Determining T_g via Fluorescence:

Linear fits of the integrated fluorescence data to glassy and rubbery regimes were determined from at least four data points at each of the extreme ends of the temperature range. Data points were included moving inward to insure $R^2 > 0.99$. Once this condition was no longer reached, due largely to changes in the curvature related to the glass transition, data points were no longer included in determining linear fits.

Exponential Fits to Bilayer Annealing data:

In order to quantify and clearly compare the recovery of T_g(bulk) between these systems, the data in Figure 7 was fit to the exponential function:

$$T_g = A \cdot e^{-\frac{t_{Bann}}{\tau}} + T_g(bulk) \tag{S1}$$

where the fitted prefactor A (< 0), represents the initial deviation from T_g(bulk) after consolidating the bilayer (fitted values all within error of $t_{Bann} = 0$ measurement), t_{Bann} is the bilayer annealing time at 150°C, and τ represents an intrinsic timescale of the T_g recovery process. Reasonable fits, adjustable parameters τ and A, are obtained from fitting the bilayer anneal data to Equation S1, as illustrated by the solid lines in Figure S1. The intersection of these fits with T_g(bulk) − 1 (to account for error in T_g(bulk) and avoid effect of asymptotes) is then used to determine the recovery time, t_{Bann}^*, which is plotted in Figure 7D.
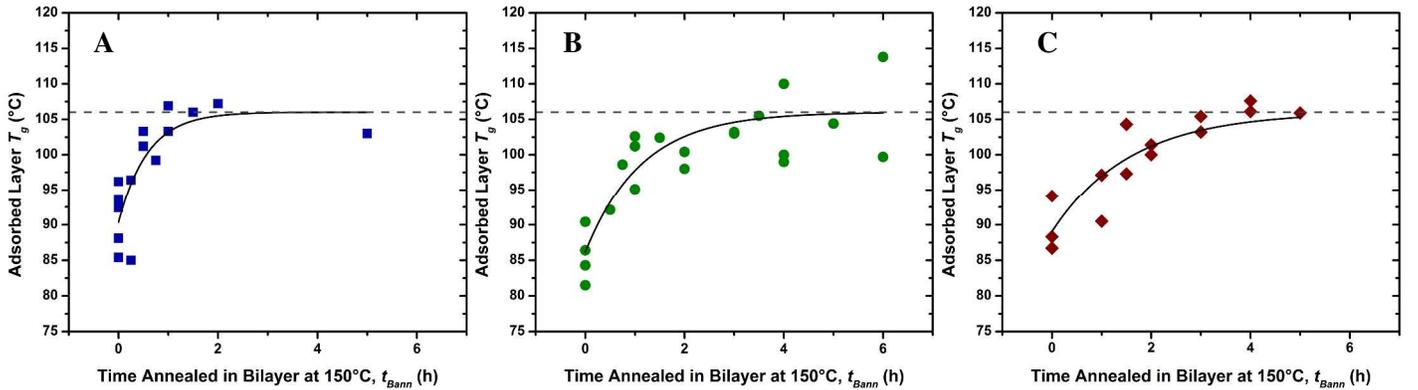
Figure S1. Exponential fits (solid lines) to (A) 4-hour (B) 6-hour and (C) 10-hour bilayer annealing systems. Averaged data are also shown in Figure 7. Dashed lines represent T_g(bulk).

FVHD Model Derivations:

For Figure 4:

$D(T)$ for free volume holes in bulk PS has been previously reported to follow the relationship:[1,2]

$$D(T) = D_0(VFT) \cdot e^{\left(-B/T-T_0\right)} + D_0(Arr) \cdot e^{\left(-E/kT\right)} \tag{S2a}$$

Where $D_0(VFT)$ = 302 cm2/s, B = 1000 K, T_0 = 341 K , $D_0(Arr)$= 1.80 x 10^{15} cm2/s, E= 190 kJ/mol, and k is the Boltzmann constant.[2,3] Comparing $D(T)$ calculated at the average T_g of our long-annealed adsorbed layers (90°C) to that calculated at the average T_g of bulk films (106°C), we found that $D(T_g\_ads) = D(T_g\_bulk)/343$. We then used this relationship to arrive at $D_{ads}(T_g) = D_{bulk}(T_g)/343$. Therefore, for our calculations,

$$D_{ads}(T) = \frac{1}{343} \cdot \left(D_0(VFT) \cdot e^{\left(-B/T-T_0\right)} + D_0(Arr) \cdot e^{\left(-E/kT\right)} \right) \qquad (S2b)$$

In order to relate the measured thickness of the irreversibly adsorbed layer to the free interface available as a sink for diffusing free volume, we use geometric arguments:

We know

$$h_{ads} = \frac{2V}{A_{total}} \qquad (S3a)$$

Where h_{ads} is the thickness of the adsorbed nanolayer, A_{total} is the area of both surfaces parallel to the substrate, and V is the volume of the adsorbed layer. We also define an effective thickness h_{eff} that corresponds to the amount of free interface, A_{free}:

$$h_{eff} = \frac{2V}{A_{free}} \qquad (S3b)$$

Now, holding volumes equal and rearranging S3a and S3b gives us the relationship

$$h_{eff} = h_{ads} \cdot \left(\frac{A_{free}}{A_{total}} \right)^{-1} \qquad (S4)$$

We have measured values for h_{ads}, and A_{free}/A_{total} can be calculated employing Equation 4 from the text,

$$\frac{A_{free}}{A_{total}} = \left(\frac{A_{free}}{A_{total}} \right)_{max} - a \cdot t_{ann} \qquad (4)$$

Using the boundary conditions (A_{free}/A_{total}) = 0.5 at t_{ads} = 6 hours, corresponding to no free interface at the substrate and a complete free interface at the free surface, allows us to define:

$$a = \frac{1}{6} \left[\left(\frac{A_{free}}{A_{total}} \right)_{max} - 0.5 \right] \qquad (S5)$$

Thereby reducing the fitting parameters to one: $(A_{free}/A_{total})_{max}$. For a selected value of $(A_{free}/A_{total})_{max}$ (selection is explained later), A_{free}/A_{total} can then be calculated from Equation 4 and input into Equation S4 with measured h_{ads} value to solve for h_{eff}.

After slight modifications to account for bulk behavior,[2] values of h_{eff} (calculated from measured values of h_{ads} and fitted parameter $(A_{free}/A_{total})_{max}$) were used in Equation 3 from the text:

$$\left(\frac{h_{eff}}{2}\right)^2 = 2D(T_g)q^{-1} \tag{3}$$

where $D(T_g)$ is the diffusion coefficient of free volume holes at T_g and q is the cooling rate. In order to determine the T_g corresponding to calculated values of $D(T_g)$, and thus the T_g predicted by the FVHD model, the temperature, T, was found to match $D(T_g)$ to $D_{ads}(T)$, calculated in Equation S2b. Therefore, T_g(FVHD) is defined:

$$T_g(FVHD) = \{T : D(T_g) = D_{ads}(T)\} \tag{S6}$$

The equality can be interpreted as $T_g(FVHD)$ is the temperature at which free volume holes have effectively diffused out of the film, given the assumed diffusion coefficient for free volume holes in adsorbed layers.

Selection of $(A_{free}/A_{total})_{max}$:

Many values of $(A_{free}/A_{total})_{max}$ were used to calculate T_g(FVHD), and these values were then compared to T_g(fluor). The $(A_{free}/A_{total})_{max}$ value that provided the lowest mean squared error (MSE) was selected, a value of 0.55.

For Figure 6:

Similar logic was followed as outlined for Figure 4 calculations. However, to describe the fractional free surface as a function of original annealing time for capped films, we used the equation:

$$\frac{A_{free}}{A_{total}} = \left(\frac{A_{free}}{A_{total}}\right)_{min} + b \cdot t_{ann} \tag{S7}$$

Where $(A_{free}/A_{total})_{min}$ is the amount of free interface at $t_{ads} = 0$, when we expect maximum interpenetration of the top layer (complete coverage of the free surface). This value was determined by the initial condition of Equation 4, with only the free interface from the substrate contributing, ie. $(A_{free}/A_{total})_{min} = 0.05$. We expect less penetration of the top layer with increased degree of adsorption until $A_{free}/A_{total} = 0.5$ at $t_{ads} = 6$ hours, when we expect full coverage at the substrate and no interpenetration of the top bilayer. Using these conditions, $b = 0.075$ h^{-1}. Once again, defining T_g(FVHD) in accordance with Equation S6, we determined the predicted values shown in the text.

For Figure 7:

Once again, the difference in derivation for FVHD model predictions for Figure 7a-c lies in the description of the fractional free volume changes with annealing time. We use the equation:

$$\frac{A_{free}}{A_{total}} = \left(\frac{A_{free}}{A_{total}}\right)_{max} - c \cdot t_{Bann} \tag{S9}$$

Where c is the rate of filling with bilayer annealing time and t_{Bann} is the bilayer annealing time. For each system (4, 6, and 10-hour irreversibly adsorbed layers), $(A_{free}/A_{total})_{max}$ is determined from the value of (A_{free}/A_{total}) for the corresponding t_{ads} in Figure 6. The other boundary condition, we define as $A_{free}/A_{total} = 0$ when $t_{Bann} = t_{Bann}^*$, where t_{Bann}^* is the T_g(bulk)

recovery time. The determination of $t_{Bann}{}^{*}$ was described previously. Based on the boundary conditions, FVHD model fits to Figures 7a-c were established with no additional fitting parameters.

References

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