Electronic Supplementary Information

Tetra-sensitive Graft Copolymer Gels with High Volume Changes

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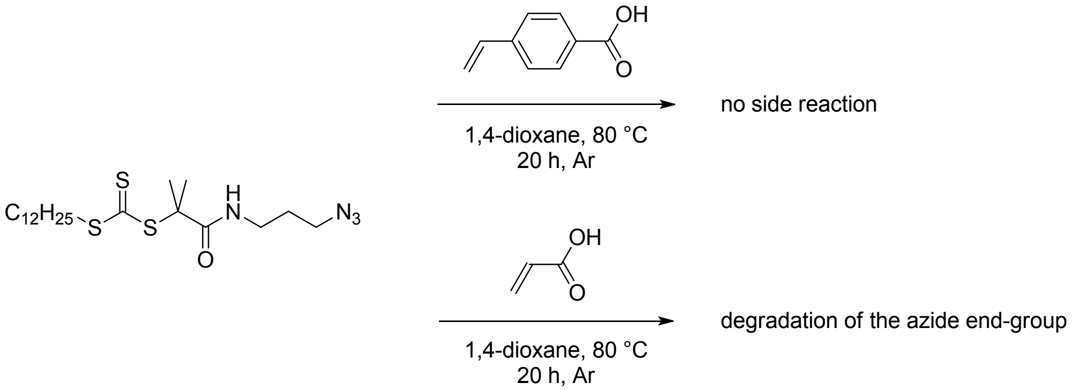
Control experiment to exclude degradation of the azide end-group



Scheme SI-1. Control experiment to exclude the loss of the azide end-group after polymerization of vinylbenzoic acid (top) and acrylic acid (botton)

In order to exclude the loss of the azide end-group after polymerization, a control experiment was carried out wherein the reaction of the azide functionalized chain transfer agent with 4-vinylbenzoic acid and acrylic acid was tested. Due to the fact that DMF is difficult to remove completely from the reaction mixture 1,4-dioxane was used (**Scheme SI-1**). The reaction mixture was investigated by FTIR before and after conducting the control experiment. In **Figure SI-1** (left) the FTIR spectrum with acrylic acid is shown and reveals that the azide stretch at 2100 cm^{-1} is completely degraded. In contrast, no degradation of the azide stretch with 4-vinylbenzoic acid is detected (**Figure SI-1**; right). For this reason, we decided to use 4-vinylbenzoic acid as monomer for the synthesis of the macromonomer.

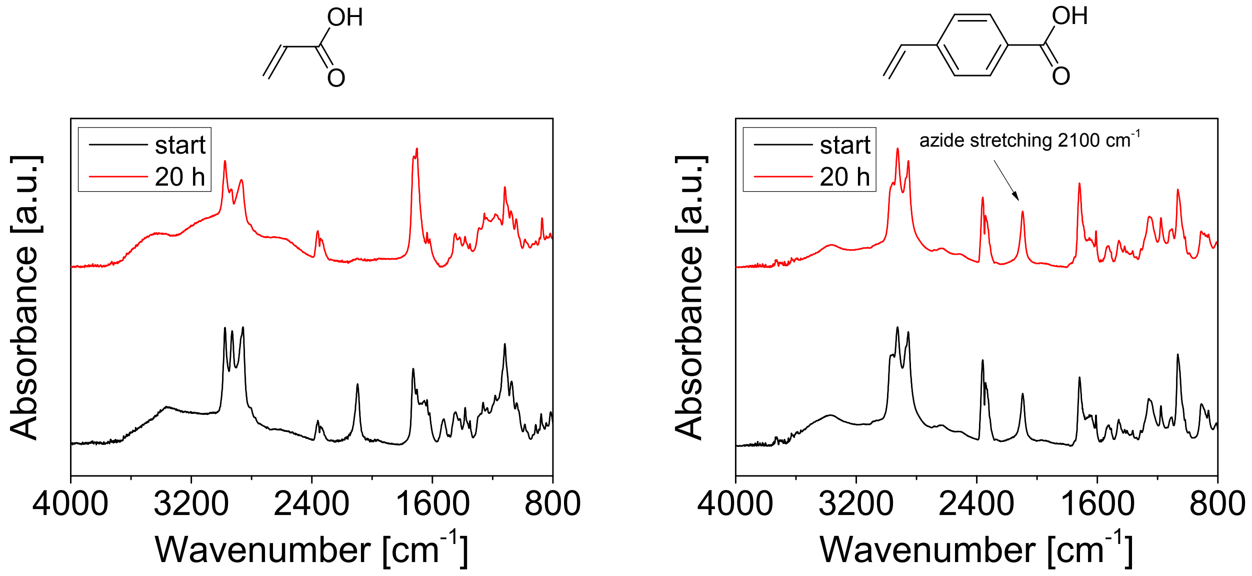


Figure SI-1. FTIR spectra of the reaction mixture before and after the control experiment using acrylic acid (left) and 4-vinylbenzoic acid (right).

Further analytic information of PVBA-N_3 and PVBA-AAm

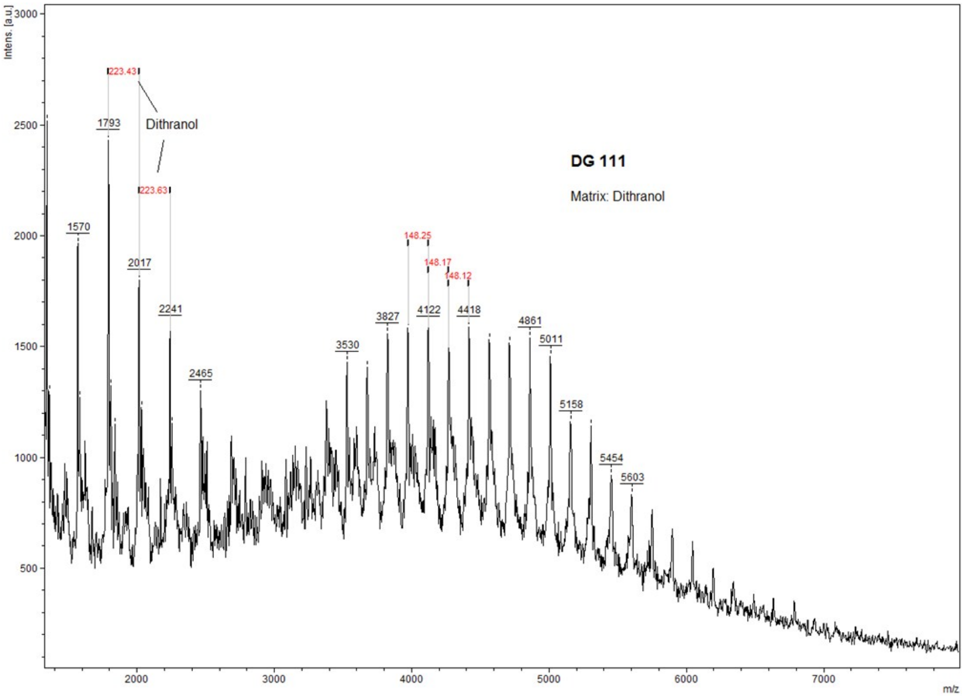


Figure SI-2. MALDI TOF MS spectrum of PVBA-N_3.

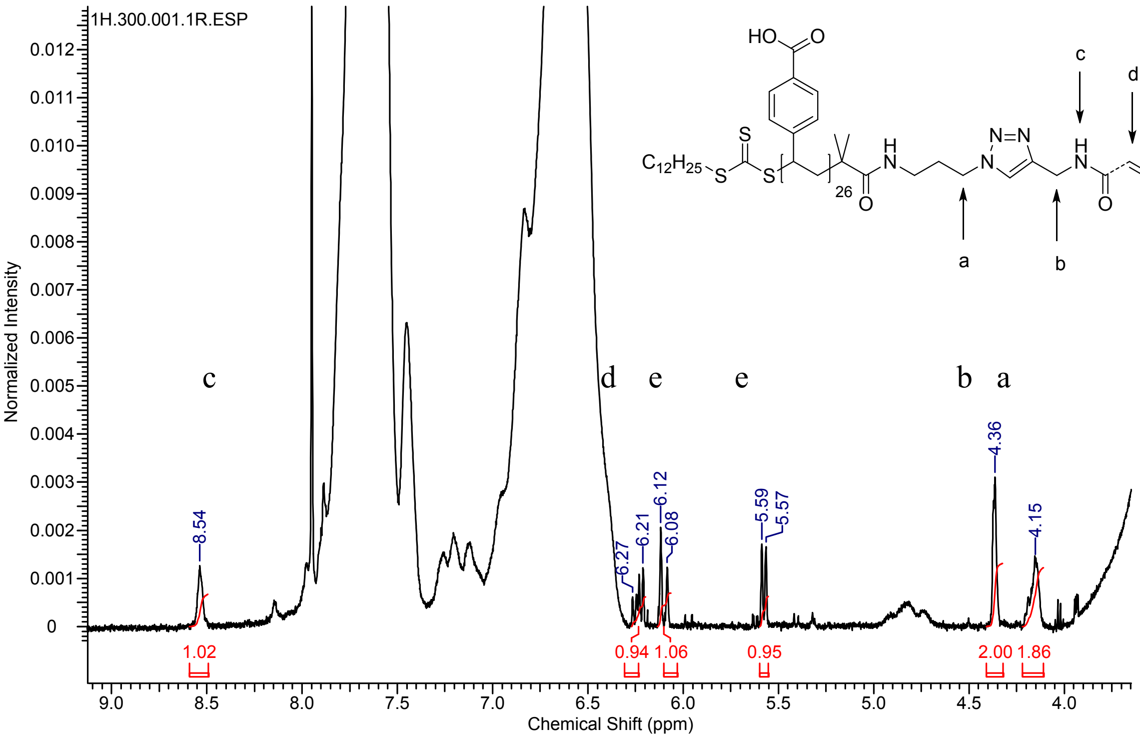


Figure SI-3. Selected and magnified part of the ^{1}H NMR spectrum of PVBA-AAm.

Determination of the hydrogel composition

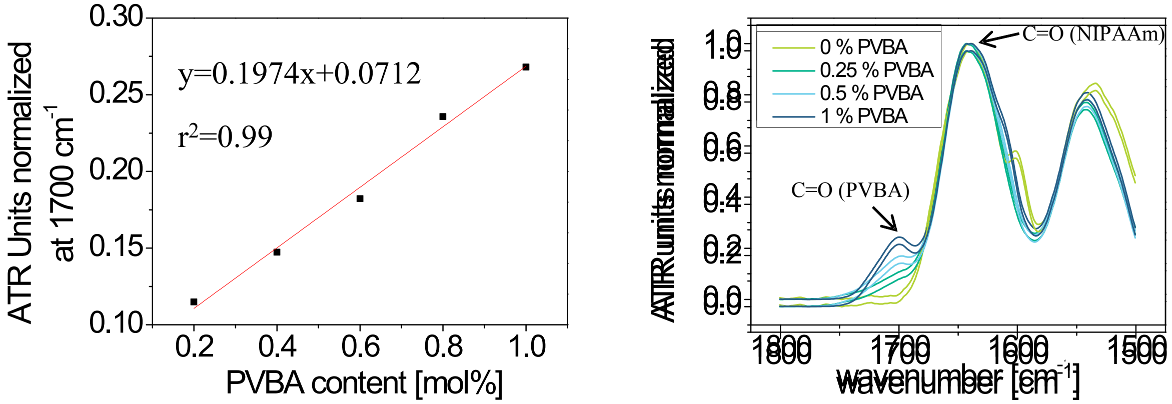


Figure SI-4. (Left) Normalized ATR Units at 1700 cm^{-1} as a function of PVBA content. (Right) Selected and magnified part of the IR spectrum of the prepared *net*-PNIPAAm and *net*-PNIPAAm-*g*-PVBA hydrogels.

The characteristic band of the C=O stretch of PVBA is shown in figure 3 right at 1700 cm^{-1}. The intensity of this band was normalized using the C=O stretching of NIPAAm at 1645 cm^{-1}. Then, a calibration curve was prepared using mixed samples of PVBA and NIPAAm in the predetermined weight ratio. The resulting calibration curve is given in figure 3 left and was used to quantify the hydrogel composition of the prepared hydrogels (**Table SI-1**).

Table SI-1. Determined hydrogel composition by FTIR spectroscopy

sample	ATR units at 1700 cm^{-1}	PVBA content [mol%]	grafting efficiency [%]	Ratio of	
				NIPAAm units	VBA units
0 % PVBA	-	-	-	100	-
0.25 % PVBA	0.107	0.18	72	96	4
0.5 % PVBA	0.168	0.49	99	89	11
1 % PVBA	0.244	0.87	87	82	18

Further analytic information of the prepared *net*-PNIPAAm-*g*-PVBA

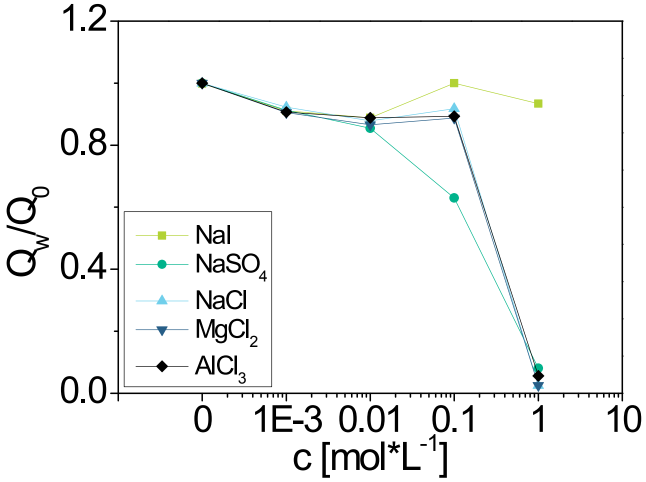


Figure SI-5. Change in swelling as function of various salts at different concentrations for *net*-PNIPAAm.

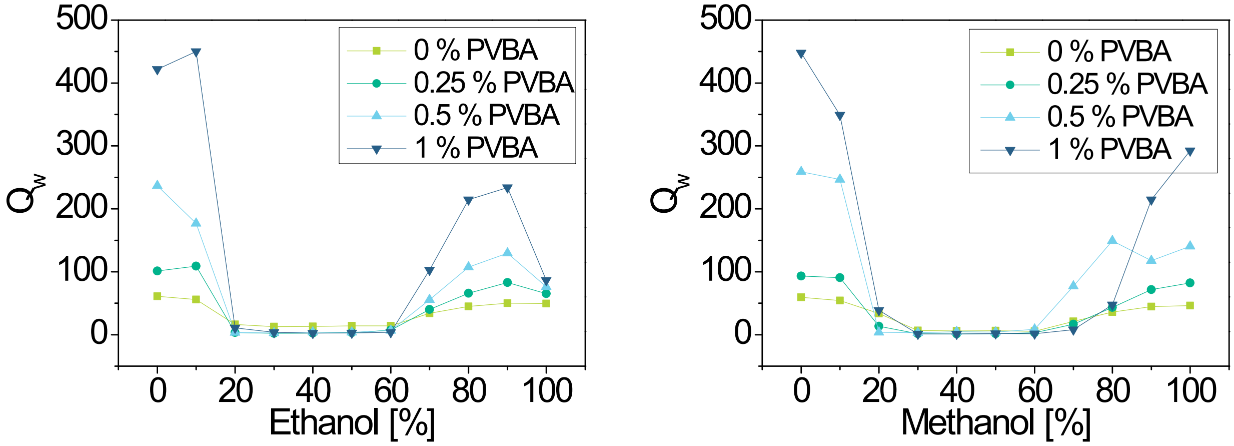


Figure SI-6. Equilibrium swelling behaviour at r.t. as function of ethanol concentration (left) and methanol concentration (right).

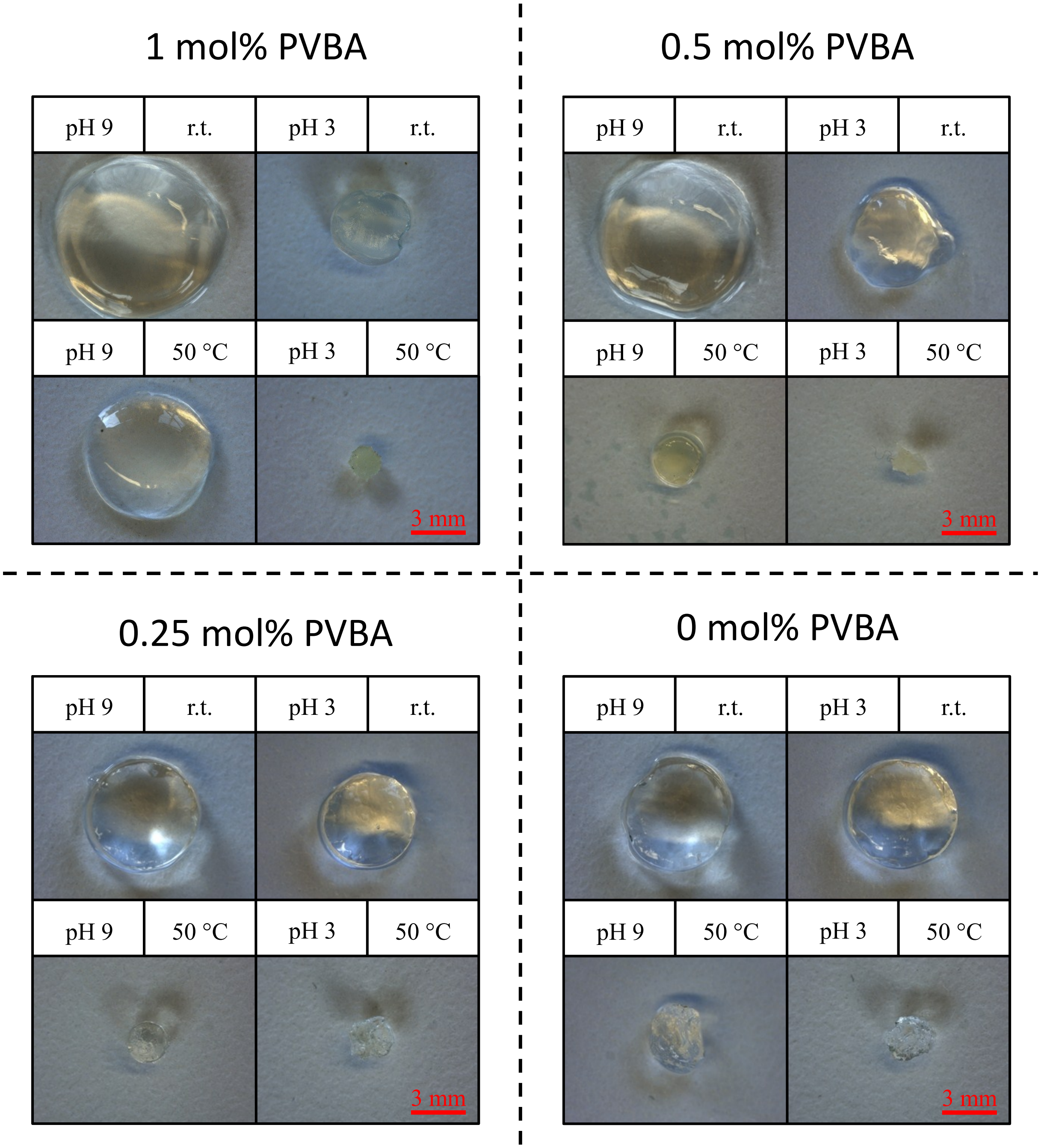


Figure SI-7. Microscope images of the prepared *net*-PNIPAAm and *net*-PNIPAAm-*g*-PVBA.