Tuning The Properties Of Soft Materials Through Extreme Nanoconfinement

Haonan Wang

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Tuning The Properties Of Soft Materials Through Extreme Nanoconfinement

Abstract
Polymers and small molecules under nanoconfinement can show significantly deviated properties from bulk. While the effect of nanoconfinement has been studied for several decades, the origin of the deviation is yet to be investigated and different people can observe very different effects in similar systems. Capillary Rise Infiltration (CaRI) enables the fabrication of polymer-infiltrated nanoparticle (NP) films in which extreme nanoconfinement can be achieved.

In this thesis, we first use CaRI films as the model system to study the glass transition of soft materials under extreme nanoconfinement. In-situ spectroscopic ellipsometry with a temperature-control stage is used to monitor the glass transition process. We show that in CaRI films the Tg of confined polystyrene (PS), which interacts weakly with SiO2 NPs, significantly increases with decreasing pore size such that the Tg increases by up to 50 K in 11 nm NP packings, while Tg is close to the bulk Tg in 100 nm NP packings. Such effect on Tg is almost independent of molecular weight. For Poly(2-vinylpyridine)(P2VP)/SiO2 CaRI films, a ~100 K increase in Tg can be achieved with a huge gradient of dynamics. We then studied the thermal degradation of polymers in CaRI films. We demonstrate that as the NP size is decreased, increasing the degree of confinement, the isothermal degradation time of PS is dramatically increased due to the slowed dynamics and diffusion in CaRI films. In addition to the slowed diffusion, the small pore size can suppress the carbonization reactions. The competition of these two effects results in a non-monotonic trend of the thermal degradation of some polymers. Finally, we characterized the molecular conformation of a small molecule glass N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) to investigate the origin of the different confinement effects in nanoporous media with different pore geometries. We show that TPD has a more planer conformation in CaRI films with concave pores while no change in conformation is observed when TPD is confined in controlled pore glass (CPG) with convex pores. The results indicate that pore geometry is an essential factor in Tg nanoconfinement effects and highlight the role of intramolecular degrees of freedom in the glass transition, which have not been extensively explored.

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TUNING THE PROPERTIES OF SOFT MATERIALS THROUGH EXTREME NANOCONFINEMENT

Haonan Wang

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in

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TUNING THE PROPERTIES OF SOFT MATERIALS THROUGH EXTREME NANOCONFINEMENT

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ABSTRACT

TUNING THE PROPERTIES OF SOFT MATERIALS THROUGH EXTREME NANOCONFINEMENT

Haonan Wang

Zahra Fakhraai

Polymers and small molecules under nanoconfinement can show significantly deviated properties from bulk. While the effect of nanoconfinement has been studied for several decades, the origin of the deviation is yet to be investigated and different people can observe very different effects in similar systems. Capillary Rise Infiltration (CaRI) enables the fabrication of polymer-infiltrated nanoparticle (NP) films in which extreme nanoconfinement can be achieved.

In this thesis, we first use CaRI films as the model system to study the glass transition of soft materials under extreme nanoconfinement. In-situ spectroscopic ellipsometry with a temperature-control stage is used to monitor the glass transition process. We show that in CaRI films the $T_g$ of confined polystyrene (PS), which interacts weakly with SiO$_2$ NPs, significantly increases with decreasing pore size such that the $T_g$ increases by up to 50 K in 11 nm NP packings, while $T_g$ is close to the bulk $T_g$ in 100 nm NP packings. Such effect on $T_g$ is almost independent of molecular weight. For Poly(2-vinylpyridine)(P2VP)/SiO$_2$ CaRI films, a $\sim$100 K increase in $T_g$ can be achieved with a huge gradient of dynamics. We then studied the thermal degradation of polymers in CaRI films. We demonstrate that as the NP size is decreased, increasing the degree of confinement, the isothermal degradation time of PS is dramatically increased due to the slowed dynamics and diffusion in CaRI films. In addition to
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1.1. Polymers and polymer nanocomposites

A polymer or a macromolecule is a very large molecule composed of many repeating subunits called monomers. Polymers can have a broad spectrum of properties, depending on their chemical formulation, molecular weight and the producing process. Polymers can range from biopolymers such as DNA and proteins to synthetic plastics such as polyethylene (PE), polypropene (PP) and polystyrene (PS). Their large molecular weight, relative to small molecules, gives them unique physical properties including toughness, elasticity, and viscoelasticity. Also because of the large size and usually irregular molecular structures, polymers tend to form amorphous and semicrystalline structures rather than crystals. Polymers play important and irreplaceable roles in our everyday life.

In order to expand the range of properties that polymeric materials can have, a variety of additives can be added to the polymer matrix to make polymer microcomposites and nanocomposites, depending on the size of the fillers. When at least one spatial dimension of the filler is less than or around 100 nm, the composite material is called polymer nanocomposites (PNC). With smaller nanoparticle fillers, the interfacial area in PNCs grows dramatically, which can significantly influence the properties of the polymer matrix even at very small loading of the nano-fillers, especially the mechanical properties. Since the very first application of PNCs of rubber polymers with carbon black filler for tires, PNCs have expanded to a wide range of polymers and nano-fillers for various applications, such as electronics, energy storage, sensing, catalysis, etc.

Current applications of PNCs usually have small NP loadings, that is, the major-
ity of the PNCs is the polymer matrix. The NP loadings are typically less than 50 vol% (124; 101; 92; 13; 82). PNCs with high NP loadings are still relatively unexplored. Conventional method of making polymer nanocomposites are melt- or solution-compounding. NPs are mixed in polymer melts or solutions, followed by a cooling or drying step. However, this approach is difficult to control when the NP loading is high, because of the high viscosity and the tendency of NP aggregation. As such, a simple and widely applicable way of making PNCs with high NP loadings is desired. Capilari-rise Infiltration (CaRI) is a recently-developed method to address this problem.

1.2. Introduction to Capillary-rise Infiltration (CaRI)

Capillary rise infiltration (CaRI) is a simple yet powerful method of making PNC films. To make a CaRI film, a nanoparticle (NP) layer and a polymer layer are deposited on a substrate, such as Si and glass, with simple film deposition techniques including spin coating, dip coating, blade coating and spray coating. The packing of nanoparticles is produced on top of the polymer layer. The inverted geometry can also be fabricated by depositing the nanoparticle film first and then the polymer film, by directly using a solution-based deposition technique (e.g., spin coating) or by placing a free-standing polymer film.

If a solution-based technique is used to deposit the polymer layer on top of the NP layer, the pores of the NP film can be partially filled with polymers from the solution, depending on the molecular weight of the polymers and the viscosity of the solution. Regardless of the method by which a bilayer is prepared, the solvent of the second deposition should not influence the integrity of the first layer, e.g., the polymer film should not dissolve in the solvent of the NP solutions. In addition, the solutions should have good wetting on the surface to be deposited on. For example,
an aqueous NP solution doesn’t wet the surface of a hydrophobic polymer, which makes it impossible to cast the NP layer on the top. A surface modification of the first layer such as plasma treatment of the polymer film may be necessary.

The NP films deposited by spin-coating have random close packing with high surface area and interconnected nanopores. For example, a film of spherical SiO\(_2\) nanoparticles has the porosity of \(\sim 37\%\) regardless of particle size when the film thickness is significantly larger than the size of the NPs.(125; 14) NP films with fewer layers of NPs (e.g. less than 4) can have higher overall porosity due to the large fraction of the surface region. The average pore diameter of the random packings of spherical particles is around 30% of the particle diameter.

After the deposition of the two layers, the film is annealed above the glass transition temperature (\(T_g\)) of the polymer to induce infiltration. Most polymers have relatively low surface energy and favorable contact angles (i.e., \(< 90^\circ\)) on the inorganic NP surface. Capillary forces make the infiltration of polymers into the pores of the NP film a favorable process. This capillary-rise process continues until the pores in the NP film is completely saturated or all the polymers are inside the pores. The same principle has been used to induce infiltration of polymers into cylindrical pores of anodized aluminium oxide (AAO) substrate or controlled pore glass (CPG). For SiO\(_2\) NPs, which is most widely studied in CaRI films, there are hydroxyl groups (-OH) on the NP surface, resulting in hydrogen bonding between the NPS. The strong inter-particle interactions of the NP packings as well as the small thermal expansion coefficient of SiO\(_2\) make the NP film very rigid. The infiltration of polymer does not change the thickness of the NP layer significantly. The center-to-center distance of NPs after polymer infiltration does not change as well. Figure 1.1 shows the schematic illustration of a typical CaRI process as well as scanning electron microscopic (SEM)
Figure 1.1: (a) Schematic illustration showing the process of Capillary-rise Infiltration (CaRI) of polystyrene (PS) into the pores of TiO$_2$ NP film. (b) Scanning electron microscopy (SEM) images showing CaRI of a bilayer film consisting of PS ($M_n = 8000$ g/mol) and a TiO$_2$ NP layer. From left to right, the SEM images are taken after the bilayer is annealed at 403 K for 0, 2 and 20.5 h, respectively. Reproduced from Ref(60) with permission from The Royal Society of Chemistry.

The CaRI method has been used to make polymer-infiltrated NP films with a variety of polymers, from hydrophobic polymers, such as polytetrafluoroethylene (PTFE) to hydrophilic polymers, such as polymethyl methacrylate (PMMA) and poly(2-vinyl pyridine) (P2VP), from very low molecular weight (or small organic molecules) to as high as 2 million g/mol, together with NPs of various composition, size and shapes. Polymers can infiltrate NP films up to several micros thick in several seconds to days or even longer, depending on the size of the NPs, the thickness of the NP film, the molecular weight of the polymers and the polymer-NP interfacial interactions.

1.3. Glass transition of polymers in confined geometries

One of the most important properties of most polymeric materials is the formation of glasses instead of crystals at solid state. Figure 1.2 shows the specific volume $V_{sp}$ as a
function of temperature for a typical glass-forming liquid. As the liquid is cooled from high temperature, it may crystallize at the melting point \( T_m \) and cause reduction in the specific volume. If the crystallization is avoided below \( T_m \), the liquid is called a supercooled liquid, of which the thermodynamic properties can be expected from extrapolating the liquid state above \( T_m \). As the supercooled liquid is further cooled to lower temperatures, the viscosity keeps increasing and the relaxation of the molecules gets slower. Because the rearrangement of the molecules is necessary for the supercooled liquid to reach the equilibrium state at the temperature, the experimentally observed \( V_{sp} \) will begin to deviate below some temperature when the rearrangement is too slow. The liquid is kinetically trapped at some non-equilibrium state that is called the glassy state. The temperature of the transition from a supercooled liquid to glass is called the glass transition temperature \( T_g \). Because the glassy state is non-equilibrium and continuously relaxing to lower energy states, the properties of glass depend on how the glassy state is reached. For example, by changing the cooling rate, different \( T_g \)s and glassy state can be observed for the same supercooled liquid; through physical vapor deposition, where the glassy state is achieved by surface equilibrium during the deposition process, the final glass have significantly higher density and kinetic stability than a liquid-quenched glass.(116; 102; 79)

Investigating the glass transition behaviors of polymers at nanometer length scale and how \( T_g \) is influenced by nanoconfinement has been of interest for almost 3 decades.(87) Typical nanoconfined systems include 1D (thin films), 2D (pores) and 3D (spheres), where at least one length scale of the three dimensions is less than \( \sim 100 \) nm. When polymers are confined at nanometer scale, the conformations of the chains are affected by both the finite size effects and interfacial effects. There are other factors, such as polymer shape, sample preparation and thermal history, that can have influence on
the properties of the polymers. These effects are always convoluted in the systems of nanoconfinement and make it difficult to get a simple picture of the glass transition in nanoconfinement.

Polymer thin films (1D confinement) are the simplest and most understood systems. There are typically two interfaces: polymer-air interface and polymer-substrate interface. The polymer-air interface can provide additional free volume and mobility, resulting in lower $T_g$ when the film thickness is small. Depending on the strength of the polymer-substrate interfacial interaction, different systems can have increased or decreased $T_g$s. Figure 1.3 shows the change in $T_g$ values as a function of film thickness of three polymers with different interfacial interactions with SiO$_2$ substrate. Poly(2-vinylpyridine) (P2VP) and Polymethyl methacrylate (PMMA) can form hydrogen bonds with the surface hydroxyl groups on SiO$_2$ substrate while Polystyrene (PS)
only has weak Van der Waals interactions. When the free surface (polymer-air interface) is removed by capping the polymer thin film, the $T_g$ of PS film is recovered.\textsuperscript{(111)} The competing of the two interfaces can even result in two distinct $T_g$s in P2VP films on SiO\textsubscript{2}.\textsuperscript{(46)} We note that the measured $T_g$ values are not consistent for systems with strong interfacial interactions and significantly different $T_g$s are reported for the same P2VP-SiO\textsubscript{2} systems.

Because of the difficulty in preparing 3D-nanoconfined polymers in nanospheres with ultra-small size, there are much fewer studies focusing on this system. 3D confinement of polymers with a hard cover can result in isochoric boundary condition rather than isobaric boundary condition. Instead of $T_g$, Silica-capped PS shows a significant decrease in the dynamic fragility of PS, which indicates that the temperature dependence of the structural relaxation close to $T_g$ is weakened with isochoric
Polymers confined in nanoporous materials (2D confinement) are of broad interest in modern science and technology. The great selection of materials and variable degree of nanoconfinement make 2D confinement widely studied. Since the pore size can vary from hundreds of nanometers to as small as several nanometers, nanoporous materials offer a model system to study the dynamic properties of polymers under different degrees of confinement. Conventionally used nanoporous media include anodic aluminum oxide (AAO) with cylindrical pores and controlled pore glass (CPG) made from phase separation of borosilicate glass. The polymers can fill the pores by polymerization inside the pores or infiltration of polymers driven by capillary force. Lack of control of sample preparation and characterization methods of the polymers confined in nanopores makes the confinement effects not consistent even for very similar systems. Increase, decrease or unaffected $T_g$s have all been observed.(87; 77; 69; 78; 76)In many cases, two $T_g$s are measured for polymers and small molecules confined in nanoporous media, one lower than bulk value and one above bulk $T_g$. However, the trend of the observed $T_g$ changes for different systems do not always follow the strength of interfacial interactions, which may indicate the existence of some hidden factors that are not well controlled and studied.(133; 1; 94; 142; 131; 141; 80)

1.4. Thesis outline

In this thesis, we use CaRI as the model system to systematically study the effect of different factors on the glass transition and other properties of polymers and small organic molecule glasses under 2D extreme nanoconfinement. The factors include pore size, interfacial interactions, irreversible adsorption and pore geometry, which is proven to be an essential factor that is ignored so far.
In Chapter 2, we study the glass transition of polymers confined in CaRI films. With careful control of the factors, we show dramatic increase in $T_g$ under extreme nanofinacement even in weakly interacting systems. Strong interfacial interactions can further increase the $T_g$ and the effect is stronger under stronger nanoconfinement. Such high $T_g$s are entropic in nature and have never been observed in other systems like AAO and CPG. We show the importance of spacial confinement over free surface effect using underfilled CaRI (UCaRI) films. The reduced relaxation and mobility of polymers in CaRI films can result in deviation of other related properties.

In Chapter 3, we study the thermal degradation of polymers in CaRI films. In stead of measuring the overall mass loss with the conventional Thermogravimetric analysis (TGA) method, we performed in-situ ellipsometry measurement and demonstrated the detailed thermal degradation process of polymers in CaRI films with careful ellipsometry modeling. We show that the thermal stability and activation energy for PS can be significantly enhanced due to the reduced mobility. At the same time, the limited pore size can suppress the carbonization reactions of other polymers and accelerate the thermal degradation. The competition of the two factors results in non-monotonic trend for the thermal degradation of Polyethersulfone (PES).

In Chapter 4, we try to answer the question whe the confinement effects in CaRI films are different from other nanoporo (AAO and CPG) at the molecular scale. We study the molecular conformation of a small molecule glass former (N,N’-Bis(3-methylphenyl)-N,N’-diphenylbenzidine, TPD) confined in CaRI and CPG and demonstrate the importance of pore geometry on the confinement effects. We show that the TPD molecules tend to have a more planer conformation in CaRI films than in bulk and CPG. Such change in molecular conformations, which has potential influence in more optical and electrical properties, has never been observed elsewhere. Because of
the entropic origin of the unique nanoconfinement effects in CaRI system, this study can be extended to other molecules.

In Chapter 5, we demonstrate the application of the CaRI films in enhancing the adhesion between polymers and glass substrate. We show the preliminary data of enhanced adhesion between the hydrophilic glass surface and a superhydrophobic polymer, indicating the wide scope of applicable systems of the CaRI films.

Finally, Chapter 6 summarizes the content of thesis and proposes future directions of the research and application of the CaRI systems.
CHAPTER 2: GLASS TRANSITION OF POLYMERS UNDER EXTREME NANOCONFINEMENT IN NANOPARTICLE FILMS

2.1. Abstract
Properties of polymers in polymer nanocomposites and nanopores have been shown to deviate from their respective bulk properties due to chain confinement as well as polymer-particle interfacial interactions. However, separating the confinement effects from the interfacial effects under extreme nanoconfinement is experimentally challenging. Capillary Rise Infiltration (CaRI) enables polymer infiltration into nanoparticle (NP) packings, thereby confining polymers within extremely small pores and dramatically increasing the interfacial area, providing a good system to systematically distinguish the role of each effect on polymer properties. In this study, we investigate the effect of spatial confinement on the glass transition temperature \( T_g \) of polystyrene (PS) infiltrated into SiO\(_2\) NP films. The degree of confinement is tuned by varying the molecular weight of polymers, the size of NPs (diameters between 11 nm-100 nm, producing 3 nm-30 nm average pore sizes), as well as the fill-fraction of PS in the NP films. We show that in these dense NP packings the \( T_g \) of confined PS, which interacts weakly with SiO\(_2\) NPs, significantly increases with decreasing pore size such that for the two molecular weights of PS studied, the \( T_g \) increases by up to 50 K in 11 nm NP packings, while \( T_g \) is close to the bulk \( T_g \) in 100 nm NP packings. Interestingly, as the fill-fraction of PS is decreased, resulting in the accumulation of the polymer in the contacts between nanoparticles, hence increased specific interfacial area, the \( T_g \) further increases relative to the fully-filled films by another 5-8 K, indicating the strong role of geometrical confinement as opposed to the interfacial
effects on the measured \( T_g \) values.

2.2. Introduction

Thin polymer films and polymer nanoparticle (NP) composites have become increasingly important in modern technology, such as microelectronics(91), separation membranes(130), protective coatings(24), and photovoltaic cells(129). At the nanometer scale, the reduction in size of the polymers in these systems results in a deviation of physical properties, such as the physical aging rate(59; 96; 97; 7; 99), viscosity,(17) and the glass transition temperature \( (T_g) \)(39; 65; 11; 31; 103; 48), from their bulk values. These deviations from bulk properties could be due to either chain and segmental confinement effects(132; 142) or the increased role of interfacial effects on the properties of the system(48; 34; 35). In particular, \( T_g \) of supported polymer thin films have been shown to be influenced by both the substrate and the free surface(104; 121; 93; 65; 33; 32). The free surfaces of polymer films show enhanced mobility(31; 35; 100) which can result in lower average film \( T_g \)s. The effects are quite significant when the film thickness is reduced below \( \sim 30 \) nm in both polymer and small molecule glass systems(93; 47; 31; 111; 39; 136; 135). When the polymer has strong interactions with the substrate (such as hydrogen bonding), the substrate-polymer interactions can dominate and the \( T_g \) increases with decreasing film thickness(93; 121; 85; 42). The competing interfacial effects can even give rise to two distinct \( T_g \)s for ultra-thin films at low cooling rates(46).

Polystyrene (PS) on Silicon substrate with native oxide (Si/SiO\(_2\)) is one of the most investigated systems with weak polymer-substrate interactions. Decreasing \( T_g \) of PS with film thickness was observed in early 1990s(65). Since then, a large number of both experimental and theoretical studies have focused on the confinement and interfacial effects on PS glassy dynamics(65; 111; 68; 3; 21; 70; 27; 114; 115). In sup-
ported PS films, $T_g$ typically decreases with decreasing film thickness due to strongly enhanced dynamics at the free surface. After the removal of the free surface, $T_g$ recovers to the bulk value (111; 132). As such, most studies have attributed the observation of $T_g$ changes in supported PS thin films to the free surface effects that are the dominant factor in these films. Even the formation of highly adsorbed PS layers on native Silicon Oxide substrate has a moderate effect on $T_g$ in this geometry (88; 86; 19).

Distinguishing interfacial effects from pure confinement effects is even more challenging when it comes to PS/SiO$_2$ nanocomposites. Increase (62), decrease (8), or no change (110) in composite $T_g$ with increasing SiO$_2$ NP loading have all been observed. In these systems, the highest possible NP loadings are around 40% volume fraction (82; 13; 8; 62), limiting the degree of confinement. Furthermore, the dispersion conditions and possible aggregation of SiO$_2$ NPs can complicate data interpretation.

Recently, a new method of making polymer NP films with extremely high NP loadings has been reported via capillary rise infiltration (CaRI) (60). In this method, a NP film is placed on top of a polymer film. During annealing at high temperature, capillary forces drive the polymer to infiltrate into the interstices between the NPs without disturbing the dense ($\sim$ 63% volume fraction) NP film packing. The viscosity and dynamics of unentangled polymers during infiltration have been studied using experiments and molecular dynamics simulations and have shown extreme slowedown of the dynamics under nano-confinement (60; 112; 57). We have recently shown that the viscosity increase in unentangled systems is independent of the polymer/NP interactions and correlates well with the increased $T_g$ (57).

Here, we study the glass transition temperature of PS/SiO$_2$ CaRI films with various NP diameters, PS molecular weights, and PS fill-fractions in under-saturated CaRI (UCaRI) (55) films. Spectroscopic ellipsometry was used to measure the thickness and
the index of refraction of CaRI films as a function of temperature to determine $T_g$ of PS confined in these films ($T_g$ (confined)). The results show that under these extreme confinement conditions, $T_g$ (confined) is significantly increased for CaRI films with NP diameters smaller than 100 nm. For UCaRI films, where there is insufficient PS to fully fill the interparticle space, PS forms capillary bridges between NPs, resides in the most confined regions, and $T_g$ is further increased, despite having larger free surface area. The dewetting of PS on the NPs under these conditions indicates that the interfacial effects are still minimal in these systems and the $T_g$ increase can be strongly attributed to the geometrical confinement effects due to modifications in segmental relaxation dynamics in small spaces.

2.3. Materials and methods

2.3.1. Preparation of PS/SiO$_2$ CaRI films

The sample preparation scheme for CaRI and UCaRI films in various geometries (PS-top or NP-top) are schematically shown in Figure 2.1. One sided-polished silicon wafers (100) purchased from Virginia Semiconductor were cut to approximately by 1 cm × 1 cm squares. Polystyrene (PS, $M_n = 7.5$ kg/mol, PDI = 1.06 (PS(8K)), and 1900 kg/mol, PDI = 1.18 (PS(2M)), Polymer Source, Inc.) solutions were prepared by dissolving PS in toluene. SiO$_2$ (25 nm) NPs were purchased dispersed in water (Ludox TM-50, Sigma Aldrich). SiO$_2$ (11 nm) and SiO$_2$ (100 nm) NPs were purchased dispersed in isopropanol (IPA) (free samples from Nissan Chemical). The suspensions were further diluted with their respective solvents. No other treatment was applied to the NPs.

To generate the nanoporous CaRI films, a PS layer was first spin-coated (Laurell, WS-400BZ-6NPP/Lite spin-coater) onto the silicon wafer. Then PS film was room air plasma-treated for $\sim 2$ seconds (Expanded Plasma Cleaner PDC-001, Harric Plasma)
to render the film surface hydrophilic. For SiO$_2$ in IPA, this latter step was not necessary. The SiO$_2$ NP suspensions were then spin-coated onto the PS layer to form a bilayer film. The bilayer films were then annealed at 423-453 K to induce PS infiltration and homogeneous distribution throughout the voids of the SiO$_2$ NP packings. These films are designated as \textit{NP-top CaRI} films (Figure 1a). In some experiments, in order to prevent crack formation, an inverted geometry was used, where the NP film was spin-coated first, followed by the PS film. These samples are designated as \textit{PS-top CaRI} films (Figure 1c). Fully-filled CaRI films are prepared such that they have a residual PS layer after full infiltration. CaRI films were made with 11 nm, 25 nm, and 100 nm diameter SiO$_2$ NPs in both PS-top and NP-top geometries.

The porosity of fully-filled NP films were calculated based on the thickness change of the PS layer after infiltration and was determined to be $37 \pm 3\%$ (See Table 2.1). The average pore size was calculated to be $0.3d$, where $d$ is the diameter of the NPs(14). As such, the volume occupied by the NPs is 63\%.
Table 2.1: Thickness of PS and NP layers before and after infiltration. Porosity of the NP film was calculated to be $\Delta h_{PS}/h_{NP}$.

In order to avoid crack formation during thermal infiltration of CaRI films, the method of making PS-top samples is introduced in this study. In this method, the PS is spin-coated on top of the NP film and subsequently infiltrated. Figure 2.2 shows the index of refraction of SiO$_2$(11 nm)/PS(8K) and SiO$_2$(11 nm)/PS(2M) films immediately after spin-coating of the PS layer and after the thermal infiltration. For PS(8K), PS can fill part of the pores during the spin-coating process. The solvent-induced infiltration leaves more PS closer to the top of the NP layer resulting in a gradient of index of refraction. For PS(2M), because of the high molecular weight and viscosity of the solution, much less filling of the pores occurs during spin-coating. After annealing above $T_g$, both molecular weight chains can fully fill the pores of the NP layer, forming uniform CaRI films.

2.3.2. The effect of plasma treatment and irreversible absorption on properties

In order to spin coat a good NP film on PS for the NP-top geometry, the solvent of the SiO$_2$ suspension must wet the surface of PS. Hence, for aqueous suspension, $\sim 2s$ room air plasma treatment on the PS film surface were performed to increase the surface energy. To rule out the influence of the surface plasma treatment on the final properties of the films, SiO$_2$(11 nm) in isopropanol (IPA) was used as a control because IPA wets the PS surface well. PS(8K) can fully infiltrate the SiO$_2$(11 nm)
Figure 2.2: Index of refraction of the film as a function of the distance from the substrate before and after thermal infiltration for PS-top CaRI films with different PS molecular weights.

NPs in 15 s when annealed at 433 K. For spin coated films, it takes hours for the irreversibly adsorbed layer to grow at that temperature. Thus, by controlling the annealing time, we are able to examine the influence of the adsorbed layer.

2.3.3. Preparation of under-saturated CaRI (UCaRI) films

UCaRI films were prepared where the initial thickness of the PS layer was varied such that the desired fill-fraction could be achieved after all of the polymer was infiltrated in the system, leaving no residual PS layer under the NP film (Figure 1b). The PS fill-fraction, the ratio of PS volume compared to the fully-filled PS volume, was defined as \( \frac{h_{PS}}{37\% \times h_{SiO_2}} \), where \( h_{PS} \) is the PS-layer thickness before infiltration and \( h_{SiO_2} \) is the thickness of the NP layer. However, due to the formation of cracks in the NP-top geometry this method is subject to error.

UCaRI samples were prepared with 25 nm SiO\(_2\) NPs and NP-top geometry only, except for SEM images where 100 nm diameter was used to highlight capillary bridges.
For UCaRI films with fill-fractions > 70%, the assumption was made that the polymer is uniformly distributed in the NP films and a single-layer model with uniform index was used in ellipsometry measurements. The model is compared with an alternative model with a gradient in the refractive index and it is observed that for high filling fractions the uniform index assumption is reasonable (Figure 2.3a). This is consistent with previous observations(117). Using a linear regression, we can obtain the fill-fraction from $n$. This method is used for the data shown in Figure 2.17. Lower fill-fractions where this assumption fails have not been included in this study (Figure 2.3b).

2.3.4. Preparation of CaRI films with binary NP mixtures

Two methods for making NP films were used.

Method 1- Making mixtures of 11 nm and 100 nm NP at varying ratios The NP mixture solutions were prepared with varying concentrations of 11nm and 100nm NPs. Six solutions were made with weight ratios of 100 nm:11 nm NP size (1:0.05, 1:0.1, 1:0.15, 1:0.2, 1:0.25, 1:0.3) The NP solutions were bath sonicated for 2 hours to disintegrate the particle agglomerates into smaller and more monodisperse units then the solutions were filtered prior to use.

Method 2 – Coating the 100 nm and 11 nm NP separately The concentration of the 100 nm NP was kept constant at 100 nm NP:Ethanol = 1:4 but varied the concentration of the 11 nm NP; 11 nm:isopropanol = 1:40 & 1:60. The NP solutions were bath sonicated for 2 hours to disintegrate the particle agglomerates into smaller and more monodisperse units then the solutions were filtered prior to use. The 100 nm NP solution was spin coated first at 6000 rpm then the 11 nm NP solution was applied to the same silicon wafer and incubated for 3 minutes before spin coating at 6000 rpm.
2.3.5. Ellipsometry $T_g$ measurements

The thickness and refractive index values were measured using spectroscopic ellipsometry (M-2000V, J.A. Woollam). The raw ellipsometry data $\Psi(\lambda)$ and $\Delta(\lambda)$ were fit to a Cauchy model ($n(\lambda) = A + B/\lambda^2, k(\lambda) = 0$), where $n$ and $k$ are the real and imaginary parts of index of refraction. Depending on the sample, either two-layer (for CaRI) or one-layer (UCaRI) Cauchy model on Si substrate with 1 nm native oxides were used. Optical constants of Si substrate and the native oxide layer were taken from previous publication(53). The properties of both the PS residual layer
Figure 2.4: PS fill fraction calculated from initial PS thickness vs. refractive index at 632.8 nm at 423 K for different PS(8K)/SiO$_2$(25 nm), NP-top UCaRI films with $\sim$ 200 nm thickness. Error bars are calculated from error of NP layer thickness before and after infiltration. The straight line is the linear fit of the data points.

and the NP films were modeled to fit the ellipsometry data. Different models were compared to make sure all the key parameters were included without over-fitting of the insensitive ones (Figure 2.5). Figure 2.6 shows a typical SE data and the results of the model used to fit the data. Samples were mounted onto a temperature-controlled stage (Linkam THMS 600) that was attached to the ellipsometer. The ellipsometry sampling rate was 1 s with high-accuracy zone averaging. Heating and cooling ramps under dry nitrogen flow were run for each sample (Figure 2.7). Cooling rate was held at 10 K/min. All $T_g$ measurements are reported upon cooling.

In addition to the fitting parameters mentioned above, the offset of angle of incidence was also fit when necessary to ensure that any uncertainty in the angle does not affect the data. The beam size was reduced to 0.3 $\times$ 1.2 mm using focusing optics. Before mounting the focusing optics, the ellipsometer was aligned to ensure a direct light path
Figure 2.5: (a) Typical ellipsometry model used for CaRI films, including all the fitting parameters (bold blue fonts). (b) Fitting parameter uniqueness test of incident light angle offset shows that angle offset is a necessary parameter in the fitting. (c) Comparing different optical models for each layer confirms that the layers are uniform and ellipsometry is not sensitive to the surface roughness for over-filled CaRI films.

with a 70° reflection off of the sample. Calibrations were performed after mounting the optics using Si wafers with a thermally grown oxide layer of a known thickness to correct for any changes due to the focusing optics. The spectroscopic wavelength range during the measurement was set to 600-1600 nm to maintain imaging in the transparent region of the spectrum and avoid scattering by NPs.

To ensure good thermal contact between the samples and the temperature controller stage (Linkam THMS600), the heating element was coated with Arctic Alumina thermal paste (Arctic Silver, Inc.), and the samples were clamped tightly to the heating element. Due to the use of the ellipsometer’s high-accuracy setting (zone averaging), the actual temperature was the average of the listed temperature and the previously listed temperature. This was corrected post acquisition. A small temperature lag (<1 K for 10 K/min cooling rate) was observed in both indium melting tests, and in the thickness data. This temperature shift, which was the same for all samples, was
Figure 2.6: Ellipsometric angles $\Psi$ (red) and $\Delta$ (green) vs. wavelength for an over-filled PS(8K)/SiO$_2$ (25 nm) CaRI film measured at $T = 303$ K. The dashed line shows the fit to the two-layer model used. The film thickness of the NP layer and the residual PS layer were determined to be $h_{PS} = 106.1 \pm 0.5$ nm and $h_{NP} = 206.1 \pm 0.5$ nm, respectively. The spectroscopic wavelength range of 600–1700 nm was used to maintain imaging in the transparent region of the spectrum and avoid scattering by NPs. Incident light angle offset was also fit to correct the tilt angle of the sample.
Figure 2.7: (a) Ellipsometry model for PS (8K)/SiO$_2$(25nm) CaRI film. Layers 2 and 3 are the residual PS layer and the NP layer, respectively. (b) During heating and cooling ramps, the thickness of layer 3 (NP film) was not sensitive to temperature. To avoid over-fitting, the thickness of layer 3 was kept constant for data presented in the manuscript. (c) The mean square error (MSE) of the fitting with fitting layer 3 (black) and without fitting layer 3 (red). (d) The calculated refractive index of the NP layer with (black) and without (red) fitting layer 3. It shows that both MSE and Index values are insensitive to the fitting of layer 3.
taken into account post acquisition.

2.3.6. Scanning electron microscopy (SEM)

SEM images were taken using a JEOL 7500F HRSEM at University of Pennsylvania Materials Research Science & Engineering Center (MRSEC). Before imaging, each sample was sputter-coated with a thin gold/palladium layer using a Cressington sputter-coater 108 to prevent charging. The samples were imaged at an accelerating voltage of 5.0 kV, emission current of 20 µA, and a working distance of approximately 8 mm.

2.4. Results and discussion

2.4.1. Glass transition of polystyrene under extreme nanoconfinement in CaRI films

$T_g$ of these films were determined via Spectroscopic Ellipsometry (SE) upon cooling the films at 10 K/min. This is the nominal cooling rate typically used in differential scanning calorimetry measurements and typically corresponds to a segmental relaxation time of $\sim 10^2$ seconds for bulk polymers.(52; 43; 87; 4; 30; 84). The thickness of the NP layer, in all three geometries shown in Figure 2.1 was found to be insensitive to the temperature changes and was fixed at a constant initial value to avoid over-fitting (Figure 2.7. This is consistent with the previous observations that, once the NP film is formed, it does not expand upon polymer infiltration. This is due to strong interactions between the NPs(60). As such, the changes in the index of refraction ($n$) vs. temperature ($T$) were monitored to measure $T_g$(confined).

Figure 2.8 shows an example of the calculated thickness and refractive index change with temperature for a PS(8K)/SiO$_2$(11 nm) NP-top, CaRI sample, with $h_{PS} = 242 \pm 1$ nm and $h_{NP} = 204 \pm 1$ nm. The $T_g$ of each layer was determined as the intersection of the linear fitting of the glass and the super-cooled liquid (SCL) regions in the plot of $n$ vs. $T$. The $T_g$s of the PS and NP films were determined to be $T_g$(PS)
= 362 ±3 K and \( T_g(\text{confined}) = 403 ±4 \) K, respectively. We note that because of water absorption, there is a deviation from linear behavior of the refractive index of the NP layer at low temperatures. Therefore, only the linear region was fitted as shown in Figure 2.8a.

In Figure 2.8b two inflection points can be observed at 363 ± 2 K and 401 ± 7 K in the plot of \( h_{PS} \) vs. \( T \). These values are the same as \( T_g(PS) \) and \( T_g(\text{confined}) \) within the error, as measured by the index of refraction, respectively. This is because as the film is cooled above \( T_g(\text{confined}) \) (\( T > 403 \) K), the PS chains in both layers are in the SCL state and can further infiltrate into the NP film while \( h_{NP} \) remains constant due to the rigidity of the nanoparticle film. This generates an apparent expansion coefficient in the PS layer that is larger than the expansion coefficient of the SCL of bulk PS. Below \( T_g(\text{confined}) \) (\( T < 403 \) K), the PS layer recovers the expansion coefficient of bulk material and goes through a glass transition upon further cooling below \( T_g(PS) \).

Measurements of both the index of refraction and the film thickness as shown in Figure 2.8 indicate an increase of \( \sim 41 \) K in \( T_g \) of PS(8K) upon confinement in SiO\(_2\)(11 nm) NP films. In this system the average pore diameter is estimated to be \( \sim 3 \) nm (14) and the polymer radius of gyration is roughly 2.5 nm(118). To investigate the changes of \( T_g \) (\( \Delta T_g \)) upon further confinement, CaRI films with various NP sizes were tested, with PS of two molecular weights. Figure 2.9 shows \( T_g \) of PS(8K) and PS(2M), NP-top CaRI films, in NP packings with various sizes (11 nm-100 nm). In the original CaRI geometry (NP-top), \( T_g \) values are fairly similar to the corresponding bulk values in SiO\(_2\)(100 nm) NP films, increasing dramatically with decreasing NP size for both molecular weights, up to \( \Delta T_g = 41 ± 3 \) K increase for PS(8K)/SiO\(_2\)(11 nm) and \( \Delta T_g = 23 ± 3 \) K increase for PS(2M)/SiO\(_2\)(11 nm). However, we note that
Figure 2.8: (a) Index of refraction $n$ (at $\lambda = 632.8$ nm) vs. $T$ for the PS (black) and NP (red) films of a PS(8K)/SiO$_2$(11 nm) NP-top CaRI film. The inset shows the geometry of the sample. The $T_g$ of these layers are measured to be $T_g$(PS)=362±3 K and $T_g$(confined)=403±4 K, respectively. (b) Normalized thickness vs. temperature for PS (black) and NP (red) films. The thickness of these layers were measured to be $h_{PS} = 242 \pm 1$nm and $h_{NP} = 204 \pm 1$nm, respectively. $h_{NP}$ was held constant during fitting. The inset shows the mean-squared error (MSE) vs. $T$, which shows reliable fitting throughout this temperature range. Two inflection points are observed in $h_{PS}$ vs. $T$ plot. The first inflection point occurs at the $T_g$(confined) upon cooling, where material is no longer sipped into the NP film at lower temperatures.
in this geometry the polymer and NP films have mismatching expansion coefficients upon heating and the polymer infiltration results in the formation of cracks in the NP films during infiltration (Figure 2.10). As such, there are some free polymers in the cracked areas and the measured \( T_g(\text{confined}) \) is a weighted average between the confined \( T_g \) and the \( T_g \) of PS in the cracked regions. In contrast, in the PS-top geometry where cracks are absent, the measured \( T_g(\text{confined}) \) is dramatically larger, up to \( \Delta T_g = 51 \pm 3 \) K for SiO\(_2\)(11 nm)/PS(8K) and \( \Delta T_g = 57 \pm 3 \) K for SiO\(_2\)(11 nm)/PS(2M).

Figure 2.9: \( T_g \) as a function of NP diameter for CaRI films at two different geometries (NP-top with open symbols and PS-top with solid symbols), with PS with two molecular weights PS(8K) (black) and PS(2M) (red). Black and red dashed lines show the bulk \( T_g \) values of PS(8K) \((T_g = 362 \pm 2 \) K) and PS(2M) \((T_g = 373 \pm 2 \) K), respectively as measured for thick PS films. Error bars represent standard error of at least 3 samples. Thicknesses of the NP and the residual PS layers are \( h_{NP} \sim 250 \) nm and \( h_{PS} \sim 200 \) nm, respectively.

The observations of up to \( \sim 57 \) K increase in \( T_g \) in CaRI films (for SiO\(_2\)(11 nm)/PS(8K))...
Figure 2.10: Cracks after the infiltration from the bottom-up for (a) PS(8K)/SiO$_2$(11 nm), (b) PS(8K)/SiO$_2$(25 nm), and (c) PS(8K)/SiO$_2$(100 nm) NP-top films. All samples were CaRI films with $\sim$300 nm NP layer and $\sim$250 nm residual PS layer. Cracks start to appear at the beginning of the infiltration at $\sim$378K. (d) SiO$_2$(11 nm)/PS(2M) PS-top film does not show evidence of crack upon top-down infiltration. Scale bars are 2 mm in all figures.

nm)/PS(2M) PS-top sample) is quite remarkable. SiO$_2$ is typically considered as a substrate with weak interactions with PS. As such, in previous studies, the free surface effects were considered as the dominant factor in the observed $T_g$ reduction of PS thin films. In these studies after the free surface was removed, bulk $T_g$ was recovered but still no increase in $T_g$ for films as thin as $\sim$7 nm were observed(111). The conventional method of making polymer nanocomposites is by evaporating the solvent of polymer-NP mixture suspension. In these types of nanocomposite systems, low acces-
sible NP loadings and tendency of NPs to aggregate can reduce the effect interfacial area and the spatial confinement. The force generated by extremely confined chains precludes NPs from creating regions of significant confinement, unless the polymer chain is depleted from that region. As a result, \( T_g \) of PS is either reduced or is to within a few degrees from the bulk value in conventional nanocomposites(62; 8; 110).

To put the degree of CaRI film confinement in context, the thinnest films studied in \( T_g \) measurements are typically 5-10 nm. PS in anodic aluminum oxide (AAO) templates can be confined down to a diameter of 55 nm(23). In CaRI films, NPs are closely packed with strong interparticle interactions before the infiltration process. The space occupied by NPs is \( \sim 63\% \) of the CaRI film volume (Table 2.1), which is very close to random close packing of uniform spheres (64%). As such, the PS/SiO\(_2\) interfacial area and spatial confinement is significantly larger than achievable by co-mixing of the polymer and NPs. By changing the diameter of NPs from 100 nm to 11 nm, the average pore diameter can be varied from 30 nm down to 3 nm (calculated as \( \sim 0.3 \) of the NP diameter(14)), with much smaller areas close to the NP junctions. Moreover, there is almost no free surface in these films and virtually all of the polymer chains are close to a SiO\(_2\) surface.

2.4.2. Fine control of \( T_g \) using binary NP mixtures

The porosity of the NP layer with randomly packed monodispersed NPs is 37\%. To reduce the pore size and hence reduce the index of refraction, bidispersed NP were made by mixing 11 nm NP with 100 nm NP. The solutions were prepared with varying weight ratios of 100 nm:11 nm NP size (1:0.05, 1:0.1, 1:0.15, 1:0.2, 1:0.25, 1:0.3) and their index of refraction were measured. Figure 2.11 shows the expected index of refraction (black) of each mixture if the 11 nm NP fills the pores of the 100 nm NP packing. However, the actual measured index of refraction (red) deviated from the
expected trend as the concentration of the 11 nm NP in the mixture increased.

![Graph showing expected and measured refractive indices of binary NP mixture films with 100 nm and 11 nm SiO₂ NPs.]

Figure 2.11: Expected and measured refractive indices of binary NP mixture films with 100 nm and 11 nm SiO₂ NPs.

Scanning electron microscopy (SEM) imaging was used to see the morphology of the NPs and how they were distributed on the Si wafer for ratios 1:0.15, 1:0.2 and 1:0.25. As shown in Figure 2.12, the ratio with the highest concentration of 11 nm NP (1:0.25), showed that the smaller 11 nm NP would aggregate at the bottom layer instead of being evenly distributed throughout the larger 100 nm NP packing. The 1:0.2 ratio also showed some 11 nm NP aggregation at the bottom layer but they were slightly more distributed amongst the 100 nm NP than the 1:0.25 ratio. The 1:0.15 ratio, in contrast, showed that the 11 nm NP were almost evenly distributed amongst the 100 nm NP. Therefore, the deviation of the measured index of refraction from the expected index of refraction trend was due to the small NP aggregating at the bottom as the 11 nm concentration increased.

CaRI films in varying geometries (PS-top or NP-top) were prepared using the NP
Figure 2.12: SEM images of binary NP mixture films with different ratio of the two sizes of NPs.

mixture solutions and measured to get the $T_g$. As shown in Figure 2.13, for the CaRI films made with the PS-top geometry, the $T_g$ gradually increased with increasing concentration of 11 nm NP ratios. This follows a similar trend shown in their previous research that $T_g$ increasing with decreasing NP size. With the bidispersed NP mixtures, the properties of $T_g$ can be controlled more accurately as opposed to when using monodispersed NPs.

2.4.3. Origin of $T_g$ increase in CaRI films

There are a few possible origins for the dramatic increase of $T_g$ in these highly confined CaRI films. Interfacial effects at the SiO$_2$/PS boundary, geometrical confinement of the chains, and a change in the boundary conditions from isobaric (P,N,T) to isochoric (V,N,T) can result in changes in the properties of PS in these highly confined systems.

We can first rule out the effect of the boundary conditions. As shown in Figure 2.8b, PS can freely expand in and out of the film upon heating/cooling at temperatures above $T_g$(confined). This effect is observed as an apparent change in the expansion coefficient of the adjacent residual PS layer. As such, it is unlikely that the boundary conditions are isochoric (V,N,T) during these experiments. Similarly, in the NP-top geometry, PS can freely expand to the free surface, as well as the bottom PS surface,
yet significantly increased $T_g$ values are still observed. This is consistent with previous studies where it was observed that isochoric confinement for PS nanoparticles, of 100 nm diameter or larger, does not significantly affect $T_g$ (132).

Another possibility is the formation of highly adsorbed PS layer during the infiltration/annealing process. Previous studies have shown that during annealing at elevated temperatures, large molecular weight PS can be irreversibly adsorbed on SiO$_2$ surface with slower dynamics. These studies have shown that the $T_g$ of the interfacial layer is below bulk $T_g$ before adsorption and gradually recovers to the bulk $T_g$ with the growth of the irreversibly adsorbed layer (89; 19). The irreversibly adsorbed PS layer takes hours of annealing to grow at the infiltration temperature of 433 K used in this study (58). Thus, by controlling the annealing time, we are able to examine the potential influence of the adsorbed layer on $T_g$ (confined) values. Figure 2.14 and Figure 2.15 show that extended annealing of the samples (3 hours at 433
Figure 2.14: (a) Temperature profile and change of index of refraction during infiltration, annealing and \(T_g\) measurement of PS(2M)/SiO\(_2\)(25nm) PS-top CaRI sample. Index of refraction is stable after 20 min annealing at 433 K. (b) 10 K/min cooling ramps after annealing at 433 K for 20 ~ 150 min. Good overlap of the curves indicates no influence of the adsorbed layer.

K) does not significantly affect the value of \(T_g\) and thus there is no visible evidence that the growth of a highly-adsorbed layer has an influence on the observed values of \(T_g\)(confined) for either PS(8K) and PS(2M) samples.

An interfacial layer with slower dynamics is also expected to broaden the width of the glass transition(1; 83) or even result in two glass transitions(46; 94; 78; 1; 83). In order to calculate the width of the glass transition, the slope of the refractive index change vs. temperature (\(dn/dT\)) was calculated. The refractive index data was first smoothed with the adjacent average method. Then, the 1st order derivative was calculated followed by another adjacent average smoothing. \(T_+\) and \(T_-\), the start and end point of transition, respectively, were determined to be the intersection of the linear fits of the regions before, during and after transition as shown in Figure 2.16.

Figure 2.16 shows \(T_+\) and \(T_-\), the high and low onsets of the glass transition, as a function of NP diameter for CaRI films. It is observed that there is no significant difference in the transition width (\(\Delta T = T_+ - T_-\)) between confined PS and bulk...
Figure 2.15: $T_g$ of PS(8K)/SiO$_2$(11nm) NP-top CaRI film and PS(2M)/SiO$_2$(25nm) PS-top CaRI film at a cooling rate of 10 K/min for different annealing times at 433 K with and without room air plasma treatment of the PS surface prior to infiltration. Error bars of PS(8K) samples represent average standard deviation of more than three samples. Error bars of PS(2M) samples represent 95% confidence level of linear fit.
PS, which indicates that the range of dynamical heterogeneity of PS inside the NP packings is similar to the bulk within our ability to resolve.

Figure 2.16: (a) The slope of refractive index change ($dn/dT$) of bulk PS(8K) and PS in PS (8K)/SiO$_2$ films of different NP sizes. Dashed lines show linear fit of the regions before, during and after glass transition. (b) Calculated $T_+$ (black) and $T_-$ (red) values for PS(8K) NP-top CaRI samples with various NP diameters and selected UCaRI PS(8K)/SiO$_2$(25nm) samples. Dashed lines show the corresponding values of bulk PS. There is no significant change in the width of the glass transition width in the confined state and both $T_+$ and $T_-$ shift with a similar relative value inside the NP films.

To further confirm whether spatial or interfacial effects are responsible for $T_g$ changes, series of under-saturated (UCaRI), NP-top films (Figure 2.1b) of PS(8K)/SiO$_2$(25 nm) with various PS fill-fractions were studied(55). In this geometry, free surfaces are introduced due to underfilling. Unlike the porous glass systems used in the past(94), underfilling of NP films forces the polymer to be confined to the narrowest regions of the pores due to capillary effects and at the same time have free surfaces. As such one can differentiate the role of interface/free surface vs. confinement on the measured $T_g$(confined). If interfacial effects are dominant one would expect the $T_g$(confined) to decrease. In contrast, because of the dewetting on SiO$_2$ surface, PS is expected to form capillary bridges and occupy more constricting regions in the interstices of the NPs, further spatially confining the chains, resulting in increased $T_g$(confined).
is because, while the PS chains can eventually fill all the pores of 100 nm NPs with enough material, they fill the smaller pores (i.e., the regions of higher curvature) first and form capillary bridges between SiO$_2$ NPs(55). The inset of Figure 2.17 shows an SEM images of the capillary bridges formed for a PS(8K)/SiO$_2$(100 nm) NP-top UCaRI film with $\sim$ 50% PS fill-fraction. Here, the fill-fraction is defined as the ratio of PS content compared to the PS content of the fully-filled CaRI films. Thus 100% fill-fraction is analogous to 37% total PS volume in the NP film. Larger SEM images of both CaRI and UCaRI films can be viewed in Figure 2.18. Figure 2.17 shows $T_g$ values of UCaRI films with various fill-fractions. As the fill-fraction is decreased, $T_g$(confined) further increases. This observation indicates that the stronger geometric confinement has much stronger effect than the increased free surface in changing the $T_g$ values in CaRI films. The $T_+$ and $T_-$ values for UCaRI samples of two UCaRI samples are also shown in Figure 2.16. It is observed that both $T_+$ and $T_-$ shift uniformly with decreasing PS fill-fraction within error and the width of the transition remains constant, consistent with the negligible effect of free surfaces, which would have broadened the width of the transition(48; 66).

Geometric confinement is thus the most likely explanation for the dramatically increased $T_g$(confined) values. Considering the configurational entropy theory of glass transition(44; 29), $T_g$ should increase when the material is confined in small pores, as the confinement decreases the configurational entropy(2). Previous simulations(54; 15; 106; 123; 107; 108) have shown that hard walls can slow the dynamics close to interfaces thus increasing the local $T_g$. Geometric curvature of the hard wall was also considered as an important factor that can significantly increase the $T_g$(23) and even induce ordering of bonds and affect the glassy structure near the substrate. (127; 11). However, it is worth noting that in previous studies of
Figure 2.17: $T_g$(confined) at a cooling rate of 10 K/min vs. fill-fraction for PS(8K)/SiO$_2$(25 nm), NP-top UCaRI films with $\sim$ 200 nm thickness. The fill-fraction is defined as the ratio of PS volume in UCaRI vs. the PS volume in fully-filled CaRI NP films. Error bars represent average ±1 standard deviation of linear fits for three separate cooling ramps. The insets show the schematic of the UCaRI sample and the SEM image of a capillary bridge observed in a PS(8K)/SiO$_2$(100nm) NP-top UCaRI film ($\sim$ 50% PS fill-fraction). Scale-bar is 100 nm.

Figure 2.18: SEM images of (a) UCaRI film ($\sim$ 50% PS fill fraction) and (b) CaRI film of PS (8K)/SiO$_2$(100nm) CaRI films. The amount of PS was controlled by changing the rate of spin-coating.
the thermal glass transition of molecules confined in controlled pore glass (CPG) or AAO templates by differential scanning calorimetry (DSC), decreasing $T_g$ with decreasing pore size was observed (2; 61; 133; 3; 87). Some studies also observed two $T_g$s, one below the bulk $T_g$ (due to the "size effect") and the other above the bulk $T_g$ value (80; 78; 94), where the higher $T_g$ was attributed to the adsorbed layer on the surface of the pores. In these studies, there is very weak pore size-dependence on the higher $T_g$ value (94), which is qualitatively different from the data reported here. We note that these DSC measurements were performed upon heating. The out of equilibrium glass can show lower $T_g$ due to stress induced by thermal expansion mismatch (98) and potentially reduced density, which could result in reduction and broadening of the $T_g$ transition (83). In the current study, we measure the glass transition upon cooling from the equilibrium state and thus thermal expansion mismatch does not affect the results as the polymer can move out of the NP film as observed in Figure 2.8. We have also ruled out the $T_g$ broadening as shown in Figure 2.16. As such, the strong increase in $T_g$ under isobaric conditions can be attributed to the entropic confinement effects. Since the glass transition is primarily due to the arrest of segmental dynamics in polymers, the significant increase in $T_g$ transition indicates significantly slower segmental dynamics in these systems, which is consistent with our previous measurements of increased viscosity in unentangled polymers in CaRI (57). Future studies that directly measure the relaxation dynamics in these systems can elucidate the exact nature of the confinement effects in these systems.

2.4.4. Glass transition of Poly(2-vinylpyridine) (P2VP) in CaRI films: the effect of interfacial interactions

After we have elucidated the effect of spacial confinement on the $T_g$ of polymers, we can study how the interfacial interactions matters in CaRI films. Poly(2-vinylpyridine) (P2VP) is a polymer with similar structure as PS. In P2VP, just one
C is replaced by N in each monomer, which enables hydrogen bonding with the hydroxyl groups on the surface of SiO\textsubscript{2} NPs. With the same molecular weight, bulk P2VP and PS have almost the same \( T_g \) and glass transition width. Hence, it is a perfect candidate to study the effect of interfacial interactions with good control of other factors. P2VP(\( M_w = 8000 \) g/mol, PDI = 1.6) is used to study the effect of interfacial interactions here to compare with the PS(8K) described previously.

Figure 2.19a shows the \( T_g \) values of P2VP(8K) and P2(8K) confined in CaRI films with different NP sizes. While P2VP shows similar glass transition behaviors as PS in large NP packings (100 nm), the \( T_g \) further increases a lot when the NP sizes are smaller, up to 93 K in 11 nm NP packings, which is 42 K more increase than PS in the same condition.

To check the origin of the further-increased \( T_g \) for P2VP, we plot the \( T_+ \) and \( T_- \) values in Figure 2.19b. We can see that \( T_+ \) have much larger increase than \( T_- \) for P2VP in CaRI films, which indicates that the segmental dynamics at the interface is further suppressed because of the hydrogen bonding between P2VP and SiO\textsubscript{2} while the molecules at the center of the pores are not influenced as much. The gradient in segmental dynamics is larger under stronger confinement.

2.5. Conclusion

In summary, polymers confined in NP packings using Capillary Rise Infiltration (CaRI) are great model systems to systematically study the role of confinement effects vs. interfacial effects on the glass transition temperature values measured upon cooling under isobaric conditions. In this study, we demonstrated significantly increased \( T_g \) values of PS in densely-packed SiO\textsubscript{2} NP films, with weak interfacial interactions. \( T_g(\text{confined}) \) of PS increases with decreasing pore size (increasing confinement), as well as by under-filling the polymer in UCaRI films. In this weakly interacting system,
Figure 2.19: (a) $T_g$ and (b) $T_\pm$ v.s. NP size for P2VP and PS in CaRI films. The dashed lines mark the bulk values. The top sketches show the interfacial interactions between PS/P2VP and SiO$_2$ NPs and the effect on the gradient of segmental dynamics. Darker color indicates slower dynamics of polymers in the pores.

Extreme geometric confinement presents a larger effect on the segmental relaxation dynamics and therefore $T_g$ than the free surface effects that can act to reduce $T_g$. The dramatic increase in $T_g$ has potential impact in applications where nanocomposites are used at elevated temperatures, but a glassy behavior is required.
3.1. Abstract

Extreme nanoconfinement has been shown to significantly affect properties of materials. Here we demonstrate that extreme nanoconfinement can significantly improve thermal stability of polystyrene (PS) and reduce its flammability. Capillary Rise Infiltration (CaRI) is used to infiltrate PS into films of randomly-packed silica nanoparticles (NPs) to produce highly confined states. We demonstrate that as the NP size is decreased, increasing the degree of confinement, the isothermal degradation time is dramatically increased, by up to a factor of 30 at 543 K for PS confined in ~3 nm pores. The activation energy of PS degradation is also increased, by 50 kJ/mol in the most confined state (~3 nm pores). We demonstrate that the degradation proceeds through the film surface and from the center of large holes towards NP surfaces, an indirect evidence that the process is diffusion limited. The surface-driven process dramatically reduces char formation even in large NP packings that show no significant changes in their dynamics and glass transition temperature ($T_g$) compared to the bulk.

3.2. Introduction

Material properties deviate from bulk significantly when confined at nanometer length scale. For polymeric materials, the reduction in the size and interfacial effects such as enhanced free surface dynamics (31; 35) can significantly modify the physical aging rate (59; 96; 97; 7; 99), viscosity (17; 57; 56) and the glass transition temperature ($T_g$) (39; 65; 11; 31; 103; 48; 125). Confinement and interfacial
effects can also significantly influence chemical reactions at nanometer length scale. (138; 75; 139; 12; 80; 140; 141; 120). Unlike polymerization reactions, which have been extensively studied in confinement, little attention has been paid to polymer degradation reactions under extreme nanoconfinement. Understanding degradation under nanoconfinement is important for various applications, such as designing thermally- and photo-stable coatings and organic electronics. Changing reaction pathways can also modify the reaction products and change the flammability of the confined polymer.

Degradation of polymers, in particular polystyrene (PS) in polymer nanocomposites (PNCs), can provide some insight into the degradation under confinement. PNCs made with PS and clay show enhanced thermal stability at low nanoparticle (NP) loadings (between 0.75% to 18%) (25; 13; 18; 122; 74; 6). The enhanced stability is believed to be due to the decrease in chain mobility and char promotion of clay, which acts as mass transport barriers for the volatile products. (25) The existence of an optimal loading is because of NP aggregation at high loadings that changes the structure from nanocomposite to microcomposite. The enhancement of thermal stability of PS/SiO$_2$ nanocomposites is less significant, probably due to SiO$_2$’s lack of catalytic ability as char promoter. (13; 122) In general, PNCs made by conventional mixing methods have low loadings and poor control of NP dispersion.

Highly confined polymers with exceptionally high NP loadings can be achieved by capillary rise infiltration (CaRI)(60). In CaRI, polymers are infiltrated into the pores of a film of randomly-packed NPs by annealing the system above the polymers’ $T_g$. Due to the ultra-high loading ($\sim$ 63% volume fraction for randomly-packed NPs), uniform dispersion of NPs, and the rigidity of the NP film, CaRI is a good model system to study the effect of extreme nanoconfinement on polymer properties. We have
recently demonstrated that in CaRI, viscosity(57; 56) and $T_g$(125) are dramatically increased.

In this study, CaRI films made with unentangled PS and SiO$_2$ NPs are used to investigate the thermal degradation of highly confined polymers in ambient conditions. We demonstrate that the thermal degradation is significantly suppressed and the activation energy for degradation is increased with decreasing pore size. The effect strongly correlates with the increased $T_g$, which is correlated with the loss of degrees of freedom of the segmental motion, and is thus entropic in origin.(125)

3.3. Materials and methods

3.3.1. Preparation of PS/SiO$_2$ CaRI films

One sided-polished silicon wafers (100) purchased from Virginia Semiconductor were cut to approximately by 1 cm $\times$ 1 cm squares. Polystyrene (PS, $M_n = 8000$ g/mol, PDI = 1.10 (PS(8K)), $M_n = 345.5$ kg/mol, PDI = 1.07 (PS(345K)) Polymer Source, Inc.) solutions were prepared by dissolving PS in toluene. SiO$_2$(25 nm) NPs were purchased dispersed in water (Ludox TM-50, Sigma Aldrich). SiO$_2$(11 nm) and SiO$_2$(100 nm) NPs were purchased dispersed in isopropanol (IPA) (Nissan Chemical). The suspensions were further diluted with their respective solvents. No other treatment was applied to the NPs. All solutions were filtered with a 0.45$\mu$m PTFE syringe filter (Fisher brand) and settled overnight before spin-coating.

To generate the nanoporous CaRI films, a NP layer was first spin-coated (Laurell, WS-400BZ-6NPP/Lite spin-coater) onto the silicon wafer. The NP film was annealed at 773 K for 30 min to remove the solvent and stabilize the film. The PS layer was then spin-coated from a toluene solution onto the NP layer to form a bilayer film. The bilayer films were then annealed in ambient condition at 423 K to induce PS infiltration and homogeneous distribution throughout the voids of the SiO$_2$ NP
packings. By controlling the concentration and spin-coating rate, fully-filled CaRI films with a thin residual PS layer (< 50 nm) after infiltration were prepared. CaRI films were made with 11 nm, 25 nm, and 100 nm diameter SiO$_2$ NPs.

3.3.2. Ellipsometry measurements of thermal degradation of CaRI films

The thickness, refractive index and the index variations in CaRI films were measured using spectroscopic ellipsometry (SE, M-2000V, J.A. Woollam) with high-accuracy zone averaging. Samples were mounted onto a temperature-controlled stage (Linkam THMS 600) that was attached to the ellipsometer. The ellipsometry sampling rate were set according to the degradation rate of each sample. To fit the raw SE data of $\Psi(\lambda)$ and $\Delta(\lambda)$ data, a four-layer stack was considered, PS, NP, and a 1 nm native oxide layer on a silicon substrate. A transparent Cauchy model ($n(\lambda) = A + B/\lambda^2$, $k(\lambda) = 0$, where $n$ and $k$ are the real and imaginary parts of the index of refraction) was used for fitting the optical properties of either the NP and PS layers before degradation. Optical constants of the Si substrate and the native oxide layer were obtained from a previous publication(53). During the degradation, for each stage, different models were used to fit the index of refraction of the NP layer to ensure that all the key parameters were included without over-fitting of the insensitive variables. The procedure of fitting is described below.

3.3.3. Thermogravimetric analysis (TGA) of bulk PS

The degradation of bulk PS was measured with TGA (TA instruments, SDT-Q600 Simultaneous DSC/TGA). ~3 mg of PS was put in a standard Aluminum pan. The temperature was raised to 543 K at 20 K/min and then held at constant for 120 min. The measurement was performed in room air with the flow rate of 100 mL/min.
3.3.4. Scanning electronic spectroscopy (SEM) and X-ray photoelectron spectroscopy (XPS) characterization of CaRI films

Scanning electron microscopy (SEM) images were taken using a FEI-600 Quanta ESEM to observe the morphology of the half-degraded CaRI samples. Before imaging, each sample was coated with a 4 nm iridium layer to prevent charging using a sputter coater (Q150T S/E/ES, Quorum Technologies). The SEM images were captured at an accelerating voltage of 30 kV, spot size of 3.0 and working distance around 10 mm.

X-ray photoelectron spectroscopy (XPS) (Physical Electronics VersaProbe 5000 spectrometer) with a microfocused monochromatic scanned X-ray beam equipped with an Al Kα X-ray source (1486 eV photons), was used to quantify elements of the spin-coated bare silica nanoparticles layer and the CaRI thin-film after degradation. The spot size was 100 µm at 25 W and 15 kV.

3.4. Results and discussion

3.4.1. Isothermal degradation of confined PS in CaRI films

Figure 3.1 schematically shows the steps used for the preparation of PS(8 kg/mol)/SiO₂ CaRI samples and the measurements of the thermal degradation. Spectroscopic Ellipsometry (SE) was used to determine the thickness and indices of refraction of each of the NP and PS layers. Due to its rigid structure, the thickness of the NP layer does not change as the degradation proceeds.(125) As such, the degree of PS degradation inside the NP layer was evaluated based on the layer’s index of refraction, which has a linear relationship with the volume fraction of PS(55). To ensure that the NP layer was fully filled before the beginning of the experiments, an excess amount of PS was used, which resulted in a pure top PS layer, with a thickness less than 30 nm,. The degradation of the top PS layer was monitored by changes in its thickness.
Figure 3.1: Schematic representation of the sample preparation and isothermal degradation measurements of PS/SiO$_2$ CaRI samples.

Figure 3.2 shows a typical measurement of the isothermal degradation of a PS(8K)/SiO$_2$(100nm) CaRI sample at 543 K. Here 8K is the molecular weight of PS in kg/mol, and 100nm is the diameter of the NP particles used. The plots show the degradation of the top PS layer (blue), which precedes the degradation of the confined PS inside the NP layer (black). Before the top PS layer is fully degraded ($h_{PS} = 0$ nm set as $t = 0$ s), the index of refraction of the NP layer stays constant, indicating that the confined PS is not degrading during this stage. The confined PS only begins to degrade after the full degradation of the top layer. Another interesting feature of this data is the observation of inhomogeneous degradation once the degradation of the confined PS begins (inset of Figure 3.2). Using a model with linearly graded index of refraction for $n_{NP}$, we can see that the index inhomogeneity initially grows sharply and then decreases as the degradation proceeds. The inhomogeneity is negative, meaning that the index of refraction is lower near the free surface of the NP film. The delayed and inhomogeneous degradation is observed in all CaRI films with various NP diameters ($11$ nm < $D$ < 100 nm). Significantly, the rate of degradation is slower as the NP size is decreased, indicating enhanced thermal stability for PS.
confined in smaller pores.

3.4.2. Modeling the isothermal degradation process with ellipsometry

During isothermal measurements, before the full degradation of the top PS layer, properties of both PS and NP layers were fit to the SE angles at each measurement time, while keeping the optical properties of the Si substrate with 1 nm native oxide constant. Due to the small pathway of light, the SE angles become insensitive to the value of the index of refraction when the thickness of a film (the PS layer here) is smaller than $\sim 10$ nm. As such the index value for the top PS layer was fixed as the initial fit value measured when the temperature first reached the target value of the isothermal degradation. This helps avoid over-fitting at subsequent time points. For this layer, only the thickness was fit during the isothermal degradation. The lower limit of the thickness of the PS layer was set as 0 nm to ensure physical fits during the degradation. We have previously also demonstrated that the thickness of the NP layer does not change due to its rigidity(125). As such, the thickness of the top PS layer and the index of refraction of the NP layer were the only fitted variables during the isothermal degradation studies. Remarkably, we observed that the index of refraction of the NP layer also stays constant and uniform before the full degradation of the top PS layer. Thus, a simple Cauchy fit was adequate to the NP layer index of refraction up to this point.

Time $t = 0$ sec is defined as the time at which the thickness of the top PS layer became equal to zero ($h_{PS=0}$ nm), which signifies the full degradation of the top PS layer and the start of the degradation of the confined polymer in the NP layer Figure 3.2. For each CaRI film, the thickness of the NP layer was measured at this point by fitting with a one-layer model (i.e. one Cauchy layer on Si substrate with 1 nm native oxide). Figure 2 in the main paper shows the typical fitting results for both the top
Figure 3.2: (a) The index of refraction of the NP layer ($n_{NP}$, black, left axis) and the thickness of the top PS layer ($h_{PS}$, blue, right axis) of a PS(8K)/SiO$_2$ (100nm) film during isothermal degradation at 543 K. The degradation of PS inside the NP layer (confined PS) begins once the top PS layer is completely degraded ($h_{PS} = 0$, set as time $t = 0$ s). The red curve is an empirical stretched exponential decay fit to the data. The initial thickness of the PS and NP layers were $\sim 15$ nm and $\sim 200$ nm, respectively. The thickness of the NP layer was held constant. (b) The %inhomogeneity of the index of refraction of the NP layer during degradation.
Figure 3.3: (a) The average index of refraction and (b) %inhomogeneity during isothermal degradation at 543 K. The blue curves are fit to a stretched exponential decay function.

PS layer degradation and the confined layer degradation, as measured by changes of the index of refraction.

However, unlike the isothermal degradation of bulk PS, which follows a simple exponential decay function as measured by thermogravitometric analysis (TGA), the degradation of PS in CaRI films follows an apparent stretched exponential decay as shown in Figure 3.3a. The change of the inhomogeneity during the degradation indicates a faster degradation rate of PS close to the free surface compared to the substrate region at the beginning of degradation, potentially explaining the apparent stretched exponential decay. (Figure 3.3b) As such, this simple decay model is not entirely accurate in representing the degradation data and a more sophisticated analysis of the data is needed.

Due to the complex pattern of degradation, various models were used to fit the index of refraction of the NP layer at times $t > 0$ sec. Figure 3.4 summarizes the details of these models. Based on Figure 3.4a, a model with a uniform NP layer does not fit the raw data well (large value of the mean square error, MSE). As such a gradient of
the index of refraction must be introduced. A model with simple linear gradient was first assumed (Figure 3.4b). This significantly reduced the MSE values of the fitting. The negative %Inhomogeneity indicates that the index of refraction on the top of the film is lower than the value at the bottom. Because of the linear relationship between the volume fraction of PS in CaRI and the index of refraction, the gradient the index of refraction represents the distribution of PS during the degradation. Although the model with simple linear gradient could fit the data better, there was still room to further reduce the MSE. This was achieved by assuming a function to describe the profile of the index of refraction through the film. Two more models were assumed for these samples: a two-segment model and an exponential profile model. The two-segment model (Figure 3.4c) assumes two linear sections with different gradients. The exponential model (Figure 3.4d) assumes that the index of refraction follows an exponential function where \( A \propto [\text{Pos}]^{[\text{Exponent}]} \times \frac{[\%\text{Grade}]}{100} \), where [Pos] is the position within the film as shown in Figure 3.4e, \( 0 \leq [\text{Pos}] \leq 1 \), and [Pos] = 0 signifies the silicon substrate. Both of these two models further reduce the MSE to significantly lower values. We note that the MSE of these two models are quite similar, which indicates that the SE cannot distinguish between them. Figure 3.4e shows the profiles of index of refraction predicted by the two models. Both models show an index gradient close to the NP layer surface and a uniform bottom layer. By plotting the profiles using either 100 or 1000 number of slices within the film we observe that it is adequate to use 100 slices to estimate the profile. Considering the spherical shape of the NPs and the fitting efficiency, we chose the exponentially graded model with 100 slices for the fitting during the degradation at this stage. We note however that either of these four models yield similar conclusions in the observed behavior of the confined PS.
Figure 3.4: Typical fitting results using different models during the degradation of confined PS in CaRI film made with 25 nm NPs held isothermally at 543 K. The models are (a) uniform layer, (b) linearly graded model, (c) two-segment model and (d) exponentially graded model. (e) The profiles of the index of refraction from two-segment and exponential models with different number of slices.
Figure 3.5: Profiles of the index of refraction obtained from exponential model during isothermal degradation at 543 K for CaRI films made with (a) 11 nm (b) 25 nm and (c) 100 nm NPs.

Figure 3.5 shows how the profiles of index of refraction change during the isothermal degradation. Although the model with linear gradient is not the best one to describe the film, its high efficiency and qualitative accuracy enable the analysis of the overall properties. Figure 3.3 shows the change of the average index of refraction and %inhomogeneity of CaRI films with various NP sizes during isothermal degradation at 543 K. The blue curves are stretched exponential fit to the data. The rise and fall of the inhomogeneity in this simple fit correlates with the strong changes in the gradients of index observed with exponential fits shown in Figure 3.5. However we note that the stretched exponential includes both the surface and bulk degradation modes and as such overestimates the degradation rates inside these films.

3.4.3. A two step process for thermal degradation

To gain more insight into the degradation mechanism and kinetics, the SE data at each time point was fit to a model with an exponentially-graded index of refraction for the NP film described above. This model presents a more accurate fit to the experimental data with large inhomogeneity compared to the linearly graded model used in Figure 3.2. Figure 3.6a shows typical results of the index of refraction as a function of the distance from the surface, in the NP layer of a PS(8k)/SiO\(_2\)(25nm) sample at different annealing times at 543 K. There are two steps of degradation. In
the first ∼600 sec, the index of refraction at the film’s surface drops rapidly while it remains constant at the film’s center. The film center index value starts to decrease uniformly with a much slower rate after the full degradation of the surface layer, observed as a reduction of the index gradient. The same steps are observed for degradation at various temperatures and for all NPs sizes studied here (Figure 3.5).

3.4.4. The film center degradation process

Focusing first on the film center degradation process, Figure 3.6b shows the mass loss during isothermal degradation of three CaRI samples at 543 K in ambient conditions, along with degradation of bulk PS at the same temperature, measured using thermogravitometric analysis (TGA). Figure 3.7 shows the influence of sample mass on the degradation rate of TGA, indicating that a sample with comparable mass as the CaRI film would degrade even faster. This data is extracted from the index of refraction at the center of the film, i.e. the plateau value of index as shown in Figure 3.6a. The residual mass of both bulk and confined PS can be fitted to a simple exponential decay function \( \frac{m}{m_0} = \exp(-t/\tau) + \frac{m_{\text{inf}}}{m_0} \), where \( m, m_0 \) and \( m_{\text{inf}} \) are the mass of PS during, before, and after degradation, respectively. \( t \) is the annealing time, and \( \tau \) is the characteristic degradation time. Figure 3.6b shows that \( \tau \) is slowed by about a factor of 30 in 11 nm NPs compared to the 100 nm NPs, or the bulk PS at this temperature.

Due to char formation during isothermal degradation of bulk PS in ambient conditions\( (71; 45) \), the final residual mass \( m_{\text{inf}} \) is non-zero for the bulk TGA data. \( m_{\text{inf}} \) is thus assumed to be a fitting parameter and is measured to be ∼8% of the initial mass. Significantly, no charring is observed in degradation of confined PS, even for the large NP sizes (more detailed discussions in later section). As such, \( m_{\text{inf}} \) is set to zero for the confined PS measurements. SEM imaging of CaRI films

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Figure 3.6: (a) Index of refraction as a function of distance from the substrate of the NP layer for a PS(8K)/SiO\(_2\) (25nm) CaRI film at various times during isothermal degradation at 543 K in ambient condition. The NP layer thickness was \(\sim 190\) nm. Time \(t = 0\) s is defined as when the top PS layer is fully degraded as shown in Figure 3.2. (b) Mass loss of PS(8K)/SiO\(_2\) CaRI films of various NP sizes during isothermal degradation at 543 K. The gray hollow symbols show isothermal degradation of bulk PS(8K) measured by TGA. The curves show a simple exponential decay fit to the data with the corresponding color. The initial mass of the the bulk (TGA) and confined (CaRI) PS are \(\sim 2\) mg and \(\sim 0.01\) mg, respectively.
Figure 3.7: Isothermal degradation of bulk PS(8K) at 543 K with different initial mass values measured using TGA.

(Figure 3.8) also does not show any evidence of charring. The absence of char, along with improved thermal stability is in contrast to the previous observations in PS-Clay nanocomposites, where the char formation was considered the main mechanism for improved thermal stability. (71; 45)

Isothermal degradation measurements were performed at various temperatures on CaRI films with various NP layer thicknesses (120-500 nm). Figure 3.9a shows a plot of the characteristic time for degradation of confined PS, log(τ), as a function of 1/T for NPs of various diameters. Despite the variations in film thickness values, as long as a bulk-like layer is observed in the film, the degradation rate appears to follow an Arrhenius equation in the temperature range of our measurements. The activation energies for the degradation for the NP film center were measured based on the slopes of the Arrhenius lines to be 102 ± 13 kJ/mol, 129 ± 5 kJ/mol, and 157 ± 16 kJ/mol for PS confined in 100 nm, 25 nm, and 11 nm NPs, respectively (Figure 3.9c).
measurements show that under extreme nanoconfinement conditions, the barrier for thermal degradation of the confined PS is significantly higher than the corresponding barrier for PS confined in larger NPs, as well as bulk PS, reported to be $\sim 125$ kJ/mol ($M_w = 280$ kg/mol)(95).

Polystyrene degrades through free radical diffusion and chain scission.(25) In the presence of $O_2$ in ambient conditions, the formation of highly active peroxy radicals significantly accelerates the degradation, making PS a highly flammable material.(124) Since the rate limiting step of the thermo-oxidative degradation of PS is the bimolecular decomposition of the peroxides,(95) the slower dynamics of the confined PS can decrease the rate of this reaction. Reduced diffusion of both oxygen and the free radicals under confinement increases the thermal stability and reduces the flammability.

According to our previous studies, the segmental dynamics is suppressed and the viscosity is increased with increased degree of confinement(57; 125; 56), consistent with the observation of slower degradation and higher barrier to degradation in this study. Longer lifetime of radicals and reduced termination rate during free-radical polymer-
Figure 3.9: (a) Characteristic time for the isothermal degradation in the film center \((\log \tau)\) vs. \(1/T\) of PS(8K) and in CaRI films with three different NP sizes. (b) The time to reach maximum inhomogeneity during isothermal degradation \((\log t)\) vs. \(1/T\), of the same CaRI films. The lines show linear fit to each data set in a and b. (c) Activation energy of the film center and surface degradation vs. \(T_g\) of PS in CaRI films.

Oxidation in controlled pore glass was also observed in previous studies, consistent with our observations.\(^{120; 90; 139}\)

We have previously shown that undersaturated CaRI (UCaRI) films can be made with insufficient amount of top PS. In UCaRI the \(T_g\) further increases due to the stronger confinement.\(^{125; 55}\) Figure 3.10 shows the characteristic degradation time at 573 K in UCaRI films with 11 nm NPs and different initial PS fill fractions. Indeed the thermal stability is further enhanced under stronger confinement in UCaRI films, further indicating the important role of the slow-down of oxygen and free radical diffusion in this enhancement of thermal stability.

3.4.5. \textit{The surface degradation of confined PS}

In order to evaluate the thickness and the degradation rate of the surface layer, index of refraction profiles were measured on various NP sizes and film thicknesses. Figure
Figure 3.10: (a) Isothermal degradation curves of PS(8K)/SiO$_2$(11nm) UCaRI measured at 573 K. (b) Characteristic degradation time at 573 K log $\tau$ vs. initial index of refraction of the NP layer (% filling of PS) for UCaRI films made with 11 nm NPs.

3.11a shows the profiles of the index of refraction, at the time point where the index of refraction shows the strongest inhomogeneity. The data shows that for each particle diameter, the thickness of the surface layer, where the rate of degradation is faster than bulk, roughly corresponds to one NP diameter. This is independent of the total thickness of the NP layer, as shown in Figure 3.12. The faster rate of surface degradation is likely due to imperfections at the free surface of the CaRI film as well as more oxygen availability compared to the film center. As the NP diameter is decreased, the thickness of the surface layer also decreases and its degradation slows, resulting to exceedingly more stability in the layer as a whole, because the film center degradation does not start until the surface layer is degraded (Figure 3.6).

Figure 3.9b shows the plot of the surface degradation time, the time to reach maximum inhomogeneity (inset of figure 3.2), vs. 1/T. Unlike the film center mass loss, where the degradation is independent of the NP layer thickness, the surface degradation appears to be a layer-by-layer material loss process. Thus, the total degradation time for the 100 nm NPs can be longer than that of 25 nm NPs at some temperatures,
Figure 3.11: (a) Profile of the index of refraction at the same stage after the beginning of the film center degradation of CaRI samples with different NP sizes and film thicknesses. The scale bars represent the diameter of the NPs. The degradation temperature is 543 K. (b) Proposed mechanisms of thermal degradation in CaRI films. The hollow arrows shows the zoomed-in version of the schematics.

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while the activation energy remains lower.

Figure 3.9c shows the activation energy for the degradation of the confined PS in the film center as well as the surface vs. $T_g$ (125). It is remarkable that both the surface and film center degradation rates correlate well with the $T_g$ increase, with reasonably similar activation energies at smaller particle sizes, indicating that both processes are slowed due to the slow-down of the kinetics of the confined PS itself. The slower characteristic time of degradation in the NP film center compared to the surface likely stems from slower oxygen diffusion towards the center of the film as well as the slower diffusion of the products. Combined, this data indicates that the degradation process in these highly confined systems is diffusion-limited and proceeds through free surfaces.
3.4.6. **Diffusion-limited degradation in extreme confinement**

Based on the data shown in Figure 3.9 we propose a two-step diffusion-limited degradation in CaRI films, schematically sketched in Figure 3.11b. After the full degradation of the top PS layer, i.e. the beginning of the degradation of confined PS, the PS at the surface layer of NPs, which has better access to oxygen degrades first. The products of the reaction for this layer can readily diffuse out of the layer, with a rate that is dependent on the viscosity of the layer and thus correlates with the $T_g$.

After the removal of the first layer, the film essentially becomes an under-filled (UCaRI) layer, where there is a gradient of mobility in the dynamics. The material in the center of the larger pores has lower viscosity and higher diffusion, and thus degrades first, while the remaining PS moves towards smaller pores and becomes more confined, as previously reported in UCaRI systems.\(^{(125)}\) In UCaRI films, the spatial confinement has a stronger effect on the dynamics of the confined PS increasing $T_g$, and thus its effective viscosity.\(^{(125)}\) As shown in Figure 3.10, this also results in slower rate of degradation in UCaRI films. As such, it is reasonable to assume that the material in the center of the pores degrades first, slowly removing products as the degradation continues towards the NP surfaces.

To verify this hypothesis, SEM images were obtained of a PS(8K)/SiO\(_2\)(25nm) sample where $\sim 40\%$ of the PS in the film center is degraded. From the cross-section SEM image (Figure 3.8a), it is observed that the sample contains large pores and the PS is uniformly distributed throughout the film, as expected. Moreover, no PS is seen in the first layer from the top-view image, indicating the complete degradation of the surface layer (Figure 3.8b). These observations indicate that even in the film’s center, the degradation is through the free surface and proceeds towards the NP surfaces, meaning that the availability of oxygen and product diffusion are rate-limiting steps.
even in the film center.

The diffusion-limited degradation process, even in relatively large 100 nm NP particles, means that the process is distinctly different than bulk PS degradation, despite the fact that the activation energy of degradation in 100 nm NPs is reasonably similar to that of bulk PS. This difference has important consequences in the molecular weight distribution of the products as well as the flammability of PS in CaRI films. Since diffusion is strongly dependent on the size of the reaction products, it is expected that the smaller products would diffuse out of the film faster, allowing time for the larger products to break apart. As such, we hypothesize that the distribution of the molecular weight in CaRI films will be weighted towards smaller products such as styrene and toluene. This will be explored in our future work.

Remarkably, the cross-linking of the reaction products that results in char formation as well as the auto-acceleration of the degradation reaction and therefore PS flammability, also slows-down in CaRI. This is because the degradation is primarily occurring at the free PS surfaces even in the film center. As such, unlike the bulk PS, the degradation in CaRI proceeds until all the material is removed without leaving any noticeable residual layer or char (Figures 3.13 and Figure 3.14). This suppression of char formation is potentially of interest in developing flame-retardant coatings using flammable polymers, by producing highly confined states.

Figure 3.13b shows the raw SE data for a PS(8K)/SiO$_2$(11nm) sample with 270 nm NP layer thickness measured at 573 K after isothermal degradation at 573K and cleaning at 773 K. The amount of PS in the NP layer is equivalent to a 100 nm film. The difference between the raw data is almost negligible, especially in the low wavelength region where the absorption of light from chars should be significant, and the residual mass of PS calculated from fitted indices of refraction is less than 3%.
The lack of char formation is also supported by x-ray photoelectron spectroscopy (XPS). Figure 3.14 shows the XPS measurements of a PS(345K)/SiO₂ sample after isothermal degradation at 593 K in ambient condition and a pure SiO₂ NP film after annealing at 773 K. The Carbon contents are 12.99% and 15.81%, respectively. The Carbon likely originates from the stabilizer in the NP solution that appears in both samples. The lower Carbon content after degradation of PS indicates complete degradation under nanoconfinement. In contrast, as shown in Figure 3.13a and inset of Figure 3.14, if a pure film of PS is produced with similar amounts of PS, as the CaRI films studied here, char is easily observed, indicating that if chars were present we would have been able to observe and measure them. This is also supported by electron exposure with SEM. (Figure 3.15)

These observations are in sharp contrast with the degradation of PS in the PNC systems reported previously, where the thermal stability of PS/SiO₂ nanocomposites is not as significant as PS/clay nanocomposites. In our study, the degradation rate at 573 K of PS in 11 nm NP packings is significantly slower than the rate at 543 K in 100 nm NPs or bulk PS. To our knowledge, this is the highest reported degree of improvement of the thermal stability of PS/SiO₂ composite systems. In CaRI systems without significant interaction between the NPs and PS, we have previously demonstrated that entropic effects result in increase viscosity(56; 57) and T_g,(125) which are in turn promoting enhanced thermal stability here. The enhanced thermal stability is also observed for PS well above entanglement molecular weight (Figure 3.16). It remains to be explored how NP/polymer interactions and molecular weight in extreme confinement would affect these observations.

Different polymers have different tendency of char formation (carbonization) during thermal degradation. In addition to the slowed diffusion in CaRI films, the limited
Figure 3.13: (a) Microscopic image of dewetting and charring of a 66 nm PS(8K) film after isothermal degradation at 573 K. (b) Image of a PS(8K)/SiO$_2$(100nm) sample after isothermal degradation at 573 K. (c) Raw ellipsometry data of a PS(8K)/SiO$_2$(100nm) sample with 350 nm NP layer thickness measured at 573 K after isothermal degradation at 573 K and cleaning at 773 K. (d) Raw ellipsometry data of a PS(8K)/SiO$_2$(11nm) sample with 270 nm NP layer thickness. The initial amount of PS in the NP layers of the films in c and d are equivalent to a 130 nm and 100 nm pure PS film, respectively.
Figure 3.14: (a) X-ray photoelectron spectroscopy for a PS(345k)/SiO$_2$ CaRI sample after degradation at 593 K at ambient condition and a pure SiO$_2$ NP film sample without adding polymer. The lower Carbon content in the post-degraded CaRI film indicates complete degradation of PS under nanoconfinement. (b) Charring of 0.4 mg PS(345K) after isothermal degradation at 593 K with TGA in 100 mL/min air flow.
Figure 3.15: (a) Cross-section SEM image of a PS(8K)/SiO$_2$(11nm) CaRI film before degradation showing full infiltration. (b) Top-view SEM image of the PS(8K)/SiO$_2$(11nm) CaRI film. The darker area are from exposure of electrons, indicating the existence of PS close to the surface. There will be a thin top layer at $\sim$3 nm at the degradation temperature. (c) Cross-section and (d) top-view SEM images of a PS(8K)/SiO$_2$(25nm) CaRI film after degradation. No darker area appeared after the same exposure process in (d).
space in the pores could suppress the carbonization process and the formation of
chars. Because the carbonized products have much higher thermal stability than
the original polymers, polymers with high tendency of carbonization have multi-step
thermal degradation: a fast carbonization step followed with a slower degradation
step of the carbonized products.

Suppression of carbonization can reduce the formation of the highly stable species
and accelerate the thermal degradation. Polyethersulfone (PES) is a example. PES
is a highly rigid polymer and the oxygen atoms in PES can form hydrogen bondings
with SiO₂. Figure 3.17a shows the $T_g$ of thin PES films on SiO₂ substrates. Despite
the hydrogen bonding, the $T_g$ of PES slightly drops when the film thickness is smaller
than 50 nm, highlighting the effect of the free surface. When confined in CaRI
films with SiO₂ NPs, the $T_g$ dramatically increases with decreasing NP size, by up
to 105 K in 11 nm NPs with 30 min sintering of the NP films at 823 K before

Figure 3.16: Isothermal degradation of PS(345K)/SiO₂ CaRI films at 593 K measured
by ellipsometry and in bulk measured by TGA.
infiltration of the polymer. (Figure 3.17b) The hydroxyl groups that are closely in contact on the NP surface can undergo a dehydration condensation reactions forming Si-O-Si bonds between the NPs, which results in stronger confinement especially at the connection parts of the NPs. Figure 3.17c shows the center degradation process during isothermal degradation of PES in CaRI films at ambient condition. Different from what is observed for PS, with decreasing NP sizes, the thermal degradation rate first increased and then decreased. We hypothesize that this is because of the competition of the two factors in CaRI films: the reduced dynamics slow down the degradation while the suppression of the formation of highly stable chars accelerates the degradation.

3.5. Conclusion

In summary, we studied the thermal degradation of PS under extreme nanoconfinement using CaRI as a model system. The degree of confinement is controlled using SiO$_2$ NPs with diameters ranging from 11 nm to 100 nm, resulting in the pore diameters ranging from $\sim$3 nm to $\sim$30 nm. We show that in this weakly-interacting system, strong spatial confinement results in unprecedented enhancement of the thermal stability of PS in ambient conditions. In isothermal degradation experiments both the characteristic time of degradation and the activation energy for degradation increase, with values that correlate with increased $T_g$ in these systems. The details of degradation indicates that the degradation proceeds through surfaces and from the center of larger holes towards NP surfaces, reducing the flammability and the ability of the system to form char. These observations indicate that even in relatively large pores for the 100 nm NPs, the process of degradation is diffusion limited and is stabilized due the slower diffusion of the free radicals, oxygen, and the reaction products.
Figure 3.17: (a) $T_g$ of PES ultra-thin films on SiO$_2$ substrate. (b) $T_g$ of PES in CaRI films with SiO$_2$ NPs. (c) Isothermal degradation of PES in CaRI films showing non-monotonic effect of nanoconfinement.
CHAPTER 4 : EFFECT OF NANOPORE GEOMETRY IN THE
CONFORMATION AND VIBRATIONAL DYNAMICS
OF A HIGHLY-CONFINED MOLECULAR GLASS

4.1. Abstract
The effect of nanoporous confinement on the glass transition temperature ($T_g$) strongly depends on the type of porous media. Here, we study the molecular origins of this effect in a molecular glass, N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD), highly-confined in concave and convex nanoporous geometries. When confined in controlled pore glass (CPG) with convex pores, TPD’s vibrational spectra, measured by Raman spectroscopy, remained unchanged. In these systems, two $T_g$s were observed, consistent with previous studies. In contrast, when confined in densely-packed silica nanoparticles with concave pores, Raman peaks were shifted due to more planar conformations, as predicted by density functional theory (DFT). This confinement in the motion of dihedral angles also resulted in strong $T_g$ increases, indicating significantly slower relaxation dynamics compared to CPG. These effects are stronger as the degree of nanoconfinement is increased. Given that TPD interacts weakly with silica, this effect is entropic in nature. These results indicate that pore geometry is an essential factor in $T_g$ nanoconfinement effects and highlight the role of intramolecular degrees of freedom in the glass transition, which have not been extensively explored.

4.2. Introduction
It has been shown that the physical and chemical properties of soft materials can be significantly modified when confined in nanoporous media. For example, glass transition temperature ($T_g$) of both polymers and small molecules confined in anodic aluminum oxide (AAO)
and controlled pore glass (CPG) deviates significantly from their bulk values. Two $T_g$s are typically measured, one higher than the bulk value and the other lower. In some systems with weak interactions only the lower $T_g$ value is observed, which may depend on the rate of cooling/heating. This phenomenon is usually attributed to interfacial interactions and unknown intrinsic size effects.

Recently, another method called capillary-rise infiltration (CaRI) has been developed to produce extreme nanoconfinement conditions. In this method a polymer is infiltrated into a densely-packed nanoparticle (NP) film. In contrast to AAO or CPG systems, polymers confined in CaRI show both increased viscosity and significantly higher $T_g$ values with decreasing pore size, regardless of the strength of the interfacial interactions. $T_g$ values lower than bulk have not been observed in CaRI films. Given the extremely high $T_g$ values even in the absence of strong interfacial interactions, it is hypothesized that this effect is entropic in origin and is due to the constrained molecular motion.

Given the geometry of CaRI, where a dense packing of spherical NPs are produced, CaRI films have concave curvatures, while CPG and AAO have convex cylindrical pores. Pore geometry thus could play an important role in determining the effect of nanoconfinement on the glassy dynamics. Another example of the potential geometry effects on nanoconfinement is polymerization reactions. Polymerization of methyl methacrylate (MMA) can result in different molecular weights, polydispersities, and tacticities when confined in CPG with weak interfacial interactions, indicating restriction of chain-scale orientation and conformation, while at the monomer scale, there is no evidence of conformational change in CPG with weak interfacial interactions. In addition, thermal degradation of polymers can be significantly suppressed in
CaRI, (126) while the thermal decomposition of some small molecules are accelerated in CPG. (9; 10)

In this study, we focus on the molecular glass system, N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD). We measured $T_g$ and vibrational spectroscopy of TPD confined in both CaRI and CPG systems with various pore sizes. Using Raman spectroscopy and density functional theory (DFT) calculations, we show that CaRI films, with concave pores, can restrict the molecular motion of TPD, specifically the range of the motion of dihedral angles, and reduce its available conformations under extreme nanoconfinement, while no such conformational change is observed in CPG with convex pores. This reduction in conformational degrees of freedom results in large increases in $T_g$ of TPD in CaRI films as the pore size is decreased, while a similar effect is not observed in CPG, where two $T_g$s are observed, one below bulk $T_g$ which decreases with pore size, and a second above bulk $T_g$ which is not sensitive to the pore size. These observations directly connect the molecular degrees of freedom and the resulting loss of configurational entropy to the slow-down of dynamics in CaRI systems. The direct relationship between the configurational entropy of intra-molecular degrees of freedom and $T_g$ dynamics to our knowledge has not been established. Constraining molecular conformation using geometric routes without adding specific intermolecular interactions, e.g. hydrogen bonding, can be a universal design rule for many other nanoconfined glassy systems. (28; 81; 51; 138) This motivates further studies of the behavior of soft materials confined in CaRI system to control macroscopic properties such as optical, thermal, and electronic effects.
4.3. Materials and methods

4.3.1. Preparation and \( T_g \) measurement of TPD CaRI films

N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) was purchased from Sigma-Aldrich and used without further purification. TPD \( T_g \) was measured using spectroscopic ellipsometry (SE, M-2000, J.A. Woollam) to be \( 330 \pm 3 \) K at the cooling rate of 10 K/min.

Single-side-polished silicon wafers (100) (Virginia Semiconductor, 1 cm \( \times \) 1 cm squares) were cleaned with room-air plasma before use. TPD solutions were prepared using toluene. SiO\(_2\) NPs (25 nm) (Ludox TM-50, Sigma Aldrich) were dispersed in water. SiO\(_2\)(11 nm) and SiO\(_2\)(100 nm) NPs (IPA-ST and IPA-ST-ZL, Nissan Chemical) were dispersed in isopropanol (IPA). The suspensions were further diluted with their respective solvents. No further treatment was applied to the NPs. The TPD solutions and NP solutions were filtered with 0.45\( \mu \)m PTFE syringe filters (Fisherbrand) and 0.7\( \mu \)m GMF filters (Thermo scientific), respectively, before spin-coating.

To make the CaRI films, the NP layer was first spin-coated (Laurell, WS-400BZ-6NPP/Lite spin-coater) onto the silicon wafer. The TPD layer was then spin-coated onto the NP layer. The thickness of both layers were controlled with the concentration of solutions (typically 5% - 10%) and the rate of spin-coating (typically 2000 - 6000 rpm). The bilayer films were then annealed in ambient condition at 373 K to induce infiltration of TPD into the NP packings. By controlling the concentration and spin-coating rate, fully-filled CaRI films with a residual TPD layer or slightly undersaturated CaRI films with no top layer after infiltration were prepared. Typical film thicknesses were 200 - 800 nm.

In order to measure the \( T_g \) of TPD in CaRI films, the thickness and refractive index
<table>
<thead>
<tr>
<th>Pore diameter (nm)</th>
<th>7.5</th>
<th>26.7</th>
<th>38.3-102.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volumen (mL/g)</td>
<td>0.49</td>
<td>1.14</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 4.1: Pore volumen of used controlled pore glass

values were measured using spectroscopic ellipsometry (J.A. Woollam, M-2000). The raw ellipsometry data Ψ(λ) and Δ(λ) were fit to a Cauchy model \( n(λ) = A + B/λ^2, k(λ) = 0 \), where \( n \) and \( k \) are the real and imaginary parts of index of refraction.

The optical constants of the Si substrate with native oxide layer were taken from literature(53). In-situ SE with controlled cooling rate (10 K/min) using a Linkam THMS600 stage was performed. Because of the small thermal expansion coefficient of SiO\(_2\) NPs, the thickness of the NP layer was fixed at the initial value. The thickness of the top TPD layer, as well as the Cauchy parameters of both layers, were fitted to study their temperature dependence.

4.3.2. Infiltration of TPD into CPG and DSC \( T_g \) measurements

The \( T_g \) of TPD confined in controlled-pore glass (CPG) was measured by differential scanning calorimetry (DSC, TA instruments, Q2000). The CPG was purchased from Millipore (7.5 nm and 26.7 nm), 3-Prime (38.3 nm and 53.6 nm) and Vitra-Bio (15.4 nm, 72.4 nm and 102.6 nm). The pore size and volume were determined by the vendors (Table 4.1). The mass of each component was measured so that a ∼ 100% filling was achieved. First, powders of TPD crystal and CPG were mixed in DSC pans. Next, samples were annealed at 523 K for 2 h to melt the TPD crystals and induce infiltration of TPD into CPG. The samples were then ramped between 173 K and 523 K at the heating/cooling rate of 10 K/min for 3 cycles. The \( T_g \) was measured during heating. Scanning electronic microscopy (SEM, FEI-600 Quanta ESEM) was used to check the infiltration condition after DSC measurements. The SEM images were captured at an accelerating voltage of 30 kV, spot size of 3.0 and working distance around 10 mm.
4.3.3. Raman Spectroscopy of TPD

The Raman spectroscopy of TPD confined in CaRI and CPG was measured using a JASCO NRS-5500 Raman Spectrometer with a 532 nm laser in confocal mode with 100x objective lens. In order to prevent the influence of the top TPD layer of CaRI films and get enough Raman signals, slightly under-filled CaRI samples (600-800 nm, over 90% filling) with no top layer were made. All samples were measured on Si substrates. The Raman spectrum of Si was collected simultaneously and used to calibrate the TPD spectra. Because TPD can be damaged during long-time laser irradiation, the acquisition parameters were optimized for each sample to get good signal intensity and resolution. Typical parameters used are: L300/B860nm grating, 200×1000μm slit, d-4000μm aperture, 0.4 mW laser power, 5% (OD1.3) attenuator, 1 second acquisition with 10 accumulations.

4.3.4. DFT calculation of TPD conformation change

In order to understand the conformational changes that cause the shift in Raman peaks of TPD, density functional theory (DFT) calculations were performed using Gaussian 16 program with B3LYP functional and 6-31g(d) basis set. (41) Raman spectroscopy was calculated with the assignment of vibrational modes.

4.3.5. Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) was performed in order to check the influence of molecular conformation on the packing of TPD molecules. Due to the small amount of materials on a typical CaRI film, we cannot get enough signal from the thin films. Thus, the CaRI samples for WAXS measurements were prepared with a similar method as the TPD-CPG samples. The solvent of the NP solution was first evaporated slowly to generate NP xerogels, which should have similar packing as the spin-coated thin NP films. TPD crystals were first melted at 473 K in vacuum and cooled down naturally to create liquid-quenched glass. The SiO₂ NP xerogels and
pre-melted TPD glass were ground to micron-size powders to enhance the thermal infiltration. The mass of TPD and NPs were measured so that an overall of $\sim 150\%$ filling was achieved because of the slow and nonuniform infiltration when the NP packing is large.

Before WAXS measurement, the samples were packed into a Kapton cell. WAXS data was collected with Xeuss 2.0 X-ray Scattering Machine from Xenocs using a copper source in transmission mode. An empty Kapton cell was measured with the same amount of acquisition time and used as a background. The Kapton background was already subtracted from the raw data for all of the WAXS data shown in the following sections.

4.4. Result and discussion

4.4.1. Glass transition of TPD confined in pores with different geometries

TPD-CaRI films were prepared as schematically shown in Figure 4.1a. The typical initial thicknesses of the NP and TPD layers were about 200-400 nm and 100 nm, respectively. In CaRI films, the NP layer is a random close packing of NPs and as such has an average pore diameter of $\sim 0.3$ times the NP diameter.(14; 125; 55; 57; 56) Thus, by varying the NPs diameter (11 - 100 nm in this study), the degree of TPD confinement can be varied to an extreme extent (3 - 30 nm average pore diameter).

The $T_g$ of CaRI films were determined using in-situ spectroscopic ellipsometry (SE, Woollam M-2000V) with an attached Linkam THMS600 temperature stage. $T_g$s were measured upon cooling at a rate of 10 K/min. Indices of refraction of each layer, which is related to the material density, were used to monitor the glass transition. Figure 4.1c shows a typical measurement of $T_g$ of a TPD/SiO$_2$(25nm) CaRI sample with a top TPD layer. By linearly fitting the supercooled liquid (SCL) and the glass regions of each curve, the $T_g$s of TPD in bulk ($330 \pm 3$ K) and confined ($355 \pm 3$ K) states
could be determined. Similar $T_g$ values are obtained for CaRI samples if measurements were performed during heating, immediately after a cooling cycle (Figure 4.2). Figure 4.1d shows the $T_g$ values of TPD confined in CaRI films with various NP sizes. It is observed that $T_g$ is close to bulk values in TPD/SiO$_2$(100nm) films (30 nm pores), but dramatically increases with decreasing NP/pore size, up to 30 K in TPD/SiO$_2$(11nm) films (3 nm pores). Since TPD has weak interfacial interactions with SiO$_2$ and ultrathin TPD films on SiO$_2$ substrates show decreased $T_g$ with decreasing film thickness due to the enhanced mobility of the free surface(137; 135). The significantly increased $T_g$ in CaRI systems is due to the influence of the geometric confinement. This is in line with the significant effects observed for polymers confined in CaRI systems.(125; 57; 56) Figure 4.2 shows the heating and cooling curves and the first order derivatives. The same $T_g$ is measured upon heating and cooling.

The effect of nanoconfinement in CaRI systems is not the same as what have been observed in other mesoporous media, such as controlled pore glass (CPG). CPG is another commonly used porous media where the pores are generated through metastable phase separation in borosilicate glasses. The glass transition of a variety of different molecules, from small molecules to polymers, has been studied for decades. Most studies have shown decreased $T_g$ in smaller pores, while some molecules have two $T_g$s in CPG, one above bulk $T_g$ and the other below bulk $T_g$. The higher and lower $T_g$s are usually attributed to the interfacial interactions and ”size effect”, respectively.

We use differential scanning calorimetry (DSC) to measure the onset glass transition of TPD confined in CPG at 10 K/min heating rate immediately after cooling from SCL at 10 K/min. Figure 4.1b shows the sample preparation process. The average pore diameters of CPG range from 7.5 nm to 102.6 nm. Figure 4.3 shows sample DSC curves and their first order derivatives. The measured $T_g$s are plotted in Figure
Figure 4.1: Schematic representation of preparation procedures for (a) the TPD-CaRI film and (b) TPD-CPG sample preparation. (c) Index of refraction vs. temperature of the top TPD layer (100 nm, black symbols) and the bottom TPD-NP layer (250 nm, red symbols) of a TPD/SiO$_2$(25nm) film measured during cooling at 10 K/min. The inset shows the schematic structure of the sample and the TPD molecular structure. (d) $T_g$ of TPD vs. average pore size in CaRI films (measured by ellipsometry, black symbols) and CPG (measured by DSC, red symbols). The bulk $T_g$ is marked by a dashed line with corresponding colors.
4.1d. In agreement with previous studies of nanoconfinement effects using CPG as the mesoporous media, two $T_g$s are observed in most of the TPD-CPG samples, one higher than bulk value ($T_{g1}$) and the other below bulk ($T_{g2}$). While $T_{g1}$ shows no significant change, $T_{g2}$ slightly decreases with decreasing pore diameter. Although the average pore size of NP films made with 25 nm NPs is comparable with CPG with 7.5 nm pore diameter, the glass transition behavior of TPD is very different when confined in the two systems.

4.4.2. Molecular conformation of TPD confined in pores with different geometries

In order to find the origin of the different behaviors in the two porous media, we measured the Raman scattering spectra of TPD under nanoconfinement. To make sure there is no top TPD layer that can complicate the analysis, slightly underfilled CaRI films and TPD-CPG samples are used. Figure 4.4 shows the Raman spectra of TPD in different conditions. There are 3 sets of peaks at $\sim$1200 cm$^{-1}$, $\sim$1300 cm$^{-1}$ and $\sim$1600 cm$^{-1}$ for TPD in the plotted range. The dashed lines are a guide to the eye of the relative position of the peaks. In Figure 4.4a, we can see that there is no
Figure 4.3: (a) Sample DSC curves of TPD-CPG samples upon heating at 10 K/min. (b) 1st order derivatives of the DSC curves and $T_g$ assignments.

difference between crystallized TPD and liquid-quenched TPD glass. When confined in CaRI films, changes in the vibrational frequencies become more significant when the NP size is smaller. Under stronger confinement in CaRI, the relative intensity of some vibrational modes around 1300 cm$^{-1}$ and 1600 cm$^{-1}$ invert, while the peak at 1200 cm$^{-1}$ blue shifts. The change in the vibrational modes indicates change of molecular conformations of TPD in CaRI films. In CPG, as is shown in Figure 4.4b, the positions of the Raman peaks are exactly the same as TPD crystal and glass, even in the smallest pores (7.5 nm, which is comparable to the pore size of 25 nm NP films). Thus, the molecular conformation of TPD does not change when it is confined in CPG.

The geometry was first optimized to get the vibrational modes of each Raman peak. Five major peaks that show the impact of nanoconfinement in CaRI films are labeled in Figure 4.5a. While peak 2-5 are from the stretching vibrational modes of the C-C bonds of the molecules, peak 1 is from the symmetric scissoring vibration of the 8 C-H bonds in the middle of the molecule. Blue shift of peak 1 indicates that the TPD
Figure 4.4: Raman spectra of TPD in (a) CaRI films and (b) CPG, compared with TPD crystal and liquid-quenched glass. Dashed lines mark the position of major peaks. The inset in (b) shows that the 1200 cm$^{-1}$ peak corresponds to the scissoring vibration of the C-H bonds of the middle two benzene rings.
molecules may have more planer conformation in CaRI films.

To show how the molecular conformation of TPD changes in CaRI system, we performed Density Functional Theory (DFT) calculations on the vibrational modes and Raman spectra of TPD using b3lyp/6-31g(d) method. Because of the steric effect, the most stable conformation of TPD has a twisted structure: the two rings in the biphenyl moiety have a 35° dihedral angle ($\alpha$); the dihedral angle between one ring of the biphenyl and the methylphenyl group is 40° ($\beta$). The Raman scattering peak at $\sim$1200 cm$^{-1}$ corresponds to the symmetric scissoring vibration of the 8 C-H bonds of the middle two benzene rings. (Inset of figure 4.4b) The other two major peaks are from the stretching vibrations of the carbon chain of the molecule.

It is obvious that the energy of the scissoring vibration of the C-H bonds can be easily influenced by the steric effect. The more coplaner the benzene rings are, the stronger steric repulsion the C-H bonds has, which results in higher energy of the corresponding vibrational modes. Thus, the significant blue shift of the 1200 cm$^{-1}$ peak for TPD confined in CaRI films (Figure 4.4a) indicates the more planer molecular conformations compared with bulk TPD. The dihedral angles $\alpha$ and/or $\beta$ should be smaller in CaRI films at the most stable conformations.

To check this hypothesis, the two dihedral angles ($\alpha$ and $\beta$, marked in red boxes in figure 4.5) were manually modified without changing the relative coordinates of other atoms. Figure 4.5b (4.5c) shows how the Raman spectrum of TPD changes with one angle while the other angle is kept at the original value. The calculated Raman spectra were then compared with experimental data.

There are several features of the measured change of Raman spectroscopy of TPD in CaRI films: (1) blue shift of peak 1, (2) suppression of peak 2 and rise of peak
Figure 4.5: (a) Experimental Raman spectra of TPD in different conditions. The dashed lines mark the major peaks that change in CaRI films. (b) Calculated Raman spectra when the side dihedral angle changes. The center angle is fixed at 35°. (c) Calculated Raman spectra when the center dihedral angle changes. The side angle is fixed at 40°. The angles changed are marked by the red boxes. Small black arrows on the side of (b) and (c) point the spectrum of the original conformation.
3, (3) reduction of the intensity ratio between peak 1 and peak 3, (4) rise of peak 4 compared with peak 5. Through reducing the center dihedral angle, feature 1 and 4 can be reproduced. By reducing the side dihedral angle, feature 1, 2 and 3 can be obtained. Thus, simultaneously reducing the two dihedral angles is required to fully reproduce the experimental result. We note that although there could be other changes of molecular conformation, such as the rotation of the end phenyl groups, simply reducing the two dihedral angles can provide results consistent with the experiments. Figure 4.6b shows the calculated Raman spectra of TPD with the originally optimized conformation ($\alpha = 35^\circ, \beta = 40^\circ$) and a more planer conformation ($\alpha = 20^\circ, \beta = 10^\circ$).

By just changing the two dihedral angles, we can reproduce the change in the experimental Raman spectra. This confirms that the most stable molecular conformations of TPD changes significantly in CaRI films but not in CPG. With more planer conformations, TPD molecules in CaRI can have denser packing and stronger intermolecular interactions.

Molecular conformation changes have been observed in nanoporous systems with specific intermolecular interactions, such as ion-dipole interactions and hydrogen bonding.(28; 81; 51; 138) Molecules that form liquid crystals also have different phase behavior when confined in nanoporous media.(109; 26; 36; 50; 49) While the conformation change of polymers and bio-molecules confined in nanoporous media are common because of the large size of the molecules,(64; 115; 40; 134; 16; 38; 37) to our best knowledge, such change in conformations of small molecules is never observed with only van der Waals interactions. Vapor deposited ultra-stable glass, which has significantly enhanced kinetic stability, also shows no change in the molecular conformation from liquid-quenched glass. When CaRI films and CPG have the same
average pore size, the most significant difference should be the shape of the pores. Figure 4.6c shows the sketches of cross-sections of the pores in CaRI films and CPG. The packing of the NPs in CaRI films results in concave pores. With the same average pore size, the connection parts of the NPs can have significantly stronger confinement effect. Pores in CPG and most of the other mesoporous materials, on the other hand, have grid structures made of near cylindrical convex pores. Such pore structures have narrow pore size distribution but the effect of spatial confinement is limited at the same time. Figure 4.6c also shows the conditions in which the pores are not fully filled in light blue color. Because of the capillary forces and surface tension, the filler tends to stay in smaller pores or the connection parts in CaRI films, while the filler just forms a uniform thin film in CPG. In both systems, underfilling the pores can introduce a free surface, which can enhance the mobility of the molecules close to it.

We used Scanning Electronic Microscopy (SEM) to check the filling conditions of the CPG samples (Figure 4.7). The SEM picture shows an overall underfilled TPD-CPG sample with 72.6 nm pore diameter. We can see that the TPD partially fills the right side forming thin films covering the pores, while there is excess amount of TPD on the left side. The non-uniformity in filling of CPG may result in more complicated DSC results. For CaRI films, the TPD can be uniformly distributed through the film. In addition to the free surface effect, the degree of nanoconfinement in underfilled CaRI films is significantly enhanced. This results in further increase in $T_g$.

4.4.3. Physical vapor deposition (PVD) of TPD ultrastable glass and its Raman spectroscopy

Vapor-deposited small molecule glass is another system that shows significantly enhanced kinetic stability compared with the liquid-quenched glass.(116; 79; 102) Stable glass (SG) films of TPD was prepared by physical vapor deposition (PVD), a technique known to produce glasses with exceptionally high thermodynamic and kinetic
Figure 4.6: (a) The two dihedral angles changed in DFT calculation to simulate the effect of nanoconfinement in CaRI system. (b) Calculated Raman spectra of original TPD and a more planer TPD by reducing the two dihedral angles. (c) Sketch of the cross section of the pores in CaRI films and CPG at the partially-filled condition.

Figure 4.7: SEM image of an overall under-filled TPD/CPG(72.6nm) sample showing non-uniform filling.
stability.(116; 79) Glasses undergo structural rearrangements at their surface during PVD to approach energetically lower states and more densely packed configurations; a stable glass is characterized as having a higher onset temperature of transformation into supercooled liquid than a liquid-quenched glass. Spectroscopic ellipsometry is used for characterizing glassy films by providing information on the thickness and refractive index of a film. Through a heat-and-cool dilatometry experiment, a stable glass formed by PVD can be transformed to a supercooled liquid and subsequently cooled to liquid-cooled glass. The thickness of the glass film is monitored by SE throughout the dilatometry process; by comparing the thickness before and after transformation, the difference in density between the vapor deposited stable glass and the liquid-cooled glass can be measured. Figure 4.8 shows an illustration of a dilatometry experiment performed on TPD stable glasses used in this study.

An important property of stable glasses, that is relevant to the current study is their exceptionally high onset temperature of transformation. Due to their kinetic stability, these glasses need to be heated significantly above \( T_g \) before transforming into supercooled liquid. As shown in Figure 4.8, for the 200 nm thick TPD film deposited at \( 0.85T_g \) (280 ± 1 K), the transformation is conducted at 353 K, which is more than 20 K above \( T_g \).

Raman spectroscopy was taken for the TPD stable glass. As is shown in figure 4.9, there is almost no difference between liquid-quenched glass and vapor-deposited stable glass for TPD. The Raman peak at 521 cm\(^{-1}\) from the Si substrate is plotted to rule out any possible error from the equipment calibration between measurements. Clearly the molecular conformation in TPD SG does not change and the enhanced kinetic stability is achieved by density increase from surface relaxation during deposition. In CaRI films, the molecular conformation change can result in significantly denser
Figure 4.8: Dilatometry process of a 200-nm stable glass film of TPD, deposited at (280 ± 1) K (equivalent to 0.85 $T_g$) at a deposition rate of (0.20 ± 0.02) nm/s under a high vacuum of $3 \times 10^{-7}$ Torr. The vapor deposited glass was fully transformed to supercooled liquid at a temperature of 353 K ($= T_g + 23$ K) before cooling down; heating and cooling ramp rates were 10 K/min. At 298 K, the vapor deposited glass was found to be 1.6% denser than the liquid-cooled glass, indicating a higher thermodynamic stability than liquid-cooled glass.
packing with a regular liquid-quench process.

4.4.4. Molecular packing of liquid-quenched TPD glass confined in pores with different geometries

Figure 4.10a shows the WAXS spectra of pure TPD and SiO$_2$ NPs. All NPs and CPG used have similar spectra since they are all composed of SiO$_2$. Although the peak positions are different for TPD and SiO$_2$, there is a broad range of spectra that they overlap and SiO$_2$ has much stronger scattering signal than TPD when they are mixed. The spectrum of a mixture of TPD and SiO$_2$ will be similar to pure SiO$_2$ with slightly different peak position and a larger shoulder on the low q side. In order to separate the TPD signal from SiO$_2$, the powders of TPD and SiO$_2$ were thoroughly mixed first and divided into two samples. One sample was annealed at 473 K overnight in a vacuum oven to induce infiltration and cooled down naturally. The two samples should then have the same ratio of TPD and SiO$_2$ and the only difference is the position of TPD. The WAXS spectra of two samples were measured successively to rule out the error.
Figure 4.10b,d show the WAXS spectra for a TPD-CaRI(11nm) sample and a TPD-CPG(7.5nm) sample. While the CPG samples show almost no difference before and after infiltration, the shoulder of the CaRI sample peak significantly shift to larger $q$ after infiltration. In order to separate the TPD signal with the SiO$_2$ signal, the spectrum of pure SiO$_2$ was subtracted from the raw data with a scaling factor. A range of scaling factors were tried until the ”mix only” spectrum can overlap perfectly with the bulk TPD glass spectrum. The determined scaling factors were then used to subtract SiO$_2$ signals from the ”infiltrated” samples. Typical factors range from 0.55 to 0.8, depending on the relative amount of TPD and SiO$_2$. The results are shown in figure 4.10c,e. It is clear that the scattering peaks of TPD shift to higher $q$ only in the CaRI samples, indicating a denser packing of molecules in CaRI samples. Figure 4.11 shows the pair distribution function $g(r)$ of TPD in different conditions derived from the WAXS data in Figure 4.10c,e using the PDFgetX3 software.(63) Because of the limited $q$ range of our measurement, $g(r)$ at small $r$ values (shadowed area) is not accurate and we don’t have the resolution at atomic length scale for higher $r$. Nevertheless, the intermolecular distribution can be derived based on the WAXS data. The arrows indicate that TPD shows $g(r)$ peaks around the intermolecular distance at smaller $r$ only in CaRI films.

Figure 4.12 shows the Wide Angle X-ray Scattering (WAXS) of TPD in different conditions. While the XRD pattern of TPD confined in 7.5 nm CPG stays almost the same as bulk glass, the peak shifts to larger wave vector $q$ when TPD is confined in CaRI samples. This indicates denser packing of molecules in CaRI films, which can be one of the origins of the increased $T_g$ in CaRI films without strong interfacial interactions.
Figure 4.10: WAXS spectra of (a) pure SiO$_2$ NPs, TPD glass and a typical mixture; (b) TPD-CaRI(11nm) sample before and after infiltration; (d) TPD-CPG(7.5nm) sample before and after infiltration. (c)(e) TPD WAXS spectra after subtraction of SiO$_2$ signals under each condition.
4.5. Conclusion

In summary, we measured the glass transition of TPD confined in CaRI films and CPG to study how the pore geometry influences the nanoconfinement effect. While the $T_g$ shows similar trend as other molecules in CPG (one higher and one lower than bulk value), the $T_g$ significantly increases with decreasing pore size in CaRI films by up to 30 K without strong interfacial interactions. Combining Raman spectroscopy and DFT calculations, we show that the molecular conformations of TPD can be significantly modified in CaRI films but not in any other systems. Because of its geometric origin, the observation for TPD in this paper can be easily expanded to other soft materials. Thus, by changing the NP size in CaRI films, we are able to control the molecular conformation and dynamics of soft material fillers in a broad range. This can further enable the modification of optical and electronic properties of soft materials with CaRI films.
Figure 4.12: WAXS of TPD glass in different conditions. The shift of the peak to larger q (smaller d) indicates denser packing.
5.1. Introduction

Functional coatings are important in modulating the properties of materials, especially at the surface. While a large part of the coatings are small organic molecules and polymers, the durability of the coatings can limit their applications and lifetime. Because of the hydrophilic nature of surface of most inorganic materials (such as glass and metals), the adhesion of hydrophobic organic coatings can be a problem. In order to enhance the adhesion of polymers, a variety of methods have been developed. Here are some examples of the existing methods of enhancing the adhesion of polymers on other surfaces. (1) The micro-mechanical interlocking method: It uses micro-electromechanical system (MEMS) or laser-structuring to make micro patterns on the substrate surface that can physically lock the polymer coating. (73; 20) (2) Modification of the substrate surface: The surface chemistry and surface energy of the substrate can be modified by chemical treatment. (113) (3) Modification of the polymer surface: Typically through plasma treatment, the surface energy of the polymer film can be enhanced for better adhesion. (22) (4) Adhesion layer: Adhesion layers are widely used to improve adhesion of various substrates and coatings. (67)

In this section, we describe a method with similar principle as the micro-mechanical interlocking using NP films as the adhesive layer through CaRI process. Significantly stronger polymer-substrate adhesion can be achieved using single- or multi-layer NP films. Example substrates include silicon, glass, quartz, etc. The polymers should be thermoplastic and can range from hydrophilic polymers to superhydrophobic poly-
mers with any molecular weight.

5.2. Materials and methods

We demonstrate the enhanced adhesion between glass (microscope glass slides) and a superhydrophobic polymer PTFE AF 1600 (Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene] dioxole 65 mol%, $T_g = 160$ °C, purchased from Sigma-Aldrich). SiO$_2$ NPs used in previous sections are used in this study.

The glass microscope slides were first cleaned with room air plasma. Nanoparticle films with different nanoparticle diameters were blade coated on half of the cleaned glass slides, leaving half of the slides bare glass substrate as control. Some of the NP films were then sintered at different temperatures (600 - 800 °C). Polymer solutions were then dropped on the glass surface to make small dots (1µL per dot) and the samples were annealed at 200 °C to induce infiltration. Finally, the taping method and IPA wiping test were used to examine the adhesion and durability of the polymer dots. To perform the tape peel test, a Scotch tape is put and pushed on the glass surface. When the tape is peeled off, some of the loosely bonded PTFE dots are removed from the glass. To do the IPA wipe test, cheesecloth moistened with IPA is used to rub the PTFE dots. The strength of adhesion was evaluated based on the number of polymer dots on the glass slides after the tests.

5.3. Results and discussion

Previous studies have shown that CaRI films have enhanced mechanical properties and thermal properties compare with bare polymer films.(60; 57; 56; 125; 126) Because of the strong inter-particle interactions of the SiO$_2$ NPs, especially after sintering, NP films can be used to enhance the adhesion of polymers with substrates such as glass.

The mechanism of the enhanced adhesion is mechanical interlocking. Thus the in-
interactions between the NPs and glass is the key factor for the adhesion performance. The SiO$_2$ NPs have surface hydroxyl groups that can form hydrogen bonds with each other. In order to build hydrogen bonds between the glass surface and the NPs, room air (or Oxygen) plasma treatment of the glass surface can be applied to introduce more Oxygen atoms and activate the glass surface. To further enhance the interactions and avoid failure of the NP films, a sintering process can be performed before the coating of the polymers. According to published data which shows the transition of SiO$_2$ NPs with increasing temperature (Figure 5.1), 400–800 °C is the temperature range to induce the reaction. Figure 5.2 shows the cross-section SEM images of 100 nm NPs sintered at different temperatures for 15 min. Due to the low $T_g$ the glass substrate used here, the NPs can sink into the glass when the temperature is above ~700 °C. In order to have most fusion and avoid the melting of the glass substrate, we used 650 °C/15 min as the sintering condition to test the adhesion properties.

We show the effectiveness of this method with the example of adhesion of PTFE AF 1600 (Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene] dioxole 65 mol%) on glass substrate with SiO$_2$ NPs. Figure 5.3
Figure 5.2: Cross-section SEM of 100 nm SiO$_2$ nanoparticles on microscope glass slides after sintered at different temperatures. Scale bars are 200 nm.

shows the process of making CaRI films described above as well as the molecular structure of PTFE AF 1600. As a superhydrophobic polymer, PTFE AF 1600 has very weak interfacial interactions with glass. As a result, this polymer coating is not durable on a glass surface. With the NP layer in the middle, the polymer can be physically locked on the glass surface.

A tape peel test and an IPA (isopropanol) wipe test can be performed to test the durability of the PTFE coating on glass. The bottom half of each glass slide is coated with a layer of SiO$_2$ NPs while the top half is just bare glass. Several drops of PTFE solution are deposited uniformly on the glass to test the adhesion at different positions. Figure 5.4 shows the preliminary adhesion experiment results. After the same tests on the same glass slides, all the PTFE dots on the top halves are removed while all the dots on the bottom stay bonded, regardless of the size of the NPs and the thickness of the NP films. This example shows that this method can significantly enhance the adhesion between polymer and substrate even with very weak interfacial interactions.

Using CaRI films as the adhesive layer is a facile method for durable coatings, especially on glass substrates. There is no need for chemical adhesives or HF etching of
the glass. With the NP layer applied, the coating can be physically interlocked on
the substrate. This method is specifically good for solution-based film preparation
methods, in which the coating is applied from solution and modifying the coating
interface is not possible. Because of the mechanical interlocking mechanism, this
method is suitable for almost any type of NPs and coating materials, either polymers
or small molecules. This method is low-cost, environmentally friendly and easy for
large area applications. Because of the stability of the inorganic NPs, the film can
be easily repaired after the polymer layer is damaged or degraded using the same
coating method. Besides the enhanced adhesion, the polymer-infiltrated NP films
have enhanced thermal and mechanical properties, which can improve the durability
of the coatings.
Figure 5.4: PTFE AF 1600 (dots) on glass substrate before and after (top) tape peel test and (bottom) IPA wipe test. The bright stripes are reflection from the room light.
5.4. Conclusion

In this chapter, we show that CaRI films can be potentially used to enhance the adhesion between organic materials and inorganic substrates. Although the data are preliminary and qualitative, they show that the adhesion between the superhydrophobic polymer, PTFE AF 1600, and a hydrophilic glass surface can be significantly enhanced with a few or mono layer of SiO$_2$ NPs. This method requires polymers to be thermalplastic and is especially good for solution-based process. More experiments are required in the future to quantitatively evaluate the enhancement of adhesion energy and characterize the failure behavior of the CaRI film for better performance.
CHAPTER 6 : SUMMARY AND OUTLOOK

This thesis focuses on the behavior of polymers and small organic molecules under extreme nanoconfinement using CaRI films as a model system. Compared with other nanoporous media, such as CPG and AAO, CaRI films show qualitatively different confinement effects that were never observed before, including dramatically increased $T_g$, enhanced thermal stability with potentially more complete degradation, and the change in molecular conformation.

In Chapter 1, we present an overview of polymer nanocomposites and the development of CaRI as a simple and robust method to make PNCs with ultra-high NP loading. We show that the CaRI method is widely applicable to a variety of polymer and NP combinations. With careful design and fabrication, CaRI films can have many good properties such as enhanced hardness/modulus, scratch resistance, anti-reflection, anti-icing and have potential applications in water-oil separation, anti-corrosion, Bragg reflector sensors, etc. Despite the material engineering of the CaRI films as a whole and all these applications, there is lack of fundamental understanding about how the properties of the polymer filler are influenced by the extreme nanoconfinement in the pores of the NP packings.

In Chapter 2, we study the glass transition behavior of polymers under extreme nanoconfinement in CaRI films. There have been a number of research about the glass transition of polymers in confined environment, yet there are always several factors that cannot be well separated, such as size effect and interfacial interactions. Inconsistent observations have been reported by different people. In addition, the shape of pores, which we prove to be a critical factor that can influence the properties of the polymer fillers, were never studied. CaRI films provide a good model system
that can study the effect of these factors with good control of other parameters. We show dramatically increased $T_g$ from the spacial confinement in CaRI films while interfacial interactions have more significant effects under stronger confinement.

In Chapter 3, thermal degradation of polymers in CaRI films are investigated. We show the thermal degradation of polymers in CaRI films are controlled by the competing effects: reduced dynamics can slow down the degradation, while the size effect of the pores can limit the formation of carbonization products and in turn accelerate the degradation. As such, CaRI films are good candidates when enhanced thermal stability of polymers is desired. CaRI films also show potential applications for polymer recycling.

In Chapter 4, we dig more into the fundamental origins of the behavior of polymers and small molecules under nanoconfinement by studying the molecular conformation using vibrational spectroscopy. We show that pore shape is the crucial factor that determines the effect of nanoconfinement in nanoporous media. Significant change in molecular conformation of TPD molecules is observed only in CaRI films. This observation enables the modification of electronic and optical properties of the molecules without changing their nature in chemistry. More research should focus on this aspect in the future.

In Chapter 5, we describe one potential application of the CaRI films by showing the enhancement of the adhesion between polymers and glass substrate. The solution-based process makes it easy to apply CaRI films in industry. The mechanical interlocking mechanism makes CaRI films suitable for almost any type of NPs and coating materials, either polymers or small molecules.

The unique effects of nanoconfinement make CaRI films good candidates of tuning
the properties of soft materials and expand their application area. For example, in photovoltaic cells, the increased $T_g$ can expand the selection of the organic materials with relatively low $T_g$ and thus not applicable in regular conditions. The change in molecular conformation can result in variation of optical and electronic properties that can be tuned by the degree of nanoconfinement. Such effects and applications of CaRI films require future study.

In summary, CaRI films provide a unique platform to study physical and chemical properties of polymers under extreme nanoconfinement. These fundamental studies have led to some interesting and unexpected results that inspire further investment. As a novel type of PNC materials, CaRI films also show great potential in a wide range of applications that need to be developed in the future.
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