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Supporting Information for

# Thiol-ene "Click" Networks from Amphiphilic Fluoropolymers: Full synthesis and characterization of a benchmark anti-biofouling surface

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## PeakForce$^{TM}$ Quantitative Nanomechanical Mapping (QNM$^{TM}$) Atomic Force Microscopy

Atomic force microscopy (AFM) measurements were taken using a Bruker Multimode 8 system in PeakForce$^{TM}$ tapping mode. This imaging method also provides direct surface maps of modulus, dispersion, deformation and adhesion[1]. In brief, the PeakForce$^{TM}$ QNM$^{TM}$ imaging mode that uses a modified Hertzian model, the DMT[2] model (Equation 1), to directly extract a reduced Young's modulus ($E_r$). The DMT model takes into account surface-tip interactions neglected in the Hertz model.

$$E_r = \frac{3(F_t - F_a)}{4\sqrt{Rd^3}} \tag{1}$$

In equation 1 for the DMT reduced Young's Modulus: $F_t$ is the force on the probe tip, $F_a$ is the adhesive force between the probe tip and the sample, R is the working tip radius, and d is the depth of surface deformation below the zero-force contact point. The reduced Young's modulus is related to the sample modulus by equation 2 and reduces to equation 3 where the modulus of the probe tip is much greater than the sample being measured.

$$\frac{1}{E_r} = \frac{(1-v^2)}{E} - \frac{(1-v_t^2)}{E_t} \tag{2}$$

$$\frac{1}{E_r} \cong \frac{(1-v^2)}{E} \tag{3}$$

This is where $v$ is the sample Poisson's ratio, $v_t$ is the probe tip Poisson's ratio, $E_t$ is the probe tip modulus and E is the sample modulus. Force curve fitting after tip contact provides a reduced modulus value which can then be converted to a Young's modulus using a sample surface Poisson's 0.35, as it is very difficult to determine the Poisson's Ratio of a coating or thin film. As crosslinked, shape-persistent organic materials have Poisson ratios almost exclusively between 0.3 and 0.4 (0.5 for completely uncompressible materials), this assumption limits the possible error in the on conversion of reduced moduli to the final Young's moduli to *ca.* 3% from misassignment of the surface's Poisson's ratio. While this error is relatively small, the authors ask readers to take this into account when interpreting the moduli results. The difference in force curve minima during approach and retraction provides adhesion force. The absolute minimum in tip Z position after contact dictates deformation. Finally, the hysteresis in the after-contact approach and before-release retraction force curves provides dispersion values.

This is where $v$ is the sample Poisson's ratio, $v_t$ is the probe tip Poisson's ratio, $E_t$ is the probe tip modulus and E is the sample modulus. Force curve fitting after tip contact provides a reduced modulus value which can then be converted to a Young's modulus using a sample surface Poisson's ratio of 0.3 for samples with moduli of 1 MPa or below, 0.4 for samples with moduli of 1 GPa or above and scaling linearly between 1 MPa and 1 GPa. For this system, a ratio of 3.5 was selected. As crosslinked, shape-persistent organic materials have Poisson ratios almost exclusively between 0.3 and 0.4 (0.5 for completely uncompressible materials), this assumption limits the possible error in the on conversion of reduced moduli to the final Young's moduli to *ca.* 3% from misassignment of the surface's Poisson's ratio. The PeakForce$^{TM}$ method dictates a selection of either 0.3 or 0.4 without a gradient. It was the author's decision that this was inappropriate, potentially leading to error levels as high as 12% and so a gradient was used. While the error from the assigned Poisson's ratio is relatively small, the authors ask readers to take this into account when interpreting the moduli results. The difference in force curve minima during approach and retraction provides adhesion force. The absolute minimum in tip Z position after contact dictates deformation. Finally, the hysteresis in the approach and retraction force curves provides dispersion values.

In these measurements a Scanasyst-air probe with nominal manufacturer mechanical specifications of k = 0.4 N/m, F = 70 kHz and tip radius = 2 nm was used. Calibration of the system was first done using two reference samples, a homogeneous PDMS film with a known modulus of 3.5 MPa and homogeneous spin-cast polystyrene film of a known modulus of 2.7 GPa in order to confirm calibration over moduli spanning ~3 orders of magnitude. Calibration was performed on each independently and the modulus values were found to be within 5% of the known value for both samples for the calibration. Calibration was further confirmed through independent determination of the probe cantilever spring constant, deflection sensitivity and tip geometry. Tip geometry/radius was determined with the use of a known surface of titanium crystals. After independent calibration, the two standards were measured again and confirmed to have Young's moduli within 5% of the known value.

## Film Thickness and 2D Fluorescence

As measured by optical cross-section, coating thicknesses for **LH** were 220 μm, **LP** were 310 μm and **PH** were 320 μm as cast.

In regards to the lack of solvent emission from 1% LFPene solutions in the 2D spectra, a cause can be assigned as follows:
The ratio of LFPene to 1,2-dioxane is 1:16000 molecules at the 1% ratio. This easily puts all solvent molecules within FRET range of the polymer. However, at lower concentrations the molecules of 1,2-dioxane are in sufficient excess to not be entirely within FRET range of the polymer. At 0.01% and 0.001% almost none of the solvent would be close enough to a polymer acceptor.

A description to the motivation for and application of the 2D fluorescence work for identifying microregion chemistry follows:
It has been found that fluorescence microscopy of these films consistently show contrast that cannot be explained from AFM of microfeatures. This indicates that the chemical differences in this contrast are not correlated to surface features explicitly. However, it has also been noted that some BSA binding events happen more frequently above some microregions. Identifying these regions, and their chemical makeup is therefore important to the ultimate performance of the film and should be accounted for. Previous work with fluoropolymers shows this to be typical of other systems and it was the authors intent to not only address the identification of these regions for this system, but to outline a method for assessing work in the future by others.

## Extracted Excitation and Emission Spectra and Peak Deconvolution

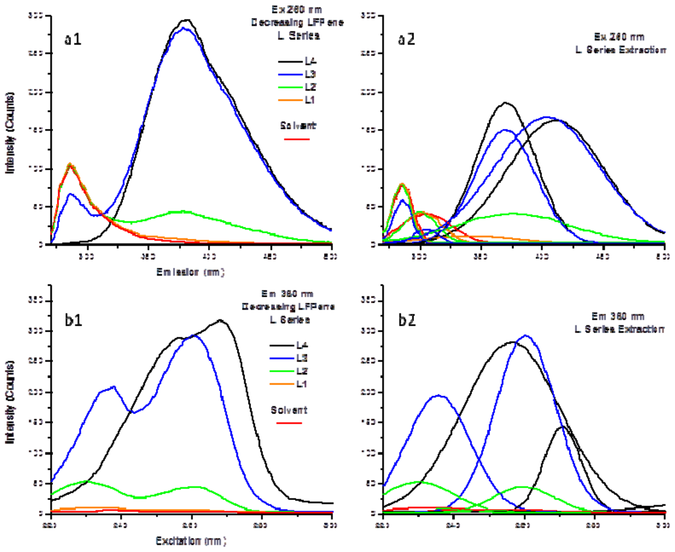

**Figure S1.** 260 nm Emission (a1) and 380 nm Excitation (b1) Spectra of **L4-L1** and **S**.

*Peak extractions for both the emission (a2) and excitation (b2) are provided.*

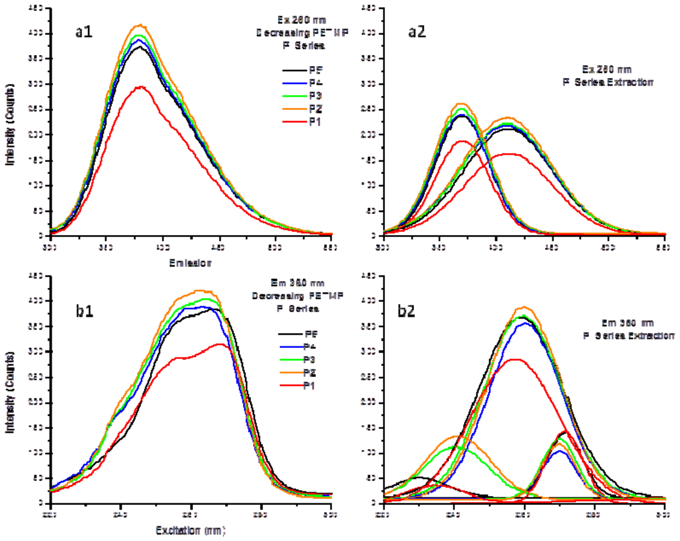

**Figure S2.** 260 nm Emission (a1) and 380 nm Excitation (b1) Spectra of **P5-P1**

*Peak extractions for both emission (a2) and excitation (b2) are provided.*

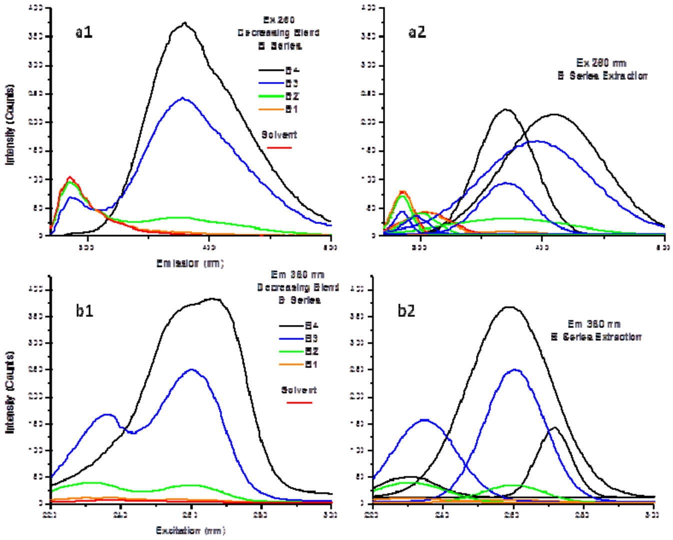

**Figure S3.** 260 nm Emission (a1) and 380 nm Excitation (b1) Spectra of **B4-B1** and **S**.

*Peak extractions for both the emission (a2) and excitation (b2) are provided.*

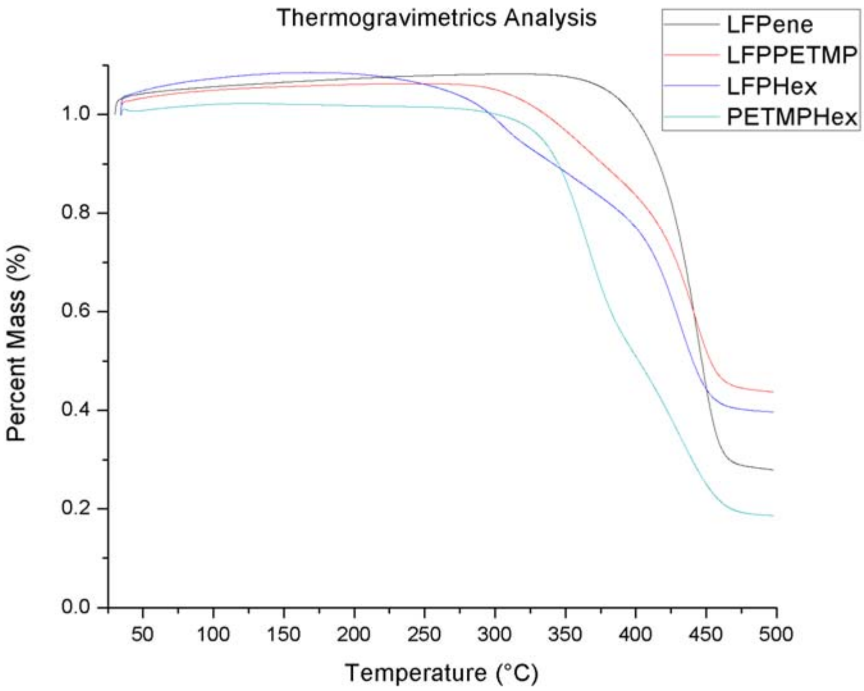

**Figure S4.** Combined thermal decomposition curves for LFPene, LFP-PETMP (**LP**), LFP-Hex (**LH**) and PETMP-Hex (**PH**).

Note: The increase in mass observed from 25 to 100 °C is related to increased water uptake on warming.

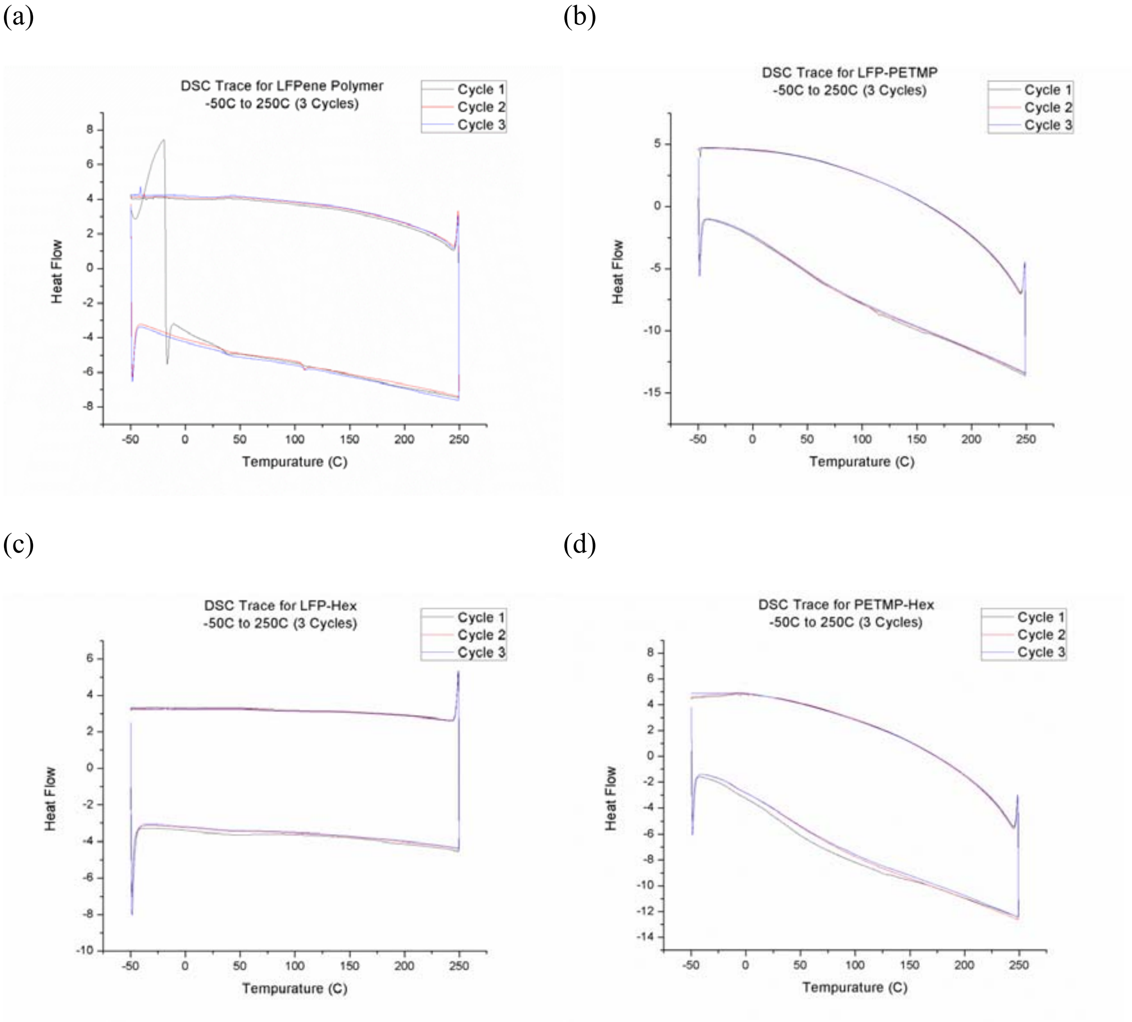

**Figure S5.** DSC traces for (a) LFPene, (b) LFP-PETMP (**LP**), (c) LFP-Hex (**LH**) and (d) PETM-PHex (**PH**).

## References

1. T. J. Young, M. A. Monclus, T. L. Burnett, W. R. Broughton and S. L. Ogin, *Meas. Sci. Technol.*, *The Use of the PeakForce™ Quantitative Nanomechanical Mapping AFM-based Method for High-resolution Young's Modulus Measurement of Polymers*, 2011, **22**, 125703.
2. B.V. Derjaguin, V. M. Muller and Y. P. Toporov; *J. Colloid Interface Sci.*, *Effect of contact deformations on the adhesion of particles*, 1975, **53**, 314.