Electronic Supplementary Material (ESI) for Soft Matter.

Selective Hydrogen Bonding Controls Temperature Response of Layer-by-Layer Micellar Assemblies

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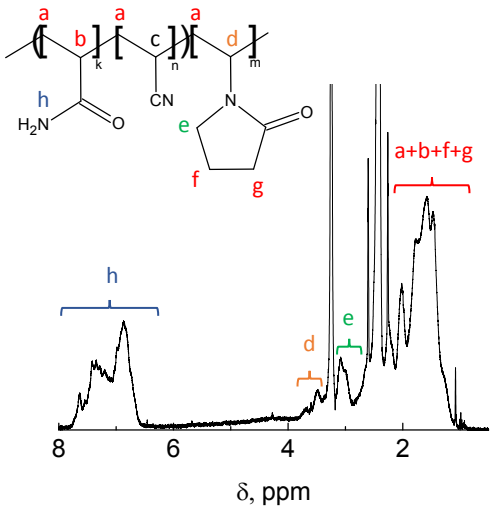

Figure S1. ^{1}H NMR of P(AAm-*co*-AN)-*b*-PVP in d_6-DMSO.

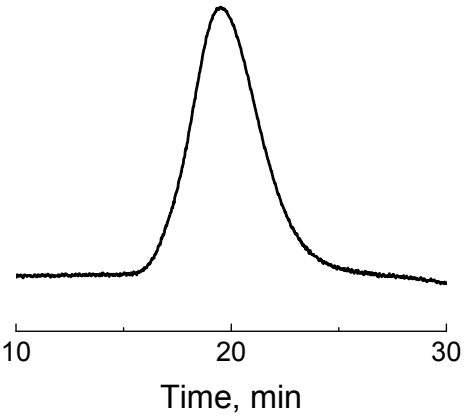

Figure S2. A GPC trace of 2 mg/ml P(AAm-*co*-AN)-*b*-PVP in DMSO. Flow rate of the eluent was 0.1 ml/min at 45 °C.

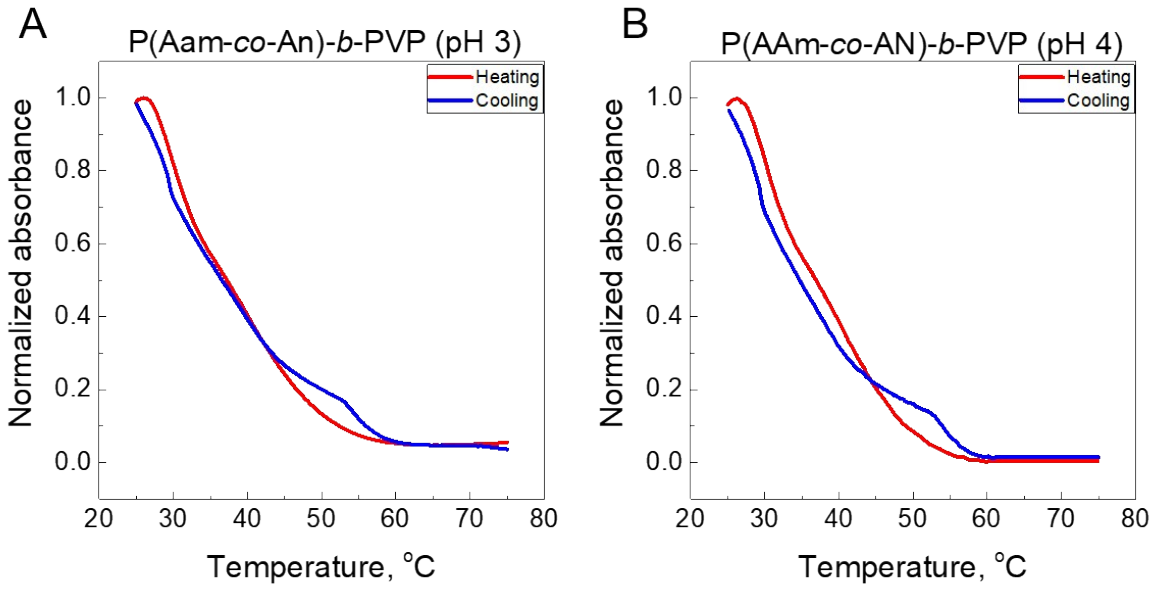

Figure S3. Temperature dependent turbidity in 1 mg/ml P(AAm-*co*-AN)-*b*-PVP solutions in PBS at pH 3 (A) and pH 4 (B).

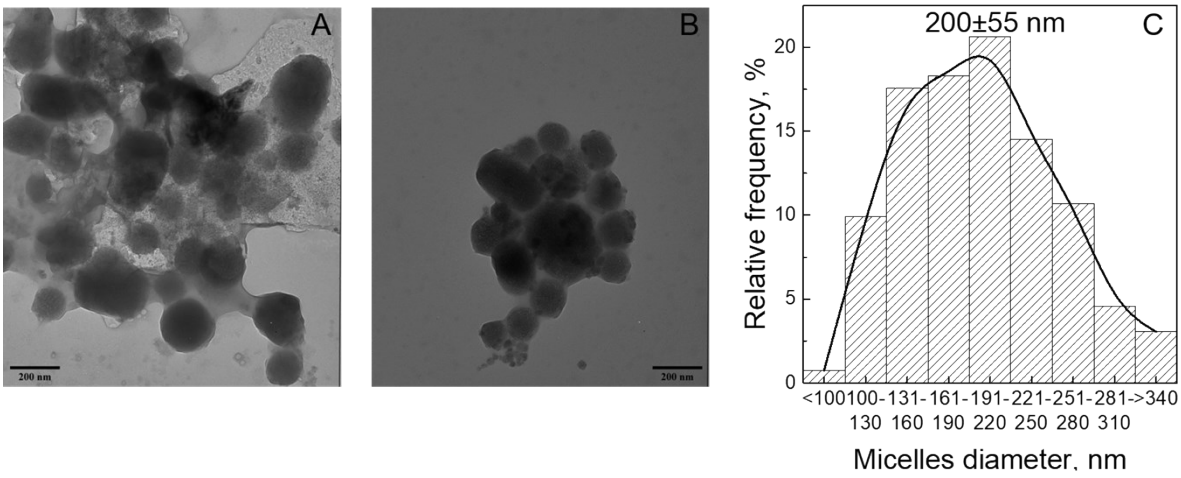

Figure S4. TEM images of UCSTMs dried from solutions at pH 3 (A) and pH 4 (B), as well as the micellar size distribution (C) dried from pH 4 solution.

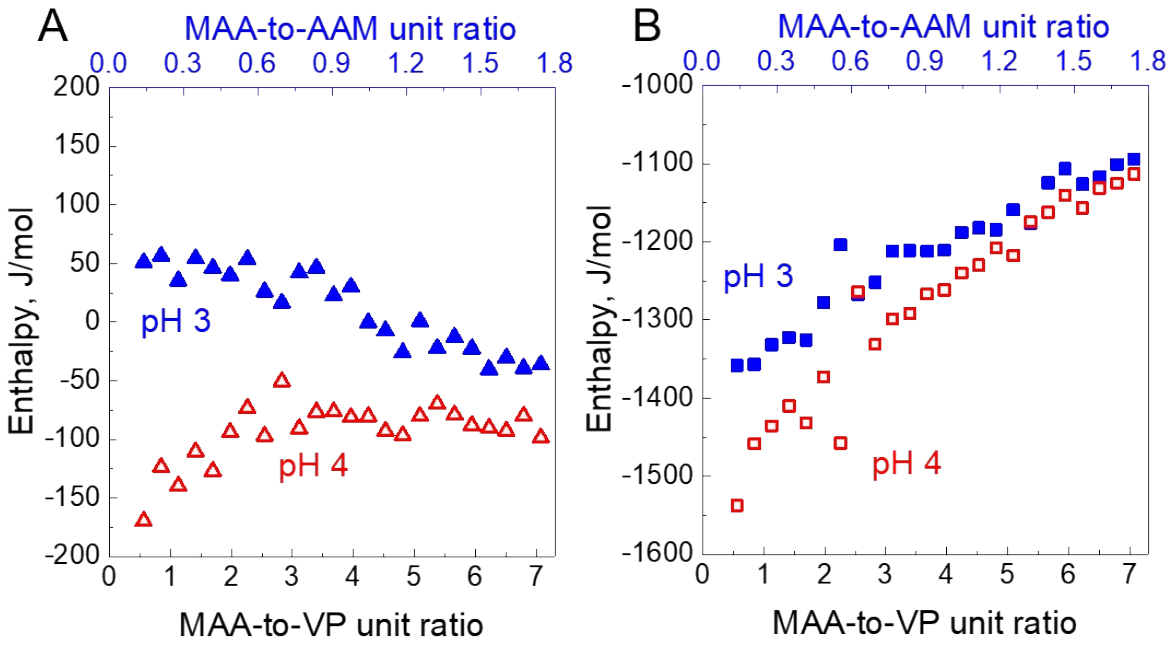

Figure S5. Enthalpy of dilution for PMAA to PBS at pH 3 and pH 4 at 25 °C (A) and 55 °C (B).

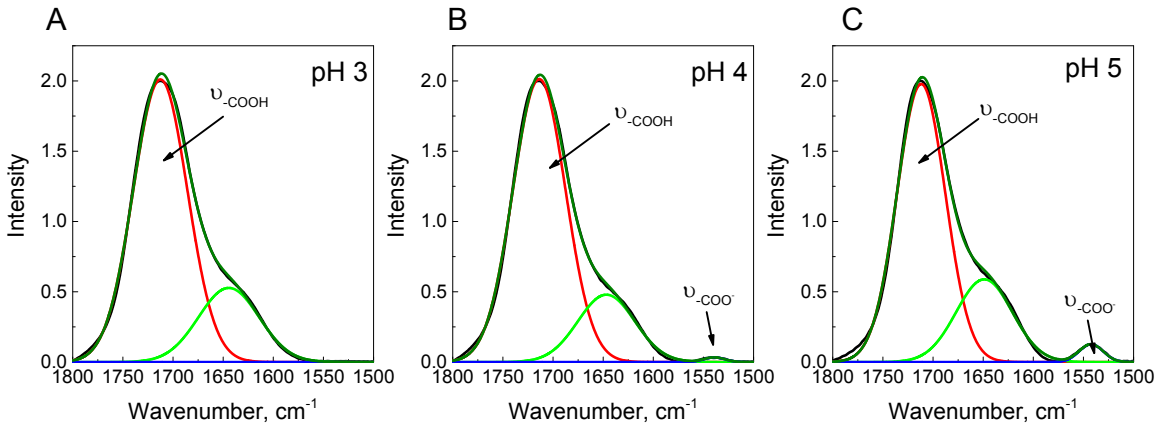

Figure S6. FTIR spectra of PMAA freeze-dried at pH 3 (A), pH 4 (B) and pH (5). Assuming that the extinction coefficients of stretching carbonyl vibrations of ionized and nonionized PMAA are equal, ionization of PMAA was determined as 0.6 ± 0.1 % at pH 4 and 3.8 ± 0.2 % at pH 5 from the ratio of 1540 cm^{-1} to the sum of two 1540 and 1720 cm^{-1} peaks in the 1500-1800 cm^{-1} region.

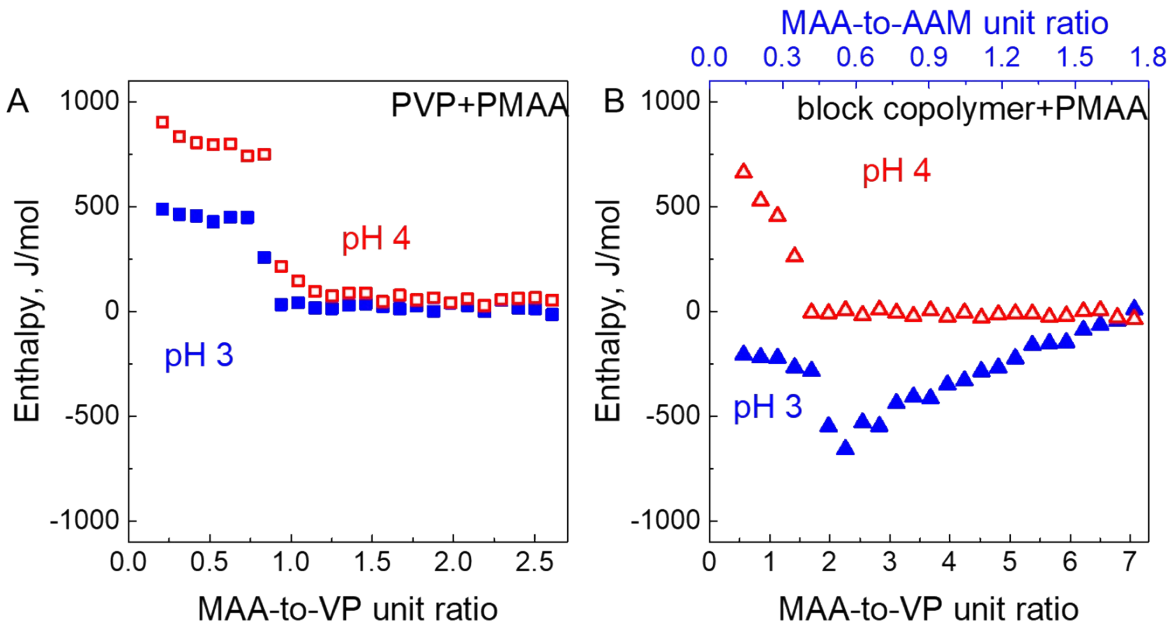

Figure S7. ITC titration of PVP (A), and P(AAm-*co*-AN)-*b*-PVP (B) with PMAA at pH 3 (closed symbols) and pH 4 (open symbols) at 55 °C.

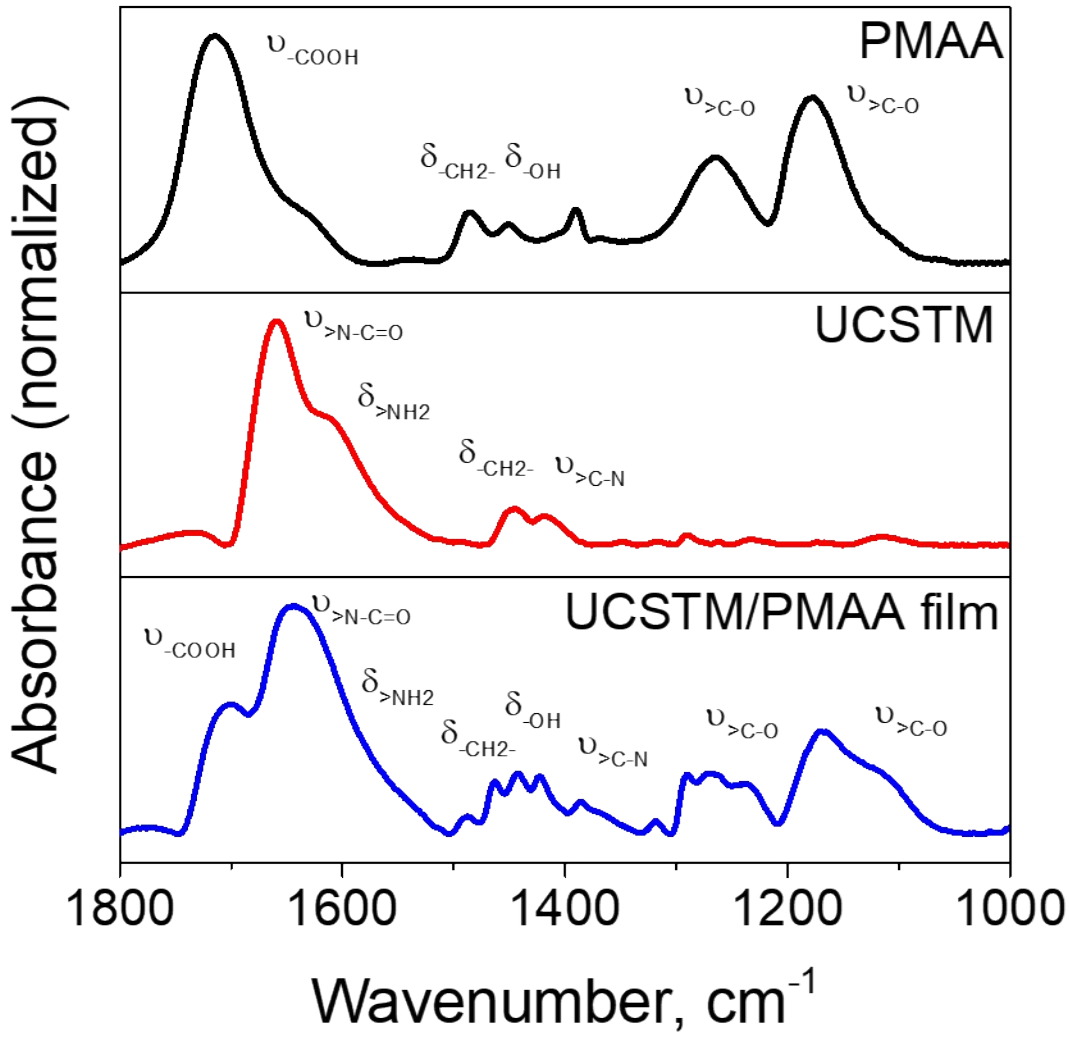

Figure S8. FTIR spectra of PMAA and UCSTM drop casted and dried on pre-cleaned silicon wafers, as well as UCSTMs/PMAA films deposited at pH 3.

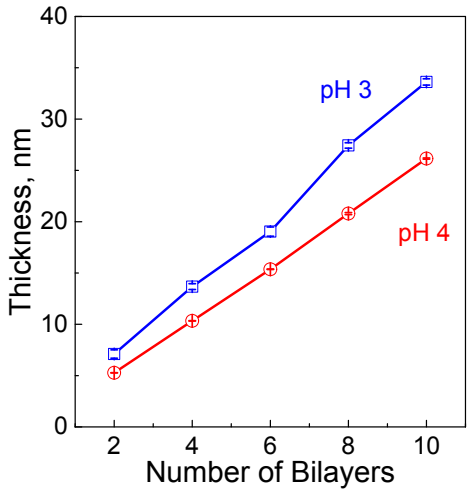

Figure S9. Ellipsometric dry thickness of PVP/PMAA films deposited at pH 3 (open squares, blue) and pH 4 (open circles, red) at room temperature.

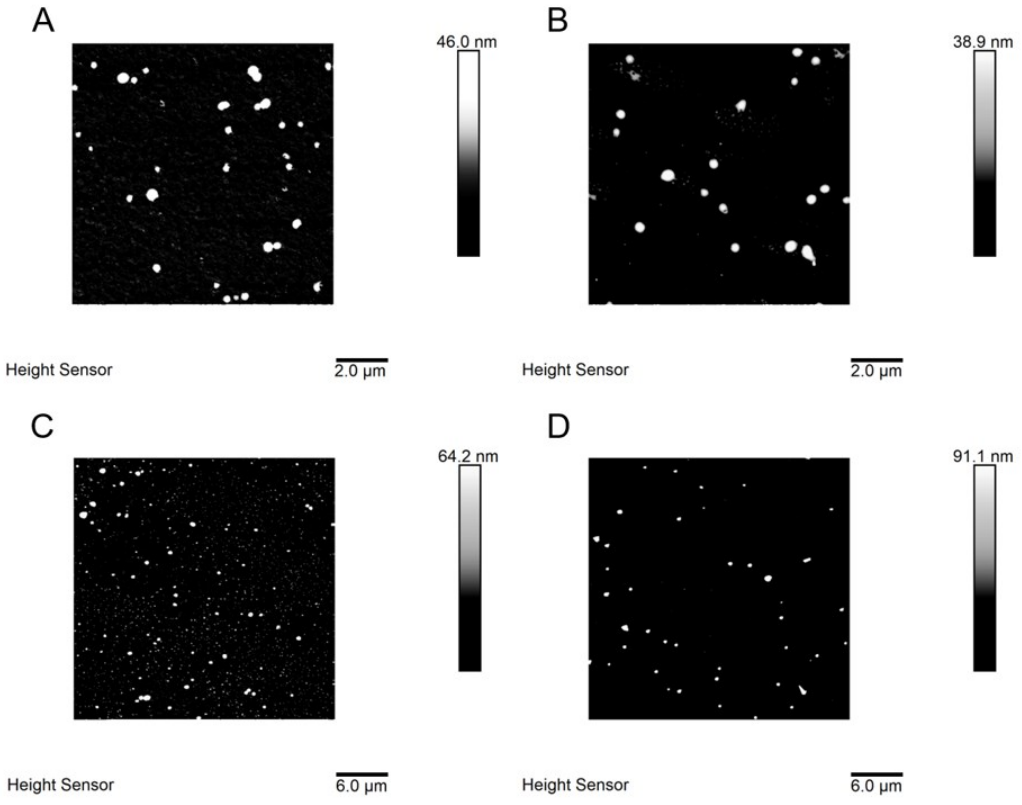

Figure S10. AFM images of monolayer of micelles deposited at pH 3 (A) and 4 (B) and 2 bilayer (UCSTM/PMAA) films deposited at pH 3 (C) and 4 (D) on silicon substrate. All substrates were primed with BPEI/PMAA layer prior to the micelles deposition.

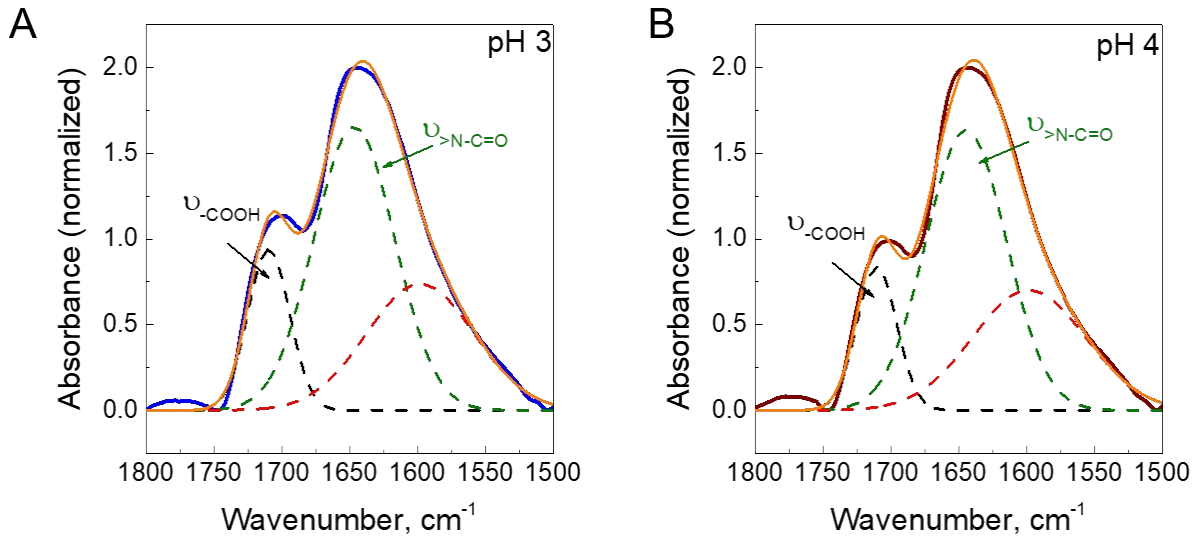

Figure S11. Deconvolution of FTIR spectra of UCSTM/PMAA films deposited at pH 3 (A) and pH 4 (B) in the 1500-1800 cm^{-1} region. The ratio of integrated intensities of stretching vibrations of PMAA ($\nu_{\text{-COOH}}$) to those of stretching vibrations of P(AAm-*co*-AN) block of UCSTMs ($\nu_{\text{>N-C=O}}$) is 0.3±0.01 and 0.25±0.01 at pH 3 and 4, respectively, suggesting a lower content of PMAA in films deposited at pH 4.

Fitting Model For Neutron Reflectometry Data:

Below is the model used for fitting the data obtained from neutron reflectometry experiments. The thicknesses of the three stacks are then:

$$d_H^{pure} = \sum_{l=0}^{7} d_l$$

$$d_D^{pure} = \sum_{l=8}^{9} d_l$$

$$d_{H1}^{pure} = \sum_{l=10}^{17} d_l,$$

where the initial bilayer thickness d_l (or d_0) is a fitted parameter.

If the material deposited in sharply defined bilayers, the summation results in the total thickness of the film. The marker layer, d_D, yields information on how much the bilayers intermix with preceding and subsequently deposited material, so we can fit d_D as well and then we can get the thicknesses of the H-blocks, where in addition to d_0 and ϵ we now fit d_D.

$$d_H = \sum_{l=0}^{8} d_l - d_D/2,$$

$$d_{H1} = \sum_{l=9}^{17} d_l - d_D/2,$$

To breakdown the SLD data, the varying film density should be taken into account and can be represented as:

$$\Sigma = \rho \frac{N_A \sum_j b_j}{M} \equiv \rho S,$$

where ρ is the mass density, N_A Avogadro's number, $\sum_j b_j$ the sum of the scattering lengths in the formula unit (e.g. monomer), and M the atomic mass of the formula unit. In this way, we can separate the mass density from the stoichiometry S for each of the components of the film (PMAA, *d*PMAA, UCSTMs, and H_2O) and treat mass density as a fitted parameter.

The non-deuterated strata of the film follow the same hydration and mixing, except with PMAA rather than dPMAA,

$$\Sigma_H = \rho(f_{H2O} S_{H2O} + (1 - f_{H2O})[f_{PMAA} S_{PMAA} + (1 - f_{PMAA}) S_{UCSTM}]),$$

where f_{H2O} is the water volume fraction, f_{PMAA} the fraction of PMAA deposited per bilayer. The SLD of marker layer is the following:

$$\Sigma_D^{pure} = \rho(f_{H2O} S_{H2O} + (1 - f_{H2O})[f_{PMAA} S_{dPMAA} + (1 - f_{PMAA}) S_{UCSTM}]),$$

The ratio between the fitted thickness of the marker layer and thickness of an unmixed marker bilayer d_D^{pure} can be used to constrain the SLD of the marker layer. The actual marker layer does not go down as a perfectly sharp, pure layer, but is instead distributed over a greater thickness so that the marker layer has mixed into the material from the adjacent layers,

$$f_d = d_D^{pure}/d_D$$

$$\Sigma_D = f_d \Sigma_D^{pure}$$

Parameters obtained from and used in the fit are presented in Table S1 and S2

Table S1. Model parameters for a $(UCSTM/PMAA)_8/(UCSTM/dPMAA)_2/(UCSTM/PMAA)_8$ film deposited from buffer solution at pH 3.0.

Layer	*Nb*, (Å^{-2})	*d*, (Å)	σ_{int}, (Å)	d_0, (Å)	f_{PMAA}	f_{H2O}	ρ, g/cm^3	f_d
$(UCSTM/PMAA)_8$	1.07e-6	285.7	230.8	44.7	0.82	0.10	1.11	0.62
$(UCSTM/dPMAA)_2$	2.52e-6	144.1	126.3					
$(UCSTM/PMAA)_8$	1.07e-6	285.7	77.6					
BPEI	5.0e-7	27.3	27.3	N/A	N/A			
SiO2	3.23e-6	21.6	6.0			N/A	N/A	N/A
Si	2.05e-6	100.0	10.0					

Table S2. Model parameters for a $(UCSTM/PMAA)_8/(UCSTM/dPMAA)_2/(UCSTM/PMAA)_8$ film deposited from buffer solution at pH 4.0.

Layer	*Nb*, (Å^{-2})	*d*, (Å)	σ_{int}, (Å)	d_0, (Å)	f_{PMAA}	f_{H2O}	ρ, g/cm^3	f_d
$(UCSTM/PMAA)_8$	1.11e-6	207.0	173.5	24.2	0.65	0.09	1.10	0.69
$(UCSTM/dPMAA)_2$	2.37e-6	70.7	62.9					
$(UCSTM/PMAA)_8$	1.11e-6	207.0	44.5					
BPEI	4.95e-7	15.1	15.1	N/A	N/A			
SiO2	3.2e-6	24.3	10.0			N/A	N/A	N/A
Si	2.02e-6	100.0	5.0					