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

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ABSTRACT: Free radical polymerization of ethylene in an intermediate pressure and temperature range ($P_{ethylene}$ < 250 bar and 50°C < T < 90°C) in the presence of an organic solvent has been studied. Under these conditions a phase transition occurred between a biphasic medium (polymerization takes place in the liquid phase in which radical initiator and some ethylene are dissolved) and a supercritical monophasic medium (polymerization takes place in an unique supercritical phase (solvent + ethylene)). This transition allows the experimental observations such as activity evolution vs. solvent volume to be rationalized and can be also predicted by thermodynamic calculations.

Free radical polymerization of ethylene is industrially conducted under high pressures (1000-4000 bar) and temperatures (200-300°C).[1,2] Under these conditions, polymerization occurs in a monophasic supercritical medium without any use of solvent. A polymerization of ethylene with an organic solvent as diluent can be considered under milder conditions but free radical polymerization of ethylene is usually assumed to be inefficient except when some strong Lewis acids are used to activate the monomer.[3-5] We have recently reported that the solvent was not spectator and that a simple change of solvent can increase drastically the efficiency of the free radical polymerization of ethylene[6] under mild conditions (ethylene pressure up to 250 bar; T = 70°C).

Low molecular weight polyethylenes (Mn<5000 g/mol) have been produced exhibiting a slightly branched microstructure (7 branches/1000C in toluene and 9 branches/1000C in THF) and a melting temperature between 110°C and 120°C. The crystallinity is below catalytic PEHD but higher than for standard LDPE produced at high temperature and pressure by free radical process (~70%). The development of the free radical polymerization of ethylene under mild conditions is an attractive challenge, because it could be a new tool to create new functionalized polyethylenes (e.g. using chain transfer to solvent) with a better controlled molecular weight distribution and microstructure as it was described in our previous paper.[6]

Actually there is a lack of study on ethylene polymerization in this intermediate range of pressure. As a consequence, all the data allowing to understand in which conditions the chemistry takes places are not available and cannot be extrapolated from the two better known reaction ranges. Polyethylene synthesis is performed by catalysis[7,8] in the low pressure range (up to 100 bar), while free radical polymerization is performed much over 1000 bar at high temperature. An important issue for our intermediate conditions is the determination of the phase diagram of the polymerization medium: whether the polymerization takes place in a biphasic or in a monophasic medium. The first case is a well known biphasic system at low pressure and temperature, with a polymerization located in the liquid phase where some ethylene is dissolved from a surrounding ethylene gas phase. The solubility of ethylene in a broad wide range of organic solvents has been fully determined under 40 bar of ethylene pressure.[9-11] At

high pressure and high temperature, the system is constituted by a unique supercritical phase (usually ethylene is used without any additional solvent). In the intermediate pressure range the two aforementioned systems could be envisaged depending on the ethylene pressure, the amount of solvent (slurry conditions) and the temperature. The biphasic or monophasic medium will not lead to the same polymerization activity and polyethylene microstructure. Therefore the determination of the phase transition is of great interest.

In the present paper, the transition has been evidenced experimentally and confirmed using simple thermodynamic calculations leading to a complete description of our polymerization system with for example the exact composition of the polymerization medium.

Experimental evidence of the transition

Polymerization of ethylene was performed in batch reactor by increasing amounts of THF as organic solvent at 70°C under a pressure of 100 bar of ethylene (Figure 1). Note that at this pressure and this temperature free radical polymerization of ethylene is usually assumed to be inefficient and this unusual activity observed has been directly related to the presence of THF.[6]

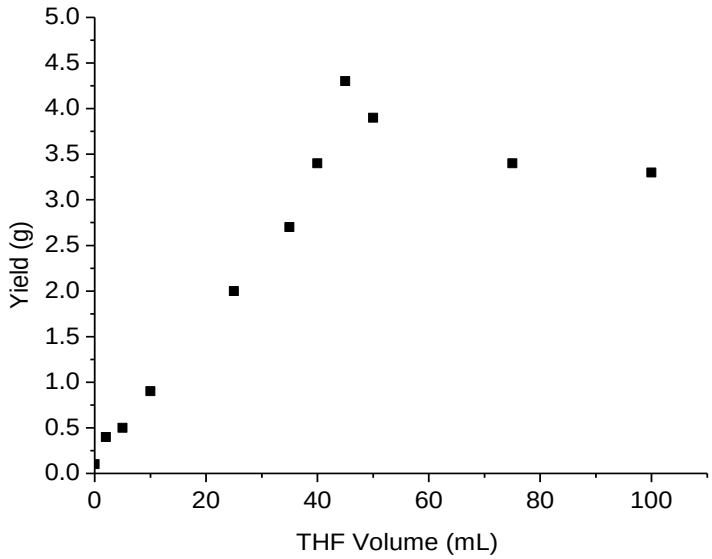

Figure 1: Influence of THF content on radical polymerization of ethylene

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

The results showed a break of behavior between 40 and 45 mL of tetrahydrofurane (THF). At low amount of THF, yield increased according to the volume of the solvent. On the contrary it decreased slightly for higher volume of THF. This behavior cannot be due to the THF by itself because no polyethylene was synthesized without AIBN in THF in the same experimental conditions. The highest conversion was reached around the break between 40-45 mL where the yield was over 4.5g.

These observations could be compatible with a phase transition between a monophasic medium at low THF volume, where the reaction takes place in a single supercritical phase (ethylene + THF= 1 phase), and a biphasic medium at higher volume, where the polymerization takes place in the liquid phase in which ethylene is dissolved.

In the case of a biphasic medium, no AIBN is in the gaseous phase and thus polymerization occurred only in the liquid phase.[12,13] Over 45 mL of THF, the polymerization became less efficient due to a dilution of the initiator while the ethylene concentration remains constant with increasing amounts of THF. Below 40 mL of THF, reaction seems to be accelerated by a solvent activation effect evidenced in our previous work.[6] In this case initiator concentration remains constant and ethylene concentration decreases with increasing amounts of THF (the partial pressure of ethylene P_E decreases while total pressure P_{tot} remains constant: $P_{tot} = P_E + P_{THF}$). Without solvent the reaction is almost inefficient and activation with THF is almost proportional to THF amount. Radical polymerization occurred efficiently only in the presence of THF for solvating the propagating radical.[6] Note that at this state the conversion of our system is unknown as the real fraction of THF and ethylene, due to the complexity of the polymerization medium.

A similar set of experiment was also performed in toluene (see Supporting Information Figure S1). The same behavior was observed with toluene, but the activation was less impacted. Polymerization

yield slightly increased with increasing amounts of toluene until a maximum again around 40-45 mL of solvent and then finally decreased. The ratio between activation with THF and toluene did not remain constant with the solvent amount. Below 40 mL of solvent the relative activation (yield in THF vs yield in toluene) increased up to a factor 6, and remained constant above this volume.

The produced polyethylenes had a melting point between 110°C and 117°C and a crystallinity of 50-60% (see supporting information Table S1 and S2). As expected polyethylene molecular weight decreased with increasing solvent volumes due to transfer of propagating radical to the solvent. In addition, molecular weight dropped over 45 mL due to the sudden increase of solvent concentration in the liquid phase after the assumed phase transition. Moreover, low polydispersity index (PDI) were measured and the molecular weight distributions of polyethylenes were always monomodal, which strongly suggests that polymerization occurred in one phase, respectively in the supercritical phase (solvent + ethylene) for a monophasic medium and in the liquid phase for a biphasic system.

In order to confirm this phase transition, polymerizations were performed at 70°C under 100 bar of ethylene with 50 mL of THF and various amounts of AIBN (see Supportion Information Table S3). If no phase transition occurs this set of experiment could be related to the previous one (same amount of AIBN but various volume). For this purpose we plotted yield vs the initial ratio AIBN/THF (Figure 2).

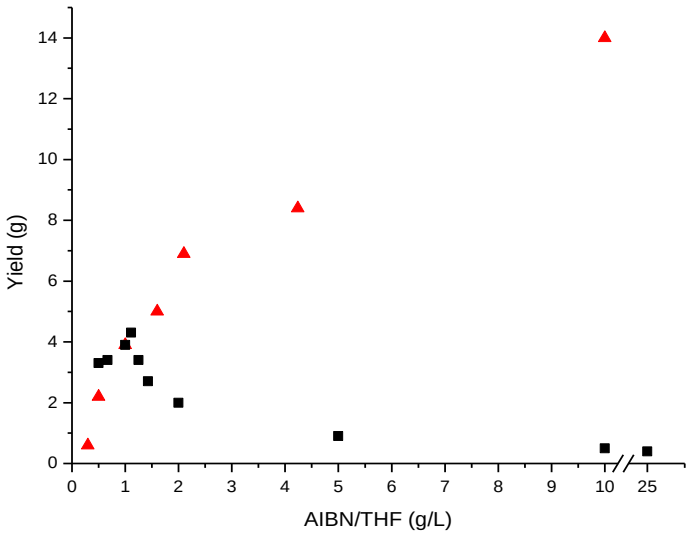

Figure 2: Influence of AIBN/THF ratio on radical polymerization of ethylene

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

▲ : 50 mL of THF, 4h at 70°C under 100 bar of ethylene pressure, various amount of AIBN

The two set of experiments diverge from the ratio AIBN/THF of 1.25 g/L corresponding to 45 mL of THF (50 mg AIBN). This could be related to the phase transition aforementioned. Below this amount both set of experiments follow the same curve (biphasic medium). It implies that the proportion of AIBN in the supercritical phase of the biphasic medium is negligible as the PE formed in this phase.

How to determine this phase transition theoretically?

The previous findings highlighted the importance of the reaction medium. To determine theoretically this transition in order to valid our hypothesis we need as prerequisite to calculate experimentally the solubility of ethylene in the solvent phase. As far as we know ethylene solubility was well determined up to 40 bar in organic solvent.[9-11]

Ethylene solubility determination (40-130 bar)

To determine ethylene solubility at higher pressure we assume that solubilization is a slow kinetic process when there is no stirring. The reactor was thus charged with ethylene at a desired pressure and then stirring was started until thermodynamic equilibrium. Pressure and temperature evolution were recorded during all the experiment (see Supporting Information Figure S2).

A Peng-Robinson equation of state,[14] was chosen after examination of numerous available equations of state as an excellent compromise between simplicity and efficiency. According to it, the density of ethylene (d) is known in the supercritical phase for each P, T (equations 1-2). The difference in density between the initial step (i) (before stirring) and the equilibrium (f) is due to the solubilization of ethylene in the solvent (s_E). To perform the calculation the total inner volume of the reactor has been determined

(V_R = 230 mL).[15] The volume of the solvent being known (V_S), solubility was calculated by mass balance through the equation 3. The dilatation of solvent (V_E) due to the solubilization of ethylene was determined by varying the volume of solvent at a constant P_f.

$$d_i = EOS(P_i, T_i) \quad (1)$$

$$d_f = EOS(P_f, T_f) \quad (2)$$

$$\underbrace{d_i(V_R - V_S)}_{\text{initial } m_E \text{ in gaseous phase}} - \underbrace{d_f(V_R - V_S - V_E)}_{\text{final } m_E \text{ in gaseous phase}} = \underbrace{s_E V_S}_{\text{final } m_E \text{ in liquid phase}} \quad (3)$$

According to this modus operandi, ethylene solubility in toluene and THF was determined up to 130 bar of pressure of ethylene at 70°C (Figure 3) in toluene. The solubility at 50°C and 90°C in toluene was also measured.

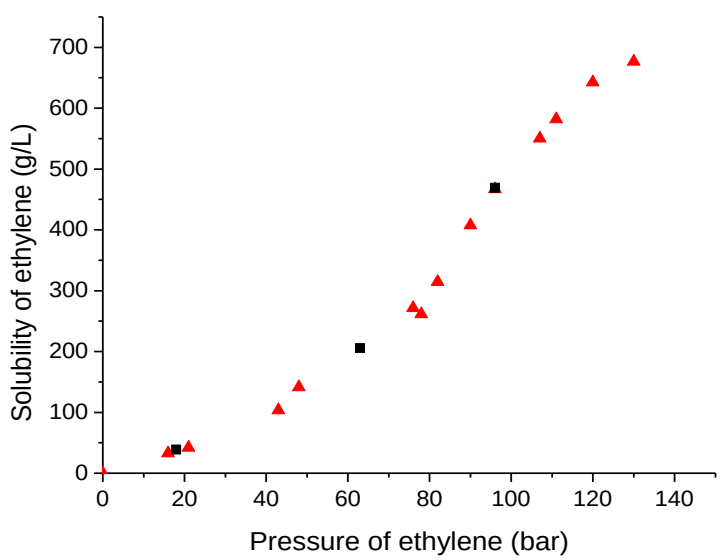

Figure 3: Solubility of Ethylene at 70°C (in grams of ethylene per initial volume of solvent)

■ : in THF, ▲ : in Toluene

As an illustration, at 100 bar about 24 g of ethylene are dissolved at 70°C in 50 mL of solvent initially introduced (usual conditions of our polymerization experiments). At low pressure the slope was about 2

g/L/bar according to the literature. Over 50 bar an increase of the slope to 9 g/L/bar was observed. The solubility seems to be mostly independent to the nature of solvent. Solubility varies linearly with density of ethylene with a slope of 3.04 (see Figure 4). This linear relationship is valid whatever the temperature and the nature of solvent.

A linear relationship also occurred between ethylene density and the effective ethylene solubility, i.e. the solubility in the ethylene expanded solvent. The liquid phase is about 1.8 times more concentrated in ethylene than the supercritical phase (ethylene) which explains in part (in addition to solvent activation effect) why the free radical polymerization of ethylene is more efficient in a solvent than without any solvent in this pressure range.

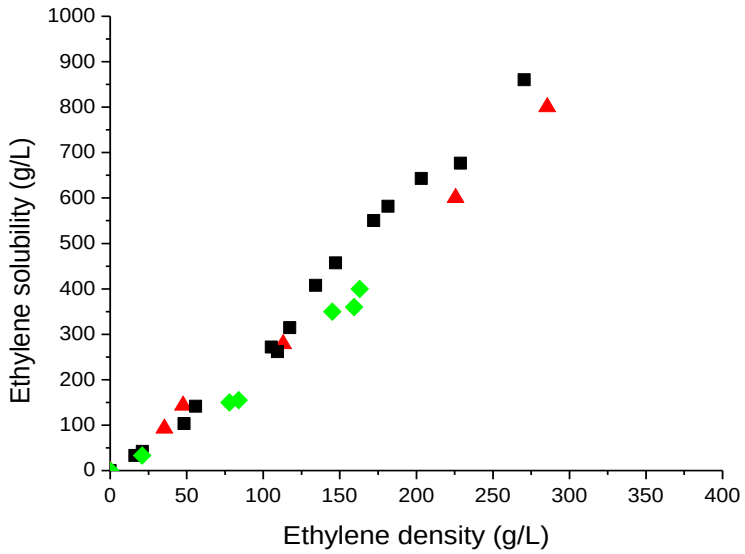

Figure 4: Correlation between ethylene density and solubility in toluene

▲: at 50°C; ■ : at 70°C; ♦: at 90°C

Phase transition determination

Ethylene solubility has been determined up to 130 bar, but the phase transition between a biphasic medium at low pressure and a monophasic medium at higher pressure still has to be determined. This

was done using the Peng-Robinson equation of state[16] (equations 4-6) and the standard mixing rules for a and b coefficients (equations 7-8)[16] for a bicomponent system (ethylene and solvent).

Peng – Robinson equation of state

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \quad (4)$$

$$a = \frac{0.45724 R^2 T_c^2}{P_c}\left[1 + f\omega\left(1 - T_r^{1/2}\right)\right]^2 \quad (5)$$

where $f\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$ and $T_r = \frac{\mathrm{T}}{\mathrm{T_c}}$

$$b = \frac{0.07780 R T_c}{P_c} \quad (6)$$

Mixing rules

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j a_{ij} \text{ where } a_{ij} = \sqrt{a_i a_j} \quad (7)$$

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \text{ where } b_{ij} = \frac{b_i + b_j}{2} \quad (8)$$

where P is the pressure, T the absolute temperature, v the molar volume, R the ideal gas constant, Pc the pressure at the critical point, Tc the absolute temperature at the critical point, ω the acentric factor,[17] x_i the molar fraction of compound i (solvent or ethylene).

To calculate the transition we have to determine at each temperature (because a depends of T), critical pressure and temperature of the ethylene-solvent mixture using equations 5-8 for all compositions.

Mixture composition depends on three parameters only: temperature, pressure of ethylene (which determines the amount of ethylene),[18] and volume of solvent (which determines the amount of solvent). For each composition and temperature a and b were thus calculated using equations 7 and 8. Then critical parameters of the mixture have been determined (equations 5 and 6). These critical parameters also depend on ethylene pressure, temperature and solvent volume. At a given temperature if $Tc_{mixture}<T$ and $Pc_{mixture}<P$, the medium is supercritical and monophasic. If $Tc_{mixture}>T$ it is biphasic system with a

liquid phase of solvent containing dissolved ethylene. $Pc_{mixture}>P$ and $Tc_{mixture}<T$ never occur due to the intrinsic properties of the mixture.

From these calculations a phase transition surface can be obtained depending on temperature, ethylene pressure, and amount of solvent as shown in Figure 5 and the medium composition can be precisely determined for each coordinate.

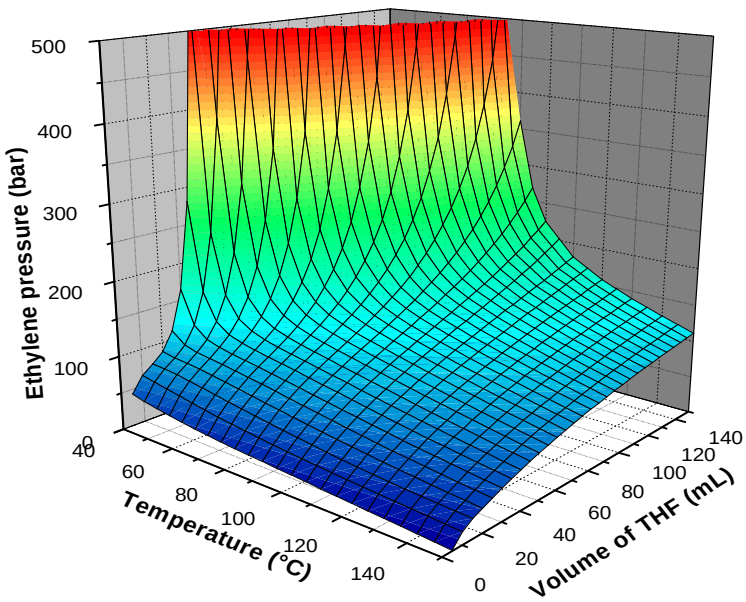

Figure 5: Phase diagram for Ethylene/THF mixture

Above the phase transition surface the system will be a supercritical monophasic medium (THF and ethylene in a unique supercritical phase) and below the surface it will be biphasic (2 phases with ethylene in both). Note that the transition surface possesses a certain thickness (second order transition) which cannot be precisely determined using our calculation method.

Our method was also used for various solvents such as toluene and the phase transition was determined for each solvent (see on Figure 6 for a comparison of transition between THF and toluene at a constant volume of solvent: 50 mL).

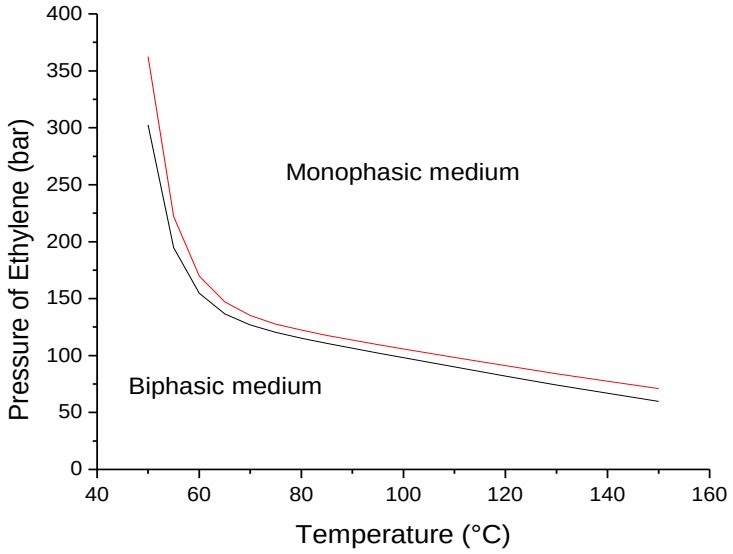

Figure 6: Phase diagram of Ethylene/Solvent system

—: with 50 mL THF, —: with 50 mL Toluene

At iso-volume, THF and toluene present almost the same phase transition. For example at 70°C, 50 mL of solvent, the transition is at 128 bar in THF and at 135 bar in toluene. This transition could explain the impossibility of measuring ethylene solubility over 130 bar.

Are these calculations accurate?

Calculations show a phase transition under 100 bar at 70°C for THF between 36 and 37 mL (39-40 mL for toluene) which is in good agreement with experimental behavior in ethylene free radical polymerization (Figure 1). As proposed, the break in activity corresponds to the phase transition which experimentally occurs between 40 and 45 mL solvent using these polymerization conditions (100 bar,

70°C). To validate our calculations we performed polymerization at different pressure (25-250 bar) at 70°C to experimentally determine the transition between monophasic and biphasic medium (Figure 7) by varying the volume of THF to identify the break in activity.

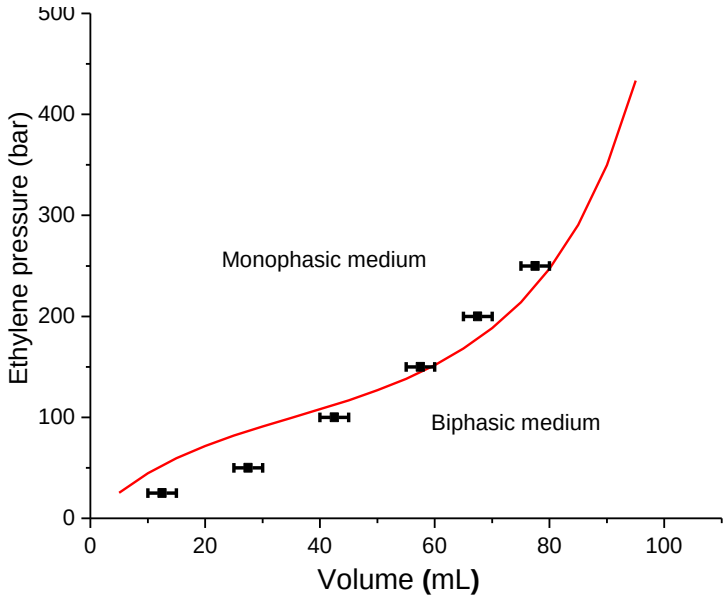

Figure 7: Phase diagram for Ethylene/THF mixture at 70°C

—: Theoretical measure, ■: Experimental measure

Our methodology seems to predict the transition of the system with a good correlation. The difference between theoretical and experimental transition could originate from the non-ideality of the THF/ethylene mixture. But the accuracy of the cubic Peng-Robinson equation of state seems to be a good enough to describe the mixture of ethylene and solvent in our range of temperature and pressure.

In summary, the activity profile for free radical polymerization of ethylene show a break that could be related to a phase transition between a biphasic medium (two phases with ethylene in both) and a supercritical monophasic medium (solvent + ethylene). This phase transition depending on ethylene pressure, temperature and amount of organic solvent was fully determined by thermodynamic calculations using Peng-Robinson EOS and mixing rules for a bicomponent system (ethylene and

solvent). For this purpose solubility of ethylene was determined up to 130 bar in various solvents: solubility was mostly found to be independent of solvent properties. The full description of the polymerization medium proposed from these calculations allow to better understand the free radical polymerization of ethylene in the intermediate pressure range ($20 < P_{Ethylene} < 300$ bar) and opens the door to accurate copolymerization studies, the comonomers playing the role of a solvent. Note that our calculation method is not restricted to ethylene but could be applied for other supercritical fluids.

Acknowledgment: E.G. thanks the "Ministère de la Recherche et de l'Enseignement Supérieur" for fellowship.

Supporting Information Available: Text giving experimental details, figures and tables showing the influence of toluene or THF volume on radical polymerization of ethylene, modus operandi to calculate ethylene solubility. This material is available free of charge via the Internet at http://pubs.acs.org

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(13) When the condensable fractions of the gaseous phase corresponding to a mixture of 500 mg of AIBN in 50 mL of THF at 70°C and under 100 bar of ethylene were recovered in glass vial, no significant amount of AIBN was detected.

(14) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. In *The properties of gases and liquids*, 4th ed.; Reid, R. C.; Prausnitz, J. M.; Poling, B. E., Eds ; McGraw-Hill Book Company: Singapore, 1988, p 29-35.

(15) Total reactor volume was calculated by studying the pressure fall of the intermediate tank when we charge the empty reactor. A mass balance gives us: $d_i(V_T) = d_f(V_T + V_R)$ with V_T the tank volume.

(16) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. In *The properties of gases and liquids*, 4th ed.; Reid, R. C.; Prausnitz, J. M.; Poling, B. E., Eds ; McGraw-Hill Book Company: Singapore, 1988, p 74-84.

(17) Critical parameters for ethylene (Tc=282.4 K, Pc=50.4 bar, ω=0.089), THF (Tc=540.1 K, Pc=51.9 bar, ω=0.217), and toluene (Tc=591.8 K, Pc=41 bar, ω=0.263) from Reid, R. C.; Prausnitz, J. M.; Poling, B. E. In *The properties of gases and liquids*, 4th ed.; Reid, R. C.; Prausnitz, J. M.; Poling, B. E., Eds ; McGraw-Hill Book Company: Singapore, 1988, p 656-732.

(18) The amount of ethylene was calculated thanks to the Peng-Robinson EOS for the gaz phase and the solubility in the hypothetical liquid phase, because $m_{Etotal} = m_{E\ gaseous} + m_{E\ liquid}$.

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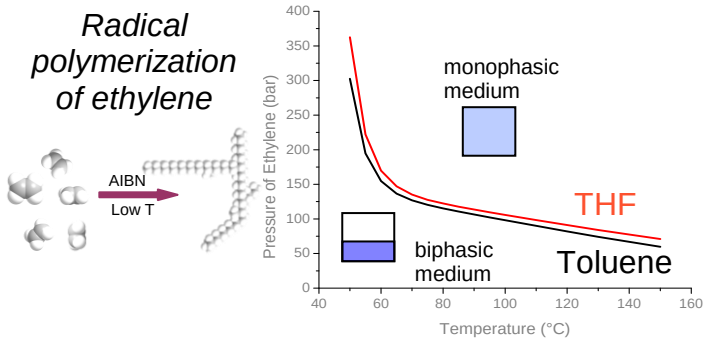

Electronic Supplementary Information

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.

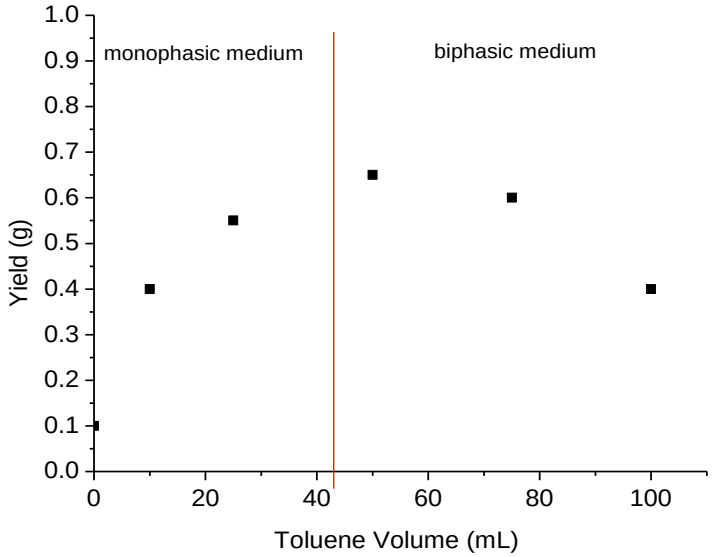

Figure S1: Toluene volume influence on radical polymerization of ethylene

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

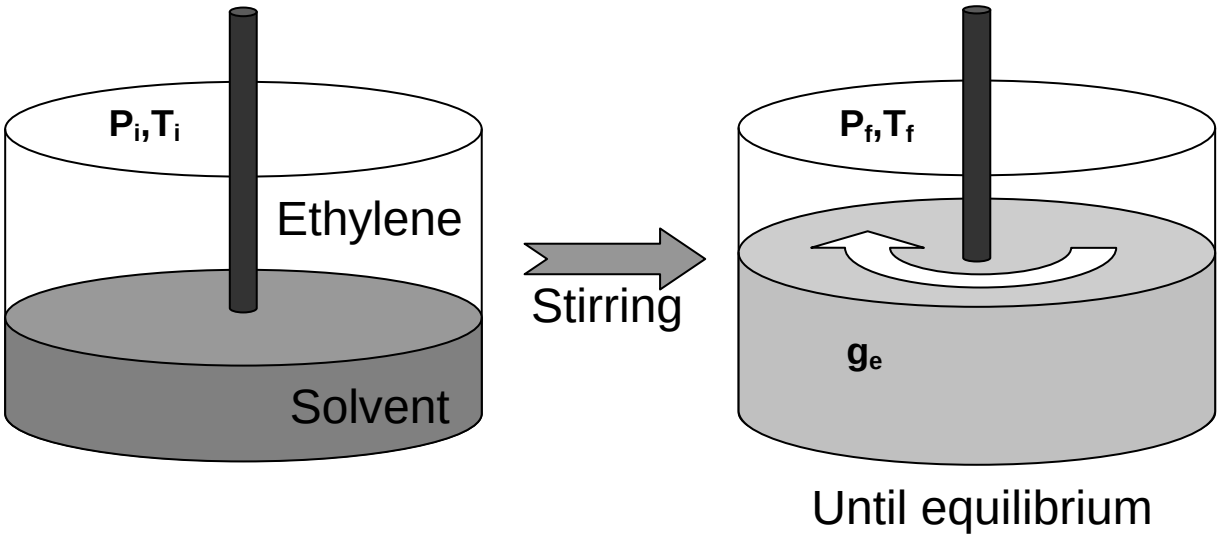

Figure S2: Modus operandi to calculate ethylene solubility

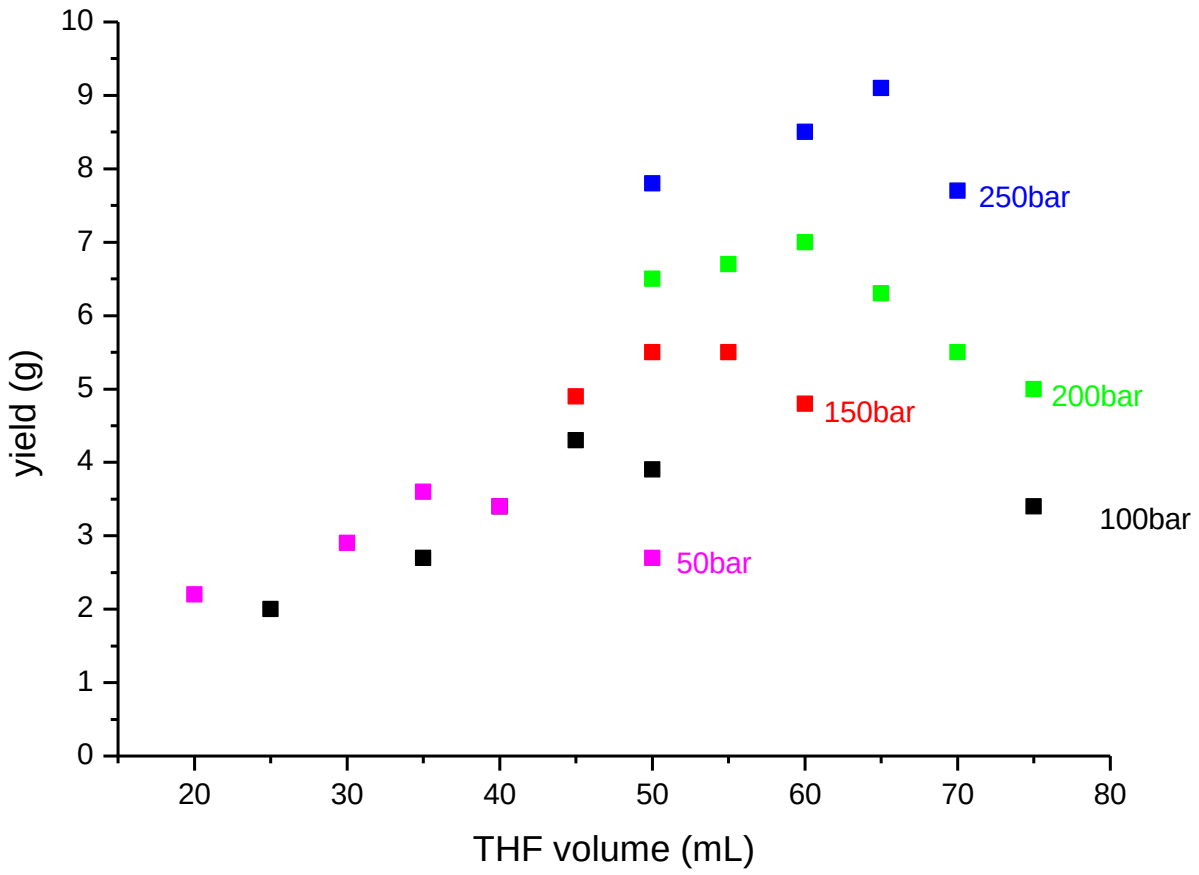

Figure S3: THF volume influence on radical polymerization of ethylene at different pressures

■ : 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