Supplementary Information for:

Flattened chains dominate the adsorption dynamics of loosely adsorbed chains on modified planar substrates

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Author Contributions

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1. Experimental detail

1.1 The calculation of phenyl content by the Cassie equation

The surface fraction of phenyl groups on the substrate was estimated by the Cassie equation[1], as described in our previous work[2]:

$$\cos\theta = f_{\text{-}OH}\cos\theta_{\text{-}OH} + f_{\text{-}phenyl}\cos\theta_{\text{-}phenyl} \quad (f_{\text{-}OH} + f_{\text{-}phenyl} = 1) \qquad \text{Eq. S1}$$

where θ, $\theta_{\text{–OH}}$, and $\theta_{\text{–phenyl}}$ are water contact angles on the PTS modified substrate, the silicon surface covered with −OH groups (i.e., 7°), and the substrate fully covered with phenyl groups (i.e., 91°), respectively, and $f_{\text{–OH}}$ and $f_{\text{–phenyl}}$ are areal fractions for hydroxyl and phenyl groups on the PTS- modified substrate, respectively.

Table S1. Details for modify reaction and obtained phenyl contents.

No.	C_{PTS} (vol%)	Reacting time (min)	Reacting temperature (K)	Water Contact angle (°)	Phenyl Content (%)
PTS-1	**0.25**	**15**	**333**	**38 ± 1**	**20**
PTS-2	**0.25**	**30**		**60 ± 1**	**49**
PTS-3	**0.25**	**45**		**72 ± 1**	**69**
PTS-4	**0.25**	**60**		**76 ± 1**	**75**

1.2 XPS and SFG characterization of PTS-modified substrates.

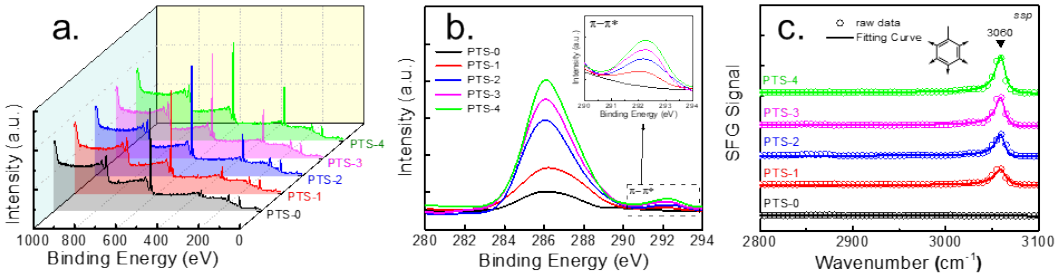

Fig. S1. (a) XPS of PTS-modified substrates and (b) High-resolution XPS spectrum in the C1s region for PTS-modified substrates with varying phenyl group contents. The graph in the inset shows the amplified region around π-π* vibrational peak. (c) SFG spectra of PTS-modified substrates surfaces with different phenyl contents.

2. To obtain and characterize adsorbed layer on the substrate

2.1 Solvent rinsing experiment

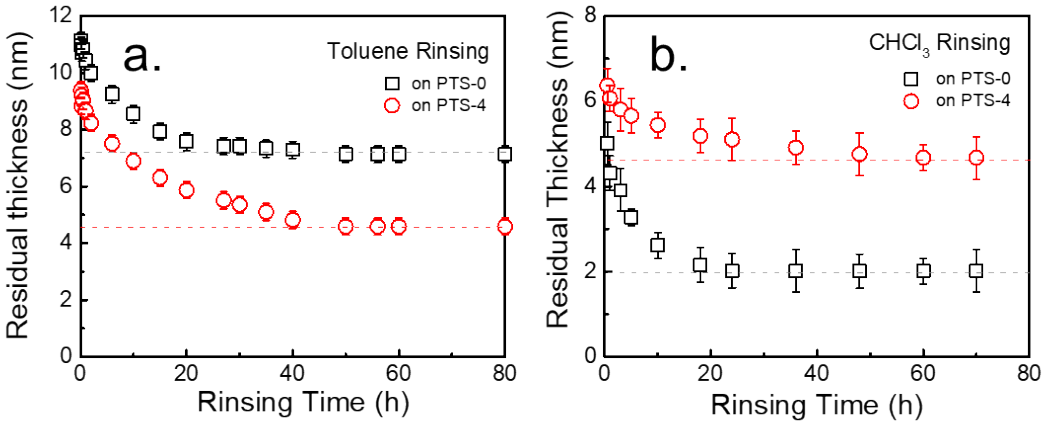

Fig. S2. The residual thickness of the PS (M_w=225 kDa) films on the neat SiO_2-Si substrate (annealing at 423 K for 48 h) and PTS-4 modified substrate (annealing at 423 K for 200 h) rinsed by (a) toluene and (b) $CHCl_3$ as a function of rinsing time.

2.2 XR test for the adsorbed layer on SiO_2-Si substrate obtained by different solvent elution.

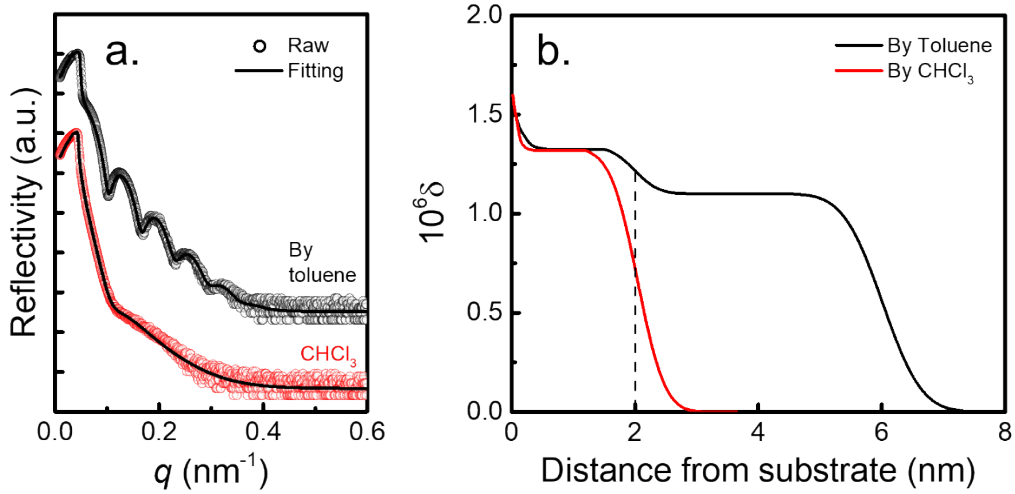

Fig. S3. (a) XR curves of the entire adsorbed layer and flattened layer on SiO_2-Si substrate obtained by annealing the PS (M_w=225 kDa) film at 423 K for 48 h and then leaching to equilibrium using toluene and $CHCl_3$, respectively. (b) The dispersion (δ) profiles correspond to the best-fits to the data against the distance (z) from the SiO_2 surface.

Table S2. The fitting parameters of XR profiles for Fig. S3.

Leaching solvent	Fitting model	Low-density PS layer			High-density PS layer			SiO_2			Si Substrate	χ^2
		Thickness (nm)	Roughness (nm)	δ×10⁶	Thickness (nm)	Roughness (nm)	δ×10⁶	Thickness (nm)	Roughness (nm)	δ×10⁶	Roughness (nm)	
Toluene	4-layer	6.3	0.43	1.14	1.9	0.36	1.31	1.9	0.34	7.12	0.25	0.007
$CHCl_3$		/	/	/	2.1	0.78	1.29	2.0	0.42	7.12	0.33	0.005

2.3. Fitting parameters of the XR data in Fig. 2

Table S3. The fitting results of a three-layer model of XR profiles for Fig. 2.

No.	Fitting model	PS adsorbed layer			SiO_2			Si Substrate	χ^2
		Thickness (nm)	Roughness (nm)	δ×10⁶	Thickness (nm)	Roughness (nm)	δ×10⁶	Roughness (nm)	
PTS-0	3-layer	8.5	0.25	1.21	1.9	0.24	7.12	0.46	0.037
PTS-2		5.2	0.76	1.61	2.0	0.31	7.12	0.52	0.042
PTS-4		4.6	0.98	1.69	2.1	0.43	7.12	0.43	0.007

Table S4. The fitting results of a four-layer model of XR profiles for Fig. 2.

No.	Fitting model	Low-density PS layer			High-density PS layer			SiO_2			Si Substrate	χ^2
		Thickness (nm)	Roughness (nm)	δ×10⁶	Thickness (nm)	Roughness (nm)	δ×10⁶	Thickness (nm)	Roughness (nm)	δ×10⁶	Roughness (nm)	
PTS-0	4-layer	6.3	0.36	1.14	2.0	0.28	1.31	2.1	0.32	7.12	0.48	0.007
PTS-2		2.4	0.48	1.14	2.7	0.45	1.53	2.0	0.28	7.12	0.47	0.008
PTS-4		2.4	0.66	1.66	2.3	0.87	1.68	2.0	0.45	7.12	0.36	0.037

For the fitting of XR data, we carefully checked the fitting parameters and contrastively analyzed the goodness-of-fit for models with three- or four-layer model. That is, a four-layer model of Si/SiO_2/high-density PS/low-density PS and a three-layer model of Si/SiO_2/PS adsorbed layer were both employed by using *REFLEX* software. In the fitting, the thickness, X-ray refractive index (δ) (which is proportional to mass density) and roughness of the PS layers, as well as the thickness and roughness of SiO_2 layer, were allowed to refine. While the δ of SiO_2 layer was fixed as a reported data of 7.13×10^{-6}.[3] A refinement procedure was used to minimize the differences between the model and experimental data (i.e. minimize χ^2). The results were displayed in Table S3 and Table S4. By comparing the fitting results of three-layer and four-layer model, it is clearly shown that for the PS interfacial sublayer on PTS-0 (SiO_2-Si) and PTS-2 substrates, four-layer model is preferable than three-layer

model with much smaller χ^2 (about an order of magnitude smaller), while for PTS-4 substrate, three-layer model was better. However, the fitting results of four-layer model show that the δ of both high-density PS layer and low-density PS layer on PTS-4 substrate were very close, which means four-layer model is equals to three-layer model at this situation. Consequently, a four-layer model was chosen for PTS-0 and PTS-2 substrates, while a three-layer model was chosen for PTS-4 substrate (marked by light yellow).

2.4 Adsorption kinetics of PS on various PTS-modified substrates.

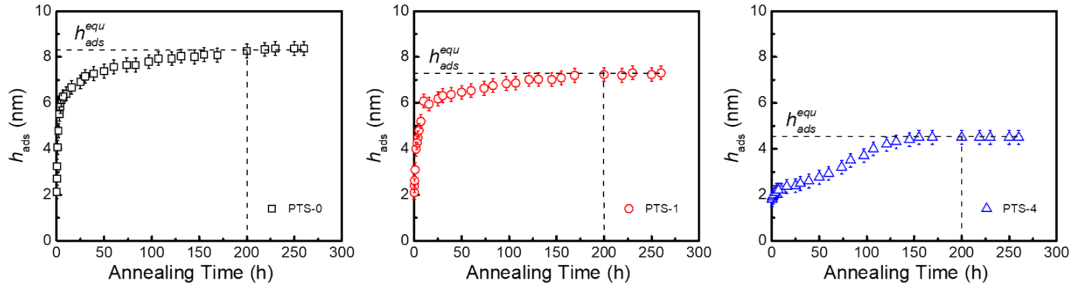

Fig. S4. Variation in h_{ads} of PS (M_w =225 kDa) with annealing time in a linear scale at 423 K on PTS-0, PTS-1, and PTS-4.

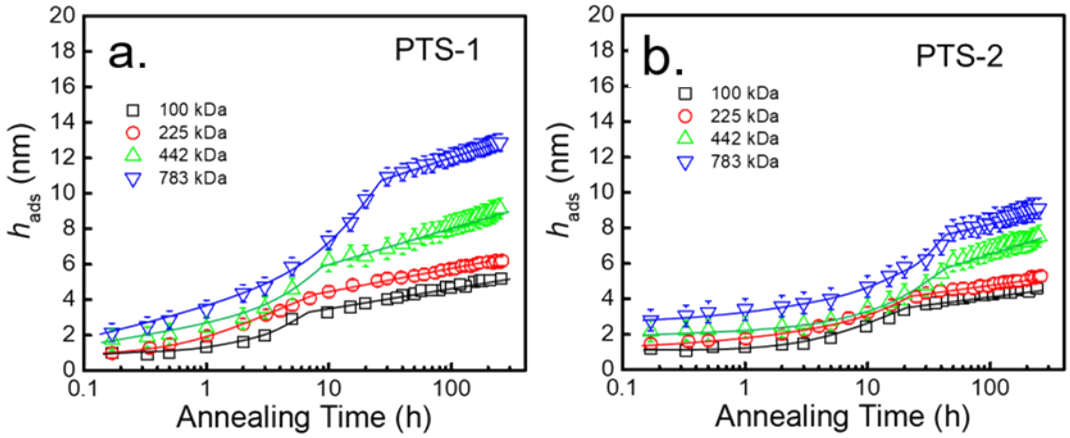

Fig. S5. The thickness of the whole adsorbed layer on PTS-1 and PTS-2 substrates against annealing time in a logarithmic scale at 423 K for PS with various molecular weights.

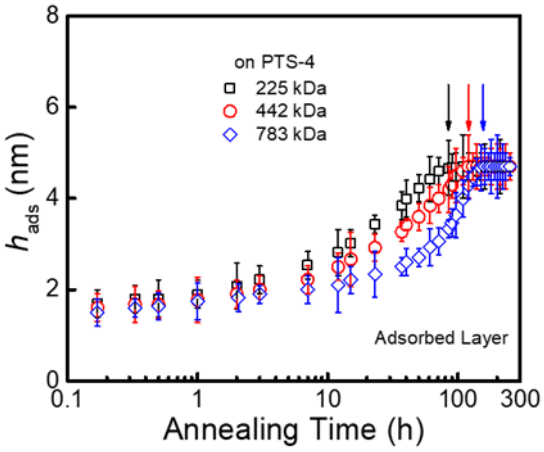

Fig. S6. The thickness of the whole adsorbed layer on PTS-4 (75 % phenyl content) substrates against annealing time in a logarithmic scale at 423 K for PS with various molecular weights. It was confirmed that at sufficiently annealing time for PTS-4, $h_{ads}=h_{flat}$.

3. The surface coverage of the flattened chains by AFM

In order to estimate the surface coverage of the PS (Mw=225 kDa) flattened chains, we applied bearing area analysis using NanoScope Analysis software (version 1.40, Bruker).[4] A bearing area gives a percentage of the surface above a critical threshold. For this analysis, AFM height images were used and we set the critical threshold (i.e., the polymer/PTS-modified substrate interface) to 0 nm.

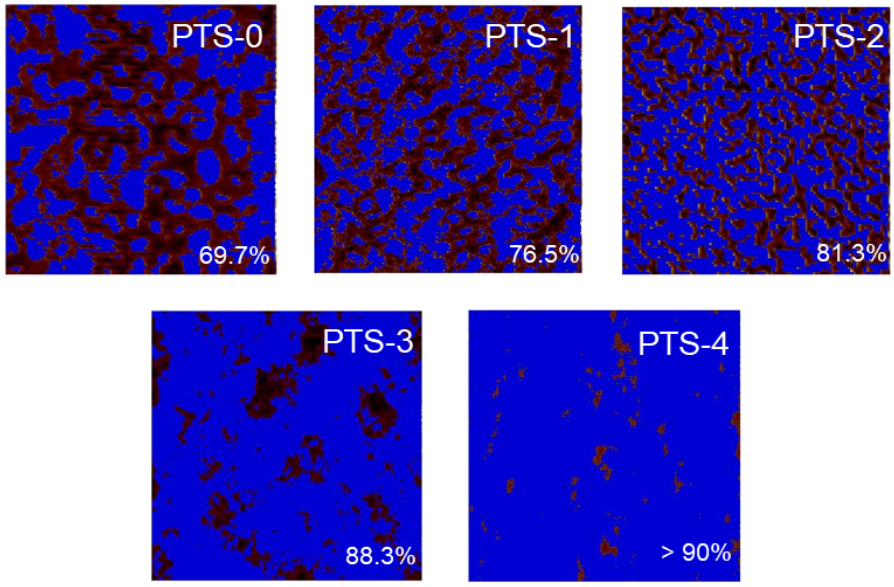

Fig. S7. The representative bearing analysis results of the AFM image for Fig. 5.

References

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