Final Report

PD 105270

Title: **Synergetic Chemomechanical Patterns in Deformable Chemically Active Media**

Duration: **2013-01-01 – 2015-12-31 (36 months)**

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Institution: **Eötvös Loránd University**
Research unit: **Institute of Chemistry**

SUMMARY

I made further progress in the construction of synergistic chemomechanical oscillators, beyond the ones operational in the acid region. After returning home from France after 5 years, first, I set up labs for gel synthesis and time-lapse imaging of experiments operated under continuous flow. This was made possible both from the present fund and the equipment donated by the French research group.

Employing the new setup, I assembled a gel oscillator with a non-redox pH-clock reaction, the formaldehyde-sulfite reaction, which produces OH-ions instead of H-ions. An appropriate pH-responsive gel with a swollen to shrunken transition between pH 8.00 to 9.25 was synthesized. For such sharp response in the alkaline region, not only the H-binding functional groups but the initiator couple of the polymerization required proper match. Gels with fast and slow swelling-shrinking responses were synthesized at different network structures by tuning the solvent composition.

As a result, chemomechanical oscillations in a 1 mm gel filament, loaded ten times than its own weight, were sustained over 33 hours with 4h period and between 15 to 11 mm in length.

Thereby, I extended the synergistic concept from acid-producing to base-producing clock-reactions. This progress opened the way towards an enzymatic clock-reaction, the OH-producing urease-urea reaction. This could be the first gel oscillator operating with no permanent inflow and no oscillatory chemical reaction – mimicking biology.

1^{st} year: Setting up of laboratories and shipping of equipment from France

The main aim of the present project was the transfer of intellectual heritage and equipment from the *Nonlinear Structures and Dynamics Group* (Centre de Recherche Paul Pascal, CNRS Bordeaux, France) after the retirement of the last two founding members (especially Dr. Patrick De Kepper's) of the group at the end of the year 2012.

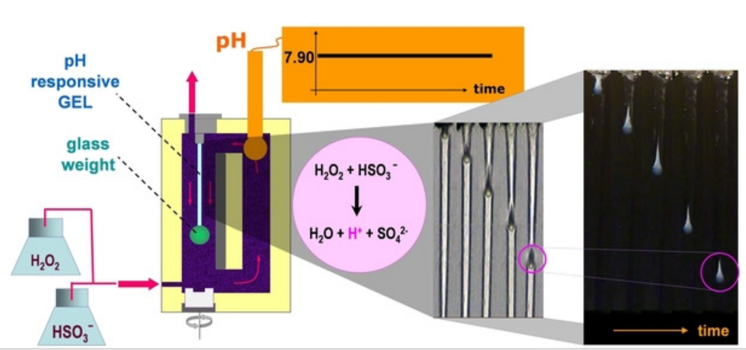
The most important items I received from Bordeaux:

- The continuously-fed stirred reactor with observation windows on two sides, made of Plexiglas, specially designed and machined for the chemomechanical experiments.
- Several precision piston pumps (one per stock solution is required at a time for an experiment), which are not manufactured any more but are the most convenient models for this kind of experiments.

For the complete list and selected photos see the Annex of this Report. The shipping cost of these material was covered from the present grant.

At ELTE, I had two recirculating baths (ultrathermostats) and two balances. Temperature stabilization over day and night within ±0.20 °C is of crucial importance during my chemomechanical experiments, as my gels are not only pH-responsive but the exact pH-window of this response is strongly temperature dependent. Conditions were not ideal, as the laboratories at the Institute of Chemistry are not air conditioned, plus both baths showed problems after prolonged operation (instability or inability of modifying the originally set temperature). This made my work difficult, because only one side of the reactor plus the entering solutions are thermostatted (because of imaging).

Equipment bought from the present grant:
a cooling recirculator to be independent of tap water cooling for the ultrathermostat;
LED light sources for stabilized and powerful illumination; photo cameras with timer and computer-controlled machine vision camera for time-lapse imaging; a pH-meter; two fast magnetic stirrers; an analytical balance.



Scheme of the chemomechanical reactor with time-lapse image series of a downward propagating acid front followed by a contraction front in a long gel filament.

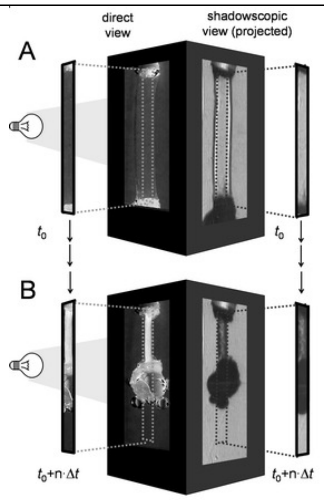


FIGURE Images clarifying why two kinds of observation (direct view + shadowscopic view) are simultaneously necessary and give complementary information

Please, see the Annex for photos documenting the setting up of the laboratories.
The comparative photos show what changes were necessarily made since my arrival till the labs were fully operational.

2nd year: Conceiving a new synergistic chemomechanical oscillator

Autonomous operation of pH-actuators can be achieved in an *ordinary* way when oscillatory chemical reactions are utilized as (internal) pulse generator. In oscillatory chemical reactions the (+) and (–) feedbacks in the mechanism, a necessary condition for oscillations, are both of chemical nature.

Chemomechanical oscillators, with no oscillatory chemical reaction, are feasible based on a *synergistic* concept. Here, oscillations arise from a positive chemical feedback and a negative physical feedback. A clock-reaction induces a pH-switch in a swollen pH-responsive material while the environment is maintained in the unreacted state. The subsequent spontaneous shrinking in size can lead to the “resetting” of the unreacted chemical state in the gel. The “resetting” is the result of a sufficient reduction of the diffusion time of reactants and products between the core of the gel and the steady environment. As a consequence, reswelling to the original size occurs and a new period can start.

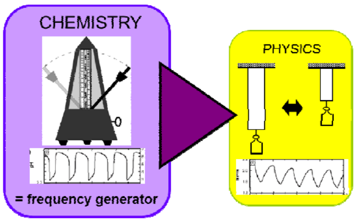
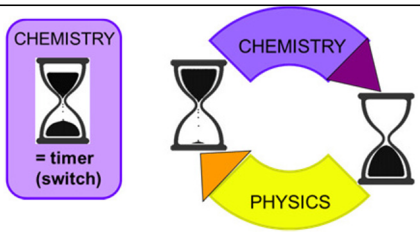
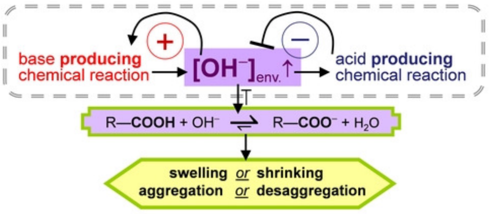
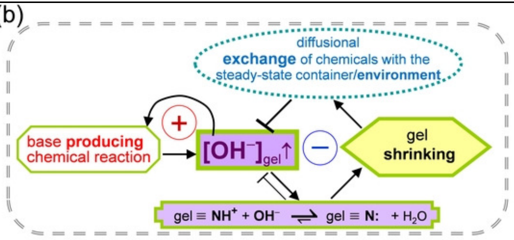
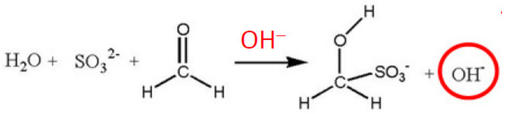
Conventional chemomechanical oscillator	Synergistic chemomechanical oscillator
	
(a) 	(b) 

FIGURE Positive and negative feedback loops in chemically driven (a) and synergistic (b) chemomechanical oscillators. □ stands for activation, □ for inhibition. Grey dashed frame denotes the smallest (sub)system which is oscillatory in itself. Green frames indicate processes that take place within the gel.

The synergistic concept is clear and general, and by now, I have a strategy how to find experimentally the right conditions for a given new chemical reaction.

After the succesful assembly of 3 synergistic chemomechanical oscillators with acid producing pH-clock reactions (bromate–sulfite, BS; iodate–sulfite, IS; hydrogen peroxide – sulfite, HPS), I wished to extend the chemistry to less investigated reactions. A special member of the family of the pH-oscillators is the formaldehyde-sulfite-gluconolactone reaction, which is an *organic-based* pH-oscillator composed of *non-redox* steps. However, the *spiky* oscillations in the formaldehyde-sulfite-gluconolactone oscillatory reaction do not make this reaction particularly appropriate to drive a *conventional* chemomechanical oscillator with high amplitude. On the other hand, utilizing the pH-clock behavior of the formaldehyde – sulfite reaction alone with the synergistic concept is feasible.

The brutto reaction produces hydroxide ions in an autocatalytic-like cascade, thus the clock produces a pH-jump:



$$CH_2(OH)_2 \xrightarrow{slow} HCHO + H_2O \qquad (R1)$$

$$\mathrm{HCHO} + \mathrm{SO_3^{2-}} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{CH_2(OH)SO_3^-} + \mathrm{OH^-} \tag{R2}$$

$$\mathrm{HSO_3^-} + \mathrm{OH^-} \leftrightarrow \mathrm{SO_3^{2-}} + \mathrm{H_2O} \tag{R3}$$

I used the strategy that I worked out during the assembly of my previous synergistic chemomechanical oscillators with the acid clock-reactions. The first step was to explore how the two distinct chemical states (reacted and unreacted states, *that is,* the high pH-state and low pH-state) of the pH-clock reaction shift and shrink in the presence of a buffer. This buffer imitates the H^+-binding functional groups unavoidably present in the gel and responsible for the pH-size response. I chose *N*-methyldiethanolamine (MDEA) which is a water soluble liquid and has $pK_a = 8.52$. Taking into account the pH-jump in the formaldehyde–sulfite clock, *tertiary* amine functions were the appropriate candidates whose degree of protonation would considerably change in this pH-domain.

Buffers cause the two pH-states to near to each other, till the transition becomes continuous. We needed **to experimentally determine the pH values at the limit of stability of the two states**, just before they merge. These limits gave us the pH-values in between the pH-responsive gel should undergo a large enough size-change, thus an important hint for conceiving the gel. In the acid clock-reactions, the shift was usually not symmetrical and not theoretically predictable.

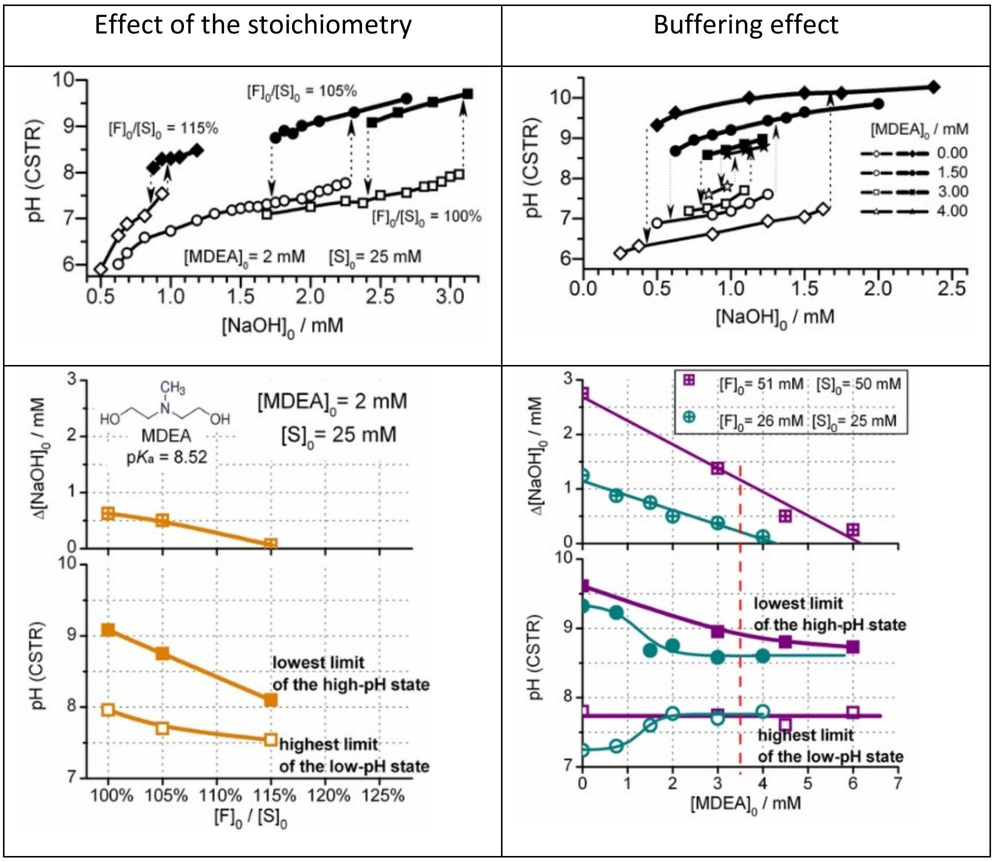


FIGURE Nearing of the two distinct chemical states to each other in a CSTR on the addition of a weak base, *N*-methyldiethanolamine (MDEA), $pK_a = 8.52$. Open symbols: flow-state; full symbols: thermodynamic state. Residence time 8.44 min; temperature 30.0 °C.

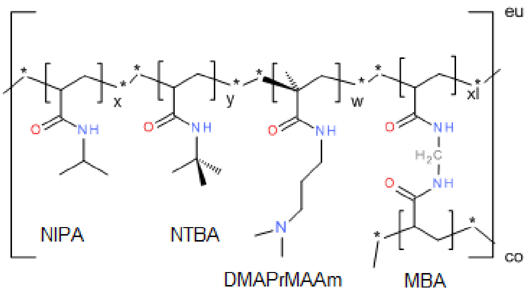
In the formaldehyde–sulfite reaction, the two pH states shift quite symmetrically, roughly from pH 9.3 down to **pH 8.6** and from pH 7.24 up to **pH 7.8**. MDEA **totally buffered** the bistability at **4 mM** and 6 mM concentration at sulfite concentrations of 25 mM and 50 mM, respectively. **This MDEA**

concentration gives the approximate average concentration of the H-binding functional groups in the swollen gel that cannot be exceeded.

The most suitable ratio of the reactants formaldehyde and sulfite was also explored. The most robust behavior against buffering was found when the reactants were in *stoichiometric* ratio. This is similar to the IS reaction, but contrary to the HPS reaction where 10–20% excess HP resulted in the highest robustness.

Next step was the **elaboration of an appropriate pH-responsive gel**. Without large enough difference in the smallest linear size (here, diameter) of the gel in its swollen and shrunken state, no periodic behavior can emerge at all because a sufficient size-change is a condition (and not only a consequence) to operate according to the synergistic concept. Higher amount (monomer ratio) of the H^+-binding functional groups would result in higher degree of swelling when these groups are charged but their applicable amount is limited by the above discussed buffering effect.

FIGURE Comonomers in the polybase network with tertiary amine functional groups:



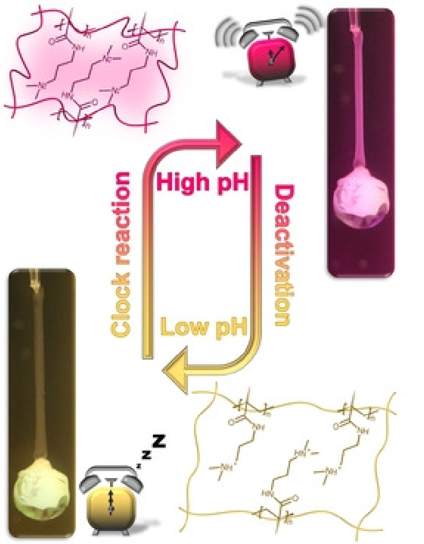


FIGURE →
Volume change (shrinking and swelling) of a hydrogel filament made of a pH-responsive pNIPA-based network containing tertiary amine functional groups. Background color is provided by Phenol Red pH-indicator. The gel filament is suspended from a plastic holder and a load (glass bead) is glued to its lower end.

Two major changes had to be made in the chemical composition of the network compared to the previous ones used with the acid clock-reactions.

1. **H^+-binding functional group:** The tertiary amine *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPrMAA) was used in 1.5% *n/n* of total monomers to maintain a *shrinking* response when the pH changes from 8 to 9.

2. **Initiator pair:** TEMED is a commonly used component with potassium persulfate (KPS) to initiate free-radical polymerization in aqueous solution. At the same time, DMAPrMAA and TEMED are both tertiary amines, and they might be present in a comparable amount in the network because TEMED radicals are incorporated at chain start or termination. DMAPrMAA gels initiated by TEMED (colored lines below) did not give a same sharp pH-response (that is, within 1–1.5 pH units) that we had got in our previous works for gels operational in different pH-regions below pH 7. Even by optimizing the temperature to get a maximal size-change, the transition from swollen to shrunken spread over more than 2 pH units. This problem was overcome by omitting TEMED and using the inorganic sulfite ion as reducing agent. This necessary change together with a slight adjustment of the amount of the crosslinker resulted in a sharp swollen to shrunken transition, that is to 38% of the initial diameter, within 1.25 pH units (from pH 8.00 to 9.25).

Composition: 3.00% DMAPrMAAm	**Composition: 1.50% DMAPrMAAm**

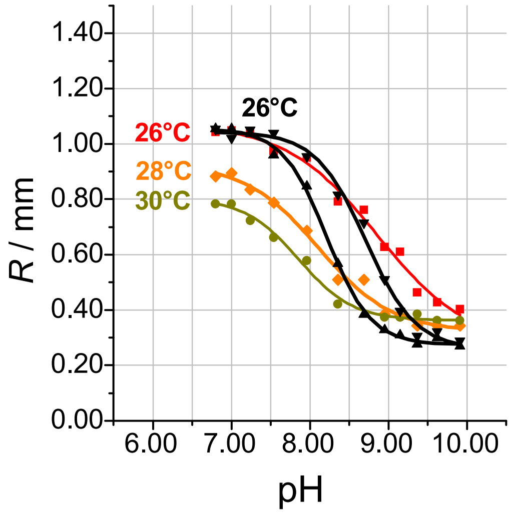
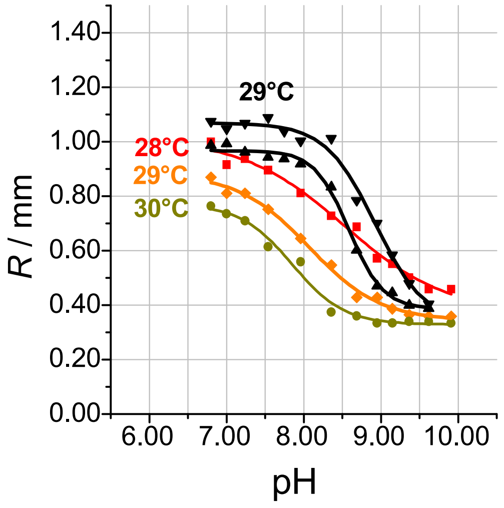
/ NTBA:NIPA = 20:80	**/ NTBA:NIPA = 10:90**
	

FIGURE Radius of cylindrical gels (R_0 = 0.750 mm at synthesis) in swelling equilibrium in Britton–Robinson buffers with $[Na^+]_{tot}$ = 50 mM. **Black lines**: gels initiated by KPS/sulfite redox pair (swelling/deswelling). Colored lines: gels initiated by KPS/TEMED redox pair.

Temperature and monomer composition:

In order to have a large enough swelling-shrinking response closer to room temperature, the more hydrophobic monomer *N-tert* butylacrylamide (NTBA) was added to NIPA.

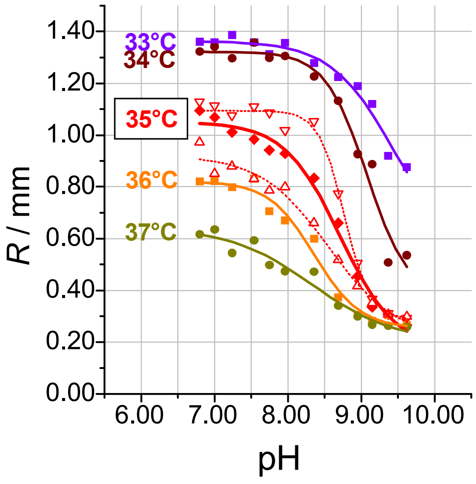
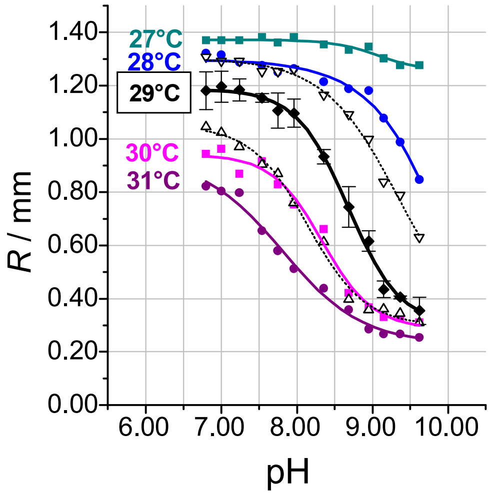
Composition: 1.50% DMAPrMAAm **/ NTBA:NIPA = 00:100**	Composition: 1.50% DMAPrMAAm **/ NTBA:NIPA = 10:90**
	

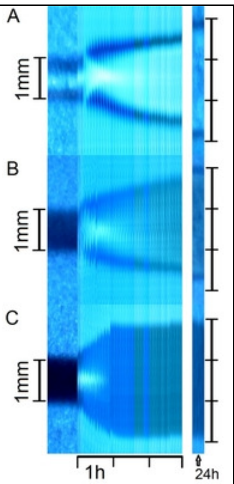
FIGURE Radius of cylindrical gels (R_0 = 0.750 mm at synthesis) in swelling equilibrium in Britton–Robinson buffers with $[Na^+]_{tot}$ = 50 mM.

Gels with fast and slow swelling-shrinking response

The rate of swelling and shrinking of gels is limited by the transport of the swelling medium and the collective motion of the network chains. Higher rates can be obtained by microstructured (macroporous) gels that contain denser and looser regions on the microscale. They behave like a sponge and expel water relatively unhindered from their inner core through their pore system. When microphase separation should occur during the polymerization, the dense domains of aggregates are fixed by crosslinking and loosely connected by several longer network chains.

We got microphase-separated porous structured gels (at the same time keeping the appropriate pH-response) by **tuning the solvent composition for the crosslinking polymerization**. The microstructure of the resulting polymer network depends sensitively on the solvent composition. In a so called "good solvent" (2:1 *t*BuOH/water ratio) the forming chains are expanded, well-solvated, the gel is transparent (clear), and the network is homogeneous (gel A). The quality of the solvent rapidly decreases by increasing the ratio of water, therefore the forming gel is translucent in 7:4 *t*BuOH/water (gel B) and opaque in 3:2 *t*BuOH/water (gel C).

Swelling of the porous gel is facilitated by the fact that water can penetrate inside the collapsed gel through the pore system thus the contact area with water is higher than in a conventional gel. At the same time, swelling remains much slower than the collapse which is a general observation in pNIPA-based gels.

<table>
<tr>
<td rowspan="2">Solvent composition at the synthesis of gels: <i>t</i>BuOH : water =
2:1 (A),
7:4 (B),
3:2 (C) "fast" gel</td>
<td rowspan="2">
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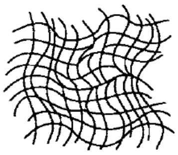
<td></td>
<td>Sketch of the homogeneous structure of a conventional hydrogel and the heterogeneous structure of a macroporous network.</td>
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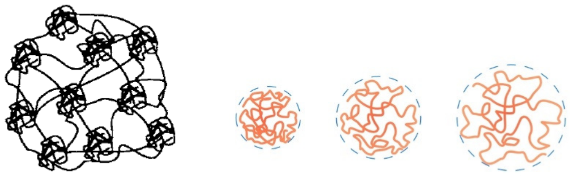
<td colspan="2"></td>
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FIGURE Kinetics of swelling after a temperature drop of the surrounding buffer solution from 32.0 °C to 23.0 °C at constant pH 8.36. *N.B.* The "fast gel" remains turbid even swollen.

Swelling kinetics measurements reveal a striking difference between gel C ("fast gel") and A and B ("normal" gels). Swelling equilibrium of the "fast gel" C (from 0.95 mm to 2.70 mm) is reached in 55-60 min. For comparison, the normal network gel A swells only to 66% of its final diameter in 1 hour and to 80% in 3 hours (finally the fully swollen 2.70 mm diameter is reached in 24 h).

The opposite process (not shown), the shrinking of the "fast gel" C (from 2.45 mm to 1.00 mm, so to 40% of the swollen diameter) is complete in 10 minutes. During the same time, the normal gel A shrinks from 2.45 mm to only 2.20 mm, so it still has 90% of its initial diameter (and still 81% after 20 min).

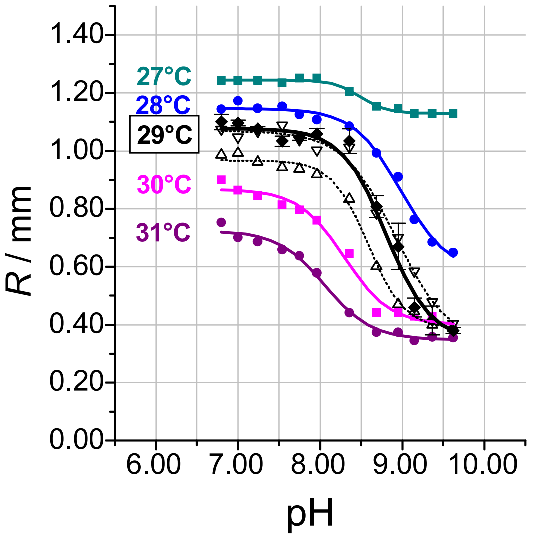
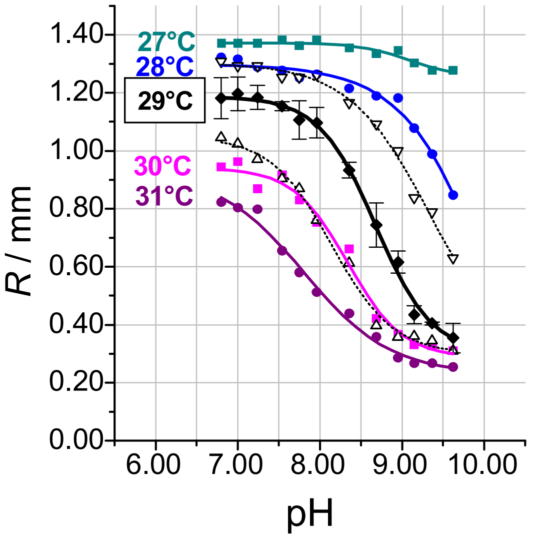
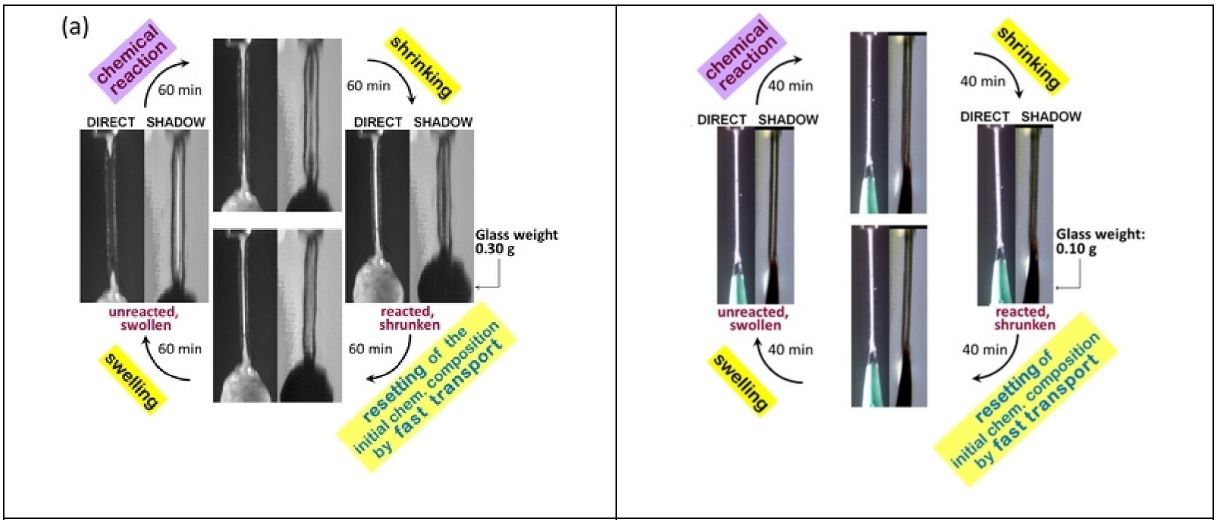
Composition: 1.50% DMAPrMAAm / NTBA:NIPA = 10:90	Composition: 1.50% DMAPrMAAm / NTBA:NIPA = 10:90
FAST gel	**gel with NORMAL swelling kinetics**
	

FIGURE Similarity between the equilibrium swelling degree of fast and normal gels of the same monomer composition. Dotted black lines are swelling/deswelling curves taken 1h after temperature change.

3rd year: Chemomechanical oscillations

Synergistic chemomechanical oscillations

Reaction-diffusion-mechanics experiments under flow require the careful stabilization of the experimental parameters in order to obtain a stable operation with regular periods. Not all of them is obvious, as the experiments run several days long. I successfully **overcome the problem how to stabilize the sulfite/bisulfite stock solution** over extended time: contrary to previous papers, I only used a sulfite stock solution (sulfite ions react by orders of magnitude slower with oxygen than hydrogen sulfite ion) and, separately, a sulfuric acid stock solution, and I premixed these two stoichiometrically *in flow* in 1 mL volume, just before entering the reactor. Keeping the sulfite stock solution in ice, its concentration was sufficiently stable for 12–14 hours. The sulfite/bisulfite ratio was set by the controlled feed of NaOH solution, used as control parameter to find the proper induction time where the chemomechanical oscillations arise. The results present **regular operation even over 33 hours**. The gels did not show any degradation even under a load exceeding ten times their own weight.



Variations in length: 15.0–11.00 mm (= –27%) Variations in diameter: 1.33–1.00 mm (= –25%) Feed conditions: $[HCHO]_0 = [HSO_3^-]_0 = 25.00$ mM $[NaOH]_0 = 2.31$ mM **const. pH = 6.40 in the CSTR** residence time = 8.44 min; temp. = 29.1 °C	Variations in length: 20.0–17.50 mm (= –12.5%) Variations in diameter: 1.25–0.95 mm (= –24%) Feed conditions: $[HCHO]_0 = [HSO_3^-]_0 = 28.60$ mM $[NaOH]_0 = 2.86$ mM **const. pH = 6.50 in the CSTR** residence time = 6.43 min; temp. = 28.9 °C

FIGURE Synergistic chemomechanical oscillations in suspended polybase gel cylinders. Snapshots of the four characteristic phases within one period.

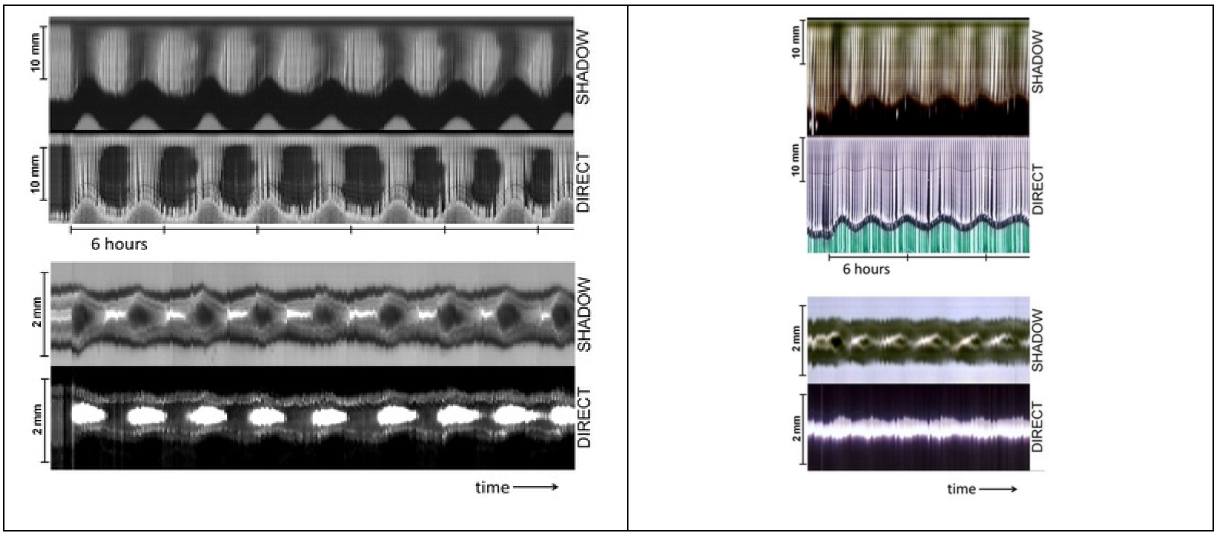


FIGURE Synergistic chemomechanical oscillations of the suspended polybase gel cylinder. Space-time plots of the periodic changes in length and diameter.

The above results were obtained with the gel with “normal” swelling/shrinking kinetics. No synergistic chemomechanical oscillations were obtained with the “fast” gel. This finding demonstrates the significance of the **condition of time-delay** between the chemical reaction (positive feedback) and the size-response of the gel (negative feedback). With no delay (so with too fast size-response), the system is able to find a stationary state. It also demonstrates that the period of the synergistic chemomechanical oscillations cannot be significantly reduced by the faster response of the gel.

Nevertheless, the performance of the “fast” gel was tested in a time-program that is reminiscent of the “conventional” (ordinary) type chemomechanical oscillator, where the negative feedback is in the chemistry.

Time-programmed chemomechanical actuation with the “fast” gel

As mentioned, the spiky oscillations in the formaldehyde-sulfite-gluconolactone oscillatory reaction do not make this reaction particularly appropriate to drive a conventional chemomechanical oscillator with high amplitude. Changing the chemical negative feedback reaction from gluconolactone (GL) to valerolactone (VL), it broadened the relaxation phase of the pH-peak, thus prolongated the time spent in the high-pH state. This new version of the reaction can be more appropriate to drive an actuator. The response time of the driven subsystem (here, the time scale of the self-assembly) is crucial in time-programmed processes. I.e., the driven building blocks should be able to perform the desired rearrangement within the time domain (time window) of the transient chemical command for “activation”. The above elaborated “fast” gel was able to **follow this time-program**. Moreover, we showed that the gel is capable of **performing mechanical work** (e.g., pulling and releasing a lever) following the imposed time-program. The load (glass bead) on the gel filament is 10–14 times the weight of the swollen gel itself.

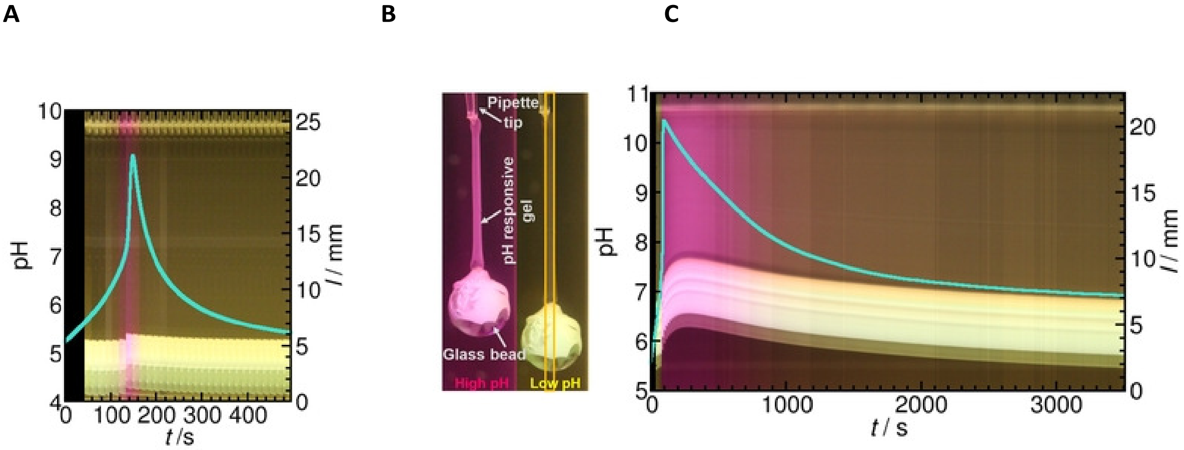


FIGURE (A) Space-time plot of the gel length and the synchronous pH-change (blue line) in the MGS and GL system (B) Snapshots of the suspended gel cylinder in its shrunken and elongated states. Background color is provided by Phenol Red pH-indicator. The yellow frame indicates the vertical cut taken to create the space-time plot. (C) Space-time plot of the gel length and the synchronous pH-change (blue line) in the MGS and VL system. [Phenol Red]$_0$ = 0.0145 mM, [VL]$_0$ = 0.0100 M, [CH$_2$OH$_2$]$_0$ = 0.1125 M, [SO$_3^{2-}$]$_0$ = 0.0050 M, [HSO$_3^-$]$_0$ = 0.0500 M. The diameter of plastic tip and glass bead were 0.750 mm and 5.00 ± 0.10 mm, respectively. The system was unstirred and θ = 25 ± 0.5 °C.

Turing-patterns in a closed system – improving a demonstration experiment

Somewhat deriving from the original plan, during Dr. Patrick De Kepper's (Bordeaux) 3rd-year visit we envisioned some improvements in his demonstration experiment to make it publishable in the *Journal of Chemical Education*. This experiment has been a popular project work in preparatory classes in French high schools for years.

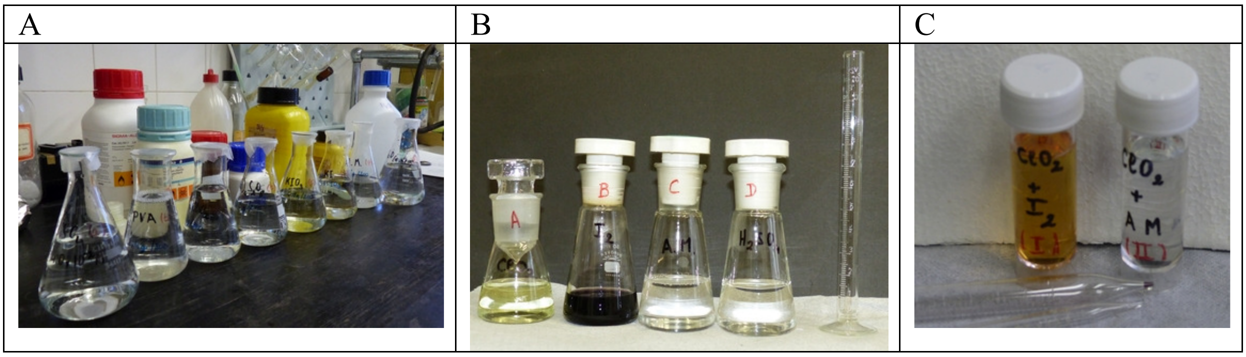
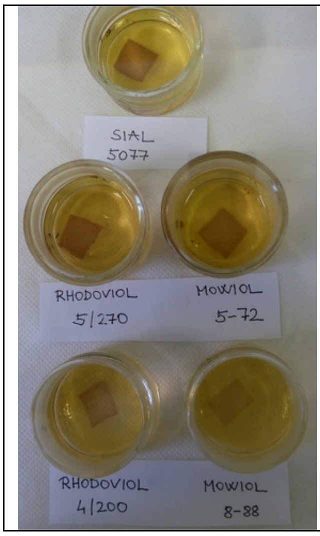


FIGURE (A) The eight primary solutions. (B) The four secondary solutions made from the combination of the primary solutions. (C) The two solutions, prepared by combining secondary solutions, that serve to impregnate the two gel sheets, respectively.

A good visual indication of the patterns is crucial. We tested different PVA-s as color indicator for triiodide ions as we possess a large collection of different brands and types. PVA of appropriate composition is a more powerful indicator and chemically more resistant than starch. At the same time, often the availability of an appropriate one is the "bottleneck" of the experiment.

	The best I_3^- indicator remains PVA No.5077 by Sigma-Aldrich. The vinyl acetate to vinyl alcohol ratio is 20:80.	
	The ratio of the monomers vinyl acetate to vinyl alcohol is 27:73 and 28:72 in Rhodoviol 5/270 and Mowiol 5-72, respectively. These PVA-s are practically as good indicators as the PVA 5077 by SIAL.	
	Rhodoviol 4/200 contains only 20% acetate groups. The weaker colour is due to less acetate groups.	Mowiol 8-88 contains only 12% acetate groups. The weak colour is caused by the low acetate content and/or by the high degree of polymerization.

Two criteria for the PVA in order to work as a I_3^- indicator:

- The PVA should contain 20–30% vinyl acetate monomers. (More acetate content makes the PVA insoluble in water. Less acetate gives weak colour.)
- The chain length should be low (M < a few 10.000 g/mol) in order to diffuse into the agarose or other gel structure from a solution.

Another improvement was that green light considerably enhanced the contrast:

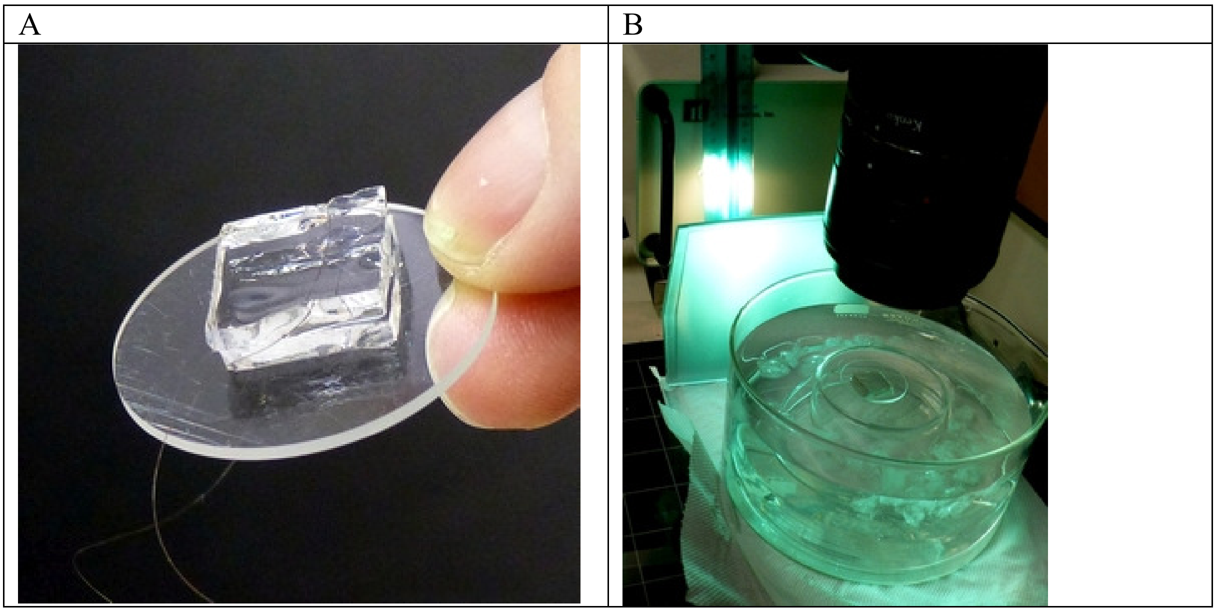


FIGURE (A) Two PVA gel sheets placed together. Turing-patterns are expected to emerge near the contact surface of the two gels (the two solutions). A human hair between the two gel sheets serves as orientation to find this plane (without the patterns yet) when focusing the camera. (B) Setup for observation of Turing-patterns in the "closed" configuration. The gel sheets are covered with a transparent plastic plate (heat insulator + to avoid escaping ClO_2) and placed on the flat bottom of an upside-down glass crystalizing dish (heat conductor) submerged in ice water. The gels are illuminated with green light to enhance the contrast of the patterns that emerge in white with brownish red background. The white light of the projector is passed through a green plastic object then through a translucid grey plastic plate serving as diffusor.

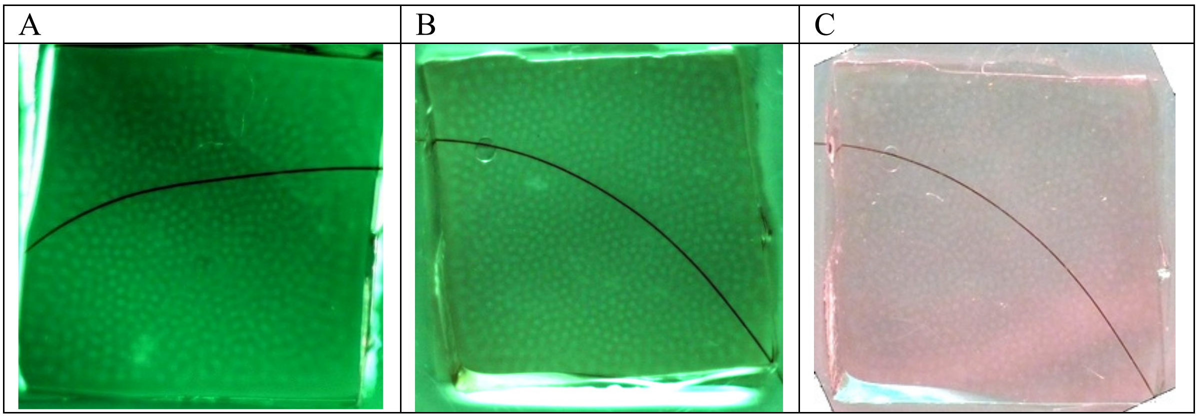


FIGURE (A) and (B) Turing-patterns observed in green light. (C) The gel in B under white light. The contrast is not sufficient even after image treatment.

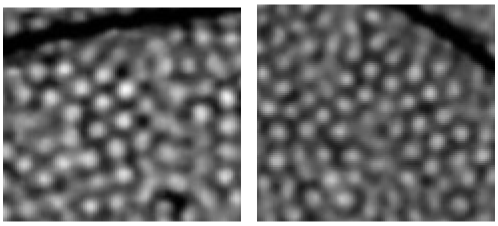


FIGURE Spot-type Turing-patterns with hexagonal arrangement zoomed from the previous photos.

FOLLOW-UP

Collaboration with Prof. John Anthony Pojman (Macromolecular Studies Group, Department of Chemistry, Louisiana State University, Baton Rouge, USA).

Prof. Pojman's research group works principally on practical aspects of combining nonlinear chemistry and polymerization, such as polymer products by frontal polymerization.

One of Prof. Pojman's research interests is to find practical applications with the timed pH-jump in the urease-urea enzymatic clock reaction. A synergistic chemomechanical oscillator based on this reaction would not require a continuous feed of chemicals to maintain a steady far-from-equilibrium environment because the enzyme (catalyst) can be immobilized in the gel so the reaction cannot proceed in the surrounding solution. This actuator would be the first one after the BZ-gels that could work in a closed system. In case of success, this synthetic experimental model would be — from the theoretical point of view — a very significant result for a broad audience (biologists, physicists) and would initiate diverse engineering ideas based on the prototype (polymer chemists, flow engineers).

We discussed my research plan in detail last summer when I spent 3 months in Prof. Pojman's lab. Currently, I am going to utilize his financial support to work on this project at ELTE.

The setting-up of the chemomechanics laboratory at the Institute of Chemistry ELTE was successful, however it is uncertain how to maintain it with no permanent position. This is my current concern.

PAPERS

1. Horvath J
Sustained Large-Amplitude Chemomechanical Oscillations Induced by the Landolt Clock Reaction
JOURNAL OF PHYSICAL CHEMISTRY B 118:(29) pp. 8891-8900. (2014)
IF 3.302
http://dx.doi.org/10.1021/jp5050964

2. Szalai I , Horvath J , De Kepper P
Contribution to an effective design method for stationary reaction-diffusion patterns
CHAOS 25:(6) Paper 064311. (2015)
IF 2.049
http://dx.doi.org/10.1063/1.4921721

3. Horvath J
Synergistic Chemomechanical Oscillators: Periodic Gel Actuators without Oscillatory Chemical Reaction
MACROMOLECULAR SYMPOSIA 358: pp. 217-224. (2015)
IF –
http://dx.doi.org/10.1002/masy.201500034

4. Horvath J
Peristaltic waves in a responsive gel sustained by a halogen-free non-oscillatory chemical reaction
POLYMER 79: pp. 243-254. (2015)
IF 3.586
http://dx.doi.org/10.1016/j.polymer.2015.09.081

PAPERS IN PREPARATION

1. Tóth-Szeles Eszter, Horváth Judit, Holló Gábor, Szűcs Rózsa, Nakanishi Hideyuki, Lagzi István
Chemically coded autonomous self-assembly from molecular and nanoscopic level to material level
PHYSICAL CHEMISTRY CHEMICAL PHYSICS (manuscript to be submitted)
IF 4.449

2. Horváth Judit
Sustained chemomechanical oscillations in a polybase gel through the competition between an alkaline clock-reaction and diffusion time
CHEMICAL COMMUNICATIONS (manuscript to be submitted)
IF 6.567

3. \+ A review paper on invitation in the Special Issue « Stimuli-Responsive Gels » in the open access journal GELS (MDPI, ISSN 2310-2861) by guest editor Prof. Dirk Kuckling (Dresden), as an outcome of my paper in Polymer.

CONFERENCE TALKS (INTERNATIONAL)

1. Judit Horváth, István Szalai, Jacques Boissonade and Patrick De Kepper
The Responsive Elastic Medium as a Source of Negative Feedback to Build Chemomechanical Oscillators (invited)
Workshop on Patterns and Hydrodynamic Instabilities in Reactive Systems
organized by the International Solvay Institutes Brussels
Université Libre de Bruxelles, Solvay Room, Brussels, Belgium, May 15–17, 2013

2. Judit Horváth
   Synergetic Chemomechanical Oscillators: Periodic Gel Actuators without Oscillatory Chemical Reaction
   PN&G 2014, the joint symposium of the *22nd Polymer Networks Group Meeting* (PNG) and the *10th Gel Symposium*
   Tokyo, Japan, November 10–14, 2014

3. Judit Horváth
   Recent Advances in the Design of Synergistic Chemomechanical Oscillators
   CCS'15 Conference on Complex Systems
   Tempe, Arizona, USA, September 28 – October 2, 2015

POSTERS

1. Judit Horváth, István Szalai, Jacques Boissonade and Patrick De Kepper
   The Responsive Elastic Medium as a Source of Negative Feedback for Building Chemomechanical Oscillators
   Engineering of Chemical Complexity - International conference; Berlin Center for Studies of Complex Chemical Systems (BCSCCS), Warnemünde, Germany; June 10–13, 2013

2. Judit Horváth and Patrick De Kepper
   Chemomechanical Oscillations without Oscillatory Chemical Reaction, based on a Synergistic Concept
   Nature Inspires - Chemistry Engineers: NICE 2014 the 2nd International Conference on Bioinspired and Biobased Chemistry and Materials
   Nice, France, October 15–17, 2014

3. Judit Horváth
   Sustained chemomechanical oscillations induced by the formaldehyde – sulfite clock reaction
   2016 Gordon Research Conference on Oscillations & Dynamic Instabilities in Chemical Systems; Stowe, Vermont, USA; July 17–22, 2016

ORAL PRESENTATIONS AT HUNGARIAN SCIENTIFIC MEETINGS

1. "**Chemomechanical Oscillators with no Oscillatory Chemical Reaction**" (in Hungarian)
   Spring Meeting of the Reaction Kinetics and Photochemistry Working Committee of the Hungarian Academy of Sciences (HAS)
   Siófok, 25-26 April 2013

2. "**The Rational Design of Chemomechanical Oscillators without Oscillatory Chemical Reaction**" (in Hungarian)
   Autumn Meeting of the Colloid Chemistry Working Committee of the HAS
   Science Research Centre of the HAS
   Budapest, 14 November 2013

ANNEX

Final Report

PD 105270

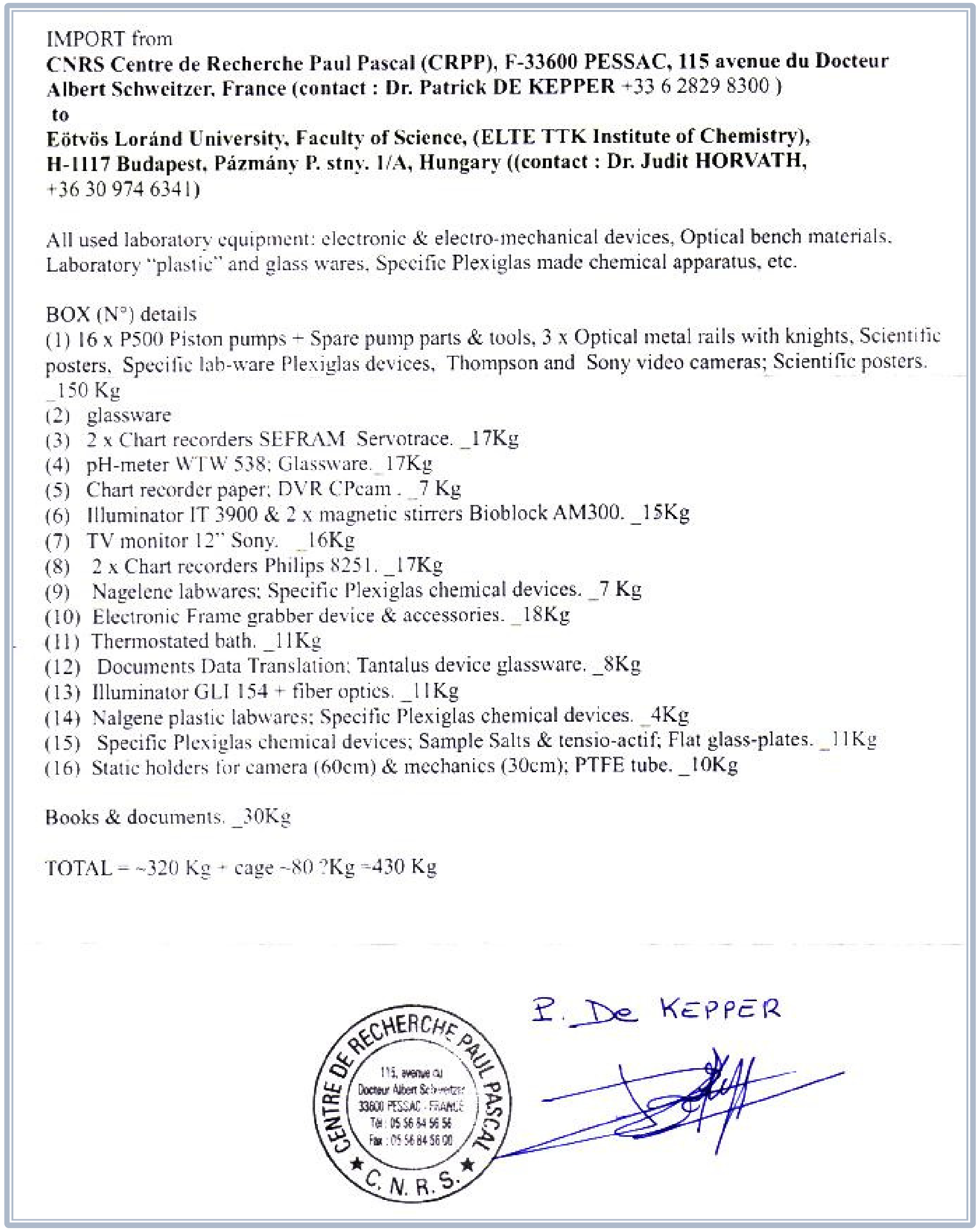
Title: **Synergetic Chemomechanical Patterns in Deformable Chemically Active Media**

Duration: **2013-01-01 – 2015-12-31 (36 months)**

Principal Investigator: **Dr. Judit Horváth**

Institution: **Eötvös Loránd University**
Research unit: **Institute of Chemistry**

List of equipment recieved as donation from the French laboratory:



IMPORT from
CNRS Centre de Recherche Paul Pascal (CRPP), F-33600 PESSAC, 115 avenue du Docteur Albert Schweitzer, France (contact : Dr. Patrick DE KEPPER +33 6 2829 8300)
to
Eötvös Loránd University, Faculty of Science, (ELTE TTK Institute of Chemistry), H-1117 Budapest, Pázmány P. stny. 1/A, Hungary ((contact : Dr. Judit HORVATH, +36 30 974 6341)

All used laboratory equipment: electronic & electro-mechanical devices, Optical bench materials. Laboratory "plastic" and glass wares, Specific Plexiglas made chemical apparatus, etc.

BOX (N°) details
(1) 16 x P500 Piston pumps + Spare pump parts & tools, 3 x Optical metal rails with knights, Scientific posters, Specific lab-ware Plexiglas devices, Thompson and Sony video cameras; Scientific posters. _150 Kg
(2) glassware
(3) 2 x Chart recorders SEFRAM Servotrace. _17Kg
(4) pH-meter WTW 538; Glassware. _17Kg
(5) Chart recorder paper; DVR CPcam . _7 Kg
(6) Illuminator IT 3900 & 2 x magnetic stirrers Bioblock AM300. _15Kg
(7) TV monitor 12" Sony. _16Kg
(8) 2 x Chart recorders Philips 8251. _17Kg
(9) Nagelene labwares; Specific Plexiglas chemical devices. _7 Kg
(10) Electronic Frame grabber device & accessories. _18Kg
(11) Thermostated bath. _11Kg
(12) Documents Data Translation; Tantalus device glassware. _8Kg
(13) Illuminator GLI 154 + fiber optics. _11Kg
(14) Nalgene plastic labwares; Specific Plexiglas chemical devices. _4Kg
(15) Specific Plexiglas chemical devices; Sample Salts & tensio-actif; Flat glass-plates. _11Kg
(16) Static holders for camera (60cm) & mechanics (30cm); PTFE tube. _10Kg

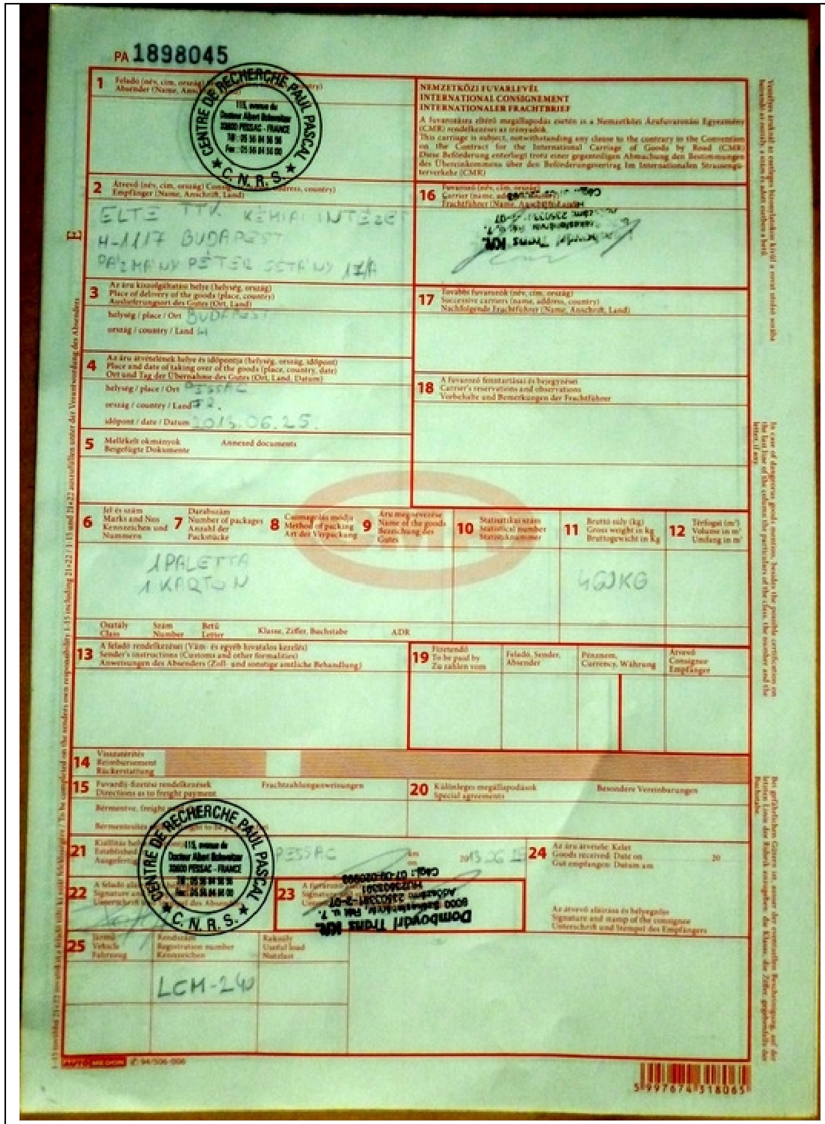
Books & documents. _30Kg

TOTAL = ~320 Kg + cage ~80 ?Kg =430 Kg

115, avenue du
Docteur Albert Schweitzer
33600 PESSAC - FRANCE
Tél : 05 56 84 56 56
Fax : 05 56 84 56 00

P. De KEPPER

Shipping of donated equipment from CRPP Bordeaux to ELTE Budapest (June 2013)



PA 1898045

1 Feladó (név, cím, ország) / Absender (Name, Anschrift, Land)

CENTRE DE RECHERCHE PAUL PASCAL
115, avenue du Docteur Albert Schweitzer
33600 PESSAC - FRANCE
C.N.R.S.

NEMZETKÖZI FUVARLEVÉL
INTERNATIONAL CONSIGNEMENT
INTERNATIONALER FRACHTBRIEF

A fuvarozásra eltérő megállapodás esetén is a Nemzetközi Árufuvarozási Egyezmény (CMR) rendelkezései az irányadók.
This carriage is subject, notwithstanding any clause to the contrary to the Convention on the Contract for the International Carriage of Goods by Road (CMR).
Diese Beförderung unterliegt trotz einer gegenteiligen Abmachung den Bestimmungen des Übereinkommens über den Beförderungsvertrag im Internationalen Strassengüterverkehr (CMR)

2 Átvevő (név, cím, ország) / Consignee (name, address, country) / Empfänger (Name, Anschrift, Land)

ELTE TTK KÉMIAI INTÉZET
H-1117 BUDAPEST
PÁZMÁNY PÉTER SÉTÁNY 1/A

16 Fuvarozó (név, cím, ország) / Carrier (name, address, country) / Frachtführer (Name, Anschrift, Land)

3 Az áru kiszolgáltatási helye (helység, ország) / Place of delivery of the goods (place, country) / Auslieferungsort des Gutes (Ort, Land)
helység / place / Ort BUDAPEST
ország / country / Land H

17 További fuvarozók (név, cím, ország) / Successive carriers (name, address, country) / Nachfolgende Frachtführer (Name, Anschrift, Land)

4 Az áru átvételének helye és időpontja (helység, ország, időpont) / Place and date of taking over of the goods (place, country, date) / Ort und Tag der Übernahme des Gutes (Ort, Land, Datum)
helység / place / Ort PESSAC
ország / country / Land F.
időpont / date / Datum 2013.06.25.

18 A fuvarozó fenntartásai és bejegyzései / Carrier's reservations and observations / Vorbehalte und Bemerkungen der Frachtführer

5 Mellékelt okmányok / Beigefügte Dokumente / Annexed documents

6 Jel és szám / Marks and Nos / Kennzeichen und Nummern	7 Darabszám / Number of packages / Anzahl der Packstücke	8 Csomagolás módja / Method of packing / Art der Verpackung	9 Áru megnevezése / Name of the goods / Bezeichnung des Gutes	10 Statisztikai szám / Statistical number / Statistiknummer	11 Bruttó súly (kg) / Gross weight in kg / Bruttogewicht in kg	12 Térfogat (m³) / Volume in m³ / Umfang in m³
	1 PALETTA 1 KARTON				460 KG	

Osztály / Class · Szám / Number · Betű / Letter · Klasse, Ziffer, Buchstabe · ADR

13 A feladó rendelkezései (Vám- és egyéb hivatalos kezelés) / Sender's instructions (Customs and other formalities) / Anweisungen des Absenders (Zoll- und sonstige amtliche Behandlung)

19 Fizetendő / To be paid by / Zu zahlen vom · Feladó, Sender, Absender · Pénznem, Currency, Währung · Átvevő, Consignee, Empfänger

14 Visszatérítés / Reimbursement / Rückerstattung

15 Fuvardíj-fizetési rendelkezések / Directions as to freight payment / Frachtzahlungsanweisungen

20 Különleges megállapodások / Special agreements / Besondere Vereinbarungen

21 Kiállítás helye / Established in / Ausgefertigt in PESSAC 2013.06.25

24 Az áru átvétele: Kelet / Goods received: Date on / Gut empfangen: Datum am 20

22 A feladó aláírása / Signature and stamp of the sender / Unterschrift und Stempel des Absenders

23 A fuvarozó aláírása / Signature and stamp of the carrier

Dombovári Trans Kft.

Az átvevő aláírása és bélyegzője / Signature and stamp of the consignee / Unterschrift und Stempel des Empfängers

25 Jármű / Vehicle / Fahrzeug · Rendszám / Registration number / Kennzeichen · Raksúly / Useful load / Nutzlast

LCM-240

<— rail optique chimio-mécanique

Installation of the Chemomechanics Lab at Institute of Chemistry ELTE

BEFORE (January 2013)	(July 2013)
	
AFTER ↓	↓
	

Installation of the Gel synthesis Lab

BEFORE (January 2013)	**January 2013**
	
AFTER ↓	↓
	

Installation of a General Lab (for preparing solutions, testing of gels, repairing pumps, etc.)

BEFORE (January 2013)	
	
AFTER ↓	↓