combined mass of the adjacent fabrics, and either

- a) place it between a 40mm x 100mm piece of the multifiber adjacent fabric and a 40mm x 100mm of the non-dyeable fabric and sew them along all four sides; or
- b) place it between a 40mm x 100mm piece of each of the two specified single-fiber fabrics and sew along all four sides.

### **Procedure**

1. Place the composite specimen in the container and add the necessary amount of soap solution, previously heated to  $40 \pm 2^\circ\text{C}$ , to give a liquor of 50:1
2. Treat the composite specimen for 30 min.
3. Remove the composite specimen, rinse it twice in cold grade 3 water and then in cold, running tap water for 10 min, and squeeze it. Open out the composite specimen and dry it by hanging it in air at a temperature not exceeding  $60^\circ\text{C}$ , with the two or three parts in contact only at the line of stitching.
4. Assess the change in color of the specimen and the staining of the adjacent fabric with the grey scales.

### **2.10 Literature reviews**

These studies focused on the assemblies of dye into PEM mainly on flat surfaces such as glass slides or quartz surfaces. Hereafter is described some work already published.

Dongsik Yoo et al.[13] studied about new electro-active self assembled multilayer thin films based on alternately adsorbed layers of polyelectrolytes and functional dye molecules and found that alternate spontaneous adsorption of polyelectrolytes and ionic dyes from dilute solutions. Combinations of different functional dyes such as Ponceau SS and Infrared dye 125 were successfully incorporated into self-assembled multilayer heterostructures. In this research, the fabrication of heterostructure thin films containing two different functional dye molecules will be presented as well as the fabrication of multilayer thin film light emitting diodes.

Katsuhiko Ariga et al.[14] studied the assembly of alternate dye-polyion molecular films by electrostatic layer-by-layer adsorption and found that Electrostatic alternate adsorption was successfully employed for low-molecular-weight dyes, leading to a large variety of dye-polyion layer-by-layer assemblies. The assembling process of individual dye-polyion layers of Congo Red (CR) poly(diallyldimethylammonium chloride) (PDDA) was investigated by using a quartz

crystal microbalance (QCM). The *in-situ* QCM measurement revealed that the dye adsorption occurred at a rate similar to that of conventional polyanion adsorption. Successful assembly of the CR layer was confirmed also by increasing intensities in the UV adsorption.

Victoria E. Campbell et al.[15] studied the coadsorption of a polyanion and an azobenzene dye in self-assembled and spin-assembled polyelectrolyte multilayers and found that the integration of a photochromic azobenzene dye into electrostatically bound polyelectrolyte multilayers was described. Two different deposition techniques are compared: electrostatic self-assembly (ESA) and polyelectrolyte spin-assembly. The polyelectrolytes used were PEI (polyethylenimine) and PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt]). Successful incorporation of the azobenzene dye Direct red 80 (DR80) into ESA and spin-assembled multilayered films (PEI/DR80) is demonstrated. Coadsorption of DR80 and PAZO on a PEI surface occur in different proportions and packing densities, depending on the assembly technique selected was found. Using DR80 as a coadsorbing agent can dramatically enhance the rate of PAZO adsorption was found, and different deposition rates for DR80 and PAZO when the two materials adsorb simultaneously from a common solution was observed.

Sung-Hoon Kim et al.[16] studied the electrostatic layer-by-layer self assembly of anionic squarylium and cationic polyelectrolyte and found that Alternating thin films of the anionic squarylium (SQ) dye and poly(diallyldimethylammonium chloride) (PDDA) were formed by the sequential deposition of SQ and PDDA from aqueous solution onto a glass substrate. UV-vis absorbance measurements reveal that the bilayer deposition process was linear and highly reproducible from layer to layer.

From these relevant articles PEM from polyelectrolyte and small dye molecules 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: construction and deconstruction [18] and found that the growth of multilayers made from a combination of a weak polyacid and a strongly dissociated polycation is studied as a function of salt concentration and molecular weight. 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.

Schlenoff et al.[19] studied effect of molecular weight on the construction of polyelectrolyte multilayers: stripping versus sticking and found that combinations of a polyanion and a polycation, with different molar masses but narrow molar mass distributions, are employed to construct thin films by the polyelectrolyte multilayering technique. All polyelectrolytes are assembled in the presence of added salt. Even highly charged polymers in the 104 Da range of molar mass exhibit a typical multilayering characteristics. If the molar mass, MM, of either of the polymers is in this range, the thickness increment realized on addition of the shorter polymer is partially lost on exposure to the solution of longer polymer, as surface polyelectrolyte is stripped off by its oppositely charged partner. Complete loss of low MM polyanion on exposure to low MM polycation inhibits multilayer growth altogether. The role of salt is elucidated in the balance between multilayer growth, which relies on kinetically irreversible adsorption, and polyelectrolyte stripping, which produces a stable solution dispersion of polyelectrolyte complex. Subtleties in the irreversibility of commonly employed combinations of high molar mass polymers are revealed by in situ waveguide measurements.

Bjoern Schoeler et al.[20] studied investigation 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). Multilayer buildup is monitored by UV-vis and FTIR spectroscopies, and with a quartz crystal microbalance (QCM) and is correlated with structural information obtained using atomic force microscopy. 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.

Hazel L. Tan et al.[21] studied temperature dependence of polyelectrolyte multilayer assembly and found that the thicknesses of polyelectrolyte multilayer thin films (PEM) are reported as a function of deposition temperature and ionic strength. PEM fabricated at high salt and elevated temperatures are significantly thicker than similar films deposited at room temperature. These trends in the multilayer films are not observed in single-layer films of PDDA directly deposited onto Si substrates. Based on the results of this study, a new mechanism is proposed to explain the dependence of PEM thickness on temperature. It is believed that elevated temperature swells the existing film and allows for increased trapping of solution phase polymer within the already-existing layers. The results and interpretation have bearing on the present understanding of PEM film deposition and also on the ability to control interpenetration between individual polymer layers.

Some PEM were sensitive with pH condition this point are the advantages for some application which want the swelling of PEM such as the swelling of capsule for drug delivery. So the relevant articles were studied as follow,

Susan E. Burke et al.[22] studied pH-dependent loading and release behavior of small hydrophilic molecules in weak polyelectrolyte multilayer films and found that the pH-dependent loading and release behavior of small hydrophilic molecular probes in polyallylamine and hyaluronic acid multilayer films was investigated. These studies were carried out using the water-soluble dyes Indoine Blue and Chromotrope 2R, and their loading and release profiles were followed with UV-vis spectroscopy. The results of these studies suggest that the incorporation and release of material from such films depend on the degree of film swelling, the ability of the dye molecules to aggregate in the film, as well as the attractive and repulsive interactions occurring between the probe molecules and the acid-base functional groups in the films. Both the degree of dissociation of the acid base functional groups and the extent of film

swelling are pH-sensitive. As a result, the amount of each dye incorporated in the film also depends on the pH conditions, with a maximum loading capacity of  $3.8 \cdot 10^{-3}$  mg/cm<sup>3</sup> of Chromotrope 2R and  $5.7 \cdot 10^{-2}$  mg/cm<sup>3</sup> of Indoine Blue. In turn, they found that by manipulating the pH of the release solution it is possible not only to control the rate of the release of the molecular probes but also to regulate the amount of probe material released. In fact, completely trapping the incorporated probes in the multilayer films was also successfully demonstrated. These findings can be rationalized by examining the interactions of the dye molecules with the polyelectrolytes, the ability of molecules to form J-aggregates, and pH-dependent physicochemical properties of the multilayer system, such as the acid-base equilibria of the polyelectrolytes and the swelling behavior of the films. It is believed that this information is fundamentally important to understanding of how to effectively manipulate the films for potential controlled release applications.

Byoung-Suhk Kim et al.[23] studied pH-controlled swelling of polyelectrolyte multilayer microcapsules and found that the effect of pH on the osmotically induced swelling of polyelectrolyte multilayer microcapsules filled with solutions of a strong polyanion were explored. The shells of the microcapsules are composed of strong polyanions and weak polycations via a layer-by-layer electrostatic self-assembly. The equilibrium radius of the swollen capsules was found to be the same at low and neutral pH but increases at high pH, indicating the softening of the capsule shell. Such a softening probably reflects a decrease in the charge density of a polycation, which leads to a reduction in the number of ionic cross-links. The dramatic increase in size and softening of the capsules at high pH is accompanied by polyanion release from the capsule interior. No release was observed at low and neutral pH.