

Supporting Information for

Electrochemically-Initiated Polymerization of Reactive Monomers via 4-Fluorobenzenediazonium Salts

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1. Experimental Section

Materials

Glycidyl methacrylate (Sigma Aldrich, 97%) was passed through basic aluminum oxide prior to use. Acetone (AnalaR NORMAPUR), acetonitrile (Acros Organics, 99.9%, anhydrous), acryloyl chloride (Alfa Aesar, 96%), 2,2'-azobis(2-methylpropionitrile) (AIBN) (Sigma Aldrich, 98%), cyclohexane (AnalaR NORMAPUR), diethyl ether (Fisher, $\geq 99\%$), ethyl acetate (AnalaR NORMAPUR), 2,6-difluorophenol (Sigma Aldrich, 98%), *N,N*-dimethylformamide (Acros Organics, 99.8%, anhydrous), 4-fluoroaniline (Sigma Aldrich, 99%), magnesium sulfate (Roth, $\geq 99\%$), methanol (AnalaR NORMAPUR), pentafluorophenol (abcr, 99%), petroleum ether (AnalaR NORMAPUR), sodium nitrite (Honeywell, $\geq 99\%$), tetrabutylammonium tetrafluoroborate (Sigma Aldrich, 99%), tetrafluoroboric acid (Sigma Aldrich, 48 wt%), tetrahydrofuran (Acros Organics, 99.5%, anhydrous), tetrahydrofuran (AnalaR NORMAPUR), triethylamine (Acros Organics, 99%), and 2,2,2-trifluoroethylamine (TCI, $>97\%$) were used as received.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Ascend III 400 MHz spectrometer at a frequency of $\nu = 400$ MHz, $\nu = 101$ MHz, and $\nu = 377$ MHz, respectively. All samples were dissolved in deuterated solvents, chemical shifts are reported relative to the residual solvent signals.

Size-Exclusion Chromatography (SEC) using THF as eluent

SEC measurements with THF as eluent were performed on an Agilent 1200 Series System, comprising an autosampler, a differential Refractive Index (RI) detector, three PLgel 5 μm Mixed C columns (300×7.5 mm) and a PLgel 3 μm Mixed E column (300×7.5 mm). The measurements were performed at a temperature of $T = 35$ °C and a flow rate of 1.0 mL min^{-1} . Samples were measured at a concentration of 2 mg mL^{-1} and filtered prior to measurement. All number-average molar mass M_n and dispersity D values were extrapolated from a range of linear poly(methyl methacrylate) standards between 800 and 2.2×10^6 g mol^{-1} and linear polystyrene standards between 370 and 2.52×10^6 g mol^{-1} .

Size-Exclusion Chromatography (SEC) using DMAc as eluent

SEC measurements with DMAc as eluent were performed on an Agilent 1200 Series System, comprising an autosampler, a differential Refractive Index (RI) detector and two PLgel 5 μm

Mixed C columns (300 × 7.5 mm). The measurements were performed at a temperature of $T = 50\text{ }^{\circ}\text{C}$ and a flow rate of 0.5 mL min^{-1} . Samples were measured at a concentration of 2 mg mL^{-1} and filtered prior to measurement. All number-average molar mass M_n and dispersity D values were extrapolated from a range of linear poly(methyl methacrylate) standards between 800 and $2.2 \times 10^6\text{ g mol}^{-1}$ and linear polystyrene standards between 370 and $2.52 \times 10^6\text{ g mol}^{-1}$.

Attenuated Total Reflection (ATR) Fourier-Transform (FT) Infrared (IR) Spectroscopy

ATR-FT-IR spectra were recorded on a Bruker Vertex 80 from $500 - 4000\text{ cm}^{-1}$ at $25\text{ }^{\circ}\text{C}$.

Gas Chromatography – Mass Spectrometry (GC-MS)

GC-MS measurements were performed on a Varian 431 GC instrument with a capillary column FactorFour™ VF-5 ms ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) and a Varian 210 ion trap mass detector.

Electrochemical Equipment

The commercially available IKA ElectraSyn 2.0 potentiostat as well as the respective IKA vial (5 mL) equipped with a septum on the outlet and an argon-filled balloon on top were used for the electrochemically-initiated polymerization of DFPA, PFPA, and GMA. Commercially available zinc and graphite electrodes from IKA were employed as anode and cathode material, respectively. After completion of the reaction, the electrodes were detached from the vial cap, rinsed with THF and acetone, and wiped with an acetone-soaked wipe. Thereafter, the surfaces of the electrodes were carefully scratched off with an APOLLO Ever-Sharp Blade and eventually wiped with an acetone-soaked wipe again. For the case of DFPA, the electrode was subsequently placed in a vial filled with acetone and placed in an ultrasonic bath. The acetone was changed three times and the electrode was again wiped with an acetone-soaked wipe.



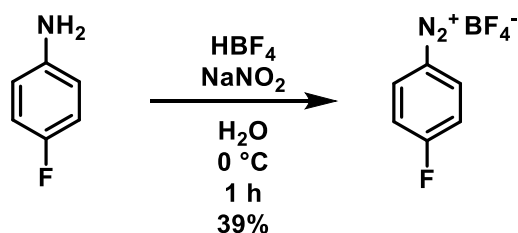
Figure S1. A fully commercial IKA ElectraSyn 2.0 setup involving an undivided cell was used for the electrochemically-initiated polymerization of reactive monomers.

Cyclic Voltammetry (CV)

CV measurements were performed on a Metrohm Autolab PGSTAT128N potentiostat featuring a glassy carbon working electrode, a Pt-wire counter electrode and an Ag/AgCl reference electrode with a scan rate of 50 mV s^{-1} . Therefore, the analytes (10 mM) and tetrabutylammonium tetrafluoroborate (0.1 M) were dissolved in anhydrous acetonitrile (10 mL) and the solution was deoxygenated by nitrogen purging for 15 minutes.

2. Initiator Synthesis

2.1 Synthesis of 4-fluorobenzenediazonium tetrafluoroborate



4-Fluoroaniline (0.566 g, 5.00 mmol, 1.00 eq.) was dissolved in distilled water (2.5 mL) and 48 wt% solution of tetrafluoroboric acid (HBF₄) in water (1.7 mL). The solution was cooled to 0 °C and sodium nitrite (0.345 g, 5.00 mmol, 1.00 eq.) in distilled water (1.0 mL) was added dropwise. The reaction was stirred for 1 hour at 0 °C and the mixture was filtered. The solid obtained thereafter was dissolved in a minimum amount of acetone. Diethyl ether was added until precipitation of the diazonium salt. The precipitate was washed thoroughly with diethyl ether and dried under vacuum giving a colorless solid (0.41 g, 39%).

¹H NMR (acetone-*d*₆): δ / ppm = 8.98 – 9.04 (m, 2H, H_a), 7.87 – 7.94 (m, 2H, H_b).

¹³C NMR (acetone-*d*₆): δ / ppm = 170.43, 138.06, 120.59, 112.21.

¹⁹F NMR (acetone-*d*₆): δ / ppm = -86.66 (tq, J = 8.3, 4.2 Hz, 1F, F_a), -151.09 (d, J = 20.3 Hz, 4F, F_b).

ATR-FT-IR: $\tilde{\nu}$ / cm⁻¹ = 3116, 2360, 2295, 1579, 1484, 1432, 1330, 1305, 1260, 1250, 1167, 1118, 1013, 850, 836, 807, 769, 685, 668.

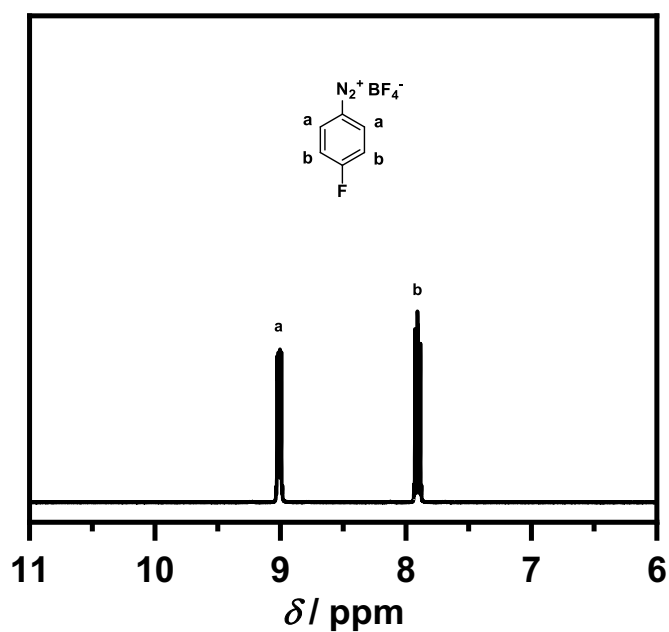


Figure S2. ^1H NMR spectrum of 4-fluorobenzenediazonium tetrafluoroborate; solvent: acetone- d_6 .

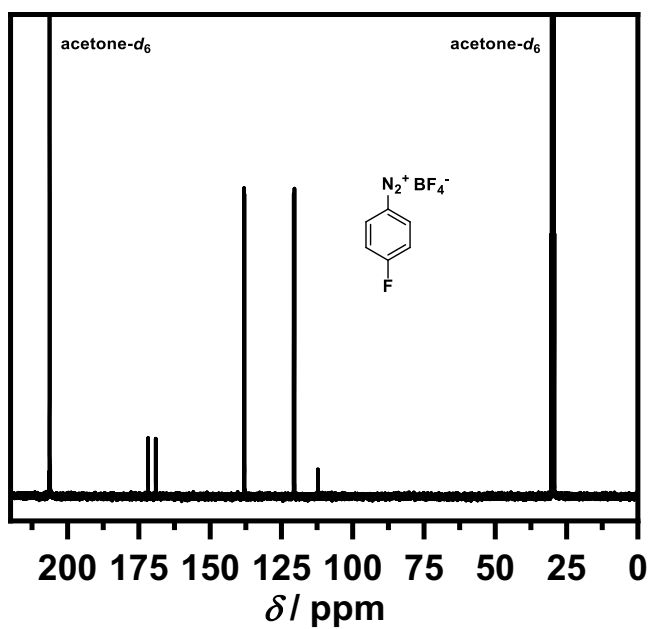


Figure S3. ^{13}C NMR spectrum of 4-fluorobenzenediazonium tetrafluoroborate; solvent: acetone- d_6 .

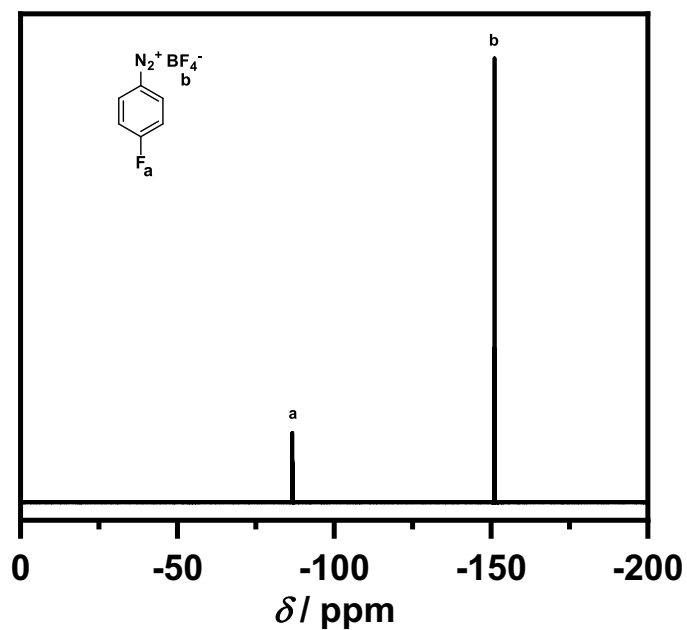


Figure S4. ^{19}F NMR spectrum of 4-fluorobenzenediazonium tetrafluoroborate; solvent: acetone- d_6 .

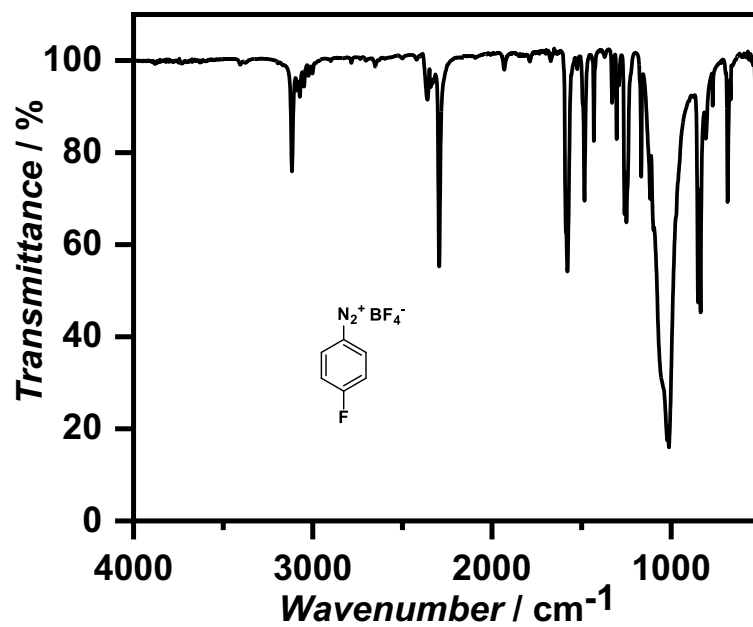


Figure S5. ATR-FT-IR spectrum of 4-fluorobenzenediazonium tetrafluoroborate.

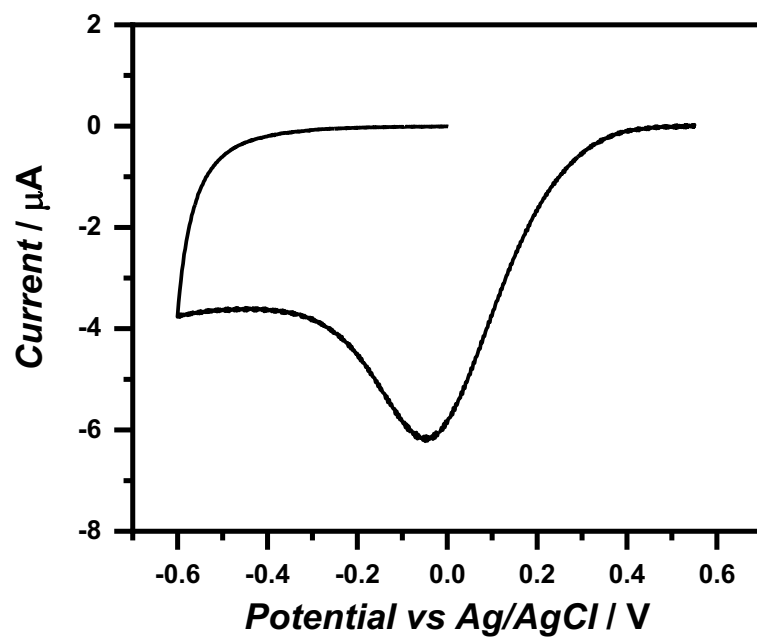
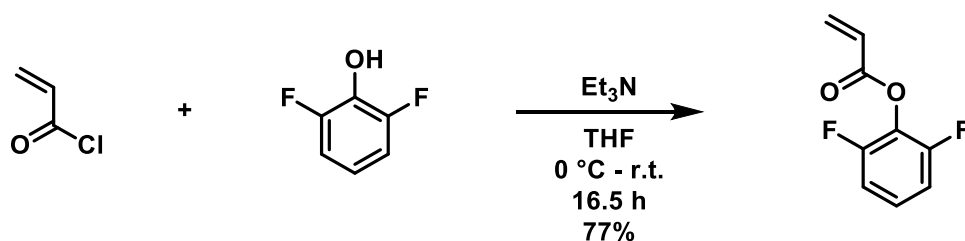


Figure S6. Cyclic voltammogram of 4-fluorobenzenediazonium tetrafluoroborate against an Ag/AgCl reference electrode with a scan rate of 50 mV s^{-1} .

3. Monomer Synthesis

3.1 Synthesis of 2,6-difluorophenyl acrylate (DFPA)



2,6-Difluorophenol (2.00 g, 15.37 mmol, 1.00 eq.) was dissolved in anhydrous THF (30 mL). The solution was cooled to 0 °C and triethyl amine (2.6 mL, 1.87 g, 18.45 mmol, 1.20 eq.) was added. A solution of acryloyl chloride (1.5 mL, 1.67 g, 18.45 mmol, 1.20 eq.) in anhydrous THF (10 mL) was added slowly and the mixture was stirred for one hour at 0 °C and for 15.5 hours at ambient temperature. The solvent was removed under reduced pressure and diethyl ether (50 mL) was added. The organic phase was washed with water (3 × 50 mL) and with brine (1 × 50 mL). The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using a 20:1 mixture of cyclohexane / ethyl acetate as eluent giving a yellowish liquid (2.19 g, 77%).

R_f (CH / EE 20:1) = 0.39

¹H NMR (acetone-*d*₆): δ / ppm = 7.34 – 7.43 (m, 1H, H_a), 7.15 – 7.23 (m, 2H, H_b), 6.68 (dd, J = 17.3, 1.2 Hz, 1H, H_c), 6.48 (dd, J = 17.3, 10.4 Hz, 1H, H_d), 6.24 (dd, J = 10.4, 1.2 Hz, 1H, H_c).

¹³C NMR (CDCl₃): δ / ppm = 162.52, 155.35, 134.12, 127.13, 126.43, 126.28, 112.09.

¹⁹F NMR (acetone-*d*₆): δ / ppm = -128.34 – -128.47 (m, 2F).

ATR-FT-IR: $\tilde{\nu}$ / cm⁻¹ = 1755, 1611, 1479, 1405, 1294, 1246, 1202, 1127, 1069, 1012, 981, 888, 775, 735, 697.

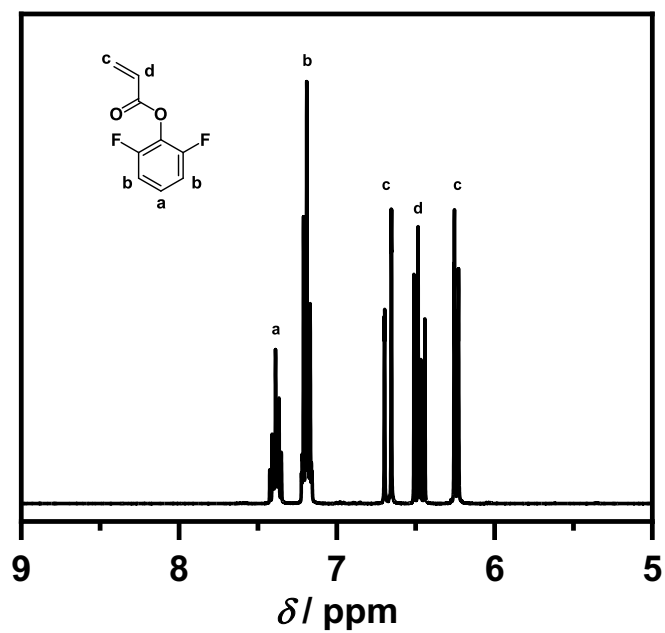


Figure S7. ^1H NMR spectrum of 2,6-difluorophenyl acrylate (DFPA); solvent: acetone- d_6 .

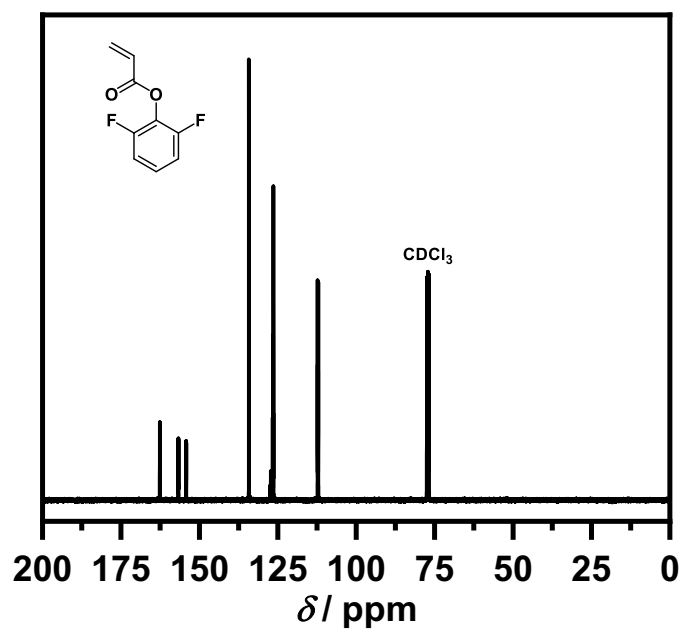


Figure S8. ^{13}C NMR spectrum of 2,6-difluorophenyl acrylate (DFPA); solvent: CDCl_3 .

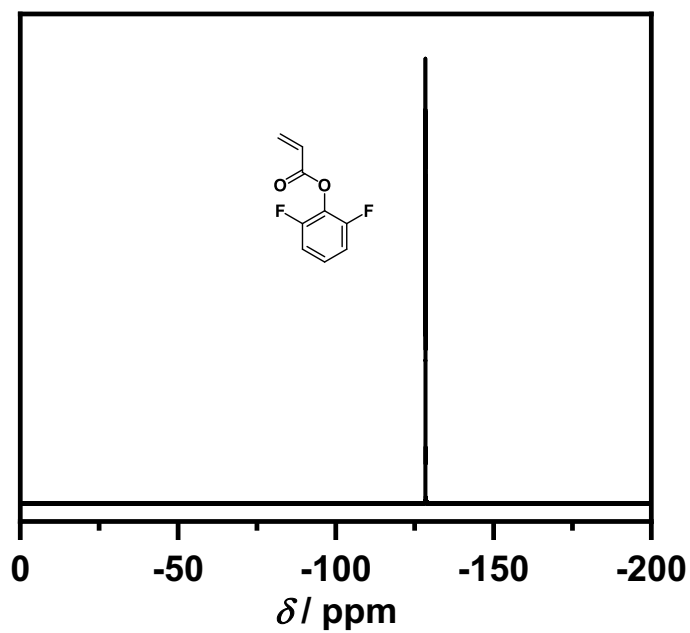


Figure S9. ^{19}F NMR spectrum of 2,6-difluorophenyl acrylate (DFPA); solvent: acetone- d_6 .

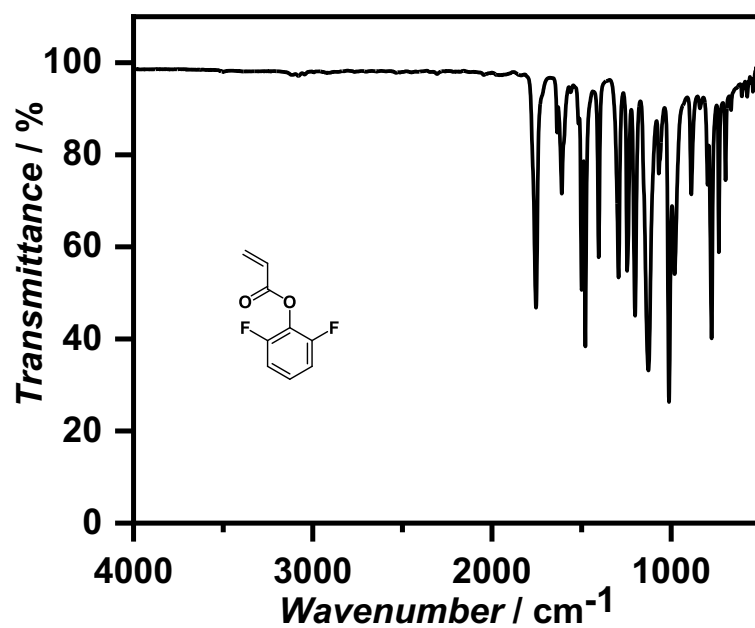


Figure S10. ATR-FT-IR spectrum of 2,6-difluorophenyl acrylate (DFPA).

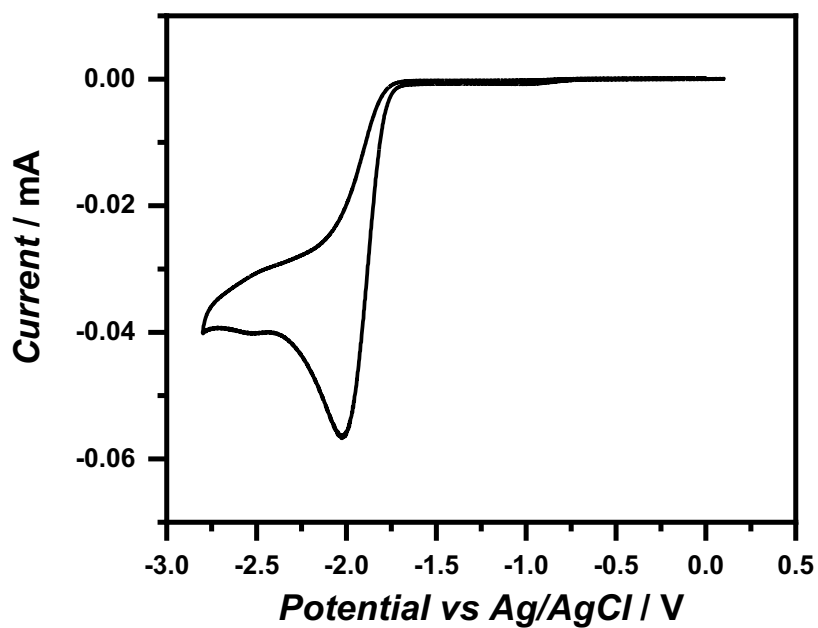


Figure S11. Cyclic voltammogram of DFPA against an Ag/AgCl reference electrode with a scan rate of 50 mV s^{-1} .

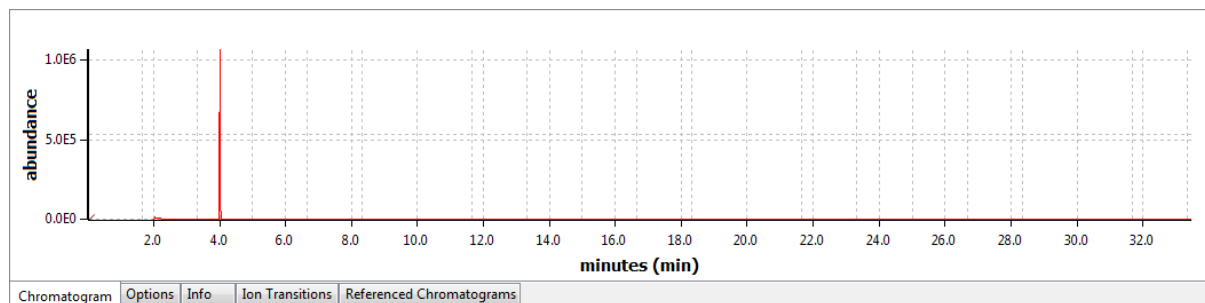
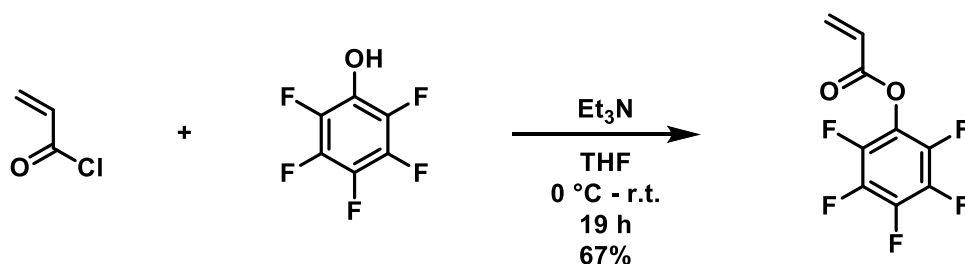


Figure S12. Gas chromatogram of DFPA.

3.2 Synthesis of pentafluorophenyl acrylate (PFPA)



Pentafluorophenol (6.00 g, 32.60 mmol, 1.00 eq.) was dissolved in anhydrous THF (40 mL). The solution was cooled to 0 °C and triethylamine (5.5 mL, 3.96 g, 39.12 mmol, 1.20 eq.) was added. A solution of acryloyl chloride (3.2 mL, 3.54 g, 39.12 mmol, 1.20 eq.) in anhydrous THF (10 mL) was added slowly and the mixture was stirred for one hour at 0 °C and 18 hours at ambient temperature. The solvent was removed under reduced pressure and diethyl ether (75 mL) was added. The organic phase was washed with water (3 × 75 mL) and with brine (1 × 75 mL). The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using petroleum ether as eluent giving a colorless liquid (5.20 g, 67%).

R_f(PE) = 0.31

¹H NMR (CDCl₃): δ / ppm = 6.72 (dd, *J* = 17.3, 0.9 Hz, 1H, H_a), 6.37 (dd, *J* = 17.3, 10.5 Hz, 1H, H_b), 6.18 (dd, *J* = 10.5, 1.0 Hz, 1H, H_a).

¹³C NMR (CDCl₃): δ / ppm = 161.83, 142.64, 140.99, 140.14, 139.31, 138.44, 136.81, 135.63, 125.49, 124.94 – 125.38.

¹⁹F NMR (CDCl₃): δ / ppm = -152.21 – -152.65 (m, 2F, F_a), -157.93 (t, *J* = 21.8 Hz, 1F, F_b), -162.24 – -162.162.42 (m, 2F, F_c).

ATR-FT-IR: $\tilde{\nu}$ / cm⁻¹ = 1771, 1634, 1516, 1472, 1406, 1292, 1218, 1112, 1070, 1030, 994, 870, 796.

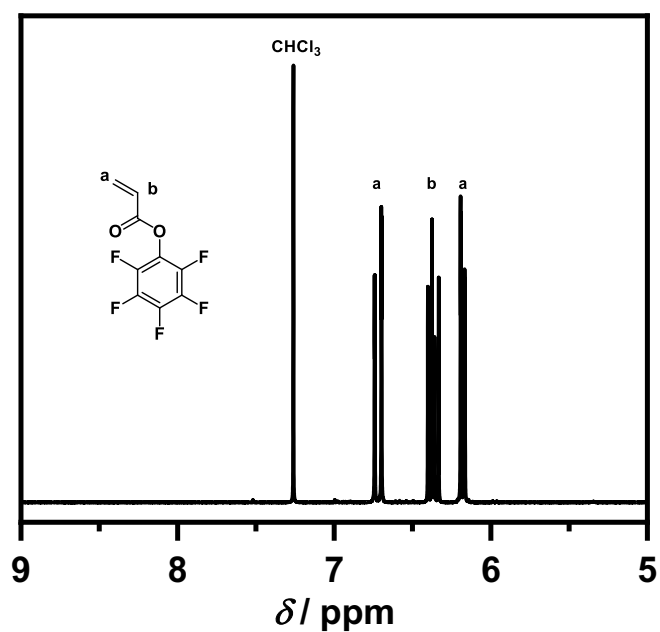


Figure S13. ^1H NMR spectrum of pentafluorophenyl acrylate (PFPA); solvent: CDCl_3 .

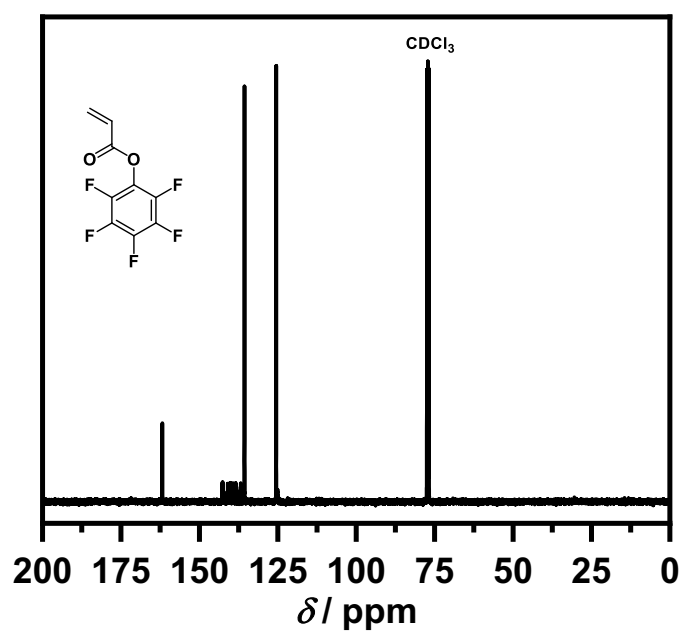


Figure S14. ^{13}C NMR spectrum of pentafluorophenyl acrylate (PFPA); solvent: CDCl_3 .

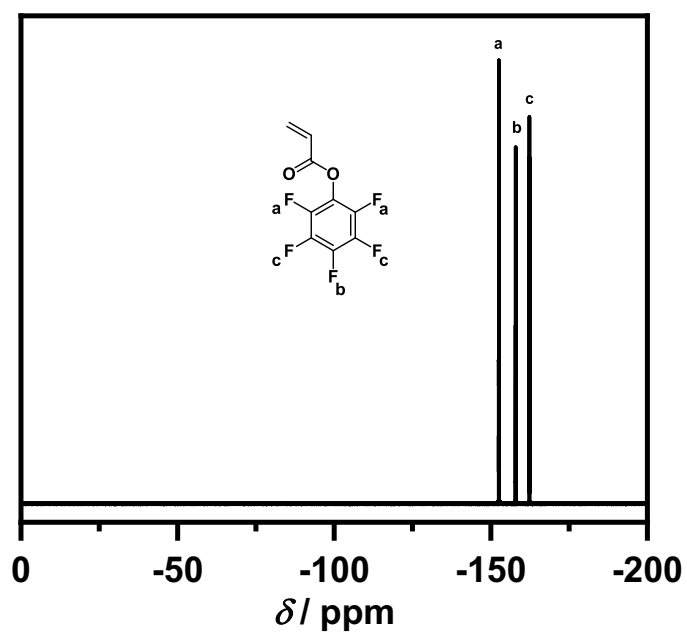


Figure S15. ^{19}F NMR spectrum of pentafluorophenyl acrylate (PFPA); solvent: CDCl_3 .

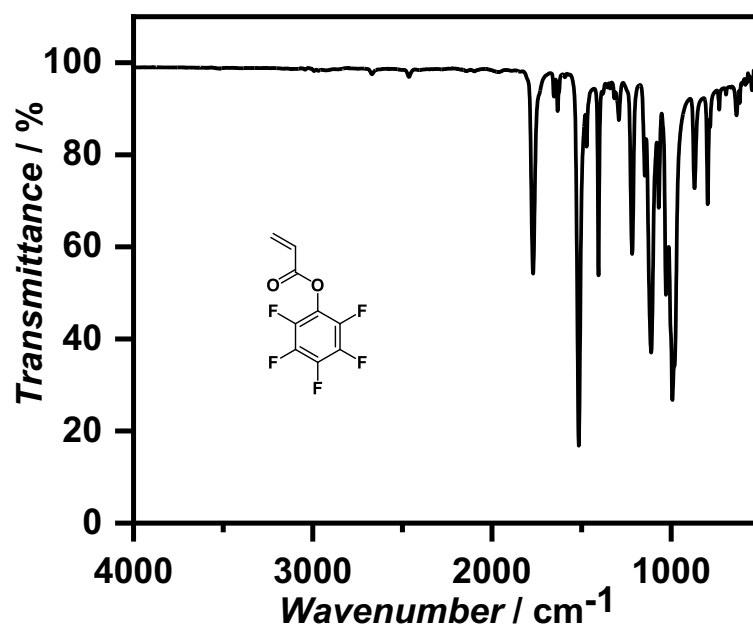


Figure S16. ATR-FT-IR spectrum of pentafluorophenyl acrylate (PFPA).

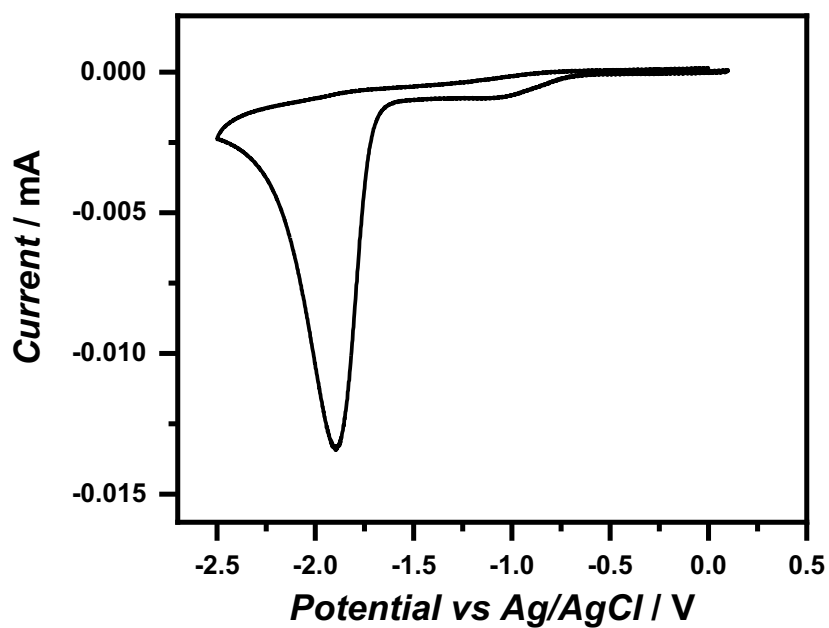


Figure S17. Cyclic Voltammogram of PFPA against an Ag/AgCl reference electrode with a scan rate of 50 mV s^{-1} .

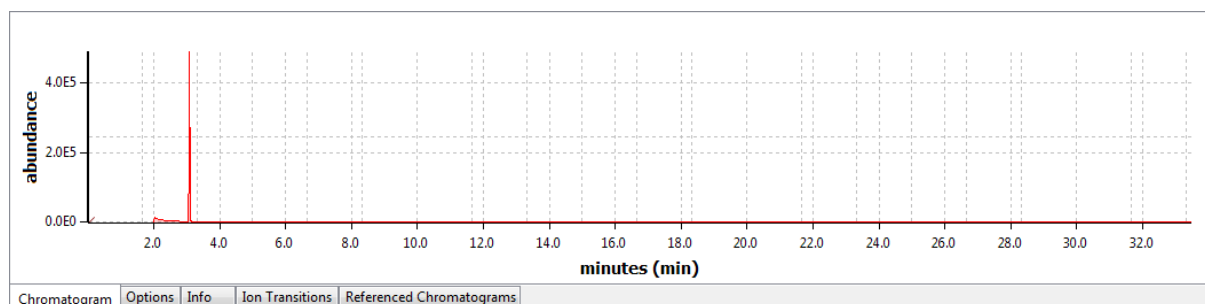
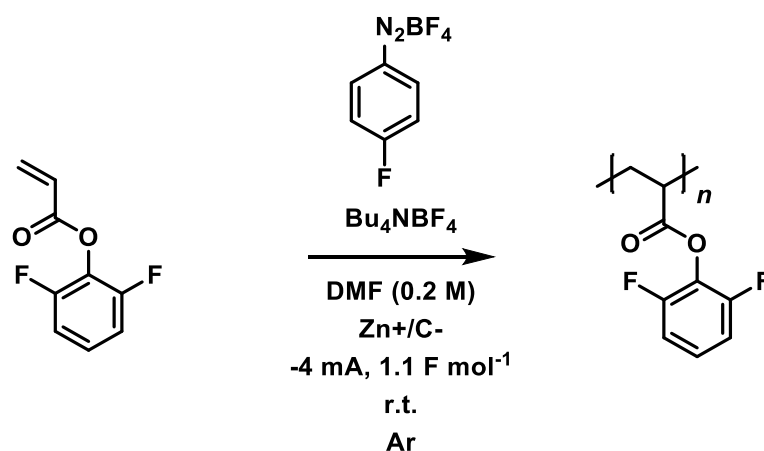


Figure S18. Gas chromatogram of PFPA.

4. Polymerization Procedures

4.1 Electrochemically-Initiated Polymerization of DFPA



A dry ElectraSyn vial (5 mL) was charged with DFPA (see Table for equivalents), tetrabutylammonium tetrafluoroborate (0.132 g, 0.40 mmol, 0.2 M), 4-fluorobenzenediazonium tetrafluoroborate (0.025 g, 0.12 mmol, 1.00 eq.), and anhydrous DMF (2 mL). The vial was closed with the respective IKA ElectraSyn cap bearing a zinc sacrificial anode and a graphite cathode and the solution was deoxygenated by argon purging for 15 minutes. A constant current of -4 mA was applied until 1.1 F mol^{-1} passed through the system. The electrodes were rinsed with THF and acetone. The mixture was precipitated in cold methanol, the solids obtained by centrifugation were dissolved in acetone and filtered (to remove graphite from the mixture) prior to a second precipitation in cold methanol. The solids were obtained by centrifugation and dried under vacuum giving a yellowish solid.

Table 1. Experimental details and results of the electrochemically-initiated polymerization of DFPA. ^a Determined by ¹H NMR spectroscopy; ^b determined by ¹⁹F NMR spectroscopy; ^c determined by SEC using THF as eluent; ^d determined by SEC using DMAc as eluent; ^e PMMA calibration; ^f PS calibration.

Entry	Eq. DFPA	M_n^a g mol ⁻¹	M_n^b g mol ⁻¹	M_n^c g mol ⁻¹	\mathcal{D}^c	M_n^d g mol ⁻¹	\mathcal{D}^d
1	10.00	-	35250	16800 ^e	1.83 ^e	14600 ^e	2.49 ^e
				15300 ^f	1.75 ^f	17300 ^f	2.23 ^f
2	5.00	-	21330	11300 ^e	1.58 ^e	8900 ^e	2.13 ^e
				10500 ^f	1.50 ^f	11000 ^f	1.89 ^f

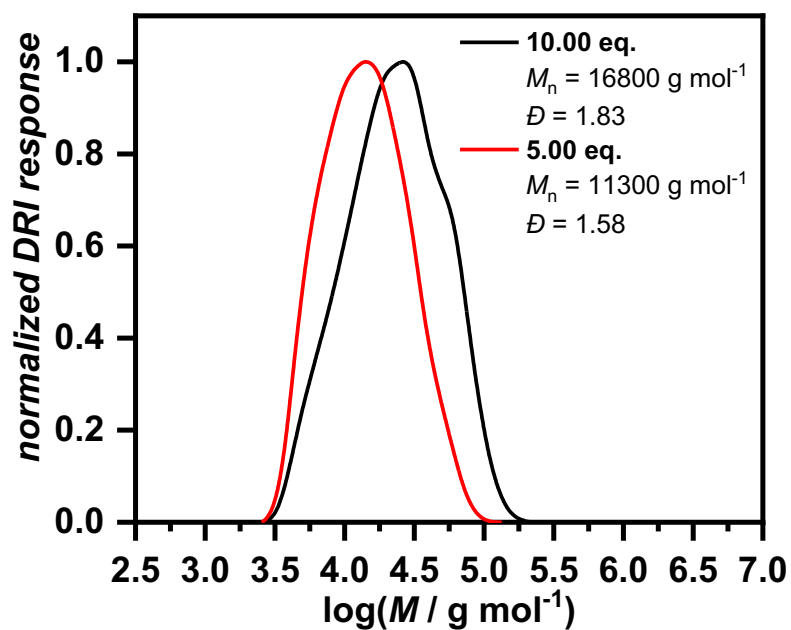


Figure S19. Comparison of SEC traces using THF as eluent (PMMA calibration) of the polymers obtained by the electrochemically-initiated polymerization of DFPA.

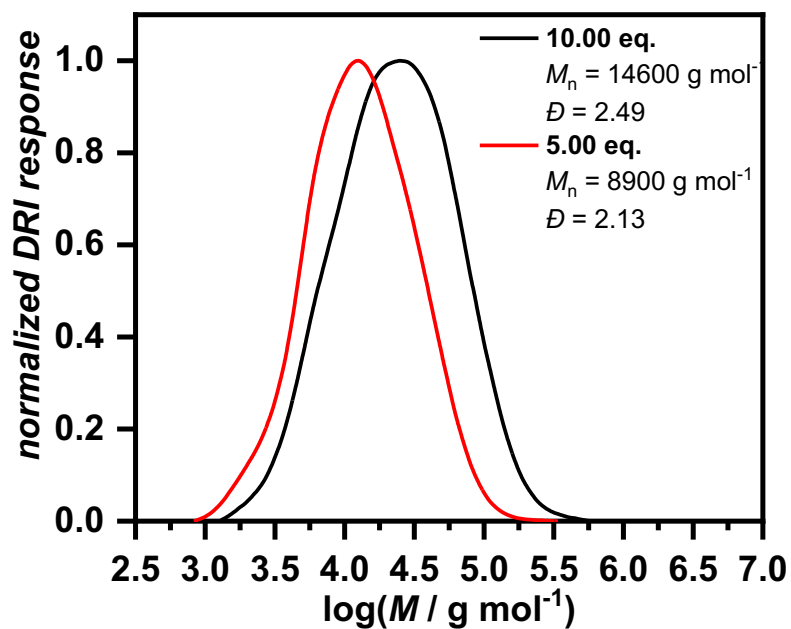


Figure S20. Comparison of SEC traces using DMAc as eluent (PMMA calibration) of the polymers obtained by the electrochemically-initiated polymerization of DFPA.

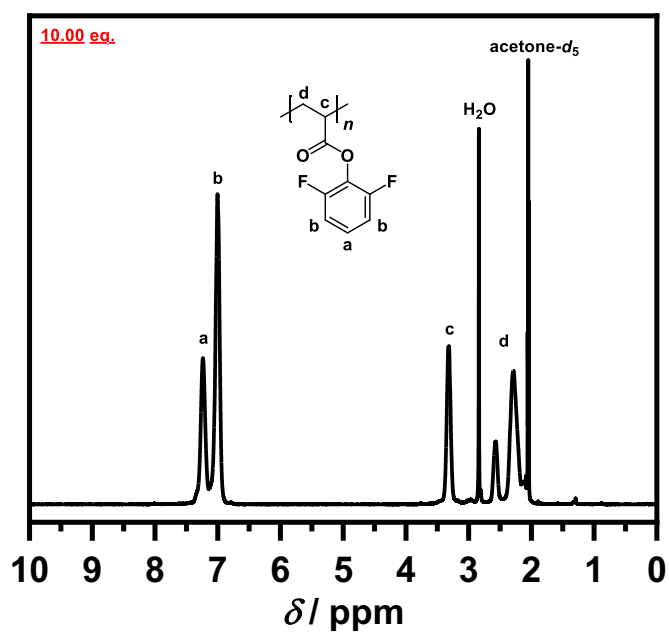


Figure S21. ^1H NMR spectrum of PDFPA obtained by the electrochemically-initiated polymerization of DFPA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

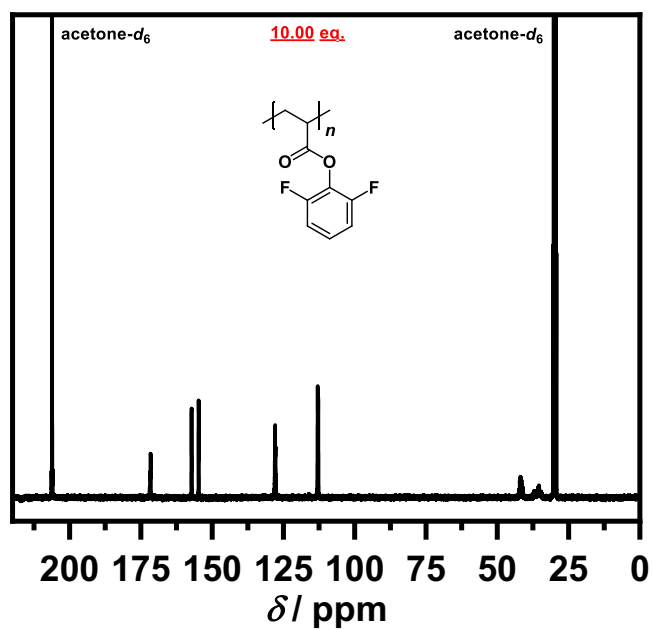


Figure S22. ^{13}C NMR spectrum of PDFPA obtained by the electrochemically-initiated polymerization of DFPA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

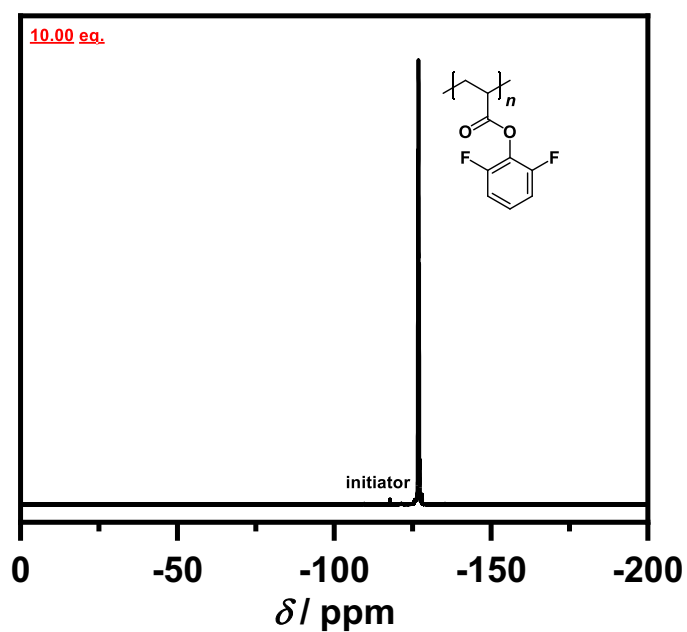


Figure S23. ^{19}F NMR spectrum of PDFPA obtained by the electrochemically-initiated polymerization of DFPA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

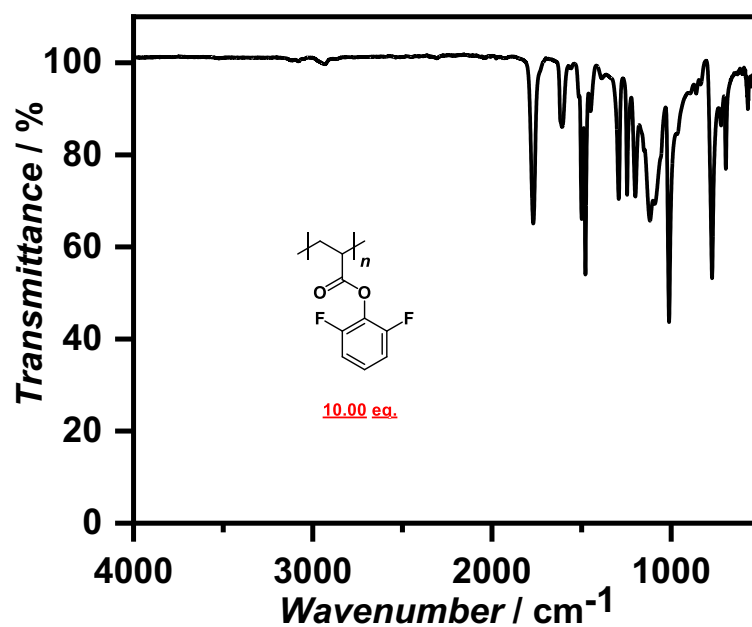


Figure S24. ATR-FT-IR spectrum of PDFPA obtained by the electrochemically-initiated polymerization of DFPA (10.00 eq. with respect to the initiator).

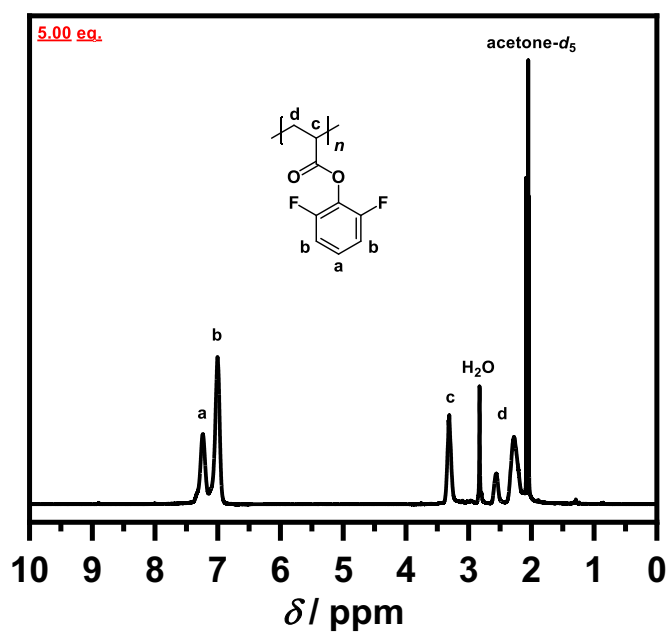


Figure S25. ^1H NMR spectrum of PDFPA obtained by the electrochemically-initiated polymerization of DFPA (5.00 eq. with respect to the initiator); solvent: acetone- d_6 .

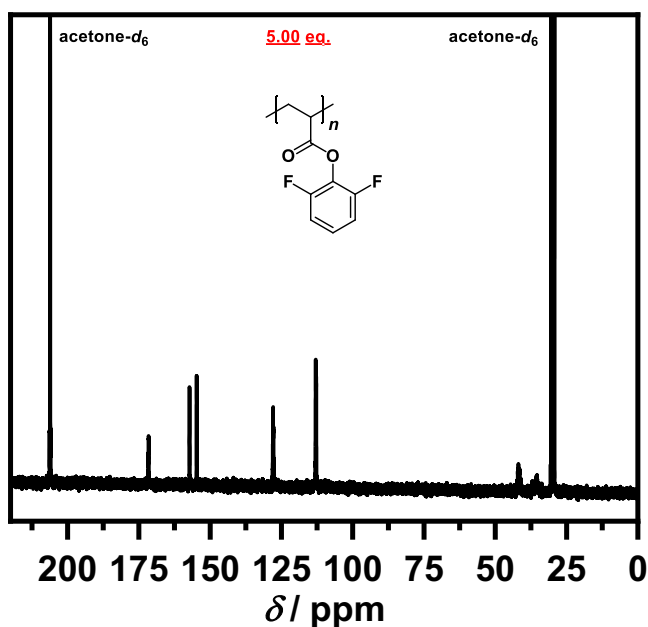


Figure S26. ^{13}C NMR spectrum of PDFPA obtained by the electrochemically-initiated polymerization of DFPA (5.00 eq. with respect to the initiator); solvent: acetone- d_6 .

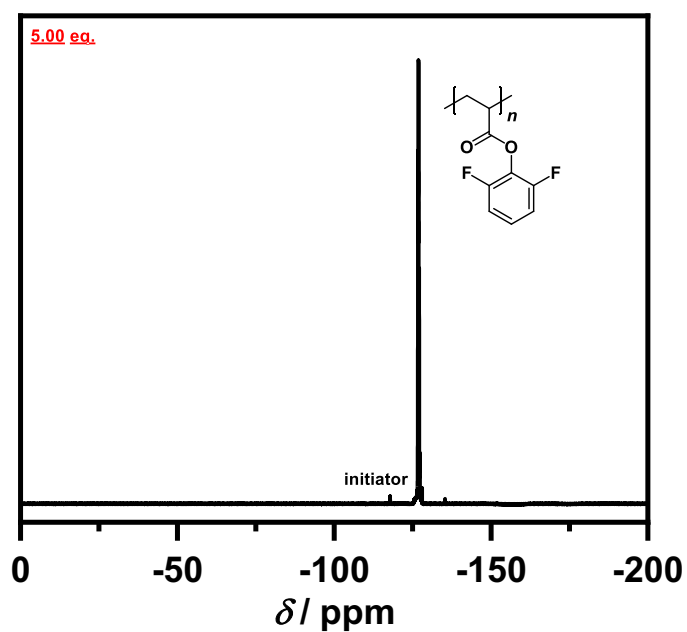
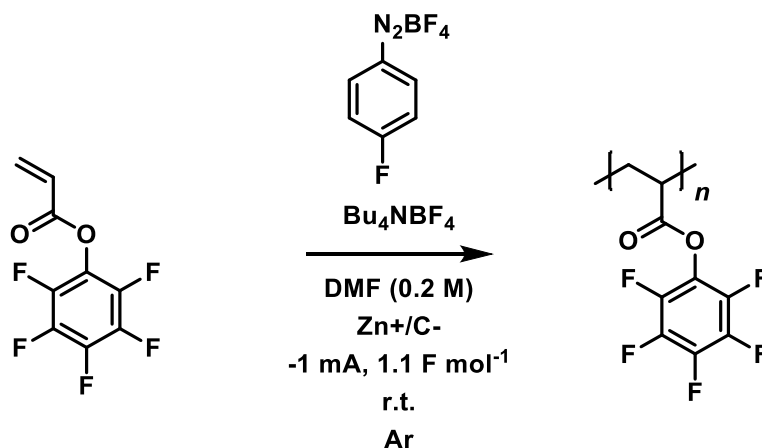


Figure S27. ^{19}F NMR spectrum of PDFPA obtained by the electrochemically-initiated polymerization of DFPA (5.00 eq. with respect to the initiator); solvent: acetone- d_6 .

4.2 Electrochemically-Initiated Polymerization of PFPA



A dry ElectraSyn vial (5 mL) was charged with PFPA (see Table for equivalents), tetrabutylammonium tetrafluoroborate (0.132 g, 0.40 mmol, 0.2 M), 4-fluorobenzenediazonium tetrafluoroborate (0.025 g, 0.12 mmol, 1.00 eq.), and anhydrous DMF (2 mL). The vial was closed with the respective IKA ElectraSyn cap bearing a zinc sacrificial anode and a graphite cathode and the solution was deoxygenated by argon purging for 15 minutes. A constant current of -1 mA was applied until 1.1 F mol⁻¹ passed through the system. The electrodes were rinsed with THF and acetone. The mixture was precipitated in cold methanol, the solids obtained by centrifugation were dissolved in acetone and filtered (to remove graphite from the mixture) prior to a second precipitation in cold methanol. The solids were obtained by centrifugation and dried under vacuum giving a yellowish solid.

Table 2. Experimental details and results of the electrochemically-initiated polymerization of PFPA. ^a Determined by ¹H NMR spectroscopy; ^b determined by ¹⁹F NMR spectroscopy; ^c determined by SEC using THF as eluent; ^d determined by SEC using DMAc as eluent; ^e PMMA calibration; ^f PS calibration; ^g monomer concentration too high, viscous mixture and formation of hardly soluble material between electrodes; ^h -2 mA instead of -1 mA.

Entry	Eq. PFPA	M_n^a g mol ⁻¹	M_n^b g mol ⁻¹	M_n^c g mol ⁻¹	D^c	M_n^d g mol ⁻¹	D^d
<i>1</i> ^g	40.00	33240	40180	41800 ^e	2.30 ^e	30300 ^e	2.48 ^e
				37000 ^f	2.28 ^f	34300 ^f	2.29 ^f
2	10.00	22630	35030	19200 ^e	1.83 ^e	13900 ^e	2.03 ^e
				17400 ^f	1.76 ^f	16500 ^f	1.83 ^f
3	5.00	14170	24480	13600 ^e	1.61 ^e	9900 ^e	1.82 ^e
				12500 ^f	1.53 ^f	12000 ^f	1.65 ^f
<i>4</i> ^h	5.00	14290	22500	13200 ^e	1.59 ^e	9500 ^e	1.72 ^e
				12100 ^f	1.52 ^f	11500 ^f	1.57 ^f

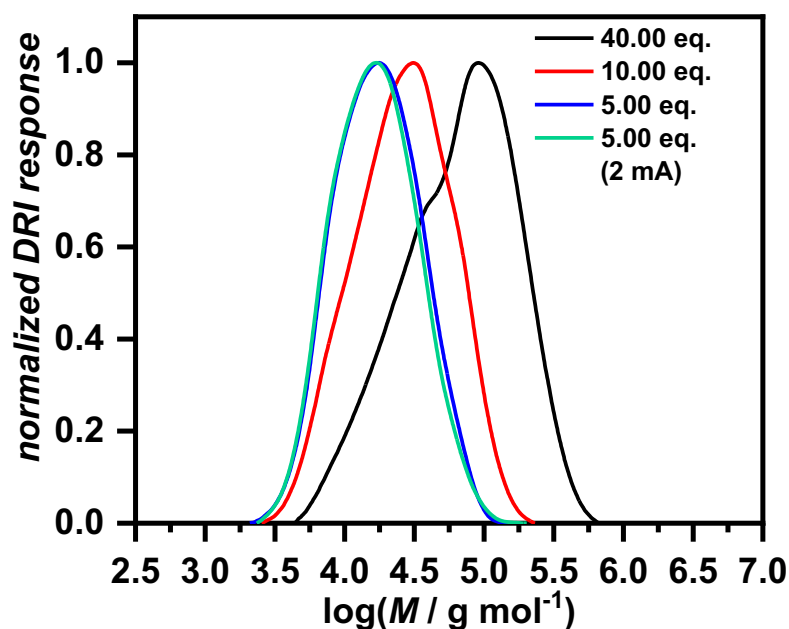


Figure S28. Comparison of SEC traces using THF as eluent (PMMA calibration) of the polymers obtained by the electrochemically-initiated polymerization of PFPA.

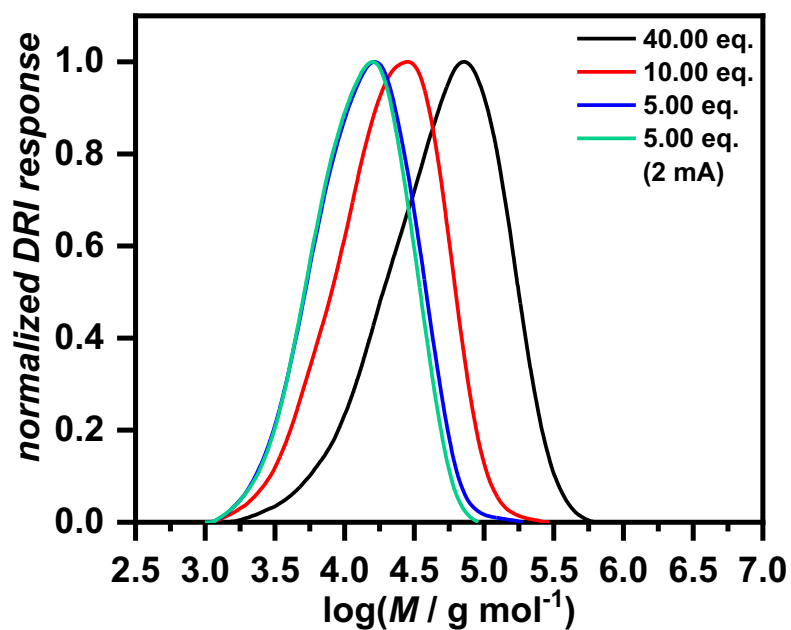


Figure S29. Comparison of SEC traces using DMAc as eluent (PMMA calibration) of the polymers obtained by the electrochemically-initiated polymerization of PFPA.

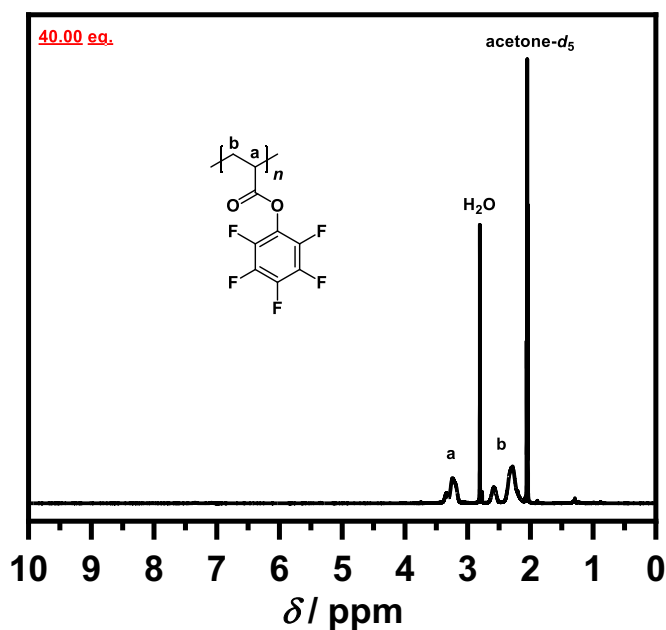


Figure S30. ^1H NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (40.00 eq. with respect to the initiator); solvent: acetone- d_6 .

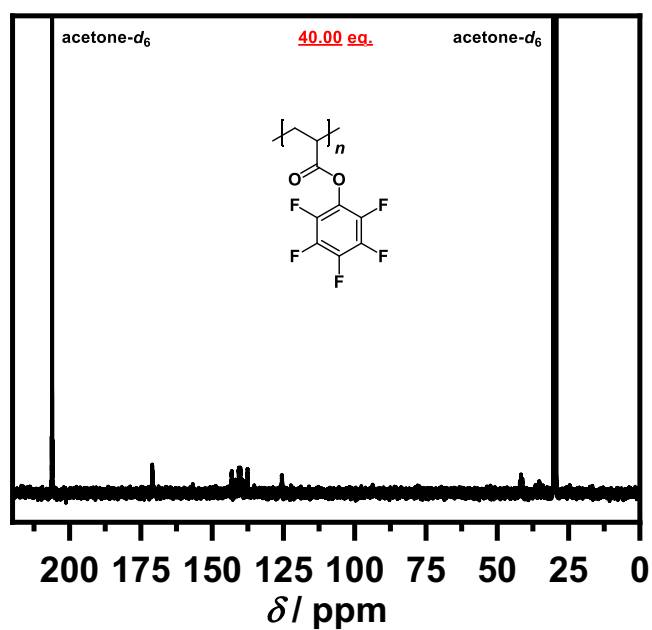


Figure S31. ^{13}C NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (40.00 eq. with respect to the initiator); solvent: acetone- d_6 .

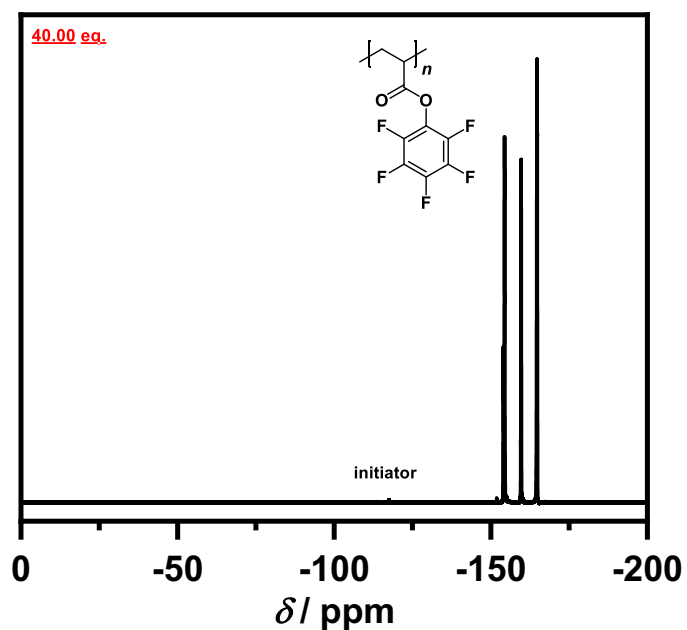


Figure S32. ^{19}F NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (40.00 eq. with respect to the initiator); solvent: acetone- d_6 .

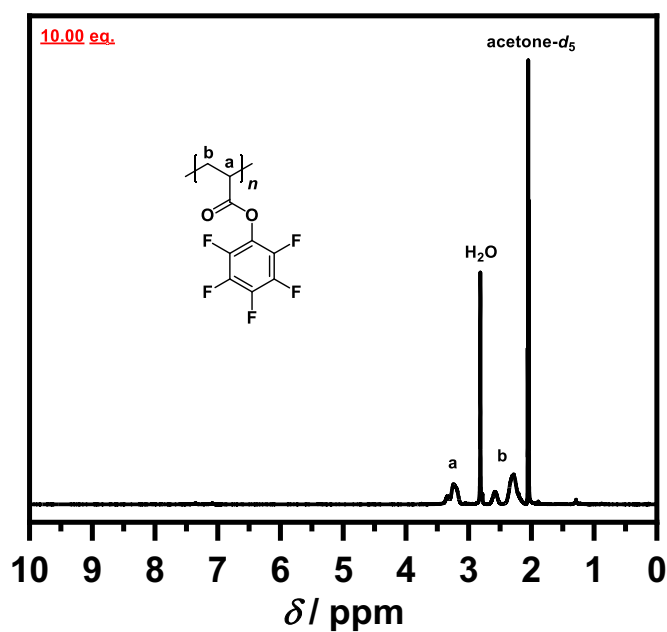


Figure S33. ^1H NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

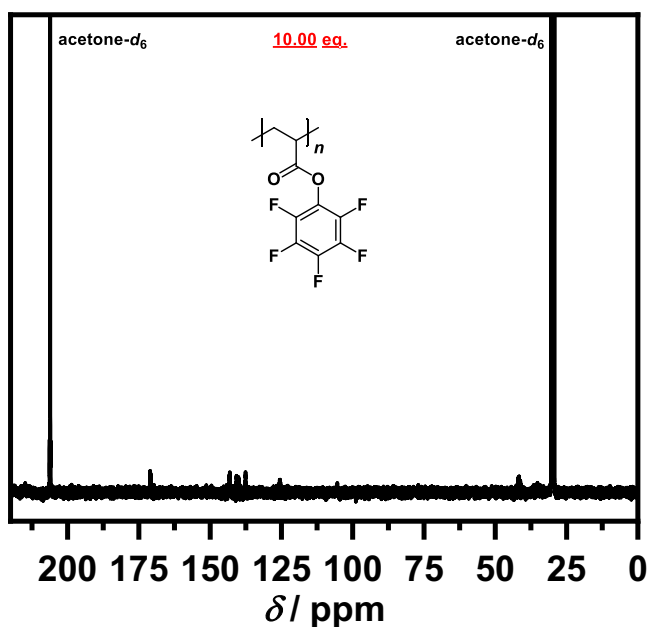


Figure S34. ^{13}C NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

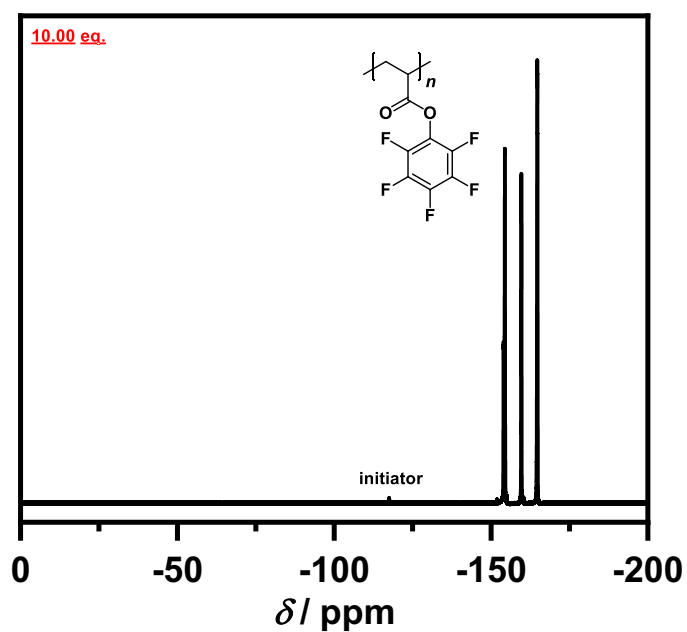


Figure S35. ^{19}F NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

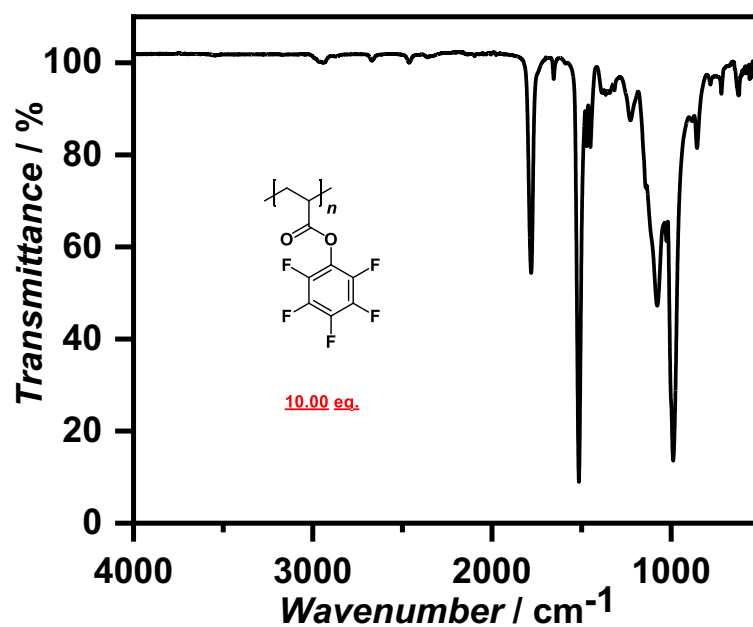


Figure S36. ATR-FT-IR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (10.00 eq. with respect to the initiator).

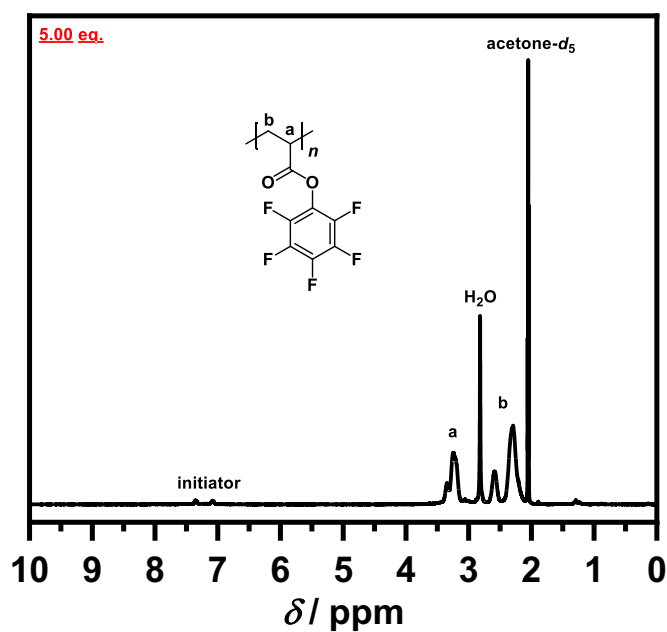


Figure S37. ^1H NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (5.00 eq. with respect to the initiator); solvent: acetone- d_6 .

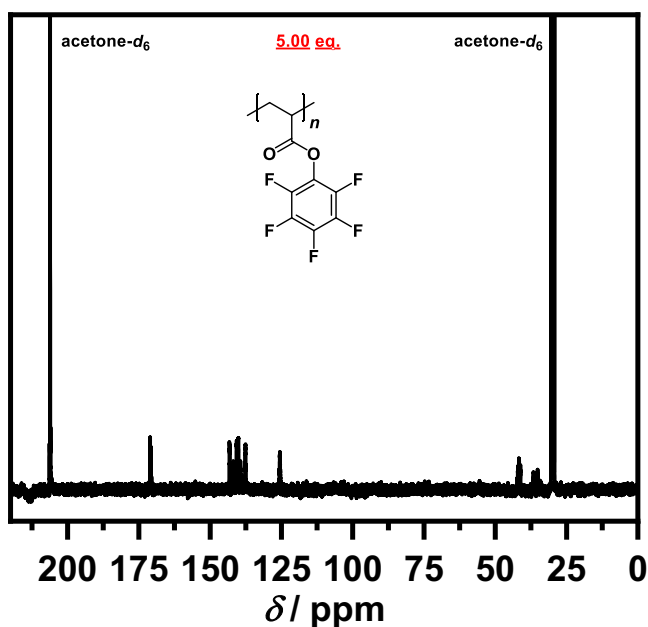


Figure S38. ^{13}C NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (5.00 eq. with respect to the initiator); solvent: acetone- d_6 .

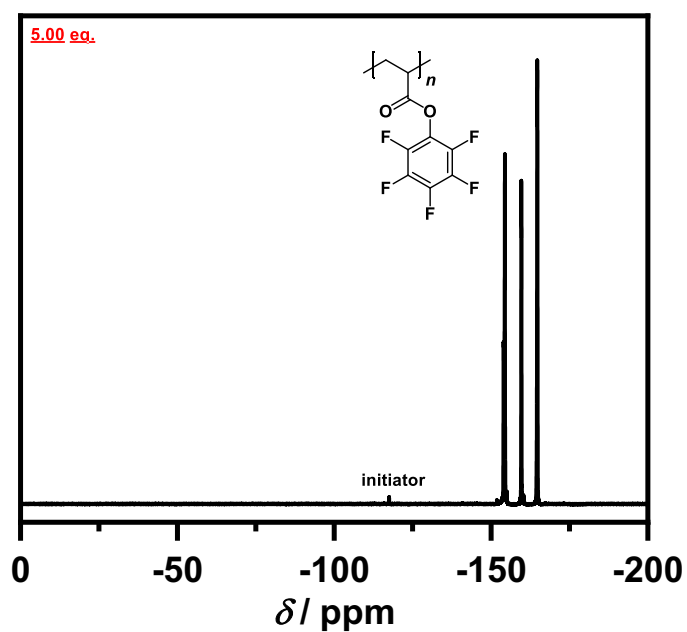


Figure S39. ^{19}F NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (5.00 eq. with respect to the initiator); solvent: acetone- d_6 .

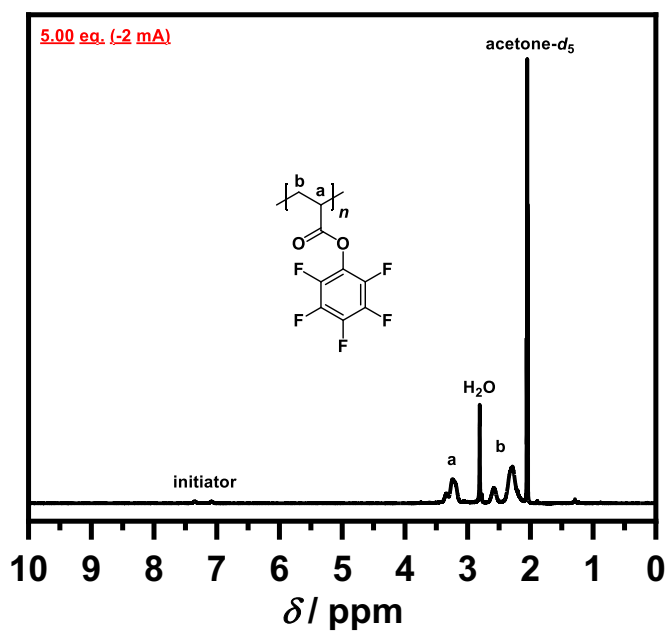


Figure S40. ^1H NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (5.00 eq. with respect to the initiator, -2 mA); solvent: acetone- d_6 .

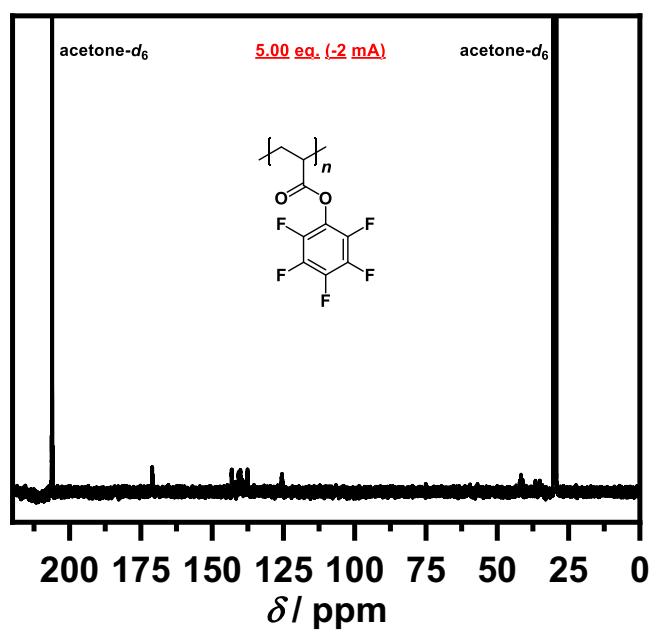


Figure S41. ^{13}C NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (5.00 eq. with respect to the initiator, -2 mA); solvent: acetone- d_6 .

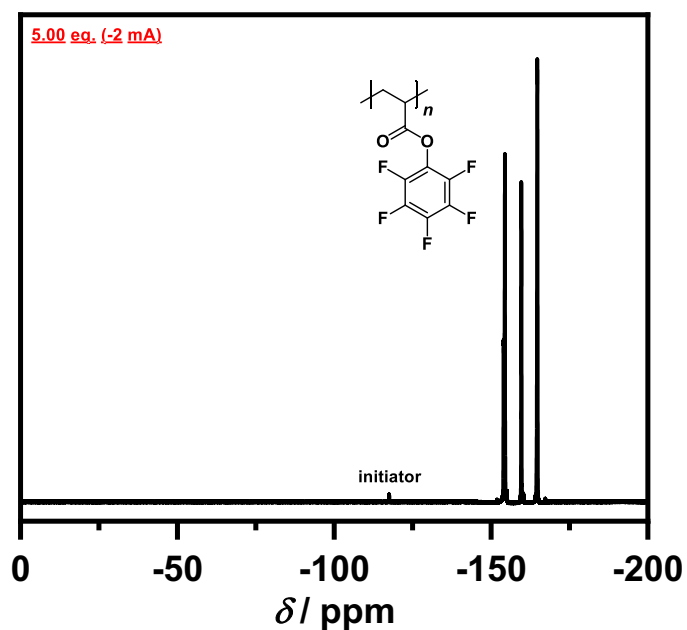


Figure S42. ^{19}F NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (5.00 eq. with respect to the initiator, -2 mA); solvent: acetone- d_6 .

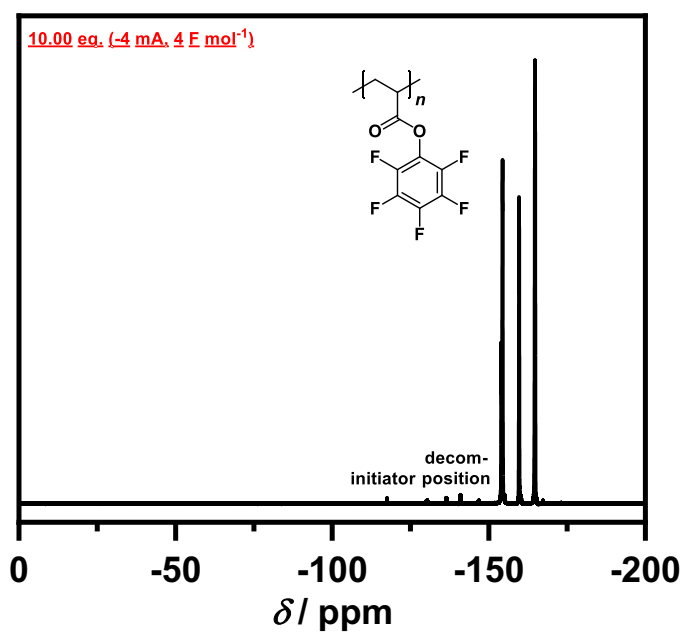
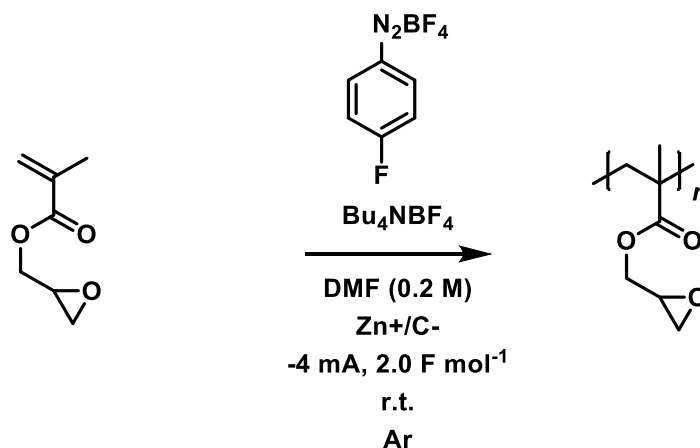


Figure S43. ¹⁹C NMR spectrum of PPFPA obtained by the electrochemically-initiated polymerization of PFPA (10.00 eq. with respect to the initiator, -4 mA for 4 F mol⁻¹), showing signs of decomposition and thus exhibiting the fragile nature of PPFPA; solvent: acetone-d₆.

4.3 Electrochemically-Initiated Polymerization of GMA



A dry ElectraSyn vial (5 mL) was charged with GMA (see Table for equivalents), tetrabutylammonium tetrafluoroborate (0.132 g, 0.40 mmol, 0.2 M), 4-fluorobenzenediazonium tetrafluoroborate (0.025 g, 0.12 mmol, 1.00 eq.), and anhydrous DMF (2 mL). The vial was closed with the respective IKA ElectraSyn cap bearing a zinc sacrificial anode and a graphite cathode and the solution was deoxygenated by argon purging for 15 minutes. A constant current of -4 mA was applied until 2.0 F mol⁻¹ passed through the system. The electrodes were rinsed with THF and acetone. The mixture was precipitated in cold methanol, the solids obtained by centrifugation were dissolved in acetone and filtered (to remove graphite from the mixture) prior to a second precipitation in cold methanol. The solids were obtained by centrifugation and dried under vacuum giving an off-white solid.

Table 3. Experimental details and results of the electrochemically-initiated polymerization of GMA. ^a Determined by ¹H NMR spectroscopy; ^b determined by ¹⁹F NMR spectroscopy; ^c determined by SEC using THF as eluent; ^d determined by SEC using DMAc as eluent; ^e PMMA calibration; ^f PS calibration.

Entry	Eq. GMA	M_n^a g mol ⁻¹	M_n^b g mol ⁻¹	M_n^c g mol ⁻¹	\mathcal{D}^c	M_n^d g mol ⁻¹	\mathcal{D}^d
1	20.00	10350	-	8200 ^e	1.85 ^e	6200 ^e	2.40 ^e
				7900 ^f	1.71 ^f	8000 ^f	2.06 ^f
2	40.00	14500	-	15700 ^e	2.40 ^e	12600 ^e	3.10 ^e
				14700 ^f	2.24 ^f	15400 ^f	2.68 ^f
3	10.00	6970	-	6800 ^e	1.60 ^e	5200 ^e	2.00 ^e
				6500 ^f	1.50 ^f	6700 ^f	1.76 ^f

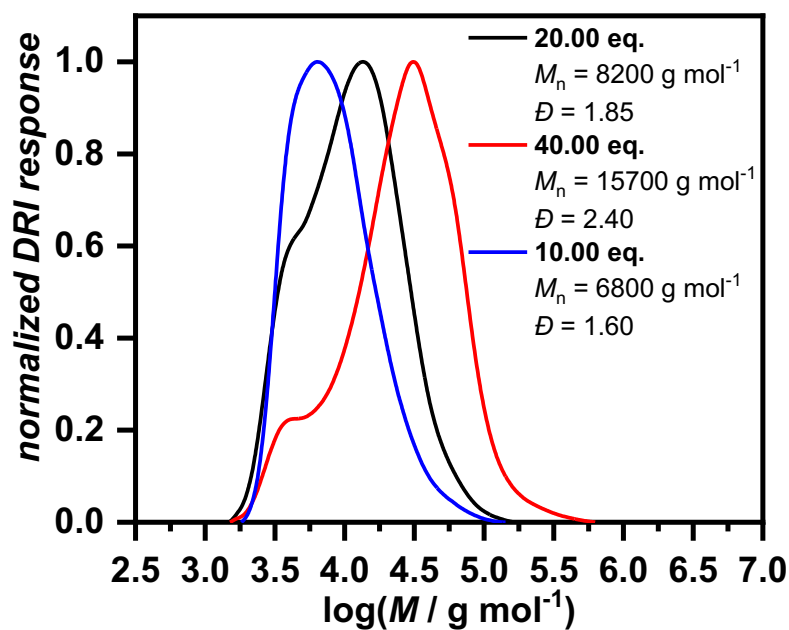


Figure S44. Comparison of SEC traces using THF as eluent (PMMA calibration) of the polymers obtained by the electrochemically-initiated polymerization of GMA.

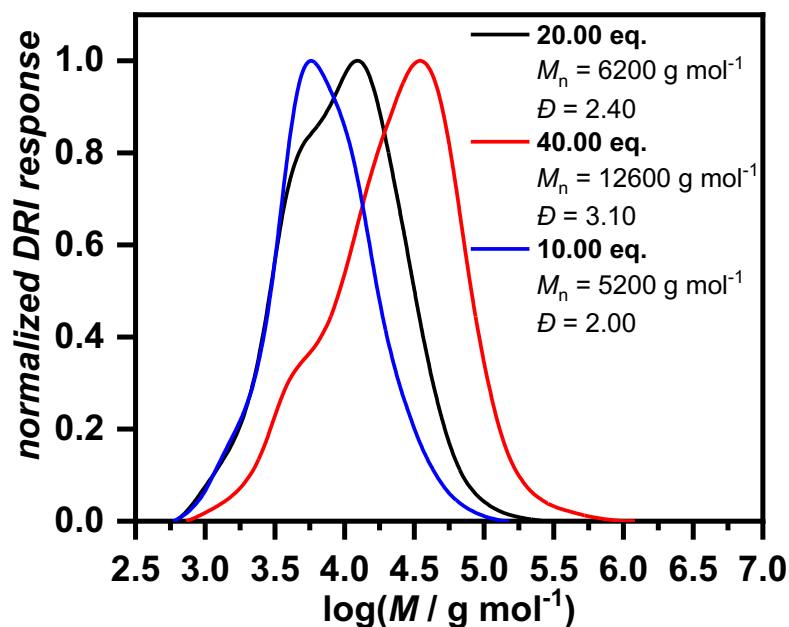


Figure S45. Comparison of SEC traces using DMAc as eluent (PMMA calibration) of the polymers obtained by the electrochemically-initiated polymerization of GMA.

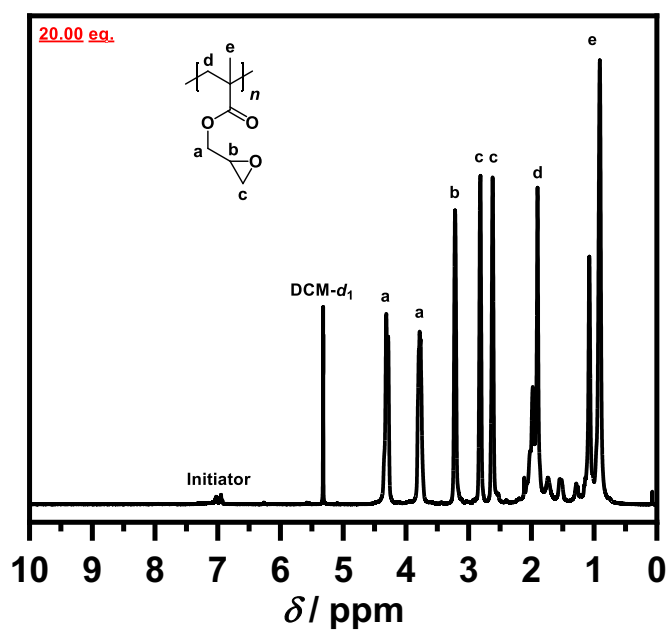


Figure S46. ^1H NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (20.00 eq. with respect to the initiator); solvent: $\text{DCM-}d_2$.

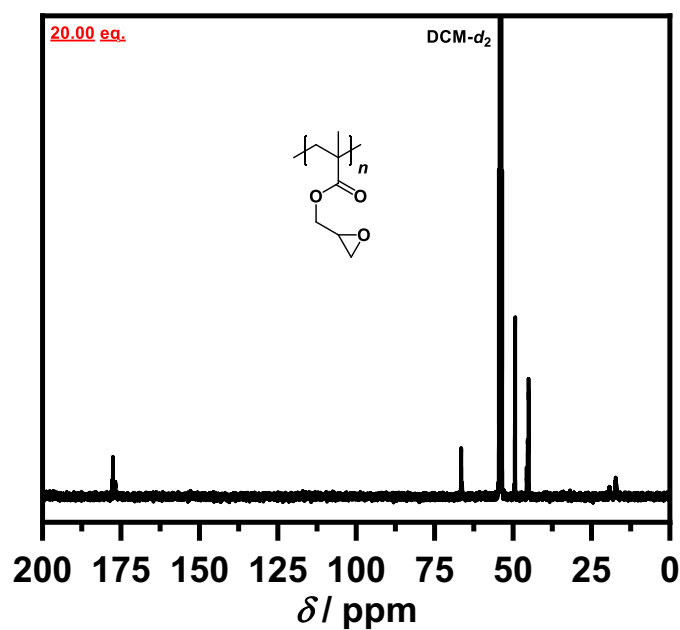


Figure S47. ^{13}C NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (20.00 eq. with respect to the initiator); solvent: $\text{DCM-}d_2$.

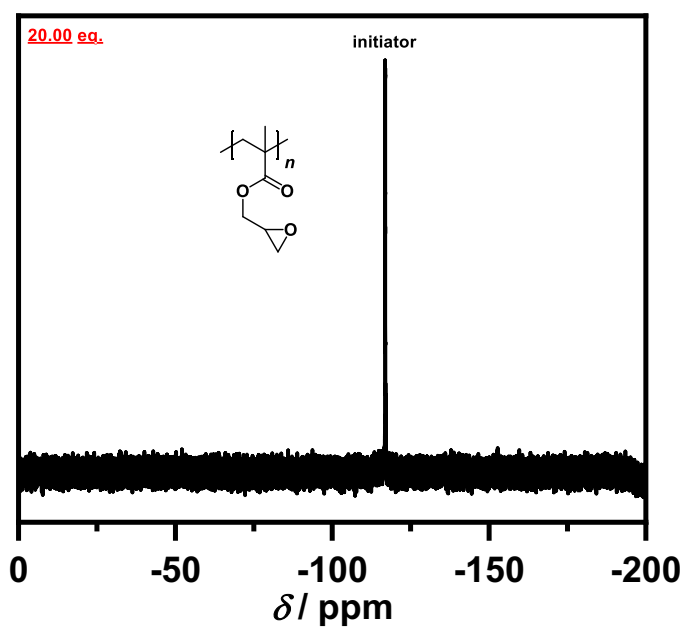


Figure S48. ^{19}F NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (20.00 eq. with respect to the initiator); solvent: $\text{DCM-}d_2$.

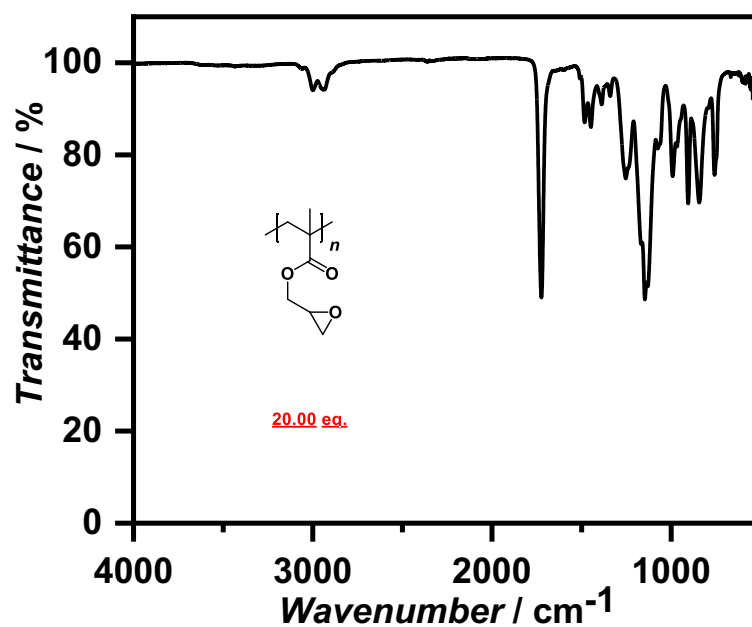


Figure S49. ATR-FT-IR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (20.00 eq. with respect to the initiator).

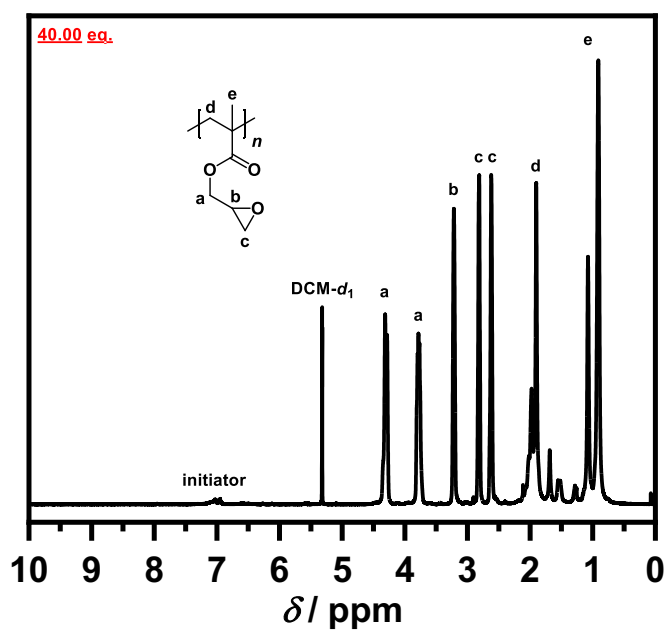


Figure S50. ^1H NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (40.00 eq. with respect to the initiator); solvent: DCM- d_2 .

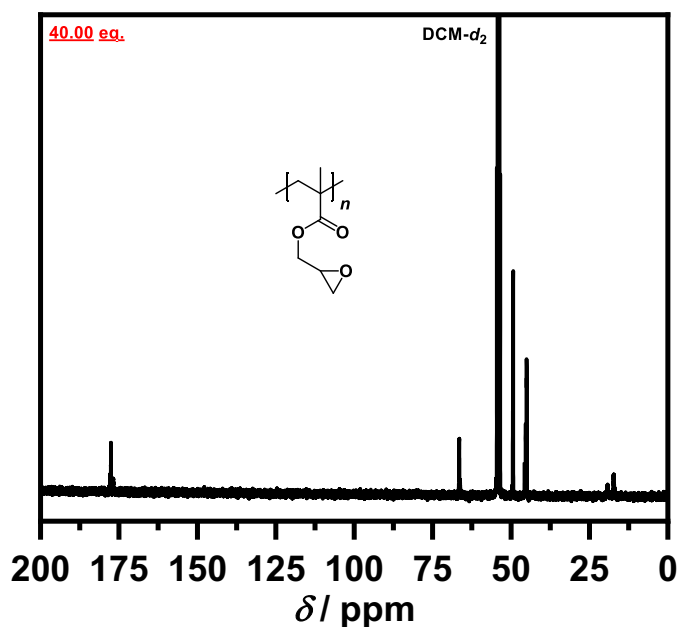


Figure S51. ^{13}C NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (40.00 eq. with respect to the initiator); solvent: DCM- d_2 .

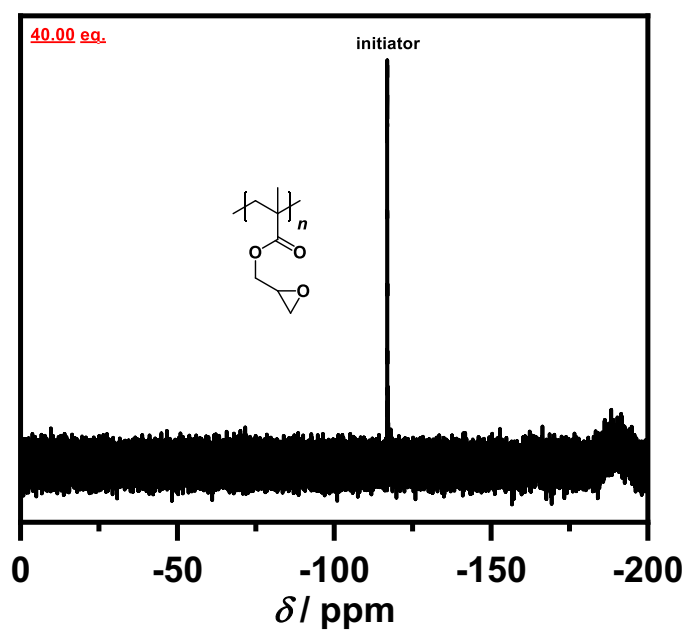


Figure S52. ^{19}F NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (40.00 eq. with respect to the initiator); solvent: $\text{DCM-}d_2$.

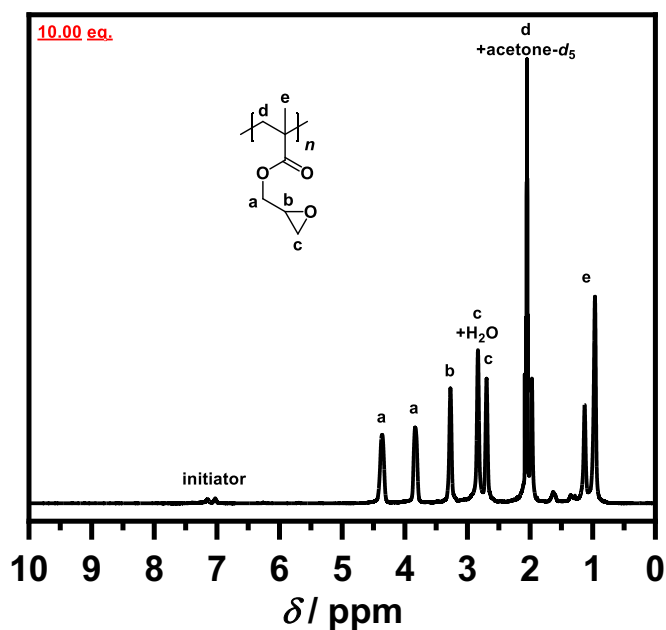


Figure S53. ^1H NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

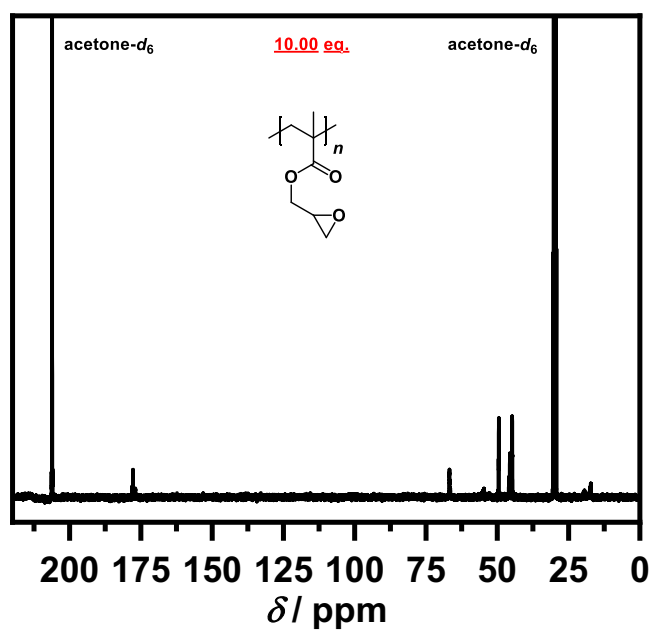


Figure S54. ^{13}C NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

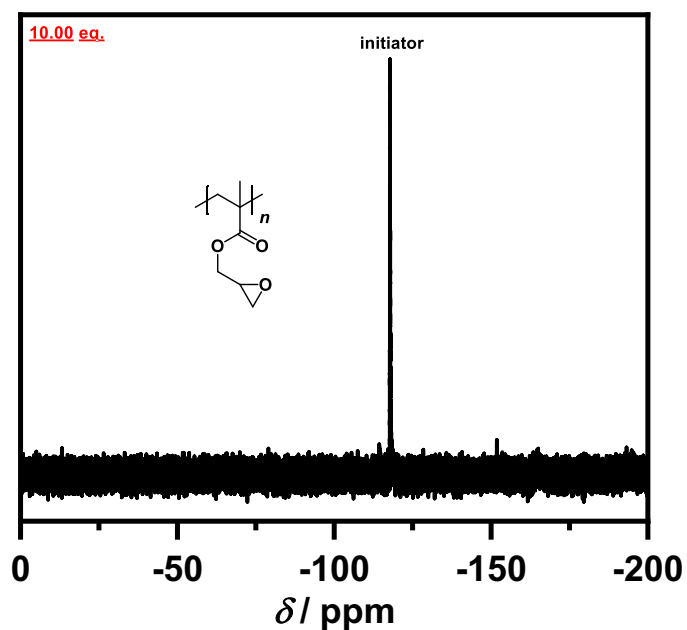
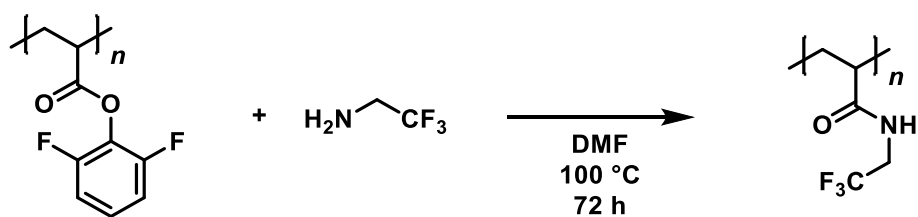


Figure S55. ^{19}F NMR spectrum of PGMA obtained by the electrochemically-initiated polymerization of GMA (10.00 eq. with respect to the initiator); solvent: acetone- d_6 .

5. Post-Polymerization Modification (PPM) Procedures

5.1 PPM of PDFPA



PDPFA (0.040 g, 0.217 mmol of repeating units, 1.00 eq.) was dissolved in anhydrous DMF (0.4 mL) and 2,2,2-trifluoroethylamine (0.43 mL, 0.538 g, 5.431 mmol, 25.00 eq.) was added. The solution was stirred for 72 hours at $100\text{ }^\circ\text{C}$ and the solvent was removed under reduced pressure. The residue was dissolved in acetone and precipitated in petroleum ether. The solids obtained by centrifugation were dissolved in acetone and filtered prior to a second precipitation in petroleum ether. The solids were obtained by centrifugation and dried under vacuum.

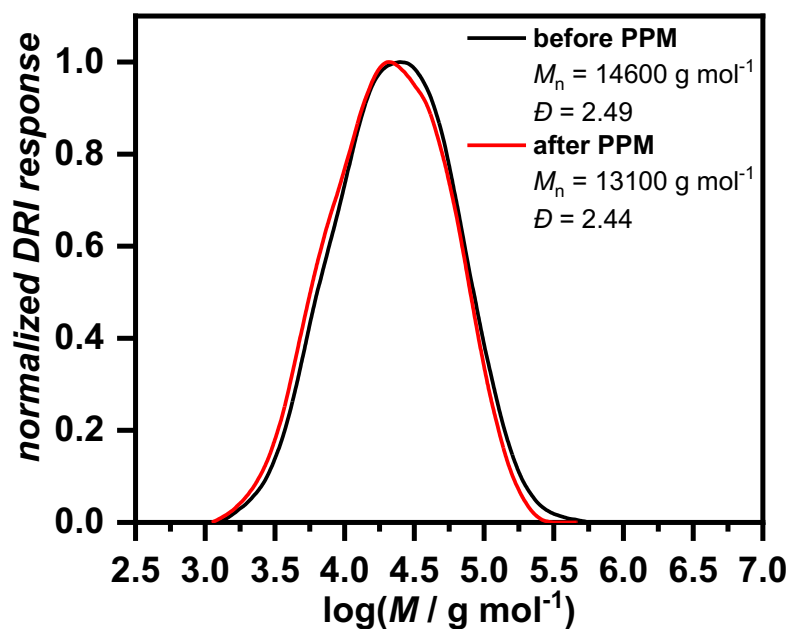


Figure S56. Comparison of SEC traces using DMAc as eluent (PMMA calibration) of PDFPA before (black line) and after PPM (red line).

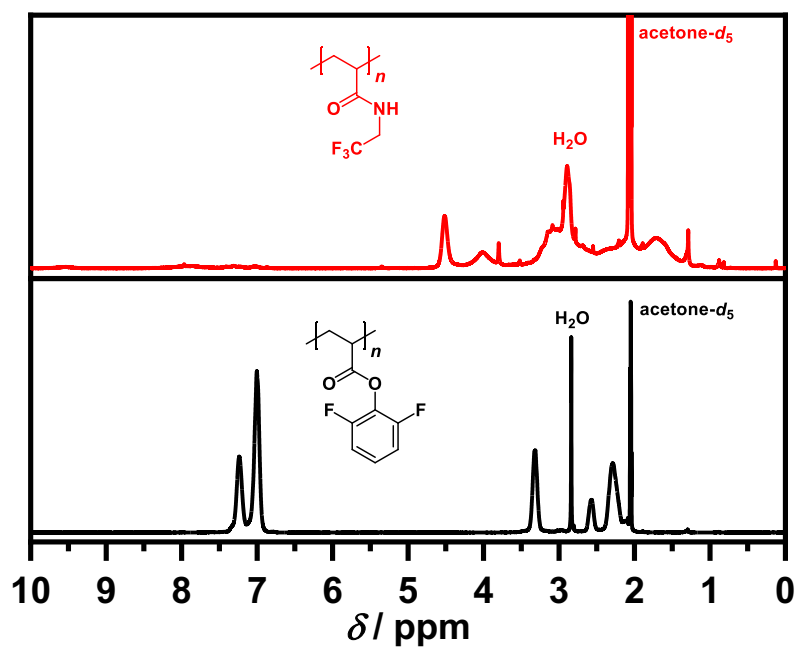


Figure S57. ^1H NMR spectroscopical comparison of PDFPA before (black line, bottom) and after PPM (red line, top); solvent: $\text{acetone-}d_6$.

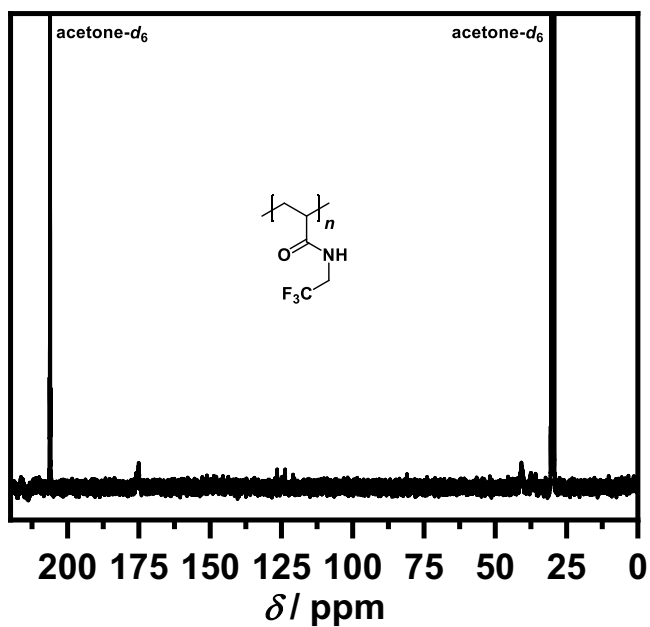


Figure S58. ^{13}C NMR spectrum of the polymer obtained after PPM of PDFPA; solvent: $\text{acetone-}d_6$.

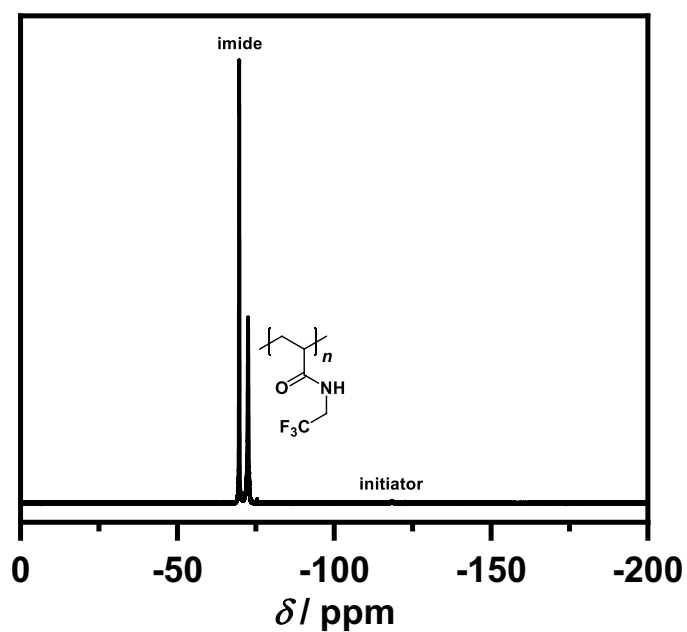


Figure S59. ^{19}F NMR spectrum of the polymer obtained after PPM of PDFPA; solvent: acetone- d_6 .

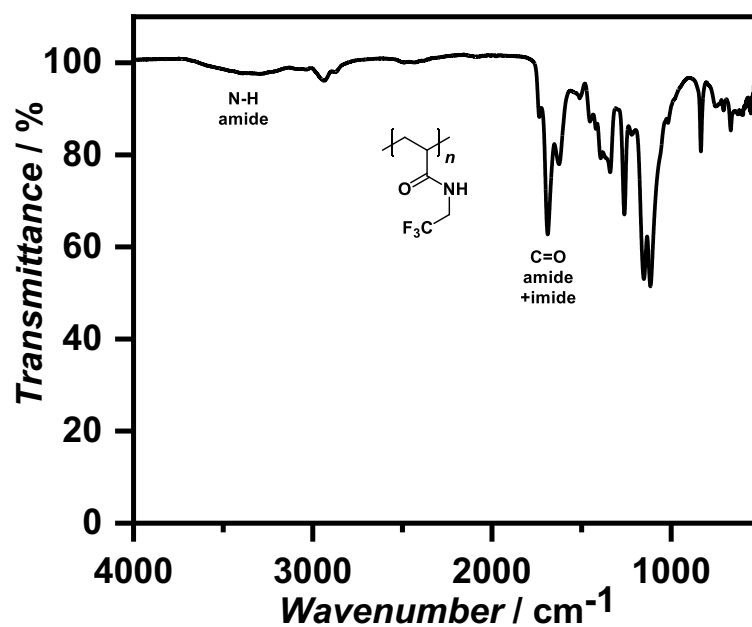
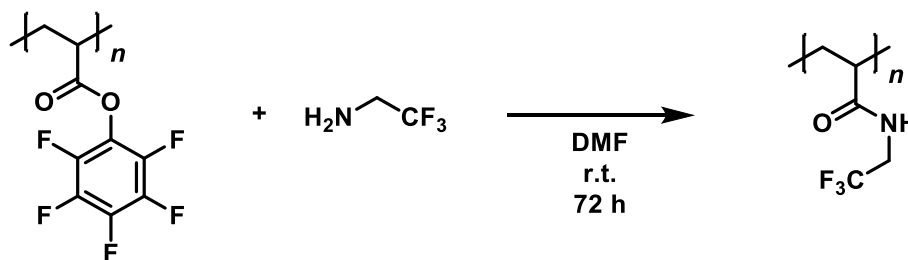


Figure S60. ATR-FT-IR spectrum of the polymer obtained after PPM of PDFPA.

5.2 PPM of PPFPA



PPFPA (0.040 g, 0.168 mmol of repeating units, 1.00 eq.) was dissolved in anhydrous DMF (1 mL) and 2,2,2-trifluoroethylamine (0.33 mL, 0.416 g, 4.200 mmol, 25.00 eq.) was added. The solution was stirred for 72 hours at ambient temperature and the solvent was removed under reduced pressure. The residue was dissolved in acetone and precipitated in petroleum ether. The solids obtained by centrifugation were dissolved in acetone and precipitated a second time in petroleum ether. The solids were obtained by centrifugation and dried under vacuum.

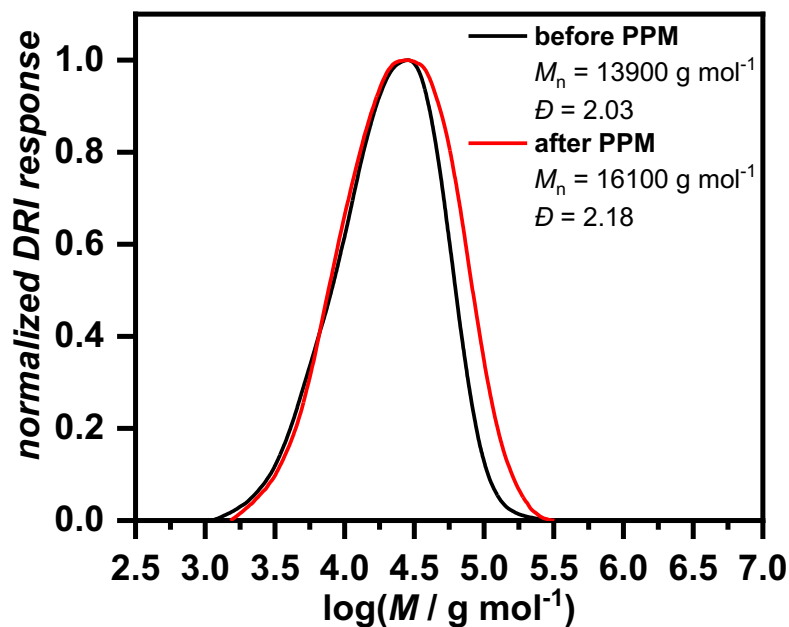


Figure S61. Comparison of SEC traces using DMAc as eluent (PMMA calibration) of PPFPA before (black line) and after PPM (red line).

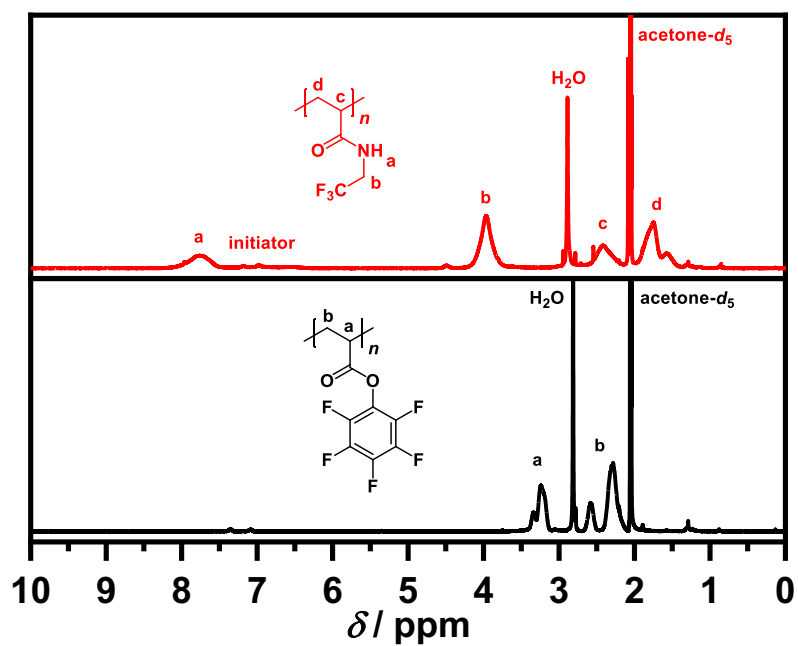


Figure S62. ^1H NMR spectroscopical comparison of PPFPA before (black line, bottom) and after PPM (red line, top); solvent: $\text{acetone-}d_6$.

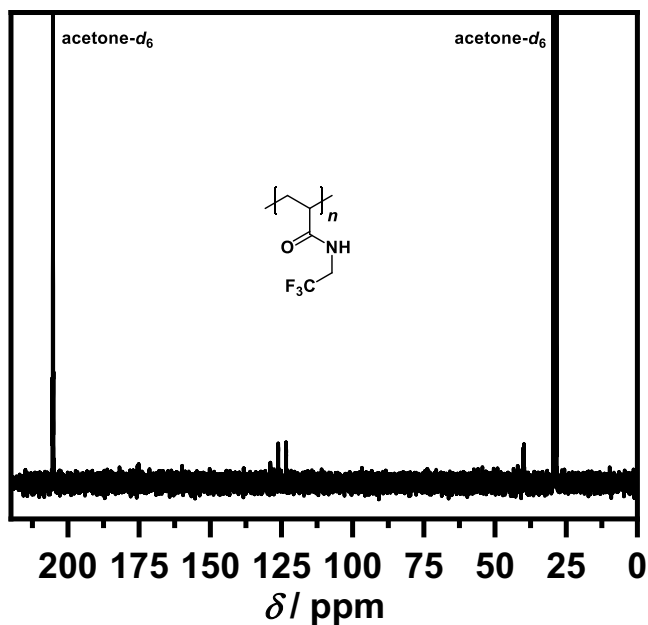


Figure S63. ^{13}C NMR spectrum of the polymer obtained after PPM of PPFPA; solvent: $\text{acetone-}d_6$.

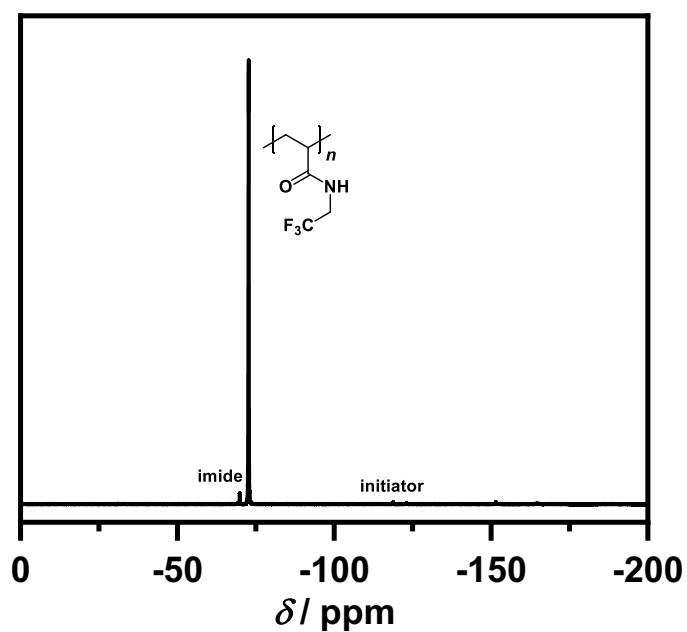


Figure S64. ^{19}F NMR spectrum of the polymer obtained after PPM of PPFPA; solvent: acetone- d_6 .

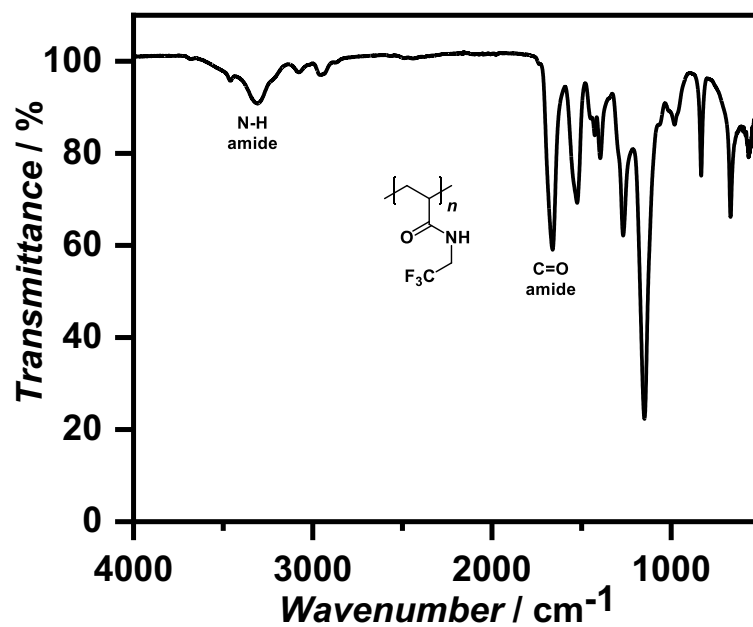
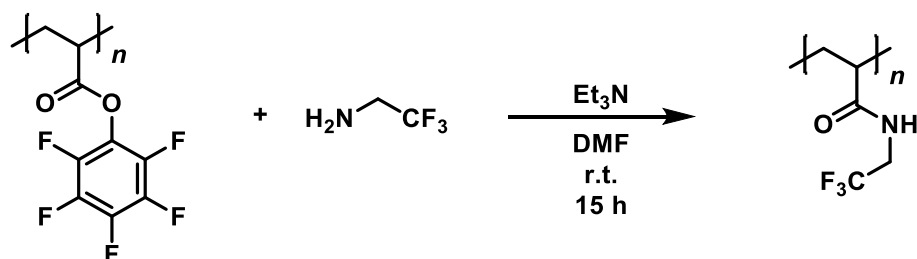


Figure S65. ATR-FT-IR spectrum of the polymer obtained after PPM of PPFPA.

Prior to this PPM procedure, we conducted experiments with the addition of triethylamine as base, resulting in the formation of imide functionalities in considerable amounts:



PPFPA (0.050 g, 0.210 mmol of repeating units, 1.00 eq.) was dissolved in anhydrous DMF (1 mL) and triethylamine (0.09 mL, 0.064 g, 0.630 mmol, 3.00 eq.) and 2,2,2-trifluoroethylamine (0.05 mL, 0.062 g, 0.630 mmol, 3.00 eq.) was added. The solution was stirred for 15 hours at ambient temperature and the solvent was removed under reduced pressure. The residue was dissolved in acetone and precipitated in petroleum ether. The solids obtained by centrifugation were dissolved in acetone and precipitated a second time in petroleum ether. The solids were obtained by centrifugation and dried under vacuum.

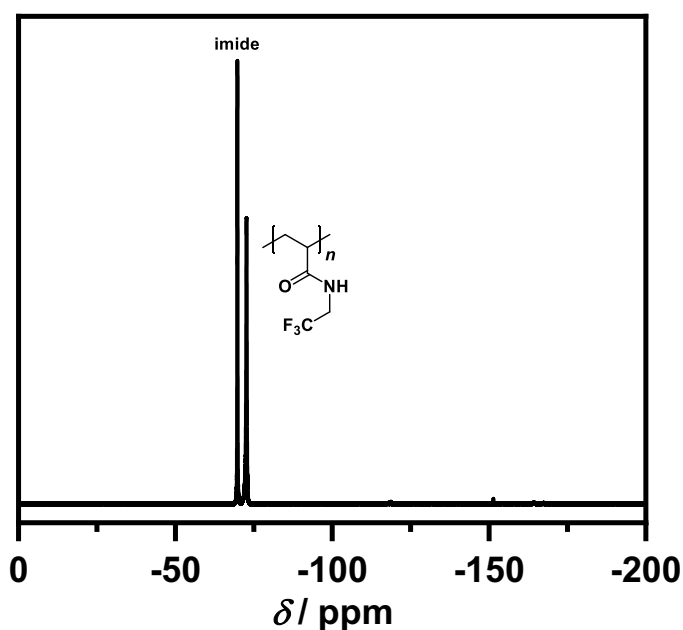
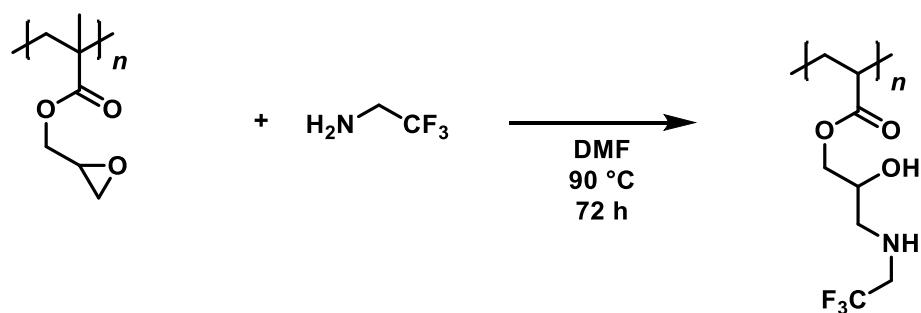


Figure S66. ^{19}F NMR spectrum of the product obtained by PPM with additional use of triethylamine as base; solvent: acetone- d_6 .

5.3 PPM of PGMA



PGMA (0.040 g, 0.281 mmol of repeating units, 1.00 eq.) was dissolved in anhydrous DMF (0.6 mL) and 2,2,2-trifluoroethylamine (0.55 mL, 0.697 g, 7.035 mmol, 25.00 eq.) was added. The solution was stirred for 72 hours at $90\text{ }^\circ\text{C}$ and the mixture was precipitated in cold diethyl ether. The solids obtained by centrifugation were dissolved in acetone and precipitated a second time in cold diethyl ether. The solids were obtained by centrifugation and dried under vacuum.

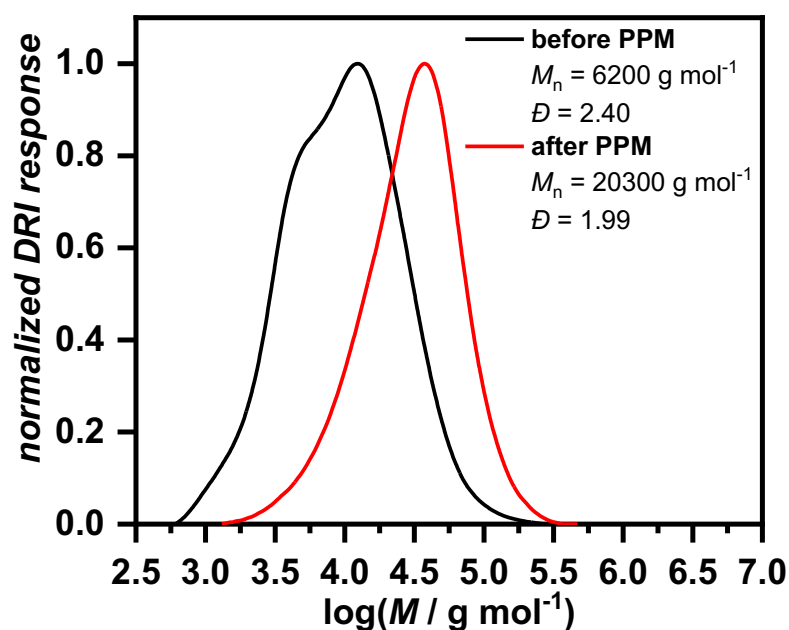


Figure S67. Comparison of SEC traces using DMAc as eluent (PMMA calibration) of PPFPA before (black line) and after PPM (red line).

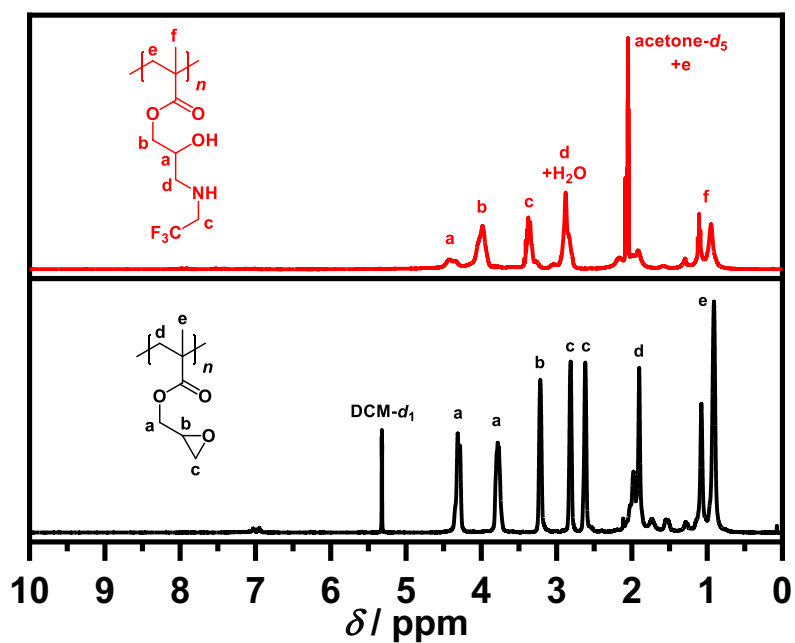


Figure S68. ^1H NMR spectroscopical comparison of PGMA before (black line, bottom) and after PPM (red line, top); solvent: DCM- d_2 (black line, bottom) and acetone- d_6 (red line, top).

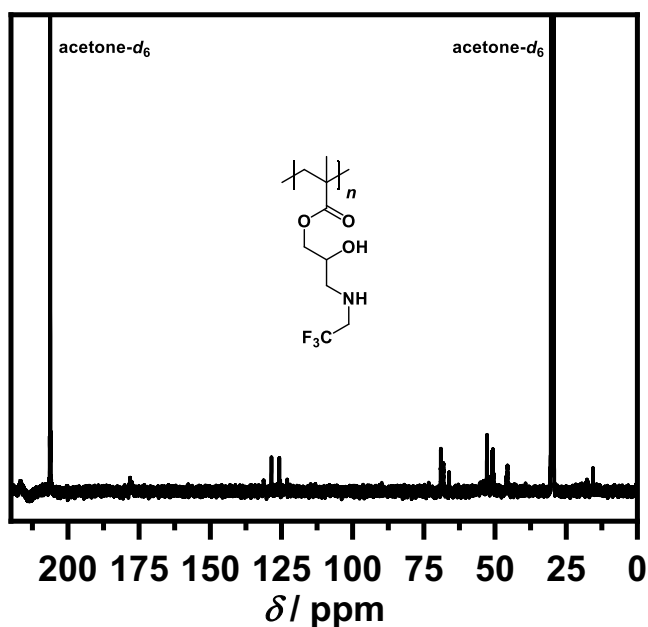


Figure S69. ^{13}C NMR spectrum of the polymer obtained after PPM of PGMA; solvent: acetone- d_6 .

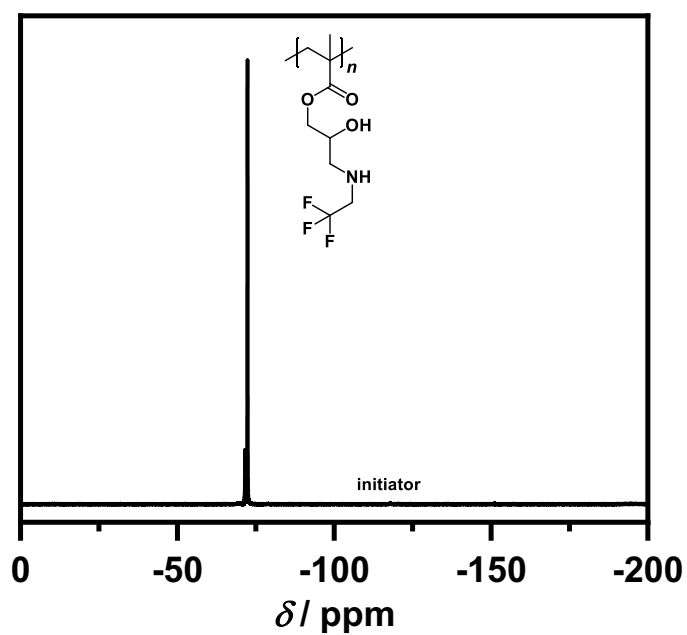


Figure S70. ^{19}F NMR spectroscopical comparison of PGMA before (black line, bottom) and after PPM (red line, top); solvent: $\text{DCM-}d_2$ (black line, bottom) and $\text{acetone-}d_6$ (red line, top).

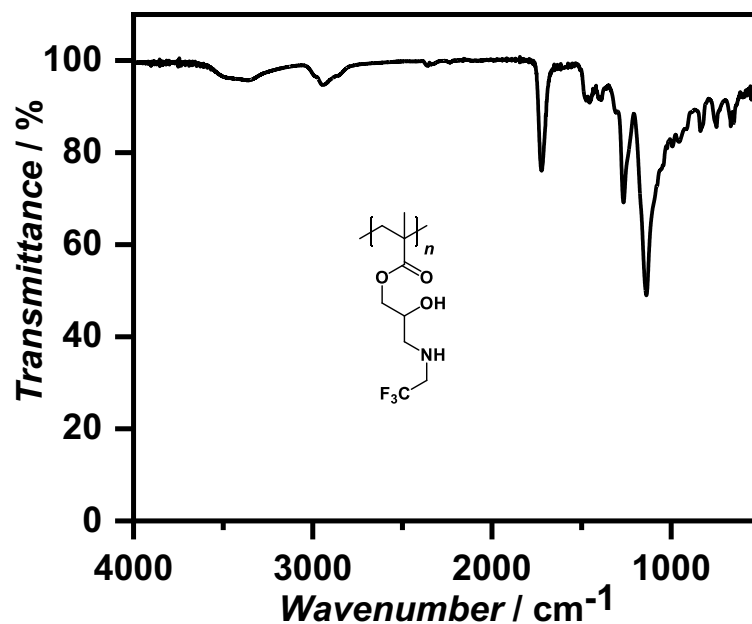
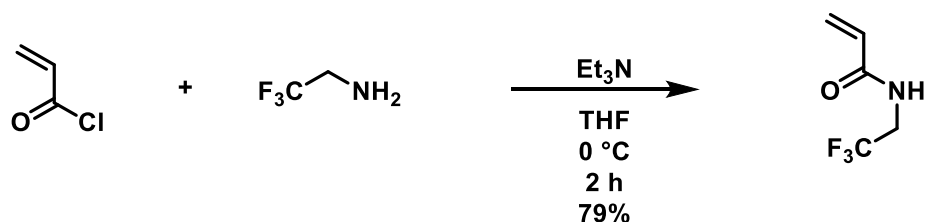


Figure S71. ATR-FT-IR spectrum of the polymer obtained after PPM of PGMA.

6. Appendix

6.1 Synthesis of *N*-(2,2,2-trifluoroethyl)acrylamide



2,2,2-Trifluoroethylamine (1.0 mL, 1.26 g, 12.72 mmol, 1.00 eq.) was dissolved in anhydrous THF (5 mL). The solution was cooled to 0 °C and triethylamine (2.2 mL, 1.54 g, 15.26 mmol, 1.20 eq.) was added. A solution of acryloyl chloride (1.2 mL, 1.26 g, 12.72 mmol, 1.20 eq.) in anhydrous THF (3 mL) was added slowly and the mixture was stirred for two hours at 0 °C. The solvent was removed under reduced and the crude product was purified by column chromatography using a 3:2 mixture of cyclohexane / ethyl acetate giving a slightly yellowish solid (1.50 g, 79%).

$R_f(\text{CH} / \text{EE } 3:2) = 0.33$

¹H NMR (acetone-*d*₆): $\delta / \text{ppm} = 7.90$ (bs, 1H, H_a), 6.24 – 6.40 (m, 2H, H_b+H_c), 5.69 (dd, $J = 9.6, 2.6$ Hz, 1H, H_c), 4.06 (qd, $J = 9.5, 6.5$ Hz, 2H, H_d).

¹³C NMR (acetone-*d*₆): $\delta / \text{ppm} = 166.05$ (s), 131.45 (s), 129.91 (s), 127.38 (s), 127.15 (s), 124.38 (s), 40.77 (q, $J = 34.2$ Hz).

¹⁹F NMR (acetone-*d*₆): $\delta / \text{ppm} = -72.99$ (t, $J = 9.5$ Hz, 3F).

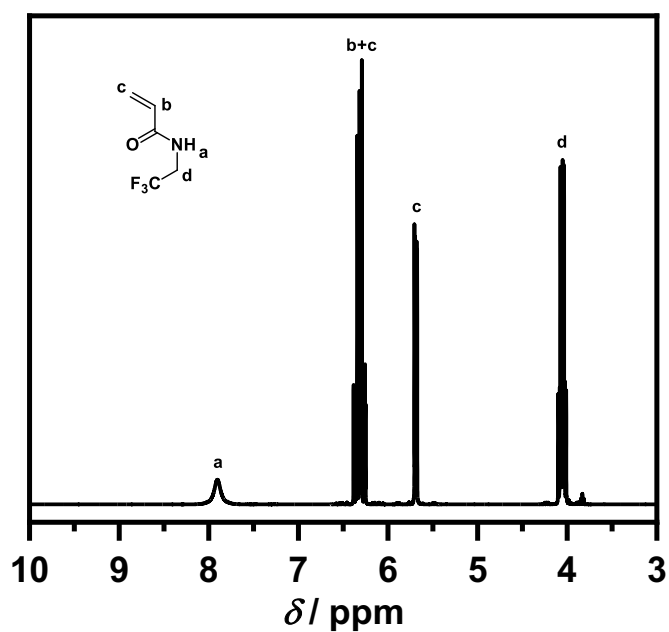


Figure S72. ^1H NMR spectrum of *N*-(2,2,2-trifluoroethyl)acrylamide; solvent: acetone- d_6 .

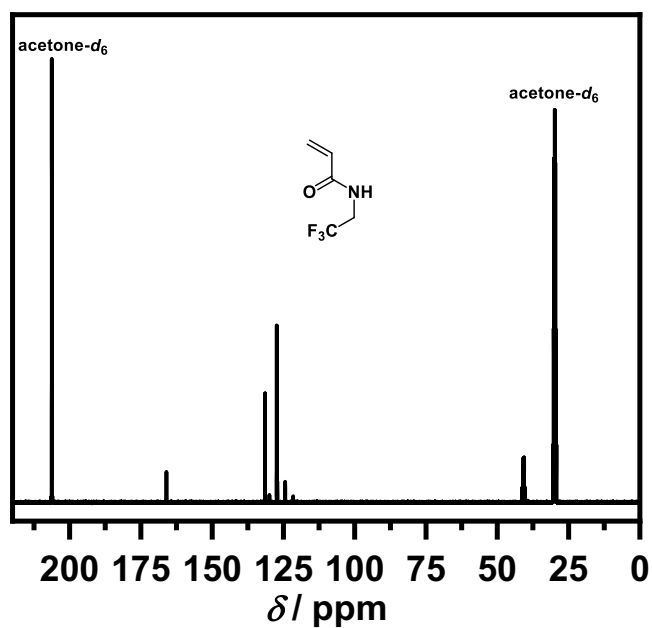


Figure S73. ^{13}C NMR spectrum of *N*-(2,2,2-trifluoroethyl)acrylamide; solvent: acetone- d_6 .

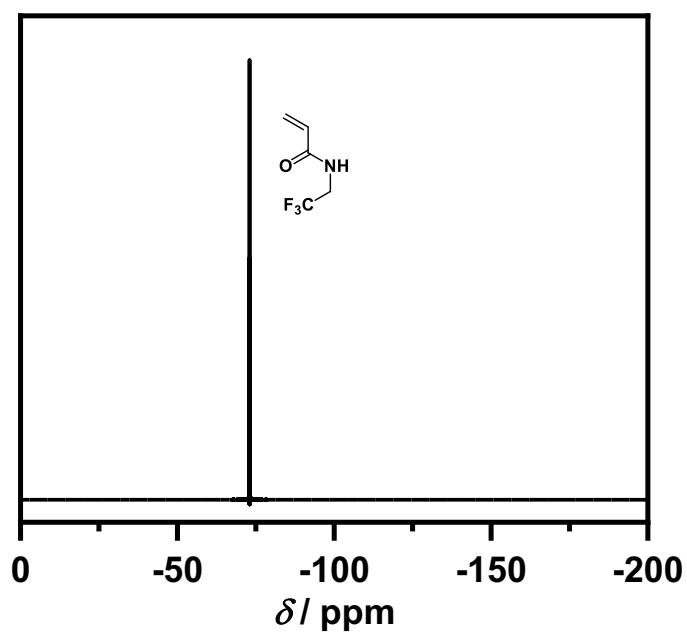


Figure S74. ^{19}F NMR spectrum of *N*-(2,2,2-trifluoroethyl)acrylamide; solvent: acetone- d_6 .

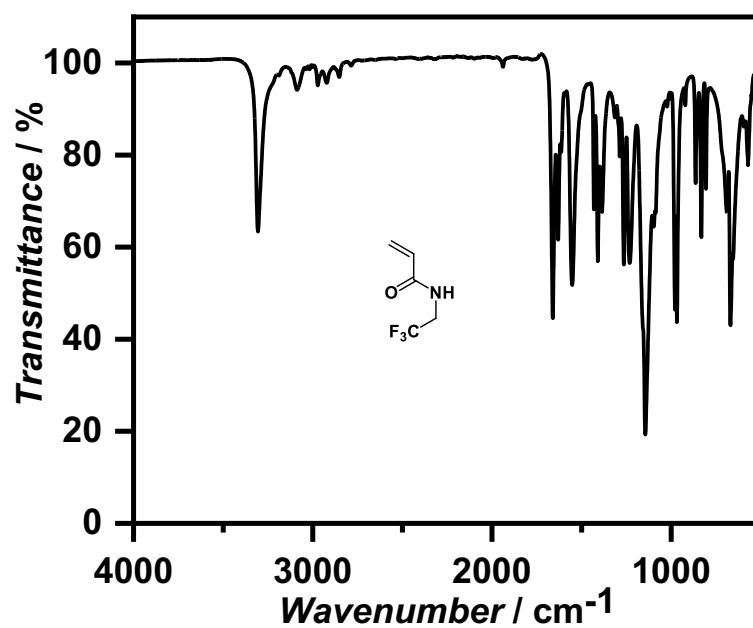
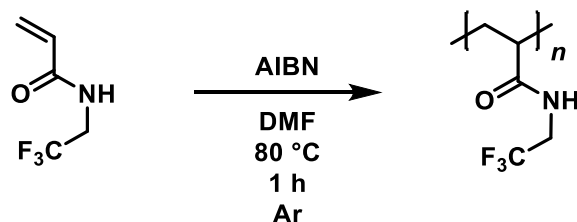


Figure S75. ATR-FT-IR spectrum of *N*-(2,2,2-trifluoroethyl)acrylamide.

6.2 Polymerization of *N*-(2,2,2-trifluoroethyl)acrylamide



N-(2,2,2-Trifluoroethyl)acrylamide (0.200 g, 1.306 mmol, 20.00 eq.) and AIBN (0.011 g, 0.065 mmol, 1.00 eq.) were dissolved in anhydrous DMF (1.5 mL). The solution was deoxygenated by argon purging for 15 minutes. The flask was placed in a preheated oil bath at 80 °C for one hour. The mixture was precipitated in cold diethyl ether, the solids obtained by centrifugation were dissolved in acetone and precipitated a second time in cold diethyl ether. The solids were obtained by centrifugation and dried under vacuum.

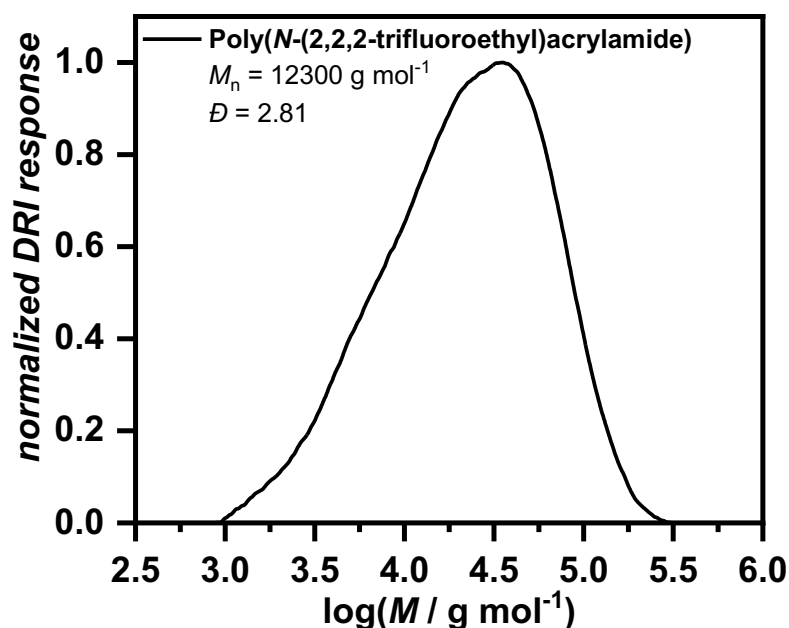


Figure S76. Size-exclusion chromatogram using DMAc as eluent (PMMA calibration) of poly(*N*-(2,2,2-trifluoroethyl)acrylamide) obtained by direct polymerization of its respective monomer.

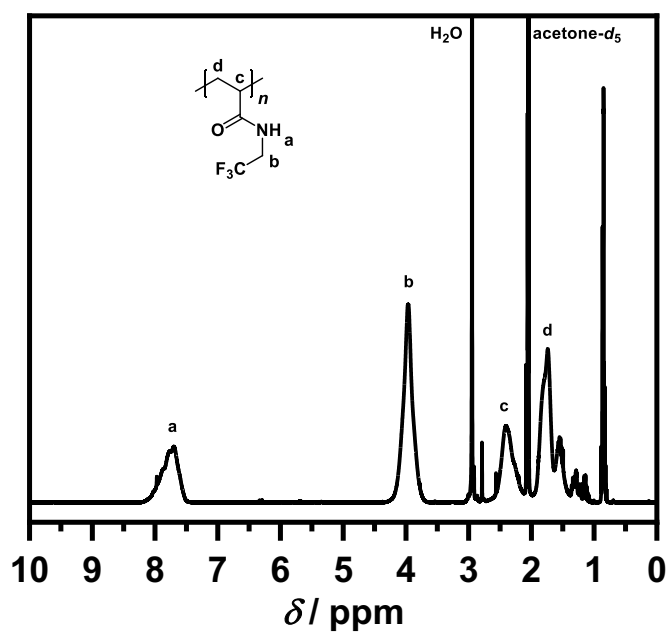


Figure S77. ^1H NMR spectrum of poly(*N*-(2,2,2-trifluoroethyl)acrylamide) obtained by direct polymerization of its respective monomer; solvent: acetone- d_6 .

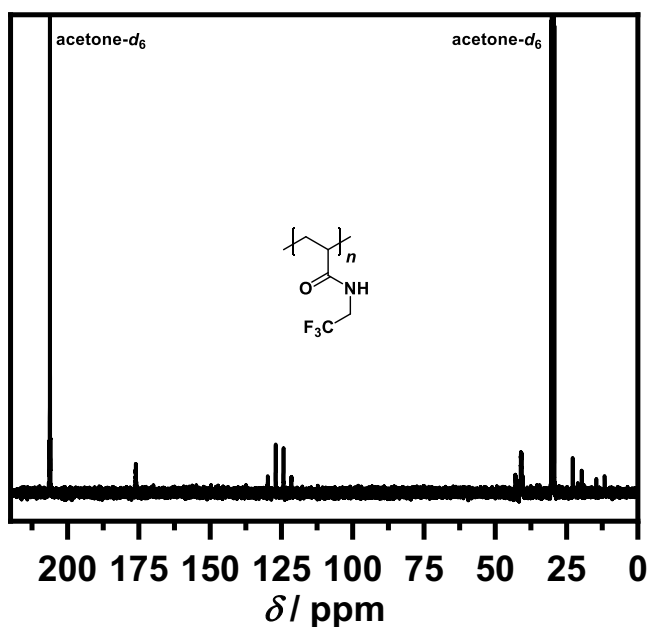


Figure S78. ^{13}C NMR spectrum of poly(*N*-(2,2,2-trifluoroethyl)acrylamide) obtained by direct polymerization of its respective monomer; solvent: acetone- d_6 .

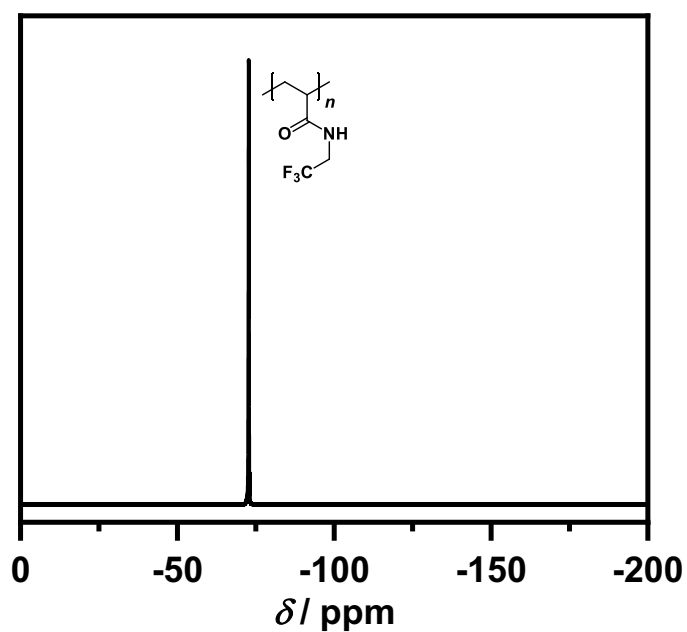


Figure S79. ^{19}F NMR spectrum of poly(*N*-(2,2,2-trifluoroethyl)acrylamide) obtained by direct polymerization of its respective monomer; solvent: acetone- d_6 .

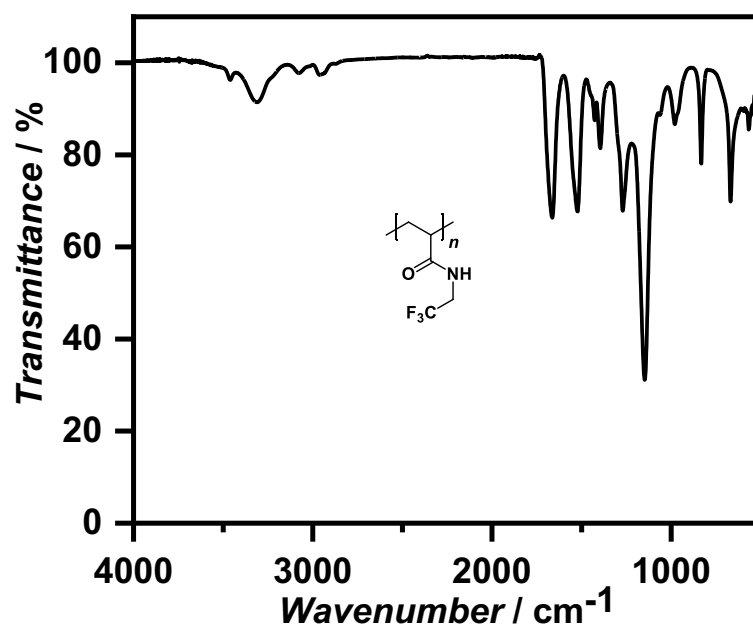


Figure S80. ATR-FT-IR spectrum of poly(*N*-(2,2,2-trifluoroethyl)acrylamide) obtained by direct polymerization of its respective monomer.