

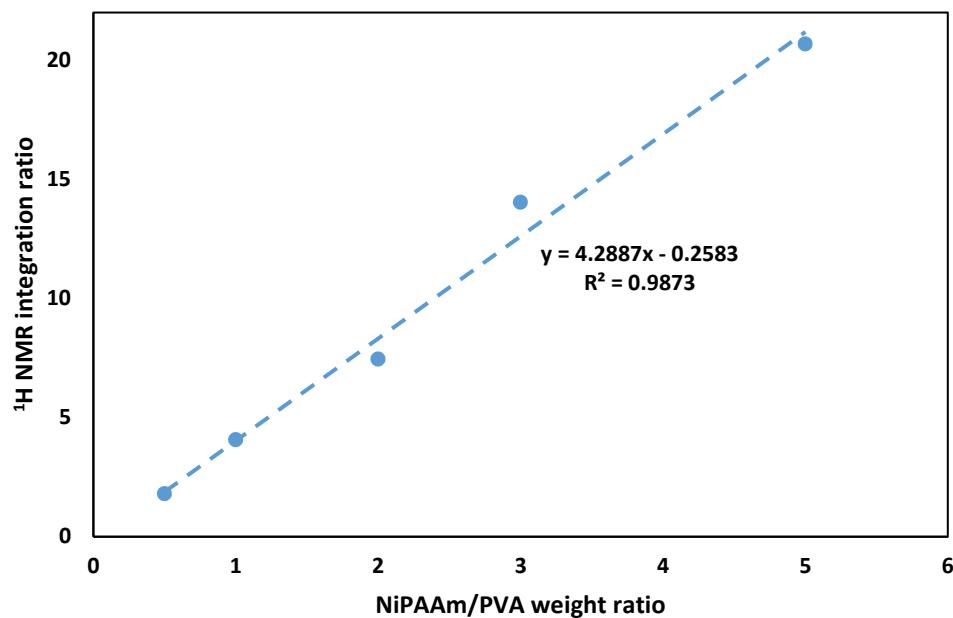
## Supporting Information

### Novel Poly(Vinyl Alcohol)-Based Amphiphilic Nanogels by Non-Covalent Boric Acid Crosslinking of Polymeric Micelles

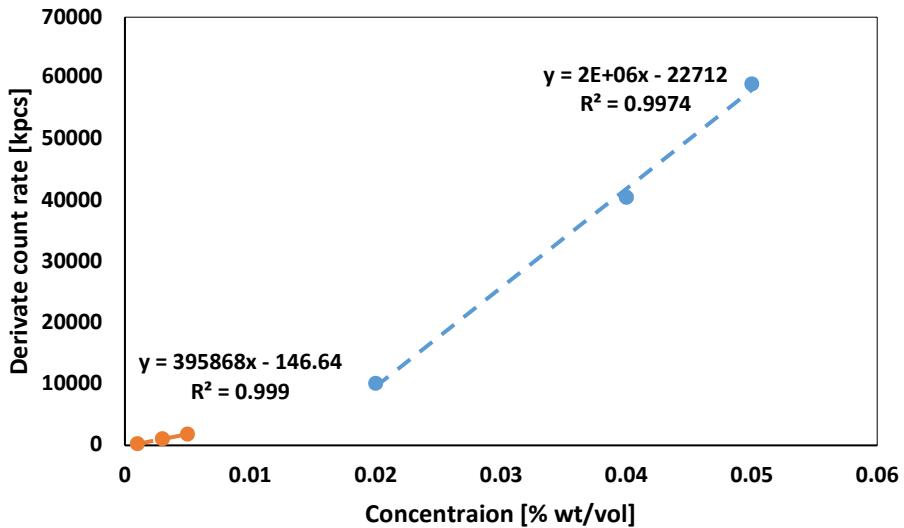
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**Table S1.** Reaction feed ratios of the different PVA-g-pNiPAAm copolymers.

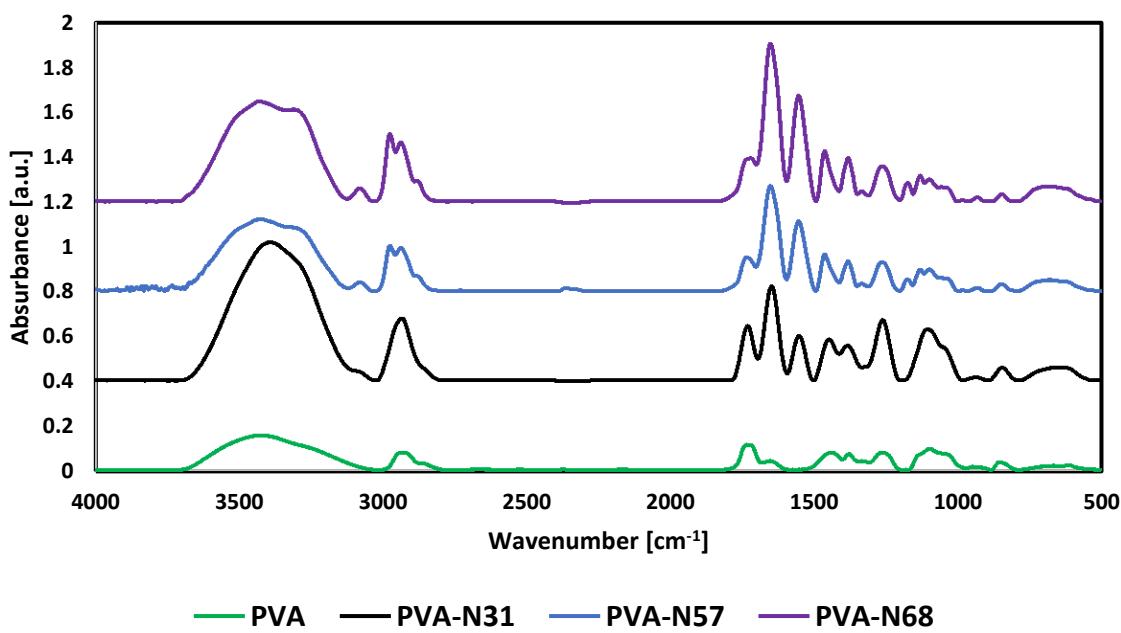
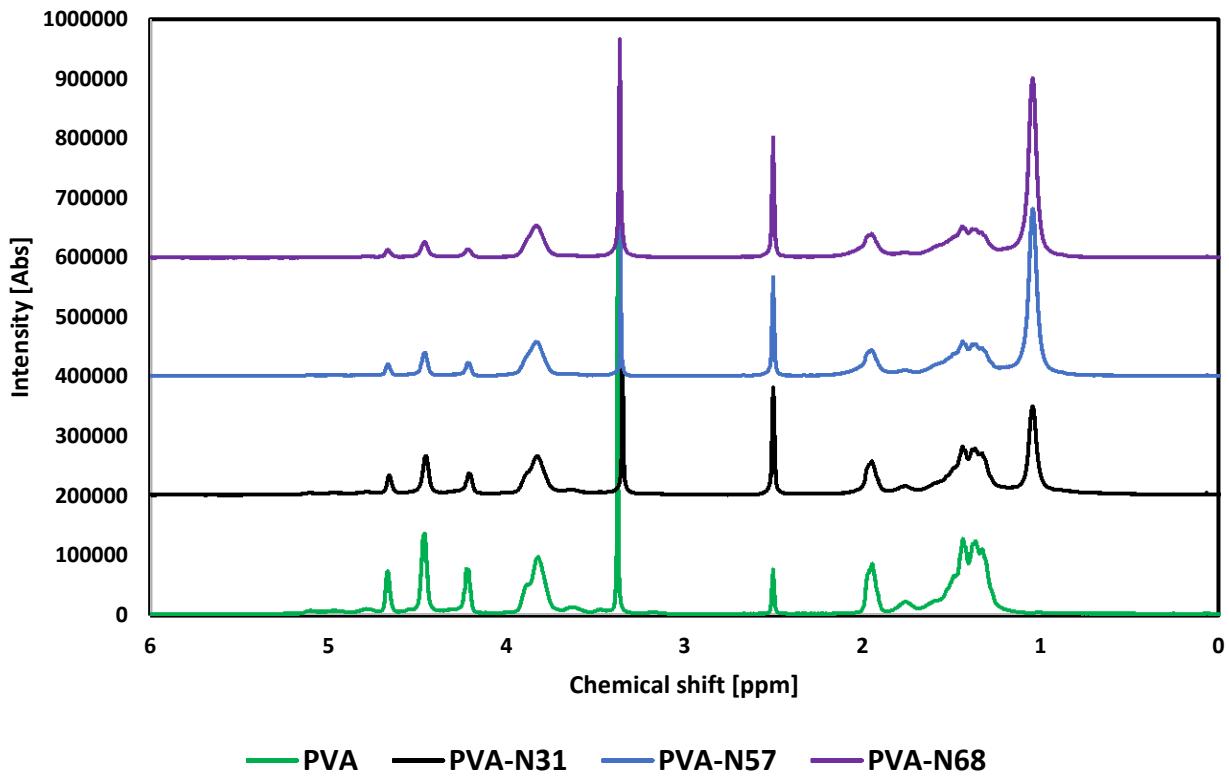
Copolymer	Reaction feed amounts (g)		Theoretical NiPAAm/PVA weight ratio
	PVA	NiPAAm	
PVA-N31	0.4	0.4	1
PVA-N57	0.4	0.8	2
PVA-N68	0.4	1.2	3

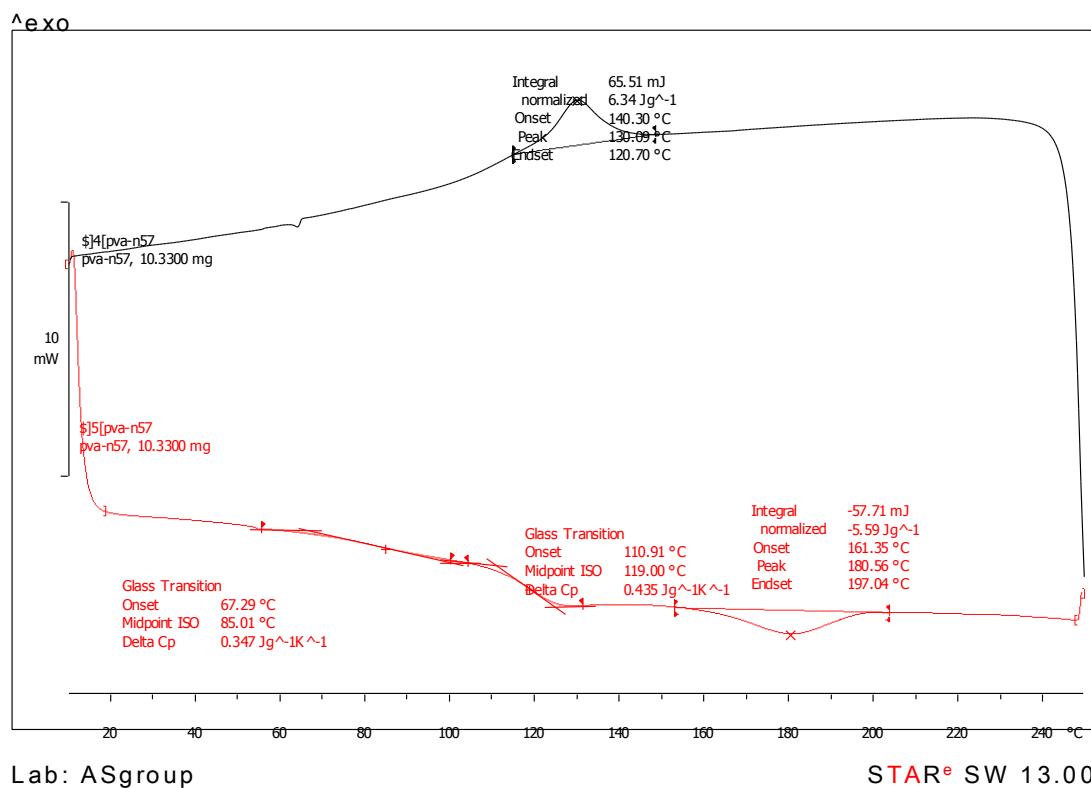
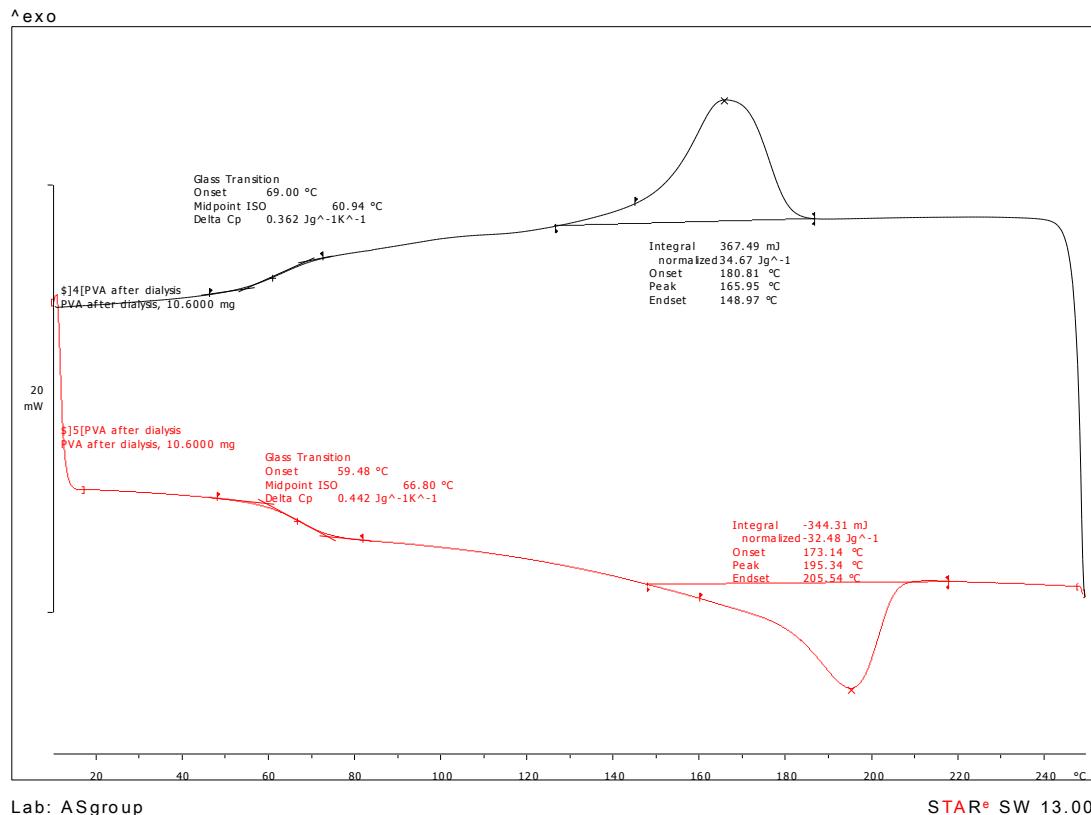


**Figure S1.** Calibration curve of NiPAAm/PVA physical mixtures, as determined by  $^1\text{H}$  NMR. Integration ratios obtained for the different copolymers were interpolated in the curve to determine the content of PNiPAAm in the corresponding copolymer.



**Figure S2.** Representative plot used for the determination of the critical micellar concentration (CMC) of the copolymer PVA-N57. The concentration versus the intensity of the scattered light at 37°C, as measured by DLS, is plotted. The CMC is established at the intersection between the two straight lines. Plots of 2-3 independent experiments were obtained for each copolymer and the CMC value expressed as the average. The S.D. was usually in the 15-20% range.





**Figure S5.** Thermograms of pure PVA and PVA-N57, as measured by DSC. The cooling ramp is represented in black and the second heating ramp in red.

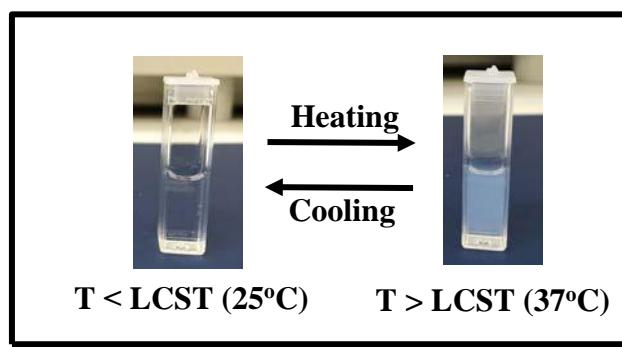
**Table S2.** Thermal analysis of PVA-*g*-PNiPAAm copolymers, as measured by DSC.

Copolymer	$T_g$ [°C] <sup>a</sup>		$T_c$ [°C] <sup>b</sup>	$T_m$ [°C] <sup>a</sup>	$\Delta H_m$ [J/g] <sup>a,c</sup>
	$T_{g1}$	$T_{g2}$			
PVA	67	-	166	195	32
PVA-N31	83	107	118	164	15
PVA-N57	-	119	130	181	13
PVA-N68	-	126	119	169	6

<sup>a</sup> Determined in the second heating ramp.

<sup>b</sup> Determined in the cooling ramp.

<sup>c</sup> Values of <sup>1</sup>H were normalized to the content of PVA in the copolymers, as determined by <sup>1</sup>H NMR.

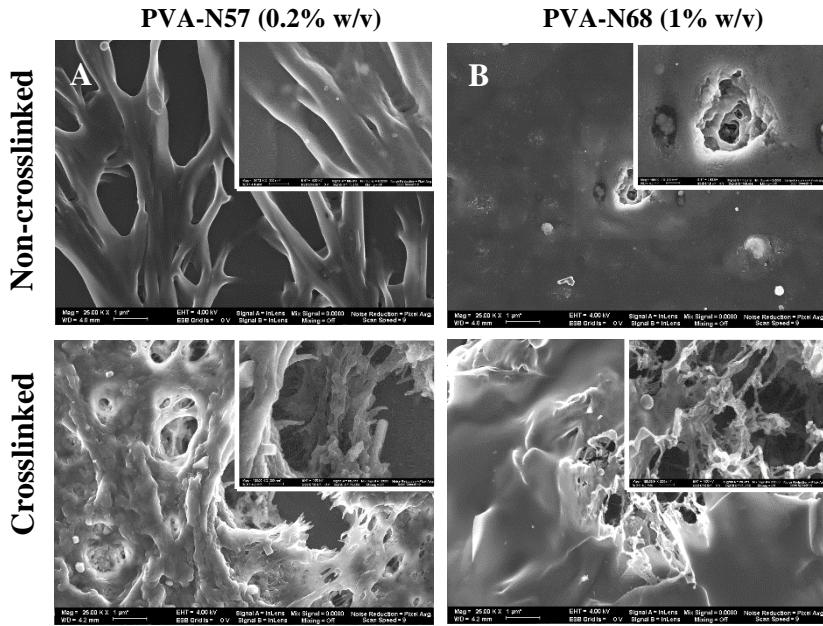


**Figure S6.** Opalescence upon heating of the copolymers to 37°C due to the hydrophilic-to-hydrophobic transition of PNiPAAm blocks.

**Table S3.** Physical stability of non-crosslinked and non-covalently crosslinked PVA-N57 and PVA-N68 polymeric micelles as estimated from size ( $D_h$ ) and size distribution (PDI) of data obtained by DLS. Crosslinking was performed by the addition of 6  $\alpha$ L of 1% w/v boric acid solution per mL of micellar suspension.

Copolymer	Copolymer concentration (% w/v)	T (°C)	Incubation time (Days)	Crosslinking	$D_h$ (nm) ( $\pm$ S.D.)		Intensity distribution (%)	PDI ( $\pm$ S.D.)
					Intensity distribution	Number distribution		
PVA-N57	0.02	37	1	No	111 (4)	72 (3)	100	0.089 (0.023)
			1	Yes	194 (10)	62 (29)	100	0.191 (0.005)
		25	1	No	600 (317)		56	
					93 (58)	6 (2)	25	0.651 (0.124)
					12 (5)		15	
	0.01	37	1	Yes	193 (16)	107 (8)	100	0.301 (0.018)
			14	Yes	167 (8)	85 (25)	100	0.280 (0.037)
		25	1	No	96 (1)	63 (3)	100	0.081 (0.015)
			1	Yes	184 (15)	78 (29)	100	0.231(0.014)
			1	No	211 (122)		59	
PVA-N68	0.01	37			18 (26)	5 (2)	24	0.690 (0.223)
					35 (21)		15	
		25	1	Yes	176 (6)	106 (7)	100	0.274 (0.022)
			14	Yes	162 (9)	86 (7)	100	0.301 (0.054)
			1	No	179 (4)	117 (10)	100	0.126 (0.029)
	0.005	37	1	Yes	210 (4)	126 (4)	100	0.156 (0.021)
			1	No	445 (291)		70	
		25			10 (3)	6 (1)	26	0.908 (0.115)
					28 (30)		4	
			1	Yes	175 (7)	88 (7)	100	0.316 (0.015)
		14	Yes		176 (29)	85 (14)	100	0.381 (0.070)
		37	1	No	156 (15)	102 (3)	100	0.161 (0.055)
			1	Yes	178 (12)	121 (7)	100	0.179 (0.024)

25	1	No	305 (131)		87	
			27 (22)	14 (12)	10	0.875 (0.096)
			9 (1)		3	
	1	Yes	162 (5)	101 (5)	100	0.223 (0.025)
	14	Yes	156 (4)	85 (7)	100	0.214 (0.007)



**Figure S7.** HR-SEM micrographs of non-crosslinked and crosslinked polymeric micelles casted onto carbon tape directly upon formation.