Electronic Supplementary Information

Supercritical Behavior in Free Radical Polymerization of Ethylene in the Medium Pressure Range

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Polyethylene characterizations

Molecular weights of polyethylenes were determined by size exclusion chromatography (SEC) using a Waters Alliance GPCV 2000 instrument (columns: PLgel Olexis); two detectors (viscosimeter and refractometer) in trichlorobenzene (flow rate: 1 mL/min) at 150°C. The system was calibrated with polystyrene standards using universal calibration. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1 at a heating rate of 5 K/min. Two successive heating and cooling of the samples were performed. We have considered data (Tm values, crystallinity) obtained during the second heats.

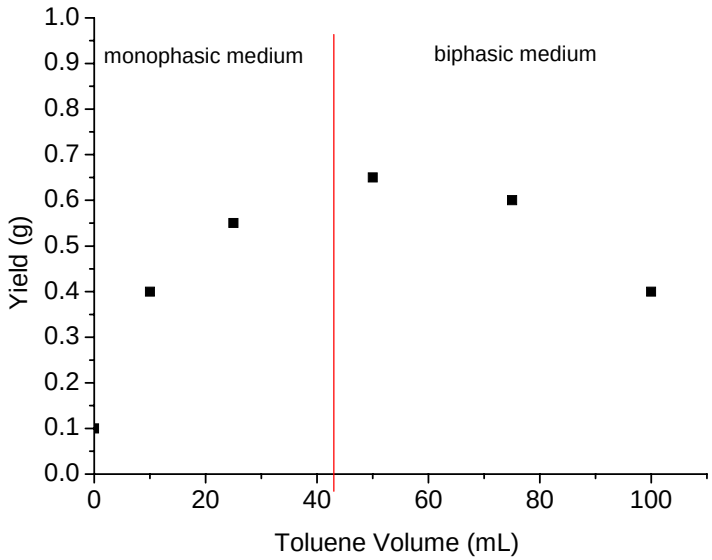

Figure S1: Toluene volume influence on radical polymerization of ethylene

■ : 50mg AIBN, 4h at 70°C under 100 bar of ethylene pressure

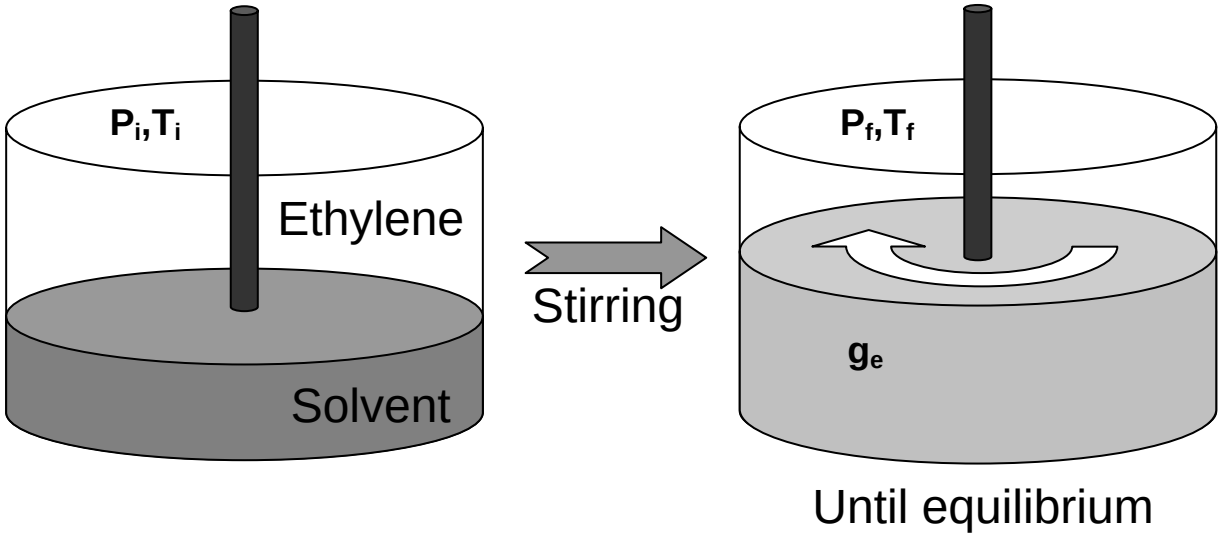

Figure S2: Modus operandi to calculate ethylene solubility

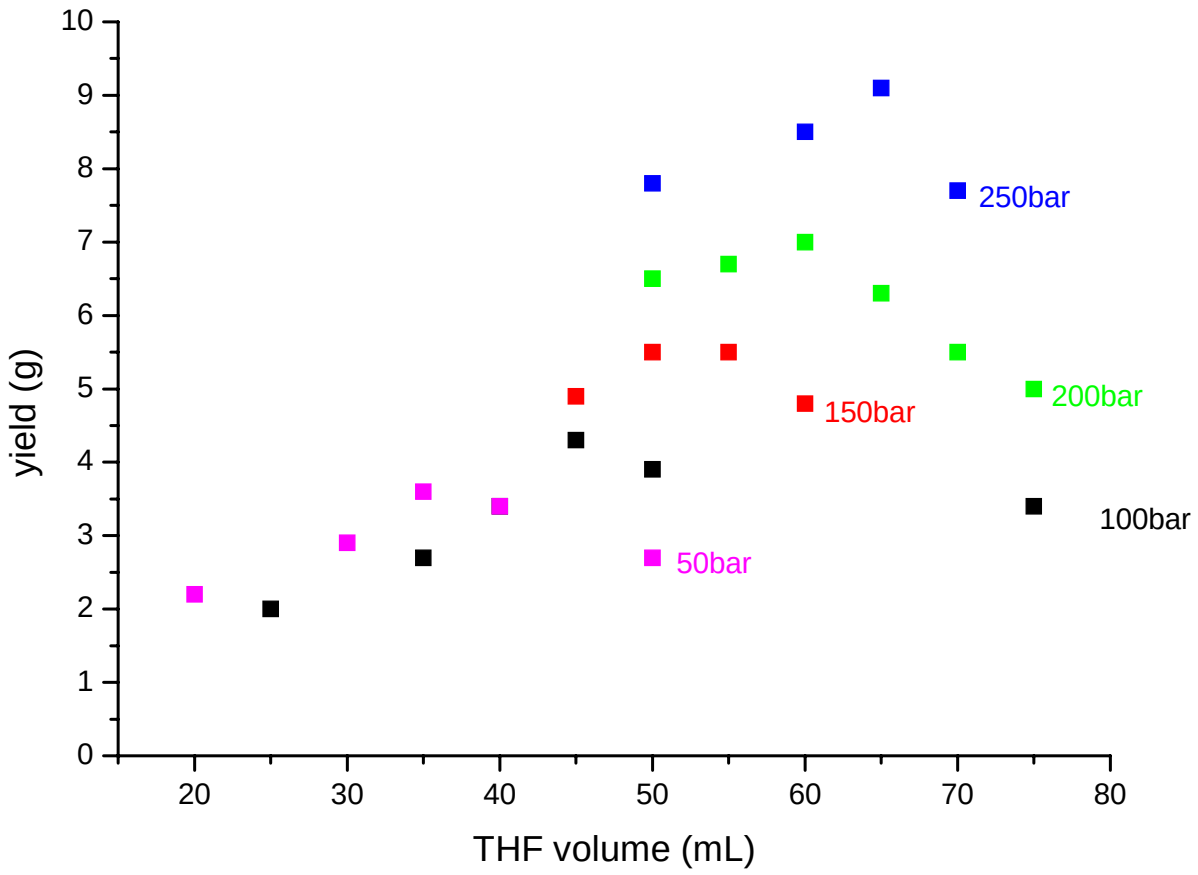

Figure S3: THF volume influence on radical polymerization of ethylene at different pressures

■ : 50mg AIBN, 4h at 70°C under 50 bar of ethylene pressure

■ : 50mg AIBN, 4h at 70°C under 100 bar of ethylene pressure (figure 1)

■ : 50mg AIBN, 4h at 70°C under 150 bar of ethylene pressure

■ : 50mg AIBN, 4h at 70°C under 200 bar of ethylene pressure

■ : 50mg AIBN, 4h at 70°C under 250 bar of ethylene pressure

Table S1 : THF volume influence on radical polymerization of ethylene (experimental data of Figure 1)

Run	THF volume (mL)	Yield (g)	Melting point (°C)	Crystallinity (%)	Mn (g/mol)	PDI
1	0	0.1	105.3	46	3010	1.3
2	2	0.4	113.6	64	4440	1.8
3	5	0.5	115.7	65	4660	1.3
4	10	0.9	116.1	61	3600	1.9
5	25	2.0	115.7	58	3350	1.7
6	35	2.7	115.6	58	2380	1.3
7	40	3.4	115.4	60	2760	1.6
8	45	4.3	115.3	62	2240	1.3
9	50	3.9	115.2	58	1190	1.9
10	75	3.4	105.7	55	820	1.5
11	100	3.3	101.9	55	740	1.5

Reactions were carried at 70°C under ethylene pressure (100 bar) during 4h with 50 mg AIBN

Table S2 : Toluene volume influence on radical polymerization of ethylene (experimental data of Figure S1)

Run	Toluene volume (mL)	Yield (g)	Melting point (°C)	Crystallinity (%)	Mn (g/mol)	PDI
12	0	0.1	105.3	46	3010	1.3
13	10	0.4	114.7	55	4120	1.5
14	25	0.55	116.1	52	2670	1.5
15	50	0.65	115.9	63	2340	1.9
16	75	0.6	113.7	57	2500	1.4
17	100	0.4	108.7	62	1470	1.4

Reactions were carried at 70°C under ethylene pressure (100 bar) during 4h with 50 mg AIBN

Table S3 : Influence of the concentration of initiator on radical polymerization of ethylene (experimental data of Figure 2)

Run	Solvent	AIBN (mg)	Yield (g)
17	THF	15	0.6
18	THF	25	2.2
19	THF	50	3.9
20 (9)	THF	80	5.0
21	THF	105	6.9
22	THF	212	8.4
23	THF	500	14
24	Toluene	10	0.3
25	Toluene	20	0.4
26 (15)	Toluene	51	0.7
27	Toluene	70	0.9
28	Toluene	224	1.5
29	Toluene	512	2

Reactions were carried at 70°C under 100 bar of ethylene during 4 hours in 50 mL of solvent

Table S4 : Experimental determination of the transition at different ethylene pressure (experimental data of Figure 7)

Run	Pressure (bar)	Volume (mL)	Yield (g)
30	25	10	0.6
31	25	20	1.2
32	25	25	1.7
33	25	30	1.5
34	25	50	1.3
35	50	20	2.2
36	50	30	2.9
37	50	35	3.6
38	50	40	3.4
39	50	50	2.7
40	150	45	4.9
41	150	50	5.5
42	150	55	5.5
43	150	60	4.8
44	200	50	6.5
45	200	55	6.7
46	200	60	7.0
47	200	65	6.3
48	200	70	5.5
49	200	75	5.0

50	250	50	7.8
51	250	60	8.5
52	250	65	9.1
53	250	70	7.7

Reactions were carried at 70°C under ethylene pressure during 4 hours in THF