Supporting Information

Interfacial Adsorption Competing with Thermal Mixing in Confined Hydrogen-Bonded Polymer Bilayers

Authors

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Table S6. Relative Fractions of PMMA and PVPh Obtained from LCF Analysis of NeXAFS Spectra

Table S1. Parameters (SLD, thickness, and roughness) Used for XRR Calculation in Figure 1

Silicon substrate	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Silicon oxide	1.07	18.9	0.2
Silicon	infinite	20.1	0.2

PVPh	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Layer 1	19.2	9.86	0.78
Silicon oxide	1.0	18.9	0.2
Silicon	infinite	20.1	0.5

PVPh and dPMMA bilayer film	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Layer 1	35.5	9.73	1.4
Silicon oxide	1.0	18.9	0.2
Silicon	infinite	20.1	0.5

After immersion in toluene solvent	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Layer 1	20.2	9.07	0.56
Silicon oxide	1.0	18.9	0.2
Silicon	infinite	20.1	0.5

After immersion in PGME solvent	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Layer 1	7.3	9.92	0.79
Silicon oxide	1.0	18.9	0.2
Silicon	infinite	20.1	0.5

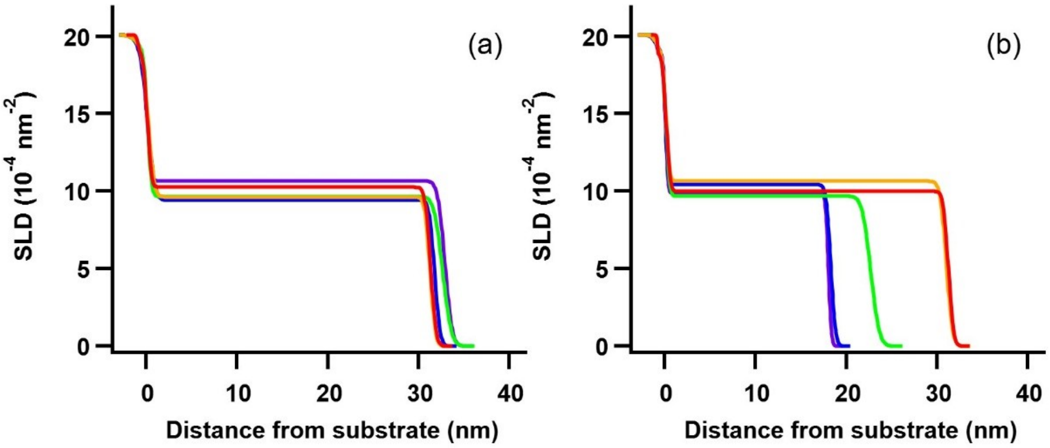

Figure S1. X-rays SLD profiles of PMMA and PVPh bilayer films after annealing at various temperatures of 180°C (red), 160°C (orange), 140°C (green), 120°C (blue), and not annealed (purple), before (a) and after (b) toluene dissolution.

Table S2. Parameters (SLD, thickness, and roughness) Used for XRR Calculation in Figure 2 (a)

Not annealed	**thickness nm**	**SLD 10^{-4}nm^{-2}**	**roughness nm**	**120^{o}C**	**thickness nm**	**SLD 10^{-4}nm^{-2}**	**roughness nm**
Layer 1	32.8	10.7	0.63	**Layer 1**	31.6	9.43	0.48
Silicon oxide	1.0	18.9	0.36	**Silicon oxide**	1.0	18.9	0.6
Silicon	infinite	20.1	0.68	**Silicon**	infinite	20.1	0.77

140 ^{o}C	**thickness nm**	**SLD 10^{-4}nm^{-2}**	**roughness nm**	**160 ^{o}C**	**thickness nm**	**SLD 10^{-4}nm^{-2}**	**roughness nm**
Layer 1	32.5	9.76	0.76	**Layer 1**	31.0	9.64	0.46
Silicon oxide	1.0	18.9	0.34	**Silicon oxide**	1.0	18.9	0.51
Silicon	infinite	20.1	0.78	**Silicon**	infinite	20.1	0.78

180 ^{o}C	**thickness nm**	**SLD 10^{-4}nm^{-2}**	**roughness nm**
Layer 1	31.2	10.3	0.48
Silicon oxide	1	18.9	0.35
Silicon	infinite	20.1	0.21

Table S3. Parameters (SLD, thickness, and roughness) Used for XRR Calculation in Figure 2 (b)

Not annealed	**thickness nm**	**SLD $10^{-4}nm^{-2}$**	**roughness nm**	**120^{o}C**	**thickness nm**	**SLD $10^{-4}nm^{-2}$**	**roughness nm**
Layer 1	17.9	9.89	0.26	**Layer 1**	18.2	10.4	0.41
Silicon oxide	1.0	18.9	0.2	**Silicon oxide**	1.0	18.9	0.24
Silicon	infinite	20.1	1.5	**Silicon**	infinite	20.1	0.48
140 ^{o}C	**thickness nm**	**SLD $10^{-4}nm^{-2}$**	**roughness nm**	**160 ^{o}C**	**thickness nm**	**SLD $10^{-4}nm^{-2}$**	**roughness nm**
Layer 1	22.6	9.69	0.75	**Layer 1**	30.9	10.7	0.54
Silicon oxide	1.0	18.9	0.31	**Silicon oxide**	1.0	18.9	0.31
Silicon	infinite	20.1	0.24	**Silicon**	infinite	20.1	0.45
180 ^{o}C	**thickness nm**	**SLD $10^{-4}nm^{-2}$**	**roughness nm**				
Layer 1	31.1	10	0.45				
Silicon oxide	1.0	18.9	0.34				
Silicon	infinite	20.1	0.46				

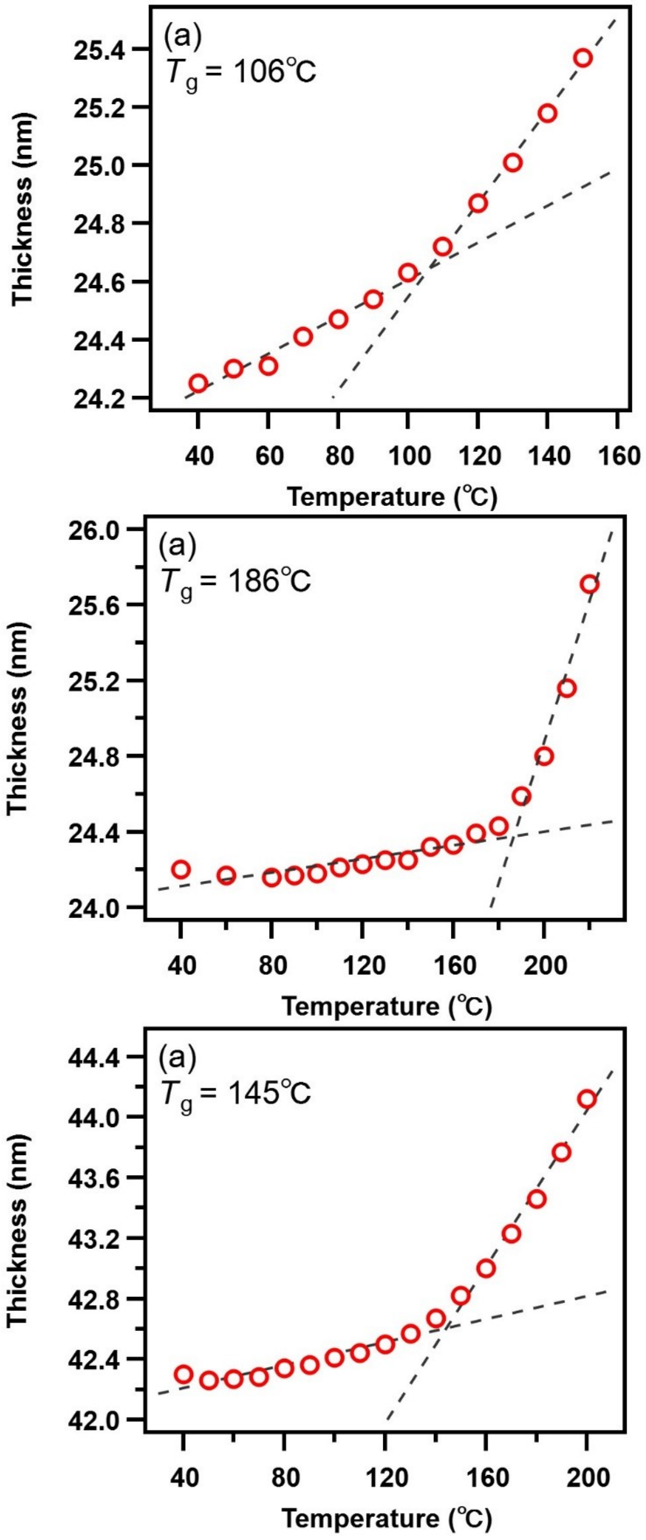

Figure S2. Temperature dependence of film thickness measured by X-ray reflectivity during cooling: (a) PMMA, (b) PVPh, (c) PMMA, and PVPh multilayer films.

Table S4. Parameters (SLD, thickness, and roughness) Used for NR Calculation in Figure 4.

130°C	thickness nm	SLD $10^{-4}nm^{-2}$	roughness nm	160°C	thickness nm	SLD $10^{-4}nm^{-2}$	roughness nm
Layer 1	24.6	6.47	2.15	Layer 1	33.6	5.73	0.78
Layer 2	0.4	4.19	0.86	Layer 2	55.6	3.08	2.31
Layer 3	0.7	2.48	1.18	Layer 3	57.6	3.03	7.69
Layer 4	22.8	1.86	2.37	Layer 4	75.9	2.62	8.84
Layer 5	4.1	1.65	3.67	Layer 5	7.9	1.00	1.60
Silicon oxide	1.0	3.47	0.10	Silicon oxide	1.0	3.47	0.10
Silicon	infinite	2.07	0.10	Silicon	infinite	2.07	0.10

180°C	thickness nm	SLD $10^{-4}nm^{-2}$	roughness nm
Layer 1	48.3	3.95	1.37
Layer 2	4.0	4.02	4.89
Layer 3	0.6	1.67	2.35
Layer 4	0.8	3.02	3.30
Layer 5	1.5	1.22	0.56
Silicon oxide	1.0	3.47	0.10
Silicon	infinite	2.07	0.10

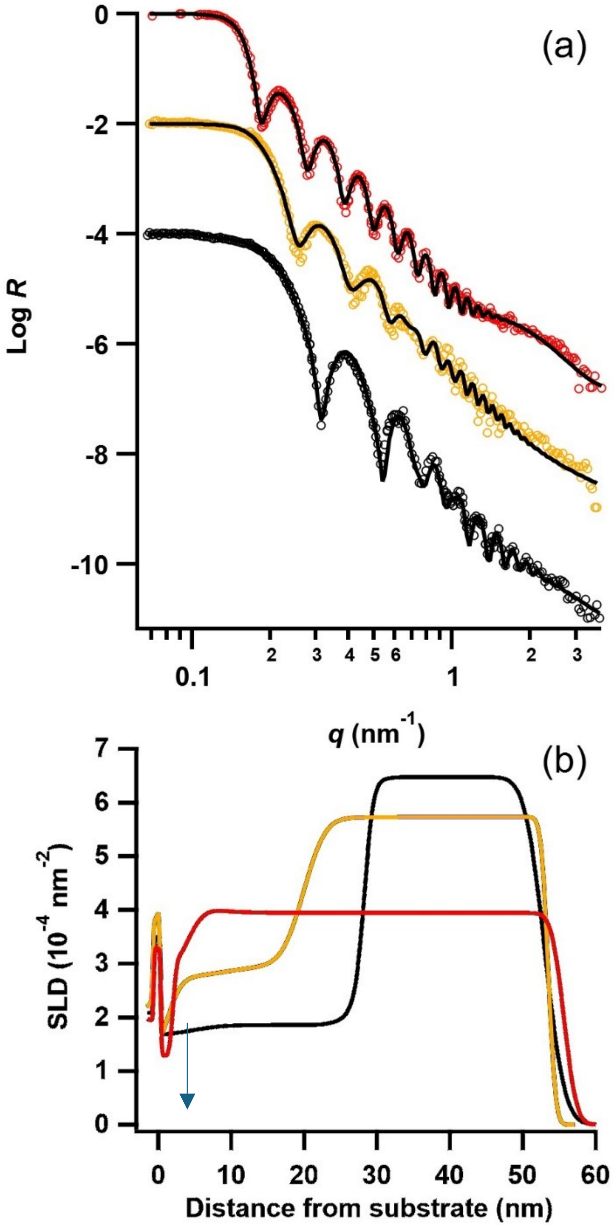

Figure S3. NR profiles (a) and corresponding SLD profiles (b) for a dPMMA/PVPh thin film on a silicon wafer, measured in situ during heating at 130 °C (black), 160 °C (orange), and 180 °C (red). Solid black lines represent the calculated curves used to derive the SLD profiles without the interfacial layer with low SLD value. NR profiles were vertically shifted to avoid overlapping.

Table S5. Parameters (SLD, thickness, and roughness) Used for NR Calculation in Figure S3.

130°C	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Layer 1	24.6	6.47	2.15
Layer 2	0.4	4.19	0.86
Layer 3	0.7	2.48	1.18
Layer 4	27.5	1.65	4.72
Layer 5	-	-	-
Silicon oxide	1.0	3.47	0.10
Silicon	infinite	2.07	0.10

160°C	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Layer 1	33.6	5.73	0.78
Layer 2	55.6	3.08	2.31
Layer 3	0.4	3.03	7.69
Layer 4	12.7	1.65	8.84
Layer 5	-	-	-
Silicon oxide	1.0	3.47	0.10
Silicon	infinite	2.07	0.10

180°C	thickness nm	SLD 10^{-4}nm^{-2}	roughness nm
Layer 1	48.3	3.95	1.37
Layer 2	4.0	4.02	4.89
Layer 3	0.6	1.67	2.35
Layer 4	2.6	3.02	3.30
Layer 5	-	-	-
Silicon oxide	1.0	3.47	0.10
Silicon	infinite	2.07	0.10

Table S6. Relative Fractions of PMMA and PVPh Obtained from LCF Analysis of NeXAFS Spectra

Annealing Temperature (°C)	After annealing (TFY) (%)		After annealing (TEY) (%)		After Toluene Dissolution (TEY) (%)		After PGME Dissolution (TEY) (%)	
	PMMA	PVPh	PMMA	PVPh	PMMA	PVPh	PMMA	PVPh
30	36.0	64.0	93.7	6.3	11.7	88.3	2.5	97.5
130	35.6	64.3	92.8	7.2	38.4	61.6	0	100
150	35.4	64.6	77.6	22.4	45.1	49.9	4.3	95.7
160	38.1	61.9	59.7	40.3	55.0	45.0	8.4	91.6
180	35.6	64.4	54.0	46.0	51.1	48.9	10.0	90.0