Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Reinvestigation of the Mechanism of Polymerization of β- Butyrolactone from 1,5,7-Triazabicyclo[4.4.0]dec-5-ene.

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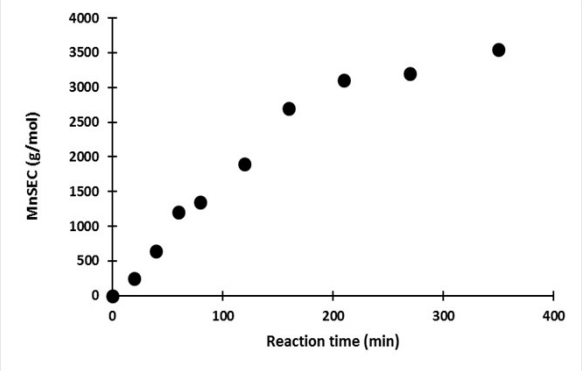
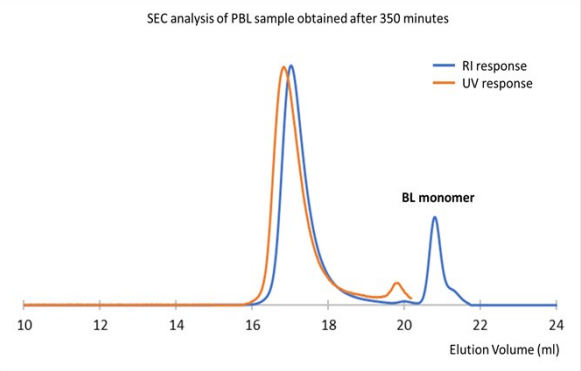
Polymerization of BL from a PyCOOH/TBD mixture (bulk, 60°C, $[BL]_0/[TBD]_0$ = 190)

In a glove box, a dried vial was charged with 200 mg of BL (n = 2.32 x 10^{-3} mol), 6 mg of PyCOOH (n = 2.44 x 10^{-5} mol) and a stirring bar. After solubilization of the PyCOOH (2 hours), 200 mg of BL were added in order to target a final DP of 190. 3.2 mg of TBD (n = 2.3 x 10^{-5} mol) were then introduced and the vial was sealed. Out of the box, the medium was immersed in a 60°C oil bath to start the polymerization. A kinetic experiment was started after 2 minutes of thermal homogenization. Samples were withdrawn after precise reaction times and analyzed by SEC analysis using a DRI/UV detector.

Polym. time (min)	M_nSEC (g.mol^{-1})	$Đ_M$
20	250	1.08
40	640	1.19
60	1200	1.25
80	1350	1.24
120	1900	1.27
160	2700	1.23
210	3100	1.25
270	3200	1.30
350	3550	1.30





Tables

Table S1. Molecular characterizations of *cyclo*-PdMMLABe obtained from ZROP of dMMLABe by IMes carbene in THF at r.t. ($[dMMLABe]_0$ = 1.45M; $[dMMALBe]_0/[IMes]_0$ = 116)

Polym. time (min)	Conv. (%)	M_nSEC (g.mol^{-1})	$Đ_M$
8	31.5	4220	1.32
28[a]	59	7880	1.34
72	90	12000	1.29
104	94.4	14700	1.26
150	95.7	16400	1.26

a) The MALDI analysis of that sample presents a Mn of 13600 g/mol^{-1} and a cyclic structure as demonstrated by isotopic simulations

Figures

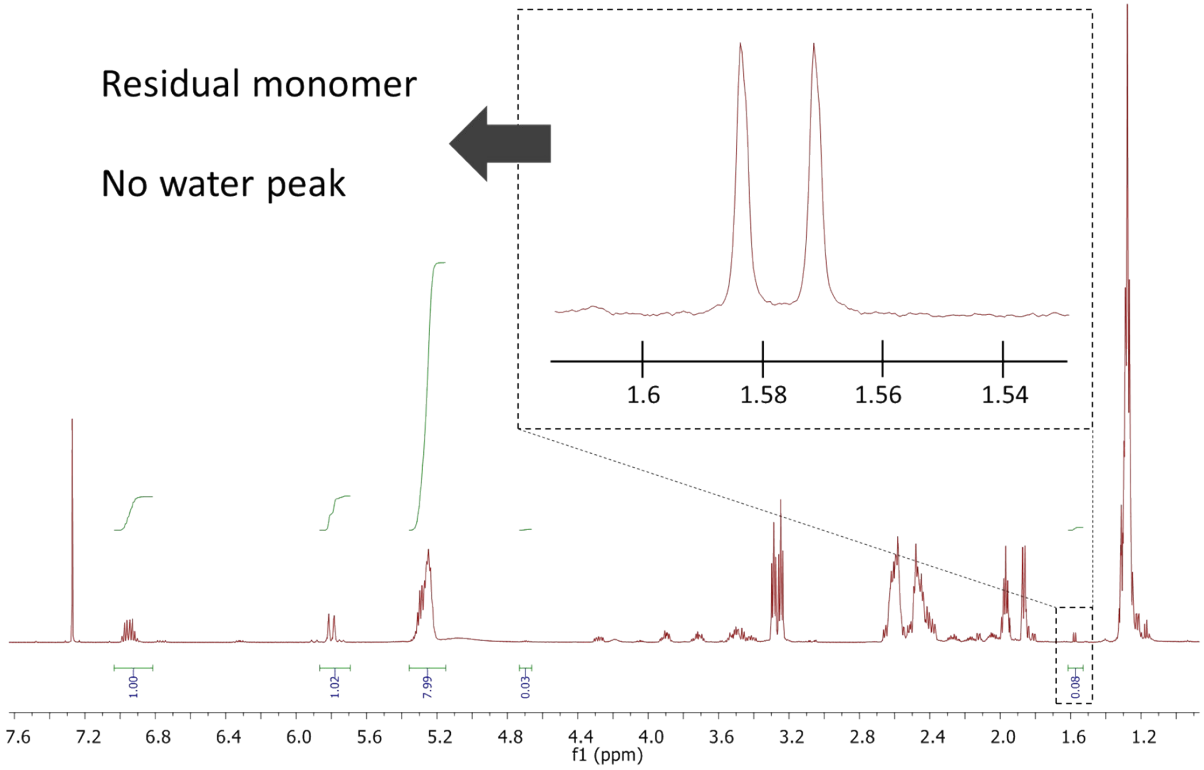


Figure S1-a. ^{1}H-NMR analysis of the PBL_8 crude medium (recorded in $CDCl_3$ at 21°C)

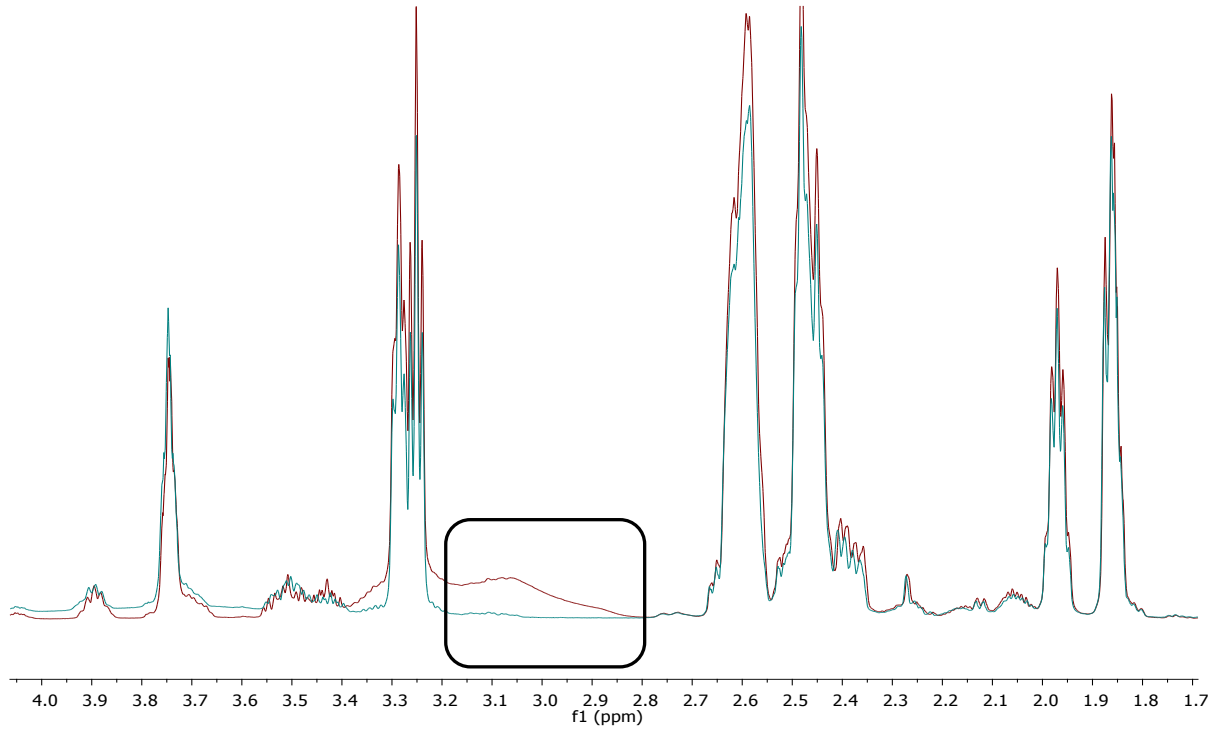


Figure S1-b. ^{1}H-NMR comparison (recorded in $CDCl_3$ at 21°C) of the PBL_8 crude medium before (blue spectrum) and after addition of 10 mol% of water (red spectrum)

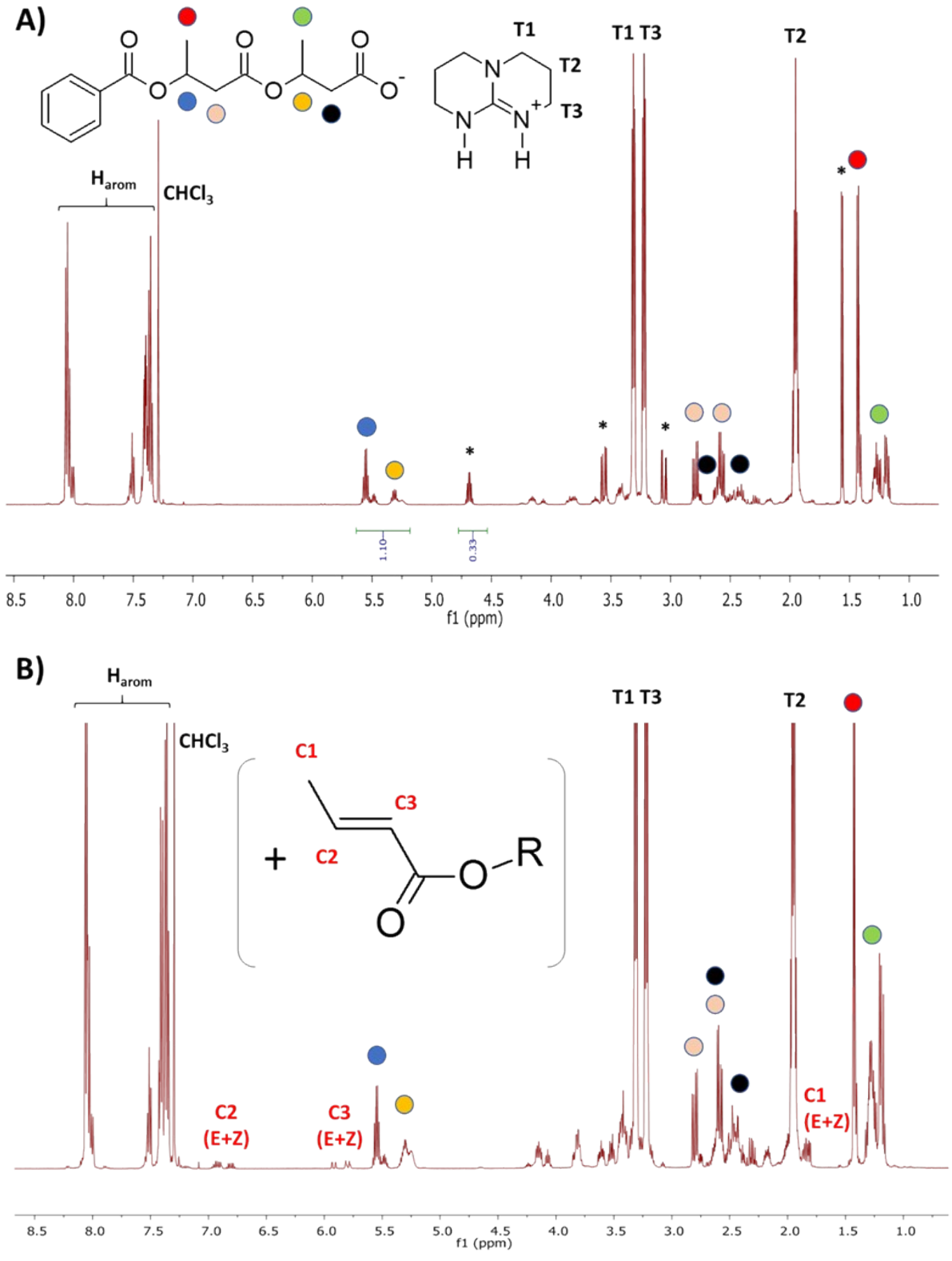


Figure S2. ^{1}H-NMR spectra of a mixture of benzoic acid/TBD salt and BL (1/1.5) recorded after 12 hours at r.t. (A) and 12 hours at r.t. + 1 hour at 60°C (B). * correspond to BL monomer signal. R corresponds to H or a BL unit. *E* and *Z* represent both crotonate isomers. Signals appearing between 3.2 and 4 are hypothetically attributed to TBD protons from TBD interacting with crotonic acid, butyric acid and benzoic acid (if any).

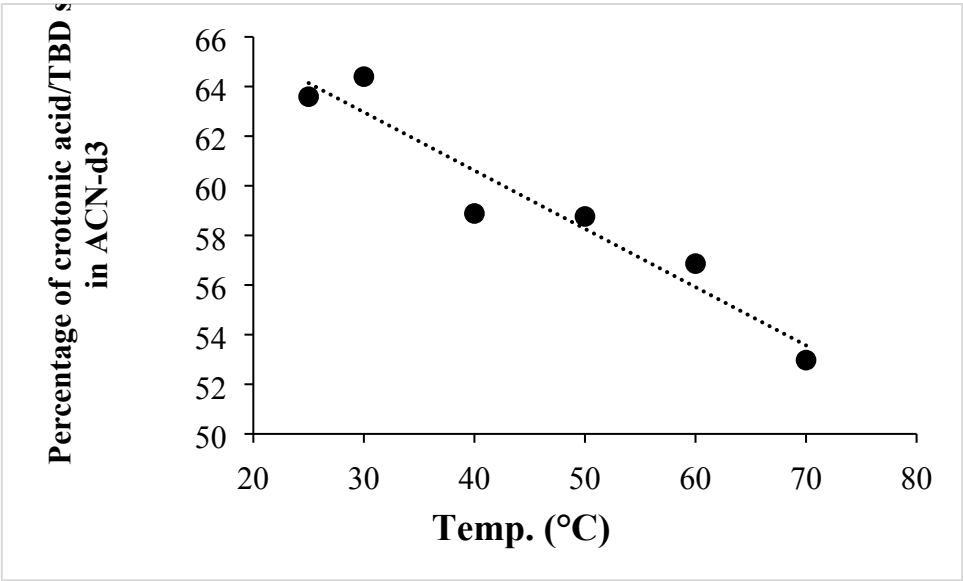


Figure S3. Percentage of crotonic acid/TBD salt calculated by ^{1}H-NMR analyses in CD_3CN in function of the temperature from a 1:1 crotonic acid/TBD mixture.

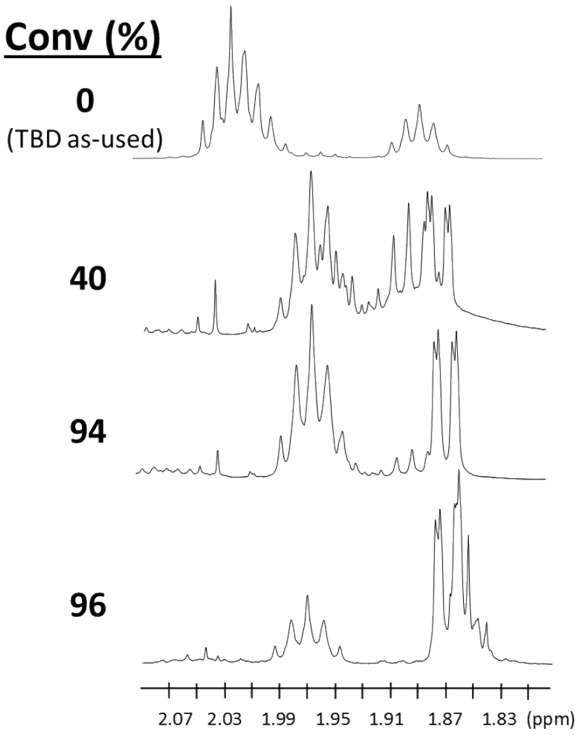


Figure S4. Evolution of TBD protonic signals (centered between 1.8 and 2.1 ppm, in $CDCl_3$) in function of the conversion as recorded during the BL bulk ROP ($[BL]_0/[TBD]_0$ = 50, 60°C)

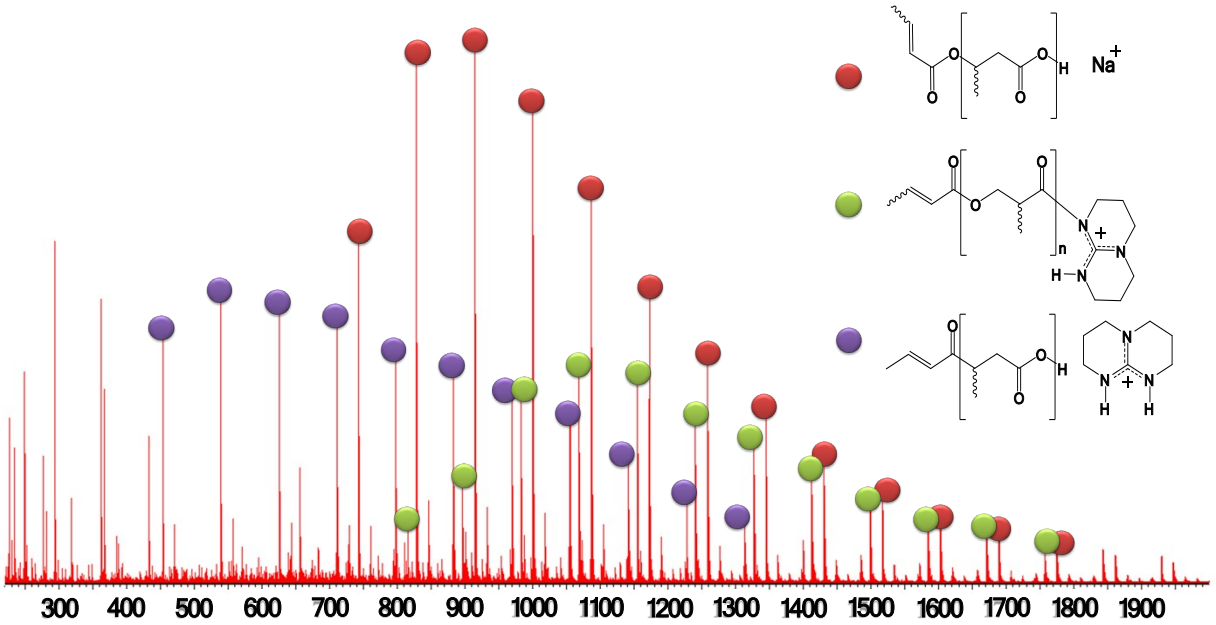


Figure S5. ESI-MS analysis of PBL_8 (realized without addition of NaI)

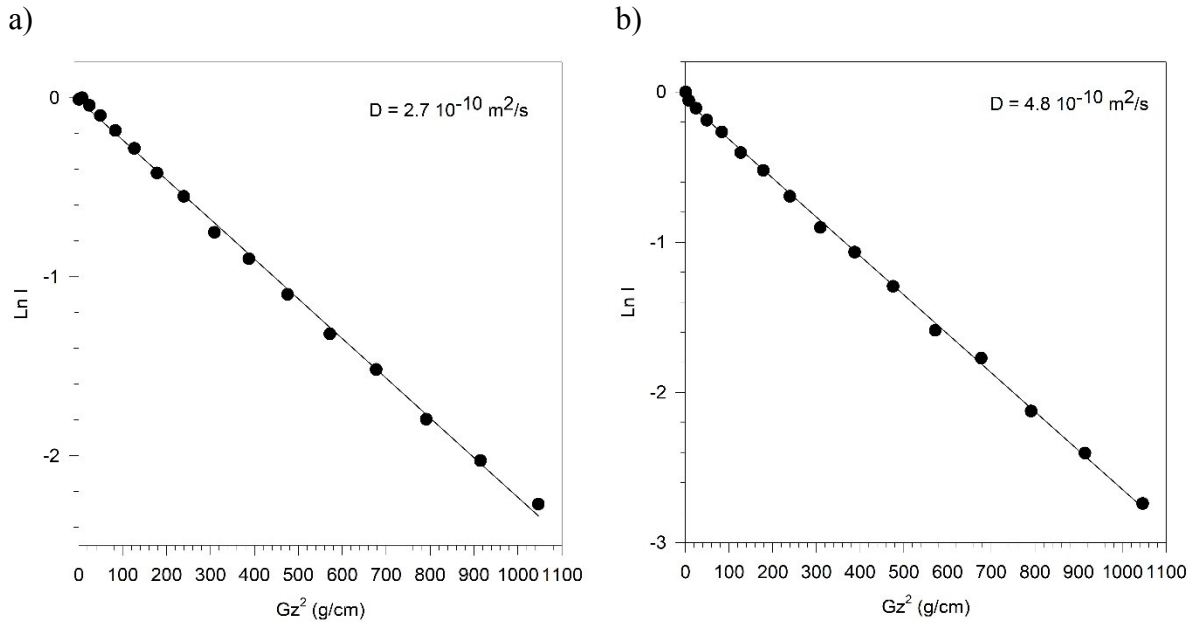


Figure S6. Examples of diffusion curves obtained on a solution of PBL_{48} in CD_3CN, a) on one of the peaks of the polymer at 1.2 ppm and b) on one of the peaks of TBD at 3.15 ppm. The linear evolution is, according to equation 1 (see experimental part), typical of a mono-diffusing species.