

## Effect of Confinement on Solvent-Driven Infiltration of the Polymer into Nanoparticle Packings

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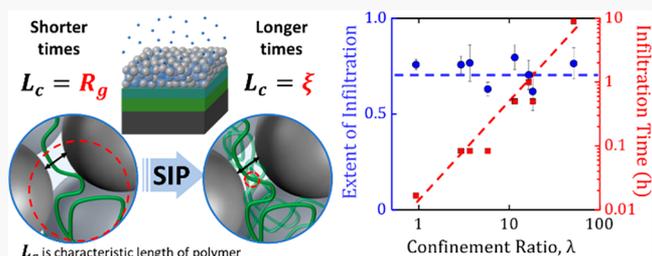
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**ABSTRACT:** Nanocomposite films containing a high volume fraction (>50 vol %) of nanoparticles (NPs) in a polymer matrix are promising for their functionality and use as structural coatings and also provide a unique platform to understand polymer behavior under strong confinement. Previously, we developed a novel technique to fabricate such nanocomposites at room temperature using solvent-driven infiltration of polymer (SIP) into NP packings. In the SIP process, a bilayer made of an underlying polymer film and a dense packing of NPs is exposed to solvent vapor which induces condensation of the solvent into the voids of the packing. The condensed solvent plasticizes the underlying polymer film, inducing polymer infiltration into the solvent-filled voids in the NP packing. In this work, we study the effect of confinement on the kinetics of SIP and the final partitioning of the polymer into the interstices of the NP packing. We find that, while the dynamics of infiltration during SIP are strongly dependent on confinement, the final extent of infiltration is independent of confinement. The time for infiltration obeys a power law with confinement, as defined by the ratio of the chain size and the pore size. Qualitatively, the observed time scale is attributed to changes in concentration regimes as infiltration proceeds, which lead to shifting characteristic length scales in the system over time. When the concentration in the pore exceeds the critical overlap concentration, the characteristic length scale of the polymer is no longer that of the entire chain but rather the correlation length, which is smaller than the pore size. Therefore, at long times, the extent of infiltration is independent of the confinement ratio. Furthermore, favorable surface interactions between the polymer and the NPs enhance partitioning into the NP packing.



## INTRODUCTION

Nanocomposite films composed of inorganic nanoparticles (NPs) in a polymer matrix provide important routes to form functional materials, as they combine the functionality of the NPs and the toughness and processability of the polymer. Composite films with high loadings (>50 vol %) of NPs are of particular interest because of their superior mechanical and transport properties; however, such nanocomposites are challenging to make using conventional blending approaches because of the thermodynamic incompatibility of the two materials and high elasticity of such mixtures. Surface functionalization or polymer grafting onto NPs are intensively investigated strategies to improve the dispersibility of NPs in a polymer matrix but, even with these modifications, volume fractions of NPs greater than 50 vol % are rarely attained.<sup>1–4</sup>

A method to bypass this hurdle is to form polymer-infiltrated NP films (PINFs), which relies on preassembled nanostructures that are subsequently filled with polymer. Such composites are used as novel functional materials in energy storage,<sup>5–9</sup> separations,<sup>10,11</sup> and optical devices.<sup>12–14</sup> Their superior mechanical properties also enable their use as protective structural coatings.<sup>15–20</sup> Currently available methods for PINF fabrication include melt processing,<sup>16</sup> infiltration

from bulk solution,<sup>6,10,12,15,18</sup> initiated chemical vapor deposition,<sup>9</sup> and *in situ* polymerization.<sup>14,17</sup>

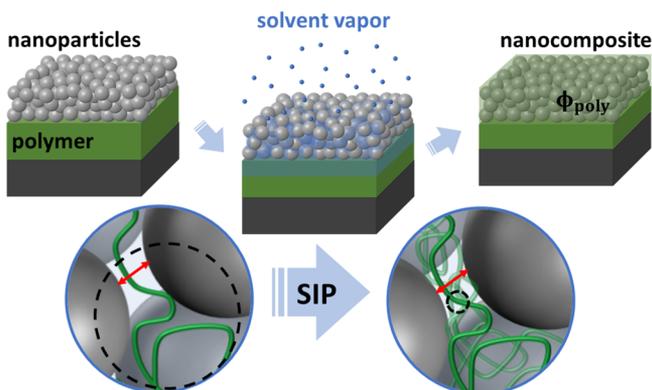
To form PINFs *via* a scalable route, our group has recently developed the process of capillary rise infiltration (CaRI), in which a polymer infiltrates into the voids of a pre-assembled layer of densely packed NPs *via* capillarity.<sup>13,19</sup> This process is achieved by heating a bilayer thin film of polymer beneath a layer of densely packed NPs above the glass transition temperature ( $T_g$ ) of the polymer. Capillarity-driven wicking of the polymer melt into the interstitial voids of the NP packing ensues. The CaRI technique requires systems where the  $T_g$  is accessible<sup>21,22</sup> and settings in which an increase in temperature does not affect the quality of the NP assembly.

As a complementary method to induce polymer infiltration into the interstices of NP packing, we have recently presented solvent-driven infiltration of polymer (SIP) into NP packings.

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In this method, a bilayer film composed of an underlying polymer layer and a densely packed NP layer is exposed to solvent vapor, leading to capillary condensation of the solvent in the interstitial voids of the NP packing. This condensed solvent subsequently plasticizes the polymer layer below and leads to infiltration of polymer into the NP layer (Figure 1).<sup>23</sup>



**Figure 1.** Schematic of SIP into NP packings. The vapor solvent condenses within the NP packing, leading to swelling and infiltration of the underlying polymer film. As the concentration of the polymer within the NP packing increases, the relevant length scales defining confinement within the system change as well. The red arrows indicate the constant pore size, while the black dashed circles indicate shifting polymer characteristic lengths, from the  $R_g$  (left) at early times to the correlation length,  $\xi$  (right) at later times.

The SIP technique is exciting as a potentially scalable and versatile method to fabricate PINFs with very high NP content and can also be utilized to prepare nanoblends of the polymer in NP packings.<sup>24</sup> Moreover, this room-temperature method can be particularly useful to prepare PINFs with very high  $T_g$  polymers. To enable widespread utilization of this method, it is critical to understand the dynamics and underlying mechanism of this technique.

Here, we explore the dynamics of polymer infiltration and partitioning of the polymer into the interstices of the NP packing to gain insights into 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 the polymer from the bulk solution to a pore and the relative mobility of the 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.<sup>25–28</sup> 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 NP 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 the polymer and the average pore size ( $\lambda = R_g/\langle R \rangle_{\text{pore}}$ ). 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 the polymer within the NP packing is not dependent on the degree of confinement, indicating that at long times, confinement does not hinder 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 ( $\text{SiO}_2$ ) NPs.

## EXPERIMENTAL METHODS

**Bilayer Fabrication.** PS of four different molecular weights ( $M_n = 8,000, 80,000, 173,000, \text{ and } 1,000,000 \text{ g/mol}$ ; polydispersity index  $\leq 1.10$ ) is purchased from Polymer Source, Inc.  $\text{SiO}_2$  NPs of two average diameters (LUDOX brand TM-50:  $\langle D \rangle_{\text{NP}} = 22 \text{ nm}$ , and SM:  $\langle D \rangle_{\text{NP}} = 7 \text{ nm}$ ) are purchased from Sigma-Aldrich. PS solutions are prepared by bath sonication of a PS/toluene mixture for 3 h up to one day (depending on molecular weight), followed by syringe microfiltration (hydrophobic, pore size  $0.2 \mu\text{m}$ ). The filtered solution is then spin-coated onto  $\text{O}_2$  plasma-treated silicon wafers to obtain  $\sim 250 \text{ nm}$  thickness films. NP dispersions are diluted in deionized  $\text{H}_2\text{O}$  and bath sonicated for 3 h, followed by syringe microfiltration (pore size  $0.45 \mu\text{m}$ ). The NP dispersions are then spin-coated onto the previously prepared PS thin films to obtain a densely packed layer with a thickness of  $\sim 250 \text{ nm}$ . PS-only thin films with no NP coating are used for *in situ* swelling studies.

**Scanning Electron Microscopy 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 (SEM) images. Images are obtained at 25 kV at high vacuum using an Everhart Thornley detector.

**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.<sup>23</sup> *Ex situ* measurements are carried out by placing samples on a mesh holder suspended directly above a large reservoir of the solvent (toluene) within a sealed container. Because of the time it takes for opening and closing this chamber during sample placement, the maximum resolution of the *ex situ* measurements is  $\sim 1 \text{ min}$ . The SIP process is quenched by the removal of the sample from the chamber followed by placement in a vacuum oven for  $\sim 12 \text{ h}$ . The dried samples are then measured under ambient conditions, using a simple two-layer Cauchy model as previously described.<sup>23</sup>

**Quartz Crystal Microbalance with Dissipation Mode.** Quartz crystal microbalance with dissipation (QCM-D) measurements are conducted using a QSense E4 system to find shifts in the frequency and dissipation because of mass adsorbing onto an oscillating quartz crystal. In QCM-D, periodic pulses of power are applied to the system and the resulting frequency ( $f$ ) and decay time ( $\mathcal{T}$ ) are monitored as a function of time for each oscillation cycle. The dissipation factor is calculated as  $D = \frac{1}{\pi f \mathcal{T}}$ , where  $\mathcal{T}$  is the decay time of oscillation. The dimensionless dissipation factor is defined as  $D \equiv \frac{\text{energy lost per cycle}}{2\pi \times \text{energy stored per cycle}}$  and describes the energy dissipation per oscillation cycle. The sensor crystal used is a QSX 303  $\text{SiO}_2$ , which has a 100 nm Au electrode coated with 50 nm of  $\text{SiO}_2$ . Prior to experiments, the crystal is rinsed with distilled water and isopropanol, and then  $\text{O}_2$  plasma-treated for 10 min. The crystal is connected to a flow cell with the  $\text{SiO}_2$  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 0.05 wt % PS ( $M_n = 173,000$  g/mol) in toluene solution flowing at 50 sccm. The frequency and dissipation shifts are monitored with a continuous flow of the PS 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 shifts in frequency and dissipation factor are then modeled using a modified viscoelastic model *via* the QTools software package (see Supporting Information, Figures S2 and S3 for more information). The dry thickness of an irreversibly adsorbed PS 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 the polymer in the wet layer.

## RESULTS & DISCUSSION

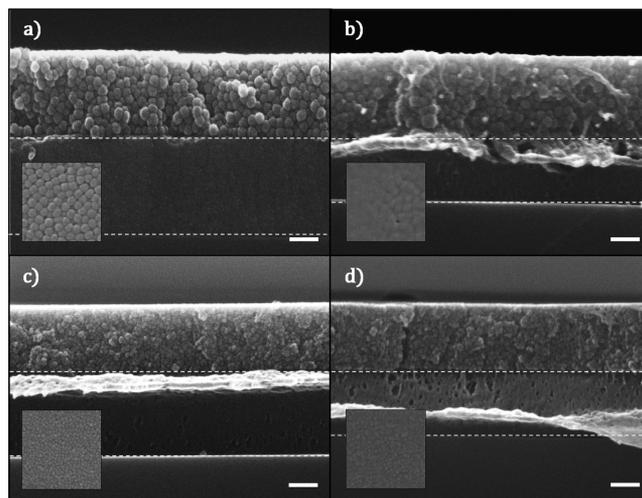
A range of confinement ratios ( $\lambda = 1-50$ ) is studied by varying the PS molecular weight and SiO<sub>2</sub> NP size. For the systems considered in this study, the radius of gyration ( $R_g$ ), critical overlap concentration in a bulk solution ( $\phi^*$ ), and that adjusted for confinement ( $\phi_c^*$ ),<sup>30</sup> as well as the confinement ratios ( $\lambda$ ) are provided in Table 1. Only one of the molecular

**Table 1. Characteristics of PS and SiO<sub>2</sub> NPs Used in This Study**

$M_n^a$ (kg/mol)	$R_g^b$ (nm)	$\phi^{*c}$	$\phi_c^{*d}$		$\lambda^e$	
			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
1000	45	0.001	0.234	0.051	52	16

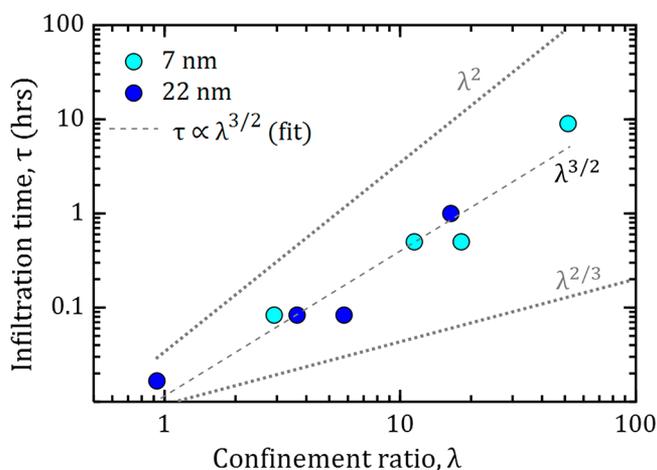
<sup>a</sup>The number average molecular weights ( $M_n$ ) as provided by the supplier. <sup>b</sup>The calculated radius of gyration for unconfined PS in toluene.<sup>29</sup> <sup>c</sup>The unconfined critical overlap volume fraction ( $\phi^*$ ). <sup>d</sup>The calculated confined critical overlap volume fraction ( $\phi_c^*$ ) for a polymer in a capillary.<sup>30</sup> <sup>e</sup>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.<sup>31</sup>

weights ( $M_n = 8000$  g/mol) is below the entanglement threshold for PS, whereas the other three ( $M_n = 80,000$ ; 173,000; 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.<sup>29</sup> 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 SiO<sub>2</sub> NPs with average diameters of 7 and 22 nm are used in this study, and the volume fraction of SiO<sub>2</sub> in the resulting NP assemblies is close to the random close packing limit for spherical particles. 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.<sup>31</sup> Previous experiments have shown that packings of NPs larger than 70 nm induce partial capillary condensation because of the decrease in the negative curvature of condensed fluid interfaces within the packing.<sup>23,32</sup> SIP occurs in all the systems studied (Figure 2). 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,  $\lambda$ .



**Figure 2.** SEM images before and after SIP. (a) 22 nm SiO<sub>2</sub> NPs, PS ( $M_n = 80,000$  g/mol) bilayer before infiltration and (b) after infiltration using toluene and (c) 7 nm SiO<sub>2</sub> NPs, PS ( $M_n = 80,000$  g/mol) bilayer before infiltration and (d) after infiltration using toluene. Insets show top down images of each NP packing. Scale bar: 100 nm. Upper dashed line indicates the interface between the NP and polymer layers; lower dashed line indicates the interface between the polymer layer and Si wafer.

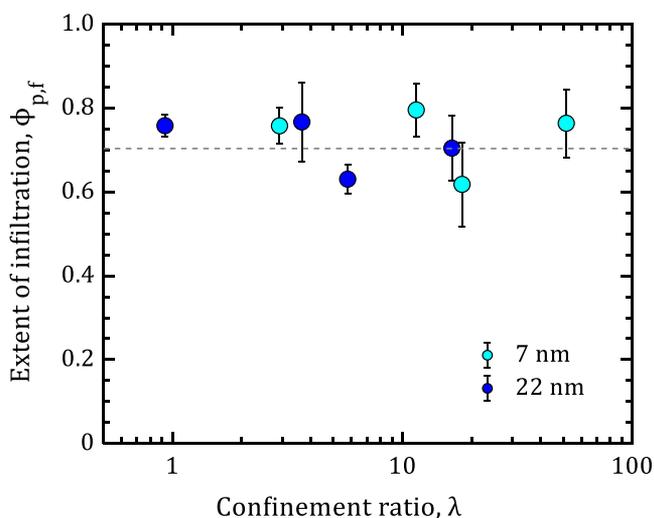
In the SIP system, the polymer infiltrates from a solvated polymer film, which serves as a concentrated polymer reservoir, into solvent-filled voids between the NPs. Initially, these voids are empty of polymer, and the infiltrating polymer experiences a very dilute environment. As infiltration progresses, however, and more chains enter the voids, the chains begin to overlap and experience more crowding within the voids. Infiltration kinetics therefore reflect the polymer passing through various concentration regimes. Figure 3 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



**Figure 3.** Infiltration time (log scale) plotted as a function of the confinement ratio (log scale). The dashed line indicates a power law fit, with the critical exponent displayed on the plot ( $\lambda^{3/2}$ ). The infiltration times for bilayers of various MW with SiO<sub>2</sub> NPs with  $\langle D \rangle_{\text{NP}} \approx 7$  nm (light blue circles) and  $\langle D \rangle_{\text{NP}} \approx 22$  nm (dark blue circles) are shown. The dotted gray lines indicate scaling behavior for melts ( $\lambda^2$ ) and for dilute solutions ( $\lambda^{2/3}$ ).<sup>33,34</sup>

concentrated reservoir, which would only be a function of the polymer molecular weight. The infiltration time also depends strongly on the pore size because the same molecular weight of PS takes longer to infiltrate into the packing with smaller pores. This can be seen in Figure 3, where the highest molecular weight PS ( $M_n = 1,000,000$  g/mol) takes roughly 1 h to infiltrate into the 22 nm NP packing (dark blue circle,  $\lambda = 16$ ) but takes 10 h to fully infiltrate the 7 nm NP packing (light blue circle,  $\lambda = 52$ ). This result indicates that the transport of polymer chains within the highly confined solvent-filled pores strongly influences SIP dynamics. As the 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, which in turn impacts the infiltration kinetics of the polymer.

The infiltration time ( $\tau$ ) as a function of the 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 ( $\tau \sim \lambda^{2/3}$ ).<sup>34</sup> 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 because of confined chains occupying less volume than bulk chains (Table 1).<sup>30</sup> When the SIP process nears completion, the concentration of the polymer within the pore will be significantly higher, as will be discussed in detail below (Figure 4). 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 ( $\tau \sim N^1$ ).<sup>33</sup> Because  $R_g \sim N^{1/2}$  in



**Figure 4.** Extent of infiltration (volume fraction of the polymer in voids of the NP packing) as a function of the confinement ratio (log scale). The final extent of infiltration  $\phi_{p,f}$  for bilayers of various MW with SiO<sub>2</sub> 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. The value of  $\phi_{p,f}$  from SIP does not vary with the confinement ratio and has a value  $\sim 0.7$ , indicated by the grey dashed line (partition coefficient,  $K \approx 1.55$ ).

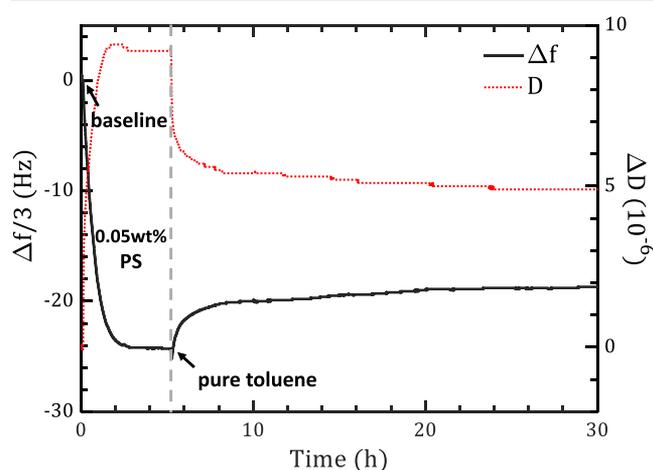
an ideal melt, with a confinement ratio defined by the radius of gyration ( $\lambda = R_g / \langle R \rangle_{\text{pore}}$ ), the dynamics should scale as  $\tau \sim \lambda^2$  (Figure 3). The SIP system passes dynamically from empty to crowded environments within the pore, obeying a power law bounded by the predicted scaling exponents in the dilute and melt regimes. Moreover, interactions with the NP surface could play a role in these dynamics because 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 the chain length than that observed in the SIP process.<sup>35</sup>

At long times, the polymer eventually stops partitioning into the NP packing, 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 the polymer in the SIP systems is defined by two values: the volume fraction of the polymer in the external swollen polymer film at equilibrium ( $\phi_{p,e}$ ) and the final volume fraction of the polymer inside the voids of the NP packing ( $\phi_{p,f}$ ) (Figures S1 and 4, respectively).  $\phi_{p,f}$  is obtained from the ratio of the volume fraction of the polymer in the NP layer, obtained from the change in the refractive index of the NP layer after infiltration, to the original void fraction within the NP packing. To our surprise, all the systems considered in this study infiltrated to the same extent, independent of the confinement ratio, as shown in Figure 4, indicating that confinement has little effect on the final partitioning of the polymer into the solvent-filled pore.  $\phi_{p,f}$  upon completion of infiltration is approximately 0.7, regardless of  $\lambda$ . Based on the ratio of this value and the volume fraction of the polymer in the swollen film, a partition coefficient  $K = \phi_{p,f} / \phi_{p,e}$  for the SIP system can be calculated. The equilibrium volume fraction of the polymer in the swollen film ( $\phi_{p,e}$ ), determined from *in situ* ellipsometry of PS films exposed to toluene, is  $\sim 0.45$  and does not depend strongly on the molecular weight of the polymer (Figure S1). Therefore, the partition coefficient for this system is roughly  $K \approx 1.55$ , 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.<sup>25,30,36</sup> This trend is attributed to the osmotic pressure outside the pore at higher concentrations overcoming the entropic barrier of confinement within the pore.<sup>25</sup> However, these studies typically use polymer/pore systems that have purely repulsive interactions. Previous simulation studies indicate that the polymer can partition more strongly into confined spaces ( $K > 1$ ) when there are strong interactions between the polymer and pore surface.<sup>37,38</sup> Although PS has been observed to interact with and adsorb onto unfunctionalized SiO<sub>2</sub> surfaces under theta conditions,<sup>39–41</sup> there are a significantly smaller number of studies that investigate the adsorption behavior of PS onto SiO<sub>2</sub> surfaces from a very good solvent (toluene). A previous report suggests that some interactions exist between PS and SiO<sub>2</sub>.<sup>42</sup>

To test whether PS in toluene can adsorb on the surface of SiO<sub>2</sub>, we perform QCM-D experiments. In this experiment, a SiO<sub>2</sub>-coated quartz crystal is exposed to a continuous flow of PS dissolved in toluene ( $M_n = 173,000$  g/mol,  $c = 0.05$  wt %)

and the resulting changes in the frequency ( $\Delta f$ ) and dissipation ( $\Delta D$ ) are monitored *in situ*. We observe substantial changes in  $f$  and  $D$  when the PS solution is flowing over the crystal, as shown in Figure 5. Once the shifts are stabilized, the sensor



**Figure 5.** Change in frequency (third overtone  $\Delta f/3$ —black solid line) and dissipation factor ( $\Delta D$ —red dashed line) during PS adsorption and desorption in solution from *in situ* QCM-D measurements. A 0.05 wt % solution of PS ( $M_n = 173,000$  g/mol) dissolved in toluene is exposed to the  $\text{SiO}_2$ -coated sensor crystal ( $t = 5$  min) and quenched with pure toluene at the point indicated by the grey dashed line ( $t = 5$  h). The frequency and dissipation do not recover to their original values, indicating irreversible adsorption of PS on the  $\text{SiO}_2$  surface.

crystal is exposed to pure toluene to allow any loosely adsorbed chains to desorb. Even after  $\sim 1$  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  $\text{SiO}_2$  surface from the toluene solution. Modeling 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 (Figure S2). It has been postulated that interactions between PS and the untreated  $\text{SiO}_2$  surface could be attributed to  $\text{SiOH}-\pi$  hydrogen bonds forming between the phenyl ring of the PS and the silanol groups on the  $\text{SiO}_2$  surface.<sup>42</sup> Such an interaction has been observed previously in gas adsorption studies of benzene and toluene onto  $\text{SiO}_2$ .<sup>43</sup>

Unlike the dynamics, the partitioning behavior of the polymer into the interstitial voids of the NP packings in the SIP system does not strongly depend on the confinement ratio (Figure 4). We attribute the independence of partitioning on the confinement ratio to the fact that, at long times, the concentration within the pores exceeds the critical overlap concentration. The polymer chain's characteristic length scale in such a system becomes the length of the 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 the polymer. The correlation length of PS at the final concentration ( $\xi \approx 2$  nm),<sup>44</sup> 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  $R_g$  is significantly larger than the size of the pore

as the concentration of the polymer increases above the critical overlap concentration.

## CONCLUSIONS

In summary, we find that the extent of confinement in the SIP system affects the kinetics of polymer infiltration into the NP packing but not the final extent of infiltration in a good solvent. The infiltration time is found to scale with the confinement ratio ( $\tau \sim \lambda^{3/2}$ ), which is bounded between the behavior of confined polymer melts ( $\lambda^2$ ) and that of confined single polymer chains ( $\lambda^{2/3}$ ). However, the final volume fraction of the infiltrated polymer is independent of the extent of confinement, because the fully infiltrated SIP system is at concentrations well above the critical overlap concentration, where the correlation length scale is smaller ( $\xi \approx 2$  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  $\text{SiO}_2$  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  $\text{SiO}_2$  surface, which shows irreversible adsorption of a thin polymer layer onto the surface.

Future work will focus on probing how tuning the strength of the polymer–surface interaction impacts the dynamics of infiltration in the SIP system and the final extent of infiltration. Molecular dynamics simulations on the SIP system have found that by inducing stronger adhesion between the polymer and NP, a transition from dissolution-dominated infiltration to adhesion-dominated infiltration occurs.<sup>45</sup> Our future work will probe experimentally how altering the nature of the surface interactions affects the extent of infiltration and the infiltration dynamics. To better understand partitioning and kinetics in such systems, an entropic barrier model using self-consistent field theory simulations is currently being investigated.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.0c01057>.

*In situ* ellipsometry measurements of PS thin film swelling upon toluene vapor exposure, QCM-D modeling, and further PS adsorption experiments using *ex situ* ellipsometry (PDF)

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### Author Contributions

The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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