Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Supporting information

Photochemical crosslinking of hyaluronic acid confined in nanoemulsions: towards nanogels with a controlled structure

Léa Messager[a], Naira Portecop[a], Emilie Hachet[b], Véronique Lapeyre[a], Isabelle Paintrand[b], Bogdan Catargi[c], Rachel Auzély-Velty[b], Valérie Ravaine[a]*

[a] Université de Bordeaux, ISM, UMR 5255, ENSCBP, 16 avenue Pey Berland, 33607 Pessac, France

[b] Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), affiliated with Université Joseph Fourier, 601 rue de la Chimie, 38041 Grenoble, France

[c] CBMN UMR 5248, Université Bordeaux, Allée de Saint-Hilaire, 33600 Pessac, France

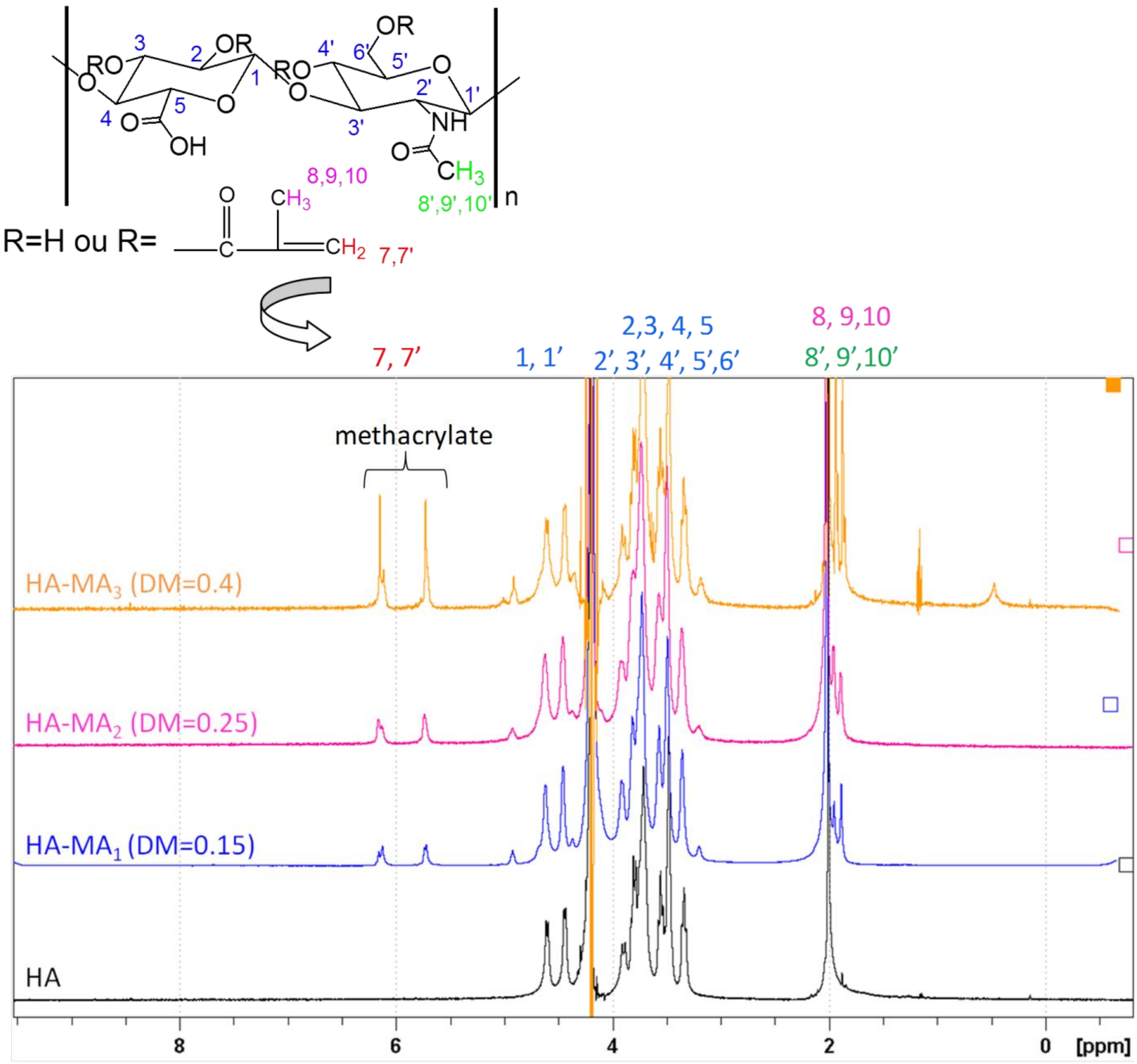

Figure S1. ^{1}H-NMR spectra of HA-MA derivatives with varying degrees of methacrylation. Conditions: 400 mHz, T=80°C, c = 8 mg/mL in D_2O.

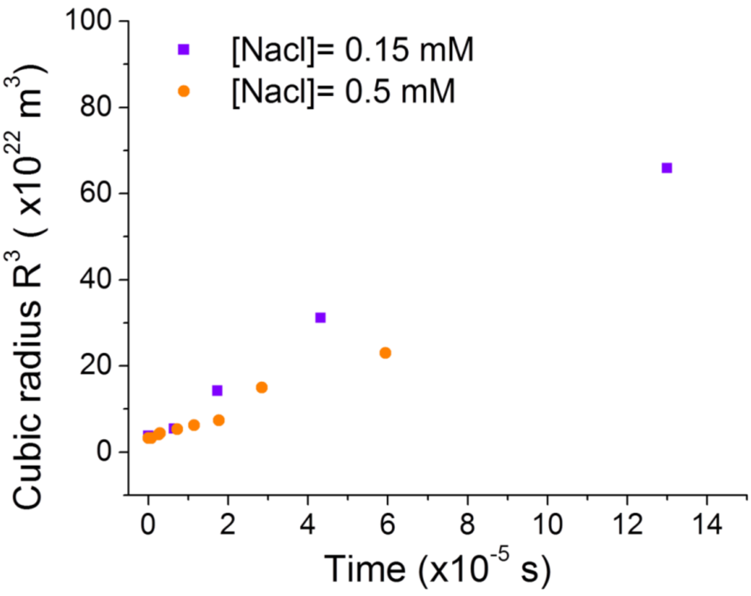

Figure S2. Evolution of the cubic radius of the emulsion over time (5 days), as a function of salt concentration in the droplets.

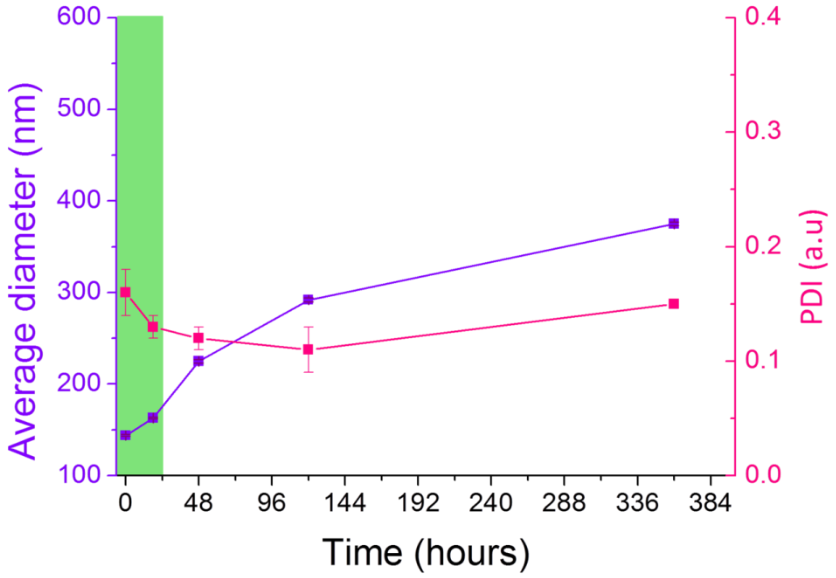

Figure S3. Evolution of the emulsion size over 1 week. After 7 days, both size and size distribution increase. The colored zone corresponds to the time scale useful for photopolymerization.

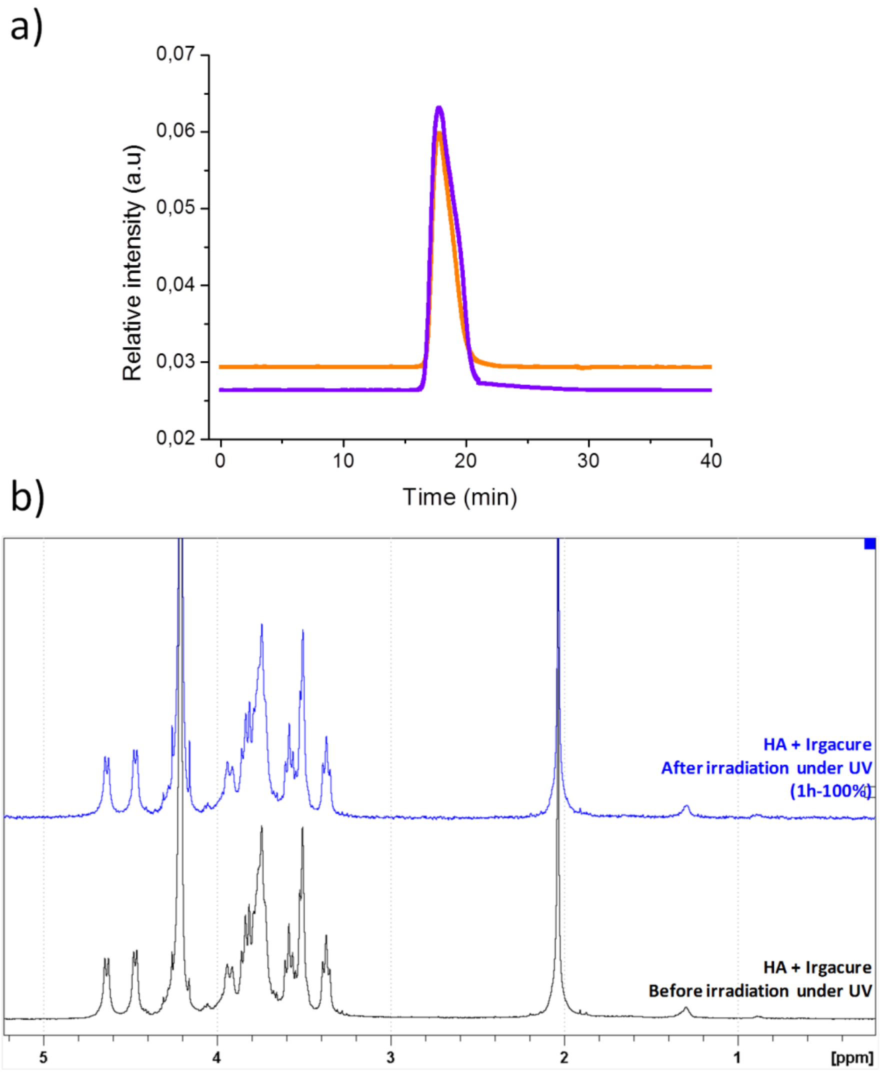

Figure S4. GPC (a) and ^{1}H-NMR (b) traces of HA before and after been confined in water-in-oil nanoemulsion. HA samples were analyzed by means of a GPC equipment made of a JASCO PU980 pump, equipped with a double detector (RI OptolabrEX from Wyatt Technolgu and MALS DAWN Heleos II). PLaquagel-OH columns (Polymer Laboratories) were eluted with a PBS buffer, at a flow rate of 0.6 mL/min. An injection loop of 100 µL was used. HA solutions (3 g/L) were prefiltered before injection with a 0.2 µm syringe filter.

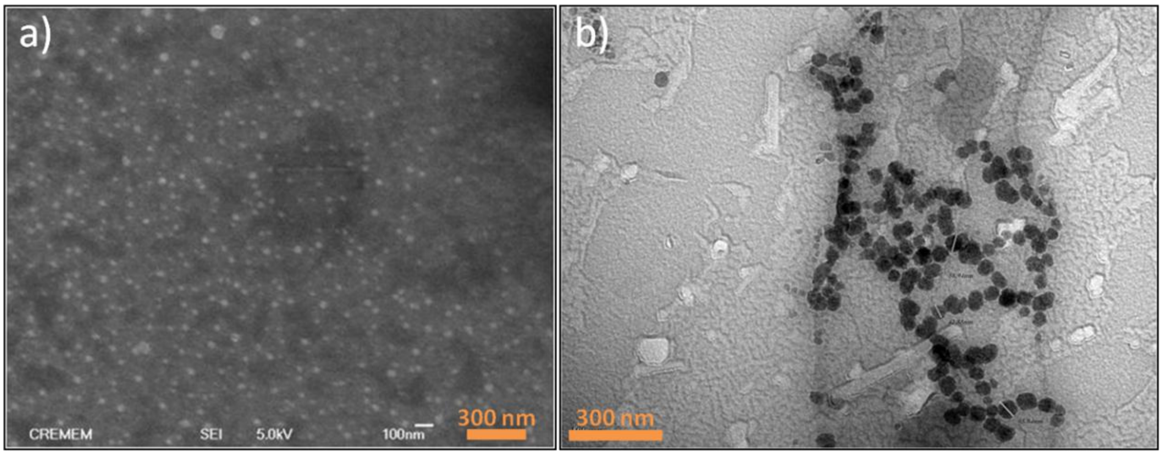

Figure S5. a) SEM and b) TEM images of nanogels in cyclohexane. Conditions : HA-MA_2, DM=0.25, irradiation under UV 2H-100% Pmax.

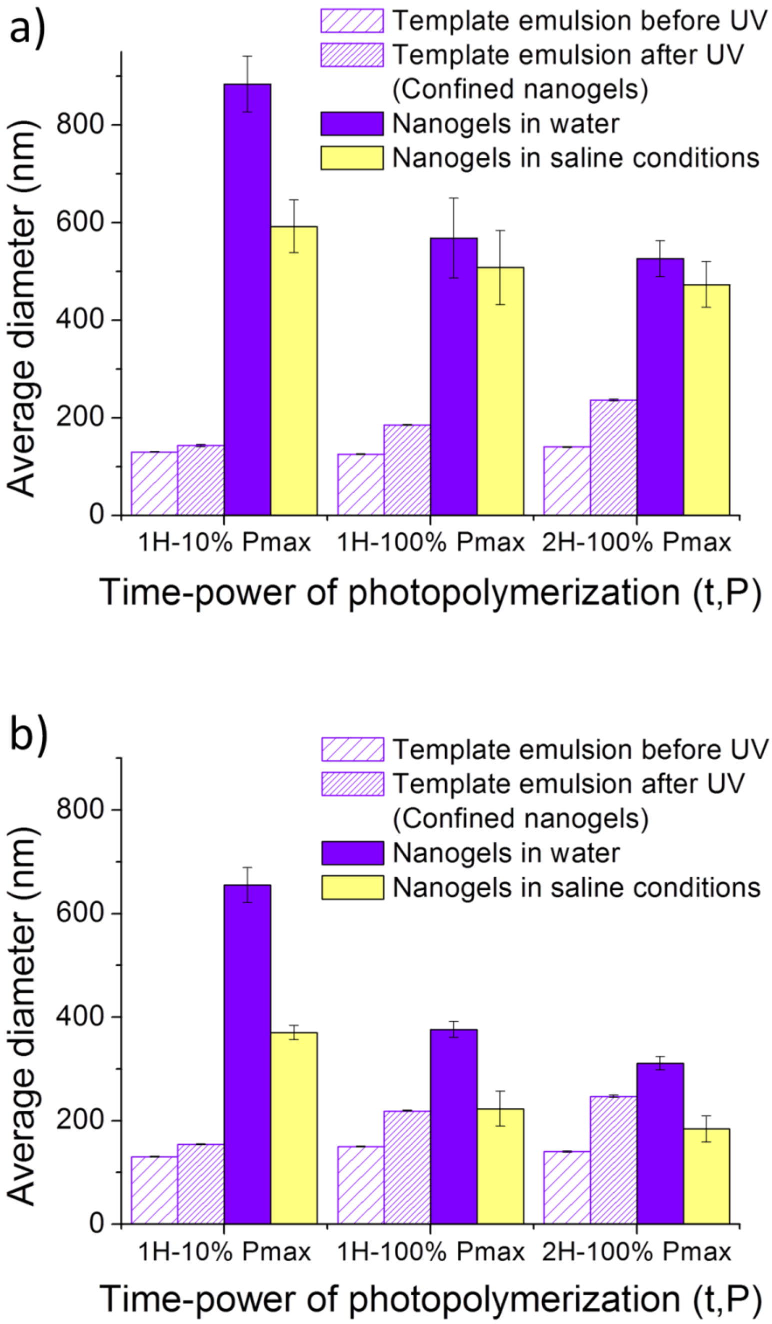

Figure S6. Summary of the size evolution of the emulsion (before and after photopolymerization) and of the nanogels as a function of photopolymerization conditions. Samples: HA-MA a) DM=0.15; b) DM=0.40.

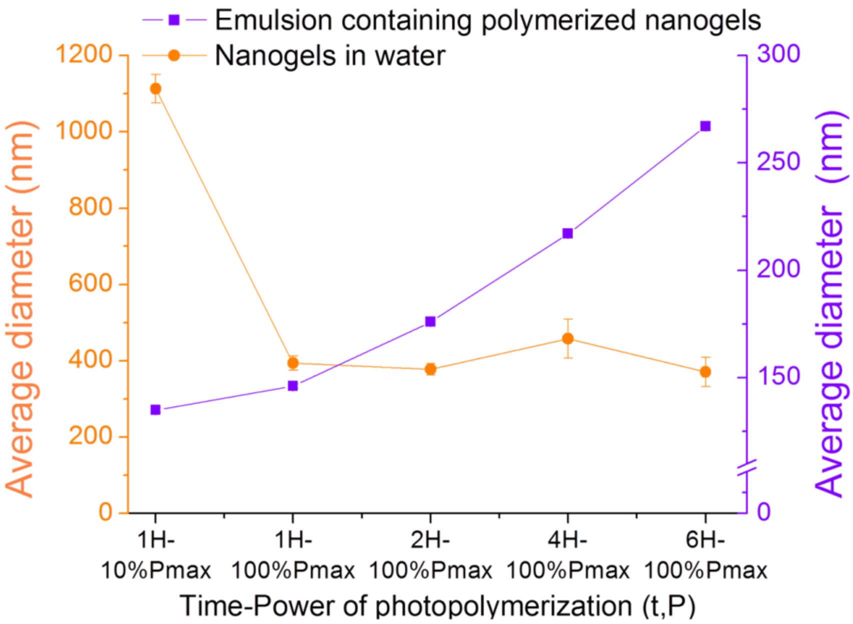

Figure S7. Summary of the size evolution of the emulsion after photopolymerization and of the resulting nanogels as a function of photopolymerization conditions. Sample: HA-MA, DM=0.25.

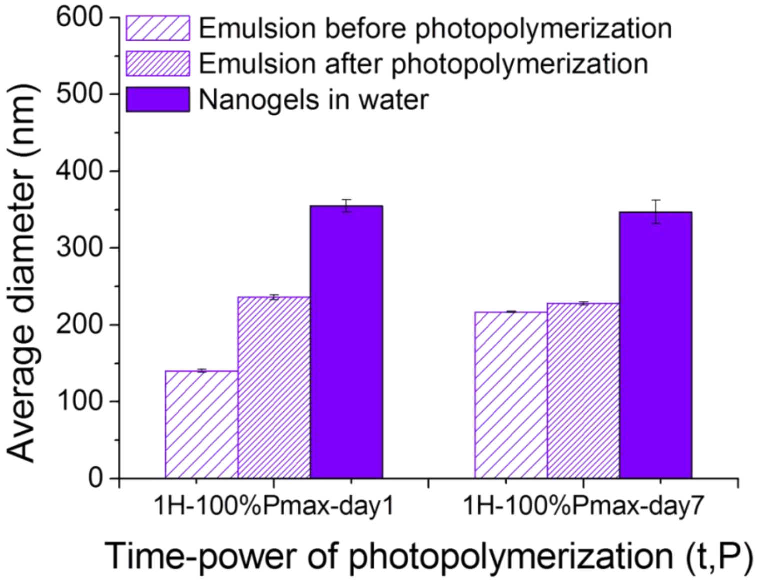

Figure S8. Summary of the size evolution of the emulsion (before and after photopolymerization) in similar photopolymerization conditions using a fresh or an aged emulsion. Sample: HA-MA, DM=0.25.

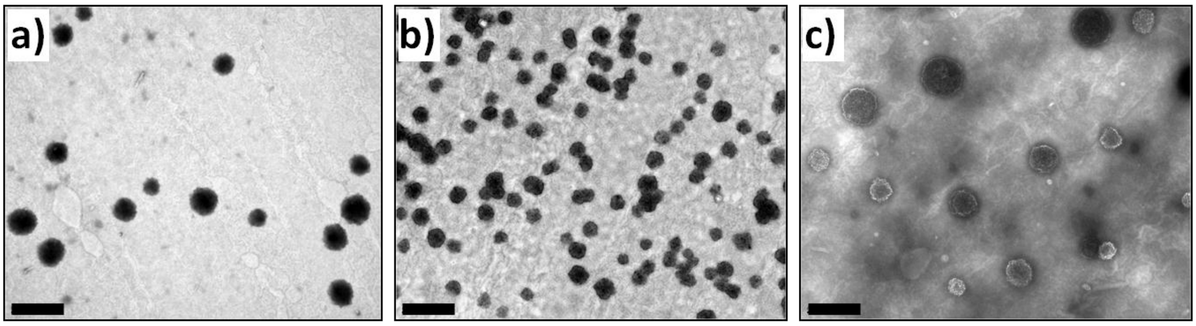

Figure S9. TEM morphologies of HA-MA nanogels: a) at t_0; b) after 2 weeks and c) after 1 month. Respective scale bars are 800 nm; 1 µm and 700 nm. Sample: HA-MA, DM=0.4.

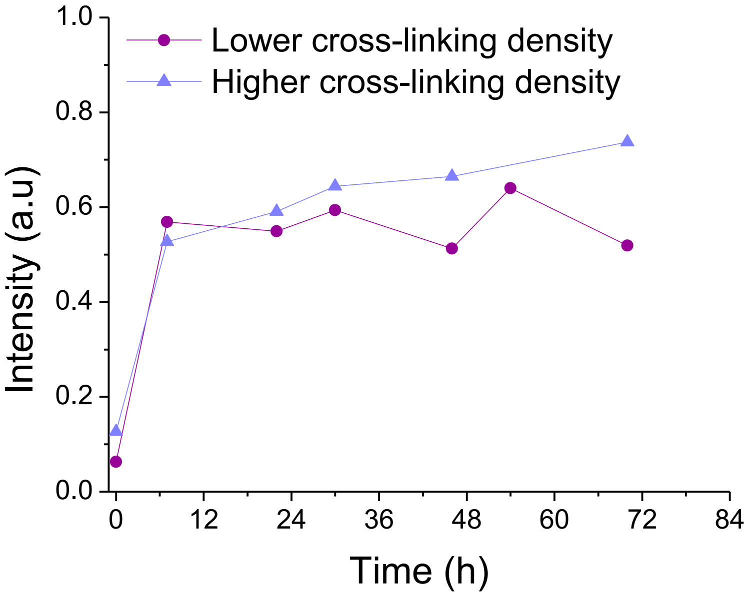

Figure S10. Enzymatic degradation of nanogels with varying crosslinking density monitored by carbazole assay. Conditions : HA-MA_2, DM=0.25, Photopolymerization 1h-100% and 2h-100%, [Nanogel]=2g/L, [Hase]=100UI/mL.