Supporting Information for

Manipulating Protein Adsorption Using a Patchy Protein-Resistant Brush

By
S. Gon, M. Bendersky, J.L. Ross, and M.M. Santore

Demonstration of Patch Deposition and Retention.

Figure S-1 demonstrates the PLL deposition portion of the procedure used to create patchy brushes, here with a 5 ppm solution of PLL at a wall shear rate, γ, of 5 s^{-1}. In the top curve, PLL adsorbs at its transport-limited rate, up to saturation of 0.4 mg/m^2, at which point the kinetic trace spontaneously turns horizontal. The adsorption process takes 9-10 minutes at these conditions. Injecting buffer before surface saturation, in the lower curves, halts adsorption prematurely. The resulting unsaturated layers are well-retained in flowing buffer. At these conditions, we found it possible to tightly control the amount of PLL deposited on the surface, with precision of .025 mg/m^2. Greater precision for the creation of surfaces with larger spacing between adsorbed PLL coils was obtained by employing a more dilute PLL solution. Indeed, with some systems, such as 11 nm nanoparticles we find it possible to reproducibly place as few as 10 surface elements or polycation coils per um^2 on the substrate though, in the current work, we found it necessary only to go down to a few hundred PLL patches / um^2, which corresponds to 0.01 mg/m^2. Notably the flatness of the buffer rinsing portions of the curves indicates stable PLL layers and patches in these conditions.

Figure S-2 demonstrates the retention of PLL following exposure to buffer, PLL-PEG, and fibrinogen. These data, measured using total internal reflectance fluorescence (TIRF), as used extensively in the Santore lab, were generated using a lightly fluorescein-tagged PLL sample.

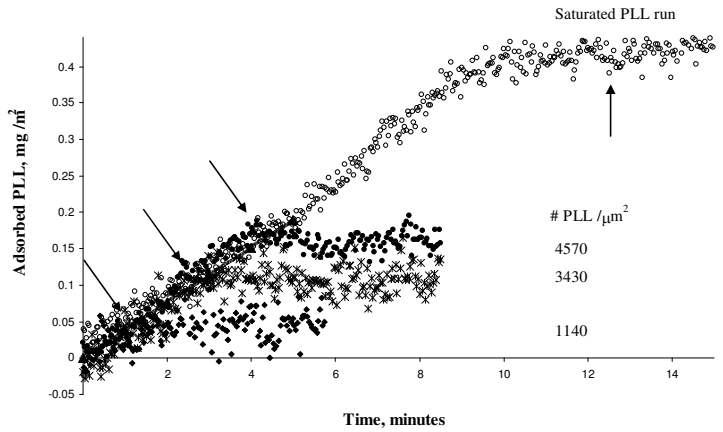
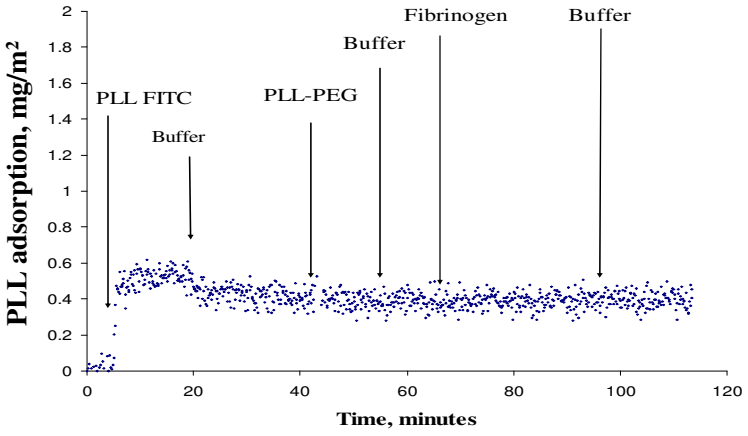


Figure S-1. Controlled PLL deposition to make cationic patches. Buffer injection at arrows limits the amount of PLL deposited. Buffer injection at the arrow for the saturated run demonstrates good retention of the fully saturated layer

Because TIRF sees only fluorescent species, any adsorption of PLL-PEG or fibrinogen is not visible in Figure S-2; however, there is no confusion about the signal being exclusively due to the PLL, which is well-retained on the surface. Of note in Figure S-2, there is a small and rapid decrease in fluorescence signal upon buffer reinjection following the initial PLLadsortpion. This signal decrease is not seen in the reflectometry runs of Figure S-1, and we therefore conclude it results from washing of a small amount of fluorescent material from the near-surface (but not adsorbed) region excited by the evanescent wave, which is about 100 nm deep. After this intial flushing of fluorescent PLL from the chamber, the signal level is maintained upon exposure to the other challenging species.

Figure S-2. TIRF experiment for the adsorption of fluorescently-labeled PLL, subsequently challenged by flowing buffer, PLL-PEG, and fibrinogen. The PLL-PEG and fibrinogen are unlabeled and therefore not visible in the experiment, which shows the retention of the labeled PLL.



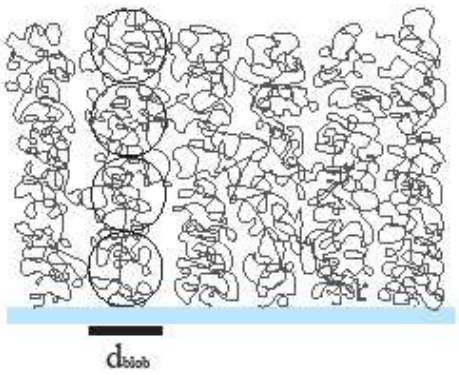
Calculation of Brush Height

The calculation of the brush height follows the "blob" approach put forth by Alexander and DeGennes,[1,2,3] in which sections of the chain, each possessing about a kT of energy, termed "blobs," extend normal to the surface (Figure S-1). The brush height is the blob diameter times the number of blobs:

$$\text{Height} = (N / N_{blob})\, d_{blob} \qquad \text{(S-1)}$$

The number of blobs in a chain is equal to the number of statistical segments in a chain divided by the number statistical segments in a blob, N/N_{blob}. The blob diameter corresponds to the spacing of the PEG anchors, 1.85 nm, calculated from the experimentally adsorbed amount of PLL-PEG coverage at saturation.

Using data from the handbook,[4] C-infinity = 3.8, we determine that for PEG a statistical segment length, b, is 0.57 nm and the molecular weight of a statistical segment is 59. Therefore a 2000 molecular weight PEG chain contains 34 statistical segments while $N_{blob} = 7.1$, based on a good solvent (blob diameter = 1.85 nm= $b\, N_{blob}^{3/5}$). From Equation S-1 follows a brush height of 9 nm.



[1] S. Alexander J. Phys. (Paris) 38 (1977) 977.
[2] P.G. De Gennes J. Phys. (Paris) 28 (1976) 1443.
[3] S.T. Milner, Science 251 (1991) 905.
[4] J. Brandup and E.H. Immergut "Polymer Handbook," 4ed. J. Wiley and Sons, NY 1999.