Polymer thin films: transport phenomena and surface forces
Garcia Turiel, J.

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POLYMER THIN FILMS

TRANSPORT PHENOMENA AND SURFACE FORCES

JAVIER GARCÍA TURIEL
POLYMER THIN FILMS

TRANSPORT PHENOMENA AND SURFACE FORCES

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JAVIER GARCÍA TURIEL

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PROMOTOR       Prof. Dr. B.T.L. JÉRÔME  
van’t Hoff Institute for Molecular Sciences, 
Universiteit van Amsterdam

COMMISSIELEDEN   dr. A. DEL CAMPO BÉCARES  
Max Planck Institute for Metal Research, 
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DSM Research, Geleen, The Netherlands

prof. dr. O. I. VINOGRADOVA  
Max Planck Institute for Polymer Research, 
Mainz, Germany and the Russian Academy of 
Sciences, Moscow, Russia

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A mi padre, a mi madre y a mi hermana.
"Para ir a donde no se sabe, hay que ir por donde no se sabe"

SAN JUAN DE LA CRUZ, s.XVI
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CHAPTER 1

Giant Molecules in Tiny Spaces

Progress in thin film research is a remarkable example of the interplay between basic studies and practical applications. The demands for improved methods and properties have helped to drive new discoveries, which, in turn, have opened even more opportunities for applications.

1.1. General Introduction.

Electronic devices, coatings, displays, sensors, optical equipment, and numerous other technologies all depend on the deposition of thin films. Even when well-established methods exist for the production of high-quality films, there is still considerable interest in alternative methods that may be less expensive, more reliable, or capable of producing films with novel or improved properties. For instance, comparing inorganic light-emitting diodes (LEDs) with organic and polymer LEDs, the potential advantages of the latter, such as low cost, full-color capabilities, efficiency and lifetime, have been crucial for industrial developments [1]. Another example is hard inorganic coatings, originally developed for cutting tools. Nowadays metal carbides, nitrides, and oxides are used on wearing elements, such as bearings, and even as decorative or protective coatings on doorknobs and pens. In these hard superlattices the properties of individual materials are greatly improved by the deposition of thin alternating layers of a second material [2]. Even nature takes advantage of thin-film approaches: for example, seashells are built up of inorganic and organic components through a complex deposition chemistry. This deposition can be reproduced by a low-temperature biomimetic process in which directed nucleation and growth of inorganic layers on self-assembled organic templates produce continuous films of single-phase ceramics [3].

One type of very interesting materials used to produce thin films are polymers. These materials are so widely used in technological applications that their absence would literally change the face of the world. The major advantage of using polymers over non-polymeric materials in some technologies is that polymers are cheap and easy to fabricate. Polymers can be synthesized in a virtually unlimited range of chemistries, providing opportunities to literally “tailor” many physical properties of the material. In many applications, polymers are processed into films or other confined geometries, e.g. in structured composite materials, coatings, synthetic membranes, fibers, and thin optical devices. These applications require polymers to meet diverse performance criteria that range from electronic and optical performance to adhesive and mechanical performance. In all these systems, interfaces play a crucial role in the behavior of the whole system. As the degree of miniaturization continuously increases, these confinement effects become increasingly important. These effects can either help reaching a given goal, or be undesirable, in which case one needs to reduce these effects. Understanding the changes in the morphology and the dynamic behavior of polymers and the resulting properties of the material is a prerequisite to any controlled processing and functioning, and for ensuring the long-term stability of these materials.
1.2. A Brief Introduction to Polymers.

Polymers are giant molecules in which at least a thousand atoms are linked together by covalent bonds. For this reason they are frequently referred to as “macromolecules”. They may be linear chains or three-dimensional networks. Many natural substances, especially the biological construction materials, are polymer chains (e.g. DNA, proteins). On the other hand many materials and devices we commonly use everyday are made by synthetic macromolecules (e.g. polystyrene, polyethylene). They all consist of constitutional repeating structural units called monomers. If the basic units are identical, we speak of a homopolymer; if the chains are made of different kinds of monomers, we speak of a copolymer.

1.2.1. Polymer Chains. Polymer chains are complex molecules; a simplified model to describe them is the random walk model [4, 5]. This model considers the chains to be made of a number \( N_k \) of segments of length \( \sigma_k \) (called Kuhn length). These segments do not have a specific volume, are free to rotate with respect to each other and have no interactions with each other. These chains are also called ideal chains, as they are the equivalent of ideal gases. The Kuhn length is significantly larger than the length \( l \) of the chemical bonds in the actual chain (figure 1.1) to ensure that the segments are free to rotate. Although this is a very simple model, ideal chains describe very well the behavior of many polymer systems, in particular that of polymer melts.

**Figure 1.1.** Schematic picture of a polymer chain approximated by a random walk. \( R_{ee} \) is the end-to-end distance, \( l \) the bond length, \( \sigma_k \) the Kuhn length and \( N_k \) the total amount of Kuhn segments.
The collection of Kuhn segments of a given chain follows a random walk in space to form a coil. The size of the coil can be characterized by the root-mean-square value of the end-to-end distance $R_e$, which is equal to [6]:

$$\sqrt{\langle R_e^2 \rangle} = \sigma_k \sqrt{N_k}$$  \[1\]

This is essentially the diameter of the coil. Another measure of the coil size is the radius of gyration $R_g$, which is equal to [7]:

$$R_g = \sqrt{\langle R_g^2 \rangle} = \sigma_k \sqrt{\frac{N_k}{6}} \approx 0.41 \sigma_k \sqrt{N_k}$$  \[2\]

For typical commercial polymers having molecular weights in the range of $10^5$ g/mol, $R_g$ is of the order of 10 nm.

1.2.2. Molecular Weights of Polymers. While the exact minimum molecular weight required for a molecular chain to be called a polymer is not really established, polymer scientists often use the limit of 25 000 g/mol [8]. Because of their large size, polymer chains cannot be synthesized all exactly with the same length. A given “pure” polymeric material is therefore characterized by a distribution of molecular weights of the constituting chains (figure 1.2).

![Graphs showing molecular mass distribution for two polymers](image)

**Figure 1.2.** Molecular mass distribution for two of the polymers used in this thesis: (left) polystyrene with a narrow distribution ($M_w/M_n=1.03$) and (right) poly(sodium 4-styrene sulfonate) with a wide distribution ($M_w/M_n=3.12$).

This distribution may vary greatly in shape and width, depending on the method of synthesis of the polymer. From this distribution, one can calculate different types of averages. The two most important are the number-average molecular weight ($M_n$) and the weight-average molecular weight ($M_w$):

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$  \[3\]

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$  \[4\]
where \( N_i \) is the number of molecules of molecular weight \( M_i \). For single-peaked distributions, \( M_n \) is usually near the peak. The weight-average molecular weight is always larger. The ratio \( M_w/M_n \), sometimes called the polydispersity index, provides an indication of the degree of polydispersity of a material. If it is close to 1, the polymer exhibits narrow molecular weight distribution, while larger values correspond to wider distributions (see figure 1.2).

### 1.2.3. Morphology and Thermodynamics of Pure Polymers

At high enough temperature, all polymers are in a liquid state, generally referred to as melt. When the melt is cooled down, two main types of behavior are observed. In the first case, the polymer never crystallizes. One speaks of amorphous polymers. As temperature decreases, the purely viscous melt first becomes visco-elastic (one speaks of rubbery state). Then both the viscosity and elastic modulus strongly increase and the polymer reaches the glassy state. Although this increase is continuous and there is no thermodynamic transition between the melt (viscous or rubbery) and the glass, one speaks of the glass transition, taking place by convention at the temperature \( T_g \) at which the viscosity reaches the value of \( 10^{13} \text{ Pa.s} \). This temperature depends in particular on the rate at which the system is cooled, showing the importance of the system dynamics in the appearance of the glassy state.

A different behavior is observed in the so-called semi-crystalline polymers. As these polymers are cooled down from the melt, some regions crystallize through the ordering of the chains. This crystallization is, however, never complete and crystallites are always surrounded by amorphous regions. Just below the melting temperature \( T_m \), these regions are molten but, as temperature decreases further, they become glassy.

The major factor determining whether a polymer can crystallize is the occurrence of successive units in the chain in a configuration of high geometrical regularity. If the chain elements are small, simple and of equal size, as in linear polyethylene, a large proportion of the material will crystallize: one speaks of a high degree of crystallinity. If however, the chain elements are complex, containing bulky (side) groups, as in polystyrene, the material can crystallize only if these groups are arranged in an ordered configuration. The melting point \( (T_m) \) is theoretically the highest temperature at which polymer crystallites can exist. Normally, crystallites appear in a polymer melt in a certain temperature range. Suitable methods for studying the transitions in the crystalline state are X-ray diffraction measurements and differential thermal analysis.

### 1.3. Thin Polymer Films

Whether a film is thin or not can be defined from a physical point of view from the properties of the system. Thin films have a behavior that differs from “bulk” behavior, with different structural features and/or different dynamics resulting in important differences in properties. This difference
arises from the fundamental difference between the environment of molecules (or chain segments) in bulk and the environment of these molecules at the interface with another phase. How far the influence of this interface reaches into the material depends very much on the material itself, but also on external parameters such as temperature. When this influence extends over a significant proportion of a film, it can be defined as thin. In the case of polymers, “thin” films can have thicknesses up to micrometers, because of the large size of the polymer coils.

There are many known techniques to prepare thin polymer films. We will limit ourselves here to two techniques that we have used in our work: spin-coating from a solution, and adsorption from a solution.

1.3.1. Spin Coating. In the spin coating process, a polymer solution is deposited on the substrate, and the substrate is then accelerated rapidly to the desired rotation rate (normally 1000 – 4000 rpm) during a certain time (figure 1.3). The liquid flows radially, owing to the action of the centrifugal force, and the excess is ejected off the edge of the substrate. The film continues to thin slowly until disjoining pressure effects cause the film to reach an equilibrium thickness or until it turns solid-like due to a dramatic rise in viscosity caused by solvent evaporation. The final thinning of the film is only due to solvent evaporation [9].

![Figure 1.3. Schematic picture of the spin-coating deposition.](image)

The final thickness of the deposited polymer film depends on several parameters [10, 11], among which the initial viscosity of the polymer solution, the spinning speed, and the concentration of the solution. This deposition technique will be used in the first part of the thesis, playing with the solution concentration to vary the thickness.

1.3.2. Dip Coating: Multilayer Films. This technique is based on the adsorption from a solution [12-14]. Its principle uses electrostatic self-assembly and finds its broadest application in the polyelectrolyte world. A monolayer of polyelectrolyte is assembled on a charged substrate through ionic bonding, by dipping the substrate in the ionic solution (figure 1.4). After rinsing, this coated substrate is set in an oppositely-charged polyelectrolyte solution to adsorb the next molecular monolayer. The resulting coated substrate is again rinsed in ultrapure water. Repeating this process, one gets multilayer structures. This is why this technique is
also called _Layer-by-Layer_ (LbL) deposition. The composition and structure of each layer can be controlled by appropriately choosing the molecules and adjusting the deposition parameters. A wide variety of molecules, including nonlinear optical chromophores, conducting polymers, biological macromolecules, magnetic materials, dielectrics, and metallic oxide nanoparticles can be incorporated into the film to achieve specific functionalities. This makes electrostatic self-assembly practical for a wide variety of applications such as optics, electronics, bio-sensing and surface modification. This technique will be used in the second part of this thesis.

Figure 1.4. Schematic picture of the alternate adsorption of polyelectrolytes in the dip coating technique.

1.4. Scope of this Thesis.

Despite the great importance of confined polymers for applications, there is still very little known with certainty about the deviation from bulk behavior in polymer films, in particular when the dimension of the films is of the same order of magnitude as the size of the chains. For a full understanding of these systems, it is essential to make a link between the behavior of the polymer chains and the resulting mesoscopic and macroscopic properties of these systems. This is the approach we have used in this thesis to study different aspects of the effect of confinement and interfaces in thin polymer films. The key parameters in all our studies is the thickness of the films, that is varied between a few nm and a few 100 nm to observe the changes in behavior this variation induces.

The work presented here is divided into two parts dedicated to two different types of materials and focusing on different properties. The first
part considers glassy polymers and the behavior of guest molecules in thin films of these materials, while the second part considers polyelectrolytes, their layer by layer deposition into films, and the interaction properties of these films with other surfaces.

**Glassy polymers** often contain some small guest molecules such as solvents or water. The latter plays a particularly important role in applications, as it is essentially omnipresent. For example, in coatings, multilayer electronic modules and composites in the presence of humidity, the concentration profiles of these guest molecules across the interfaces between the polymer and solid phases determines the stability of these devices against debonding at interfaces [15]. The dynamics of the absorption process is determined by the diffusivity of the guest molecules in the material, which is therefore an important parameter to control. Both the solubility and the diffusivity also play a crucial role in synthetic membranes, through which specific species are required to permeate [16]. In all cases changes in the size of the polymeric system should have an influence on the absorption (solubility) and transport (diffusivity and permeability) of guest molecules. This is what we have investigated in two types of systems: polystyrene/solvent and polyamide/water.

**Polyelectrolytes** have the ability of forming multilayer films by electrostatic self-assembly [17]. Recently these multilayers have been used to make microcapsules by layer-by-layer adsorption of polyelectrolytes on the surfaces of colloidal particles that are subsequently removed [18]. These microcapsules are very promising nanocontainers to induce confinement or to serve as vehicles for drug delivery for instance. Many questions need yet to be answered concerning the structure and properties of the multilayers forming the capsules [19]. We have addressed a number of them by studying model multilayers deposited on flat surfaces, focusing on the multilayer growth and structure, as well as their adhesion and interaction properties.

### List of Abbreviations and Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units [MKS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LbL</td>
<td>Layer-by-Layer technique</td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>Bond length</td>
<td>[m]</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
<td>[kg mol$^{-1}$]</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight-average molecular weight</td>
<td>[kg mol$^{-1}$]</td>
</tr>
<tr>
<td>$N_k$</td>
<td>Number of Kuhn segments</td>
<td>[-]</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$R_{ee}$</td>
<td>End-to-end distance</td>
<td>[m]</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Radius of gyration</td>
<td>[m]</td>
</tr>
<tr>
<td>$\sigma_k$</td>
<td>Kuhn length</td>
<td>[m]</td>
</tr>
<tr>
<td>$x$</td>
<td>Position in the film in the direction of diffusion</td>
<td>[m]</td>
</tr>
</tbody>
</table>
References:

PART I

Glassy Polymers
“Es un error hablar de ciencia pura y ciencia aplicada. No hay dos clases de ciencia sino una, y el resto son aplicaciones que se hacen de esta ciencia. La opinión pública y los gobernantes piensan que sólo es útil la ciencia aplicada. Están equivocados. La gente tendría que darse cuenta de que todo el conocimiento en el que se basa la ciencia aplicada viene de alguna ciencia teórica pura.”

BERNARDO ALBERTO HOUSSAY
The behavior of polymers in thin films or close to interfaces is far from being understood. Many observations, encompassing both structural and dynamical behavior, indicate that the properties of polymers in thin films deviate from what we know from the bulk. Questions about the density (irreversible and reversible changes after annealing even above the bulk glass transition temperature), film stability and dewetting, glass transition temperature, diffusion coefficient and chain conformation and relaxation are intensively debated. In particular, it is not yet clear how the size of such chain-like molecules (their molecular weight) comes into play, especially if the thickness of the film is less than the radius of gyration of these molecules. In addition, due to the high surface-to-volume ratio the influence of surface and interfacial properties become important if not dominant. This interfacial sensitivity highlights the importance of the properties of the near surface region in polymer films; a topic whose importance is beginning to be recognized.

2.1. Introduction.

Amorphous polymers belong to the family of glass-forming molecules. The behavior of these systems and in particular the mechanisms at the origin of the glass transition are still poorly understood despite numerous studies [1]. How these materials behave close to interfaces and under confinement is also hardly understood.

Among all glass-forming materials, polymers receive a special attention, due to their importance for applications. They are also special because of the chain character of their constitutive molecules. All kinds of effects related to the conformation of the chains, that are irrelevant for other glassy materials, can take place in polymers.

The least that we can say is that there is little known with certainty about the behavior of confined glassy polymers. Experimental results reported in the literature are often contradictory, which makes it very difficult to validate possible models. In the following, we review the essential aspects of this behavior, first in terms of structure and dynamics of amorphous polymer films, and then in terms of transport of guest molecules.

2.2. Structure and Dynamics of Polymer Films.

2.2.1. Structure of Thin Polymer Films. Little is known about the conformation of polymer chains and the structure of thin polymer films. In a bulk polymer a particular “test chain”, as might be isolated through selective deuteration and measured by neutron scattering, exhibits a Gaussian distribution of the distance between chain ends. About 1% of the volume within the roughly spherical domain encompassing this test chain is filled by the chain itself. One expects this conformation to be modified by the presence of limiting surfaces over an interfacial region which thickness should be of the order of a few times the radius of gyration \( R_g \) [2, 3]. In particular chains should have a flatter conformation [4]. Shuto et al. [5, 6] reported that when the film thickness was lower than \( 2R_g \), the radius of gyration of a chain along the direction parallel to the film surface was larger than the radius of gyration of an unperturbed chain. The interpenetration of the chains was weaker than in the bulk [5, 6], which is expected for systems becoming two dimensional [7]. Jones et al. [8], however, came to the contradictory conclusion that the radius of gyration in the direction parallel to the film maintains almost its bulk value for thicknesses down to \( 2R_g \), the Gaussian configuration being also preserved parallel to the film.

Another issue is whether the polymer keeps its bulk density or not. Direct density measurements with neutron reflectivity have shown that polystyrene
films deposited on silicon wafers keep their bulk density for thicknesses down to 6.5 nm [9, 10]. On the other hand, positron annihilation measurements, which are sensitive to the amount of voids present in between polymer chains, have detected an increase of this free volume close to the free surface of polymer films [11, 12], although this was not the case in the first measurements with this technique [13]. The reverse effect, i.e. a densification of the polymer, has even been observed at the interface with substrate supporting the films, in the case the polymer strongly interacts with the substrate [14, 15].

**2.2.2. Dynamics of Polymer Chains under Confinement.** Because of the importance of dynamics in glass-forming materials, the dynamic behavior of polymer films has been extensively studied [16, 10]. Despite many inconsistencies in the reported results, a number of facts are now well established. One distinguishes two main effects in the dynamics of polymer films.

The first effect comes from the interaction between the polymer and a limiting solid surface, generally a supporting substrate. If this interaction is strong, it immobilizes the chain segments in the vicinity of the substrate, slowing down the dynamics of the system. This shows up as an increase of the glass transition temperature as film thickness decreases [17-19].

The second effect comes from the reduction of the size of the material. It is ideally observed in free-standing films, but dominates also in films supported by substrates with little interaction with the polymer. This effect leads to an acceleration of the dynamics and a decrease of the glass transition temperature as thickness decreases [20-23]. For instance, for supported polystyrene films, all measurements report rather consistently a decrease of the glass transition by approximately 30K as thickness decreases down to 0.6 nm [10] (**figure 2.1**).

![Figure 2.1. Trend observed in measured $T_g$ values for supported PS films. Reproduced data from references 10, 22, 24, 25 and 26.](image)
Note that this decrease is even larger (~70 K) in free-standing films [21]. While this effect is well established, there is still a lot of debate about the mechanisms leading to this acceleration of dynamics. It seems that the presence of a free surface is necessary to observe this effect [27]. A mechanism that is often evoked is the presence of a layer at the free surface with a lower glass transition temperature and faster dynamics than in bulk [10, 28]. While such a surface layer was indeed observed [29-31], several experimental results are in contradiction with its existence [13, 32-34].

2.3. Guest Molecules in Thin Films.

Polymeric films often contain some small guest molecules dissolved in the material. These molecules might be some solvent used in the processing of the material that has not evaporated out during drying. It can also be molecules that have penetrated into the polymer from a vapor or a liquid phase. This is typically the case of coatings or foils in which water from the atmosphere absorbs, or membranes through which some molecules are forced to diffuse by a pressure gradient [35].

In most applications, however, polymer films have thicknesses of the order of 10 \(\mu\)m or larger. They are considered as having the same properties as bulk materials, and possible interfacial effects are neglected. There is hardly anything known about the behavior of thinner films containing guest molecules, how changes in thickness affect this behavior, and which specific properties the interfaces might have.

As far as we know, only two results have been reported in the literature. The first one concerns the absorption of water in polyimide films deposited in silicon wafer [36, 37]. It was shown that the water absorbs preferentially at the interface with the substrate. The second study concerns the diffusion of water through polyelectrolyte films, which are highly hydroscopic [38]. The diffusion coefficient was then found to decrease by three orders of magnitude when the film thickness decreases down to 10 nm. No explanation was given for this observation.

So, to try to understand the behavior of guest molecules in thin films, we can only refer to what is known from the bulk behavior. We present below the main concepts needed to understand our work.

In a non-equilibrated isolated system consisting of a polymer surrounded by other phases, mass and heat exchange between the phases takes place until thermodynamic equilibrium is achieved, in other words until the thermodynamic properties (for instance pressure or concentration) are equal in all phases. Mass transfer occurs via a bimodal process. Sorption is responsible for the transfer of species from the other phase into the polymer, taking place at the interface between the polymer and the rest. Molecular diffusion is responsible for the mobility of molecules from the interface
through the polymer matrix and determines the kinetics of the mass exchange [39, 40].

2.3.1. Sorption. When a polymer contacts a fluid (liquid or gas), sorbates present in both phases are exchanged until their chemical potentials become equal. The equilibrium for every sorbate can be characterized by the sorbate concentration in each phase, generally expressed as a partial vapor pressure in gas phases. When the system is formed by a single organic compound partitioned between a gas phase and a homogeneous polymeric material, the system is fully characterized by the corresponding sorption isotherm giving the concentration of the solvent in the polymer versus sorbate partial vapor pressure in the gas [41]. Experimentally, sorption of a single component is determined by exposing a pre-weighed polymeric sample to a controlled atmosphere with a given temperature and partial pressure of the sorbent, and weighing after equilibration. Each experiment provides a single isotherm datum. Repeating the process under different partial pressures of sorbent at the same temperature provides the full isotherm. Brunauer et al. [42-44] developed a still leading classification (the so-called “BET classification”) of the equilibrium sorption behavior of porous materials, as reflected by the shape of their sorption isotherms.

Independently of the isotherm shape, there is always a concentration range (low sorbate concentrations) in which the profile can be assumed to be linear. Henry’s law expresses this proportionality (equation 1) between the sorbate concentration in the condensed phase, $C$, and the partial vapor pressure ($p_v$) through the solubility coefficient, $S$ [45]:

$$C = S \cdot p_v$$  \hspace{1cm} [1]

2.3.2. Diffusion. In many uniform materials, the unidirectional diffusion of species present with a concentration $C$ is well described by the so-called Fick’s law [46]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D(C) \frac{\partial C}{\partial x} \right)$$  \hspace{1cm} [2]

where $t$ is the time, $x$ the position in the direction of diffusion and $D$ is the diffusion coefficient or diffusivity of the penetrant in the polymer, which determines the rate of transport. In principle, this coefficient depends on both the penetrant concentration $C$ and temperature. Isothermal diffusion of organic penetrants in polymers is however, in good approximation, concentration independent at low concentrations over a wide temperature range, and for higher concentrations at low enough temperatures [47].

The so-called Fickian diffusion (following equation 2) in polymers is an ideal case of penetrant transport, corresponding to free diffusion of penetrant
without interference of structural relaxations in the polymer. This happens if the polymer relaxation is much faster than the penetrant diffusion. Diffusion of the penetrant is then followed by instantaneous response of the system. This is generally the case of polymers above their glass transition temperature, and for slow diffusion in the glassy state.

The rate of diffusion through a material is the limiting factor for the permeation kinetics through a film. In a permeation experiment, a vapor is forced to cross the film by creating a pressure (or concentration) gradient between both sides of the film. In general the mass flux $F$ of permeant depends linearly on the pressure gradient $\Delta p/\Delta x$ through a permeability coefficient $P$:

$$ F = P \frac{\Delta p}{\Delta x} $$  \[3\]

If the diffusion coefficient in the material is assumed to be Fickian and the diffusion coefficient is independent on the concentration, Fick’s law implies that the mass flux $F$ is proportional to the concentration gradient $\Delta C/\Delta x$ through the diffusion coefficient:

$$ F = D \frac{\Delta C}{\Delta x} $$  \[4\]

If the concentrations are small enough, we can use Henry’s law (equation 1) to obtain:

$$ F = D S \frac{\Delta p}{\Delta x} $$  \[5\]

Comparing this equation with equation 3, we get:

$$ P = D \times S $$  \[6\]

This is a simple mathematical expression of the fact that the permeation of species through a membrane implies, first, the absorption in the polymer on one side of the membrane, and then, its diffusion to the other side of the membrane. This is the so-called solution-diffusion model of permeation [48]. The relationship $P = D \times S$ has been shown to describe very well the permeability behavior of membranes, even in cases where it is not obvious that the assumptions made above to derive it are valid (e.g. for pervaporation where permeation occurs between a liquid and a gas phase).

2.3.3. Free volume. There is clear evidence that penetrant absorption and transport in polymers may be connected to free volume existing in between
the polymer chains. Vrentas et al. [49-51] have suggested that the volume inside a polymer can be divided into three elements (figure 2.2):

- **i) Occupied volume.** This is basically the “van der Waals” volume [52] occupied by the polymer chains at given instant. This volume is independent of temperature.

- **ii) Interstitial free volume.** This free volume stems from the vibrational motion of polymer bonds, and increases slightly with temperature. This volume is inaccessible to other molecules.

- **iii) Hole free volume.** This is the volume stemming from chain relaxations. This free volume is accessible for penetrant absorption and transport, and may be altered by absorption and desorption of penetrants. Changes in the total polymer volume upon temperature changes are largely governed by changes in the whole free volume.

In the liquid and rubbery state, the total volume corresponds to that dictated by the thermodynamic equilibrium, since chains relaxations are fast. Glassy polymers, however, are non-equilibrium liquids in which relaxations are slow. Consequently, glassy polymers may occupy a larger volume that would be the case at equilibrium, and extra hole free volume is trapped in the polymer (figure 2.2).

![Figure 2.2](image-url)

**Figure 2.2.** Schematic picture of the polymer volume as a function of temperature. Reproduced from Duda and Zielinski [53].
Although polymers seem to be porous viewed in this way, this trapped free is continuously redistributed through the material [53], so that there are no physical pores actually present in the material. Using this concept of free volume, it is clear that changes in the available free volume due to confinement effects will induce changes in the solubility and in the diffusivity of guest molecules inside the film. However, as we have seen in section 2.2.1, it is not clear yet how the free volume is affected by confinement. Interfaces can also influence the concentration of guest molecules because their possible preferential affinity for the inside of the polymer or rather the proximity of another phase. This effect will also lead to variations in free volume across the thin film, and influence the dynamic properties of the film. What is the outcome of these difference effects in terms of solubility, diffusivity, and film properties is essentially unknown.

2.4. Scope of the First Part of this Thesis.

It is obvious from the previous section that studies of the effect of confinement on the behavior of guest molecules in polymers are badly needed. In the first part of this thesis, we study the absorption and transport properties of guest molecules through polymer films in different systems: polystyrene/toluene (chapter 3 and 4), polystyrene/tetrahydrofuran (chapter 4) and polyamide/water (chapter 5).

We mainly focus on the dependence on the film thickness of the amount of solvent present in the films after drying (chapter 3) or after exposition to vapor (chapter 4 and 5), of the diffusion coefficient (chapter 3 and 5), and of the permeability (chapter 5). Despite the different nature of the studied systems, and the different experimental conditions (supported films in the presence of vapor, and membranes on porous substrates submitted to a concentration gradient), similar effects of confinement are observed. First, the diffusivity and permeability decreases by several orders of magnitude when the film thickness decreases down to the 10 nm range. Second, the solubility varies little with film thickness. Qualitative explanations of these effects can be given in terms of the polymer behavior under confinement.
Chapter 2

List of Abbreviations and Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units [MKS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Penetrant concentration</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>[m$^{2}$ s$^{-1}$]</td>
</tr>
<tr>
<td>F</td>
<td>Mass flux through a film</td>
<td>[kg m$^{-2}$ s$^{-1}$]</td>
</tr>
<tr>
<td>P</td>
<td>Permeability</td>
<td>[m$^{3}$ m$^{-1}$ s$^{-1}$]</td>
</tr>
<tr>
<td>$p_v$</td>
<td>Partial vapor pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Radius of gyration</td>
<td>[m]</td>
</tr>
<tr>
<td>$S$</td>
<td>Solubility</td>
<td>[m$^{3}$ m$^{-3}$]</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>[s]</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>$x$</td>
<td>Position in the direction of diffusion</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pressure difference</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$\Delta C$</td>
<td>Concentration difference</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>Film thickness</td>
<td>[kg m$^{-3}$]</td>
</tr>
</tbody>
</table>

References:

CHAPTER 3

Thin Polystyrene Films: Solvent Evaporation and Retention

Ultrathin polymer films of Polystyrene were produced by spin coating from solutions in Toluene. Some solvent was found to remain in the polymer network after spin coating and drying, and this quantity was measured using Gas Chromatography. The total amount of retained toluene was found to depend mainly on the thickness of the film and the supporting substrate. The thickness and substrate dependence show that the solvent is retained at the polymer-substrate interface. While thicker films (thickness > 200nm) can essentially be considered as dry, the proportion of toluene in the thinnest films (10nm) goes up to 35% in weight. For thicknesses below 200nm, the diffusion coefficient of toluene after film formation drops down, probably due to strong confinement effects dominating in the behavior of the film.
3.1. Introduction.

Thin and ultra-thin films are usually fabricated by spin casting from solutions (see section 1.3.1). It is expected that most of the solvent evaporates during the last step of the spin coating. But some solvent can still remain inside the polymer network, even after annealing the sample at temperatures above the boiling point of the solvent. For polymer films, either free-standing or supported by rigid substrates, the presence of guest molecules (e.g. solvent molecules or moisture) is known to influence the properties of the material [1-3]. For instance retained solvent in solution-cast films of PMMA shifted the glass transition temperature to lower temperatures [4]. However the question of where the solvent is retained in the film has hardly been addressed [5, 6].

Moreover most studies have been performed in thick films (thicknesses larger than 1 µm) in which bulk behavior dominates. For thinner films, interfacial effects can play a significant role, as we have seen in chapter 2. We have therefore studied the amount of solvent retained in polystyrene films spin-coated from a solution in toluene as a function of film thickness in the range of 10-500 nm. As the interaction between the polymer and the substrate is expected to play an important role, we have also varied the type of substrate using both hydrophilic bare fused quartz and hydrophobic silinated fused quartz. The absolute amounts of retained solvent were investigated using Gas Chromatography, which appears to be a very useful technique to perform residual solvent analysis, even for the minute volumes of our thin films.

We have also examined the time dependence of the amount of retained solvent in the course of the drying process. Understanding this process and how it is influenced by the thickness of the film is important for its optimization in the industrial processing of polymer products. Moreover the structure and properties of the final product can be greatly influenced by the course of the drying [7]. The most critical parameter in the drying process is the diffusion coefficient of the solvent in the polymer. Unfortunately most of the studies concerning diffusion of solvent in polymers do not pay much attention to the case of thin polymer films. Here we study the influence of the film thickness in the slow diffusion in the last step of evaporation.

3.2. Experimental.

3.2.1. Sample preparation. Polystyrene (PS) films were prepared by spin-coating from solutions of PS in Toluene. Standard atactic polystyrene ($M_n=178$ kDalton, $M_n/M_p=1.03$, $T_g=100^\circ$C, Polymer Standards Service-USA Inc.) was used to prepare several PS solutions in Toluene (Rathburn Chemicals Ltd., $\rho=0.867$g/cm$^3$, $T_b=110.6^\circ$C). Toluene was chosen as solvent
since it is one of the most commonly used solvents for the spin-coating of PS films.
The films were spin-cast on fused quartz substrates. Substrates had to be thoroughly cleaned. As PS is well soluble in ketones, substrates with an old film were first put in acetone in an ultrasound bath for a few minutes to destroy the film chemically and mechanically. The substrates were then cleaned with ethanol and dried. To oxidize any impurities still present, the substrates were placed in Chromosulphuric acid for at least twelve hours, rinsed with double distilled water, dried in an oven at 120°C for at least two hours, and cooled in air until room temperature is reached.
To modify the interaction between the polymer film and the substrate, we have also used silinated fused quartz substrates [8]. For this the clean substrates were placed inside a chamber under vacuum at 0.01 mBar pressure and 200°C for 24h. After this treatment 5μl of Hexamethyldisilane (HMDS, Acros Organics Ltd.) was injected in the chamber keeping the temperature at 70°C for 25 minutes. The excess of HMDS was evacuated and the system brought at room temperature. With this chemically treated fused quartz substrates we increase the hydrophobicity of the glass surface because of the presence of a uniform methyl group layer. It is therefore expected that the interaction between the polystyrene and the substrate will decrease.
To make films, toluene solutions of PS were filtered and spin-cast at 2500rpm for 30s. The concentration of PS in the solution determines the thickness of the films obtained after spin-coating, which can be measured by ellipsometry [9], see appendix A. The thickness of the films varied from 10nm up to 500nm. The films were prepared at room temperature. Spun films were placed under Nitrogen (to prevent oxidation) and heated at different temperatures for further drying and annealing. The films were dried for different times, ranging from 10 minutes to 6 hours, to observe the kinetics of the evaporation process.

Figure 3.1. AFM pictures of a 10nm film with some defects (a) and an exceptional picture of 20nm film showing defects (b).
We have checked the uniformity of the films by AFM imaging (figure 3.1). For thicknesses of 20nm and upwards the films were perfectly uniform with the exception of rare defects. The 10nm films showed some small dewetted spots and pinholes with diameter less than 0.16 µm, but the percentage of the area occupied by these spots is small enough (~1.5 %) to be negligible. These defects are expected to have little influence on the retention measurements.

3.2.2. Measurement Techniques. To determine the amount of toluene retained in the films, we dissolved the annealed films with a good solvent (Cyclohexanone) for both PS and toluene. The composition of the obtained mixture was then determined with Gas Chromatography (GC). This technique has been already used to perform residual solvent analysis with bulk systems [10, 11].

The measurements were performed with a Carlo Erba GC 6000 Vega Series gas chromatographer (figure 3.2), with a flame ionization detector (FID) coupled to a Hewlett Packard HP3394A integrator. The injection temperature and the temperature of the column were 200ºC; the temperature at the detector was 230ºC.

Because the dependence of the signal given by the detector on the toluene quantity is not known, a calibration curve was made of the column response versus toluene concentration using solutions of toluene in cyclohexanone, with known concentrations in the range of 0.05-10µl/ml. A fixed amount of acetonitril was also added as a reference to be able to correct for the differences in the quantities injected into the column of the gas chromatographer.

![Figure 3.2. Schematic picture of a Gas Chromatographeter.](image-url)
The amount of toluene in the films was expected to be very small. To avoid systematic errors due to uncertainties on the base line of the detector, we dissolved films with 50µl of a toluene-cyclohexanone-acetonitrile solution with a known concentration of toluene. This ternary solution, called working solution (WS), was beforehand analyzed with GC to use its toluene response as a reference. Then 2 µl of the solution resulting from the dissolution of the film was injected in the GC to determine the total concentration of toluene. This concentration had two contributions: (1) the toluene present in the working solution and (2) the toluene present in the dissolved film. The difference between this last concentration and the concentration in the working solution gives then the amount of toluene present in the film (figure 3.3). To obtain good statistics, the analysis of a given solution with GC was repeated three times, and for each film parameters (thickness, drying time and temperature) between 5 and 10 films were prepared and analyzed. The error bars given in the results show the standard deviation of the measurements.

We have checked the amounts of toluene measured with this method in the case of clean bare substrates (without any film) and bare substrates after spin-coating with pure toluene. The measured amounts of toluene were then zero within the measurement errors.

![Chromatogram for WS](image1)

![Chromatogram for WS + Film](image2)

**Figure 3.3.** Schematic picture of the gas chromatogram of the working solution (left) and working solution with dissolved film (right). Peak 1 corresponds to the acetonitrile, peak 2 to the toluene in the WS, peak 3 to the cyclohexanone, peak 4 to the toluene retained in the film and the recorded signal, peak 2+peak 4 is the total amount of toluene.

### 3.2.3. Studied dependences

From the GC we obtained absolute values of the amount of toluene found inside the polymer films. The first parameter that we have varied is the *drying time*. The system was annealed at 115°C for
different times and then cooled down to room temperature. At this moment, the films were dissolved in the working solution and the absolute solvent retention calculated.

The second parameter we have varied is the annealing temperature. For a fixed annealing time of 60 minutes the samples were dried at different temperatures from 25°C to 115°C and the retained solvent extracted after cooling the system back to room temperature.

The last parameters are the film thickness and the type of substrate. For a fixed annealing temperature of 115°C and annealing time of 60 minutes, desorption experiments were done with films of thicknesses ranging from 10 to 500nm, deposited both on hydrophilic bare fused quartz and hydrophobic silinated quartz.

3.2.4. Determination of Diffusion Coefficients. The solvent that diffuses out of the polymer film during drying is assumed to have a Fickian behavior (see section 2.3.2). The diffusion equation writes in this case:

\[ \frac{\partial C}{\partial t} = D \nabla^2 C \]  

where \( C \) is the concentration of the diffusing species and \( D \) the diffusion coefficient. Crank [12] has shown that the appropriate solution of this equation may be written as:

\[ \ln |M_\infty - M_i| = -\lambda_i D t + \ln M_i \]  

where \( M_\infty \) is the equilibrium or steady state mass of solvent in the film after infinite time (experimentally taken as the average of several values extracted after periods of time longer than 360 minutes), \( M_i \) is the mass of solvent in the film at a given time, \( \lambda_i \) is a parameter dependent on geometry, and “\( \ln M_i \)” is a constant. By fitting the dependence of \( \ln |M_\infty - M_i| \) on time \( t \), one obtains the diffusion coefficients \( D \). This method will be called “Crank’s method”. Depending on the dimensions of the diffusion specimen it takes a long time (hours, days or weeks) to measure \( M_\infty \). Therefore, the measured data may be treated using the so-called Guggenheim’s elimination method [13], which suppresses the need for a value of \( M_\infty \). The time-dependence of the mass of solvent can then be expressed as:

\[ \ln |\Delta M_i| = -\lambda_i D t + \text{const}. \]  

where \( \Delta M_i \) is the difference \( M_{i+\Delta t} - M_i \) and \( \text{const.} \) is a constant. The interval \( \Delta t \) is chosen so that the differences \( \Delta M_i \) are large enough while the number of points remains adequate for good statistics. This method will be called
“Passiniemi’s method”. The geometry parameter $\lambda_i$ in the case of a supported film with a free surface and thickness $\Delta x$ is:

$$\lambda_i = \left( \frac{\pi}{l} \right)^2$$  \[4\]

where $l=\Delta x$ for Crank’s method and $l=2\Delta x$ for Passiniemi’s method.

### 3.3. Results and Discussion.

#### 3.3.1. Dependence on drying time.

The drying time of the films made on bare quartz substrates was varied to obtain desorption curves. The slopes of the desorption curves give the desorption rates $k$ defined as:

$$k = \frac{dC}{dt}$$  \[5\]

where $C$ is the concentration of toluene. The results coming from a selected set of 4 film thicknesses is shown in figure 3.4.

![Figure 3.4](image)

**Figure 3.4.** Mass of toluene in films versus drying time for different film thicknesses: (Neal) 10nm, (▲) 20nm, (●) 100nm, (■) 200nm. The substrate is bare quartz and annealing temperature 115°C. Time $t=0$ corresponds to samples just spin-cast. The lines are linear fits.

The mass of toluene present in the films varies little with time. This means that at the time when our measurements are performed, we are in the latest stage of the desorption process (close to steady state) where the changes in
mass are slow. This is also observed in the value of the desorption rates (table 3.1). So we can conclude that the solvent mainly evaporates while the films are being formed during the spin coating process. Further evaporation during drying is not significant.

<table>
<thead>
<tr>
<th>Film Thickness (nm)</th>
<th>Desorption Rate (µg/min)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-2.9E-04</td>
<td>0.10</td>
</tr>
<tr>
<td>20</td>
<td>-7.0E-04</td>
<td>0.34</td>
</tr>
<tr>
<td>100</td>
<td>-1.0E-03</td>
<td>0.77</td>
</tr>
<tr>
<td>200</td>
<td>-3.2E-03</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 3.1. Desorption rate of toluene as a function of film thickness obtained from figure 3.4. $r^2$ is the correlation coefficient of the linear fits.

Applying equations 2 to 4 to the desorption curves we calculate the diffusion coefficients with the Crank’s and Passimiemi’s methods. The results for all measured thicknesses and for the two types of substrates are shown in figure figure 3.5.

![Figure 3.5](image)

Figure 3.5. Diffusion coefficient of toluene in polystyrene thin films calculated from two different methods: (●) Crank’s method, (■) Passimiemi’s method, (▲) Crank’s method for silinated samples.

With Passimiemi’s method it was only possible to calculate the diffusion coefficient for two thicknesses for which the differences $\Delta M_i$ were large enough. With Crank’s method it was possible to calculate the diffusion coefficient for every single film thickness ranging from 10 to 500nm.
The diffusion coefficient decreases by almost 3 orders of magnitude when the film thickness falls from 200 to 10 nm, while it is essentially constant for thicker films. The decrease of the diffusion coefficient as thickness decreases is probably due to the confinement of the polymer chains that tend to align parallel to the surface. This makes the system anisotropic, with two different diffusion coefficients, one for diffusion parallel to the surface and the other one for diffusion perpendicular to the surface. The alignment of the chains parallel to the surface increases the barrier to transport in the direction perpendicular to the surface and decreases therefore the diffusion in this direction, which is the one we measure in our experiments. An effect of chain alignment on diffusion has also been found in polystyrene films aligned by rubbing [14]. However the observed decrease in diffusion coefficient was only by a factor of 2 with respect to non-oriented films.

Another possible explanation would be a decrease of polymer mobility due to the substrate supporting the films (see section 2.2.2). However, as the glass transition temperature of the films decreases as film thickness decreases, the overall mobility in the film should rather increase than decrease. We will discuss the decrease in diffusion coefficient under confinement further in chapter 5 concerning the transport of water through polyamide films, as a similar decrease in transport was observed in these films.

3.3.2. Dependence on drying temperature. To evaluate the effect of temperature, the drying temperature of the films made on bare quartz substrates was varied. The annealing temperature has little influence on the amount of solvent retained in the films, as it can be seen in the results shown in figure 3.6.

![Figure 3.6](image.png)

**Figure 3.6.** Mass of toluene in films versus drying temperature for different film thicknesses: (◆) 10nm, (▲) 20nm, (●) 100nm, (■) 200nm. The substrate is bare quartz and the drying time 60 minutes.
3.3.3. Dependence on film thickness and type of substrate. Several films were prepared with thickness ranging from 10nm up to 500nm to study the relationship between solvent retention in the films and film thickness. Both bare and silinated fused quartz substrates were used to see the effect of the interaction between the polymer film and the substrate. The mass of toluene found in the films as a function of the film thickness is shown in figure 3.7.

We clearly observe two different regimes. The first domain corresponds to film thicknesses larger than 200 nm, in which the solvent retention is essentially independent of thickness and type of substrate. The second domain corresponds to film thicknesses smaller than 200 nm. In the latter region, both the film thickness and the type of substrate have an influence on the amount of retained solvent, although the observed variations are relatively small. There is also a systematic difference on the standard deviation of the measurements performed with both substrates: this deviation is systematically larger for quartz substrates than for silinated substrates. This comes from the fact that it is more difficult to obtain a reproducible quality in glass cleaning than in silinazation.

Figure 3.7. Mass of toluene retained films versus film thickness for two types of substrates: (●) bare quartz, (■) silanated quartz. The annealing temperature is 115°C.

The results can also be translated in terms of the relative amount of solvent retained:

\[
M_r = \frac{M_T}{M_T + M_F}
\]  

where \(M_T\) stands for the absolute amount of toluene retained in the film and \(M_F\) stands for the mass of the film, which is defined as:
where $\rho$ is the bulk density of the film, considered to be independent of film thickness [15, 16], $\Delta x$ is the film thickness and $A$ the area of the substrate. The relative amount of solvent retained (figure 3.8.) significantly increases as the film thickness decreases below 100nm. For the thinnest films the relative amount of toluene retained goes up to 35%. These ultra-thin samples were also observed under the optical microscope to look for a possible dewetting or breaking of the film, but no sign of it was found.

There are several interesting features in the dependence of the amount of toluene retained in polystyrene films on the type of substrate and the film thickness. First of all, this amount has only a small dependence on the film thickness, which indicates that the solvent must be mainly located at the interface of the film, most probably in the vicinity of the substrate. This is confirmed by the fact that the amount of solvent retained and the standard deviation on the amount measured depend on the nature of the substrate. Also silanating the quartz substrate is known to increase the hydrophobicity of the substrate and decrease the interaction with polystyrene. This is consistent with the fact that in the case of silanated substrates, the amount of retained toluene is larger.

\[ M_f = \rho V = \rho A \Delta x \]  

Figure 3.8. Relative amount of toluene retained versus film thickness for two types of substrates. The inset shows the same results in a log-log plot. The substrate is: (●) bare quartz, (■) silanated quartz.

Another interesting feature is the fact that the solvent retention clearly shows two distinct regimes, below and above 200nm, respectively. This limit of 200 nm corresponds well to the thickness below which the glass transition
temperature of supported polystyrene films departs from the bulk glass transition temperature [17]. 200nm is also the thickness below which the diffusion coefficient depends on the film thickness. This shows that this limit corresponds to the thickness below which confinement effects become important. In the non-confined regime (thickness > 200 nm), the amount of solvent retained is independent of film thickness and type of substrate, while in the confined regime (thickness < 200 nm), the amount of solvent retained does depend on film thickness and type of substrate. A possible explanation for the latter is that, as confinement increases, the solvent becomes more segregated from the polymer chains. Direct data on the location of the solvent in the films is however needed to confirm this hypothesis.

The relative amounts of solvent found in the films show that films with thicknesses above 200 nm can essentially be considered as free of solvent. This dry state is already reached at the end of the deposition process, and further drying for up to six hours at temperatures up to 115ºC (above the glass transition temperature of PS and the boiling point of toluene) does not decrease further the amount of solvent in the film.

As the film thickness decreases below 200nm, the relative amount of solvent in the film becomes important. The large relative amounts of solvent in the thinnest films raise the question whether these films are still stable. We could not find any sign of instability or dewetting. This is consistent with reports in the literature that polystyrene films with thicknesses above 2nm are continuous [17, 18]. The fact that the relative amount of solvent is high does not mean that the behavior of the whole film should be affected by the presence of the solvent, since this solvent is concentrated at the interface with the substrate. One could in particular wonder whether the large amount of solvent present could not be responsible for the decrease of the glass transition temperature observed in supported polystyrene films [16]. This decrease in glass transition temperature has however been proven to be caused by the presence of the free surface [19]. It is therefore likely that the presence of solvent at the interface with the substrate plays little role (if any) in the decrease of the glass transition temperature of the films.

3.4. Conclusions.

Ultrathin polymer films of polystyrene were produced by spin coating from solutions in toluene and Gas Chromatography was used to evaluate the absolute amount of toluene found inside of the films after drying. The dependence of this amount on the drying time and temperature, the type of substrate, and the film thickness was studied.

The drying time and temperature have little influence on the amount of retained toluene. This toluene amount depends mainly on the thickness of the film and on the nature of the supporting substrate. While thicker films (thickness > 200nm) can essentially be considered as dry, the proportion of
toluene in the thinnest films (10nm) goes up to 35% in weight. The thickness and substrate dependence show that the solvent is retained at the polymer-substrate interface.
For thicknesses below 200nm changes in both the solvent retention and the diffusion coefficient are observed, due to confinement effects. In particular, the diffusion coefficient decreases significantly as thickness decreases, probably because of the alignment of polymer chains and/or a decrease of their mobility.

List of Abbreviations and Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units [MKS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Area of the film</td>
<td>[m²]</td>
</tr>
<tr>
<td>C</td>
<td>Solvent concentration</td>
<td>[mol l⁻¹]</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>[m²/s]</td>
</tr>
<tr>
<td>HDMS</td>
<td>Hexamethyldisilane</td>
<td></td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>Desorption rate</td>
<td>[kg s⁻¹]</td>
</tr>
<tr>
<td>Mₐ</td>
<td>Number-average molecular weight</td>
<td>[kg mol⁻¹]</td>
</tr>
<tr>
<td>Mₘ</td>
<td>Weight-average molecular weight</td>
<td>[kg mol⁻¹]</td>
</tr>
<tr>
<td>M∞</td>
<td>Absolute mass of toluene retained in the steady state</td>
<td>[kg]</td>
</tr>
<tr>
<td>M₊</td>
<td>Absolute mass of the polymer film</td>
<td>[kg]</td>
</tr>
<tr>
<td>Mᵣ</td>
<td>Relative mass of the Toluene retained</td>
<td>[kg]</td>
</tr>
<tr>
<td>Mₜ</td>
<td>Absolute mass of the Toluene retained</td>
<td>[kg]</td>
</tr>
<tr>
<td>Mᵣₜ</td>
<td>Absolute mass of toluene retained at time t</td>
<td>[kg]</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methylmethacrylate)</td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>[s]</td>
</tr>
<tr>
<td>Tₘ</td>
<td>Boiling Temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>Tₜ</td>
<td>Glass Transition Temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>V</td>
<td>Film volume</td>
<td>[m³]</td>
</tr>
<tr>
<td>Δx</td>
<td>Film thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>λᵢ</td>
<td>Geometry parameter</td>
<td>[m⁻²]</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
<td>[kg m⁻³]</td>
</tr>
</tbody>
</table>

References:

This chapter studies the uptake of solvent in supported polystyrene films exposed to a saturated vapor. Gas chromatography was used to measure the amount of solvent absorbed in the films and its dependence on film thickness, time of exposure to the vapor, temperature and type of solvent. The results indicate that the uptake of Tetrahydrofuran increases with increasing film thickness at room temperature, the solubility coefficient being roughly constant in the studied thickness range. The exposure time (larger than 20 min.) seems not to have any influence, probably due to a fast absorption dynamics. In the case the absorption is done at temperatures above the glass transition temperature and the sample is cooled fast enough in the presence of solvent vapor, more solvent is found in the films, probably trapped by the fast increase in barrier properties induced by cooling. Finally, Tetrahydrofuran gets slightly more absorbed than Toluene (at room temperature for film of 100 nm), probably because of is smaller size.
4.1. Introduction.

As we have mentioned in chapter 2, very little is known about how the solubility of guest molecules varies in thin films as their thickness decreases. As these systems are highly inhomogeneous, the question arises whether the guest molecules mainly absorb at the interfaces or in the “bulk” part of the films.

To shed some light on this problem, we have investigated the absorption of solvent from a vapor in supported polystyrene films, and its dependence on the time of exposure to the vapor, film thickness, thermal history and type of solvent.

4.2. Experimental.

4.2.1. Solvent Up-Take. The polystyrene films were prepared and annealed as described in chapter 3 (see section 3.2.1.). To perform absorption experiments, the Nitrogen flowing into the cell was mixed with vapor of THF using the set-up shown in figure 4.1.

Figure 4.1. Schematic picture of the experimental set-up used for the absorption experiment.

Nitrogen was blown from the general stream (1) to a container filled with THF (2). The THF was purchased from Acros Organics Ltd. ($\rho=0.80\text{ g/cm}^3$, $T_b=66^\circ\text{C}$). The Nitrogen flow was measured with a flow meter (3) and kept constant to 7.39 ml s$^{-1}$. The THF container was sealed with openings for the inlet Nitrogen flow and the outlet THF-saturated Nitrogen flow. The temperature inside was tuned by a water bath (Thermomix® ME) (4) in which the container was submerged. The temperatures of both the water bath and THF container (5, 6) were kept 5 degrees above the one measured in the
absorption cell. The Nitrogen flow left the container saturated with THF vapor and arrived to the annealing cell (7) where the samples are kept at 25 °C for most of the experiments, and at 115°C for the others. This temperature was well controlled by a temperature controller (Eurotherm Temperature controller type 902) (8). The saturated stream left the annealing cell and the THF was recovered in another container (9).

The solvent uptake was carried out under saturated conditions for all the experiments, probably very near the saturation-condensation boundary, although, condensation was never observed inside the annealing cell.

4.2.2. Determination of Absorbed Mass. The mass of THF present in the films after the absorption process was determined by gas chromatography, using the same procedure as for the determination of the amount of toluene retained in spin-coated films (see section 3.2.2.). The relative sorbate uptake ($M_t$) after an absorption time $t$ is defined as follows:

$$M_r(t) = \frac{m_p^t - m_p^0}{m_p^0} = \frac{M_t}{m_p^0},$$  \[1\]

where $m_p^0$ is the mass of the film free of sorbate, $m_p^t$ is the mass of the polymer film after equilibration in the presence of the THF vapour, and $M_t=m_p^t-m_p^0$ is the absolute mass of solvent absorbed. Using Henry’s law (see section 2.3.1) we can determine the solubility coefficient:

$$S = \frac{M_t}{m_p^0} \frac{1}{p_v},$$  \[2\]

where $p_v$ is the partial vapor pressure of THF. Since we work in saturation conditions, it is equal to the saturation vapor pressure $p_v^0$. Another way of expressing the results is in terms of the volume fraction $\phi_s$ of absorbent in the polymer at equilibrium ($t\rightarrow\infty$):

$$\phi_s = \frac{M_t \rho_p}{m_p^t \rho_s}$$  \[3\]

where $\rho_s$ is the density of absorbent and $\rho_p$ the density of the polymer with the absorbent. In our experiments the density of the polymer with the absorbent will be considered the same as the density of the dry polymer film.

4.2.3. Studied Dependences. The first parameter that we have varied is the absorption time. The polymer film continuously absorbs solvent and eventually reaches saturation at equilibrium. We have examined the absorbed amounts after different times ranging from 20 minutes up to 140 minutes after the introduction of THF vapor.
The second parameter we have varied is the *film thickness*. For a fixed exposure time of 20 minutes to the vapor the experiment was repeated for films of different thicknesses: 10, 20, 100 and 200 nm. The third parameter was the *temperature*. Sorption experiments were carried out both at 25°C and at 115 °C for a fixed film thickness of 100 nm. For the absorption at 115°C, the absorbed amount was measured following two different procedures. *Method 1* involved i) absorbing solvent at high temperature, ii) cooling the film for one minute in a Petri dish at room temperature and iii) eventually dissolving and injecting the dissolved film in the gas chromatographer. *Method 2* involved i) absorbing solvent at high temperature, ii) cooling down to RT at 1°C min⁻¹ in the presence of THF vapor and iii) dissolving and analyzing as before. The fourth and last dependence we have studied was the type of solvent absorbed. To vary the interactions between the solvent and the polymer films, the same type of experiments was performed using Toluene as a solvent. The water bath was then heated up to 40°C to reach the saturation-condensation barrier for Toluene, the temperature of the cell was kept at 25°C.

### 4.2.4. Stability of films in THF vapor

To check for a possible roughening and instability of the films exposed to solvent vapor, several films of 200 nm were observed after their exposure to THF with an Atomic Force Microscope (for shorter exposure times) and under an optical microscope (for longer exposure times). The root mean square roughness measured from AFM imaging of the films without any exposure to THF and those ones exposed to the THF (up to 120 minutes) did not change and it was always less than 1 nm. Only after 3 hours of exposure the films start to show macroscopic holes and depletions around some impurities that probably act as dewetting nuclei (figure 4.2). This proves the stability of the thicker films under the presence of THF. The fact that no change in the surface roughness was observed does not prove that no roughening takes place. This effect could occur at a smaller scale than the diameter of the AFM tip (3-10 nm).

**Figure 4.2.** Typical AFM pictures of a PS film annealed 24 h under vacuum (a) and exposed to THF vapor for 120 minutes (b). Pictures (c) and (d) are microscope pictures of PS films exposed to THF for more than 3 hours, with some holes indicated by the arrows.
4.3. Results and Discussion.

4.3.1. Time dependence. Polystyrene films were saturated with THF vapor for different exposure times ranging from 20 minutes up to 140 minutes at room temperature (25°C). The data shows that there is essentially no dependence of the amount of THF absorbed on time (figure 4.3), which implies that saturation is reached after an absorption time smaller than 20 minutes. We therefore assume that the mass uptake after any absorption time ca. 20 minutes is equal to the equilibrium mass uptake $M_\infty$. Note that the data gets more scattered as the film thickness increases.

![Figure 4.3](image.png)

**Figure 4.3.** Plot of the time dependence of the THF solvent uptake $M_t$ at 25°C in supported PS films of different thickness. Solid lines represent the values averaged over all times.

4.3.2. Film thickness dependence. PS films of different thicknesses were exposed to a saturated atmosphere of THF vapor at room temperature for 20 minutes. The absolute amounts were averaged over all measurements and the data is shown in figure 4.4. Except for the thinnest films, the THF uptake increases approximately linearly with the film thickness. This translates in a relative uptake $M_r$ (defined by equation 1) that is essentially independent of film thickness (figure 4.5).
Figure 4.4. Absolute THF solvent uptake $M_t$ versus film thickness in supported PS films after an exposure of 20 minutes to THF vapor. The error bars correspond to the standard deviation of the data.

Figure 4.5. Relative THF solvent uptake $M_r$ versus film thickness in supported PS films: (○) 200 nm, (●) 100 nm, (○) 20 nm and (●) 10 nm. The error bars correspond to the standard deviation of the data.
This indicates that at least part of the THF is absorbed in the “bulk” of the film. Another contribution (essentially independent of film thickness) can come from adsorption at the polymer/substrate and/or polymer/air interfaces. This contribution is obviously small with respect to the bulk contribution, except perhaps for the thinnest films.

The relative uptake $M_r$ can be translated into a solubility coefficient (equation 4) and a volume fraction (equation 6) of THF in PS (table 4.1).

<table>
<thead>
<tr>
<th>Film Thickness (nm)</th>
<th>Solubility of THF $S$ ($\mu g_{thf} \mu g_{PS}^{-1} Pa^{-1}$)</th>
<th>Volume Fraction of THF $\phi_s$ ($\mu g_{thf} \mu g_{PS}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$(6.82\pm2.42) \times 10^{-6}$</td>
<td>0.15$\pm$0.05</td>
</tr>
<tr>
<td>20</td>
<td>$(2.71\pm1.02) \times 10^{-6}$</td>
<td>0.06$\pm$0.02</td>
</tr>
<tr>
<td>100</td>
<td>$(1.94\pm0.52) \times 10^{-6}$</td>
<td>0.04$\pm$0.02</td>
</tr>
<tr>
<td>200</td>
<td>$(3.64\pm0.97) \times 10^{-6}$</td>
<td>0.08$\pm$0.02</td>
</tr>
</tbody>
</table>

Table 4.1. Solubility and Volume Fraction of THF in PS at 25 °C.

It is known that in PS films phenyl groups are ordered at the free surface [1, 2] and tilted away from the surface with angle of 60° [3]. In the presence of toluene vapor, it has been shown that toluene preferentially coats the film surface and induces a disorder of the phenyl groups at the free surface [4]. THF molecules might show the same behavior, with THF molecules both adsorbed at polystyrene free surface and absorbed in the bulk. The ordering of the PS phenyl groups originally at the air interface is then probably lost.

As we have discussed in section 2.3.3, the solvent absorbs in the polymer in the available free volume. There have been some direct measurements of the amount of free volume at the interface between PS and vacuum using positron annihilation. While the first reported measurement did not find any evidence for an increase of this amount close to the interface [5], such an increase was found in a subsequent study at distances from the surface smaller than 20 nm [6]. This work also shows that the distribution of hole sizes is significantly broader at the interface than in bulk. Similar effects were observed at the surface of other polymers [7, 8]. More recent studies with the same technique found that the density varies only over thicknesses of few nanometers at the free surface [9, 10]. One should however keep in mind that the translation of raw positron annihilation data into information on free volume requires some significant modeling and is subject to different interpretations [6]. This can explain the difference in results reported in the literature. One should also note that density measurements performed with neutron reflectivity found no sign of density changes in polystyrene film on silicon with thicknesses down to 6.5 nm [11]. This contradicts the assumption that there is an enhancement of the free volume at the free surface.
There are also some arguments leading to assume a decrease of free volume due to confinement. The presence of a limiting surface is known to align the chains preferentially parallel to the surface [12]. For bulk polymers that have been stretched to align the chains, it has been shown, both experimentally [13, 14] and with computer simulations [15], that this stretching decreases the overall amount of free volume but widens the distribution of void sizes. In particular the number of larger voids increases, while their shape becomes more elongated. Put together, these results suggest that the amount of free volume would rather decrease at the free surface.

In view of all these literature results, our finding that the relative amount of THF absorbed in the films is essentially independent of the film thickness, implying that the solvent in uniformly distributed in the films, is not inconsistent with known results.

4.3.3. Temperature dependence. Sorption experiments were also carried out at 115°C (above \( T_g \)) for films of 100nm. Two methods were tested to study the variation of the amount of absorbed solvent on the thermal history. With the first method, consisting in cooling the sample outside the cell before dissolving the film, the average amount of THF in the film was almost zero. This is probably because when the films are put in the presence of an atmosphere without THF (zero partial pressure of THF), the THF that was initially absorbed in the film evaporates out of the film. This backward process can take place because, due to the thermal inertial of the substrate, the film remains sufficiently long at high temperature where the diffusion of THF is fast. The results for method 2 (cooling in the presence of THF vapor) are shown in table 4.2, together with the results of the absorption at 25°C (section 4.3.1).

<table>
<thead>
<tr>
<th>Temperature T (°C)</th>
<th>Absolute Solvent Uptake ( M_t ) (µg\text{THF})</th>
<th>Relative Solvent Uptake ( M_r ) (µg\text{THF} µg\text{PS}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>2.46±1.11</td>
<td>0.06±0.03</td>
</tr>
<tr>
<td>25</td>
<td>1.42±0.75</td>
<td>0.04±0.02</td>
</tr>
</tbody>
</table>

Table 4.2. Absolute and relative solvent uptake of THF in 100nm-thick PS films after absorption at 115 °C (method 2) and at 25 °C.

The average amount of solvent uptake with method 2 increases with about 1 µg with respect to uptake at room temperature. This can be explained as follows: the solubility of THF is significantly higher above \( T_g \) than below, so that more THF absorbs in the films at 115 °C than at 25 °C. When the films were cooled again below \( T_g \), the solubility decreases, which should lead to an evaporation of THF out of the film. The presence of saturated THF vapor, however, makes the driving force for evaporation small. During cooling, the diffusivity of the molecules also significantly decreases. If this effect is fast
enough, THF molecules will get trapped in the film and more THF will be found in the film than after absorption at 25 ºC. It is probable that this difference will increase if the cooling rate increases, and decrease if the cooling rate decreases.

4.3.4. Dependence on the Type of Solvent. Sorption experiments were carried out using Toluene as absorbent and comparing it to THF. THF is found to absorb approximately 4 times more than toluene (table 4.3).

<table>
<thead>
<tr>
<th>Type of Solvent</th>
<th>Absolute Solvent Uptake $M_t$ ($\mu g$)</th>
<th>Relative Solvent Uptake $M_r$ ($\mu g \mu g^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>1.42±0.75</td>
<td>0.036±0.019</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.39±0.25</td>
<td>0.009±0.003</td>
</tr>
</tbody>
</table>

Table 4.3. Absolute and relative solvent uptake at 25 ºC of THF compared with Toluene for supported PS films of 100nm after 20 minutes absorption time.

Quantitatively, the solubility of one component in another is governed by the Gibbs free energy of mixing: $\Delta G_m = \Delta H_m - T \Delta S_m$, where $\Delta H_m$ is the enthalpy of mixing, $T$ is the absolute temperature, and $\Delta S_m$ is the entropy of mixing. A negative value of $\Delta G_m$ indicates that the solution process will occur spontaneously. The term $T \Delta S_m$ is always positive because there is an increase in the entropy of mixing. $\Delta H_m$ is generally positive, proportional to $(\delta_1 - \delta_2)^2$, where $\delta_i$ is the solubility parameter of component $i$ [16]. Better solvents for a given polymer have therefore a solubility parameter closer to that of the polymer ($\delta_1 \approx \delta_2$). For our system, the values of this parameter are: 9.1 (cal/cm$^3$)$^{1/2}$ for THF, 8.0 (cal/cm$^3$)$^{1/2}$ for Toluene, and 8.7 (cal/cm$^3$)$^{1/2}$ for PS [17]. Although the compatibility of both solvents with PS is pretty similar, THF absorbs more than Toluene, probably because THF molecules are smaller than Toluene molecules (figure 4.6). THF can therefore access more free volume of the film than Toluene.

4.4. Conclusions.

In this chapter, the solvent uptake of THF in supported polystyrene films (PS) was studied as function of several dependences: exposure time, film thickness, temperature (thermal history) and type of solvent. Gas Chromatography results have indicated that the relative solvent absorption was not influenced by film thickness. When the solvent was absorbed at high temperature, higher amounts could be trapped in the films by cooling them in the presence of THF vapor. Finally, the solubility of THF was compared with the one of Toluene. The latter showed a lower solubility, probably because of its larger size.
Figure 4.6. Two views of the solvent molecules: THF (7a, 7c) and Toluene (7b, 7d). The average radii of the molecules are 3.76 Å for THF and 4.65 Å, calculated from ACD Chemsketch Software v. 5.0.

List of Abbreviations and Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
<td></td>
</tr>
<tr>
<td>$M_t$</td>
<td>Absolute Solvent uptake at time $t$</td>
<td>[kg]</td>
</tr>
<tr>
<td>$m_p^0$</td>
<td>Mass of the polymer before absorption</td>
<td>[kg]</td>
</tr>
<tr>
<td>$m_p^t$</td>
<td>Mass of the polymer after absorption</td>
<td>[kg]</td>
</tr>
<tr>
<td>$p_r$</td>
<td>Partial vapor pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$p_v^0$</td>
<td>Saturation vapor pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
<td></td>
</tr>
<tr>
<td>$S$</td>
<td>Solubility coefficient</td>
<td>[kg kg$^{-1}$ Pa$^{-1}$]</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydroduran</td>
<td></td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>[s]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>[°C] or [K]</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>$M_r$</td>
<td>Relative Sorbate uptake</td>
<td>[kg solvent kg$^{-1}$ film]</td>
</tr>
<tr>
<td>$\delta_i$</td>
<td>Solubility parameter</td>
<td>[(J/m$^3$)$^{1/2}$]</td>
</tr>
<tr>
<td>$\Delta G_m$</td>
<td>Change in Gibbs's free energy through mixing</td>
<td>[J]</td>
</tr>
</tbody>
</table>
Entropy of mixing $\Delta S_m$ [J]
Enthalpy of mixing $\Delta H_m$ [J]
Volume fraction of penetrant $\phi_s$ [m$^3$ m$^{-3}$]
Density of absorbent $\rho_s$ [kg/m$^3$]
Density of the polymer containing absorbent $\rho_p$ [kg/m$^3$]

References:

John Wiley and Sons, New York, Table 7 (VII_694) and Table 10 (VII/702)
CHAPTER 5

Transport phenomena in Thin Polyamide Films

We have studied the influence of film thickness and polymer morphology on the water absorption and transport (permeability, solubility and diffusivity) through thin polyamide films. Water vapor permeability measurements were performed on polymer films spin-coated from a solution onto porous γ-Alumina plates. The experiments were run at different temperatures and for several film thicknesses. The water vapor permeability was found to decrease by several orders of magnitude as film thickness decreases. Possible explanations for this effect are an increase of the chain alignment due to confinement or a decrease of the chain mobility due to strong interactions with the substrate.

Solubility measurements were performed on supported films with a Quartz Crystal Microbalance. The solubility was found to increase as film thickness increases but this could be due to adsorption of water molecules on top of the film. These absorption experiments also allowed us to estimate the diffusion coefficient that was found to decrease as film thickness decreases. This shows that the decrease observed in the permeability is essentially due to a reduction in transport and not in solubility.
5.1. Introduction.

Many polymers such as polyolefins (polyethylene, polypropylene), aliphatic polyamides and polycarbonate are used as protective barrier against the mass transport of small molecules in vapor and liquid form [1]. The barrier properties of a film depend on many factors such as [2]: the nature of the polymer (density, morphology, etc), the nature of the fluid, area and thickness of the polymer film, the partial pressure of the gas, temperature, or the fluid concentration, permeation time and the development of steady conditions. An important example of small molecules is water and, in particular, humidity of the air. Up to date little interest has been paid to the influence of the film thickness on the transport properties of polymer films from (sub)micron to nano scale, and in particular on the transport of water.

5.1.1. Polyamides as barrier materials. Water transport through polymeric barrier materials or membranes is of major industrial importance. Applications can be found in the drying of natural gas [3], drying of compressed air [4], clothing [5], packaging materials, protective coatings, and the humidity control in closed spaces (air conditioning in buildings, aviation and space flight). Depending on the application, a high or low permeability or selectivity for water is preferred. One class of materials often used as barrier against gases and vapors is polyamides, commonly known as Nylons. These polyamides are commonly combined with other polymers (e.g. polyethylene) in multilayer films to achieve an optimal barrier performance against water and oxygen. This performance is of great importance to many applications. The most typical example of polyamides is nylon 6 (figure 5.1), which is a semicrystalline material. The key advantages of nylon 6 for packaging are, among others, its high-temperature resistance, toughness, puncture resistance, stiffness, and dimensional stability. In addition, it provides an excellent barrier to oil and fats and does not absorb or transmit most flavors.

![Figure 5.1. Chemical structure of the repeating unit of the semicrystalline polyamide Akulon® f132-e (Nylon-6).](image)

The main deficiencies of nylon are processing difficulties, poor water barrier, and stiffness variations changes in with relative humidity. These factors and the fact that the permeability to oxygen of Nylon 6 is very sensitive to the presence of water (e.g. humidity) limit the use of nylon 6 in packaging. Recently new amorphous nylons have been developed to overcome these problems. While Nylon 6 presents strong plasticizing effects originated by the
presence of water molecules, amorphous nylons do not show these strong effects and this is the reason why amorphous nylons are broadly used in industry as additives to semicrystalline nylons. For film processing, for instance, when a film of Nylon 6 is stretched, it will harden. By blending Nylon6 6 with amorphous nylons, the film becomes less stiff, making the processing of the material easier. They maintain all the advantages of nylon 6, such as high temperature resistance and toughness. But they also exhibit a consistently high stiffness at all relative humidity levels. Their stiffness actually increases slightly as the equilibrium moisture content goes up. This is in sharp contrast to the semicrystalline nylons that can lose 75% of their dry stiffness at high humidity.

The barriers to oils and flavors are as good as or better than nylon 6 and the barriers to gases and water are much higher. They are transparent and show a wide processing latitude in a variety of melt processes [6]. Grivory® G21 is one of these amorphous nylons. It is a copolymer (figure 5.2) intended for barrier films and bottles.

\[
\text{Figure 5.2. Chemical structure of the repeating unit of the amorphous polyamide Grivory® G21.}
\]

The permeability of polyamides to gases has been fairly well studied although up to date the influence of film thickness has not been reported, in particular when the thickness of polyamide coatings is lower than the micron scale. The purpose of the present work is to study the water vapor transport through thin polyamide film and the influence of the morphology of the film and film thickness on this transport.

5.1.2. Characterizing Transport Properties. As we have seen in section 2.3, the permeation of a species through a film requires, first, the dissolution of the molecules from the vapor into the polymer at one interface of the film, and then, the diffusion of the molecules through the film towards the other interface. This means that a full characterization of the transport properties of system requires the measurement of three coefficients: the permeability, the diffusion coefficient, and the solubility coefficient.

5.1.2.1. Permeability. One way to evaluate experimentally the permeability coefficient is derived from Darcy’s law. If only one gas (e.g. water) is driven through a porous membrane the mass flux (\( F \)) through the membrane per unit area of the membrane is given by:
\[ F = \frac{M}{A\Delta t} = P_m \frac{\Delta p}{\Delta x} \]  

where \( M \) is the mass of water crossing the membrane, during a time \( \Delta t \), \( A \) is the area of the membrane, \( \Delta p \) is the pressure difference between both sides of the membrane, and \( \Delta x \) is the membrane thickness (figure 5.3). \( P_m \) refers to the permeability expressed in mass with units [kg m m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)]. This can be converted in permeability \( P \) expressed in volume of liquid water transported with units [m\(^3\) m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)]. Ideally, the measurements would be made with free-standing polymer membranes. But only thick films are strong enough for this. Thin films as the ones we study need to be supported by a porous substrate in our case an alumina plate.

![Figure 5.3. Schematic representation of a typical permeability set up.](image)

Experimentally, the system is exposed to a vapor at a given temperature \( T \) saturated in water (with a saturation vapor pressure \( p_v^o(T) \)) with the polymeric membrane in direct contact with the vapor, while vacuum is created on the other side. Water transport through the polymeric membrane is created by the gradient in the partial pressure between both sides of the membrane. The water that has permeated condenses in a cold trap and its mass \( M \) accumulated during a time interval \( \Delta t \) is measured, giving the mass flux (equation 1). These measurements are done both for the bare alumina substrate (to give \( F_{sub} \)) and every single system (substrate + coated film),
giving \( F_{\text{system}} \). From these mass fluxes we can calculate the permeability coefficients using equation 1:

\[
\begin{align*}
P_{\text{substrate}} &= F_{\text{substrate}} \frac{\Delta x_{\text{substrate}}}{\Delta p_{\text{substrate}}} \\
P_{\text{system}} &= F_{\text{system}} \frac{\Delta x_{\text{system}}}{\Delta p_{\text{system}}}
\end{align*}
\]

where \( \Delta x_{\text{substrate}} \) is the substrate thickness, and \( \Delta x_{\text{system}} = \Delta x_{\text{film}} + \Delta x_{\text{substrate}} \) is the thickness of the coated substrate.

Our goal is to calculate the permeability of the coated film. For this, we have to decompose the resistance of the system to the mass transport into two independent resistances in series. Mathematically this can be expressed as:

\[
\frac{\Delta x_{\text{substrate}}}{P_{\text{substrate}}} + \frac{\Delta x_{\text{film}}}{P_{\text{film}}} = \frac{\Delta x_{\text{system}}}{P_{\text{system}}}
\]

This approximation is totally independent of the pressure profile across the membrane. Although equation 4 is only valid for the regime where Henry’s law applies (possible deviations from Henry’s law regime will not be critical for the extraction of the results), it allows us to extract the permeability of the polymer film:

\[
P_{\text{film}} = \frac{\Delta x_{\text{film}}}{P_{\text{system}} - \frac{\Delta x_{\text{substrate}}}{P_{\text{substrate}}} - \frac{\Delta p_{\text{system}}}{F_{\text{system}}}} = \frac{\Delta x_{\text{film}}}{F_{\text{substrate}} - \frac{\Delta p_{\text{substrate}}}{F_{\text{substrate}}}}
\]

This permeability is the intrinsic permeability of the material.

For many polymers, the highly selective transport of water, in contrast to mixtures of permanent gases, can cause concentration polarization phenomena [7]. This is schematically depicted in figure 5.4. Concentration polarization occurs in gas mixtures if the flux of water through a polymer membrane is larger than the concentration profile from the bulk of the feed to the gas/polymer surface. This flux imbalance creates a boundary layer near the membrane surface on the feed side, with a lower water concentration (or partial pressure) than in the rest of the feed. A similar effect can occur on the vacuum side of the membrane, but instead of a boundary layer depletion as observed at the feed side, mass accumulation at the permeate side may occur. As a result the actual pressure drops (\( \Delta p \)) through the membrane, which is the driving force for water permeation, is smaller than the one imposed on the membrane. The resistance of the membrane to water transport appears then larger than the actual one.

To measure reliable values of membrane permeation, one needs to ensure that such effects do not take place, or to estimate the resistance to transport
of the boundary layers to extract the resistances of the membrane itself from the overall resistance that is measured experimentally.

![Figure 5.4](image)

**Figure 5.4.** Schematic representation of the partial vapor pressure \( (p) \) and concentration \( (C) \) profiles for water in the stagnant boundary layers and the membrane for a water / nitrogen mixture, when concentration polarization occurs.

### 5.1.2.2. Solubility

The principle of the solubility measurements we have performed here is the following: the system is put in the presence of water with a certain partial pressure (in our case at the saturation vapor pressure). Some water absorbs in the system, leading to an increase of the mass of the system, which is monitored by Quartz Crystal Microbalance. After sufficient time, equilibrium is reached and the corresponding mass uptake after equilibration measured. We can calculate the solubility coefficient of water in the polymer film \( (S_w) \) from the (water) mass uptake after equilibration at a given temperature \( (M_x) \) and the dry weight of the sample \( (m_p^0) \):

\[
S_w = \frac{M_x}{m_p^0 p_v^o}
\]

where \( p_v^o \) is the saturation pressure. For a given temperature, \( p_v^o \) is known and the mass of the dry film is calculated directly from:

\[
m_p^0 = \rho_{\text{film}} V = \rho_{\text{film}} (A \Delta x_{\text{film}})
\]
where \( \rho_{\text{film}} \) is the density of the polymer film (bulk value), \( A \) is the active area of the microbalance electrode, and \( \Delta x_{\text{film}} \) is the thickness of the polymer film.

5.1.2.3. Diffusivity. The uptake process described in the previous section actually involves two simultaneous mechanisms: the sorption of the sorbate at the polymer film surface, and the one-dimensional diffusion of the sorbate in the polymer due to the sorbate concentration gradient between the surface and the rest of the film. This assumption is not always true, however for the model used in this chapter we will consider it valid. Because this diffusion process limits the speed at which the sorbate can permeate the film, the amount of sorbate in the polymer film increases gradually with time until an equilibrium weight is reached. Assuming a Fickian diffusion (see section 2.3.2) and the diffusion coefficient to be independent of the water vapor concentration, the solvent uptake after a time \( t \) in a film of thickness \( \Delta x \) is given by:

\[
\frac{M_t}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \times \exp \left[ -D_w \frac{(2n+1)^2 \pi^2 t}{\Delta x^2} \right] \tag{8}
\]

where \( D_w \) is the diffusion coefficient. This gives an isotherm of the absorbed mass \( M_t \) as a function \( t \) with the characteristic shape shown in figure 5.5. From this equation 8, the diffusion coefficient can be determined by setting \( M_t/M_{\infty} = 0.5 \), taking the first two terms of the series and solving for \( D_w \):

\[
D_w = \frac{0.049 \Delta x^2}{t_{0.5}} \tag{9}
\]

where \( t_{0.5} \) is the time required to reach the value \( M_t/M_{\infty} = 0.5 \) [8].

From the absorption isotherms obtained with the quartz microbalance, we can then determine the diffusion coefficient of water in the films.

---

**Figure 5.5.** Plot of a typical fickian isotherm.
5.2. Experimental.

5.2.1. Materials. Polyamides were provided (as pellets) by DSM Research Laboratories (Geleen, The Netherlands). We have used an aliphatic nylon (figure 5.1): Akulon® f132-e (Nylon 6) with molecular weights $M_n$=20 kg/mol, $M_w$=40 kg/mol, and an aromatic nylon (figure 5.2) copolymer Grivory® G21. The first one is semicrystalline and the second one is amorphous, and in the following, they will be referred to by these morphologies (amorphous and semicrystalline). Films were processed in two ways: compression molding and spin-coating. For spin-coating, these polymers were dissolved in formic acid obtained from Aldrich with a purity of 97%, molecular weight of $M_w$=46.03 g/mol and a density of $\rho$=1.220 g/ml.

5.2.2. Sample Preparation. For compression molding, the pellets were molded using a Lauffer & Botscher Mühlen press. The pellets were pressed between brass plates and aluminum foil into a sheet of 50mm×75mm×0.005mm at 250 °C. Compression was performed in 3 steps: 2 min at 5 MPa, 3 min at 10MPa and 5 min at 20 MPa at 250 °C and subsequently the samples were cooled to room temperature.

Thin polymer films were deposited by spin-coating onto porous alumina flat disks of 39 mm diameter and 2.0 mm thick (provided by IMS Laboratories, Faculty of Science & Technology, University of Twente, Enschede, the Netherlands). The bottom of the plates is made of $\alpha$-alumina with pore sizes around 80nm in diameter. The top is made of a layer of $\gamma$-alumina with pores of approximately 4-7 nm in diameter. These membranes allow the formation of thin films by spin-coating due to small pore size and its surface properties [9]. A series of four solutions of semicrystalline and amorphous polyamides of concentrations between 0.81-16.39% were prepared in formic acid and then spin-coated at 1000rpm during 30s onto the alumina plates using a laboratory spinner. Drying and annealing of the samples was done in a vacuum oven for at least 24 h at 80 °C (for the semicrystalline polyamide) and 150 °C (for the amorphous polymer), which is in both cases above the glass transition temperature. The same procedure was also followed using as substrates Silicon (100) wafers or quartz resonators for measurements with a Quartz Crystal Microbalance.

5.2.3. Sample Characterization. The polyamides in the form of pellets and processed films were characterized by X-Ray Diffraction (IMS Laboratories, Faculty of Science and Technology, University of Twente, the Netherlands), Differential Scanning Calorimeter (Max Planck Insitute for Polymer Research, Mainz, Germany) and Scanning Electron Microscopy (MESA+ Institute, University of Twente, the Netherlands).
5.2.3.1. X-Ray Diffraction (XRD) was used to study the degree of crystallinity and its variation with the film thickness. The samples were spin-coated on Si-wafers. X-Ray diffraction data were collected on a Philips PW3710 based X’Pert-1 diffractometer in Bragg-Brentano geometry, using a $\theta$ compensating divergence slit. Diffraction data collection was performed at room temperature, using a “zero”-background spinning specimen holder. Peak positions and peak intensities were extracted using pattern decomposition program PROFIT available in the PC software X’PERT LINE supplied by Philips (Eindhoven, The Netherlands). The observed individual lines and clusters of lines were fitted with Pearson VII functions to get the relative intensities of the different peaks.

Making a precise measure of the degree of crystallinity is a major challenge because of the difficulty in precisely defining the crystalline and amorphous phases within the polymer precisely [10]. Since intercrystalline defects are either crystalline or amorphous material, and criteria to fix the interface position are complex, the degree of crystallinity can be understood by simplified models [11, 12]. In that respect the two-phase model (crystallinity + amorphous phases) is still the most widely used [13]. Using this model, we have calculated the degree of crystallinity with the graphic multipeak resolution method [14].

5.2.3.2. Differential Scanning Calorimeter (DSC). Thermodynamic values of the melting temperature ($T_m$) and the glass transition temperature ($T_g$) of bulk polymers (pellets) were determined using a Setaram Setsijs 16 Differential Scanning Calorimeter (DSC). The temperature was calibrated with Iridium. Sample weights were between 10-15 mg. The samples were heated quickly (at 10 °C/min) to 20-30°C above the melting temperature, kept constant for 10min to eliminate residual crystals and then cooled to room temperature, while recording the heat flow to and from the system. Transitions appear then as accidents in dependence of the flow on temperature.

5.2.3.3. Scanning Electron Microscopy (SEM) was used to evaluate the thickness of the films on fractured membranes. Micrographs were produced in a LEO 1550 (Germany) high-resolution low-voltage SEM equipped with an in-lens detector. The samples were both spin-cast on Si-wafer and $\gamma$-alumina flat disks.

5.2.4. Permeability Set-up. Permeability experiments were performed at the IMS Laboratories (Faculty of Science and Technology, University of Twente, the Netherlands) in a temperature range of 30-90°C. The feed vessel contained pure liquid water which is pressurized under nitrogen. The water stream pressurized with Nitrogen that left the feed vessel was continuously pumped through the feed compartment of the permeability unit (figure 5.6.). At the feed side the liquid water is in equilibrium with the vapor phase that is transported through the membrane. The permeability
unit and membrane were kept at desired temperature using a thermostatic oil bath. On the feed side of the membrane, the partial pressure of water is equivalent to the saturation pressure of water at the given temperature. On the other side, it is maintained very low (less than 20 mbar) by a vacuum pump. This vapor pressure difference is the driving force for the water vapor transport. Steady state fluxes were determined by collecting the water driven through the polymer film-alumina system in a dry ice cold trap and measuring the weight increase with time. Every measurement took around 20-30 minutes (short enough to have no influence of a possible aging of the polymeric membrane).

**Figure 5.6.** Schematic picture of the permeability set-up used for the water permeability experiment.

### 5.2.4. Quartz Crystal Microbalance (QCM).

The solubility measurements were performed on a Quartz Crystal Microbalance (QCM) with Dissipation monitoring (QCM-D) in the Max Planck Institute for Polymer Research, Mainz, Germany. The Device is a Q-Sense D300 system (Q Sense AB, Germany) (see figure 5.7).

**Figure 5.7.** Picture of the Q-Sense D300 system: (a) PC with QSoft software, (b) Electronics unit, (c) Measurement chamber containing the sensor crystal and (d) active sensor side of a quartz crystal. Reproduced with permission of Q-SENSE AB.
The quartz microbalance was part of an open flow system to perform absorption experiments (see figure 5.8.).

![Diagram of absorption set-up](image)

**Figure 5.8.** Schematic picture of the absorption set-up.

Nitrogen was blown (1) to a container filled with distilled water (3). The Nitrogen flow was measured with a flow meter (2) and kept constant to 0.1mlmin⁻¹ to minimize distortions due to pressure fluctuations. The distilled water container was sealed (it is only open with an inlet for the inlet Nitrogen flow and the outlet water saturated Nitrogen flow). The temperature inside was tuned by a water bath (4) where the container was submerged to minimize temperature fluctuations. The temperatures of both the water bath and water container were measured and controlled (5, 6). The Nitrogen flow left the container saturated with water and arrived to the microbalance cell (7) where the samples are kept at the desired temperature (8). This temperature was well controlled by a temperature controller inside the measurement chamber. The saturated stream left the microbalance cell and the water is recovered in a waste receptacle (9).

The samples were prepared by spin coating, using the quartz sensors as supports. The crystals were 5.0 MHz AT-cut quartz resonators with silica coated gold electrodes (see figure 5.9).
The crystals were washed in methanol, then in acetone, and cleaned with UV ozone for 2 min prior to use. The mass of water absorbed in the film can be determined from the change in the resonance frequency of the quartz resonator using the Sauerbrey’s equation [15], relating the frequency shift, $\Delta f$, to the change in mass, $\Delta m$.

$$\Delta f = -\frac{2 f_0^2 \Delta m}{nA_e (\mu_q \rho_q)^{0.5}} = -C_f \frac{\Delta m}{nA_e}$$

where $f_0$ is the measured resonant frequency or overtone, $n$ is the number of the overtone, $A_e$ is the electrode area (0.20 cm$^2$), $\mu_q$ and $\rho_q$ are the shear module (2.947×10$^{11}$g cm$^{-1}$ s$^{-2}$) and the density of quartz (2.648 g cm$^{-3}$) respectively, and $C_f$ is the integral sensitivity constant. To use this equation a basic assumption needs to be made: the incremental change in mass from the deposited film is treated as if it were really an extension of the underlying quartz. The film is considered rigid and so thin that is does not experience any shear forces during vibration. As a result the sensitivity factor, $C_f$, is a fundamental property of the quartz crystal.

5.3. Results and Discussion.

5.3.1. Characterization. The characterization of the bulk materials and the processed films (obtained by compression molding and spin coating) was
done to evaluate certain relevant parameters and morphological features. These parameters are needed to understand the transport properties through films of these materials.

5.3.1.1. X-Ray Diffraction (XRD). The XRD spectra of both bulk polyamides (pellets) are shown in figure 5.10. For the semicrystalline polymer (figure 5.10a), two sharp peaks are clearly seen at ca. $2\theta=20.8^\circ$ and $24.3^\circ$ (indexed as 200 and 002/202 reflections), which are characteristic of the $\alpha$-crystalline form of nylon-6 and are labeled $\alpha_1$ and $\alpha_2$ respectively [16, 17]. The $\gamma$-form of nylon-6 gives peaks centered around $2\theta=22^\circ$ (001) and $23^\circ$ (200/201) [18]. On the other hand the single broad peak of figure 5.10b (amorphous polymer) centered around $2\theta=22^\circ$ corresponds, as expected, to an amorphous structure.

![XRD spectra](image)

**Figure 5.10.** XRD spectra of both polyamides as pellets: (a) semicrystalline polyamide and (b) amorphous polyamide.

For the semicrystalline polyamide, XRD experiments were performed also on compression molding films and spin coating films (on Silicon wafers). The results are shown in figure 5.11. Fitting the XRD profiles gives the degree of crystallinity (see figure 5.12).

Unfortunately the signal intensity decreases with the sample volume and it was not possible to obtain a fitteable signal for the thinnest films. It is, however, very interesting to observe the increase of degree of crystallinity of the semicrystalline polymer, as film thickness decreases. Below 10 $\mu$m there is jump from 35 % to 55 % in the degree of crystallinity. It is indeed known that the substrate may influence the crystallinity of the films [19]. From the values at which the crystalline peaks center, we can obtain the lattice parameters of the crystal structures using Bragg’s equation:

$$2d \sin \theta = \lambda$$  \[11\]

where $d$ is the lattice parameter, $\theta$ is the angular position of the peaks, and $\lambda$ is the wavelength of the X-Ray beam (1.54059 Å).
Figure 5.11. XRD spectra of pellets, compression molded film and several spin coated films made with the semicrystalline polyamide.

Figure 5.12. Plot of the degree of crystallinity for pellets, compression molded film and several spin coated films made with the semicrystalline polyamide.

Results are shown in table 5.1. Contrary to the degree of crystallinity, almost no changes are observed in the lattice parameters, which are close with those found in the literature [20].

<table>
<thead>
<tr>
<th>thickness</th>
<th>lattice parameter $d_{\alpha1}$ (Å)</th>
<th>lattice parameter $d_{\alpha2}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk pellets</td>
<td>4.44</td>
<td>3.79</td>
</tr>
<tr>
<td>50 µm</td>
<td>4.37</td>
<td>3.72</td>
</tr>
<tr>
<td>13.36 µm</td>
<td>4.41</td>
<td>3.67</td>
</tr>
<tr>
<td>3.26 µm</td>
<td>4.41</td>
<td>3.70</td>
</tr>
<tr>
<td>0.938 µm</td>
<td>4.41</td>
<td>3.67</td>
</tr>
</tbody>
</table>

Table 5.1. Values for the lattice parameters (calculated from Bragg’s equation) corresponding to the $\alpha_1$ and $\alpha_2$ peaks in figure 5.11.

5.3.1.2. Differential Scanning Calorimeter (DSC). The first and second DSC heating and cooling scans of pellets of the semicrystalline and amorphous polyamide are shown in figure 5.13. During the first heating, the sample relaxes initial internal stresses and only the second scan was used to analyze the thermodynamic behavior of the materials.

The semicrystalline polyamide shows a sharp melting peak at 228 °C while the melting process starts at ca. 190 °C. The glass transition temperature is slightly observed at 50 °C (faster cooling rates are needed to enhance the $T_g$ peak). The amorphous polyamide shows only a transition at 125 °C that corresponds to the glass transition temperature.
Figure 5.13. First and second DSC heating (negative heat flow) and cooling (positive heat flow) scans for the pellets of the semicrystalline polyamide (a) and the amorphous polyamide (b).

5.3.1.2. **Scanning Electron Microscopy** (SEM). Spin coated samples are observed with SEM to evaluate the film thickness of the coating. The supported membrane is cut in several pieces and the cross-sections are recorded. Examples of typical micrographs recorded are shown in figure 5.14.

![Figure 5.14. SEM micrographs showing typical crossed sections of the coated membranes. Micrographs (a), (b), (c) and (d) correspond to semicrystalline films of 13.36 μm, 3.26 μm, 938nm and 10 nm respectively. Micrographs (e), (f), (g) and (h) correspond to amorphous films of 11.59 μm, 971 nm, 404 nm and 10 nm.](image)
From these cross-sections we can observe the macroporous α-alumina plate at the bottom of every SEM picture, the mesoporous γ-alumina and coated on top, the homogeneous polymer layer, either spherulitic (semicrystalline) or smooth (amorphous).

5.3.2. Permeability Coefficient. The measured fluxes through blank substrates and polymer-coated substrates are represented in figure 5.15. The alumina substrates used for the semicrystalline polyamide had 3 coatings of γ-alumina (mesoporous material), while the ones used for the amorphous polyamide had only one. This explains the lower flux for the bare substrate in the first case. The system substrate + polymer show lower fluxes than the bare substrate, in particular for the amorphous polyamide. For both polyamides, the higher the temperature (and therefore the pressure gradient), the higher the mass flux across the system. In the results for the semicrystalline polyamide, the flux of the system with the thickest film is smaller than the rest of the membranes. In the case of the amorphous system, the values are all very similar and with small errors.

The values of the permeabilities of the polymer films calculated using equation 5 are shown in figure 5.16. There is only a slight effect of temperature on the permeability, with a decrease as temperature increases (more visible for the amorphous polymer). Although for most polymers the permeability increases as temperature increases, the permeability of water through polylactic acid films has also been found to decrease as temperature increases [21]. This variation can be understood using the solution-diffusion model (section 2.3.2). While the diffusion coefficient increases as temperature increases, the solubility decreases (within a given phase). If the
latter dependence is stronger than the increase of the diffusion, the permeability decreases as temperature increases.

In both polyamides, there is a clear thickness effect. In the case of the semicrystalline polyamide the variation is more abrupt than in the amorphous polyamide. This effect can be clearly appreciated if we plot the permeability as a function of the film thickness (figure 5.17).

For the semicrystalline polyamide, there are some values available in the literature to compare with. According to reference [22], the permeability of a Nylon 6 film at 38 °C is of the order of $7 \times 10^{-11}$ cm$^3$ cm cm$^{-2}$ s$^{-1}$ Pa$^{-1}$.

![Figure 5.16. Permeability coefficients (intrinsic permeabilities) of water vapor through the polyamide films: (left) semicrystalline polyamide and (right) amorphous polyamide.](image)

![Figure 5.17. Permeability coefficients (for all the temperatures) plotted as a function of film thickness: (left) semicrystalline polyamide and (right) amorphous polyamide. The dashed line represented the average bulk value for the thickest films.](image)

Another reference [23] published a value of 275 Barrer ($=2.06 \times 10^{-11}$ cm$^2$ s$^{-1}$ Pa$^{-1}$). Although the thickness is not reported in neither of the references, neither the method used to obtain these values, this permeability is close to the one we have found for the thickest films, which using the same units is: $(1.10 \pm 0.68) \times 10^{-11}$ cm$^3$ cm cm$^{-2}$ s$^{-1}$ Pa$^{-1}$. Literature values for Nylon 6 (semicrystalline polyamide) are available as well from general handbooks.
[24]. One of them at 40 °C, 90% relative humidity (close to saturation) and 0.017 mm thickness was: 1 g ml/100 in² day (≈3.0 ×10⁻¹² m³ m⁻² s⁻¹). This value was not given by pressure units, therefore we can compare with our values multiplying our values of the permeability $P$ with the pressure difference $\Delta p$. Our experimental value for the thickest semicrystalline film at 42 °C is then 4.58 ×10⁻¹² m³ m⁻² s⁻¹, which is of the same order of magnitude. Another reference appearing in another handbook [25] gives a value at 38 °C and 90% humidity of 4.3 g mm⁻² day⁻¹ (≈5.0 ×10⁻¹⁴ m³ m⁻² s⁻¹), which is significantly higher. For the amorphous polyamide, the same handbook gives a value for reference (but it does not specify the temperature neither the humidity): 7 g m⁻² day⁻¹ for a film of 0.05 mm (4.1 ×10⁻¹⁵ m³ m⁻² s⁻¹). So there is some scatter in the literature values, but our results for thick films are at least of the same order of magnitude. We have to understand that permeability being a much less fundamental constant than the diffusion coefficient, it is less reported in the scientific literature.

Before trying to find an explanation for the thickness effect we observe in the permeability, we should ask ourselves whether this effect is real or whether it is an artifact due to an extra resistance to transport not taken into account in equation 6. The relative importance of this spurious resistance could become larger for the thinner films, making their permeability appear smaller than it actually is. There are several possible effects that could give rise to such a resistance.

i) As explained in section 5.1.2.1, concentration polarization can take place because the air layers adjacent to the film may have a higher resistance than the film. Literature has reported some experimental evidence for this effect [26]. In our set-up, such a layer depleted in water vapor cannot appear at the feed side since there is a continuous flow of water. This prevents the formation of layers with a different composition close to the film. At the vacuum side, we cannot exclude totally the presence of a stagnant layer of water vapor close to the sample. However the pressure drop through the membrane is small: the pressure at the vacuum side is 17.19±3.57 mbar (averaging all experiments) and the water vapor pressure at the feed side goes in our experiments from 34.57 to 540 mbar at the maximum. This makes the appearance of a layer of water vapor with a higher pressure than measured by the vacuum pump improbable, especially at low pressure. It is also unlikely that this polarization effect would take place with the alumina substrate covered with a film and not with the bare alumina plates. If this effect happens, it should already be taken into account in the permeability of the bare alumina plates.

ii) More likely than a resistance at the vacuum side, it could happen that in our experiments there is a mass transport limitation of water in the
substrate, i.e. that water condenses somehow in the pores of the substrate. This is not very likely because we keep a very low pressure at the vacuum side, but it might happen if we have very large water flux going through the polymer membrane. In this case, the pressure might be higher in the substrate than what we measure with the pump. But we can estimate that with our experimental conditions, this effect is negligible (see appendix B). Moreover it is, once again, very unlikely that this condensation would happen in the alumina covered with a film and not in the bare alumina.

So having excluded possible sources of extra resistance in our system, we conclude that the observed decrease in permeability as film thickness decreases is a real effect. If we want to explain the possible reasons of this thickness effect we must first recall changes in the morphology of the membranes as film thickness decreases. In particular, the semicrystalline polyamide has got crystalline domains that do not contribute to the transport. As film thickness decreases the degree of crystallinity increases from 35% to 55%, as we have already seen in figure 5.12. This increase in the crystallinity of the film decreases the permeability, but this effect alone cannot explain the large variation in permeability observed experimentally. Also, for the amorphous polyamide, the permeability decreases as film thickness decreases as well. So changes in the degree of crystallinity cannot be the main effect.

Two other effects can be at the origin of the observed thickness dependence. Firstly, as film thickness decreases the polymer chains tend to align parallel to the limiting surfaces. This ordering would enhance the resistance to the transport in the direction perpendicular to the substrate. This is schematically depicted in figure 5.18.

![Figure 5.18](image1)

**Figure 5.18.** Schematic path of water molecules through the free volume of the polymer membrane.

![Figure 5.19](image2)

**Figure 5.19.** Schematic picture showing the possible increase of the polymer density and decrease of the mobility at the vicinity of the coated support.
The arrows show that in the case of the thinner membrane, the molecules will travel more easily in the direction parallel to the surface but with more difficulties in the direction perpendicular to the supporting surface. As mentioned in section 3.3.1, this effect might not be strong enough to explain the large decrease we have observed. A second effect could come from a strong decrease of the polymer mobility in the vicinity of the substrate due to strong interactions with the substrate (see section 2.2). It has also been shown that in this case the density of the polymer at the substrate interface is larger than in the bulk [27, 28]. This immobile interfacial layer could actually be the main barrier in the amorphous polymer, leading to a flux through the film essentially independent of film thickness (see figure 5.19.).

5.3.3. Solubility Coefficient. The values of the absolute mass uptake obtained from our Quartz Crystal Microbalance measurements are shown figure 5.20. The thinner the film, the lower the amount of water absorbed. As we have done in chapter 4, we can convert these absolute amounts in a relative mass uptake:

\[ M_r = \frac{M_\infty}{m_p^0} \]  

[12]

and a volume fraction of water in the polymer \((V_w)\):

\[ V_w = \frac{M_\infty \rho_{film}}{(m_p^0 + M_\infty) \rho_w} \]  

[13]

where \(\rho_w\) is the density of water and \(\rho_{film}\) is the density of the polymer containing water at the given volume fraction (which is taken as approximately the same value of the bulk density of the polymer).

![Figure 5.20](image-url)  

**Figure 5.20.** Absolute mass uptake of water vapor by polyamide films: (left) semicrystalline polyamide and (right) amorphous polyamide.
The relative mass uptake and the volume fraction are shown in figure 5.21. We could not measure over a large enough temperature range to see a clear dependence on this parameter. Nevertheless it can be seen, especially for the amorphous polyamide, that from 25 °C to 35 °C the volume fraction decreases.

Figure 5.21. Relative mass uptake and volume fraction of water vapor by the polyamide films: (left) semicrystalline polyamide and (right) amorphous polyamide.

The values for the solubility coefficient (equation 8) at 35 °C for both polyamides are summarized in figure 5.22, showing a clear increase of the solubility coefficient with decreasing film thickness. However this effect is much smaller than the thickness effect on the permeability.

Figure 5.22. Solubility coefficient at 35 °C for both series of polyamide films.
Some of the water added to the film may actually not be absorbed inside but adsorbed at the surface. The water molecules absorbed inside the films fill the free volume of the polymer film. As discussed in chapter 4 about the polystyrene/THF system (section 4.3.2), it is not clear whether we should expect an increase or decrease of free volume when thickness decreases. We have found no variation of the solubility of THF in PS with film thickness. The fact that the volume fraction is observed to increase could be an indication of the presence of water adsorbed at the surface. The amount of water adsorbed can be expected to be approximately constant (in absolute value) with the film thickness, leading to an increase in relative value as the film thickness decreases.

The fact that part of the water is adsorbed at the surface of the film would introduce some error in the measured value of the solubility coefficient. We can however compare the obtained values for the semicrystalline polyamide (table 5.2) with the solubility data from Hernandez et al. [29] for a semicrystalline film of 25.4 µm (100% humidity): 10 kg kg⁻¹ atm⁻¹ (5 °C), 3 kg kg⁻¹ atm⁻¹ (23 °C) and 1 kg kg⁻¹ atm⁻¹ (40 °C). Pressure units refer to partial water pressure. This last value is very close to the one we have found for the thickest film at 35 °C. This gives us a clear indication that the measurements done for the thickest films are very realistic, because the ratio absorbed water /adsorbed water is anyway large. For the thinnest film this ratio would become smaller and the error on the measured solubility large.

<table>
<thead>
<tr>
<th>Δx (µm)</th>
<th>$S_w$ (kg kg⁻¹ atm⁻¹) at 25°C</th>
<th>$S_w$ (kg kg⁻¹ atm⁻¹) at 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.36</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>3.26</td>
<td>15.8</td>
<td>3.0</td>
</tr>
<tr>
<td>0.94</td>
<td>11.5</td>
<td>5.5</td>
</tr>
<tr>
<td>0.46</td>
<td>16.7</td>
<td>5.7</td>
</tr>
<tr>
<td>0.30</td>
<td>1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>0.01</td>
<td>-</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Table 5.2. Values for the solubility coefficient for the semicrystalline polyamide films at two different temperatures.

5.3.4. Diffusion Coefficient. Direct application of equation 14 in the isotherms recorded for 35 °C allows us to extract the diffusion coefficient and to study the dependence of this coefficient with the thickness of the films (table 5.3). This method is only reliable if the isotherms have a purely fickian shape (see figure 5.5.). Unfortunately most of the isotherms found in our experiments deviate from classical fickian behavior. Examples of typical deviations from a fickian behavior are shown in figure 5.23. Only the values from the semicrystalline polyamide can be compared with literature values. The diffusion coefficient from Hernandez et al. [29] for a nylon-6 film of 25 µm
at 40 °C is in the order of $2.4 \times 10^{-14}$ m$^2$s$^{-1}$, very close to the ones found in our thicker films. This shows that, despite the imperfections of the absorption isotherms, our experiments give diffusion coefficients with the right order of magnitude.

![Figure 5.23](image)

**Figure 5.23.** Examples of deviations from a fickian absorption behavior. On the right, the film absorption follows a two stage sorption; on the left, water absorbs and then desorbs again until steady state is reached.

It is clear that for both polyamides there is a decrease in the diffusion coefficient (as it was already observed in section 3.4.1 on supported thin polystyrene films) as film thickness decreases. This effect has been previously observed in the diffusion coefficient of water in a polyelectrolyte with absorption experiments performed with a quartz microbalance [30]. These experiments show a decay of three orders when the thickness is decreased from 120 nm to and below 10 nm.

<table>
<thead>
<tr>
<th>semicrystalline films</th>
<th>amorphous films</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta x$ (µm)</td>
<td>$\Delta x$ (µm)</td>
</tr>
<tr>
<td>$D_w$ (m$^2$s$^{-1}$)</td>
<td>$D_w$ (m$^2$s$^{-1}$)</td>
</tr>
<tr>
<td>13.36</td>
<td>6.1x10$^{-13}$</td>
</tr>
<tr>
<td>3.26</td>
<td>4.9x10$^{-14}$</td>
</tr>
<tr>
<td>0.94</td>
<td>1.3x10$^{-15}$</td>
</tr>
<tr>
<td>0.46</td>
<td>2.01x10$^{-16}$</td>
</tr>
<tr>
<td>0.30</td>
<td>2.8x10$^{-17}$</td>
</tr>
<tr>
<td>0.01</td>
<td>4.4x10$^{-19}$</td>
</tr>
<tr>
<td>11.59</td>
<td>5.0x10$^{-14}$</td>
</tr>
<tr>
<td>0.97</td>
<td>2.9x10$^{-15}$</td>
</tr>
<tr>
<td>0.41</td>
<td>3.8x10$^{-16}$</td>
</tr>
<tr>
<td>0.37</td>
<td>3.6x10$^{-16}$</td>
</tr>
<tr>
<td>0.34</td>
<td>3.4x10$^{-16}$</td>
</tr>
<tr>
<td>0.01</td>
<td>2.3x10$^{-19}$</td>
</tr>
</tbody>
</table>

**Table 5.3:** Diffusion coefficient ($D_w$) at 35°C for several film thicknesses. The values in bold come from the isotherms that showed undoubtedly a fickian behavior.

Together with the fact that the solubility tends rather to increase as film thickness decreases (if it all varies, see section 5.3.3), these results show...
that the reduction in permeability we have observed is due to a reduction in diffusivity.

5.3.5. Comparison of Permeability Coefficients. We have seen in section 2.3.2. that the permeability is simply the product of the diffusion coefficient and solubility coefficient. From the diffusion coefficient \(D_w\) and the solubility coefficient \(S_w\) obtained from the isotherms at 35ºC, we can use this relationship to calculate the value of the permeability given by the Quartz Microbalance \(P^*\):

\[ P^* = D_w \times S_w \]  

This permeability can be compared with the value \(P\) obtained by permeation measurements for a similar temperature (section 5.3.2). The values of both permeabilities are listed in table 5.4 and table 5.5. The values of the permeabilities \(P\) and \(P^*\) differ substantially.

<table>
<thead>
<tr>
<th>(\Delta x (\mu m))</th>
<th>(P^*(m^2 s^{-1} Pa^{-1}))</th>
<th>(P(m^3 m^{-2} s^{-1} Pa^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.36</td>
<td>1.0x10^{-17}</td>
<td>1.3x10^{-15}</td>
</tr>
<tr>
<td>3.26</td>
<td>1.5x10^{-18}</td>
<td>8.2x10^{-15}</td>
</tr>
<tr>
<td>0.94</td>
<td>7.1x10^{-20}</td>
<td>1.4x10^{-15}</td>
</tr>
<tr>
<td>0.46</td>
<td>1.1x10^{-20}</td>
<td>-</td>
</tr>
<tr>
<td>0.30</td>
<td>6.0x10^{-22}</td>
<td>-</td>
</tr>
<tr>
<td>0.01</td>
<td>7.3x10^{-23}</td>
<td>6.1x10^{-18}</td>
</tr>
</tbody>
</table>

Table 5.3. Comparison of values for the Permeability calculated from QCM measurements \(P^*\) and Permeability calculated from the permeability measurements \(P\) for the semicrystalline polyamide films.

<table>
<thead>
<tr>
<th>(\Delta x (\mu m))</th>
<th>(P^*(m^2 s^{-1} Pa^{-1}))</th>
<th>(P(m^3 m^{-2} s^{-1} Pa^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.59</td>
<td>4.6x10^{-19}</td>
<td>1.1x10^{-14}</td>
</tr>
<tr>
<td>0.97</td>
<td>3.7x10^{-20}</td>
<td>8.7x10^{-16}</td>
</tr>
<tr>
<td>0.41</td>
<td>1.2x10^{-20}</td>
<td>3.1x10^{-16}</td>
</tr>
<tr>
<td>0.37</td>
<td>1.0x10^{-20}</td>
<td>-</td>
</tr>
<tr>
<td>0.34</td>
<td>3.6x10^{-21}</td>
<td>-</td>
</tr>
<tr>
<td>0.01</td>
<td>2.9x10^{-23}</td>
<td>2.8x10^{-17}</td>
</tr>
</tbody>
</table>

Table 5.4. Comparison of values for the Permeability calculated from QCM measurements \(P^*\) and Permeability calculated from the permeability measurements \(P\) or the amorphous polyamide films.

A simple calculation can be made from the data from Hernandez et al., if the diffusion coefficient for 40 °C is in the order of 2.4x10^{-10} cm²s⁻¹ and the
solubility coefficient for the same temperature is 1.25 g g\(^{-1}\) atm\(^{-1}\), then a permeability of the order of \(3 \times 10^{-19}\) m\(^2\) s\(^{-1}\) Pa\(^{-1}\), which is closer to the one we found from the results of the QCM for the thickest semicrystalline film. On the other hand, we have seen in section 5.3.2. that several literature values for the permeability of Nylon 6 (semicrystalline polyamide) as measured directly are close to the values of \(P\) we have obtained by permeability measurements. The scatter of the literature data is therefore too large to be able to say which of the permeabilities \(P\) or \(P^*\) is in better agreement with reported data. A possible source of discrepancies between \(P\) and \(P^*\) would be that equation 18 is actually not valid for our system. But considering that this equation is well reproduced by experiments reported so far, this is rather unlikely.

### 5.4. Conclusions.

In this chapter we have observed the following effect of thickness on the transport properties of water in polyamides:

1) the permeability coefficient as measured in a permeability experiment decreases as thickness decreases.

2) the diffusion coefficient as measured with absorption experiments with a Quartz Microbalance decreases as film thickness decreases.

3) the calculated permeability coefficient as a product of the diffusion and solubility coefficients measured with absorption experiments with a Quartz Microbalance decreases as film thickness decreases.

4) the solubility hardly varies, tending to increase as film thickness decreases.

Despite the uncertainties that remain on certain measurements and the fact that the permeability values cannot really be compared with literature data, the trend we observe is always the same and very clear: the transport of water through polyamide is reduced in thin films. A possible explanation is the presence of an immobile layer close to the substrate which would have a significantly larger resistance to transport through the film, and would actually be mainly responsible for the barrier properties of the film. The alignment of the polymer chains in the direction parallel to the film could also reduce the transport in the direction perpendicular to the surfaces.
## List of Abbreviations and Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units [MKS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Surface of the membrane</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$A_e$</td>
<td>Electrode area</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$C_f$</td>
<td>Integral sensitivity constant</td>
<td>[s$^{-1}$ m$^2$kg$^{-1}$]</td>
</tr>
<tr>
<td>$D_w$</td>
<td>Diffusion coefficient of water</td>
<td>[m$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$d$, $d_{a1}$, $d_{a2}$</td>
<td>Lattice parameter</td>
<td>[m]</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimeter</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>Mass flux</td>
<td>[kg m$^{-2}$s$^{-1}$]</td>
</tr>
<tr>
<td>$F_{substrate}$</td>
<td>Water flux through alumina</td>
<td>[kg m$^{-2}$s$^{-1}$]</td>
</tr>
<tr>
<td>$F_{system}$</td>
<td>Water flux through alumina + film</td>
<td>[kg m$^{-2}$s$^{-1}$]</td>
</tr>
<tr>
<td>$f_o$</td>
<td>Resonant frequency</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$m_o$</td>
<td>Weight of dry film</td>
<td>[kg]</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass of permeated water</td>
<td>[kg]</td>
</tr>
<tr>
<td>$M_r$</td>
<td>Relative mass uptake</td>
<td>[-]</td>
</tr>
<tr>
<td>$M_t$</td>
<td>Mass uptake at time $t$</td>
<td>[-]</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number averaged molecular weight</td>
<td>[kg mol$^{-1}$]</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight averaged molecular weight</td>
<td>[kg mol$^{-1}$]</td>
</tr>
<tr>
<td>$M_\infty$</td>
<td>Mass uptake after equilibration (QCM)</td>
<td>[kg]</td>
</tr>
<tr>
<td>$n$</td>
<td>Overtone number (QCM)</td>
<td></td>
</tr>
<tr>
<td>$P_m$</td>
<td>Permeability (in mass)</td>
<td>[kg m$^{-2}$s$^{-1}$Pa$^{-1}$]</td>
</tr>
<tr>
<td>$P$</td>
<td>Permeability (in volume)</td>
<td>[m$^3$ m$^{-2}$s$^{-1}$Pa$^{-1}$]</td>
</tr>
<tr>
<td>$P^*$</td>
<td>Permeability from QCM data</td>
<td>[m$^3$ m$^{-2}$s$^{-1}$Pa$^{-1}$]</td>
</tr>
<tr>
<td>$p_o$</td>
<td>Saturation vapor pressure</td>
<td>[Pa]</td>
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<tr>
<td>$P_{vacuum}$</td>
<td>Vacuum pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Microbalance</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>$S_o$</td>
<td>Solubility coefficient of water</td>
<td>[kg kg$^{-1}$Pa$^{-1}$]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$T_w$</td>
<td>Water temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>[s]</td>
</tr>
<tr>
<td>$V_w$</td>
<td>Volume fraction of water in the polymer</td>
<td>[-]</td>
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<td>XRD</td>
<td>X-Ray Diffraction</td>
<td></td>
</tr>
<tr>
<td>$\Delta f$</td>
<td>Frequency shift (QCM)</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pressure difference</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Time interval</td>
<td>[s]</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>Sample thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta x_{substrate}$</td>
<td>Thickness of the substrate</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta x_{film}$</td>
<td>Thickness of the polymer film</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta x_{system}$</td>
<td>Thickness of the system (substrate + film)</td>
<td>[m]</td>
</tr>
<tr>
<td>$\theta$</td>
<td>XRD angle</td>
<td>[$^\circ$]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of the X-Ray beam</td>
<td>[m]</td>
</tr>
<tr>
<td>$\rho_{film}$</td>
<td>Density of polymer film</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\rho_q$</td>
<td>Density of quartz</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>Density of water</td>
<td>[kg m$^{-3}$]</td>
</tr>
</tbody>
</table>
References:

[06] www.emsgrivory.com
[22] www.goodfellow.com/csp/active/static/A/AM30.html
PART II
Polyelectrolytes
“El alfabeto del ADN contiene solo cuatro letras pero el número de mensajes que es posible escribir con ellas es infinito”

M. HOAGLAND
A whole new range of phenomena in interface science happens around the effect of surface forces. Many practical applications in colloid science come down to the problem of controlling the force between colloidal particles, between particles and surfaces, and in particular between two surfaces. For this reason scientists have devoted considerable effort to understanding surface forces and being able to influence them.

(from H.J. Butt, K. Graf and M. Kappl, Physics and Chemistry of Interfaces 2003, Wiley-VCH Verlag & Co.)
6.1. Introduction.

The name “surface forces” refers to the forces acting between microscopic or even macroscopic bodies, usually when they are in close proximity. The properties of many materials are determined by the interaction between elements that are larger than molecules, for example micrometer-sized or even millimeter-sized grains, crystals, layers, fibers, cells, or other components (table 6.1.). A lot of effort is therefore dedicated to understanding these different forces and their relation to the nature of the interacting elements.

<table>
<thead>
<tr>
<th>Colloid Science</th>
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<td>Composites, coatings, thin films</td>
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<td>Electronic packaging</td>
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<td>Friction and wear</td>
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<td>Medicine</td>
<td>Drug delivery systems</td>
</tr>
<tr>
<td></td>
<td>Implant materials, biocompatibility</td>
</tr>
</tbody>
</table>

Table 6.1. Partial list of processes, products and phenomena in which surface forces play an important role.

Conversely, measuring the force a sample surface exerts on another probe surface as the distance between the two decreases and the surfaces are eventually pressed against each other, is a way of getting information about the studied sample. This is the main technique we have used in this part of the thesis to study polyelectrolyte multilayers and their interactions with other surfaces. In the following we review the equipments that have been developed to be able to measure surfaces, and the signature of the different forces acting between surfaces in this type of measurements.

6.2. The Measurement of Surface Forces.

Measuring surface forces is experimentally challenging. Direct methods using model surfaces are difficult because of the short distances, the small magnitude of the forces, and the ever-present danger of surface contamination. Indirect methods are hampered by other factors (mainly the difficulty in interpreting the results).

There are two main methods for measuring surface forces directly. The first one is using a surface force apparatus (SFA), whose development was a
big step forward [1, 2]. It allowed one to measure directly the force law between two surfaces separated by a liquid or a vapor, with a spatial resolution of the order of 1Å [3]. The first type of SFA used two crossed cylinders of roughly 1cm in radius covered by atomically smooth mica sheets between which the interaction forces are measured. One mica cylinder is mounted on a piezoelectric translator that adjusts the distance between the two surfaces. The other mica surface is attached to a spring of known and adjustable spring constant. The separation between the two surfaces is measured by interferometry. Knowing the position of one cylinder and the separation between the two surfaces, the deflection of the spring and the force acting on the second cylinder can be calculated. Later, non-interferometric SFA were developed [4] in which the distance between the surfaces is measured by an electronic device. It is then possible to change the nature of the interacting surfaces.

Another device with which forces can be measured directly and relatively universally is the atomic force microscope (AFM) [5, 6]. In the AFM one measures the deflection of a cantilever terminated by a tip as it approaches a sample surface (figure 6.1).

Knowing the spring constant of the cantilever, its deflection can be converted into the force between the surface and the tip. This tip is either microfabricated with a radius at the end between 10 and 100 nm, or is made of a sphere glued to the cantilever, with a radius between 0.5 µm and several 100µm. The practical advantage of the atomic force microscope is that measurements are quick and simple. Also, the interacting surfaces are substantially smaller than in the surface force apparatus. Thus the problem
of surface roughness, deformation, and contamination, is reduced. However this reduced interaction area significantly reduces the sensibility with respect to the SFA. As non-interferometric SFA, the AFM allows one to study surfaces of different materials. This is the technique we have used in the following to measure surface forces.

In force measurements with an AFM the sample is moved up and down by applying a voltage to the piezoelectric translator, onto which the sample is mounted, while measuring the cantilever deflection (figure 6.1). The direct results of such a force measurement are the cantilever deflection, $z_c$, versus position of the piezo, $z_p$, in the direction normal to the surface (figure 6.2a). To obtain a plot of the force $F$ acting between the tip carried by the cantilever and the sample as a function of the distance $D$ between them (figure 6.2b), $z_c$ and $z_p$ have to be converted into these quantities. The force $F$ is obtained by multiplying the deflection $z_c$ of the cantilever with its spring constant. The tip-sample separations calculated by adding the deflection $z_c$ to the piezo position $z_p$ [7].

Figure 6.2. Schematic drawing of a typical force vs. distance curve. The collected raw data is represented in (a) and the data converted into a force vs. distance curve in (b).

Independently of the forces acting between the tip and the sample, the tip eventually ends up being pressed against the sample that appears rigid. The deflection $z_c$ varies then linearly with the piezo position $z_p$ (left part of the plot in figure 6.2a). The force $F$ increases then while the distance $D$ remains constant (figure 6.2b). At the beginning of the retraction, the $F(D)$ curve is superimposed on the approach curve.
6.3. Types of Forces.

Forces between two surfaces separated by a third medium can arise due to a variety of phenomena. We review here the most important ones and their signature in the force vs. distance curves. To focus our discussion, we will consider the case of a sphere attached to an AFM cantilever interacting with a flat sample, which is the geometry we have used in our experiments.

6.3.1. Van der Waals Forces. We call under the name of van der Waals interactions a collection of interactions between molecules based on dipole-dipole, dipole-induced dipole and induced dipole-dipole interactions [8-10]. These interactions are present between all molecules, and therefore between all materials. Integrating all these molecular interactions over the system surface 1/surface 2/intermediate medium, taking the geometry of the surfaces into account, gives the resulting van der Waals force between the two surfaces through the intermediate medium. In case of a sphere of radius $R$ interacting with a flat surface, this force can be expressed as:

$$F_{vdw} = -\frac{A_H}{6D^2} R$$  \[1\]

where $D$ is the minimum distance between the sphere and the surface, and $A_H$ is the so-called Hamaker constant. This constant depends on the media involved. It is usually positive, so that the force is attractive. If the two interacting surfaces are made of different materials, $A_H$ can be negative and the force repulsive.

In force vs. distance curves measurements, attractive van der Waals forces lead to an attraction of the cantilever towards the surface as it approaches (figure 6.3).

![Figure 6.3](image_url)

**Figure 6.3.** Typical force vs. distance curve in the case of attractive van der Waals forces. (a) Raw data , (b) force vs. distance curve.
If the slope of the $F(D)$ curve exceeds the spring constant $k_c$ of the cantilever before the sphere gets into contact with the sample surface, the elastic force of the cantilever cannot compensate anymore the force acting on the cantilever and the cantilever gets out of equilibrium. The sphere jumps then into contact, instead of following the actual shape of the force vs. distance curve. The jump can however be very short and not really discernable in experimental curves.

6.3.2. Electrostatic Forces. If the surfaces carry some charges, electrostatic forces will come into play. The basic electrostatic interaction is the Coulomb force between charges that is attractive between charges of different signs and repulsive in the case of identical sign, and is inversely proportional to the square of the distance between the charges. This force is extremely long range and is relevant when making force measurements in air. We have performed all our measurements in liquids, which means that the two interacting surfaces are separated by an electrolyte. In this case the surface charges are screened by the ions of the solution that are attracted towards the surfaces. The electrostatic force between two surfaces carrying charges of the same sign, generally called double-layer repulsion in this case, takes then the following form (for a sphere of radius $R$ interacting with a flat surface of the same material):

$$F_{elec}(D) = 128\pi R k_B T n_0 \kappa^{-1} Y_0^2 \exp\left(-\frac{D}{\kappa^{-1}}\right)$$  \hspace{1cm} [2]

with

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2 q^2 n_0}\right)^{1/2}$$  \hspace{1cm} [3]

and

$$Y_0 = \left(\frac{\exp(e \psi_0 / k_B T) - 1}{\exp(e \psi_0 / k_B T) + 1}\right)$$  \hspace{1cm} [4]

where $k_B$ is the Boltzman constant, $T$ the temperature, $n_0$ the number density of ions in the solution, $\varepsilon$ the relative dielectric permittivity of the medium, $\varepsilon_0$ the dielectric permittivity of vacuum, $q$ the charge of the ions, and $\psi_0$ the electric potential of the surfaces. $\kappa^{-1}$ is the Debye screening length, which is the distance over which the double layer repulsion decays. It is typically around 100 nm in “pure water” and 1 nm in concentrated (0.1 M) electrolyte solutions. In this last case, the electrostatic interactions are totally screened and play only a role at very short distances.
Since van der Waals forces are always present, it is not possible to observe electrostatic forces alone, but only the combination of van der Waals and electrostatic forces. This combination is referred to as *DVLO forces*, after Derjaguin, Landau, Verwey and Overbeek who came up with the first theory to explain colloidal stability based on these two forces.

In force vs. distance curve measurements, the DVLO forces results at long distances into a slight attraction (figure 6.4), which is often not observed because it is too weak with respect to the elastic force of the cantilever. As the sample gets closer to the sphere, the force becomes repulsive and the cantilever deflects away from the surface. At very short distances, the van der Waals forces will eventually dominate, so that the force goes through a maximum and decreases again as the distance decreases.

![Figure 6.4. Typical force vs. distance curve in the case of DVLO forces. (a) Raw data, (b) force vs. distance curves.](image)

In most cases, the slope of the force vs. distance curve reaches the value of the spring constant $k_c$ of the cantilever before the maximum if the force vs. distance curve is reached. The sphere jumps then into contact and the rest of the force vs. distance curve cannot be observed experimentally.

Note that in the case of surfaces with charges of opposite sign, the electrostatic force is attractive. The sum of the electrostatic and van der Waals forces looks then qualitatively the same as the van der Waals force (figure 6.3).

### 6.3.3. Specific Forces

Besides the two main types of interactions we have just discussed, some systems exhibit surface forces specific to their particular nature [8]. These forces can become much stronger than the DVLO forces and dominate the behavior of the system. For instance, solids often induce a molecular order of the liquid close to their surface. The first few molecular layers of liquid show then a certain packing. This order can give rise to short-
range oscillatory forces acting between two solid surfaces that are pressed together [11, 12].
Another category of forces is the one arising when the liquid acts as a solvent for the surfaces. As the solvation shells of the two surfaces get closer, a monotonic attractive or repulsive force appears. In the case of water, hydrophobic surfaces repel each other [13-15] while hydrophilic surfaces attracted each other [14, 16].
Finally let us mention the steric repulsion of surfaces covered by adsorbed or grafted polymer chains. Due to the steric repulsion between the polymer chains, the polymer layers repel each other as they start interpenetrating. The strength and exact shape of this repulsion strongly depend on the solvent quality of the liquid for the specific polymer used.

6.3.4. Deformation and Adhesion. Once the sphere has got into contact, it applies a certain pressure to the sample, which depends on the contact area between the sphere and the sample. This pressure has two contributions:

i) If the cantilever is deflected upwards, it applies a force proportional to this deflection.

ii) For many systems, the sphere sticks to the sample because of an adhesion force that presses it on the sample.

Under this pressure, the sample deforms. If the sample is rigid, there will be only a slight deformation that increases the contact area. This has been described theoretically by Johnson, Kendall and Robert [17] (the so-called JKR model), which is generally the most relevant model to SFA and AFM measurements. This slight deformation will, however, not appear in the measured force vs. distance curves (figure 6.5a and b).
If the sample is soft, the deformation will be significant, and one speaks of indentation. As a result the measured force vs. distance curve in contact will not be straight but concave (figure 6.5c and d).
The exact shape of this curve depends on the profile of mechanical properties of the sample in its depth. In the extreme case of a liquid layer, the viscoelastic response of the sample is the dominating factor. The results depend then on the speed at which the sample is moved during the approach, as force vs. distance curve measurements are actually performed dynamically.
If there is no adhesion, when the sample is retracted away from the sphere, the force vs. distance curve follows the same path as during the approach. If there is some adhesion between the sphere and the sample, the sample exerts an attractive force (pull-off force) on the sphere over a longer distance than during the approach (figure 6.5).
CHAPTER 6

Figure 6.5. Typical force vs. distance curves in contact in the case of rigid and soft samples with adhesion. (a, c) Raw data, (b, d) force vs. distance curves.

If the sample is rigid, the sphere will eventually jump off the surface to follow again the approaching curve. If the sample is soft, it will move up with the sphere. The contact area generally reduces gradually, and so does the pull-off force till the sphere totally detaches. If the sample is made of polymer chains (or other entities) that attach to the sphere by discrete contact points, the individual detachments of these contacts can be observed as a series of jumps in the force vs. distance curves.

6.3.5. **Hydrodynamic Forces.** When surfaces are driven towards each other, the rate of approach is affected not only by equilibrium forces, but also by the hydrodynamic flow of the fluid between them and the boundary conditions at the interfaces. As a result there is a hydrodynamic drag force acting on the sphere as it moves.

To avoid these spurious forces, one should choose the speed of approach and retraction small enough. As the hydrodynamic force is proportional to the viscosity of the fluid, larger speeds can be used when measuring in air instead of in a liquid.
6.4. Scope of the Second Part of this Thesis

In this second part of the thesis, we study and characterize the build up of supported polyelectrolyte coatings (multilayers) onto flat surfaces and their mechanical properties, having in mind their application as polyelectrolyte capsules. Firstly, in chapter 7, we study the Multilayer Growth Characterization of Polyelectrolye Films by Surface Plasmon Resonance spectroscopy (SPR) and Atomic Force Microscopy (AFM). This characterization is essential to understand the surface properties of these multilayers. Planar supported DNA/poly(allylamine hydrochloride) (PAH) multilayers are compared with standard poly(sodium 4-styrenesulfonate)/poly(allylamine hydrochloride) multilayer films. The conditions of the multilayer growth using semiflexible DNA chains are found to be dramatically different from what was previously observed in the case of flexible polyelectrolytes.

Subsequently we study the interaction/adhesion of these multilayers in chapter 8, using AFM-related force measurements. As in chapter 7, the results given by multilayers made out of typical polyelectrolyes such as poly(sodium 4-styrenesulfonate) and poly(allylamine hydrochloride) is compared with multilayers made using biologically interesting materials like DNA.

List of Abbreviations and Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units [MKS]</th>
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<tbody>
<tr>
<td>( A_H )</td>
<td>Hamaker Constant</td>
<td>[J]</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
<td></td>
</tr>
<tr>
<td>DVLO</td>
<td>Derjaguin, Landau, Verwey and Overbeek</td>
<td></td>
</tr>
<tr>
<td>( D )</td>
<td>Distance</td>
<td>[m]</td>
</tr>
<tr>
<td>( F )</td>
<td>Interaction Force</td>
<td>[N]</td>
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<tr>
<td>( F_{elec} )</td>
<td>Electrostatic Force</td>
<td>[N]</td>
</tr>
<tr>
<td>( F_{vdw} )</td>
<td>Van der Waals Force</td>
<td>[N]</td>
</tr>
<tr>
<td>JKR</td>
<td>Johnson, Kendall and Robert</td>
<td></td>
</tr>
<tr>
<td>( k_B )</td>
<td>Boltzmann Constant</td>
<td>[J K(^{-1})]</td>
</tr>
<tr>
<td>( k_c )</td>
<td>Spring constant of cantilever</td>
<td>[N m(^{-1})]</td>
</tr>
<tr>
<td>( n_0 )</td>
<td>Number density of ions</td>
<td>[-]</td>
</tr>
<tr>
<td>( q )</td>
<td>Electric Charge</td>
<td>[C]</td>
</tr>
<tr>
<td>( R )</td>
<td>Radius of sphere</td>
<td>[m]</td>
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<tr>
<td>SFA</td>
<td>Surface force apparatus</td>
<td></td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>( z_c )</td>
<td>Cantilever deflection</td>
<td>[m]</td>
</tr>
<tr>
<td>( z_p )</td>
<td>Position of the piezo</td>
<td>[m]</td>
</tr>
<tr>
<td>( \kappa' )</td>
<td>Debye Length</td>
<td>[m]</td>
</tr>
<tr>
<td>( \varepsilon_0 )</td>
<td>Dielectric Permittivity of the Vacuum</td>
<td>[C(^2) J(^{-1}) m(^{-1})]</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Relative dielectric Permittivity of the Medium</td>
<td>[-]</td>
</tr>
<tr>
<td>( \psi_0 )</td>
<td>Surface Potential</td>
<td>[V]</td>
</tr>
</tbody>
</table>
References:

We report the preparation and characterization of DNA/poly(allylamine hydrochloride) (DNA/PAH) and poly(sodium 4-styrenesulfonate)/poly(allylamine hydrochloride) (PSS/PAH) multilayer films. The multilayers were constructed on a planar support to examine their layer-by-layer build-up. AFM morphology and roughness studies revealed clear DNA loops and porous morphology at the surface of DNA/PAH multilayers. Surface plasmon resonance spectroscopy showed a non-linear growth of the assembly. While the thickness of the deposited layers was found to be independent of salt concentration, a weak increase of the film thickness with the DNA concentration was detected. The conditions of the multilayer growth were found to be dramatically different from what was previously observed in the case of flexible polyelectrolytes as building blocks (e.g. PSS/PAH) for which a linear growth of the multilayer thickness was found. This suggests that the unique properties of DNA-based supported multilayers reflect the semiflexible character of the DNA molecules.
7.1. Introduction.

The alternated deposition of polycations and polyanions on a charged surface leads to the build-up of films known as polyelectrolyte multilayers [1-4]. These films have received considerable attention during the past decade not the least due to their potential applications in various fields, ranging from nanomechanical composites and electrochemical devices to biomaterial and optical coatings [5]. This has opened a whole new area of surface engineering dealing with coated colloids, polyelectrolyte microcapsules [6-10], and nanotubes [5, 11, 12]. Recently it appeared particularly interesting to make these multilayers with DNA as polyanions to take advantage of the biological functionality of this polyelectrolyte. In viruses and cells, DNA is organized in tightly packed structures [13]. Much research has been carried out to get insight into the mechanism of condensation and aggregation of DNA [14, 15]. This can be induced by a variety of positive ions, which could interact electrostatically with the oppositely charged phosphate groups on the DNA backbone. DNA molecules are indeed known to form complexes with multivalent cations [16], linear polycations [17, 18], cationic dendrimers [19-22], proteins [23, 24], colloidal particles [25, 26] and lipids [27, 28]. Most of the cationic agents forming these complexes and aggregates are potentially useful as DNA vectors in novel gene therapies. The past few years have seen a rapid development of effective non-viral drug delivery systems [29], and several DNA systems have been employed for gene delivery applications [30]. In this context, DNA-containing multilayer films on colloidal particles [31] or microcapsules filled with DNA [32] might also be considered as promising gene therapy carriers. Another strategy might take advantage of using DNA-containing multilayer micro-shells or so-called “hollow” polyelectrolyte multilayer microcapsules.

To get to understand under which conditions these DNA-containing multilayers can be build and what their actual structure is, we focus in this chapter on the build-up of ultrathin multilayer films composed of layers alternating DNA and poly(allylamine) hydrochloride (PAH) supported by a planar substrate. The multilayer growth study will be done by means of Surface Plasmon Resonance Spectroscopy. Several dependences will be studied such as the concentration of DNA and the effect of electrolyte concentration on the DNA solution. The morphology of the multilayers will be examined by means of Atomic Force Microscopy.

These results provide the necessary information to prepare DNA/synthetic polyelectrolyte multilayer microcapsules, exploiting electrostatic interactions [33]. To date, multilayer microcapsules were made of oppositely charged synthetic linear polyelectrolytes [34], polyelectrolyte/inorganic nanoparticles [35], polyelectrolyte/dye [36] and polyelectrolyte/dendrimer [37-39] pairs. Multilayer microcapsules containing DNA as a building block represent a new system of special interest. Moreover, the results of this growth
characterization will help us to understand the interaction and adhesion properties of these multilayers, studied in chapter 8.

7.2. Experimental.

7.2.1. Materials. The polyelectrolytes used for the preparation of the self-assembled films were poly(ethylenimine) (PEI, 50 % w/v, $M_w \approx 1.2$ kg/mol), poly(allylamine hydrochloride) (PAH, $M_w \approx 70$ kg/mol) as polycations, and poly(sodium 4-styrenesulfonate) (PSS, $M_w \approx 70$ kg/mol) and deoxyribonucleic acid (DNA double helix, $M_w \approx 6.000$ kg/mol, sodium salt, from calf thymus) as polyanions (figure 7.1). All were purchased from Sigma-Aldrich Chemie GmbH (Germany) and were used as received. No additional buffers were added to the polyelectrolyte solutions to adjust the pH value. NaCl was purchased from Aldrich (purity > 99 %). 3-mercaptopropionic acid (3MPA) was purchased from Aldrich. The ultrapure water used in all experiments was obtained by using a commercial Milli-Q system containing ion-exchange and charcoal stages and had a resistivity higher than 18 MΩ/cm.

Figure 7.1. Chemical structures of PAH, PSS, branched PEI and the double DNA helix.

7.2.2. Sample Preparation. Substrates for Surface Plasmon Resonance (SPR) measurements consisted of a gold layer with a thickness of 50 nm thermally evaporated on high refractive index (n=1.8) LaSFN9 (Hellma Optik GmbH, Germany) substrates. The gold film was functionalized by a self-assembled monolayer of 3-mercaptopropionic acid (3MPA), by immersing the substrates in a 0.03 mol/l solution of 3MPA for 24 hours. Such a modified surface is negatively charged in water due to the dissociation of the carboxylic
groups belonging to the 3MPA. The multilayer deposition of polyelectrolytes was conducted in a teflon flow cell, attached to the sample surface allowing measurements in solution. Briefly, the appropriate polymer solution was injected into the flow cell and a certain time (10 min) for deposition was allowed. Then the sample was washed with a sufficient volume of Milli-Q water and a SPR scan was performed. At least three measurements, at different positions on the surface of the sample, were done after the deposition of each layer, to check the homogeneity of the growth.

For imaging by Atomic Force Microscopy (AFM), the multilayers were assembled on microscope glass slides (76×26 mm², Menzel-Glaser, Germany). They were cleaned following a two step procedure. The first step included cleaning in a piranha solution, i.e. submerging the slides under a 3:1 (vol %) mixture of sulfuric acid and hydrogen peroxide at least 20 minutes at 80ºC to remove organic residues from substrates. The second step was performed according to the RCA protocol [40], and included immersion in 5:1:1 (vol %) H₂O/H₂O₂/NH₃ mixed solution at 80 ºC for ca. 15 min. and followed by extensive rinsing with Milli-Q water. After this cleaning procedure the slides were completely hydrophilic. In all experiments, a prelayer of PEI was adsorbed on the glass substrate by immersion (30 min.) into a 1.0 mg/ml aqueous solution of PEI. After adsorption, the films were rinsed by dipping them three times for 5 min. each in Milli-Q water.

Multilayer films were formed on the PEI-coated glass substrates by sequential deposition of polyanions and polycations. All polyelectrolyte solutions, except DNA, were prepared at a concentration of 1 mg/ml and containing 0.5 M NaCl. The adsorption of DNA was performed from 0.5 mg/ml solutions and also containing 0.5 M NaCl [31]. The samples were manually dipped into the polyelectrolyte solutions for 20 min. (PSS/PAH film) and 40 min. (DNA/PAH film) each. After rinsing with water three times for 5 min. each, the multilayer was dipped into the solution of polyelectrolyte with opposite charges immediately without drying [41].

### 7.2.3. Surface Plasmon Resonance Spectroscopy

A home built Surface Plasmon Resonance Spectrometer (SPR) was used for the thickness measurements of the multilayer films deposited on a plane surface (see figure 7.2). The sample is attached to the base of a glass prism (Hellma Optik GmbH, Germany) optically matched by index matching oil (Winopal Forschungsbedarf GmbH, Germany) in a Kretschmann configuration. A beam of a HeNe Laser (λ=632.8 nm, JDS Uniphase Corporation, USA) with transverse-magnetic polarization (p-polarization) is directed through the prism. The angle θₑₓ of the incident beam relative to the surface normal is adjusted by rotating the prism. Collection of the reflected light with a photodiode (PD) mounted on a second, co-linear goniometer, allows for angle-resolved reflectivity measurements [42] (figure 7.3).
The optical thickness and refractive index of each layer in the sample was obtained by fitting the reflectivity curves with a “Winspall” software based on the Transfer Matrix Evaluation Method. Since these two quantities cannot be uniquely determined by this method, one of them must be measured by an independent method. The refractive index of the polyelectrolyte layers was assumed to be 1.54, based on a previous work [43] where the refractive index of PAH/PSS multilayer system was determined by SPR as the thickness was measured by Small Angle X-ray Reflectivity. Similar values for the refractive index of PAH/PSS multilayers system were found by others [44].
7.2.4. Atomic Force Microscopy Imaging. The morphology and roughness of the multilayer was analyzed by Atomic Force Microscopy (AFM), with a Nanoscope IIIa (Digital Instruments). AFM measurements were performed in air using tapping mode working with commercial silicon cantilevers (Olympus Inc., spring constant of 42 N/m and tip radius < 10nm).

7.3. Results and Discussion.

7.3.1. Multilayer Growth. The DNA/PAH multilayers were constructed using different DNA concentrations in the primary solutions. The concentration of PAH is set to 1.0 mg/ml with 0.5 M NaCl and the concentration of NaCl in DNA is fixed to 0.5 M NaCl. Figure 7.4 shows the equilibrium optical thickness of the film as a function of the number of the deposition cycles. The majority of previous experiments using DNA have shown a regular linear growth of the film [44]. A clear non-linearity is, however, seen for the DNA/PAH combination. The curve appears linear only at higher layer numbers.

The data presented in figure 7.4 show a weak increase in thickness with the concentration of DNA in the chosen interval. Higher concentrations of DNA were not explored due to a very high viscosity of more concentrated DNA solutions. Since the use of a concentration of 0.5 mg/ml provides nearly the maximal film thickness and since this concentration gives a solution with a low viscosity, we have chosen this concentration of DNA for further studies.

![Figure 7.4. Equilibrium optical thickness of a DNA/PAH film assembled from solutions of different DNA concentrations as a function of deposited layers. Odd layers are from PAH. Even layers are from DNA.](image-url)
Fixing the concentration of PAH to 1.0 mg/ml with 0.5 M NaCl and the concentration of DNA to 0.5 mg/ml as mentioned above, the same experiment was repeated changing the concentration of NaCl in the DNA solutions. **Figure 7.5.** shows the equilibrium thickness of the different assembled multilayers. In contrast to all systems studied before [42, 45, 47], we find here that the thickness of the DNA/PAH multilayer films immersed in water does not depend on the amount of salt in the original DNA solutions. Below we use a concentration of 0.5 mol/l of NaCl, as commonly accepted for other polyelectrolyte solutions.

![Figure 7.5.](image)

**Figure 7.5.** Equilibrium optical thickness of a DNA/PAH film assembled from solutions of different NaCl concentrations as a function of deposited layers. Odd layers are from PAH. Even layers are from DNA.

We have also compared the equilibrium optical film thickness of PSS/PAH and DNA/PAH multilayers as a function of layer numbers. Both films were assembled on a PEI prelayer (figure 7.6). The thickness of the first deposited bilayer was found to be the same for PSS/PAH and DNA/PAH films. The clear linear growth of the assembly in the case of a PSS/PAH system suggests similar adsorption properties of both polyelectrolytes. The thickness of PSS monolayer is found to be roughly 2 nm and of PAH monolayer about 1.5 nm. These results are in agreement with previous studies performed with different techniques [48, 49].
Figure 7.6. Equilibrium optical thickness of the PSS/PAH and DNA/PAH multilayers. The concentration of the aqueous polyelectrolyte solutions were all 1 mg/ml except for DNA (0.5 mg/ml) with the NaCl concentration of 0.5 M. The solid line represents the best polynomial (2nd order) fit and the dashed line a linear fit through the data of DNA/PAH after the 5th layer.

Finally, one feature is interesting to note in the kinetics of deposition of PAH on a DNA-based film (figure 7.7). In contrast to previous SPR measurements on adsorption of PAH on a PSS/PAH film, where the adsorption resulted in an abrupt increase in reflectivity followed by a horizontal plateau, here the true plateau regime was often established after 30 min or more, although the main jump in reflectivity was as fast as before. This might indicate that the adsorption of PAH cause some slow conformational changes in the underlying DNA layer.
Figure 7.7. Time dependence of the reflectivity for an incidence angle $\theta_e = 62^\circ$ during the deposition of the third monolayer of PAH for different concentration of DNA solutions.

7.3.2. Morphology and Roughness of the Multilayer Films. To investigate more closely the changes in the surface morphology and roughness during the multilayer build-up, we have taken AFM images of multilayers. DNA/PAH films always had a highly porous morphology (figure 7.8a and 7.8b). In contrast, a homogeneous coating with low roughness was observed in the case of PSS/PAH multilayers (figure 7.8c and 7.8d). An outer DNA layer always contained large domains of parallel oriented elongated “hills” similar to what was previously observed on colloidal spheres coated by DNA/PAH films [33].

Figure 7.8. AFM images of (a) PEI-(DNA/PAH)$_2$-DNA, (b) PEI-DNA-PAH, (c) PEI-(PSS/PAH)$_2$-PSS and (d) PEI-PSS-PAH multilayers. The sample was assembled without drying and measured in air. The scan area is 1$\mu$m×1$\mu$m.

The Root-Mean-Square (RMS) roughness for DNA/PAH and PSS/PAH multilayers is shown in figure 7.9 as a function of the number of deposited layers. The changes in roughness are much more significant in the case of
DNA/PAH films, especially after two bilayers. The RMS roughness is larger for an outer DNA layer, than for the preceding and subsequent PAH layers. This indicates that PAH adsorbs into the “valleys” between “hills” formed by ordered DNA loops and is in agreement with the SPR results. An interesting observation is that the roughness increases with the number of bilayers. In contrast, there are little roughness changes with the layer number for PSS/PAH films. The RMS value is of the same order of magnitude as that for bare glass. Also, no dependences of RMS on the polyelectrolyte charge and/or layer number was observed for PSS/PAH films under the present assembly conditions.

**Figure 7.9.** Root Mean Square roughness of PSS/PAH film and DNA/PAH multilayer estimated from AFM height images.

7.3.3. **Conformation of DNA Chains.** For the chosen DNA and NaCl concentration, the bilayer thickness in the quasi-linear regime (after 5 layers) is found to be approximately equal to 8-10 nm. Here, the thickness of a DNA monolayer \( \delta \) is \(~6-8\) nm and that of a PAH monolayer is \(~2-3\) nm. Thus, in contrast to the case of PSS/PAH self-assembled films (see section 7.3.1), the steps of growth for DNA are much bigger that the ones for PAH. Previous measurements of the thickness of DNA/PAH multilayers reported a smaller monolayer thickness [50, 51]. This is likely due to the use of more diluted solutions of DNA and NaCl. Another reason could be that in references [50] and [51] the thickness of dried films was studied, while we are measuring multilayers immersed in water.

The cross section of the DNA double helix is \(~2\) nm [52]. The measured thickness \( \Delta \) of the DNA layer in the film corresponds therefore to 3-4 diameters of the DNA, but it is much smaller than the persistence length of DNA \( \lambda_p \sim 50 \) nm. It has been previously suggested that the high molecular
weight semiflexible DNA molecules can form surface (vertical) loops during
the adsorption [42] (figure 7.10). Both the DNA layer thickness and the AFM
images of DNA upper layers are in agreement with this concept.

We note that the contour length \( L \) of DNA chains (~3 \( \mu \text{m} \)) is much bigger than
the persistence length: \( L >> \lambda_p \). In this case DNA chains are known to form
loops in bulk DNA solutions [53]. The radius of bulk DNA coils is given by
\( R_{\text{DNA}} \sim \lambda_p^{1/5} \kappa^{-1/5} L^{3/5} \) [54], where \( \kappa^{-1} \) is the Debye screening length and is roughly
equal to 300-400 nm for a system in pure water [55]. This gives \( R_{\text{DNA}} \sim 800 \text{ nm} \).
This means that the DNA coils present in the bulk of the solution need to
unfold during the adsorption. Considering the length of \( R_{\text{DNA}} \), the surface loops
are not likely to have intramolecular intersections. The distance between two
closest contacts of DNA molecules with the support, the so-called deflection
length \( \lambda \), can be evaluated as \( \lambda \sim \delta^{2/3} \lambda_p^{1/3} \) [56], which gives ~15 nm.

\[ \delta \]
\[ \lambda \]

**Figure 7.10.** Schematic picture of a DNA chain forming vertical in a layer when the
persistence length is larger than the layer thickness \( \delta \). \( \lambda \) is the deflection length.

An increase of the thickness of the DNA layer is observed as the layer
number increases. This almost likely indicates that DNA may take different
configuration with the growing of the multilayer. While the first DNA layer
may form horizontal loops (i.e. lie flat on the surface) to maximize the contact
with the substrate [57], the next DNA layers form vertical loops. It has
however also been suggested that the smaller layer thickness observed for the
first layers is actually due to an insufficient charged substrate, leading to the
deposition of less DNA and PAH in the first layers [58].

Since the DNA monolayer thickness (5-6 nm) is much larger than the PAH
monolayer thickness (1-3 nm), one could speculate that PAH molecules, due
to their flexibility, adsorb mostly into “valleys” in between the DNA loops.
The kinetics of adsorption of PAH layers, which reaches only slowly the
equilibrium thickness (see section 7.3.1), is also in agreement with this idea:
this intermixing of PAH with the DNA is likely to require some
rearrangement of the DNA chains, which is a rather slow process with
respect to the adsorption itself.
7.4. Conclusions.

We have demonstrated the successful formation of DNA/PAH multilayer films on planar substrates and have studied the morphology of these films. The Surface Plasmon Resonance results show a linear and non-linear film growth for PSS/PAH and DNA/PAH multilayers, respectively. There is no effect of the salt concentration of the DNA solution on the deposition, and only little effect of the DNA concentration. AFM morphology and roughness studies reveal homogeneous film surfaces for PSS/PAH and clear DNA loops and a porous morphology for DNA/PAH multilayer surfaces.

The conditions of the multilayer growth were found to be dramatically different from what was previously observed in the case of flexible polyelectrolytes as building blocks. This suggested that the unique properties of DNA-based supported multilayers reflect the semiflexible character of the DNA molecules.

List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units [MKS]</th>
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<td>Dsoxyribonucleic acid</td>
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<td>$L$</td>
<td>Contour length</td>
<td>[m]</td>
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<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
<td>[kg mol$^{-1}$]</td>
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<td>$n$</td>
<td>Refractive index</td>
<td></td>
</tr>
<tr>
<td>PAH</td>
<td>Poly(allilamine hydrochloride)</td>
<td></td>
</tr>
<tr>
<td>PD</td>
<td>Photodiode</td>
<td></td>
</tr>
<tr>
<td>PEI</td>
<td>Poly(ethylenimine)</td>
<td></td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(sodium 4-styrenesulfonate)</td>
<td></td>
</tr>
<tr>
<td>$R_{\text{DNA}}$</td>
<td>Radius of bulk DNA coils</td>
<td>[m]</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
<td></td>
</tr>
<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance spectroscopy</td>
<td></td>
</tr>
<tr>
<td>3MPA</td>
<td>3-mercaptopropionic acid</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>Thickness of DNA monolayer</td>
<td>[m]</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Debye screening length</td>
<td>[m]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Deflection length</td>
<td>[m]</td>
</tr>
<tr>
<td>$\lambda_p$</td>
<td>Persistence length of DNA</td>
<td>[m]</td>
</tr>
<tr>
<td>$\theta_{\text{ex}}$</td>
<td>Incidence beam</td>
<td>[°]</td>
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The interaction and adhesion properties of supported poly(sodium 4-styrenesulfonate)/poly(allylamine hydrochloride) (PSS/PAH) and DNA/PAH multilayers were investigated by means of force measurements with an atomic-force-microscopy-related device. Multilayers were assembled on a pre-layer of poly(ethylenimine) both with and without drying between each layer deposition. Measurements of forces acting between a bare glass sphere and a multilayer have revealed repulsive or attractive forces, depending on the surface charge. This indicates that, upon approach, electrostatic forces dominate. Upon retraction we have observed large pull-off forces in the case of positively charged multilayers, and weak or no pull-off forces in case of negatively charged multilayers. Multiple adhesions and plateau regions observed upon retraction were interpreted in terms of a bridging between the glass particle and the multilayer by multiple polymer chains, and a stretching of the polyelectrolyte loops. The dependence of the pull-off force on the number of deposited layers shows regular oscillations, especially when the multilayers were dried after the deposition of each other, revealing the regularity of the multilayer structure.
8.1. Introduction.

Despite numerous publications on the assembly and characterization of the polyelectrolyte multilayers, information about interaction and adhesion properties of multilayer-coated surfaces is to date rather scarce. There have been only a few publications focusing on the subject [1-5]. Nearly all of them focused on the interaction properties of poly(styrenesulfonate)/poly(allylamine hydrochloride) (PSS/PAH) multilayers [6-8]. These multilayers are known to grow linearly with the number of deposition steps [9] (see also section 7.3.1), and their structure is often assumed to be stratified [10].

Direct force measurements on these systems have first been performed with the interferometric surface force apparatus (SFA) technique [11]. Although these experiments have tried to explain some questions concerning the interaction behavior of PSS/PAH multilayers, there have been some limitations. In contrast to the commonly used conditions of multilayer assembly [12], the multilayers reported by Lowack et al. [1] were prepared from diluted polyelectrolyte solutions with low ionic strength. This research was recently extended into studying the PSS/PAH multilayers deposited in more standard conditions [2]. Both interferometric SFA and non-interferometric surface forces apparatus [11] have been used. The number of adsorbed monolayers was limited to two [1] or four [2], so that this should be considered as a precursor, but not a true multilayer, and the results of both publications might strongly be influenced by the substrate (mica and/or glass). Indeed, an atomic force microscope (AFM) study [3] suggested that the true PSS/PAH multilayer regime, where the influence of substrates disappears, corresponds to a least six deposited layers. This is in agreement with a recent interferometric SFA study [4] of the interaction and adhesion properties of PSS/PAH multilayers performed with films consisting of eight or nine polyelectrolyte monolayers, which led to results different from early publications [1, 2]. Beside this research focused on PSS/PAH films, the interaction between exponentially growing poly-(L-glutamic acid)/poly-(L-lysine) multilayers have been studied with the interferometric SFA technique [5].

In this chapter we study the interaction between a bare glass sphere with multilayer-coated glass surfaces. This experimental configuration is different from all previous studies, where both surfaces were coated by polyelectrolyte films [1-5]. Both the commonly used PSS/PAH multilayers and similarly prepared DNA/PAH multilayers were studied by force measurements. Since all previous publications on the subject have dealt with flexible polyelectrolytes, the work presented in this chapter represents most probably one of the first attempts to study and compare the interaction/adhesion properties of multilayers based on flexible polyelectrolytes (PSS/PAH) and a semi-flexible polyelectrolyte (DNA). The clear non-linearity of the film growth
we found for DNA/PAH multilayers (see chapter 7) also makes them different from linearly [2-4] and exponentially [5] growing films. In the present work we have measured the interaction and adhesion properties for systems consisting of up to five bilayers of polyelectrolytes, which allows us exploring both the “pre-cursor” and the real “true” multilayer regimes. We also address the issue of the influence of drying on the properties of multilayers: the films we study here are assembled both with and without drying after each layer deposition.

8.2. Experimental

8.2.1. Sample Preparation. We have used the same materials as in chapter 7 (see section 7.2.1.), following the same procedure for multilayer preparation as for the samples for AFM imaging (section 7.2.2). The only difference is that some multilayers were dried in air after the deposition of each layer.

8.2.2. Force-Distance Curve Measurements. The interaction and adhesion properties of the multilayers were studied with a home-made AFM-related setup (figure 8.1) described in details before [8, 13, 14]. Briefly, glass substrates coated with polyelectrolyte multilayers were placed onto the bottom of a Teflon cuvette. The Teflon cuvette was filled with Milli-Q water. To measure the force curves, the cuvette was moved vertically towards the cantilever with a 12 µm range piezoelectric translator (Physik Instrumenten, Germany). This translator is equipped with integrated capacitance position sensors, which provides measurements of their actual position and further adjustment of piezo movement. This feature leads to an accuracy of 0.005 %, which means that for a piezo travel of 12 µm the maximum error is 0.6 nm. During the movement the deflection of the cantilever was measured with an optical lever technique. For this, the light of a laser diode (3 mW, 670 nm) was focused onto the back of the gold coated cantilever using microfocusing optics (the spot diameter is about 8 µm). After reflection of the beam on the cantilever and another mirror, the position of the reflected laser spot was measured with a two-dimensional position sensitive detector (SiTek, Sweden, active area 2×2 cm²).

Dry borosilicate glass microspheres of radius 10±1.0µm (Duke Scientific Corporation, Palo Alto, California, USA) were glued onto the apex of tipless V-shaped cantilevers (NanoProbes™, Santa Barbara, USA), using epoxy glue (UHU plus, Germany). The spring constant of the cantilever (0.58 N/m) was calculated from the thermal noise power spectra measured in a Molecular Force Probe 1D (Asylum Co, Santa Barbara, USA). All force-distance measurements were done at the driving speed of 200 nm/s to avoid the influence of hydrodynamic drag forces [15, 16]. The results will be reported as normalized force \( F/2\pi R \) or \( F/R \) vs. distance \( D \) where \( F \) is the force applied on
the cantilever as deduced from its deflection (see section 6.2), and $R$ is the microsphere radius.

Figure 8.1. The AFM-related setup used for force measurements.

8.3. Results and Discussion

8.3.1 Force-Distance Profiles. To study the interaction and adhesion properties of the multilayers, force-distance curves were measured after the deposition of each monolayer. Figure 8.2 shows two typical force-distance curves for (PSS/PAH)$_2$-PSS and (PSS/PAH)$_3$ multilayers assembled with drying steps in the deposition cycle. It can be seen that when the outer layer is formed by polyanions (PSS), the forces are repulsive. There is no hysteresis between forces measured on approach and retraction, and no pull-off force was detected. This confirms that the multilayer is negatively charged due to the overcompensation of the surface charges of the underlying assembly by the last monolayer deposited [17]. When the outer layer is formed by polycations (PAH), the approach curves show a long range attraction (up to 100 nm away from the surface). This is likely caused by strong electrostatic attractive forces between the negatively charged glass particle and the positively charged multilayer. Since the interacting surfaces are separated by pure water, the Debye screening length over which electrostatic interactions decay is indeed expected to be of the order of 100nm (see section 6.3.2).
In the retraction curve, strong adhesion with a saw tooth pattern is observed (dashed lines in figure 8.2b). The range of the adhesion force is above 600 nm, which is much larger than the contour length of PAH (187 nm) and PSS (91 nm) [18]. Therefore, the multiple adhesions can be attributed to a bridge between the particle and the multilayer, formed by entangled PAH and PSS chains, as depicted in figure 8.4a. The detachment of the different polymer chains leads to the saw-tooth pattern of the retraction curve. A similar effect was observed during the extention of fused phospholipid bilayers [19]. An important point to note is that the multiple adhesion is only observed in the
case of an outer PAH layer, which indicates that the adsorption of the positive charges present on the PAH chains on the negatively charged glass particle is essential for this kind of the multiple chain bridges. All the other curves measured with different numbers of layers in the film have the same characters, although the values of pull-off forces vary.

**Figure 8.3** shows the typical force-distance curves obtained for DNA/PAH multilayers assembled with drying. If the outer layer was formed by DNA, the force-distance curves always show an electrostatic repulsion force on approach reflecting the negative surface charge of the multilayer. Nevertheless there could be a small attraction close to contact. Besides, the concave shape of the curve after contact suggests that the film is soft. This can be expected if the upper DNA layer is made of vertical loops, as the results of chapter 7 suggest (see section 7.3.3). These loops are very likely compressible.

![Figure 8.3](image-url)

**Figure 8.3.** Force-distance curves for the multilayer of PEI-(DNA/PAH)$_2$-DNA and PEI-(DNA/PAH)$_3$ assembled with drying. The dashed lines indicate the plateau regions in the retract curves.
This observation is different from what we had for PSS/PAH multilayers, where the straight line after contact indicates a rigid surface. In the retract curve, in the case of a DNA upper layer, an attractive force is observed with some plateau regions as indicated by the dashed lines (figure 8.3a).

If the outer layer was formed by PAH, we have observed strong attractive forces on approach. However, they were of much shorter range than in case of PSS/PAH multilayers. One could speculate that this is connected with the lower surface charge density. The retract curves always show a large single adhesion peak. The range of the pull-off force is ca. 600 nm. This value exceeds the contour length of PAH, but is well below the contour length of DNA (which is ca. 3 \( \mu \)m). This pull-off force is likely due to a partial detachment of one DNA chain from the multilayer, connected to the glass sphere by one PAH chain (figure 8.4b).

![Figure 8.4](image)

**Figure 8.4.** Schematic illustration of the bridges formed between the glass particle and a (PSS/PAH)_n multilayer (a) and a (DNA/PAH)_n multilayer (b).

Similar measurements were performed with the multilayers assembled without drying and similar trends were observed in the results. As a rule, the picture was qualitatively the same except for the first PSS layer, where we sometimes have seen attractive force on approach. This is probably due to some heterogeneity in the surface charge.
8.3.2. Adhesion Forces. As described qualitatively above, the force-distance curves are different for positively and negatively charged multilayers. Figure 8.5. shows the pull-off force, defined as the minimum of the retraction curve, as a function of the deposited layer number for PSS/PAH multilayers. The data include the measurements performed with the multilayers assembled both with and without drying. Every point represents an average of several (minimum four) values of the pull-off force. The error bars show the standard deviation over these values. We observe both similarities and differences between multilayers deposited with and without drying. In the case of multilayers assembled with drying, regular oscillations in the pull-off force with increasing layer number are observed. No pull-off forces are observed when PSS made the outer layer, while a discernible adhesion is found when PAH served as an outer layer. For the multilayers assembled without drying, some irregularities are observed for the first few monolayers in the alternation of low and high pull-off force. One can conclude that the assembly with drying allows creating a more regular multilayer structure.

Figure 8.5. Pull-off forces for deposited PSS/PAH multilayers assembled with and without drying. The error bars represent the spreading of the data obtained from different areas in the sample.
Figure 8.6. shows the pull-off forces measured for DNA/PAH multilayers as a function of the number of layers. We again observe a regular oscillation of pull-off forces. Much stronger adhesive forces are however observed in the case of positively charged DNA/PAH multilayers than for positively charged PSS/PAH. Moreover, the pull-off forces increase with the layer number. We note that the scatter in the pull-off force data is much larger in the case of PAH as an outer layer, especially in the case of the assembly without drying. This can again be expected if the upper PAH layer is entangled with the underlying DNA layer (see section 7.3.3), as heterogeneities in the surface charges can then easily appear.

Figure 8.6. Pull-off forces for deposited DNA/PAH multilayers assembled with and without drying. The error bars represent the spreading of the data obtained from different areas in the sample.

8.4. Conclusions.

The interaction and adhesion properties of PSS/PAH and DNA/PAH multilayers with a glass sphere were studied in this chapter. Electrostatic repulsion and attraction were observed on the approaching force-distance curves for polyanion and polycation surfaces, respectively. The retraction
curves show weak adhesion forces on the negatively charged surfaces and strong adhesion on the positively charged surfaces. These features indicate that the surface charges were overcompensated by the last polyelectrolyte layer deposited and that the electrostatic interactions dominate the surface forces.

The shape and range of adhesion forces with PAH upper layers suggest that in the case of PSS/PAH assemblies a bridge of entangled PSS and PAH chains forms between the multilayer and the glass sphere. In the case of DNA/PAH assemblies, it is probably a single DNA chain attached to the glass via a PSS chain that forms the bridge.

The pull-off force variation as the multilayer grows, shows regular oscillations between positive and negative charged surfaces although irregularities were observed for the films assembled without drying. Assembly without drying might lead to a heterogeneous surface charge distribution and, therefore, to large deviations in the measured pull-off forces, while assembly with drying allows creating a more regular multilayer structure.

List of Abbreviations and Symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units [MKS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
<td></td>
</tr>
<tr>
<td>DNA</td>
<td>Desoxyribonucleic acid</td>
<td></td>
</tr>
<tr>
<td>F/(2\pi R)</td>
<td>Normalised force [Force/Particle Radius] [Nm⁻¹]</td>
<td></td>
</tr>
<tr>
<td>PAH</td>
<td>poly(allilamine hydrochloride)</td>
<td></td>
</tr>
<tr>
<td>PEI</td>
<td>poly(ethylenimine)</td>
<td></td>
</tr>
<tr>
<td>PSS</td>
<td>poly(sodium 4-styrenesulfonate)</td>
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<tr>
<td>SFA</td>
<td>Surface force apparatus</td>
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</table>

References:


APPENDIX
APPENDIX A: Spin-coated Polystyrene Films: Thickness-Concentration Relationship.

The thickness of PS ($M_w=178$ 000 Dalton) films spin coated from solutions in toluene with different concentrations on unstriped Si (100) has been reported in the literature, as measured by ellipsometry [1] (see figure A.1). The solutions were spin-cast at 2500 rpm for 30s as for the films we have used.

![Figure A.1. Film thickness of spin-cast PS films vs concentration in toluene, as determined by ellipsometry [1].](image)

We have imaged PS films spin-cast on quartz substrates by means of Atomic Force Microscopy. The films were mostly continuous although some pinholes were observed in the thinnest films (see figure A.2). Studying the profile of these defects, we checked the thickness of the films finding almost no deviations from the values given in figure A.1.
Figure A. 2. AFM pictures of defects found in the thinnest films (a and c); (b) and (d) show the cross sections of the defects in the films.

References to Appendix A

APPENDIX B: Mass transport limitations in porous substrates.

To evaluate the possible limitations to the mass transport in the porous alumina substrates we have used in permeation experiments (see chapter 5), we should address two critical issues: the possible capillary condensation in the pores and the limitations to transport in meso- and macropores.

B.1. Capillary Condensation. This effect could occur in the alumina mesopores under the polymer film. The pore size of the γ-alumina layer is ~4 nm or larger. We can calculate the Kelvin radius of the pores that will get filled with water using the Kelvin equation:

\[
r_k < \frac{-\gamma_{sw} V_m}{RT \ln(p_v / p_v^0)}
\]  

[1]

In this equation, \( r_k \) is the largest pore radius that will still be filled, \( \gamma_{sw} \) is the surface tension of water (73 mN/m), \( V_m \) the molar volume of water (18·10^{-6} m³/mol), \( R \) is the gas constant (8.31 J K^{-1} mol^{-1}), \( T \) is the temperature and \( p_v/p_v^0 \) the relative pressure of water: actual pressure \( p_v \), divided by saturation pressure \( p_v^0 \) at temperature \( T \) (pressure at the feed side). We can estimate what would occur at high and low temperatures.

At high temperatures, for instance \( T = 70 \, ^\circ\) C, then \( p_v = 311.57 \, \text{mbar} \) (roughly 31150 N/m²). At the permeate side (vacuum) we have a pressure of ~20 mbar so \( p_v/p_v^0 = 0.065 \), then \( r_k = 1.6 \, \text{Å} \). The size of the pores in the γ-alumina is significantly larger (> 4nm), so under these conditions no condensation will occur. At lower temperatures the situation might be different, because \( p_v^0 \) decreases substantially. For instance, taking \( T = 28 \, ^\circ\) C, where \( p_v^0 = 39 \, \text{mbar} \), and \( p_v = 20 \, \text{mbar} \), we have \( p_v/p_v^0 =0.5 \); then \( r_k = 7.6 \, \text{Å} \). No condensation will occur under these conditions either.

In reality, however, the situation is more complicated because of two main reasons: firstly we are not measuring under equilibrium conditions, where the Kelvin equation is strictly speaking valid. In our particular case there are net flows, forces, etc. These particular effects help to keep pores open that would otherwise (in equilibrium situation) be flooded because of capillary condensation. The other reason is that near the polymer film/γ-alumina interface, the local pressure of water may be higher. For instance when \( p_v/p_v^0 \) would be 0.9 there, we would have condensation already in pores of 10 nm or larger. However this is rather unlikely.

B.2. Transport in Meso- and Macropores. The second question to be answered is if the removal of water from the meso- and macropores occurs fast enough to prevent the occurrence of a “stagnant” layer somewhere in the porous support through which water diffuses more slowly.
The transport through a stagnant layer (a very common problem in engineering) can be described by Fick’s first law:

\[
J = -D \frac{dc}{dx} = -\frac{D}{RT} \frac{dp}{dx}
\]  

[2]

where \( c = \frac{n}{V} = \frac{p}{RT} \) and \( D \), the diffusion coefficient, can be estimated from kinetic gas theory: \( D \sim \frac{v \lambda}{3} \), where \( v = \sqrt{\frac{8RT}{\pi M}} \) is the molecular speed of the water molecules. For water at \( T = 300 \text{ K} \), \( v \sim 600 \text{ ms}^{-1} \). The parameter \( \lambda \) is the mean free path between intermolecular collisions:

\[
\lambda = \frac{\bar{c}}{z} = \frac{k_B T}{\sigma \sqrt{2} p}
\]  

[3]

Here \( \sigma \) is the collision cross-section and \( p \) the pressure. Considering water as a small molecule we can approximate \( \sigma_{H_2O} \sim \sigma_{He} \) (0.21 nm²). Let us assume that we are at saturation. This means that at \( T = 300 \text{ K} \) then \( p \sim 40 \text{ mbar} \). This would give a mean free path \( \lambda = 3.5 \mu \text{m} \) and a diffusion coefficient of \( D = 7 \cdot 10^{-4} \text{ m}^2/\text{s} \). So \( D/RT \sim 2.8 \cdot 10^{-7} \text{ m}^2/(\text{s J mol}^{-1}) \).

Since the water is moving through a porous medium with a porosity \( \varepsilon < 1 \) and a tortuosity \( \tau > 1 \), the effective diffusion coefficient is smaller than the coefficient in free air, and has to be corrected. For \( \gamma \)-alumina we estimate that \( \varepsilon = 0.55 \) and \( \tau \sim 5 \). This would give: \( (D\varepsilon)/(RT\tau) \sim 2.8 \cdot 10^{-8} \text{ m}^2/(\text{s J mol}^{-1}) \). The factor \( (D\varepsilon)/(RT\tau) \), which expresses essentially a permeability, has to be compared with the permeability of the films.

The value of \( (D\varepsilon)/(RT\tau) \) is \( 3.6 \cdot 10^{-7} \text{ s J / (mol m}^2) \). The maximum film permeability \( P \) that we find in our data is \( \sim 3 \cdot 10^{-14} \text{ m}^3 / (\text{m}^2 \text{ s Pa}) \). Converting the \( \text{m}^3 \text{ H}_2\text{O} \) to moles \( \text{H}_2\text{O} \) leads to \( P = 15 \cdot 10^{-10} \text{ mol m} / (\text{m}^2 \text{ s Pa}) \). This is (at least) 2 orders of magnitude lower than the permeability of the porous layer for gas diffusion. Since \( (D\varepsilon)/(RT\tau) \) is much larger than the permeability of the films, the resistivity effect due to a “stagnant” layer is negligible: water is transported quickly away from the polymer/\( \gamma \)-alumina interface.

So in conclusion **no capillary condensation will occur**, so no liquid transport, but only vapor transport. And vapor transport is much faster than in the polymer film, so we can neglect its resistive effect.
Summary

Electronic devices, coatings, displays, sensors, optical equipment, and numerous other technologies all depend on the deposition of thin films. A very particular type of thin films is polymer thin films. The behavior of polymers in thin films or close to interfaces is far from being understood. Many observations, encompassing both structural and dynamical behavior, indicate that the properties of polymers in thin films deviate from what we know from the studied done in bulk. Questions about the density, film stability and de-wetting, glass transition temperature, diffusion coefficient and chain conformation and relaxation are intensively debated. The piece of experimental work presented here tackles open issues concerning two different types of thin polymer films: glassy polymers and polyelectrolytes.

In the case of glassy materials where we have studied the effect of guest molecules, from several perspectives: solvent evaporation and retention after film formation, solvent absorption, and finally transport of guest molecules across thin polymeric membranes. This is relevant to understand the behavior of desired or undesired guest molecules in many applications involving thin polymer films, such as coatings, foils and membranes.

It is known that in polymer films cast from solutions, some solvent can be found to remain in the polymer network. This quantity was measured using Gas Chromatography (GC) for Polystyrene (PS) films. The total amount of retained solvent (Toluene) was found to depend mainly on the thickness of the film and the supporting substrate. The thickness and substrate dependence showed that the solvent is retained at the polymer-substrate interface. While thicker films (thickness > 200 nm) could essentially be considered as dry, the proportion of toluene in the thinnest films (10 nm) went up to 35% in weight. A strong confinement effect was observed in the diffusion coefficient of toluene out of the films with a significant decrease as film become thinner than 200 nm.

The inverse problem was subsequently studied: how much solvent does absorb in these films absorb? Gas Chromatography was again used to measure the amount of Tetrahydrofuran (THF) and Toluene uptake by PS films. The solvent uptake increased with increasing film thickness at room temperature, with a relative solvent absorption essentially independent of film thickness. The exposure time (above 20 minutes) seemed not to have any influence, probably due to a fast absorption dynamics. When the solvent was absorbed at high temperature, higher amounts could be trapped in the films by cooling them in the presence of THF vapour. Finally, the solubility of THF was found to be larger than that of Toluene, probably because of its larger size.
After considering the system PS/solvent, we have studied the case of polyamide materials, often used in applications for their properties. Water vapour transport is of major industrial importance, much effort is dedicated to controlling this process. We have studied the influence of film thickness and polymer morphology on the water vapor transport (permeability, solubility and diffusivity) through thin polyamide films. The water vapor permeability was found to decrease by several orders of magnitude as film thickness decreases. The solubility was found to increase slightly as film thickness increases, but this increase should also be due to the presence of water adsorbed at the surface of the films. These absorption experiments also allowed us to estimate the diffusion coefficient which, was found to decrease as film thickness decreases.

So in both systems we have studied, polystyrene/solvent and polyamide/water, we consistently observe the same effects: the diffusion strongly decreases as film thickness decreases, while the solubility hardly changes. The latter suggests that there is a little change in the overall free volume available in the film. The strong decrease in diffusion could be due to the alignment of the polymer chains parallel to the film surface. This would decrease the diffusion perpendicular to the surfaces, which is the one we probed by our experiments. Another possible effect is the presence of a layer with decreased mobility at the interface with the substrate supporting in the film. Such a layer could be main barrier to transport in the film.

Moving to the second group of polymers studied in this thesis, polyelectrolytes, we have also tackled a different type of problem: the conformation and interaction properties of multilayers upon their building-up though layer-by-layer deposition. These layers could have very promising applications as walls of nano-sized objects, such as microcapsules. Our work on model flat multilayers provides the necessary fundamental information on the properties of such films.

Firstly we report the successful formation of DNA/polyallylamine hydrochloride) (DNA/PAH) multilayer film formation on planar substrates and the study of the growth and morphology of these films. This was made by means of Surface Plasmon Resonance spectroscopy (SPR) and Atomic Force Microscopy (AFM) imaging. The SPR results show the linear and non-linear film thickness growth for poly(sodium 4-styrenesulfonate)/poly(allylamine hydrochloride) (PSS/PAH) and DNA/PAH multilayers, respectively. AFM imaging revealed that the surface of DNA layers is very rough, probably due to the presence of vertical DNA loops sticking out. Overall the growth conditions of DNA/PAH multilayers were found to be dramatically different from what was previously observed in the case of flexible polyelectrolytes as building blocks for multilayer formation. This suggests that the unique properties of DNA-based supported multilayers reflect the semiflexible character of the DNA molecules.
Secondly, the interaction/adhesion properties of supported PSS/PAH and DNA/PAH multilayers were investigated. This was done by means of Atomic Force Microscope (AFM) related force measurements. Electrostatic repulsion and attraction were observed on the approaching force-distance curves for polyanion and polycation surfaces, respectively. This indicates that the last layer deposited overcompensates the charge of the rest of the film. The retraction curves showed weak adhesion forces on the negatively charged surfaces and strong adhesion on the positively charged surfaces, which indicates that the electrostatic interactions dominate the surface forces. Multiple adhesions and plateau regions were observed on the PAH surfaces of PSS/PAH multilayer and DNA surfaces. This suggests that some polymer chains from bridges between the AFM probe and the film. In the case of DNA based multilayers, it even seems that some DNA loops are pulled out of the film. The pull-off force variation with the multilayer growth shows regular oscillations between positive and negative charged surfaces although irregularity was observed for the films assembled without drying. Assembly without drying might lead to a heterogeneous surface charge distribution and, therefore, to large deviations in the measured pull-off forces, while assembly with drying allows creating a more regular multilayer structure.

The work presented here has demonstrated several effects of confinement in polymeric systems, some of them quite dramatic. While qualitative explanations could be given, for most of them still require the development of satisfactory models to describe them. Hopefully the present work will stimulate this development.
**Resumen**

Las propiedades de las películas delgadas de polímeros no están bien entendidas y a menudo se desvían de las propiedades del *bulk*. La densidad, la estabilidad, la temperatura de transición vítrea, el coeficiente de difusión o la conformación de las cadenas poliméricas varían cuando la macromolécula está próxima a una interfaz. Esta tesis presenta un estudio de algunas de estas propiedades (absorción y desorción de disolventes, propiedades de transporte, adhesión y conformación) en películas de polímeros vítreos y de polielectrolitos.

En el caso de los polímeros vítreos, se ha analizado la retención, absorción y transporte de moléculas de disolvente en películas delgadas de Poliestireno (PS) y Poliamida, así como su dependencia con el espesor de la película, el tipo de disolvente y el tiempo de exposición. Los experimentos fueron efectuados en películas preparadas por evaporación del disolvente.

Experimentos realizados con películas de PS depositadas por evaporación de Tolueno demuestran que la cantidad absoluta de Tolueno residual depende principalmente del grosor de la película y la naturaleza del sustrato sobre el cual es depositada. Las películas con un grosor superior a 200 nm pueden ser consideradas libres de disolvente mientras que la proporción de tolueno en las películas más finas (10 nm) asciende hasta un 35% en peso. La cantidad de Tolueno residual es ligeramente superior en el caso se sustratos tratados con sustancias hidrófobas. Estos resultados indican que el disolvente podría quedar retenido preferentemente en la interfaz polímero-sustrato.

El coeficiente de difusión de tolueno pudo ser calculado a partir de los métodos aproximados de absorción y desorción de moléculas en capas unidimensionales (difusión desde dentro hacia afuera del film). Su valor decrece significamente cuando el grosor de la película disminuye por debajo de los 200 nm. Esto prueba el diferente comportamiento de los polímeros en estado “confinado” frente al comportamiento en *bulk*.

Con estas películas se efectuaron experimentos de reabsorción de disolvente usando tolueno y tetrahidrofurano. Los resultados demuestran que la cantidad de disolvente absorbido aumenta con el espesor de la película. Tiempos de exposición al disolvente superiores a 20 minutos no causan ningún cambio en la cantidad de disolvente absorbida, lo que indica que la cinética del proceso de absorción es rápida. Cuando el disolvente es absorbido a temperaturas por encima de la transición vítrea del polímero, la cantidad de disolvente absorbida aumenta considerablemente. Finalmente, la solubilidad del tetrahidrofurano es ligeramente superior a la del tolueno, probablemente debido al menor tamaño molecular.
En el caso de las poliamidas, se ha estudiado el transporte (permeabilidad, solubilidad y difusión) de vapor de agua a través de películas finas de distintas morfologías. Para el estudio se escogieron dos tipos de poliamidas: una amorfa y una semicristalina. Se observó que la permeabilidad al vapor de agua decrece tres órdenes de magnitud al pasar de películas de 10 μm a 10 nm de grosor. La solubilidad también aumenta ligeramente con el grosor de la película. A partir de los resultados de absorción se pudo estimar el coeficiente de difusión que también decrece con el espesor de la película.

En conclusión ambos sistemas estudiados, poliéster/disolvente y poliamida/vapor de agua, muestran una disminución de la difusión cuando el grosor de la película polimérica disminuye, mientras que la solubilidad a penas varía. Este último efecto sugiere que el volumen libre de las moléculas en la película polimérica a penas varía con el grosor. El hecho de que la difusión disminuya drásticamente podría tener relación con el alineamiento de las cadenas poliméricas, paralelamente a la superficie de la película. Esto haría que el coeficiente de difusión decrezca en la dirección perpendicular a la superficie, que es la dirección que hemos investigado en nuestros experimentos. Otro posible efecto es la presencia de una película con una menor movilidad en la interface con el substrato usado como soporte. Tal película podría ser la principal barrera al trasporte a través del film. Estos resultados son bastante interesantes desde el punto de vista práctico, ya que el papel de la deposición de películas finas está presente en la composición de aparatos electrónicos, recubrimientos, sensores, equipos ópticos, así como en la microelectrónica y en otras tecnologías.

El segundo grupo de polímeros estudiado en esta tesis son los polielectrolitos. Primeramente se ha estudiado el proceso de formación de multicapas por deposición sucesiva de películas de un polianión (poli(estireno sulfonato de sodio) (PSS) o ácido desoxirribonucleico (ADN)) y del policación poli(hidrocloruro de alilamina) (PHA) sobre una superfi cies plana. El grosor de la multicapa fue analizado mediante espectroscopia de resonancia de plasmones de superficie (SPR) después de cada paso de deposición. La morfología de la superfi cie de la multicapa fue analizada mediante microscopía de fuerza atómica.

Los resultados de SPR muestran que el grosor de la multicapa de PSS/PHA aumenta linealmente en cada paso de deposición. Por el contrario, en el caso de multicapas de ADN/PHA el grosor de las películas aumenta exponencialmente con el número de pasos de deposición. La microscopía de fuerza atómica revela que la superfi cie de las multicaps ADN/PHA es más rugosa que la superfi cie de PSS/PHA y otros sistemas encontrados en la literatura. Este efecto es debido probablemente a la presencia de bucles de ADN que sobresalen de la multicapa, y sugiere que la menor flexibilidad de la
cadena de ADN confiere propiedades singulares a los recubrimientos fabricados con ella.

Finalmente se han estudiado las propiedades de adhesión de estas multicapas mediante microscopía de fuerza atómica. Esta técnica permite medir la fuerza entre la superficie de la multicapa y la superficie de una partícula cargada negativamente pegada a la punta del cantilever. Las curvas de Fuerza vs. Distancia detectan repulsión cuando el cantilever se aproxima a superficies polianiónicas y atracción cuando la superficie es poliacatiónicas. Esto indica que la última película depositada compensa la carga del resto de la multicapa. Las curvas de retracción mostraron una fuerza de adhesión débil sobre superficies cargadas negativamente, y adhesión fuerte hacia las superficies cargadas positivamente, lo cual indica que las interacciones electrostáticas dominan las fuerzas de superficie. Cuando la última capa depositada en la superficie es de PHA se observan adhesiones múltiples y regiones meseta. Esto nos sugiere que algunas cadenas de los polímeros forman puentes entre la partícula del cantilever del microscopio de fuerza atómica y la multipelícula. En el caso las multipelículas fabricadas con ADN, incluso algunos bucles de ADN son arrancados del film. La variación de la fuerza de adhesión con respecto al número de capas depositadas en la multipelícula muestra oscilaciones regulares entre las superficies cargadas positiva- y negativamente. Por otro lado, ciertas irregularidades surgen dependiendo si las deposiciones se realizaron secando o no las películas previa deposición de una nueva película de signo contrario. Si el ensamblado es continuo (sin secar las multicapas) podría originar una distribución de carga heterogénea en la superficie, y por lo tanto una mayor dispersión en la medida de las fuerzas de adhesión. Por el contrario, si las multipelículas se secan el ensamblado permite crear una estructura más regular en las multicapas.

El trabajo aquí presentado demuestra las propiedades singulares de películas poliméricas delgadas como consecuencia del confinamiento de las macromoléculas. Los efectos encontrados se han podido explicar cualitativamente y ponen de manifiesto la necesidad de modelos nuevos que describan el comportamiento de estos sistemas. El autor confía en que los resultados presentados despierten la curiosidad de la comunidad científica y contribuyan a su desarrollo.
Samenvatting

Elektronische apparaten, coatings, beeldschermen, sensoren, optische apparaten en vele andere technologieën zijn allemaal afhankelijk van de afzetting van dunne coatings. Een speciaal type coating is de polymeer coating. Het gedrag van polymeren in coatings en in het bijzonder de polymeren dicht bij het grensvlak met het substraat is grotendeels onbegrepen.

Vele observaties, die beide structureel en dynamisch gedrag omvatten, duiden erop dat de eigenschappen van polymeren in coatings afwijken van de eigenschappen van polymeren in bulk. De dichtheid, coatingstabiliteit, vochtigheid, glasovergangstemperatuur, verspreidingscoëfficiënt, conformatie van ketens en de relaxatie zijn onderwerpen die momenteel intensief bediscussieerd worden.

Het experimentele werk dat hier gepresenteerd wordt behandelt de nog openstaande vragen over twee verschillende typen van dunne polymeer coatings; glasachtige polymeren en polyelectrolieten.

In het geval van glasachtige materialen hebben we het effect van gast moleculen vanuit verschillende oogpunten bestudeerd; verdamping van het oplosmiddel en binding na de vorming van de film, het absorberen van het oplosmiddel en als laatste het transport van de gast moleculen door dunne polymeer membranen.

Dit is belangrijk om het gedrag te begrijpen van de gewenste of ongewenste gastmoleculen in de vele toepassingen van dunne polymere films, zoals coatings, folies en membranen.

Het is bekend dat in polymeerfilms, gemaakt met behulp van oplossingen, een beetje oplosmiddel achterblijft in het polymere netwerk. De hoeveelheid hiervan is gemeten voor Polystyreen (PS) films met Gas Chromatografie (GC). De totale hoeveelheid aan achtergebleven oplosmiddel (tolueen) bleek voornamelijk af te hangen van het ondersteunende substraat en de dikte van de film.

De dikte- en substraatafhankelijkheid laten zien dat het oplosmiddel achterblijft op het grensvlak van de polymeerfilm en het substraat. Terwijl dikkere films (dikte > 200 nm) in wezen kunnen worden beschouwd als droog, was het gewichtspercentage van tolueen in de dunste films (10 nm) 35%. De diffusie coëfficiënt wijst er duidelijk op dat de tolueen aan het grensvlak opgesloten is. Dit effect nam af indien de films dunner werden dan 200 nm.

Het volgende probleem dat bestudeerd werd was de vraag hoeveel oplosmiddel deze films absorberen. Gas chromatografie werd weer gebruikt om de hoeveelheid aan THF en tolueen te meten die door de polystyreen films opgenomen wordt. De absorptie van oplosmiddel bij kamertemperatuur nam ongeveer evenredig toe met de toename van de film dikte. Na ongeveer 20
minuten was de film verzadigd. Wanneer het oplosmiddel bij een hoge temperatuur geabsorbeerd werd, werden grotere hoeveelheden oplosmiddel opgenomen in de film, door af te koelen in aanwezigheid van THF damp. De oplosbaarheid van THF ten slotte was hoger dan die van tolueen, waarschijnlijk doordat THF een groter molecuul is.
Na bestudering van het systeem PS/oplosmiddel hebben we polyamide films bestudeerd. De transportatie van waterdamp is een proces dat van groot industriëel belang is, veel moeite wordt gedaan om dit proces te controleren. We hebben de invloed van de film dikte en de conformatie van het polymeer op het transport van waterdamp (o.a. de permeabiliteit, oplosbaarheid en diffusie) door dunne polyamide films bestudeerd. De permeabiliteit van de waterdamp nam met meerdere ordegroottes af naarmate de film dunner werd. De oplosbaarheid nam in de film toe met de dikte van de film, maar deze toename was deels te wijten aan de absorptie van water aan het oppervlak van de films. Deze absorptie experimenten maakte het voor ons mogelijk de diffusie coëfficiënt te schatten, welke afnam met de dikte van de film.
In beide systemen die we bestudeerden hebben, polystyreen/oplosmiddel en polyamide/oplosmiddel, hebben we consequent dezelfde effecten waargenomen. De diffusie nam sterker af met toenemende dikte van de film, terwijl de oplosbaarheid nauwelijks veranderde. Dit wijst er op dat er weinig verandering in het totale vrije volume in de film was. De sterke afname in diffusie kan te wijten zijn aan de uitrusting van de polymeerketens parallel aan het filmoppervlak. Hierdoor neemt de diffusie door de film loodrecht op het oppervlak af. Dit is de diffusie die wij onderzocht hebben. Een andere mogelijke oorzaak zou de aanwezigheid van een laag met verminderde doorlatbaarheid aan het polymeer-substraat grensvlak kunnen zijn. Een dergelijke laag zou een ernstige barrière voor transport in de film zijn.

Bij de tweede groep van polymeren die we bestudeerden hebben, polylektrolieten, hebben we een ander type probleem aangepakt: de conformatie en interactie eigenschappen van multilagen tijdens hun laag-bij-laag deposietie. Deze lagen zijn veelbelovend als bouwstenen voor nano-objecten, zoals micro-capsules. Ons werk aan het model van platte multilagen levert de noodzakelijke fundamentele informatie over de eigenschappen van deze films.
Ten eerste rapporteren wij de succesvolle synthese van DNA/polyallylamine hydrochloride (DNA/PAH) multilagen op vlakke substraten en verder een studie naar de groei en morfologie van deze films. Dit werd gedaan met behulp van oppervlakte plasmon resonantie spektroskopie (SPR) en atoomkracht mikroskopie (AFM). SPR toont lineaire film groei bij poly(natrium 4-styreensulfonaat)/poly(allylamine hydrochloride) en niet-lineaire film groei bij DNA/PAH multilagen. AFM toonde aan dat het oppervlak van DNA lagen erg ruw is, waarschijnlijk doordat DNA lussen uit
Het oppervlak steken. Over het algemeen waren de groei condities voor DNA/PAH multilagen geheel anders in vergelijking met wat tot nu toe gemeld is voor flexibele polyelektrolieten die als bouwstenen voor multilagen gebruikt werden. Dit wijst op een unieke eigenschap van op DNA-gebaseerde gedragen multilagen, namelijk het semiflexibele karakter van DNA-moleculen.

Tevens werden de interactie/adhesie eigenschappen van gedragen PSS/PAH en DNA/PAH multilagen onderzocht, m.b.v. AFM. Bij polyanion oppervlakken werden bij de toenaderende kracht-afstandscurves elektrostatische afstoting geconstateerd, terwijl bij de polycationoppervlakken elektrostatische aantrekkingswaargenomen werd. Dit wijst er op dat de laatste laag die gedeponeerd is de lading van de rest van de film overcompenseert. De terugtrekkingscurves lieten zwakke adhesie krachten bij de negatief geladen oppervlakken en sterke adhesie bij de positief geladen oppervlakken zien, wat er op wijst dat de elektrostatische interacties de oppervlakte krachten domineren. Meervoudige adhesies en plateau regionen waren zichtbaar bij PAH-oppervlakken van PSS/PAH multilagen en bij de DNA oppervlakken. Dit suggereert dat sommige polymereketens bruggen vormen tussen de AFM-tip en de film. In het geval van op DNA-gebaseerde multilagen lijkt het er zelfs op dat sommige DNA-lussen uit de film getrokken worden. De variatie in de verwijderingskracht bij de groei van de multilaag toonde regelmatig oscillaties tussen positief en negatief geladen oppervlakken, alhoewel onregelmatigheid geconstateerd werd bij de films die zonder drogen geassembleerd waren. Samenstellen zonder drogen zou kunnen leiden tot een heterogene oppervlakte lading verdeling, en daardoor tot grote afwijkingen in de gemeten verwijderingskrachten. Lagen assembleren met drogen zorgt voor een meer regelmatige multilaagstructuur.

Het werk dat hier gepresenteerd wordt heeft een aantal dramatische effecten bij opsluiting in polymere systemen getoond. Alhoewel kwalitatieve verklaringen gegeven kunnen worden, moeten er nog bevredigende modellen ontwikkeld worden om deze effecten te beschrijven. Hopelijk zal dit werk dat hier gepresenteerd wordt deze ontwikkeling stimuleren.
ABOUT THE AUTHOR

Javier García Turiel was born in La Bañeza, León (Spain) the 13th of December of 1976. After graduating from high school, he did his university entrance examination in 1994 to study Chemistry at the University of Salamanca (Spain). During his studies, he spent a year under the European Program “Socrates” in 1997-1998 at the University of Bristol. In July 2000 he obtained the degree of “Licenciado en C.C. Químicas” (M.Sc. Chemistry) with a specialisation in organic chemistry.

After his graduation he worked, under the European program “Leonardo Da Vinci“, at DOW BENELUX N.V. Terneuzen (The Netherlands). He worked there at the Polyurethane R&D Department taking part in the “Performance Evaluation of Urethane Acrylate Based Coatings Project” at the Polyurethane New Business Development Research Group.

In the year 2001 he joined the “Complex Fluids” group of Prof. B. Jérôme at the University of Amsterdam as a PhD student to work on the project: “The effect of guest molecules in thin polymer films”. During his PhD, he graduated as Register Polymeerkundige (Expert in Polymer Science and Technology) at the National Dutch Graduate School of Polymer Science and Technology (PTN) in 2003. In 2003 and 2004 he was benefited from the Marie Curie Training Site Programme of the EU to spend two research stays at the Max Planck Institute for Polymer Research, Mainz (Germany), within the group of prof. dr. O.I. Vinogradova. The results of these 4 years of work are described in this thesis.
PUBLICATIONS

SCIENTIFIC PAPERS:

2005  J. Garcia-Turiel, J.E. ten Elshof, A. Stroeks and B. Jérôme, Transport Phenomena in Thin Polyamide Films (submitted) (Chapter 5)

2005  J. Garcia-Turiel, B. Jérôme, Solvent Retention in Thin Polymer Films (submitted) (Chapter 3)


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“Aprendamos a soñar, quizás así encontraremos la verdad. Pero guardémonos de publicar nuestros sueños sin antes haberlos sometido a prueba y haberlos hecho comprensibles.”

AUGUST FRIEDRICH KEKULÉ VON STRADONITZ

[Signature]

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