Supporting Information

Synthesis of Fluorinated Phosphorus-Containing Copolymers and their Immobilization and Properties on Stainless Steel

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Synthesis of Poly(HDFDMA) Homopolymer

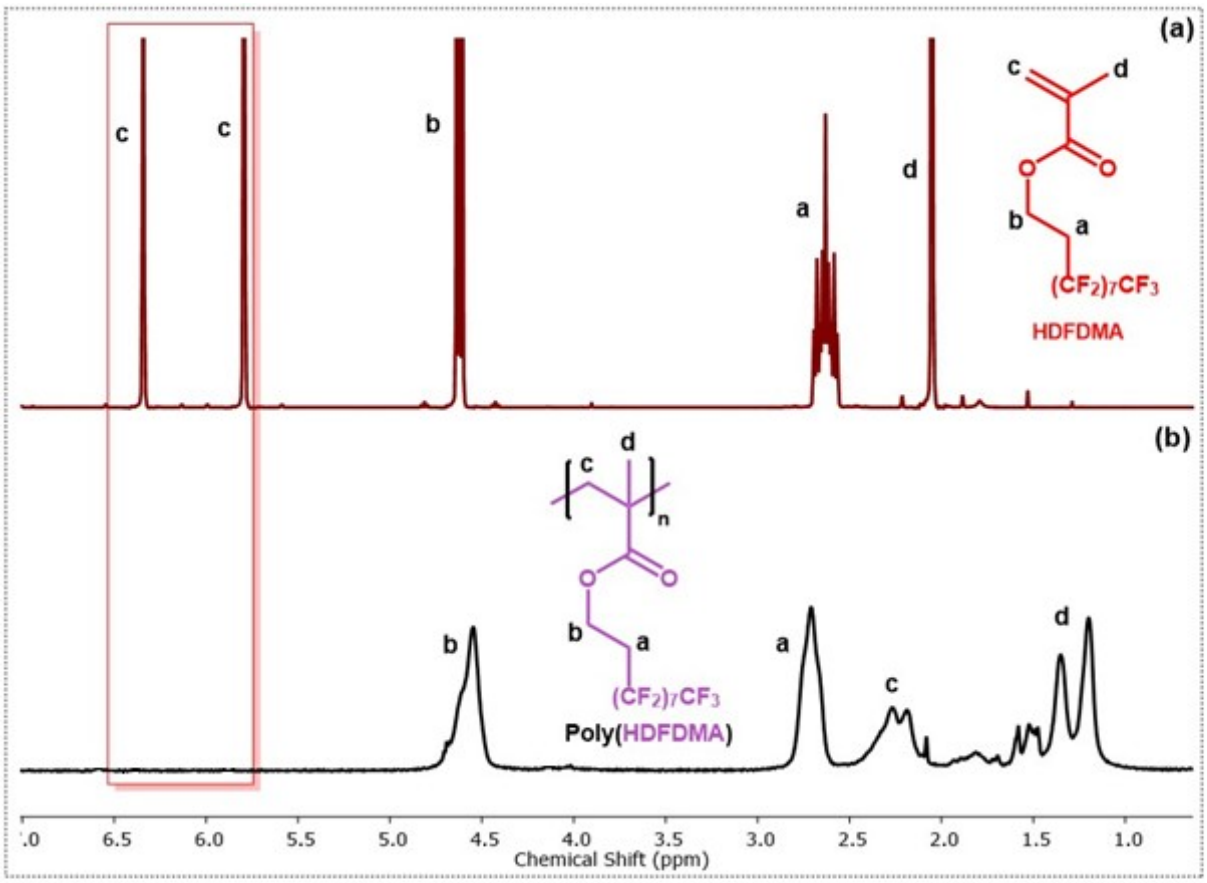

Figure S1. ^{1}H NMR (400- MHz) spectra of HDFDMA monomer (**a)**, and poly(HDFDMA) polymer **(b)**. Both spectra were taken in deuterated TFA (CF_3CO_2D). The bar shows the disappearance of monomer peaks in the spectra.

^{19}F Spectra of Poly(HDFDMA) Homopolymer

^{19}F NMR spectra of monomer and homopolymer further support the successful polymerization of HDFDMA (see Figure S2 (a)). A shift in spectra towards lower numbers and broadening of the fluorine signals (CH_2CH_2–CF_2) was observed in the poly(HDFDMA) spectrum (Figure S2 (b) as compared to the monomer ((Figure S2 (a)) support the successful polymerization of HDFDMA.

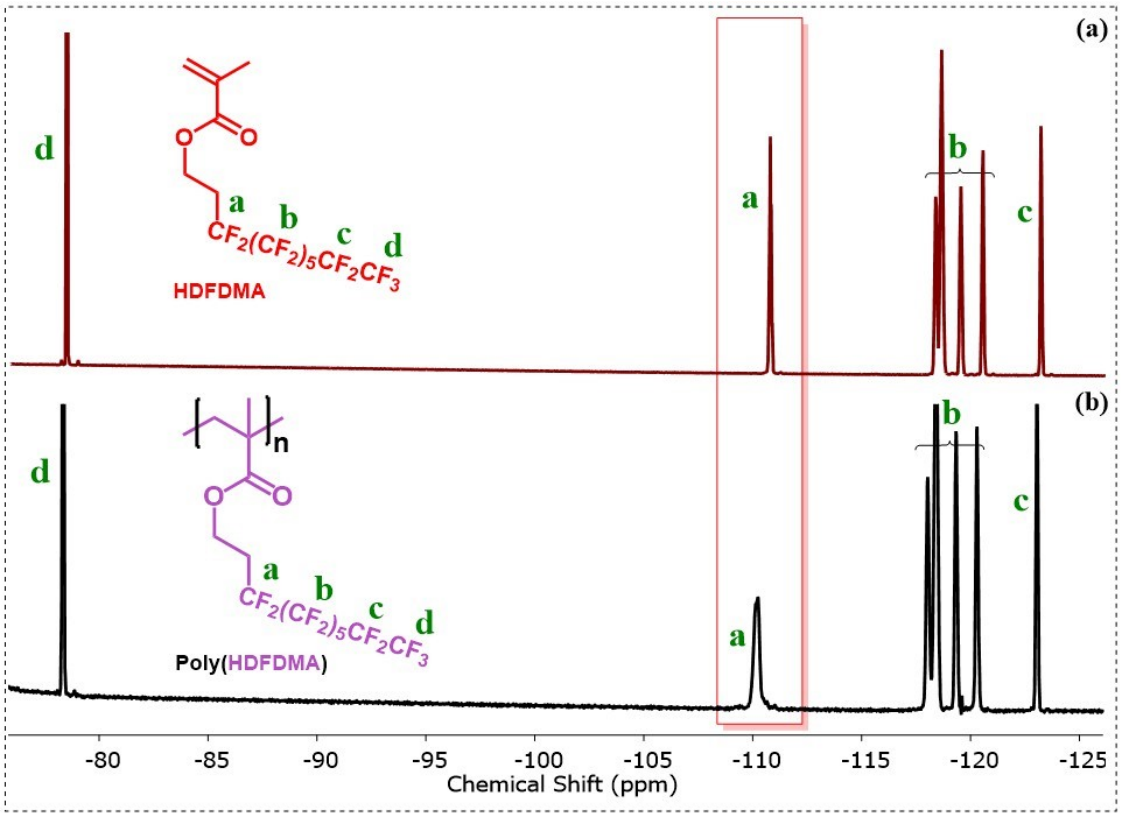

Figure S2. ^{19}F NMR (400- MHz) spectra of HDFD monomer (red color) **(a)**, and the resulting poly(HDFDMA) homopolymer (black color) after purification **(b)**. Both spectra were taken in deuterated TFA. The bar shows the broadening of the fluorine resonances in the poly(HDFDMA) homopolymer.

Synthesis of Poly(PMM) Homopolymer

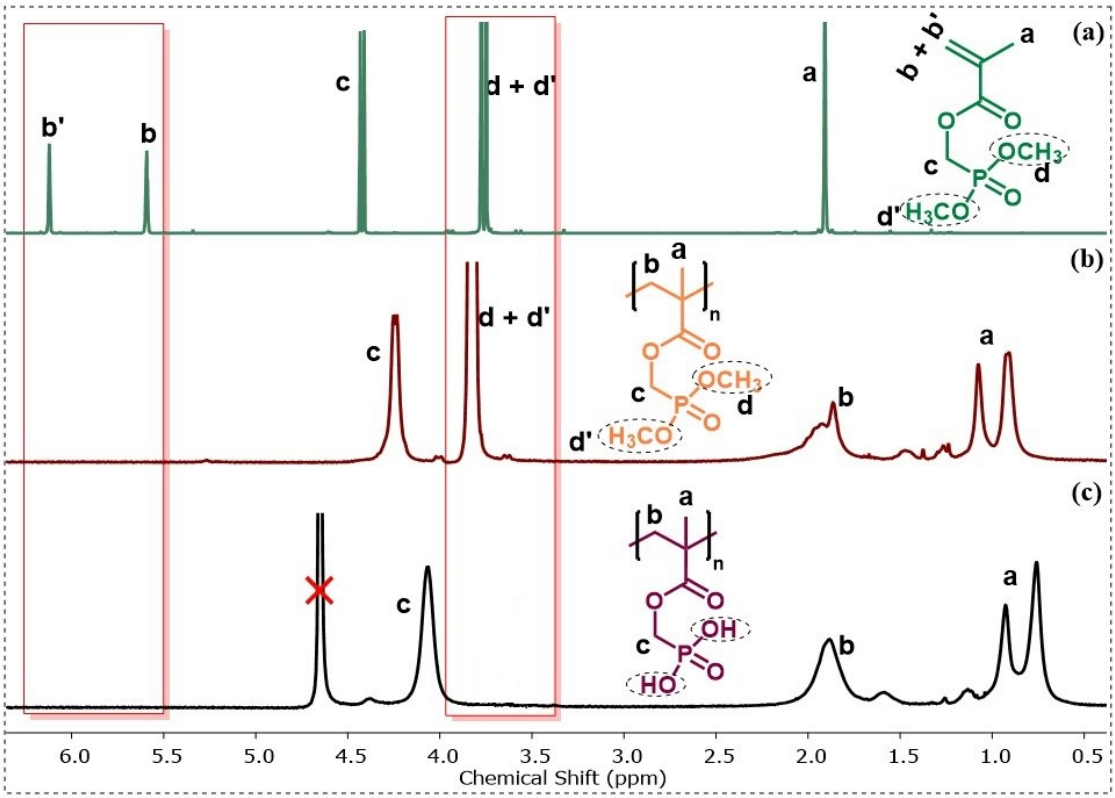

Figure S3. ^{1}H NMR (400- MHz) spectra of DMPMM monomer ($CDCl_3$) **(a)**, poly (DMPMM) homopolymer in its protected form ($CDCl_3$) **(b)**, and the resulting hydrolyzed (deprotected) poly(PMM) homopolymer (D_2O) **(c)**. The bar is showing the disappearance of the phosphonate methyl peaks in the spectra.

^{31}P NMR of Poly(PMM) Homopolymer

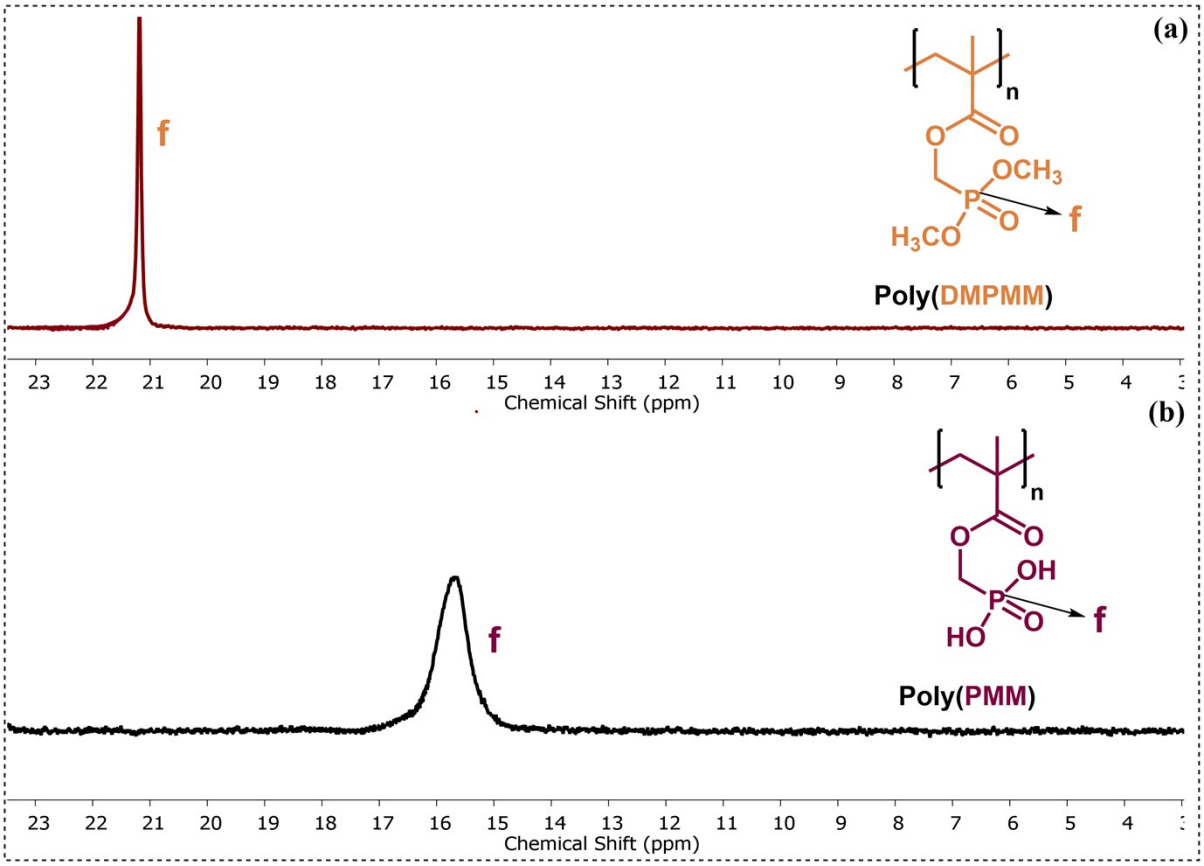

Figure S4. ^{31}P NMR (400- MHz) spectrum of poly(DMPMM) phosphonate ester homopolymer in $CDCl_3$, **(a)**, and the deprotected poly(PMM) phosphonic acid homopolymer in D_2O **(b)**.

^{1}H NMR Spectrum of poly(HDFDMA-co-PMM) Copolymer

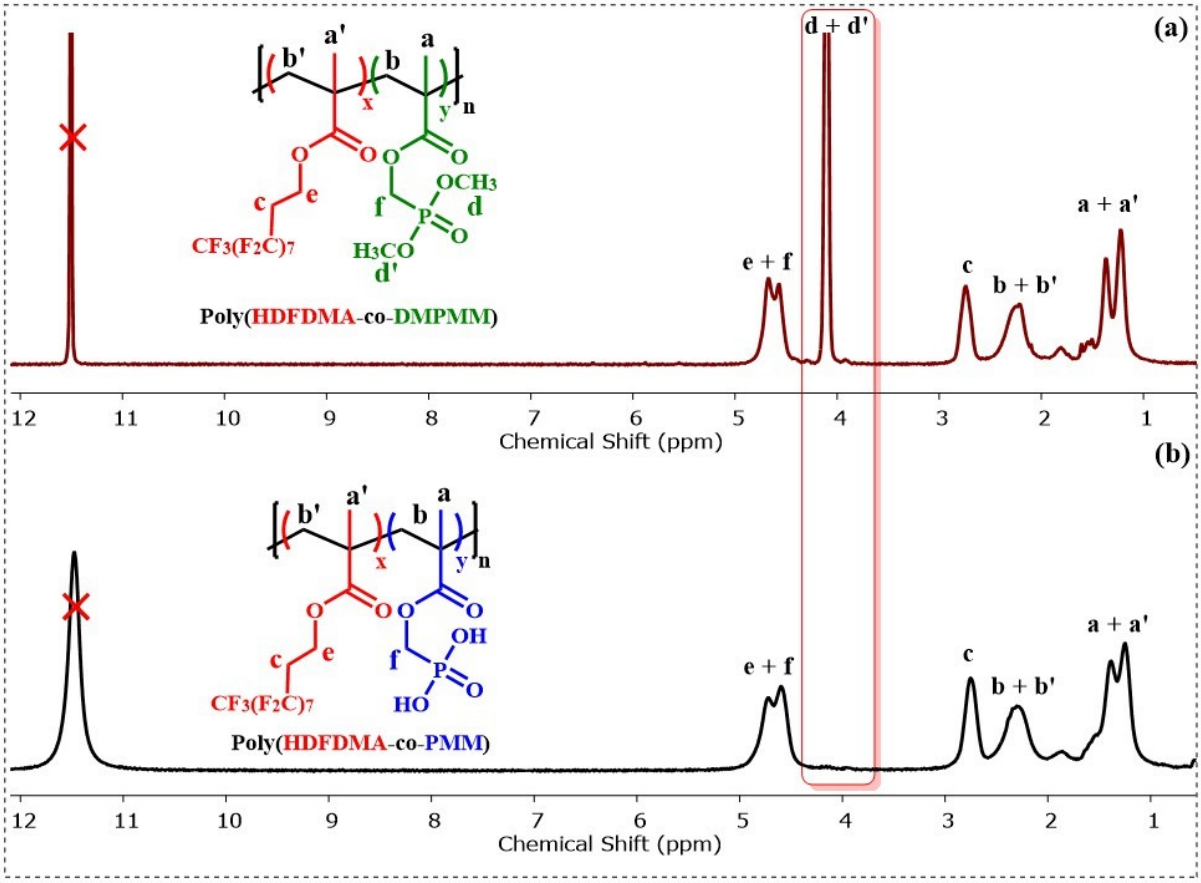

Figure S5. ^{1}H NMR (400- MHz) spectra of poly(HDFDMA-co-DMPMM) protected copolymer with mol ratio [1:1] **(a)**, and the resulting hydrolyzed poly(HDFDMA-co-PMM) copolymer in its deprotected form **(b)**. Both spectra were taken in deuterated trifluoroacetic acid. The bar is showing the disappearance of the phosphonate methyl peaks in the spectra.

^{19}F Spectra of Poly(HDFDMA-co-PMM) Copolymer

^{19}F NMR spectra support the successful copolymerization of HDFDMA and PMM to form poly(HDFDMA-co-PMM). A broadening of the fluorine resonances was observed in the poly(HDFDMA-co-PMM) copolymer spectrum (Figure S6 (b)) as compared to the monomer (Figure S6 (a)). This broadening of the fluorine signal has also been shown in the inset which corresponds to CH_2–CF_2 functional group, together with a small shift.

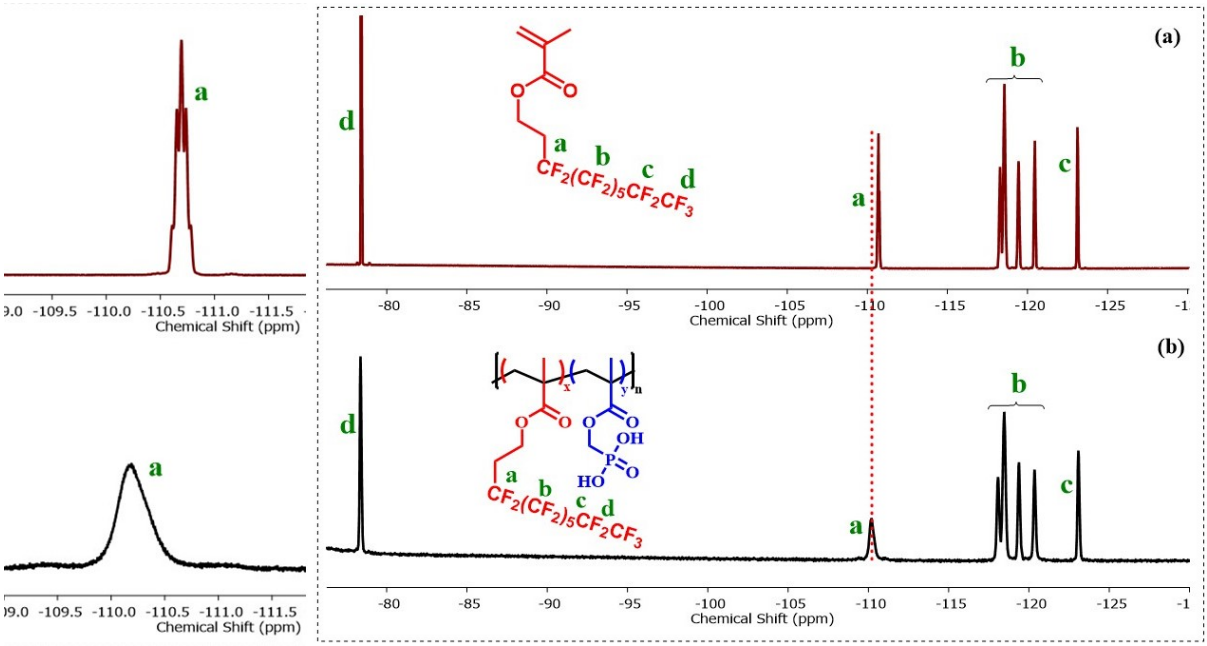

Figure S6. (a) ^{19}F NMR (400- MHz) spectra of the protected poly(HDFDMA-co-DMPMM) copolymer **(a),** and the resulting hydrolyzed (deprotected) poly(HDFDMA-co-PMM) copolymer **(b)** for mol ratio [1:1]. Both spectra were taken in deuterated trifluoroacetic acid.

TGA thermograms of poly(HDFDMA-co-PMM) Copolymers

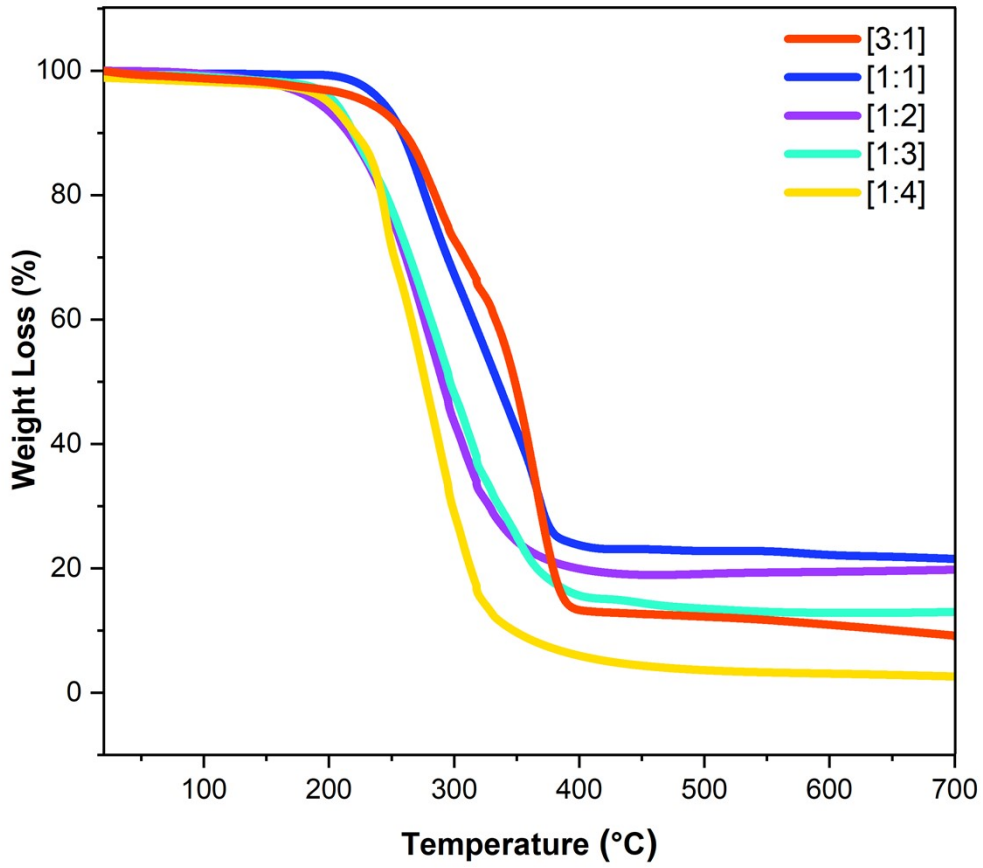

Figure S7. TGA thermograms of poly(HDFDMA-co-PMM) copolymers with mol ratio [3:1], [1:1], [1:2], [1:3], and [1:4], heated at 10 °C min^{-1} under nitrogen.

Contact Angle of Uncoated SS Surface

The wettability of the uncoated SS substrate was tested in water via contact angle measurements. AR-SS denotes the as-received SS, SS represents the chromic acid cleaned substrate, and the SS-TFA depicts the SS coupon cleaned with chromic acid solution and left in TFA solution for 30 minutes in order to observe the change in wettability of the coupon surface.

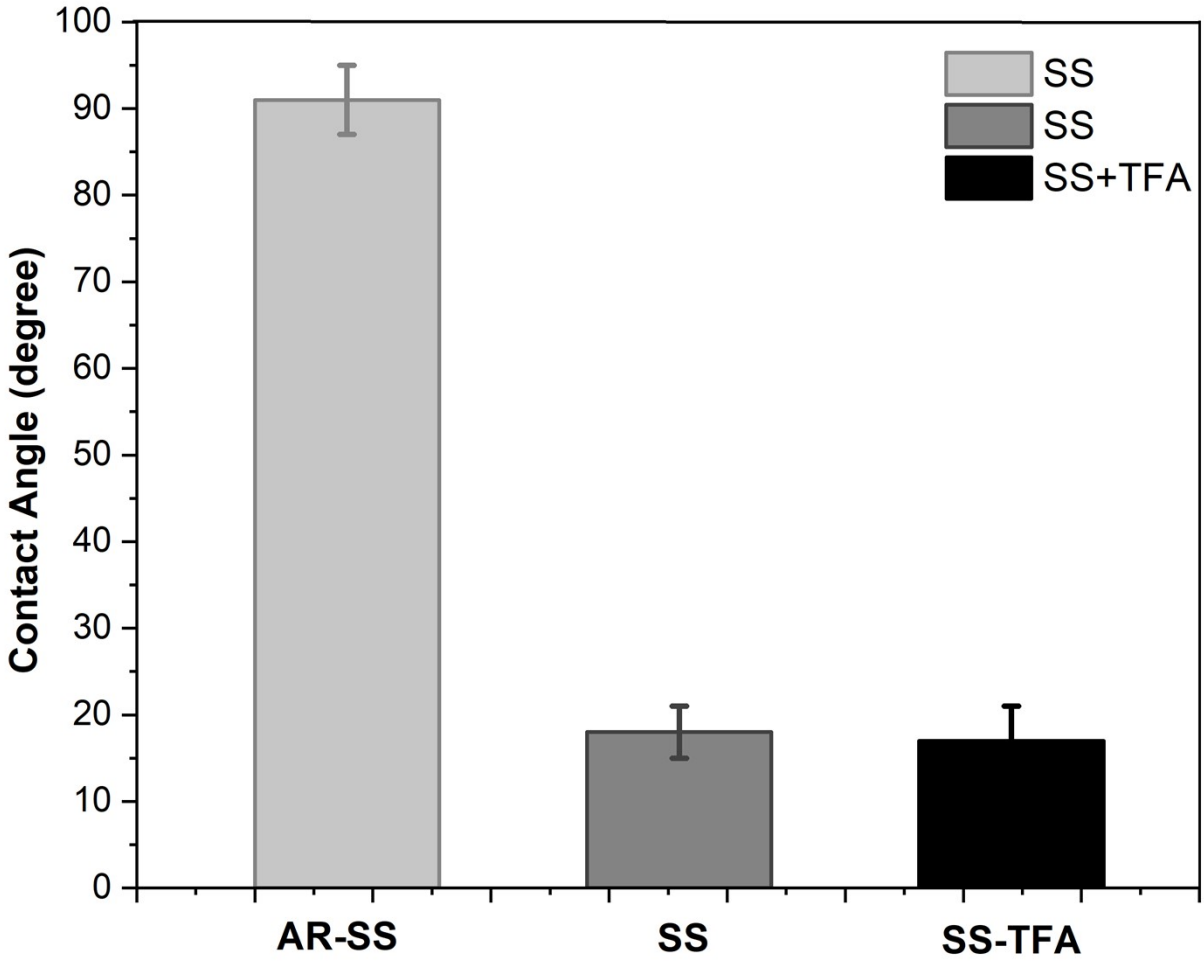

Figure S8. Water contact angles on as-received (AR-SS) surface, chromic acid cleaned (SS) surface, and chromic acid cleaned and immersed in TFA for 30 minutes (SS-TFA) surfaces. Data are presented as mean ± standard deviation (N=3).

The Contact Angles of Uncoated and Polymer Coated SS Surfaces

Table S1. The Contact Angles of Uncoated and Polymer Coated SS Surfaces		
Samples	**Mol ratio of HDFDMA to PMM**	**WCA (°)**
AR-SS	-	87 ± 4
SS	-	17 ± 4
Poly(HDFDMA)	[1:0]	72.3 ± 2
Poly(PMM)	[0:1]	55.4 ± 5
Poly(HDFDMA-co-PMM)	[3:1]	126 ± 1
	[1:1]	128.2 ± 2
	[1:2]	102.5 ± 3
	[1:3]	97 ± 2
	[1:4]	86 ± 1

Statistical Analysis of the Contact angle of Uncoated and Polymer Coated SS Surfaces

The statistical significance was assessed for the uncoated and polymer coated SS coupon surfaces using one way ANOVA test and the results are shown in Figure S9. Results revealed that a decrease in the hydrophilicity of the surface was observed when the fluorinated compounds were used and the changes in C.A for all polymer coated surfaces were statistically different.

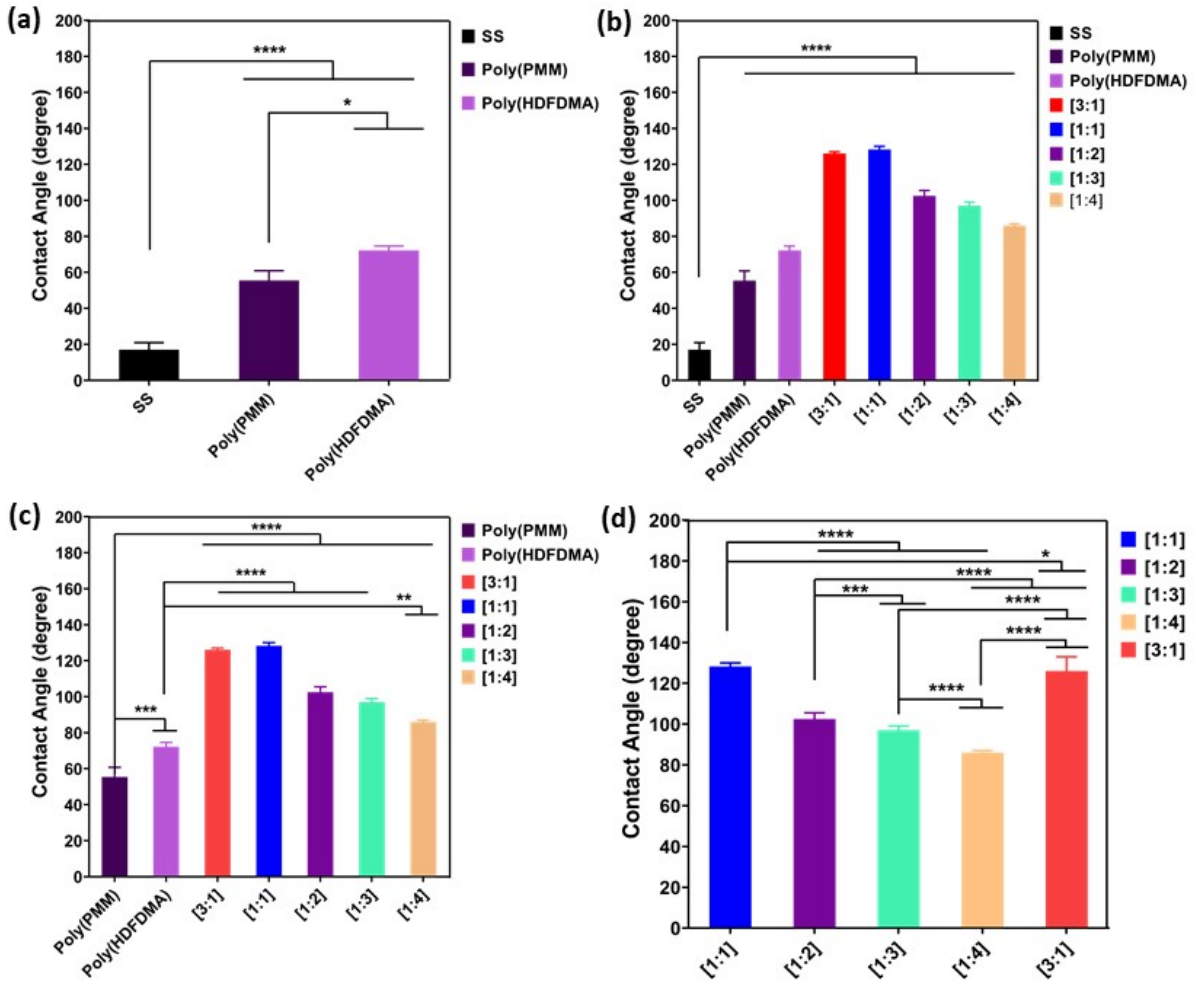

Figure S9. Contact angles of uncoated and polymer coated SS surfaces. The films were deposited from TFA at a concentration of 1 wt. % of the polymer solution. **** P<0.0001, *** P=0.001, ** P<0.01, * P<0.05. Data are presented as mean ± standard deviation (N=3).

Contact angle of Uncoated and Polymer Coated SS Surfaces Deposited from DMSO Solution

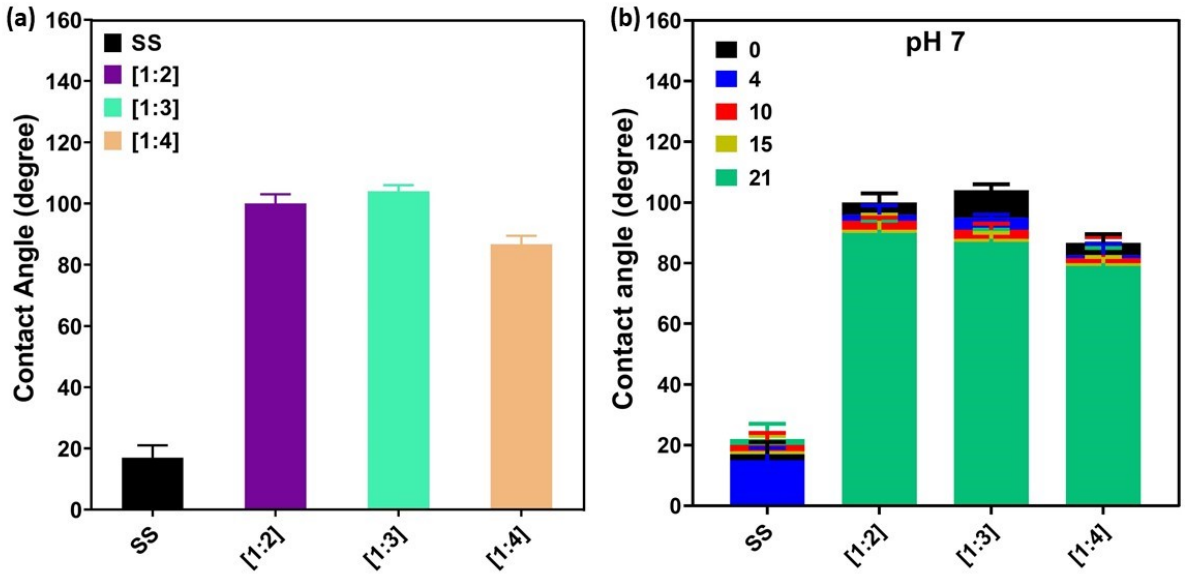

Figure 10. (a) Contact angles of uncoated and polymer coated SS surfaces. **(b)** Long-term stability study of copolymers coated SS along with uncoated SS surfaces (control) as measured by their static contact angles under the water rinsing conditions: neutral solution (milli-Q water). The SCA was measured after formation (black), and water rinsing after 4 days (blue), 10 days (red), 15 days (yellow), and 21 days (green). Data are presented as mean ± standard deviation (N=3).

ATR-IR spectrum of poly(HDFDMA-co-PMM) copolymer on Stainless Steel Surfaces

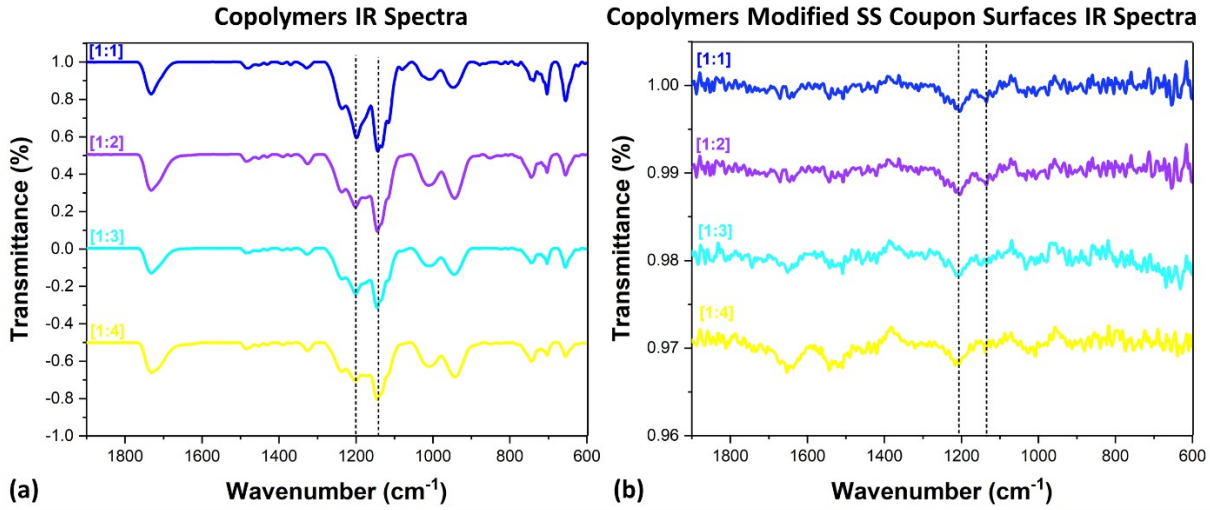

Figure S11. ATR-IR spectra of poly(HDFDMA-co-PMM) copolymer with various mol ratios in solid form **(a)** and on stainless steel surfaces **(b)**.

XPS Survey Spectra of Uncoated and Polymer Coated SS Surface

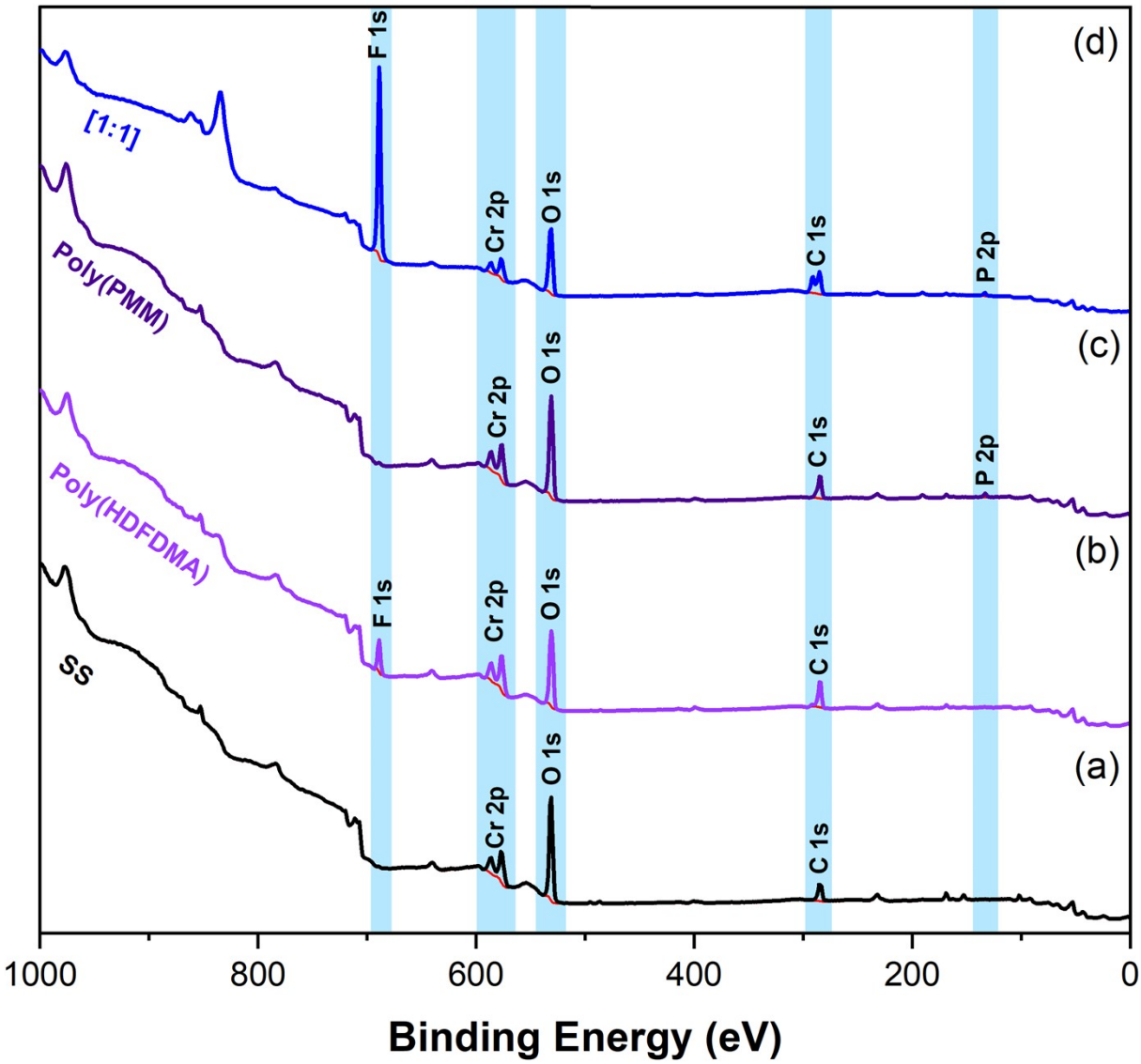

Figure S12. (a) XPS survey spectra of uncoated SS coupons, **(b)** poly(HDFDMA) homopolymer coated SS coupons, **(c)** poly(PMM) homopolymer coated SS coupons, and **(d)** poly(HDFDMA-co-PMM) copolymer with mol ratio [1:1] coated SS coupons. Note the difference in P signal intensity: for the poly(PMM) phonic acid, the P/C ratio is 0.094, while for the poly(HDFDMA-co-PMM) fluorinated phonic acid copolymer, the ratio is 0.098. For reference, a fully assigned and Cr 2p XPS spectrum for stainless steel are given in the Supporting Information (Figure S17-18).

High-resolution C 1s XPS Spectra of Poly(HDFDMA-co-PMM) Copolymer Coated SS Surfaces

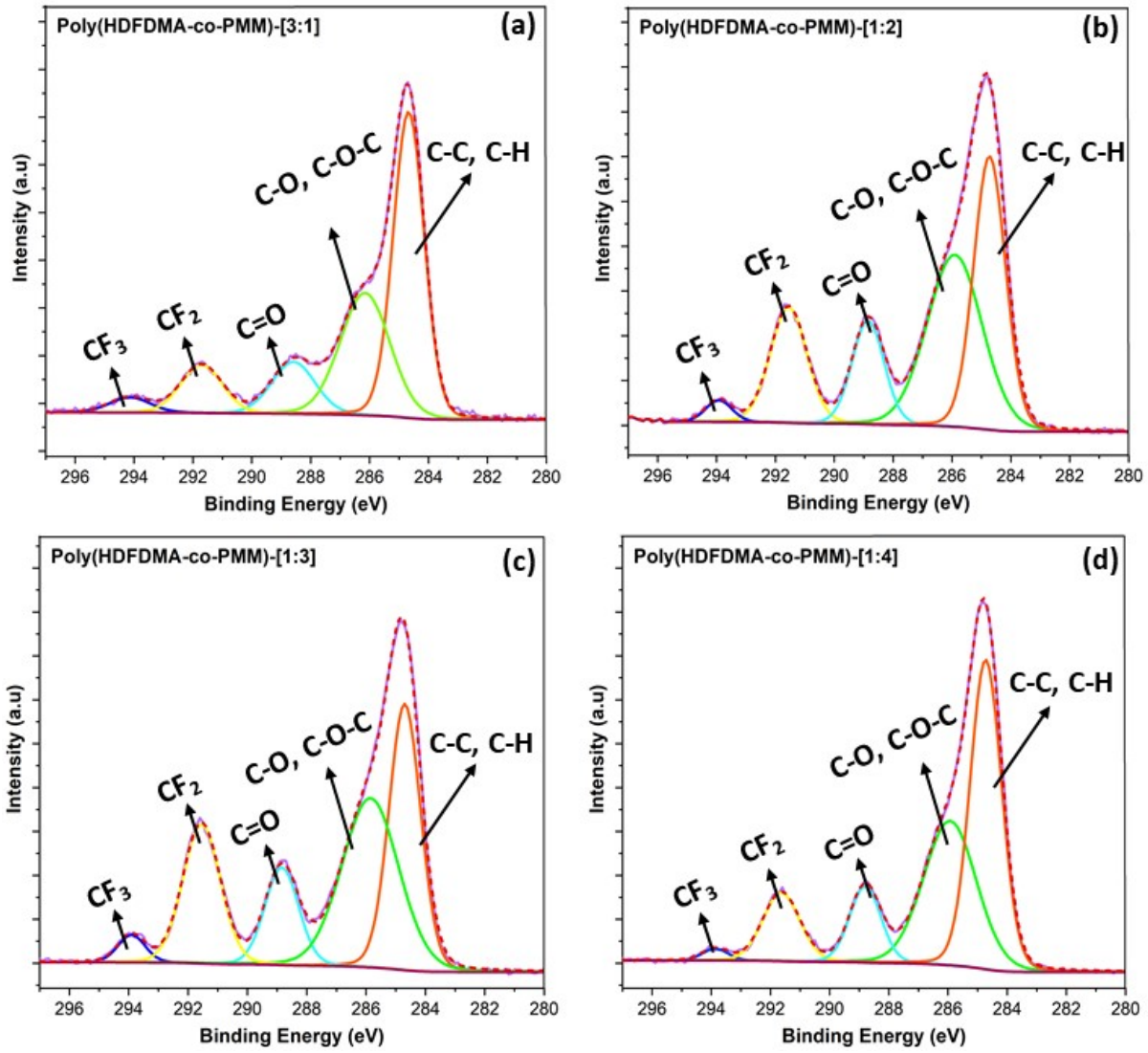

Figure S13. XPS core-level C 1s scans for poly(HDFDMA-co-PMM) copolymer coated SS coupons with mol ratio [3:1] **(a),** [1:2] **(b),** [1:3] **(c),** and [1:4] **(d)**. The purple solid line indicates the raw data line whereas the dotted line shows the peak fitting. The red color lines show the background.

Binding Energies of the Peak Fittings of High-resolution C 1s Spectra

Table S2. Chemical compositions of the various possible components after deconvolution of C 1s peak.

Sample	C-C, C-H (%)	C-O, C-O-C (%)	C=O (%)	CF_2 (%)	CF_3 (%)
SS	68.49	25.64	5.88	-	-
Poly(PMM)	52.30	34.47	13.23	-	-
Poly(HDFDMA)	61.0	28.10	5.70	4.76	0.44
[3:1]	46.45	29.73	11.02	9.75	3.04
[1:1]	23.63	33.06	15.74	23.64	3.93
[1:2]	33.23	35.93	12.59	16.09	2.16
[1:3]	30.88	35.13	12.05	19.20	2.74
[1:4]	43.14	33.78	10.52	11.22	1.33

Binding Energies of the Peak Fittings of High-resolution C 1s Spectra

Table S3. Curve-fitting Binding Energies on the XPS C1s spectra of uncoated and polymer coated SS coupons

Atom	**Groups**	**SS**	**Poly (HDFDMA)**	**Poly (PMM)**	**[3:1]**	**[1:1]**	**[1:2]**	**[1:3]**	**[1:4]**
C 1s	C-C, C-H	284.8	284.7	284.6	284.7	284.7	284.7	284.7	284.7
	C-O, C-O-C	285.6	285.9	285.8	286.2	285.9	285.9	285.8	285.9
	C=O	288.4	288.7	288.7	288.6	288.8	288.8	288.8	288.8
	CF_2	-	291.7	-	291.7	291.5	291.5	291.5	291.6
	CF_3	-	293.9	-	294.2	293.8	293.9	293.9	293.8
P 2p	$2P_{3/2}$	-	-	133.2	133.3	133.3	133.2	133.4	133.2
	$2P_{1/2}$	-	-	134.0	134.5	134.2	134.2	134.4	134.0
F 1s	CF_2, CF_3	688.2	688.7	688.2	688.8	688.6	688.6	688.6	688.6
O 1s	O 1	530	530.0	530.0	530.0	530.0	530.0	530.0	530.0
	O 2	531.7	531.6	531.8	531.5	531.6	531.7	531.6	531.7
	O 3	-	533.4	533.7	533.2	533.9	533.4	533.4	533.5

High-resolution P 2p and F 1s Spectra of Poly(HDFDMA-co-PMM) Copolymer for all mol ratios

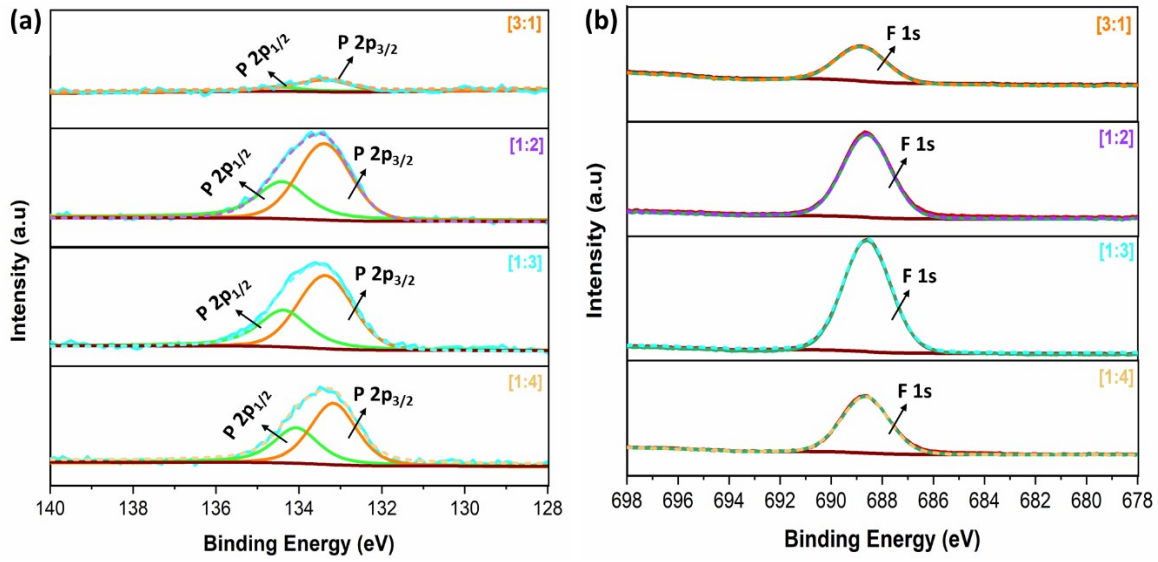

Figure S14. XPS core-level high resolution P 2p scans **(a),** and F 1s scans **(b),** for poly(HDFDMA-co-PMM) copolymer with mol ratio [3:1], [1:2], [1:3] and [1:4] coated SS coupons.

High-resolution O 1s Spectra of Poly(HDFDMA-co-PMM) Copolymer Coated SS Surfaces

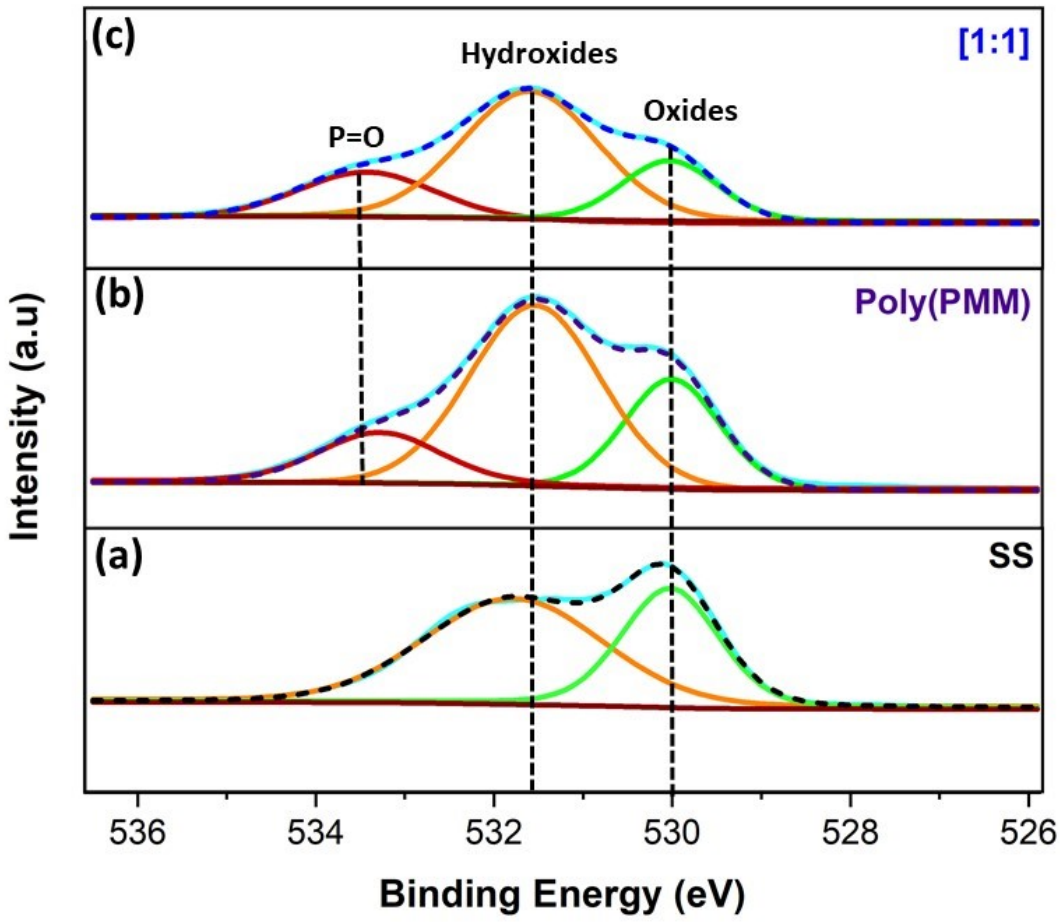

Figure S15. XPS core-level high resolution O 1s scans for **(a)** uncoated, **(b)** poly(PMM) coated**, (c)** and poly(HDFDMA-co-PMM) coated SS coupon. The appearance of the P═O peak occurs after deposition of poly(HDFDMA-co-PMM) copolymer with mol ratio [1:1].

High-resolution O 1s Spectra of Poly(HDFDMA-co-PMM) Copolymer for all mol ratios

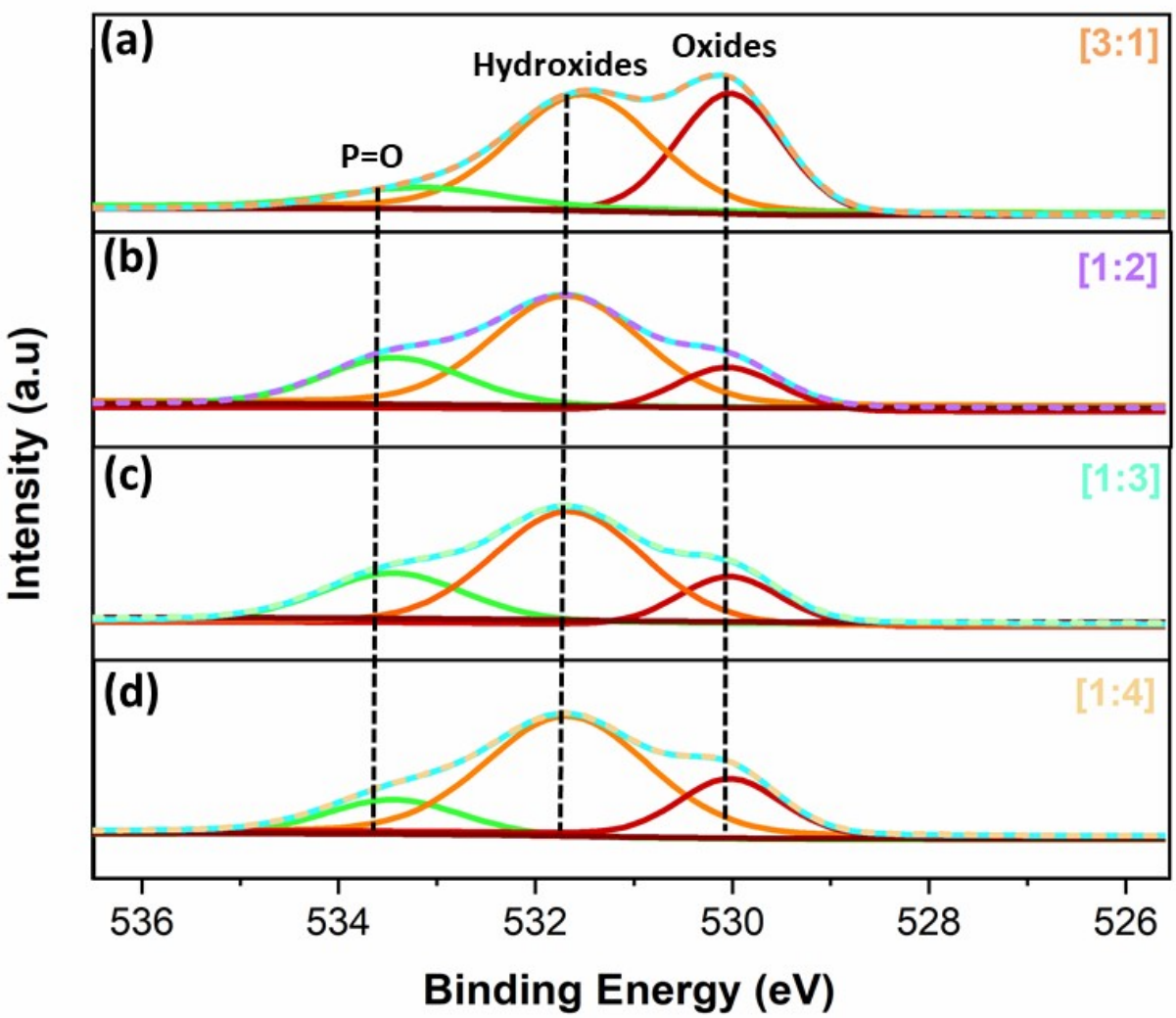

Figure S16. XPS core-level high resolution O 1s scans for poly(HDFDMA-co-PMM) coated SS coupons with mol ratio **(a)** [3:1], **(b)** [1:2], **(c)** [1:3] and **(b)** [1:4].

Full Survey XPS Spectrum of Uncoated SS Surface

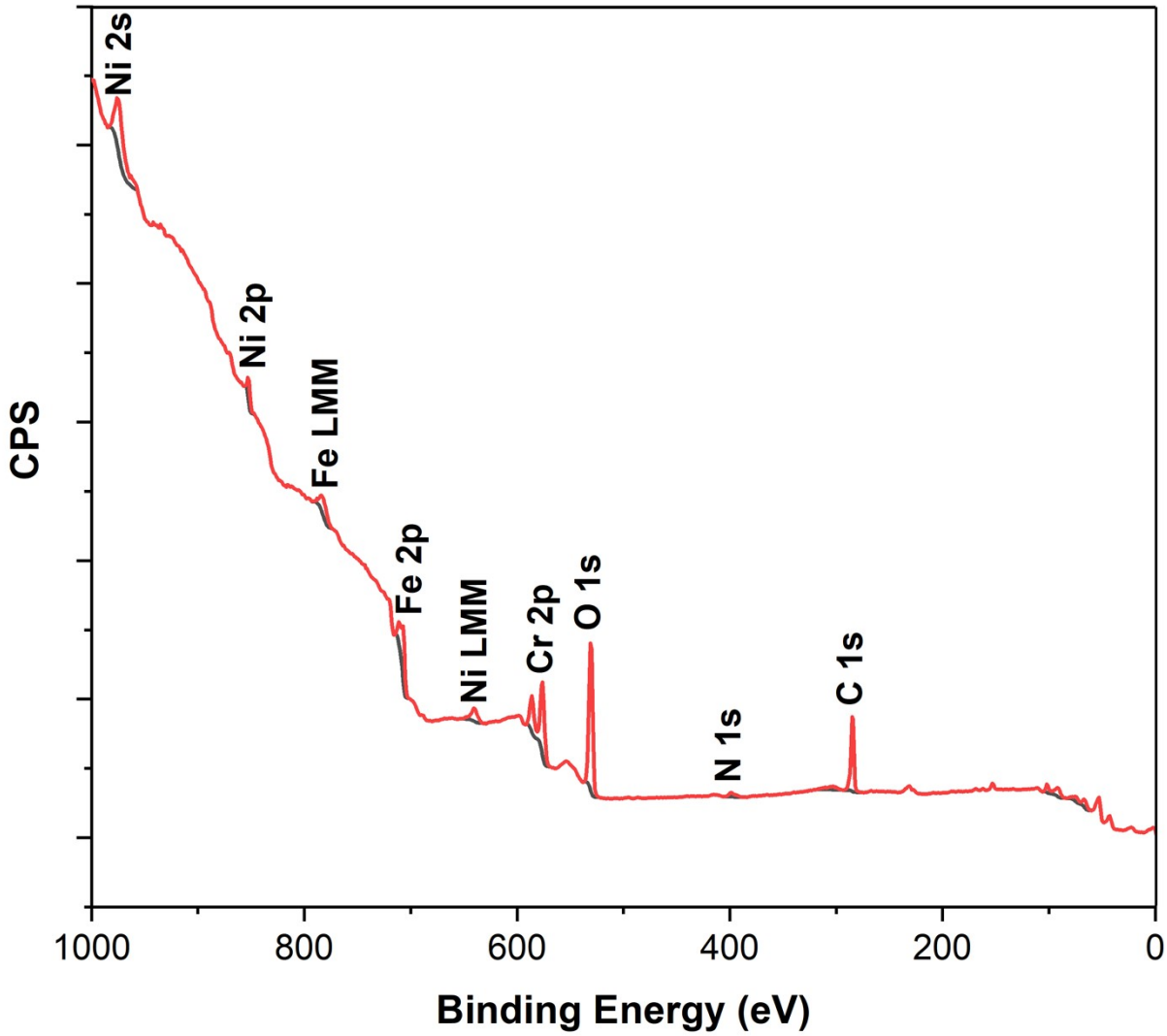

Figure S17. Detailed full survey XPS scans of uncoated SS Surface

High-resolution Cr 2p XPS Spectrum of Uncoated SS Surface

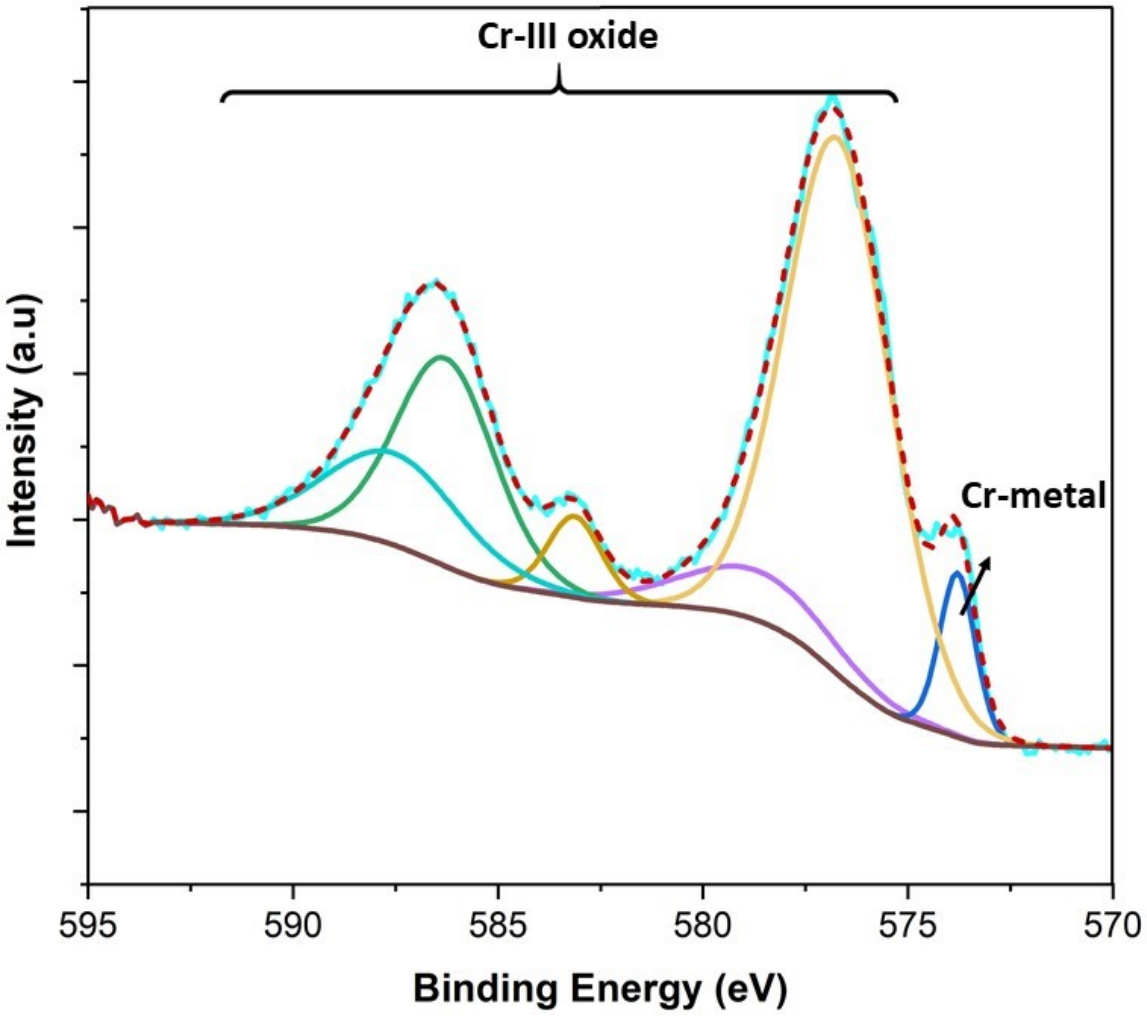

Figure S18. High-resolution Cr 2p XPS spectrum of uncoated SS surface