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## SUPPORTING INFORMATION

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### Highly efficient grafting of hetero-complementary amidinium and carboxylate hydrogen-bonding/ionic pairs onto polymer surfaces

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## SI.0. Materials and methods

**Starting materials.** Chemicals were purchased from commercial suppliers and used without further purification. Solid hygroscopic reagents were dried in a vacuum oven before use. Reaction solvents were thoroughly dried before use using standard methods. Butyl Acrylate (BA, ≥99%), Ethyl Acrylate (EA; 99%), Hexyl Acrylate (HEA, 98%), Methyl Acrylate (MA, ≥99.5%), 2,2'-azobis(2-methylproprionitrile) (AIBN, 98%), Triethylsilane (Et<sub>3</sub>SiH, 99%) were purchased from Sigma-Aldrich. Sodium n-dodecyl sulfate (SDS, 98%), potassium persulfate (KPS, ≥99%), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 99%), Triethylamide (Et<sub>3</sub>N, 99%), Trifluoroacetic acid (TFA, 99.5%), Potassium Carbonate (K<sub>2</sub>CO<sub>3</sub>, ≥99%) were supplied by Acros Organics.

**Column chromatography** was carried out on silica gel Merck-60 (230-400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F254 (Merck).

**Nuclear Magnetic Resonance Spectroscopy (NMR):** <sup>1</sup>H and <sup>13</sup>C and <sup>19</sup>F NMR measurements were carried out with deuterated chloroform and dimethyl sulfoxide (CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub>, Aldrich) as solvents using a BRUKER AVANCE-II spectrometer operating at 300 MHz. The temperature was actively controlled at 298 K.

**High Resolution Mass Spectra (HR-MS):** HR-MS were determined on a BRUKER ULTRAFLEXIII (MALDI-TOF/TOF) equipment. The data are in mass units m/z.

**Fourier-transform infrared spectroscopy (FT-IR):** FT-IT spectra were recorded with an Agilent Technologies Cary 630 FT-IR spectrometer.

**Scanning Electron Microscopy (SEM):** The morphology of the surface of the grafted polymers were analysed upon drying by Scanning Electron Microscopy using a SEM S-3000N-EDX spectrometer.

**Differential Scanning Calorimetry (DSC):** Glass Transition temperatures (T<sub>g</sub>s) of the precursors copolymers and resulted grafted materials were determined by DSC analysis. DSC were performed using a TA instruments Q600 device, by a series of heating and cooling cycles from -80 °C to 120 °C at 10 °C min<sup>-1</sup> under nitrogen atmosphere.

**Gel Permeation Chromatography (GPC):** The molecular weight of the precursor polymers was determined by GPC. The samples were first dried, then dissolved in THF to achieve a concentration of about 0.1% (g mL<sup>-1</sup>) and filtered (polyamide 45 μm) before injection into the GPC, which consisted of a pump (Shimadzu LC-20AD), three columns (Styragel HR2, HR4 and HR6), and a refractive index detector (Waters 2410). Chromatograms were obtained at 35 °C using a THF flow rate of 1 mL min<sup>-1</sup>. The molecular weights obtained were related to polystyrene standards. Monomer conversion was determined gravimetrically (polymerizable surfactants/stabilizer were not considered as monomer) using the equation below. An aliquot of the reaction was thoroughly dried to remove solvent and unreacted monomer, and the weight of the dry capsule was compared to the weight of the wet capsule.

$$\text{Conversion (\%)} = \frac{m_{\text{monomer}} + m_{\text{initiator}} + m_{\text{solvent}}}{m_{\text{monomer}} + m_{\text{initiator}}} \times \frac{m_{\text{dry}} - m_{\text{empty}}}{m_{\text{wet}} - m_{\text{empty}}}$$

## **SI.1. Preparation of the Precursor Copolymers**

### **SI.1.1. Emulsion Copolymerization**

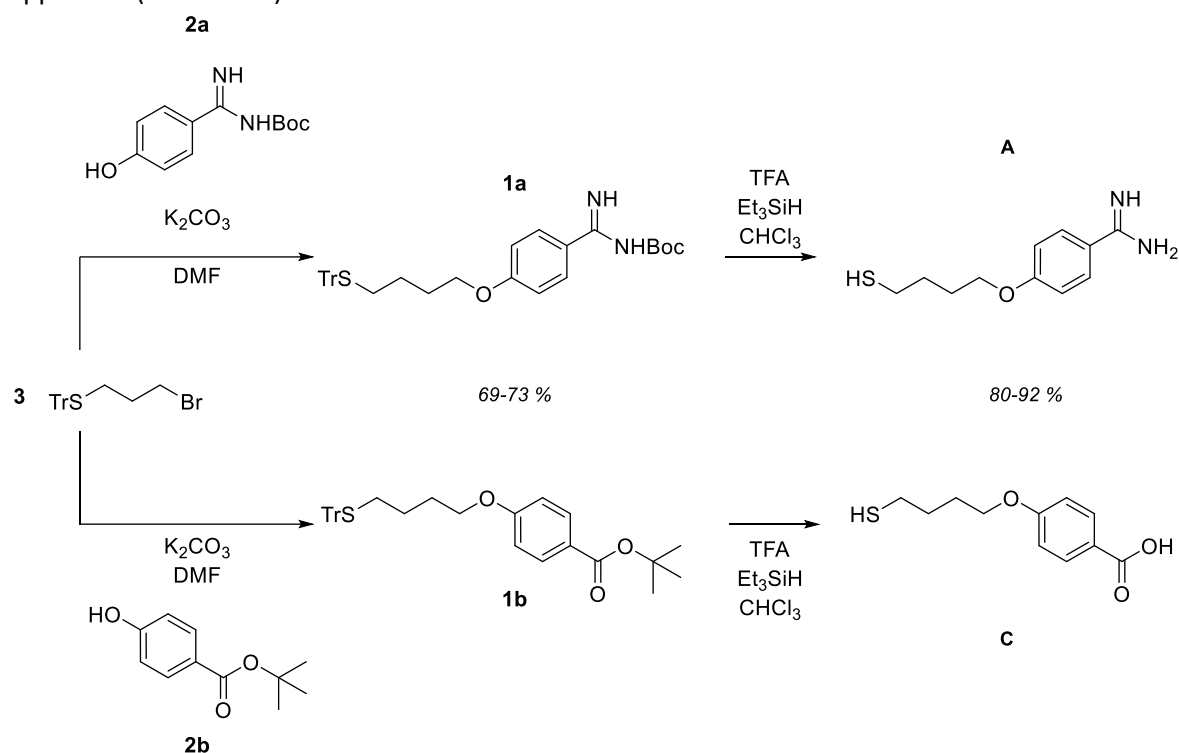
Different random copolymers polybutylacrylate-co-pentafluorostyrene (PBA-co-PFS), polyethylacrylate-co-pentafluorostyrene (PEA-co-PFS), polyhexylacrylate-co-pentafluorostyrene (PHA-co-PFS) or polymethylacrylate-co-pentafluorostyrene (PMA-co-PFS) were prepared by aqueous emulsion polymerization by varying the amount of monomers in the system (BA, EA, HA or PFS). In a standard reaction, 10 % solid content latexes, with monomers of different acrylic nature (BA/PFS, EA/PFS, MA/PFS or HEA/PFS) using monomer ratios of 95/5, 90/10, 80/20, 70/30 and 50/50 were added to a solution containing the emulsifier (SLS, 2% wbm, where wbm is the weight based on the monomer weight) in deionized water (Milli-Q quality) and the mixture was purged with Argon for 15 minutes. The mixture was heated to 65 °C, and then the initiator (KPS or AIBN, 1% wbm) was injected in a shot. The polymerization was allowed to react for 24 h under constant stirring (330 rpm), so as to ensure full conversion, although kinetic studies demonstrated that in about 6 hours no free monomer remained in the system. After the synthesis, the copolymers can be extracted from water solution by extracting with chloroform to concentrate the copolymer particles from water solution, concentrating, and then washing the polymer several times with methanol. The final product was filtered and dried under high vacuum to yield a white, sticky solid. The final monomer conversion was calculated by gravimetry.

### **SI.1.2. Solution Free Radical Copolymerization**

In a standard reaction 50 wt.% (where wt. is the total weight) of a 70/30 monomer ratio was dissolved in anhydrous THF in a round-bottomed flask equipped with a magnetic stir bar under Argon atmosphere, and AIBN 1% wbm was added until complete dissolution. Then, the reaction flask was placed in an oil bath at 70 °C, and the mixture was stirred at this temperature for 24 hours under argon atmosphere. The reaction was stopped by cooling down to room temperature, before cold methanol was added to precipitate the copolymer. The final product was washed with methanol, filtered by removing the supernatant, and dried under high vacuum to yield a clear, sticky solid. The final monomer conversion was calculated by gravimetry.

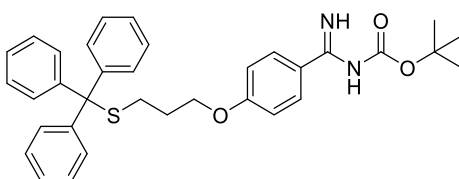
## SI.2. Synthesis of the Stickers

The synthesis of the thiol-amidine (A) and thiol-acid (C) was performed in a straightforward approach. (Scheme S1)



**Scheme S1.** Schematic illustration showing the preparation of the thiol-amidine (A) and thiol-acid (C).

### SI.2.1. Synthesis of tert-butyl (imino(4-(3-(tritylthio)propoxy)phenyl)methyl) carbamate (1a)



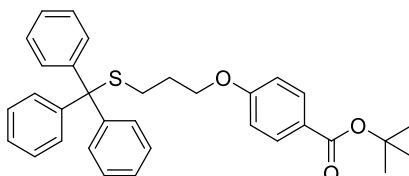
For the synthesis of *tert-butyl (imino(4-(3-(tritylthio)propoxy)phenyl)methyl)carbamate (1a)*: *N*-Boc *p*-amidinophenol (**2a**, 1.90 g, 8.04 mmol) and (3-bromopropyl)(*S*-trityl)sulfane (**3**, 5.11 g, 12.87 mmol, 1.6 equiv.) were stirred in 40 mL of DMF at r.t. for 10 min and then,  $K_2CO_3$  (2.22 g, 16.08 mmol, 2 equiv.) was added. The mixture was stirred at r.t. for 24 h. After that, the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica (cyclohexane/ethyl acetate 8:2) to obtain **1a** (3.05 g, 5.52 mmol, 69%) as a white solid.

$^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.80 – 7.70 (m, 2H,  $H_{ortho}$ ), 7.40 – 7.27 (m, 6H,  $H_{trityl}$ ), 7.27 – 7.06 (m, 9H,  $H_{trityl}$ ), 6.88 – 6.71 (m, 2H,  $H_{meta}$ ), 3.87 (t,  $^3J_{1,2} = 6.2$  Hz, 2H, H1), 2.29 (t,  $^3J_{2,3} = 7.0$  Hz, 2H, H3), 1.75 (dt,  $^3J_{1,2} = 6.2$  Hz,  $^3J_{2,3} = 7.0$  Hz, 2H, H2), 1.48 (s, 9H,  $CH_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.09 ( $\text{CO}_2$ ), 144.80 ( $\text{C}_{\text{ipso-Triyl}}$ ), 129.59 ( $\text{C}_{\text{ortho}}$ ), 128.99 ( $\text{C}_{\text{meta-Triyl}}$ ), 127.92 ( $\text{C}_{\text{ortho-Triyl}}$ ), 126.69 ( $\text{C}_{\text{para-Triyl}}$ ), 114.40 ( $\text{C}_{\text{meta}}$ ), 77.25 ( $\text{C}(\text{CH}_3)_3$ ), 66.69 ( $\text{CPh}_3$ ), 66.35 ( $\text{C1}$ ), 28.32 ( $\text{C2/C3}$ ), 28.27 ( $\text{CH}_3$ ), 28.18 ( $\text{C2/C3}$ ). Three  $^{13}\text{C}$  resonances were not detected.

**HRMS (ESI-TOF):** Calculated for  $\text{C}_{34}\text{H}_{37}\text{N}_2\text{O}_3\text{S}$ : 553.2525  $[\text{M}+\text{H}]^+$ ; Found: 553.2519.

### SI.2.2. Synthesis of *t*-butyl *p*-[3-(tritylthio)propoxy]benzoate (**1b**) (HRMS)



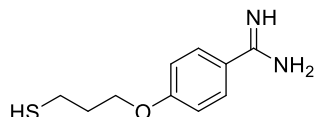
(3-bromopropyl)(*S*-trityl)sulfane (**3**, 3.40 g, 8.56 mmol), and *tert*-butyl 4-hydroxybenzoate (**2b**, 4.99 g, 25.67 mmol, 3 equiv.) and  $\text{K}_2\text{CO}_3$  (7.10 g, 6 equiv.) were suspended in DMF and the mixture was stirred at r.t. for 3 days. Then, the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica (cyclohexane/ $\text{CHCl}_3$  1:1) to obtain 3.20 g (6.27 mmol, 73 %) of **1b** as colorless viscous oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89-7.76 (m, 2H,  $\text{H}_{\text{ortho}}$ ), 7.41-7.26 (m, 6H,  $\text{H}_{\text{trityl}}$ ), 7.23-7.05 (m, 9H,  $\text{H}_{\text{trityl}}$ ), 6.80-6.66 (m, 2H,  $\text{H}_{\text{meta}}$ ), 3.86 (t,  $^3J_{1,2} = 6.1$  Hz, 2H, H1), 2.29 (t,  $^3J_{2,3} = 7.1$  Hz, 2H, H3), 1.74 (dt,  $^3J_{1,2} = 6.1$  Hz,  $^3J_{2,3} = 7.1$  Hz, 2H, H2), 1.50 (s, 9H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.76 ( $\text{CO}_2$ ), 162.31 ( $\text{C}_{\text{para}}$ ), 144.91 ( $\text{C}_{\text{ipso-Triyl}}$ ), 131.43 ( $\text{C}_{\text{ortho}}$ ), 129.68 ( $\text{C}_{\text{meta-Triyl}}$ ), 128.00 ( $\text{C}_{\text{ortho-Triyl}}$ ), 126.76 ( $\text{C}_{\text{para-Triyl}}$ ), 124.51 ( $\text{C}_{\text{ipso}}$ ), 113.99 ( $\text{C}_{\text{meta}}$ ), 80.61 ( $\text{C}(\text{CH}_3)_3$ ), 66.76 ( $\text{CPh}_3$ ), 66.37 ( $\text{C1}$ ), 28.44 ( $\text{C2/C3}$ ), 28.39 ( $\text{CH}_3$ ), 28.28 ( $\text{C2/C3}$ ).

**HRMS (ESI-TOF):** Calculated for  $\text{C}_{33}\text{H}_{34}\text{NaO}_3\text{S}$ : 533.2126  $[\text{M}+\text{Na}]^+$ ; Found: 533.2130.

### SI.2.3. Synthesis of *p*-(3-mercaptopropoxy)benzenecarboximidamide (**A**)

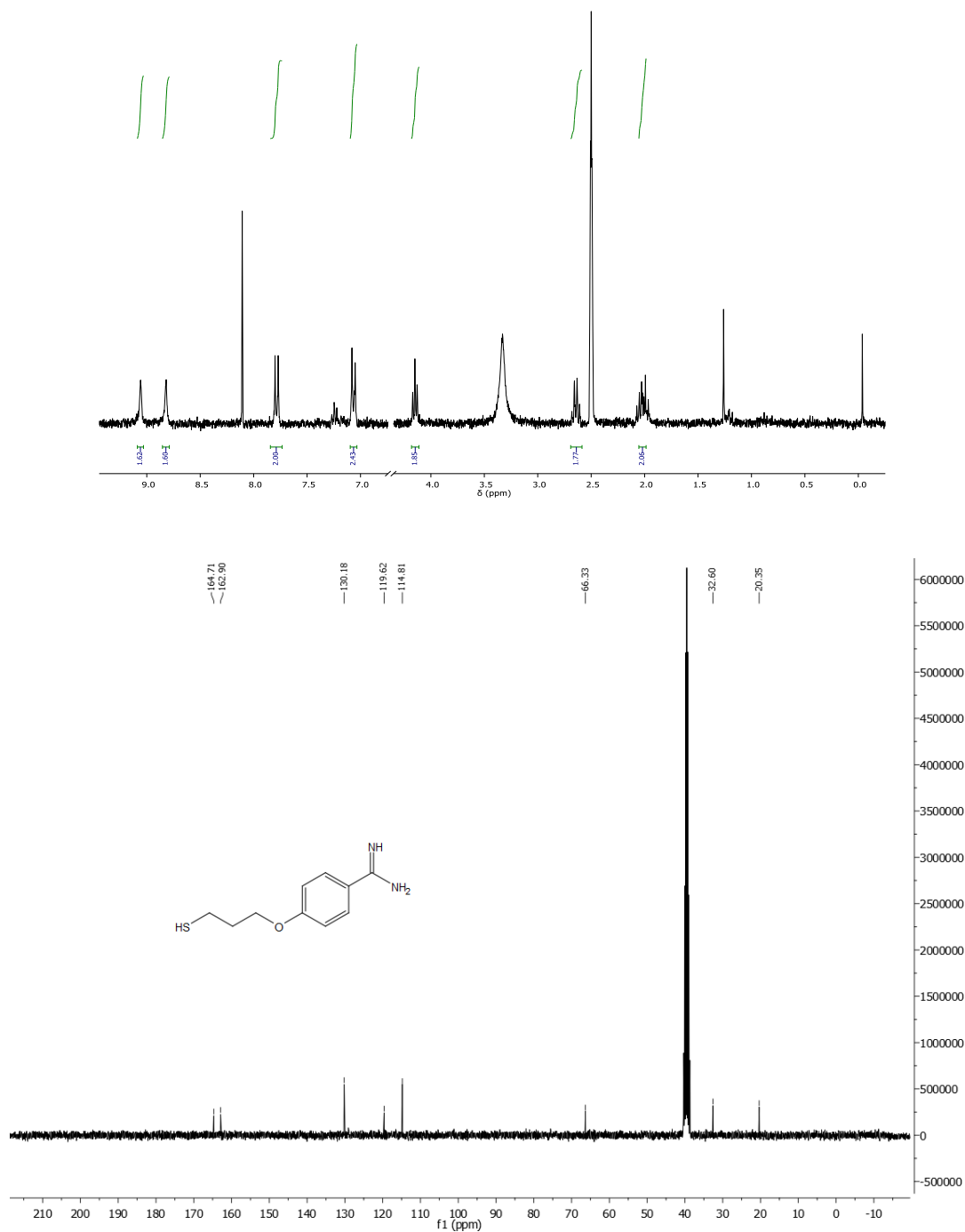


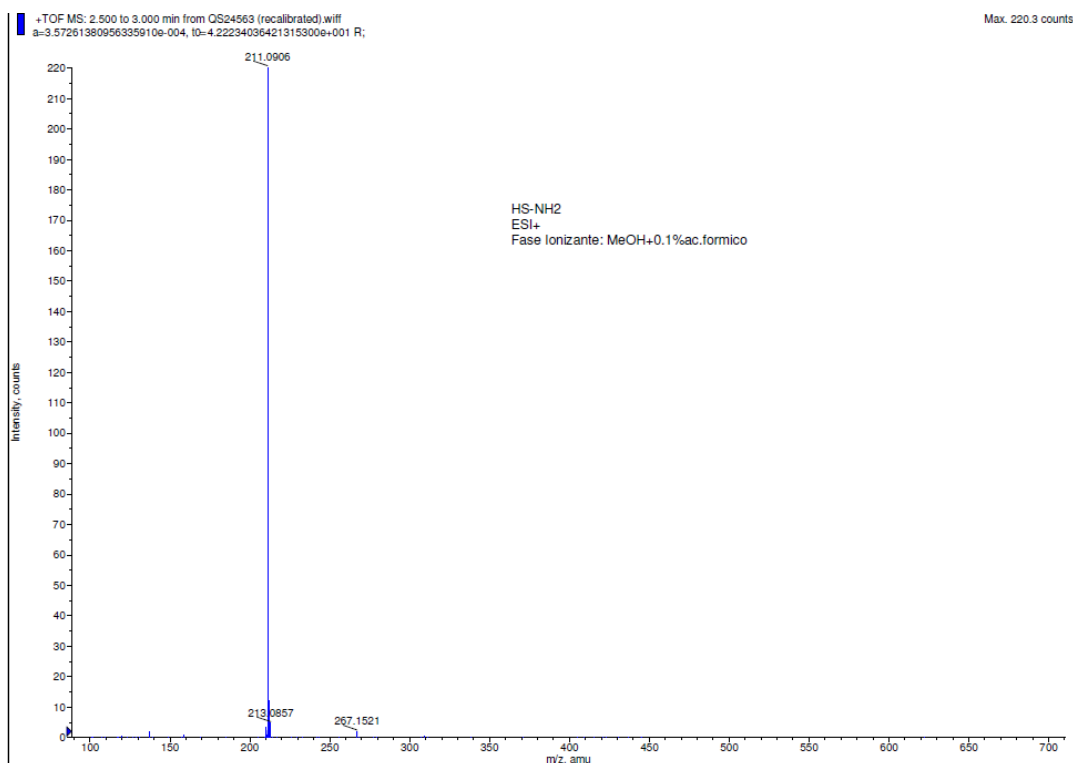
*p*-(3-mercaptopropoxy)benzenecarboximidamide (**A**): **1a** (3.00 g, 5.43 mmol) was dissolved in  $\text{CHCl}_3$  (50 mL) at r.t.,  $\text{Et}_3\text{SiH}$  (20 mL, 124.83 mmol, 23 equiv.) was added and then trifluoroacetic acid\* (30 mL, 396.21 mmol, 73 equiv.) dropwise. A transient yellow color was observed during addition of trifluoroacetic acid. The mixture was stirred at room temperature for 2 h. After that, cyclohexane/diethyl ether 1:1 was added slowly until a white precipitate was formed. The precipitate was filtered off and washed with cyclohexane/diethyl ether 1:1 (small volume) and cyclohexane. The precipitate was collected and dried under vacuum to obtain 1.05 g of **A** (4.99 mmol, 92 %) as a white solid.

$^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.15 (bs, 2H,  $\text{NH}_2$ ), 9.05 (bs, 2H,  $\text{NH}_2$ ), 7.82 (d,  $^3J_{o,m} = 8.9$  Hz, 2H,  $\text{H}_{\text{ortho}}$ ), 7.17 (d,  $^3J_{o,m} = 8.9$  Hz, 2H,  $\text{H}_{\text{meta}}$ ), 4.18 (t,  $^3J_{1,2} = 6.2$  Hz, 2H,  $\text{CH}_2\text{O}$ ), 2.64 (dt,  $^3J_{2,3} = 7.0$  Hz,  $^3J_{3,SH} = 7.4$  Hz, 2H,  $\text{CH}_2\text{S}$ ), 2.49 (t,  $^3J_{3,SH} = 7.4$  Hz, SH, overlapped with solvent signal), 2.02 (tt,  $^3J_{1,2} = 6.2$  Hz,  $^3J_{2,3} = 7.0$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ).

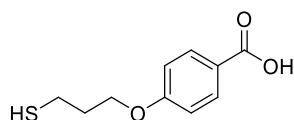
$^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  164.71 ( $\text{CNH}\text{NH}_2$ ), 162.90 ( $C_{para}$ ), 130.18 ( $C_{meta}$ ), 119.62 ( $C_{ipso}$ ), 114.81 ( $C_{ortho}$ ), 66.33 ( $\text{CH}_2\text{O}$ ), 32.60 ( $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 20.35 ( $\text{CH}_2\text{S}$ ).

HRMS (ESI-TOF): Calculated for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{OS}$ : 211.0905  $[\text{M}+\text{H}]^+$ ; Found: 211.0906.





#### SI.2.4. Synthesis of *p*-(3-mercaptopropoxy)benzoic acid (**C**):

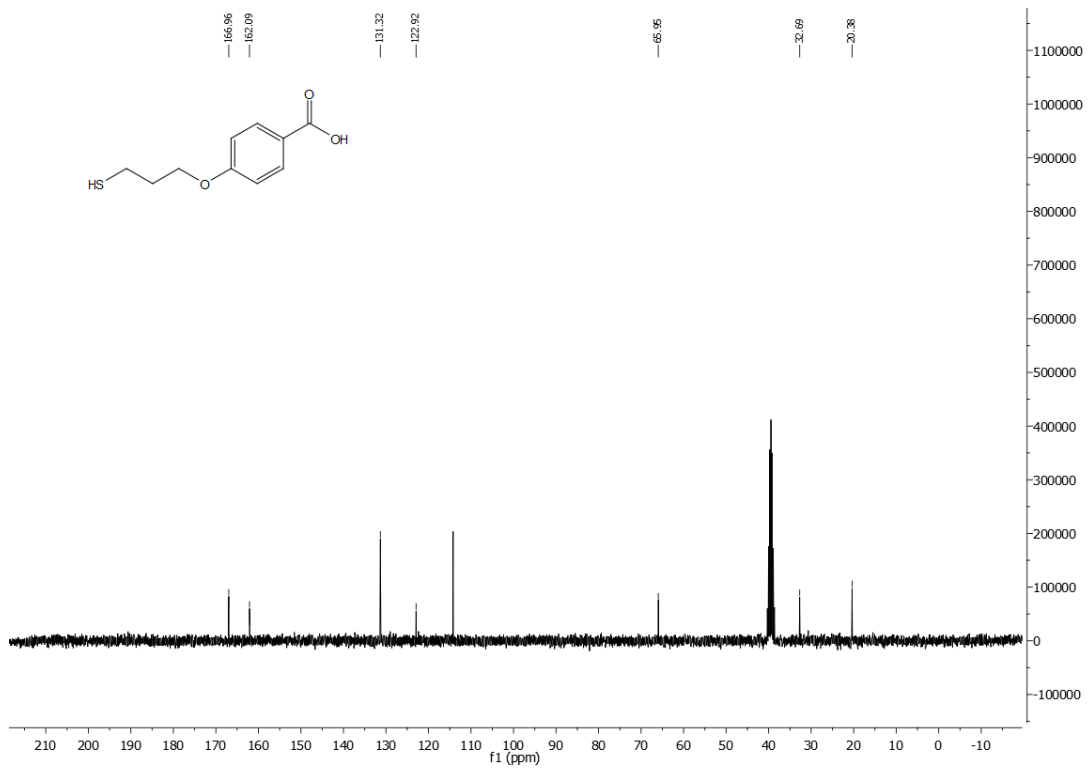
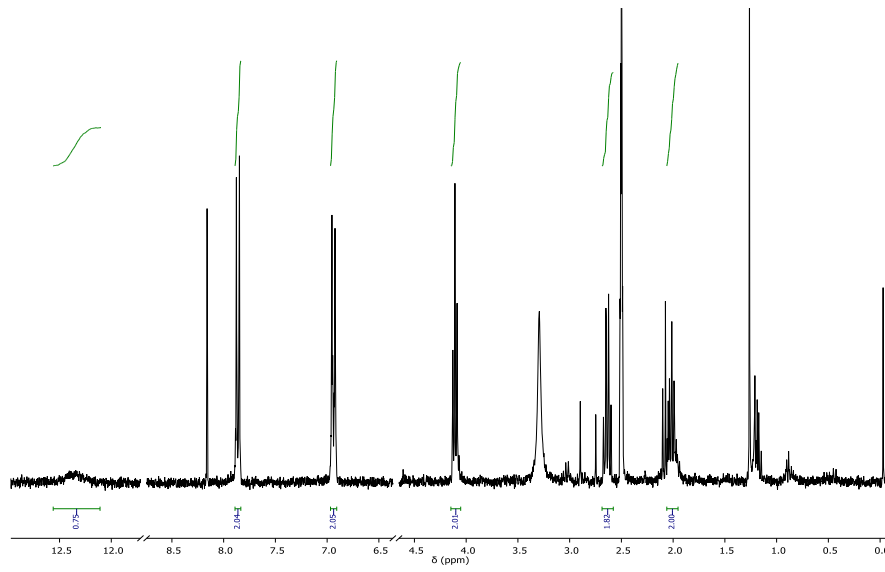


*p*-(3-mercaptopropoxy)benzoic acid (**C**): **1b** (3.00 g, 5.87 mmol) was dissolved in  $\text{CHCl}_3$  (50 mL) at r.t.,  $\text{Et}_3\text{SiH}$  (22 mL, 137.46 mmol, 23 equiv.) was added and then trifluoroacetic acid\* (33 mL, 428.88 mmol, 73 equiv.) dropwise. A transient yellow color was observed during addition of trifluoroacetic acid. The mixture was stirred at room temperature overnight. After that, solvents were evaporated under vacuum and the crude was purified by column chromatography on silica ( $\text{CHCl}_3$  to  $\text{CHCl}_3/\text{Acetone}$  10:1) to obtain 1.00 g of **C** (4.71 mmol, 80 %) as a white solid.

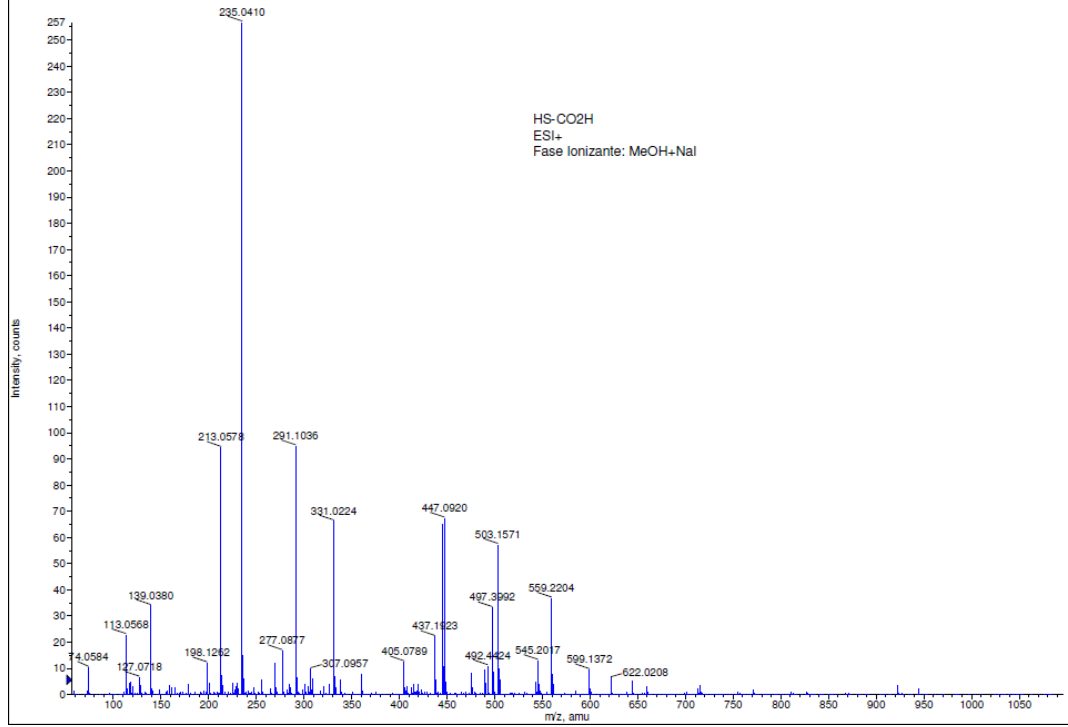
$^1\text{H NMR}$  (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  12.57 (bs, 1H,  $\text{CO}_2\text{H}$ ), 8.37 – 7.66 (m, 2H,  $\text{H}_{ortho}$ ), 7.19 – 6.22 (2H,  $\text{H}_{meta}$ ), 4.07 (t,  $^3J_{1,2} = 6.1$  Hz, 2H,  $\text{CH}_2\text{O}$ ), 2.58 (ddt,  $^3J_{2,3} = 6.9$  Hz,  $^3J_{3,SH} = 7.4$  Hz,  $^3J_{3,SH} = 8.4$ , 2H,  $\text{CH}_2\text{S}$ ), 2.38 (dd,  $^3J_{3,SH} = 7.4$  Hz,  $^3J_{3,SH} = 8.4$  Hz, 1H, SH), 1.95 (tt,  $^3J_{1,2} = 6.1$  Hz,  $^3J_{2,3} = 6.9$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ).

$^{13}\text{C NMR}$  (75 MHz,  $\text{DMSO}-d_6$ )  $\delta$  166.96 ( $\text{CO}_2\text{H}$ ), 162.09 ( $\text{C}_{para}$ ), 131.32 ( $\text{C}_{meta}$ ), 122.92 ( $\text{C}_{ipso}$ ), 114.20 ( $\text{C}_{ortho}$ ), 65.95 ( $\text{CH}_2\text{O}$ ), 32.69 ( $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 20.38 ( $\text{CH}_2\text{S}$ ).

**HRMS (ESI-TOF)**: Calculated for  $\text{C}_{10}\text{H}_{12}\text{NaO}_3\text{S}$ : 235.0405  $[\text{M}+\text{Na}]^+$ ; Found: 235.0410. Calculated for:  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{S}$ : 213.0585  $[\text{M}+\text{H}]^+$ ; Found: 213.0578.







## SI.3. Grafting Reactions in Solution

The grafting reaction was performed at 50 °C, using 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as the base. Triethylamine was also tested as the base with negative results. A 1:1 mixture of DMSO and CHCl<sub>3</sub> was utilized as solvent in order to dissolve both reactants: the polar grafting agent, on one hand, and the apolar copolymer, on the other. Total conversion, as monitored by <sup>19</sup>F-NMR (see Figure S2), <sup>1</sup>H-NMR and FT-IR, required 24 h in our standard conditions. Lower temperatures (*i.e.* room temperature) can be employed, but at the expense of using longer reaction times to achieve full conversion.

### SI.3.1. Preparation of the Thiol-Amidine grafted Copolymers in Solution

Different grafted copolymers of PBA-co-PFS-g-**A**, PMA-co-PFS-g-SH-**A**, PHA-co-PFS-g-**A** and PEA-co-PFS-g-**A** were synthesized by varying the monomer ratio of the precursors copolymers. In a standard reaction, the precursor copolymer (PBA-co-PFS), (PMA-co-PFS), (PHA-co-PFS) or (PEA-co-PFS) (40 mg), with different amounts of pentafluorostyrene, was dissolved in chloroform (2 mL) in a round-bottomed flask equipped with a magnetic stir bar under argon atmosphere until complete dissolution. Then, DBU (3 eq. in respect to pentafluorostyrene groups) was added to the mixture. Afterwards, **A** (3 eq. in respect to pentafluorostyrene groups) was dissolved in DMSO (2 mL) and added to the reaction flask. The reaction was allowed to react during 1 day at 50 °C. After CHCl<sub>3</sub> was evaporated and the residue was purified by precipitation in acidic water (HCl 1M) and then washed with methanol. The final product was filtered by removing the supernatant and dried under high vacuum to yield a yellow, sticky solid.

### SI.3.2. Preparation of the Thiol-Acid Grafted Copolymers in Solution

Different grafted copolymers of PBA-co-PFS-g-**C**, PMA-co-PFS-g-**C**, PHA-co-PFS-g-**C** and PEA-co-PFS-g-**C** were synthesized by varying the monomer ratio of the precursors copolymers. In a standard reaction, the precursor copolymer (PBA-co-PFS), (PMA-co-PFS), (PHA-co-PFS) or (PEA-co-PFS) (40 mg) was dissolved in chloroform (2 mL) in a round-bottomed flask equipped with a magnetic stir bar under argon atmosphere until complete dissolution. Then, DBU (3 eq. with respect to pentafluorostyrene groups) was added to the mixture. Afterwards, **C** (3 eq. with respect to pentafluorostyrene groups) was dissolved in DMSO (2 mL) and added to the reaction flask. The reaction was allowed to react during 1 day at 50 °C. After CHCl<sub>3</sub> was evaporated and the residue was purified by precipitation in basic water (NaHCO<sub>3</sub> 1M) and then washed with methanol. The final product was filtered by removing the supernatant and dried under high vacuum to yield a yellow, sticky solid.

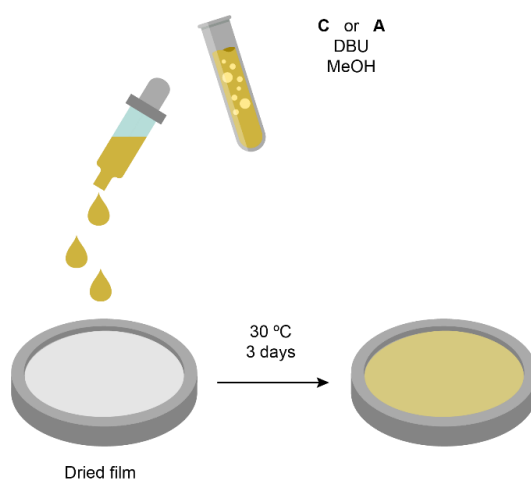
## SI.4. Grafting Reactions on the Film Surface (Scheme S2)

### SI.4.1. Preparation of the Thiol-Amidine Grafted onto the Film Surface

Different grafted copolymers of PBA-co-PFS-g-**A**, PMA-co-PFS-g-**A**, PHA-co-PFS-g-**A** and PEA-co-PFS-g-**A** were synthesized onto the precursors dried films. In a standard reaction, the precursor copolymer (PBA-co-PFS), (PMA-co-PFS), (PHA-co-PFS) or (PEA-co-PFS) (40 mg) was dissolved in chloroform (2 mL) and placed in a petri dish. After the evaporation of  $\text{CHCl}_3$ , **A** (1 eq. with respect to pentafluorostyrene groups) and DBU (2 eq. with respect to pentafluorostyrene groups) were dissolved in methanol (2 mL) and dropwise added onto the film surface. The mixture was allowed to react during 2 days at 30 °C in a closed system under argon atmosphere. The final film surface was washed with acidic methanol, then with methanol, and dried under high vacuum to yield a yellow solid.

### SI.4.2. Preparation of the Thiol-Acid Grafted onto the Film Surface

Different grafted copolymers of PBA-co-PFS-g-**C**, PMA-co-PFS-g-**C**, PHA-co-PFS-g-**C** and PEA-co-PFS-g-**C** onto the precursors dried films. In a standard reaction, the precursor copolymer (PBA-co-PFS), (PMA-co-PFS), (PHA-co-PFS) or (PEA-co-PFS) (40 mg) was dissolved in chloroform (2 mL) and placed in a petri dish. After the evaporation of  $\text{CHCl}_3$ , **C** (1 eq. with respect to pentafluorostyrene groups) and DBU (2 eq. with respect to pentafluorostyrene groups) were dissolved in methanol (2 mL) and dropwise added onto the film surface. The mixture was allowed to react during 2 days at 30 °C in a closed system under argon atmosphere. The final film surface was washed thoroughly with basic methanol, then with methanol, and dried under high vacuum to yield a yellow solid.



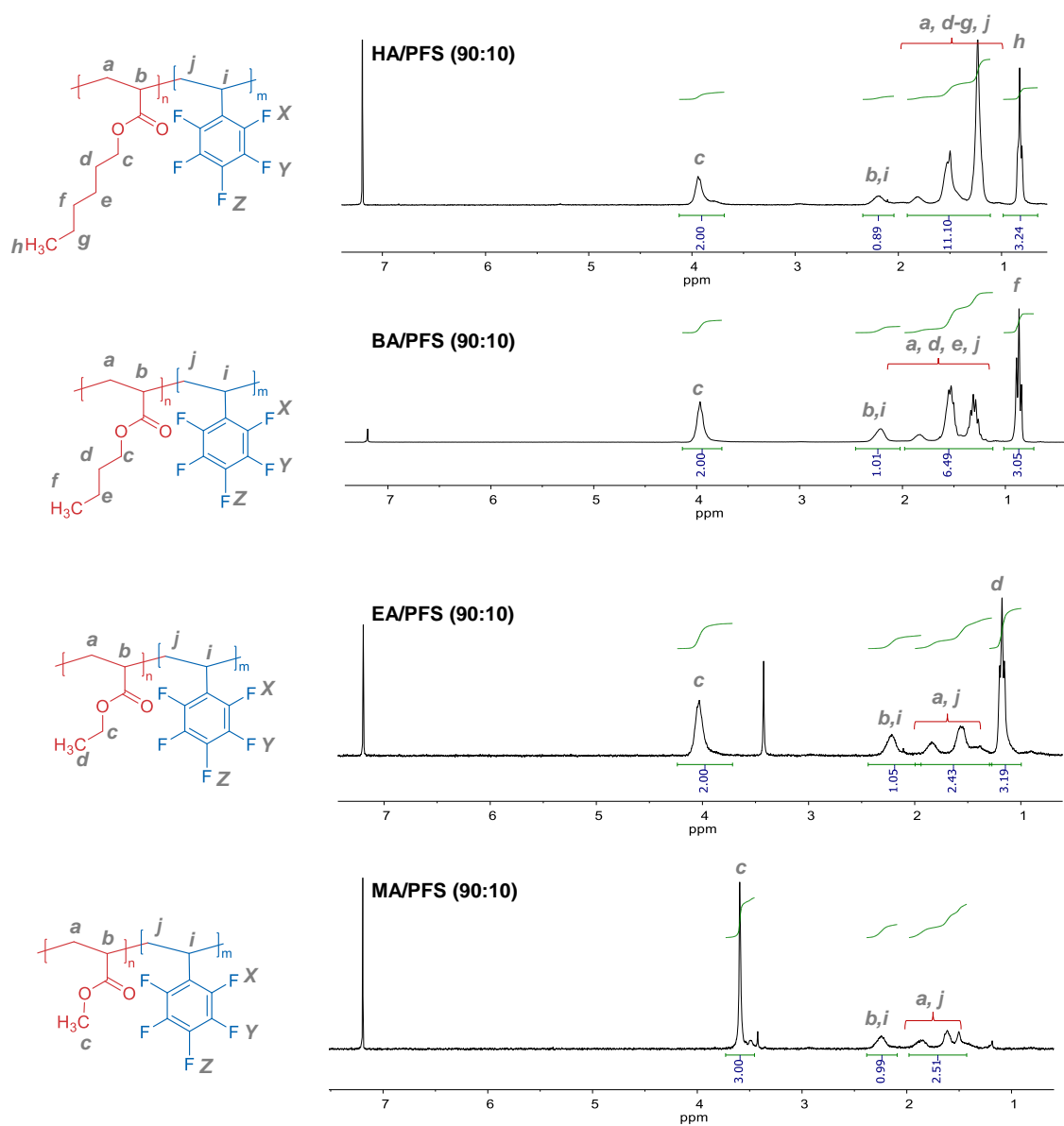
**Scheme S2.** Schematic illustration about the preparation of grafted copolymers onto the dried polymer.

## Figures S1-S8

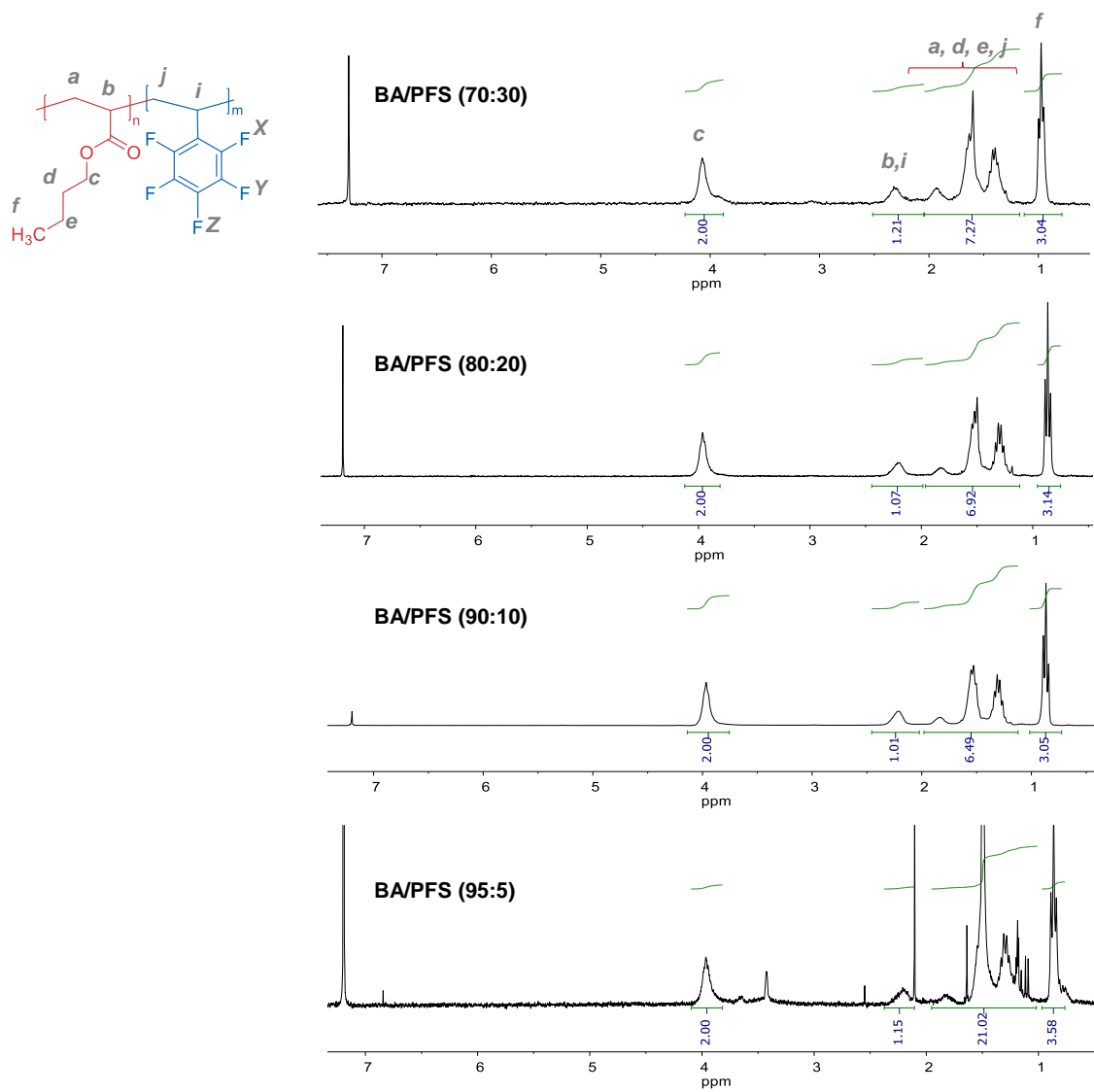
	HA:PFS	$I(c)$	$I(h)$	1H(HA)	$I(b,i)$	$I(a,d,g,j)$	1H(PFS)	X(HA)	X(PFS)	
$= (I(c)/2 + I(h)/3)/2$	90-10	2	3,24	1,04	0,89	11,1	0,1	0,912	0,088	$= 1H(PFS)/(1H(HA)+1H(PFS))$ $= 1H(HA)/(1H(HA)+1H(PFS))$ $= ((I(b,i)-1H(HA)) + (I(a,d,g,j) - (10 \times 1H(HA))))/2)/2$
$= (I(c)/2 + I(f)/3)/2$	BA:PFS	$I(c)$	$I(f)$	1H(BA)	$I(b,i)$	$I(a,d,e,j)$	1H(PFS)	X(BA)	X(PFS)	
	95-5	2	3,58	1,0967	1,15		0,05333	0,954	0,046	$= ((I(b,i)-1H(BA)) + (I(a,d,e,j) - (6 \times 1H(BA))))/2)/2$ $= I(b,i) - 1H(BA)$ [ $I(a,d,e,j)$ could not be integrated properly due to the presence of impurities in that ppm region]
	90-10	2	3,05	1,0083	1,01	6,49	0,11083	0,901	0,099	
	80-20	2	3,14	1,0233	1,07	6,92	0,21833	0,824	0,176	
	70-30	2	3,04	1,0067	1,21	7,27	0,40917	0,711	0,289	
$= (I(c)/2 + I(d)/3)/2$	EA:PFS	$I(c)$	$I(d)$	1H(EA)	$I(b,i)$	$I(a,j)$	1H(PFS)	X(EA)	X(PFS)	
	90-10	2	3,19	1,0317	1,05	2,43	0,10083	0,911	0,089	$= ((I(b,i)-1H(EA)) + (I(a,j) - (2 \times 1H(EA))))/2)/2$
	80-20	2	3,07	1,0117	1,07	2,83	0,23083	0,814	0,186	
$= (I(c)/3)$	MA:PFS	$I(c)$		1H(MA)	$I(b,i)$	$I(a,j)$	1H(PFS)	X(MA)	X(PFS)	
	95-5	3		1	1,01	2,21	0,0575	0,946	0,054	$= ((I(b,i)-1H(MA)) + (I(a,j) - (2 \times 1H(MA))))/2)/2$
	90-10	3		1	0,99	2,51	0,1225	0,891	0,109	
	80-20	3		1	1,13	2,83	0,2725	0,786	0,214	
	50-50	3		1	1,74	4,16	0,91	0,524	0,476	

$I(x)$  → Integral value of proton x  
 $1H(AA) / 1H(PFS)$  → Relative value of each proton in the alkyl acrylate / pentafluorostyrene moieties  
 $X(AA) / X(PFS)$  → Molar fraction of alkyl acrylate / pentafluorostyrene

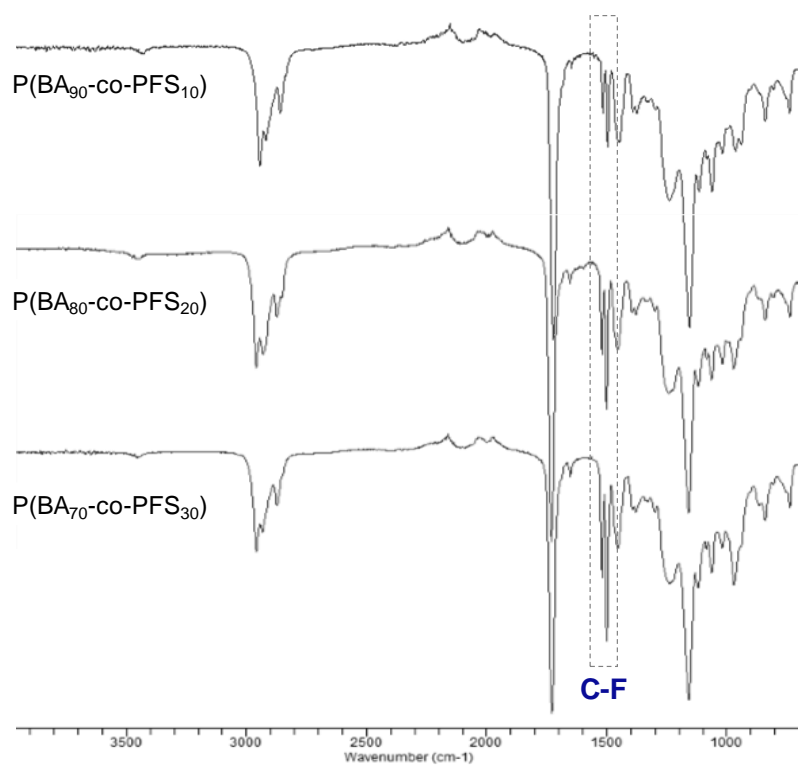
**Table S1.** Integral values obtained from the  $^1H$  NMR spectra of poly(AA-co-PFS) copolymers (see examples in Figure S1 below), as listed in Table 1 in the main text, and formulas employed for the calculation of the molar fraction of the AA and PFS moieties integrated in the polymer.



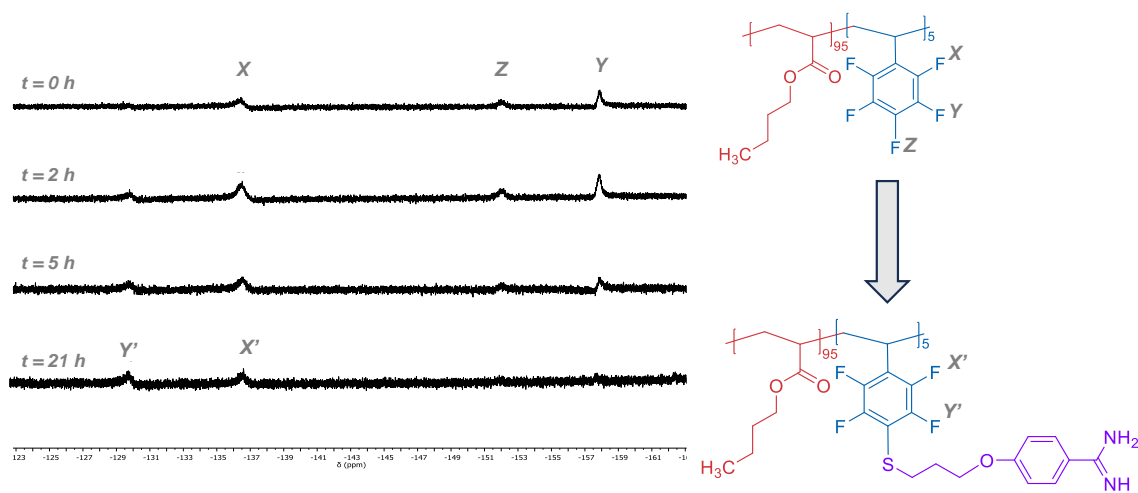
**Figure S1A.**  $^1\text{H}$  NMR spectra of the different poly(AA-co-PFS) copolymers obtained at a AA/PFS 90:10 feed ratio and integral values ( $I(x)$ ) for the different proton signals, as listed in Table S1.



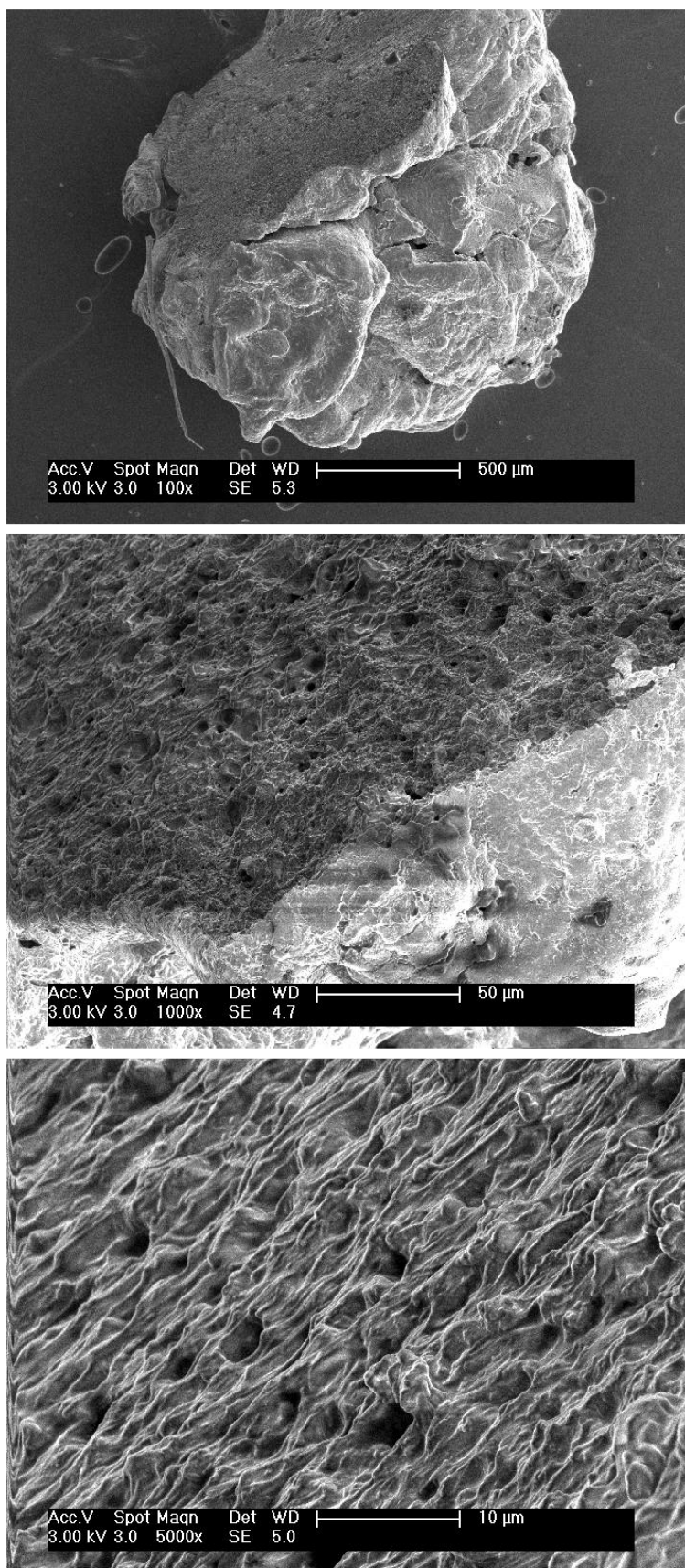
**Figure S1B.**  $^1\text{H}$  NMR spectra of poly(BA-co-PFS) copolymers obtained at different BA/PFS feed ratio and integral values ( $I(x)$ ) for the different proton signals, as listed in Table S1.



**Figure S2.** FT-IR spectra of **a)** PBA<sub>90</sub>-co-PFS<sub>10</sub> **b)** PBA<sub>80</sub>-co-PFS<sub>20</sub> and **c)** PBA<sub>70</sub>-co-PFS<sub>30</sub>.

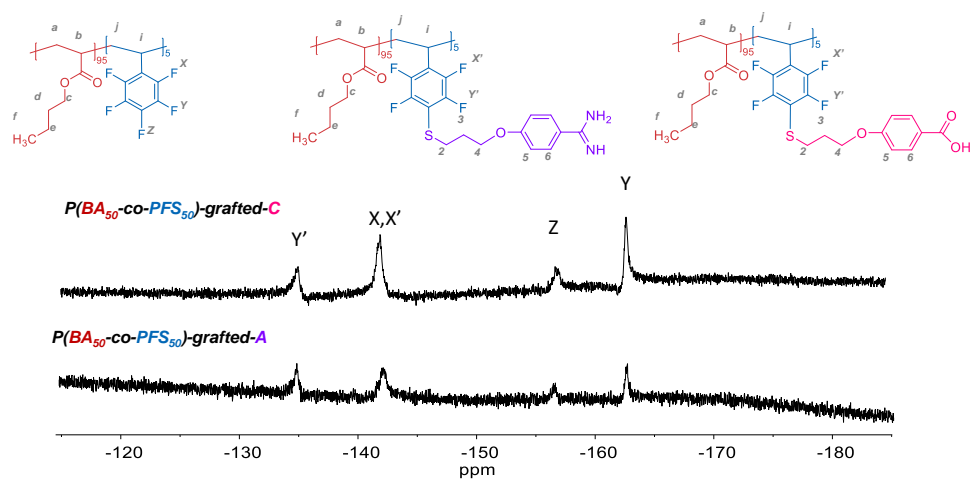


**Figure S3.** Example of <sup>19</sup>F-NMR spectra of a grafting reaction using thiol-amidine at different reaction times.

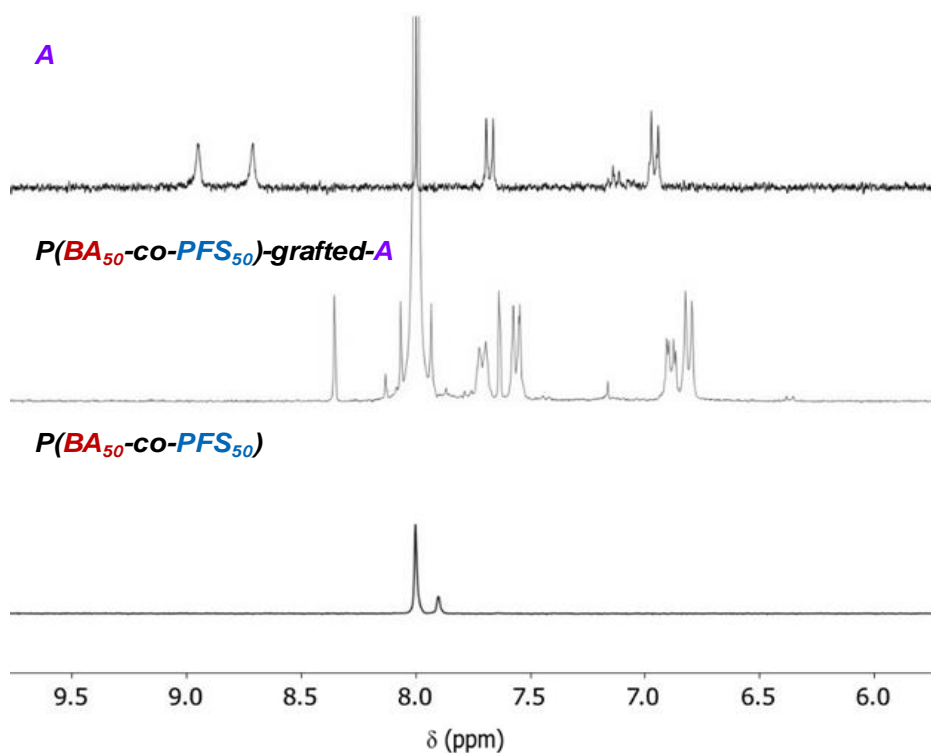


**Figure S4.** SEM micrographs of dried PBA70-co-PFS30 grafted **A** at different scales showing the interior of a cross section and the dried surface.

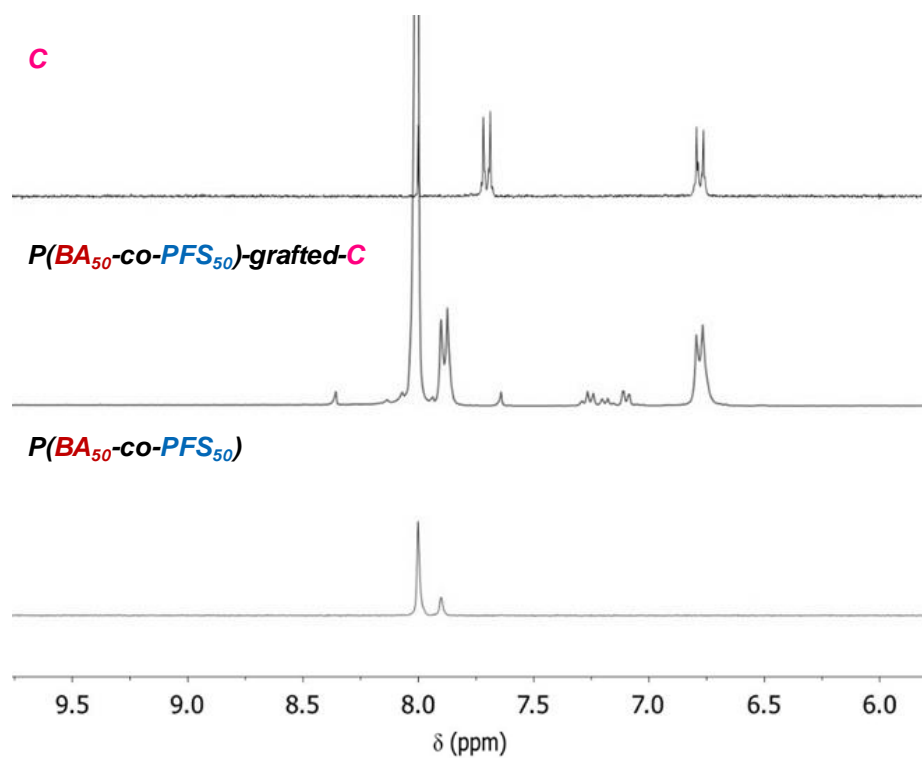




**Figure S5.**  $^{19}\text{F}$ -NMR spectra of the polymer films modified on the surface with **C** (top) and **A** (bottom). The top part of the polymer was dissolved in  $\text{CDCl}_3/\text{DMSO-}D_6$  1:1, showing both reacted and unreacted PFS moieties.



**Figure S6.**  $^1\text{H}$ -NMR spectra of **A** (top), polymer film modified with **A** (middle) and unmodified polymer (bottom) in  $\text{CDCl}_3/\text{DMSO-}D_6$  1:1.



**Figure S7.** <sup>1</sup>H-NMR spectra of **C** (top), polymer film modified with **C** (middle) and unmodified polymer (bottom) in CDCl<sub>3</sub>/dimethylsulfoxide-d<sub>6</sub> 1:1.

Preliminary *ad hoc* qualitative adhesion tests were performed from these surface-functionalized films. Rectangular pieces, with a surface of approximately 2 cm x 1 cm and a thickness of 1 mm, were cut from the films of the **A**-grafted and **C**-grafted copolymers. Only one of the two surfaces of each film, hereafter called the “top surface”, was functionalized with these H-bonding units. A control film was also prepared by treatment of the top surface under exactly the same conditions, but in the absence of thiol. The functionalized “top surfaces” of the films, but not (or to a much lower extent) the “bottom” non-functionalized surfaces or the control films, were able to stick onto smooth planar surfaces of different nature, like metal, glass, or plastic. Bottom surfaces or control films could not withstand such weight at all. Remarkably, the complementary surfaces of the films, *i.e.* carboxylate- and amidinium-functionalized surfaces, stick to each other stronger than all other tested surfaces (see Supplementary Video). When the interaction was made between top and bottom surfaces, a similar adhesion strength as in the direct adhesion experiments was noted. Future work will focus on characterizing quantitatively and optimizing the adhesion process.



**Figure S8.** Pictures demonstrating the adhesion of the A- and C-grafted polymer surfaces. Left: lifting a 2 euro coin after contact with the treated surface. Middle and right: contact of A- and C-grafted polymer surfaces followed by stretching.