Supplementary information for

The Role of the Molecular Weight of the Adsorbed Layer at a Substrate in the Suppressed Dynamics of Supported Thin Polystyrene Films

Weizhao Ren,[a] Xin Wang,[a] Jiahui Shi,[a] Jianquan Xu,[*a] Hidenobu Taneda,[b] Norifumi L. Yamada,[c] Daisuke Kawaguchi,[bd] Keiji Tanaka,[*bd] and Xinping Wang[*a]

[a]Department of Chemistry, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China

[b]Department of Applied Chemistry, Kyushu University, Fukuoka, 819-0395, Japan

[c]Neutron Science Laboratory, High Energy Accelerator Research Organization, 203-1 Shirakata, Tokai, Naka-gun, Ibaraki 319-1106, Japan

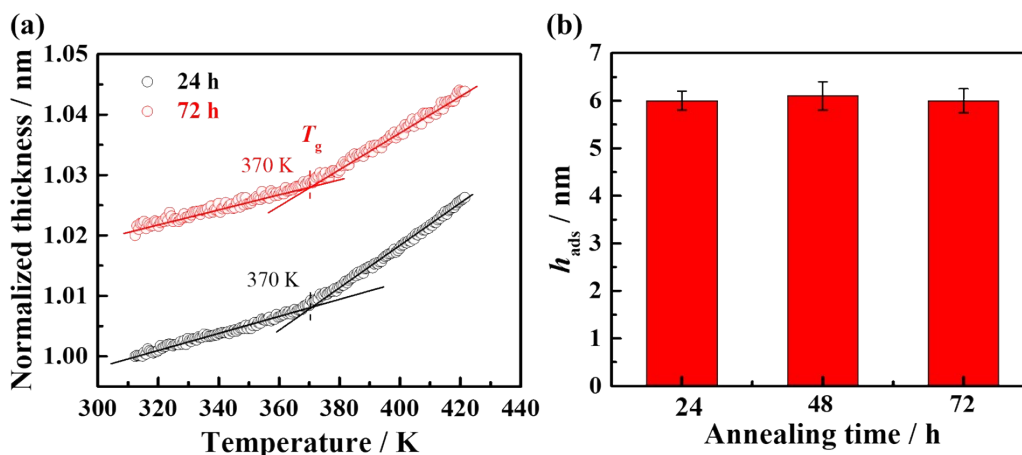[d]Center for Polymer Interface and Molecular Adhesion Science, Kyushu University, Fukuoka, 819-0395, Japan

Fig. S1 (a) Temperature dependence of normalized thickness for 60 nm thick PS films supported on the 6 nm adsorbed layer after annealing at 393 K for 24 h and 72 h, respectively. (b) The thickness of adsorbed layer (h_{ads}) as a function of annealing time. (A 60 nm thick PS film was directly spun cast on top of the 6 nm adsorbed layer and then annealing at 393 K for 24 h, 48 h, 72 h, and followed by toluene leaching.)
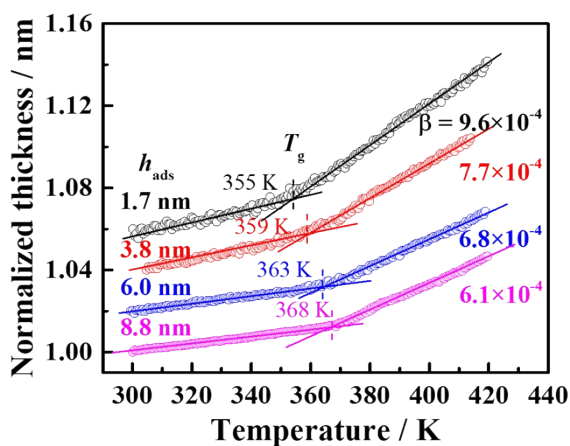

Fig. S2 Representative temperature dependence of normalized thickness for PS films supported on adsorbed layer with various h_{ads}. The β value is thermal expansivity above T_g. 25 nm thick PS films are used here and the molecular weight of upper PS films and bottom adsorbed layer are both 222 kg/mol.
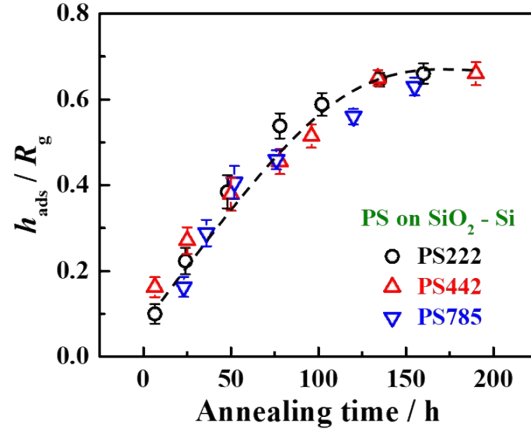
Fig. S3 Growth of the adsorbed layer on SiO$_2$-Si prepared by PS with different molecular weights against annealing time at 423 K. The dotted line corresponds to the best-fit of the power-law growth described in the text. The solid line is the best-fit for the linear the adsorption part. The initial thickness of the PS film for preparation of the adsorbed layer was larger than 8 R_g.
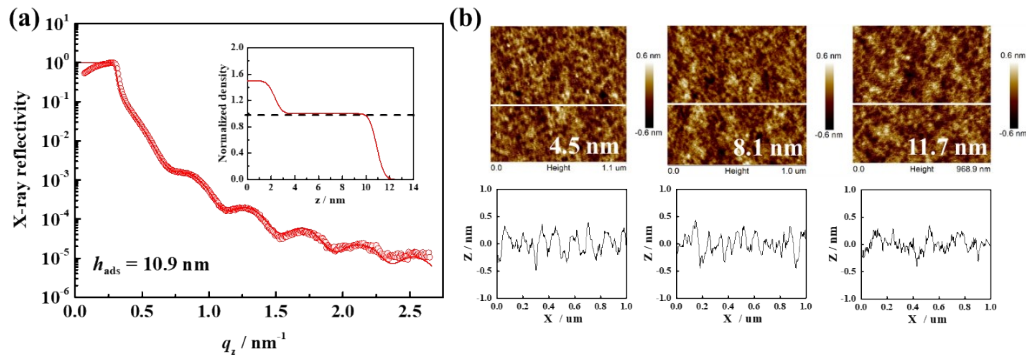

Fig. S4 (a) XRR profile of the PS442 adsorbed layer with h_{ads}=10.9 nm. Open circles denote the experimental data. The solid curve denotes the calculated reflectivity from a density profile shown in the inset. The dotted line in the inset corresponds to the value of bulk PS. (b) AFM height images of the PS adsorbed layer with various h_{ads}. The corresponding height profiles along the white line in part are plotted below each image.
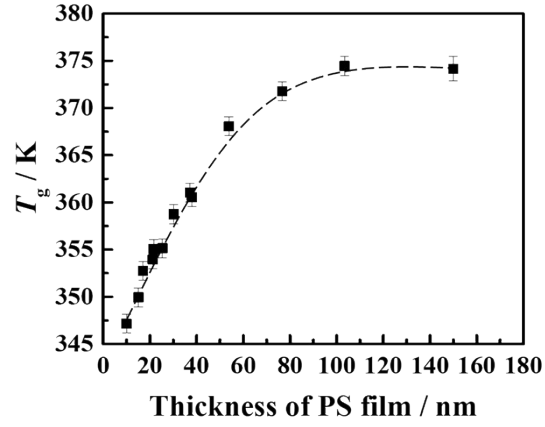
Fig. S5 T_g for PS222 films supported on neat SiO_2-Si substrate as a function of the film thickness.
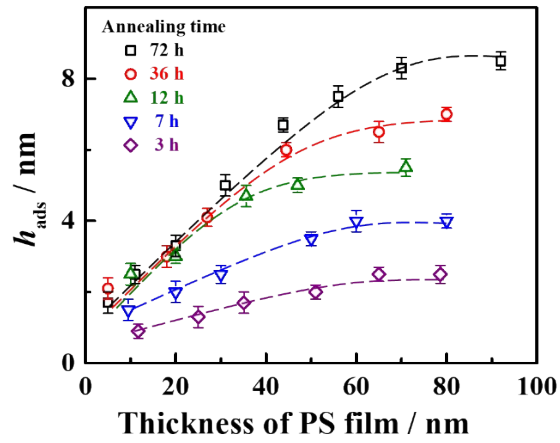

Fig. S6 Thickness of PS222 adsorbed layer (h_{ads}) on SiO_2-Si substrate vs. thickness of PS films for preparation of adsorbed layer with annealing at 423 K.
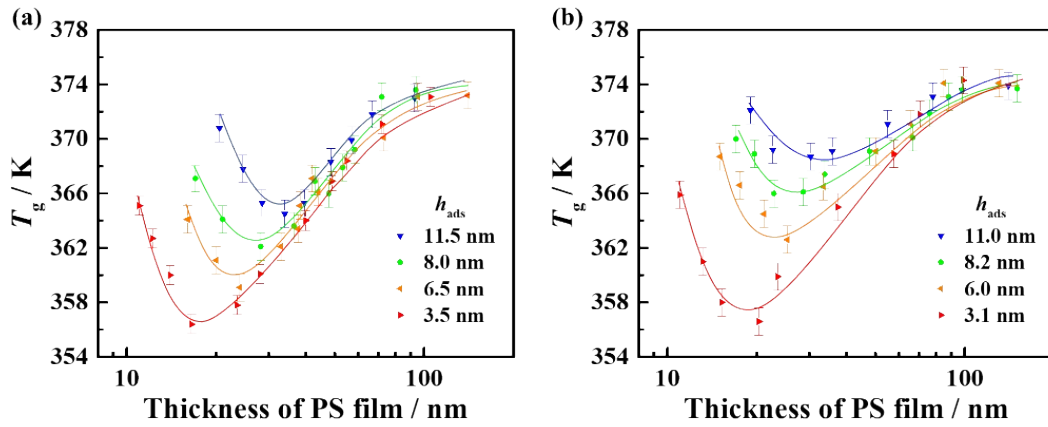
Fig. S7 T_g for PS222 films supported on the adsorbed layer as a function of the film thickness. M_w of PS adsorbed layer was (a) 442 kg/mol, (b) 785 kg/mol.
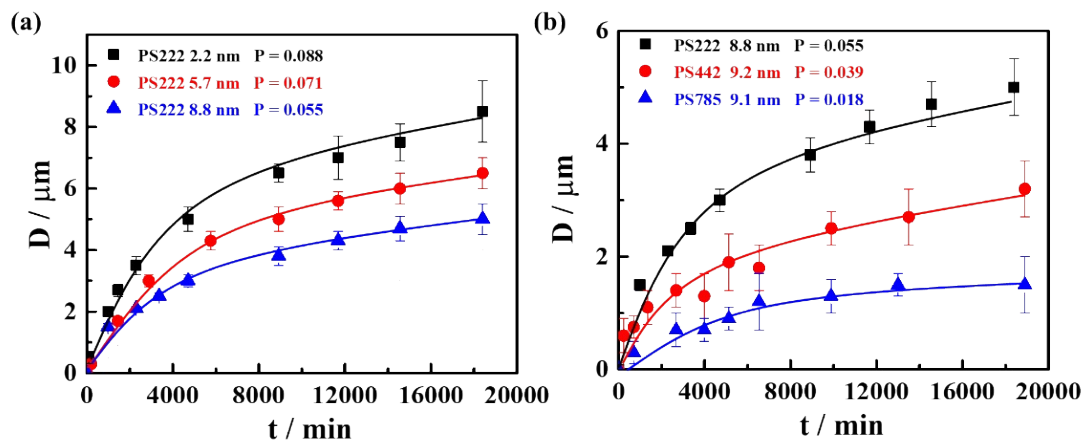

Fig. S8 Time evolution of hole diameter (D) for dewetting of a 45 ± 2 nm thick PS40 film on various adsorbed layers. The data are fitted by the power law D = $P\,t^{2/3}$. (a) The M_w of adsorbed layer is 222 kg/mol. (b) Adsorbed layers of similar thickness with various M_w.
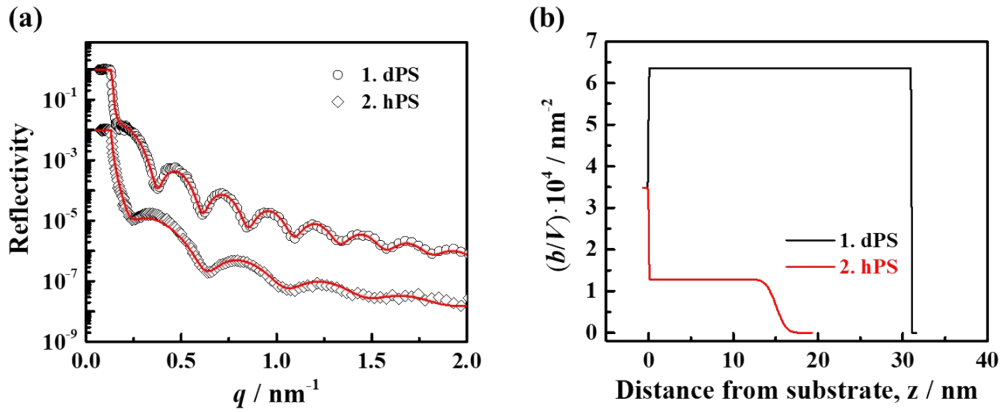
Fig. S9 (a) NR profiles of a 31 nm-thick dPS film and a PS442 adsorbed layer with h_{ads}=12.9 nm. Solid curves are the best-fits to the data based on model (b/V) profiles shown in (b). (b) Scattering length density profiles for dPS film supported on SiO_2-Si and hPS adsorbed layer on SiO_2-Si against the distance from the SiO_2-Si surface.
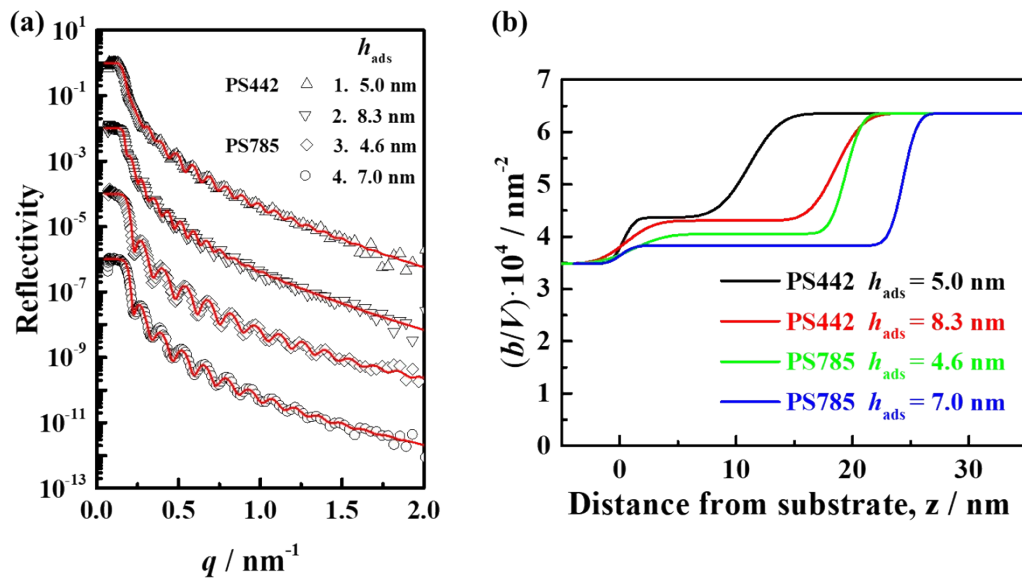

Fig. S10 (a) NR profiles of dPS film supported on various hPS adsorbed layers after annealing at 393 K for 24 h. Solid curves are the best-fits to the data based on model (b/V) profiles shown in (b). (b) (b/V) profiles for these supported dPS films against the distance from the SiO_2 surface after annealing at 393 K for 24 h.

Table S1. Structure parameters of dPS thin films retained on the hPS adsorbed layer after annealing at 393 K for 24 h (the molecular weight of the PS adsorbed layer was 222 kg/mol).

| Code | h_{ads} (nm) | top layer | | | bottom layer | | | substrate | overlap region |
		roughness (nm)	$(b/V) \times 10^4$ (nm^{-2})	thickness (nm)	roughness (nm)	$(b/V) \times 10^4$ (nm^{-2})	thickness (nm)	roughness (nm)	h^{OR} (nm)
1	3.1	0.71	6.36	36.9	1.3	4.65	3.3	1.36	9.1
2	5.0	0.58	6.36	36.6	2.9	4.05	5.9	0.48	13
3	6.8	0.59	6.36	32.4	3.1	5.38	6.5	1.3	16.5
4	8.8	0.55	6.36	34.9	5.5	4.56	9.2	1.6	21.2

Table S2. Structure parameters of dPS thin films supported on the hPS adsorbed layer after annealing at 393 K for 24 h (Code 1,2: the molecular weight of the PS adsorbed layer was 442 kg/mol and Code 3,4: the molecular weight of PS adsorbed layer was 785 kg/mol).

| Code | h_{ads} (nm) | top layer | | | bottom layer | | | substrate | overlap region |
		roughness (nm)	$(b/V) \times 10^4$ (nm^{-2})	thickness (nm)	roughness (nm)	$(b/V) \times 10^4$ (nm^{-2})	thickness (nm)	roughness (nm)	h^{OR} (nm)
1	5.0	0.74	6.36	51.2	3.0	5.01	10.5	0.8	16.8
2	8.3	0.70	6.36	72.7	1.81	4.31	18.1	1.9	23.5
3	4.6	0.42	6.36	44.5	1.1	4.05	18.2	1.7	22.3
4	7.0	0.43	6.36	42.9	0.95	3.88	21.5	0.9	27.5