Autonomic Composite Hydrogels by Reactive Printing: Materials and Oscillatory Response

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Supplementary Methods:

FE Implementation

A FE simulation was used to investigate the effects of constrained vs free swelling behavior of Ru immobilized gel. The model geometry consisted of cube with height H divided into an active and inactive layer. We set the active layer to isotropically swell 10% to simulate the Ru catalyst oxidation process. The swelling was prescribed using a thermal expansion coefficient of $\alpha = 0.1$ and an adjusted temperature of 1 degree. We used a temperature independent hyperelastic material law to ensure this loading approach would not affect mechanical behavior. The specific material law used was the Neo Hookean

$$W = \frac{\mu}{2}\left(\bar{I}_B - 3\right) + \frac{K}{2}\left(J - 1\right)^2$$

where W is the free energy, μ the initial shear modulus, I_B is the 1st invariant of the left Cauchy-Green stretch tensor, J is the jacobian of the deformation gradient, and K is the bulk modulus. The shear modulus used was $\mu = 10$. We assume the material to be incompressible ($K \sim \infty$), which is enforced using a mixed displacement-pressure (u-p) formulation. The hydrostatic pressure associated the incompressibility constraint is solved over a separate mesh made up of a center node from each element. A total of 8000 8-node brick elements were used. The simulation was computed using commercial FE package ANSYS v12.1.

Analysis of BZ wave direction:

The transition in wave direction under thermal loading was quantified by comparing the times of Ru oxidation between three uniformly spaced locations on the polymer. The spacing was chosen so that each set of oxidation peaks corresponded to the same wave traveling through the three

nodes. This constrained the time differences to always be less than a full period. A positive Δt indicates that it the wave traveled through that node before the center black node, while a negative Δt indicates the wave traveled through that node later. The parameters used in this measurement are outlined in the schematic of supplemental Figure S2.
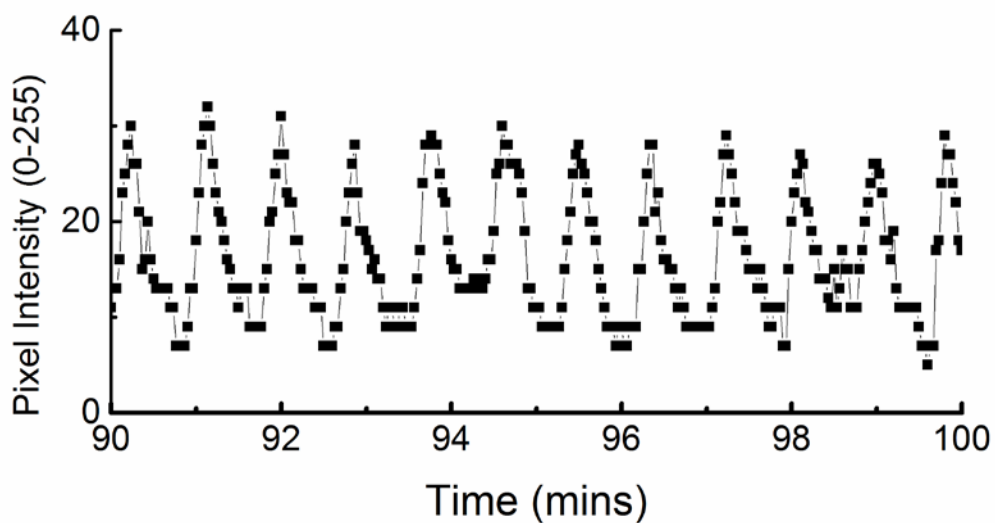
Figure S1. Oscillations in the blue channel intensity of a single pixel located within a printed spot. This shows an example of the raw data used to create the period dependence on BZ reactant concentrations in the text. The section of data shown here begins 90 minutes after the sample has been placed in the reaction solution and has reach a steady state.
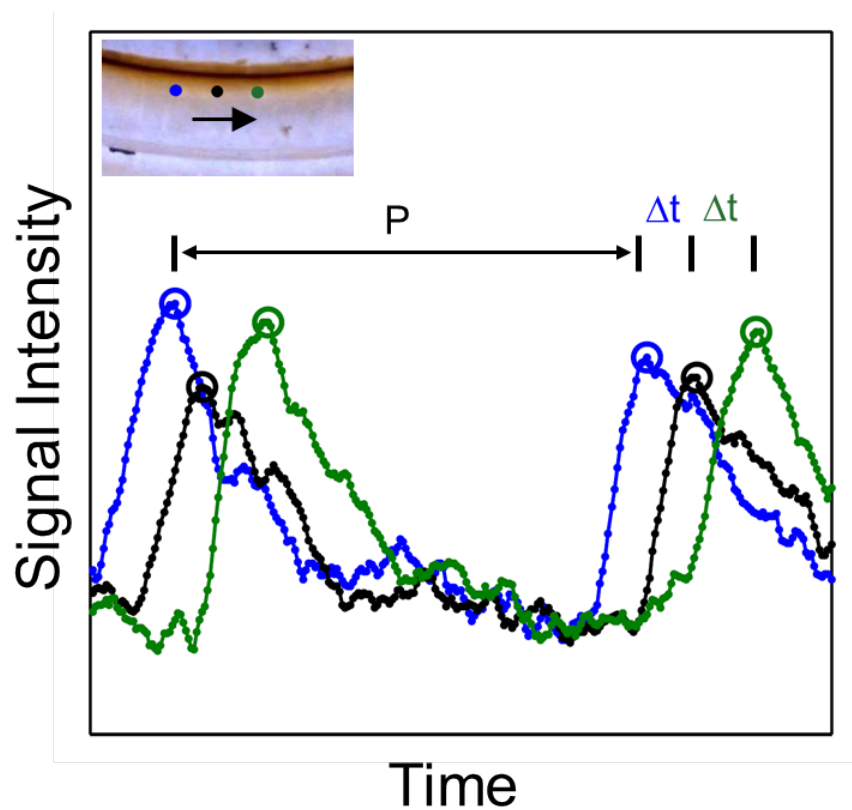
Figure S2 Schematic of relative phase parameter calculation. P denotes period and the color coded time difference, Δt, corresponds to time difference between black node and the blue and green, respectively.
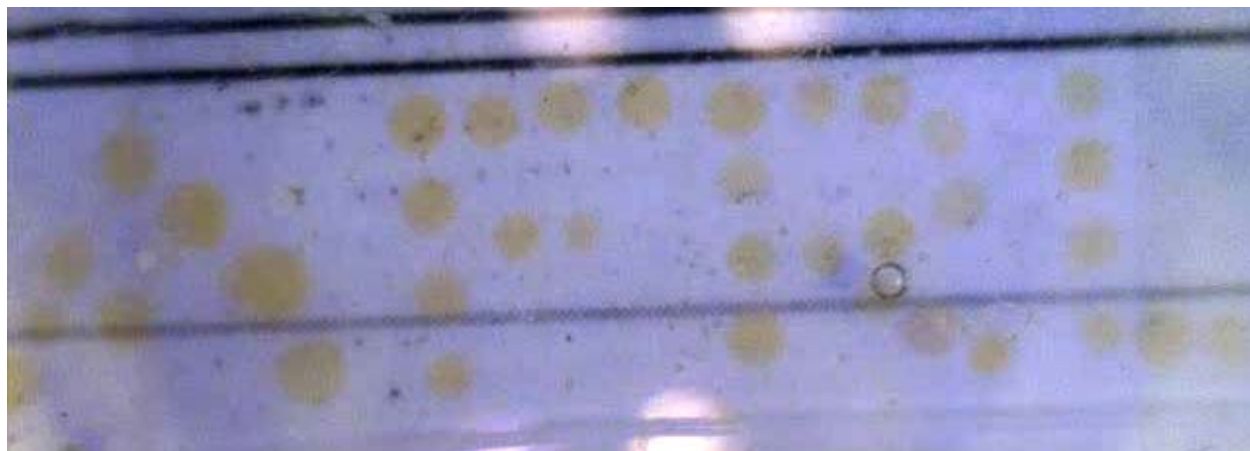
Movie S1. Oscillations of printed spots in the shape of letters. Substrate materials is PAAm-co-PAPMAm, and reactant concentrations are 0.2M SB, 0.1M MA, 1.0MNA. Black lines in the background are separated by 1mm.
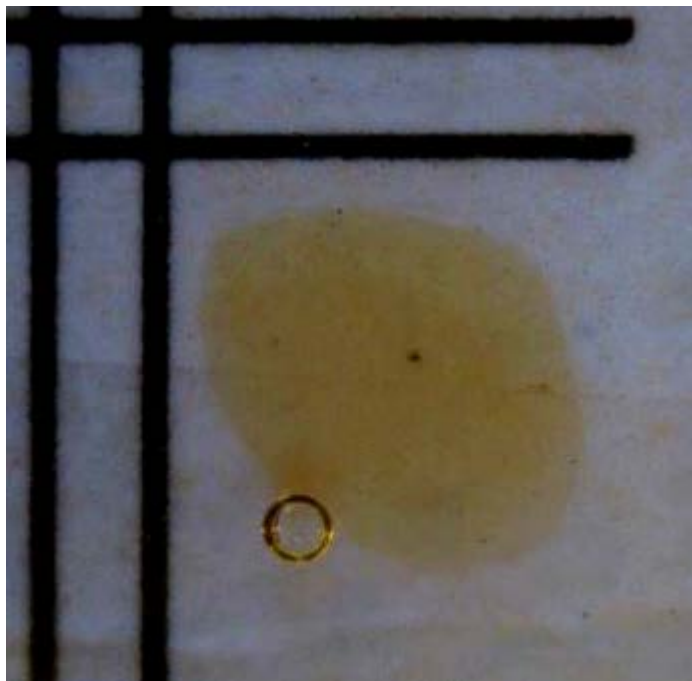
Movie S2. Oscillations in color of a printed spot in the BZ reaction. Substrate materials is PAAm-co-PAPMAm. BZ concentrations for this movie are 0.175M SB, 0.1M MA, 1.0M NA and oscillations have a period of approximately 35 seconds. Black lines in the background are separated by 1mm.

Movie S3. Side view of a strip of PAAm-co-PAPMAm with Ru catalyst printed on the top face. The sample had been moved from a uniform 20°C Peltier plate to two separate plates. On the left, the temperature is set to 35°C and the right plate remains at 20°C. Initially, waves move from right to left as they were at a uniform 20°C, but after a lag time of about 10 minutes, faster oscillations begin traveling from left to righ due to the higher temperature on the left side.