Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

PPEGMEMA-based Cationic Copolymers Designed for Layer-by-Layer Assembly

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S1 Characterization of P(PPEGMEMA-*stat*-AMA) Copolymers

S1.1 ^{1}H NMR spectra of s-PPEGMEMA and l-PPEGMEMA

The 1H NMR spectra of all three synthesized copolymers were measured to characterize the three PPEGMEMA copolymers synthesized. A Brucker 400 MHz NMR spectrometer was used, with D2O as the solvent. The TopSpin software from Brucker was used to process the NMR data obtained. The NMR spectra of s-PPEGMEMA, m-PPEGMEMA and l-PPEGMEMA are presented in Figure S1, Figure 1 and Figure S2, respectively.

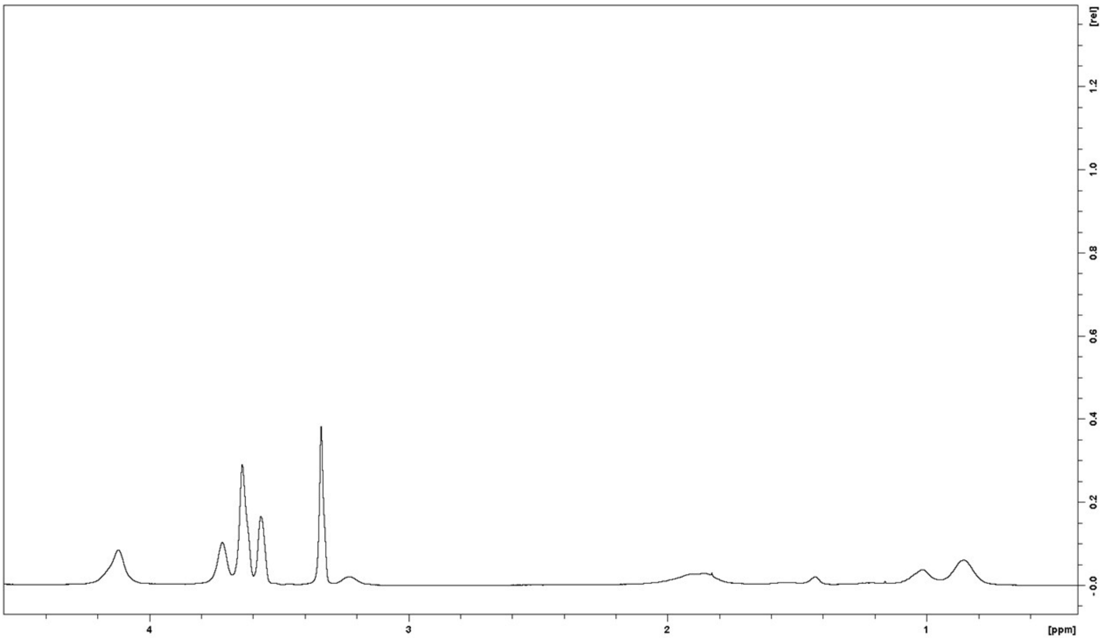


Figure S1 ^{1}H NMR spectrum of s-PPEGMEMA

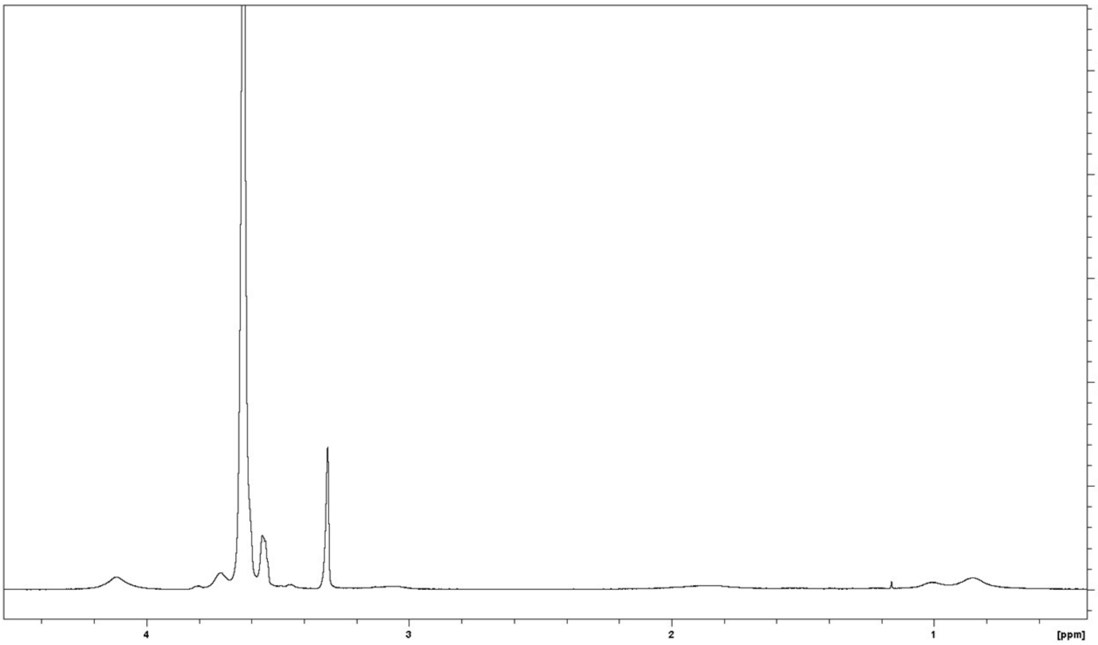


Figure S2 ^{1}H NMR spectrum of l-PPEGMEMA

S1.2 AF4 chromatograms of P(PEGMEMA-*stat*-AMA)

The molecular weight and polydispersity of the three P(PEGMEMA-*stat*-AMA) polymers were determined by AF4 with a Wyatt Eclipse instrument with UV (Agilent 1230 infinity, Agilent), refractive index (Optilab rex, 633 nm, Wyatt) and multi-angle light scattering (MALS) (Dawn Heleos-II, 662 nm, Wyatt) detectors. The Optilab RI detector was used to precisely determine the refractive index increment (dn/dc) values of the three polymers. A concentration series of 0.05, 0.1, 0.25, 0.5 and 1 mg/ml were used and the corresponding dRI values were plotted and fitted linearly. The slope was calculated as the dn/dc value and accurate MW were calculated accordingly.

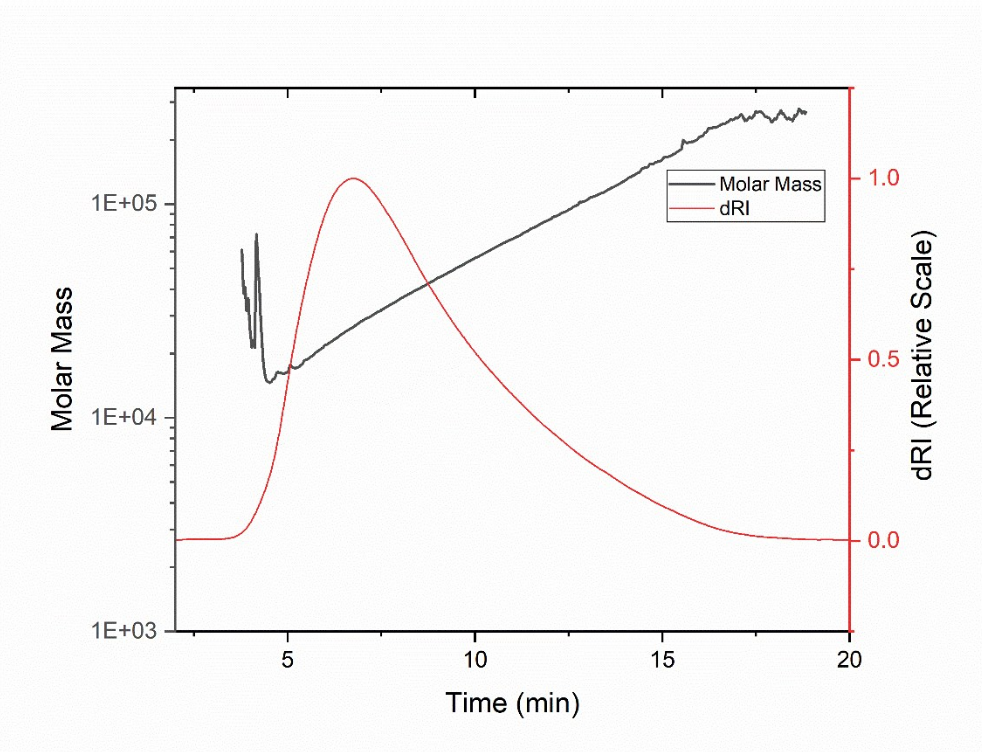


Figure S3 AF4 chromatogram of s-PPEGMEMA

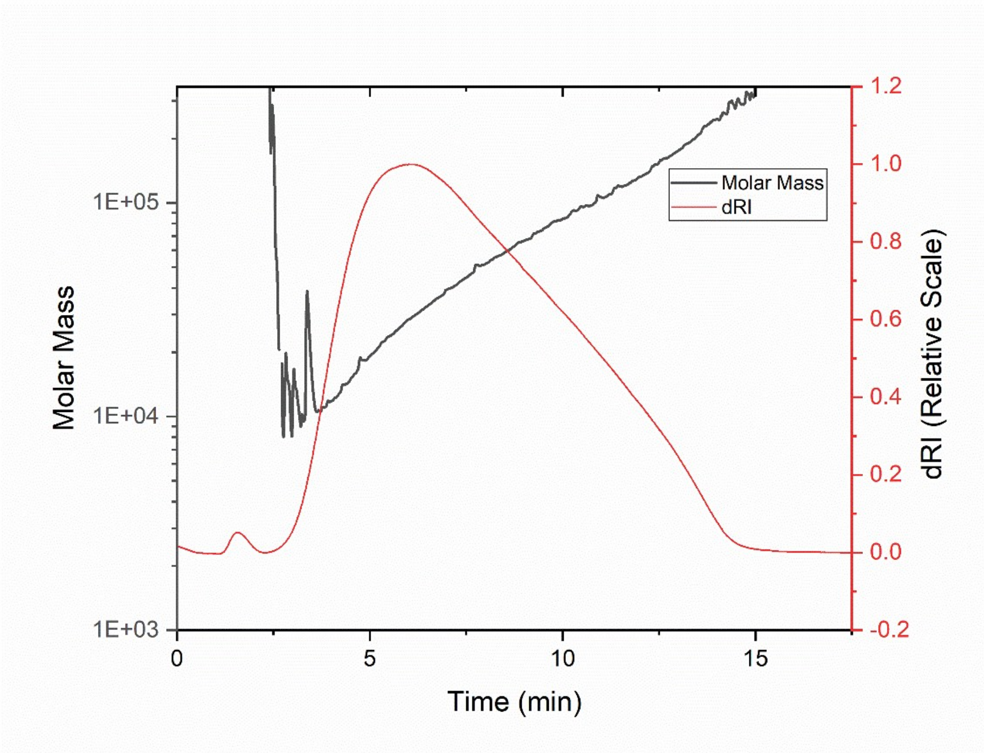


Figure S4 AF4 chromatogram of m-PPEGMEMA

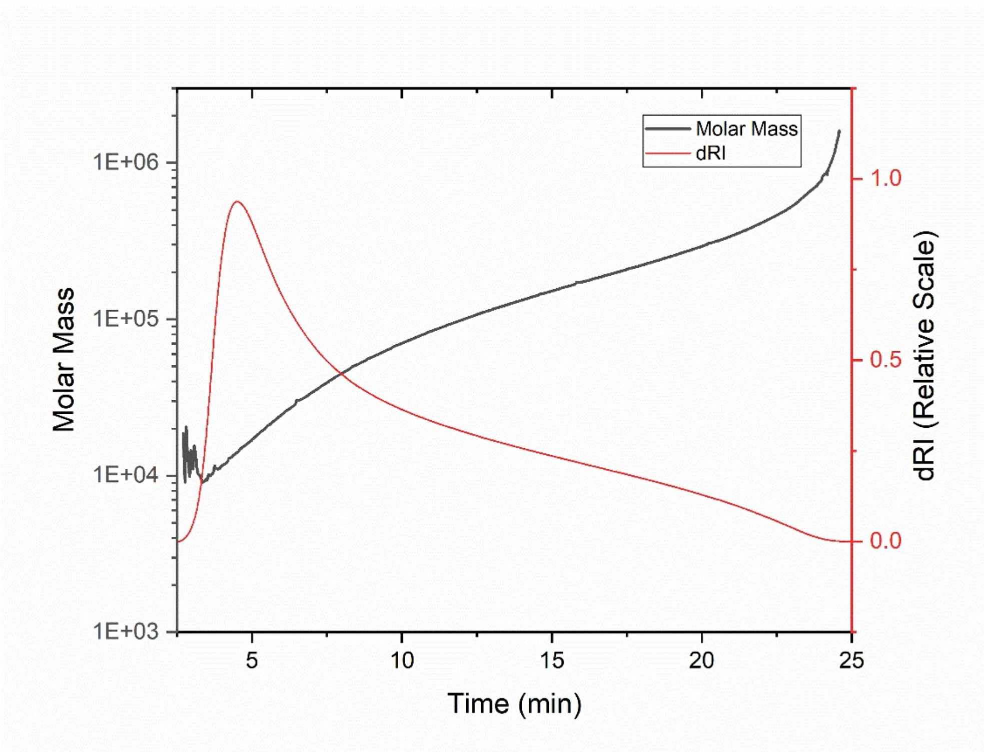


Figure S5 AF4 chromatogram of l-PPEGMEMA

S2 Estimation of Hydrated PPEGMEMA/alginate Multilayered Film Density

The volume fraction of the solvent, f_s, in the PPEGMEMA/alginate multilayered film were estimated with the BEMA model from our ellipsometry data. The hydrated PPEGMEMA/alginate multilayered film density ρ_f was estimated according to the following equation:

$$\rho_f = \rho_s f_s + \rho_p(1 - f_s)$$

Where ρ_s and ρ_p are the densities of solvent and dry polymer, respectively. Herein ρ_s is 999 g/mL, and ρ_p is 1.4 g/cm^3, estimated as an average of the polymer density of PEG (1.2 g/mL) and sodium alginate (1.6 g/cm^3). The hydrated PPEGMEMA/alginate multilayered film density was finally calculated to be 1080 g/cm^3, 1060 g/cm^3 and 1040 g/cm^3 for s-PPEGMEMA/alginate, m-PPEGMEMA/alginate and l-PPEGMEMA/alginate multilayered films, respectively.

S3 Ellipsometry

S3.1 Bare QCM sensor modelling

To reduce the number of layers that contribute to the optical properties of the QCM sensor substrate and simplify the modeling process, a tailor-made sensor (QSX335) with a thick opaque interlayer of titanium was used. The optical model for substrate then consists of a titanium substrate and a layer of silica. To avoid overparameterization, the thickness of silica coating was fixed as 25 nm, and only the optical constants of the titanium substrate was fitted with a B-Spline model (resolution 0.2 eV, parameterized initially from Ti optical constants from software library).

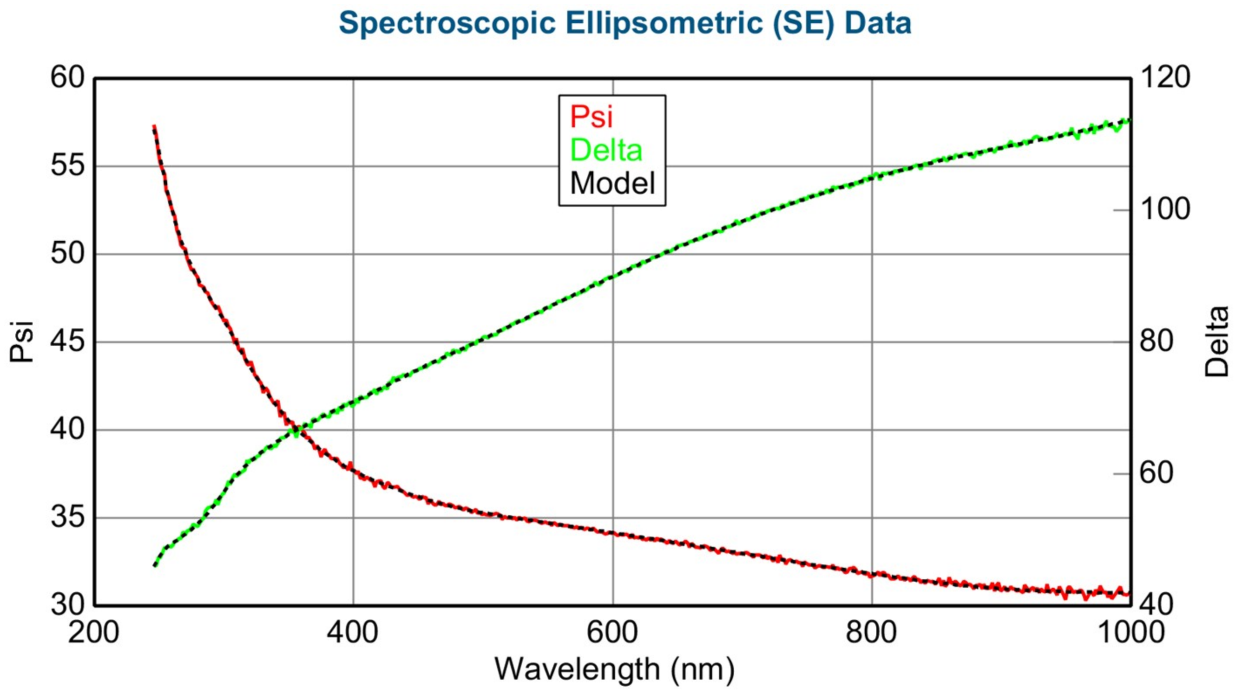


Figure S6 QCM bare sensor Psi and Delta in air with the fitted model described (dashed line)

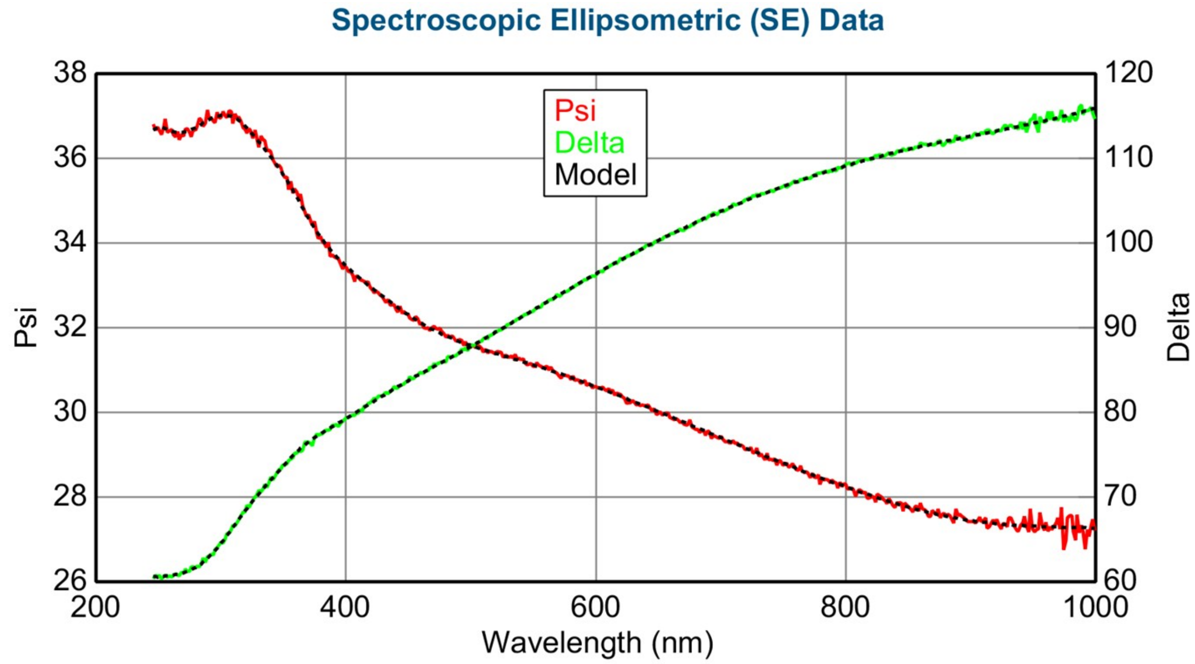


Figure S7 QCM bare sensor Psi and Delta in buffer with the fitted model described

S3.2 Ellipsometry data modelling of PPEGMEMA/alginate multilayered film

As has been discussed in the Experimental section, the PPEGMEMA/alginate multilayered film was modeled with single-component Cauchy and two-component BEMA models. Detailed Psi and Delta spectra of all three PEM films are shown in Figure S8-13. The effect of several parameters such as surface roughness, grading, and thickness nonuniformity were tested, where only the latter was found to significantly improve the fitting quality and thus included in the model.

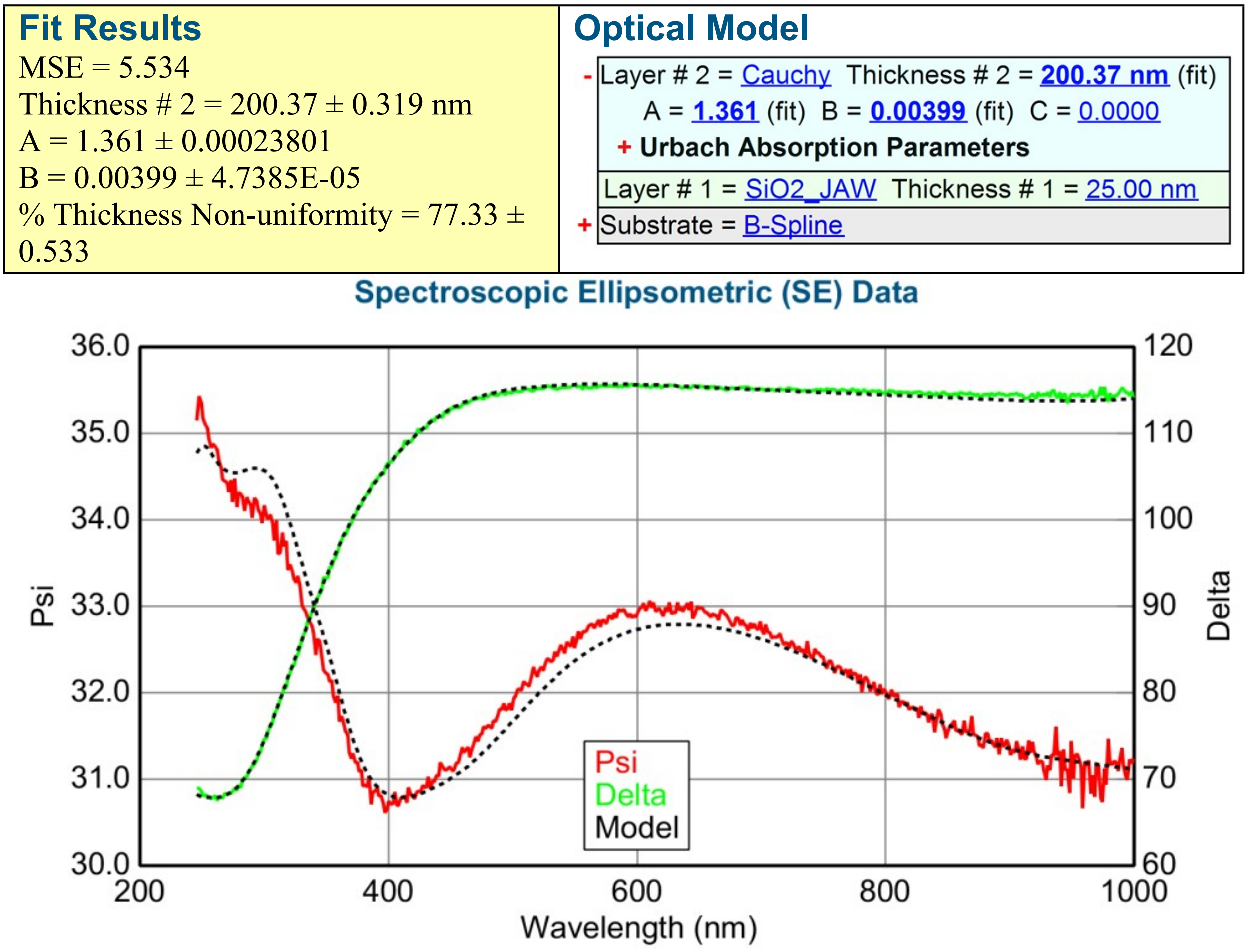


Figure S8 Ellipsometry data as well as the Cauchy modelling for s-PPEGMEMA/alginate multilayered film

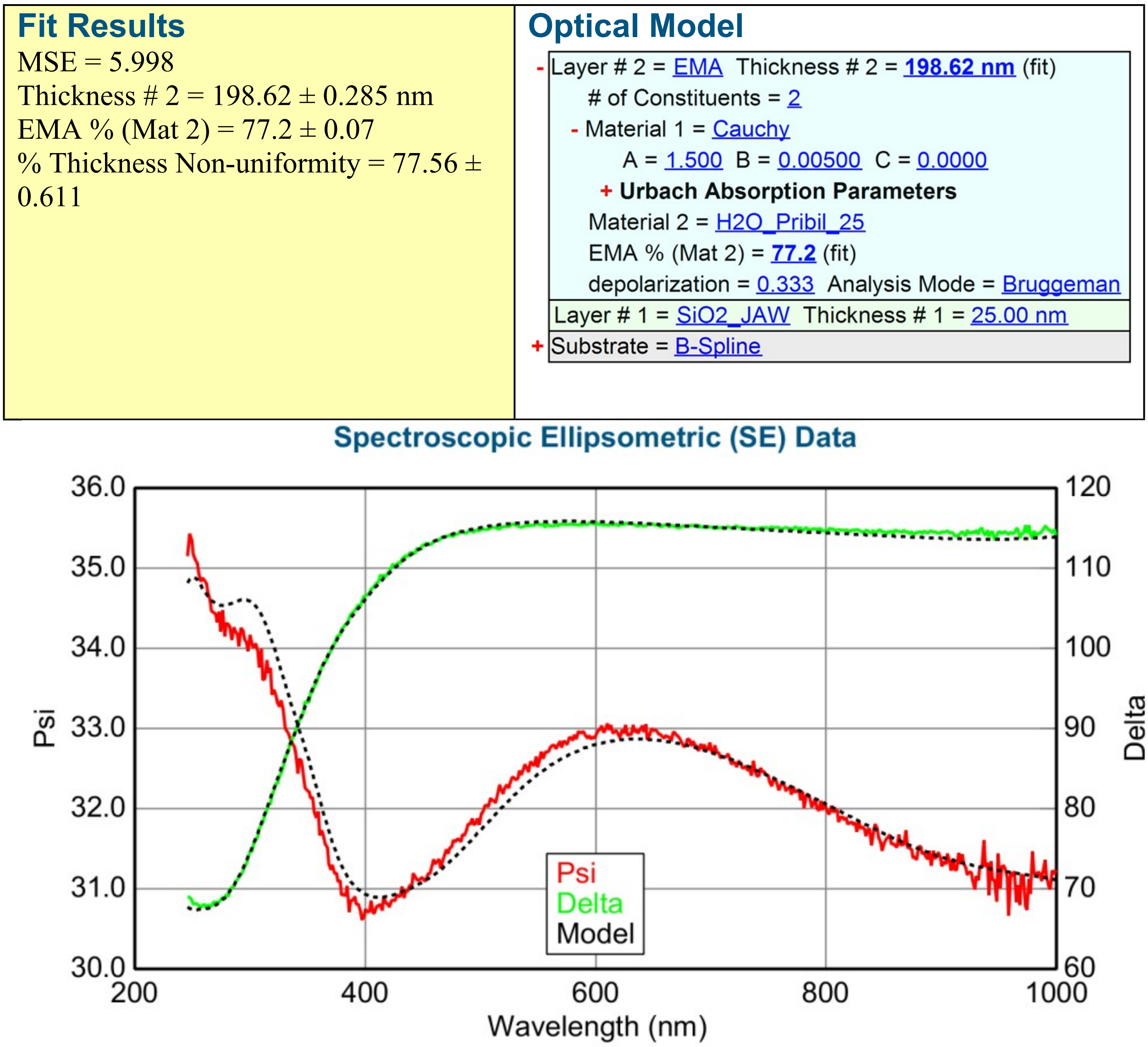


Figure S9 Ellipsometry data as well as the BEMA modelling for s-PPEGMEMA/alginate multilayered film

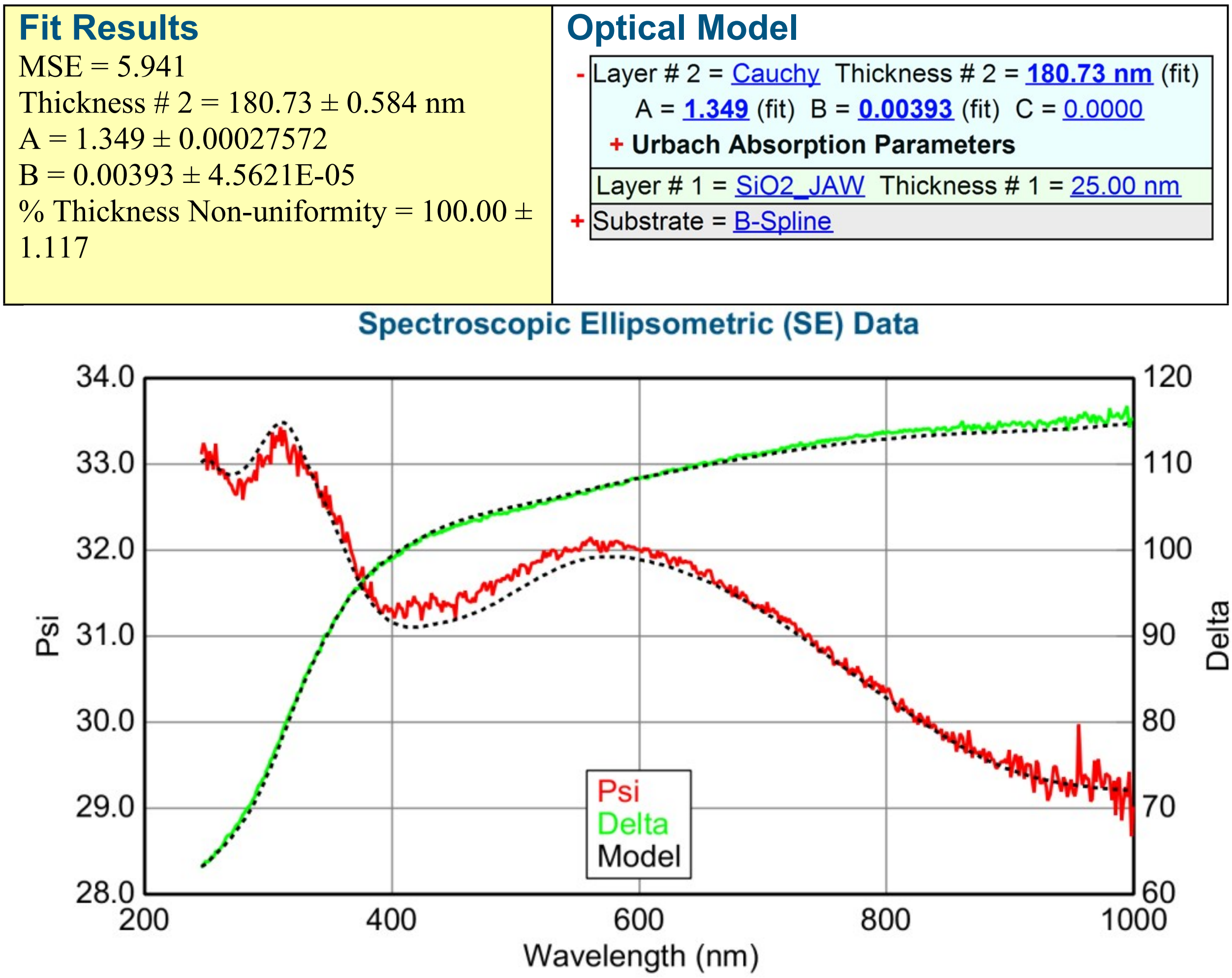


Figure S10 Ellipsometry data as well as the Cauchy modelling for m-PPEGMEMA/alginate multilayered film

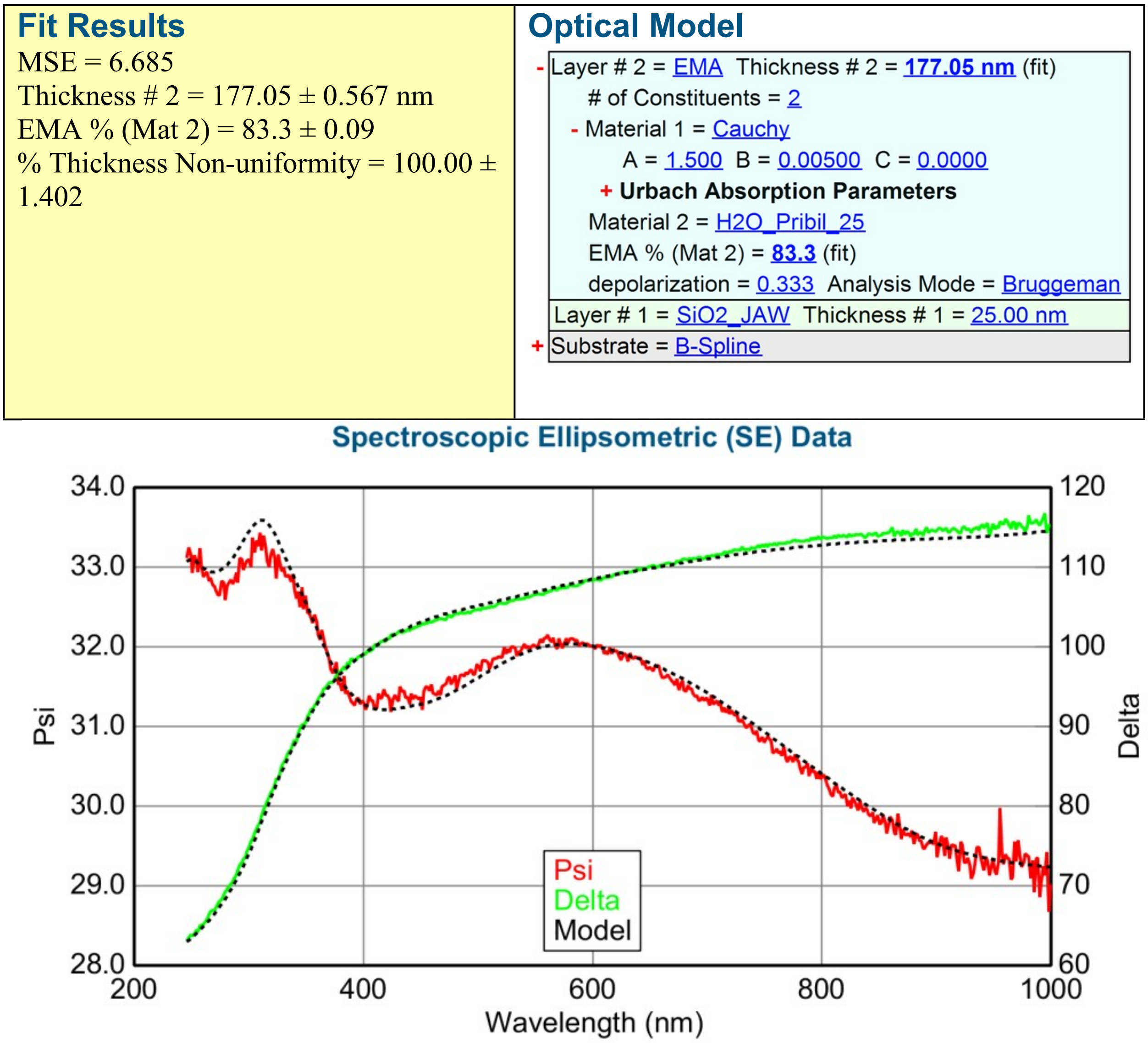


Figure S11 Ellipsometry data as well as the BEMA modelling for m-PPEGMEMA/alginate multilayered film

Fit Results	**Optical Model**
MSE = 13.713 Thickness # 2 = 159.46 ± 2.948 nm A = 1.337 ± 0.00059798 B = 0.00341 ± 7.0185E-05 % Thickness Non-uniformity = 100.00 ± 8.130	- Layer # 2 = Cauchy Thickness # 2 = **159.46 nm** (fit) A = **1.337** (fit) B = **0.00341** (fit) C = 0.0000 + **Urbach Absorption Parameters** Layer # 1 = SiO2_JAW Thickness # 1 = 25.00 nm + Substrate = B-Spline

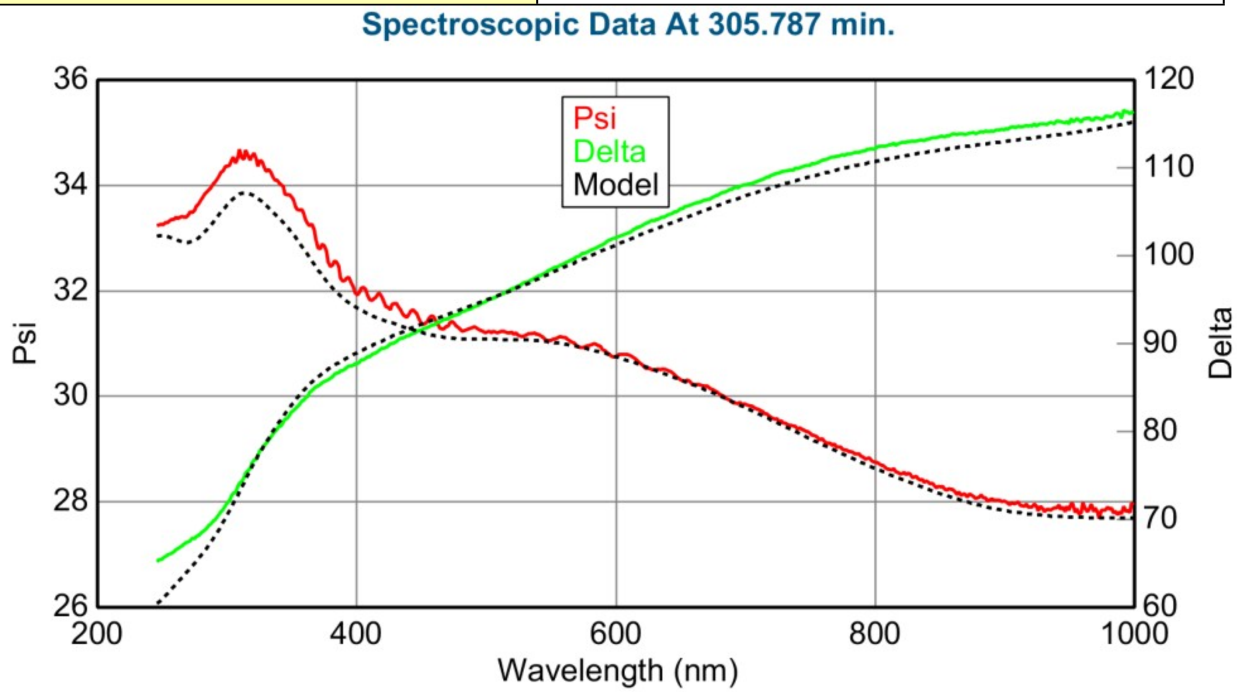


Figure S12 Ellipsometry data as well as the Cauchy modelling for l-PPEGMEMA/alginate multilayered film

Fit Results	Optical Model
MSE = 13.432 Thickness # 2 = 153.25 ± 2.711 nm EMA % (Mat 2) = 91.4 ± 0.22 % Thickness Non-uniformity = 100.00 ± 8.742	- Layer # 2 = EMA Thickness # 2 = **153.25 nm** (fit) # of Constituents = 2 - Material 1 = Cauchy A = 1.500 B = 0.00500 C = 0.0000 + **Urbach Absorption Parameters** Material 2 = H2O_Pribil_25 EMA % (Mat 2) = **91.4** (fit) depolarization = 0.333 Analysis Mode = Bruggeman Layer # 1 = SiO2_JAW Thickness # 1 = 25.00 nm + Substrate = B-Spline

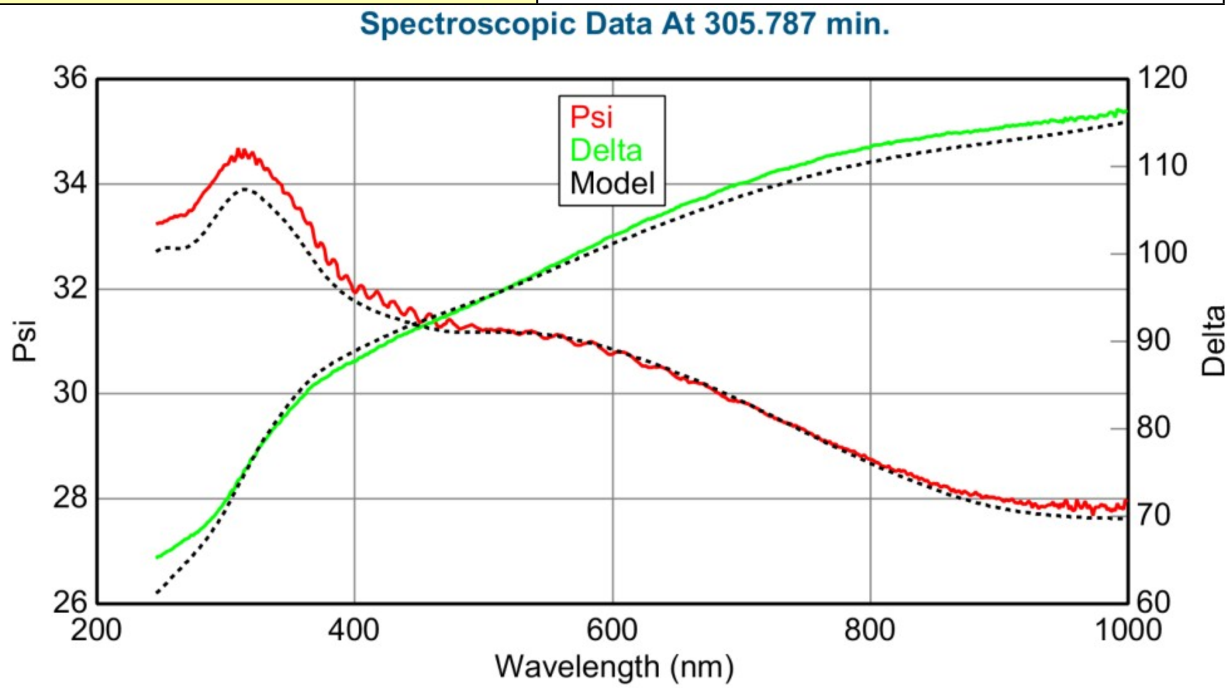


Figure S13 Ellipsometry data as well as the BEMA modelling for l-PPEGMEMA/alginate multilayered film

Fit Results	Optical Model
MSE = 63.300 Thickness # 2 = 48.87 ± 0.059 nm	- Layer # 2 = Cauchy Thickness # 2 = **48.87 nm** (fit) A = 1.500 B = 0.00500 C = 0.0000 + **Urbach Absorption Parameters** Layer # 1 = SiO2_JAW Thickness # 1 = 25.00 nm + Substrate = B-Spline

Experimental and Model Generated Data Fits

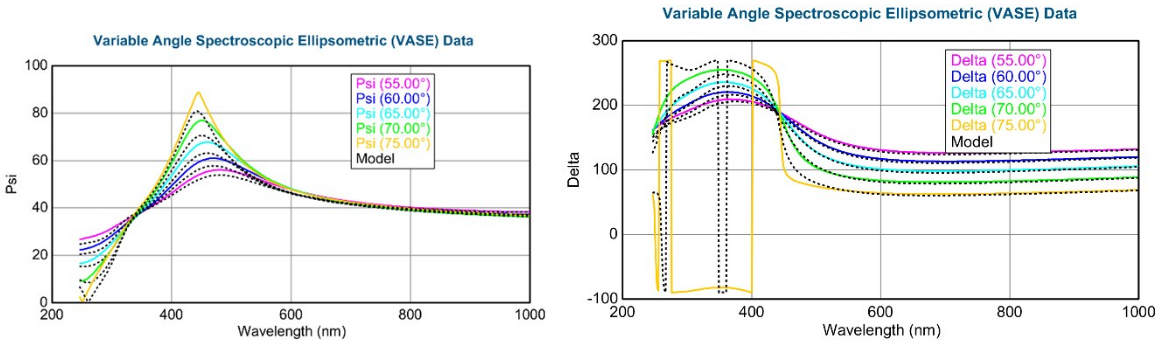
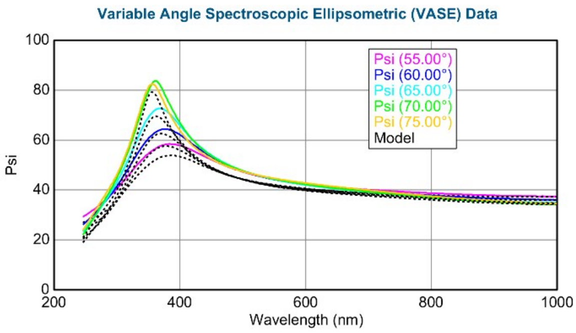


Figure S14 Ellipsometry data as well as the Cauchy modelling for dry s-PPEGMEMA/alginate multilayered film in air

Fit Results	Optical Model
MSE = 97.154 Thickness # 2 = 29.37 ± 0.086 nm	- Layer # 2 = Cauchy Thickness # 2 = **29.37 nm** (fit) A = 1.500 B = 0.00500 C = 0.0000 + **Urbach Absorption Parameters** Layer # 1 = SiO2_JAW Thickness # 1 = 25.00 nm + Substrate = B-Spline

Experimental and Model Generated Data Fits



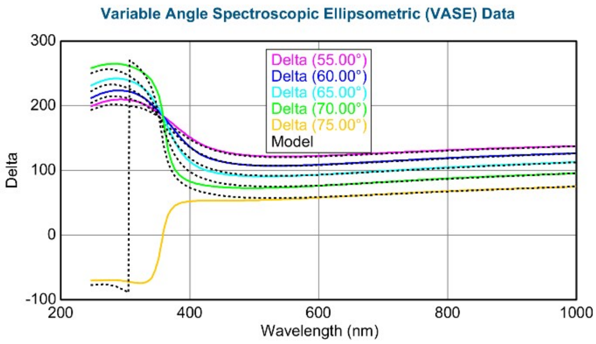


Figure S15 Ellipsometry data as well as the Cauchy modelling for dry m-PPEGMEMA/alginate multilayered film in air

Fit Results	Optical Model
MSE = 43.426 Thickness # 2 = 17.58 ± 0.029 nm	- Layer # 2 = Cauchy Thickness # 2 = **17.58 nm** (fit) A = 1.500 B = 0.00500 C = 0.0000 + **Urbach Absorption Parameters** Layer # 1 = SiO2_JAW Thickness # 1 = 25.00 nm + Substrate = B-Spline

Experimental and Model Generated Data Fits

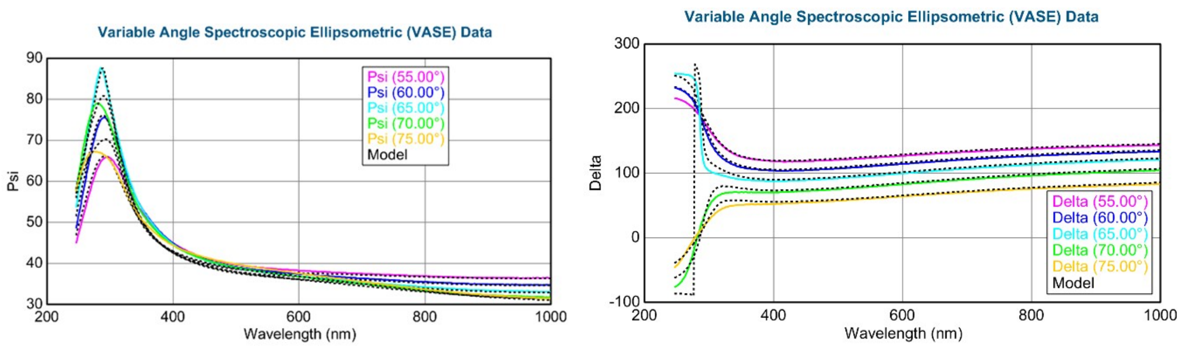


Figure S16 Ellipsometry data as well as the Cauchy modelling for dry l-PPEGMEMA/alginate multilayered film in air

S4 PPEGMEMA/alginate Multilayered Film Stability Before Glutaraldehyde Crosslinking

The pH stability of the m-PPEGMEMA/alginate multilayered film before crosslinking of glutaraldehyde was examined by flushing a pH 8 buffer over the prepared film. As is shown in Figure S17, an immediate disassembly of the film was observed, evidenced by a drastic decrease in frequency and dissipation shifts.

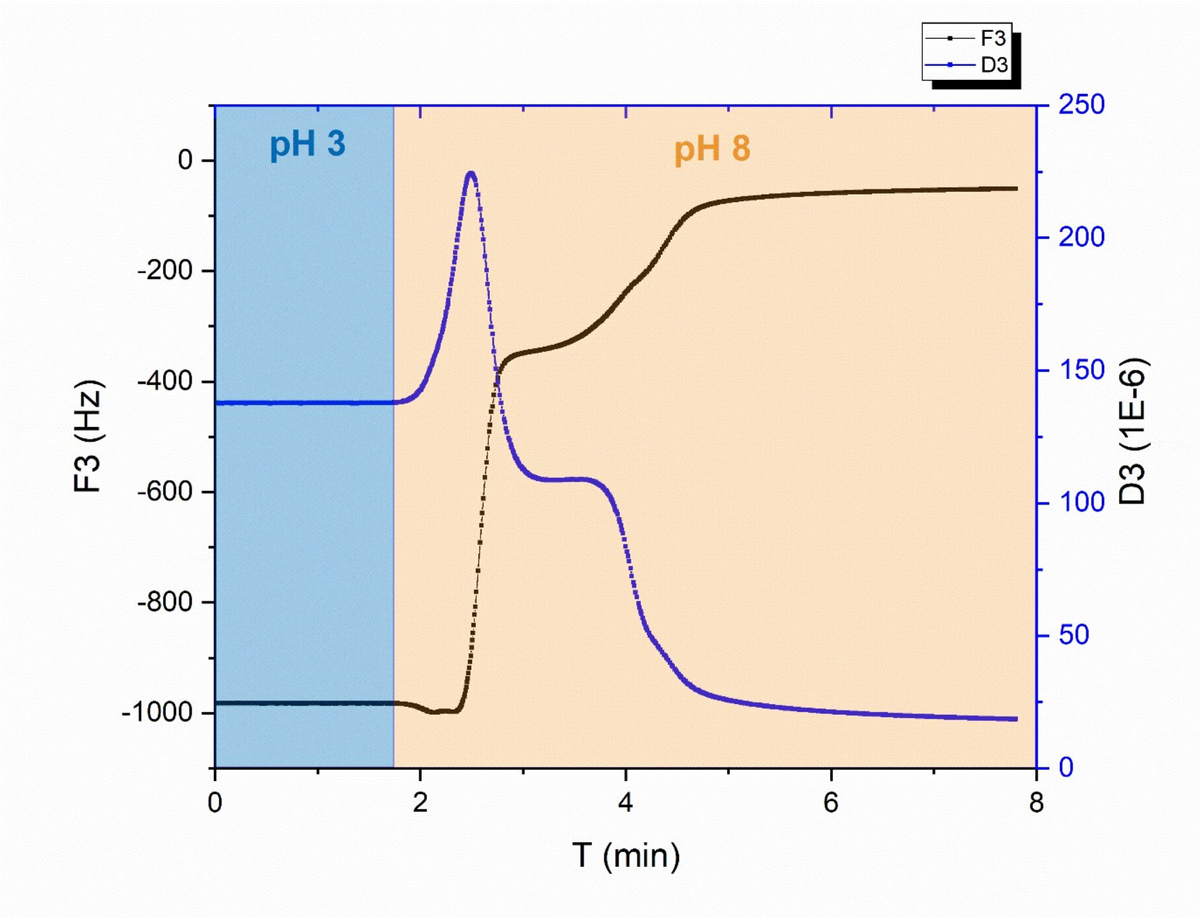


Figure S17 QCM-D Frequency and dissipation shifts after inflow of pH 8 carbonate buffer before crosslinking of glutaraldehyde