gels

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Article

Interplay of the Influence of Crosslinker Content and Model Drugs on the Phase Transition of Thermoresponsive PNiPAM-BIS Microgels

Daniel Schlattmann and Monika Schönhoff *

Institute of Physical Chemistry, University of Münster, Corrensstr. 28-30, 48149 Münster, Germany
* Correspondence: schonhoff@uni-muenster.de

Supplementary Materials

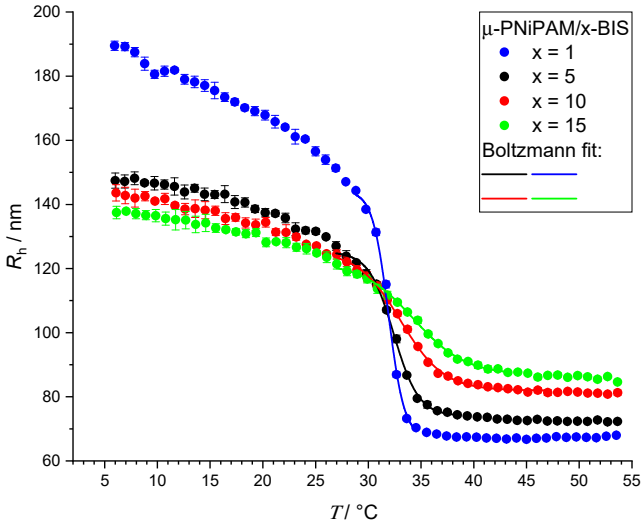

Figure S1. Temperature dependent hydrodynamic radii R_h of microgel structures containing different amounts of crosslinker. Results shown from a heating cycle starting at low temperatures. Lines are fits according to equation (4).

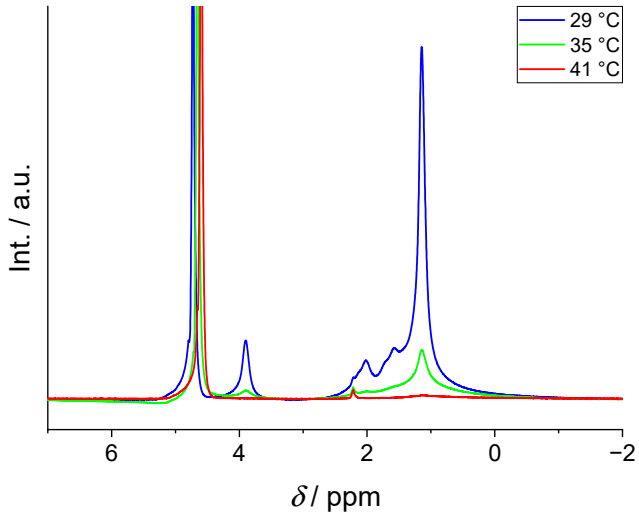

Figure S2. ^{1}H-NMR temperature series of a microgel acquired with equal spectral parameters.

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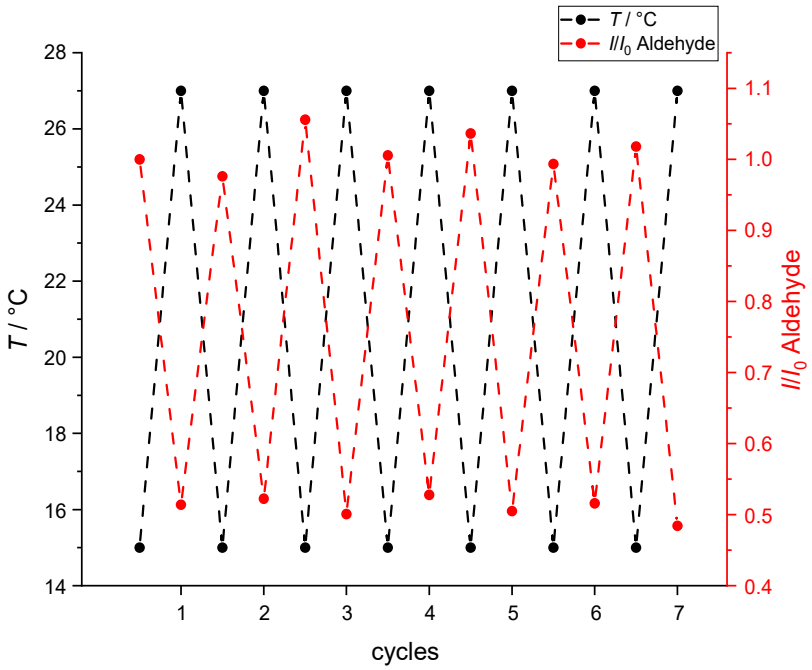

Figure S3. Integrated aldehyde ^{1}H signal for μ-PNiPAM/1-BIS with 20 mM *m*-HBA for a series of temperature jumps. Integrals are normalized to the value measured at 15 °C.

It could be shown, that the incorporation of additive is fully reversible and can be accomplished in the investigated time intervals.

NMR also revealed that incorporation of additives is *not* time dependent in the investigated period of time (2.5 h). Integrals are normalized to 15 °C. Equilibration time was 30 min at least. Data show no significant deviation from reached value at 27 °C and is forming a plateau, indicating no further reduction of $P_{inc.}$ with time:

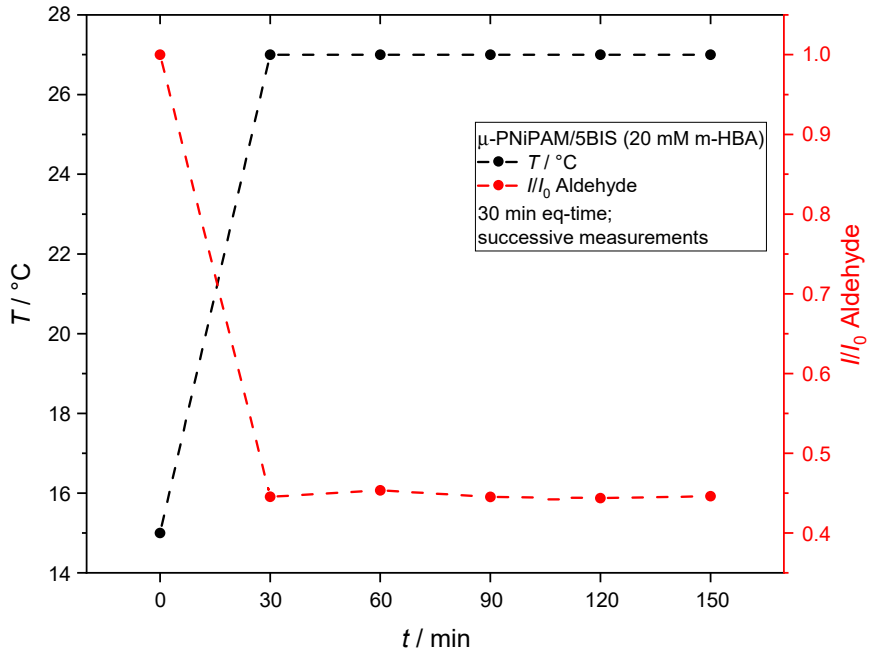

Figure S4. Integrated aldehyde signal for μ-PNiPAM/1-BIS with 20 mM *m*-HBA in dependency of time, following a temperature jump.

DSC

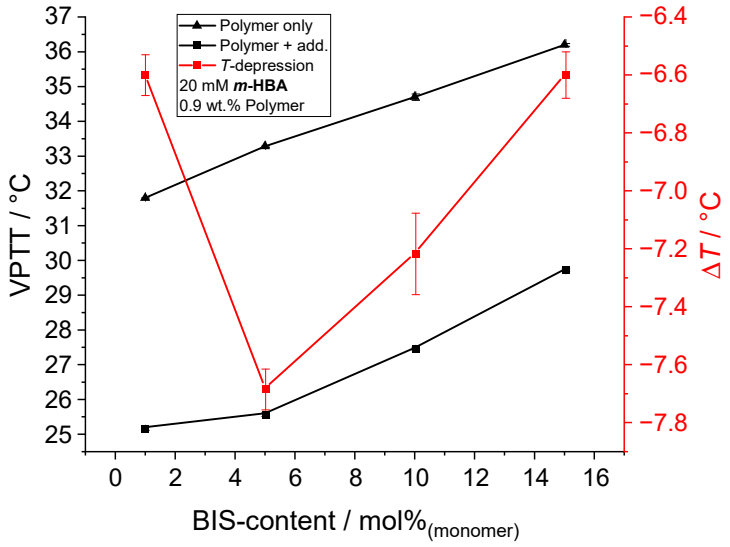

Figure S5. Plot of the VPTT (triangles: polymer only, black squares: depressed temperature) and calculated ΔT (red squares) against the crosslinker content for *m*-HBA.

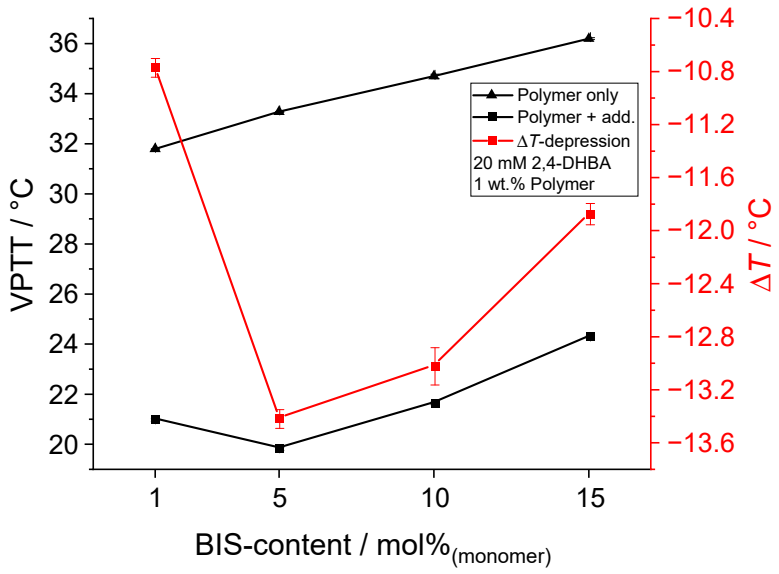

Figure S6. Plot of the VPTT (triangles: polymer only, black squares: depressed Temperature) and calculated ΔT (red squares) against the crosslinker content for *2,4*-DHBA.

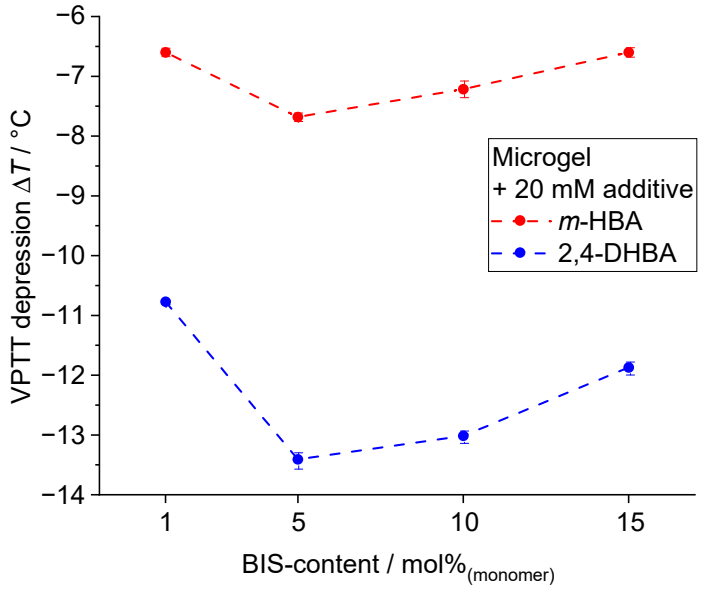

Figure S7. Calculated microgel VPTT depression Δ*T* from DSC data in presence of two different aromatic additive structures. Concentrations were 1 wt.% for the microgels and 20 mM for each additive. Error bars do reflect standard deviation. Colorcode corresponds to the microgels VPTT influenced by additives relative to each other (low *T* = blue; high *T* = red).

DLS

Table S1. Summary of DLS data for neat μ-PNiPAM/x-BIS microgels in H_2O and comparison with reported data from Friesen et al.

	$R_{h,15\,°C}$ / nm	$R_{h,50\,°C}$ / nm	$R_{sw,15°C/50°C}$	VPTT/°C	VPTT/°C	$PDI_{25°C}$ ± 0.02
μ-PNiPAM/1BIS	176	67	2.6	31.9	-	0.06
μ-PNiPAM/2.5BIS	-	-	-	-	34.1*	-
μ-PNiPAM/5BIS	143	72	2.0	32.4	35.7*	0.02
μ-PNiPAM/10BIS	138	81	1.7	33.0	37.1*	0.04
μ-PNiPAM/15BIS	132	87	1.5	34.3	38.6*	0.03

*Friesen, S., et al., Accounting for Cooperativity in the Thermotropic Volume Phase Transition of Smart Microgels. Gels, 2021. **7**(2): p. 42.

We note that absolute phase transition temperatures may differ, caused by different synthesis protocols. Nonetheless, temperature shifting trend remains the same.

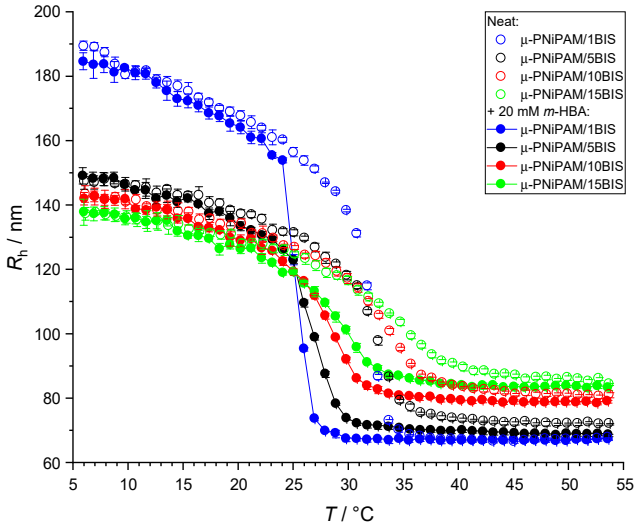

Figure S8. Temperature dependent hydrodynamic radii R_h of microgel particles containing different amounts of crosslinker (hollow circles: neat Polymer; solid circles: 20 mM *m*-HBA). Results shown from a heating cycle starting at low temperatures. Lines are guide to the eye.

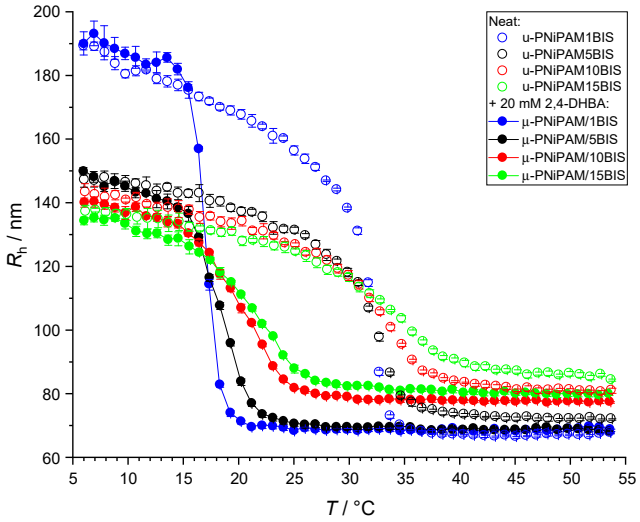

Figure S9. Temperature dependent hydrodynamic radii R_h of microgel particles containing different amounts of crosslinker (hollow circles: neat Polymer; solid circles: 20 mM 2,4-DHBA). Results shown from a heating cycle starting at low temperatures. Lines are guide to the eye.

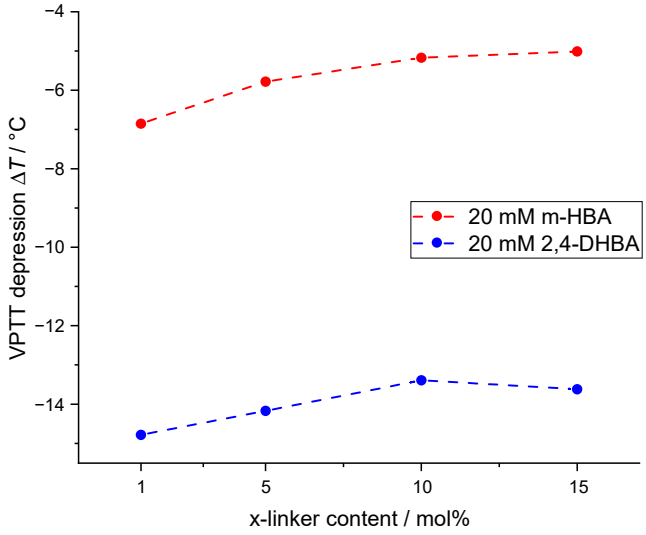

Figure S10. Calculated microgel VPTT depression ΔT from DLS data in presence of two different aromatic additive structures. Concentrations were 1 wt.% for the microgels and 20 mM for each additive. Error bars do reflect standard deviation. Colorcode corresponds to the microgels VPTT influenced by additives relative to each other (low T = blue; high T = red).

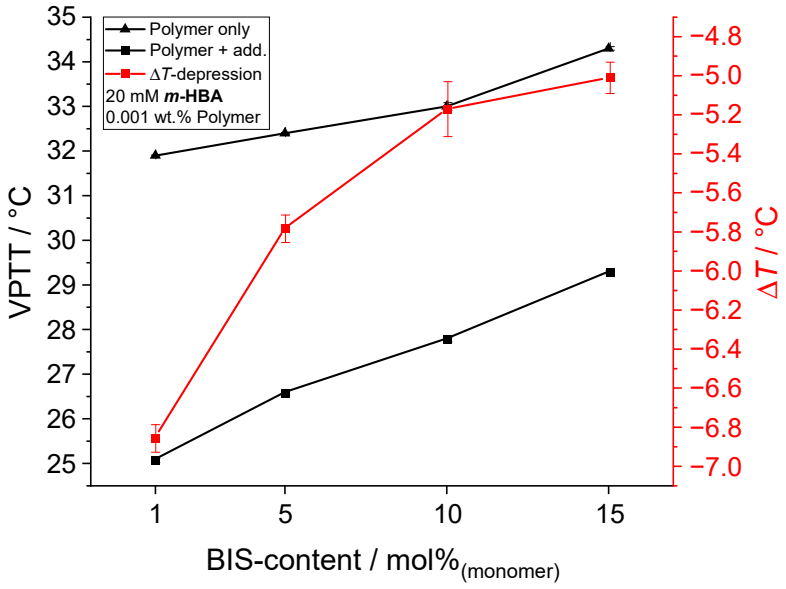

Figure S11. Plot of the VPTT (triangles: polymer only, black squares: depressed Temperature) and calculated ΔT (red squares) against the crosslinker content for *m*-HBA.

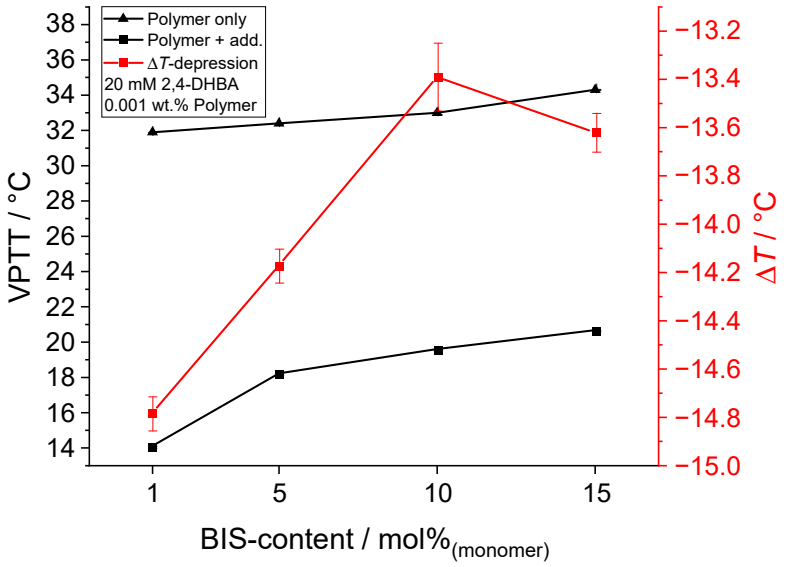

Figure S12. Plot of the VPTT (triangles: polymer only, black squares: depressed Temperature) and calculated ΔT (red squares) against crosslinker content for 2,4-DHBA.

NMR

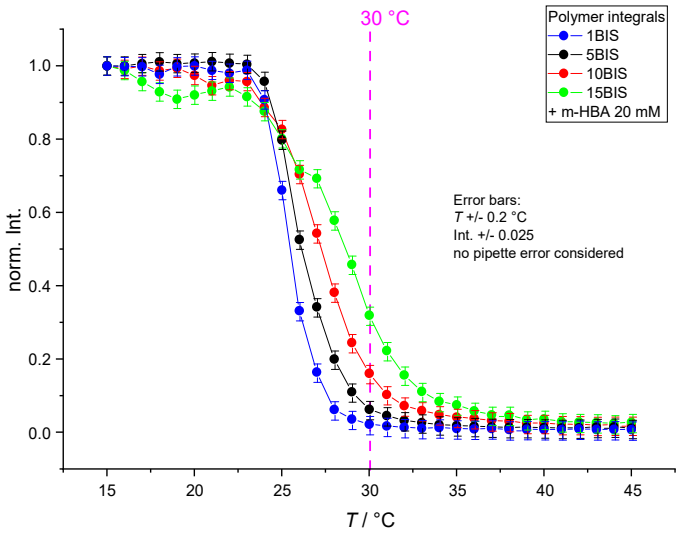

Figure S13. Integrated normalized polymer signals as acquired in ^{1}H-NMR temperature series for neat microgels containing different crosslinker content and 20 mM of *m*-HBA. Lines are guide to the eye.

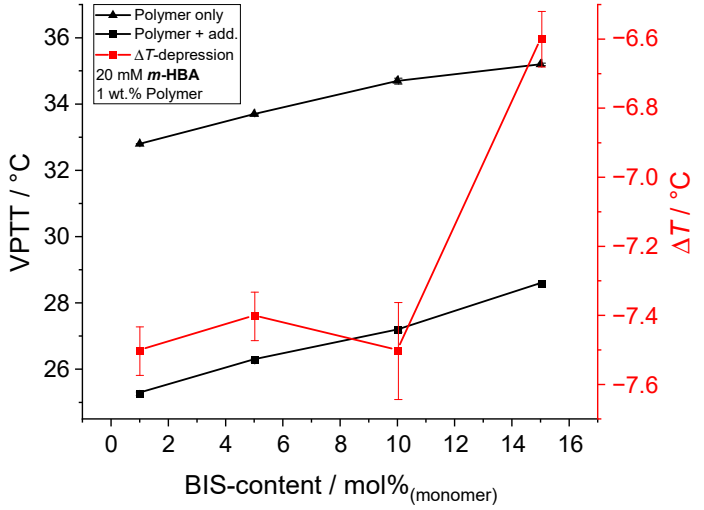

Figure S14. VPTT (triangles: polymer only, black squares: depressed Temperature) and calculated ΔT (red squares) against the crosslinker content for *m*-HBA.

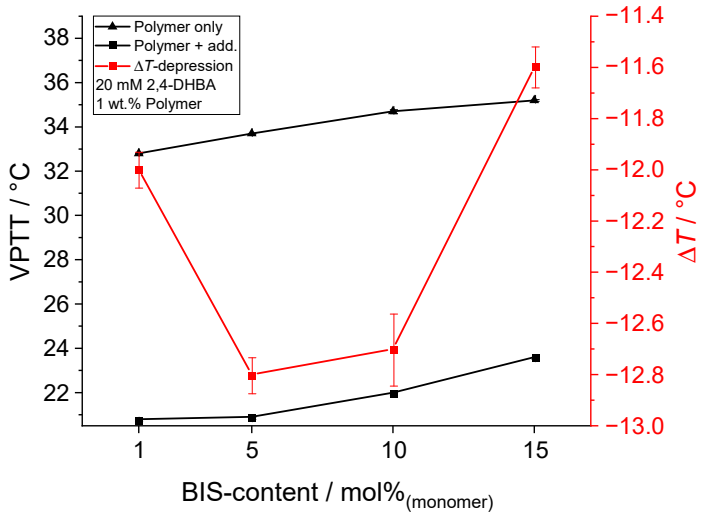

Figure S15. Plot of the VPTT (triangles: polymer only, black squares: depressed Temperature) and calculated ΔT (red squares) against crosslinker content for 2,4-DHBA.

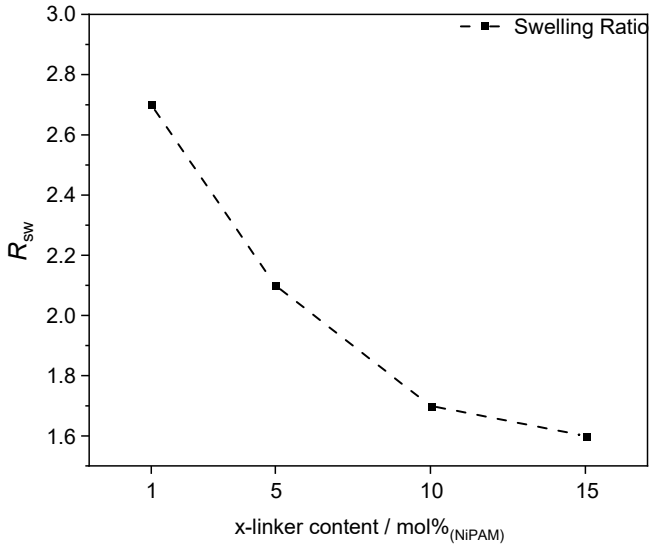

Figure S16. Swelling ratios R_{sw} for differently crosslinked microgels.