Supporting Information for

Synthesis of Block Polymer *Mikto*brushes

Adam O. Moughton,[a] Takanori Sagawa,[a,b] William M. Gramlich,[a,b,‡] Myungeun Seo,[a] Timothy P. Lodge*[a,b], and Marc A. Hillmyer*[,a]

[a]Department of Chemistry and [b]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0431

[‡]Current address: Department of Bioengineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

*To whom correspondence should be addressed. E-mail: lodge@umn.edu (T.P.L.), hillmyer@umn.edu (M.A.H.).

Experimental Section

Materials

All reagents were used as received unless otherwise stated. *2',2'*-azo-*bis*-*iso*-butyronitrile (A.I.B.N) was purchased from Sigma-Aldrich Co. and purified by re-crystallization from *n*-hexanes. Poly(ethylene oxide) (PEO) methyl ether was purchased from Polymer Source, Inc. and purified by re-precipitation into *n*-hexanes from dichloromethane. The PEO has a molecular weight, M_n = 21 kg/mol and a dispersity ($Đ$, M_w/M_n) = 1.09. *S*-1-Dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate chain transfer agent (CTA) was synthesized following a literature procedure.[1] Tetrahydrofuran (THF) was purified by passing through an alumina column. Freon-113 (1,1,2-trichlorofluoroethane), *α,α,α*-trifluorotoluene (TFT), and methoxy-nonafluorobutane (HFE-7100®, 99%, 3M Company) were stirred over calcium hydride (CaH_2) and vacuum distilled prior to use. Poly(Dmap)® was purchased from Reilly Industries. Mono-carboxylic acid end-capped poly(perfluoropropylene oxide) (PFPO-COOH, Krytox®) was obtained from E.I. Du Pont De Nemours and Company. The molecular weight of the PFPO-COOH sample was determined by ^{19}F NMR spectroscopy to be 2.5 kg mol^{-1} using the intensity ratio of the peak at –131.2 ppm to that at −132.8 ppm. 4-vinyl-benzyl alcohol was synthesized from 4-vinyl-benzyl-chloride in a one step procedure as reported in the literature previously.[2]

Characterization

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian 300-MHz spectrometer in deuterated chloroform ($CDCl_3$), Freon-113, or $CDCl_3$/Freon-113 mixtures unless otherwise stated. Size exclusion chromatography (SEC) analysis was performed on a Hewlett-Packard 1100 series liquid chromatography system equipped with a Hewlett–Packard 1047A refractive index detector, Wyatt MALS and UV-vis detection systems. SEC measurements were performed at a flow rate of 1.00 mL min^{-1}, and THF was used as the mobile phase unless otherwise stated.

Synthetic Procedures

Synthesis of PEO-CTA

The PEO-CTA macroinitiator was prepared as follows: CTA (0.768 g, 2.11 mmol) was dissolved in dry CH_2Cl_2 (5 mL) under argon atmosphere and oxalyl chloride (0.09 mL, 1.05 mmol) was added. The reaction mixture was stirred at room temperature until gas evolution had stopped (~ 4 h). Excess reagents were removed under vacuum, and the residue was redissolved in dry CH_2Cl_2 (5 mL), followed by the addition of PEO-mono methyl ether (4.00 g, 0.19 mmol) under argon. The reaction was stirred for 48 hours at room temperature, after which time the PEO-CTA product was isolated from the crude reaction mixture by repeated precipitations in *n*-hexanes at room temperature. The PEO-CTA product was dried under vacuum. Yield = 3.2 g (80%). End group conversions to CTA were always > 95% and were quantified by integrating the CTA and PEO ester linkage end group peaks at $\delta = 0.82$ and $\delta = 4.18$ with respect to PEO peaks at $\delta = 3.6$ and 3.32. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 0.82 (t, 3H, –$CH_2\mathit{CH}_3$ in CTA), 1.19 (m, 18H, –$CH_2(\mathit{CH}_2)_9CH_3$ in CTA), 1.56 (m, 2H, –C(S)S–$CH_2\mathit{CH}_2CH_2$– in CTA), 1.64 (s, 6H, –$C(\mathit{CH}_3)_2SC(S)S$–, in CTA), 3.29 (t, 2H, –SC(S)SCH_2CH_2– in CTA), 3.32 (s, 3H, CH_3OCH_2– in PEO), 3.6 (m, 1900H, CH_3O–$(\mathit{CH}_2\mathit{CH}_2\mathit{O})_{475}$– in PEO), 4.18 (t, 2H, –$CH_2\mathit{CH}_2OC(O)C(CH_3)_2$– in PEO). Elemental analyses: Calc. C = 54.57%, H = 9.15%, S = 0.46% Found. C = 54.37%, H = 8.96%, S = 0.20%.

Synthesis of MI-PMCL

The poly(methyl-caprolactone) or PMCL macromonomer was typically prepared as follows. In a N_2 atmosphere dry box, MI (567 mg), $Sn(Oct)_2$ (127 mg), and 6MCL (20 g, contains 4 mol % 2MCL) were combined in a 75 mL pressure vessel. Once the MI and $Sn(Oct)_2$ dissolved, the vessel was sealed, removed from the dry box, and placed in a 130 °C oil bath. After 2 h, the flask was removed and placed in an ice bath to stop the reaction. The viscous polymer was diluted with CH_2Cl_2 and subsequently precipitated in a 10-fold excess of cold (0 °C) 60/40 methanol/H_2O solution. Once the product had settled, the viscous material was collected and dried under vacuum at 50 °C for several days (93 % monomer conversion, 95.4 % yield). The product was analyzed by ^{1}H NMR spectroscopy and SEC calibrated with polystyrene standards. ^{1}H NMR spectroscopy ($CDCl_3$, 300 MHz, δ ppm): **δ** 6.73 (s, -C*H*=C*H*- end group), 4.88 (m, -C*H*- 6MCL repeat unit), 4.22 (t, *J* = 5.3 Hz, NCH_2CH_2O end group), 4.04 (t, *J* = 6.8 Hz, -C*H*- 2MCL repeat unit), 3.79 (br m, NCH_2CH_2O and -C*H*- end groups), 2.26 (t, *J* = 7.4 Hz, $OCCH_2$- repeat unit), 1.68-1.24 (br m, -CH_2- repeat unit), 1.186 (d, *J* = 5.5 Hz, -CH_3 6MCL repeat unit), and 1.126 (d, *J* = 6.8 Hz, -CH_3 2MCL repeat unit). Elemental analyses: Calc. C = 65.22%, H = 9.32%, N = 0.26% Found. C = 64.97%, H = 9.20%, N = 0.22%

Synthesis of Monoacyl Chloride-Functionalized PFPO (PFPO-COCl)

A typical procedure for the preparation of Poly(perfluoropropylene oxide) acid chloride (PFPO-COCl) is described. PFPO-COOH (50.0 g, 20 mmol) was added to a 250 mL round bottom flask with a Teflon inlet valve. The flask was evacuated overnight at RT with stirring from a glass magnetic stirrer bar. Purified HFE-7100 (100 mL) and oxalyl chloride (25.0 g, 200 mmol) were then added under positive argon flow. The reaction flask was fitted with a condenser and heated to reflux (*ca.* 65 °C) under a slow dry nitrogen purge for 48 h. After cooling to RT, the mixture excess oxalyl chloride and solvent were removed using a vacuum manifold setup and a secondary liquid nitrogen trap. The product was then dried in vacuum to constant weight at RT for 3 days and stored under a dry argon atmosphere in sealed vessel.

Synthesis of Sty-PFPO

A typical coupling reaction between 4-vinyl-benzyl alcohol and PFPO-COCl is described. The reaction was performed in a sealable 50-mL pressure vessel to minimize any loss of the volatile HFE-7100 solvent over the course of the reaction, which may compromise the homogeneity of the reaction mixture. PFPO-COCl (22.1 g, 8.84 mmol) and 4.0 g Poly(DMAP) resin were added to a sealable 50-mL pressure vessel fitted with a Teflon inlet valve along with a glass magnetic stirrer bar and the contents were dried under high vacuum for 4 h with stirring. HFE-7100 (15 mL) was added to the reaction mixture under argon flow to dissolve PFPO-COCl to give a clear solution. 4-vinyl-benzyl alcohol (3.7 g, 27.6 mmol) was added to the reaction mixture as a solution in trifluorotoluene (20 mL) under argon flow. *Tert*-butyl catechol (*ca.* 50 mg) was added to the reaction mixture to act as a radical inhibitor and prevent any polymerization of 4-vinyl-benzyl alcohol at elevated temperatures. Prior to heating, the reaction mixture was stirred vigorously under argon flow to ensure homogeneity. Small amounts of trifluorotoluene (5 mL) or HFE-7100 (5 mL) were added to the reaction mixture accordingly in case of cloudy solutions, which was dependent upon the scale of the reaction performed. The reaction vessel was sealed under argon and heated and stirred at 65 °C for 48 h. Upon reaction completion and cooling to room temperature, the Poly(DMAP) was removed by suction filtration and the Poly(DMAP) was washed with HFE-7100. The solvents were then removed from the crude reaction mixture under vacuum. The remaining cloudy oil was dissolved in HFE-7100 (*ca.* 100 mL) and passed through a thin layer of basic alumina. The resulting cloudy solution was then allowed to stand for 24 h at room temperature to allow any insoluble impurities to precipitate from the solution. The resultant clear solution was then decanted from the precipitated insoluble impurities and dried under vacuum to obtain the product. Yield = 18.1 g (78%), higher yields were obtained for smaller scale reactions. End group conversions to styrene were always > 95% as determined by ^{1}H and ^{19}F NMR spectroscopy. ^{1}H NMR (Freon-113, 300 MHz, δ ppm): 7.46 (d, J = 8.06 Hz, 2H), 7.37 (d, J = 8.06 Hz, 2H), 6.74 (dd, J = 11.0, 17.5 Hz, 1H), 5.80 (dd, *J* = 17.5 Hz, 1.6 Hz, 1H), 5.37 (s, 2H), 5.32 (dd, *J* = 1.6 Hz, 11.0 Hz, 1H). ^{13}C NMR (Freon-113, δ ppm): 136.6, 129.4, 128.6, 126.9, 124.1, 118.4, 117.9, 116.5, 114.6, 112.6, 104.9, 101.3, 70.1. ^{19}F NMR (Freon-113, 300 MHz, δ ppm): -80.8(br s), -81.5(s), -81.6(s), -83.1(br s), -83.2, -83.8(d), -83.9(d), -85.9(s), -131.2(s, 3F), -132.9(m, 1F), -146.1(m, 1F). Elemental analyses: Calc. C = 24.90%, H = 0.35%, F = 64.92% Found. C = 24.66%, H = 0.21%, F = 64.93%.

Synthesis of μ-O(CF)$_n$ Terpolymers

A typical copolymerization is as follows: AIBN and PEO-CTA were weighed into a vial followed by MI-PMCL and Sty-PFPO. $CHCl_3$ and HFE-7100 were added to give a cloudy solution followed by TFT (1:1:1 v/v/v) and mixing which gave a clear solution. The polymerization solution was then placed in a pressure vessel with a small stirrer bar under argon. The vessel was then subjected to 4 x freeze/pump/thaw cycles to de-gas the solution prior to polymerization. The vessel was released to and sealed under 5 psi of argon and allowed to reach room temperature and placed into an oil bath heated at 85 °C for an appropriate amount of time. After 73 hrs, the solution was precipitated into hexanes and the μ-O(CF)$_n$ terpolymers were decanted. The terpolymers were then dissolved in $CHCl_3$ and then repeatedly precipitated into toluene:*n*-hexanes (9:1 v/v). The collected μ-O(CF)$_n$ terpolymers were analyzed by ^{1}H, ^{13}C, ^{19}F NMR, SEC and elemental analyses. In the ^{1}H NMR, the PEO signals at 3.7 ppm were used as an integration calibration which enabled determination of the number of PMCL and PFPO chains and thus the molar mass and composition. This was achieved as follows. Peaks corresponding to the PMCL backbone were present between δ = 0.5-2.3 and at δ = 4.9 ppm. The peak at δ = 4.9 ppm is due to one backbone proton adjacent to the ester linkages and the methyl group within each repeating unit. Since there are 38 repeating units in the 5.3 kDa MI-PMCL, the integral of this peak was equal to the number of PMCL chains within the terpolymer x 38. This value corroborated well with signal integrals for 2 x PMCL protons at δ 2.3 ppm, which was always integrated to 76, i.e. twice the value at 4.9 ppm. The integral value of the peak at δ = 4.9 ppm was divided by 38 to give the number of PMCL chains polymerized/incorporated into the backbone of the μ-O(CF)$_n$ terpolymer. PMCL chains in the μ-O(CF)$_n$ terpolymer were distinguishable from MI-PMCL MM, since no peaks remained for the vinyl group on the MI end group (at δ = 6.5 ppm) when it was polymerized. The number of PFPO chains incorporated was determined by integrating the peak at δ = 5.3-5.5 ppm with respect to PEO and PMCL peaks. This peak corresponded to the $-C\boldsymbol{H}_2-$ methylene group adjacent to the ester linkage between the Sty group and PFPO.

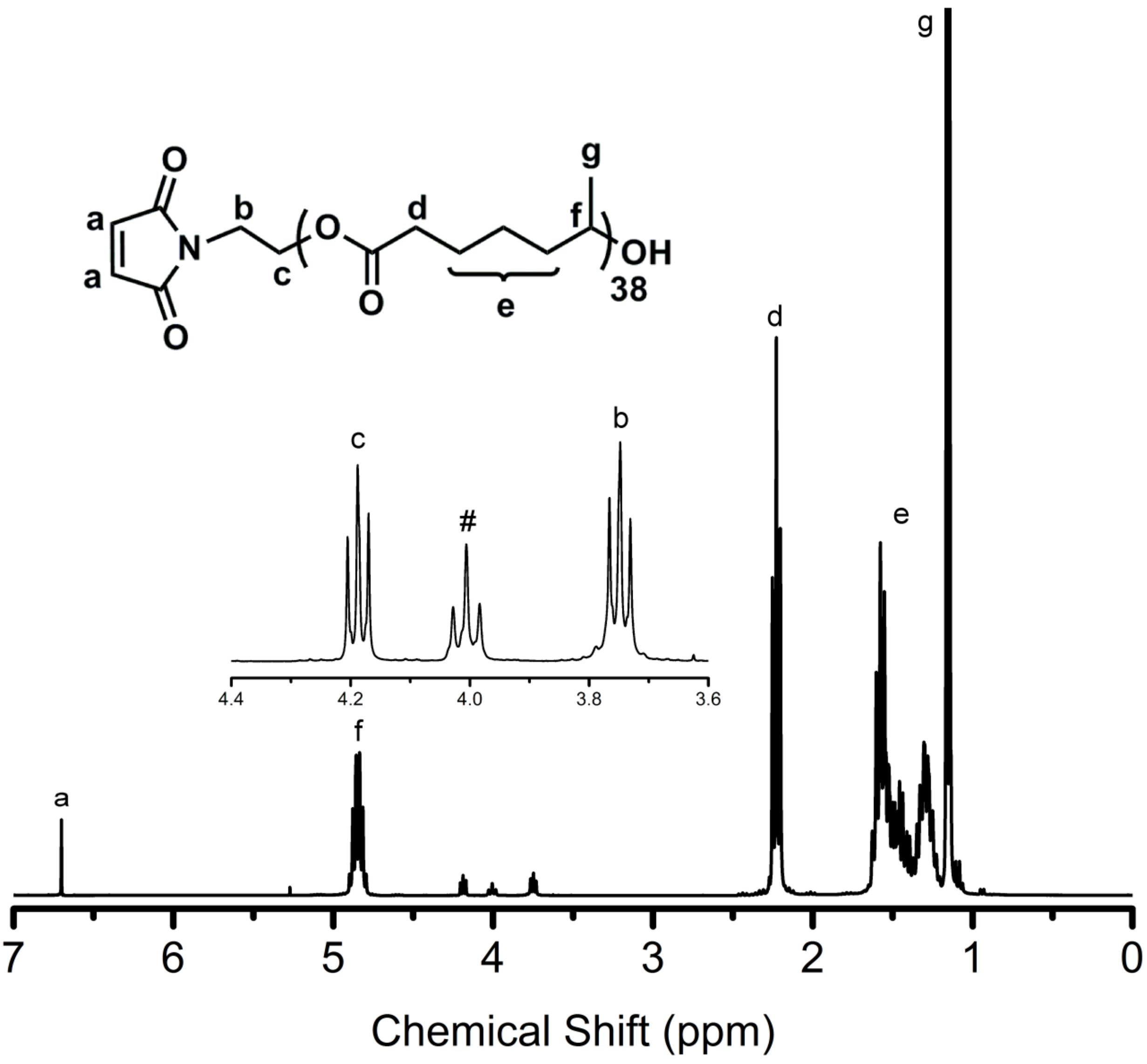


Figure S1. Assigned ^{1}H NMR spectrum of MI-PMCL macromonomer, in $CDCl_3$. # denotes the presence of the other regio isomer within PMCL backbone. Inset shows region indicating presence of MI end group.

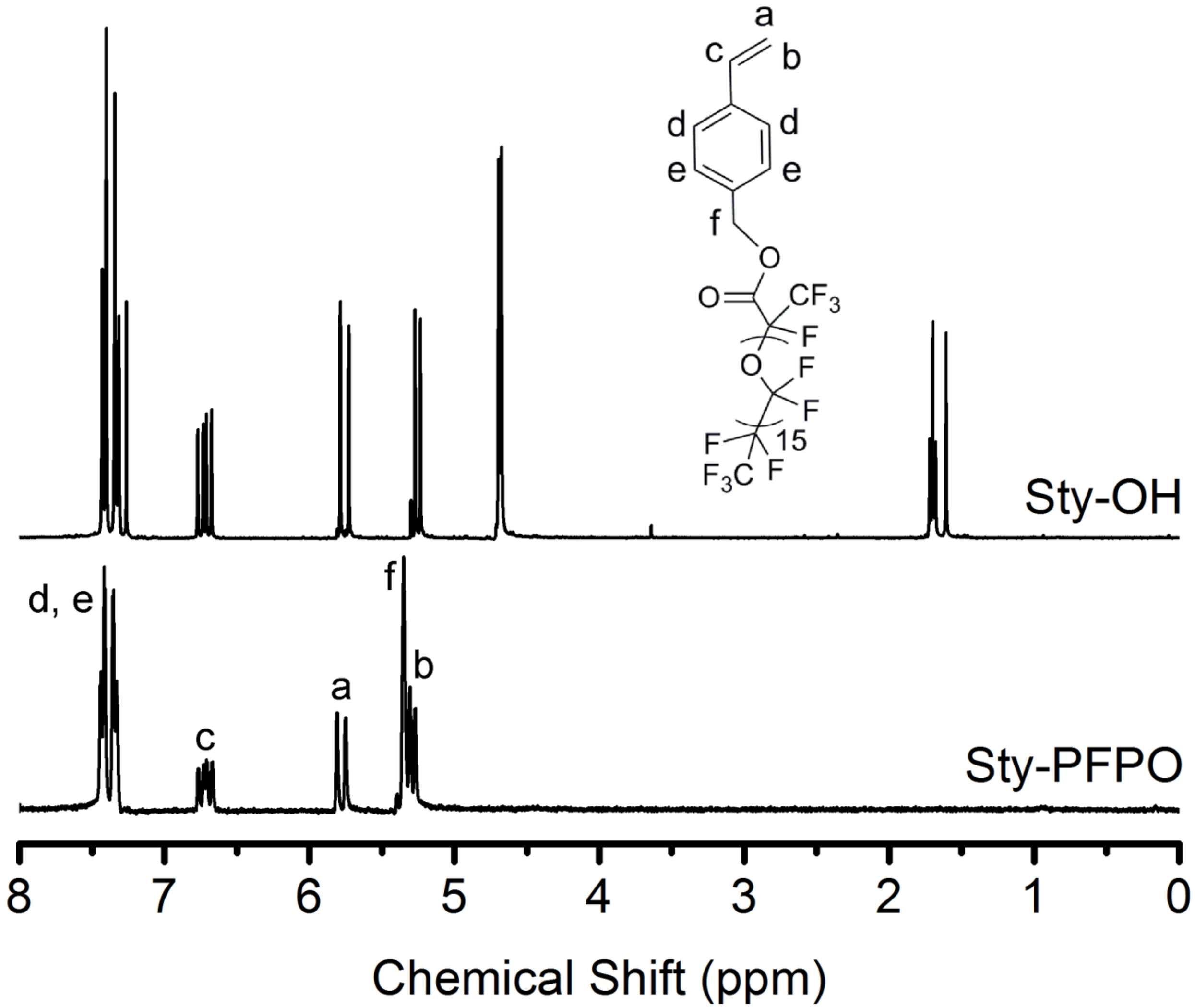


Figure S2. Assigned ^{1}H NMR spectrum of Sty-PFPO in Freon-113/$CDCl_3$ compared to 4-vinyl benzyl alcohol starting material (in Freon-113/$CDCl_3$).

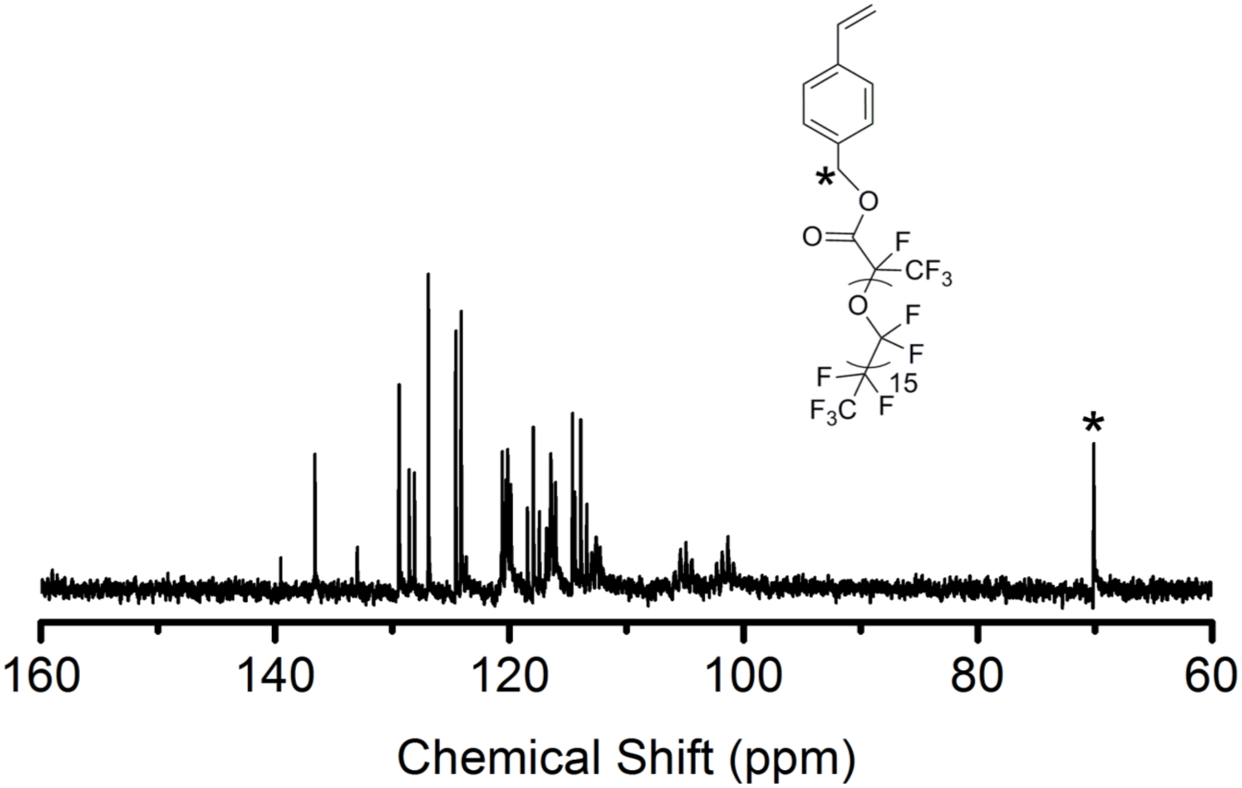


Figure S3. Assigned ^{13}C NMR spectrum of Sty-PFPO MM in Freon-113. * indicates end group signal for linkage between PFPO and styrene.

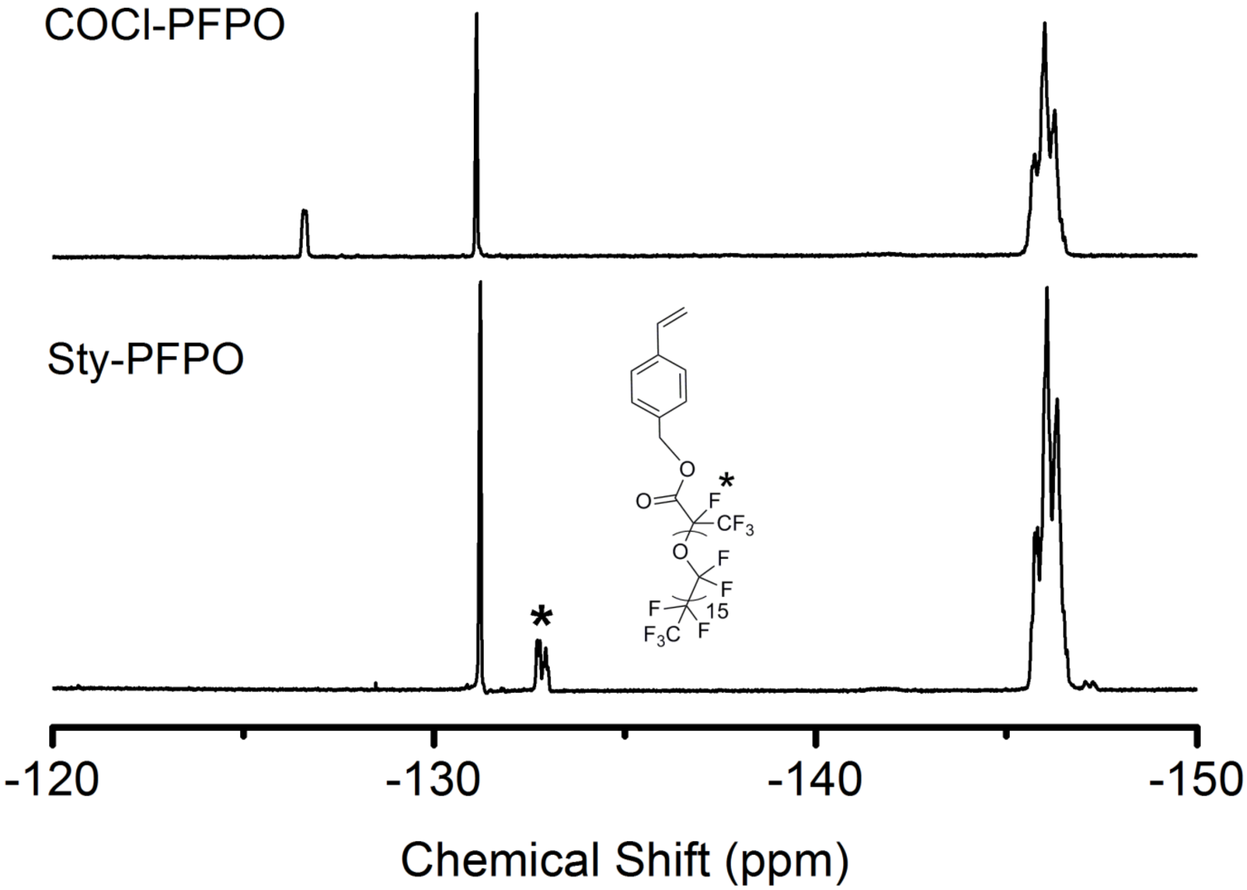


Figure S4. ^{19}F NMR spectrum of Sty-PFPO and COCl-PFPO in Freon-113. * indicates the signal corresponding to the fluorine atom adjacent to the styrene end group. The multiplicity of this peak in Sty-PFPO is due to micellization in the NMR solvent, consistent with our previous reports for PFPO end functionalization.[3,4]

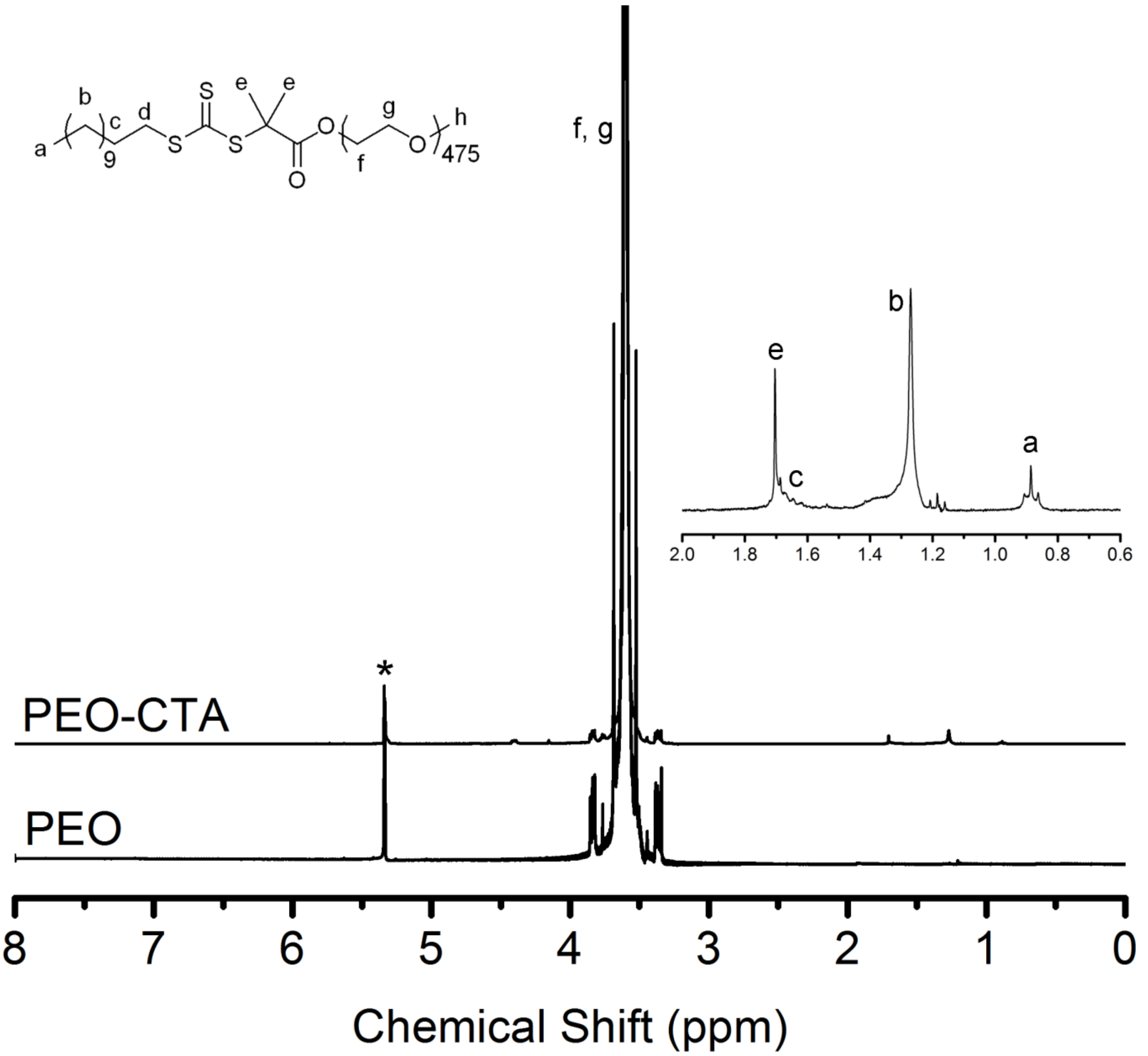


Figure S5. Assigned ^{1}H NMR spectrum of PEO-CTA and original PEO block, in CD_2Cl_2. Inset shows region indicating presence of CTA end group in PEO-CTA. * indicates residual CH_2Cl_2 solvent.

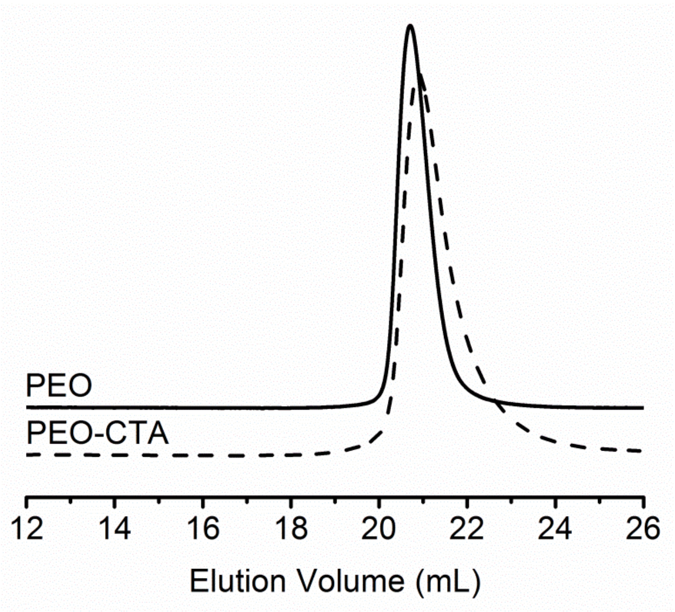
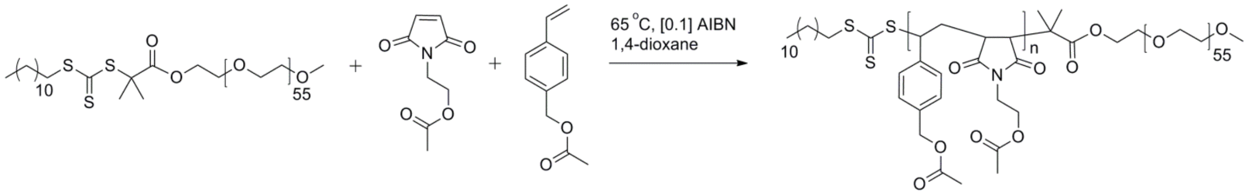


Figure S6. SEC chromatogram of PEO CTA run in $CHCl_3$.



Scheme S1. Model alternating copolymerization of small molecule monomers SAc and MIAc with (2.5 KDa) PEO-CTA.

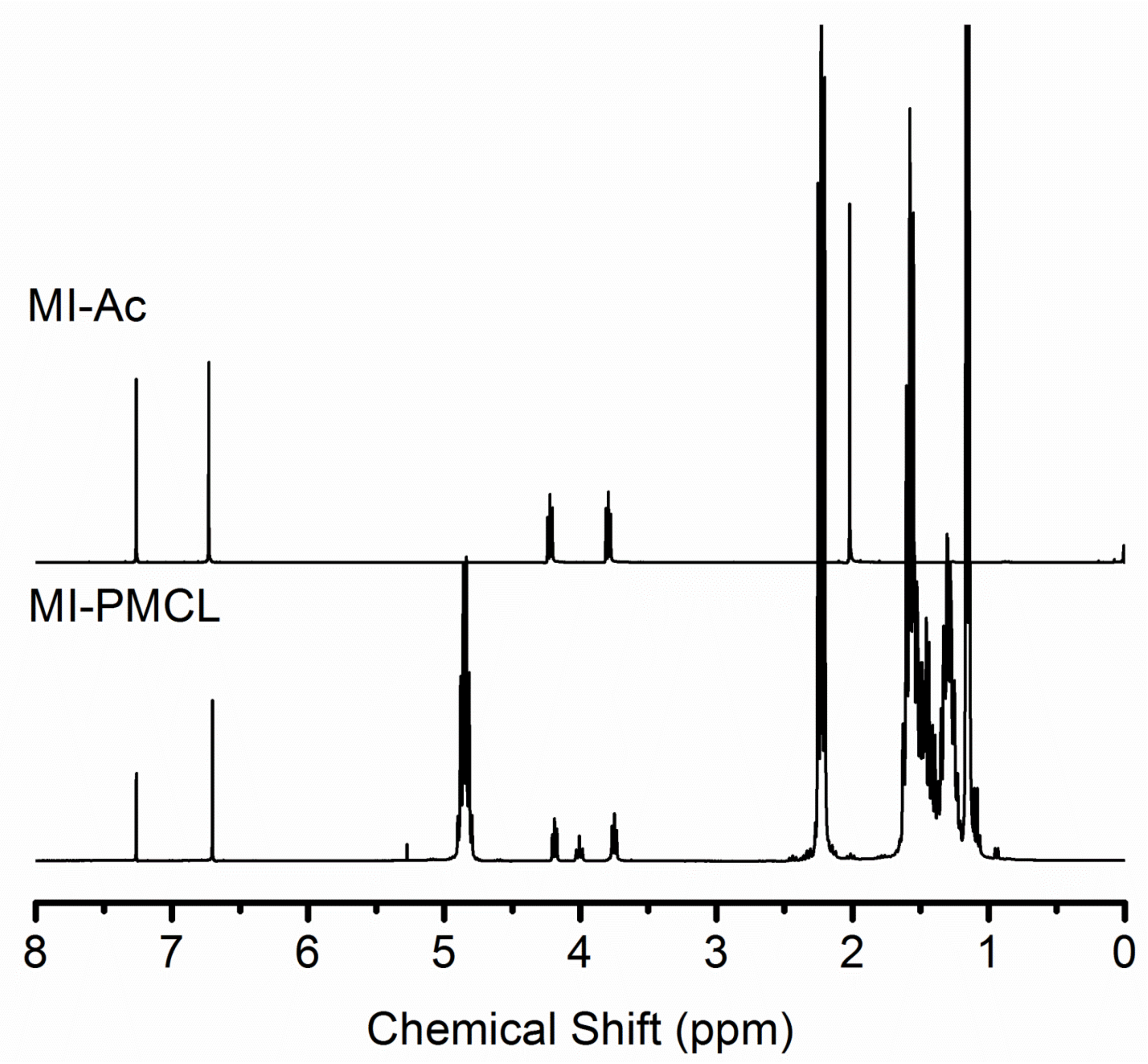


Figure S7. ^{1}H NMR spectra comparison of MI-Ac and MI-PMCL in $CDCl_3$

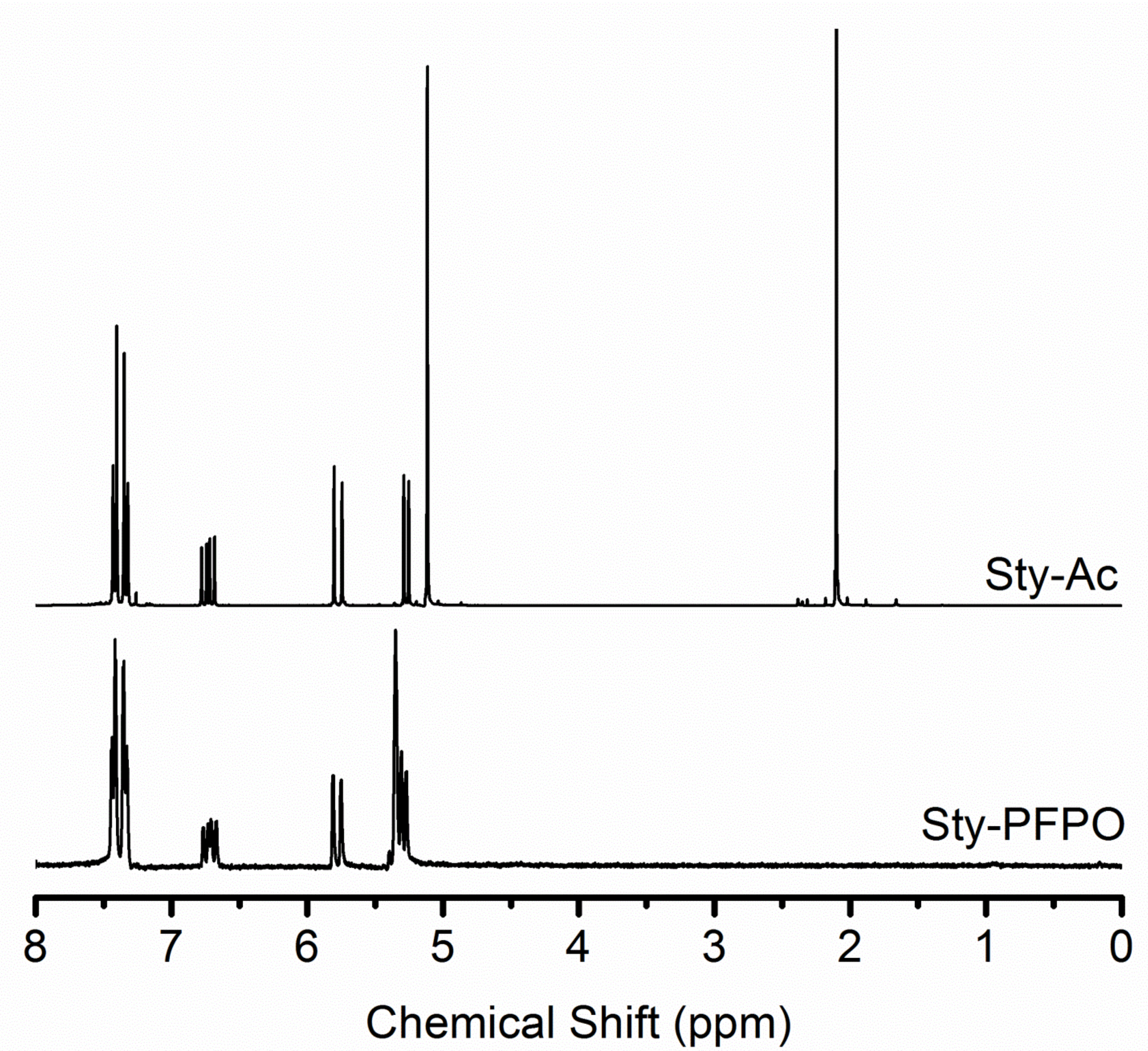


Figure S8. ^{1}H NMR spectra comparison of Sty-Ac and Sty-PFPO in 1:1 (v/v) Freon-113/$CDCl_3$.

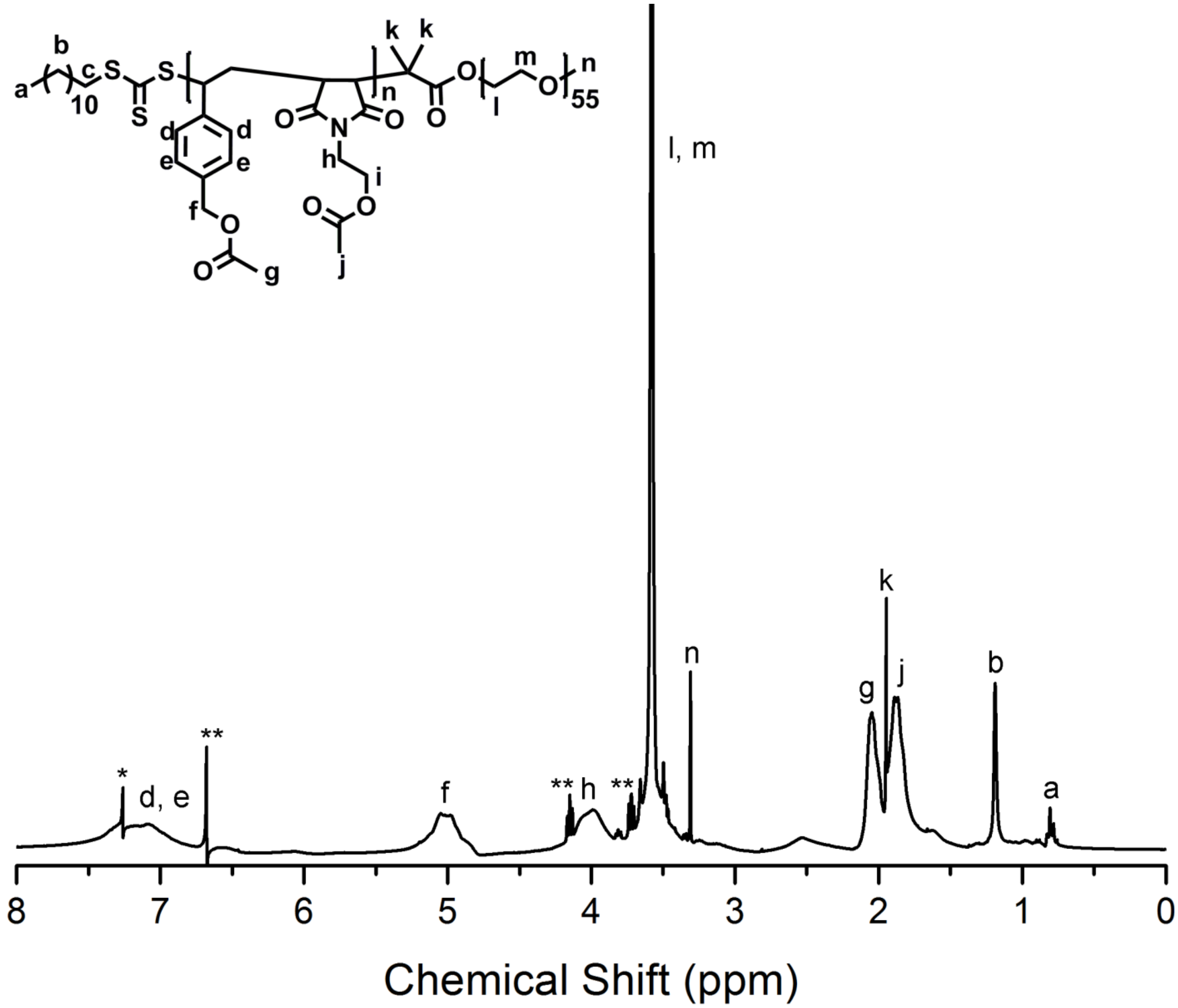


Figure S9. Assigned ^{1}H NMR spectrum of model alternating copolymer PEO-*b*-(P(S-Ac)-*alt*-P(MI-Ac)) CDCl$_3$. * and ** indicate residual CHCl$_3$ solvent peaks and residual MI-Ac monomer respectively.

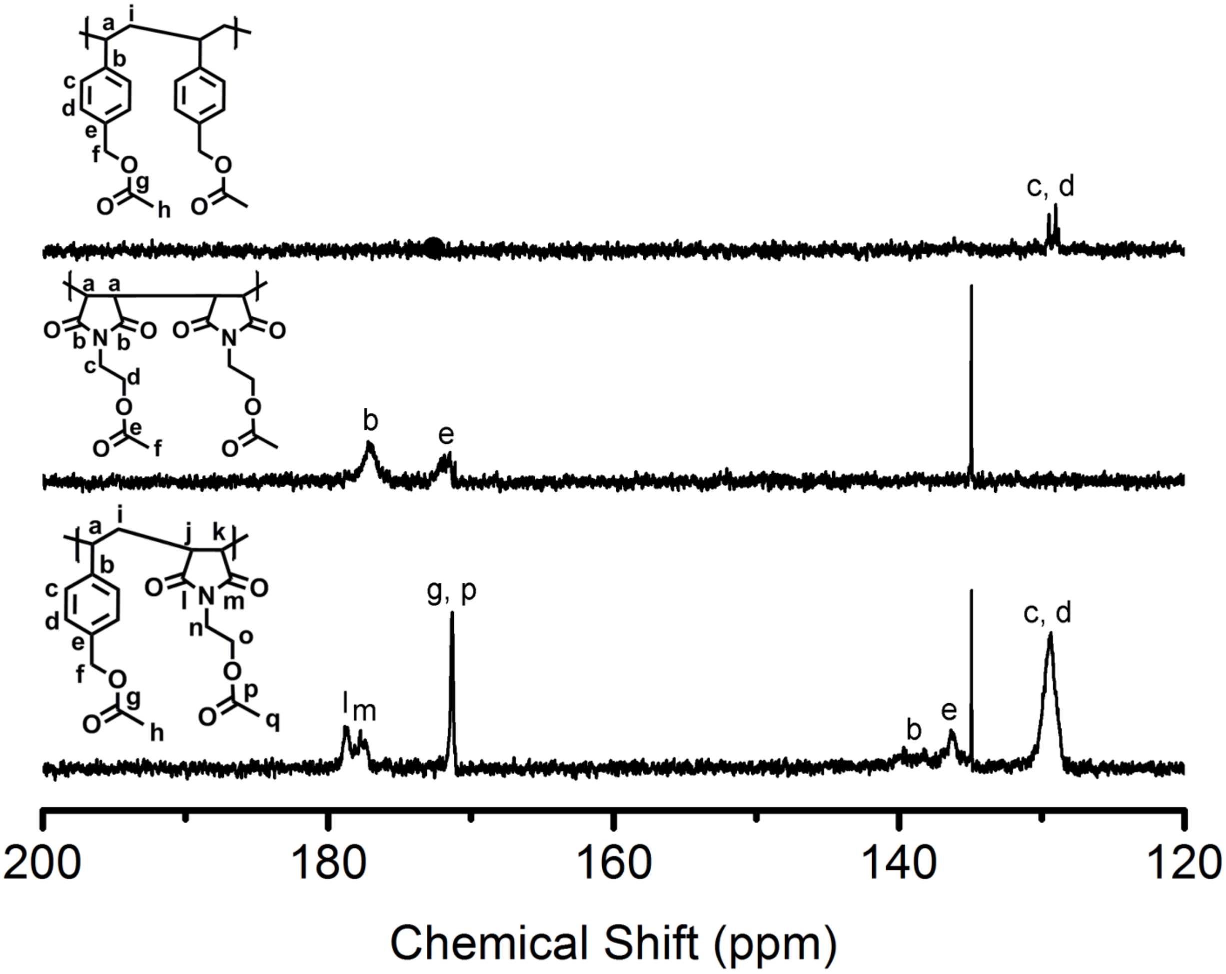


Figure S10. Assigned ^{13}C NMR spectra of poly(styrene acetate), poly(maleimide acetate) and poly(styrene acetate-*alt*-maleimide acetate) in $CDCl_3$

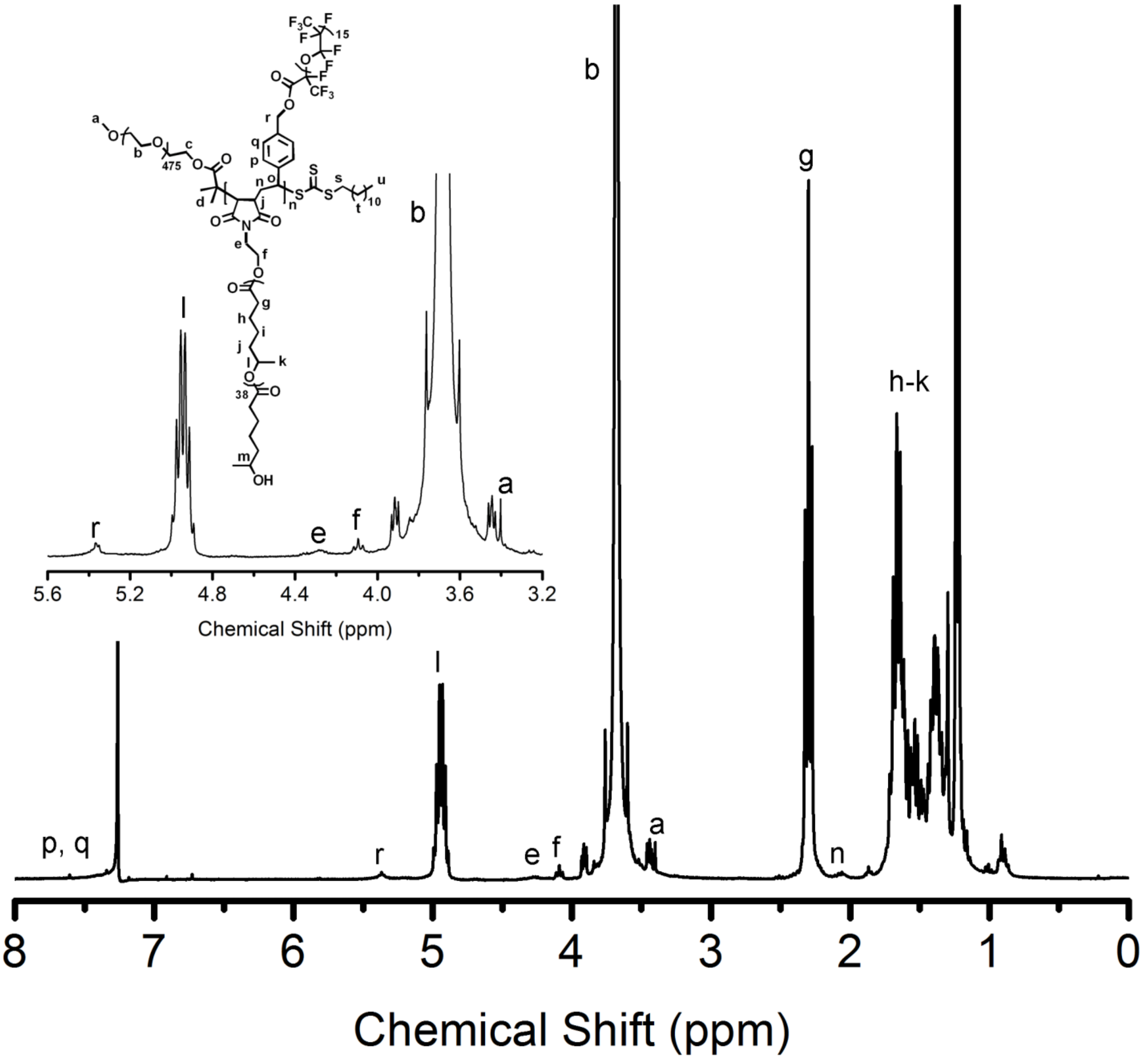


Figure S11. Assigned ^{1}H NMR spectrum of μ-O(C_2F_3) terpolymer in 9:2 (v/v) Freon-113/$CDCl_3$.

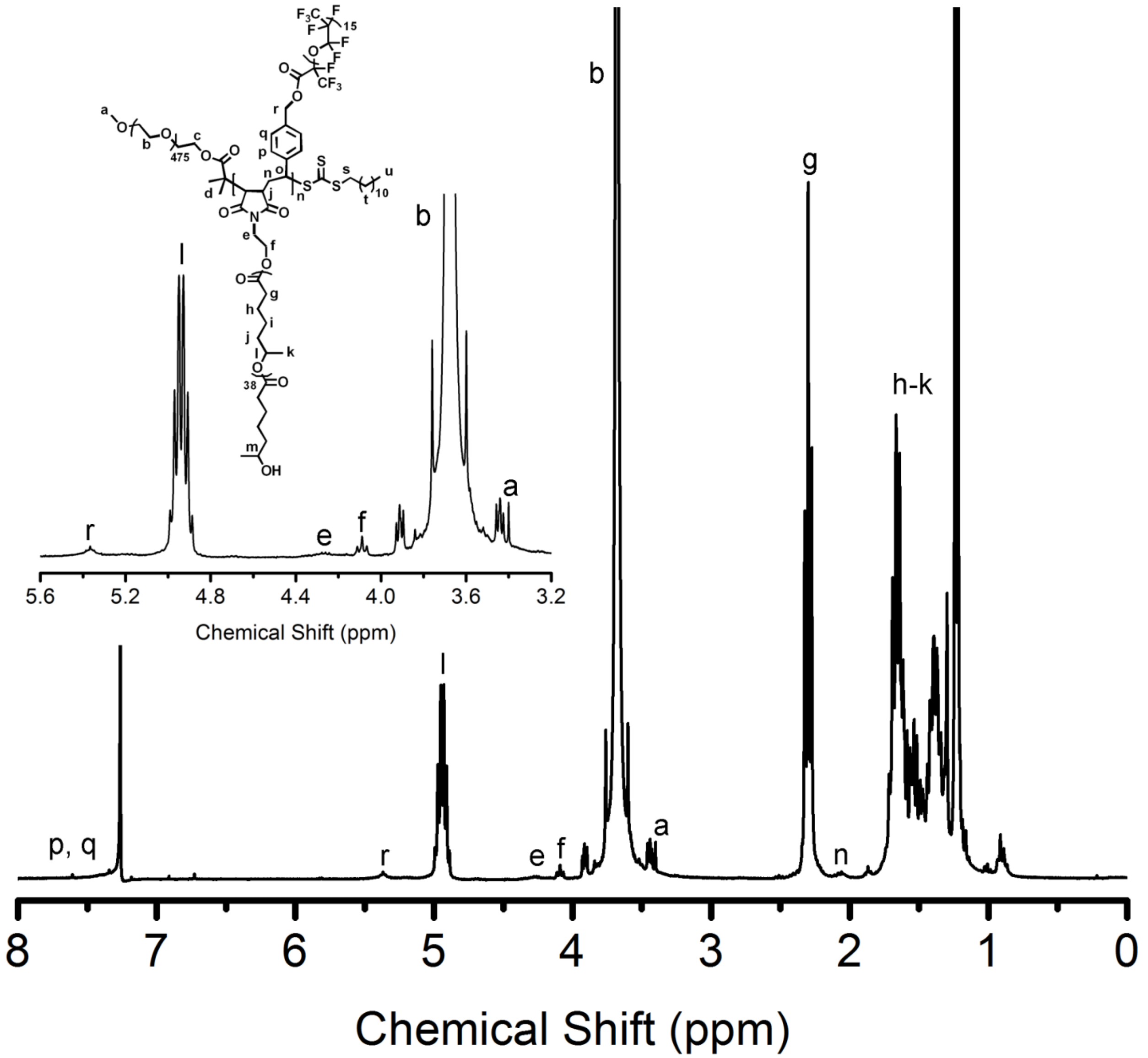


Figure S12. Assigned ^{1}H NMR spectrum of μ-O(C_3F_2) terpolymer in 9:2 (v/v) Freon-113/$CDCl_3$.

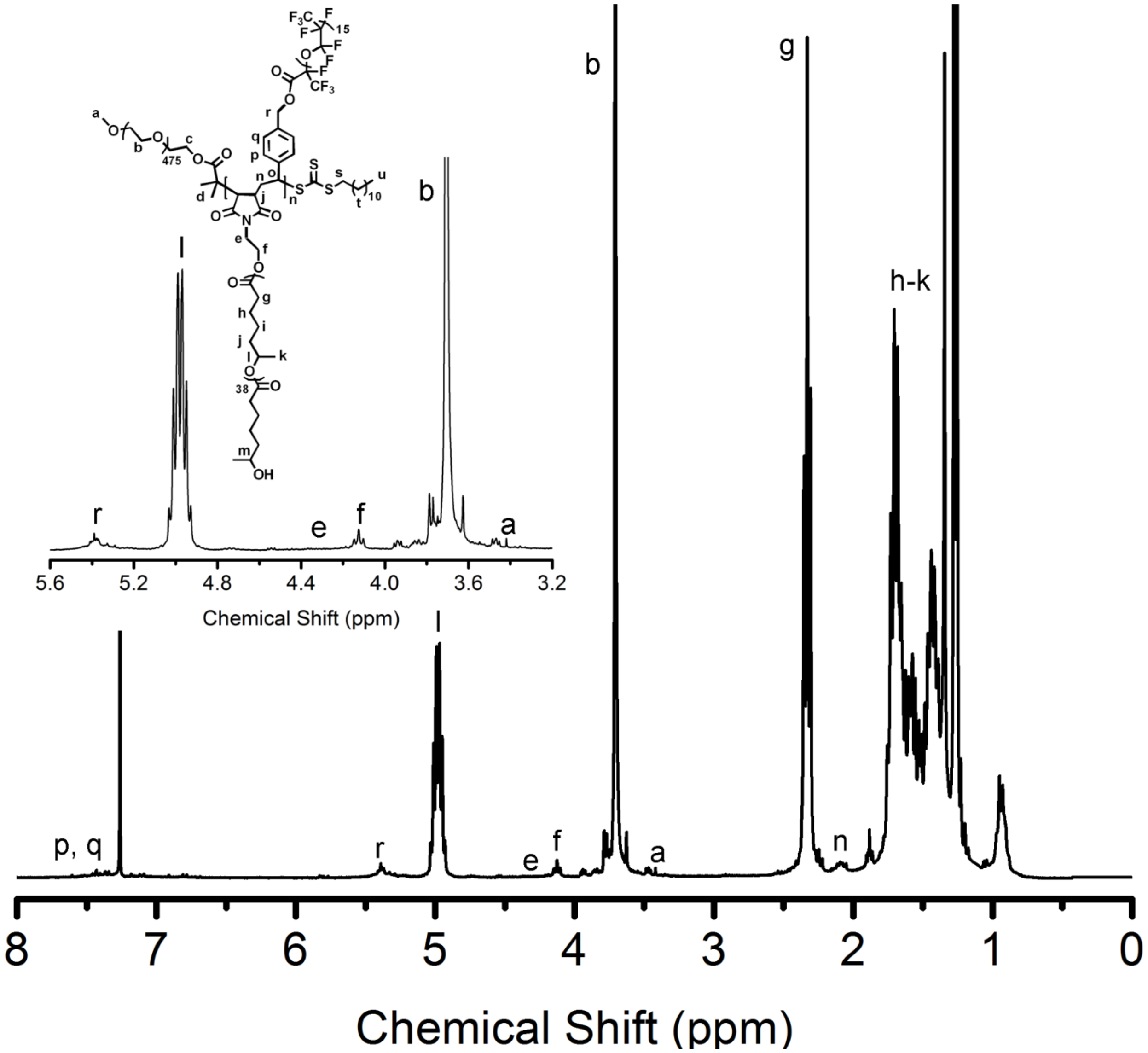


Figure S13. Assigned ^{1}H NMR spectrum of μ-O($C_{15}F_{20}$) terpolymer in 9:2 (v/v) Freon-113/$CDCl_3$.

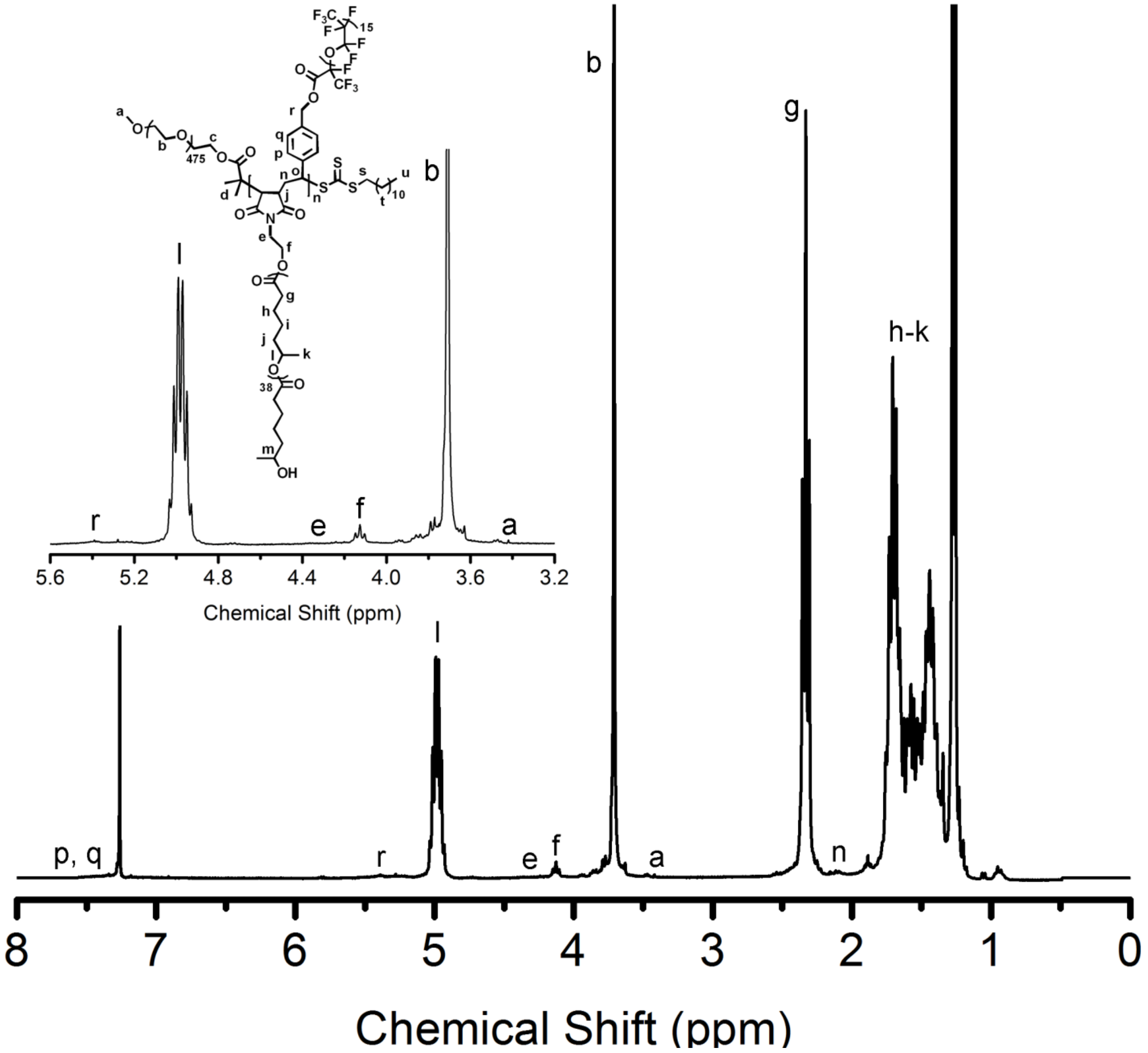


Figure S14. Assigned ^{1}H NMR spectrum of μ-O($C_{33}F_{38}$) terpolymer in 9:2 (v/v) Freon-113/$CDCl_3$.

Table S1. Elemental analyses of μ-O(CF)$_n$ terpolymers synthesized.

Sample		% C	% H	% F	% N	% S
μ-O(C_2F_3)	Calculated	53.8	8.0	8.9	0.1	0.3
	Found	53.6	7.9	8.9	0.1	0.3
μ-O(C_3F_2)	Calculated	55.3	8.2	7.8	0.1	0.2
	Found	54.7	8.1	7.6	0.2	0.2
μ-O(C_2F_4)	Calculated	50.2	7.0	16.1	0.1	0.2
	Found	50.2	7.1	16.2	0.1	0.0
μ-O(C_3F_4)	Calculated	52.0	7.3	14.3	0.1	0.2
	Found	51.9	7.5	13.9	0.2	0.0
μ-O(C_5F_8)	Calculated	50.1	6.6	19.8	0.1	0.2
	Found	50.1	6.5	21.0	0.2	0.5
μ-O(C_7F_{13})	Calculated	48.4	6.0	23.9	0.1	0.2
	Found	47.0	5.8	24.1	0.1	0.0
μ-O($C_{15}F_{20}$)	Calculated	50.6	6.3	22.2	0.1	0.3
	Found	48.1	5.9	23.5	0.1	0.0
μ-O($C_{33}F_{38}$)	Calculated	51.6	6.3	21.8	0.2	0.4
	Found	49.8	6.1	22.5	0.2	0.0

References

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(3) Zhu, S.; Edmonds, W. F.; Hillmyer, M. A.; Lodge, T. P. *J. Polym. Sci. Part B: Polym. Phys.* **2005**, *43*, 3685-3694.

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