

# [Mechanisms that lead to dynamic self-organization](https://assignbuster.com/mechanisms-that-lead-to-dynamic-self-organization/)

SELF-ORGANIZATION AND GROWTH OF NANOSTRUCTURED BRANCHED CRYSTAL PATTERN IN BELOUSOV-ZHABOTINSKY TYPE CHEMICAL REACTIONS

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1. Introduction

The self-assembly of structural motifs and the self-organization of dynamic motifs into highly ordered one-, two-, or three-dimensional patterns with controlled structures have received much attention in recent years, because of their importance in basic research and their potential applications [1, 2]. The spontaneous formation of nano-scale patterns represents a significant way to control the structure and morphology of various functional materials [3, 4]. This area is of significant interest because of its possible relevance in improving the materials properties. It can be achieved readily by organizing the nanostructure building blocks by reacting chemical systems over a broad spectrum of space and time [5]. The recent application of nonlinear chemical phenomena has been found in the designing of modern materials of advanced functionality [6-8]. The reacting chemical systems have also been found useful to fabricate and design of diverse optoelectronic nano-devices and nano-catalysts. The role of self-organization has been exemplified to control the orders and hierarchy of such intricate patterns [9-12]. Self-organization, based on interplay between reactions and diffusion, has been found to occur in a range of physical and chemical systems. The recent development of non-equilibrium crystallization phenomena enables one to forms spontaneous, coherent, and periodic patterns which are accompanied by molecular interactions. Among the different nanostructures, the dendritic, diffusion-limited-aggregation (DLA) and spherulitic crystal patterns are attracting the attention of scientific community due to their importance in connection to some fractal growth phenomena and crystallography research [13-15]. The growth of dendritic crystals is also an example which mimics several pattern-forming phenomena encountered in nature and biology.

The aim of our research is to understand the mechanisms that lead to dynamic self-organization in nature in order to anticipate the development of some interesting bio-inspired materials and devices that function far from equilibrium. The present research is also helpful to understand, design and control chemical systems that exhibit complex, non-linear, dynamical behavior in time and space. These behaviors include periodic oscillations, chaos, wave propagation and pattern formation. Such system may provide some insights into related phenomena encountered in biology, physics, mathematics, polymer and material science. The Belousov-Zhabotinsky (BZ) reaction provides a classical platform for investigation of these phenomena. The work described here is an experimental study of growth of nanostructured branched crystal patterns by utilizing three different types of BZ systems. In liquid phase, we observed the reaction system to result into well distinguishable intermediate spatial patterns leading to the formation of DLA and spherulitic structures as the final product. The oscillatory behavior, exhibited by UV-Visible spectroscopy, was found to be interrelated to the DLA and spherulitic structures formed in the BZ system. On the basis of these results, a general mechanism for the synchronized formation of the ordered DLA and spherulitic structures is proposed. In another chemical system chaotic oscillations have been observed experimentally in dual–frequency oscillator o-Hydroxyacetophenone–cerium–bromate–sulphuric acid (OAP–Ce 4+ – BrO 3 − –H 2 SO 4 ) in CSTR.

2. Scope of the study

. Recently there has been increasing interest in fractal and self-organized nanostructured branched crystal growth phenomenon under non-equilibriums conditions. Laplacian growth phenomenon in pattern formation has attracted considerable attention . . DLA and spherulitic crystal patterns have also been observed in various crystallization phenomena usually at far from equilibrium conditions, such as electrodeposition, bacterial colonies, colloidal aggregates, dendrite formation, viscous fingering, and many others. Our research interests are to elucidate the mechanistic aspects of aggregation in macromolecules related to the biological pattern formation. The growth of nanostructured dendritic crystals is also a profound example among a wide range of pattern-forming phenomena in nature and biology.

The study of chemical and biological pattern and their shapes have considerable current interest due to its close resemblance with morphology of growing bodies. Irreversible aggregation of small particles to form large clusters is technologically and scientifically important. Far from, equilibrium growth phenomena have been reported in electrochemical deposition, physicochemical and biological systems. The study of chemical waves, rhythmic crystallization in gel media and crystal growth, will be helpful in understanding morphological stability of growing bodies.

3. Objectives

The present study includes the objectives systematically, from following angles

1. To investigate new types of multiple patterns in mixed organic substrate of Belousov-Zhabotinsky reaction.
2. To investigate stationary-like spatial patterns in dual organic substrate of a micro-emulsion system.
3. To study the transition from stripe to hexagonal spatial pattern by varying the temperature and concentration of the BZ reactants.
4. To study the growth of nanostructured DLA and spherulitic crystal pattern in BZ type oscillatory chemical reaction.
5. To study the chemistry of undertaken BZ reactions and proposed the reaction mechanism.
6. To study the entertainment phenomena between co-existing oscillators and continuously stirred tank reactor (CSTR).
7. To study the dynamics of the spatiotemporal pattern formation by varying the chemical and physical parameters.
8. To elucidate the role of reaction-diffusion mechanism and self-organization process for the growth and morphological study of predictable crystal patterns with help of various analytical methods.

4. Organization of thesis

The organization of thesis has been classified into following chapters.

Chapter 1provides an introduction to the thesis. This chapter outlines, in brief, self-organization in nonlinear chemical dynamics and its relation with the material science. The work conducted and presented as part of this thesis rely upon previous research conducted across a broad range of scientific disciplines; which include an understanding of the concept of nonlinear chemical dynamics; the nonlinear reaction kinetics of the BZ reaction; and materials science. In this context, the workflow of the thesis is outlined in this chapter. One of the initial objectives of the research was to become familiar with the chemistry of the BZ system, with a particular interest in identifying the reaction parameters that control and affect the types of patterns that are formed. Pattern formation and chemical chaos in the BZ system was studied individually in different systems.

Chapter 2provides the literature survey from the historical background of the BZ reaction to recent development in pattern formation in oscillatory reaction media. This chapter includes the following subheadings.

1. Historical background of the BZ reaction
2. Oscillatory chemical reaction and chemical chaos
3. Patterns and wave
4. Substitutes of the BZ reaction
5. Recent development in pattern formations in oscillatory reaction media

Chapter 3describes the detailed experimental procedure adopted for the growth of self-organized nanostructured spherulitic patterns and their morphological investigation in combination of dual substrates (adipic acid and acetyl acetone) and dual catalysts (cerium and ferroin) by utilizing a number of characterization techniques e. g. optical microscopy (OPM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), X-ray diffractometer and Fourier transform infrared spectroscopy (FT-IR) spectroscopy. The oscillatory behavior was also investigated by using UV-Visible spectroscopy. On the basis of these results clues are sought for explaining the observed growth of nanostructured spherulitic patterns inlight of self-organization phenomenon.

Chapter 4deals with the detailed experimental procedure for the growth of self-organized nanostructured diffusion-limited-aggregation (DLA) crystal patterns. The DLA crystal patterns were characterized OPM, SEM, TEM, XRD, Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric (TG) analysis. The oscillatory behavior, exhibited by UV-Visible spectroscopy, was found to be interrelated to the DLA structures formed in the reaction system. This chapter elucidates the roles of the various possible factors behind such phase-transformation along with the plausible explanation of the corresponding reaction pathways.

Chapter 5furnishes the detailed experimental procedure and analysis for the growth of nanostructured DLA patterns in microemulsion consisting of water, styrene, cetyltrimethylammonium chloride (CTACl), potassium persulfate (PS) and oscillating Belousov-Zhabotinsky (BZ) reactant. The chapter describes the analysis of formation of a variety of spatiotemporal patterns viz. concentric wave, spatial (stripe) and chaotic pattern in the used BZ reaction system and has employed TEM, XRD and particle size analyzer to study the morphology, crystallinity and particle size of the associated structure formed.

Chapter 6of the thesis represents the detailed experimental procedure and associated studies for the investigation of chaotic oscillations observed experimentally in dual–frequency oscillator.

Chapter 7is the conclusion, which summarizes the research findings and also provides a future perspective of the work undertaken.

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List of publications

1. Rohit Srivastava\*and P. K. Srivastava, Self-organized nanostructured spherulitic crystal pattern formation in Belousov-Zhabotinsky type reaction system, Chemical Physics , 426(2013) 59-73.
2. Rohit Srivastava\*, P. K. Srivastava and Jayeeta Chattopadhayay, Choas in a chemical system, European Physical Journal Special Topic , 222(2013) 777-783.
3. Rohit Srivastava\*, Jayeeta Chattopadhyay, P. K. Srivastava, Narendra Yadav, Growth of nanostructured Diffusion-Limited-Aggregation (DLA)-Grass like branched patterns in a Belousov-Zhabotinskii (BZ ) type reaction system, International Journal of Chemistry , 34 (2013)1119.
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Conference Publications:

1. Rohit Srivastavaand P. K. Srivastava ” Chaos in a chemical system” Proceed. 7 th National conference on Nonlinear Systems and Dynamics (NCNSD), Organized by Department of Physics, Indian Institute of Science Education and Research (IISER) Pune, (12-15 July, 2012).
2. Rohit Srivastavaand P. K. Srivastava ” Self-organized nanostructured Diffusion-Limited-Aggregation (DLA) crystal pattern formation in Belousov-Zhabotinsky (BZ) type reaction system” Proceed. 8 th National conference on Nonlinear Systems and Dynamics (NCNSD), Organized by Department of Physics, Indian Institute of Technology (IIT Indore) Indore (12-15 December, 2013).