

Supplementary Information

Figures and Tables:

Reloading of three times is enough:

Table S1. Variation of absolute frequency values due to reloading of chips

Chip	Surface condition	$f_d/3 \pm SE$		
		Reloading 10 times	Reloading 3 times	Difference
1	SAM ^a	4986316 ± 6	4986311 ± 10	-5 ± 12
2	SAM	4980337 ± 3	4980342 ± 2	5 ± 4
3	SAM	4981246 ± 2	4981245 ± 1	-1 ± 2
3	OEGMA ^b	4981179 ± 2	4981180 ± 6	1 ± 6

^a each quartz chip was coated with a SAM of 100% initiator, ^b chip 3 was polymerized for OEGMA, the resulted polymer brush has a dry thickness of 8.7 ± 0.1 nm, and corresponding Δf^{iii} value of 67 and 65 Hz for reloading of 10 and 3 times, respectively, ^c each chip was reloaded for 10 times and randomly picked 3 values among the 10 values for calculation, ^d differences between the average values of 3 and 10 times reloading.

Vacuum dry is not necessary:

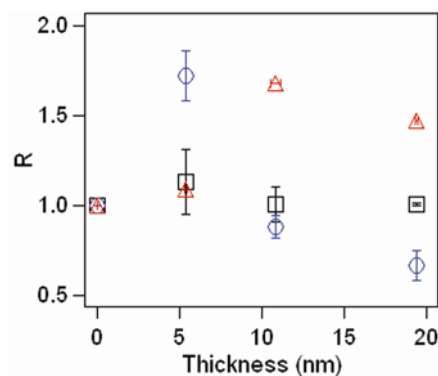


Figure S1. Three types of ratios between vacuum dried polymer (VDP) and nitrogen flow dried polymer (NDP) were plotted against dry film thickness for OEGMA: black square for dry film thickness-T (T_{VDP}/T_{NDP}), blue circle for $\Delta f^{iii}_{VDP}/\Delta f^{iii}_{NDP}$ and red triangle for $\Delta f^v_{VDP}/\Delta f^v_{NDP}$. The R value (mostly close to 1) indicated the differences between VPD and NDP were negligible at tested humidity (15%).

The optical constant An in the Cauchy model has minimal impact on $t_{f, dry}$:

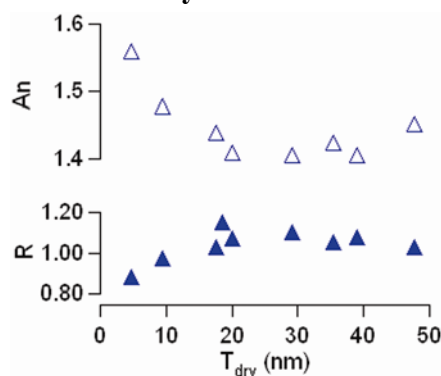


Figure S2. The dry film thickness was measured by ellipsometry at air-solid interface and evaluated using a Cauchy model for thickness with either fixed An (1.46) value or varied An value. The ratio ($R = t_{f, dry, An} / t_{f, dry, 1.46}$) between $t_{f, dry, 1.46}$ at fixed An and $t_{f, dry, An}$ with varied An (indicated in the upper Y axis) was plotted against $t_{f, dry, 1.46}$ for OEGMA. $R \sim 1$ indicated negligible impact of optical constant for $t_{f, dry, 1.46}$.

Viscosity of water can be measured and $\Delta f^i / \Delta D^i$ is very reproducible:

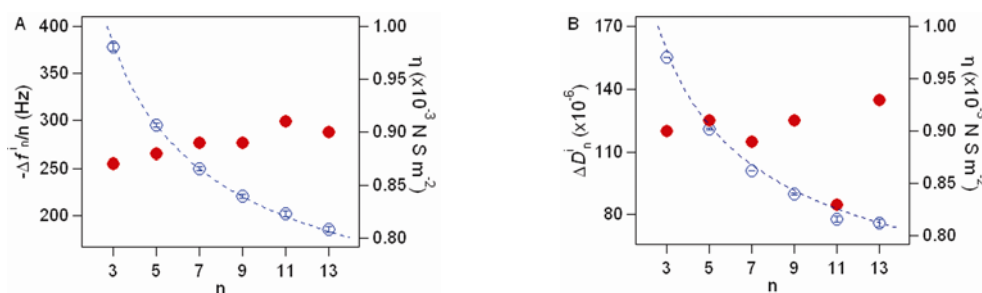


Figure S3. The viscosity of water at 25 °C calculated from QCM-D measurement: (A) frequency change (Δf^i , 8.9×10^{-4} N s m $^{-2}$) and (B) dissipation change (ΔD^i , 9.1×10^{-4} N m $^{-2}$) agreed well with literature values (8.9×10^{-4} N s m $^{-2}$).

The linear relations between dissipation/frequency and thickness changes:

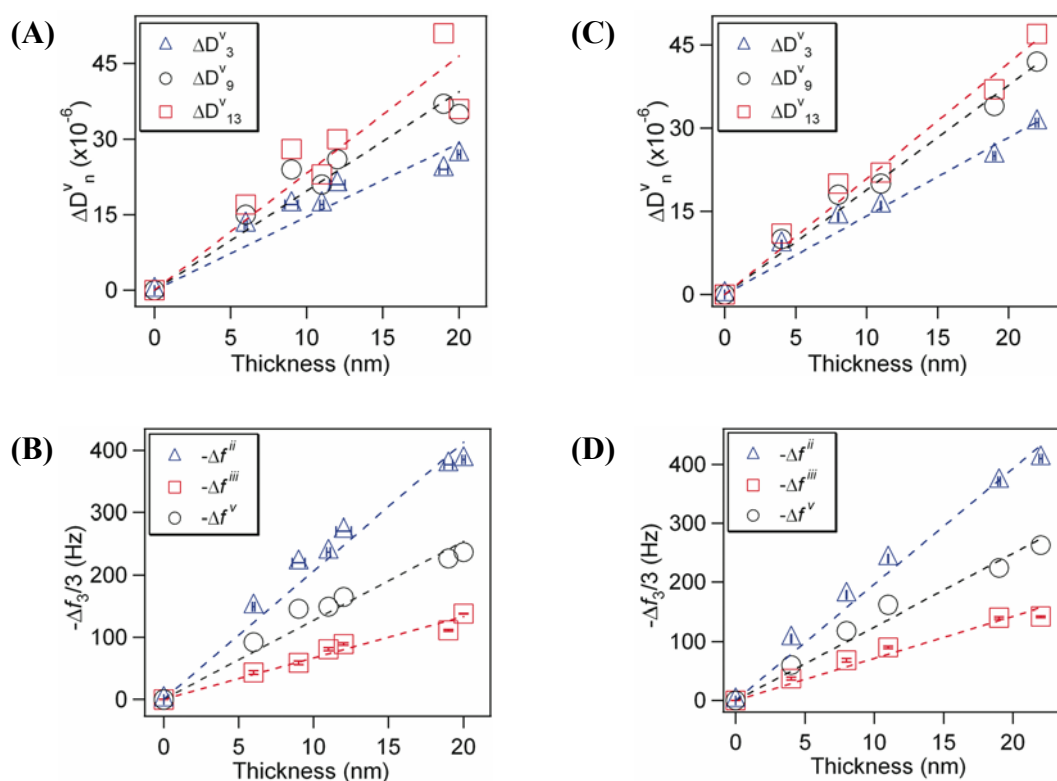


Figure S4. Linear relations between dissipation/frequency changes and thickness changes. Poly(OEGMA) brushes were grown from QCM chips at two different initiator densities: (A) dissipation changes and (B) frequency changes for 0.42 initiator density, (C) dissipation changes and (D) frequency changes for 0.15 initiator density ($R^2 > 0.95$).

The calculated viscoelasticity properties:

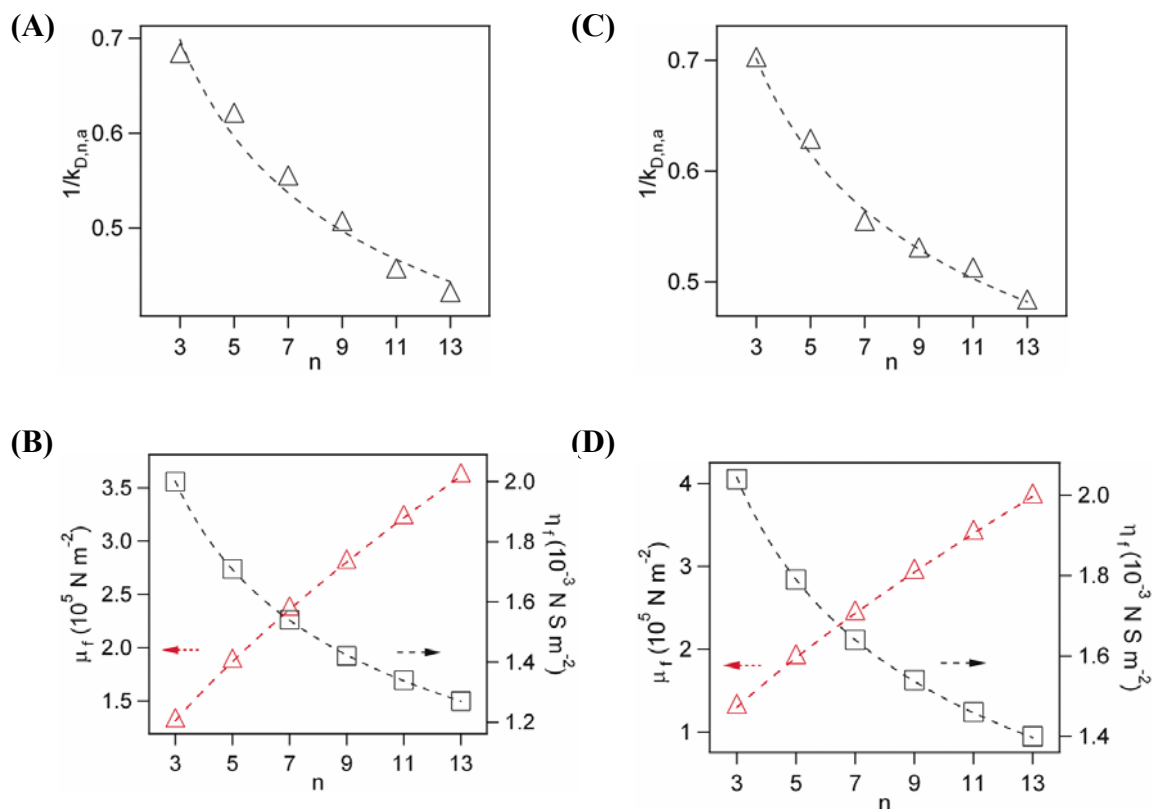


Figure S5. Calculated viscosity and elasticity values (See Table 1). Poly(OEGMA) brushes were grown from QCM chips of 0.42 and 0.15 initiator densities and the viscoelasticity properties were fitted according equations (21) for (A)~(B) and (C)~(D), respectively, ($R^2 > 0.99$). $R = t_{f,wet}/t_{f,dry}$ was assumed to be 2.

Assuming viscoelasticity was independent on frequency.

From equation (17) in text, we have

$$\frac{R_{wet/dry}}{nk_{D,n,dry}} = \frac{1}{6.4 \times 10^{-11} \mu_f} \left(\frac{\mu_f}{2\pi f_{q,1}} \right)^2 \left(\frac{1}{n} \right)^2 + \frac{\eta_f^2}{6.4 \times 10^{-11} \mu_f} \quad (S1)$$

Let

$$\frac{1}{nk_{D,n,dry}} = c \left(\frac{1}{n} \right)^2 + d \quad (S2)$$

$$c = \frac{1}{6.4 \times 10^{-11} R_{wet/dry} \mu_f} \left(\frac{\mu_f}{2\pi f_{q,1}} \right)^2 \quad (S3)$$

$$d = \frac{\eta_f^2}{6.4 \times 10^{-11} R_{wet/dry} \mu_f} \quad (S4)$$

where $R_{wet/dry}$, c and d were experimentally determined (**Figure S6 and Table S2**). We

have:

$$\mu_f = 6.26 \times 10^4 R_{wet/dry} c \quad (S5)$$

$$\eta_f = 2 \times 10^{-3} R_{wet/dry} \sqrt{cd} \quad (S6)$$

Table S2. Viscoelasticity calculated from equation (S2).

Overtone ^a	c	d	η ^b	μ ^c
3,5,7,9,11,13	2.96	0.055	1.61	3.71
5,7,9,11,13	4.08	0.038	1.58	5.11

^a the fitted range was indicated by the listed overtone numbers, ^b viscosity with a unit of $\times 10^{-3}$ N s m⁻², ^c elasticity with a unit of $\times 10^5$ N m⁻².

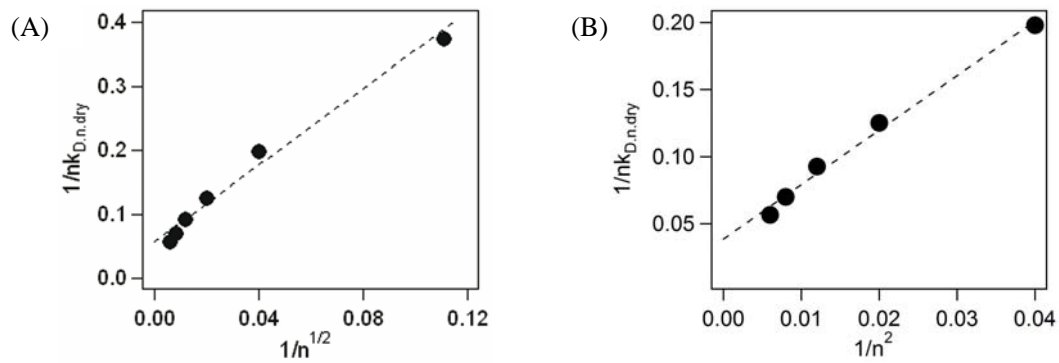


Figure S6. Linear fit for viscoelasticity according equation (S2). (A) fitted for $n = 3 \sim 13$ and (B) fitted for $n = 5 \sim 13$. The change of fitting range had great impact on elasticity but not viscosity. The value of slope and intersection were 4.08 and 0.038, respectively, $R^2 = 0.999$.

Assuming viscoelasticity was independent on frequency, the resulting viscosity and elasticity were similar to the case where the viscoelasticity was dependent on frequency (equations (21)~(25), Figure 5 and Table 1).

The $k_{2,dry}$ value was independent on thickness and initiator density.

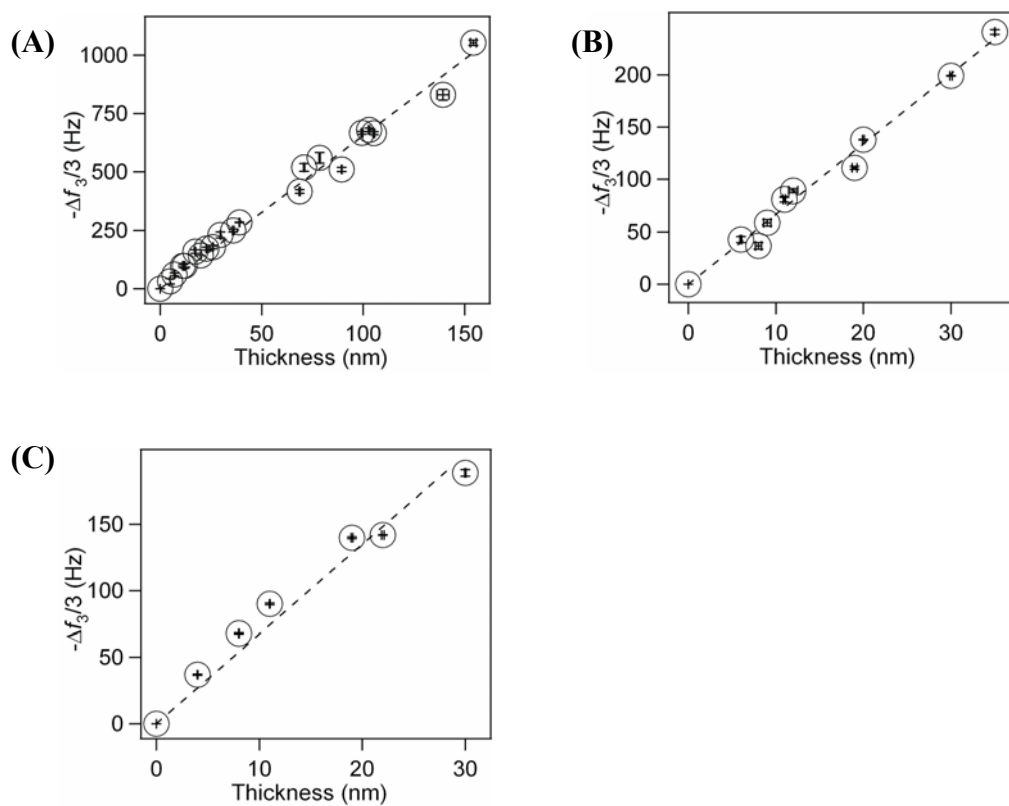


Figure S7. The linear $f-t$ relation ($k_{2,dry}$) for three initiator densities. (A) initiator density was 1.00 and $k_{2,dry} = 6.55$, (B) 0.42 and $k_{2,dry} = 6.60$ and (C) 0.15 and $k_{2,dry} = 7.15$, respectively ($R^2 > 0.98$).

Deduction of Equations for $\rho_{wet,f}$:

From equation (S7) and (S8), we have equation (S9):

$$\Delta D_{f,L,n} = \frac{6.4 \times 10^{-11}}{n} \frac{\mu_f}{\left(\frac{\mu_f}{2\pi f_{q,1}}\right)^2 \left(\frac{1}{n}\right)^2 + \eta_f^2} t_{f,wet} \quad (\text{S7}) \text{ corresponding to (17) in text}$$

$$\frac{\Delta f_{f,L,n}}{n} = 4.99 \times 10^{-3} \eta_f \frac{1}{\left(\frac{\mu_f}{2\pi f_{q,1}}\right)^2 \left(\frac{1}{n}\right)^2 + \eta_f^2} t_{f,wet} \quad (\text{S8}) \text{ corresponding to (33) in text}$$

$$\frac{\Delta D_{f,L,n}}{\Delta f_{f,L,n}/n} = \frac{6.4 \times 10^{-11}}{4.99 \times 10^{-3}} \frac{\mu_f}{n \eta_f} \quad (\text{S9})$$

Substituting equation (S9), (S10), (S11) to equation (S12), we have equation (S13)

$$\frac{\Delta f_{f,n}}{n} = -5.60 \times 10^{-3} \rho_{f,wet} t_{f,wet} \quad (\text{S10}) \text{ corresponding to (32) in text}$$

$$\frac{\Delta f_{f,L,n}}{n} = \frac{4.99 \times 10^{-3}}{6.4 \times 10^{-11}} \frac{n \eta_f}{\mu_f} \Delta D_{f,L,n} \quad (\text{S11})$$

$$-\frac{\Delta f_n^{ii}}{n} = -\left(\frac{\Delta f_{f,L,n}}{n} + \frac{\Delta f_{f,n}}{n}\right) = k_{1,n,a} t_{f,dry} \quad (\text{S12}) \text{ corresponding to (4) in text}$$

$$\rho_{f,wet} = \left(k_{1,n,a} + \frac{4.99 \times 10^{-3}}{6.4 \times 10^{-11}} \frac{\eta_0}{\mu_0} n^{d-c/2} k_{D,n,dry}\right) \frac{1}{5.60 \times 10^{-3} R_{wet/dry}} \quad (\text{S13})$$

corresponding to (37) in text, which was used to calculate the density of wet films.

Table S3. List of fitted values and viscoelastic properties for poly(OEGMA) at different initiator densities (R = 4).

<i>Initiator Density</i>	$an^c + bn^d$	η_f (N s m ⁻²)	μ_f (N m ⁻²)
1.00	$0.79n^{-0.28} + 0.79n^{-0.28}$	$6.3 \times 10^{-3} n^{-0.28}$	$2.0 \times 10^5 n^{0.72}$
0.42	$0.49n^{-0.31} + 0.49n^{-0.31}$	$3.9 \times 10^{-3} n^{-0.31}$	$1.2 \times 10^5 n^{0.69}$
0.15	$0.46n^{-0.26} + 0.46n^{-0.26}$	$3.7 \times 10^{-3} n^{-0.26}$	$1.2 \times 10^5 n^{0.74}$

Table S4. List of calculated density values for poly(OEGMA) at different initiator densities (R=4).

<i>Initiator Density</i>	$k_{2,dry}$	$\rho_{f,dry}$ (Kg m ⁻³)	$\rho_{f,wet}$ (Kg m ⁻³)
1.00	7.64	1364	883
0.42	6.60	1179	1070
0.15	7.15	1277	989

Table S5. List of calculated k values for poly(OEGMA) at 0.42 initiator densities.

<i>n</i>	<i>k</i> _{1,<i>n</i>} ^{<i>a</i>}	<i>k</i> _{2,<i>n</i>} ^{<i>b</i>}	<i>k</i> _{3,<i>n</i>} ^{<i>c</i>}
3	10.40	13.01	2.61
5	10.03	12.91	2.88
7	9.68	12.90	3.22
9	9.45	12.98	3.53
11	9.21	13.13	3.92
13	8.86	13.01	4.16

^{*a*} $k_{1,n} = k_{1,n,a}/R$ ($R = t_{f,wet}/t_{f,dry} \approx 2$), ^{*b*} $k_{2,n} = k_{1,n} + k_{3,n}$, ^{*c*} calculated according equation (33).

Table S6. List of calculated k values for poly(OEGMA) at 0.15 initiator densities.

<i>n</i>	<i>k</i> _{1,<i>n</i>} ^{<i>a</i>}	<i>k</i> _{2,<i>n</i>} ^{<i>b</i>}	<i>k</i> _{3,<i>n</i>} ^{<i>c</i>}
3	9.85	12.48	2.63
5	9.36	12.30	2.94
7	8.90	12.23	3.33
9	8.60	12.09	3.49
11	8.34	11.95	3.61
13	8.02	11.84	3.82

^{*a*} $k_{1,n} = k_{1,n,a}/R$ ($R = t_{f,wet}/t_{f,dry} \approx 2$), ^{*b*} $k_{2,n} = k_{1,n} + k_{3,n}$, ^{*c*} calculated according equation (33).