

Supplementary Information

Dual-responsive biocompatible microgels as high loaded cargo: Understanding of encapsulation/release driving forces by NMR NOESY

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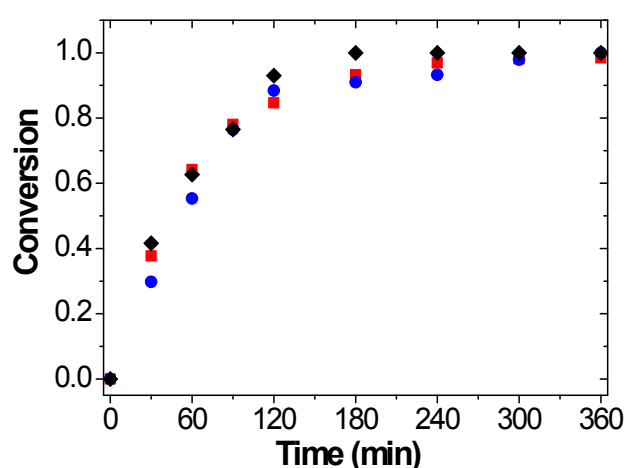


Figure S1. Evolutions of the partial conversions of ■ MeO₂MA, ● MAA, and ◆ OEGDA.

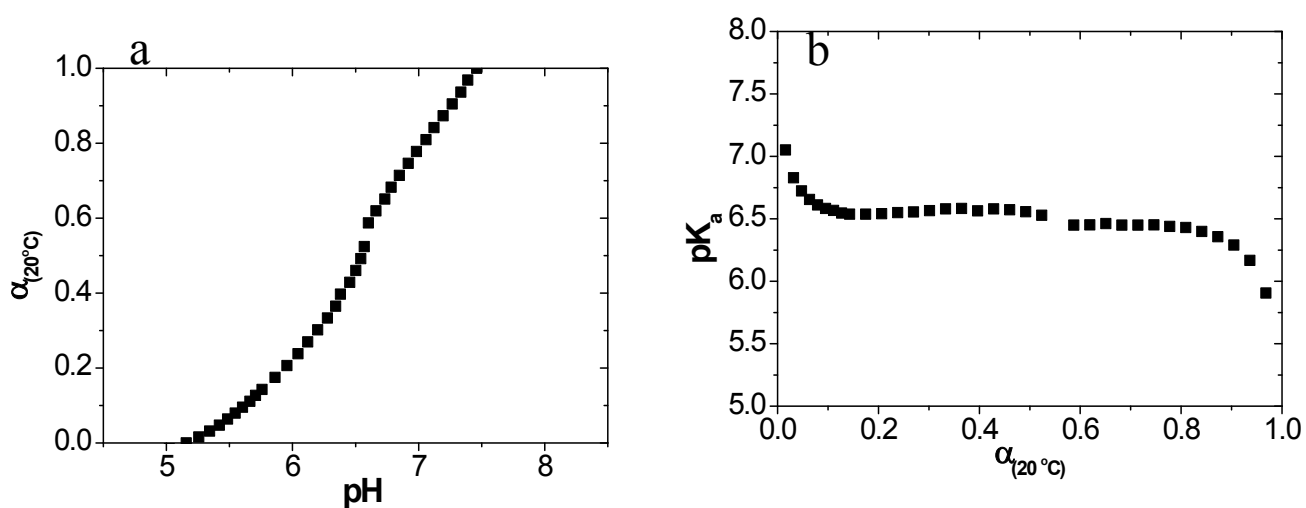


Figure S2. Degree of ionization (α) of MAA as a function of pH (a) and pK_a value for carboxylic acid group as a function of α of the microgel particles.

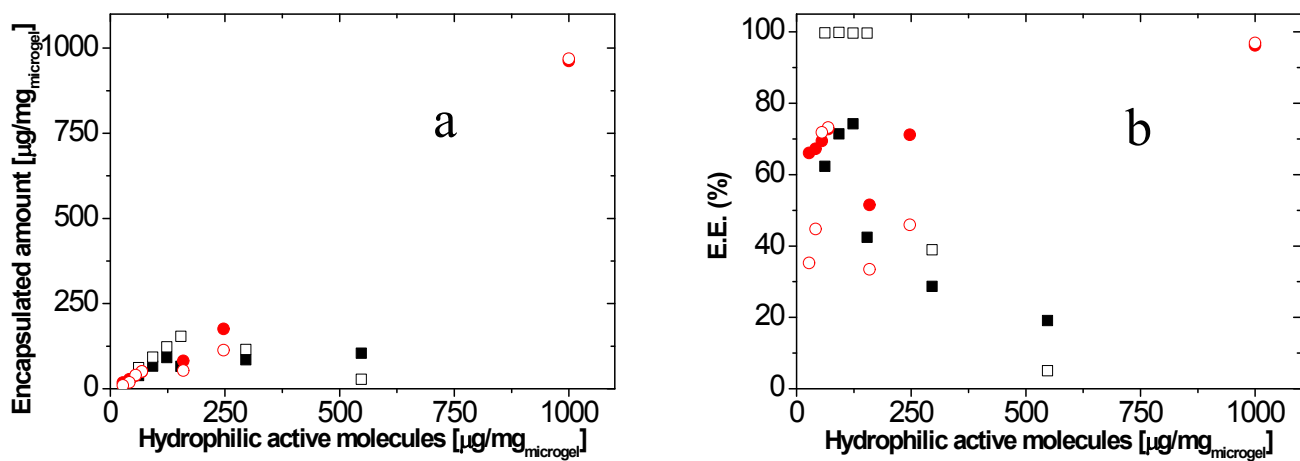


Figure S3. Encapsulated amounts (a) and entrapment efficiencies (E.E.) (b) as a function of hydrophilic active molecules concentration and pH for microgel particles using hydrophilic protocol. ■ Benzophenone-4 at pH 4.4; □ Benzophenone-4 at pH 7; ● Salicylic acid at pH 4.4; ○ Salicylic acid at pH 7.

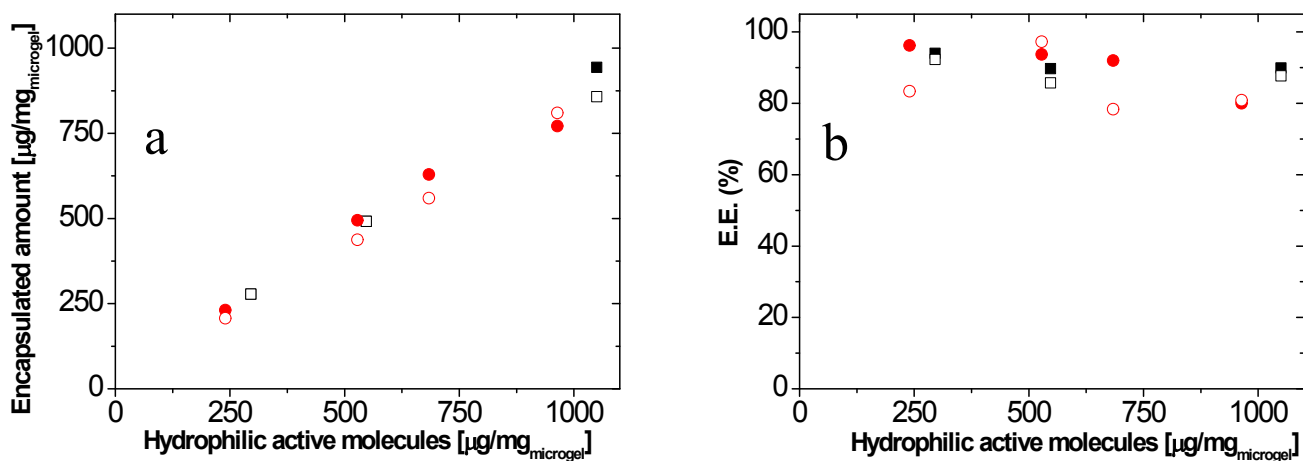


Figure S4. Encapsulated amounts and entrapment efficiencies (E.E.) as a function of hydrophilic active molecules concentration and temperature for microgel particles using hydrophobic protocol. ■ Benzophenone-4 at 20 °C; □ Benzophenone-4 at 50 °C; ● Salicylic acid at 20 °C; ○ Salicylic acid at 50 °C.

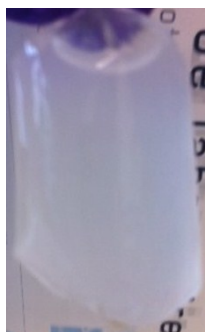


Figure S5. Escalol 587 precipitates/aggregates formation after dialyzing against deionized water for 48 h.

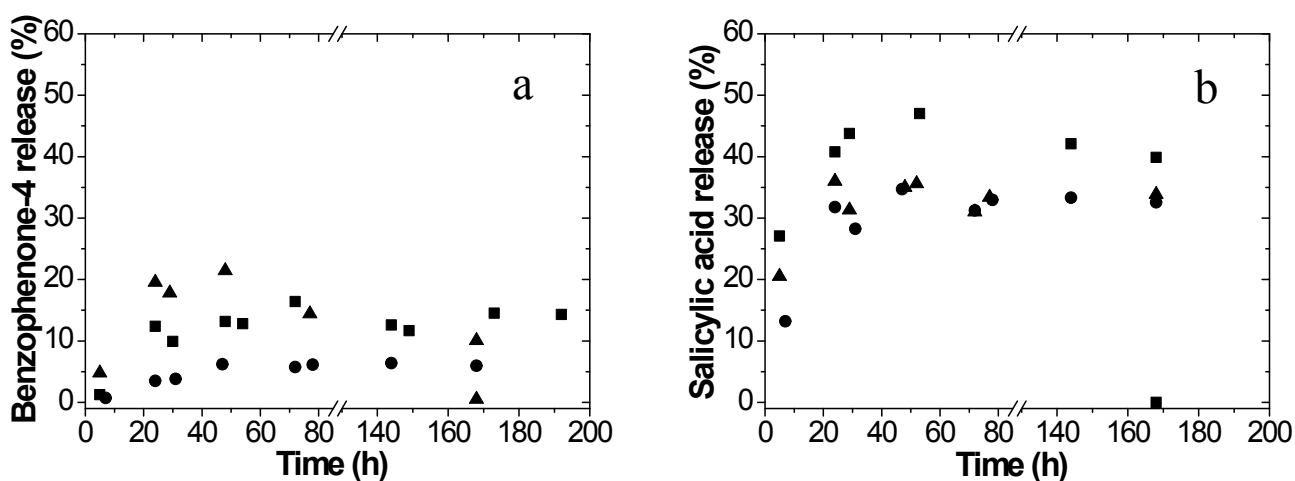


Figure S6. Benzophenone-4 (a) and Salicylic acid (b) release as a function of pH and temperature. ■ pH 4.5 and 25 °C; ● pH 6 and 25 °C; ▲ pH 4.5 and 37 °C.

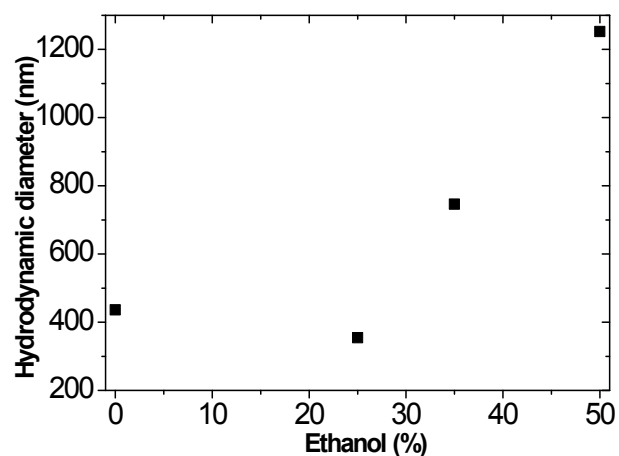


Figure S7. Average hydrodynamic diameters as a function of ethanol percentage.

Table S1. Fitting parameters for Peppas and Peppas model as a function of pH and temperature.

Active molecule	pH 4.5		pH 6		25 °C		37 °C	
	k	n	k	n	k	n	k	n
Uvinul-A	0.035	0.13	0.040	0.38	0.034	0.13	---	---
Escalol	---	---	---	---	---	---	---	---
Benzophenone-4	0.012	0.34	0.029	0.30	0.041	0.24	0.068	0.23
Salicylic acid	0.217	0.12	0.115	0.22	0.278	0.09	0.198	0.12

Table S2. Fitting parameters for Peppas and Peppas model as a function of medium hydrophobicity.

Active molecule	25 % of ethanol		35 % of ethanol		50 % of ethanol	
	k	n	k	n	k	n
Uvinul-A	0.060	0.07	0.027	0.51	0.049	0.72
Escalol	0.042	0.06	0.74	0.09	0.759	0.08
Benzophenone-4	0.023	0.35	0.040	0.29	0.021	0.43
Salicylic acid	0.432	0.19	---	---	---	---

Table S3. Fitting parameters for Peppas-Sahlin model as a function of medium pH.

Fitting parameters	Uvinul-A		Benzophenone-4		Salicylic acid	
	pH 4.5	pH 6	pH 4.5	pH 6	pH 4.5	pH 6
k_1	0.0130	0.0107	0.0154	0.0031	0.1931	0.0605
k_2	-0.0006	-0.0011	-0.0004	-0.0001	-0.0205	-0.0027
n	0.54	0.81	0.58	0.80	0.37	0.51

Table S4. Fitting parameters for Peppas-Sahlin model as a function of medium temperature.

Fitting parameters	Uvinul-A		Benzophenone-4		Salicylic acid	
	25 °C	37 °C	25 °C	37 °C	25 °C	37 °C
k_1	0.0129	---	0.0226	0.0194	0.1931	0.1583
k_2	-0.0006	---	-0.0089	-0.0004	-0.0205	-0.0183
n	0.54	---	0.53	0.77	0.37	0.32

Table S5. Fitting parameters for Peppas-Sahlin model as a function of medium hydrophobicity for hydrophobic active molecules.

Fitting parameters	Uvinul-A			Escalol		
	25 %	35 %	50 %	25 %	35 %	50 %
k_1	0.0685	0.0266	0.0689	0.0643	---	---
k_2	-0.0139	0.0024	-0.0012	-0.0178	---	---
n	0.24	0.41	0.83	0.19	---	---

Table S6. Fitting parameters for Peppas-Sahlin model as a function of medium hydrophobicity for hydrophilic active molecules.

Fitting parameters	Benzophenone-4			Salicylic acid		
	25 %	35 %	50 %	25 %	35 %	50 %
k_1	0.0232	0.0209	0.0020	0.3470	---	---
k_2	-0.0001	-0.0007	0.0024	-0.0319	---	---
n	0.35	0.56	0.35	0.38	---	---

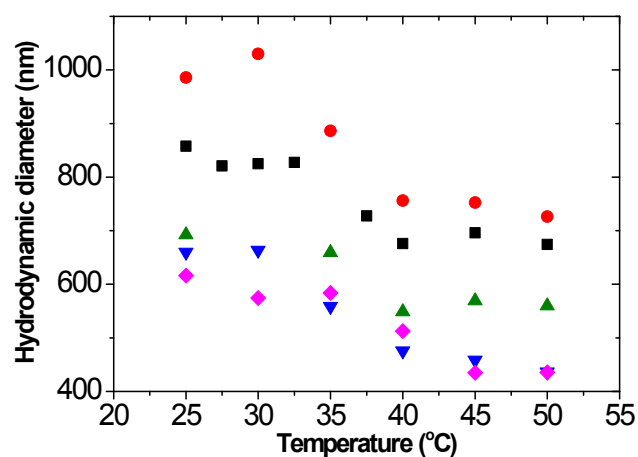


Figure S8. Average hydrodynamic diameters as a function of temperature at pH 6 and in buffered medium with an ionic strength of 1mM. ■Bare microgel particles, ●Uvinul-A loaded-microgel particles, ▲Escalol loaded-microgel particles, ▼Benzophenone-4 loaded-microgel particles, and ◆Salicylic acid loaded-microgel particles.

Table S7. VPTT values for bare and loaded-microgel particles.

Sample	VPTT (°C)
Bare microgel-particles	37.4
Uvinul-A-loaded microgel	35.0
Escalol 587-loaded microgel	35.1
Benzophenone-4-loaded microgel	39.9
Salicylic acid-loaded microgel	39.9