

Supporting Information

Synthesis, characterization, thermal and surface properties of co- and terpolymers based on fluorinated α -methylstyrenes and styrene

Justyna Walkowiak-Kulikowska,^{,1} Anna Sz wajca,¹ Véronique Gouverneur,² Bruno Ameduri,^{*,3}*

¹Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland,

²Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, United Kingdom, ³Institut Charles Gerhardt, Ingénierie et Architectures Macromoléculaires, UMR CNS 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'École Normale, 34296 Montpellier, France.

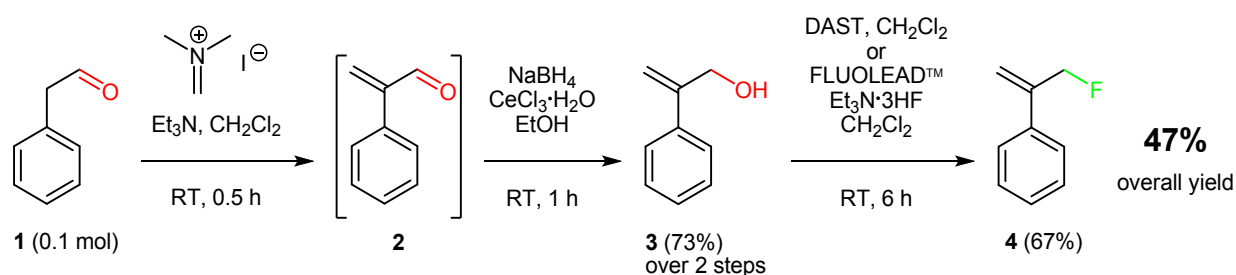
Table of content

1.	Synthesis of Fluorostyrenic monomers (F-STs)	3
1.1.	Synthesis of α -fluoromethylstyrene (FMST)	3
1.2.	Synthesis of α -trifluoromethylstyrene (TFMST)	4
2.	Spectroscopic characterization of poly(α -fluoromethylstyrene- <i>co</i> -styrene) copolymers	6
2.1.	Description of ST and FMST monomers ^1H NMR spectra presented in Figure 1 (main manuscript)	6
2.2.	^1H NMR spectra of poly(FMST- <i>co</i> -ST) copolymers	6
2.3.	^{19}F NMR spectra of poly(FMST- <i>co</i> -ST) copolymers	7
2.4.	Determination of comonomer content in poly(FMST- <i>co</i> -ST) obtained in bulk radical copolymerizations of FMST with ST	8
3.	Spectroscopic characterization of poly(α -trifluoromethylstyrene- <i>co</i> -styrene) copolymers	11
3.1.	Description of ST, TFMST monomers and poly(TFMST- <i>co</i> -ST) copolymer ^1H NMR spectra presented in Figure 2 (main manuscript)	11
3.2.	^1H NMR spectra of poly(FMST- <i>co</i> -ST) copolymers	12
3.3.	^{19}F NMR spectra of poly(FMST- <i>co</i> -ST) copolymers	13
3.4.	Determination of comonomer content in poly(TFMST- <i>co</i> -ST) obtained in bulk radical copolymerizations of TFMST with ST	14
4.	Determination of reactivity ratios of F-ST and ST by Fineman-Ross, Kelen-Tüdös and extended Kelen-Tüdös linear least squares methods	17
5.	Spectroscopic characterization of poly(α -trifluoromethylstyrene- <i>ter</i> -styrene- <i>ter</i> - α -fluoro-methylstyrene) terpolymers	21
5.1.	Description of ST, FMST, TFMST monomers and poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers ^1H NMR spectra presented in Figure 5 (main manuscript)	21
5.2.	The comparison of ^{13}C NMR spectra of FMST and TFMST monomers with poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers	22
5.3.	The comparison of ^{19}F NMR spectra of FMST and TFMST monomers with poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers	23
5.4.	^1H NMR spectra of <i>poly</i> (TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers	25
5.5.	^{13}C NMR spectra of <i>poly</i> (TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers	26
5.6.	^{19}F NMR spectra of <i>poly</i> (TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers	27
5.7.	Determination of comonomer content in poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) termonomers obtained in bulk radical terpolymerizations of TFMST and FMST with ST	28
6.	Determination of average molecular weights of poly(FMST- <i>co</i> -ST) copolymers from GPC with polystyrene standards	33
7.	Determination of average molecular weights of poly(TFMST- <i>co</i> -ST) copolymers from GPC with polystyrene standards	34
8.	Determination of average molecular weights of poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST) terpolymers from GPC with polystyrene standards	35
9.	Thermostability of poly(fluorinated α -methylstyrene-styrene) co- and terpolymers	36
10.	Contact Angle Measurements	40

1. Synthesis of Fluorostyrenic monomers (F-STs)

1.1. Synthesis of α -fluoromethylstyrene (FMST)

Alternatively to previous two-step sequence reported by Kostov et al.¹, the monofluorinated monomer FMST was prepared following the most convenient large-scale synthesis that began with the 2-phenylacetaldehyde **1**.² α -Methylenation was performed, reacting the aldehyde with the Eschenmoser's salt (*N,N*-dimethylmethyleammonium iodide) in the presence of a large excess of triethylamine. Without isolation, the resulting product **2** was reduced, leading uneventfully to the desired allylic alcohol **3** in good yield (73%) over two steps. The alcohol was converted into corresponding fluorinated monomer **4** by direct nucleophilic fluorination. In comparative studies, both DAST and FLUOLEADTM, a more stable reagent used in combination with Et₃N·HF, were employed.³ The yields for the fluorination of alcohol **3** were consistent and comparable, independent of the reagent or the scale of the reaction, averaging 67% for allylic fluoride **4**. This three-step synthetic route towards monofluoromethylstyrene (FMST) using a direct nucleophilic fluorination was found to be easy to implement, selective, cost-effective and easily scalable (up to 100 mmol) giving the desired allylic fluoride **4** in 47% overall yield (Scheme 1).



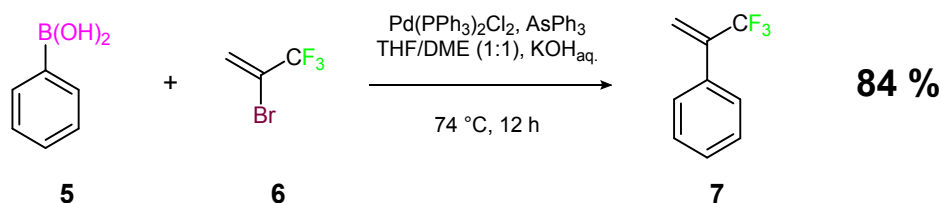
Scheme S1. Preparation of α -fluoromethylstyrene (FMST) by direct nucleophilic deoxofluorination.

Synthetic procedure of α -fluoromethylstyrene (FMST).² To a solution of FLUOLEADTM (11.7 g, 46.9 mmol) and Et₃N·3HF (7.56 g, 7.68 mL, 46.9 mL) in dry CH₂Cl₂ (75 mL) at 0 °C was added dropwise a solution of 2-phenylprop-2-en-1-ol (5.03 g, 37.5 mmol) in dry CH₂Cl₂ (75 mL). The reaction was then brought to room temperature and stirred for 6 hours (monitored by TLC). Saturated

aqueous K_2CO_3 (190 mL) was then slowly added and the mixture was additionally stirred for 1 hour, then extracted with CH_2Cl_2 (3 x 120 mL). The combined organic layers were dried ($MgSO_4$ or Na_2SO_4) and concentrated under reduced pressure. The residue was purified by silica gel column chromatography or by Biotage SP-4 System using PE 30-40 as eluent, or by short-path distillation under reduced pressure (bp 80-81 °C, 17 mbar) to yield 3.42 g (25.1 mmol, 67% yield) of FMST as a colorless liquid. This compound was stable to silica gel chromatography and no apparent elimination of fluorine was observed (the walls of the glassware were not etched). 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46–7.48 (m, 2 H, H_{Ar}), 7.32–7.41 (m, 3 H, H_{Ar}), 5.63 (s, 1 H, $C=CH_2$), 5.44 (m, 1 H, $C=CH_2$), 5.26 (d, $^2J_{H-F} = 47.1$ Hz, 2 H, CH_2F); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.0 (d, $^2J_{C-F} = 14.4$ Hz, $H_2C=CCH_2F$), 137.3 (C_{Ar}), 128.5 (C_{Ar}), 128.2 (C_{Ar}), 125.9 (C_{Ar}), 115.3 (d, $^3J_{C-F} = 10.6$ Hz, $H_2C=CCH_2F$), 84.3 (d, $^1J_{C-F} = 169.0$ Hz, CH_2F); ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –212.7 (t, $^2J_{F-H} = 47.1$ Hz, 1 F, CH_2F); HRMS (CI): m/z $[M]^+$ calcd for C_9H_9F : 136.0688; found: 136.0685.

1.2. Synthesis of α -trifluoromethylstyrene (TFMST)

Trifluoromethyl styrene (TFMST) was synthesized in 84% yield using the palladium-catalyzed coupling reaction of organoboron compound **5** with electrophile **6** in the presence of a base (Scheme 1).^{2,4}



Scheme S2. Preparation of α -trifluoromethylstyrene (TFMST) by palladium-catalyzed Suzuki-Miyaura coupling

The Suzuki reaction^{5,6} has been selected from a number of reported^{7–11} synthetic methods for the preparation of α -trifluoromethylstyrene derivatives due to its attractive features, such as: high yields,

milder condition, many functional groups surviving under reaction conditions, and the ability to remain unaffected in the presence of water.^{2,4}

Synthetic procedure of α -trifluoromethylstyrene (TFMST). α -Trifluoromethylstyrene (TFMST) was prepared according to literature procedure.^{2,4} In a pressure tube to a solution of 2-bromo-3,3,3-trifluoropropene (7.87 g, 0.045 mol, 1.5 eq.) in tetrahydrofuran (THF)–dimethoxyethane (DME) (1 : 1; v/v; 90 ml) and potassium hydroxide (KOH) (aq, 2M, 60 ml), phenylboronic acid (3.66 g, 0.030 mol, 1 eq.), bis(triphenylphosphine)palladium(II) dichloride PdCl₂(PPh₃)₂ (0.632 g, 0.9 10⁻³ mol, 0.03 eq.) and AsPh₃ (1.38 g, 4.5 10⁻³ mol, 0.15 eq.) were added under inert atmosphere. The reaction mixture was sealed and stirred at 74 °C for 12 h. After being cooled to room temperature, water (300 ml) was added, then the mixture was extracted with diethyl ether (2 × 300 ml). The combined organic layers were washed with brine (3 × 100 ml) and dried over MgSO₄. After removing the solvent, the residue was purified by short-path distillation under reduced pressure (bp 55-57 °C, 17-19 mbar), giving 4.34 g (25.2 mmol, 84 %) of TFMST as colorless liquid. **¹H NMR** (CDCl₃) δ [ppm]: 7.52 (m, 2 H, H_{Ar}), 7.44 (m, 3 H, H_{Ar}), 6.01 (m, 1 H, C=CH₂), 5.81 (m, 1 H, C=CH₂); **¹³C NMR** (CDCl₃) δ [ppm]: 139.0 (q, ²J_{C-F} = 30.0 Hz, H₂C=CCF₃), 133.6 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 127.4 (C_{Ar}), 123.4 (q, ¹J_{C-F} = 273.9 Hz, H₂C=CCF₃), 120.4 (q, ³J_{C-F} = 5.8 Hz, H₂C=CCF₃); **¹⁹F NMR** (CDCl₃) δ [ppm]: -65.3 (s, 3F, CF₃); **HRMS** (CI): m/z [M⁺] calcd for C₉H₇F₃: 172.0500, found 172.0504.

2. Spectroscopic characterization of poly(α -fluoromethylstyrene-*co*-styrene) copolymers

2.1. Description of ST and FMST monomers ^1H NMR spectra presented in Figure 1 (main manuscript)

The ^1H NMR spectrum of ST (–) exhibited signals at 5.46, 5.97 and 6.94 ppm with multiplicity of doublet of doublets assigned to vinyl protons H_2 , H_3 and H_1 , respectively and characteristic multiplets attributed to aromatic protons of monosubstituted benzene ring could have been observed at 7.45, 7.52 and 7.62 ppm. In that of FMST (–), the characteristic doublet at 5.26 ppm (coupling constant of 47.1 Hz) attributed to $-\text{CH}_2\text{F}$ group was observed (H_1), beside similar chemical shifts for vinyl protons H_2 and H_3 (centered at 5.43 and 5.61 ppm), as well as for aromatic protons at 7.35 and 7.46 ppm.

2.2. ^1H NMR spectra of poly(FMST-*co*-ST) copolymers

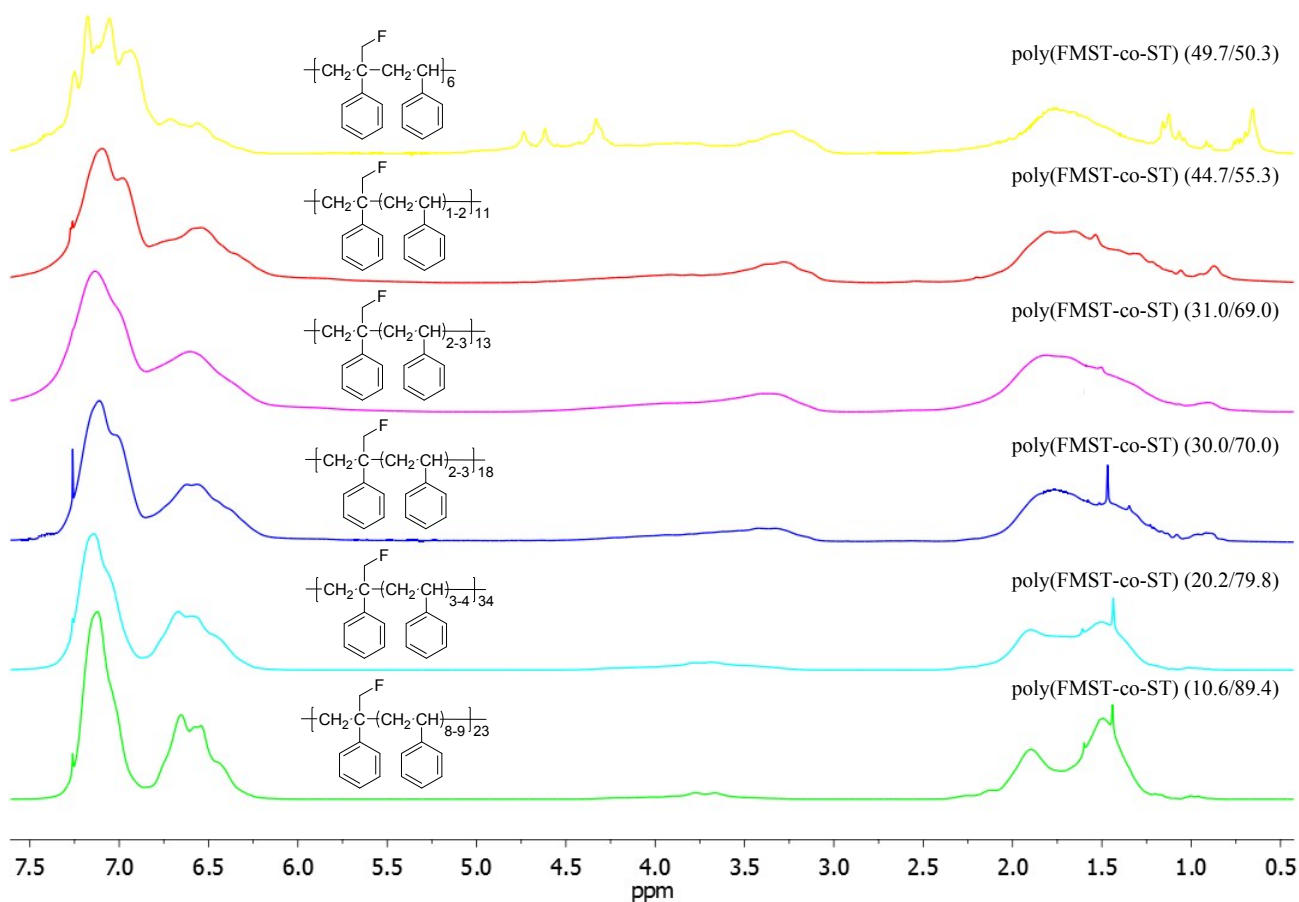


Figure S1. Stack of ^1H NMR spectra (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymers with decreasing content of FMST comonomer units in polymer structure.

2.3. ^{19}F NMR spectra of poly(FMST-*co*-ST) copolymers

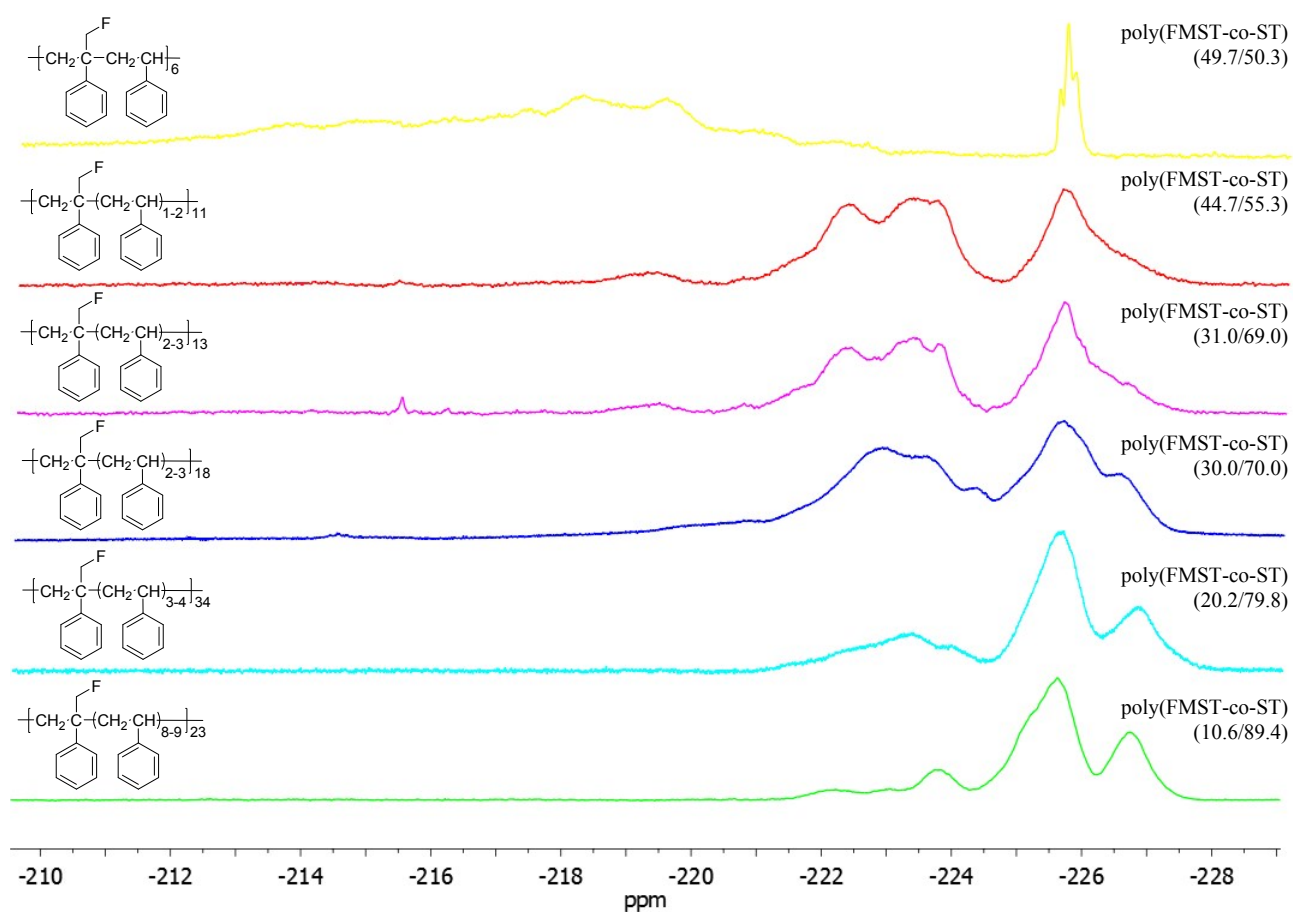


Figure S2. Stack of ^{19}F NMR spectra (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymers with decreasing content of FMST comonomer units in polymer structure.

2.4. Determination of comonomer content in poly(FMST-*co*-ST) obtained in bulk radical copolymerizations of FMST with ST

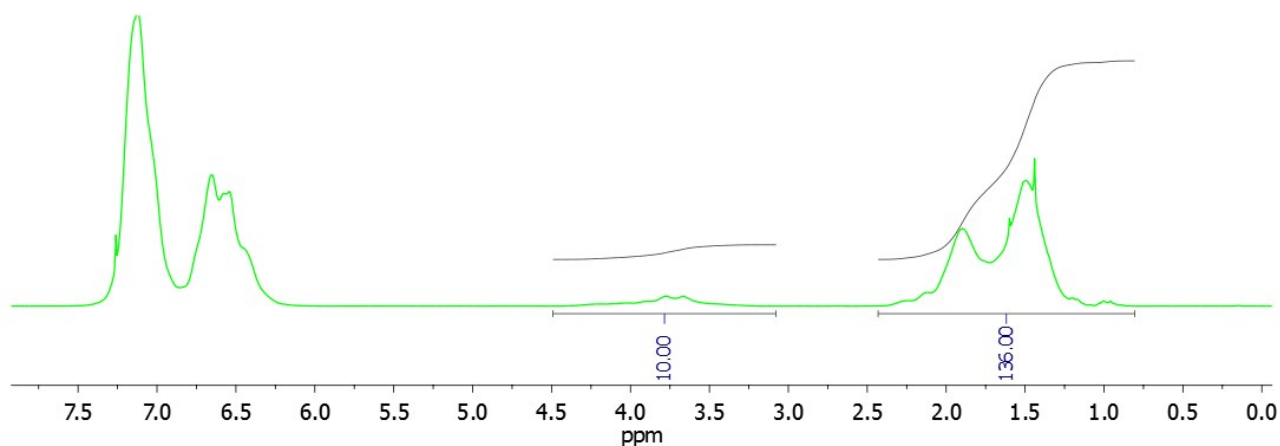


Figure S3. ^1H NMR spectrum (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymer (10.6/89.4, $M_n = 23700 \text{ g}\cdot\text{mol}^{-1}$)

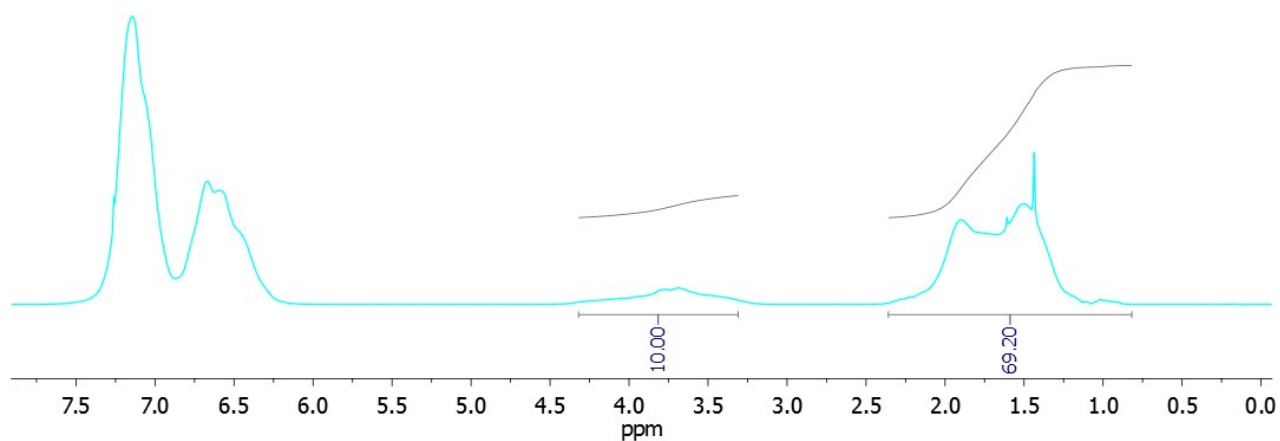


Figure S4. ^1H NMR spectrum (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymer (20.2/79.8, $M_n = 18900 \text{ g}\cdot\text{mol}^{-1}$)

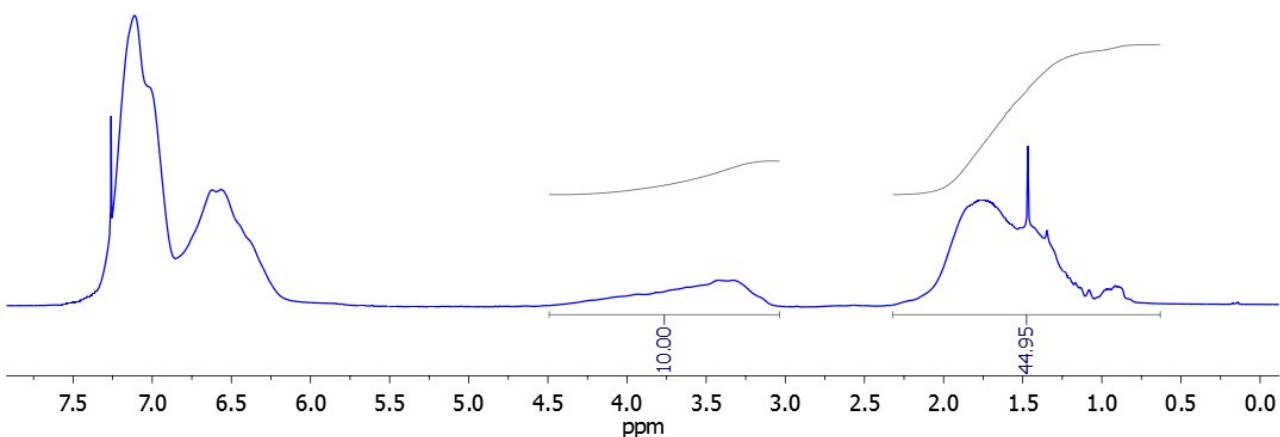


Figure S5. ^1H NMR spectrum (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymer (30.0/70.0, $M_n = 6600 \text{ g}\cdot\text{mol}^{-1}$)

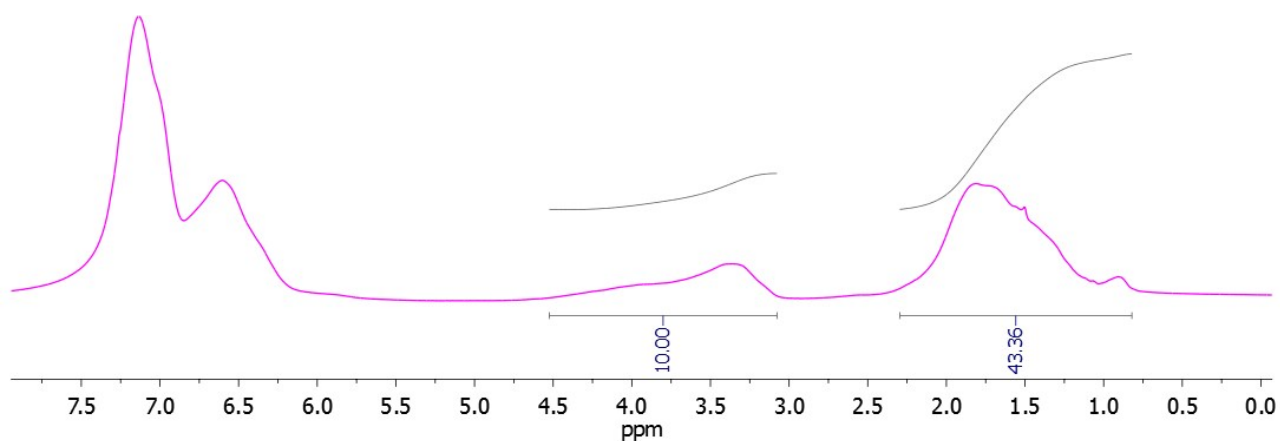


Figure S6. ^1H NMR spectrum (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymer (31.0/69.0, $M_n = 4800 \text{ g}\cdot\text{mol}^{-1}$)

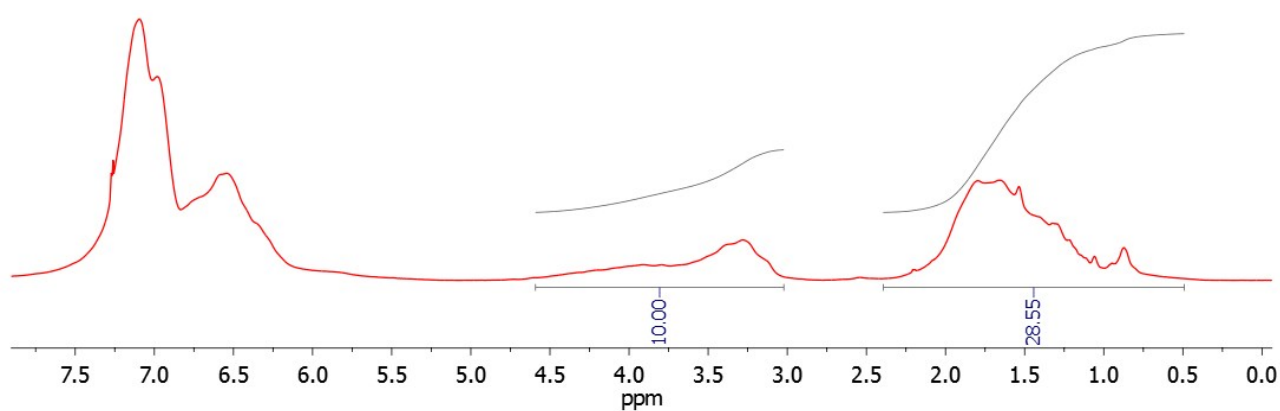


Figure S7. ^1H NMR spectrum (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymer (44.7/55.3, $M_n = 2900 \text{ g}\cdot\text{mol}^{-1}$)

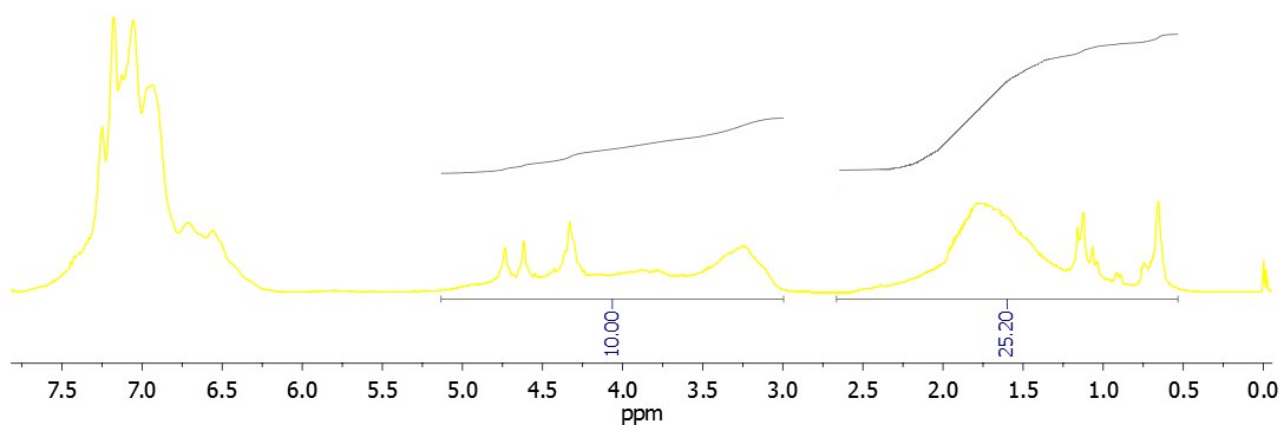


Figure S8. ^1H NMR spectrum (recorded in CDCl_3) of poly(FMST-*co*-ST) copolymer (49.7/50.3, $M_n = 1500 \text{ g}\cdot\text{mol}^{-1}$)

Table S1. Determination of copolymer composition in poly(FMST-*co*-ST) copolymers

$I_{A,B,B'}$	$I_{A'}$	% _{FMST} / % _{ST}	% _{FMST}	% _{ST}	M_n [g mol ⁻¹]
136.00	10.00	0.1190	10.6	89.4	23700
69.20	10.00	0.2534	20.2	79.8	18900
44.95	10.00	0.4292	30.0	70.0	6600
43.36	10.00	0.4496	31.0	69.9	4800
28.55	10.00	0.8086	44.7	55.3	2900
25.20	10.00	0.9868	49.7	50.3	1500

Mol% of ST in the copolymer $\%_{ST} = [(I_{A,B,B'} - I_{A'})/3] / \{[(I_{A,B,B'} - I_{A'})/3] + (I_{A'}/2)\}$

Mol% of FMST in the copolymer $\%_{FMST} = (I_{A'}/2) / \{[(I_{A,B,B'} - I_{A'})/3] + (I_{A'}/2)\}$

where $I_{A,B,B'}$ and $I_{A'}$ stands for the integrals of signals centered at 1.72 and 3.75 ppm, respectively.

3. Spectroscopic characterization of poly(α -trifluoromethylstyrene-*co*-styrene) copolymers

3.1. Description of ST, TFMST monomers and poly(TFMST-*co*-ST) copolymer ^1H NMR spectra presented in Figure 2 (main manuscript)

The ^1H NMR spectrum of ST (–) exhibits signals at 5.46, 5.97 and 6.94 ppm with multiplicity of doublet of doublets assigned to vinyl protons H_2 , H_3 and H_1 , respectively, and characteristic multiplets attributed to aromatic protons of monosubstituted benzene ring could have been observed at 7.45, 7.52 and 7.62 ppm. Similarly, in ^1H NMR spectrum of TFMST (–), the characteristic chemical shifts for H_2 and H_3 vinyl protons are observed at 5.81 and 6.01 ppm, respectively, while those of aromatic protons at 7.44 and 7.52 ppm. The ^1H NMR spectrum of poly(TFMST-*co*-ST) copolymer (–) displays broad signals centered at 1.75 and 6.95 ppm attributed to secondary and tertiary aliphatic protons of TFMST and ST units ($\text{H}_{\text{B}''}$, H_{B} , and H_{A}) and aromatic ones of ST and TFMST copolymer units (H_{C} , H_{D} , H_{E} , $\text{H}_{\text{C}''}$, $\text{H}_{\text{D}''}$, and $\text{H}_{\text{E}''}$), respectively. Most probably, due to the absence of unsaturated vinyl systems, signals of aromatic protons in copolymer were high field shifted to 6.95 ppm in comparison to H_{Ar} multiplets at 7.45, 7.52, 7.62 and 7.44, 7.52 ppm noted in spectra of ST and TFMST monomers, respectively. ^{19}F NMR spectrum of TFMST monomer (–) exhibited characteristic singlet at -65.3 ppm assigned to isolated $-\text{CF}_3$ moiety of TFMST monomer, whereas that of poly(TFMST-*co*-ST) copolymer (–) shows a broad multiplet centered at -65.5 ppm attributed to trifluoromethyl side group of TFMST monomer unit.

3.2. ^1H NMR spectra of poly(FMST-*co*-ST) copolymers

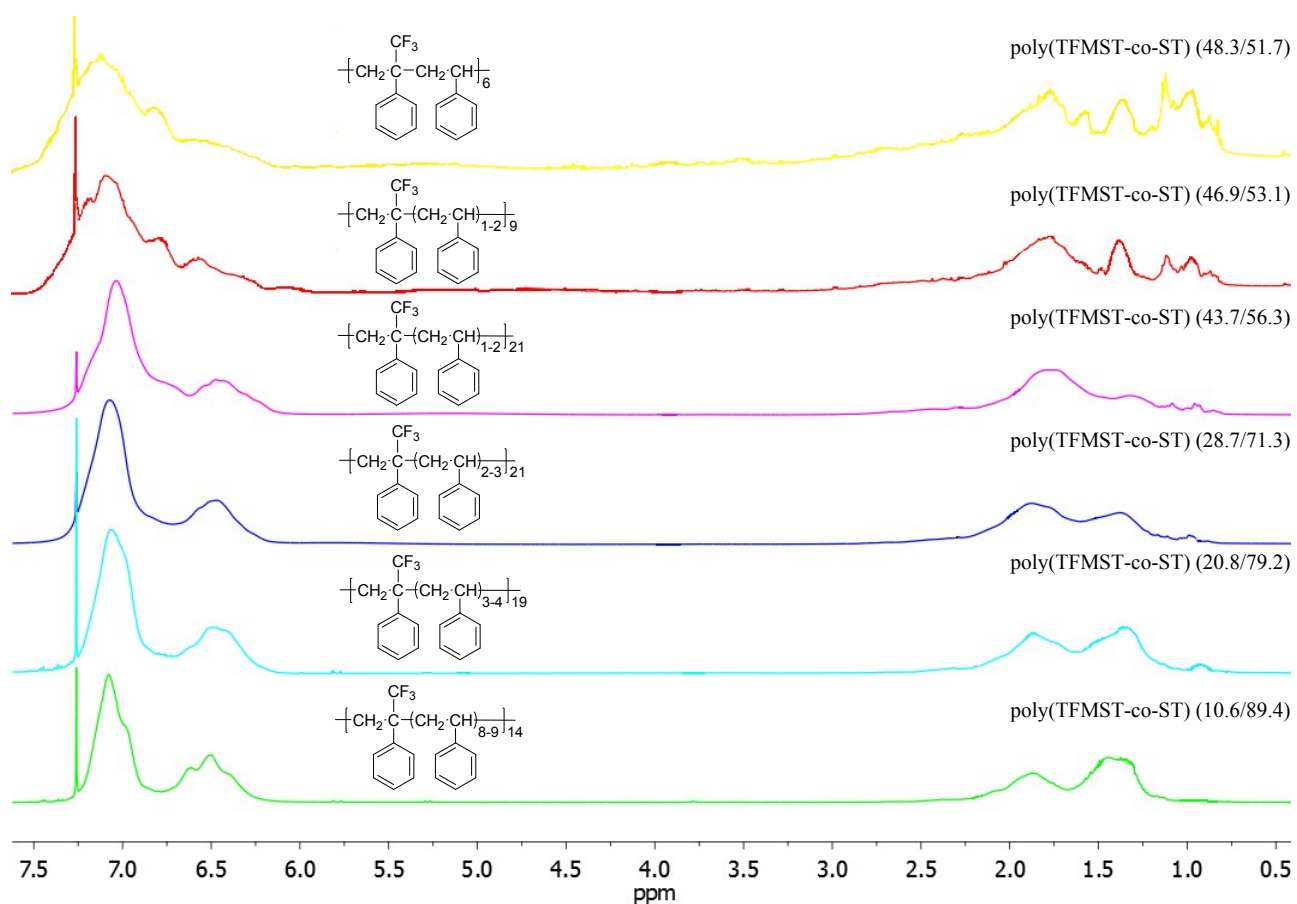


Figure S9. Stack of ^1H NMR spectra (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymers with decreasing content of TFMST comonomer units in polymer structure.

3.3. ^{19}F NMR spectra of poly(FMST-*co*-ST) copolymers

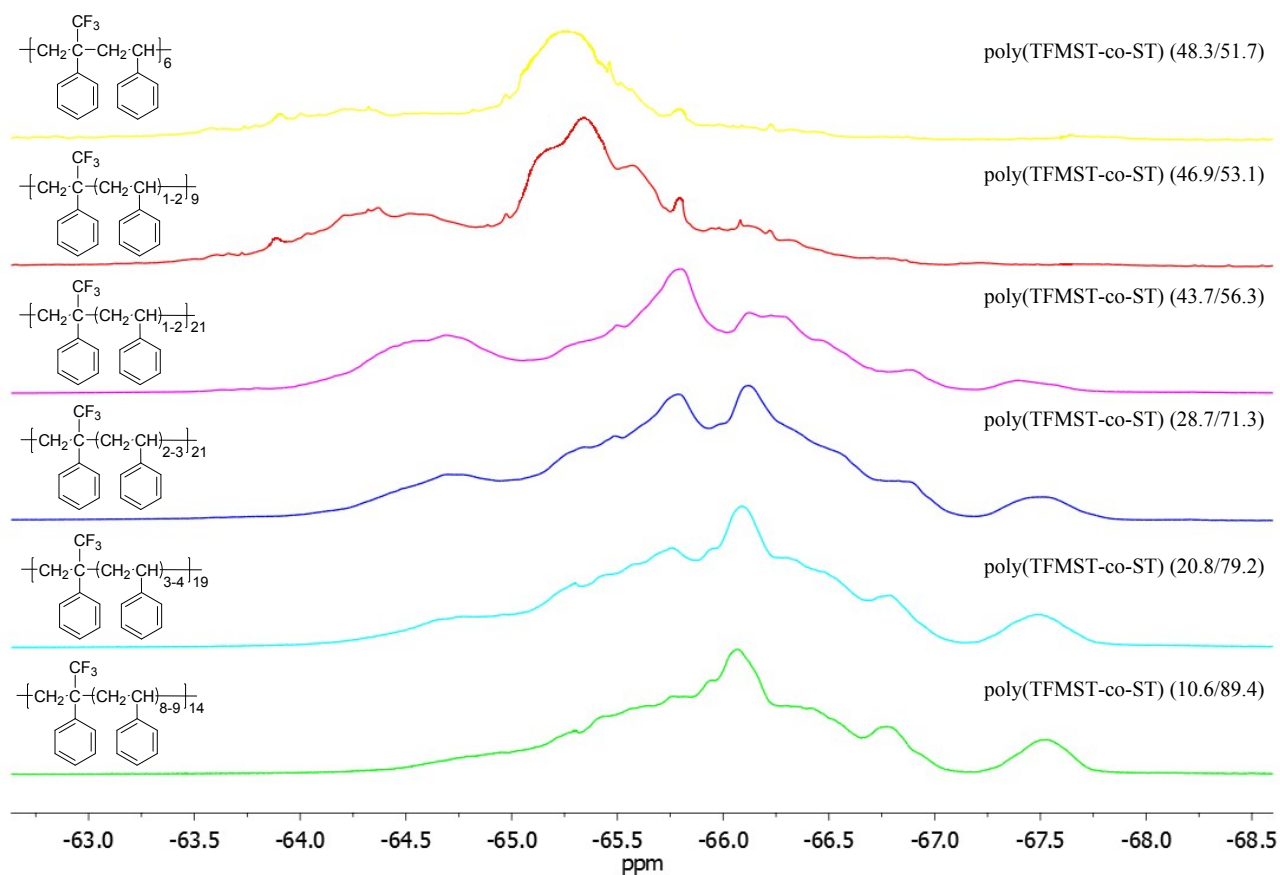


Figure S10. Stack of ^{19}F NMR spectra (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymers with decreasing content of FMST comonomer units in polymer structure.

3.4. Determination of comonomer content in poly(TFMST-*co*-ST) obtained in bulk radical copolymerizations of TFMST with ST

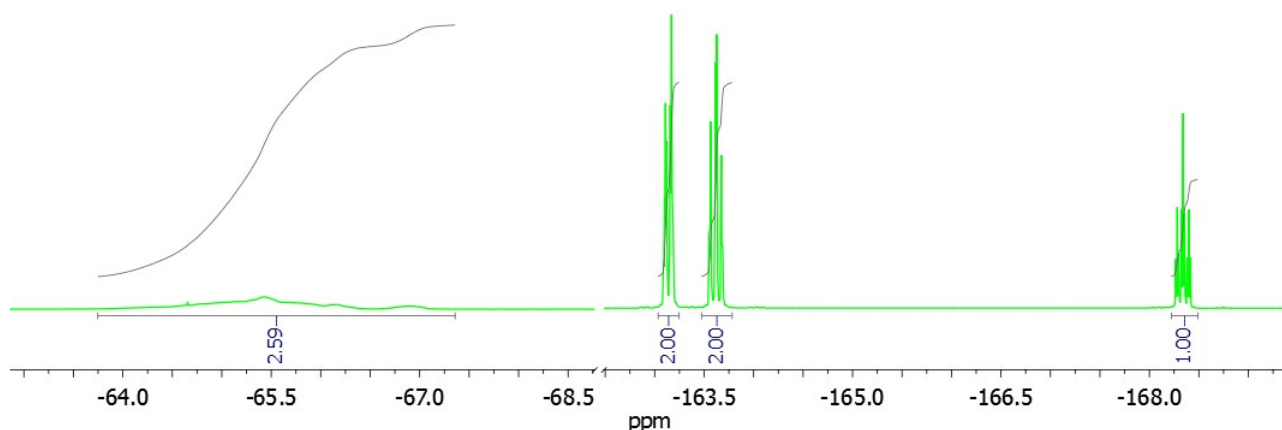


Figure S11. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymer (10.6/89.4, $M_n = 14600 \text{ g}\cdot\text{mol}^{-1}$) with pentafluorophenol (PFPhOH) as internal standard.

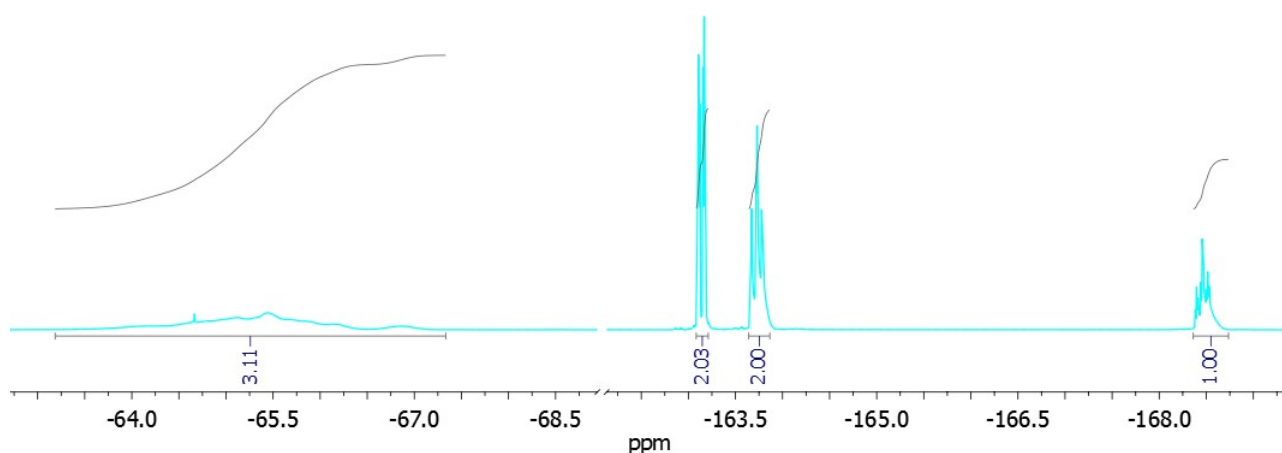


Figure S12. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymer (20.8/79.2, $M_n = 10800 \text{ g}\cdot\text{mol}^{-1}$) with pentafluorophenol (PFPhOH) as internal standard.

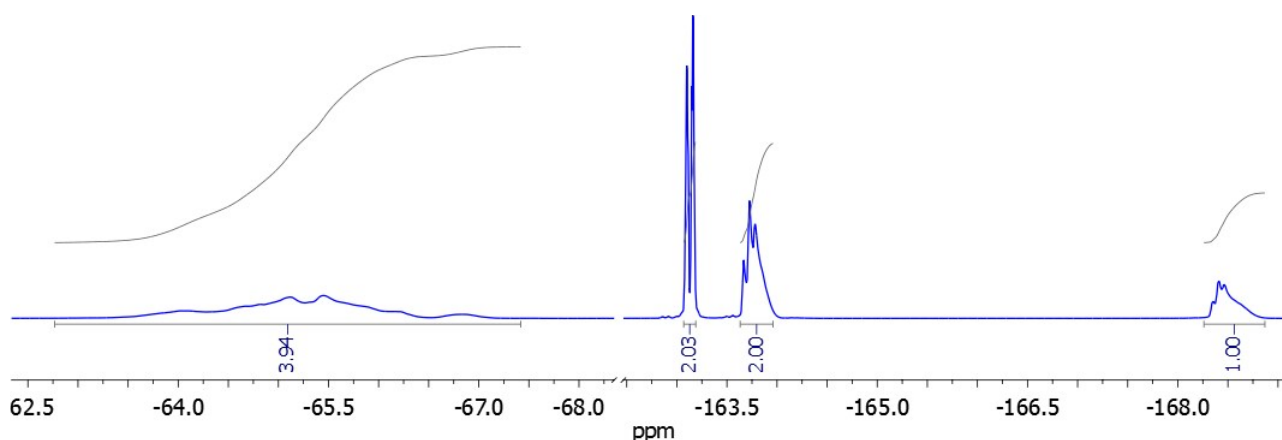


Figure S13. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymer (28.1/71.3, $M_n = 8900 \text{ g}\cdot\text{mol}^{-1}$) with pentafluorophenol (PFPhOH) as internal standard.

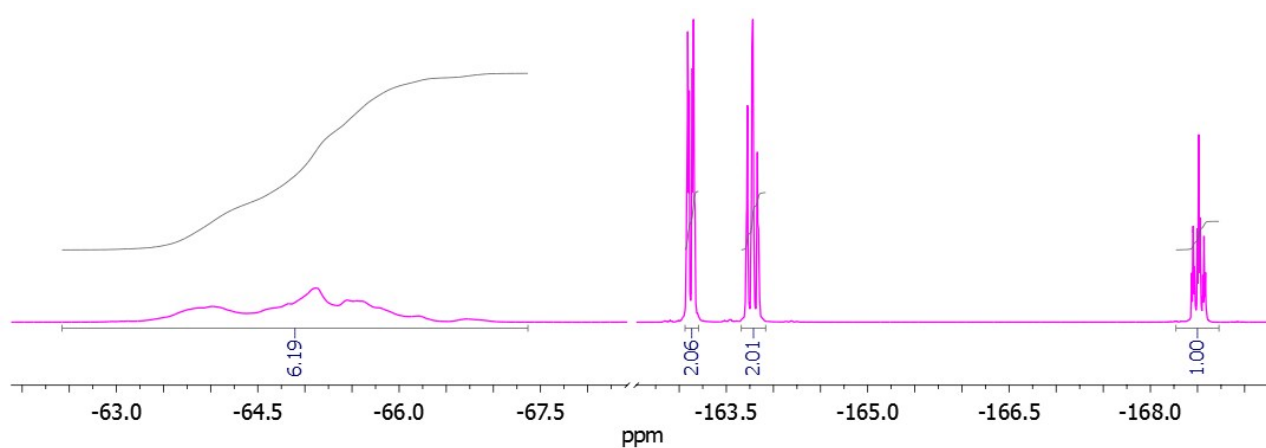


Figure S14. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymer (43.7/56.3, $M_n = 6500 \text{ g}\cdot\text{mol}^{-1}$) with pentafluorophenol (PFPhOH) as internal standard.

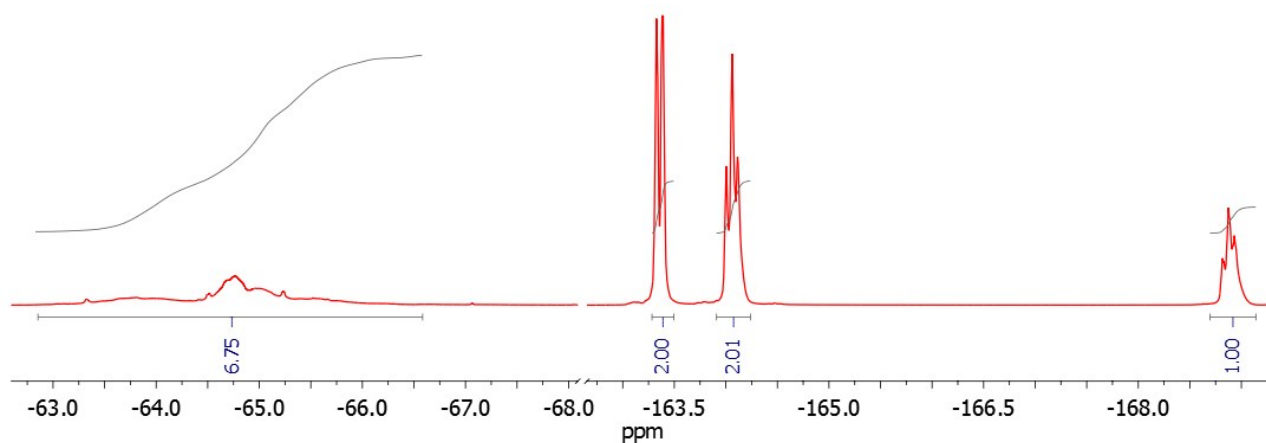


Figure S15. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymer (46.9/53.1, $M_n = 2600 \text{ g}\cdot\text{mol}^{-1}$) with pentafluorophenol (PFPhOH) as internal standard.

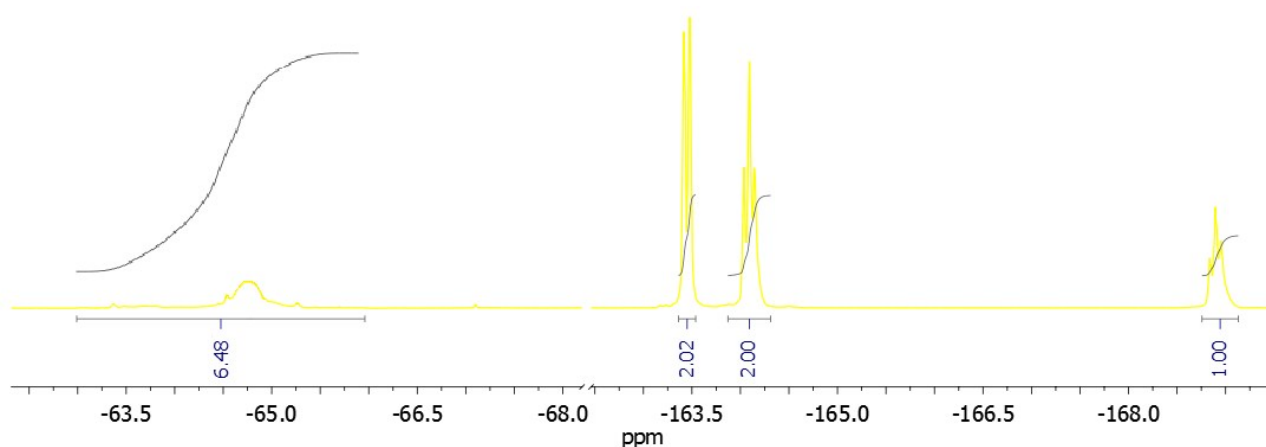


Figure S16. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*co*-ST) copolymer (48.3/51.7, $M_n = 1500 \text{ g}\cdot\text{mol}^{-1}$) with pentafluorophenol (PFPhOH) as internal standard.

Table S2. Determination of poly(TFMST-*co*-ST) copolymers composition.

I_{A^*}	I_{PFPhOH}	molar ratio ^a	n_{PFPhOH}^b [10 ⁻³ mol]	$m_{copolymer}^b$ [g]	n_{TFMST} [10 ⁻³ mol]	m_{TFMST} [g]	m_{ST} [g]	n_{ST} [10 ⁻³ mol]	%TFMST	%ST
2.59	5.00	0.863	0.16136	0.1463	0.13931	0.02398	0.12232	1.17444	10.6	89.4
3.11	5.03	1.040	0.20482	0.1208	0.21233	0.03655	0.08425	0.80891	20.8	79.2
3.94	5.03	1.313	0.21243	0.1202	0.27899	0.04803	0.07217	0.69296	28.7	71.3
6.19	5.07	2.063	0.17168	0.1085	0.35423	0.06098	0.04752	0.45625	43.7	56.3
6.75	5.01	2.253	0.17277	0.1129	0.38931	0.06702	0.04588	0.44052	46.9	53.1
6.48	5.02	2.160	0.17168	0.1052	0.37083	0.06384	0.04136	0.39714	48.3	51.7

^a Calculated based on ¹⁹F NMR analysis.

$$\text{Molar ratio} = (I_{A^*}/3)/(I_{PFPhOH}/5)$$

$$n_{TFMST} = \text{molar ratio} * n_{PFPhOH}$$

$$m_{ST} = m_{copolymer} - m_{TFMST}$$

$$m_{TFMST} = (n_{TFMST}/1000) * M_{TFMST}$$

$$n_{ST} = (m_{ST}/M_{ST}) * 1000$$

where n_{ST} , m_{ST} , M_{ST} (104.15 g·mol⁻¹), n_{TFMST} , m_{TFMST} , and M_{TFMST} (172.15 g·mol⁻¹) stand for moles, masses and molecular weight of styrene and α -trifluoromethylstyrene, respectively.

Mol% of ST in the copolymer

$$\%_{ST} = [n_{ST}/(n_{ST} + n_{TFMST})] * 100$$

Mol% of TFMST in the copolymer

$$\%_{TFMST} = [n_{TFMST}/(n_{ST} + n_{TFMST})] * 100$$

where n_{ST} and n_{TFMST} stands for the moles of styrene and α -trifluoromethylstyrene, respectively.

4. Determination of reactivity ratios of F-ST and ST by Fineman-Ross, Kelen-Tüdös and extended Kelen-Tüdös linear least squares methods

The **Fineman-Ross law**¹² (F-R) uses the following equation:

$$G = r_1H - r_2$$

With $G = x(X-1)/X$ and $H = x^2/X$.

Where, $x = f_1/f_2$ stands for the feed monomers composition,

$X = F_1/F_2$ stands for the copolymer composition.

When $r_1=0$, the equation simplifies to:

$$G = r_2H$$

With $G = (1-X)$ and $H = X/x$.

The **Kelen-Tüdös law**¹³ (K-T) uses the following equation:

$$\eta = (r_1+r_2/\alpha)\xi - r_2/\alpha$$

With $\eta = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$ and $\alpha = (H_{\min} \times H_{\max})^{1/2}$

And G and H defined by Fineman-Ross method (see above)

When $r_1=0$, the equation simplifies to:

$$\eta = r_2/\alpha(\xi-1)$$

With $\eta = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$ and $\alpha = (H_{\min} \times H_{\max})^{1/2}$

The **extended Kelen-Tüdös law**¹⁴ (EK-T) uses the following equation:

$$\eta = (r_1+r_2/\alpha)\xi - r_2/\alpha$$

With $\eta = z(X-1)/(\alpha z^2 + X)$ and $\xi = X/(\alpha z^2 + X)$ and $\alpha = (H_{\min} \times H_{\max})^{1/2}$

And $G = (X-1)/z$ and $H = X/z^2$

Where, $z = \log(1-\zeta_1)/\log(1-\zeta_2)$ stands for conversion-dependent value,

With $\zeta_2 = \zeta(1+x)/(1+X)$ and $\zeta_1 = (X/x)\zeta_2$

Where ζ_1 and ζ_2 are partial conversions of individual monomers, and while ζ stands for the experimental conversion given on the molar basis.

When $r_1=0$, the equation simplifies to:

$$\eta = r_2/\alpha(\xi-1)$$

With $\eta, \xi, \alpha, G, H, z, \zeta_1, \zeta_2$ defined as described above for the extended Kelen-Tüdös method

Table S3. Determination of (FMST;ST) and (TFMST;ST) reactivity ratios, at 70 °C, by, Finemann-Ross (F-R), Kelen-Tüdös (K-T) and extended Kelen-Tüdös (E-KT) linear least-squares methods.

Method	(FMST;ST)	(TFMST;ST)*
Finemann-Ross	$r_{\text{FMST}} = 0.05 \pm 0.02$	$r_{\text{TFMST}} = 0.00$
	$r_{\text{ST}} = 0.68 \pm 0.05$	$r_{\text{ST}} = 0.65 \pm 0.04$
Kelen-Tüdös	$r_{\text{FMST}} = 0.12 \pm 0.03$	$r_{\text{TFMST}} = 0.00$
	$r_{\text{ST}} = 0.75 \pm 0.03$	$r_{\text{ST}} = 0.65 \pm 0.01$
Extended Kelen-Tüdös	$r_{\text{FMST}} = 0.08 \pm 0.02$	$r_{\text{TFMST}} = 0.00$
	$r_{\text{ST}} = 0.72 \pm 0.04$	$r_{\text{ST}} = 0.64 \pm 0.01$

*calculated assuming that $r_{\text{TFMST}} = 0.00$, according to Ueda and Ito report¹⁵

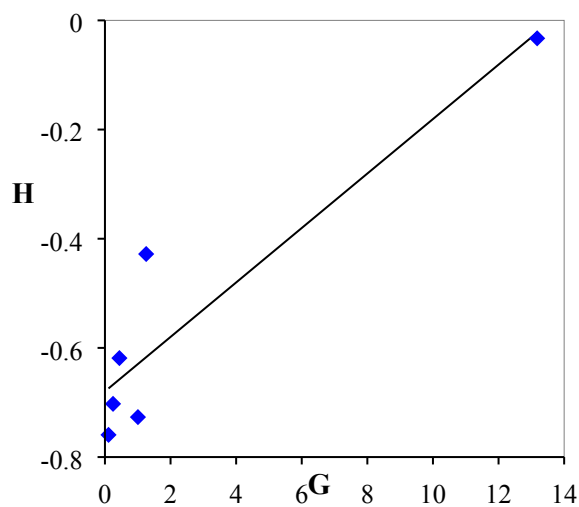


Figure S17. Fineman-Ross linear least-squares method for the determination of the reactivity ratios of FMST and ST.

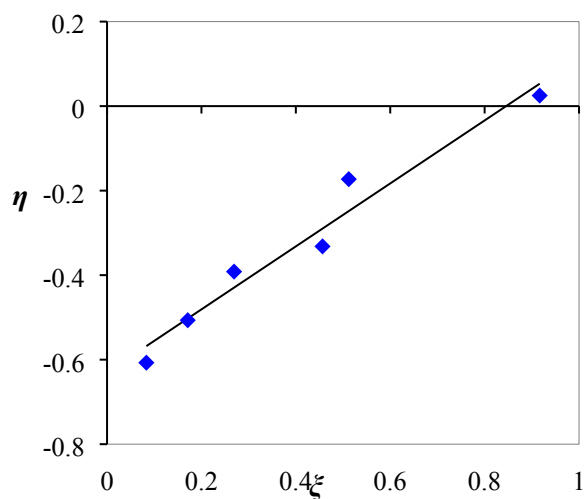


Figure S18. Kelen-Tüdös linear least-squares method for the determination of the reactivity ratios of FMST and ST.

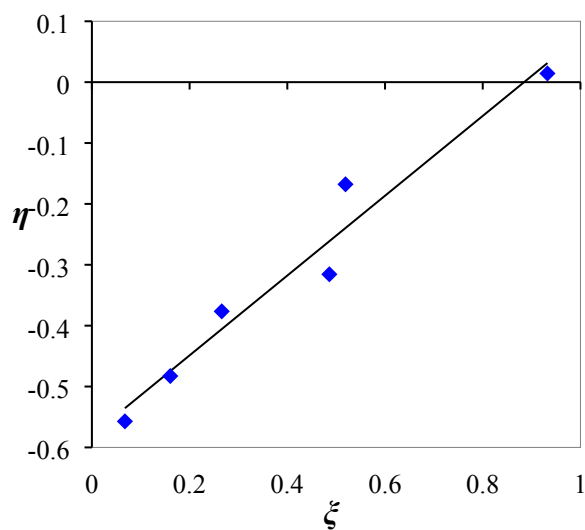


Figure S19. Extended Kelen-Tüdös linear least-squares method for the determination of the reactivity ratios of FMST and ST.

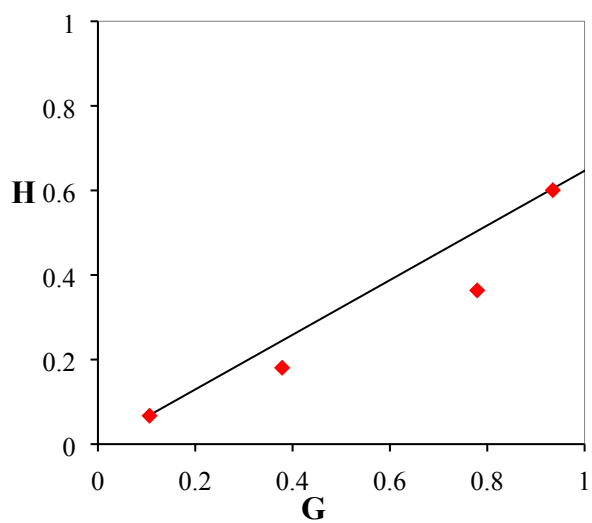


Figure S20. Fineman-Ross linear least-squares method for the determination of the reactivity ratios of TFMST and ST (when $r_1 = 0$).

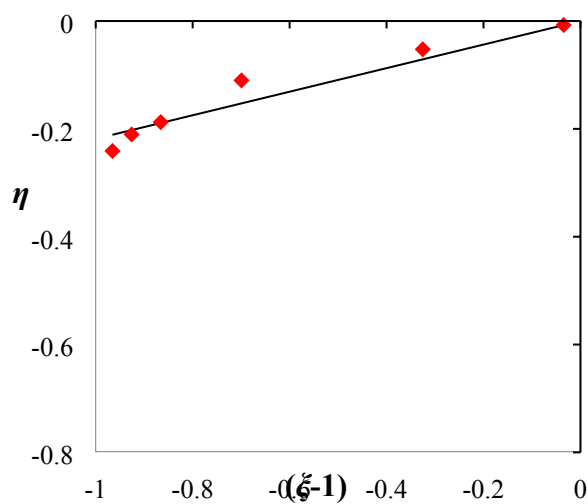


Figure S21. Kelen-Tüdös linear least-squares method for the determination of the reactivity ratios of TFMST and ST (when $r_1 = 0$).

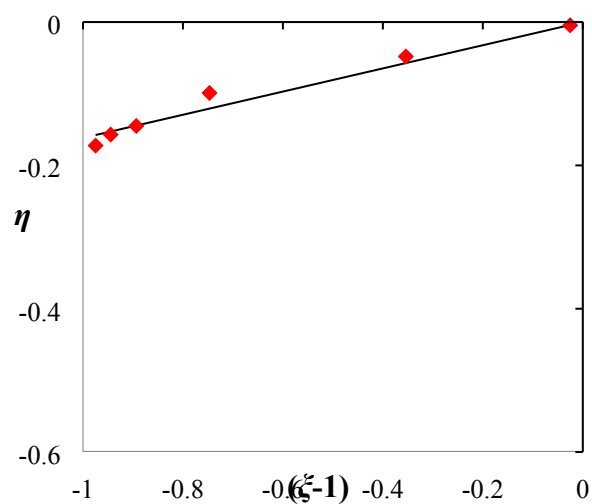


Figure S22. Extended Kelen-Tüdös linear least-squares method for the determination the reactivity ratios of TFMST and ST (when $r_1 = 0$).

The EK-T method was selected for determination of reactivity ratio values due to its applicability for systems with high level of conversions.

5. Spectroscopic characterization of poly(α -trifluoromethylstyrene-*ter*-styrene-*ter*- α -fluoromethylstyrene) terpolymers

5.1. Description of ST, FMST, TFMST monomers and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers ^1H NMR spectra presented in Figure 5 (main manuscript)

The comparison of ^1H NMR spectra of ST, FMST and TFMST monomers with poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers of different fluorinated base unit compositions 14.5/80.3/5.2 mol% and 3.7/57.9/38.4 mol% is illustrated in Figure 5 of MS. As discussed above, ^1H NMR spectrum of styrene (ST –, Figure 5) exhibited signals at 5.46, 5.97 and 6.94 ppm with multiplicity of doublet of doublets assigned to vinyl protons H_2 , H_3 and H_1 , respectively and characteristic multiplets attributed to aromatic protons of monosubstituted benzene ring could have been observed at 7.45, 7.52 and 7.62 ppm. Whereas, in ^1H NMR spectra of α -trifluoromethylstyrene (TFMST –, Figure 5) and α -fluoromethylstyrene (FMST –, Figure 5) were observed characteristic chemical shifts for vinyl protons H_2 , H_3 at 5.81, 6.01 and 5.43, 5.61 ppm, respectively, as well as for aromatic protons at 7.44, 7.52 and 7.35, 7.46 ppm, respectively. Additionally, in ^1H NMR spectrum of α -fluoromethylstyrene (FMST –, Figure 5) the characteristic doublet at 5.26 ppm with coupling constant of 47.1 Hz attributed to $-\text{CH}_2\text{F}$ group was observed (H_1).

^1H NMR spectra of all poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers (poly(TFMST-*ter*-ST-*ter*-FMST) 14.5/80.3/5.2 –, poly(TFMST-*ter*-ST-*ter*-FMST) 3.7/57.9/38.4 –, Figure 5, see also Figure S23 in Supporting Information) exhibited broad signals centered at 1.72, 3.75 and 6.88 ppm attributed to secondary and tertiary aliphatic backbone protons of all three base units (H_A , H_B , $\text{H}_{B'}$, $\text{H}_{B''}$), side chain primary protons of fluoromethyl group of FMST ($\text{H}_{A'}$) and aromatic protons of ST and FMST or TFMST termonomer units (H_{C-E} , $\text{H}_{C'-E'}$, $\text{H}_{C''-E''}$), respectively. However, the intensity of signals attributed to $-\text{CH}_2\text{F}$ moiety depends on the FMST content incorporated in polymeric chain. Furthermore, most probably due to the absence of vinyl moieties, signals of aromatic protons in

terpolymers were shifted down to 6.88 in comparison to H_{Ar} multiplets at 7.45, 7.52, 7.62 and 7.35, 7.46 or 7.44, 7.52 ppm observed in monomers spectra of ST and FMST or TFMST, respectively.

5.2. The comparison of ^{13}C NMR spectra of FMST and TFMST monomers with poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers

The comparison of ^{13}C NMR spectra of FMST and TFMST monomers with poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers of different fluorinated base unit compositions 14.5/80.3/5.2 mol% (–) and 3.7/57.9/38.4 mol% (–) is illustrated in Figure S23. ^{13}C NMR spectra of FMST (–) and TFMST (–) monomers show characteristic signals for aliphatic carbons C_1 bearing fluorine atom/s, i.e. a doublet located at 84.3 ppm ($^1J_{C-F}=169.0$ Hz) and quartet centered at 123.4 ppm ($^1J_{C-F}=273.9$ Hz) assigned to $-CH_2F$ and $-CF_3$ groups, respectively. Moreover, both spectra exhibit four singlets in the range of 125.9 to 137.3 ppm attributed to aromatic carbons (C_4-C_7), as well as signals characteristic for vinyl carbons C_3 , C_2 i.e. two doublets (FMST) at 115.3 ($^3J_{C-F}=10.6$ Hz), 143.0 ppm ($^2J_{C-F}=14.4$ Hz) and two quartets (TFMST) at 120.4 ($^3J_{C-F}=5.8$ Hz) and 139.0 ppm ($^2J_{C-F}=30.0$ Hz). The ^{13}C NMR spectra of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers show expected multiplets between 36.1 and 48.9 ppm corresponding to secondary and tertiary aliphatic carbons (C_A , C_B , $C_{B'}$, $C_{B''}$) of ST, FMST and TFMST units, respectively, as well as multiplets located in the range of 124.7 to 128.9 ppm and centered at 145.5, 142.3 or 137.1 ppm assigned to tertiary (C_{C-E} , $C_{C'-E'}$, $C_{C''-E''}$) and quaternary aromatic carbons (C_F , $C_{F'}$, $C_{F''}$) of ST, FMST and TFMST units, respectively. Additionally, the spectra of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers with high content of TFMST units (–) exhibit characteristic multiplet at 52.4 ppm and practically unnoticeable very broad quartet ($^1J_{C-F}\approx 280$ Hz) at 128.2 ppm attributed to quaternary aliphatic carbon $C_{G''}$ and CF_3 group of TFMST units, respectively. On the other hand, the spectra of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers with high content of FMST units (–) show characteristic multiplet at 49.8 ppm and broad doublet ($^1J_{C-F}\approx 167$ Hz) at 82.4 ppm assigned to quaternary aliphatic carbon $C_{G'}$ and CH_2F moiety of FMST units, respectively.

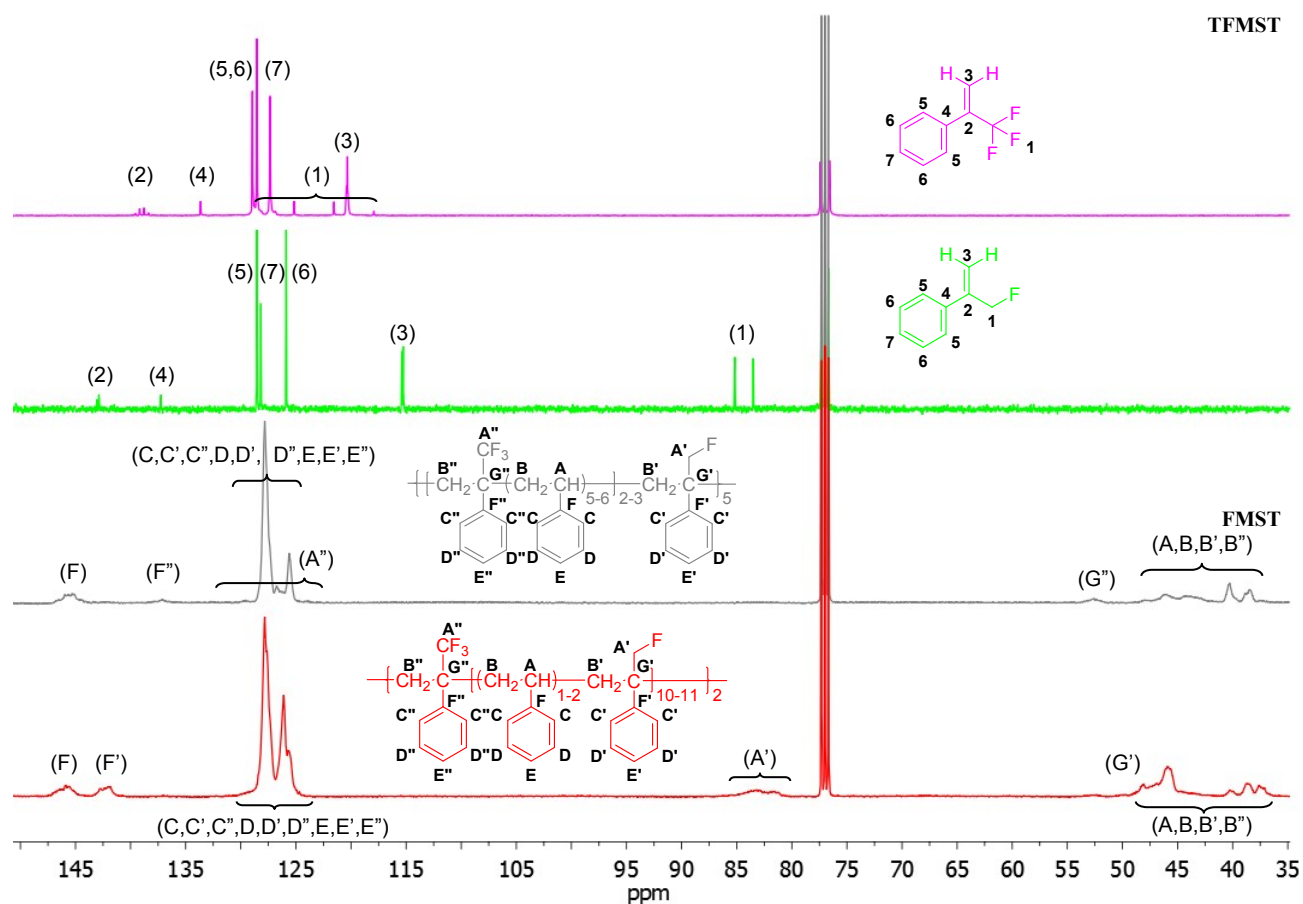


Figure S23. Comparison of ^{13}C NMR spectra (recorded in CDCl_3) of fluorinated monomers: (–) α -trifluoromethylstyrene (TFMST), (–) α -fluoromethylstyrene (FMST), and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers: (–) poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (14.5/80.3/5.2, $M_n = 10,700 \text{ g mol}^{-1}$, Table 1, Entry 13), (–) ^{13}C NMR spectrum of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (3.7/57.9/38.4, $M_n = 6,900 \text{ g mol}^{-1}$, Table 1, Entry 18).

5.3. The comparison of ^{19}F NMR spectra of FMST and TFMST monomers with poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers

The comparison of ^{19}F NMR spectra of FMST and TFMST monomers with poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers of different monomer unit compositions 14.5/80.3/5.2 mol% (–) and 3.7/57.9/38.4 mol% (–) is illustrated in Figure 7. ^{19}F NMR spectra of TFMST (–) and FMST (–) monomers exhibit characteristic signals, i.e. a singlet at -65.3 ppm assigned to isolated $-\text{CF}_3$ moiety

of TFMST and a triplet at -212.7 ppm with coupling constant of 47.1 Hz assigned to $-\text{CH}_2\text{F}$ moiety of FMST, respectively. ^{19}F NMR spectra of all poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers exhibit two broad multiplets at -65.0 and -225.5 ppm attributed to $-\text{CF}_3$ and $-\text{CH}_2\text{F}$ side groups tethered to the polymeric chain, respectively.

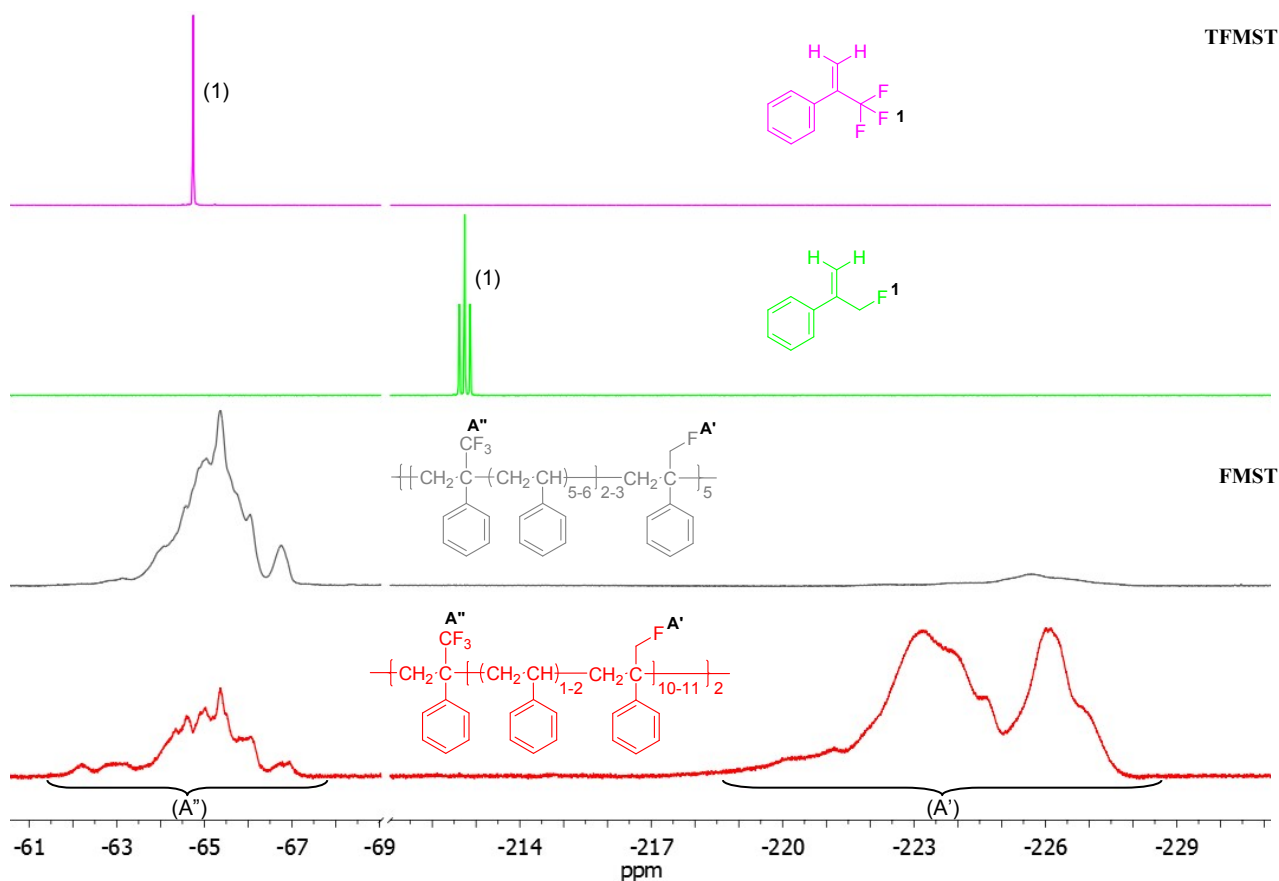


Figure S24. Comparison of ^{19}F NMR spectra (recorded in CDCl_3) of fluorinated monomers and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer: (–) ^{19}F NMR spectrum of α -trifluoromethylstyrene (TFMST), (–) ^{19}F NMR spectrum of α -fluoromethylstyrene (FMST), (–) ^{19}F NMR spectrum of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (14.5/80.3/5.2, $M_n = 10,700 \text{ g mol}^{-1}$, Table 1, Entry 13), (–) ^{19}F NMR spectrum of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (3.7/57.9/38.4, $M_n = 6,900 \text{ g mol}^{-1}$, Table 1, Entry 18).

5.4. ^1H NMR spectra of *poly*(TFMST-*ter*-ST-*ter*-FMST) terpolymers

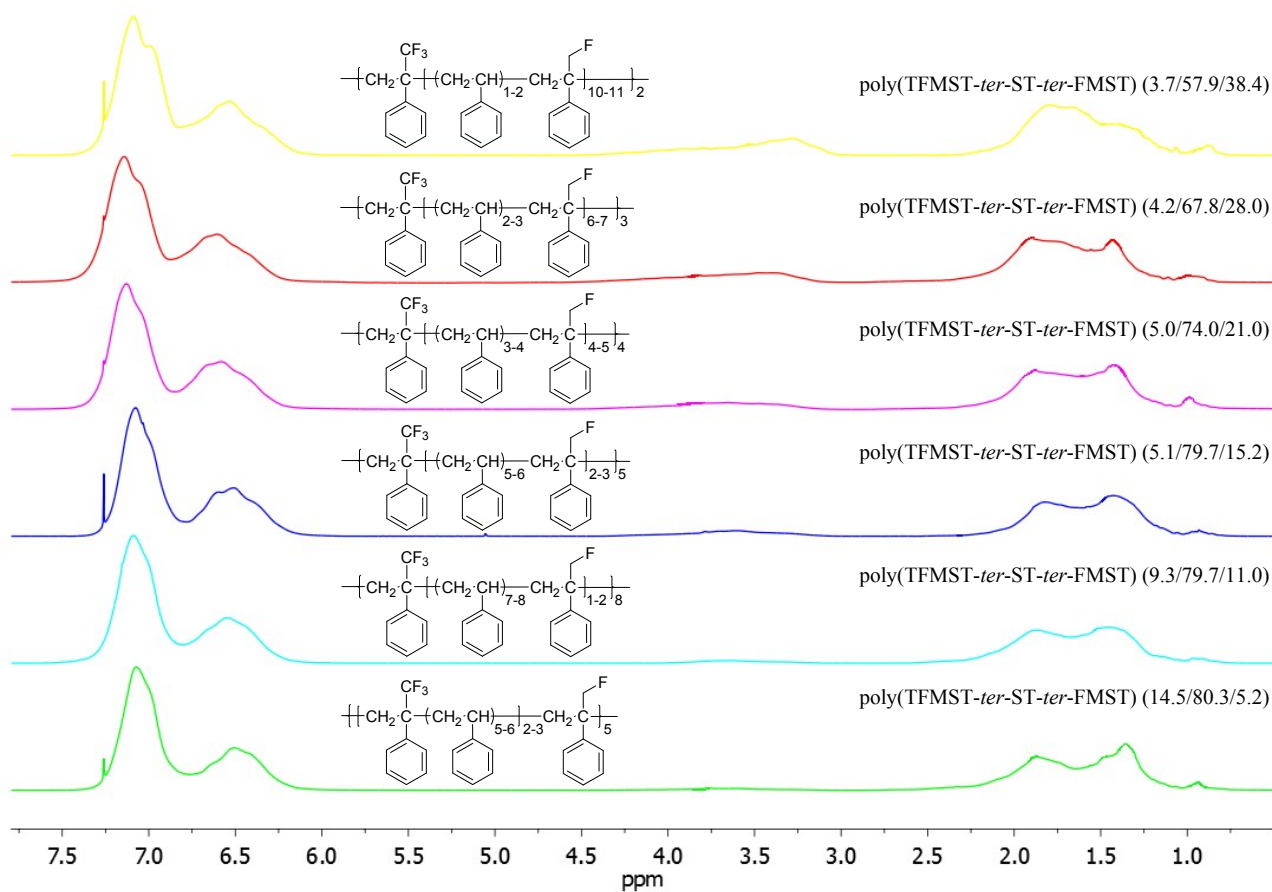


Figure S25. Comparison of ^1H NMR spectra (recorded in CDCl_3) of *poly*(TFMST-*ter*-ST-*ter*-FMST) terpolymers with decreasing content of F-ST comonomer units in polymer structure.

5.5. ^{13}C NMR spectra of *poly*(TFMST-*ter*-ST-*ter*-FMST) terpolymers

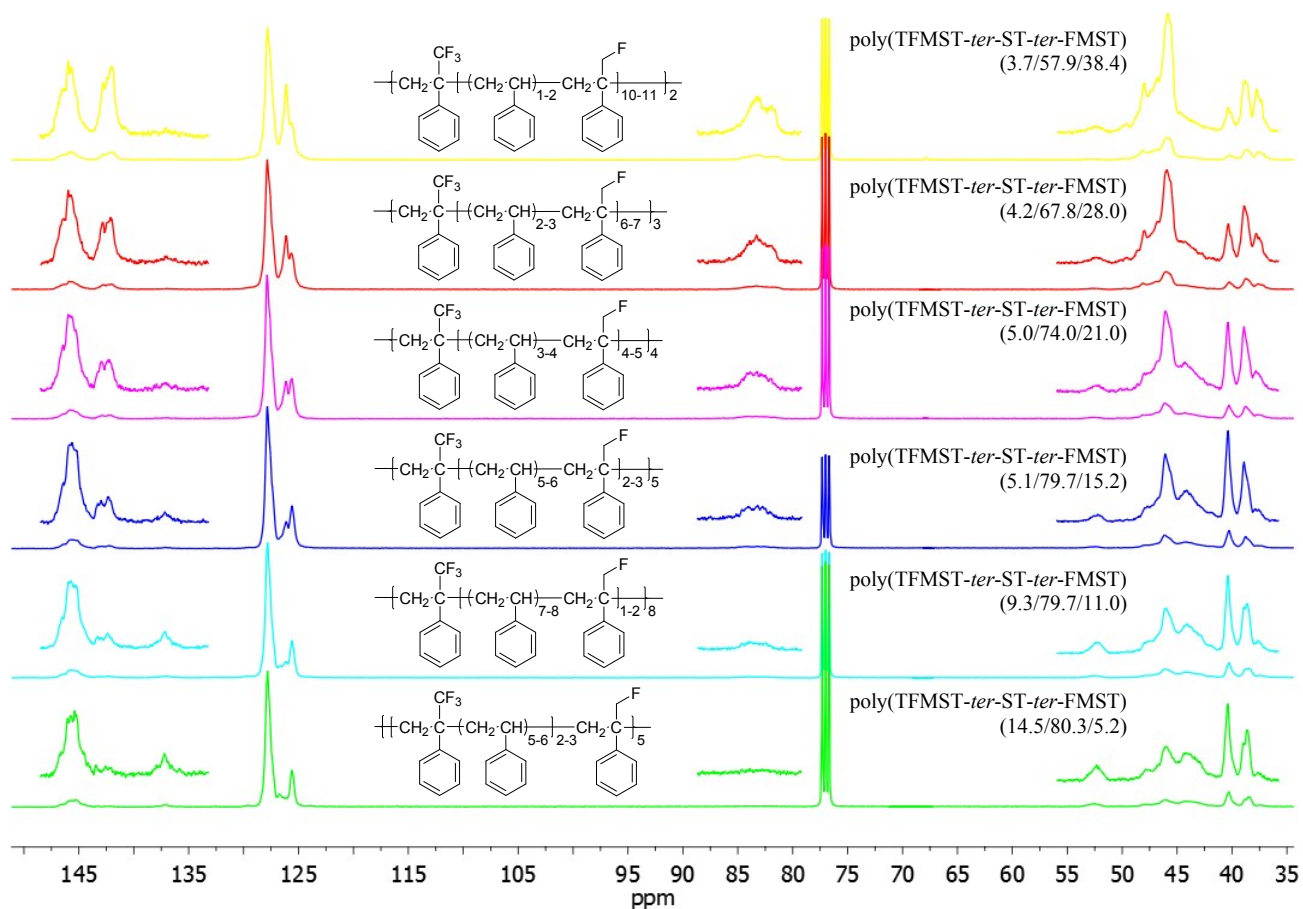


Figure S26. Comparison of ^{13}C NMR spectra (recorded in CDCl_3) of *poly*(TFMST-*ter*-ST-*ter*-FMST) terpolymers with decreasing content of F-ST comonomer units in polymer structure.

5.6. ^{19}F NMR spectra of *poly*(TFMST-*ter*-ST-*ter*-FMST) terpolymers

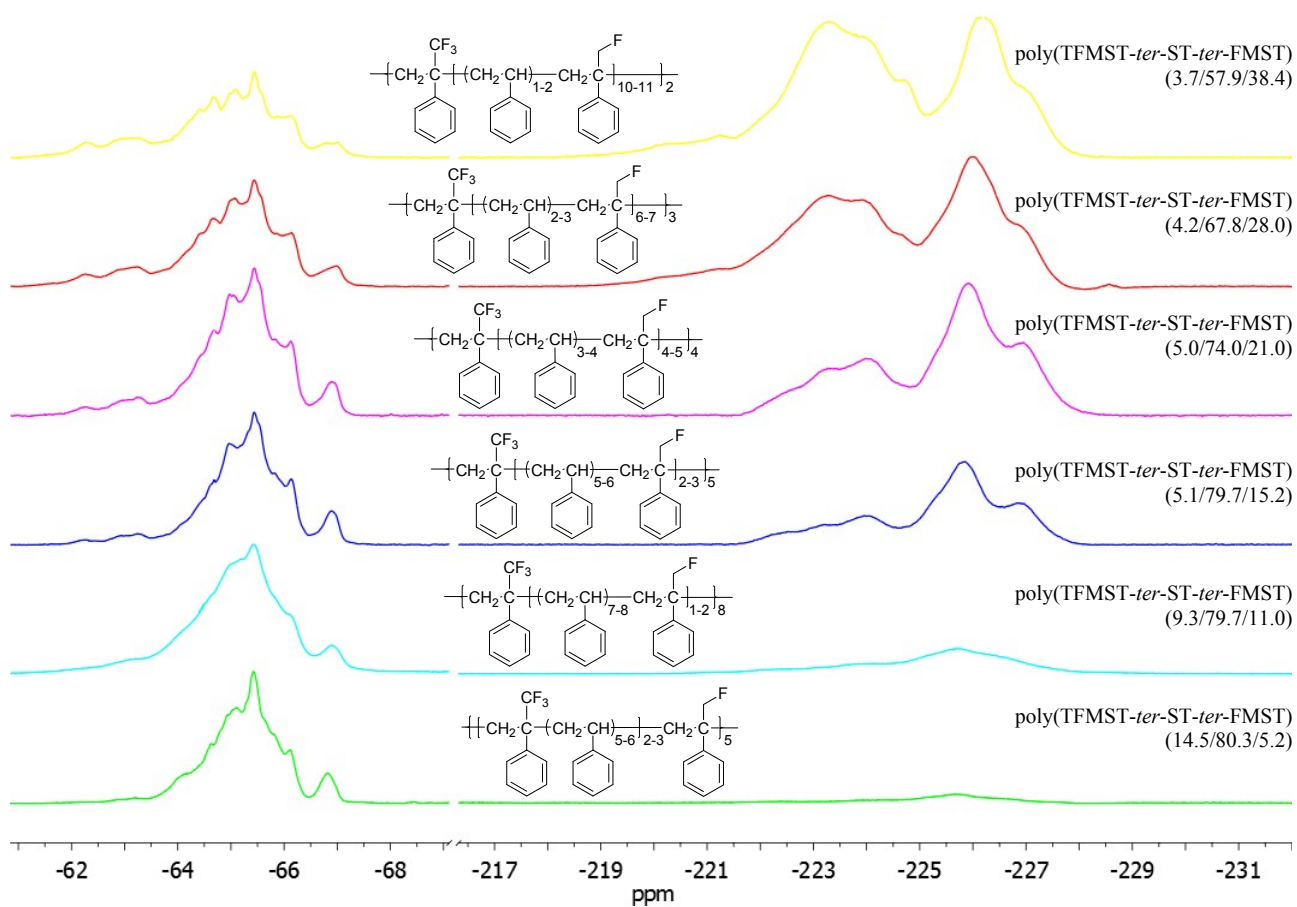


Figure S27. Comparison of ^{19}F NMR spectra (recorded in CDCl_3) of *poly*(TFMST-*ter*-ST-*ter*-FMST) terpolymers with decreasing content of F-ST comonomer units in polymer structure.

5.7. Determination of comonomer content in poly(TFMST-*ter*-ST-*ter*-FMST) termonomers obtained in bulk radical terpolymerizations of TFMST and FMST with ST

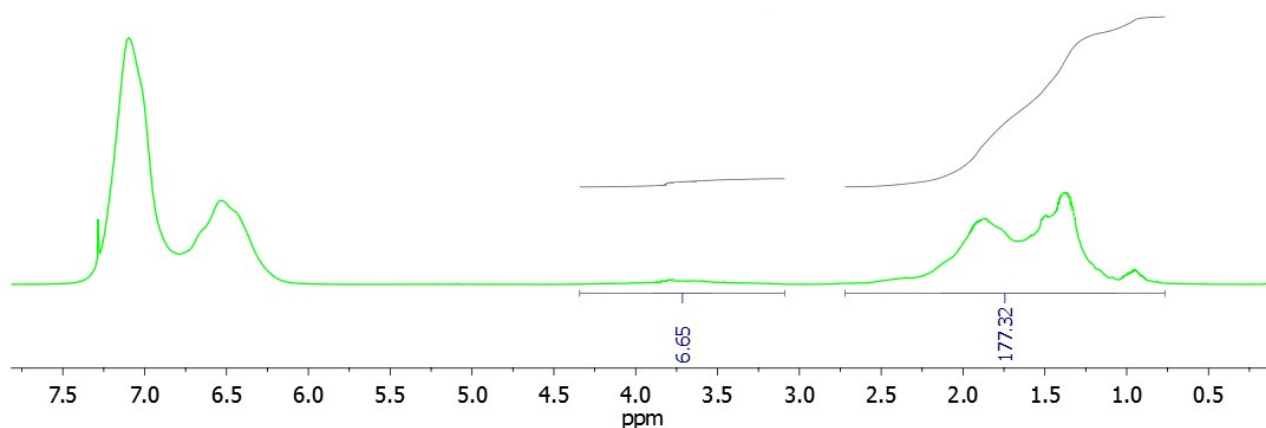


Figure S28. ¹H NMR spectrum (recorded in CDCl₃) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (14.5/80.3/5.2, $M_n = 10700 \text{ g}\cdot\text{mol}^{-1}$).

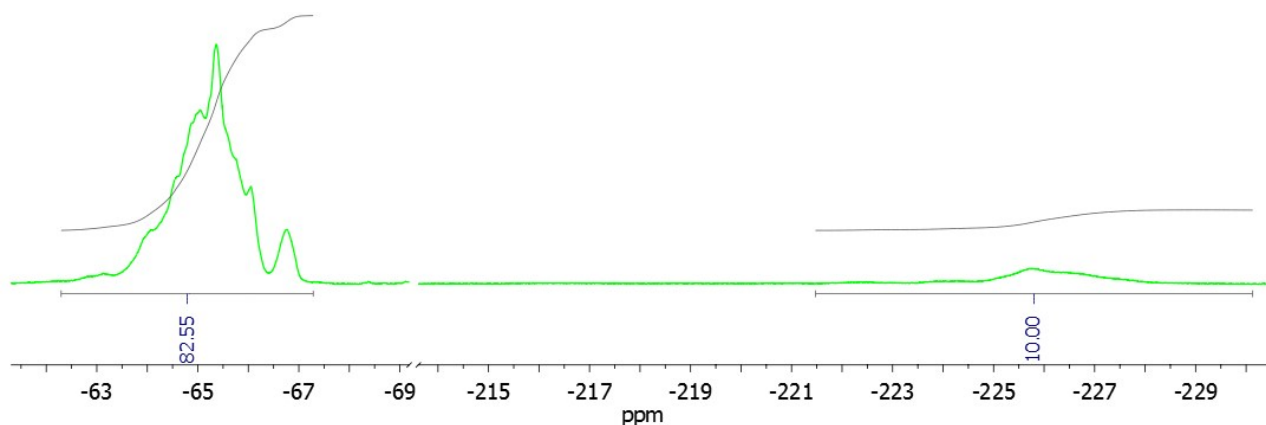


Figure S29. ¹⁹F NMR spectrum (recorded in CDCl₃) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (14.5/80.3/5.2, $M_n = 10700 \text{ g}\cdot\text{mol}^{-1}$).

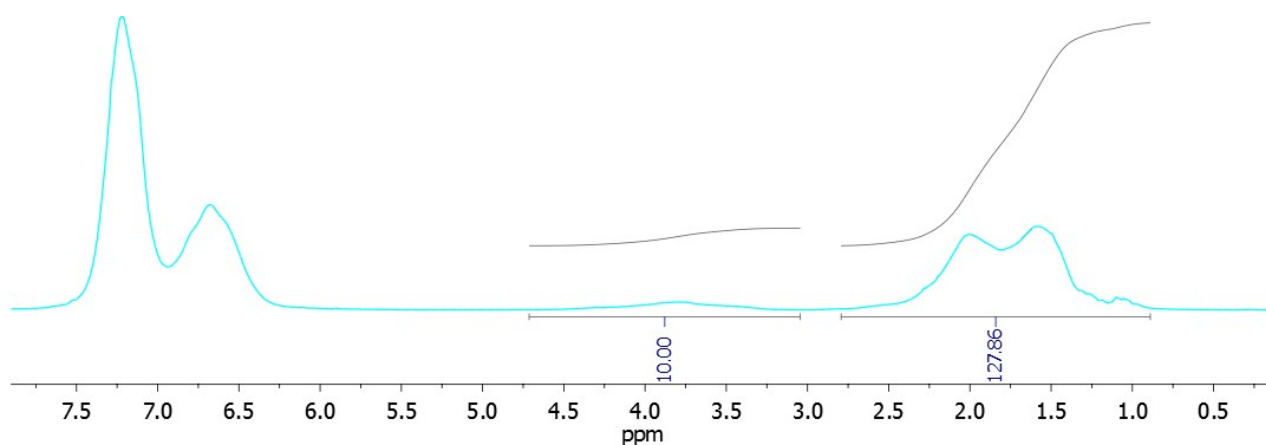


Figure S30. ¹H NMR spectrum (recorded in CDCl₃) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (9.3/79.7/11.0, $M_n = 9200 \text{ g}\cdot\text{mol}^{-1}$).

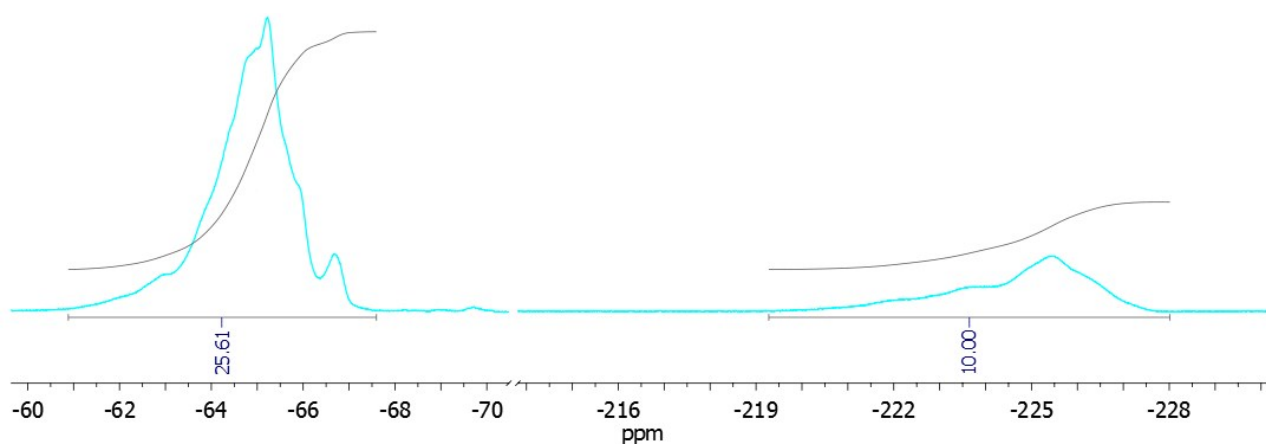


Figure S31. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (9.3/79.7/11.0, $M_n = 9200 \text{ g}\cdot\text{mol}^{-1}$).

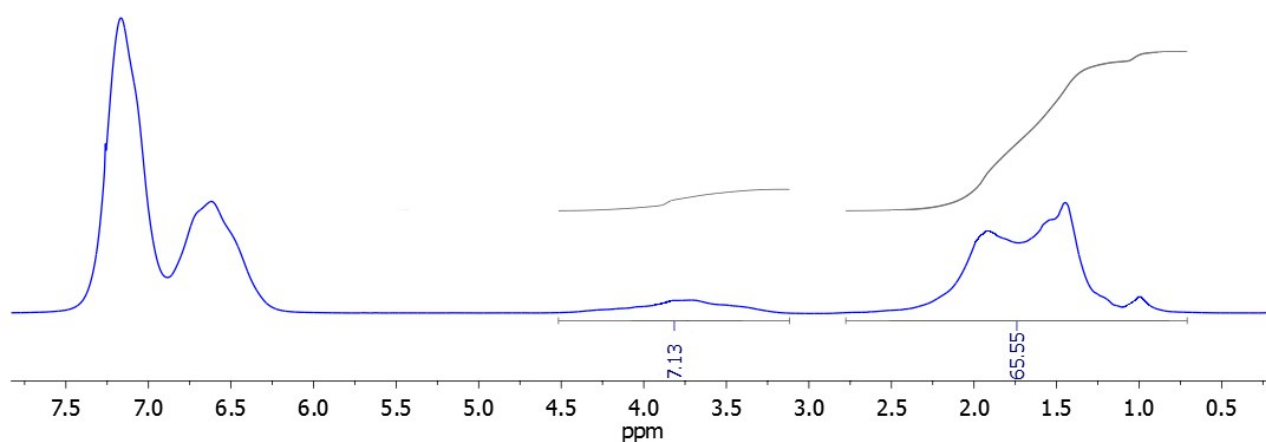


Figure S32. ^1H NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (5.1/79.7/15.2, $M_n = 10900 \text{ g}\cdot\text{mol}^{-1}$).

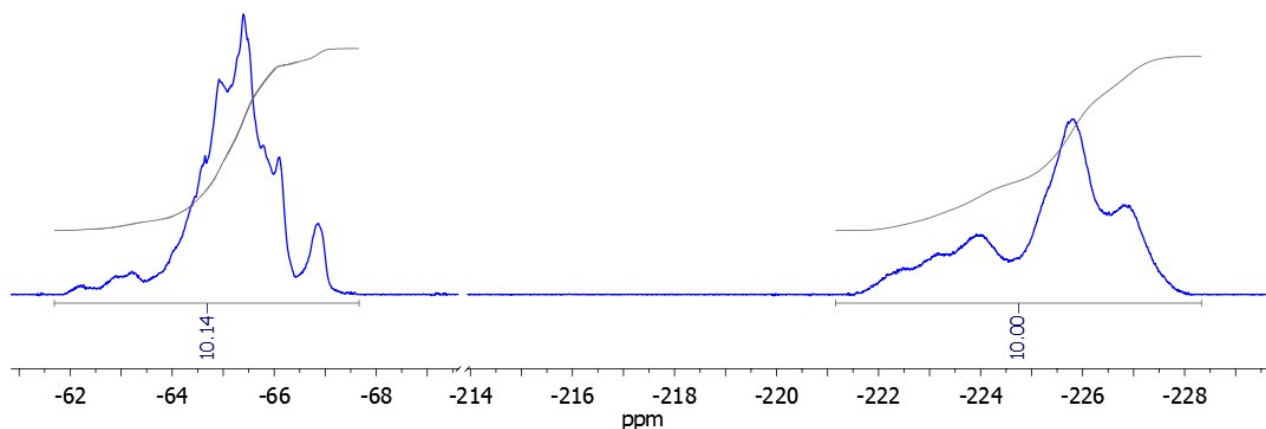


Figure S33. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (5.1/79.7/15.2, $M_n = 10900 \text{ g}\cdot\text{mol}^{-1}$).

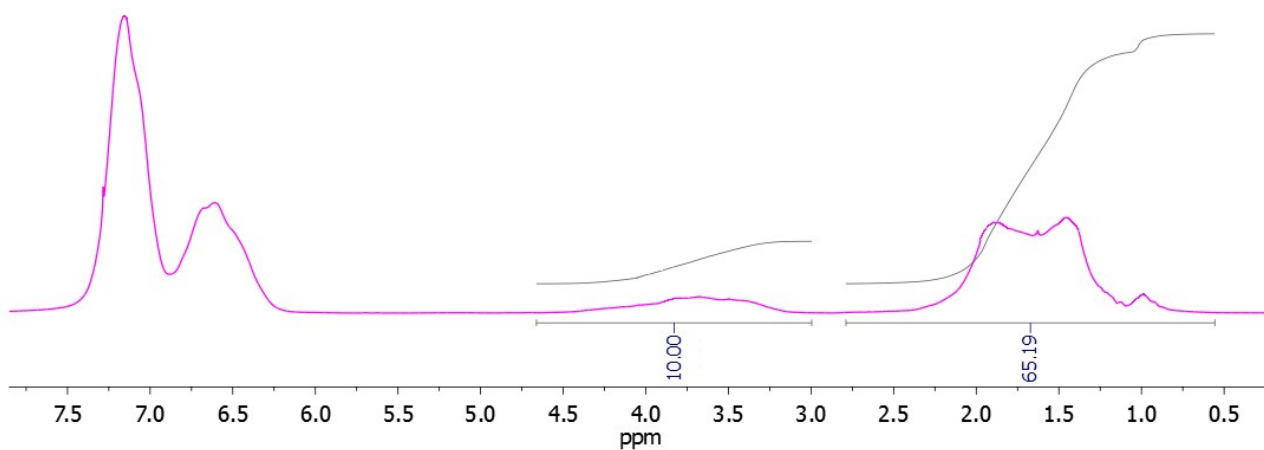


Figure S34. ^1H NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (5.0/74.0/21.0, $M_n = 9400 \text{ g}\cdot\text{mol}^{-1}$).

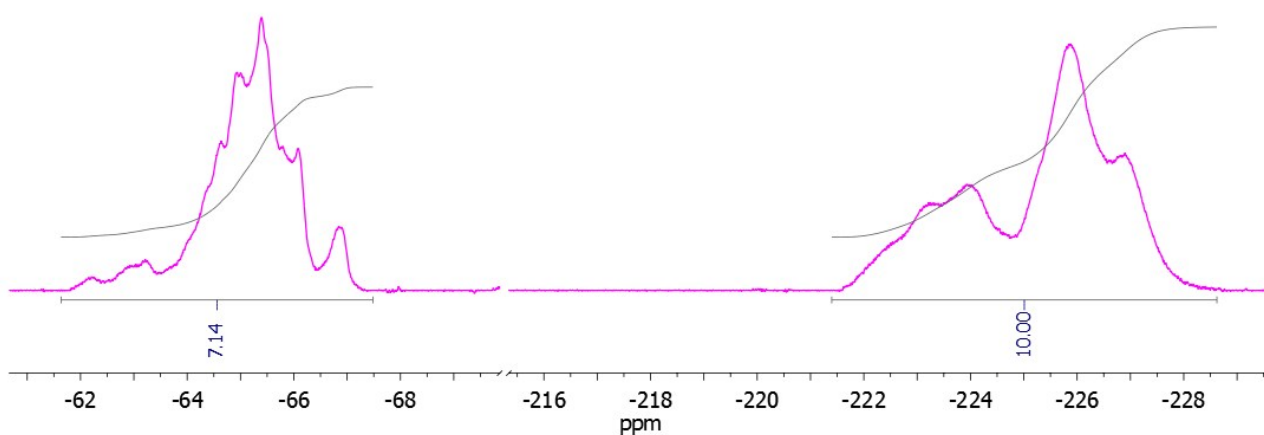


Figure S35. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (5.0/74.0/21.0, $M_n = 9400 \text{ g}\cdot\text{mol}^{-1}$).

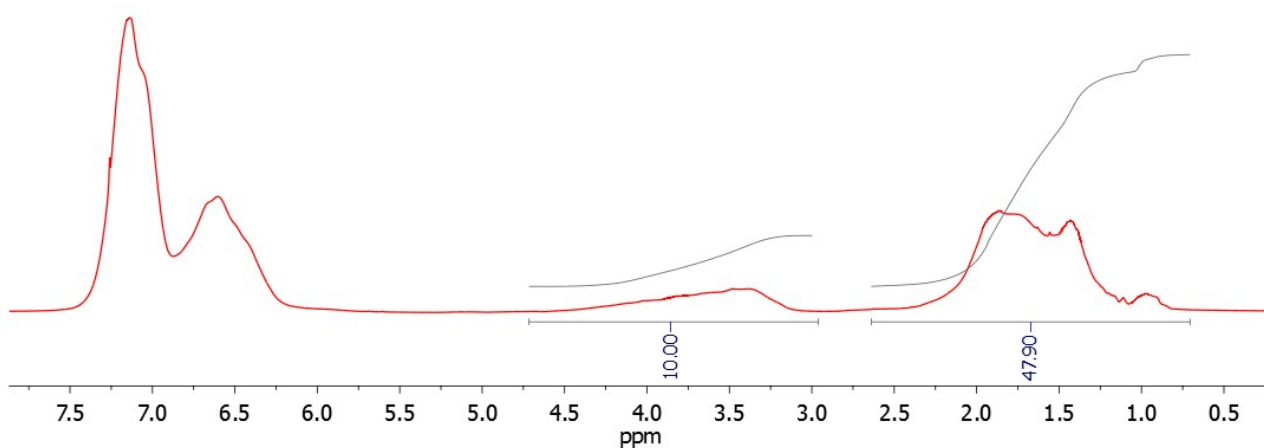


Figure S36. ^1H NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (4.2/67.8/28.0, $M_n = 8000 \text{ g}\cdot\text{mol}^{-1}$).

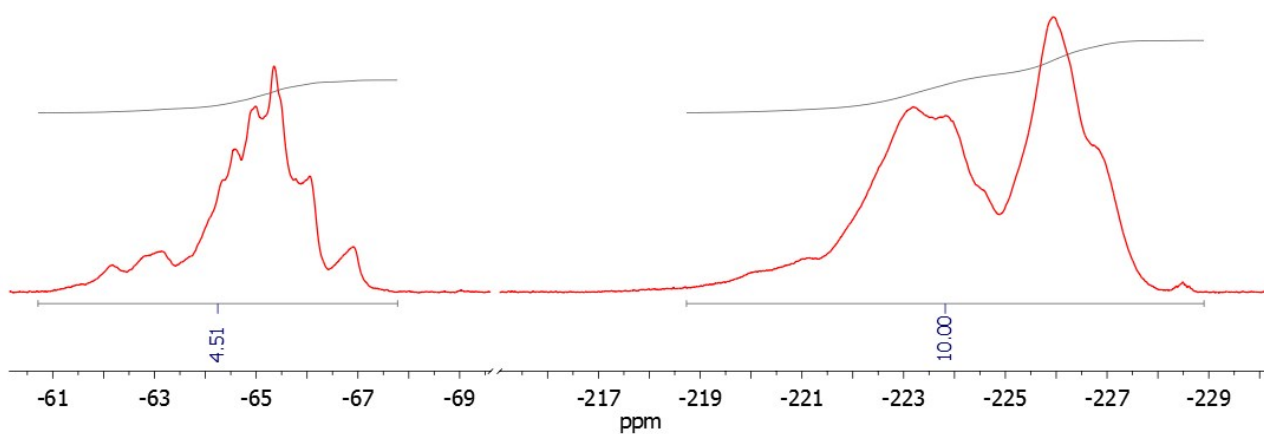


Figure S37. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (4.2/67.8/28.0, $M_n = 8000 \text{ g}\cdot\text{mol}^{-1}$).

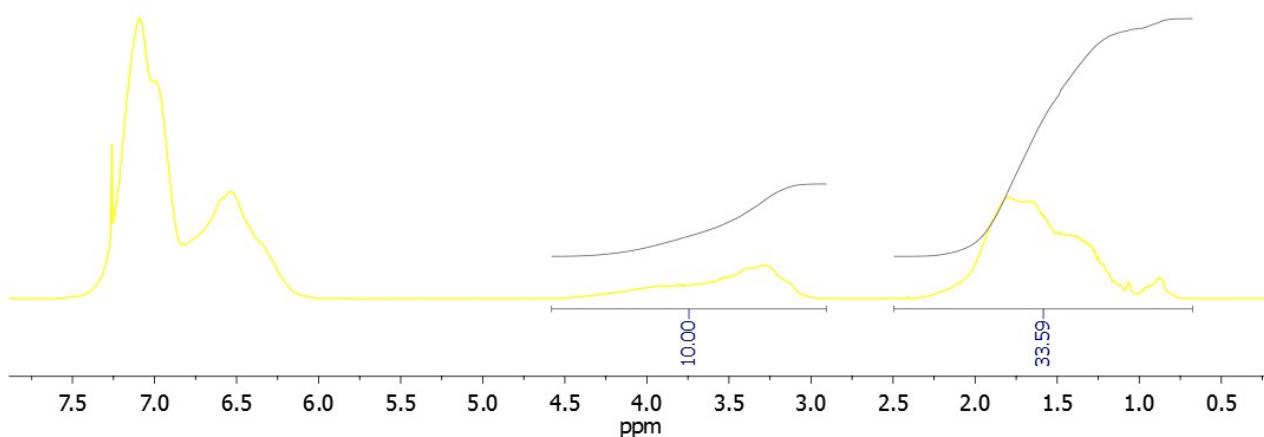


Figure S38. ^1H NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (3.7/57.9/38.4, $M_n = 6900 \text{ g}\cdot\text{mol}^{-1}$).

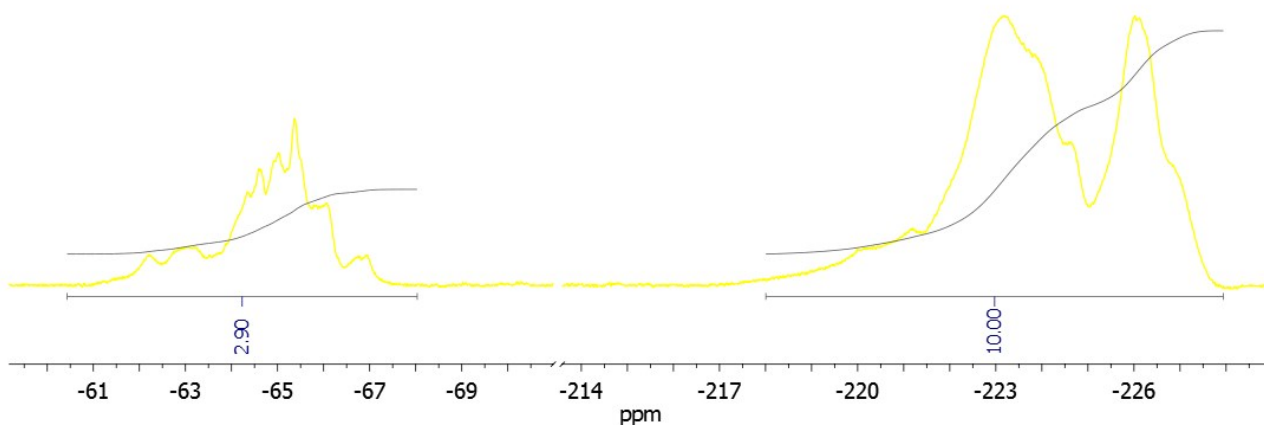
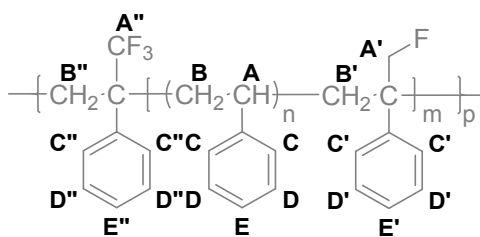


Figure S39. ^{19}F NMR spectrum (recorded in CDCl_3) of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymer (3.7/57.9/38.4, $M_n = 6900 \text{ g}\cdot\text{mol}^{-1}$).

Table S4. Determination of terpolymer composition in poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers.

I_I	I_{II}	I_{III}	I_{IV}	% _{ST}	% _{FMST}	% _{TFMST}	M_n [g mol ⁻¹]
177.32	6.65	82.55	10.00	80.3	5.2	14.5	10700
127.86	10.00	25.61	10.00	79.7	11.0	9.3	9200
65.55	7.13	10.14	10.00	79.7	15.2	5.1	10900
65.19	10.00	7.14	10.00	74.0	21.0	5.0	9400
47.90	10.00	4.51	10.00	67.8	28.0	4.2	8000
33.59	10.00	2.90	10.00	57.9	38.4	3.7	6900



Mol% of ST in the terpolymers

$$\%_{ST} = \{ [I_I - I_{II} - ((I_{II} * I_{III}) / (3 * I_{IV}))] / 3 \} / \{ [[I_I - I_{II} - ((I_{II} * I_{III}) / (3 * I_{IV}))] / 3] + (I_{II} / 2) + [((I_{II} * I_{III}) / (3 * I_{IV})) / 2] \}$$

Mol% of FMST in the terpolymer

$$\%_{FMST} = (I_{II} / 2) / \{ [[I_I - I_{II} - ((I_{II} * I_{III}) / (3 * I_{IV}))] / 3] + (I_{II} / 2) + [((I_{II} * I_{III}) / (3 * I_{IV})) / 2] \}$$

Mol% of TFMST in the terpolymer

$$\%_{TFMST} = \{ [((I_{II} * I_{III}) / (3 * I_{IV})) / 2] \} / \{ [[I_I - I_{II} - ((I_{II} * I_{III}) / (3 * I_{IV}))] / 3] + (I_{II} / 2) + [((I_{II} * I_{III}) / (3 * I_{IV})) / 2] \}$$

where I_I , I_{II} and I_{III} , I_{IV} stand for the integrals of signals centered at 1.72 ppm (H_A , H_B , $H_{B'}$, $H_{B''}$), 3.75 ppm ($H_{A'}$) in ¹H NMR spectra and -65.0 ppm ($F_{A''}$), -225.5 ppm ($F_{A'}$) in ¹⁹F NMR spectra, respectively.

6. Determination of average molecular weights of poly(FMST-*co*-ST) copolymers from GPC with polystyrene standards

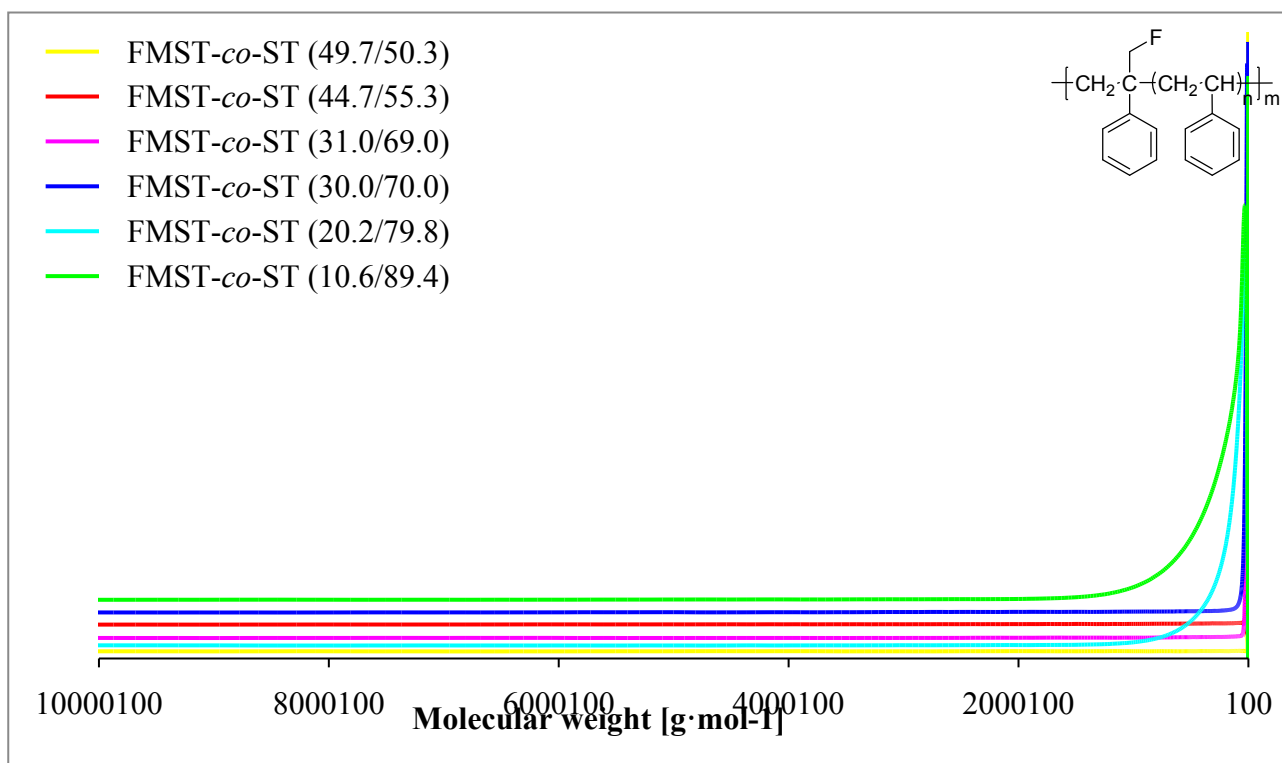


Figure S40. GPC chromatograms of series poly(FMST-*co*-ST) copolymers with different comonomer contents obtained in bulk radical copolymerizations.

Table S5. poly(FMST-*co*-ST) copolymers average molecular weights (M_n , M_w) and polydispersity indexes (\mathcal{D}) assessed from GPC with polystyrene standards.

Molar ratio in polymer [mol%]		M_n [g/mol]	M_w [g/mol]	\mathcal{D}
FMST	ST			
10.6	89.4	23727	86930	3.66376
20.2	79.8	18856	57894	3.07032
30.0	70.0	6590	12423	1.88513
31.0	69.0	4769	8446	1.77102
44.7	55.3	2914	5634	1.93342
49.7	50.3	1462	1971	1.34815

7. Determination of average molecular weights of poly(TFMST-*co*-ST) copolymers from GPC with polystyrene standards

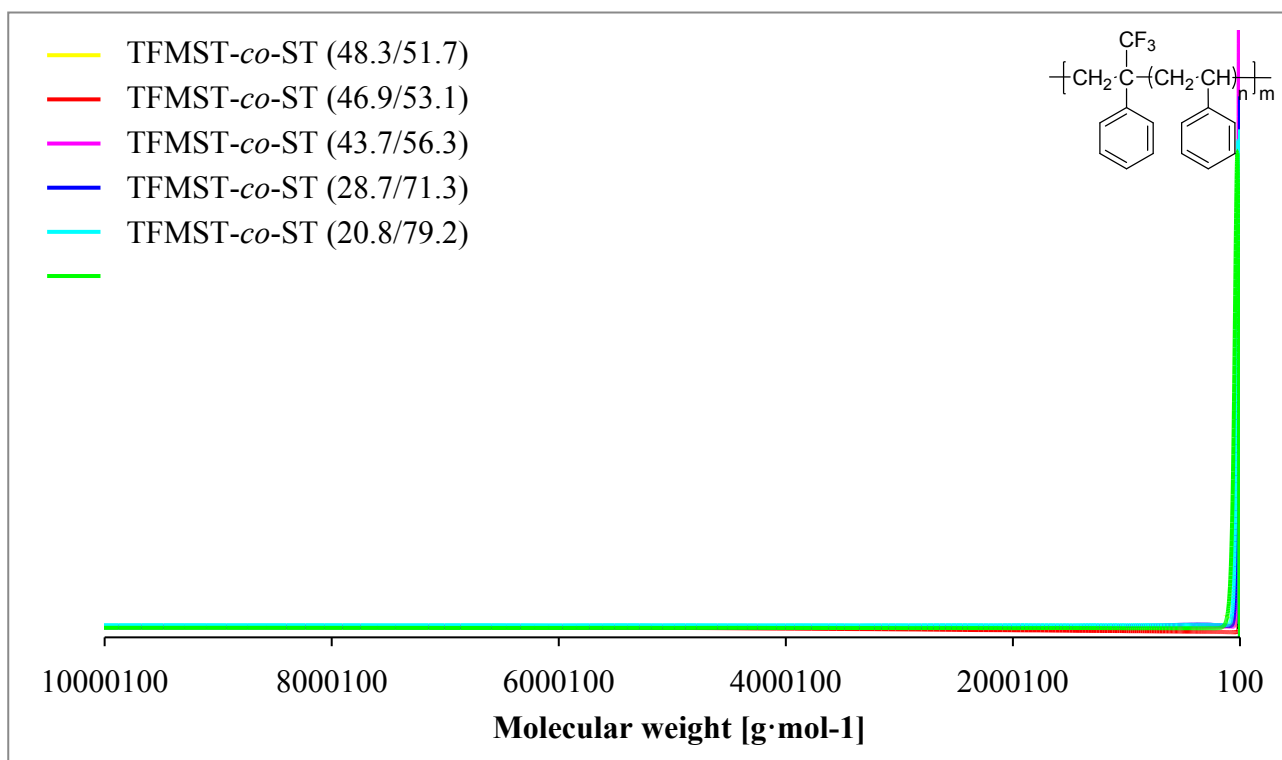


Figure S41. GPC chromatograms of series poly(TFMST-*co*-ST) copolymers with different comonomer contents obtained in bulk radical copolymerizations.

Table S6. poly(TFMST-*co*-ST) copolymers average molecular weights (M_n , M_w) and polydispersity indexes (\mathcal{D}) assessed from GPC with polystyrene standards.

Molar ratio in polymer [mol%]		M_n [g/mol]	M_w [g/mol]	\mathcal{D}
TFMST	ST			
10.6	89.4	14634	24830	1.69673
20.8	79.2	10807	16326	1.51069
28.7	71.3	8879	12867	1.44915
43.7	56.3	6549	8894	1.35807
46.9	53.1	2647	3846	1.45297
48.3	51.7	1546	2448	1.58344

8. Determination of average molecular weights of poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers from GPC with polystyrene standards

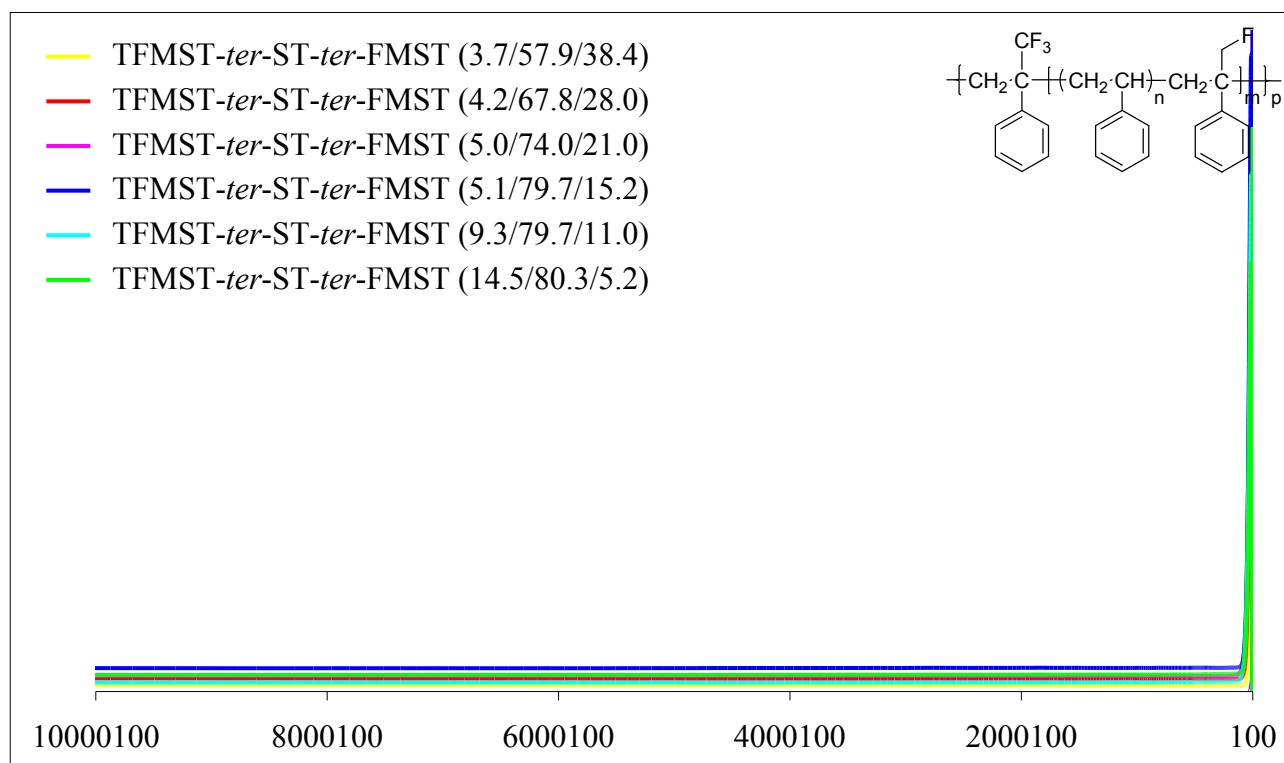


Figure S42. GPC chromatograms of series poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers with different termonomer contents obtained in bulk radical terpolymerizations.

Table S7. poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers average molecular weights (M_n , M_w) and polydispersity indexes (\mathcal{D}) assessed from GPC with polystyrene standards.

Molar ratio in polymer [mol%]			M_n [g/mol]	M_w [g/mol]	\mathcal{D}
TFMST	ST	FMST			
14.5	80.3	5.2	10684	17175	1.60754
9.3	79.7	11.0	9238	16877	1.82691
5.1	79.7	15.2	10884	17231	1.58315
5.0	74.0	21.0	9384	16039	1.70919
4.2	67.8	28.0	8006	12928	1.61479
3.7	57.9	38.4	6854	10718	1.56376

9. Thermostability of poly(fluorinated α -methylstyrene-styrene) co- and terpolymers

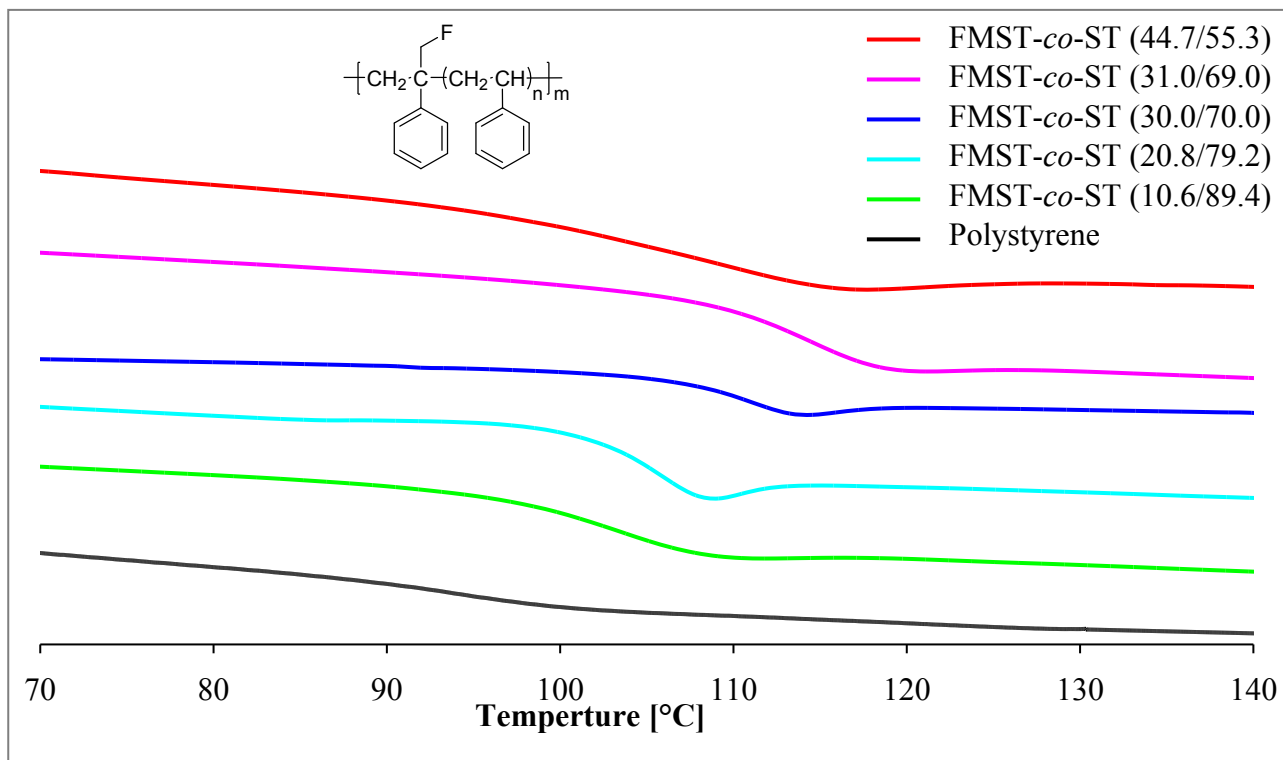


Figure S43. Comparison of glass transition temperatures (T_g) of series poly(FMST-co-ST) copolymers with different comonomer contents obtained in bulk radical copolymerizations.

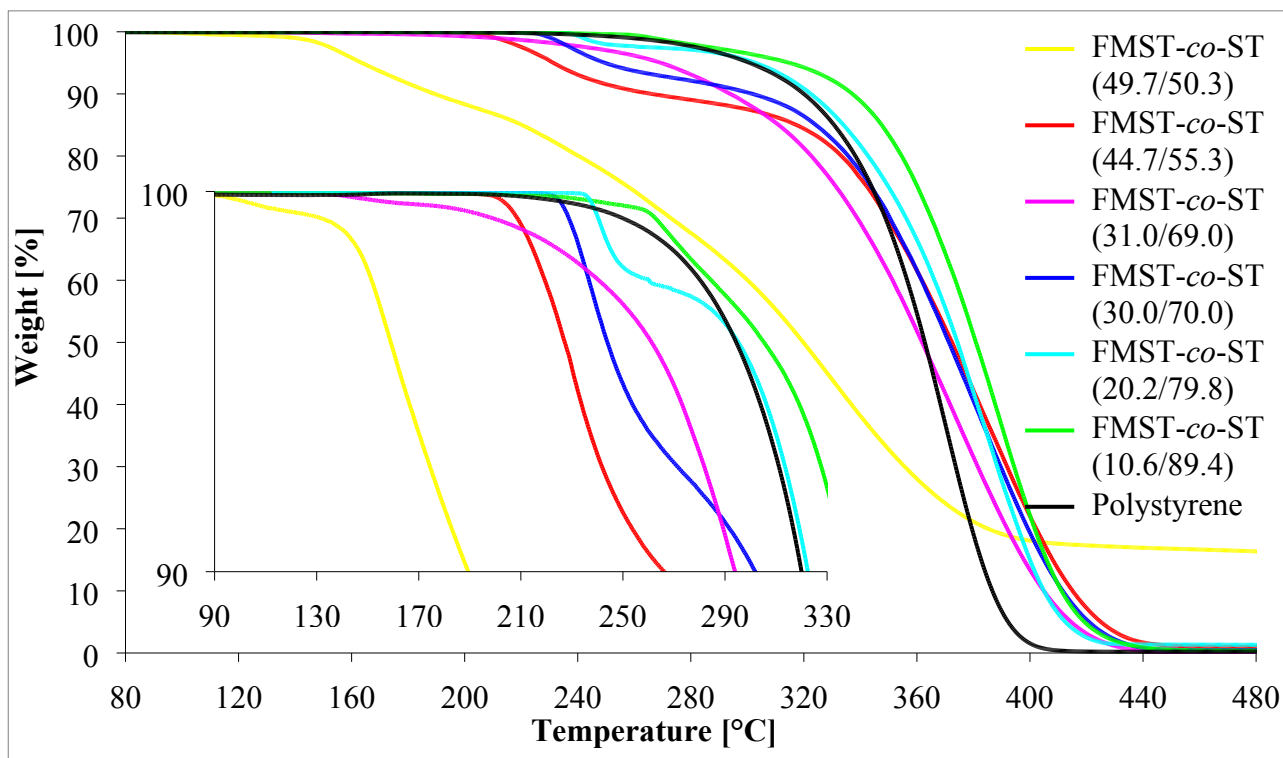


Figure S44. TGA thermograms of series poly(FMST-co-ST) copolymers with different comonomer contents obtained in bulk radical copolymerizations.

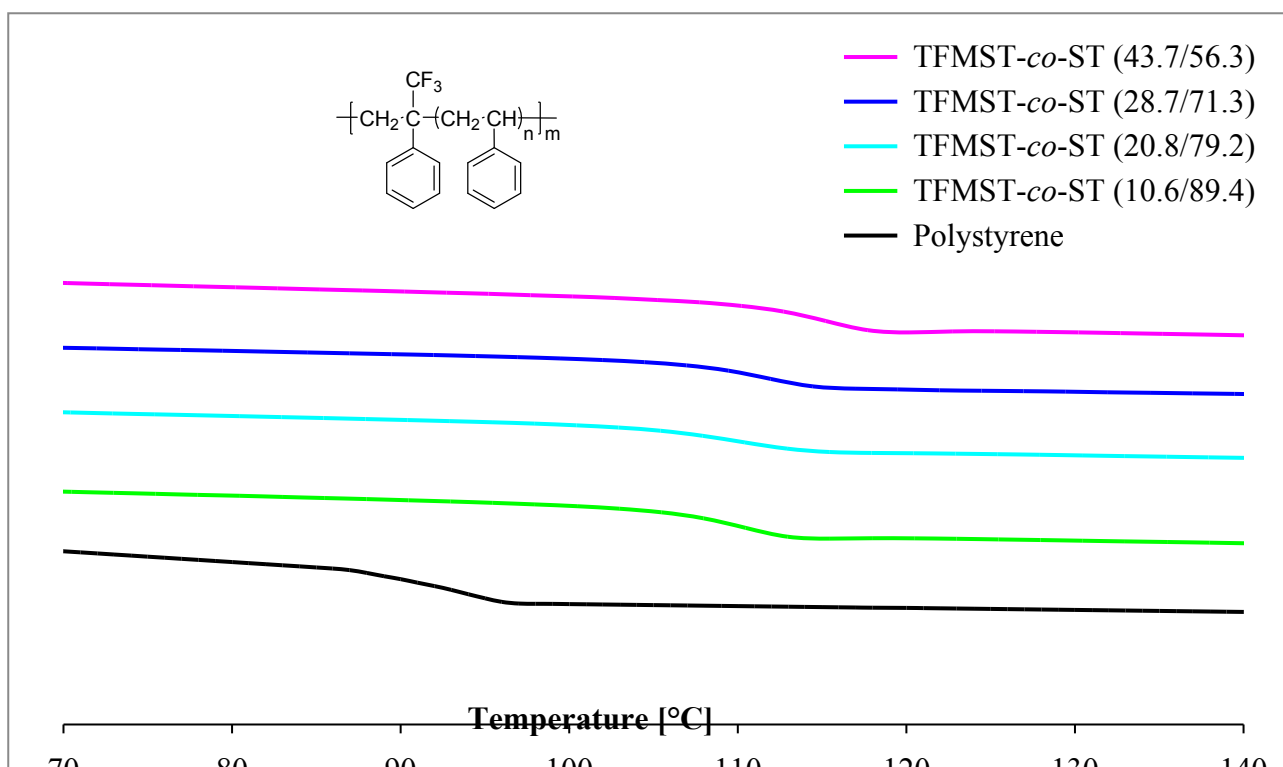


Figure S45. DSC thermograms of poly(TFMST-*co*-ST) copolymers with different comonomer contents obtained in bulk radical copolymerizations.

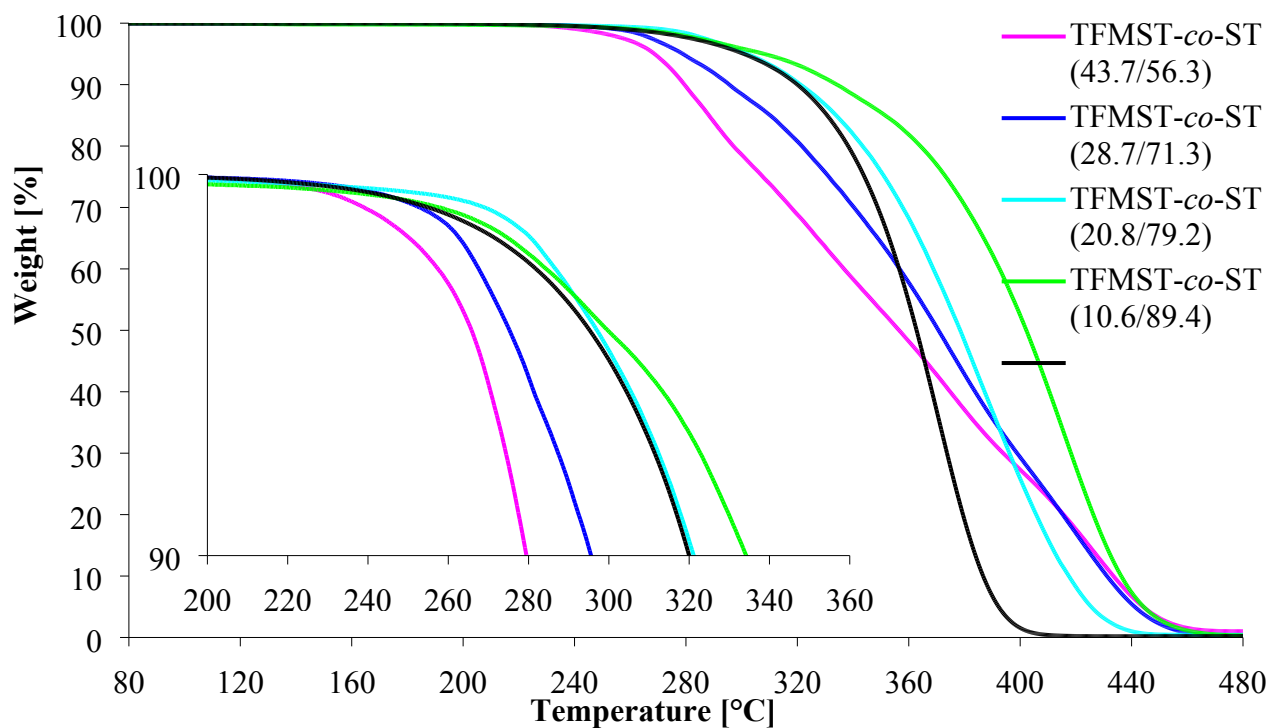


Figure S46. TGA thermograms of series poly(TFMST-*co*-ST) copolymers with different comonomer contents obtained in bulk radical copolymerizations.

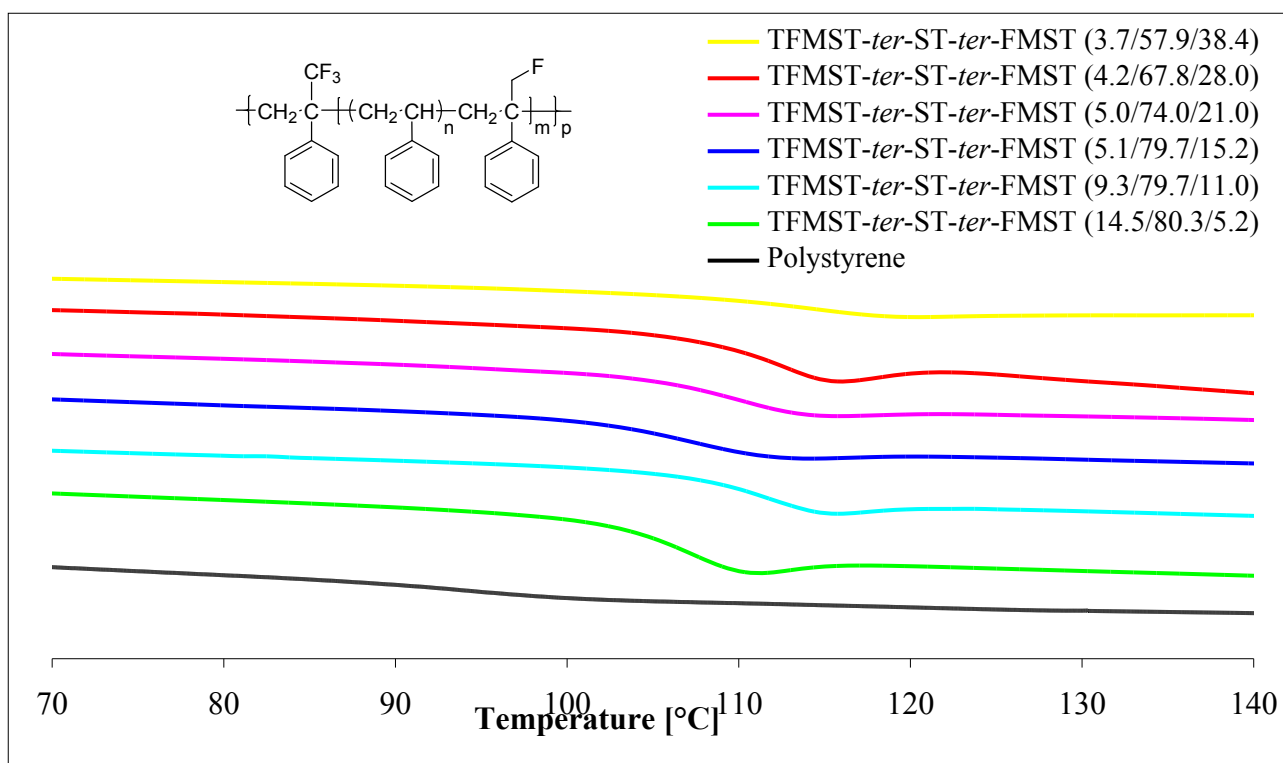


Figure S47. Comparison of glass transition temperatures (T_g) of series poly(TFMST-*ter*-ST-*ter*-ST) terpolymers with different comonomer contents obtained in bulk radical terpolymerizations.

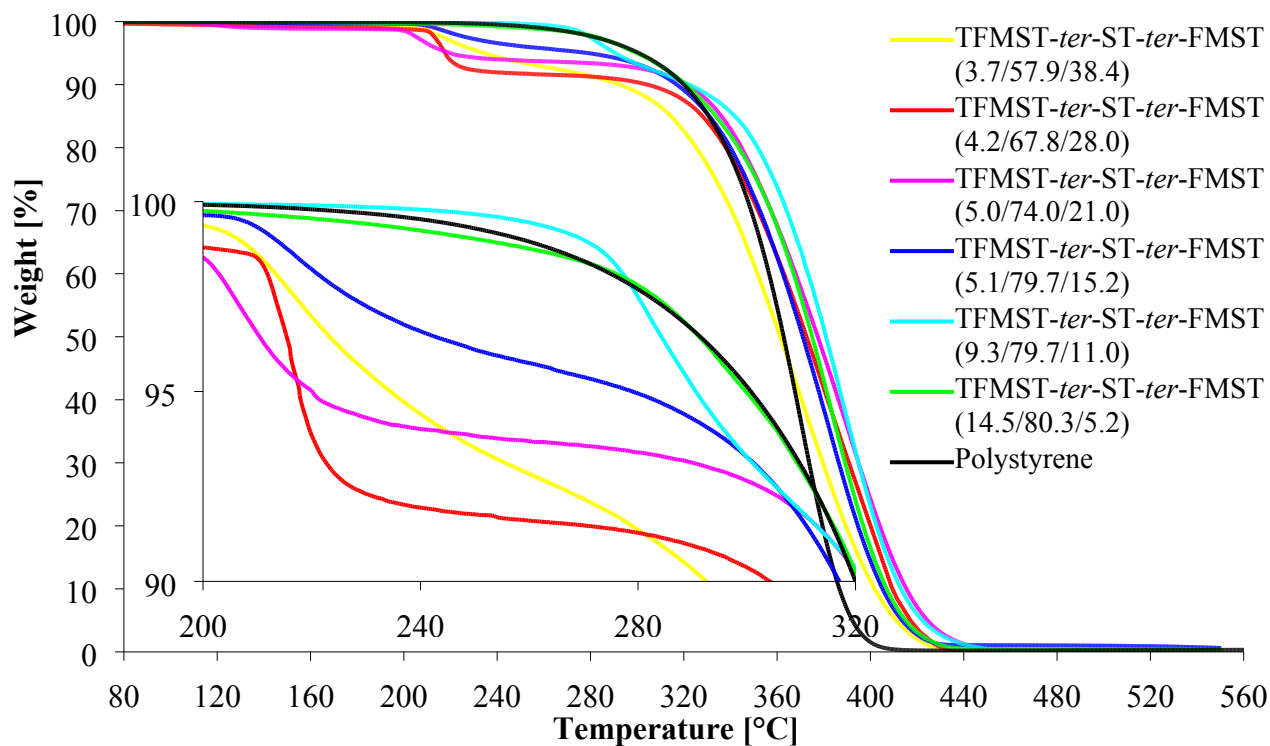


Figure S48. TGA thermograms of series poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers with different termonomer contents obtained in bulk radical terpolymerizations.

Table S8. Thermal properties of polystyrene, poly(FMST-*co*-ST), poly(TFMST-*co*-ST) copolymers, and poly(TFMST-*ter*-ST-*ter*-FMST) terpolymers obtained in bulk radical copolymerizations (from Figures S43-S48).

M_n exp. ^a [g·mol ⁻¹]	mol% in polymer			T_g^b [°C]	T_{d5}^b [°C]	T_{d10}^b [°C]	T_{d30}^b [°C]	T_{d50}^b [°C]
	TFMST	ST	FMST					
Polystyrene								
11300	-	100	-	91	304	320	349	363
15000	-	100	-	97	311	334	372	385
23000	-	100	-	101	318	342	373	384
poly(FMST- <i>co</i> -ST)								
23700	-	89.4	10.6	102	315	337	365	381
18900	-	79.8	20.2	104	303	323	356	375
6600	-	70.0	30.0	111	249	302	351	371
4800	-	69.0	31.0	113	269	294	339	362
2900	-	55.3	44.7	106	231	266	349	372
1500	-	50.3	49.7	N/A	164	190	273	319
poly(TFMST- <i>co</i> -ST)								
14600	10.6	89.4	-	109	308	334	380	402
10800	20.8	79.2	-	110	302	321	358	378
8900	28.7	71.3	-	112	279	296	340	371
6500	43.7	56.3	-	114	269	279	318	356
poly(TFMST- <i>ter</i> -ST- <i>ter</i> -FMST)								
10700	14.5	80.3	5.2	107	300	321	357	375
9200	9.3	79.7	11.0	111	291	322	364	381
10900	5.1	79.7	15.2	107	279	317	353	371
9400	5.0	74.0	21.0	110	220	321	357	377
8000	4.2	67.8	28.0	111	217	304	352	372
6900	3.7	57.9	38.4	113	234	293	340	361

^a number-average molecular weights (M_n) assessed from SEC with poly(styrene) standards.

^b TGA and DSC analyses were performed under nitrogen atmosphere

10. Contact Angle Measurements

The organic films were prepared *via* deposition of presented copolymers in THF on the glass surface modified by octadecyltrichlorosilane (OTS) surface at room temperature according to the schema in Figure S49.

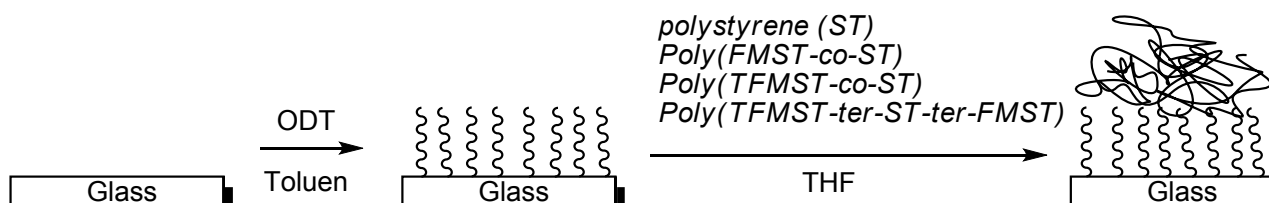


Figure S49. Schematic formation of a glass/OTS substrate and subsequent fluorinated *polystyrene* copolymers adsorption from THF solution.

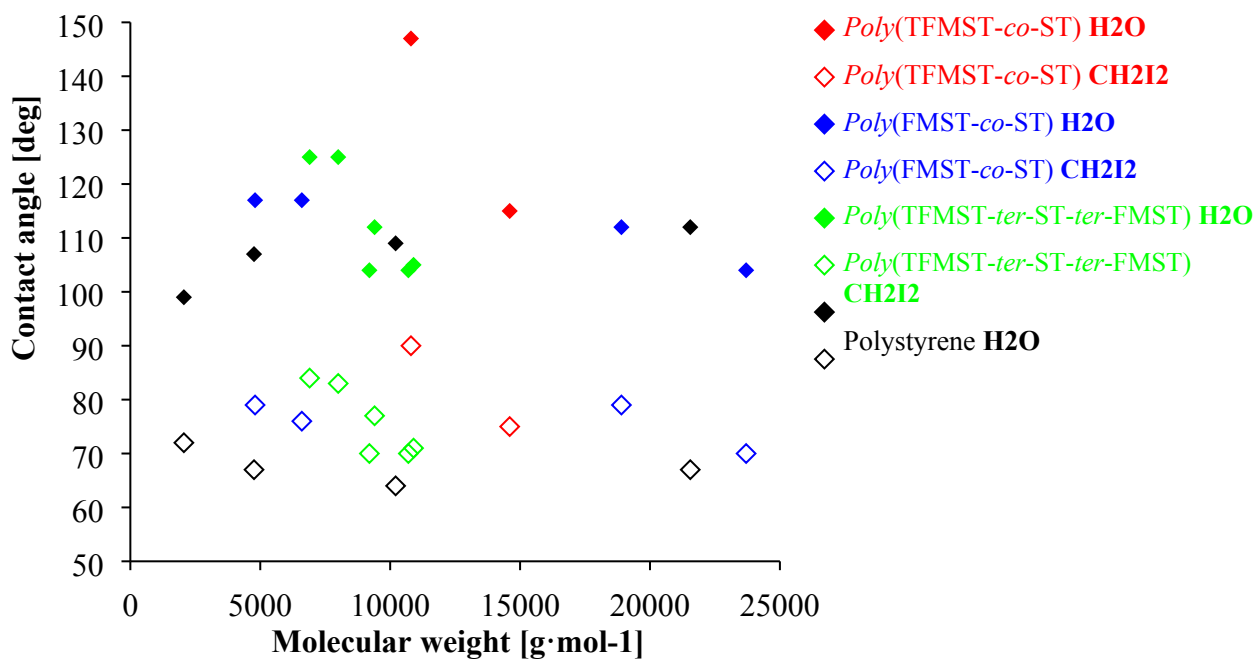


Figure S50. Advancing Water and diiodomethane Contact Angles *versus* molecular weight (M_n) of polystyrene and fluorinated copolystyrenes.

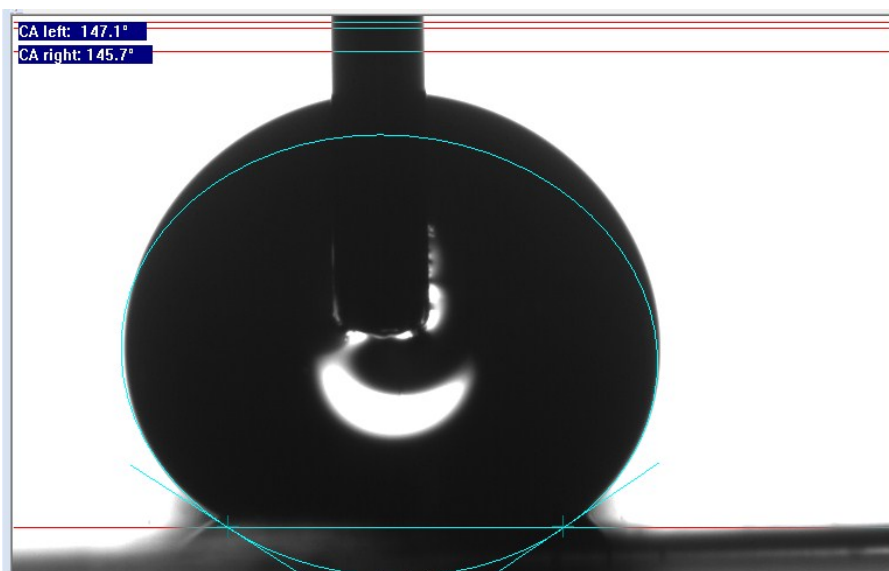


Figure S51. Picture of water droplet on a poly(TFMST-*co*-ST) copolymer (CA=147°) surface.



Figure S52. Water droplets (4 μ l) on a poly(TFMST-*co*-ST) copolymer surface.

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