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

**Olga V. Lagunova, George O. Molokanov, Olga A. Dikaia, Petr V. Shvets,
Alexander Yu. Goikhman and Eugeny G. Chupakhin**

1. Materials and methods, hydrogel preparation

Ammonium cerium(IV) nitrate $(NH_4)_2Ce(NO_3)_6$, acrylic acid, *N*,*N′*-methylenebisacrylamide, ammonium persulfate, *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA), ethanol, malonic acid, sulfuric acid, sodium bromate (Sigma-Aldrich, 99%), and distilled water were used without further purification. The square capillaries used as a mould for gel polymerization were procured from CM Scientific Ltd.

A solution of ammonium cerium(IV) nitrate (0.411 g) was prepared by dissolving it in 10.4 ml of distilled water. Subsequently, 2.5 ml of acrylic acid, 1.5 ml of 200 mM aqueous solution of *N*,*N′*-methylenebisacrylamide, and 0.137 g of ammonium persulfate were added and mixed thoroughly on Vortex 1 Biosan. Thereafter, it was purged for 10 minutes with argon to remove the oxygen that affects polymerization. Subsequently, 0.6 ml of a 1 M aqueous solution of TMEDA (polymerization promoter) was added. The resulting mixture was pipetted into 11 × 0.8 × 0.8 cm and 14.5 × 0.4 × 0.4 cm square capillaries, heated at 40 °C for one hour and then allowed to polymerize at room temperature for 24 h. Then, it was washed thoroughly with distilled water several times.

For Raman scattering and SEM/EDS, gel samples were prepared in Eppendorf tubes (sample 1.1, sample 1.2) as already described, with the quantity adjusted to accommodate a smaller volume (0.5 ml). Since visually the top portion of the gel remains transparent while the bottom one is mostly yellowish-white opaque, samples for testing were taken from sample 1.2 in two locations: 1.2-top and 1.2-bottom. For comparison, a sample was prepared containing 0.0822 g of ammonium cerium(IV) nitrate per 20 ml of the total volume of the reaction mixture, *i.e.* with a five-fold reduction in Ce^{4+} ions (sample 1.3). Sample 1.1 was subjected to freeze-drying in a Labconco FreeZone Triad Freeze Dryer for 24 h. Samples 1.2 and 1.3 were tested after washing with distilled water without drying.

2. Raman scattering

Raman scattering measurements were performed using a Horiba Jobin Yvon LabRam HR800 micro-Raman spectrometer with an 100× magnification objective lens (numerical aperture of 0.9, Horiba, Villeneuve d'Ascq, France). Measurements were conducted at room temperature in the ambient. A He-Ne laser with a 632.8 nm wavelength was used to excite Raman scattering. Laser power on the sample was 0.5 mW, and a spot diameter was about 5 μm. The total acquisition time for each sample was about 1 h to achieve good signal-to-noise ratio. We compared the Raman spectrum of hydrogel, obtained by polymerization of acrylic acid with *N*,*N*'-methylenebis(acrylamide) as a linker and ammonium persulfate as an initiator in the presence of $FeCl_3$,[S1] then with acrylic acid dimers.[S2] The Raman spectrum is exhibited in **Figure S1** and **Figure S2**.

3. Scanning electron microscopy

Scanning electron microscopy (SEM) of hydrogel samples was conducted in bright field mode on a Jeol JSM-6390 microscope using an acceleration voltage of 5 kV (high vacuum mode). Energy dispersive spectra (EDS) were collected using an Oxford Instruments X-ACT with a 10 keV electron beam and refined by a related software INCA. Before testing, the samples were subjected to freeze-drying at a temperature of −78 °C in a Thermo Scientific freezer. To create samples that were dehydrated and suitable for high vacuum conditions, the samples were lyophilized in a Labconco Triad unit for a period of 24 h.

4. Nuclear magnetic resonance

The ^{1}H and ^{13}C NMR spectra were recorded with a solid-state gel sample that had been lyophilized in a vacuum freeze dryer. The ^{1}H and ^{13}C NMR spectra are exhibited in **Figures S3** and **S4**, respectively.

5. Mechanical testing of hydrogels

Compression tests were conducted using the Instron 34TM-10 universal testing machine and axial compression test equipment. A sample with a height of 10 mm and a diameter of 12 mm was employed with five repetitions at a test speed of 10 mm/min, a preload of 0.5 N, a temperature of 21 ± 2 °C, a pressure of 757 mm Hg. The sample was trimmed to a predefined size using a surgical blade. The elastic modulus was determined with used compressive stress–strain curves. The compressive stress–strain curves for hydrogel samples are exhibited in **Figure S5**.

6. Hydrogel self-healing test

Hydrogels of cylindrical shape measuring approximately 20 × 10 mm were bisected using a surgical blade at the midpoint. Subsequently, the surfaces were joined together, wrapped it with PVC film to prevent the material from drying out and stored at a temperature of 25 °C for 120 min, followed by observation of the self-healing outcome under an optical microscope (Zeiss Stemi-2000C) equipped with a digital black-and-white camera (QImaging QICAM Fast1394).

7. Characteristics of the self-propelled properties of the gel sample

The block diagram of our experimental setup is exhibited in **Figure S6**. The movements of the gel pieces immersed in a solution containing [sodium bromate] = 0.084 M, [malonic acid] = 0.065 M and [sulfuric acid] = 0.8 M were observed using a microscope (Zeiss Stemi-2000C) equipped with a black and white camera (QImaging QICAM Fast1394). The petri dish containing the gel sample was illuminated from below using an LED light source and a long pass filter at $\lambda = 650$ nm. Images were captured at a rate of one frame per second using Labview software. A sequence of 6725 images of the gel was captured over time [for an example, see **Figure S7**(*a*),(*b*)], with pixels from the same location [see **Figure S7**(*a*),(*b*)] copied to construct an image from spatial slices taken at different points in time. On the space-time plot, it can be observed that the gel exhibits a smooth trajectory to the right, after which it abruptly returns to the starting position. Following the manual counting of the pixels using the ruler tool in the Paint program, the results of the measurements and calibration (1 pixel = 5.8 μm) were utilized to plot a graph of periodic deviation of the gel piece relative to its initial position as a function of time. For better visualization, photographs were compiled into a video accelerated by one hundred twenty-four times.

References

S1 Z. Wei, J. He, T. Liang, H. Oh, J. Athas, Z. Tong, C. Wang, Z. Nie, *Polym. Chem.*, 2013, **4**, 17, 4601; https://doi.org/10.1039/c3py00692a.

S2 C. Murli, Y.J. Song, *Phys. Chem. B,* 2010, **114**, 30, 9744; https://doi.org/10.1021/jp1034757.

Figures.

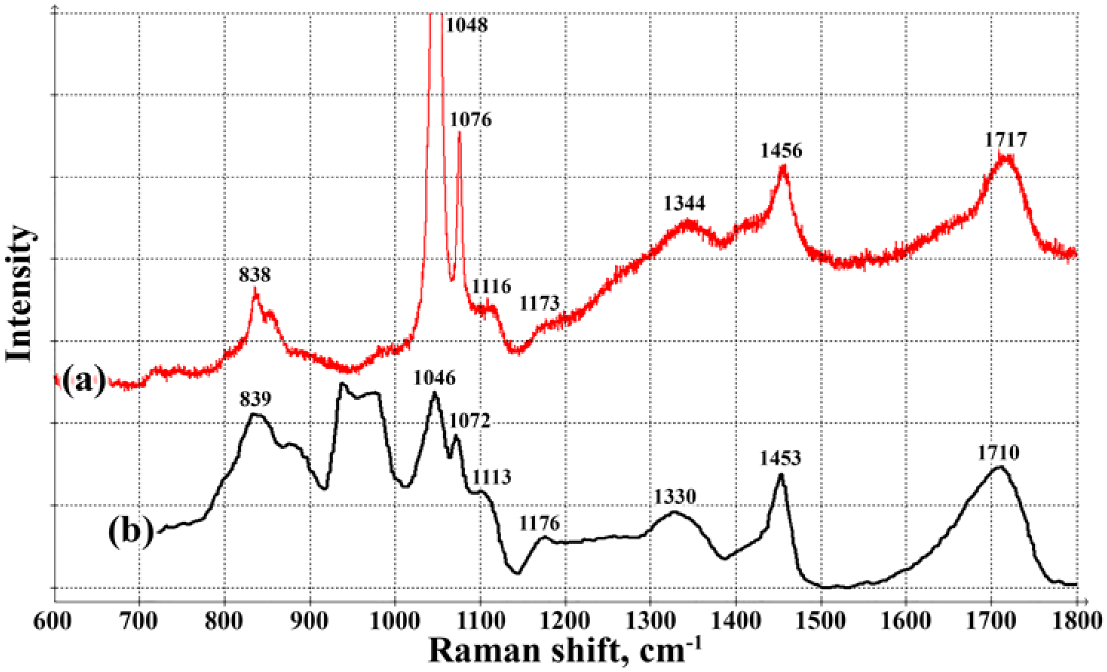

Figure S1.The Raman spectra of: (a) 1.2 – bottom, (b) hydrogel from literature.[S1]

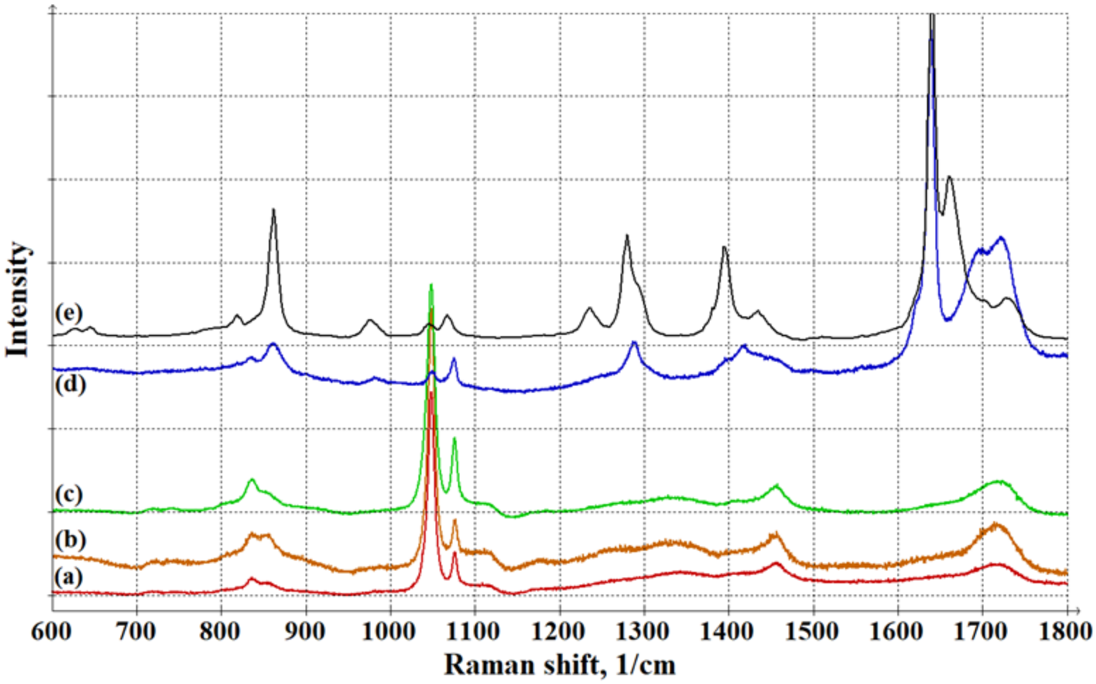

Figure S2. Raman spectra of samples: (a) 1.2-bottom; (b) 1.2-top; (c) 1.1; (d) 1.3; (e) acrylic acid, liquid (data obtained from the literature).[S2]

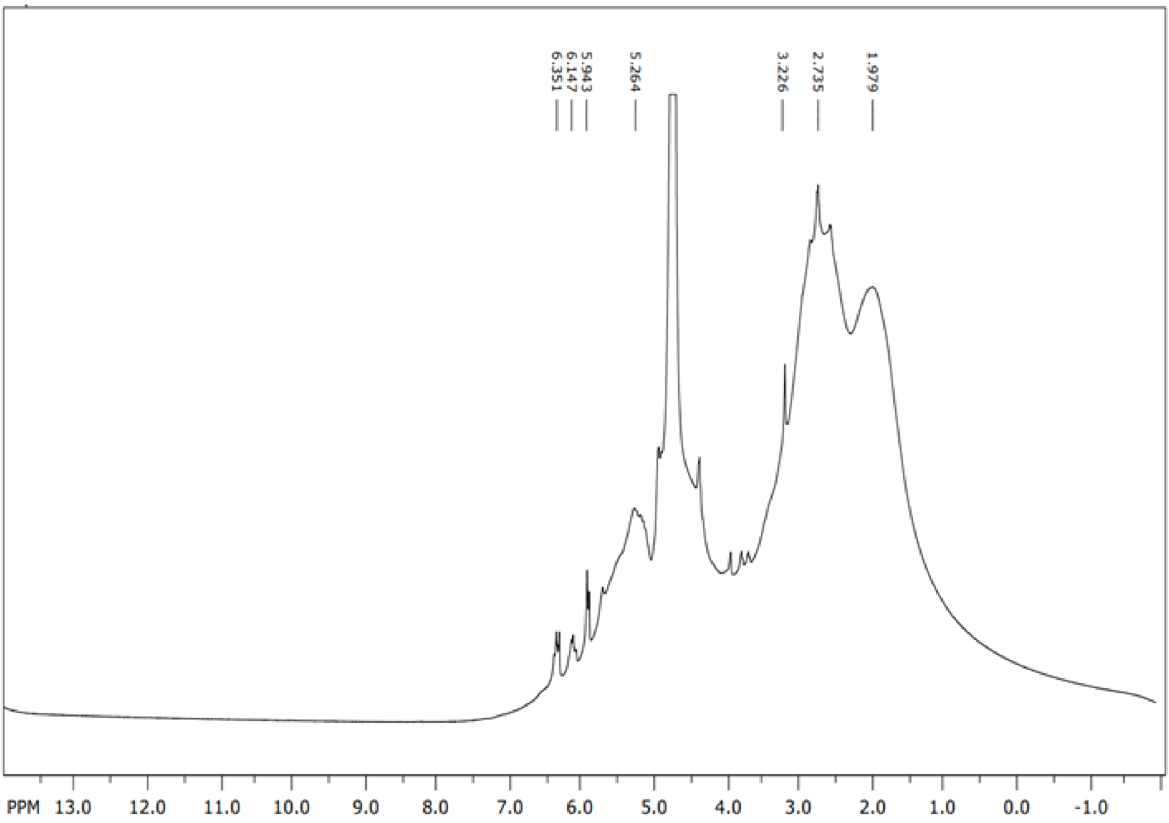

Figure S3. ^{1}H NMR spectrum of polyacrylic acid/Ce^{4+} sample.

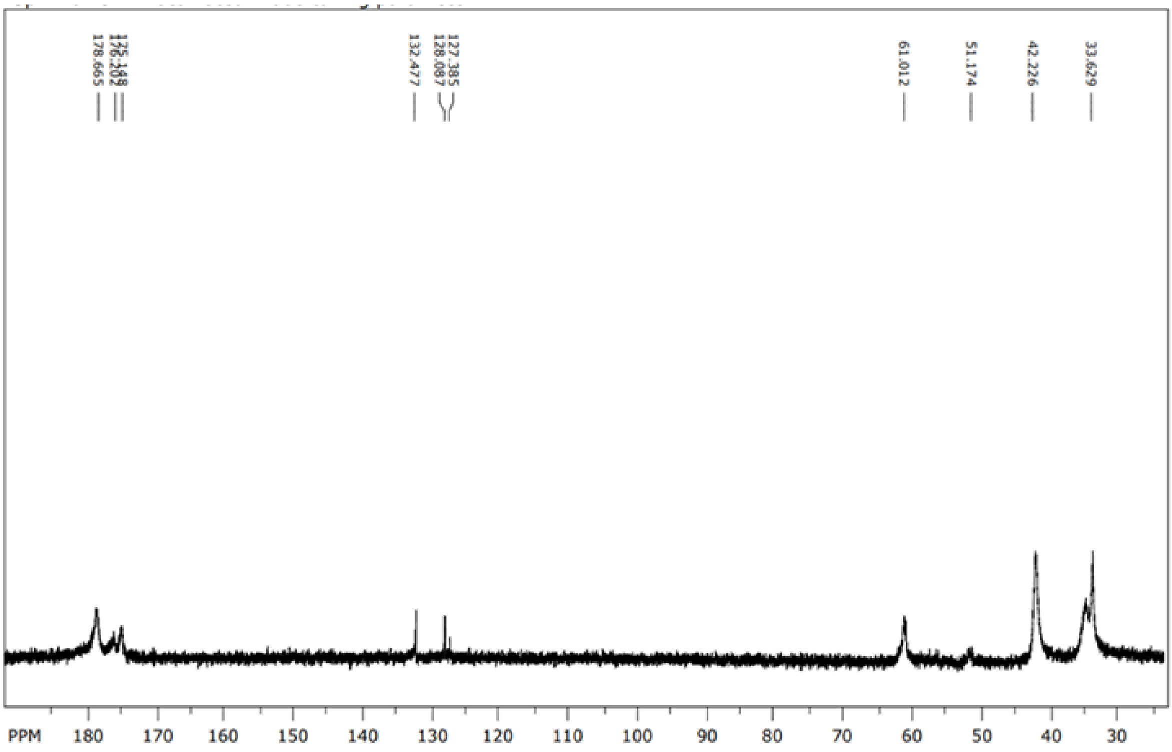

Figure S4. ^{13}C NMR spectrum of polyacrylic acid/Ce^{4+} sample.

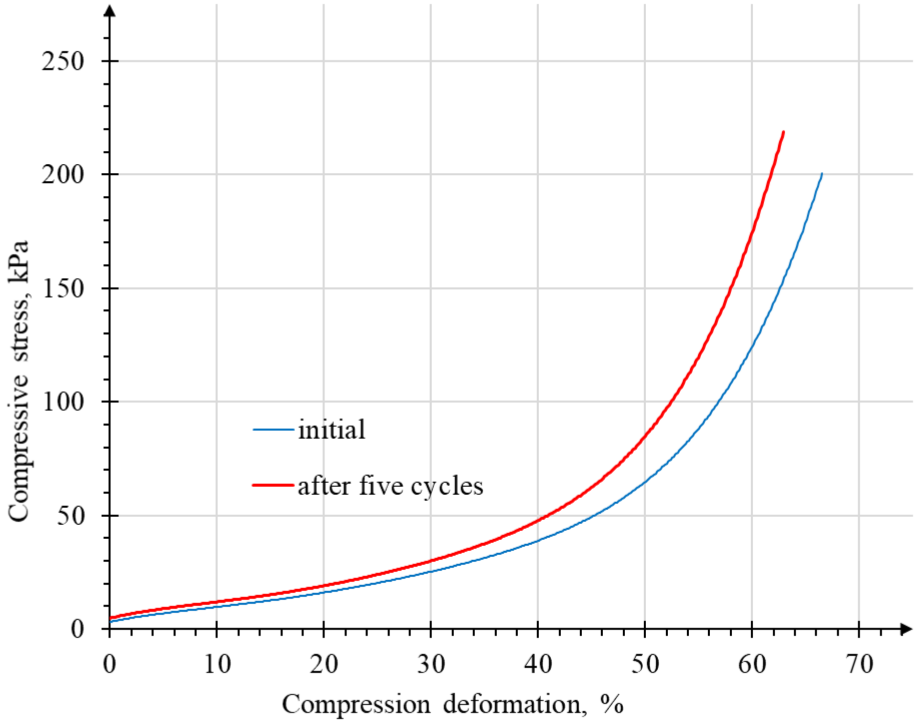

Figure S5. Compressive stress–strain curves for hydrogel samples: the initial sample and after five cycles of compression.

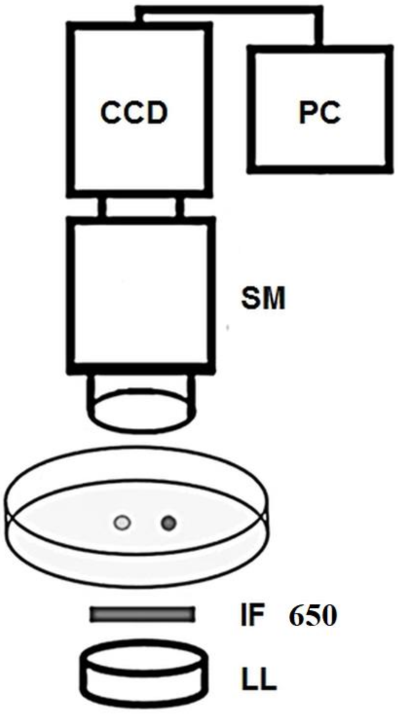

Figure S6. Experimental setup. The block diagram of the experimental setup for recording the oscillations of the pieces of the gels. Designations: SM, stereo microscope (Zeiss Stemi-2000C); CCD, a CCD video-camera (QImaging Retiga 2000R); PC, personal computer; IF 650, interference filters with the wavelength of the maximum transmission at $\lambda = 650$ nm; LL, analysing LED light.

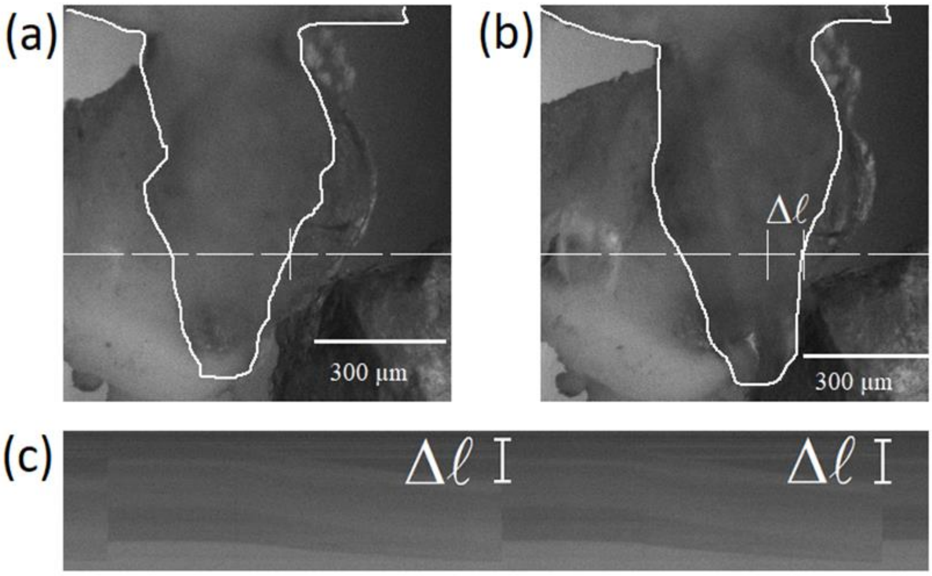

Figure S7. The initial materials used to determine the relationship between the periodic deviation of the gel piece in time and its position at the start of the experiment: (a) The initial position of the gel piece, a white dashed line represents the cross-section chosen for constructing a space-time plot; (b) the position of the gel piece after 489 s. $\Delta\ell$ is the distance from the initial position of the right edge of the gel piece to the deviated location of the right edge of the gel piece; (c) a space-time-plot fragment to build a dependence on the relative deviation of the location of the gel piece in time. In Figures (a) and (b), the white line delineates the boundaries of the gel piece selected to quantify deviation against the background of other gel pieces.