Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supporting Information

# Synthesis of PEVE-*b*-P(CTFE-*alt*-EVE) block copolymers by sequential cationic and radical RAFT polymerization

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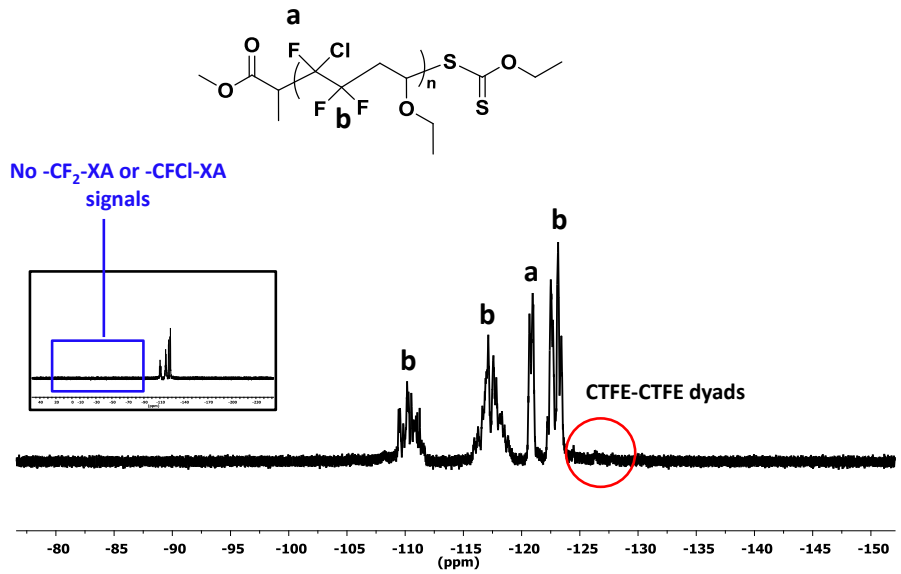


**Figure S1.** $^{19}F$ NMR spectrum in $CDCl_3$ of P(CTFE-*alt*-EVE)-XA homopolymer (P1, Table 1) synthesized by RAFT alternating copolymerization of CTFE and EVE via pathway 1.

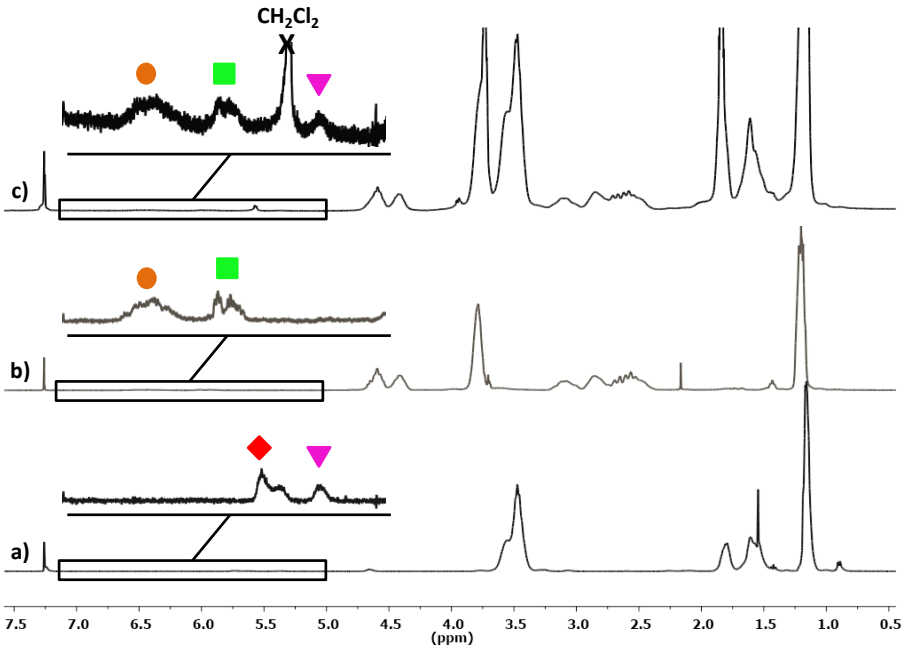


**Figure S2.** $^{1}H$ NMR spectra in $CDCl_3$ of: a) $PEVE_3$ homopolymer synthesized by RAFT cationic polymerization of EVE (P4, Table 1); b) P(CTFE-*alt*-EVE)-XA homopolymer synthesized by radical RAFT alternating copolymerization of CTFE and EVE (P1, Table 1); and c) P(CTFE-*alt*-EVE)-*b*-PEVE block copolymers synthesized using pathway 1 (first radical RAFT polymerization followed by cationic RAFT polymerization (P5, Table 1). The expanded regions show the polymer end-groups: PEVE-$CH_2$-CH(OEt)-XA (red diamond), internal C-C double bond generated by partial abstraction of the ethyloxy group during cationic polymerization (purple triangle),[1] P(CTFE-*alt*-EVE)-CFClH (orange circle), P(CTFE-alt-EVE)-$CH_2$-CH(OEt)-XA (green square).

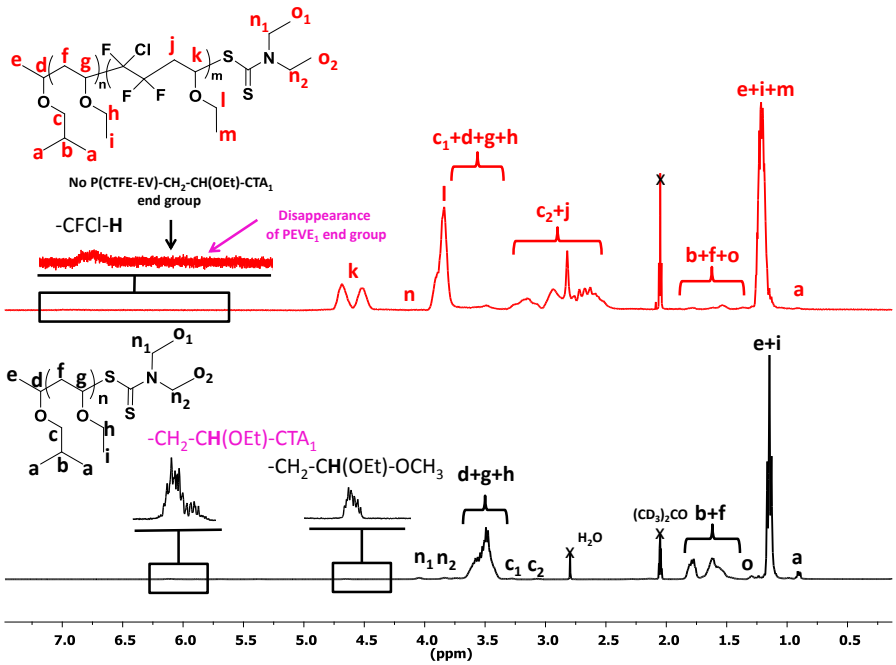


**Figure S3.** . $^{1}$H NMR spectra in $(CD_3)_2CO$ of: (bottom) $PEVE_1$ homopolymer (P2, Table1); (top) PEVE-*b*-P(CTFE-*alt*-EVE)-$CTA_1$ block copolymer (P6, Table 1) synthesized via pathway 2 (first RAFT cationic polymerization followed by RAFT cationic polymerization).

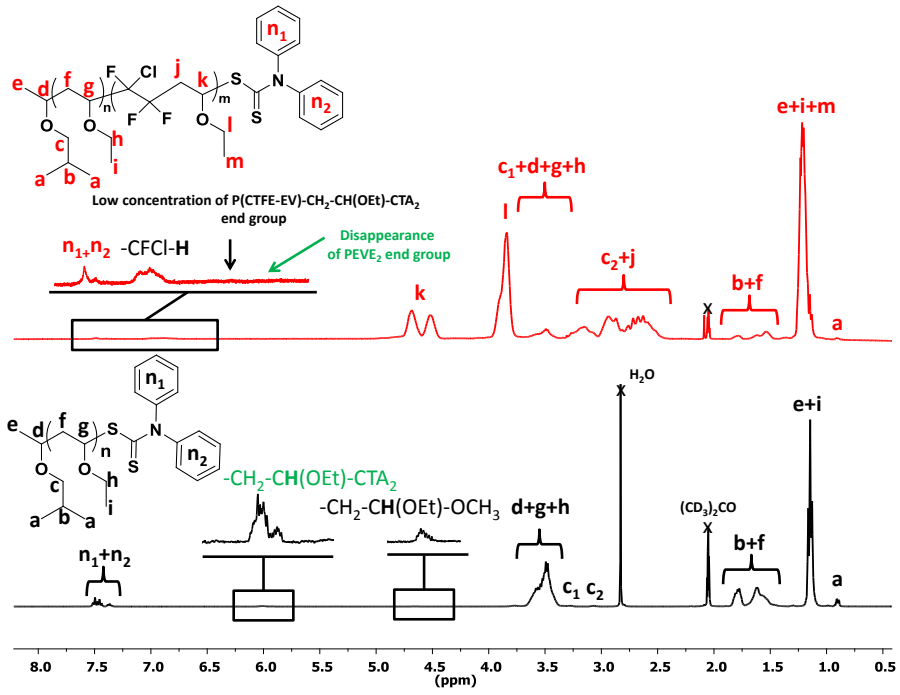


**Figure S4.** . $^{1}$H NMR spectra in $(CD_3)_2CO$ of: (bottom) $PEVE_2$ homopolymer (P3, Table 1) and PEVE-*b*-P(CTFE-*alt*-EVE)-$CTA_2$ block copolymer (P7, Table 1) synthesized via pathway 2 (first cationic RAFT polymerization followed by radical RAFT copolymerization).

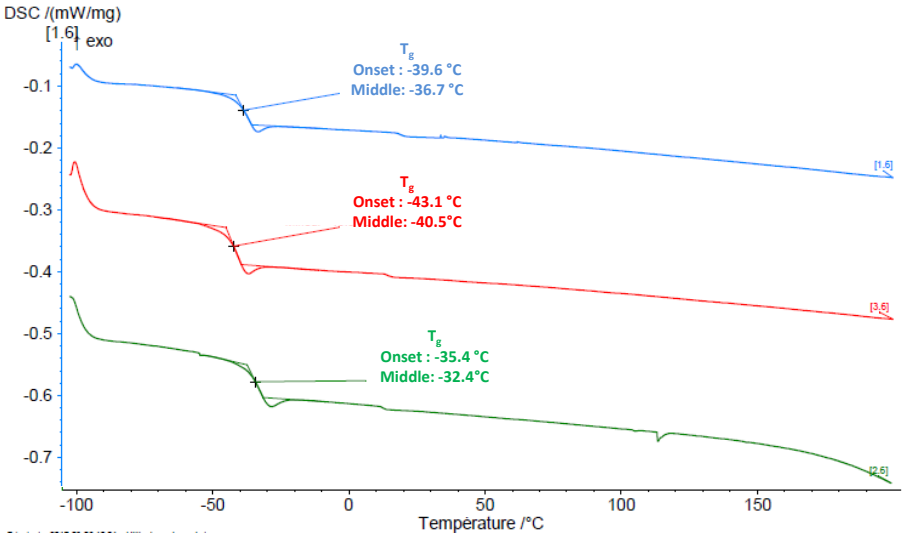


**Figure S5.** DSC thermograms of $PEVE_1$ (P2, Table 1, blue line), $PEVE_2$ (P3 Table 1, red line) and $PEVE_3$ (P4 Table 1, green line).

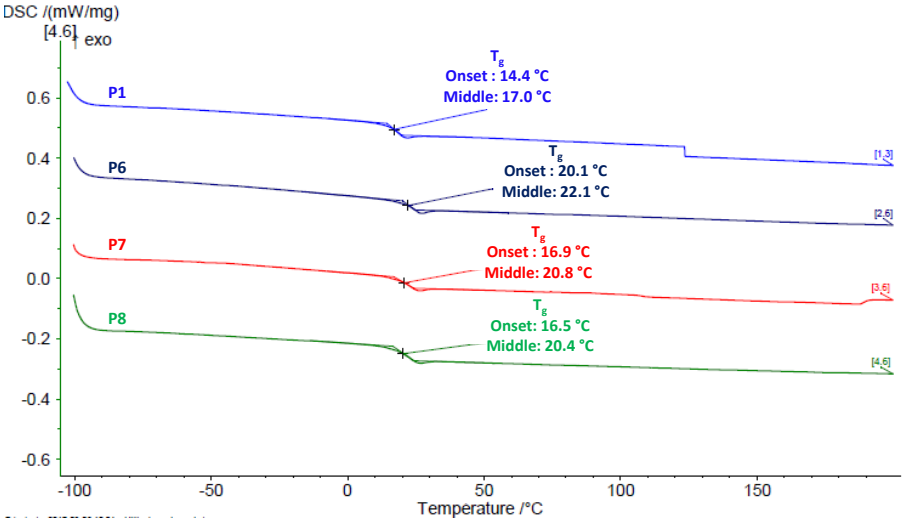


**Figure S6.** DSC thermograms of P(CTFE-*alt*-EVE)-XA (P1, Table1, blue line), PEVE-*b*-P(CTFE-*alt*-EVE)-$CTA_1$ (P6, Table 1, dark blue line), PEVE-*b*-P(CTFE-*alt*-EVE)-$CTA_2$ (P7, Table 1, red line) and PEVE-*b*-P(CTFE-*alt*-EVE)-$CTA_3$ (P8, Table 1, green line).

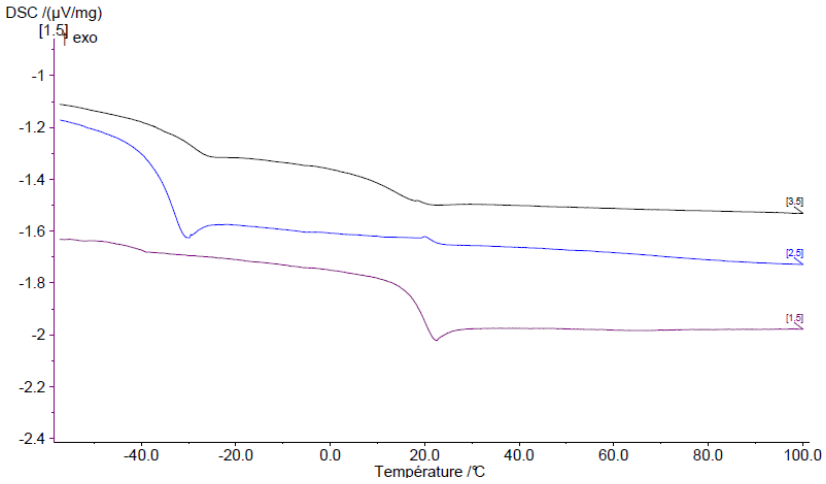


**Figure S7.** DSC thermograms of $PEVE_1$ (P2, Table 1, blue line ), P(CTFE-*alt*-EVE)-XA (P1, Table1, purple line) and blend of both ($PEVE_1$ and P(CTFE-*alt*-EVE)-XA, respectively P2 and P1 in Table 1)

References

[1] A. Kanazawa, S. Kanaoka, S. Aoshima, *J. Polym. Sci: Part A: Polym. Chem*. **2010**, 48, 3702-3708