

Supporting Information: Role of “Hard” and “Soft” Confinement on Polymer Dynamics at the Nanoscale

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Experimental Section

The polymers used in this study were poly(vinyl alcohol) (PVA) (weight-average molecular weight $M_w = 25$ kg/mol, polydispersity index $PDI = 1.9$) purchased from Polysciences Inc. and polystyrene (PS) ($M_w = 50$ kg/mol, $PDI = 1.06$) purchased from Pressure Chemical Company. PVA solutions were made using deionized (DI) water as the solvent. PS solutions were made using toluene as the solvent. The solutions were filtered using polytetrafluoroethylene (PTFE) syringe filters with $0.2 \mu\text{m}$ pore size, then agitated for 24 hours. Agitation of the PVA solutions were done under elevated temperatures (50°C) to ensure thermodynamic mixing.

Thin films of PVA and PS for the dynamics measurements were prepared and confined between two aluminum (Al) electrodes (known as double Al supported). Al electrode strips, 0.5 mm in width and ~ 100 nm in thickness, were deposited onto glass substrates by thermal evaporation under high vacuum (10^{-7} mbar) in a nitrogen (N_2) environment. Prior to evaporation, the substrates were thoroughly cleaned using DI water, glass detergent, acetone, and toluene under sonication. After Al evaporation, the substrates were brought into ambient air. Films were made by first spin-cleaning (WS-400B-6NPP/LITE/10K, Laurell Technologies) with the used solvent (DI water for PVA), and then spin-coating the previously described solutions at 5000 rpm, 2500 acc for 75 seconds. Typically, BDS film measurements are done with the polymer film confined between hard, electrically conductive electrodes or as a supported film exposing a free surface;^{1,2} for the bilayers in this study, a PS film was deposited via spin casting directly on top of the PVA film. Bilayers were made by simply spin-coating one film on top of the other. Film thicknesses and bilayer conformations were determined using a spectroscopic ellipsometer (SE) (M-2000, J.A. Wollam). Thickness changes were done by varying the weight percent concentration of the solutions.

Samples were then dried under vacuum at room temperature for 12 hours, followed by subsequent annealing at a temperature of 393 K for 24 hours under high vacuum. This temperature is above the bulk T_{gs} of both PVA and PS. Following annealing, Al strip electrodes of the same geometry were then deposited on top of the films in the counter direction under the same conditions. To ensure that the sample geometry is known (area of film in contact with the electrodes), the Al strip electrodes are cut in such a way to ensure that only the directly overlaying parts of the top and bottom electrodes are available for charge transfer. Further details on sample preparation are described elsewhere.²

Measurements of the dynamics were performed using a broadband dielectric spectrometer (BDS) (GmbH, Novocontrol Technologies). Because of probable air and moisture exposure during sample transport, the samples were annealed again within a BDS cryostat (Active Sample Cell ZGS, Novocontrol Technologies) under a N_2 flow environment for 10 hours to ensure that any residual moisture was removed. After in situ annealing, each sample was cooled at a rate of 3 K/min. The BDS sweeps were performed upon step heating in a frequency range of 0.1 Hz to 1MHz with an AC voltage of 0.3V per 100 nm of polymer film. The temperature range was 270K to 420K at a 3K step.

The T_{gs} of the polymers were measured using differential scanning calorimetry (DSC, Q200, TA Instruments) by first heating above the component T_{gs} and holding isothermally for 10 minutes, cooling at 10 °C/min below the component T_{gs} , and then performing the measurement upon heating at 10 °C/min. The glass transition was extracted from the step-like change in the endothermic heat flow baseline, where the baseline before and after the transition were extrapolated to a temperature where the change in heat capacity was at 50% completion. This result was compared to the peak position in the derivative heat flow.

Samples for Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700, Thermo Scientific) were prepared on silicon (Si) substrates with a thin layer of native oxide, thoroughly sonicated with acetone, isopropanol, and water prior to use. Al deposition was done as described previously, except now it covered the entire substrate. PVA films were prepared in the same manner as the dynamic samples, including the same annealing conditions. Reflective measurements were done with a resolution of 4.0 cm^{-1} by averaging 128 scans in the range of $4000 - 400\text{ cm}^{-1}$.

Analysis of BDS Data in the Temperature Representation

In the manuscript, the dynamic data is displayed as a typical frequency sweep experiment - $\epsilon''(\omega)$ is measured at constant T . As long as the experiment is conducted within the linear response regime (small electric field strengths and a time-dependent response based solely on linearity and causality), representation as a temperature sweep - $\epsilon''(T)$ at constant ω - provides identical dielectric information.³ The temperature sweep experiments can be noted for the relative ease of identification of the relaxation processes - frequency sweep measurements, particularly in thin films, can suffer from electrode and interfacial polarization, which convolutes the dielectric response at low frequencies and/or high temperatures.³

An example of the raw dielectric loss curves as a function of temperature for a $h = 70$ nm PVA film confined between two Al electrodes - Al/PVA(70 nm)/Al - obtained using BDS is shown in Figure S1a. As with its corresponding frequency representation (Figure 1a), the peak that appears is due to the segmental, or α , relaxation process, and shifts to lower temperatures with decreasing frequencies of the applied AC voltage, as expected for pure polymers under isochronal measurement conditions. These curves are well described using a modified version⁴ of the Havriliak -Negami (HN) function (not shown). From this empirical fit to the data, a characteristic relaxation temperature associated with the dielectric loss peak maximum of the imaginary portion of the permittivity $\epsilon''(T)$ can be identified. The relaxation rates as calculated from both the frequency and temperature representations are plotted as $1/\tau$ vs. $1/T$ in Figure S1b. The results are in excellent agreement, confirming that both types of experiments yield the same results.

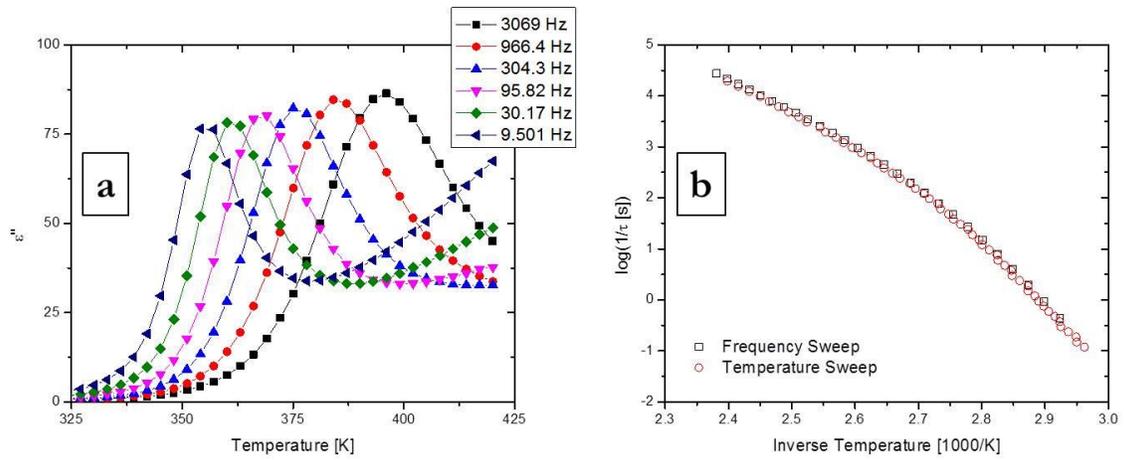


Figure S1: (a) Raw dielectric loss curves at different frequencies of the applied AC electric field for a 70 nm PVA film capped between two Al electrodes (Al/PVA(70 nm)/Al). (b) Temperature dependencies of the inverse PVA segmental relaxation times in Al/PVA(70 nm)/Al as calculated from the peaks in the dielectric loss curves of both the frequency sweep and the temperature sweep.

Modeling for Dielectric Properties in Series

The simplest model to describe the inhomogeneous bilayer system is as a double layer arrangement where each layer is characterized by a complex dielectric permittivity. It is well known that capacitive properties can be modelled in the following manner:

$$\frac{1}{C_{equivalent}} = \frac{1}{C_1} + \frac{1}{C_2} \quad (S1)$$

Of course, the relationship between parallel plate capacitance and permittivity is defined as follows:

$$C = \varepsilon \frac{A}{D} \quad (S2)$$

where A is area of the capacitor perpendicular to current flow and D is the spacing between the plates (in our case the thickness of the layer). Because the area is unchanged throughout the sample, the complex permittivity can be defined as:

$$\frac{1}{\varepsilon_{total}^*(\omega)} = \frac{\phi}{\varepsilon_{PVA}^*(\omega)} + \frac{1-\phi}{\varepsilon_{PS}^*(\omega)} \quad (S3)$$

where $\varepsilon_{total}^*(\omega)$ is the dielectric response of the entire bilayer system, $\varepsilon_{PVA}^*(\omega)$ and $\varepsilon_{PS}^*(\omega)$ are the contributions from the PVA and PS layers respectively, and ϕ is the thickness ratio of PVA to the whole bilayer. Algebraic manipulation can get the PVA dielectric response as:⁵

$$\varepsilon_{PVA}^*(\omega) = \phi \left[\frac{1}{\varepsilon_{total}^*(\omega)} - \frac{1-\phi}{\varepsilon_{PS}^*(\omega)} \right]^{-1} \quad (S4)$$

In the experimental analysis in the manuscript, equation S4 is applied for all the bilayer systems across all measured frequencies at all the temperatures. The PS contribution used in this equation is obtained by measuring double Al capped PS films – Al/PS(L)/Al – of the appropriate thickness (except for the 5 nm PS case, in which the 15 nm PS complex permittivities are used). These PS films are measured under different experimental conditions than exist in the bilayer – double Al cap rather than asymmetric Al and PVA confining interfaces.

For modelling purposes, we are interested in two effects: (1) how does the PVA dielectric response compare to the total bilayer dielectric response and (2) what effect does the PS dielectric response have on the PVA dielectric response. As such, consider a model bilayer system in which the film thicknesses are equal ($\Phi = 0.5$). Each component response in our frequency and temperature range is modelled as a single relaxation described by the HN function:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1+(i\omega\tau)^{\alpha})^{\beta}} \quad (\text{S5})$$

Relative values for the parameters for the total bilayer response and PS contribution can be estimated from the bilayer and single PS film experimental data, respectively, at an arbitrary temperature. These complex permittivities can then be applied to equation S3 to calculate the corresponding PVA dielectric contribution. Note that, for this particular model, we consider material conductance to be equal and therefore negligible for all samples and focus solely on dielectric properties.

Figure S2 shows the frequency dependent dielectric losses peaks of the bilayer, PS with varying parameters, and the correspondingly calculated PVA at an arbitrary temperature. First note that the PVA response is shifted from the total bilayer response in both peak and permittivity – despite the much stronger PVA signal, the PS permittivity still has a contribution and therefore should be taken into account. However, note what happens when the PS dielectric strength or relaxation time is varied – even varying these parameters by an order of magnitude leaves the PVA dielectric response as extracted from the same total bilayer dielectric response relatively unchanged. Thus, even though in our analysis we use the experimental data from PS films under double aluminum confinement rather than asymmetric confinement, in which the

interface change may have effects on the PS dynamics, such changes appear to be negligible for the extraction of PVA dynamics.

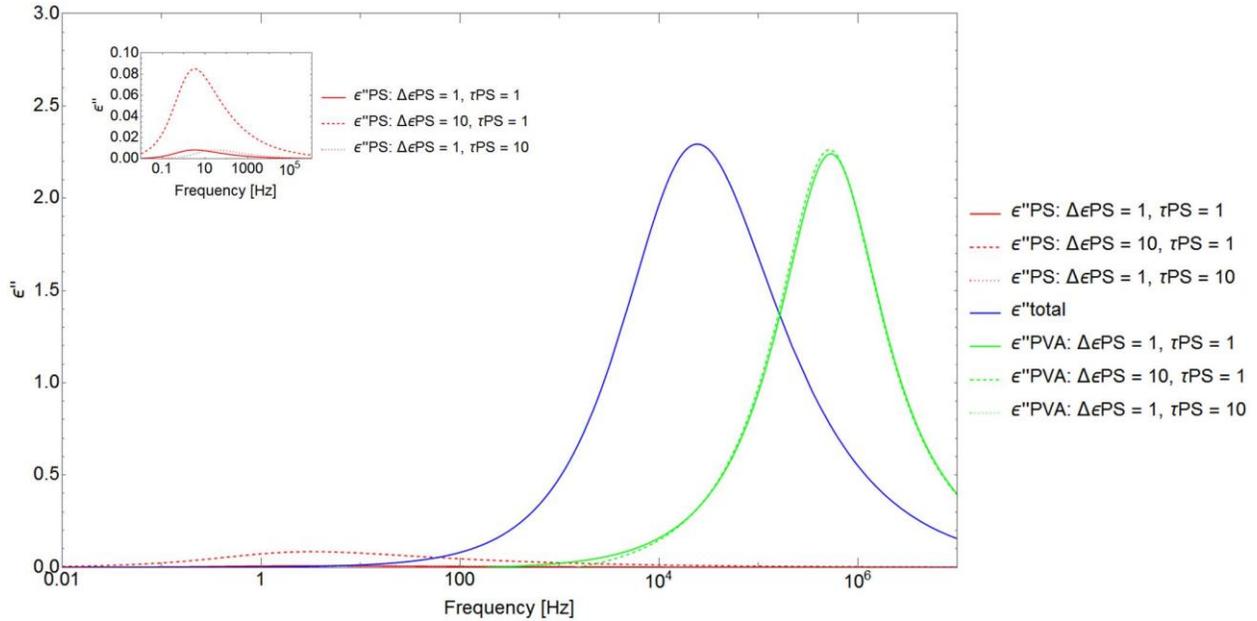


Figure S1: Model of the dielectric loss response of 0.5 PS film and 0.5 PVA film in series. Red lines represent the PS dielectric loss, green lines represent the PVA dielectric loss, and the blue line represents the series total dielectric loss. Model is based on equation S3, in which the complex permittivities of PS and the bilayers are inputs and the PVA contribution is calculated. Red dashed and dotted lines represent shifts of one order of magnitude in the PS dielectric strength and characteristic relaxation time, respectively, and corresponding green dashed and dotted lines show how the PVA dielectric loss is affected. Inset plot shows an enlarged version of the PS dielectric loss.

It is noteworthy that, because there is an inner dielectric boundary layer, Maxwell/Wagner polarization will occur due to a buildup of charge carriers at said boundary layer. This gives rise to an additional conductivity contribution and a relaxation process due to charge build-up, creating an internal dipole moment. However, because charge carrier transport is a temperature dependent process that takes place at higher temperatures than molecular relaxation processes, it does not affect the measurements in our temperature and frequency range.

Moisture and Crystallinity Concerns

We address the potential effects that moisture and changes in the degree of crystallinity might have on the reliability of our measurements of PVA dynamics. It has been suggested that moisture, if not carefully eliminated, could lead to a shift in the relaxation times and the appearance of a secondary Arrhenius relaxation.⁶ These were determined to not be issues in our study – we used a more stringent annealing procedure than proposed in the literature to remove moisture from our samples: 120 °C for at least 24 hours under high vacuum, followed by additional in situ annealing. Only a single VFT-type relaxation was observed in the dynamics, which is consistent with the absence of moisture. Moreover, confirmation of the the removal of moisture was evident by the absence of a BDS signal associated with water.⁷ Certain studies suggest that deviations of the dynamics might be due to improper annealing conditions;^{8–10} we have observed no unusual changes or fluctuations that would be due to annealing in our experiments.

The second factor that has been suggested to be potentially problematic is the crystallinity of PVA. Fourier-transform infrared spectroscopy (FTIR) was used to identify quantitative correlations between the intensity of the crystalline band normalized to the intensity of the C-O stretching band (see Figure S3).¹¹ Our measurements indicate a degree of crystallinity of roughly 57%, which is well within literature values for dried PVA¹² and does not vary across all PVA film thicknesses.

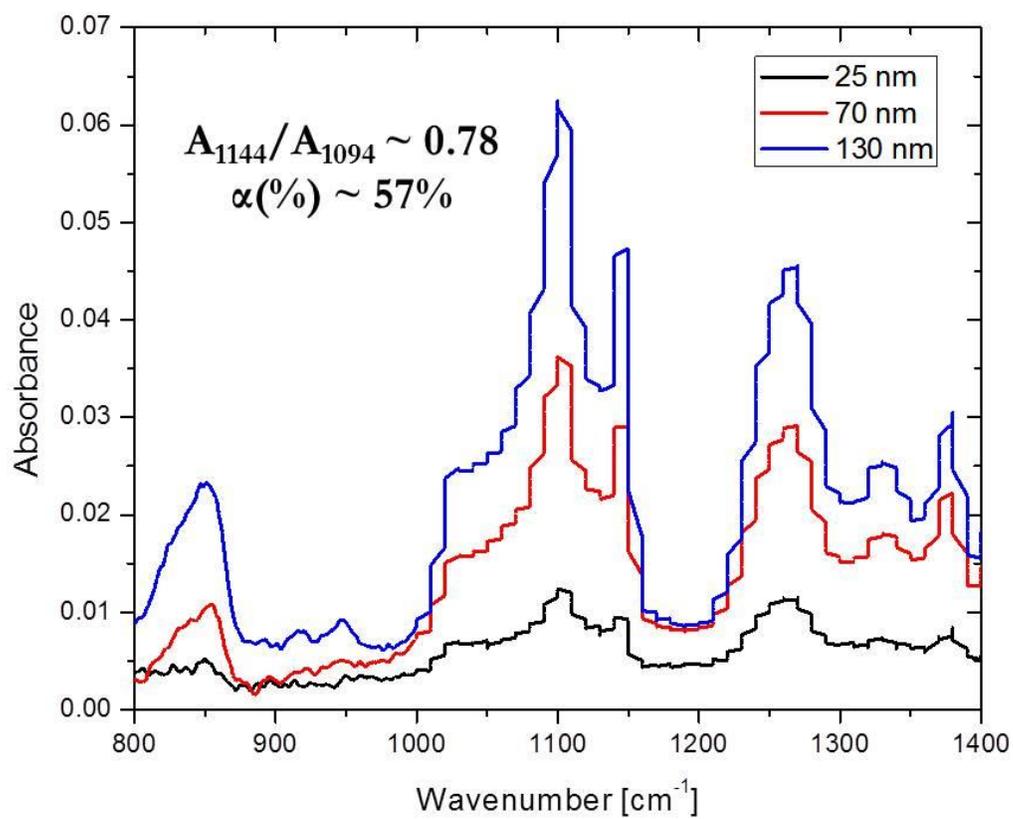


Figure S3: IR spectrum of 3 different PVA films showing the C-C stretching band (A_{1144}) and the C-O stretching band (A_{1094}). The ratio between the two relates to the degree of crystallinity, giving a value of roughly 57%.

References

- (1) Fukao, K. Glass Transitions and Dynamics in Thin Polymer Films: Dielectric Relaxation of Thin Films of Polystyrene. *Phys. Rev. E* **2000**, *61* (2), 1743–1754.
- (2) Serghei, A.; Kremer, F. Metastable States of Glassy Dynamics, Possibly Mimicking Confinement-Effects in Thin Polymer Films. *Macromol. Chem. Phys.* **2008**, *209* (8), 810–817.
- (3) Kremer, F.; Schönhals, A. *Broadband Dielectric Spectroscopy*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2003.
- (4) Kipnusu, W. K.; Elmahdy, M. M.; Tress, M.; Fuchs, M.; Mapesa, E. U.; Smilgies, D.-M.; Zhang, J.; Papadakis, C. M.; Kremer, F. Molecular Order and Dynamics of Nanometric Thin Layers of Poly(styrene-*B*-1,4-Isoprene) Diblock Copolymers. *Macromolecules* **2013**, *46* (24), 9729–9737.
- (5) Casalini, R.; Zhu, L.; Baer, E.; Roland, C. M. Segmental Dynamics and the Correlation Length in Nanoconfined PMMA. *Polymer* **2016**, *88*, 133–136.
- (6) Betzabe Gonzalez-Campos, J.; Garcia-Carvajal, Z. Y.; Prokhorov, E.; Luna-Barcenas, J. G.; Mendoza-Duarte, M. E.; Lara-Romero, J.; del Rio, R. E.; Sanchez, I. C. Revisiting the Thermal Relaxations of Poly(vinyl Alcohol). *J. Appl. Polym. Sci.* **2012**, *125* (5), 4082–4090.
- (7) Urakawa, O.; Fuse, Y.; Hori, H.; Tran-Cong, Q.; Yano, O. A Dielectric Study on the Local Dynamics of Miscible Polymer Blends: poly(2-Chlorostyrene)/Poly(vinyl Methyl Ether). *Polymer* **2001**, *42* (2), 765–773.
- (8) Kremer, F.; Tress, M.; Mapesa, E. U. Glassy Dynamics and Glass Transition in Nanometric Layers and Films: A Silver Lining on the Horizon. *J. Non-Cryst. Solids* **2015**, *407*, 277–283.
- (9) Boucher, V. M.; Cangialosi, D.; Yin, H.; Schönhals, A.; Alegría, A.; Colmenero, J. Tg Depression and Invariant Segmental Dynamics in Polystyrene Thin Films. *Soft Matter* **2012**, *8*, 5119.
- (10) Sharp, J. S.; Forrest, J. A. Dielectric and Ellipsometric Studies of the Dynamics in Thin Films of Isotactic Poly(methylmethacrylate) with One Free Surface. *Phys. Rev. E Stat. Nonlin. Soft Matter Phys.* **2003**, *67* (3 Pt 1), 031805.
- (11) Tretinnikov, O. N.; Zagorskaya, S. A. Determination of the Degree of Crystallinity of Poly(vinyl Alcohol) by FTIR Spectroscopy. *J. Appl. Spectrosc.* **2012**, *79* (4), 521–526.
- (12) Hassan, C. M.; Peppas, N. A. Structure and Applications of Poly(vinyl Alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing/Thawing Methods. In *Biopolymers · PVA Hydrogels, Anionic Polymerisation Nanocomposites*; Advances in Polymer Science; Springer Berlin Heidelberg, 2000; pp 37–65.