

Electronic Supporting Information

Functional Selenium Modified Microgels: Temperature-Induced Phase Transition and Network Morphology

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S1. Proton NMR spectrum of Bis(11-hydroxyundecyl) diselenide ($\text{HO-C}_{11}\text{SeSeC}_{11}\text{-OH}$). Proton NMR (Fig. S1) was performed to check the final product in the synthesis of Bis(11-hydroxyundecyl) diselenide, i.e., (CDCl_3 , 400 MHz): δ 3.57 (t, 4H, HOCH_2), 2.84 (t, 4H, CH_2Se), 1.65 (q, 4H, $(\text{CH}_2)_7\text{CH}_2\text{CH}_2\text{Se}$), 1.50 (q, 4H, $\text{HOCH}_2\text{CH}_2(\text{CH}_2)_7$), 1.34–1.11 (br, 28H, $\text{CH}_2(\text{CH}_2)_7\text{CH}_2$).

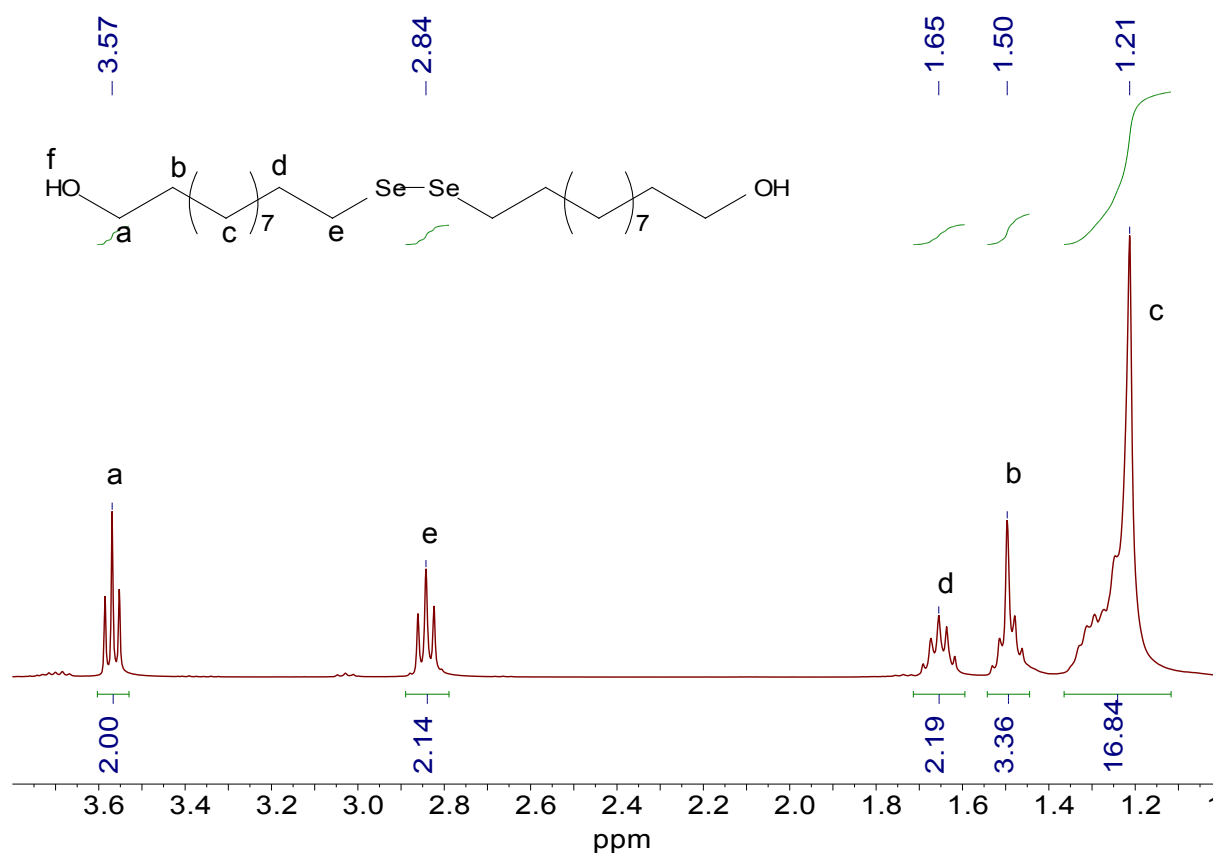


Fig. S1 Proton high-resolution spectrum of Bis(11-hydroxyundecyl) diselenide. The proton TMS resonance was used as chemical shift reference.

S2. Proton NMR spectrum of Bis(11-acryloyloxyundecyl) diselenide $[\text{C}=\text{CC}(=\text{O})\text{OC}_{11}\text{SeSeC}_{11}\text{OC}(=\text{O})\text{C}=\text{C}]$. Proton NMR spectrum of Bis(11-acryloyloxyundecyl) diselenide (Fig. S2) (CDCl_3 , 400 MHz) is shown in figure below and the

peaks chemical shifts are: δ 6.35-6.30 (dd, 2H, *cis*-HHC=CHC(=O)), 6.09-6.02 (dd, 2H, H₂C=CHC(=O)), 5.76-5.73 (dd, 2H, *trans*-HHC=CHC(=O)), 4.08 (t, 4H, OCH₂CH₂(CH₂)₇), 2.84 (t, 4H, (CH₂)₇CH₂CH₂Se), 1.65 (m, 4H, (CH₂)₇CH₂CH₂Se), 1.60 (m, 4H, OCH₂CH₂(CH₂)₇), 1.34–1.11 (br, 28H, CH₂(CH₂)₇CH₂).

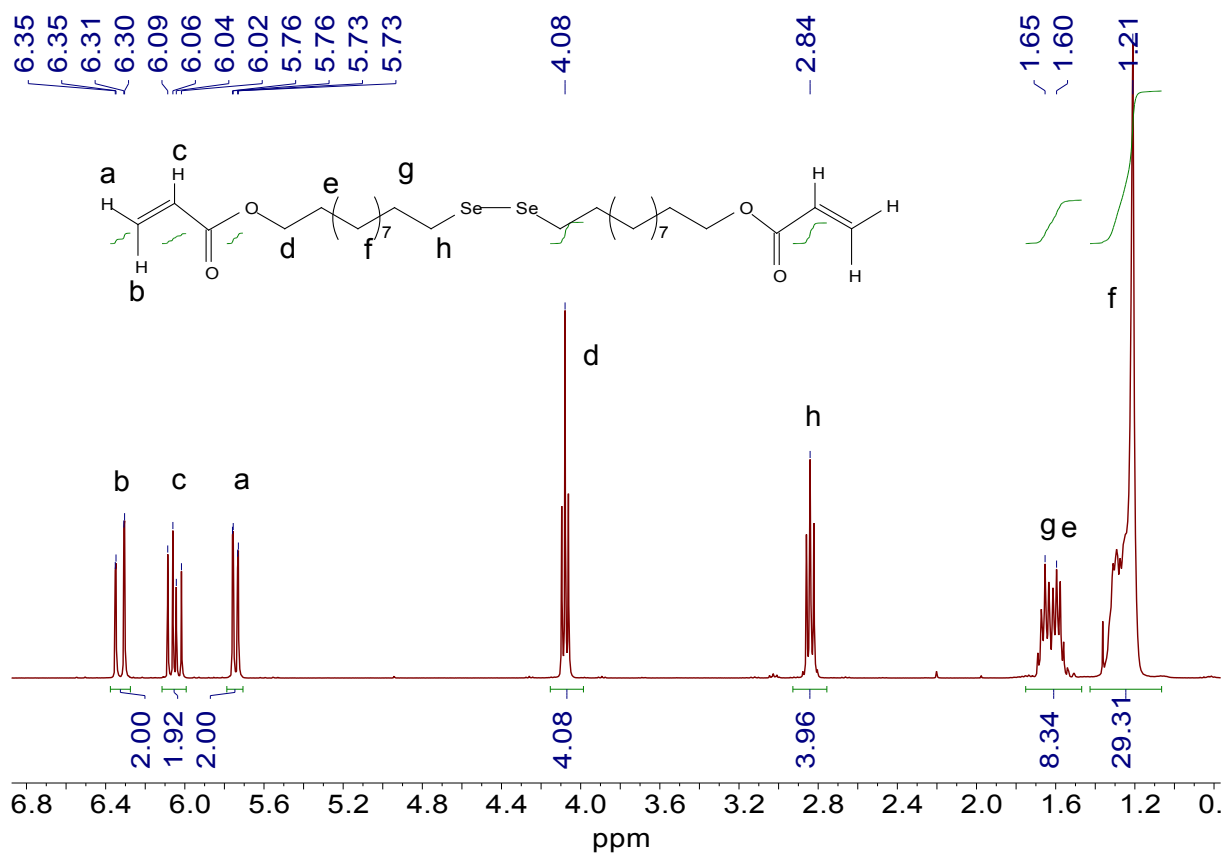


Fig. S2 Proton high-resolution spectrum of Bis(11-acryloyloxyundecyl) diselenide. The proton TMS resonance was used as chemical shift reference.

S3. Incorporation efficiency of diselenide crosslinker.

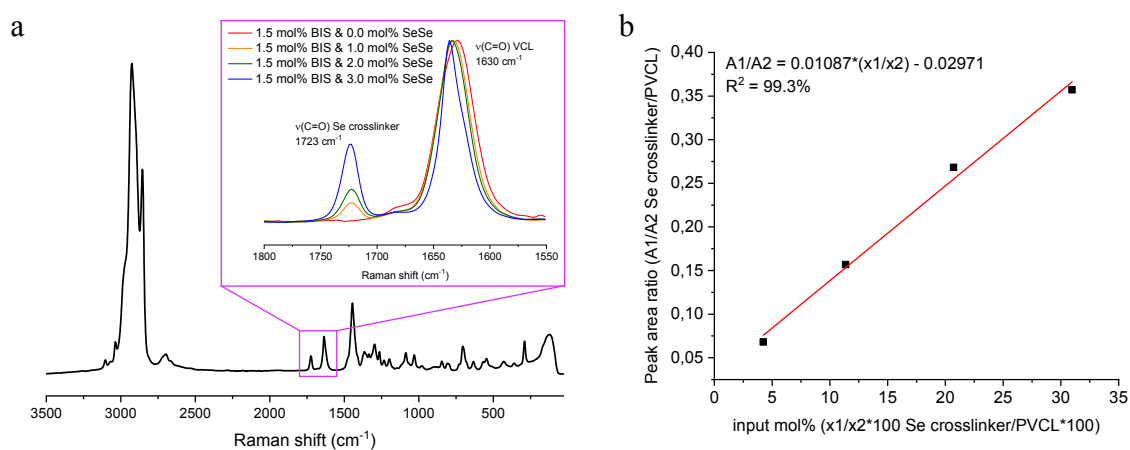
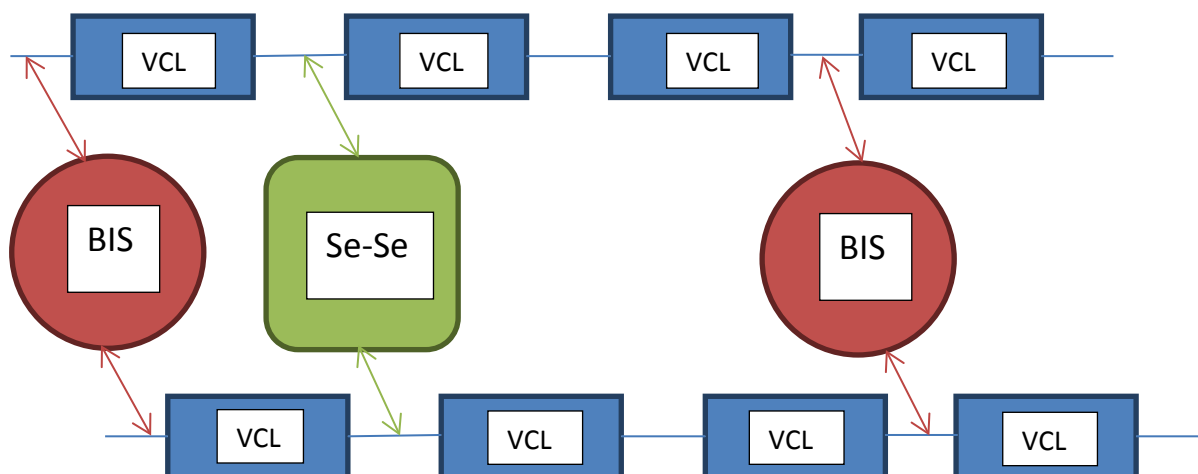


Fig. S3 Raman spectrum of the PVCL microgels 1.5mol% BIS 3.0 mol% SeSe with the inset shows the Raman spectra between 1800 and 1550 cm⁻¹ of all microgels.

Table S1 Comparison between the input contents of Se crosslinker during synthesis with the content determined by the Raman calibration method (see Fig. S3b).		
Sample	Se crosslinker input (mol%)	Se crosslinker Raman (mol%)
1.5 mol% BIS & 1.0 mol% SeSe	1.0	0.9
1.5 mol% BIS & 2.0 mol% SeSe	2.0	2.6
1.5 mol% BIS & 3.0 mol% SeSe	3.0	4.3

S4. Simplified dual crosslinker distribution into microgel (PVCL).



Scheme S1 Two-dimensional simplified sketch of the dual crosslink polymer network. Two PVCL subchains of the network are shown crosslinked by BIS (first crosslinker specie), i.e., $N_1=2$ (see eqn (3), and the text in the paper). The number of Se-Se crosslinker (the second specie) between two BIS is in this case $n_2=1$. The total number of network strands is given by $N=N_1(1+n_2)$, (eqn (3)) and finally we get $N=4$. The incorporation of both crosslinkers (BIS and Se-Se) into the microgel network follows similar mechanism. Both crosslinkers contain two polymerizable acrylamide (BIS) and acrylate (Se-Se crosslinker) groups, which can copolymerize with vinyl groups of VCL monomers. Thus, in the ideal case both crosslinkers become randomly incorporated in the main chain of PVCL macromolecules. Due to the fact that both crosslinkers contain two polymerizable groups in each molecule, they can get incorporated in two different PVCL chains leading to the formation of covalent crosslinks in the microgel network.

S5. Temperature dependence of hydrodynamic radius fits with Boltzmann function and two-state model for bimodal crosslinked PVCL hydrogel.

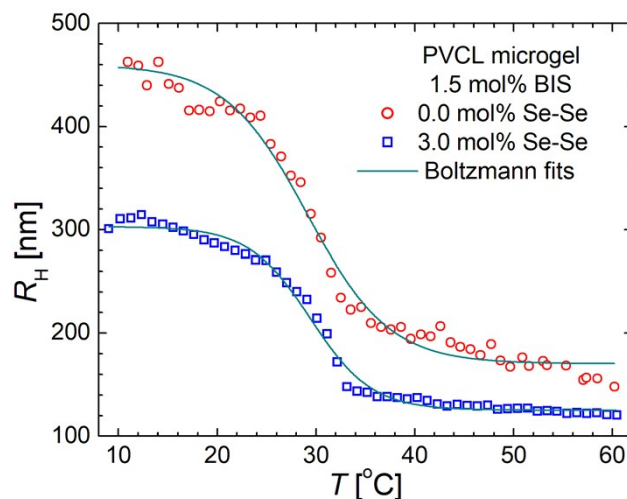


Fig. S4 The Boltzmann function fits of R_H versus temperature dependence measured by DLS. Different PVCL microgels with 1.5 mol% BIS and two concentrations of diselenide is shown.

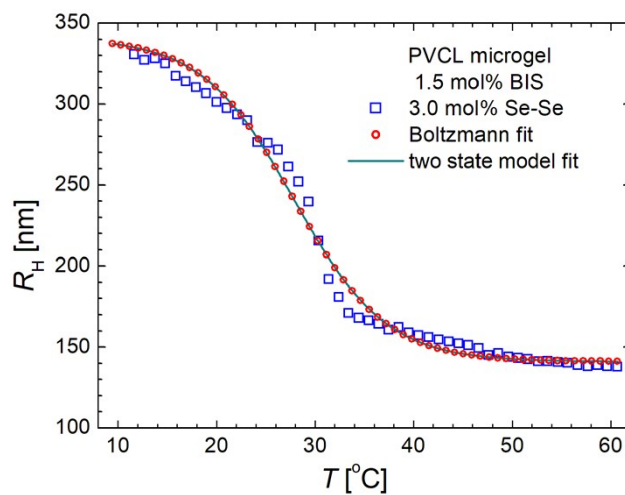


Fig. S5 Comparison between the fits made by two-state model (continuous line) and Boltzmann sigmoidal function (circles) of the $R_H(T)$ (square) measured by DLS. The molar concentrations of crosslinkers were 1.5 mol% BIS and 3.0 mol% diselenide.

S6. Temperature-induced phase transition by ^1H MAS HRNMR spectroscopy analyzed by Boltzmann sigmoidal function.

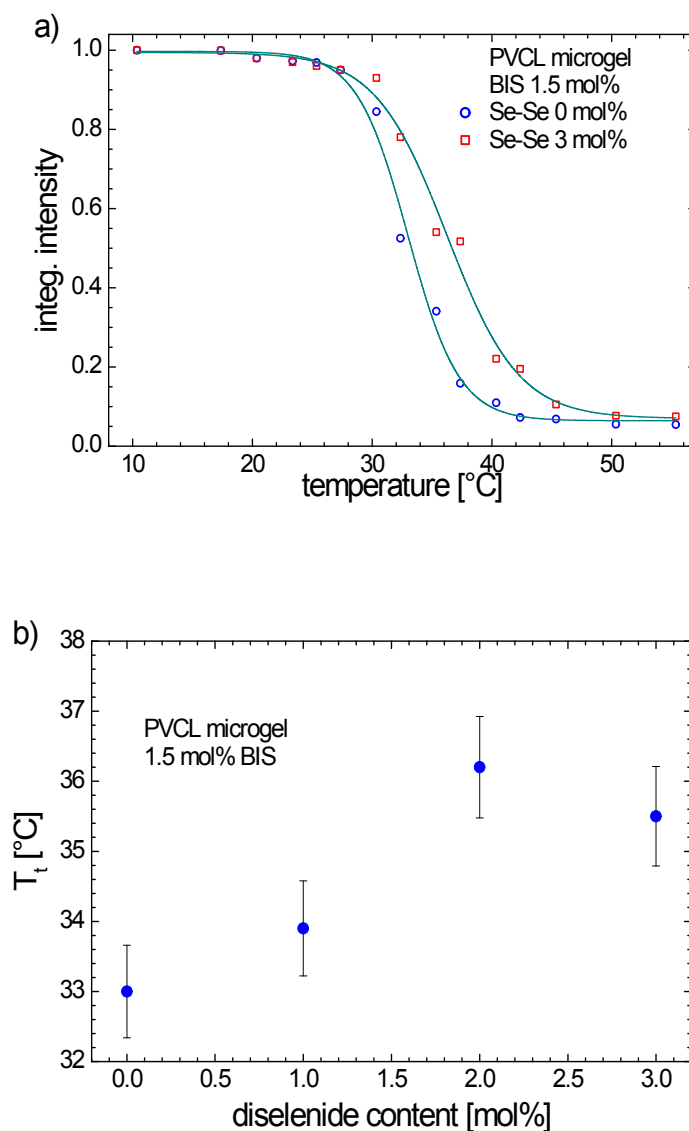


Fig. S6 (a) Volume-temperature phase transition measured by integral intensity of the proton HRMAS NMR spectra edited by the spin-echo for PVCL microgel (5 wt% in D₂O) bimodal crosslinked with 1.5 mol% BIS and two values of diselenide 0 mol% (circles) and 3 mol% (squares). Proton NMR spectra were measured at 23 °C. The fits shown by continuous lines were made using a Boltzmann sigmoidal function. (b) The dependence of transition temperature (T_t) upon diselenide content obtained by sigmoidal Boltzmann fits.

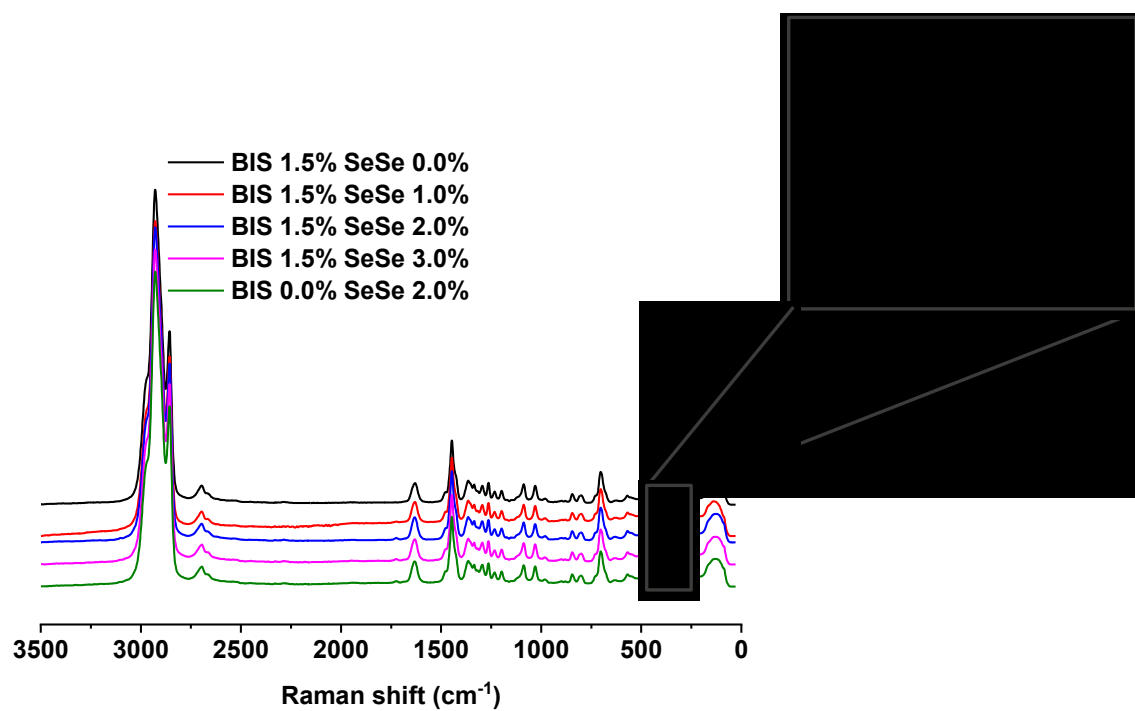
S7. Incorporation of diselenide crosslinker in microgels.

Fig. S7 Raman spectra of microgels synthesized with bisacrylamide and diselenide crosslinker revealing the diselenide band (inset).

S8. Raman spectra of PVCL microgel in the process of diselenide crosslinkers oxidation.

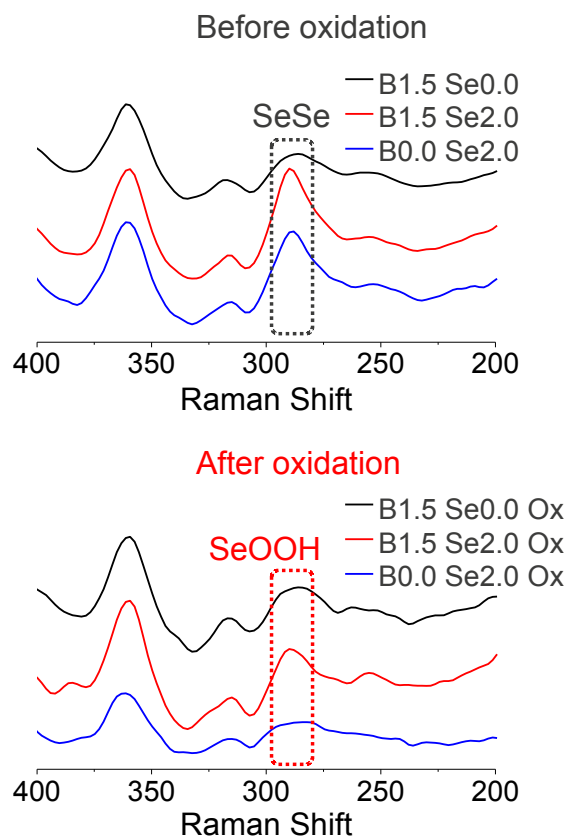


Fig. S8 Raman spectra of microgels before and after oxidation with H₂O₂.

S9. Phase transition temperature and transition width of PVCL microgel in the process of diselenide crosslinkers oxidation.

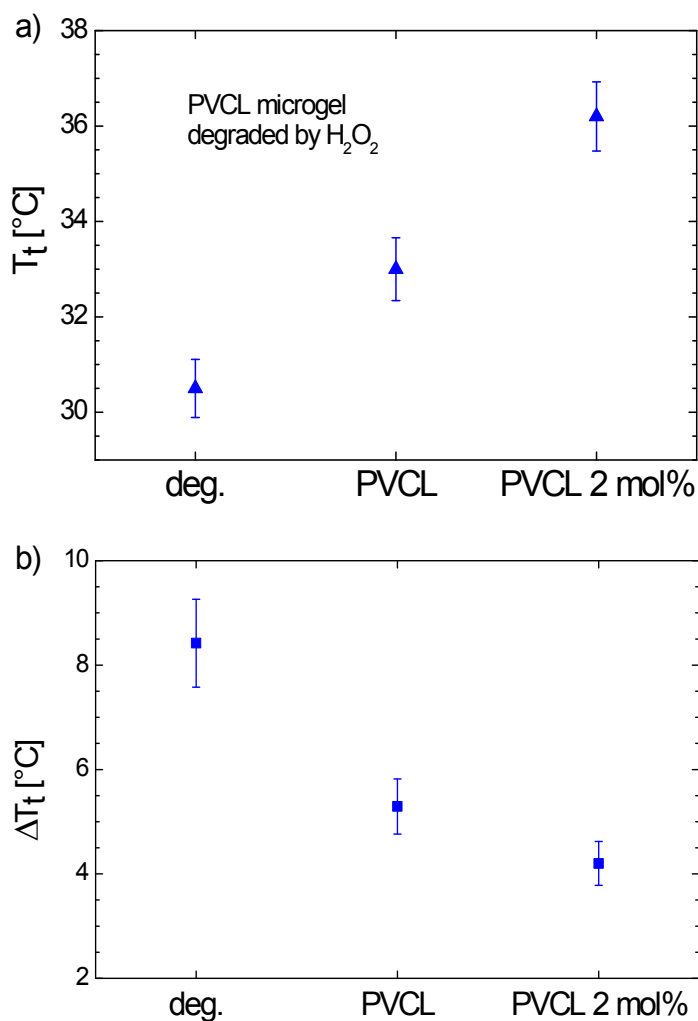


Fig. S9 (a) Volume-phase transition temperature (T_t) of degraded and non-degraded PVCL microgel measured by ^1H MAS HRNMR spectroscopy as a function of temperature. (b) Full width of volume-phase transition temperature (ΔT_t) degraded and non-degraded PVCL microgel. On the horizontal axis the degraded microgel is denoted by deg., PVCL notation corresponds to the microgel with 1.5 mol% BIS crosslinker and PVCL 2 mol% designates the microgel with 2 mol% diselenide as a second crosslinker. The degradation was made on PVCL microgel using 1.0 wt% H_2O_2 . The phase transition widths were obtained by Boltzmann function fits of the NMR integral spectral intensity of PVCL microgel in the aliphatic region.

S10. Scanning transmission electron microscopy (STEM) of PVCL microgels in the process of diselenide crosslinkers oxidation.

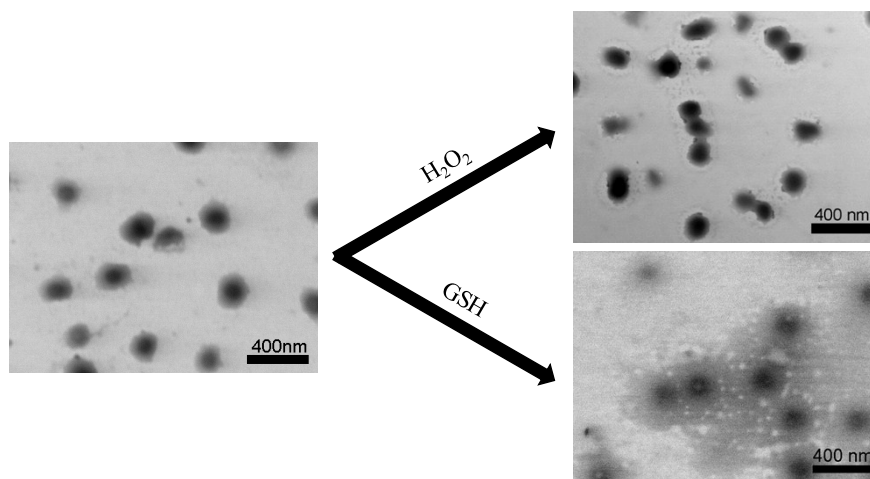


Fig. S10 STEM images of PVCL microgels containing BIS 1.5 mol% and SeSe 2.0 mol% (left), after oxidation by H_2O_2 (right top) and reduction by GSH (right bottom) at 20 °C.