SUPPORTING INFORMATION

Direct Nanoscopic Measurement of Laminar Slip Flow Penetration of Deformable Polymer Brush Surfaces: Synergistic Effect of Grafting Density and Solvent Quality

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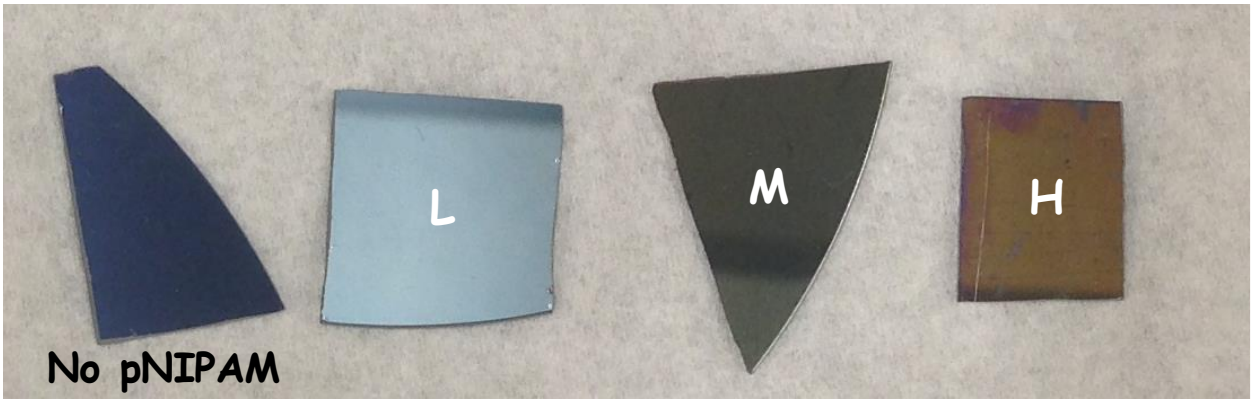

Figure S1. Photographs of bare silicon wafer containing native oxide layer with no pNIPAM film and covered by low (0.27 chain/nm^2), medium (0.38 chain/nm^2), and high (0.60 chain/nm^2) grafting densities of pNIPAM.

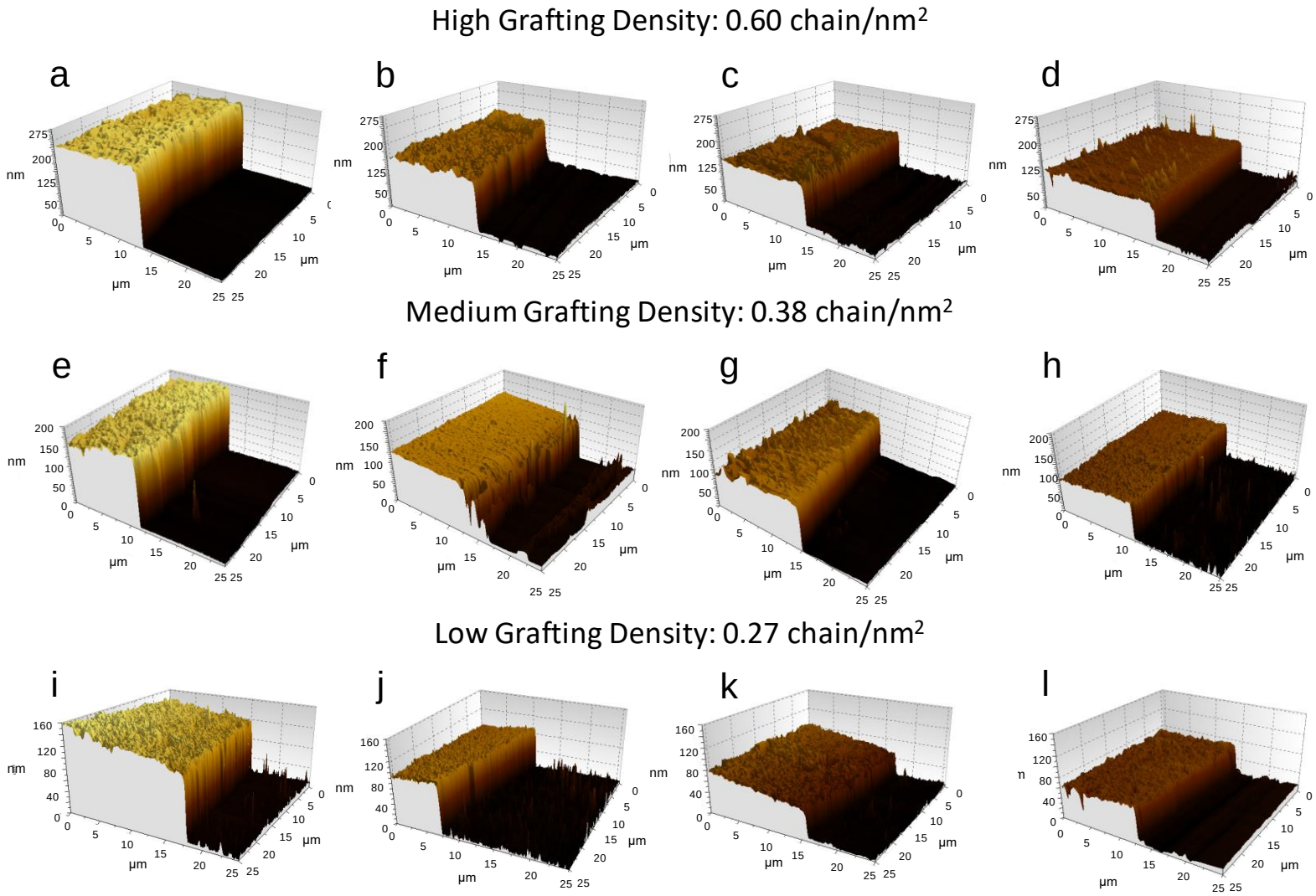

Figure S2. AFM images from high-, medium-, and low-density pNIPAM films in solvents of different quality. a), e), i) Films in good solvent (100% MeOH); b), f), j) films in theta solvent (13 mol% MeOH/H_2O);c), g), k) films in first poor solvent (20 mol% MeOH/H_2O);and d), h), l) films in second poor solvent (31 mol% MeOH/H_2O).

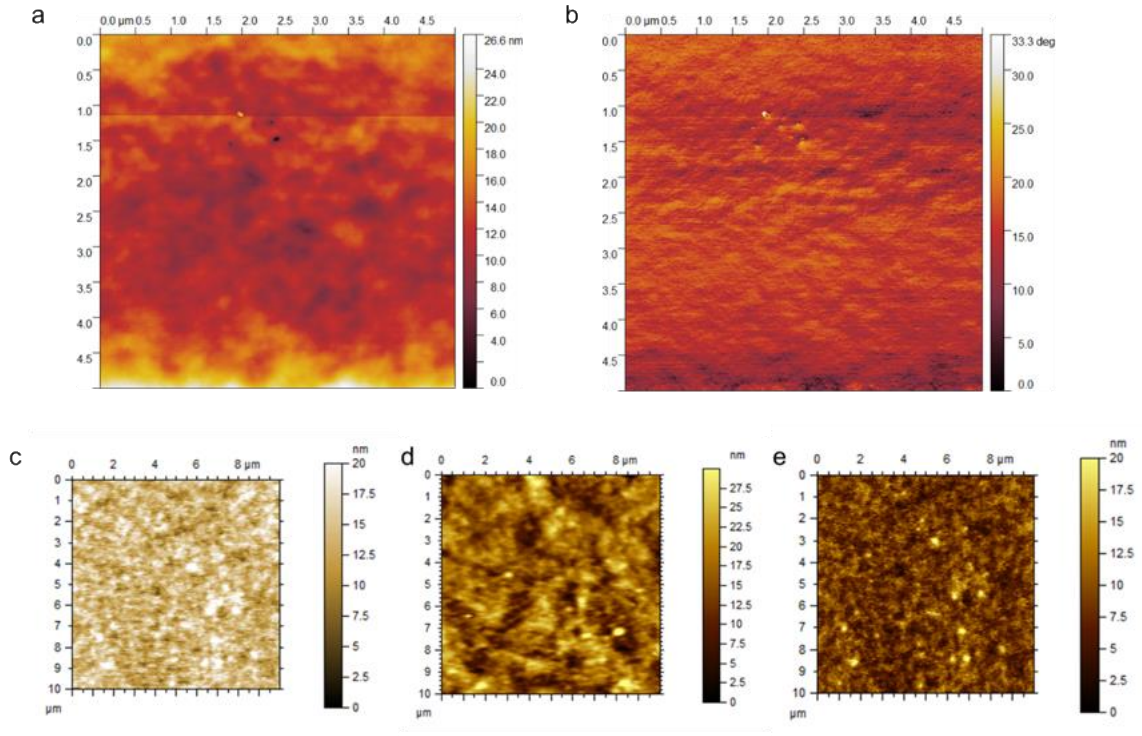

Figure S3. Higher resolution AFM images of pNIPAM films. High density (0.60 chain/nm^2) film imaged in air a) height contrast, b) phase contrast. Methanol-swollen film of c) low- (0.27 chain/nm^2), d) medium- (0.38 chain/nm^2), and e) high-density (0.60 chain/nm^2) pNIPAM films showing film uniformity.

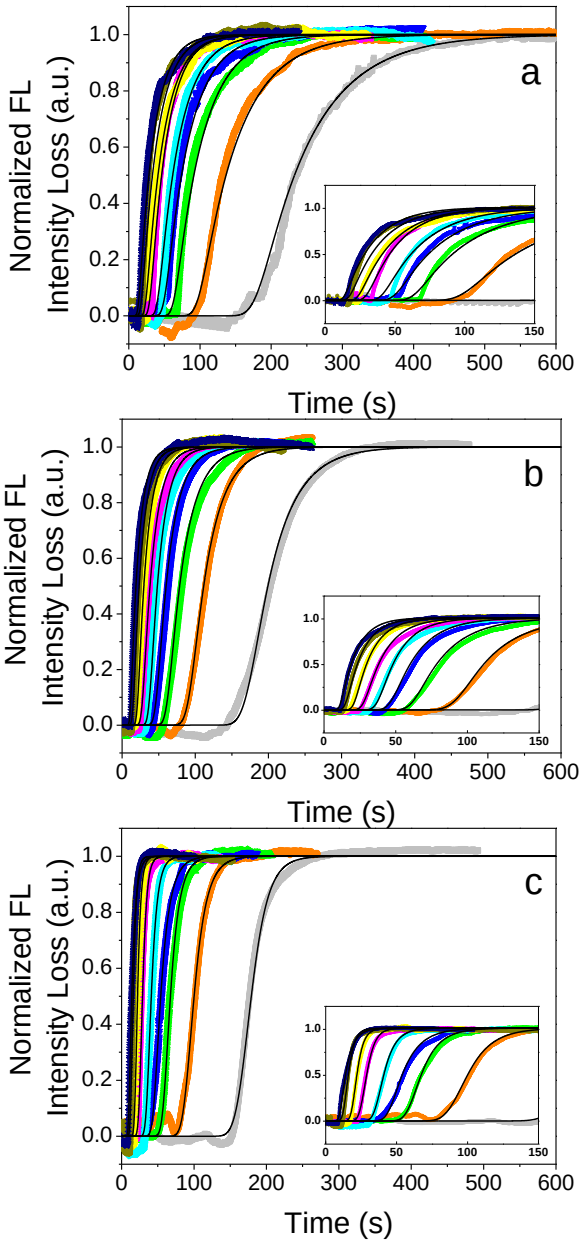

Figure S4. FRET breakthrough curves for RhB in FITC-modified pNIPAM films in a theta solvent (13 mol% MeOH/H_2O) for pNIPAM grafting densities that are a) high, b) medium, and c) low.

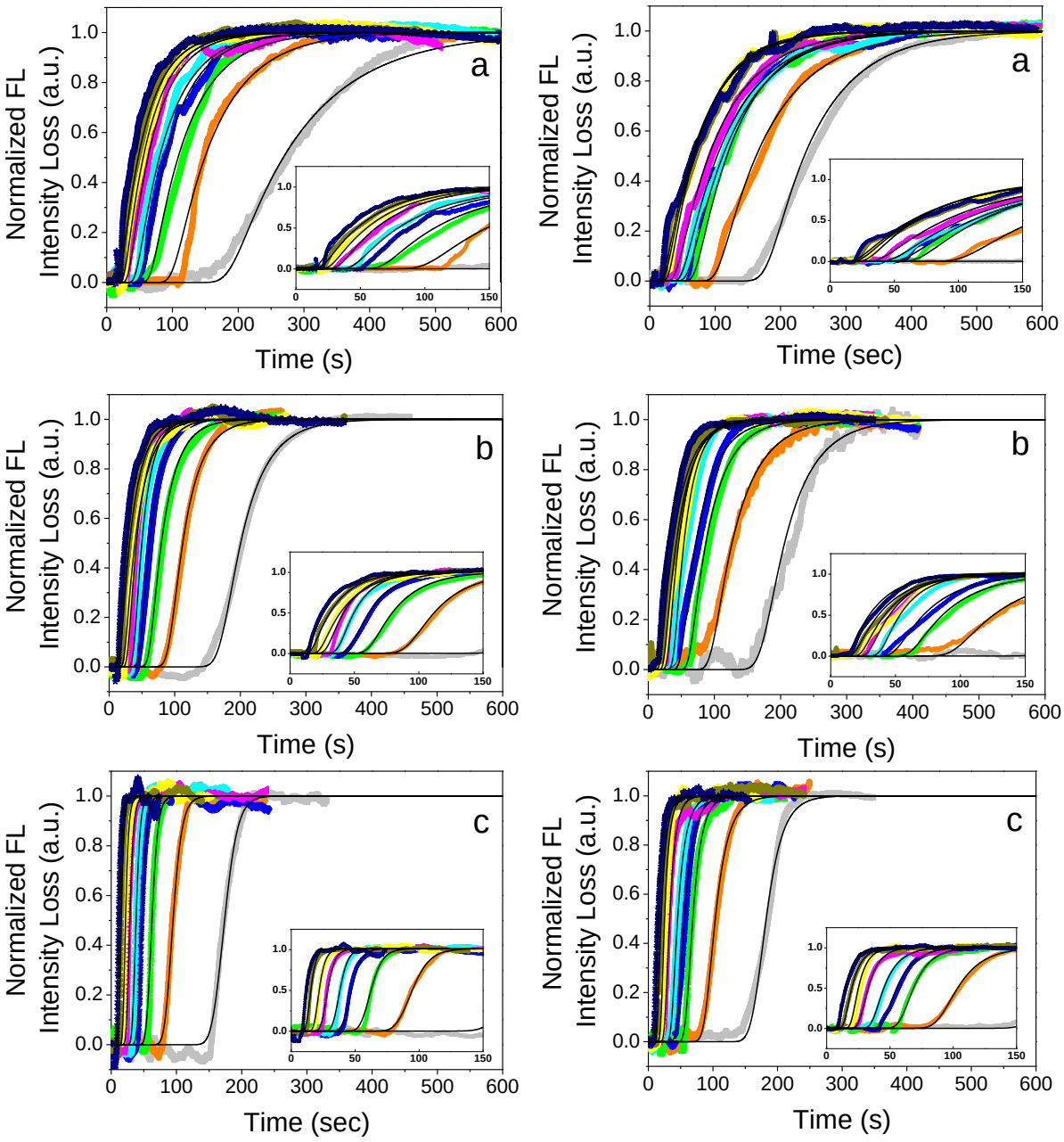

Figure S5. FRET breakthrough curves for RhB in FITC-modified pNIPAM films in poor (left: 20 mol% MeOH/H_2O and right: 31 mol% MeOH/H_2O) solvents for pNIPAM grafting densities that are a) high, b) medium, and c) low.

Table S1. Apparent diffusion coefficients for pNIPAM films of different grafting density and solvent quality conditions.

	High-density Films D_{app} **x** 10^{12} **cm**^{2}**/s**		**Medium-density Films** D_{app} **x** 10^{12} **cm**^{2}**/s**		**Low-density Films** D_{app} **x** 10^{12} **cm**^{2}**/s**	
Flow Condition	**192 µm/s**	**2,952 µm/s**	**192 µm/s**	**2,952 µm/s**	**192 µm/s**	**2,952 µm/s**
100% MeOH	1.9	9.3	2.4	12.3	2.7	15.0
13 mol% MeOH/H_2O	1.4	4.8	1.6	6.4	2.0	9.6
20 mol% MeOH/H_2O	0.8	2.0	1.0	2.2	1.9	6.1
31 mol% MeOH/H_2O	1.0	1.5	0.9	1.9	0.9	2.8

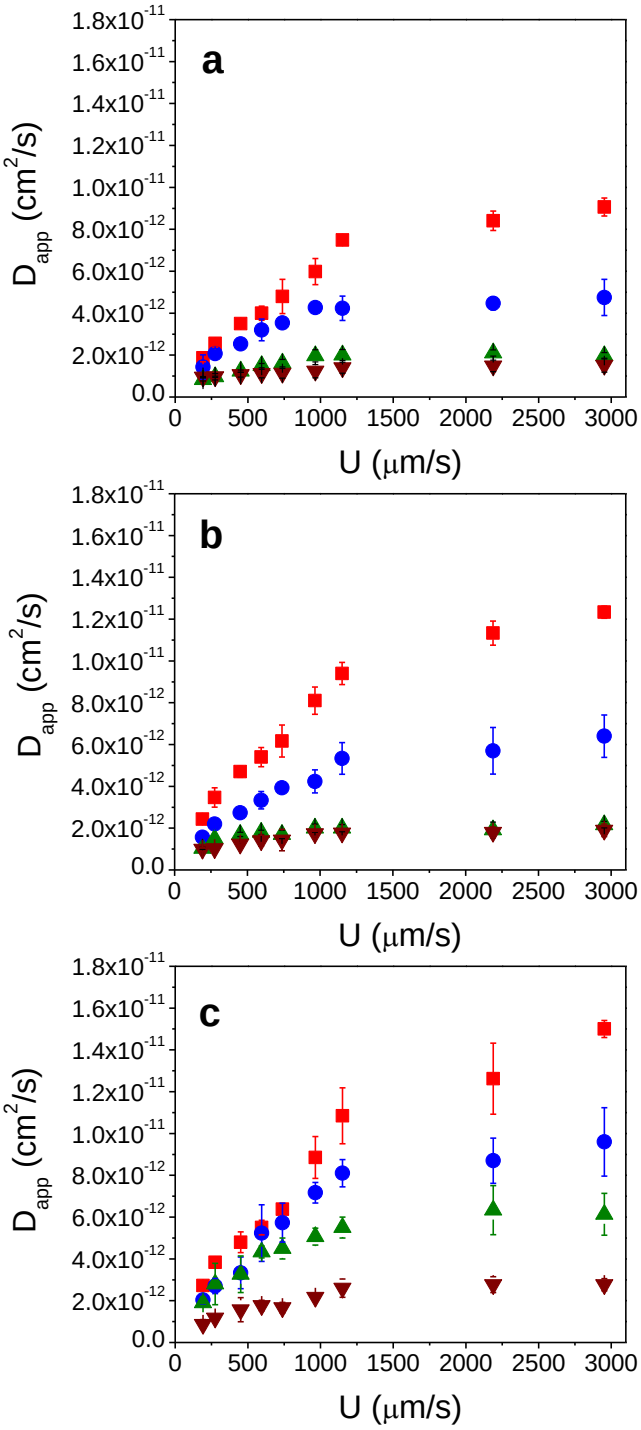

Figure S6. Apparent diffusion coefficients for RhB (D_{app}) as a function of linear flow velocity (U) for pNIPAM grafting densities that are a) high, b) medium, and c) low. Experimental data points correspond to different solvent quality: good solvent (100 % MeOH, red squares), theta solvent (13 mol% MeOH/H_2O, blue circles), and poor solvents (20 mol% MeOH/H_2O, green triangles; 31 mol% MeOH/H_2O, maroon triangles.)

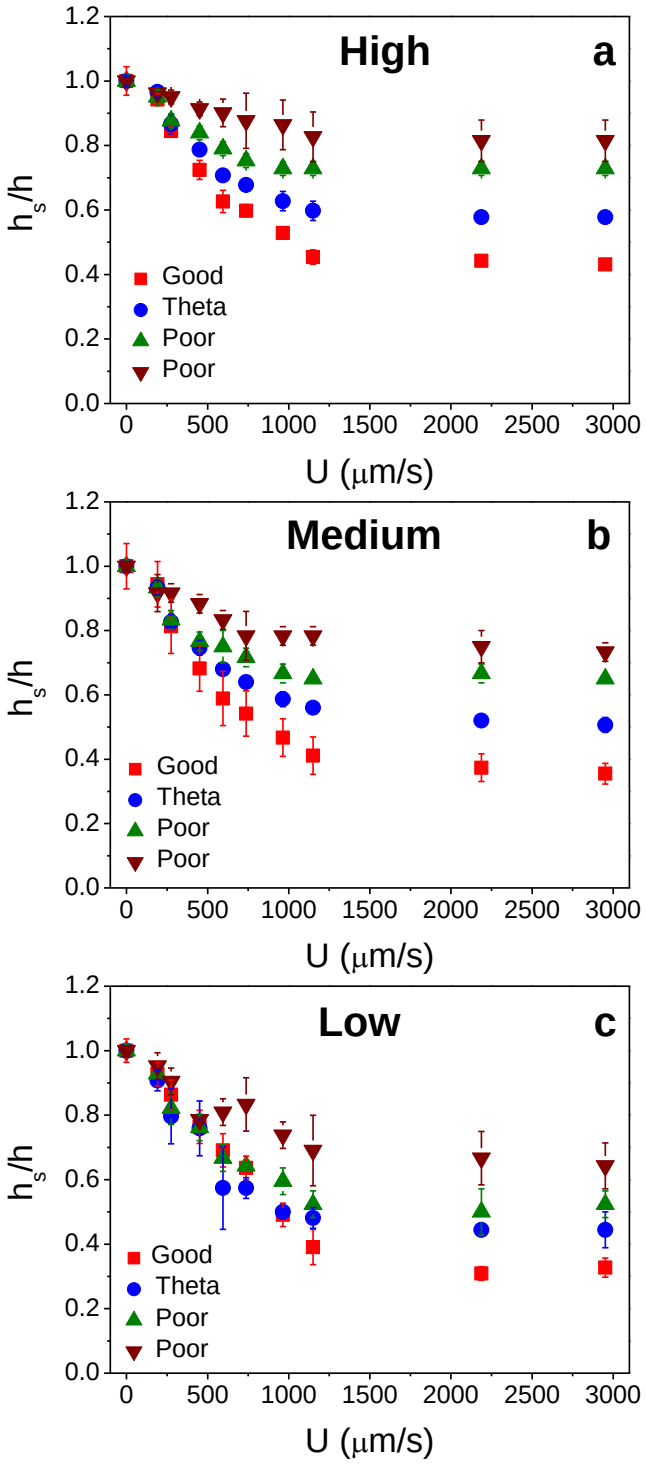

Figure S7. Fractional film thickness unaffected by flow field (h_s/h) as a function of applied linear flow velocity for pNIPAM film grafting densities that are a) high, b) medium, and c) low. Experimental data points correspond to different solvent quality: good (100% MeOH, red squares), theta (13 mol% MeOH/H_2O, blue circles), and poor solvents (20 mol% MeOH/H_2O, green triangles; 31 mol% MeOH/H_2O, maroon triangles.)

Consideration of resolution and measurement error in FRET-TIRFM

For a polymer film that is perfectly homogeneous in all solvent conditions such that mass transport of a reporter molecule can be reduced to a single value (here, the apparent diffusion coefficient, D_{app}), the vertical resolution is limited to a distance of 1.5 times the Förster radius of the FRET process, which in this case corresponds to a value of ~ 8 nm for a Förster radius of 5.5 nm. Thus, ideally, the slip length values would be good to about ± 8 nm. The measured standard deviations indeed reflected this, except for the high density film in methanol wherein film swelling occurs to the largest extent (to 225 nm), and the error is 15 nm or ~7% of the film swollen thickness, wherein the swelling uncertainty overwhelms the error from FRET. However, since it is known that these polymer brush films exhibit density gradients along the vertical direction that vary by solvent quality, the reality is that the true resolution is system-dependent and is a function of how well the value of D_{app} for a given film maps onto the range of real diffusion coefficient values across the density range of the film. Nonetheless, because the density gradient is not as severe under poor solvent conditions compared to good solvent conditions, the vertical resolution is expected to be better in poor solvents than in good solvents, although one would expect errors from limited resolution under all solvent conditions.

Further, we considered the possible error from differences in the rate of energy transfer in different solvents, and hence the Förster radius (which scale as n^{-4}) and whether this effect could lead to misinterpretation of solvent quality effects. One unique benefit of taking advantage of the co-nonsolvency effect for this work is that the refractive indices of methanol and water differ only slightly, 1.331 and 1.333, respectively. Given that we have quite high grafting densities, we estimate that, using an effective medium approximation for refractive index, the Förster radius should vary by no more than 10-15% across the three grafting densities, which is insufficient to alter our conclusions in any way. We further note that our measurements indicate in all cases that the stagnant layer thickness is greater than 20 nm, more than twice the Förster radius of ~8 nm. Therefore, any effects from the slight differences in refractive indices for the different grafting densities is unlikely to have a significant effect on our data analysis. Thus, while the absolute values of slip length reported here are probably only good to within 20-30%, the relative values and trends in the values observed are well validated by the quality of the fits to the Taylor-Aris-Fickian model used to fit the breakthrough curves.

For completeness, we further note that the resolution is additionally limited to a small extent by error that comes from fitting of the experimental data to a numerical solution to the Taylor-Aris-Fickian diffusion model. As we could not obtain an analytical solution to this model, a finite element boundary condition has to be satisfied to obtain a numerical solution, which depends on D_{app} and the polymer film thickness being measured. In general, the thicker the film, the smaller D_{app}, and the smaller the finite element that can be used, which translates to better accuracy. In the reported study, 5 nm was used as the finite element for fitting; therefore, this finite element size contributes an additional error of 2% and 4% for good and poor solvents, respectively. Since these errors from fitting are smaller than the % error obtained from the reproducibility of the measurements from multiple samples of 5-10%, we conclude that these contributions are negligible.