—Supporting Information—

The Azide–*para*-Fluoro Substitution on Polymers: Multi-purpose Precursors for Efficient Sequential Postpolymerization Modification

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—Content—

Experimental Section

Instrumentation

NMR spectroscopic measurements were performed on 300, 400, or 500 MHz Bruker instruments in 5 mm NMR tubes. Residual solvent signals of $CHCl_3$ (δ_H = 7.26 ppm, δ_C = 77.2 ppm), DMSO-d_5 (δ_H = 2.51 ppm) and CD_2HCN (δ_H = 1.94 ppm) were used as references. Fourier transform infrared spectroscopy (FT-IR) was performed on a Bruker IFS 66/S spectrometer or an Agilent Cary 600 Series spectrometer, in both cases under attenuated total reflectance (ATR).

Size exclusion chromatography (SEC) was performed on one of two instruments: a Shimadzu system using *N*,*N*-dimethylacetamide (DMAc) (equipped with four 300 × 7.8 mm^2 linear phenogel columns operating at 50 °C and a flow rate of 1 mL/min, and calibrated with PS standards) or a Viscotek GPCMax VE 2001 setup using tetrahydrofuran (THF) (equipped with three linear 7.5×300 mm PLgel mixed-D columns operating at 35 °C and a flow rate of 0.7 mL/min, and calibrated with PMMA standards). For both instruments, samples were prepared at concentrations of 2–3 g/L in the respective solvents and filtered through 0.2 µm regenerated cellulose syringe filters before injection. Plotted traces are from the respective refractive index detectors.

Differential scanning calorimetry (DSC) was done on a TA Instruments DSC Q1000 instrument using a heat–cool–heat cycle between 27 °C and 210 °C at heating/cooling rates of 10 °C/min.

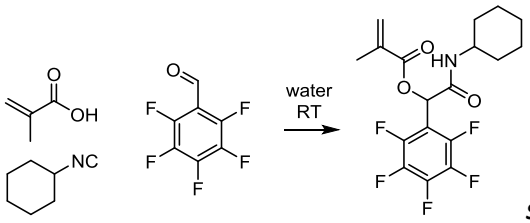
Thermogravimetric analysis (TGA) was done on a TA Instruments TGA Q500 instrument by heating from RT to 600 °C at a rate of 10 °C/min under nitrogen.

Synthesis: General Remarks

Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored in a freezer. RAFT agent 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPPA) was purchased from Sigma-Aldrich and used as received. The commercial monomers 2,3,4,5,6-pentafluorostyrene and oligo(ethylene glycol) methyl ether acrylate (PEGA, monomer M_n = 480 g/mol) were deinhibited by passing through a short plug of basic alumina directly before polymerization. Copper(I) bromide was stirred in boiling acetic acid, then filtered and washed with acetic acid and ethanol to extract copper(II) bromide impurities. The preparation of RAFT agent benzyl propyl trithiocarbonate (BPTC) is described in the literature.[1]

Synthesis: Pentafluoroaryl-functional polymers

Poly(2,3,4,5,6-pentafluorobenzyl methacrylate), **1a**. Several batches were prepared according to a literature procedure,[2] see table below for details. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 5.16, 5.07, 5.03 (2 H, CH_2COO, splitting due to tacticity), 1.90, 1.83, 1.76, 1.56, 1.36 (2 H, CH_2), 1.14, 0.95, 0.90, 0.79, 0.74 (3 H, CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm = −142.4 (2 F, *ortho*), −151.9 (1 F, *para*), −161.5 (2 F, *meta*). FT-IR ν/cm^{-1} = 2956 (w, C–H stretch), 1734 (m–s, C=O stretch), 1656 (m, C=C stretch), 1523, 1502 (s, C=C stretch), 1128 (m, C–F stretch), 933 (m, C=C bending).



Scheme S1. *Synthesis of monomer* ***1b***.

Poly[2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl methacrylate], **1b**. The monomer (Scheme S1) was prepared as follows. Pentafluorobenzaldehyde (1.00 g, 0.63 mL, 5.1 mmol, 1 eq.) was weighed into a 10 mL round bottom flask and water (1.7 mL) and methacrylic acid (0.44 g, 0.43 mL, 5.1 mmol, 1 eq.) were added. The mixture was stirred for a few minutes and cyclohexyl isocyanide (0.56 g, 0.63 mL, 5.1 mmol, 1 eq.) was added slowly. The mixture was stirred overnight at room temperature. The water was decanted and the sticky solid residue was dried under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate–hexane 2:3 to afford the title compound in quantitative yield (2.0 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ/ppm = 6.45 (s, 1 H, -COOC*H*-), 6.29 (d, 1 H, -CON*H*-), 6.20 (s, 1 H, H*H*C=C(CH$_3$)-), 5.74 (t, 1 H, *H*HC=C(CH$_3$)-), 3.85 (m, 1 H, -NHC*H*-Cy), 1.99 (s, 3 H, -C(CH_3)-), 1.94-1.16 (m, 10 H, cyclohexyl); ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm = 164.9 (*C*OO), 164.7 (*C*ONH), 135.0 (-*C*(CH$_3$)-), 127.9 (H$_2$*C*=C-), 65.4 (-OCO*C*H-), 48.4 (-NH*C*H-cyclohexyl), 32.7, 32.6 (Cy), 25.4 (Cy), 24.6, 24.5 (Cy), 18.2 (-C(*C*H$_3$)-); ^{19}F NMR (282 MHz, $CDCl_3$), δ/ppm = −141.4 (m, 2 F, *ortho*), −151.9 (t, 1 F, *para*), −161.4 (m, 2 F, *meta*); FT-IR ν/cm^{-1} = 3363 (w, N-H, stretch), 2939, 2860 (w, C-H alkyl, C=CH$_2$, stretch), 1736 (m/s, C=O, ester, stretch), 1655 (s, C=O, amide, stretch), 1505 (s, C=C, stretch), 1129 (s, C-N, stretch), 997 (s, C-F, stretch).

The polymer **1b** was prepared in analogy to procedure in the literature.[3] DP = 60; SEC (DMAc, PS calibration, 19.5 kg/mol, *Đ* = 1.26). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 6.06 (bs, 2 H, N*H*, ArC*H*), 3.79 (bs, 1 H, NHC*H*), 1.90, 1.72, 1.37, 1.18, 0.61 (m, 15 H, Cy, backbone). ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm = −141.0 (2 F, *ortho*), −151.1 (1 F, *para*), −161.0 (2 F, *meta*). FT-IR ν/cm^{-1} = 2932, 2854 (w, C–H stretch), 1740 (C=O ester stretch), 1683 (C=O amide stretch), 1521, 1504 (s, C=C stretch), 1125 (m, C–F stretch).

Poly[2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acrylate], **1c** was prepared in analogy to a literature procedure using BPTC as RAFT agent.[3] DP = 55; SEC (DMAc, PS calibration, 8.9 kg/mol, *Đ* = 1.45). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 6.17 (bs, 1 H, ArC*H*), 3.75 (bs, 1 H, NHC*H*), 2.54 (bs, 1 H, backbone C*H*), 1.89, 1.64, 1.33, 1.13 (m, 12 H, backbone CH_2, Cy); ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm = −141.9 (2 F, *ortho*), −151.6 (1 F, *para*), −161.2 (2 F, *meta*). FT-IR ν/cm^{-1} = 2931, 2854 (w, C–H stretch), 1747 (C=O ester stretch), 1670 (C=O amide stretch), 1521, 1506 (s, C=C stretch), 1128 (m, C–F stretch).

Poly[(2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acrylate)$_{0.30}$-*co*-(oligo (ethylene glycol) methyl ether acrylate)$_{0.70}$], **1c**-*co*-PEGA (shown above) was prepared in analogy to a literature procedure using BPTC as RAFT agent and a 30:70 molar ratio of the respective monomers.[3] DP = 30 + 62 = 92. SEC (DMAc, PS calibration, 28.5 kg/mol, $Đ$ = 1.39). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 6.28 (bs, ArC*H*), 4.17 (bs, COOCH_2), 3.84–3.52 (m, NHC*H*, PEG), 3.37 (bs, OCH_3), 2.30 (bs, backbone C*H*), 1.98–1.11 (m, backbone CH_2, Cy); ^{19}F NMR (282MHz, $CDCl_3$) δ/ppm = −140.6 (2 F, *ortho*), −152.3 (1 F, *para*), −161.3 (2 F, *meta*). FT-IR ν/cm^{-1} = 2934, 2854 (m, C–H stretch), 1740 (m, C=O ester stretch), 1684 (s, C=O amide stretch), 1523, 1508 (s, C=C stretch), 1097 (s, C–O stretch).

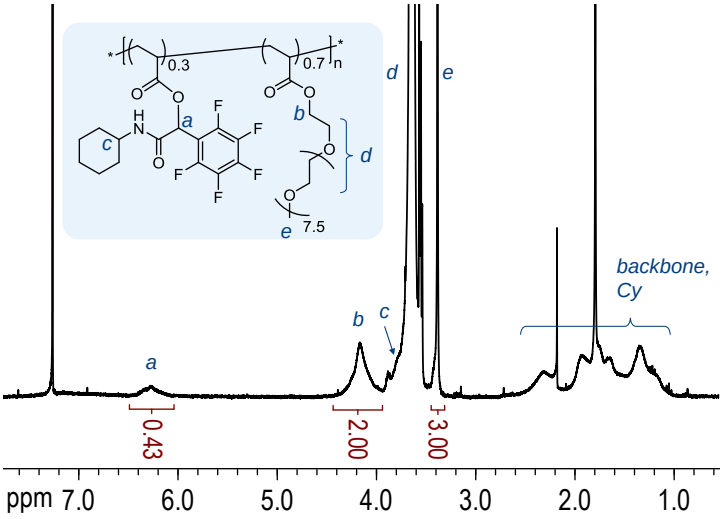


Figure S1. *^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1c**-co-PEGA with assignments.*

Reaction 1 → 2 see main paper.

Poly(2,3,4,5,6-pentafluorostyrene), **3**, Several samples were prepared by RAFT using BPTC as RAFT agent, see table below for details. ^{1}H NMR (400 MHz, CDCl3) δ/ppm = 2.73, 2.40 (1 H, C*H* backbone), 2.01 (2 H, CH_2 backbone); ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm = −143.1 (2 F, *ortho*), −154.1 (1 F, *para*), −161.0 (2 F, *meta*). FT-IR ν/cm^{-1} = 1653 (m, C=C stretch), 1522, 1496 (s, C=C stretch), 1128 (C–F stretch).

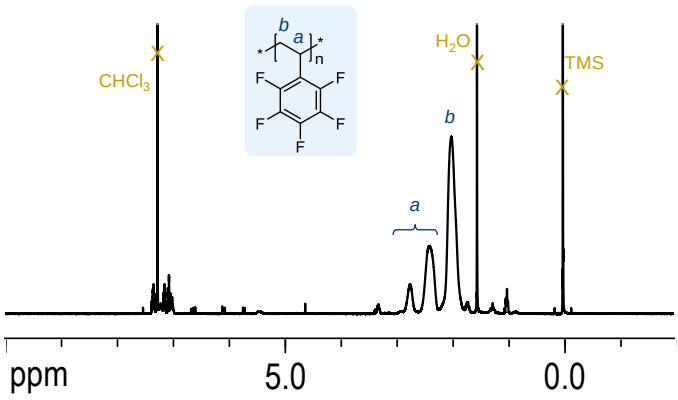
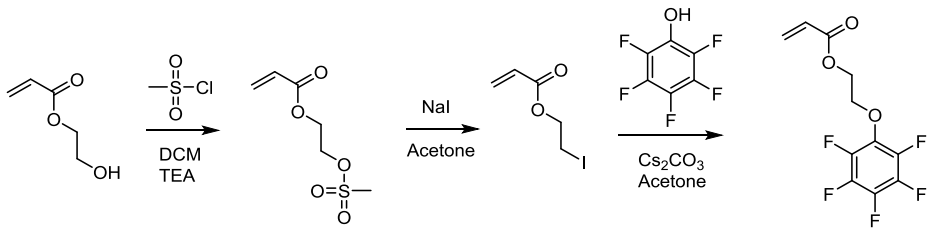


Figure S2. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of poly(2,3,4,5,6-pentafluorostyrene) **3**.*

Reaction 3 → 4 see main paper.

The synthesis of polymer poly(2,3,4,5,6-pentafluorophenyl acrylate) **5** (DP = 178, $Đ$ = 1.23) is described elsewhere.[4] Its attempted modification with sodium azide followed the same procedure as for **1a**.

Poly[(ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate)$_{0.42}$-*co*-(oligo(ethylene glycol) methyl ether acrylate)$_{0.58}$] **6**-*co*-PEGA. The monomer ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate was prepared in three steps from 2-hydroxyethyl acrylate (Scheme S2).



***Scheme S2**. Synthesis of monomer **6**.*

Step 1 (2-methylsulfonyl ethyl acrylate): Hydroxyethyl acrylate (HEA) (15.00 g ,129 mmol, 14.83 mL) was dissolved in CH_2Cl_2 (150 mL) in a 500 mL two-necked flask equipped with a with a dropping funnel, drying tube, and thermometer. The solution was cooled to 0–5°C with an ice–water bath before triethylamine (19.61 g ,193 mmol, 27.01 mL, 1.5 eq.) was added into the flask. Then, methanesulfonyl chloride (22.20 g ,193 mmol, 1.5 eq.), dissolved in 50 mL CH_2Cl_2 (50 mL) was added dropwise from the dropping funnel under vigorous stirring while the temperature was not allowed to exceed 10 °C. A white salt precipitated and the mixture was allowed to warm to RT and stirred overnight. Diethyl ether (50 mL) and aq. $NaHCO_3$ (100 mL) were added and stirring was continued for 5 min upon which the salt re-dissolved. The phases were separated, the aqueous phase was washed with diethyl ether (2 × 50 mL) and the combined organic phases were washed with water (100 mL), aqueous $NaHCO_3$ (100 mL), aqueous NH_4Cl (100 mL), aqueous Na_2CO_3 (100 mL) and aqueous NaCl (2 × 100 mL). The organic phase was dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. The product was dried in vacuum. Yield: 96 %, yellow oil. ^{1}H NMR (300MHz, $CDCl_3$) δ/ppm = 6.47 (1 H d, C*H*), 6.15 (1 H, q, = C*H*), 5.90 (1 H, d, C*H*), 4.44 (4 H, m, CH_2CH_2), 3.05 (3 H, s, –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 165.6 (>*C*=O), 131.9 (=*C*H–), 128.6 (=*C*H_2), 67.5 (–*C*H_2–), 61.9 (–*C*H_2–), 37.5 (–*C*H_3); FT-IR, ν/cm^{-1} = 3050–2950 (C–H stretch (CH_2)), 1722 (C=O stretch), 1637 (C=C stretch), 1350, 1167 (S=O), 1297 (C–O), 750 (CH_2 rocking).

Step 2 (2-iodo ethyl acrylate): 2-methylsulfonyl ethyl acrylate (10.00 g ,51 mmol) was dissolved in anhydrous acetone (280 mL) in a 500 mL two-necked flask equipped with a reflux condenser. Sodium iodide (15.44 g, 102 mmol, 2 eq.) and inhibitor BHT (a few crystals) were added and the solution was heated to reflux overnight during which the colour changed from light yellow to yellow. A precipitated salt was removed by filtration and the solvent was removed under reduced pressure. The residual crude product was diluted with CH_2Cl_2 (100 mL) and washed with water (3 × 150 mL). The organic phase was dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure. The product was dried in vacuum. Yield: 96 %, yellow-brown liquid. ^{1}H NMR (300MHz, $CDCl_3$) δ/ppm = 6.46 (1 H, d, C*H*) 6.14 (1 H, q, C*H*), 5.88 (1 H, d, C*H*), 4.42 (2 H, t, CH_2), 3.33 (2 H, t, CH_2).

Step 3 (ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate): In a 250 mL round bottom flask equipped with a reflux condenser Cs_2CO_3 (9.51 g, 29 mmol, 1.1 eq.) was added to anhydrous acetone (100 mL) and stirred for several days. 2,3,4,5,6-Pentafluorophenol (5.37 g, 29 mmol, 1.1 eq.) was added and stirred for 20 min before 2-iodo ethyl acrylate (6.00 g, 27 mmol, 1 eq.) was added. The suspension was refluxed overnight. A white precipitate was removed by filtration and the solvent was removed under reduced pressure. The yellow-brown filtrate was dissolved in CH_2Cl_2 (150 mL) and washed with water (3 × 150 mL), aqueous $NaHCO_3$ (100 mL), and aqueous NaCl (100 mL). The organic phase was dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure. The residual liquid was purified by silica gel column chromatography using hexane–ethyl acetate 4:1 v/v. The product was dried in vacuum. Yield: 12.8 g (73% (step 3)), yellow liquid. ^{1}H NMR (300MHz, $CDCl_3$) δ/ppm = 6.40 (1 H, dd, C*H*), 6.11 (1 H, q, C*H*), 5.86 (1 H, dd, C*H*), 4.43 (4 H, m, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 165.8 (*C*=O), 135.9–143.5 (*C*F), 131.5 (=*C*H-), 127.8 (=CH_2), 73.0 (*C*H_2), 62.9 (*C*H_2); ^{19}F NMR (282 MHz, , $CDCl_3$) δ/ppm = −156.7 (2 F, d, *ortho*), −162.9 (1 F, t, *para*), −163.3 (2 F, t, *meta*); FT-IR, ν/cm^{-1} = 2955 (C–H stretch (CH_2)), 1728 (C=O stretch), 1637 (C=C stretch), 1510–1474 (C–H bending (CH_2), 1268 (C–O stretch), 1161 (C–F) cm^{-1}. UV-Vis (0.1 mmol/L in MeCN): λ_{max1} = 236 nm, λ_{max1} = 260 nm. Soluble in methanol, acetonitrile, acetone, chloroform, dichloromethane, diethyl ether, hexane. Insoluble in water.

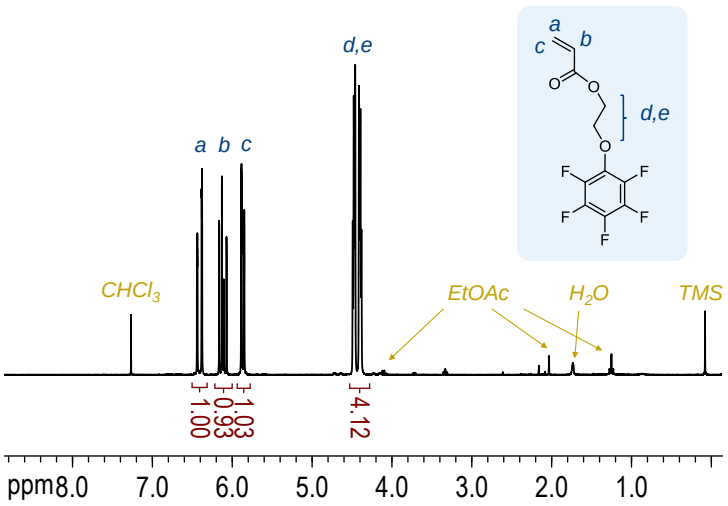


***Figure S3**. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate with assignments.*

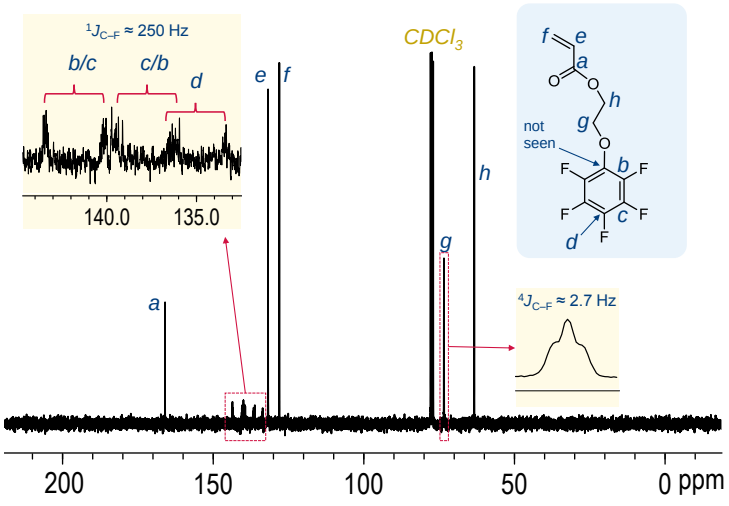


Figure S4. *^{13}C NMR spectrum (75 MHz, $CDCl_3$) of ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate with assignments. The C–F (d) was assigned based on the lower estimated integral (1 C). The quaternary aromatic carbon did not give a signal strong enough to be discerned in the noise.*

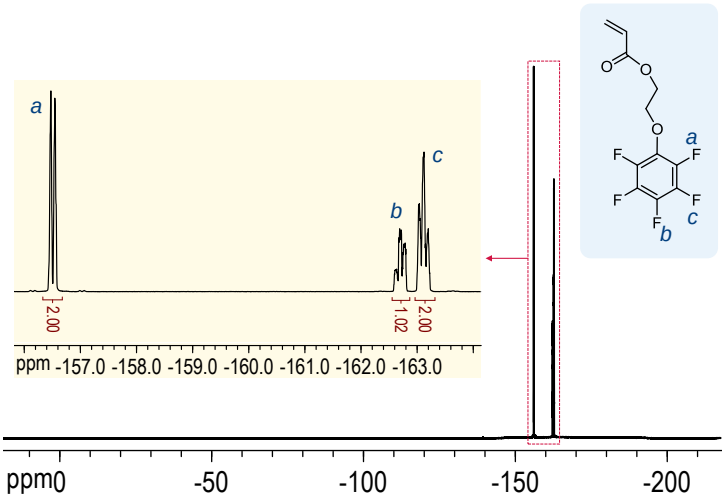
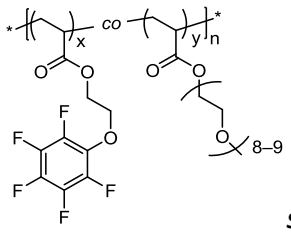


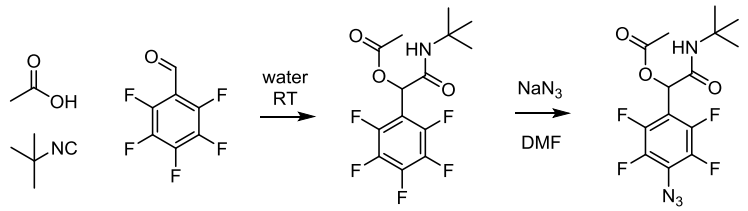
Figure S5. *^{19}F NMR spectrum (282 MHz, $CDCl_3$) of ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate with assignments.*



Scheme S3. *Structure of **6**-co-PEGA.*

The polymer **6**-*co*-PEGA (Scheme 3) was prepared in analogy to a literature procedure using an ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate–PEGA feed ratio of 40:60.[3] DP = 33 + 45 = 78. SEC (DMAc, PS calibration, 23.9 kg/mol, $Đ$ = 1.27). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 4.33 (bs, CH_2CH_2OAr), 4.14 (bs, CH_2CH$_2$OPEG), 3.37 (m, PEG), 3.37 (s, OCH_3), 2.34 (bs, CH), 1.88–1.25 (m, CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm = −156.6 (2 F, *ortho*), −161.1 (3 F, *meta* + *para*).
As **6**-*co*-PEGA did not undergo the desired para-fluoro substitution with sodium azide (see main paper), further homo-/copolymers of **6** were not investigated in this study.

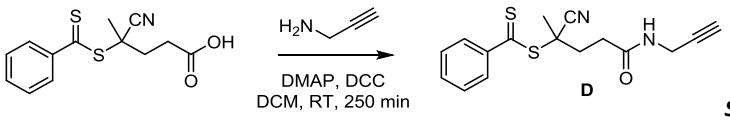
Synthesis: Azide-functional model compound



Scheme S4*. Synthesis of an azide-functional model compound.*

2-(*tert*-Butylamino)-2-oxo-1-(4-azido-2,3,5,6-tetrafluorophenyl) ethyl acetate was prepared in two steps (Scheme S4).
Step 1 (2-(*tert*-Butylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acetate): Pentafluorobenzaldehyde (0.5 g, 0.31 mL, 2.6 mmol, 1 eq.) was added to water (1.0 mL) in a 5 mL round bottom flask before acetic acid (0.16 g, 0.15 mL, 2.6 mmol, 1 eq.) was added. The mixture was stirred for a few minutes and *tert*-butyl isocyanide (0.21 g, 0.29 mL, 2.6 mmol, 1 eq.) was added slowly to the mixture which was left to stir overnight at room temperature. The water was decanted and remaining solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate–hexane 1:3 to obtain the product as a slight yellow liquid (0.73 g, 2.2 mmol, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$), δ/ppm = 6.29 (s, 1 H, -COOC*H*-), 6.24 (s, 1 H, -CON*H*-), 2.17 (s, 3 H, CH_3CO-), 1.40 (s, 9 H, -C(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm = 168.3 (*C*OO), 164.8 (*C*ONH), 65.3 (*C*H), 52.0 (*C*(CH$_3$)$_3$), 28.5 (-C(*C*H$_3$)$_3$), 20.7 (*C*H$_3$); ^{19}F NMR (282 MHz, $CDCl_3$), δ/ppm = −140.9 (m, 2 F, *ortho*), −152.4 (t, 1 F, *para*), −161.5 (m, 2 F, *meta*).
Step 2 (2-(*tert*-Butylamino)-2-oxo-1-(4-azido-2,3,5,6-tetrafluorophenyl) ethyl acetate): The product of the previous step (0.3 g, 0.884 mmol, 1 eq) was dissolved in DMF (15 mL) and sodium azide (143.7 mg, 2.21 mmol, 2.5 eq) was added. The solution was stirred in the dark for 2 h at 80 °C. Completion was confirmed by ^{19}F NMR spectroscopy of a withdrawn sample (100 µL) diluted with $CDCl_3$ (500 µL). The product was isolated by adding water (15 mL) and extracting the product with diethyl ether (3 × 50 mL), followed by drying ($MgSO_4$), and removing the solvent by blowing air into the solution. ^{1}H NMR (300 MHz, $CDCl_3$), δ/ppm = 6.27 (s, 1 H, -COOC*H*-), 6.24 (s, 1 H, -CON*H*-), 2.17 (s, 3 H, CH_3CO-), 1.39 (s, 9 H, -C(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm = 168.4 (*C*OO), 164.9 (*C*ONH), 65.5 (*C*H), 52.0 (*C*(CH$_3$)$_3$), 28.5 (-C(*C*H$_3$)$_3$), 20.8 (*C*H$_3$); ^{19}F NMR (282 MHz, $CDCl_3$), δ/ppm = −141.7 (m, 2 F, *ortho*), −152.2 (m, 2 F, *meta*). FT-IR, ν/cm^{-1} = 2120 (s, azide N=N=N). ESI MS: 363.1 (100%, M+H$^+$).

Synthesis: *N*-propargyl-4-cyano 4-(dithiobenzoyl)valeramide



Scheme S5*. Synthesis of alkyne-functional RAFT agent*

4-Cyano-4-dithiobenzoylvaleric acid (Scheme S5) (460 mg, 1.65 mmol, 1 eq) was dissolved in anhydrous dichloromethane (8 mL) in a flask under nitrogen atmosphere. 4-*N*,*N*-dimethylaminopyridine (41.6 mg, 0.34 mmol, 0.21 eq), propargyl amine (96.5 mg, 1.75 mmol, 1.06 eq), and dicyclohexyl carbodiimide (455 mg, 2.20 mmol, 1.33 eq) were added in that order. The solution was stirred until TLC control indicated completion (250 min). The product was purified by column chromatography yielding 298 mg (57%) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$), δ/ppm = 7.88 (d, 2 H, Ar), 7.56 (t, 1 H, Ar), 7.38 (t, 2 H, Ar), 6.13 (bs, N*H*), 4.06 (app. q (1:1:1:1), J = 2.6 Hz, 2 H, CH_2CCH), 2.69–2.37 (m, 4 H, CH_2CH_2), 2.23 (t, J = 2.6 Hz, 1 H, CC*H*), 1.93 (s, 3 H, CH_3).

List of all Polymers

***Table S1**. List of all Polymers with Calculated Molar Masses and SEC-determined Molar Masses and Dispersities*

Code	Full Name	Details of Synthesis (conversion)	M_n^{calc} [a]	M_n^{SEC} [b]	$Đ$ [b]
3	Poly(2,3,4,5,6-pentafluorostyrene)	DP [c] = 48	9.5	n.d.	n.d.
4	Poly(4-azido-2,3,5,6-pentafluorostyrene$_{0.90}$-*co*-2,3,4,5,6-pentafluorostyrene$_{0.10}$)	azide–*para* fluoro substitution of **3** (DP = 48) (90%)	9.7	n.d.	n.d.
3	Poly(2,3,4,5,6-pentafluorostyrene)	DP = 62	12.3	n.d.	n.d.
4	Poly(4-azido-2,3,5,6-pentafluorostyrene$_{0.89}$-*co*-2,3,4,5,6-pentafluorostyrene$_{0.11}$)	azide–*para* fluoro substitution of **3** (DP = 62) (89%)	12.4	n.d.	n.d.
3	Poly(2,3,4,5,6-pentafluorostyrene)	DP = 170	33.2	8.3 T [d]	1.32
4	Poly(4-azido-2,3,5,6-pentafluorostyrene$_{0.89}$-*co*-2,3,4,5,6-pentafluorostyrene$_{0.11}$)	azide–*para* fluoro substitution of **3** (DP = 170) (89%)	33.7	8.0 T	1.29
3	Poly(2,3,4,5,6-pentafluorostyrene)	DP = 30	6.2	5.0	1.14
4	Poly(4-azido-2,3,5,6-pentafluorostyrene$_{0.91}$-*co*-2,3,4,5,6-pentafluorostyrene$_{0.09}$)	azide–*para* fluoro substitution of **3** (DP = 30) (91%)	6.8	19.3	1.22
9	Poly(4-amino-2,3,5,6-pentafluorostyrene$_{0.91}$-*co*-2,3,4,5,6-pentafluorostyrene$_{0.09}$)	same-pot amine reduction of **4** (DP = 30)	6.1	18.8	1.19
5	Poly(2,3,4,5,6-pentafluorophenyl acrylate)	DP = 178	42.6	69.6	1.23
6-*co*-PEGA	Poly[(ethylene glycol 2,3,4,5,6-pentafluorophenyl ether acrylate)$_{0.42}$-*co*-(oligo(ethylene glycol) methyl ether acrylate)$_{0.58}$]	DP = 78	37.7	23.9	1.27
1a	Poly(2,3,4,5,6-pentafluorobenzyl methacrylate)	DP = 40	10.9	10.5	1.15
2a	Poly(4-azido-2,3,5,6-tetrafluorobenzyl methacrylate)	azide–*para* fluoro substitution of **1a** (DP = 40) (quant.)	11.8	14.4	1.47
7a/A	Poly[4-(4-decyl-1*H*-1,2,3-triazol-1-yl)-2,3,5,6-tetrafluorobenzyl methacrylate]	CuAAC modification of **2a** (DP = 40) with 1-dodecyne	18.5	21.8	1.62
1b	Poly[2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl methacrylate]	DP = 60	23.7	19.5	1.26
2b	Poly[2-(cyclohexylamino)-2-oxo-1-(4-azido-2,3,5,6-tetrafluorophenyl) ethyl methacrylate]	azide–*para* fluoro substitution of **1b** (quant.)	25.1	18.4	1.32
7b/A	Poly[2-(cyclohexylamino)-2-oxo-1-(4-(4-decyl-1*H*-1,2,3-triazol-1-yl)-2,3,5,6-tetrafluorophenyl) ethyl methacrylate]	CuAAC modification of **2b** with 1-dodecyne (96% conversion)	35.1	48.7	1.37
7b/B	Poly[2-(cyclohexylamino)-2-oxo-1-(4-(4-acryloxymethyl-1*H*-1,2,3-triazol-1-yl)-2,3,5,6-tetrafluorophenyl) ethyl methacrylate]	CuAAC modification of **2b** with propargyl acrylate (97% conversion)	30.7	33.1	1.34
7b/C	Poly[2-(cyclohexylamino)-2-oxo-1-(4-(4-butyl-1*H*-1,2,3-triazol-1-yl)-2,3,5,6-tetrafluorophenyl) ethyl methacrylate]	CuAAC modification of **2b** with 1-hexyne (95% conversion)	30.0	47.0	1.35
7b/D	Poly[2-(cyclohexylamino)-2-oxo-1-(4-(4-(4-cyano 4-(dithiobenzoyl)valeramido methyl)-1*H*-1,2,3-triazol-1-yl)-2,3,5,6-tetrafluorophenyl) ethyl methacrylate]	CuAAC modification of **2b** with *N*-propargyl-4-cyano 4-(dithiobenzoyl)valeramide (quant.)	44.1	54.1	1.35
1a	Poly(2,3,4,5,6-pentafluorobenzyl methacrylate)	DP = 65	17.5	10.3 T	1.13
2a	Poly(4-azido-2,3,5,6-tetrafluorobenzyl methacrylate)	azide–*para* fluoro substitution of **1a** (DP = 65) (quant.)	19.0	9.6 T	1.16
8a	Poly(4-acetamido-2,3,5,6-tetrafluorobenzyl methacrylate)	azide–thioacetate modification of **2a** (DP = 65) (quant.)	20.1	4.1 T	1.23
1c	Poly[2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acrylate]	DP = 55	21.0	8.9	1.45
2c	Poly[2-(cyclohexylamino)-2-oxo-1-(4-azido-2,3,5,6-tetrafluorophenyl) ethyl acrylate]	azide–*para* fluoro substitution of **1c** (quant.)	22.3	n.d.	n.d.
10c	Poly[2-(cyclohexylamino)-2-oxo-1-(4-amino-2,3,5,6-tetrafluorophenyl) ethyl acrylate]	azide-to-amine reduction of **2c** (quant.)	20.8	13.5	1.39
1c-*co*-pPEGA	Poly[(2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acrylate)$_{0.30}$-*co*-(oligo(ethylene glycol) methyl ether acrylate)$_{0.70}$]	DP = 92	41.4	28.5	1.39
2c-*co*-pPEGA	Poly[(2-(cyclohexylamino)-2-oxo-1-(4-azido-2,3,5,6-tetrafluorophenyl) ethyl acrylate)$_{0.32}$-*co*-(oligo(ethylene glycol) methyl ether acrylate)$_{0.68}$]	azide–*para* fluoro substitution of **1c**-*co*-pPEGA (quant.)	42.1	30.3	1.40
10c-*co*-pPEGA	Poly[(2-(cyclohexylamino)-2-oxo-1-(4-amino-2,3,5,6-tetrafluorophenyl) ethyl acrylate)$_{0.32}$-*co*-(oligo(ethylene glycol) methyl ether acrylate)$_{0.68}$]	azide-to-amine reduction of **2c**-*co*-pPEGA (quant.)	41.3	31.0	1.40
1a	Poly(2,3,4,5,6-pentafluorobenzyl methacrylate)	DP = 145	38.8	19.2	1.34
2a	Poly(4-azido-2,3,5,6-tetrafluorobenzyl methacrylate)	azide–*para* fluoro substitution of **1a** (DP = 145) (quant.)	42.2	n.d.	n.d.
10a	Poly(4-amino-2,3,5,6-tetrafluorobenzyl methacrylate)	same-pot amine reduction of **2a** (DP = 145)	38.4	41.4	1.20
11a/E	Poly(4-acrylamido-2,3,5,6-tetrafluorobenzyl methacrylate)	amidation of **10a** (DP = 145) with acryloyl chloride	46.2	77.9	1.31
11a/F	Poly(4-(3,5-dinitrobenzamido)-2,3,5,6-tetrafluorobenzyl methacrylate)	amidation of **10a** (DP = 145) with 3,5-dinitrobenzoyl chloride	66.5	136.3	1.29

[a] Molar mass calculated from degree of polymerization and mass of end groups
[b] Determined by size exclusion chromatography in DMAc (PS calibration)
[c] Degree of polymerization determined from crude NMR measurement by quantifying the amount of residual monomer
[d] T = Size exclusion chromatography in THF (PMMA calibration)

Results and Discussion

Azide–*para*-fluoro substitution on 2,3,4,5,6-pentafluorobenzyl-functional polymers

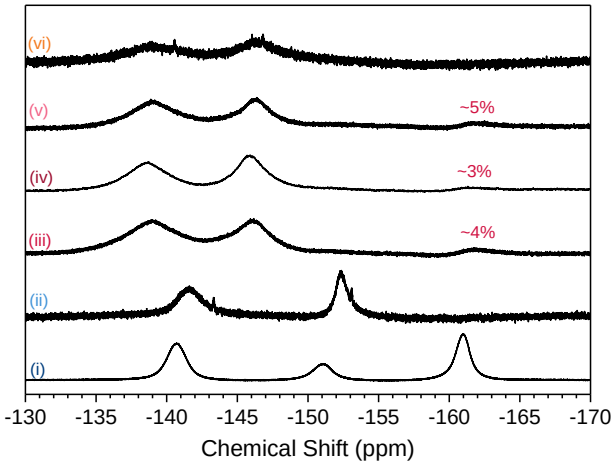


Figure S6. *^{19}F NMR spectra (376 MHz, $CDCl_3$) of (i) poly[2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl methacrylate]* ***1b****, (ii) its azide derivate* ***2b*** *and triazoles* ***7b*** *after CuAAC modification with (iii) 1-dodecyne (****7b/A****), (iv) propargyl acrylate (****7b/B****), (v) 1-hexyne (****7b/C****), and (vi) the propargyl-functional dithioester (****7b/D****). The inset figures indicate the approximate molar ratio of a side produce with a chemical shift of −163 ppm. The spectra show broad signals presumably due to poor solvation around the sterically crowded methacrylic repeat units. This broadening was already observed in our previous study[3] and the attachment of further functionality through CuAAC, while (nearly) quantitative, leads to further peak broadening.*

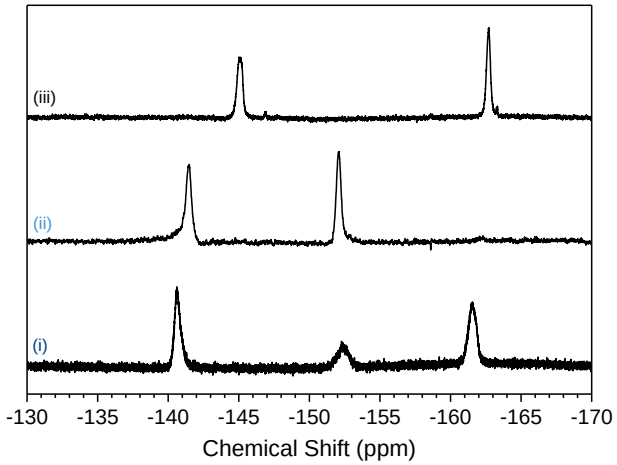


Figure S7. *^{19}F NMR spectra (282 MHz, $CDCl_3$) of (i) poly[(2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acrylate)$_{0.32}$-co-(oligo(ethylene glycol) methyl ether acrylate)$_{0.68}$]* ***1c****-co-pPEGA; (ii) its azide derivate* ***2c****-co-pPEGA, and (iii) after reduction to the 2,3,5,6-tetrafluoroaniline derivative* ***10c****-co-pPEGA.*

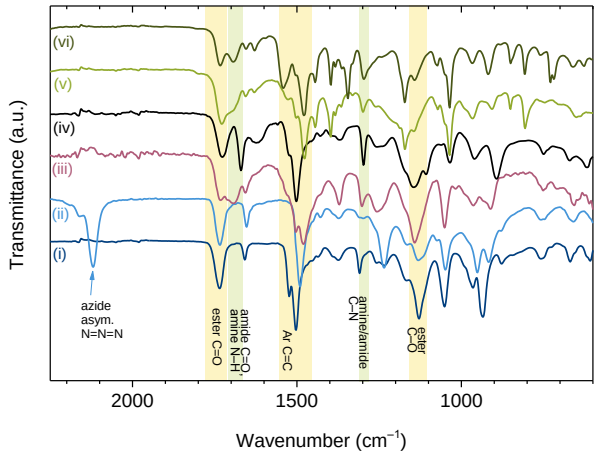


Figure S8. *FT-IR spectra of (i) poly(2,3,4,5,6-pentafluorobenzyl methacrylate)* ***1a****, (ii) its azide derivative* ***2a****, (iii) 2,3,5,6-tetrafluoroacetanilide* ***8a****, (iv) 2,3,5,6-tetrafluoroaniline* ***10a****, and after acylation with (v) acryloyl chloride,* ***11a/E*** *and (vi) 3,5-dinitrobenzoyl chloride,* ***11a/F*** *with relevant vibrations highlighted.*

Azide–*para*-fluoro substitution on poly(2,3,4,5,6-pentafluorostyrene)

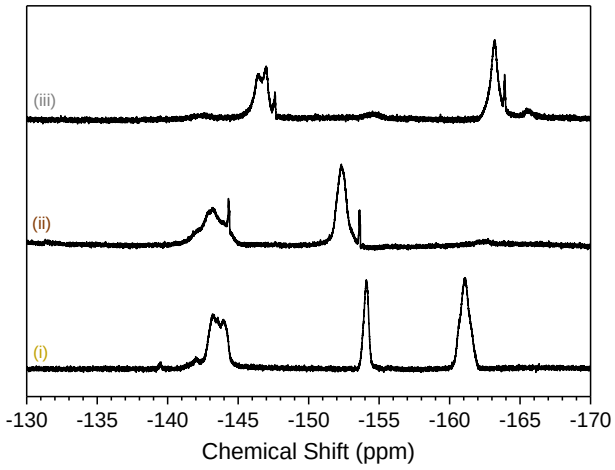
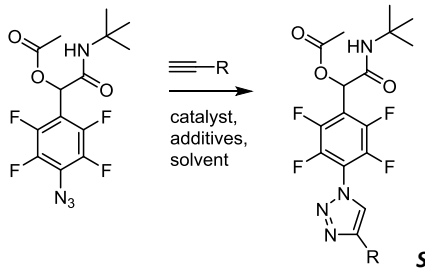


***Figure S9**. ^{19}F NMR spectra (376 MHz) of (i) poly(2,3,4,5,6-pentafluorostyrene) **3** ($CDCl_3$); (ii) after substitution of approx. 91% of the para-fluorides with azide, **4** (DMAc–$CDCl_3$ 1:3) and (iii) following same-pot azide-to-amine reduction to give the aniline-derivative **9** (DMAc–$CDCl_3$ 1:3). The sharp signals in spectra (ii) and (iii) originate from approx. 5 mol-% of residual 2,3,4,5,6-pentafluorostyrene monomer that had not been removed before modification but which indicates that the modification also took place on the small molecules. The small broad signals in the same spectra originate from unmodified 2,3,4,5,6-pentafluorostyrene repeat units.*

CuAAC Modification: Optimisation of conditions using a small molecule model azide



***Scheme S6**. CuAAC model reactions.*

***Table S2**. Overview of CuAAC reactions on a small molecule model (Scheme S6)*

Entry	Yne	Catalyst	Additives	Solv.	Temp.	Time	Triazole
1	1-Pentyne (1.2 eq)	CuBr (0.08 eq)	4,4'-Dinonyl-2,2'-dipyridyl (0.16 eq), Pyridine (1 eq)	$CDCl_3$	0 °C → RT	19 h	0%
2	1-Pentyne (1.2 eq)	CuBr (0.12 eq)	Et_3N (1.2 eq), Diisopropylamine (1.2 eq)	$CDCl_3$	RT	16 h	13%
3	1-Pentyne (2 eq)	$Cu(PPh_3)_3Br$ (0.4 eq)	Piperidine (4 eq), Ethyldiisopropylamine (0.8 eq)	THF	RT	4 h	0% (mixture of products)
4	1-Dodecyne (1.2 eq)	CuBr (0.12 eq)	Et_3N (1.8 eq)	$CDCl_3$	40 °C	a) 2 h b) 22.5 h	a) 46% b) 85%
5	1-Dodecyne (1.2 eq)	CuBr (0.12 eq)	Et_3N (1.8 eq)	$CDCl_3$	40 °C[a]	a) 1.75 h b) 5.25 h c) 23.5 h d) 4 d e) 5 d	a) 9 % b) 25 % c) 79 % d) 94 % e) 95 %
6	1-Dodecyne (1.2 eq)	CuBr (0.12 eq)	Et_3N (1.8 eq)	DMF	80 °C	20.5 h	100%

[a] reaction in NMR tube; not stirred

CuAAC Modification on azide-functional polymer

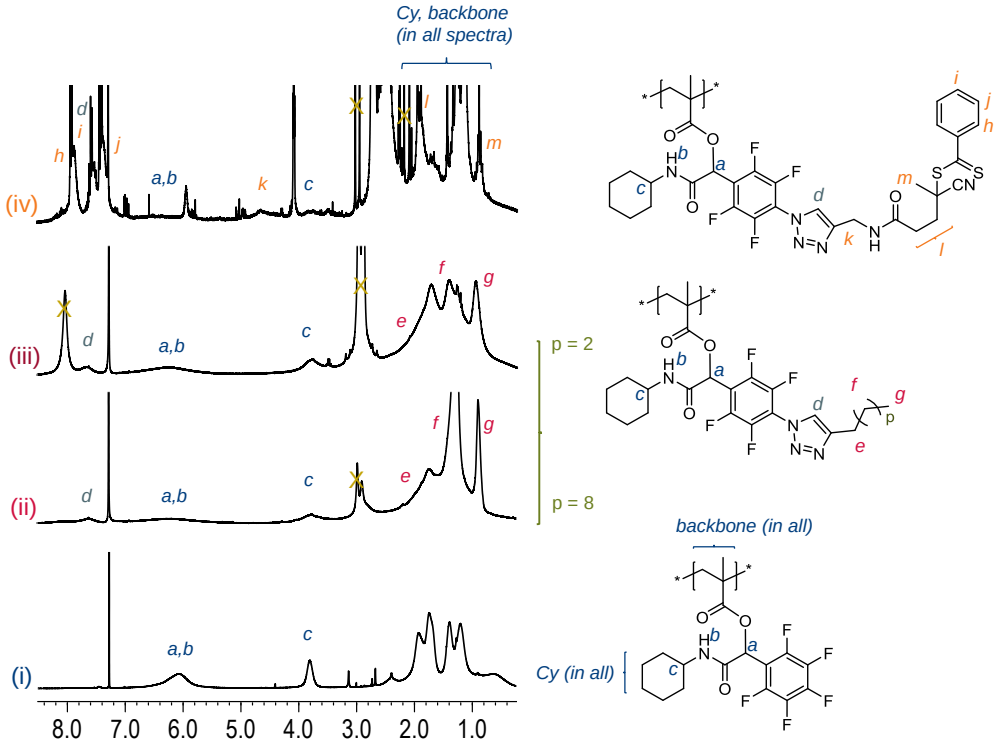


Figure S10. *^{1}H NMR spectra (400 MHz, $CDCl_3$) of (i) poly[2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl methacrylate]* ***1b*** *and following azide substitution and CuAAC modification with (ii) 1-dodecyne,* ***7b/A****; (iii) 1-hexyne,* ***7b/C****; (iv) an alkyne-functional RAFT agent,* ***7b/D****.*

Azide-to-amine reduction

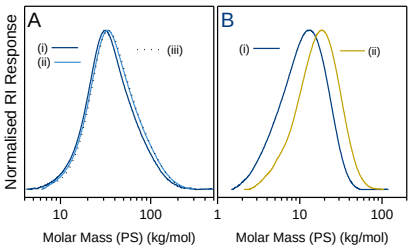


Figure S11. *Size exclusion chromatograms of (**A**) (i) poly[(2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acrylate)$_{0.32}$-co-(oligo(ethylene glycol) methyl ether acrylate)$_{0.68}$]* ***1c****-co-pPEGA (DP = 92), (ii) its azide derivate* ***2c****-co-pPEGA, and (iii) after reduction to the 2,3,5,6-tetrafluoroaniline derivative* ***10c****-co-pPEGA; (**B**) (i) poly[2-(cyclohexylamino)-2-oxo-1-(2,3,4,5,6-pentafluorophenyl) ethyl acrylate]* ***1c*** *(DP = 55) and (ii) its 2,3,5,6-tetrafluoroaniline derivative* ***10c*** *after one-pot substitution–reduction.*

Solubility Tests

***Table S3**. Observed solubilities of four methacrylic polymer examples in a variety of aqueous and organic solvents. The insolubility of aniline-functional polymer **10a** in aqueous HCl demonstrated the low basicity of the nitrogen lone pair. Importantly, all below polymers were soluble in solvents of intermediate polarity.*

Solvent	1a (pentafluoro)	2a (azide)	10a (aniline)	11a/F (dinitrobenzamide)
Water	no	no	no	
Aq. HCl (pH 2–3)	no		no	
Methanol	no	no	yes	no
Ethanol	no	no	yes	no
Dimethylsulfoxide	yes		yes	yes
N,*N*-Dimethylformamide	yes	yes	yes	yes
N,*N*-Dimethylacetamide	yes	yes	yes	
Acetonitrile	yes		yes	yes
Acetone	yes			yes
Tetrahydrofuran	yes	yes	yes	yes
Ethyl acetate	yes		yes	yes
Chloroform	yes	yes	no	yes
Dichloromethane	yes		no	yes
Toluene	yes		no	no
Diethyl ether	yes		no	
Hexane	no		no	no

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