# On the nature of patterns arising during polymerization of acrylamide in the presence of the methylene blue-sulfide-oxygen oscillating reaction

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**Abstract**

Transient Turing-like spatial patterns were recently reported by Münster et al. when the components of the methylene blue oscillator are mixed with acrylamide and a polymerization initiator to form a polyacrylamide gel. We have qualitatively reproduced these results, but we demonstrate that, although the observed patterns have the appearance of Turing structures, they actually result from Rayleigh–Benard convection in a mixture of acrylamide, N,N′-methylene-bisacrylamide, triethanolamide, sulfide ions and ammonium peroxodisulfate during the polymerization and gelation process. Neither methylene blue nor sulfite is required for patterns to develop. © 1998 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

The many efforts to find Turing structures [1] in chemical systems were unsuccessful until experiments on the CIMA ($ClO_2^-$-$I^-$-malonic acid-starch) reaction carried out in a specially designed gel reactor demonstrated unambiguously the existence of such patterns [2–4]. The other oscillatory chemical system that has been reported to be capable of forming Turing-like structures in a gel matrix [5–7] is the methylene blue oscillator (MBO), which consists of methylene blue (Mblue), sulfide ($S^{2-}$), sulfite ($SO_3^{2-}$) and oxygen [8].

In this paper we reexamine the results obtained in the study of the methylene blue oscillator-polyacrylamide gel system. Our main aim is to reproduce and analyze the previously observed patterns with an eye toward clarifying their origin.

## 2. Experimental

### 2.1. Chemicals

All reagents were of the highest grade commercially available. These were: acrylamide (AA), Sigma, electrophoresis reagent, $\geq 99\%$; N,N′-methylene-bis-acrylamide (Bis), Sigma, electrophoresis reagent, $\geq 98\%$; triethanolamine (TEA), Fisher,

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99%; ammonium peroxodisulfate ($S_2O_8^{2-}$), Sigma, electrophoresis reagent, $\geq$ 98%; sodium sulfide ($S^{2-}$), Merck, 35% $Na_2S$; methylene blue (Mblue), Fisher, p.a. In some initial experiments, we used sodium sulfite ($SO_3^{2-}$) (Sigma, 99%), which is a non-essential but suggested component of the methylene blue oscillator [8]. Since this compound produced no noticeable effect on the behavior of the MBO-polyacrylamide gel system, we ceased to employ it. Recrystallization of sodium sulfide was suggested in Ref. [5] in order to remove polysulfide impurities present in the commercial product. We observed no difference between the results obtained with unpurified and with recrystallized sulfide. Therefore instead of purification, we used newly purchased Merck product in our experiments. We note that polysulfide, $S_x^{2-}$, is formed in any case as an intermediate during the reaction between $S_2O_8^{2-}$, and $S^{2-}$.

For preparation of stock solutions, the chemicals were dissolved in deionized water. All stock solutions but $(NH_4)_2S_2O_8$ and $Na_2S$ could be stored for many days without decomposition. The following stock solutions were made: [AA] = 2.37 M; [Bis] = 0.13 M; [TEA] = 1.62 M; [$(NH_4)_2S_2O_8$] = 0.79 M; [$Na_2S$] = 0.16 M; [Mblue] = 0.01 M.

### 2.2. Procedure

The gel components, AA, Bis and TEA, were mixed with Mblue and $S^{2-}$, and $(NH_4)_2S_2O_8$ was then added to initiate the gelation process. The final volume, composed of the stock solutions and water, was 12.6 $cm^3$, which formed an approximately 2 mm thick solution layer in a 9 cm i.d. Petri dish. In most experiments the concentration of the gel components was kept constant ([AA] = 1.035 M, 5.50 $cm^3$ of stock solution; [Bis] = $4.85 \times 10^{-3}$ M, 0.47 $cm^3$; [TEA] = 0.055 M, 0.47 $cm^3$). The [Mblue] was either $4 \times 10^{-4}$ M (0.5 $cm^3$) or the mixture was free of this component. The time of polymerization was found to be unaffected by [Mblue] but changed significantly with [$S^{2-}$] and [$S_2O_8^{2-}$]. For example, at [$S^{2-}$] = $1.5 \times 10^{-2}$ M (1.20 $cm^3$), $3 \times 10^{-2}$ M (2.40 $cm^3$) and $5 \times 10^{-2}$ M, (3.94 $cm^3$), and [$S_2O_8^{2-}$] = 0.113 M (1.80 $cm^3$) or 0.226 M, (3.60 $cm^3$), gelation took about 10 min, 20 min and 3–4 h or 5 min, 10 min and 40–50 min, respectively. After

the mixture became solid, the gel layer was covered either with a solution of methylene blue, ($4 \times 10^{-4}$ M, 0.5 $cm^3$ stock solution plus 5.5 $cm^3$ water, which resulted in a 1 mm thick solution layer) as suggested in Ref. [5] or with water (6 $cm^3$), and the system was exposed to air. Observations were made visually from above using illumination (light box) from below. Images were recorded with a video camera, and the data were processed with an OPTI-MAS image analysis system (Bioscan).

## 3. Results

### 3.1. Reproducing Münster and Watzl's results

Münster et al. present a phase diagram in the [Mblue] vs. [$Na_2S$] plane showing the concentration domains in which colorless and blue hexagons and stripes develop in the polyacrylamide-methylene blue oscillator system [5–7]. The stationary patterns shown in the photographs in Refs. [5] and [6] strongly resemble the Turing structures seen in the CIMA system.

We had difficulties in directly reproducing Münster et al.'s observations for two reasons:

(i) Phase diagrams with the same experimental points are shown in Refs. [5] and [6], but the scales of the axes (i.e. the concentrations of Mblue and $Na_2S$) differ significantly, by a factor of 25 for [Mblue] and 3.1 for [$Na_2S$]. One of the diagrams, we believe it to be the one presented in Ref. [5], must be erroneous.

(ii) Assuming the phase diagram in Ref. [6] to be correct, we still had to use concentrations different from those given for the reagent $S^{2-}$ and/or the initiator $(NH_4)_2S_2O_8$ in order to transform the mixture of AA, Bis, TEA, Mblue, $S^{2-}$ and $S_2O_8^{2-}$ to a gel state. The concentrations of sulfide and peroxodisulfate were found to influence strongly the time needed for gelation. Higher [$S^{2-}$] results in longer polymerization times, and no gelation at all occurs at many compositions where a gel state and pattern formation are expected to appear according to the phase diagram in Ref. [6].

With proper variation of the concentration ratio of sulfide to peroxodisulfate we finally succeeded in

reproducing qualitatively most of the observations described in Ref. [5]. Keeping $[S^{2-}]$ as in Ref. [6] and using a new set of concentrations for peroxodisulfate (0.113–0.226 M, i.e. one order of magnitude higher than in Ref. [6]), we observed blue and colorless spots and stripes in the polyacrylamide gel 20–30 min after covering it with Mblue solution. The patterns changed in time and persisted for many hours.

Münster et al. assert that the pattern observed in the polyacrylamide gel layer is a Turing structure that arises from the reaction-diffusion interaction between the components of the methylene blue oscillator and the gel matrix. They suggest that an adduct formed between methylene blue and the gel serves as the activator, while an unspecified, rapidly-diffusing sulfur species acts as the inhibitor. Such a scheme implies that the pattern arises from the interaction of the MBO with the polyacrylamide gel.

We checked this hypothesis by submerging 2 mm polyacrylamide gel layers in a solution containing all soluble components of the MBO with a volume ratio of solution to gel of 100:1 under an argon atmosphere. After 12 h the gel layers were taken from the reagent solution, rinsed with distilled water and placed in contact with air. During the subsequent oxidation we did not observe any spatial pattern formation.

The studies reported here demonstrate that the observed pattern is not a Turing structure, and the components of the methylene blue oscillator are not required for development of the pattern seen in the polyacrylamide gel layer. In the following sections we describe experiments that show that the structures seen in the methylene blue oscillator-polyacrylamide system are of convective origin and the major factors that bring about these patterns are the heat evolved during polymerization and the interaction between sulfide and the gel components.

### 3.2. Pattern formation in the AA-Bis-TEA-$S_2O_8^{2-}$-$S^{2-}$ system

In the experiments described in Refs. [5] and [6], two components of the MBO, Mblue and $S^{2-}$, were mixed with the gel components prior to polymerization, and the gel layer was covered with a $4 \times 10^{-4}$

M solution of Mblue, the same [Mblue] as in the gel. Two purposes were suggested for covering the gel surface with Mblue solution: a) to prevent the drying out of the gel; and b) to enhance the transport of oxygen, the oxidizing agent in the MBO, from the air into the gel.
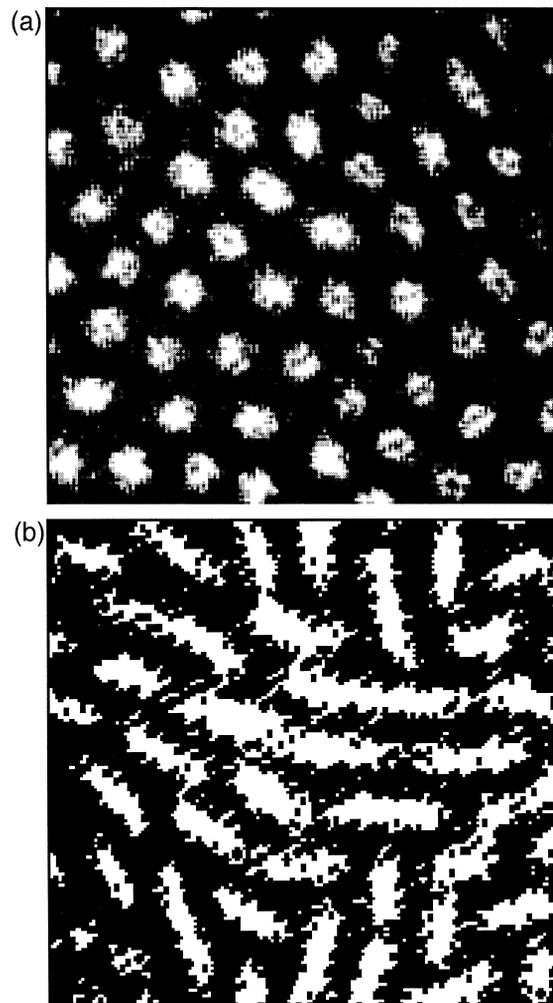


Fig. 1. (a) Spotted pattern in the AA-Bis-TEA-$S_2O_8^{2-}$-$S^{2-}$ gel system. Composition of the gel mixture: [AA] = 1.035 M; [Bis] = $4.85 \times 10^{-3}$ M; [TEA] = 0.055 M; $[S_2O_8^{2-}]$ = 0.112 M; $[S^{2-}]$ = $3 \times 10^{-2}$ M. Covering solution: water. The domain size is 27 mm × 25 mm. The average diameter of the spots is about 1.5–2 mm. (b) Striped pattern in the AA-Bis-TEA-$S_2O_8^{2-}$-$S^{2-}$ gel system. All conditions and concentrations, except $[S^{2-}]$ = $5 \times 10^{-2}$ M as in (a).

(a)



(b)

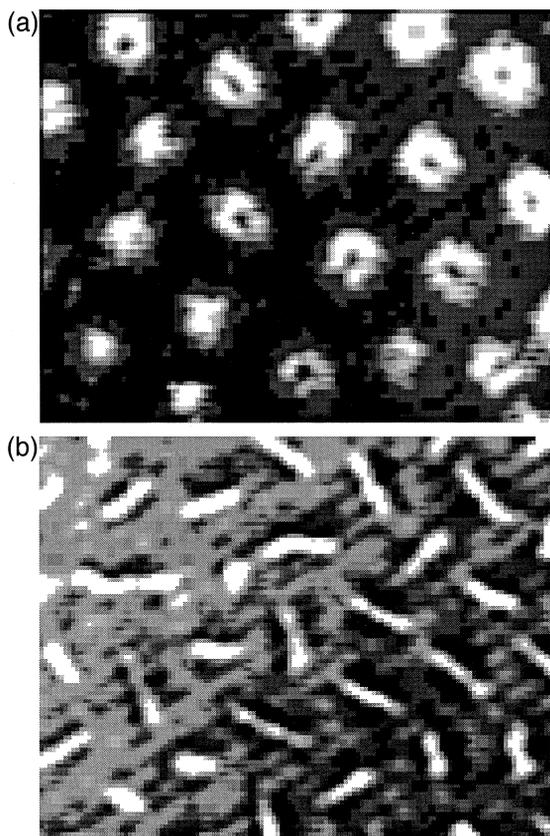

Fig. 2. (a) Spotted pattern in the AA-Bis-TEA-$S_2O_8^{2-}$-MBO (methylene blue-$S^{2-}$-oxygen) gel system. Composition of the gel mixture as in Fig. 1a, plus [Mblue] = $4 \times 10^{-4}$ M. The domain size is 19 mm × 14 mm. Covering solution: $4 \times 10^{-4}$ M Mblue. (b) Striped pattern in the AA-Bis-TEA-$S_2O_8^{2-}$-MBO gel system. All conditions and concentrations as in (a) except [$S^{2-}$] = $5 \times 10^{-2}$ M.

In one set of our experiments the gel was prepared with sulfide but without Mblue, and pure water instead of Mblue solution was spread on the surface of the gel. Surprisingly, the same type of structures appeared in these experiments, and even the dependence of the character of the patterns on the concentration of sulfide resembled the results reported in Refs. [5] and [6].

Fig. 1(a) and (b) show the spots and stripes that developed with a single composition of gel matrix containing different concentrations of sulfide. To examine the similarity between these structures and the reported Turing-like patterns, we repeated our

experiments with all components of the MBO present. The results are shown in Fig. 2(a) and (b).

We note that patterns can be formed in a mixture of polyacrylamide components, sulfide and methylene blue when the mixture remains in a liquid state for an extended time (1–2 h or longer) if the concentration of initiator is low (e.g. 0.01 M). Similar patterns arise when solutions of methylene blue and sulfide are mixed and spread in a Petri dish in the absence of any gel component. Such patterns, shown in Fig. 3(a) and (b) certainly arise from convection and are not related chemically to the patterns in Figs. 1 and 2.
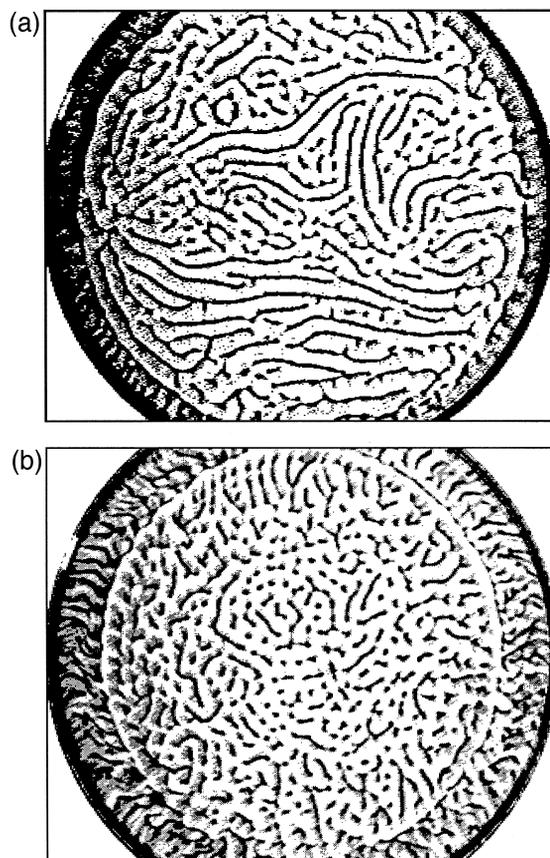
(a)



(b)



Fig. 3. (a) Convective pattern in Mblue-$S^{2-}$ solution layer exposed to air. [Mblue] = $4 \times 10^{-4}$ M; [$S^{2-}$] = $3 \times 10^{-2}$ M. Picture was taken 10 min after mixing the components and layering the solution into a Petri dish. (b) Convective pattern in Mblue-$S^{2-}$ solution layer exposed to air. Conditions as (a) in but picture was taken at 30 min after mixing.

## 4. Discussion

Münster et al., who first observed pattern formation in an MBO–polyacrylamide gel layer [5,6], suggest that it occurs only if all components of the methylene blue oscillator are included in the gel. They propose that the chemistry of these species combines with the interaction between methylene blue and the gel to provide the activator-inhibitor pair that leads to the formation of a reaction-diffusion based Turing pattern.

Here we have shown that the chemistry of the methylene blue oscillatory system does not contribute to bringing about pattern formation in the gel. The patterns that develop in the polyacrylamide gel layer resemble Turing structures, but they are almost certainly convection-generated phenomena rather than genuine reaction-diffusion based Turing structures. It worth noting that many similar, chemically driven convective patterns were reported earlier [9], and several of these were initially confused with Turing patterns.

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