Supporting Information:

Ethylene Free Radical Polymerization in scCO$_2$

Ali Al Rida Hmayed, Sebastien Norsic, Vincent Monteil*, and Jean Raynaud*

*C2P2-LCPP/ CNRS-UCBL-CPE Lyon/ 43 Bd du 11 Nov. 1918/ 69616 Villeurbanne cedex- France.
vincent.monteil@univ-lyon1.fr; jean.raynaud@univ-lyon1.fr

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# Comparison between DMC- and CO$_2$-mediated experiments

The reaction conditions for the control experiments conducted in DMC are almost identical to those for the CO$_2$-mediated reactions:

- For AIBN- and lauroyl peroxide-initiated reactions in DMC: 0.3 mmol of initiator was added, the reactor was pressurized by 110 bar of ethylene at 35 °C, the reaction temperature was 70 °C (the pressure at 70 °C was equal to 237 bar for AIBN-initiated reaction and 225 bar for LP-initiated reaction), and the reaction lasted for 3 hours; which are very close to those of the CO$_2$-mediated reactions.

- For benzoyl peroxide-initiated reaction in DMC: 0.3 mmol of BP was added, the reactor was pressurized by 90 bar of ethylene at 45 °C, the reaction temperature was 90 °C (the pressure at 90 °C was equal to 215 bar), and the reaction lasted for 3 hours; which are also very close to those of the CO$_2$-mediated reactions.

Nuclear Magnetic Resonance (NMR)

NMR analyses (^{1}H and ^{13}C) were recorded using a Bruker Avance II 400 MHz spectrometer, equipped with a 10mm ^{13}C-^{1}H selective probe (PSEX13C) with z-gradient coil. All samples (100 mg) were dissolved in 3 mL of C_6D_6/tetrachloroethylene (1:2). The spectra were recorded at 90°C (363 K) with 256 scans for ^{1}H-NMR and 4096 scans for ^{13}C-NMR. Chemical shifts (in ppm) were expressed relative to the resonance of tetramethylsilane TMS (δ = 0 ppm).

-CH$_2$-

AIBN-initiated PE produced in DMC

AIBN-initiated PE produced in CO$_2$
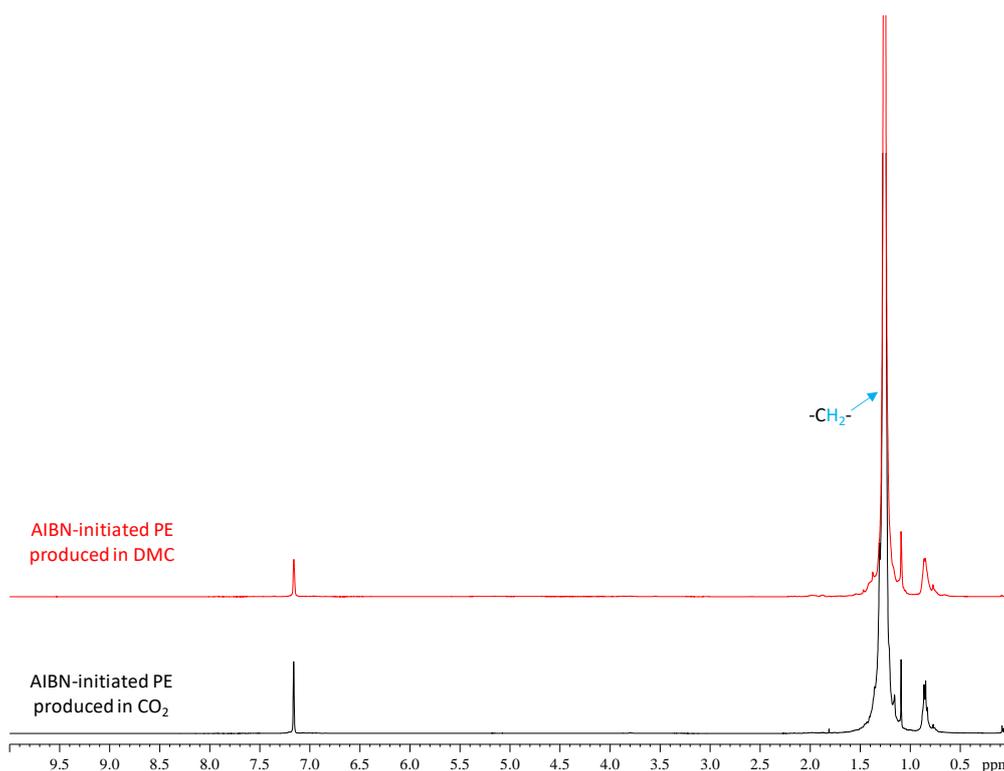
S1. ^{1}H-NMR spectra of the AIBN-initiated PE produced in CO$_2$ (80 bars at 35 °C) and in DMC, the massif at ~1.2-1.3ppm represents the methylene protons of the PE backbone.

Calculation of the number of branches:

See Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32* (5), 1620–1625

From ^{13}C-NMR spectrum (**see Figure 3**): (*I= integration*)

- I_a= Integration of the peak at 38.05 ppm= Integration of the peak corresponding to "$^{br}B_4$ + $^{br}B_5$ + $^{br}B_n$".
- I_b= Integration of the peak corresponding to any C atom of the PE backbone or branches; then ΣI_b= summation of all the integration of the peaks corresponding to C atoms of the PE.
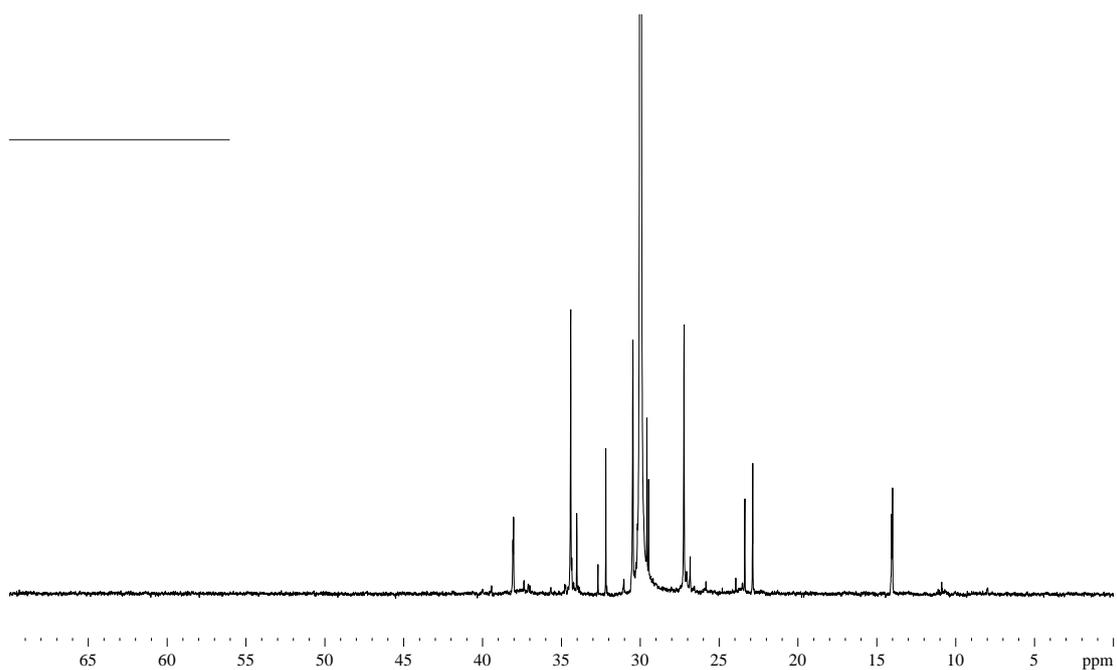
Number of branches= I_a/ΣI_b.

Then: *"number of branches per 1000 C atoms"= I_a × 1000/ΣI_b.*
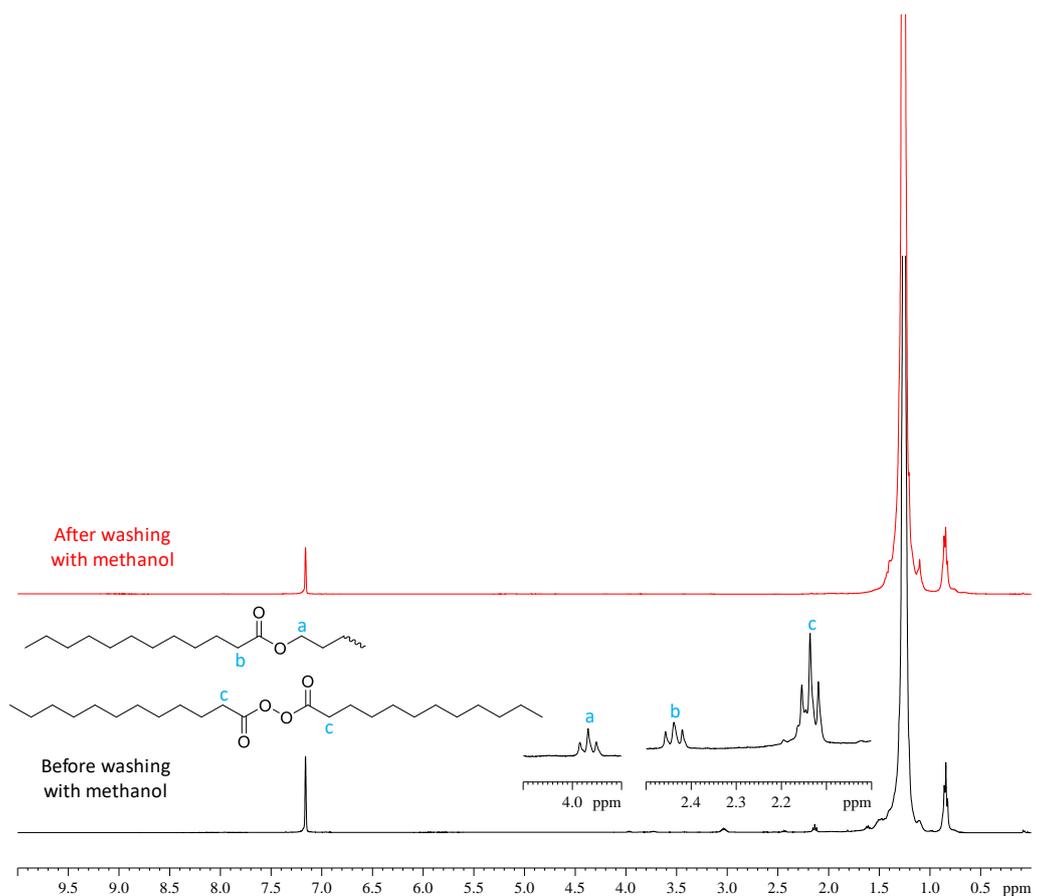
S2. ^{1}H-NMR spectra of the lauroyl peroxide-initiated PE produced in CO_2 before and after washing with methanol.
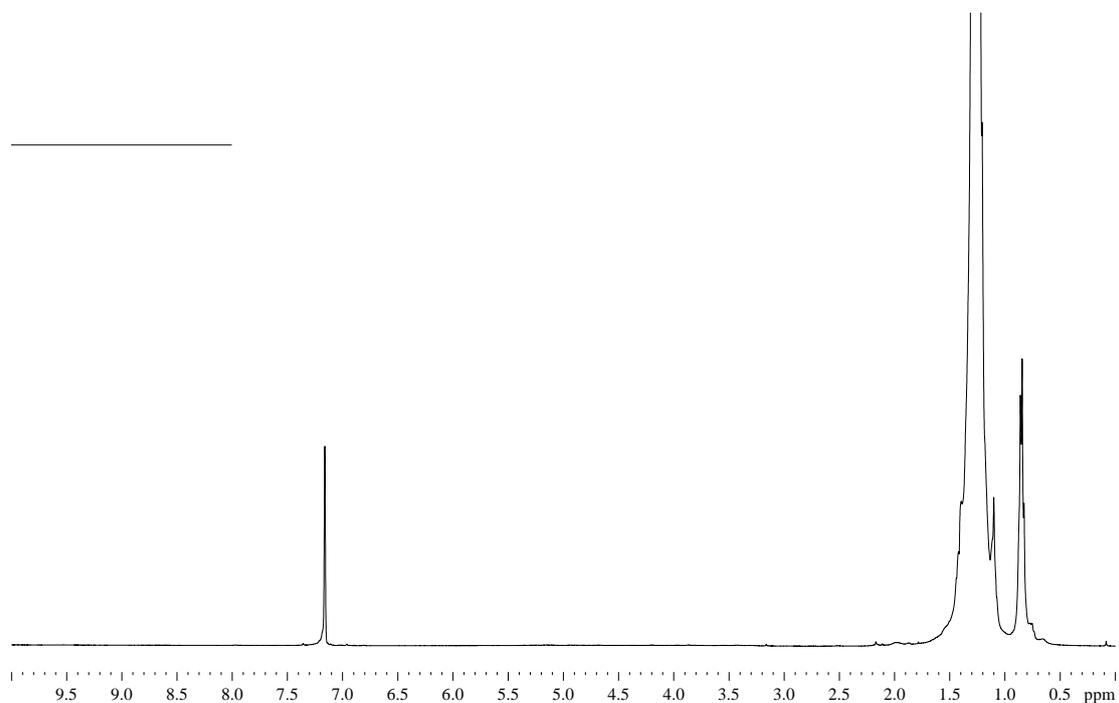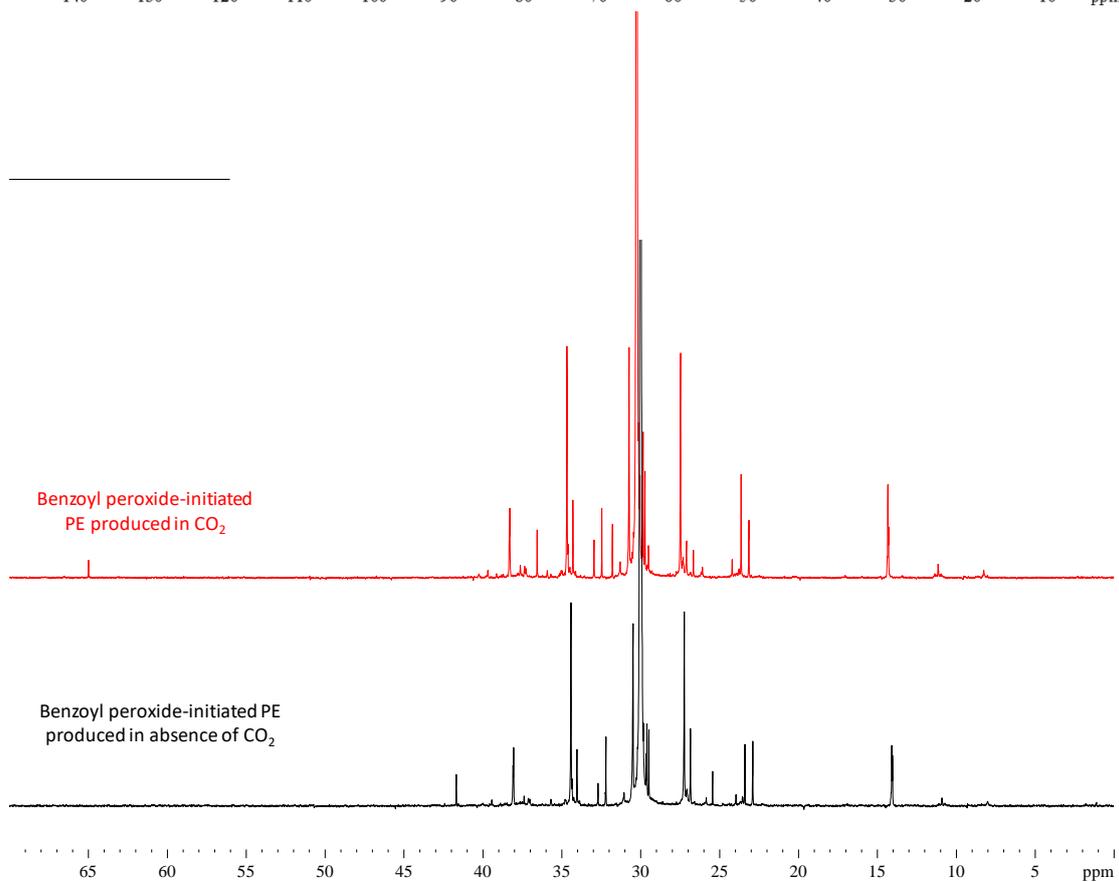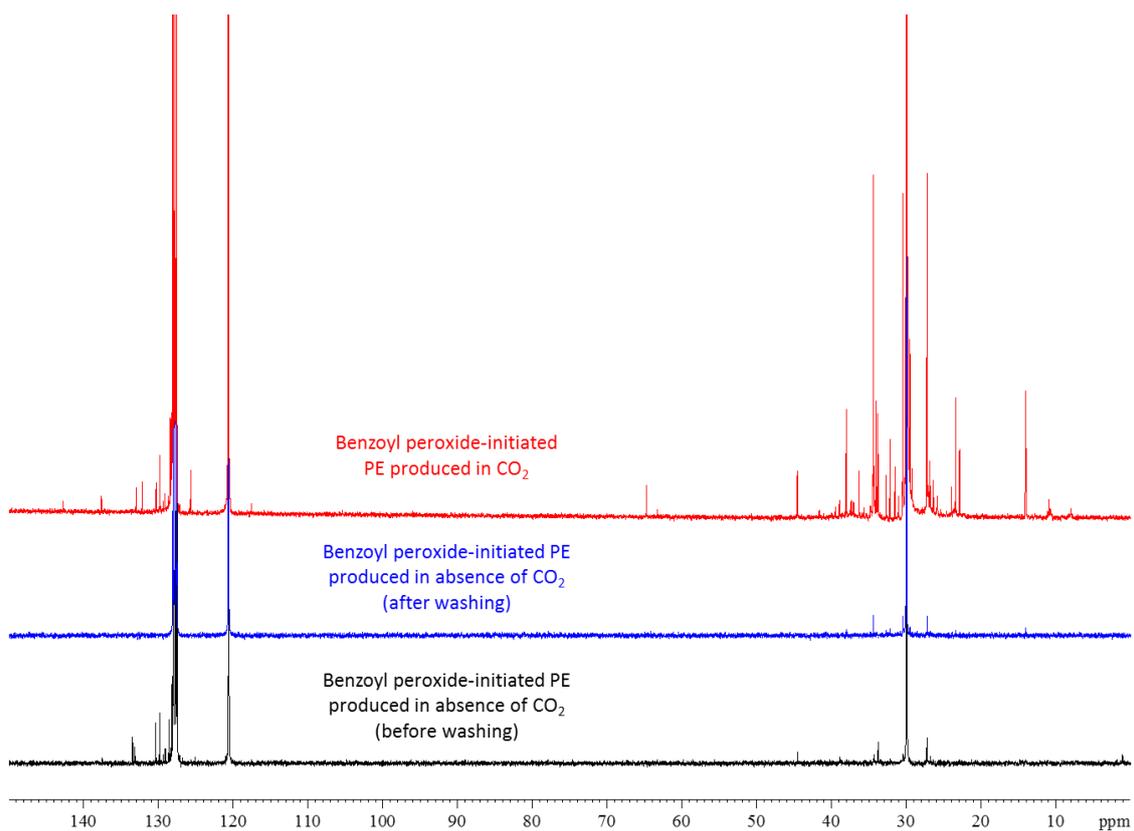

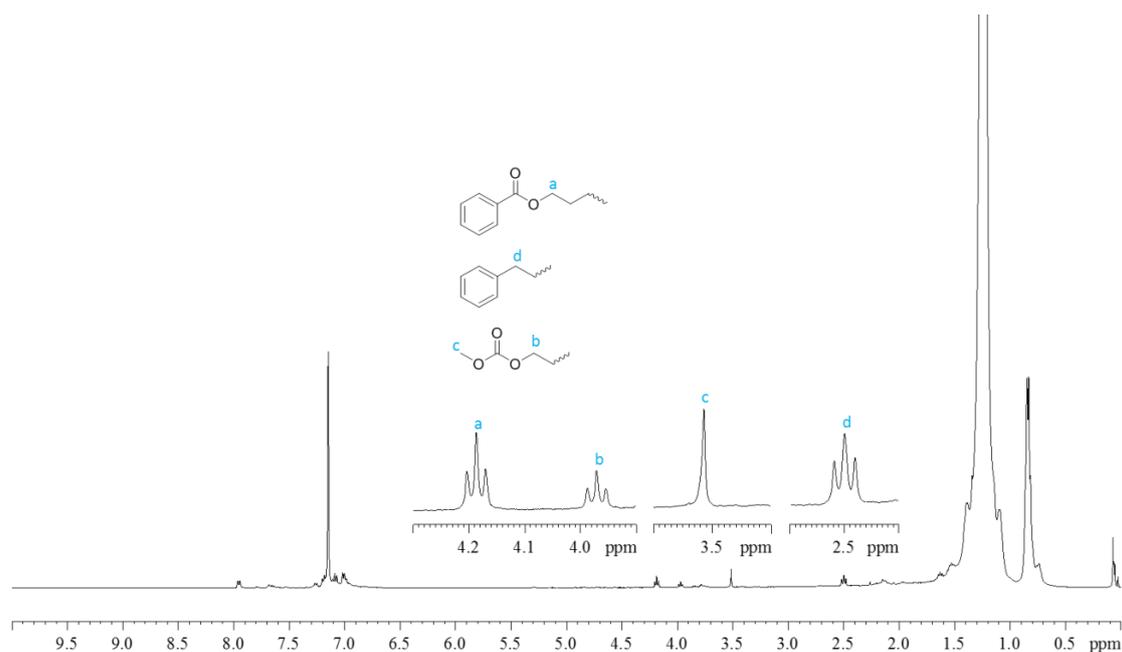**S3**. ^{1}H-NMR spectrum of the lauroyl peroxide-initiated PE produced in DMC.

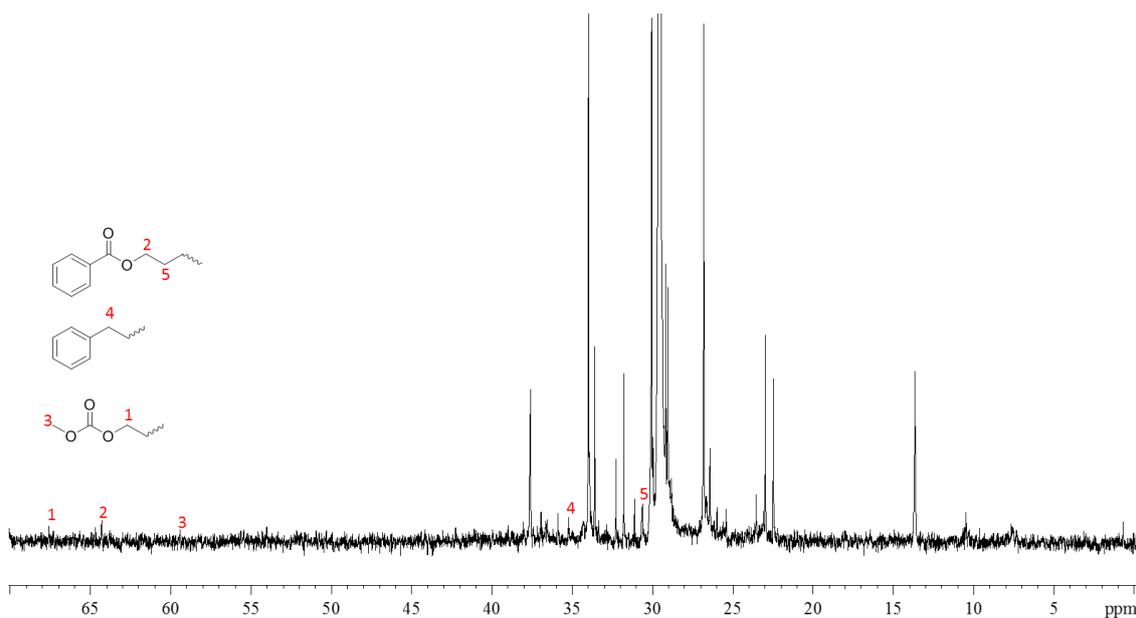**S4**. Aliphatic region of the ^{13}C-NMR spectrum of the lauroyl peroxide-initiated PE produced in DMC.

Benzoyl peroxide-initiated
PE produced in CO$_2$

Benzoyl peroxide-initiated PE
produced in absence of CO$_2$
(after washing)

Benzoyl peroxide-initiated PE
produced in absence of CO$_2$
(before washing)
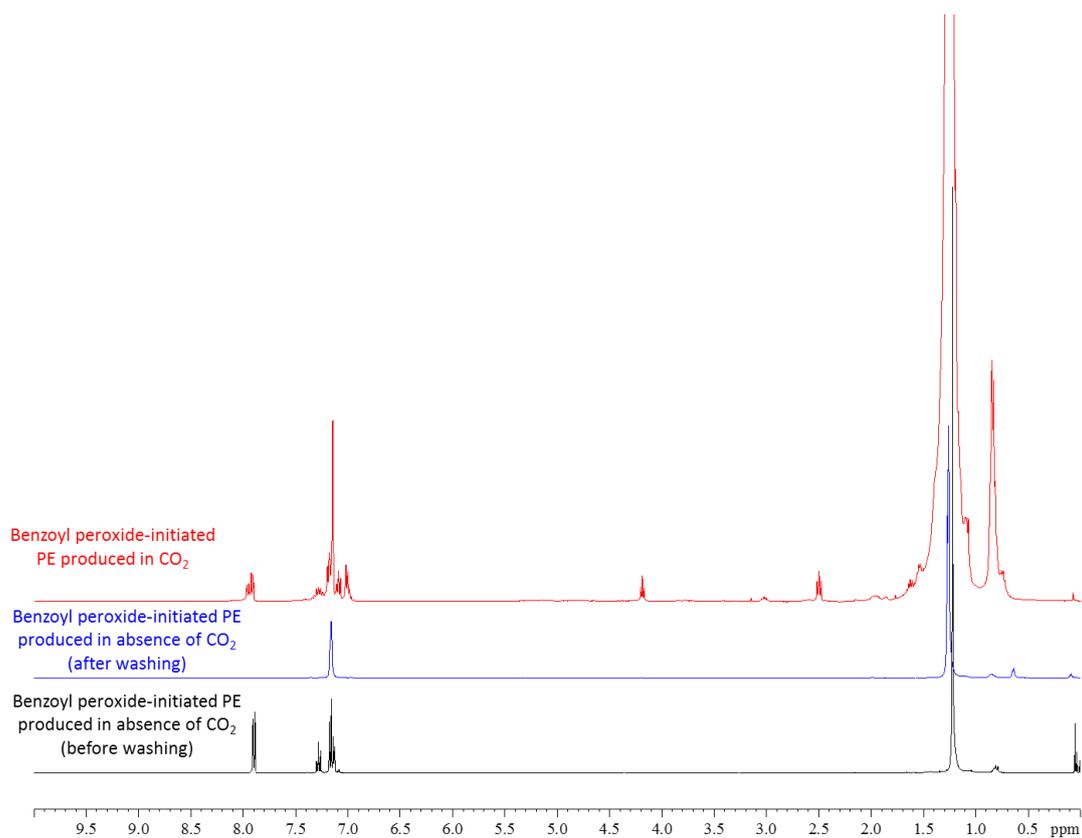
S5. ^{1}H-NMR spectra of the benzoyl peroxide-initiated PE produced in presence and absence of CO$_2$.

S6. Full superimposition of ^{13}C-NMR spectra & aliphatic region of ^{13}C-NMR spectra of the benzoyl peroxide-initiated PE produced in presence and absence of CO_2 (after washing you even see the disappearance of the signal at 41.5ppm characteristic of leftover unreacted benzoyl peroxide).
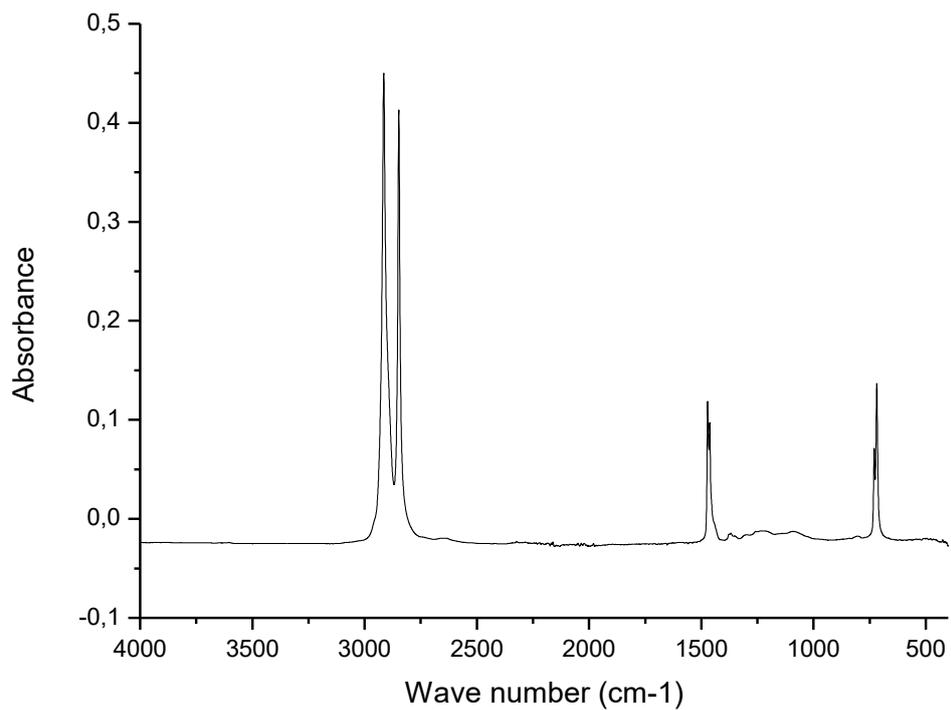
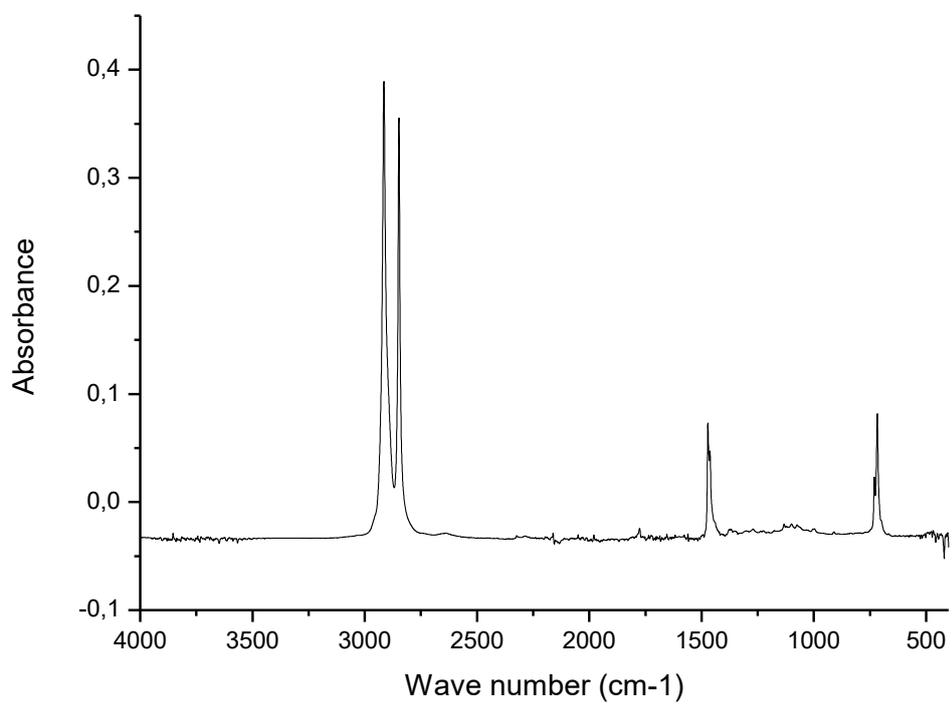**S7**. ^{1}H-NMR spectrum of the benzoyl peroxide-initiated PE produced in DMC.

S8. ^{13}C-NMR spectrum of the benzoyl peroxide-initiated PE produced in DMC.

Fourier Transform Infrared Spectroscopy (FTIR)

The device used for infrared analysis is a Nicolet iS50 infrared spectrometer from Thermo Fisher Scientific. The infrared spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} with 32 scans and a resolution of 4. A background spectrum is collected and subtracted from the spectrum of the sample. Samples do not require any prior preparation and were analyzed directly by the ATR module. The software used here for the analysis is OMNIC from Thermo Fisher Scientific.

**S9**. IR spectrum of the AIBN-initiated PE produced in CO_2.

S10. IR spectrum of the lauroyl peroxide-initiated PE produced in CO_2.

Differential Scanning Calorimetry (DSC)

DSC analyses were carried out on a DSC 3+- Differential Scanning Calorimetry apparatus from METTLER TOLEDO equipped with an auto sampler. This device has a wide temperature range from -70 to 700 °C. A computer controls the device and retrieves the results using STARe software from METTLER TOLEDO. For all the polyethylene samples, a heating-cooling-heating (25 °C $\leftrightarrow$ 180 °C) process was performed with a heating rate of 10 °C/min and N_2 flow of 30 mL/min.

Lauroyl peroxide-initiated PE in CO_2
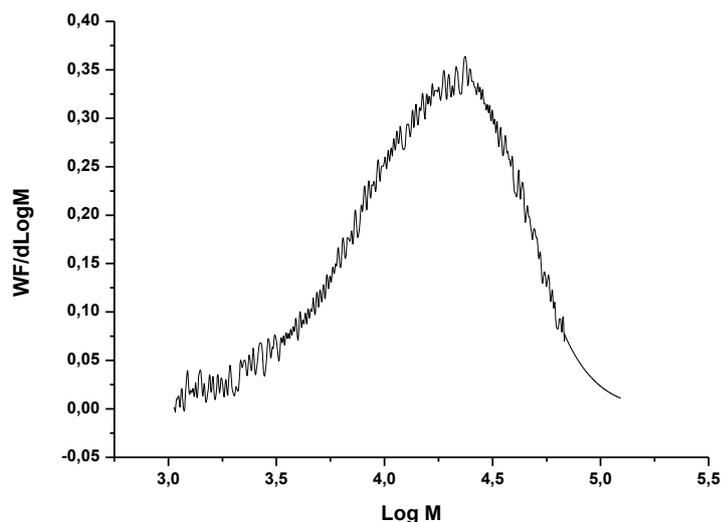Benzoyl peroxide-initiated PE in CO_2
AIBN-initiated PE in CO_2
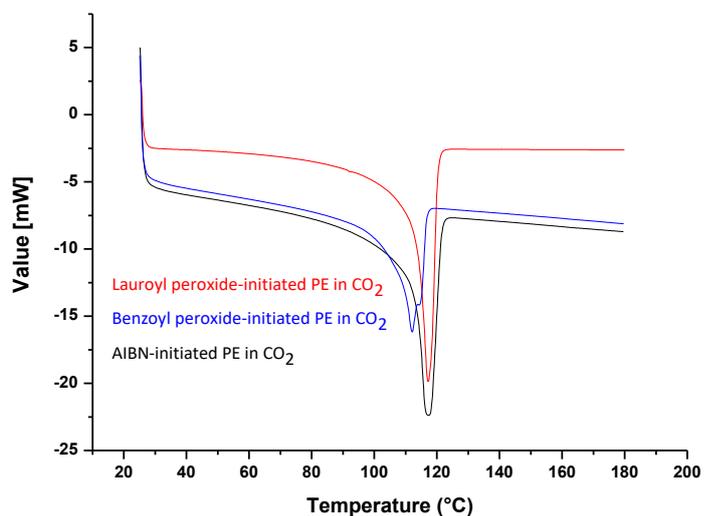
S11. DSC thermograms of the AIBN, lauroyl peroxide, and benzoyl peroxide-initiated PE produced in CO_2 (80 bars at the desired temperature).

AIBN-intiated PE in DMC
Lauroyl peroxide-intiated PE in DMC
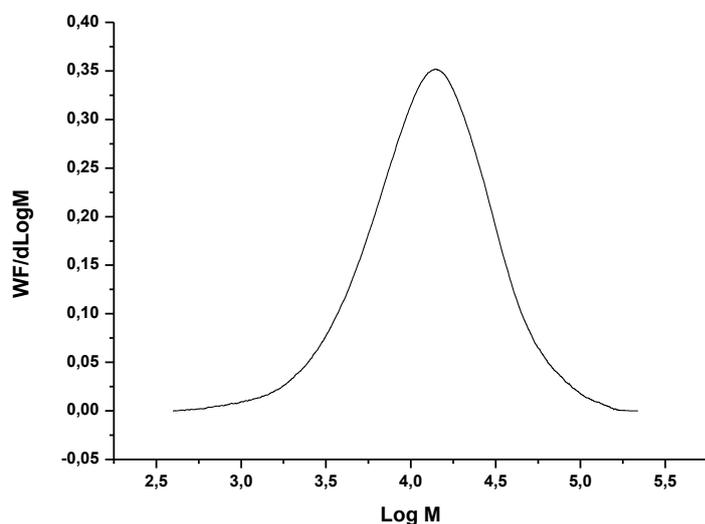Benzoyl peroxide-intiated PE in DMC
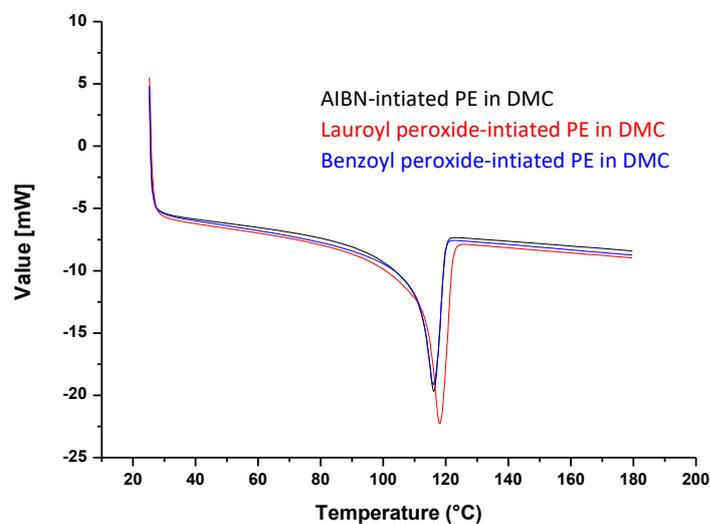
S12. DSC thermograms of the AIBN, lauroyl peroxide, and benzoyl peroxide-initiated PE produced in DMC.

# Size-Exclusion Chromatography (SEC)

The high temperature size-exclusion chromatography (gel-permeation chromatography (GPC)) analyses were performed using a "Viscotek-Malvern instrument high temperature GPC system" equipped with a differential refractive index detector, viscometer and light scattering detector: Column set: 4 x PLgel Olexis 20 µm columns; Injection volume: 200 µL; Eluent: 1,2,4 trichlorobenzene at 150 °C + 2,6-di-*tert*-butyl-4-methylphenol (0.2 g.L^{-1}); flow rate: 1.0 ml/min; OmniSEC software (ver. 5.12) was used for data interpretation.

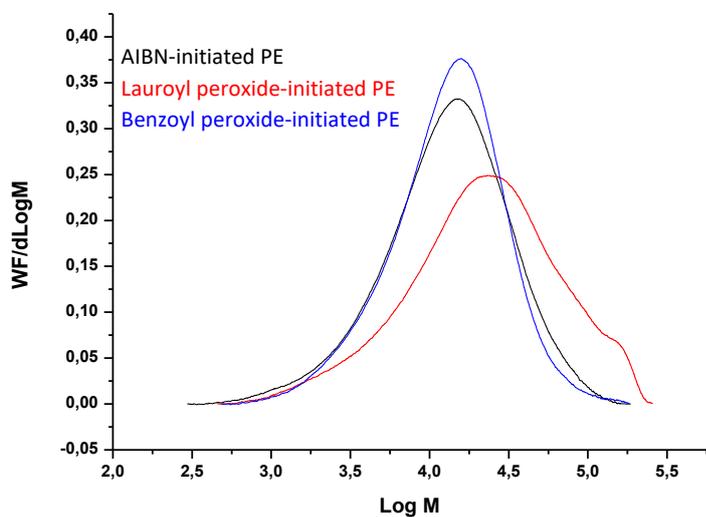**S13**. Molar mass distribution of the AIBN-initiated PE produced in CO_2 (80 bars CO_2 at 35 °C).

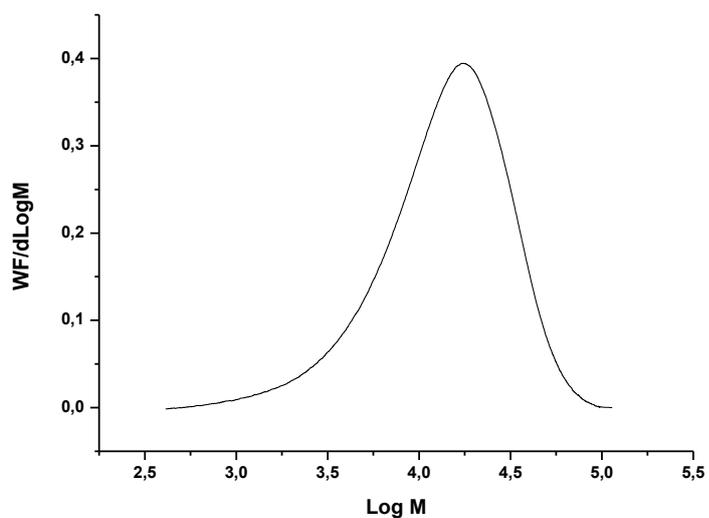**S14**. Molar mass distribution of the lauroyl peroxide-initiated PE produced in CO_2 (20 bars CO_2 at 35 °C).
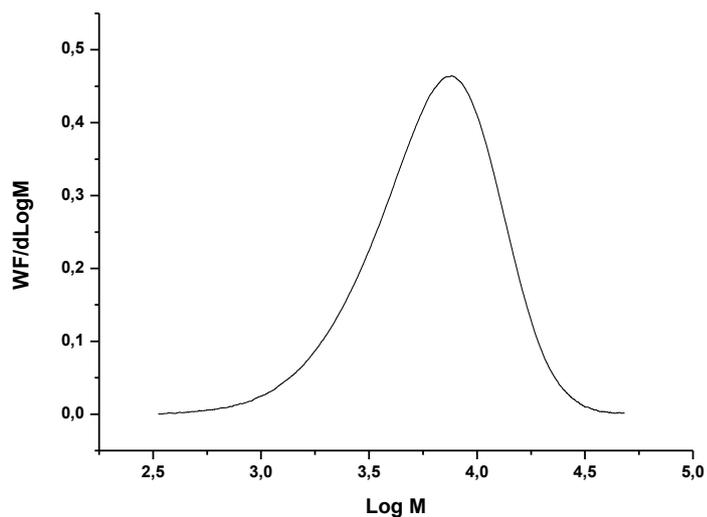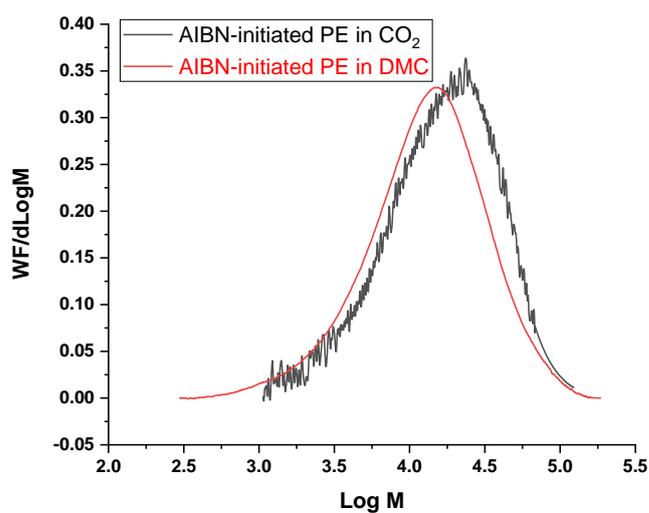
S15. Molar mass distribution of the benzoyl peroxide-initiated PE produced in CO_2 (80 bars CO_2 at 45 °C).
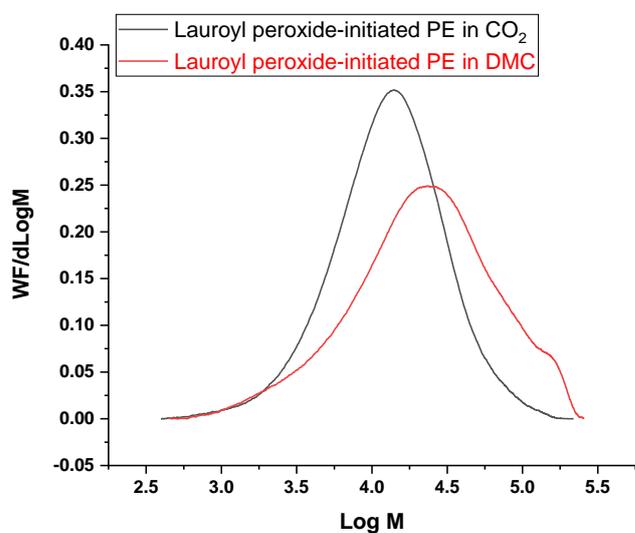

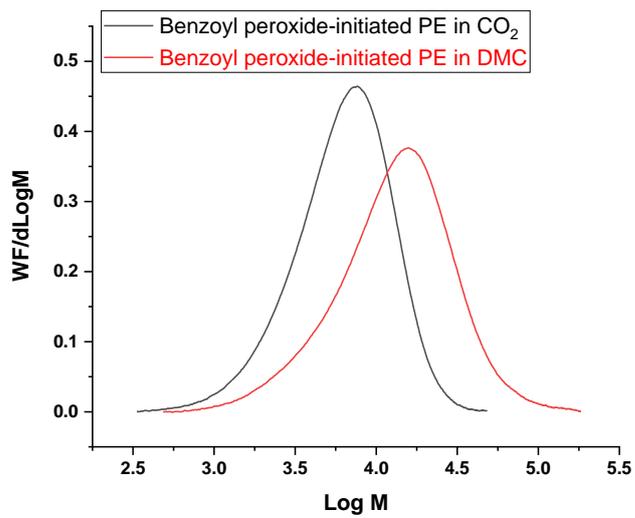**S16.** Molar mass distributions of the AIBN, lauroyl peroxide, and benzoyl peroxide-initiated PE produced in DMC.

S17. Molar mass distribution of the benzoyl peroxide-initiated PE produced in CO_2 (80 bars CO_2 at 35 °C) at 70 °C.

S18. Overlays of molar mass distributions of the AIBN-initiated PE produced in CO_2 (80 bar CO_2 at 35 °C) versus that of the AIBN-initiated PE produced in DMC under the same conditions.

S19. Overlays of molar mass distributions of the LP-initiated PE produced in CO_2 (20 bar CO_2 at 35 °C) versus that of the LP-initiated PE produced in DMC under the same conditions.
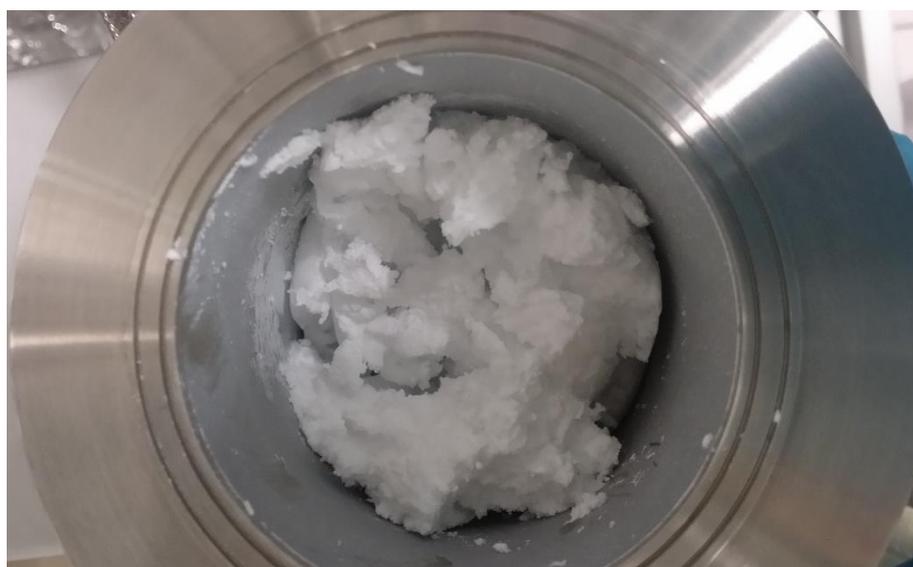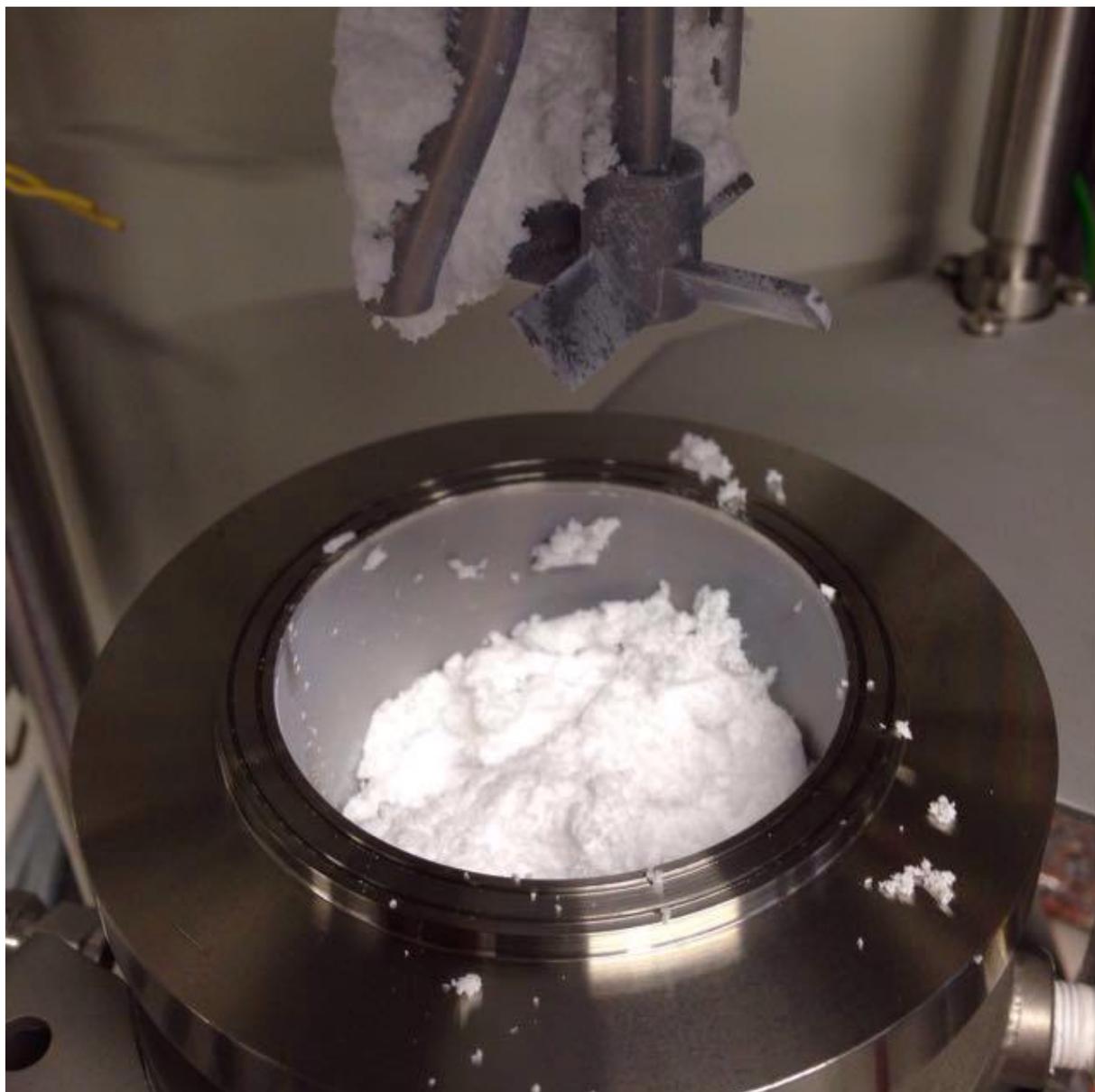
S20. Overlays of molar mass distributions of the BP-initiated PE produced in CO_2 (80 bar CO_2 at 45 °C) versus that of the BP-initiated PE produced in DMC under the same conditions.

Ethylene Free Radical Polymerization in scCO$_2$: Photos

S21. Ethylene free radical polymerization in scCO$_2$ in the sapphire-windowed reactor.

S22. Dry PE obtained when opening the reactor (no need for additional purification).

Scanning Electron Microscopy (SEM) Characterization

Scanning electron microscope (SEM) observations of the polymer particles were made with a FEI Quanta FEG 250 scanning electron microscope. Micrographs were taken at 5 KV acceleration voltage. The samples for SEM observation were prepared by sticking the polyethylene powder directly from the reactor on conductive tape, without any precipitation/filtration/drying steps. Before the SEM observations, all the sample surfaces were coated with a layer of 15 nm of copper.
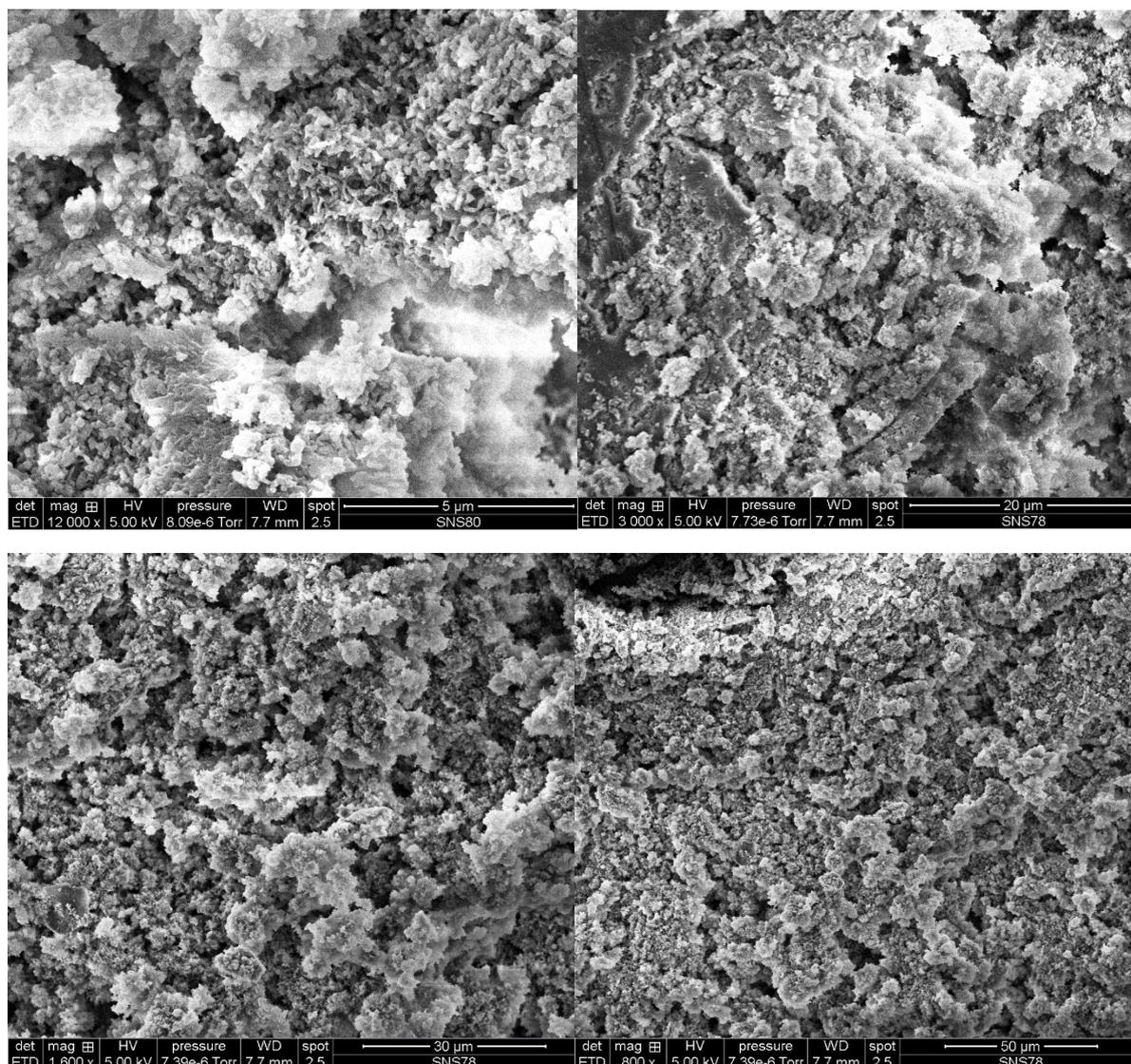
S23. SEM pictures of PE obtained from AIBN-initiated polymerization in $scCO_2$ at various scales.