Supporting Information:

Switching the Interpenetration of Confined Asymmetric Polymer Brushes.

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Further experimental details

PDMAEMA Brush Formation: For ARGET-ATRP polymerisation, 30.0 ml propan-2-ol, 30.0 ml 2-(dimethylamino)ethyl-methacrylate (DMAEMA, 28 g, 178 mmol), 82.1 mg 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 0.356 mmol) and 1.58 ml water were first mixed in a round-bottomed flask sealed with a septum and deoxygenated by bubbling through nitrogen for at least 15 minutes. 16 mg $CuBr_2$ (0.072 mmol) and 125 mg ascorbic acid (AA, 0.710 mmol) were then added, the headspace purged with nitrogen and the mixture magnetically stirred and briefly sonicated to dissolve the solids. A very light yellow solution resulted. Meanwhile, a silicon block was placed in a beaker which was sealed inside a vacuum desiccator. The desiccator was filled with nitrogen using at least three pump/refill cycles. The polymerisation solution was then syringed over the silicon block. After the desired polymerisation time, typically 16 hours, the block was removed from the desiccators. The sample block was then washed with propan-2-ol and again with water, afterwards the sample was dried under a nitrogen stream.

Data Analysis: Fitting of the neutron reflectivity data was achieved using an optical matrix method[2] in RasCAL.[3] A custom model was developed for analysing the sample, whereby the unconfined polymer brush is split into 4 layers. A sub-phase and an incident medium are also required. Each of these regions is described by a thickness, roughness and scattering length density (SLD) parameter. In addition, the brush layer also requires a parameter for the water volume fraction.

The incident medium in this model is always a semi-infinite silicon layer, i.e. it only has one boundary interface in the optical calculations. The material of the sub-phase depends on the

confinement and which polymer brush is being analysed. For unconfined PEO brushes, the sub-phase is considered to be a semi-infinite layer of H_2O. When PDMAEMA brushes are examined the sub-phase is a semi-infinite D_2O layer. The SLD of each of these materials is listed in Table S1, unless noted otherwise these values were determined by fitting this model to the experimental data.

Between the incident and sub-phase regions are the layers of the polymer brush sample. The first layer required is to represent a thin SiO_2 layer present on the Si block; the SLD listed in Table S1 is lower than the SLD for pure SiO_2 due to its porosity. A second layer is then required to account for the PS intermediate layer necessary to graft a polymer brush to the substrate. The thicknesses of these layers are determined by ellipsometry measurements between the samples' fabrication stages. The roughness values are determined by fitting the unconfined sample data.

After grafting the brushes to the PS, only a single additional layer is required to describe the additional polymer. The PS component of the co-polymer used to make the brushes is indistinguishable from the PS intermediate layer. Therefore, to account for it, the thickness of the PS intermediate layer, which was determined by ellipsometry, is increased by 15 Å; the expected thickness of the PS component of the brush based on the brush's grafting density, this is approximately the thickness of a single PS monolayer. The thickness of the additional layer used to describe the brush is determined by ellipsometry measurements of a dry sample. The key model parameter is the hydration of this polymer brush layer. The uptake of water both swells the layer's thickness and alters its SLD. The SLD (s) and thickness (δ) of a wet layer are those used in the fitting model. The wet and dry values are related by:

$$s = s_{H_2O}\phi + s_p(1-\phi) \quad \text{(S1)}$$

$$\delta_{wet} = \delta_{dry}/(1-\phi) \quad \text{(S2)}$$

where s_{H_2O} is the SLD of H_2O, s_p is the SLD of the polymer, and ϕ is the volume fraction of the water in the layer (often referred to as hydration).

With this model there are 4 free fitting parameters for unconfined brush data sets, the 3 internal roughnesses and the brush hydration. To account for the rough interfaces in the model, a Gauss error function is used with the roughness parameter listed as the value used to scale this function appropriately. However, the exception to this is the roughness of an unconfined polymer brush, which is modelled using a parabolic function, $1\text{-}ax^2$. To more easily compare the brush's parabolic profile to the sample's internal roughness's, an equivalent Gauss error function value that closely estimates the parabolic shape of the brush is instead provided in Table S2. No dispersity in thickness of any layer of the sample is required to match the experimental data. Compression of the brush significantly alters the roughness and hydration of the brush layer.

When confined, an additional layer is added in order to model the presence of the confining brush. This layer represents the dPEO brush, and the material of the sub-phase is changed to dPS to account for the >50 nm layer deposited onto the Melinex® sheet and the dPS component of the co-polymer used to fabricate the brush. The comparatively large thickness of the dPS means we

can consider this layer to be semi-infinite. The value for the thickness of the dPEO layer was determined from the thickness obtained from previous work with brushes fabricated in the same way with equivalent grafting densities.[4] The thickness of the brushes on the Melinex® cannot be determined directly by ellipsometry due to the transparent nature of the materials and their comparative thicknesses.

The effect of confinement on the brushes depends on whether a sample has charged groups on one of the brushes. Without charged groups only the hydration of the two brushes and the roughness between them are variables, the thicknesses of the layers are not altered and the remaining internal roughness values are kept constant from the unconfined data. Hence there are 3 free parameters for these data sets. If a charged group is present on one of the brushes in the sample then an additional variable needs to be introduced representing the thickness reduction of the sample due to interpenetration. The interpenetration value, *i*, reduces the thickness of both the dPEO and PDMAEMA layers by *i*/2. Interpenetrating samples also have a much higher roughness at the interface of the two brushes. Therefore, there are 4 free parameters for interpenetrating samples. The values used for all these parameters are listed in Table S2.

Using error analysis within the program to calculate the standard deviation error, the uncertainty in the polymer brushes' water volume fraction is ±4% v/v when unconfined and is ±1.5% v/v when confined. The error in the fitted roughness values is ±1 Å.

References

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(2) Born, M.; Wolf, E. *Principles of optics*; Pergamon Press: Oxford, UK, 1970.

(3) Hughes, A. RasCAL http://sourceforge.net/projects/rscl/.

(4) Abbott, S. B.; de Vos, W. M.; Mears, L. L. E.; Cattoz, B.; Skoda, M. W. A.; Barker, R.; Richardson, R. M.; Prescott, S. W. *Macromolecules* **2015**, *48* (7), 150319144329000.

Neutron reflectivity model parameters

Table S1: Scattering Length Density (SLD) Values

Material	SLD ($\times 10^{-6}$ Å^{-2})	Material	SLD ($\times 10^{-6}$ Å^{-2})
Si	2.07*	d-PEO	5.70
SiO_2	2.75	d-PS	6.0
Initiator	1.128	H_2O	- 0.56*
PDMAEMA	1.33		

*value determined theoretically†

†Sears, V. F., *Neutron News*, **1992**, *3*, 26-37.

Table S2: Layer Parameters

pH	SiO_2 thickness	SiO_2 roughness	Initiator thickness	Initiator roughness
2	25 Å	4 Å	60 Å	4 Å
5	36 Å	4 Å	65 Å	4 Å
10	35 Å	8 Å	65 Å	4 Å

pH	PDMAEMA dry thickness	PDMAEMA roughness	PDMAEMA hydration	dPEO thickness
2	61 Å	16 Å	19 %	35 Å
5	67 Å	16 Å	20 %	34 Å
10	97 Å	3 Å	0 %	34 Å

pH	dPEO roughness	dPEO hydration	Interpenetration, *i*	Dispersity
2	3 Å	0 %	34 Å	±5 %
5	4 Å	1 %	27 Å	±5 %
10	3 Å	0 %	0 Å	±5 %

Only the values for the interpenetrating (pH2 and pH5) or compact (pH10) case are presented.

Scattering Length Density (SLD) profiles

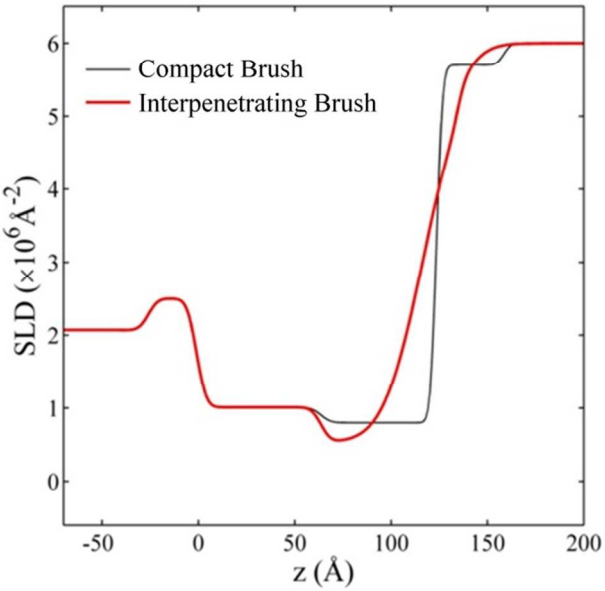

Figure S1: SLD profiles for the pH 2 neutron reflectivity data. The origin (z=0) is at the SiO_2-PS interface. The thick red line is the profile for an interpenetrating brush that results in the ideal fit. The thin black line is the alternative compact profile that results in a poor fit.

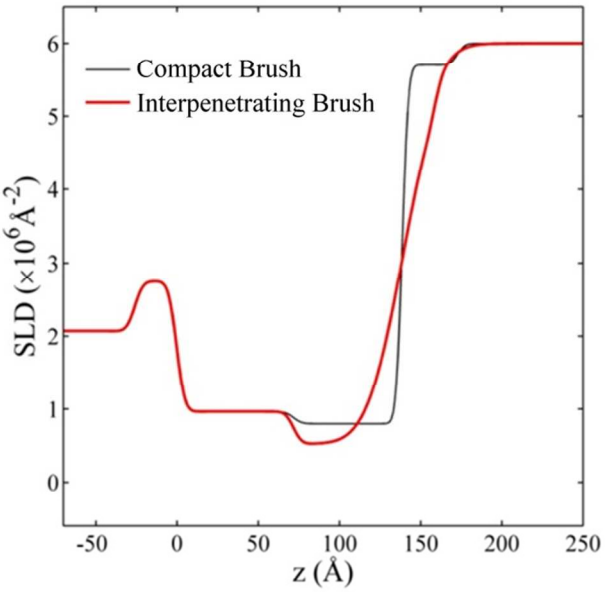

Figure S2: SLD profiles for the pH 5 neutron reflectivity data. The origin (z=0) is at the SiO_2-PS interface. The thick red line is the profile for an interpenetrating brush that results in the ideal fit. The thin black line is the alternative compact profile that results in a poor fit.

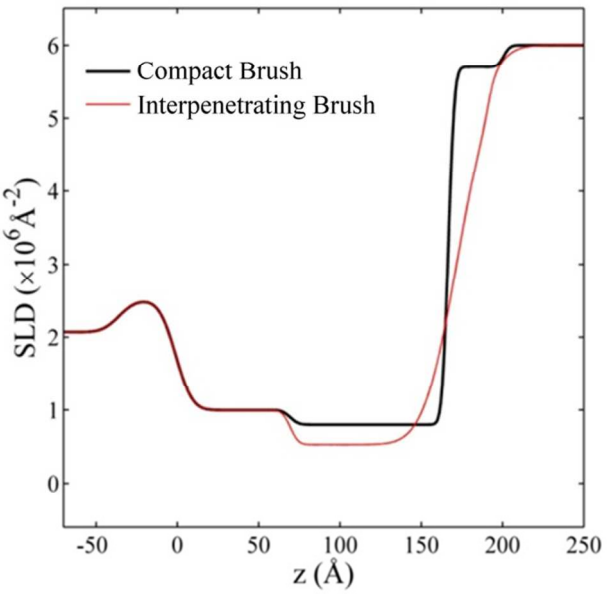

Figure S3: SLD profiles for the pH 10 neutron reflectivity data. The origin (z=0) is at the SiO_2-PS interface. The thick black line is the profile for a compact brush that results in the ideal fit. The thin red line is the alternative interpenetrating profile that results in a poor fit.

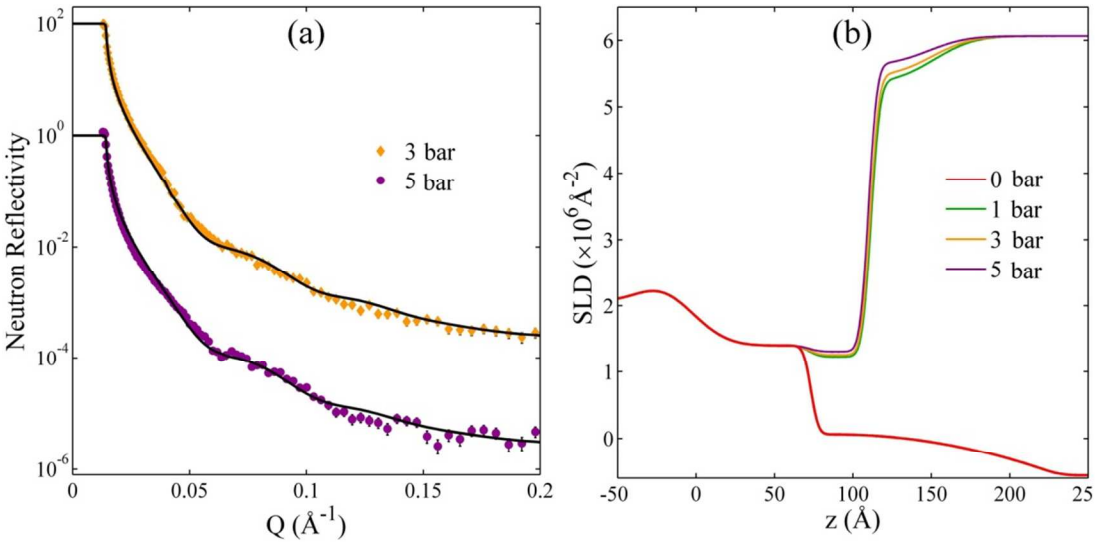

Figure S4: (a) Neutron reflectivity data and fits for the 0.2nm^{-2} d-PEO brush confined at higher pressures. (b) SLD profiles for all the 0.2nm^{-2} PEO:d-PEO neutron reflectivity data. The origin (z=0) is at the SiO_2-PS interface. The majority of the compression occurs with the application of 1 bar, further pressure increases have minimal additional effect.

Unconfined PDMAEMA

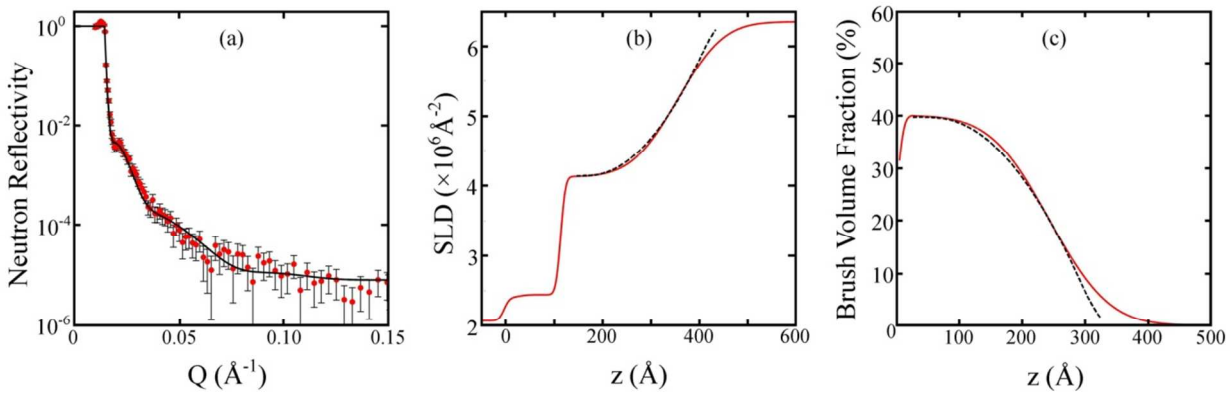

Figure S5: (a) Experimental neutron reflection data for an unconfined PDMAEMA brush hydrated with D_2O. The black line is a fit generated from optical calculations using the SLD profile presented in (b). This results in a volume fraction distribution presented in (c). In both (b) and (c) the black dashed line demonstrates the parabolic like profile of the brush, $1-(3.15\times10^{-5}\ z^2)$. At higher z, at the end of the brush, the volume fraction deviates from the parabolic profile due to the highly dispersed polymer chain length for a brush made by ATRP.

Alternative Plots of Neutron Reflectivity Fits

This figure has the neutron reflectivity multiplied by Q^4, and then plotted on a log-log axis. This removes the Q^4 bias from the plot presented in the main manuscript.

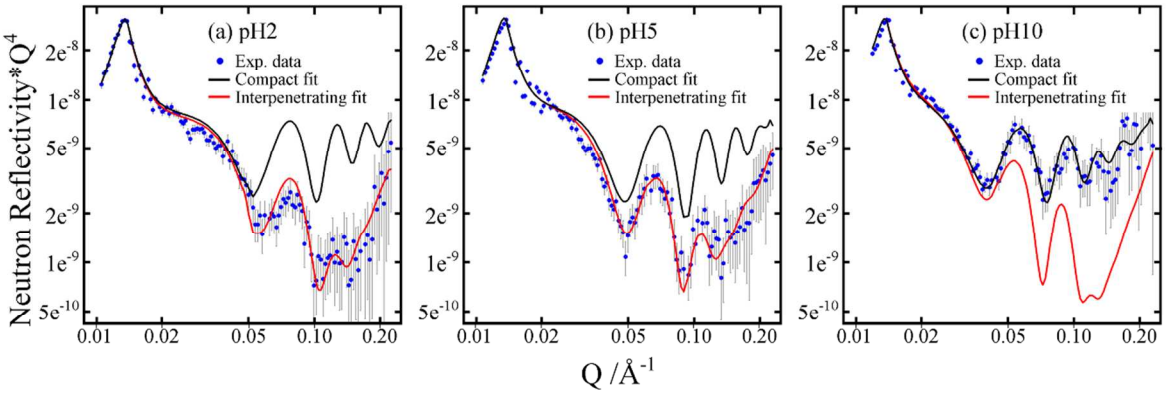

Figure S6: Neutron reflectivity data and potential fits for PDMAEMA and dPEO brushes confined with a pressure of 6 bar when the hydrating solution is (a) pH 2, (b) pH 5 and (c) pH 10. Both a compact and interpenetrating case is presented to illustrating the clear difference in the fit between non-interpenetration and interpenetration.