

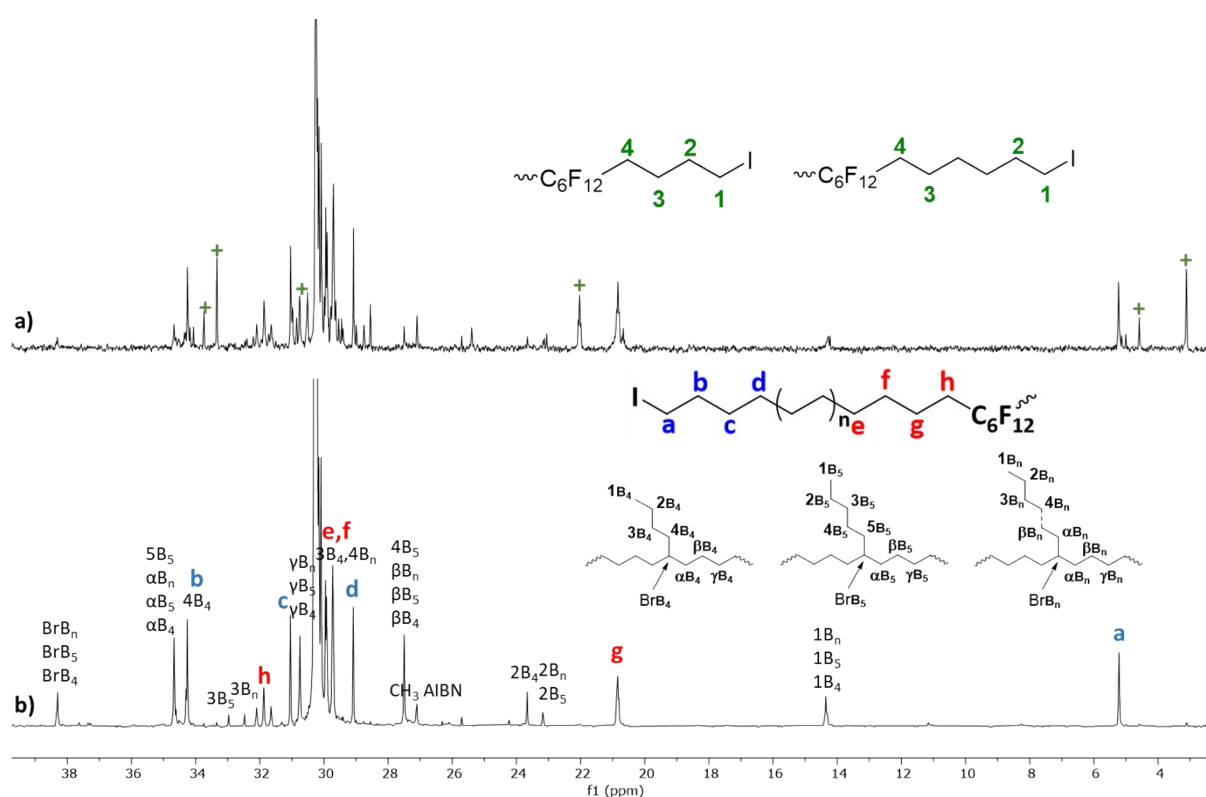
## SUPPORTING INFORMATION

### **Telechelic polyethylene, poly(ethylene-co-vinyl acetate) and triblock copolymers based on ethylene and vinyl acetate by iodine transfer polymerization.**

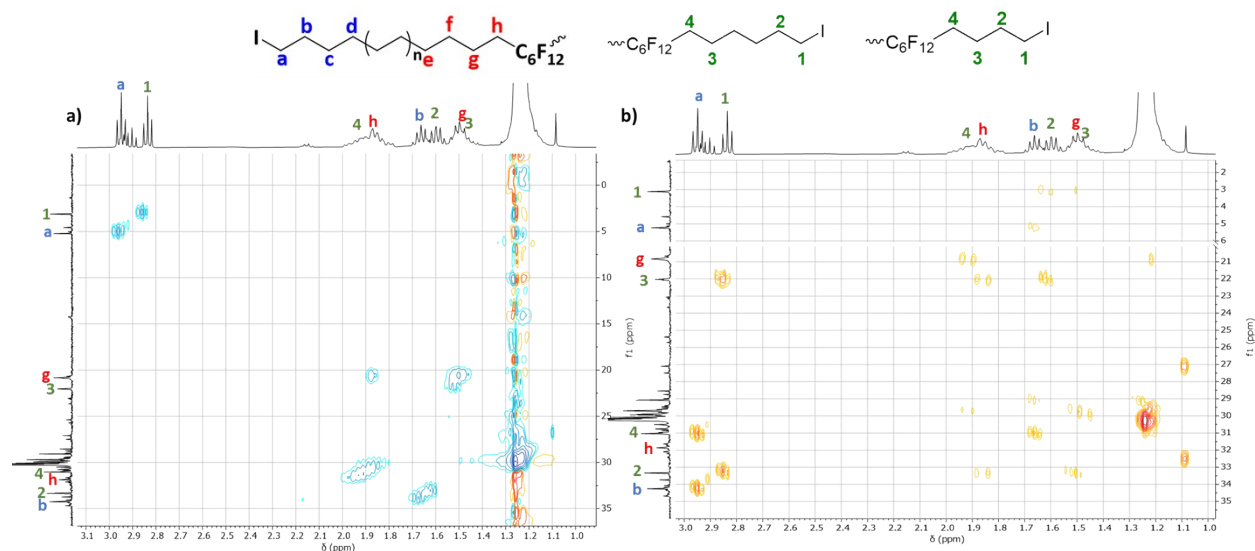
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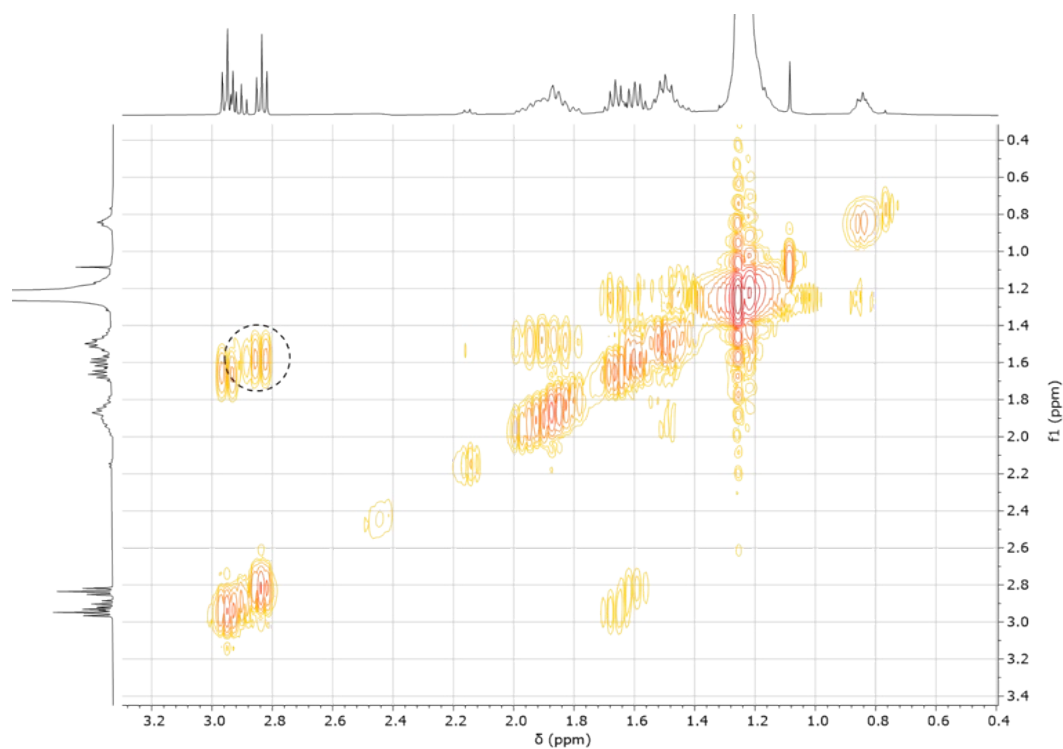
$^{13}\text{C}$  NMR (**Figure S1**) and  $^1\text{H}$ - $^{13}\text{C}$  HSQC and HMBC (**Figure S2**) analyses were performed to confirm the presence of PE oligomers after 45 min of polymerization performed with CTA-1 (at 70 °C, 80 bar). All the signals could be assigned for the polymer after precipitation (**Figure S1b**). The spectrum is like the one obtained for a PE produced with CTA-2, confirming the absence of side reaction and the good chain-end fidelity. Branching was studied using  $^{13}\text{C}$  NMR analyses. The data obtained when CTA1 was used are similar to those previously reported when CTA-F was employed (i.e. 6 branches per 1000 C atoms, out of those, approximately 55% are butyl, 15% are pentyl and 30% are branches containing more than five carbons.<sup>1</sup> However, for the filtrate residue in **Figure S1a**, several additional signals are present (annotated by +). With a DEPT 135 analysis (data not shown), it was shown that these additional signals are all  $\text{CH}_2$  carbons. Moreover, the chemical shifts correspond to protons and carbon atoms next to an iodine atom and a perfluorinated alkyl group. From the 2D experiments in **Figure S2** it is possible to say that all the protons 1-4 are connected and form only one molecule. Furthermore, protons 1 have a distance correlation to protons 4 (**Figure S2b**), confirming that oligomers are present. It is also in accordance with the number of ethylene units inserted measured by  $^1\text{H}$  NMR for the filtrate residue.



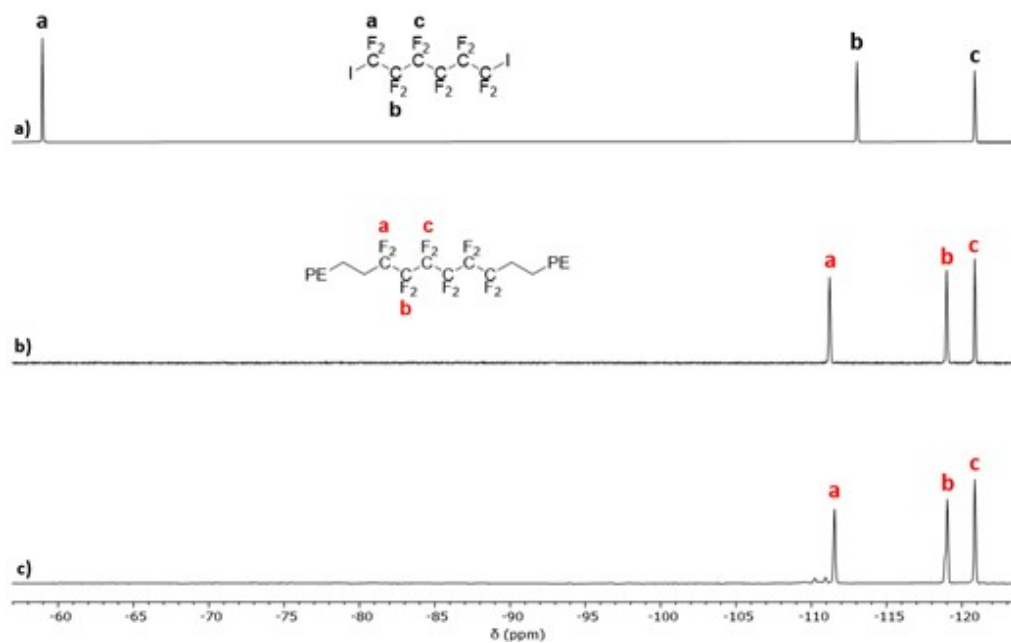
**Figure S1.**  $^{13}\text{C}$  NMR spectra (in TCE/ $\text{C}_6\text{D}_6$  at 90 °C) of the PE after precipitation, synthesized in the presence of CTA-1 at 80 bar, 70 °C and after 45 min: a) filtrate residue, and b) solid part. Notations of branches are taken from the literature.<sup>1</sup>



**Figure S2.** a)  $^1\text{H}$ - $^{13}\text{C}$  HSQC, and b)  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectra of the filtrate residue after the precipitation of the PE synthesized in the presence of CTA-1 at 80 bar, 70 °C and after 45 min (in TCE/ $\text{C}_6\text{D}_6$  at 90 °C).



**Figure S3.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum (in TCE/ $\text{C}_6\text{D}_6$  at 90 °C) of the filtrate residue after precipitation of the PE synthesized in the presence of CTA-1 and stopped after 45 min (Figure 4b).



**Figure S4.**  $^{19}\text{F}$  NMR spectra (in TCE/ $\text{C}_6\text{D}_6$  at 90 °C) of a) CTA-1, and b) of the solid part of the precipitated PE and c) EVA from run 1 in **Table 1**.

1. G. B. Galland, R. F. de Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*, 1999, **32**, 1620-1625.