Electronic Supplementary Material (ESI) for Soft Matter.
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Electronic Supplementary Material for "Interrelation between swelling, mechanical constraints and reaction-diffusion processes in molecular responsive hydrogels"

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S1 Experimental

Fitting of data from the numerical modelling to experimental data on molecular responsive hydrogels exploited selected examples of DNA-co-AAm and Morpholino-co-AAm hydrogels reported previously[1,2]. For the convenience of the readers, we here summarize core aspects of experimental approach, but refer to the publications for a more in-depth description.

S1.1 Materials

Acrylamide $\leq$ 99% (Aam), N, N'-methylenbis-(acrylamide) $\leq$ 99.5% (Bis), squalane oil, dimethyl sulfoxide (DMSO), 3-(trimethoxysilyl) propyl methacrylate 98% (linker), 1-hydroxycyclohexyl phenyl ketone 99% (HCPK), 2-amino-2hydroxymethyl-propane-1,3-diol (Tris) and 7-[4-(trifluoromethyl)coumarin]-acrylamide (Aam-coumarin) were obtained from Sigma-Aldrich; ethylenediaminetetraacetic acid (EDTA) and sodium chloride (NaCl) were obtained from VWR. DNA-oligonucleotides and Morpholino oligonucleotides with custom base sequence were purchased from Integrated DNA Technologies (IDT, Coralville, U.S.A) and Gene Tools (Philomath, OR, U.S.A), respectively. Some of the oligonucleotides were functionalized with an acrydite group and/or labeled with a fluorescent tag by the manufacturer. All materials were used without further purification. Deionized water with a resistivity of 18.2 mΩ cm (Millipore Milli-Q) was used throughout. The bp sequences of the DNA and morpholino oligonucleotides included in the hydrogels as well as the respective probes used as molecular stimuli to induce dissociation of the physical crosslinks in the resulting hydrogels are shown in Table S1.

S1.2 Pregel and Target Solutions

An aqueous buffer (10 mM Tris, 1 mM EDTA and 150 mM NaCl, adjusted to pH 7.5) was used throughout for preparation of the pregel and target solutions.
Pregel solutions contained 10 wt % Aam (in some cases also including 0.05 mol % Aam-coumarin), 0.6 mol % Bis, 0.13 mol % HCPK and 0.2 mol % of dsDNA or 0.4 mol % of dsMO, dissolved in the buffer solution. HCPK was dissolved in DMSO at 0.1 M prior to addition to the pregel solution and Aam-coumarin was similarly first dissolved in DMSO at 0.11 M.

Table S1: Base sequences of the DNA and morpholino oligonucleotides used for inclusion of a duplex based crosslinked made of a sensing and blocking strand, and target strands designed destabilize the SB-duplexes through a competitive displancement reaction, with baisepair overhangs referred to as lenghts of the toehold. Areas of B and T strands complementary to the S strand are shown in red.

DNA sequences															
S					3'	CCA	CCG	GAC	GCG	GGT	GCC	TA	5'		
B	5'	G	TGC	TAG	CGA	GGT	GGC	CTG	C	3'					
T3					5'	GGT	GGC	CTG	CGC	CGG	TTG	3'			
T7					5'	GGT	GGC	CTG	CGC	CCA	CGA	3'			
T0					5'	TAA	GCT	TGC	CGT	AGG	TTG	3'			
Morpholino sequences															
S					3'	CGT	AAG	TAA	CTA	TCG	ACT	TCA	GTC	GTC	A 5'
B	5'	TT	CAG	TCG	TCA	GCA	TTC	ATT	GAT	AGG	AC	3'			
T2					5'	GCA	TTC	ATT	GAT	AGC	TAA	TGA	CAT	A	3'
T10					5'	GCA	TTC	ATT	GAT	AGC	TGA	AGT	CAG	A	3'
T0					5'	TAT	CGT	AGC	AGG	CTA	CAG	GAC	TCA	A	3'

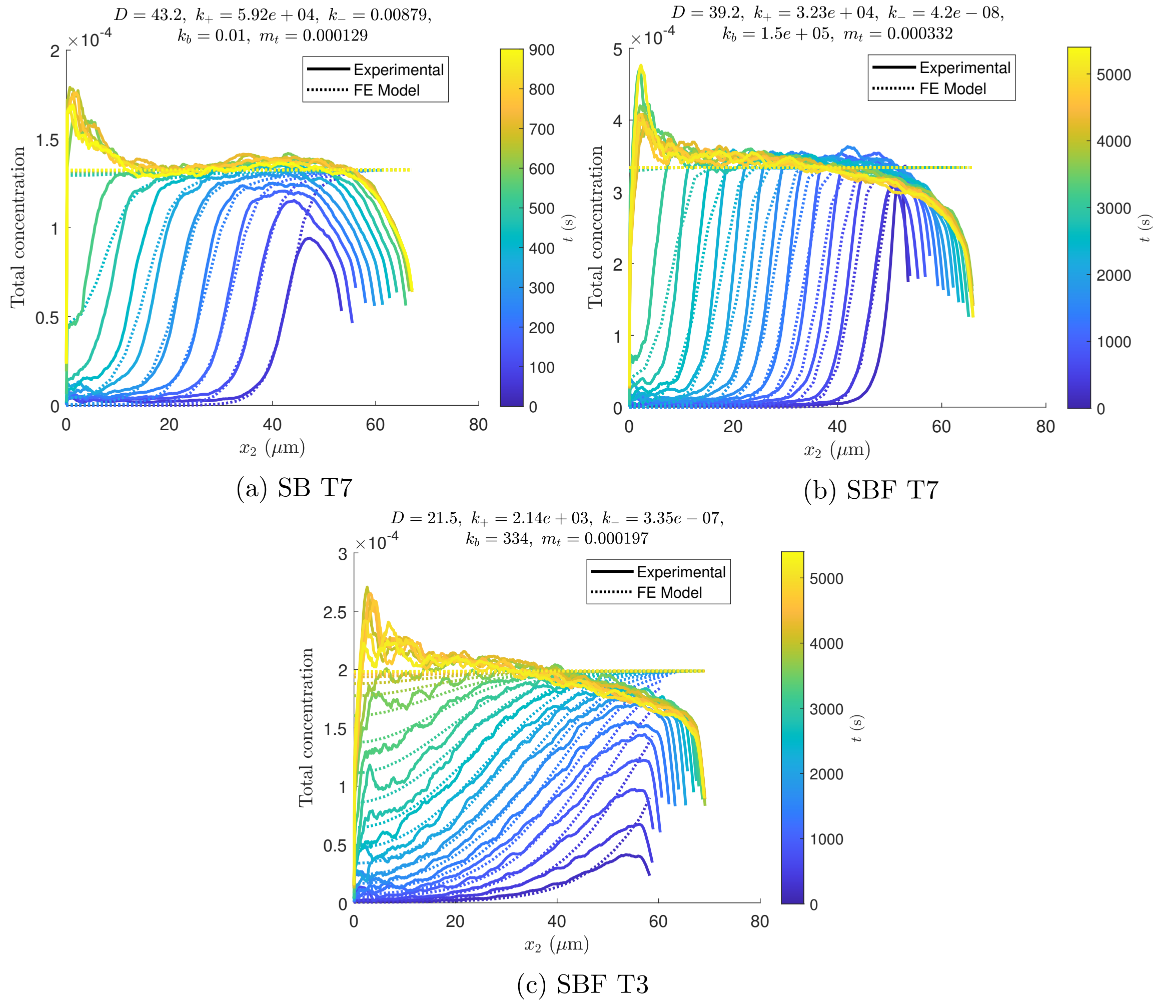
Various types of pregel solutions were prepared. For DNA, 3 different fluorescent labeling strategies were used: SB hydrogels contained the SB duplex without fluorescent dyes, CoumSB hydrogels contained the SB duplex without fluorescent dyes, but the acrylamide network was carrying 0.05 mol % Aam-coumarin dye, and SBF hydrogels contained 10 % of the B strands labeled with Fluorescein dT.
In case of Morpholinos, no dyes were used on the duplex.

Stock solutions of target ssDNA and ssMO were prepared by dissolving the target strands T in buffer to a concentration of 30 (Morpholinos) or 60 μM (DNA). The target solutions consisted of 90 % unlabeled and 10 % labeled oligonucleotides.

S1.3 Gel Preparation

Hydrogels of a quasi-hemispherical shape were prepared at the end face of optical fibers stripped of their coating (SMF-28-J9, ThorLabs, diamter of 125 μm). This setup was used to allow for an interferometric readout of the hydrogel's size. The interferometry is described in detail elsewhere[3], but the results obtained with this readout are not relevant in the present study. The fiber was stripped of its coating and the end of it was cut (Fitel model S323 cutter, Furukawa Electric Co. Ltd., Tokyo, Japan), cleaned with ethanol and functionalized with methacrylate groups by silanization. The silanization consisted of treating the end of the fiber with a 0.1 M HCl solution for 20 minutes, cleaning with ethanol and soaking the fiber for 15 minutes in a 2 vol % solution of the linker dissolved in degassed Mili-Q water at pH 3.5. The end face of the fiber was then cleaned with ethanol and duct tape, in order to remove dust.

The end of the functionalized fiber was inserted into a droplet of a squalane oil saturated with 2.6 mg/mL of HCPK. A small amount of the pregel solution (approx. 0.3 nL) was deposited manually on the end face of the fiber with the use of a pipette while inspection the set-up using a stereo microscope. The polymerization was then triggered by UV light exposure of 5 minutes. Two different sources of UV light were used for the various experiments: a fiber coupled LED UV source M340F3 with a nominal wavelength 340 nm from ThorLabs or a UV lamp Dymax Bluewave, 50W.



(a) SB T7

(b) SBF T7

(c) SBF T3

Figure S1: Comparison between the experimental and obtained FE total concentration ($c+m_c+m_0$) (M) profiles along the vertical edge of the gel for SB and SBF gels a) SB T7, b) SBF T7, c) SBF T3.

S2 Additional comparisons between experimental data and FE modeling

References

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