Supplementary Material for “Flexible thermoresponsive nanomembranes at the aqueous-air interface” by Ashley D. Cramer\textsuperscript{a}, Filippo Gaminossi\textsuperscript{a}, Erik Wischerhoff\textsuperscript{b}, Andre Laschewsky\textsuperscript{b,c}, Reinhard Miller\textsuperscript{d}, and James K. Ferri\textsuperscript{a,*}

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Experimental. Surface tension and dilational rheology at the air-water interface.

Surface tension values were determined from the shape of the axisymmetric menisci using the axisymmetric drop shape analysis (ADSA) technique. Assuming that the experimental drop is Laplacian and axisymmetric, ADSA finds the theoretical profile that best matches the drop profile extracted from the image of a real drop, from which the surface tension, contact angle, drop volume, and surface area can be computed. The strategy employed is to fit the shape of an experimental drop to a theoretical drop profile according to the Laplace equation of capillarity, using the surface tension as an adjustable parameter.\textsuperscript{1}

The dilational rheological parameters of the interface are obtained using areal oscillations.\textsuperscript{2} In these experiments, the surface area, $A$, of a pendant drop periodically changed causing compression and expansion of the interface. The relative area variation imposed by the apparatus and the interfacial tension response are recorded in order to evaluate the complex dilatational interfacial elasticity $E^*$:

$$E^* = \frac{d\gamma^*}{d\ln A} \quad \text{(eq. S1)}$$
where \( A^* \) is the complex area of the drop and \( \gamma^* \) is the complex interfacial tension. Then one can evaluate the real part \( G' \) and the imaginary part \( G'' \) of the complex dilatational interfacial elasticity, which encompass surface elasticity \( E_s \) and the viscosity \( \eta_s \), respectively:

\[
E^* = G^i + jG^ii = E_s + j\omega\eta_s \tag{eq. S2}
\]

with \( j = \sqrt{-1} \).

**Section S1. Synthesis of DMPG/PDADMAC/PSS/PDADMAC/MA01/P(MEO₂MA₉₇-co-OEGMA₃) nanomembranes at the surface of a pendant water drop in air.**

The synthesis of freestanding Layer-by-Layer (LbL) nanocomposites at the air-water interface was followed monitoring the time evolution of surface tension using axisymmetric drop shape analysis (ADSA). Details of the preparation are reported elsewhere.³ A lipid solution of 1,2-dimyristoyl-sn-glycero-3-phosphoglycerol (DMPG, 99%, Avanti Polar Lipids) was prepared using a mixture of ultrapure chloroform and methanol (3:1 v:v, J.T. Baker). Briefly \( V=0.17\mu L \) of DMPG was deposited on the surface of a pendant drop. The drop was inflated and compressed to ensure the surface was clean, the surface tension after compression was \( \gamma=(41\pm0.1)\text{mN/m} \). Polydiallyldimethylammonium chloride (PDADMAC, \( \text{Mw} \approx 200-350\text{kDa} \)) and polystyrene sulfonate (PSS, \( \text{Mw} \approx 70\text{kDa} \)) were purchased from Aldrich and prepared at 1mg/mL in 0.5M NaCl, pH = 3. The PSS was dialyzed before use (Mw 50kDa cut off). The subphase of the drop was then exchanged, maintaining constant surface area (\( A_0=25\text{mm}^2 \)) with an aqueous solution containing a polyelectrolyte of opposite charge. The subphase was exchanged with PDADMAC, PSS, and PDADMAC (\( V=500\mu L \)). Between polyion exchanges the subphase was washed with 0.5M NaCl (\( V=700\mu L \)). After exchange with the last PDADMAC layer, the macroinitiator, MA01, (1mg/mL, pH=3, 0.5M NaCl) was introduced then washed with 0.5M NaCl. After this wash the chamber was evacuated of oxygen through the introduction of a strong argon sweep for 2 minutes, followed by a continuous low flow sweep during polymerization. A solution of \( \text{CuBr}_2 \) (Aldrich, 99%), oligo(ethylene glycol) methacrylate (OEGMA 475, Aldrich, \( \text{Mn} = 475\text{gmol}^{-1} \)), 2-(2’-methoxyethoxy)
ethyl methacrylate (MEO₂MA, Aldrich, 95%), 2,2’-bipyridyl (Fluka, 98%), and sodium L-ascorbate (Aldrich, 99%) in 15mL of H₂O and 15mL of ethanol was prepared in a flask with a septum and degassed by purging with argon. The as prepared solution was exchanged at a volumetric flow rate \( Q=0.33\mu l \text{ s}^{-1} \) for polymerization at the interface. The reaction was quenched by the introduction of oxygen into the chamber (upon removal of the glass cuvette) for a total of 20 minutes and then exchanged with 50% ethylene glycol (\( V=700\mu L \)) and a final wash with 0.5M NaCl. The final layer sequence was DMPG/PDADMAC/PSS/PDADMAC/MA01/P(MEO₂MA_{97}-co-OEGMA_{3}). The overall thickness of the polymer layer has been estimated through ellipsometry on solid supports to be \( \delta\approx25\text{nm} \). Figure S1 shows the evolution of drop shape and surface tension against time during all the reaction steps.

![Figure S1](image)

**Figure S1.** (a-d) Drop interfacial morphology and freestanding nanomembrane evolution: (a) DMPG lipid layer, (b) Layer-by-Layer (LbL) adsorption of PDADMAC/PSS bilayer, (c) growth of the macroinitiator, MA01, LbL layer, (d) end of polymerization with MEO₂MA/OEGMA copolymer. (e) Surface tension (left) and surface area (right) vs. time during the synthesis steps.

Upon addition of PDADMAC we observe an increase of surface tension \( \Delta\gamma=(10.1\pm0.1)\text{mN/m} \) due to charge condensation (neutralization) at the interface. Subsequent additions of alternating
polyelectrolytes have negligible effects on the surface tension while keeping constant the surface area (region I).

On the contrary, the exchange with a subphase containing the macroinitiator MA01 leads to a strong decrease of the surface tension, \( \Delta \gamma = -(10 \pm 0.1) \text{mN/m} \), suggesting charge density and conformational changes of the freestanding nanocomposite (region II). After the addition of the \( \text{MEO}_2\text{MA/OEGMA} \) monomers the surface tension decreases again while the software fails to maintain the surface area constant because of the non-homogeneous reaction at the interface (region III) – see main text for discussion. Upon removal of the reaction chamber (oxygen flows) the polymer growth stops immediately and the drop recovers the original shape. The total variation of surface tension due to the polymer growth is \( \Delta \gamma = -(14.8 \pm 0.1) \text{mN/m} \).

**Section S2. Temperature-induced dilational rheology change for the freestanding nanomembranes.**

Figure S2 shows the dependence of the complex surface elasticity on frequency.

**Figure S2.** Complex dilational surface elasticity against frequency for the nanomembrane at (a) \( T=24^\circ C \) and at (b) \( T=37^\circ C \): (left axis) real part, \( G' \), and (right axis) imaginary part, \( G'' \).

Independent of temperature, both \( G' \) and \( G'' \) increase almost linearly with frequency. However, while at \( T=24^\circ C \) the real part has approximately the same value as the dissipative term, \( G' \approx G'' \), upon heating the
The nanomembrane becomes more elastic, \( G' > G'' \), for all the frequencies studied. To better examine the frequency behavior of the system we also calculated the dilational elastic modulus, \(|E|\), and the loss angle, \( \phi \), given by:

\[
|E| = \sqrt{(G')^2 + (G'')^2}
\]  
(eq. S3)

\[
\phi = \tan^{-1}\left(\frac{G''}{G'}\right)
\]  
(eq. S4)

The dependence of both modulus and phase on frequency is shown in Figure S3.

![Figure S3](image)

**Figure S3.** (a) Dilational elastic modulus (\(|E|\), close symbols) and phase (\(\phi\), open symbols) as a function of frequency, \( \omega = 2\pi f \), for the nanomembrane at \( T=24 \, ^\circ C \) (blue) and at \( T=37 \, ^\circ C \) (red). (b) Logarithmic plot of the elastic modulus against frequency.

While the phase is independent from the temperature variation, the modulus increases one order of magnitude upon heating. We found the nanomembrane turns from a liquid-like to a solid-like system upon heating following a power law dependency over frequency, \( \log(E) \propto \log(\omega) \).
References


