

## Experimental Evidence of a Sustained Standing Turing-Type Nonequilibrium Chemical Pattern

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We report the experimental observation of a sustained standing nonequilibrium chemical pattern in a single-phase open reactor. Considering the properties of the pattern (symmetry breaking, intrinsic wavelength), it is interpreted as the first unambiguous experimental evidence of a Turing structure.

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Because of their supposed role in morphogenesis, the possible emergence of Turing structures in single-phase chemical systems maintained far from equilibrium by a permanent supply of reactants, first asserted in 1952,<sup>1</sup> has been the subject of a tremendous amount of theoretical study summarized in various textbooks.<sup>2-7</sup> As some confusion prevails about this term, let us make clear what we mean by "Turing structures" and what are their main properties. These are *stationary* concentration patterns, originating in the sole coupling of *reaction* and *diffusion* processes. In particular, patterns involving convection or any type of hydrodynamic motion are excluded. The Turing patterns result from spontaneous *symmetry-breaking* phenomena associated with bifurcations of steady states (often known as nonequilibrium phase transitions or self-organization phenomena). They correspond to *stable* stationary solutions of a set of *reaction-diffusion* equations,

$$\partial c_i / \partial t = f_i(\dots, c_j, \dots) + D_i \Delta c_i,$$

where the nonlinear functions  $f_i$  of the concentrations  $c_i$  represent the contribution of reactive processes, the  $D_i$  are the diffusion coefficients, and  $\Delta$  is the Laplacian operator which brings in the spatial dependence. The patterns are characterized by an *intrinsic* wavelength which does not depend on the geometrical parameters but only on the concentrations or input rates of the reactants, the diffusion coefficients, and the macroscopic reaction rates. This distinguishes the Turing patterns from the other well-known nonequilibrium structures like the convective Bénard cells or the Taylor vortices in Couette flows, which depend on some geometric length of the system.<sup>8</sup> In Turing patterns such a dependence occurs only when the size of the system is smaller than a few wavelengths—due to the necessary fit with the boundary conditions—but disappears at larger sizes. In most studies, the pattern originates, as in Ref. 1, from the instability of the homogeneous steady state in a system where the concentrations of input and output reactants are assumed to be kept constant in space and time, but Turing patterns can also form in systems fed by diffusion of reactants from the boundaries.<sup>9-12</sup> The latter are more relevant for our experiments.

The necessary conditions for Turing patterns are

stringent. First, the kinetics should include a positive feedback—such as autocatalysis—on a species called activator and an inhibitory process. Such conditions are readily fulfilled in the few reactions which exhibit bistable or oscillatory behavior.<sup>5,13</sup> Moreover, the inhibitor  $h$  should diffuse much faster than the activator  $a$  (see Ref. 4, Chap. 3) so that  $D_h \gg D_a$ . Pearson and Horsthemke have shown that when the diffusion coefficients are *nearly* equal—a common situation since most simple chemicals have diffusion coefficients of same order of magnitude  $\sim 10^{-5}$  cm<sup>2</sup>/s—the pattern still exists but only over a narrow range of control parameters in the vicinity of a Takens-Bogdanov point.<sup>14</sup> The necessity for different diffusion coefficients can be dropped when the pattern results from a secondary bifurcation and is initiated through finite perturbations.<sup>15</sup> Because of the above-mentioned difficulties, joined to the lack, until recently, of open spatial reactors able to sustain such structures in the laboratory, no unambiguous experimental observation of a Turing pattern had been reported so far. There has even been a growing skepticism about their reality in the physical world. Moreover, computations on the popular Belousov-Zhabotinskii reaction<sup>16</sup> predict pattern formation only when the relative values of the diffusion coefficients are in contradiction with physical arguments.<sup>17</sup> Recently, several types of open spatial reactors have been developed to produce and sustain chemical dissipative structures.<sup>18-22</sup> In particular, a first stationary structure has been obtained in a reactor where the molecular diffusion was replaced by a turbulent diffusion (all diffusion coefficients are equal in this case), but the pattern which develops parallel to an imposed gradient of concentration is not of the Turing-type.<sup>21,23</sup> Other reactors made of a thin flat piece of gel, the edges of which are in contact with different chemical reservoirs, have been used to study sustained wave patterns.<sup>19,24,25</sup> It had already been pointed out that this type of reactor should be well suited to evidence a Turing pattern.<sup>12</sup> In this paper, we report on the observation in a similar reactor of a stationary chemical pattern which exhibits all the characteristics of a Turing structure.

The reactor is made of a narrow rectangular flat piece of a transparent chemically inert hydrogel (polyacrylamide) which avoids any parasitic convective

motion in the reaction cell. The dimensions of the gel strip are length  $L=20$  mm, width  $l=3$  mm, and thickness  $e=1$  mm. The two opposite long edges are, respectively, in contact with two chemical reservoirs  $A$  and  $B$  where the concentrations of reactants are kept constant and uniform by appropriate mixing and a continuous flow of fresh solutions [Fig. 1(a)]. The reactants are distributed in such a way that neither solution  $A$  nor  $B$  is separately reactive: The chemicals diffuse from the edges into the gel where the actual reaction takes place. The typical diffusion time to establish stationary concentration profiles across the gel strip is about 3 h. The chemical system selected in our study is a variant of the chlorite-iodide reaction (malonic acid was added) which is known to exhibit a rich dynamical behavior.<sup>21,26,27</sup> To make the concentration changes visible, the gel was loaded with a soluble starchlike color indicator which does not diffuse through the gel. The color changes from yellow to blue with the changes of the  $[I_3^-]/[I_2]$  ratio during the redox reaction. The color pattern is monitored with a video camera.

At the beginning of the experiment, the development of a series of clear and dark stripes parallel to the edges reveals the emergence of a concentration pattern in the central region of the reactor. Although this pattern is nontrivial and could be related to a Turing pattern,<sup>9</sup> this identification remains uncertain since the stripes preserve the symmetry imposed by the feed and since other types of patterns can develop in the direction of the concentration gradient.<sup>28</sup> But over a well-defined range of the malonic-acid concentration in  $B$ , all the stripes—except

for the first clear one located close to reservoir  $B$ —ultimately break up into lines of periodic spots [Fig. 1(b)]. This constitutes a genuine symmetry-breaking phenomenon in the direction transverse to the imposed gradient. A similar line of spots parallel to the main front has been obtained in a numerical study of the Turing bifurcation of the “Brussellator” in analog conditions.<sup>12</sup> In the experiments, the pattern can be sustained indefinitely and was actually found to remain unchanged for more than 20 h. Moreover, the wavelength  $\lambda \sim 0.2$  mm seems to be really intrinsic and exclusively characterized by nongeometric properties;  $\lambda$  is much smaller than any geometric size of the reactor (including thickness) by at least 1 order of magnitude. The pattern develops along large sections of the reactor, often extending to the whole length ( $L > 100\lambda$ ) and reappears with the same wavelength after it has been destroyed by a temporary perturbation or when produced in an annular reactor of same radial width but where periodic boundary conditions prevail. On the contrary, the pattern is sensitive to the temperature which controls the reaction rates and forms only over a well-defined range of concentration. To set the ideas, with all other control parameters fixed at the values given in Fig. 1, the malonic-acid concentrations for which the pattern is observed range from  $8 \times 10^{-3}$  to  $13 \times 10^{-3}$  mole/l. Over this range of concentrations, the number of detectable rows of spots changes from 2 to 4 while, within these limits, the wavelength  $\lambda$  does not change by more than 20%. Within the accuracy of the present experimentation the patterns appear and disappear reproducibly as a function of the con-

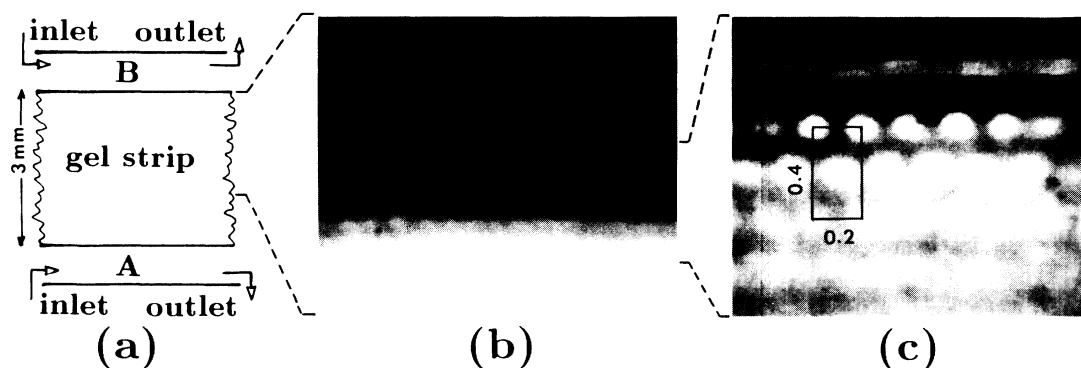


FIG. 1. Sustained chemical pattern in the gel strip reactor. (a) Sketch of the reactor: The gel strip is tightly squeezed between two flat plates 1 mm apart. Reactants are fed through the well-mixed reservoirs  $A$  and  $B$ . (b) Contrast-enhanced image: Dark regions correspond to reduced states colored in blue; clear zones correspond to oxidized states. (c) Enlarged image of the region of pattern (dimensions in mm). Experimental conditions: The gel is prepared by dissolving in 100 ml of water: 17.1 g acrylamide, 0.10 g  $N,N'$ -methylene-bisacrylamide, 0.70 g ammonium persulfate, 1.0 g triethanolamine, and 2.8 g thiodène (iodine color indicator from PROLABO). A thin uniformly flat layer of the solution is left to polymerize at  $0^\circ\text{C}$  for 1 h. The resulting sheet of polymer is then thoroughly washed and set to swell in water for 24 h before the reactor strip is cut off. After swelling of the gel, the concentration of the color indicator (taken as amylose) is  $\sim 10^{-4}$  mole/l and does not significantly decay during the experiments. Boundary feed compositions: in  $A$ ,  $[\text{NaClO}_2]_0^A = 2.6 \times 10^{-2}$  mole/l,  $[\text{KI}]_0^A = 3.0 \times 10^{-3}$  mole/l,  $[\text{NaOH}]_0^A = 3 \times 10^{-3}$  mole/l,  $[\text{Na}_2\text{SO}_4]_0^A = 3 \times 10^{-3}$  mole/l; in  $B$ ,  $[\text{CH}_2(\text{COOH})_2]_0^B = 9 \times 10^{-3}$  mole/l,  $[\text{KI}]_0^B = 3.0 \times 10^{-3}$  mole/l,  $[\text{H}_2\text{SO}_4]_0^B = 10^{-2}$  mole/l,  $[\text{NaOH}]_0^B = 3 \times 10^{-3}$  mole/l,  $[\text{Na}_2\text{SO}_4]_0^B = 3 \times 10^{-3}$  mole/l. Temperature:  $7^\circ\text{C}$ .

tol parameter. In order to definitely dismiss a spurious gel structure caused by swelling effects in an ionic strength gradient<sup>29</sup> as the possible pattern source, this ionic strength was buffered in test experiments by increasing the sodium-sulfate concentration in both *A* and *B* by 1 order of magnitude without producing any significant change in the pattern.

The study of the vicinity of the bifurcation leading to the patterns is presently out of reach because of the low contrast due to the thinness of the gel and to the dilution of chemicals. Moreover, the color indicator switches only at a given level of the  $[I_3^-]/[I_2]$  ratio. Thus only the variations large enough to go across this level can be visualized which makes the distinction between first- and second-order transitions (supercritical or subcritical bifurcations) hazardous. Only fully developed patterns can be reliably observed. On the basis of a generic Landau theory of nonequilibrium phase transitions, Walgraef, Dewel, and Borckmans<sup>30</sup> have shown that in a three-dimensional space only Turing patterns where wave vectors satisfy a definite angular relation should remain, the most stable being the body-centered cubic patterns. Our patterns are actually three dimensional since  $\lambda \ll e$  (here  $e \geq 5\lambda$ ). In the region where the pattern can be observed, one clearly distinguishes a spot distribution in qualitative agreement with such a bcc structure. However, the parallel versus transverse wavelength ratio may change as a function of the control-parameter value and the actual unit cell is more like a body-centered quadratic structure, as shown in the enlarged picture [Fig. 1(c)], due to the natural concentration gradient introduced by the edge-feed conditions, instead of the space-uniform feed hypothesized in the theoretical calculation. Note that it has been shown in theoretical one-dimensional studies<sup>31</sup> that a continuous transcritical ramp variation of control parameter—as induced by our edge-feeding technique—can lead to a strong wavelength selection. Although the extension to higher dimensionalities is an open question, this could provide an explanation for our observation of a reproducible value and small changes of wavelength along the width of the pattern.

All these properties—stationarity, spontaneous symmetry breaking, intrinsic wavelength, and patterning in good agreement with theoretical predictions<sup>11,12,30</sup>—support the interpretation of this pattern as the first experimental evidence of a genuine Turing structure. It is still unclear if the intermediate species of this specific reaction have already significantly different diffusion coefficients in aqueous solution or if small differences in diffusion coefficients are enhanced by the diffusion processes in the gel. Our observations further highlight the unquestionable advantage of the new open spatial reactors over the more traditional batch reactors to evidence a wealth of hitherto experimentally undocumented sustained patterns such as those described in this Letter.

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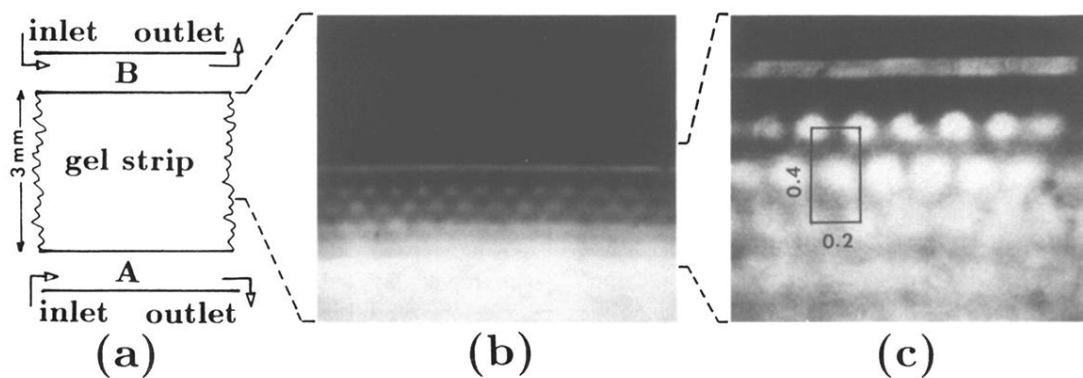


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