

*Supporting Information for:*

# Tosyl iodide – a new initiator for the photo-controlled iodine transfer polymerization of methacrylates under sunlight irradiation

*João R. C. Costa, Joana R. Góis, José R. Fernandes, Krzysztof Matyjaszewski, Jorge F.J. Coelho and Arménio C. Serra \**

## Table of Contents

1. Experimental Section .....	S1
1.1. Materials.....	S1
1.2. Techniques.....	S1
1.3. Synthesis of Tosyl iodide (Ts-I) <sup>1</sup> .....	S2
1.4. General procedure for the photocontrolled iodine polymerization of methyl methacrylate (MMA) .....	S3
2. Additional Figures .....	S4
3. Reference.....	S7

# 1. Experimental Section

## 1.1. Materials

Alumina (basic, Fisher Scientific), anisole ( $\geq 99\%$ , Fluka), deionized purified water (Milli-Q®, Millipore, resistivity  $>18\text{ M}\Omega\cdot\text{cm}$ ) was obtained by reverse osmosis, dimethylacetamide (DMA,  $\geq 98.8\%$ , Fluka), dimethylformamide (DMF,  $\geq 99.5\%$ , Fischer Chemical), dimethyl sulfoxide (DMSO,  $99.9\%$ , Fischer Chemical), ethanol ( $96\%$ , José Manuel Gomes dos Santos, LDA), iodine ( $99.8\%$ , Sigma-Aldrich), iodoform ( $+99\%$ , Acros Organics), iodomethane ( $\geq 99\%$ , Fluka), methanol ( $100\%$ , José Manuel Gomes dos Santos, LDA), petroleum ether ( $100-140\text{ p.}$ , Chem-Lab Analytical), potassium iodide ( $99.9\%$ , Alfa Aesar), sodium *p*-toluenesulfinate ( $>98\%$ ; TCI (Tokyo Chemical Industry Co. LTD)), 2-cyanopropyl iodide ( $>96\%$ , TCI (Tokyo Chemical Industry Co. LTD)), 4-iodophenyl isocyanate ( $97\%$ , Alfa Aesar), and 2,2,6,6-tetramethylpiperidine-1-xyloxy (free radical) (TEMPO,  $98\%$ , Sigma-Aldrich) were used as received.

Methyl methacrylate (MMA,  $99\%$  stabilized, Acros Organics), glycidyl methacrylate (GMA,  $97\%$  stabilized, Alfa Aesar), *n*-butyl methacrylate (*n*-BMA,  $99\%$  stabilized, BDH Chemicals), and ethyl methacrylate (EMA,  $99\%$  stabilized, Sigma-Aldrich) were passed over a sand/alumina column before use to remove the radical inhibitor.

2-hydroxyethyl methacrylate (HEMA,  $>95\%$ , TCI (Tokyo Chemical Industry Co. LTD)) was purified by first dissolving the monomer in water ( $25\%$  by volume). The solution was extracted with hexane to remove diacrylates. The aqueous solution was salted ( $250\text{ g/L NaCl}$ ) and the monomer was then separated from the aqueous phase by ether extraction ( $4$  times). Hydroquinone ( $200\text{ ppm}$ ) was used as a radical inhibitor. The organic solvent was removed under reduced pressure. The purified monomer was kept refrigerated and it was passed through a sand/alumina column, in order to remove the radical inhibitor, immediately prior to use.

Deuterated chloroform ( $\text{CDCl}_3$ ,  $+1\%$  tetramethylsilane (TMS); Euriso-top), polystyrene (PS) standards (Polymer Laboratories) for THF GPC and poly(methyl methacrylate) (PMMA) standards (Polymer Laboratories) for DMF GPC, were used as received. Tetrahydrofuran and dimethylformamide (THF and DMF, high-performance liquid chromatography (HPLC) grade; Panreac) were filtered ( $0.2\text{ }\mu\text{m}$  filter) under reduced pressure before use.

## 1.2. Techniques

The molecular weight and dispersity parameters of PMMA, PBMA, PGMA and PEMA were determined by high-performance size exclusion chromatography HPSEC; Viscotek (Viscotek TDMax) with a differential viscometer (DV), right-angle laser-light scattering (RALLS,

Viscotek), low-angle laser-light scattering (LALLS, Viscotek), and RI detectors. The column set consisted of a PLgel 5  $\mu\text{m}$  guard column ( $50 \times 7.5 \text{ mm}^2$ ) followed by one Viscotek T2000 column (6  $\mu\text{m}$ ), one Viscotek T3000 column (6  $\mu\text{m}$ ), and one Viscotek LT4000L column (7  $\mu\text{m}$ ). HPLC dual piston pump was set with a flow rate of  $1 \text{ mL}\cdot\text{min}^{-1}$ . The eluent (THF) was previously filtered through a 0.2  $\mu\text{m}$  filter. The system was also equipped with an on-line degasser. The tests were carried out at 30  $^\circ\text{C}$  using an Elder CH-150 heater. Before the injection (100  $\mu\text{L}$ ), the samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2  $\mu\text{m}$  pore. The system was calibrated with narrow polystyrene standards. Molecular weight ( $M_n^{\text{SEC}}$ ) and  $\mathcal{D}$  ( $M_w/M_n$ ) of the synthesized polymers were determined by multidetectors calibration ( $\text{dn}/\text{dc}$  PMMA =  $0.089 \text{ mL}\cdot\text{g}^{-1}$ ;  $\text{dn}/\text{dc}$  PBMA =  $0.0903 \text{ mL}\cdot\text{g}^{-1}$ ;  $\text{dn}/\text{dc}$  PGMA =  $0.087 \text{ mL}\cdot\text{g}^{-1}$ , and  $\text{dn}/\text{dc}$  PEMA =  $0.0905$ ), using the OmniSEC software version: 4.6.1.354.

The chromatographic parameters of PHEMA were determined using a size exclusion chromatography (SEC) set-up from Viscotek (Viscotek TDAmix) equipped with a differential viscometer (DV) and right-angle laser-light scattering (RALLS, Viscotek) and refractive index (RI) detectors. The column set consisted of a PLgel 5  $\mu\text{m}$  guard column followed by one Viscotek T5000 column and one Viscotek T4000 column. A dual piston pump was set with a flow rate of  $1 \text{ mL}/\text{min}$ . The eluent (DMF with 0.03% LiBr) was previously filtered through a 0.2  $\mu\text{m}$  filter. The system was also equipped with an on-line degasser. The tests were done at 60  $^\circ\text{C}$  using an Elder CH-150 heater. Before the injection (100  $\mu\text{L}$ ), the samples were filtered through a PTFE membrane with 0.2  $\mu\text{m}$  pore. The system was calibrated with narrow PMMA standards. Molecular weight ( $M_n^{\text{SEC}}$ ) and dispersity ( $\mathcal{D} = M_w/M_n$ ) of the synthesized polymers were determined by multidetectors calibration (PHEMA =  $0.0902 \text{ mL}\cdot\text{g}^{-1}$ ) using the OmniSEC software version: 4.6.1.354.

400 MHz  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra of reaction mixture samples were recorded on a Bruker Avance III 400 MHz spectrometer, with a 5-mm TIX triple resonance detection probe, in  $\text{CDCl}_3$  with TMS as an internal standard, or in  $\text{D}_2\text{O}$  for the sample of PHEMA. Conversions of the monomer were determined by integration of monomer and polymer peaks using MestRenova software version: 12.0.0-20080.

### 1.3. Synthesis of Tosyl iodide (Ts-I)<sup>1</sup>

Three grams of pure sodium *p*-toluenesulfinate (16.50 mmol) was dissolved in 150 mL of distilled water at around 20  $^\circ\text{C}$ . Posteriorly, a saturated solution of 2.45 g. (9.65 mmol) of iodine in 96 % ethanol was prepared and gradually added into the sulfinate solution until a slight excess of iodine was present. The yellow precipitated formed, was then filtered by vacuum, washed with cold water, and recrystallized from petroleum ether. After

recrystallization, the light-yellow crystals were filtrated and dried under nitrogen atmosphere. Finally, the product (tosyl iodide) was stored on a closed vial with a septum under nitrogen, protected from light and on the freezer prior to use. The  $^1\text{H}$  NMR of the pure initiator is presented in Figure S2.

#### 1.4. General procedure for the photocontrolled iodine polymerization of methyl methacrylate (MMA)

A 10 mL vial equipped with a stir bar was charged with Ts-I (39.56 mg, 0.14 mmol, 1 equiv.). The vial was then sealed with a rubber septum, and it was subjected to vacuum and backfilled with nitrogen. MMA monomer (1.50 mL, 14.02 mmol, 100 equiv.) and DMA (1 mL, 40 vol %) were degassed in with nitrogen for 15 min in separate containers, and posteriorly added to the vial under nitrogen atmosphere. The vial was irradiated under violet LEDs ( $\lambda = 400$  nm) or sunlight to start the photopolymerization (a fan ventilation was used to prevent an increase of temperature due to the LEDs light irradiation). During the polymerization, different reaction mixture samples were collected by using an airtight syringe. The samples were analyzed by  $^1\text{H}$  NMR spectroscopy to determine the monomer conversion and by SEC, to determine the  $M_n^{\text{SEC}}$  and  $\bar{D}$  of the polymers. The PMMA was purified by dissolving the final product in THF, precipitated in methanol, twice, collected by filtration, and finally dried in vacuum.

Natural sunlight irradiation experiments were performed on the rooftop of the Chemical Engineering Department in University of Coimbra. A working day was estimated from 10:00 am to 6:00 pm.

## 2. Additional Figures

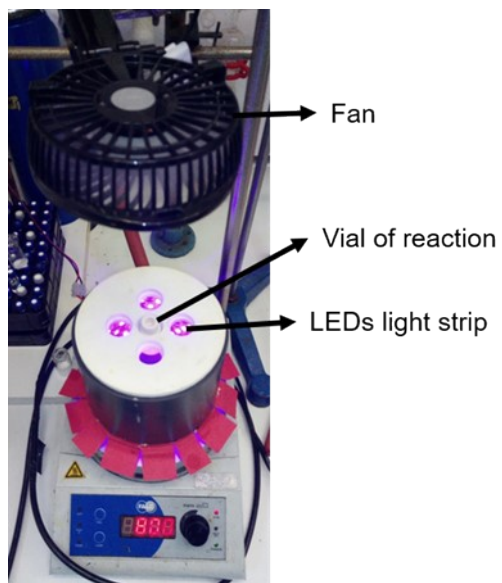


Figure S1 – Reaction setup for the iodine-mediated photopolymerization.

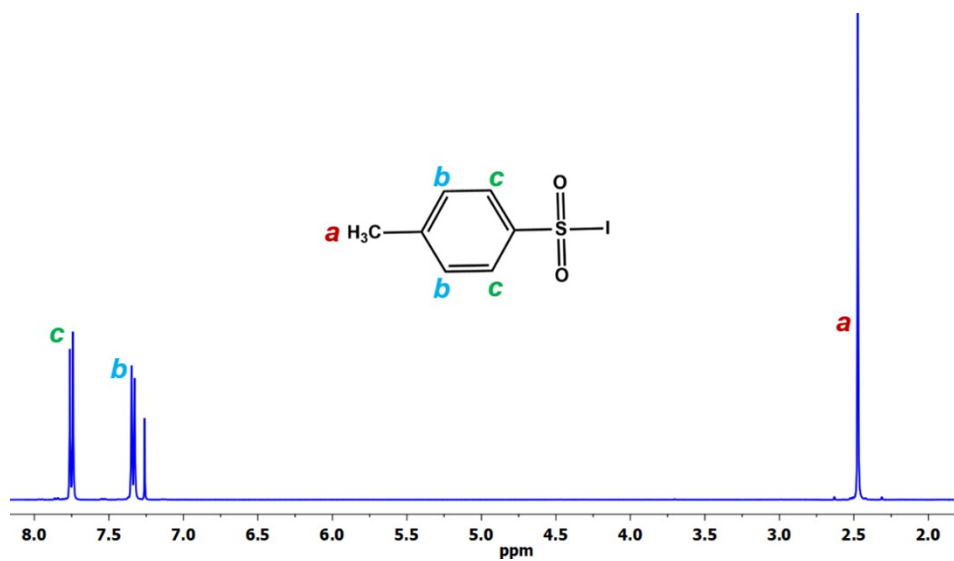
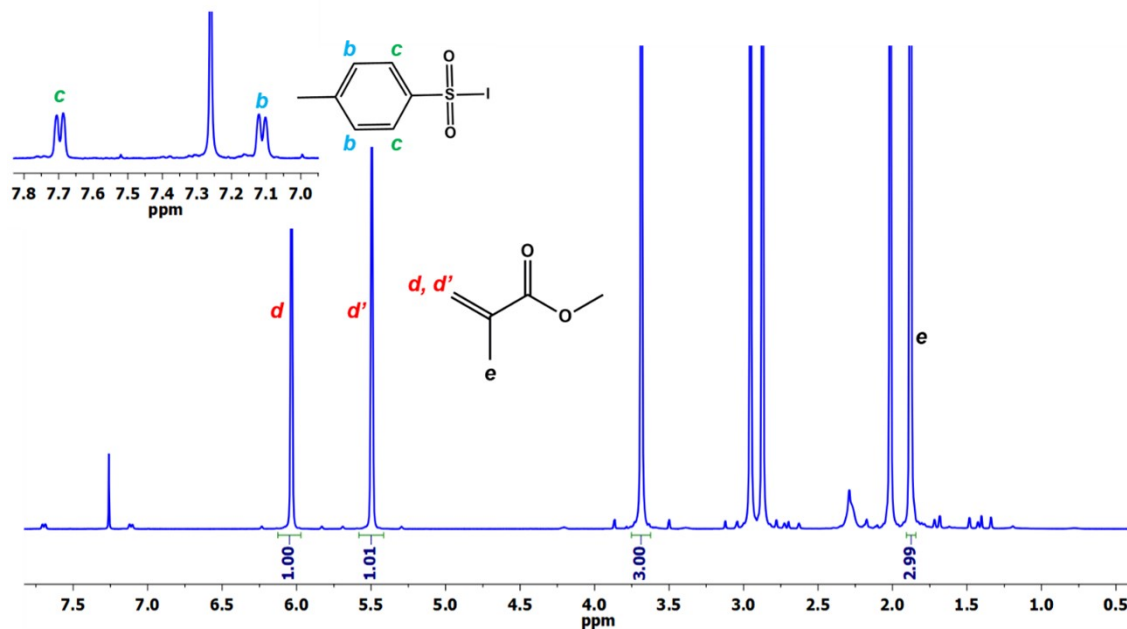
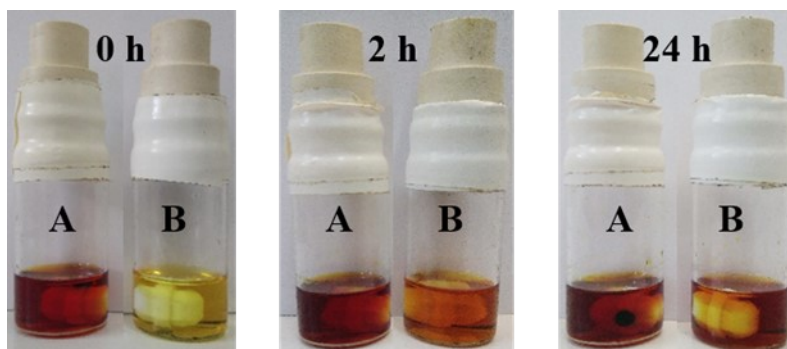


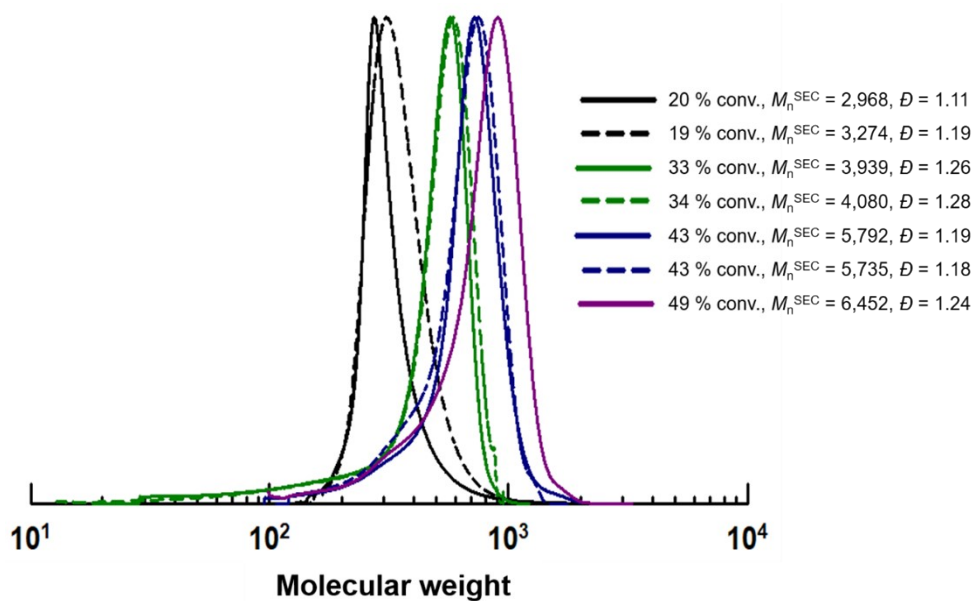
Figure S2 – <sup>1</sup>H NMR of pure tosyl iodide.



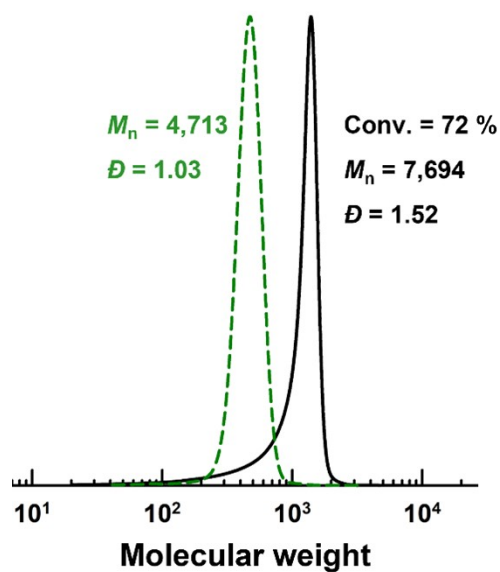
**Figure S3** – <sup>1</sup>H NMR spectra of the MMA polymerization using TEMPO as radical scavenger. Polymerization conditions:  $[MMA]_0/[Tosyl\ iodide]_0/[TEMPO]_0 = 100/1/1.5$ , under violet LEDs irradiation ( $\lambda_{max} = 400\text{ nm}$ ,  $0.85\text{ mW}\cdot\text{cm}^{-2}$ ) at room temperature.



**Figure S4** – Color change photography's of the polymerization system at different reaction times. Polymerization conditions:  $[MMA]_0/[Solvent]_0 = 1/1.5$  (v/v);  $[MMA]_0/[Initiator]_0 = 100/1$ , under violet LEDs irradiation ( $\lambda_{max} = 400\text{ nm}$ ,  $0.85\text{ mW}\cdot\text{cm}^{-2}$ ) at room temperature. Reaction A using dimethyl sulfoxide (DMSO) as solvent; Reaction B using dimethylacetamide (DMA) as solvent.



**Figure S5** – SEC traces of temporal control in photo-controlled iodine polymerization of MMA demonstrating “on-off” cycles of polymerization under violet LEDs irradiation ( $\lambda_{\text{max}} = 400 \text{ nm}$ ,  $3.19 \text{ mW}\cdot\text{cm}^{-2}$ ). Solid lines correspond to 2 h of “light on” period and dashed lines correspond to 1 h “light off” period. Polymerization conditions:  $[\text{MMA}]_0/[\text{DMA}]_0 = 1/1.5 \text{ (v/v)}$ ;  $[\text{MMA}]_0/[\text{Initiator}]_0 = 100/1$ , at room temperature.



**Figure S6** – SEC traces of photo-controlled iodine polymerization of MMA under sunlight irradiation (full black line), and polystyrene standard (dashed green line). Polymerization conditions:  $[\text{MMA}]_0/[\text{DMA}]_0 = 1/1.5 \text{ (v/v)}$ ;  $[\text{MMA}]_0/[\text{Initiator}]_0 = 100/1$ .

### 3. Reference

1. F. C. Whitmore and N. Thurman, *J. Am. Chem. Soc.*, 1923, **45**, 1068-1071.