Supporting Information

**Polymer Synthesis and Characterization**

Determining Monomer Feed Ratio

Feed compositions for the different polymerization reactions were determined by desired polymer composition, approximately following the copolymerization equation:[1]

$$F_s = \frac{r_s f_s^2 + f_s f_m}{r_s f_s^2 + 2 f_s f_m + r_m f_m^2} \quad \text{(S1)}$$

Where $F_s$ is the instantaneous molar fraction of styrene in the polymer, $f_s$ and $f_m$ are instantaneous molar fractions of styrene and methyl methacrylate in the monomer feed, and $r_s$ and $r_m$ are reactivity ratios of the two monomers. While these are instantaneous calculations, our initial monomer feed composition makes a good approximation due to the similarity of $r_s$ and $r_m$ and the low extent of conversion maintained in our synthesis reactions.

NMR analysis: Composition and Tacticity

Composition for the copolymers was calculated from their 1H-NMR spectra (shown in figure S1). In order to determine composition, the integrated areas of the aromatic (6-8 ppm) and aliphatic (0-4 ppm) portions of the spectrum were compared in a system of equations:

$$5x_s = kA_{Ar} \quad \text{(S2a)}$$

$$3x_s + 6x_m = kA_{Al} \quad \text{(S2b)}$$

$$x_s + x_m = 1 \quad \text{(S2c)}$$

Where $x_s$ and $x_m$ are the molar fractions of styrene and methyl methacrylate in the polymer, respectively, $A_{Ar}$ and $A_{Al}$ are the integrated areas of the aromatic and aliphatic regions, and k is a multiplication factor to account for the absolute intensity.

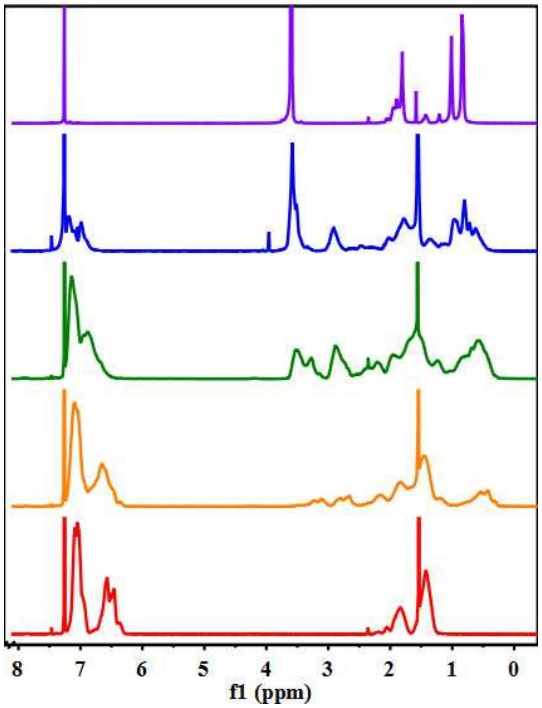


Figure S1. [1]H-NMR spectra of the polymers used in this study, arranged from the top down in order of increasing styrene content. Integrated intensities of the aromatic and aliphatic regions

were used to calculate their compositions. The spectra were normalized by their residual solvent peak at 7.26 ppm for $CDCl_3$.

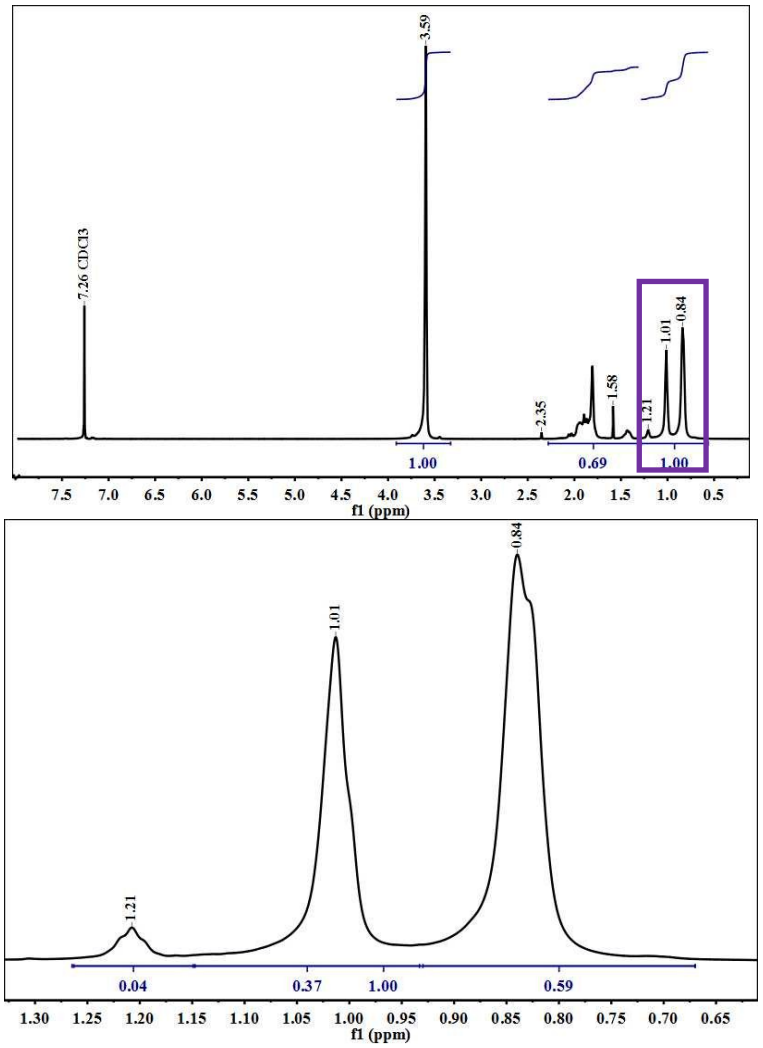


Figure S2. Tacticity of PMMA is determined by comparing the peaks in the α-methyl region of the $^1$H-NMR spectrum.[2] (above) full $^1$H-NMR spectrum of PMMA, with area of interest boxed in purple. (below) magnified view of area of interest showing the integrated peaks used to determine tacticity.

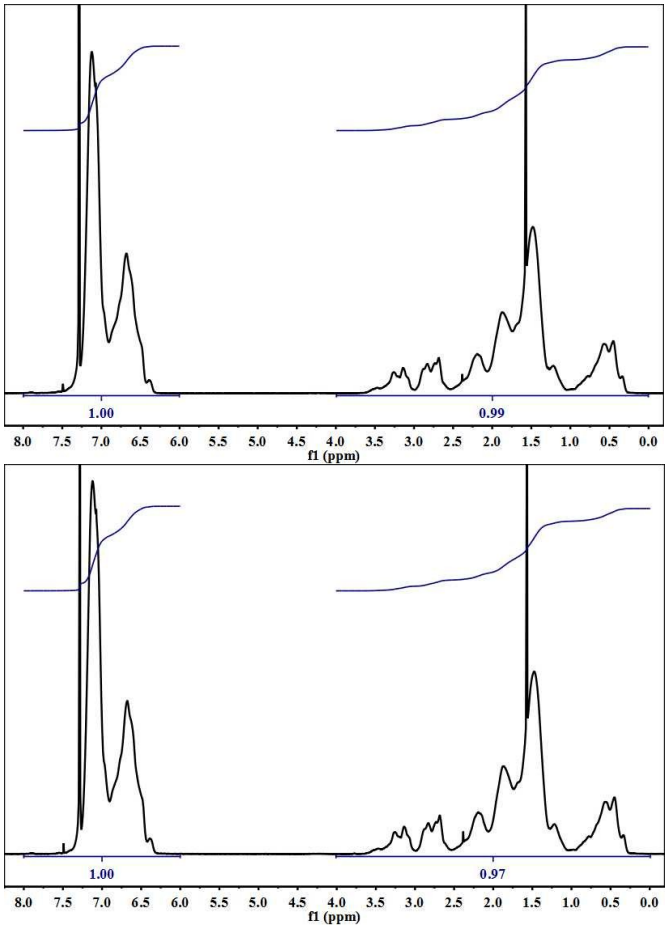


Figure S3. Minimal compositional drift is observed at <10% conversion. P(S-r-MMA) prepared with the same monomer feed concentrations, but run to 8% (top) and 3% (bottom) conversion give P(S-r-MMA) with compositions of (75:25) and (76:24), respectively. This 1% composition difference is within experimental error, and could be due to the contribution of residual solvent peaks. No compositional drift is observed.

**Measuring Thickness of Adsorbed Layers**

A Cauchy model was used to measure the thickness of adsorbed layers via spectroscopic ellipsometry, of the form:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \cdots \tag{S3}$$

The parameters used, based on measurements of 200 nm films were:

| Polymer | A | B | C |
|---|---|---|---|
| **PS100** | 1.563 | 0.0083 | 0.003 |
| **PMMA25** | 1.545 | 0.0087 | 0.00005 |
| **PMMA50** | 1.524 | 0.0085 | 0 |
| **PMMA75** | 1.501 | 0.0069 | 0.000001 |

| | | | |
|---|---|---|---|
| **PMMA100** | 1.478 | 0.0055 | 0 |

Thicknesses of adsorbed layers were also measured via AFM, and their thicknesses were compared to those for the same samples via ellipsometry in Figure S4. As previously reported for PS,[3] films below ~2-3nm dewetted due to spinodal decomposition. Select AFM images are included in Figure S5.

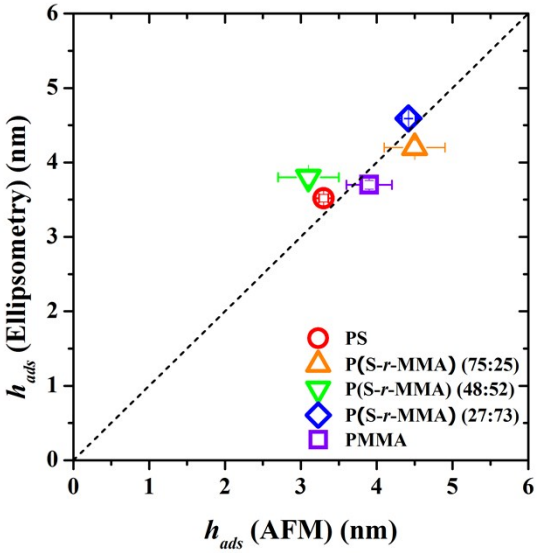


Figure S4. Comparison of adsorbed layer thickness measured via AFM and ellipsometry

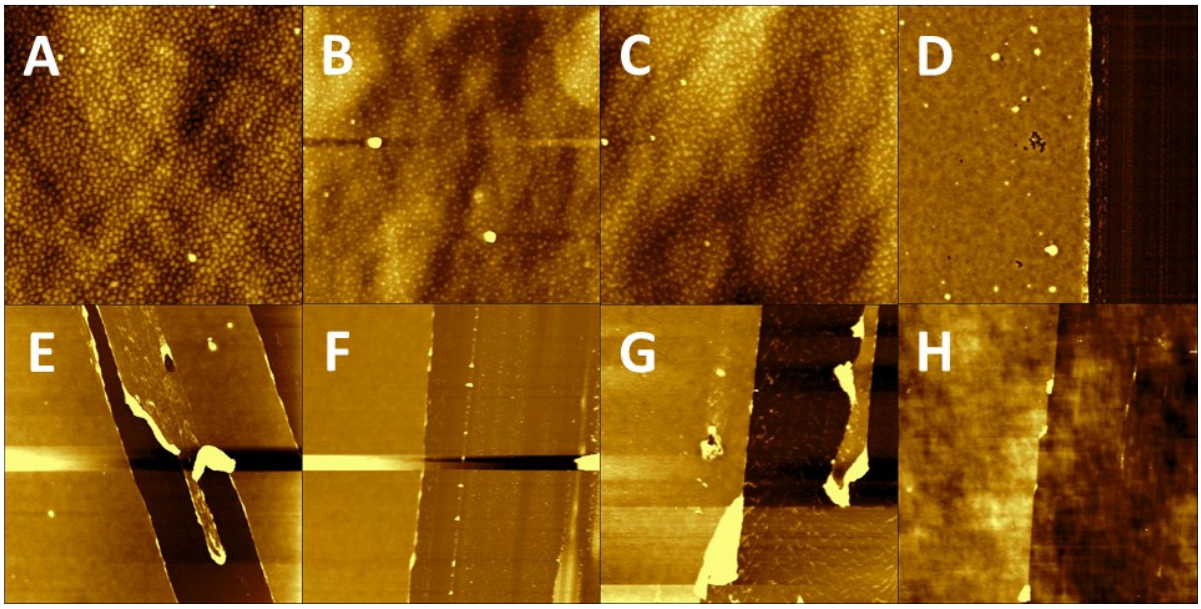


Figure S5. AFM images of adsorbed layer morphologies. All images are 5 x 5 μm, with the exception of H, which is 10 x 10 μm; D-H were scraped with a razor blade to determine thicknesses reported in Figure S4. (A) 1-h PS adsorbed layer, $T_{ann}$ = 423 K, $h_{ads}$ = 1.5 nm (B) 1-h P(S-*r*-MMA) (75:25) adsorbed layer, $T_{ann}$ = 423 K, $h_{ads}$ = 0.9 nm (C) 1-h P(S-*r*-MMA) (48:52) adsorbed layer, $T_{ann}$ = 423 K, $h_{ads}$ = 1.3 nm (D) 1-h PS adsorbed layer, $T_{ann}$ = 443 K, $h_{ads}$ = 3.5 nm (E) 1-h P(S-*r*-MMA) (75:25) adsorbed layer, $T_{ann}$ = 443 K, $h_{ads}$ = 4.2 nm (F) 1-h P(S-*r*-MMA) (48:52) adsorbed layer, $T_{ann}$ = 443 K, $h_{ads}$ = 3.8 nm (G) 1-h P(S-*r*-MMA) (27:73) adsorbed layer, $T_{ann}$ = 443 K, $h_{ads}$ = 4.6 nm (H) 1-h PMMA adsorbed layer $T_{ann}$ = 443 K, $h_{ads}$ = 3.7 nm

**Calculating $R_g$**

The radius of gyration for PS and PMMA were calculated based on the polymer Mw using empirical relations published in the literature. Details on the determination of the $R_g$ of PS have previously been published.[3]

For PMMA, we used the value published by Fetters et al:[4]

$$\langle R^2\rangle_0 \Big/ _M = 0.425 \frac{\text{Å}^2 mol}{g} \tag{S4}$$

As determined by SANS, combined with the relation

$$\langle R_g^2\rangle_0 = \frac{1}{6}\langle R^2\rangle_0 \tag{S5}$$

Where $M$ is the weight-average molecular weight, $\langle R^2\rangle_0$ is the unperturbed mean-square end-to-end distance, and $R_g$ is the radius of gyration in Å.

**Fitting Adsorption Kinetics**

Adsorption data was fit to a saturated exponential of the form

$$h_{ads} = h_0 + \Delta h\left(1 - e^{-t/t_c}\right) \tag{S6}$$

As suggested by Nieto et al.[5] $h_0$, $\Delta h$, and $t_c$ were all fit to the data. With the exception of P(S-r-MMA) (75:25), this equation fit the data well, and the approximation for $h_p$

$$h_p = h_0 + \Delta h \tag{S7}$$

agrees well with that calculated by averaging adsorbed layer thicknesses for $t_{ads}$ > 15 h, as shown below in Figure S6.

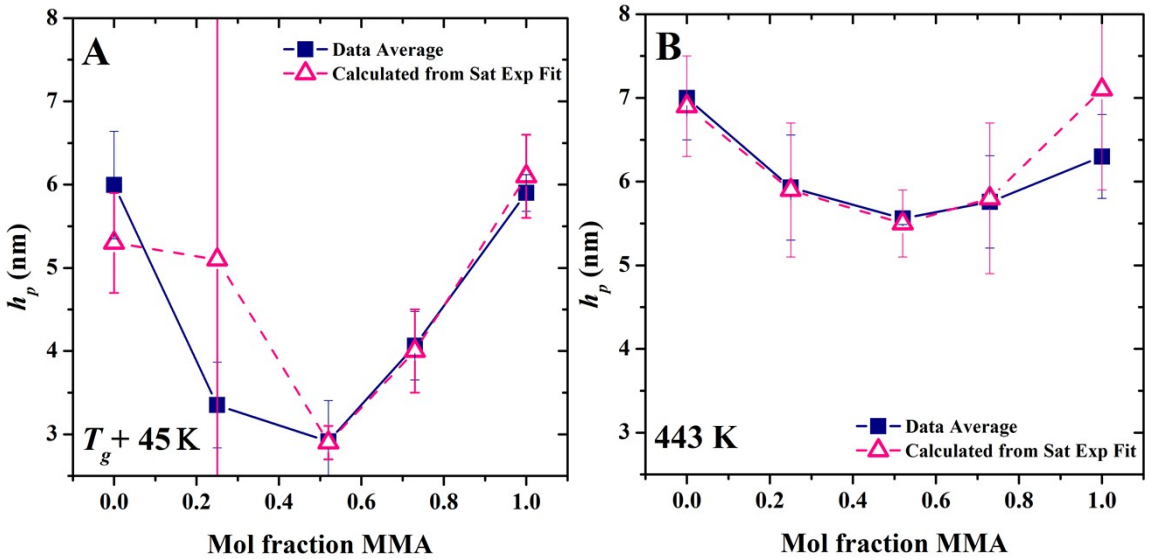


Figure S6. Comparison of $h_p$ calculated by different methods as a function of composition at (A) $T_{ann} = T_g + 45$ K and (B) $T_{ann} = 443$ K. Blue squares indicate $h_p$ listed in the text, calculated from averaging $h_{ads}$ after 15 hours of annealing. Pink triangles are $h_p$ calculated from saturated exponential fit to the data and Equation S7.

The characteristic values of adsorption, $t_c$, calculated for each polymer were used as approximations for determining $t_{cross}$ in linear and logarithmic fits representing the two growth regimes of adsorption. These fits to the data are shown below in Figures S7 and S8, with dashed lines representing 95% confidence intervals to the fits.

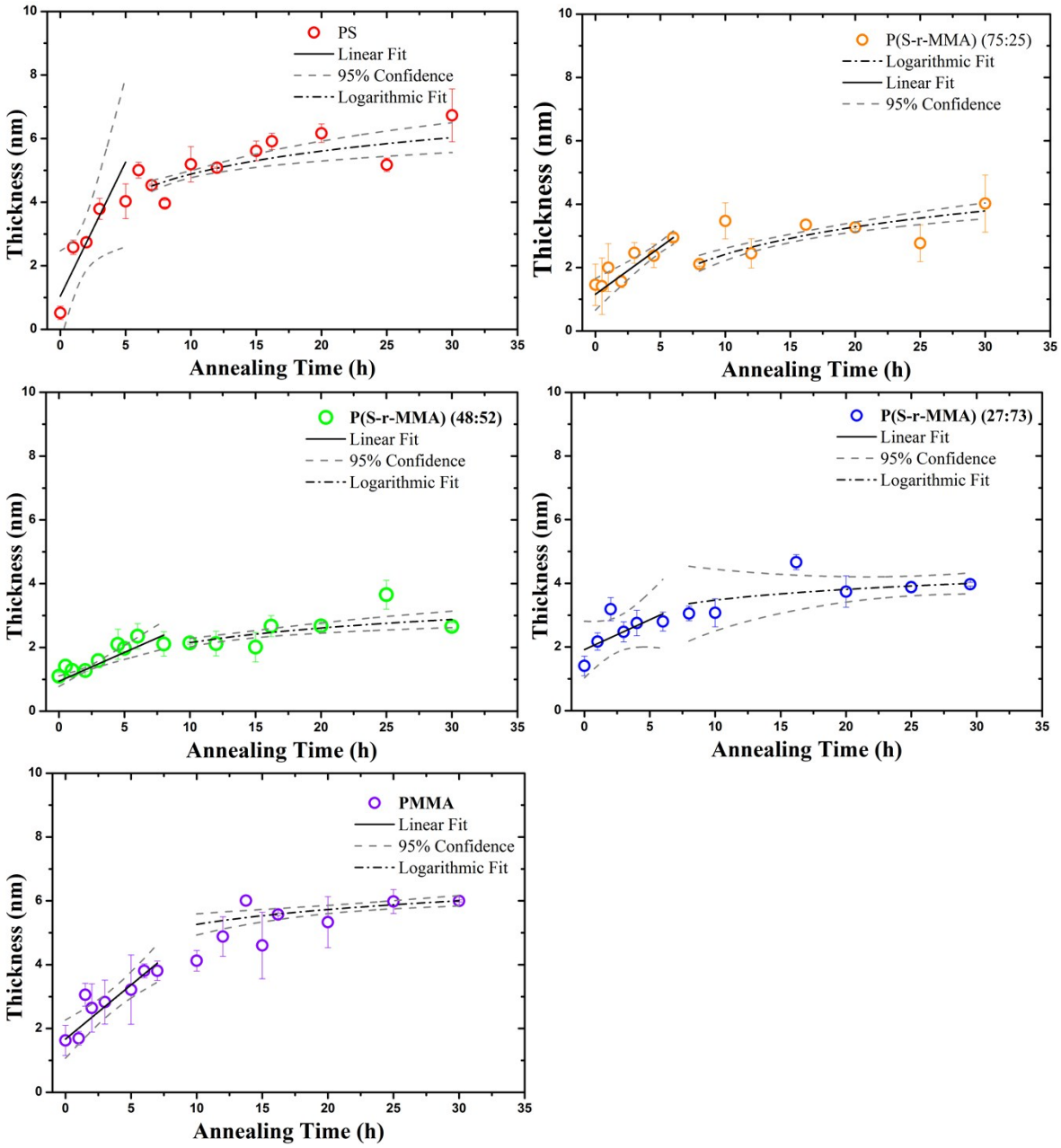


Figure S7. Linear and Logarithmic fits to adsorbed layer thickness after being growth at $T_g$ + 45 K. Linear fits are shown by solid black lines; logarithmic fits are shown by dash-dot black lines. Gray dashed lines represent 95% confidence intervals for the fits.

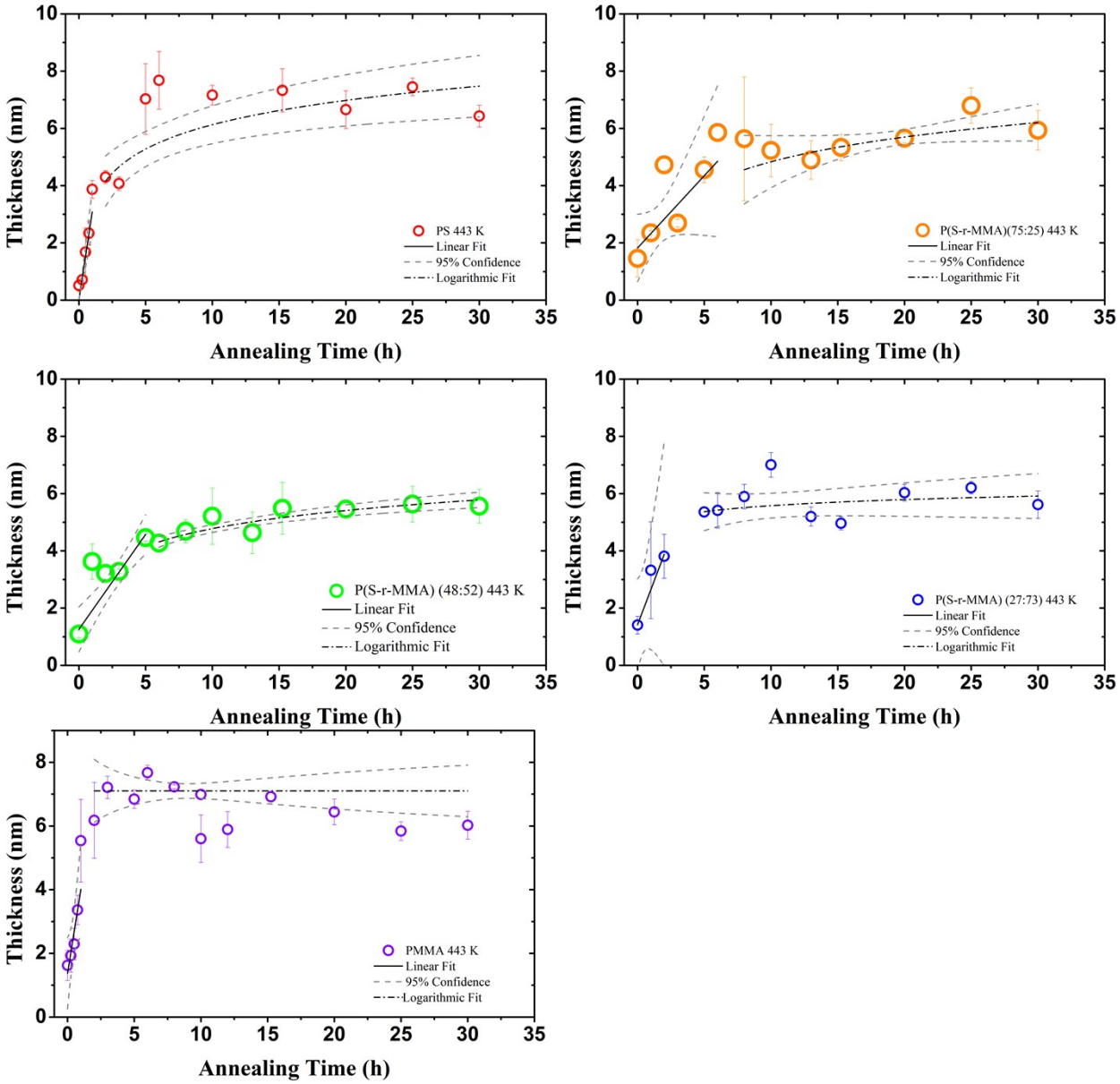


Figure S8. Linear and Logarithmic fits to adsorbed layer thickness after being grown at 443 K. Linear fits are shown by solid black lines; logarithmic fits are shown by dash-dot black lines. Gray dashed lines represent 95% confidence intervals for the fits.

**Annealing Copolymers Longer at 423 K**

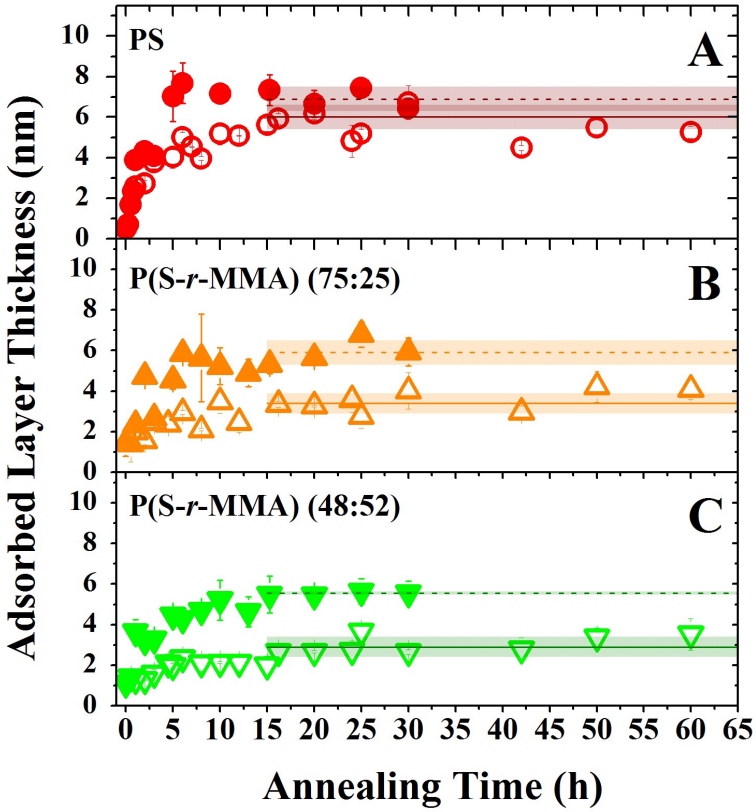


Figure S9. PS and P(S-r-MMA) were annealed at 423 K for up to 60 h with no change in $h_p$ apparent. $h_p$ calculated from 423 K data is shown by the solid lines and $h_p$ calculated from 443 K data is shown by the dashed line. This indicates that slow kinetics at 423 K are not responsible for the difference in $h_p$ observed in copolymers when annealed at different temperatures.

1. Brazel, C. & Rosen, S. *Fundamental Principles of Polymeric Materials*. (Wiley, 2012).
2. Smith, L. M. & Coote, M. L. Effect of temperature and solvent on polymer tacticity in the free-radical polymerization of styrene and methyl methacrylate. *J. Polym. Sci. Part A Polym. Chem.* **51,** 3351–3358 (2013).
3. Burroughs, M. J., Napolitano, S., Cangialosi, D. & Priestley, R. D. Direct Measurement of Glass Transition Temperature in Exposed and Buried Adsorbed Polymer Nanolayers. *Macromolecules* **49,** 4647–4655 (2016).
4. Fetters, L. J., Lohse, D. J., Richter, D., Witten, T. A. & Zirkelt, A. Reviews Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties. *Macromolecules* **27,** (1994).
5. Simavilla, D. N., Panagopoulou, A. & Napolitano, S. Characterization of Adsorbed Polymer Layers: Preparation, Determination of the Adsorbed Amount and Investigation of the Kinetics of Irreversible Adsorption. *Macromol. Chem. Phys.* **219,** 1700303 (2017).