Electronic Supplementary Information (ESI)

Structure-induced switching of interpolymer adhesion by polymer chains adsorbed onto a planar solid

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1. X-ray reflectivity results of the PEO adsorbed layers

Figure S1 shows the XR results of the 46kPEO interfacial sublayer and flattened layer before the interdiffusion experiment. The XR data was fit using a standard multilayer fitting routine with three parameters (thickness, dispersion value (δ in the X-ray refractive index), and interfacial roughness) for each layer. The parameters including their standard deviations were obtained from non-linear least squares regression on the experimental reflectivity curves. From the best fits to the data, the thicknesses of the 46kPEO interfacial sublayer and flattened layer were found to be 11.6 ± 0.2 nm and 2.6 ± 0.2 nm, respectively. Based on the AFM cross sectional analysis of the interfacial sublayer shown in Figure 2b, we can then conclude that finger-like crystals of about 9 nm in height were grown on top of the 2.6 nm-thick flattened layer. The dispersion (δ) value of the interfacial sublayer and flattened layer were estimated to be $5.6 \pm 0.1 \times 10^{-6}$ and $4.6 \pm 0.1 \times 10^{-6}$, respectively. The bulk dispersion (δ_{bulk}) with the X-ray energy of E = 8.04keV is 4.0 × 10⁻⁶ such that the δ value of the flattened layer is about 10 - 15 % higher than that of the bulk. On the other hand, in the case of the interfacial sublayer, due to its rough surface (Figure 2b), the dispersion value may not be accurate. Also, we were not able to validate the formation of the high-density flattened layer in the interfacial sublayer, possibly due to the limited q-range and flux in the XR measurements performed with a lab source at NIST.



Figure S1. XR profiles of the 46kPEO interfacial sublayer (red) and flattened layer (blue). The solid lines correspond to the best-fits to the data based on the dispersion (δ) profiles against the distance (z) from the HF-etched Si surface shown in the inset.

2. Surface Morphology of 100kPEO interfacial sublayer and flattened layer

Figure S2(a) and (b) show representative AFM height and phase images of the 95kPEO interfacial sublayer. The thickness of the 95kPEO was estimated to be 15 nm based on the AFM height image (Table 1). We can see dendrite crystalline pattern with branching angles of ~ 90 deg, which is slightly different from the seaweed-like crystalline pattern observed from the interfacial sublayer composed of 20kPEO (Figure 5a) and 46kPEO (Figure 3b). Such molecular weight dependence on the crystalline morphology is in good agreement with previous findings by Zhang et al.¹. The height profile shown in Figure S2c demonstrates that the dendrite crystals are grown on top of the 2.5 nm-thick flattened layer, as discussed for the 46kPEO interfacial sublayer (Figure 3). Namely, the dark region in the height image is not the substrate surface, but the flattened layer surface. At the same time, it is clear that the dendrite structures are less dense than the seaweed-like patterns of the 46kPEO interfacial sublayer. According to Cheng and co-workers², when chain lengths become longer, segment-solid contact points per chain are greater. This implies that chain folding for longer polymer chains adsorbed on the substrate surface becomes hindered, resulting in a less densely packed interface. Further experiments are currently in progress to clarify the hypothesis and will be summarized in a forthcoming publication. On the other hand, the surface morphology of the flattened laver (Figure S2(d)) is smooth and featureless, which is in line with the surface morphology of the 46kPEO flattened layer (Figure 3a).



Figure S2 AFM height (a) and phase (b) images of the 95kPEO interfacial sublayer. The scan sizes of the images are 5 μ m×5 μ m. The height scale is 0-16 nm. (c) Cross-sectional height profile along the dotted line shown in (a). (d) The AFM height image of the 95kPEO flattened layer. The scan size is 1 μ m×1 μ m and the height scale is 0-1 nm.

3. Contact angle measurements and surface tension measurements

The static contact angles of the 20kPEO spin cast thin films and adsorbed layers were measured with the KSV CAM 200 optical contact angle meter.³ The volume of each liquid droplet was fixed to 2 μ L. The static contact angles were collected 1 min after the liquid droplet was dropped onto the sample surface, and we did not observe any change in the static contact angles for up to 5 min. The calculation of the surface tension was based on the two-component theory, i.e., the polar component and the dispersion component. Based on Young's equation (eq. S1), Fowkes theory equation (eq. S2), and reference parameters of the test liquids tabulated in Table S1, the polar and dispersion component refers to the total surface tension.

$$\sigma_{s} = \sigma_{sl} + \sigma_{l} * \cos\theta \quad (S1)$$

$$\sigma_{sl} = \sigma_{s} + \sigma_{l} - 2*(\sqrt{\sigma_{s}^{D} * \sigma_{l}^{D}} + \sqrt{\sigma_{s}^{P} * \sigma_{l}^{P}}) \quad (S2)$$

(σ_s and σ_l are the total surface tension of the solid and liquid, respectively. σ_{sl} is the interfacial energy between solid and liquid. θ is the static contact angle of the liquid. σ_s^D and σ_s^p are the dispersion and polar parts of the surface energy of the solid, respectively. σ_l^D and σ_l^p are the dispersion and polar parts of the surface energy of the liquid, respectively.)

 Table S1. Surface tensions and contact angles of the testing liquids at room temperature

Chemical	Surface	Dispersion	Polar	Contact
	Tension	Component Componen		angle (θ)
	$(\sigma_l, \mathrm{mJ/m}^2)$	$(\sigma_l^D, \mathrm{mJ/m}^2)$	$(\sigma_l^P, \text{mJ/m}^2)$	
1, 4-butanediol	44	24	20	$19 \pm 2^{\circ}$
Glycerol	64	34	30	$53 \pm 1^{\circ}$

Based on the liquid contact angle measurements, we found that the static contact angles of the 20kPEO flattened layer, the interfacial sublayer, the 20 nm-thick film and the 100 nm-thick film were nearly identical ($\theta = 53 \pm 1^{\circ}$ for glycerol and $\theta = 19 \pm 2^{\circ}$ for 1, 4-butanediol, respectively). The surface tension (γ) of all the PEO samples was estimated to be 43 mJ/m² with a dispersion part (γ_d) of 31 mJ/m² and a polar part (γ_p) of 12 mJ/m², which is consistent with the value reported from literature⁴. Note that the surface tension of PEO was found independent of molecular weight.

4. Coarse-Grained Molecular Dynamics Simulation and Calculation of the Potential of Mean Force

We performed coarse-grained molecular dynamics simulations of a polymer thin film sandwiched by highly adsorbing substrates to determine the potential of mean force of separating one of the substrates from the film. The initial configuration of the thin film was taken from the simulations of Carrillo et al.,⁵ for the case of fully flexible polymer chains, with degree-of-polymerization, N = 50 (which is below the critical entanglement length, $N_e = 85^6$), and in contact with an analytical Lennard-Jones wall with well depth equal to $\varepsilon_{LJ} = 8 kT$ (Here, kT is the thermal energy and σ is the bead diameter). From this initial configuration, all the polymer chains within an interval, d, away from both substrates were retained, while the rest of the chains were removed (see, Figures S3c and S3d). The conformation of the chains within d (see Figure S3d) were used to create a new simulation box, where new substrates composed of Lennard-Jones (LJ) beads are introduced, as shown in Figures S3d and S3e. The new simulation box has periodic boundary conditions in all directions and a vacuum spanning ~ 70σ was added between the top surface of the top substrate to the periodic image of the bottom surface of the bottom substrate to ensure no contacts between the periodic images of the substrates during the delamination process. To minimize finite size effects, the x and y dimensions were set to a much larger value (i.e., 21.8σ) than the bulk value of the square root of the mean square end-to-end distance of the polymer (= 9σ). The top and bottom substrates were composed of randomly packed LJ beads with number density of $1\sigma^{-3}$. During the delamination process, the beads of the bottom substrate were frozen, while those beads belonging to the top substrate were free to move but were bonded to its nearest neighbor in order to keep the substrate's shape.

The truncated-shifted Lennard-Jones (LJ) potential describes the interaction between all beads,

$$U_{WCA}(r) = \begin{cases} 4\varepsilon_{LJ} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} - \left(\frac{\sigma}{r_{cut}} \right)^{12} + \left(\frac{\sigma}{r_{cut}} \right)^{6} \right] & r < r_{cut} \\ 0 & r \ge r_{cut} \end{cases}$$
(S3)

where r_{ij} , is the distance between the i^{th} and j^{th} bead, ε_{LJ} is the well depth and r_{cut} is the cutoff, which is equal to 2.5 σ . The ε_{LJ} between monomer beads and between monomer and substrate beads are 1 kT and 8 kT, respectively.

The connectivity of monomers into polymer chains was maintained by the finite extension nonlinear elastic (FENE) potential:

$$U_{FENE}(r) = -\frac{1}{2}k_{s}R_{m}^{2}\ln\left(1 - \frac{r^{2}}{R_{m}^{2}}\right)$$
(S4)

with the spring constant $k_s = 30.0 kT/\sigma^2$, and maximum bond length $R_m = 1.5\sigma$. Also, to maintain the structure of the top substrate, each bead in the top substrate is bonded to its nearest neighbor using a harmonic bond,

$$U_H(r) = k_h (r - r_o)^2,$$
 (S5)

where the harmonic spring constant (k_h) is set to 200 kT/σ^2 and the equilibrium bond length, r_o is 1 σ . The simulations were carried out in a constant number of particles and temperature ensemble (canonical or *NVT* ensemble). The constant temperature was maintained by coupling the system to a Langevin thermostat implemented in LAMMPS^{7, 8}. In this case, the equation of motion of the *i*th particle is

$$m\frac{d\overline{v_i}(t)}{dt} = \vec{F_i}(t) - \xi_L \overline{v_i}(t) + \vec{F_i}^R(t)$$
(S6)

where $\overline{v}_{l}(t)$ is the bead velocity and $\vec{F}_{l}(t)$ is the net deterministic force acting on the bead with mass, m which is set as unity for all particles. $\vec{F}_{l}^{R}(t)$ is the stochastic force with zero average value $\langle \vec{F}_{l}^{R}(t) \rangle = 0$ and δ -functional correlations $\langle \vec{F}_{l}^{R}(t)\vec{F}_{l}^{R}(t') \rangle = 6\xi k_{B}T\delta(t-t')$. The velocity-Verlet algorithm with a time step of 0.01 τ was used for time integration.

Prior to the delamination procedure, the two substrates along with their associated polymer thin films are kept at a distance of 5σ away from each other and equilibrated in a separate step (1000 τ) to let the Guiselin brush develop further in each interface, and also to prevent bridging or prevent a chain from being adsorbed in both substrates (see Figure S3d). The top substrate is then translated such that the two polymer films barely touch, after which, because of the attractive interactions between the top and bottom films, the films merge and further equilibration (5000 τ) was performed to equilibrate the film thickness or *h* as shown in Figure S3e.

To calculate the potential of mean force (PMF), we performed umbrella sampling and used the weighted histogram analysis method.⁹ Here, we applied a biasing harmonic potential,

$$U_{Bias}(z) = \frac{1}{2}k_{bias}(z - z_o)^2$$
(S7)

where k_{bias} is 50,000 kT and z_0 is scanned at an interval of 0.01 σ . The PMF was calculated using the WHAM code developed by Grossfield.¹⁰ During the umbrella sampling procedure, the top substrate is moved to its specified z location, z_0 , and the simulations was equilibrated for 500 τ prior to data gathering (see, Figure S4). For

populating the histogram used in WHAM, the position of the top substrate was collected every τ for a 500 τ interval. Here, τ is the characteristic time defined as $\tau = \sigma (m/kT)^{1/2}$.



Figure S3. Density distribution (a) and snapshot (b) of polymer chains (red beads) confined to a highly adsorbing bounding wall where the data and polymer configurations were taken from Carrillo et al.⁵ Polymer chains with center-of-mass located in the interval, d, (c and d) are then used to create a new simulation box with new substrates composed of LJ beads (e). The top and bottom films were equilibrated separately for up to 1000 τ to allow chains to fully coat their respective substrate (d). Then, the coordinates of the top film were translated such that the top film comes into contact with the bottom film. We performed another equilibration step (5000 τ) of the merged film to equilibrate the film thickness, h (see, (e)). Also, the top substrate (cyan beads) and bottom substrate (magenta beads) are shown in (e).



Figure S4. Equilibrium conformation of a polymer thin film (red beads) adsorbed to highly adsorbing substrates (cyan and magenta beads) is shown in the leftmost image. Middle and rightmost images show the top substrate (cyan beads) being moved away from the film by applying a harmonic biasing potential acting on the center-of-mass of the top substrate. The histograms of the fluctuations of the location of the center-of-mass of the top substrate are used in calculating the PMF.



Figure S5. Monomer density distribution of free segments, trains, loops and tails (ρ_{free} , ρ_{train} , ρ_{loop} , and ρ_{tail} , respectively) along the z-direction, where $z = 0\sigma$ is the position of the interface between the bottom substrate and the polymer film for the systems with $d = 5\sigma$ (left column) and $d = 10\sigma$ (right column). Here, Δz pertains to the displacement (relative to the equilibrium position) of the position of the harmonic potential that pegs the position of the center-of-mass of the top substrate during the delamination process.

5. Formation of the PEO flattened layer

Figure S5 shows representative AFM height images of the 46kPEO flattened layer pre-annealed at 85 °C with different annealing times: (a) 0 h, (b) 0.5 h, (c) 1 h, and (d) 2 h. The original thickness of the 46kPEO film was 50 nm before rinsing. As seen from the images, a homogeneous PEO flattened layer was observed after annealing for more than 2 h, which is in line with previous findings⁴. In contrast, the flattened layers with pre-annealing time of less than 2 h were inhomogeneous with low surface coverage.



Figure S6. AFM height images of 46kPEO flattened layer pre-annealed at 85 °C with different annealing times: (a) 0 h, (b) 0.5 h, (c) 1 h, and (d) 2 h. The corresponding height profiles along the white lines obtained from cross sectional analysis are shown below each image. The dotted line corresponds to the surface of the HF-etched Si substrate.

6. AFM phase images of the 46kPEO flattened layer and interfacial sublayer.



Figure S7. The AFM phase images of (a) the 46kPEO flattened layer and (b) 46kPEO interfacial sublayer prepared on Si substrates. The phase scale is fixed from -10 to 10 deg. The corresponding AFM height images are shown in Figure 3 in the main text.

7. Surface morphology of the 20kPEO flattened layer before and after the adhesion measurement.



Figure S8. AFM height images of the 20kPEO flattened layer: (a) before and (b) after the adhesion experiment. The scale bars correspond to 10 μ m. The height scales for both images are 0-2 nm. The local surface topology of the 20kPEO flattened layer after the adhesion experiment is shown in (c). The scan size is 1 μ m × 1 μ m and the height scale is 0-1 nm. The height profile along with the red line shown in (c) is plotted in (d).

8. Adhesion experiments for the PS flattened layers and interfacial sublayers

Three different molecular weights of polystyrene (PS) ($M_w = 100$ kDa, 221 kDa and 650 kDa, $M_w/M_n < 1.15$, Pressure Chemical Co. and Scientific Polymer Product Inc.) were used. To produce the PS interfacial sublayer and flattened layer, 60 nm-thick PS spin-cast films were prepared on HF-etched Si substrates via spin coating and then annealed at a temperature (T = 150 °C) far above the bulk glass transition temperature (~ 100 °C) under vacuum below 10⁻³ Torr for 2-5 days. The details have been described elsewhere¹²⁻¹⁴. The thickness of the thin films was characterized by ellipsometry technique (Rudolf Auto EL- II) with a refractive index of 1.589 for PS. These films were then leached in baths of a fresh good solvent (chloroform for the flattened layer and toluene for the interfacial layer) at room temperature until the resultant film thickness remained unchanged. This selective extraction of the two different adsorbed chains is due to the large difference in the desorption energy between the loosely adsorbed chains and the flattened chains, which is proportional to the number of segment-surface contacts¹⁵. The resultant PS flattened layers and interfacial sublayers were post-annealed at a temperature above T_g in a vacuum oven overnight to remove any excess solvent molecules trapped in the adsorbed layers.

The PS flattened layers and interfacial sublayers prepared on the Si substrates (1 cm × 1 cm in a surface area) were first pressed together with an upper 200 nm-thick PS film on the Si substrate with a constant pressure of 40 MPa at 170 °C (>> T_g). The bottom adsorbed layers were then fixed to a dial caliper with the same glue used for the PEO films, while the upper 200 nm thick film was attached to one end of a mechanical spring with a spring constant of either 4 or 0.55 N/cm with the same glue.

It should be noted that, as reported previously^{11, 12, 14}, the flattened layers (about 2 nm in thickness) composed of these high M_w PS did not cover the HF-etched Si substrates completely (the surface coverage was about 70%), while the interfacial sublayers covered the substrate entirely. However, we also confirmed that the flattened layer composed of low M_w PS ($M_w = 30$ kDa), which covered the HF-etched Si substrate entirely, did not show any adhesion either with the same adhesion testing device. This indicates that the effect of the exposed Si surface (for the flattened layers composed of the three high M_w PS) on the adhesion measurements can be ignored.

measurements for the PS adsorbed layers						
Bottom sample	Critical normal stress (kPa)					
Interfacial sublayer	$M_{\rm w}$ =100kDa (h_{int} = 5 nm)	$M_w=221$ kDa ($h_{int}=7$ nm)	$M_{\rm w}$ =650kDa (h_{int} = 10 nm)			
	90	92	106			
Flattened layer	$M_{\rm w}$ =100kDa	M _w =221kDa	M _w =650kDa			
	N/A	N/A	N/A			

 Table S2. Summary of the critical normal stress obtained from adhesion

 measurements for the PS adsorbed layers

9. GIXD result for the 20kPEO flattened layer measured at 25 °C



Fig. S9 GIXD profile for the 20kPEO flattened layer measured at 25 °C.

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