Supporting Information

Synthesis of PEVE-\textit{b}-P(CTFE-\textit{alt}-EVE) block copolymers by sequential cationic and radical RAFT polymerization

Marc Guerre,\textsuperscript{a,\dagger} Mineto Uchiyama,\textsuperscript{b} Gerald Lopez,\textsuperscript{a} Bruno Améduri,\textsuperscript{a} Kotaro Satoh,\textsuperscript{bc} Masami Kamigaito,\textsuperscript{b,\ast} and Vincent Ladmiral\textsuperscript{a,\ast}

\textsuperscript{a}ICGM, University of Montpellier, CNRS, ENSCM, Montpellier, France. 240 av du Professeur Emile Jeanbrau, 34296 Cedex 5 Montpellier, France.
\textsuperscript{b}Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.
\textsuperscript{c}Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.
\textsuperscript{\dagger}Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281, B-9000, Ghent, Belgium.
**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 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), 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$_3$)$_2$CO of: (bottom) PEVE$_1$ homopolymer (P2, Table 1); (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$_3$)$_2$CO 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 PEVE₁ (P2, Table 1, blue line), PEVE₂ (P3 Table 1, red line) and PEVE₃ (P4 Table 1, green line).

Figure S6. DSC thermograms of P(CTFE-alt-EVE)-XA (P1, Table 1, blue line), PEVE-b-P(CTFE-alt-EVE)-CTA₁ (P6, Table 1, dark blue line), PEVE-b-P(CTFE-alt-EVE)-CTA₂ (P7, Table 1, red line) and PEVE-b-P(CTFE-alt-EVE)-CTA₃ (P8, Table 1, green line).
Figure S7. DSC thermograms of PEVE₁ (P2, Table 1, blue line), P(CTFE-alt-EVE)-XA (P₁, Table 1, purple line) and blend of both (PEVE₁ and P(CTFE-alt-EVE)-XA, respectively P2 and P1 in Table 1)

References