Electronic Supplementary Material (ESI) for Soft Matter.

Metal Cation Responsive Anionic Microgels: Behaviour Towards Biologically Relevant Divalent and Trivalent Ions

Vittoria Chimisso, Simona Conti, Phally Kong, Csaba Fodor and Wolfgang P. Meier*

University of Basel, Department of Chemistry, Mattenstrasse 24/a, 4002 Basel

Nuclear Magnetic resonance (NMR)

^{1}H NMR were recorded in deuterated solvents ($CDCl_3$ or D_2O) on a Bruker 400 MHz spectrometer at room temperature, utilizing 256 scans with a 0.1 wt% microgel concentration. The chemical shifts (δ) are reported in ppm and are calibrated to the residual peaks of the main solvent. The collected spectra were analysed using MestReNova (v 9.1) (Mestrelab Research S.L.).

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	-	-	0.053	0.19	0.060	0.38	0.010	0.027
N1	95:5	1.983	14.24	0.118	0.75	0.053	0.19	0.060	0.38	0.010	0.027
N2	90:10	7.879	13.50	0.237	1.50	0.053	0.19	0.060	0.38	0.010	0.027
N3	80:20	1.670	12.00	0.474	3.0	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	IADME mol%			Sample	TITRATION COOH mol%
	Theoretical value	NMR value	ATR-FTIR value		
N1	5	5	5.775	**M1**	5.8
N2	10	10	9.395	**M2**	10
N3	20	20	22.950	**M3**	19

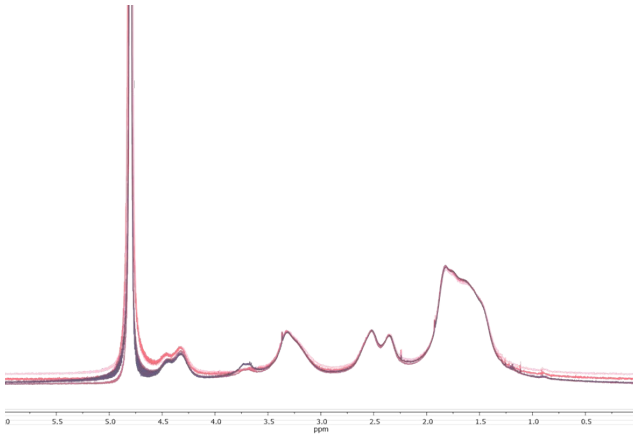

Figure S1. ^{1}H NMR spectrum of **M***n* microgels recorded in $CDCl_3$. **M**1 *(light pink),* **M**2 (pink) and **M**3 (purple).

Table S3. R_g/R_H ratio of M1, M2 and M3 taken at 20°C, at pH 7, 1 mM Mg^{2+} and pH=2.

Microgel	pH 7	1 mM [M^{2+}]	pH 3
M1	0.44	0.59	0.56
M2	0.49	0.64	0.64
M3	0.45	0.66	0.65

Table S4. D_H of homopolymeric VCL microgel N0 in pure water and in the presence of 1mM $M^{2+/3+}$ ions at 10 °C and neutral pH.

Sample	H_2O	Mg^{2+}	Sr^{+2}	$Cu^{(II)}$	$Fe^{(III)}$
N0	375 ± 19	355 ± 20	355 ± 22	360 ± 27	340 ± 35

Table S5. Amount of Mg^{2+} ion bonded at ambient condition in PBS

Microgel	% Mg^{2+}	% Fe^{3+}
M1	0	100
M3	0	100

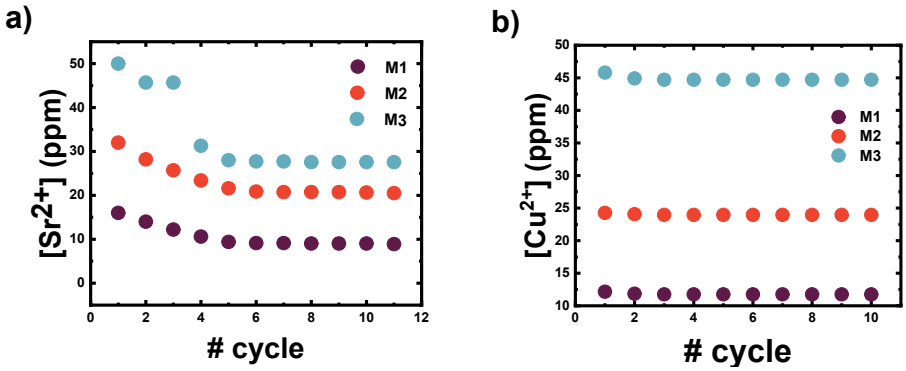

Figure S2. Amount in ppm of (a) $Sr^{2+}$and (b) Cu^{2+} retained by a 0.1 wt% microgel solution at room temperature and neutral pH. Microgels used ae M1 (5.8 mol% COOH), M2 (10 mol% COOH) and M3 (18 mol% COOH).