

Supporting Information to:

"Non-Fouling Poly(ethylene oxide) Layers End-Tethered to Polydopamine"

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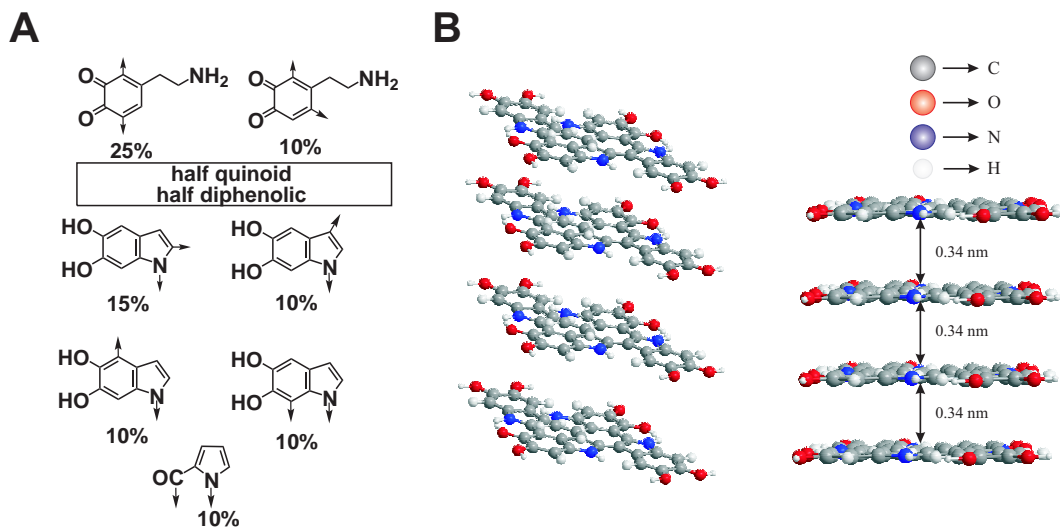
Radius of Gyration of Different PEO's

Table S1: Molecular weight (M_n) of polymers used in this study, hydrodynamic radius (R_h) determined by DLS, as well as calculated radius of gyration (R_g) assuming random coiling of PEO chains in good solvent.

Abbreviation	M_n [g/mol]	R_h [nm]	R_g^\dagger [nm]
PEO(2000)-SH	2015	1.4	2.5
PEO(2000)-NH ₂	1930	1.3	2.3
PEO(5000)-SH	5118	2.1	3.9
PEO(5000)-NH ₂	5079	2.1	3.7
PEO(10000)-SH	11153	3.3	5.9
PEO(10000)-NH ₂	11065	3.3	5.9
PEO(20000)-SH	22271	4.1	7.3
PEO(20000)-NH ₂	22359	4.2	7.5

$^\dagger R_g = 1.78 \times R_h.$

Covalent Structure of PDA



Scheme S1: Proposed covalent structure of PDA. (A) Model depicting PDA as a high molecular weight polymer made up of randomly linked monomer units.^{1,2} (B) Model suggesting the ultrastructural organization of 4–5 π -stacked oligomeric sheets.^{3,4}

Calculations of the Interpenetration Zone Thickness

The thickness of the interpenetration zone between PDA and PEO of different molecular weights was approximated by:⁵

$$I_{\text{thickness}} = \frac{2a}{\sqrt{6 \left[\chi - 2 \ln 2 \left(\frac{1}{N_{\text{PDA}}} + \frac{1}{N_{\text{PEO}}} \right) \right]}}, \quad (\text{S.1})$$

where a is the geometric mean of PDA and PEO statistical segment lengths, N_{PDA} and N_{PEO} are the degrees of polymerization of PDA and PEO, respectively. Since N_{PDA} is not known *a priori*, it was set as a variable for the calculation of the interpenetration zone thickness. χ is the Flory-Huggins interaction parameter of PDA and PEO, and is defined as:⁶

$$\chi = \frac{V_m (\delta_{\text{PDA}} - \delta_{\text{PEO}})^2}{RT}, \quad (\text{S.2})$$

where V_m is the molar volume taken as the geometric mean of PDA and PEO monomer units, while δ_{PDA} and δ_{PEO} are the solubility parameters of PDA and PEO, respectively. R is the universal gas constant and T is the temperature (in K) at which the grafting of PEO was performed. The molar volumes of the monomer units were estimated using "back-of-the-envelope" method,⁷ whereas the solubility parameters were estimated using the atomic increment approach.⁸ Calculated values of the solubility parameters were $23.82 \text{ (J/cm}^{-3}\text{)}^{1/2}$ for PEO, and $32.29 \text{ (J/cm}^{-3}\text{)}^{1/2}$ and $\sim 35.40 \text{ (J/cm}^{-3}\text{)}^{1/2}$ for PDA having covalent structure of randomly linked monomer units (Scheme S1A)^{1,2} and ultrastructural organization (Scheme S1B),^{3,4} respectively. The obtained interpenetration zone thickness for the proposed models of the PDA covalent structure is reported in Figure S1.

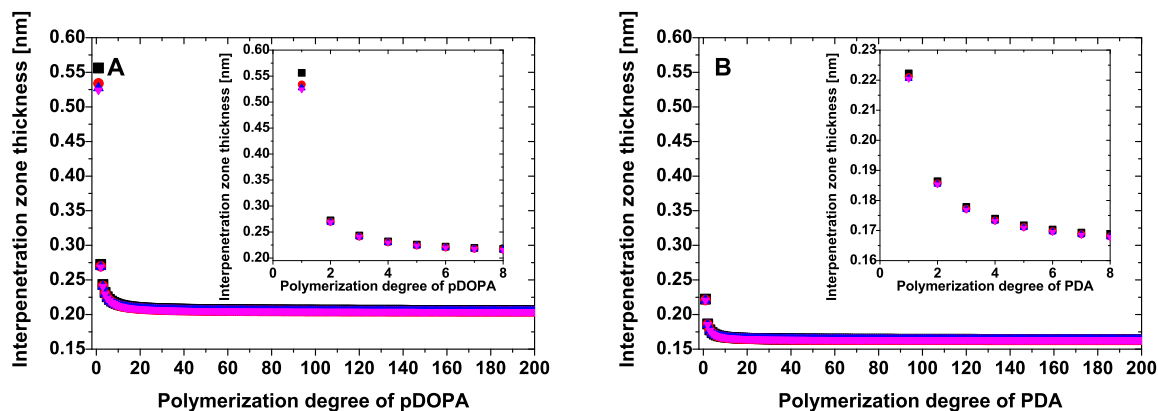


Figure S1: Variations of PEO/PDA interpenetration zone thickness for PDA having covalent structure of randomly linked monomer units (Scheme S1A) and ultrastructural organization (Scheme S1B). The thickness was calculated for PEO with different molecular weights: 2 000 (*black*), 5 000 (*red*), 10 000 (*blue*), and 20 000 (*pink*). Insets report the interpenetration zone thickness for low polymerization degrees of PDA.

Ellipsometric Data on PEO Layer Thickness and Surface Chain Density

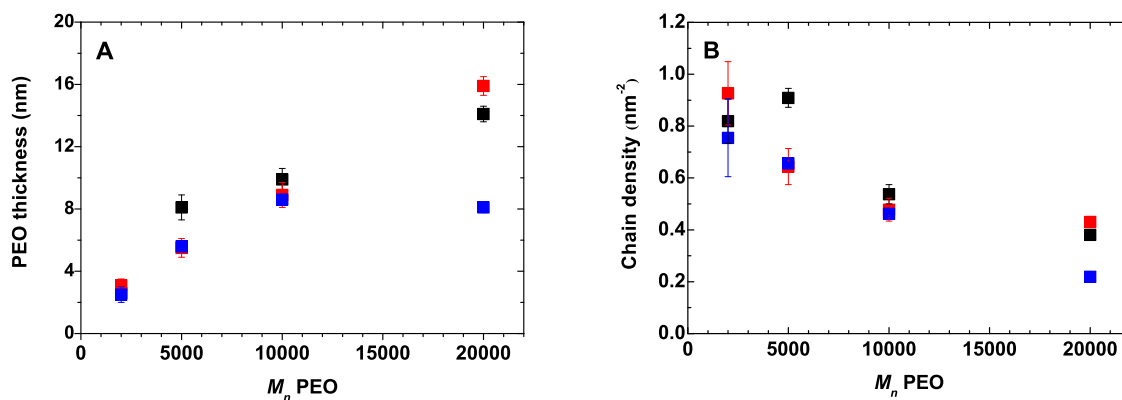


Figure S2: Variations of PEO (A) layer thickness and (B) surface chain density with increasing number average molecular weight of PEO. PEO-N(H)-PDA (*black*), PEO-S-PDA (*red*), and PEO-S (*blue*) anchoring on gold are shown. The thickness of the PDA film was ~ 11 nm.

VSFG Spectra of PDA Layer in the C–H Region in Air and in Water

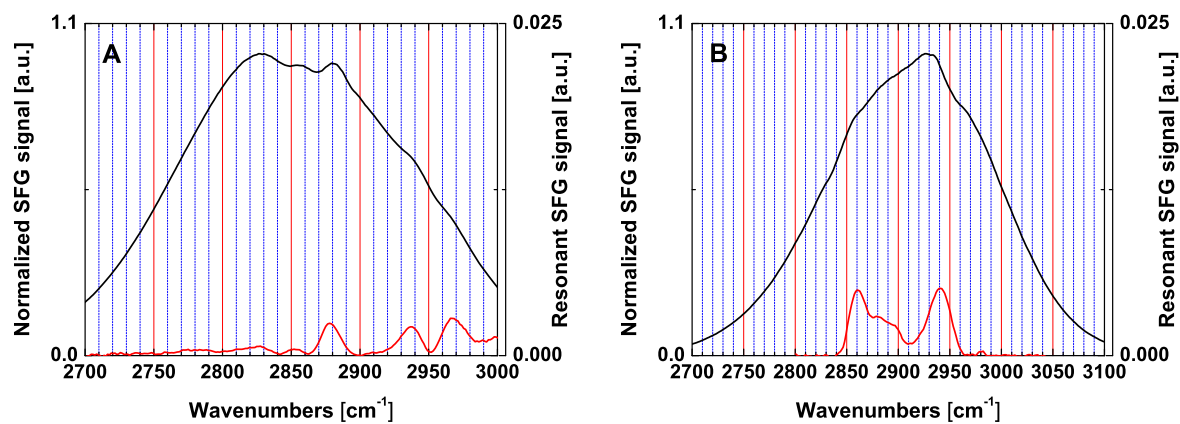


Figure S3: Measured (*black*) and delay-shifted (*red*) VSFG spectra in the CH stretching region of neat PDA films in air (A) and in H₂O (B).

Measured and delay-shifted VSFG Spectra of PEO-S-Au Layers in the C–H Region in Air

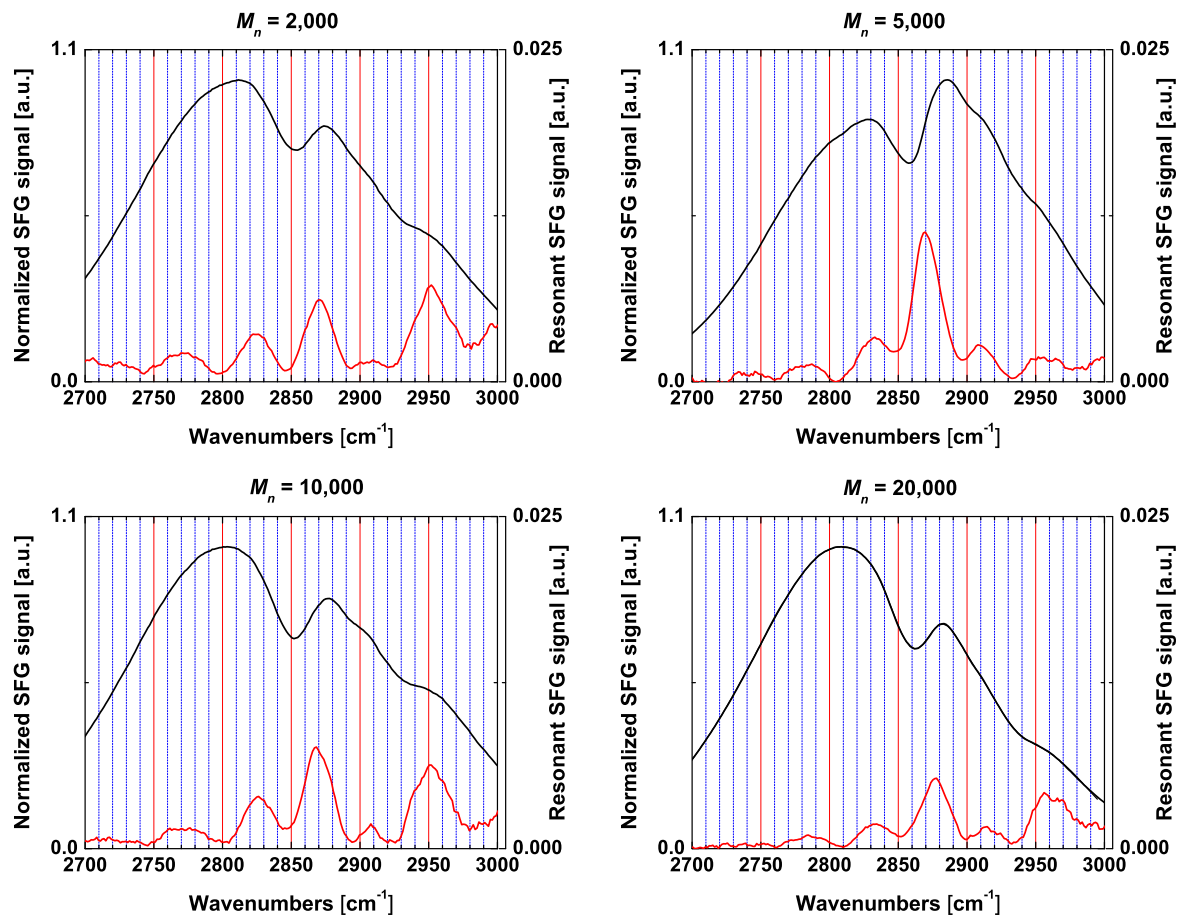


Figure S4: Measured (*black*) and delay-shifted (*red*) VSFG spectra in the C–H region of PEO-S-Au layers with different number average molecular weights: 2 000, 5 000, 10 000 and 20 000 in air.

Measured and delay-shifted VSFG Spectra of PEO-S-Au Layers in the C–H Region in Water

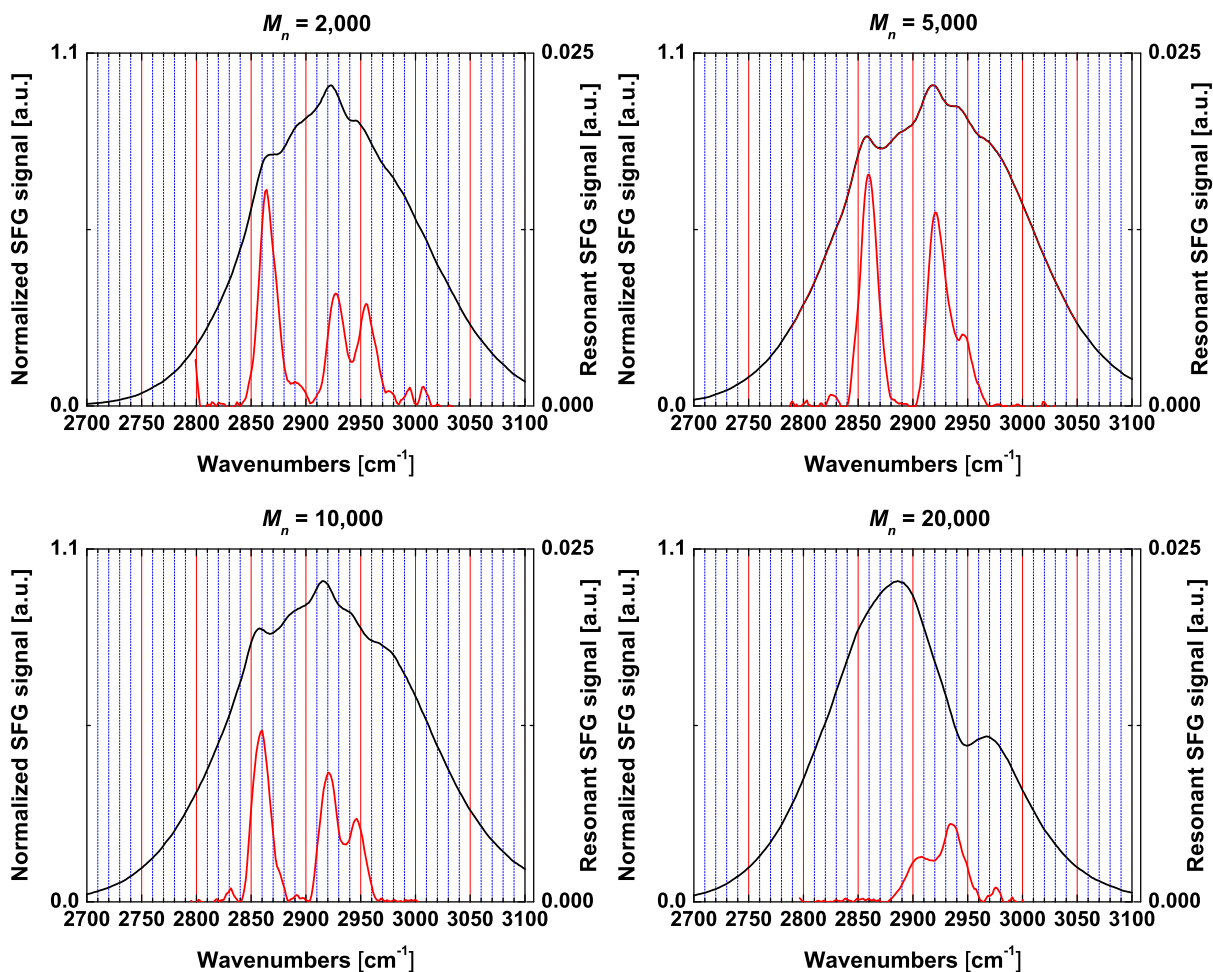


Figure S5: Measured (*black*) and delay-shifted (*red*) VSFG spectra in the C–H region of PEO-S-Au layers with different number average molecular weights: 2 000, 5 000, 10 000 and 20 000 in H_2O .

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