# Supporting Information

**Effect of Divalent Cation on Swelling Behavior of Anionic Microgels: Quantification and Dynamics of Ion Uptake and Release**

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#### Table S1. Synthetic conditions for the polymerization of neutral microgels with various *N*-vinylcaprolactam (VCL) and dimethylitaconate (IADME) ratios.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample ID | VCL/IADME ratio | VCL |  | IADME |  | AMPA |  | BIS |  | CTAB |  |
|  |  | g | mmol | g | mmol | g | mmol | g | mmol | g | mmol |
| N0 | 100:0 | 2.087 | 15.00 | 0 | 0 | 0.053 | 0.19 | 0.060 | 0.38 | 0.010 | 0.027 |
| N5 | 95:5 | 1.983 | 14.24 | 0.118 | 0.75 | 0.053 | 0.19 | 0.060 | 0.38 | 0.010 | 0.027 |
| N10 | 90:10 | 7.879 | 13.50 | 0.237 | 1.50 | 0.053 | 0.19 | 0.060 | 0.38 | 0.010 | 0.027 |
| N15 | 85:15 | 1.774 | 12.75 | 0.355 | 2.25 | 0.053 | 0.19 | 0.060 | 0.38 | 0.010 | 0.027 |
| N20 | 80:20 | 1.670 | 12.00 | 0.474 | 3.0 | 0.053 | 0.19 | 0.060 | 0.38 | 0.010 | 0.027 |
| N30 | 70:30 | 1.461 | 10.50 | 0.711 | 4.5 | 0.053 | 0.19 | 0.060 | 0.38 | 0.010 | 0.027 |

**Table S2. Amount of dimethylitaconate (IADME) incorporated and itaconic acid (IA) groups.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample ID | Theoretical value | NMR value | ATR-FTIR value | Sample | IR value | TITRATION |
| N0 | 0 | 0 | 0 | NA | NA | NA |
| N5 | 5 | 5 | 5.775 | M4 | 4.089 | 3.8 |
| N10 | 10 | 10 | 9.395 | M7 | 5.471 | 6.5 |
| N15 | 15 | 15 | 16.013 | M11 | 7.429 | 11 |
| N20 | 20 | 20 | 22.950 | M13 | 10.474 | 12.5 |
| N30 | 30 | 30 | 31.068 | M15 | 15.711 | 14.5 |

**Table S3. *Rg*/*RH* of P(VCL-*co*-IADME) (N*n*) microgels in pure water at pH 7 and P(VCL-co-IA) (M*n*) microgels in pure water at pH 7 and pH 3.**

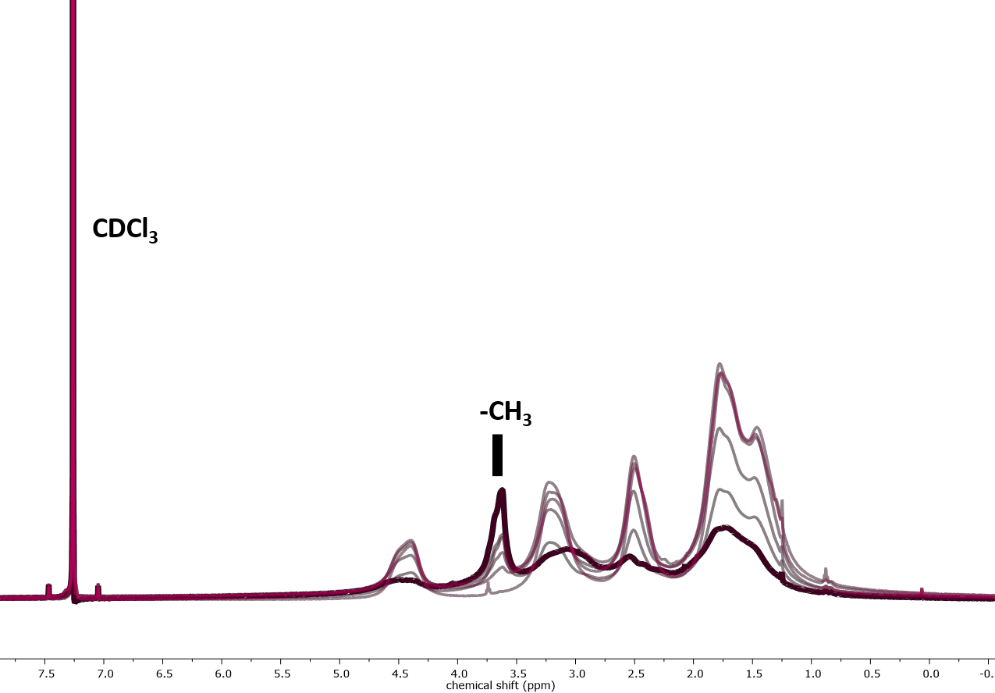
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample ID | *R*g/*R*H  (pH=7) | Code | *R*g/*R*H  (pH=3) | *R*g/*R*H  (pH=7) |
| **N0** | 0.55 |  |  |  |
| **N5** | 0.52 | M4 | 0.63 | 0.37 |
| **N10** | 0.61 | M7 | 0.60 | 0.38 |
| **N15** | 0.61 | M11 | 0.63 | 0.42 |
| **N20** | 0.66 | M13 | 0.63 | 0.52 |
| **N30** | 0.74 | M15 | - | 0.37 |

**Table S4. Comparison of the *D*H of P(VCL-co-IA) (M) microgels in the presence of Ca2+ and at pH 3 at T=20 °C.**

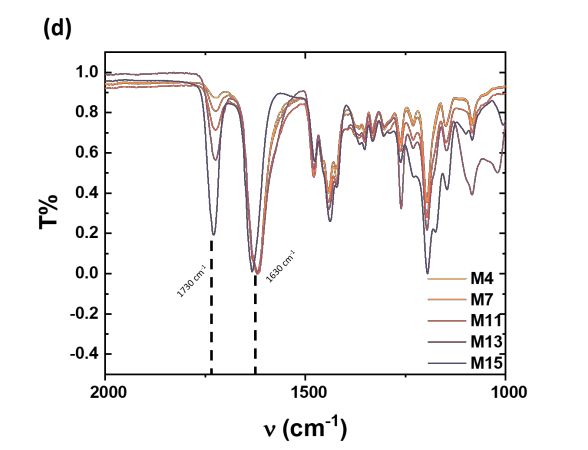
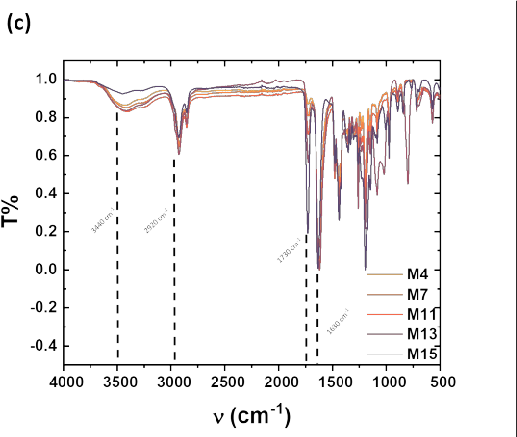
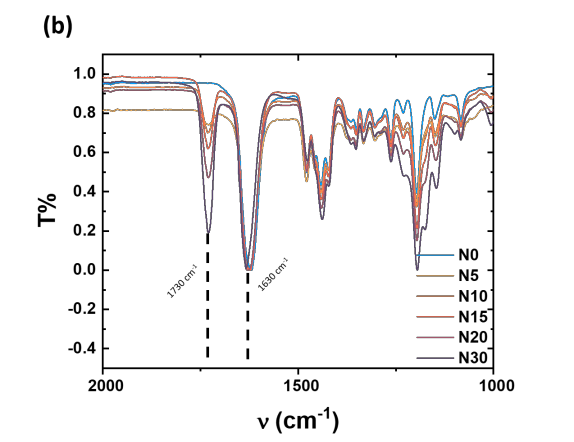
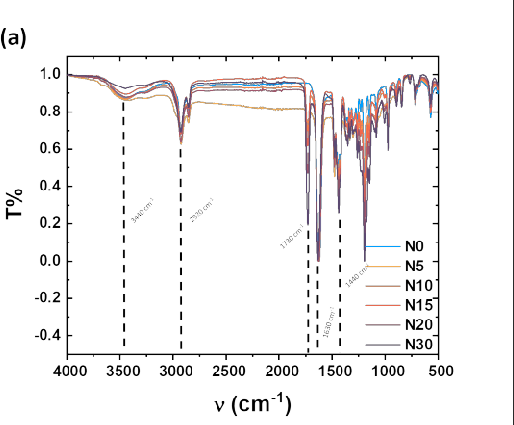
|  |  |  |  |
| --- | --- | --- | --- |
| Sample ID | *D*H  [Ca2+]= 10 mM  (pH= 7) | *R*g*/R*H  [Ca2+]= 10 mM  (pH= 7) | *D*H  [Ca2+]=0 mM (pH= 3) |
| M4 | 319 ± 18 | 0.66 | 244 ± 2 |
| M7 | 320 ± 10 | 0.64 | 264 ± 4 |
| M11 | 298 ± 8 | 0.62 | 230 ± 4 |
| M13 | 308 ± 3 | 0.43 | 204 ± 2 |
| M15 | 278 ± 4 | 0.53 | NA |

**Table S5. ζ-potential of P(VCL-*co*-IA) (M*n*) microgels samples in pure water and loaded with Ca2+ ions.**

|  |  |  |
| --- | --- | --- |
| **Ζ-potential (mV)** | | |
| **Sample ID** | **empty gels** | **loaded gels** |
| **M4** | -16.2 ± 0.5 | -11.9 ± 0.8 |
| **M7** | -18.8 ± 0.4 | -16.9 ± 0.3 |
| **M11** | -19.8 ± 0.6 | -18.4 ± 0.2 |
| **M13** | -24.3 ± 0.6 | -20.3 ± 1.0 |
| **M15** | -28.9 ± 0.9 | -26.6 ± 0.8 |



**Figure S1** 1H-NMR spectrum of PVCL (pale pink) no signal at 3.64 ppm, P(VCL-*co*-IADME) 5 mol% (pale pink), 10 mol% (pale violet), 15 mol% (violet), 20 mol% (purple) and 30 mol% (black).



**Figure S2** (a) full ATR-FTIR spectra of P(VCL-*co*-IADME) (b) ATR-FTIR spectra of P(VCL-*co*-IADME) zoomed on relevant ester groups of itaconate (1730 cm-1) and amide band of VCL (1630 cm-1) (c) full ATR-FTIR spectra of P(VCL-*co*-IA) (d) ATR-FTIR spectra of P(VCL-*co*-IA) zoomed on relevant ester groups of itaconate (1730 cm-1) and amide band of VCL (1630 cm-1) .

**550**



**N Microgel M Microgel**

**500**

**450**

**DH (nm)**

**400**

**350**

**300**

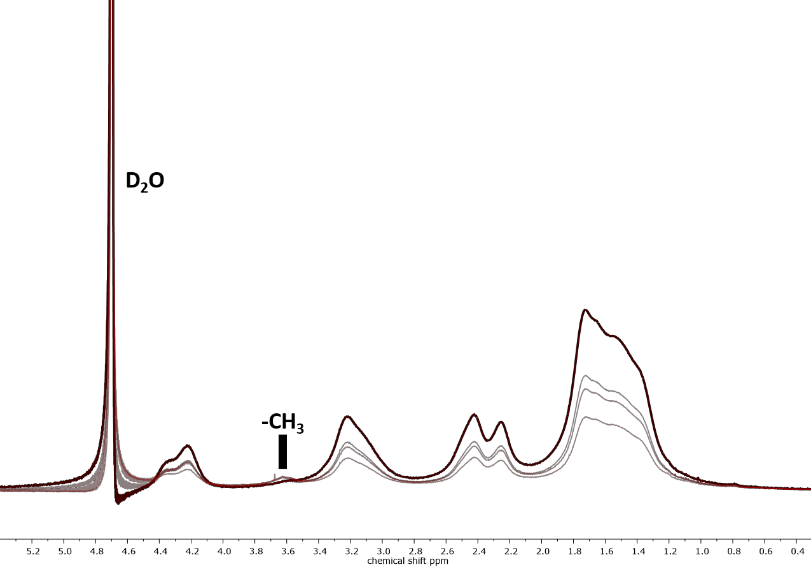
**250**

**200**

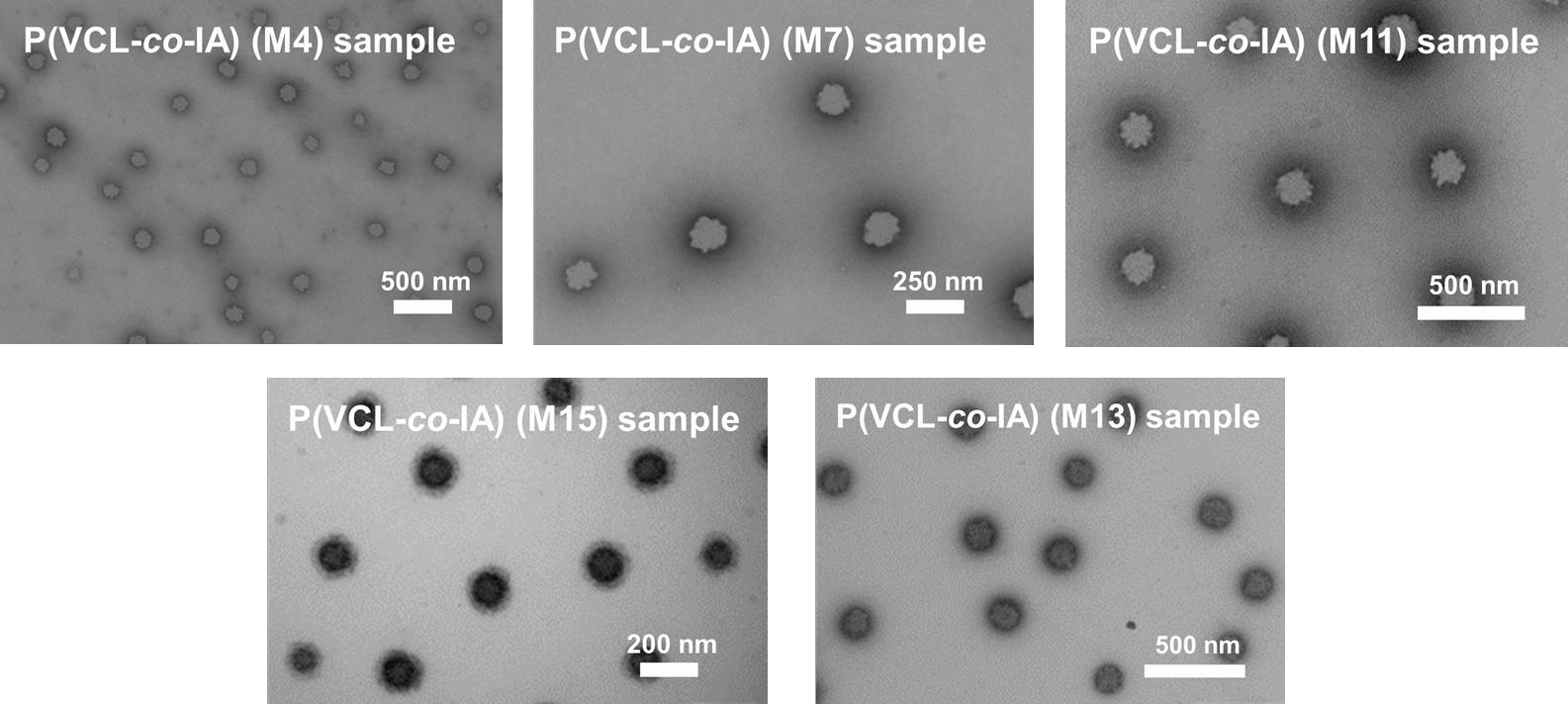
**0 5 10 15 20 25 30 35**

**mol% (a.u.)**

**Figure S3**. *D*H of P(VCL-*co*-IADME) (**N***n*) and P(VCL-*co*-IA) (**M***n*) microgels in water at T= 10 °C according to the IADME mol% (**N** microgels) and COOH moieties (**M** microgels) measured at pH=7.



**Figure S4**. 1H NMR of P(VCL-*co*-IA) in D2O, peak at 3.65 ppm corresponds to the remaining methoxy protons of dimethylitaconate.



**Figure S5**. TEM images recorded of P(VCL-*co*-IA) **M4**, **M7**, **M11**, **M13** and **M15** microgels by staining them with PTA.

**550**



**N sample 0 mM Ca2+ N sample 10 mM Ca2+ M sample 0 mM Ca2+ M sample 10 mM Ca2+**

**500**

**450**

**400**

**DH (nm)**

**350**

**300**

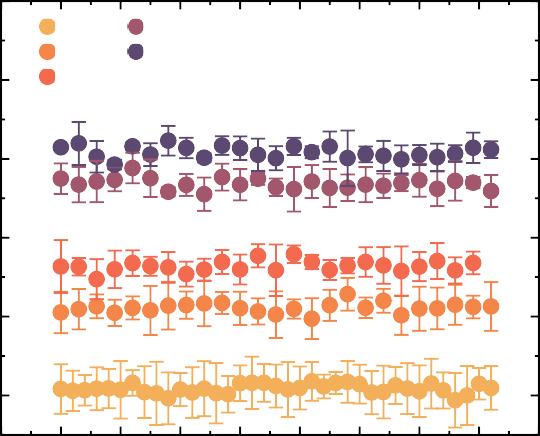
**250**

**200**

**0 5 10 15 20 25 30**

## COO- mol%

**Figure S6**. *D*H of P(VCL-*co*-IADME) (**N***n*) microgels (orange) and P(VCL-*co*-IA) (**M***n*) microgels (purple) recorded in pure water at pH=7 (hollow symbols) and in 10 mM Ca2+ solution, recorded at T= 10°C.

**340**

**M4 M13**

**M7 M15**

**320 M11**

**300**

**DH (nm)**

**280**

**260**

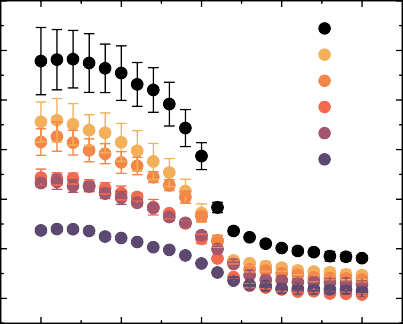
**240**

**-50 0 50 100 150 200 250 300 350 400**

## t (s)

**Figure S7**. *D*H of P(VCL-*co*-IA) (**M***n*) microgel samples against time, at a Ca2+ concentration of 10 mM and T= 32 °C.

##### (a)

**450**

**400**

**350**

**DH (nm)**

**300**

**250**

**200**

**150**

**N0 N5 N10 N15 N20 N30**

**(b)**

**550**

**500**

**450**

**DH (nm)**

**400**

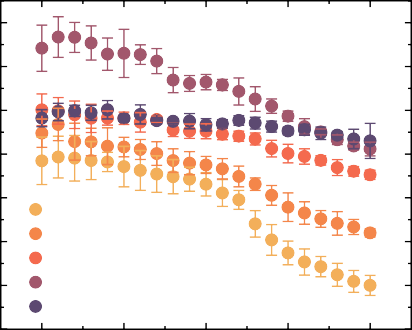
**350**

**300**

**250**

**200**

**M4 M7 M11 M13 M15**

**10 20**

**30 40 50**

##### T (°C)

**10 20 30 40 50**

##### T (°C)

**Figure S7**. *D*H of P(VCL-*co*-IADME) (**N***n* samples) against temperature measured in pure water and (b) *D*H of P(VCL-*co*-IA) (**M***n* samples) against temperature measured in pure water at pH=7.

**18**



**M11**

**M13 M15**

**M4 M7**

**16**

**14**

**[Ca2+] (ppm)**

**12**

**10**

**8**

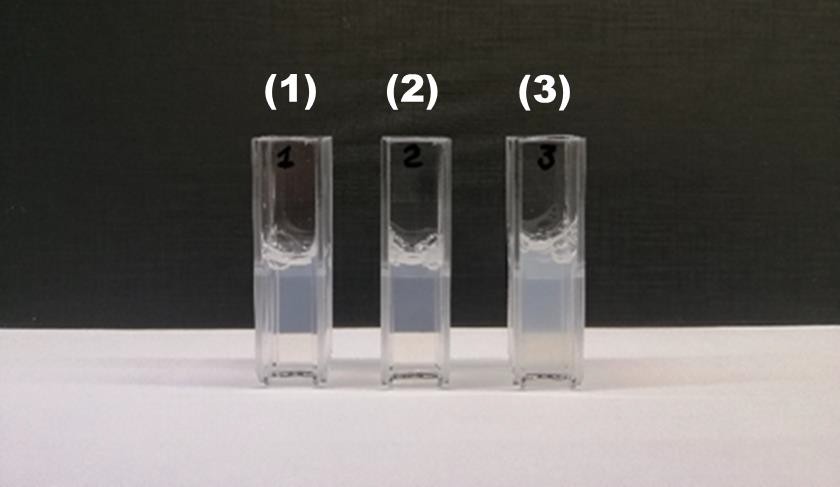
**6**

**4**

**-200 0 200 400 600 800 1000 1200 1400**

**t (s)**

**Figure S9**. Amount of Ca2+ retained overtime at pH 7 and T= 20 °C of P(VCL-*co*-IA) (**M***n*) microgels.

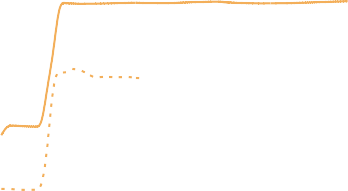


**Figure S10**. Turbidity of 0.1 wt% P(VCL-*co*-IA) (**M15**) microgel samples in (1) water, (2) after the addition of 1 mM Ca2+ to the solution and (3) after the addition of acid to equilibrate to pH 3.

**(a)**

**(b)**

**0.2**



**M4 10 mM Ca2+  M4 pH 3**

**0.15**



**M4 10 mM**

**M4 1 mM**

**M4 0.1 mM**

**Abs**

**Abs**

**0.10**

**0 10 20 30 40 50 60**

**t (s)**

**0.1**

**0 10 20 30 40 50 60**

##### t (s)

**(c)**

**0.25**

**(d)**

**0.3**



**M7 10 mM Ca2+  M7 pH 3**

**0.20**



**M7 10 mM**

**M7 1 mM**

**M7 0.1 mM**

**0.2**

**Abs**

**Abs**

**0.15**

**0.10**

**0 10 20 30 40 50 60**

##### t (s)

**0.1**

**0 10 20 30 40 50 60**

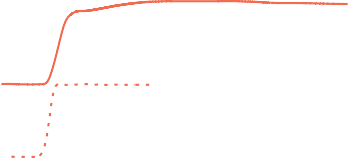
**t (s)**

##### (e)

**0.25**

**(f)**

**0.4**



**M11 10 mM Ca2+  M11 pH 3**

**0.20**

**Abs**

**0.3**

**0.15 0.2**

**Abs**

**0.10**

**0 10 20 30 40 50 60**

**M11 10 mM**

**M11 1 mM**

**M11 0.1 mM**

##### t (s)

**0.1**

**0 10 20 30 40 50 60**

##### t (s)

**(g)**

**0.45**

**M13 10 mM M13 1 mM**

**M13 0.1 mM**

**0**

**10**

**20**

**30**

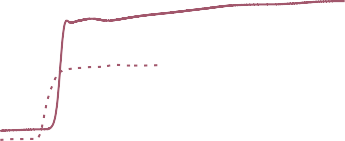
**40**

**50**

**60**

**(h)**

**0.4**



**M13 10 mM Ca2+  M13 pH 3**

**0.40**

**0.35**

**Abs**

**0.25**

**0.3**

**0.20**

**Abs**

**0.2**

**0.15**

**0.10**

##### t (s)

**0.1**

**0 10 20 30 40 50 60**

##### t (s)

**(i)**

**0.45**



**(j)**

**1.0**

**0.40**

**0.9**

**0.35 0.4**

**Abs**

**Abs**

**0.25**

**0.20**

**0.3**

**0.15**

**0.10**

**M15 10 mM M15 1 mM**

**0 10 20 30 40 50 60**

**t (s)**

**0.2**

**0.1**

**M15 10 mM Ca2+  M15 pH 3**

**0 10 20 30 40 50 60**

**t (s)**

**Figure S11.** Absorbance spectra measured in function of time of a 0.1 wt% microgel solution, measured with a scanning rate of 1 measurement per second; (a),(c),(e),(g),(i): measurements were made at T= 20°C and pH= 7, (b),(d),(f) and (j): measurements were performed in the same cuvette at T= 20 °C, with a starting pH= 7.