polymers

Bis(formylphenolato)cobalt(II)-Mediated Alternating Radical Copolymerization of *tert*-Butyl 2-Trifluoromethylacrylate with Vinyl Acetate

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SUPPORTING INFORMATION

Table S1. Data for bulk VAc polymerization initiated by V-70 in presence or absence of Co(SAL)$_2$ at 30 °C.[a]

Entry	Initiating system	Time (h)	Conversion (%)[b]	$10^{-4} \cdot M_{n,theo.}$ (g mol^{-1})[c]	$10^{-4} \cdot M_{n,SEC}$ (g mol^{-1})[d]	$Đ$[d]
1	V-70/Co(SAL)$_2$	0.5	0	-	-	-
		1	1	0.07	-	-
		2	5	0.24	-	-
		3	10	0.46	-	-
		4	16	0.72	-	-
		5	22	0.98	3.50	1.62
		20.25	67	2.90	3.87	1.66
2	V-70	0.5	3	n.a.	-	-
		1	7	n.a.	-	-
		2	14	n.a.	-	-
		3	24	n.a.	-	-
		4	32	n.a.	-	-
		5	37	n.a.	4.88	1.60
		21.5	85	n.a.	4.05	1.99

[a]Conditions: {[VAc]$_0$/[V-70]$_0$ = 500/2, [V-70]$_0$/[Co(SAL)$_2$]$_0$ = 2/1. [b]Determined by ^{1}H NMR spectroscopy. [c]The theoretical molar masses of the polymers ($M_{n,theo}$) were calculated using the following equation:

$$M_{n,theo.} = \left(\frac{[VAc]_0}{[Co(SAL)_2]_0} \times \text{conv. of VAc} \times M_{VAc} \right) + (M_{TEMPO} - 1) + \quad \text{contribution of V} - 70 \text{ part (S1)}$$

[d]Determined by SEC in THF with multiangle DLS detection and analysis on the basis of the dn/dc.

Table S2. Data for the copolymerization of VAc and MAF-TBE mediated by Co(SAL)$_2$ at 40 °C.[a]

Time (h)	VAc conversion (%/no. of moles)[b]	MAF-TBE conversion (%/no. of moles)[c]	Total conversion (%)	$10^{-3} \cdot M_{n,theo.}$ (g mol^{-1})[d]	$10^{-3} \cdot M_{n,SEC}$ (g mol^{-1})[e]	$Đ$[e]
2	4/3.4	4/3.1	4	3	17.8	1.75
5	15/12.1	14/11.7	14.5	11.3	28.9	1.65
7	26/20.5	25/20.0	25.5	18.9	42.5	1.61
10	32/26.4	31/25.1	31.5	23.4	48.9	1.59
12	42/33.8	41/33.2	41.5	31.7	57.5	1.58
30	76/61.2	77/62.0	76.5	57.4	83.0	1.55

[a]Conditions: {[VAc]$_0$ + [MAF-TBE]$_0$}/[V-70]$_0$/[**3**]$_0$ = 537/3/1, [VAc]$_0$/[MAF-TBE]$_0$ = 1/1, [V-70]$_0$/[Co(SAL)$_2$]$_0$ = 3/1. [b]Determined by ^{1}H NMR spectroscopy. [c]Assessed by ^{19}F NMR spectroscopy. [d]The theoretical molar mass of the polymers ($M_{n,theo}$) were calculated using the following equation:

$$M_{n,theo.} = \left(\frac{[VAc]_0}{[Co(SAL)_2]_0} \times \text{conv. of VAc} \times M_{VAc} \right) + \left(\frac{[MAF - TBE]_0}{[Co(acac)_2]_0} \times \text{conv. of MAF} - TBE \times M_{MAF-TBE} \right)$$

$$+ (M_{TEMPO} - 1) + M_{V70 \, fragment} \text{(S2)}$$

With M_{VAc} = 86 gmol^{-1}, $M_{MAF-TBE}$ = 196 gmol^{-1}, M_{TEMPO} = 155 gmol^{-1} and $M_{V70 \, fragment}$ = 141 gmol^{-1}.

[e]Determined by SEC in DMF (containing 0.1 wt% LiCl), system was calibrated using poly(methyl methacrylate) standards.
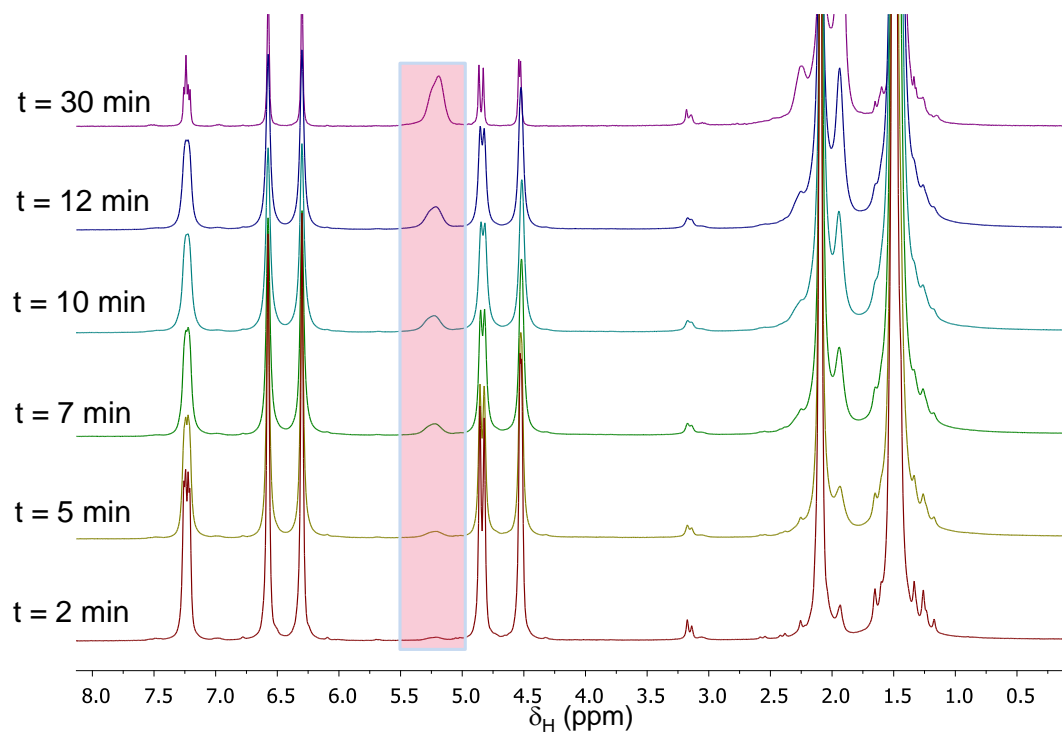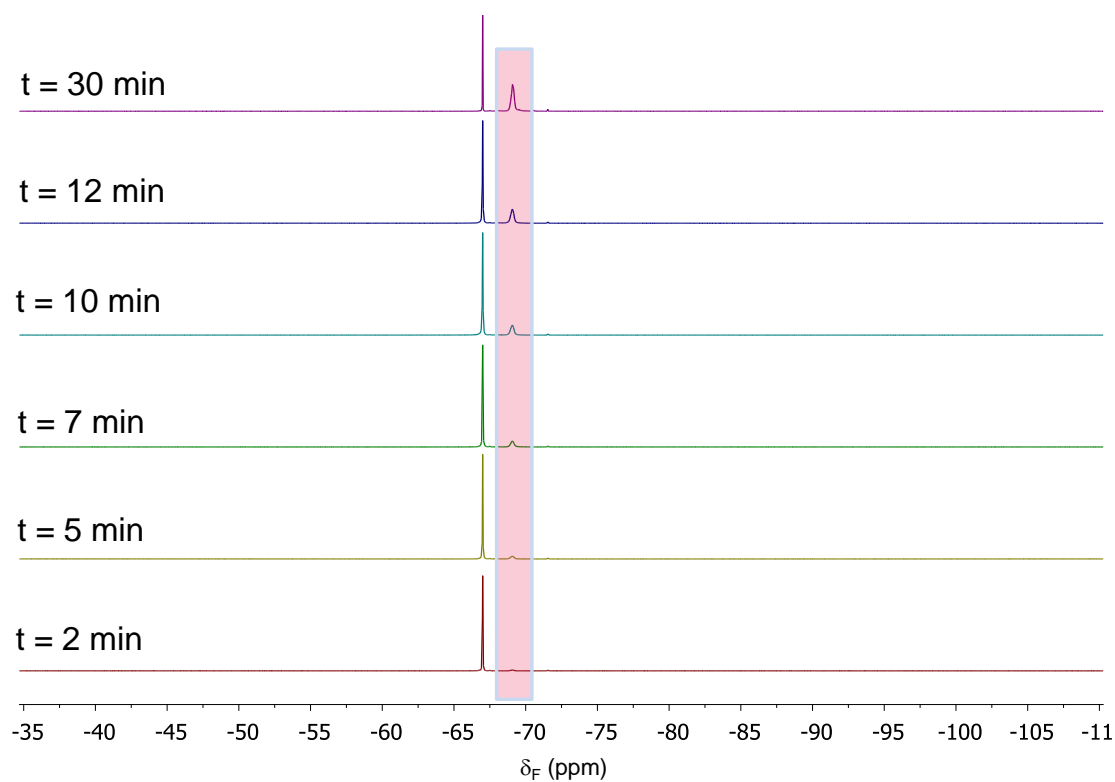
Figure S1. Time evolution of the ^1H NMR spectra (in acetone-d_6, 20 °C) of the bulk copolymerization of VAc and MAF-TBE at 40 °C initiated by V-70 in the presence of Co(SAL)$_2$. {[VAc]$_0$+[MAF-TBE]$_0$}/[V-70]$_0$/[**3**]$_0$ = 537/3/1, [VAc]$_0$/[MAF-TBE]$_0$= 1/1 (Table S2).

Figure S2. Time evolution of the ^{19}F NMR spectra (acetone-$d6$, 20 °C) during the bulk copolymerization of VAc and MAF-TBE at 40 °C initiated by V-70 in presence of Co(SAL)$_2$ {[VAc]$_0$+[MAF-TBE]$_0$}/[V-70]$_0$/[**3**]$_0$ = 537/3/1, [VAc]$_0$/[MAF-TBE]$_0$= 1/1 (Table S2).
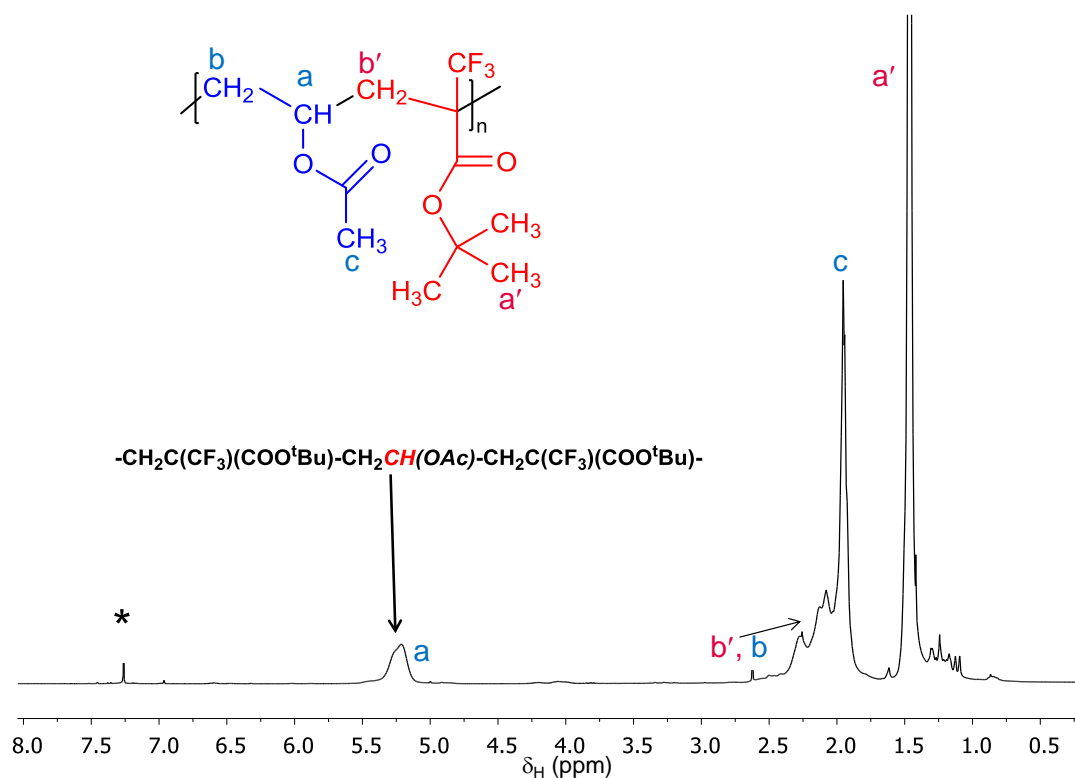
Figure S3. Representative[1]H NMR spectrum (400 MHz) of poly(VAc-*alt*-MAF-TBE) copolymer prepared by OMRP of VAc with MAF-TBE mediated by V-70/Co(SAL)$_2$ at 40 °C in bulk (Table S2), recorded in CDCl$_3$ at 20 °C. Peaks are centered at δ 1.45 (a′), 1.90 (c), 2.05 to 2.75 (b and b′), 5.20 (a). (*) Solvent (CHCl$_3$) peak.
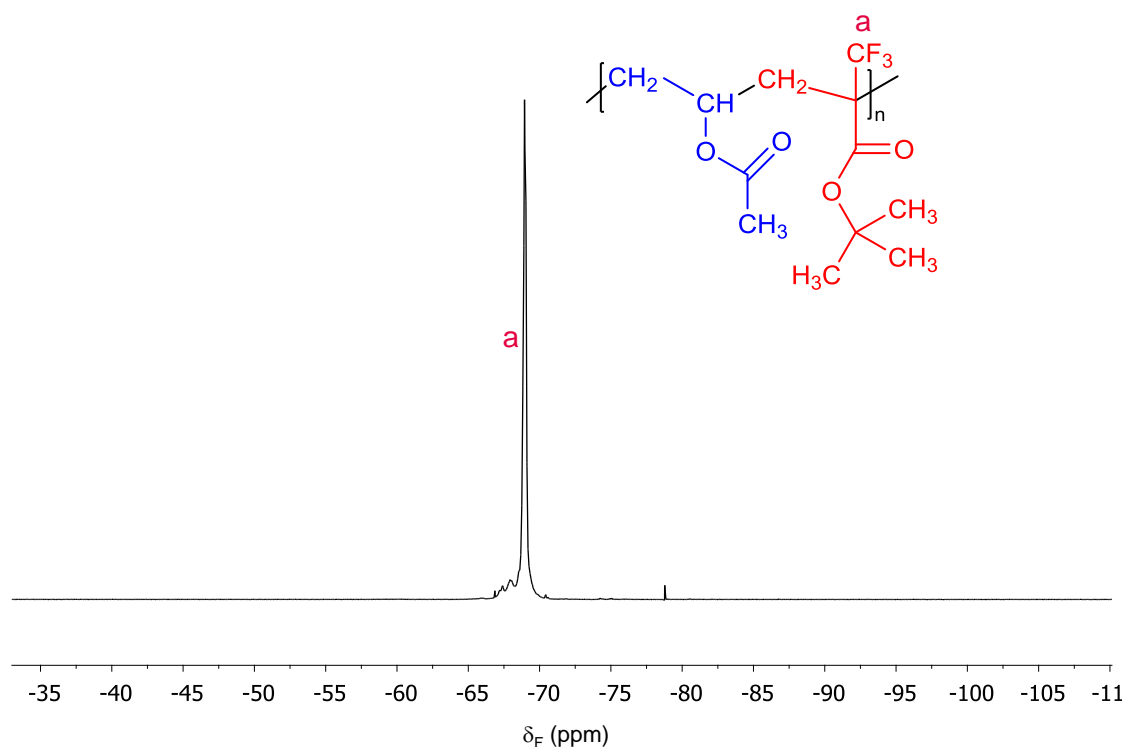

Figure S4. Representative ^{19}F NMR (376 MHz) spectrum of poly(VAc-*alt*-MAF-TBE) copolymer prepared by OMRP of VAc with MAF-TBE mediated by V-70/Co(SAL)$_2$ at 40 °C in bulk (Table S2), recorded in CDCl$_3$ at 20 °C. The peak is centered at -69 ppm.
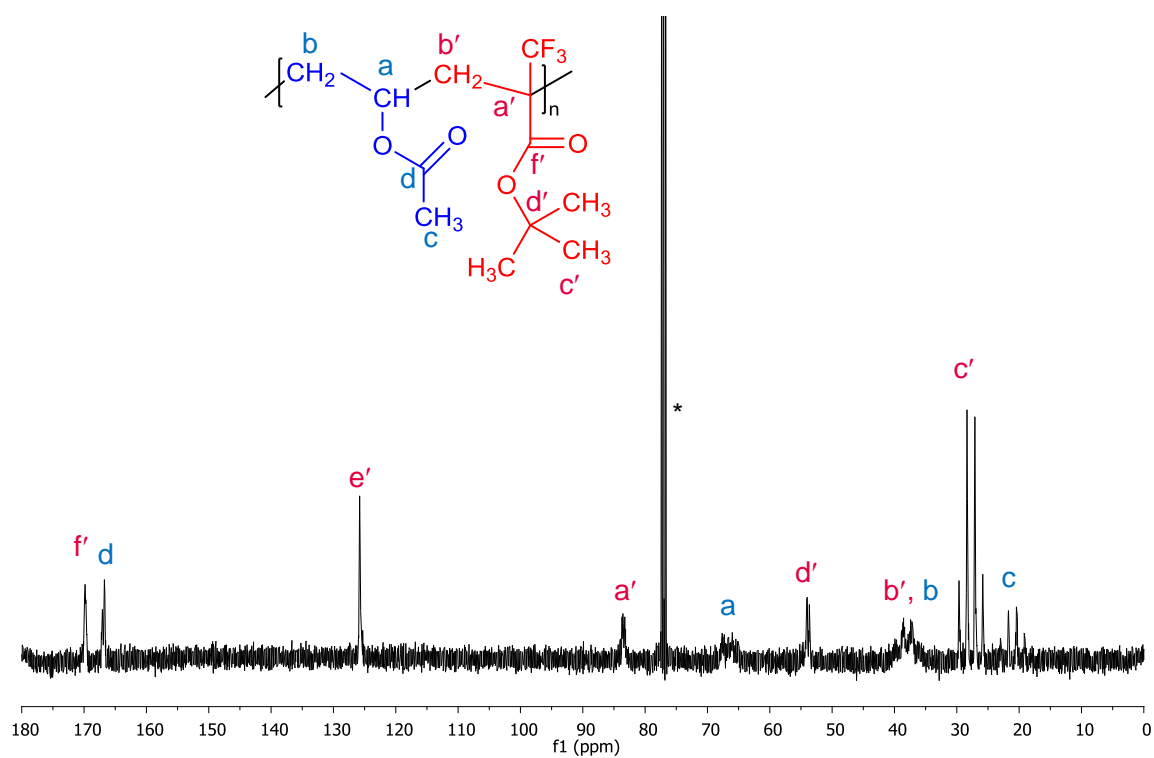
Figure S5. Representative $^{13}C\{^{19}F\}$ NMR spectrum (100 MHz) of poly(VAc-*alt*-MAF-TBE) copolymer prepared by OMRP of VAc with MAF-TBE mediated by V-70/Co(SAL)$_2$ at 40 °C in bulk (Table S2), recorded in CDCl$_3$ at 20 °C. Peaks are centered at δ 20.8 (c); 27.8 (c′), 38.4 (b and b′), 53.5 (d′), 67.5 (a), 83.2 (a′), 125.8 (e′), 167.0 (d), and 170.0 (f′). (*) CDCl$_3$ peak.