

Supporting Information

Fitting ellipsometric data with an error function

Following R  he and co-workers,¹ the function used for fitting ellipsometric data with an error function was:

$$\varphi_p(z) = \varphi_0 \operatorname{erf} \left(\frac{\frac{z}{d} - i}{w} \right) \quad [\text{S1}]$$

where φ_0 is a normalisation constant, z the distance from the surface, d the total thickness of the 10-slab model, i the location of the point of inflection and w a variable controlling how ‘box-like’ the profile is (the ‘interface width’). By varying φ_0 , d and w , density profiles which are step-like (Figure S1), exponential-like (Figure S2) or parabolic-like (Figure S3) can be reproduced.

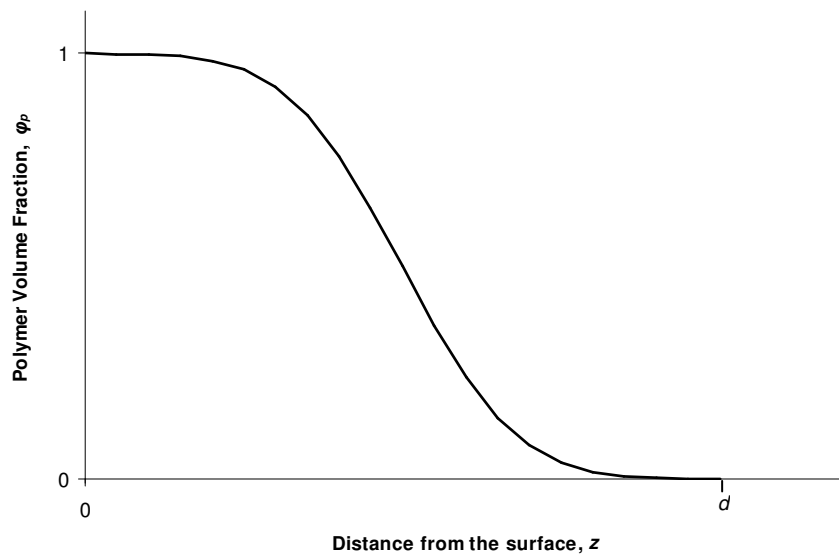


Figure S1. Step-like density profile given by the error function in equation S1, with $\varphi_0 = 0.5$, $i = 0.5$ and $w = 0.2$

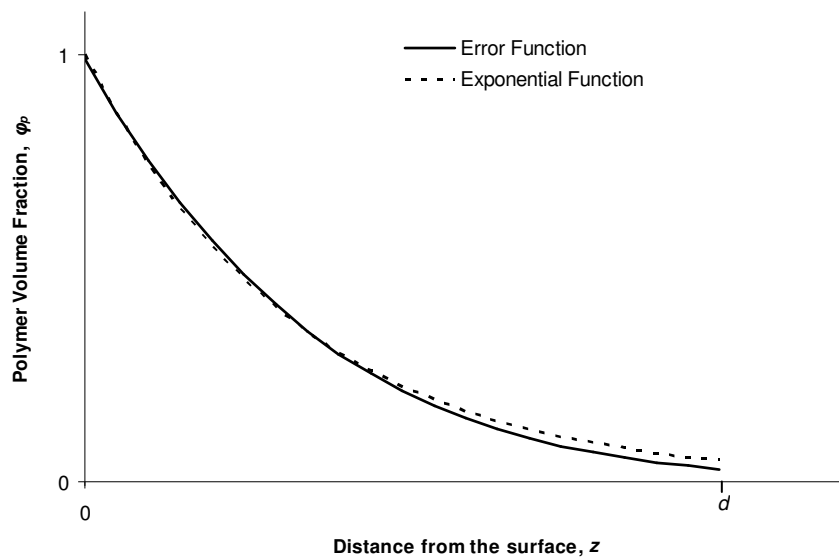


Figure S2. Exponential-like density profile given by the error function in equation S2, with $\varphi_0 = 6.28$, $i = -1$ and $w = 1$. A typical exponential decay function is shown with a dotted line.

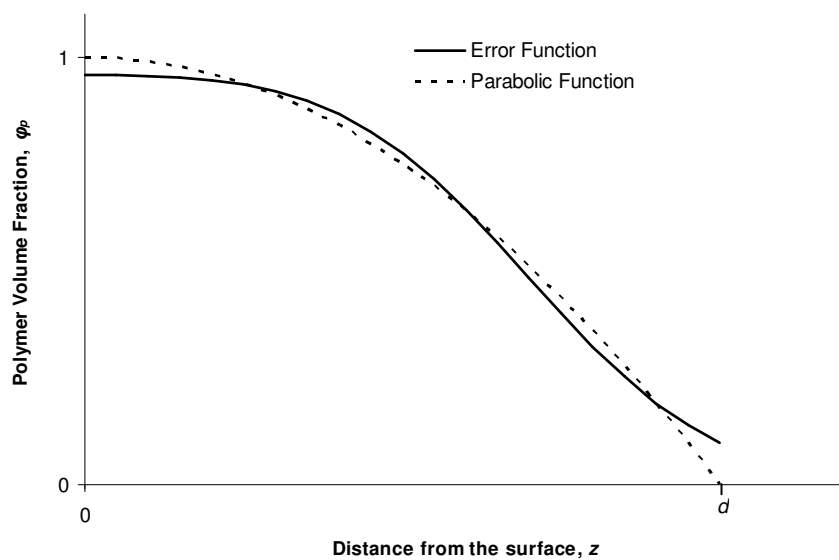


Figure S3. Parabolic-like density profile given by the error function in equation S2, with $\varphi_0 = 0.48$, $i = 0.70$ and $w = 0.33$. A parabolic function is shown with a dotted line.

Justification for Equation 4

The result derived by R  he and co-workers² (who apply a Flory-type expression for the free energy of the polymer networks³) for the volumetric degree of swelling for unconstrained and surface-attached polymer networks of the same polymer with the same crosslink density is:

$$S_{uc} \approx \left(\frac{1}{\phi_0 N_c} \right)^{-3/5} \quad \text{for unconstrained swelling in three dimensions} \quad [S2]$$

and

$$S_{sa} \approx \left(\frac{1}{\phi_0 N_c} \right)^{-1/3} \quad \text{for constrained swelling of surface-attached networks} \quad [S3]$$

where S_{uc} is the volumetric degree of swelling for an unconstrained network, S_{sa} that for a surface-attached network, ϕ_0 the polymer volume fraction in a reference state (e.g. $\phi_0 = 1$ for dry polymer) and N_c the number of segments between crosslinks.

However, we will allow the crosslink density for these systems to differ, giving:

$$S_{uc} \approx \left(\frac{1}{\phi_0 N_{c,uc}} \right)^{-3/5} \quad [S4]$$

and

$$S_{sa} \approx \left(\frac{1}{\phi_0 N_{c,sa}} \right)^{-1/3} \quad [S5]$$

Where $N_{c,uc}$ and $N_{c,sa}$ the number of segments between crosslinks for the unconstrained and surface-attached networks respectively. Assuming ϕ_0 is equal for the two systems, we can combine equations S4 and S5 to give

$$S_{sa} = \left(\frac{N_{c,sa}}{N_{c,uc}} \right)^{1/3} S_{uc}^{5/9} \quad [S6]$$

which is the result used in equation (4) in the main text, with $A = \left(\frac{N_{c,sa}}{N_{c,uc}} \right)^{1/3}$.

Justification for Equation 6

Assuming that the brush can be treated as a surface-attached, cross-linked network, equation [S6] can be rewritten as:

$$S_{brush} = A S_{gel}^{5/9} \quad [S7]$$

where S_{brush} is the volumetric degree of swelling for the brush, and S_{gel} is that for the gel (which undergoes unconstrained swelling).

We can introduce a new quantity 'relative volume' V_{rel} which is the sample volume in a given solvent mixture V normalised with respect to the sample volume in pure water V_0 . That is,

$$V_{rel} = \frac{V}{V_0} \quad [S8]$$

The volumetric swelling ratio can be expressed as the ratio of the sample volume in a given solvent mixture to the volume in the dry state V_{dry} :

$$S = \frac{V}{V_{dry}} \quad [S9]$$

We can define S_0 as the volumetric swelling ratio of the sample in pure water, that is:

$$S_0 = \frac{V_0}{V_{\text{dry}}} \quad [\text{S10}]$$

which allows us to relate the relative volume V_{rel} to the volumetric swelling ratio S in a given solvent by combining equations S8, S9 and S10:

$$V_{\text{rel}} = \frac{S}{S_0} \quad [\text{S11}]$$

Considering the relative volume for the brush $V_{\text{rel,brush}}$, equation S11 can be written as:

$$V_{\text{rel,brush}} = \frac{S_{\text{brush}}}{S_{0,\text{brush}}} \quad [\text{S12}]$$

where $S_{0,\text{brush}}$ is the volumetric swelling ratio for the brush in pure water. Substituting for S_{brush} and $S_{0,\text{brush}}$ using equation [S7]:

$$V_{\text{rel,brush}} = \frac{AS_{\text{gel}}^{5/9}}{AS_{0,\text{gel}}^{5/9}} = \frac{S_{\text{gel}}^{5/9}}{S_{0,\text{gel}}^{5/9}} = V_{\text{rel,gel}}^{5/9} \quad [\text{S13}]$$

where $S_{0,\text{gel}}$ is the volumetric swelling ratio for the gel in pure water and $V_{\text{rel,gel}}$ the relative volume for the gel at a given solvent composition, which is the result used in equation 6 in the main text.

Typical ellipsometric kinetics data for swelling

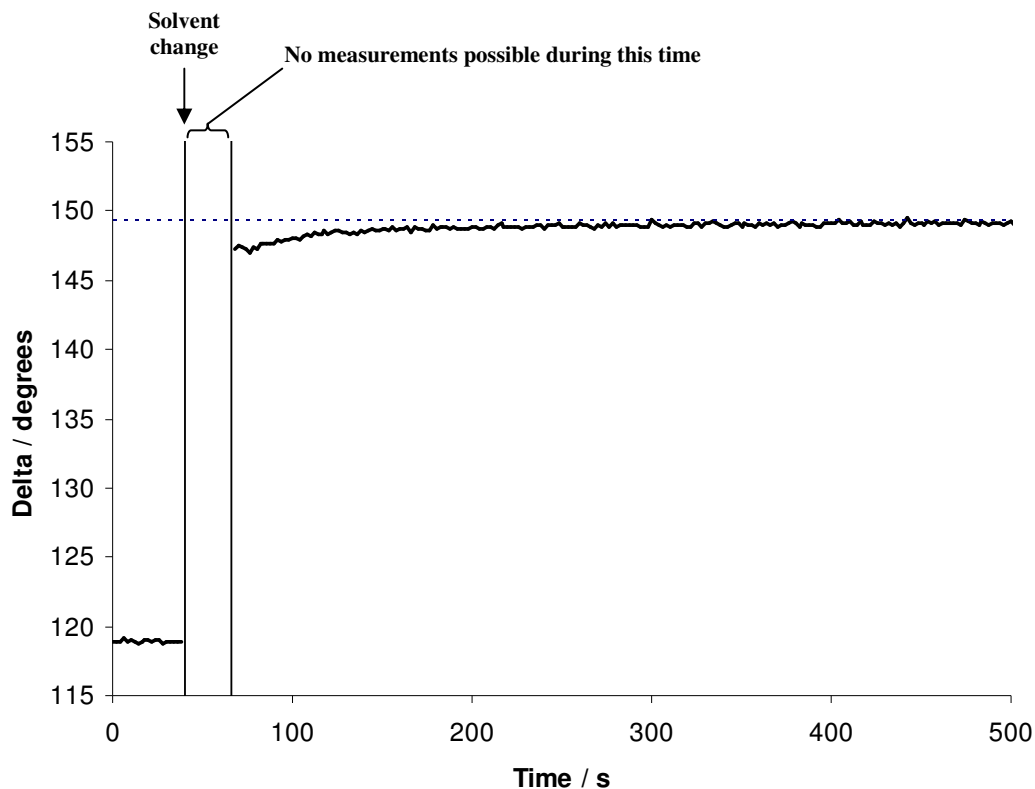


Figure S4. Typical ellipsometric data from a swelling event of PMPC brushes upon a solvent change. The ellipsometric angle Δ at 500 nm wavelength is shown as a function of time. At the point indicated on the plot, the solvent was changed from 8:92 v/v water:ethanol (a poor solvent for the brush) to pure ethanol (a good solvent for the brush). No measurements were possible immediately after the solvent change due to lack of beam alignment on the ellipsometer. The dotted line is a guide to the eye to show the eventual value of Δ . The relationship between Δ and swollen brush thickness is complex in general; however for this system it is approximately linear, with Δ increasing with thickness.

References

- (1) Habicht, J.; Schmidt, M.; Ruhe, J.; Johannsmann, D. *Langmuir* **1999**, *15*, 2460-2465.
- (2) Toomey, R.; Freidank, D.; Ruhe, J. *Macromolecules* **2004**, *37*, 882-887.
- (3) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.