The background is an abstract composition of overlapping, semi-transparent geometric shapes in various colors including blue, orange, yellow, green, and purple. A central, dark, circular lens-like shape is positioned in the middle, with a small, dark, circular spot inside it. The overall effect is a complex, layered visual texture.

Swelling of Thin Polymer Films

Understanding the Mechanisms and Dynamics

Kristianne Tempelman

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By Kristianne Tempelman

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SWELLING OF THIN POLYMER FILMS
UNDERSTANDING THE MECHANISMS AND DYNAMICS

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Prof. dr. ir. N.E. Benes (promotor)

*"Science is not only a disciple of reason but,
also, one of romance and passion."*

- Stephen Hawking (1942-2018)

Theoretical physicist, cosmologist and mathematician

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Summary

Thin polymer films applied in organic solvent applications, such as coatings or thin selective membrane layers, often show a decline in their performance over a period of time which makes them unsuitable for long-term applications. The reason for this decline in performance can often be attributed to the swelling and instability of thin polymer films in organic solvents. Currently, there is still a poor understanding of the mechanisms behind the swelling and instability of high-performance polymers when in contact with an organic solvent and how these mechanisms change over time. As a result, predictions on the performance of thin polymer films in organic solvent applications are limited, preventing significant improvements in the membrane performance. The work described in this thesis provides a contribution to the understanding of the swelling dynamics of thin polymer films exposed to an organic solvent.

An introduction to all the concepts related to swelling in thin polymer films is provided in **Chapter 1**. In the first part a distinction is made between glassy and rubbery polymer films. Also, the role of the glass transition on the sorption and diffusion behavior of a penetrant into a polymer is described. In the second part, the application of thin polymer films in membrane applications and the challenges to overcome for organic solvent nanofiltrations are highlighted. In the last part of **Chapter 1**, the concept of using *in situ* characterization techniques to study sorption in thin polymer films is explained. The theory and use of spectroscopic ellipsometry, quartz crystal microbalance with dissipation monitoring and broadband dielectric spectroscopy are described in more detail. Finally, an outline of the thesis is provided.

Chapter 2 describes the applicability and limitations of *in situ* spectroscopic ellipsometry in liquid media. The effect of the presence of a liquid ambient and experimental non-idealities such as window birefringence, is investigated for its influence on the accuracy of the spectroscopic ellipsometry measurement. It is shown that the inaccuracy of the measurement is amplified when measuring in relatively high refractive index ambients. In particular, it is shown that for films thinner than ~100 nm, the implications on the accuracy of the measurement of even small non-idealities are substantial, and large deviations in the thickness and refractive index are found.

In **Chapter 3**, *in situ* spectroscopic ellipsometry is used to measure the penetrant induced swelling in five glassy polymers with excess free volume fractions ranging from 3-12 % in three different organic solvents. The role of the excess free volume is assessed by implementing a dual mode sorption concept. It is shown that for each

polymer/solvent combination, the excess free volume is completely filled around a swelling of ~5 %, independent of the type of penetrant or polymer used. Upon further dilation, irreversible structural changes within the polymer matrix occur, changing the sorption properties of the polymer. This is found to be in correspondence with literature reports on the dual mode sorption model where it is shown that Langmuir sorption only contributes up until a swelling of ~6 % and there is only a small contribution of Henry sorption.

In **Chapter 4**, evidence of the presence of a transition layer between the free surface and the bulk of a polystyrene is provided. By measuring the swelling of thin polystyrene films at 22 °C in *n*-hexane, three different diffusion regimes are observed. The first regime, representing the free surface layer extends for approximately 2.5 nm into the dry film and displays a rubbery behavior. The second regime is the transition layer, displaying a Case II diffusion and extending for ~11 nm below the free surface into the dry film. The last regime represents the bulk polymer and here *n*-hexane diffuses into the layer according to Fickian diffusion. The length of the transition layer remains constant for thicknesses above the macromolecular size of the polymer, but for thicknesses below $\sim 2R_g$, the length of the transition layer decreases.

Chapter 5 addresses the problem of the failure of water treatment membranes in hydrocarbon contaminated water mixtures. Desalination membranes with a mechanical polysulfone support fail when exposed to water saturated with toluene. In **Chapter 5**, the interaction of the polysulfone support with the toluene saturated water mixture is studied in more detail. In water, the polysulfone does not swell, while in toluene polysulfone swells excessively. In water saturated with toluene, it is shown that the non-ideality of the system induces a dewetting of the polysulfone layer. With this insight, the dewetting of the selective polyamide layer from the polysulfone was identified as the main cause of membrane failure in desalination membranes in hydrocarbon contaminated water.

Chapter 6 introduces poly(PDMS-POSSimide) films, which are synthesized in a localized fashion via interfacial polymerization, as a new high performance polymer material for solvent applications. Compared to conventional PDMS elastomers, the highly cross-linked poly(PDMS-POSSimide) films possessed a dramatically reduced swelling upon contact with *n*-hexane vapor (~15-fold decrease) and ethyl acetate vapor (~5-fold decrease). Due to an enhanced affinity for polar solvent of these poly(PDMS-POSSimide) films as a result of the presence of positively charged ammonium groups, an increased swelling in ethanol (~4-fold increase) is observed. Nonetheless, an extremely low ethanol permeance ($<0.1 \text{ L m}^{-2}$

$\text{h}^{-1}\text{bar}^{-1}$) was found, making these poly(PDMS-POSSimide) films suitable as potential barrier materials in for example microfluidic devices.

Broadband dielectric spectroscopy (BDS) in combination with spectroscopic ellipsometry and infrared spectroscopy (IR) was used to study the molecular interactions between Matrimid 5218, toluene and *n*-hexane in **Chapter 7**. It is shown that dry Matrimid 5218 films possess two overlapping β -relaxations, which split up upon interaction with a penetrant. The extent of the splitting of the β -relaxations indicated that toluene only interacts with one specific group in the molecular structure of Matrimid 5218, while *n*-hexane interacts with non-specific groups. Infrared spectroscopy measurements implied that toluene can interact with the diamine in Matrimid 5218 via π - π interactions. *n*-Hexane on the other hand interacts with Matrimid 5218 via weak Van der Waals interactions at non-specific sites. As a result, Matrimid 5218 can swell seven times more in toluene than in *n*-hexane.

Chapter 8 reflects on the results presented in this thesis and discusses possible new research directions in terms of studying the swelling behavior of thin polymer films with *in situ* characterization techniques. In this thesis, the first steps of directing fundamental swelling studies more towards obtaining information vital in membrane applications have been presented. **Chapter 8** provides a discussion on what follow up steps should be taken. Also, a reflection is provided on the use of quartz crystal microbalance with dissipation monitoring and broadband dielectric spectroscopy in combination with spectroscopic ellipsometry. Finally, **Chapter 8** provides a general conclusion of the work described in this thesis.

Samenvatting

De prestaties van dunne polymeerlagen zoals coatings of membranen nemen in de loop van der tijd af wanneer deze lagen worden toegepast in een omgeving van organische oplosmiddelen. Vele polymeercoatings en polymerische membranen zijn dan ook vaak ongeschikt om gedurende een langere tijd te worden toegepast in organische oplosmiddelen. Dunne polymeerlagen zijn vaak instabiel in organische oplosmiddelen omdat de lagen gaan zwellen door de aanwezigheid van dit oplosmiddel. Hoe dit zwelgedrag precies werkt en waarom de lagen instabiel worden na een bepaalde periode, is op dit moment nog onduidelijk. Door deze lacune in kennis, zijn de prestatievoorspellingen gelimiteerd en kunnen dunne polymeerlagen voor toepassingen in organische oplosmiddelen maar beperkt worden verbeterd. In dit proefschrift staat het begrijpen van het zwelgedrag van dunne polymeerlagen in oplosmiddelen centraal, om zo uiteindelijk betere materiaalkeuzes te kunnen maken voor toepassingen in organische oplosmiddelen.

Alle concepten die zijn gerelateerd aan het zwellen van dunne polymeerlagen worden toegelicht in **Hoofdstuk 1**. In het eerste deel van dit hoofdstuk wordt er een onderscheid gemaakt tussen glasachtige en rubberachtige polymeren en wordt er beschreven wat de rol van de glastransitie is met betrekking tot het sorptie- en diffusiegedrag van een penetrant in een polymeer. In het tweede deel van **Hoofdstuk 1** wordt de toepassing van een dunne polymeerlaag als een membraan verder toegelicht. Er wordt uitgelegd hoe membranen kunnen worden toegepast in nanofiltraties met organische oplosmiddelen en waarom dit nog niet op grote schaal gebeurt. In het laatste deel van **Hoofdstuk 1** wordt er meer aandacht besteed aan de mogelijkheden om de sorptie van een penetrant in een dunne polymeerlaag *in situ* te meten. Spectroscopische ellipsometrie, kwarts-microbalans met dissipatie registratie en breedband dielectrische relaxatie spectroscopie zijn uitgelichte karakterisatietechnieken die meer gedetailleerd zijn beschreven. **Hoofdstuk 1** eindigt met een overzicht van de indeling van dit proefschrift, waarbij kort de overige hoofdstukken worden toegelicht.

Hoofdstuk 2 beschrijft de toepasbaarheid en beperkingen van *in situ* spectroscopische ellipsometrie voor het meten van sorptie van dunne polymeerlagen in een natte of vloeibare omgeving. Door het gebruik van een vloeistof en een vloeistofcel, worden er extra parameters geïntroduceerd, die de accuraatheid van de meting kunnen aantasten. Dit is met name het geval wanneer de vloeistof waarin wordt gemeten een relatief hoge brekingsindex heeft. Daarnaast, voor polymeerlagen dunner dan ~100 nm wordt het effect uitvergroot en zullen zelfs

kleine afwijkingen van het ideale gedrag van de parameters leidden tot grote fouten in de bepaalde dikte en brekingsindex van de polymeerlaag.

In **Hoofdstuk 3** is *in situ* spectroscopische ellipsometrie gebruikt om de zwelling te meten in vijf verschillende glasachtige polymeren. Deze polymeren hebben een exces vrij volume variërend van 3-12 % en de zwelling van deze polymeren is gemeten in drie verschillende organische oplosmiddelen. De exacte rol van het exces vrij volume met betrekking tot het zweelgedrag van een glasachtige polymeer is onderzocht door middel van het "dual mode" sorptie concept. **Hoofdstuk 3** laat zien dat voor elke polymeer/penetrant combinatie, het exces vrij volume volledig opgevuld is wanneer er een zwelling van 5 % wordt waargenomen. Dit gedrag is onafhankelijk van het soort penetrant of polymeer dat gebruikt wordt. Zodra de zwelling meer dan ~5 % is, treden er onomkeerbare veranderingen op in de polymeerstructuur met als gevolg dat ook het sorptiegedrag van het polymeer is veranderd. Het geobserveerde generieke vulgedrag van het exces vrij volume wordt ook indirect beschreven in de literatuur. Bevindingen gerapporteerd over de sorptie in glasachtige materialen, beschreven met behulp van het "dual mode" sorptie model, laten zien dat tot een zwelling van ~6 %, er voornamelijk sorptie optreedt door middel van het Langmuir sorptie mechanisme. Tot ~6 % zwelling is er maar een kleine contributie van sortie door middel van het Henry sorptie mechanisme. Voor een zwelling meer dan 6 % wordt het sorptie gedrag volledig gedomineerd door het Henry sorptie mechanisme.

In **Hoofdstuk 4** wordt er bewijs geleverd van de aanwezigheid van een transitie laag tussen het vrije oppervlak en de bulklaag van een polystyreenlaagje. De zwelling van dunne polystyreenlagen is gemeten op 22 °C in *n*-hexaan, waarbij er drie verschillende diffusieregimes zijn waargenomen. Het eerste regime, het vrije oppervlak, laat een rubberachtig gedrag zien en loopt tot ongeveer 2,5 nm in de droge laag. Het tweede regime, de transitie laag, laat een Case II diffusiegedrag zien. Deze transitie laag zit onder het vrije oppervlak en is ongeveer 11 nm dik. In het laatste regime, de bulklaag, vindt er *n*-hexaan diffusie plaats volgens de wetten van Fick. Tot hoeverre de transitie laag doorloopt in de bulk is afhankelijk van de dikte van totale polystyreenlaag. Wanneer de dikte van de polystyreen laag dikker is dan de macromoleculair grootte van het polymeer ($\sim 2R_g$), dan is de dikte van de transitie laag constant en ongeveer 11 nm dik. Voor polystyreenlagen dunner dan $2R_g$ neemt de dikte van de transitie laag af.

Hoofdstuk 5 beschrijft het probleem van het gebruik van waterzuiveringsmembranen in mengels van water vervuild met koolwaterstoffen. Membranen die worden gebruikt voor het ontziltten van water, zijn vaak niet toepasbaar voor het zuiveren van water dat vervuild is met koolwaterstoffen, omdat

deze defect raken. In **Hoofdstuk 5** wordt er gedemonstreerd hoe ontziltingsmembranen die een polysulfon draaglaag hebben, defect raken in water dat verzadigd is met tolueen. De interactie tussen de polysulfon en het mengsel van verzadigd water met tolueen is onderzocht met *in situ* spectroscopische ellipsometrie, een optische microscoop en met atoomkrachtmicroscopie. Er wordt aangetoond dat polysulfon niet in puur water zwelt en een sterke zwelling laat zien in puur tolueen. Wanneer polysulfon wordt blootgesteld aan water verzadigd met tolueen, laat de polysulfonlaag los van de draaglaag. Dit proces wordt geïnduceerd door het feit dat een mengsel van water en tolueen een niet-ideaal systeem is. Voor ontziltingsmembranen die een polysulfon draaglaag bevatten, is delaminatie van de polyamide laag boven op de polysulfon de aangewezen hoofdoorzaak van het defect raken in water vervuild met koolwaterstoffen.

In **Hoofdstuk 6**, wordt de grensvlakpolymerisatie en karakterisatie van dunne poly(PDMS-POSSimide) lagen beschreven. Poly(PDMS-POSSimide) is een geschikt hybride polymeermateriaal voor gebruik in toepassingen met organische oplosmiddelen. In vergelijking met een conventioneel PDMS elastomeer, zwellen deze inherent dunne poly(PDMS-POSSimide) lagen ongeveer 15 keer minder in *n*-hexaan en 5 keer minder in ethyl acetaat. Echter, door de aanwezigheid van positief geladen ammonium groepen is de polariteit van de poly(PDMS-POSSimide) laag hoger in vergelijking met conventioneel PDMS, waardoor er een verhoogde zwelling wordt waargenomen in ethanol (ongeveer 4 keer hoger). Desondanks wordt er een extreem lage ethanol permeatie waargenomen ($0,1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), waardoor deze poly(PDMS-POSSimide) lagen zeer geschikt zijn als barrièrematerialen in bijvoorbeeld microfluidische componenten.

De moleculaire interacties tussen Matrimid 5218, tolueen en *n*-hexaan zijn onderzocht in **Hoofdstuk 7** met behulp van breedband dielectrische relaxatie spectroscopie (BDS) in combinatie met spectroscopische ellipsometrie (SE) en infrarood spectroscopie (IR). BDS laat zien dat er twee overlappende β -relaxaties plaatsvinden in een droge Matrimid 5218 laag, welke opsplitsen als Matrimid 5218 wordt blootgesteld aan een penetrant. Bij blootstelling aan tolueen laat BDS zien dat tolueen een interactie heeft met één specifieke groep, terwijl bij blootstelling aan *n*-hexaan beide β -relaxaties worden beïnvloedt er geen groep specifieke interactie plaatsvindt. IR metingen suggeren dat tolueen π - π bindingen kan vormen met de diamine groep in Matrimid 5218. *N*-hexaan daarentegen kan alleen via zwakke Van der Waals bindingen een interactie vormen met Matrimid 5218. Als gevolg hiervan zwelt Matrimid 5218 zeven keer meer in tolueen ten opzichte van *n*-hexaan.

In **Hoofdstuk 8** wordt er gereflecteerd op de resultaten beschreven in dit proefschrift en worden er suggesties beschreven voor nieuwe onderzoeksrichtingen met

betrekking tot het bestuderen van zwellings in dunne lagen met *in situ* karakterisatietechnieken. In dit proefschrift zijn er stappen gezet om de informatie die kan worden verkregen via fundamentele zwellingsstudies te vertalen naar de bruikbaarheid in toepassingen zoals membranen. In **Hoofdstuk 8** wordt er beschreven wat de vervolgstappen kunnen zijn om fundamentele zwellingsstudies en het gebruik ervan in het verbeteren van bijvoorbeeld membranen, nog dichter bij elkaar te brengen. Ook wordt er in **Hoofdstuk 8** gereflecteerd op het gebruik van karakterisatietechnieken zoals de kwarts-microbalans en BDS in combinatie met spectroscopische ellipsometrie. **Hoofdstuk 8** wordt afgesloten met een algehele conclusie van dit proefschrift.

Chapter 1

Thin Polymer Films in Fluids

1.1 Introduction

In our everyday lives we encounter thin polymer films as coatings or adhesives and also as membranes, sensors or detectors. In the Merriam-Webster dictionary, a thin film is described as 'a very thin layer of a substance on a supporting material' ^[1], but an explicit thickness range is not specified. In literature, depending on the research field, the definition of thin varies from anywhere between a few nanometer to several micrometers ^[2,3]. In this thesis, thin films are defined to have a thickness in the range from ~20 nm to 1 μ m thick films; this corresponds well with the typical thicknesses of membranes for molecular separations ^[4]. When the thickness is below ~20 nm, the film is referred to as ultrathin. Compared to bulk polymers, polymers confined to a thin film on a substrate can possess different physical properties. The important factors governing this bulk-deviating behavior are the thin film uniformity, stability, and its adhesion to the substrate ^[5].

For many applications, a thin polymer film is exposed to gases or liquids that can penetrate into the polymer (i.e. penetrants) and may alter the film properties, including the stability and performance. To know the extent to which the performance and stability are changed, and to have an understanding of the underlying causes, is essential to improve the thin polymer film properties. Other than that, the ability to predict the penetrant uptake, and the resulting change in properties of the thin polymer film, will allow for a more accurate evaluation of the potential polymers for application as a thin film.

When a polymer is exposed to a penetrant, the penetrant will diffuse into the polymer matrix and swelling can often be observed. For example, a hydrogel can grow extensively beyond its original size when exposed to water and the swollen hydrogel can consist up to ~99 % of water ^[6]. The properties of this swollen hydrogel are distinctly different compared to the dry hydrogel. For thin polymer films, the swelling is restricted to a unidirectional swelling in the perpendicular direction of the substrate, because the film is confined to a substrate ^[7,8]. When considering swelling, it is important to make a distinction between **dilation** and **penetrant mass uptake**. Dilation is referred to as an increase in polymer volume due to additional volume occupied by the penetrant. The penetrant mass uptake is referred to as the concentration of penetrant within the polymer matrix (see Figure 1.1). Depending on the type of polymer and penetrant, the dilation and penetrant mass uptake do not relate to each other in a linear manner. In order to understand the difference between dilation and penetrant mass uptake, and to be able to study the swelling dynamics of these thin polymer films, the physical and thermodynamic states of the polymer need to be considered.

Figure 1.1 – A schematic illustration, showing the definition of mass uptake (left), 3D dilation (middle) and 1D dilation of a polymer film confined to a substrate (right).

1.2 The Glass Transition

The thermodynamic state of a polymer and its properties are not only governed by the intrinsic properties of the polymer, but to a large extent also by the processing parameters^[9]. Most polymers are processed in the liquid state. This can be achieved by either dissolving the polymer using a suitable solvent, or by melting the solid material. In both cases, a solid material is brought into a liquid state, allowing it to flow. In case of melt-processing, upon cooling down, the molecular motions of the polymer chains slow down and eventually, the motions are slowed down to such an extent, that the polymer appears as a solid^[10]. When the cooling rate is sufficiently low, allowing enough time at each temperature for the polymer chain motions to relax, a crystalline solid is obtained^[9,11]. The point at which a liquid is transformed into a crystalline solid is known as the melting point. The transition of a liquid into a crystalline solid is described as a first-order phase transition. At a first-order phase transition discontinuities can be observed in the physical properties of the polymer such as the heat capacity and the specific volume, which are first derivative properties (i.e. properties that can be derived from a thermodynamic equation of state by the first derivative)^[12].

Upon supercooling of the liquid, the molecular polymer chain motion will cool rapidly (i.e. quenching) and an amorphous solid or glass is obtained. The point at which the polymer chain motions seem to be frozen in place is referred to as the glass transition. The glass transition is one of the most important physical properties of an amorphous polymer, as many material properties change at the glass transition. For example, above the glass transition, the heat capacity and the thermal expansion coefficient increase, optical properties such as the refractive index change, mechanical properties and viscosity decrease^[9]. In Figure 1.2, the

glass transition is schematically depicted by showing the change in a physical property as function of temperature.

Figure 1.2 – A schematic depiction of a physical property as function of the temperature. At a sufficient low cooling rate, the material can be cooled down from above the melting temperature, T_m via the crystallization range to a crystalline solid. When the material is cooled down too fast, an undercooled liquid can be obtained, which forms below the glass transition temperature, T_g , an amorphous or glassy material.

The glass transition takes place over a range of temperatures, referred to as the ‘transformation range’^[12]. As a result, no discontinuous change in the physical properties can be observed and the glass transition is not a first-order phase transition. In terms of thermodynamic stability, the crystalline solid is described to be in a thermodynamic equilibrium, while an amorphous glass is thermodynamically unstable as its equilibrium state is only reached when all polymer chains are fully relaxed^[11]. However, for glasses the relaxation times of the molecular motions of the glass are far lower than the experimental timescales (i.e. relaxations can occur over decades^[13]). Often, a glass is therefore considered kinetically stable as no changes are observed within a typical experimental time frame^[12].

Although the glass transition is a well-researched topic within polymer physics, there are still deficiencies in understanding the dynamics of the glass transition and its relation to the glassy polymer properties^[14–19]. This is the result of the many factors that influence thermodynamics of a glassy polymer. The time span, thermal history and pressure of the measurement are external factors that influence the glass transition and the relating physical properties. Intrinsic factors include the cross-linking density, the average molecular weight, presence of additives or

impurities, interchain and intrachain effects such as hydrogen bonding and chain stiffness ^[9].

When heating a glassy polymer to its T_g , sufficient thermal energy is provided to overcome the resistance of the cohesive forces and the resistance to viscous flow ^[9]. This allowed for the T_g to be defined as the temperature at which the polymer viscosity, η , equals $10^{12} \text{ kg m}^{-1} \text{ s}^{-1}$ ^[20]. In 1965, Adam and Gibbs ^[21] proposed that the decrease in viscosity upon heating a glassy polymer is the result of a cooperative rearranging region (CRR). Within the CRR, the polymer chain configuration can be rearranged independently from the environment, provided the fluctuation in energy is sufficient. At the glass transition, the length scale of cooperative motion is believed to be between 1-4 nm ^[22] and the existence of the CRR has been observed in several computational studies ^[23–25].

1.2.1 Measurement of the T_g in thin polymer films

Since a distinct but continuous change in many physical properties can be observed below and above the T_g , a wide variety of techniques can be applied to measure the T_g experimentally. By far the most common employed technique for the characterization of bulk materials is differential scanning calorimetry (DSC), where a change in the heat capacity of the sample versus temperature is measured. Another bulk characterization technique is dilatometry, which measures a change in the thermal expansion. Both techniques require a polymer powder for the measurement. However, a thin polymer film confined to a substrate may result in a glass transition deviating from bulk behavior ^[26,27]. For this reason, in order to measure the T_g of thin polymer films confined on a substrate, other techniques need to be employed. Most surface characterization techniques probe the thermal expansivity of the polymer film. The most common technique used to measure the T_g of thin films is spectroscopic ellipsometry (SE) ^[20,28]. SE measures the film thickness and the refractive index as function of the temperature. By measuring the discontinuity in the film thickness at a certain temperature, the T_g can be determined. SE is the most common used technique for thin polymer films because of its fast acquisition time and high sensitivity ^[29,30]. However, any technique that measures a physical property of a thin polymer film that changes upon the glass transition can in principle be utilized. Other techniques include, X-ray reflectivity (XRR) ^[31,32], Brillouin light scattering (BLS) ^[33–35] and positron annihilation lifetime spectroscopy (PALS) ^[36].

In literature, the results reported on structurally confined polymers such as thin films confined to a substrate, and on free standing films show contradictory behavior ^[30,33,35–40]. It is suggested that strong interactions between polymer and substrate result in increasing glass transition temperatures with decreasing film

thicknesses. For weak polymer substrate interactions, the glass transition temperature decreases ^[20]. When considering free standing films, in general a larger decrease in glass transition and a certain molecular weight dependence was observed. More recently, it has been suggested that the reported deviations in the reported glass transition temperatures are more likely due to preparation conditions and thermal history, since only films thinner than ~10 nm are likely to show a deviation from bulk behavior ^[41].

1.2.2 The specific volume of a (glassy) polymer

The specific volume is a very important property for glassy polymers, it is directly connected to the mass and packing density of the polymer and influences for example the penetrant sorption, elastic modulus and viscosity. The specific volume of a rubbery polymer consists of four parts, while for a glassy polymer the specific volume consists of five parts (see Figure 1.3). The first part is the **Van der Waals volume** (also known as the **hard-core volume**). The Van der Waals volume (V_w) of a molecule is the space occupied by the molecule and is impenetrable to other molecules ^[42]. The second is the **packing volume** or additional empty space that is imposed by the packing constraints of the atoms. Together, the Van der Waals volume and packing volume sum up to the **occupied volume** of the polymer. As a general rule, the occupied volume (V_{occ}) is approximately $1.3 V_w$ ^[42,43]. The third part is the **expansion volume**, **vibrational volume** or **interstitial free volume** (V_{vib}). This expansion volume is free volume spread amongst all molecules and is created by the thermal motions of the atoms and therefore shows a temperature dependency. The expansion volume is the difference between molar volume at a specific temperature, T and the hypothetical molar volume at 0 K. When considering a crystal, the specific volume is the sum of V_{occ} and V_{vib} . The final contributor to the specific volume amorphous equilibrium polymers is the **hole free volume** (V_{hole}) or often referred to as the free volume, which is created by the non-ideal stacking of the polymer chains. The hole free volume is a localized volume element but can be redistributed due to polymer chain motions. ^[9,43,44]

When considering a glassy polymer, one additional volume part exists, which is referred to as the **excess free volume** (V_{EFV}). Where the hole free volume can readily be redistributed, the excess free volume is the additional free volume that is created within a glassy polymer upon quenching of the polymer to a temperature below T_g and is fixed. Whether the excess free volume is a frozen part of the hole free volume, or additionally created void volume due to the limited mobility of the polymer chains, is not clearly described in literature. Over time, excess free volume will disappear by a process known as isothermal volume recovery or ageing ^[45,46]. As the amount of free volume ($V_{EFV} + V_{hole}$) govern the non-equilibrium properties of the

glassy polymer, any change in the EFV over time changes the glassy polymer properties.

Figure 1.3 – A schematic depiction of the different volume constituents that add up to the total specific volume as function of temperature for a polymer. Below the glass transition, excess free volume is created by the sudden decrease in polymer chain mobility. It is not clear whether it represents the frozen holes of the hole free volume, or whether it is additional created volume.

It is difficult to measure the exact amount of free volume and excess free volume available inside the glassy polymer. In order to assess the total amount of free volume and excess free volume, a deduction from other measurements is necessary^[47]. Measurement techniques from which information on the free volume can be deduced include small-angle X-ray scattering (SAXS)^[48,49] and positron annihilation spectroscopy (PALS)^[50,51]. SAXS measures the size of the free volume based on density fluctuations, while PALS can be used to determine the size, size distribution and concentration of the free volume holes. From both techniques an indication of the free volume size can be deduced.

Measurement techniques based on the measurement of the thermal expansivity, such as spectroscopic ellipsometry, provide for a straightforward determination of the excess free volume. The excess free volume can be deduced from the difference between the total specific volume or thickness and the specific volume or thickness of the hypothetical liquid polymer (see Figure 1.3). The volume or thickness of the hypothetical liquid polymer can be determined by extrapolating the measured

specific volume or thickness temperature dependence above the T_g to the desired temperature below the T_g [52].

1.2.3 Influence of a penetrant

1.2.3.1 Penetrant sorption

As mentioned in section 1.1, in order to understand the swelling dynamics of thin polymer films, the physical and thermodynamic state of the polymer needs to be considered. When the polymer is in liquid or rubbery state ($T > T_g$) the polymer is in equilibrium and any change that occurs, will bring the polymer immediately into a new equilibrium state. In terms of sorption, this means that the penetrant will mix with the rubbery polymer into a new equilibrium state almost instantaneously. For rubbery polymers, the extent to which dilation occurs is determined by the amount of sorption of the penetrant into the polymer and the partial molar volume of the penetrant inside the polymer. The partial molar volume of the penetrant indicates to what extent volume expansion occurs upon adding one mole of the penetrant to the total polymer volume. In the case of sorption in a rubbery polymer, the partial molar volume of the penetrant is almost constant. As a result, dilation and penetrant mass uptake can be linearly related to each other when considering rubbery polymers.

The extent to which the two liquids (polymer and penetrant) will mix, is governed by the molecular affinity between the two components as can be expressed by interaction and solubility parameters based on their molecular composition. For rubbery polymers, the Flory-Huggins theory [53] can be used to predict the equilibrium penetrant fraction inside the polymer as function of the penetrant activity (Eq. 1.1) [54]. The Flory-Huggins theory describes the free energy of mixing for polymers and solutes, taking into account the large difference in molecular sizes. The Flory-Huggins theory described the free energy of mixing of polymers and solutes according to an entropic (ΔS^M) and an enthalpic term (ΔH^M) (Eq. 1.1, shown for a single polymer-solvent combination). The entropic term describes the increase of configurations available for the polymer chains upon mixing with the solute. The enthalpic term describes the energy change that occurs upon mixing due to the formation of new polymer-solute contacts. The enthalpic term can either be negative, stimulating the mixing of the polymer and solute, or positive which opposes mixing. The difference in energy between a solute immersed in a pure solvent or in the polymer is described by the interaction parameter, χ . In general, if the interaction parameter is smaller than 0.5, the polymer will dissolve in the solute, and the solute can be considered a "good" solvent for the polymer. The interaction parameter is inversely dependent on the temperature and increases with an increase in polymer concentration.

$$\Delta G^M = \Delta H^M - T\Delta S^M = RT[(x_1 \ln \varphi_1 + x_2 \ln \varphi_2) + N\varphi_1\varphi_2\chi(T)] \quad [1.1]$$

φ_1 and φ_2 are the solute and polymer volume fraction respectively, $x_{1,2}$ are the mole fractions and N is the total number of sites or segments.

The Flory-Huggins theory is a lattice-based equation of state (EoS) approach. Another commonly used EoS based on a lattice model is the Sanchez and Lacombe EoS [55]. The Sanchez and Lacombe EoS differs from the Flory-Huggins EoS in that Sanchez and Lacombe introduces holes into the lattice, representing the hole free volume, and accounts for variations in compressibility and density. Sanchez and Lacombe is therefore more often used as a basis to predict solvent sorption in glassy polymers [56]. However, the Sanchez and Lacombe EoS requires knowledge and assumptions on the characteristic temperature (T^*), characteristic pressure (p^*) and characteristic close-packed density (ρ^*), which are the state parameters to be derived from the pure component properties.

An EoS provides a description on the sorption behavior of a solute and polymer in equilibrium but glassy polymers are in a non-equilibrium state. For this reason, modifications to the equations of state are necessary to account for the non-equilibrium contributions present in a glassy polymer. The non-equilibrium factors of a glassy polymer are the presence of the excess free volume and the ability of the glassy polymer to age towards equilibrium over a certain period of time. In fact, the excess free volume is additional volume present in which penetrant sorption can take place, without dilating the polymer. When the penetrant diffuses into the void spaces of the excess free volume, the partial molar volume of the penetrant is almost zero and almost no dilation will be observed, while there is a penetrant mass uptake. Here it is important to note that this is a simplification to enhance the understanding of the concept of sorption in glassy polymers. In reality, there is likely an interplay between the excess free volume and the hole free volume. To what extent each volume element contributes to sorption is complicated and not completely understood. To describe penetrant sorption inside glassy polymers, many models in literature have been developed. The two most common used models include the non-equilibrium lattice fluid model (NELF) [56] and the Dual Mode Sorption (DMS) model, as well as various modified versions of this model [57].

The NELF or nonequilibrium thermodynamics for glassy polymers (NET-GP) model describes the sorption of a penetrant within a glassy polymer as a uniform nonequilibrium metastable phase, and all penetrant molecules are treated as dissolved into the polymer. The chemical potential of the penetrant-polymer mixture in the nonequilibrium state ($\mu_1^{NE}(T, p, \Omega_1, \rho_2^{NE})$) is considered equal to the chemical potential of an equilibrium gas-polymer mixture which is evaluated in the hypothetical equilibrium state ($\mu_1^{Eq}(T, p, \Omega_1)$) at the same temperature, composition

and polymer density as determined by the Sanchez and Lacombe EoS. When considering glassy polymers, the density of the polymer mixture, ρ_2^{NE} is introduced as the nonequilibrium parameter and can be considered equal to the value of the pure unpenetrated polymer in the case of non-swelling penetrants. When the penetrant induces swelling of the polymer matrix, the density of the polymer should be retrieved at every sorption pressure from dilation experiments in order to describe the penetrant sorption inside the glassy polymer accurately with the NET-GP model. [56,58]

The DMS model was initially proposed by Barrer et al. in 1958 [57] and describes two modes of sorption; Langmuir mode and Henry mode. The Langmuir sorption mode occurs via the void spaces of the polymer matrix and assumes no contribution to volume dilation. The Henry sorption mode describes the sorption of the solvent molecules into the polymer matrix, contributing to the volume dilation. The DMS is a simplified model and assumes no modification of the polymer matrix. Over the years, many modifications of the DMS model have been proposed to account for its deficiencies [59–62]. However, in all cases, the history effect, solvent concentration dependence and temperature dependence are often deduced in an empirical or semi-empirical way [63].

1.2.3.2 Penetrant diffusion

The equations of state can be used to predict how much penetrant will be taken up by the polymer in equilibrium conditions, however they do not describe the uptake mechanism and diffusion of the penetrant into the polymer. The simplest mode of diffusion follows Fick's laws of diffusion (Eq. 1.2 and 1.3) and is referred to as Fickian diffusion. The first law of Fick (Eq. 1.2) describes the flux (J) as proportional to the gradient in concentration (c) with the diffusion coefficient (D) as the proportionality constant. The second law of Fick (Eq. 1.3) describes how the concentration changes as function of time from the change in flux with respect to the position.

$$J = -D \frac{\partial c}{\partial x} \quad [1.2]$$

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \quad 0 < x < l \quad [1.3]$$

When considering a polymer film, the boundary conditions are defined at the film surfaces as $c(0, t) = c_0$, the initial concentration (1), $c(l, t) = c_1$, the concentration at the boundary (2) and $c(x, 0) = c(x)$ (3). [64,65] The solution to the complete set of boundary conditions is referred to as Fickian diffusion.

The diffusion dependent penetrant sorption or mass uptake can be divided in three different regimes: Fickian diffusion, anomalous Fickian diffusion and Case II diffusion. In Table 1.1, an overview of the different diffusion regimes and the related

mass uptake relation is shown. In this section, the difference between the three different regimes will be further discussed.

Table 1.1 – An overview of the different diffusion regimes and their mass uptake relation as function of time. k is a constant related to the diffusivity, R_{diff} represents the rate of diffusion, and R_{relax} the relaxation rate of the polymer. ^[64,66,67]

Regime	Mass uptake (M_t) relation	Features
Fickian	$M_t = k\sqrt{t}$ (Eq. 1.4)	$R_{\text{diff}} \ll R_{\text{relax}}$
Anomalous Fickian diffusion	$M_t = kt^n$ where $\frac{1}{2} < n < 1$ (Eq. 1.5)	$R_{\text{diff}} \sim R_{\text{relax}}$
Case II	$M_t = kt$ (Eq. 1.6)	$R_{\text{diff}} \gg R_{\text{relax}}$

Fickian diffusion

Following Fickian diffusion, the mass uptake (M_t) can be described as a function of the square root of time (Eq.1.4) ^[64]. Penetrant sorption following Fickian diffusion will occur when a sorption equilibrium can be achieved at the film surface. Fickian diffusion is often observed in the penetrant transport in rubbery polymers, due to the high mobility in the polymer chains (see also section 1.2), which will cause the solvent diffusion rate to be slower than the polymer relaxation rate ($R_{\text{diff}} \ll R_{\text{relax}}$). In this case, the penetrant transport and uptake for sufficiently low characteristic diffusion times (i.e. low Fourier numbers, a dimensionless number for the diffusion time) is solely dependent on the diffusion.

Anomalous Fickian diffusion

In the case of penetrant diffusion into glassy polymers, the relaxation times of the polymer chains have slowed down significantly because $T < T_g$. As a result, the diffusion rate of the penetrant will be in the same order of magnitude or faster than the polymer relaxation rate. When the diffusion rate is approximately equal to the relaxation rate of the polymer ($R_{\text{diff}} \sim R_{\text{relax}}$), the diffusion process is referred to as anomalous Fickian diffusion ^[66] (Eq. 1.5), which is the most common diffusion process in glassy polymers ^[66,67].

For anomalous Fickian diffusion, the diffusion of the penetrant into the polymer is governed by both the diffusion rate of the penetrant and the relaxation rate of polymer itself and is often referred to as Fickian Relaxation. In 1977 Berens and Hopfenberg ^[68] developed a model which allows the contribution of the diffusion and relaxation parameters to be separated. By using the Berens and Hopfenberg model, it was shown that initially the penetrant sorption into a dry polymer is dominated by a Fickian diffusion process, which is followed by a slower relaxation process.

Case II diffusion

When $R_{\text{diff}} \gg R_{\text{relax}}$, the diffusion process is referred to as Case II diffusion ^[66] and will occur in glassy polymers when exposed to a strong interacting penetrant within a specific temperature range. Case II diffusion is characterized by a rapid increase in the solvent concentration in the swollen region, and therefore a sharp solvent penetration front between the swollen region and the dry inner polymer core will exist. What happens is that penetrant induces a localized glass transition. This solvent front will advance at a constant rate, and the penetrant uptake will linearly increase with time (Eq. 1.6) ^[67]. Ogieglo et al. showed the existence of the sharp penetrant front in Case II diffusion experimentally for *n*-hexane sorption in a thin film of polystyrene ^[69].

In Figure 1.4, a schematic illustration of the total penetrant mass uptake as function of time and square root of time according to Fickian diffusion, anomalous Fickian diffusion and Case II diffusion is presented.

Figure 1.4 – The penetrant mass uptake following a Fickian diffusion (A1,2), Anomalous Fickian diffusion (B1,2) and Case II diffusion (C1,2) process as function of time (1) and square root of time (2).

1.2.3.3 Penetrant induced T_g depression

As shown for Case II diffusion, in some cases the penetrant is able to depress the T_g to such an extent that the T_g is below the measurement temperature and, therefore the penetrant induces a glass transition upon diffusion into the polymer. This

process is also known as plasticization of the glassy polymer. In most cases, when the penetrant has a lower glass transition than the polymer, the penetrant will cause a small depression of the T_g . However, it will not induce a glass transition immediately. Over the years, many approaches have been suggested to estimate the T_g of the polymer-penetrant mixture based on the pure component properties. Gordon and Taylor proposed the following expression based on the weighted averages of the pure components [70]:

$$T_{g,mix} = \frac{w_1 T_{g1} - k w_2 T_{g2}}{w_1 + k w_2} \quad [1.7]$$

where $T_{g,mix}$ is the glass transition temperature of the mixture, w_1, w_2 the weight fractions of the component 1 and 2 respectively in the mixture, k is a parameter that is dependent on the thermal expansion coefficient, α .

In order to apply Eq. 1.7, it is assumed there is an ideal volume of mixing and the volume is assumed to linearly change with temperature [71]. Eq. 1.7 is a simple approach to obtain an estimation of the change in the glass transition temperature upon penetrant sorption. However, Eq. 1.7 does not account for any heat effects occurring upon mixing of the polymer and penetrant. An improved expression, derived based on mixture thermodynamics was developed by Chow in 1980, accounting for the heat change occurring upon mixing the penetrant and the polymer [72]:

$$\ln\left(\frac{T_{g,mix}}{T_{g2}}\right) = \beta[(1 - \theta) \ln(1 - \theta) + \theta \ln(\theta)] \quad [1.8]$$

$$\beta = \frac{zR}{M_p \Delta C_p} \quad [1.9]$$

$$\theta = \frac{M_p w_1}{z M_1 (1 - w_1)} \quad [1.10]$$

where M_p is the molecular weight of the polymer repeating unit, ΔC_p is the change of the isobaric specific heat capacity of the polymer at T_{g2} and z is the lattice coordination number. R is the ideal gas constant.

1.2.4 High-performance polymers

As polymers are versatile, easy processable and light-weight materials compared to metals, they are often the material of choice in many applications such as in the aerospace industry, packaging, construction, etc., However, for many applications extreme environments such as high temperatures, high pressures and harsh chemical environments cause many polymers to be unsuitable for the application. For this reason, the development of high-performance polymers has gained more and more attention over the past years [73,74]. High performance polymers are polymers that can outperform 'conventional' polymers in harsh environments for a

long period of time. Properties include high thermal decomposition temperatures ($>450\text{ }^{\circ}\text{C}$), no or little change in chemistry, and a long-term durability ($>10,000\text{ h}$) at temperatures above $150\text{ }^{\circ}\text{C}$ [75]. High-performance polymers therefore typically have a high glass transition ($>150\text{ }^{\circ}\text{C}$) and can roughly be divided into two categories; thermoplastics and thermosets.

Thermoplastics are high molecular weight linear or branched polymers and are either amorphous or crystalline. Therefore, thermoplastics can have both a melting temperature and a glass transition temperature. Their increased performance is gained from their high molecular weight, which causes the polymer chains to form non-covalent cross-links. Polymer chains can still flow, allowing them to orient and to form a semi-crystalline state. Thermoplastics are soluble and can be melt-processed up their critical molecular weight of entanglements (CME). Examples of well-known thermoplastics include poly(ether ether ketone) (PEEK), poly(etherimides) (PEIs), polyethersulfone (PES) and polyethylene terephthalate (PET).

Thermosets require the use of covalent cross-linking and are in general amorphous polymers, however they are also known to form crystalline networks. However, typically thermosets only have a glass transition temperature and do not possess a melting point temperature. Above the glass transition temperature, depending on the degree of cross-linking, the thermoset can be reshaped to a certain extent. Cross-linking prevents that thermosets dissolve and only allows for a certain extent of swelling. In order to process a thermoset, it is processed in its pre-cross-linked form and once in the desired shape, a curing treatment, which involves the cross-linking either by means of a chemical, thermal or radiation treatment. [76]. Thermosets are considered high-performance polymers, as their high degree of cross-linking allows them to have a high chemical and temperature resistance. The drawback of thermosets is their poor processability. [77,78] Examples of thermosets include phenol-formaldehyde resins (e.g. Novolac) which are often used as bonding material in plywood or as electrical insulation [79] and epoxy resins, which are often applied as structural applications, as bonding materials or coatings and also for electrical insulation [80].

When a certain elasticity or flexibility is required from the polymer, elastomers can be the polymers of choice. Elastomers or rubbers are slightly cross-linked polymers of which the glass transition temperature is generally very low (around or below room temperature). Elastomers show a high flexibility and mobility of the polymer chains and they show a viscoelastic behavior [11]. A common used elastomer is polydimethylsiloxane (PDMS) which is often used in microfluidics [81], medical applications [82] and sensing applications [83].

All of the above described materials show different swelling dynamics. To apply these polymers in a wide variety of applications, it is crucial to understand the fundamentals of swelling and the penetrant induced property changes.

1.3 Membrane Technology and Applications

In this thesis, the focus is on high-performance polymers applied in the field of membrane separations. A membrane can be described as a barrier that selectively separates one or more components from a mixture ^[84]. Based on either size selectivity, chemical affinity or charges, a membrane is able to selectively let one component permeate through the material, while retaining the rest of the mixture. The amount of transported component per unit surface area per unit time through the membrane is referred to as the **flux** (J) of the membrane. The **permeance** of the membrane is the flux per unit pressure and the **permeability** (P) of the membrane is the permeance corrected for the membrane thickness. The performance of a membrane is often expressed in terms of its permeability and **permselectivity** (F_α). The selectivity of the membrane is defined as the ratio of the permeabilities of the components in a mixture (Eq. 1.11) ^[84,85].

$$F_{\alpha_{ij}} = \frac{P_i}{P_j} \quad [1.11]$$

When designing a membrane, there is in general a trade-off between the selectivity of the membrane and the permeance of the membrane.

The extent to which a membrane retains a solute is described by the rejection. The **rejection** (R) of the membrane is expressed in terms of the feed (c_f) and permeate (c_p) concentration of the solute:

$$R = \frac{c_f - c_p}{c_f} \cdot 100\% \quad [1.12]$$

Membranes are used for gas separations, electrodialysis, pervaporation, carrier facilitated transport, controlled drug delivery and for pressure driven liquid separation processes^[84]. There are four different types of liquid separation processes defined: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (see also Figure 1.5) ^[84].

Figure 1.5 – A schematic depiction of the different pressure driven liquid separation processes and their separation abilities. The indicated length scale represents the size of the retained solute.

A membrane is either symmetric or asymmetric and the type of membrane used depends on its application. Symmetric membranes are either porous, non-porous dense membranes or charged membranes. In the case of a **porous** membrane (see Figure 1.6A), the membrane has a high void fraction that consists of randomly distributed and interconnected pores. The pore size, depending on the size of the component that needs to be retained are in the order of 2 nm to 10 µm in diameter [84,86]. UF and MF membranes are often porous membranes and their separation occurs based on size-exclusion. Materials commonly used for UF and MF membranes include polyacrylonitrile (PAN), polyethersulfone (PES) and polysulfone (PSf). The transport of a solute through a porous membrane can be described as a viscous flow and is driven by a pressure gradient over the membrane, as described by Darcy's law (Eq. 1.13).

$$J = -\frac{k}{\eta} \left(\frac{dp}{dx} \right) \quad [1.13]$$

where k is the Darcy's law coefficient, η is the viscosity and $\left(\frac{dp}{dx} \right)$ is the pressure gradient over the membrane. [84,87,88]

Membranes used for NF, RO and gas separation applications have in general a **dense** or **microporous** (pore size < 2 nm) separating top layer mechanically supported by a porous UF or MF layer. **Dense** membranes do not possess discrete pores and a component will be transported through the membrane via dissolution of the component into the membrane, followed by diffusion through the membrane, which

is a statistical process. This type of transport is referred to as the solution-diffusion process. The selectivity and separation for dense membranes is governed by the difference in the solubility (S) and diffusion coefficient (D) of the different components through the membrane (see Eq. 1.14).^[84,89]

$$F_{\alpha_{ij}} = \frac{D_i \cdot S_i}{D_j \cdot S_j} \quad [1.14]$$

Equilibrium polymers (i.e. rubbers) such as polydimethylsiloxane (PDMS) can be used to create a dense polymer membrane film. As it concerns an equilibrium material any pressure applied on the feed site of the membrane will be equal to the pressure in the membrane film itself. As a result, no pressure gradient over the membrane film exists (see Figure 1.6B).^[84,90] Also, the diffusion coefficients of the different components through the membrane will be similar. As a result, in dense polymer membrane films, the selectivity is dominated by the difference in solubility coefficients between the different components. The magnitude of the solubility coefficient is dependent on the affinity of the component for the membrane material.

Extreme glassy polymers (i.e. high T_g) with a high excess free volume and inorganic materials such as zeolites and silica can be used to create a **microporous** membrane (Figure 1.6C)^[43,86,91]. In microporous membranes, the pores are immobilized and as a result, the energy threshold for the “jumping” of a molecule from one diffusion site to another diffusion site is increased. Consequently, the diffusion coefficient can differ substantially between different components diffusing through the membrane film and the selectivity of the membrane film is dependent on both the solubility and diffusivity.^[86,91]

Figure 1.6 – Schematic depiction of a porous (A), dense (B) and microporous (C) membrane film.

Many NF, RO and gas separation membrane materials are glassy high-performance polymers such as polyimides and polyamides ^[92–94]. For glassy polymers, the amount of EFV available inside the polymer, will determine the penetrant transport rate through the polymer. In an equilibrium polymer, the hole free volume is the largest free volume element (see section 1.2.2). The hole free volume elements fluctuate as a result of the thermal motion of the polymer chains and are not fixed inside the polymer structure. The motion of the penetrants in this case is assumed to occur at about the same timescale as the fluctuation of these hole free volume elements, and diffusion occurs through the polymer material^[95]. When considering a glassy polymer, a part of the hole free volume is fixed (i.e. the excess free volume) and can be considered as void space available for diffusive transport. For polymers with a very high T_g (>~400 °C, e.g. PIM's or PTMSP), there is a high amount of EFV available, increasing the statistical jumping rate, allowing for a high diffusion rate ^[43]. For polymers with a lower amount of EFV, the availability of void spaces will be lower, decreasing the rate of diffusion. For a sufficient low EFV, also the hole free volume elements will influence the penetrant diffusion. For many glassy polymer membrane materials, the exact role of the excess free volume and hole free volume elements and their interaction with the penetrant is still poorly understood. ^[89,95,96]

1.3.1 Thin film composite membranes

For dense NF and RO membranes, a thicker membrane has a higher resistance and will require an increased feed pressure to maintain the same flux. For this reason, reducing the membrane thickness is preferred. In the 1960s, Loeb and Sourirajan introduced integrally skinned cellulose acetate membranes ^[97], which consisted of

a thin dense layer on top of a thick porous mechanical support, manufactured out of one material through a process now known as the phase inversion process. It was found that the thin dense layer limited the membrane resistance, allowing for a much high flux compared to symmetrical membrane available at that time ^[97]. Nowadays, most asymmetric membranes are thin film composite (TFC) membranes. TFC membranes are made out of two different materials. Often a thin dense polymer film consisting of one material is coated or formed on top of a microporous support, usually from a different material (see Figure 1.7) ^[98]. This allows for fine-tuning of the properties of the separation layer and the microporous support layer separately and independently from each other. Also, the thickness of the dense separation layer can be made ultrathin, allowing for higher fluxes. For this reason, almost all commercial reverse osmosis and nanofiltration processes operate using thin film composite membranes ^[99–101]. In thin film composite membranes, the separation is governed by the thin polymer film. Understanding how penetrants interact with this separation layer and how it changes the separation properties, is crucial to the design of new thin film composite membranes.

Figure 1.7 – A schematic representation of a thin film composite or anisotropic membrane. A thin dense separation layer is formed on top of a mechanical porous support, often a microfiltration or ultrafiltration membrane. The non-woven is the backing material.

1.3.2 Interfacial Polymerization

A common technique for the fabrication of a thin dense film, which is also commercially applied for the fabrication of thin film composite RO and NF membranes, is interfacial polymerization (IP) or interfacial polycondensation. IP is the localized polymerization reaction of two reactants on the interface of commonly two immiscible liquids, such as an aqueous phase and an organic phase. A reaction based on the Schotten-Baumann reaction occurs between an acyl halide and a compound with an active hydrogen, such as an amide ^[102]. The acyl halide is dissolved in the organic phase, while the amide is dissolved in the aqueous phase, at the interface the reactants will meet and react, forming a polymer (see Figure 1.8). Since the polymerization reaction is confined to the interface between the two phases, the reactants are more likely to react with the reactive chain end of the

polymer, rather than with free monomers. As a result, IP yields in high molecular weight, low polydispersity and defect free polymer films, compared to bulk polymerization reactions under mild conditions ^[103]. The IP reaction occurs on the scale of seconds to minutes, and as the formed polymer film will form a barrier for the diffusion of the reactants, the typical obtained film thicknesses for IP can range from a few nanometers to a few micrometers ^[104]. For this reason, IP is a very efficient method to synthesize high performance thin film polymers.

Figure 1.8 – The concept of interfacial polymerization. A represents the reactant with an active hydrogen dissolved in the aqueous phase, for membranes commonly an amide. B represents the acyl halide dissolved in the organic phase. At the interface between the aqueous and organic phase, a reaction occurs, and a thin polymer film is formed.

IP can be applied for the manufacturing of thin film composite membranes, by immersing a microporous support in the aqueous solution, creating a reservoir for the aqueous phase. The surface of the microporous support is then dried (while maintaining an aqueous solution inside the pores) and subsequently placed in the organic phase. As a result, a thin film is formed on top of the microporous support.

The formation and performance of the IP film as a thin film composite membrane is dependent on many parameters. The interface of the IP film is defined by the thin film composite support and therefore, the support of the thin film composite membrane is very important ^[105]. A small pore size combined with a good wettability of the support by the aqueous phase will provide for a stable interface and a better adhesion of the IP film to the support ^[106–108]. Most commercial IP membranes are synthesized on top of an organic support such as Polysulfone (PSf), poly(ether sulfone) (PES), polyvinylidene fluoride (PVDF), polypropylene (PP), polyacrylonitrile (PAN), or polyimides (PI) ^[95,109]. In case of extreme temperatures or harsh chemical environments, inorganic supports have also been utilized. Other parameters that influence the IP reaction include the type of solvents used, the reaction time and temperature, the use of additives and surfactants and the type of monomers ^[104,110,111].

The first IP membrane was described by Cadotte in 1981^[112] who prepared a RO membrane using *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC). As of today, most commercialized IP thin film composite membranes for NF and RO are synthesized from an aromatic or semi-aromatic multifunctional amine and TMC^[94,113]. However, IP can be applied to a wide variety of monomers, and thus a wide variety of new materials can be synthesized using IP. Over the years, many new monomers with increased functionality have been proposed for the development of novel and functional IP membranes. For a comprehensive overview on IP and the development of new IP chemistries, the reader is referred to the review of Raaijmakers et al.^[104]

Although the different chemistries of IP synthesized films have been widely explored as shown by Raaijmakers et al.^[104], there is a poor fundamental understanding on how IP synthesized films interact with a penetrant. Most IP films are characterized based on their separation and flux performance^[111,114–116]. However, there is only little literature available which specifically study the sorption performance of typical IP polymerized films such as polyamides^[117–119].

1.3.3 Organic solvent nanofiltration

The work in this thesis focusses on thin film composite membranes applied in organic solvent nanofiltration. Therefore, the concept of organic solvents and the challenges of applying membranes in organic solvent nanofiltrations will be discussed.

Organic solvents are non-aqueous substances that have the ability to dissolve another compound. In the pharmaceutical industry, petrochemical industry and the chemical industry in general, organic solvents are widely applied. Organic solvents are used as a means to transport, process or purify a single component or multiple components. At this moment, the main means to ensure a separation of organic solvents from a mixture, is thermal distillation. One of the major disadvantages of distillation however, is the high energy consumption required to ensure separation. Other than the high energy consumption, heat sensitive compounds cannot be separated using thermal distillation. As membranes have been applied and successfully commercialized for desalination and water treatment applications, membrane technology is being considered as a high potential candidate to be used for energy efficient organic solvent separation applications^[95]. Although membranes have a high theoretical potential towards these types of separations, only a limited amount of commercialized organic solvent nanofiltration (OSN) or solvent resistant nanofiltration (SRNF) processes can currently be found. The first large scale industrial process was the MAX-DEWAX process from ExxonMobil^[120].

At this moment, 94 % of OSN applications fall under purifications such as pharmaceutical polishing and catalyst recovery ^[95].

In order to apply OSN in large scale industrial processes, a number of challenges need to be overcome. Unlike with membranes used for water treatment, OSN involves a wide variety of solvents, that each of which can interact with the membrane in a different way. As a result, a membrane could retain a certain solute in one solvent, but not in a different solvent ^[121]. Additionally, there is lack of general multipurpose membrane, because the robustness of these membranes towards swelling and leaching in a variety of environments is still poorly understood ^[95,121]. At this moment, a deeper understanding of the interaction between solvent, solute and membrane material is necessary in order to increase the capability to predict the performance of the NF membrane by means of modelling and thus to improve the process design ^[95]. Unpredicted behavior such as the sudden flux decline upon a reduction in membrane thickness ^[122], the inclusion of nanofillers ^[123–125] or the effect of post-treatments ^[126] still require further research to better understand and to induce these type of phenomena on purpose.

Over the past two decades, a great deal of research has been done to improve the membrane performance and to develop new membranes to be used for OSN applications. Excellent reviews on the developments in the field of OSN were provided by Vandezande et al. (2007) ^[105] and by Marchetti et al. (2014) ^[95], and a review more specifically on the development of thin film composite membranes was provided by Hermans et al. (2015) ^[121]. As stated by Marchetti et al. and by Hermans et al., to make OSN an appealing alternative to conventional separation techniques there is a general need for a better understanding of the membrane structure and the interaction with the solvents and dissolved components at a molecular level. Eventually, this will allow for a better prediction of the membrane performance and improvement in the membrane design. In order to accomplish this, the membrane should not only be characterized based on its performance in terms of permeance and retention or molecular weight cut-off (MWCO) as is commonly reported for OSN membranes, but also the structure and solvent interaction should be characterized and evaluated ^[95,127].

The work in this thesis provides new fundamental understandings on the interaction between the different components in OSN systems. Also, alternative methods as to measuring the membrane performance are presented to improve the fundamental understanding of thin polymer films in OSN applications.

Figure 1.9 – The possible interaction that exist between the solvent, solute and membrane material itself. Adapted with permission from the American Chemical society¹.

In the following sections, different characterization techniques that can be used to study the interaction of a penetrant and the membrane material will be discussed.

1.4 Characterization Techniques to Study Sorption

In order to study the penetrant sorption in membrane materials, many studies have typically utilized gravimetric methods ^[54,128–131] to determine the solvent mass uptake, or the measurement of size changes to determine the dilation ^[131–134]. Although often effective for the measurement of penetrant sorption in bulk materials in a (semi-)equilibrium, these two techniques cannot provide an accurate description of penetrant concentration inside the thin polymer film of a thin film composite membrane over time. Additionally, bulk properties cannot be assumed to be the same as that of a thin film, as the thin film is confined to a substrate, which restricts the swelling of the film to one dimension ^[135–137] and a larger fraction of the molecules are exposed to a free surface. Nano-confinement effects or diffusion effects can occur that are not present for bulk materials ^[138–140]. Also, since many of the membrane materials are glassy polymers ^[141,142], the penetrant sorption is expected to change continuously over time. For the abovementioned reasons, to understand the penetrant sorption, it is important to measure the penetrant sorption of thin polymer films in conditions that are similar to the real membrane conditions. One characterization technique that allows for derivation of the solvent

¹ Marchetti et al. (2014) (<https://pubs.acs.org/doi/pdf/10.1021/cr500006j>) ^[95]

mass uptake and thickness dilation simultaneously of thin polymer films confined to a substrate, is spectroscopic ellipsometry (SE). To probe the underlying molecular chain dynamics during penetrant sorption, broadband dielectric spectroscopy (BDS) poses as a possible technique. In the coming sections, the theory and applications of both techniques, and techniques complementary to SE and BDS will be discussed.

Table 1.2 – An overview of the different characterization techniques discussed in detail in this section.

Characterization technique	Obtained information	Methodology
Spectroscopic ellipsometry	Changes in thickness and optical properties	Optical
Quartz crystal microbalance	Mass changes and viscoelasticity	Mechanical
Broadband dielectric spectroscopy	Polymer chain relaxation times	Electrical

1.4.1 *In situ* spectroscopic ellipsometry

Spectroscopic ellipsometry is a non-destructive optical technique where a sample is exposed to a beam of linearly polarized light. It provides information on the thickness and optical properties (refractive index) of the measured sample. The concept of ellipsometry is based on the change in the polarization state of the transmitted light. During the ellipsometry measurement a linearly polarized light beam is either reflected or transmitted through the sample and the change in the polarization state is measured by using the amplitude ratio ψ (Ψ) and the phase difference δ (Δ) between p - and s -polarized light waves. p -Polarization refers to the polarization waves in the plane of incidence and s -polarization refers to the polarization waves normal to the plane of incidence. In general, the reflected light has an elliptical polarization state, hence the name ellipsometry. Using the parameters Ψ and Δ , a ratio ρ can be determined:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) \cdot e^{i\Delta} \quad [1.15]$$

where r_p is the reflectivity of p -polarized light and r_s is the reflectivity of s -polarized light. The reflectivity and transmittance of the p - and s -polarization can be predicted by the Fresnel equations, which predict the behavior of the p - and s -polarized waves when in contact with a material interface. As there is a difference in electric dipole radiations of the different materials, the amplitude reflection coefficients for p - and s -polarizations differ significantly. ^[143,144]

Although SE is a real-time monitoring and fast technique, it is based on indirect characterization. An optical model with fit parameters is required to interpret the raw data. The optical model is defined by the optical parameters and the layer thicknesses of the measured sample. Often a multi-layer optical model is used to represent the whole sample. This model includes information about the layer thicknesses, the refractive index, n , and the absorption, k of each layer in the model. In case of an optical transparent polymer film, a Cauchy description is used for the determination of n as function of the wavelength (Eq. 1.16).

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad [1.16]$$

A gives an indication of the range of the refractive index and the parameters B and C determine the shape or curvature of the refractive index versus the wavelength.

When studying sorption, information on the composition of the polymer/penetrant mixture can be obtained based on the determined changes in the refractive index and in case of equilibrium polymers, assuming volume additivity, also based on the change in thickness. Mixing rules such as Effective Medium Approximations (EMA's) can be employed to determine the penetrant volume fraction [8,144,145]. The Clausius-Mossotti relation applied to mixtures (Eq. 1.17) can be used to determine the mass concentration of a penetrant as commonly used in gas sorption measurements. However, an assumption about the density of the penetrant in the mixture is required [8].

$$\frac{n_{mix}^2 - 1}{n_{mix}^2 + 2} = \frac{R_{penetrant}}{M_{w,penetrant}} \cdot C_{penetrant} + \frac{R_{polymer}}{M_{w,polymer}} \cdot C_{polymer} \quad [1.17]$$

Where n_{mix} is the refractive index of the mixture, R is the molar refractivity, M_w the molecular weight and C the mass concentration of the penetrant and polymer respectively.

Since SE involves an indirect characterization, the quality of the fit should be evaluated. The fit quality can be quantified by calculating the Mean Squared Error (MSE) of each fit. The MSE is defined as

$$MSE = \sqrt{\frac{1}{2n_\lambda - M} \cdot \left[\left(\frac{\psi_t^{Mod} - \psi_t^{Exp}}{\sigma_{\psi,t}^{Exp}} \right)^2 + \left(\frac{\Delta_t^{Mod} - \Delta_t^{Exp}}{\sigma_{\Delta,t}^{Exp}} \right)^2 \right]} \quad [1.18]$$

where n_λ is the number of wavelengths and M the number of fit parameters. In general, a good fit is obtained when the MSE is minimized and the fit curve overlaps the experimental data. For a measurement over a broad wavelength range (300-1000 nm), a MSE between 1 and 5 is considered acceptable or a layer thickness of up to 500 nm, however for a layer thickness in the range of 1000-2000 nm, an MSE above 10 can be obtained [8]. However, a low MSE does not indicate that the fit obtained is

unique and physically realistic. The behavior of the optical constants should be checked as function of the wavelength. For non-absorbing materials, the value for the refractive index is physical when n increases with shorter wavelengths.

SE measurements can be performed *in situ*, since for modern ellipsometers the light intensity ratios are measured and not the individual intensities of the *s*- and *p*-polarized light waves. For this reason, *in situ* swelling or temperature measurements, which generally result in a loss of the absolute intensity, can still be measured using *in situ* SE. Advantages of *in situ* SE are the high precision and high acquisition times that can be accomplished by the modern ellipsometers. For this reason, swelling dynamics of thin polymer films when exposed to a penetrant can be followed with a high resolution. Disadvantages of SE are the limitation in the choice of substrate and the requirement of a well-defined optical model. The substrate should be optically non-transparent and preferably it has a high optical contrast with the analyzed polymer. Typically a silicon wafer ($n=3.9$) is used as the substrate, because the optical properties are well-documented and there is a high optical contrast with most polymers ($n = 1.4\text{--}1.6$ ^[8]). In literature alternative substrates have been reported as well, for example gold is used when also the mass uptake is studied with combined quartz crystal microbalance (QCM), and in the case of membrane applications, reports on porous substrates have been published ^[96,146,147].

An extensive review of *in situ* SE applied to thin polymer films and membranes is provided by Ogieglo et al ^[8] and in the book "Ellipsometry of Functional Organic Surfaces and Films" by Hinrichs and Eichorn ^[148]. When characterizing thin polymer films for membrane applications, SE can provide insight on penetrant induced swelling and plasticization processes. For example, *in situ* SE was used to determine the transport mechanism of *n*-hexane through PDMS membranes under non-equilibrium conditions ^[96], to study the polymer relaxations in the vicinity of the penetrant or temperature induced glass transition ^[149] and to discriminate between Fickian diffusion and Case II diffusion mechanisms for *n*-hexane sorption in polystyrene ^[69]. From a more application focused point of view, *in situ* SE has also been widely applied to measure gas and vapor sorption in thin polymer films and membranes ^[118,150–153].

1.4.1.1 Techniques complementary with spectroscopic ellipsometry

Since SE is a model-based technique and over-interpretation or over-parameterization of the model is often one of the main drawbacks of SE, complementary techniques to confirm the SE findings should be performed. Many characterization techniques can be used complementary to SE. In most cases this involves separate measurements on different samples to obtain additional

information on the sample material. In the review on *in situ* SE by Ogieglo et al.,^[8] an overview of (*in situ*) techniques complementary to SE is provided. Although many of the techniques mentioned in this review can be performed *in situ*, only two of these techniques have been combined with SE, as such that different information can be obtained simultaneously on the same sample. This includes IR-ellipsometry^[154,155] and QCM with dissipation monitoring (QCM-D). In this thesis, the potential of combining QCM-D with SE was investigated, for this reason, QCM-D will be discussed in more detail.

Quartz Crystal Microbalance with dissipation monitoring (QCM-D)

Where SE measures the change in volume and optical properties of the sample material, a measurement with QCM-D yields information on the mass change and mechanical properties of the sample material. The principle of QCM is based on the piezoelectricity of the quartz crystal. An alternating voltage is applied to the quartz crystal, which will result in an oscillatory motion of the crystal. A so-called standing wave is generated when the AC voltage frequency matches the resonance frequency of the crystal. In QCM AT-cut crystals are used that cause the crystal to vibrate in a thickness shear mode at a resonance frequency (f_n) of:

$$f_n = \frac{nc}{2d} \quad [1.19]$$

Where n is the overtone order, c is the speed of sound in quartz and d is the crystal thickness^[156]. Whenever the mass on the quartz surface changes, the resonance frequency will change. The mass changes (Δm) can be related to the change in the resonance frequency (Δf) by the Sauerbrey relationship (Eq. 1.20)^[157].

$$\Delta f_n = -\frac{n}{C} m_f = -\frac{n}{C} \rho_f h_f \quad [1.20]$$

Where C is the mass sensitivity constant related to the properties of quartz, and ρ_f and h_f are the density and thickness of the absorbed film^[156]. Eq. 1.20 is valid when the adsorbed film is a rigid film and no decay of the frequency was observed. However, when measuring in liquids and gases, the shear frequency of the quartz crystal decays rapidly, this decay in frequency is referred to as dissipation (D_n) (Eq. 1.21). Dissipation also occurs when the adsorbed film has a low viscosity, as illustrated in Figure 1.10.

$$D_n = \frac{1}{\pi f_n \tau} \quad [1.21]$$

Figure 1.10 – The difference in QCM frequency signal between a rigid film and a soft/viscoelastic film. Upon the addition of a soft or viscoelastic layer on top of the rigid film, the frequency lowers and a stronger decay in frequency can be observed.

In a QCM-D measurement, the dissipation can be measured by intermittently turning off the external AC voltage. The voltage the quartz crystal generates during this period as a result of the decaying oscillations, is measured from which the dissipation factor can be obtained. When $\frac{\Delta D_n}{\Delta f_n} \ll 4 \times 10^{-7} \text{ Hz}^{-1}$ for a quartz crystal with $f_n = 5\text{MHz}$, the dissipation of the signal can be neglected and the Sauerbrey equation is valid and can be used to extract the areal mass density of the adsorbed film ^[158]. When measuring in liquids, the areal mass density in this case will include the mass density of the adsorbate itself, but also the mass density of the penetrant. Independent thickness or mass measurements, for example with SE, can be used to determine the mass density of the adsorbate. With QCM, the weight fraction of the penetrant inside the film can then be determined ^[156]. In case of a viscoelastic film, $\Delta D_n > 0$, the Sauerbrey relation will overestimate the mass density of the adsorbate film, and the viscoelastic properties must be considered. The viscosity of a material, η , is the measure of the material's resistance to flow. When considering viscoelastic materials, the viscosity is represented by modelling a dashpot, while the elasticity is modelled as a spring. To model the viscoelastic behavior of a material, typically simple combinations of spring and dashpot are considered. This can be done in series (Maxwell model) or in parallel fashion (Voigt-Voinova model ^[159]) (see Figure 1.11). The Maxwell model is applicable when the polymer solution demonstrates purely liquid-like behavior at the low shear rates. The Voigt model is more applicable to polymers which are able to conserve their shape and do not flow ^[159].

Figure 1.11 – A schematic representation of the Maxwell model and Voigt-Voinova model. The viscosity, η , is represented by a dashpot and the elasticity, E , by a spring.

The viscoelastic behavior is represented as:

$$G^* = G' + iG'' = \mu + i2\pi f\eta \quad [1.22]$$

Where G^* is the complex shear modulus, G' the storage modulus, G'' the loss modulus, μ the modulus of elasticity, f the frequency and η the viscosity. When performing a QCM-D measurement, one can measure the frequency change and dissipation change, and by using the layer density, fluid density and viscosity as additional input parameters, information on the thickness, viscosity and shear modulus of the adsorbed layer can be obtained. As shown in Eq. 1.22, the viscoelastic behavior is frequency dependent. It is therefore important to realize that the thickness of the adsorbed material cannot be properly modelled when the frequency dependency of the viscoelastic properties is unknown.

Combining a QCM-D measurement with SE can overcome the weaknesses of either technique when used individually. For SE swelling measurements, the mass uptake can be extracted based on the changes in the refractive index. Combining with QCM-D will provide additional and reliable information on the penetrant mass uptake. Also, additional information on the change in the viscoelastic properties, as a result of the penetrant uptake can be obtained. In literature, the combination of QCM-D and SE has grown more popular over the years. Especially in the field of polymer brushes, QCM-D with SE has been utilized extensively. In the fully swollen state the refractive index of the swollen brush is comparable to the refractive index of the medium, and individual SE measurements are not reliable ^[154,160–163]. Applied to membranes, Lin et al. ^[164] studied the void structure of commercial polyamide membranes and the water uptake by these void fractions using QCM-D and SE. Dishari et al. ^[165] studied the humidity uptake as function of film thickness for S-

radel with varying film thicknesses from 25-250 nm and showed that water accumulated at the substrate interface and interfacial effects were less pronounced for thicker films. More information on studies of QCM-D combined with SE is provided in ^[148].

1.4.2 Broadband Dielectric Spectroscopy

Broadband dielectric spectroscopy (BDS) measures the interaction between an external electric field with the electric dipole moment and charges of the sample. Upon oscillating the electric field over a broad range of frequencies (10^{-6} Hz to 10^{12} Hz), the dielectric response of the sample material is measured and connected to the molecular dynamics.

In the field of membrane science, BDS can prove to be a very useful tool, since it can provide insight on the relaxation phenomena that occur within the membrane as function of temperature. Also, it can prove to be very useful for the study of penetrant induced swelling of the membrane. Although there are few studies available to date on the effect of a penetrant on the molecular dynamics of polymers using BDS ^[166–168], BDS in combination with other techniques such as SE and infrared spectroscopy can provide a fundamental understanding of the penetrant induced molecular dynamics within a thin polymer film.

1.4.2.1 BDS theory

Dielectric materials are electrical insulators that can be polarized when exposed to an applied electric field. Unlike in conducting materials, charges cannot flow in the material, but can only shift from their equilibrium positions in the direction of the electric field (see Figure 1.12). As a result, the charge distribution is distorted and an electric dipole is created. The dielectric relaxation of a material is the delayed response to a change in the electric field. The electric response of a dielectric material can be categorized in three processes ^[169]:

1. Electronic/atomic polarization: electrons react very fast to the electric field and the electronic polarization is responsible for the optical properties of the sample (e.g. refractive index in UV range). Atomic polarization is what can be measured with IR spectroscopy. The magnitude of atomic polarization is usually quite small but the response is considered instantaneous (linear response).
2. Orientational polarization: orientational polarization arises due to the rotation of pre-existing molecular dipole moments when exposed to an applied electric field. The timescale is dependent on the effective viscosity, since it involves the motion of larger entities.

3. Propagation of charge carriers: a buildup of charges at a boundary such as a dielectric interface or electrode, often referred to as the Maxwell Wagner polarization or electrode polarization.

Figure 1.12 – Schematic illustration of the orientation of the dipole moments inside a polymer film upon the application of an electric field.

The dependence of the polarization on the electric field is described by the susceptibility, χ , a constant proportionality that is dependent on the material structure and properties. The extent to which a material can be polarized upon the application of an electric field, is expressed in the polarizability of the material (α ($\text{C}^2 \text{m}^2 \text{J}^{-1}$)). As a dielectric material is effectively a capacitor, it has an ability to store energy when an electric field is applied. The extent to which it can store this energy is described by the permittivity (ϵ (F m^{-1})) of the material. The capacitance, C is therefore dependent on the relative permittivity of the material (ϵ_r), the permittivity of vacuum (ϵ_0) and the area (A) and thickness (d) of the dielectric material (Eq. 1.23 and Eq. 1.24).

$$C = \epsilon_r \frac{\epsilon_0 A}{d} \quad [1.23]$$

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad [1.24]$$

The permittivity of a material is a macroscopic property which can be measured, but it can be related to microscopic properties such as the polarization via the Clausius-Mossotti relation (Eq.1.25) and to the dipole moment of the molecule via the Kirkwood-Fröhlich equation ^[170,171] which is based on Onsager's dielectric equation ^[172] (Eq. 1.26).

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} \cdot \frac{N}{V} \alpha \quad [1.25]$$

Where N is the number of dipole moments, and V the volume of the dielectric material.

$$g \mu_0^2 = \epsilon_0 kT \frac{V}{N} \frac{9(2\epsilon_r + \epsilon_\infty)}{\epsilon_r(\epsilon_\infty + 2)^2} (\epsilon_r - \epsilon_\infty) \quad [1.26]$$

g is known as the Kirkwood correlation factor to account for orientational correlations and μ_0 is the dipole moment of an isolated molecule.

By applying the Clausius-Mossotti relation and the Kirkwood-Fröhlich equation, dielectric relaxation spectroscopy can provide information on microscopic changes within the polymer molecules.

The dielectric response

When performing a BDS measurement, it is the complex capacity (including storage and loss factors) that is measured as function of the AC voltage frequency, while it is the complex permittivity that is provided as the output. The complex dielectric function represents the dielectric response of the material, which includes information on the dipole displacement as shown in Eq. 1.26. As mentioned above, the dielectric response is a complex function and it includes a storage and a loss component. The dipole displacement, $\vec{D}(t)$, is time dependent and upon the application of an electric field, there will be an instantaneous response, which will be in-phase with the AC frequency of the electric field, and there will be a delayed response caused by the orientational dynamics of the dielectric material (see Figure 1.13).

Figure 1.13 – Left: the stepwise application of the electric field. Right: The displacement as measured as a result of the applied electric field. An instantaneous response is followed by a delayed response over time.

When translated to a frequency dependent response via a Fourier transformation, the dipole displacement can be described as:

$$\vec{D}(t, \omega) = \varepsilon^*(\omega) \varepsilon_0 \vec{E}(t, \omega) \quad [1.27]$$

Where $\varepsilon^*(\omega)$ is the frequency dependent complex dielectric function described as:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad [1.28]$$

$\varepsilon'(\omega)$ is the in-phase response of the system (dispersion), while $\varepsilon''(\omega)$ accounts for the delay in response to the excitation (Loss) (see Figure 1.14). At high frequencies, internal rearrangements occur, and at the low frequencies conductivity can occur.

To describe the dispersion and loss factor of the dielectric function as function of the frequency and to extract the relaxation time of the relaxation, The Havriliak Negami relaxation function can be used (Eq. 1.29).

$$\varepsilon^* = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1+(i\omega\tau)^{\alpha})^{\beta}} \quad [1.29]$$

Where ε_{∞} is the value of the dielectric function in absence of polarization processes, $\Delta\varepsilon$ is the dielectric strength and τ is the relaxation time, α and β are shape parameters quantifying the symmetric and asymmetric broadening of the relaxation time distribution function. ^[169]

Figure 1.14 – ε' and ε'' as function of frequency.

The Kramer-Krönig relations can be used to check for linearity and physical behavior of the dielectric function (Eq. 1.30 and 1.31). Many dielectric polymers show a linear dielectric behavior, meaning there is direct correlation between the displacement, $\vec{D}$ as function of the applied electric field ^[173].

$$\varepsilon'(\omega) - \varepsilon_{\infty} = -\frac{2}{\pi} \int_0^{\infty} \frac{\omega' \varepsilon''(\omega')}{\omega'^2 - \omega^2} d\omega' \quad [1.30]$$

$$\varepsilon''(\omega) = -\frac{2\omega}{\pi} \int_0^{\infty} \frac{\varepsilon'(\omega') - \varepsilon_{\infty}}{\omega'^2 - \omega^2} d\omega' \quad [1.31]$$

Dielectric relaxations

In section 1.2 the glass transition in a material was described as a transition where cooperative motion up to length scale of 1-4 nm is able to occur as the so-called cooperative rearranging region (CRR) ^[22]. The polymer relaxation associated with the CRR is the α -relaxation. By convention, the dielectric glass transition temperature is set as the temperature when the α -relaxation time, $\tau_\alpha(T_g) = 100$ s. The temperature dependence of τ_α is described by the Vogel-Fulcher-Tammann empirical dependence (Eq. 1.32) ^[174,175].

$$\frac{1}{\tau(T)} = \frac{1}{\tau_\infty} \exp\left(-\frac{CT_0}{T-T_0}\right) \quad [1.32]$$

Where τ_∞ is the relaxation time in the high temperature limit, C is a constant and T_0 is the Vogel-Fulcher temperature. On a more local scale, slow and fast β -relaxations can occur. In general, β -relaxations occur at lower temperatures than α -relaxations, which occur in an amorphous polymer. β -relaxations are due to the motions of groups present in the side chain around the main polymer backbone (fast β -relaxations) or motions of groups in the main chain itself. β -relaxations is a thermally activated motion between two potential wells, and the temperature dependence can therefore be described with an Arrhenius relation (Eq. 1.33).

$$\frac{1}{\tau(T)} = \frac{1}{\tau_\infty} \exp\left(-\frac{E_A}{kT}\right) \quad [1.33]$$

Where E_A is the activation energy and k the Boltzmann constant. ^[169,176]

Figure 1.15 – A schematic overview of the dielectric loss as function of the frequency, indicating the different types of relaxations that can occur within a material. Adapted with permission from Elsevier².

² Kremer (2002) ([https://doi.org/10.1016/S0022-3093\(02\)01083-9](https://doi.org/10.1016/S0022-3093(02)01083-9))^[176]

1.4.2.2 BDS applied to soft matter

BDS measurements can be performed in different configurations, of which the parallel plate configuration is most commonly applied, but also interdigitated electrodes are used. In both cases, the material functions as a capacitor that is placed between two counter electrodes. In the case of a parallel plate configuration, ultrathin films ^[177–179] and even isolated polymer chains ^[180] can be probed. The minimum film thickness of the sample is in case of the interdigitate electrodes limited by the spacing of the comb electrodes ^[181]. In both cases, a permanent dipole in the sample material is required.

As BDS provides information on the molecular dynamics within a material, it has been widely applied in many different fields of research. The most common applications include the monitoring of chemical reactions, ageing and curing processes ^[182–184], pharmaceutical applications such as drug characterization or biosensing ^[185,186], studying of material properties like the glass transition, crystallization or phase composition ^[138,187–190], study of charge transport and charge mobility ^[191,192]. However, when using BDS as a measurement tool, it should be taken into mind that the dipoles within the materials are probed. For this reason, one cannot exactly point out the process responsible for the relaxation peak, but additional complementary measurement methods are required (e.g. calorimetry, FTIR, or NMR). In this thesis, BDS is applied to study the induced molecular interactions induced by the sorption of a penetrant.

1.5 Thesis Outline

In order to improve the prediction and understanding of a thin polymer film in organic solvent applications, an investigation into the polymer-penetrant interaction is required. The work described in this thesis provides a contribution to the understanding of the swelling dynamics of thin polymer films exposed to an organic penetrant. Throughout this thesis, *in situ* characterization techniques have been applied as a means to study the swelling behavior of thin polymer films in organic solvent applications.

First, the applicability of *in situ* spectroscopic ellipsometry on thin polymer films in liquid media is discussed in **Chapter 2**. The effect of introducing a liquid medium and windows in front of the measurement light beam on the accuracy of the optical model is discussed. It was shown that the reliability of the swelling quantification decreases when measuring films thinner than ~100 nm in liquid environments.

In **Chapters 3 to 6**, *in situ* spectroscopic ellipsometry has been used as a tool to study and characterize the swelling behavior of different membrane materials. **Chapters 3 and 4** discuss more on the mechanisms of swelling in glassy polymers, while

Chapters 5 and 6 focus more on the dynamics of swelling. In **Chapter 7**, the potential of broadband dielectric spectroscopy in combination with spectroscopic ellipsometry and infrared spectroscopy as *in situ* characterization techniques is shown.

In **Chapter 3**, the role of the excess free volume on the swelling behavior of glassy polymers was investigated. The swelling behavior of three different solvents was measured in five different glassy polymers. It was shown that independent of the type of solvent or polymer, the excess free volume was filled at a swelling of ~5 %.

Chapter 4 describes the presence of a stratified swelling behavior in thin polystyrene films exposed to *n*-hexane. It was shown that within a thin polystyrene film at a specific temperature, both a Fickian diffusion regime and a Case II diffusion regime were present. As a result, three layers could be identified within the polystyrene film: a free surface layer behaving like a rubber, a transition layer showing Case II diffusion and a bulk layer displaying Fickian diffusion. The thickness of the transition region and its dependence on the total polymer film thickness was determined.

Chapter 5 addresses the problem of the failure of water treatment membranes in hydrocarbon contaminated water mixtures. The interaction of thin polysulfone films in a water solution saturated with toluene was studied and compared to pure component solutions. It was shown that the non-ideality of the system induces a dewetting of the polysulfone layer.

In **Chapter 6**, the disadvantages of using a rubber like polydimethylsiloxane (PDMS) in organic solvent applications is discussed. The thin film formation of poly(PDMS-POSSimides) via interfacial polymerization is proposed as a novel approach to form hyper-cross-linked thin PDMS films. The swelling behavior of these poly(PDMS-POSSimides) was studied and compared to the swelling behavior of conventional PDMS films.

In **Chapter 7**, the interaction of two organic solvents with Matrimid 5218 was investigated by employing a combination of spectroscopic ellipsometry, broadband dielectric spectroscopy and infrared spectroscopy. It was shown for the first time that broadband relaxation spectroscopy can be used to study the different interactions between the penetrant and the polymer chains.

Chapter 8 reflects on the results presented in this thesis and discusses on possible new research directions in terms of studying the swelling behavior of thin polymer films with *in situ* characterization techniques.

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Chapter 2

Inaccuracies in the Analysis on Solvent-induced Swelling of Transparent Thin Films using *in situ* Spectroscopic Ellipsometry

This chapter is adapted from:

Kristianne Tempelman, Emiel J. Kappert, Michiel J. T. Raaijmakers, Herbert Wormeester, Nieck E. Benes, *Dealing with inaccuracies in the analysis on solvent-induced swelling of transparent thin films using in situ spectroscopic ellipsometry in the visible wavelength range*, Surface and Interface Analysis **2016**, accepted manuscript, DOI: 10.1002/sia.6191

Abstract

The accuracy of spectroscopic ellipsometry studies of transparent polymer films in the visible wavelength range is greatly reduced in the presence of a liquid ambient. The relatively high refractive index of a liquid ambient strongly amplifies the effects of experimental non-idealities, such as window birefringence and an unknowingly inaccurate description of the optical properties of the ambient. In particular for thin films (approximately <100 nm), the implications of even small non-idealities are substantial, and large deviations in the thickness and refractive index are found. The concurrent low root mean square error (*MSE*) values show that a good *MSE* does not show that the optical model is correct, it just shows a good agreement between the experimental and fitted data. This implies that quantitative *in situ* ellipsometry studies for thin films are intricate, and derived properties like sorption behavior should be treated with caution. Here, we show that quantitative *in situ* ellipsometry swelling measurements in solvents require a very accurate solvent dispersion relation, a high-quality temperature control, especially to prevent temperature differences between the cell, its content and exterior ambient, and accurate quantification of window effects, in particular for polymer films with thicknesses of approximately below 100 nm, depending on the optical contrast of the polymer-solvent system.

2.1 Introduction

Applications of thin films are widespread. In many instances, these films are formed from, or can be exposed to, solvents or their vapors. In thin film production, solvents are for instance used during coating,^[1] in solvent annealing,^[2] or in characterizing a material by ellipsometric porosimetry^[3]. Some films find their application in solvents, for instance as a sensor,^[4,5] or as a membrane.^[6,7] Typically, the structure of a thin film changes when it is exposed to a solvent. Tracking its structure *in situ* during exposure can provide crucial insights into the stability and properties of the film. The required accuracy for such measurements depends on whether one is only interested in trends or in accurate recorded values. Depending on the desired accuracy, a suitable technique can be chosen to track the *in situ* changing of the thin film structure. A diverse range of techniques is available for characterizing thin films in solvents, including spectroscopic ellipsometry,^[8,9] infrared/Raman spectroscopy,^[10] quartz crystal microbalance,^[11] white light interferometry^[12], x-ray reflectivity^[13] and atomic force microscopy.^[14]

Spectroscopic ellipsometry has proven to be a powerful technique for studying thin films in solvents, because it allows for determining both the thickness and the refractive index of the film, it is fast, and it can be applied both *in situ* and *in operandi*.^[8] When used correctly it can effectively capture features such as solvent gradients,^[15] anisotropy^[16] and solvent volume fractions^[17] that can develop and/or disappear from films upon solvent exposure.

In addition to the wide variety of possible measurement configurations, modern spectroscopic ellipsometers are, in theory, sensitive to measure changes in layers with a resolution Δd of 0.1 Å.^[18] For simple, transparent thin films on a well-defined substrate such as a silicon wafer, this sensitivity can be reached, as measurement accuracy is mainly limited by the precision of the ellipsometer in determining Ψ and Δ . For more complex samples, the choice of the optical model used to describe the film can have a strong impact on the accuracy.^[18] Here, precision is referred to as a random error, an inherent error which cannot be prevented and will always be there. Accuracy is a systematic error and is the result of the experimental design.

Figure 2.1 – A schematic representation of either an accurate, precise or both an accurate and precise measurement. A precise measurement represents some tight grouping on a part of the dartboard, while an accurate measurement represents measurements that are in or close to the center.

Deriving accurate information from *in situ* measurements, of a film exposed to a liquid solvent or vapor, is even more intricate than for dry systems. This is, among many other factors, due to the presence of a measurement cell (with windows), the presence of a solvent, temperature offsets, and temperature gradients within the measurement cell. Also the behavior of the thin polymer film itself, such as the development of a gradient upon solvent exposure, is often unknown beforehand. Corresponding inaccuracies that are introduced by non-idealities that can be avoided are here referred to as systematic errors; when they are due to non-idealities that are difficult or impossible to avoid, we refer to them as random errors. The accuracy of *in situ* swelling experiments is in general not limited by the resolution of the apparatus itself, but by these additional random errors. These random errors will differ for each polymer-solvent system.

Although the accuracy of modern measurement equipment is widely discussed in the literature (see for instance, ^[19], ^[20] or ^[21]), the topic of measurement accuracy within measurement cells has received far less attention.^[22,23] The loss of accuracy

that one will experience during experiments involving measurement cells filled with a liquid solvent remains largely undocumented.

Information about the impact of common non-idealities is required to interpret the final data values. This requires careful judgement of which errors should be prevented during measurement, which parameters should be compensated for during modelling, and which parameters have to be accepted as random errors. During an ellipsometry measurement, the polarized light beam has to pass through the transparent windows of the measurement cell. These windows are often subjected to strain, which causes optical retardance of the light. The resulting change in the polarization state of the light results in an offset in the value of Δ , one of the two angles that describe the ellipticity of the polarized light beam.^[24] For a well-designed cell filled with air the delta offset can be very low. For a cell that is filled with a liquid, the increased refractive index of the ambient strongly enhances the offset.^[22,23,25–29] To prevent a delta offset, a perfect alignment of the polarizer source to cell, and of the cell to the receiver unit is needed. This is only possible when the spectroscopic ellipsometer has the possibility to adjust the angle of the source and receiver unit separately, a luxurious ability only a few ellipsometry devices possess.

The use of a solvent, also introduces systematic and random errors in the optical model. An accurate quantification of the swelling of a polymer film, induced by a solvent, requires very accurate information about the optical dispersion of the solvent. We learned that this is by no means trivial, as the literature reports many inconsistent data sets, resulting in the use of erroneous values for solvent dispersions in the optical model. In the case of the optical model, the solvent has two roles; as an ambient and as a dilutant in the polymer film. For this reason, changes in the optical dispersion, caused by variations in temperature or impurities, will affect the measured values of the thickness and the refractive index of the swollen film. When dealing with very thin films, the interaction with the solvent and the interface of the polymer will also have an effect on the optical dispersion of both the solvent and polymer. As a result, deriving the concentration of the solvent in the swollen film from an effective medium approach is also strongly affected. Finally, the use of a cell can affect the angle of incidence of the light beam. In particular, the effects of non-normal light incidence of the beam through the cell windows will cause an offset in the angle of incidence, which is amplified by an increased refractive index of the cell content.^[22] A slight tilt of the sample resulting from solvent flow will also affect the error in the angle of incidence.

The effect of a delta offset, the angle of incidence and the overall presence of a liquid inside a measurement cell, makes the design of such a measurement cell far from

trivial. Also much care should be taken to limit the errors that can occur during *in situ* ellipsometry solvent swelling experiments. Table 2.1 gives an overview of possible random and systematic errors that are relevant for *in situ* ellipsometry solvent swelling experiments.

This paper discusses in detail the importance of uncertainties in *in situ* ellipsometry studies involving liquid solvents. The impact of uncertainties will strongly depend on the sample characteristics (e.g., the substrate, the film thickness, and the refractive indices of the solvent and the film). We selected a model system that is representative for an artificial membrane, consisting of a transparent film on a silicon substrate. The transparent film either has a low refractive index (reminiscent of polydimethylsiloxane, PDMS, $n = 1.41$) or a high refractive index (reminiscent of a state-of-the-art polyimide, P84, $n = 1.69$).^[6,7] The film thicknesses are varied in the range of 5 to 1000 nm, to cover ultra-thin to micron-thick films. A silicon wafer is chosen as the substrate, because of its widespread use in this type of measurements.^[8] Silicon wafers can be considered as ideal substrates; they provide a smooth surface, well-known optical parameters, and a high refractive index. Water ($n = 1.33$) and toluene ($n = 1.49$) are selected as a low- and a high-refractive-index-solvent, respectively.

2.2 Theory

2.2.1 Ψ and Δ

During a spectroscopic ellipsometry measurement the change in the polarization state of the propagating light is measured. The change in polarization state is described by ratio of the reflectivities of linearly polarized light parallel to the plane of incidence ($\tilde{r}_p$) and perpendicular to the plane of incidence ($\tilde{r}_s$):

$$\rho = \tan(\Psi) \exp(i\Delta) = \frac{\tilde{r}_p}{\tilde{r}_s} \quad [2.1]$$

where the Ψ is the relative amplitude of the propagating p - and s -waves and Δ resembles the phase change along the propagation axis.^[30] The sign of Δ determines the sense of motion of the ellipse: $\Delta > 0$ corresponds to a right-handed polarization and $\Delta < 0$ to a left-handed polarization.

The Ψ, Δ -spectra obtained in a spectroscopic ellipsometry experiment relate to the properties of the sample and the ambient in which it is situated. To illustrate this, Figure 2.2 shows the Ψ, Δ -trajectories (generated with Woollam CompleteEase software) for polymer films in liquid water or toluene as ambient. For a high-index polymer, thicknesses changes affect both the Ψ and Δ signals. For a low-index polymer the changes in Ψ are significantly smaller than those observed for a high-index polymer. For low thicknesses (<10 nm), changes in Δ can be observed, but little

or no changes in Ψ are recorded. This difference in sensitivity towards signal changes of Ψ and Δ is known as the thin film approximation^[30]. Figure 2.3 illustrates the optical contrast between polymers and solvents. In the case of low optical contrast (e.g., a low-refractive-index-polymer in a high-refractive-index-solvent), changes in Δ are more pronounced than changes in Ψ . Given sufficient optical contrast (high-refractive-index-polymer in low-refractive-index-solvent), changes in Ψ become more significant than in case of low optical contrast, and already at thicknesses higher than 5 nm both Ψ and Δ changes will be observed.

A retardation of the light is the result of a generated phase difference between the *p*- and *s*-polarizations (Δ).^[18] Light retardation can be the result of density changes of the polymer film, but also windows of the measurement cell can introduce small retardations of the light, due to the presence of strain within these windows. In the Supplementary Information, Table S2.1 and Table S2.2 provide an indication of the delta-offset, a quantification of the window strain, for different measurement cells. It should be noted that the determination of a delta offset, especially in a liquid ambient is not always straightforward. In Figure 2.2, the simulated changes in Δ , ranging from -10° to 10° , induced by the presence of strain in the windows, for a bare silicon wafer are represented by the red diamonds. Due to the window effects it appears as if a thin film is present, whereas the sample in reality does not comprise such a film. As a consequence, for measurements with a low optical contrast between the polymer film and the liquid ambient, different film thicknesses are difficult to distinguish from the presence of window effects. In this case higher inaccuracies in the results will be obtained. Also, in Figure 2.2 an identical behavior of the low index polymer for both a toluene and water ambient is shown, indicating that the Ψ and Δ behavior is strongly dependent on the difference in the refractive index between the ambient and the polymer film.

Figure 2.2 – Simulated Ψ, Δ -trajectories at $\lambda=632.8$ nm, of a high index polymer (squares) and a low index polymer (circles) in a toluene ambient (left panel) and in a water ambient (right panel) for various polymer film thicknesses (0-50nm) on a silicon wafer. The red symbols represent the effect of an in-plane optical retardance by a window (simulated delta offsets in the range -10° to 10°) on Ψ and Δ for a bare Si wafer.

Figure 2.3 – Ambient indices and polymer refractive indices. When the indices of the ambient and polymer are overlapping or are close to each other, as is displayed by the grey squares, there is a low optical contrast.

2.2.2 Angle of incidence offsets

The highest sensitivity for a spectroscopic ellipsometry measurement is obtained when the difference between $\tilde{r}_p$ and $\tilde{r}_s$ is maximized, because then the ratio of the amplitude $\left(\frac{\tilde{r}_p}{\tilde{r}_s}\right)$ is the largest. For this reason, an ellipsometric measurement is performed at the angle where the largest variation between Ψ and Δ is to be seen. The highest amplitude ratio can be achieved when measurements are performed at an angle of incidence that is at about the Brewster angle (θ_B), where $\tilde{r}_p$ is equal or close to zero.^[18] When the sample is slightly tilted, or when the incoming light beam is not aligned exactly perpendicular to the windows, or when the polarizer and the analyzer are not exactly aligned, an additional offset in the ratio between the two reflectivities is measured. Small angle changes will mainly result in an offset in Δ , while larger changes will also cause an offset in Ψ .^[30] Therefore, the offsets in the angle of incidence should be kept to a minimum.

Table 2.1 – An overview on the type of errors/uncertainties that can occur during a measurement and their effects on the final results.

Source of error	Influence	Effect
Glass windows in measurement cell	Optical in-plane light retardance, resulting in delta offset	In air or gasses (low n): small effect. Solvents and compressed gasses (higher n): the effect can be significant.
<ul style="list-style-type: none"> - Errors in optical dispersion solvent: Unknown dispersion - Incorrect dispersion - Impure solvent - Temperature deviations - Interaction solvent with polymer 	Erroneous dampening effect in the optical model on the Ψ and Δ values. Error in solvent concentrations determined from effective medium approaches.	Particularly significant for films smaller than ~100 nm (vide infra)
Offset in the angle of incidence <ul style="list-style-type: none"> - Angle offset of full cell - Angle offset of cell bottom compared to windows - Non-normal incidence in cell windows 	Misalignment of the polarizer and analyser, resulting in offsets of the Ψ and Δ values.	Apparent in all cases and should be avoided. Effect is amplified by higher value of the refractive index of the cell content.

2.3 Data Simulation

2.3.1 Representative base cases

The impact of measurement uncertainties is assessed from data simulations for selected base case systems. All base case systems are based on a hypothetical sample that consists of a silicon wafer (with 2 nm native oxide layer), a thin homogeneous transparent film, and a transparent solvent as ambient. The differences between the base cases are the refractive indices of the film and the solvent. For each base case, Ψ and Δ spectra were generated for an idealized system (no errors) using the Simulate Data option of the software package CompleteEase (J.A. Woollam Co.). Subsequently, the spectra were fitted using the same software, while introducing a certain deviation in the value of the systematic error of interest. For instance, the value of the offset in Δ is held $\neq 0$. Fitting parameters are the thickness of the polymer film, and the A and B constants of the Cauchy relation that describes the dispersion of this film. In all simulations and data fits a wavelength range of 370 nm - 1000 nm was used. Cauchy dispersions were used to generate a polymer film with a low refractive index (resembling PDMS) and a polymer film with a high refractive index (resembling P84). Thicknesses of 5, 20, 100, 200 and 1000 nm were selected to represent the relevant thickness range for thin film applications.

Water, using an optical dispersion fitted to the data published by Pribil and Synowicki,^[31] (H2O_high_purity_20_deg.mat, from the CompleteEase library), and toluene based on refractive index data published in ^[32], were selected as solvents with low and high refractive indices, respectively. In Table 2.2 an overview of the Cauchy parameters of the materials used for the representative base cases is presented.

Three combinations of the refractive indices of the polymer and the ambient have been studied:

1. Low index polymer – high index solvent ($n_p^{low} n_s^{high}$);
2. High index polymer – low index solvent ($n_p^{high} n_s^{low}$);
3. High index polymer – high index solvent ($n_p^{high} n_s^{high}$).

Two of these cases represent sufficient to high optical contrast between the polymer layer and the solvent (case 2 and 3). Case 1 represents a case with low optical contrast.

Table 2.2 – An overview of the Cauchy parameters of the materials used for the simulation of the representative base cases.

	<i>A</i>	<i>B</i>	<i>C</i>	<i>k</i>
Low-refractive-index-polymer	1.397	0.0004	0	0
High-refractive-index-polymer	1.63	0.022	0	0
H2O high purity 20 degC*	1.323	0.00316	$7.6761 \cdot 10^{-6}$	0
Toluene (Samoc)**	1.475	0.00699	0.000218	0

*A Cauchy relation fitted to the optical dispersion data in ^[31].

**A Cauchy relation fitted to the optical dispersion data in ^[32].

2.3.2 Introducing non-idealities

The simulation data of the base cases as described above, was generated using known ambient dispersions and without window offsets. To quantify non-ideality effects on the final thickness and refractive index, non-idealities were introduced during subsequent fitting of the modelled base cases. The obtained values for the root mean squared error (*MSE*) are shown as obtained. The *MSE* is a quantity that indicates the agreement between the optical model and the original experimental data. In the CompleteEase software, the *MSE* is defined as:^[33]

$$MSE = \sqrt{\frac{1}{3l-m} \sum_{i=1}^l \left[(N_{E_i} - N_{G_i})^2 + (C_{E_i} - C_{G_i})^2 + (S_{E_i} - S_{G_i})^2 \right]} \times 1000 \quad [2.2]$$

where $\mathcal{L}$ is the total number of wavelengths, m the number of fit parameters, and $N = \cos(2\Psi)$, $C = \sin(2\Psi) \cos(\Delta)$, $S = \sin(2\Psi) \sin(\Delta)$. Parameters subscripted with E represent the experimental (here: simulated) data while parameters subscripted with G represent the fit data (that are fitted to the E data).

The changes in thickness and refractive index from the original thickness and from the refractive index are expressed by:

$$\delta_n = \frac{n_{\text{fit}} - n_0}{n_{\text{fit}}} \times 100\% \text{ and } \delta_d = \frac{d_{\text{fit}} - d_0}{d_{\text{fit}}} \times 100\% \quad [2.3]$$

where δ describes the deviation between the simulation thickness (d_0) or simulation refractive index (n_0) and the fitted thickness (d_{fit}) or fitted refractive index (n_{fit}).

2.3.2.1 Effects of an inaccurate optical dispersion for the ambient

Inaccuracies in the optical dispersion of the ambient were introduced as a constant offset or via a change in the shape of the dispersion. For toluene, the deviations in the optical dispersion were taken from literature. Here, the dispersion of Samoc,^[32] which is based on a meta-analysis of multiple studies, was considered the correct dispersion. The deviating dispersion given by Rubio ^[34] was assumed to be

inaccurate in this work. To create two other cases, two false dispersions were created by applying an offset of +0.005 and -0.005 in the Cauchy parameter A . These offsets correspond to a $\pm 8^\circ\text{C}$ temperature deviation in the toluene ambient.

In Table 2.3 an overview of the Cauchy parameters of the deviating toluene optical dispersions are given.

Table 2.3 – An overview of the Cauchy parameters of the deviating optical dispersions for toluene.

	A	B	C	k
Toluene (Rubio)*	1.471	0.00656	0.000258	0
Toluene (Offset +0.005)	1.480	0.00699	0.000218	0
Toluene (Offset -0.005)	1.470	0.00699	0.000218	0

* A Cauchy relation fitted to the optical dispersion data in ^[34].

For water, the dispersions available in the CompleteEase materials library, H₂O high purity 20degC.mat, H₂O.mat, H₂O (Sellmeier).mat and H₂O Pribil at 25 °C, were taken as the optical dispersions. Of these, H₂O high purity 20degC.mat is based on an extensive dataset and was considered the 'correct' dispersion. In Table 2.4 an overview of the Cauchy parameters of the deviating water optical dispersions are given.

Table 2.4 – An overview of the Cauchy parameters of the deviating optical dispersions for water.

* A Cauchy relation based on a Sellmeier fit of data from ^[35].

	A	B	C	k
H ₂ O (Sellmeier)*	1.319	0.00502	$-1.5129 \cdot 10^{-5}$	0
H ₂ O (Pribil 25)	1.323	0.00316	$7.6760 \cdot 10^{-6}$	0
H ₂ O**	1.319	0.00518	$-3.1206 \cdot 10^{-5}$	0

**Best fit by using Cauchy relation. Based on data from ^[35].

2.3.2.2 Swollen films

A generated data set of 20, 40, 200 and 2000 nm films in toluene for which the refractive index was mapped by a Bruggeman Effective Medium Approximation (EMA) with 50 % solvent fraction, indicating the film contained of 50 % toluene and 50 % polymer materials, and was used to simulate swollen films in toluene with a swelling degree (SD) of 100 %.

The swelling degree is defined as:

$$SD = \left(\frac{d_{\text{swollen}}}{d_{\text{dry}}} - 1 \right) \times 100\% \quad [2.4]$$

where d_{swollen} is the thickness of the swollen polymer and d_{dry} is the thickness of the dry polymer. The refractive index of the polymer film was held fixed, while both the thickness of the polymer film and the solvent volume fraction were fitted for the different Cauchy dispersions of the ambient (see 2.3.2.1) to resemble the situation of tracking the swelling of a polymer film with a known index.

The change in the solvent volume fraction with respect to the original solvent volume fraction is expressed by:

$$\delta_{\phi} = \left(\frac{\phi_{\text{fit}} - \phi_0}{\phi_{\text{fit}}} \right) \times 100\% \quad [2.5]$$

where δ describes the deviation between the simulation volume fraction (ϕ_0) and the fitted volume fraction (ϕ_{fit}).

2.3.2.3 Delta offsets

The influence of in-plane optical retardance introduced by the glass windows of a measurement cell was simulated by generating a data set without delta offset. Then the simulated data was fitted for the thickness, and the A and B parameters of the thin film while introducing a forced delta offset of -10° to 10° .

2.4 Results and Discussion

2.4.1 Inaccurate optical dispersion of the ambient

A change in temperature or the presence of an impurity will cause a change in the optical dispersion of the ambient (the solvent), which will influence the oscillation pattern of Ψ and Δ . When the film becomes substantially swollen by the ambient, the optical contrast is generally lowered and the accuracy of model-derived parameters is further reduced, as will be shown in paragraph 2.4.2.

2.4.1.1 Non-swollen films

In this section, the films are modelled not to swell in the presence of the solvent. To approach representative systems as used in, for example, membrane applications or coatings, a high index polymer in a low index solvent (i.e., P84 in water) and a low index polymer in a high index solvent (i.e., PDMS in toluene) have been simulated. The first system represents high optical contrast, whereas the latter system represents low optical contrast.

In Figure 2.4, the *MSE*, the normalized thickness change (δ_d), and the normalized refractive index change (δ_n) are shown as a function of the film thickness, for several (incorrect) optical dispersions of the ambient. The left panel shows the case of high optical contrast (i.e., P84 in water) and the right panel shows the case of low optical contrast (i.e., PDMS in toluene). In the Supplementary Information, Figure S2.1, a third case is presented where the optical contrast is moderate (i.e., P84 in toluene). The curves assigned “original” present the results of the fitting, when using the solvent dispersion parameters identical to that used for creating the simulated data. In this case, an *MSE* close to one was obtained, implying a small inherent deviation between fitted and simulated data. The “original” curve represents the measurement of precision, while the other curves represent the accuracy you can obtain for a certain thickness. In general, the *MSE* increased upon introduction of a deviation in the optical dispersion of the ambient.

Figure 2.4 – The MSE (upper row), δ_d (middle row) and δ_n (lower row) as a function of the simulated film thickness for various refractive index dispersions of a low-refractive-index-solvent (left panel) and a high-refractive-index-solvent (right panel). Red symbols indicate negative values, i.e., an underestimation of the original values. The curve labelled original represents the inherent deviation that is obtained when using fitting parameters values identical to that used for creating the data. The other curves represent deviating optical dispersions.

In general a high correlation between the A parameter and thickness was observed for all 5 and 20 nm films (ranging from -0.91 to 0.997) indicating that there is a relative high error margin for the thickness and refractive index obtained for 5 and 20 nm films compared to thicker films. This corresponds with the literature which described the correlation between the refractive index and the thickness for thin films.^[30]

In the case of **high optical contrast** (Figure 2.4, left panel), an overall low MSE was obtained ($MSE < 6$) for a deviating optical dispersion of the ambient. The MSE

remains low for the thinnest films and only shows a slight deviation (<0.5) from the *MSE* obtained using the original index dispersion. With an increasing polymer film thickness, a higher *MSE* (~ 5.3) for the deviating ambient optical dispersions was obtained. For δ_d and δ_n , an opposite trend was visible; for a film of 5 nm, δ_d up to 30% and δ_n up to 8% were observed, while for a film of 1000 nm only a δ_d and δ_n of 0.03% were observed. This can be explained by the fact that for thicker films, more polymer material will interfere with the light and thus the polymer contribution for the Ψ and Δ signal increases. For thin films (approximately <100 nm), the amount of polymer that interferes with the light is lower, and the ambient will have a relative larger contribution to the light interference compared to thick films. In that case, the presence of the ambient is more pronounced and a change in the ambient will have more effect on the final results. The lack of Ψ and Δ oscillations in these thin films, partly dampened by the larger amount of the ambient, causes the *MSE* to remain low. For the refractive index, a similar effect as that of the film thickness was observed. Also δ_n increases with decreasing simulated film thicknesses, but the changes in δ_n are one order of magnitude smaller as compared to δ_d . The modelled thickness has a higher sensitivity to the changes in the ambient dispersions than the refractive index.

For **low optical contrast** cases (i.e., PDMS in toluene) (Figure 2.4, right panel), the *MSE* shows an opposite effect as observed for the case with high optical contrast. The *MSE* increases for decreasing film thicknesses and in general remains low (<2). The generally low *MSE* can be explained by the fact that in case of low optical contrast, the Ψ and Δ oscillations are strongly dampened, decreasing the sensitivity of the *MSE* to differences between the fit results and the experimental data. The trend observed in δ_d and δ_n is comparable to the case with high optical contrast, but the deviations observed were significantly higher. For δ_d , deviations up to 585 % were observed for 5 nm and values up to 0.6 % for 1000 nm. For δ_n , values up to 26 % were observed for 5 nm and 0.3 % for 1000 nm. The observation of the high δ_d and δ_n values in combination with the low *MSE* for the case of low optical contrast, shows that the *MSE* can be misleading regarding the quality of the fit when working with thin films in an ambient (approximately <100 nm). In case of moderate optical contrast (See also Supplementary Information, Figure S2.1), the results for δ_d and δ_n are in between the values in case of high and low optical contrast. Also, the *MSE* in general lowers with a decrease in optical contrast. This lowering shows that a small change in the ambient dispersion can result in significant deviations of the final interpreted results. It is therefore important to carefully control the environment of the experiments to cancel out any undesired ambient effects caused by external features such as temperature changes. Also, it is very important to obtain an accurate description of the ambient index dispersion. The literature does raise

awareness on the complications that arise for the simultaneous determination of the optical constants and thickness of thin films (approximately <100 nm),^[18,19,36] but the effects of deviating ambient dispersions also have dramatic consequences on the final data interpretation.

2.4.2 Swollen films

In the previous sub-section, no swelling of the polymer was assumed. However, when a polymer is exposed to a solvent such as toluene, the solvent will penetrate into the polymer and the polymer will start to swell to a certain extent. In this case, a change in the ambient causing a deviation in the refractive index dispersion will not only have an effect on the ambient simulation itself, but also on the refractive index of the swollen polymer.

In Figure 2.5, the *MSE*, δ_d and δ_ϕ are shown as a function of the film thickness, for several (incorrect) optical dispersions of the ambient. The left panel shows the case of high optical contrast (i.e., P84 in toluene) and the right panel shows the case of low optical contrast (i.e., PDMS in toluene).

The *MSE* of the fits of the swollen films, in the case of both sufficient and low optical contrast, shows a similar behavior as observed for the non-swollen films in a liquid ambient with high optical contrast. For both **moderate and low optical contrast**, the *MSE* increases with increasing film thicknesses to *MSE*~6, when a deviating optical dispersion of the ambient was introduced.

In case of **moderate optical contrast** (i.e., P84 in toluene) (Figure 2.5, left), δ_d is 85 % for 10 nm swollen films and 0.15 % for 2000 nm swollen films. This is lower than for the non-swollen film. For δ_ϕ large deviations were observed. For very thin swollen films (i.e., a 10 nm swollen film), δ_ϕ shows that no solvent was detected in the polymer film (i.e., $\phi=0$), resulting in an infinite δ_ϕ . The dependency on the optical dispersion of the ambient by the solvent volume fraction can be explained by the dependency of the solvent volume fraction on the refractive index of the solvent and the refractive index of the polymer. The polymer refractive index was assumed to be constant for all cases, therefore every change in the refractive index of the solvent will largely influence the solvent volume fraction in the polymer. An alternative to obtaining the solvent volume fraction based on the refractive index, is by means of dilation based on the thickness data:

$$\phi_s = 1 - \frac{d_{\text{dry}}}{d_{\text{swollen}}} \quad [2.6]$$

ϕ_s is the solvent volume fraction, d_{dry} the dry thickness of the polymer and d_{swollen} the equilibrated thickness of the swollen polymer. The dilation approach assumes that no excess free volume is present within the thin polymer film, there is no

change in molar volume of the polymer, and solvent-induced volume changes are forced to occur only in the direction perpendicular to the substrate. Although in practice a calculation on the solvent volume fraction based on the dilation approach is often less reliable due to the presence of free volume and the confinement of the swelling direction, it allows for a rough estimate. In the case of the simulation results in this paper, the solvent volume fraction calculated based on the dilation approach should coincide with the solvent volume fraction based on the Bruggeman effective medium approximation, as no excess free volume is incorporated in the model. For films thicker than approximately 100 nm the deviation from the actual data is a factor ten lower using the dilation approach (see Supplementary Information, Figure S2.2). For thinner films, the use of EMA is more reliable. In case of very thin films (approximately lower than 20 nm) both the EMA method and dilation method become very unreliable.

In the case of **low optical contrast** (i.e., PDMS in toluene) (Figure 2.5, right), for both δ_d and δ_ϕ values comparable to the case of moderate contrast were obtained. To conclude, the inaccuracies in the refractive index and/or solvent volume fraction increase for swollen polymer systems compared to non-swollen polymer systems, while the inaccuracies in the thickness decrease compared to non-swollen systems but remain overall high.

Figure 2.5 – Simulation results for swollen films in a solvent. The MSE (upper row), δ_d (middle row), δ_ϕ (lower row) as a function of the simulated film thickness for various refractive index dispersions of a high-index solvent. Red symbols indicate negative values, i.e., an underestimation of the original values. The curve labelled original represents the inherent deviation that is obtained when using fitting parameters values identical to that used for creating the data.

2.4.3 Cell window effects in a liquid ambient

In Figure 2.6 the MSE , δ_d and δ_ϕ are shown as a function of an induced delta offset in the optical model, as described in section 2.3.2.3. The left panel shows the case of high optical contrast (i.e., P84 in water) and the right panel shows the case of low optical contrast (i.e., PDMS in toluene).

Small disturbances in the optical light path, such as stresses in the optical windows, will result in a large change of the measured Ψ and Δ signal. The effects will be more pronounced for thin films in comparison with thick films. For a disturbance in the optical light path to be detected in the measured signal of thick films, the disturbance must be significantly larger than for thin films as for thick films, the

higher amount of polymer material will have a larger contribution to the light interference compared to the surrounding. In the case of thick films, small optical retardances of the light will give an offset in the Δ curve, contributing to an increase in the *MSE*. In general a decrease in the optical contrast dampens the Ψ and Δ oscillations, resulting in a decrease of the *MSE*. This is shown in Figure 2.6 where the *MSE* of a 100 nm film strongly increases with increasing delta offsets for a case with **high optical contrast**, but overall remains low for a case with **low optical contrast**.

For δ_d (Figure 2.6, middle row), it can be observed that in the case of **high optical contrast**, the modelled thickness is an underestimation of the original simulated film thickness for positive delta shifts. The consequence of a delta shift is that the measured delta signal has an offset, shifting the Δ signal upwards (positive delta shift) or downwards (negative delta shift).

Also, δ_d increases with decreasing simulated film thicknesses, a behavior similar to the trends witnessed in Figure 2.4 and Figure 2.5. The highest increases were observed for the first degree (-1° and 1° delta shift) in the delta shift; after this, the deviations increase gradually. This indicates that not correcting for a small delta offset (which can be due to additional strain in the windows due to O-ring swelling), will result in a large deviation for the modelled thickness of thin films (Approximately < 100 nm). For the case in which there is **low optical contrast**, this effect is even more pronounced and also occurs for thick films. Figure 2.6 shows that even for a simulated 1000 nm film, a δ_d of 3 % for a delta change of only 1° was observed.

For δ_n , in case of **high optical contrast**, an underestimation of the simulated refractive index was observed at a negative delta shift. This is presumably a compensation effect of the overestimated thickness at this point, and in order to maintain the same optical density, the refractive index is underestimated. In the case of **low optical contrast** (Figure 2.6, right panel), δ_n for a 1000 nm and 100 nm film is an order of magnitude higher compared to the cases with high optical contrast. This indicates that in case of low optical contrast, no accurate measurements can be performed for films thinner than approximately 100 nm. This is in contradiction with the suggestion of a good fit by the low *MSE* (< 4) for 100 nm or thinner films.

The values for the delta shifts that have been used in this study, 1-5, are quite realistic for the rather aggressive solvents, such as the toluene considered here. Typical data for window strain effects of different kind of cells are listed in the Supplementary Information. The data imply that, especially at elevated temperatures, delta offsets of our homebuilt cells can be high. This is due to several reasons, such as interaction between the solvent and the glue used to seal the cell,

the temperature gradients from the outside to the inside of the cell, the combination of materials with distinct thermal expansion coefficients (e.g., glass body and quartz windows), and the large volumes (~100 mL). The large volumes are chosen to facilitate fast insertion of samples into the liquid at $t=0$ s. The volume of modern commercial liquid cells is much smaller and is completely filled with the solvent. This reduces the existence of temperature gradients within the liquid itself. Also, the construction of commercial cell bodies out of stainless steel negates thermally induced stresses at the working temperatures of maximum 50 °C. The windows of the commercial cells are relative small and sealed with O-rings. This sealing makes them sensitive to strain when exposed to an aggressive solvent. In this study Kalrez O-rings were used and still delta offsets increased upon solvent exposure. This indicates that the importance of sealants should be carefully considered.

The delta-offsets in the range of 5-10 are an extreme case and imply that one has not carefully considered the liquid cell design. As shown in Figure 2.6, the consequence of a badly designed cell on the final obtained thickness and optical constants is large.

Figure 2.6 – The MSE (upper row), δ_d (middle row), and δ_n (lower row) as a function of the delta shift (°) for a case of high optical contrast (left column) and low optical contrast (right column). Red symbols indicate negative values, i.e., an underestimation of the original values. The absence of a symbol in the deviation from the refractive index graphs indicate that the deviation is smaller than 10^{-3} .

2.5 General Considerations

For all the results shown in the previous sections, polymer films were considered that are ideal in the sense that surface roughness and solvent gradients are considered neglectable. For rubbery polymers like PDMS, which swell instantaneously when exposed to a solvent, this might be the case. However, for glassy polymers where swelling of the polymer film will be time dependent, the parameters such as surface roughness and gradients within the polymer film will change. This requires that these parameters must be included in the analysis and have a certain correlation with the index and thickness. Although more parameters may improve the match between model and the experimental data, the correspondence between the fitted and the actual values may decrease. Thus after adding a fit parameter, the fitted values should be treated with even more caution.

2.6 Conclusions

In this study, we discuss the reduced accuracy of *in situ* spectroscopic ellipsometry studies of polymer films, due to the exposure to a liquid ambient. It is shown that the relatively high refractive index of the liquid ambient strongly amplifies the effects of experimental non-idealities, such as window birefringence and an inaccurate optical dispersion relation for the liquid ambient. The effects of even small non-idealities are in particular large for thin films (Approximately < 100 nm). For such thin films, large deviations in the thickness and refractive index are found, while the concurrent low *MSE* values erroneously suggest a good fit of the optical model to experimental data. This implies that a low *MSE* will not necessarily indicate an improved fit result, and that quantitative *in situ* ellipsometry studies for these thin films should be treated with caution. For films that do not substantially swell, the value of the thickness of the films is more sensitive to non-idealities than the refractive index. For films that do show substantial uptake of the liquid there is a very pronounced effect on the value of the solvent uptake, calculated from an effective medium approximation approach. For thin films, this value should be considered inherently inaccurate.

Our results demonstrate that quantitative *in situ* ellipsometry polymer swelling measurements in solvents require a very accurate solvent dispersion relation, a high-quality temperature control, especially to prevent temperature differences between the cell, its content and exterior ambient, and accurate quantification of window effects, in particular for polymer films of thicknesses up to 100 nm. Multi-wavelength refractometry experiments on solvent (mixtures) and extensive window calibrations are crucial for quantitative *in situ* ellipsometry solvent swelling experiments. Although the quantitative results shown in this paper cannot be generalized for each swelling system used for spectroscopic ellipsometry, it shows that the accuracy is strongly dependent on the swelling system and it is vital to perform an accuracy analysis as shown above.

2.7 Acknowledgements

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2.8 Supplementary Information

2.8.1 Delta offsets

In Table S2.1 and Table S2.2, the delta offsets of different measurement cells were determined using a Si with 25 nm SiO₂ calibration wafer. It should be noted that the *MSE* varied between 0.8-2 for the determination of delta-offsets in air, but the *MSE* increased drastically upon the determination of delta offsets in a toluene ambient. In particular for the homemade glass cell, the determination of the delta offsets in a toluene ambient is very difficult and the *MSE* goes up to 9. In general, it should be realized that also due to the increased of the refractive index of the ambient, the determination of the delta offset in liquid environments is not trivial.

Table S2.1 – Delta offsets in air for different commercial and home-made measurement cells 25 °C, 30 °C and 40 °C.

Type of measurement cell	Delta offset
Commercial liquid cell for Woollam α-SE	-0.139
Commercial Heated liquid cell for Woollam M2000x at 25 °C	0.314
Commercial Heated liquid cell for Woollam M2000x at 30 °C	0.217
Commercial Heated liquid cell for Woollam M2000x at 40 °C	-0.0748
Home-made glass cell at 25 °C	0.299
Home-made glass cell at 30 °C	2.733
Home-made glass cell at 40 °C	4.638

Table S2.2 – Delta offsets in toluene for different commercial and home-made measurement cells at 25 °C and 40 °C.

Type of measurement cell	Delta offset
Commercial liquid cell for Woollam α-SE	-2.316
Commercial Heated liquid cell for Woollam M2000x at 25 °C	0.450
Commercial Heated liquid cell for Woollam M2000x at 40 °C	0.0654
Home-made glass cell at 25 °C	-6.695 (<i>MSE</i> =9.202)
Home-made glass cell at 40 °C	-1.243 (<i>MSE</i> =9.321)

2.8.2 Non-swollen polymer film in an incorrect ambient dispersion

In Figure S2.1, the MSE , δ_d and δ_n for a high-refractive-index-polymer (i.e., P84) are shown as a function of the film thickness, for several (incorrect) optical dispersions of the ambient (i.e., toluene).

Figure S2.1 – The MSE (upper row), δ_d (middle row) and δ_n (lower row) as a function of the simulated film thickness for various refractive index dispersions of a high-refractive-index-solvent. Red symbols indicate negative values, i.e., an underestimation of the original values. The curve labelled original represents the inherent deviation that is obtained when using fitting parameters values identical to that used for creating the data. The other curves represent deviating optical dispersions.

2.8.3 Solvent volume fraction calculations

The solvent volume fraction (ϕ_s), of a solvent within a swollen polymer can be calculated in different ways. One method is using the solvent induced increase in thickness of the swollen polymer, known as the dilation method:

$$\phi_s = 1 - \frac{d_{\text{dry}}}{d_{\text{swollen}}} \quad [\text{S2.1}]$$

ϕ_s is the solvent volume fraction, d_{dry} the dry thickness of the polymer and d_{swollen} the equilibrated thickness of the swollen polymer. The dilation approach assumes that no excess free volume is present within the thin polymer film, there is no change in molar volume of the polymer, and solvent-induced volume changes are forced to occur only in the direction perpendicular to the substrate.

A different method is utilizing the change in the refractive index of the swollen polymer which is the result of the different refractive index of the solvent:

$$\Phi_s = \frac{n_s^2 - n_{\text{swollen}}^2}{n_s^2 + 2n_{\text{swollen}}^2} + (1 - \Phi_s) \frac{n_p^2 - n_{\text{swollen}}^2}{n_p^2 + 2n_{\text{swollen}}^2} = 0 \quad [\text{S2.2}]$$

where n_s is the refractive index of the solvent, n_p the refractive index of the dry polymer and n_{swollen} the refractive index of the swollen polymer. Eq. S2.2 is known as the Bruggeman Effective Medium Approximation (EMA).

In Figure S2.2 a comparison between the dilation method (closed symbols) and EMA method (open symbols) for a high-refractive-index (e.g. P84, left panel) swollen polymer and a low-refractive-index (e.g. PDMS, right panel) swollen polymer in toluene is shown for different thicknesses and different deviating optical dispersions. At thicknesses approximately thicknesses lower than 20 nm, both methods become very unreliable, while at thicknesses higher than 100 nm, the dilation method is more accurate than the EMA.

Figure S2.2 – The deviation in the solvent volume fraction in a high refractive index swollen polymer (left panel) or low refractive index polymer (right panel) in toluene based on the dilation method (closed symbols) and on EMA calculations (open symbols) for different given film thicknesses and different optical dispersions of toluene. For higher film thicknesses, the dilation method is factor 10 more accurate.

2.8.4 Raw data

In Figure S2.3, the Ψ , Δ -data of 5 and 1000 nm non-swollen polymer films are shown. Also the Ψ , Δ -data of 10 and 2000 nm swollen polymer film and the corresponding model results fits using different optical dispersions of the ambient, toluene.

Figure S2.3 – Ψ , Δ -data of non-swollen and swollen films in a toluene ambient.

In Figure S2.4, Ψ , Δ -data of 5 and 1000 nm non-swollen polymer films in water (left panel) and in toluene (right panel) are shown. Also the fits of a -2° , -10° , 2° , and 10° delta offset are shown.

Figure S2.4 – The Ψ , Δ -data of non-swollen films with the implementation of different delta offsets in a toluene and water ambient.

2.9 References

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Chapter 3

On the Generic Swelling Behavior of Glassy Polymers

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Abstract

Literature on dual mode sorption shows that a relation between the Langmuir type of penetrant sorption, Henry type of penetrant sorption and the extent of swelling exists. Langmuir sorption only contributes up until a swelling of ~6 % and there is only a small contribution of Henry sorption. For swelling degrees higher than ~6 %, the excess free volume is filled and only Henry sorption will occur. In this work, *in situ* spectroscopic ellipsometry was used to measure the penetrant induced swelling in five glassy polymers with excess free volume fractions ranging from 3-12 % in three different organic solvents. Evidence of a generic relation between the filling of the excess free volume and the swelling factor for all distinct polymer/solvent combination was provided. For each polymer/solvent combination, the excess free volume was completely filled around a swelling of ~5 %, independent of the type of penetrant or polymer used. Upon further dilation, irreversible structural changes within the polymer matrix occurred, changing the penetrant sorption properties of the polymer.

3.1 Introduction

Polymers are commonly used materials in thin film applications such as coatings, membranes and sensors. They are often widely available, easy to process and allow for fine-tuning of properties such as elasticity, thermal and chemical stability. At present, many polymeric materials that allow for a high thermal or chemical stability are in a glassy state, in particular high-performance polymers such as polyimides or polyketones. The glassy state of a polymer is observed below its glass transition temperature; here, the dynamics of the polymer chains are slowed down to such an extent that the polymer chains are frozen in and their relaxation times slow down by decades in time^[1]. As a result, on a short timescale compared to their relaxation time, the polymer chains are not optimally relaxed below the glass transition and an excess “empty space” persists between the polymer chains (see section 1.2.2). This additional empty space is referred to as the excess free volume (EFV). The EFV depends on the glass transition temperature and the dynamic fragility of the polymer (i.e. how fast do the relaxations slow down at the glass transition). The EFV has a large influence on the physical properties of the glassy polymer and it influences the diffusivity of small molecules within the polymer matrix, impacting the transport properties of the polymer material^[1,2]. The excess free volume is a non-equilibrium property and is dependent on the temperature and history of the polymer. Consequently, it is difficult to describe the solvent sorption behavior in a glassy polymer.

Over the years, many models have been developed to approximate the penetrant sorption in glassy polymers. A widely used model on penetrant sorption in glassy polymers is the dual mode sorption model. The dual mode sorption model was proposed by Barrer et al. (1958)^[3] who observed that in ethyl cellulose, the existence of voids in the polymer network plays a role in the solvent sorption. It is a simple model and many modifications have been proposed. Vrentas and Vrentas (1991)^[4] coupled the dual mode sorption model to the temperature dependence of the polymer properties, taking into account the stiffening of polymer chains around the glass transition. Leibler and Sekimoto (1993)^[5] coupled the excess sorption that is observed, relative to a rubbery polymer, to the Young’s modulus of the bulk polymer. In all cases, the history effect, solvent concentration dependence and temperature dependence are often deduced in an empirical or semi-empirical manner.^[6] For this reason, the dual mode sorption model has been heavily criticized in literature. However due to its simple approach, the dual mode concept remains widely used. A more accurate description of gas and vapor permeability in glassy polymers can be obtained by using the well-established Non-Equilibrium Lattice Fluid (NELF) model^[7]. Other thermodynamic approaches include modifications of the Flory-Huggins model^[8–10]. Both the dual mode sorption model and the thermodynamic models

have been widely applied to explain the experimental results on solvent and gas sorption in glassy polymers. [11–16]

In this study, we use the dual mode sorption because of its simple and intuitive character. The dual mode sorption model identifies only two modes of sorption. The first sorption mode is the Langmuir sorption mode, which occurs via the void spaces of the polymer matrix and is assumed to make no contribution towards volume dilation. The second mode is the Henry sorption mode, which describes the sorption of the solvent molecules into the polymer matrix, contributing to the volume dilation. In the Henry sorption mode, the partial molar volume of the solvent is typically assumed to be equal to the molar volume at infinite dilution in the liquid state. The total solvent concentration inside the polymer can then be described by:

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad [3.1]$$

where p is the pressure (bar), C_D the concentration of the penetrant that is dissolved into the polymer matrix, C_H the concentration of penetrant inside the holes, k_D is the Henry constant ($\text{cm}^3 \text{ solvent cm}^{-3} \text{ polymer bar}^{-1}$), C'_H the maximum Langmuir capacity ($\text{cm}^3 \text{ solvent cm}^{-3} \text{ polymer}$) and b the hole affinity constant (bar^{-1}).

Punsalan and Koros (2005) [12] for the first time observed increased swelling in an aged bisphenol A –Polycarbonate sample and attributed this to a reduced amount of void space available compared to the unaged sample. They also found that the partial molar volume of CO_2 converged to a similar constant value for the unaged and aged samples in the high penetrant uptake regime. This suggests that the CO_2 occupies some critical number of Langmuir sorption sites, and until this point both Langmuir sorption and Henry sorption occur simultaneously. Once all Langmuir sites are occupied, additional sorption occurs via Henry sorption, dilating the polymer matrix. A relationship between the glass transition temperature and the partial molar volume of CO_2 , at low CO_2 uptakes, was established by Wijmans [17] based on the data from Wessling et al. [18]. Their data shows that with increasing glass transition temperatures, the partial molar volume of CO_2 decreases. This implies that with increasing glass transition temperatures, more excess free volume can be occupied by the CO_2 .

Within the dual mode sorption model, Koros and Paul [19] found that the maximum Langmuir capacity constant (C'_H) for CO_2 sorption, can be described by

$$C'_H = \frac{V_g - V_l}{V_g} \rho^* = \frac{22414 \rho_{\text{penetrant}}}{M_w} = \text{EFFV} * \frac{22414}{V_{\text{penetrant}}} \quad [3.2]$$

where V_g is the molar volume ($\text{cm}^3 \text{ mole}^{-1}$) of the polymer at a certain temperature in the glassy state, V_l is the molar volume of the polymer in the hypothetical equilibrium state ($\text{cm}^3 \text{ mole}^{-1}$), ρ^* is the molar density of gas sorbed into the

Langmuir sites, $\rho_{\text{penetrant}}$ is the mass density of the polymer (g cm^{-3}), M_w is the molecular weight of the penetrant (g mole^{-1}), EFFV is the excess fractional free volume and $V_{\text{penetrant}}$ is the partial molar volume (mole cm^{-3}) of the penetrant inside the polymer matrix.

When the EFV is filled by the penetrant the right term of the equation in Eq. 3.1 (Langmuir sorption) is no longer increasing and C_H is approximately equal to C'_H . The extent to which a penetrant molecule is able to fill up the empty void space created by the excess free volume is dependent on the penetrant its packing fraction or packing density, ρ^* . In 1968, Bondi^[20] stated that the packing density of a crystal at 0 K can vary from 0.52 to 0.74 for open- and close-packed cubic structures which are the most common structures for small penetrants. CO_2 for example has a packing density of 0.76^[20]. Assuming that the EFV is filled up by the penetrant using its maximum packing density, one can make an estimation of the concentration of penetrants that are sorbed via Langmuir mode:

$$C_H = \rho^* C'_H \quad [3.3]$$

Here it is assumed that the penetrant is able to fill the void spaces up to its maximum capacity. In the Supplementary Information, a literature overview of CO_2 sorption inside different polymers is provided, and an approximation of the ratio between C_H and C'_H was made assuming no further contribution of penetrants sorbed via Henry dilation. When no concentration contribution via Henry dilation is assumed the packing density equals 0.69 ± 0.03 for CO_2 sorption. This obtained packing density is lower than the maximum theoretical packing density for CO_2 as calculated by Bondi ($\rho^*=0.76$ for CO_2). The underestimation of the calculated packing factor based on the dual mode sorption data, can be explained by the fact that the packing density is based on the Langmuir contribution only. However, in reality there is a small contribution from the Henry sorption mode. For this reason, the Bondi packing densities are a suitable estimate to determine the Langmuir contribution, C_H .

Based on Eq. 3.1 and Eq. 3.3, when b and the packing density are known, the pressure corresponding to a completely filled Langmuir capacity, $p_{H,\text{filled}}$, can be estimated:

$$p_{H,\text{filled}} = \frac{\rho^*}{b - \rho^* b} \quad [3.4]$$

Once the pressure has reached the value of $p_{H, \text{filled}}$, the penetrant concentration has reached a critical concentration, C^* . Up to the critical concentration, both Langmuir sorption and Henry sorption occurred alongside, with Langmuir sorption being the dominating mode of sorption. Penetrant concentrations higher than C^* , are the result of only Henry sorption, dilating the polymer matrix.

$$C^* = k_D p_{H, \text{filled}} + \frac{C_H' b p_{H, \text{filled}}}{1 + b p_{H, \text{filled}}} \quad [3.5]$$

To determine to what extent the Henry sorption plays a role in the total penetrant concentration when the free volume has not yet been filled, the ratio between the concentration of penetrant dissolved into the polymer matrix, C_D , and the penetrant concentration that has filled up the voids, C_H can be determined at $p_{H, \text{filled}}$.

In literature, the dual mode parameters of several polymer/penetrant systems together with their sorption behavior are documented. An overview of some of the dual mode parameters, combined with the determined $p_{H, \text{filled}}$, C_D and C_H is presented in Table S3.2 in the Supplementary Information.

Figure 3.1 – The ratio the concentrations of penetrant sorbed via Henry sorption over the concentration penetrant sorbed via Langmuir sorption, C_D/C_H , as function of the glass transition temperature based on dual mode values reported in literature. At $\frac{C_D}{C_H} < 1$, Langmuir sorption dominated, while at $\frac{C_D}{C_H} > 1$, Henry sorption dominates. The closed black symbols represent CO_2 gas sorption, the open symbols represent hydrocarbon gases and the closed grey symbols are organic solvent vapors. The glass transition temperature of PIM-1 and PTMSP was estimated to be $\sim 400^\circ\text{C}$. When the glass transition temperature was not reported, it was estimated based on other literature reports. Data taken from [21–35].

In general, the glass transition temperature may be used as an indication of the magnitude for the EFFV. The higher the glass transition temperature of a polymer, the further away the polymer will be from equilibrium at room temperature and the higher the EFV will be as indicated in Figure 3.2. When considering swelling and/or plasticizing penetrants such as CO_2 , a negative correlation between the ratio of C_D/C_H versus the glass transition was observed, as shown in Figure 3.1. With increasing glass transition temperatures, the amount of penetrant that is sorbed via the Henry mode decreases relative to the amount of penetrant sorbed via the Langmuir mode. This observation is similar as to what was observed by Wijmans^[17] based on the data of Wessling^[36], where it is shown that with a higher glass transition temperature, more CO_2 is sorbed into the void spaces of the polymer, showing a dependence between C_D/C_H and the EFFV.

To further strengthen the presence of a general relation between the EFFV and the penetrant sorption mode independent of the type of polymer used, literature data where the EFFV was either reported or could be derived from, was used to estimate the swelling of the polymer at $p_{H, \text{filled}}$ assuming:

$$\text{Swelling}(\%) = \frac{c_D}{c_H} \text{EFFV}(\%) \quad [3.6]$$

In other cases, the swelling of the polymer was reported as function of pressure and the swelling of the polymer when the Langmuir sites were filled, could be derived using $p_{H, \text{filled}}$. An overview of the swelling ratios of a polymer exposed to CO₂ is provided in Table 3.1.

Table 3.1 – Overview of CO₂ induced reported or calculated swelling at $p_{H, \text{filled}}$.

Polymer/CO ₂	EFFV (%)	T_g (°C)	Swelling (%)
PC slow ^[22]	4.9	147	3.6
PC quench 190 ^[22]	5.6	147	4.3
PC quench 200 ^[22]	5.4	147	3.8
PC quench -94 ^[22]	5.2	147	4.4
PPO Slow ^[22]	9.1	219	4.6
PPO 220 ^[22]	9.3	219	4.4
PPO 240 ^[22]	9.4	219	4.4
PPO 250 ^[22]	9.4	219	4.2
ODPA – P1 ^[37]	-	243	2.0
ODPA – P2 ^[37]	-	214	1.8
ODPA – P3 ^[37]	-	208	1.5
PET 25 °C ^[19]	1.9	85	1.0
PET 35 °C ^[19]	1.4	85	1.0
PET 45 °C ^[19]	1.2	85	0.9
PET 55 °C ^[19]	1.0	85	1.0
PET 65 °C ^[19]	0.7	85	1.2
PET 75 °C ^[19]	0.5	85	1.5
PIM-1 ^[26]	0.25	>350	5.5

Although a scatter in the swelling data can be observed, the data suggests that the swelling does not exceed ~6 % upon complete filling of the EFV. This suggests that above a swelling of ~6 %, the EFV is filled and further sorption of the penetrant occurs only via Henry dilation. This observation is in agreement with the findings of Visser and Wessling^[38] who investigated the sorption of different gases in Matrimid 5218. They found that above a dilation of ~2 %, sorption relaxations are induced, indicating that the penetrant starts dilating the polymer matrix via the Henry sorption mode, independent of the type of penetrant. Also, in a very recent publication of Ogieglo et al.^[39] it was found that for CO₂ sorption in four different ultra-high EFFV PIMs the matrix dilation starts to dominate at about ~5-8 % dilation, supporting the finding above based on the dual mode sorption model.

In this study we will provide experimental evidence for the presence of a relation between the EFFV and the penetrant sorption mechanism in glassy polymers as found in the literature, resulting in a universal swelling behavior among glassy polymers when relating the swelling to the filling of the EFV. We used five glassy polymers with excess free volume fractions ranging from 3-12 % in three different organic solvents to determine the amount of swelling in relation to the filling of the excess free volume, utilizing *in-situ* spectroscopic ellipsometry. The concept of the dual mode sorption model was used to distinguish between the different volume fractions available for penetrant sorption and demonstrates a general relation between swelling and the EFV.

3.2 Theoretical Considerations

3.2.1 Excess free volume

Here we refer to the excess free fractional volume (EFFV) as the fraction between the specific volume of the equilibrium liquid polymer below the glass transition and the total specific glassy volume of the polymer (Figure 3.2). The EFFV fraction can be determined by measuring the thickness as function of the temperature using spectroscopic ellipsometry. The abrupt change in the thermal expansion coefficient at the glass transition temperature causes the polymer to display a different temperature-thickness dependence above and below the glass transition temperature as illustrated in Figure 3.2.

Figure 3.2 – The specific volume, thickness-Temperature relation of an amorphous polymer [40–42] and the schematic representation of the excess free volume, which is the part of the Hole free volume that is frozen into the polymer matrix (see also section 1.2.2).

As previously described by Ogieglo et al. [43] the EFFV can be determined by two approaches. The first approach is based on the change in thickness, dilation:

$$\phi_{EFFV}^{dil} = \frac{h_{DG} - h_{hyp}}{h_{DG}} \quad [3.7]$$

Where h_{DG} is the dry glass thickness and h_{hyp} is the extrapolated hypothetical liquid polymer thickness at 25 °C as shown in Figure 3.2. It is assumed that the volume expansion is confined to perpendicular direction in respect to the substrate^[44–47] and thus the volume dilation is equal to the thickness dilation, allowing for the calculation of the EFFV using the thickness as a parameter.

The second approach determines the EFFV based on combining the refractive indices of the components present inside the glassy polymer film using the Bruggeman effective medium approximation (BEMA) which is commonly used in polymer swelling studies^[48]:

$$\phi_{EFFV}^{BEMA} \cdot \frac{n_{void}^2 - n_{DG}^2}{n_{void}^2 + 2n_{DG}^2} + (1 - \phi_{EFFV}^{BEMA}) \cdot \frac{n_{hyp}^2 - n_{DG}^2}{n_{hyp}^2 + 2n_{DG}^2} = 0 \quad [3.8]$$

Where n_{void} , n_{DG} , and n_{hyp} are the refractive index of void ($n=1$), dry glassy polymer and of the extrapolated hypothetical liquid polymer respectively. For example, for Matrimid 5218 at 25 °C, $n_{DG} = 1.632 \pm 0.001$ and $n_{hyp} = 1.698 \pm <0.001$, resulting in a $\phi_{EFFV}^{BEMA} = 0.092 \pm 0.001$ (error indicates standard error).

3.2.2 Excess free volume filling

In Figure 3.3 a schematic representation of a dry and a swollen polymer film is shown. A dry polymer film consists of a polymer fraction and a certain void fraction (i.e. EFFV). In analogy to the definition of the EFFV using the respective volume fractions of the glassy polymer and the hypothetical liquid at room temperature, the total film thickness of the glassy polymer can be divided into the thickness contribution from the dense polymer matrix (i.e. hypothetical liquid) and from the void.

When the polymer is exposed to the solvent (Figure 3.3, swollen polymer), the solvent volume fraction can be subdivided into two fractions: the Langmuir fraction (φ_L) and the Henry fraction (φ_H). As the sum of the fractions represent the total swollen thickness, the sum of the four fractions equals 1:

$$\varphi_P + \varphi_{\text{void}} + \varphi_L + \varphi_H = 1 \quad [3.9]$$

$$SF = \frac{h_{\text{sw}}}{h_{\text{dry}}} \quad [3.10]$$

The different volume fractions can be expressed as a function of the swelling factor (SF) (Eq. 3.10) of the swollen polymer. The complete derivation is provided in the Supplementary Information.

$$\varphi_P = \frac{1-E}{SF} \quad [3.11]$$

$$\varphi_H = 1 - \frac{1}{SF} \quad [3.12]$$

$$\varphi_L = \frac{E \cdot x}{SF} \quad [3.13]$$

$$\varphi_{\text{void}} = \frac{(1-x)E}{SF} \quad [3.14]$$

E is the EFFV as determined in a T_g measurement, and x is defined as the filling factor, the extent to which the excess free volume is filled with solvent and ranges from 0 (dry polymer) to 1 (EFFV is filled with solvent). By applying a three component BEMA (void, polymer and solvent volume fractions), the filling factor, x can be calculated by Eq. 3.15. For a complete derivation, the reader is referred to the Supplementary Information.

$$x = \frac{(E-1)I_{\text{hyp}} - EI_{\text{void}} + (1-SF)I_{\text{solvent}}}{E(I_{\text{hyp}} - I_{\text{void}})} \quad [3.15]$$

In Eq. 3.15, the filling factor, x is expressed as function of the swelling factor (SF), the EFFV (E) and the refractive indices of the void (n_{void}), the solvent (n_{solvent}), the swollen polymer (n_{swollen}) and hypothetical liquid polymer (n_{hyp}) as present in the

Clausius-Mossotti factors: $I_{\text{hyp}} = \frac{n_{\text{hyp}}^2 - n_{\text{swollen}}^2}{n_{\text{hyp}}^2 + 2n_{\text{swollen}}^2}$, $I_{\text{void}} = \frac{n_{\text{void}}^2 - n_{\text{swollen}}^2}{n_{\text{void}}^2 + 2n_{\text{swollen}}^2}$ and $I_{\text{solvent}} = \frac{n_{\text{solvent}}^2 - n_{\text{swollen}}^2}{n_{\text{solvent}}^2 + 2n_{\text{swollen}}^2}$.

This means the extent to which the EFV is filled can be determined by determining the swelling factor and when knowledge about the EFFV and the refractive indices are available. This allows for the analysis of a wide variety of polymers with different EFFV and thermal histories and to compare their swelling behavior.

Once x is known, the solvent volume fraction inside the polymer film can be determined by using Eq. 3.16.

$$\varphi_{\text{solvent}} = \varphi_H + \varphi_L = 1 - \frac{1}{SF} + \frac{Ex}{SF} \quad [3.16]$$

Figure 3.3 – A schematic representation of a swollen polymer film, divided into the different volume constituents.

3.3 Materials and Methods

3.3.1 Materials

Polysulfone Udel® P-3500 (Amoco), polystyrene (Sigma Aldrich), Matrimid® 5218 US (Huntsman), P84® 325 mesh (HP Polymer), and polyetherimide Ultem™ 1000 (GE Plastics) were used as received.

Cyclopentanone (ReagentPlus®, ≥99 %, Sigma-Aldrich), toluene (anhydrous, ≥ 99.8 %, Sigma-Aldrich), N-methyl-2-pyrrolidone (anhydrous, 99.5%, Sigma-Aldrich), and chloroform (anhydrous, ≥99 %, Sigma-Aldrich) were used for dissolving the polymers.

Silicon wafers (100, front side polished, CZ test grade, Silchem) were used as a substrate for the spin-coated layer. The wafers were stored under clean-room conditions prior to being diced. Prior to use, the wafers were cleaned with Acetone (Chromasolv® plus, for HPLC 99.9 %, Sigma-Aldrich).

Ethyl Acetate (anhydrous, 99.8 %, Sigma-Aldrich), *n*-hexane (EMPLURA®, >95 %,Merck), ethanol (EMSURE®, ACS, ISO, Reag. Ph Eur; Merck), and toluene (EMPLURA®, >99 %,Merck) were used as received for the swelling experiments. In Table 3.2 the properties of the solvents used for the swelling study are listed.

Table 3.2 – Solvent properties; Molecular weight, Lennard-Jones length parameter (σ), δ_d (dispersive), δ_p (permanent dipole), δ_H (hydrogen bonding) are the Hansen solubility parameters taken from^[49], dipole moment^[50] and the vapor pressure at 25 °C

Solvent	Mw (g mol ⁻¹)	Density (kg m ⁻³)	σ (Å)	$\delta_d, \delta_p, \delta_H$ (MPa) ^{1/2}	Dipole moment (D)	Vapor pressure at 25 °C (bar)
Ethanol	46.07	789	4.299 ^[51]	15.8; 8.8; 19.4	1.7	0.078
Ethyl acetate	88.11	897	5.153 ^[51]	15.8; 5.3; 7.2	1.9	0.125
Hexane	86.18	655	6.269 ^[52]	14.9; 0.0; 0.0	0	0.200
Toluene	92.14	867	5.923 ^[52]	18.0; 1.4; 2.0	0.4	0.038

3.3.2 Sample preparation

Thin polymer films were prepared by spin-coating a 4 mL polymer solution on a complete silicon wafer under a nitrogen atmosphere. The polymer solutions were prepared according to the concentrations as given in Table 3.3 and were filtered with a 0.2 μm PTFE filter. The solutions were spin-coated using a Laurell WS-400B-6NPP-Lite spin-coater as described below.

For solutions in cyclopentanone, the dope was deposited while spinning for 10 seconds at 500 rpm, then the spinning speed was increased to 10 minutes at 1000 rpm. For solutions in toluene, a one step program of 30 seconds at 3000 rpm was applied and the polymer solution was deposited during spinning. For polymer solutions in NMP, a three-step spinning program was applied. The polymer solution was deposited during the first step of 10 seconds at 500 rpm. The the spinning speed was then increased to 3000 rpm for 30 s, and the final step was spinning for 10 minutes at 1000 rpm. For polymer solutions in chloroform, a one step program of 30 seconds at 3500 rpm was applied and the polymer solution was deposited during spinning. In all cases an acceleration of 1710 rpm s⁻¹ was used.

After spin-coating, the polymer films were annealed in a low temperature furnace (Carbolite HTMA 5/28) for 8 hours under a nitrogen atmosphere to remove any residual solvents at an annealing temperature as given in Table 3.3. The annealing temperature was set above the glass transition temperature where possible, but when in risk of degradation or cross-linking of the polymer through exposure to a high temperature for 8 hours, the annealing temperature was instead set at least higher than the boiling point of the solvent as a compromise to attempt to avoid

thermal degradation or cross-linking while still removing residual solvent. After annealing, the wafer with the polymer film was diced into pieces of $5 \times 2 \text{ cm}^2$.

Table 3.3 - Polymer properties, concentrations and temperatures used for preparation.

Polymer	M_w (g mol^{-1})	$\rho_{\text{bulk, pol}}$ (kg m^{-3})	Solvent	C_{pol} (wt %)	$T_{\text{annealing}}$ ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)
Polysulfone	77,000-86,000	1240	$\text{C}_5\text{H}_8\text{O}^*$	3	215	300
Polystyrene	280,000	1047	Toluene	3	130	150
Matrimid 5218	80,000 ^[53]	1200	$\text{C}_5\text{H}_8\text{O}^*$	3	250	400
P84	146,400	1380	NMP	6	335	400
PEI	30,000	1280	CHCl_3	1.5	235	300

* Cyclopentanone

3.3.3 Characterization

3.3.3.1 Glass transition temperature measurement

Prior to solvent exposure, for each sample the glass transition temperature, the EFFV and the hypothetical refractive index of the liquid polymer were determined using temperature dependent spectroscopic ellipsometry. A Linkam heatcell in combination with a M2000XI (J.A. Woollam Co., Inc.) was used to determine the layer thickness and refractive index from the (Ψ, Δ) -spectra as function of temperature. The samples were heated to T_{max} (Table 3.3) at a rate of $75 \text{ }^{\circ}\text{C min}^{-1}$ and held at T_{max} for 10 minutes. The samples were then cooled down at a rate of $12.5 \text{ }^{\circ}\text{C min}^{-1}$ to $25 \text{ }^{\circ}\text{C}$. A nitrogen flow of 100 mL min^{-1} into the cell was used to create a nitrogen atmosphere. The properties of the samples were determined from the cooling down curve of the temperature measurement. The glass transition temperature, EFFV, and the hypothetical refractive index of the liquid polymer were determined at $25 \text{ }^{\circ}\text{C}$, by determination of the slopes of both thickness and refractive index above the glass transition temperature and below the glass transition temperature, as described in section 3.2.1. Prior to each glass transition measurement, the window offsets of the heat cell were determined with a 25 nm SiO_2 calibration wafer.

3.3.3.2 Solvent swelling

The solvent induced swelling of the samples was determined by measuring the layer thickness and refractive index using a M2000XI spectroscopic ellipsometer (J.A. Woollam Co., Inc.) in combination with a 5 mL heated liquid cell. The temperature of the cell was fixed at $25 \text{ }^{\circ}\text{C}$. Prior to the exposure to solvent vapor, the sample was placed in the Linkam heatcell and given the same temperature treatment as described in section 3.3.2. for the glass transition temperature

measurement. The sample was measured outside the cell, and inside the cell at 25 °C. The solvent vapor was generated by using two bubblers in series, both filled with solvent to ensure oversaturation of the solvent in the nitrogen gas. One bubbler was placed in a water bath at 30 °C, the second bubbler was placed at room temperature. Two mass flow controllers (Brooks GF40) were used to control the solvent saturated nitrogen flow through the bubblers and the pure nitrogen flow (see Figure 3.4 for flow scheme). The pure and the saturated nitrogen flows were mixed at different ratios to introduce solvent vapor with activities varying between 0-1 with steps of 0.1 into the cell as calculated by Eqs. 3.17 and 3.18. The solvent activity represents the effective solvent concentration inside the measurement cell. A total flow (Φ_{tot}) of 100 mL min⁻¹ for the activity measurements was used and the total pressure (p_{tot}) was set at 1 atm.

$$\Phi_{\text{tot}} = \Phi_1 + \Phi_2 \frac{p_{\text{tot}} - p_{\text{sat}}}{p_{\text{tot}}} \quad [3.17]$$

$$a_s = \left(\frac{\Phi_{\text{tot}} - \Phi_1}{\Phi_{\text{tot}}} \right) p_{\text{tot}} \quad [3.18]$$

Where p_{sat} is the saturation pressure as determined by the Antoine equation, a_s is the solvent activity, and Φ_1 and Φ_2 are the volume flows of the pure nitrogen and solvent respectively.

The following measurement protocol was followed:

1. Determination of window offsets heated liquid cell using a 25 nm SiO₂ calibration wafer.
2. Measure sample outside the cell at 25 °C.
3. Measure sample inside the cell at 25 °C
4. Start in-situ measurement
5. Measure dry for ~2 min
6. Connect vapor flow to the measurement cell and start with an activity of 0.1.

The activity was increased after a minimum of 30 minutes.

Figure 3.4 – Scheme of the used set-up. Pure nitrogen gas was bubbled through two bubblers and mixed with pure nitrogen to obtain the desired solvent activity.

3.3.3.3 Hysteresis effects

To test for hysteresis effects upon filling and emptying the EFV, multiple activity runs were performed on a Matrimid 5218 and polystyrene film in ethyl acetate vapor. For the first run, the activity was increased up to $a=0.2$, followed by a drying step with pure nitrogen (100 mL min^{-1}). In the second run the activity was increased to $a=0.4$, followed by another drying step of pure nitrogen (100 mL min^{-1}). In the third run the activity was increased to $a=0.6$ followed by a drying step with pure nitrogen (100 mL min^{-1}). In the fourth run, the activity was increased to $a=0.8$ followed by a drying step with pure nitrogen (100 mL min^{-1}). In the fifth and sixth run the activity was increased to $a=1$ and both runs were followed by a drying step with pure nitrogen (100 mL min^{-1}).

3.3.3.4 Optical Modelling

For the analysis of the measured (Ψ, Δ) -spectra, an optical model was used. The polymer film was modelled with a Cauchy dispersion (fit parameters: A , B , and thickness d) on top of a silicon wafer with a 2 nm native oxide layer. If a significant enhanced quality of the fit was obtained upon including the Urbach absorption tail k , then also absorption was included. In the Supplementary data, an overview of the exact models used for the different samples is provided.

The refractive index of the solvent was determined for 7 different wavelengths (365.0 nm, 400.0 nm, 450.0 nm, 500.0 nm, 590.0 nm, 700.0 nm, 800.0 nm) by using a digital multiple wavelength refractometer (Schmidt Haensch ATR-L) at 25 °C. A Cauchy dispersion relation was fitted to the obtained data to determine the refractive index at 632.8 nm. The measured refractive indices of the solvents are provided in Table S3.4 in the Supplementary Information.

For each measurement, the standard error was determined based on the correctness the fit of the optical model. For the complete error analysis, the reader is referred to the Supplementary Information.

3.4 Results and Discussion

3.4.1 Glass transition measurement

The glass transition temperature and the EFFV were determined for each polymer using temperature dependent spectroscopic ellipsometry. In Table 3.4 an overview of the glass transition results is shown.

Table 3.4 – The EFFV according to the dilation method ($\Phi_{E,dil}$), the BEMA method ($\Phi_{E,BEMA}$) and the T_g of the different polymers. The error margins represent the standard error.

Polymer	$\Phi_{E,dil}$	$\Phi_{E,BEMA}$	T_g (°C)
P84 (n=5)	0.122 ± 0.001	0.095 ± 0.001	330.8 ± 2.8
Matrimid 5218 (n=6)	0.125 ± 0.001	0.093 ± 0.001	323.9 ± 0.9
Polyetherimide (n=5)	$0.076 \pm <0.001$	0.060 ± 0.001	212.6 ± 0.4
Polysulfone (n=5)	$0.066 \pm <0.001$	0.051 ± 0.001	187.0 ± 0.1
Polystyrene (n=5)	$0.032 \pm <0.001$	$0.030 \pm <0.001$	100.3 ± 0.2

For higher T_g polymers a larger standard error is found. This is because the kink in the temperature versus time curve, indicating the T_g is less pronounced for more glassy polymers, and because for high T_g polymers a larger extrapolation to EFFV at room temperature is required. For a low EFFV (e.g. 3 %), there is a good agreement between the dilation method and the BEMA method. For an increased EFFV, the EFFV based on the dilation and BEMA methods start to deviate from each other. This is in agreement with the results as observed by Ogieglo et al.^[43], where also the extrapolated EFFV show larger deviations for higher EFFV values. As any systematic errors that are introduced into the system will be squared in the BEMA method, the dilation method will be further on used for the determination of the EFFV.

3.4.2 Solvent vapor swelling

3.4.2.1 Filling of the EFV

In Figure 3.5, the EFV filling factor, x is plotted as function of the swelling factor for the five different polymers, in ethyl acetate, ethanol, and *n*-hexane. The separate data per polymer are available in the Supplementary Information. Figure 3.5 depicts very similar trends for all described polymer/solvent combinations. This is

remarkable, as it indicates that even for distinct polymers that are in different non-equilibrium states and exposed to different solvents, the relation between filling of the EFV and the degree of swelling appears universal. Around a swelling factor of ~ 1.05 (swelling of 5 %), in all polymers the EFV is completely filled and further sorption results in dilation as observed in a rubbery polymer. This observation is in agreement with the literature on gas sorption as described in the introduction (see section 3.1) and suggests that by measuring the dilation of a polymer one can make an estimation when matrix dilations start to dominate the sorption behavior.

Figure 3.5 – The EFFV filling factor, x as function of the swelling factor for the five different polymers in ethyl acetate, ethanol, and n -hexane. At approximately $SF=1.05$, the EFV appears to be filled. The points represent the average of the last 10 datapoints for each activity step. The shades around the curves represent the standard error of the measurement.

However, although the similarity of the EFV filling for each glassy polymer is striking, the obtained values for the filling factor rise *above* 1 with increasing swelling factors, and with a stronger tendency to exceed unity for polymer with a lower glass transition temperature. Values of x exceeding 1 are physically not possible within the dual mode sorption model. A possible explanation might be that the dual mode sorption model is too simplistic to accurately describe the sorption characteristics, and hence our calculations based on Figure 3.3 are also inadequate for a reliable quantitative analysis. As mentioned in section 1.2.2, the free volume sites in a glassy polymer are either frozen into the matrix or they fluctuate along the polymer chain, and the EFV is considered as the frozen part of the hole free volume. However, in reality the difference between the hole free volume and the EFV will not be that distinct. Additional frozen or fluctuating free volume inside the glassy polymer can function as a sorption site, but possibly via a different sorption mode than as described in the dual mode sorption model. In addition, it should be noted

that the (non-equilibrium) properties of the glasses are changing upon filling of the EFV of the polymer with the penetrant. To test this, a hysteresis test has been performed on Matrimid 5218 and polystyrene during which the EFV has been filled and emptied for several times at different activities of ethyl acetate.

In Figure 3.6 the EFV filling of both Matrimid 5218 and polystyrene are shown as function of the swelling factor. The open symbols represent activity runs up till the point that the EFV has been filled for the first time. The closed symbols represent the activity runs after the EFV of the polymer has been filled completely once and subsequently dried with nitrogen. A hysteresis is visible in the EFV filling curve once the EFV has been filled with the penetrant at least once, while the activity runs before completely filling the EFV show no hysteresis. This is the case for both Matrimid 5218, a high EFFV polymer and Polystyrene, a low EFFV polymer. The presence of the shift to higher swelling factors in the EFV filling curve, supports the hypothesis that upon completely filling of the EFV, the polymer matrix is changed, reducing the amount of EFV in the polymer matrix. As polystyrene is a low EFFV polymer, one would expect that a change in the EFV upon filling the void spaces with a penetrant, will have a strong effect on the filling factor, x as is shown in Figure 3.5.

Figure 3.6 – The EFFV filling factor as function of the swelling factor for Matrimid 5218 (left) and polystyrene (right) in ethyl acetate vapor. The different symbols represent the different activity runs. The open symbols represent four activity runs up to $a=0.8$. In the fourth run up to $a=0.8$, the EFV has been filled and upon drying with nitrogen and repeating the run up to an activity of $a=1$ (fifth and sixth run, closed symbols), a change in the filling curve is visible. The presence of this hysteresis is an indication of change in the polymer matrix upon free volume filling.

With Figure 3.5 it is shown that all the measured polymer-solvent systems behave in a similar way and that the errors introduced by the optical modelling with spectroscopic ellipsometry are small (small error margins). However, the general assumptions that are made within the dual mode sorption model (e.g. no modifications of the polymer matrix upon penetrant sorption), indicate a general trend but cannot prove the existence of a master curve. The use of a thermodynamic model, such as the non-equilibrium lattice fluid model [7], and incorporating modifications of the polymer structure upon EFV filling could be beneficial to improve the general trend. Here, we limit ourselves to the simple dual mode sorption model to illustrate the proof of concept.

3.4.2.2 Solvent volume fraction

The solvent volume fraction inside the polymer film can be determined by using Eq. 3.16. In Figure 3.7, the solvent volume fraction is shown as a function of the swelling factor. The data for each separate solvent-polymer combination is provided in the Supplementary Information.

Figure 3.7 – The solvent volume fraction inside the polymer film as function of the swelling factor for each polymer-solvent combination. The data points represent the average value of the last 10 data points of each activity step. With an increasing EFFV in the polymer, a higher solvent volume fraction was observed.

In Figure 3.7 it is shown that more solvent is present in higher EFFV polymers at the same swelling factor, compared to low EFFV polymers. Also, it should be noted that for polymers with a higher EFFV, there is already a significant solvent uptake while almost no swelling was observed (i.e. $SF=1.005$). This is in agreement with the observations by Visser and Wessling [38], where it is shown that at the first contact with the penetrant, no polymer relaxations occur and the penetrant only diffuses

into the empty void spaces of the polymer. A higher EFFV, therefore results in a relative higher amount of solvent concentration inside the polymer compared to a low EFFV, while the dilation is the same. This is significant for polymers applied for solvent related applications, as even though the polymer might not yet show significant swelling the polymer properties will have changed due to the change in the thermodynamic state.

3.4.2.3 Toluene

A deviation from the general trend was observed when the polymer films were exposed to toluene. While for polystyrene a similar trend was observed as for the other solvents, for polysulfone, polyetherimide, Matrimid 5218 and P84 a lower solvent uptake in the free volume combined with higher swelling factors was observed as is shown in Figure 3.8. This would indicate that toluene has a tendency to dilate the polymer matrix rather than to fill up the available free volume inside the polymer film. An explanation for the deviating behavior of toluene compared to the other solvents might be found in the fact that toluene is an aromatic solvent; it has an ability to have a π - π interaction with each polymer, as each polymer contains at least one aromatic ring in the repeat unit. Although much is yet still unknown about the nature of the aromatic interactions, recently it has been shown that aromatic solvents are able to induce specific conformations in *o*-cresol, a compound with different binding sites for different solvents ^[54,55]. Polystyrene however has a small repeating unit, allowing for intramolecular aromatic group interactions. Matrimid 5218, polysulfone, P84 and PEI have a more bulky repeating unit, allowing a larger interaction with aromatic penetrants. As a result, toluene will interact at specific sites and shows a lower occupation of the EFV.

Figure 3.8 – The EFFV filling factor (left) and solvent volume fraction (right) as function of the swelling factor for the different polymer films for the solvent vapor swelling in toluene.

3.5 Conclusions

At present, no relation has been established between the excess free volume and solvent sorption inside glassy polymers. This study shows that for distinct polymers with varying non-equilibrium characteristics, exposed to different penetrants, a universal relation between the filling of the excess free volume and the degree of swelling exists. For each polymer/solvent combination, the excess free volume is completely filled around a swelling of ~5 %. This degree of swelling is in agreement with literature reported on penetrant sorption in glassy polymers, where it was shown that within the dual mode sorption model, the upper limit of the Langmuir sorption can be coupled to a swelling ~6 %. This work shows that upon further dilation, the structure of the polymer is irreversibly changed, resulting in a change of the excess free volume available for penetrant uptake. Also, it was shown that by interpreting the sorption in terms of Langmuir sorption and Henry sorption, a good approximation of the excess free volume filling master curve could be obtained. However, further research into the available free volume available for sorption in the different glassy polymers and the changes in the polymer structure in the vicinity of completely filling the EFV, is necessary to obtain an accurate description of the EFV filling behavior in glassy polymers.

Based on the findings in this work, a rough prediction on the type of penetrant sorption in thin polymer films is possible, when knowledge on only the swelling factor is available. From an engineering perspective this is important, thin glassy polymer films find their application in many industries and often endure exposure to a wide selection of penetrants. Therefore, knowledge on the swelling behavior of such a thin polymer film is necessary to allow for a more accurate prediction of the thin film performance in non-aqueous media.

3.6 Acknowledgements

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3.7 Supplementary Information

3.7.1 Packing density calculated from dual mode

The packing density based on the dual mode sorption data can be calculated assuming that the total penetrant concentration inside the polymer, C equals the Langmuir maximum capacity, C'_H . Based on the total concentration, the critical pressure, P_{cr} could be determined from the concentration as function of pressure data. The packing density can then be calculated:

$$\rho^* = \frac{bP_{cr}}{1+bP_{cr}} \quad [S3.1]$$

In Table S3.1 an overview of the packing density for CO₂ sorption based on dual mode sorption data reported in the literature, is provided. The average packing density was calculated to be 0.69 ± 0.03 at 95 % confidence. The packing density for CO₂ as taken from Bondi^[20] is equal to 0.76. The difference can partially be explained by the fact that the packing density calculated from the dual mode data assumes no sorption via Henry dilation occurs within the polymer. In reality however, there is a small contribution from the Henry sorption mode. As a result, the calculated average packing density is then an underestimation of the real packing density making the Bondi estimation a very suitable estimate.

Table S3.1 – Calculated packing factor based on the dual mode data of CO₂ sorption as reported in literature. The calculated average packing factor was 0.69 ± 0.03 based on a 95 % confidence interval.

Type of polymer	Packing factor	Source	Type of polymer	Packing factor	Source
PI (slow)	0.71	[22]	CA 1.75	0.62	[56]
PI Quench	0.72	[22]	CA 2.45	0.61	[56]
PC Slow	0.68	[22]	CA 2.84	0.58	[56]
PC quench 190	0.66	[22]	PI4	0.80	[30]
PC quench 200	0.67	[22]	PIM-1	0.81	[30]
PC quench -94	0.67	[22]	PIM-1	0.79	[26]
PC	0.69	[21]	ODPA-P1	0.76	[37]
PC (Lexan unaged)	0.63	[12]	ODPA-P2	0.65	[37]
PC (Lexan aged)	0.65	[12]	ODPA-P3	0.62	[37]
PPO Slow	0.71	[22]	PSf	0.67	[30]
PPO 220	0.71	[22]	PSf untreated	0.71	[32]
PPO 240	0.71	[22]	PSf ozone treated	0.75	[32]
PPO 250	0.72	[22]	PSf 35 °C	0.66	[35]
PS	0.62	[29]	Matrimid 5218	0.79	[33]
PTMSP	0.49	[57]	Matrimid 5218 + C60	0.73	[33]
PET	0.66	[19]			

3.7.2 Dual Mode sorption parameters

Table S3.2 – An overview of the dual mode parameters and calculated C_D as observed in literature.

System	T_g (°C)	K_d^a	C'_H^b	b^c	$p_{H, \text{filled}}$ (atm)	C^{*d}	C_D^d	C_D/C_H	
PI (slow) - CO2	227	1.3	14.4	0.7	4.3	16.7	5.8	0.5	[22]
PI Quench - CO2	227	1.3	15.7	0.8	4.1	17.3	5.4	0.5	[22]
PC Slow - CO2	147	0.8	16.2	0.3	11.9	21.3	9.0	0.7	[22]
PC quench 190 - CO2	147	0.8	22.5	0.2	17.4	30.3	13.2	0.8	[22]
PC quench 200 - CO2	147	0.8	24.7	0.2	16.7	32.0	13.2	0.7	[22]
PC quench -94 - CO2	147	0.8	24.9	0.2	17.4	32.9	14.0	0.7	[22]
PPO Slow - CO2	219	0.9	26.1	0.3	10.4	29.3	9.5	0.5	[22]
PPO 220 - CO2	219	1.0	27.7	0.3	11.0	31.5	10.5	0.5	[22]
PPO 240 - CO2	219	0.9	28.9	0.3	11.0	32.3	10.3	0.5	[22]
PPO 250 - CO2	219	0.9	30.3	0.3	11.0	33.2	10.2	0.4	[22]
Matrimid 5218 non-annealed - Heptane	305	292.7	19.8	142.7	0.0	19.6	5.3	0.4	[28]
Matrimid 5218 annealed - Heptane	305	270.6	9.2	473.5	0.0	8.5	1.9	0.2	[28]
Matrimid 5218 non-annealed - Toluene	305	995.6	55.8	136.8	0.0	52.1	14.4	0.4	[28]
Matrimid 5218 annealed - Toluene	305	1233.8	22.2	510.3	0.0	20.0	5.0	0.3	[28]
PS-CO2	100	0.7	7.7	0.4	8.6	11.5	5.7	1.0	[29]

Table S3.2 (continued)

System	T_g (°C)	K_d^a	$C_H'^b$	b^c	$p_{H, \text{filled}}$ (atm)	C^{*d}	C_D^d	C_D/C_H	
PI4 - CO2	380	1.6	54.6	0.6	5.8	50.6	9.1	0.2	[30]
PIM-1 - CO2	400 ^a	1.7	78.6	0.5	6.5	70.5	10.8	0.2	[30]
ODPA-P1 - CO2	243	0.4	32.0	0.2	13.6	30.2	5.9	0.2	[37]
ODPA-P2 - CO2	214	0.4	25.0	0.2	14.2	24.0	5.0	0.3	[37]
ODPA-P3 - CO2	208	0.3	18.0	0.2	16.5	18.5	4.8	0.4	[37]
PSf untreated - CO2	185	0.3	16.0	0.2	15.1	17.3	5.1	0.4	[58]
Matrimid 5218 - CO2	338	1.4	35.0	0.7	4.5	33.0	6.4	0.2	[33]
Matrimid 5218 + C60 - CO2	352	1.4	28.5	0.5	6.7	30.9	9.2	0.4	[33]
PET 35 degC - CO2	85	0.3	5.8	0.3	9.8	7.6	3.2	0.7	[19]
PC - CO2	147	0.7	18.8	0.3	12.1	22.7	8.4	0.6	[21]
Polysulfone - CO2	190	0.6	19.4	0.2	17.8	25.4	10.7	0.7	[35]
PET butane	78	1.3	1.3	2.2	1.2	2.4	1.5	1.6	[23]
PSf C - CO2	179	0.6	12.0	0.4	8.6			0.5	[24]
PSf D - CO2	173	0.6	10.3	0.4	8.6			0.7	[24]
PSF N - CO2	155	0.6	8.2	0.4	8.6			0.9	[24]
PC - CO2	145	0.8	7.6	0.4	8.6			1.2	[24]
PEI - CO2	215	0.8	12.4	0.5	5.9			0.5	[24]
PET methane	79	63.1	0.7	144.4	0.0			1.9	[25]
PET ethane	79	64.6	1.0	308.5	0.0			0.7	[25]

Table S3.2 (continued)

System	T_g (°C)	K_d^a	C'_H^b	b^c	$p_{H, \text{filled}}$ (atm)	C^*^d	C_D^d	C_D/C_H	
PET - n-propanol	79	159.8	2.3	104.5	0.0			2.3	[25]
PET - i-propanol	79	80.6	0.5	415.3	0.0			1.4	[25]
PIM-1 - CO2	400 ^a	2.4	105.8	0.4	7.5	98.1	17.7	0.2	[26]
PIM-1 - C2H4	400 ^a	1.8	93.5	0.6	3.7	69.2	6.6	0.1	[26]
PIM-1 - C2H6	400 ^e	2.8	81.1	1.1	2.0	60.5	5.4	0.1	[26]
PIM-1 - C3H6	400 ^e	10.1	88.7	2.6	0.8	67.3	7.9	0.1	[26]
PIM-1 - C3H8	400 ^e	10.5	78.1	3.4	0.7	61.3	7.0	0.1	[26]
MPD - butane	548	17.1	14.1	6.1	25.4	15.1	5.7	0.6	[27]
TrMPD - butadiene	649	32.0	29.4	45.9	3.4	21.1	1.4	0.1	[27]
5CMPD - butadiene	550	18.4	21.3	9.6	16.1	18.2	3.9	0.3	[27]
44'DPE - butadiene	564	17.2	19.8	10.5	14.7	16.6	3.3	0.3	[27]
34'DPE - butadiene	510	17.0	7.4	2.6	60.6	18.5	13.6	2.8	[27]
44'DDM - butadiene	559	19.8	19.6	11.5	13.5	16.6	3.5	0.3	[27]
BAAF - butadiene	573	18.7	27.4	15.9	9.7	20.8	2.4	0.1	[27]

^a K_d in $\text{cm}^3(\text{STP}) \text{cm}^{-3} \text{atm}^{-1}$ ^b C'_H in $\text{cm}^3(\text{STP}) \text{cm}^{-3}$ ^c b in atm^{-1} ^d C^* and C_D in $\text{cm}^3 \text{cm}^{-3}$ ^e PIM-1 decomposes below its glass transition temperature. The glass transition temperature given here is an estimation and cannot be measured.

3.7.3 Excess free volume filling

For a swollen polymer system, the separate volume fractions can be calculated based on the thickness. Here it is assumed that the swelling of the polymer sample on the substrate is restricted to a one-directional swelling, perpendicular to the substrate. As a result, the volume fractions can be defined in terms of the swollen thickness (h_{sw}) and dry thickness (h_{dry}) of the polymer film.

The dry polymer fraction, φ_p is defined as

$$\varphi_p = \frac{h_{hyp}}{h_{swollen}} = \frac{(1-E)h_{dry}}{h_{swollen}} \quad [S3.2]$$

where $(1 - E)$ represents the fraction of dry polymer as represented in Figure S3.1.

The total void fraction, φ_{void} is defined as

$$\varphi_{void} = \frac{(1-x)E h_{dry}}{h_{swollen}} \quad [S3.3]$$

where x is the fraction of void space (excess free volume) filled (filling factor), varying from 0 to 1 and will be derived later in this section.

Subsequently, the total Langmuir fraction, φ_L , the amount of solvent that is sorbed into the void space of the polymer, is defined as

$$\varphi_L = \frac{E \cdot x \cdot h_{dry}}{h_{swollen}} \quad [S3.4]$$

$$\varphi_p + \varphi_{void} + \varphi_L + \varphi_H = 1 \quad [S3.5]$$

Knowing that the sum of all the separate volume fractions adds up to 1 (Eq. S3.5), the Henry fraction, φ_H can be calculated (Eq. S3.6).

$$\varphi_H = 1 - \frac{h_{dry}}{h_{swollen}} \quad [S3.6]$$

By defining a swelling factor, SF, all volume fractions can be rewritten as a function of the swelling factor (Eq. S3.8-S3.11).

$$SF = \frac{h_{sw}}{h_{dry}} \quad [S3.7]$$

$$\varphi_p = \frac{1-E}{SF} \quad [S3.8]$$

$$\varphi_H = 1 - \frac{1}{SF} \quad [S3.9]$$

$$\varphi_L = \frac{E \cdot x}{SF} \quad [S3.10]$$

$$\varphi_{void} = \frac{(1-x)E}{SF} \quad [S3.11]$$

To determine the value of the filling factor, χ , a three component Bruggeman effective medium approximation (BEMA) can be utilized. In this case, the swollen polymer system consists of three components: void (φ_{void}), dry polymer (φ_p) and solvent ($\varphi_H + \varphi_L$). The BEMA can then be defined as

$$\varphi_p \cdot I_{\text{hyp}} + \varphi_{\text{void}} \cdot I_{\text{void}} + (\varphi_H + \varphi_L) \cdot I_{\text{solvent}} = 0 \quad [\text{S3.12}]$$

Where $I_{\text{hyp}} = \frac{n_{\text{hyp}}^2 - n_{\text{swollen}}^2}{n_{\text{hyp}}^2 + 2n_{\text{swollen}}^2}$, $I_{\text{void}} = \frac{n_{\text{void}}^2 - n_{\text{swollen}}^2}{n_{\text{void}}^2 + 2n_{\text{swollen}}^2}$ and $I_{\text{solvent}} = \frac{n_{\text{solvent}}^2 - n_{\text{swollen}}^2}{n_{\text{solvent}}^2 + 2n_{\text{swollen}}^2}$ are the Clausius-Mossotti factors.

where n_{hyp} is the refractive index of the equilibrium polymer extrapolated below the glass transition temperature as determined from the T_g measurement, n_{swollen} the refractive index of the swollen polymer as measured, n_{void} the refractive index of the void (=1.000), and n_{solvent} the refractive index of the solvent.

Combining Eq. S3.8-S3.11 with S3.12, the following equation can be obtained:

$$\frac{1-E}{SF} \cdot I_{\text{hyp}} + \frac{(1-\chi)E}{SF} \cdot I_{\text{void}} + \left(1 - \frac{1}{SF} + \frac{E \cdot \chi}{SF}\right) \cdot I_{\text{solvent}} = 0 \quad [\text{S3.13}]$$

By measuring the SF and the refractive index of the swollen polymer film independent from each other, using spectroscopic ellipsometry, the extent to which the EFV has been filled by the solvent can be determined by rewriting Eq. S3.13 into Eq. S3.14:

$$\chi = \frac{(E-1)I_{\text{hyp}} - EI_{\text{void}} + (1-SF)I_{\text{solvent}}}{E(I_{\text{hyp}} - I_{\text{void}})} \quad [\text{S3.14}]$$

Figure S3.1 – A schematic representation of a swollen polymer film, divided into the different volume constituents.

3.7.4 Solvent swelling measurements

A typical measurement, polysulfone exposed to ethanol vapor, is shown in Figure S3.2, left. While the thickness of polysulfone gradually increases, the refractive index (Figure S3.2 Left, right axis) of the thin polysulfone film first increases, and then decreases. On the right hand side in Figure S3.2, the degree to which the EFV is filled by the ethanol in the polysulfone film, calculated based on Eq. S3.14, is given as function of the swelling factor. The refractive index of the swollen polysulfone film has a maximum at an estimated solvent activity around 0.7 (point 3 in Figure S3.2), upon increasing the solvent activity further, the refractive index decreases again. This indicates that the polymer film has a stronger dilation and the EFV is nearly filled. This corresponds with the data in Figure S3.2 right. Initially there is a strong increase in x , while the swelling factor shows only a small increase. However, with increasing solvent activities ($> \sim 0.7$), a higher increase in swelling factor is observed, corresponding with the start of the dilation of the polymer matrix. At this point, the EFV is nearly filled.

Figure S3.2 – Left: Polysulfone exposed to ethanol vapor, an example of a typical solvent vapor swelling experiment. The black line represents the thickness (left axis), while the grey line represents the refractive index (right axis). The activity is increased from 0 to 1 by step of 0.1. **Right:** the filled EFV, x plotted as function of the swelling factor. The points 1-3 indicated on both the graphs represent corresponding data points in the left and right graph.

3.7.4.1 Activity measurements

In Figure S3.3 the solvent activity measurements for each polymer are presented.

Figure S3.3 – Overview of solvent activity measurements per polymer. The graphs on the left side show the EFFV filling factor as function of the swelling factor and the right side shows the solvent volume fraction as function of the swelling factor.

3.7.4.2 Non-equilibrium measurements

In Figure S3.4, an overview of the EFFV fillings factor (left) and the solvent volume fraction (right) at an apparent solvent activity of 1 is provided for each polymer.

Figure S3.4 – Overview of solvent measurements with apparent solvent activity of 1 per polymer. The graphs on the left side show the EFFV filling factor as function of the swelling factor and the right side shows the solvent volume fraction as function of the swelling factor. The two lower graphs display all the polymers combined.

3.7.5 Spectroscopic ellipsometry – Additional data

3.7.5.1 Modelling

All polymer samples were modelled with a Cauchy model using only A , B , and the thickness as the main fitting parameters on top of a temperature dependent Silicon wafer with a 2 nm native oxide layer. When the MSE was improved by at least 50 %, the Urbach absorption tail, k , was included. In Table S3.3, a detailed overview of the fit parameters used for modelling is provided. Prior to the glass transition temperature measurement, anisotropy was observed in the Matrimid 5218 sample. Once annealed above the T_g , the anisotropy has disappeared. The anisotropy was most likely induced by the spin-coating procedure. As Matrimid 5218 was not annealed above its glass transition temperature prior to the glass transition temperature measurement, the anisotropy was still visible. Once Matrimid 5218 was heated above its T_g , the polymer chains were able to relax and the anisotropy was removed.

Table S3.3 – An overview of the fit parameters used for both the T_g measurements and the solvent measurements.

Polymer	Cauchy Fit parameters for T_g measurement	Cauchy Fit parameters for solvent measurement
P84	d , A , B , k and Si T-dependent	d , A , B , k and Si 25 °C
Matrimid 5218	Anisotropic model with ΔA , d , A , B , k and Si T-dependent	d , A , B , k and Si 25 °C
Polyetherimide	d , A , B , k and Si T-dependent	d , A , B , k and Si 25 °C
Polysulfone	d , A , B , and Si T-dependent	d , A , B , and Si 25 °C
Polystyrene	d , A , B , and Si T-dependent	d , A , B , and Si 25 °C

3.7.5.2 Solvent refractive indices

The determined solvent refractive indices are provided in Table S3.4. The error displayed is an estimated standard error based on the Cauchy fit using the least squares method.

Table S3.4 – An overview of the measured refractive index for each solvent as used in the three component BEMA calculations.

Solvent	n at 632.8nm $\pm$ 0.001
Ethanol	1.358
Ethyl acetate	1.368
Toluene	1.491
Hexane	1.373
Methyl ethyl ketone	1.375
Isopropylalcohol	1.374

3.7.5.3 Error Analysis

In Table S3.5, an overview of the average error for each parameter per polymer is provided to give an indication for the order of magnitude of the errors. For the error calculations, the specific error belonging to the polymer/solvent combination was used for further error analysis.

Table S3.5 – Overview of calculated average standard errors for the different parameters per polymer.

Parameter	Matrimid 5218	P84	PEI	PSf	PS
d_{glass}	0.0084	0.0074	0.0056	0.0044	0.0063
n_{glass}	0.000035	0.000033	0.000019	0.000018	0.000023
d_{hypliq}	0.07	0.078	0.025	0.019	0.024
n_{hyp}	0.00034	0.00057	0.00013	0.00005	0.00013
d	0.02	0.030	0.036	0.012	0.030
d_{dry}	0.02	0.030	0.036	0.012	0.030
n_{swollen}	0.00016	0.00055	0.00043	0.00024	0.00022

The filling factor can be calculated by:

$$x(E, n_{\text{hyp}}, n_{\text{swollen}}, n_{\text{void}}, n_{\text{solvent}}, SF) = \frac{(E-1) \frac{n_{\text{hyp}}^2 - n_{\text{swollen}}^2}{n_{\text{hyp}}^2 + 2n_{\text{swollen}}^2} - E \frac{n_{\text{void}}^2 - n_{\text{swollen}}^2}{n_{\text{void}}^2 + 2n_{\text{swollen}}^2} + (1-SF) \frac{n_{\text{solvent}}^2 - n_{\text{swollen}}^2}{n_{\text{solvent}}^2 + 2n_{\text{swollen}}^2}}{E \left(\frac{n_{\text{hyp}}^2 - n_{\text{swollen}}^2}{n_{\text{hyp}}^2 + 2n_{\text{swollen}}^2} - \frac{n_{\text{void}}^2 - n_{\text{swollen}}^2}{n_{\text{void}}^2 + 2n_{\text{swollen}}^2} \right)}$$

As all errors provided are statistic errors, for a function $f = f(y, z)$, the error function is provided by Eq. S3.15. Here it assumed that all variables are independent and uncorrelated.

$$s_f^2 = \left(\frac{\partial f}{\partial y} \right)^2 s_y^2 + \left(\frac{\partial f}{\partial z} \right)^2 s_z^2 \quad [\text{S3.15}]$$

Thus the error function for the filling factor can be defined as:

$$s_f = \sqrt{\left(\frac{\partial f}{\partial E} \right)^2 \Delta E^2 + \left(\frac{\partial f}{\partial n_{\text{hyp}}} \right)^2 \Delta n_{\text{hyp}}^2 + \left(\frac{\partial f}{\partial n_{\text{swollen}}} \right)^2 \Delta n_{\text{swollen}}^2 + \left(\frac{\partial f}{\partial n_{\text{void}}} \right)^2 \Delta n_{\text{void}}^2 + \left(\frac{\partial f}{\partial n_{\text{solvent}}} \right)^2 \Delta n_{\text{solvent}}^2 + \left(\frac{\partial f}{\partial SF} \right)^2 \Delta SF^2} \quad [\text{S3.16}]$$

Δn_{void} is considered to be negligible and ΔSF is calculated as:

$$\Delta SF = SF \sqrt{\left(\frac{\Delta d_{\text{swollen}}}{d_{\text{swollen}}} \right)^2 + \left(\frac{\Delta d_{\text{hyp}}}{d_{\text{hyp}}} \right)^2} \quad [\text{S3.17}]$$

ΔE is calculated as:

$$\Delta E = \sqrt{\left(\frac{d_{\text{hyp}}}{d_{\text{glass}}^2} \right)^2 \Delta d_{\text{glass}}^2 + \left(-\frac{1}{d_{\text{glass}}} \right)^2 \Delta d_{\text{hyp}}^2} \quad [\text{S3.18}]$$

The error in ϕ_s is determined as:

$$\Delta \phi_s = \sqrt{\left(\frac{1}{SF^2} - \frac{Ex}{SF^2} \right)^2 \Delta SF^2 + \left(\frac{x}{SF} \right)^2 \Delta \varepsilon^2 + \left(\frac{\varepsilon}{SF} \right)^2 \Delta x^2} \quad [\text{S3.19}]$$

3.8 References

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Chapter 4

Stratified Swelling Dynamics in Ultrathin Polystyrene Films

This chapter is adapted from:

Wojciech Ogieglo, Kristianne Tempelman, Simone Napolitano, Nieck E. Benes, *Evidence of a transition layer between the free surface and the bulk*, Journal of Physical Chemistry Letters **2018**, accepted manuscript, DOI: 10.1021/acs.jpcllett.8b00076

Abstract

The free surface, a very thin layer at the interface between polymer and air, is considered the main source of the perturbations in the properties of ultrathin polymer films, *i.e.* nanoconfinement effects. The structural relaxation of such layer is decoupled from the molecular dynamics of the bulk. The free surface is, in fact, able to stay liquid even below the temperature where the polymer resides in glassy state. Importantly, this surface layer is expected to have a very sharp interface with the underlying bulk. Here, by analyzing the penetration of *n*-hexane into polystyrene films, we report on the existence of a transition region, not observed by previous investigations, extending for a maximum ~ 12 nm below the free surface. Presence of such layer permits reconciling the behavior of interfacial layers with current models and has profound implications on the performance of ultra-thin membranes. We show that the expected increase in the flux of the permeating species is actually overruled by nanoconfinement.

4.1 Introduction

In polymer films, molecules sitting at the very interface with air (or a gas, or vacuum) exhibit peculiar properties that strongly differ from those of the bulk. Particles can, for example, diffuse faster on surfaces than towards the interior. This feature is shared by polymers, where within the first 2-10 nm ^[1,2] (i.e. the interfacial layer, usually referred to as free surface ^[3-5]) structural relaxation occurs at rates exceeding by up to 12 orders of magnitude the bulk rate. The free surface is, hence, capable of demonstrating liquid-like behavior also below the glass transition temperature, T_g , of the bulk material. In addition to this, evidence for enhanced flow was confirmed by ingenious viscosity measurements. ^[6,7] Recent work has, furthermore, shown that it is possible to tune the properties of the free surface by controlling macromolecular architecture (molecular weight, ^[8] branching, ^[9] ...) and the processing conditions (notably the degree of adsorption on the supporting substrate ^[10-12]). Remarkably, extensive investigation has shown that the structural relaxation at the free surface is totally disentangled from the molecular dynamics of the underlying bulk layer. ^[3,13] The extreme sharpness of the interface between the surface layer and the bulk is furthermore strengthened by models defined on step-like functions ^[1,2,6] – thus with an interfacial width virtually equal to zero.

While such a steep transition could be rationalized for small molecules, in the case of high molecular weight polymers, where the macromolecular size ($2R_g$, where R_g is the gyration radius of the polymer) easily exceeds 10 nm, a broader transition region would be expected. It is puzzling to think that a transition region between the free surface and the bulk does not exist. Considering the expected small contrast between the transition region and the bulk region, it is likely that thus far, current methods have failed to identify this transition region. In this work, to identify the presence of a transition layer, the diffusion of vapor molecules at temperatures around the glass transition of the swollen film has been followed. Polymer chains swell when surrounded by molecules of a good solvent; this process is usually associated with an increase in molecular mobility due to plasticization. Penetration of small molecules into a glass, induces a transition to the rubbery state and as a consequence the diffusion coefficient increases by 3-4 orders of magnitude. Such a tremendous difference in penetrant mobility can induce an anomalous mechanism, known as Case II, where diffusion of small molecules inside the polymer matrix is not limited by diffusion of the penetrant, but by chain relaxations at the interface between the rubbery swollen outer layer and the glassy dry inner layer. Swelling, hence, proceeds linearly with time, which sets the signature of Case II anomalous diffusion ^[14]. In sub mm-thick films, anomalous diffusion occurs at temperatures high enough to ensure plasticization upon swelling; at lower temperatures, the swollen portion of the film remains glassy and diffusion of penetrants proceeds via

conventional Fickian dynamics^[15]. As the temperature where this change in diffusion mechanism occurs is just above the T_g of the swollen polymer, a stratified swelling within the polymer film is to be expected, displaying both Case II and Fickian diffusion.

Diffusion of small molecules inside a polymer film can be followed by monitoring in time the swelling of the layer^[15,16]. Consequently, information on the spatial variation in the dynamics of the polymer chains and in distribution of the free volume can be obtained^[16]. This is relevant, since at the interface between polymer and air the reduced topological constraints provide an increase in polymer chain mobility with respect to the bulk.^[17,18] The changes in the free volume content however, are small (<0.2%) and it is therefore difficult to detect them with the current state of the art techniques¹.

In this work, the strong coupling between the polymer chain mobility and temperature^[19–21] was utilized to overcome these limitations. By utilizing *in situ* spectroscopic ellipsometry, we introduce a novel method allowing to determine fine variations in the structure of a polymer film, which permitted to verify the existence of a transition region between the free surface and the bulk. Using *n*-hexane vapor, as opposed to a liquid ambient^[16], we forced the transport of penetrant molecules in the interfacial layer of polystyrene (PS) via Case II diffusion^[15]. In these conditions, the presence of a layer with a polymer chain mobility compared to the bulk was observed. Within this layer, swelling proceeds linearly with time, sitting on top of a bulk-like region, where a small reduction in the polymer chain mobility was sufficient to inhibit Case II diffusion. The neat passage from linear to the usual square root dependence of swelling with time allowed for a precise measurement of the thickness of the transition layer. The careful choice of the experimental conditions allowed for the very high sensitivity of our method, as the precision of our method (0.5 – 1 nm) significantly exceeded that of other investigations by fluorescence^[22–24] or by dielectric spectroscopy^[25] because we were not limited by the minimum dimensions of the labeled layer (15-25 nm). Additionally, we studied the vapor penetration at the film interface not only as function of film thickness but also polymer molecular weight which gave insight into the physical origin of the transition layer.

¹ We considered a thermal expansion coefficient of the free volume content of $75 \times 10^{-4} \text{ K}^{-1}$,^[41] and a shift in T_g by 4 K between bulk and surface layer

4.2 Materials and Methods

4.2.1 Film preparation

Polystyrene (PS, M_w ranging from 280 kg mol⁻¹ to 1 million g mol⁻¹) ultra-thin films were spin coated onto clean silicon wafers from toluene (Merck, analytical grade). Prior to the deposition the substrates were treated with a mixture of sulfuric acid and 30 % hydrogen peroxide (3:1 v:v) and rinsed with ultra-pure water. The film thickness was adjusted via the solution concentration; the spin coating speed was fixed at 2000 rpm. The freshly formed films were dried for one week at room temperature under nitrogen. Prior to the swelling experiments the films were heated to 150 °C (PS bulk $T_g \approx 100$ °C), for a period of time sufficient to ease structural relaxation yet short enough to avoid dewetting of especially the thinnest films (5 minutes for 280 kg mol⁻¹ and 2 h for 1000 kg mol⁻¹). Afterwards, the films were quenched at room temperature, and kept aging in ambient atmosphere for exactly 3 minutes or 3 weeks before the swelling experiments started.

4.2.2 Swelling experiments

Swelling experiments were performed using an M-2000X spectroscopic ellipsometer (J. A. Woollam Co., Inc.). Dynamic data were acquired in a fast mode resulting in a temporal resolution of ~ 2 scans s⁻¹. A trapezoidal stainless steel cell with quartz windows was stabilized at 22 ± 0.1 °C. *n*-Hexane vapors were generated by flowing purified nitrogen through a bubbler at 21 ± 0.1 °C. The nitrogen flow rate was kept constant throughout each series of measurements.

4.2.3 Data extraction and modeling

The optical model comprised the silicon substrate with a ~ 2 nm native silicon oxide and atop a single uniform layer with a Cauchy optical dispersion. The wavelength range was limited to 370–1000 nm, where the polymer can be assumed fully transparent. The ambient refractive index was set to 1.000, assuming no effect of the *n*-hexane vapor. The window birefringence was carefully corrected for. Even though for ultrathin films the accuracy of the simultaneous thickness and refractive index determination is limited, relative variations in thickness can be monitored with a very high precision (<1 %). Further information on the ellipsometry analysis can be found in the Supplementary Information. The thickness of the adsorbed layer was obtained by literature data^[26] of experiments of PS adsorbed on silicon oxide, the same system considered in this work.

4.3 Results and Discussion

n-Hexane in the vapor phase is able to swell PS and upon penetration of these small molecules the T_g of PS drops to 292 K. The induced swelling of *n*-hexane into polystyrene of film thicknesses varying from 7 to 166 nm was measured with *in situ* spectroscopic ellipsometry using a very high data acquisition rate (~ 2 spectrum s^{-1}). No film wrinkling or dewetting as a result of solvent vapor penetration occurred because of the relatively high molecular weight and high viscosity of the used polymer, as well as comparatively low degree of plasticization and swelling. Such morphological changes would have been detected by our experimental technique either by significant loss of signal intensity (light scattering) or deviations in the ellipsometric delta parameter at shorter wavelengths of probing light.

In Figure 4.1, the time evolution of the increase in film thickness upon swelling, $\Delta h = h_{\text{swollen}} - h_{\text{dry}}$ is plotted. Three distinct swelling regimes with distinctly different swelling dynamics are present, which confirms the presence of three regions with distinct properties inside the PS film. The first layer swells almost instantly and is identified as the free surface layer. The second regime swells linearly with time and is regarded as the Case II layer. Finally, on top of the Case II layer, a bulk region can be identified where dilation occurs following Fickian diffusion at the rate of very thick films. For all films, the free surface swells by $\Delta h_{\text{fs}} = 1.5$ nm in approximately 3 seconds, i.e., with a speed of ~ 1 nm s^{-1} , that is more than 2 orders of magnitude faster than the bulk films ($0.003 - 0.005$ nm s^{-1}).

Figure 4.1 – Increase in film thickness upon swelling, $\Delta h = h_{\text{swollen}} - h_{\text{dry}}$, as a function of time for polystyrene thin films with $M_w = 280$ kg·mol $^{-1}$; data show stratification of dynamics with an almost instantly swollen free surface, linear in time transition region (Case II layer), and bulk regions going from shortest to longest time.

In Figure 4.2 the thickness of the dry layer was plotted as function of the swelling factor, $SF = h_{\text{swollen}} / h_{\text{dry}}$. The thickness of the outer free surface layer and of the transition layer can be determined based on the swelling factor and the increase in film thickness upon swelling for the free surface layer, Δh_{fs} and transition layer, Δh_{tr} . The free surface layer swells instantaneously to its maximum swelling factor and represents the outer layer of the polymer film. For this reason, the swelling factor extrapolated to a thickness of 0 nm (see Figure 4.2), represents the swelling factor of the free surface layer and the thickness of the free surface layer (L_{fs}) can be calculated according to Eq. 4.1.

$$\Delta h_{\text{fs}} + L_{\text{fs}} = L_{\text{fs}} \cdot SF_{h=0} \quad [4.1]$$

Extrapolating SF to $h = 0$, it was determined that $SF_{h=0} = 1.6$ and thus the free surface layer, L_{fs} , extends for 2.5 nm into the dry film. Also, it should be noted that the SF of the free surface layer, corresponds to a swelling four times the relative change compared to the bulk of the polystyrene films ($SF_{h=0} = 1.6$ for free surface versus 1.15 for bulk). By considering the extent and time of dilation, the thickness of this surface layer (~ 2.5 nm) is in excellent agreement with previous reports on the altered behavior at the free surface.^[7,27,28] This behavior of the free surface might be related to the enhanced conformational freedom of the free interfaces of glassy systems, where the matrix expansion is not as much restricted by the neighboring chains and entanglement density is reduced.

After the first 3 seconds characterized by fast dynamics of the free surface, a second regime, of ~ 1.5 minutes, takes place. Here swelling slows down, and proceeds linearly with time, which is still unlike the bulk swelling, which proceeds with the square root of time. Linear thickness dilation is associated with the progressive motion of a sharp front between swollen and non-swollen parts of the film, via Case II diffusion. In a similar fashion as the determination of the thickness of the free surface layer, the dry thickness of the transition layer (L_{tr}) can be determined (Eq. 4.2).

$$\Delta h_{\text{tr}} + L_{\text{tr}} = L_{\text{tr}} \cdot SF_{\text{tr}} \quad [4.2]$$

Since the transition layer swells much less compared to the free surface layer, due to an inhibition of the polymer chain mobility, it was assumed that the swelling factor of the transition layer is comparable to the swelling factor of the bulk (i.e. $SF_{\text{tr}} \approx SF_{\text{bulk}} \approx 1.15$). In reality, this assumption results into a slight underestimation of the real swelling factor of the transition layer as the polymer chain mobility in the transition layer is higher than in the bulk layer. From Figure 4.1, The extent of the transition layer-related swelling was determined to be ~ 2 nm and based on $SF_{\text{bulk}} \approx 1.15$, the transition layer thickness, L_{tr} was determined to be

11 ± 2 nm. This value for the transition layer thickness agrees very well with results of recent molecular dynamics simulations^[29,30].

Figure 4.2 – Equilibrium swelling factor, $SF = h_{swollen} / h_{dry}$, dependence on h_{dry} for polystyrene thin films of $M_w = 280$ (squares), 500 (triangles), and 1000 (circles) $\text{kg}\cdot\text{mol}^{-1}$ exposed to *n*-hexane vapor.

To determine the dependence of the L_{tr} on the molecular weight of the polymer, experiments were performed on PS samples with different molecular weights. In Figure 4.3 it is shown that for polystyrene films with a dry thickness thicker than $2R_g$, the thickness of the transition region, L_{tr} , is independent of the molecular weight. Below a dry film thickness of $2R_g$, the thickness transition layer shrinks and the velocity of swelling decreases (see also Figure 4.1). Fast swelling dynamics are inhibited while approaching the polymer/substrate interface, most likely due to a reduction in the polymer chain mobility. In line with recent work,^[12,31,32] it is expected that the presence of a layer of PS chains irreversibly adsorbed on the supporting substrate, would favor densification of the film. As the polymer chain mobility decreases upon adsorption,^[33,34] the reduction in L_{tr} should be sensitive to the adsorbed amount, Γ , that is, number of monomers present in the chains adsorbed per unit surface. This idea is confirmed by Figure 4.3, where datasets of different molecular weights superimpose when plotting the values of L_{tr} as a function of the film thickness normalized to thickness of the adsorbed layer ($\approx 0.5 R_g$), a quantity directly proportional to the adsorbed amount. Measurements in films thinner than 15 nm did not show a presence of a bulk-like layer. Based on these observations, the structure and extension of the transition layer depend on the boundary conditions at both the polymer/air and the polymer/substrate interfaces, while its molecular origin should be attributed to the upper interface only: L_{tr} is

indeed constant for films where the surface layer is far enough from the supporting substrate.

Figure 4.3 – Transition layer thickness, L_{tr} , as a function of h_{dry} normalized by the thickness of the adsorbed layer h_{ads} ($\approx 0.5 R_g$); Symbol designation as in Figure 4.2; R_g values used are 14.6, 19.5 and 27.6 nm for M_w of 280, 500 and 1000 kg·mol⁻¹, respectively (taken from literature^[35]).

4.4 Conclusions

In literature, experimental evidence of a transition layer between the free surface and the bulk of a polymer film has never been shown, due to the lack in measurement resolution. In this work we have shown that by measuring the kinetics of dilation induced by the penetration of *n*-hexane vapor inside thin films of polystyrene (PS) of different thicknesses and molecular weights, stratified swelling dynamics could be observed. We have shown that the first 15 nm from the interface with air show a peculiar stratification. This region can be divided into two sub layers with distinct extent and dynamics of swelling. The first layer of ~ 2.5 nm, attributable to the free surface, behaves as a liquid and swells almost 4 times as much as the bulk. Underneath the free surface, a transition layer, swelling just ~ 20 % more than the bulk, extends for 11 nm independently on the molecular weight. We have shown that the extension of the transition layer into the bulk is both dependent on the polymer/air and polymer/substrate interfaces. The presence of the transition layer has profound implications on the fabrication of polymer coatings designed to be responsive towards contact with small molecules, such as sensors^[36], or to affect the diffusional transport of small molecules, as in the case of barriers and artificial membrane films for molecular separations^[37–39]. In particular, current fabrication trends push towards a reduction in the thickness of membrane films, aiming at an increase of the flux of the permeating species. Here, the supported character of these membranes is very important, as freestanding films would lack of mechanical stability. Commercial devices with a thickness in the

20-40 nm range for air separation exist already for years and recently, sub-10 nm membranes have been introduced for organic solvent nanofiltration^[40]. Depending on the molecular weight of the polymer used, the effect of nanoconfinement-induced stratified dynamics will dominate the separation performance. For such thin films the properties will exclusively be determined by the nanoconfinement, and bulk materials properties are of limited predictive potential for membrane separation performance.

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4.6 Supplementary Information

Figure S4.1 shows the influence of selected measurement parameters on the obtained film swelling. It is obvious that the cell windows birefringence (window delta offset) has a major influence on the film swelling factor ($SF = h_{\text{swollen}} / h_{\text{dry}}$), especially for the thinnest films, as seen from Figure S4.1a. It is absolutely critical that this parameter is accurately corrected for by using a calibration wafer measured inside of the measurement chamber. In this study the determined window delta offset was 4.976° for the 280 kg mol^{-1} and 0.250° for the 500 and 1000 kg mol^{-1} samples. On the other hand, the obtained swelling is virtually insensitive to the film refractive index, Figure S4.1b. The sensitivity increases slightly for thicker films, however in those cases the index can be determined simultaneously with the thickness at sufficiently high accuracy and does not need to be fixed in the optical model.

Figure S4.1 – The influence of optical modeling parameters on the obtained swelling factor, SF
a) SF versus fixed window delta offset parameter #1 with simultaneous fit for the film thickness and index b) SF versus fixed values of the film refractive index during fitting for the film thickness with window offset determined from calibration against a calibration wafer

In Figure S4.2 the non-Fickian behavior of the transition layer is shown by the non-linear dependence on the square root of time.

Figure S4.2 – Increase in film thickness upon swelling, $\Delta h = h_{\text{swollen}} - h_{\text{dry}}$, as a function of the square root of time for polystyrene thin films with $M_w = 280 \text{ kg}\cdot\text{mol}^{-1}$. The non-Fickian behavior of the transition layer is visible.

4.7 References

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Chapter 5

The Effect of Hydrocarbon Pollution on Polysulfone-based Membranes in Aqueous Separations

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Abstract

This work investigates the influence of hydrocarbon pollution on the performance of desalination membranes with a polysulfone support. Toluene was chosen as the model hydrocarbon compound and permeation measurements were performed on two commercial membranes with a polysulfone support in water saturated with toluene. Over time, the TriSep TS80 membrane under analysis broke down and the delamination of the separation layer was observed. The influence of the polysulfone layer on the membrane deterioration was studied in detail by the use of a model system of a thin polysulfone film on top of a silicon wafer. *In situ* spectroscopic ellipsometry, and *in situ* optical microscopy revealed that the non-ideality of the hydrocarbon in water system initiates a dewetting of the polysulfone layer and is the root cause of the membrane failure.

5.1 Introduction

Purification of water contaminated with hydrocarbons poses a challenging problem and is required to prevent release of hydrocarbons into the environment ^[1-3]. In the oil and gas industry, three to four barrels of contaminated water are produced for the production of one barrel oil or gas ^[4]. In this case, the so-called “produced water” is a by-product in the recovery of oil and gas from a well ^[5], which needs a pretreatment in order to be released in the environment. Today, common water treatment processes include the use of membranes. Reverse osmosis (RO) membranes and nanofiltration (NF) membranes are a well-established and energy efficient separation technique and widely applied ^[4,6,7]. The use of a one-step treatment using RO or NF membranes for waste water or produced water treatment would be a simple and low-cost operation ^[4,5,8,9]. However, at this moment, membrane fouling when in contact with the wastewater is still a large problem, limiting the membrane process efficiency and the use of RO or NF membranes in general ^[10-14]. Pre-treatment steps such as adsorption, gravity settling or coagulation techniques have shown to be effective in reducing the membrane fouling ^[15], but even after the pre-treatment step significant fouling could still be observed.

The industrial wastewater streams and produced water from the petroleum industry have been analyzed thoroughly and one of components present in these water streams appointed as the cause for membrane fouling and degradation in wastewater or produced water treatments is the presence of organic contaminants (TOC content) ^[16,17]. The underlying phenomena of membrane fouling and degradation when in contact with TOCs is still poorly understood. It was suggested that the fouling was caused by interactions between dissolved and suspended solutes in the feed and the membrane surface, resulting in large flux declines ^[11]. Van der Bruggen et al. (2001) found that both the membrane surface charge and the membrane hydrophobicity play a role in the adsorption of solutes onto the membrane surface, lowering the water solubility ^[17,18].

Microfiltration (MF) and ultrafiltration (UF) membranes are often integrally skinned and asymmetric in nature. In most cases they are fabricated out of a single polymer material without an additional mechanical support. NF and RO membranes on the other hand, to limit the operation pressure, are in the vast majority of cases thin film composite membranes, with typically a separating layer thickness of 50-200 nm. Often these membranes are made by either coating a single membrane layer or by interfacial polymerization on top of an UF support for mechanical stability^[5]. For the treatment of produced water it has been found that the use of NF membranes is the most beneficial, considering the trade-off between the applied operating pressure and the separation factor obtained ^[5] especially when the water is to be reused within the operational process.

For NF and RO membranes, the most common used selective barrier consists of a highly cross-linked (semi) aromatic polyamide layer ^[19]. Polyamides are known for their enhanced durability, their reasonable chemical resistance, and can effectively reject inorganic solutes ^[19]. The support layer is typically a UF membrane made from polysulfone or polyethersulfone ^[20].

In this work, the interaction between the dissolved hydrocarbons, the separating polyamide layer and the supporting polysulfone layer was studied. The performance of two commercial membranes, TriSep TS80 and DOW FILMTEC NF270, were compared in water using toluene as the model hydrocarbon solute. The interaction between the support and the solute was studied in further detail with *in situ* spectroscopic ellipsometry, atomic force microscopy and optical microscope monitoring using a model system existing of a thin polysulfone layer on top of a silicon wafer in both a water, toluene and water saturated with toluene ambient.

5.2 Materials and Methods

5.2.1 Materials

Polysulfone Udel[®] P-3500 (Amoco), Cyclopentanone (ReagentPlus[®], ≥99 %, Sigma-Aldrich), toluene (anhydrous, ≥ 99.8 %, Sigma-Aldrich) were used as received.

Silicon wafers (100, front side polished, CZ test grade, Silchem) were used as a substrate for the spin-coated layer. The wafers were stored under clean-room conditions until being cut. Prior to use, the wafers were cleaned with Acetone (Chromasolv[®] plus, for HPLC 99.9 %, Sigma-Aldrich).

The purchased commercial membranes TriSep TS80 (flat sheet, Microdyn Nadir) and DOW FILMTEC[™] NF270 (flat sheet, DOW) were used for permeance measurements. Both membranes are a semi-aromatic polyamide based thin film composite membrane with a polysulfone support.

Unless otherwise stated, deionized water (18.2 MΩ cm, Milli-Q Advantage A10, Millipore) was used.

5.2.2 Sample preparation

Thin polysulfone films (~250 nm) were prepared on silicon wafers by spin-coating a solution of polysulfone in cyclopentanone (3wt%) using a two-step spinning program:

1. 30 s 500 rpm
2. 5 min 1000 rpm

After spin-coating, the samples were annealed in a chamber over (Carbolite HTMA 5/28) at 215 °C for 8 hours under a constant nitrogen flow (5 mL min⁻¹).

5.2.3 Permeation measurements of TriSep TS80 and DOW NF270

Prior to the permeance experiments, both the TriSep TS80 and DOW NF270 membranes were placed in water at least one day before the measurement, in order to remove the glycerol inside the membranes. After soaking, the membranes were rinsed with water and placed into the permeance set-up.

Permeance experiments in demi-water and in demi-water saturated with toluene were performed on a custom-built setup (Convergence, The Netherlands). All measurements were performed at a constant feed pressure of 15 bar and at a constant temperature of 25 °C, in cross-flow operation with a membrane area of 46 cm². Permeate fluxes were measured using an M13 mini-Coriflow Coriolis mass-flow meter (Bronkhorst, The Netherlands). For each permeance measurement, the sample was first measured in demi-water for at least one hour before the feed was changed to water saturated with toluene. A water solution saturated with toluene was obtained by mixing ~4.5 L of demi-water with ~250 mL of toluene for at least one day. Saturation was accomplished when a thin layer of toluene remained on top of the water solution.

After the measurement, to remove the water and prevent collapse of the pore structure, the membranes were placed in ethanol for at least 2 hours, washed with ethanol and subsequently placed in hexane for at least 2 hours. The membranes were then washed with hexane and dried to the air.

Scanning electron micrographs of the membranes used for permeation experiments were taken with a JEOL JSM-7610 field emission scanning electron microscope (FE-SEM). Samples were coated with a 10 nm chromium layer (Quorum Q150T ES prior to imaging. Cross-section samples were cut after immersing in liquid nitrogen.

5.2.4 Characterization

5.2.4.1 *In situ* spectroscopic ellipsometry

In situ swelling experiments were performed with spectroscopic ellipsometry using an alpha-SE from J.A. Woollam Co., in combination with a custom-built glass cell (V = 100 mL) with quartz windows with an incident angle of 70°. The cell temperature was controlled with an external water-bath (LAUDA-Brinkmann, LP.), allowing water to flow through the outer walls of the cell. An external temperature control, with a temperature sensor inside the cell was used for temperature control. To correct for the optical retardance of the quartz windows, a calibration with a 60 nm SiO₂ wafer was performed prior to each measurement.

Prior to each *in situ* swelling measurement, the polymer sample was measured outside the cell, inside the cell and then the *in situ* measurement was started. After

2 minutes dry, 70 mL of the temperature calibrated liquid (water or toluene) was poured into the cell. For the measurement in water saturated with toluene solution, water was first poured into the cell and on top of the water, a small amount of toluene (~2 mL) was carefully added. In this case, the toluene slowly diffuses into the water until the maximum solubility limit is reached. The maximum solubility of toluene in water at 25 °C is in average 547 ± 8.5 ppm ^[21].

The data was modelled using the CompleteEase software package (J.A. Woollam Co.) and in the wavelength range of 370-900 nm. The silicon substrate was modelled using the built-in optical properties of a silicon wafer, on top of which a 2 nm native oxide layer was modelled. The thickness and refractive index of the polysulfone film was modelled using a Cauchy dispersion with the thickness, A , B and C as fit parameters. An ambient was added to the model based on the Cauchy dispersion of the solvent. The optical dispersion of water, toluene and water-toluene was determined by measuring the refractive index at 7 different wavelengths (365.0 nm, 400.0 nm, 450.0 nm, 500.0 nm, 590.0 nm, 700.0 nm, 800.0 nm) using a digital multiple wavelength refractometer (Schmidt Haensch ATR-L) at 22 °C. The determined Cauchy constants of each solvent are provided in the Supplementary Information.

The swelling degree of a polymer film upon swelling was calculated using Eq.5.1.

$$SD = \left(\frac{d_{\text{swollen}}}{d_{\text{dry}}} - 1 \right) \cdot 100\% \quad [5.1]$$

Where SD is the swelling degree, and d_{dry} and d_{swollen} are the dry and swollen thickness of the film, respectively.

The normalized refractive index upon swelling in solvents was calculated using Eq.5.2.

$$n_{\text{norm}} = \frac{n_{\text{swollen}} - n_{\text{solvent}}}{n_{\text{dry}} - n_{\text{solvent}}} \quad [5.2]$$

Where n_{norm} is the normalized refractive index, n_{dry} is the refractive index of the non-swollen polymer film, n_{swollen} is the refractive index of the swollen polymer film in a solvent, and n_{solvent} is the refractive index of the pure solvent.

5.2.4.2 Optical microscopy

An inverted optical microscope (Zeiss Axiovert 40 MAT microscope) in combination with a Hamamatsu ORCA-Flash4.0 LT camera was used to image the swelling of a spin-coated polysulfone film in toluene and in water saturated with toluene as function of time. The sample was placed topside down in a transparent flask filled with the solvent, using a 1 mm thick spacer between the bottom of the flask and the sample. Images were taken at a ten minutes interval at 20x magnification.

5.2.4.3 Atomic Force Microscopy

Spin-coated polysulfone samples that were immersed in water saturated in toluene for 8 and 24 hours, or immersed in pure toluene for 24 hours and a dry polysulfone sample were used for Atomic Force Microscopy (AFM) measurements. After solvent exposure, the samples were dried in a vacuum oven at 50 °C for 4 hours. AFM measurements were performed with Multimode 8 AFM (Bruker) with a NanoScope V controller and a JV vertical engage scanner in tapping mode at room temperature. A silicon cantilever (model NCH, Nanoworld, Switzerland), with a resonance frequency of 320 kHz, a force constant of 42 N m⁻¹ and a polygon-based pyramid shape with a tip radius of 8 nm was used. The samples were scanned at a rate of 1 Hz. The NanoScope software (version 8.15) was used for image processing and analysis.

5.3 Results and Discussion

5.3.1 Permeation measurements

Figure 5.1 shows the permeation results of the commercial TriSep TS80 in demineralized water, followed by water saturated with toluene at a constant pressure of 15 bar. The water permeance for the TriSep TS80 is ~4 L m⁻² h⁻¹ bar⁻¹. Upon the introduction of the water-toluene solution, the permeance decreases immediately within the first 15 minutes to ~3 L m⁻² h⁻¹ bar⁻¹, after which a sharp progressive increase with time is observed. This sharp progressive increase with time as observed for the water-toluene permeance, indicates a breakdown of the membrane.

Figure 5.1 – The permeance (left axis) of a commercial TriSep TS80 nanofiltration membrane at a constant pressure of 15 bar. The first 1.2 hours shows the permeance of demineralized water. At 1.2 hours a saturated solution of water with toluene was introduced.

A similar experiment as done for the TriSep TS80 membrane was performed for the commercial DOW NF270 membrane, also a nanofiltration membrane. For the DOW NF270 membrane a constant decline in the H₂O-toluene permeance was observed over a period of six days as is shown in Figure 5.2. The initial decline from $\sim 12 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ to $\sim 7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ can be attributed to the introduction of toluene, as also observed in literature [17]. The slower decline over time was attributed to membrane fouling due to pollution as was also observed in a clean water permeance measurement (see Figure S5.1 in Supplementary Information) and is caused by contamination present in the set-up itself [22].

Figure 5.2 – The permeance (left axis) of a commercial DOW NF270 nanofiltration membrane at a constant pressure of 15 bar. The first 1 hour shows the permeance of demineralized water. At ~1 hour a saturated solution of water with toluene was introduced.

Although both TriSep TS80 and DOW NF270 are semi-aromatic polyamide-based membranes on a polysulfone support, their performance in water saturated with toluene was observed to be entirely different. In previous studies it was shown that with both an increased surface charge and an increased hydrophobicity of the membrane, cause a higher interaction with the organic solute, decreasing the performance of the membrane [17]. The hydrophobicity of both TriSep TS80 and DOW NF270 have already been studied widely in literature and the reports on the contact angles vary from 15° to 43° for DOW NF270 [12,23–25] and from 48° to 57° for TriSep TS80 [23,25,26]. In general, TriSep TS80 was always found to be less hydrophilic compared to DOW NF270. Also, previous studies have shown that DOW NF270 exhibits a higher surface charge compared to TriSep TS80 [23,25]. The higher hydrophobicity of the TriSep TS80 membrane compared to the DOW NF270,

explained the stronger effect of the presence of toluene on the membrane performance of the TriSep TS80 membrane. Other than the hydrophobicity and surface charge of the two commercial membranes, also the membrane structure was studied using scanning electron microscopy (SEM).

In Figure 5.3 the cross-section and top view SEM images of the TriSep TS80 (A,C,E,G) and DOW NF270 membrane (B,D,F,H) are displayed for a virgin membrane (A-D) and the membrane used for H₂O-toluene permeation (E-H). A clear difference in structure between the TriSep TS80 and the DOW NF270 was observed. The TriSep TS80 has a high roughness and the separation layer is approximately 260 nm thick. The interfacial polymerization layer appears to be formed on top of the polysulfone support and little interconnection between the polysulfone support and the polyamide layer is visible. The DOW NF270 on the other hand shows a smooth layer with a low macroscopic roughness with a separating layer of approximately 40 nm thick.

Upon exposure to a saturated mixture of water with toluene at 15 bar, the separating layer for the TriSep TS80 has delaminated from the polysulfone support (Figure 5.3C). On the surface (Figure 5.3G) a collapse of the interfacial polymerization structure could be observed. Most likely caused by the swelling of the layer in toluene, followed by a collapse and change in morphology upon drying. For the DOW NF270, contamination is present on the surface, confirming that the decay in permeance over a long time is the result of fouling due to pollution present in the feed. Other than the pollution, no significant changes in structure were observed.

Figure 5.3 – FE-SEM at 50000x magnification cross-section (A-D) and top-view (E-H) images of TriSep TS80 (A,C,E,G) and DOW NF270 (B,D,F,H) of a clean non-used membrane (A,B and E,F) and when exposed to water saturated with toluene (C,D and G,H).

5.3.2 *In situ* spectroscopic ellipsometry

As polyamide layers are known to have a good chemical resistance to organic solvents ^[27] and the polysulfone is prone to swelling in organic solvents ^[28], the swelling behavior of the polysulfone support in a water-hydrocarbon mixture was the main focus of this study. To investigate the effect of the polysulfone layer on the separation performance of a polysulfone based membrane in water polluted with hydrocarbons in detail, a model system was designed. The model system consists of a spin-coated polysulfone film on top a silicon wafer which was investigated with *in situ* spectroscopic ellipsometry.

In Figure 5.4 the swelling degree and normalized refractive index as function of the experiment time are shown for polysulfone in MilliQ water, pure toluene and water saturated with toluene. No significant swelling was observed for the polysulfone layer in water, while a swelling degree of almost 80 % was obtained in toluene followed by a slow dissolution process as both the thickness and the refractive index show a decline with increasing experiment time. In the water-toluene solution, with increasing experiment time, an excessive swelling occurs. For longer experiments times (>1000 min), the fitting error increases to such an extent that a fit of the raw data is no longer possible. This indicates a change in the sample which cannot be captured by the optical model.

In Figure 5.5 the raw Ψ -data as measured for the water-toluene solution is shown. The Ψ -data is based on the p- and s-reflectivities of the bare substrate and the polymer film in an ambient. It is shown that at $t=1252$ min, the Ψ -data has collapsed onto the so-called optical envelope, which represents the substrate. The oscillatory pattern that is observed in the Ψ -data represents the transparent polysulfone film and is the result of the interference of the thin film with the light. From Figure 5.5 it can therefore be concluded that the polysulfone has been removed from the substrate. In contradiction to a polysulfone film in pure toluene, the polysulfone film in water saturated with toluene first shows excessive swelling and then it appears to be removed as a whole from the substrate, no evidence of a continuous dissolution process such as was observed for polysulfone in pure toluene, was detected in water saturated with toluene.

Figure 5.4 – *In situ* spectroscopic ellipsometry data as function of the experiment time for 230 nm polysulfone film on a silicon wafer. Swelling degree (Left) and the normalized refractive index (Right) of polysulfone in MilliQ water, pure toluene and water saturated with toluene.

Figure 5.5 – Ψ -spectra for a polysulfone film on top of a silicon wafer in an ambient of water saturated with toluene as recorded during the *in situ* measurement. The oscillatory pattern indicates the presence of the polymer film. With increasing experiment time, the polysulfone film is being removed from the substrate. At $t = 1252$ min, the Ψ -signal collapsed onto the so-called optical envelope of the silicon wafer (dashed line).

5.3.3 Dewetting effect

Figure 5.6 – *In situ* optical microscopy images of a ~200 nm film on top of a Si wafer initially and at 10, 20 and 30 hours in toluene (Top row). Bottom row shows a ~200 nm film on top of a Si wafer initially and at 10, 20 and 30 hours in water saturated with toluene. Here a dewetting mechanism was observed.

For both the TriSep TS80 membrane and the polysulfone layer on top of the silicon wafer, a similar delamination process was observed. Indicating that the non-ideality of the water-toluene solution induces a separation between the substrate and the polysulfone layer. This hypothesis is further confirmed by the optical microscopy results shown in Figure 5.6. Figure 5.6 shows the *in situ* progression of a ~200 nm thick polysulfone film on top of a silicon wafer in toluene (top) and water saturated with toluene (bottom) using optical microscopy. In toluene no changes were observed over the course of time. In the water-toluene solution however, small holes start to appear around 16-20 hours, which merge and eventually result in an almost complete removal of the polysulfone film around 30 hours. In order to confirm the observations in Figure 5.6, atomic force microscopy (AFM) measurements have been performed. A non-swollen spin-coated polysulfone film was compared to a polysulfone film immersed in water saturated with toluene for 8 hours and 24 hours and to a polysulfone film immersed in pure toluene for 24 hours (Figure 5.7). A neat polysulfone film has a roughness of 0.36 ± 0.03 nm and immersion in solvent increases the roughness of the film. In Figure 5.7 it is shown that small holes on the surface are already present at an 8 hours exposure in a water-toluene mixture and they grow with longer immersion times. Also, for polysulfone exposed to pure liquid toluene for 24 hours, small holes could be detected.

Figure 5.7 – AFM images of spin-coated polysulfone films without solvent exposure (A), 8 hours immersion in water oversaturated with toluene (B), 24 hours immersion in water oversaturated with toluene (C) and 24 hours immersion in toluene (D). The roughness of the film increases with the immersion time. For polysulfone in pure toluene, also holes are visible, indicating some dewetting. The error margin displays a 95% confidence interval based on 9 3x3 μm spots on the surface.

The removal of the polysulfone film from the silicon wafer is similar to the commonly observed dewetting process. When a liquid is placed on top of a non-wettable surface, it will flow and dewetting occurs. A similar process is often observed for coated glassy polymers on top of a silicon wafer when heated to temperatures above the glass transition temperature, T_g . Above the glass transition temperature, the polymer becomes liquid and has gained sufficient mobility to dewet the surface. This is known as thermal dewetting. Dewetting can also be induced by the exposure of a thin polymer film to a penetrant, known as solvent dewetting. When the penetrant is able to sufficiently dilute the polymer matrix, the glass transition temperature is decreased and an increase in the mobility of the polymer film can be observed. The stability of a polymer film on top of a substrate is either defined as stable, metastable or unstable. In case of a stable film, the film is in the lowest energy state. For a metastable film, a potential barrier has to be overcome to reach the lowest energy state. Unstable films dewet immediately. Both metastable and unstable films can dewet via nucleation, known as heterogeneous dewetting or via spinodal dewetting, also known as homogeneous nucleation.^[29]

As shown with the *in situ* spectroscopic ellipsometry measurement, polysulfone swells up to 80% more than its initial thickness in pure toluene. Based on the almost instant diffusion of toluene into the polysulfone matrix and the high solvent content inside the polymer matrix, one can assume that the presence of the solvent has sufficiently depressed the glass transition temperature to around the measurement temperature^[30]. For this reason, at very long immersion times (>24 hours) of the polysulfone to toluene, dewetting could be observed (Figure 5.7D). In this case however, the dewetting rate is much slower compared to the dewetting in water-toluene mixtures.

For polysulfone in water saturated with toluene, the dewetting rate is much faster compared to the dewetting as observed in pure toluene. In the case of water saturated with toluene, the water to toluene ratio is very large and as a result, when polysulfone swells the polysulfone, water will tag along. As the affinity between water and polysulfone is lower than the affinity of water for the silicon substrate^[31,32], a thin water film is formed between the substrate and the polymer film, resulting in the dewetting of the polysulfone film.

In order to inhibit dewetting of the polymer film, several approaches can be used^[29]. Chemical surface modification can be used to increase the substrate surface energy or surface tension. Cross-linking of the polymer can be used to fixate the polymer chains and to decrease the mobility of the polymer. For polysulfone it has been shown before that cross-linking using UV-radiation works to immobilize the polymer and to reduce swelling in order to prevent dewetting^[33]. A different approach to prevent dewetting is by adding nanofillers in the polymer, changing the interfacial interactions.

5.3.4 Membrane dewetting

As shown in section 5.3.1, the commercial TriSep TS80 membrane shows a dewetting of the interfacial polymerization layer from the polysulfone substrate upon exposure to a water solution saturated with toluene. The commercial DOW NF270 membrane however, shows no such dewetting and remains stable over the timespan of six days. The main reason for this contradiction in behavior between these two membranes is the integration of the interfacial polymerization layer into the polysulfone support and the hydrophobicity of the membranes. The IP layer of the TriSep TS80 is formed on top of the polysulfone support and the growth of the film has occurred in the organic phase as shown by the lobes on top of the membrane. In case of the DOW NF270 membrane, the IP layer is significantly thinner than for the TriSep TS80 membrane and it seems to be better integrated into the polysulfone support. The higher hydrophobicity of the TriSep TS80 membranes caused that more toluene was able to diffuse through the polyamide layer and swell the polysulfone support. Because of the high availability of water, for which the affinity for the polyamide layer is much higher than the affinity for the swollen polysulfone, a thin water film can be formed between the polyamide separating layer and polysulfone support resulting in the delamination of the polyamide layer. In order to increase the stability of membranes used for the separation of industrial waste water polluted with hydrocarbons, the adhesion between the IP layer and the support layers has to be promoted.

5.4 Conclusions

Membranes used for water treatment often show a high instability and mechanical failure when traces of hydrocarbons are present in the water, making the use of cheap NF and RO membranes unsuitable for water treatment of industrial waste streams. We have shown that the stability of the thin film composite membrane is strongly dependent on the stability of the support material and the adhesion between the separating layer and the mechanical support. The polysulfone does not dissolve in water saturated with toluene, but instead a dewetting mechanism was observed. By improving the adhesion of the interfacial polymerization layer to the mechanical support, the dewetting of the IP film can be inhibited, allowing for a higher stability of the thin film composite membrane in industrial waste water streams containing traces of hydrocarbons. This would allow for the use of cheap and easy producible polysulfone supports for the use of industrial wastewater treatment membranes.

5.5 Acknowledgements

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5.6 Supplementary Information

5.6.1 Clean water permeance DOW NF270

To compare the permeance of a DOW NF270 membrane in water saturated with toluene to the permeance in clean water, a permeance experiment in clean demi-water for 3 days was performed at 15 bar (Figure S5.1). Over time a constant decline in the H₂O permeance was observed, while the density of the permeate remained constant. This decline was attributed to contamination present in the set-up that fouled the membrane. FE-SEM pictures (Figure S5.2) confirm that the membrane shows clear contaminations after permeating water for three days and that fouling has occurred.

Figure S5.1 - The permeance (left axis) of a commercial DOW NF270 nanofiltration membrane at a constant pressure of 15 bar in demi-water. A constant decline over time of the H₂O permeance was observed.

Figure S5.2 – Top-view FE-SEM images at 50 000x magnification of DOW NF270 membrane before (Left) and after H₂O permeation for 3 days at 15 bar (Right). A clear cake layer has formed on top of the membrane, confirming that the membrane has been fouled.

5.6.2 Refractive indices

The refractive indices of water, toluene and water oversaturated with toluene used for the modelling of the *in situ* spectroscopic ellipsometry data were determined based on the refractive index of the solvents measured at 7 different wavelengths (365.0 nm, 400.0 nm, 450.0 nm, 500.0 nm, 590.0 nm, 700.0 nm, 800.0 nm). A Cauchy relation was used to fit the optical constants of the three solutions. An overview of the optical constants is shown in Table S5.1.

Table S5.1 – The optical constants A , B , and C for the different solvent solutions as determined from a Cauchy fit of the refractive indices at 7 different wavelengths.

	A	B	C	n at 632.8 nm ± 0.001
H ₂ O	1.3229	0.0035	0	1.3316
Toluene	1.4743	0.0066	0.0003	1.4927
H ₂ O-Toluene	1.323	0.0035	0	1.3317

5.6.3 Optical Microscopy

In Figure S5.3 and Figure S5.4, the *in situ* optical microscopy images of a polysulfone film in liquid toluene and in water saturated with toluene are shown respectively. In toluene, over a timespan of two days, no hole formation was observed. In water saturated with toluene, the first holes were visible at about 16 hours. Around 30 hours, most of the polysulfone film was removed from the silicon substrate.

Figure S5.3 – *In situ* optical microscopy images of a polysulfone film in liquid toluene. Over a timespan of two days, no hole formation was observed.

Figure S5.4 – *In situ* optical microscopy images of a polysulfone film in water saturated with toluene. At 16 hours the hole formation was visible at a 20x magnification. Over a timespan of about 30 hours, most of the polysulfone has been removed from the silicon surface.

5.7 References

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Chapter 6

Hyper-cross-linked Thin Polydimethylsiloxane Films

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Abstract

Polydimethylsiloxane (PDMS) elastomers are widely used in many applications, such as in microfluidic devices or as membranes. These slightly cross-linked PDMS networks suffer from severe swelling upon contact with, especially non-polar, organic solvents, thereby drastically reducing the performance of the device. Here, we report on a new method to prepare ultra-thin, highly cross-linked PDMS films in a localized fashion by the interfacial polymerization of PDMS with polyhedral oligomeric silsesquioxane (POSS). The resulting thin poly(PDMS-POSSimide) films (~ 150 nm) show to have a drastic reduction in swelling upon contact with *n*-hexane vapor (~ 15 fold decrease) and ethyl acetate vapor (~ 5 fold decrease). These poly(PDMS-POSSimide) films show an increase in swelling upon contact with ethanol vapor (up to a 4 fold increase) as compared to conventional PDMS. We attribute this increase in swelling to the enhanced affinity for polar solvents of these poly(PDMS-POSSimide) films due to the presence of positively charged ammonium groups. Despite the highest swelling in ethanol, the poly(PDMS-POSSimide) films are found to have extremely low ethanol permeances ($< 0.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), thereby making them suitable as potential barrier materials.

6.1 Introduction

Polydimethylsiloxane (PDMS) is an organosilicon polymer, that has the general formula $[\text{Si}(\text{CH}_3)_2\text{O}]_n$. PDMS is widely used because it is optically transparent, flexible, inert, bio-compatible, and non-flammable. Most applications require the cross-linking of PDMS chains. Typically, cross-linked PDMS is prepared from the hydrosilylation of a liquid divinyl-terminated PDMS, with a multifunctional organosilane cross-linker, followed by a (thermal) curing step ^[1]. The reaction rate of this cross-linking reaction at ambient conditions is sufficiently low to allow for processing the PDMS by methods such as spin-coating, molding, or casting. Example application areas of PDMS are sensors, medical devices, microfluidics, or membranes ^[2,3]. In microfluidic devices, thin PDMS films are commonly applied as, e.g., microlenses ^[4–6], valves ^[7,8], or actuators ^[9,10]. In addition, thin PDMS films are used as membranes in organic solvent nanofiltration (OSN), or as gas separation membranes ^[11].

For microfluidic devices and membrane applications, PDMS is often the preferred material of choice, due to its excellent optical properties, low cost and ease in fabrication, ease of bonding and high permeability of organic solvent vapors or liquids ^[12,13]. Despite these advantages, PDMS also has some major drawbacks. For the use of PDMS in microfluidic devices the main problem is the high hydrophobicity and low zeta-potential. In the case of organic solvent applications, the high affinity of PDMS for non-polar solvents and the rubbery nature of PDMS, causes PDMS to swell substantially, especially in non-polar solvents. This severe swelling could significantly reduce the performance of any PDMS-based device. Literature has reported swelling of PDMS more than two times its original volume ^[14,15]. For PDMS membranes the excessive swelling causes a loss of selectivity in organic solvents since high molecular weight solutes can permeate through the swollen membrane. In an extreme case, the selective PDMS layer can be peeled off from the support due to severe swelling of the PDMS ^[13]. In the case of PDMS swelling in microfluidic devices, it can cause deformation or even collapse of the microfluidic channels, resulting in leakage of the device ^[16,17].

Several approaches focusing on the reduction of swelling in membranes can be found in literature. These methods could also be applied to other PDMS-based devices. One of these methods is the inclusion of inorganic nanofillers in the PDMS matrix ^[18–22]. These nanofillers physically interact with the PDMS matrix, thereby restricting the swelling of PDMS ^[11]. However, the use of inorganic nanofillers can result in phase separation, or particle agglomeration, which can reduce the performance of the device ^[23].

An improved control over the swelling of the PDMS network could be obtained when the nanofiller is covalently bound to the PDMS matrix. An interesting nanofiller that could be covalently cross-linked to PDMS is polyhedral oligomeric silsesquioxane (POSS). Typical POSS molecules have a cage structure with the general formula $R_8Si_8O_{12}$, where the organic end-groups R can be tailored [24]. POSS is of high interest due to its excellent thermal and chemical stability of the inorganic core and flexible end-group chemistry. Many examples of the cross-linking of PDMS with partially condensed [25,26] or fully condensed [26–30] POSS cages can be found in literature. These PDMS-POSS nanocomposites are even used as membranes for gas separation, although the preparation of these membranes by casting [13] results in relatively thick (200–250 μm) PDMS layers [26].

A method to obtain defect-free thin films is interfacial polymerization (IP). IP is the localized polycondensation of two or more monomers at the interface of two immiscible solvents [11,31,32] resulting in a perfectly alternating cross-linked polymeric film. POSS has already been successfully used in the preparation of hybrid polyamide [33,34], or polyimide [35] films, prepared from POSS and small organic monomers. However, POSS has not yet been applied in the preparation of cross-linked PDMS films by interfacial polymerization.

Here, in order to improve the swelling behaviour of PDMS in organic solvent, a thin (~ 150 nm) hyper-cross-linked PDMS-POSS film was prepared by IP. The swelling dynamics of these poly(PDMS-POSSimide)s were studied by *in situ* spectroscopic ellipsometry and compared to the swelling of conventional PDMS.

6.2 Materials and Methods

6.2.1 Materials

OctaAmmonium POSS (POSS) was obtained from Hybrid Plastics, USA, Polydimethylsiloxane, succinic anhydride terminated; viscosity 75-100 cSt (PDMS) was obtained from ABCR, Germany. Ethanol (absolute) was obtained from Merck. Sodium hydroxide (NaOH, >98%), *n*-hexane (anhydrous, 99.8%), and ethyl acetate (anhydrous, 99.8%) were obtained from Sigma-Aldrich (The Netherlands). PDMS, Permacol RTV 615 A/B type was obtained from Permacol B.V. as a two-component system, consisting of a vinyl-terminated siloxane polymer and cross-linker (RTV A) and a polydimethyl hydrogen siloxane with a catalyst (RTV B).

6.2.2 Preparation of PDMS films

Thin PDMS films were prepared on silicon wafers by spin-coating a pre-polymer solution (2.5 wt% in *n*-hexane) containing the cross-linker in a ratio of RTV A/RTV B of 10:1 at 3000 rpm for 30 seconds. To facilitate the crosslinking, the thin films were placed in a chamber oven (Carbolite HTMA 5/28) under a nitrogen flow (5 mL min⁻¹). The samples were heated to 80 °C for 8 h.

6.2.3 Synthesis of poly(PDMS-POSSamic acid) networks by interfacial polymerization

Both powdered and supported poly(PDMS-POSSamic acid) networks were prepared by interfacial polymerization (IP). For both, POSS was dissolved in Milli-Q grade water and the pH of the solution was adjusted to pH 8.5 or 9.5 using 1.5 M NaOH. Powdered poly(PDMS-POSSamic acid) was prepared by vigorously stirring equal amounts of an aqueous solution of POSS (0.9 wt%) and an organic solution of PDMS (0.5 wt% in toluene) for 1 hour. The formed solids were filtered and washed with excess water and toluene, respectively. The precipitate was dried overnight in a vacuum oven at 50 °C, and ground to a fine powder. The powder was stored under nitrogen until further use.

Poly(PDMS-POSSamic acid) membranes were prepared by interfacial polymerization on top of porous α -alumina disks, coated with two layers of γ -alumina (Pervatech, The Netherlands). The support was soaked with aqueous POSS solution (0.9 wt%) and dried for 15 minutes to remove excess aqueous solution. Afterwards, the organic solution of PDMS (0.5 wt% in toluene) was poured onto the porous disk. After 5 minutes reaction time, the toluene solution was removed, and the membrane surface was washed with toluene.

Thin poly(PDMS-POSSamic acid) films deposited on silicon wafers were prepared for spectroscopic ellipsometry experiments. A silicon wafer was fixed in the middle of a petri dish and aqueous POSS solution (0.9 wt%, pH=9.5) was poured into the petri dish, just covering the wafer. Then PDMS solution (0.5 wt% in toluene) was gently poured from the side over the POSS solution, allowing it to float on top of the aqueous solution. A thin film formed immediately. After ten minutes reaction time, most of the toluene was removed with a pipet and the petri dish was slowly decanted, allowing for the water solution to flow out of the petri dish, and the formed poly(PDMS-POSSamic acid) film was carefully deposited on the fixed wafer. The wafer with the poly(PDMS-POSSamic acid) film was removed from the petri dish and air dried. Once dried, the wafer with the film was carefully placed in a petri dish filled with ethanol, to remove unreacted monomers.

6.2.4 Imidization of poly(PDMS-POSSamic acid) networks

Both poly(PDMS-POSSamic acid) powder and supported films were placed in a chamber oven (Carbolite HTMA 5/28) under a nitrogen flow (5 mL min⁻¹). The samples were heated to 100 °C for 1 h, followed by an 18 minutes dwell at 250 °C with a heating rate of 10 °C min⁻¹. The imidization time and temperature were determined from combined TGA-MS experiments. The samples were cooled to room temperature without a specified cooling rate.

6.2.5 Characterization

The chemical structure of poly(PDMS-POSSamic acid) and poly(PDMS-POSSimide) powders was analyzed by fourier transform infrared spectroscopy (FTIR) in attenuated total reflectance (ATR) mode on an ALPHA spectrometer (Bruker, Germany). All powders were used without further sample preparation.

Combined thermogravimetric analysis (TGA) and mass spectroscopy (MS) measurements were performed on poly(PDMS-POSSamic acid) powders using an STA 449 F3 Jupiter TGA with an aluminium sample cup (Netzsch, Germany) and QMS 403 D Aeolos MS (Netzsch, Germany). Mass loss measurements were performed from 50 to 1000 °C with a heating rate of 20 °C min⁻¹ under both air and nitrogen atmospheres. Isothermal analysis was performed at 250 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Streaming current measurements were performed on a SurPASS (Anton Paar, Austria) analyzer equipped with an adjustable gap cell. Poly(PDMS-POSSimide) films were deposited on silicon wafers of 1 × 2 cm². The wafers were attached to the adjustable gap cell by double sided adhesive tape. The pH of the electrolyte solution (5 mM KCl) was automatically adjusted using 0.1 M NaOH. From the streaming current, the zeta potential could be derived using Eq. 6.1:

$$\zeta = \frac{dl}{dp} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{A_{\text{channel}}} \quad [6.1]$$

where ζ is the zeta potential, $\frac{dl}{dp}$ is the slope of the streaming current versus pressure, η and ε are the viscosity and dielectric constant of the electrolyte, here taken as that of water, ε_0 is the permittivity of vacuum, L is the length of the streaming channel, and A_{channel} is the cross sectional area of the channel.

The contact angle of poly(PDMS-POSSimide) films deposited on silicon wafers was measured with an OKA 15 (DataPhysics, Germany) set-up by applying the sessile drop method. A Milli-Q water droplet ($V=1 \mu\text{L}$) was deposited onto the surface and the contact angle was obtained 3 s after deposition. The average contact angle and 95% confidence interval were calculated from 5 individual measurements.

Ethanol permeation measurements were performed on a custom-built dead-end permeation setup. A feed vessel was pressurized to 20 bar using ultra-pure nitrogen. Permeate streams were measured with a mass balance.

6.2.6 *In situ* spectroscopic ellipsometry

Thickness and refractive index measurements of films were done with spectroscopic ellipsometry on an M2000XI spectroscopic ellipsometer (J.A. Woollam Co.), with focusing probes. *In situ* data was recorded at least once every 15 seconds. The data was modelled using the CompleteEase software package (J.A. Woollam Co.) in the wavelength range of 370-1000 nm. The substrate was modelled using the built-in temperature-dependent optical properties of silicon, on top of which a 2 nm native oxide layer was modelled. The refractive index of the poly(PDMS-POSS) film was modelled at 632.8 nm wavelength using a Cauchy dispersion (fit parameters: A , B , k , and thickness).

The ellipsometry data for imidization was collected with a Linkam heating stage with quartz windows with an incident angle of 70°. The non-imidized films, used for imidization measurements with ellipsometry, were stripped of residual solvents in a furnace at 110 °C for 20 minutes. The temperature measurements were performed under ultra-pure nitrogen at a flow rate of 100 mL min⁻¹. A temperature correction was performed according to the procedure described by Kappert et al. [36]. The optical retardance of the windows of the measurement cell was included using calibrated delta off-sets. Prior to heating, the samples were flushed at 25 °C under nitrogen flow for 30 minutes. Then, the samples were heated to 250 °C at 5 °C min⁻¹ and remained at 250 °C for 20 minutes. The samples were cooled down with a cooling rate of 20 °C min⁻¹.

The obtained thickness was divided by the thickness measured at time $t=0$ resulting in the relative thickness as shown by Eq. 6.2.

$$d_{\text{relative}} = \frac{d_t}{d_0} \quad [6.2]$$

Where d_{relative} is the relative thickness at a certain point of time, d_0 and d_t are the thicknesses at the starting time or at a certain point of time, respectively. The relative refractive index was obtained similarly from the refractive index at the starting time and at a certain point of time.

The ellipsometry swelling measurements were performed with a custom-built Teflon liquid flow cell with quartz windows with an incident angle of 70°. The cell volume was 25.5 cm³. The cell temperature was controlled with an external water bath (LAUDA-Brinkmann, LP.), allowing water at 25 °C to flow through the outer walls of the cell. The optical retardance of the windows of the measurement cell was corrected for using calibrated delta offsets. Ethanol, ethyl acetate and *n*-hexane

were the solvents used for swelling and their properties are provided in Table 6.1. The solvent vapor flow was generated using two identical bubblers in series, both at 25 °C. The carrier gas was an ultra-pure nitrogen gas, with a gas flow of 100 mL min⁻¹. The dry sample thickness and refractive index were based on the last ten data points before the solvent vapor was introduced into the cell. The swelling degree of a polymer film upon swelling in solvents was calculated using Eq. 6.3.

$$SD = \left(\frac{d_{\text{swollen}}}{d_{\text{dry}}} - 1 \right) \cdot 100\% \quad [6.3]$$

Where SD is the swelling degree, and d_{dry} and d_{swollen} are the dry and swollen thickness of the film, respectively.

The normalized refractive index upon swelling in solvents was calculated using Eq. 6.4.

$$n_{\text{norm}} = \frac{n_{\text{swollen}} - n_{\text{solvent}}}{n_{\text{dry}} - n_{\text{solvent}}} \quad [6.4]$$

Where n_{norm} is the normalized refractive index, n_{dry} is the refractive index of the non-swollen polymer film, n_{swollen} is the refractive index of the swollen polymer film in a solvent, and n_{solvent} is the refractive index of the pure solvent.

The poly(PDMS-POSSimide) films show a significant spread in the refractive index, that can originate from the preparation of the films on a silicon wafer. The preparation involves a free-standing film that is deposited onto the silicon wafer by decanting the solutions. As a result, an inhomogeneous thin film was deposited onto the wafer, with different thicknesses and refractive indices, depending on the local reaction time. For this reason, a note on treating the refractive index of the poly(PDMS-POSSimide) films is necessary. The inhomogeneity of the thin poly(PDMS-POSSimide) films causes the measured refractive index to have a reduced accuracy and the measurements should therefore be treated based on the qualitative trends and not on the exact quantity.

The apparent solvent activity in the cell was determined by assuming the solvent cell as a continuous ideally stirred tank reactor (CISTR), with the boundary condition at time $t = 0$, the apparent activity a is 0 and the activity of the in-going stream equal to 1. As a consequence, $\lim_{t \rightarrow \infty} a(t) = 1$. The apparent solvent activity at time t can be calculated using Eq. 6.5.

$$a(t) = 1 - \exp\left(-\frac{t}{\tau}\right) \quad [6.5]$$

Where a is the apparent solvent activity, and τ is the residence time which can be determined as:

$$\tau = \frac{V_{\text{cell}}}{\phi_{\text{gas}}} \quad [6.6]$$

where V_{cell} is the volume of the cell (25.5 cm³), and ϕ_{gas} is the flow of the solvent vapor into the cell.

Table 6.1 – Solubility parameters, dielectric constants, molar volumes and vapor pressure of the solvents used in this study, the solubility parameter of PDMS is 7.3 cal^{1/2} cm^{-3/2} [14].

Solvent	δ (cal ^{1/2} cm ^{-3/2})	Dielectric constant (-) ^[37]	Molar volume (cm ³ mol ⁻¹) ^[38]	Vapor pressure (bar)
<i>n</i> -hexane	7.3	1.89	310	0.20
Ethyl acetate	9.0	6.08	284.35	0.13
ethanol	12.7	25.3	173.55	0.08

6.3 Results and Discussion

6.3.1 Imidization of poly(PDMS-POSSamic acid)

The imidization process of a thin poly(PDMS-POSSamic acid) film has been studied by spectroscopic ellipsometry. Figure 6.1 shows the relative thickness (a,b) and relative refractive index (c,d) as a function of temperature and time. Three regimes can be distinguished when looking at the thickness of the film during the heating phase. First, a small decrease in film thickness was observed at temperatures up to 50 °C. This decrease has been attributed to the drying of the film and thus the release of physically bound water. The second stage is characterized by a plateau in the film thickness. At this stage the thermal expansion of the film is equal to the mass loss due to the release of water, as confirmed by the observed decrease in the refractive index during this stage and accompanying TGA-MS data (see Figure S6.4, Supplementary Information). The last stage can be defined as the onset of imidization, starting from 180 °C with a significant decrease in film thickness. As water is formed and released during the imidization process, the imidization process can also be tracked by performing a combined thermogravimetric analysis (TGA) and mass spectroscopy (MS) analysis on powder samples. From the TGA-MS analysis it was shown that the imidization of this poly(PDMS-POSSamic acid) starts at 150 °C, with a peak in water release at 195 °C. Above 250 °C no more water is released, indicating that the imidization is finished at this temperature (see Figure

S6.4 Supplementary Information). The peak of water release at 195 °C corresponds well with the onset decline of thickness between 180 °C and 200 °C. The steepened decline in thickness between 200 °C and 250 °C can be attributed to reorganization of the polymer network, while the decrease in index can be attributed to the conversion of the amic acid groups into imide groups [39]. At the isothermal stage (Figure 6.1b,d) both the thickness and refractive index keep decreasing over time. Since there is no more thermal expansion of the material, the decrease in both thickness and refractive index is attributed to the continuing imidization. During the imidization, progressively less amic acid groups remain and thereby the decrease in thickness levels off.

Figure 6.1 – The relative thickness and refractive index of poly(PDMS-POSSamic acid) films during imidization studied by spectroscopic ellipsometry. (a) The relative thickness during heating to 250 °C as function of temperature. (b) The relative thickness during the isothermal stage as function of time. (c) The relative refractive index during heating to 250 °C as function of temperature. (d) The relative refractive index during the isothermal stage as function of time.

Infrared spectroscopy measurements (see Figure S6.3 in Supplementary Information), confirmed the conversion of the covalent amic acid bonds to imide bonds between the PDMS and POSS after the thermal treatment.

6.3.2 Swelling in organic solvents

The swelling of both conventional PDMS films and poly(PDMS-POSSimide) films in *n*-hexane, ethyl acetate, and ethanol vapors was studied. Figure 6.2 shows the swelling behavior of a conventional PDMS film as function of the “apparent solvent activity” (Figure 6.2a), as a function of time at solvent activity 1 (Figure 6.2b) and as a function of square root of time at solvent activity 1 (Figure 6.2c). The extent of solvent induced swelling of a PDMS film is correlated to the affinity of the PDMS chains for the solvent. The conventional PDMS film has the highest swelling degree for *n*-hexane, with a stable swelling degree at 72 %. The second highest swelling degree is observed for ethyl acetate (25 %), and the lowest for ethanol (3 %). This order of the swelling degrees corresponds well with the affinity of PDMS for organic solvents, based on Hildebrand solubility parameters (see Table 6.1) and the polarity of the solvents. The diffusion of the solvent into a rubbery polymer is based on the Fickian mode of transport. This means that a linear increase in volume is observed with the square root of time through the bulk of the film, until an equilibrium value is reached. In Figure 6.2c, a linear increase of the swelling degree as function of the square root of time was observed for the swelling of PDMS in ethyl acetate. In the case of *n*-hexane, a new equilibrium was obtained almost instantaneously, while in ethanol the swelling is only limited, but a very small, but constant increase over the square root of time was observed. While *n*-hexane is the largest penetrant (see Table 6.1), it has the fastest diffusion into PDMS. For this reason, the diffusion into PDMS is governed by the polarity of the penetrant rather than by the size of the penetrant [40,41].

Figure 6.2 – (a) The swelling degree of pure PDMS as a function of solvent vapor activity in the cell. (b) The swelling degree as function of time at an apparent activity of 1. (c) The swelling degree as function of the square root of time at an apparent activity of 1. A linear dependence of the swelling degree as function of the square root of time indicates Fickian diffusion. The swelling degree of PDMS is the highest for *n*-hexane (72 %), followed by ethyl acetate (25 %), and ethanol (3 %).

The absolute magnitude of swelling is lower than the swelling values reported in literature for both liquids and vapors [14,42,43]. The observed lower swelling values for PDMS in the solvent vapors can be attributed to various reasons. First of all, the type of PDMS and the amount of cross-linking used, influences the swelling behavior of PDMS in organic solvents. The PDMS comes in two components and is commonly crosslinked in a 10:1 ratio (base:curing agent). PDMS RTV 615 (used in this study) and Sylgard 184 are the two most commonly types of PDMS used. Sylgard 184 is known to have a lower density, more constant and purer composition and lower curing times compared to PDMS RTV 615 [44,45]. For this reason, Sylgard 184 which is most commonly used in swelling studies is likely to have higher swelling degrees. Furthermore, since the measurements have been performed in vapors rather than in liquids, a solvent activity of 1 is hard to realize. The quantitative control of the activity is generally less accurate, in particular close to an activity of 1, the extent of swelling is a strong function of the activity. For this reason, the activity of the solvent is referred to as the 'apparent solvent activity', since there might be a small discrepancy from the actual solvent activity and the assumed solvent activity. The use of vapors however, was necessary to allow for a higher optical contrast for the ellipsometry measurements; highly swollen films have a refractive index that is relatively similar to that of the liquid ambient, whereas for vapors the ambient refractive index remains close to 1.

In Figure 6.3 the swelling degree as function of apparent activity, time and square root of time of the poly(PDMS-POSSimide) films in *n*-hexane (Figure 6.3a-c), ethyl

acetate (Figure 6.3d-f) and in ethanol (Figure 6.3g-i) is shown. Poly(PDMS-POSSimide)s films show a stable swelling degree of 4-6 % in *n*-hexane. This swelling degree is approximately fifteen times lower compared to that of the conventional PDMS. This can be caused by the successful cross-linking of the PDMS chains, as well as by the reduced affinity for *n*-hexane due to the inclusion of the POSS molecules. The swelling degree of poly(PDMS-POSSimide) films in ethyl acetate (3-7 %) is comparable to that obtained for *n*-hexane. This swelling degree is approximately five times lower compared to that of conventional PDMS in ethyl acetate. Surprisingly, in the most polar solvent, ethanol, a swelling of 4-11 % was observed for the poly(PDMS-POSSimide) films, which is higher than the swelling in the non-polar solvent *n*-hexane and the swelling in conventional PDMS (3 %). The reason for the increased swelling in ethanol for the poly(PDMS-POSSimide) films is attributed to the increased surface charge compared to conventional PDMS. More clarification on the increased affinity for polar solvent of the poly(PDMS-POSSimide) films is provided in 6.3.3.

Also, as shown in Figure 6.3, three different samples with different refractive indices were measured for each solvent. The refractive index correlates to the density of the sample and the density increases with an increased refractive index^[46]. In all three solvents, a lower refractive index of the poly(PDMS-POSSimide) film corresponds to a higher swelling degree and this effect is more pronounced for an increased solvent polarity. An increased refractive index indicates an increase of the POSS content inside the poly(PDMS-POSSimide) film, as was shown by Raaijmakers et al.^[47], thus increasing the affinity for polar groups.

Figure 6.3 – The swelling degree of poly(PDMS-POSSimide) films measured by spectroscopic ellipsometry for (a,b) *n*-hexane, (c,d) ethyl acetate, and (e,f) ethanol vapors. Panels a, c, and e show the swelling degree as function of the apparent solvent vapor activity in the cell. Panels b, d, and f show the swelling degree as function of time at an apparent activity of one. For every solvent, three different samples with varying refractive indices were measured.

Figure 6.4 shows the normalized refractive index for poly(PDMS-POSSimide) films in *n*-hexane (Figure 6.4a-b), ethyl acetate (Figure 6.4c-d), and ethanol (Figure 6.4e-f) as function of solvent activity and time. In case of lower POSS concentrations, ($n < 1.50$), the normalized refractive index shows an immediate decrease as function of time, as observed with conventional PDMS (see Figure S6.5, Supplementary Information). This indicates that any solvent molecule that is absorbed in the poly(PDMS-POSSimide) film has a certain molar volume, diluting the polymer matrix and thereby decreasing the refractive index. For the poly(PDMS-POSSimide) films with an increased POSS concentration ($n > 1.50$), an initial increase with time in the normalized refractive index was observed. A behavior which is more commonly observed in glassy polymers, where solvent initially first replaces void in the polymer matrix, causing the overall index of the polymer film mixture to increase. Over time more and more solvent is being absorbed into the polymer matrix, reducing the polymer to solvent ratio and thus the overall refractive index. In the case of poly(PDMS-POSSimide) films, the initial increase in the refractive index indicates an increased rigidity of the polymer matrix, which is the result of an increased POSS concentration. This effect is apparent in all three studied solvents, indicating that an increased incorporation of POSS molecules into the poly(PDMS-POSSimide) network, increases the rigidity of the polymer matrix and restricts the swelling in organic solvents.

Figure 6.4 – The normalized refractive index of poly(PDMS-POSSimide) films measured by spectroscopic ellipsometry for (a,b) *n*-hexane, (c,d) ethyl acetate, and (e,f) ethanol vapors. Panels a, c, and e show the normalized refractive index as function of the apparent solvent vapor activity in the cell. Panels b, d, and f show the normalized refractive index as function of time at an apparent activity of one. For every solvent, three different samples with varying refractive indices were measured.

6.3.3 Surface properties of poly(PDMS-POSSimide)

An increased swelling of a poly(PDMS-POSSimide) film was observed in ethanol compared to conventional PDMS, indicating an increased affinity between the a poly(PDMS-POSSimide) and a polar solvent such as ethanol. This increased affinity was explained by the presence of unreacted partially deprotonated ammonium

side-groups within the poly(PDMS-POSSimide) network. The PDMS chains are cross-linked by POSS containing ammonium side-groups. These side-groups are partially deprotonated towards the reactive free amine groups prior to interfacial polymerization. However, only 3-4 ammonium groups are converted at the pH of the aqueous solution (pH=9.5) and thus POSS is a positively charged monomer at these conditions. Figure 6.5 shows the zeta potential of a poly(PDMS-POSSimide) film supported on a silicon wafer, proving the positive charge of the poly(PDMS-POSSimide) film at neutral pH. This in comparison to conventional PDMS, which has a strong negative surface charge at neutral pH^[48,49]. Therefore, the higher swelling degree of poly(PDMS-POSSimide) films in ethanol could be explained by the presence of positively charged ammonium groups. Despite the positively charged surface, the poly(PDMS-POSSimide) films show to have an average water contact angle of $110^{\circ} \pm 6^{\circ}$ and can therefore still be considered as hydrophobic.

Figure 6.5 – Zeta potential of poly(PDMS-POSSimide) films supported by silicon wafers, measured in duplicate.

6.3.4 Barrier properties

Poly(PDMS-POSSimide) films were prepared by interfacial polymerization on top of γ -alumina coated porous α -alumina supports. The use of these ceramic supports allow for the imidization at 250 °C. Due to the hydrophilic nature of the support, only polar solvents will be permeating through the support. Clean ethanol fluxes were measured for three separate membranes in dead-end mode at 20 bar transmembrane pressure for at least 27 hours. All membranes showed almost no permeation, with ethanol permeances between 0.004 and $0.011 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (Figure 6.6), which is surprising regarding the substantial swelling in ethanol observed for films with a lower cross-linking degree. The extremely low ethanol permeance of

the poly(PDMS-POSSimide) membrane could be explained by a combination of a high cross-link density, and the relatively short PDMS oligomer used ($M_n \approx 900 \text{ g mol}^{-1}$ as determined by $^1\text{H-NMR}$).

Figure 6.6 – The permeate mass increase during ethanol permeation at 20 bar in dead-end mode. The steps are caused by dripping of the permeate onto the mass balance.

The low permeance of these poly(PDMS-POSSimide) films could be of benefit when applied in microfluidic devices. In microfluidic devices, the swelling of PDMS causes deformation or even leakage of the microfluidic channels, making the material unsuitable for microfluidic organic solvent applications. Also the extremely low surface charge is often considered a problem [12,14,50]. The poly(PDMS-POSSimide) film can act as a barrier layer, while maintaining the hydrophobic and optical properties of PDMS, in microfluidic devices where the swelling and surface charge of the PDMS pose a problem. By using the conventional PDMS as a reservoir for the organic phase, the synthesis of the poly(PDMS-POSSimide) film via interfacial polymerization on top of the PDMS substrate is easily realized.

6.4 Conclusion

Here, we showed the preparation of hyper-cross-linked poly(PDMS-POSSimide) films. Swelling measurements in *n*-hexane, ethyl acetate and ethanol vapors show that the presence of the hybrid cross-links significantly restrict the swelling of poly(PDMS-POSSimide) films in *n*-hexane and ethyl acetate as compared to conventional PDMS. A ~15 fold decrease in swelling in *n*-hexane vapor, and a ~5 fold decrease in ethyl acetate vapor was observed for these poly(PDMS-POSSimide) films. The presence of unreacted positively charged ammonium groups promote a slightly higher swelling of poly(PDMS-POSSimide) films in ethanol compared to

PDMS. In general, the swelling of these hyper-cross-linked poly(PDMS-POSSimide) films is limited to less than 12 %, showing that these films have only a limited swelling in a wide variety of solvents.

Despite the substantial swelling in ethanol, poly(PDMS-POSSimide) films did not show ethanol permeance ($<0.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). This low permeance can be attributed to a combination of a high cross-linking degree and the relatively short PDMS oligomer used and makes poly(PDMS-POSSimide) films a suitable barrier material to be applied in microfluidic devices.

6.5 Acknowledgements

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6.6 Supplementary Information

6.6.1 Synthesis of poly(PDMS-POSSimide) networks

Ultra-thin poly(PDMS-POSSimide) films were made by the interfacial polymerization of octaAmmonium POSS and succinic anhydride terminated PDMS. OctaAmmonium-POSS was deprotonated to form its reactive free amine, and subsequently reacted with succinic anhydride terminated PDMS resulting in a poly(PDMS-POSSamic acid). This poly(amic acid) was thermally imidized in the corresponding poly(PDMS-POSSimide) (Figure S6.1).

Figure S6.1 – The synthesis of hyper-cross-linked poly(PDMS-POSSimide) by interfacial polymerization of amine functionalized POSS with succinic anhydride functionalized PDMS. After film formation, the resulting poly(PDMS-POSSamic acid) was thermally imidized to the stable poly(PDMSPOSS imide).

To partially activate the eight available ammonium groups, the POSS was treated with sodium hydroxide. The number of converted ammonium groups to primary amine groups depends on the amount of sodium hydroxide added and is thus dependent on the pH of the aqueous solution. Dalwani et al. ^[33] showed that below pH 7 there is no significant conversion of ammonium groups. With increasing pH, the number of converted ammonium groups increases. At a pH value of 9–10, about 4 to 5 amine groups have been formed. At increasing pH simultaneous hydrolysis of the Si–O–Si bonds occurs.

6.6.2 Synthesis of poly(PDMS-POSSimide) networks at different pH-values of the aqueous solution

Figure S6.2 shows FTIR spectra of poly(PDMS-POSSamic acid) powders from 1800 to 1400 cm^{-1} . All spectra are normalized to the absorbance peak at 1530 cm^{-1} . Poly(PDMS-POSSamic acid) powders were prepared with various pH values of the aqueous solution. The absorbance peaks of the N–H bending and C=O stretching, originating from the amic acid bonds, can be clearly distinguished at 1640 and 1530 cm^{-1} , respectively. In addition to these characteristic amic acid peaks, a small absorbance peak, which magnitude is dependent on the synthesis pH, appears at 1705 cm^{-1} . This peak can be assigned to the C=O stretching of a carboxylic acid. This carboxylic acid can be formed by the reaction of a succinic anhydride group with

water. A relatively high amount of these carboxylic acid groups is present at a “low” pH (pH 8.3), while a “high” pH (pH 9.5) results in almost none of these carboxylic acid groups. This corresponds perfectly well to the amount of available reactive amine groups at a certain pH. To conclude, a “low” pH of the aqueous phase results in relatively few reactive amine groups, and thus a high amount of unreacted succinic anhydride groups that eventually convert into carboxylic acid groups.

Figure S6.2 – ATR-FTIR spectra for poly(PDMS-POSSamic acid) powders from 1800 to 1400 cm^{-1} . The pH of the aqueous solution was varied from pH 8.3 to 9.5.

6.6.3 Infrared spectroscopy on poly(PDMS-POSSamid acid) and poly(PDMS-POSSimide) powders

To confirm that poly(PDMS-POSSamic acid) indeed imidized into poly(PDMS-POSSimide) after thermal treatment, infrared spectroscopy has been performed on poly(PDMS-POSS) powder before (Figure S6.3 bottom) and after (Figure S6.3 top) the imidization step. Sharp absorbance peaks at 795 and 1260 cm^{-1} can be observed in both spectra, indicating the presence of Si-CH₃ bonds and thus the presence of PDMS. Absorbance peaks at 1015 and 1080 cm^{-1} can be attributed to the asymmetric stretching of Si-O-Si, a bond that is present in both PDMS and in POSS. The spectrum of the poly(PDMS-POSSamic acid) shows peaks at 1640 and 1530 cm^{-1} , which are assigned to the N-H bending and C=O stretching of the amic acid, respectively. These peaks vanish after the thermal treatment, indicating the conversion of amic acid bonds into imide bonds. Peaks at 1700 and 1670 cm^{-1} appear after this thermal treatment. These peaks are assigned to the C=O symmetric and asymmetric stretching present in the poly(PDMS-POSSimide). In addition, a small peak at 1780 cm^{-1} can be observed in the spectrum of the poly(PDMS-POSSimide). This peak can be attributed to a small fraction of isoimide bonds formed during imidization.

Figure S6.3 – FTIR of poly(PDMS-POSSamic acid) (bottom) and the corresponding poly(PDMS-POSSimide) (top). The characteristic amic acid absorbance peaks have been replaced by characteristic imide absorbance peaks upon thermal imidization. The absorbance peaks characteristic for both PDMS and POSS (*i.e.*, absorbance peaks caused by Si-O-Si and Si-CH₃ bonds) have been unchanged, indicating the thermal stability of the network.

6.6.4 Thermogravimetric analysis of poly(PDMS-POSSamic acid) powders

The imidization of poly(PDMS-POSSamic acid) to poly(PDMS-POSSimide) is an important step to ensure stability of the material against hydrolysis. Poly(PDMS-POSSamic acid) powder has been thermally treated during a thermogravimetric analysis combined with mass spectroscopy (TGA-MS) to study the onset of imidization and the stability of the material during thermal treatment. Figure S6.4 shows the TGA-MS graphs of poly(PDMS-POSSamic acid) powders. The upper panels show the mass loss as a function of temperature, while the lower panels show the corresponding gases evolved tracked with a MS. During imidization, the amic acid ring is closed while water is eliminated (Figure S6.1) and the onset of imidization can be determined from the $m/z=18$ MS signal. From Figure S6.4 it can be concluded that the imidization of this poly(PDMS-POSSamic acid) starts at 150 °C, with a peak in water release at 195 °C. Above 250 °C no more water is released, indicating that the imidization is finished at this temperature. The imidization and thermal degradation of a poly(PDMS-POSSamic acid) powder in an air atmosphere is shown in Figure S6.4a, and that in a nitrogen atmosphere is shown in Figure S6.4b. Both in an air and a nitrogen atmosphere, the peak in water evolved associated with imidization is present at 215 °C. However, when the imidization is carried out in air, almost immediately after this imidization peak a significant release of CO₂ and more H₂O is detected. Those are typical degradation

products under air atmosphere. Thus, although the onset of imidization seems not to depend on the atmosphere, the onset of thermal degradation strongly does (250 °C in air, 400 °C in nitrogen). To avoid thermal degradation of the material during imidization, the imidization temperature chosen should be well below the onset of thermal degradation. This can only be achieved when imidization is carried out in a nitrogen atmosphere.

In addition to the onset of thermal degradation, the mass loss pattern of the poly(PDMS-POSSimide) powders does strongly depend on the atmosphere as well. This dependence of atmosphere is similar to that found for conventional PDMS [51]. Thermal degradation in air occurs in multiple steps, with a stable weight of 50 % of the original mass reached at 500 °C. In contrast, the main degradation in nitrogen occurs in a single step at 470 °C, after which the mass slowly further decreases with increasing temperature. A residual mass of less than 10 % is found at 1000 °C. Camino et al. report that conventional PDMS degrades to volatile cyclic oligomers upon heating by the scission of Si-O bonds. The authors state that oxygen can catalyze this depolymerization reaction, resulting in a reduced temperature of the first weight loss observed in air [51,52]. The higher residual weight in air can be a result of further cross-linking of the PDMS chains in the presence of oxygen, and thereby stabilizing the material against thermal degradation. The poly(PDMS-POSSimide) networks prepared in this work are prepared with a relatively low molecular weight PDMS ($M_n \approx 900 \text{ g mol}^{-1}$), making the formation of volatile cyclic compounds less likely. However, the further cross linking of the PDMS chains in the presence of oxygen can still occur, and thus explain the dependence of degradation behavior on the atmosphere.

In addition to the imidization temperature, the imidization time could be determined from the TGA-MS experiments. Figure S6.4c and d show the heating and isothermal stage of the imidization, respectively. Some minor traces of H₂O are observed around 90 °C. This can be attributed to the release of physically bound water. The release of H₂O due to the imidization process starts at 150 °C, with a peak around 195 °C. Besides imidization, H₂O can be released because of silanol condensation [39]. Simultaneously, small traces of CO₂, CH₄, and NO are detected. The release of CO₂ can be caused by the decarboxylation reaction of unreacted carboxylic acid groups [39]. Despite these minor peaks of decomposition gasses, the network is considered to be stable at this imidization process. This is proven by the lack of a signal originating from the CH₃CH₂CH₂ fragment. Due to the sp³ hybridization, the propyl groups are considered to be the thermally most weakest links. The isothermal analysis (Figure S6.4d) reveals that after 18 minutes at 250 °C there is no more loss of H₂O detected. That means that after 18 minutes the

imidization process is finished, and therefore the imidization of poly(PDMSPOSSamic acid) is performed at 250 °C for 18 minutes.

Figure S6.4 – TGA-MS data for poly(PDMS-POSSamic acid) powders. (a) Imidization and thermal degradation in an air atmosphere. (b) Imidization and thermal degradation in a nitrogen atmosphere. (c) The imidization in a nitrogen atmosphere. (d) Isothermal analysis of the imidization under nitrogen atmosphere at 250 °C. All upper panels show the mass loss as function of temperature. All lower panels show the evolved gases during heating. The following gases are traced: CH_4 ($m/z=15$, green, -), H_2O ($m/z=18$, blue, -), NO ($m/z=30$, pink, -), $CH_3CH_2CH_2$ ($m/z=43$, orange, -), and CO_2 ($m/z=44$, black, -).

6.6.5 The refractive index of poly(PDMS-POSSimide) films upon solvent swelling

From spectroscopic ellipsometry both the film thickness and refractive index could be obtained. The change in normalized refractive index for conventional PDMS upon swelling in solvent vapor is shown in Figure S6.5. Figure S6.5a shows the normalized refractive index as function of apparent solvent activity, while Figure S6.5b shows the normalized refractive index (hereafter called “index”) at activity 1 as function of time. The index of PDMS decreases upon exposure to solvents, which fits perfectly well with the swelling measured. Upon solvent swelling, the PDMS matrix gets diluted with the solvent that has a lower refractive index than the PDMS matrix, and therefore decreasing the index of the swollen film. The extent of this reduction of the index is directly related to the swelling degree in the specific solvent. A higher swelling degree results in more solvent in the polymer matrix, and thus a lower index.

Figure S6.5 – The normalized refractive index of PDMS in solvent vapors (a) as a function of the apparent solvent activity in the cell, and (b) as a function of time at a constant activity of 1.

6.7 References

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Chapter 7

Relaxation Dynamics of Thin Matrimid 5218 Films in Organic Solvents

This chapter is adapted from:

Kristianne Tempelman, Jeffery A. Wood, Friedrich Kremer, Nieck E. Benes, *Relaxation dynamics of thin Matrimid 5218 films in organic solvents*, Manuscript in preparation

Abstract

Polyimides are interesting polymer materials for organic solvent nanofiltration (OSN) applications, because of their high chemical resistance. Challenges of glassy polymer materials (such as polyimides) are their tendency to swell in organic solvents. An understanding on how swelling influences the polymer properties and performance is then of crucial importance for assessing polyimide suitability in OSN applications. Here, the combination of *in situ* spectroscopic ellipsometry, broadband dielectric spectroscopy and infrared spectroscopy is applied to study the molecular interaction of two organic penetrants, toluene and *n*-hexane, with Matrimid 5218 in detail. *In situ* spectroscopic ellipsometry shows that slightly cross-linked Matrimid 5218 swells approximately seven times more in toluene (swelling degree ~28%) compared to in *n*-hexane (swelling degree ~4%). Broadband dielectric spectroscopy at room temperature reveals two overlapping β -relaxations that separate upon exposure to a penetrant. Diffuse reflectance infrared spectroscopy indicates that the origin of the β -relaxations is most likely in the axial stretch of the C-N-C connection between the diamine and diamine of Matrimid 5218. Although only small changes are observed with infrared spectroscopy, the results indicate that toluene interacts with the benzene ring present in the diamine through π - π interactions, while *n*-hexane likely fills up the excess free volume, forming local Van der Waals interactions. This obtained knowledge on the exact nature of the molecular interactions between the penetrant and polymer allow for a more accurate assessment of swelling in polymers to be used for OSN applications.

7.1 Introduction

High performance materials such as polyimides are interesting candidates when requiring a high chemical and temperature resistance in, for example coating or membrane applications [1]. Polyimides are known for their rigid structure, high temperature resistance and high chemical resistance. Due to their rigid structure and their tendency to crystallize, many polyimides are nearly insoluble after the imidization treatment. However by incorporating a copolymer structure or steric hindrance by introducing a bulky molecular group, the linearization of the rigid backbone is disrupted and the solubility of the polyimide can be increased.^[2,3] An example of such a non-homogenous polyimide is Matrimid 5218, from here onwards referred to as matrimid. For processing purposes, the possibility to dissolve the polymer is preferred but as a result the polymer will be more receptive to plasticization as well. In the field of membrane technology, plasticization is a common problem that causes a lower selectivity of the membrane. For this reason, the origin of plasticization in polyimides such as matrimid is a well-researched topic. As polyimides are considered to have a high potential as gas separation membranes, most of these studies involve the plasticization induced by CO₂ [4–9]. However, because of their high chemical resistance, polyimides are also considered either as support material or as a selective layer in organic solvent nanofiltration applications^[10]. Consequently, more research is required into the plasticization and swelling induced by organic solvents.

Typically in plasticization studies, the penetrant mass uptake, swelling or performance of the polyimide are studied as function of the penetrant pressure^[11–15]. Generally, these techniques measure the consequences of the penetrant-polymer interactions, but provide no direct insight on the underlying physical phenomena and the specific changes in the dynamics of the penetrant and the polymer. By studying the penetrant induced relaxation dynamics, information on the site-specific interactions of the penetrant with the molecular groups inside the polymer can potentially be provided. To the best of our knowledge, no research on the penetrant-induced relaxation dynamics for polyimides has been presented to date.

The temperature dependent relaxation dynamics of polyimides and the influence of the two monomers of a polyimide, the dianhydride and diamine, have already been studied in literature^[2,3,16–19]. Typically for temperatures at room temperature or higher, a β -relaxation and an α -relaxation have been observed. In 1999 Li et al., observed for the first time for a polyimide three relaxations above room temperature. They appointed the lower temperature relaxations as β_1 and β_2 , and the third process was the α -relaxation corresponding with the glass transition. The β_1 -relaxation was attributed to the local motion of the diamine constituents, while the β_2 -relaxation is considered to be caused by local motion of the dianhydride

constituents. Li et al. showed, by employing the Starkweather theory, that the β_2 -relaxation can transform from a non-cooperative process to a cooperative process upon increasing the size and anisotropic shape of the substituted groups on the dianhydride. The two β -relaxations were in 2001 confirmed by Qu et al.^[2]. The observed cooperative characteristics of the β -relaxation was also observed for other polyimides^[16,17,19,20].

In the case of matrimid, the dynamic polymer chain relaxations of matrimid have been studied by Comer et al.^[21] and Konnertz et al.^[22] as a function of temperature. Both studies utilized broadband dielectric spectroscopy and the β -relaxation was assigned to be local in nature, but cooperative in origin due to the rigid backbone of the matrimid structure. Konnertz et al. proposed that the cooperativity of the β -relaxation was the result of the π - π stacking of the phenyl rings. Also, a temperature history dependent relaxation behavior of matrimid was observed. At this point, the temperature dependence of the dynamic polymer chain relaxations of matrimid is well understood. However, it is unknown to what extent the introduction of a penetrant will influence the dynamic polymer chain relaxations and which interactions between the penetrant and polymer dominate the swelling behavior.

In this work the interaction of toluene and *n*-hexane with matrimid was studied. *In situ* spectroscopic ellipsometry was used to study the swelling upon exposure to the two different penetrants. Broadband dielectric spectroscopy was applied *in situ* to probe the dynamic polymer chain relaxations on matrimid while exposed to the penetrants. *In situ* diffuse reflectance infrared spectroscopy was used to obtain a molecular interpretation of the different chain relaxations observed upon penetrant exposure. The combination of the three *in situ* characterization techniques allowed for an interpretation of the difference in interaction between *n*-hexane and toluene with matrimid.

7.2 Materials and Methods

7.2.1 Materials

Matrimid® 5218 US (Huntsman), Cyclopentanone (ReagentPlus®, ≥99 %, Sigma-Aldrich), toluene (EMPLURA®, >99 %, Merck), *n*-hexane (EMPLURA®, >95 %, Merck), toluene anhydrous (99.8 %, Sigma Aldrich) and *n*-hexane anhydrous (95 %, Sigma Aldrich) for the BDS experiments were used as received.

Silicon wafers (100, front side polished, CZ test grade, Silchem) were used as a substrate for the spin-coated layer. The wafers were stored under clean-room conditions until being cut. Prior to use, the wafers were cleaned with acetone (Chromasolv® plus, for HPLC 99.9 %, Sigma-Aldrich).

Figure 7.1 – Molecular structure of Matrimid 5218

7.2.2 Sample preparation

Cyclopentanone was used as a solvent to prepare 5 wt% and 20 wt% solutions of matrimid. The solutions were spin-coated (Laurell WS-400B-6NPP-Lite spin-coater) on a silicon wafer with a native oxide. For the preparation of the spectroscopic ellipsometry and dielectric samples, a two-step spin-coating program was used. During the first step, 10 s at 500 rpm, a 0.1 ml 5 wt% solution was deposited on the wafer. The second step involved an acceleration of 1710 rpm s⁻¹ to 3000 rpm at which it was kept for 1 minute. The samples for broadband dielectric spectroscopy were prepared inside a dust free room (ISO Class 6) to prevent contamination of the polymer film. For infrared spectroscopy, a spin-coating program of 5 min at 3000 rpm with an acceleration of 1710 rpm s⁻¹ was used. The 20 wt% solution was deposited prior to spin-coating due to the high viscosity.

After spin-coating, the samples have been annealed in a low temperature furnace (Carbolite HTMA 5/28) under a nitrogen atmosphere at a temperature of 250 °C for 1 hour, followed by a relaxation step at 350 °C for 6 hours using a ramp rate of 5 °C min⁻¹. To enable a controlled cooldown of the samples, the samples were cooled down to 25 °C with a rate of 0.1 °C min⁻¹.

7.2.3 *In situ* spectroscopic ellipsometry

Temperature dependent and penetrant dependent thickness and refractive index measurements of the spin-coated matrimid films were performed with spectroscopic ellipsometry. The data was modelled in the CompleteEase software package (J.A. Woollam Co.) in the wavelength range of 400-1000 nm. The substrate was modelled using the built-in temperature-dependent optical properties of silicon, on top of which a 2 nm native oxide layer was modelled. The matrimid films were modelled using an anisotropic Cauchy dispersion (fit parameters: ΔzA (anisotropy), A , B , C , k , and thickness). In case of penetrant induced swelling, an ambient with the optical constants of the penetrant was added to the model. Additional modelling details are provided in the Supplementary Information.

Temperature dependent measurements were performed with a M2000XI spectroscopic ellipsometer (J.A. Woollam Co.) equipped with a Linkam heating stage with quartz windows at an incident angle of 70°. The temperature measurements were performed under ultra-pure nitrogen at a flow rate of 100 mL min⁻¹. Temperature correction for the actual temperature of the sample was applied according to the procedure described previous by Kappert et al. [23] The optical retardance of the windows of the measurement cell was included using calibrated delta off-sets. The freshly spin-coated matrimid films were heated to 250 °C at a ramp of 5 °C min⁻¹ and hold at 250 °C for 1 hour, followed by another temperature ramp of 5 °C min⁻¹ to 350 °C at which the sample was held for another 6 hours. Finally, the sample was cooled down to 25 °C at a rate of 0.1 °C min⁻¹.

Penetrant induced swelling measurements were performed with an Alpha-SE ellipsometer (J.A. Woollam Co.) and a 500 µL liquid cell at a 70° angle of incidence. Measurements were performed in liquid *n*-hexane and toluene¹ at room temperature for approximately 24 hours. The liquid cell was filled with the penetrant using a 20 mL glass syringe. *In situ* data was recorded once every ~15 seconds. The optical retardance of the windows of the measurement cell were included using calibrated delta off-sets (see Supplementary Information).

For each penetrant induced swelling measurement, the swelling degree (Eq. 7.1) and the normalized refractive index (Eq. 7.2) were determined.

$$SD = \left(\frac{d_{\text{swollen}}}{d_{\text{dry}}} - 1 \right) \cdot 100 \% \quad [7.1]$$

where *SD* is the swelling degree, and d_{dry} and d_{swollen} are the dry and swollen thickness of the film, respectively.

$$n_{\text{norm}} = \frac{n_{\text{swollen}} - n_{\text{solvent}}}{n_{\text{dry}} - n_{\text{solvent}}} \quad [7.2]$$

where n_{norm} is the normalized refractive index, n_{dry} is the refractive index of the non-swollen polymer film, n_{swollen} is the refractive index of the swollen polymer film in a solvent, and n_{solvent} is the refractive index of the pure solvent.

¹ Toluene has a low dipole moment of 0.375 D and a very small electron donor parameter [43] and is therefore considered as a non-polar molecule.

7.2.4 *In situ* broadband dielectric spectroscopy (BDS)

BDS experiments were performed using a high resolution Novocontrol Alpha-A analyzer with a ZG4 test interface (Novocontrol technologies). A homemade sample cell from Leipzig University was used and could be immersed in the liquid penetrants. For the measurements, a parallel plate configuration was used where the bottom electrode was an 8 x 8 mm² silicon wafer (30 nm oxide on top) with a 200 nm sputtered aluminum layer on the backside and the spin-coated matrimid film on the top side. The 1 x 1 mm² top counter electrode was also a 30 nm SiO₂ on a silicon wafer with a 200 nm sputtered aluminum layer on the backside (see Figure 7.2).

Figure 7.2 – A schematic representation of the parallel plate electrode configuration used for the BDS measurements.

For each sample, the complex dielectric function was measured in a frequency range of 8×10^{-2} to 10^6 Hz at room temperature and the AC voltage was set at 1.0 V. Prior to each measurement, the sample was purged with dry nitrogen for 1 hour. For the penetrant induced swelling measurements, the BDS sample cell was completely immersed into the liquid penetrant and continuous frequency sweeps over a range of 24 hours were performed. To dry the sample, a continuous dried nitrogen flow over the sample was used to evaporate the residual penetrant. All measurements were performed in an environmental controlled dust free room with a temperature of 20 °C and humidity variations between 45-50 %.

To determine the specific relaxation times, τ , the dielectric loss peaks were fitted with the Havriliak-Negami relation (Eq. 7.3) using WinFit (Novocontrol technologies).

$$\varepsilon^* = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1 + (i\omega\tau)^{\alpha})^{\beta}} \quad [7.3]$$

7.2.5 *In situ* FTIR diffuse reflectance spectroscopy (DRIFT-FTIR)

DRIFT-FTIR spectra of ~3 µm thick matrimid films were obtained with a Tensor 27 FTIR spectrometer (Bruker optics) equipped with a high temperature reaction chamber used in conjunction with the Praying Mantis™ accessory (Harrick). Absorption measurements were performed in the range of 400-4000 cm⁻¹ with a resolution of 2 cm⁻¹ and the sample scan time was 1 min. A background

measurement was performed prior to each measurement using a clean silicon wafer with a native oxide.

For the temperature dependent measurements, an annealed 3 μm thick matrimid sample was heated as with the annealing of the thin film samples. An additional temperature dependent measurement was performed with a ramp of $1\text{ }^{\circ}\text{C min}^{-1}$ from 25 to 350 $^{\circ}\text{C}$ with steps of 25 $^{\circ}\text{C}$. At each temperature step, the sample was held for 30 min. The sample was then cooled down again at a rate of $1\text{ }^{\circ}\text{C min}^{-1}$ and a 30 min isothermal plateau was set at 325 $^{\circ}\text{C}$, 300 $^{\circ}\text{C}$, 250 $^{\circ}\text{C}$, 150 $^{\circ}\text{C}$, 125 $^{\circ}\text{C}$, 75 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$.

For the penetrant induced swelling measurement, the cell was kept at constant temperature of 25 $^{\circ}\text{C}$. Prior to the exposure of the penetrant, a dry measurement of the matrimid was taken. Next, the sample cell was filled with the liquid penetrant, with care taken to not cover the sample. After this, by using two bubblers in series, saturated penetrant vapor was flowed through the cell at a rate of 200 mL min^{-1} , and over a period of 24 hours, a spectrum was recorded every ten minutes. To account for the signal of the penetrant vapor during the penetrant induced swelling measurement, a reference measurement on a bare silicon wafer was performed using the same settings.

7.3 Results and Discussion

7.3.1 Thermal history effects

Matrimid is a glassy polymer, consequently the thermal history of the polymer will influence the physical properties. Upon heating a polyimide above its glass transition temperature, both crystallization^[24–27] and cross-linking^[28–30] phenomena have been reported. When considering matrimid, a polyimide with steric hindrance to linearization, reports of cross-linking can be found in literature^[30–33]. To determine whether cross-linking took place and to gain more information on the thermal properties of the sample after the thermal annealing, the annealing was followed *in situ* with temperature dependent spectroscopic ellipsometry. In Figure 7.3 the thickness and optical properties of a freshly spin-coated 290 nm matrimid film as function of temperature and time are shown. Based on the optical modelling of the matrimid film, anisotropy was observed in the freshly spin-coated film (see Supplementary Information for modelling details), which can be the result of stress induced during the spin-coating process. Upon heating, the decrease in thickness caused by the removal of the spin-coating solvent competes with the thermal expansion induced by the increase in temperature as is shown in Figure 7.3. Isothermal annealing of the matrimid above 350 $^{\circ}\text{C}$ removed the anisotropy within the sample and a small decrease in thickness ($\sim 1\text{ nm}$) was observed. Upon cooling down from 350 $^{\circ}\text{C}$ to 25 $^{\circ}\text{C}$, a glass transition

temperature was observed at 309 °C and the anisotropy increased. The complete thickness and refractive index dependence as function of the annealing process is provided in the Supplementary Information.

Figure 7.3 – The thickness (left axis), ordinary refractive index (n_o) and extraordinary refractive index (n_e) (right axis) as function of the annealing temperature and time. Upon heating to 250 °C (left), during 6 hours isothermal stage at 350 °C (middle), and upon cooling to 25 °C (right). A glass transition temperature was observed at 309 °C.

After the thermal heat treatment, the matrimid films were found to be insoluble in cyclopentanone. In Figure 7.4, the *in situ* temperature dependent DRIFT-FTIR absorbance as measured during the annealing treatment are shown. Upon the evaporation of the spin-coating solvent, cyclopentanone, strong changes in the absorbance spectra for each specific vibration were observed. Cyclopentanone has a broad and strong absorbance peak at 1750 cm^{-1} , and a strong absorbance peak at 1150 cm^{-1} , which are both visible in the fresh spin-coated sample but disappear after the first heating ramp to 250 °C, showing that the cyclopentanone was removed. Upon subsequent heating to 350 °C, the strongest change was observed for the C-N-C axial stretch, which shifts to the lower wavenumbers. This can indicate that polymer chains are brought in closer proximity to each other and a more conjugated system was obtained. This is in agreement with literature, where it is suggested slight cross-linking occurs via the formation of charge transfer complexes between the benzene rings and the imide rings, allowing the transfer of π -electrons [27,34–36].

Figure 7.4 – Temperature dependent DRIFT-FTIR absorbance spectra of matrimid during the annealing of a freshly spin-coated film at 25 °C to 350 °C. Black line: 25 °C, freshly spin-coated. Blue: 55 min at 250 °C, all cyclopentanone is removed (left and right figure), Orange: 5 min at 350 °C, Dark red: 5 hours and 55 min at 350 °C, dashed blue: 250 °C upon cooling, dashed black: 25 °C after the heat treatment. For the C-N-C axial stretch (middle) a strong shift to the lower wavelengths was observed upon heating to 350 °C, which was reversed on cooling.

7.3.2 Penetrant induced swelling

7.3.2.1 *In situ* spectroscopic ellipsometry

The swelling degree and the normalized ordinary and extraordinary refractive indices as measured with *in situ* spectroscopic ellipsometry are shown in Figure 7.5. Matrimid swells about seven times more in toluene (Swelling degree, $SD = 28\%$) than in *n*-hexane ($SD = 4\%$), which is comparable to what has been observed before^[37]. The absolute observed swelling degrees are lower compared to previous literature results, due to the difference in annealing temperatures used (250 °C in literature versus 350 °C in this study). Interestingly, the anisotropy within the matrimid film remained and even increased upon exposure to the penetrant. This observed strengthening of the degree of anisotropy within the matrimid film upon swelling is likely the result of the cross-linking of the matrimid film during the annealing treatment, allowing for a stronger swelling effect in the direction of the optical axis (n_e) compared to the swelling perpendicular to the optical axis (n_o). This indicates that the matrimid chain structure is different in the *z*-direction as compared to the *x-y* direction of the substrate.

Figure 7.5 – The swelling degree (SD , left) and the normalized refractive indices (right) as function of time in a ~ 260 nm matrimid film. The filled black symbols represent the swelling data in toluene, while the open symbols represent the swelling data in n -hexane. The grey area refers to the removal of the solvent from the matrimid film by applying a nitrogen flow over the sample. It can be observed that upon drying $SD > 0$, hence, not all the penetrant is removed.

7.3.2.2 Broadband dielectric spectroscopy

In order to understand the difference in swelling degree of matrimid in n -hexane and in toluene, broadband dielectric spectroscopy (BDS) was applied *in situ* to probe the interactions of the polymer chains with the two different penetrants. In literature, for matrimid 5218, Comer et al. observed a γ -relaxation, a β -relaxation and an α -relaxation. Konnertz et al. observed a broad β^* -relaxation and an additional conductivity term. Further mechanical measurements showed that the observed broad β^* -relaxation consisted of two processes which merge together at higher frequencies or temperatures. Both Comer et al. and Konnertz et al. studied non-crosslinked matrimid, and thus the behavior they observed is strongly dependent on the thermal history of the matrimid, which partly explains the differences in the relaxation behavior between these two studies.

In Figure 7.6A,B the dielectric behavior of dry matrimid and of matrimid exposed to toluene at room temperature is shown. For a dry matrimid sample after annealing, two overlapping β -relaxations were observed. Upon exposure to toluene, the two β -relaxations separated with β_2 shifting to higher frequencies. As shown during the ellipsometry measurements, at room temperature the toluene could not completely be removed upon drying with a dried nitrogen flow. For this reason, upon drying with a continuous dried nitrogen flow, β_2 shifts back to a lower frequency, but not to the original frequency. In Figure 7.6C, the relaxation times as obtained by the Havriliak-Negami fits of the β_1 - and β_2 -relaxation are shown as function of the

exposure time to toluene. Within the first few hours of penetrant exposure, a continuous shift of the β_2 -relaxation to the higher frequencies was observed, but after ~ 5 hours the dielectric behavior of matrimid in toluene was stable. The shift of the β_2 -relaxation to the higher frequencies was shown to be consistent over two different experiments as shown in the Supplementary Information. Furthermore, upon exposure to toluene, at the lower frequencies an increase in the dielectric loss was observed. This increase may be a conductivity effect due to the presence of traces of contaminants in the toluene solution, which diffused into the matrimid due to the high swelling degree of matrimid in toluene.

Figure 7.6 – ϵ'' (A) and ϵ' (B) for a ~ 260 nm dry matrimid film (closed black squares), exposed to toluene for 1 hour (blue open circles), 22.5 hours (orange open circles) and after 2 hours of drying in a nitrogen flow after toluene exposure (open square). (C) The relaxation times of the two β -relaxations were determined for each frequency sweep time step and shown as function of exposure time. The grey margin above the symbols represent the standard error of the fit (in positive direction only).

In Figure 7.7A,B the dielectric behavior of dry matrimid and of matrimid exposed to *n*-hexane at room temperature is shown. The dielectric changes observed for matrimid exposed to *n*-hexane are not repeatable for each measured sample, unlike the case for toluene exposure. However, it is shown that in the case of *n*-hexane, both β_1 - and β_2 -relaxations are influenced by the presence of *n*-hexane and this behavior is not reversible as shown by the removal of *n*-hexane by a nitrogen flow. Also, in the case of *n*-hexane exposure, no additional increase in the dielectric loss at the low frequencies was observed. The difference for *n*-hexane compared to toluene is that the swelling degree of matrimid in *n*-hexane is much lower compared to in toluene, inhibiting diffusion of contaminants into the matrimid.

Figure 7.7 – ϵ'' (A) and ϵ' (B) for a ~260 nm dry matrimid film (closed black squares), exposed to *n*-hexane for 1 hour (blue open circles), 22.5 hours (orange open circles) and after 2 hours of drying in a nitrogen flow after *n*-hexane exposure (open square). (C) The relaxation times of the two β -relaxations were determined for each frequency sweep time step and shown as function of exposure time. The grey margin above the symbols represent the standard error of the fit (in positive direction only).

The fact that toluene only effects the β_2 -relaxation, namely through speeding up the relaxation time, while in *n*-hexane both β_1 and β_2 are effected and can both be slowed down or speed up, shows that both penetrant molecules have different interactions with matrimid.

7.3.2.3 Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT-FTIR)

DRIFT-FTIR was used to gain a better understanding on the molecular origin of the β -relaxations as observed in matrimid [38,39]. In Figure 7.8 the C-N-C axial stretch absorbance of matrimid as function of the *n*-hexane vapor exposure time (A) and toluene vapor exposure time (B) is shown. For toluene exposure, with increasing toluene exposure times, a tendency to shift to lower wavenumbers with decreasing intensities (see Figure 7.8) was visible. In the case of *n*-hexane, no such trend was observed. In none of the other matrimid vibration modes a significant change or trend was detected as function of the penetrant exposure times. Although a similar change in the C-N-C axial shift was observed during the temperature dependent measurement (see Figure 7.4), the changes observed during the penetrant dependent measurement were less strong than as would have been expected based on the strong changes that were observed in the BDS spectra and the expected swelling degrees for toluene and *n*-hexane respectively. This is most likely due to the limited swelling that could be obtained during the penetrant induced swelling measurement with DRIFT-FTIR. Unlike for the spectroscopic ellipsometry and BDS experiments, here the swelling was induced using toluene and *n*-hexane vapor, generated by two bubblers in series. The design of the *in situ* cell was not optimal as such that it was highly likely a solvent activity lower than 1 (which is the solvent activity in a pure liquid), was obtained. As shown by Favre et al.^[40] lower solvent activities result in significantly lower sorption of the penetrant. The lower sorption of the penetrant can result in smaller changes in the relaxation behavior of the polymer chains, decreasing the sensitivity of the DRIFT-FTIR measurement.

Figure 7.8 – C-N-C axial stretch for a $\sim 3\ \mu\text{m}$ matrimid film on top of a silicon wafer in *n*-hexane and in toluene. The dashed black line represents the background signal of the penetrant used as measured using a bare silicon wafer. The indicated time represents the exposure time to the penetrant. In case of toluene swelling, after ~ 24 hours, additional toluene was added to in the cell, to enhance the penetrant activity and to enhance the swelling and visualize the trend in swelling. In case of *n*-hexane, the hexane was already added in the beginning in order to ensure significant swelling for detection. The measurement was therefore continued for 3 days in order to detect a trend if present.

7.3.2.4 Interpretation penetrant induced swelling in matrimid

When exposed to toluene, a strong penetrant induced swelling could be observed ($\sim 28\%$) with spectroscopic ellipsometry, and the relaxation time of β_2 -relaxation was decreased as observed with BDS. This decrease in relaxation time, indicates a decrease in energy, a trend which was observed for the C-N-C axial stretch in the DRIFT-FTIR spectra. Together with the high swelling degree, it is speculated that toluene interacts in particular with the benzene group in the diamine (DAPI), breaking intersegmental interactions as the π - π interaction between the toluene molecule and the benzene ring in the matrimid polymer chain are stronger than the intersegmental interactions between the benzene rings (see also Figure 7.9). The role of the benzene ring and its accessibility to the toluene molecule is also confirmed by the reported lower sorption rates in literature for toluene in for example P84^[37,41]. P84 is a composite polyimide, where the diamine group is much less bulky, improving the alignment of the molecule. As a result, however, the benzene groups are much more difficult to access. A similar phenomenon based on polarity strength was suggested for the sorption of CO_2 in cellulose acetate and polymethylmethacrylate (PMMA). Koros et al.^[42] showed that with an increasing easily accessible carboxyl concentration inside the polymer, the sorption of CO_2 increased. It was therefore concluded that the interactions of CO_2 with the polar

groups carboxyl groups in the matrimid chain are stronger than the intermolecular interactions between the matrimid chain segments.

In the case of *n*-hexane sorption, the hexane is not able to interact with the matrimid polymer via either polar interactions or π - π interactions and can only interact with the matrimid chains via Van der Waals interactions. Other than that, *n*-hexane will fill up the excess free volume available (see also Chapter 3), providing only for a limited interaction with the matrimid polymer chains. The fact that in the BDS spectra of matrimid in *n*-hexane non-consistent changes were observed is probably governed by how locally the *n*-hexane molecule can penetrate in-between the matrimid polymer chains. Possible interaction sites are the methyl groups in the diamine (DAPI). However, due to the overlapping strong signal of *n*-hexane itself, this could not be confirmed via the DRIFT-FTIR measurements. Also, since Van der Waals interactions are much weaker interactions compared to the π - π interactions, the current sensitivity of the DRIFT-FTIR measurement may be too low to measure noiseless signal changes as a result of *n*-hexane interactions with matrimid. In order to improve the sensitivity of the DRIFT-FTIR measurement, the signal intensity ought to be improved by ensuring that the *in-situ* cell allows for liquid measurements.

To confirm the role of the π - π interaction between the toluene and matrimid, swelling experiments with bulky aromatic solvent such as mesitylene or xylene should be performed. Bulky aromatic solvents are more prone to steric hindrance, reducing the π - π interactions and as a result a lower swelling should be observed.

Figure 7.9 – A schematic illustration of the different interactions between toluene and *n*-hexane with Matrimid 5218.

7.4 Conclusions

In this work, the molecular origin of the different penetrant interactions with matrimid were investigated using a combination of *in situ* characterization techniques: SE, BDS and DRIFT-IR). The thermal annealing treatment applied to the matrimid films resulted in a small degree of cross-linking of the matrimid films, which caused the films to become insoluble in cyclopentanone. At room temperature, two overlapping β -relaxations were observed for dried matrimid films. Upon exposure to a penetrant, a separation of the two different β -relaxations was observed. In case of toluene exposure, a strong penetrant induced swelling was observed ($\sim 28\%$), and the relaxation time of β_2 -relaxation was decreased. Toluene is speculated to break up intersegmental interactions and to form a π - π interaction with the benzene rings in the diamine, resulting in a decrease in energy of the C-N-C axial stretch as observed during the DRIFT-FTIR measurements. When matrimid was exposed to *n*-hexane, a swelling degree $\sim 4\%$ was observed, however BDS results show that *n*-hexane interacts with multiple molecular moieties in the matrimid chain, changing both β -relaxations. Unlike toluene, the β -relaxations were found to inconsistently change (speed up or slow down) versus toluene where relaxation time consistently decreased. *n*-Hexane fills up the excess free volume available inside the polymer matrix and the induced relaxation time changes are likely governed by the local penetration of *n*-hexane in-between the matrimid polymer chains. The exact interaction of the *n*-hexane molecules with the different groups in matrimid could not be revealed due to the limited sensitivity that was obtained during the DRIFT-FTIR measurement, which motivates further investigation into the improvement of *in situ* infrared spectroscopy cells designed for liquid measurements.

7.5 Acknowledgements

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7.6 Supplementary Information

7.6.1 Spectroscopic ellipsometry

To determine the best optical model for matrimid, different optical models were compared for a dry matrimid sample. In Table S7.1, an overview of the outcomes of the different optical models is presented.

Table S7.1 – Overview of the different optical models and their fit parameters for 5 random spots on a dry matrimid sample. The error margins indicate the standard deviation. #Fit indicates the number of fit parameters used in the optical model, *RMSE* is the root mean squared error for the fit, n_0 is the refractive index determined at 632.8 nm, k is the absorption parameters and %grading represents the thickness inhomogeneity perpendicular to the substrate.

Model choice:	#Fit	<i>RMSE</i>	Thickness (nm)	n_0 at 632.8 nm	k	%grading
d , Cauchy A, B, C	4	21.9 ± 0.4	256.5 ± 0.5	1.648		
d , Cauchy A, B, k	4	10.0 ± 0.2	263.5 ± 0.5	1.617	0.009	
d , Cauchy A, B, C, k	5	8.5 ± 0.1	263.3 ± 0.4	1.619	0.009	
d , Cauchy A, B, k, dzA (anisotropy)	5	9.8 ± 0.2	263.5 ± 0.5	1.618	0.009	
d , Cauchy A, B, C, dzA (anisotropy)	5	19.3 ± 0.6	257.3 ± 0.5	1.648		
d , Cauchy A, B, k, C, dzA (anisotropy)	6	4.9 ± 0.2	263.7 ± 0.5	1.621	0.008	
d , Cauchy $A, B, C, k, grading$	6	8.0 ± 0.2	264.1 ± 0.4	1.616	0.010	4.0 ± 0.9

7.6.1.1 Thermal annealing

In Figure S7.1 the change in the refractive indices and the thickness is shown as function of the complete annealing treatment. Upon heating, the decrease in thickness caused by the removal of the spin-coating solvent competes with the thermal expansion induced by the increase in temperature as is shown in Figure S7.1A. After an isothermal timestep at 250 °C, all residual solvent was removed and thermal expansion upon heating to 350 °C was observed (Figure S7.1C). At the same time, as 350 °C is above the glass transition of matrimid, the anisotropy decreased. A small but continuous decrease in thickness (~1 nm) and no significant changes occurred in the refractive index during the isothermal stage at 350 °C. The small change in thickness and no change in refractive index during this isothermal stage indicate that any structural changes that occur, such as cross-linking or

crystallization, are of a very small degree. During a slow cooling to 25 °C (Figure 7.3E), a glass transition temperature was observed at ~309 °C and the anisotropy within the sample again increased.

Figure S7.1 – The thickness (right axis), ordinary refractive index (n_o) and extraordinary refractive index (n_e) as function of the annealing temperature and time. Upon heating to 250 °C (A) followed by an isothermal stage at 250 °C (B), residual solvent was evaporated. Upon further increase in temperature, anisotropy in the sample was being removed and thermal expansion was observed (C). During the 6 hours isothermal stage (D), a slight decrease in thickness (~1 nm) and no changes in the refractive indices were observed. Upon cooling to 25 °C (E), a glass transition temperature was observed at 309 °C and anisotropy was increased.

7.6.1.2 Penetrant induced swelling

For the *in situ* swelling measurements, to avoid over parameterization, a wavelength range of 450 nm to 900 nm was used. This allowed for removal of eliminating the absorption, k , which is strongly correlated with the thickness. For swelling measurements with toluene, an additional gradient was considered, as shown in Figure S7.2.

Figure S7.2 – Swelling degree (SD) and mean squared error (MSE) as function of time, as a result of a simple/normal optical model (left) and the application of a gradient in the optical model (right). The application of a gradient yielded in an improved optical model for the first ~2-3 hours. Afterwards, the inhomogeneity was close to 0.

The calibration of the window offsets during the liquid swelling measurements was performed using a 60 nm SiO_2 calibration wafer which was measured *ex situ*, *in situ* dry and *in situ* with the liquid penetrant. The optical constants of *n*-hexane and toluene were determined with a digital multiple wavelength refractometer (Schmidt Haensch ATR-L) at 20°C for 7 different wavelengths (365.0 nm, 400.0 nm, 450.0 nm, 500.0 nm, 590.0 nm, 700.0 nm, 800.0 nm). A Cauchy dispersion relation was fitted to the obtained data to determine the refractive index at 632.8 nm. The fixed optical parameters used for the optical modelling in the liquid penetrants are shown in Table S7.2.

Table S7.2 – The optical constants as used for toluene and *n*-hexane in the optical model at 20°C.

Penetrant	n at 632.8 nm ± 0.001	A	B	C	Window offset
Toluene	1.494	1.4755	0.0066	0.0003	-0.825
<i>n</i> -hexane	1.374	1.3665	0.0031	0	1.431

7.6.2 DRIFT-FTIR temperature dependence

The DRIFT-FTIR absorbance spectra for each characteristic IR vibration of matrimid before, during and after annealing treatment are shown in Figure S7.3.

Figure S7.3 – Temperature dependent DRIFT-FTIR absorbance spectra of matrimid during the annealing of a freshly spin-coated film at 25°C to 350 °C. Black line: 25°C, Blue: 55 min at 250 °C, Orange: 5 min at 350 °C, Dark red: 5 hours and 55 min at 350 °C, dashed blue: 250 °C upon cooling, dashed black: 25 °C after the heat treatment.

In Figure S7.4, the FTIR temperature dependence of an *annealed* ~3 μm matrimid film is shown. The C-N-C axial stretch and the C=C aromatic stretching are strongly influenced by the temperature and show a decrease in wavenumbers. This indicates a lower amount of energy is required to vibrate these specific groups. The effect is reversible, as with decreasing temperatures, the original wavenumbers were obtained again.

Figure S7.4 – Temperature dependent IR spectra of ~3 μm matrimid film. Strong shifts to the lower energies were observed for the C-N-C axial stretch and the C=C aromatic stretching. The dashed black line indicates the FTIR spectrum at 25°C after the heat treatment. Resolution is 2 cm^{-1}

7.6.3 Reproducibility of the broadband dielectric spectroscopy measurements

In Figure S7.5, the BDS results of toluene induced swelling in the second matrimid film is shown. As also shown in Figure 7.6, Toluene consistently speeds up the β_2 -relaxation, while the β_1 -relaxation remains unchanged.

Figure S7.5 – Reproducibility of ϵ'' (A) and ϵ' (B) for a ~260 nm dry matrimid film (closed black squares), exposed to toluene for 1 hour (blue open circles), 24 hours (orange open circles) and after drying with a continuous nitrogen flow after *toluene* exposure (open square). (C) The relaxation times of the two β -relaxations were determined for each frequency sweep time step and shown as function of exposure time. The grey margin above the symbols represent the standard error of the fit (positive direction only). For both samples, no changes in the β_1 -relaxation was detected, and the β_2 -relaxation shifts to the higher frequencies.

In Figure S7.6, the BDS result for the second sample of *n*-hexane induced swelling in a matrimid film is shown. *n*-Hexane influences the relaxation dynamics of both β -relaxations, but no consistent change was observed when considering the results of both matrimid samples (Figure 7.7 and Figure S7.6).

Figure S7.6 – Reproducibility of ϵ'' (A) and ϵ' (B) for a ~260 nm dry matrimid film (closed black squares), exposed to *n*-hexane for 1 hour (blue open circles), 16.5 hours (orange open circles) and after drying with a continuous nitrogen flow after *n*-hexane exposure (open square). (C) The relaxation times of the two β -relaxations were determined for each frequency sweep time step and shown as function of exposure time. The grey margin above the symbols represent the *positive* standard error of the fit. Both β -relaxations interact with the *n*-hexane, but the effect is not consistent.

7.6.4 DRIFT-FTIR penetrant induced absorbance spectra

For both *n*-hexane and toluene *in situ* DRIFT-FTIR measurements, a reference measurement was performed on a bare silicon wafer using the same measurement conditions. In Figure S7.7 (*n*-hexane) and Figure S7.8 (Toluene), the IR absorbance spectra for different matrimid samples are shown. In these figures, the *in situ* was corrected for the absorbance of the penetrant by subtracting the reference signal of the pure penetrant on a bare silicon wafer.

Figure S7.7 – Corrected IR-absorbance spectra for 2 different matrimid samples exposed to *n*-hexane. The dashed black line represents the reference measurement of a bare silicon wafer exposed to *n*-hexane. The black line is the original dry matrimid sample. The dashed red line represents the longest exposure time (i.e. 3 days for Hexane-2) and the red line represents 26 and 33 hours exposure respectively for hexane-1 and hexane-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).

Figure S7.8 - Corrected IR-absorbance spectra for 2 different matrimid samples exposed to toluene. The dashed black line represents the reference measurement of a bare silicon wafer exposed to toluene. The black line is the original dry matrimid sample. The dashed red line represents the adsorbance spectra after the addition of extra liquid toluene into the measurement cell (i.e. 3 hours after additional toluene was added) and the red line represents 26 and 27 hours exposure respectively for toluene-1 and toluene-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).

7.6.4.1 Original data

In Figure S7.9 and Figure S7.10 the original absorbance spectra of matrimid for *n*-hexane and toluene exposure respectively are shown.

Figure S7.9 – Original IR-absorbance spectra of 2 different matrimid samples exposed to *n*-hexane. The dashed black line represents the reference measurement of a bare silicon wafer exposed to *n*-hexane. The black line is the original dry matrimid sample. The dashed red line represents the longest exposure time (i.e. 3 days for hexane-2) and the red line represents 26 and 33 hours exposure respectively for hexane-1 and hexane-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).

Figure S7.10 – Original IR-absorbance spectra of 2 different matrimid samples exposed to toluene. The dashed black line represents the reference measurement of a bare silicon wafer exposed to toluene. The black line is the original dry matrimid sample. The dashed red line represents the absorbance spectra after the addition of extra liquid toluene into the measurement cell (i.e. 3 hours after additional toluene was added) and the red line represents 26 and 27 hours exposure respectively for toluene-1 and toluene-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).

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Chapter 8

Reflection and Perspectives

"Tactics is knowing what to do when there is something to do;

Strategy is knowing what to do when there is nothing to do."

- Savielly Tartakower (1887-1956) -
Polish and French Chess Grandmaster

The overall objective of this thesis is to work towards an improved understanding of the swelling dynamics and mechanisms of thin polymer films, such as membranes exposed to an organic penetrant. A sole characterization based on performance tests of the polymer material will not provide the required insight on what material properties dominate the material performance and therefore limit the opportunity to improve the process design. In order to understand the performance of a polymer material when exposed to an organic penetrant, the interaction between the penetrant and the polymer material should be studied in detail. In this thesis, *in situ* swelling studies have been used as the method of choice to obtain an enhanced understanding of the interaction between a penetrant and the polymer material over time under realistic operating conditions.

In situ spectroscopic ellipsometry (iSE) and broadband dielectric spectroscopy (BDS) have been utilized and assessed as tools to reveal the swelling dynamics of thin glassy polymer films. It was shown that iSE can be used reliably for thin polymer films with a minimum thickness of 100 nm in a liquid environment, but care should always be taken to correct for the non-idealities such as changing window offsets and errors in the optical constants of the liquid medium. Taking the inaccuracies of iSE for measurements on films thinner than 100 nm in a liquid medium into account, iSE has been applied successfully to reveal a general swelling behavior in glassy polymers and to reveal the presence of a transition layer between the free surface and the bulk in (ultra)thin polystyrene films. From an application point of view, in this thesis iSE has been applied to study the swelling behavior of a hyper-cross-linked poly(PDMS-POSSimide), an interfacial polymerized film, to assess its potential in environments containing organic solvents. Additionally, iSE in combination with microscopy techniques has been applied to reveal the underlying problem of the application of nanofiltration desalination membranes which utilize a polysulfone support in hydrocarbon polluted wastewater environments. Dewetting between the polysulfone support and the selective thin film top layer of the composite membrane was determined to be the cause of membrane failure in non-ideal water solutions such as water-toluene. Finally, from a more fundamental point of view, the use of broadband dielectric spectroscopy to reveal the underlying polymer chain relaxations and interaction upon exposure to a penetrant was investigated. It was shown that *n*-hexane is likely to interact only via Van der Waals contributions, while toluene can interact through π - π interactions with matrimid. As a result, seven times higher swelling was observed for matrimid in toluene compared to matrimid in *n*-hexane.

In the following sections, a reflection on the findings within this thesis and suggestions and perspectives for future research are provided. In the first section, the perspectives of extending the research presented in this thesis more towards

membrane applications are discussed. Suggestions are given on studying multicomponent mixtures in general and non-ideal mixtures of water specific alone. Also, the potential of combining spectroscopic ellipsometry experiments with quartz crystal microbalance with dissipation monitoring experiments is discussed. In the second section, a reflection on the information obtained on the swelling dynamics from a fundamental point of view is provided and a review is given on the future potential of using BDS as a tool to study penetrant-polymer interactions. Finally, the strength of theoretical modelling in terms of supporting, understanding and designing experimental measurements is discussed and an overall conclusion is provided.

8.1 Towards Membrane Applications

8.1.1 Non-ideal mixtures: organic contaminants in water

In Chapter 5, it is shown that for a non-ideal mixture of water saturated with toluene an enhanced transport of water through the polysulfone film occurs. This eventually results in the delamination of the polysulfone layer. For wastewater treatment membrane applications, this interplay between toluene, water and the polysulfone support, is shown to have a dramatic effect on the membrane performance. In addition to Chapter 5, to gain a better understanding of the interactions between water and contaminant and water/contaminant mixture with polysulfone, measurements of a thin polysulfone film in water saturated with *n*-hexane and in water saturated with methylethylketone (MEK, polar and aprotic) were performed. In Table 8.1, the properties of the water/contaminant mixture and the Hildebrand solubility parameters of the different organic contaminants are shown. For neither the water/*n*-hexane and water/MEK mixture a dewetting mechanism of polysulfone was observed. For a water/toluene mixture, dewetting of the polysulfone layer occurs. The activity coefficient of toluene in water is very high compared to *n*-hexane and MEK, indicating a strong deviation from ideal behavior for the water/toluene mixture. This, in combination with a relative high toluene solubility in water and the proximity of the solubility constants of toluene and polysulfone, allows for sufficient toluene to diffuse into the polysulfone film, inducing a substantial swelling. In addition, there is a high availability of water for which sorption into the swollen polymer is unfavorable, while it does have an affinity for the silicon interface. Over time, accumulation of water between the silicon interface and the swollen polymer results in dewetting. For a system in which toluene is saturated with water, similar observations are made (results not presented here), but on a much longer timescale; this is due to the lower availability of water. For water/*n*-hexane mixtures, this dewetting is not likely to occur due to the limited *n*-hexane induced swelling. In case of the water/MEK mixture, MEK

induces sufficient swelling of the polysulfone film (similar to toluene), however MEK is miscible with water, rendering water sorption into the swollen polymer less unfavorable as compared for the water/toluene system.

Table 8.1 – Properties of organic contaminants in water and their Hildebrand solubility parameter (δ_s). For water $\delta_s=47.9 \text{ MPa}^{0.5}$ [1] and for polysulfone $\delta_s=23.7 \text{ MPa}^{0.5}$ [2].

Organic contaminant	Activity coefficient (γ^∞) at 25 °C [3]	Solubility in water (mg/L) at 25 °C	$\delta_s(\text{MPa}^{0.5})$ [1]
Toluene	9186 [4]	517 [5]	18.2
<i>n</i> -Hexane	2940 (at 20°C) [6]	9.5 [7]	14.9
MEK	27.8 [8]	26.7x10 ⁴ [9] (miscible)	19.0

Until now, for membranes used in wastewater treatment applications, it has been difficult to predict the membrane performance and possible failure mechanisms, due to the strong deviation from ideal behavior that is often observed for dissolved organic compounds in water. Also, mixtures are often complex and do not possess a constant composition. Within such a multi-component mixture, the unknown interplay between different components is what makes the membrane performance unpredictable [10–14].

In Chapter 5 it was shown that the unpredicted membrane failure of desalination membranes with a polysulfone support is the result of a combination of factors, such as the non-ideality of the mixture, solubility of the contaminant in water and affinity for the different membrane materials. Future research should be focused on creating an improved understanding of different interactions between different components in the non-ideal system. Which interaction or combination of interactions result in phase separation between the organic component and water upon diffusion into the polymer film? Which interactions dominate diffusion of the organic contaminant into the polymer film? Is it possible to assign design parameters and threshold values in terms of non-ideality, solubility in water and affinity between the contaminant and the polymer film in order to predict unexpected behavior of the membrane such as failure or excessive swelling? To answer this, a systematic swelling study on the sorption behavior of typical membrane materials used for wastewater treatment is required, utilizing a wide variety of possible organic contaminants in varying concentrations.

8.1.2 Sorption studies with more than one penetrant

Throughout this thesis, iSE was used as a tool to study the swelling behavior in a wide variety of polymer/penetrant combinations. In Chapter 3, the generic characteristics of solvent induced swelling of glassy polymers have been

discussed., with a particular focus on a universal interconnection between the extent of the filling of the excess free volume and the dilation of the polymer matrix. In Chapter 4, iSE is utilized to reveal stratified solvent swelling dynamics that can occur at a thin outer region of glassy polystyrene films. Both chapters provide a fundamental insight in the swelling behavior of thin polymer films, which both contribute to the improvement of predicting the behavior of thin polymer films exposed to a penetrant. However, both chapters deal with simple systems that involve only a single type of penetrant, while membrane applications by definition involve mixtures of multiple components ^[15,16]. In addition to the changes that a single species can induce in the dynamics of the polymer, the presence of additional species further complicates understanding and predicting of the mass transport through polymer films. Among the strategies for describing multi-component mass transport through a dense membrane the generalized Maxwell-Stefan model is often used^[18,19]. This model explicitly considers the friction forces between the different species within a mixture. However, the friction between different mobile species is negligible, because of the predominant friction between the polymer material and each species. Nonetheless, the very presence of a mobile species can affect the molecular dynamics of the polymer and consequently also the mobility of other species that are present. Incorporating these mobility changes in models describing the diffusion coefficients ^[20,21] is not straightforward, which limits the accuracy of the mass transport predictions. Especially in glassy polymers, where the diffusion coefficient is 3-4 orders of magnitude smaller as compared to in rubbery polymers ^[25], an estimation error in the mobility will have a large impact ^[14].

In addition, swelling of a glassy polymer by one type of species can also affect the solubility of any other species that are present. Although the generalized Maxwell-Stefan approach is based on the appropriate thermodynamic driving forces for diffusion, it cannot easily account for the mutual interrelations between sorption of different species. As a consequence, even the Maxwell-Stefan approach for describing solution-diffusion has limited value for predicting the membrane performance in organic solvent nanofiltration applications ^[18,23,26-28]. Steps towards improved predictions include experimental multi-component sorption experiments, which should be combined with fundamental thermodynamics describing the mixture including the non-equilibrium polymer.

Chapter 3 describes a systematic study on the generalized behavior of penetrant sorption in glassy polymers. Future research should focus on extending the research in chapter 3 to multi-component mixtures. Specifically, on the specific interactions between the different penetrants, the free volume and the polymer itself. Will all penetrants diffuse into the free volume, will one penetrant enhance the sorption of another penetrant, inducing higher swelling degrees? iSE

measurements can provide experimental results on the sorption behavior, but it is an indirect characterization technique. Therefore, introducing additional parameters (i.e. additional penetrants) into the system will make the results harder to interpret. For this reason, a combination of *in situ* characterization methods should be addressed to obtain additional information. Here quartz crystal microbalance with dissipation monitoring (see also section 8.1.4) and *in situ* infrared spectroscopy can be considered as useful complementary techniques to iSE. Both techniques have advantages and disadvantages which should be considered carefully. In the case of *in situ* infrared spectroscopy it has the strong potential to provide more information on the chemical interactions^[29], but in order for it to be applied successfully in multi-component penetrant studies, the sensitivity of the technique towards thin polymer films should be researched (see also section 8.2.1).

Additionally, when studying the sorption of multi-component mixtures in polymers, the in-line monitoring of the outgoing composition and a good control on the composition of the ingoing composition is required. This will allow for completing the mass balance of the in- and outgoing components in the measurement cell, providing information on the amount of penetrant that interacts with the polymer. For an accurate quantification of the concentration of the different penetrants, gas chromatography combined with mass spectroscopy (GC-MS) could be used. However, from a practical point of view, GC-MS is an expensive technique and requires a substantial investment. An indirect measurement of the outgoing composition can also be obtained by incorporating an inline density measurement by using for example a Coriolis mass flow meter^[30]. Although not as accurate as a GC-MS, a Coriolis mass flow meter can be used for both liquid and gas measurements and from the density a deduction of the different concentrations can be made^[31].

8.1.3 Characterization of interfacially polymerized films

In order to limit the operating pressure in reverse osmosis (RO) and nanofiltration applications (NF), to obtain the desired flux, the thickness of the separating layer needs to be controlled and the thickness should be ~200 nm or less^[32]. For this reason, membranes applied in RO and NF applications are often thin film composite membranes (TFC). As described in section 1.3.2, these thin films are often synthesized via an interfacial polymerization (IP) technique in a localized fashion^[33]. Since the reaction conditions, such as the reaction time, availability of the reactants, temperature, etc. govern the final properties of the thin IP film, it is important that upon characterizing IP film, the preparation conditions are similar to conditions used for membrane fabrication. To illustrate, in Chapter 6, the swelling behavior of an interfacial polymerization derived poly(PDMS-POSSimide) film was

studied, by depositing a free standing film onto a silicon wafer. Although a significant swelling in ethanol was observed, permeation experiments with ethanol showed a complete retention of ethanol. Possible reasons for these contradictory results can be the difference in the POSS concentration in the researched film via iSE and in the thin film composite membrane itself, due to the difference in preparation methods (free standing vs. supported). Also, the free-standing film formed, is mechanically very fragile, making the deposition of the free-standing IP film onto the silicon substrate very hard. The deposited IP film on top of the silicon wafer always showed some folds, wrinkling and a large thickness inhomogeneity. Preferably, the swelling behavior of the poly(PDMS-POSSimide) film is to be studied as a TFC membrane, meaning that the alumina support functions as the substrate, with the IP film on top, similar as to the membrane studied in Chapter 6. Raaijmakers et al.^[34] showed that for gas separations, such studies are possible. However, for the ellipsometric analysis, measuring a thin film composite system consisting of an α -alumina layer, a γ -alumina layer and an IP film on top requires a complicated optical model for which knowledge about the void fraction of both the α -alumina and γ -alumina is required.

In general, knowledge about the porosity can be obtained by measuring each layer independently. However, when immersing the full thin film composite membrane into a liquid or vapor, the penetrant can condense in the pores of the substrate, changing the optical constants, making the interpretation of the iSE measurement very difficult. For this reason, there is a need for a simpler system that mimics the localized formation of an IP film on top of a substrate. To simplify the optical modeling in an iSE measurement, and to simulate the formation of an IP layer on top of another layer which functions as a reservoir, a suitable layer can be coated on top of an optically well-defined silicon wafer (see Figure 8.1). This layer should be a dense layer with known optical constants and a good chemical resistance. Preferably, the layer can be removed after the formation of the IP layer, to obtain a simple single layer system, while the IP film is formed in a similar fashion as to an IP film in a TFC membrane. For a removable polymer layer, one can for example consider polymers with an upper critical solution temperature (UCST) which are insoluble in water below a certain temperature^[35]. Upon heating above the UCST, this polymer will become soluble, allowing for a removal of the UCST polymer layer. Furthermore, in order to successfully form an IP layer on top of the reservoir layer, it is important that it can swell sufficiently in the aqueous phase to allow for the uptake of the monomer dissolved in the aqueous phase. Also, the reservoir layer should be stable in organic solvents to prevent dissolution of the layer when brought in contact with the organic phase. In case the reservoir layer cannot be removed after the IP film formation, the requirements for SE in order to perform

accurate swelling measurements are that the reservoir is to be an optically smooth transparent film and the optical constants of the layer are distinctly different from the IP layer, to guarantee an optical contrast between the IP layer and the reservoir layer.

A. Dry reservoir layer on top of a silicon wafer.

B. immersing in aqueous phase

Requirements reservoir layer:

- Homogeneous and dense
- Optically transparent
- Stable in organic solvents
- Swellable in water
- Easy removal of aqueous phase after IP formation
- $n_{\text{reservoir}} \neq n_{\text{IP}}$
- Poor molecular weight cut-off

C. In between drying to remove water from the outer surface of the layer

D. immersing in organic phase

Figure 8.1 – Schematic illustration of the principle of using a reservoir layer for IP formation on top of a silicon wafer and an overview of the requirements in order for the reservoir layer to be suitable for iSE. Preferably, the reservoir layer is removed after IP formation.

An interesting system that has proven to function as a successful reservoir for IP, is a multilayer polyelectrolyte complex ^[36], which can be deposited on a substrate via a layer-by-layer dip-coating of the cation and anion respectively. The advantage of using multilayers polyelectrolytes is that the thickness and surface properties of the polyelectrolyte layer can easily be tuned by the numbers of layers deposited and the choice of polyelectrolyte ^[37]. However, there are some challenges that need to be overcome in order to apply multilayer polyelectrolyte complexes as a reservoir layer. First of all, to allow for the bulky IP monomers such as octa-ammonium POSS (>1,200 g mol⁻¹), and also for branched polymers such as poly(ethylene imine) (25,000 g mol⁻¹) to sorb into the polyelectrolyte layer, the multilayer polyelectrolyte complex should have a poor molecular weight cut-off (i.e. the minimum molecular weight of the solute in which 90 % of the solute is retained by the membrane ^[17]). Furthermore, the polyelectrolyte layer should be homogeneous and any unreacted monomer inside the reservoir should be removed after the formation of the IP film. This is important, as the monomers can change the optical properties of the reservoir layer. The reservoir layer should also be sufficiently dried prior to the contact with the organic phase to form the IP film. Any water still present on the surface will cause an interference with the light, resulting in scattering of the optical beam. The IP film will become opaque, limiting the quality of the iSE

analysis. A systematic study into which polyelectrolyte combination is most suitable is required. Once the above mentioned challenges have been overcome, the use of multilayer polyelectrolytes can improve the *in situ* swelling analysis, but also they can have potential as an additional coating on ceramic hollow fibers, to aid the IP film formation on hollow fibers^[38].

8.1.4 Potential of combining spectroscopic ellipsometry with quartz crystal microbalance and dissipation monitoring (QCM-D)

In order to move the characterization of membrane materials more toward real membrane applications, for example studying mixed penetrant sorption and the measurement of ultrathin films as discussed in sections 8.1.1 and 8.1.2, only iSE data will not be sufficient. In this thesis, it is shown that a great deal of information can be revealed by utilizing iSE (Chapter 3 and 4), but there are limits towards what extent iSE can be used. Chapter 2 shows that for films thinner than 100 nm, external effects such as the window birefringence and the correctness of the optical description of the ambient reduce the accuracy of the swelling measurement. Therefore, measurements for films thinner than 100 nm and also for mixed penetrant sorption measurements where the ambient description will be challenging, complementary swelling measurement techniques are necessary to interpret the swelling dynamics in thin polymer films. In the introduction of this thesis, the potential of combining SE with QCM-D is briefly described. However, throughout this thesis there was no further mention of QCM-D. Here, a reflection on the use of SE combined with QCM-D will be made.

When considering swelling, a combined measurement of SE with QCM-D is commonly applied in the field of stimuli-responsive polymer brushes^[39–43]. In these studies, a discrepancy between the QCM-D and SE measurements can be detected in terms of adsorbate mass, which is the result of a density profile occurring within the swollen brush from the substrate/polymer interface to the polymer/ambient interface^[39,40]. Where QCM measures changes based on an acoustic contrast and is therefore sensitive to total adsorbate mass changes (polymer and penetrant), SE measures an optical contrast and is a surface sensitive technique. In case of SE, only information on surface changes in the polymer can be obtained^[44]. In the field of stimuli-responsive brushes, this difference in sensitivity between QCM-D and SE in terms of adsorbate mass, is utilized to obtain information on the different phase transitions or stages occurring upon applying external stimuli, such as a temperature or pH change inside the swollen brush^[39,41–43] and to obtain more information on the density profile^[45]. In terms of modelling for QCM, a constant density is assumed, which is often set equal to the ambient, for brushes in the solvated state. Further mechanical properties are often obtained for viscoelastic films by modelling the films with a Voigt-Voinova model.

The combination of QCM-D and SE has also successfully been applied in studying the sorption of rigid (ultra)thin polymer films^[46,47]. For ultrathin films, the refractive index, n and the thickness, d cannot be determined independently of each other. By combining information obtained from QCM-D and SE, information on the ultrathin film thickness and the porosity can be obtained by means of a virtual separation approach^[45,48–50]. In this approach, the information from QCM is used to decouple n and d to eventually obtain an effective refractive index, n_{eff} and effective thickness, d_{eff} of the polymer film with the sorbed penetrant. Here, it is important that the polymer film does not become viscoelastic upon penetrant sorption, in order for the Sauerbrey relation to suffice. When the penetrant induces a viscoelastic behavior, that is when the penetrant plasticizes the rigid polymer, a viscoelastic model is necessary to obtain information on the adsorbent mass, requiring additional information on the density changes inside the polymer film.

For the application of QCM-D/SE characterization towards membrane applications, there are multiple considerations to be made. First of all, it is important to realize that both QCM-D and SE are indirect characterization techniques, requiring a model to translate the measured signal changes (frequency or light polarization) into a physical parameter such as adsorbed mass or thickness. Also, as mentioned above, QCM-D and SE probe different changes and absolute surfaces of the polymer film (total mass on substrate for QCM versus local surface changes for SE), the derived penetrant sorption or penetrant sorbed mass will not be the same for QCM-D and SE. For this reason, one technique cannot be used to verify the results of the other technique.

Furthermore, considering penetrant sorption in glassy polymer films, depending on the exact penetrant/polymer interaction, over time the rigid polymer film can become viscoelastic. This has implications for the modelling of the QCM-D data. When it is not exactly known at what point the Sauerbrey regime ends (rigid to viscoelastic conversion), the application of the wrong model can give significant discrepancies from the actual adsorbent mass values for films thicker than 100 nm^[51]. In case of Chapter 3, this discrepancy between the two models can possibly be used as an advantage. In Chapter 3, SE measurements show that at ~5% swelling, all excess free volume was filled with the penetrant. Until this point it is expected that the polymer film plus penetrant behave as a rigid mass. Upon further dilation, the rigidity of the polymer structure will change and it is expected that the viscoelasticity of the mixed polymer/penetrant film will increase. In this case, QCM-D can be used to provide additional insight in the shift of viscoelastic behavior, using the discrepancy between the Sauerbrey model and the viscoelastic model.

Overall, when designing new penetrant induced swelling experiments imitating operating membrane conditions, the combination of QCM-D/SE can be applied, provided sufficient knowledge on the measurement system is available. For this, knowledge about the density and viscosity of the dry polymer film and the penetrating medium is required. Information about the density changes or viscosity changes inside the polymer film as function of penetrant sorption is needed to apply the correct model. When this knowledge is available, QCM-D and SE can be used complementary and provide additional insight on the different stages in penetrant sorption, such as shown in Chapter 3 and 4 in this thesis and improve the understanding of penetrant sorption mechanisms and phenomena. Additional *in situ* atomic force measurements can be used as a verification of the swelling measurements and to obtain information on the mechanical properties of the swollen polymer film ^[52–54].

8.2 Understanding the Mechanisms and Dynamics of Swelling

8.2.1 The potential of broadband dielectric spectroscopy in sorption studies

In Chapter 7, broadband dielectric spectroscopy (BDS) was introduced as a new method to study the penetrant induced swelling in thin polymer films. Two non-polar penetrants, *n*-hexane and toluene were shown to interact differently with Matrimid 5218, resulting in distinctly different swelling degrees (i.e. SD= ~28 % in toluene, SD=~4 % in *n*-hexane). The combination of SE, BDS and infrared spectroscopy allowed for a detailed insight into the exact interaction between the penetrants and the polymer and the specific chemical moieties involved.

The results presented in Chapter 7 show that BDS is a suitable technique to probe and unravel the different relaxations that occur within the polymer chains upon an external stimulation such as temperature or a penetrant. However, although the current measurement set-up functioned well enough as a proof of concept, a number of changes are required to enhance the reproducibility and quality of the BDS measurements. At this moment, the measurement set-up does not allow for an accurate temperature and ambient control, resulting in estimated temperature deviations of ~2 °C and humidity deviations of ~5 % between the different measurements. As a result, the measurement conditions differ for each measurement, and the presence of water can ‘pollute’ the measurement^[55]. For pursuing penetrant induced swelling measurements with BDS, an enclosed measurement environment is necessary, which can easily be filled with a liquid penetrant in a dried nitrogen atmosphere. Also, an accurate temperature control is required. BDS is a temperature sensitive technique and any fluctuations in

temperature will be reflected in the measurement results. Other than enhance the reproducibility of the measurement results, temperature control can also provide additional information. By measuring the relaxation dynamics at different temperatures, a temperature dependent behavior can be obtained. This can provide information on the activation energy of the different dipole relaxations and also, it helps in distinguishing between an artifact, conductivity, β -relaxation and α -relaxation, as all display a different temperature dependence^[56] (see section 1.4.2). Based on the Starkweather approach, coupling the activation energy (E_A) to an activation entropy ($\Delta S^\ddagger$), the extent of cooperativity of a specific relaxation can be determined^[57]. The extent of cooperativity can provide information on the origin of the induced relaxation, and information on the total mobility of the polymer chains.

Other factors that strongly influence the BDS measurements, are concerned with the preparation of the measurement sample^[58]. Other than the temperature dependent history of Matrimid 5218, it was also shown in Chapter 7 that the deposition of the thin film through spin-coating induced an anisotropy which was not completely removed after the annealing treatment. When considering BDS measurements, the sample preparation should be taken into account and a reproducible sample preparation should be ensured.

As mentioned, although the results in Chapter 7 point toward the different interactions of the diamine in Matrimid 5218 with toluene and *n*-hexane, the sensitivity of the performed infrared spectroscopy measurements was too low to provide conclusive proof. Infrared spectroscopy is a good complementary technique to BDS and allows for studying the specific interactions of the penetrant with the different chemical groups within the polymer structure. However, the DRIFT-FTIR set-up used in Chapter 7, did not allow for a controlled vapor environment and control of the thin film swelling, resulting in a likely much lower swelling degree than as was measured with ellipsometry. To use infrared spectroscopy as a complementary technique, it is important that the measurement conditions and sample preparation conditions are similar to the samples as prepared for the BDS measurements. In case of DRIFT-FTIR, a thicker sample ($\sim 3\ \mu\text{m}$) than as was used for the BDS measurement ($\sim 260\ \text{nm}$) was required to obtain enough sensitivity to measure the absorbance, possibly introducing preparation effects. Preferably, similar samples as to the samples used for BDS are analyzed with infrared spectroscopy, and therefore also other infrared measurement techniques should be investigated. Suitable candidates are FTIR -Attenuated Total Reflection (ATR) and infrared spectroscopy combined with spectroscopy ellipsometry (IR-SE)^[59,60]. Both techniques have been applied successfully *in situ* for swelling studies of thin polymer films or brushes^[59,61–64]. However, in the case of FTIR-ATR, similar as for DRIFT FTIR, the sensitivity for films thinner than $1\ \mu\text{m}$ is often low, and a careful

consideration of the prism, incident angle, and wavelength of the light source is needed to obtain the highest signal to noise ratio ^[65]. For IR-SE, an expensive investment into a new set-up is required.

For a continuation of using BDS and FTIR to study the molecular interactions between the penetrant and the polymer, the focus should first be on improving the experimental set-up as used in Chapter 7 according to the suggestions as mentioned above. When the reproducibility of the BDS measurements is ensured, and the sensitivity of the FTIR measurement increased, the combination of FTIR/BDS and SE swelling studies will be a powerful tool in future swelling studies. Especially when considering multicomponent mixtures, the combination of BDS/FTIR can possibly allow for locating the specific interactions between the different penetrants and the specific molecular groups in the polymer chain, making a distinction between the different penetrants which is not possible with SE alone. In the case of high excess free volume polymers (e.g. polymer with intrinsic microporosity (PIM), FTIR/BDS can possibly provide more information on the exact origin of plasticization or a concentration induced glass transition. Which molecular groups are interacting with the penetrant and how are their relaxation dynamics changing upon contact with the penetrant? How is this different for polymers with a low excess free volume? It should be kept in mind however, BDS studies for studying swelling as discussed above are thus far limited to non-polar penetrants, to avoid 'drowning out' of the material signal by the polar penetrant signal.

8.2.2 From experimental observations to prediction of membrane performance

In this thesis the experimental observations have aided into a better understanding on the dynamics and mechanisms on sorption in thin polymer films, but ultimate goal of this research is to aid in the prediction of the performance of organic solvent nanofiltration membranes. In the introduction of this thesis, section 1.2.3.1, several models that describe the sorption of a penetrant in the polymer have been discussed. Also, modes of diffusion of the penetrant into the polymer and finally a translation to transport models for membrane applications have been discussed.

In Chapter 3, the different sorption modes for the sorption of a penetrant in a glassy polymer are discussed in terms of the dual mode sorption model. Penetrant sorption was discussed to occur either in the excess free volume of the polymer or into the polymer matrix itself via the mobile hole free volume. In terms of penetrant transport this is important, because it will determine whether the diffusivity or solubility will dominate the transport and selectivity ^[17,66].

In Chapter 3, the simple approach based on the dual mode sorption model was not sufficient to describe the generalized behavior of the free volume filling in polymers

in detail. There is a need for a better understanding on the role of free volume and the change in the thermodynamic state of the polymer as related to the penetrant. Here a non-equilibrium model such as the non-equilibrium lattice fluid model (NELF) applied for glassy polymers ^[67] can be used as a starting point. When the experimental data can be matched to the general behavior of the NELF model, information on the changing thermodynamic state of the polymer can be obtained. The results in Chapter 3 show that it is possible to make a distinction between the different modes of sorption. When the contribution and type of sorption can be predicted based on the amount of penetrant present inside the polymer or the extent of swelling observed, a link can be made to the type of transport occurring within the membrane. For example, the data in Chapter 3 indicates that below a swelling of ~5 % the dominating sorption occurs in the free volume of the polymer. Therefore, for polymers with swelling degrees below 5 %, it is more likely that penetrant transport occurs via the free volume of the polymer. For future research, the extent to which the NELF model can be used to describe the generalized sorption in glassy polymers as observed in Chapter 3 should be investigated. Can additional information from the NELF model be obtained to describe the change in the thermodynamic state? For this, the applicability of a non-equilibrium description based on the density alone should be researched. How can the change in partial molar volume of the penetrant be described correctly and how does this reflect in the density? In order to obtain information on the change of the penetrant's partial molar volume, it is important that an understanding of the availability of the free volume sites is obtained. For this, the challenging question as to what extent is the EFV representative for the 'frozen' part of the hole free volume, needs to be answered.

In Chapter 4, it was shown that the penetrant diffusion in polymers is different for ultrathin films compared to bulk films of polystyrene. Although models had predicted the presence of a transition layer, it was never measured before. In Chapter 4, it was shown a transition layer exists between the free surface and the bulk of the polymer film, but the length of the transition layer decreases for ultrathin films. As a result, current prediction models based on data of a bulk material, should be adjusted for predicting diffusion into ultrathin films. In order to do this, the dominant parameters influencing the mobility of the polymer chains on the substrate should be studied. Parameters that should be considered are the interaction parameters of the substrate and polymer, but also external effects such as annealing temperature and the solvent used for deposition of the polymer layer.

8.3 Overall Conclusion

In this thesis it was shown that *in situ* swelling studies contribute to the understanding of the mechanisms and dynamics of swelling in thin polymer films. In this work I have tried to show that by performing advanced *in situ* swelling studies, information on the different interactions between the penetrant and the thin polymer film could be obtained. By linking the swelling behavior of the thin polymer film to the molecular structure and thermodynamic state, predictions on the performance of the thin film polymer in a non-aqueous environment could be improved. Throughout this thesis, different *in situ* characterization techniques have been used and their limits in the application in sorption studies investigated. The insights obtained during the four years of research bundled in this thesis has provided for new research directions which will bring us closer to comprehending and eventually predicting the performance of thin film polymers in non-aqueous environments. In the end, the improved understanding of a material's performance in a non-aqueous environment will result in an enhanced material selection for applications such as OSN.

Figure 8.2 – Schematic illustration connecting the structure and thermodynamic state of a polymer to the performance of the polymer by performing *in situ* swelling studies.

8.4 References

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Acknowledgements

"Tell me and I forget.

Teach me and I remember.

Involve me and I learn."

- Benjamin Franklin (1706-1790) -

One of the Founding Fathers of the United States

When I had accepted the 4-year PhD adventure, I was not sure what was waiting for me. During the past 4 years, there were many people directly or indirectly involved in my project and who made sure I successfully finished it. To all of them I owe many thanks and I am very grateful, for they shaped me into the person I am today. There are several people who I would like to thank in particular.

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Although my main hobbies are chess and badminton, my colleagues made sure I got enough physical exercise to stay physically and mentally fit. It started with running, but every now and then, I joined a Futsal match (and I did score once!). At the end Timon and Rian also introduced me to Padel. I would like to thank all my running buddies, Padel buddies and Futsal buddies for keeping me fit!

Of course, working without a break is not possible, and I always very much appreciated the coffee and lunch breaks at the MST coffee corner. Although the conversations sometimes went a bit over the top, were too controversial or just simply out of bounds, they always allowed me to relax and gather new energy for the rest of the working day. Thank you all in the membrane cluster for your direct or indirect input.

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About the Author

Kristianne Tempelman was born on the 25th of May 1991 in Apeldoorn, The Netherlands. In 2009 she obtained her VWO diploma and international baccalaureate diploma at the Koninklijke scholengemeenschap in Apeldoorn. In the same year she started her bachelor studies in Chemical Engineering at the University of Twente. She performed her final bachelor thesis in the group of Inorganic Membranes, University of Twente. After her bachelor studies, she continued with the master studies in Chemical Engineering in the Molecules and Materials Engineering track. In 2013 she performed a four-month professional internship at Teijin Aramid, Arnhem, The Netherlands. In 2014, she graduated cum laude from the University of Twente on a master thesis entitled: "An experimental study into the kinetics of interfacial polymerization, utilizing a microfluidic platform."

During both her bachelor and master studies, she was active in several educational committees within the study association C.T.S.G. Alembic and she was active in the organization of the study tour of C.T.S.G. Alembic to Chile. Additionally, she was active as a chess teacher for children at S.G. Max Euwe.

Starting from November 2014, she has been working as a PhD candidate in the Films in Fluids group, University of Twente, under the supervision of prof. dr. ir. Nieck E. Benes. She has presented her research at various conferences in Europe, including a poster presentation at International Conference on Spectroscopic Ellipsometry (ICSE-7) in Berlin, a poster presentation at Euromembrane (2018) in Valencia and a plenary presentation at the Dutch Polymer Days (2018) in Lunteren, The Netherlands.

List of publications

Per January 2019

Peer-reviewed international journals

- Submitted* **K. Tempelman**, W. Ogieglo, J. A. Wood, N. E. Benes, *On the generic swelling behavior of glassy polymers*, submitted to Macromolecules
- Submitted* **K. Tempelman**, S. Casanova, N. E. Benes, *The effect of hydrocarbon pollution on polysulfone-based membranes in aqueous separations*, submitted to Separation and Purification Technology
- 2018 E.J. Kappert, M.J.T. Raaijmakers, **K. Tempelman**, F.P. Cuperus, W. Ogieglo, N.E. Benes, *Swelling of 9 polymers commonly employed for solvent resistant nanofiltration membranes: a comprehensive dataset*, Journal of Membrane Science, 569 (2019) 177-199. doi: 10.1016/j.memsci.2018.09.059
- 2018 E. Maaskant, **K. Tempelman**, N.E. Benes, *Hyper-cross-linked thin polydimethylsiloxane films*, European Polymer Journal, 109 (2018) 214-221. doi: 10.1016/j.eurpolymj.2018.09.052
- 2018 W. Ogieglo, **K. Tempelman**, S. Napolitano, N.E. Benes, *Evidence of a Transition layer between the Free Surface and the Bulk*, Journal of Physical Chemistry Letters, 9 (2018) 1195-1199. doi: 10.1021/acs.jpclett.8b00076
- 2017 **K. Tempelman**, E.J. Kappert, M.J.T. Raaijmakers, H. Wormeester, N.E. Benes, *Dealing with inaccuracies in the analysis on solvent-induced swelling of transparent thin films using in situspectroscopic ellipsometry in the visible wavelength range*, Surface and Interface Analysis, 49 (2017) 538-547. doi: 10.1002/sia.6191
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- 2013 W. Ogieglo, H. van der Werf, **K. Tempelman**, H. Wormeester, M. Wessling, A. Nijmeijer, N.E. Benes, *n-Hexane induced swelling of thin PDMS films under non-equilibrium nanofiltration permeation conditions, resolved by spectroscopic ellipsometry*, Journal of Membrane Science, 431 (2013) 233-243. doi: 10.1016/j.memsci.2012.12.045

PROPOSITIONS

Accompanying the thesis

Swelling of Thin Polymer Films ***Understanding the Mechanisms and Dynamics***

by Kristianne Tempelman

1. Data in reports on *in situ* spectroscopic ellipsometry swelling measurements regarding polymer films thinner than 100 nm in liquid media have a large error margin and cannot always be considered reliable. (Chapter 2)
2. Advances in predicting glassy polymer swelling behavior require knowledge of the distribution of the free volume and its relation to penetrant sorption. (Chapter 3)
3. Sorption properties as measured for a bulk polymer cannot be assumed to be the same as the sorption properties of an ultrathin polymer film. (Chapter 4)
4. Multi-component sorption experiments show that the interplay between the different penetrants and the thin polymer film can yield in unexpected phenomena, which are not present in a single-component sorption system. (Chapters 5 and 8)
5. The peer review system of journals should be double-anonymous, to prevent prejudices and favors, allowing a manuscript to be judged solely on its contents.
6. To prevent reinventing the wheel, sharing of unsuccessful research experiments should be encouraged.
7. The emotional impact on the mental state of mind of pursuing a PhD degree should be discussed more openly and requires professional attention.
8. Although presenting your research to a large group of people (>100 persons) is an honor, presenting your research to a small group of peers is more valuable.
9. By providing a full English education only, scientific employees will have less command of the Dutch language.
10. In today's modern society, in which we are continuously stimulated by and aware of our (social) environment, more investment into mental healthcare is required.

STELLINGEN

Behorende bij het proefschrift

Swelling of Thin Polymer Films *Understanding the Mechanisms and Dynamics*

door Kristianne Tempelman

1. Gerapporteerde resultaten van *in situ* spectroscopische ellipsometrie metingen in een vloeistof kunnen niet altijd worden vertrouwd als het gaat om het meten van zwellen van polymeerlagen die dunner zijn dan 100 nm. (Hoofdstuk 2)
2. Om de voorspelling van het zwelgedrag in glasachtige polymeren te verbeteren, is er meer kennis nodig over de verdeling van het vrij volume en over de rol van het vrij volume met betrekking tot sorptie van een penetrant. (Hoofdstuk 3)
3. De sorptie-eigenschappen van een bulk-polymeer kunnen niet worden vergeleken met de sorptie eigenschappen van een extreem dunne polymeerlaag. (Hoofdstuk 4)
4. Experimenten met multi-component systemen laten zien dat de samenwerking en interactie tussen verschillende penetranten en de dunne polymeerlaag kan leiden tot onverwachte manifestaties die niet optreden in een enkel-component system. (Hoofdstuk 5 en 8)
5. Een wetenschappelijk artikel kan alleen volledig op zijn inhoud worden beoordeeld, zonder vooroordelen of voorkeursbehandelingen, door het peerreview systeem van wetenschappelijke tijdschriften dubbel anoniem te maken.
6. Om te voorkomen dat het wiel telkens opnieuw wordt uitgevonden, moet ook het delen van niet-succesvolle experimenten worden aangemoedigd.
7. Emoties en gevoelens die men ervaart tijdens het doen van een PhD verdienen professionele aandacht en moeten beter bespreekbaar worden gemaakt.
8. Het is een eer om je onderzoek te mogen presenteren aan een grote groep mensen (>100 mensen), maar het is waardevoller om je onderzoek te presenteren aan een kleine groep collega's.
9. Door alleen nog maar een volledig Engelstalige opleiding aan te bieden, zal het beheersen van de Nederlandse taal onder hoogopgeleid personeel gaan verloederen.
10. Grotere investeringen in de psychische gezondheidszorg zijn noodzakelijk, doordat we in de huidige maatschappij continu worden geprikkeld en bewust zijn van onze (sociale) omgeving.

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