Investigation into the mechanism of photo-mediated RAFT polymerization involving the reversible photolysis of the chain-transfer agent

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Supporting Information

I - Synthesis and characterization of methyl 2-((9*H*-carbazole-9-carbonothioyl)thio)-2-methylpropanoate (DTC)

1) Synthesis

Materials

Carbazole (Sigma-Aldrich; ≥ 95 %), carbon disulfide (CS_2; Sigma-Aldrich; ≥ 99.9 %), methyl α-bromoisobutyrate (Sigma-Aldrich; ≥ 99 %) and sodium hydroxide (NaOH; Sigma-Aldrich; 97 %) were used as received.

Experimental procedure

In a flask of 500 mL, 4.00 g of NaOH ($1.00.10^{-1}$ mol) were dissolved under stirring in 250 mL of dimethylsulfoxide. Carbazole (16.7 g; $1.00.10^{-1}$ mol) was then added and the mixture was stirred for 1 h. The solution became brown. Then, CS_2 (6.0 mL; $1.0.10^{-1}$ mol) was added to the mixture which was stirred during 2.5 h, taking a red color. Finally, methyl α-bromoisobutyrate (13 mL; $1.0.10^{-1}$ mol) was added. The solution was stirred during 24 h before being poured in 1 L of distilled water. The suspension was divided in 3 portions of ~400 mL. For each portion, 4 extractions with 100 mL each of dichloromethane were performed, before the organic phases were gathered and washed 4 times with 100 mL of distilled water (the 4th aqueous phase was transparent). The solvent was evaporated and the product was recrystallized in methanol (MeOH). Total yield after purification: 42 %.

2) ^1H NMR Spectrum

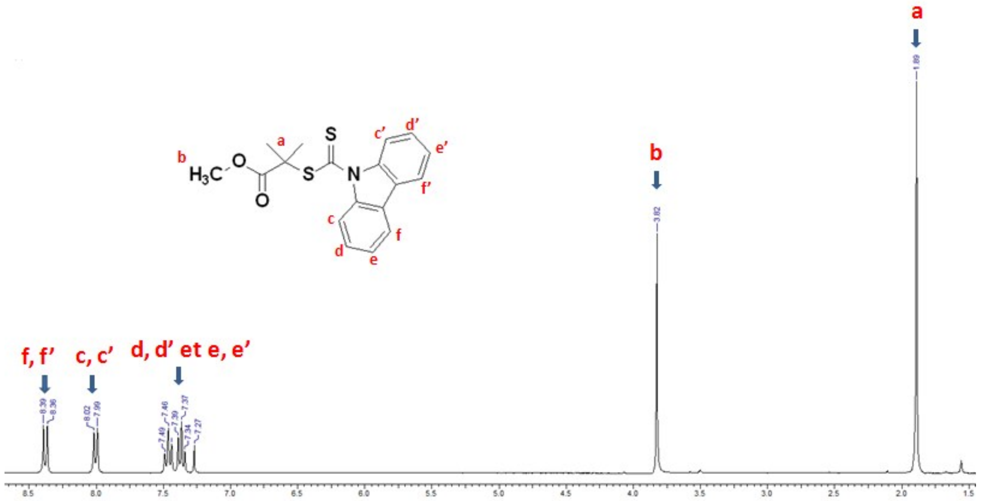


Figure S1. ^1H NMR spectrum of DTC

II - Polymerization tests by conventional thermal RAFT using DTC

1) Polymerization procedures

Synthesis of a PS

149.5 mg of DTC (4.35×10^{-1} mmol, 1 eq.) and 4530 mg of S (100 eq.) were added in this order into a dried Schlenk flask. The solution was thoroughly deoxygenated by three freeze-pump-thaw cycles. The flask was filled with nitrogen gas and placed in an oil bath maintained at 110 °C for 24 h under magnetic stirring. Solvent was then evaporated under vacuum.

Synthesis of a PMMA

10.2 mg of AIBN (0.15 eq.), 142.1 mg of DTC (4.14×10^{-1} mmol, 1 eq.), 2070.5 mg of MMA (50 eq.) and dioxane (5.00 mL) were added in this order into a dried Schlenk flask. The solution was thoroughly deoxygenated by three freeze-pump-thaw cycles. The flask was filled with nitrogen gas and placed in an oil bath maintained at 70 °C for 7 h under magnetic stirring. Solvent was then evaporated under vacuum.

Synthesis of a PBA

8.2 mg of AIBN (0.15 eq.), 113.6 mg of DTC (3.30×10^{-1} mmol, 1 eq.), 2120.4 mg of BA (50 eq.) and dioxane (5.00 mL) were added in this order into a dried Schlenk flask. The solution was thoroughly deoxygenated by three freeze-pump-thaw cycles. The flask was filled with nitrogen gas and placed in an oil bath maintained at 80 °C for 6 h under magnetic stirring. Solvent was then evaporated under vacuum.

Synthesis of PNVC

3.6 mg of AIBN (0.25 eq.), 29.8 mg of DTC (8.6×10^{-2} mmol, 1 eq.), 839.2 mg of NVC (50 eq.) and dioxane (2.00 mL) were added in this order into a dried Schlenk flask. The solution was thoroughly deoxygenated by three freeze-pump-thaw cycles. The flask was filled with nitrogen gas and placed in an oil bath maintained at 80 °C for 24 h under magnetic stirring. Solvent was then evaporated under vacuum.

2) Characterization by SEC

	M_n (g/mol)	**M_w (g/mol)**	**$Đ = M_w/ M_n$**	**DP_n**
PS	5.20×10^3	5.48×10^3	1.05	47
PMMA	1.29×10^4	1.49×10^4	1.16	126
PBA	6.81×10^3	7.56×10^3	1.11	50
PNVC	4.82×10^3	5.90×10^3	1.22	23

Table S1. Results of the preliminary syntheses realized with DTC under thermal conditions

III - Effect of light intensity

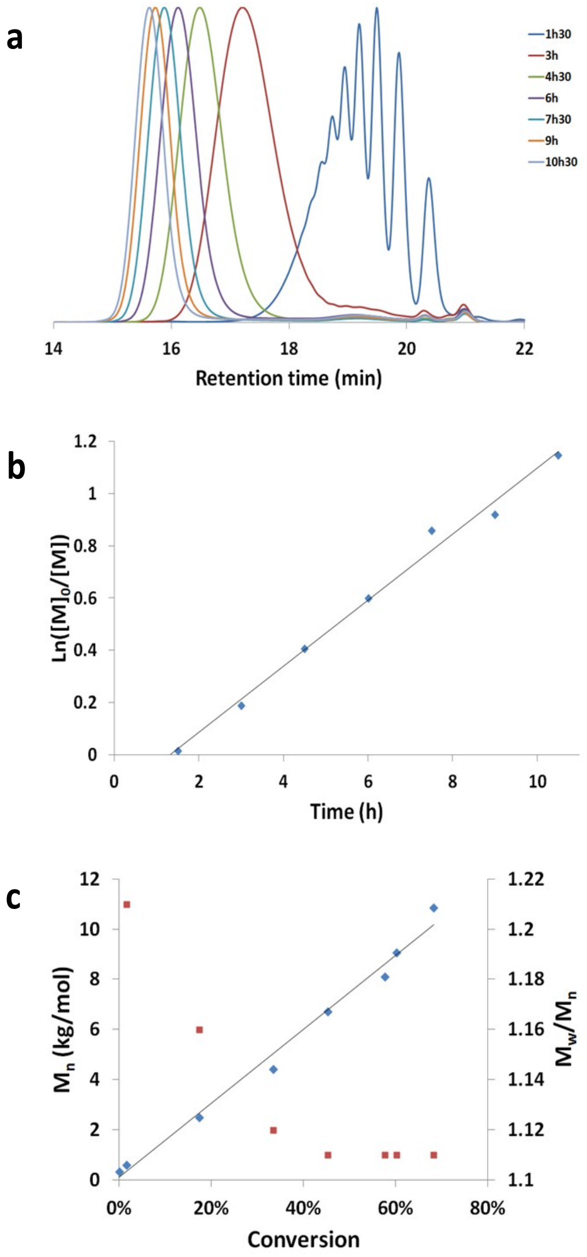
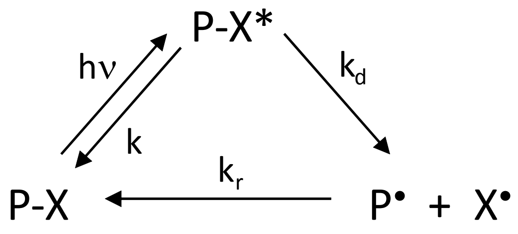


Figure S2. Kinetic monitoring of the photo-mediated RAFT polymerization of BA using a blue LED (0.9 W, $\lambda_{em,max}$ = 465 nm). a. SEC chromatograms (RI detector). b. Polymerization kinetics. c. Evolution of number average molecular weight (M_n) and dispersity ($Đ = M_w/M_n$) with conversion; line: theoretical molecular weight. $[BA]_0/[DTC]_0 = 120$; Dioxane/BA: 3/1 in volume

IV - Kinetic modeling of a reversible photolysis

The kinetic scheme can be represented as follows:



With PX being the dormant species (macroCTA), PX* the corresponding excited state generated under irradiation, $P^\bullet$ the propagating species (carbon-centered radical) and $X^\bullet$ the thiocarbonylthiyl (sulfur-centered radical).

Making the approximation that the light source is monochromatic, the rate of disappearance of PX due to light irradiation is:

$$-\left(\frac{d[PX]}{dt}\right)_{h\nu} = I_{abs}\frac{A_{PX}}{A}$$

With I_{abs} being the absorbed intensity, A the total absorbance and A_{PX} the absorbance due to PX only.

Considering the establishment of a steady state, the following relations are obtained:

- Steady state approximation applied to the dormant species at the ground state:

$$-\frac{d[PX]}{dt} = I_{abs}\frac{A_{PX}}{A} - k[PX^*] - k_r[P^\bullet][X^\bullet] \approx 0$$

- Steady state approximation applied to the dormant species at the excited state:

$$\frac{d[PX^*]}{dt} = I_{abs}\frac{A_{PX}}{A} - k[PX^*] - k_d[PX^*] \approx 0$$

- Steady state approximation applied to the active species:

$$\frac{d[P^\bullet]}{dt} = k_d[PX^*] - k_r[P^\bullet][X^\bullet] \approx 0$$

These relations lead to the following equation, governing the reversible photolysis process:

$$I_{abs}\frac{A_{PX}}{A}\phi_d = k_r[P^\bullet][X^\bullet]$$

Where the quantum yield of photodissociation is introduced:

$$\phi_d = \frac{k_d}{k_d + k}$$

The law of conservation of matter can be summarized as follows:

	PX	PX*	$P^\bullet$	$X^\bullet$
Initially:	C_0			
Equilibrium:	$C_0.[1 - (x + y)]$	$C_0.y$	$C_0.x$	$C_0.x$

With C_0 being the initial concentration of the CTA.

The 2 following approximations can be then introduced:

- The concentration of PX* is negligible (short-lived excited state): $x \gg y$
- Only the absorptions of PX and $X^\bullet$ are considered (which implies no other absorbing species):

$$\frac{A_{PX}}{A} = \frac{\varepsilon_{PX}[PX]}{\sum_i \varepsilon_i[i]} \approx \frac{\varepsilon_{PX}[PX]}{\varepsilon_{PX}[PX] + \varepsilon_{X^\bullet}.[X^\bullet]}$$

The following equation is thus obtained:

$$\frac{I_{abs}.\phi_d}{C_0^2.k_r} = \left(1 + \frac{\varepsilon_{X^\bullet}}{\varepsilon_{PX}} \frac{x}{1 - x}\right)x^2$$

If we assume that (only a low fraction of active species): $1 \gg x$

The equation becomes:

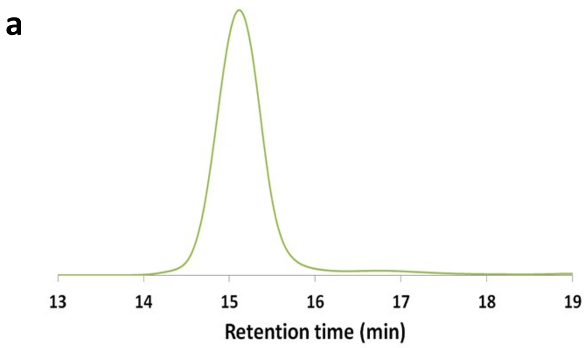
$$\frac{I_{abs}.\phi_d}{C_0^2.k_r} = \left(1 + \frac{\varepsilon_{X^\bullet}}{\varepsilon_{PX}} x\right)x^2$$

And finally, expressing I_{abs} as a function of the absorbance A and incident intensity I_0:

$$\frac{I_0.(1 - 10^{-A}).\phi_d}{C_0^2.k_r} = \left(1 + \frac{\varepsilon_{X^\bullet}}{\varepsilon_{PX}} x\right)x^2$$

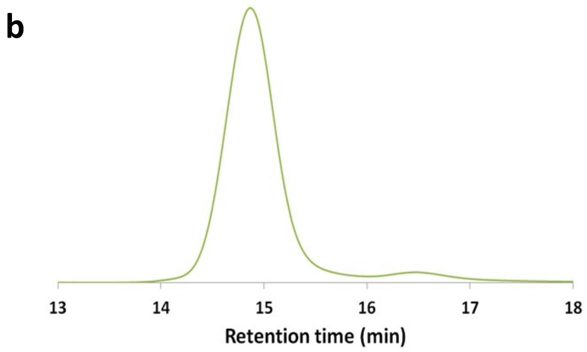
V - Reinitiation efficiency

- Chain-extension with BA starting from a PBA macroCTA synthesized by conventional thermal RAFT (RI chromatogram after 3 h of reaction):



The comparison of the areas of the peaks corresponding to the chain-extended product "PBA-*b*-PBA" and to the residual PBA macroCTA, considering a same dn/dC, enables the estimation of the residual fraction of PBA precursor: 3.5 %.

- Chain-extension with BA starting from a PS macroCTA synthesized by conventional thermal RAFT (RI chromatogram after 3 h of reaction):



The comparison of the areas of the peaks corresponding to the block copolymer PS-*b*-PBA and to the residual PS macroCTA, considering their respective dn/dC values, enables the estimation of the residual fraction of PS precursor: 9.4 %.

For the PS, the dn/dC value used was 0.185 mL/g. For the PS-*b*-PBA copolymer, an average value was calculated considering the number average degree of polymerization of each block (PS block: 43; PBA block: 131): dn/dC = 0.091 mL/g.

VI - Effect of the wavelength

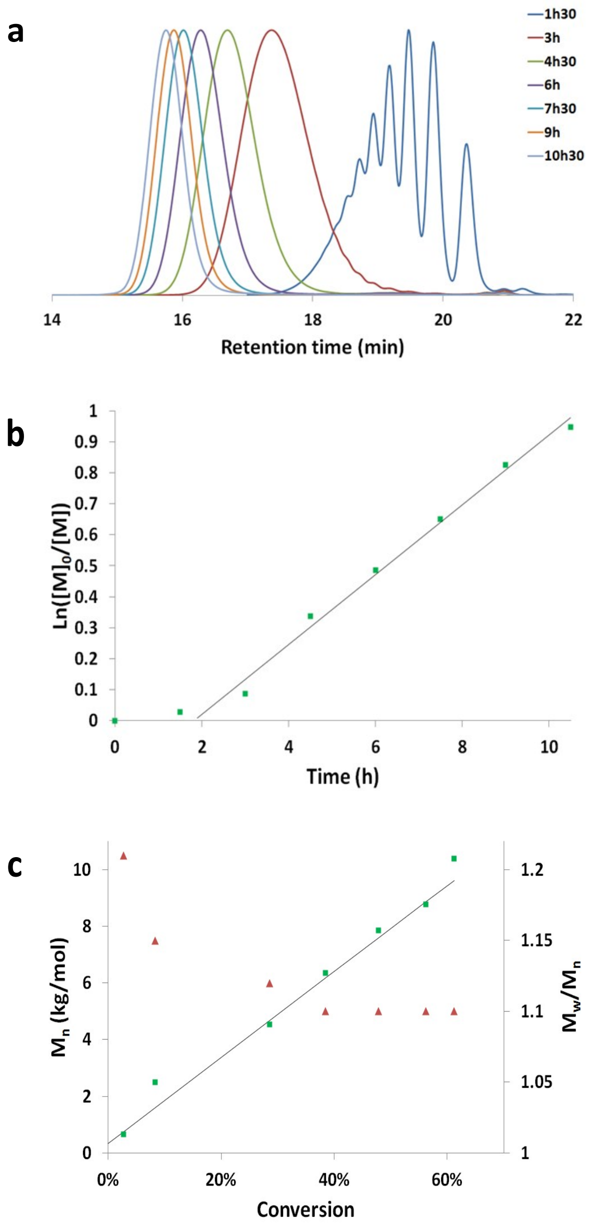


Figure S3. Kinetic monitoring of the photo-mediated RAFT polymerization of BA using a green LED (3 W, $\lambda_{em,max}$ = 525 nm). a. SEC chromatograms (RI detector). b. Polymerization kinetics. c. Evolution of number average molecular weight (M_n) and dispersity (Đ = M_w/M_n) with conversion; line: theoretical molecular weight. $[BA]_0/[DTC]_0$ = 120; Dioxane/BA: 3/1 in volume

VII – Chain-end fidelity

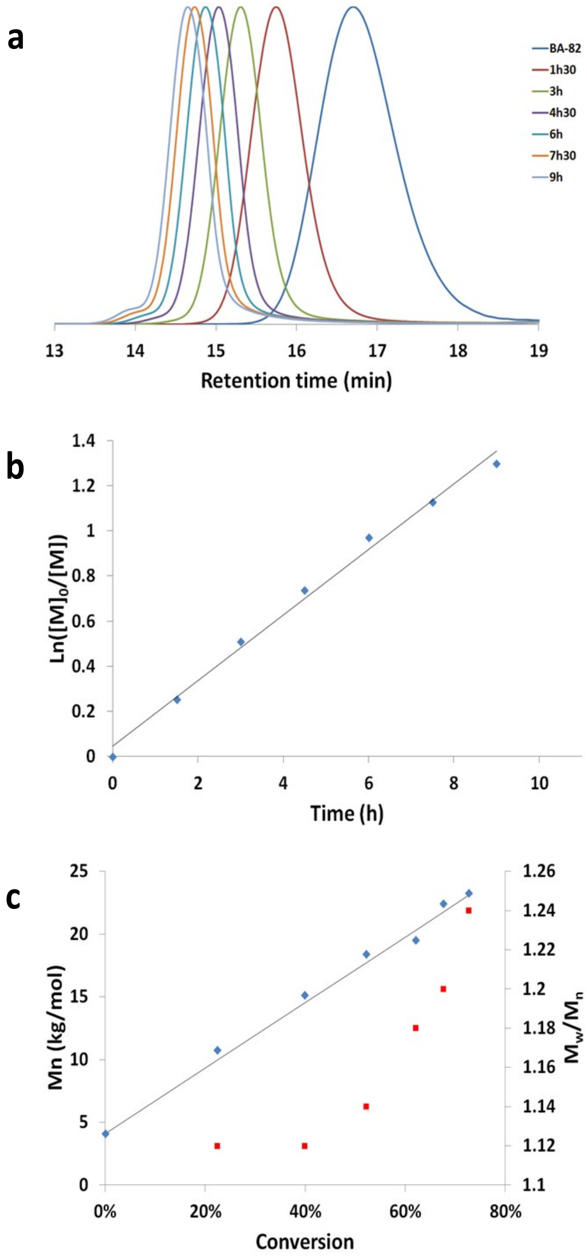


Figure S4. Kinetic monitoring of the photo-mediated RAFT polymerization of BA using a blue LED (3 W, $\lambda_{em,max}$ = 472 nm) starting from a PBA (M_n = 4.10×10^3 g.mol^{-1}; Đ = 1.16) synthesized by photo-mediated RAFT as a macroCTA. a. SEC chromatograms (RI detector). b. Polymerization kinetics. c. Evolution of number average molecular weight (M_n) and dispersity (Đ = M_w/M_n) with conversion; line: theoretical molecular weight. $[BA]_0/[PBA]_0$ = 200; Dioxane/BA: 3/1 in volume