

Supporting Information

Smart self-assembled microgel films as encapsulating carriers for UV-absorbing molecules.

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EXPERIMENTAL SECTION

Materials. Di(ethylene glycol) methyl ether methacrylate (MeO₂MA 95%, Aldrich), oligo(ethylene glycol) methyl ether methacrylate (OEGMA, monomethyl terminated with 8 EG repeat units, number average weight $M_n = 475$ g mol⁻¹, Aldrich), methacrylic acid (MAA, Aldrich), oligo(ethylene glycol) diacrylate (OEGDA, number average weight $M_n = 250$ g mol⁻¹, Aldrich), potassium persulfate (KPS 99%, ABCR), and ethanol (VWR Chemicals) were used as received. Hydrochloric acid (HCl, 36 w/w, ABCR) and potassium hydroxide (KOH, Aldrich) were used to control the pH of dispersions. Citric acid (Sigma-Aldrich) and sodium phosphate dibasic (Na₂HPO₄, Sigma-Aldrich) were used to prepare the buffers. Deuterium oxide (D₂O, EurosiTop) was used for NMR characterization. Diethylamino hydroxybenzoyl hexyl benzoate (Uvinul A), octyl salicylate (Escalol), benzophenone-4, and salicylic acid were supplied by LVMH. "Milli-Q" grade water was used throughout work.

Self-assembled microgel films formation. Prior to the film formation, oligo(ethylene glycol)-based microgels were synthesized following the method described by Boularas et al.¹ Briefly, self-assembled microgel films were formed *via* an easy handling procedure based on water evaporation under ambient conditions. 30 mL of purified or non-purified (presence of water soluble polymers, WSP) aqueous microgel dispersion (1.4 wt% solid content) were introduced into inert plastic mold and dried for 48 h at 35 °C (±3 °C) at atmospheric pressure. The effect of the presence and concentration of different salts (citric acid/sodium phosphate dibasic and potassium carbonate) in film formation was studied following the same protocol.

Swelling behavior of self-assembled microgel films. The swelling behavior of films was studied varying the medium conditions such as hydrophobicity, temperature, and pH. To study the effect of pH different buffered media were prepared and for the study of the effect of hydrophobicity different compositions of water/ethanol and water/isopropanol were used. The films were immersed into different media for 24 h the swelling ratio was calculated by gravimetric method following the next equation□

$$\begin{aligned} \text{Swelling ratio (\%)} \\ &= \frac{W_t - W_o}{W_o} \times 100 \end{aligned} \quad (1)$$

where W_t is the mass of the swollen film and W_o is the mass of the dry film.

Characterization of self-assembled microgel films. Images by Atomic Force Microscopy (AFM) of self-assembled microgel films were recorded on a Multi mode 8 (BrukerNano) using silicon-nitride cantilevers from Bruker-probe (ScanAsyst-Air). For that, the self-assembled microgel films were deposited on wafer silicon substrate prior to be observed by AFM surface mapping. Films were formed using purified and non-purified microgel dispersions in order to study the effect of WSPs.

Differential scanning calorimetry (DSC) measurements were done using a DSC Q 100 (TA instruments). Approximately 5 mg of dried self-assembled microgel films were sealed in aluminum pans and measured from -70 to

130 °C and under nitrogen flow (50 mL.min⁻¹). For all samples, two heating and two cooling runs were performed and the glass transition temperature was taken from the second heating run.

In vitro encapsulation of cosmetic active molecules. The loaded amounts of cosmetic active molecules into films were determined immersing the films in active molecules water/ethanol (1□0.25) solution and allowing them to rehydrate during 24 h. Then, the loaded-films were separated and the solutions containing non-encapsulated cosmetic active molecules were analyzed by UV-Vis to determine the amount of non-encapsulated cosmetic active molecules.

Entrapment efficiency (E.E.) was calculated as follows□

$$E.E.\% = \frac{\text{weight of active molecule in film}}{\text{weight of feeding active molecule}} \times 100$$

Characterization of loaded-film. Transmittance data of loaded-films were collected using Shimadzu UV-2101 spectrometer from 300 to 500 nm. Loaded-films were enough sticky to hold themselves to sample holder and therefore, air was used as reference.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded on a Spectrum One (PerkinElmer) spectrometer. Four scans were made for each measurement and all spectra were recorded at 25 °C and atmospheric pressure.

The interactions between different cosmetic active molecules and self-assembled microgel particles were studied by Nuclear Overhauser Enhancement Spectroscopy (NOESY-NMR). All NMR experiments were performed at 25 °C and 60 °C on a Bruker Avance 400 spectrometer equipped with a Bruker 5 mm BBFO probe and a gradient amplifier, which provides a z-direction gradient strength of up to 47.5 G/cm. The temperature was maintained constant within ± 0.1 °C by means of the BCU 05 unit. The proton chemical shifts were referenced to the HOD signal at 4.70 ppm. For these measurements cosmetic active molecules were loaded at 2000 µg/mg_{film} concentration and loaded-films were allowed to rehydrate in D₂O overnight. Then, all 2D NOESY spectra were recorded using a 1H spectral width of 12 ppm and acquired with the Bruker standard pulse program (noesygpph) of the Avance 400 spectrometer. For each NOE spectrum, 256 slices were recorded in the t₁ dimension, and the number of scan was 32 (2048 data points for each scan). The FID was treated by square-shifted sine bell weighting functions in both dimensions using TopSpin 2.1. The mixing time and the relaxation time were set to 400 ms and 2 s, respectively.

The distribution of cosmetic active molecules into self-assembled microgel films was studied by confocal microscopy. For that, samples were visualized with a confocal microscope (Confocal Leica SP2, Leica Microsystems, Germany) with laser excitation line at 405 nm and acquiring the emission signals in the range of 400-600 nm together with the transmitted light simultaneously. An objective HC-PL APO CS 20.0x0.70 UV was used for these analysis.

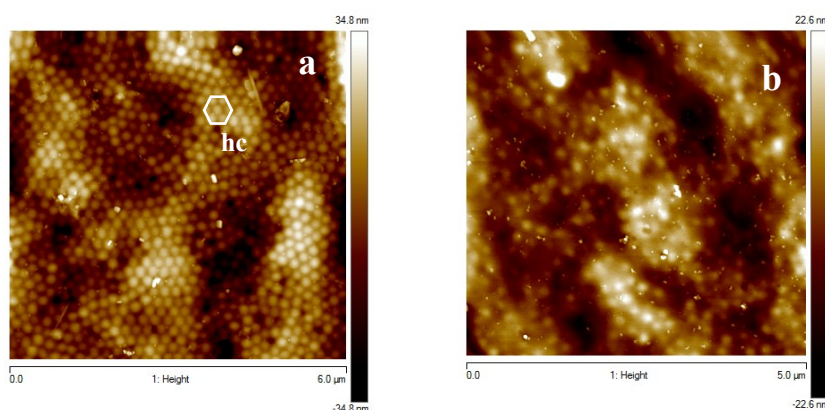


Figure S1. AFM micrographs of the surface of self-assembled oligo(ethylene glycol)-based purified (a) and non-purified (b) microgel films.

Table S1. Tg values as type of salt at 1 mM

Type of salt	pH	Without WSP	With WSP
		Tg	Tg
None	6	-20	-19
	4.5	-29	-30
Citric acid/sodium phosphate dibasic	6	-12	-12
	7	-11	-12
Potassium carbonate	9	-19	---

a function of pH and ionic strength.

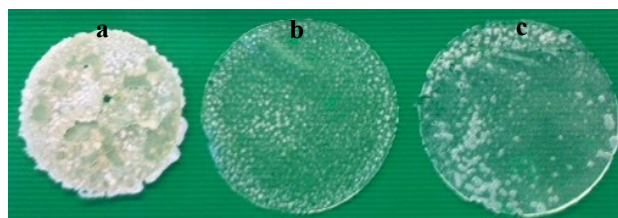


Figure S2. Images of oligo(ethylene glycol)-based microgel films prepared at 10 mM ionic strength and at different microgel solid contents. a) 1.4 wt%, b) 2.5 wt%, c) 5 wt%.

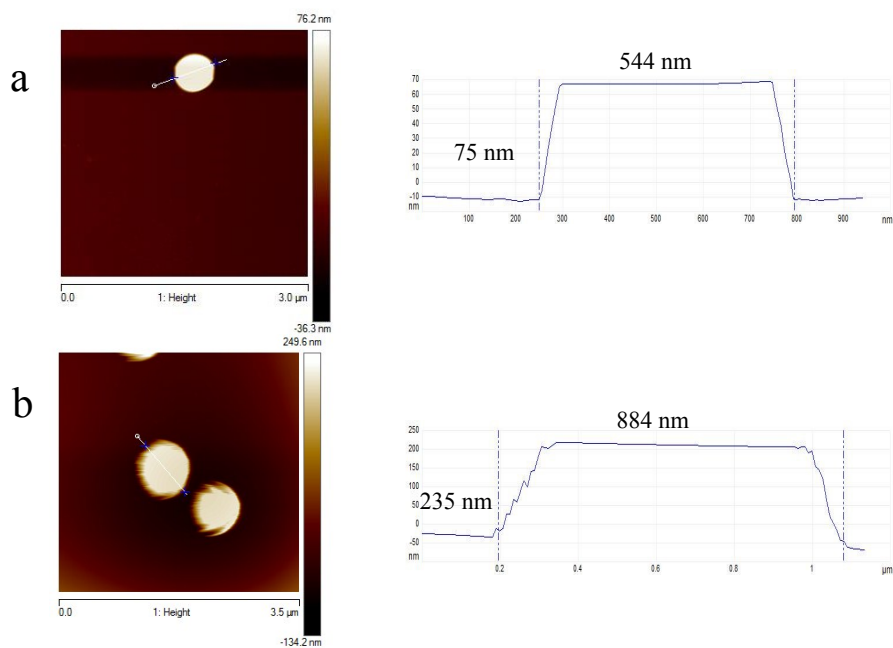


Figure S3. AFM images of oligo(ethylene glycol)-based microgel and size (nm) of indicated cross-section in dried state (a) and immersed in alkaline solution at pH 9 (b).

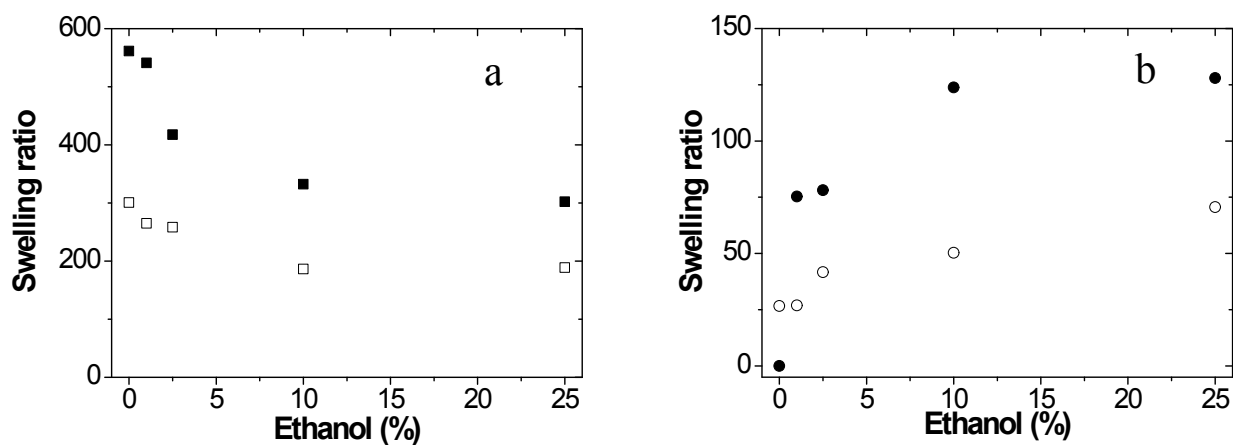


Figure S4. Swelling ratio of self-assembled microgel films at 20 °C (a) and 50 °C (b) using purified microgel dispersion (■, ●) and non-purified microgel dispersion (□, ○).

Table S2. Entrapment efficiencies (E.E.) as a function of the presence of WSP.

Active molecules (1000 $\mu\text{g}/\text{mg}_{\text{film}}$)	Entrapment efficiency (E.E.) (%)	
	Without WSP	With WSP
Uvinul A	81	84
Escalol	83	99
Benzophenone-4	82	81
Salicylic acid	72	69

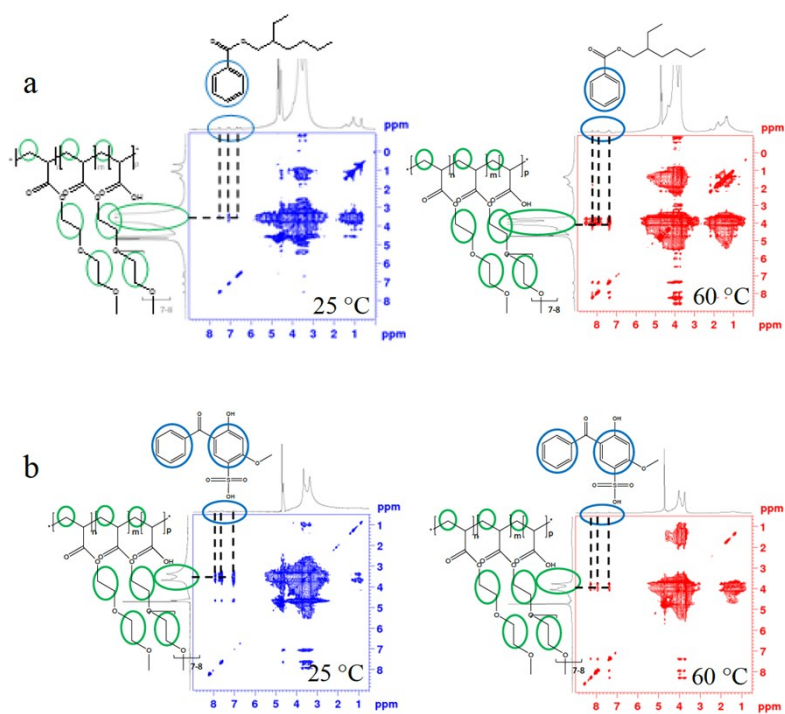


Figure S5. NOESY-NMR spectra of Escalol-loaded (a) and Benzophenone-4-loaded (b) film as a function of temperature.

REFERENCES

- (1) M. Boularas, E. Deniau-Lejeune, V. Alard, J.-F. Tranchant, L. Billon, M. Save, Dual stimuli-responsive oligo (ethylene glycol)-based microgels: insight into the role of internal structure in volume phase transitions and loading of magnetic nanoparticles to design stable thermoresponsive hybrid microgels, *Polym. Chem.*, **2016**, *7*, 350.