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**Supporting information for the article**

# Photochemically induced formation of adhesive hydrogels from sodium alginate, acrylamide, and iron sandwich complex

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## Author contributions

A.S. Sokolov, V. A. Korabelnikova, D.A. Michurov, D.S. Perekalin – investigation; V.P. Ananikov - supervision, resources, writing – review & editing; V.I. Lozinsky, D.S. Perekalin – conceptualization, writing original draft.

## General

Sodium alginate had the following properties: MM 150 kDa, the viscosity of the 1% aqueous solution 0.63 × Pa·s (23 °C), mannuronic blocks – 30%, guluronic blocks – 20%, and mixed sequence blocks – 50%. All other reagents were purchased from commercial sources (Aldrich, Acros, J&K Scientific, or Vekton) and used as received. All aqueous solutions were prepared using deionized water. Visible light irradiation was carried out using a household LED lamp (15 W, 1300 Lumen, 4000 K color temperature). Green laser pointers (1W) can also be used. Red-light irradiation was carried out using incandescent lamp (100 W) together with 600−800 nm optical glass filter. $^1$H NMR spectra were measured using a 60 MHz Benchtop NMR spectrometer (Nanalysis 60e). UV-visible spectra were recorded from aqueous solutions using a Varian Cary 50 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) were performed using a DSC-60 Plus instrument (Shimadzu) under argon flow.

### Synthesis of iron complex $[(C_5H_5)Fe(toluene)]BF_4$ (1).

Complex **1** was prepared according to the published procedure (*Helv. Chim. Acta* **2022**, *105*, e202100246). For convenience of the readers, we copy it here. A mixture of ferrocene (2.5 g, 13 mmol), ground $AlCl_3$ (6.9 g, 52 mmol), and Al powder (0.4 g, 13 mmol) was suspended in toluene (40 ml) and flushed with argon. The mixture was efficiently stirred at 85 °C for 2 hours, then aqueous HCl (0.5 ml, ≈12 M) was added dropwise, and stirring at 85 °C continued for additional 3 hours. Alternatively, $TiCl_4$ (1 ml, ca. 9 mmol) can be added instead of HCl (following the published procedure: *Inorg. Chim. Acta*, 2004, **357**, 1909), which led to a cleaner mixture during the isolation stage. After cooling to room temperature cold water (40 ml) was carefully added (exothermic hydrolysis occurred). The aqueous layer was separated and the organic layer was additionally extracted three times with water (100 ml). The combined aqueous extracts were treated with a concentrated solution of $Na_2CO_3$ until the beginning of the precipitate formation. Then, $NaBF_4$ (2.2 g, 20 mmol) was added, the mixture was stirred for 1 hour, and the water was evaporated by a rotary evaporator. The solid residue was transferred into a Soxhlet apparatus and extracted by acetone for 4 hours. Evaporation of acetone and triturating the residue with ether gave a dark yellow crystalline powder of the complex **1** (2.82 g, 72% yield). To ensure the absence of iron salts we advise to re-precipitate the product from acetone solution by ether and to store it in the dark. Complex **1** was isolated as tetrafluoroborate salt to ensure high solubility in water (in contrast, a more common $PF_6$ salt is insoluble in water). $^1H$ NMR (400 MHz, $D_2O$): δ 6.20 (bs, 5H, Ph), 5.00 (s, 5H, $C_5H_5$), 2.53 (s, 3H, Me). $^{13}C$ NMR (100 MHz, $D_2O$): δ 103.53 (ipso-Ph), 88.35 (Ph), 87.20 (Ph), 85.92 (Ph), 76.47 ($C_5H_5$), 19.97 (Me).

### Photochemical formation of iron alginate

Typically, complex **1** (66 mg, 0.22 mmol) and $K_2S_2O_8$ (30 mg, 0.11 mmol) were dissolved under stirring in water (1.5 ml). The undissolved admixtures (if present) were removed by centrifugation and the clear yellow solution was added dropwise to the stirred 3% aqueous solution of sodium alginate (3 ml, which corresponds to 90 mg of dry sodium alginate, 0.45 mmol of carboxylic groups). The resulting solution was placed in a vial and was irradiated using a household LED lamp (15 W, 1300 Lumen) from 10 cm distance to give a stable amber-colored hydrogel after 2 min. The irradiation was continued for 30 min to ensure the complete reaction (Figure S1). The resulting gel sample was soaked in distilled water for 10 min and blotted with filter paper. The freshly prepared hydrogels have slight characteristic odor of unsaturated hydrocarbons (cyclopentadiene and toluene), which disappears after several hours. One of the referees has noted that aggregation cyclopentadiene and toluene into oil droplets may influence the porosity of the hydrogels.

Other samples were prepared similarly by using corresponding amounts of complex **1** and $K_2S_2O_8$ (Table S1). Note, that in the case of the **FeAlg1** sample, complete dissolution of reagents was problematic due to high concentration. This may have contributed to the lower homogeneity of the **FeAlg1** samples.

Irradiation of similar solutions without $K_2S_2O_8$ initially gives green $Fe^{2+}$-hydrogels, which are then slowly oxidized to amber $Fe^{3+}$-hydrogels by atmospheric oxygen (Figure S2).

**Table S1**. Ratio of reagents for preparation of iron alginate hydrogels.

| Hydrogel | Iron: carboxylate molar ratio | Complex **1** | $K_2S_2O_8$ | Water to dissolve **1** and $K_2S_2O_8$ | 3% solution of sodium alginate |
|---|---|---|---|---|---|
| **FeAlg1** | 1:1 | 132 mg | 60 mg | 1.5 ml | 3 ml |
| **FeAlg2** | 1:2 | 66 mg | 30 mg | 1.5 ml | 3 ml |
| **FeAlg3** | 1:3 | 44 mg | 22 mg | 1.5 ml | 3 ml |
| **FeAlg4** | 1:4 | 33 mg | 15 mg | 1.5 ml | 3 ml |

**Figure S1**. UV-vis monitoring of the photochemical reaction of aqueous sodium alginate (2%) with complex **1** (1.5%) and $K_2S_2O_8$ (1%) in a quartz cuvette (1 mm optical path). The general increase in the absorption with time is mainly due to the light scattering, and not to the specific absorption of the gel. Minimal changes between spectra after 20 min and 30 min of irradiation indicate the end of the reaction.

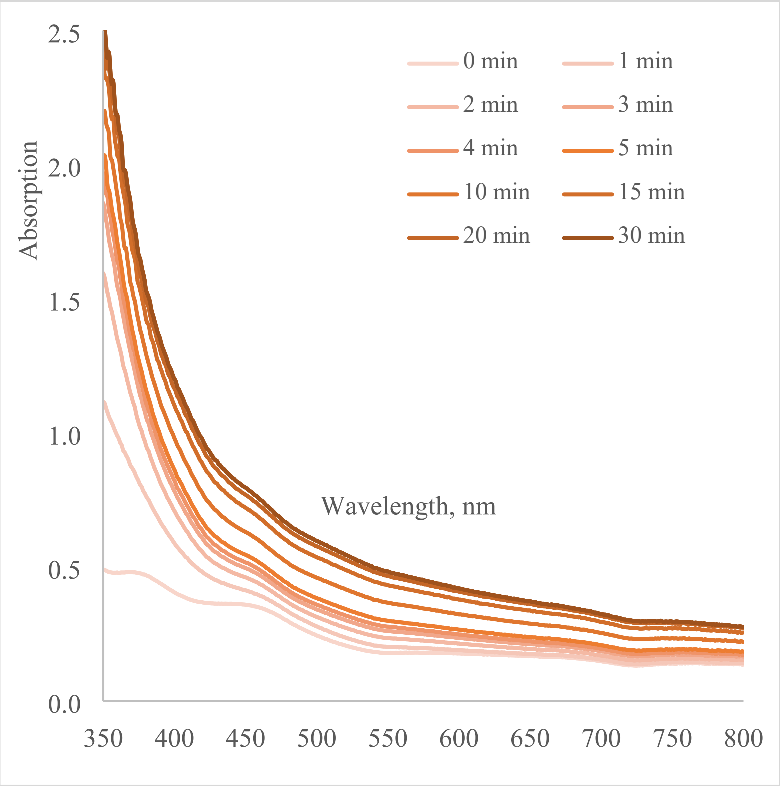


**Figure S2**. Photos of different stages of the photochemical reaction of sodium alginate with complex **1** in the absence of $K_2S_2O_8$. Left: starting yellow solution of sodium alginate (2% by mass) and complex **1** (1.5% by mass; molar ratio of alginate to complex **1** is 2:1) in water (3 ml) before irradiation. Center: green gel containing $Fe^{2+}$ ions, after 1 hour of irradiation; orange color appears in the thin film on the wall due to further oxidation of $Fe^{2+}$ to $Fe^{3+}$ ions. Right: final orange gel containing $Fe^{3+}$ ions, after standing open to air for 24 hours.

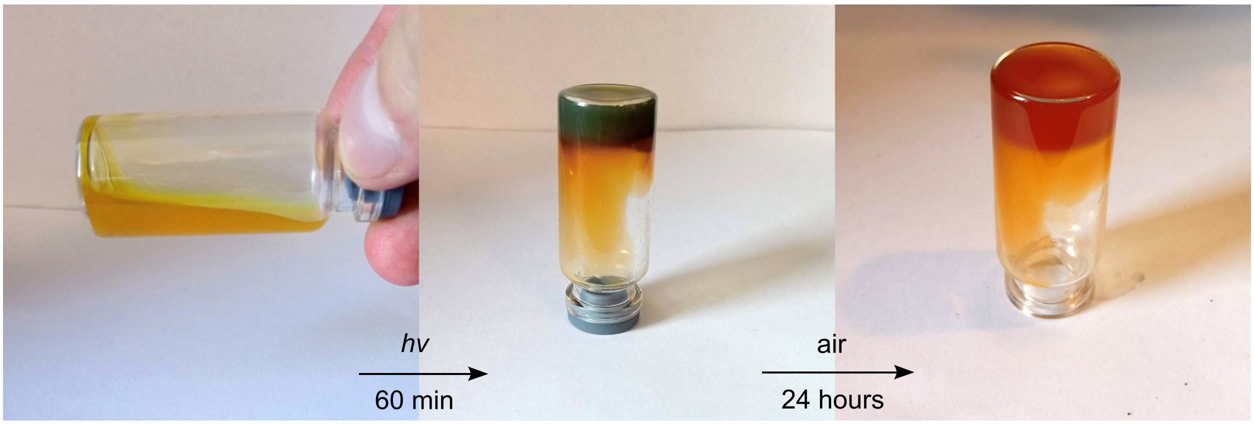
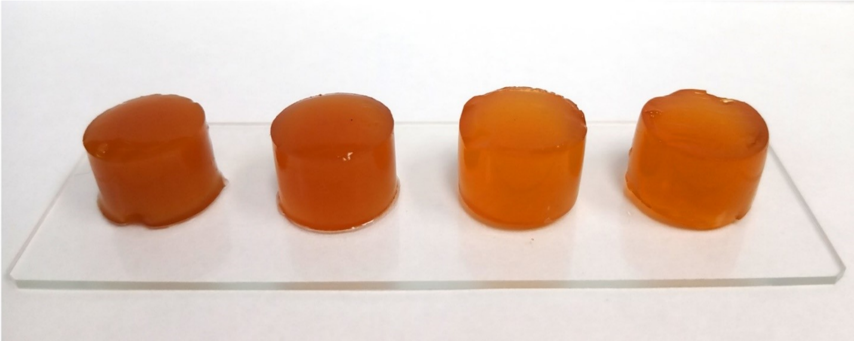


**Figure S3**. Samples of gels. From left to right: **FeAlg1**, **FeAlg2**, **FeAlg3**, **FeAlg4**.



### Dissolution of iron alginate

A sample of **FeAlg2** hydrogel (2 g) was placed in a vial in water (3 ml) and sodium citrate (150 mg) was added. The mixture was gently shaken every 5 minutes. Most of the sample was dissolved after 10 min and complete dissolution was observed after 20 min (Figure S4). Using sodium ascorbate instead of sodium citrate gave similar results.

**Figure S4**. From left to right: Original sample of **FeAlg2** hydrogel; residual sample after 10 min in aqueous sodium citrate; completely dissolved sample after 20 min.

### Swelling studies

Swelling of the hydrogel samples was estimated using the gravimetric procedure. The samples of **FeAlg1−FeAlg4** gels (ca. 1.4 g mass, cylinder shape, 4 samples of each type for averaging the results) were kept in vials in 10 ml water for various periods of time. The swollen samples were transferred to a glass Petri dish and free water was carefully removed from the surfaces by blotting with filter paper, and the sample was weighed. Then the samples were transferred back into vials with freshly changed water for further storage. The changes in the sample weights are given in the Table S2.

**Table S2**. Average mass of samples (in g) used for the swelling experiments.

| Hydrogel | As prepared | After 24h | After 72h | After 6d | After 12d | After 30d |
|---|---|---|---|---|---|---|
| **FeAlg1** | 1.430 | 0.922 | 0.833 | 0.791 | 0.716 | 0.701 |
| **FeAlg2** | 1.372 | 1.285 | 1.313 | 1.387 | 1.459 | 1.497 |
| **FeAlg3** | 1.363 | 1.396 | 1.613 | collapsed | | |
| **FeAlg4** | 1.420 | 1.687 | 2.465 | collapsed | | |

### Mechanical tests

Cylindrical samples of hydrogels (9 mm height, 12 mm diameter, 1 ml volume) were prepared following the general procedure. The values of Young's modulus (E) for the samples were measured in a mode of uniaxial compression at a 0.2 mm/min loading rate using a TA-Plus automatic texture analyzer (Lloyd Instruments, Fareham/Hampshire, UK) by linear approximation of the stress-strain dependence. The tests were performed until 20% deformation (Figure S5). The E values were measured for at least three samples of each type and the results were averaged.

**Figure S5.** Typical stress-strain curves of the samples of **FeAlg1–4** hydrogels.

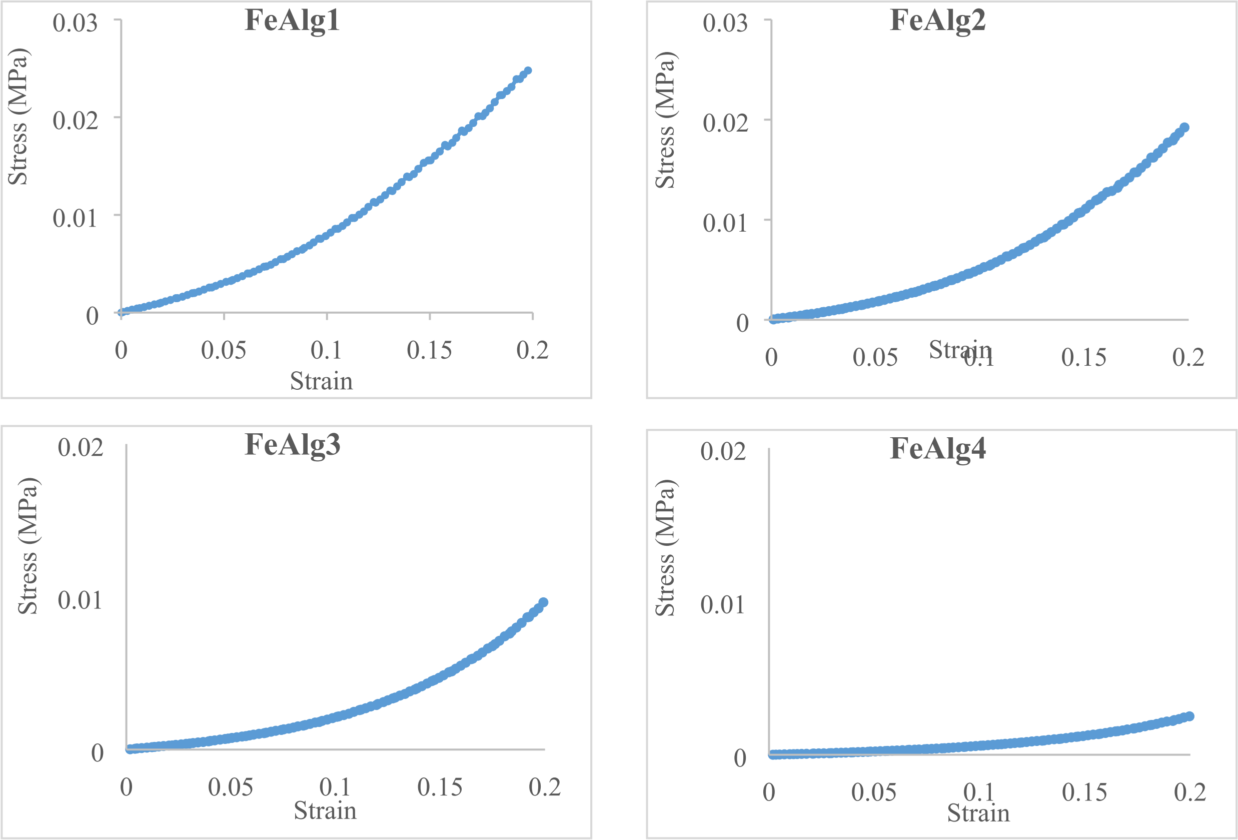
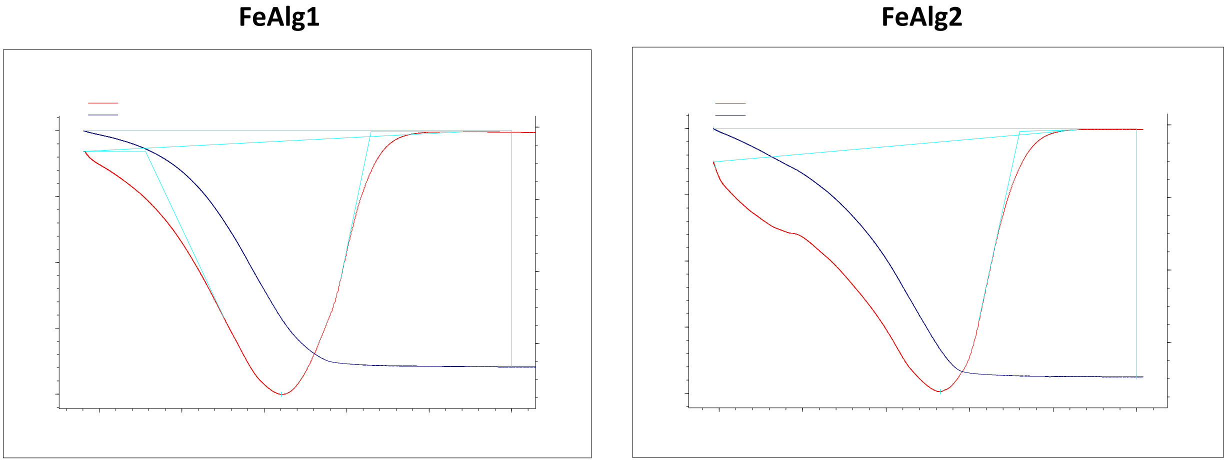
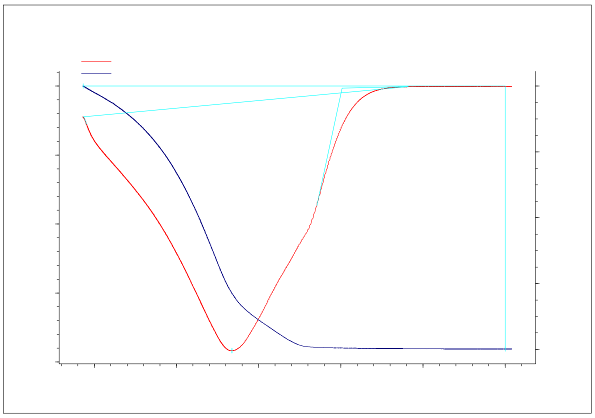


**Figure S6.** Thermogravimetric analysis of the samples of **FeAlg1–4** hydrogels in argon atmosphere at 5 °C min$^{-1}$ heating speed. Blue curves show the loss of mass (water evaporation), while red curves indicate the inverted speed of water evaporation.

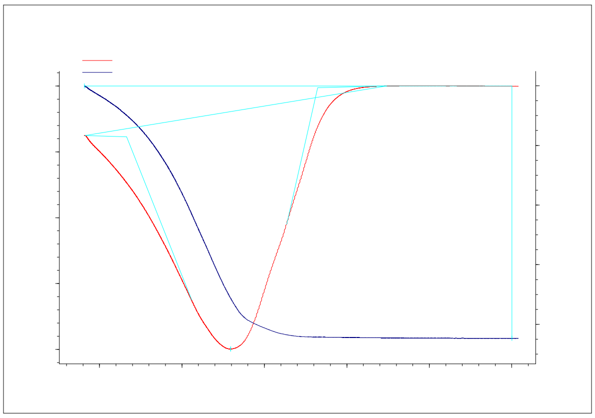

**FeAlg1**

**FeAlg2**

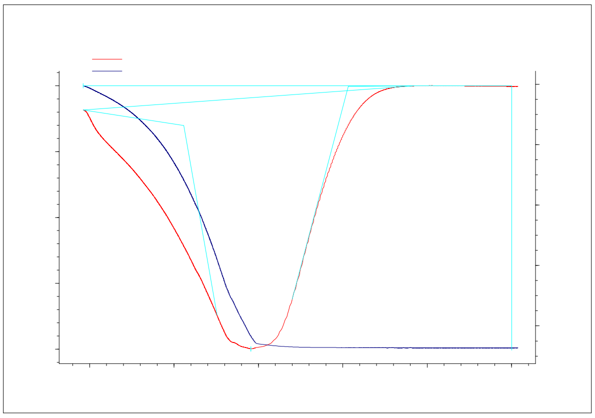
## FeAlg3



## FeAlg4



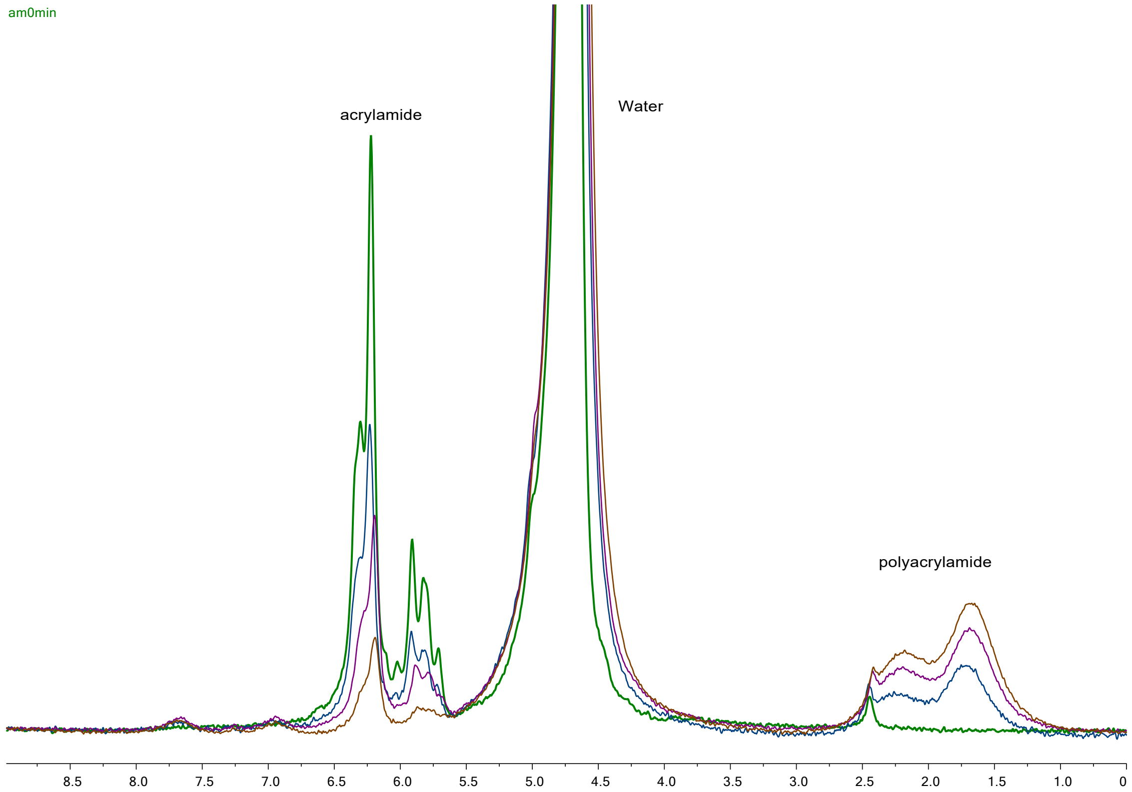
Data for pure water under the same conditions



### Photochemical polymerization of acrylamide

Acrylamide (60 mg), complex **1** (1 mg) and $K_2S_2O_8$ (1 mg) were dissolved in $D_2O$ (0.5 ml) in NMR tube in the dark. The $^1$H NMR spectrum was measured, the solution was irradiated for 20 seconds, and the spectrum was measured again (Figure S7). The tube was then kept in the dark, and the additional spectra were measured after several periods of time.

**Figure S7.** $^1$H NMR monitoring of acrylamide polymerization initiated by complex **1** and $K_2S_2O_8$. Green – initial solution; blue – after 20 seconds of irradiation; purple – after 8 min in the dark; brown – after 20 min in the dark.

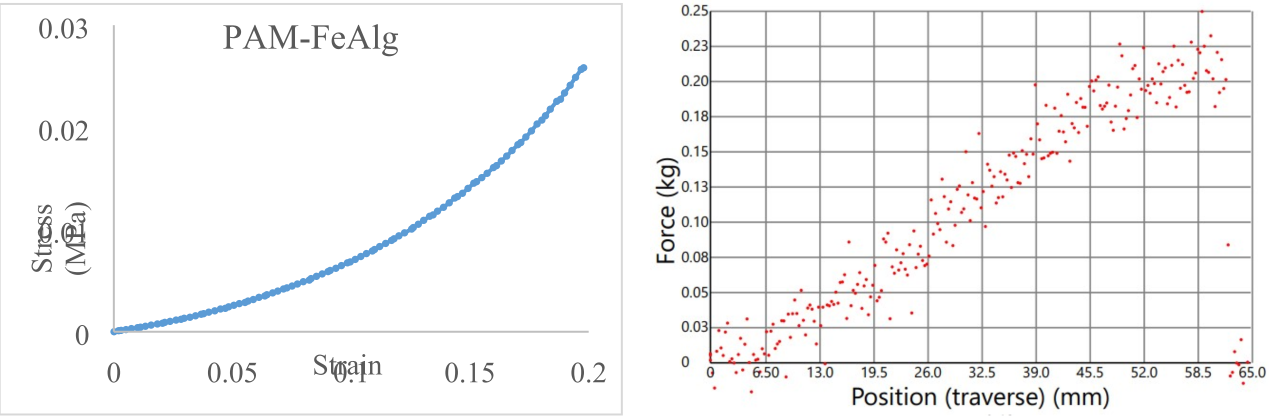


### Preparation of iron alginate-acrylamide hydrogels

Acrylamide (720 mg), N,N'-methylene-bis-acrylamide (3 mg), and complex **1** (60 mg) were dissolved in water (1.8 ml). This solution was added to a stirred 3% aqueous alginate solution (3 ml), followed by dropwise addition of an aqueous solution of $K_2S_2O_8$ (30 mg in 0.4 ml $H_2O$) to give a total of 6 ml of the mixture. It is important to add $K_2S_2O_8$ slowly as the last component to avoid premature polymerization. The vial with the mixture was protected from light by aluminum foil, but the solution can still undergo slow polymerization (gel formation is typically apparent after 24 hours in the dark). The resulting solution was poured into a mold and irradiated by visible light for 30 min in air to give amber transparent elastic hydrogel **PAM-FeAlg**, which was soaked in water (3 times for 10 min) to remove any unreacted components.

The compression tests were carried out as described above using cylindrical samples of hydrogels (9 mm height, 12 mm diameter, 1 ml volume) and a TA-Plus automatic texture analyzer (Lloyd Instruments, Fareham/Hampshire, UK) (Figure S8). The tensile tests were carried out using dog-bone shaped samples of hydrogels (the dimensions of the tested area were 60×11×3 mm) using the tensile machine Tinius Olsen 25ST at the testing speed of 40 mm min$^{-1}$ (Figure S8). All values were measured for at least three samples of each type, and the results were averaged. The Young's modulus (E) of **PAM-FeAlg** was measured as 106±20 kPa (from compression tests) and 90±20 kPa (from tensile tests). The maximal elongation before rupture was 90±10%.

**Figure S8.** Typical stress-strain curves of the samples of **PAM-FeAlg** hydrogel samples. On the left: compression; on the right: elongation (initial sample length 60 mm).



## Adhesion tests

Acrylamide (240 mg), N,N’-methylene-bis-acrylamide (2 mg), and complex **1** (20 mg) were dissolved in water (0.54 ml) making a total of 0.80 g of the solution. This solution was added to a stirred 3% aqueous alginate solution (1 ml), followed by dropwise addition of an aqueous solution of $K_2S_2O_8$ (10 mg in 0.2 ml $H_2O$). It is important to add $K_2S_2O_8$ slowly as the last component to avoid premature polymerization. The vial with the mixture was protected from light by aluminum foil, but the solution can still undergo slow polymerization (gel formation is typically apparent after 24 hours in the dark).

The adhesion properties of the hydrogels were investigated by glass lap shear tests using a Tinius Olsen 25ST tensile machine at the testing speed of 1 mm min$^{-1}$. Flexible clamps were used to avoid non-axial deformation of the samples. The glass slides (L×W×H = 75×25×2 mm) were rinsed with deionized water. Then the freshly prepared solution of hydrogel precursor (40-50 µL) was applied on the surface of one glass slide and covered with another slide, so that the overlap area was equal to 500 mm$^2$ (L×W = 20×25 mm; Figure S9). These slides were irradiated by a household LED lamp (15 W, 1300 Lumen, 4000 K color temperature) for 30 min and then measured immediately or after storage in ambient air or water for a particular time period. The measurements of each type of sample were repeated at least four times (Table S3).

**Table S3.** Results of shear lap tests of samples stored in water.

| Time in water (days) | Shear strength (kPa) |
|---|---|
| 0 | 95±2 |
| 1 | 194±8 |
| 2 | 220±5 |
| 4 | 126±10 |
| 12 | 90±5 |
| 2 days in air | >500 |

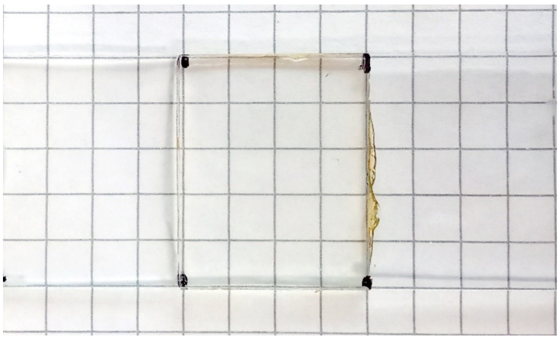


**Figure S9.** Photo of the glued glass slides on the checkered paper demonstrates the transparency of the adhesive.

**Typical force-strain diagrams for lap sheer tests of glues glass samples (overlap area = 5 cm²).**

**Figure S10.** Lap sheer test (overlap area = 5 cm$^2$) of glues glass samples immediately after preparation.

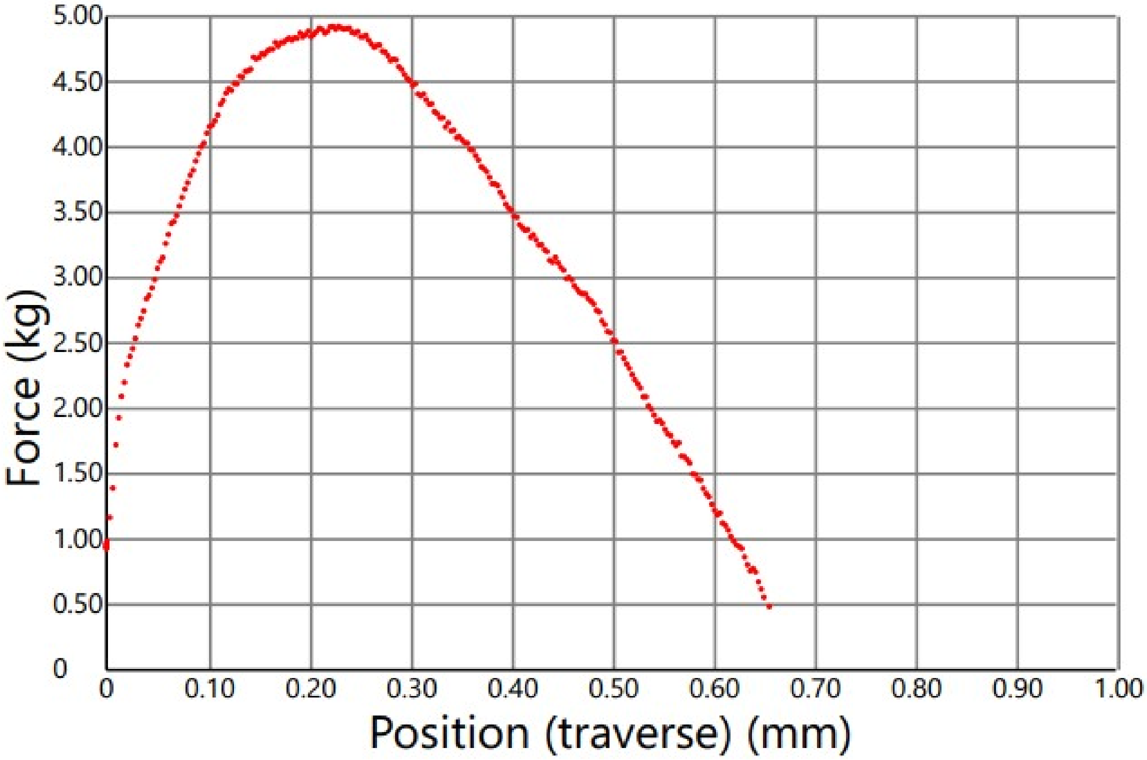


**Figure S11.** Lap sheer test (overlap area = 5 cm$^2$) of glues glass samples after storage for 1 day in water.

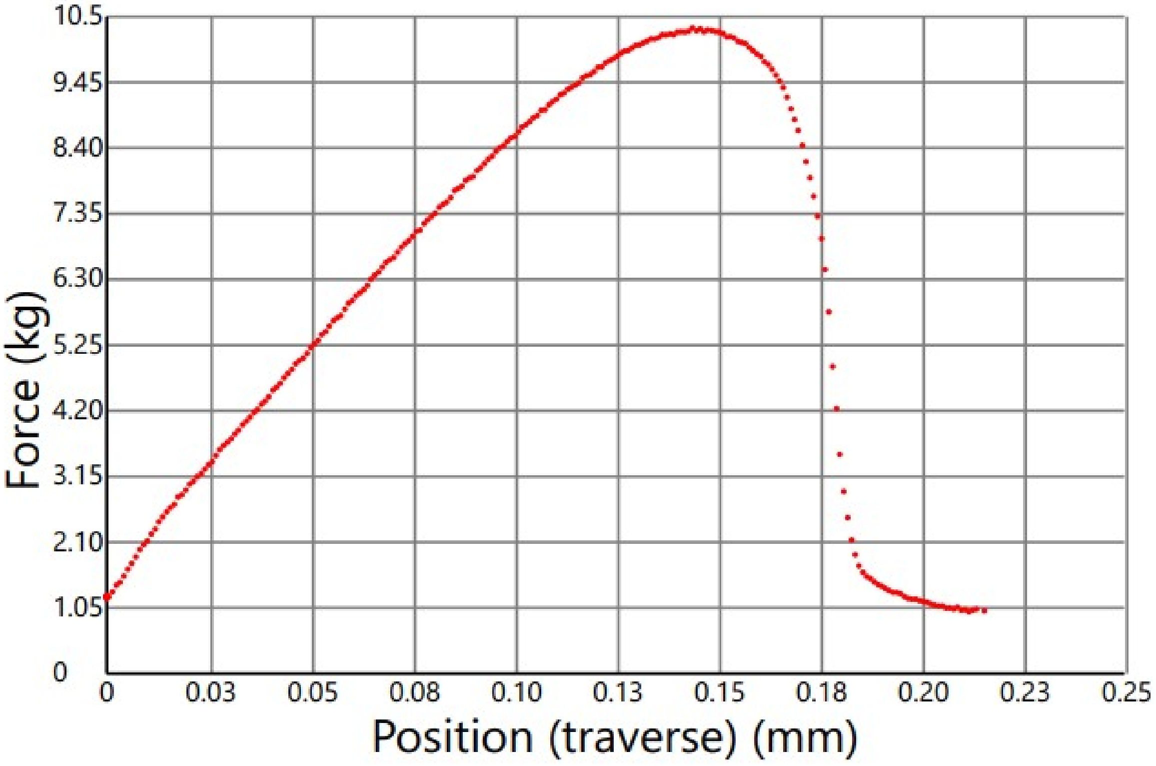


**Figure S12.** Lap sheer test (overlap area = 5 cm$^2$) of glues glass samples after storage for 2 days in water.

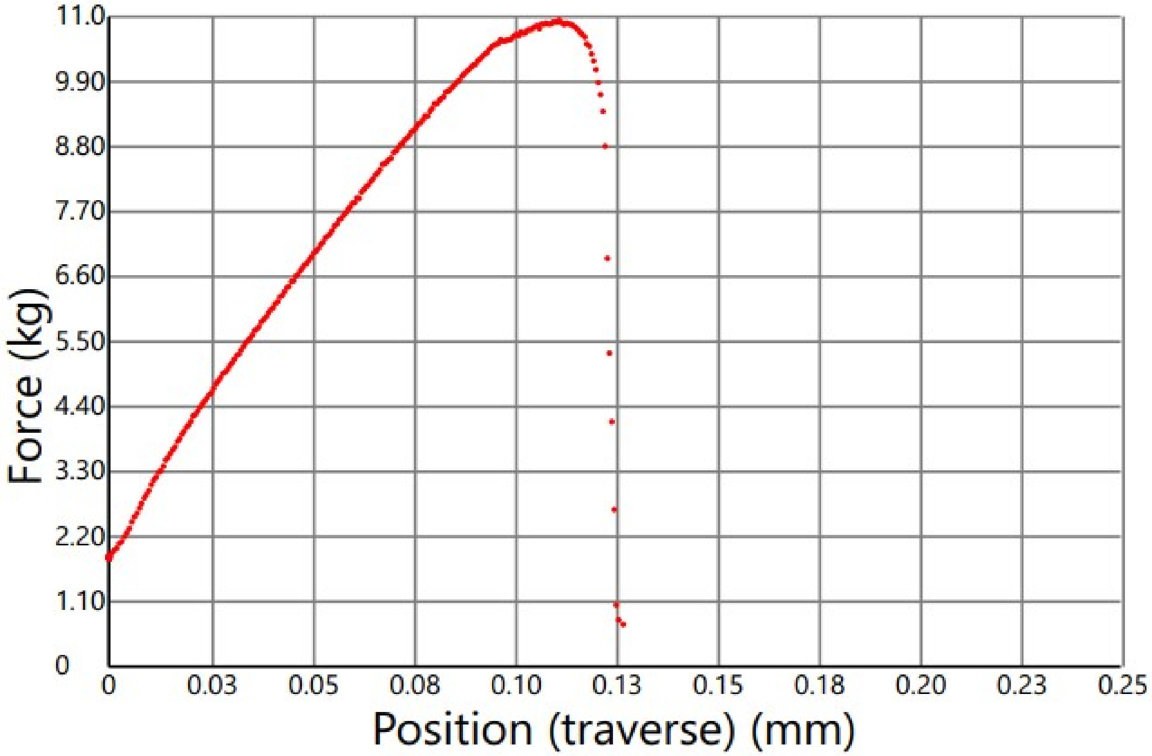


**Figure S13.** Lap sheer test (overlap area = 5 cm$^2$) of glues glass samples after storage for 4 days in water.

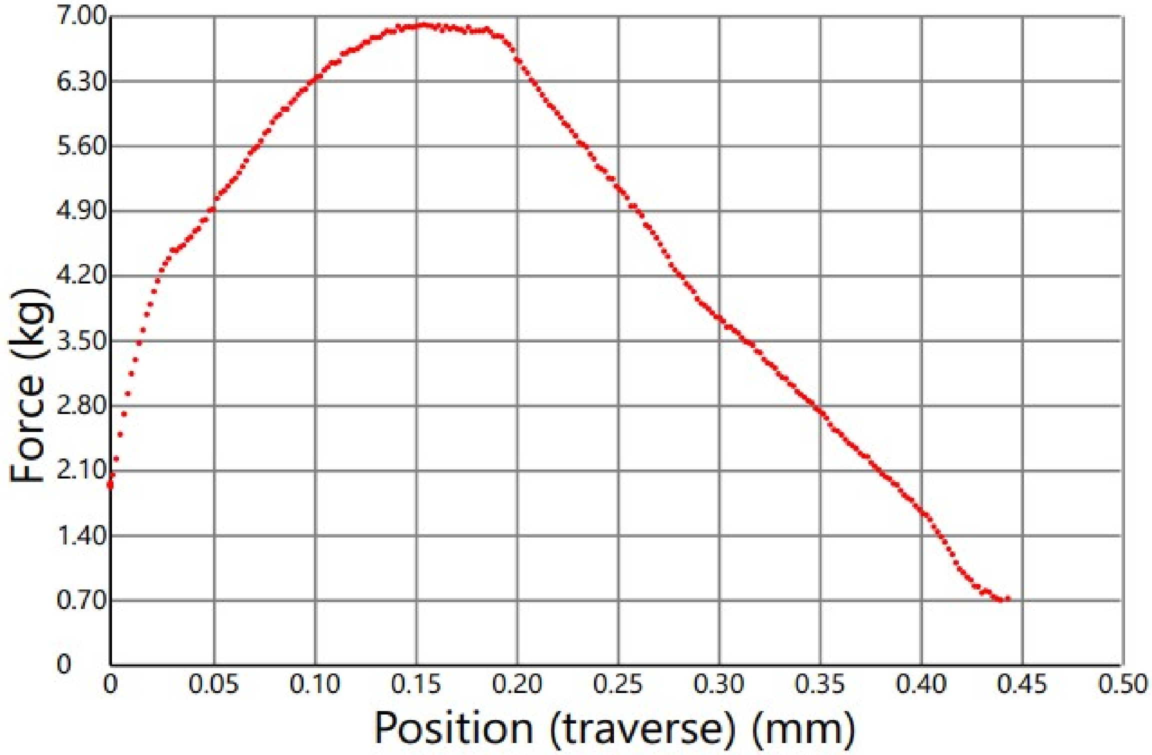


**Figure S14.** Lap sheer test (overlap area = 5 cm$^2$) of glues glass samples after storage for 12 days in water.

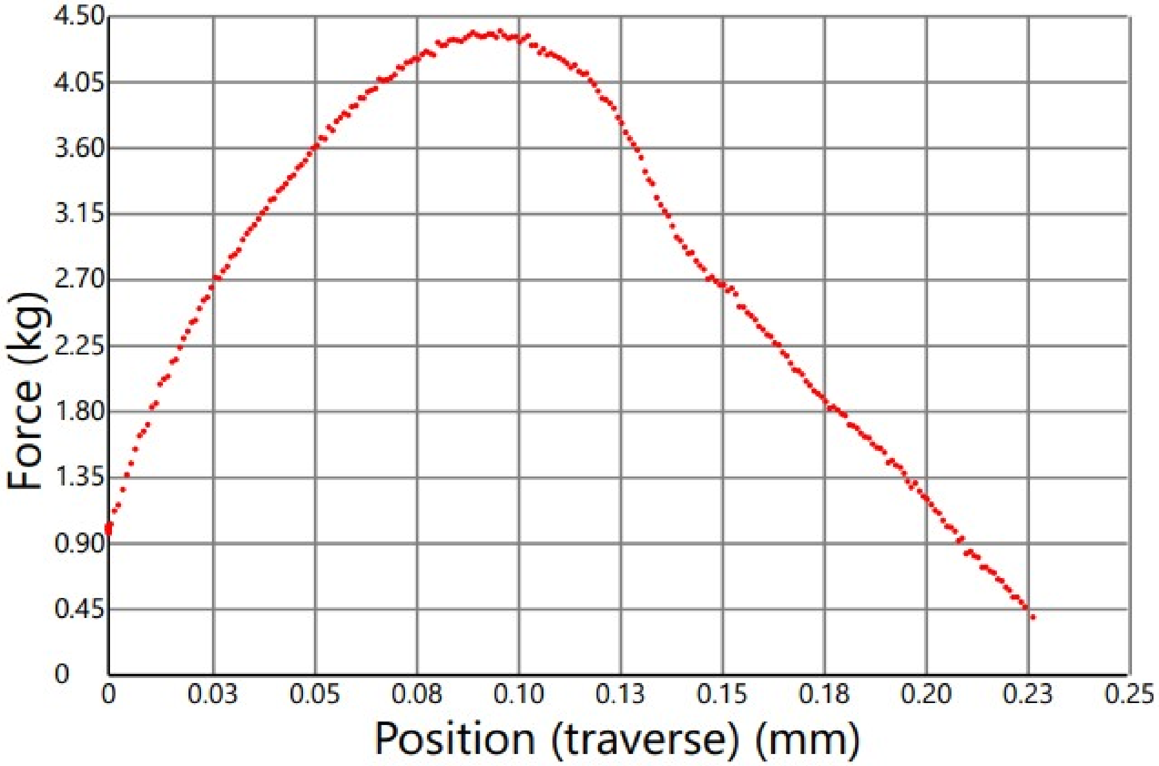


**Figure S15.** Lap sheer test (overlap area = 5 cm$^2$) of glues glass samples after storage for 2 days in air (glass was broken before the colapse of adhesion layer).