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Abstract

Nanocomposite films containing a high volume fraction ($> 50\text{vol}\%$) of nanoparticles (NPs) in a polymer matrix are promising for their functionality and use as structural coatings, and also provide a unique platform to understand polymer behavior under strong confinement. In this work, we present a one-step, room temperature method for the fabrication of such films through solvent-driven infiltration of polymer (SIP) into NP packings from a bilayer film composed of a densely packed layer of NPs atop a polymer film. Upon exposure to solvent vapor, capillary condensation occurs in the NP packing, leading to plasticization of the polymer layer and subsequent infiltration of polymer into the NP layer. Infiltration proceeds from a swollen polymer film into the highly confined interstitial voids of the NP packing, providing a novel system for the study of polymer solutions infiltrating into confinement.

We show that the extent of polymer infiltration depends on the quality of solvent, the extent of confinement, and polymer-NP interactions through experimental work and theoretical modelling. We find that decreasing solvent quality leads to less infiltration, but if given enough time to infiltrate, even slightly poor solvents ($\chi = 0.7$) can lead to significant infiltration. The use of a slightly poor solvent enables SIP via liquid solvent annealing. We study the effect of confinement on SIP by varying polymer molecular weight and NP size. While the dynamics of infiltration during SIP are strongly dependent on confinement, the final extent of infiltration is not. This is attributed to changes in concentration regimes as infiltration proceeds, which lead to shifting characteristic length scales in the system over time. Finally, we probe the effect of polymer-NP interactions on the kinetics of confined polymer translocation through an entropic barrier and investigate how this effect varies with solvent quality and confinement. It is found that τ is strongly dependent on the strength of the polymer-wall interactions and shows a nonmonotonic dependence with interaction strength which qualitatively agrees with the MD simulations. The SIP technique is a versatile and tunable method to fabricate high filler-fraction nanocomposite films of controlled porosity. This work aims to understand the mechanism of polymer infiltration during SIP, which provides insights into polymer solution behavior under strong nanoconfinement.

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Neha Manohar

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PACKINGS**

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Neha Manohar

To my parents, Sadhana and Sanjeev Manohar.

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ABSTRACT

SOLVENT-DRIVEN INFILTRATION OF POLYMER (SIP) INTO NANOPARTICLE PACKINGS

Neha Manohar

Daeyeon Lee and Kathleen J. Stebe

Nanocomposite films containing a high volume fraction ($> 50\text{vol}\%$) of nanoparticles (NPs) in a polymer matrix are promising for their functionality and use as structural coatings, and also provide a unique platform to understand polymer behavior under strong confinement. In this work, we present a one-step, room temperature method for the fabrication of such films through solvent-driven infiltration of polymer (SIP) into NP packings from a bilayer film composed of a densely packed layer of NPs atop a polymer film. Upon exposure to solvent vapor, capillary condensation occurs in the NP packing, leading to plasticization of the polymer layer and subsequent infiltration of polymer into the NP layer. Infiltration proceeds from a swollen polymer film into the highly confined interstitial voids of the NP packing, providing a novel system for the study of polymer solutions infiltrating into confinement.

We show that the extent of polymer infiltration depends on the quality of solvent, the extent of confinement, and polymer-NP interactions through experimental work and theoretical modelling. We find that decreasing solvent quality leads to less infiltration, but if given enough time to infiltrate, even slightly poor solvents ($\chi = 0.7$) can lead to

significant infiltration. The use of a slightly poor solvent enables SIP via liquid solvent annealing. We study the effect of confinement on SIP by varying polymer molecular weight and NP size. While the dynamics of infiltration during SIP are strongly dependent on confinement, the final extent of infiltration is not. This is attributed to changes in concentration regimes as infiltration proceeds, which lead to shifting characteristic length scales in the system over time. Finally, we probe the effect of polymer-NP interactions on the kinetics of confined polymer translocation through an entropic barrier and investigate how this effect varies with solvent quality and confinement. It is found that τ is strongly dependent on the strength of the polymer-wall interactions and shows a nonmonotonic dependence with interaction strength which qualitatively agrees with the MD simulations. The SIP technique is a versatile and tunable method to fabricate high filler-fraction nanocomposite films of controlled porosity. This work aims to understand the mechanism of polymer infiltration during SIP, which provides insights into polymer solution behavior under strong nanoconfinement.

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Chapter 1. Introduction to SIP

1.1. Polymer Nanocomposites

Polymer nanocomposites are a unique class of materials that combine the functionality of inorganic nanoparticles (NPs) with the toughness and processability of a surrounding matrix polymer. These materials can have synergistic electronic, optical, and mechanical properties which can enable their use in membrane separations, energy storage devices, electrochemical sensors and as structural coatings.¹⁻⁹

These properties are typically further enhanced with higher loadings of well-dispersed NPs.¹⁰⁻¹⁵ However, achieving higher NP loadings can be a challenge with conventional blending methods due to the thermodynamic incompatibility of the two materials and the high elasticity of such blends. Several methods have been proposed to eliminate this issue, such as introducing polymer grafts on the NP surface to improve dispersibility within the polymeric matrix. However, such techniques can be cumbersome and limited to low volume fractions of NPs (<50vol%).¹⁶⁻¹⁹

1.2. Polymer-Infiltrated Nanoparticle Films (PINFs)

The infiltration of polymers into the interstices of dense nanoparticle (NP) packings opens new opportunities for fabrication of functional composites with extremely high fractions of NPs (> 50 vol%) and circumvents issues associated with dispersal or mixing of NPs into polymers.²⁰⁻²⁵ Like composite structures found in nature such as nacre, polymer-infiltrated nanoparticle films (PINFs) have high strength and toughness and also

exhibit high scratch and wear resistance, making them ideal protective and structural coatings.^{26–28} Moreover, many working electrodes in energy storage and conversion devices such as fuel cells, lithium ion batteries and solid-state dye-sensitized solar cells exploit PINF structures;^{29–32} in these settings, a small volume of ion-conducting polymers is dispersed in dense packings of NPs with catalytic properties. PINFs also have great potential for producing gas barrier layers.^{25,33} The introduction of nanoporosity in PINFs could further enhance their functionality by tuning their optical properties, for example, to generate anti-reflection coatings with high mechanical strength.^{1,28,34}

Previous attempts to infiltrate polymer into porous structures and NP packings have involved either immersion in a polymer melt or solution,^{20,21} exposure to monomer vapor followed by *in situ* polymerization,^{22,23} or infiltration with resin solutions that are subsequently crosslinked.^{24,25} However, such approaches can lead to low and inhomogeneous loadings or require multi-step complex methods that could result in the presence of residual monomers and uncontrolled polymer fill fractions.^{20–25} Initiated chemical vapor deposition also has been used for the generation of PINFs used in dye-sensitized solar cells; however, this method requires vacuum processing.³⁵ There is need, therefore, for a scalable, facile technique for PINF fabrication that retains polymer quality and consistent loading within the NP packings to enable their use in a variety of applications.

Recently, a novel technique to overcome these obstacles has been developed by preparing a bilayer made of a packing of NPs and a polymer layer, and subsequently

thermally annealing the bilayer above the polymer's glass transition temperature (T_g) to induce capillary-rise infiltration (CaRI) of the polymer into the voids of the NP packing.²⁶ Moreover, by varying the amount of polymer relative to the void fraction in the NP film, it is possible to manufacture nanoporous PINFs that can be exploited for optical and mechanical applications.¹ The CaRI approach relies on the use of a polymer with a low or accessible glass transition, which may not be the case for several glassy polymers used in industrial applications which can decompose before reaching their T_g .^{36–38} Additionally, high temperatures can lead to loss of structural integrity of some NPs that are made of metal or ceramics,^{39–41} creating a need for viable room-temperature alternatives for porous PINF fabrication, which would also significantly reduce the energy requirement.

1.3. Solvent-driven Infiltration of Polymer (SIP) into Nanoparticle Packings

In order to meet this need, we have developed a room-temperature method called Solvent-driven Infiltration of Polymer (SIP) into nanoparticle packings. This technique involves starting with a thin bilayer film composed of a polymer layer underneath a densely packed layer of NPs, similar to the CaRI system. This bilayer is exposed to solvent vapor, which undergoes capillary condensation within the interstices of the NPs, and subsequently seeps into and swells the polymer layer underneath. This provides the polymer with sufficient mobility to infiltrate into the solvent-rich voids within the NP packing.⁴²

Figure 1.1. A schematic illustration of the SIP process.

A schematic illustration of the SIP system is provided in Figure 1.1. Upon exposure of the bilayer to solvent vapor, the NP packing becomes flooded with condensed liquid solvent, which begins to swell the underlying polymer layer and initiates infiltration. As infiltration proceeds, the SIP system provides a unique opportunity to study the infiltration behavior of polymer solutions under strong nanoconfinement. Furthermore, the concentration of polymer within the “pores” (voids of the NP packing) evolves with time, transitioning from dilute, with polymer initially encountering a solvent-rich environment, to concentrated, where the polymer is crowded by other chains within the cavity. The SIP system is studied to understand the kinetics and thermodynamics of polymer solutions

under nanoconfinement, and how they are impacted by solvent quality, extent of confinement, and polymer-cavity interactions.

1.4. Introduction to Polymer Solutions Under Confinement

Polymer behavior in solutions when experiencing geometric constraints has been of great interest within the polymer community.^{43,44} Specifically, the diffusion and partitioning of polymer solutions under nanoscale confinement is very relevant in phenomena such as size exclusion chromatography (SEC),⁴⁵ nanocomposite fabrication,^{46,47} nanopatterning,⁴⁸ and ultrafiltration membranes.^{49,50} Fundamental studies of polymer solutions under confinement have typically been limited to dilute solutions in porous media with negligible interactions with the pore wall.⁴³ These studies use dynamic light scattering (DLS) to obtain the diffusivity of polymers trapped in a porous media relative to the bulk polymer solution, as well as the extent of partitioning of polymer into the porous media from the bulk. Several studies have found that polymer diffusivity decreases with increasing confinement (defined as $\lambda = R_g / \langle R \rangle_{\text{pore}}$), and that this effect scales strongly with molecular weight.^{51,52} Simulations studies of such systems observe similar behavior with confinement for polymer diffusivity, and further find that polymers partition less into pores with greater confinement.⁵³ A few studies consider semi-dilute polymer solutions above the critical overlap concentration ($\leq 5c^*$), and observe that diffusivity increases with polymer concentration.^{54,55} Furthermore, the partitioning of polymer into confinement in these systems has been found to undergo a transition from weak to strong as concentration increases beyond the critical overlap threshold.^{56,57} The

highest partitioning achievable in these cases is the concentration of polymer within the porous media reaching the bulk polymer concentration. Higher partitioning has been achieved in Monte Carlo simulations in cases where the polymer-pore interactions are highly attractive.⁵⁸

In the SIP system, the swollen polymer film as well as the concentration of polymer in the voids of the NP after infiltration (Chapter 3) reach significantly higher concentrations than those considered in existing studies. The extents of confinement considered in the SIP studies ($\lambda \approx 1 - 50$) are also significantly higher than those previously considered ($\lambda \leq 10$), with most prior work exploring a maximum confinement of $\lambda \approx 2$. Through the study of the infiltration dynamics and partitioning behavior in the SIP system, we hope to improve understanding of concentrated polymer solutions that are highly confined.

1.5. Outline of Thesis Chapters

Infiltration of polymer in the SIP system relies on several factors, including solvent quality, degree of confinement, and polymer-NP interactions. Herein, I describe the SIP technique and explore the effect of varying conditions on polymer infiltration through experiments and theoretical modelling.

In Chapter 2, we study the role that solvent capillary condensation and solvent quality play in polymer infiltration during SIP. We probe the capillary condensation in the system using in situ ellipsometry and find that larger NPs have incomplete condensation within the NP packing. The solvent quality is systematically varied via the use of solvent with different Flory-Huggins interaction parameters with polystyrene. We find that

decreasing solvent quality leads to less infiltration, but if given enough time to infiltrate, even slightly poor solvents ($\chi = 0.7$) can lead to significant infiltration. Such poor solvents also enable the use of liquid solvent exposure, which has the same infiltration kinetics as vapor solvent exposure, indicating complete capillary condensation in the vapor system. Finally, the extension of SIP via the use of a monomer as the solvent and the subsequent photopolymerization of the solvent to form polymer nanoblends is described.

In Chapter 3, we explore the effect of confinement on the kinetics and final extent of infiltration during SIP. This effect is studied by defining a confinement ratio ($\lambda = R_g / \langle R \rangle_{\text{pore}}$) and studying a broad range of λ by using different polymer molecular weights and NP sizes. The kinetics of polymer infiltration is found to have a strong power law dependence on the confinement ratio ($\tau \sim \lambda^{3/2}$), which lies between the scaling relationship with confinement for melts and dilute solutions. The partitioning of polymer into the pore of the NP packing, calculated as the ratio of final extent of infiltration of polymer within the NP packing to the volume fraction of polymer in the swollen polymer film, is not a function of confinement and significantly greater than unity. This finding is attributed to interactions between the polymer and the NPs, and the fact that, at high concentrations, the polymer's characteristic length scale is the correlation length, which is smaller than the average pore sizes of the NP packings considered.

In Chapter 4, we consider the role of polymer-NP surface interactions on polymer infiltration kinetics and develop a model to study the synergistic effects of these interactions with solvent quality and confinement. An entropic barrier model is developed

using self-consistent field theory (SCFT) calculations with excluded volume interactions and polymer-wall surface interactions. The mean translocation time τ for a polymer trapped in a cavity to escape into a second cavity through a segment-size hole is calculated as a function of the surface interaction potential between the polymer and the cavity wall; this time scale is found to have a nonmonotonic dependence. This trend is in qualitative agreement with our molecular dynamics (MD) simulations study of the SIP system, which shows a similar dependence of the kinetics of infiltration on surface interaction strength. Finally, asymmetric translocation is considered with increasing and decreasing cavity size, where the nonmonotonic behavior with ϵ_{P-NP} is replaced by a monotonic trend favoring higher confinement with increasing surface interaction strength.

Finally, Chapter 5 summarizes the findings related in this thesis. The open questions remaining in this topic are discussed and future work is proposed to gain further understanding of the mechanism and breadth of the SIP technique.

Chapter 2. Role of Solvent in SIP

Content in this chapter is reprinted (adapted) with permission from N. Manohar, K. J. Stebe, and D. Lee. Solvent-driven Infiltration of Polymer (SIP) into Nanoparticle Packings. *ACS Macro Lett.* **2017**, 6, 1104-1108.

2.1. Introduction

The SIP process is heavily dependent on the solvent used to induce polymer infiltration into the NP packing. The presence of condensed solvent in the interstitial voids of the NP packings is expected to play a major role in the infiltration process. The role of solvent is considered in this chapter by exploring two major factors: the condensation of solvent via capillary condensation and the quality of solvent within the voids as characterized by a Flory-Huggins interaction parameter (χ).

Capillary condensation is a well-known and well-studied phenomenon in (meso)porous materials,^{59,60} and has been exploited to modify the surface properties of such materials.²³ Capillary condensation occurs when a vapor starts to condense within small pores; the vapor-liquid interface which forms has very high curvatures, leading to a depressed saturation vapor pressure and promoting condensation within the porous media. The relationship between the vapor pressure and interfacial curvature is described by the Kelvin equation:²³

$$RT \ln \left(\frac{P_0^{\text{Capillary}}}{P_0} \right) = \gamma^{LV} V_m \left(\frac{1}{x} - \frac{1}{r_c} \right) \quad \text{Eq. 2.1}$$

where P_0 is the standard vapor pressure, V_m is the molar volume of condensate, and γ^{LV} is the surface tension. Here, x and r_c represent the principle curvatures of a saddle shaped vapor-liquid interface between two NPs (see Figure 2.1). In NP packings, the curvature of the interface increases with decreasing NP size, leading to complete flooding of the interstitial voids when the NPs are small enough. The extent and speed of condensation is expected to play a role in infiltration for different SIP systems.

Figure 2.1. A schematic illustration of capillary condensation between two NPs. The radius of the NP (r) and the principle curvatures of the vapor-liquid interface (x and r_c) are labelled in the diagram.

The quality of condensed solvent with respect to the infiltrating polymer solubility will also play a major role in the SIP process. The solvent quality will determine the enthalpic driving force for mixing of the swollen polymer into the solvent-rich voids within the NP packing, and therefore is expected to have strong impact on infiltration behavior. In this chapter, polystyrene is exposed to various solvents with a range of Flory-Huggins interaction parameters in order to study the impact of solvent quality on infiltration.

1.1. Methods

2.1.1. Experimental Setup

Figure 2.2. Schematic illustration of solvent annealing setup. A pure nitrogen stream flows into a mass flow controller (MFC) which then flows into a stainless steel solvent bubbler. The solvent stream flows into an aluminum chamber for in situ ellipsometry measurements of the infiltration process. A second pure nitrogen stream is used as a purge stream for the system.

A plasma-treated silicon wafer is coated with a 250 nm thick polystyrene ($M_n = 8,000$ g/mol, 21,000 g/mol, 173,000 g/mol; $PDI \leq 1.1$) film, which is subsequently coated with a 250 nm layer of SiO₂ (average size = 23 nm) nanoparticles. The void fraction within the coated nanoparticle film is roughly 0.31. This sample is then placed in an aluminum chamber and exposed to a nitrogen purge stream using a home-built controlled vapor flow setup (Figure 2.2). Once purged with nitrogen for 10 min, the sample is then exposed to solvent vapor for 30 min followed by another 15 min of quenching with nitrogen. The sample is then placed in a vacuum oven overnight for drying. The longer exposure experiments were run using a setup in which the sample is exposed to a stagnant saturated vapor environment (or submerged directly in solvent for liquid annealing experiments) for

an extended time and then vacuum dried overnight before characterization. Since these experiments are not conducted in the controlled vapor flow setup, there is no nitrogen purging before or after annealing.

The experiments are characterized using a J.A. Woollam Alpha-SE spectroscopic ellipsometer. Measurements are taken at a 70° angle of incidence in the wavelength range of 380-900 nm and are analyzed using the CompleteEASE software package. The model consists of two transparent layers with a Cauchy dispersion equation on top of a silicon substrate.^{1,26,61} The refractive index of the polymer layer ($n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$, where the optical constants A, B, and C are fitted to determine the refractive index of the film) and the thickness of the nanoparticle layer remain constant and therefore only the thickness of the polymer layer and refractive index of the nanoparticle layer are estimated using the two-layer Cauchy model before and after the SIP experiments. The volume fraction of polystyrene in the nanoparticle packing after SIP is estimated by determining the change in the thickness of the bottommost polymer layer according to:

$$\varphi_p = \frac{h_{PS,initial} - h_{PS,final}}{h_{SiO_2}}. \quad \text{Eq. 2.2}$$

This quantity can also be estimated from the change in the NP layer refractive index.

More information on this setup is provided in Appendix A.

2.1.2. Calculation of the Flory-Huggins χ Parameter

To calculate the Flory-Huggins χ parameter to estimate the solvent quality, the Hansen three-dimensional solubility parameters are found for each solvent and for polystyrene.⁶²⁻⁶⁴

The following equations are used to calculate χ from the values of these solubility parameters:^{64,65}

$$\chi = \frac{V * (Ra)^2}{4RT} + 0.34 , \quad \text{Eq. 2.3A}$$

$$Ra = \sqrt{4(\delta_d^p - \delta_d^s)^2 + (\delta_h^p - \delta_h^s)^2 + (\delta_p^p - \delta_p^s)^2} \quad \text{Eq. 2.3B}$$

where δ_d , δ_h and δ_p represent the square root of the cohesive energy density from dispersion, hydrogen bonding and dipolar intermolecular forces between molecules, respectively and V, R and T are molar volume of the solvent, ideal gas constant and temperature, respectively. Here, Ra is the “distance” between the solubility parameters and defines a spherical radius of solubility in “Hansen space”.⁶⁵

2.2. Capillary Condensation in Different NP Packings

Figure 2.3. Percent filling (open symbols) of NP packing by condensed solvent and NP film thickness (closed symbols) for SiO₂ NP packings on Si wafers upon exposure to toluene vapor. Two NP packings are characterized by average particle radius 23 nm (red) and 77 nm (black), respectively. Samples were purged in nitrogen for ten minutes prior to exposure to toluene vapor at the 5-min mark in this graph.

Capillary condensation in NP packings occurs due to the high negative curvature associated with the voids between two small spheres in contact, and has been shown to occur to a greater extent as the size of the NP is decreased.²³ We use SiO₂ NPs with average diameters of 23 nm and 77 nm, which are small enough that a significant driving force for condensation within the respective packings exists. To show that capillary condensation indeed occurs readily in this system, a 225 nm thick film comprised of 23 nm SiO₂ NPs

and a 235 nm thick film comprised of 77 nm SiO₂ NPs are exposed to solvent vapor after an initial nitrogen purge for ten minutes and observed using *in situ* ellipsometry.

Subsequently, the refractive index of the NP film increases significantly upon exposure to the solvent vapor stream, indicating the capillary condensation of the solvent in the interstices of the NP film. The thickness of the NP film does not change upon exposure to solvent vapor as shown in Figure 2.3. This indicates that the solvent is condensing within the film and not on top of the film, which allows for the use of a simple mixing rule to estimate the percent of the voids filled with solvent (Figure 2.3). This change in refractive index upon solvent vapor exposure corresponds to near-complete filling of the pores in the 23 nm particle packing for all the solvents used in this study; for reference, the void fraction within the densely packed NP film is approximately 0.31. We also observe capillary condensation within the packing of 77 nm particles. However, owing to the larger pores in the packings of these larger particles, less than a quarter of the void space is filled with liquid solvent as shown in Figure 2.3.

2.3. Effect of Flory-Huggins χ Parameter

2.3.1. Low Molecular PS Infiltration

The bilayer samples are exposed to solvent vapor through an apparatus that allows a nitrogen stream that has been bubbled through a liquid-state solvent to come in contact with the bilayer sample (Figure 2.1). The SEM images of as-prepared bilayers are compared to those of bilayers after solvent vapor exposure in Figure 2.4. In the infiltrated sample, polymer (PS, $M_n = 8,000$ g/mol) within the interstitial voids in the NP packing is

evident in the SEM images. Furthermore, in the infiltrated sample, one can observe a decrease in the thickness of the polymer layer, indicating polymer infiltration. The top-view SEM image of the infiltrated sample for the smaller NPs (Figure 2.4B, inset) also shows NPs that appear to be embedded in polymer. The average distance between the NP centers for the infiltrated smaller NP film ($\langle d \rangle \approx 26$ nm) does not change significantly compared to the un-infiltrated sample ($\langle d \rangle \approx 27$ nm), but the visible portion of the NPs shrinks, indicating polymer filling the spaces between the NPs. We do not observe any polymer overlayer on top of these NPs, which also agrees with our ellipsometry measurements.

Figure 2.4. Cross-sectional SEM images of PS/23 nm SiO₂ particles (A, B) and PS/77 nm SiO₂ particles (C, D). (A) and (C) show the bi-layer films before solvent exposure; (B) and

(D) show the films after infiltration using SIP. Inset: top-down SEM images. All scale bars are 100 nm.

Table 2.1. Flory-Huggins χ parameters between PS and different solvents used in this study.

Solvent	toluene	cyclohexane	1,4-dioxane	morpholine	hexane	diacetone alcohol	ethanol
χ	0.35	0.53	0.55	0.80	1.03	1.90	2.37

Solvent quality has a significant impact on the thermodynamics and dynamics of polymers in solvents. To investigate the effect of solvent quality on SIP (**Table 2.1.** Flory-Huggins χ parameters between PS and different solvents used in this study. Table 2.1), PS-SiO₂ NP bilayers are exposed to seven different solvent vapors with varying polymer-solvent Flory-Huggins interaction parameter (χ). The polymer-solvent χ parameter ranges from that for very good solvents ($\chi = 0.35$) to non-solvent systems ($\chi = 2.37$), where $\chi_c = 0.61$ is the calculated critical value that indicates a theta solvent for the polymer.⁶⁴ The Flory-Huggins interaction parameter is calculated using the method described by Hansen which emphasizes the dispersion interactions between molecules (see Eq. 2.3-2.4).⁶⁵ The volume fraction of PS in the NP film (ϕ_p) upon SIP is estimated based on changes in the thickness of the bottommost PS layer (see Eq. 2.2). The top composite layer is modelled as a homogenous layer since there is no clear evidence of a gradient and no clear infiltration front is observed based on ellipsometry modeling.¹ The thickness of the NP packing does not change after SIP (Figure 2.4).

The polymer volume fraction in the top layer (ϕ_p) is also dependent on the size of the nanoparticles in the packing, with larger nanoparticles leading to less infiltration

irrespective of solvent quality (Figure 2.5). This behavior is attributed to the decrease in the extent of capillary condensation observed for larger nanoparticle packings (Figure 2.3). From this we infer that, if the interstitial voids of the nanoparticle packing are not completely filled with solvent, the polymer does not fully infiltrate into those voids. The lack of polymer between the NPs in the top-down SEM images of the infiltrated sample for the larger nanoparticles also indicates that infiltration is incomplete in this system (Figure 2.4D).

Figure 2.5. Volume fraction of PS in the NP packing (ϕ_p) for PS ($M_n = 8,000$ g/mol) into 23 nm particle packings (circles) and 77 nm particle packings (diamonds), after 30 minutes (closed) or 24 hours (open) of vapor exposure for various solvents at different χ .

The extent of infiltration depends on the solvent quality, as estimated by χ , the size of the nanoparticles, and the duration of annealing. The poorer the solvent (i.e., the higher the χ), the smaller ϕ_p is found in the PINF for a constant annealing time of 30 min. When the samples are exposed to solvent vapors for 24 hours, ϕ_p is increased, as can be seen for the cases of cyclohexane ($\chi = 0.53$) and hexane ($\chi = 1.03$). For the case of very good solvents such as toluene (i.e., low χ), infiltration occurs rapidly. Extended exposure of bilayers to some of these very good solvents, however, can induce dewetting of PS from the substrate (i.e., the Si wafer), complicating precise sample characterization. For non-solvents (e.g., diacetone alcohol), no infiltration is observed even after a 24-hr exposure. The highest calculated fill fraction of polymer possible in the NP film, found by completely filling the interstices of the NP film using CaRI, is $\phi_{p,max} \approx 0.31$. Using SIP, the maximum volume fraction of polymer in the composite is roughly $\phi_p \approx 0.25$, indicating that the SIP PINFs are porous.

2.3.2. Infiltration of Higher Molecular Weights

One intriguing question is whether polymers of high molecular weight can be induced to undergo SIP, especially when the characteristic size of polymer chains is larger than the average pore size in the NP packing. To examine this possibility, we use bilayers composed of intermediate and high molecular weight PS ($M_n = 21,000$ and $173,000$ g/mol; for both polymers $PDI < 1.1$) and 23 nm SiO_2 NPs. The 21k and 173k PS have estimated radii of gyration of 4 nm and 12 nm in cyclohexane, respectively, whereas the estimated average pore radius in random close packing of 23 nm SiO_2 NPs is 3 - 5 nm.^{66,67} The 173k

PS also represents a fully entangled system in its melt state. We find, remarkably, that these high molecular weight polymer chains are able to undergo SIP into the NP film provided that they are exposed to a good solvent vapor (Figure 2.6). Furthermore, even with a solvent of moderate quality such as cyclohexane ($\chi = 0.53$), after 24 hours of vapor annealing, the 21k PS infiltrates fully into the packing and the 173k PS begins to infiltrate the packing (Appendix B). Additionally, for a poor solvent such as hexane ($\chi = 1.03$), the 21k PS infiltrates to a small degree after 24 hours (Appendix B). This result suggests that while infiltration dynamics are slowed by molecular weight, SIP is thermodynamically favored despite the increase in confinement within the NP packing.

Figure 2.6. Volume fraction of PS in the NP packing (ϕ_p) for PS into 23 nm SiO₂ NP packings (circles) using different good solvents ($\chi < \chi_c$) as a function of PS molecular weight after 30 min of vapor exposure.

2.4. SIP with Liquid Solvent

The fact that even slightly poor solvents such as hexane can induce SIP at long exposure times (Figure 2. 5) could provide a significant advantage; by using poor solvents instead of good solvents, bilayers might be directly submerged in liquid solvent without compromising sample integrity. The use of liquids instead of vapors could also offer significant advantages in manufacturing processes, since solvent vapors may pose health and safety hazards. Furthermore, liquid phase processes such as dip coating are far simpler to implement than are processes that rely on annealing in vapor chambers. To test this possibility, a bilayer is directly submerged in liquid hexane. PS indeed infiltrates the NP packing, as shown in Figure 2.7. In contrast, direct submersion in good solvents such as toluene leads to immediate dissolution of the bilayer from the substrate.

The dynamics of infiltration, as represented by the volume fraction of polymer in PINF as a function of time, in vapor SIP and liquid SIP are quite similar to each other as shown in Figure 2.7. These trends suggest that capillary condensation occurs rapidly in the vapor annealing case and that the condensed liquid in the interstices plasticizes the polymer and induces SIP, making both systems essentially identical from the perspective of the polymer layer. However, when the bilayers are liquid-annealed in hexane for much longer times, the polymer layer is completely lost from the bilayer structure, whereas the refractive index changes indicate that the volume fraction of polymer in the PINF layer (ϕ_p) stays constant around 0.25. This result indicates that once polymer infiltrates the NP packing,

there is a continuous flux of polymer dissolving into the solvent bath from the top of the packing.

Figure 2.7. Volume fraction of PS ($M_n = 8,000$ g/mol) in SiO_2 NP packing (ϕ_p) after annealing with hexane ($\chi = 1.03$) via vapor annealing (black circles) and liquid annealing (blue squares) as a function of time.

2.5. SIP with Monomer as Solvent

In place of a typical solvent, a monomer which can undergo capillary condensation and plasticize the underlying polymer layer can also be used to induce SIP. Furthermore, upon the infiltration of the solvated polymer, the monomer can be photopolymerized to form a polymer blend-filled NP film (Figure 2.8A). In this study, a bilayer of PS and SiO_2 NPs is exposed to a vapor phase mixture of initiator and monomer, in this case 2-hydroxy-

2-methylpropiophenone (HMP) and methyl methacrylate (MMA), respectively. Infiltration is monitored using *in situ* ellipsometry, and once complete, the bilayer film is exposed to UV light, resulting in the condensed MMA polymerizing into polymethylmethacrylate (PMMA). The sample is subsequently dried and characterized.

We find that independent control of the volume fraction of each polymer can be achieved by tuning the ratio of initial thicknesses of the polymer and NP layers (h_{PS}/h_{NPs}) as well as the duration of UV exposure during photopolymerization (Figure 2.8B-C). As seen in Figure 2.8B, with increasing h_{PS}/h_{NPs} , the volume fraction of PS in the composite increases and the void fraction decreases, while the volume fraction of PMMA remains constant. At constant h_{PS}/h_{NPs} , with increasing UV exposure time, we see that the volume fraction of PMMA increases and the void fraction decrease, while the volume fraction PS remains constant (Figure 2.8C). This method enables the design and engineering of polymer blend/NP ternary composite films with high loadings of NPs and tunable compositions.

Figure 2.8. (A) Schematic illustration of a NP/polymer bilayer being annealed with the monomer and photoinitiator vapor, leading to capillary condensation of the monomer and photoinitiator within the NP packing, followed by the infiltration of polymer. The subsequent UV exposure leads to the polymerization of the monomer and a blend of two polymers in the interstices of the packing. The volume fraction of each component (PS, PMMA and void) in the polymer blend-filled NP films upon (B) varying h_{PS}/h_{NPs} from ~ 0.08 to ~ 0.24 while keeping UV exposure constant at 30 min., and (C) varying the UV exposure duration while keeping h_{PS}/h_{NPs} constant at ~ 0.12 . Figure is reprinted (adapted)

with permission from Y. Qiang, N. Manohar, K. J. Stebe, and D. Lee, *Mol. Sys. Des. Eng.*, **2018**, 3, 96-102.⁶⁸

2.6. Conclusions

In conclusion, solvent-driven infiltration of polymer (SIP) in polymer/NP bilayers yields high filler-fraction nanocomposite films of varying porosity, which can be tuned by controlling the capillary condensation of solvent, solvent quality, and solvent exposure time. Polymers undergo SIP even when slightly poor solvents are used, and high molecular weight polymers can also be induced to undergo SIP upon extended exposure. The use of slightly poor solvents provides a significant advantage, in that they enable liquid submersion (dip processing) to induce SIP, potentially providing a route to a room-temperature, industrially-viable continuous fabrication process to prepare porous PINFs. However, further optimization is required before the technique can meet industrially relevant time scales. Furthermore, if a monomer is used as solvent to induce SIP, the condensed solvent can be photopolymerized after infiltration is complete to produce polymer nanoblend composite films.

Chapter 3. Role of Confinement in SIP

Content in this chapter is reprinted (adapted) with permission from N. Manohar, K. J. Stebe and D. Lee. Effect of Confinement on Solvent-driven Infiltration of Polymer (SIP) into Nanoparticle Packings. *Macromolecules* **2020**, in press.

3.1. Introduction

Here, we explore the dynamics of polymer infiltration and partitioning of polymer into the interstices of NP packings to gain insight on how confinement affects SIP. Different molecular weights and particle sizes are used to probe a range of confinement ratios under a good solvent condition (polystyrene (PS) in toluene, Flory-Huggins parameter, $\chi = 0.34$). This SIP system provides a unique platform to investigate the effect of extreme nanoconfinement on the behavior of highly solvated polymers. Although the partitioning of polymer from bulk solution to a pore and the relative mobility of polymer within a confining pore have been studied, the concentration regimes have been limited to dilute solutions and solutions just above the critical overlap concentration (see Section 1.4).^{52,54–56} However, prior studies are lacking in regimes where the characteristic size of the polymer chains is significantly larger than that of confinement, and the concentration of confined polymer transitions from dilute to concentrated regimes.

We show that the kinetics of polymer infiltration into the nanoparticle packing strongly depends on the degree of confinement, whereas the final extent of infiltration into the packing does not. The infiltration time scales strongly with the confinement ratio, which

we define as the ratio of the radius of gyration of polymer and the average pore size within the NP packing ($\lambda = R_g / \langle R \rangle_{\text{pore}}$) (Figure 3.1). The infiltration dynamics in SIP are slower than chain dynamics predicted for a single chain under cylindrical confinement but faster than the diffusion dynamics in a polymer melt. In contrast, the final volume fraction of polymer within the NP packing is not dependent on the degree of confinement, indicating that at long times, confinement does not hinder the final extent of infiltration. We postulate that in the SIP system, the environment surrounding the infiltrating polymer shifts over time from dilute to concentrated, leading to changes in relevant polymer length scales, which at long times eliminates the effect of confinement imposed on the polymer chains by the NP packing. We show that the polymer partitions strongly into the voids of the NP packing, which is attributed to the affinity, albeit weak, of PS to the surface of the silicon dioxide (SiO_2) NPs.

Figure 3.1. A schematic illustrating important length scales in the system. The radius of gyration of an unperturbed polymer in solution (R_g) and the average pore radius in the NP packing ($\langle R \rangle_{\text{pore}}$).

3.2. Methods

3.2.1. Bilayer Fabrication

PS of four different molecular weights (M_n = 8,000 g/mol, 80,000 g/mol, 173,000 g/mol and 1,000,000 g/mol; $PDI \leq 1.10$) is purchased from Polymer Source, Inc. SiO₂ NPs of two average diameters (LUDOX brand TM-50: $\langle D \rangle_{NP} = 22$ nm, and SM: $\langle D \rangle_{NP} = 7$ nm) are purchased from Sigma Aldrich. PS solutions are prepared by bath sonication of a PS/toluene mixture for three hours up to one day (depending on molecular weight), followed by syringe microfiltration (hydrophobic, pore size 0.2 microns). The filtered solution is then spin-coated onto O₂ plasma-treated silicon wafers to obtain ~250 nm thickness films. NP dispersions are diluted in DI H₂O and bath sonicated for three hours, followed by syringe microfiltration (pore size 0.45 microns). The NP dispersions are then spin-coated onto the previously prepared PS thin films to obtain a densely packed layer with a thickness of ~250 nm. PS-only thin films with no NP coating are used for in situ swelling studies.

3.2.2. Scanning Electron Microscopy (SEM) Imaging

Cross-section samples are obtained by cleaving pristine or infiltrated samples in half. Top-down and cross-section samples are sputtered with a 4 nm layer of iridium prior to imaging. A FEI Quanta 600 ESEM is used to take scanning electron microscopy images. Images are obtained at 25 kV at high vacuum using an Everhart Thornley detector.

3.2.3. Ellipsometry Measurements

A J. A. Woollam alpha-SE spectroscopic ellipsometer is used for in situ and ex situ measurements. In situ measurements are carried out using a vapor annealing chamber setup

previously described (see Section 2.2.1.).⁴² Ex situ measurements are carried out by placing samples on a mesh holder suspended directly above a 100 mL reservoir of solvent (toluene) within a sealed container (Figure 3.2). Due to the time it takes for opening and closing this chamber during sample placement, the maximum resolution of the ex situ measurements is ~1 min. The SIP process is quenched by removal of the sample from the chamber followed by placement in a vacuum oven for ~12 hrs. The dried sample is then measured under ambient conditions, using a simple two-layer Cauchy model as previously described (Section 2.2.1.).⁴²

Figure 3.2. A) A schematic illustration of the ex situ SIP setup, and B) the extent of infiltration (ϕ_p) vs toluene exposure time for PS ($M_n = 80$ kg/mol) into 22 nm SiO₂ NP packing.

3.2.4. Quartz Crystal Microbalance with Dissipation Mode (QCM-D)

QCM-D measurements are conducted using a QSense E4 system to find shifts in the frequency and dissipation due to mass adsorbing onto an oscillating quartz crystal. The

sensor crystal used is a QSX 303 SiO₂, which has a 100 nm Au electrode coated with 50 nm of SiO₂. Prior to experiments, the crystal is rinsed with distilled water and isopropanol, and then O₂ plasma-treated for ten minutes. The crystal is connected to a flow cell with the SiO₂ surface exposed, and a baseline frequency and dissipation factor are obtained in air. A wet baseline is collected after flowing toluene over the sensor at 50 sccm for an hour to allow for stabilization. The sensor crystal is then exposed to 0.05wt% polystyrene ($M_n = 173,000$ g/mol) in toluene solution flowing at 50 sccm. The frequency and dissipation shifts are monitored with continuous flow of the polystyrene solution until stabilization. The sensor crystal is then flushed with pure toluene at 50 sccm for a day to induce desorption of loosely bound polymer. The final shift in frequency and dissipation factor are then modelled using a modified viscoelastic model via the QTools software package (see Appendix C). The dry thickness of an irreversibly adsorbed polystyrene layer on a silicon wafer was obtained using ellipsometry measurements. This value is then used to confirm the wet layer density from the QCM-D model, as the dry layer thickness provides an estimate for the volume fraction of polymer in the wet layer.

3.2.5. Confinement and Concentrations in System

Table 3.1. Characteristics of PS and SiO₂ NPs used in this study.

M_n^a (kg/mol)	$R_g^†$ (nm)	ϕ^{*b}	$\phi_I^{*\ddagger}$		λ^c	
			7 nm	22 nm	7 nm	22 nm
8	2.5	0.054	0.224	0.049	2.9	0.9
80	9.9	0.009	0.229	0.050	11	3.7
173	16	0.005	0.230	0.050	18	5.8
1,000	45	0.001	0.234	0.051	52	16

^aThe number average molecular weights (M_n) as provided by the supplier; [†]the calculated radius of gyration for unconfined PS in toluene⁶⁷; ^bthe unconfined critical overlap volume

fraction (ϕ^*); ‡the calculated confined critical overlap volume fraction (ϕ_I^*) for a polymer in a capillary⁶⁹; °the confinement ratio ($\lambda = R_g/\langle R \rangle_{\text{pore}}$) for each system considered, with $\langle R \rangle_{\text{pore}} \approx 0.9$ for the 7 nm NPs and $\langle R \rangle_{\text{pore}} \approx 2.7$ for the 22 nm NPs.⁶⁶

The confinement ratio, λ , is defined as the ratio of the radius of gyration of polymer and the average pore size ($\lambda = R_g/\langle R \rangle_{\text{pore}}$) (Figure 3.1). A range of confinement ratios ($\lambda = 1-50$) is studied by varying PS molecular weight and SiO₂ NP size. For the systems considered in this study, the radius of gyration (R_g), critical overlap concentration in a bulk solution (ϕ^*) and that adjusted for confinement (ϕ_I^*),⁶⁹ as well as the confinement ratios (λ) are provided in Table 3.1. Only one of the molecular weights ($M_n = 8,000$ g/mol) is below the entanglement threshold for PS, whereas the other three ($M_n = 80,000$ g/mol; 173,000 g/mol; and 1,000,000 g/mol) are entangled systems. The radius of gyration of unconfined PS in toluene is determined from the molecular weight using empirical relationships determined via light scattering studies.⁶⁷ The NP sizes are chosen such that the curvature is large enough to induce complete capillary condensation within the NP packing; that is, the pores are completely filled with condensed solvent. Two commercially available SiO₂ NPs with average diameters of 7 and 22 nm are used in this study. The average pore size within the packing $\langle R \rangle_{\text{pore}}$ is estimated from simulations of void volumes in random close packings of spheres.⁶⁶ Previous experiments have shown that packings of NPs larger than 70 nm induce partial capillary condensation due to the decrease in the negative curvature of condensed fluid interfaces within the packing.^{23,42} SIP occurs in all the systems studied (Figure 3.3). The SIP experiments are run to completion, and the time it takes for infiltration to plateau as well as the final value of the plateau are found via ex

situ quenching experiments and studied as a function of the confinement ratio, λ (Figure 3.2).

Figure 3.3. Cross sectional SEM images before and after SIP. A) 22 nm SiO₂ NPs, PS ($M_n = 80,000$ g/mol) bilayer before infiltration and B) after infiltration using toluene, C) 7 nm SiO₂ NPs, PS ($M_n = 80,000$ g/mol) bilayer before infiltration and D) after infiltration using toluene. Insets show top down images of each nanoparticle packing. Scale bar: 100 nm. Upper dashed line indicates the interface between the NP and composite layers; lower dashed line indicates the interface between the polymer layer and Si wafer.

3.3. Kinetics of Infiltration

In the SIP system, polymer infiltrates from a solvated polymer film, which serves as a concentrated polymer reservoir, into solvent-filled voids between the nanoparticles. Initially, these voids are empty of polymer, and the infiltrating polymer experiences a very dilute environment. As infiltration progresses, however, and more chains enter the voids, the chains begin to overlap and experience more crowding within the voids. Infiltration kinetics therefore reflect polymer passing through various concentration regimes. Figure 3.4 shows that the time it takes for complete infiltration to occur in each system is strongly dependent on the confinement ratio of the system. This effect cannot be attributed solely to the rate of chain escape from the concentrated reservoir, which would imply an increase in infiltration time with molecular weight as longer chains would require longer times to escape. The observed dependence of infiltration time on pore size indicates that such a time scale cannot be the controlling mechanism, since the same molecular weight of PS takes longer to infiltrate into the packing with smaller pores. For example, in Figure 3.4, the highest molecular weight PS ($M_n = 1,000,000$ g/mol) takes roughly one hour to infiltrate into the 22 nm NP packing (dark blue circle, $\lambda = 16$) but takes ten hours to fully infiltrate the 7 nm NP packing (light blue circle, $\lambda = 52$). This result indicates that the transport of polymer chains within the solvent-filled pores control the SIP dynamics. As polymer partitions from the crowded swollen film into solvent-rich voids within the packing, the extreme nanoconfinement likely affects the chain conformation and leads to some loss of conformational entropy.

Figure 3.4. Infiltration time (log scale) is plotted as a function of confinement ratio (log scale) for bilayers of various MW with SiO₂ NPs with $\langle D \rangle_{NP} \approx 7$ nm (light blue circles) and $\langle D \rangle_{NP} \approx 22$ nm (dark blue circles). The dashed line indicates a power law fit, with the critical exponent displayed on the plot ($\lambda^{3/2}$). The dotted gray lines indicate scaling behavior for melts (λ^2) and for dilute solutions ($\lambda^{2/3}$).^{44,70}

The infiltration time (τ) as a function of confinement ratio can be described by a power law with an exponent of 3/2 ($\tau \sim \lambda^{3/2}$). Although this exponent has not been predicted by an existing theory, prior studies provide scaling for limiting cases. According to a scaling model for infiltration of a single polymer chain into cylindrical confinement, the dynamics are expected to scale with confinement with an exponent of 2/3 ($\tau \sim \lambda^{2/3}$).⁴⁴ In the SIP system, however, polymer infiltration eventually progresses into much higher

concentration regimes than this model system as the pore is filled with additional polymer chains from the reservoir. The overlap of polymers confined in capillaries is expected to occur at higher concentrations than that of bulk critical overlap due to confined chains occupying less volume than bulk chains (Table 3.1).⁶⁹ When the SIP process nears completion, the concentration of polymer within the pore reaches ~ 0.7 , which is well above the overlap concentration under confinement (Table 3.1) and very close to the melt state. Thus, the infiltration behavior in the late stage of SIP likely has some resemblance to the dynamics of confined polymer melts. In such systems, infiltration time is predicted to follow a linear relationship with chain length ($\tau \sim N^1$).⁷⁰ Since $R_g \sim N^{1/2}$ in an ideal melt, with a confinement ratio defined by the radius of gyration ($\lambda = R_g / \langle R \rangle_{\text{pore}}$), the dynamics should scale as $\tau \sim \lambda^2$ (Figure 3.4). The SIP system passes dynamically from empty to crowded environments within the pore, obeying a power law bounded by the predicted scaling exponents in the dilute and melt regimes. Moreover, interactions with the NP surface could play a role in these dynamics, since the extent of surface coverage presumably evolves as infiltration proceeds. The surface diffusion of polymer melts on attractive surfaces is predicted to have the scaling behavior $\tau \sim N^{5/2}$, while for weak interactions, the relationship is identical to bulk reptation dynamics, namely $\tau \sim N^3$, which both predict a stronger dependence on chain length than that observed in the SIP process.⁷¹

3.4. Partitioning into Confinement

3.4.1. Partition Coefficient (K)

Figure 3.5. A) Swelling of PS thin films (~250 nm) of two different MWs ($M_n = 80,000$ g/mol – grey diamonds; $M_n = 1,000,000$ g/mol – black circles) upon exposure to toluene vapor observed using in situ ellipsometry. B) The extent of infiltration (volume fraction of polymer in voids of the NP packing) as a function of confinement ratio (log scale). The final extent of infiltration $\phi_{p,f}$ for bilayers of various MW with SiO₂ NPs with $\langle D \rangle_{NP} \approx 7$ nm (light blue circles) and $\langle D \rangle_{NP} \approx 22$ nm (dark blue circles) are shown.

At long times, the polymer eventually stops partitioning into the pore, which is observed experimentally as a plateau in the change in the refractive index of the NP packing and the thickness of the underlying polymer layer. The partitioning of polymer in the SIP systems is defined by two values: the volume fraction of polymer in the external swollen polymer film at equilibrium ($\phi_{p,e}$), and the final volume fraction of polymer inside the

voids of the NP packing ($\phi_{p,f}$) (Figure 3.5). $\phi_{p,f}$ is obtained from the ratio of the volume fraction of polymer in the NP layer (ϕ_p), obtained from the change in refractive index of the NP layer after infiltration, to the original void fraction within the NP packing ($\phi_p = \frac{\phi_p}{\phi_{\text{void}}}$). To our surprise, all the systems considered in this study infiltrated to the same extent, independent of the confinement ratio, as shown in Figure 3.5B, indicating that confinement had little effect on the final partitioning of polymer into the solvent-filled pore. $\phi_{p,f}$ upon completion of infiltration is approximately 0.7, regardless of λ . Based on the ratio of this value and the volume fraction of polymer in the swollen film, a partition coefficient $K = \frac{\phi_{p,f}}{\phi_{p,e}}$ for the SIP system can be calculated. The equilibrium volume fraction of polymer in the swollen film ($\phi_{p,e}$), determined from *in situ* ellipsometry of PS films exposed to toluene, is ~ 0.45 and does not depend strongly on the molecular weight of polymer (Figure 3.5A). Therefore, the partition coefficient for this system is roughly $K = 1.55$, which indicates that despite strong confinement, the polymers prefer to be in the solvent-filled pores than in the solvent-swollen polymer film phase.

Prior studies have shown that when polymer partitions from a solution phase into a confined space, K is less than 1 and approaches unity as the concentration in the solution phase increases.^{43,54,69} This trend is attributed to the osmotic pressure outside the pore at higher concentrations overcoming the entropic barrier of confinement within the pore.⁵⁴ However, these studies typically use polymer/pore systems that have purely repulsive interactions. Previous simulation studies indicate that polymer can partition more strongly

into confined spaces ($K > 1$) when there are strong interactions between the polymer and pore surface.^{58,72} Although PS has been observed to interact with and adsorb onto unfunctionalized SiO₂ surfaces under theta conditions,^{73–75} there are a far fewer studies that investigate the adsorption behavior of PS onto SiO₂ surfaces from a very good solvent (toluene). A previous report suggests that some interactions exist between PS and SiO₂.⁷⁶

3.4.2. Surface Adsorption in PS/toluene/SiO₂ System

Figure 3.6. Change in frequency (third overtone $\Delta f/3$ – black solid line) and dissipation factor (ΔD – red dashed line) during PS adsorption and desorption in solution from in situ

QCM-D measurements, with schematics below. Initially (1), pure toluene is flowing over a bare SiO₂-coated sensor crystal, followed by (2) exposure to a 0.05wt% solution of PS ($M_n = 173,000$ g/mol) dissolved in toluene which continues to adsorb until it plateaus (3), and finally the system is quenched with pure toluene immediately after. The frequency and dissipation do not recover (4) to their original values, indicating irreversible adsorption of PS on the SiO₂ surface.

To test whether PS in toluene can adsorb on the surface of SiO₂, we perform quartz crystal microbalance with dissipation (QCM-D) experiments. In this experiment, a SiO₂-coated quartz crystal is exposed to a continuous flow of dilute PS dissolved in toluene ($M_n = 173,000$ g/mol, $c = 0.05\text{wt}\%$) and the resulting changes in the frequency (Δf) and dissipation (ΔD) are monitored in situ. The concentration of PS (0.05wt%) is chosen such that the system is expected to be past the plateau of the adsorption isotherm, but not high enough to significantly impact the viscosity of the fluid phase.^{74,77} We observe substantial changes in f and D when the PS solution is flowing over the crystal, as shown in Figure 3.6. Once the shifts are stabilized, the sensor crystal is exposed to pure toluene to allow any loosely adsorbed chains to desorb. Even after ~ 1 day of toluene flow, the frequency and dissipation do not fully recover to the original baseline values. This observation indicates that irreversible adsorption of PS occurs onto the SiO₂ surface from the toluene solution. Modelling of this final adsorbed layer using an extended viscoelastic model indicates that the solvated adsorbed layer is roughly 12 nm thick, which is comparable to

the R_g of the PS in solution (Appendix C). It has been postulated that interactions between PS and the untreated SiO_2 surface could be attributed to $\text{SiOH}-\pi$ hydrogen bonds forming between the phenyl ring of the PS and the silanol groups on the SiO_2 surface.⁷⁶ Such an interaction has been observed previously in gas adsorption studies of benzene and toluene onto SiO_2 .⁷⁸

3.4.3. Effect of Confinement on Partitioning

Figure 3.7. A schematic illustrating the shifting characteristic length scale of polymer within the pore (L_{poly}) as infiltration proceeds, from initially R_g due to the pore being an empty/ dilute environment, to finally ξ as the pore becomes more crowded with overlapping polymer chains.

Unlike the dynamics, the partitioning behavior of polymer into the interstitial voids of the nanoparticle packings in the SIP system does not strongly depend on the confinement ratio (Figure 3.5). We believe that the independence of partitioning on the confinement ratio is attributed to the fact that, at long times, the concentration within the pores exceeds

the critical overlap concentration (Figure 3.7). The polymer chain's characteristic length scale in such a system becomes the length of unperturbed polymer between chain overlaps, known as the correlation length, which is not a function of molecular weight, but rather of the concentration and stiffness (Kuhn length) of polymer. The correlation length of PS at the final concentration ($\xi \approx 2 \text{ nm}$)⁷⁹, which represents the longest unperturbed chain dimension between overlaps with other polymer chains, is likely to be smaller than the effective pore sizes; in essence the polymer does not feel extra confinement even though the R_g is significantly larger than the size of the pore as the concentration of polymer increases above the critical overlap concentration.

3.5. Conclusions

In summary, we find that the extent of confinement in the SIP system affects the kinetics of polymer infiltration into the nanoparticle packing, but not the final extent of infiltration in a good solvent. The infiltration time is found to scale with confinement ratio ($\tau \sim \lambda^{3/2}$), which is bounded between the behavior of confined polymer melts (λ^2) and that of confined single polymer chains ($\lambda^{2/3}$). However, the final volume fraction of infiltrated polymer is independent of the extent of confinement, since the fully infiltrated SIP system is at concentrations well above the critical overlap concentration, where the correlation length scale is smaller ($\xi \approx 2 \text{ nm}$) than the average pore sizes within the NP packings and thus dominates the partitioning. Furthermore, the partitioning from the swollen polymer film into the voids of the NP packing is very high ($K \approx 1.55$), indicating that some surface

adsorption of PS onto the SiO₂ NP surface from toluene occurs in the SIP system. This interaction is confirmed qualitatively via QCM-D studies of a PS solution in contact with a SiO₂ surface, which shows irreversible adsorption of a thin polymer layer onto the surface.

Chapter 4. Role of Polymer-NP Interactions in SIP

Content in this chapter is adapted from work that is under preparation for publication and has been performed in collaboration with Robert A. Riggleman from the Department of Chemical and Biomolecular Engineering at the University of Pennsylvania.

4.1. Introduction

As described in Chapters 2 and 3, the kinetics of the SIP process is strongly influenced by the quality of solvent and the degree of confinement in the system, but the role of interactions between the polymer and the NP surface has yet to be explored. The strength of polymer-NP interactions is expected to play a major role due to the high surface to volume ratio inherent to a NP packing. Previous studies of the dynamics and partitioning of polymer solutions under confinement either completely neglect surface interactions by using only non-adsorbing polymer-pore systems,^{43,52} or neglect the effect of solvent quality.^{58,80} A more holistic theory on polymer solution infiltration into confinement which takes into account both solvation effects and surface effects is not readily available. The effect of surface interactions on polymer infiltration under confinement in melt systems has been studied,^{76,81} but the impact of surface interaction strength on infiltration and polymer dynamics is not fully understood. Infiltration during the SIP process is further complicated by the presence of solvent, and will depend on the competition between adsorption, solvation and confinement effects within the system.

4.1.1. Molecular Dynamics (MD) Simulations

The effect of polymer-NP interactions on infiltration during SIP has been explored using molecular dynamics (MD) simulations (Figure 4.1), and indicates that three regimes can emerge, solvent-mediated infiltration where the polymer-NP interactions are very weak, surface-mediated infiltration when there are strong polymer-NP interactions present, and an intermediate regime where both modes of infiltration occur (Figure 4.2).⁸² These regimes are explored by changing the Lennard-Jones (LJ) interaction energy (ϵ_{P-NP}) between polymer beads and the NP surface as defined by a 12-6 LJ potential, where σ is the bead size and r is the distance between the interacting beads:

$$U_{LJ} = 4\epsilon_{P-NP} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{Eq. 4.1}$$

In Figure 4.1C, it can be seen that with $\epsilon_{P-NP} = 0.6$, infiltration proceeds faster and has a more diffuse front, whereas with $\epsilon_{P-NP} = 1.1$, infiltration is considerably slower and has a more coherent infiltration front. The fastest kinetics are predicted to occur in an intermediate polymer-NP interaction regime (Figure 4.1D), which is further confirmed by entropic barrier model studies. This nonmonotonic dependence on polymer-NP interactions is postulated to be due to low polymer-NP interactions providing additional pathways for infiltration, allowing for faster infiltration, while at higher polymer-NP interaction strengths the polymer begins to adsorb to the NP surface, which slows infiltration. Experimentally, it is expected that SIP occurs in this intermediate regime where infiltration is fast and can utilize both pathways without being hindered by strong adsorption (Figure 4.2).

This study does not take into consideration the effect of changing solvent quality (polymer-solvent interactions), which is kept constant in the MD simulations, and also does not investigate the effect of confinement on kinetics. In order to probe these different phenomena simultaneously, a less computationally expensive model is needed that can provide information on kinetics as surface interactions, solvent quality, and confinement extent are tuned.

Figure 4.1. A) Model system for SIP MD simulations. B) Choice of interaction potential between polymer and NP in the model system. C) Front position indicators H_{85} and H_{99} for the two systems – blue curves depict data for weakly ($\epsilon\epsilon_{P-NP} = 0.6$) interacting system and the red curves depict data for strongly interacting system ($\epsilon_{P-NP} = 1.1$) for $T = 0.6$. D) Squared front position (H_{99}^2) vs interaction parameter (ϵ_{P-NP}) at three different times during infiltration for $T = 0.7$. Figure is reprinted (adapted) with permission from R. B. Venkatesh, T. Zhang, N. Manohar, K. J. Stebe, R. A. Riggleman and D. Lee, *Mol. Sys. Des. Eng.*, **2020**, 5, 666-674.⁸²

Figure 4.2. Schematic illustration of polymer infiltration in an adhesion-dominated regime (left), an intermediate regime (center) and a dissolution-dominated regime (right).

4.1.2. Entropic Barrier Model for Polymer Translocation

The entropic barrier model is a simple methodology to understand how polymers overcome entropic barriers to go from one cavity to another.^{83,84} By calculating the free energy of a polymer with one end tethered to a “hole”, and allowing this polymer to escape into a second region through this single-segment width “hole” (Figure 4.3), a mean translocation time can be calculated that in essence derives kinetic information for entropic hopping from the thermodynamic landscape experienced by the polymer on either side of the hole.^{84,85} Previously, this model has been used to study ideal polymer translocation through a pore in a planar membrane,⁸⁵ escape from a spherical vesicle,⁸³ between two cavities of different sizes, translocation through an adsorbing hole,⁸⁶ and translocation through single-segment width channels of varying lengths.⁸⁷ Polymer chains with excluded

volume interactions have also been considered, and require a shift to numerical methods in order to accommodate many body interactions.⁸⁸ In order to approximate the SIP system, translocation of a polymer with excluded volume interactions between two circular cavities is considered, with the incorporation of interactions between the polymer chain and the wall of the cavity, which has not been previously done.

Figure 4.3. Schematic illustration of polymer translocation in the entropic barrier model. N is the chain length of the polymer, R is the cavity radius, and m is the number of segments which have translocated into the second cavity.

In this study, we probe the effect of polymer-wall interactions on the kinetics of polymer translocation through an entropic barrier and investigate how this effect changes with solvent quality (excluded volume interactions) and confinement. The free energy landscape within the cavities is obtained by self-consistent field theory (SCFT) calculations, and these free energies are used to determine the mean translocation time (τ) of polymer from one cavity to another. It is found that the τ is strongly dependent on the strength of the polymer-wall interactions and shows a nonmonotonic dependence with interaction strength which qualitatively agrees with the MD simulations. Kinetics initially get faster with increasing surface interactions, but eventually slow down as interactions become strong enough for adsorption to occur. Interestingly, as solvent quality is improved,

this transition into slower kinetics shifts toward stronger interaction strengths. Furthermore, under asymmetric confinement conditions, the behavior with increasing polymer-cavity interactions is monotonic, with the more strongly confined cavity becoming more favorable at higher interaction strengths due to proximity of polymer to the attractive cavity wall.

4.2. Methods

4.2.1. Entropic Barrier Model to Obtain τ

In this model, a polymer chain escapes from cavity 1 to cavity 2 via a hole that is the width and length of a single polymer segment. The free energy of a polymer chain of N segments translocating can be calculated as a function of m , or the number of segments translocated into cavity 2. This free energy $F(m)$ is found by:

$$F(m) = F_1(N - m) + F_2(m) \quad \text{Eq. 4.2}$$

In order to obtain $F(m)$ for any m , the free energy in each cavity as a function of chain length of polymer within that cavity must be calculated for chain lengths from 1 to $N-1$.

The transport of the polymer chain through an entropic barrier can be described by a Fokker-Planck style equation around the probability density of stochastic variable m .⁸⁴

$$\frac{\partial W_m(t)}{\partial t} = \frac{\partial}{\partial m} \left[\frac{k_0}{k_B T} \frac{\partial F(m)}{\partial m} W_m(t) + k_0 \frac{\partial^2 W_m(t)}{\partial m^2} \right] \quad \text{Eq. 4.3A}$$

$$\frac{\partial W_m(t)}{\partial t} = \mathcal{L}_{FP}(m) W_m(t) \quad \text{Eq. 4.3B}$$

$W_m(t)$ represents the probability density function for the fluctuating variable m , and $\mathcal{L}_{FP}(m)$ is the Fokker Planck operator. The first term on the right-hand side of Eq. 4.2A represents the diffusion term, which is determined by the derivative of the free energy field calculated earlier. The second term on the right-hand side of Eq. 4.2A represents a drift term which is multiplied by the drift coefficient k_0 . This coefficient is treated as a constant which represents the friction experienced by the polymer segment translocating through the hole.

The mean first passage time (τ) is defined as the average time for diffusion from a single segment translocated ($m = 1$) to all-but-one segment translocated ($m = N-1$). This value is obtained by applying the adjoint Fokker Planck operator to τ and using the reflecting boundary condition at $m = 0$ and absorbing boundary condition at $m = N$:⁸⁹

$$\tau = \frac{1}{k_0} \int_1^{N-1} dm e^{\beta F(m)} \int_1^m dm' e^{-\beta F(m')} \quad \text{Eq. 4.4}$$

4.2.2. SCFT Simulations

In order to find $F(m)$ for the translocating polymer, a canonical model A (implicit solvent) homopolymer field theory in two dimensions is developed.⁹⁰ A particle to field transformation is used to circumvent the many body problem in the calculation of the partition function for a polymer system with excluded volume interactions, resulting in the following forms of the partition function ($\mathcal{Z}$) and the effective Hamiltonian ($\mathcal{H}$):

$$\mathcal{Z}(n, V, T) = \mathcal{Z}_0 \int D\omega \exp(-\mathcal{H}[\omega]) \quad \text{Eq. 4.5A}$$

$$\mathcal{H}[\omega] = \frac{1}{2u_0} \int d\mathbf{r} [\omega(\mathbf{r})]^2 - n \ln Q[i\omega] \quad \text{Eq. 4.5B}$$

Here, Q is the chain propagator for the system and u_0 is the excluded volume parameter, which can be defined as:

$$u_0 = v_0(1 - 2\chi_{PS}), \quad \text{Eq. 4.6}$$

where v_0 is the molar volume of a monomer unit, and χ_{PS} is the Flory-Huggins interaction parameter between the polymer and solvent. Since the solvent is implicit, we can only have u_0 values greater than zero (good solvents). However, a range of solvent quality can still be accessed, from near- θ ($u_0 = 0.03$, $\chi_{PS} = 0.49$) to very good ($u_0 = 0.5$, $\chi_{PS} = 0.25$).

The mean field approximation is taken, where a single field configuration (ω^*) is assumed to dominate the functional integral in the partition function or minimize the free energy. In order to find ω^* , the method of continuous steepest descent is used.

This set of equations is solved iteratively until the error between iterations reaches a set tolerance. From here, the chain propagator is recalculated for a tethered chain (one end fixed at the wall) to find the free energy of the chain tethered to the wall.

4.2.3. Integrated L-J potential for Surface Interactions

Figure 4.4. A schematic illustration of A) a bead (blue) interacting with a 2D circular cavity of radius R , where the bead is at some point (ρ, θ) within the cavity and some distance r from the cavity wall. B) A schematic illustration showing the integration of the interaction potential beyond the surface of the cavity wall.

In order to introduce surface interactions to the model, a wall density term is introduced. This term is applied when calculating the fields in each iteration of the SCFT code. In order to find the appropriate form of this term, a 12-6 Lennard-Jones (L-J) potential for a monomer or segment that is distance ρ from the center of the cavity, and r from the cavity wall (of radius R), is integrated over every point in the circular wall (Figure 4.4A):

$$\epsilon_{\text{shell}} = \int_0^{2\pi} d\theta n_e \left(4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \right) R \quad \text{Eq. 4.7}$$

Using the law of cosines to replace r with ρ and with $a = \rho / R$, the resulting form is:

$$\begin{aligned} \varepsilon_{\text{shell},2D} = 8\pi n_e \epsilon R \left\{ \left(\frac{\sigma}{R} \right)^{12} \left[\frac{a^{10} + 25a^8 + 100a^6 + 100a^4 + 25a^2 + 1}{(a-1)^{11}(a+1)^{11}} \right] \right. \\ \left. - \left(\frac{\sigma}{R} \right)^6 \left[\frac{a^4 + 4a^2 + 1}{(a-1)^5(a+1)^5} \right] \right\} \end{aligned} \quad \text{Eq. 4.8}$$

This potential is then integrated out over all possible wall radii (Figure 4.4B) to determine the interaction potential of the polymer with the particles in the wall beyond those on the wall surface:

$$\varepsilon_{\text{wall}} = \int_{R_w}^{\infty} dR \varepsilon_{\text{shell}} \quad \text{Eq. 4.9A}$$

$$\begin{aligned} \varepsilon_{\text{wall},2D} = 4\pi n_e \epsilon R^2 \left\{ \left(\frac{\sigma}{R} \right)^{12} \left[\frac{5a^8 + 40a^6 + 60a^4 + 20a^2 + 1}{5(1-a)^{10}(1+a)^{10}} \right] \right. \\ \left. - \left(\frac{\sigma}{R} \right)^6 \left[\frac{2a^2 + 1}{2(1-a)^4(1+a)^4} \right] \right\} \end{aligned} \quad \text{Eq. 4.9B}$$

This equation is the final form of the cavity wall density implemented in the SCFT model.

Depending on the value of the surface interaction potential, defined here as $\epsilon_{P-NP} \equiv n_e \epsilon$, the resulting radially averaged segment density profiles shift from being mostly centered within the cavity and avoiding the walls to mostly clustered near the walls (Figure 4.5). ϵ_{P-NP} is tuned from 0.005-0.05 in order to explore a full range of polymer behavior.

Figure 4.5. The radially averaged polymer density profile (ρ_{poly}) as a function of distance from cavity center, r at different polymer-wall interaction strengths: A) $\epsilon_{P-NP} = 0.0005$ (red), B) $\epsilon_{P-NP} = 0.005$ (blue), and C) $\epsilon_{P-NP} = 0.02$ (green). The chain length is $N = 100$ and the radius of the cavity is 5 with $u_0 = 0.1$.

4.3. Effect of Surface Interactions on τ

In order to elucidate the effect of polymer-wall interactions on the polymer's ease of escape from the cavity, the free energy change upon tethering is determined:

$$\Delta F = F_t(N) - F_{\text{free}}(N) \quad \text{Eq. 4.10}$$

In the mostly repulsive case ($\epsilon_{P-NP} = 0.0005$, $u_0 = 0.1$), ΔF initially increases with increase in chain length due to the loss of conformational entropy, but as chain length continues to increase, ΔF approaches a maxima before eventually beginning to decrease again (Figure 4.6A, red curve). This eventual decline is attributed to the polymer chain becoming long enough to reach the wall, which allows for easier escape of polymer from the cavity, and has been reported in previous studies which incorporate excluded volume interactions.⁸⁸ The trend for the intermediate interaction strength is similar, with an initial increase in ΔF followed by a maximum and a slow decline due to this wall segregation effect. However, at higher interaction strength (Figure 4.6A, green curve), this decrease in ΔF only occurs at intermediate chain length and is followed by a sharp increase at the highest chain length values. This trend is attributed to polymer adhering to the cavity wall at these chain lengths, which leads to a significant loss of conformational entropy for longer chains. These three competing effects are expected to drive the kinetics of translocation.

Figure 4.6. A) The change in free energy upon tethering (ΔF) is plotted against chain length and B) the free energy profile $F(m)$ plotted against the number of segments translocated for symmetric cavities for a $N = 100$ polymer chain in a cavity of radius $R = 5$, with $u_0 = 0.1$ and surface interaction values: $\epsilon_{P-NP} = 0.0005$ (red), $\epsilon_{P-NP} = 0.005$ (blue), and $\epsilon_{P-NP} = 0.02$ (green).

Figure 4.7. The mean translocation time τ as a function of the surface interaction potential ϵ_{P-NP} for a $N = 100$ polymer chain translocating from cavity to cavity, with both cavity radii at $R = 5$, and $u_0 = 0.1$.

The free energy profile as a function of number of segments translocated (Figure 4.6B) is shown for three different value of the interaction parameter. The free energy minima at the center which is expected for cases with excluded volume interaction⁸⁸ is found for the lower interaction strengths (red and blue curves), but eventually inverts into an energy maximum at the highest interaction strength ($\epsilon_{P-NP} = 0.02$, green curve). The free energy profiles for the weakly interacting systems indicate that they are dominated by the excluded volume effect, which pushes longer polymer chains nearer to the wall, leading to the free energy minimum when both cavities have relatively large polymer chains ($N = 50$) within them. However, the free energy profile for the strongly interacting case (Figure 4.6B, green curve) turns into a maximum at $m = 50$ for the strongly interacting case, indicating that the polymer chain strongly prefers to be in one cavity completely, since maximizing the chain length allows for the strongest adsorption.

The resulting mean translocation times show a nonmonotonic dependence of τ with increasing ϵ_{P-NP} (Figure 4.7). Initially, τ decreases with increasing ϵ_{P-NP} since the magnitude of the free energy profile decreases (Figure 4.6B) with increasing interaction strength, which also in turn lowers the magnitude of the free energy minimum halfway through translocation. However, as ϵ_{P-NP} continues to increase to higher values, τ begins to sharply increase due to adsorption of polymer to the cavity wall, which hinders translocation from one cavity to another.

4.4. Synergistic Effect with Solvent Quality (u_0)

Figure 4.8. The radially averaged polymer density profile (ρ_{poly}) as a function of distance from cavity center, r at different excluded volume parameters (background color): A) $u_0 = 0.03$ (midnight blue), B) $u_0 = 0.1$ (navy blue), and C) $u_0 = 0.3$ (blue) and D) $u_0 = 0.5$ (light blue). The chain length is $N = 100$ and the radius of the cavity is 5 with $\epsilon_{P-NP} = 0.0005$ (red), $\epsilon_{P-NP} = 0.005$ (blue), and $\epsilon_{P-NP} = 0.02$ (green).

When the excluded volume parameter is increased, the polymer density expands and more uniformly occupies the space within the cavity. This behavior leads to less strong segregation away from and near the wall with polymer-wall interactions for the high excluded volume case (Figure 4.8D, $u_0 = 0.5$) compared to the low excluded volume case (Figure 4.8A, $u_0 = 0.03$). This behavior is attributed to the excluded volume disallowing

crowding of polymer in the center or at the wall, effectively dampening the effect of polymer-wall interactions on polymer density.

Figure 4.9. The mean translocation time τ as a function of the surface interaction potential ϵ_{P-NP} for a $N = 100$ polymer chain translocating from cavity to cavity, with both cavity radii at $R = 5$, for $u_0 = 0.03$ (midnight blue), $u_0 = 0.1$ (navy blue), $u_0 = 0.3$ (blue) and $u_0 = 0.5$ (light blue).

This competition between excluded volume and polymer-wall interaction strength is also apparent in the behavior of τ with respect to the interaction parameter, ϵ_{P-NP} (Figure 4.9). Most apparent is the increase in τ with increasing excluded volume at low surface interaction potentials, which is due to lower energy minima in the free energy profiles $F(m)$ of higher excluded volume chains. Such chains have lower energy minima when $m = 50$

because they are more expanded, and therefore closer to the wall and more able to escape into the receiving cavity. However, the first system to begin feeling the effect of the interaction potential is the one with the lowest excluded volume, which agrees with the density profiles (Figure 4.8), indicating that stronger excluded volume interactions dampen the surface interaction. Therefore, the transition in τ from faster to slower with increasing ϵ_{P-NP} shifts to higher values of ϵ_{P-NP} for higher excluded volume systems (Figure 4.9).

4.5. Asymmetric Translocation

Here, we consider the dynamics when the environment in the receiving cavity differs from the feeding cavity. Specifically, we probe how increasing surface interactions with the cavity wall affect translocation kinetics between cavities of different sizes. In the case where there are no surface interactions or excluded volume effects (ideal chain), polymer escapes into larger cavities faster, and translocates more slowly into smaller cavities.^{83,87} This trend is intuitively appealing; the polymer must lose conformational entropy to enter a smaller cavity, which is reflected in a higher free energy barrier for this process. When excluded volume is introduced, this trend is exacerbated with increasing excluded volume (slower to enter smaller cavities, faster to enter larger cavities) when compared to an ideal chain.⁸⁸ In the following studies, we consider how introducing a surface interaction potential with the cavity wall (ϵ_{P-NP}) impacts this behavior.

4.5.1. Decreasing Confinement ($R_1 = 5$, $R_2 = 10$)

Figure 4.10. A) The free energy profile $F(m)$ plotted against the number of segments translocated (m) for a $N = 100$ polymer chain ($u_0 = 0.5$) translocating from $R_1 = 5$ to $R_2 = 10$, and surface interaction values: $\epsilon_{P-NP} = 0.0005$ (red), $\epsilon_{P-NP} = 0.005$ (blue), and $\epsilon_{P-NP} = 0.02$ (green). B) τ as a function of ϵ_{P-NP} for a $N = 100$ polymer chain ($u_0=0.5$) translocating from $R=5$ to $R=10$ (solid light blue) and $R_1 = R_2 = 5$ (dashed light blue). C) Schematic illustration of decreasing confinement case for surface interaction values: $\epsilon_{P-NP} = 0.0005$ (red), $\epsilon_{P-NP} = 0.005$ (blue), and $\epsilon_{P-NP} = 0.02$ (green).

The kinetics of infiltration from a small cavity ($R_1 = 5$) to a larger cavity ($R_2 = 10$) for a high excluded volume ($u_0 = 0.5$, $\chi = 0.25$) polymer is considered in this section. Initially, at low surface interaction values, the behavior is similar to that in the absence of

surface interaction, with a strong inducement for polymer to escape the feeding cavity in order to gain conformational freedom. In Figure 4.10A, the $F(m)$ is plotted for the weakly interacting case (red curve), there is a downward free energy slope which will favor faster translocation. However, as surface interaction strength is increased, this slope flattens and eventually reverses sign indicating a free energy barrier. This barrier is attributed to the onset of adsorption of the polymer to the cavity wall; this adsorption alters the free energy within the smaller cavity ($R_1 = 5$) most significantly where there will be more contact between the polymer and the wall. This effect is weaker in the larger cavity ($R_2 = 10$), where polymer is less likely to find the cavity wall for adsorption (Figure 4.10C). When ϵ_{P-NP} is large enough, very strong adsorption to the walls of the smaller cavity leads to a lower free energy in the smaller cavity than the larger cavity.

The kinetics for this system is shown in Figure 4.10b (solid line), where τ is found to increase with increasing ϵ_{P-NP} . When compared to the kinetics of the symmetric case ($R_1 = R_2 = 5$, dashed line), the kinetics of the decreasing confinement case is initially faster at lower ϵ_{P-NP} , since there is a strong entropic gain by translocating into the larger cavity. At intermediate surface interaction values, the symmetric case goes through a minimum while τ for the decreasing confinement case continues to increase due to adsorption in the smaller cavity, leading to a crossover at $\epsilon_{P-NP} \approx 0.02$ where the symmetric case has a lower τ value. At higher ϵ_{P-NP} , τ increases sharply in both cases, but the decreasing confinement case remains slower due to the asymmetry and favorable adsorption in the smaller cavity.

4.5.2. Increasing Confinement ($R_1 = 10$ to $R_2 = 5$)

Figure 4.11. A) The free energy profile $F(m)$ plotted against the number of segments translocated (m) for a $N = 100$ polymer chain ($u_0 = 0.5$) translocating from $R_1 = 10$ to $R_2 = 5$, and surface interaction values: $\epsilon_{P-NP} = 0.0005$ (red), $\epsilon_{P-NP} = 0.005$ (blue), and $\epsilon_{P-NP} = 0.02$ (green). B) τ as a function of ϵ_{P-NP} for a $N = 100$ polymer chain ($u_0 = 0.5$) translocating from $R_1 = 10$ to $R_2 = 5$ (solid light blue) and $R_1 = R_2 = 5$ (dashed light blue). C) Schematic illustration of increasing confinement case for surface interaction values: $\epsilon_{P-NP} = 0.0005$ (red), $\epsilon_{P-NP} = 0.005$ (blue), and $\epsilon_{P-NP} = 0.02$ (green).

Conversely, we can consider the case of increasing confinement, where the polymer escapes from a larger cavity ($R_1 = 10$) into a smaller one ($R_2 = 5$). As shown in Figure 4.11A, the free energy profiles during translocation all start from similar free energy values

$F(m)$, which is relatively unaffected by the changing surface interaction strength. This lack of change is because the feeding cavity in this case is the larger cavity ($R_1 = 10$), where access to the wall is limited due to the cavity size, preventing strong polymer-wall interactions. However, the free energy within the smaller cavity ($R_2 = 5$) is much more strongly affected by increasing surface interaction, leading to an initial energy barrier to entry when there are very weak interactions (dominated by the confinement effect), which eventually turns into a free energy decrease at higher interaction strengths due to strong adsorption of polymer to the cavity wall in the smaller receiving cavity. Therefore, at low ϵ_{P-NP} , τ for the increasing confinement case is higher than the symmetric case, but eventually decreases and becomes faster (at $\epsilon_{P-NP} \approx 0.02$) than the symmetric case as escape into the smaller cavity is made more favorable by strong surface interactions. The increasing confinement case described in this section is the only case where the minimum translocation time, and therefore the fastest kinetics, occur at the highest interaction strength value.

4.5.3. Lower Excluded Volume Polymer

The asymmetric translocation of a polymer with lower excluded volume interactions ($u_0 = 0.1$, $\chi = 0.45$) is considered. Figure 4.12A compares the kinetics for the symmetric, decreasing confinement and increasing confinement cases. At low ϵ_{P-NP} , the decreasing confinement case is the fastest, followed by the symmetric and the increasing confinement cases, respectively. However, as surface interactions increase, the decreasing confinement case get slower until it is equivalent to the symmetric case at intermediate

interaction strengths. This behavior is attributed to strong adsorption in the smaller cavity, which leads to a lower free energy for the tethered polymer. Conversely, the increasing confinement case becomes faster as surface interactions make escape into the smaller receiving cavity more favorable, until it crosses over with the other two cases (Figure 4.12B). Compared to the higher excluded volume ($u_0 = 0.5$), this crossover occurs at lower ϵ_{P-NP} values. For $u_0 = 0.5$, this crossover occurs around $\epsilon_{P-NP} \approx 0.02$, but for $u_0 = 0.1$, the crossover in τ occurs at $\epsilon_{P-NP} \approx 0.005$. This could be attributed to the observation made in Section 4.4, where it is found that the excluded volume interactions appear to dampen the surface interaction effect. This could also be why, for both $u_0 = 0.5$ and $u_0 = 0.1$, this crossover occurs near the same ϵ_{P-NP} value where the symmetric translocation case undergoes a minimum and transitions into surface-dominated behavior.

Figure 4.12. A) τ as a function of ϵ_{P-NP} for a $N = 100$ polymer chain ($u_0 = 0.1$) translocating from $R_1 = R_2 = 5$ (solid line), $R_1 = 5$ to $R_2 = 10$ (long dashed line), and $R_1 =$

10 to $R_2 = 5$ (short dashed line). B) Schematic illustration of decreasing (top) and increasing (bottom) confinement cases for surface interaction value $\epsilon_{P-NP} = 0.005$ and $u_0 = 0.1$.

4.6. Conclusions

In summary, we have developed an entropic barrier model to explore the kinetics of polymer translocation in the presence of surface interactions of polymer with the cavity wall and excluded volume interactions due to solvation. The kinetics for a polymer translocating between two identical cavities shows a nonmonotonic dependence on the surface interaction potential (ϵ_{P-NP}). This can be attributed to two competing effects: (1) the chain length/ excluded volume effect which leads to an energy minimum at the halfway point of translocation, and (2) the surface adsorption effect which leads to an energy minima when the polymer is fully in one or the other cavity, and an energy maximum at the halfway point. Both these effects hinder translocation, with the excluded volume effect dominating at low surface interaction strengths, and the surface adsorption effect dominating at higher surface interaction strengths. These effects cancel out at intermediate interaction strength values, leading to a minimum in mean translocation time τ at an intermediate ϵ_{P-NP} value. This qualitatively mirrors what is observed in the MD simulations of the SIP system, with intermediate polymer-NP interactions leading to the fastest infiltration dynamics.⁸²

As excluded volume interactions in the system increase, this minimum occurs at higher ϵ_{P-NP} values, which is attributed to the hindering of surface adsorption by the excluded volume interactions, leading to a dampening of the surface interaction effect. In

cases of asymmetrical confinement, there is no free energy minimum so there is monotonic behavior. As surface interactions increase, the smaller, more highly confined cavity becomes more favorable, leading to slower kinetics with increasing ϵ_{P-NP} for decreasing confinement, and conversely, faster kinetics with increasing ϵ_{P-NP} for increasing confinement. The entropic barrier model developed in this study can provide insight into the kinetics of confined polymer solutions under varying solvation, surface interaction, and confinement conditions.

The insight gained from this study can guide the design of SIP systems to optimize infiltration time scales. The nonmonotonic dependence of τ on the interaction strength between the polymer and the cavity wall show that fastest kinetics are obtained when the interaction strength is not too weak to hinder entropic hopping, and not too strong to lead to polymer adsorption on the surface of the cavity (Figure 4.2). By changing the polymer/NP interactions in the SIP system, the interaction strength can be tuned via surface modification to find this “sweet spot” of minimum infiltration time. For a given polymer/NP system, the kinetics can also be tuned by changing the solvent quality and improving solvent quality can either hinder or improve the kinetics depending on which side of the minimum τ the system is on. Finally, in systems with very strong interactions, where infiltration is very slow, having an increasing confinement gradient could potentially push polymer further into a NP film.

Chapter 5. Summary and Outlook

5.1. Thesis Summary

Solvent-driven infiltration of polymer (SIP) into NP packings provides a robust, effective route to nanocomposites with high fractions of NPs. The work reported in this thesis aimed to provide insight into the mechanism of the SIP process, and explore the role of solvent, confinement and polymer-NP interactions on infiltration during SIP through experiments and theoretical modelling.

Chapter 2 provides an understanding of the role of solvent quality, capillary condensation, and exposure time on the infiltration of polymer using SIP. It was found that capillary condensation occurs only partially in packings of larger NPs, which is reflected in lower polymer infiltration into such packings via SIP. The extent of infiltration of polymer is found to depend strongly on solvent quality, as characterized by the Flory-Huggins interaction parameter (χ). As solvent quality is decreased, less infiltration occurs. However, given long enough solvent exposure times, polymer eventually infiltrates to a comparable extent with both good and poor solvents. The use of poor solvents enables liquid solvent exposure, which is found to follow the same infiltration kinetics as with vapor exposure, which is attributed to the vapor undergoing complete capillary condensation in NP packing. A monomer can be used as the solvent for polymer infiltration in SIP, which can then be polymerized to obtain unique polymer blend nanocomposites.

Chapter 3 probes the effect of confinement on the kinetics and final extent of infiltration for the SIP process. A range of confinement ratios (λ) is accessed by varying the polymer molecular weight and the NP size. The time for infiltration to occur was found to follow a power law relationship with λ ($\tau \sim \lambda^{3/2}$), which is weaker than that predicted for confined polymer melts ($\sim \lambda^2$) but stronger than that predicted for dilute polymer solutions under confinement ($\sim \lambda^{2/3}$). This trend is attributed to the shifting concentration regimes as polymer infiltrates into the NP packing, with polymer going from dilute to very concentrated during the course of SIP. The final extent of infiltration is not dependent on confinement, which is likely due to the high concentration of polymer at longer times, for which the correlation length (ξ) rather than the radius of gyration (R_g) is the dominant length scale of the system. Since ξ is smaller for PS than the average cavity sizes within the NP packings, confinement is effectively not felt even at the higher λ values. The partitioning of polymer from the swollen polymer film into the voids of the NP packing below is also greater than unity ($K \approx 1.55$), which indicates that there are favorable interactions between the polymer and the NP surface.

Chapter 4 introduces a model for studying the role of polymer-NP interactions and considers the interplays of surface interactions with solvation and confinement effects. An entropic barrier model using SCFT calculations incorporating excluded volume interactions and a L-J integrated potential for surface interactions is described. For polymer translocation between identical cavities ($R = 5$), the mean translocation time (τ) is found to have a nonmonotonic dependence on the surface interaction potential between the polymer

and cavity wall (ϵ_{P-NP}). This nonmonotonic behavior is due to two competing effects (excluded volume and adsorption) that cancel out at intermediate ϵ_{P-NP} values, leading to the fastest translocation occurring at these values. As excluded volume interactions are increased, this minimum τ occurs at higher values of ϵ_{P-NP} , which indicates that the excluded volume interactions hinder polymer adsorption to the cavity wall. Polymer translocation between cavities of different sizes ($R = 5$ and $R = 10$) is found to also have a strong dependence on surface interactions, with smaller cavities and therefore stronger confinement becoming more favorable (lower free energy) than the larger, less confined cavities at higher ϵ_{P-NP} values.

5.2. Open Questions and Outlook

5.2.1. Probing the Effect of Polymer-NP Interactions in SIP

Based on the simulations from Chapter 4, increasing the interaction strength between the polymer and the NP surface is expected to make the kinetics faster, but eventually lead to a pronounced retardation of the kinetics once the adsorption effect begins to dominate. In the PS/SiO₂/toluene SIP experimental system, it is found that there is some irreversible surface adsorption (Section 3.4.2.), but these interactions are not strong enough to hinder infiltration. In order to probe stronger interaction strengths, we have used poly(2-vinylpyridine) (P2VP) in place of PS to induce specific hydrogen bonding interactions between the ring nitrogen in P2VP and the silanol groups on the SiO₂ NP surface. The effect of solvent quality on infiltration of P2VP after 30 min. of solvent vapor exposure is considered.

Figure 5.1. Volume fraction of polymer in the NP packing (ϕ_p) for PS ($M_n = 8,000$ g/mol, dark blue circles) and P2VP ($M_n = 9,000$ g/mol, red circles) into 23 nm SiO₂ NP packings after 30 minutes of vapor exposure for various solvents at different χ .

The results in Figure 5.1 indicate that P2VP partitions much more strongly than PS into the NP packing given the same amount of solvent exposure time (30 min.). Furthermore, the effect of solvent quality is much less pronounced, indicating that the infiltration mechanism for the P2VP is quite different from that of the PS, or that the kinetics are so much faster in the P2VP system that the 30 minute time scale is too long to capture the solvent quality effect. The fact that P2VP appears to have faster kinetics than PS indicates surface interactions are not so strong that adsorption impedes this process.

Stronger specific interactions, such as ionic interactions, may be required to enter the surface-dominated regime. Future fundamental studies might use polyelectrolytes and/or modified NP surfaces in order to probe the surface dominated regime and predicted nonmonotonic kinetics.

5.2.2. The Infiltration Profile in the SIP System

The dynamics of infiltration during SIP were studied by finding the time for infiltration to fully occur in the system (Chapter 3). However, the exact form of the infiltration front is not discernible through ellipsometry measurements, where the contrast between the polymer and the solvent is very low. In the CaRI system, where surface forces drive infiltration, there is a sharp infiltration front which can be used to elucidate the dynamical properties of the infiltrating polymer from the Lucas-Washburn equation.^{1,26} In the SIP system, understanding the form of the infiltration front may help identify the regime of infiltration and separate solvation-mediated and surface-mediated time scales.

In order to distinguish the infiltrating polymer front from the solvent-filled NP packing, neutron reflectivity studies are proposed where deuterated polymer is used to provide higher contrast. Preliminary neutron reflectivity studies of ex situ samples before and after SIP (Figure 5.2) in highly interacting (P2VP/SiO₂/methyl ethyl ketone) indicate that the infiltration is more complex than the two-layer model used in ellipsometry (Section 2.2.1.). However, further studies are needed to understand if multiple time scales of infiltration can be uncovered and if an infiltration front can be identified in situ.

Our previous studies were performed on samples which were too thick (> 500 nm) and substrates which had previously been used, which limited modelling accuracy. Furthermore, a precise mass flow controller for vapor exposure with the instrument (ILL, D17) was unavailable. Future studies should be done on thinner films (< 500 nm), with precise mass flow control of solvent vapor, and with pristine substrates.

Figure 5.2. Scattering length density (SLD) as a function of distance from the top of the NP packing for a d-P2VP ($M_n = 9,000$ g/mol)/ 22 nm SiO₂ NP bilayer A) before and B) after SIP using methyl ethyl ketone (MEK) as solvent.

5.2.3. Polymer Escape from Reservoir (EBM/SCFT)

The time scale obtained from the entropic barrier model considered in Chapter 4 describes the kinetics of a polymer translocating from one dilute confined environment to another. With respect to the SIP process, this only accounts for the kinetics once polymer has entered the NP packing from the swollen polymer film. However, the rate of chain escape from the swollen polymer film into the pores of the NP packings is expected to

significantly contribute to the overall kinetics of the SIP process. A model system to take this important time scale into account is depicted in Figure 5.3, where the polymer escapes from a reservoir of polymers into a cavity containing only solvent. The rate of translocation of polymer from this reservoir into the cavity is expected to be a reasonable approximation for polymer chains escaping from the polymer film into the first layer of voids in the NP packing during SIP. The comparison of this time scale and the time scale developed in

Chapter 4 is expected to provide a more holistic model for the kinetics of polymer infiltration in the SIP system.

Figure 5.3. A schematic illustration of an entropic barrier model where polymer translocates from a concentrated polymer reservoir (left) into a circular cavity (right).

APPENDIX A: In Situ Ellipsometry Setup

A.1. Mass Flow rate of solvent

Figure A.14. A) Volume fraction of polymer in NP layer vs solvent vapor exposure time for a P2VP ($M_n = 70,000$ g/mol)/ 22 nm SiO₂ NP bilayer exposed to MEK for ex situ measurements (black diamonds), in situ measurements with a 200 sccm solvent flow rate (blue squares) and 25 sccm solvent flow rate (red circles). B) In situ thickness values (left y-axis) for the polymer (green line) and NP (blue line) layers upon periodic exposure to

MEK and subsequent quenching with N₂ over time. The grey line indicates the mean-squared error for the model (right y-axis).

The in situ spectroscopic measurements described in Chapter 2 (Section 2.2.1.) cannot directly provide information on the dynamics of infiltration with SIP due to the lack of significant contrast between the refractive indices of the component materials (polymer, silicon dioxide and solvent). Furthermore, the swelling of the polymer layer with solvent makes it intractable to estimate infiltration from polymer layer thickness in situ. However, some kinetic information can be gained by periodically quenching infiltration in the in situ system with a 20 minute N₂ purge. This is shown in Figure A.1B, where a bilayer film of P2VP/ SiO₂ NPs is exposed to MEK vapor. The resulting volume fraction of infiltration during each purge cycle is calculated and shown in Figure A.1A, with two different solvent flow rates (25 sccm and 200 sccm) compared to an ex situ experiment as described in Section 3.2.3. The infiltration kinetics appear to be strongly dependent on the flow rate of solvent, likely due to the solvent activity in the chamber being affected by this flow rate. However, it is uncertain how accurate these measurements are, since solvent may still be present in the bilayer film after 20 minutes of N₂ purge, which would allow for continued infiltration even after quenching, and skew the volume fraction calculations. In order to avoid these issues, the ex situ method in Section 3.2.3 is used for estimating kinetics in the SIP system.

A.2. Activity calculations

The activity of solvent in the in situ ellipsometry chamber at a given flow rate can be estimated using polymer swelling studies, based on the Flory-Huggins lattice theory for polymer solutions. The following equation is used to compute the activity (p/p_0):

$$\ln \frac{p}{p_0} = \chi \phi_{p,e}^2 + \ln(1 - \phi_{p,e}) + \left(1 - \frac{V_s}{V_p}\right) \phi_{p,e} \quad \text{Eq. A.1}$$

where χ is the Flory-Huggins interaction parameter, $\phi_{p,e}$ is the equilibrium swelling fraction of polymer, and V_s and V_p are the molar volumes of solvent and polymer, respectively.⁹¹

Figure A.2 shows the in situ swelling of a PS ($M_n = 8,000$ g/mol) film with a thickness of ~ 280 nm upon exposure to toluene vapor at 25 sccm. Based on Eq. A.1 and the volume fraction of polymer in the film after one hour of solvent exposure (~ 0.6), the activity of toluene in the system is roughly 0.43. However, the film has not yet reached an equilibrium swelling ratio, which could not be obtained due to dewetting (rising MSE in Fig A.1). Higher activities are achieved when the flow rate of solvent is increased to 200 sccm and higher molecular polymers are considered (Figure 3.5A, $\phi_{p,e} \approx 0.45$), but the resulting activity is still below saturation (~ 0.6). This could be an issue with the χ value used to determine these activities, since χ is challenging to estimate for polymer-solvent systems. Potential ways to overcome this challenge in the future could include directly

measuring the vapor content using a gas analyzer, or by adding a fritted end to the solvent bubbler to ensure the stream reaches saturation.

Figure A.25. In situ ellipsometry measurements of a PS ($M_n = 8,000$ g/mol) thin film upon exposure to toluene vapor (blue line) as a function of time using. A) The modelled thickness of the PS film (left axis, blue line) and the mean-squared error (right axis, grey line). B) The modelled change in refractive index of the PS film (left axis, blue line) and the mean-squared error (right axis, grey line).

APPENDIX B: Solvent Quality Effect on Higher Molecular

Weights

In cyclohexane and hexane, the higher molecular weight polystyrenes ($M_n = 21k$ g/mol and $172k$ g/mol) infiltrate to lesser degrees than the lower molecular weight ($M_n = 8k$ g/mol) in 30 minutes. Given longer annealing times (24 hrs), however, the infiltration of these higher molecular weight polymers increases significantly, indicating that infiltration is slower but not halted by the increased confinement of these longer polymers in the NP packing (Figure B.1).

Figure B.16. Volume fraction of PS in NP packing for polystyrene of molecular weight 8,000 g/mol (blue circles), 21,000 g/mol (red diamonds) and 173,000 g/mol (black squares) after 24 hrs of vapor annealing.

APPENDIX C: Supporting Information for QCM-D Studies

C.1. Modelling of QCM-D Adsorption Experiments

Figure C.17. The modelled adsorbed layer thickness (thick black line, left y-axis) values for the first ten hours of in situ QCM-D data along with the corresponding χ^2 values (thin grey line, right y-axis).

The final solvated or “wet” layer thickness is found by applying an extended viscoelastic model using the QTools software package (Biolin Scientific, Inc.) to the quartz crystal microbalance with dissipation mode (QCM-D) data presented in the main text (Figure 5) for PS ($M_n = 173$ kg/mol) adsorption from a 0.05wt% solution in toluene onto a silicon dioxide (SiO_2)-coated sensor crystal. A Voigt viscoelastic model with fixed fluid density, fluid viscosity, and adsorbed layer density and with fitted adsorbed layer viscosity,

shear, and thickness is used to model the 3rd, 5th, 7th, 9th and 11th harmonic frequency and dissipation data. The model error is reported as a χ^2 value.

Figure C.1 shows that the final wet layer thickness after desorption is ~ 12 nm. In order to obtain this value, a fixed layer density of 900 kg/m^3 was used. This density is corroborated using dry layer thickness measurements from ex situ spectroscopic ellipsometry, described in SI Section III.

C.2. Ex Situ Adsorption Measurements Using Ellipsometry

Figure C.28. The dry adsorbed layer thickness values from ex situ ellipsometry measurements of PS ($M_n = 173 \text{ kg/mol}$) adsorbing onto silicon wafer, plotted against exposure time in hours (log scale).

To corroborate the in situ QCM-D measurements, ex situ adsorption studies are performed using spectroscopic ellipsometry. Fresh silicon wafers are cut into 2 cm x 2 cm squares and cleaned with water and isopropanol, followed by oxygen plasma treatment for five minutes to form a native oxide (SiO₂) layer. The wafers are then immediately placed inside a 0.05wt% bath of PS (M_n = 173 kg/mol) in toluene. After a given amount of time, the samples are removed from the bath and washed in toluene for five minutes and left in pure toluene for an hour to allow for desorption. The sample is then dried under nitrogen and measured using ellipsometry. A simple Cauchy model is used with oxide (SiO₂) layer thickness and angle offset fixed in all measurements based on the values for a bare silicon wafer immediately after oxygen plasma treatment. The polymer layer refractive index is fixed at 1.58, while the thickness is allowed to fit. The results are shown in Figure C.2.

The final thickness of PS adsorbed onto the oxygen plasma-treated silicon wafer is ~1.7 nm. Based on this value, and the value of the wet adsorbed layer of PS from the QCM-D measurements, the wet PS layer density can be estimated. If the volume fraction of polymer in the adsorbed layer is calculated from the dry layer thickness divided by the wet layer thickness, $\phi_{\text{poly}} = \frac{\text{Dry thickness}}{\text{Wet thickness}}$, the volume fraction of polymer in the wet layer is ~0.14. With a pure PS density of 1,060 kg/m³ and a pure toluene density of 867 kg/m³, we obtain an estimated solvated or “wet” layer density of 897 kg/m³. This closely matches the fixed adsorbed layer density used in the QCM-D modelling of 900 kg/m³ (see Section A.1).

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