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Modeling Polymer Gels Exhibiting Self-Oscillations Due to the Belousov−Zhabotinsky Reaction

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Polymer gels exhibit a unique capability of undergoing significant volume changes in response to chemical, mechanical, and electrical stimulation.[1−3] For example, gels can undergo rhythmic swelling and deswelling in response to variations in the pH of the surrounding solution caused by an oscillatory chemical reaction.[4,5] In recent experiments, the pH oscillations were generated by the Landolt reaction[6] or by an enzymatic reaction.[7] Periodic volume changes were also observed in a pH-responsive swollen gel, which exhibited bistability with diffusion of a reactive substrate into the gel.[8] In all of these studies, the cause of the complex behavior—the chemical reaction—was *external* to the gels. Furthermore, the chemical reactions were carried out under nonequilibrium conditions provided, for example, by precisely controlled continuous-flow stirred tank reactors.[6,8]

The only known responsive polymer gels that exhibit autonomous volume oscillations under stationary conditions are those involved in the Belousov−Zhabotinsky (BZ) reaction.[9,10] In these systems, a ruthenium catalyst, which participates in the BZ reaction, is covalently bonded to the polymer chain, and the rest of the reagents are dissolved in the solvent.[11,12] The BZ reaction in the swollen gel generates periodic redox changes of the metal ion catalyst, and the gel undergoes an expansion and contraction at the oxidized and reduced states of the catalyst, respectively.[11] The cause of oscillations is purely internal because all of the necessary ingredients are present within the swollen gel; there is no chemical reaction outisde the gel. Self-oscillating gels driven by the BZ reaction have been fabricated not only as submicron-sized beads[13] but also in larger, centimeter-sized cylinders and rectangular slabs, in which traveling waves of swelling were observed.[12,14] These self-oscillating polymer gels could potentially be utilized in fabricating miniature peristaltic pumps, autonomously functioning membranes for pulsating drug release, and distributed actuator systems.[4,12,15]

Despite their potential utility and intrinsically fascinating behavior, there have been only a few theoretical studies of polymer gels exhibiting self-oscillating reactions.[16,17] The studies are restricted to considering spatially uniform swelling and deswelling behavior. In the case of the bistable chemical reaction,[18] the model for the nonuniform radial swelling of the 3D spherical gel does not adequately capture the gel elasticity.[19] It is noteworthy that there are currently no models in the literature to describe the BZ reactions in polymer gels. Herein, we present a model for a polymer gel undergoing the BZ reaction. Using this model, we first pinpoint regions in parameter space where the gels exhibit self-oscillations and then, after incorporating the spatially nonuniform gel dynamics, study one-dimensional traveling waves in the reacting gel.

The polymer gel, which contains the anchored catalyst, occupies a volume fraction ϕ. Correspondingly, $1 - \phi$ is the volume fraction of solvent, which contains the remaining dissolved BZ reagents. To mathematically describe the BZ reaction, we adapted the well-known "Oregonator" model,[10] implementing the version introduced by Tyson and Fife.[20] According to this model, the reaction kinetics can be described in terms of two dimensionless variables, u and v, where u is the concentration of reagent in solution and v gives the concentration of the oxidized catalyst. We modified the original Oregonator model to explicitly take into account how the evolution of these species depends on ϕ (see below) and thereby describe the effect of gel swelling and deswelling on the reaction kinetics. The final form of the equations depends on the size of the gel. If the gel particle is sufficiently small that the solvent transport can be considered as essentially instantaneous, then the dimensionless equations that describe the dynamics of a reacting gel undergoing the BZ reaction have the following form:

$$\mathrm{d}u/\mathrm{d}t = -u(1-\phi)^{-1}(\mathrm{d}\phi/\mathrm{d}t) + F(u,v,\phi) \tag{1}$$

$$\mathrm{d}v/\mathrm{d}t = v\phi^{-1}(\mathrm{d}\phi/\mathrm{d}t) + \epsilon G(u,v,\phi) \tag{2}$$

The first terms on the right-hand side of eqs 1 and 2 describe the concentration variations due to swelling and deswelling (see also ref 17); they are proportional to the rate of swelling, $\mathrm{d}\phi/\mathrm{d}t$. The reaction rate functions F and G are the modified terms from the Oregonator model:[21]

$$F(u,v,\phi) = (1-\phi)^2 u - u^2 - fv(1-\phi)[u - q(1-\phi)^2][u + q(1-\phi)^2]^{-1} \tag{3}$$

$$G(u,v,\phi) = (1-\phi)^2 u - (1-\phi)v \tag{4}$$

The BZ reaction kinetics now explicitly depends on ϕ. Setting $\phi = 0$ in the above equations recovers the expressions introduced by Tyson and Fife.[20] The stoichiometric factor f and the dimensionless parameters ϵ and q have the same meaning as in the original Oregonator model.

Equations 1−4 must be supplemented by an equation that specifies the equilibrium volume fraction of the polymer at a given concentration of the oxidized catalyst, v. The swollen state of the gel reaches equilibrium when the osmotic pressure, π_{osm}, becomes equal to the elastic stress in the gel, σ_{el}. According to ref 22, the electrolyte effects are quite small. We assume, therefore, that π_{osm} only depends on the polymer volume fraction ϕ and the concentration of oxidized catalyst v. To calculate π_{osm}, we employ the Flory−Huggins theory[23]

$$\pi_{\mathrm{osm}}(\phi,v) = -{v_0}^{-1} k_{\mathrm{B}} T[\phi + \log(1-\phi) + \chi(\phi)\phi^2 - \chi^* \phi v] \tag{5}$$

where k_{B} is the Boltzmann constant, T is temperature, and v_0 is the volume of one monomeric unit. The function $\chi(\phi) = \chi_0 + \chi_1\phi$ describes the polymer−solvent interactions that depend on the volume fraction ϕ,[24] where χ_0 is temperature-dependent and χ_1 is a constant. The BZ reaction and the gel dynamics are coupled through the last term on the right-hand side of eq 5. This term mimics the hydrating effect of the oxidized catalyst that causes the swelling of the gel ($\chi^* > 0$).[22]

We also need to calculate the elastic stress in the gel, σ_{el}, to obtain the equilibrium volume fraction of polymer in this system. We assume that a reactive gel swells uniformly in all three dimensions and employ the Flory model of gel elasticity to

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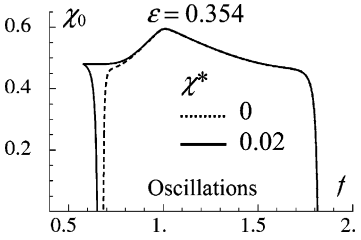

Figure 1. Map of the oscillatory regime of the BZ reaction within the gel in the $\chi_0 - f$ plane as obtained from eqs 1−6 at $\epsilon = 0.354$. Loci of the Hopf bifurcation points for a reactive gel ($\chi^* = 0.02$) (solid line) and for a nonreactive gel ($\chi^* = 0$) (dashed line). Solid and dashed lines coincide at $f > 1$. The widening of the domain of oscillations is seen for $f < 1$, with the strongest effect located in the vicinity of the swelling−deswelling transition (at $\chi_0 \approx 0.47$).

obtain in this case[25]

$$\sigma_{\mathrm{el}}(\phi) = c_0 k_B T[(\phi/\phi_0)^{1/3} - \phi/(2\phi_0)] \tag{6}$$

Here, c_0 is the cross-link density and ϕ_0 is the volume fraction of gel in the undeformed state. The values selected for c_0 and ϕ_0 are typical for gels used in the experiments, i.e., $c_0 v_0 = 1.3 \times 10^{-3}$ and $\phi_0 = 0.139$.[22]

We employed eqs 1−6 to analyze the conditions for the self-oscillations of a reactive gel under the assumption of instantaneous equilibration; i.e., assuming $\pi_{\mathrm{osm}}(\phi,v) = \sigma_{\mathrm{el}}(\phi)$ is valid for any moment of time. At $\chi^* \neq 0$, we solved this condition to obtain $v = v(\phi)$, which allowed us to describe the gel dynamics only in terms of u and ϕ. The polymer−solvent interactions were controlled by varying the parameters χ_0 (from 0 to 1.0) and χ^* (from 0 to 0.05) at the constant value of $\chi_1 = 0.518$.[24] An increase in χ_0 at $\chi^* = 0$ leads to a gradual decrease in the degree of gel swelling everywhere except in the vicinity of $\chi_0 \approx 0.47$, where a steep deswelling occurs (the swelling−deswelling transition). If $\chi^* > 0$, bistability could be observed near the swelling−deswelling transition if χ^* is sufficiently large.

The regime of the BZ reaction kinetics was controlled through the parameters ϵ and f at $q = 9.52 \times 10^{-5}$. The stoichiometry of the BZ reaction in gels[14] and the experimental data on the BZ reaction rate constants in solutions[26] have been used to estimate the value of q.

The stoichiometric factor f is known to be the key parameter that controls the transition between the oscillatory and nonoscillatory regimes of the BZ reaction. As the factor f is varied, the system crosses a Hopf bifurcation point, which separates these two regimes.[10] We determined the loci of the Hopf bifurcation points in the $\chi_0 - f$ and $\epsilon - f$ planes for the case of a nonreactive gel ($\chi^* = 0$) and a responsive gel ($\chi^* = 0.02$). (Within the oscillatory region of the BZ reaction, a "nonreactive" gel will not exhibit self-oscillations.)

We found that the oscillatory regime of the BZ reaction in a gel is only possible when the gel is swollen to a certain degree. As shown in Figure 1, the BZ reaction in both nonreactive and responsive gels exhibits oscillations at $\chi_0 < 0.6$, with the major region of the oscillatory regime being located at $\chi_0 < 0.47$, i.e., below the swelling−deswelling transition. Compared to the BZ reaction in the nonreactive gel, the BZ reaction in the responsive gel exhibits self-oscillations for a wider range of the parameters. As shown in Figures 1 and 2, the region where the responsive gels exhibit self-oscillations expands near the swelling−deswelling transition ($\chi_0 \approx 0.47$). This effect is clearly seen in Figure 2, which shows the loci of the Hopf bifurcation points plotted in the $\epsilon - f$ plane for both the nonreactive and responsive gels for $\chi_0 = 0.47$. These studies indicate that kinetics of the BZ reaction could be significantly affected by coupling the reaction to the polymer gel dynamics.

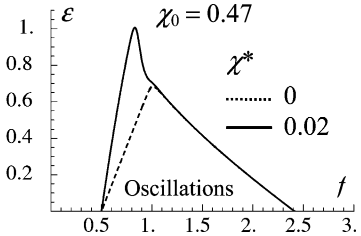

Figure 2. Map of the oscillatory regime of the BZ reaction within the gel in the $\epsilon - f$ plane as obtained from eqs 1−6 at $\chi_0 = 0.47$, i.e., in the vicinity of the swelling−deswelling transition. Notation is the same as in Figure 1. Coupling the BZ reaction to the gel dynamics significantly widens the domain of self-oscillations for $f < 1$. The solid and dashed lines coincide for $f > 1$.

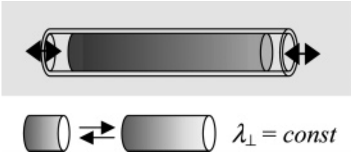

Figure 3. Schematic of the reactive gel confined in a tube. Only gel ends are in contact with the external solution, as indicated by the arrows in the top image. The gel deformations are purely one-dimensional along the tube; the gel size in the transverse direction, $\lambda_\perp$, remains constant (see image at the bottom).

In the above section, we assumed that the gel particle is sufficiently small that the solvent transport can be considered as essentially instantaneous. However, if the gel size is relatively large, the swelling−deswelling of the reactive gel cannot be considered as an instantaneous process. As a result, traveling waves of swelling−deswelling can exist in the reactive gels provided that the BZ reaction is in or sufficiently close to the oscillatory regime. Below, we simulate and study one-dimensional waves propagating along the reactive gel.

We employed the two-fluid model of gel dynamics[27] to describe the swelling dynamics in the reactive polymer gels. We considered a reacting gel confined in a tube (see Figure 3); the swollen gel is assumed to fill this tube, and the right-hand side of the sample is pinned in space. (The remainder of the gel is assumed to slip freely along the tube walls but does not detach.) We further assumed that swelling or deswelling results in purely one-dimensional longitudinal deformations of the polymer network. This assumption allows for significant simplifications in the theoretical description. The gel dynamics is described by a diffusion-like equation for ϕ

$$\partial_t \phi = -\partial_x J_\phi \tag{7}$$

$$J_\phi = -\Lambda(\phi)\partial_x(\pi_{\mathrm{osm}} - \sigma_{\mathrm{el}}^{(1D)}) \tag{8}$$

J_ϕ is the flux of the polymer units, which is proportional to the nonfrictional forces acting on the polymer network, and $\Lambda(\phi)$ is the kinetic coefficient.[21] The term $\sigma_{\mathrm{el}}^{(1D)}$ is the elastic stress caused by the 1D deformations:[21,27a]

$$\sigma_{\mathrm{el}}^{(1D)} = c_0 k_B T[\lambda_\perp^{-4}(\phi_0/\phi) - \phi/(2\phi_0)] \tag{9}$$

In eq 9, $\lambda_\perp$ = constant is the degree of gel swelling in the transverse direction. Equation 9 is used instead of eq 6 because the latter provides the elastic stress for uniform swelling in all three dimensions and is not applicable for 1D deformations.

The diffusion fluxes of the reacting species u and v are determined if the flux of polymer units, J_ϕ, is known, and the

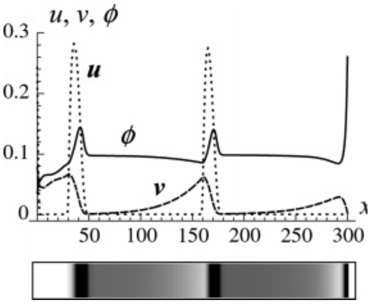

Figure 4. Propagation of a 1D wave along the confined gel undergoing the BZ reaction as obtained by numerical integration of eqs 7, 10, and 11. The wave fronts are generated at the left boundary of the gel via a time-independent boundary condition at the gel−solvent interface. The wave front travels from left to right with a constant velocity. The distributions of the reactive species *u* (dotted line) and *v* (dashed line) in the wave are typical for a traveling wave in the BZ reaction in solutions.[10] The chemical wave is coupled to the distortions of the local volume fraction of polymer ϕ (solid line) traveling along the gel. The graph at the bottom is a schematic of what would be observed in experiments.

final form of the reaction−diffusion equations is as follows:

$$\partial_t u = \partial_x[(1-\phi)\partial_x(u(1-\phi)^{-1})] + \partial_x[u(1-\phi)^{-1}J_\phi] + F(u,v,\phi) \quad (10)$$

$$\partial_t v = -\partial_x(v\phi^{-1}J_\phi) + \epsilon G(u,v,\phi) \quad (11)$$

The expressions for F and G are given in eqs 3 and 4, respectively. The diffusion flux of the reactant u has contributions from the diffusion of the reactant in the solvent and from the transport of the reactant with the solvent flux in the course of polymer−solvent interdiffusion.[21] The flux of the oxidized metal ions is simply proportional to J_ϕ because the catalyst is attached to the polymer network.

By numerically integrating eqs 7, 10, and 11, we simulated the propagation of waves of local swelling along the confined reactive gel.[21] Figure 4 shows the volume fractions of the reactants (u and v) and polymer, ϕ, along the X direction at one instant of time. In the corresponding graph at the bottom, the dark regions indicate areas of low solvent content, while the light regions mark areas of high solvent content.

The calculations reveal a novel 1D propagating wave, with alternating periodic regions of gel contraction and expansion. In particular, regions of gel contraction (or solvent-depleted zones) travel at the front of regions of gel expansion. In experiments, this effect would be observed as the formation of distinct dark stripes (i.e., contracted polymer) preceding the bright areas of the swollen gel (as shown in the bar in Figure 4). The regions of gel contraction appear because of the confinement of the gel within the tube. In other words, the polymer can only take up solvent from the ends of the tube, and thus, the polymer−solvent interdiffusion occurs solely inside the confined gel. Note that the simulations also reveal how the distribution of the reactive species along the length of the tube is coupled to the swelling−deswelling of the gel.

In summary, we developed a model for the BZ reaction within polymer gels. We found that the extent of the oscillatory regime was enhanced by coupling this reaction to a responsive gel. We also uncovered a novel form of periodic expansion and contraction within confined gels. The findings from this study can enhance our fundamental understanding of the interplay between nonlinear chemical dynamics and the finite deformations of a responsive medium. Herein, we assumed that one end of gel is fixed in the confining tube. If, however, this were not the case, the entire gel could potentially exhibit locomotion down the length of the tube, opening up new possibilities for controlling the dynamic behavior of polymeric gels in confined systems.[28]

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Supporting Information Available: Kinetics of the BZ reaction, 1D elastic stress, gel dynamics, and numerical simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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