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Electronic Supplementary Information

Syntheses of 2-(trifluoromethyl)acrylate-containing Block Copolymers via RAFT Polymerization using a Universal Chain Transfer Agent

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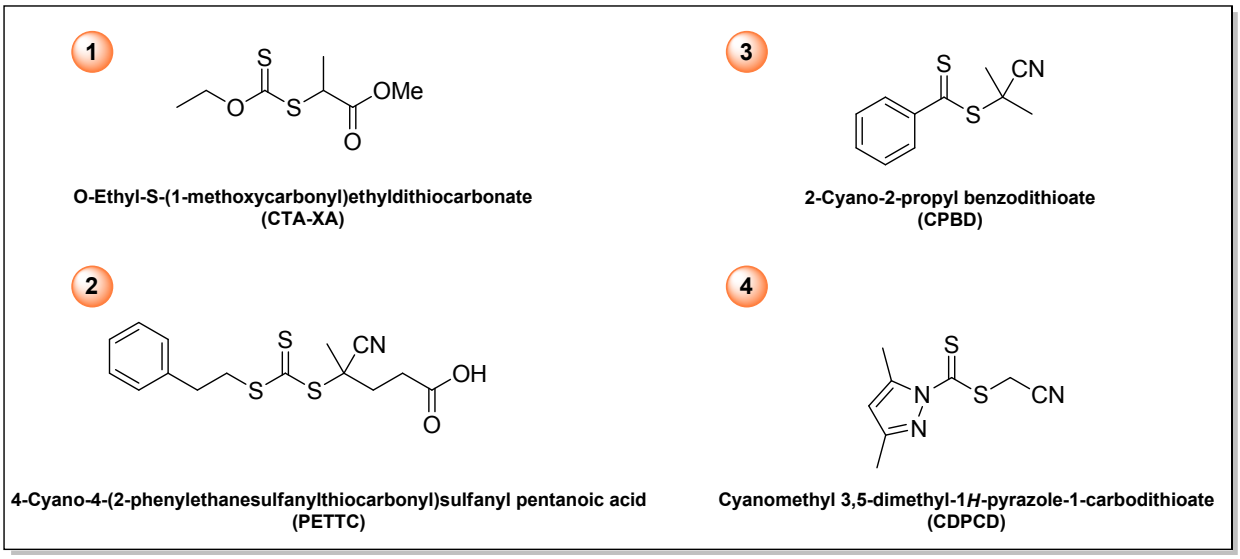
Table S1 Reaction conditions and results of the RAFT copolymerizations of MAF-TBE and VAc in bulk at 40 °C in the presence of cyanomethyl-3,5-dimethyl 1H-pyrazole-1-carbodithioate (CDPCD).[a]

entry	time (h)	VAc conv[b] (% / no. of moles)	MAF-TBE conv[c] (% / no. of moles)	total conv (%)	$M_{n,SEC}$[d] (g/mol)	$Đ$[d]
1	1	7 / 2.8	6 / 2.4	7	1300	1.31
2	2	13 / 5.2	13 / 5.2	13	1900	1.25
3	3	20 / 8.0	21 / 8.4	21	2700	1.21
4	4	31 / 12.4	30 / 12.0	31	3500	1.18
5	5	40 / 16.0	40 / 16.0	40	4200	1.17
6	6	45 / 18.0	44 / 17.6	45	4800	1.17
7	7	49 / 19.6	50 / 20.0	50	5400	1.16
8	15	66 / 26.4	66 / 26.4	66	6600	1.15
9	24	86 / 34.4	85 / 34.0	86	7900	1.13

[a]*Reaction Conditions:* $[VAc]_0/[MAF\text{-}TBE]_0/[CTA]_0/[V\text{-}70]_0$ = 15/15/1/0.1. [b]determined by ^1H NMR spectroscopy. [c]determined by ^{19}F NMR spectroscopy. [d]determined by SEC in DMF (containing 0.1 wt% LiCl), system was calibrated using PMMA standards.



Scheme S1 Chemical structures of the CTAs employed in this study.

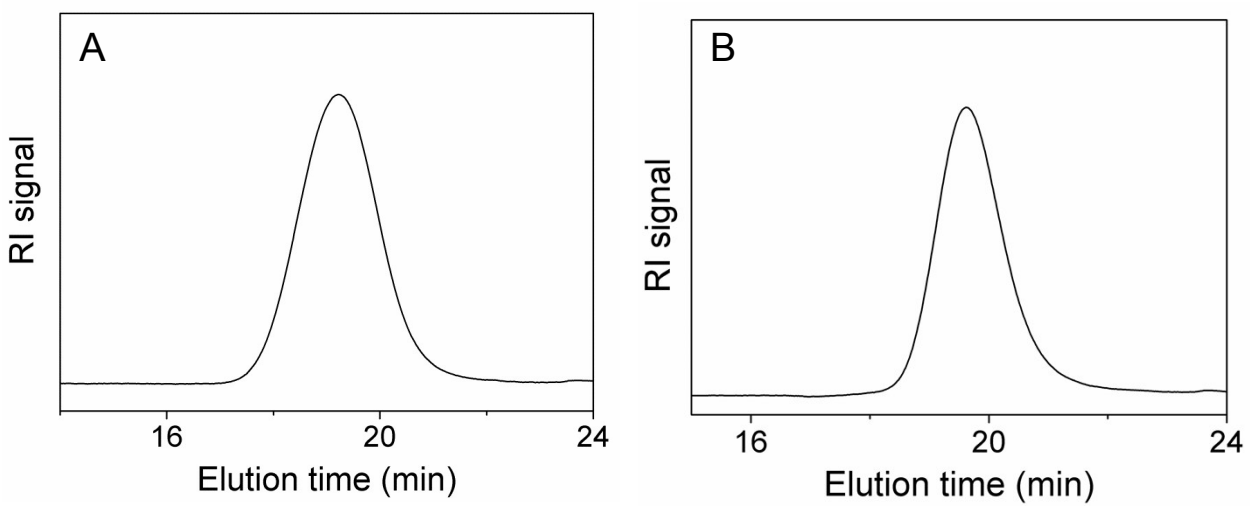


Figure. S1 SEC traces of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by RAFT copolymerization of VAc and MAF-TBE carried out at 40 °C in bulk using V-70 as initiator in the presence of: (A) CTA-XA (P1, Table 1) and (B) cyanomethyl-3,5-dimethyl 1H-pyrazole-1-carbodithioate (CDPCD) (P4, Table 1).

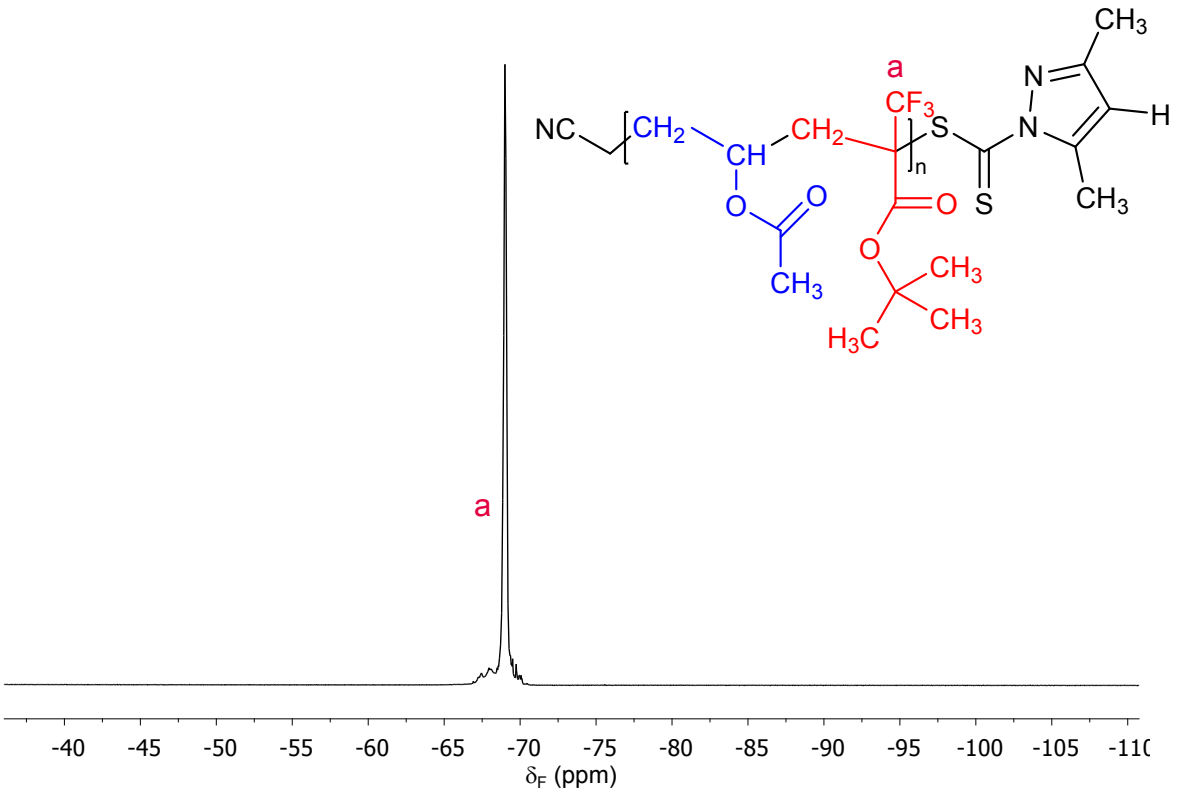


Figure. S2 ^{19}F NMR spectrum (recorded in $CDCl_3$ at 20 °C) of poly(VAc-*alt*-MAF-TBE) alternating copolymer prepared by RAFT copolymerization of VAc and MAF-TBE ($f_{MAF\text{-}TBE}$ = 0.5) carried out at 40 °C in bulk using V-70 as initiator in the presence of cyanomethyl-3,5-dimethyl 1H-pyrazole-1-carbodithioate (CDPCD) (P4, Table 1).

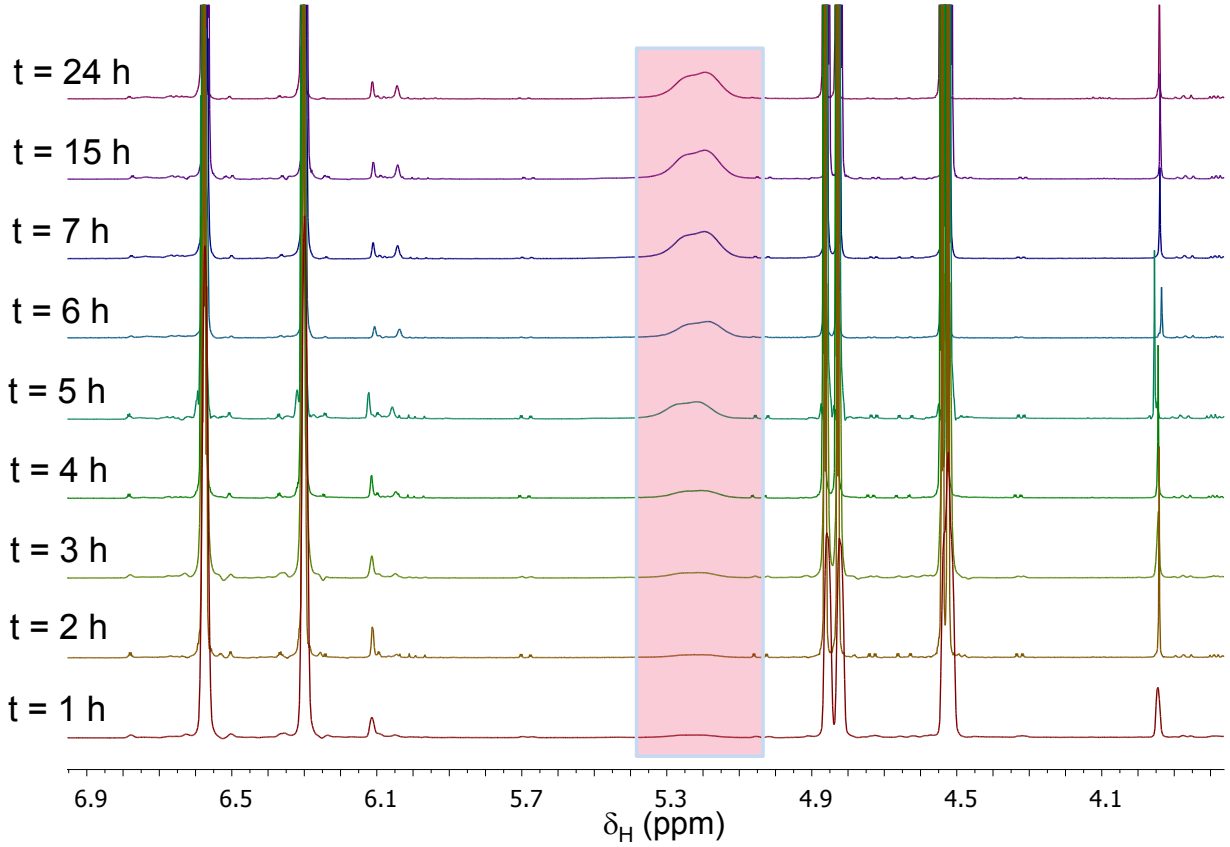


Figure. S3 Evolution of the ^{1}H NMR spectra (recorded in $CDCl_3$, 20 °C) during the RAFT copolymerization of VAc and MAF-TBE ($f_{MAF\text{-}TBE}$ = 0.5) carried out at 40 °C in bulk using V-70 as initiator in the presence of cyanomethyl-3,5-dimethyl 1H-pyrazole-1-carbodithioate (CDPCD) (Table S1).

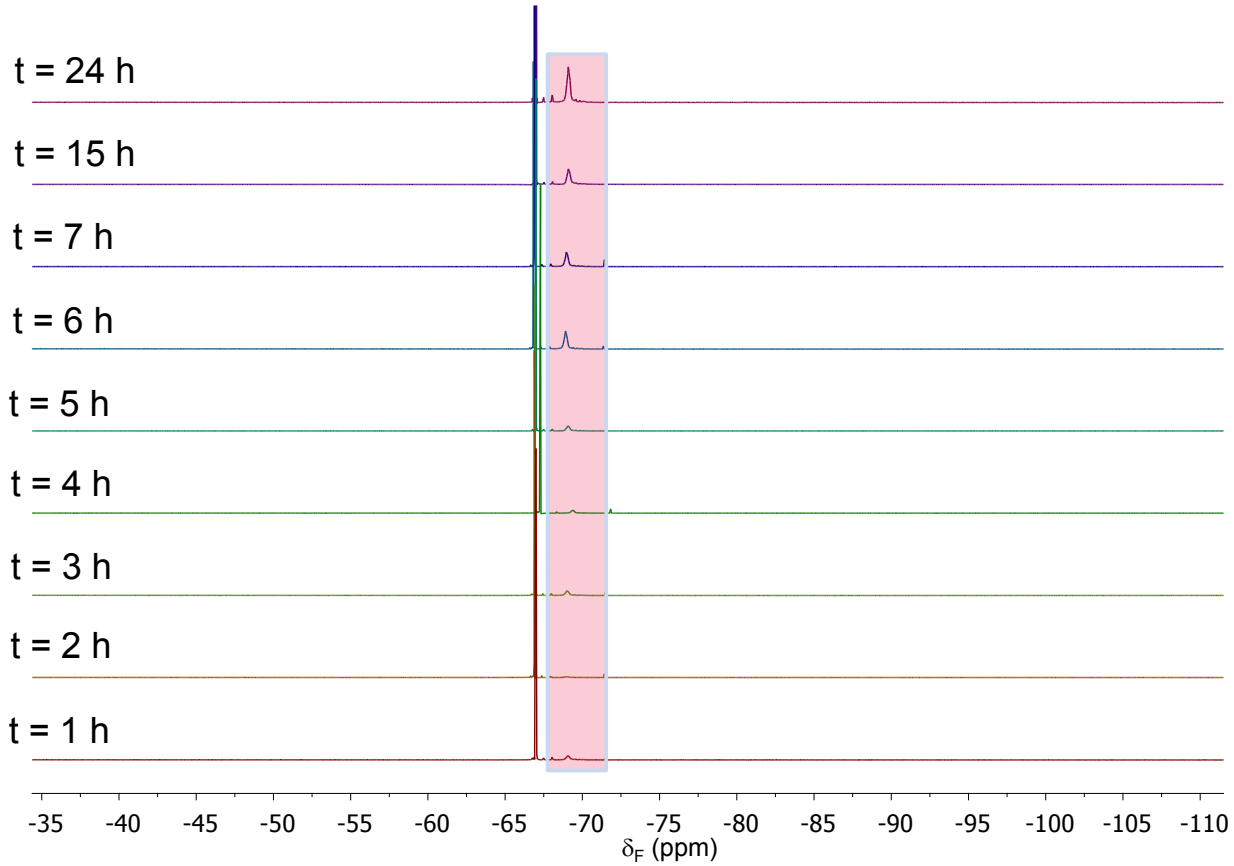


Figure. S4 Evolution of the ^{19}F NMR spectra ($CDCl_3$, 20 °C) during the RAFT copolymerization of VAc and MAF-TBE ($f_{MAF\text{-}TBE}$ = 0.5) carried out at 40 °C in bulk using V-70 as initiator in the presence of cyanomethyl-3,5-dimethyl 1H-pyrazole-1-carbodithioate (CDPCD) (Table S1).

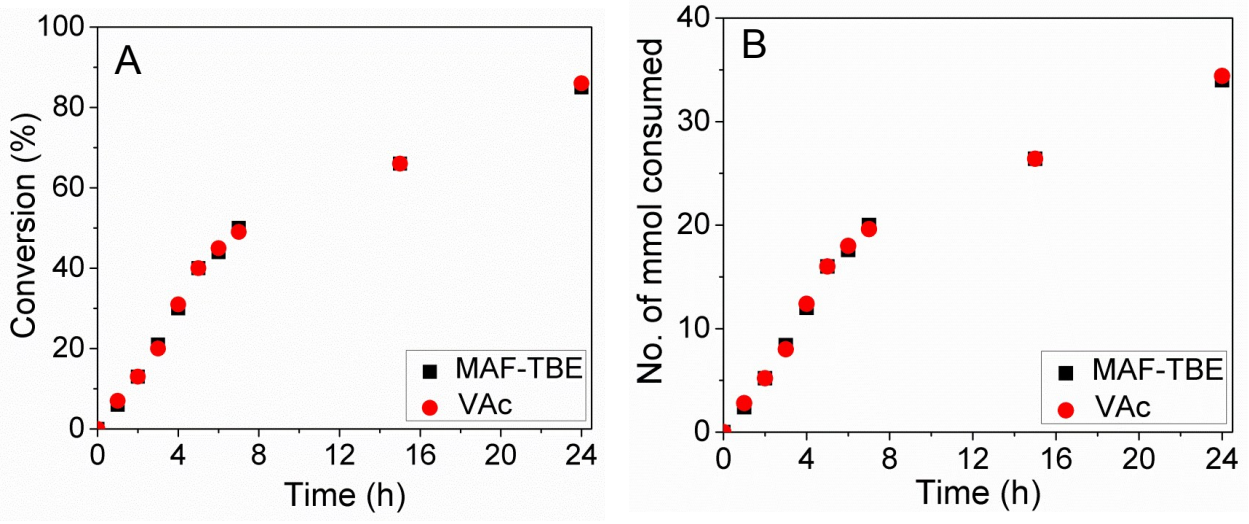


Figure. S5 Conversion *vs* time plots of VAc and MAF-TBE during their RAFT copolymerization ($f_{MAF\text{-}TBE}$ = 0.5) carried out at 40 °C in bulk using V-70 as initiator in the presence of CDPCD: (A) conversion expressed in %, (B), conversion expressed in amount of mmol consumed.

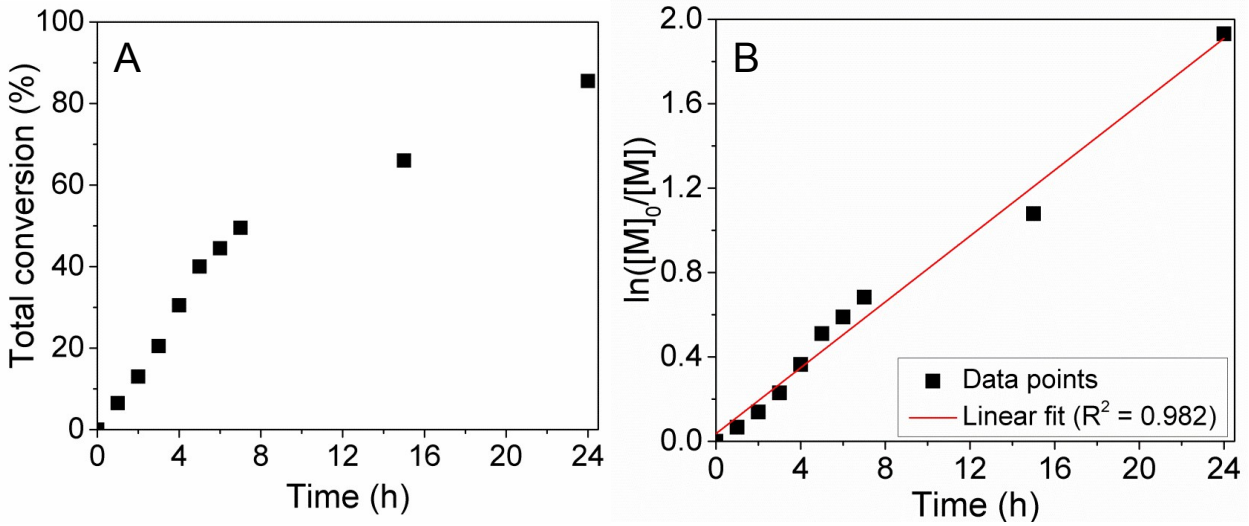


Figure. S6 (A) Total conversion *vs* time and (B) $\ln[M]_0/[M]$ *vs* time plot for the RAFT copolymerization of VAc and MAF-TBE ($f_{MAF\text{-}TBE}$ = 0.5) carried out at 40 °C in bulk using V-70 as initiator in the presence of CDPCD (Table S1).

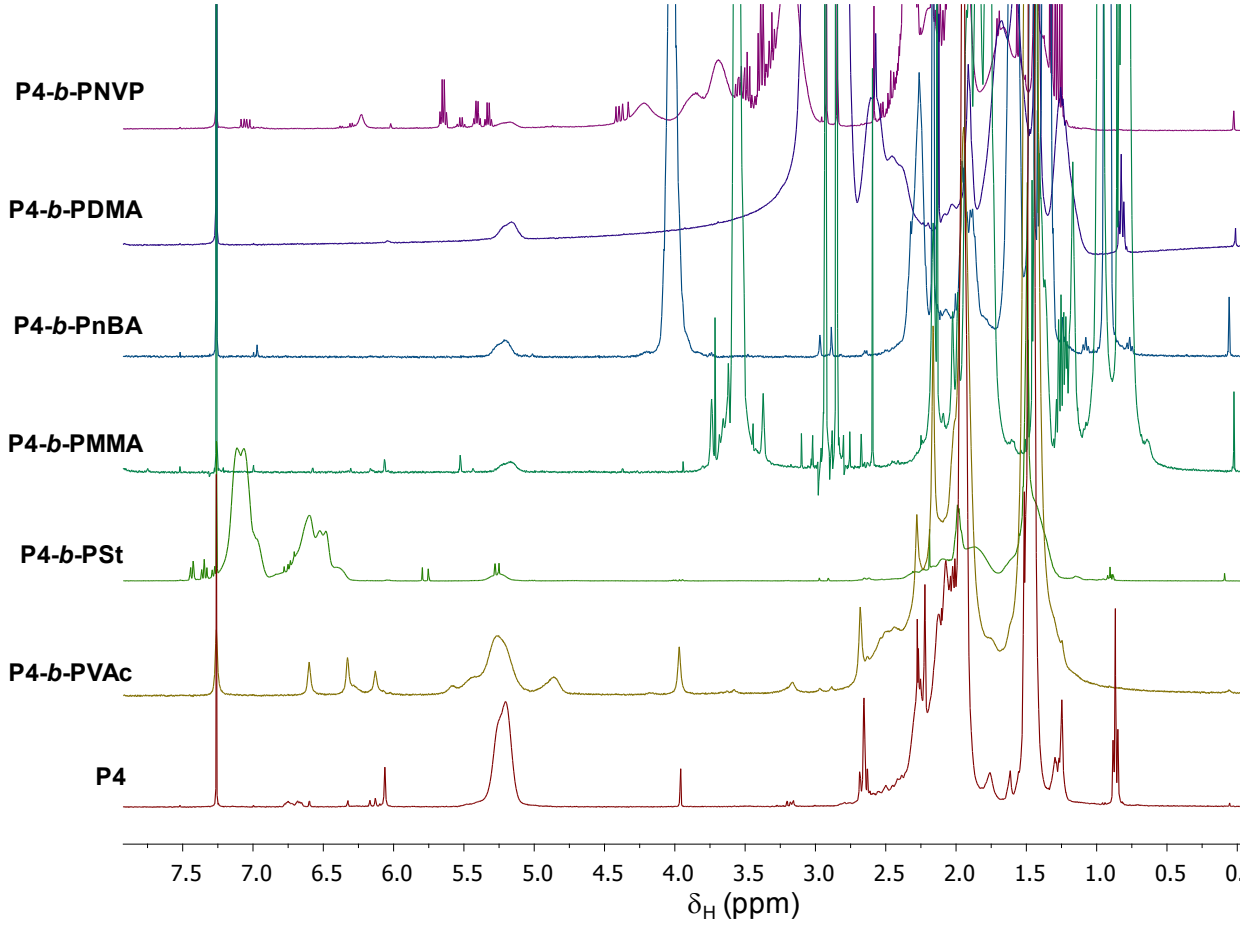


Figure. S7 Expansion of the 0 to 7.5 ppm region of the ^{1}H NMR spectra of poly(VAc-*alt*-MAF-TBE)-DPCD (P4, Table 1) and the derived block copolymers (P5-P10, Table 1), recorded in $CDCl_3$ at 20 °C.

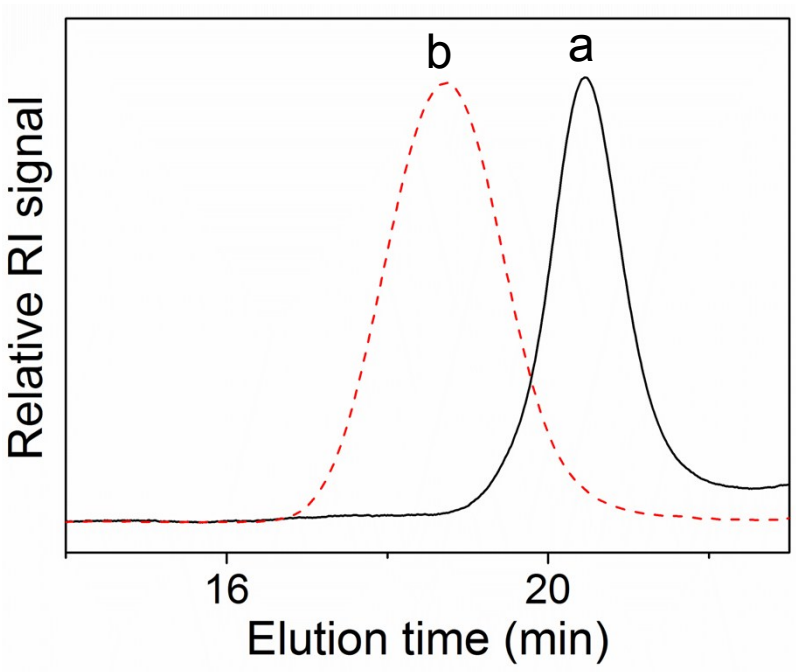


Figure. S8 SEC traces of (a) PVAc-DPCD (P11, Table 1) and (b) the resulting PVAc-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P17, Table 1).

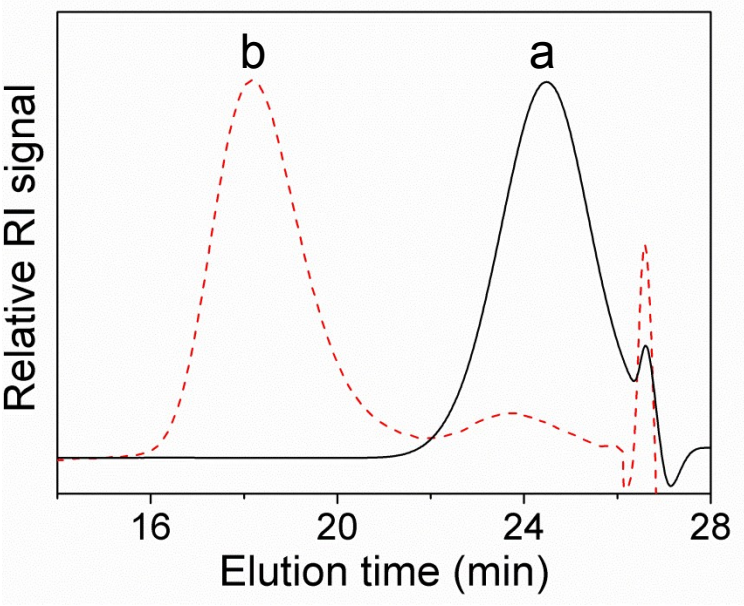


Figure. S9 SEC traces of (a) PSt-DPCD (P12, Table 1) and (b) the derived PSt-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P18, Table 1).

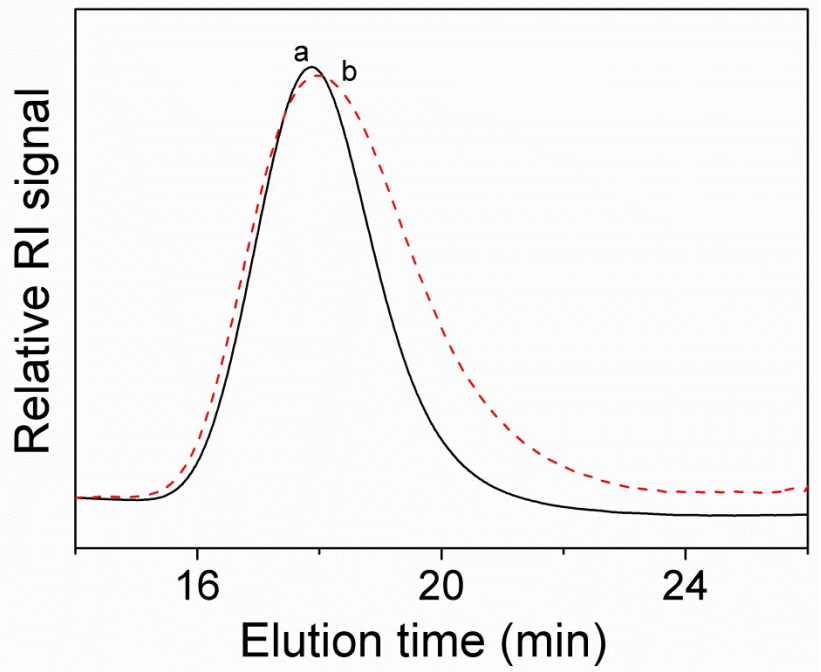


Figure. S10 SEC traces of (a) PMMA-DPCD (P13, Table 1) and (b) the derived PMMA-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P19, Table 1).

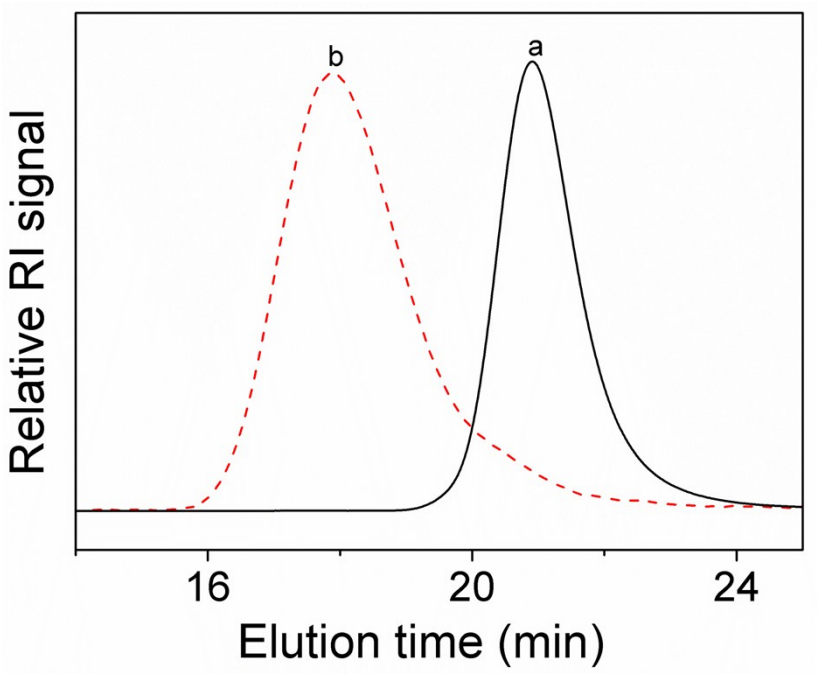


Figure. S11 SEC traces of (a) PnBA-DPCD (P14, Table 1) and (b) the derived PnBA-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P20, Table 1).

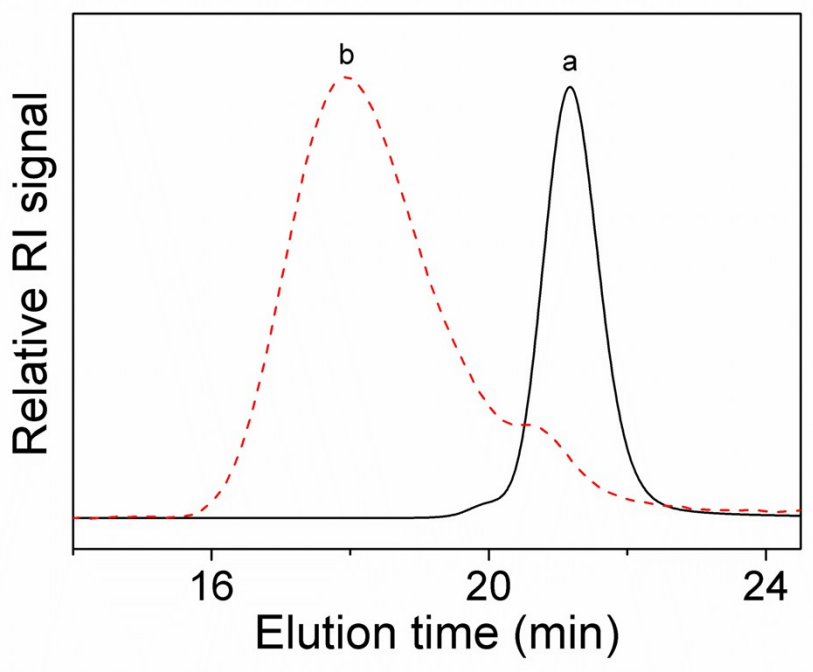


Figure. S12 SEC traces of (a) PDMA-DPCD (P15, Table 1) and (b) the derived PDMA-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P21, Table 1).

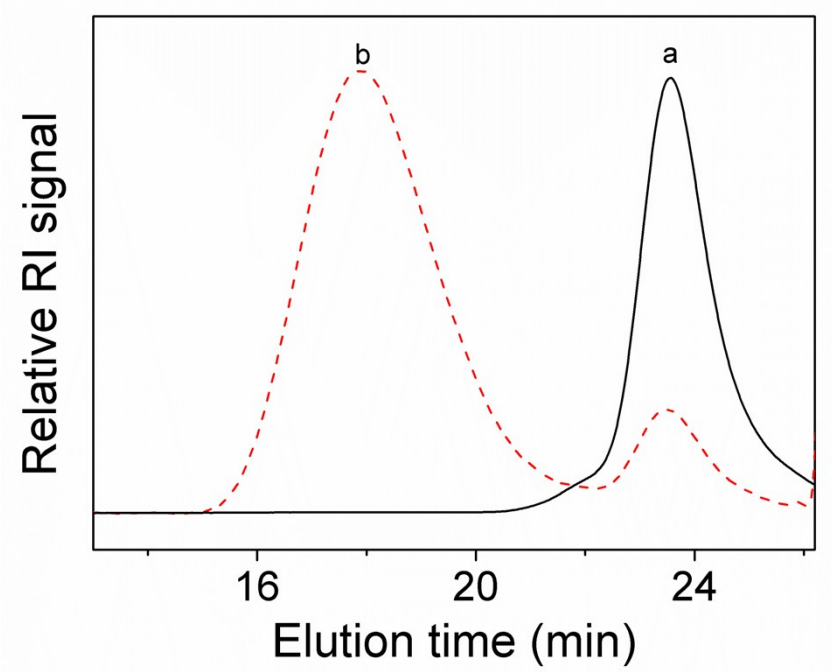


Figure. S13 SEC traces of (a) PNVP-DPCD (P16, Table 1) and (b) the derived PNVP-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P22, Table 1).

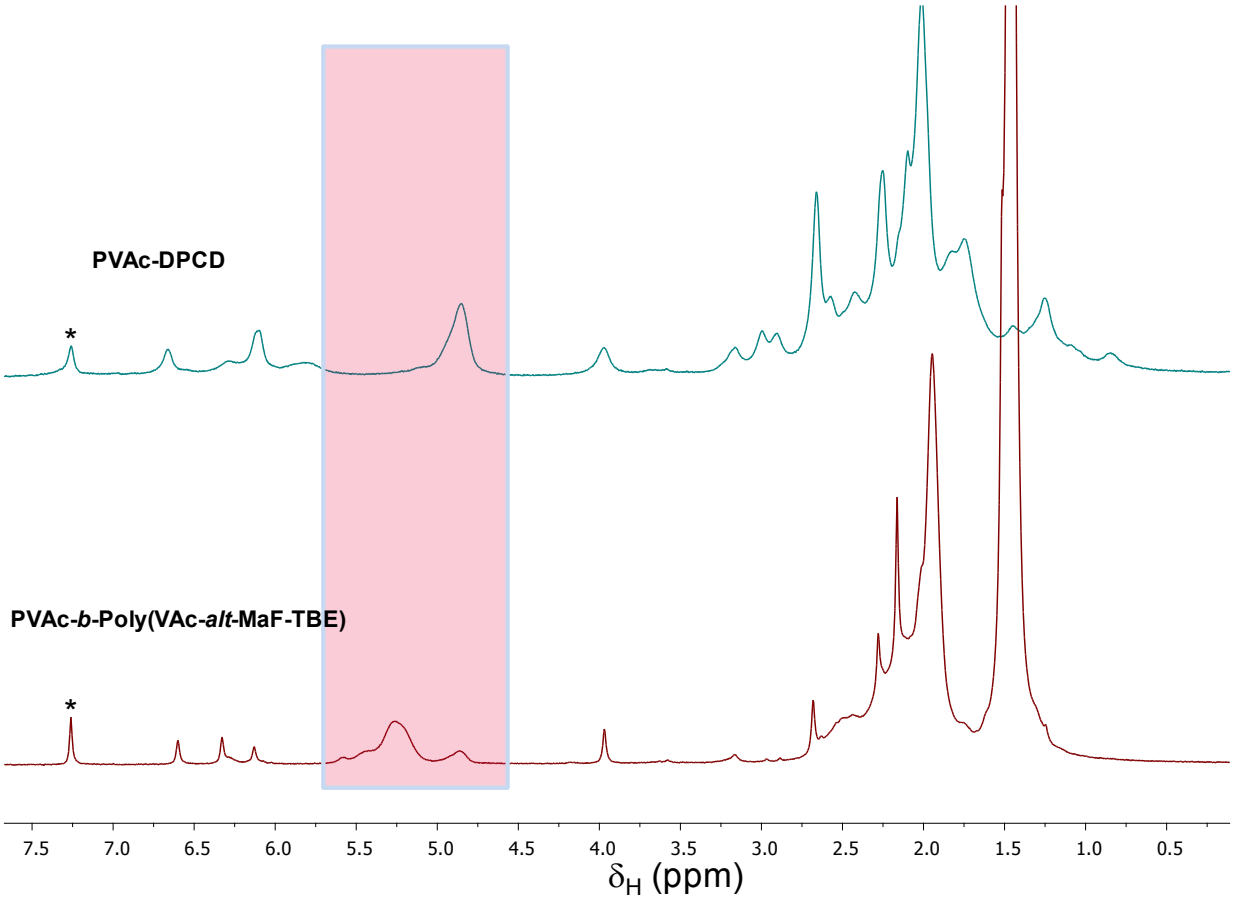


Figure. S14 Expansion of the 0.5 to 7.5 ppm region of the ^{1}H NMR spectra of PVAc-DPCD (P11, Table 1) and of the derived PVAc-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P17, Table 1) recorded in $CDCl_3$ at 20 °C).

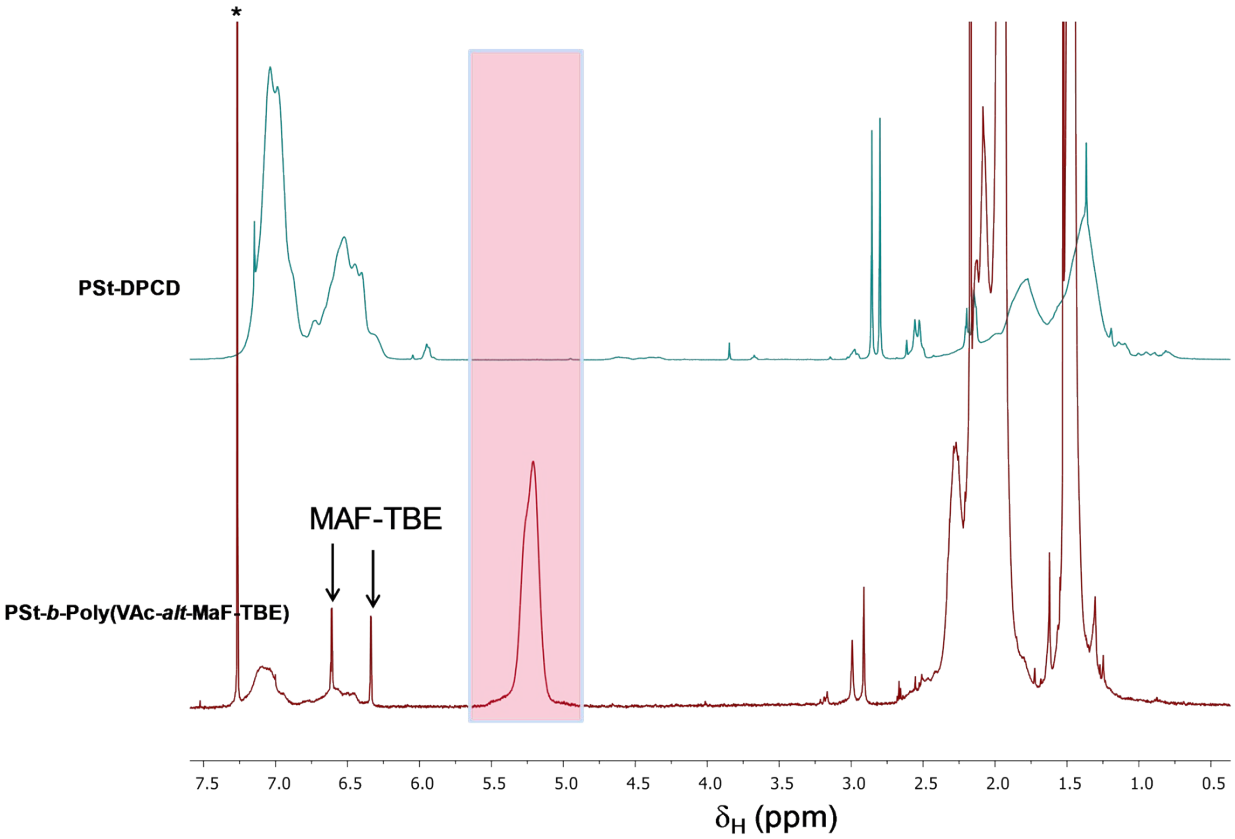


Figure. S15 Expansion of the 0.5 to 7.5 ppm region of the ^{1}H NMR spectra of PSt-DPCD (P12, Table 1) and of the derived PSt-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P18, Table 1), recorded in $CDCl_3$ 20 °C. (*) Solvent ($CDCl_3$) peak.

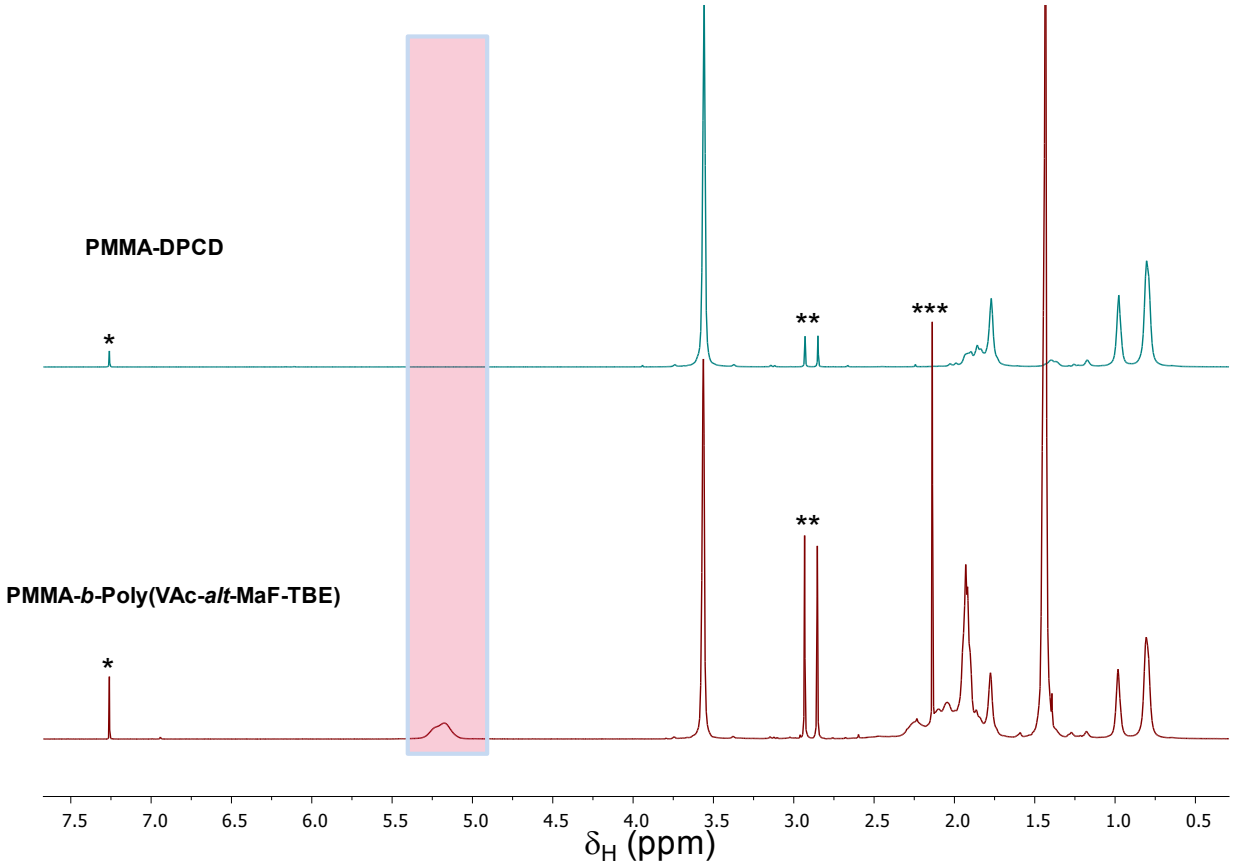


Figure. S16 Expansion of the 0.5 to 7.5 ppm region of the ^{1}H NMR spectra of PMMA-DPCD (P13, Table 1) and of the derived PMMA-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P19, Table 1), recorded in $CDCl_3$ 20 °C. (*) Solvent ($CDCl_3$), (**) solvent (DMF) and (***) solvent (acetone) peaks.

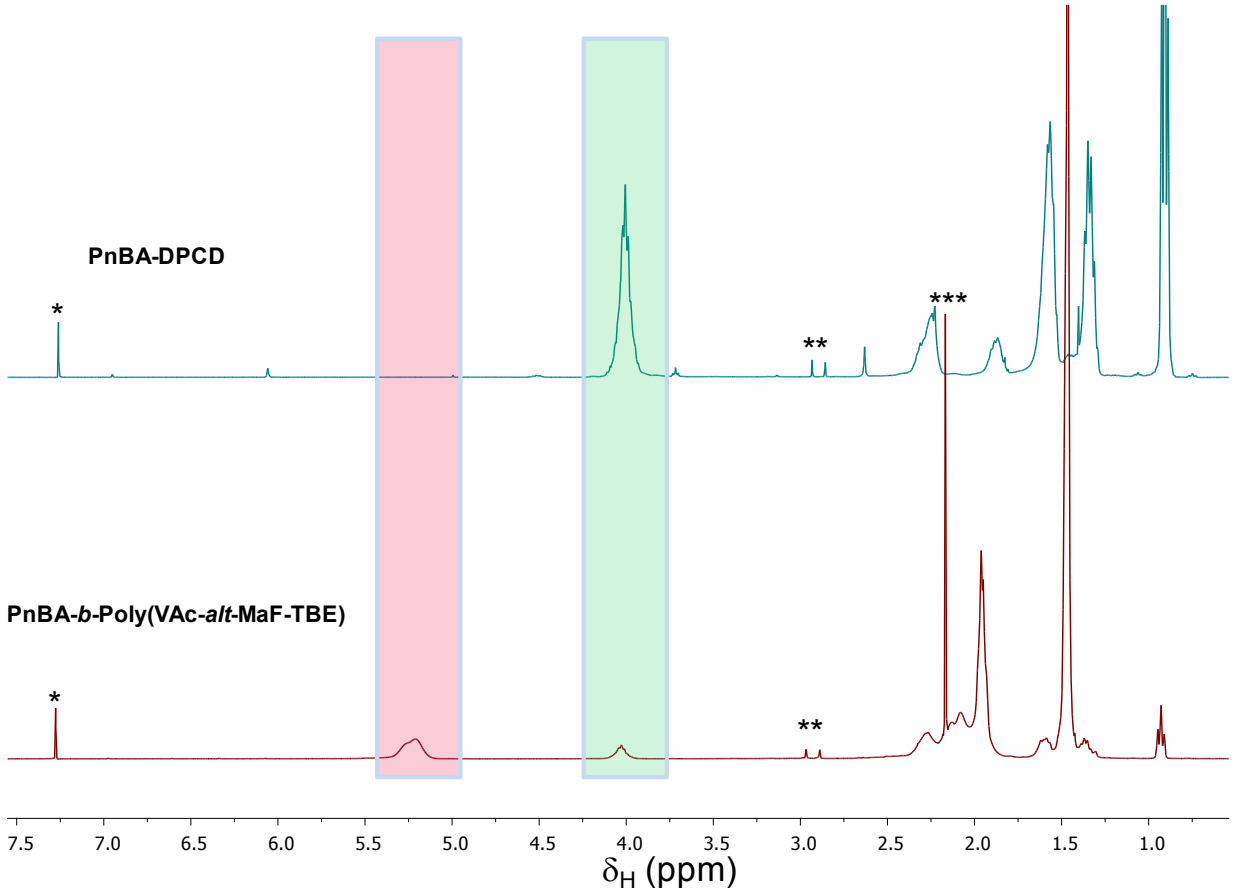


Figure. S17 Expansion of the 0.5 to 7.5 ppm region of the ^{1}H NMR spectra of PnBA-DPCD (P14, Table 1) and of the derived PnBA-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P20, Table 1), recorded in $CDCl_3$ 20 °C. (*) Solvent ($CDCl_3$) (**) solvent (DMF) and (***) solvent (acetone) peaks.

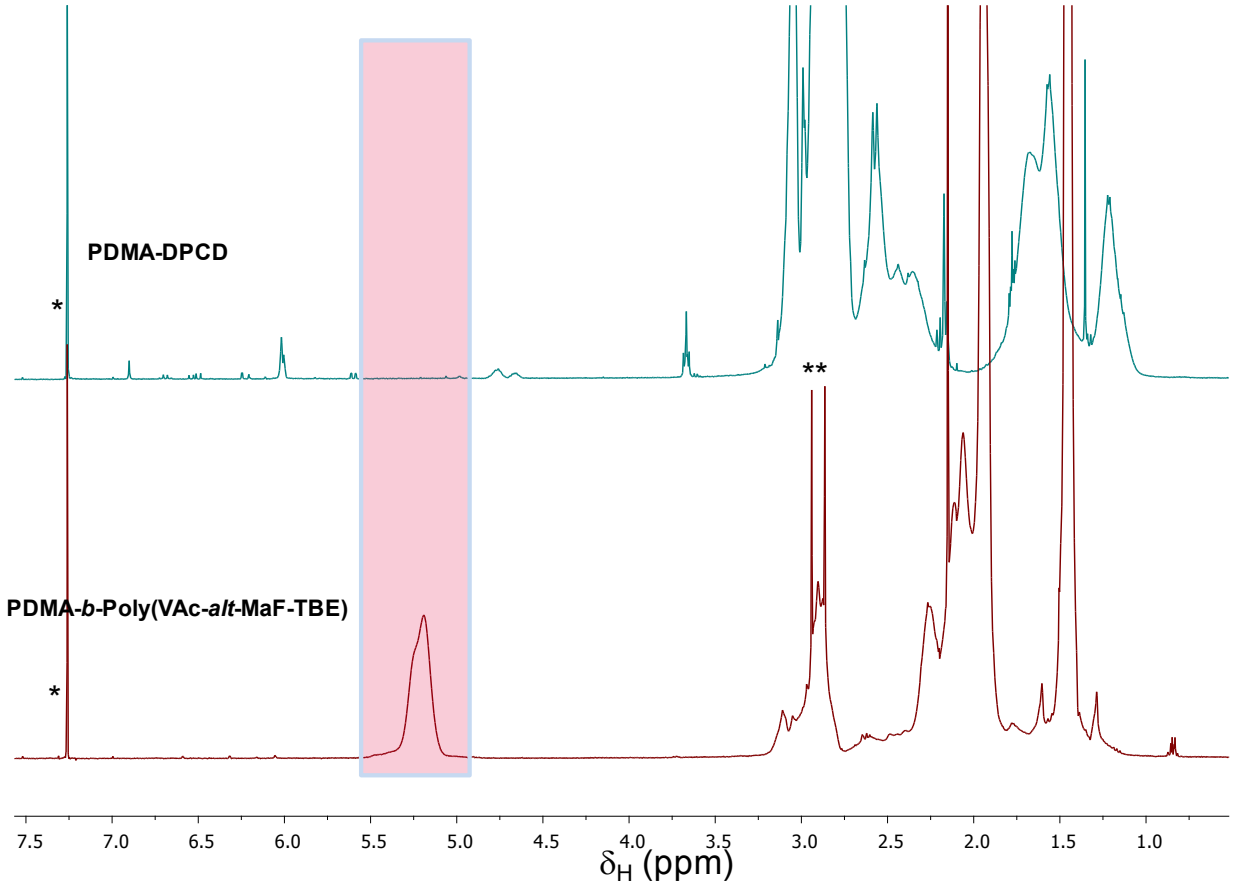


Figure. S18 Expansion of the 0.5 to 7.5 ppm region of the ^{1}H NMR spectra of PDMA-DPCD (P15, Table 1) and of the derived PDMA-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P21, Table 1) recorded in $CDCl_3$ 20 °C. (*) Solvent ($CDCl_3$) and (**) solvent (DMF) peaks.

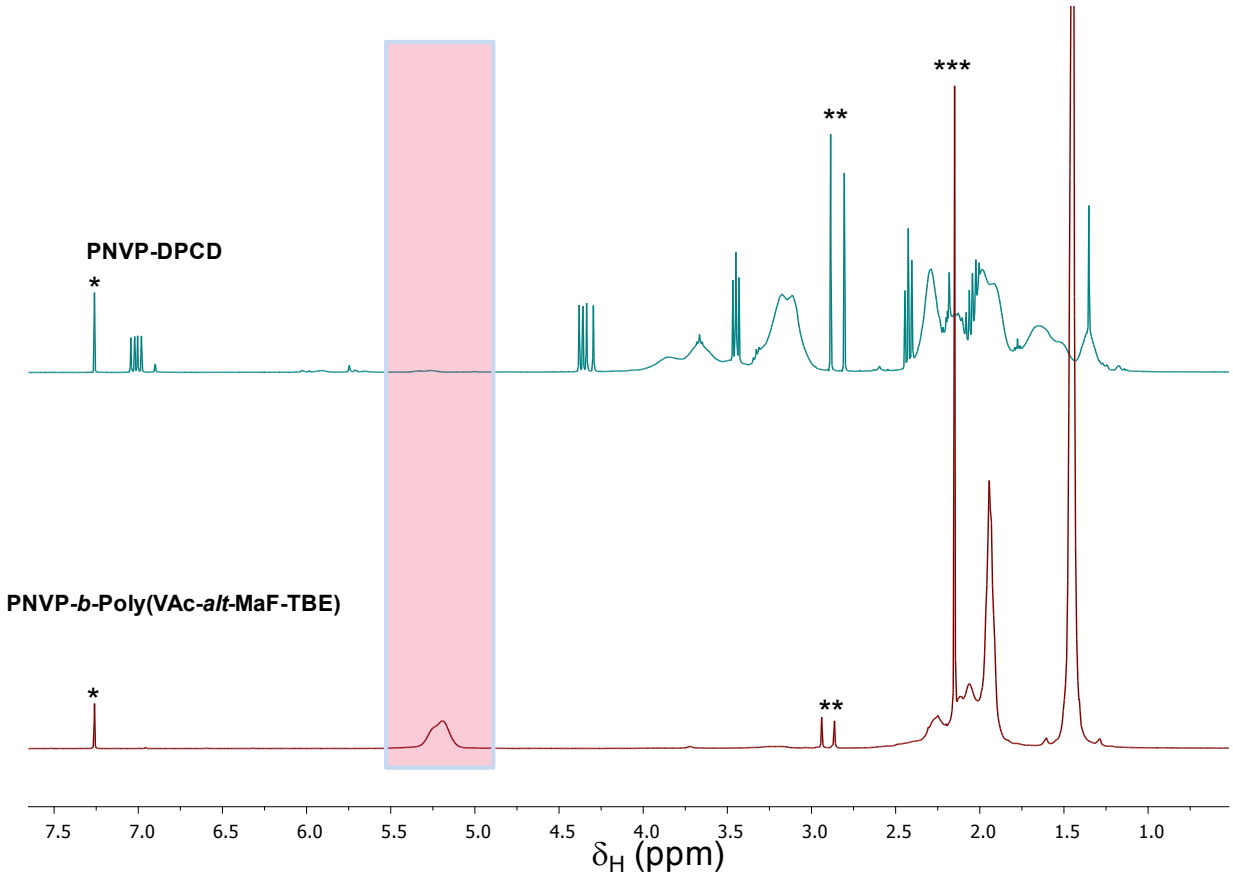


Figure. S19 Expansion of the 0.5 to 7.5 ppm region of the ^{1}H NMR spectra of PNVP-DPCD (P16, Table 1) and of the derived PNVP-*b*-poly(VAc-*alt*-MAF-TBE) block copolymer (P22, Table 1) recorded in $CDCl_3$ 20 °C. (*) Solvent ($CDCl_3$), (**) solvent (DMF) and (***) solvent (acetone) peak.