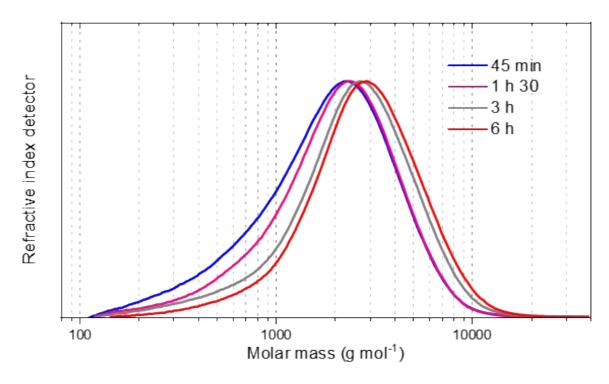
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## **SUPPORTING INFORMATION**

## Polyethylene and poly(ethylene-co-vinyl acetate) star polymers by iodine transfer polymerization.

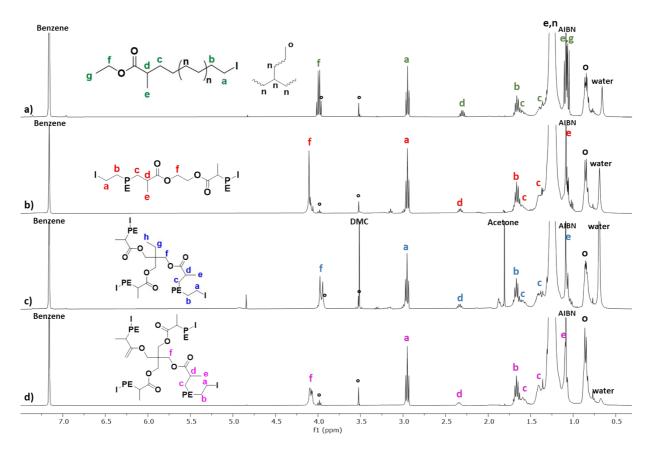
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**Figure S1.** Molar mass distributions of PE obtained during ITP of ethylene mediated by CTA-S1 at 70 °C and 80 bar of ethylene pressure after the indicated polymerization time. A conventional calibration using PE standards was applied.

## Comparison of <sup>1</sup>H NMR spectra of the PE synthesized with the four different CTAs

Similarly to CTA-S1 and CTA-S4, the use of CTAS2-3 led to PE chains for which the multiplet from proton *d* at 2.35 ppm presents an integral around half of the expected value. Moreover, multiplets at 2.05 and 2.45 ppm at short polymerization times, which disappear over increased reaction times, can also be observed.



**Figure S2**.  $^1$ H NMR spectra (in TCE/C<sub>6</sub>D<sub>6</sub> at 90  $^{\circ}$ C) of and PE synthesized at 70  $^{\circ}$ C, 80 bar and stopped after 6 hours in the presence of a) CTA-S1, b) CTA-S2, c) CTA-S3, and d) CTA-S4. The end group -CH<sub>3</sub> stems from intramolecular and intermolecular chain transfer inherent in ethylene radical polymerization.  $^{\circ}$  transfer to polymerization solvent DMC. AIBN stands for the methyls from the chainends of the PE chains initiated by AIBN. The water is coming from the NMR solvent.