Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Potassium-sensitive poly(*N*-isopropylacrylamide)-based hydrogels for sensor applications

Dominic Büning[#], Franka Ennen[#], Sarah Verena Walter[#], Tobias Hennecke, Mathias Ulbricht*

Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, Universitätsstr. 7, 45141 Essen, Germany

Table SI 1. Overview of parameters of synthesized hydrogels

assigned as		Comonomer		$B_{15}C_5Am$ content	TMC[a]	yield
			[mol%]	[mol%]	[M]	[%]
	M9.9M'0.1DC05	AAm	1.5	-	0.92	97.2
		SPE	0.4	-	0.91	99.0
		SPP	0.4	-	0.91	97.1
	M9.85M'0.15DC05	AAm	2.3	-	0.92	98.1
		SPE	0.6	-	0.91	99.3
		SPP	0.6	-	0.91	98.7
	M9.8M'0.2DC05	AAm	3.0	-	0.93	98.8
		SPE	0.8	-	0.91	98.7
		SPP	0.8	-	0.91	99.3
	M9.75M'0.25DC05	AAm	3.8	-	0.93	97.9
		SPE	1.0	-	0.90	98.6
		SPP	0.9	-	0.90	99.3
	M9.7M'0.3DC05	AAm	4.5	-	0.93	98.2
		SPE	1.2	-	0.90	98.4
		SPP	1.1	-	0.90	99.1
	M9.65M'0.35DC05	AAm	5.3	-	0.93	99.1
	M9.6M'0.4DC05	AAm	6.0	-	0.94	99.1
HG1	M9.6M'0.4DC05CE10	AAm	5.8	3.1	0.97	94.3
	M9.55M'0.45DC05	AAm	6.0	-	0.93	98.9
	M9.5M'0.5DC05	AAm	7.5	-	0.94	96.7
		SPP	1.5	-	0.89	98.9
	M9.45M'0.55DC05	AAm	8.2	-	0.94	98.6
HG2	M9.45M'0.55DC05CE10	AAm	7.9	3.0	0.97	97.2
	M9.4M'0.6DC05	AAm	8.9	-	0.95	99.0
		SPP	2.3	-	0.88	94.9
HG3	M9.4M'0.6DC05CE10	AAm	8.6	3.0	0.98	97.5
HG4		SPP	2.2	3.2	0.91	97.2
	M9.35M'0.65DC05	AAm	9.6	-	0.95	98.8
		SPE	2.6	-	0.88	94.9
HG5	M9.35M'0.65DC05CE10	AAm	9.3	3.0	0.98	98.2
HG6		SPE	2.6	3.3	0.91	95.0
	M9.25M'0.75DC05	SPE	3.1	-	0.88	97.1
		SPP	2.9	-	0.88	99.7
HG7	M9.25M'0.75DC05CE10	SPE	3.0	3.3	0.91	93.7
HG8		SPP	2.8	3.3	0.91	97.9
	M9.2M'0.8DC05	AAm	11.7	-	0.96	98.2
HG9	M9.2M'0.8DC05CE10	AAm	11.4	3.0	0.99	96.2
	M9M'1DC05	AAm	14.5	-	0.97	98.6
		SPE	4.1	-	0.86	98.7
		SPP	4.0	-	0.86	99.2
HG10	M9M'1DC05CE10	AAm	14.1	3.0	1.00	96.8
HG11		SPE	4.0	3.3	0.89	98.4
HG12		SPP	3.8	3.3	0.89	97.8
HG13	M10DC05	-	-	-	0.92	97.1
HG14	M10DC05CE10	-	-	3.1	0.95	95.9
HG15	M9M'1DC05CE10[b]	AAm	14.2	3.0	0.74	99,5
HG16	M7M'0.75DC05CE15[b]	AAm	13,8	5.8	0.77	98,4
HG17	M7M'0.7DC05CE25	AAm	13.3	9.6	0.80	88,6
HG18	M9M'1.2DC05CE10[b]	AAm	16.7	2.9	1.03	99,6
HG19	M9M'1DC05CE15[b]	AAm	16.9	4.4	1.01	98,7
HG20	M11.3M'1.25DC05CE12.5	AAm	14.3	3.2	1.25	99.4
HG21	M11.3M'1.3DC05CE25	AAm	14.2	6.3	1.29	99.4
HG22	M9M'1DC05[b]	AAm	14.5	-	1.03	100,0
HG23	M9.1M'0.9DC05CE10	SPP	3.6	3.3	0.90	98.5
HG24	M10DC05CE10	-	-	3.1	0.95	98.7

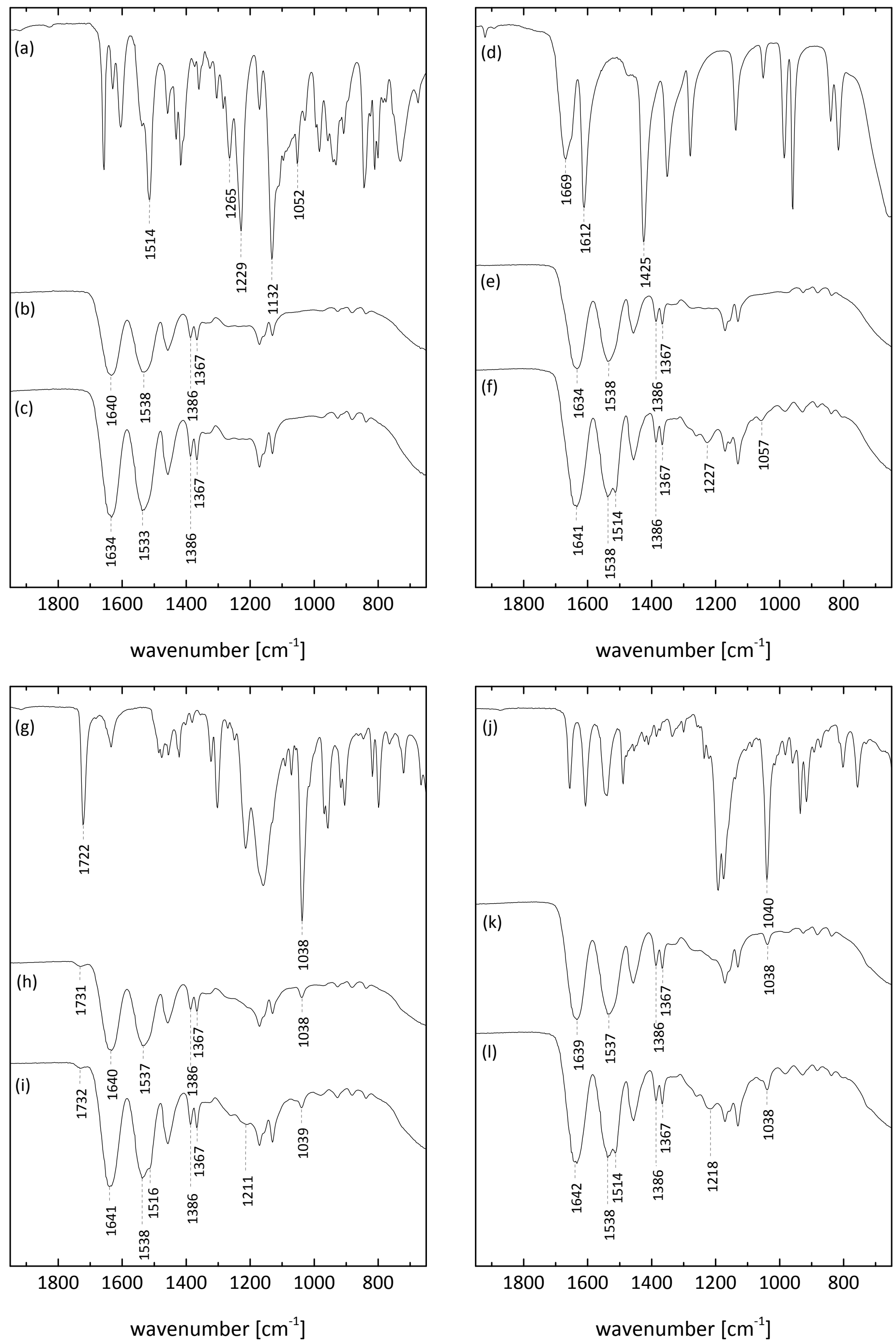


Figure SI-1. ATR-IR spectra of a) $B_{15}C_5Am$; b) PNIPAAm hydrogel with 0 mol% BCAm; c) PNIPAAm hydrogel with 3.1 mol% BCAm; d) AAm; e) PNIPAAm hydrogel with 11.8 mol% AAm; f) PNIPAAm hydrogel 11.4 mol% AAm and 3.0 mol% BCAm; g) SPE; h) PNIPAAm hydrogel with 2.6 mol% SPE; i) PNIPAAm hydrogel with 2.6 mol% SPE and 3.3 mol% BCAm; j) SPP; k) PNIPAAm hydrogel with 2.3 mol% SPE; l) PNIPAAm hydrogel with 2.2 mol% SPE and 3.2 mol% BCAm.

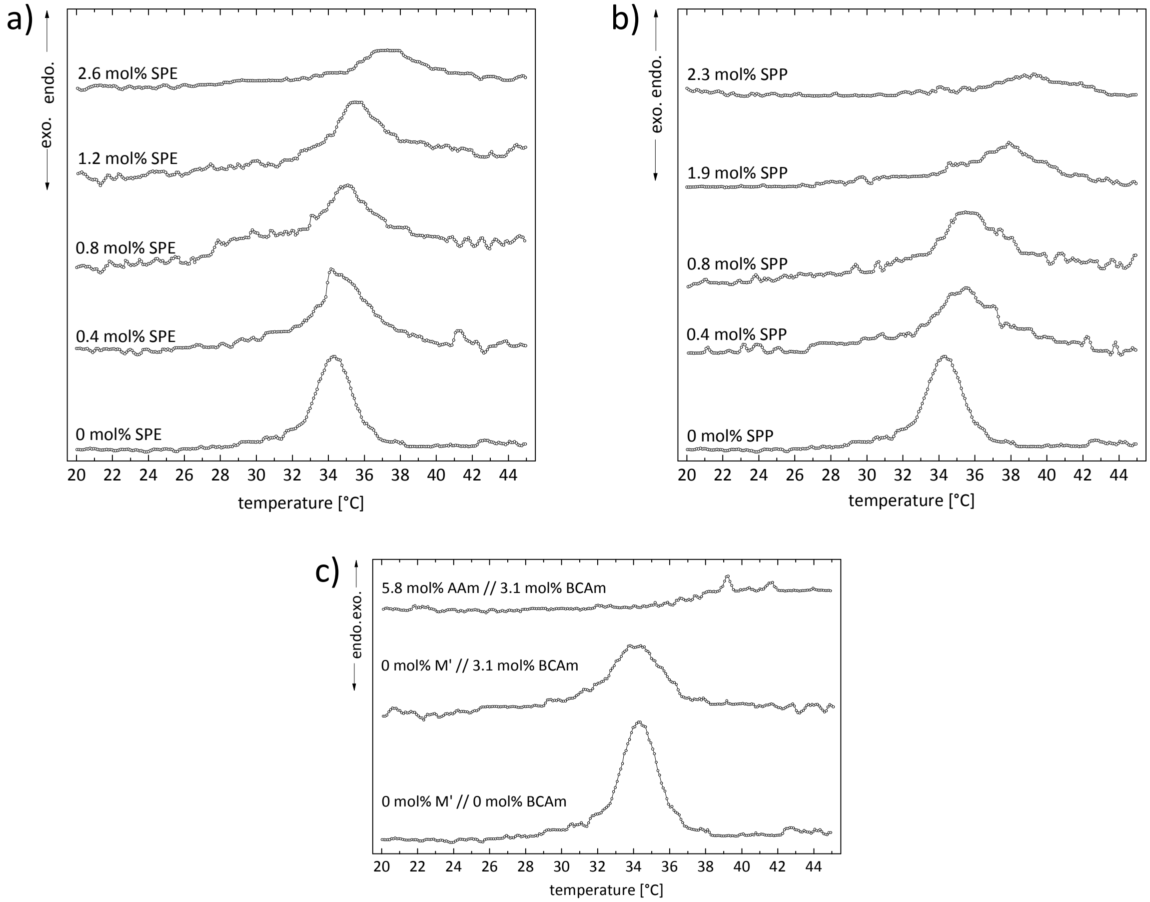


Figure SI-2. DSC thermograms of PNIPAAm hydrogels containing different amounts of a) SPE, b) SPP and c) BCAm and AAm.

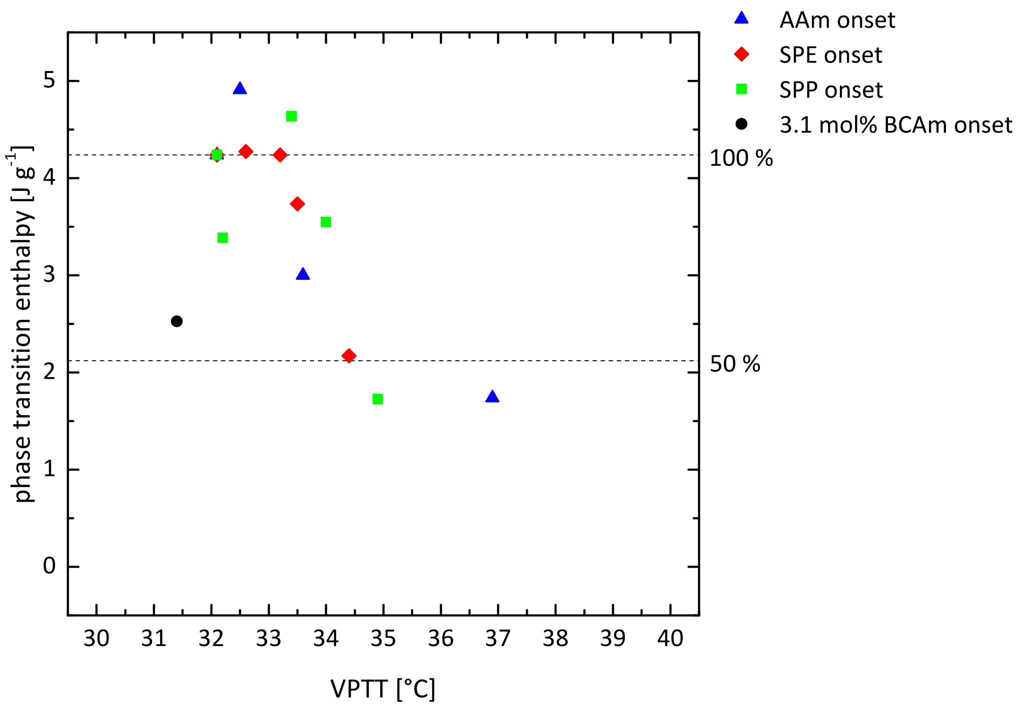


Figure SI-3. Dependence of phase transition enthalpy from VPTT for different hydrophilic comonomers as a measure for hydrogel performance. With respect to experimental errors AAm, SPP and SPE show similar VPT shift efficiency.

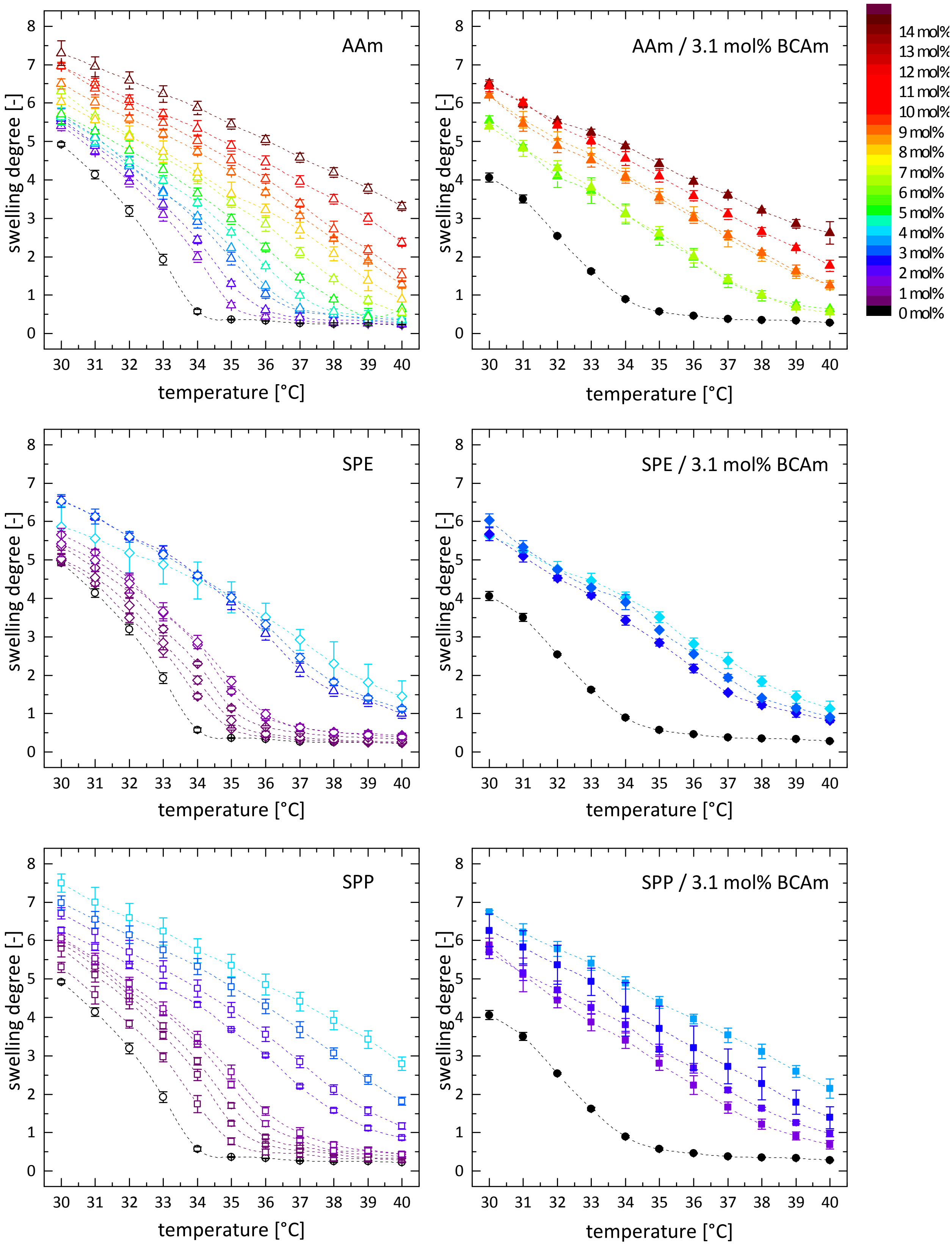


Figure SI-4. SD-T curves of various differently composed HGs.

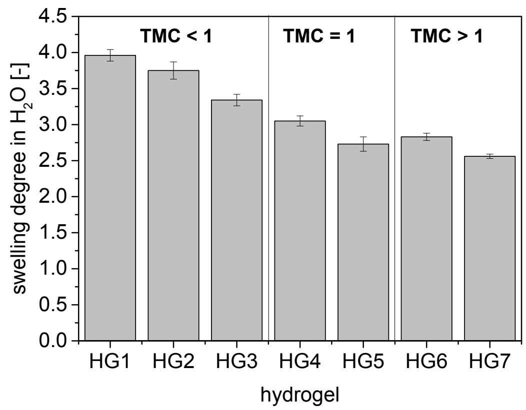
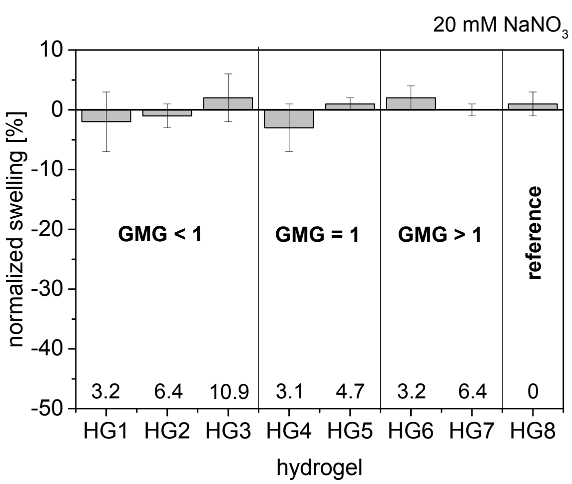


Figure SI-5. Swelling degrees of BCAm containing HGs in water.



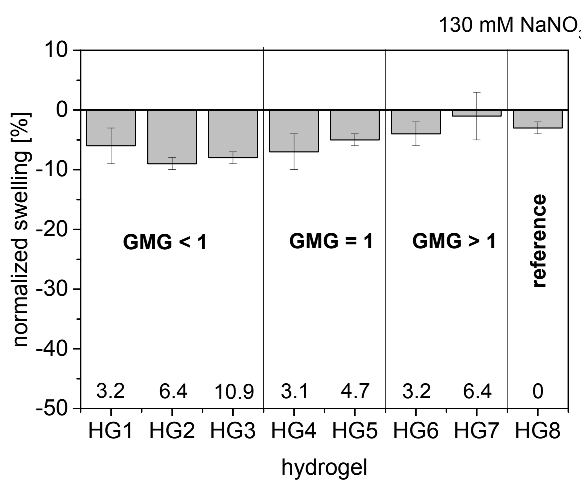


Figure SI-6. Normalized swelling of HGs containing different BCAm contents after equilibration in different sodium nitrate concentrations at 39° C; numbers below the columns indicate the amount of BCAm in the HG in mol%.

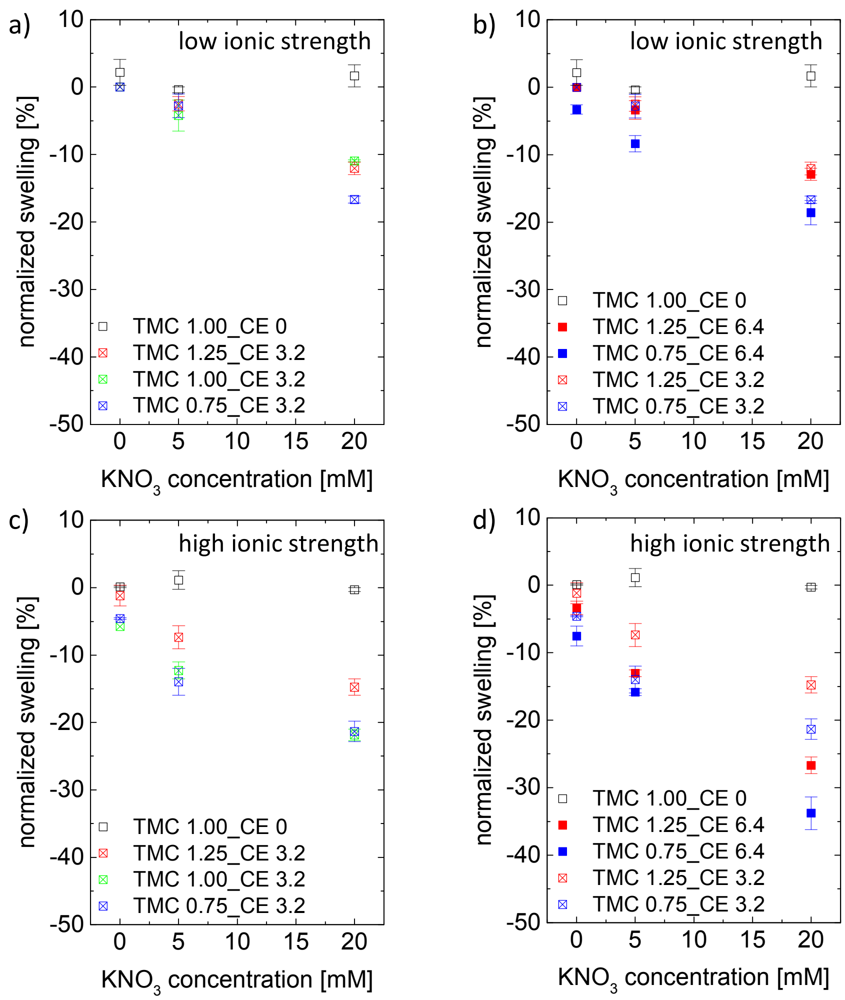


Figure SI-7. Normalized swelling plotted against potassium concentration, different samples with different TMC [M] and crown ether content (CE), given in mol%, are compared. A and b measured without sodium nitrate background; c and d are measured at a background of sodium nitrate, total ionic strength I = 130 mM. AAm containing hydrogels were imprinted with BCAm to KNO_3 ratio of 1:1.1 (except TMC 1.00_CE 3.2, this hydrogel was only imprinted with ratio of 1.5:1).

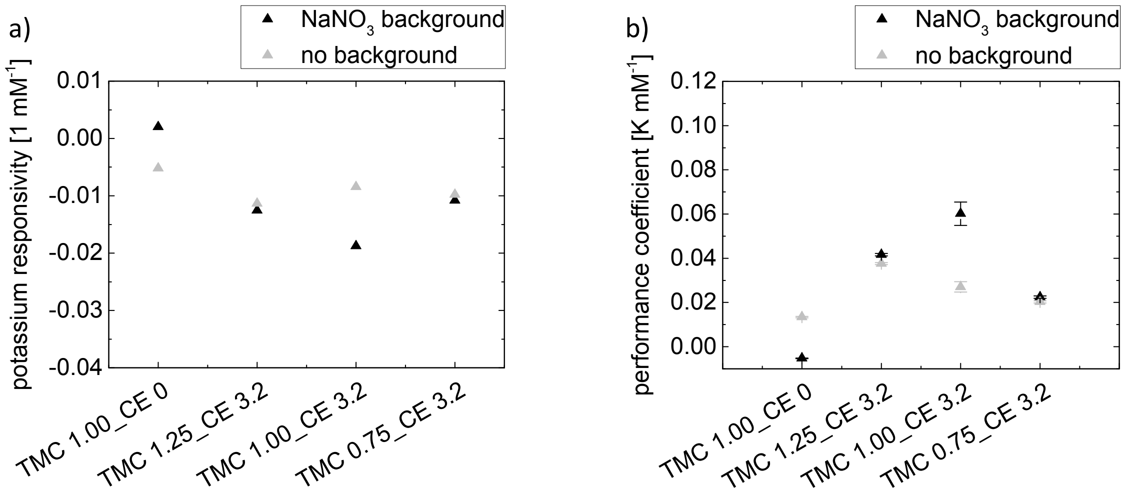


Figure SI-8. Left: Potassium responsivity K_{K^+} of different HGs, influence of TMC and crown ether content on potassium responsivity. Right: Performance coefficient K_{HG} calculated from tangent slope of swelling degree vs. potassium concentration (0 mM – 5 mM) K_{K^+} and tangent slope from VPT curves K_T. Both diagrams include measurements without sodium nitrate background and measurements with overall ionic strength I = 130 mM due to adjustment of sodium nitrate concentration. Hydrogels were imprinted with BCAm to KNO_3 ratio of 1.5:1.

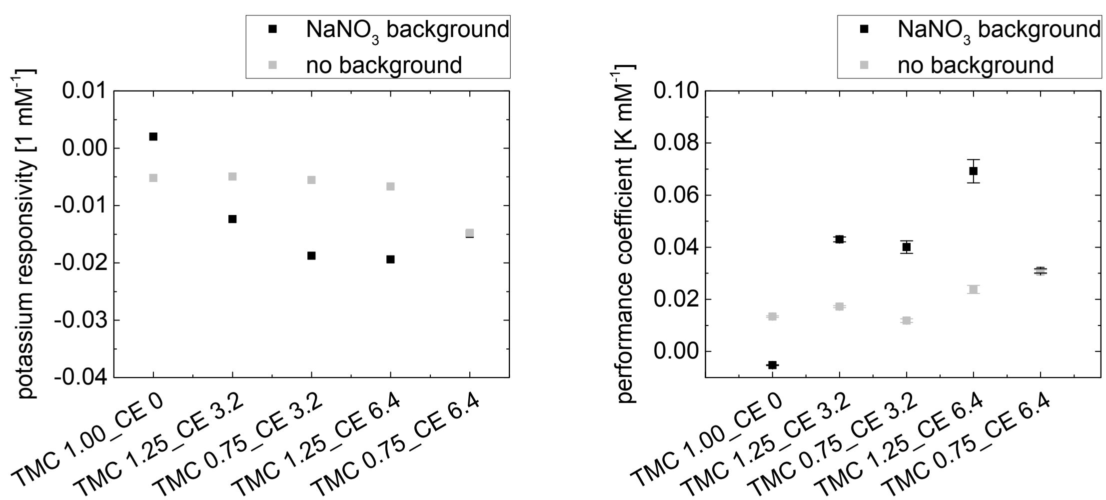


Figure SI-9. Left: Potassium responsivity K_{K^+} of different HGs, influence of TMC and crown ether content on potassium responsivity. Right: Performance coefficient K_{HG}. Both diagrams include measurements without sodium nitrate background and measurements with overall ionic strength I = 130 mM due to adjustment of sodium nitrate concentration. Hydrogels were imprinted with BCAm to KNO_3 ratio of 1:1.1.

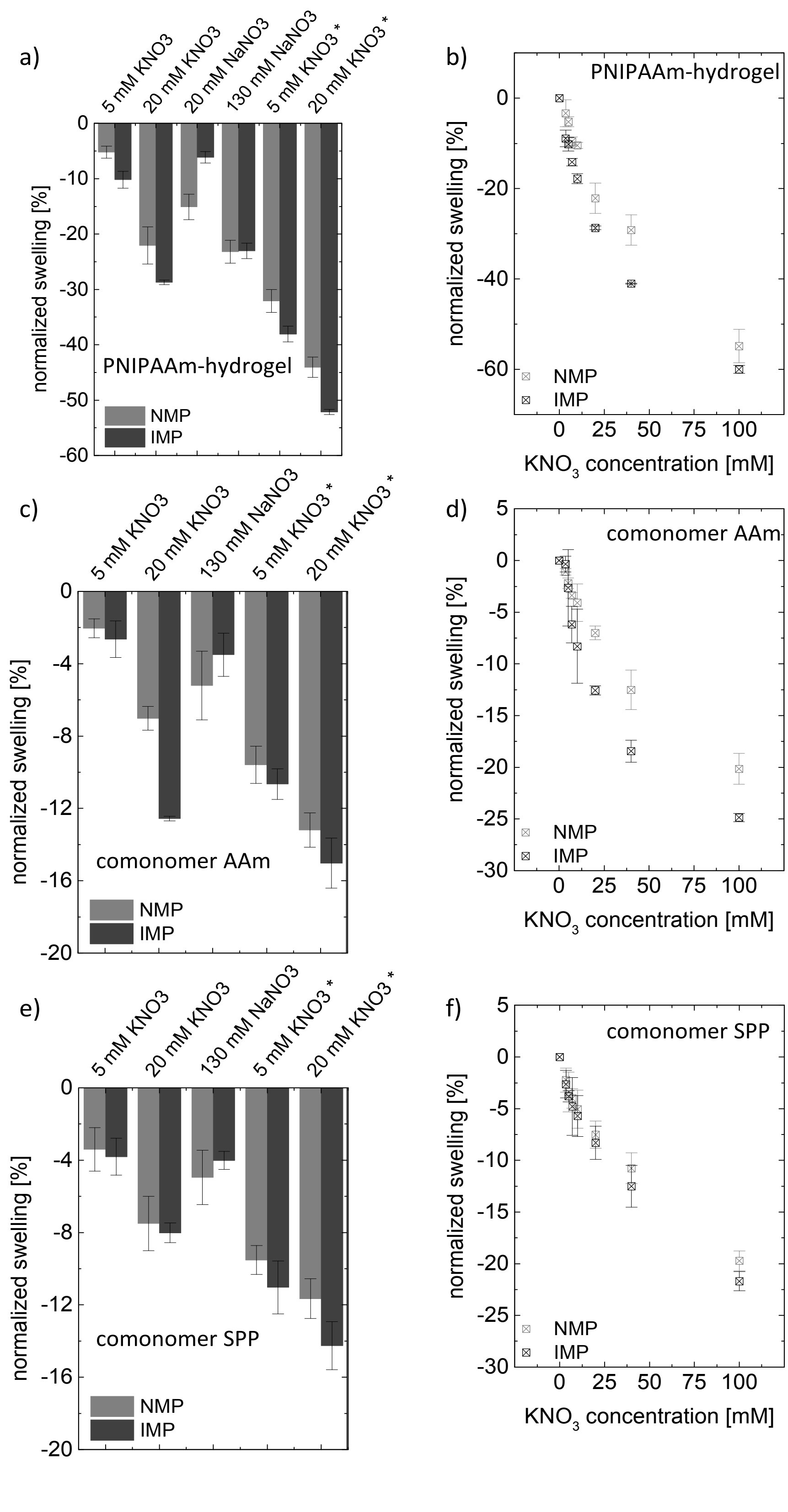

a)
5 mM KNO3
20 mM KNO3
20 mM NaNO3
130 mM NaNO3
5 mM KNO3*
20 mM KNO3*
normalized swelling [%]
PNIPAAm-hydrogel
NMP
IMP
b)
PNIPAAm-hydrogel
normalized swelling [%]
NMP
IMP
KNO$_3$ concentration [mM]
c)
5 mM KNO3
20 mM KNO3
130 mM NaNO3
5 mM KNO3*
20 mM KNO3*
normalized swelling [%]
comonomer AAm
NMP
IMP
d)
comonomer AAm
normalized swelling [%]
NMP
IMP
KNO$_3$ concentration [mM]
e)
5 mM KNO3
20 mM KNO3
130 mM NaNO3
5 mM KNO3*
20 mM KNO3*
normalized swelling [%]
comonomer SPP
NMP
IMP
f)
comonomer SPP
normalized swelling [%]
NMP
IMP
KNO$_3$ concentration [mM]

Figure SI-10. Normalized deswelling plotted against potassium and/or sodium nitrate concentration, thereby imprinted hydrogels (IMP) are compared with non-imprinted hydrogels (NMP); imprinting ratio of 1.5:1 BCAm to K^+.

Figure SI-10 a) and **b)** show the results of a *poly*-NIPAAm-*co*-BCAm (TMC 0.95_CE 3.1) hydrogel analyzed at 32°C.

Figure SI-10 c) to **f)** show the effect of imprinting of comonomer containing hydrogels; all hydrogels were analyzed at a temperature of 37°C; **Figure SI-11 c)** and **e)** present data for a hydrogel containing 11.4 mol% AAm (TMC 0.99_CE 3.0); **Figure SI-11 d)** and **f)** present data for a hydrogel containing 3.6 mol% SPP (TMC 0.90_CE 3.3)).

In **Figure SI-10 a)**, **c)** and **e)**, different salt compositions and concentrations are compared, * highlights hydrogels analyzed in a salt solution containing both KNO_3 and $NaNO_3$ with a total ionic strength of 130 mM. In **Figure SI-10 b)**, **d)** and **f)** the effect of KNO_3 concentration on normalized swelling is demonstrated.