A Chemical Oscillation Model
for a Copolymerization

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Abstract

In many two variables chemical oscillator models, the sigmoidal form of the characteristic nullcline plays an important role making intuitive the presence of hysteresis cycles in the variables (concentrations). Although in this type of models the use of steps of the form $A + X_j \rightarrow 2X_j$, or $X_i + X_j \rightarrow 2X_i$, has been frequently used, Seelig and Denzel designed a hysteresis model without autocatalysis, which has been taken as a base for this work by applying it to a copolymerization reaction.

The context includes the copolymerization of two monomers, the first which supplies the first propagator and the second produces a third compound which acts as a terminator. The concentrations of the second monomer and the terminator change very little during the reaction which reduces the number of variables to two. By mathematical analysis of the kinetic equations reduced to two main variables (the total concentrations of the propagator and that of the first monomer), it can be shown that in a flowing system the sigmoidal characteristic proposed by Seelig and Denzel can be reached, and that the two concentrations can exhibit sustained oscillations of the limit cycle type. For high flows, relaxation oscillations are possible.

Keywords: Copolymerization, Stationary State, Chemical Oscillator Models, Limit Cycle
INTRODUCTION

Autocatalytic steps are common to many chemical dissipative structure models [1] and they show a tendency to destabilize the stationary state since they generate in the Jacobean matrix for the system [2] one element of the form

\[
\left( \frac{\partial (X_i)}{\partial X_i} \right)_0 > 0
\]

\( X_i \) is a certain variable of the studied system; the subindex 0 indicates stationary state. This effect is often achieved with steps of the form \( A + X_i \rightarrow 2 X_i \), or \( X_i + X_j \rightarrow 2 X_i \).

However, Seelig and Denzel [3] have already presented a model, based in the cooperative properties of allosteric enzymes which does not require such steps. In this paper the formalism of this model is adapted to a copolymerization reaction [4–6].

MECHANISM

Monomers \( M_1 \) and \( M_2 \) are copolymerized, where the monomer \( M_2 \) is much less reactive than monomer \( M_1 \) which is the source of the first propagator \( R_1 \); the successive propagators \( R_j \) can incorporate any of the monomers. Starting with monomer \( M_2 \) the \( Z \) specie is produced which acts as a terminator of the propagators. An open system is assumed, with inlet flows of both monomers and exit flows of \( M_1 \), \( M_2 \), \( R_j \) and \( Z \):

\[
\begin{align*}
A & \rightarrow M_1 \xrightarrow{F} \text{exit} \\
B & \rightarrow M_2 \xrightarrow{F} \text{exit} \\
M_1 & \xrightarrow{k_{n1}} R_1 \\
R_j + M_1 & \xrightarrow{k_{n2}} R_{j+1} \quad (j = 1, 2, ..., \infty) \\
R_j + M_2 & \xrightarrow{k_{n2}} R_{j+1} \quad (j = 1, 2, ..., \infty) \\
M_2 & \xrightarrow{k_i} Z \\
Z + R_j & \xrightarrow{k_0} \quad (j = 1, 2, ..., \infty) \\
R_j & \xrightarrow{F} \text{exit} \quad (j = 1, 2, ..., \infty) \\
Z & \xrightarrow{F} \text{exit}
\end{align*}
\]

the kinetic equations for (1) are:
Chemical oscillation model

\[
\begin{align*}
\dot{M}_1 &= A - F \cdot M_1 - k_{i_1} \cdot M_1 - k_{p_1} \cdot R \cdot M_1 \\
\dot{R} &= k_{i_1} \cdot M_1 - k_{r_1} \cdot R \cdot Z - F \cdot R \\
\dot{M}_2 &= B - F \cdot M_2 - k_{i_2} \cdot M_2 - k_{p_2} \cdot R \cdot M_2 \\
\dot{Z} &= k_{i_2} \cdot M_2 - k_{r_2} \cdot R \cdot Z - F \cdot Z
\end{align*}
\]

(2)

this system is reduced to two variables by assuming a quasi–stationary state for the “slower varying” variables \(Z\) and \(M_2\):

\[
\begin{align*}
\dot{R} &= k_{i_1} \cdot M_1 - \frac{k_{i_1} \cdot k_{i_2} \cdot B \cdot R}{(k_{r_1} \cdot R + F)(k_{p_1} \cdot R + k_{r_1} + F)} - FR \\
\dot{M}_1 &= A - (k_{i_1} + F) \cdot M_1 - k_{p_1} \cdot R \cdot M_1
\end{align*}
\]

(3)

If \(R = R_0\), \(M_1 = (M_1)_0\), is a stationary state of (3), for these values, \(\dot{R} = 0, \dot{M}_1 = 0\).

ANALYSIS

A normalization [2] of system (3) was carried out, with the new variables and the following definitions it became:

\[
\begin{align*}
X &= \frac{R}{R_0} ; Y = \frac{M_1}{(M_1)_0} \\
\frac{k_{i_1} \cdot (M_1)_0}{R_0} &= \gamma ; F = \frac{1}{\mu} ; \frac{k_{i_1} \cdot k_{i_2} \cdot B \cdot R}{\mu} = \frac{\beta}{\mu} ; n = \frac{k_{i_1} + F}{k_{p_1} \cdot R_0} \\
a = \frac{A}{(M_1)_0} ; g = k_{i_1} + F ; h = k_{p_1} \cdot R_0 \\
m &= \frac{F}{k_{i_1} \cdot R_0}
\end{align*}
\]

(4)

From where It is obtained:

\[
\begin{align*}
\mu \dot{X} &= \gamma Y - X - \frac{\beta X}{(X + m)(X + n)} = \sigma (X, Y) \\
\dot{Y} &= a - g Y - hXY
\end{align*}
\]

(5)

Obviously, the stationary state is now \(X = X_0 = 1, Y = Y_0 = 1\) and then
\[
\begin{align*}
\begin{cases}
\gamma = 1 + \frac{\beta}{(1 + m)(1 + n)} \\
a = g + h
\end{cases}
\end{align*}
\] (6)

Now the Jacobian matrix (5) takes the form

\[
J = \begin{bmatrix}
\frac{\beta(1 - m \cdot n)}{\mu (1 + m)^2 (1 + n)^2} - 1 & \frac{\gamma}{\mu} \\
- h & - (g + h)
\end{bmatrix}
\] (7)

The J determinant is positive if

\[
1 + \frac{\beta}{(1 + m)(1 + n)} > \left(1 + \frac{g}{h}\right)\left(\frac{\beta(1 - m \cdot n)}{(1 + m)^2 (1 + n)^2} - 1\right)
\] (8)

(for example, if \(h \gg g\)). J’s trace is positive, for \(\mu\) small enough (\(\mu \to 0\)), if

\[
\begin{cases}
\beta > \frac{(1 + m)^2(1 + n)^2}{1 - m \cdot n} \\
(m \cdot n < 1)
\end{cases}
\] (9)

If the determinant and trace J are positive, the stationary state \(X = X_0 = 1, Y = Y_0 = 1\) is a node of unstable focus [7]. As a numerical example (all values for the parameters are given in the appropriate units), let’s consider the system

\[
\begin{align*}
\dot{X} &= 31 \cdot Y - X - \frac{90X}{(X + 1)(X + 0.5)} \\
\dot{Y} &= 3 - 2Y - XY
\end{align*}
\] (10)

whose determinant is \(D_{st} = 19 > 0\), its trace is \(T_r = 1 > 0\), and the discriminant \(T_r^2 - 4D_{st} = -75 < 0\), such that the stationary state \(X = X_0 = 1, Y = Y_0 = 1\) is an unstable focus.

The nullcline \(\dot{X} = 0\) of system (5), that is, the characteristic curve \(\sigma(X, Y) = 0\), is

\[
Y = \frac{1}{\gamma} \left( X + \frac{\beta X}{(X + m)(X + n)} \right)
\] (11)

and has an oblique asymptote \(Y = X/\gamma\); besides, sometimes it shows a “sigmoidal shape” with a maximum and a minimum. The nullcline \(\dot{Y} = 0\) of the system (5) is
\[ Y = \frac{a}{g + hX} \]  

and intersect the Y axes at \( Q_2(a/g,0) \). Figure 1 shows both nullclines, and the presence of only one stationary state (at \( X_0 = 1, Y_0 = 1 \)).

Line \( \Gamma = Q_1Q_2Q_3Q_4Q_1 \) is built, which is the frontier of an enclosure (a rectangle) from which phase trajectories cannot emerge [8]. This is confirmed by examining the flow \( \Phi \) of the vector \( \begin{pmatrix} X \\ Y \end{pmatrix} \) of (5), through \( \Gamma \). If \( \vec{n} \) is a vector defined on each point of \( \Gamma \), perpendicular to \( \Gamma \) and out of the rectangle, the flow \( \Phi \) is calculated from

\[ \Phi = \vec{n} \otimes \begin{pmatrix} \dot{X} \\ \dot{Y} \end{pmatrix} \]  

(where \( \otimes \) is the scalar product). The confirmation requires that \( \Phi \) is not positive for any point of \( \Gamma \).

Starting at the origin \( Q_1(0,0) \), the segment \( Y = Q_1Q_2 \), up to \( Q_2(a/g,0) \), has \( \vec{n} = (-1,0) \), \( \dot{X} \geq 0 (= at Q_1) \), then \( \Phi = -\dot{X} \leq 0 (= at Q_1) \).

Continuing on the horizontal \( Q_2Q_3 \) to \( \dot{X} = 0 \) (it will probably be close to the oblique asymptote; as \( Q_3 \approx (ya/g, a/g) \)). At \( [Q_2Q_3[, \vec{n} = (0,1) \), \( \dot{Y} \leq 0 (= at Q_2), \Phi = -\dot{Y} \leq 0 (= at Q_2) \). Now, continuing on the vertical to the X axis. At \( [Q_3Q_4[, \vec{n} = (1,0) \), \( \dot{X} \leq 0 (= at Q_3), \Phi = \dot{X} \leq 0 (= at Q_3) \). Last, on the segment \( [Q_4Q_1[ \) on the X axis, \( \vec{n} = (0,-1) \), \( \dot{Y} > 0 \), then \( \Phi = -\dot{Y} < 0 \).
Applying the Poincaré–Bendixson theorem, if the single stationary state enclosed in the rectangle is unstable (focus or node type), there is at least a limit cycle [9] for the system (5). The concentration of all the propagators \( R \sim X \) and that of monomer \( M_1 \sim Y \) will show sustained oscillations.

Besides, given the characteristic sigmoidal form, it is easy to predict the form of the limit cycle for \( \mu \rightarrow 0 \) (Figure 2). It is the relaxation oscillations regime [10], with quick jumps of the “trigger” variable \( X \) (propagators), parallel to the \( X \) axis, alternating between the two lateral stable branches of the characteristic, in which a relatively slow movement occurs; oscillations with smaller and slower fluctuations of the “recovery” variable \( Y \) (monomer \( M_1 \)).

4. SUMMARY AND CONCLUSIONS

A copolymerization of two monomers is proposed: \( M_1 \) supplies the first propagator and \( M_2 \) produces a terminator \( Z \) for the propagators. The \( Z \) specie is produced which acts as a terminator of the propagators. The process occurs in an open system, with feed flow of both monomers, and exit flow of monomers, propagators and terminator.

It is assumed that concentrations for \( M_2 \) and \( Z \) are practically constant, which reduces the number of variables to two, and the analysis takes place on the phase plane \( \{R, M_1\} \). The possibility of a unique stationary state of the focus or node type is shown. The possibility of drawing a confinement region for the trajectory–solution on the phase plane is also shown. Therefore, cycle limit sustained oscillations on the main variables are possible. For high flows,
relaxation oscillations are possible, where the concentration of the propagators is a fast variable, and that of monomer $M_1$ is a slow variable.

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