

## Polymers synthesized by RAFT as versatile macrophotoinitiators

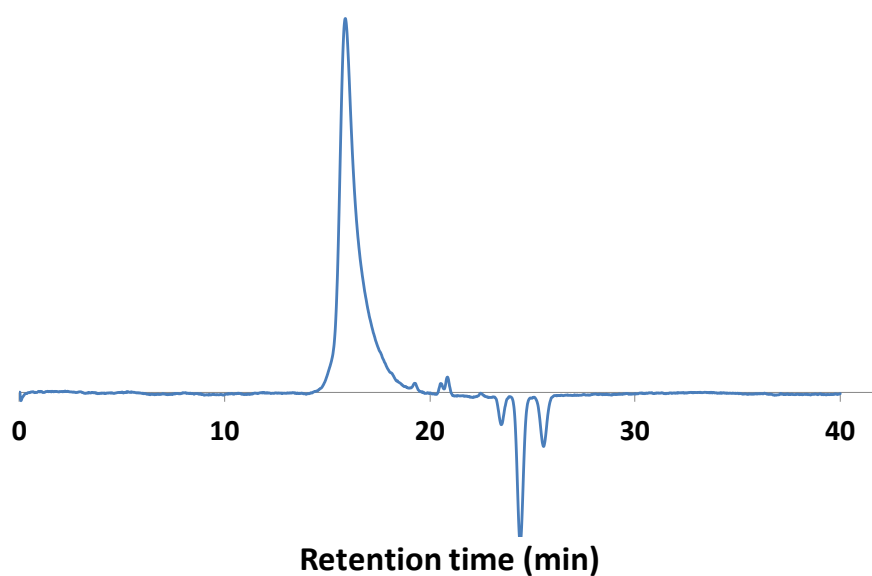
J. Poly,\* B. Cabannes-Boué, L. Hebinger, R. Mangin, A. Sauvage, P. Xiao, F. Morlet-Savary & J. Lalevée

### Supporting Information

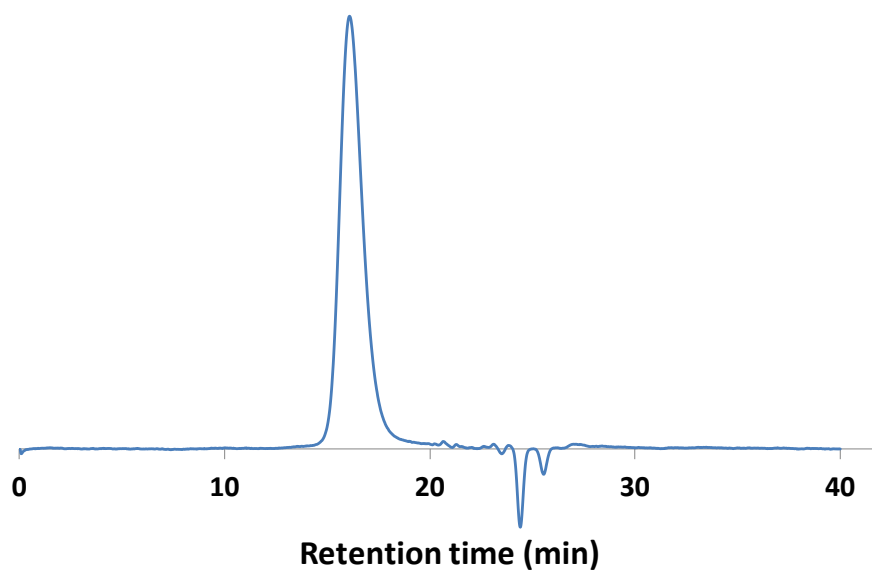
#### Characterization of the polymers by SEC

Chromatograms corresponding to the polymers described in the manuscript (signals of the refractive index detector).

- **PVAc**  
 $M_n = 4.28 \cdot 10^3$  g/mol;  $M_w/M_n = 1.15 \rightarrow$  degree of polymerization (DP)  $\approx 47$



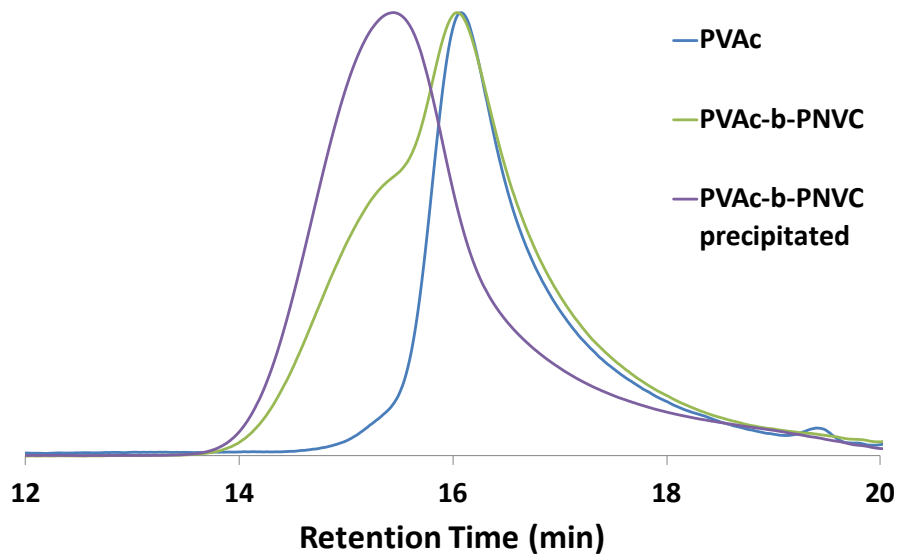
- **PNVC**  
 $M_n = 5.16 \cdot 10^3$  g/mol;  $M_w/M_n = 1.25 \rightarrow$  DP  $\approx 26$



- **Block copolymer: PVAc-b-PNVC**

Chromatograms corresponding to the PVAc precursor and the products of the chain-extension experiment, before and after purification by selective precipitations.

- PVAc precursor:  
 $M_n = 4.28 \cdot 10^3$  g/mol;  $M_w/M_n = 1.15$
- Purified product:  
 $M_n = 6.40 \cdot 10^3$  g/mol;  $M_w/M_n = 1.33 \rightarrow$  DP (PNVC block)  $\approx 11$



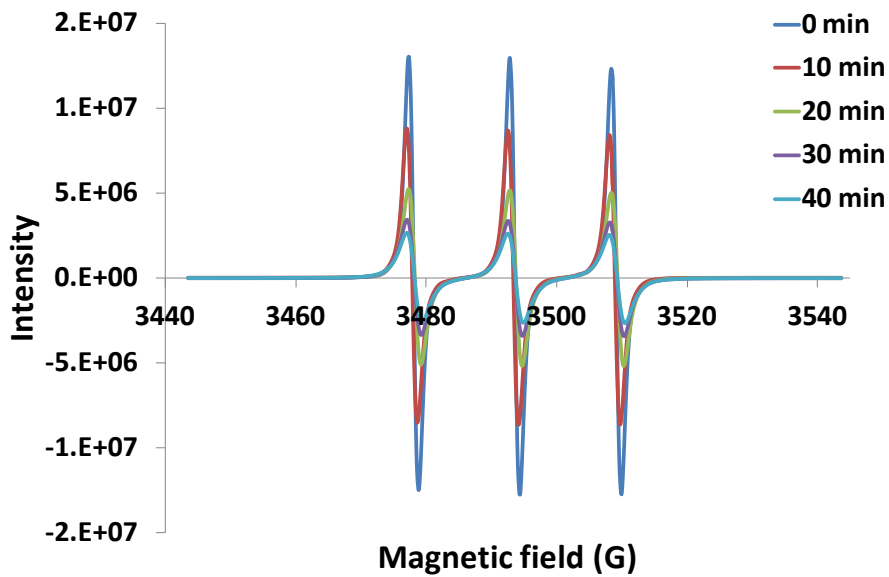
## Photodissociation of the chain-end functions

### ESR spectra

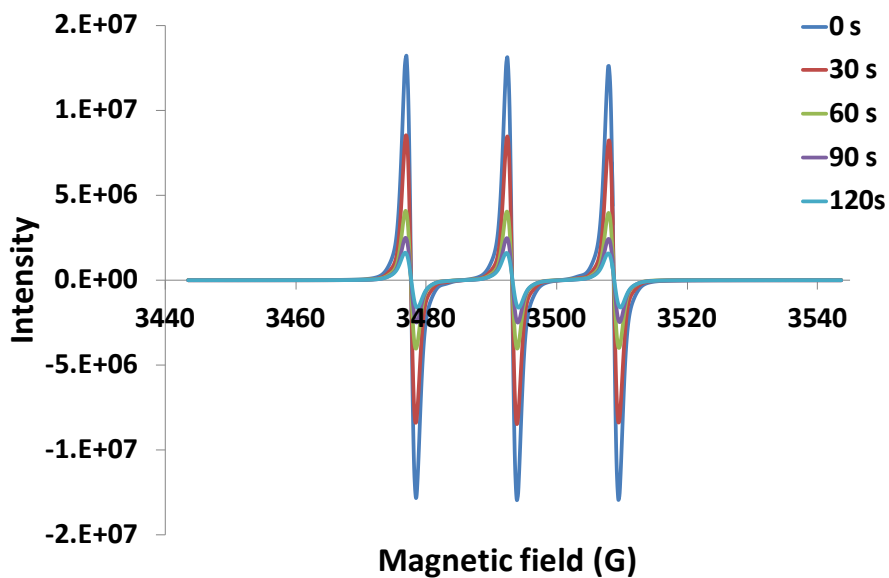
Photodissociation of the xanthate chain-ends evidenced by a spin-trap experiment using TEMPO.

Only one spectrum out of two is shown for a better visibility.

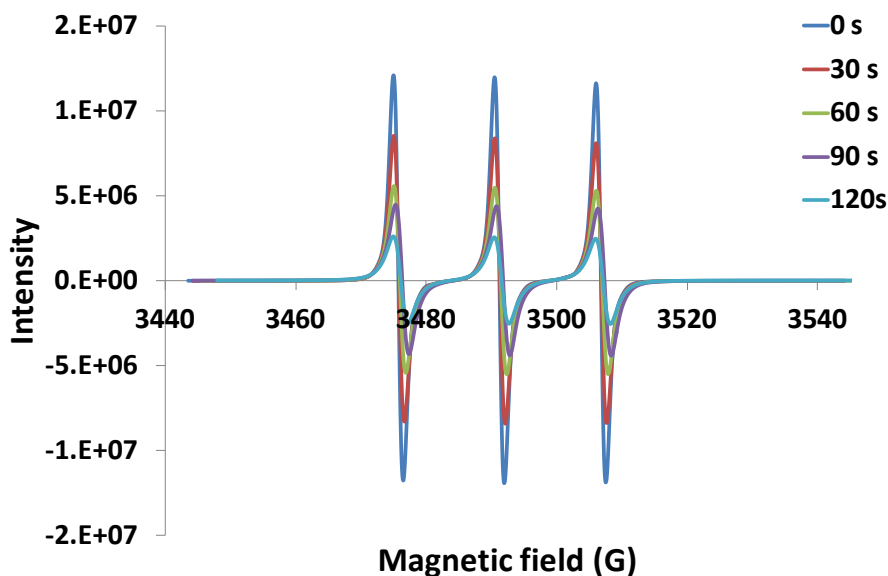
- PVAc



- PNVC



- PVAc-*b*-PNVC



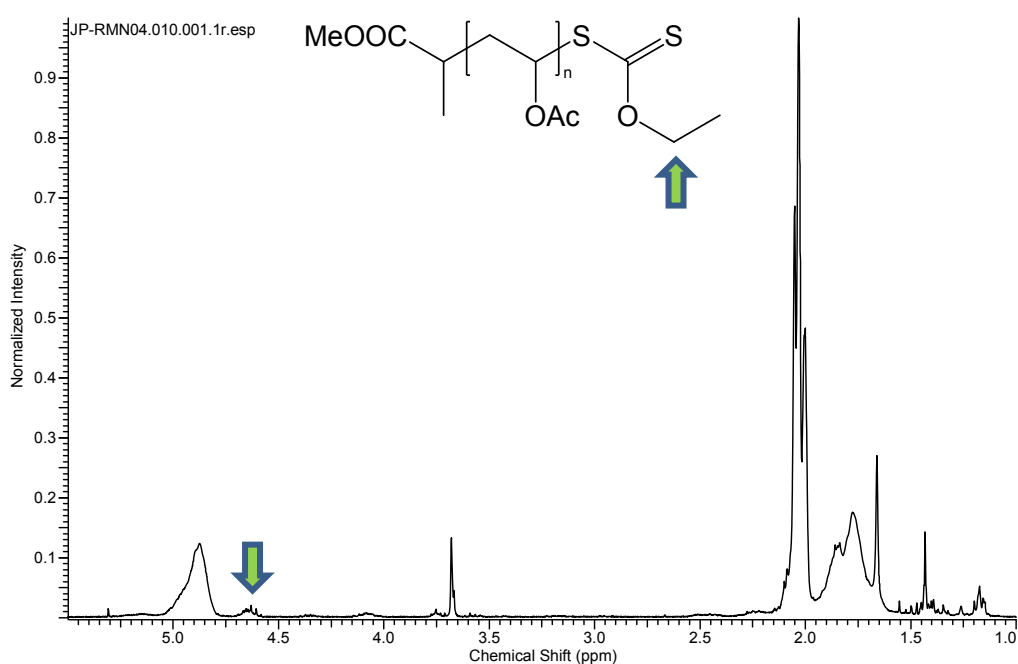
### NMR spectra

The photodissociation of chain-ends can be also directly evidenced by  $^1\text{H}$  NMR on similar products but with shorter lengths: PVAc of DP  $\approx 25$  and PNVC of DP  $\approx 10$ .

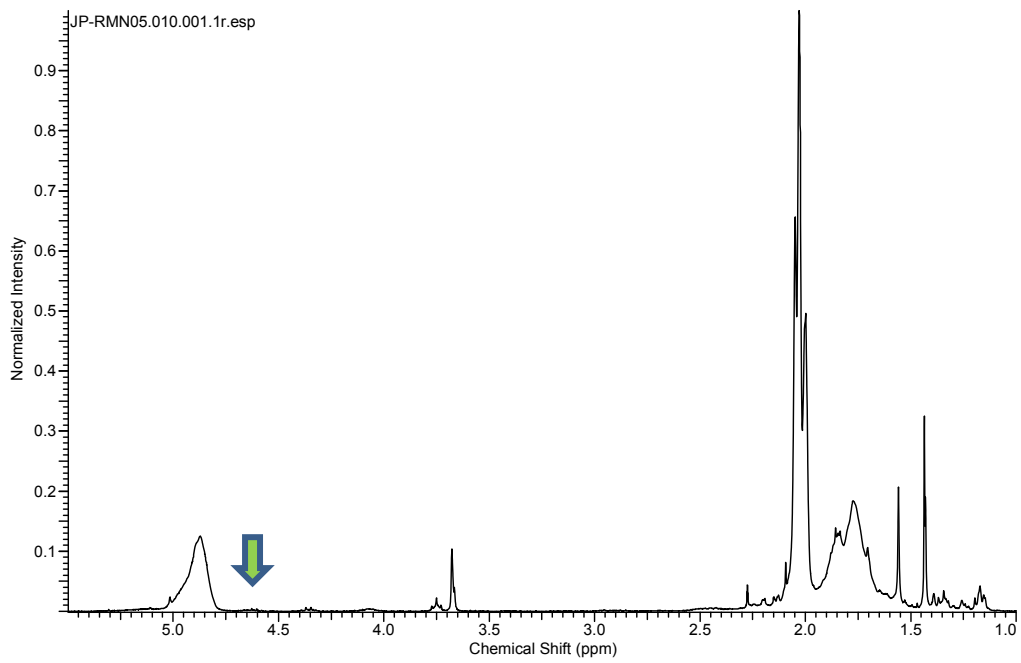
In order to collect enough polymer for further characterizations, the experiment was not performed directly in an ESR tube but in a Schlenk tube, using a larger volume (30 mL) of solution at the same concentration ( $5.0 \cdot 10^{-4}$  mol/L; 3 equivalents of TEMPO). Irradiation was stopped when the ESR spectrum of TEMPO reached its minimum intensity.

- PVAc

- Before irradiation:

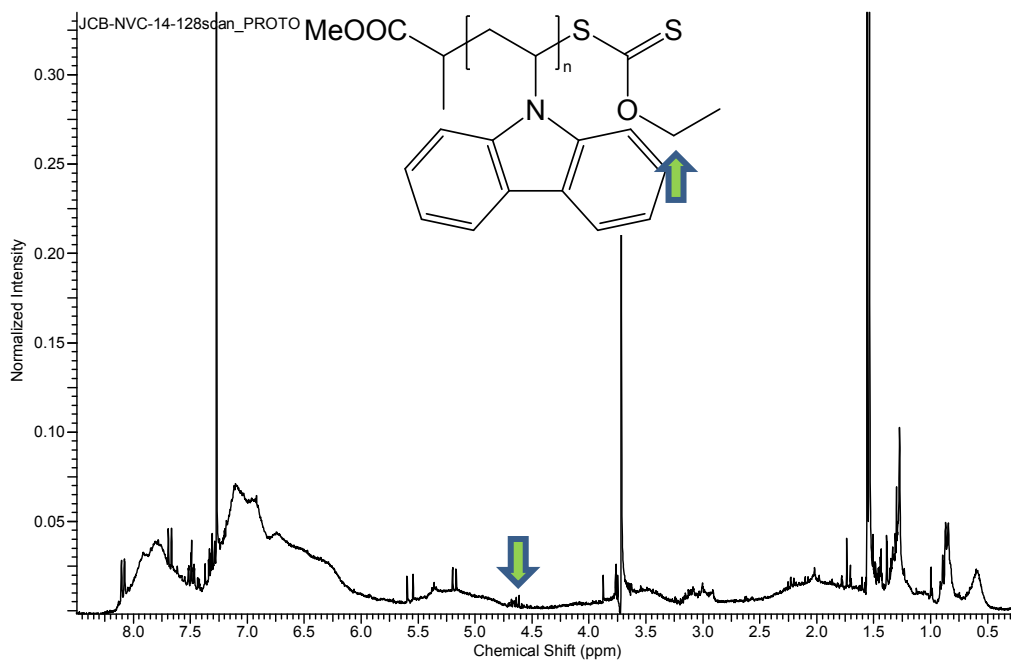


- *After irradiation and recovery of the product by precipitation:*

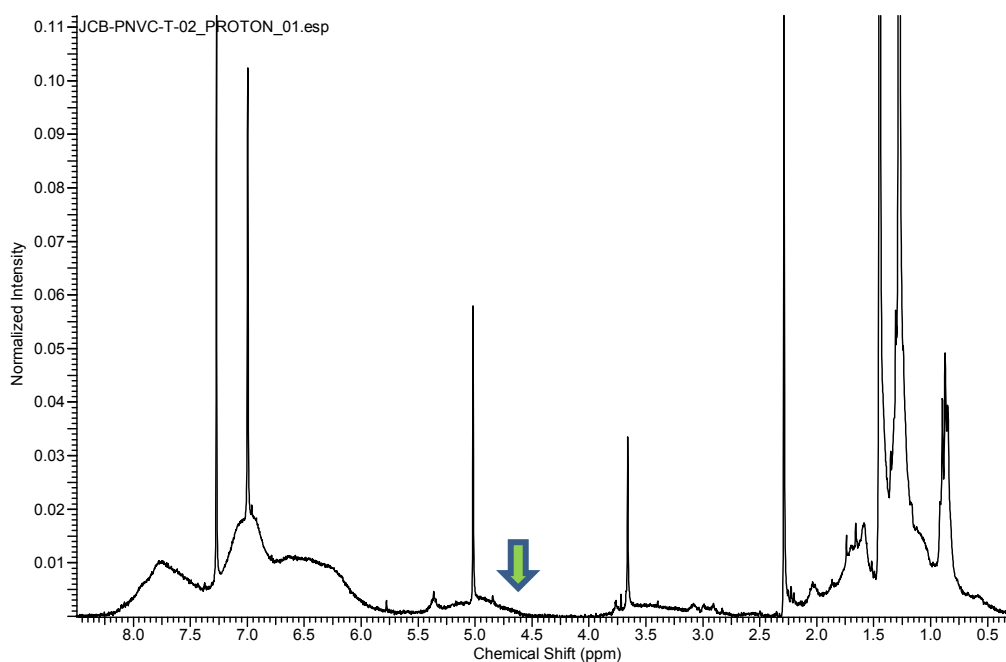


- PNVC

- *Before irradiation:*

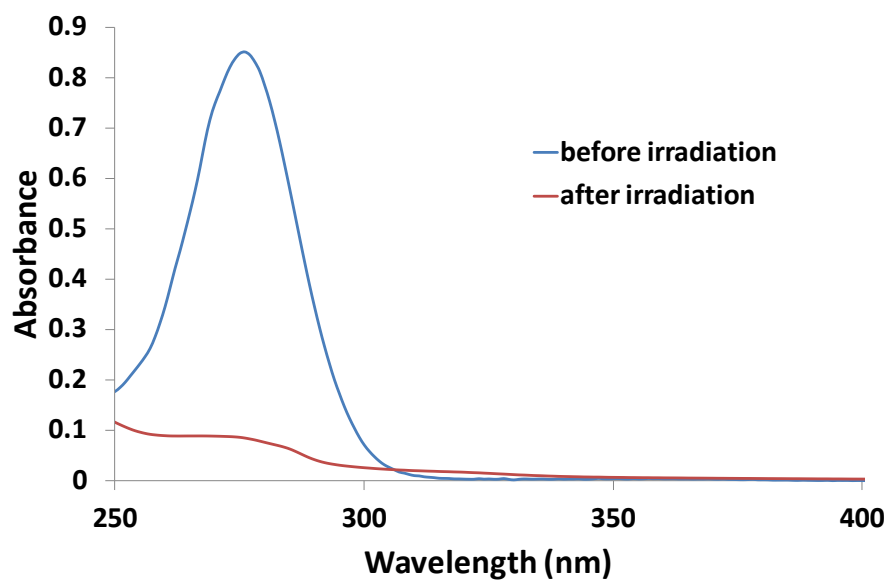


- After irradiation and recovery of the product by centrifugation:



### UV-visible spectra

In the case of the PVAc described in the previous section, the removal of the xanthate chain-end can be more simply and clearly evidenced by UV-visible spectroscopy through the decrease of the characteristic absorbance of the xanthate function at  $\lambda \approx 290$  nm (solutions in toluene at  $1.0 \cdot 10^{-4}$  mol/L).

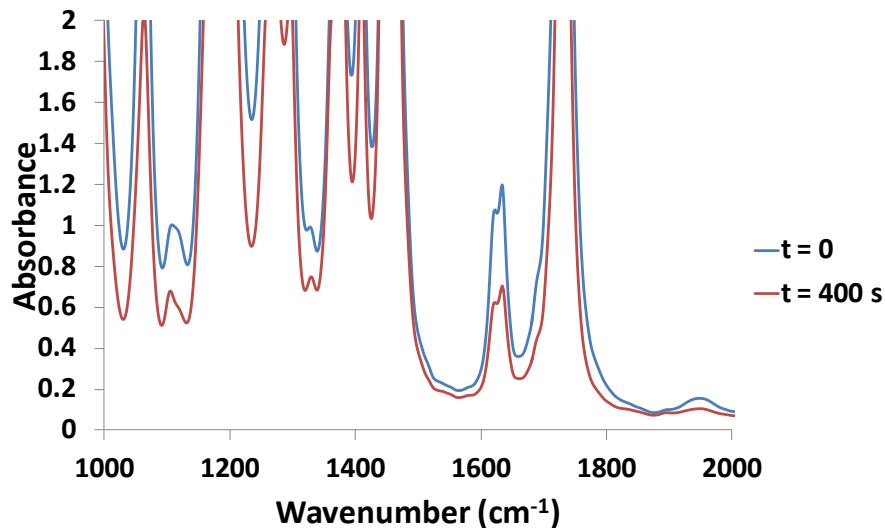


## Photopolymerizations

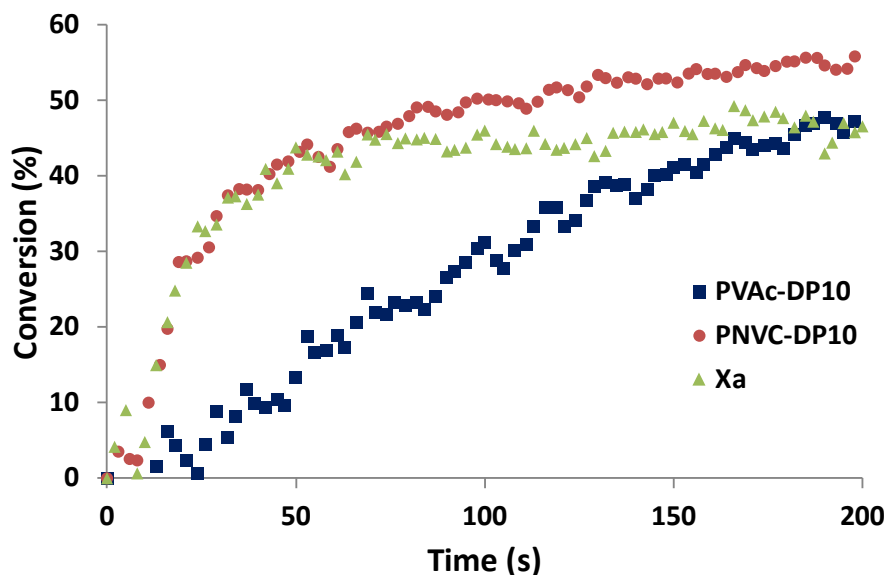
### Photopolymerization of TMPTA

A formulation containing 10 mg of PNVC in 1 g of TMPTA was prepared before being deposited (thickness: 35  $\mu\text{m}$ ) on a  $\text{BaF}_2$  pellet in laminate conditions (the formulation is sandwiched between two polypropylene films). The conversion of the acrylate functions (band at  $1630\text{ cm}^{-1}$ ) occurring during the irradiation of the film was followed by real time Fourier Transform InfraRed spectroscopy (JASCO FTIR 4100 spectrometer). A Xe-Hg lamp (Hamamatsu LC8;  $100\text{ mW}\cdot\text{cm}^{-2}$ ) was used.

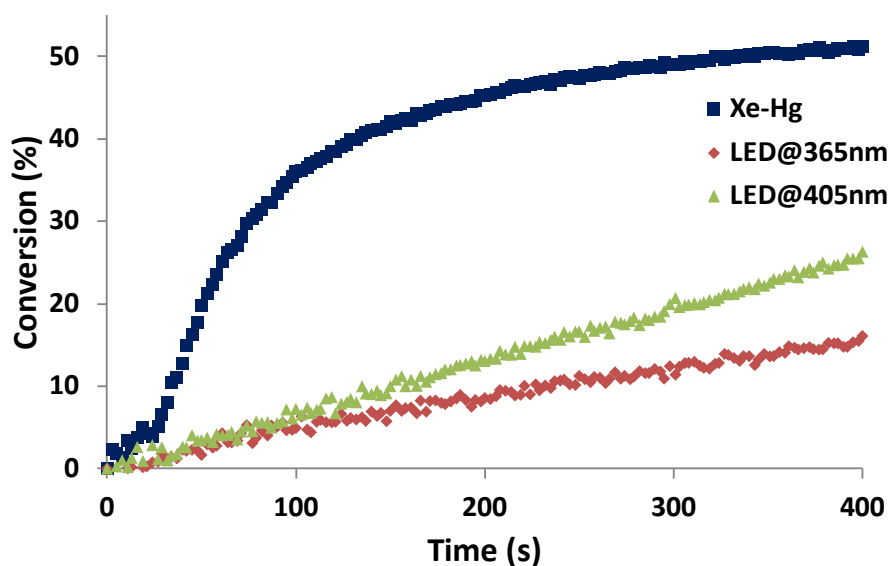
- Formulation based on the PNVC of DP  $\approx 26$ : initial and final FT-IR spectra



- Formulation based on the PNVC of DP  $\approx 10$ : comparison with PVAc (DP  $\approx 10$ ) and xanthate used at the same molar concentration



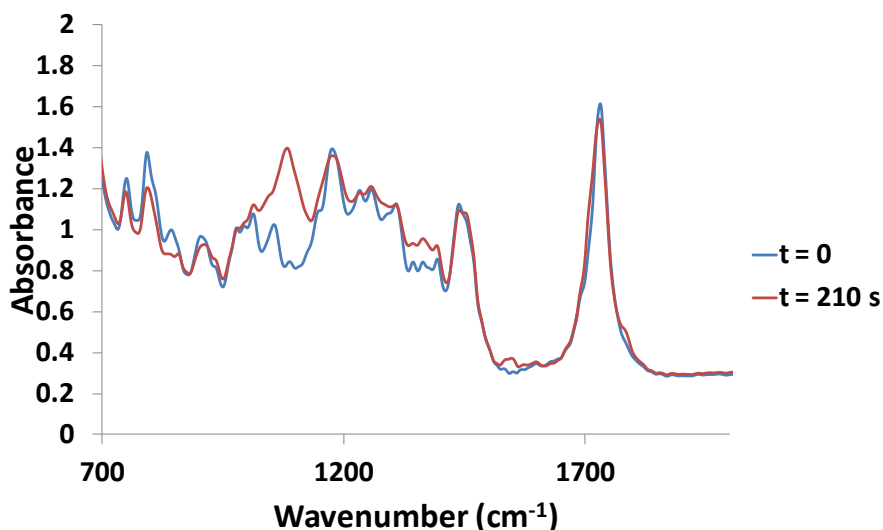
- Formulation based on the PNVC of DP  $\approx$  26: other lamps  
The same experiment was tested using two other light sources: LED at 365 nm (M365L2 – ThorLabs; 31 mW.cm<sup>-2</sup>) and LED at 405 nm (M405L2 – ThorLabs; 110 mW.cm<sup>-2</sup>).



#### Photopolymerization of EPOX

A formulation containing 10 mg of PNVC and 10 mg of Ph<sub>2</sub>I<sup>+</sup>,PF<sub>6</sub><sup>-</sup> in 1 g of EPOX was prepared. The procedure was the same as for TMPTA, except that the photopolymerization was performed in air with the formulation being directly deposited (thickness: 35  $\mu$ m) on the BaF<sub>2</sub> pellet. The conversion of the epoxide functions was monitored following the evolution of the band at 790 cm<sup>-1</sup>.

- Formulation based on the PNVC of DP  $\approx$  26: initial and final FT-IR spectra





- Formulation based on the PNVC of DP  $\approx$  26: other lamp  
The same experiment was tested using another light source: LED at 365 nm (M365L2 – ThorLabs; 31 mW.cm<sup>-2</sup>).

