

Chapter 1

Hierarchical Self-organization and Self-assembly: Metal Nanoparticles in Polymer Matrices

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Abstract Although thermodynamically different, self-assembly and dissipative structure formation often work together to bring about highly ordered structures in an open system. This mutual assistance between self-assembly and dissipative structure formation is regarded as self-organization for a system to increase the degrees of hierarchy and complexity. An example for this comprehensive idea is given by hierarchic self-organization of organo-passivated metal nanoparticles in dissipatively isolated polymer matrices.

1.1 Introduction

The concept of self-organization was originated by Schrödinger [1], who reconstructed the long issue on life as a problem of order in a living system. He thought that an order in a living system was brought about via *order from order* and *order out of disorder*. Order from order is related to the structure of biomolecules such as DNA and to the openness of the system, as well (i.e., getting order from the surroundings as *negative entropy* to maintain its order). Order out of disorder is related to spatio-temporal pattern formation under the conditions far from equilibrium. The latter has been named as dissipative structure by Prigogine [2] and has been studied intensively since the 1970s. On the other hand, there have been extensive studies on molecular biology and on biomimetic chemistry such as host-guest chemistry and

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supramolecular chemistry, and self-organization in chemistry is often referred to as *self-assembly* of (tailor-made) molecules in order to realize a higher hierarchy via non-covalent intermolecular forces between molecular components [3].

1.2 Self-organization in Chemistry

1.2.1 Self-assembly and Dissipative Structure

Thus, we know two principles of self-organization (that we can label with the term self-organization): self-assembly near equilibrium conditions and dissipative structure formation under conditions far from equilibrium. As summarized in Table 1.1, these are considerably different in time and spatial scales, order of driving force, existence of potential function, and so on. Because of these particular thermodynamical differences and their quite independent historical backgrounds, they seem to have been studied almost independently in different research fields.

1.2.2 Advantages of Each Self-organization

A self-assembled structure is a static structure stable against thermal fluctuations. Recent progress in molecular chemistry enables us to design a self-assembled supramolecular structure by designing and synthesizing component molecules, and handling them like pieces of toy blocks. Driving forces of self-assembly are hydrogen bonds, salt bridges and solvation forces. Geometrical and topological characteristics of molecules enhance these forces. Self-assembly requires no introduction of energy or matter into the system of concern under thermal equilibrium conditions. In most practical cases, however, self-assembly takes place near equilibrium conditions,

Table 1.1 Self-assembly and dissipative structure

	Self-assembly	Dissipative structure
Periodicity	Spatial	Spatial and temporal
Wavelength ^a	10^0 – 10^1	10^2 – 10^6
Driving force ^b	10^1	10^2
Entropy production	Minimum	No universality
Potential function	Exists	Not known
Reversible	Yes	No
Described by	Phase transition	Instability and bifurcation

^aWith respect to the size of components

^bWith respect to thermal noise

where continuous flows of heat and chemical reaction exist. These thermodynamical fluxes must remain in a linear regime because of the constraint of minimum entropy production. Theoretically, the most stable structure should be selected; however, it is still very difficult to predict even crystallographic structures from given structures of organic compounds [4].

Dissipative structures have some interesting characteristics from the viewpoint of pattern formation:

1. The global structure of dissipative structure may be controlled by its local structure. This is because of entrainment between coupled oscillators distributed in space. As shown in Fig. 1.1, for example, the shape of a spiral in the Belousov-Zhabotinsky (BZ) reaction is reversibly transformed from Archimedian to logarithmic by changing the core size of the spiral [5]. It is a kind of information processing in dissipative structure (transduction and amplification of external information). Mathematically, the core includes the singular point where the phase of the periodic reaction is not defined. This nature of global control via the singular point is universal among so-called excitable media with temporal periodicity.
2. Stationary patterns are not specific to self-assembly. Turing structures [6] are time-independent dissipative structures. Their characteristic wavelengths are intrinsically determined by the reaction rates and the diffusion coefficients, and are independent of boundary conditions. In addition to an ordinary route to the Turing structure via global noise-driven diffusion-induced instability, there has been found a unique route through the self-duplication of spots that finally cover the whole active medium to result in a stationary Turing structure (Fig. 1.2) [7].
3. Some of the spatio-temporal and time-evolving patterns in dissipative structures can be frozen to obtain stationary structure. Addition of Ag^+ ions to the BZ reaction records the spiral pattern [8], and quenching the photoinduced phase separation in a polymer mixture results in a Turing-type structure [9].

1.2.3 Self-organization of Hierarchy by Mutual Assistance Between Self-assembly and Dissipative Structure

Under many practical situations such as those in biological systems, the above-mentioned two self-organization principles are not always so clearly distinguishable. By contrast, they often play their roles on different spatio-temporal scales to bring about highly complicated structures in open systems. Any biological system may be a good but not the only example; we can find suitable examples in very simple systems, as well.

For example, one can see dissipative structure-assisted self-assembly of molecules or ions in dendritic crystal growth. When the driving force (the degree of supercooling) is large enough and the system is set far from the equilibrium condition (i.e., the melting point), the smoothly growing surface of a crystal loses its stability and

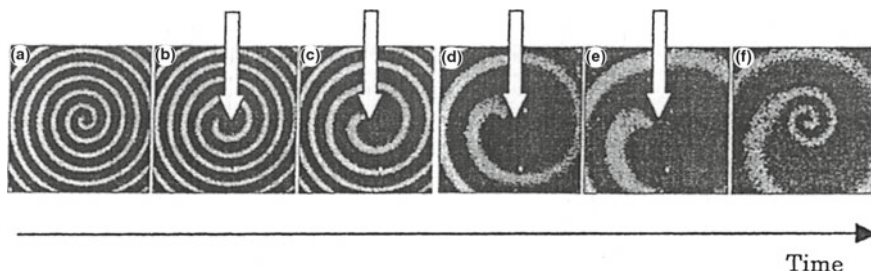


Fig. 1.1 Control of the spiral shape in the oscillatory Belousov-Zhabotinsky reaction. $\text{Ru}(\text{bpy})_3^{2+/3+}$ was used as catalyst. An Ar^+ laser beam (illustrated by white arrow) was directed to the core of the rotating spiral to increase the size of the core region. The morphology of the spiral changed reversibly from Archimedean to logarithmic, and the wave profile from a trigger wave to a phase wave. Controlling a global structure by local control of a singular region is characteristic for dissipative structures



Fig. 1.2 A new route to reach to a stationary structure (the Turing structure) via self-duplication of dots. The Gray-Scott model [10] is used for calculations. The last panel is still not symmetrical because of the influence of noise initially added randomly at each pixel

is replaced by a new mode of dendritic growing surface. Its characteristic wavelength is subject to the transport of latent heat from the growing interface. This is known as Mullins-Sekerka instability [11]. The interface of a growing dendritic crystal provides an open system to support the dissipative structure with its characteristic wavelength(s), and the molecules or ions incorporated into the growing crystal are regarded to be self-assembled into the specific coordinate of the dendritic crystal by the assistance of the dissipative structure.

This complex process of dissipative structure-assisted self-assembly plays an important role for pattern formation in biological systems and many other artificial systems. As far as the authors know, this concept was firstly proposed by Lefever in 2000 [12]. We may extend his idea to think of an alternative concept: a self-assembly assisted dissipative structure. It is obvious that most biological dissipative structures such as traveling waves along giant axons and wavy beating of cilia are realized on the basis of self-assembled substructures of biomolecules.

What is the fruit of this complicated picture of self-organization? The answer is: the approach to the increase in degree of hierarchy and complexity (see Fig. 1.3). As shown in Table 1.1, self-assembly and dissipative structure are in a complementary relationship with respect to structural, temporal, and conditional senses. This

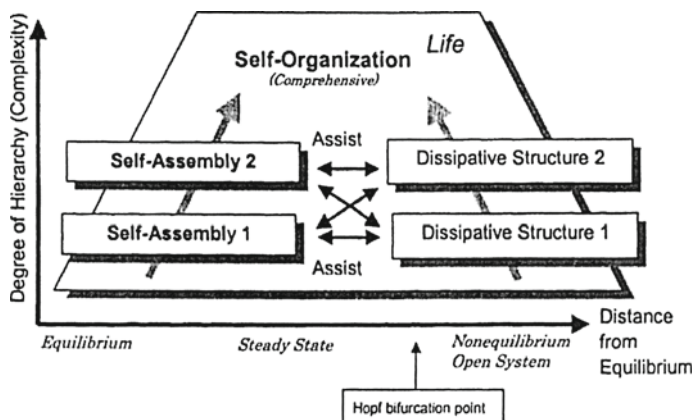


Fig. 1.3 Two well-known principles of self-organization, i.e., self-assembly and dissipative structure, and a new concept of comprehensive self-organization. The abscissa indicates the distance from thermal equilibrium. Temporal dissipative structure appears at the Hopf bifurcation point. Self-assembly and dissipative structure are complementary, and their mutual assistance makes it easier for the system to step up the stair of hierarchy and complexity. Both dissipative structure-assisted self-assembly and self-assembly assisted dissipative structures are possible

complementarity is the basis of the mutual assistance between self-assembly and dissipative structure formation. A system might increase its complexity either by a self-assembly scenario only or by the scenario of dissipative structure formation only. The system might increase the number of its hierarchic levels by these independent scenarios, as well. But in some cases (or in most cases) the comprehensive scenario of self-organization based on the mutual assisting relation will provide more simple and powerful strategies for stepping up the stair of hierarchy. It could be a strategy to be chosen by abiotic systems towards the origins of life (the prebiotic chemical evolution), and the succeeding evolution of life. This strategy would be supportive to answer the request of bottom-up procedures in recent nanotechnology. Therefore, recent interest among researchers in materials science has been focusing on the mutually assisting relations between self-assembly and dissipative structure [13]. Figure 1.3 summarizes the present idea. Further below we will present some of our original results as an example relevant in this sense to materials science.

1.3 Self-organization of Hierarchic Structure

1.3.1 Metal Nanoparticle as Conducting Material

In the years 1981–1986, a pioneering research on metal nanoparticles had been carried out in Tsukuba, Japan. This project was called Hayashi Ultrafine Particle Project. The researchers' interest was not only directed to pure science but also to

practical application of metal nanoparticles. They succeeded in producing well-defined crystalline metal nanoparticles by high-temperature evaporation of Au, Ag, Cu and so on under a well-controlled Ar stream. Coating with some organic compounds allows these metal nanoparticles to be dispersed in an appropriate organic solvent. These dispersed nanoparticles in organic solvents are now commercially available.

So far as passivated Ag nanoparticles are concerned, a convenient one-pot preparation method is known [14]. Silver salt of carbonic acid such as myristate is heated up to about 620 K without any solvent. Pyrolytically reduced Ag atoms then self-assemble to form metal clusters of about 5 nm in diameter, which are surrounded by remaining Ag myristate to form organo-passivated Ag nanoparticles with a yield of 70 %. This type of self-organization may be called reaction-induced self-assembly.

One of the interesting features of metal nanoparticles is their melting at very low temperature. The melting point of bulk Au and Ag is 1,337 and 1,235 K, respectively, but their organo-passivated nanoparticles with diameter less than 10 nm melt at a temperature below or much lower than 500 K. If line-fused, a resulting metal-color line shows good electric conductivity even though the nanoparticles are initially passivated by organic compounds. By use of this low-temperature melting property, we can draw electric circuits on many practical substrates including polymers and papers. Metal nanoparticles are therefore expected to bring about a technological innovation in the near future.

The most practical way to draw lines and dots by nanoparticle-ink is to use a PC-controlled ink jet printer. However, we can propose an alternative method based on a new concept of self-organization, i.e., dissipative structure-assisted self-assembly.

1.3.2 Dissipative Structure-Assisted Self-assembly of Metal Nanoparticles

1.3.2.1 Strategy to Realize Hierarchic Structure

Suppose we want to obtain a dot or line-shaped pattern composed of metal nanoparticles, the characteristic wavelength of which is in the order of μm . It is a typical problem to realize a hierarchic structure, as the wavelengths in the resulting structure are different by 3 orders of magnitude. So we attribute the resulting μm -scale pattern formation of dots or lines to the phenomenon in an upper layer of hierarchy. Aggregation of nano-size particles into a shape of dots or lines attributes to that in another layer (sub-layer), and different strategies are to be applied to different layers.

Aggregation of nanoparticles is an issue of self-assembly in the sub-layer. Once the boundary conditions are fixed, aggregation will proceed to reach the equilibrium state. The pattern formation in the super-layer simultaneously provides the initial and boundary conditions for the aggregation process in the sub-layers. In order to obtain in the super-layer a characteristic wavelength that is sufficiently larger than the size

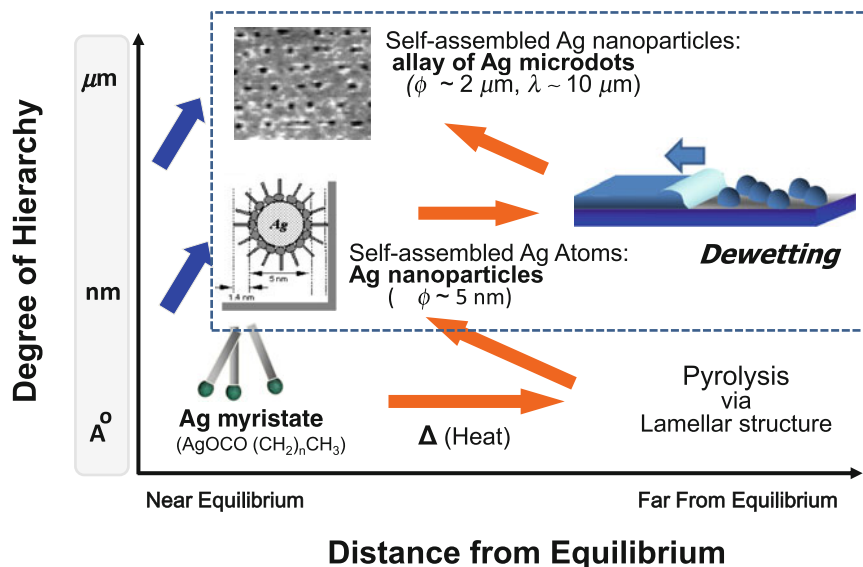


Fig. 1.4 Experimental design based on the new concept of self-organization to obtain a hierarchic *dot* or *stripe* pattern composed of metal nanoparticles. Here a polymer is used for constructing the super-layer structure with the wavelength λ that is chosen by dewetting instability. The patterned polymer islands simultaneously provide the initial and boundary conditions of the sub-layer, i.e., the conditions for self-assembly of nanoparticles

of the compounds, we introduce a dissipative structure principle. Such a dissipative pattern is known in the dewetting process of a dilute polymer solution [15]. Behind the receding front of polymer solution an array of polymer dots is left with a few μm in diameter and with a lateral spacing of about $10 \mu\text{m}$. If nanoparticles are left within polymer dots that still contain solvent to some extent, the nanoparticles must start to aggregate in accordance with further evaporation of solvent (Fig. 1.4, within the dotted square).

1.3.2.2 Experiments and Discussion

Polystyrene (M_w : 166,400–187,200) was purchased from Wako Pure Chemicals. Toluene of reagent grade was used without purification. Organo-passivated Cu and Ag nanoparticles dispersed in toluene were gifts from Harima Chemicals Inc. (concentrations of metals: $<40 \text{ wt\%}$) [16]. Metal core diameter of nanoparticles is about 5 nm , and total diameter is about $7\text{--}8 \text{ nm}$.

A thin toluene solution of metal nanoparticles and polystyrene (1:1 in weight) was evaporated on a clean glass plate at room temperature (299 K). The glass was kept almost vertically, 70° , until toluene evaporated completely.

The self-assembled hierarchic patterns of nanoparticles were observed with an optical microscope (Olympus STM, object lens ULWD MSPlan50).

A typical example of dissipative structure-assisted self-assembly of nanoparticles is shown in Fig. 1.4. The dark dots and lines are aggregates of organo-passivated Cu nanoparticles, and the light surroundings are polystyrene matrices. The dewetting process determines first the wavelength of spatial pattern (frozen dissipative structure) of polymer matrices that are isolated between one another, then followed by the self-assembly process of nanoparticles in each polymer island matrix. Apparently, the aggregates of nanoparticles locate at the center of each polymer matrix. This suggests that gradual evaporation of solvent caused precipitation and aggregation (phase separation) of hydrocarbon-passivated nanoparticles in the matrix of polystyrene-toluene mixture island. By choosing other combinations of passivating organic layer and polymer, we may obtain homogeneous dispersion of nanoparticles in polymer matrices.

In Fig. 1.4(top), there exist several line-shaped structures. These lines run along the moving direction of receding fronts. One may notice that some lines look as if they are going to split. This observation suggests a possible route of producing a dot pattern via instability of line-shaped structures.

Basically, line-shaped structures can be organized in both directions, parallel and normal to the direction of the receding front, depending on experimental conditions. Interestingly, we can occasionally obtain a specimen, where polymer lines run orthogonal with different wavelengths in the dewetting process of polymer solution [17]. Similar patterns with two orthogonal waves have been observed in a crystallization process of L-ascorbic acid from a sparsely distributed methanol solution, as well.

The dewetting pattern of polymer on glass is highly sensitive to a number of experimental parameters (the primary factors): the initial concentration of polymer solution, the thickness of solution, solvents, temperature, the conditions of the glass surface, air humidity, and others. As the pattern formation via dewetting is a physical process and is observable in many other polymeric systems, we can reasonably expect that these experimental factors are included in the secondary factors such as the viscosity and the velocity of the receding front, by which the cubic shape of the receding front is described. If the shape is known, the controllability of the dewetting process may be improved based on the knowledge on the instability of the receding front. The authors, therefore, consider this modeling approach important, and its further consideration is in progress in our laboratory in parallel to the laboratory experiments.

1.3.2.3 Further Possibilities of Dissipative Structure-Assisted Self-assembly in Polymeric Systems

Once we notice and recognize the action of dissipative structure-assisted self-assembly, we can find many examples in the literature, typically in the field of

materials sciences and molecular biology. Listed below are some examples related to polymeric systems.

1. The spin-mode frontal polymerization resulting in a helicoidal structure [18]
2. A record of the traveling BZ spiral as a spiral deposition of AgBr in a gel membrane [8], although this required an additional assistance of experimentalists
3. Photoinduced phase separation in a polymer mixture that results in a Turing-type structure [9]
4. Periodic radical polymerization in the BZ media [19]
5. Microscale patterns induced by laser ablation [20]
6. Clustering of receptor molecules in a biological cell [21]
7. Pattern formation in most convecting systems
8. Treadmilling of actin microdilaments, if controlled by coexisting dissipative structures.

This list is certainly not complete. Nevertheless, it will be a guide for readers to understand correctly the potentials of the dissipative structure-assisted self-assembly mechanism, and to provide ideas to design new experimental systems and practical applications, in particular to polymeric systems.

1.4 Conclusions

Self-assembly and dissipative structure formation are complementary self-organizing processes. Making better use of these two principles, we designed and realized a hierarchic structure composed of metal nanoparticles. The present comprehensive idea of self-organization is a useful concept to design and realize a hierarchic order, especially in nano-scale technology, and also to understand some of the complexity in biological systems.

Acknowledgments TY thanks Olaf Karthaus and Masatsugu Shimomura for stimulating discussions and Kinko Tsuji for helpful comments. This research has been supported partly by the Shorai Foundation for Science and Technology. This chapter is reprinted with permission from: *Nonlinear Dynamics in Polymeric Systems*, J.A. Pojman and Q.T.-C. Miyata (eds.), ACS Symposium Series 869, 16–27 (2003). Copyright (2004) American Chemical Society.

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<http://www.springer.com/978-3-319-19409-7>

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Advances

Müller, S.C.; Parisi, J. (Eds.)

2015, XIV, 293 p. 163 illus., 90 illus. in color., Hardcover

ISBN: 978-3-319-19409-7