

## Pattern formation in the polyacrylamide-methylene blue-sulfide-oxygen system

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**SUMMARY:** In an experimental study of the polyacrylamide-methylene blue-sulfide-oxygen (PA-MBO) system a variety of complex concentration patterns have been observed. Chevron and white-eye patterns develop from hexagons in a slow, continuous transition process. Honeycombs form a third type of structure that develops from either white-eye or hexagonal patterns. The motion of suspended tracer particles during the process of pattern formation was recorded under a microscope. This motion provides information about the possible role of hydrodynamic convection and/or mechanical deformation of the gel matrix. Quantitative data on surface undulations of the gel are also presented. The structure of the gel surface resembles the structure of the observed methylene blue patterns. It is concluded that plastic or elastic phenomena may play a role in later stages of the pattern formation.

### Introduction

The formation of regular stationary concentration patterns in reactive systems has been discussed since the publication of Turing's pioneering work "On the chemical basis of morphogenesis" which appeared in 1952<sup>1)</sup>. An experimental verification of such patterns in the chemical laboratory was realized almost 40 years later using the chlorite-iodide-malonic acid (CIMA) reaction<sup>2)</sup> as the result of long lasting efforts. Another reaction which exhibits spatial organization of this kind is the methylene blue-sulfide-oxygen (MBO) system embedded in a polyacrylamide (PA) gel, which reveals a variety of complex Turing-like concentration patterns<sup>3)</sup>. Stationary patterns like stripes and hexagons as well as chevron, zig-zag and white-eye patterns can be observed in this system<sup>4)</sup>. Recently, the question has been asked whether these patterns arise from a Turing-like chemical instability<sup>1-3, 5, 6)</sup> or from convection phenomena<sup>7, 8)</sup> during the gelation of the polymer gel, and this issue remains under discussion in the current literature<sup>9, 10)</sup>. In the present article some properties of the PA-

MBO system are described; we focus on the transition between white-eye and honeycomb patterns, on the measurement of particle motion associated with this transition and on the surface deformation which occurs after completion of the patterning process. Possible implications of the presented results for the ongoing discussion on the nature of the patterns in the PA-MBO reaction are pointed out.

## Materials and Methods

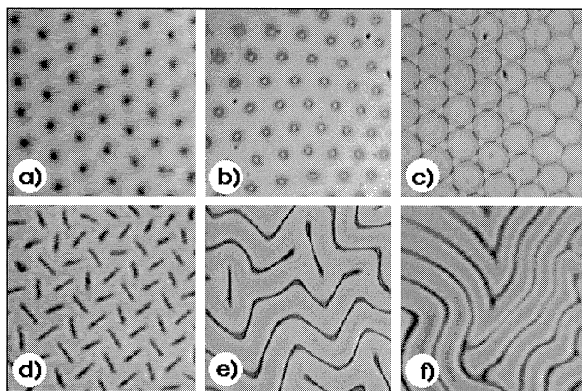
The MBO reaction is the methylene blue-catalyzed oxidation of  $\text{HS}^-$  by oxygen in basic aqueous solution<sup>11, 12</sup>. Methylene blue (MB) exists in three oxidation states: the blue  $\text{MB}^+$  ion, the colorless MBH (leukomethylene blue), and the  $\text{MB}^\bullet$  radical. In homogenous, well-stirred solutions, this reaction system displays sustained oscillations. We are interested in studying spatiotemporal patterns, therefore we immobilize the components of the MBO system in a polyacrylamide gel.

For the preparation of the system the chemicals of the MBO reaction and the monomer mixture for the PA gel were mixed together in a thermostated Petri dish of 7 cm diameter. Then the polymerization was initiated by adding ammonium peroxodisulfate and exposing the system to illumination with white light from below<sup>3</sup>). The addition of peroxodisulfate to the reaction mixture always marks the begin of the experiment (i.e.  $t=0$ ). The Petri dish containing the reaction mixture was placed on a light box at room temperature and the pattern formation was monitored by a charge coupled device (CCD) camera. In order to obtain different patterns, the initial sulfide concentration was varied in a certain range<sup>4</sup>). Once started, the system cannot change its initial concentrations; the system is semiclosed, since only the reactant oxygen is supplied from the air, while sulfide as well as MB are continuously consumed in the course of the reaction.

It is important to note that this kind of preparation of the PA-MBO system is necessary to generate spatiotemporal patterns in the MBO system. No pattern formation could ever be detected by placing the MBO reactants into a 'ready made' PA gel<sup>7</sup>). This fact is especially important for the question about the origin of the pattern formation process.

## Results

Our observations have shown that stripes and hexagonal patterns arise approximately 10 min after preparation of the gel and have a typical wavelength of about 2-3 mm, as determined by two-dimensional fast Fourier transform (FFT)<sup>4)</sup>. In the course of the reaction we observed a transition from the initially formed hexagonal patterns to white-eye, chevron and zig-zag patterns. They develop from simple hexagons in a slow, continuous transition process lasting for about 14 min across the entire Petri dish. The white-eye patterns consist of small rings of high MB<sup>+</sup> concentration with each ring located on a hexagonal lattice. Figure 1 shows examples of the observed patterns.

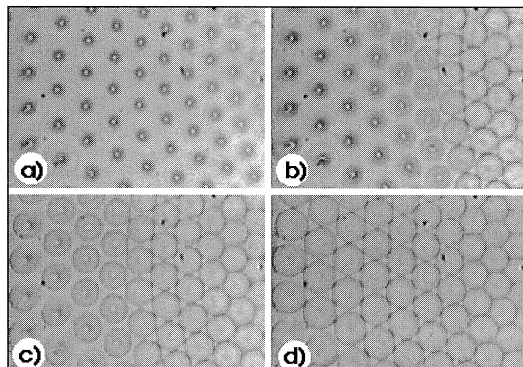


**Fig. 1.** Different types of patterns in the PA-MBO system: a) hexagonal pattern, b) white-eye pattern, c) honeycombs, d) chevrons, e) zig-zag pattern, f) stripes; image area: 16.3 x 16.3 mm<sup>2</sup>, except e) 16.1 x 16.1 mm<sup>2</sup>.

A particularly interesting pattern consists of honeycombs that form from either white-eye or hexagonal patterns about 25 min after preparation of the gel. The transition to this structure occurs rapidly along propagating fronts<sup>4)</sup> ( $\approx 1$  min for each line of patches). Figure 2 shows snapshots of the MBO system during the formation of the honeycombs in the wake of a front moving from right to left across the array of white-eye patterns. Looking more closely at a single patch of the pattern one can observe an expansion of a single white-eye spot until it collides with neighboring patches. The expansion of the patches stops with the formation of the honeycomb pattern. During this transition the patches lose their central 'white-eye'.

The various types of patterns observed in the course of the experiments can be grouped in a schematic phase diagram that characterizes the pattern geometry in dependence of reaction

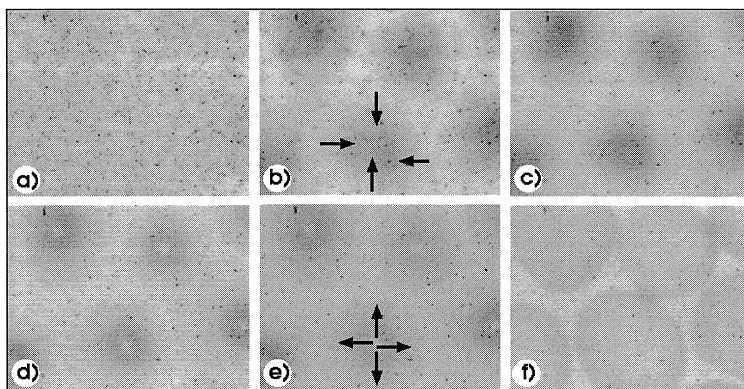
time and initial sulfide concentration. Despite the apparent complexity of some of these patterns one can show by use of two-dimensional Fourier analysis that a simple underlying geometry prevails and that the wave vectors of the initial hexagons are conserved in all transitions <sup>4)</sup>.



**Fig. 2.** Transition from white-eye to honeycomb structures. The snapshots are taken: (a) 19 min, (b) 23 min, (c) 27 min, and (d) 34 min after preparing the PA-MBO system. Image area:  $23 \times 16.1 \text{ mm}^2$ .

In order to obtain more information about the possible influence of hydrodynamic flow and/or mechanical deformations of the gel matrix, experiments were made where talcum particles were added to the solution. We carried out measurements of this particle motion during different phases of the pattern formation process. The determination of particle movement was made with computational particle tracking.

Figure 3 shows snapshots of the same area taken at different stages, starting from spatial homogeneity and leading via hexagons and white-eyes to honeycomb structures <sup>13)</sup>. Initially, one can detect the formation of a hexagonal pattern in the gel which has a wavelength of about 2 mm in Fig. 3b. A motion of the small particles towards the center of the patches is associated with the evolution of these patches. This motion stops as the evolution of white eye patches sets in (Fig. 3d). During the transition from the white-eye pattern to honeycombs one can observe a second stage of particle motion in the patches, but this time it is directed away from the patch centers (Fig. 3e). This outward motion is much slower than the first inward flow of the particles during the formation of the blue patches of a hexagonal pattern.



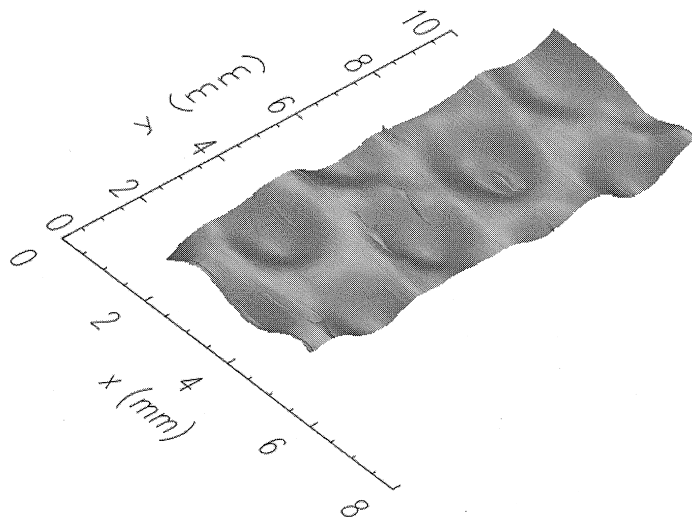
**Fig. 3.** Sequence of snapshots: a) shows a homogenous phase (note that the black speckles are talcum particles used to trace motion on the gel). Transition to hexagonal patterns is shown in frames b,c), followed by the formation of 'white-eyed' structures in d). Frames e,f) show the subsequent transformation of the white-eyed structures to honeycomb patterns. The arrows mark the direction of particle motion in a single patch of the pattern. Temporal sequence after preparing the system: a) 9 min, b) 9.5 min, c) 10 min, d) 17 min, e) 24 min, f) 26 min.

In the context of particle motion the gelation stage of the PA-MBO system plays a prominent role. At a certain point during the polymerization, the gel point, there is a drastic change in the physical properties of the reaction system, like in viscosity, elasticity, and permeability<sup>14, 15)</sup>. Different suggestions on how to detect the gel point are given in references<sup>14, 15)</sup>. Since the gel point of the PA-MBO system depends on the intensity of illumination, its measurement using the proposed methods is especially difficult. This being the case, we decided to monitor the state of the system by a simple test: we slowly move a glass rod in the fluid until the gelation is reached. This stage of polymerization is characterized by a throw up of the gel in front of the rod. We found that the gel point occurs about 20 seconds before detecting the first visible patterns. From the close temporal sequence between the onset of polymerization and of pattern formation process ( $\approx 20$  s) a close connection between these two processes can be inferred.

In order to further characterize these patterns we measured the typical length scale, i.e. the typical average distance between the dark dots of the initial hexagons. It turns out that this 'wavelength' shows a linear dependency on the layer thickness of the gel which is in contrast to a statement in reference<sup>9)</sup>, where no dependency was observed. This point needs further experimental clarification. Following our finding and since for Turing structures no

dependency on the layer thickness is expected, one can ask the question whether other physical phenomena are involved in the process of pattern formation. In particular, the formation of convection cells during the polymerization and gelation stage of the reaction has been considered in the recent literature <sup>8, 10)</sup> as a possible mechanism for the pattern formation process and would be consistent with the linear dependency on the layer thickness.

We found that nearly synchronously with the onset of pattern formation remarkable changes in the surface of the gel occur. These changes consist of a local swelling and/or shrinking of the gel which can be easily seen with the naked eye. To further analyze the undulations, we performed a series of experiments where the gels, containing patterns, were allowed to dry out over 1 day. These experiments revealed that the resulting surface undulations remain present even in the completely dried-out polymer. In the dry film the maximal height differences amount to 4  $\mu\text{m}$  (measured with a surface profiler) and the relative locations of the valleys yield a wavelength of about 2-3 mm. The surface structure in Fig. 4 resembles the structure of the observed methylene blue pattern (compare Fig. 3f). As one can see, areas with high  $\text{MB}^+$  concentration are associated with shrunken gel zones while areas of low  $\text{MB}^+$  concentration belong to swollen regions of the dried gel.



**Fig. 4.** Surface profile of a dried PA-MBO system gel. The height differences amount up to 4  $\mu\text{m}$ . Scanned gel surface: 3.75 x 10.0 mm<sup>2</sup>.

## Conclusion

The semiclosed polyacrylamide-MBO system was shown to reveal transitions of the initial hexagonal patterns towards white-eye and honeycomb patterns. These patterns have not been predicted in the past, possibly because pattern formation in this system is linked to mechanical and/or chemical changes of the polyacrylamide network which are not considered in the classical reaction-diffusion approach. A remarkable and unexpected finding of this study are the changes in the surface of the gel matrix. Also eminent is the detection of particle motion closely connected with the process of pattern formation. The inward motion is most probably an indicator of fluid convection during the still incomplete exothermic gelation process of the polyacrylamide. The remarkable, subsequent reversal of particle motion, however, which is associated with the transition to a pattern of higher complexity, is observed at a later stage after gelation. It cannot be explained on the basis of hydrodynamic considerations. We suggest that an elastic or plastic instability is responsible for a mechanical deformation of the system leading to a displacement of the tracer particles. Further experimental evidence is necessary to collect on this phenomenon of mechano-chemical coupling in a polymeric network induced by an oscillatory reaction.

## Acknowledgment

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