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Triple-crosslinked self-propelled hydrogel with self-healing properties: preparation and characteristics

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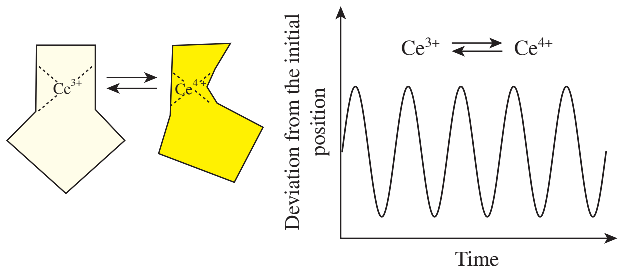
A polyacrylic acid hydrogel containing Ce^{4+} ions acting as a catalyst for the Belousov–Zhabotinsky reaction with self-healing and self-propelled properties was prepared by a one-pot synthesis. By using cerium ammonium nitrate as a radical polymerization initiator, a significant simplification of the synthesis of stimuli-responsive polymers was achieved. The compressive strain and elastic modulus were calculated to describe the mechanical properties of the hydrogel during compression.



Keywords: self-propelled gels, self-oscillating gels, Belousov–Zhabotinsky reaction, cerium catalyst, stimuli-responsive polymers, smart materials.

Modern polymer materials, referred to as 'smart' or stimuli-responsive, are currently attracting considerable attention in the field.[1–9] Their applications are wide, including use in the fabrication of logic elements and more complex neuromorphic networks.[10–14] However, despite substantial advancements, it is evident that the production of such polymers with a specific set of properties remains a significant challenge. To address the task of creating neuromorphic elements for a network of micro-oscillators, our research group focused on the development of hydrogels that would exhibit self-propelled and self-healing properties, in addition to the ability to maintain the shape and size of the micro-oscillator for long periods of time.

We define self-propelled or autonomous systems as transport systems that directly convert chemical energy into mechanical energy without using additional thermal energy, similar to biological systems. Such a system generates its own motion using chemical energy and does not require an external driving force, *i.e.*, it is chemomechanical.[15] We are particularly interested in the most complex and at the same time intriguing system that spontaneously breaks its symmetry and exhibits nonlinear behavior, namely the oscillatory motion of hydrogels during the Belousov–Zhabotinsky (BZ) reaction.[16] This reaction can be broadly described as the bromination and oxidation of an organic substrate such as malonic acid by bromate in the presence of a redox catalyst such as ferroin or cerium ions in a concentrated solution of sulfuric or nitric acid.

The fundamental principle of swelling of a polymer material is that when the material is immersed in a specific solvent, the free energy of mixing due to the gain in the entropy of translational motion contributes to the osmotic pressure causing the diffusion of the solvent into the body of the material. The absorption of the solvent continues until the complete solvation of the polymer occurs.[17] We hypothesized that by immobilizing cerium ions as heterogeneous inclusions within the crosslinked polymer network of a pH-sensitive hydrogel, specifically polyacrylic acid, the periodic protonation and deprotonation during the oscillatory reaction could create a concentration gradient of mobile ions within the hydrogel relative to the external solution (osmotic pressure). The energy from this gradient absorbed by the polymer matrix could cause periodic movements of the gel sample in the solution, thereby demonstrating self-propelled properties (Figure 1).

The material must have a certain modulus of elasticity to ensure that the energy from the redox transitions of the catalyst is not dissipated by vibrations of the polymer chains inside the body, while maintaining its original shape after receiving a chemical signal.

Guided by these considerations, the material was synthesized through crosslinking involving three types of interactions: ionic interactions between cerium ions and hydroxyl groups of the polymer network allowing for self-healing and chemomechanics, hydrogen bonding and chemical crosslinking with *N,N'*-methylene-bisacrylamide (MBA) to enhance the mechanical strength of the resulting material.

Thus, a hydrogel based on polyacrylic acid/Ce^{4+} was obtained (Scheme 1).

The concentrations of the main monomer (2.5 M), the crosslinking agent MBA (0.01 M or 0.4 mol%) and the catalyst

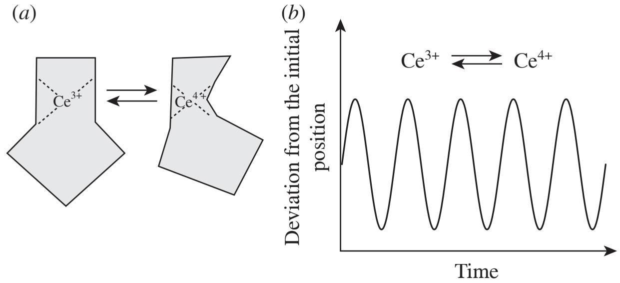
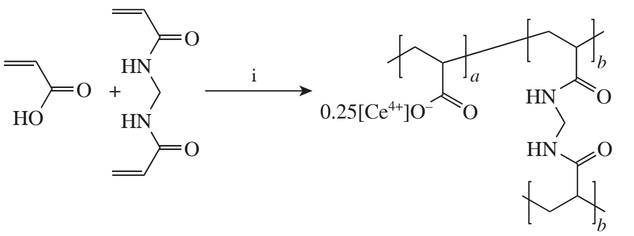


Figure 1 (*a*) Schematic representation of the movement of a piece of gel in space. (*b*) Dependence of the deviation of a piece of gel from its initial position over time (example).



Scheme 1 *Reagents and conditions*: i, $(NH_4)_2Ce(NO_3)_6$, $(NH_4)_2S_2O_8$, TMEDA, H_2O, 40 °C, 1 h, Ar.

(0.05 M) were determined experimentally in order to obtain a material with sufficient elasticity to form a body exhibiting pronounced self-propelled and self-healing properties. A quantitative assessment of the effect of the initial concentrations of the components requires detailed investigation and will be presented in subsequent publications. The use of cerium ammonium nitrate for radical polymerization, which is itself a strong one-electron oxidizer, made it possible to create a material with a non-homogeneous distribution of cerium ions, which can be seen by analyzing the scanning electron microscopy (SEM) images in Figure 2 and the energy dispersive spectra (EDS) in Figure 3 (Table 1).

Cerium ions are likely to be inhibitors of the polymerization reaction, since attempts to introduce cerium ions into the polymerization mixture in the form of other salts such as cerium sulfate did not result in a reaction (for details, see Online Supplementary Materials). Cerium ions were chosen as catalysts for the oscillatory reaction after unsuccessful attempts to find catalytic activity in the BZ reaction of other lanthanides, such as samarium, europium, terbium and ytterbium, which will be reported in another publication.

To investigate the chemomechanical properties, a gel sample (1.2×0.7 mm) containing immobilized cerium ions is immersed in a catalyst-free BZ mixture containing 0.065 M malonic acid, 0.084 M $NaBrO_3$ and 0.8 M H_2SO_4, initiating the diffusion of the reagents into the gel. This process triggers an oscillatory reaction. During the reaction, the oxidation state of the catalyst periodically changes from +4 to +3, correspondingly increasing and decreasing the number of crosslinks, and causing protonation and deprotonation of the polymer. The concentrations of the components of the catalyst-free BZ mixture were chosen experimentally based on literature data.[18]

Since the observation of the movements is complicated by the movements of the adjacent samples, we selected a part resembling a protrusion from a larger piece of gel that remains stationary. Subsequently, to determine the dependence of the displacement of the gel piece on time, we plotted a space–time plot using the Plotto software.[19] In the space–time plot, it can be seen that the gel exhibits a smooth trajectory to the right, after which it abruptly returns to its starting position. The space–time plot was used to

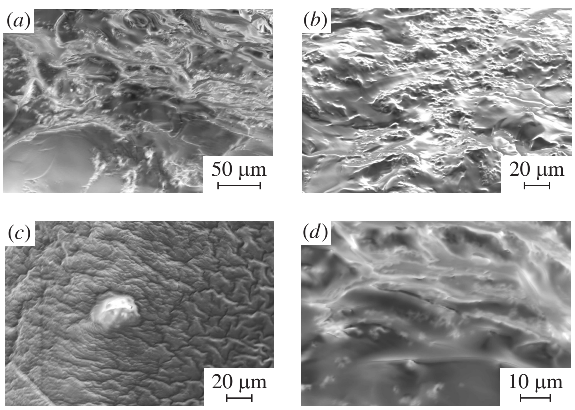


Figure 2 SEM images of hydrogel morphology: (*a*) bottom, (*b*) top, (*c*) heterogeneous inclusion and (*d*) probable inclusions of cerium salts.

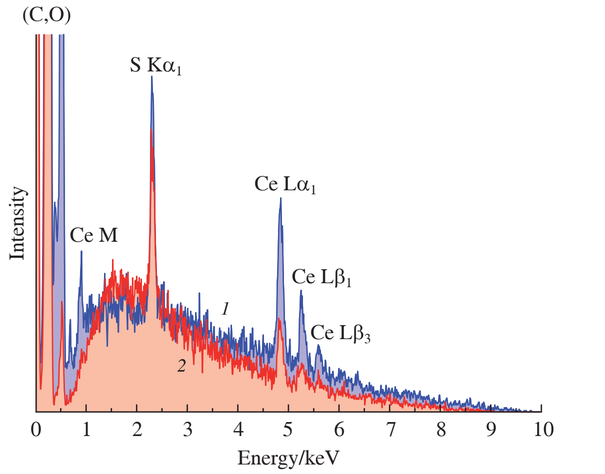


Figure 3 EDS spectra of (*1*) a heterogeneous inclusion and (*2*) the bulk of the hydrogel sample.

Table 1 EDS analysis of points of interest in the hydrogel sample.

Points of interest	Concentration (at%)			
	C K	O K	S K	Ce L,M
Heterogeneous inclusion	79.87	17.82	0.73	1.58
Arbitrary point	75.94	23.89	0.12	0.00

plot a graph depicting the periodic displacement of the gel piece relative to its initial position over time (Figure 4), characterizing the self-propelled properties of the material during the BZ reaction. After 2500 seconds, the sample moved out of the field of view of the optical microscope, but chemomechanical processes continued to occur in it for several hours.

For better visualization, the photographs were compiled into a video accelerated by 124 times. Detailed information about the experimental setup for capturing images of gel pieces and measuring their sizes, as well as videos and the procedure for constructing space–time plots, are contained in Online Supplementary Materials.

The self-propelled properties of the polymer are combined with high self-healing capabilities, as expected for a polyacrylic acid-based material.[20] We found that cerium ions introduced as cerium ammonium nitrate do not significantly affect the self-healing ability. After only 120 min, a cut sample of approximately 3×1 cm is completely re-crosslinked and restored itself (Figure 5). This phenomenon can be explained by the reversible nature of ionic crosslinking.

Using dynamic loading methods, the elastic modulus of the material was calculated (see Online Supplementary Materials), and its value (Table 2) suggests that this material could be utilized as a signal transmission medium in a neuromorphic network of micro-oscillators, for example, as a 'chemical diode' logic element. A suitable material must have specific properties, namely stability

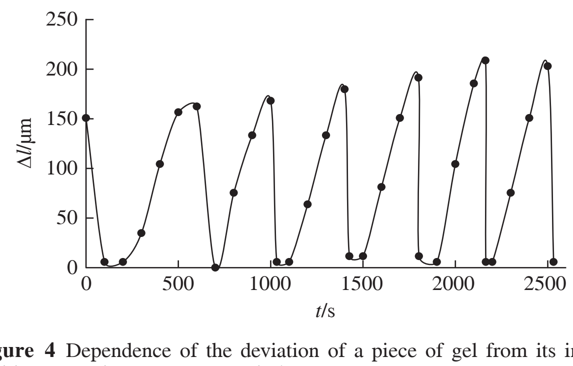


Figure 4 Dependence of the deviation of a piece of gel from its initial position Δl on time t (average period T = 480 s).

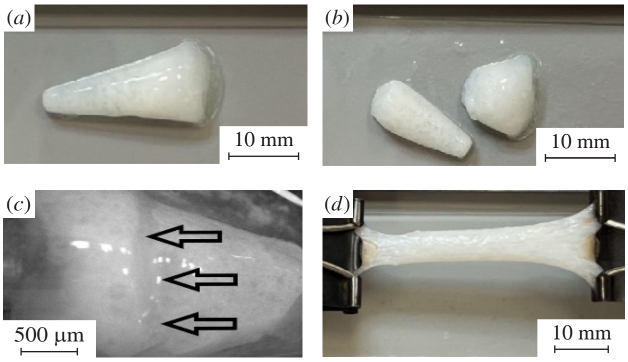


Figure 5 Self-healing properties of polyacrylic acid/Ce^{4+} hydrogel. Images of hydrogel pieces: (*a*) intact sample, (*b*) cut sample, (*c*) incision site on the sample after 120 min (taken with an optical microscope) and (*d*) maximally stretched sample before rupture.

Table 2 Results of compression of the hydrogel sample calculated with 95% confidence.

Sample type	Stress at ε = 40%, σ_{40}/kPa	Compressive stress, σ_{max}/kPa	Relative compression strain, σ_{max} (%)
Initial sample	79.87	17.82	0.73
After 5 compression cycles	75.94	23.89	0.12

under the BZ reaction conditions, *i.e.* it must retain its shape and size over long periods of time.[7]

Thus, a polyacrylic acid hydrogel containing Ce^{4+} ions exhibiting self-healing and self-propelled properties was prepared by a one-pot synthesis. The use of cerium ammonium nitrate as a radical polymerization initiator allows the synthesis of a stimuli-responsive polymer with a heterogeneous distribution of cerium ions. The physical and chemical properties of the resulting material were characterized using Raman spectroscopy, NMR spectroscopy, scanning electron microscopy and mechanical compression testing followed by calculation of the relative compression strain and elastic modulus. Furthermore, the demonstrated chemo-mechanical properties of oscillatory behavior during the BZ reaction and self-healing capability make the obtained hydrogel a promising material for creating logic elements in neuromorphic networks of micro-oscillators.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7681.

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