Electronic Supplementary Information (ESI) for:

The effect of fluorination on chain transfer reactions in the radical polymerization of oligo ethylene glycol ethenesulfonate monomers

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Monomer syntheses

Synthesis of ethyl ethenesulfonate (EES). EES was prepared as described previously with slight modifications.[1-3] A solution of 2-chloroethanesulfonyl chloride (15.00 mL, 142.8 mmol, 1.0 eq) in DCM (180 mL) was cooled down to 0 °C. Under stirring, a solution of dry ethanol (9.99 mL, 171.4 mmol, 1.2 eq) and triethylamine (43.79 mL, 314.2 mmol, 2.2 eq) in DCM (20 mL) was added dropwise within 1 h. The mixture was stirred at room temperature for another 19 h resulting in a yellowish suspension containing a white solid. After filtration and washing the filter cake with DCM (30 mL), the alkaline filtrate was washed with hydrochloric acid (1 N, 50 mL) and water (60 mL twice) until neutrality. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Further purification was carried out by vacuum distillation (bp 32 °C/1.24 Pa), yielding EES as a colorless and transparent oil (12.0 g, 69 %). Anal. Calcd for $C_4H_8O_3S$: C, 35.3; H, 5.9; N, 0.0; S, 23.5. Found: C, 34.9; H, 5.9; N, 0.0; S, 23.2 %. ^{1}H NMR ($CDCl_3$) δ 6.52 (dd, J = 16.6, 9.7, 1H, H_2C = C*H*-), 6.38 (d, J = 16.6, 1H, *H_2*C = CH-), 6.12 (d, J = 9.7, 1H, *H_2*C = CH-), 4.17 (q, J = 7.1, 2H, -SO_2-O-C*H_2*-), 1.37 (t, J = 7.1, 3H, *H_3*C-), Fig. S1. ^{13}C NMR ($CDCl_3$) δ 132.4 (H_2C = *C*H-), 130.1 (H_2*C* = CH-), 67.1 (-SO_2-O-*C*H_2-), 14.8 (H_3*C*-), Fig. S2.

Chain transfer agent (CTA) synthesis

Synthesis of *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate (OEMDTC). The synthesis of OEMDTC was performed similarly to the literature,[4] but with an excess of methyl 2-bromopropionate instead of potassium ethyl xanthogenate to prevent a second nucleophilic substitution by the ethyl xanthogenate. The latter reaction was expected to yield the double substituted by-product 2-(ethoxy-carbonothioylthio)propanoic (*O*-ethyl carbonothioic) thioanhydride (EPETA) which could also act as a chain transfer agent (CTA). It turned out, that the removal of excess methyl 2-bromopropionate was easier in comparison to the removal of EPETA.

A solution of methyl 2-bromopropionate (9.96 g, 59.6 mmol, 1.05 eq) in ethanol (300 mL) was cooled down to 0 °C. Under stirring, potassium ethyl xanthogenate (9.08 g, 56.6 mmol, 1.00 eq) was added in portions within 1 h. The mixture was stirred at room temperature overnight yielding in a yellowish suspension containing a white solid. The suspension was diluted by a mixture of diethyl ether/pentane (2/1 by volume, 400 mL) and washed with water (twice 150 mL). The aqueous phase was extracted with a mixture of diethyl ether/pentane (2/1 by volume, 100 mL). The combined organic phases were washed with water (twice 150 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The product was purified by column chromatography on silica with a mixture of *n*-hexane/ethyl acetate (10/1 by volume) as an eluent and drying in high vacuum at room temperature for two days yielding OEMDTC as a yellow oil (9.3 g, 79 %). The product was stored under argon. The density of the product was determined by weighing thrice a volume of 1 mL and calculating the arithmetic mean (1.183 g/mL at 22 °C). We observed two different ^{1}H NMR quartet signals of the methylene protons in OEMDTC which had not been noted in previous studies. We assume that this splitting arises from the presence of (*R*)- and (*S*)-OEMDTC. ^{1}H NMR ($CDCl_3$) δ 4.60 and 4.59 (q, J = 7.1, 2H, (*R*)- and (*S*)-OEMDTC, H_3C-CH_2-), 4.35 (q, J = 7.4, 1H, *H*-C(CH_3)($COOCH_3$)-), 3.71 (s, 3H, H_3C-O-), 1.53 (d, J = 7.4, 3H, H_3C-CH($COOCH_3$)-), 1.38 (t, J = 7.1, 3H, H_3C-CH_2-), Fig. S13. ^{13}C NMR ($CDCl_3$) δ 211.76 (=*C*(OC_2H_5)-), 171.72 (=*C*(OCH_3)-), 70.35 – 69.94 (m, H_3C-*C*H_2-), 52.62 (q, J = 6.1, H_3*C*-O-), 46.81 (d, J = 7.6, -*C*H(CH_3)-), 16.69 (H_3*C*-CH(CH_3)($COOCH_3$)-), 13.51 (H_3*C*-CH_2-), Fig. S14.

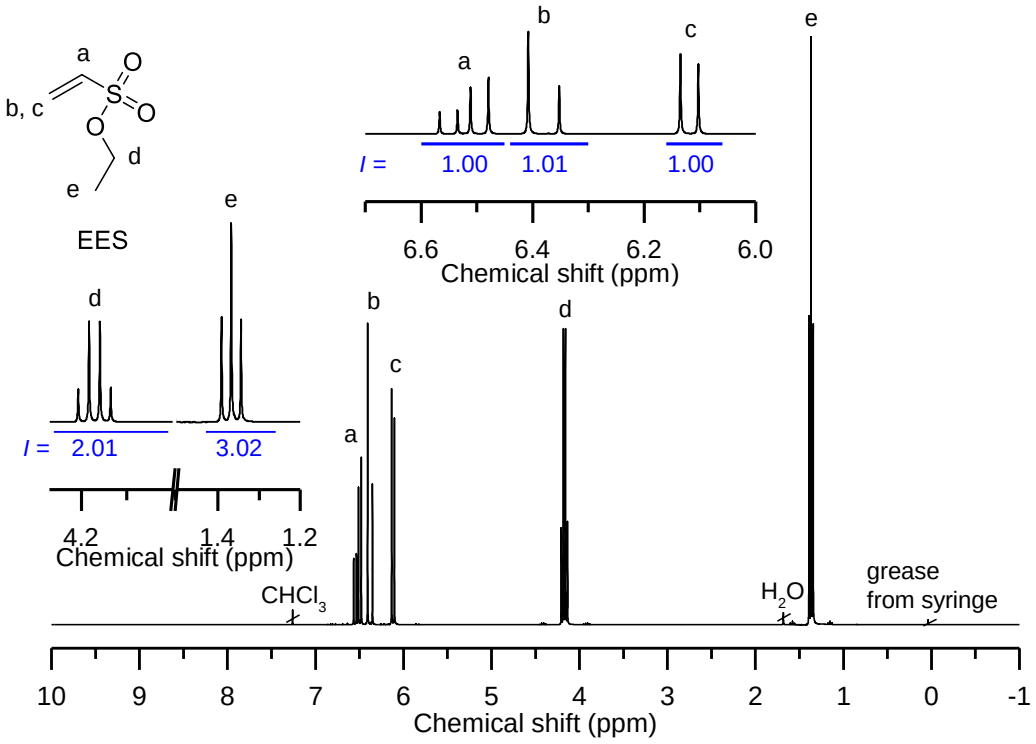


Fig. S1 ^{1}H NMR spectrum of EES in $CDCl_3$.

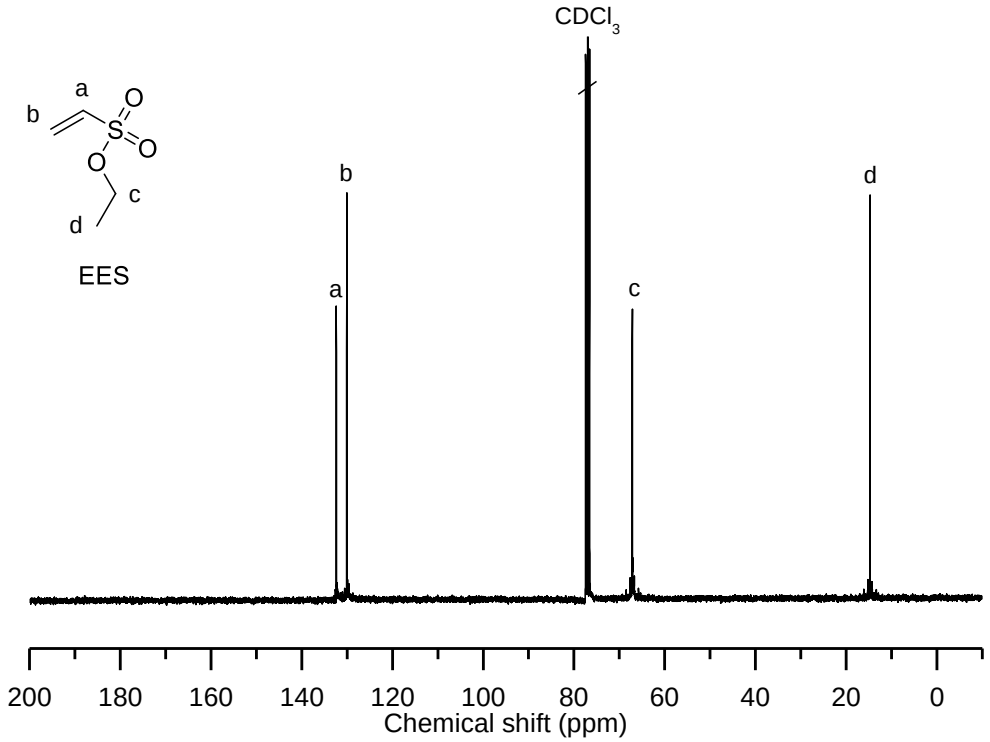


Fig. S2 ^{13}C NMR spectrum of EES in $CDCl_3$.

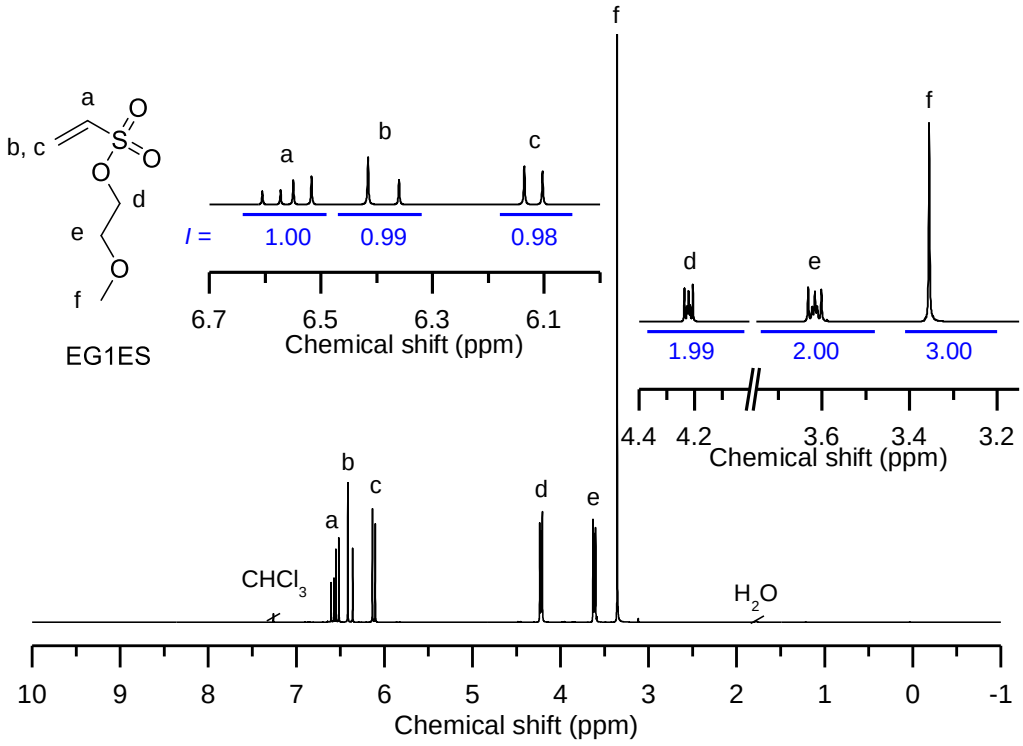


Fig. S3 ^{1}H NMR spectrum of EG1ES in $CDCl_3$.

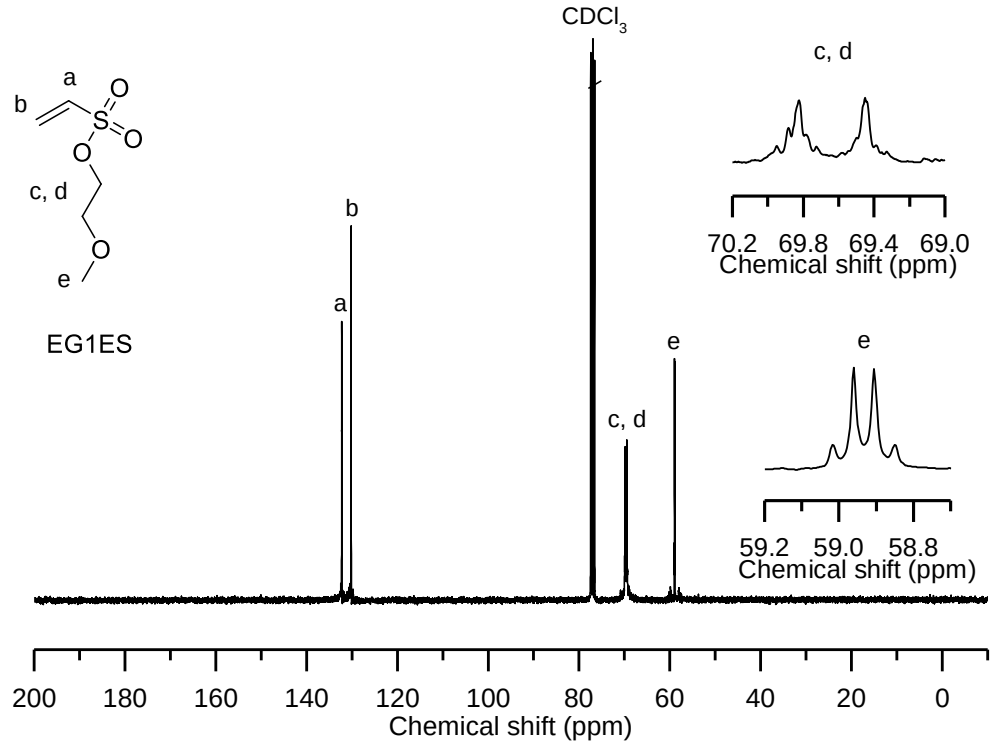


Fig. S4 ^{13}C NMR spectrum of EG1ES in $CDCl_3$.

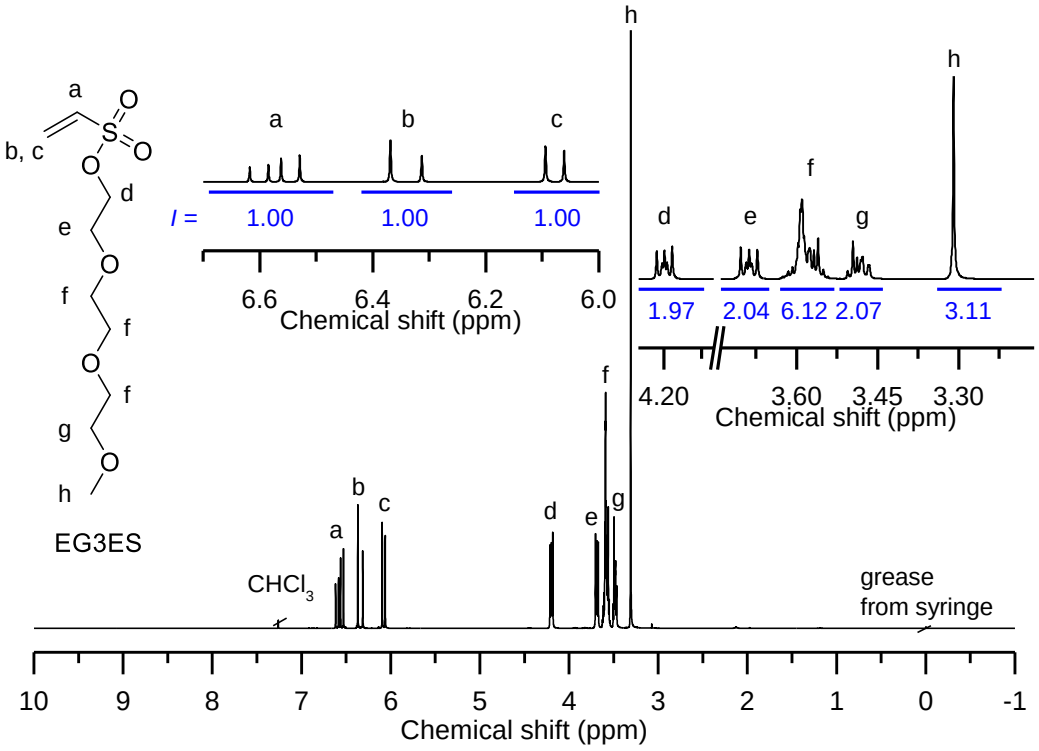


Fig. S5 ^{1}H NMR spectrum of EG3ES.

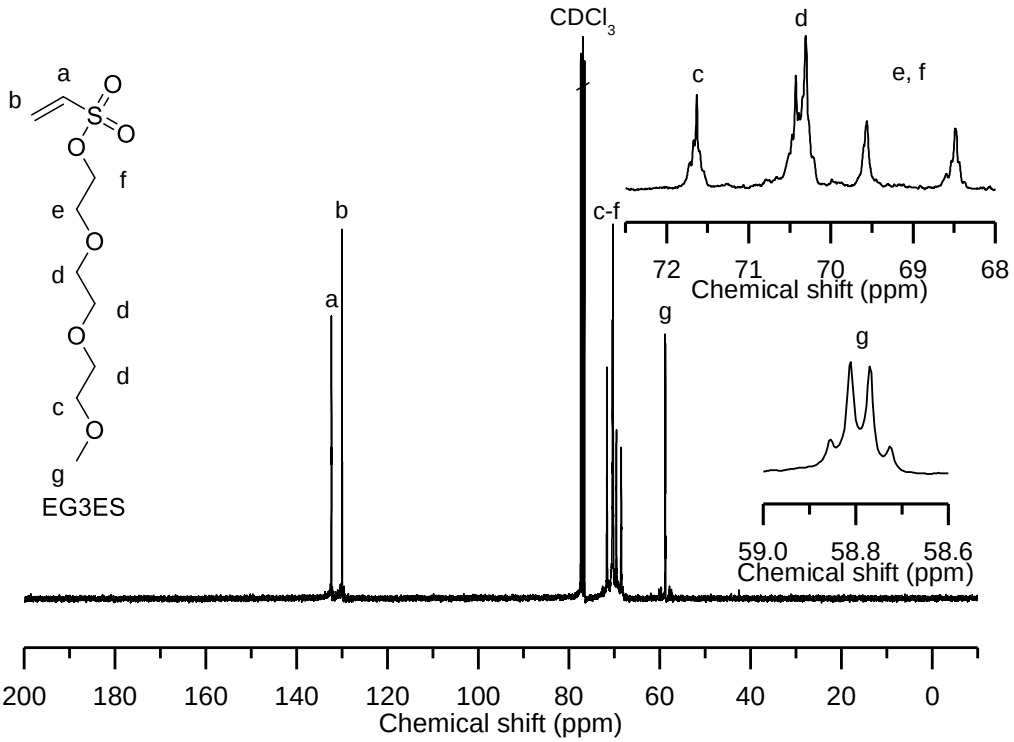


Fig. S6 ^{13}C NMR spectrum of EG3ES in $CDCl_3$.

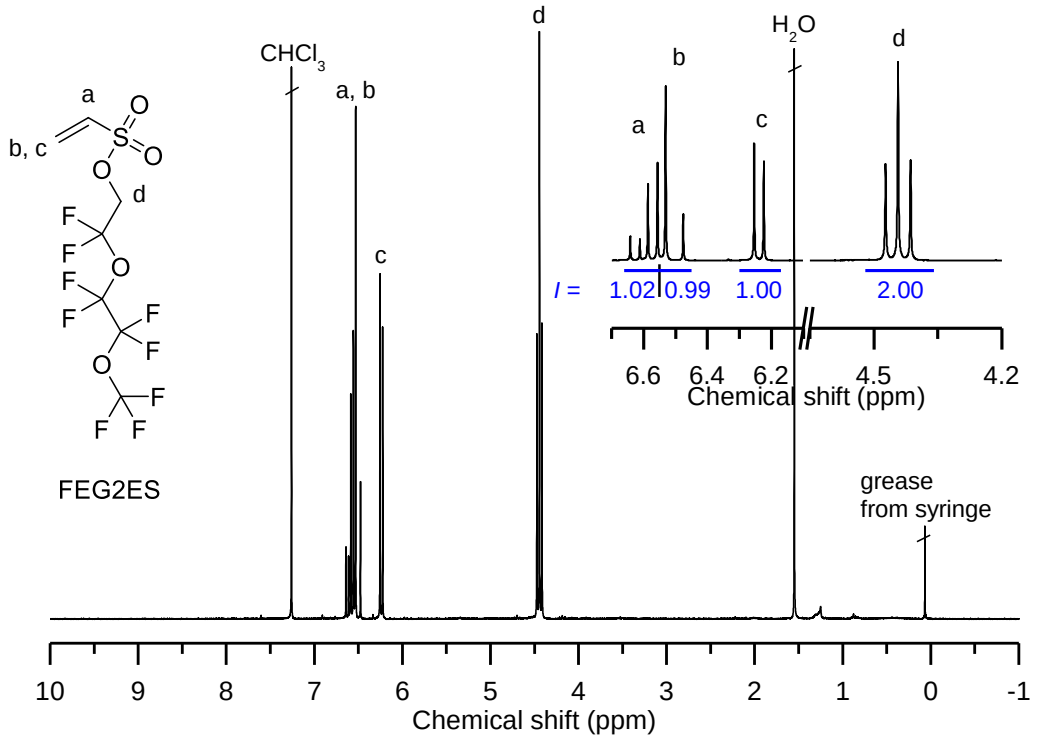


Fig. S7 ^{1}H NMR spectrum of FEG2ES in $CDCl_3$.

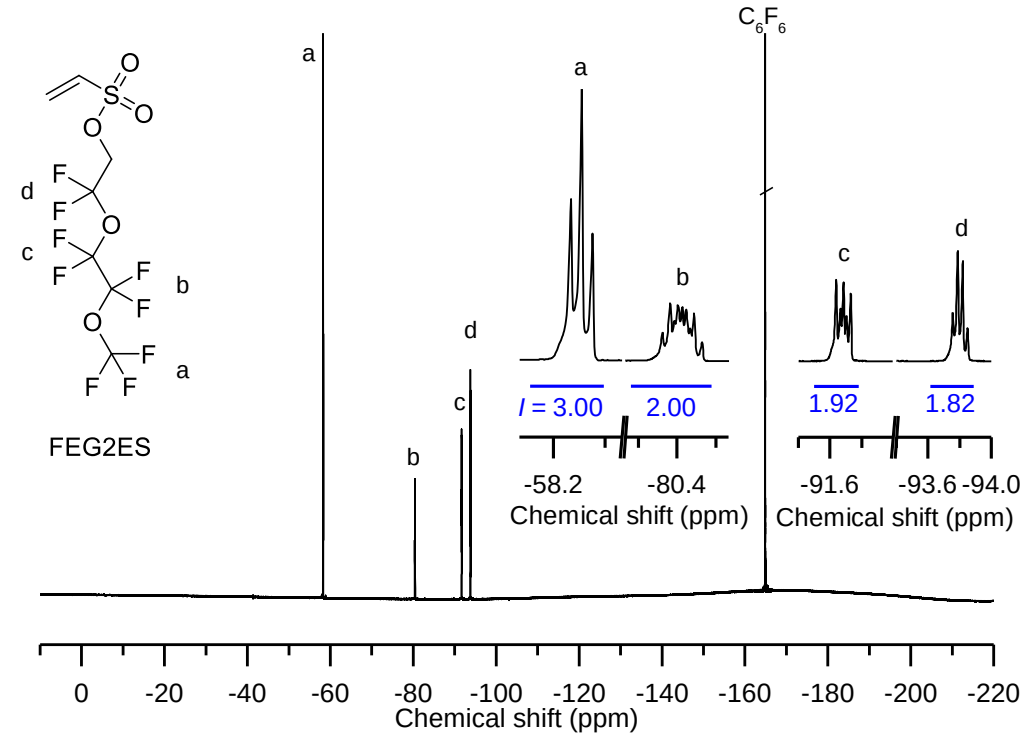


Fig. S8 ^{19}F NMR spectrum of FEG2ES in $CDCl_3$ with C_6F_6 as an internal reference.

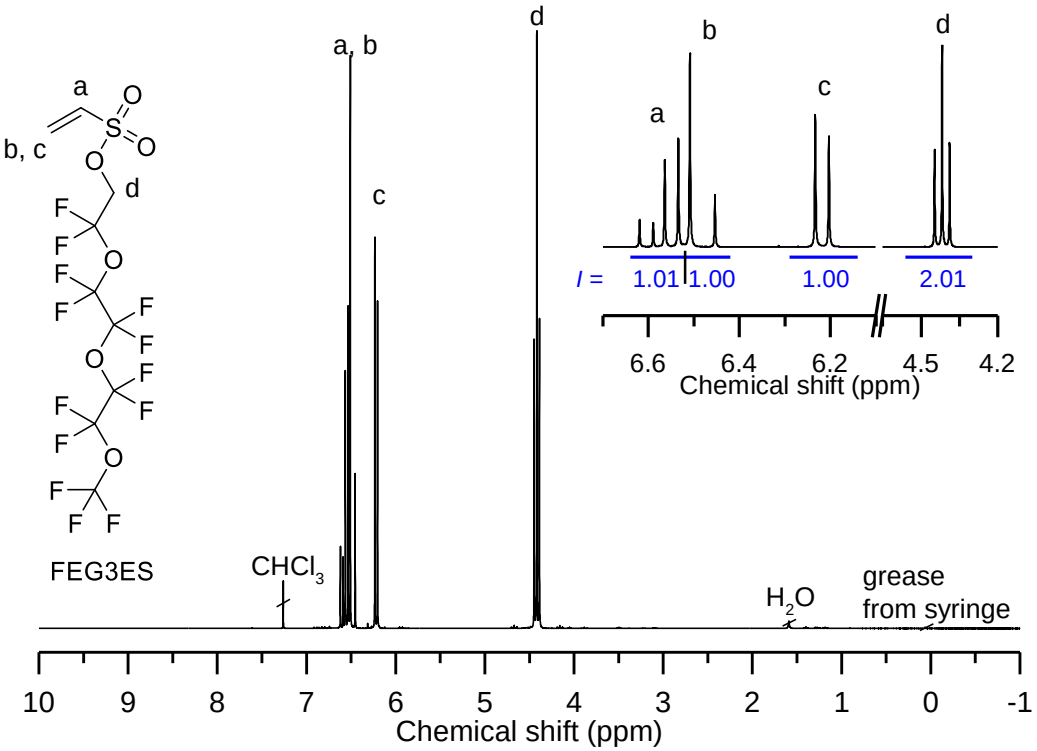


Fig. S9 ^{1}H NMR spectrum of FEG3ES in $CDCl_3$.

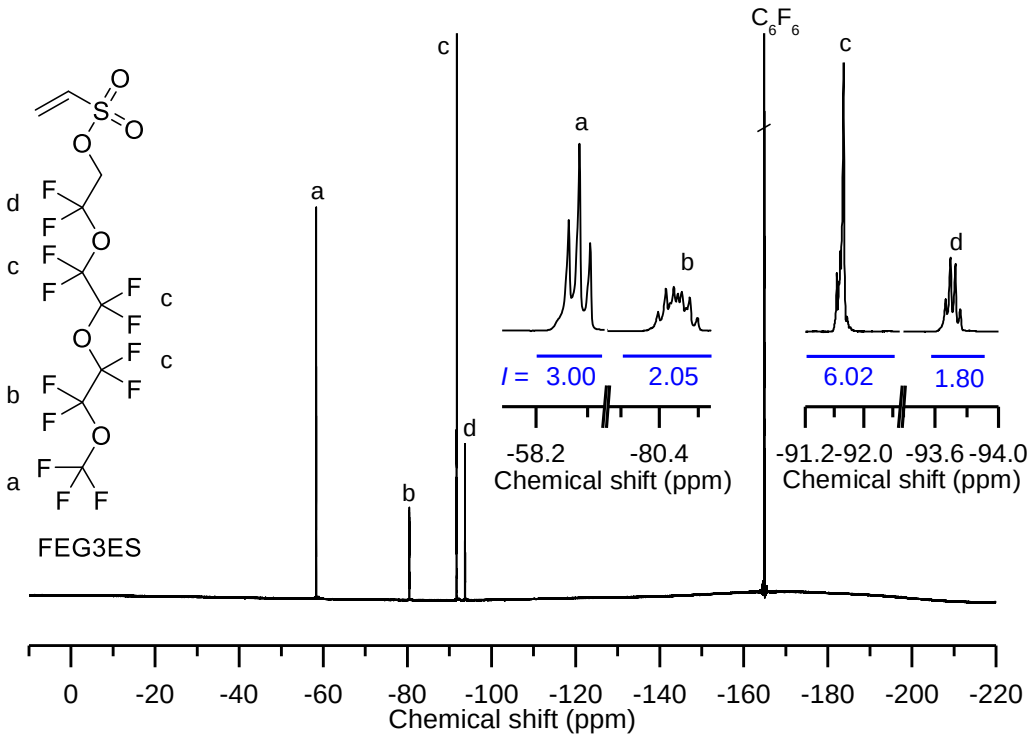


Fig. S10 ^{19}F NMR spectrum of FEG3ES in $CDCl_3$ with C_6F_6 as an internal reference.

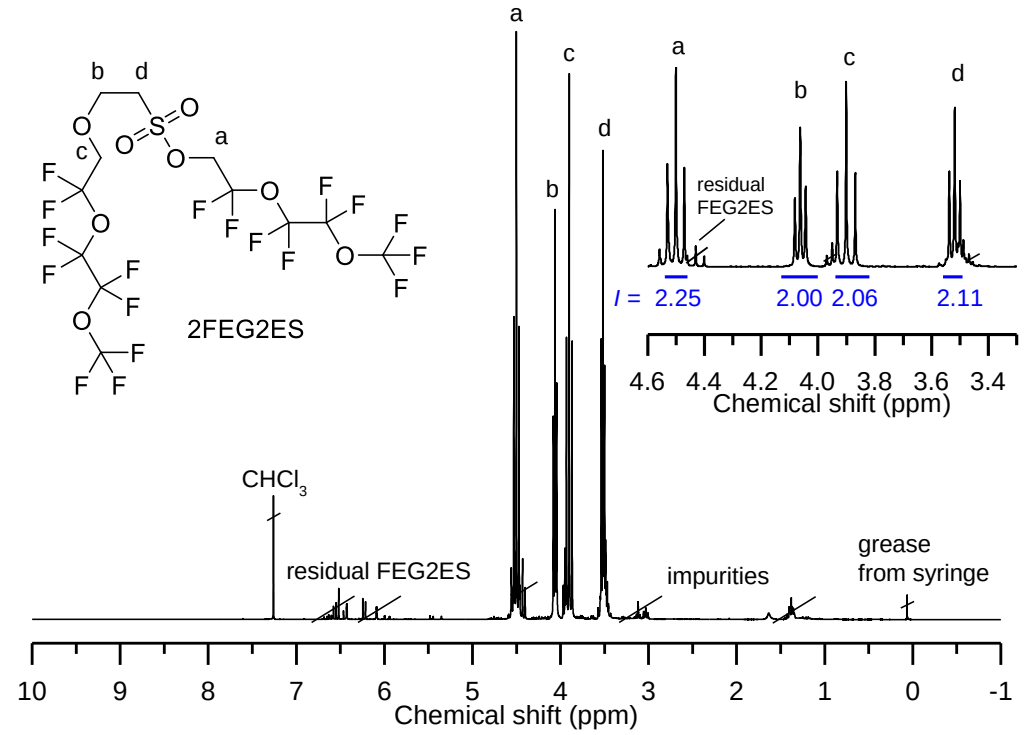


Fig. S11 ^{1}H NMR spectrum of the by-product 2FEG2ES from the synthesis of FEG2ES in $CDCl_3$. The sample was taken from the residue after distillation of the product FEG2ES.

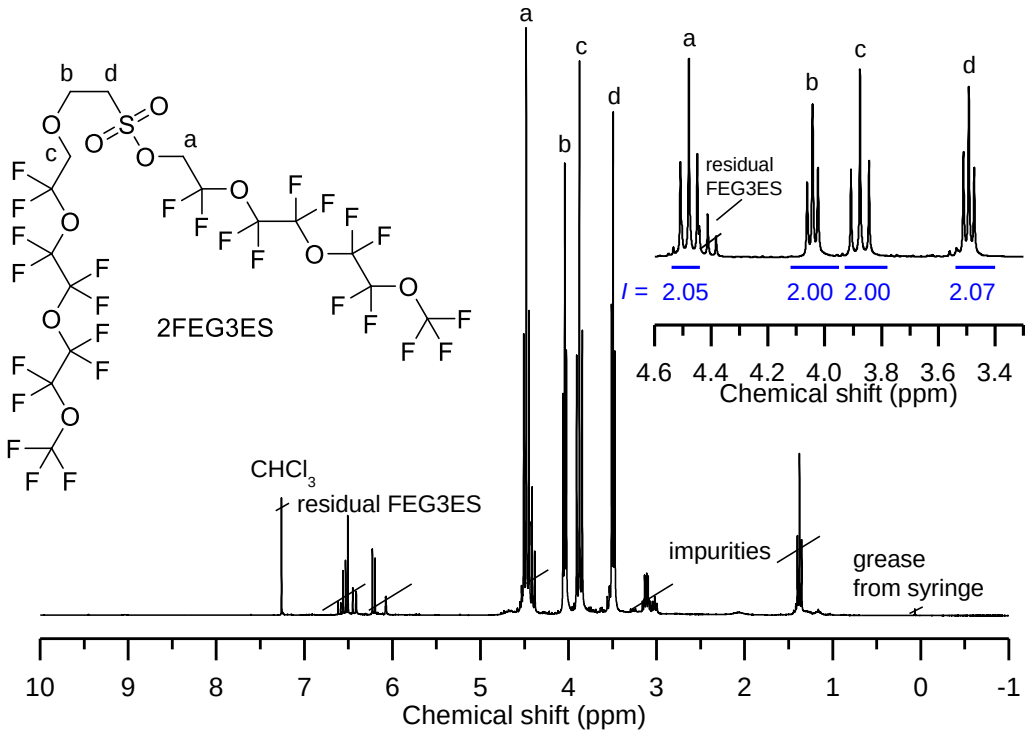


Fig. S12 ^{1}H NMR spectrum of the by-product 2FEG3ES from the synthesis of FEG3ES in $CDCl_3$. The sample was taken from the residue after distillation of the product FEG3ES.

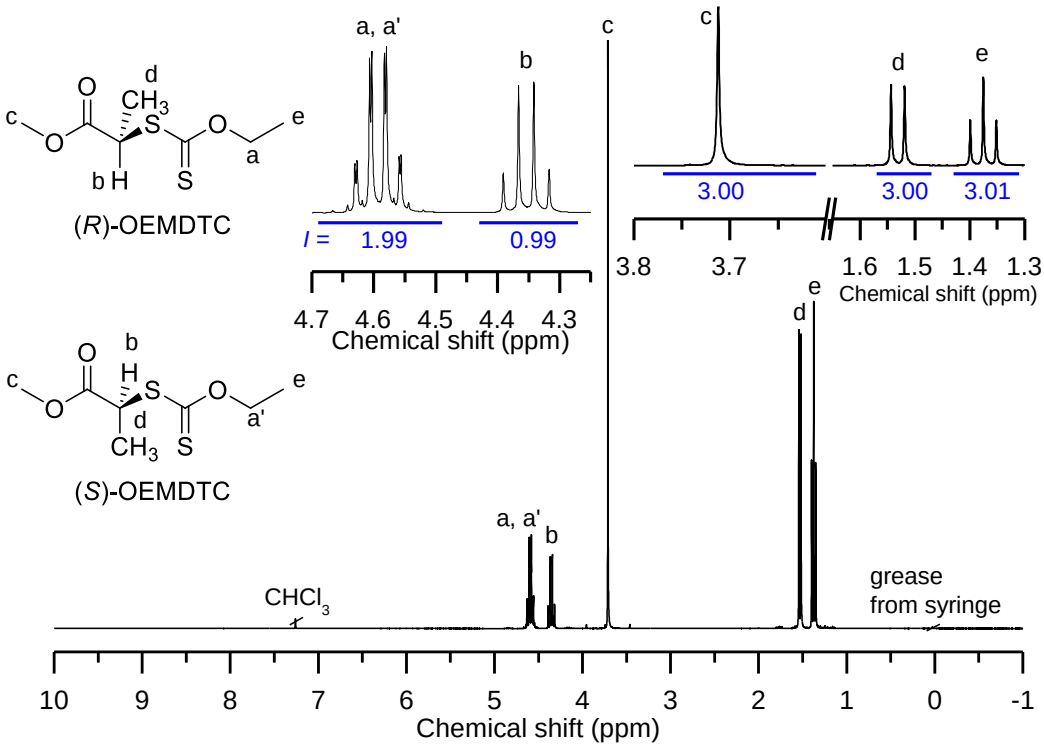


Fig. S13 ^{1}H NMR spectrum of OEMDTC in $CDCl_3$.

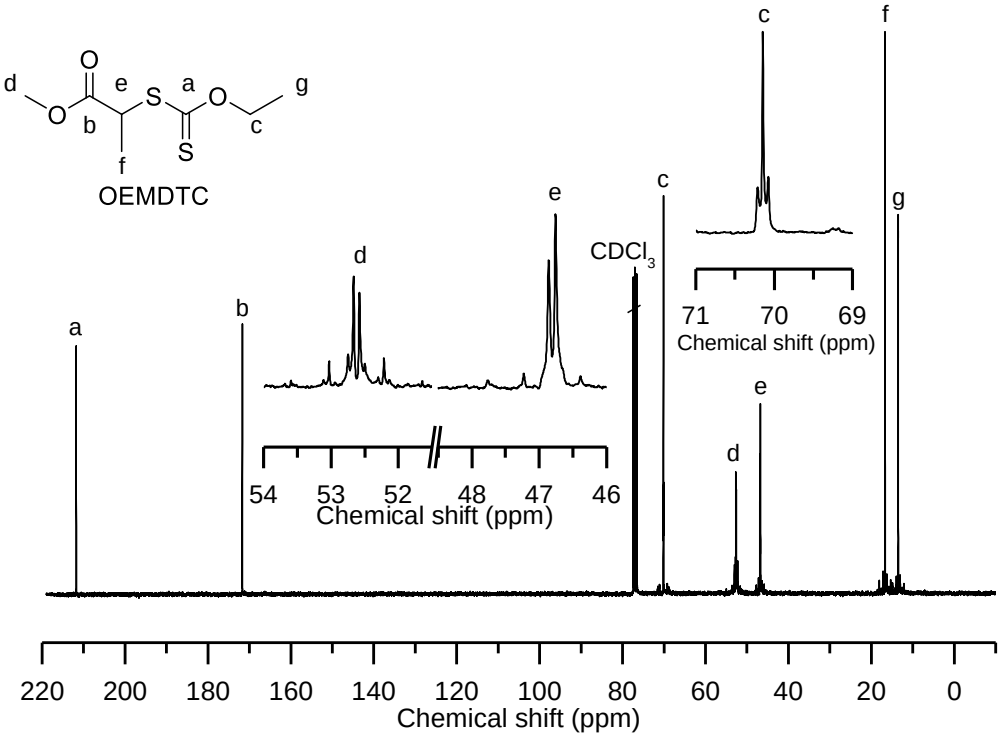


Fig. S14 ^{13}C NMR spectrum of OEMDTC in $CDCl_3$.

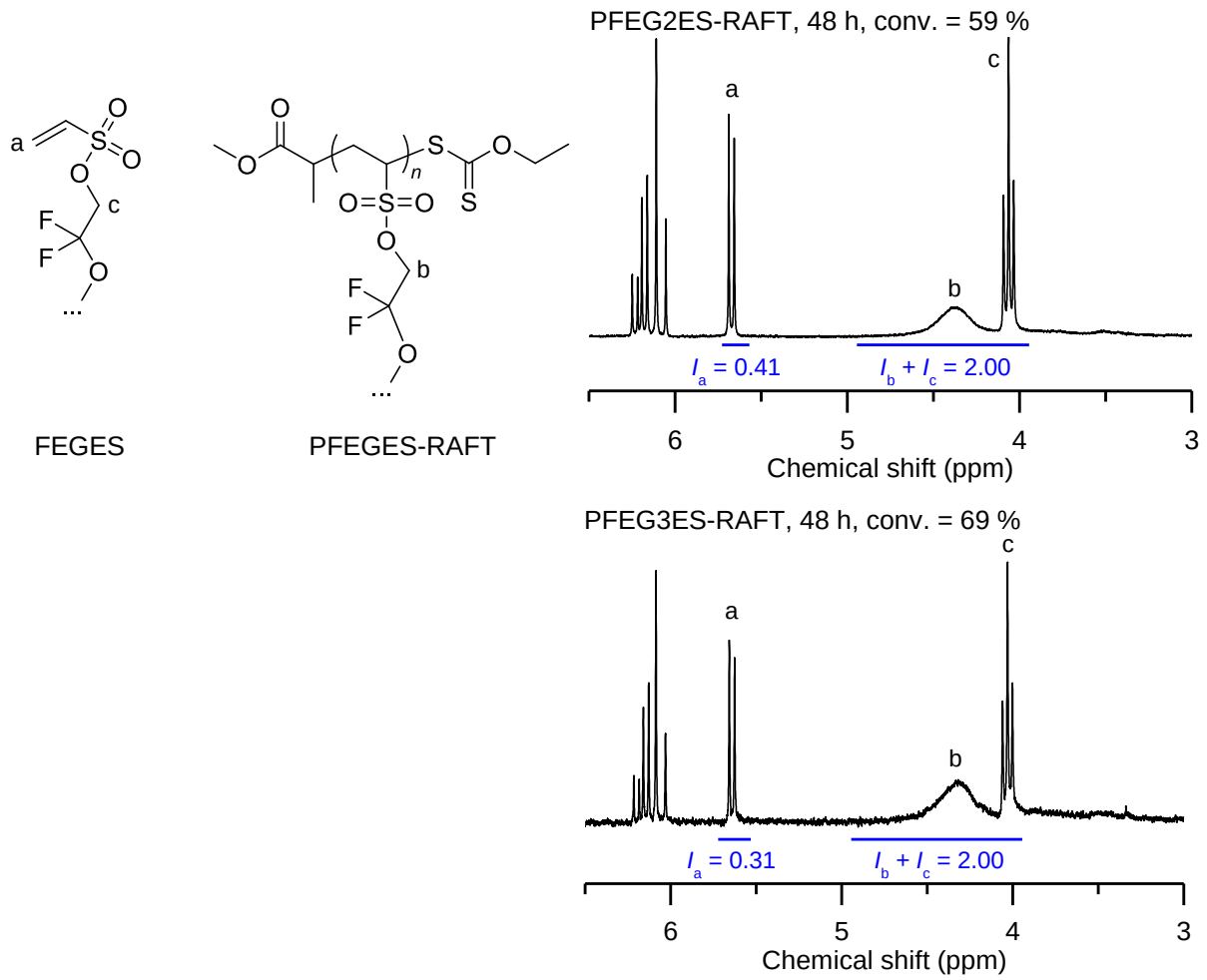


Fig. S15 ^{1}H NMR spectrum taken during the synthesis of (above) PFEG2ES-RAFT and (below) PFEG3ES-RAFT after a reaction time of 48 h. The monomer conversion (conv.) was calculated by equation 1 with the integration of the vinyl proton of the monomer I_a (5.73-5.57 ppm for PFEG2ES-RAFT and 5.72-5.53 ppm for PFEG3ES-RAFT) and the integration of the methylene protons adjacent to the sulfonate group of both the polymer I_b and the monomer I_c (4.95-3.94 ppm for PFEG2ES- and PFEG3ES-RAFT).

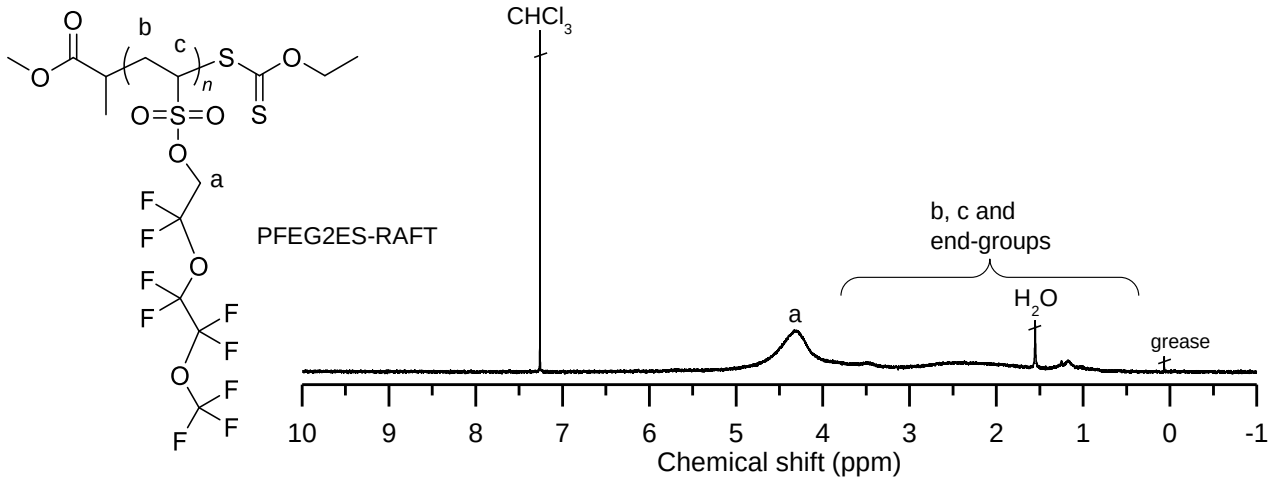


Fig. S16 ^{1}H NMR spectrum of purified PFEG2ES-RAFT synthesized by RAFT polymerization in bulk at 60 °C using AIBN as a thermal initiator and OEMDTC as a CTA. The measurement was performed in perfluorodecalin with $CDCl_3$ in a coaxial insert. The shown end-groups are derived from OEMDTC.

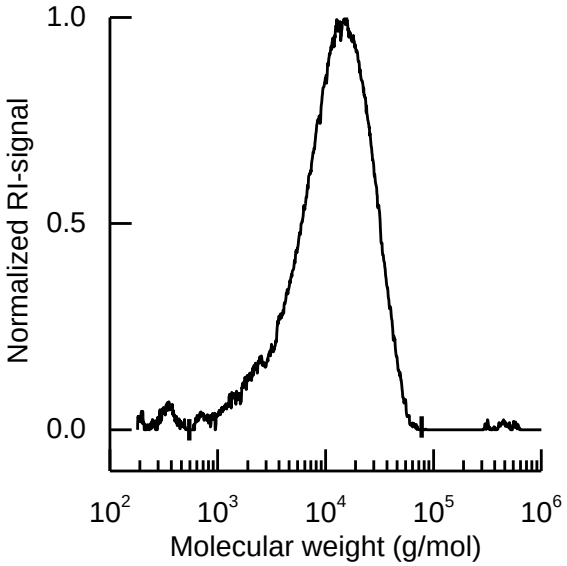


Fig. S17 SEC molecular weight distribution of crude PEES-FRP synthesized by FRP in bulk at 60 °C using AIBN as a thermal initiator after a reaction time of 24 h. The measurement was performed with THF as an eluent and PS standards for calibration.

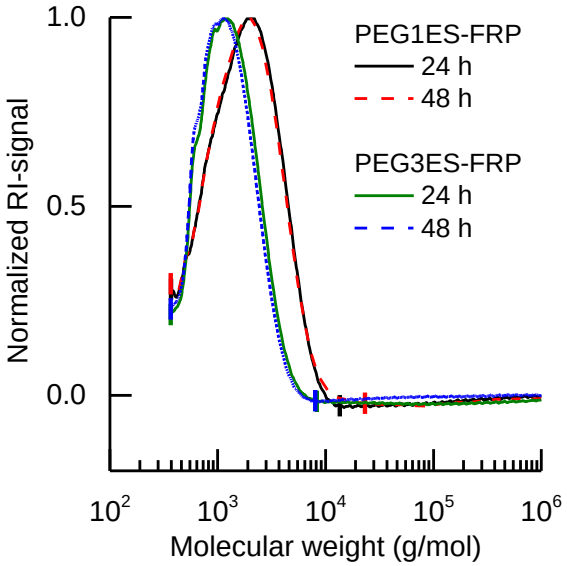


Fig. S18 SEC molecular weight distributions of crude PEG1ES-FRP and PEG3ES-FRP each after a reaction time of 24 h and 48 h. The syntheses were performed by FRP in bulk at 60 °C using AIBN as a thermal initiator. The measurements were performed with THF as an eluent and PS standards for calibration. The traces were limited by the PS calibration to 366 g/mol in the low molecular weight region.

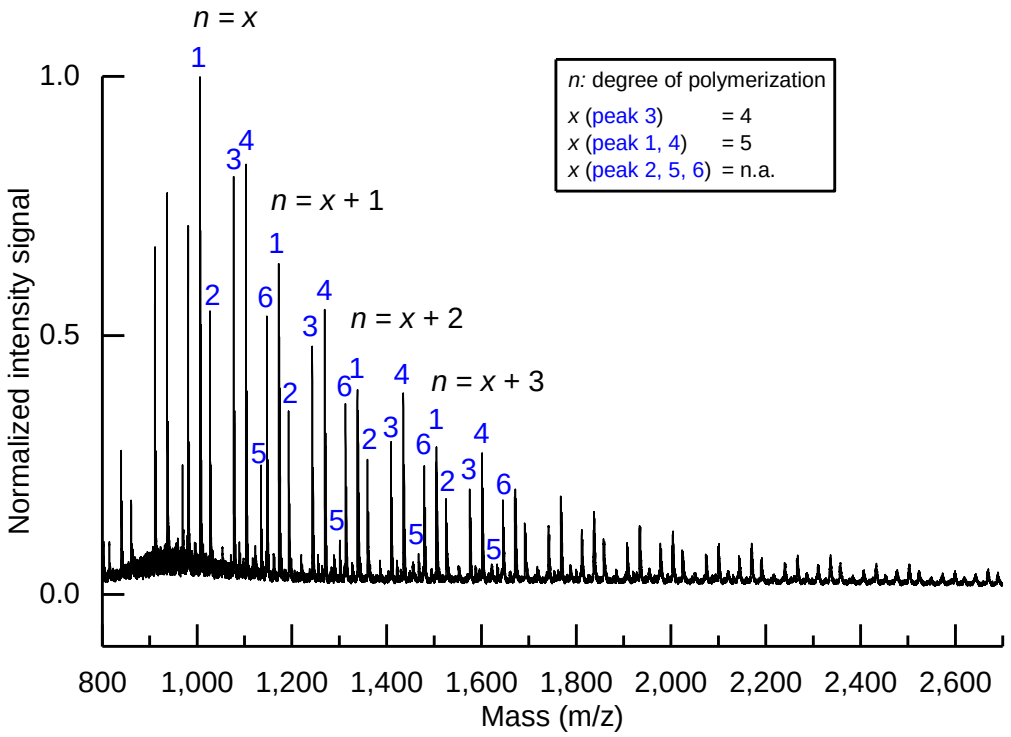
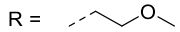
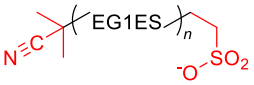


Fig. S19 MALDI-ToF MS spectrum of crude PEG1ES-FRP synthesized by FRP in bulk at 60 °C using AIBN as a thermal initiator after a reaction time of 24 h. The measurement was performed in reflectron negative mode with DCTB as a matrix.

Table S1 Isotopic mean values for crude PEG1ES-FRP. The measurement was performed in reflectron negative mode with DCTB as a matrix.

Peak number	$n = x$	$n = x + 1$	$n = x + 2$	$n = x + 3$
1 (x = 5)	1007.1	1173.4	1339.6	1505.8
2 (x = n.a.)	1027.9	1194.1	1360.2	1526.4
3 (x = 4)	1077.8	1244.0	1410.2	1576.3
4 (x = 5)	1103.8	1270.0	1436.2	1602.4
5 (x = n.a.)	1136.0	1302.3	1468.5	1634.6
6 (x = n.a.)	1147.9	1314.1	1480.3	1646.5

Table S2 End-group analysis of crude PEG1ES-FRP synthesized by FRP in bulk at 60 °C using AIBN as a thermal initiator after a reaction time of 24 h. The measurement was performed in reflectron negative mode with DCTB as a matrix.

Peak number	Observed mass[a] (m/z)	Mass of end-group (*E*)[b] (m/z) R = 		Calculated mass[c] (m/z)
1	176.0		176.23	$[E^-]^-$ = 176.2
2	n.a.	n.a.	n.a.	n.a.
3	413.0		136.22	$[E + CN^- + DCTB]^-$ = 412.6
4	272.9		235.31	$[E + K^+ – 2 \times H^+]^-$ = 272.4
5	n.a.	n.a.	n.a.	n.a.
6	n.a.	n.a.	n.a.	n.a.

[a]See Table S1 for raw data. Isotopic mean values of the end-groups averaged for each peak series shown in Fig. S19. [b]M_{EG1ES} = 166.20 g/mol. [c]M_{DCTB} = 250.34 g/mol. n.a. = not assigned.

Table S3 Isotopic mean values for crude PEG3ES-FRP. The measurement was performed in reflectron negative mode with DCTB as a matrix.

Peak number	$n = x$	$n = x + 1$	$n = x + 2$	$n = x + 3$	$n = x + 4$	$n = x + 5$	$n = x + 6$	$n = x + 7$
1 (x = 0)	843.6	1098.0	1352.4	-	-	-	-	-
2 (x = 2)	869.8	1124.2	1378.5	1632.8	1887.1	2141.6	2395.7	2649.9
3 (x = 0)	913.8	1168.2	1422.7	1677.0	1931.2	-	-	-
4 (x = 3)	939.2	1193.7	1448.0	-	-	-	-	-
5 (x = 0)	990.1	1244.2	1498.5	-	-	-	-	-
6 (x = 1)	1035.8	1290.1	1544.3	-	-	-	-	-

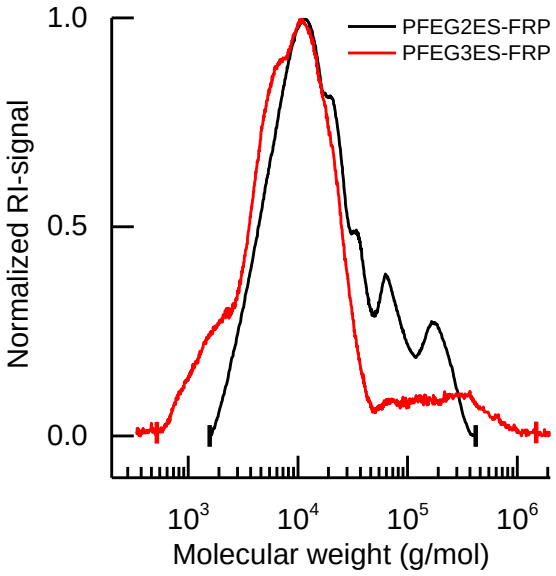


Fig. S20 SEC molecular weight distributions of crude PFEG2ES-FRP and PFEG3ES-FRP synthesized by FRP in bulk at 60 °C using AIBN as a thermal initiator. The measurements were performed with HFIP (with 0.5 % w/w KTFA) as an eluent and PMMA standards for calibration.

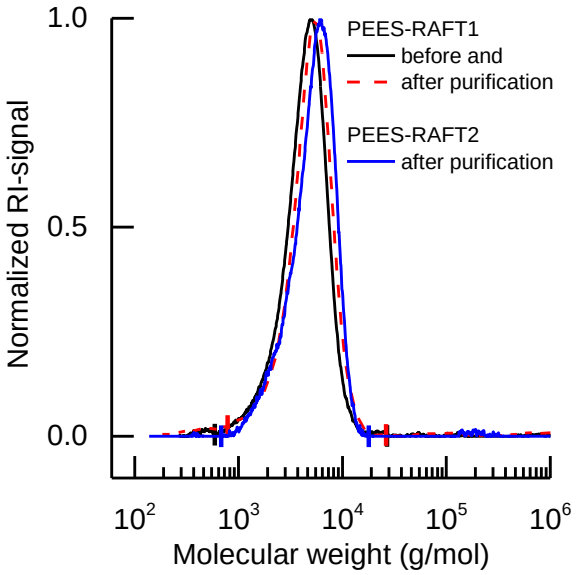


Fig. S21 SEC molecular weight distributions of PEES-RAFT1 before and after purification and of purified PEES-RAFT2. The syntheses were performed by RAFT polymerization in bulk at 60 °C using AIBN as a thermal initiator and OEMDTC as a CTA. The measurements were performed with THF as an eluent and PS standards for calibration.

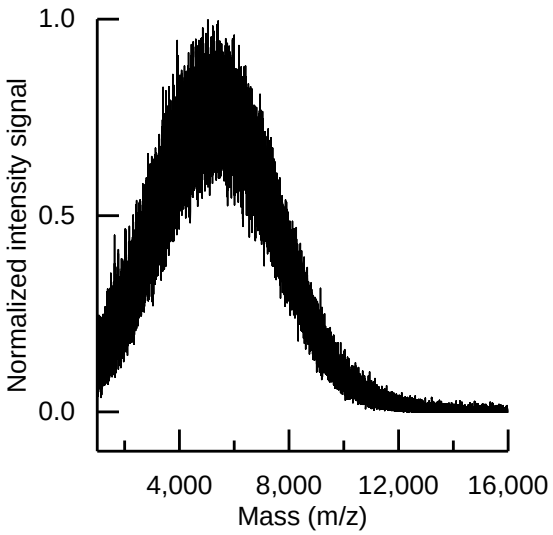


Fig. S22 MALDI-ToF MS spectrum of purified PEES-RAFT2 synthesized by RAFT in bulk at 60 °C using AIBN as a thermal initiator and OEMDTC as a CTA. The measurement was performed in reflectron positive mode with IAA as a matrix.

Table S4 Isotopic mean values (Gaussian fit) for purified PEES-RAFT1. The measurement was performed in reflectron positive mode with IAA as a matrix.

Peak number	*n* = 32	*n* = 33	*n* = 34
1	4558.6	4695.0	4832.3
2	4582.9	4719.6	4854.9
3	4602.5	4738.8	4874.9
4	4626.5	4762.1	4899.2

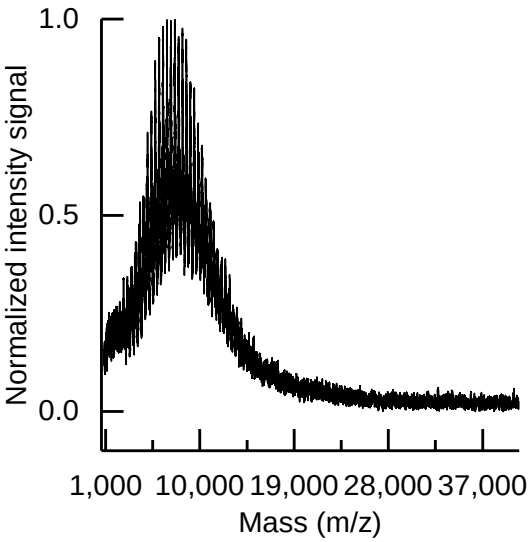


Fig. S23 MALDI-ToF MS spectrum of purified PFEG2ES-RAFT synthesized by RAFT in bulk at 60 °C using AIBN as a thermal initiator and OEMDTC as a CTA. The measurement was performed in linear negative mode with DHB as a matrix.

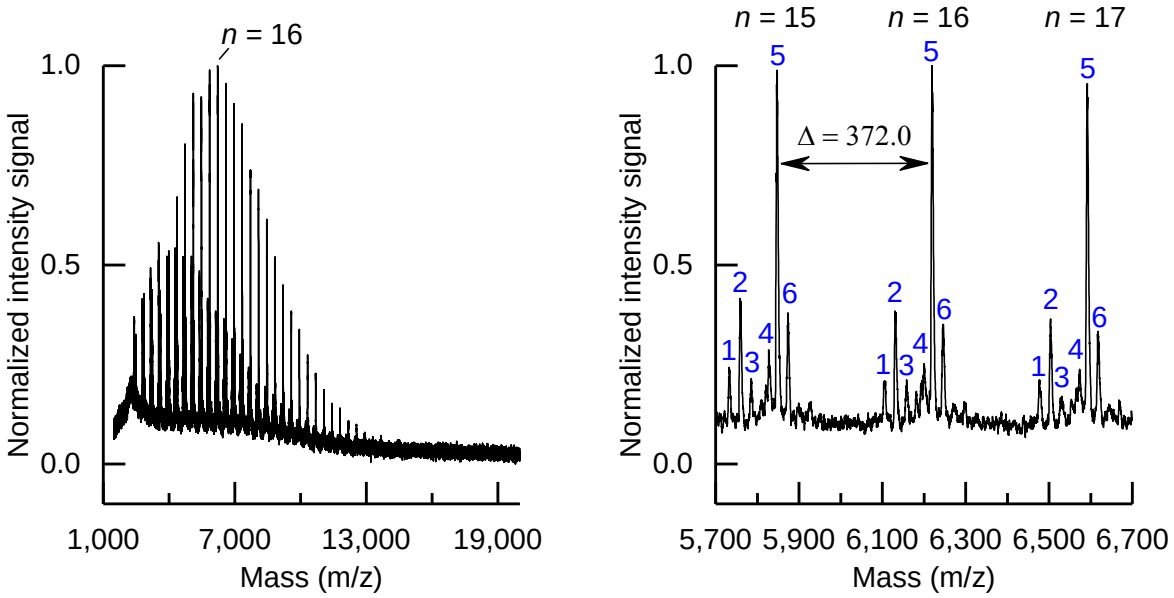


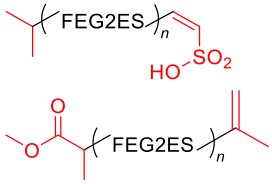
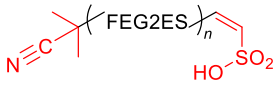
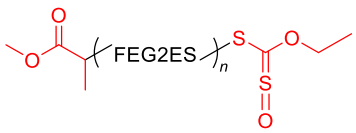
Fig. S24 MALDI-ToF MS spectrum of purified PFEG2ES-RAFT synthesized by RAFT polymerization in bulk at 60 °C using AIBN as a thermal initiator and OEMDTC as a CTA. The measurement was performed in reflectron positive mode with DHB as a matrix.

Table S5 Isotopic mean values for purified PFEG2ES-RAFT. The measurement was performed in reflectron positive mode with DHB as a matrix.

Peak number	*n* = 12	*n* = 13	*n* = 14	*n* = 15	*n* = 16	*n* = 17	*n* = 18	*n* = 19	*n* = 20	*n* = 21
1	4617.1	4989.1	5361.4	5732.4	6104.3	6477.4	6849.9	7223.6	7595.0	7966.2
2	4642.2	5014.2	5386.4	5759.4	6130.5	6503.7	6875.9	7248.8	7619.8	7993.4
3	4669.1	5040.3	5412.3	5785.3	6158.5	6529.5	6903.5	7277.6	7646.5	8019.1
4	4712.1	5084.2	5457.1	5827.5	6200.6	6573.4	6944.6	7318.0	7689.5	8063.9
5	4730.2	5102.3	5475.3	5847.4	6219.4	6591.8	6963.8	7336.5	7708.6	8080.9
6	4756.2	5128.2	5500.5	5873.5	6246.6	6617.8	6990.8	7362.9	7734.2	8107.3

n = 22	*n* = 23	*n* = 24
8339.3	8711.8	-
8365.8	8737.8	9108.4
8391.0	-	-
-	-	-
8453.4	8825.8	9198.3
8480.4	8851.7	9224.1

Table S6 End-group analysis of purified PFEG2ES-RAFT synthesized by RAFT polymerization in bulk at 60 °C using AIBN as a thermal initiator and OEMDTC as a CTA. The measurement was performed in reflectron positive mode with DHB as a matrix.

Peak number	Observed mass[a] (m/z)	Mass of end-group (*E*)[b] (m/z)		Calculated mass[c] (m/z)
1	151.2		150.23 128.19	[*E* + H⁺]⁺ = 151.2 [*E* + Na⁺]⁺ = 151.2
2	177.0		175.24	[*E* + H⁺]⁺ = 176.3
3	203.5		180.26	[*E* + Na⁺]⁺ = 203.3
				
4	246.4		224.31 196.23 208.31	[*E* + Na⁺]⁺ = 247.3 [*E* + 2CN – 2H + H⁺]⁺ = 247.3 [*E* + K⁺]⁺ = 247.4
				
5	265.3		111.20	[*E* + H⁺+ DHB]⁺ = 266.3
6	291.4		136.22	[*E* + H⁺+ DHB]⁺ = 291.4

[a]See Table S5 for raw data. Isotopic mean values of the end-groups averaged for each peak series shown in Fig. S24 (for *n* = 12-24). [b]M_{FEG2ES} = 372.16 g/mol. [c]M_{DHB} = 154.12 g/mol.

Table S7 Isotopic mean values for purified PFEG3ES-RAFT. The measurement was performed in reflectron positive mode with DHB as a matrix.

Peak number	*n* = 17	*n* = 18	*n* = 19	*n* = 20	*n* = 21	*n* = 22	*n* = 23	*n* = 24	*n* = 25	*n* = 26	*n* = 27	*n* = 28	*n* = 29
1	8445.1	8932.8	9419.6	9909.0	10397.3	10884.5	11371.4	11861.7	12347.1	-	-	-	-
2	8472.6	8960.2	9447.2	9935.8	10421.7	10910.1	11400.1	11885.5	12373.4	-	-	-	-
3	8533.3	9020.9	9509.6	9996.7	10484.7	10971.7	11460.2	11948.2	12436.4	12923.1	13411.1	13898.0	14387.8
4	8559.3	9047.9	9535.3	10023.0	10510.7	10999.3	11486.8	11975.0	12462.4	12949.3	13437.1	13925.5	14413.3
5	8615.8	9104.1	9590.0	10077.3	10566.6	11056.5	11542.0	12031.7	12518.6	-	-	-	-
6	8644.2	9130.9	9618.1	10108.0	10594.0	11082.0	11571.6	12061.0	12547.4	-	-	-	-
7	8671.8	9158.7	9646.0	10134.2	10621.1	11110.3	11599.6	12089.6	12573.9	-	-	-	-

Table S8 Conventional free radical polymerization (FRP)[a] and RAFT[b] polymerization of FEG3ES in hexafluorobenzene as a solvent at different monomer concentrations $[M]_0$ and at 60 °C using AIBN as a thermal initiator (I) and in case of RAFT polymerization OEMDTC as a CTA.[c]

Polymerization method	$[M]_0$ (mol/L)	Conv.[d] (%)	$M_{n,\,theor}$[e] (g/mol)	$M_{n,\,SEC}$[f] (g/mol)	$Đ_{SEC}$[f]	$M_{p,\,SEC}$[f] (g/mol)
FRP	16	24	-	6,300	1.65	9,500
FRP	32	29	-	-[g]	-[g]	1,700[g]
RAFT	16	24	6,100	-[g]	-[g]	1,500[g]
RAFT	32	37	9,200	7,200	1.72	12,900
RAFT	128	30	7,500	-[g]	-[g]	2,100[g]

[a] $[M]_0/[I]_0$ = 100/1. [b] $[M]_0/[CTA]_0/[I]_0$ = 100/2/1. [c] All data were measured from the crude reaction mixture. [d] Determined by ^{1}H NMR spectroscopy and calculated according to equation 1 after a reaction time of 48 h. [e] Calculated according to equation 2. [f] Determined by SEC using HFIP containing 0.5 % w/w KTFA as an eluent and calibrated with PMMA standards. [g] Molecular weight peak was low and overlapped with the peak of the internal standard.

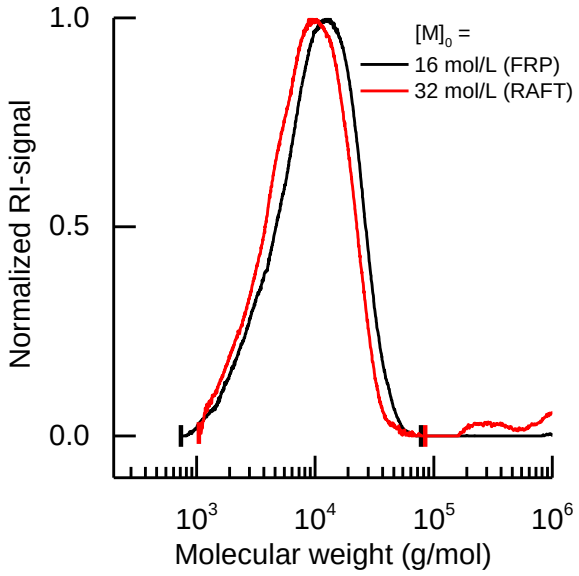


Fig. S25 SEC molecular weight distributions of crude PFEG3ES synthesized by FRP or RAFT polymerization in hexafluorobenzene as a solvent at different monomer concentrations $[M]_0$ and at 60 °C using AIBN as a thermal initiator. The measurements were performed with HFIP (with 0.5 % w/w KTFA) as an eluent and PMMA standards for calibration.

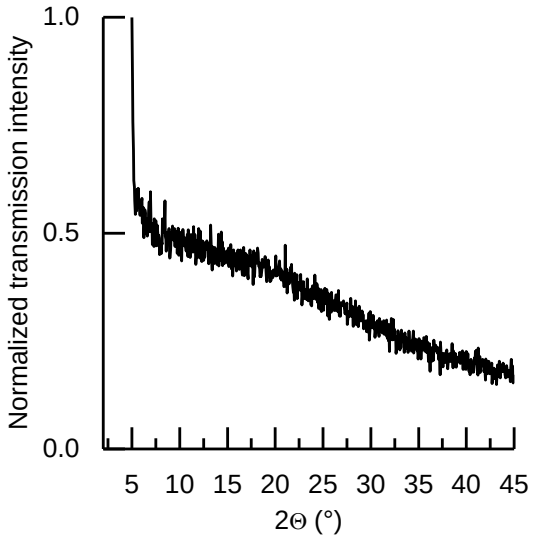


Fig. S26 WAXS diffractogram of PFEG3ES-RAFT measured at room temperature.

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