NMR Study of the Chain End and Branching Units in Poly(vinylidene fluoride-*co*-tetrafluoroethylene)
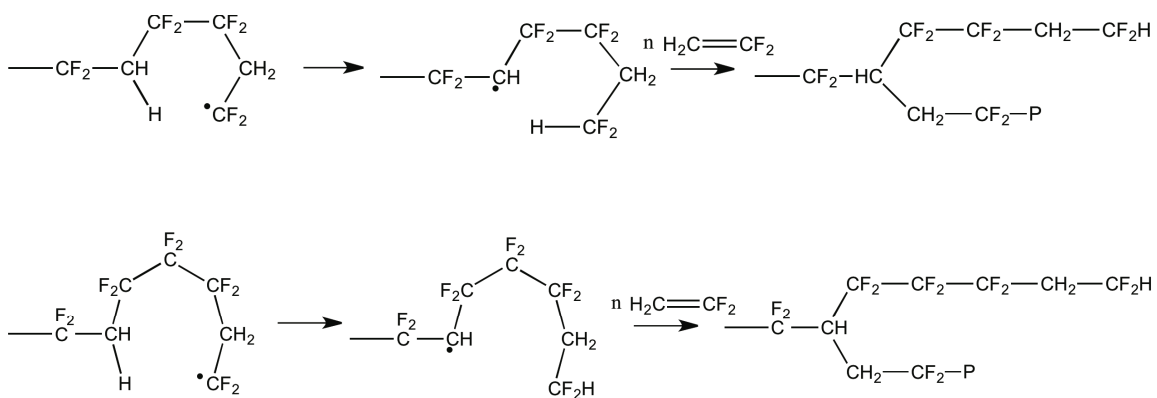
Supporting Material

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Top reaction series:

CF_2—CF_2 / —CF_2—CH / H / •CF_2 / CH_2 $\longrightarrow$ CF_2—CF_2 / —CF_2—ĊH / H—CF_2 / CH_2 $\xrightarrow{\text{n } H_2C=CF_2}$ CF_2—CF_2—CH_2—CF_2H / —CF_2—HC / CH_2—CF_2—P

Bottom reaction series:

F_2 / C / F_2C CF_2 / $\overset{F_2}{C}$—CH / H / •CF_2 / CH_2 $\longrightarrow$ F_2 / C / F_2C CF_2 / $\overset{F_2}{C}$—ĊH / CH_2 / CF_2H $\xrightarrow{\text{n } H_2C=CF_2}$ CF_2—CF_2—CF_2—CH_2—CF_2H / $\overset{F_2}{C}$—CH / CH_2—CF_2—P

Scheme S1: Other possible intramolecular chain transfer reactions via n-membered ring transition state.

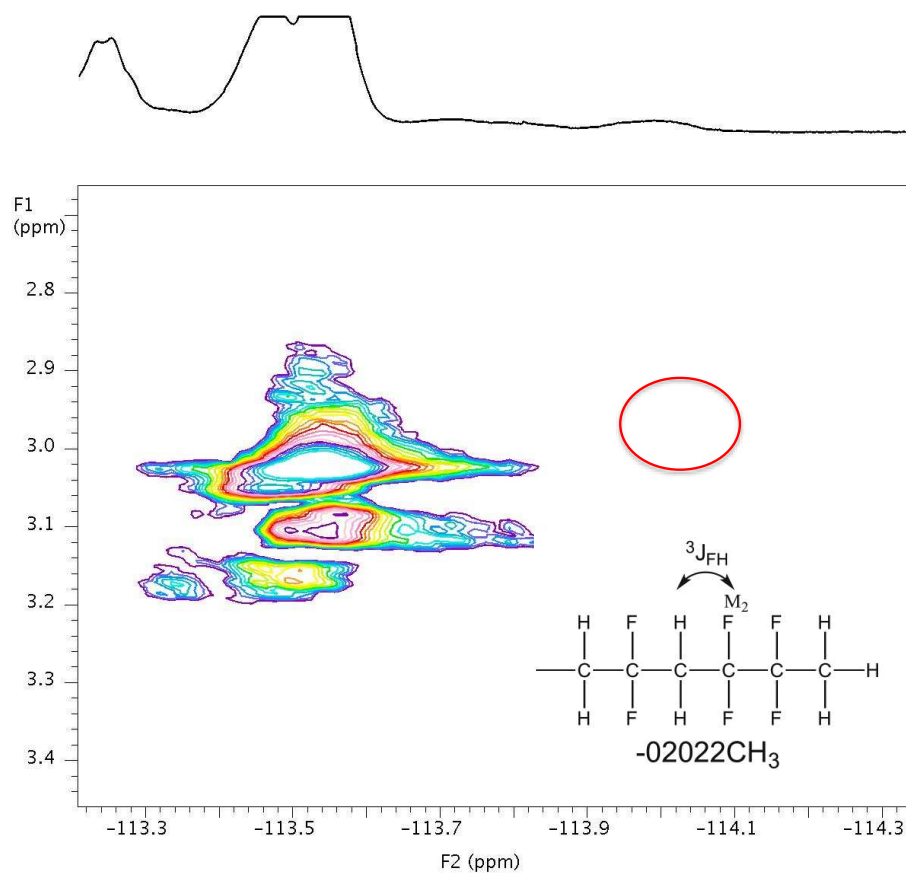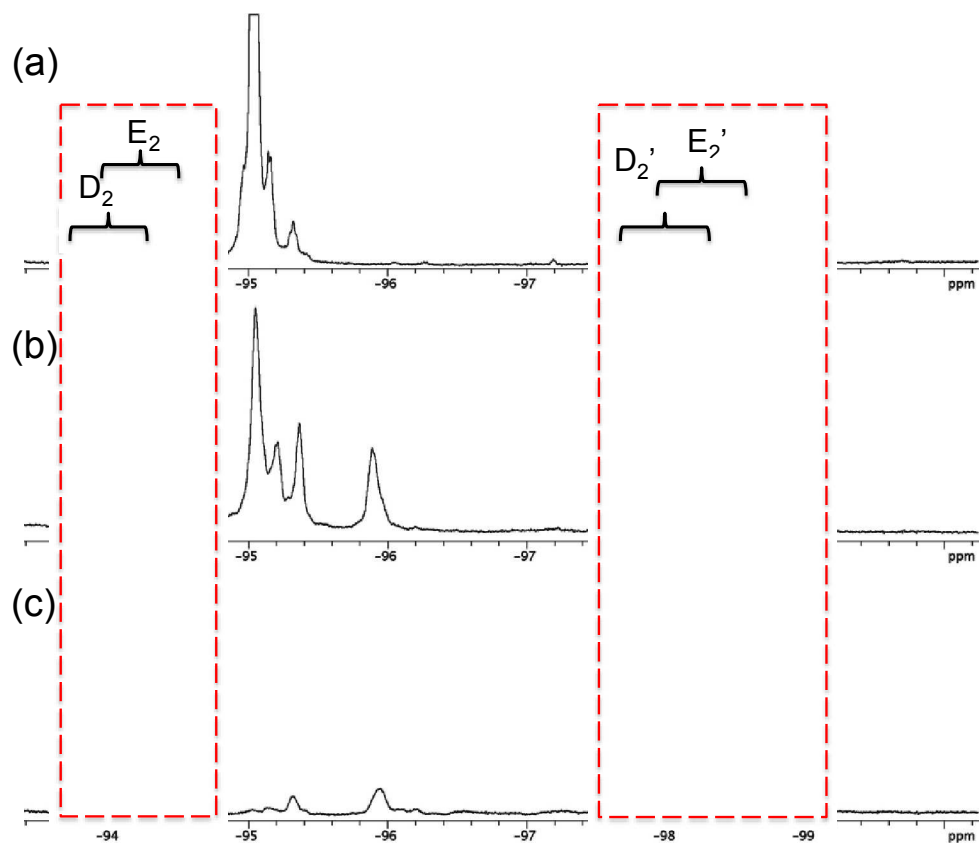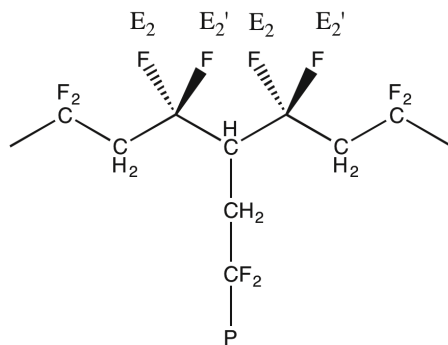**Figure S1.** Selected region from the 470MHz $^{19}F\{^1H\}$ gHETCOR 2D-NMR spectrum of poly(VDF-*co*-TFE) (84:16 mole %).

Figure S2. 470 MHz quantitative $^{19}F\{^1H\}$ 1D-NMR spectrum of (a) PVDF, (b) poly(VDF-co-TFE) (84:16 mol%) and (c) poly(VDF-co-TFE) (58:42 mol%) (* The assignments of resonances from LCB in PVDF are based on the work of Eric B. Twum et al. 's work, Macromolecules, 2012, 45, 5501-5512.).
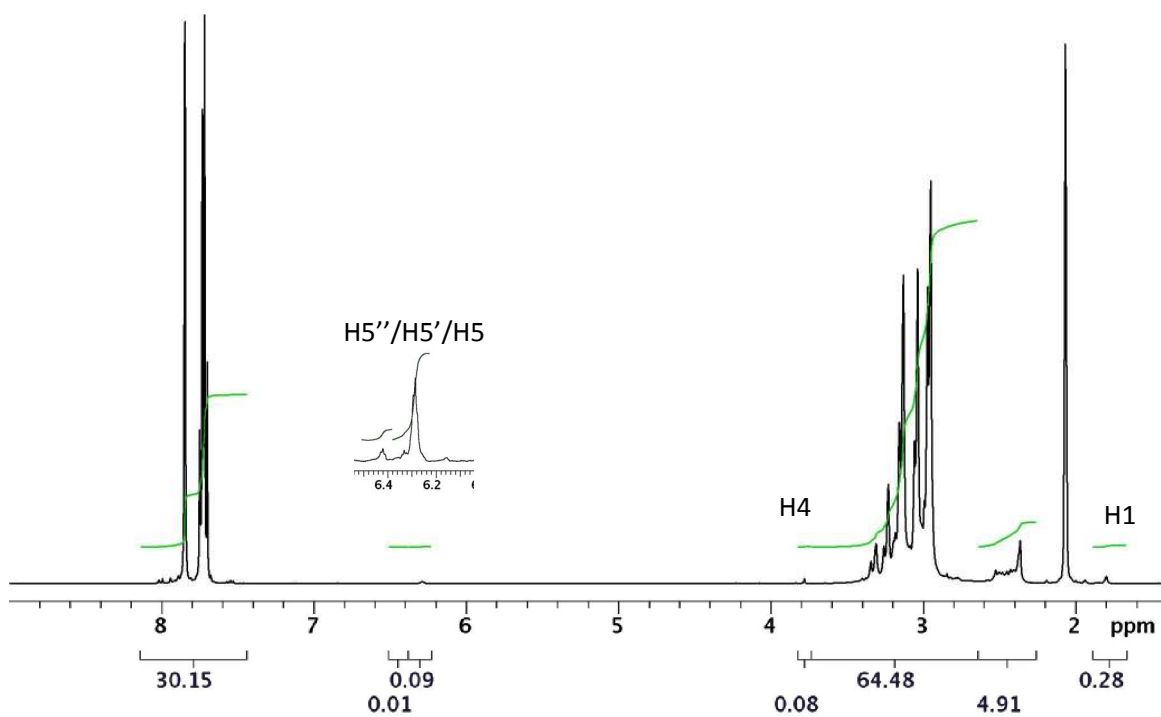
Figure S3. 500 MHz quantitative $^1H\{^{19}F\}$ 1D-NMR spectrum of poly(VDF-co-TFE) (84:16 mol%).

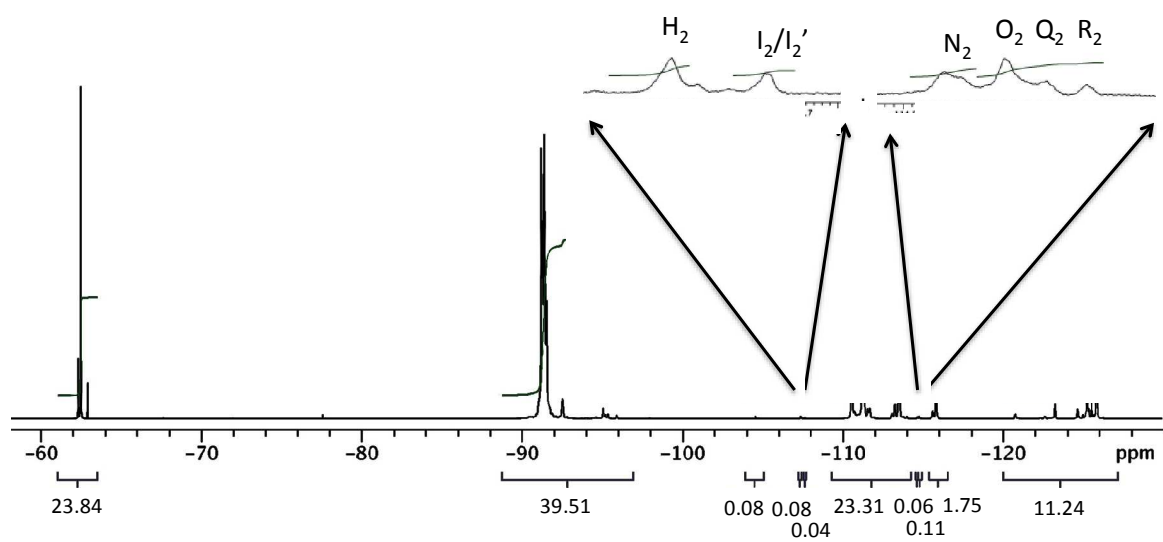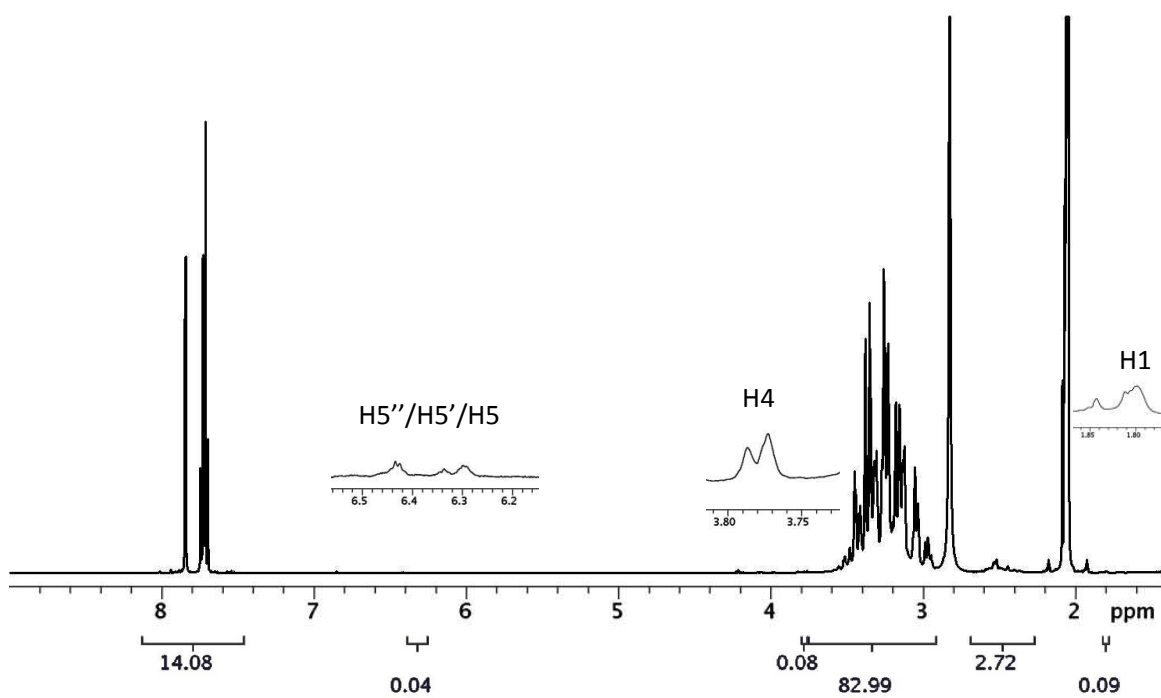**Figure S4.** 470 MHz quantitative $^{19}F\{^1H\}$ 1D-NMR spectrum of poly(VDF-co-TFE) (84:16 mol%).

Figure S5. 500 MHz quantitative ^{1}H{^{19}F} 1D-NMR spectrum of poly(VDF-co-TFE) (58:42 mol%).

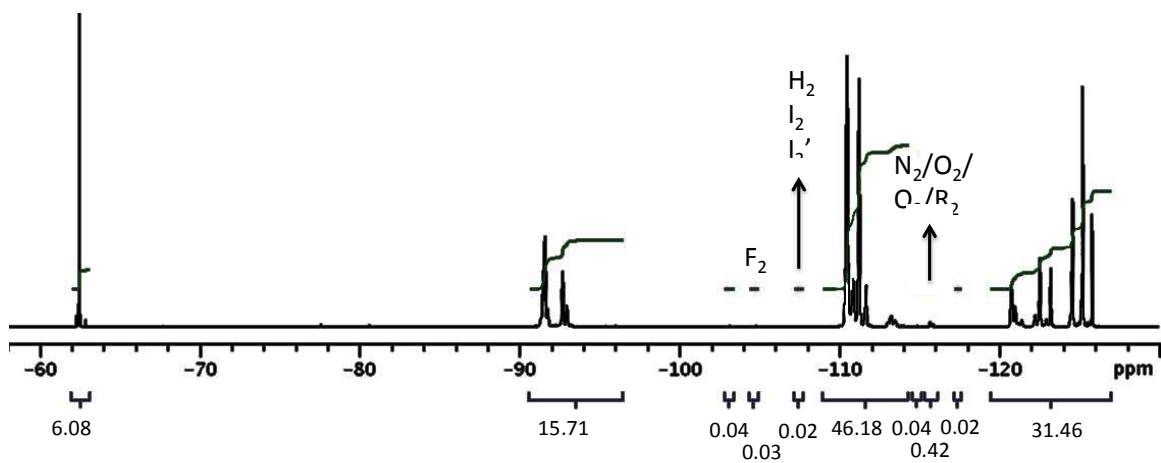**Figure S6.** 470 MHz quantitative $^{19}F\{^1H\}$ 1D-NMR spectrum of poly(VDF-co-TFE) (58:42 mol%).
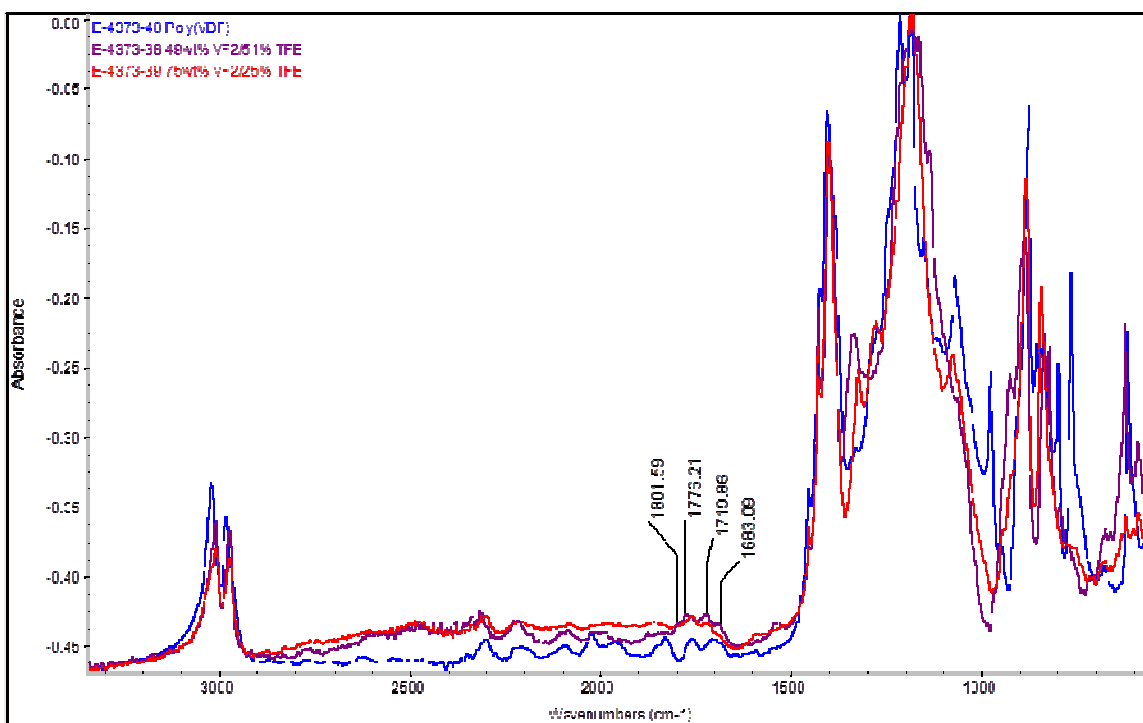
Figure S7. FT-IR spectra of VDF-containing polymers. (The Infrared spectra of poly(VDF-co-TFE) shows low levels of carboxylic acid dimer, mixed dimer, and carboxylate ions. Slightly higher levels of carboxylate species were observed in the sample containing higher concentrations of TFE. The peaks in the 1700-1800 cm^{-1} range might also be combination bands from the C-H stretch (ca 3000 cm^{-1}) and the C-F stretch (1200-1300 cm^{-1}).)
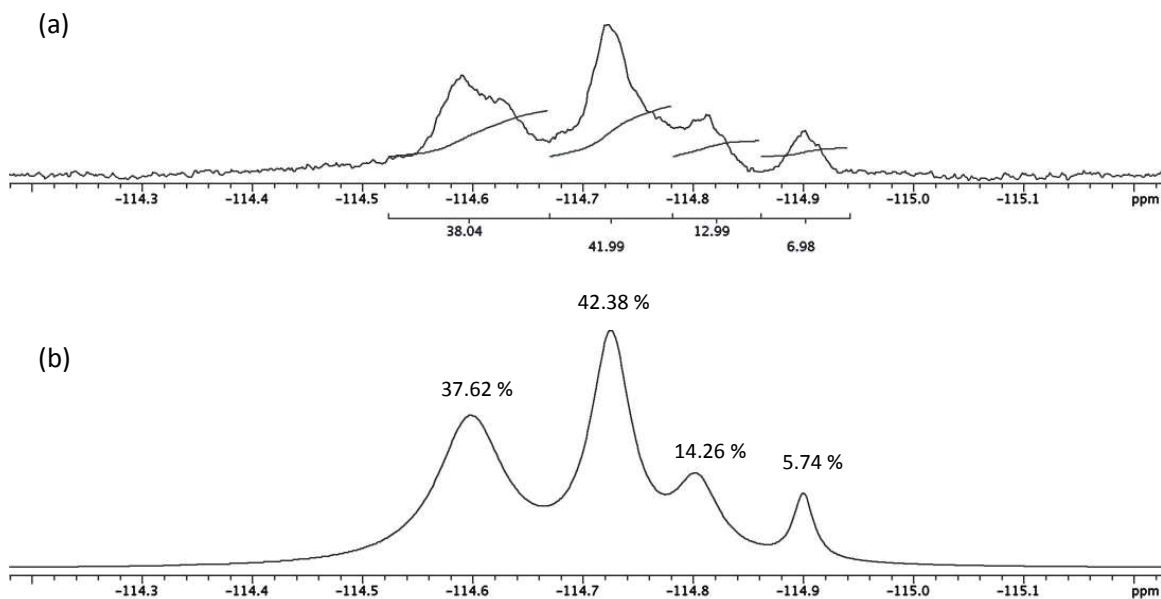
Figure S8. (a) 470 MHz quantitative $^{19}F\{^{1}H\}$ 1D-NMR spectrum of poly(VDF-co-TFE) (84:16 mol%), and (b) The simulated NMR spectrum of (a) after deconvolution. (Deconvolution was performed with the processing tool in Vnmrj 2.2D. From these spectra, it can be seen that a good fitting was obtained for this polymer.)