Supporting Information

An organocatalytic perfluoroalkylation of commodity polymers

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Materials and Methods

General Considerations

NMR spectra were recorded using a Bruker DRX 400 MHz spectrometer. Chemical shifts δ (ppm) are referenced using the unified scale relative to the absolute frequency for ^{1}H of 0.1% TMS in $CDCl_3$ (^{19}F). Gel permeation chromatography (GPC) was performed on either a Tosoh EcoSEC Elite GPC system equipped with a TSKgel Super HM-M (17392) column maintained at 40 °C with an RI detector or a Waters 2695 separations module liquid chromatograph equipped with either four Waters Styragel HR columns (WAT044225, WAT044231, WAT044237, and WAT054460) arranged in series or two Agilent Resipore columns (PL1113-6300) maintained at 35 °C, and a Waters 2414 refractive index detector at room temperature. Tetrahydrofuran was used as the mobile phase at a flow rate of 0.5 mL/min (Tosoh GPC) or 1.0 mL/min (Waters GPC). Molecular weight and dispersity data are reported relative to polystyrene standards.

Material Synthesis

All starting materials were used as purchased without further purification. Polystyrene (**1**) and catalysts **2**-**11** were synthesized according to literature procedure.[1–6]

GPC trace of starting material

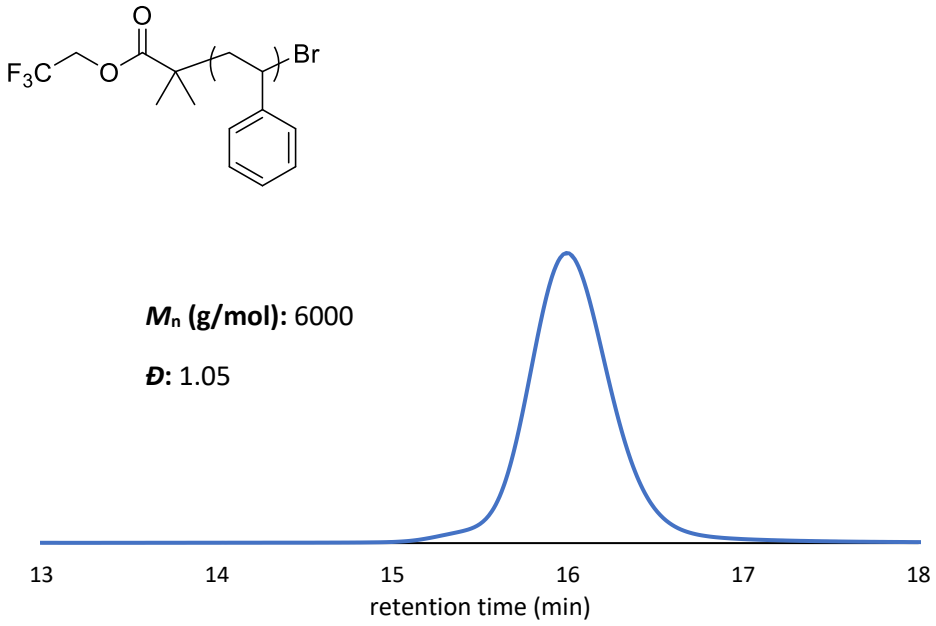


Figure S1: GPC trace of polystyrene (**1**) starting material for catalyst screening and optimization studies.

GPC traces of catalyst screening reactions

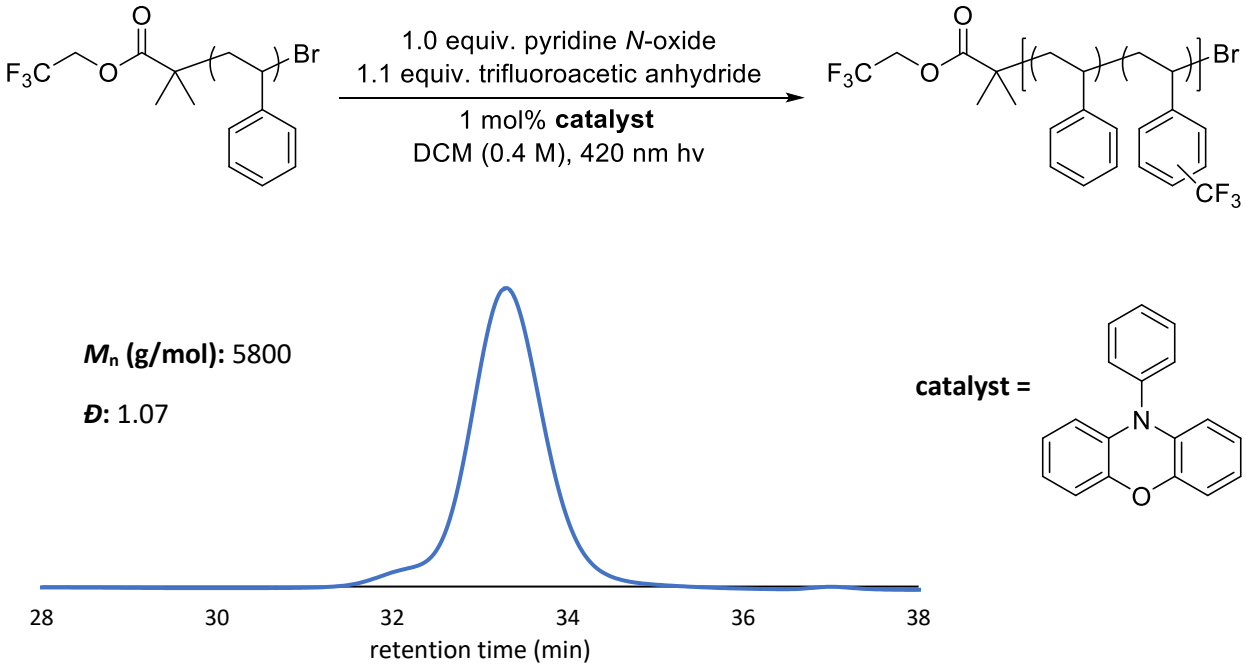


Figure S2: GPC trace of trifluoromethylated polystyrene using **2** as the organic catalyst.

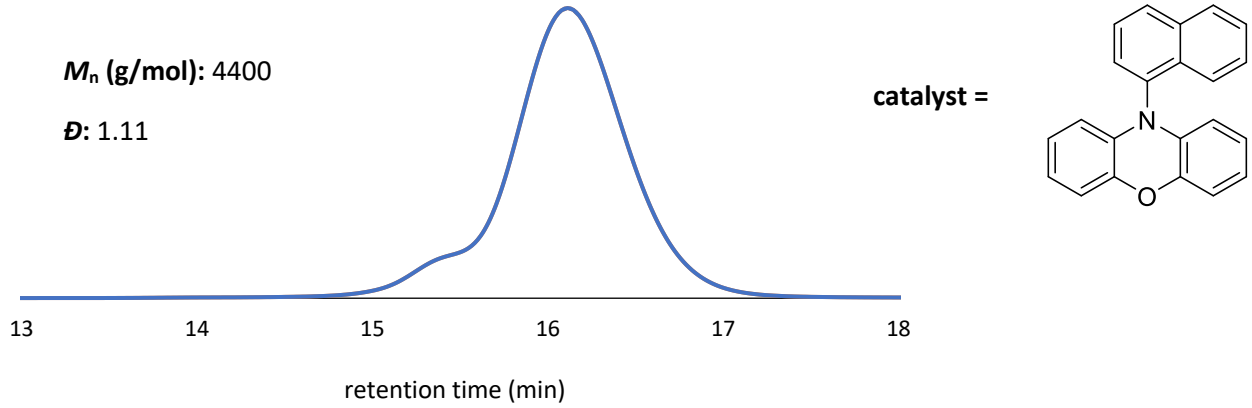


Figure S3: GPC trace of trifluoromethylated polystyrene using **3** as the organic catalyst.

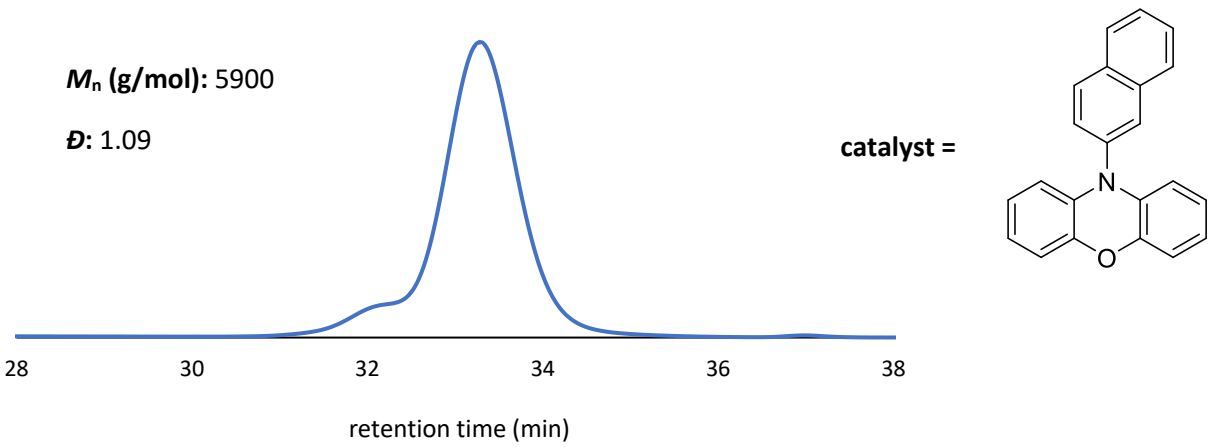


Figure S4: GPC trace of trifluoromethylated polystyrene using **4** as the organic catalyst.

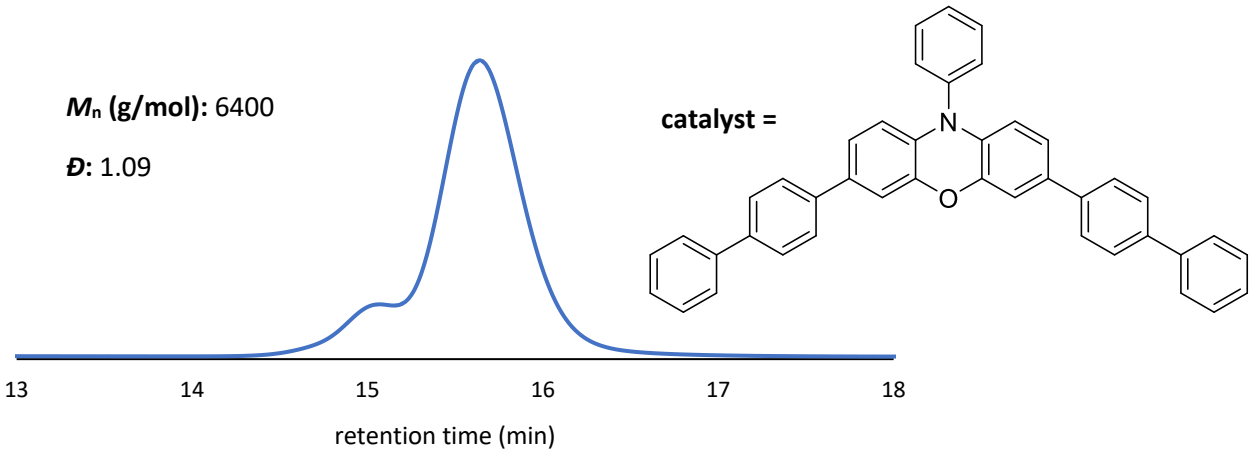


Figure S5: GPC trace of trifluoromethylated polystyrene using **5** as the organic catalyst.

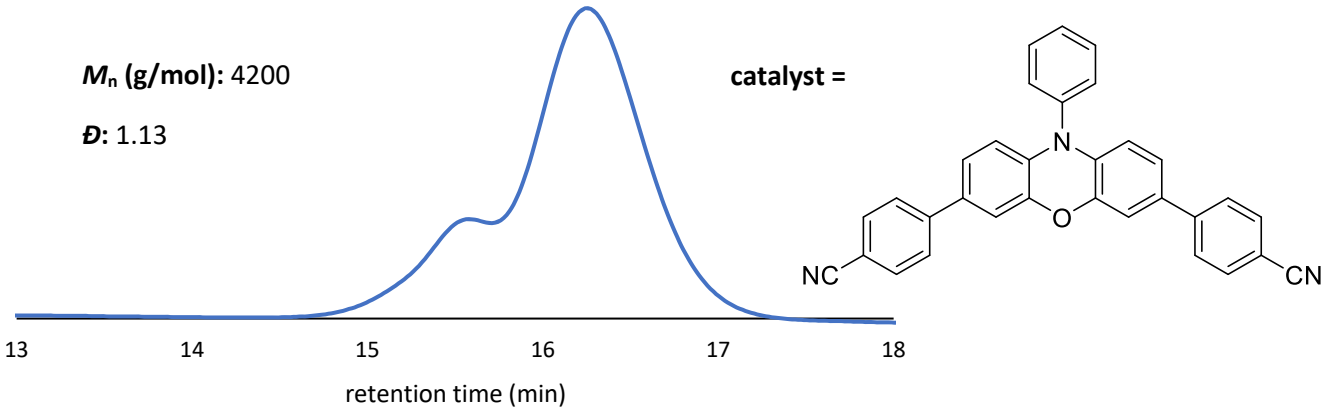


Figure S6: GPC trace of trifluoromethylated polystyrene using **6** as the organic catalyst.

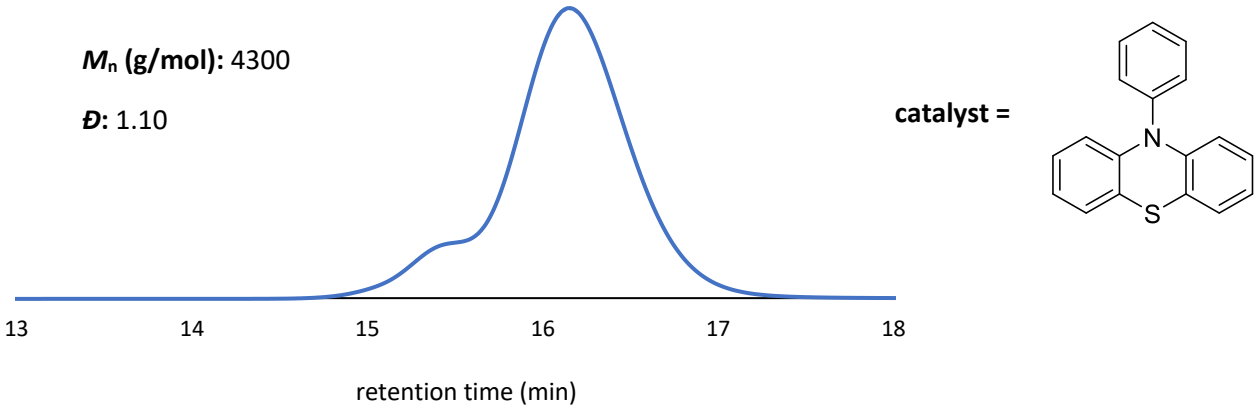


Figure S7: GPC trace of trifluoromethylated polystyrene using **7** as the organic catalyst.

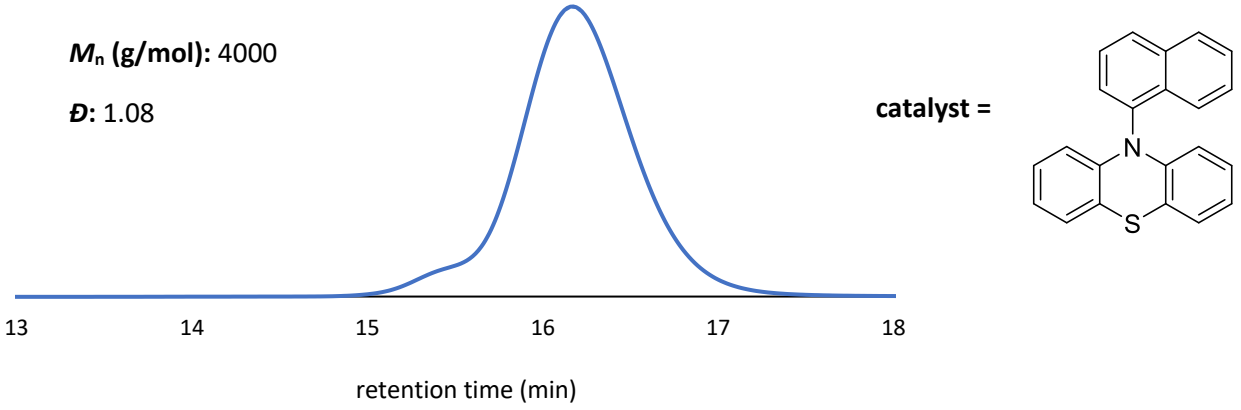


Figure S8: GPC trace of trifluoromethylated polystyrene using **8** as the organic catalyst.

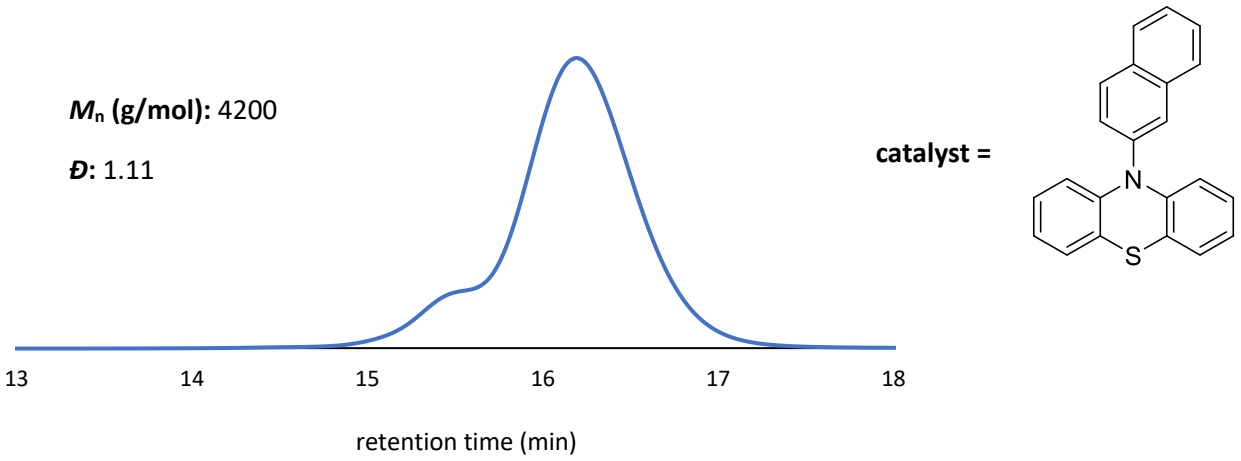


Figure S9: GPC trace of trifluoromethylated polystyrene using **9** as the organic catalyst.

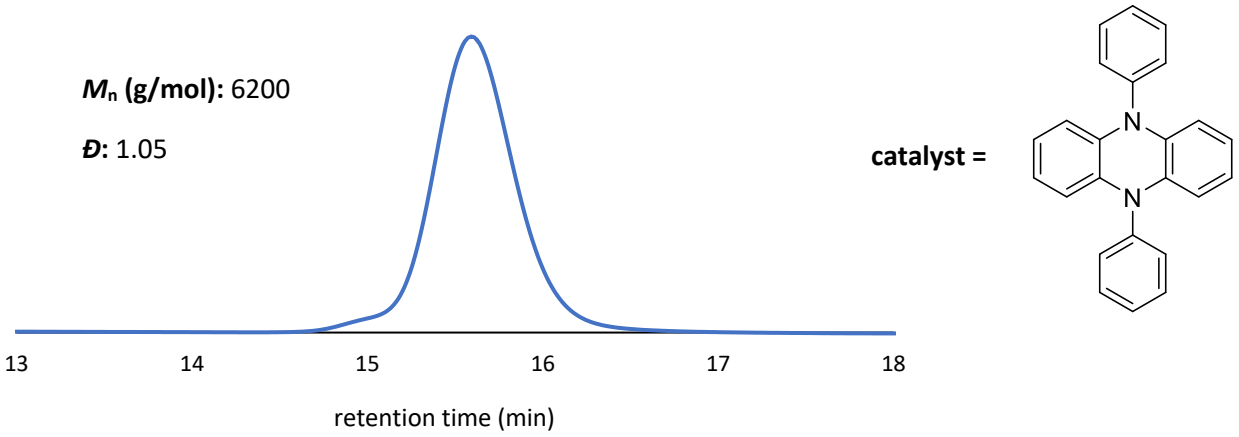


Figure S10: GPC trace of trifluoromethylated polystyrene using **10** as the organic catalyst.

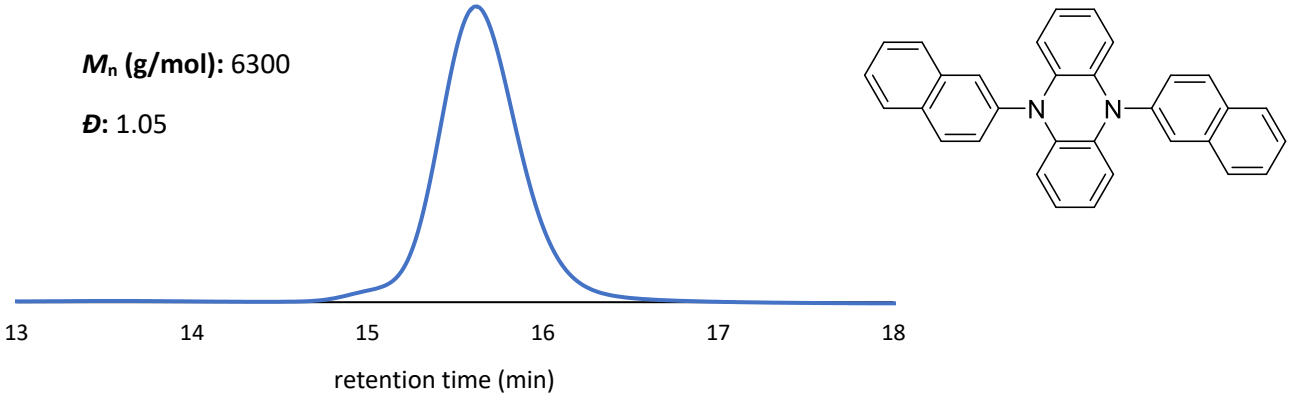


Figure S11: GPC trace of trifluoromethylated polystyrene using **11** as the organic catalyst.

Table S1 Optimization of trifluoromethylation of polystyrene

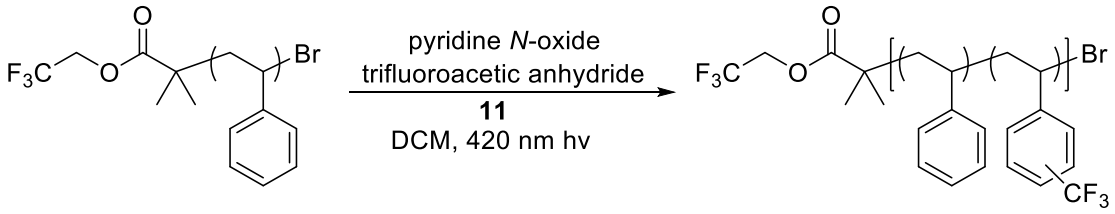
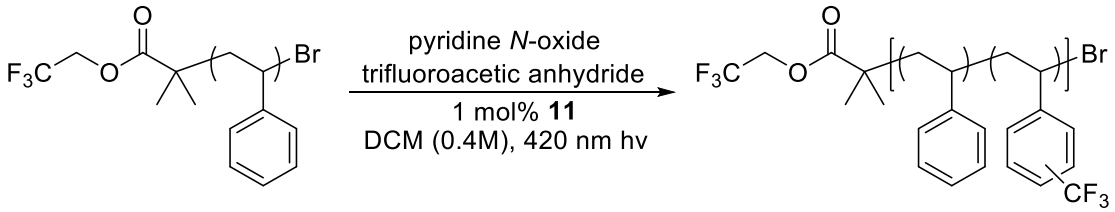


Table entry	equiv pyridine *N*-oxide	equiv TFAA	[repeat unit] (M)	Mol% 11	Reaction Time (hr)	Average CF_3 per 100 repeat units
1	1.0	1.1	0.4	1	16	18
2	1.0	1.1	0.4	0.1	16	12
3	1.0	1.1	0.4	0.5	16	18
4	1.0	1.1	0.4	2	16	20
5	1.0	1.1	0.4	5	16	16
6	1.0	1.1	0.4	1	16	16
7	1.0	1.1	0.4	2	16	16
8	1.0	1.1	0.8	1	16	20
9	1.0	1.1	0.2	1	16	12
10	1.0	1.1	0.1	1	16	11
11	1.0	1.1	1.2	1	16	25
12	1.0	1.1	1.6	1	16	8.4
13	5.0	5.5	0.8	1	16	8.3
14	5.0	5.5	1.2	1	16	3.3
15	2.0	2.2	0.4	1	16	27
16	2.0	2.2	0.8	1	16	28
17	1.0	1.1	0.4	1	1	1.9
18	1.0	1.1	0.4	1	3	5.9
19	1.0	1.1	0.4	1	5	7.6
20	1.0	1.1	0.4	1	7	10
21	3.0	3.3	0.4	1	16	31
22	5.0	5.5	0.4	1	16	33
23	7.0	7.7	0.4	1	16	27

GPC traces of increased reagent loading studies



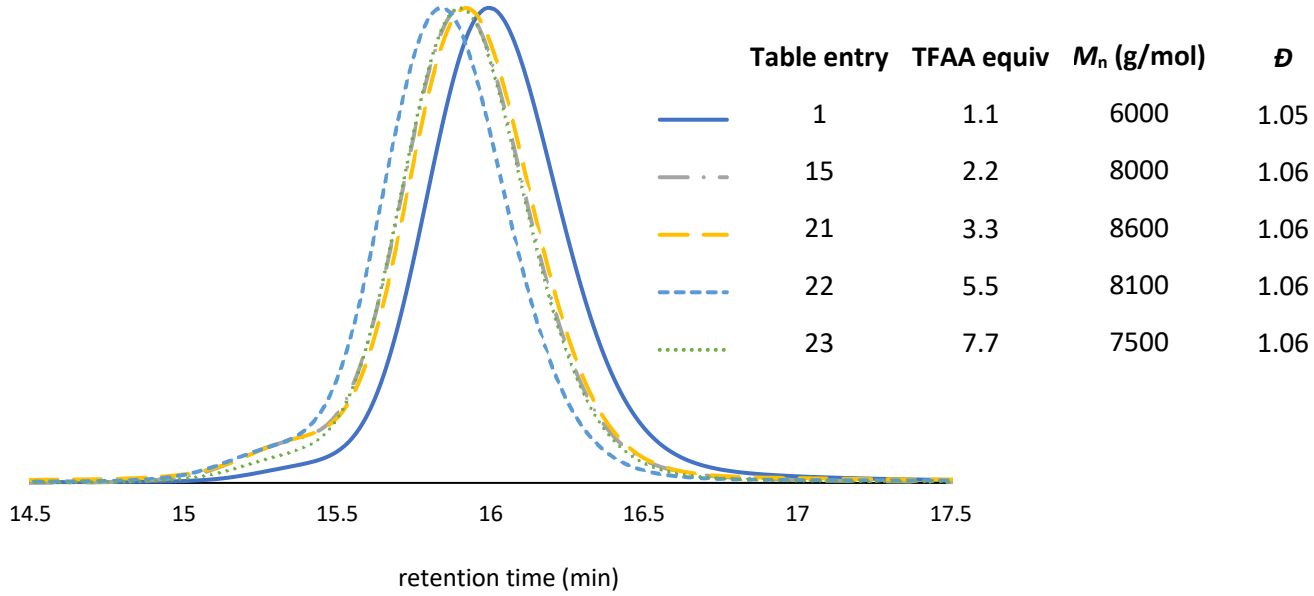
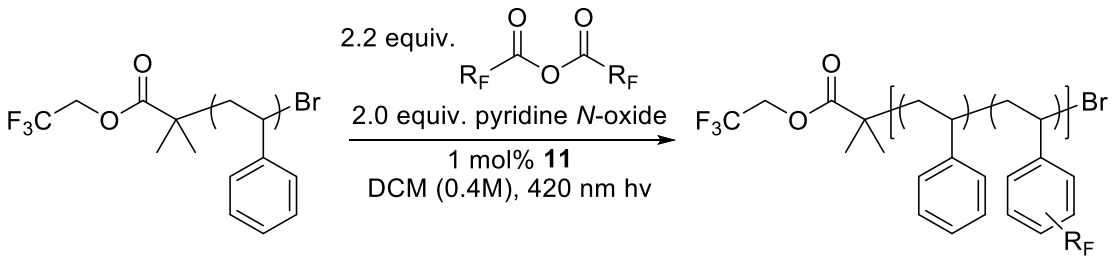
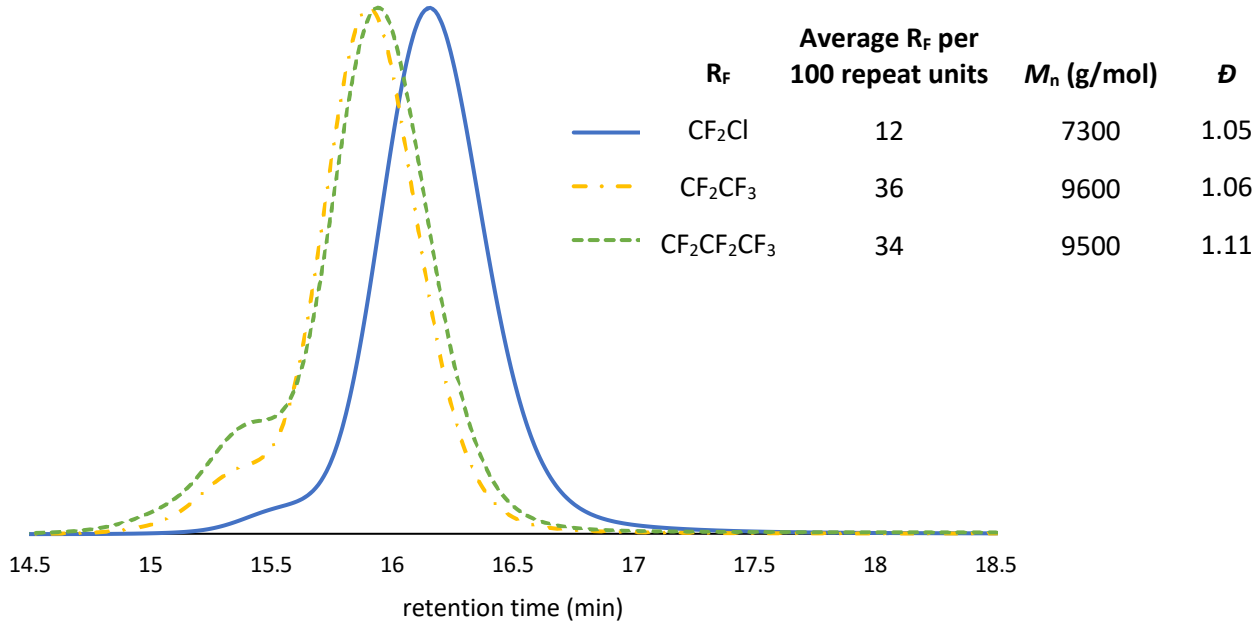


Table entry	TFAA equiv	M_n (g/mol)	$Đ$
1	1.1	6000	1.05
15	2.2	8000	1.06
21	3.3	8600	1.06
22	5.5	8100	1.06
23	7.7	7500	1.06

Figure S12: GPC overlay of increasing TFAA/pyridine *N*-oxide equivalents in the trifluoromethylation of polystyrene, reference **table S1** for reaction conditions. The starting M_n and $Đ$ for these reactions was 6000 g/mol and 1.05, respectively

GPC traces of anhydride scope





R_F	Average R_F per 100 repeat units	M_n (g/mol)	$Đ$
CF_2Cl	12	7300	1.05
CF_2CF_3	36	9600	1.06
$CF_2CF_2CF_3$	34	9500	1.11

Figure S13: GPC overlay of anhydride scope. The starting M_n and $Đ$ for these reactions was 6000 g/mol and 1.05, respectively

GPC traces of commodity polymer functionalization reactions

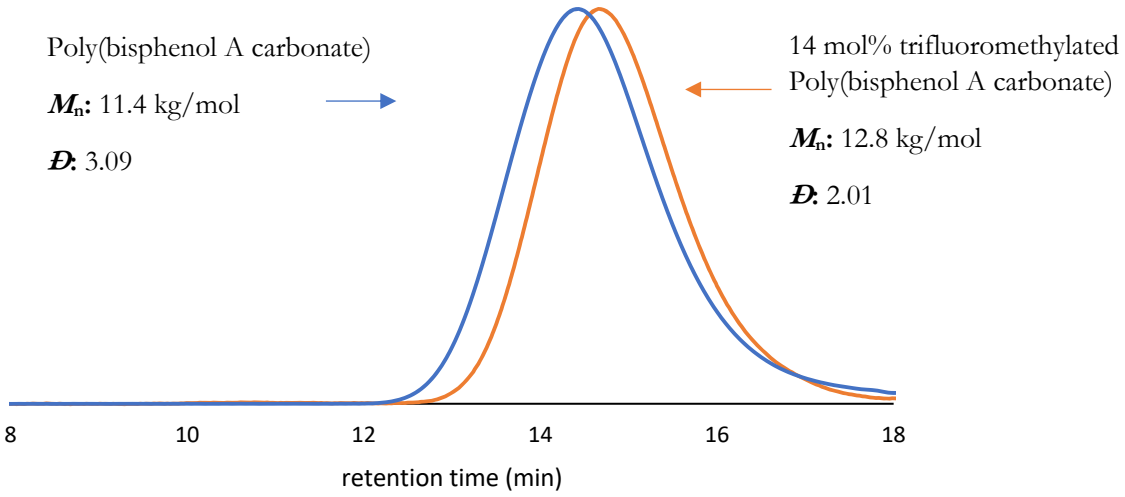


Figure S14: GPC overlay of poly(bisphenol A carbonate) and functionalized poly(bisphenol A carbonate). The shift in retention time is attributed to a decrease in the hydrodynamic radius of the polymer upon trifluoromethylation.

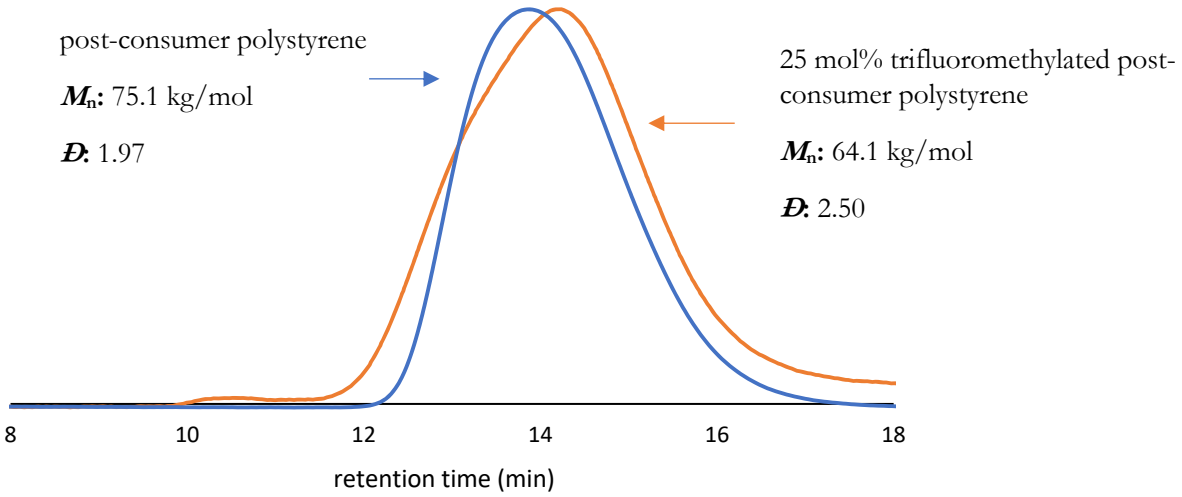


Figure S15: GPC overlay of post-consumer polystyrene and functionalized post-consumer polystyrene. The shift in retention time is attributed to a decrease in the hydrodynamic radius of the polymer upon trifluoromethylation.

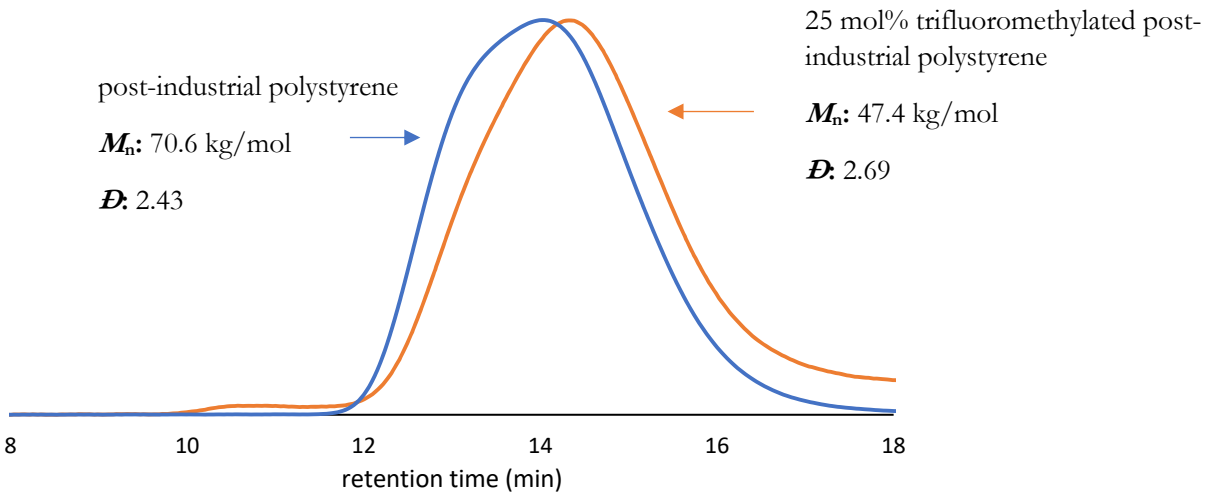
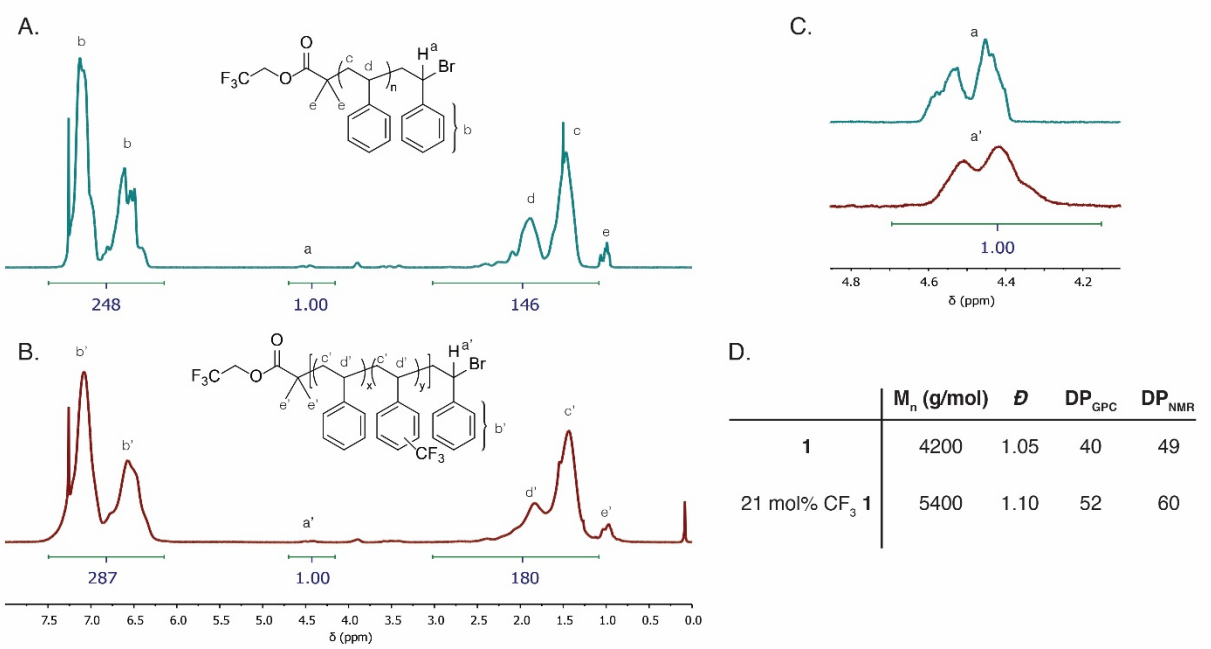


Figure S16: GPC overlay of post-industrial polystyrene and functionalized post-industrial polystyrene. The shift in retention time is attributed to a decrease in the hydrodynamic radius of the polymer upon trifluoromethylation.

^{1}H NMR study of the Br chain-end

The chemoselectivity of the fluoroalkylation in terms of retention of the bromine end-group was studied experimentally. Figure S17 demonstrates that the hydrogen alpha to the bromine chain-end is clearly seen in the ^{1}H NMR before and after functionalization indicating that the bromine is retained. By integrating the H^a and $H^{a'}$ protons to 1.00, a degree of polymerization (DP) was determined for both polymer samples using the signals produced from H^c + H^d and $H^{c'}$ + $H^{d'}$. Additionally, accounting for the weight of the chain-ends, the DP from the GPC data was also calculated, shown in part D. In both cases, the NMR DP values are similar to the GPC values. The combination of this experimental data indicates that the bromine chain-end is retained during the functionalization reaction on the majority of the polymer chains.



	M_n (g/mol)	$Đ$	DP_{GPC}	DP_{NMR}
1	4200	1.05	40	49
21 mol% CF_3 **1**	5400	1.10	52	60

Figure S17: (A) ^{1}H NMR spectra of an unfunctionalized PS **1** containing a bromine on the omega chain-end. (B) ^{1}H NMR spectra of a 21 mol% trifluoromethylated PS sample. (C) expansion of the ^{1}H NMR spectra of the region containing the proton alpha to the bromine (H^a and $H^{a'}$). (D) a table containing the M_n, $Đ$, and degree of polymerization (DP) values calculated from NMR and GPC data.

^{19}F NMR spectra of functionalized products

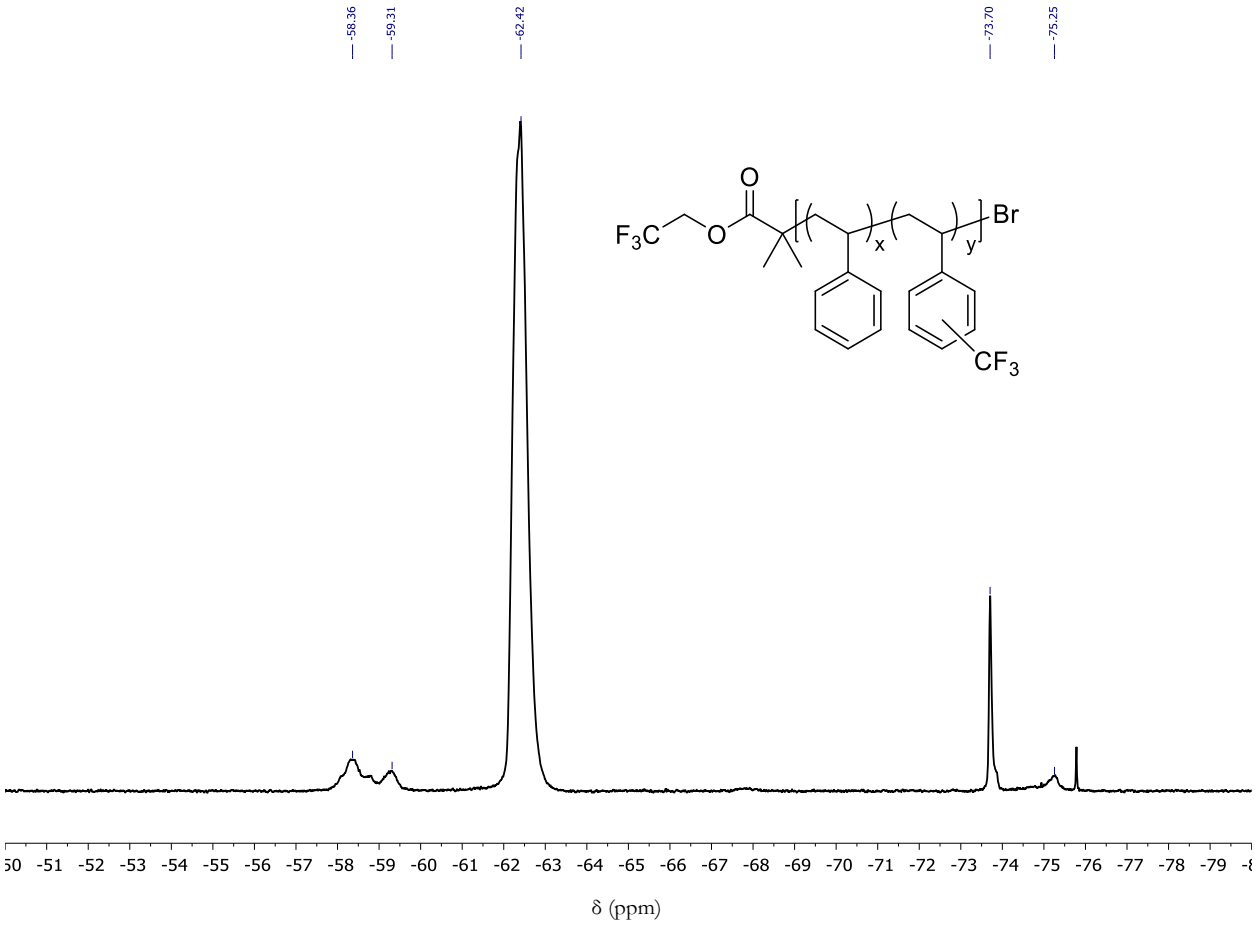


Figure S18: ^{19}F NMR ($CDCl_3$) of trifluoromethylated polystyrene. δ -58.36, -59.31, -62.42, -73.70, -75.25 ppm

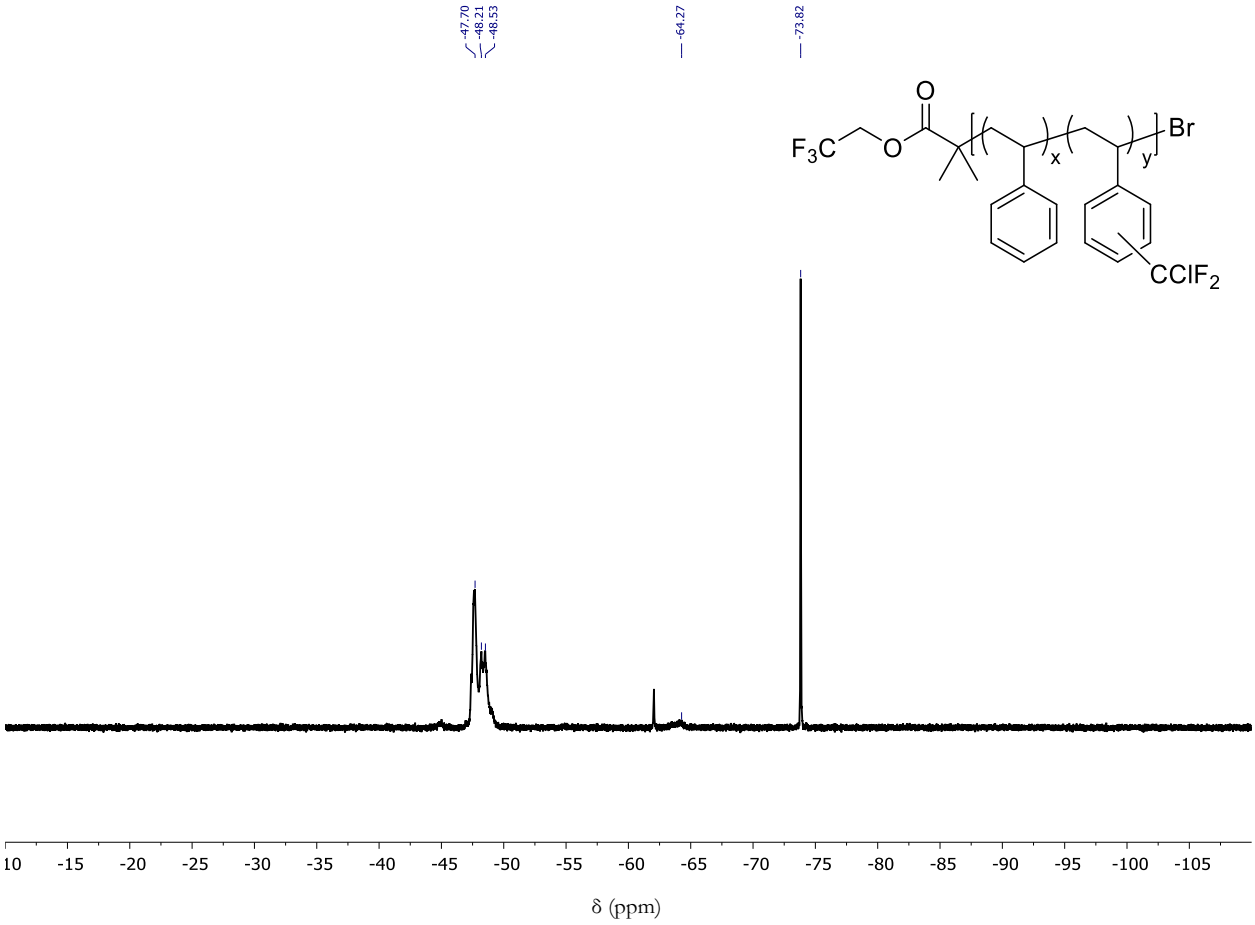


Figure S19: ^{19}F NMR ($CDCl_3$) of chlorodifluoromethylated polystyrene. δ -47.70, -48.21, -48.53, -64.27, -73.82 ppm

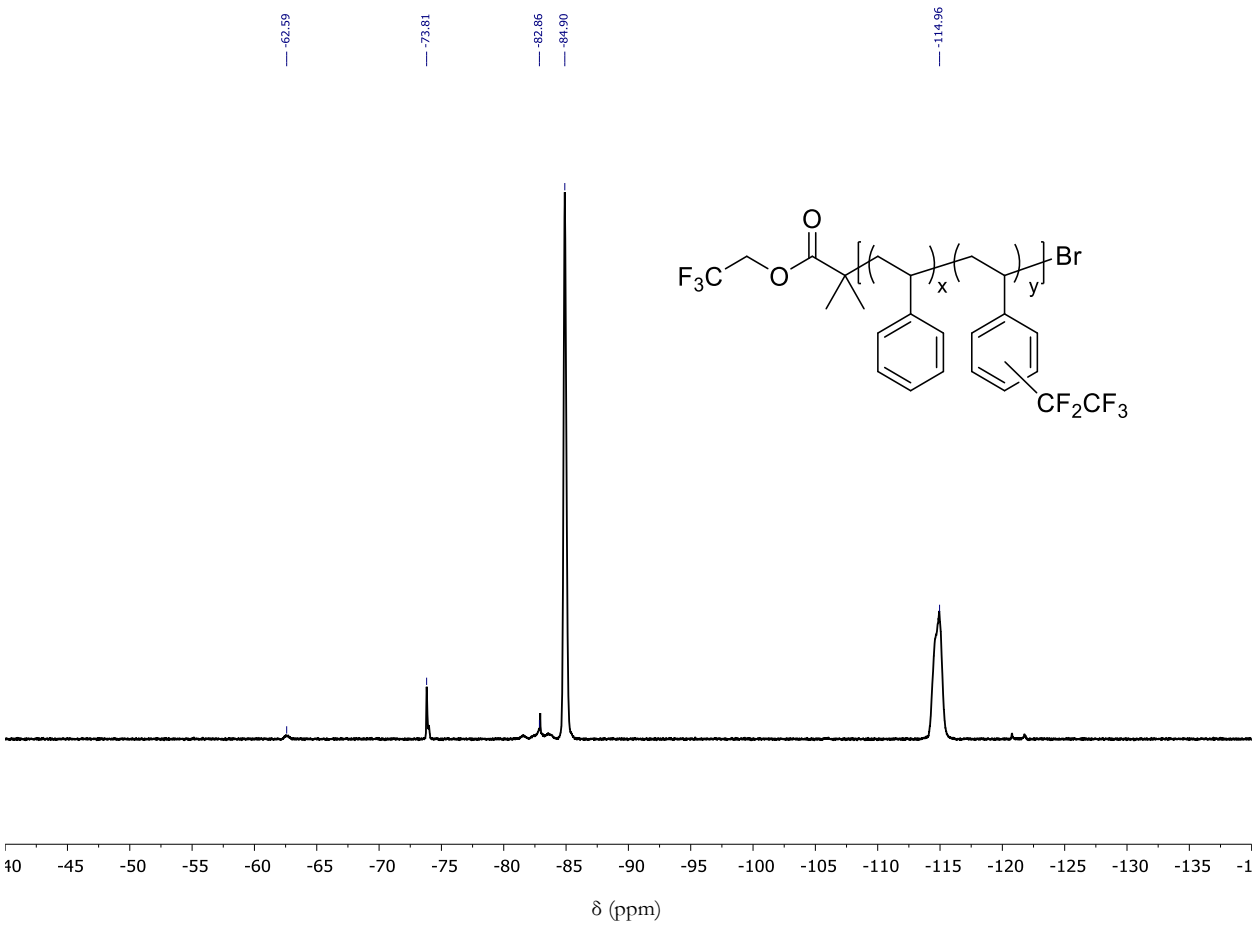


Figure S20: ^{19}F NMR ($CDCl_3$) of perfluoroethylated polystyrene. δ -62.59, -73.81, -82.86, -84.90, -114.96 ppm

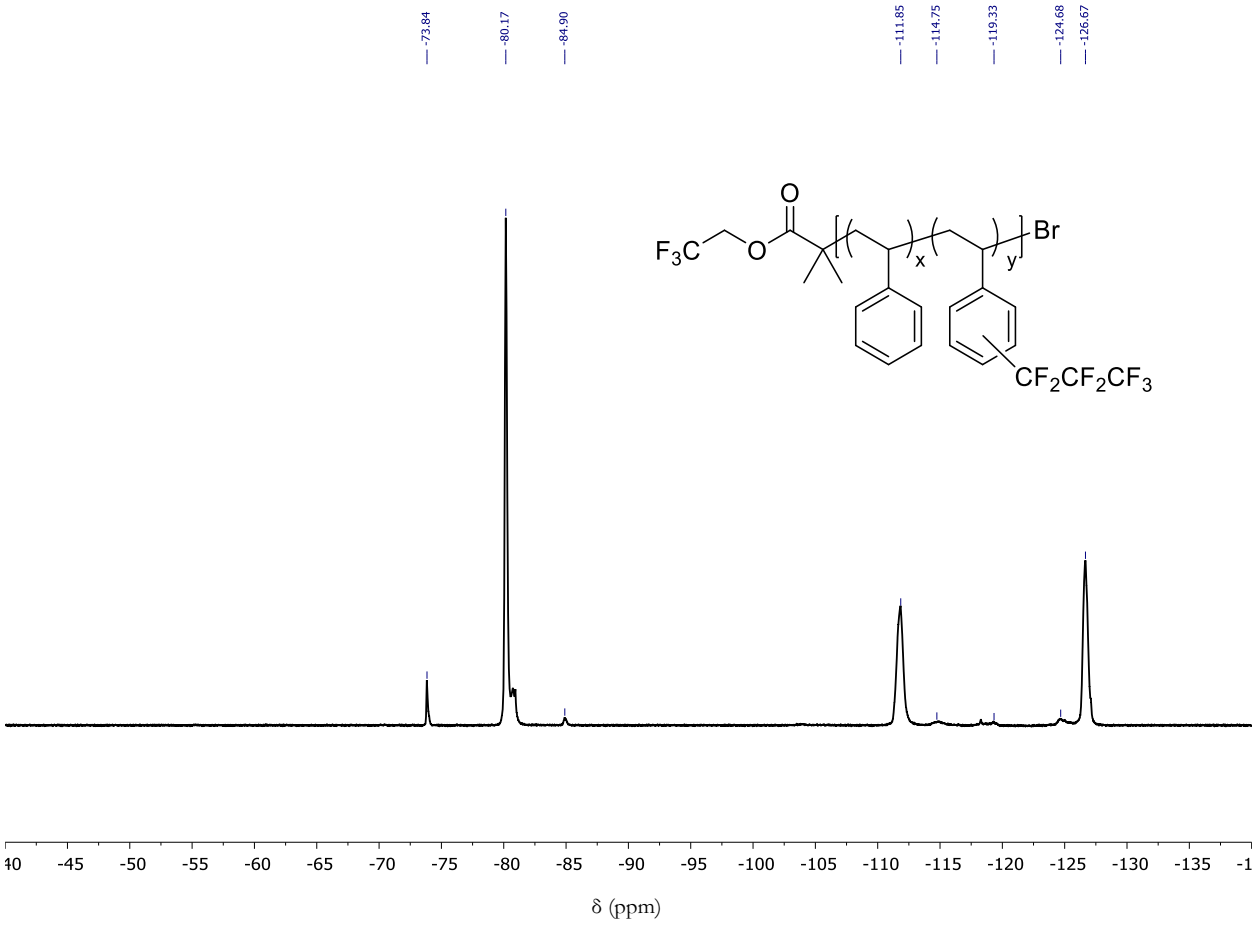


Figure S21: ^{19}F NMR ($CDCl_3$) of perfluoropropylated polystyrene. δ -73.84, -80.17, -84.90, -111.85, -114.75, -119.33, -124.68, -126.67 ppm

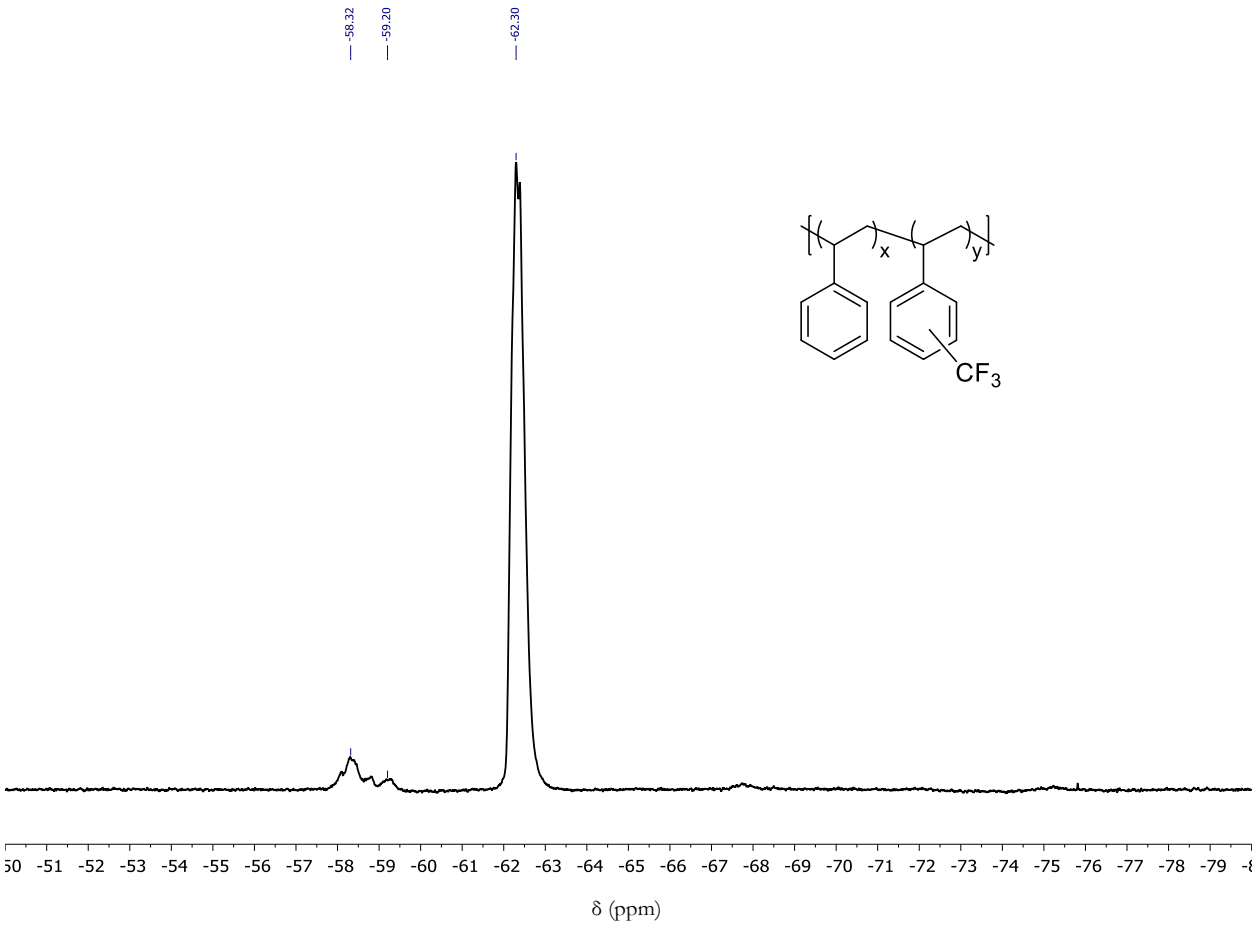


Figure S22: ^{19}F NMR ($CDCl_3$) of trifluoromethylated post-industrial waste polystyrene. δ -58.32, -59.20, -62.30 ppm. Fluorobenzene (-113.15 ppm) was used as a standard for functionalization calculations.

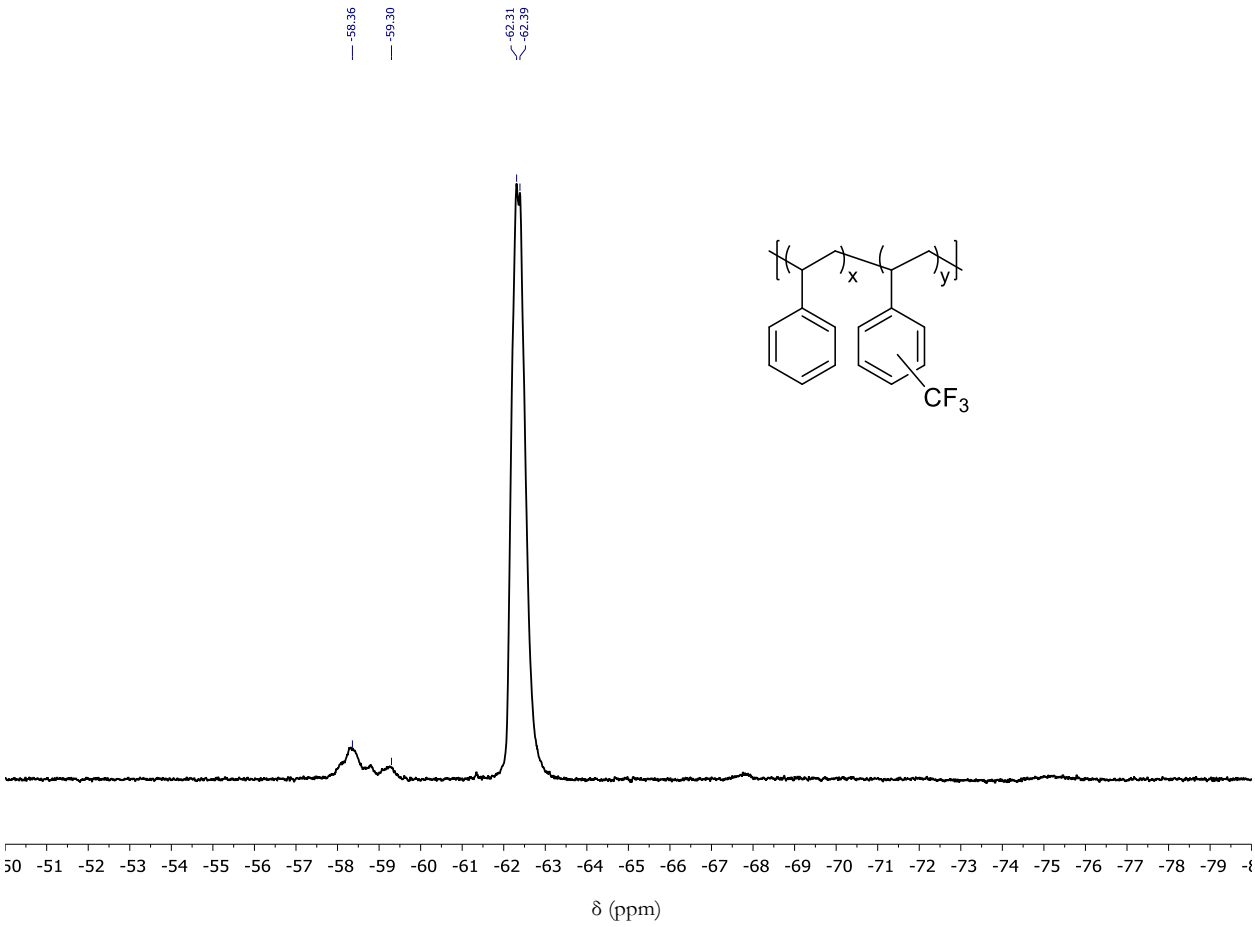


Figure S23: ^{19}F NMR ($CDCl_3$) of trifluoromethylated post-consumer waste polystyrene. δ -58.36, -59.30, -62.31, -62.39 ppm. Fluorobenzene (-113.15 ppm) was used as a standard for functionalization calculations.

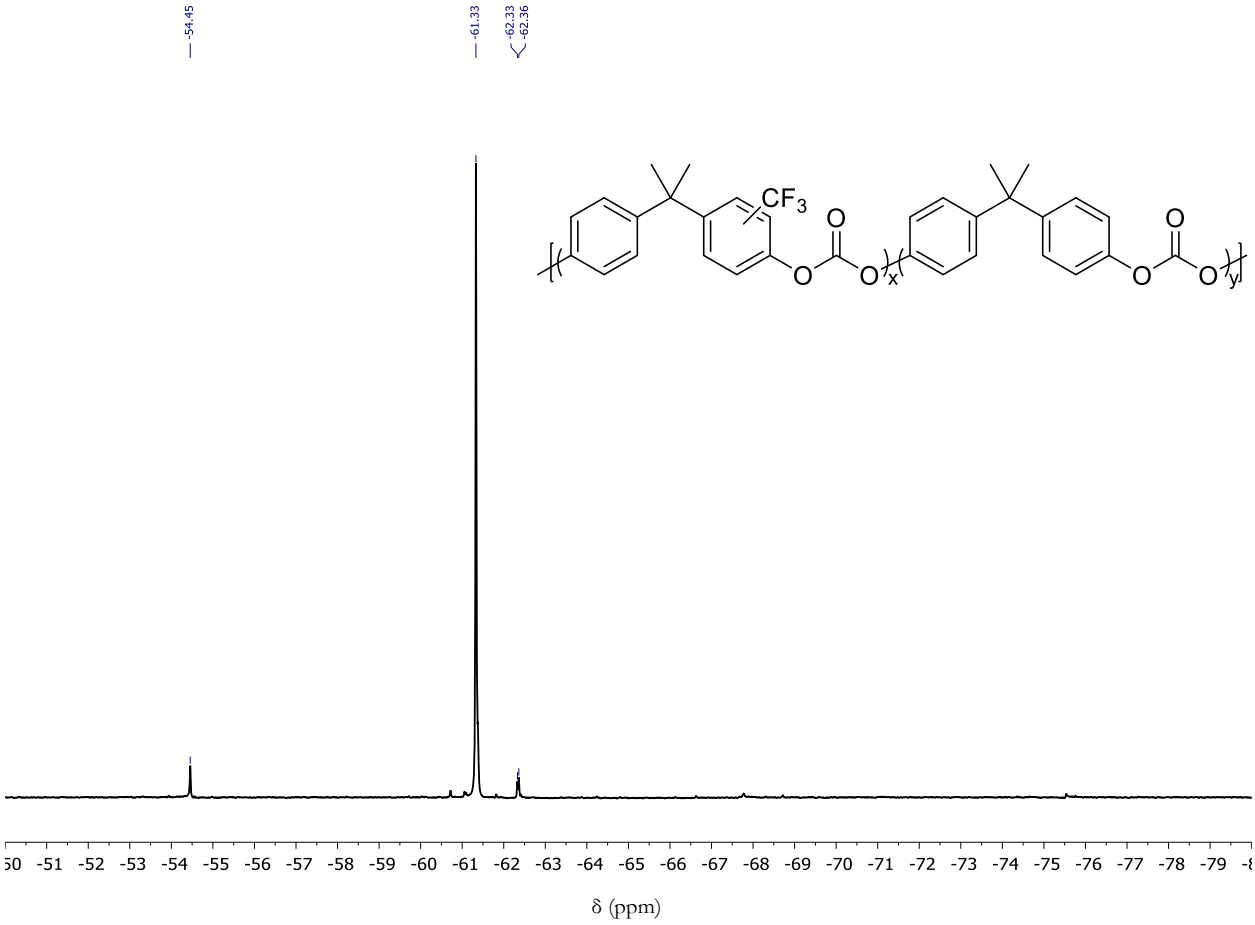


Figure S24: ^{19}F NMR ($CDCl_3$) of trifluoromethylated poly(bisphenol A carbonate). δ -54.45, -61.33, -62.33, -62.36 ppm. Fluorobenzene (-113.15 ppm) was used as a standard for functionalization calculations.

References

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