

Electronic Supplementary Information

Unusual Activation by Solvent of the Ethylene Free Radical

Polymerization

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Details of calculation of the optimum of solvent properties thanks to the Arrhenius parameters.

Free radical polymerization kinetics law link monomer conversion to the global kinetic constant. Thanks to the set of experiments we now the Arrhenius parameters dependence to the solvent properties $\left(\frac{\mu}{\varepsilon}\right)^2$.

$$\ln \frac{1}{1-x} \propto k_{tot}$$

$$\ln k_{tot} = \ln A_{tot} - \frac{E_{tot}}{RT}$$

$$X = \left(\frac{\mu}{\varepsilon}\right)^2 > 0$$

$$\ln A_{tot} = a \frac{1}{X} + b$$

$$E_{tot} = cX + d$$

Then we can calculate the optimum dependence with the temperature.

$$\frac{\partial \ln k_{tot}}{\partial X} = 0$$

$$\frac{\partial \ln k_{tot}}{\partial X} = \frac{\partial \ln A_{tot}}{\partial X} - \frac{1}{RT} \frac{\partial E_{tot}}{\partial X}$$

$$0 = -a \frac{1}{X^2} - \frac{c}{RT}$$

$$X = \sqrt{-\frac{aRT}{c}}$$

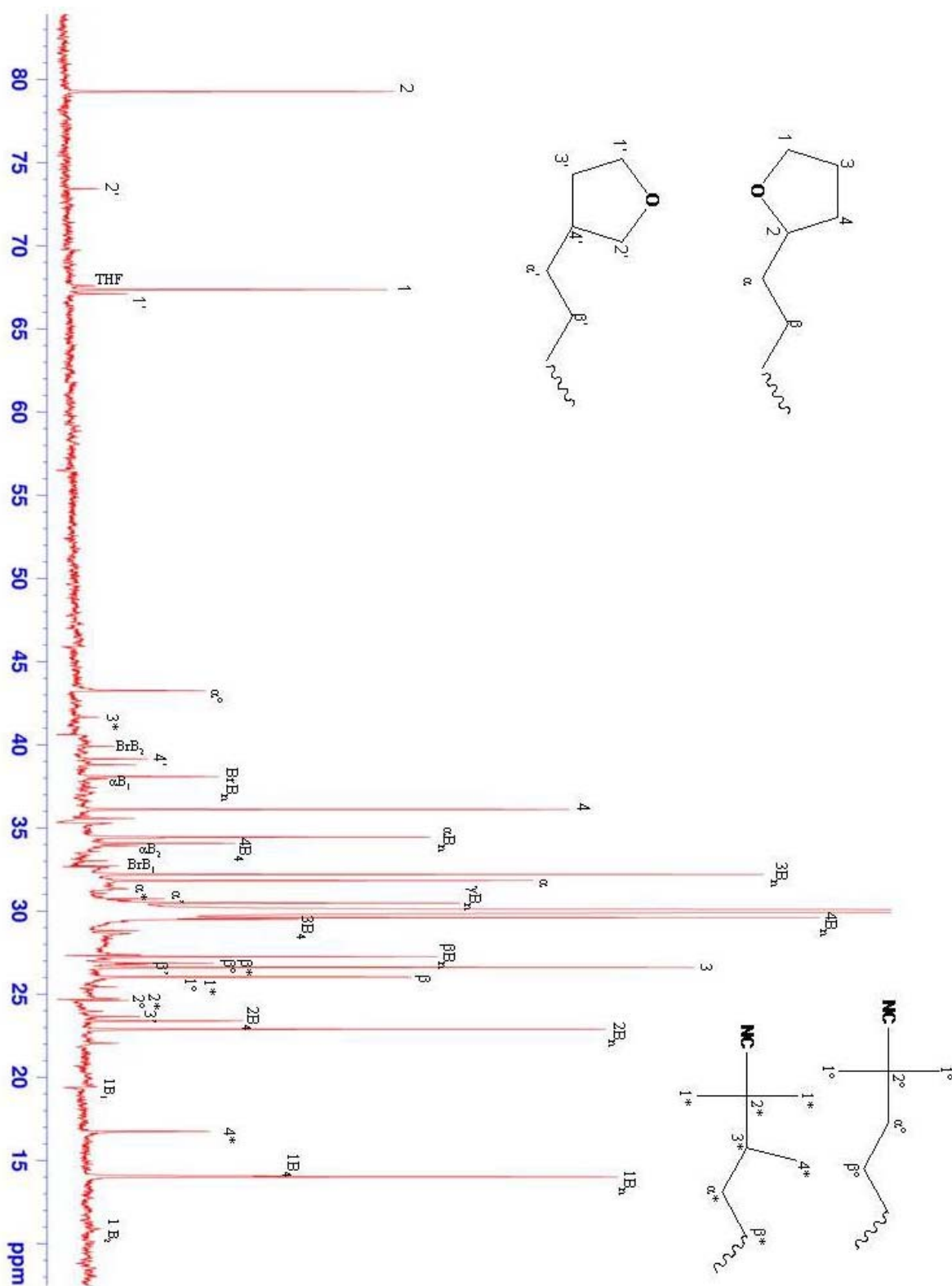


Figure S1: Typical ^{13}C NMR of polyethylene prepared in THF (notations from Galland et al for branching description ref 22 and ref 5 of the article)

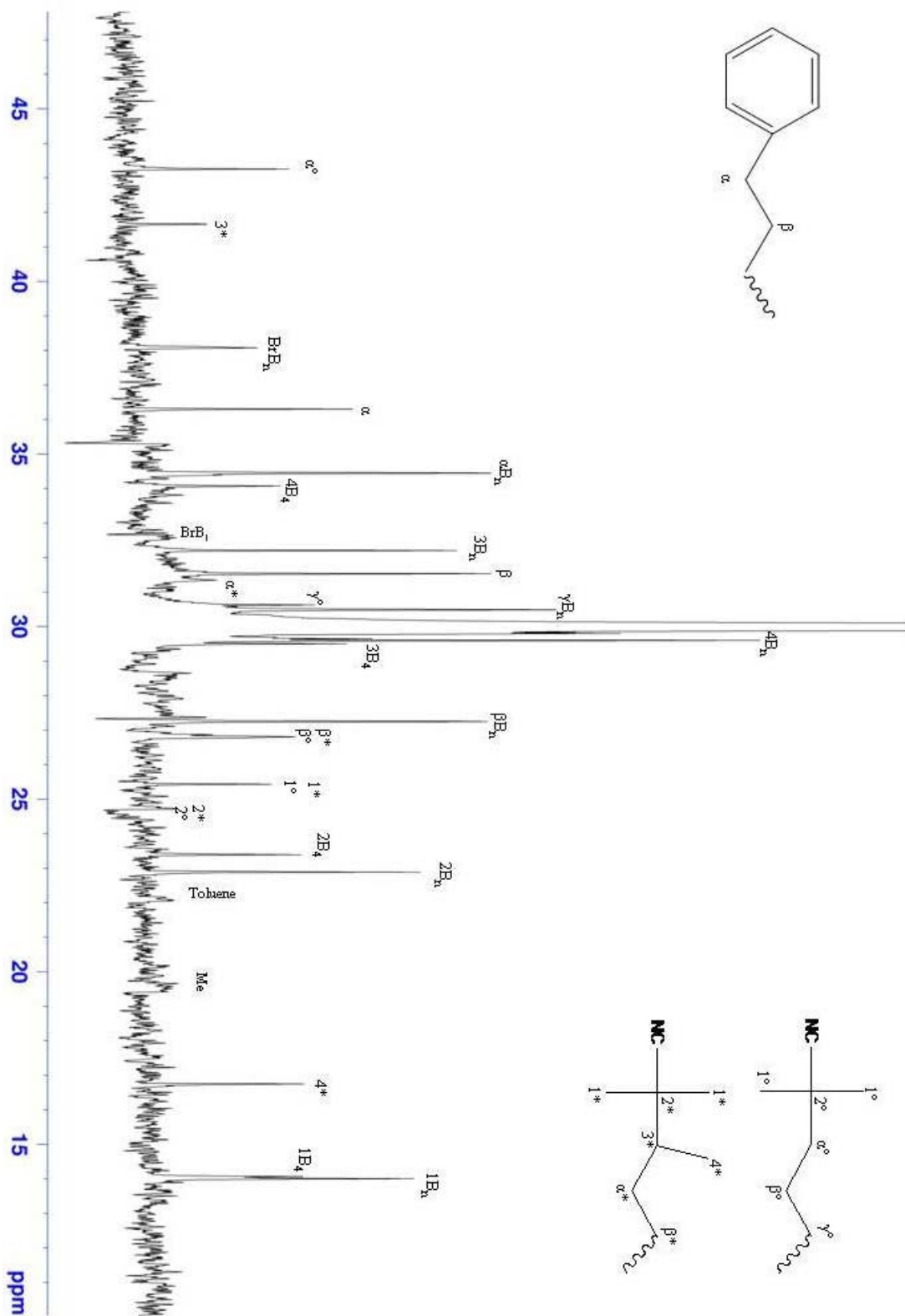


Figure S2: Typical ^{13}C NMR of polyethylene prepared in toluene (notation from Galland et

al)

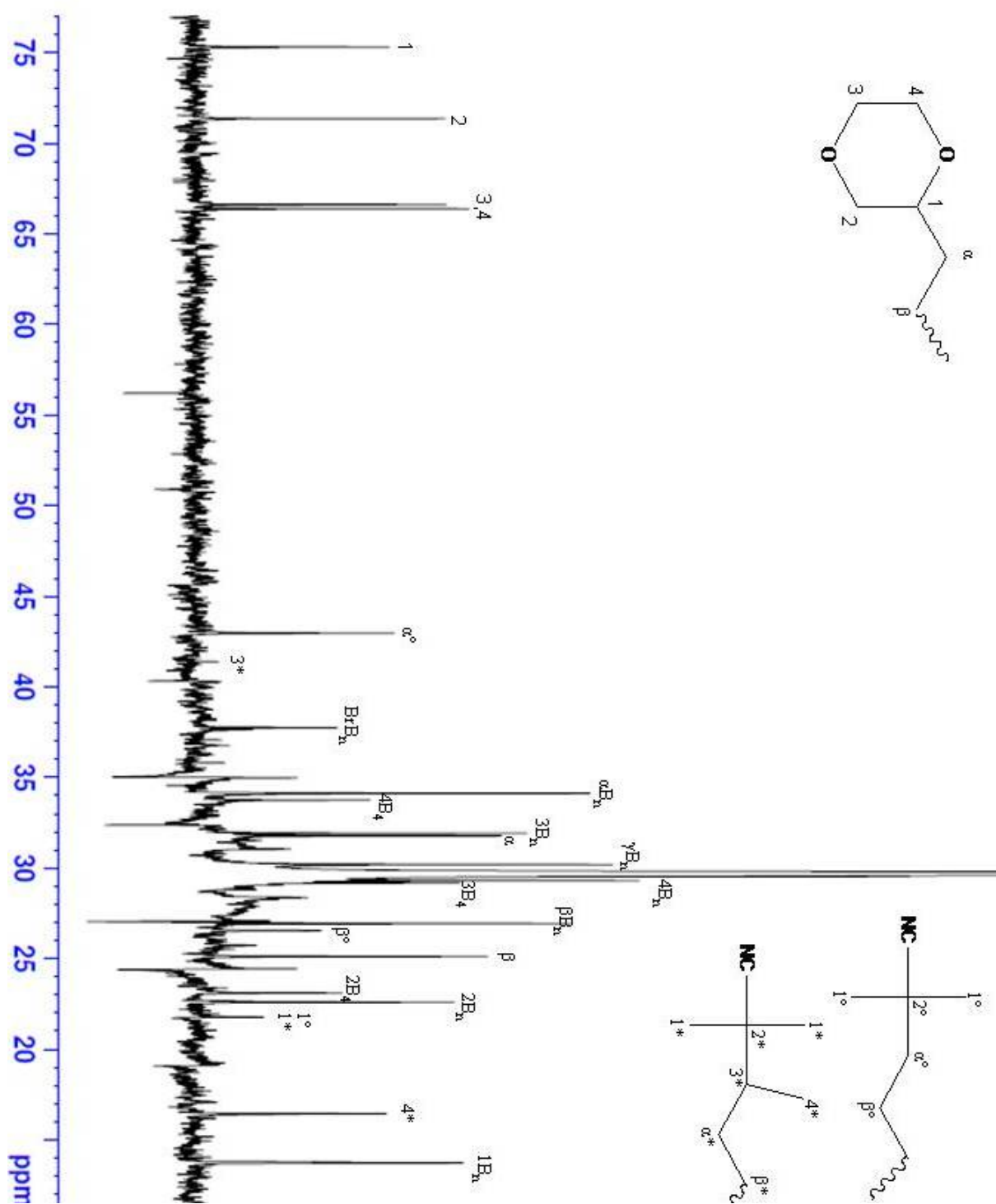


Figure S3: Typical ^{13}C NMR of polyethylene prepared in dioxane (notation from Galland et al)

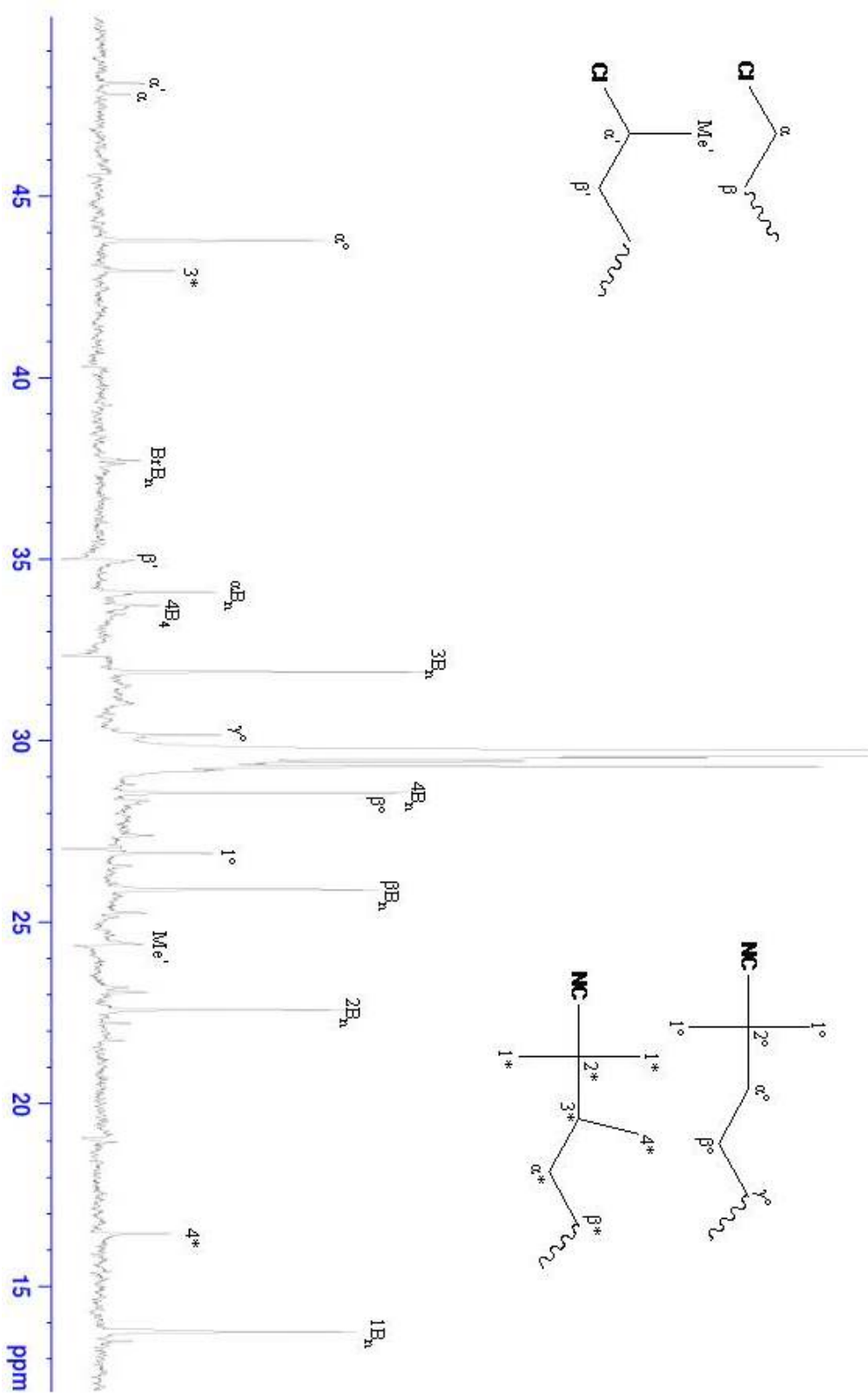


Figure S4: Typical ^{13}C NMR of polyethylene prepared in dichloromethane (notation from Galland et al)

Table S1 : Solvent mixture composition effect on radical polymerization of ethylene^a

Run	Solvent composition in volume (% toluene / % THF/ % DEC)	Yield (g)	Mn (g/mol)	PDI
21 (=4)	100/0/0	0.65	2340	1.9
22	90/10/0	0.75	1840	1.8
23	70/30/0	0.8	1260	2.
24	50/50/0	1.1	1190	2.1
25	30/70/0	1.8	1170	2.1
26	10/90/0	3.1	1190	1.9
27 (=21)	0/100/0	3.9	1190	1.9
28	0/90/10	4	1270	1.8
29	0/70/30	3.8	1560	2.1
30	0/50/50	3.3	2490	1.7
31	0/30/70	2.4	2700	2.1
32	0/10/90	1.9	5360	2.4
33 (=7)	0/0/100	1.2	7150	2.5
34	10/0/90	1.8	6630	2.4
35	30/0/70	2.5	4650	2.1
36	50/0/50	4	3210	2.6
37	70/0/30	1.8	2640	2.1
38	90/0/10	0.7	2340	2.1
39	40/40/20	2	2650	1.6
40	40/20/40	4.1	5970	2
41	20/40/40	3.7	2010	2.2

^a Reactions were carried at 70°C under 100 bar of ethylene pressure during 4h with 50 mg AIBN in 50 mL of solvent

Table S2 : Temperature impact on radical polymerization of ethylene^a

Run	Solvent	Temperature (°C)	Ethylene pressure (bar)	Yield (g) [conversion %]
42	Toluene	50	50	0.05 [0.5%]
43	Toluene	70	50	0.25 [2.7%]
44	Toluene	90	50	0.4 [4.8%]
45	Toluene	50	100	0.15 [0.4%]
46 (=4)	Toluene	70	100	0.7 [2.6%]
47	Toluene	90	100	1.3 [6.5%]
48	Toluene	50	150	0.15 [0.4%]
49	Toluene	70	150	0.8 [2%]
50	Toluene	90	150	1.7 [5.2%]
51	Toluene	50	200	0.2 [0.4%]
52	Toluene	70	200	1 [2.1%]
53	Toluene	90	200	2 [4.8%]
54	Toluene	50	250	0.25 [0.4%]
55	Toluene	70	250	1.3 [2.5%]
56	Toluene	90	250	2.5 [5.3%]
57	THF	50	50	0.4 [3.7%]
58	THF	70	50	2.9 [31.2%]
59	THF	90	50	4.1 [49.4%]
60	THF	50	100	0.6 [1.8%]
61 (=21)	THF	70	100	3.9 [15.7%]
62	THF	90	100	9 [44.7%]
63	THF	50	150	0.8 [1.7%]

64	THF	70	150	5.9 [15%]
65	THF	90	150	11 [33.6%]
66	THF	50	200	1 [1.9%]
67	THF	70	200	6.5 [13.8%]
68	THF	90	200	14.5 [35%]
69	THF	50	250	1.2 [2.1%]
70	THF	70	250	7.8 [14.9%]
71	THF	90	250	17 [35.9%]
72	DEC	50	50	0.1 [0.9%]
73	DEC	70	50	0.7 [7.5%]
74	DEC	90	50	2.5 [30.1%]
75	DEC	50	100	0.3 [0.9%]
76 (=7)	DEC	70	100	1.2 [3.5%]
77	DEC	90	100	4.3 [12.5%]
78	DEC	50	150	0.2 [0.4%]
79	DEC	70	150	1.9 [4.8%]
80	DEC	90	150	5 [15.3%]
81	DEC	50	200	0.2 [0.4%]
82	DEC	70	200	2.9 [6.2%]
83	DEC	90	200	6.3 [15.2%]
84	DEC	50	250	0.2 [0.3%]
85	DEC	70	250	3.5 [6.6%]
86	DEC	90	250	7.2 [15.2%]

^aReactions were carried under ethylene pressure during 4 hours with 50mg AIBN in 50 mL of solvent

1-hexyl radical has been simulated using GAUSSIAN03 using restricted open shell B3LYP/6-311++G basis.

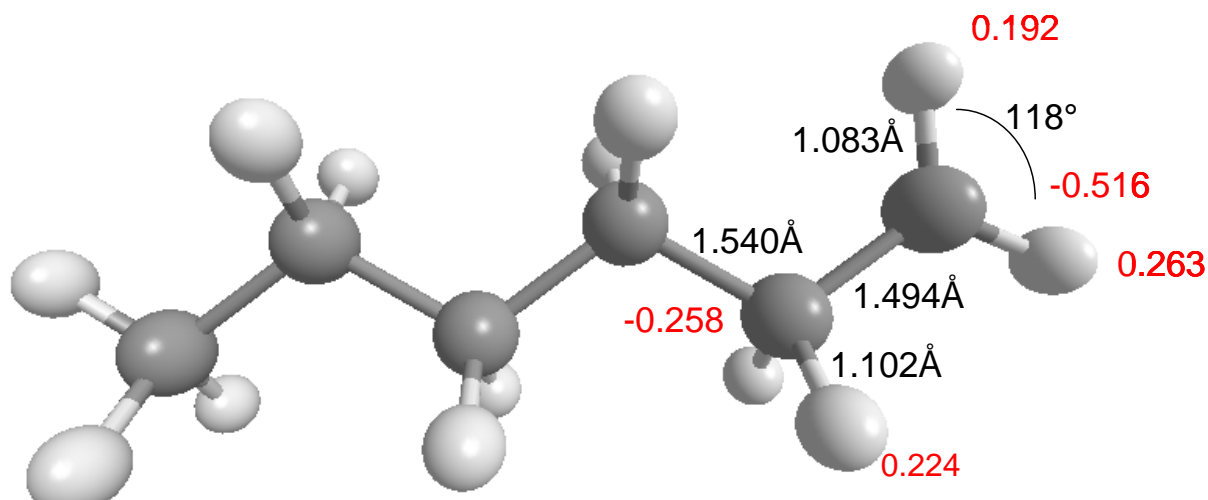


Figure S5: Relaxed 1-hexyl radical determined using GAUSSIAN03 calculation (in red are the partial Mulliken charge)

Table S3 : XYZ coordinates and mulliken charge of all atoms of 1-hexyl radical

	X (Å)	Y (Å)	Z (Å)	Mulliken charge
C	-3.068705	-0.78129438	-0.00968804	-0.936163
C	-1.899007	0.21412305	-0.00092907	-0.22222
C	-0.520477	-0.46837619	-0.00412973	-0.45143
C	0.6554958	0.52105771	0.00478151	-0.500515
C	2.035075	-0.16299197	0.00117502	-0.258503
C	3.1874262	0.78814546	0.01004793	-0.516226
H	-4.03192	-0.26585788	-0.00728355	0.239686
H	-3.038214	-1.43268143	0.8680714	0.21495
H	-3.035814	-1.41996189	-0.8966608	0.21494
H	-1.976931	0.86169144	0.87977864	0.220248
H	-1.974673	0.87445422	-0.87230679	0.220244
H	-0.442232	-1.11642707	-0.88584924	0.210398
H	-0.44459	-1.12941321	0.86810397	0.210358
H	0.5799197	1.16707995	0.88708638	0.225668

H	0.5819664	1.18047349	-0.86772897	0.225685
H	2.1035051	-0.82799116	-0.87428211	0.223605
H	2.1012486	-0.8415595	0.86636991	0.223715
H	4.2081217	0.4266013	0.00732591	0.192124
H	3.030765	1.85960971	0.01982957	0.192124

The punctual dipole momentum of the radical is calculated by $\mu_{\text{radical}} = \sum q_i r_i$ with an origine corresponding to the barycenter of the $\text{C}_2\text{H}_2^\bullet$ unit. Therefore $\mu_{\text{radical}} = 1.5009$ C.m.

AIBN fragment radical has been simulated using GAUSSIAN03 using restricted open shell B3LYP/6-311++G basis.

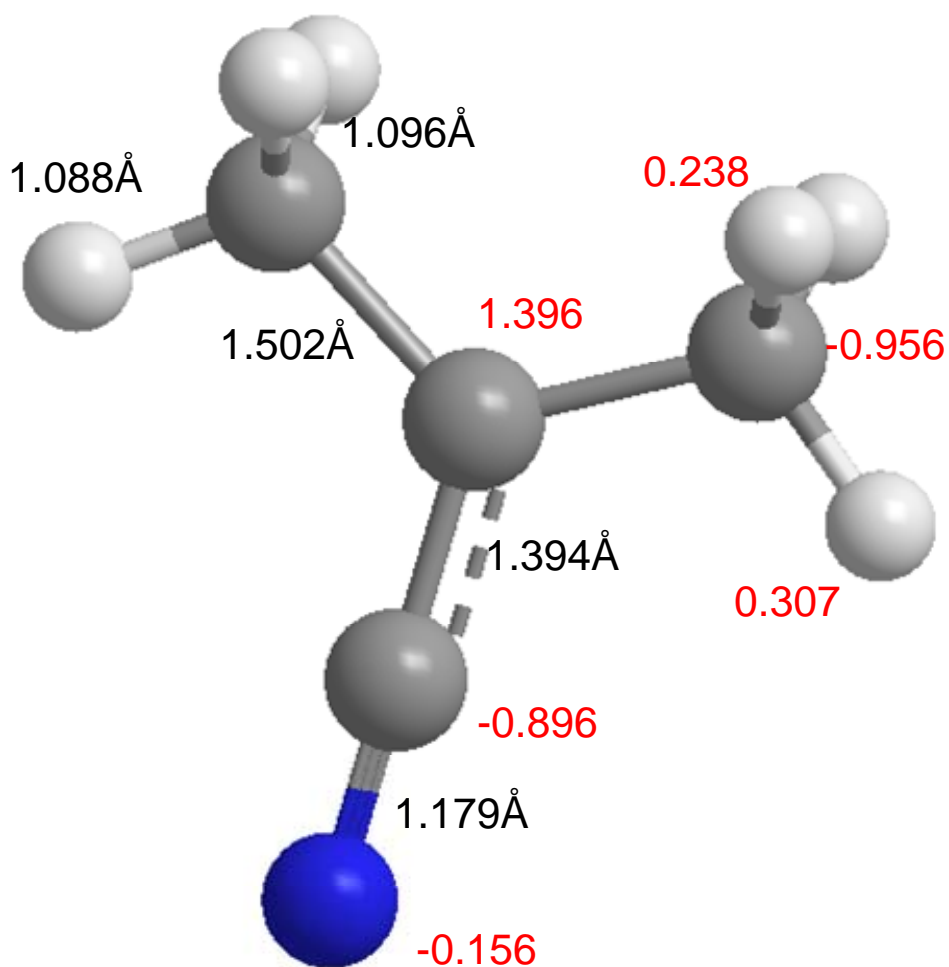


Figure S6: Relaxed AIBN fragment ($((\text{CH}_3)_2\text{C}^\bullet\text{CN})$) determined using GAUSSIAN03 calculation (in red are the partial Mulliken charge)

Table S4 : XYZ coordinates and Mulliken charge of all atoms of AIBN fragment

	X (Å)	Y (Å)	Z (Å)	Mulliken charge
C	-0.0122706683	0.2201925596	-0.2163932989	1.395675
C	0.9974644499	1.3322570133	-0.2254218486	-0.955998
C	-1.0755799762	0.1832120249	-1.2767479919	-0.955956
C	0.0395995858	-0.7697845441	0.7632715439	-0.895831
N	0.0833215632	-1.6072846018	1.5921380806	-0.156196
H	1.7067482815	1.2509183719	0.5958362627	0.307336

H	0.501442927	2.3070625122	-0.154625786	0.238347
H	1.5615569264	1.3366018246	-1.1653678806	0.238469
H	-1.7482882897	-0.6635400293	-1.1557594958	0.307338
H	-0.6263192804	0.1231975998	-2.2748916962	0.238501
H	-1.6736718546	1.1014896111	-1.2584083956	0.238315

The punctual dipole momentum of the radical is calculated by $\mu_{\text{radical}} = \sum q_i r_i$ with an origine corresponding to the barycenter of the AIBN fragment. Therefore $\mu_{\text{radical}} = 1.605$ C.m.