

Turing patterns in a simple gel reactor

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We introduce a very simple open two-dimensional gel reactor for studying chemical patterns that arise in reaction–diffusion systems. The reactor consists of a thin disk-shaped layer of polyvinyl alcohol gel with one face in direct contact with a well-stirred flow reactor containing reactants of the chlorite–iodide–malonic acid system; the other face of the gel is in contact with a piece of transparent plexiglass. We have used this reactor to study the transition from a uniform state to a hexagonal pattern; for other concentrations, striped patterns were observed. The wavelength of these structures is greater than the thickness of the gel layer, which indicates that the patterns are two-dimensional (a single layer). This reactor provides a promising new tool for studying chemical patterns since the diffusion time of reactants into and out of the gel can be made small compared to the total residence time in the stirred flow reactor. This feature facilitates the comparison between theory and experiment since the chemical concentrations leading to pattern formation are close to those in the stirred flow reactor and hence can be directly measured.

1. Introduction

Pattern formation in reaction–diffusion systems has attracted the interest of experimentalists and theorists alike during the last few decades. Until recently experimental work centered on spatio-temporal patterns in closed systems. Typically, a thin layer of reactive solution was placed in a petri dish and patterns such as spiral waves and target patterns were observed. However, since these appeared in a closed system, they were only short-lived transients.

Several open chemical reactor designs have been introduced in order to allow the study of chemical patterns at conditions maintained far from equilibrium. Most of these designs employ an inert gel reaction medium in which convection is suppressed; such a reactor has been called a CFUR (continuous flow unstirred reactor), in analogy with the acronym CSTR used for continuous flow stirred tank reactors. In 1987 Noszticzius et al. [1] used a CFUR with an annular gel that was fed at the inner and outer rims to study traveling waves in the Belousov–Zhabotinskii (BZ) reaction. Another CFUR design consists of a thin gel layer that is sandwiched between two thin porous glass plates [2]. The face of each porous glass plate opposite to the gel is in contact with a stirred

chamber that is continuously fed with chemicals; the chemicals in each chamber are chosen to be unreactive. The chemicals diffuse through the porous glass plates into the gel, forming crossed gradients in the gel. The concentrations in planes parallel to the glass plates would be uniform in the absence of

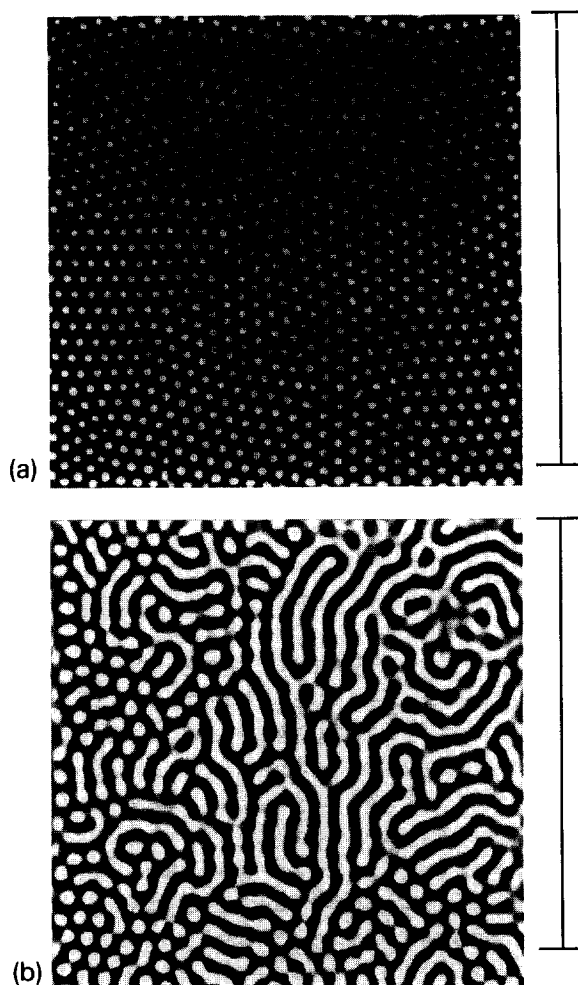


Fig. 1. Stationary chemical patterns formed in the CSTR-membrane reactor with a gel layer 0.27 mm thick. (a) Hexagonal structures with wavelength 0.32 mm ($[\text{CH}_2(\text{COOH})_2] = 1.0 \text{ mM}$). (b) Striped patterns with wavelength 0.52 mm ($[\text{CH}_2(\text{COOH})_2] = 2.2 \text{ mM}$). The parameters common to both patterns were $[\text{ClO}_2] = 6.0 \text{ mM}$, $[\text{H}_2\text{SO}_4] = 5.0 \text{ mM}$, $[\text{NaI}] = 3.5 \text{ mM}$, and temperature 7.0°C . The chlorite reservoir also contains sodium hydroxide (1 mM) to stabilize the chlorite. The bar beside each picture represents 1 cm. Wavelengths were calculated from two-dimensional Fourier transforms.

reaction, but the reaction–diffusion process can lead to the formation of spatial patterns. This membrane reactor has been used by Ouyang and Swinney [3] in the first study of the transitions from uniform concentration to stationary chemical patterns (Turing patterns). Turing had predicted stationary spatial structures four decades ago [4], but the first observation in laboratory experiments was made only in 1990 by the Bordeaux group [5–7]. The Bordeaux experiments and the subsequent experiments of Ouyang and Swinney were conducted on the chlorite–iodide–malonic acid (CIMA) reaction. Further experiments by Ouyang and Swinney [8], using the membrane reactor, led to the discovery of a transition from Turing patterns to time-dependent patterns (“chemical turbulence”).

A third design also consists of a thin gel layer, one side of which is in contact with a capillary array, which in turn is in contact with a CSTR; the other side of the gel is in contact with a glass plate. This reactor was used by Tam et al. [9] in studies of the formation of spirals in the BZ reaction and by Skinner and Swinney [10] in studies of the transition from simple to compound rotation of the spirals.

The reactor developed for the present experiments is similar to the disk reactor of Tam et al. [9], except that the capillary array has been eliminated. The capillary array was originally thought to be necessary to prevent the stirring in the CSTR from disrupting the pattern formation. Unfortunately, because of the long diffusion time through the 1 mm thick capillary array, the concentrations imposed on the gel were not accurately known, which makes it difficult to make direct connection between the experimental observations and reaction–diffusion models.

The present reactor is the ultimate in simplicity: a thin gel layer lies on one wall of a CSTR. Very high contrast Turing patterns have been observed with a gel thickness of only 0.27 mm, as fig. 1 illustrates. The diffusion time into the gel is very short; hence the concentrations of the feed chemicals for the reaction–diffusion process can be determined fairly accurately from measurements in the CSTR, and consequently it should be possible to make direct contact between the observations and reaction–diffusion models. We call this new CFUR a CSTR–membrane reactor. We will describe it and then present some results obtained using it.

2. Experimental system

A schematic diagram of the chemical reactor and data acquisition system used in this study is shown in fig. 2. Three Pharmacia P-500 precision piston pumps

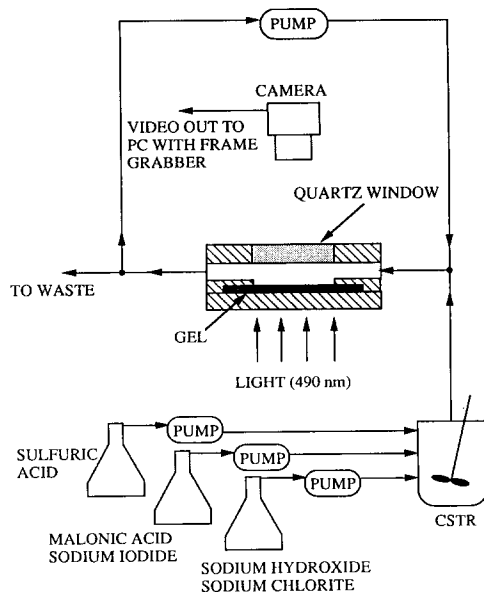


Fig. 2. Schematic of the CSTR-membrane reactor showing the configuration of the gel and reactant streams. The reactor is shown in cross section and is not to scale. The PVA gel plus Anapore thickness is 0.31 mm and the diameter is 25.4 mm (see text).

are used to feed solutions from three reservoirs containing sulfuric acid, a malonic acid-sodium iodide mixture, and a sodium chlorite-sodium hydroxide solution (the NaOH is needed to stabilize the chlorite) into a 0.5 ml stirred-tank reactor. The three reservoirs are separately unreactive and thus the reaction does not occur until the reagents are mixed in the CSTR. The reaction mixture then enters a small plexiglass chamber (1.6 ml volume) that is in direct contact with the gel (fig. 2).

The disk-shaped gel is made from polyvinyl alcohol (PVA) instead of polyacrylamide, which has been used in most previous studies. The properties of PVA differ in several important respects from those of polyacrylamide. In previous work using polyacrylamide, the gel had to be loaded with a soluble starch indicator (usually Thiodène, Prolabo) in order to make spatial variations in triiodide concentration visible. In contrast, PVA acts both as a convection-free reaction medium and is itself a triiodide indicator. This gel is also less brittle than polyacrylamide; hence the gel layer can be very thin. The thickness of the gel used in the present study was 0.27 mm; further studies could use even thinner gels. PVA gel was prepared by mixing 5 ml of 12 percent by weight PVA solution with 2 drops of 25 percent aqueous solution of glutaral-

dehyde at room temperature. Polymerization was initiated using 0.2 ml of concentrated hydrochloric acid. After one-half hour the gel set and upon subsequent immersion in water it shrunk approximately 10 percent after several hours.

Recently, Noszticzius et al. [11] have studied the role of triiodide indicators, including Thiodène and polyvinyl alcohol, in the formation of Turing patterns. They have shown that in both cases triiodide reacts with the indicator to form an optically detectable complex. It is believed that these complexes are immobile and result in a rescaling of the effective diffusivity of some of the species [12], which is a necessary condition for a Turing instability to occur. However, Thiodène contains a large amount of urea, which may interfere with other reactions [11]. The possibility of this happening can be circumvented by using PVA gel instead of polyacrylamide loaded with Thiodène.

The 0.27 mm thick gel disk is 2.54 cm in diameter and it rests on top of a transparent piece of plexiglass (see fig. 2). It is held in place around its edges by an overlaying piece of plexiglass with a circular 1.78 cm diameter opening, which exposes the gel to the small 1.6 ml chamber containing the mixed reactants that are fed from the CSTR. High contrast patterns were obtained with this arrangement, but there was some difficulty at times with buckling of the gel. To prevent this buckling, experiments were also conducted with a thin inert rigid membrane (Anapore from Whatman) placed over the PVA gel; the Anapore disc is 0.04 mm thick and has an average pore size of 0.02 μm . The Anapore membrane keeps the gel flush with the plexiglass but is so thin that no difference could be observed in the patterns formed with and without this membrane. The membrane is brittle, and we therefore impregnated it with one drop of polyacrylamide gel (no starch) in order to make it stronger and more flexible.

A peristaltic pump operating at 1000 ml/hr is used to recirculate the reactants that exit from the chamber in order to maintain well-stirred conditions in the fluid above the gel. The entire reactor assembly is immersed in a constant temperature water bath.

The PVA gel reacts with triiodide to form an immobile complex that absorbs light with a broad range of wavelengths that peaks near 490 nm, giving a color change from clear to a reddish-brown during the redox reaction. Therefore, patterns can be observed by using standard optical techniques. The gel is illuminated from below with a uniform light source with a peak intensity of 470–520 nm. A Sanyo CCD video camera fitted with a macro lens is placed above the gel to detect the intensity of transmitted light as a function of position in the plane of the gel. The video output from the camera is sent to an IBM PC-AT equipped with a 480 \times 512 frame grabber. The acquired images are then analyzed on a Silicon Graphics workstation.

3. Results

The system can be controlled by changing one or more of several control parameters including the concentration of the chemical reactants, the residence time, and the temperature. Beyond critical values of the control parameters patterns emerge spontaneously from an initially homogeneous state. For example, fig. 1 shows steady-state patterns observed at two different sets of conditions. At low concentrations of malonic acid, hexagonal patterns separated by grain boundaries are observed (fig. 1a). These patterns evolve over a period of several hours before becoming stationary with only slight changes in the grain boundary positions.

We have studied the transition from the homogeneous state to hexagons by using temperature as a control parameter while keeping all other parameters held fixed. As the temperature is decreased we find that the pattern emerges near 17°C, as shown in fig. 3. Within the experimental resolution we do not observe any hysteresis upon subsequent increase of temperature. We do not detect any critical slowing down near the transition, in contrast to previous work with a membrane reactor [3]. The wavelength of the patterns, 0.32 mm, also appears to be fairly insensitive to the temperature.

At higher concentrations of malonic acid, striped patterns are observed, as illustrated in fig. 1b. Again, these structures evolve toward a stationary state from an initially homogeneous state over a period of several hours. The

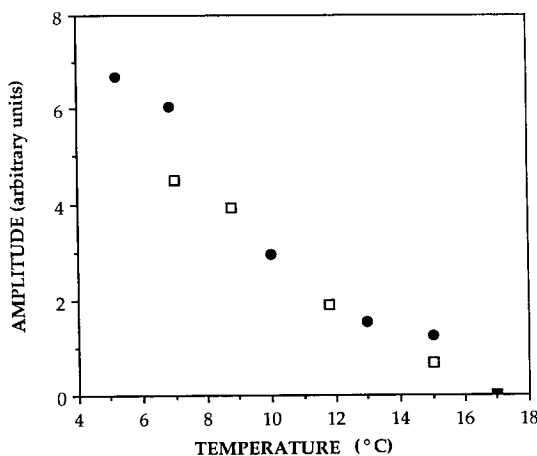


Fig. 3. The transition from a uniform state to a hexagonal Turing pattern. The amplitude of the patterns was obtained from the modulus of a two-dimensional Fourier transform. The points ● (□) were measured for temperature decreasing (increasing) in steps. The concentrations of the reactants were $[\text{ClO}_2^-] = 6.0 \text{ mM}$, $[\text{H}_2\text{SO}_4] = 5.0 \text{ mM}$, $[\text{NaI}] = 3.5 \text{ mM}$ and $[\text{CH}_2(\text{COOH})_2] = 2.0 \text{ mM}$.

appearance of stripes at larger concentrations of malonic acid is also accompanied by an increase in wavelength from 0.32 mm (at $[\text{CH}_2(\text{COOH})_2] = 1.0$ mM, hexagons) to 0.56 mm (at $[\text{CH}_2(\text{COOH})_2] = 2.5$ mM, stripes). The transition from hexagons to stripes as the concentration of malonic acid is increased was also found in the membrane reactor, but the strong dependence of the wavelength on malonic acid was not observed [3].

We have also found that the appearance of Turing structures is sensitive to the residence time in the CSTR–membrane reactor. We define the residence time, τ , to be the volume of mixed reactants divided by the total volumetric flow rate of the reactants. The volume containing the reaction mixture includes the CSTR, the tubing leading from the CSTR to the gel reactor, the small volume of reactants above the gel, and the recirculation loop. We have found patterns only when $60 \text{ s} < \tau < 180 \text{ s}$. The wavelength and character of the patterns changes very little as the residence time is varied in this range.

4. Discussion

A major advantage of the CSTR–membrane reactor over previous reactors designed for the study of reaction–diffusion patterns is the simplicity of the present design. Another advantage is the small thickness of the gel. If we neglect chemical reaction and reflections off the boundary, we can obtain an upper bound estimate on the time scale for diffusion into and out of the gel from the relation $t_z \sim z^2/2D$, where D is the diffusivity and z is the gel thickness. In our system $z = 0.031$ cm (gel + Anapore), $D \approx 10^{-5}$ cm²/s, and therefore we find $t_z \sim 50$ s. We emphasize that this is only a largest-value estimate, and that the actual value could be much less. By comparison, typical residence times in the CSTR–membrane reactor at which we observe patterns are four times greater. Hence, the chemical concentrations probably do not vary greatly across the thickness of the gel and are near those in the CSTR.

A second benefit of the short time-scale for diffusion into and out of the gel is that the spatial structures in the plane of the gel can evolve on a much shorter time-scale than they would in a membrane reactor. This could be especially important if one were interested in studying the dynamics of spatio-temporal structures such as those recently reported by Ouyang and Swinney [8].

Thirdly, it may be possible to draw a correspondence between experimental observations of temporal structures in a CSTR and spatial or spatio-temporal structures in the CSTR–membrane reactor. For example, Lengyel and Epstein [12] have argued, using certain assumptions, that the chemical conditions in a gel medium in which Turing structures are present should correspond to

oscillations in a CSTR. In order to monitor the iodide concentration, we have placed a platinum probe in the recirculation loop of the CSTR–membrane reactor, and no oscillations have been observed when Turing patterns are present. This seems to suggest that at least some of the assumptions in the analysis of Lengyel and Epstein are not fulfilled in our system.

Another important finding of our studies using the CSTR–membrane reactor is that the wavelength of the observed patterns (0.32–0.56 mm) is greater than the thickness of the gel. Thus, only a single-layer structure is present, and patterns do not depend upon the presence of structure orthogonal to the gel.

In contrast to a CSTR–membrane reactor, in the membrane with reservoirs on both sides of the reactor [2, 3] the concentration gradients are deliberately created and maintained across the thickness. The gel rests between two membranes, which further complicates the understanding of the chemical concentrations at which the spatial structures occur. Furthermore, these membranes do not simply serve as supports for the gel. As the reactants diffuse towards each other across the membranes and into the gel, a reaction front is formed at some intermediate location between the boundaries. On one side of the front the system will be in the reduced state and on the other side it will be in the oxidized state. The presence of starch indicator in the gel will render a dark color in the reduced region. Therefore patterns cannot be optically detected unless the position of the reaction front is moved to the gel-membrane boundary so that the reduced region resides in the indicator-free membrane. Consequently, there are restrictive conditions on the feed concentrations and flow rates, and it is difficult to determine if there is a single or multi-layer structure. However, the membrane reactor has a significant advantage for some studies in that the reagents in each chamber can be separately unreactive; reaction occurs only in the gel layer. Hence this reactor is complementary to the CSTR–membrane reactor we have described.

In summary, we have introduced a simple new gel reactor that consists of a thin layer of PVA that is fed uniformly over one face and which has no-flux boundary conditions on the other face. We have observed Turing patterns and transitions similar to those previously found in a membrane reactor and we have shown that these patterns are quasi two-dimensional. The CSTR-membrane reactor allows accurate characterization of the chemical conditions that lead to spatial pattern formation and thus it facilitates the comparison of reaction–diffusion models with experimental observations.

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