

Supplementary Information to „Mussel-Inspired pH-triggered Reversible Foamed Multi-Responsive Gel – the Surprising Effect of Water”

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Experimental Details

Materials

N-Isopropyl acrylamide (NIPAM, 98%, Aldrich) was recrystallized from a 65:35 (v/v) mixture of hexane and benzene before using. Dimethylformamide (DMF) was distilled under sodium wire and calcium chloride respectively and bubbled by nitrogen to remove their dissolved oxygen. Methylene chloride (CH₂Cl₂) was refluxed over CaH₂ and distilled. Dopamine methacrylamide (DMA) was synthesized based on Glass *et al.*¹ and azobisisobutyronitrile (Aldrich), sodium tetraborate, diethyl ether, and boric acid were purchased from Daejung Co and used as received. All aqueous solutions were prepared with ultrapure water purified with a Milli-Q UV-Plus water purification system (Millipore, Bedford, MA). The water had a resistivity of >10¹⁸MΩcm⁻¹.

Synthesis of poly (dopamine methacrylate-co-N-isopropyl acrylamide) (p(DMA-co-NIPAm))copolymer

Synthesis of poly (dopamine methacrylate-co-N-isopropylacrylamide) (p(DMA-co-NIPAm)): The recrystallized N-isopropylacrylamide (5.0 g, 42 mmol) and 40 mg of azobisisobutyronitrile were added to a 50 ml round bottomed flask that contain 30 ml dimethylformamide. The dopamine monomer (2.3 mmol, 514 mg) were added to the flask. The solution was bubbled with nitrogen for 30 minutes. Polymerization was carried out for 6 hours at 65°C, after which the mixture was viscous. The solution was added drop wise into 400 ml of diethyl ether with stirring to precipitate the synthesized copolymer. The obtained polymer was dissolved in methylene chloride and precipitated in diethyl ether twice to

have pure copolymer. The purified polymer was dried overnight in a vacuum oven in room temperature. The final products have white to light yellow color. The purified copolymer was obtained with 87% yield. The products were characterized by ^1H NMR, δH (400 MHz, DMSO, 273 K) 6.5-6.8 (3H, m, Ph), 3.7 (1H, s, $\text{CH}-(\text{CH}_3)_2$), 3.4 (2H, q, $\text{CH}_2-\text{NHC}(\text{O})$), 2.6 (2H, m, $\text{CH}_2\text{-ph}$), 1.9 and 1.4 (m, repeating units of the two monomers), 1.1 (6H, d for $\text{CH}_3\text{-CH}$ and 3H, s for $\text{CH}_3\text{-C}$). Further experimental details are given elsewhere.²

Synthesis of foamed gels in organic solvent

10 wt.% of the copolymer with ($M_n = 2100$ g/mol and $M_w/M_n = 2.1$, based on PS-standard) were dissolved in dried DMF (dimethylformamide). $\frac{1}{2}$ eq. of NaBH_4 was added followed by vigorous stirring. Then 2N NaOH was added drop wise until the pH was about 9 and the sample was gelified. At the same time H_2 -bubbles appeared.

Characterization Techniques

^1H and ^{11}B NMR (400 MHz) spectra were recorded in deuterated dimethyl sulfoxide (DMSO) or deuterium oxide (D_2O) with a Bruker Spectrometer AM 400 (400 MHz). The molecular weights and molecular weight distribution, M_w/M_n of copolymer samples were determined by size exclusion chromatography SEC (PL-GPC110, Polymer laboratories) equipped with refractive index detector and combination of columns with the effective molecular weight ranges from 200 to 25000 grams/mol. Linear polystyrene standards were applied for calibration in 40 °C.

The mechanical properties of the hydrogels were tested using a rheometer (Malvern KinexusPro) using a 20 mm parallel plate geometry (gap=0.3...0.6 mm) and a 20mm/1° cone/plate geometry for gels and solutions, respectively. A solvent trap with a liquid seal around the moving part of the geometry was used to ensure a solvent saturated environment. Solvent loss during testing is negligible due to the typical solvent trap, which would allow measurements with significantly more volatile solvents (e.g. acetone) for several hours.

The frequency dependence of storage $G'(\omega)$ and loss modulus $G''(\omega)$ were assessed in the linear-viscoelastic regime at a deformation $\gamma_0 = 5\%$ and found to be negligible (cf. Fig. S2). The strain-dependence and self-healing were determined from a strain sweep ($\gamma_0 = 0.1...300, 1000, 3000\%$, $\omega = 10 \text{ s}^{-1}$) followed immediately by linear viscoelastic monitoring of the mechanical property recovery (stress $\tau_0 = 10$ Pa $\rightarrow \gamma_0 \approx 0.3...1.5\%$) for 1000 s.

As the catechol groups, randomly distributed along the chain of copolymer, are intrinsically more hydrophobic than NIPAM, it is expected that the LCST of copolymer in aqueous solution is lower than LCST of PNIPAM (32.9°C^3) as shown in Figure S11, which presents a heating scan with $q = 2 \text{ K/min}$, $\omega = 0.16 \text{ s}^{-1}$, and $\gamma_0 = 1\%$ indicating that the LCST has its onset at 17°C .

The hydrophobicity of the copolymer is strongly depends on external stimuli of temperature and pH of aqueous solution and water/DMF-ratios. As all of these factors influence lead to a complex LCST-dependence, which will be discussed in a follow-up paper, all isothermal experiments were performed at 10°C to avoid any influence of the LCST. The LCST is only present in H_2O -containing systems, while DMF-solutions behave like regular polymer solutions.

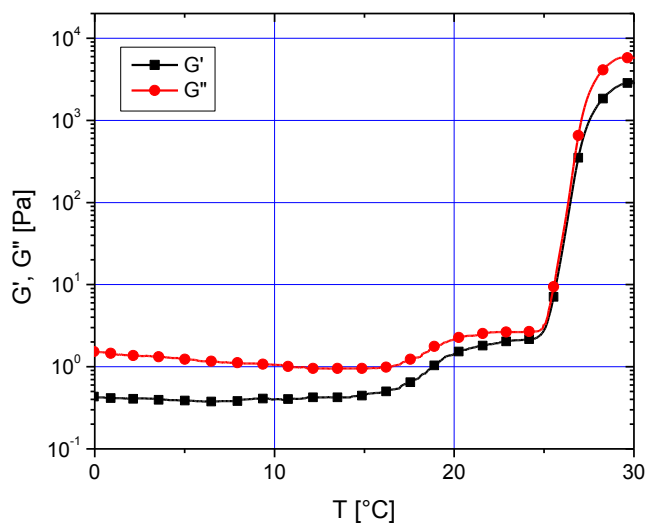


Figure S11: Temperature ramp of a solution of DMA 5% in H₂O (without ions), $q=2$ K/min, $\omega=0.16$ s⁻¹.

Oscillatory shear testing of gels as a function of frequency was performed at constant strain $\gamma_0=1\text{...}5\%$. Figure S12 shows the almost ideal rubbery behavior only having a very small frequency dependence. This is typical for gels having very few dangling chain ends and macroscopically also can be detected as ringing of the gel, when tapping it. While the ringing is quite strong for the anhydrous gel Figure S12a, adding some water changes the behavior to a lower modulus and a higher damping (Figure S12b), which weakens the ringing significantly.

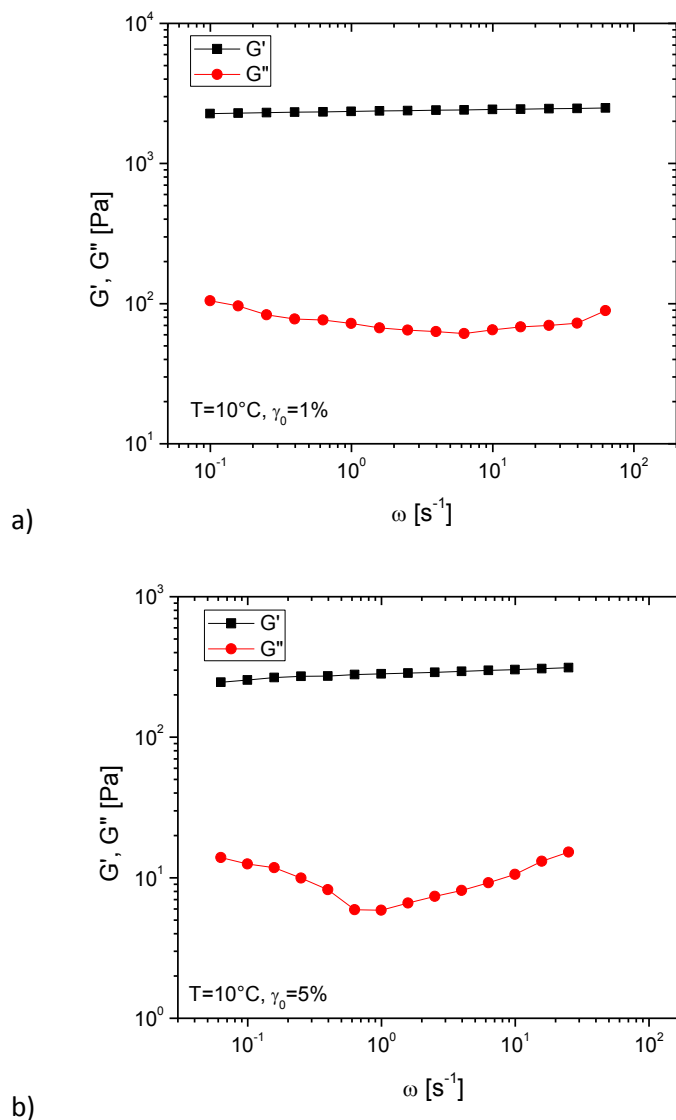


Figure S12: frequency dependence of the mechanical properties of an anhydrous gel of 10 wt.% DMA5% a) in DMF, b) in DMF with added humidity from humid air (ca. 90% DMF, 10% H_2O).

Self-healing tests were performed by straining each gel from 0.1% to a set maximum deformation of 100, 300, 1000, or 3000% ($\omega=10$ s^{-1}) immediately followed by linear conditions ($\tau_0=10$ Pa $\rightarrow \gamma_0 \approx 0.3 \dots 1.5\%$, $\omega=10$ s^{-1}) while monitoring the recovery of the storage and loss modulus (G' , G''). The self-healing test was repeated on the same sample to ensure that the self-healing persists or to monitor further damage to the sample.

Figure S13 show the effect of adding HCl-gas to an anhydrous gel (10 wt.% DMA 5% with $\frac{1}{2}$ eq. $NaBH_4$). In the beginning a gel with bubbles is obvious, which are freed by the dissolution of the gel going from top to bottom (Figure S13b), which after about 25 min leads to a fully degelated sample (Figure S13c).

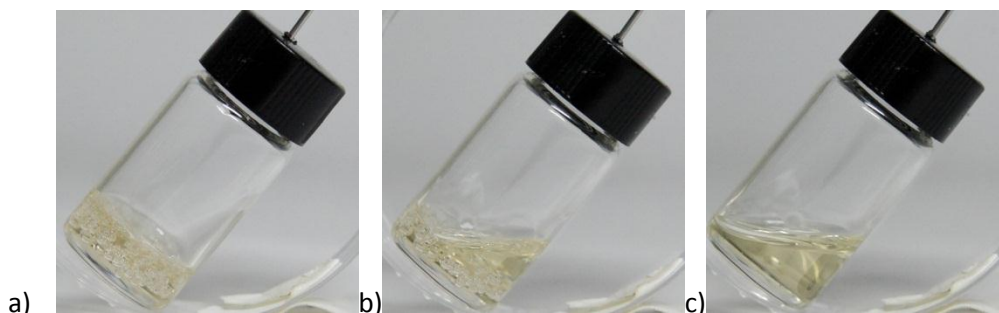


Figure S13: Images of anhydrous DMA 5% in DMF with 0.5 eq. NaBH_4 . a) before adding HCl-gas, b) after 15 min, c) after 25 min.

In order to detect the reference peak and the exact distance between NaBH_4 - and H_3BO_3 -peaks, a boron-NMR measurement for solution of H_3BO_3 and NaBH_4 in DMSO-d_6 was performed (Fig. S14). The chemical shift of the boron species in the solution containing high amount of NaBH_4 was determined to be -37.3 ppm. So the peak of boric acid (H_3BO_3) at 0.3 ppm is chosen as main reference. The difference in height of the peaks of H_3BO_3 and NaBH_4 is due to the larger amounts of NaBH_4 in solution. The high concentration of H_3BO_3 and NaBH_4 is the reason for the broad peak between -10 and -50 ppm (Figure 2) belonging to the boron in NMR tube being almost invisible due to its small relative size.

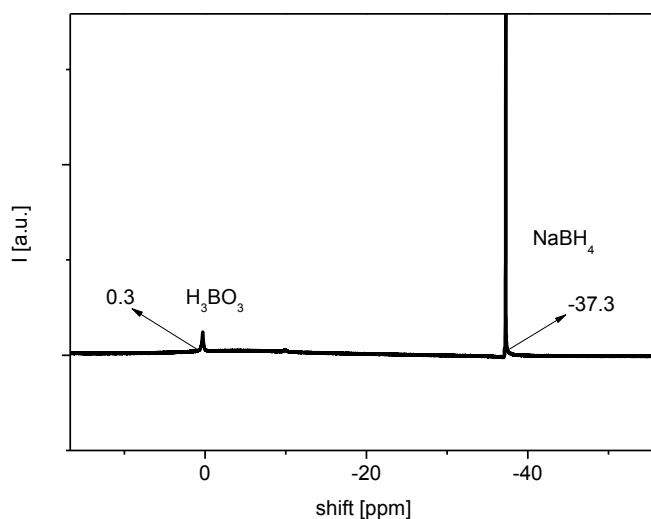


Figure S14: ^{11}B -NMR-data of mixing NaBH_4 and H_3BO_3 in DMSO-d_6

Fig. S15 shows the sample ejected from the rheometer geometry due to a shear deformation of up to $\gamma_0=1000\%$. The about 50% of the sample was broken in small pieces and ejected from the rheometer geometry. Please note that the small trench around the geometry at the outer side of the lower plate is the reservoir for the solvent trap, which saturates the air in the sample chamber.



Figure S15: image of a destroyed anhydrous gel ejected due to high shear ($\gamma_0^{\max}=1000\%$).

References

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