

## Supporting Information

# Nitroxide-Mediated Alternating Copolymerization of Vinyl Acetate with *tert*-Butyl-2-trifluoromethacrylate Using a SG1-based Alkoxyamine

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**1- Materials.** *tert*-Butyl-2-trifluoromethacrylate (MAF-TBE, kindly offered by Tosoh F-Tech Company Shunan, Japan) and vinyl acetate (VAc,  $\geq 99\%$ , Aldrich) were stored under nitrogen and purged for 30 mins with nitrogen before use. SG1-based BlocBuilder alkoxyamine (MAMA-SG1) was kindly offered by Dr. Julien Nicolas (University Paris Sud) via Arkema.

Acetone and laboratory reagent grade pentane (purity  $>95\%$ ), purchased from Sigma-Aldrich were used as received.  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$  used for NMR spectroscopy were purchased from Euroiso-top (Grenoble, France) (purity  $>99.8\%$ ).

## 2- Experimental Procedures.

**2.1. Copolymerization of VAc and MAF-TBE Using MAMA-SG1.** All polymerizations were performed using Schlenk techniques under nitrogen atmosphere. A typical copolymerization (entry 5, Table 1) of VAc with MAF-TBE was performed as follows (Scheme 1): MAMA-SG1 (34 mg, 0.09 mmol) was placed into a Schlenk flask and then purged by three vacuum-nitrogen cycles. Then, degassed VAc (0.7 mL, 8.0 mmol), MAF-TBE (1.4 mL, 8.0 mmol) and DMSO (2.0 mL) were added to the Schlenk flask under a nitrogen flux and the reaction mixture was heated at 40 °C under stirring. During the course of the polymerization, samples were withdrawn periodically from the reaction medium to determine the monomer conversions by  $^1\text{H}$  NMR spectroscopy (for VAc) and  $^{19}\text{F}$  NMR spectroscopy (for MAF-TBE) and to assess the molar masses ( $M_n$ ) and dispersities ( $D = M_w/M_n$ ) by SEC analysis. The monomer conversions were determined by  $^1\text{H}$  NMR spectroscopy (for VAc) and  $^{19}\text{F}$  NMR spectroscopy (for MAF-TBE) using equations S1 and S2, respectively:

$$\% \text{ VAc conversion} = \frac{\int_{4.80}^{5.15} \text{CH}}{(\int_{4.80}^{5.15} \text{CH} + \int_{4.30}^{4.45} \text{CH})} \times 100 \dots \dots \dots (S1)$$

where  $\int_i^j CH_x$  stands for the integral of the signal assigned to  $CH_x$  ranging from  $i$  ppm to  $j$  ppm in the  $^1H$  NMR spectrum of the reaction at time  $t$ .

$$\% \text{ MAF} - \text{TBE conversion} = \frac{\int_{-68.5}^{-70.5} CF_3}{\int_{-66.5}^{-67.5} CF_3 + \int_{-68.5}^{-70.5} CF_3} \times 100 \dots \dots \dots (S2)$$

where  $\int_{-n}^{-m} CF_3$  stands for the integral of the signal assigned to  $CF_3$  ranging from  $-n$  ppm to  $-m$  ppm in the  $^{19}F$  NMR spectrum of the reaction at time  $t$ .

After the reaction, the crude product was dissolved in acetone and precipitated twice in chilled pentane, filtered through a filter funnel, and then dried under vacuum ( $10^{-3}$  bar, 40 °C) for 12 h. The purified copolymer was characterized by  $^1H$  and  $^{19}F$  NMR spectroscopy.

$^1H$  NMR (400 MHz,  $CDCl_3$ ,  $\delta$  ppm, Figure 3): 0.85 to 1.55 {signal for the  $\alpha$ -end group containing MAMA fragment:  $-C(\underline{CH}_3)_2$  of MAMA signal  $h$ , signal for the  $\omega$ -end group containing SG1 fragment:  $-C(\underline{CH}_3)_3$  signal  $d$ ,  $\{-N-C(\underline{CH}_3)_3$  signal  $e$ ,  $-CH_2\underline{CH}_3$  signal  $f$ \}; 4.10  $\underline{CH}_2CH_3$  signal  $g$  of the  $\omega$ -end group containing SG1 fragment}; 1.40  $\{-C(\underline{CH}_3)_3$  of MAF-TBE, signal  $a'$ }; 1.90 ( $-OCO\underline{CH}_3$  of VAc, signal  $c$ ); 2.0 to 2.7 ( $-CH_2$  of VAc and MAF-TBE, signal  $b$  and  $b'$ ); 5.10 ( $-CHOAc$  of VAc in the VAc-MAF-TBE alternating dyad, signal  $a$ ); 6.55 ( $-CHOAc$  of VAc attached to the SG1 at the  $\omega$ -end group, signal  $i$ ).

$^{19}F$  NMR (376 MHz,  $CDCl_3$ ,  $\delta$  ppm of entry 5, Table S1, Figure S8): peak centered at -69 ( $-CF_3$  of MAF-TBE in the copolymer).

$^{31}P$  NMR (162 MHz,  $CDCl_3$ ,  $\delta$  ppm of entry 5, Table S1, Figure S9): peak centered at 25.02 ( $-P(O)OCH_2CH_3$  of the  $\omega$ -chain end containing SG1).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm, Figure S10): 20.83 ((-OCOCH<sub>3</sub> of VAc); 27.75 {-C(CH<sub>3</sub>)<sub>3</sub> of MAF-TBE}; 38.44 (-CH<sub>2</sub> of VAc and MAF-TBE); 53.49 {-C(CH<sub>3</sub>)<sub>3</sub> of MAF-TBE} 66.62 (-CHOAc of VAc in the VAc-MAF-TBE alternating dyad); 83.18 {-CH<sub>2</sub>C(CF<sub>3</sub>)CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub> of MAF-TBE}; 125.70 {-CH<sub>2</sub>C(CF<sub>3</sub>) of MAF-TBE}; 166.81 (-OCOCH<sub>3</sub> of VAc); 169.89 (-COOC(CH<sub>3</sub>)<sub>3</sub> of MAF-TBE).

## 2.2. Determination of the Reactivity Ratios of VAc and MAF-TBE.

Instantaneous copolymer compositions from the radical copolymerization of VAc with MAF-TBE using MAMA-SG1 at 40 °C in DMSO-*d*<sub>6</sub> in sealed NMR tube at seven different monomer feed compositions ([VAc]<sub>0</sub>/[MAF-TBE]<sub>0</sub> = 10/90, 20/80, 30/70, 50/50, 70/30, 80/20, 90/10) were determined by measuring the conversions of VAc and MAF-TBE by <sup>1</sup>H (equation S1) and <sup>19</sup>F (equation S2) NMR spectroscopies. Then monomer-copolymer composition curve (Figure S16) was constructed using these low conversions (< 5 %) composition data points. This curve was then fitted to the Mayo-Lewis copolymerization equation (S3) depicted by the red line<sup>1</sup> to determine the reactivity ratios of VAc and MAF-TBE:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \dots \dots \dots (S3)$$

where  $F_1$ ,  $f_1$ ,  $f_2$ ,  $r_1$  and  $r_2$  stands for the molar percentage of MAF-TBE in the copolymer, molar percentages of MAF-TBE and VAc, respectively in the starting comonomer feed and the reactivity ratios of MAF-TBE and VAc, respectively.

The calculation led to the following reactivity ratios:  $r_{VAc} = 0.013 \pm 0.011$  and  $r_{MAF-TBE} = 0$  at 40 °C.

### 3- Characterizations.

*Size Exclusion Chromatography (SEC) Measurements.* Molar masses ( $M_n$ s) and dispersities ( $D$ s) of the synthesized polymers were determined from size exclusion chromatography (SEC) using triple-detection GPC (Agilent Technologies). The SEC is equipped with a PL0390-0605390 LC light scattering detector operating at two diffusion angles ( $15^\circ$  and  $90^\circ$ ), a PL0390-06034 capillary viscometer, and a 390-LC PL0390-0601 refractive index detector and two PL1113-6300 ResiPore  $300 \times 7.5$  mm columns. The entire SEC-HPLC system was thermostated at  $35^\circ\text{C}$ . DMF (containing 0.1 wt % of LiCl) was used as the eluent at a flow rate of  $0.8\text{ mL min}^{-1}$  while toluene was used as the flow rate marker. Poly(methyl methacrylate) standards were used for calibration and the results were processed using the corresponding Agilent software.

*Nuclear Magnetic Resonance (NMR) Spectroscopy.* The compositions and microstructures of the synthesized polymers were determined by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectroscopies.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  1D NMR spectra were recorded on a Bruker AC 400 Spectrometer (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ , 376 MHz for  $^{19}\text{F}$  and 162 MHz for  $^{31}\text{P}$ ) using  $\text{CDCl}_3$  as a solvent using the following experimental conditions for  $^1\text{H}$  [or  $^{13}\text{C}$  or  $^{19}\text{F}$  or  $^{31}\text{P}$ ] NMR spectra: flip angle  $90^\circ$  [or  $90^\circ$  or  $30^\circ$  or  $90^\circ$ ], acquisition time 4.5 s [or 0.3 s or 0.7 s or 0.5 s], pulse delay 2 s [or 1 or 5 s or 2 s], number of scans 32 [or 8192 or 64 or 128], and a pulse width of 12.5, 9.5, 5.0 and 7.6  $\mu\text{s}$  for  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR, respectively. Coupling constants and chemical shifts are presented in Hertz (Hz) and parts per million (ppm), respectively.  $^1\text{H}$  decoupling was realized with WALTZ-16 programme.  $^{19}\text{F}$  decoupling was performed with nested loops using 0.5 ms and 1 ms chirped adiabatic pulses with 80 kHz band with in order to desynchronize and minimize decoupling artifacts.

*Thermogravimetric analysis (TGA).* TGA of the purified copolymer was performed under air

using a TGA 51 apparatus from TA Instruments at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  from room temperature to  $580\text{ }^{\circ}\text{C}$ .

*Differential Scanning Calorimetry (DSC).* DSC analysis was conducted using a Netzsch DSC 200 F3 instrument under  $\text{N}_2$  atmosphere. The instrument was calibrated with noble metals and checked just before the analysis with an indium sample ( $T_m = 156\text{ }^{\circ}\text{C}$ ). The heating or cooling range of the sample was from  $-40\text{ }^{\circ}\text{C}$  to  $160\text{ }^{\circ}\text{C}$  at a scanning rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ , and the  $T_g$  was recorded in the second heating cycle to remove the previous thermal history of the polymer.  $T_g$  was measured by the inflection point in the heat capacity jump.

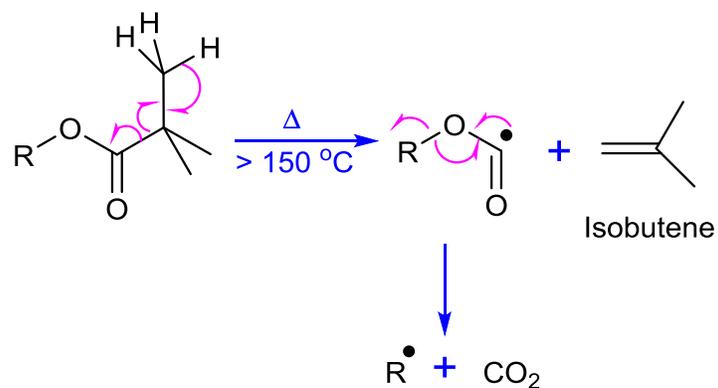
#### 4- Supplementary tables.

**Table S1.** Reaction conditions and results of nitroxide-mediated copolymerization of MAF-TBE with VAc using MAMA-SG1.<sup>a</sup>

entry	VAc/ MAF- TBE (mol%)	solvent	initiator	temp. (°C)	time (h)	VAc convn <sup>b</sup> (% / no. of moles)	MAF-TBE convn <sup>c</sup> (% / no. of moles)	total convn (%)	$M_{n,SEC}^d$ (g/mol)	$\bar{D}^d$
1	100/0	DMSO	-	40	24	0	-	0	-	-
2	0/100	DMSO	-	40	48	-	0	0	-	-
3	100/0	DMSO	-	65	24	0	-	0	-	-
4	0/100	DMSO	-	65	48	-	0	0	-	-
5	50/50	DMSO	-	40	0.5	3 / 0.24	3 / 0.24	3	1800	1.33
					1.0	8 / 0.64	7 / 0.56	8	3400	1.28
					2.0	13 / 1.00	12 / 0.92	12	4500	1.27
					4.0	19 / 1.52	19 / 1.52	19	5600	1.27
					8.0	28 / 2.24	27 / 2.16	28	7400	1.28
					16.0	50 / 4.00	49 / 3.92	50	13500	1.26
					24.0	63 / 5.04	62 / 4.96	63	17100	1.25
					24.0	63 / 5.04	62 / 4.96	63	17100	1.25
6	50/50	DMSO	-	65	0.08	37 / 2.96	36 / 2.88	37	8800	1.41
					0.16	39 / 3.12	40 / 3.20	40	9700	1.40
					0.33	42 / 3.36	43 / 3.44	43	10500	1.38
					0.5	45 / 3.60	46 / 3.68	46	11600	1.36
					1.0	50 / 4.00	48 / 3.84	49	12400	1.37
					2.0	55 / 4.40	54 / 4.32	55	13300	1.36
					4.0	60 / 4.80	60 / 4.80	60	14700	1.35
					24.0	65 / 5.20	64 / 5.12	65	15900	1.34
7	50/50	CH <sub>2</sub> Cl <sub>2</sub>	-	40	18.0	7 / 0.56	7 / 0.56	7	4500	1.55
					24.0	8 / 0.64	8 / 0.64	8	4900	1.53
					36.0	9 / 0.72	9 / 0.72	9	5100	1.60

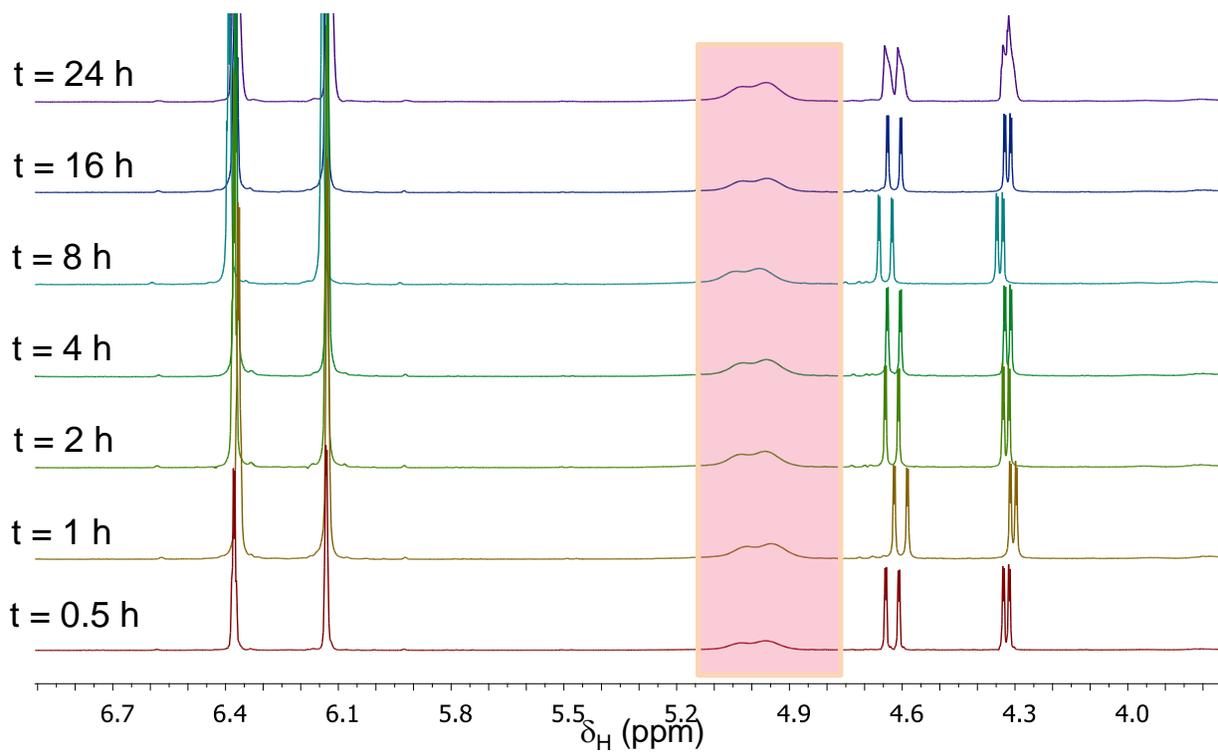
<sup>a</sup>Conditions: [VAc]<sub>0</sub>/[MAF-TBE]<sub>0</sub>/[MAMA-SG1]<sub>0</sub> = 90/90/1. <sup>b</sup>determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>determined by <sup>19</sup>F NMR spectroscopy. <sup>d</sup>determined by SEC in DMF (containing 0.1 wt% LiCl), system was calibrated using poly(methyl methacrylate) standards.

## 5- Supplementary schemes.

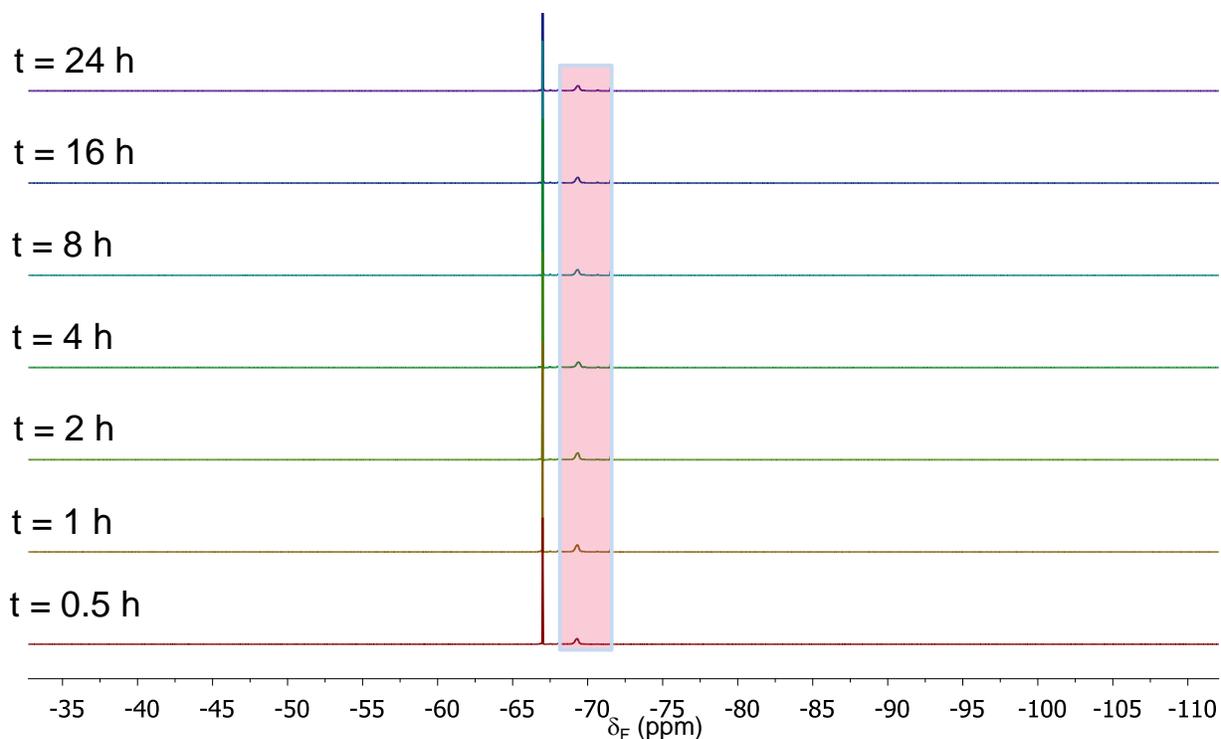


**Scheme S1.** Degradation of *tert*-butyl ester groups of the poly(VAc-*alt*-MAF-TBE) alternating copolymers upon heating under air above  $150\text{ }^{\circ}\text{C}$ .

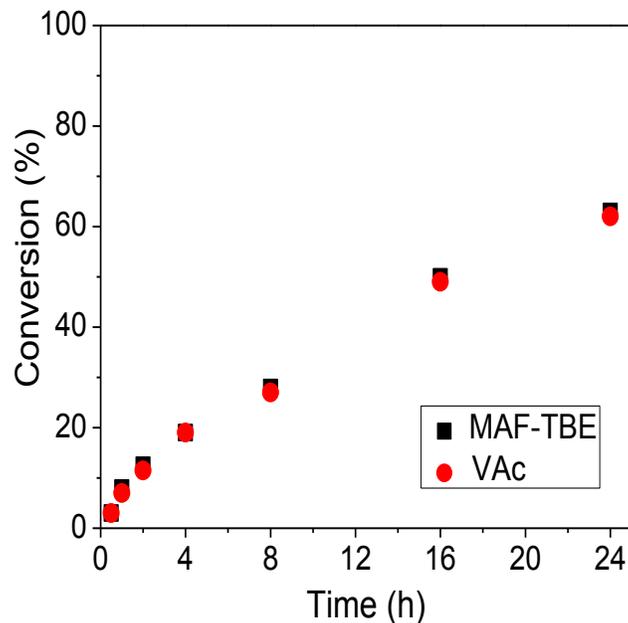
## 6- Supplementary figures.



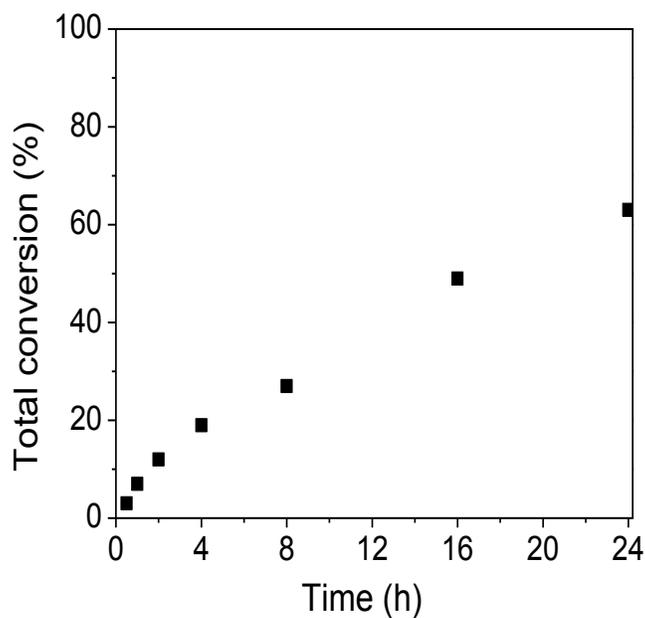
**Figure S1.** Time evolution of the  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) during the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at  $40^\circ\text{C}$  in DMSO (entry 5, Table S1).



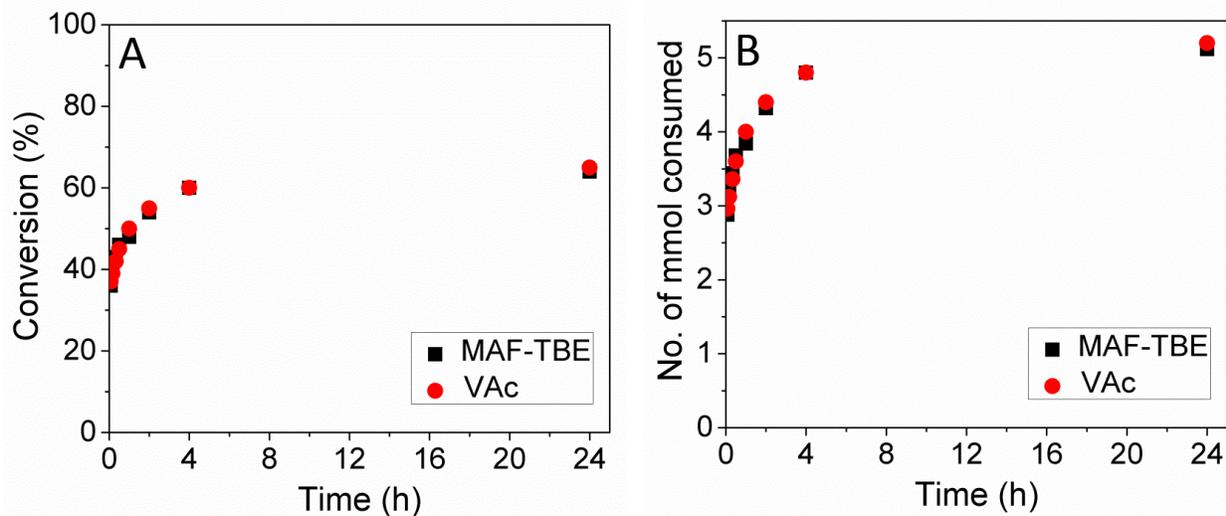
**Figure S2.** Time evolution of the  $^{19}\text{F}$  NMR spectra ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) during the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at  $40^\circ\text{C}$  in DMSO (entry 5, Table S1). The signals in the pink shade are assigned to  $\text{CF}_3$  groups in the poly(VAc-*alt*-MAF-TBE) copolymer.



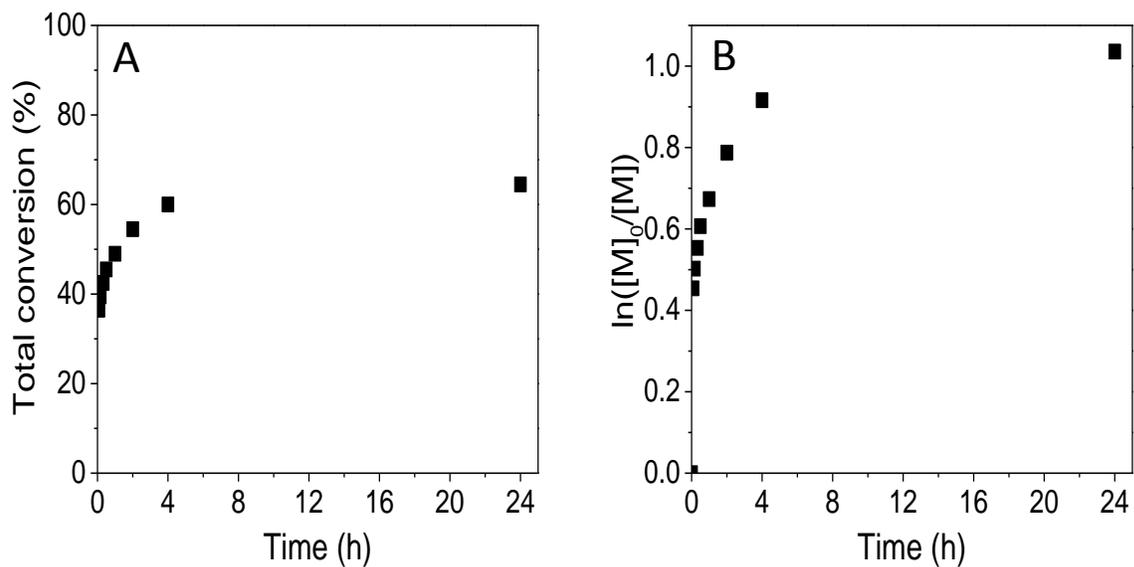
**Figure S3.** % Conversion vs. time plot of VAc and MAF-TBE during the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[VAc]_0/[MAF-TBE]_0/[MAMA-SG1]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1).



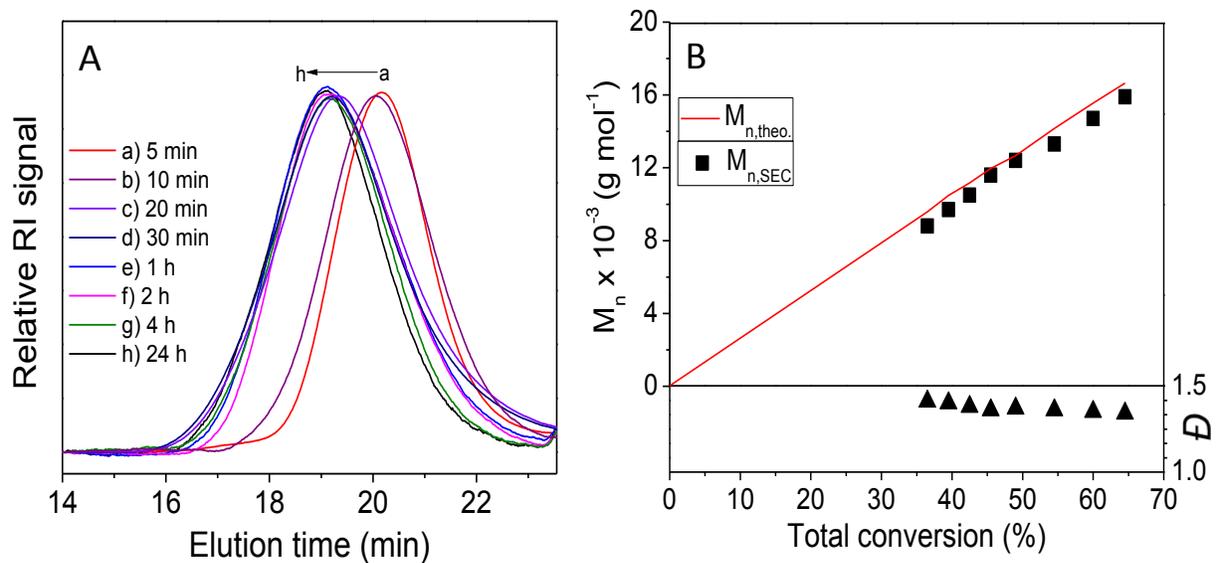
**Figure S4.** % Total conversion vs. time plot of VAc and MAF-TBE during the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[VAc]_0/[MAF-TBE]_0/[MAMA-SG1]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1).



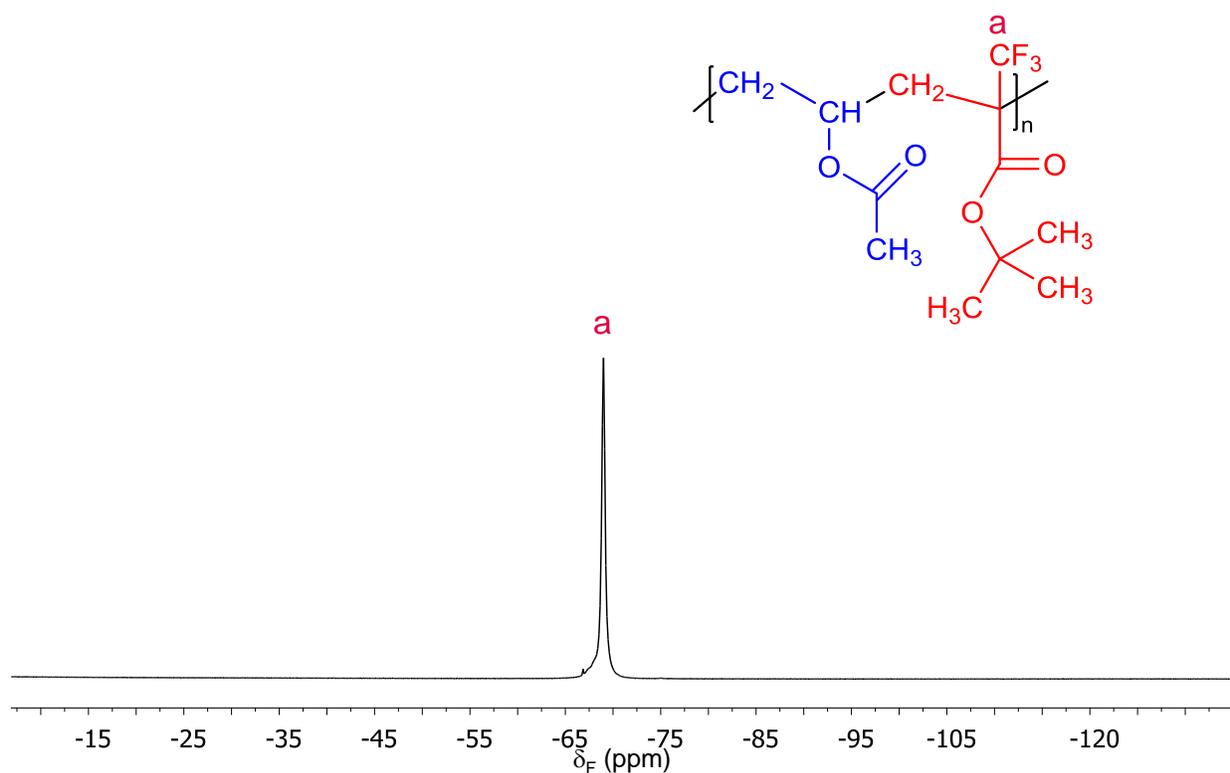
**Figure S5.** Conversion vs. time plot of VAc and MAF-TBE in terms of their % conversion (A) and no. of mmol consumed (B) during the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[VAc]_0/[MAF-TBE]_0/[MAMA-SG1]_0 = 90/90/1$ ) at 65 °C in DMSO (entry 6, Table S1).



**Figure S6.** % Total conversion vs. time (A) and  $\ln([M]_0/[M])$  vs. time (B) plots for the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[VAc]_0/[MAF-TBE]_0/[MAMA-SG1]_0 = 90/90/1$ ) at 65 °C in DMSO (entry 6, Table S1).

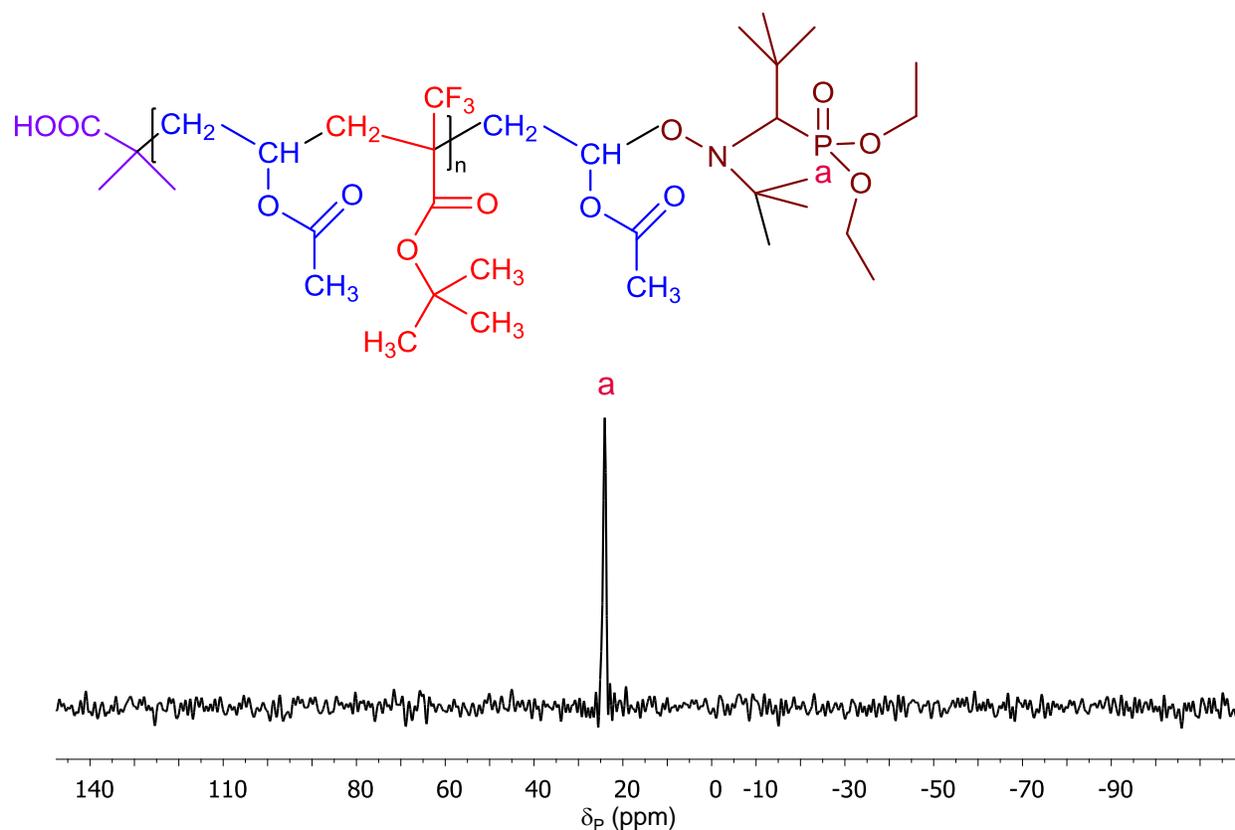


**Figure S7.** (A) Evolution of SEC traces vs. time and (B) evolution of  $M_n$  and  $D$  as a function of the total conversion for the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at 65 °C in DMSO (entry 6, Table S1).



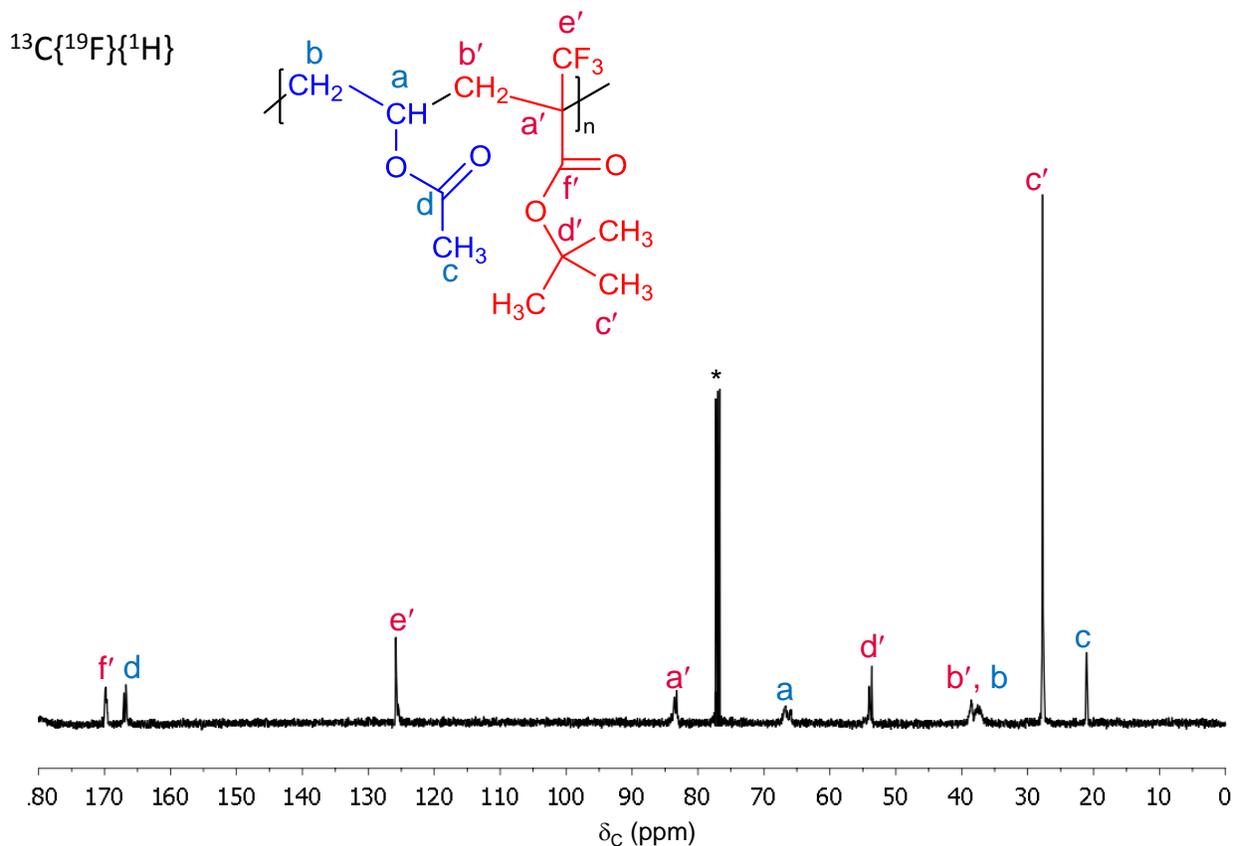
**Figure S8.** Representative  $^{19}\text{F}$  NMR spectrum of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1), recorded in  $\text{CDCl}_3$  at 20 °C.

$^{19}\text{F}$  NMR spectrum (Figure S8) reveals the characteristic signal centered at ca. -69 ppm attributed to the fluorine atoms in  $-\text{CF}_3$  of MAF-TBE in the alternating copolymer.<sup>2-4</sup>



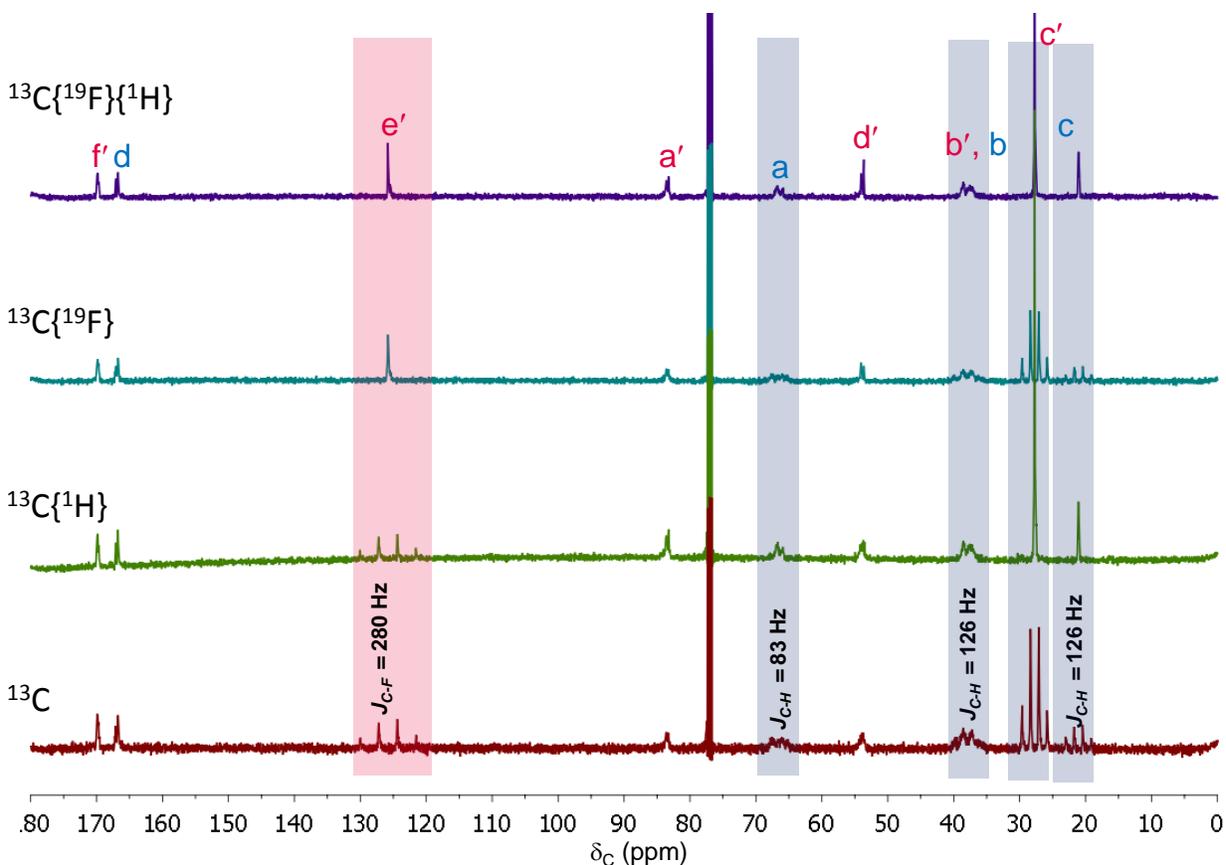
**Figure S9.** Representative  $^{31}\text{P}$  NMR spectrum of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1), recorded in  $\text{CDCl}_3$  at 20 °C.

$^{31}\text{P}$  NMR spectrum (Figure S9) reveals the characteristic signal centered at ca. 25 ppm attributed to the phosphorous atom in the  $\omega$ -chain end of the copolymer bearing SG1 fragment.



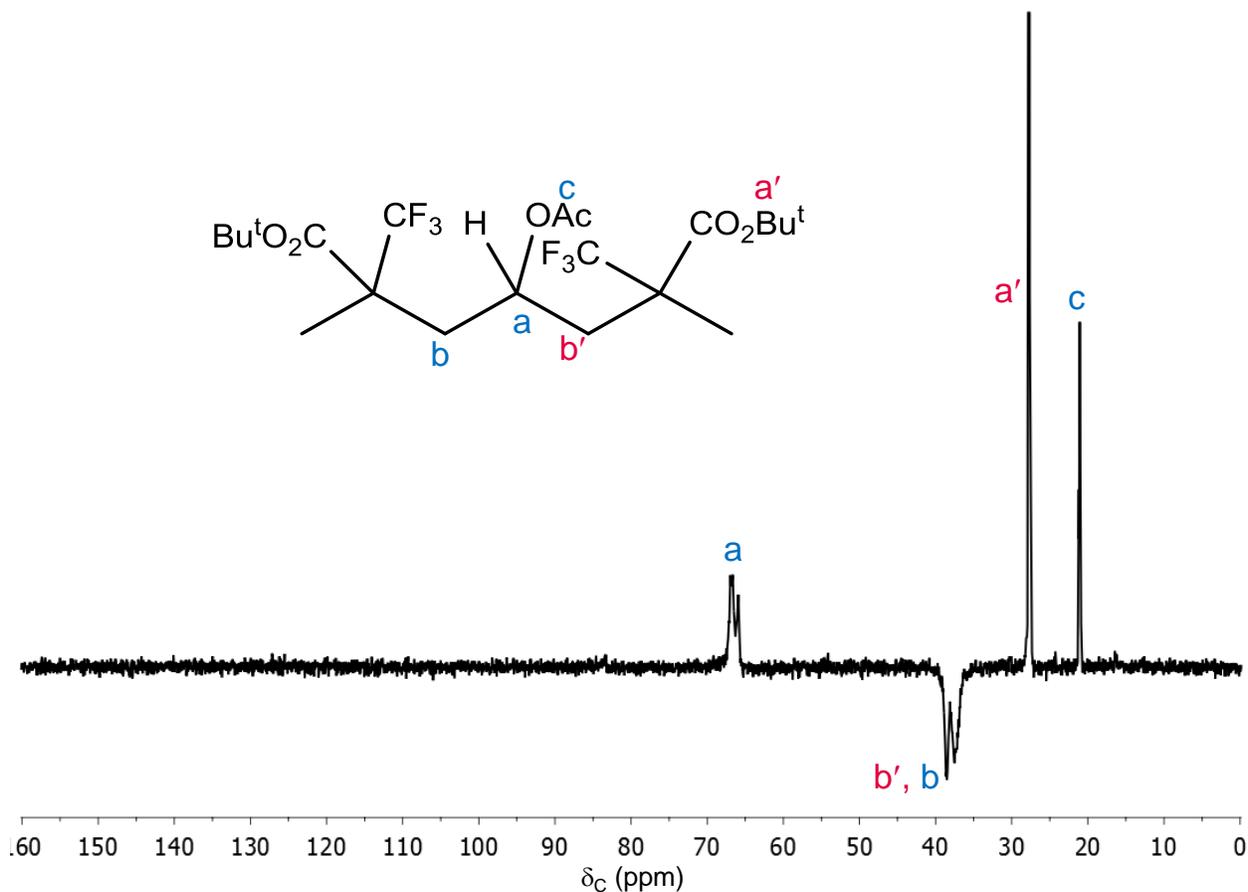
**Figure S10.** Representative  $^{13}\text{C}\{^1\text{H}\}\{^{19}\text{F}\}$  NMR ( $^1\text{H}$  and  $^{19}\text{F}$  double decoupled) spectrum of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1), recorded in  $\text{CDCl}_3$  at 20 °C.

$^{13}\text{C}\{^1\text{H}\}\{^{19}\text{F}\}$  NMR ( $^1\text{H}$  and  $^{19}\text{F}$  double decoupled) spectrum analysis (Figure S10) enabled to confirm the position of the carbon atoms of the poly(VAc-*alt*-MAF-TBE) alternating copolymer. The origin of two signals centered at ca. 67.5 ppm corresponding to the  $-\text{CH}$  of VAc in the VAc-MAF-TBE alternating dyad might be attributed to the tacticity of the copolymer. Two distinct signals centered at 166.8 and 169.9 ppm were assigned to the carbonyl carbon in VAc and MAF-TBE, respectively.



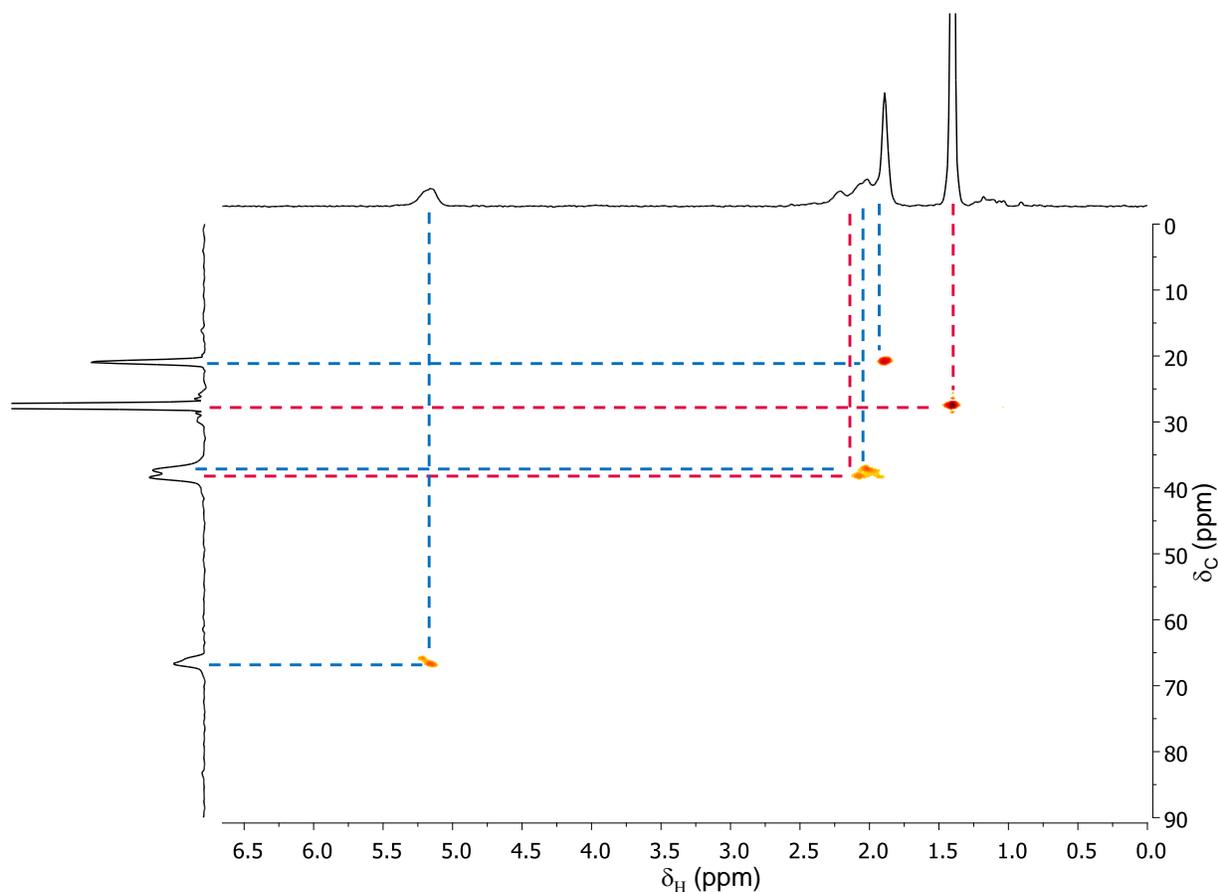
**Figure S11.** Comparison of  $^{13}\text{C}$  NMR spectrum (from bottom to top: without any decoupling, with  $^1\text{H}$  decoupling, with  $^{19}\text{F}$  decoupling and with  $^1\text{H}$  and  $^{19}\text{F}$  double decoupling) of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1), recorded in  $\text{CDCl}_3$  at 20 °C.

Comparison of  $^{13}\text{C}$  NMR spectra with or without  $^1\text{H}$  and  $^{19}\text{F}$  decoupling (Figure S11) enables us to confirm the number of H or F atoms attach to the carbon atoms the poly(VAc-*alt*-MAF-TBE) alternating copolymer. This analysis further confirms the structure of the alternating copolymer. Interestingly, both carbonyl groups in VAc and MAF-TBE are represented by two distinct signals centered at ca. 166.8 and 169.9 ppm, respectively.



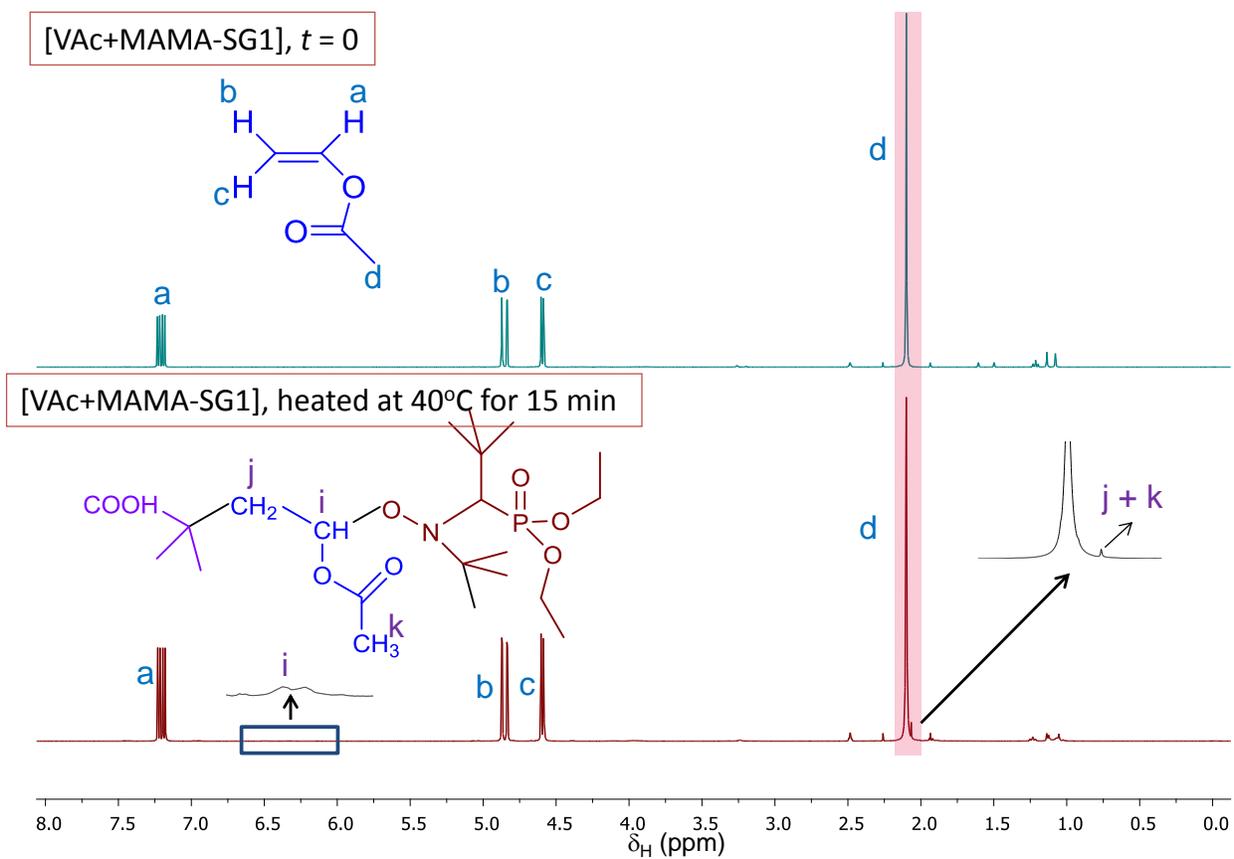
**Figure S12.** Representative Distortionless Enhancement by Polarisation Transfer-135 (DEPT-135)  $^{13}\text{C}$  NMR spectrum of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1), recorded in  $\text{CDCl}_3$  at 20 °C.

DEPT-135 NMR ( $\text{CH}_3/\text{CH}$  positive,  $\text{CH}_2$  negative) spectrum (Figure S12) enables us to confirm the position of the carbon atoms of the poly(VAc-*alt*-MAF-TBE) alternating copolymer. The origin of two signals corresponding to the  $-\text{CH}$  of VAc in the VAc-MAF-TBE alternating dyad might be attributed to the presence of stereocenters in every monomer unit.

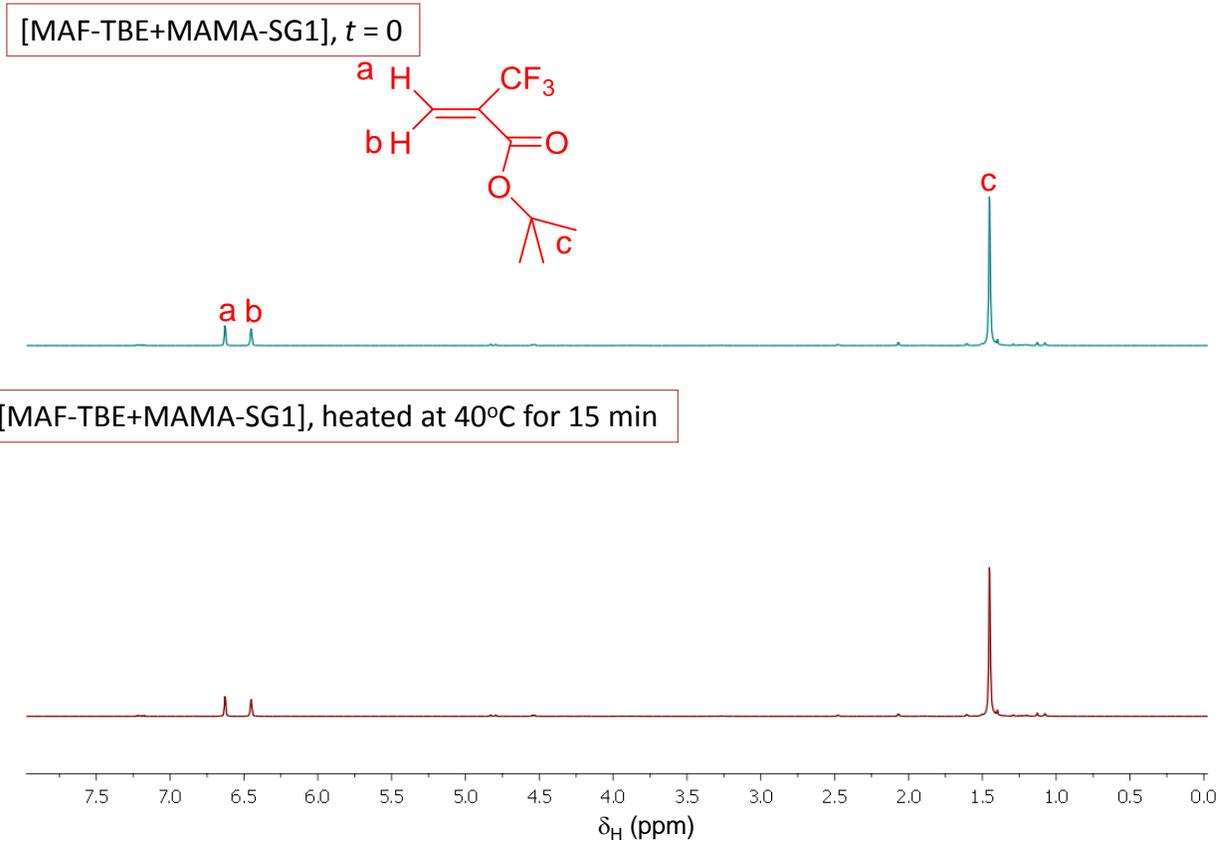


**Figure S13.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[\text{VAc}]_0/[\text{MAF-TBE}]_0/[\text{MAMA-SG1}]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1), recorded in  $\text{CDCl}_3$  at 20 °C. Multiple signals for *a* is caused by the tacticity. Horizontal axis:  $^1\text{H}$  NMR; Vertical axis:  $^{13}\text{C}$  NMR. The signals assigned to VAc are highlighted with the blue dashed lines and that for the MAF-TBE by red dashed line.

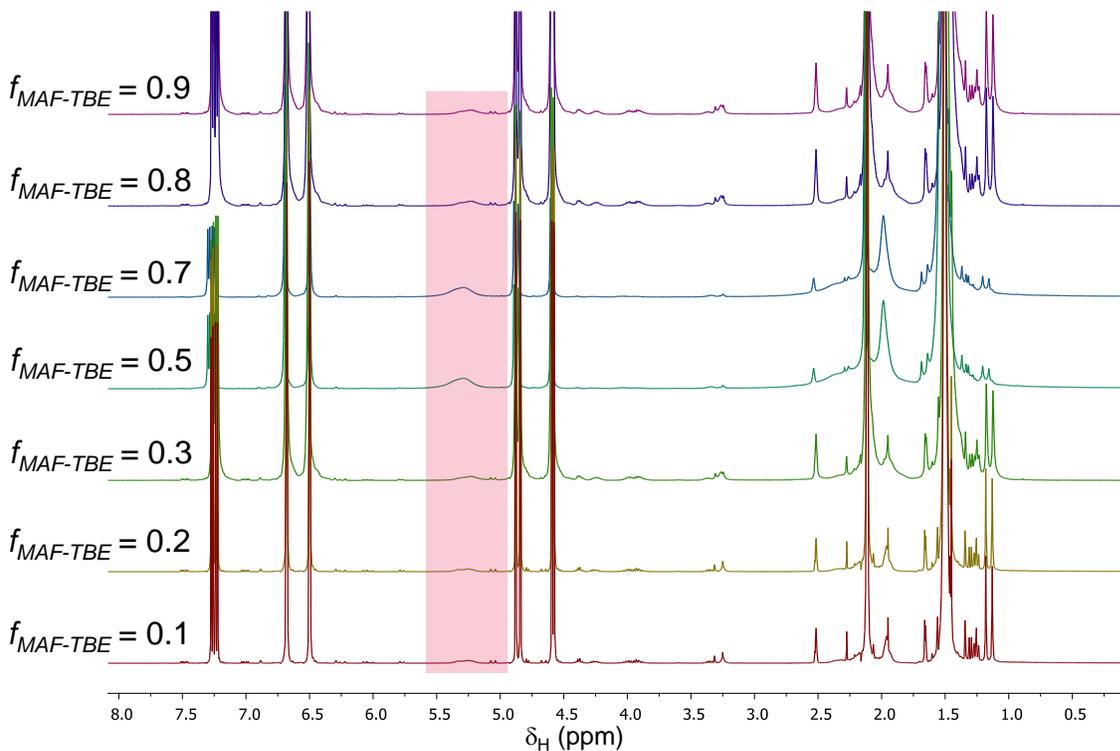
The  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum (Figure S13) of the poly(VAc-*alt*-MAF-TBE) alternating copolymer revealed four correlations between protons and carbon atoms: (i)  $-\text{C}(\text{CH}_3)_3$  protons of MAF-TBE ( $\delta_{\text{H}} = 1.40$  ppm) with carbon C(*a'*) at  $\delta_{\text{C}} = 27.75$  ppm, (ii)  $-\text{OCOCH}_3$  protons ( $\delta_{\text{H}} = 1.90$  ppm) with carbon C(*c*) at  $\delta_{\text{C}} = 20.83$  ppm, (iii)  $-\text{CH}_2$  protons of VAc and MAF-TBE ( $\delta_{\text{H}} = 2.0$  and 2.21, respectively) with carbons C(*b*, *b'*) at  $\delta_{\text{C}} = 37.32$  and 38.44 ppm, respectively, and (iv) the  $-\text{CH}_2\text{C}(\text{CF}_3)(\text{COO}^t\text{Bu})-\text{CH}_2\text{CH}(\text{OCOCH}_3)-\text{CH}_2\text{C}(\text{CF}_3)(\text{COO}^t\text{Bu})-$ protons ( $\delta_{\text{H}} = 5.10$  ppm) with carbon at C(*a*)  $\delta_{\text{C}} = 66.62$  ppm



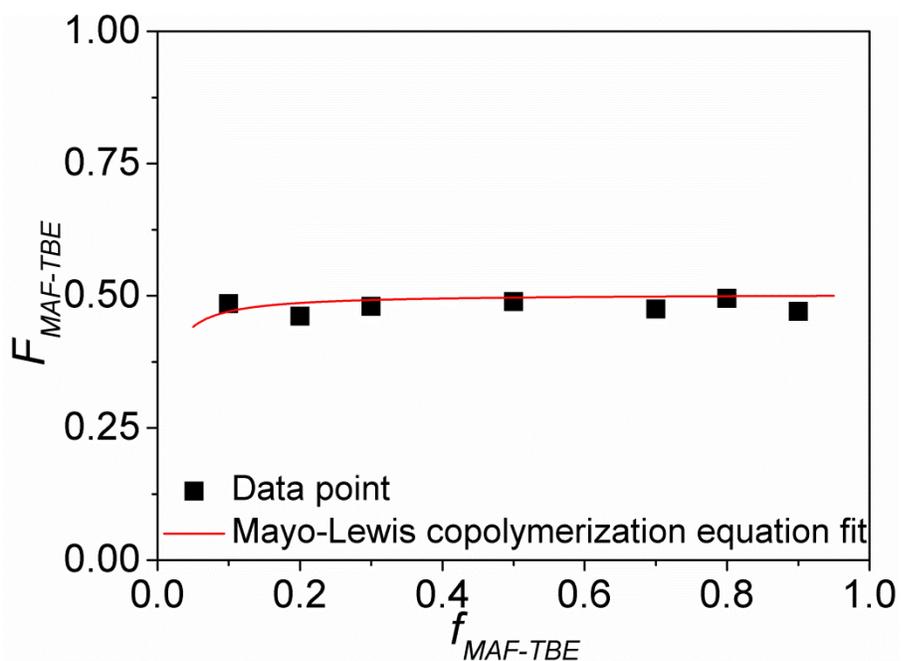
**Figure S14.**  $^1\text{H}$  NMR spectra of [VAc+MAMA-SG1], recorded at  $40^\circ\text{C}$  in  $\text{DMSO-}d_6$  during *in-situ* NMR experiment.



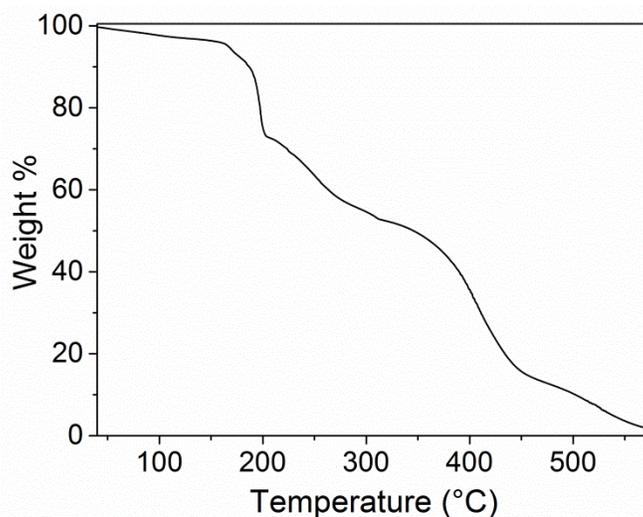
**Figure S15.**  $^1\text{H}$  NMR spectra of [MAF-TBE+MAMA-SG1], recorded at 40 °C in  $\text{DMSO-}d_6$  during *in-situ* NMR experiment.



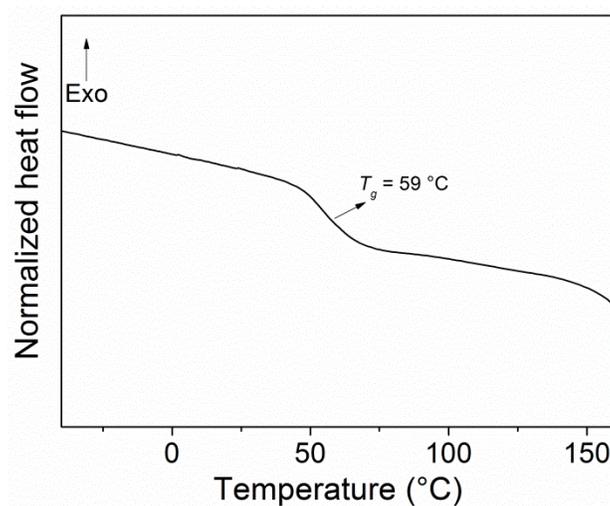
**Figure S16.**  $^1\text{H}$  NMR spectra during in situ NMR experiment for the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 in DMSO at  $40^\circ\text{C}$ .



**Figure S17.** Evolution of copolymer- monomer composition curve for the nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 in DMSO at  $40^\circ\text{C}$ .



**Figure S18.** TGA thermogram of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[VAc]_0/[MAF-TBE]_0/[MAMA-SG1]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1, polymerization time = 24 h), heated at 10 °C min<sup>-1</sup> under air.



**Figure S19.** DSC thermogram of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by nitroxide-mediated alternating copolymerization of VAc with MAF-TBE using MAMA-SG1 ( $[VAc]_0/[MAF-TBE]_0/[MAMA-SG1]_0 = 90/90/1$ ) at 40 °C in DMSO (entry 5, Table S1, polymerization time = 24 h).

## 7- References

- (1) Buback, M.; Feldermann, A.; Barner-Kowollik, C.; Lacík, I., *Propagation Rate Coefficients of Acrylate–Methacrylate Free-Radical Bulk Copolymerizations. Macromolecules* **2001**, *34*, 5439-5448.
- (2) Patil, Y.; Ono, T.; Ameduri, B., *Innovative Trifluoromethyl Radical from Persistent Radical as Efficient Initiator for the Radical Copolymerization of Vinylidene Fluoride with tert-Butyl-Trifluoromethacrylate. ACS Macro Lett.* **2012**, *1*, 315-320.
- (3) Patil, Y.; Ameduri, B., *Advances in the (Co)polymerization of Alkyl 2-Trifluoromethacrylates and 2-(Trifluoromethyl)acrylic Acid. Prog. Polym. Sci.* **2013**, *38*, 703-739.
- (4) Patil, Y.; Ameduri, B., *First RAFT/MADIX radical copolymerization of tert-butyl 2-trifluoromethacrylate with vinylidene fluoride controlled by xanthate. Polym. Chem.* **2013**, *4*, 2783-2799.