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

1) Synthesis

Materials

Carbazole (Sigma-Aldrich; ≥ 95 %), carbon disulfide (CS₂; 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, CS₂ (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

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$\bar{D} = M_w / M_n$</th>
<th>$DP_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>5.20×10³</td>
<td>5.48×10³</td>
<td>1.05</td>
<td>47</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.29×10⁴</td>
<td>1.49×10⁴</td>
<td>1.16</td>
<td>126</td>
</tr>
<tr>
<td>PBA</td>
<td>6.81×10³</td>
<td>7.56×10³</td>
<td>1.11</td>
<td>50</td>
</tr>
<tr>
<td>PNVC</td>
<td>4.82×10³</td>
<td>5.90×10³</td>
<td>1.22</td>
<td>23</td>
</tr>
</tbody>
</table>

*Table S1.* Results of the preliminary syntheses realized with DTC under thermal conditions
Figure S2. Kinetic monitoring of the photo-mediated RAFT polymerization of BA using a blue LED (0.9 W, λ_{em,max} = 465 nm). a. SEC chromatograms (RI detector). b. Polymerization kinetics. c. Evolution of number average molecular weight (M_n) and dispersity (D = 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:

\[
\begin{align*}
\text{h} & \quad \text{P-X}^* \\
\text{k} & \quad \text{P-X} \\
\text{k_d} & \quad \text{P}^* + \text{X}^*
\end{align*}
\]

With PX being the dormant species (macroCTA), PX* the corresponding excited state generated under irradiation, P* the propagating species (carbon-centered radical) and X* 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:

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

With \(I_{\text{abs}}\) being the absorbed intensity, A the total absorbance and \(A_{\text{PX}}\) 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:

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

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

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

- Steady state approximation applied to the active species:

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

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

\[I_{\text{abs}} \frac{A_{\text{PX}}}{A} \phi_d = k_r[P^*][X^*]\]
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:

<table>
<thead>
<tr>
<th></th>
<th>PX</th>
<th>PX*</th>
<th>P*</th>
<th>X*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially:</td>
<td>$C_0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium:</td>
<td>$C_0 \cdot [1 - (x + y)]$</td>
<td>$C_0 \cdot y$</td>
<td>$C_0 \cdot x$</td>
<td>$C_0 \cdot x$</td>
</tr>
</tbody>
</table>

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* are considered (which implies no other absorbing species):

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

The following equation is thus obtained:

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

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

The equation becomes:

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

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

$$\frac{I_0(1 - 10^{-A}) \phi_d}{C_0^2 k_r} = \left(1 + \frac{\varepsilon_{X*} \cdot x}{\varepsilon_{PX}}\right)x^2$$
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 ($D = M_w/M_n$) with conversion; line: theoretical molecular weight. $[BA]_0/[DTC]_0 = 120$; Dioxane/BA: 3/1 in volume.
Figure S4. Kinetic monitoring of the photo-mediated RAFT polymerization of BA using a blue LED (3 W, $\lambda_{\text{em, max}} = 472$ nm) starting from a PBA ($M_n = 4.10 \times 10^3$ g.mol$^{-1}$; $D = 1.16$) 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 ($D = M_w/M_n$) with conversion; line: theoretical molecular weight. $[\text{BA}]_0/[\text{PBA}]_0 = 200$; Dioxane/BA: 3/1 in volume.