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Regulating self-organizing nanostructures via external mechanism

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Self-organizing nanostructures are ubiquitous in both natural and synthetic materials. They are not only appealing scientifically, by revealing the intrinsic atomic and molecular interactions that might be difficult to detect otherwise, but may also hold the key for the development of novel functional structures and devices. For their technological potential to be fully realized, the size, morphology, and distribution of the self-organizing nanostructures must be regulated. In this paper, we investigate the principles under which the self-organizing nanostructures can be regulated via external mechanisms. Using nanomesa and nanowell formation in polyvinylidene fluoride trifluoroethylene copolymer film as an example, we demonstrate that the external mechanism, if appropriately applied, can not only change the structure stability and trigger pattern formation in the otherwise stable films where self-organizing nanostructure is impossible to form, but can also regulate the size, morphology, and distribution of self-organizing nanostructures in a very effective manner. While the analysis is carried out for a particular system, the principles should be applicable for a wide range of self-organizing materials and structures. © 2008 American Institute of Physics.

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I. INTRODUCTION

Self-organizing nanostructures are ubiquitous in both natural and synthetic materials, and can occur in materials over many length scales.¹ They have been observed in a wide range of material systems, including polymer blends and block copolymers,²⁻⁴ semiconducting quantum dots and lines,⁵⁻⁷ magnetic domains and nanoparticles,⁸⁻¹⁰ and martensitic twins and ferroelectric domains.¹¹⁻¹³ The phenomena are driven by competing atomic and molecular interactions to minimize the overall energy of the system, with the formation of nanostructure governed by the internal instability, and size of the nanostructure determined by the competition between the refining and coarsening mechanisms. Very often, these self-organizing nanostructures are randomly distributed with irregular morphology due to the lack of internal mechanism to regulate their morphology and distribution. While a wide range of device applications have been envisioned for self-organizing nanostructures,¹⁴ including solar cells,^{15,16} photonic crystals,^{17,18} and molecular electronics,¹⁹ the random distribution and irregular morphology often observed in self-organizing nanostructures seriously limited their technological potential. Various external mechanisms have been applied to guide the size, morphology, and distribution of self-organizing nanostructures with some success, by modulation of surface chemistry^{20,21} or external electric field,²²⁻²⁵ but most of these efforts are trial and error in nature. Motivated by these observations, we investigate the principles under which the self-organizing phenomena can be regulated by external mechanisms in this paper, with the intention to guide the experimental development in various self-organizing material systems.

To demonstrate our idea, we use nanomesa and nanowell formation in polyvinylidene fluoride trifluoroethylene [P(VDF-TrFE)] copolymer film as an example. A remarkable phenomenon of spontaneous crystalline nanomesa and nanowell formation has recently been discovered in P(VDF-TrFE) copolymer films developed by Langmuir-Blodgett deposition.^{26,27} After annealing an initially continuous 1 ML (monolayer) film at 125 °C for 1 h, arrays of predominately disk-shaped nanomesas isolated from each other appears, with average diameter of 95 ± 22 nm and average thickness of 8.7 ± 0.4 nm. As the number of the monolayers increases, more nanomesas develop, some joined into extended shapes, and tending toward percolation. The 5 ML film is mostly filled in, resulting in a complementary pattern of nanowells with diameter of 128 ± 37 nm and thickness of 9.8 ± 3.3 nm. At 8 ML and thicker, the films remain continuous without nanostructure formation even after lengthy annealing. The nanomesas are ferroelectric, with the same crystalline orientation and nearly the same transition temperature found in a continuous film, making them attractive for applications as high-density sensor and actuator arrays or ferroelectric memory cells. This would require a precise control on the size, morphology, and distribution of nanomesas and nanowells, which is very difficult to achieve by the self-organizing mechanism alone.

To help regulating self-organizing nanostructures for the desired size, morphology, and distribution, we analyze the self-organizing phenomena under the influence of an external mechanism by stability analysis and numerical simulations, using nanomesa and nanowell formation in P(VDF-TrFE) copolymer film as an example. The paper is organized as follows. Formulation of energetic model is given in Sec. II, followed by stability analysis in Sec. III. Numerical results and discussion will then be given in Sec. IV, followed by

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conclusion in Sec. V. In the end, we demonstrate that the external mechanism, if appropriately applied, can not only change the structure stability and trigger pattern formation in the otherwise stable system where self-organizing nanostructure is impossible to form, but can also regulate the size, morphology, and distribution of self-organizing nanostructures in a very effective manner.

II. MODEL FORMULATION

In order to regulate the size, morphology, and distribution of nanomesas and nanowells in P(VDF-TrFE) copolymer films, let us first examine the mechanisms leading to the nanomesa and nanowell formation. First of all, we notice that the internal energy of P(VDF-TrFE) copolymer depends on its chain morphology, and the lamellar polymeric crystalline films often possess preferred thickness due to chain folding;²⁸ this leads to pattern separation in P(VDF-TrFE) films. Second, the surface stress of the film depends on the surface concentration of P(VDF-TrFE) monomers C , which correlates with film thickness h , and an inhomogeneous distribution of C will result in an elastic field in the film that will drive the pattern refining to minimize the corresponding elastic energy. Finally, this refining mechanism is balanced by the interfacial energy that drives the pattern coarsening to minimize the interfacial area, and the competition between the refining and coarsening mechanisms determines the equilibrium size of the self-organizing nanostructures. Similar interactions and competitions exist in a wide range of material systems with self-organizing phenomena, even though the detailed atomic or molecular mechanisms might be different in different systems.

After analyzing the mechanisms responsible for the self-organizing pattern formation, it is not surprising that the morphology of the self-organizing nanostructure is often irregular, and their distribution is often random. There is usually no internal mechanism that controls the morphology and distribution of nanostructures. In order to regulate the size, morphology, and distribution of self-organizing nanostructures, external mechanism must be appropriately applied, which we seek to analyze from energetic point of view. Taking nanomesa and nanowell formation in P(VDF-TrFE) film as an example, the potential energy of the system subjected to an external force $z(\mathbf{x}, C)$ is given by²⁹

$$G = \int \left[ah_r^2 \left(\frac{C}{Ph_r} - 1 \right)^2 C^2 + \phi C_{,\alpha} C_{,\alpha} + \gamma C \varepsilon_{\alpha\alpha} + z(\mathbf{x}, C) \right] dA + \int \frac{E}{2(1+\nu)} \left[\varepsilon_{ij} \varepsilon_{ij} + \frac{\nu}{1-2\nu} (\varepsilon_{kk})^2 \right] dV, \quad (1)$$

where the first integration is over the surface area of the film A , and the second integration is over the volume of the film V . In the equation, the first term is the local internal energy density that prefers the film to have thickness h_r , where a is a constitutive parameter and P is the volume concentration of P(VDF-TrFE) monomers that is assumed to be a constant, and thus C/P gives us the thickness of the film, which minimizes the internal energy density at h_r and 0. This two-well

structure of internal energy leads to pattern separation. The second term is the short-range interfacial energy that penalizes the gradient of surface concentration, and thus drives the pattern coarsening, in which ϕ is another constitutive parameter, and the repeated Greek subscript is summed from 1 to 2. The third term is surface energy due to the strain ε in the film, with $\gamma C \delta_{\alpha\beta}$ being the surface stress and γ being the surface stress coefficient, where $\delta_{\alpha\beta}$ is two-dimensional Kronecker delta. The last term is the long-range elastic energy of the film, where E and ν are Young's modulus and Poisson's ratio of the film, respectively, and the repeated Roman subscript is summed from 1 to 3. The elastic deformation at (x_1, x_2) is caused by inhomogeneous distribution of surface stress due to the pattern separation, and can be solved using Green's function method,³⁰

$$\varepsilon_{\alpha\alpha}(x_1, x_2) = \frac{(\nu^2 - 1)\gamma}{\pi E} \int \int \frac{(x_1 - \xi_1) \frac{\partial C}{\partial \xi_1} + (x_2 - \xi_2) \frac{\partial C}{\partial \xi_2}}{[(x_1 - \xi_1)^2 + (x_2 - \xi_2)^2]^{3/2}} d\xi_1 d\xi_2. \quad (2)$$

From the divergence theorem and periodic boundary condition, we can simplify the summation of the elastic energy and surface energy due to the strain as

$$\int \frac{E}{2(1+\nu)} \left[\varepsilon_{ij} \varepsilon_{ij} + \frac{\nu}{1-2\nu} (\varepsilon_{kk})^2 \right] dV + \int \gamma C \varepsilon_{\alpha\alpha} dA = -\frac{1}{2} \int \sigma_{3\alpha} u_{\alpha} dA, \quad (3)$$

which is positive definite, and thus is minimized by maximum gradient of surface concentration, leading to pattern refining. Combining all the terms together, we have the free energy of the system given as

$$G = \int \left[ah_r^2 \left(\frac{C}{Ph_r} - 1 \right)^2 C^2 + \alpha C_{,\alpha} C_{,\alpha} - \frac{1}{2} \sigma_{3\alpha} u_{\alpha} + z(\mathbf{x}, C) \right] dA, \quad (4)$$

where the first three terms are internal mechanisms that govern the self-organizing nanomesa and nanowell formation, while the last term is the external mechanism that is applied to regulate such self-organizing pattern. It is assumed that the external mechanism is decoupled from the internal mechanisms, in the sense that it will not affect the intrinsic material properties of the film.

In order to regulate the size, morphology, and distribution of self-organizing nanomesa and nanowell formation, the external mechanism must be position dependent, which is lacking in the internal mechanisms. Thus we adopt the following representation of external mechanism:

$$z(\mathbf{x}, C) = \vartheta \Theta(x_1, x_2) C, \quad (5)$$

which varies spatially and is linear to the surface concentration C so that it can be used to regulate the size, morphology, and distribution of self-organizing nanostructures. The exact nature of this external mechanism is not important here. For polar polymers such as P(VDF-TrFE), external electric field would be a good choice.²²⁻²⁵

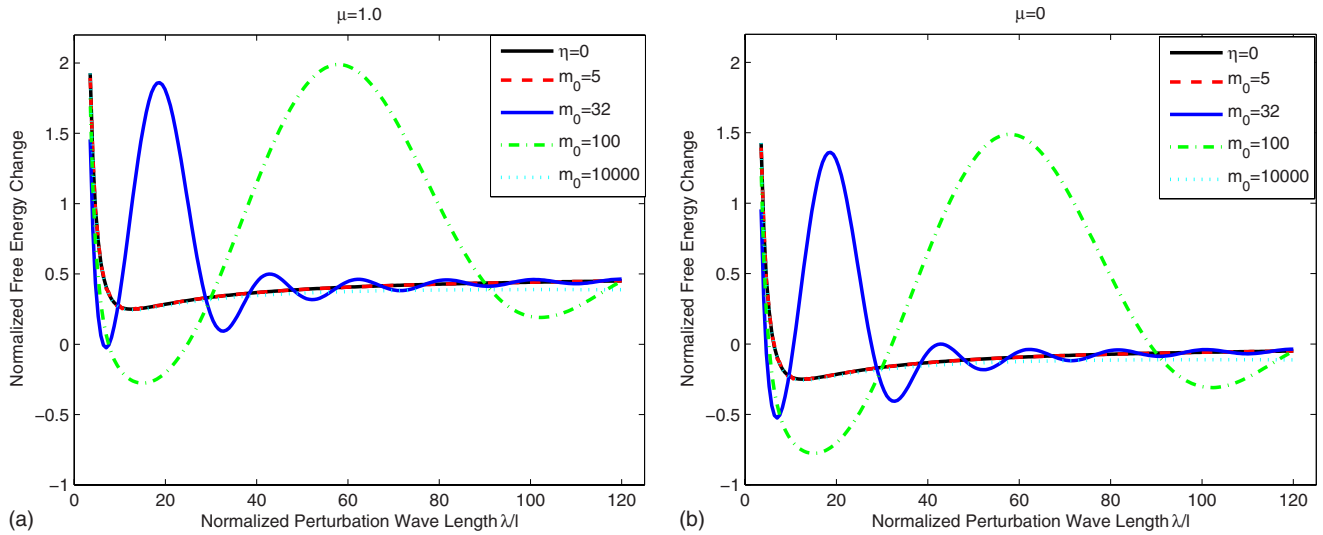


FIG. 1. (Color online) Linear stability analysis suggests that the external mechanism can change the stability of the film and lead to nanostructure formation in the otherwise stable films, where $m_0 = m/l$; left: stable film with $\mu=1$, where ΔG can be changed to negative by external mechanism; right: unstable film with $\mu=0$.

When $\vartheta=0$ and thus there is no external mechanism, Eq. (1) has been numerically implemented successfully to simulate the nanomesa and nanowell formation in P(VDF-TrFE) films.^{27,29} It remains to be seen if the external mechanism as proposed in Eq. (5) can be effective in regulating the nanostructure formation. Notice that many self-organizing phenomena can be described by essentially identical mathematical structure, incorporating local interaction that leads to pattern separation, and short- and long-range interactions that govern the nanostructure size. As a result, similar ideas can also be used to regulate the self-organizing phenomena in many different systems if it works in P(VDF-TrFE) films, even though their detailed atomic or molecular interactions and external mechanisms might be different from P(VDF-TrFE) films.

III. LINEAR STABILITY ANALYSIS

To analyze the effect of external mechanism on self-organizing nanostructure formation, we consider an initially continuous film, and check its stability under an externally applied $z(\mathbf{x}, C)$. If the energy is reduced by a small perturbation in the film thickness, then the film is unstable and the nanostructure will be formed. The size, morphology, and distribution of the nanostructures can then be compared to those without $z(\mathbf{x}, C)$, and the effect of external mechanism can be examined. To this end, we consider a film with uniform surface concentration C_0 and small sinusoidal perturbation with wavelength λ ,

$$C(\mathbf{x}, t) = C_0 + A(t) \sin\left(\frac{2\pi}{\lambda} x_1\right), \quad (6)$$

subjected to a regularly distributed external field with wavelength m ,

$$\Theta(\mathbf{x}) = \sin\left(\frac{2\pi}{m} x_1\right). \quad (7)$$

The energy variation before and after the perturbation can be easily calculated as

$$\frac{\Delta G(\lambda/l)}{\phi A^2/2l^2} = \frac{1}{2}\mu - \frac{2\pi}{\lambda/l} + \left(\frac{2\pi}{\lambda/l}\right)^2 + \eta \frac{\sin[2\pi(\lambda/m)]}{(\lambda/m)^2 - 1}, \quad (8)$$

with

$$l = \frac{E\phi}{(1-\nu^2)\gamma^2}, \quad \mu = \frac{\phi g_2}{\gamma^4} \left(\frac{E}{1-\nu^2}\right)^2, \quad \eta = \frac{\vartheta l^2}{\pi\phi A}, \quad (9)$$

where

$$g_2 = 2ah_r^2 \left[6\left(\frac{h_0}{h_r}\right)^2 - 6\frac{h_0}{h_r} + 1 \right] \quad (10)$$

is the second order Taylor coefficient of internal energy density, and h_0 is the initial thickness of the film. The last term in Eq. (8) represents the effect of external mechanism, with its magnitude scaled with η . On the other hand, the internal stability is represented by μ , which scales with initial film thickness h_0 , but also depends on constitutive parameters that characterize the internal, interfacial, and elastic energies. In order for the perturbation to grow and nanostructure to form, the energy variation must be negative. Otherwise, the film will be stable against pattern formation.

We first consider the situation where there is no external mechanism applied, i.e., $\eta=0$. Clearly ΔG is negative if and only if μ is smaller than 0.5, as shown in Fig. 1 where a stable film with $\mu=1$ and an unstable film with $\mu=0$ are shown. In addition, ΔG is minimized at $\lambda/l=4\pi$, suggesting an equilibrium pattern size of $4\pi l$. Since μ scales with the initial thickness of the film, it suggests that a uniform film thicker than a critical value is stable and without nanostructure formation. Indeed, it is observed in experiments that films of 8 ML or thicker do not form nanomesas or nanowells, despite extended period of annealing. This stability can

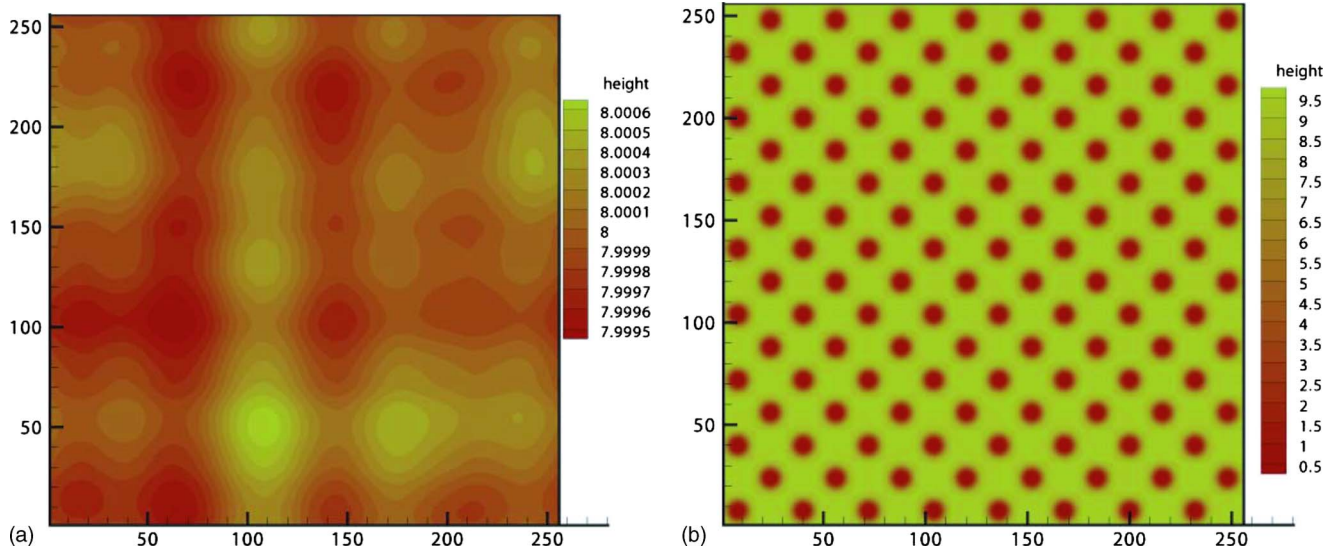


FIG. 2. (Color online) Numerical simulation of P(VDF-TrFE) film with initial thickness of 8 nm; left: the film is stable and no nanostructure formation is observed when it is subjected to no external mechanism; only small variation in film thickness is observed; right: regular array of nanowells is observed when an external mechanism of $\eta=0.1$ and $m/l=32$ is applied.

be changed by external mechanism, however, as shown in Fig. 1 for $\mu=1$, where it is observed that external mechanism with appropriate wavelength, namely, $m/l=32$ or 100, can change ΔG from positive everywhere to negative at appropriate λ . In other words, appropriately applied external mechanism can indeed change the stability of a uniform film and trigger nanostructure formation in the otherwise stable films.

For the external mechanism to be effective, it cannot be applied arbitrarily. As seen from Fig. 1, external force with wavelength $m/l=5$ or 10 000 does not change ΔG much, for both initially stable film with $\mu=1$ and initially unstable film with $\mu=0$. A closer examination on Eq. (8) reveals that the last term in Eq. (8), which represents the effect of external mechanism, converges to 0 when λ/m approaches 0 or ∞ , making the effect of external mechanism negligible. In order for the external mechanism to be effective in regulating the size, morphology, and distribution of self-organizing nanostructures, the wavelength of the external mechanism m/l , and the intrinsic length scale of the self-organizing nanostructure 4π , determined by the competition between the internal interactions, must be comparable. Indeed we observed in Fig. 1 that for $m/l=32$ and 100, the energy variation is drastically changed by the external mechanism. This gives us hope that the self-organizing nanostructure formation can indeed be regulated by external mechanism.

IV. NUMERICAL SIMULATION

To verify our hypothesis, numerical simulation based on phase field approach³⁰⁻³⁴ has been carried out to simulate the evolution of nanomesa and nanowell pattern in P(VDF-TrFE) films. The driving force of the evolution can be obtained from the variation of potential energy, and the rate of the evolution is assumed to be proportional to the driving force. From this linear kinetic assumption, the evolution equation of surface concentration can be derived as²⁹

$$\frac{\partial C}{\partial t} = M\nabla^2 \left[2ah_r^2 C_r Y(C) - 2\phi\nabla^2 C - \frac{(1-\nu^2)\gamma^2}{\pi E} H(C) + \vartheta_0 \Theta(x_1, x_2) \right], \quad (11)$$

where M is the rate constant, $C_r = Ph_r$, and

$$Y(C) = \frac{C}{C_r} \left(\frac{C}{C_r} - 1 \right) \left(2\frac{C}{C_r} - 1 \right),$$

$$H(C) = \int \int \frac{(x_1 - \xi_1) \frac{\partial C}{\partial \xi_1} + (x_2 - \xi_2) \frac{\partial C}{\partial \xi_2}}{[(x_1 - \xi_1)^2 + (x_2 - \xi_2)^2]^{3/2}} d\xi_1 d\xi_2.$$

The evolution equation is then normalized and solved on a two-dimensional lattice using fast Fourier transform and semi-implicit scheme. Details of the numerical implementation can be referred to in Li *et al.*,²⁹ where nanomesa and nanowell formation has been simulated without the influence of external mechanism.

We first consider a film that is stable without external mechanism applied, with $\eta=0$ and $h_0=8$ nm. After lengthy simulation time, no nanostructured pattern formation is observed, and only very small variation in film thickness appears, as shown in Fig. 2. On the other hand, if the same film is subjected to a two-dimensionally distributed external mechanism given by

$$\Theta(x_1, x_2) = \sin\left(\frac{2\pi}{m}x_1\right)\sin\left(\frac{2\pi}{m}x_2\right), \quad (12)$$

with $\eta=0.1$ and $m/l=32$, regularly distributed nanowells are observed in our simulation, as shown in Fig. 2. These results suggest that the stability of the films can indeed be changed by external mechanism, which triggers the nanostructured pattern formation in the otherwise stable films. This is consistent with our linear stability analysis and verifies our hypothesis on the effect of external mechanism.

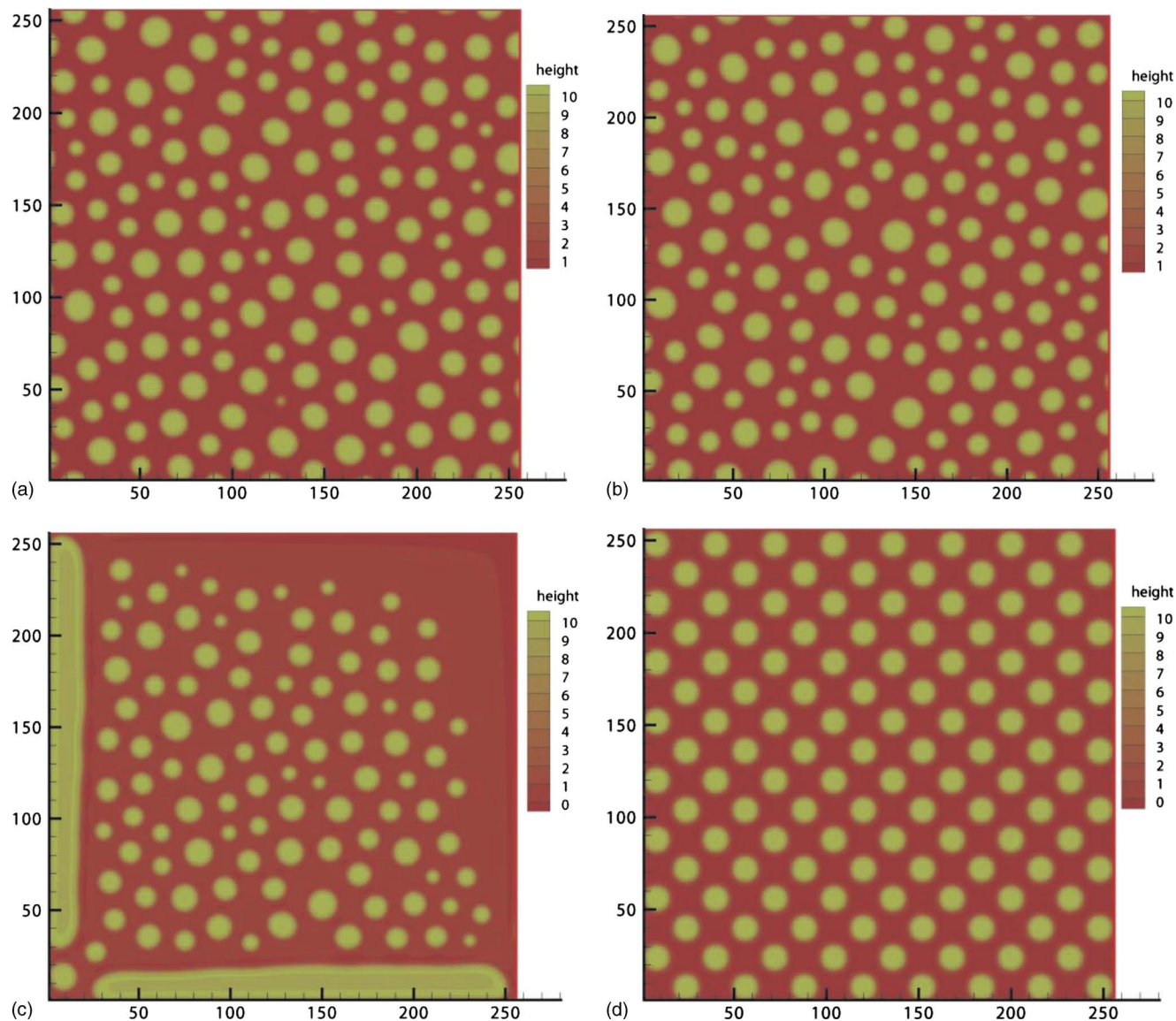


FIG. 3. (Color online) Numerical simulation of nanomesa formation in P(VDF-TrFE) film of 3 nm thick with and without external mechanism; top left: random morphology and distribution when no external mechanism is applied; top right: external mechanism of $\eta=0.1$ and short wavelength $m/l=2$ is applied, which does not change the nanomesa morphology; bottom left: external mechanism of long wavelength $m/l=1000$, which does not change the nanomesa morphology; bottom right: regular array of nanomesas is formed when the wavelength is $m/l=32$, comparable to the intrinsic size of nanomesas.

We then verify the effect of external mechanism wavelength on the pattern formation. The simulations are carried out for films with initial thickness of 3 nm, where $\eta=0$ and $\eta=0.1$ with $m/l=2$, 32, and 1000 are considered, as shown in Fig. 3. Clearly, it is observed that random nanomesas are formed when there is no external mechanism applied, i.e., $\eta=0$, as we expected. In fact, the simulation result without the external mechanism agrees with experimental observation very well.²⁹ When an external mechanism is applied with short wavelength of 2 or long wavelength of 1000, the morphology of the pattern remain essentially unchanged from the one without external mechanism, as shown in Fig. 3, which is also consistent with our linear stability analysis. Only when $m/l=32$, which is comparable with the intrinsic length scale of 4π , regular array of nanomesas is formed. This confirms that the self-organizing nanostructures can indeed be regulated by external mechanism, but only when the

wavelength of the external mechanism is comparable to the intrinsic size of the self-organizing nanostructures.

With the appropriate wavelength and distribution, the external mechanism can be used to regulate the size, morphology, and distribution of the nanomesa arrays in a very effective manner, as shown in Fig. 4, where it is observed that much smaller nanomesas are formed in regular arrays when $m/l=16$, and much larger ones are formed when $m/l=64$. When the external mechanism is varied only in one dimension instead of two, one-dimensional nanowires are formed instead of two-dimensional array of nanomesas. Without the external mechanism, these kinds of sizes and distributions would be impossible in the self-organizing nanomesas of P(VDF-TrFE) film.

V. CONCLUSION

In conclusion, the self-organizing nanostructures can be regulated by the external mechanism with appropriate wave-

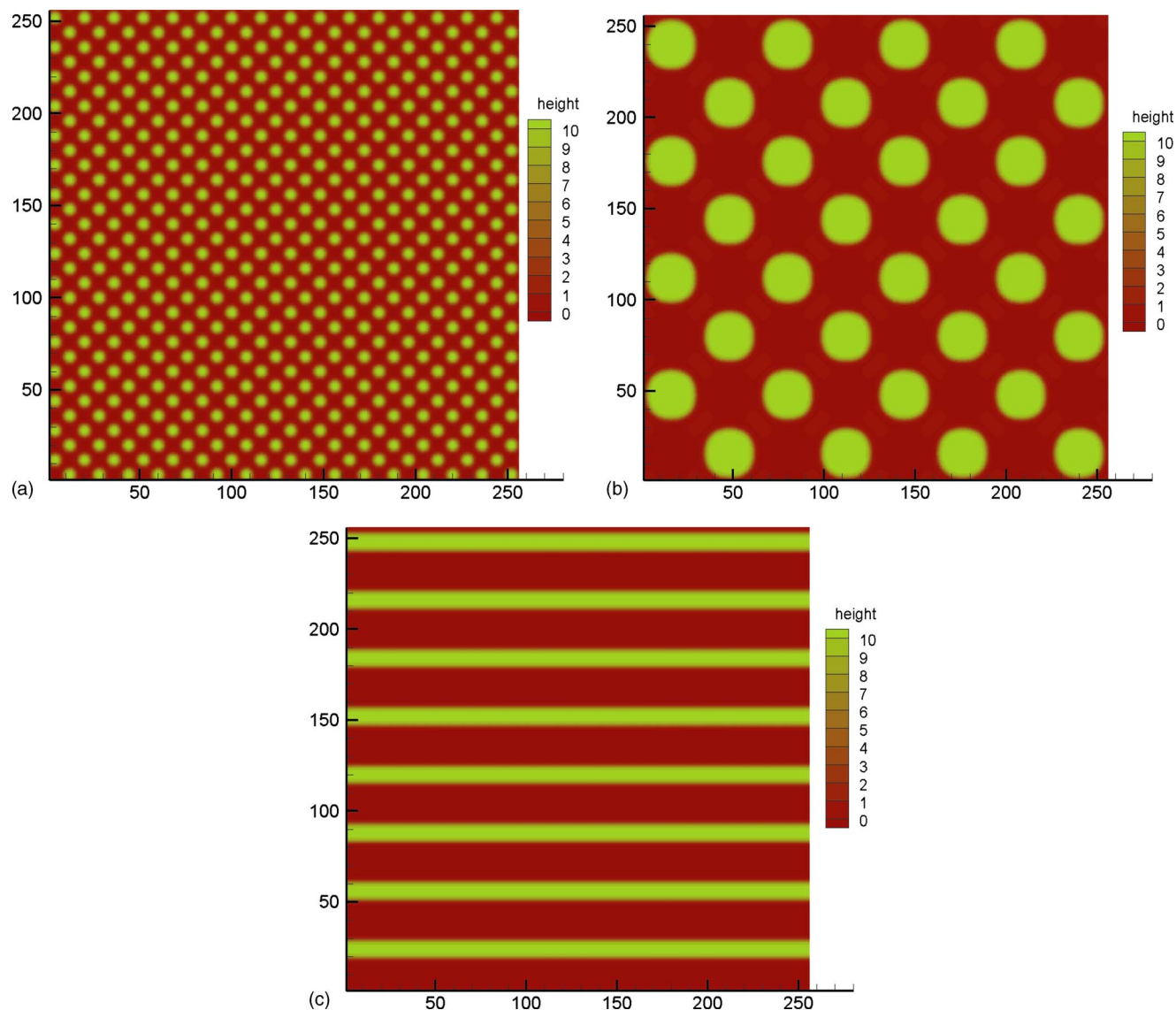


FIG. 4. (Color online) Regulating of the size, morphology and distribution of nanomesas in P(VDF-TrFE) films with initial thickness of 3 nm; top left: smaller nanomesas obtained by external mechanism with $m/l=16$; top right: larger nanomesas obtained by external mechanism with $m/l=64$; bottom: one-dimensional nanowires are obtained by an external mechanism varying only in one dimension.

lengths. The external mechanism can not only change the stability of the film and trigger nanostructured pattern formation in the otherwise stable film but can also be used to regulate the size, morphology, and distribution of the nanostructured pattern in a very effective manner.

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