Supporting Information

Photoinduced synthesis of fluorescent hydrogels without fluorescent monomers

Tugrul Cem Bicak, Maylis Garnier, Michèle Sabbah, and Nébéwia Griffete**

T. C. Bicak, M. Garnier, N. Griffete

nebewia.griffete@sorbonne-universite.fr

tugrul.bicak@sorbonne-universite.fr

Sorbonne Université, CNRS, Physico-chimie des Électrolytes et Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France

M. Garnier, M. Sabbah

Saint-Antoine Research Center (CRSA), INSERM, CNRS, Sorbonne Université, F-75012 Paris, France

Experimental:

Materials:

Rhodamine B (RhB, Aldrich, 99%), benzophenone (BP, Rhone Poulenc, 99%), acrylamide (AaM, Aldrich, 99%), N,N-methylenebis(acrylamide) (BAaM, Aldrich, 99%), 2-(N,N-diethyldithiocarbamyl)acetic acid (DCAA, Aldrich, 98%) and technical grade ethanol (EtOH, Alrich) were used as received.

Instumentation:

Fourier Transform Infra-Red (FT-IR). Infrared spectra were obtained on a Bruker Tensor 27 spectrometer on pressed KBr pellets. Spectra were obtained at regular time intervals in the MIR Region of 4000 – 400 cm^{-1} at a resolution of 4 cm^{-1} and analyzed using OPUS software. Dynamic light scattering (DLS). Hydrodynamic diameter (dh) measurements were recorded using a Malvern Instruments Nanosizer. Fluorescence spectra were recorded using a Varian Cary Eclipse fluorescence spectrophotometer (Agilent, France). Ultraviolet-visible spectrophotometry (UV-vis) absorbance measurements were carried out by Uvicon XL - Secomam UV-visible spectrophotometer, using a combined deuterium-halogen light source from 200 to 800 nm. was used. Photopolymerisations were carried out by putting reaction vessels in water bath to dissipate the heat generated in the system and approximately 5 cm above the UV light source (VL-215.L 2x15W – 365 nm tube UV lamb, Fischer Bioblock Scientific) without any stirring. UV-Vis spectrum of BP was recorded in ethanol and RhB was recorded in water using approximately 2 µM solutions. For UV-Vis spectrum of the hydrogels, 20 mg of the dried hydrogel was soaked in 3 ml of distilled water for 10 minutes prior to analysis. After swelling,

the thickness of the hydrogel was practically equal to the length of the quartz cuvette (1 cm) and UV spectrum was recorded at this stage.

Polymerisation procedure:

A typical procedure for the synthesis of fluorescent hydrogels via type II photoinitiated polymerisation is as follows (Table 1, entry 2): AaM (200 mg, 2.81 mmol) and BAaM (100 mg, 0.64 mmol) were dissolved in 16 mL deionised water containing 5% (vol%) ethanol. Next, 0.920 mL (0,0038 mmol) of RhB solution (2 mg/mL in water) and 0.832 mL (0.0219 mmol) of BP solution (5 mg/mL in EtOH) were added to a ~25 mL polyethylene vial and sonicated until a clear mixture was obtained. Next, the reaction mixture was purged with nitrogen gas for 15 min. The reaction vial was then sealed under nitrogen and put above the 2x15 W 365 nm UV light without any stirring at ambient temperature. In the end of the reaction period, product was washed thoroughly with deionized water using a dialysis membrane to remove unreacted monomers and initiators and dried overnight in at 60 °C. The yield of polymerization is calculated by weighing the hydrogel at its dry state. The corresponding non-fluorescent hydrogel was prepared via photoinitiated RAFT polymerisation by replacing RhB and BP with DCAA (0,0038 mmol). Control experiments were carried out by simply omitting RhB and BP from the procedure.

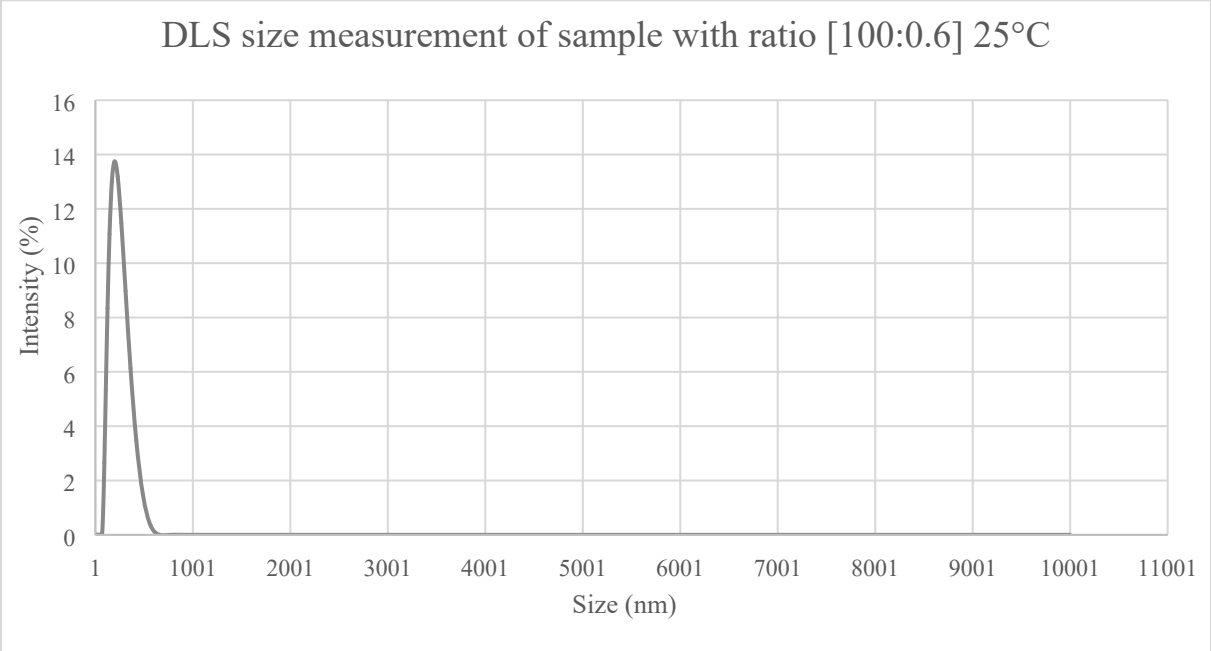

Figure S1. DLS size measurement of hydrogels prepared by type II photoinitiated polymerization using [100]:[0.6] monomer to BP mole ratio. Measurement was repeated 3 times and showed identical results.

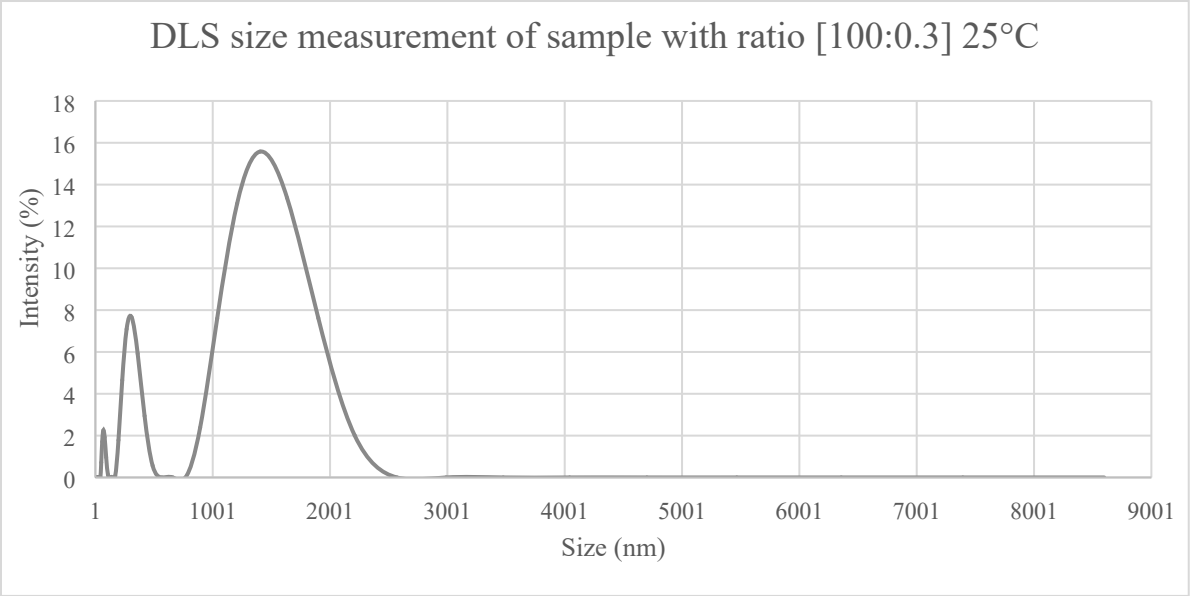

Figure S2. DLS size measurement of hydrogels prepared by type II photoinitiated polymerisation using [100]:[0.3] monomer to BP mole ratio. Measurements were repeated 3 times and the results were not reproducible probably due to the aggregation of particles during measurement (Only the first measurement is shown above).

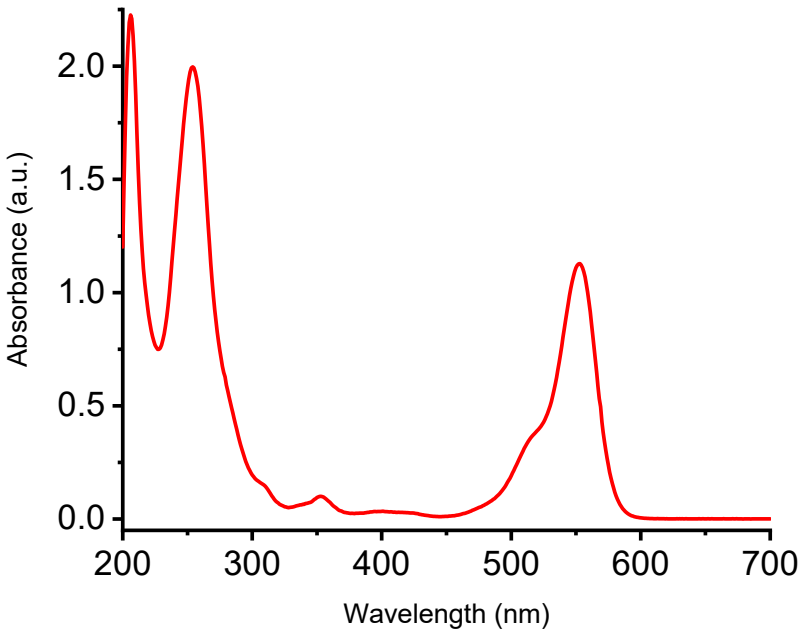

Figure S3. UV- Vis spectra of BP and RhB in ethanol.

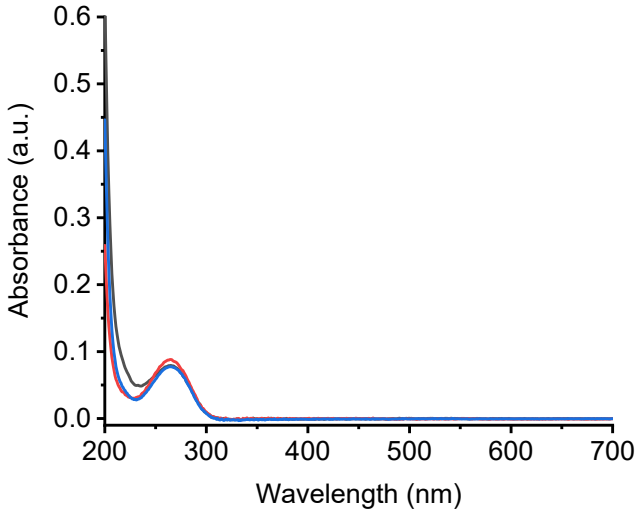

Figure S4. UV-Vis spectrum of the supernatant after 24 h (blue), 48 h (red), and 96 h (black) of incubation of hydrogels in water.