Interplay between Core and Interfacial Mobility and Its Impact on the Measured Glass Transition: Dielectric and Calorimetric Studies

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ABSTRACT: The dynamics and thermodynamics of confined triphenyl phosphite (TPP) were studied using broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC). Geometric confinement in channels having length scales commensurate with the molecular size of TPP causes bifurcation of the dynamics: two populations are observed, distinguished by their reorientational mobilities and glass transition temperatures. Upon cooling, significant changes in the relaxation process and temperature dependence occur due to the slow vitrification of the molecules in close proximity to the interface. Such a kinetic aspect of glass formation is unusual. This surface interaction alleviates constraints on the molecules, allowing their glass transition to shift to lower temperatures. Simultaneously, it was observed that the structural relaxation process shifts to lower frequencies, and the distribution of the relaxation times becomes



narrower upon annealing. This effect is especially visible at lower frequencies, indicating the decreasing contribution of those molecules characterized by slower dynamics. In addition, it was found that structural relaxation times, as well as the glass transition temperatures, can be significantly modified by annealing samples over a particular range of temperatures. This work facilitated the understanding of the interplay between different kinds of mobility and its impact on changes in the glass transition temperature for two-dimensional confined materials.

1. INTRODUCTION

The properties of soft matter on the nanoscale is a topic of great interest, engendering both scientific challenges and technological advances (e.g., photovoltaic cells,¹ microelectronics, separation membranes,^{2,3} templates for the synthesis of nanostructured polymers,^{4–6} and drug carriers^{7,8}). Despite the large number of research efforts, the physics and chemistry of spatially confined soft matter are not well understood, in part because of the complexity of the systems.

Even in the absence of confinement effects, the glass transition phenomenon remains a major unsolved problem in condensed matter physics. However, there is a growing consensus that the vitrification process and dramatic slowing of molecular motions reflect increasing intermolecular cooperativity, associated with a growing dynamic correlation length ξ .^{9–12} Notwithstanding the added complexity when soft matter is spatially confined, the changes it brings about can offer unique insights, particularly when the geometric length scale becomes commensurate with ξ . Experimental data on such systems can provide tests of models and serve as the basis for development of a more universal theory of the glass transition. Although such studies hold great promise, as shown recently,^{13–17} the situation is greatly complicated by specific

interactions of the material with surfaces of the substrate. These interactions can cause shifts in the dynamic glass transition that are unrelated to spatial restriction.¹⁷⁻²⁰ This effect is seen clearly, for example, in the different shifts of T_{σ} observed for native versus silanized pores.¹⁹ Also, the depression of the glass transition temperature varies for different materials confined in porous materials having the same geometry and diameter, emphasizing the role of the interactions.²¹ Irreversible adsorption of the material on a substrate can be followed by a decrease in the relaxation strength. The solid-liquid interactions of confined liquids can also give rise to heterogeneous dynamics.^{13,14} Previous studies have demonstrated the role of density gradients originating from packing frustration²² on the changes in molecular dynamics near a surface.¹⁵ Ediger et al. showed that anisotropy in packing can also play a significant role in the dynamics of vapor-deposited glasses.²³ In addition to studies on the interactions with a substrate, many works have studied the dynamics of polymers at the surface of thin films; the mobility of these chains is

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enhanced relative to the bulk.^{24–26} Surface effects in thin films in some cases lead to changes in the temperature dependence of the dynamics,^{25,26} while in others, no effect is observed.²⁷

In this work, we investigated the dynamics of triphenyl phosphite (TPP) confined in native aluminum oxide membranes. (Note that this compound has been reported to exhibit a prominent liquid-to-liquid transition. This putative phase transition, which has no influence on the measurements herein, will be the subject of a future paper.) We found that there are at least two groups of molecules (interfacial and core) characterized by very different temperature dependences of their relaxation times. Moreover, vitrification of the interfacial layer significantly affects the dynamics of the core (bulk) molecules, leading to shifts of the glass transition temperature larger than expected based on the pore size. Somewhat analogous behavior has been observed previously in salol.²⁸ We also show that different thermal histories and annealing procedures modify the dynamics and glass transition temperature of the core molecules.

2. EXPERIMENTAL SECTION

2.1. Materials. Triphenyl phosphite (TPP) with purity higher than 98% was supplied by Sigma-Aldrich. The chemical structure is presented in Scheme 1. The nanoporous aluminum





oxide (AAO) membranes used in this study were supplied by Synkera Co. Details concerning the porosity, pore distribution, etc., can be found in Table 1 and at the website of the producer.²⁹

Table 1. Details Concerning Porosity, Pore Diameter, and Distribution of AAO Membranes

pore diameter (nm) pore density (cm ⁻²)	18 6×10^{10}	35 1 × 10 ¹⁰	73 2×10^9	$\frac{150}{9 \times 10^8}$
pore period (nm)	44	94	243	367
estimated porosity (%)	15	13	10	15

2.2. Sample Preparation/Infiltration Procedure. Prior to being filled, AAO membranes (pore diameters 150, 73, 35, and 18 nm) were dried in an oven at 423 K under vacuum to remove any volatile impurities from the nanochannels. After cooling, the membranes were immersed in TPP, and the system was maintained at 343 K in vacuum (10^{-2} bar) for 24 h to allow the TPP to flow into the nanocavities. After completion of this infiltration process, the surfaces of the AAO membranes were dried, and excess sample was removed by patting the membranes with a paper towel.

2.3. Methods. 2.3.1. Broadband Dielectric Spectroscopy (BDS). Isobaric measurements of the complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ were carried out using a Novocontrol Alpha dielectric spectrometer over the frequency range of $10^{-2}-10^6$ Hz at ambient pressure. The temperature

was maintained with a Quatro Cryosystem using a nitrogen gas cryostat with control more accurate than 0.1 K. Dielectric measurements of bulk TPP were performed in a parallel-plate cell (diameter 10 mm, gap 0.1 mm) immediately after preparation of the amorphous sample. The AAO membranes filled with TPP were placed in a similar capacitor (diameter 10 mm, membrane 0.005 mm).^{30,31} Dielectric measurements were made in the temperature range 173–221 K for bulk and confined systems. Two temperature protocols were employed in the measurements of confined TPP: fast quenching (rate ~50 K/min) followed by slow cooling and heating.

2.3.2. Differential Scanning Calorimetry (DSC). Differential scanning calorimetry (Mettler-Toledo) was carried out on the crushed membranes filled with TPP contained in sealed crucibles. After the sample had been heated from room temperature to 173 K, data were collected during heating to above the respective melting points at 10 K/min. Each measurement was repeated three times.

3. RESULTS AND DISCUSSION

Figure 1 shows the dielectric loss spectra for the bulk and confined (150 and 18 nm, respectively) TPP obtained by heating the samples that, prior to the measurements, had been quenched below the glass transition temperature. There is a prominent structural (α -) relaxation that shifts toward lower frequencies as the temperature decreases in each sample. For the confined TPP, an additional process appears between the α peak and the rise due to dc conductivity at lower frequencies. This is illustrated in Figure 2a, which shows representative data obtained for TPP confined in pores of 35 and 18 nm. However, as stated above, due to the low amplitude of this additional process, it is almost completely masked by dc conductivity. In addition, the real part of the permittivity is shown in the inset of Figure 2a, which affirms the presence of two relaxation processes in the confined TPP. In accord with previous results on analogous systems, 32-37 we ascribe this new process to partially immobilized molecules adjacent to the pore walls and refer to it as the interfacial process. Note that immobilization due to confinement is manifested to a lesser degree as the distance from the pore boundary increases. As a consequence, the distribution of the relaxation times of the interfacial material can be quite large; for example, the stretch exponent of the KWW function can be as low as 0.20.^{38,39}

Also in Figure 2b, loss spectra measured at a lower temperature, much closer to the glass transition temperature, are shown. It can be observed that the α -loss peak shifts toward higher frequencies with decreasing pore size. This is typical behavior noted for liquids confined in pores and is consistent with depression of the glass transition temperature. The inset of Figure 2b also compares the shape of the structural process of bulk and confined TPP (the α -loss peaks were shifted vertically to superpose at the maxima). It can be seen that the distribution of relaxation times is broader under confinement. This behavior is a common feature of liquids confined in nanoporous materials, reflecting the heterogeneity of soft matter under confinement, as discussed by many authors.^{14,40,41}

The loss spectra in Figure 1 were analyzed using the Havriliak–Negami (HN) function to determine the structural relaxation times:⁴²

$$\varepsilon(\varpi)'' = \frac{\sigma_{dc}}{\varepsilon_0 \omega} + \varepsilon_{\infty} + \frac{\Delta \varepsilon}{\left[1 + \left(i \varpi \tau_{\rm HN}\right)^{\alpha_{\rm HN}}\right]^{\beta_{\rm HN}}} \tag{1}$$



Figure 1. Dielectric spectra collected for bulk TTP (a) and TPP confined in AAO membranes of diameters 150 nm (b) and 18 nm (c). Dotted lines indicate the temperature corresponding to vitrification of the interfacial molecules.



Figure 2. Dielectric loss spectra measured above (a) and below (b) the temperature where a change in the slope of the τ_{max} (*T*) is observed. In the inset of panel a, the real part of the permittivity of TPP confined in 35 and 18 nm AOO templates is shown. In the inset of panel b, superposed structural relaxation peaks measured near the glass transition for the bulk and confined TPP are shown.

where ε_{∞} is the high frequency limit of the permittivity, $\Delta \varepsilon$ is the relaxation strength, $\tau_{\rm HN}$ is the HN mean relaxation time, $\alpha_{\rm HN}$ and $\beta_{\rm HN}$ are the shape parameters characterizing the breadth and asymmetry of the loss peak, respectively, and ϖ is an angular frequency. From $\tau_{\rm HN}$, and in conjunction with the $\alpha_{\rm HN}$ and $\beta_{\rm HN}$ parameters, $\tau_{\rm max}$ values were estimated using the formula in ref 43. The relaxation times for the interfacial process were obtained via the Kramers–Kronig derivative method:⁴⁴

$$\varepsilon'' \propto -\frac{2}{\pi} \frac{\mathrm{d}\varepsilon'}{\mathrm{d}\log f} \tag{2}$$

The obtained relaxation times (τ_{max}) are plotted in Arrhenius form in Figure 3a. At high temperatures, the relaxation times have very similar behavior with no effect of confinement. However, at lower temperatures, there is a significant change in the slope of the curves (Figure 3a). The temperature associated with this change in dynamics, T_{m} , shifts higher with decreasing pore diameter. Comparable results were obtained for confined salol and ascribed to the vitrification of molecules near the interface.²⁸ Fitting our results to the VFT equation

$$\tau_{\alpha} = \tau_{\infty} \exp\left(\frac{D_{\rm T} T_0}{T - T_0}\right) \tag{3}$$

where τ_{∞} , $D_{\rm T}$, and T_0 are constants, we can calculate the glass transition temperature ($\tau_a(T_{\rm g}) = 100$ s) and $T_{\rm m}$. As seen in Table 2, with increasing severity of the confinement (decreasing pore size), $T_{\rm g}$ is reduced and $T_{\rm m}$ increases; that is, these two characteristic temperatures are anticorrelated. In addition, we plotted in Figure 3a the $\tau_{\rm max}$ evaluated for the interfacial process of two samples (d = 18 and 35 nm). The temperature of the crossover in the structural relaxation process corresponds well to the vitrification temperature of the interfacial molecules ($\tau_{\rm max} \approx 10$ s) in the smaller pores (d = 35 and 18 nm). Note that similar results have been reported for salol confined in aluminum oxide membranes.²⁸ Additionally, at



Figure 3. Panel a: relaxation map of bulk and confined TPP. Panels b-f: thermograms for bulk and confined samples (heating rate of 10 K/min). Panel g: pore diameter dependence of the melting temperature of confined samples with a solid line representing the linear fit.

Table 2. Values of the Glass Transition, Crystallization, and Melting Temperatures Obtained from Calorimetric and Dielectric Measurements

	D: measur	DSC measurements		dielectric measurements		
sample	T_{g1} (K)	$\begin{array}{c} T_{\mathrm{g2}} \\ \mathrm{(K)} \end{array}$	$T_{\rm m}$ (K)	$T_{\rm g}$ (K) for 100 s	$T_{\rm c}$ (K)	$T_{\rm m}\left({\rm K} ight)$
bulk	205.6			203.2	242.3	297.3
150 nm	196.3	214.1	211.1	194.4	260.4	294.8
73 nm	193.5	215.1	212.1	192.2	258.4	291.8
35 nm	193.2	217.5	218.1	192.2	256.1	289
18 nm	192.2	220.2	219.3	191		

 $T_{\rm m\nu}$ the amplitude of the structural process decreases as denoted by the dotted lines in Figures 1b and 1c. This result is consistent with data reported for confined salol.²⁸ The decrease in dielectric strength for the confined sample can be ascribed to a gradual freezing of the molecules in proximity to the interface upon cooling.

Complementary to the dielectric studies, DSC measurements were performed with representative thermograms obtained during heating displayed in Figures 3b–f. The confined samples exhibit two discontinuities in the heat capacity consistent with two glass transitions. Similar literature results have been interpreted as representing vitrification of material at the interface and the core.^{45–48} Two glass transitions have also been observed in systems undergoing chemical reactions. Li et al.⁴⁹ found that the T_g value of fully cured polycyanurates is depressed by more than 60 K in native-controlled pore glasses with the second glass transition detected at temperatures of 10–33 K and higher.⁴⁹ The values of the transition temperatures from the calorimetry data are in good agreement with the T_g and T_m values determined from the dielectric data for

TPP confined in aluminum oxide porous material. The separation between the two glass transition temperatures becomes greater with an increasing degree of confinement, attaining 28 K for TPP confined in 13 nm pores.

With the exception of TPP confined in the smallest pores (18 nm), crystallization followed by melting was observed in the other samples reported herein. In Figure 3g, the dependence of the melting temperature on pore size (1/d) is presented: $T_{\rm m}$ decreases with decreasing pore size (by as much as 10 K). From the data in Figure 3g, the surface energy of the solid–liquid interface ($\sigma_{\rm sl}$) was determined using the Gibbs–Thomson equation:^{50–52}

$$\Delta T_{\rm m} = (T_{\rm m} - T_{\rm m}(d)) = \frac{4\sigma_{\rm sl}T_{\rm m}}{d\Delta H_{\rm m}\rho_{\rm c}}$$
(4)

where $T_{\rm m}$ is the bulk melting point, $T_{\rm m}(d)$ is the melting temperature in pores of diameter d, $\sigma_{\rm sl}$ is the crystal–liquid surface energy, $\Delta H_{\rm m}$ is the melting enthalpy, and $\rho_{\rm c}$ is the crystal density. By substituting $\Delta H_{\rm m} = 75$ J/g and $\rho_{\rm c} = 1200$ kg/m³, we obtain $\sigma_{\rm sl} = 18$ mJ/m², which is comparable to the values calculated for *o*-terphenyl (OTP) and benzyl alcohol confined in controlled pore glasses (CPG).⁵³ Our value herein may be underestimated if the crystal density is lower than the bulk value of $\rho_{\rm c}$.

Because the glass transition is a kinetic phenomenon, different cooling rates can affect the temperature of the transition. Accordingly, we performed dielectric experiments on confined TPP using two protocols: (i) slow cooling and (ii) quenching below $T_{\rm g}$ followed by heating. In Figures 4a and b, relaxation times from the two experiments are shown for 35 and 18 nm pores. For both samples, the $\tau_{\rm max}(T)$ values are equivalent at high temperatures, while at lower temperatures, the curves for the different thermal histories diverge. This

S

 $\log_{10} \tau_{max}$ [s]

4.2

4.4

4.6

4.8

1000/Temp. [K⁻¹]

5.0



Figure 4. Panels a and b are relaxation maps of TPP confined to 18 and 35 nm channels, respectively. Panel c compares the shape of the structural relaxation peak of TPP confined to 35 nm channels measured at 213 K for a sample with a completely different thermal history.



Figure 5. Panels a and b: structural relaxation peaks during annealing (18 and 35 nm channels, respectively) at 214 K. Panel c: α -relaxation peak at the beginning of annealing and after 6000 s. Panels d and e: thermograms of both samples measured before and after aging, respectively, at 215 K.

change in the temperature dependence leads to a shift in the glass transition temperature: the lower $T_{\rm g}$ value was obtained for the quenched sample. This was accompanied by a slightly lower value (by about 1 K) for the crossover temperature (T_m) . Also, in Figure 4c, the comparison of the α -dispersions obtained for the two thermal histories is presented. The peaks do not perfectly collapse when shifted to superpose the peak maxima; there is some broadening on the low frequency side for the quenched TPP (sample measured upon heating) in 35 nm pores. The effect of thermal history on the dynamic heterogeneity is discussed below.

The change in the relaxation times with thermal history indicates that the relaxation spectra for the quenched TPP are not fully equilibrated. We see this directly in dielectric and calorimetric experiments below the crossover temperature for the quenched, confined TPP. The structural relaxation peak

shifts by more than half a decade to lower frequencies on annealing (Figures 5a and b). This slow, temperaturedependent aging process depends very weakly on pore size. With further annealing, the relaxation times (open symbols in Figure 4) reach the τ_a for samples cooled slowly. The crossover temperature shifts to slightly lower temperatures during this annealing.

10

Freq. [Hz]

10

Consistent with the shape of the loss peaks in Figure 4c, the equilibration of TPP narrows the peak (Figure 5c). This narrowing of the distribution of the relaxation times on annealing is in agreement with recent literature on aging in protic ionic liquids.⁵⁴ Calorimetric annealing measurements on the confined TPP, performed at 215 K between the two glass transition temperatures, are displayed in Figures 5d and e. The higher temperature transition decreases by 1 K, while the lower

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 $T_{\rm g}$ increases significantly, by 6–7 K. This behavior is consistent with the effect of annealing on the dielectric relaxation times.

The changes in the mobility of a fluid due to segregated vitrification under confinement, as seen herein, parallel prior work by Fakhraai et al.²⁶ and Chai et al.²⁵ on thin films. The bulk and surface populations in thin films correspond to the respective core and interfacial molecules for TPP confined in channels. In both situations, a slowing of the motion of one subset of molecules is accompanied by an enhanced mobility of the others. Bodiguel et al. 55-57 found that the viscosity displayed a decrease with respect to the bulk as the thickness of polystyrene films was reduced. Their research was further extended by Wang and McKenna, who demonstrated that, for thin films deposited on hot glycerol, the $T_{\rm g}$ starts to decrease significantly below 20 nm.^{58–60} This result agrees with the data of He et al.³⁶ and Richert,³⁷ who studied glass-forming microemulsions within a confining fluid medium. In contrast to the behavior for hard confinement (e.g., liquid adsorbed at pore walls), a significant acceleration of the relaxation was noted. These results illustrate the significance of substrate hardness on the dynamics of adsorbed molecules, involving the interplay of an interfacial layer and the core material. More recently, we have shown that changes in the crossover temperature arose from a variation in the density on vitrification.²⁸ Using high-pressure experiments, it was found that the density of the interfacial material is fixed after vitrification.⁶¹ The same conclusion was derived from positronium annihilation (PALS) studies,⁶² demonstrating that the system becomes isochoric in confined pores at some characteristic temperature.

At temperatures below vitrification of the interfacial layer, packing of the TPP is frustrated, both at the interface and within the bulk. Slow cooling or annealing allows the equilibration of local rearrangements and thus the density, resulting in a confined liquid of a slightly higher density and glass transition temperature. We expect the activation barrier for the structural process for the slowly cooled TPP to be higher than that of the quenched, confined liquid. Equilibration of materials in the glassy state very generally leads to densification. Recent studies of thin films have shown that confined material indeed densifies when annealed.^{15,24} Another interesting aspect of the present work is the more homogeneous dynamics (narrower distribution of relaxation times) for the slowly cooled (and more dense) sample in comparison to that of the quenched TPP. This reflects a smaller contribution from molecules characterized by slow dynamics. Hence, annealing and slow cooling both yield more dense and more dynamically homogeneous material under confinement, characterized by a higher glass transition temperature. In the context of our results, Zheng et al.⁶³ carried out aging experiments on liquids confined in porous silica glasses of varying internal geometry. In contrast to our results, they found that the glass transition temperature and shape of the heat capacity jump at T_g barely changed with confinement. On the other hand, Simon et al.⁶⁴ studied aging of OTP confined in CPG glasses of varying diameters and found accelerated physical aging when compared to the bulk material. At equilibrium, the fictive temperature attained a value higher than the aging temperature. To address and explain these peculiar experimental observations, the authors derived a structural recovery model from which they concluded that these anomalies were due to isochoric conditions and the development of negative pressure at temperatures around T_{σ} .

These conclusions agree qualitatively with our data, showing that the interfacial layer becomes isochoric after vitrification.⁶¹ Herein, it was surprising to find that the change in T_g of the core molecules due to aging was so large (around 7 K). This presumably reflects a dominant role of density fluctuations on the structural dynamics. Even small changes in density due to aging exert a large impact on the dynamics of the core material.

4. CONCLUSION

The dynamics of confined TPP subjected to different thermal conditions was investigated. Combined dielectric and calorimetric measurements revealed a divergence of the τ_{α} obtained via different thermal paths, likely related to heterogeneity of the packing of the molecules. Slow cooling or annealing produces more homogeneous dynamics and denser material with a higher glass transition temperature. Quenching results in a larger anisotropy and lower T_g . Our studies show the intimate relationship between dynamics and packing of the interfacial and core molecules. The insights from these experiments on confined glass-forming systems can lead to a more comprehensive understanding of the complex physics of spatially restricted soft matter, in particular the role of surface effects in controlling the dynamics.

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Notes

The authors declare no competing financial interest.

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