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Supplementary Material

High Glass Transition Temperature Fluoropolymers for Hydrophobic Surface Coatings via RAFT Copolymerization

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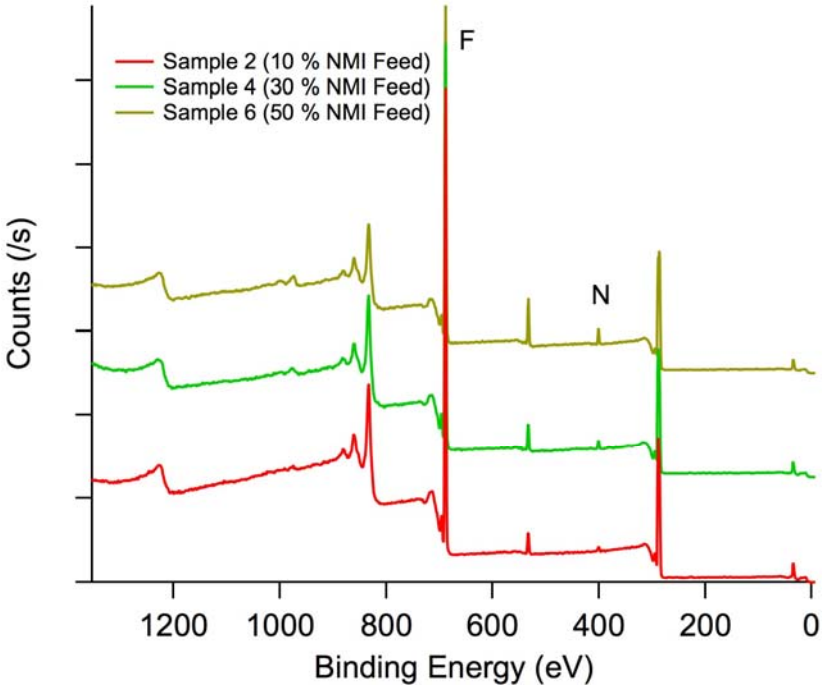

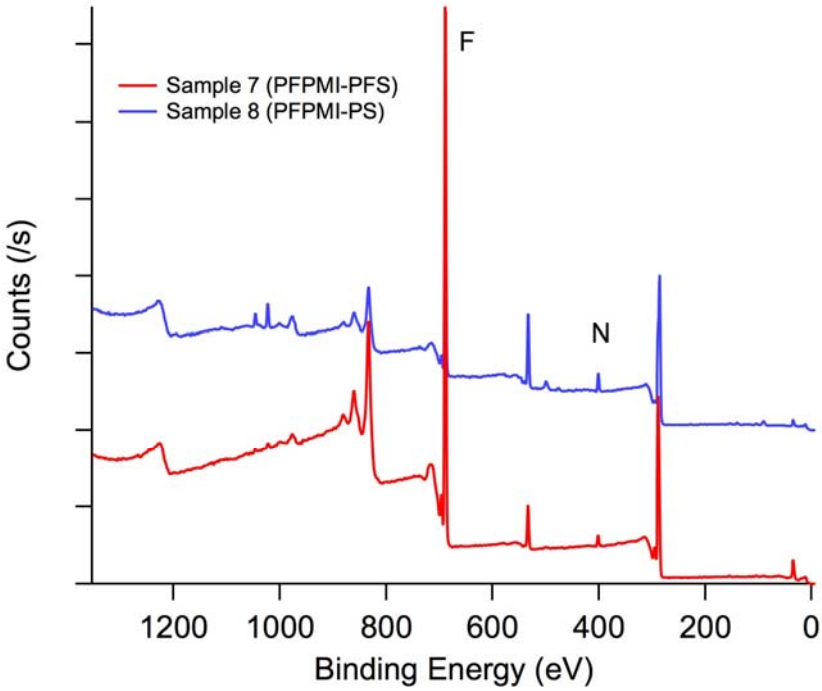

Figure S1. XPS Survey Scans for NMI-PFS copolymers (top) and PFPMI-based copolymers (bottom).

Table S1. Atomic percentages of Fluorine and Nitrogen as determined by XPS survey scans for copolymers prepared in this work.

Sample	Mole Fraction NMI (Feed)	F (atom %)	N (atom %)	Mole Fraction NMI in Copolymer
2	0.10	31.5	0.89	0.12
3	0.20	30.8	1.38	0.18
4	0.30	30.3	1.68	0.22
5	0.40	25.1	2.61	0.34
6	0.50	24.3	2.87	0.37
Sample	**Mole Fraction PFPMI (Feed)**	**F (atom %)**	**N (atom %)**	**Mole Fraction PFPMI in Copolymer**
7	0.29	37.0	1.72	0.25
8	0.30	18.6	3.65	0.46

In the case of NMI-PFS copolymers, the F/N atomic ratio was used to determine copolymer composition. As the fluorine present is within the PFS units in the polymer chain and the nitrogen present is within the NMI units (excluding any nitrogen from initiator-derived end-groups), the following calculations can be performed:

Let x = mole fraction of NMI in the copolymer.

Therefore: $$\frac{(F_{at\%}/5)}{N_{at\%}} = \frac{1-x}{x}$$

$$x = \frac{5N_{at\%}}{F_{at\%} + 5N_{at\%}}$$

Similar calculations were performed to determine the composition of PFPMI-based copolymers.

2D NMR Data Acquisition

2D NMR spectra were recorded at 300 K on a Bruker Avance III HD 600 MHz spectrometer using a 5mm TCI cryogenically cooled probe using standard Bruker pulseprograms and Topspin 3.1 software used for both acquisition and processing. Spectral widths in all datasets were set as appropriate for the observed chemical shift ranges of the relevant nuclei. Chemical shifts are referenced indirectly relevant to DSS.

^{1}H-^{1}H NOESY data (*noesygph*) were acquired with a mixing time of 250 ms with 2048 x 400 increments and 32 scans per T1 increment. Data were zero-filled to 4K x 1K with sine squared apodisation (SSB=2) in both dimensions.

^{1}H-^{13}C-HMBC data (*hmbcgpl2ndqf*) were recorded with 2048 x 256 datapoints and 128 scans per increment. The long range coupling constant was set to 10 Hz. Data were zerofilled to 4K x 1K datapoints and sine apodisation in both dimensions. Data is in magnitude mode.

^{1}H-^{13}C-HSQCme data (*hsqcedetgpsisp2.2*) were recorded with 2048 x 256 datapoints and 8 scans per increment. Data were zerofilled to 4K x 1K datapoints and sine squared apodisation (SSB=2) in both dimensions. The multiplicity editing element of the pulseprogram yields a 180 degree phase difference between CH2 protons relative to CH/CH3.

^{19}F-^{13}C-HSQC data (*hsqcetgpsp*) were recorded with 1024 x 32 datapoints and 512 scans per increment. The value for the one-bond CF coupling was set to 230 Hz (a compromise allowed through reduction homospoil gradient pulse value p16 = 800 microseconds). Data were zerofilled to 4K x 1K datapoints and sine squared apodisation (SSB=2) in both dimensions.

^{19}F-^{13}C-HMBC data (*hmbcetgpl3nd*) were recorded with 2048 x 256 datapoints and 128 scans per increment. A long-range coupling constant of 30 Hz was optimal and limits on the one-bond coupling were set between 200 Hz and 270 Hz. Data were zerofilled to 4K x 1K datapoints with sine squared apodisation (SSB=2) in F1 and Gaussian multiplication in F2 (LB = -1.0 Hzm GB = 0.3). Data are in magnitude mode.

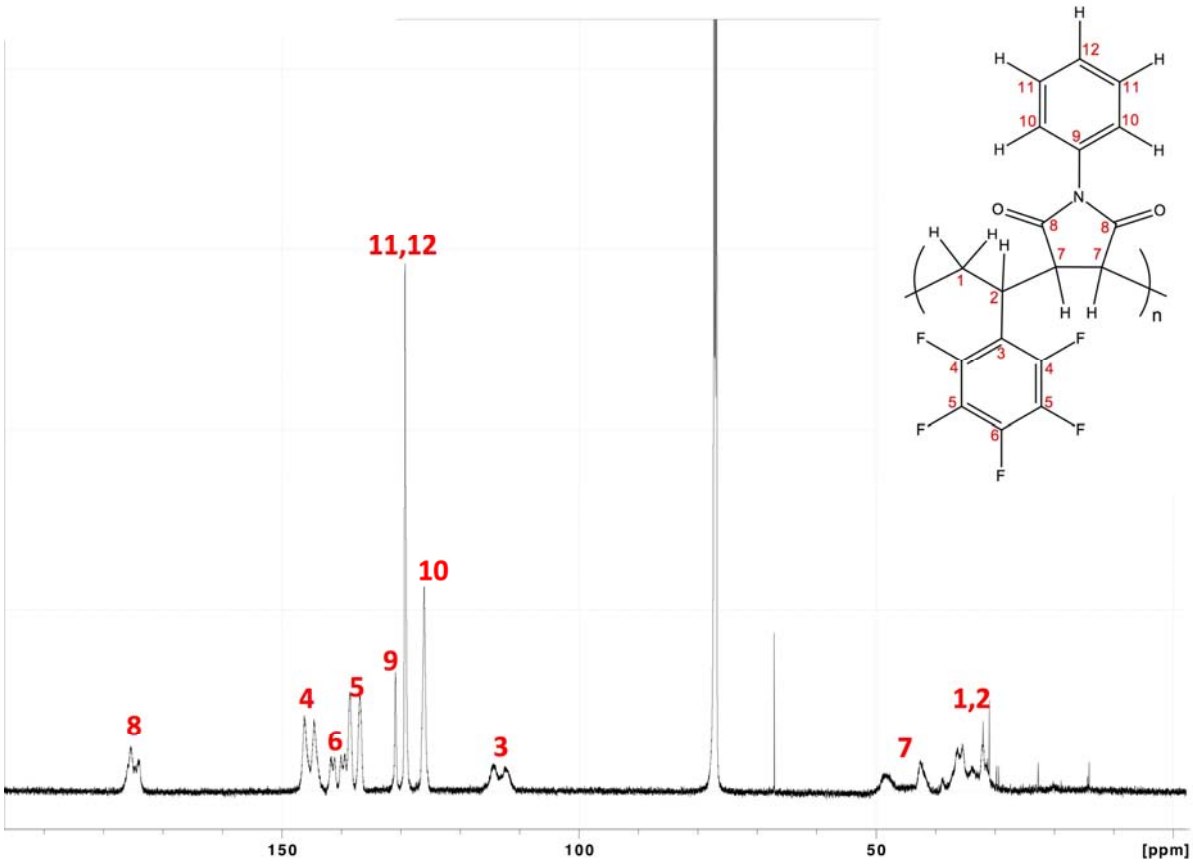

Figure S2. ^{13}C spectrum of Sample 6.

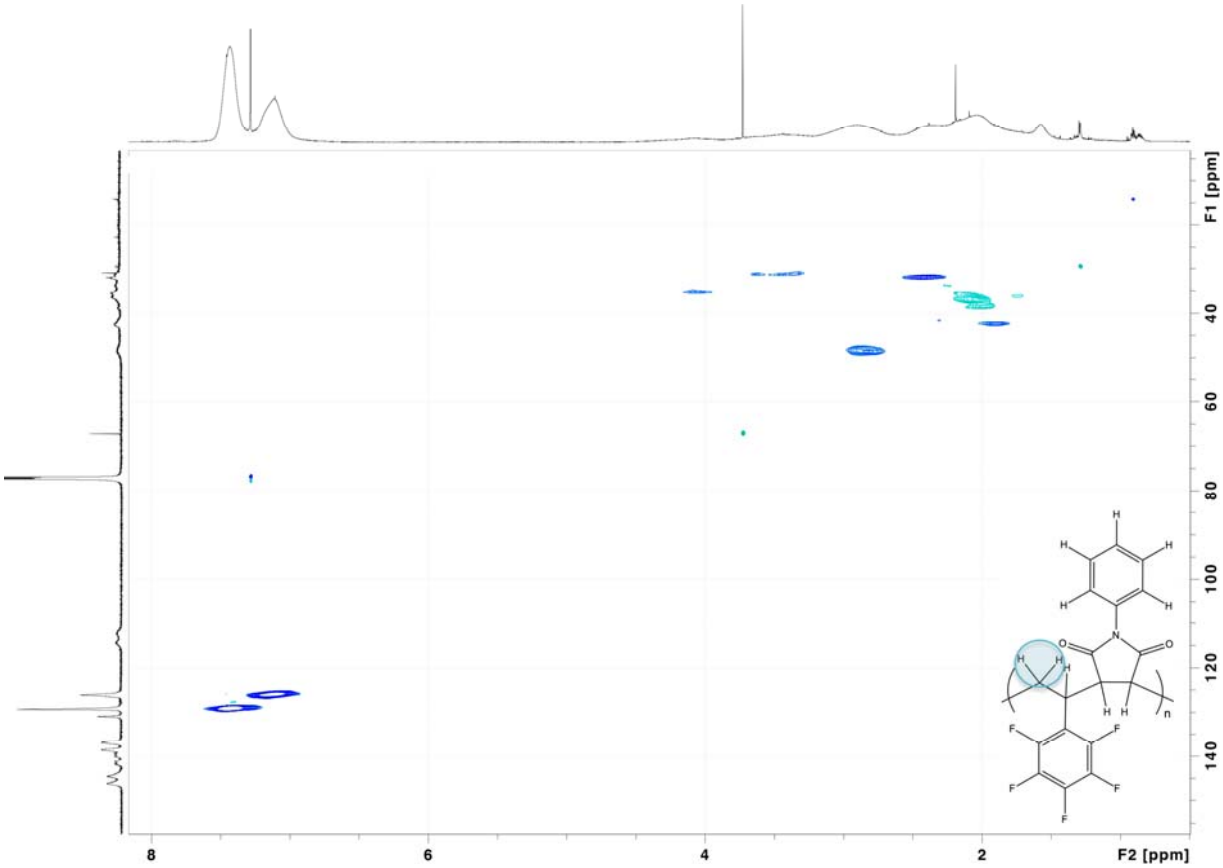

Figure S3. ^{1}H-^{13}C HSQCme spectrum of Sample 6. The methylene linkage as part of the polymer backbone is highlighted in aqua blue.

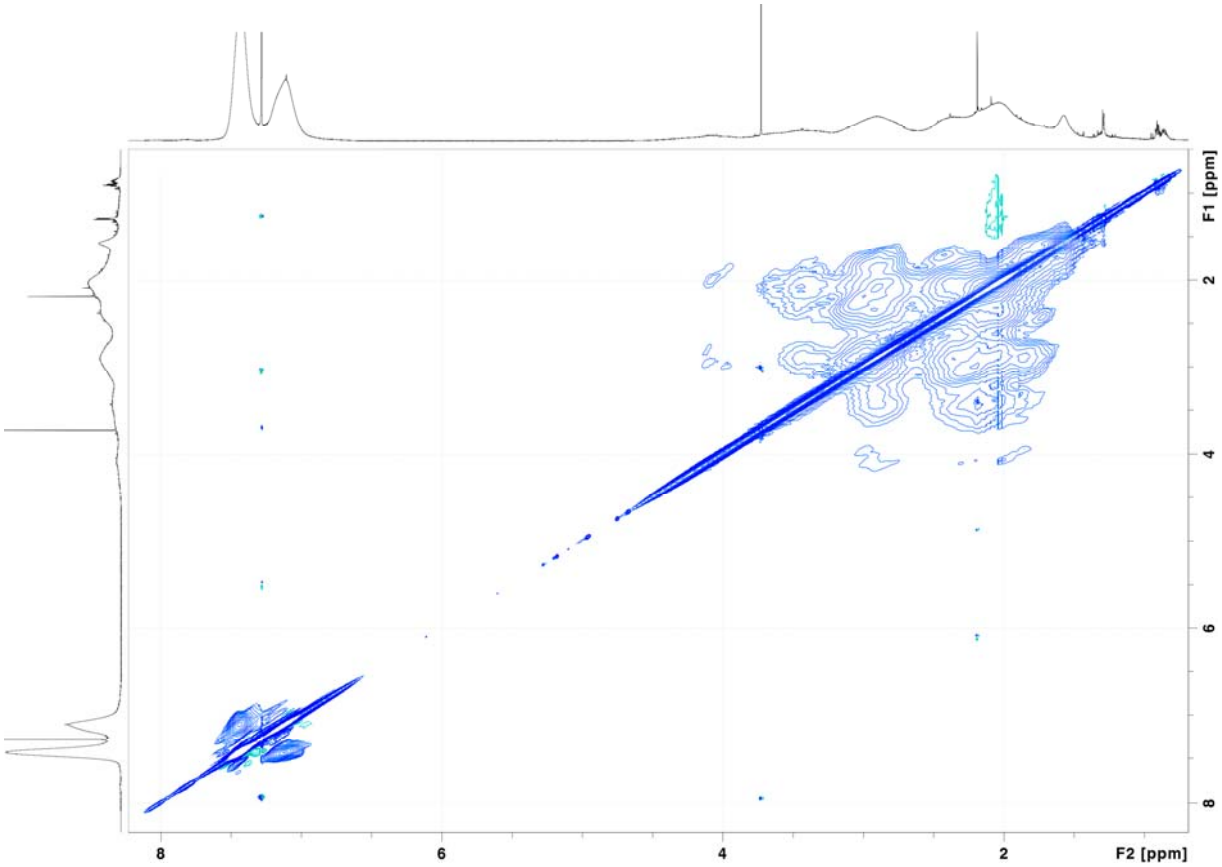

Figure S4. ^{1}H-^{1}H NOESY spectrum of Sample 6.

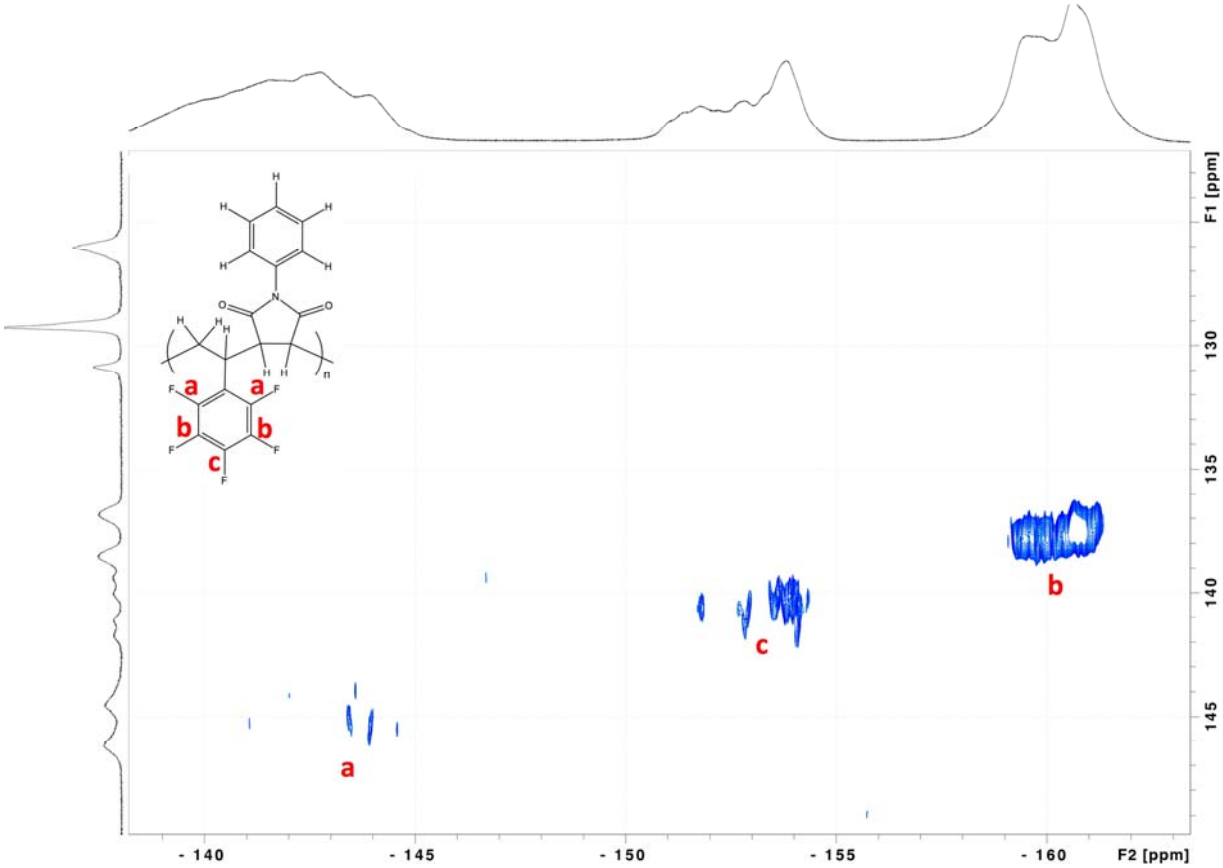

Figure S5. ^{19}F-^{13}C HSQC spectrum of Sample 6.

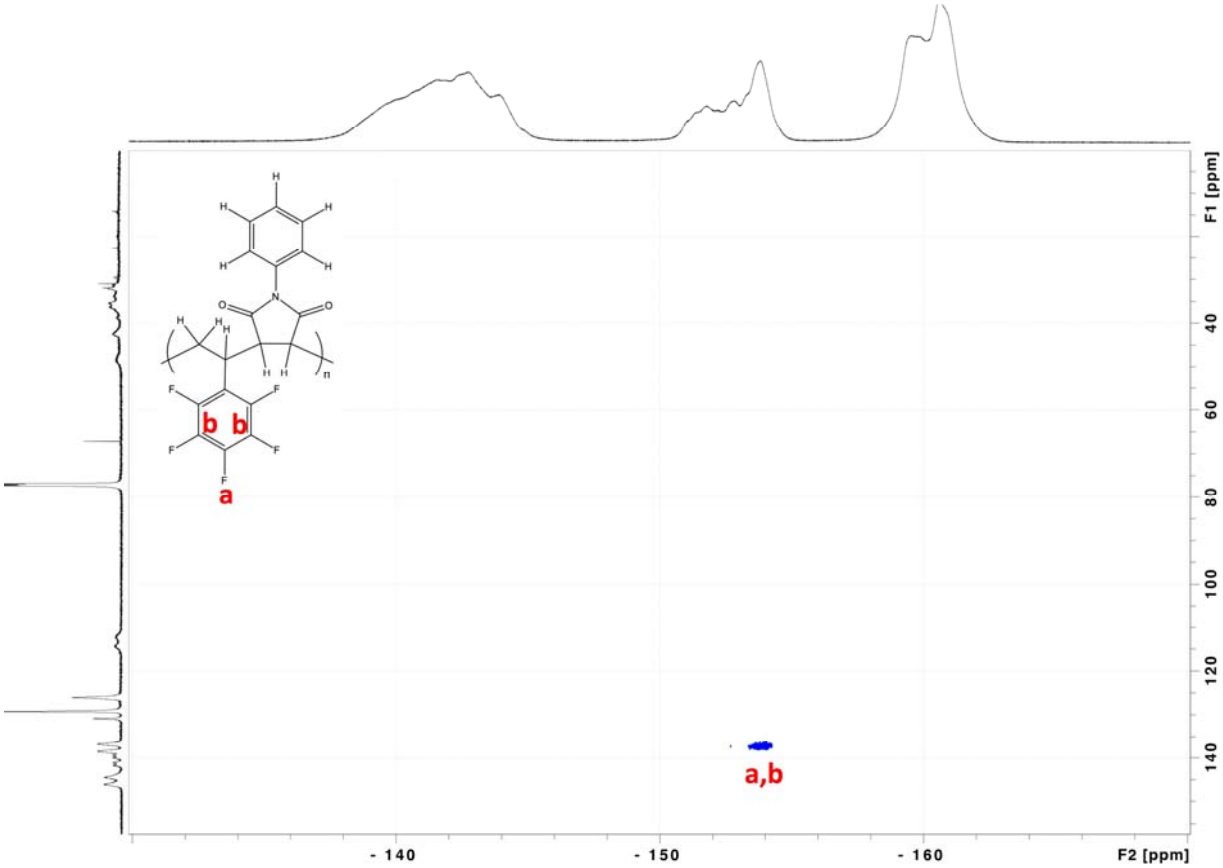

Figure S6. ^{19}F-^{13}C HMBC spectrum of Sample 6. Correlation between the *para* F and *meta* C is indicated.

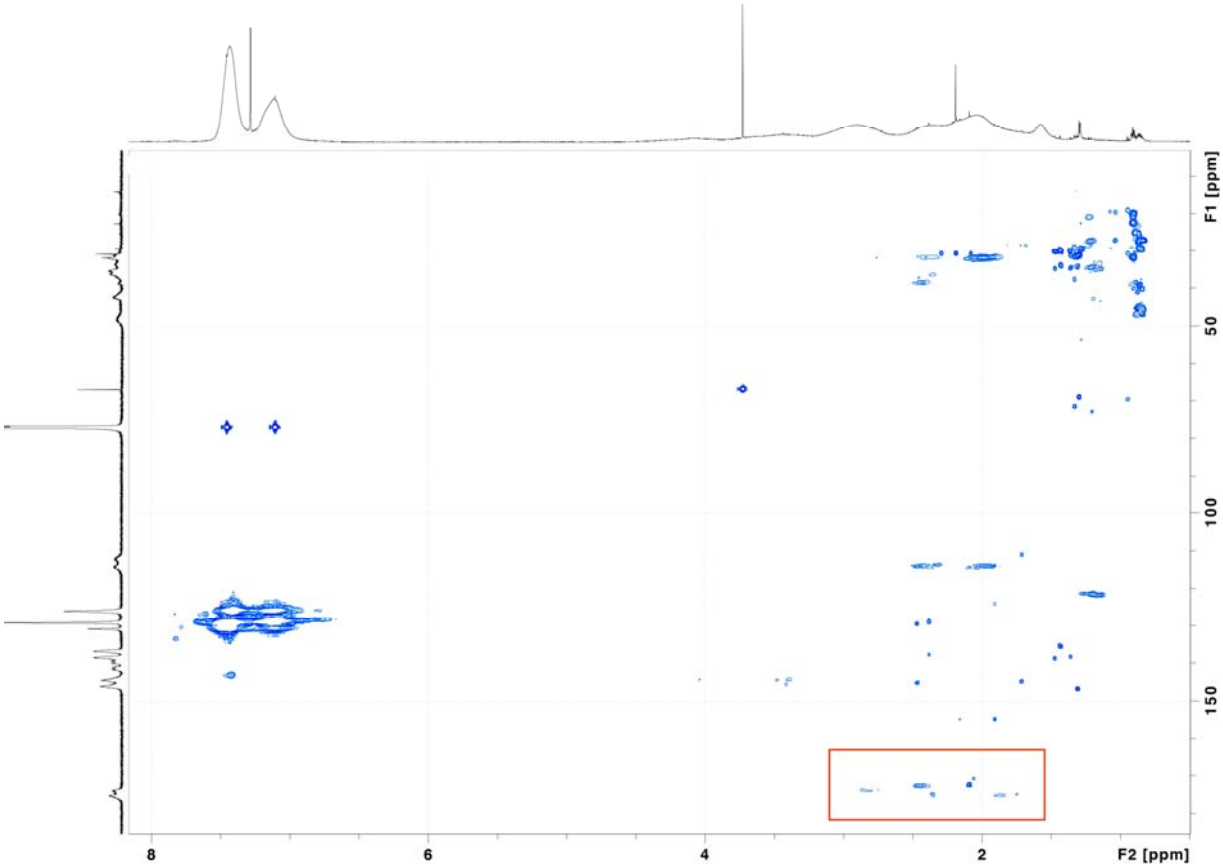

Figure S7. ^{1}H-^{13}C HMBC spectrum of Sample 6. The correlations between the carbonyl carbons and methine (NMI)/methylene(PFS) protons are highlighted.

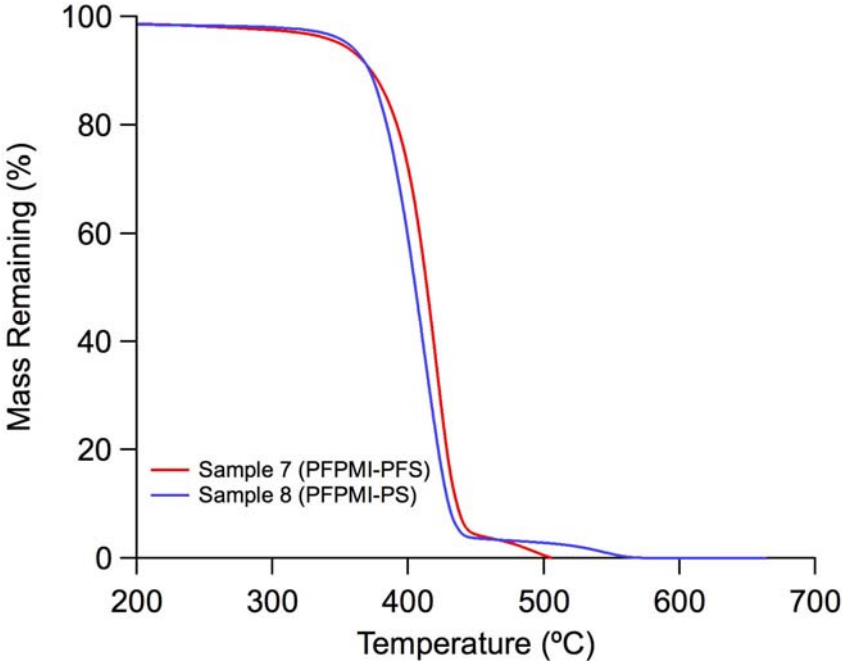

Figure S8. Thermogravimetric profile of the decomposition of PFPMI-containing copolymers prepared in this work.

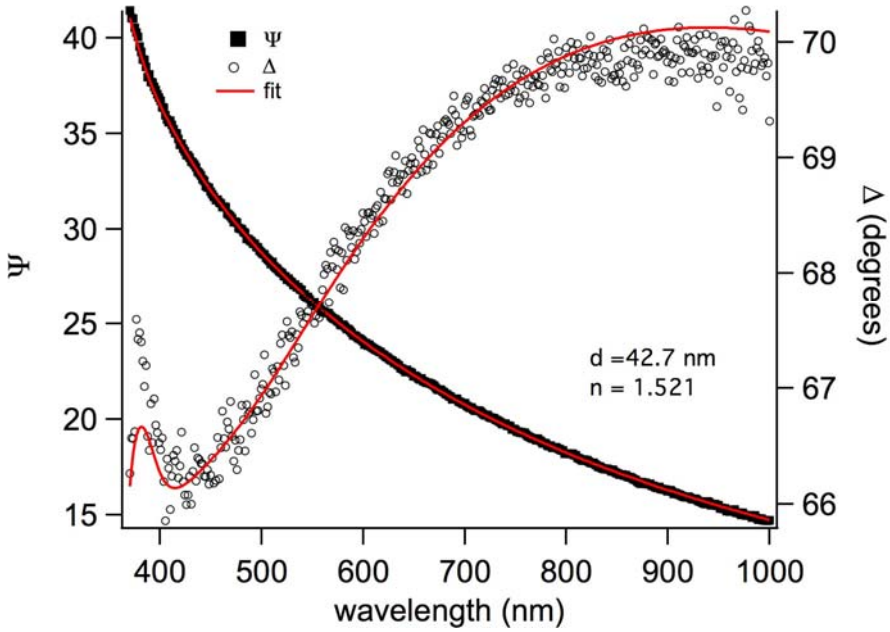

Figure S9. Ellipsometric profile for thin film of Sample 6, showing the amplitude ratio (left axis) and phase difference (right axis) as a function of wavelength. Fitting based on a monolayer with Cauchy absorption profile is shown.

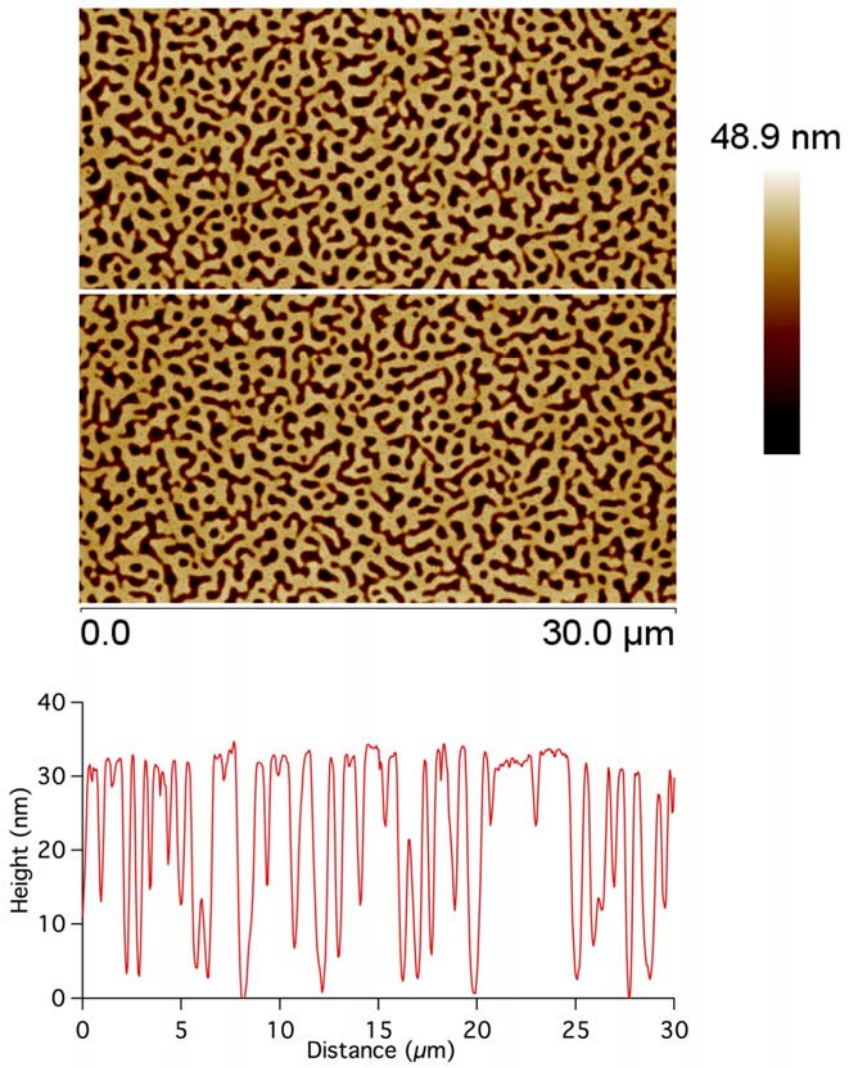

Figure S10. AFM topographical image (top) and line profile (bottom) of the as-cast thin film of Sample 6 (37 mol % NMI) on silicon.

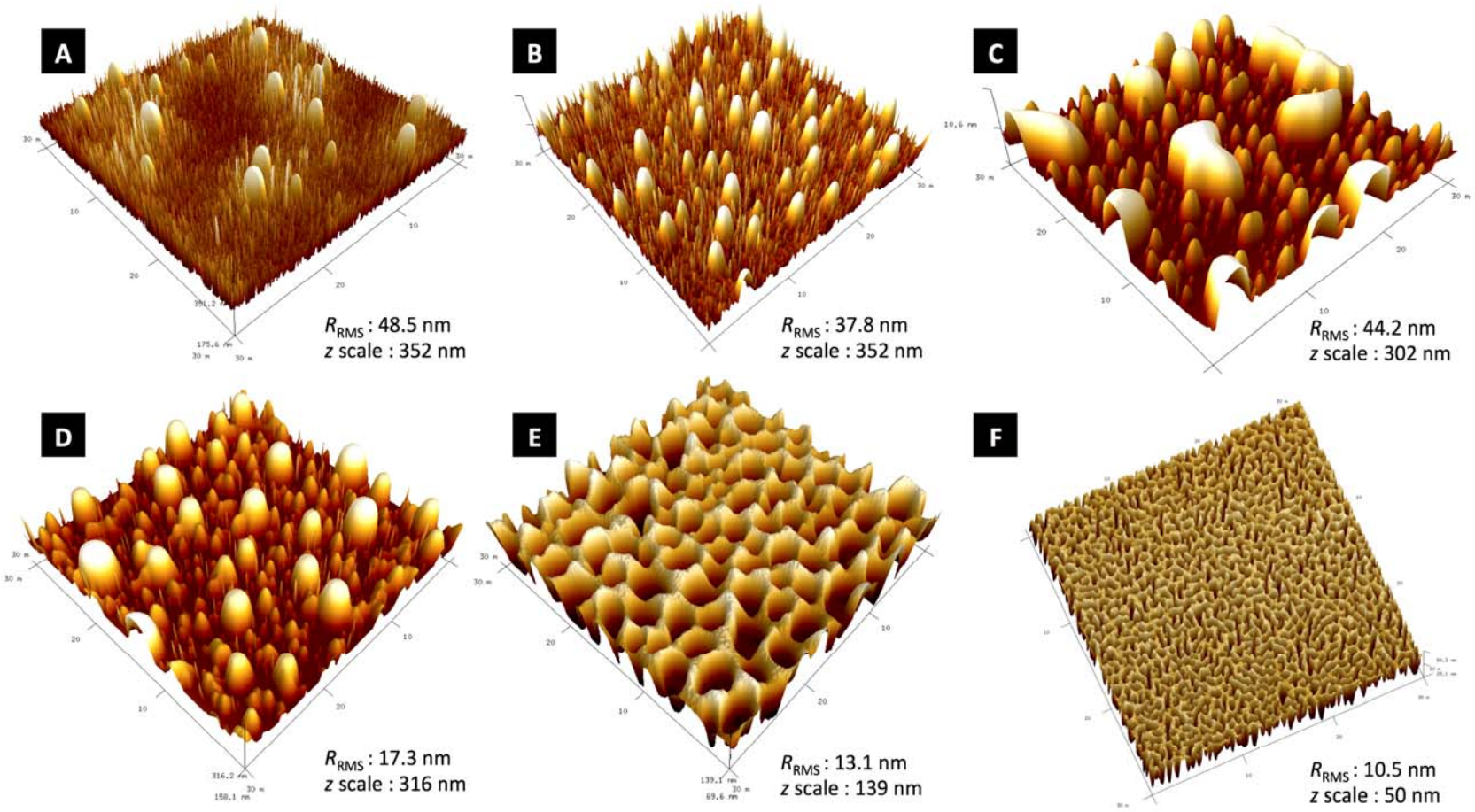

Figure S11. 3D AFM topographical images of PFS-NMI copolymer surfaces prepared by spin-coating; A) through to F) representing Samples 1 to 6 respectively (i.e. increasing NMI content). All images are 30 × 30 μm; the z-axis scale and RMS roughness for each image is indicated.

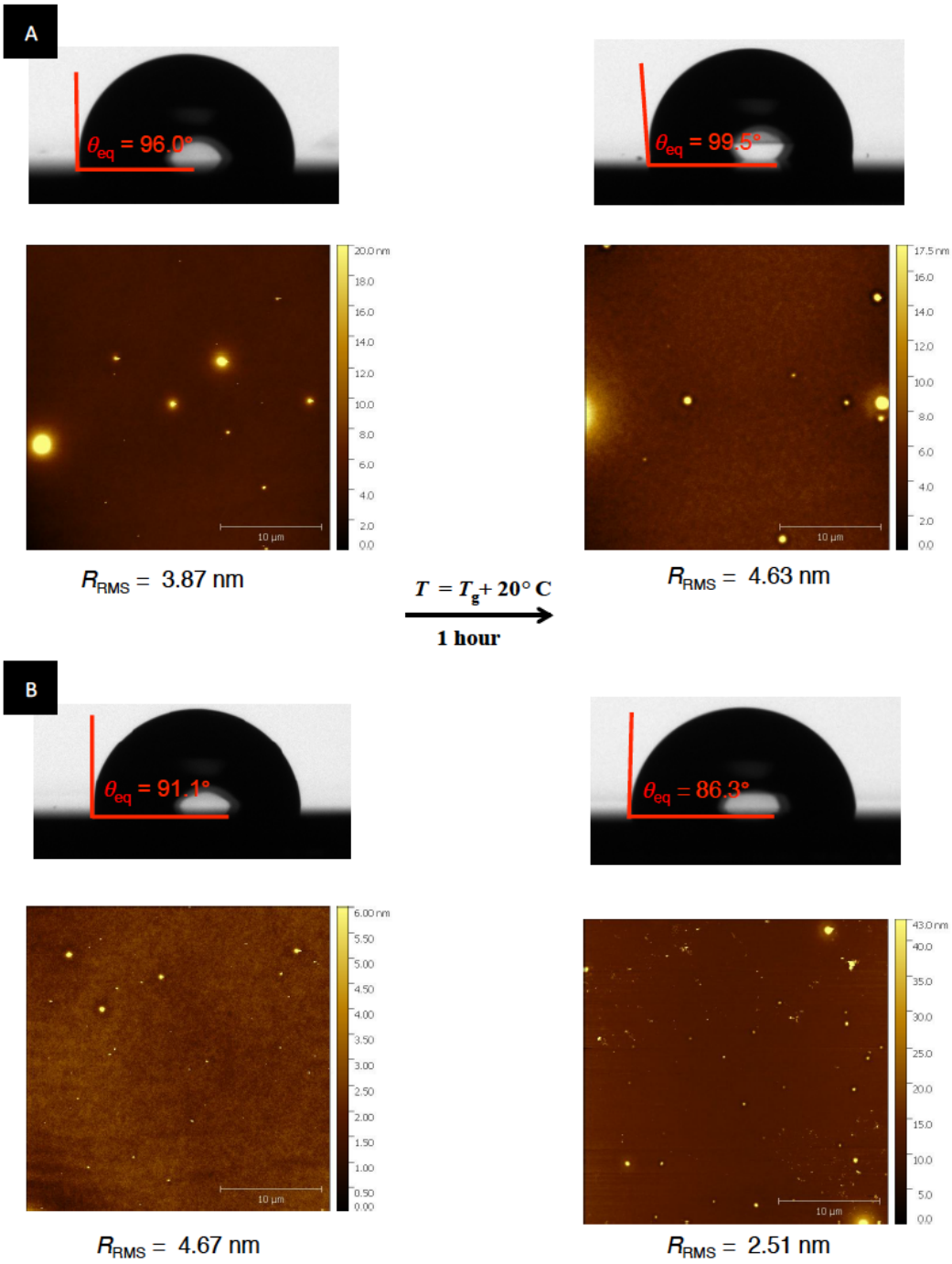

Figure S12. Static contact angle of water on surfaces (θ_{eq}), AFM image of polymer surfaces and roughness (R_{RMS}) pre- (left) and post-annealing (right); A) PFS-PFPMI copolymer (Sample 7), B) PS-PFPMI copolymer (Sample 8).