

Supporting information

Competitive Adsorption of Polyelectrolytes onto and into Pellicle Coated Hydroxyapatite Investigated by QCM-D and Force Spectroscopy

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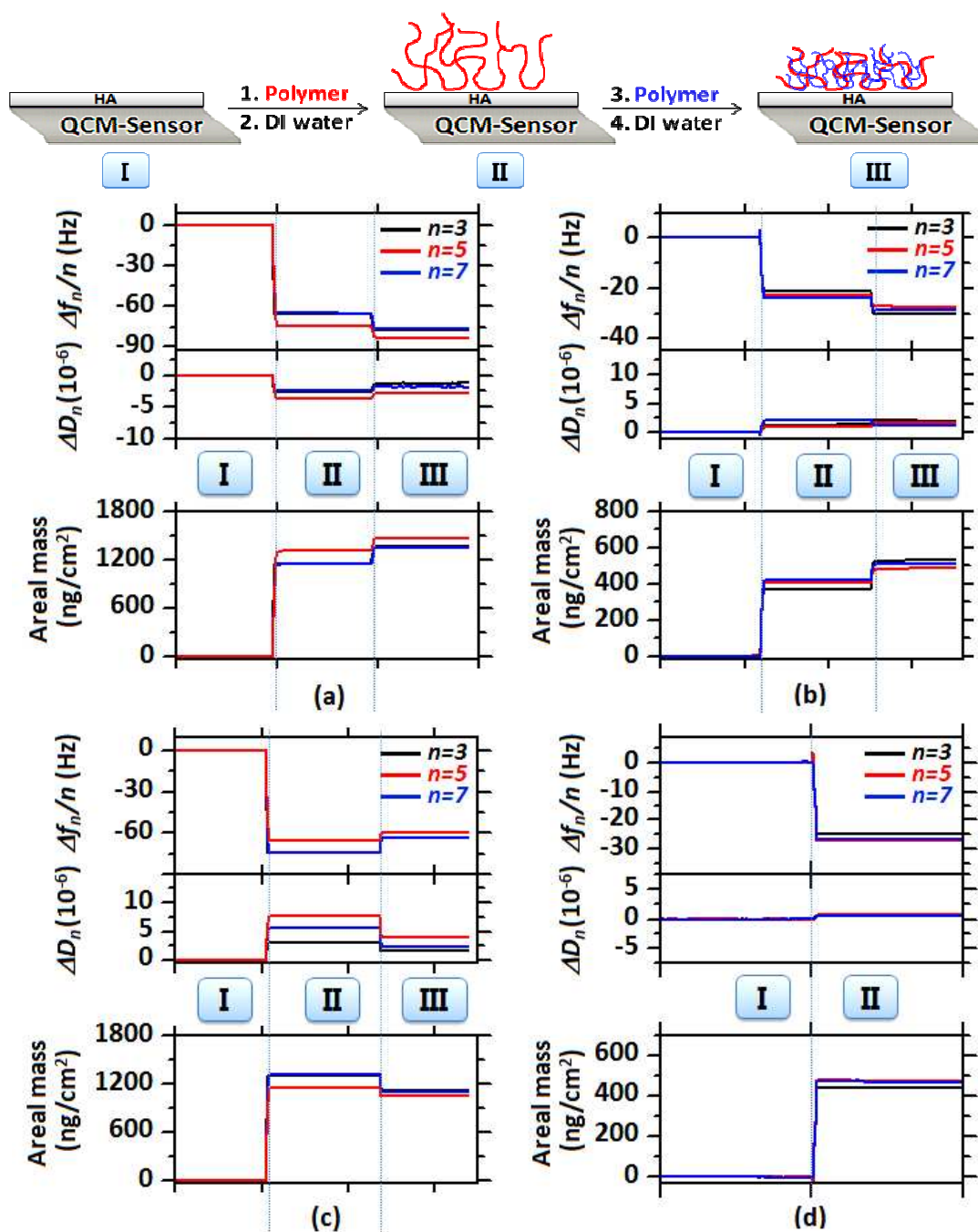


Figure S1. Traces of $\Delta f_n/n$ ($n=3, 5, 7$) and ΔD_n of bare HA-coated QCM Sensor (I), the first polymer adsorbed layer (red, II) on HA-coated QCM sensor, the sequential adsorbed polymer (blue, III) on/into the previous polymer layer under air at 21 °C, respectively. The samples were prepared using the same procedure of in-situ QCM-D in Figure 4. The data from regions I, II, and III were combined using Q-soft (Q-Sense). Dry area masses of the first polymer layer (II) and the combined polymer layer (III) in air were calculated using the Sauerbrey equation and $\Delta f_n/n$ ($n=3, 5, 7$), respectively because ΔD_n values represent both the dry layers are elastic and rigid. (a) Gantrez (II) and PAA-G75/Gantrez (III); (b) NaHa (II) and PAA-G75/NaHa (III); (c) AS (II) and PAA-G75/AS (III); (d) PAA-G75 (II).

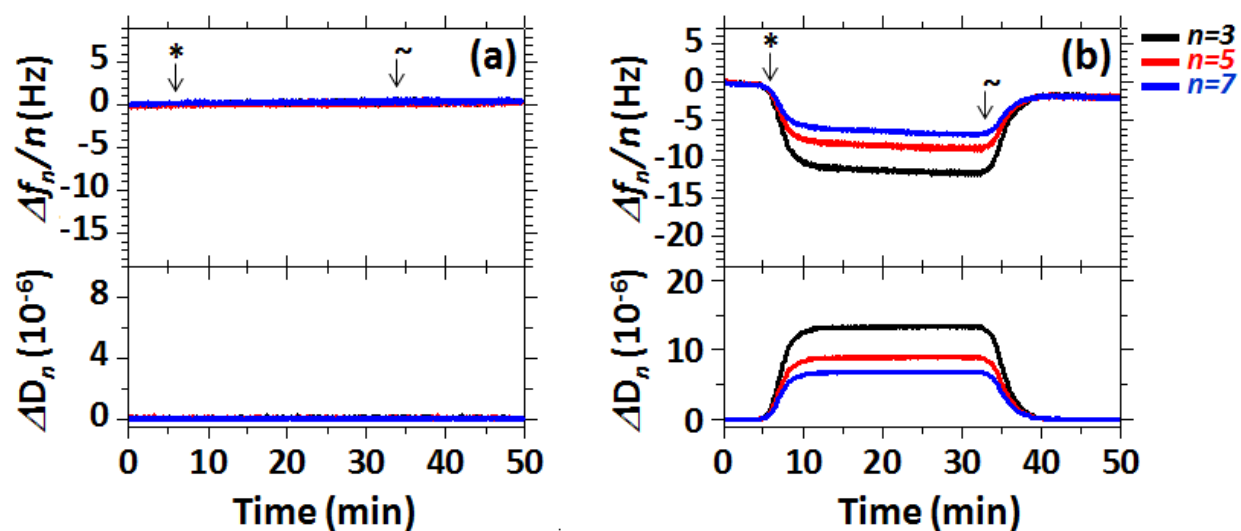


Figure S2. Response of frequency and dissipation in QCM-D to polymer adsorption and release on a surface. (a) and (b) show traces of $\Delta f_n/n$ ($n=3, 5, 7$) and ΔD_n vs. time for exposure of hydroxyapatite (HA) surfaces to 1 wt% PDMS and 1 wt% PEG, respectively, followed by exposure to DI water. Arrow * and ~ represent exposure of a surface to polymer solution and to DI water, respectively.

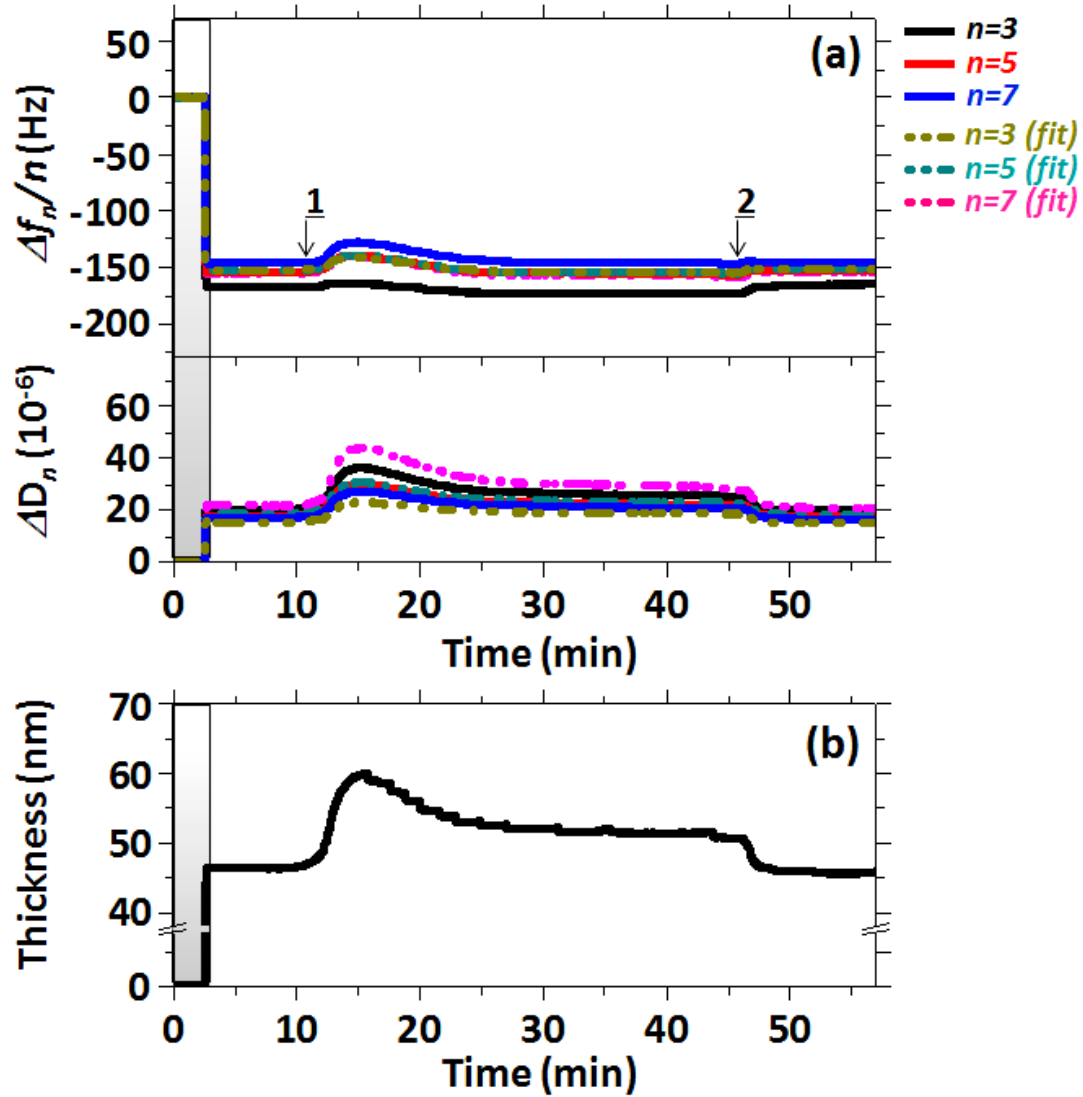


Figure S3. (a) Traces of $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n of Gantrez adsorbed layer on HA surface versus time as a function of sequential changes of solution pH; Simulated and experimental curves for $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n vs. time, showing the best fit between the experimental data and the viscoelastic model. (b) Thickness versus time determined from the fit shown in (a). Arrows 1 and 2 represent pH changes from 7 to 3.5 and 3.5 to 7, respectively.

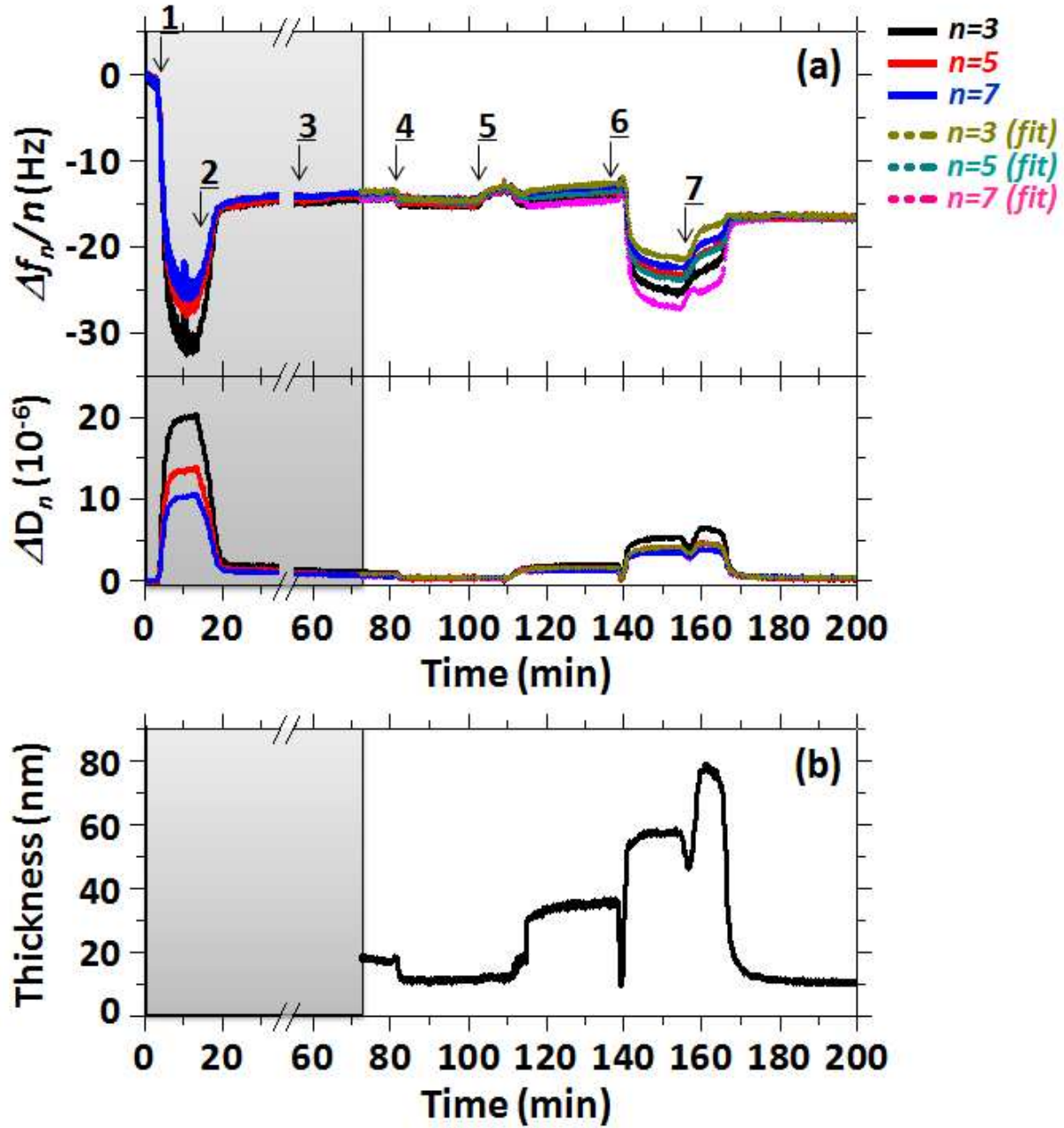


Figure S4. (a) Traces of $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n of NaHa adsorbed layer on HA surface versus time as a function of sequential changes of solution pH, followed by subsequent cross-linking by PAA-G75 polymers on a NaHa layer; Simulated and experimental curves for $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n vs. time (from 72 min to 200 min), showing the best fit between the experimental data and the viscoelastic model. (b) Thickness versus time determined from the fit shown in (a). As shown in Figure 2 (b), arrows 1 and 2 represent exposure of HA surface to 1 w% NaHa (pH 7) and to DI water (pH 7) for rinsing, respectively. Arrows 3, 4, and 5 represent pH changes from 7 to 5.5 (DI water), 5.5 (DI water) to 3.5, 3.5 to 7, respectively. Subsequent cross-linking by PAA-G75 polymers on a NaHa layer, arrow 6 and 7 represent the exposure of 1 w% PAA-G75 solution (pH 7), rinsing with DI water (pH 7), respectively.

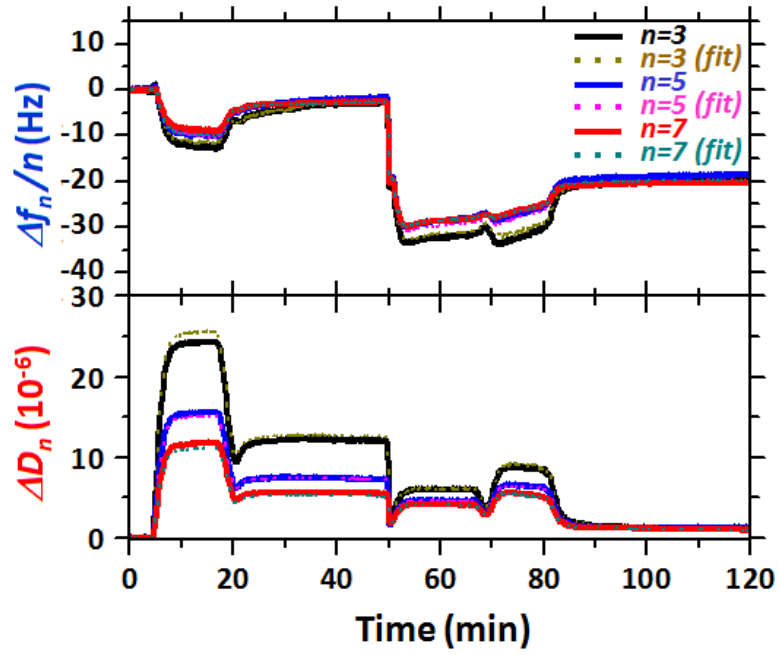


Figure S5. Simulated and experimental curves for $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n corresponding to Figure 4(a), respectively. The agreement between experiment and fit for all three vibration modes is excellent.

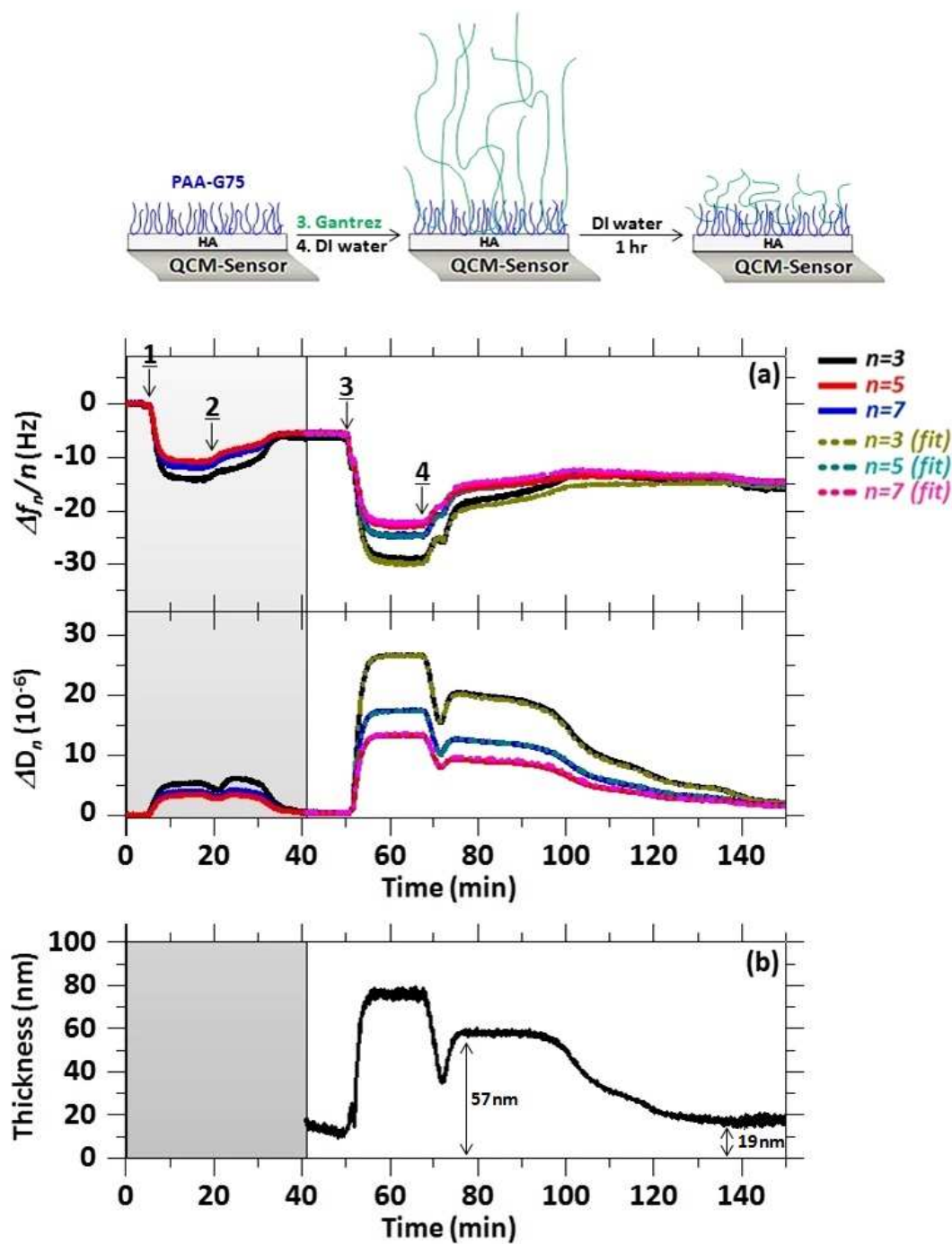


Figure S6. (a) Traces of $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n of PAA-G75 adsorbed layer on HA surface versus time, followed by adsorption of Gantrez on a PAA-G75 layer and the cross-linking process of cross-linking adsorbed Gantrez polymer and PAA-G75; Simulated and experimental curves for $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n vs. time (from 42 min to 150 min), showing the best fit between the experimental data and the viscoelastic model. (b) Thickness versus time determined from the fit shown in (a). Arrow 1, 2, 3, and 4 represent the exposure of 1 w% PAA-G75 solution (pH 7), rinsing with DI water (pH 7), the exposure of 1 w% Gantrez solution (pH 7) to HA surface, rinsing with DI water (pH 7), respectively.

Table S1. Effect of order of polymer deposition on physical properties of polymer composite layers

Polymer composite layers on HA	Thickness (nm)	Shear modulus (10^4 N/m^2)	Viscosity (10^{-3} Ns/m^2)
PAA-G75/Gantrez/HA ^a	8	2.9	2.04
Gantrez/PAA-G75/HA ^b	19 ^c	0.6 ^d	1.21 ^d

^aGantrez was first deposited on HA, followed by PAA-G75 (Figure 4); ^bPAA-G75 was first deposited on HA, followed by Gantrez (Figure S6); ^cthe polymer composite layer thickness decreased from 57 to 19 nm over a period of 1 hour; ^dshear modulus and viscosity of the stable polymer composite layer after a period of 1 hour.

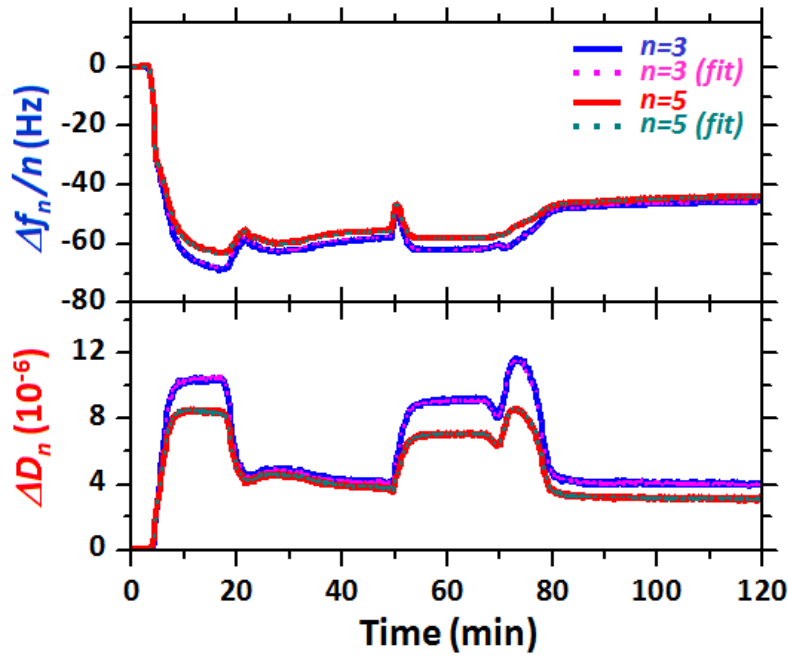


Figure S7. Simulated and experimental curves for $\Delta f_n/n$ ($n = 3, 5$) and ΔD_n corresponding to Figure 5(a), respectively. The agreement between experiment and fit for all three vibration modes is excellent.

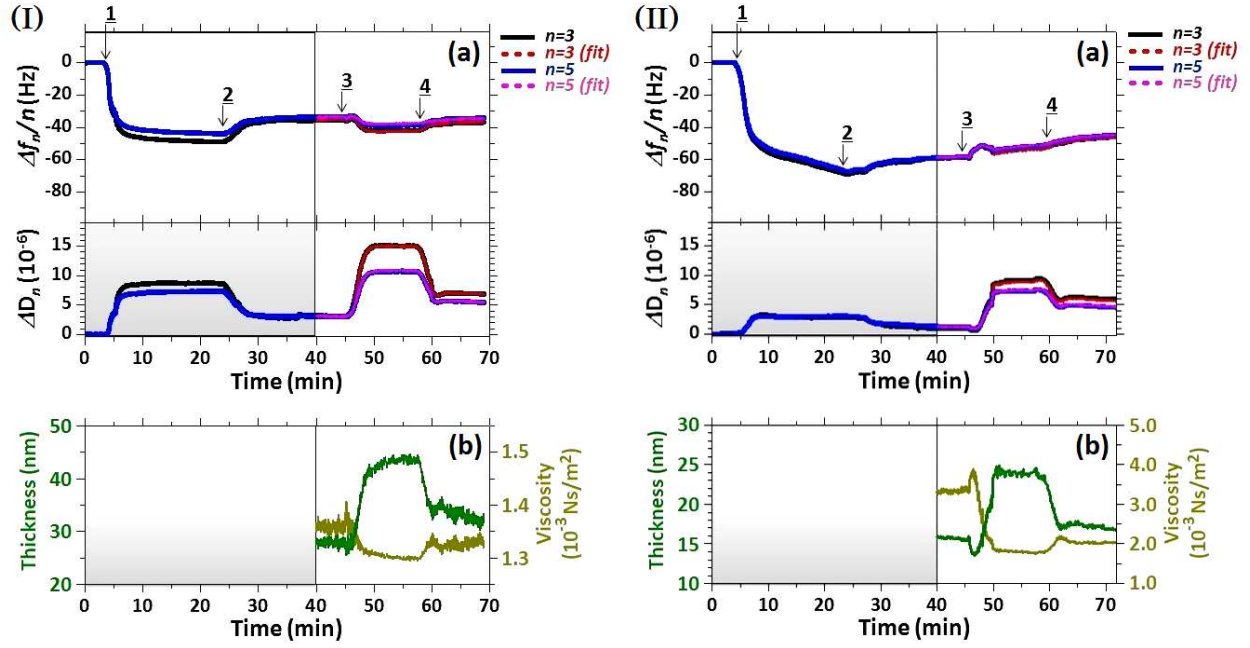


Figure S8. Simulated and experimental curves for $\Delta f_n/n$ ($n = 3, 5, 7$) and ΔD_n versus time of (I-a) an artificial saliva layer and (II-a) an pellicle layer on HA surfaces, followed by subsequent exposure to PAA-G75 polymers at 37 °C), showing a good fit between the viscoelastic model (Voigt) and the experimental data. Thickness and viscosity versus time (from 40 min to 70 min) of (I-b) an artificial saliva layer and (II-b) an pellicle layer on HA surfaces were determined from the fit shown in (I-a) and (II-a), respectively. Arrows 1, 2, 3, and 4 represent exposure of (I) artificial saliva solution and (II) human saliva solution to HA surface, DI water rinsing (pH 7), exposure of PAA-G75 solution, and DI water rinsing (pH 7), respectively.

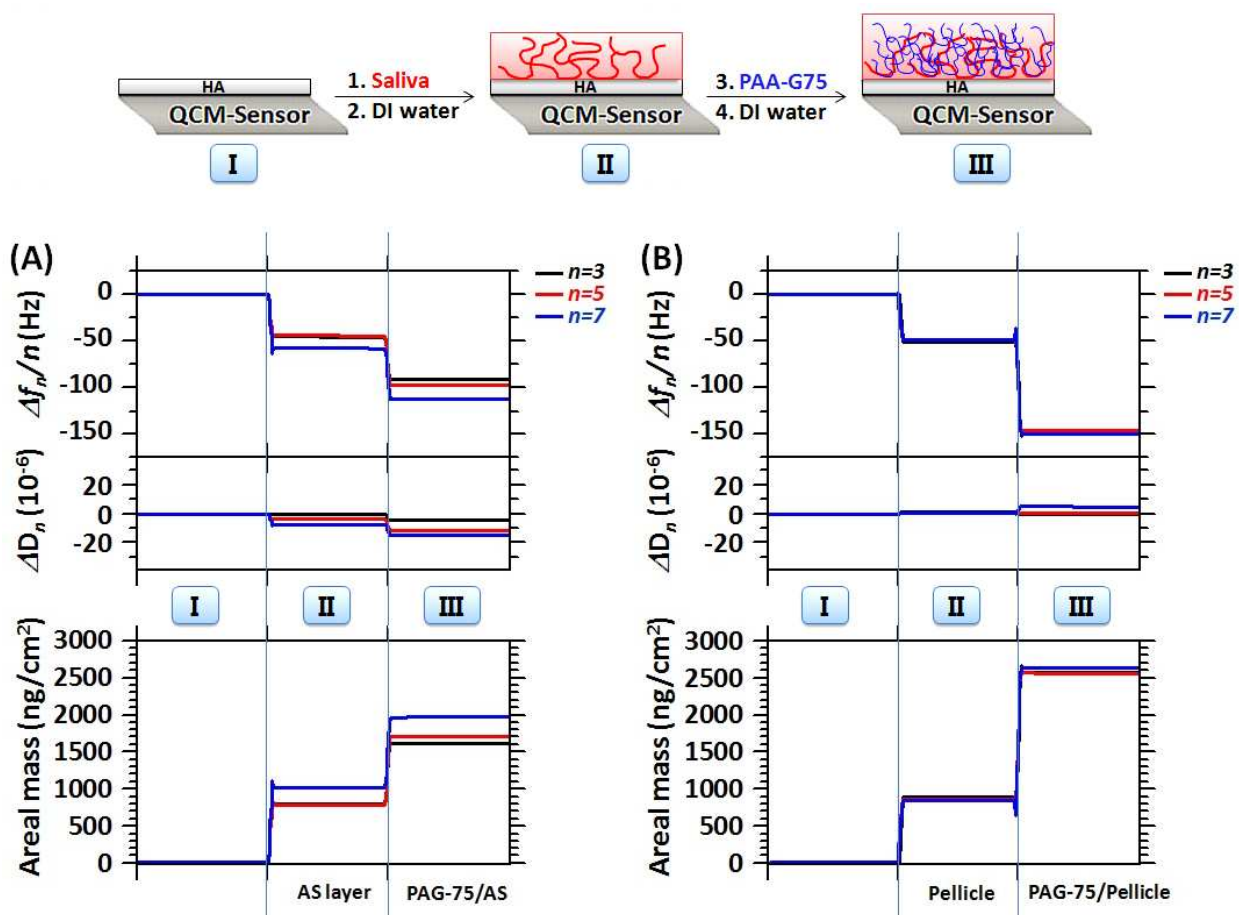


Figure S9. Traces of $\Delta f_n/n$ ($n=3, 5, 7$) and ΔD_n of (A) the first AS layer and (B) pellicle on HA-coated QCM sensor, respectively, followed by sequential exposure to PAA-G75 polymer under air at 37 °C. Samples were prepared using the same procedure as *in situ* QCM-D in Figure S7. The data from regions I, II, and III were combined using Q-soft (Q-Sense). Dry area masses of (A-II) AS layer, (B-II) pellicle layer, and (A-III and B-III) after exposure to PAA-G75 polymer in air calculated using the Sauerbrey equation and $\Delta f_n/n$ ($n=3, 5, 7$), respectively.