



Reply to Comment on “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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Watzl and Münster [1] describe Turing-like patterns in the Burger–Field (BF) oscillating reaction [2–5] run in a polyacrylamide gel layer. They assert [1] that these are Turing structures that result from the slowing down of methylene blue diffusion by the polyacrylamide gel, which would imply that the gel is macroscopically homogeneous. In his Comment, Münster [6] states that there is no prepattern arising from the polymerization procedure he employs. It would certainly be advantageous to have a photosensitive reaction–diffusion system capable of producing Turing structures. It was this possibility that initially attracted our attention to the results of Münster’s group. Unfortunately, we have been unable to obtain the anticipated results and have presented evidence [7] that the patterns observed with Münster’s procedure are formed during the polymerization of acrylamide and probably arise from chemically driven convection. While our conclusion that the observed patterns are convective in origin has not been definitively proven, we believe that the body of experimental data strongly supports this contention over the alternative that the patterns arise primarily from reaction–diffusion. To clarify this

point, we address below each of the issues raised in Münster’s Comment.

(1) Münster argues that our difficulties in reproducing his experimental results are caused by the omission of sulfite and the use of unpurified sulfide in our experiments. In fact we were able to obtain spotted and striped patterns even in the absence of sulfite ions and using commercial sulfide without purification, but only at a significantly higher concentration of initiator $(\text{NH}_4)_2\text{S}_2\text{O}_8$, than employed by Münster. Münster is correct, in principle, that sulfite should be able to decompose the polysulfides present in unpurified sulfide. However, we have not been able to obtain any evidence that sulfite enhances the range of concentrations in which patterns can be formed, or that it improves the contrast of the patterns.

Münster et al. prepared and used recrystallized, water-free sodium sulfide in order to remove the polysulfide impurity, which they claim causes gelation problems and other disturbing effects. In our view, the tedious purification procedure is unnecessary for two reasons. First, the freshly purchased Merck $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ contains negligible amounts of polysulfide. We used selected colorless crystals for preparing stock solutions and determined the sulfide content by an iodometric back titration method. The

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Merck product proved to be as pure as indicated on the label and needed no further purification. Secondly, polysulfide is formed anyway at relatively high concentrations as an intermediate of reaction (3). For example, mixing 2×10^{-2} M S^{2-} and 1.25×10^{-2} M $(NH_4)_2S_2O_8$ either in pure aqueous solution or in the gel matrix, produces an intense yellow color, which indicates the formation of polysulfides (S_x^{2-}), followed by the precipitation of white colloidal sulfur. This sequence is observed both in the absence and in the presence of 1.2×10^{-3} M sulfite. Since sulfide consumes peroxodisulfate in reaction (3), we used higher concentrations (up to 1.14×10^{-1} M) of initiator than recommended in Ref. [8] to reach a gelation time optimal for pattern formation (~ 10 min).

(2) We agree that recalibration of the axes of the figures in the two papers [8,11] does indeed yield consistent phase diagrams.

(3) Münster explains our (and his) failure to obtain patterns when the system is exposed to oxygen only after the gel is formed as follows: "...oxygen is steadily consumed by reaction with sulfide ... Patterns emerge only if the oxygen concentration is sufficiently high. This requirement is fulfilled if the components are mixed according to Ref. [8] but it cannot be met if the polymerized gel is exposed to oxygen for some time".

It is well known that the same oxygen profile is established under quasistationary conditions regardless of the initial conditions. In Münster's experiments, the first patterns appear only after 30–60 min, and patterns persist for at least 3 h. The characteristic diffusion time, l^2/D , for oxygen is ~ 30 min for a 2 mm thickness, and 2 min for a 0.5 mm gel. If the oxygen consumption due to some chemical reaction is significant, the relaxation time would be even shorter. Therefore, during the time when patterns are observed, the oxygen profile is the same, regardless of whether the experiment was started from air oxygen level or zero level. On the other hand, during the first 10 min, the period when polymerization takes place and when we assert that the prepatterning occurs, the oxygen level is critically dependent upon the initial conditions.

(4) Münster states that he sees no evidence of "any invisible prepattern which might be formed by convection in an early stage of polymerization while

the mixture is still liquid", and that he is unable to obtain patterns in the absence of methylene blue. He also argues that the relative independence of the pattern wavelength on the gel thickness and the lack of "a significant gradient of temperature which is required to drive Rayleigh–Benard convection" militate against our interpretation that convection is the source of the patterns.

Watzl and Münster's experiments with inhomogeneous illumination [1] indicate the existence of prepatterns formed during the polymerization phase. There is some ambiguity as to when the illumination was turned off, but in any case, a clear boundary between two regions subject to different levels of illumination remains hours after the cessation of illumination. This situation would be impossible in the case of reaction–diffusion Turing structures and indicates the existence of a boundary between two different states of the polymer gel. The lack of dependence of the patterns on the gel thickness is also very difficult to explain for Turing structures that are claimed to arise from a reaction with strong oxygen dependence. We note also that surprisingly small temperature gradients are sufficient to generate convective motion in thin layers of liquid solution [9].

Finally, we point out that the observed effects of light on the pattern formation may arise from the heat generated by the intense (4000–22000 lux) light applied during the gelation process [1]. We have emphasized earlier [10] the profound influence of the initial temperature of the gel matrix–sulfide systems on the development of the structure. Structures form readily at 30–40°C, but several hours are required for pattern formation at lower initial temperatures, as is true in Watzl and Münster's experiments [1] with weak illumination. High initial temperatures [10] or strong illumination [1] completely suppress pattern formation.

(5) The experiments on the electric field effect [11] are fascinating and worthy of further analysis. We would caution, however, against interpretations based on an ionic Brusselator model, whose relevance to the MBO system is tenuous at best.

While we cannot categorically rule out that the structures in question are true Turing patterns, we would offer one further, indirect argument against that interpretation. Like many chemical oscillators,

the BF reaction oscillates only in a flow reactor and does not show sustained oscillations in a batch system. The Turing-like patterns observed by Münster are sustained in a batch configuration for hours. On the other hand, all known Turing patterns arise from reactions which can oscillate in the batch for dozens of minutes and the corresponding Turing structures are sustained in the batch for approximately the same length of time. Thus, if the present system does represent a true Turing pattern, rather than a pattern of convective origin, it would be different in nature from all such systems discovered to date.

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