Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Microgel Organocatalysts: Modulation of Reaction Rates at Liquid-Liquid Interfaces

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Synthesis of Microgel-Catalysts

Reaction Scheme

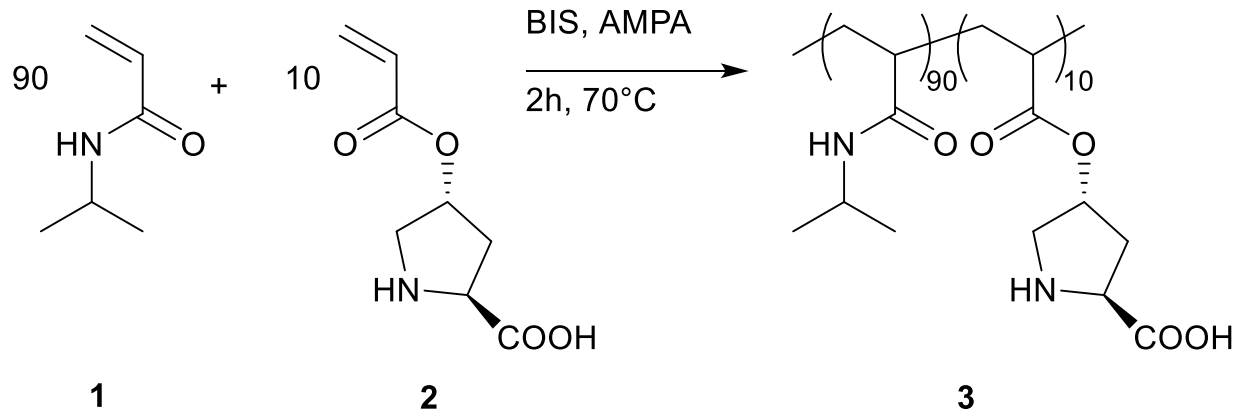

Figure S1. Reaction scheme of free radical precipitation polymerisation in water for synthesis of the microgel-catalysts. The main monomer *N*-isopropylacrylamide (NIPAM, **1**) is polymerised in presence of a polymerisable form of the L-proline organocatalyst (**2**). Synthesis of the latter can be found in literature.[1,2] As crosslinker for the co-polymer microgel (**3**), the crosslinker *N,N'*-methylenebisacrylamide (BIS) and the initiator 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AMPA) were used.

Characterisation Methods

Thermogravimetric Analysis (TGA)

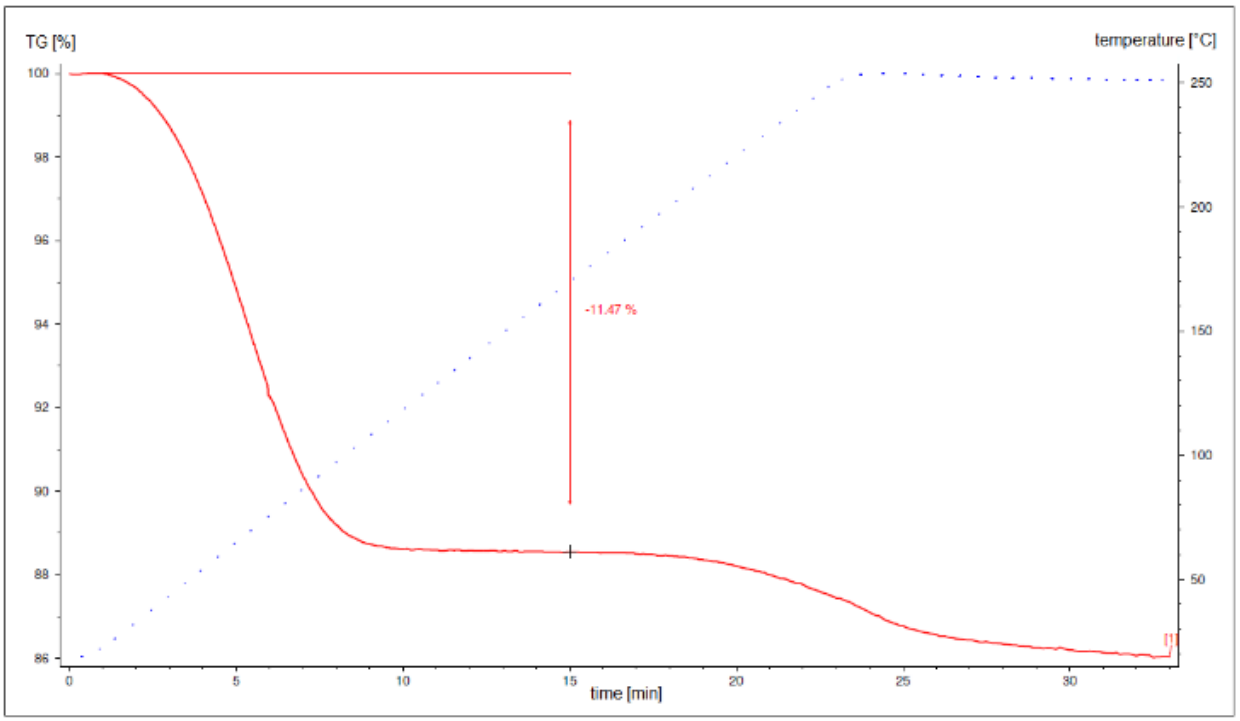

Figure S2. TGA Curve of freeze dried microgel-catalysts used in this work. The red lines represent the mass loss of sample. The blue dotted curve depicts the adapted temperature program.

Attenuated Total Reflection Fourier-transform Infrared Spectroscopy (ATR-FTIR-spectroscopy)

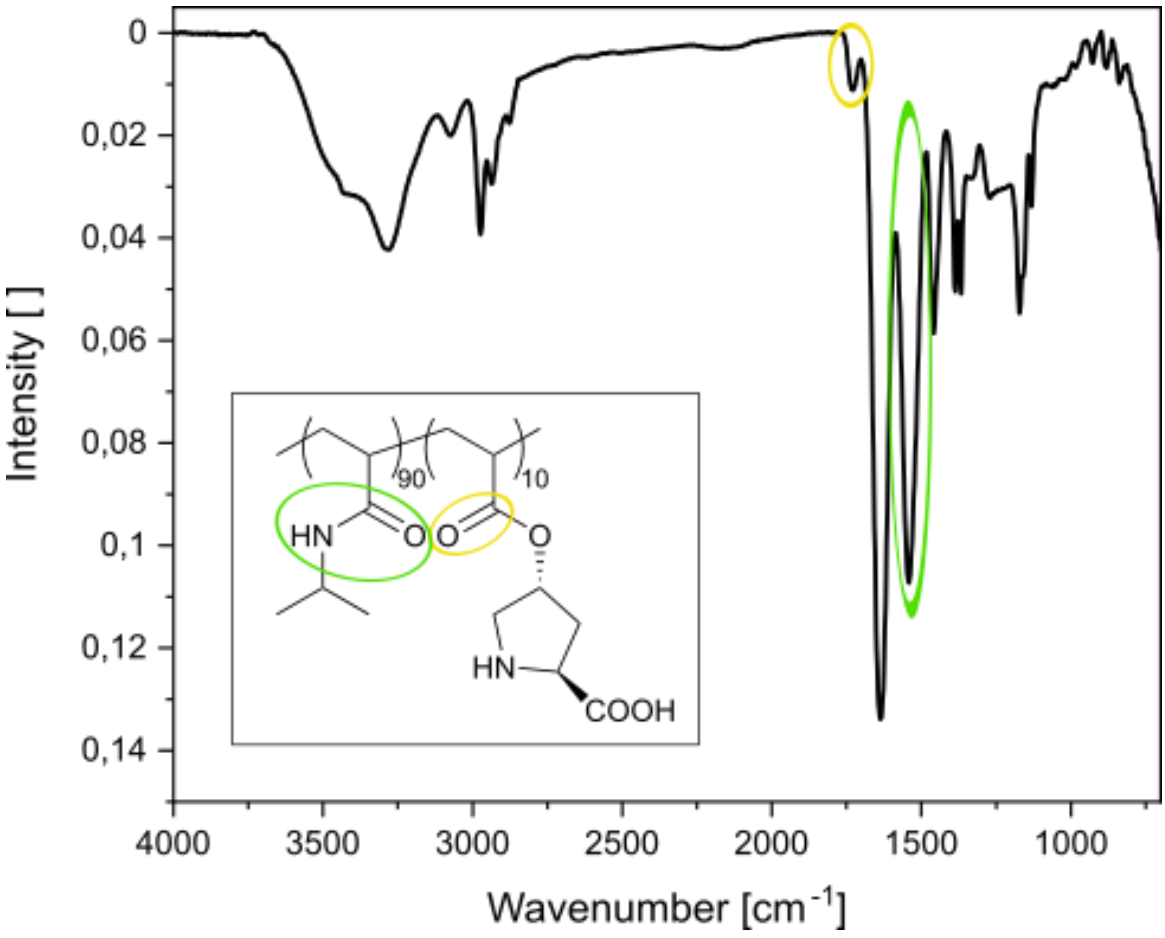

Figure S3. ATR-FTIR spectrum of microgel-catalysts. For calculation of the L-proline content, the intensity ratios of the carbonyl stretching band of the modified L-proline catalysts at 1733 cm^{-1} ($\nu(C=O)_{L\text{-}proline}$) (yellow) was referenced to the amide II band of NIPAM at 1541 cm^{-1} ($\nu(amide\ II)_{PNIPAM}$) (green). The procedure is in accordance with the literature.[2,3]

Nuclear Magnetic Resonance Spectroscopy (NMR-spectroscopy)

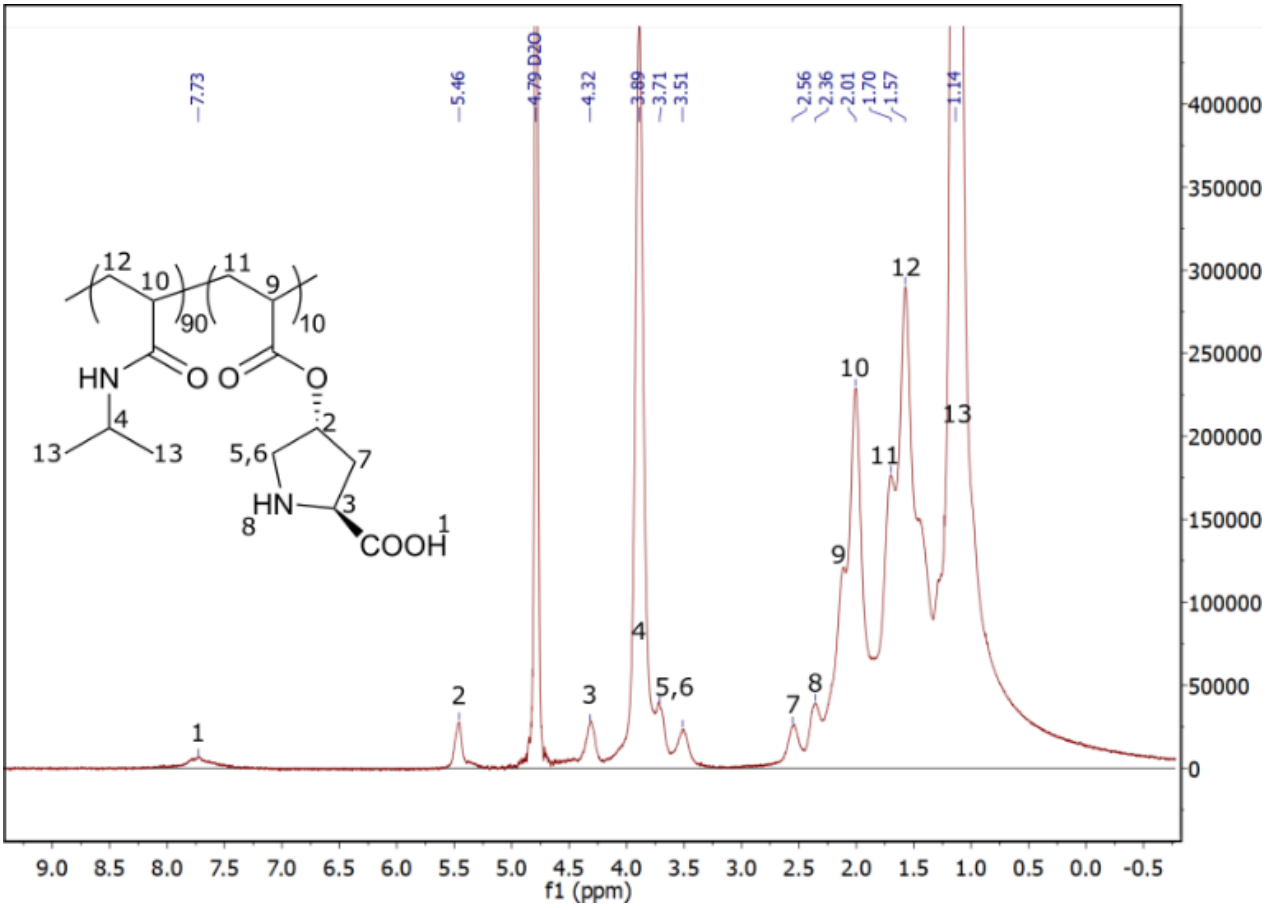

Figure S4. ^{1}H-NMR spectrum of the microgel-catalysts recorded in D_2O. Due to overlapping of signals, these data were used for qualitative analysis only.

Static Light Scattering (SLS)

SLS measurements were conducted at 25 °C in water, methanol and 20 mol% methanol. In case of water the partly collapsed state at 45 °C and in case of the mixture the partly swollen state at 10 °C were measured additionally. As aggregates were found, especially for the mixture, the 10 °C measurement in the mixture is always performed directly before the 25 °C measurement. **Figure S5a** shows the scattering intensity in dependence of the scattering vector *q*. The microgel-

catalysts are too small to obtain any minima in the q-regime of the SLS. Thus, the scattering curves are analysed with Guinier. The Guinier plots and linear fits of the microgel-catalysts in water (25, 45 °C), methanol (25 °C) and the mixture (10, 25 °C) are shown in **Figure S5b-d**. **Table S1** displays an overview of R_h, R_g and their ratio ρ in water, methanol and 20 mol% methanol at different temperatures.

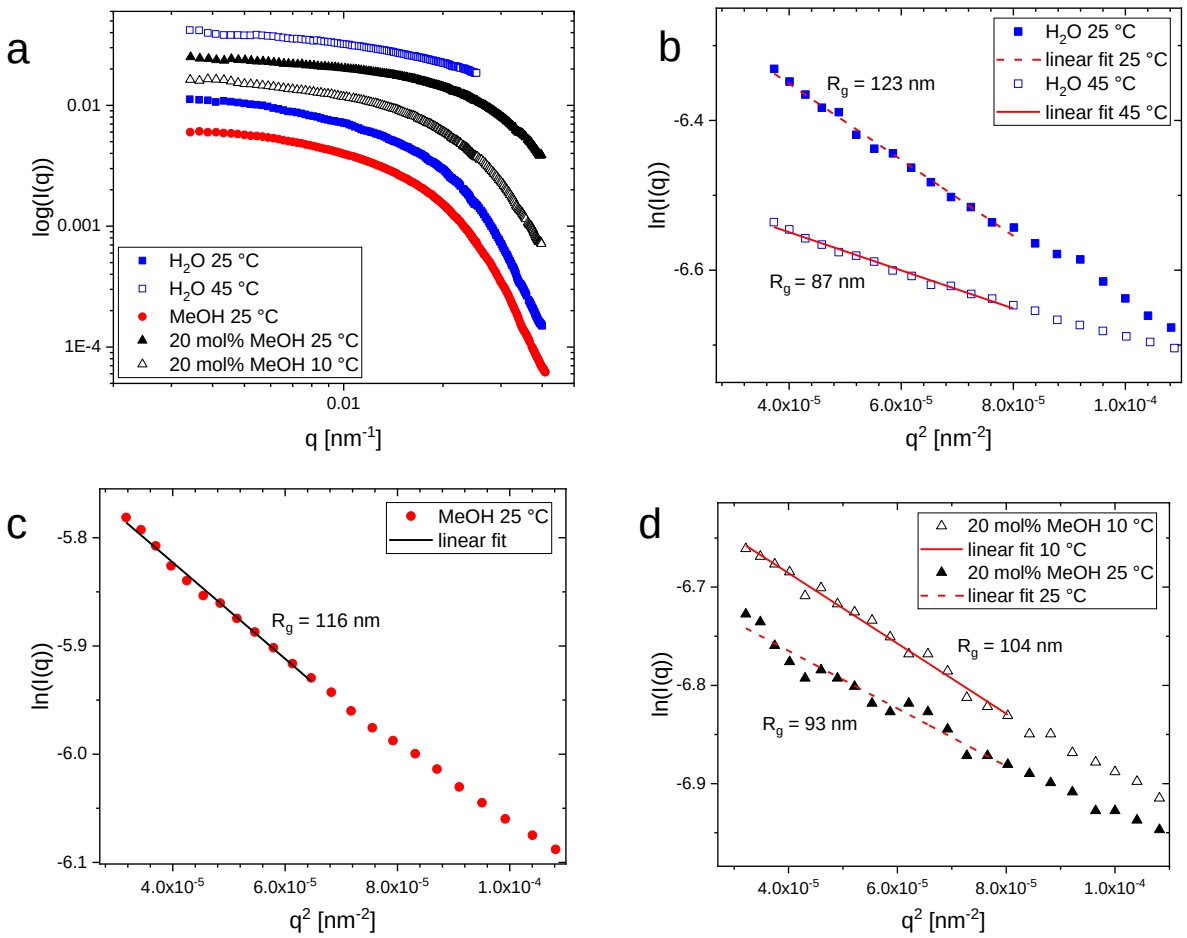

Figure S5. SLS form factors (a) of the microgel-catalysts in various solvents (the curves have been vertically shifted for better visibility) and the corresponding Guinier plots in water (b), methanol (c) and 20 mol% methanol (d).

Table S1. Comparison of the hydrodynamic radius, radius of gyration and their ratio of the microgel-catalysts in different swelling states.

Solvent	T [°C]	R_h [nm]	R_g [nm]	$\rho = R_g/R_h$
Water	25	167 ± 2	123 ± 2	0,74 ± 0.012
	45	110 ± 1	87 ± 2	0,79 ± 0.02
20 mol% MeOH	10	141 ± 1	104 ± 2	0,73 ± 0.012
	25	116 ± 2	93 ± 3	0,81 ± 0.03
MeOH	25	175 ± 7	116 ± 2	0,66 ± 0.03

In general, R_g exhibits comparable trends to R_h concerning the swelling state of the microgel-catalysts: The largest sizes are found in pure water and methanol at room temperature. At 45 °C in water and 25 °C in the 20 mol% mixture the smallest values are found for R_g. Both, R_g and R_h at high temperatures in water are smaller than in the mixture at room temperature. An intermediate value for R_g and R_h is found in the partly swollen state at 10 °C in the mixture. With respect to the ρ-ratio, it is known that a homogeneous sphere exhibits a value of 0.78. Studies by Senff et al.[4] documented ratios between 0.55 – 0.6 for PNIPAM microgels in the swollen state in water. In comparison, higher ratios close to the one of hard spheres are found in case of the microgel-catalysts. The ρ-ratios lie between 0.66 and 0.81. The smallest ratios are determined for the swollen microgel-catalysts in methanol and water, as well as for the partly swollen state at 10 °C in the 20 mol% methanol mixture. The ρ-ratios close to 0.78 indicate a less fuzzy, more homogeneous structure of the microgel-catalysts compared to pure PNIPAM microgels.

Dissipative Particle Dynamics Simulations (DPD)

Table S2. DPD interaction parameters (in units of k_BT/r_c) at T = 25 °C used in the simulations. The numbers in brackets in the non-diagonal cells are the corresponding values of Flory-Huggins parameter.

a_{ij} (χ_{ij})	P	L	N	C	W	M
P	25	26.63[a] (0.50)	30.9[a] (1.80)	27.16[a] (0.66)	25.6[b] (0.18)	25[c] (0.00)
L	26.63[a] (0.50)	25	28.37[a] (1.03)	26.7 [a] (0.52)	25[c] (0.00)	28,52[a] (1.07)
N	30.9[a] (1.80)	28.37[a] (1.03)	25	29.72[a] (1.44)	57.73[a] (10.01)	37.95[a] (3.96)
C	27.16[a] (0.66)	26.7[a] (0.52)	29.72[a] (1.44)	25	56.35[a] (9.59)	32.49[a] (2.29)
W	25.6[b] (0.18)	25[c] (0.00)	57.73[a] (10.01)	56.35[a] (9.59)	25	[d]-
M	25[c] (0.00)	28,52[a] (1.07)	37.95[a] (3.96)	32.49[a] (2.29)	[d]-	25

[a] Calculated from Hansen solubility parameter[5] [b] Calculated using the approach of Yong *et al.*[6] [c] Fixed values [d] The interactions that weren't considered both in experiments and simulations

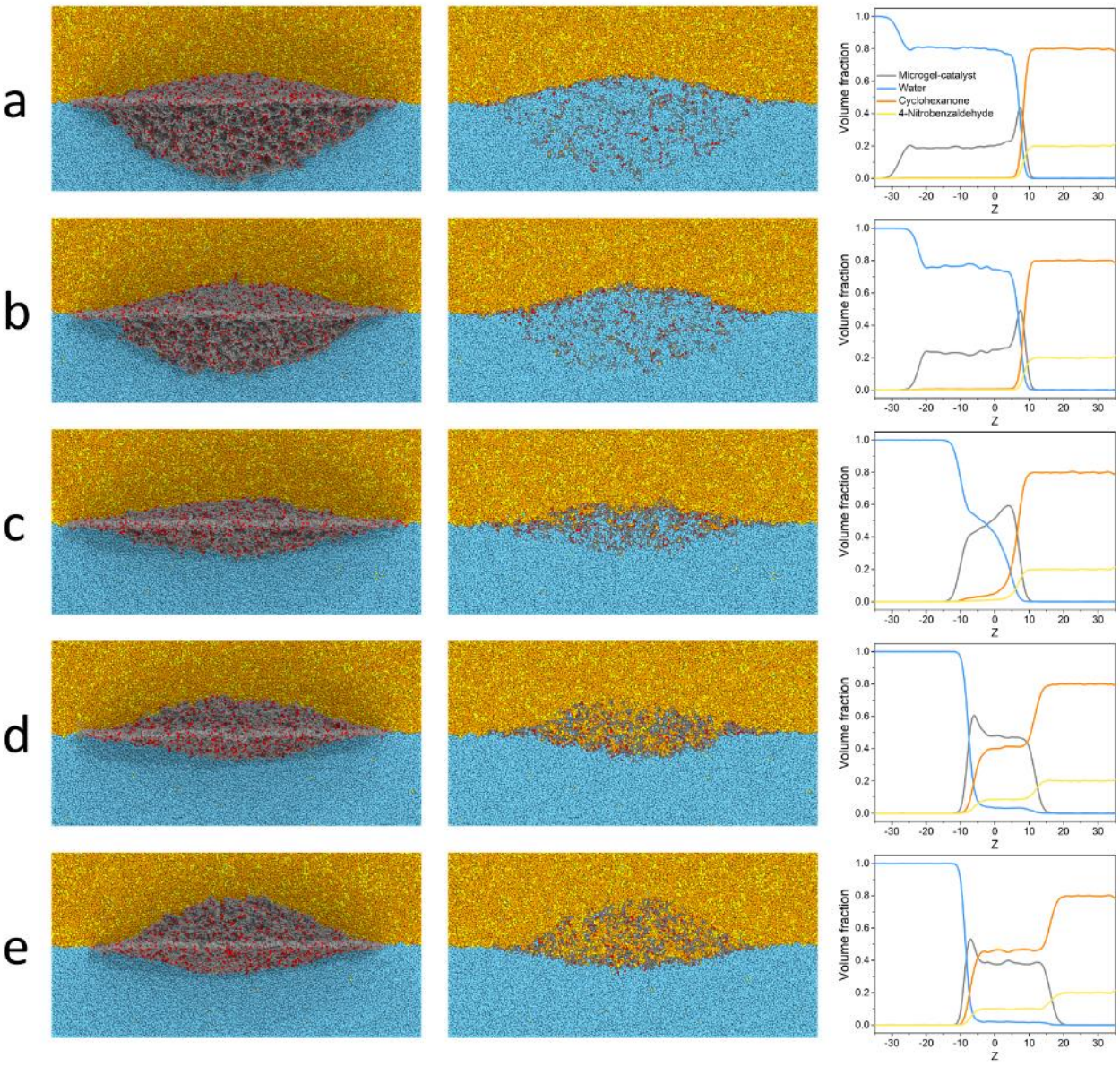

Figure S6. Side views of the adsorbed microgels (left column), cross-section of the microgels through the centre of mass and of PNIPAM (grey), L-proline (red), *4*-nitrobenzaldehyde (yellow), cyclohexanone (orange) and water (blue) beads (middle column), concentration profiles along the normal to the interface, z-axis (right column). The lines of different colours correspond to the concentrations of respective types of beads. Different rows correspond to different temperatures: T = 25 °C (a), T = 30 °C (b), T = 35 °C (c), T = 40 °C (d) and T = 45 °C (e).

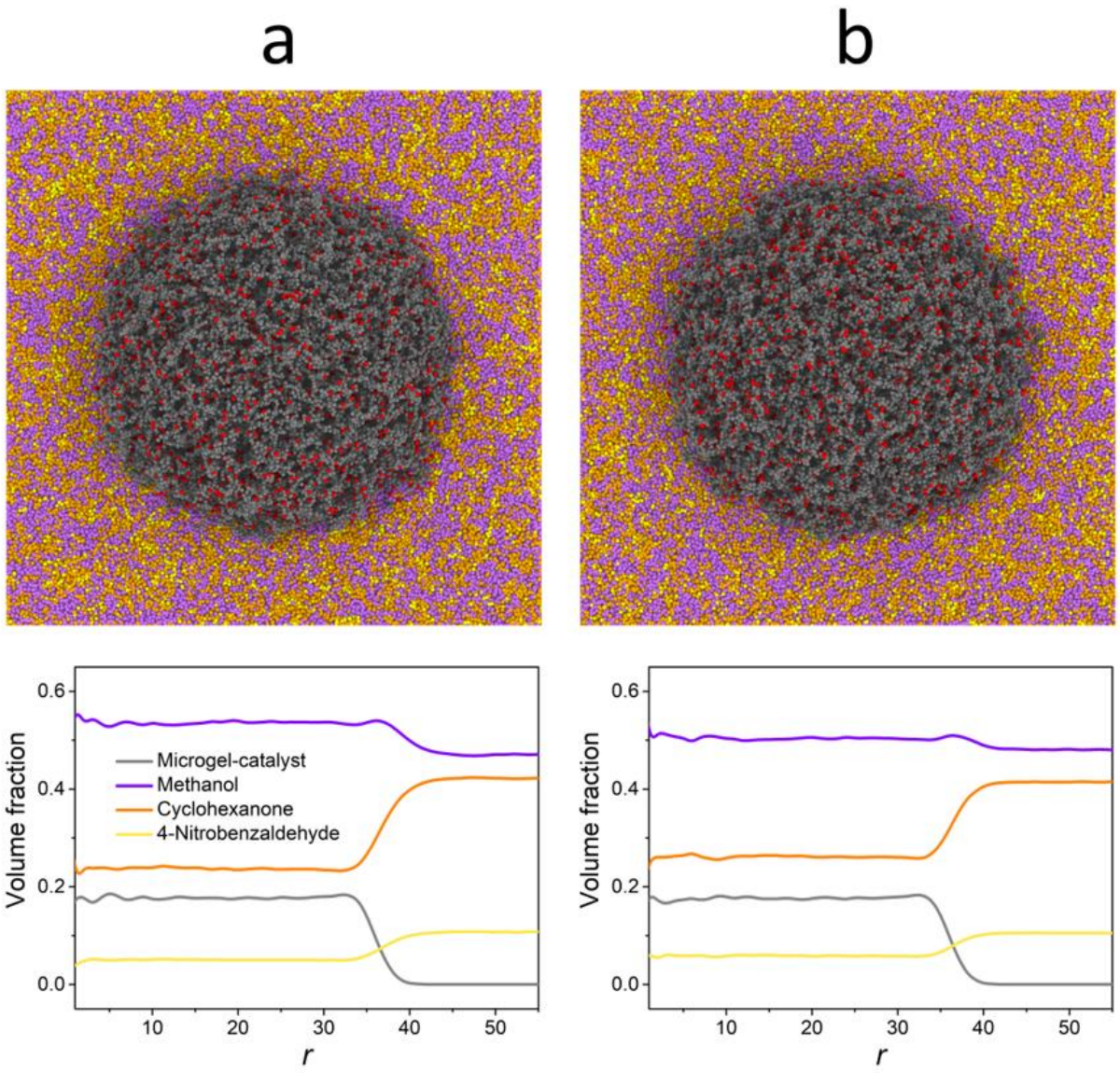

Figure S7. Snapshots of single microgels in methanol-reagents mixture (upper row) and corresponding radial concentration profiles from microgel's centre of mass (lower row) at T = 25 °C (a) and T = 45 °C (b). The lines of different colors correspond to the concentrations of respective types of beads: PNIPAM + L-proline (grey), 4-nitrobenzaldehyde (yellow), cyclohexanone (orange) and methanol (purple).

References

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