Control of Turing Structures by Periodic Illumination

Attila K. Horváth, Milos Dolnik, Alberto P. Muñuzuri,* Anatol M. Zhabotinsky,† and Irving R. Epstein
Department of Chemistry and Center for Complex Systems, Brandeis University, MS 015, Waltham, Massachusetts 02454-9110
(Received 6 April 1999)

Spatially uniform illumination of Turing structures in the chlorine dioxide-iodine-malonic acid reaction-diffusion system affects the pattern characteristics and, at larger intensities, eliminates them. Periodic illumination is more effective than constant illumination with the same average light intensity. We observe the fastest suppression of pattern at a frequency of illumination equal to the frequency of autonomous oscillations in the corresponding well-stirred system. Numerical simulations demonstrate a similar resonant behavior of periodically illuminated Turing structures.

PACS numbers: 47.54.+r, 05.70.Ln, 82.20.Mj, 82.40.Ck

The dynamics of Turing structures in autonomous reaction-diffusion systems have been investigated in great detail [1,2], yet the corresponding behavior in the presence of periodic external forcing remains almost unstudied. External periodic forcing has often been used to investigate resonant phenomena that occur in oscillatory chemical reactions both in well mixed systems [3–5] and in reaction-diffusion systems [6,7]. The photosensitivity of an oscillatory reaction is frequently employed as a convenient tool for control and external forcing. Illumination has been employed to affect Turing-like patterns obtained during polymerization in the acrylamide-methylene blue-sulfide-oxygen system [8]. The mechanism of pattern formation in this system and the possible role of convection are under discussion in the current literature [9] .

We have recently shown that the chlorine dioxide-iodine-malonic acid reaction is photosensitive to visible light [10]. Here, we demonstrate that the Turing structures can be controlled by visible illumination, and we examine the roles of frequency and intensity of periodic illumination in suppressing Turing structures.

Experiments are carried out in a thermostated continuously fed unstirred reactor (CFUR) at $4 \pm 0.3\,^{\circ}\mathrm{C}$. We use a one-sided CFUR, which consists of a polyacrylamide gel layer (thickness 0.3 mm) with immobilized starch (0.5% w/v) and a single feeding chamber, which is separated from the gel layer by two Anapore membranes (Whatman, pore size 0.2 μm) and one nitrocellulose membrane (Whatman, pore size 0.45 μm). The reagents are fed into the feeding chamber by a Rainin peristaltic pump. The input concentrations of reagents are 0.55 mM I_2 (dissolved in 40% acetic acid), 0.75 mM ClO_2, 10 mM H_2SO_4, and 1.8 mM malonic acid. The feeding chamber residence time is 360 s in all experiments. Three magnetic stirrer bars are placed directly under the membranes to maintain homogeneity of the solution in contact with the gel.

The gel layer is illuminated with unfiltered light from a tungsten-halogen lamp. We use neutral density filters to vary the intensity of actinic illumination. The light intensity is measured with a Newport 1815 Optical Power Meter. Nonuniformity of the illumination field is less than 10%. For the periodic illumination, we employ rectangular pulses of light with light and dark phases of equal duration. We use a Pulnix CCD videocamera with a Hamamatsu camera controller to record spatiotemporal patterns. The images are acquired only during the dark half period. When constant illumination is used, the actinic illumination is switched off for a few seconds during image acquisition. The intensity of light employed for the image acquisition is equal to 0.2 $\mathrm{mW/cm^2}$. We employ OPTIMAS (BioScan) software for the image analysis. We utilize two-dimensional Fourier spectra to evaluate the rate of suppression of Turing structures.

Illumination is applied to the stationary Turing structures, which are typically established within 8 h after the beginning of an experiment or 4 h after an illumination session. The total duration of an illumination session is 25 min, and data are acquired at 5 min intervals.

Figure 1 shows a pattern together with the corresponding Fourier spectra before and after 25 min of periodic illumination. The Turing structures are completely destroyed by the illumination. Figure 2 shows the effect of constant illumination at the same average intensity as in Fig. 1 (32.5 $\mathrm{mW/cm^2}$). In this case, the illumination results only in decreasing the amplitude of the pattern.

Figure 3 shows how suppression of Turing structures depends on the frequency and intensity of illumination. Figure 3a shows the state of the patterns after 25 min of illumination. Open circles correspond to cases in which the amplitude of the principal Fourier component is significantly larger than the background noise; gray circles correspond to the amplitude which is 10%–20% above the noise, i.e., the pattern is strongly suppressed but still distinguishable; filled circles designate cases when the principal component is impossible to distinguish from the noise. Both our experiments and our simulations (described below) demonstrate that forcing with a period much shorter than any of characteristic times of the system has the same effect as constant forcing with an amplitude equal to the average value of the periodic forcing. Hence, our experimental points for constant illumination are shown at $T = 0$ in Fig. 3a. The dashed line in Fig. 3a roughly depicts the boundary of the suppression domain.

 0031-9007/99/83(15)/2950(3)$15.00

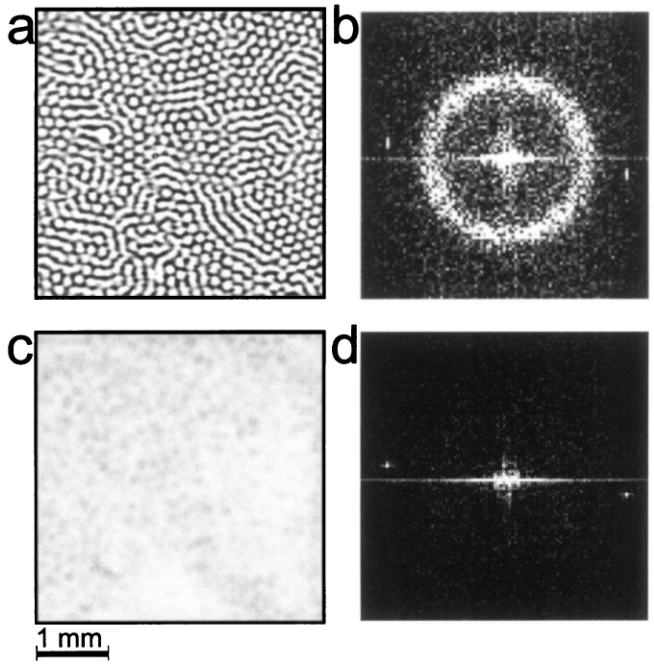

FIG. 1. Suppression of Turing structures with periodic rectangular pulses. Period of illumination is 36 s; light and dark phases have equal duration of 18 s. Light intensity during light phases is 65 mW/cm^2. (a) Initial pattern at the start of illumination—a mixture of spots and stripes; (b) Fourier spectrum of initial pattern; characteristic wavelength is 0.16 ± 0.02 mm; (c) pattern after 25 min of illumination; (d) Fourier spectrum of pattern shown in (c).

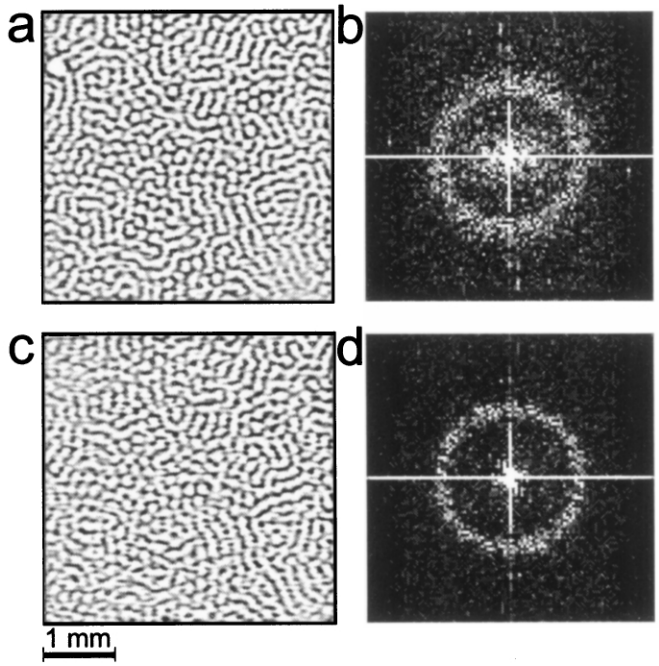

FIG. 2. Constant illumination of Turing structures. The light intensity, 32.5 mW/cm^2 (same as average light intensity of periodic illumination in Fig. 1) is not enough to suppress Turing structures. (a) Initial pattern at the start of illumination; (b) Fourier spectrum of initial pattern; (c) pattern after 25 min of illumination; (d) Fourier spectrum of pattern at the end of illumination.

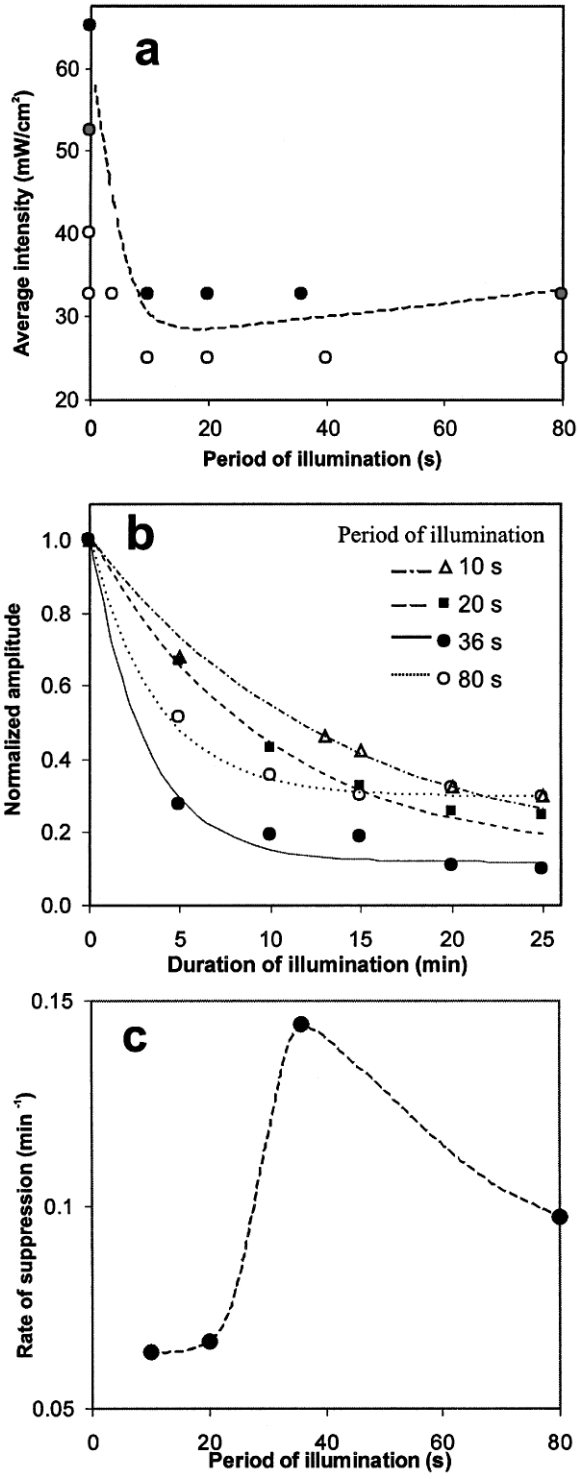

FIG. 3. Dependence of illumination effects on intensity and period of pulse illumination. (a) Filled circles—complete suppression of Turing structures; gray circles—Turing structures with strongly suppressed amplitude; open circles—Turing structures. Data shown on left vertical axis correspond to constant illumination. (b) Kinetics of Turing pattern suppression with different periods of illumination. Amplitude of patterns during illumination is evaluated from the 2D Fourier transform and compared with amplitude at the start of illumination. (c) Dependence of initial rate of Turing pattern suppression on period of illumination.

Figure 3b shows the kinetics of the suppression in a normalized plot where the amplitude of the principal Fourier component is set to 1 at the start of illumination. Figure 3c shows the dependence of the initial rate of suppression (change in pattern amplitude during the first 5 min of illumination) on the period of illumination. The most rapid rate of suppression corresponds to a period of 36 s, which is, with precision of our measurement, equal to the period of autonomous oscillations of the stirred, starch-free system.

To compare the experimental results with those of numerical simulations, we employ the Lengyel-Epstein two-variable model [11] modified to include the effect of illumination [10]. The resulting model is

$$\frac{\partial u}{\partial t} = a - u - 4\frac{uv}{1+u^2} - w + \nabla^2 u,$$

$$\frac{\partial v}{\partial t} = \sigma\left[b\left(u - \frac{uv}{1+u^2} + w\right) + d\nabla^2 v\right].$$

Here, u and v are the dimensionless concentrations of I^- and ClO_2^-, respectively; a, b, d, and σ are dimensionless parameters, and w is the dimensionless rate of the photochemical reaction, which is proportional to the light intensity. In our simulations, we fix parameters $a = 36$, $b = 2.5$, and $d = 1.2$. The rate w is a periodic function of time: $w(t) = W$ for $iT_f \le t < iT_f + T_f/2$, and $w(t) = 0$ for $iT_f + T_f/2 \le t < (i+1)T_f$. Here, $i = 0, 1, 2, \ldots$ and T_f is the period of illumination. We use two different values for the parameter $\sigma = 1 + K[I_2][S]$, where K is the association constant of the starch-triiodide complex, and $[S]$ is the concentration of the starch-triiodide binding sites [11].

Figure 4 shows the boundaries between domains of the spatially homogeneous state and the Turing structures in the amplitude period of illumination plane. The boundaries are obtained for $\sigma = 9$ and 15 by numerical integration of Eq. (1). The first minima of the curves, i.e., the points of greatest photosensitivity ($T_{crit} = 1.6$ for $\sigma = 9$ and $T_{crit} = 1.2$ for $\sigma = 15$) , are equal to the periods of intrinsic oscillation in the corresponding well-stirred systems. Comparison with Fig. 3a shows qualitative agreement of the curve calculated with $\sigma = 15$ with the experimental data.

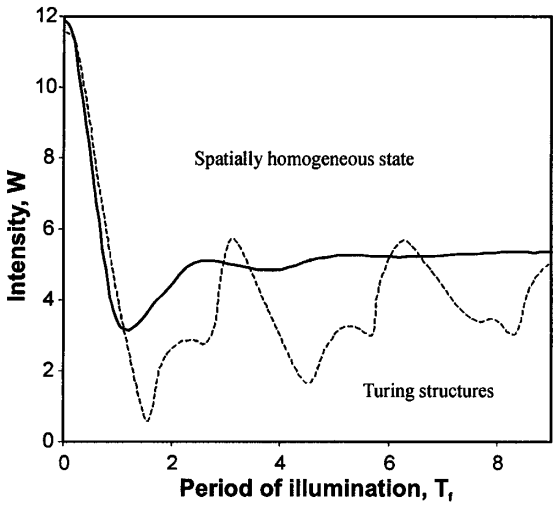

FIG. 4. Resonant dynamics of periodically forced Turing structures in two-dimensional system according to Eq. (1). Boundary between domain of Turing structures and that of spatially homogeneous state is calculated for $\sigma = 9$ (dashed line) and 15 (solid line), other parameters are $a = 36$, $b = 2.5$, and $d = 1.2$.

The boundary for $\sigma = 9$ in Fig. 4 demonstrates that, in principle, with lower starch concentrations, the resonance response of Turing structures to periodic illumination can be more pronounced and structured than in our present experiments. Unfortunately, under the present conditions, lowering the starch concentration decreases the contrast beyond the point at which the Turing structures are observable. Our results demonstrate that illumination can be used as a convenient tool for the perturbation and control of Turing structures.

This work was supported by the National Science Foundation and the W. M. Keck Foundation. We thank Arkady Rovinsky for help in developing the software used in our simulations.

*Present address: Group of Nonlinear Physics, Faculty of Physics, University of Santiago de Compostela, 15706 Santiago de Compostela, Spain.

†To whom correspondence should be addressed.

[1] J. Boissonade, E. Dulos, and P. De Kepper, *In Chemical Waves and Patterns*, edited by R. Kapral and K. Showalter (Kluwer, Dordrecht, 1995), p. 221; Q. Ouyang and H. L. Swinney, *In Chemical Waves and Patterns*, p. 269; I. Lengyel and I. R. Epstein, *In Chemical Waves and Patterns*, p. 297; P. Borckmans, G. Dewel, A. De Witt, and D. Walgraef, *In Chemical Waves and Patterns*, p. 323.

[2] R. Rudovics, E. Barillot, P. Davies, E. Dulos, J. Boissonade, and P. De Kepper, J. Phys. Chem. **103**, 1790 (1999).

[3] P. Rehmus and J. Ross, *Oscillations and Traveling Waves in Chemical Systems*, edited by R. J. Field and M. Burger (Wiley, New York, 1985), p. 287.

[4] F. W. Schneider, Annu. Rev. Phys. Chem. **36**, 347 (1985).

[5] M. Dolnik, J. Finkeova, I. Schreiber, and M. Marek, J. Phys. Chem. **93**, 2764 (1989).

[6] V. Petrov, Q. Ouyang, and H. L. Swinney, Nature (London) **388**, 655 (1997).

[7] O. Steinbock, V. Zykov, and S. C. Müller, Nature (London) **366**, 322 (1993).

[8] M. Watzl and A. F. Münster, Chem. Phys. Lett. **242**, 273 (1995); J. Phys. Chem. **A102**, 2540 (1998).

[9] K. Kurin-Csörgei, M. Orbán, A. M. Zhabotinsky, and I. R. Epstein, Chem. Phys. Lett. **295**, 70 (1998); M. Orbán, K. Kurin-Csörgei, A. M. Zhabotinsky, and I. R. Epstein, J. Phys. Chem. **B103**, 36 (1999); O. Steinbock, E. Kasper, and S. C. Müller, J. Phys. Chem. **A103**, 3442 (1999).

[10] A. P. Muñuzuri, M. Dolnik, A. M. Zhabotinsky, and I. R. Epstein, J. Am. Chem. Soc. **121**, 8065 (1999).

[11] I. Lengyel and I. R. Epstein, Science **251**, 650 (1991); **259**, 493 (1993).